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Corrosion on Mars

An Investigation of Corrosion Mechanisms under Relevant Simulated Martian Environments

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Abstract

This one-year project was selected by NASA’s Science Innovation Fund in FY17 to address Corrosion on Mars which is a problem that has not been addressed before. 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 given that there is no data regarding 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 is 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, and by performing preliminary laboratory experiments under relevant simulated Martian conditions. This project was motivated by the newly found evidence for the presence of transient liquid brines on Mars that coincided with the suggestion, by a team of researchers, that some of the structural degradation observed on Curiosity's wheels may be caused by corrosive interactions with the brines, while the most significant damage was attributed to rock scratching. An extensive literature search on data relevant to Mars corrosion confirmed the need for further investigation of the interaction between materials used for spacecraft and structures designed to support long-term surface operations on Mars. Simple preliminary experiments, designed to look at the interaction between an aerospace aluminum alloy (AA7075-T73) and the gases present in the Mars atmosphere, at 20^{o}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 effect of oxidants, the effect of radiation on their oxidizing properties and the possible catalytic effects of the clays present in the Martian regolith. The results of this one-year project provide strong justification for further investigation of the corrosion mechanism of materials relevant to long-term surface operations in support of future human exploration missions on Mars.

Introduction

Metal corrosion is the deterioration of a metal or its properties because of a reaction with its environment. Corrosion occurs mainly through electrochemical reactions. These are chemical reactions, also known as electrochemical reactions that take place when electrons are transferred from one chemical species to another in the presence of an electrolyte. An electrolyte is an aqueous solution that can carry an electrical current by the movement of the ions dissolved in it. The chemical species that loses electrons is oxidized (anodic reaction or oxidation) and the chemical species that gains electrons is reduced (cathodic reaction of reduction). When a metal corrodes, it loses electrons to form ions and its charge increases from zero to a positive number that is determined by the number of electron lost. For example, when aluminum (Al) metal corrodes (or oxidizes), by losing 3 electrons, it forms the aluminum(III) ion (Al^{3+}). This process can be expressed as an electrochemical oxidation reaction, often described as the half reaction for oxidation, in an oxidation reduction or redox reaction:

$$Al \rightarrow Al^{3+} + 3e^- \qquad (1)$$

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).

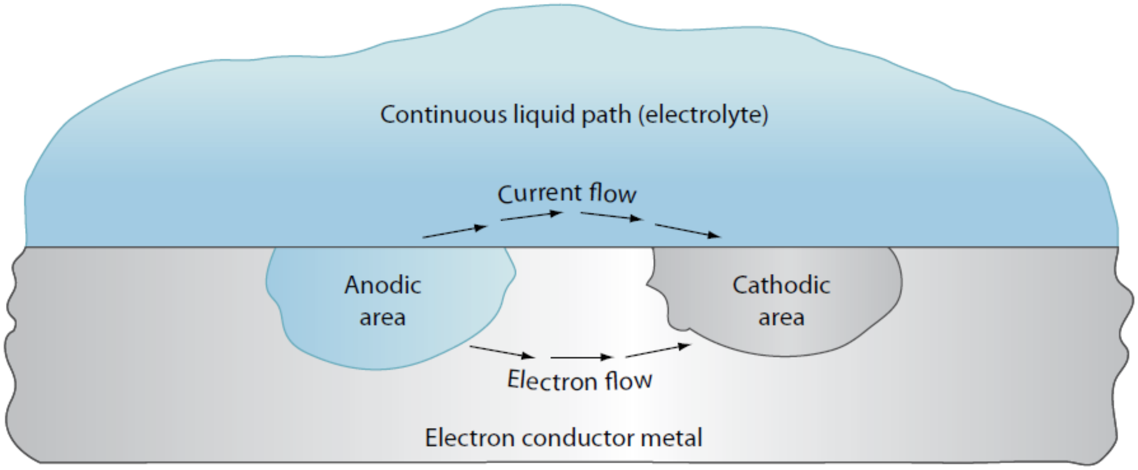

Figure 1. Illustration of the components required for corrosion to take place.[1]

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). The figure 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. 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]

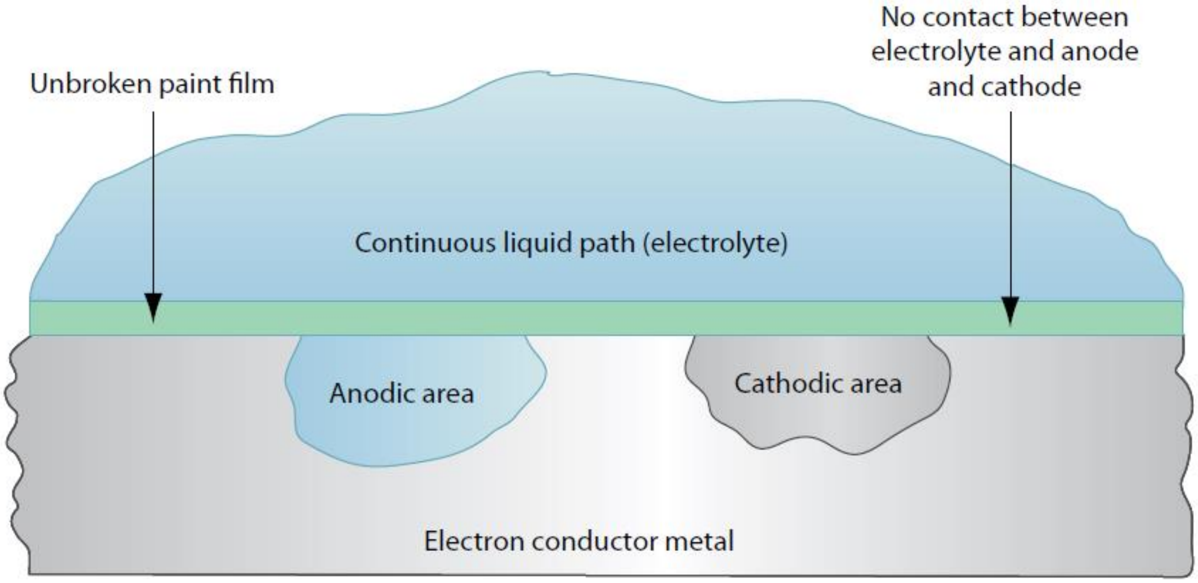

Figure 2. Illustration of a metal covered with a coating for corrosion protection.[1]

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 mankind'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, dampening, thermal management and reduced weight. "NASA could not have made it to the surface of Mars without aluminum."[5] The alloy used to make the thin-walled rigid wheel on the Mars Science Laboratory (MSL) is aluminum alloy AA7075-T7351 (Figure 3).[6] The wheel was made from a mandrel forged ring. It 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 suggested, as a low priority objective, by the Mars Exploration Program Analysis Group (MEPAG) as Investigation B7.1:[7] "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."

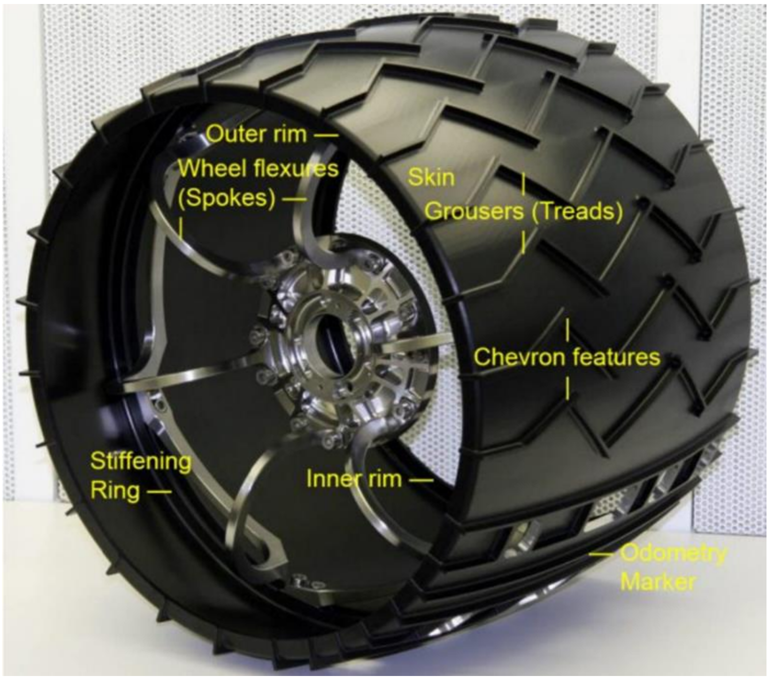

Figure 3. Curiosity's wheel made from a single piece of machined aluminum alloy AA7075-T7351. The main rim is 1.9 cm thick (0.75-inches).

Since the publication of the first evidence of liquid water on present-day Mars by Martin-Torres *et al.*,[8] according to Curiosity data, and the corroboration of the presence of brines by Ojha *et al*.,[9] a new frontier of scientific challenges has emerged, such as the corrosive interaction between brines (electrolytes) and spacecraft materials in the Mars environment.[10] On September 28, 2015, NASA issued a press release confirming that liquid water flows on today's Mars.[11] Figure 4 shows the recurring slope lineae (RSL) at Hale crater. These downhill flows have been described as possibly related to liquid water. The new findings of hydrated salts on the slopes point to what that relationship may be to these dark features. The hydrated salts would lower the freezing point of a liquid brine, just as salt on roads here on Earth causes ice and snow to melt more rapidly. Scientists say that it's likely a shallow subsurface flow, with enough water wicking to the surface to explain the darkening.

Ojha *et al.*[9] interpreted the spectral signatures as being caused by hydrated minerals called perchlorates. The hydrated salts most consistent with the chemical signatures are likely a mixture of magnesium perchlorate ($Mg(ClO_4)_2$), magnesium chlorate ($Mg(ClO_3)_2$) and sodium perchlorate ($NaClO_4$). Some perchlorates have been shown to keep liquids from freezing even when conditions are as cold as minus 70^{o}C (203K). On Earth, naturally produced perchlorates are concentrated in desserts, and some types of perchlorates can be used as rocket propellant. 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, this study of recurring slope lineae (RSL) detected perchlorates, now in hydrated form, in different areas than those explored by the landers. This also is the first time perchlorates have been identified from orbit. It should be mentioned that other researchers[12] have suggested that a dry avalanche process can explain the formation of the RSL on Mars without requiring liquid water or CO_2 frost activity.

The goal of this research is 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 and by performing preliminary laboratory experiments under relevant simulated Martian conditions.

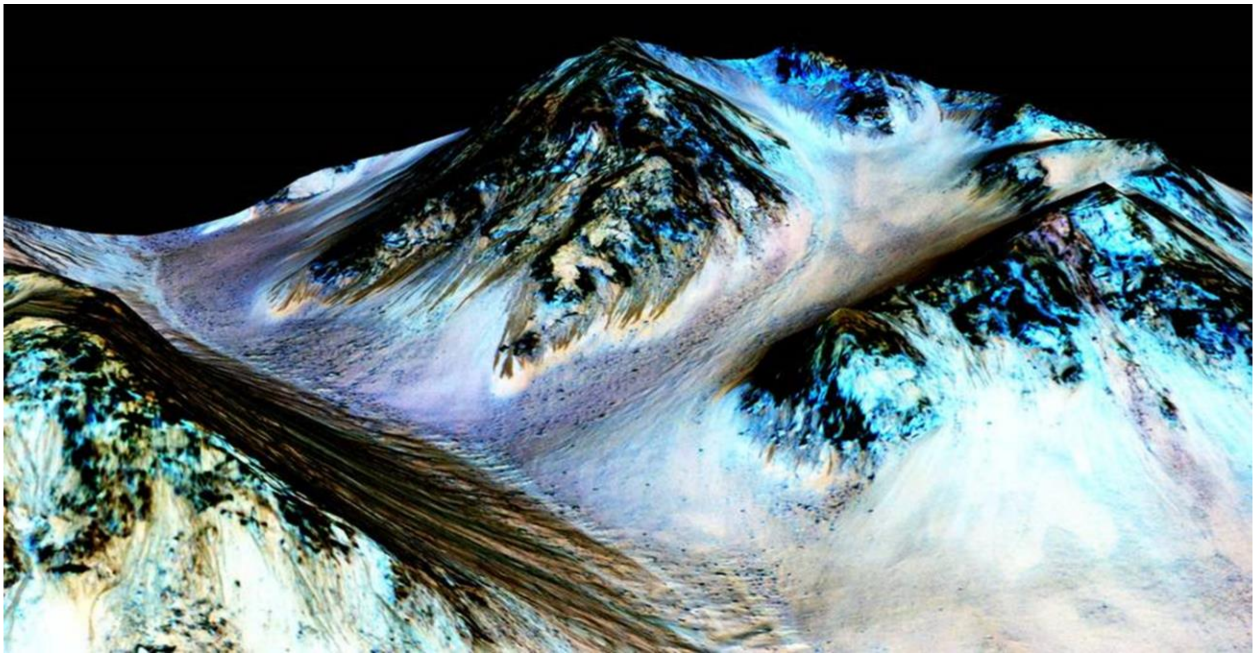

Figure 4. These dark, narrow, 100 meter-long streaks called recurring slope lineae flowing downhill on Mars are inferred to have been formed by contemporary flowing water. Recently, planetary scientists detected hydrated salts on these slopes at Hale crater, corroborating their original hypothesis that the streaks are indeed formed by liquid water. Credits: NASA/JPL/University of Arizona.[10]

Background

Mars is often called the red planet. The reddish color of the Martian surface is due to the high iron oxide (Fe_2O_3), also known as iron(III) oxide or hematite, content in its regolith (labeled as FeO in Figure 5).[13] This graph compares the elemental composition of typical soils at three landing regions on Mars: Gusev Crater, where NASA's Mars Exploration Rover Spirit traveled; Meridiani Planum, where Mars Exploration Rover Opportunity still roams; and now Gale Crater, where NASA's newest Curiosity rover is currently investigating. The data from the Mars exploration rovers are from several batches of soil, while the Curiosity data are from soil taken inside a wheel scuff mark called "Portage" and examined with its Alpha Particle X-ray Spectrometer (APXS). These early results indicate that the samples investigated by Curiosity are very similar to those at previous landing sites. Error bars indicate the variations for the given number of soils measured by the Mars exploration rovers along the traverse. Note that concentrations of silicon dioxide (SiO_2) and iron oxide (FeO) were divided by 10, and nickel (Ni), zinc (Zn) and bromine (Br) levels were multiplied by 100.

Iron oxide (rust) is formed when iron metal becomes oxidized in the presence of oxygen. This process is also known as corrosion. There is evidence that the Martian soil was capable of decomposing organic molecules and releasing O_2 upon the introduction of water vapor.[14,15] This reactivity was attributed to the possible formation of superoxide radical ions ($O_2^{-\bullet}$) in the Mars environment under ultra violet (UV) radiation[16] or to the activation of an oxidizing agent under radiation, such as perchlorate (ClO_4^-) radiolysis under gamma rays.[17]

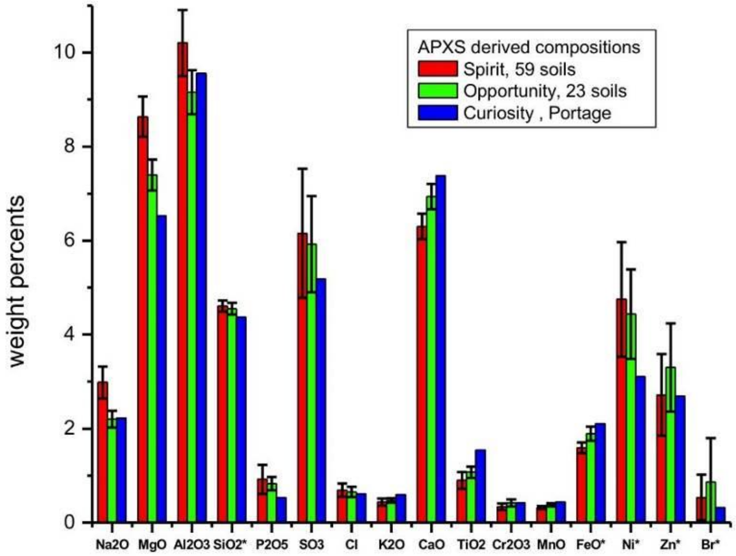

Figure 5. APXS derived compositions of rocks and soils on Mars (NASA/JPL-Caltech/University of Guelph, December 3, 2012).

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.[18] Perchlorate and chlorate (ClO_3^-) species have also been found in a Martian meteorite.[19] Its role in lowering the freezing temperature of water in Martian soil supports the presence of transient liquid water on Mars.[7] This new found evidence of liquid water (brine) coincided with the surprisingly significant damage observed on Curiosity's wheels (Figure 6 and Figure 7). 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 pointed out that, maybe the daily contact of the wheels with the corrosive perchlorate solutions during every night 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 7). A team of researchers[8] has suggested that, given the strong oxidizing character of perchlorate ions 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.[20] Although perchlorates are not as corrosive as chloride (Cl^-) anions, 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 concentrations are factors of 420 and 246 greater, respectively than a diluted copper(II) chloride ($CuCl_2$) solution (10 mM) which has been reported to cause 10-50 µm-sized blisters with copper (Cu) deposits produced after Al pitting corrosion (similar to those circled in red in Figure 7) within 10 minutes.[21] 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 internal aluminum 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. One important question to address regarding the corrosion of aluminum in the Mars environment is whether or not its protective oxide layer will repair itself, when it is scratched on Mars, as it would be the case on Earth.

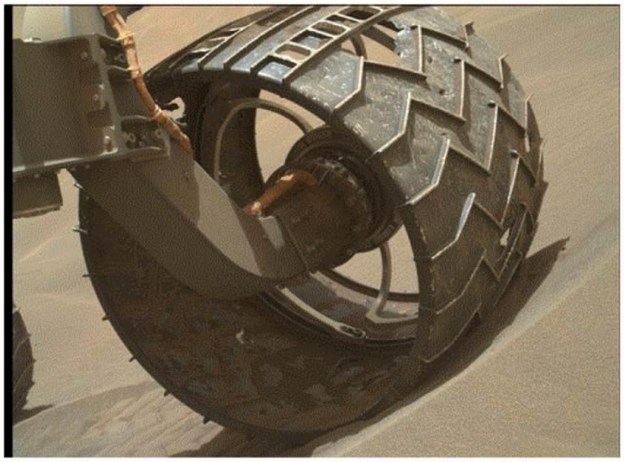

Figure 6. Curiosity's wheels showing signs of severe damage after almost 10 km of traverse.

Approach/Methodology

Considering that corrosion is the interaction between a material and its environment, it cannot be assumed that, for a given material such as aluminum alloys, this interaction is going to be the same in the terrestrial and in the Martian environments, since they are significantly different. The Martian environment includes: the composition and conditions of the atmosphere, soil composition and chemistry, radiation conditions, and the presence of transient liquid brines. This investigation was focused on the interaction between aerospace aluminum alloy AA7075-T73 (the alloy used for Curiosity’s wheels) and selected simulated Martian atmospheric environments. Understanding this interaction is very important in the selection of materials and their corrosion protection methods for their long-term performance in the Mars environment. 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.

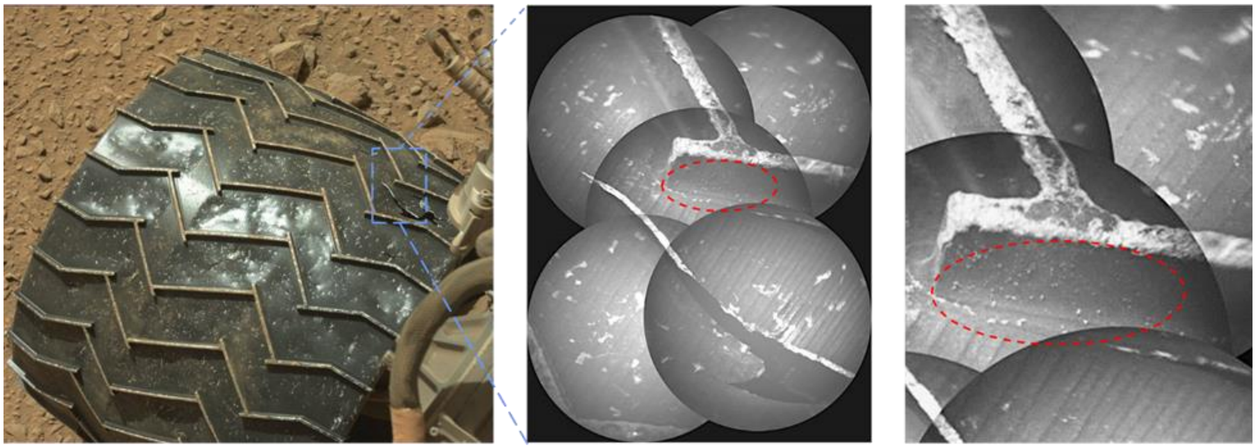

Figure 7. Curiosity's ChemCam images of a damaged area of the rover's middle right-wheel. The image shows not only a large crack in the wheel (area inside blue rectangle on left image) but some sub-millimeter-sized blisters in the vertical wall of the T-print of the wheels (circled in red on the middle 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.

Our investigation began with a literature search of available data relevant to corrosion on Mars. One important recent finding was the presence of corrosive brines and what is known about their composition and properties. These brines are known to contain perchlorates which can play an important role in the corrosion of materials under Martian conditions. This investigation also focused on what is known about perchlorates here on Earth and how their reactivity can be different in the Mars environment. The investigation concluded with some preliminary experiments designed to compare the interaction between a sample of aluminum alloy AA7075-T73, scribed *in situ*, and three different environments at room temperature (20^{o}C): Earth's atmosphere at 100 kPa (1 bar), pure carbon dioxide gas (CO_2) and Mars gas at 700 Pa (7 mbar). These pressure was selected because the average pressure on Mars is roughly 7.5 mbars.

Available Data Relevant to Corrosion on Mars

The quest to find life on Mars, by searching for organics and microbial life in the regolith, 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 part-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 are 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.[7] 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 (Figure 8)[22]. 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,[10] this finding has significant implications for spacecraft design and surface operations given the potential for corrosive interactions between the brines and spacecraft materials.

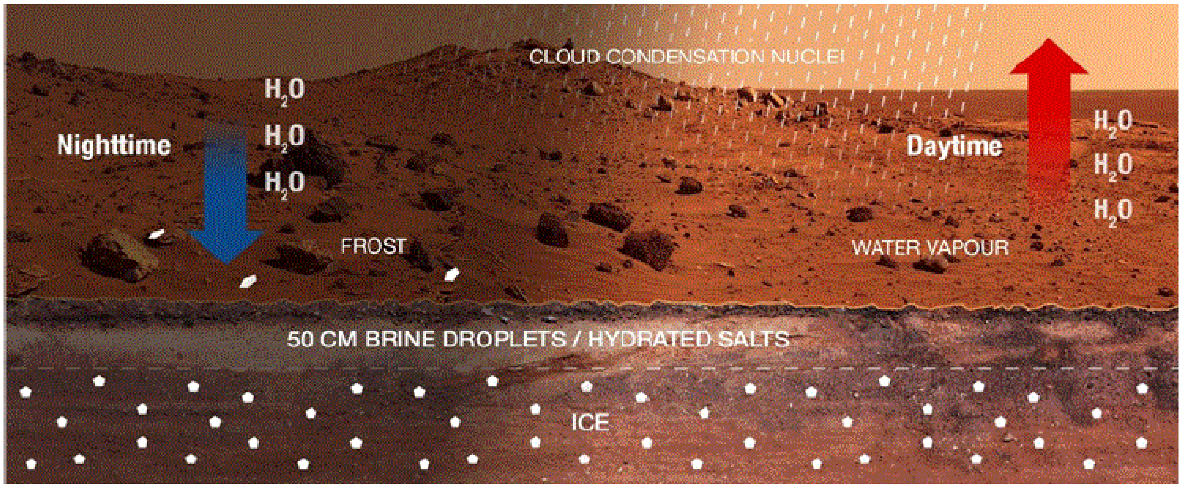

Figure 8. Schematic drawing of the water cycle on Mars and the atmosphere-regolith water interchange based on Curiosity's Rover Environmental Monitoring Station (REMS) data at Gale crater. The diurnal cycle is representative of that for a low-latitude region.

The data collected by Curiosity's Rover Environmental Monitoring Station (REMS), shown in Figure 9, Sample Analysis at Mars (SAM), and Dynamic Albedo of Neutrons (DAN) 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. The perchlorates found *in situ* are likely calcium perchlorate ($Ca(ClO_4)_2$) as detected by Curiosity at Gale[23] and magnesium (($Mg(ClO_4)_2$) (or sodium perchlorates ($NaClO_4$)) as observed at the Phoenix polar landing site.[24] Reanalysis of Viking data suggested that perchlorates could have been present there as well.[25] Chloride is distributed globally on Mars (Figure 10) as detected by the Mars Odyssey Gamma Ray Spectrometer (GRS).[26, 27] 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.[28.] 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 platforms[10] is worth of further investigation.

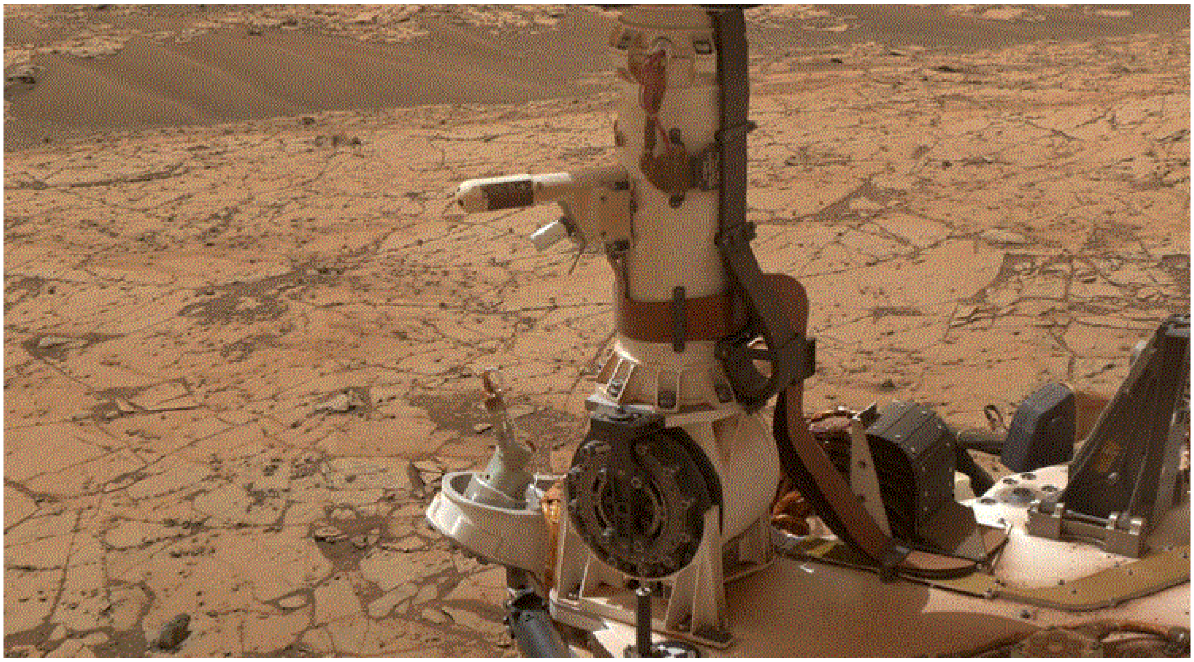

Figure 9. Image of REM's boom 2 on Curiosity's Mast.

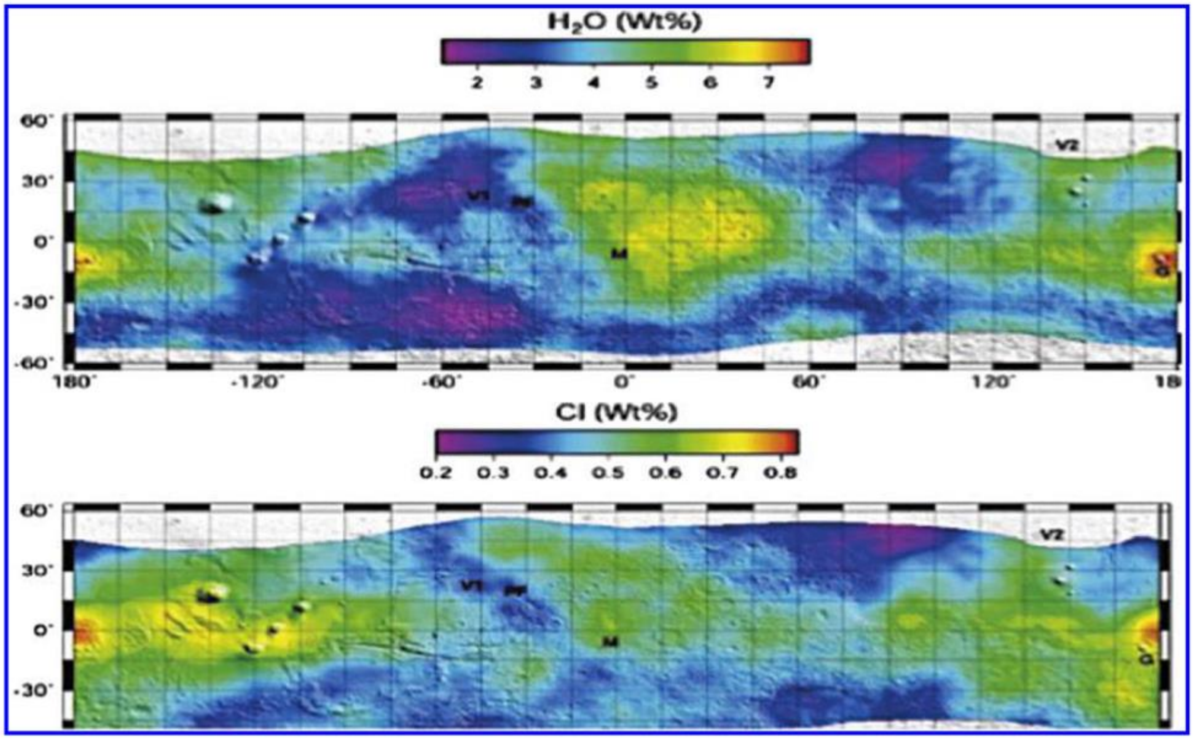

Figure 10. Equatorial and midlatitude distribution of soil equivalent-water distribution and chlorine within the top 1m of Mars as detected by NASA's Mars Odyssey GRS. (Image credit: NASA/JPL/University of Arizona).[26,27]

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 11). 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.

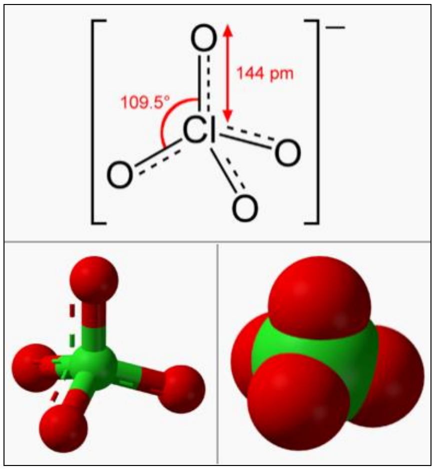

Figure 11. Chemical formula (top) and structure models (bottom) of perchlorate.

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.[29]

Even though perchlorate contains a highly oxidized central halogen atom, it exhibits low reactivity as an oxidant.[30] The low reactivity is a matter of its kinetic rather than thermodynamic stability. The standard reduction potential for the half-cell reduction reaction of perchlorate to chloride is:[31]

$ClO_4^- + 8 H^+ + 8 e^- \leftrightarrow Cl^- + 4 H_2O$ $E° = 1.287$ V (2)

The standard oxidation potential for the half-cell reaction to oxidize water to oxygen is:

$2 H_2O \leftrightarrow 4 H^+ + 4e^- + O_2$ $E° = –1.229$ V (3)

The overall reaction for the reduction of ClO_4^- to Cl^- and the oxidation of water to O_2 can be obtained by adding reactions (2) and (3):

$ClO_4^- \rightarrow Cl^- + 2 O_2$ $\Delta E = 0.058$ V (4)

The Gibbs free energy change for a combination of half-cell reactions at 25°C can be calculated from the equation:

$\Delta G = -nF\Delta E$ (5)

where ΔG is the Gibbs free energy change, n is the number of electrochemical equivalents in the reaction, F is the Faraday constant, equal to 9.6485 x $l0^4$ J V^{-1} $mole^{-1}$, and ΔE is calculated by adding the reduction potential to the oxidation potential of the half-cell reactions involved in the overall oxidation reduction (redox) reaction. A positive value of ΔE will result in a negative value of AG which means that the reaction would be spontaneous in the direction written. Spontaneity is a thermodynamic term that refers to the time-evolution of a system in which it releases free energy and moves to a lower, more thermodynamically stable, energy state (Figure 12).

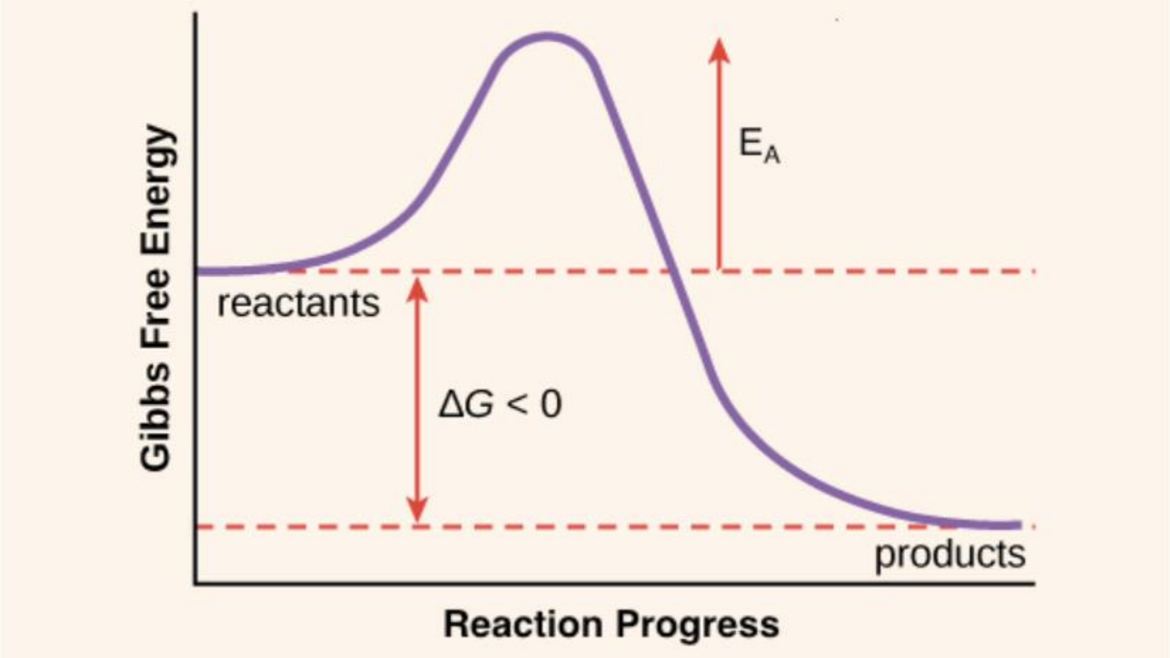

Figure 12 Activation energy of a thermodynamically spontaneous chemical reaction[32]

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 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 because of the positive value of ΔE for reaction (4). 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.[33] 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.[34] 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 than the thermal decomposition discussed above. Reaction (4) 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.[18, 35]

Aluminum and perchlorate

It is important for this project to consider the oxidation reaction of aluminum by perchlorate. Aluminum is a strong reducing agent with a standard reduction potential $E°(Al^{3+}/Al) = −1.662$ V. ΔE for the oxidation of aluminum, reaction (1), by perchlorate is obtained by adding the oxidation potential of aluminum, $E°(Al/Al^{3+}) = 1.662$ V, to the reduction potential of perchlorate, $E°(ClO_4^–/Cl^-) = 1.287$ V ,reaction (2), to obtain a ΔE value of 2.949 V for the overall reaction (6):

$$8Al + 3\,ClO_4^- + 24H^+ \rightarrow 8Al^{3+} + 3Cl^- + 12H_2O \qquad \Delta E = 2.949\text{ V} \qquad (6)$$

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 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?

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 (7). In this reaction, aluminum is oxidized to aluminum oxide (Al_2O_3) and perchlorate is reduced to Cl^-. This reaction is used in rockets (such as NASA's solid rocket boosters), explosives, pyrotechnics, flares, and ammunition.

$$10\,Al + 6\,NH_4ClO_4 \rightarrow 4\,Al_2O_3 + 2\,AlCl_3 + 12\,H_2O + 3\,N_2 \qquad (7)$$

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.[36] Several microorganisms on Earth are known to harvest energy by anaerobic reduction of the perchlorate molecule.[37]

Perchlorates and Martian Conditions

Perchlorate is widespread in Martian soils at concentrations between 0.5 and 1%.[38] Turner *et al.*[39] 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 %)[40, 41] 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.*[17] and Navarro-Gonzalez *et al.*[25] 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 suggest that ionization processing of perchlorate alone can explain the Viking Labeled Release (LR) and Gas Exchange Experiment (GEX) results. Turner *et al.*[39] conducted laboratory experiments to explore the temperature-dependent decomposition mechanisms of hydrated perchlorates, namely magnesium perchlorate hexahydrate ($Mg(ClO_4)_2{\cdot}6H_2O$), and to provide yields of the oxygen-bearing species formed in these processes at Mars-relevant surface temperatures from -108 to 37^{o}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^{o}C (260 to 160K). Perchlorate could also lead to transient, metastable brines by way of deliquescence, even under current climate conditions,[42] 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,[43,44] which has potential implications for habitability of Martian soils. Davila *et al.*[38] 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^{-}).[14] 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,[45,46] with an abundance of 4–5 wt % in the regolith, calculated from the Thermal Emission Spectrometer data of the Mars Exploration Rovers.[47] Curiosity analyzed mudstone samples in Gale Crater, which showed the presence of clays in this region.[48] 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,[18] 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[49] 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^-). Figure 13 shows the oxidation state diagram for oxychlorine species. Similar photoproducts have been previously observed in perchlorate irradiated with ionizing radiation.[17,50] C.D. Georgiou *et al*.[51] reported that γ -radiolyzed perchlorate-containing Mars soil salt analogues (in a CO_2 atmosphere) generate, upon H_2O wetting, the reactive oxygen species (ROS) superoxide radical ($O_2^{-\bullet}$), hydrogen peroxide (H_2O_2), and hydroxyl radicals ($OH^\bullet$). This study also validated that analogue radiolysis forms oxychlorine species that, in turn, can UV-photolyze to $OH^\bullet$ 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 ($ClO_2^\bullet$), and hypochlorite (ClO^-), with the formation of $^\bullet OH$ by UV photolysis of ClO^-.

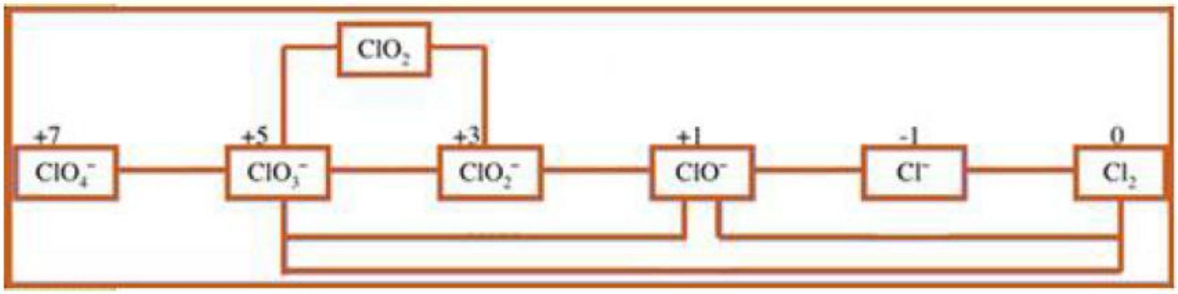

Figure 13.Oxidation state diagram for oxychlorine species[48]

A resent review paper by Lasne *et al.* [52] provides an excellent summary of the oxidants detected or proposed to be present at the surface of Mars (Table 1) 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 1. Oxidants Detected or Suggested to Be Present on Mars[51]

Group	Oxidant	Detected or Suggested	Origin
Perchlorate salt	ClO_4^-	Detected[19,24]	Produced in the atmosphere Produced by UV irradiation of chlorine-bearing minerals
Iron-bearing species	Fe_2O_3 FeO_4^{2-} Clays	Detected*[,53,54] Suggested[55] Suggested**[56]	Thermodynamically stable on Mars' surface Minor phase (thermodynamically unstable) Alteration of silicates in presence of water
Reactive oxygenated species	Peroxide or superoxide species Superoxide radical ion ($O_2^{-\bullet}$)	Suggested[15,57,58,59,60] Suggested[16,60,61,62]	Detection of species that could form superoxides or peroxides Formed in the presence of oxygen and UV radiation Formed with H_2O_2
H_2O_2	H_2O_2 in the atmosphere H_2O_2 in the regolith	Detected[63,64] Suggested[65,66,67,68]	Produced photochemically and during dust devils and storms Diffusion of H_2O_2 formed in the atmosphere Produced by interaction between minerals and water

*The Fe_2O_3 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 and Methods

Materials

10mm x 10mm x 1.5mm AA7075-T73 aluminum alloy samples (nominal composition, 5.6–6.1 wt% Zn; 2.1–2.5 wt% Mg; 1.2–1.6 wt% Cu; less than 0.5 wt% Si; and Al bal.) were polished using 800 grit grinding SiC paper. The panels were scribed using a silicon carbide (SiC) rod (1/8 inch diameter, 1.5 inch length, manufactured by Ultra-Met, Model number 1/8DX11/2-PGPC). The AA7075-T73 temper is achieved by over aging (meaning aging past the peak hardness) the material to reduce the susceptibility to stress corrosion cracking (SCC) and exfoliation.

Experimental Procedures

Atmospheric exposure environments

Three atmospheric exposure environments were performed to investigate the difference in the formation of the aluminum oxide film on a freshly scratched AA7075-T73 aluminum alloy test panel by XPS. This would simulate what happens when, for example, the wheel of a Mars rover is scratched by a sharp object such as a rock with a sharp edge. The objective was to observe if a protective film would form under Martian atmospheric conditions as it does under the Earth's atmospheric conditions. The control sample was scratched under terrestrial (sea level) atmospheric conditions in the laboratory (100 kPa) and placed immediately after in the XPS instrument chamber for analysis (0-days exposure to air) at room temperature. This sample was also analyzed after one week of exposure to air. Two other atmospheric conditions were selected to simulate the composition and pressure of the Mars atmosphere: Pure CO_2 and a Mars gas mixture. Pure CO_2 was selected since it is the main component of the Mars atmosphere (95.32 percent). The composition of the Mars gas mixture was: 0.100% oxygen, 0.100% carbon monoxide (CO), 1.59% argon (Ar), 2.70% nitrogen (N_2), and 95.5% CO_2. Both mixtures were at a pressure of 700 Pa (7 mbar). All experiments were conducted at a room temperature of 20 ^{o}C. The CO_2 and Mars gas exposures were carried out using the Mars chamber shown in Figure 14. Initial experiments on AA7075-T73 aluminum alloy samples, scribed *in situ* inside the chamber, included one week of exposure to CO_2 and one week of exposure to Mars gas. After seeing the surprising results obtained with the exposure to Mars gas, it was decided to conduct two additional experiments where the exposure to Mars gas was shorter (3 days) and longer (2 weeks). A longer exposure was planned but not carried out due circumstances beyond our control.

The Mars chamber at KSC has the capability to select the chemical composition and pressure of the atmosphere inside and to control the pressure within a few mTorr through the use of an MKS Type 640 pressure controller with an external LabView® software monitor and control.

The pressure and temperature inside the chamber were maintained at 700 Pa and 20^{o}C. To get the appropriate mix of gases in the chamber, the chamber pressure was first reduced to less than 13.3 Pa (0.133 mbar) using a Varian TriScroll 300 scroll pump. The pressure was recorded once per minute for each long-duration experiment to ensure power outages or other system anomalies were not present during testing. The pressure stability for one experiment is displayed in Figure 15.

Scribing tool design and fabrication

The aluminum alloy test panels were scribed remotely inside the Mars chamber with a scribing set up designed and fabricated specifically for this project (Figure 16). Several design iterations were necessary to develop an adequate scribing tool for the aluminum alloy coupons. Ultimately, an optics table with a mix of stainless steel and acrylonitrile butadiene styrene (ABS) 3D-printed components was used in the final design. A Micos VT-80 translation stage with LabView® control was used to move the scribing tool across the surface of the aluminum alloy sample. The optics table and stainless steel rods provided the structural rigidity needed to withstand the forces applied when scribing the aluminum alloy surface with the silicon carbide tip.

A variety of scribing tips were used to achieve the proper channel dimensions needed for the XPS analysis described in the following section. The goal was to have a wide shallow channel scribed into the aluminum alloy sample. The profiles created by these scribing tools were observed using laser confocal microscopy. To reduce the torque on the test stand, a narrow carbide wedge blade (Figure 17) was used to scratch the sample. This narrow carbide wedge scribe tool created a fairly uniform, shallow, and narrow channel (Figure 18). The channel was 12.6 µm wide and approximately 5 µm deep. However, this type of profile was not suitable for XPS analysis.

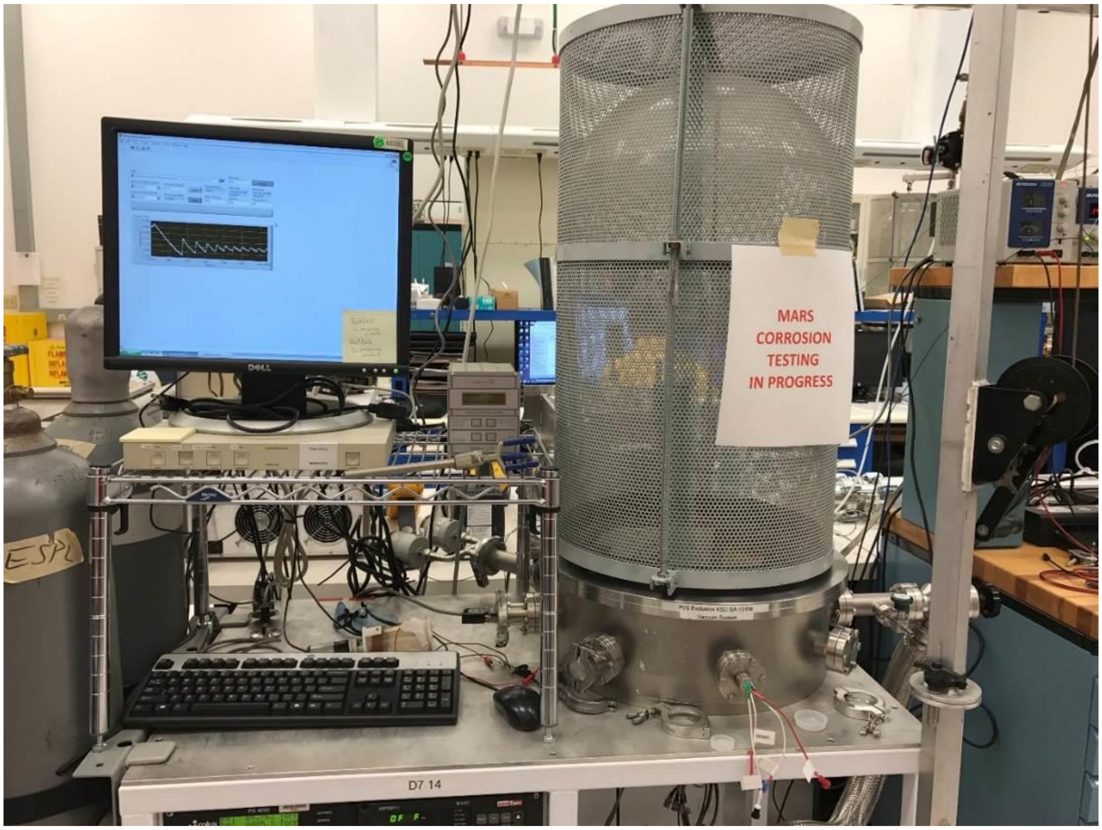

Figure 14. Mars chamber in the Electrostatics and Surface Physics Laboratory at KSC.

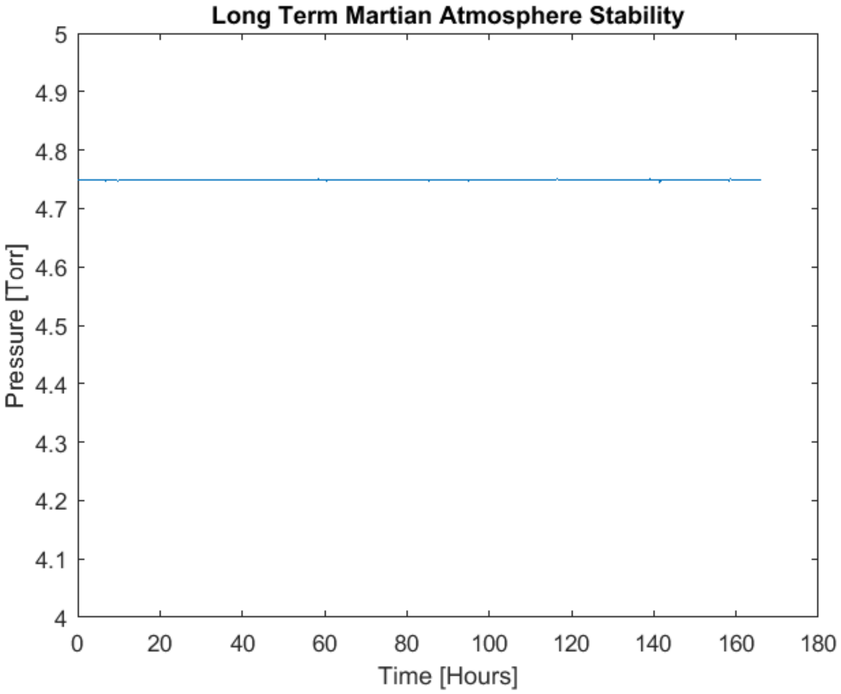

Figure 15. Pressure data from a representative long-term exposure experiment inside the Mars chamber (1 Torr = 0.13 kPa).

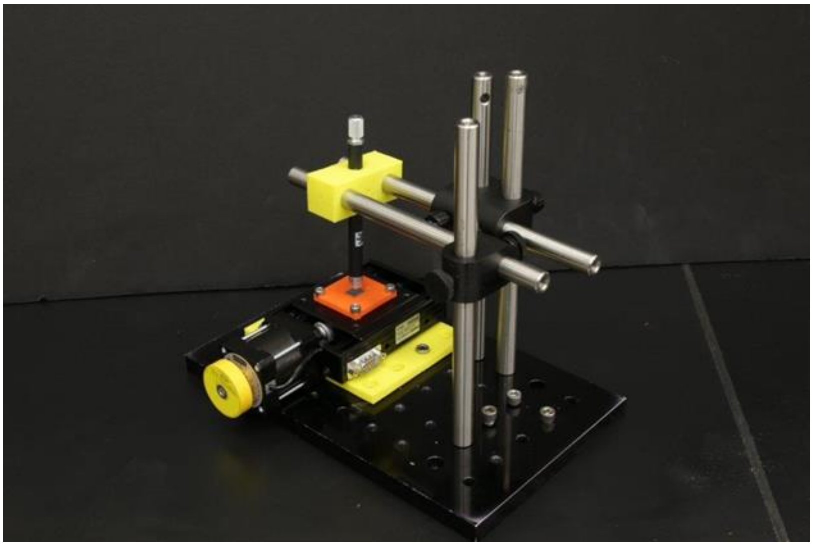

Figure 16. Sample holder with scribing tool.

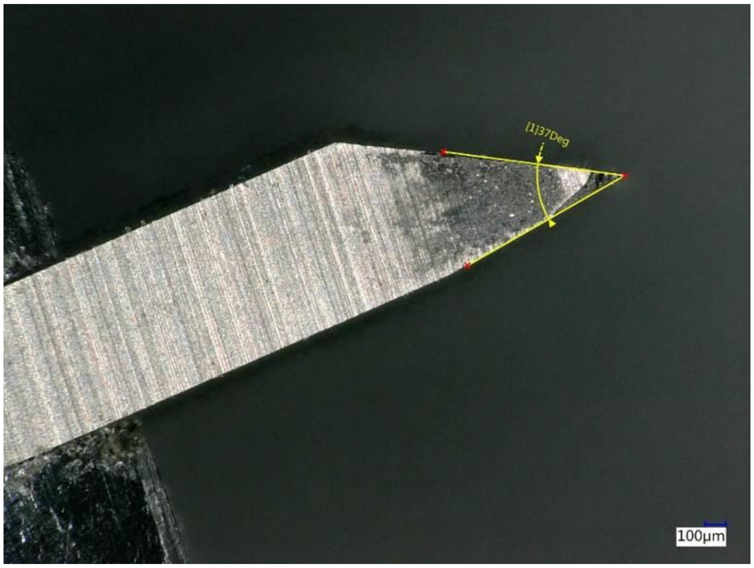

Figure 17. Narrow carbide wedge scribe tip

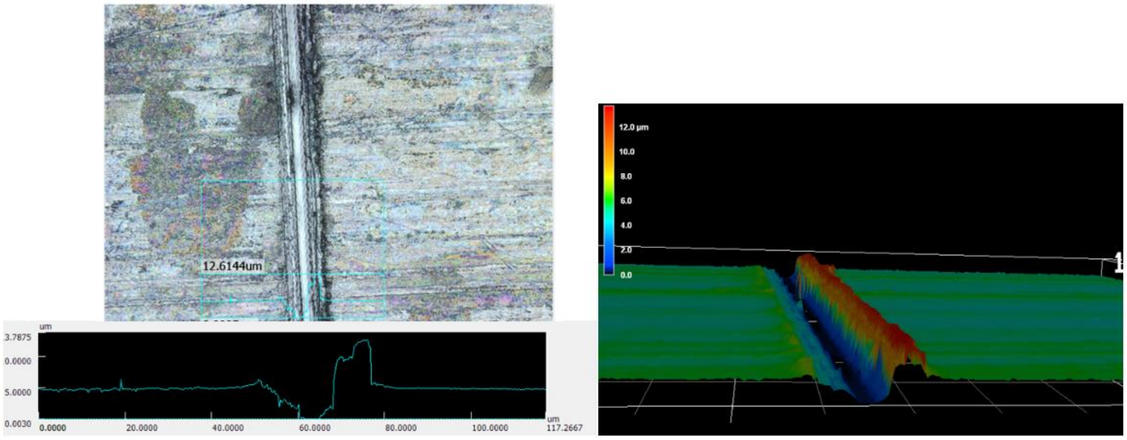

Figure 18. Narrow carbide wedge scribe profile imaged using laser confocal microscopy.

To create a wider and shallow profile, a cylindrical carbide scribe tool was used (Figure 19). The channel profile could be adjusted by angling the scribe tool. To create an adequately wide and shallow profile, as shown in Figure 20, the scribe tool was angled roughly 25 degrees from parallel to the aluminum alloy sample. The confocal microscopy images show that the scribe channel is 250 µm wide with a large radius of curvature and maximum depth of 9 µm. This profile was more suitable for XPS analysis than the profile created with the narrow carbide wedge.

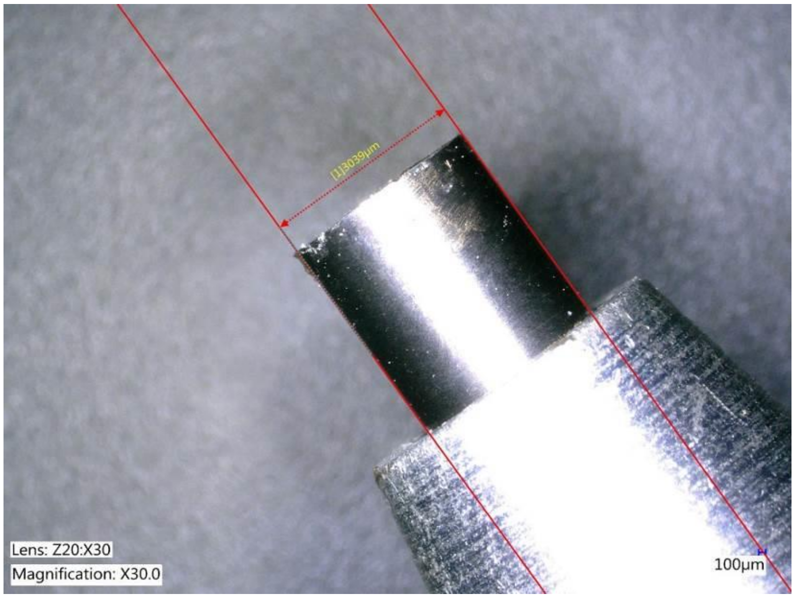

Figure 19. Cylindrical carbide scribe tool

To perform the experiments, the chamber was configured with the appropriate gas (pure CO_2 or Mars gas) at 700 Pa (7 mbar). The cylindrical carbide scribe tip was used to scribe the surface of the AA7075-T73 aluminum alloy samples inside the chamber. The scribed surface was left exposed to the low pressure environment for a pre-determined amount of time. At the end of the pre-selected time, the chamber was vented to ambient conditions and the aluminum alloy sample was vacuum-sealed until the XPS analysis was conducted.

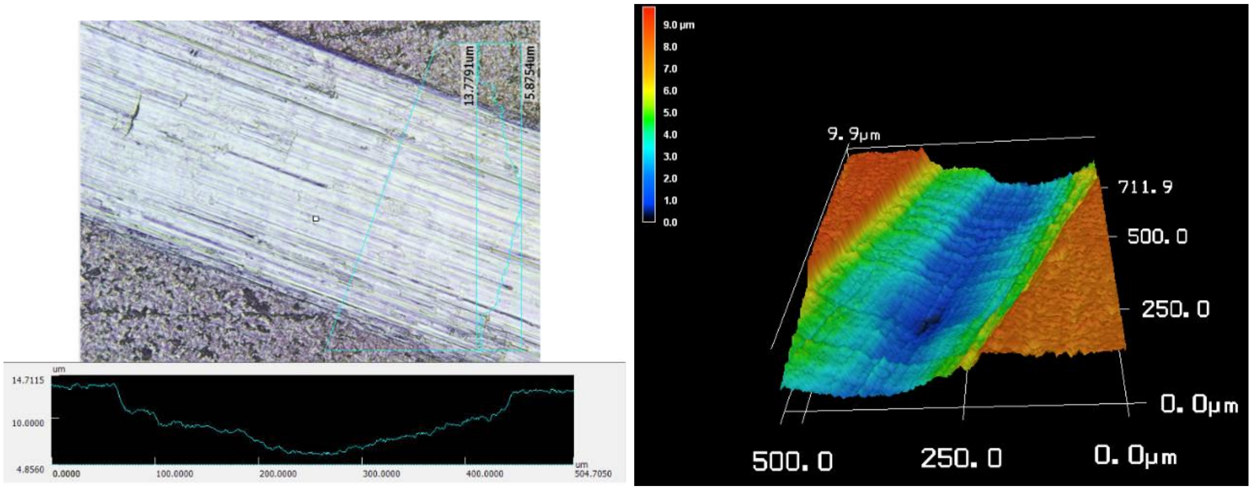

Figure 20. Cylindrical carbide scribe profile imaged using laser confocal microscopy.

XPS analysis

XPS analysis of the scribed area of the test panels was carried out using a K-alpha X-ray photoelectron spectrometer (XPS) system, a monochromatic small-spot XPS system. Depth profile data were collected for both survey and element scans.

Results and Discussion

XPS analysis

Figure 21 shows a typical survey scan of AA7075-T73 aluminum alloy where the main peaks are labeled with the elements present: Al, Mg, Zn, Cu, O, and C.

Control sample (0-days of exposure to air)

An AA7075-T73 aluminum alloy sample was polished and scribed in air, before transfer to the XPS chamber for analysis. This sample was used as a control for comparison. The scribed area was unavoidably exposed to air (for about 5 minutes) before the XPS analysis. XPS composition depth profile data was collected at the scribed area (Figure 22 and Figure 23); the total etch time was more than 2000 seconds, at an experimental setting where one second of etch time corresponds to 0.35 nm tantalum pentoxide (Ta_2O_5).

The depth profile for oxygen is indicative of slight oxidation at the scribe as a result of the brief exposure to the oxygen in the air. Below the top surface layer, the carbon content is relatively low but it is present through the whole depth profile. The high carbon content on the sample surface is due to adventitious carbon contamination. The other elements are present in the expected composition range.

Figure 24 shows selected spectra of element scans from the depth profile: series 1, 2, 10, 20, and 40 that correspond to the etch times of 0, 10, 90, 190, and 2190 seconds.

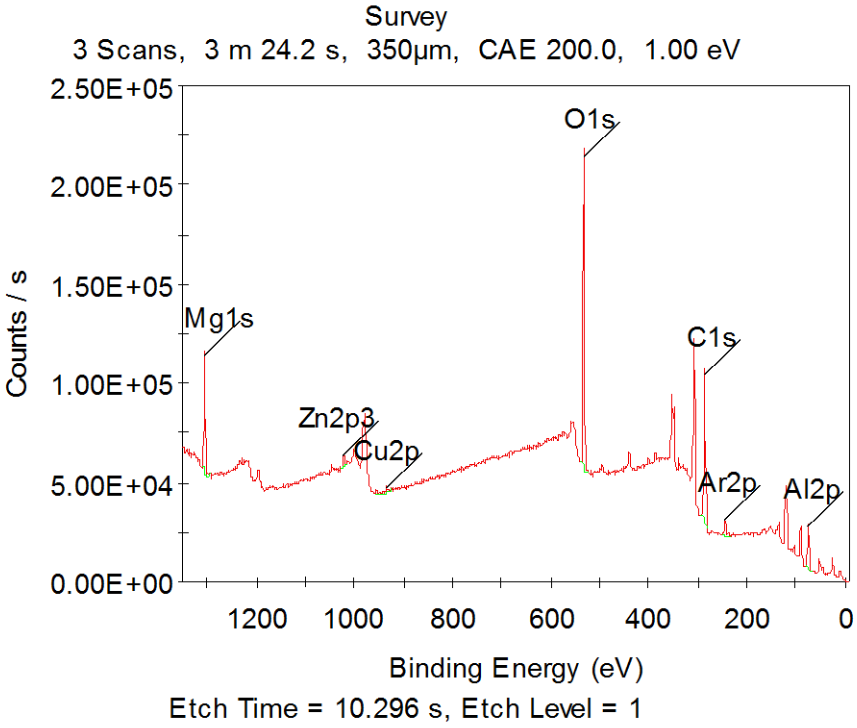

Figure 21. Typical survey scan for AA7075-T73 aluminum alloy

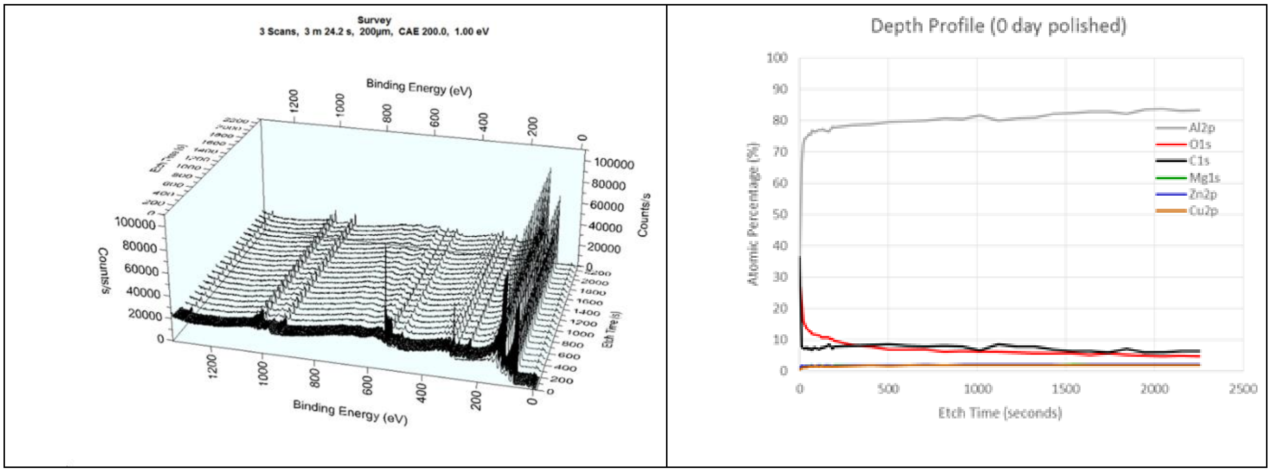

Figure 22. Survey scan and depth profile data collected over the scribed area of an AA7075-T73 aluminum alloy sample immediately after exposure to the air (“0-Day-Air” sample).

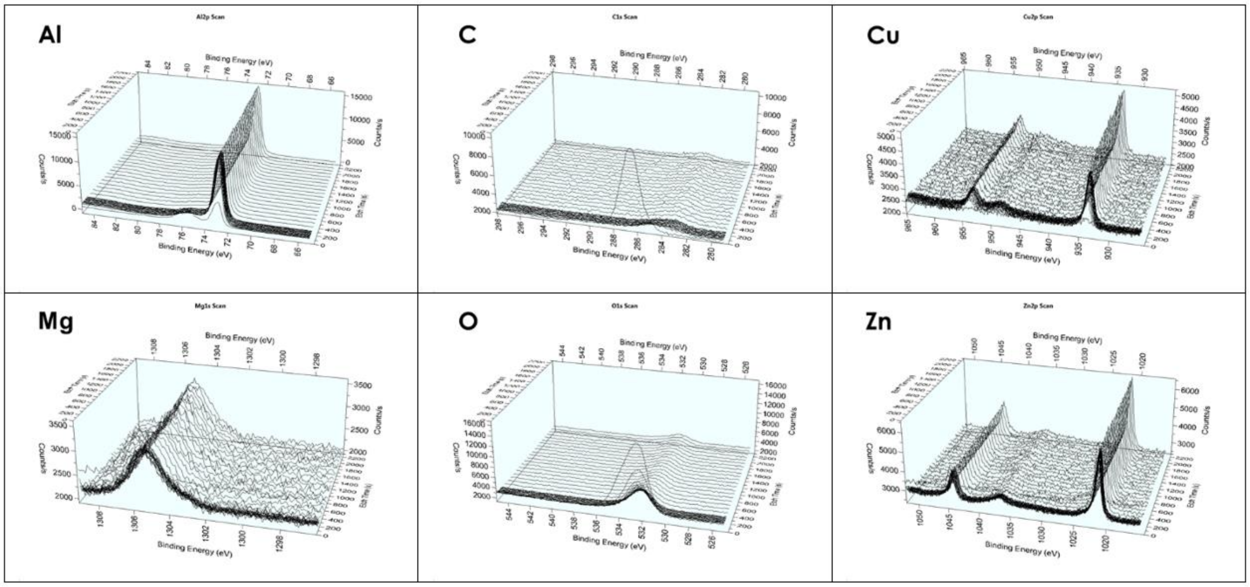

Figure 23. Depth profile data, for individual elements, collected over the scribed area of an AA7075-T73 aluminum alloy sample immediately after exposure to the air (“0-Day-Air” sample).

Figure 25 shows the same depth profile plot shown in Figure 22 zoomed in for 0-500 second etch time and for 0-10 atomic percentage to show the elements (Cu, Zn, and Mg) that are present at low level. Both sets of data show that there is some slight surface enrichment of Mg and Zn (between 0 and 100 seconds etch time). Their atomic percent compositions are relatively constant, while Al and Cu show a gradual increase as the O content decreases away from the surface.

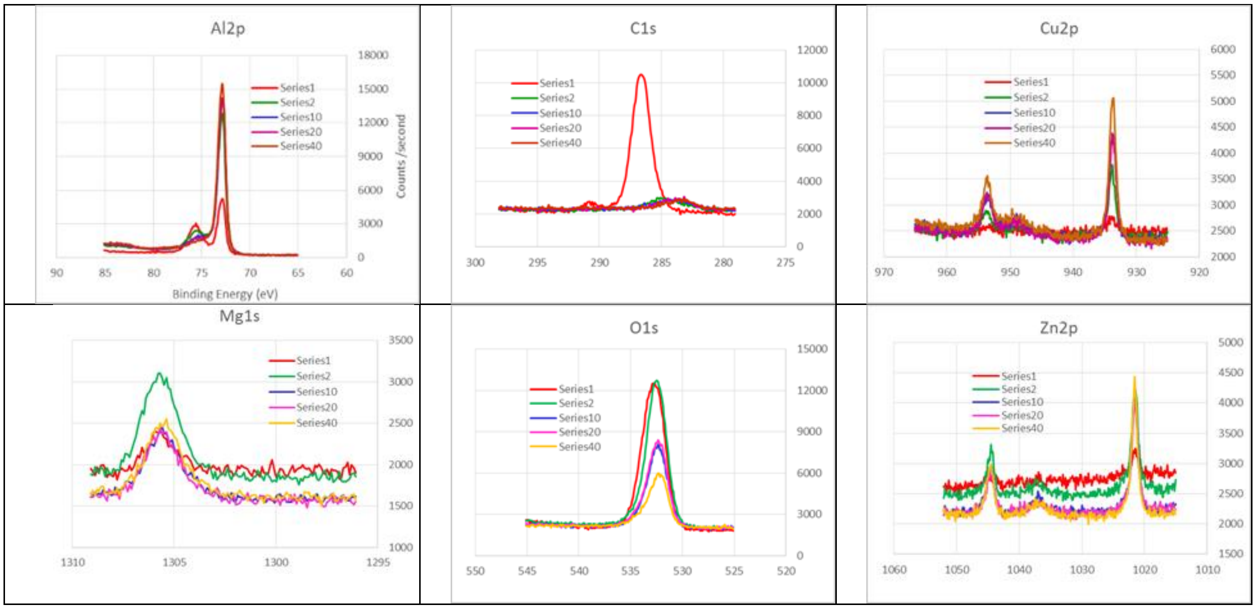

Figure 24. Selected spectra of individual element scans from the depth profile of AA7075-T73 control sample (minimal exposure to air of the scribed area).

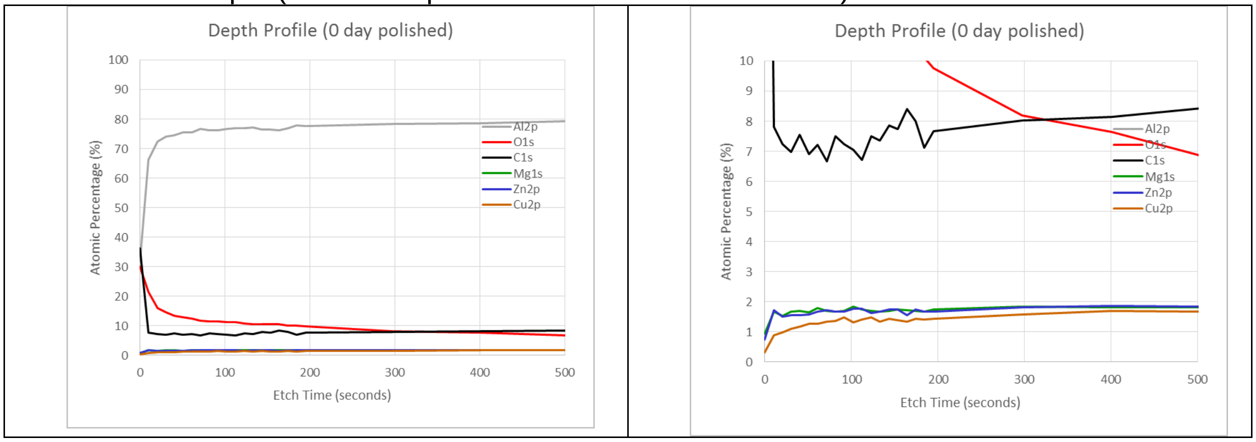

Figure 25. Depth profile data collected over the scribed area of an AA7075-T73 aluminum alloy sample, immediately after exposure to the air (“0-Day-Air” sample), zoomed in for 0-500 seconds etch time (left image) and for 0-10% atomic percentage (right image).

The observed Mg and Zn enrichment is consistent with similar results obtained by C.M. Abreu *et al.*[69] who performed an XPS study that included AA7075-T73. Their results showed a Mg^{2+} enrichment, very similar to the Mg enrichment obtained in this study, and attributed it to the formation of magnesium oxide (MgO). In summary, the results for the control (labeled as 0-day-air AA7075-T73 aluminum alloy sample), briefly exposed to air, showed a slight oxidation on the surface, a low carbon content through the depth profile (less than 1 micron from the surface) which can attributed to adventitious carbon contamination from an unknown source, and a slight surface enrichment of Mg and Zn (less than 50 nanometer from the surface).

One-week of exposure to air

The AA7075-T73 aluminum alloy sample was polished, scribed, and exposed to air for one week before transfer to the XPS chamber for analysis. Figure 26 and Figure 27 show the survey scan and depth profile data collected over the scribed area. Figure 28 shows the same depth profile plot shown in Figure 26 zoomed in for 0-500 second etch time and for 0-10 atomic percentage to show the elements (Cu, Zn, and Mg) that are present at low level. The surface shows a high oxygen content (etch time below 200 seconds) where oxygen is present through the depth profile at a higher content than that in the control (0-Day-Air sample). Aluminum also shows a larger peak component, at a higher binding energy, indicating the presence of aluminum oxide or hydroxide. Carbon content is higher at the surface, but quickly decreases to a level that is comparable to that in the control. Other elements are present in the expected composition range. There is some surface enrichment of Mg similar to that obtained for the control. There is also an enrichment of Zn that is lower than that of Mg. Figure 30 shows selected spectra of individual element scans from the depth profile data collected over the scribed area.

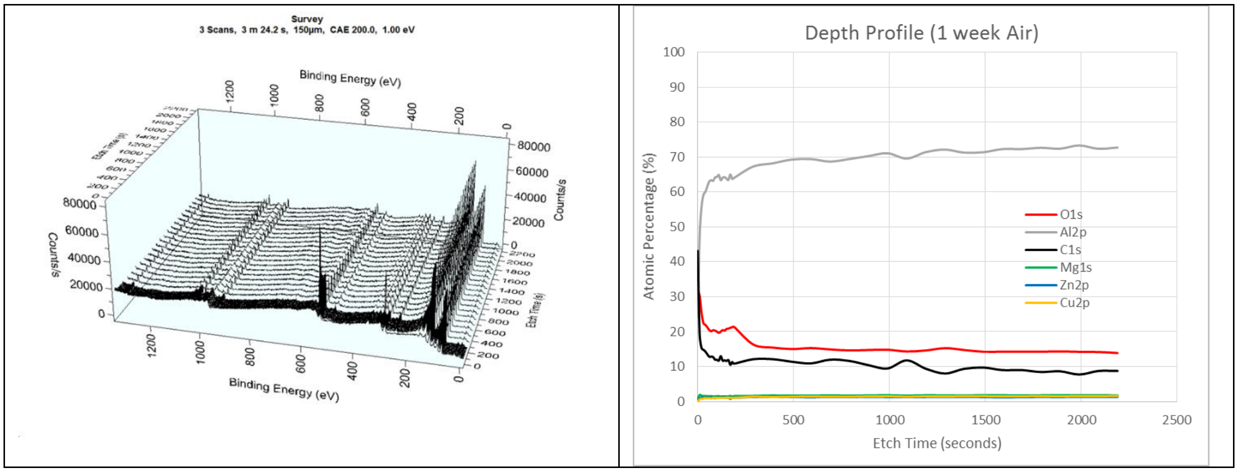

Figure 26. Survey scan and depth profile data collected over the scribed area of an AA7075-T73 alloy sample exposed to air for one week.

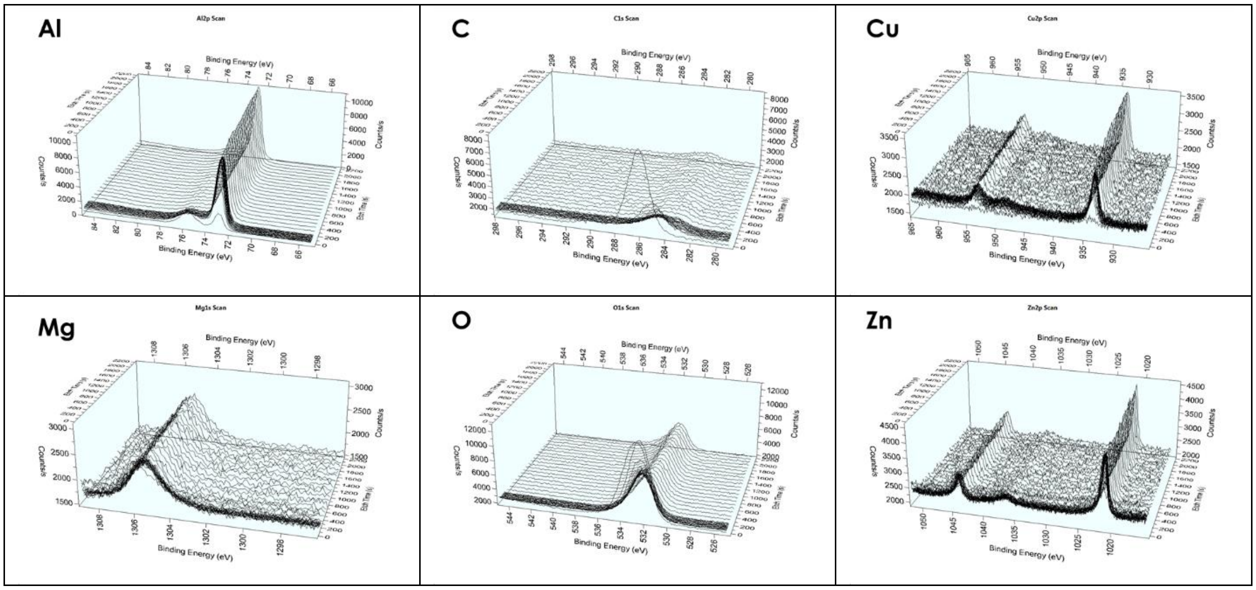

Figure 27. Depth profile data, for individual elements, collected over the scribed area of AA7075-T73 alloy exposed to air for one week.

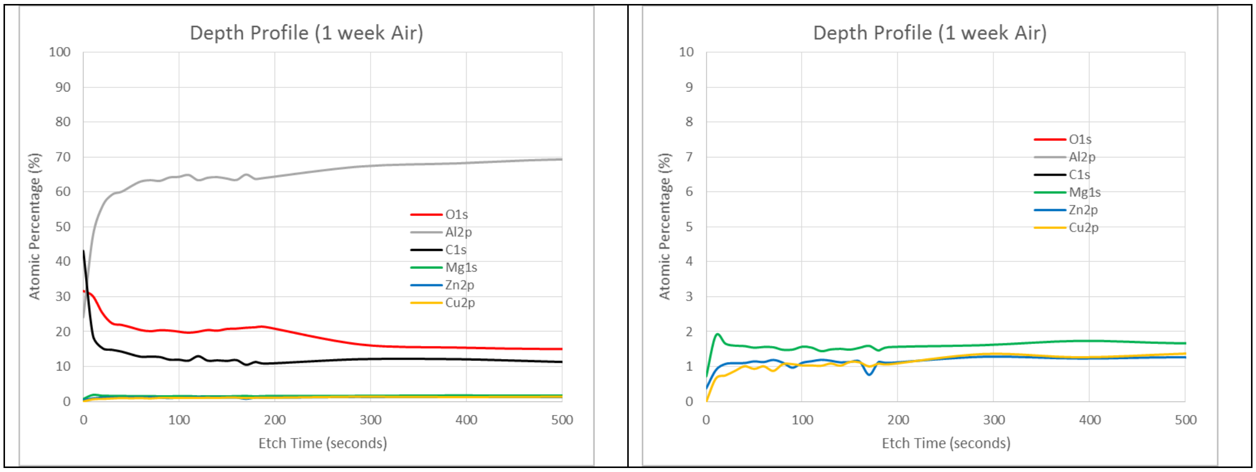

Figure 28. Depth profile data collected over the scribed area of an AA7075-T73 aluminum alloy sample, immediately after exposure to the air for one week, zoomed in for 0-500 seconds etch time (left image) and for 0-10% atomic percentage (right image).

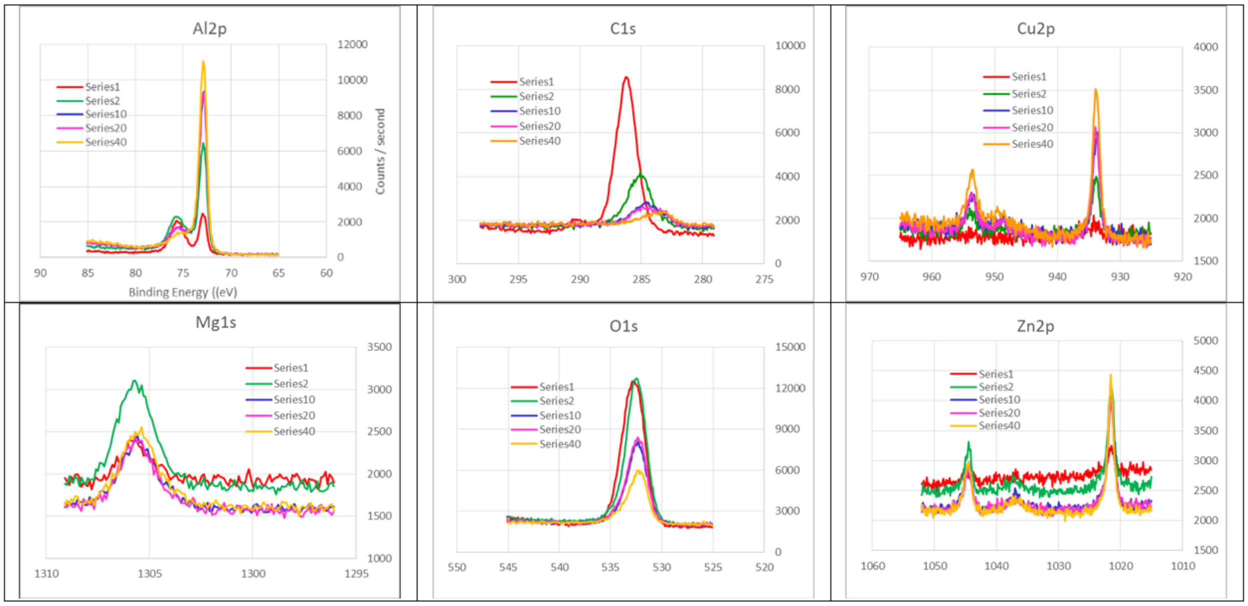

Figure 29. Selected spectra of individual element scans from the depth profile data collected over the scribed area of an AA7075-T73 aluminum alloy sample exposed to air for one week.

In summary, the XPS analysis obtained after exposing the scribed area of an AA7075-T73 aluminum alloy sample to air for one week showed that the scribed area was oxidized and that the oxide layer was enriched in Mg at a level similar to that of the control sample. There was also a slight surface enrichment of Zn that was lower than that of Mg. The carbon content was very low below the surface.

One-week of exposure to CO_2

Figure 30, Figure 31, and Figure 32 show the survey scan and depth profile data collected over the scribed area of an AA7075-T73 aluminum alloy sample after one week of exposure to CO_2 at room temperature and 700 Pa of pressure. Figure 33 shows selected spectra of element scans. As shown in Figure 30 and Figure 31, the oxygen content is lower than that of the sample exposed to air for one week but slightly higher than that of the control sample. This can be attributed to a possible chemical interaction between CO_2 and the sample. Unlike the AA7075-T73 sample that was exposed to air for one week, the aluminum peak (Figure 33) does not have a significant higher binding energy component (indicative of a metal oxide or carbonate) below the surface, which can be interpreted as an indication of a weak interaction between aluminum and the CO_2 environment. The other elements are present in the expected composition range. There is some surface enrichment of Mg and Zn where the Mg enrichment is slightly more pronounced.

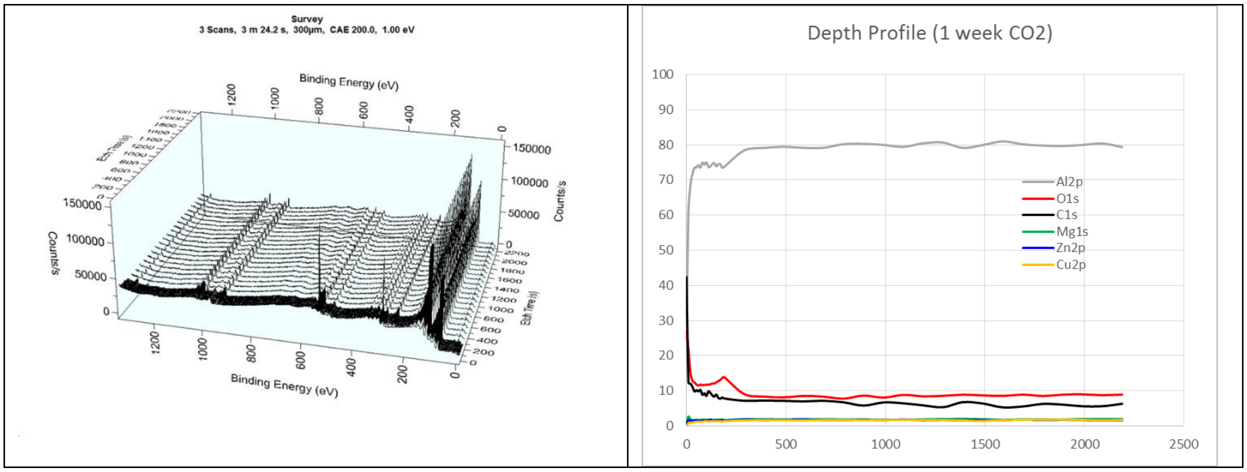

Figure 30. Survey scan and depth profile data collected over the scribed area of an AA7075-T73 alloy sample exposed to CO_2 for one week at 700 Pa (7 mbar) pressure and room temperature.

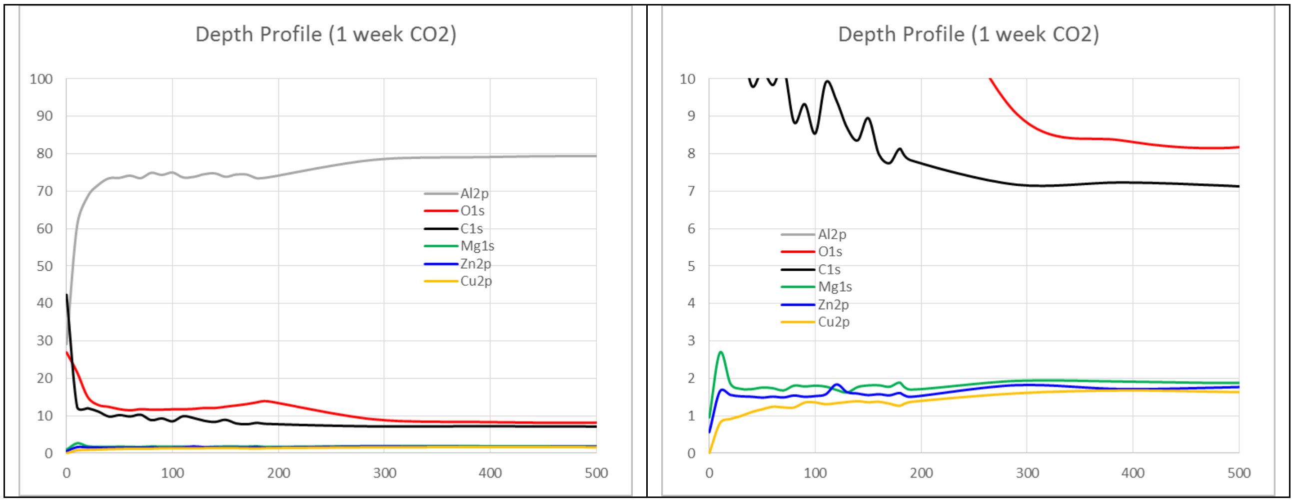

Figure 31. Depth profile data collected over the scribed area of an AA7075-T73 aluminum alloy sample, immediately after exposure to CO_2 for one week, zoomed in for 0-500 seconds etch time (left image) and for 0-10 atomic percentage (right image).

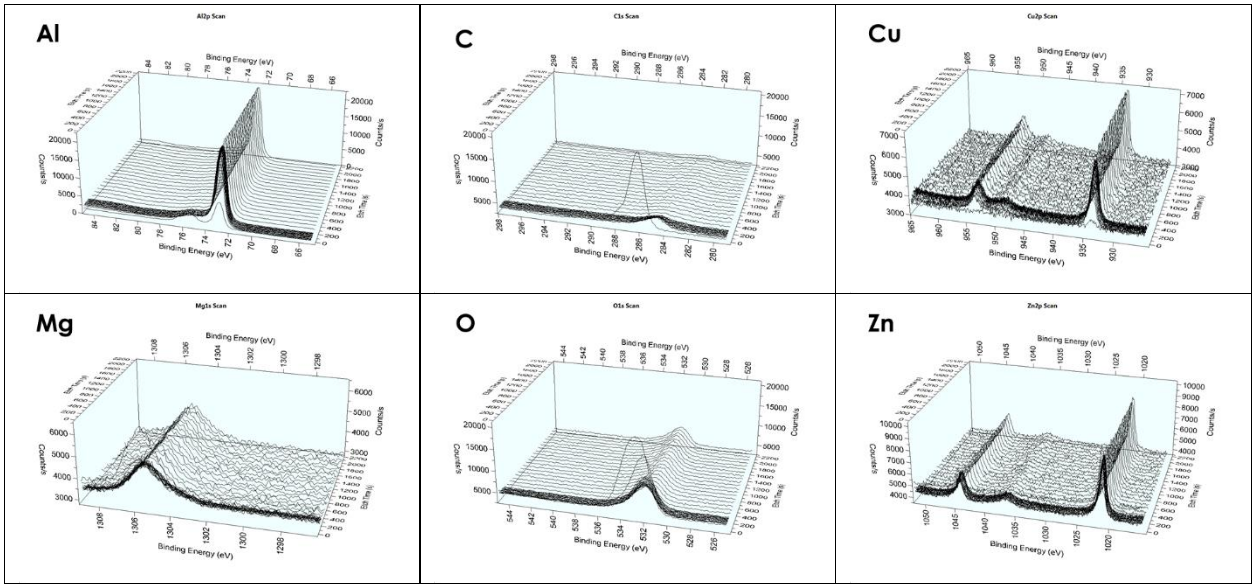

Figure 32. Depth profile data, for individual elements, collected over the scribed area of an AA7075-T73 alloy exposed to CO_2 for one week at room temperature and a pressure of 700 Pa.

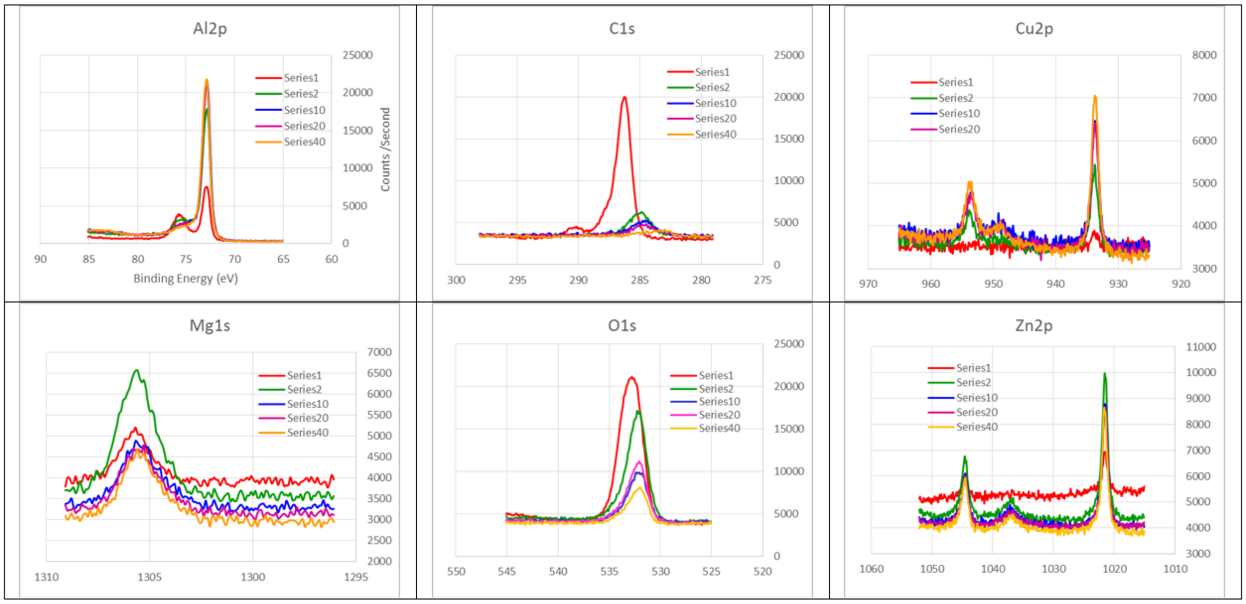

Figure 33. Selected spectra of individual element scans from the depth profile data collected over the scribed area of an AA7075-T73 alloy sample exposed to CO_2 for one week at 20 ^{o}C and a pressure of 700 Pa.

One-week of exposure to Mars gas

Figure 34, Figure 35, and Figure 36, show the survey scan and depth profile data collected over the scribed area of an AA7075-T73 aluminum alloy sample after one week of exposure to Mars gas at 20^{o}C and 700 Pa of pressure. Figure 37 shows selected spectra of element scans. Figure 35 and Figure 35 show that the content of carbon and oxygen are lower than those of the control sample (Figure 22 and Figure 25). Surprisingly, there is a noticeable difference between the one week Mars gas sample and the one week CO_2 sample. First, there is very little carbon below the sample surface (where the carbon presence is due to surface contamination) for the one week Mars gas sample that is significantly lower than that of the one week CO_2 sample. Second, the overall oxygen content is lower in the sample exposed to the Mars gas for one week, and the oxygen content drops more quickly below the surface. Furthermore, below the surface, the aluminum peak has a higher binding energy component (Figure 37), indicating the presence of aluminum oxide. When comparing the results of the sample exposed for 1 week to Mars gas to those of the sample exposed for 1 week CO_2, it appears that in the Mars gas, a thinner, yet more protective oxygen containing layer, is formed, that preventing further interaction between the metal and the gas environment. The only logical explanation for these results is the formation of thin oxide layer due to the interaction between the aluminum alloy sample and the small amount of oxygen present in the Mars gas, which prevents further interaction between CO_2 and the aluminum sample. This will result in very little carbon below the sample surface and in the overall low oxygen content. The other elements were present at the levels expected based on the composition of the alloy. There is some surface enrichment of Mg and Zn where the Mg enrichment is slightly more pronounced. In order to confirm these results, two additional exposures to Mars gas were conducted: a shorter one for two days and a longer one for two weeks.

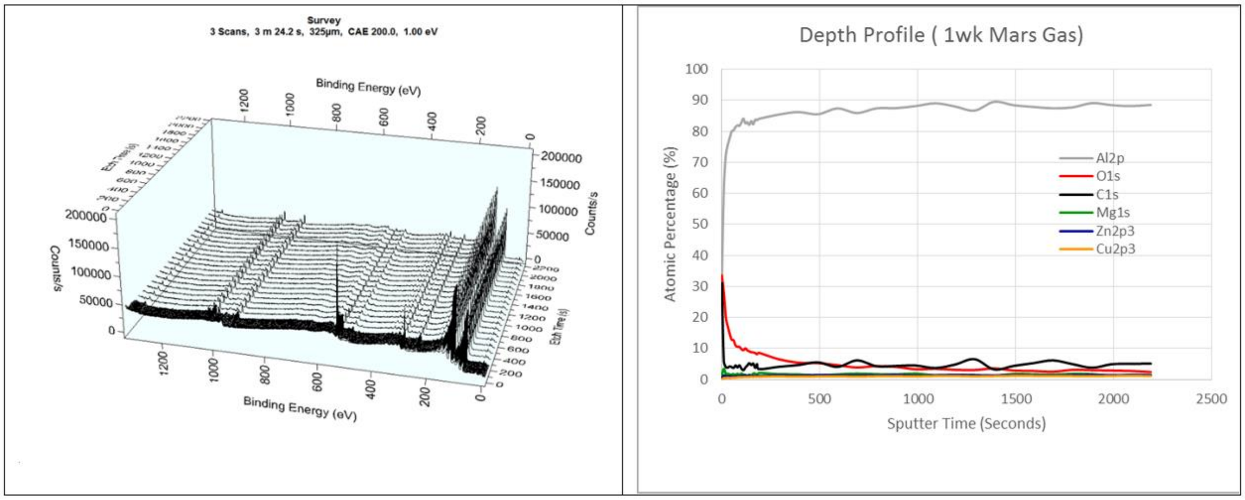

Figure 34. Survey scan and depth profile data collected over the scribed area of an AA7075-T73 alloy sample exposed to Mars Gas for one week at a temperature of 20 oC and a pressure of 700 Pa.

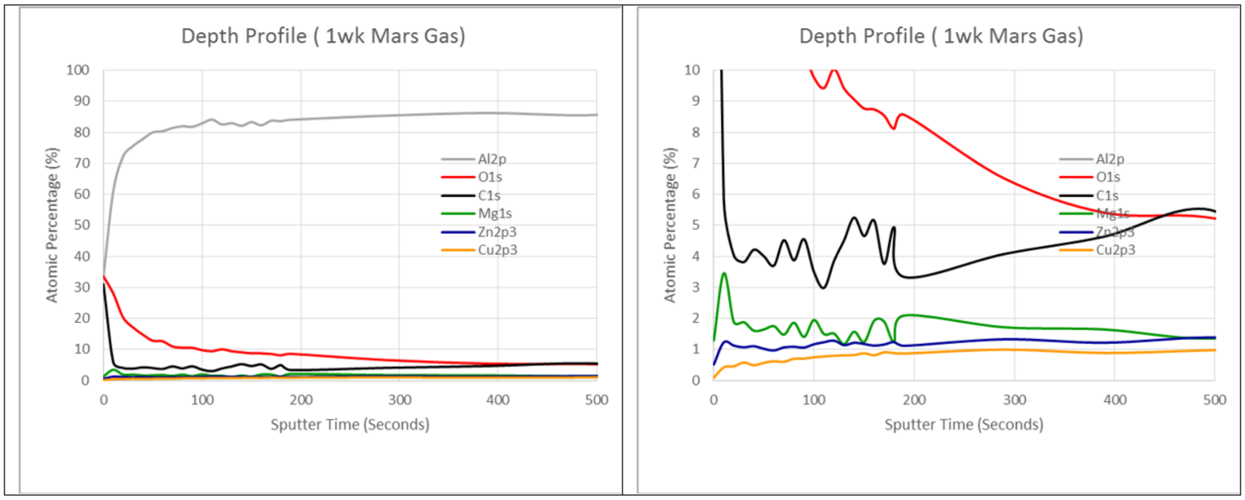

Figure 35. Depth profile data collected over the scribed area of an AA7075-T73 alloy sample, immediately after exposure to Mars gas for one week, zoomed in for 0-500 seconds etch time (left image) and for 0-10 atomic percentage (right image).

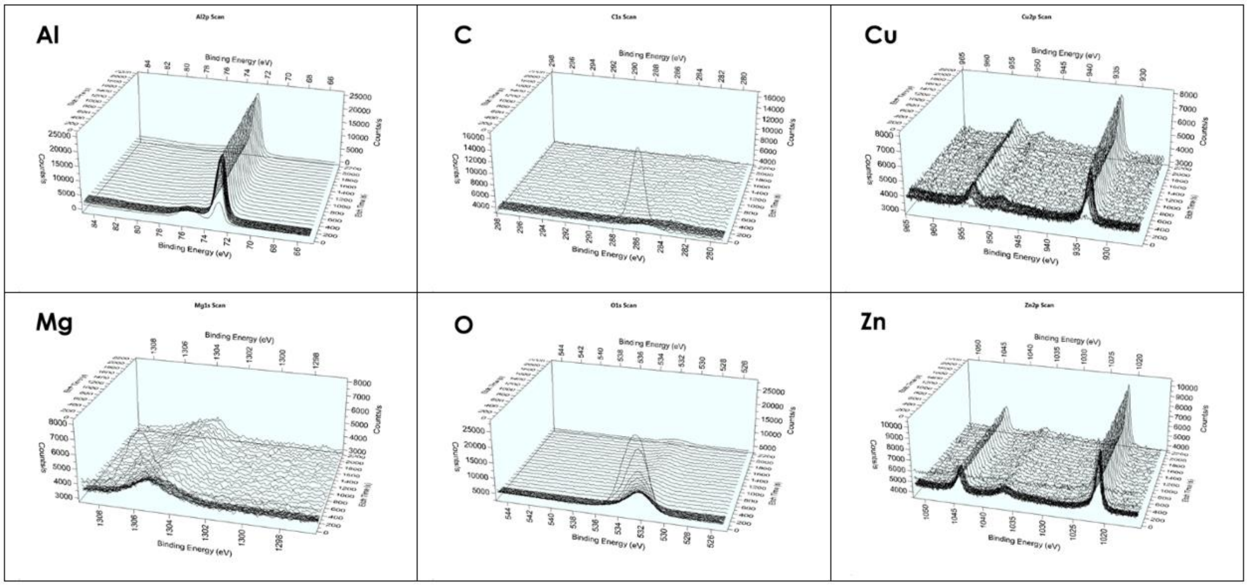

Figure 36. Depth profile data, for individual elements, collected over the scribed area of an AA7075-T73 alloy exposed to Mars gas for one week at a temperature of 20°C and a pressure of 700 Pa.

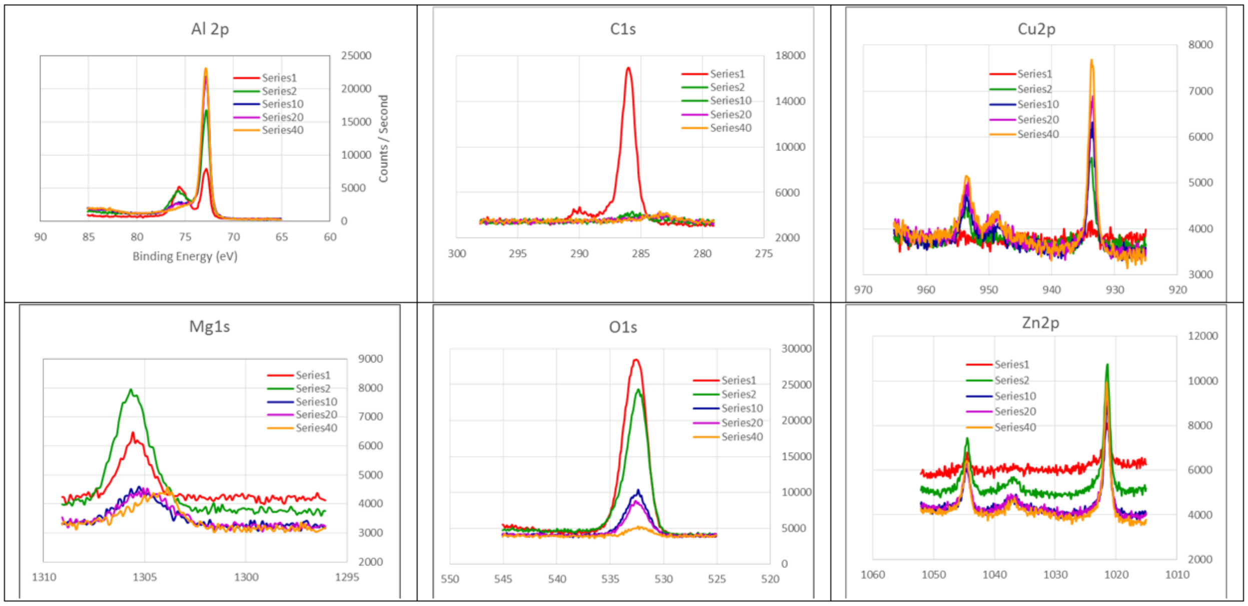

Figure 37. Selected spectra of individual element scans from the depth profile data collected over the scribed area of an AA7075-T73 alloy sample exposed to Mars gas for one week at room temperature and a pressure of 700 Pa (7 mbar).

Three-days of exposure to Mars Gas

Figure 38, Figure 39, and Figure 40, show the survey scan and depth profile data collected over the scribed area of an AA7075-T73 aluminum alloy sample after three days of exposure to Mars gas at 20^{o}C and 700 Pa of pressure. Figure 41 shows selected spectra of element scans. The data confirmed all the results obtained with the sample exposed to the Mars gas for one week. As expected, the overall oxygen content and the presence of aluminum oxide were slightly lower (Figure 38 and Figure 40)

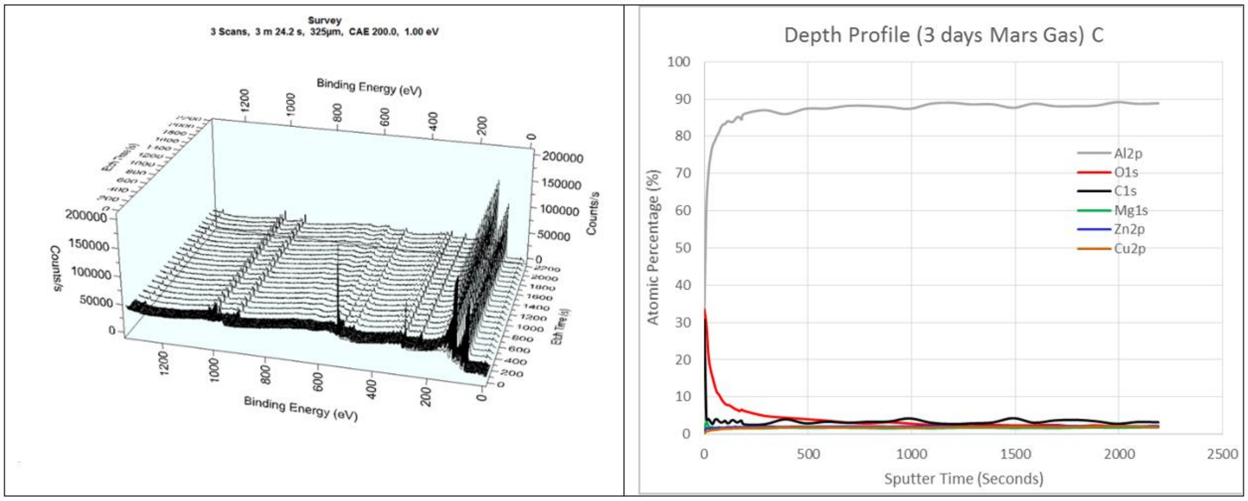

Figure 38. Survey scan and depth profile data collected over the scribed area of an AA7075-T73 alloy sample exposed to Mars Gas for 3 days at 700 Pa (7 mbar) pressure and room temperature.

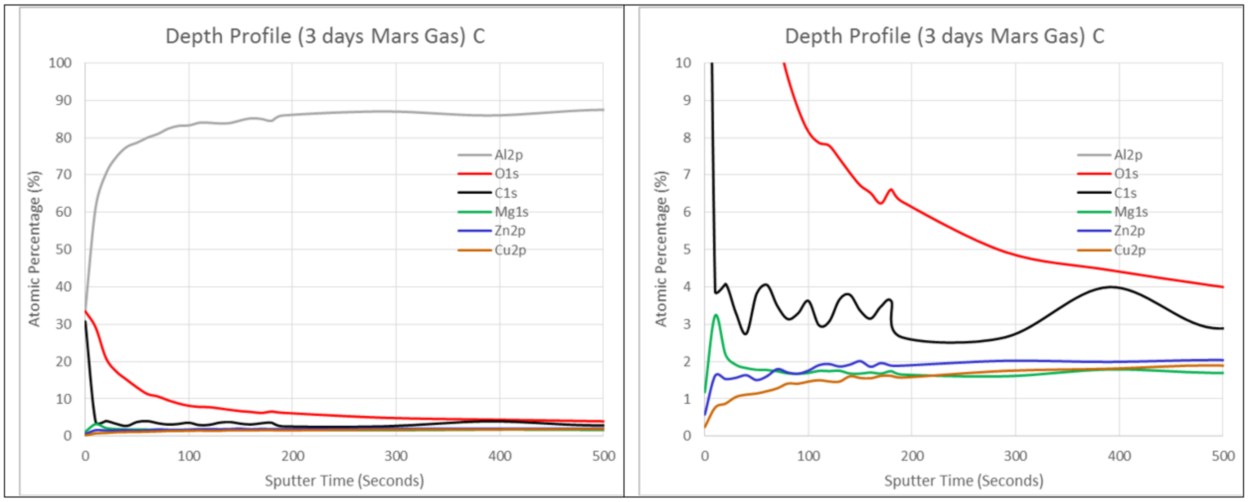

Figure 39. Depth profile data collected over the scribed area of an AA7075-T73 aluminum alloy sample, immediately after exposure to Mars gas for three days, zoomed in for 0-500 seconds etch time (left image) and for 0-10 atomic percentage (right image).

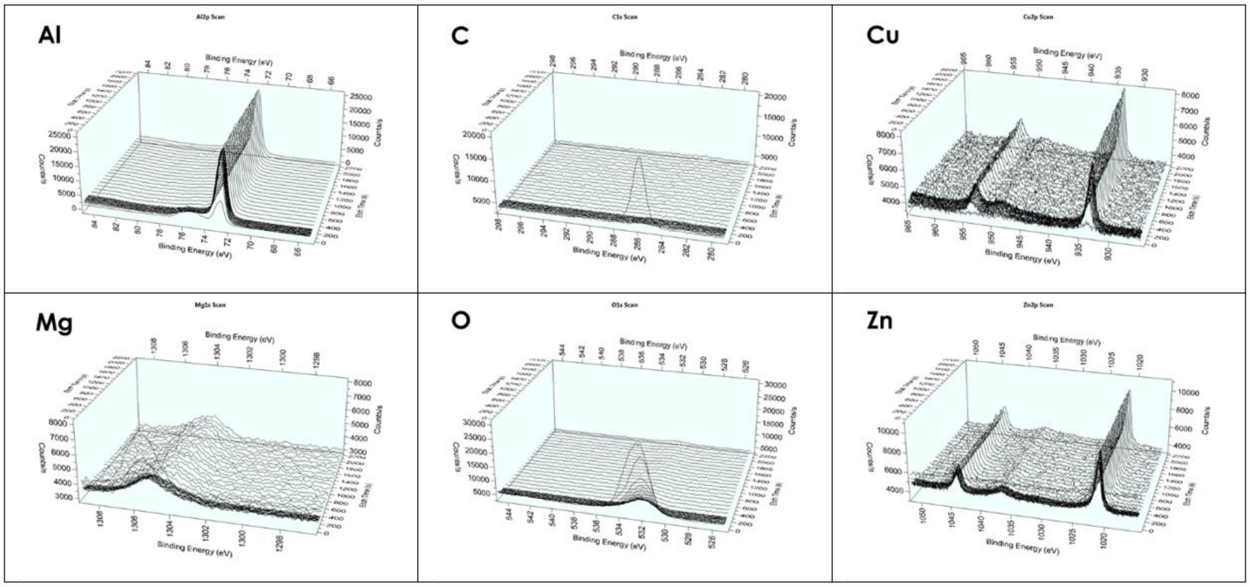

Figure 40. Depth profile data, for individual elements, collected over the scribed area of an AA7075-T73 aluminum alloy exposed to Mars gas for three days at 20 °C and a pressure of 700 Pa.

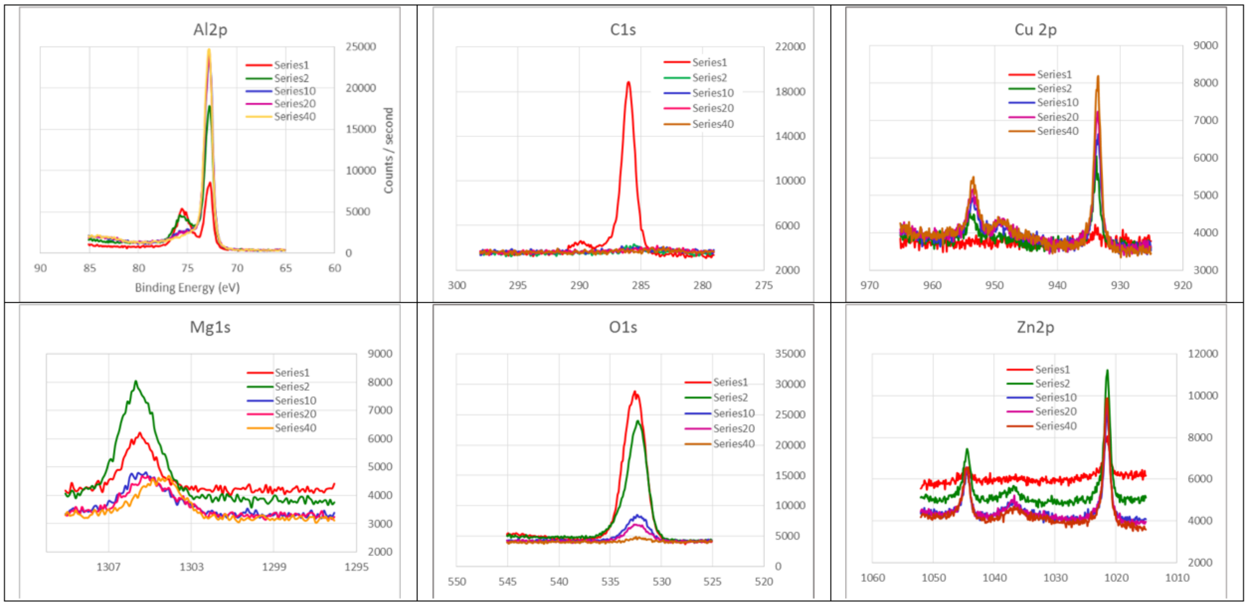

Figure 41. Selected spectra of individual element scans from the depth profile data collected over the scribed area of an AA7075-T73 alloy sample exposed to Mars gas for three days at 20°C and a pressure of 700 Pa.

Two-week exposure to Mars Gas

Figure 42, Figure 43, and Figure 44, show the survey scan and depth profile data collected over the scribed area of an AA7075-T73 aluminum alloy sample after two weeks of exposure to Mars gas at 20^{o}C and 700 Pa of pressure. Figure 45 shows selected spectra of element scans.

The data confirmed all the results obtained with the sample exposed to the Mars gas for one week: the quick drop of carbon content below the sample surface and the oxygen and aluminum peaks indicating the formation of an oxide layer. When comparing these results to those obtained for the sample exposed for 1 week, it can be seen that the oxide layer is much thicker after 2 weeks of exposure to Mars gas.

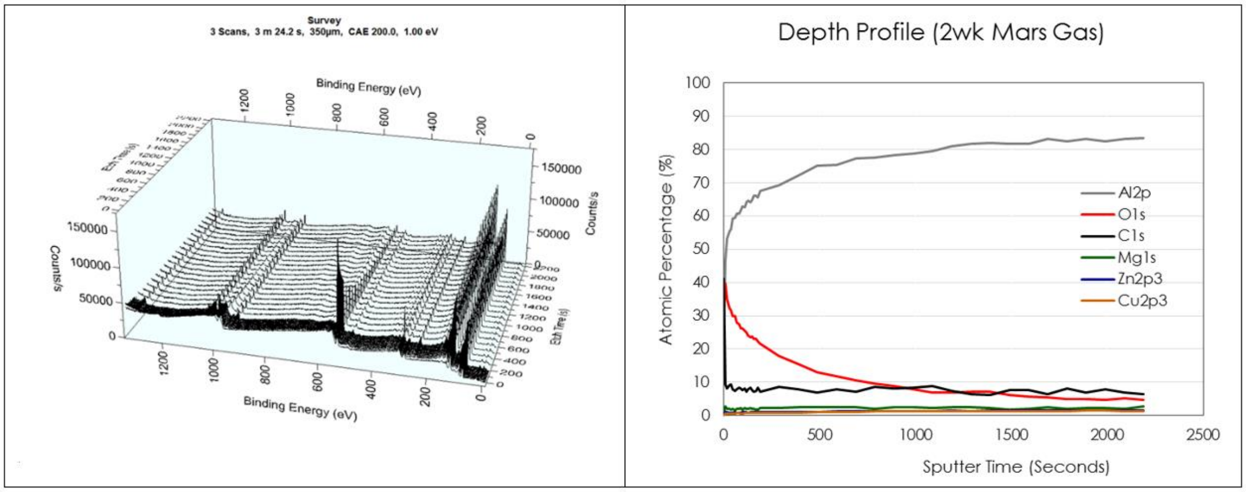

Figure 42. Survey scan and depth profile data collected over the scribed area of an AA7075-T73 alloy sample exposed to Mars Gas for two weeks at 20 ^{o}C and a pressure of 700 Pa.

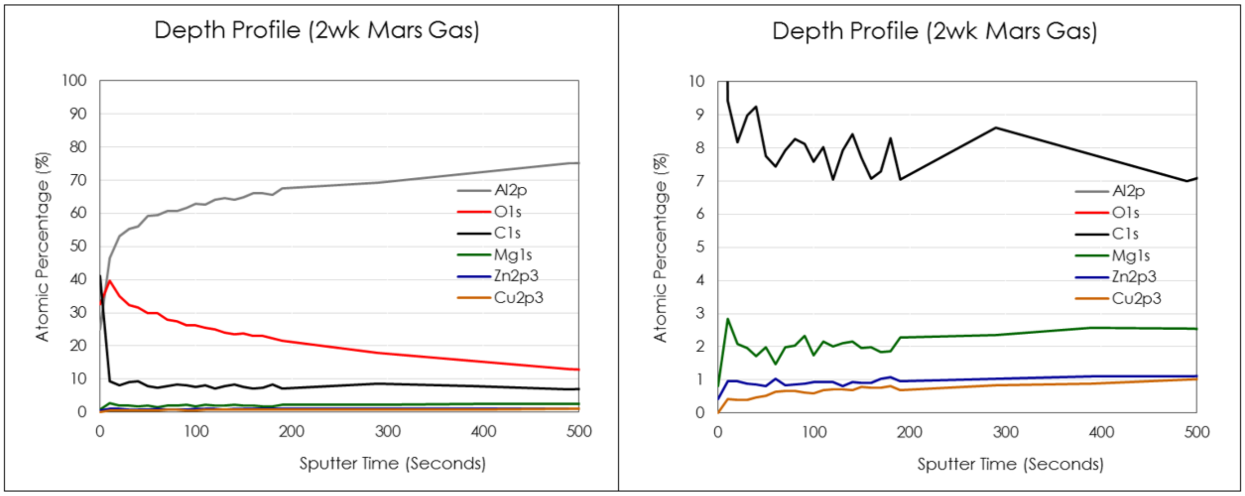

Figure 43. Depth profile data collected over the scribed area of an AA7075-T73 alloy sample, immediately after exposure to Mars gas for two weeks, zoomed in for 0-500 seconds etch time (left image) and for 0-10 atomic percentage (right image).

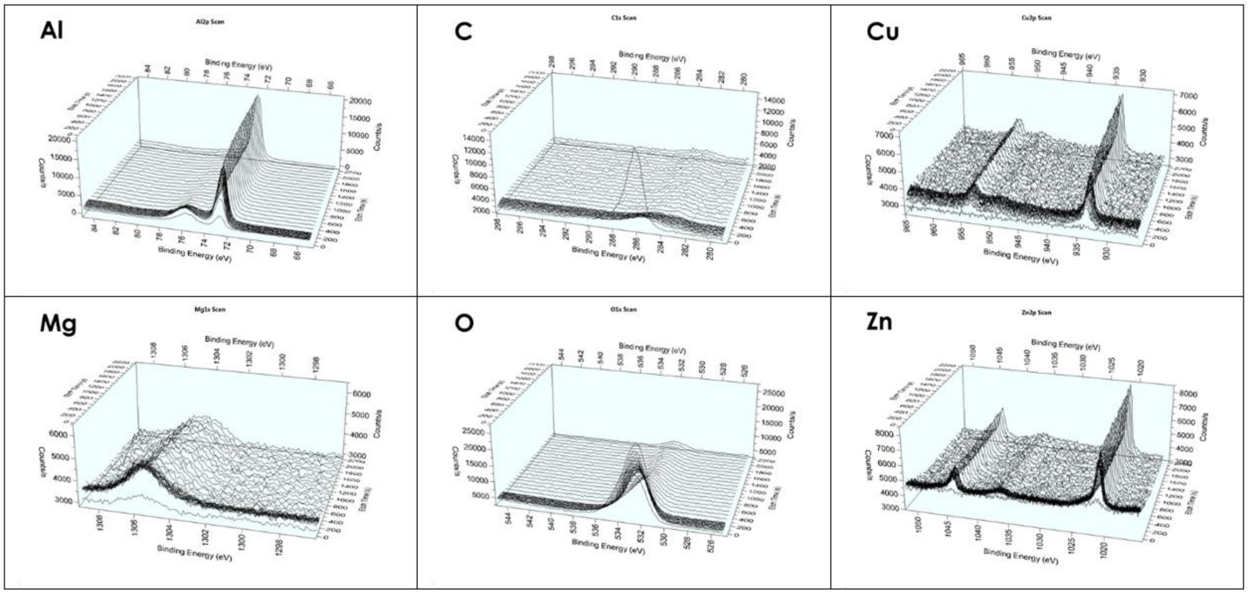

Figure 44. Depth profile data, for individual elements, collected over the scribed area of an AA7075-T73 alloy exposed to Mars gas for two weeks at 20ºC and a pressure of 700 Pa.

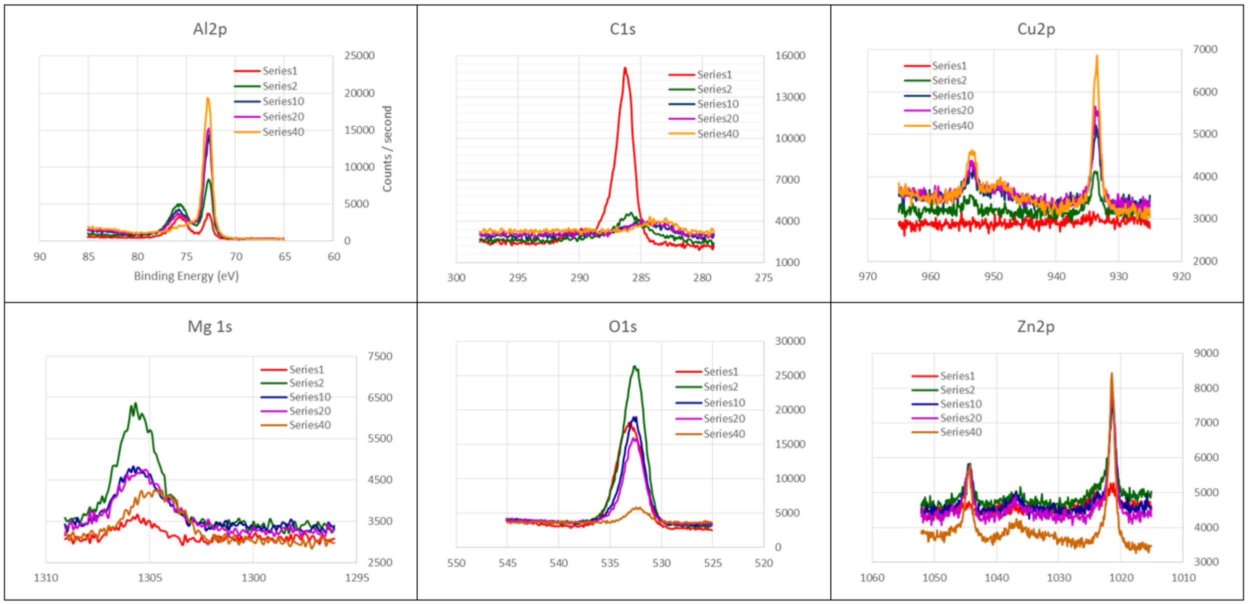

Figure 45. Selected spectra of individual element scans from the depth profile data collected over the scribed area of an AA7075-T73 aluminum alloy sample exposed to Mars gas for two weeks at 20ºC and a pressure of 700 Pa.

Conclusions

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 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 critical 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^{o}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 of the Mars environment that can affect this interaction such as: the effect of radiation on the oxidizing properties of perchlorates and the possible catalytic effects of the clays present in the Martian regolith.

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 most important finding of our preliminary experiments is the significant role of the small amount of oxygen in the interaction between Mars Gas and AA7075-T73 aluminum alloy. The XPS results showed that AA7075-T73 aluminum alloy forms an oxide layer in the presence of Mars gas and that the carbon inclusion into the oxide layer is minimal if at all. This is different from what was observed when the alloy was exposed to pure CO_2 under the same conditions of temperature and pressure. Under all three exposure conditions, surface enrichment of alloying elements was observed for magnesium and zinc but not for copper.

The results of our one-year project provide strong justification for further investigation of the corrosion mechanism of materials relevant to long-term surface operations in support of the human exploration on Mars. Based on our preliminary experimental results that show that AA7075-T73 aluminum alloy behaves differently when exposed to the gases present in the Martian atmosphere at room temperature, we propose follow on work that would include other components of the Mars environment such as regolith chemistry, radiation, brines, and clays. The goal of the follow on 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 three families of 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.

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