

Corrosion on Mars

Effect of the Mars Environment on Spacecraft Materials

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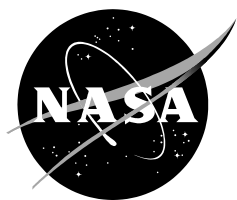
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Abstract

This report presents the results of a one-year project, funded by NASA's Kennedy Space Center Innovation Fund in FY18, to conduct a theoretical study on the effect of the Mars environment on spacecraft materials. Corrosion resistance is one of the most important properties in selecting materials for landed spacecraft and structures that will support surface operations for the human exploration of Mars. Currently, the selection of materials is done by assuming that the corrosion behavior of a material on Mars will be the same as that on Earth. This is understandable since there is no data on the corrosion resistance of materials in the Mars environment. However, given that corrosion is defined as the degradation of a metal that results from its chemical interaction with the environment, it cannot be assumed that corrosion is going to be the same in both environments since they are significantly different. The goal of this research was to develop a systematic approach to understand corrosion of spacecraft materials on Mars by conducting a literature search of available data, relevant to corrosion in the Mars environment. This project was motivated by the suggestion, by a team of researchers, that some of the structural degradation observed on Curiosity's wheels may have been caused by corrosive interactions with the transient liquid brines, reported to be present on Mars, while the most significant damage was attributed to rock scratching. An extensive literature search, on data relevant to corrosion on Mars, confirmed the need to investigate the interaction between materials, used for spacecraft and structures designed to support long-term surface operations on Mars, and the Mars environment. Previous preliminary experiments, designed to look at the interaction between aerospace aluminum alloy (AA7075-T73) and the gases present in the Mars atmosphere, at 20°C and a pressure of 700 Pa, showed that there is an interaction between the small amount of oxygen present in the Mars gas and the alloy, when there is a scratch that removes the protective aluminum oxide film. Further studies are needed to consider many other important components of the Mars environment that can affect this interaction such as: the presence of brines, the interaction between these brines and materials, the effect of radiation on these interactions, and the possible catalytic effects of the clays present in the Martian regolith. This theoretical study provides strong justification to conduct experimental work to investigate the interaction between spacecraft materials with simulated Martian environments to reduce Mars exploration costs.

Introduction

Metal corrosion is the deterioration of a metal or its properties caused by a reaction with its environment. Corrosion occurs mainly through electrochemical reactions. These are chemical reactions that take place when electrons are transferred from one chemical species to another in the presence of an electrolyte.

Corrosion of a metal requires the following components and characteristics:

- Anode: Where metal is lost and electrons are produced (oxidation).
- Cathode: Where electrons are consumed (reduction).
- Metal: Provides the path for current to flow when electrons move from the anode to the cathode.
- Electrolyte: An aqueous solution in which the electrical current is carried by ions. Negative ions (anions) flow toward the anode and positive ions (cations) flow towards the cathode.

Figure 1 shows an illustration of the four components and characteristics required for corrosion to occur. By convention, the current flows in the metal from the cathode to the anode (in the opposite direction to that shown for the electron flow in the figure).

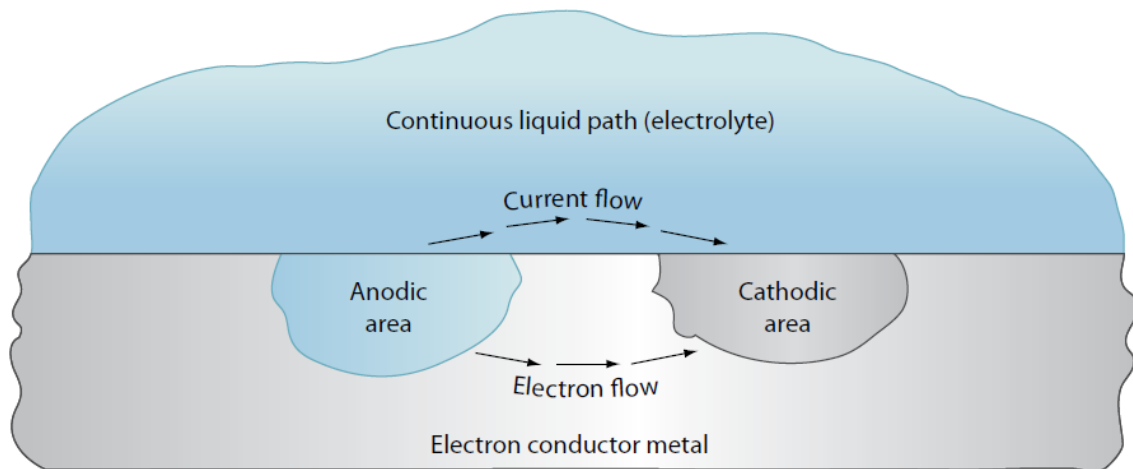


Figure 1. Illustration of the components required for corrosion to take place.¹

A metal can be protected from corrosion by covering it with a coating that isolates it from the environment, thus preventing its reaction with it. Figure 2 shows a metal being protected from corrosion by an intact paint film (coating) that prevents it from interacting with the environment (electrolyte). The metal will be protected for as long as the coating remains intact. The coating can be an applied paint or an oxide layer. When oxygen (O_2) is present in the environment, such as the Earth's atmosphere, metals react with it to form an oxide layer on the surface that may act as a coating to protect them from corrosion. Aluminum is a reactive amphoteric metal that spontaneously forms a thin but effective protective oxide layer, on contact with air, which prevents further oxidation. This oxide, unlike the oxide layers on many other metals, adheres strongly to the base metal. If damaged mechanically, the aluminum oxide layer repairs itself immediately. This layer is stable in the general pH range between 4 and 9.^{2, 3, 4} However, this oxide layer can breakdown in the presence of aggressive anions, such as the halide and perchlorate ions, resulting in the pitting corrosion of the aluminum.

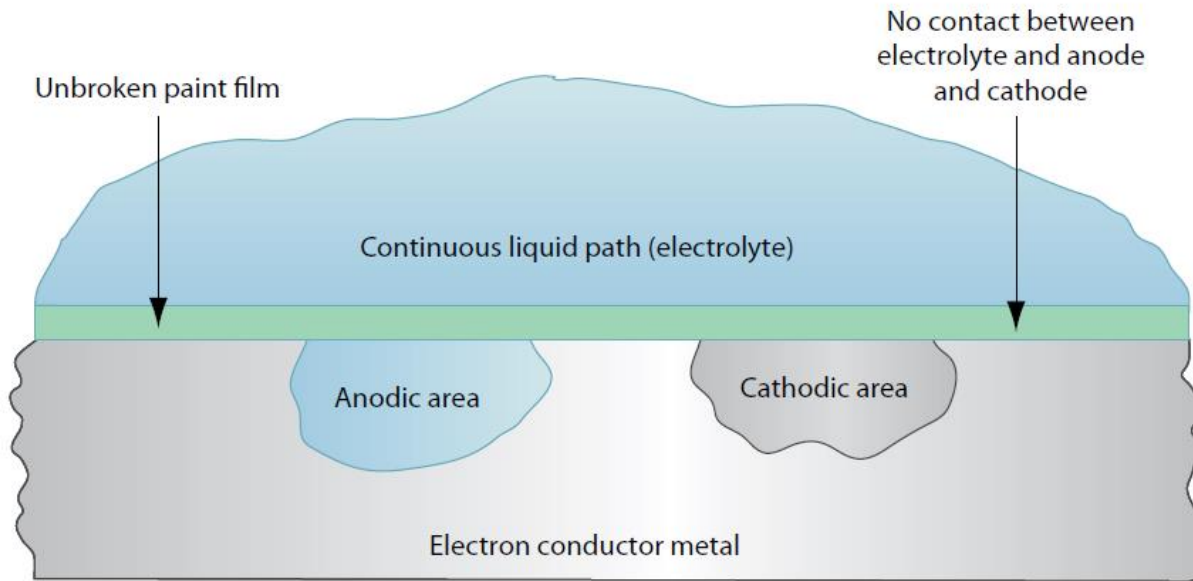


Figure 2. Illustration of a metal covered with a coating for corrosion protection.¹

Space-age aluminum alloys are lightweight, durable, extraordinarily strong, and their corrosion resistance is very good in most terrestrial environments. However, it is not known how aluminum and its alloys interact with the Martian environment. The Curiosity mission is just the latest example of aluminum's vital role in the development of modern aviation and humankind's exploration of space. Chosen for its lightweight and ability to withstand the stresses that occur during ground and launch operations, aluminum has been used on Apollo spacecraft, the Skylab, the Space Shuttles, and the International Space Station. Aluminum alloys consistently outperform other metals in areas such as mechanical stability, thermal management, and reduced weight. One example is AA7075-T7351 which is the aluminum alloy used to make the thin-walled rigid wheel on the Mars Science Laboratory (MSL). Figure 3 shows one of the six flight wheels of Curiosity.^{5, 6} Each wheel tire was machined from a single block of aluminum. It is 50 centimeters in diameter and 40 centimeters wide. It has grousers (treads) that protrude 7.5 millimeters from the wheel skin. Grousers are spaced 15 degrees apart. Unlike Spirit and Opportunity, the grousers are not straight; they have chevron features designed to prevent sideways slip. The skin of the wheel is 0.75 millimeters thick, the absolute thinnest that could be machined. The grousers provide structural strength; the skin is for floating the rover atop loose sand. There is a slight crown to the wheel to make it more robust to the moment of touchdown on Mars. There is a vertical rim on each edge of the wheel, for structural strength. There is another, double rim located about one-third of the way into the tire, the structural stiffener to which the wheel flexures (spokes) are attached. One section of the tire has a set of odometry marker holes drilled into it, which provide a way for the rover's navigational software to measure its driving progress across soft surfaces by photographing the tracks. For fun, these holes spell out "J P L" in Morse code. The wheel is hard anodized, a process used to increase the thickness of the natural oxide layer on the surface of the metal, for greater strength and improved corrosion resistance in terrestrial environments. The Mars mission scheduled to launch in 2020 will use the same type of corrosion protection. This is understandable, given the fact that one of the most important factors in the design of the wheels is the mechanical strength required to transport heavy instruments across the rugged surface of Mars. The current state of the art (SOA), regarding the selection of materials for landed spacecraft for human surface operations on Mars, is to assume that their corrosion behavior on Mars will be the same as that on Earth.

The need to investigate the corrosion behavior of materials, relevant to Mars exploration, was first suggested on a report from a workshop, sponsored by NASA Human Exploration and Operations Mission Directorate and by NASA Planetary Protection Office, on “Planetary Protection Knowledge Gaps for Human Extraterrestrial Missions,” conducted at NASA Ames Research Center, March 24-26, 2015, Moffett Field, CA. The report cites, as other areas of critical research:⁷ “those that include environment characterization and definition (properties of dust and dirt, dust storms, etc.) as well as efforts to develop suitable Mars simulants based on scientific understanding of regolith conditions (even if there is no Mars sample return in advance of a human mission). Attention should also focus on the use of additives to trace possible backward contamination, as well as chemical additives to understand materials degradation due to toxicity and corrosion.” The need to investigate the corrosion behavior of materials, relevant to Mars exploration, was also suggested, as a low priority objective, by the Mars Exploration Program Analysis Group (MEPAG) as Investigation B7.1:⁸ “Analyze regolith and surface aeolian fines (dust), with a priority placed on the characterization of the electrical and thermal conductivity, triboelectric and photoemission properties, and chemistry (especially chemistry of relevance to predicting corrosion effects), of samples of regolith from a depth as large as might be affected by human surface operations.”



Figure 3. Curiosity's wheel made from a single piece of machined aluminum alloy AA7075-T7351. The main rim is 1.9 cm thick (0.75-inches). NASA / JPL / Emily Lakdawalla.

Since the publication of the first evidence of liquid water on present-day Mars by Martin-Torres *et al.*,⁹ according to Curiosity data, and the corroboration of the presence of brines by Ojha *et al.*,¹⁰ a new frontier of scientific challenges has emerged, such as the corrosive interaction between brines (electrolytes) and spacecraft materials in the Mars environment.¹¹ The hydrated salts present in the brines would lower the freezing point, just as salt on roads here on Earth causes ice and snow to melt more rapidly. The hydrated salts, most consistent with the chemical signatures analyzed by Ojha *et al.*,¹⁰ are likely a mixture of magnesium perchlorate ($\text{Mg}(\text{ClO}_4)_2$), magnesium chlorate ($\text{Mg}(\text{ClO}_3)_2$), and sodium perchlorate (NaClO_4). Some perchlorates (salts that contain the ClO_4^- anion) have been shown to keep liquids from freezing, even when conditions are as cold as minus 70°C (203K).

Perchlorates have previously been seen on Mars. NASA's Phoenix lander and Curiosity rover both found them in the planet's soil, and some scientists believe that the Viking missions in the 1970s measured signatures of these salts. However, the study of recurring slope lineae (RSL) detected perchlorates, now in hydrated form, in areas different from those explored by the landers. This also is the first time that perchlorates have been identified from orbit. It should be mentioned that other researchers¹² have suggested that a dry avalanche process can explain the formation of the RSL on Mars, without requiring liquid water or CO₂ frost activity. On Earth, naturally produced perchlorates are concentrated in deserts, and some types of perchlorates are used as rocket propellant.

The goal of this research was to investigate the effect of the Mars environment on spacecraft materials, by conducting a literature search of available data relevant to corrosion in the Mars environment.

Background

Mars is often called the red planet. The reddish color of the Martian surface is due to the high iron oxide (Fe₂O₃), also known as iron(III) oxide or hematite, content in its regolith. Iron(III) oxide (rust) is formed when iron metal becomes oxidized in the presence of O₂. This process is also known as corrosion. The quest to find life on Mars, by searching for organic compounds, the building blocks of life on Earth, and microbial life in the regolith, has generated a great deal of data relevant to corrosion on Mars.

Missions to Mars look for evidence of organic molecules using thermal extraction techniques that involve heating soil samples to 392 degrees Fahrenheit (200 °C). The perchlorate salts in the samples break down during this heating, releasing O₂ that causes the combustion of organic molecules to form carbon dioxide (CO₂). There is evidence that this process is what caused the decomposition of organic molecules during the Viking biology experiments.^{13,14} This reactivity was attributed to the possible formation of superoxide radical ions (O₂⁻) in the Mars environment, under ultra violet (UV) radiation,¹⁵ or to the activation of an oxidizing agent, such as perchlorate (ClO₄⁻), under radiation by gamma rays. R. C. Quinn *et al.* showed that the release of trapped O₂ from radiation-exposed perchlorate salts and the reaction of hypochlorite (ClO⁻) with amino acids, that were added to the Martian soils, can explain the results of the Viking biology experiments. They concluded that neither hydrogen peroxide nor superoxide is required to explain the results of the Viking biology experiments.¹⁶

Despite the overwhelming evidence that oxidation of materials is unavoidable on Mars, corrosion of materials has not been a major concern for Mars Missions, due to its arid atmosphere and the lack of evidence of liquid water. The recent discovery of perchlorates in the equatorial Gale Crater, in addition to the Phoenix lander finding it in the Martian arctic, supports the widespread presence of perchlorates on the surface of Mars.¹⁷ Perchlorate and chlorate (ClO₃⁻) species have also been found in a Martian meteorite.¹⁸ Its role in lowering the freezing temperature of water in the Martian soil supports the presence of transient liquid water on Mars.¹⁰ This new found evidence of liquid brines coincided with the surprisingly significant damage observed on Curiosity's wheels (Figure 4 and Figure 5). Soon after its landing, disturbing cracks started to appear on some of them. This was surprising, given that the design was similar to that of the Mars Exploration Rovers (MER's), Spirit and Opportunity, which never showed such a wear and tear when experiencing the same mean pressure (i.e. platform weight over wheel area in contact with a flat terrain). It has been hypothesized that, the daily contact of the wheels with the corrosive perchlorate solutions during every night, may have weakened the scratched surface of the anodized aluminum, making it more susceptible to damage against sharp rocks. Rover engineers concluded that the damage was caused exclusively by

mechanical forces. Although the large cracks in the wheel are likely caused by mechanical damage, there is a pattern of distributed sub-millimeter sized blisters, in the vertical wall of the T-print of the wheels, that cannot be attributed to rock scratching. This pattern resembles aluminum alloy pitting corrosion, as shown on the image taken by the ChemCam remote microscopic-imager on sol 502 (Figure 5). A team of researchers⁹ has suggested that, given the strong oxidizing character of perchlorate anions and their byproducts, the damage that cannot be attributed to rock scratching may be caused by corrosive interactions of brines with the aluminum alloy wheel.¹⁹ Any Martian surface Cl⁻-containing deliquescent brine would be expected to be very corrosive. In particular, for the Martian deliquescent brines, the Cl⁻ concentration in the Ca- and Mg-perchlorate eutectic mixtures are factors of 420 and 246 greater, respectively than a diluted copper(II) chloride (CuCl₂) solution (10 mM), which has been reported to cause 10-50 μm-sized blisters with copper (Cu) deposits produced after aluminum pitting corrosion, similar to those circled in red in Figure 5, within 10 minutes.²⁰ The anodizing process increases the thickness of the natural oxide layer on the aluminum wheels, but the abrasion can wear out the external protecting layer and expose the bare aluminum metal to corrosion. The presence of chloride and perchlorate anions in brines may add stress to the aluminum wheels through pitting corrosion. Thus, it can be hypothesized that the presence of corrosive chloride-containing brines on Mars should have implications on spacecraft design for human surface operations in support of long duration exploration missions. Considering that the overall environment of Mars is more oxidizing than that of Earth, the potential challenge of metal corrosion and materials degradation should not be ignored.



Figure 4. Curiosity's wheels showing signs of severe damage after almost 10 km of traverse.

The components of the Martian environment that is relevant to corrosion include: the composition and conditions of the atmosphere, soil composition and chemistry, radiation conditions, and the presence of transient liquid brines. The corrosion resistance of aluminum alloys in the Earth's atmosphere depends on their ability to form a protective surface oxide layer. If the same alloys will be used under Martian conditions, it is important to understand their interaction with the Martian environment and to find out if a protective layer will form when the original oxide layer is damaged, as it happens here on Earth. It is also important to characterize the layer and its properties. Furthermore, it can be expected that the presence of corrosive brines on Mars should have significant implications on the selection of materials for spacecraft and structures, built to support long-term surface operations for the human exploration of Mars.

The question of whether or not an aluminum alloy will form an oxide protective layer, when its surface is scratched, under simulated Martian atmospheric conditions, was addressed in a previous investigation in which preliminary experiments were designed to study the interaction

between a sample of aluminum alloy AA7075-T73, scribed *in situ*, and three different atmospheric environments, relevant to Mars, at room temperature (20°C): Earth's atmosphere at 100 kPa (1 bar), pure carbon dioxide gas (CO₂) at 700 Pa (7 mbar), and Mars gas at 7 mbar. This pressure was selected because the average pressure on Mars is roughly 7.5 mbars.²¹ Table 1 shows the composition of the Mars gas and that of the Earth's atmosphere.

Table 1. Composition of Earth's atmosphere and Mars Gas^{21, 22}

	Nitrogen	Oxygen	Argon	CO₂	Carbon Monoxide (CO)
Earth's atmosphere (%)	78	21	0.90	0.04	-
Mars gas (%)	2.70	0.100	1.59	95.5	0.100

The most important finding of our preliminary experiments was the significant role of the small amount of oxygen present (0.13%) in the Mars gas. X-ray photoelectron spectroscopy (XPS) results showed that the oxygen in the Mars Gas reacted with the aluminum in the scratched area to form a layer of aluminum oxide and that this oxide layer prevented the interaction between the aluminum and the carbon dioxide present (95.5%). When the aluminum alloy was scribed under a 100% CO₂ atmosphere at 20°C and a pressure of 700 Pa, only a weak interaction between the aluminum in the scribe and the CO₂ was observed. Unfortunately, follow on funding was not available to continue the experimental work to investigate the interaction between the aluminum alloy and other components of the Mars environment relevant to corrosion.

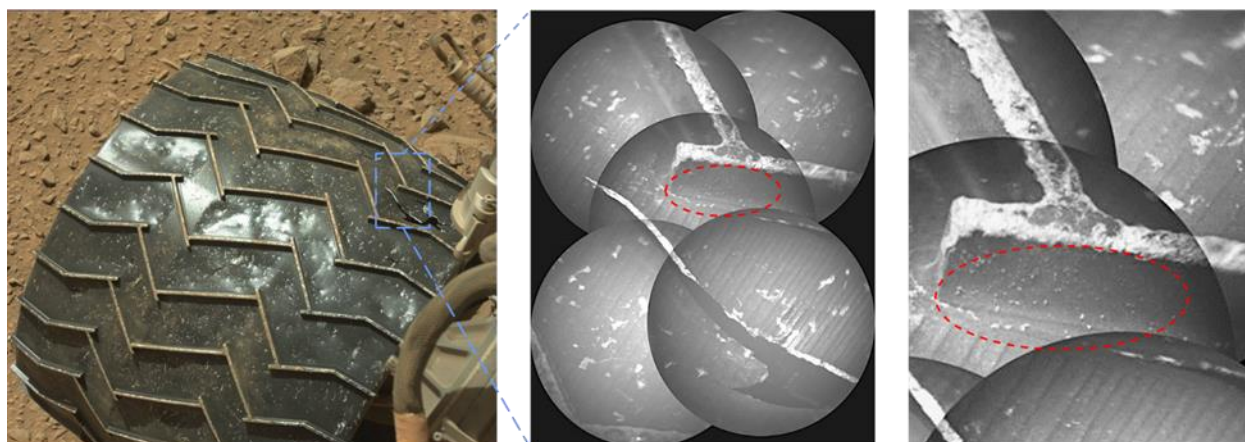


Figure 5. Curiosity's ChemCam images of a damaged area of the rover's middle right-wheel. The image shows not only a large crack in the wheel (area inside blue rectangle on left image) but some sub-millimeter-sized blisters in the vertical wall of the T-print of the wheels (circled in red on the middle and right images) which cannot be attributed to rock scratching. It has been suggested that the blisters are caused by the corrosive interaction between transient brines and the aluminum alloy.

A recent study, performed under a NASA Innovation Award at NASA Marshall Space Flight Center (MSFC) by Z.S Courtright, looked at the effects of a simulated Mars Atmosphere (without the effects of pressure or gravitational effects) on arc welding of Ti-6Al-4V and AA2219-T87 and found slight variations, such an increase in tensile strength and hardness for the simulated Martian welds.²³ These results support the importance of testing materials in the environment in which they are going to be used.

Available Data Relevant to Corrosion on Mars

The quest to find life on Mars has generated a great deal of data relevant to corrosion on Mars. Results from experiments designed to look for life have indicated that Mars' surface is lifeless and depleted of organics at the parts-per-billion levels. These results have been explained by the presence of oxidizing agents on the surface of Mars. These oxidizing agents also can cause corrosion of materials on Mars. One of the most significant recent findings, that is relevant to corrosion, is the existence of transient liquid water and water activity at Gale crater on Mars (the exploration zone of NASA's Curiosity rover) reported by a team lead by F. Javier Martin-Torres.⁹ Their observations support the formation of night-time transient liquid brines in the uppermost 5 centimeters of the subsurface that then evaporates after sunrise. There is an active exchange of water at the atmosphere/soil interface which is the area that would come in contact with landed spacecraft and structures built to support surface operations on Mars.²⁴ The research team expects that liquid brines are abundant beyond equatorial regions where atmospheric humidity is higher and temperatures are lower. As it was suggested in a recent publication,¹¹ the presence of transient liquid brines has significant implications for spacecraft design and surface operations, given the potential for corrosive interactions between the brines and spacecraft materials.

Sample Analysis at Mars (SAM),²⁵ and Dynamic Albedo of Neutrons (DAN)²⁶ instruments, over the course of a full Martian year (1.88 Earth years), has provided the largest environmental data set ever recorded *in-situ* on Mars. This data is relevant to study the interaction between spacecraft materials and the Mars environment.

Brines on Mars

Brines on Mars are produced under specific environmental conditions in the daily capture (and release) of atmospheric water vapor by deliquescent salts that exist at the surface of Mars, such as chlorides and perchlorates.²⁷ The perchlorates found *in situ* are likely calcium perchlorate ($\text{Ca}(\text{ClO}_4)_2$) as detected by Curiosity at Gale²⁸ and magnesium ($(\text{Mg}(\text{ClO}_4)_2)$ (or sodium perchlorates (NaClO_4)) as observed at the Phoenix polar landing site.²⁹ Reanalysis of Viking data suggested that perchlorates could have been present there as well.³⁰ Chloride is distributed globally on Mars as detected by the Mars Odyssey Gamma Ray Spectrometer (GRS).^{31, 32} Oxygen was one of the most abundant gases released during thermal analysis of materials at Curiosity's Rocknest site. Its release was correlated with the release of chlorinated hydrocarbons.³³ This O_2/Cl correlation makes a strong case for the presence of chlorine in the form of perchlorates. The suggestion that the presence of chloride and perchlorate anions in brines may cause pitting corrosion on Curiosity's wheels and future Martian exploration platforms⁹ is worth of further investigation.

Perchlorates

Perchlorate is a negative ion (anion) with a charge of -1 where 4 oxygen atoms are bound to a central chlorine atom in a tetrahedral geometry (Figure 6). The oxidation state of the central chlorine atom is +7, which is its highest oxidation state. This means that perchlorate has a high oxidation character because it can accept up to 7 electrons from other chemical species that will become oxidized in the process. They are powerful oxidants when heated, but are stable at room and lower temperatures. In biology, the high oxidation state of perchlorates means that they can be used as an electron acceptor by microorganisms to provide energy for growth. Early interest in the chemistry of perchlorates here on Earth was primarily motivated by their application as powerful oxidants in fireworks, military ordinance, flares, and in solid rocket fuel. These applications resulted in the presence of perchlorate as a contaminant in ground and

drinking water. This prompted research efforts aimed at the elimination of perchlorate as a contaminant. One of the main health hazards with perchlorate is that it interferes with iodide uptake in the thyroid gland. Perchlorates contamination is due to the improper disposal of solid salts of ammonium, potassium, or sodium perchlorate. These salts are very soluble in water and the perchlorate is kinetically inert to reduction (by accepting electrons). Although perchlorate is a powerful oxidizing agent when heated, its notorious lack of reactivity at room and lower temperatures can be understood from the requirement that reduction involves oxygen atom transfer. Because perchlorate is relatively unreactive, remediation schemes involving direct chemical or electrochemical reduction are not effective. There are biological systems (bacteria) that naturally reduce and degrade perchlorate. There is a renewed research interest on perchlorate as a result of its presence in the Martian environment.

Compounds that contain perchlorate include the oxidant in solid rocket fuel (ammonium perchlorate (NH_4ClO_4)) as well as that in fireworks, military ordinance, flares, airbags, and other applications, where an energetic oxidant is required. Ammonium perchlorate is among the most important propellants because it has a high oxygen content and decomposes into the gaseous phase products water, hydrochloric acid (HCl), nitrogen (N_2), and oxygen leaving no residue. Salts of perchlorate do not function well in solid-fueled rockets after the salts adsorb too much water, and improper disposal has led to environmental contamination. A great deal of research efforts have been dedicated to its removal.³⁴

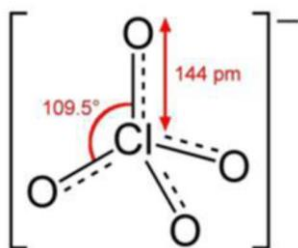


Figure 6. Structural formula and bond length of perchlorate anion.

Even though perchlorate contains a highly oxidized central halogen atom, it exhibits low reactivity as an oxidant.³⁵ The low reactivity is a matter of its kinetic rather than thermodynamic stability. The rate at which a reaction takes place (kinetics) is determined by the activation energy, E_A , temperature, and other parameters that are constant for a given reaction. The activation energy (Figure 7) is dependent on the mechanism by which a reaction takes place. For example, a catalyst causes a reaction to take place faster by lowering the activation energy. Given thermodynamics alone, we would expect perchlorate to be reduced to chloride and oxidize water to oxygen. Spontaneous reactions are those that will take place by themselves given enough time. Spontaneity refers to the direction in which the reaction will take place but it is not an indication of how fast the change will take place. The rate at which chemical reactions take place is governed by the kinetics of the reaction. The low reactivity of perchlorate is dominated largely by its kinetics.²⁹ The activation energy of ammonium perchlorate is 123.8 kJ/mol below 240°C, 79.1 kJ/mol above 240°C, and 307.1 kJ/mol between 400 and 440°C.³⁶ The decomposition of perchlorates is usually initiated using a high temperature source, such as a glow wire, to overcome the kinetic barrier (E_A). Once decomposition of some perchlorate molecules is initiated, the resulting reaction produces a large amount of heat. Between 200 and 300°C, ammonium perchlorate undergoes an autocatalytic decomposition.³⁷ At about 400°C, ammonium perchlorate decomposes very fast and suddenly explodes. The reactivity is a function of the reaction pathway. Different reaction pathways for perchlorates would have different barriers from that of the thermal decomposition discussed above.

The overall reaction for the reduction of ClO_4^- to Cl^- and the oxidation of water to O_2 is relevant to corrosion in the Mars environment since a major oxygen release, between 300 and 500°C, was detected by the Mars Curiosity rover Sample Analysis at Mars (SAM) instrument at the Rocknest eolian deposit. Thermal decomposition of perchlorate salts in the Rocknest samples is a possible explanation for this evolved oxygen release.^{17, 38}

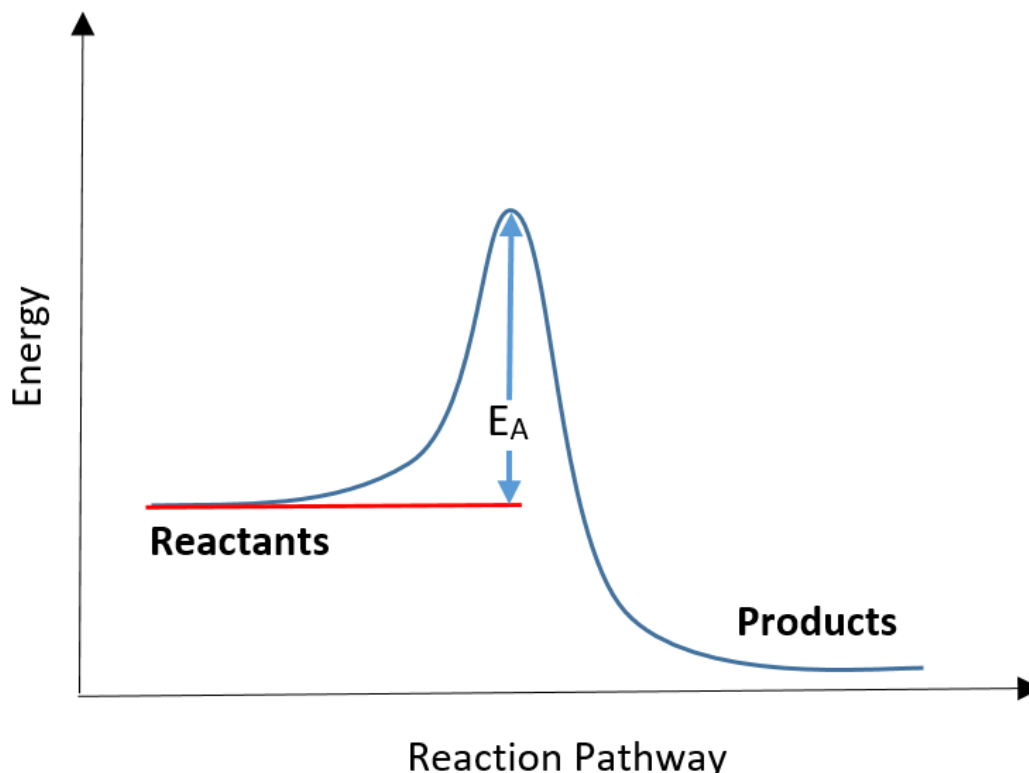
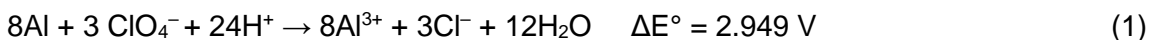


Figure 7. Activation energy, E_A , of a thermodynamically spontaneous chemical reaction

Aluminum corrosion and perchlorate

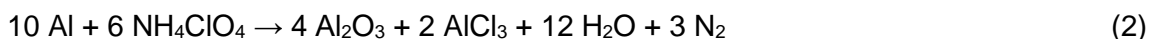
It is important for this project to consider how perchlorate affects the oxidation reaction of aluminum. Aluminum is a strong reducing agent with a standard reduction potential $E^\circ(\text{Al}^{3+}/\text{Al}) = -1.662 \text{ V}$. ΔE for the oxidation of aluminum by perchlorate is obtained by adding the oxidation potential of aluminum, $E^\circ(\text{Al}/\text{Al}^{3+}) = 1.662 \text{ V}$, to the reduction potential of perchlorate, $E^\circ(\text{ClO}_4^-/\text{Cl}^-) = 1.287 \text{ V}$, to obtain a ΔE° value of 2.949 V for the overall reaction (1):



This means that this reaction is thermodynamically favorable (spontaneous). However, aluminum metal is invariably passivated by a dense aluminum oxide film, a few nanometers thick, which can serve as a protective barrier for aluminum to react as a reducing agent. The oxide film can form instantly on the aluminum surface when exposed to air and/or water. The dense oxide film is, however, not a hurdle for employing aluminum as a reducing agent at high temperatures but it is a barrier for employing aluminum as a reducing agent in wet-chemical synthesis. This prompts the question: What is the passivation mechanism of aluminum under Martian conditions where there is only 0.13% of oxygen in the atmosphere compared to 20% here on Earth? Results from preliminary experiments, designed to answer this question, showed that AA7075-T73 aluminum alloy forms an oxide layer when scribed *in situ* under a Mars gas

atmosphere at 20°C and a pressure of 700 Pa. This was surprising given the small amount of oxygen (0.100%) gas, compared to the large amount of CO₂ gas (95.5%), present in the Mars gas.²¹

Perchlorate is present on Earth primarily as a contaminant in the environment (groundwater and drinking water). Perchlorates commonly originate as a contaminant from the disposal of solid salts such as ammonium perchlorate. These salts are very soluble in water and kinetically inert, at ambient temperatures, to reduction due to the high activation energy involved. However, the kinetic barrier can be lowered, as it happens when aluminum reacts rapidly with ammonium perchlorate, as shown in reaction (2). In this reaction, aluminum is oxidized to aluminum oxide (Al₂O₃) and perchlorate is reduced to Cl⁻. This reaction is used in rockets (such as solid rocket boosters), explosives, pyrotechnics, flares, and ammunition.



The solid rocket boosters on NASA's Space Shuttle used approximately two million pounds of solid fuel per launch. The mixture contained 70% ammonium perchlorate, 16% aluminum, and 14% of an organic polymer.³⁹ Several microorganisms on Earth are known to harvest energy by anaerobic reduction of the perchlorate molecule.⁴⁰

Aggressive anions, such as the halides, especially the chloride ions, are known to induce breakdown of the protective passive film on aluminum by a localized attack (pitting).^{41, 42, 43, 44, 45, 46, 47} There have been extensive investigations on the role of chloride ions in the breakdown of the passive film, repassivation, and initiation of localized corrosion of aluminum and high-strength aluminum-based alloys. This is understandable since aluminum and its alloys are often used in environments where chloride is present. One example is the exposure of aircraft to marine environments, where there is a high content of chloride ions. There is some evidence from the literature that supports the occurrence of pitting corrosion on the surface of some metals as a result of passivity breakdown by perchlorate ions.^{48, 49, 50} A literature survey showed that there have been a few published results concerning pitting corrosion of aluminum alloys in perchlorate solution. J. L. Trompette⁵¹ *et al.* studied the influence of the anion specificity on the electrochemical corrosion of two types of anodized aluminum substrates, a porous-type and a barrier-type. They found that in the case of Cl⁻, Br⁻, ClO₄⁻, and NO₃⁻ anions, a great number of small pits covering the surface are observed. M. A. Amin *et al.*⁵² investigated the influence of various concentrations of perchlorate ion on the pitting corrosion of aluminum and aluminum-copper alloys in neutral sulfate solutions at 25 °C. They measured the pitting corrosion susceptibility of pure aluminum and two aluminum-copper alloys, namely (Al + 2.5 wt% Cu) and (Al + 2.5 wt% Cu) alloys in 1.0M Na₂SO₄ solutions, free from and containing various concentrations of perchlorate ions, using potentiodynamic polarization, cyclic voltammetry and chronoamperometric techniques, and concluded that the rate of pitting initiation increases with increasing perchlorate concentration. They also concluded that the density of pits decreases with increasing %Cu in the aluminum samples. These findings suggest that it is important to investigate the corrosion behavior of aluminum alloys and other metals, used for spacecraft and structures to support long-term surface operations on Mars, under laboratory conditions that simulate the Mars environment, including the presence of perchlorates in the regolith.

Perchlorates and Martian Conditions

Perchlorate is widespread in Martian soils at concentrations between 0.5 and 1%.⁵³ Turner *et al.*⁵⁴ cited concentrations between 0.4-0.6 wt% discovered at the north polar landing site of the Phoenix spacecraft and at the southern equatorial landing site of the Curiosity rover. At such concentrations, perchlorate could be an important source of oxygen, but it could also become a

critical chemical hazard to astronauts and cause corrosion on landed spacecraft and ground support equipment. The amount of perchlorate in the surface regolith of Mars is significant compared to that in soils on Earth, where typical concentrations are lower (0.03 to 0.6 wt %) ^{55, 56} than on Mars.

Since its discovery on Mars, perchlorate has become a focus of research interest due to its possible role in destroying organics in the thermal stage of analytical instruments sent to Mars to detect them. Quinn *et al.* ¹⁶ and Navarro-Gonzalez *et al.* ³⁰ have shown that ionizing radiation decomposes perchlorate resulting in the formation of hypochlorite (ClO^-), other lower oxidation state oxychlorine species and production of O_2 gas that remains trapped in the salt crystal. They suggested that ionization processing of perchlorate alone can explain the Viking Labeled Release (LR) and Gas Exchange Experiment (GEX) results. Turner *et al.* ⁵⁴ conducted laboratory experiments to explore the temperature-dependent decomposition mechanisms of hydrated perchlorates, namely magnesium perchlorate hexahydrate ($\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$), and to provide yields of the oxygen-bearing species formed in these processes at Mars-relevant surface temperatures from -108 to 37°C (165 to 310K) in the presence of galactic cosmic-ray particles (GCRs). Their experiments revealed that the response of the perchlorates to the energetic electrons is dictated by the destruction of the perchlorate ion and the inherent formation of chlorates (ClO_3^-) plus atomic oxygen (O). Isotopic substitution experiments revealed that the oxygen is released solely from the perchlorate ion and not from the water of hydration (H_2O). The atomic oxygen recombines to molecular oxygen (O_2) within the perchlorates, with the overall yield of molecular oxygen increasing as the temperature drops from -13 to -113°C (260 to 160K). Perchlorate could also lead to transient, metastable brines by way of deliquescence, even under current climate conditions, ⁵⁷ and therefore plays a role in the meagre hydrological cycle on Mars. Deliquescence is the process of absorption of water vapor by salts, leading to the formation of a saturated aqueous solution. In addition, perchlorate can be used as a terminal electron acceptor by a variety of prokaryotes, ^{58,59} which has potential implications for habitability of Martian soils. Davila *et al.* ⁵³ reported that, although perchlorate is the only Cl-oxyanion that has been found on Mars, studies on Earth show that perchlorate co-occurs with chlorate (ClO_3^-) in all environments, often at equimolar concentrations. In addition, ionizing radiation can decompose perchlorate into other reactive Cl-oxyanions such as chlorite (ClO_2^-) and hypochlorite (ClO^-). ¹³ These more reactive species can cause corrosion of metallic components used on astronaut suits, instruments, landed spacecraft, and surface operations equipment.

Clays were detected on Mars by the Mars Express Orbiter, ^{60,61} with an abundance of 4–5 wt % in the regolith, calculated from the Thermal Emission Spectrometer data of the Mars Exploration Rovers. ⁶² Curiosity analyzed mudstone samples in Gale Crater, which showed the presence of clays in this region. ⁶³ Clays could be widespread on the planet and in some regions hidden under a layer of volcanic residue. Clays themselves are not oxidants, but they can catalyze oxidation reactions likely to take place in the regolith.

Since the detection of perchlorates on Mars, ¹⁷ several studies have been aimed at understanding their effects on the habitability of the planet. The recent work of J. Wadsworth and C.S. Cockell ⁶⁴ showed the significant bactericidal effects of UV-irradiated perchlorate on life at ambient temperatures and under Martian conditions. This finding is relevant to corrosion since it showed that, when irradiated with a simulated Martian UV-flux, perchlorate is more reactive at ambient temperatures and ambient conditions. The study also showed that two other components of the Martian surface, iron oxides and hydrogen peroxide, act in synergy with perchlorates to cause a 10.8-fold increase in cell death when compared to cells exposed to UV radiation after 60 seconds of exposure. The mechanism of perchlorate action on cells is likely to be its degradation to deleterious reactive oxygen species, such as hypochlorite (ClO^-), commonly known as chlorine bleach, and chlorite (ClO_2^-). Similar photoproducts have been

previously observed in perchlorate irradiated with ionizing radiation.^{16,65} C.D. Georgiou *et al.*⁶⁶ reported that γ -radiolyzed perchlorate-containing Mars soil salt analogues (in a CO_2 atmosphere) generate, upon H_2O wetting, the superoxide radical ($\text{O}_2^{\cdot-}$), hydrogen peroxide (H_2O_2), and hydroxyl radicals (OH^{\cdot}). This study also validated that analogue radiolysis forms oxychlorine species that, in turn, can UV-photolyze to OH^{\cdot} upon UV photolysis. Additionally, UV photolysis of the perchlorate γ -radiolysis product chlorite (ClO_2^-) generated the oxychlorine products trihalide (Cl_3^-), chlorine dioxide free radical (ClO_2^{\cdot}), and hypochlorite (ClO^-), with the formation of OH^{\cdot} by UV photolysis of ClO^- . Figure 8 shows the standard reduction potentials of different oxychlorine species in acidic and basic conditions, with the oxidation number of Cl shown at the top for each species.

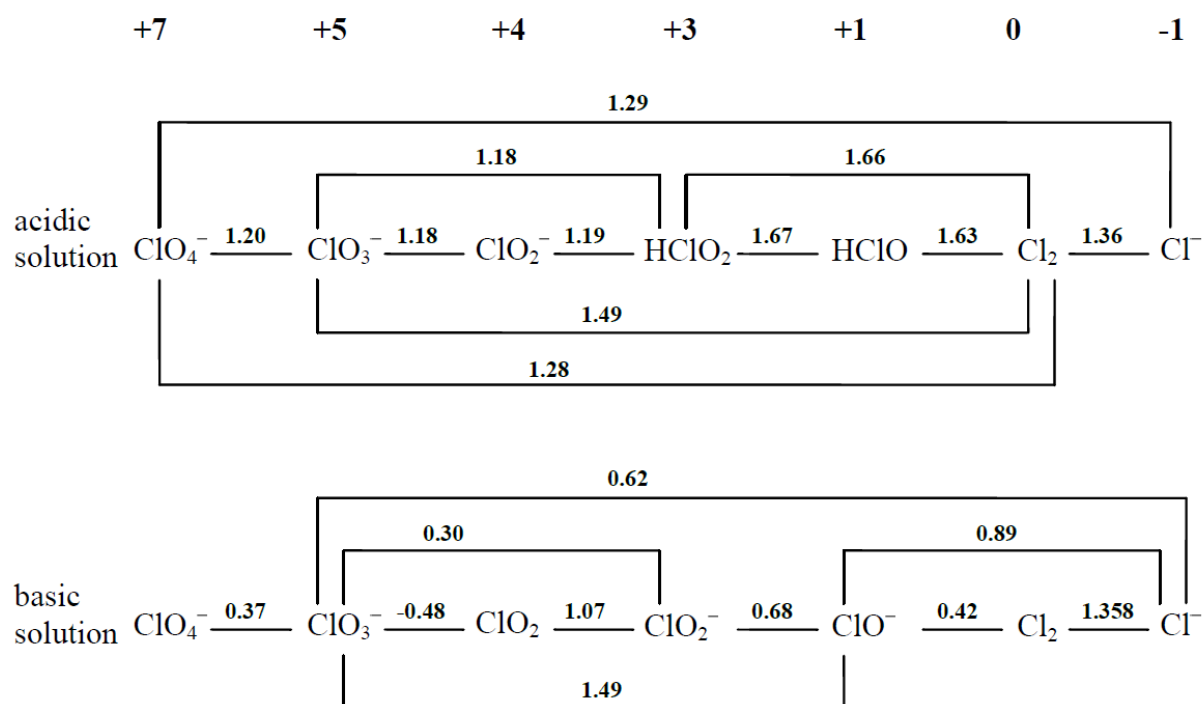


Figure 8. Standard reduction potential of oxychlorine species⁶⁷

A recent review paper by Lasne *et al.*⁶⁸ provides an excellent summary of the oxidants detected or proposed to be present at the surface of Mars (Table 2) in light of recent exploration results. These findings suggest the importance of conducting experiments to investigate the combined effects of Martian soil simulant, activated by surface photochemistry, as well as the influence of clays as catalysts, on materials relevant to long-duration surface operations on Mars.

Table 2. Oxidants Detected or Suggested to Be Present on Mars⁶⁸

Group	Oxidant	Detected or Suggested	Origin
Perchlorate salt	ClO_4^-	Detected ^{18,29}	Produced in the atmosphere Produced by UV irradiation of chlorine-bearing minerals
Iron-bearing species	Fe_2O_3	Detected ^{*,69,70}	Thermodynamically stable on Mars' surface

	FeO ₄ ²⁻	Suggested ⁷¹	Minor phase (thermodynamically unstable)
	Clays	Suggested ^{**72}	Alteration of silicates in presence of water
Reactive oxygenated species	Peroxide or superoxide species	Suggested ^{14,73,74,75}	Detection of species that could form superoxides or peroxides
	Superoxide radical ion (O ₂ ⁻)	Suggested ^{15,58,76,77}	Formed in the presence of oxygen and UV radiation Formed with H ₂ O ₂
H ₂ O ₂	H ₂ O ₂ in the atmosphere	Detected ^{78,79}	Produced photochemically and during dust devils and storms
	H ₂ O ₂ in the regolith	Suggested ^{80,81,82,83}	Diffusion of H ₂ O ₂ formed in the atmosphere Produced by interaction between minerals and water

*The Fe₂O₃ group includes hematite and maghemite; only hematite has been detected at the surface of Mars.

** The clays studied to explain the Viking results were enriched with iron; the presence of this type of clay on Mars has not been confirmed yet.

Materials Behavior in the Mars Environment

There have been previous efforts directed towards developing an electrochemical sensor to analyze the corrosive nature of the brine present under the surface of Mars.⁸⁴ These efforts were based on discussions, among planetary scientists in the early 2000s, that the subsurface of Mars is a brine-like mixture (many years before the evidence of their existence was published).^{9,10} Based upon these suppositions, it was anticipated that the sensor would be integrated into an advanced electronic tongue⁸⁵ that would be incorporated into a subsurface explorer being developed at NASA/JPL at that time. The electrochemical sensor consisted of a series of anodic materials, and a single cathodic metal (zinc) in a configuration to be exposed to various electrolytes (shown on the left picture of Figure 9). Two deposition chambers were fabricated for use with the ceramic substrates. The open sample chamber was designed to test the functionality of the device with soil samples. The fluidics chamber was fabricated for use with aqueous samples (shown on the right picture of Figure 9).

The electrochemical sensor was designed to analyze the brine present on the surface of Mars. The sensor was capable of standard electrochemical investigations which included cyclic voltammetry and anodic stripping voltammetry. In addition, a galvanic cell array was used to investigate the corrosivity of solutions. Unfortunately, the advanced electronic tongue was not included in the instrumentation that was selected as a Phoenix payload.

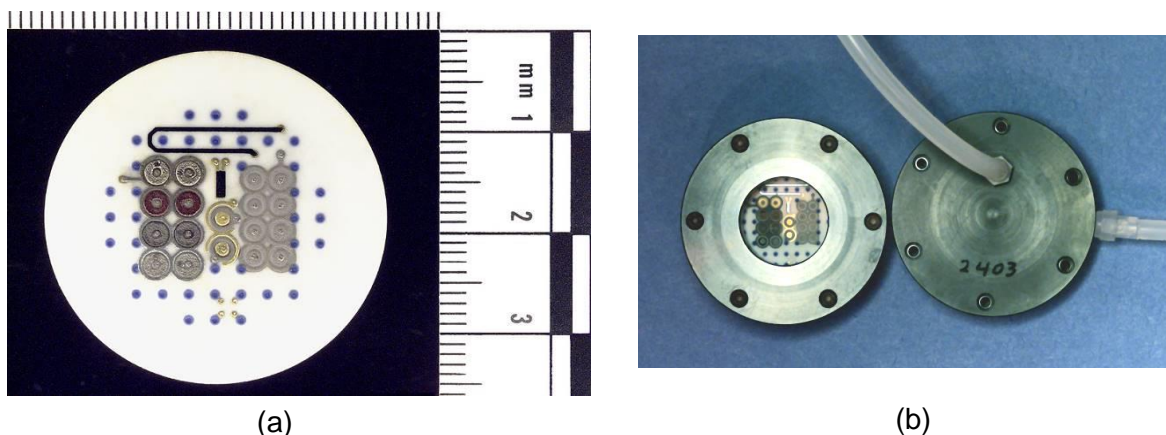


Figure 9. (a) Top-side of 3.3-cm diameter ceramic substrate showing individual sensor components. (b) Soil chamber with 3.3 cm diameter ceramic substrate inside (left) and fluidics chamber (right).

The wet chemistry laboratory (WCL) onboard Phoenix provided the first wet chemical measurements of soluble species in the Martian soil.⁸⁶ One of the most significant discoveries made by Phoenix was the high concentration of perchlorate in all three of the soil samples analyzed, roughly equivalent to about 0.6 wt%. Currently on Mars, the rover Curiosity (also known as the MSL) is refining our understanding of the Martian surface.⁸⁷ Although there are several complex science instruments aboard the rover, there are no electrochemical sensors.

The Mars 2020 mission will address high-priority science goals for Mars exploration, including key questions about the potential for life on Mars. The mission takes the next step by not only seeking signs of habitable conditions on Mars in the ancient past, but also searching for signs of past microbial life itself. The Mars 2020 rover introduces a drill that can collect core samples of the most promising rocks and soils and set them aside in a "cache" on the surface of Mars. A future mission could potentially return these samples to Earth. That would help scientists study the samples in laboratories with special room-sized equipment that would be too large to take to Mars. The mission also provides opportunities to gather knowledge and demonstrate technologies that address the challenges of future human expeditions to Mars. These include testing a method for producing oxygen from the Martian atmosphere, identifying other resources (such as subsurface water), improving landing techniques, and characterizing weather, dust, and other potential environmental conditions that could affect future astronauts living and working on Mars.⁸⁸ The European Space Agency's ExoMars rover, also slated for a 2020 launch, will be outfitted with a drill designed to sample geology at depths of up to two meters. It includes an infrared spectrometer to characterize the mineralogy in the borehole. Once collected, a sample is delivered to the rover's analytical laboratory, which will perform mineralogical and chemistry determination investigations. Of special interest is the identification of organic substances. The rover is expected to travel several kilometers during its mission.⁸⁹

The mission is timed for a launch opportunity in July/August 2020 when Earth and Mars are in good positions relative to each other for landing on Mars. That is, it takes less power to travel to Mars at this time, compared to other times when Earth and Mars are in different positions in their orbits. To keep mission costs and risks as low as possible, the Mars 2020 design is based on NASA's successful Mars Science Laboratory mission architecture, including its Curiosity rover and proven landing system.

Although the current rover on Mars, Curiosity, does not have electrochemical sensors, it has captured images that can provide a visual indication of the interaction between materials and the Mars environment. A relevant example is shown in Figure 10.⁹⁰

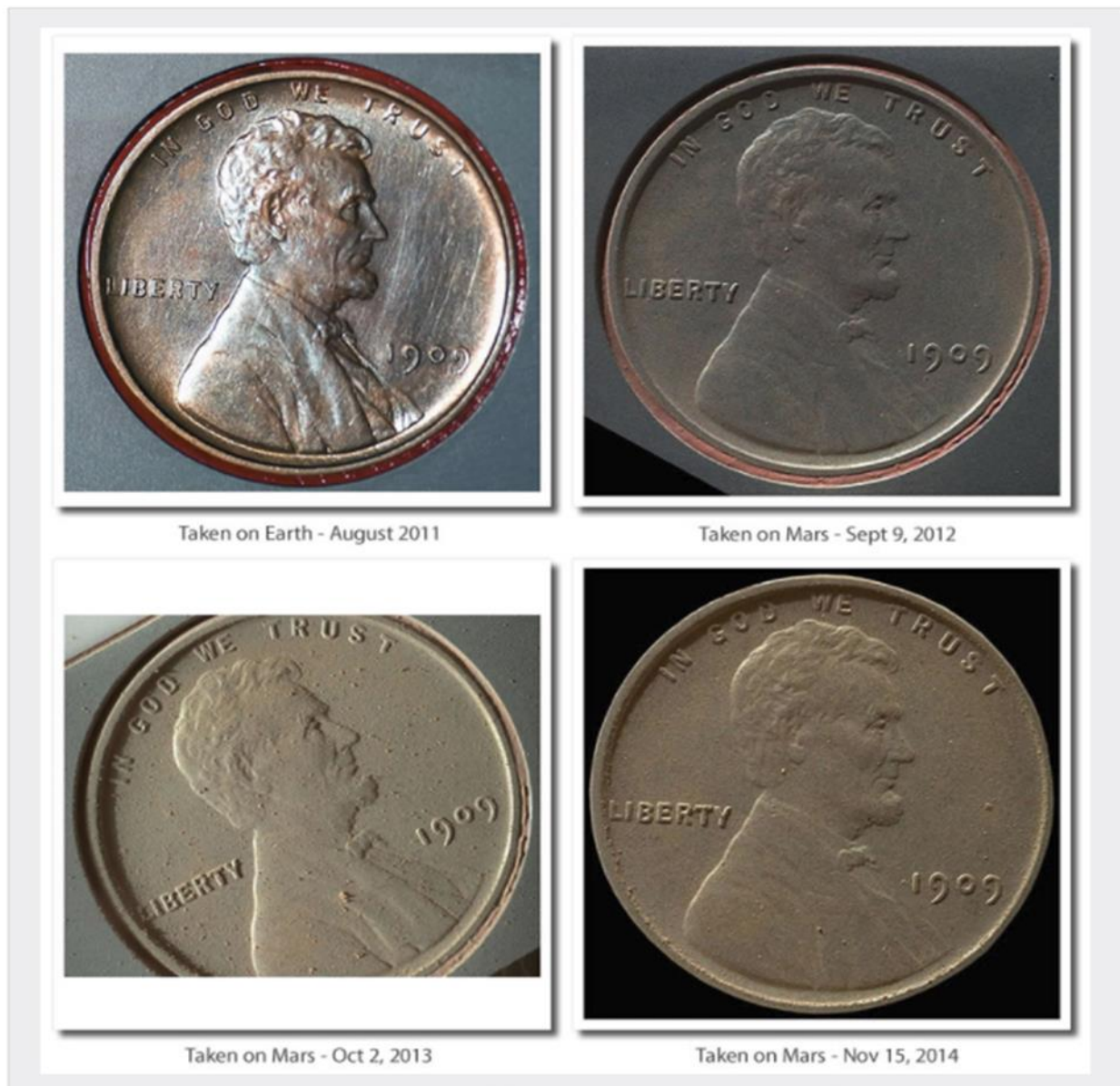


Figure 10. Four different photos of the 1909 VDB Lincoln Cent on Mars rover Curiosity. VDB are the initials of Victor David Brenner who designed the coin. The first photo was taken on Earth in August 2011. Subsequent photos were taken on Mars on September 9, 2012, October 2nd, 2013, and on November 15, 2013. Image credit: NASA, JPL-Caltech, MSSS.

The photos show the Lincoln cent that is attached to a calibration target used by the rover's camera known as the Mars Hand Lens Imager, or MAHLI (Figure 11). Curiosity was launched on Nov. 26, 2011 to search areas of Mars for past or present conditions favorable for life, and conditions capable of preserving a record of life. The rover landed on the planet on Aug. 6, 2012. It has been surveying a small portion of the planet ever since. This is the first time that a coin has been subjected to the conditions of another planet while being monitored. The only

change that can be visually observed on the pictures is the accumulation of Martian dust, which is interesting because the coin is mounted on a vertical position. Although the Lincoln cent is being used as a calibration target by the rover's camera, the photos appear to show no visual signs of corrosion of copper.

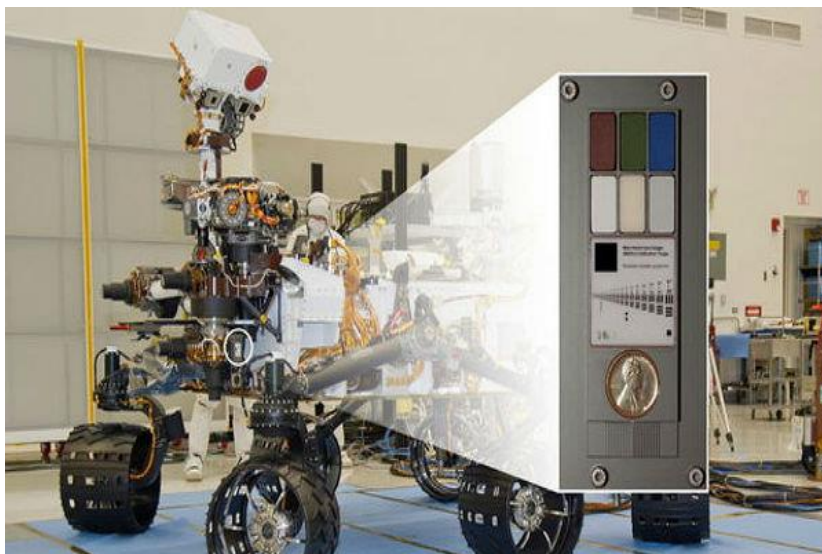


Figure 11. This image shows NASA's Mars rover Curiosity with an inset showing the calibration targets, including a 1909 Lincoln penny, at the end of its robotic arm.

Figure 12 shows a set of U.S. pennies, selected at random from a household coin jar, to show signs of corrosion. The pennies at the bottom (dated from 1999 to 2017) show very little or no visible signs of corrosion. The pennies at the top are dull and covered by corrosion products. Although the cause of corrosion is unknown, because the pennies were not subjected to a controlled experiment, it can be hypothesized that the pennies at the top were exposed to more corrosive environments than those at the bottom. When copper is exposed to air, its shiny copper color will transition to dull brown. At a later stage, the formation of copper sulfate, carbonate, and chloride salts, in varying concentrations will turn the surface green. This process is influenced by many factors such as: moisture, temperature, and the environment to which the metal has been exposed to.



Figure 12. U.S. pennies selected at random from a household jar of coins to show different states of corrosion: the pennies at the bottom (left to right) date from 1999, 2005, 2006, 2011, 2014, 2015, and 2017; the pennies at the top are corroded and only the second penny from the left has a visible date (1984).

The penny shown on Figure 10 shows no sign of corrosion. This is not surprising given that the penny has been exposed to the Martian atmosphere which contains only minor amounts of water (210 ppm).⁹¹

Chemical Weathering Rate Derived from Meteorites

Meteorites can be used to obtain information about their environment. Some meteorites are mostly iron like the “Egg Rock” meteorite found by Curiosity (Figure 13).⁹²



Figure 13. The dark, golf-ball-size object in this composite, colorized view from the ChemCam instrument on NASA's Curiosity Mars rover is a nickel-iron meteorite, as confirmed by analysis using laser pulses from ChemCam on Oct. 30, 2016. The grid of bright spots on the rock resulted from the laser pulses. Credit: NASA/JPL

The study of iron meteorites found by spacecraft exploring Mars such as the Mars Exploration rovers Spirit and Opportunity, as well as the MSL or Curiosity rover, can provide information on how the exposure to the Martian environment has affected them. Iron meteorites, like the one shown in Figure 13, will weather or oxidize as a result of their interaction with the environment. Scientists have used chemical analysis results gathered by the rovers to obtain an estimate for the rate of oxidation of the iron. C. Schroder *et al.*⁹³ used the oxidation of iron in stony meteorites, investigated by the Mars Exploration rover Opportunity at Meridiani Planum, to estimate the chemical rate of oxidation and concluded that the chemical weathering rates were about 1 to 4 orders of magnitude slower than that of similar meteorites found in Antarctica where the slowest rates are observed on Earth. The authors of the study suggest that the extremely slow weathering of meteorites, which contain metallic iron as a phase very sensitive towards chemical alteration or corrosion, is not a threat over the lifetime of a spacecraft and that the Opportunity rover is testament to that, showing no signs of corrosion after more than 12 years of operating on Mars (April 2016), in contrast to the concern expressed by Martin Torres *et al.* about the corrosive effects of chlorine-containing brines on spacecraft.¹¹

Electrochemical Corrosion of Minerals in Martian Rocks

In 2018,⁹⁴ the Curiosity rover (Figure 14) found evidence for abundant organic compounds in the ancient mudstone rocks in Gale Crater on Mars. These carbon molecules ranged from simple to fairly complex, but their actual origin was still un-known. They could be created by

abiotic processes (without life). Or they could be the molecular remains of once-living organisms. A new study⁹⁵ has shown one possible way that these or similar organics might have been created on Mars. The researchers studied organics found in three Martian meteorites – Tissint, Nakhla, and NWA 1950 – and compared them to the organics discovered by Curiosity. They found that both sets of organic carbon were quite similar, suggesting a possible similar origin and hypothesized that interactions among spinel-group minerals, sulfides, and a brine enable the electrochemical reduction of aqueous CO₂ to organic molecules.

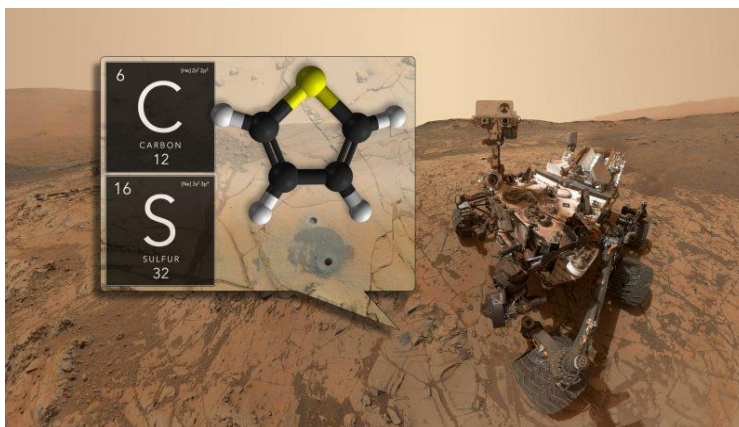


Figure 14. NASA's Curiosity rover found organic carbon compounds in ancient mudstones, similar to ones previously discovered in Martian meteorites. Credit: NASA/GSFC.

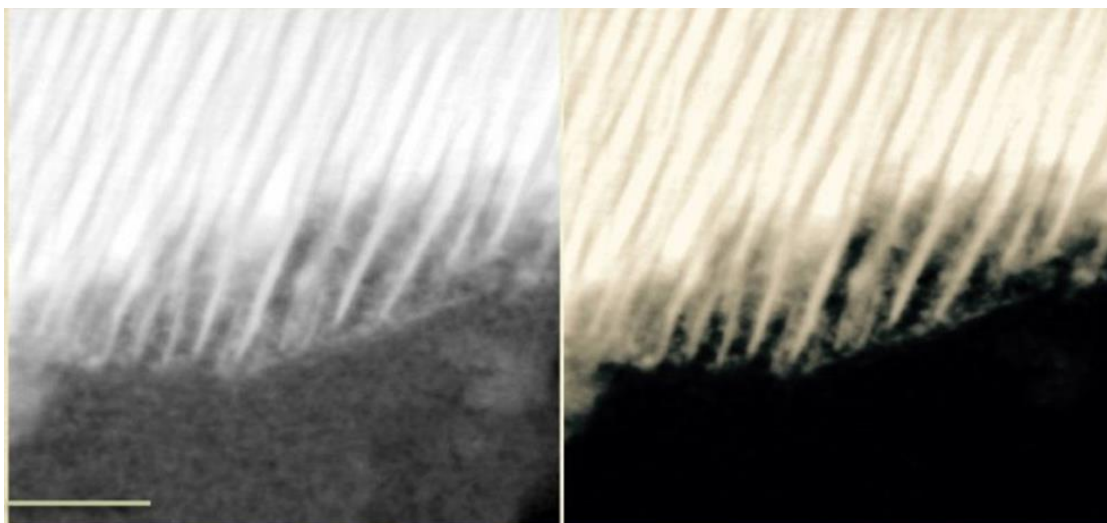


Figure 15. A high-resolution transmission electron micrograph (scale 50nm), from a transmission electron microscope, of a grain from the Martian meteorite Nakhla. The organic carbon layers are found between the intact “tines.” This texture is created when the volcanic minerals of the Martian rock interact with a salty brine and become the anode and cathode of a naturally occurring galvanic cell in a corrosion reaction. This reaction would then have enough energy – under certain conditions – to synthesize organic carbon. Image credit: Andrew Steele/Science Advances.⁹⁴

The discovery that natural systems can essentially form a small galvanic cell that drives electrochemical reactions between minerals and surrounding liquid brine has implications that need to be considered when selecting materials, relevant to surface operations on Mars. Like minerals, metallic materials, such as aluminum alloys, can react with the brines and degrade (corrode) in the process.

Summary

Our extensive literature search on the available data relevant to Mars corrosion, or the lack thereof, confirmed the need for further investigation of the interaction between materials, used for spacecraft and structures to support long-term surface operations on Mars, and the Mars environment, as it was first suggested by F.J. Martin-Torres *et al.* and recommended in the “Mars Science Goals, Objectives, Investigations, and Priorities: 2015 Version,” prepared by the Mars Exploration Program Analysis Group (MEPAG) Goals Committee.

The quest for life on Mars has been to “follow the water.” Water is critical for life as we know it and it is also critical for corrosion, given that an aqueous electrolyte solution is one of the requirements for corrosion to occur. It is important to note that a great deal of the data relevant to corrosion on Mars is available from investigations aimed at explaining the results obtained from experiments that were designed to look for evidence of life on Mars. Oxidants were hypothesized as being responsible for the lack of organics found by the Viking mission which reached Mars in 1976. The presence of perchlorates in Mars regolith was identified by NASA’s Phoenix Lander in 2009, and demonstrated as a component of transient liquid brines on September 2015. These findings are relevant to corrosion since oxidants can corrode materials and transient liquid brines can serve as the electrolyte solution that supports corrosion. Furthermore, the finding by J. Wadsworth and C. S. Cockell in 2017 that perchlorates become more bactericidal when irradiated with simulated Martian UV flux, and that other components of the Martian surface act in synergy with the irradiated perchlorates, has implications for the corrosive interaction between materials and the brines that are worth of investigation. It is well known that perchlorates here on Earth are powerful oxidants at high temperatures but stable at room and lower temperatures. However, it is not known how perchlorates interact with materials when they are activated by high energy radiation as it exists on Mars.

Our simple preliminary experiments, designed to look at the interaction between spacecraft AA7075-T73 aluminum alloy and the gases present in the Mars atmosphere, at 20°C and a pressure of 700 Pa, showed that there is an interaction between the small amount of oxygen present in the Mars gas and the aluminum alloy. Further studies are needed to consider other important components and conditions of the Mars environment that can affect this interaction such as: the presence of brines that can act as an electrolyte, the effect of radiation on the oxidizing properties of perchlorates, the possible catalytic effects of the clays present in the Martian regolith, as well as the temperature and pressure conditions.

To understand the corrosion mechanisms on Mars, the interaction between materials and the Martian environment should be studied under simulated Martians conditions that include: Martian atmospheric conditions, soil chemistry, radiation, and exposure to brine water.

The goal of the recommended work would be:

- (1) To gain a further understanding of the corrosion behavior of spacecraft materials on Mars by investigating the effect of each Martian environment parameter (individually and in combination) on their corrosion-relevant properties.
- (2) Evaluate the corrosion behavior of selected candidate materials, with different surface corrosion protection treatments, from several candidate aerospace alloys under simulated Martian conditions. These materials should include aluminum alloys, stainless steels, and titanium.
- (3) Make recommendations on corrosion resistant materials and surface treatments to enable long-term surface operations in support of human exploration missions in the Martian environment.

References

- ¹ U.S. Department of Transportation, Federal Aviation Administration, Aviation Maintenance Technician Handbook, Aircraft Cleaning and Corrosion Control, http://www.avia-it.com/act/biblioteca/libri/PDF_Libri_By_Federal_Aviation_Agency/Aviation%20Maintenance%20Technician%20Handbook%20-%20General.pdf (Accessed June 3, 2019).
- ² M. Pourbaix, “Atlas d’equilibres ‘electrochimiques,” p. 171, Gauthier-Villars & Cie, Paris (1963).
- ³ E. C. Deltombe, M. Vanleughenaghe, and M. Pourbaix, Atlas of electrochemical equilibria in aqueous solution, Pergamon Press, Oxford, UK (1966).
- ⁴ V. Vargel, Corrosion of Aluminum, Elsevier, Oxford (2004).
- ⁵ R. Whitwam, NASA reports two new breaks in Curiosity rover’s wheels, <https://www.extremetech.com/extreme/246398-nasa-reports-two-new-breaks-curiosity-rovers-wheel> (Accessed June 3, 2019).
- ⁶ Curiosity Mars rover wheel damage: The problem and solutions, <https://forums.spacebattles.com/threads/curiosity-mars-rover-wheel-damage-the-problem-and-solutions.309527/> (Accessed June 3, 2019).
- ⁷ Planetary Protection Knowledge Gaps for Human Extraterrestrial Missions Workshop Report, Conducted at NASA Ames Research Center, March 24-26, 2015, Moffett Field, CA, <https://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/20160012793.pdf> (Accessed June 3, 2019).
- ⁸ Mars Science Goals, Objectives, Investigations, and Priorities: 2015 Version, Mars Exploration Program Analysis Group (MEPAG), Finalized and Published online: June 19, 2015, Prepared by the MEPAG Goals Committee, https://mepag.jpl.nasa.gov/reports/MEPAG%20Goals_Document_2015_v18_FINAL.pdf (Accessed June 3, 2019).
- ⁹ F. J. Martin-Torres, *et al.*, Transient liquid water and water activity at Gale crater on Mars, *Nature Geoscience* 8, 357-361 (May 2015).
- ¹⁰ L. Ojha, M. B. Wilhelm, S. L. Murchie, A. S. McEwen, J. J. Wray, J. Hanley, M. Massé, and M. Chojnacki, Spectral evidence for hydrated salts in recurring slope lineae on Mars, *Nature Geoscience*, 8, 829-832 (2015).
- ¹¹ F. J. Martin-Torres and M.P. Zorzano, Should we invest in Martian brine research to reduce Mars exploration costs? *Astrobiology*, 17, (2017).
- ¹² F. Schmidt, F. Andrieu, F. Costard, , M. Kocifaj, and A.G. Meresescu, Formation of recurring slope Lineae on Mars by rarefied gas-triggered granular flows, *Nature Geoscience* 10, 270-273 (2017).
- ¹³ H. P. Klein *et al.*, the Viking Biological Investigation: Preliminary Results, *Science* 194 (4260), 99-105 (October 1, 1976).
- ¹⁴ V. I. Oyama, B. J. Berdahl, The Viking Gas Exchange Experiment Results from Chryse and Utopia Surface Samples, *Journal of Geophysical Research* 82(28), 4669-4676 (September 30, 1977).
- ¹⁵ A. S. Yen, S. S. Kim, M. H. Hecht, M. S. Frant, B. Murray, Evidence that the reactivity of the Martian soil is due to superoxide ions, *Science* 289, 1909-1912 (September 15, 2000).
- ¹⁶ R. C. Quinn, H. F. H. Martucci, S. R. Miler, C. E. Bryson, F. J. Grunthaner, and P. J. Grunthaner, Perchlorate Radiolysis on Mars and the Origin of Martian Soil Reactivity, *Astrobiology* 13 (6), 515-520 (June 2013).
- ¹⁷ R. A. Kerr, Pesky perchlorates all over Mars, *Science* 340 (6129), 138 (April 1, 2013).

-
- ¹⁸ S. Kounaves, B. L. Carrier, G. D. O'Neil, S. T. Stroble, and M.W. Claire, Evidence of Martian perchlorate, chlorate and nitrate in Mars meteorite EETA79001: Implications for oxidants and organics. *Icarus* 229, 206-213 (2014).
- ¹⁹ Curiosity's Wheel Damage, <http://www.leonarddavid.com/curiositys-wheel-damage-effects-of-corrosion/> (accessed June 3, 2019).
- ²⁰ C Vargel, M. Jacques, and M. P. Schmidt, *Corrosion of Aluminium*, Elsevier B. V., (2004).
- ²¹ L. M. Calle, W. Li, M. R. Johansen, J. W. Buhrow, and C. I. Calle, *Corrosion on Mars: An Investigation under Relevant Simulated Martian Environments*, NASA/Technical Publication, 2017-219743, 2017.
- ²² F.Cain, "Composition of the Earth's Atmosphere," <https://www.universetoday.com/26656/composition-of-the-earths-atmosphere/>, (Accessed May 7, 2018).
- ²³ S. S. Courtright, "Effects of Mars Atmosphere on Arc Welds: Phase 2," NASA Technical Publication, NASA/TM-2018-219850, 2018.
- ²⁴ J.F. Buenestado, M.P. Zorzano, and J. Martín-Torres, Liquid Water at Crater Gale, Mars, *Astrobiology Outreach*, 3: 131, (2015).
- ²⁵ SAM: Sample Analysis at Mars on the Rover Curiosity, <https://ssed.gsfc.nasa.gov/sam/> (Accessed June 3, 2019).
- ²⁶ MSL: DAN (Dynamic Albedo of Neutrons), <http://pds-geosciences.wustl.edu/missions/msl/dan.htm> (Accessed June 3, 2019).
- ²⁷ M. P. Zorzano, E. Mateo-Marti, O. Prieto-Ballesteros, S. Osuna, and N. Renno, Stability of liquid saline water on present day Mars, *Geophys. Res. Lett.*, 36, L20201, (2009).
- ²⁸ L. Leshin, *et al.*, MSL Science Team, Volatile, isotope and organic analysis of Martian fines with the Mars Curiosity rover, *Science* 341, (2013).
- ²⁹ M.H. Hecht *et al.*, Detection of perchlorate and the soluble chemistry of Martian soil at the Phoenix lander site. *Science* 325:64–67, (2009).
- ³⁰ R. Navarro-Gonzalez, E. Vargas, J. de la Rosa, A.C.Raga, and C.P. McKay, Reanalysis of the Viking results suggests perchlorate and organics at midlatitudes on Mars. *J Geophys Res* 115, (2010).
- ³¹ J.M. Keller *et al.*, Equatorial and midlatitude distribution of chlorine measured by Mars Odyssey GRS. *J Geophys. Res.* (2006).
- ³² W.C. Feldman *et al.*, Global distribution of near-surface hydrogen on Mars. *J Geophys. Res.* 109:E09006, (2004).
- ³³ P.D. Archer *et al.*, Abundances and implications of volatile-bearing species from evolved gas analysis of the Rocknest aeolian deposit, Gale Crater, Mars, *J. Geophys. Res.: Planets* 119:237–254, (2014).
- ³⁴ G.M. Brown and B. Gu, The Chemistry of Perchlorate in the Environment, in *Perchlorate: Environmental Occurrence, Interactions and Treatment*, Springer (2006).
- ³⁵ E.T. Urbansky, *Perchlorate Chemistry: Implications for Analysis and Remediation*, CRC Press, (1998) <https://clu-in.org/download/contaminantfocus/perchlorate/urbansky2.pdf> (Accessed June 3, 2019).
- ³⁶ S.K. Mendiratta, R.L. Dotson, and R.T. Brooker, Perchloric acid and perchlorates, in Kirk-Othmer *Encyclopedia of Chemical Technology*, 4th Ed., Vol.18, J.I. Kroschwitz, and M. Howe-Grant, eds. New York: John Wiley and Sons, (1996).
- ³⁷ G. Singh, I.P.S. Kapoor, and S. Dubey, Kinetics of Thermal Decomposition of Ammonium Perchlorate with Nanocrystals of Binary Transition Metal Ferrites, *Propellants, Explosives, Pyrotechnics*, **34**, 1-6, (2008).
- ³⁸ D. P. Glavin *et al.* Evidence for perchlorates and the origin of chlorinated hydrocarbons detected by SAM at the Rocknest aeolian deposit in Gale Crater, *Journal of Geophysical Research: Planets*, 118, 1955-1973, (2013).
- ³⁹ J. A. Conkling, *Chemistry of Pyrotechnics: Basic Principles and Theory*, Marcel Decker, INC., (1985).

-
- ⁴⁰ H. Attaway and M. Smith, Reduction of perchlorate by an anaerobic enrichment culture, *Journal of Industrial Microbiology*, 12, 408-412, (1993).
- ⁴¹ I.J. Polmear, *Light Alloys*, 2nd ed., Edward Arnold, London, (1969).
- ⁴² M. Elboujdaini, E. Ghali, A. and Galibois, *J. Appl. Electrochem.* 18, 257, (1988).
- ⁴³ J. Wolka and S. Virtanen, *Acta Mater.* 55 6666, (2007).
- ⁴⁴ K. Genel, *Scripta Mater.* 57, 297, (2007).
- ⁴⁵ K.-H. Na and S.-I. Pyun, *Corros. Sci.* 50, 248, (2008).
- ⁴⁶ M.K. Cavanaugh, N. Birbilis, R.G. Buchheit, F. Bovard, *Scripta Mater.* 56, 995, (2007).
- ⁴⁷ H. Ezuber, A., El-Houd, and F. El-shawesh, *Mater. Design* 29 (4), 801-805, (2008).
- ⁴⁸ J. Painot and J. Augustynski, *Electrochim. Acta*, 20, 747, (1975).
- ⁴⁹ M. Ujvari, G. Lang, and G. Horanyi, *J. Appl. Electrochem.* 31, 1171, (2001).
- ⁵⁰ M. Ujvari, G. Lang, G. Horanyi, *J. Appl. Electrochem.* 32, 581, (2002).
- ⁵¹ J.L. Trompette, L. Arurault, S. Fontorbes, and L. Massot, Influence of the anion specificity on the electrochemical corrosion of anodized aluminum substrates, *Electrochimica Acta*, 55, pp. 2901–2910, (2010).
- ⁵² M.A. Amin, S. S. Abd El Rehim, S.O. Moussa, and A. S. Ellithy, Pitting corrosion of Al and Al–Cu alloys by ClO_4^- ions in neutral sulphate solutions, *Electrochimica Acta*, 53, pp. 5644–5652, (2008).
- ⁵³ A.F. Davila, D. Willson, J.D. Coates, and C.P. McKay, Perchlorate on Mars: a chemical hazard and a resource for humans, *International Journal of Astrobiology*, 1-5, (2013).
- ⁵⁴ A.M. Turner, M.J. Abplanalp, and R. I. Kaiser, Mechanistic Studies on the Radiolytic Decomposition of Perchlorates on the Martian Surface, *The Astrophysical Journal*, 820:127, (2016).
- ⁵⁵ D. R. Parker, Perchlorate in the environment: The emerging emphasis on natural occurrence, *Environ. Chem.*, 6, 10 – 27, (2009).
- ⁵⁶ D. C., Catling, *et al.*, Possible atmospheric origins of perchlorate on Mars, *Lunar Planet. Sci. Conf.*, XL, Abstract 1567. (2009).
- ⁵⁷ N.O. Rennó, *et al.*, Possible physical and thermodynamical evidence for liquid water on the Phoenix landing site. *Geophysical Research Letters*, 114, E00E03. (2009).
- ⁵⁸ J.D. Coates and L.A. Achenbach, Microbial perchlorate reduction: rocket-fueled metabolism. *Nat. Rev. Microbiol.* 2, 569–580, (2004).
- ⁵⁹ J.D. Coates and L.A. Achenbach, The microbiology of perchlorate reduction and its bioremediative applications. In: *Perchlorate, Environmental Occurrence, Interactions and Treatment*. ed. B. Gu, and J.D. Coates, Springer, New York, p 279–295. (2006).
- ⁶⁰ J.-P., Bibring, Y. Langevin, , A. Gendrin, B. Gondet, F. Poulet, M. Berthe, A. Soufflot, R. Arvidson, N. Mangold, J. Mustard, and P. Drossart, Mars surface diversity as revealed by the OMEGA/Mars Express observations. *Science* 307: 1576–1581, (2005).
- ⁶¹ F. Poulet, J.-P. Bibring, J.F. Mustard, A. Gendrin, N. Mangold, Y. Langevin, R.E. Arvidson, B. Gondet, and C. Gomez, Phyllosilicates on Mars and implications for early martian climate. *Nature* 438:623–627. (2005).
- ⁶² H.Y. McSween, Jr., I.O. McGlynn, and A.D. Rogers, Determining the modal mineralogy of Martian soils. *J Geophys. Res: Planets* 115, (2010).
- ⁶³ D.T., Vaniman, *et al.*, MSL Science Team, Mineralogy of a mudstone at Yellowknife Bay, Gale Crater, Mars. *Science* 343, (2014). D.T., Vaniman, *et al.*, MSL Science Team, Mineralogy of a mudstone at Yellowknife Bay, Gale Crater, Mars. *Science* 343, (2014).
- ⁶⁴ J. Wadsworth and C. S. Cockell, Perchlorates on Mars enhance the bactericidal effects of UV light, *Scientific Reports* 7, published online July 7, 2017, <https://www.nature.com/articles/s41598-017-04910-3> (accessed June 3, 2019).
- ⁶⁵ H.F.H. Martucci, Characterization of Perchlorate Photostability under Simulated Martian Conditions, *Proc. Nat. Conf. Undergrad. Res. (NCUR)*, 1359-1363 (2012).

-
- ⁶⁶ C.D. Georgiou, D. Zisimopoulos, E. Kalaitzopoulou, and R.C. Quinn, Radiation-Driven Formation of Reactive Oxygen Species in Oxychlorine-Containing Mars Surface Analogues, *Astrobiology*, **17**, (2017).
- ⁶⁷ A.J. Bard, R. Parsons, and J. Jordan, Standard potentials in aqueous solutions. || IUPAC (Marcel Dekker), New York, (1985).
- ⁶⁸ J. Lasne, A. Noblet, C. Szopa, R. Navarro-Gonzalez, M. Cabane, O. Poch, F. Stalport, P. Francois, S.K. Atreya, and P. Coll, Oxidants at the Surface of Mars: A Review in Light of Recent Exploration Results, *Astrobiology*, Volume 16, Number 12, (2016).
- ⁶⁹ P.R. Christensen, J.L. Bandfield, R.N. Clark, K.S. Edgett, V.E. Hamilton, T. Hoefen, H.H. Kieffer, and R.O. Kuzmin, M.D. Lane, M.C. Malin, R.V. Morris, J.C. Pearl, R. Pearson, T.L. Roush, S.W. Ruff, and M.D. Smith, Detection of crystalline hematite mineralization on Mars by the Thermal Emission Spectrometer: evidence for near-surface water. *J. Geophys. Res.*, 105:9623–9642, (2000).
- ⁷⁰ P.R., Christensen, M.B. Wyatt, T.D. Glotch, A.D. Rogers, S. Anwar, R.E. Arvidson, J.L. Bandfield, D.L. Blaney, C. Budney, W.M. Calvin, A. Faracaro, R.L. Fergason, N. Gorelick, T.G. Graff, V.E. Hamilton, A.G. Hayes, J.R. Johnson, A.T. Knudson, H.Y. McSween, G.L. Mehall, L.K. Mehall, J.E. Moersch, R.V. Morris, M.D. Smith, S.W. Squyres, S.W. Ruff, and M.J. Wolff, Mineralogy at Meridiani Planum from the Mini-TES experiment on the Opportunity Rover, *Science* 306:1733–1739, (2004).
- ⁷¹ A.I. Tsapin, M.G. Goldfeld, G.D. McDonald, K.H. Nealson, B. Moskovitz, P. Solheid, K.M. Kemner, S.D. Kelly, and K.A. Orlandini, Iron(VI): hypothetical candidate for the Martian oxidant. *Icarus* 147:68–78, (2000).
- ⁷² J. Carter, F. Poulet, J.-P. Bibring, and S. Murchie, Detection of hydrated silicates in crustal outcrops in the northern plains of Mars, *Science* 328:1682–1686, (2010).
- ⁷³ C. Ponnamperna, A. Shimoyama, M. Yamada, T. Hobo, and R. Pal, Possible surface reactions on Mars: implications for Viking biology results. *Science* 197:455–457, (1977).
- ⁷⁴ T.R. Blackburn, H.D. Holland, and G.P. Ceasar, Viking gas exchange reaction: simulation on UV-irradiated manganese dioxide substrate, *J. Geophys. Res.* 84:8391–8394, (1979).
- ⁷⁵ H.P. Klein, The Viking biological experiments on Mars, *Icarus* 34:666–674, (1978).
- ⁷⁶ S.F.S. Chun, K.D. Pang, J.A. Cutts, and J.M. Ajello, Photocatalytic oxidation of organic compounds on Mars, *Nature* 274:875–876, (1978).
- ⁷⁷ A.P. Zent, A.S. Ichimura, R.C. Quinn, and H.K. Harding, The formation and stability of the superoxide radical ($O_2^{\cdot-}$) on rock-forming minerals: band gaps, hydroxylation state, and implications for Mars oxidant chemistry. *J. Geophys. Res.* 113, (2008).
- ⁷⁸ R.T. Clancy, B.J. Sandor, and G.H. Moriarty-Schieven, A measurement of the 362 GHz absorption line of Mars atmospheric H_2O_2 . *Icarus* 168:116–121., (2004).
- ⁷⁹ T. Encrenaz, B. Bezard, T.K. Greathouse, M.J. Richter, J.H. Lacy, S.K. Atreya, A.S. Wong, Lebonnois S., F. Lefevre, and F. Forget, Hydrogen peroxide on Mars: evidence for spatial and seasonal variations. *Icarus* 170:424–429, (2004).
- ⁸⁰ C.F. Chyba, S.W. Squyres, and C. Sagan, Depth to unoxidized material in the Martian regolith [abstract 1082]. In 20th Lunar and Planetary Science Conference Abstracts, Lunar and Planetary Institute, Houston, (1989).
- ⁸¹ M.A. Bullock, C.R. Stoker, C.P. McKay, and A.P. Zent, A coupled soil-atmosphere model of H_2O_2 on Mars, *Icarus* 107:142–154, (1994).
- ⁸² H. Hartman, and C.P. McKay, Oxygenic photosynthesis and the oxidation state of Mars. *Planet. Space. Sci.* 43:123–125, (1995).
- ⁸³ A.P. Zent, On the thickness of the oxidized layer of the Martian regolith, *J. Geophys. Res.* 103:31491–31498, (1998).
- ⁸⁴ M.R. Kolody, M.G. Buehler, and L.M. Calle, “Response of a Galvanic Cell Array to Corrosive Solutions in an Advanced electronic Tongue for Subsurface Explorers,” Paper No. 1204, 2003 IEEE Aerospace Conference, Big Sky, Montana, 2003.

-
- 85 M. G. Buehler, G. M. Kuhlman D. Keymeulen and S. Kounaves. “Advanced Electronic Tongue Concept”, 2002 IEEE Aerospace Conference, Big Sky, Montana, (2002).
- ⁸⁶ S. P. Kounaves, M. H. Hecht, J. Kapit, et al., “Wet Chemistry Experiments on the 2007 Phoenix Mars Scout Lander Mission: Data Analysis and Results. J. Geophys. Res. 115: E00E10. Doi: 10.1029/2009JEOO3424, (2010).
- ⁸⁷ K. M. McElhoney, G. D. O’Neil, and S. P. Kounaves, “Extraterrestrial,” in Environmental Analysis by Electrochemical Sensors and Biosensors: Fundamentals, Volume 1; Fundamentals, edited by L. M. Moretto and K. Kalcher, Springer, pp. 131-154, (2014).
- ⁸⁸ Mars Exploration, “2020 Mission Plans,”
<https://mars.nasa.gov/programmissions/missions/future/mars2020/> (Accessed June 3, 2019).
- ⁸⁹ European Space Agency, About Robotic Exploration, Exomars Mission 2020,
<http://exploration.esa.int/mars/48088-mission-overview/> (Accessed June 3).
- ⁹⁰ “1909 Lincoln Cent on Mars in NASA Astronomy Pic of the Day,”
<http://www.coinnews.net/2014/12/12/1909-lincoln-cent-on-mars-in-nasa-astronomy-pic-of-the-day/>
(accessed June 3, 2019).
- ⁹¹ Mars Fact Sheet, <https://nssdc.gsfc.nasa.gov/planetary/factsheet/marsfact.html>, (Accessed June 3, 2019).
- ⁹² Curiosity Mars Rover Checks Odd-looking Iron Meteorite,
<https://www.jpl.nasa.gov/news/news.php?feature=6667>, (Accessed June 3, 2019).
- ⁹³ C. Schroder, P. A. Bland, M. P. Golombek, J. W. Ashley, N. H. Warner, and J. A. Grant, “Amazonian chemical weathering rate derived from stony meteorite finds at Meridiani Planum on Mars,” Nature Communications, November 2016, <https://www.nature.com/articles/ncomms13459.pdf> (Accessed June 3, 2019).
- ⁹⁴ NASA Finds Ancient Organic Material, Mysterious Methane on Mars, <https://www.nasa.gov/press-release/nasa-finds-ancient-organic-material-mysterious-methane-on-mars>, (Accessed June 3, 2019, 2019).
- ⁹⁵ A. Steele1, L. G. Benning, R. Wirth, S. Siljeström, M. D. Fries, E. Hauri, P. G. Conrad, K. Rogers, J. Eigenbrode, A. Schreiber, A. Needham, J. H. Wang, F. M. McCubbin, D. Kilcoyne, and J. D. Rodriguez Blanco, “Organic synthesis on Mars by electrochemical reduction of CO₂,” Sci. Adv. Vol 4, No. 10, eaat5118, (2018).