8

Review Article

Rhawn G. Joseph*, Natalia S. Duxbury, Giora J. Kidron, Carl H. Gibson, and Rudolph Schild

Mars: Life, Subglacial Oceans, Abiogenic Photosynthesis, Seasonal Increases and Replenishment of Atmospheric Oxygen

https://doi.org/10.1515/astro-2020-0020 Received Sep 3, 2020; peer reviewed and revised; accepted Oct 12, 2020

Abstract: The discovery and subsequent investigations of atmospheric oxygen on Mars are reviewed. Free oxygen is a biomarker produced by photosynthesizing organisms. Oxygen is reactive and on Mars may be destroyed in 10 years and is continually replenished. Diurnal and spring/summer increases in oxygen have been documented, and these variations parallel biologically induced fluctuations on Earth. Data from the Viking biological experiments also support active biology, though these results have been disputed. Although there is no conclusive proof of current or past life on Mars, organic matter has been detected and specimens *resembling* green algae / cyanobacteria, lichens, stromatolites, and open apertures and fenestrae for the venting of oxygen produced via photosynthesis have been observed. These life-like specimens include thousands of lichen-mushroom-shaped structures with thin stems, attached to rocks, topped by bulbous caps, and oriented skyward similar to photosynthesizing organisms. If these specimens are living, fossilized or abiogenic is unknown. If biological, they may be producing and replenishing atmospheric oxygen. Abiogenic processes might also contribute to oxygenation via sublimation and seasonal melting of subglacial water-ice deposits coupled with UV splitting of water molecules; a process of abiogenic photosynthesis that could have significantly depleted oceans of water and subsurface ice over the last 4.5 billion years.

Keywords: Mars, Water, Oxygen, Oceans, Algae, Cyanobacteria, Atmosphere, Lichens, Life on Mars

1 Abiogenic vs Biology: Martian Atmospheric Oxygen

The constituents of the Martian atmosphere were unknown until 1947 when carbon dioxide was detected, followed by the observation of water vapors and 200 cm atm (20mA) of oxygen as based on the analyses of B-band spectra (Dunham 1952). Although abiotic Martian sources cannot be ruled out, the presence of atmospheric oxygen is an obvious biosignature; 70% of which, on Earth, is produced via

Corresponding Author: Rhawn G. Joseph: Astrobiology Research Center, Stanford, California, The United States of America; Email: Rhawn|oseph@gmail.com

Natalia S. Duxbury: Dept, of Physics and Astronomy, George Mason University, VA, The United States of America

Giora J. Kidron: Institute of Earth Sciences, The Hebrew University of

Carl H. Gibson: Scripps Center for Astrophysics and Space Sciences; Dept. Aerospace Engineering, University of California, San Diego, The United States of America

Rudolph Schild: Harvard-Smithsonian Center for Astrophysics (Emeritus), Cambridge, MA, The United States of America

photosynthesizing algae and cyanobacteria (Buick 2008; Sanchez-Baracaldo and Cardona 2019; Graham *et al.* 2016) and the remainder a product of water and soil dwelling plants and organisms including lichens (Canfield 2014; Ten Veldhuis *et al.* 2020).

There is now evidence, but no conclusive proof, that algae and lichens may have colonized Mars (Dass 2017; Di-Gregorio 2002; Joseph 2016; Joseph *et al.* 2019, 2020a,b,c; Krupa 2017; Levin *et al.* 1978) whereas structures resembling open-cone apertures and fenestrae have also been observed (Joseph *et al.* 2020b,c,d), and which are often formed, on Earth, secondary to the production and release of oxygen via photosynthesis (Bengtson *et al.* 2009; Freeman *et al.* 2018; Sallstedt *et al.* 2018). If these specimens are living, fossilized, or completely abiogenic, is unknown. However, if biological, they may be contributing to the production of oxygen on Mars.

2 The Discovery of Atmospheric **Oxygen: An Overview**

The detection of atmospheric oxygen was first reported in 1952 (Dunham 1952). In 1964, and as based on A-band spectra, $70 \, \text{cm}$ atm of O_2 was detected in the Martian atmosphere (Kaplan et al. 1964), whereas four years later, a value of 20 cm atm was obtained (Belton and Hunten 1968). Additional studies during the 1970s documented that oxygen levels varied over time (Strickland et al. 1973), and doubled over the course of a year; ranging from 0.5 to 1% of the total upper atmosphere (Barth 1974). However, also, in the 1970s, investigators discovered that there is much more oxygen than can be produced from the photolysis of a pure carbon dioxide atmosphere and there must be an unknown net source of oxygen relative to carbon (Carleton and Traub 1972). "Photodissociation of carbon dioxide, to produce carbon monoxide and atomic oxygen," was therefore ruled out (Barth 1974). It was suspected that these variations were related to seasonal fluctuations in water vapor (Barth 1974; Strickland et al. 1973). Thus, some investigators began to embrace the possibility that Mars is a very wet, H₂O enriched planet and that oxygen was being split off from molecules of water vapor via UV rays (Carleton and Traub 1972; McElroy et al. 2012) thereby resulting in hydrogen escape into space, with the heavier oxygen atoms being left behind. It was also determined that oxygen levels were lowest in the upper atmosphere and increased toward the surface (Barth 1974); findings that supported the possibility that oxygen and oxygen ions, like hydrogen, may be leaking into space (McElroy et al. 2012). However, as oxygen is reactive and can be destroyed, these findings, in the 1970s, led many scientists to suspect that oxygen was somehow being replenished at ground level but that water could not be the primary source of oxygen. To continually produce oxygen, the amount of water that had to be lost and converted to oxygen over the course of the last 3 billion years would require the evaporation of a planet wide ocean covering the entire surface of Mars (Barth 1974). Therefore, as it appeared, at that time, that there was insufficient surface water, then photolysis of water vapors could not account for the amount of oxygen present and its replenishment could not be explained by the evaporation of water and the splitting of H₂O molecules. This scenario only becomes plausible if ancient Mars had vast oceans and that the remnants of that planet-wide ocean was currently hidden beneath the surface.

3 The 1976 Viking Biology **Experiments**

Some investigators began to suspect that oxygen-producing, photosynthesizing organisms may have colonized the Red Planet; with the latter hypotheses leading to the 1976 Viking Labeled Release (LR) experiments which detected evidence of biological activity at two locations on the surface of Mars (Levin and Straat 1976, 1977). Specifically, prior to landing on the Red Planet, thousands of field tests were conducted and it was demonstrated that the LR experiment was capable of accurately detecting a very wide range of microorganisms including algae and lichens. Subsequently, at two locations over a thousand miles apart, a nutrient containing radioactive carbon was added to a Raw Soil Sample. As predicted radioactivity was observed in released gasses and initially this was believed to be evidence of active metabolism. By contrast, when the Control Soil Sample was heated to 50°C biological activity decreased by 65% whereas when subject to 160°C there was no evidence of biology. Thus, based on pre-mission criteria, the LR experiment had found evidence of biological activity on Mars.

These results were nevertheless rejected as due to reactive oxidizing agents within the soil including peroxide and iron oxides (Klein 1978). Later studies, however, have found that Martian perchlorates are not reactive given the parameters of the LR experiments and that the amount of hydrogen peroxide required to simulate the LR results is completely implausible (Levin and Straat 1981).

Subsequently, Bianciardi et al. (2012) performed a mathematical complexity deep analysis of the Viking LR data, employing seven complexity variables. It was determined that the Viking LR responses from the Raw Soil exhibited highly organized responses typical of biology and a different pattern from the Control Samples which resembled near-random noise. Nevertheless, the Viking LR results continued to be disputed as due to false positives (reviewed in Lanse *et al.* 2016).

The Viking "Gas Exchange" experiment was also part of the Viking biology package, and also provided evidence of active biology as well as oxygen production. Specifically, soil samples were also humidified at ~10 $^{\circ}$ C and in consequence 70-700 nmol of O2 was released (Oyama and Berdahl 1977); evidence suggestive of active biology. On Earth, the humidification of soil results in the proliferation of photosynthesizing algae/cyanobacteria and a significant increase in oxygen production due to biological activity (Lin et al. 2013; Lin and Wu 2014; Metting 1981; Zhang and Filser 2017).

Nevertheless, these results were also rejected as due to superoxides; and it was argued that the finding from the Gas Exchange experiment and the LR experiment were contradictory in that heating had opposite effects (Klein 1978). However, the LR experiment employed temperatures ranging from 50°C to 160°C which reduced "biological activity" by 65% to 100%; whereas the Gas Exchange experiment employed temperature of ~10 $^{\circ}$ C; so there is no contradiction.

It has also been argued that calcium perchlorate exposed to gamma rays decomposes in a CO₂ atmosphere to form hypochlorite (ClO⁻), chlorine dioxide (ClO₂) and trapped oxygen (O_2) . Therefore, the release of this oxygen, when percholates are subject to heating, can account for the results of the Gas Exchange experiment (Quinn et al. 2013).

On the other hand, it's been demonstrated that the release of oxygen and radioactive gasses from Martian soil samples also occurs well below the temperatures for percholate decompensation (Zent and McKay 1994; ten Kate et al. 2010; Levin and Straat 1981, 2016). Moreover, the temperature extremes employed to decompensate percholates not only might kill any bacteria present, but can destroy organics and potential biomarkers associated with oxygenproducing cyanobacteria (Montgomery et al. 2019). High temperatures produced by the LR did not increase oxygen production, but decreased and eliminated all evidence of biological metabolism. Therefore, although the results from both Viking biology experiments have been repeatedly disputed they have not been completely refuted and are still subject to debate.

4 Soil – Atmosphere Exchange and Abiogenic Oxygen?

To account for oxygen in the Martian atmosphere, a variety of hypothetical abiogenic scenarios have been proposed involving the interaction of the atmosphere with reservoirs of oxygen contained in minerals and soil (Franz et al. 2020; Livengood et al. 2020; Sutter et al. 2015, 2017) and the heating of magnesium, sodium, and potassium chlorate (Hogancamp et al. 2018). For example, the rover Curiosity's SAM instrument (Sample Analysis at Mars) has provided indirect evidence for carbonates which in turn may have served as a sink for CO₂ (Franz et al. 2020). In addition, there is 60% more atmospheric vs soil/mantle carbon thus raising the possibility that the geochemical cycling of CO₂, from the mantle is providing oxygen which is released into the soil and atmosphere (Franz et al. 2020). However, the potential

abiogenic sources for CO₂ are unknown, and the release of evolved O₂ requires substantial heating (over 218°C) well above the norm for the surface of Mars where, depending on terrain and thermal inertia (Martínez et al. 2017a; Hahn et al. 2011) heat fluxes are generally below 27.3 miliwatts per square meter (Plesa et al. 2016) whereas, according to NASA, summertime temperatures even at the equator seldom exceed 20°C (70°F).

Hogancamp et al. (2018); Sutter et al. (2015, 2017) have argued and provided experimental results, which they believe support their hypothesis that oxygen released by the SAM, and that the Martian oxygenated atmosphere, is a consequence of the decomposition of perchlorates and/or chlorates/Fe mixtures at temperatures ranging from 218°C to 755°C (Hogancamp et al. 2018); which, however, are implausibly extreme and "too high to be consistent with SAM data" (Sutter et al. 2015). These studies also assume the presence of substantial amounts of chlorate in the soil, when the amounts and different types of chlorate are unknown (Hogancamp et al. 2018). It was also found that heating Fe did not produce but consumed up to 75% of the evolved oxygen derived from chlorite decompensation (Hogancamp et al. 2018) whereas it's been well documented that the soil contains high concentration of Fe (Grotzinger et al. 2014, 2015).

A correlation between atmospheric oxygen levels and increases in ground temperature have also been reported based on data derived from spectra obtained by the Mars Atmosphere and Volatile Evolution (MAVEN) mission (Livengood et al. 2020). It was found that atmospheric oxygen production appears to be diurnal, increasing to a maximum during the afternoon, and resulting from an exchange between the atmosphere and sources at the surface. Livengood et al. (2020) hypothesize that CO2 molecules trapped in regolith, when exposed to warmth and water, releases oxygen into the atmosphere. However, they also admit that the abiogenic, physical mechanisms involved "are not obvious" and thus unknown.

On Earth, oxygen production is also diurnal, increasing with exposure to sunlight and increased temperatures, often reaching a maximum during the afternoon and is due to biological photosynthesis (Jorgensen et al. 1979). These findings parallel those of Livengood et al. (2020) whose evidence of diurnal oxygen production may also be an indication of biological activity.

The oxidation of organic matter is yet another possible abiogenic source for oxygen (Franz et al. 2020). However, the problem with this hypothesis is the dearth of organic material so far discovered; and there is little evidence that soil-atmospheric interaction can abiotically produce oxygen unless exposed to high temperatures. Thus, Franz et

al. (2020), have suggested that "biological photosynthesis" is the "best analogue" for understanding how CO₂ is converted to oxygen.

5 Ancient Mars and Meteors: **Evidence of Oxygen, Organics** and Biology

In the last 150 years, 227 meteorites have been found that are believed to have originated on Mars (Meteoritical Bulletin Database 2020). With the exception of meteors NWA 7034 (Agee et al. 2013) and NWA 7533 (Humayun et al. 2013) which are regolith breccia, most Martian meteors have a basaltic composition and have been categorized as orthopyroxenite (ALH 84001) nakhlites (N), chassignites (C), and Shergotty (S) based on chemistry, texture, mineral composition and age. The Chassigny (C) Nakhlites (N), Shergottite (S) meteorites have been respectively assigned generalized average ages of 1.3bya, 1.32 to 1.17bya, 465 to 175 mya (Nyquist et al. 2001). Yet another Martian meteorite, NWA 7034 has been dated to 2.089 bya (Agee et al. 2013) whereas ALH may be 3.8 to 4.5 billion years in age (Jagoutz et al. 1994; Nyquist et al. 1995; Ash et al. 1996; Wadhwa and Lugmair 1996). What these meteorites generally have in common is exposure to water prior to ejection from Mars and evidence of varying (ranging from negligible to relatively high) levels of oxygen (Shaheen et al. 2015; Agee et al. 2013; Nyquist et al. 2001; Clayton and Mayeda 1983, 1996; Romanek et al. 1998; Halevy et al. 2011; McKay et al. 2009; Thomas-Keprta et al. 2009).

Based on an analysis of these Martian meteorites Richter et al. (2008) have proposed a "clear progression of oxygen fugacity" from minimal (ALH) to oxidized (Nakhlites) to intermediate (Shergottite). NWA 7034, however, has been found to have "an order of magnitude of more indigenous water than most SNC meteorites" and contains evidence of "multiple oxygen reservoirs on Mars" (Agee et al. 2013). It was concluded that NWA 7034 may represent the best approximation of atmospheric and surface conditions 2 bya.

Moreover, there are distinct and different phases of Mnoxide deposition which indicates a progressive increase and "abundant molecular oxygen within the atmosphere and some groundwaters of ancient Mars" (Lanza et al. 2016). Furthermore, on Mars, Mn oxides and other indices of oxidation, indicate reactive oxygen species including O₂ that contributed to the oxidizing environment of Mars (Lanza et

al. 2016). Mars, therefore appears to have become increasingly oxygenated.

That the oxidation of the Martian surface is due primary to free oxygen is also evidenced by the significant amount of atmospheric oxygen sequestered in Fe-bearing sediments and as indicated by the massive amounts of oxidized Fe on the surface (Kolb et al. 2006; McLennan and Grotzinger 2008). The surface and various minerals were likely oxidized due to atmospheric-oxygen-groundwater-mediated diagenesis, in the ancient past, in response to heightened levels of O₂ (Lanza et al. 2016; Tosca et al. 2008).

Based on the analysis of Martian paleosol phosphorus depletion (Retallack 2014) and sulfur species in various states of redox (Parnell et al. 2018), it's been argued that sulfur oxidizing bacteria, chemolithoautotrophic bacteria and sulfur oxidizers may have dwelled on Mars between 4.1 to 3 by a under oxygenated conditions, and with sulfate the resulting end product of biologically induced sulfur oxidation (Macey et al. 2020). Parnell et al. (2018) have suggested that moist Gale Crater lake sediments may have supported a diversity of potential habitats for subsurface sulphate reducing organisms. The detection of jarosite at Meridiani Planum, also suggests water-atmosphere-biological interactions; i.e. "microbially produced jarosite via pyrrhotiteassociated sulphide oxidation" (Norlund et al. 2010). Significant amounts of atmospheric oxygen sequestered in Fe-bearing sediments has also been reported (Kolb et al. 2006; McLennan and Grotzinger 2008). There is also evidence that levels of O₂ may have been much higher than today (Lanza et al. 2016; Tosca et al. 2008).

There are also distinct and different phases of Mn-oxide deposition, and this indicates a progressive increase and "abundant molecular oxygen within the atmosphere and some groundwaters of ancient Mars" (Lanza et al. 2016). As argued by Lanza et al. (2016) the evidence based on Mx oxidation suggests aerobic respiration by microorganisms that may have been producing free oxygen via photosynthesis. As summed up by Hartman and McKay (1995) "Given the similarity of the environments on the early Mars and early Earth it is plausible that life originated on Mars and oxygenic photosynthesis also began there at a very early stage."

Although considered controversial (Steele et al. 2012; Treiman and Essen 2011) evidence of biological residue, carbonates, chains of magnetite and fossilized polycyclic aromatic hydrocarbons (PAHs) have been found in ALH 84001 (McKay et al. 2009; Clement et al. 1998) which has been dated to around 4 bya. It's been argued that at least 25% of the organic residue is biological (Thomas-Keprta et al. 2009). For example, the Martian PAHs were found in those areas of the meteor rich in carbonates (Clement et al.

1998), whereas the magnetotactic residue has the characteristic chain-like organization that is commonly biological in origin (Clement et al. 1998; McKay et al. 1996, 2009). These biological indices may have been produced by carbonate and iron-eating bacteria, magnetotactic bacteria, algae, or fungi at least 3.8 billion years ago (Thomas-Keprta et al. 2009) in an aqueous environment (Halevy et al. 2011; McKay et al. 2009; Thomas-Keprta et al. 2009) and possibly in the presence of oxygen (Shaheen et al. 2015) as also indicated by isotopic evidence of ozone (Farguhar et al. 1998) which is a product of oxygen.

In addition, structures resembling stromatolites possibly constructed by photosynthesizing-oxygen-producing algae / cyanobacteria have been observed on Mars (Bianciardi et al. 2014, 2015; Joseph et al. 2019, 2020a,c; Rizzo 2020; Rizzo and Cantasano 2009, 2016; Ruff and Farmer 2016) at least one of which is dated to 3.7 bya (Noffke 2015). Although it has been questioned if all micro-thromobolites on Earth or Mars- are truly biological, eight of the Martian





Figure 1. (Top) Lake Thetis under water stromatolite. Note fenestra. (Photo Credit: Government of Western Australia Department of Mines and Petroleum, (Bottom) Sol 122: Martian specimen with evidence of fossilized fenestrae. Several "peanut-brittle" specimens resembling thrombolite mats appear in the bottom portion of the photo. Reproduced from Joseph et al. (2020d).

sedimentary-stromatolites structures, so far reported, are nearly identical to the concentric-domical stromatolites of Lake Thetis, Australia, and may range in age from a few thousand to a few million years (Joseph et al. 2020c). Moreover, they were photographed in the presence of microbial mats and consist of numerous open-cone-apertures and fenestra (Joseph et al. 2020a,c,d). On Earth, cyanobacteria construct stromatolites; and fenestra, open cones and apertures are commonly formed in the matrix by oxygen gas bubbles produced via photosynthesis (Bengtson et al. 2009; Freeman et al. 2018; Sallstedt et al. 2018).

In addition, organic matter preserved in mudstone, dated to 3.5 by a has been detected in Gale Crater by the SAM instrument (Eigenbrode et al. 2018). These include diverse molecular structures likely derived from organic macromolecules; the source of which could be geological or biological, i.e. ancient life (Eigenbrode et al. 2018). These findings are consistent with those obtained from ALH 84001 (Thomas-Keprta et al. 2009), the detection of chlorobenzeen and dischloroalkanes previously found in Gale Crater mudstone (Freissinet et al. 2015), the chloromethanes detected during the 1976 Viking mission (Navarro-González et



Figure 2. Sol 122 (top left) and 529 (bottom). Comparisons of Gale Crater sedimentary structures with fenestra and open coneapertures with Lake Thetis stromatolite and fenestrae. Fenestra and open-cone like apertures are often formed in the surrounding matrix by the production of oxygen gas bubbles via photosynthesis. Reproduced from Joseph et al. 2020d.

al. 2010), and other indices of organics (Szopa *et al.* 2020; Wright *et al.* 1989). Organic matter not only provides an energy source and supports microbial carbon recycling, but represents the biological activity and residue of past life.

6 Oxygen Replenishment and Ancient vs Modern Mars

As reviewed in this document, there are multiple indices of biological activity, water, and oxygen beginning over 3.7 bya. That there is still a significant amount of oxygen in the soil atmosphere of Mars has been recently documented via studies conducted by NASA's robotic rovers and orbiting space craft (Alday *et al.* 2019; Leshin *et al.* 2013; Ming *et al.* 2014; Rahmati *et al.* 2015; Sutter *et al.* 2017; Valeille *et al.* 2010). Franz *et al.* (2020) have estimated that the mean volume of Martian atmospheric oxygen is 0.174%.

It is generally accepted that the lighter isotopic compositions of the Martian atmosphere are lost to space, leaving behind the heavier isotopes (Jakosky et al. 2018), including oxygen. Oxygen in the atmosphere of Mars is also a reactant and subject to the destructive effects of direct photolysis and may have a half-life of only five years (Krasnopolsky 2010; Lefèvre and Krasnopol 2017). It is well established free oxygen is too chemically reactive to remain a free element in air without being continuously replenished. It is also believed that free oxygen levels may have been much higher in the ancient past (Lanza et al. 2016; Tosca et al. 2008). Therefore, for the last 4 billion years oxygen has been continually replenished. On Earth, oxygen is replenished via the photosynthetic action of living organisms (Canfield 2014; Lane 2002). Therefore, billions of years ago, in the absence of biological photosynthesis, and after only a few decades almost all oxygen in the atmosphere of Mars would have been destroyed or lost into space.

The evidence, therefore, supports a biological basis for the production and replenishment of free oxygen on Mars for at least 4 billion years. However, the possibility of abiotic photosynthesis of water molecules originating from beneath the surface cannot be ruled out.

7 Seasonal Fluctuation in Martian Atmospheric Oxygen

Mars rotates at a rate nearly identical, albeit slightly slower than Earth, such that a Martian day (Sol) is 24 hr and 39 min long. Because of its greater distance from the sun, a Mars year is 686.93 days, almost twice as long as Earth's. However, Mars obliquity (axial tilt) of 25.2° produces seasons similar to those on Earth.

In the early 1970s, the amount of Martian atmospheric water vapor was found to vary and increase during the late spring and summer (Barth 1974); the same as on Earth. The concentrations of atmospheric oxygen were also observed to fluctuate and increase in association with these water vapors; and in 2004, and based on a reanalysis of the Viking data, distinct seasonal variation of O_2 between 2,500 and 3,300 ppmv was reported by England and Hrubes (2004).

In 2019, Trainer et al. (2019) reported that the amount of oxygen in the Martian atmosphere increases by approximately 30% in the Spring and Summer as based on atmospheric composition measurements acquired in Gale Crater at ground level by the rover Curiosity's Science Laboratory. As detailed by Trainer et al. (2019), atmospheric measurements were conducted over 3 Mars years (>5 Earth years) and major variations in oxygen over several seasonal cycles was documented: "the annual average composition in Gale Crater was measured as 95.1% carbon dioxide, 2.59% nitrogen, 1.94% argon, 0.161% oxygen, and 0.058% carbon monoxide. However, the abundances of some of these gases were observed to vary up to 40% throughout the year due to the seasonal cycle. Oxygen has been observed to show significant seasonal and year-to-year variability, suggesting an unknown atmospheric or surface process at work."

Trainer *et al.* (2019), upon analyzing all the data and reviewing the findings of other investigators, were unable to provide any abiogenic explanations for these seasonal fluctuations: " O_2 does not follow the same general pattern as the Ar and N_2 " and "do not show the annual stability or seasonal patterns that would be predicted based on the known sources and sinks in the atmosphere" and "cannot be accounted for in current chemical models." Nevertheless, Trainer *et al.* (2019) left open the possibility that oxygen production on Mars may be abiogenic.

8 The Biology of Seasonal Oxygen Fluctuations on Earth

On Earth, oxygen is produced by algae, cyanobacteria and lichens, and specimens resembling these organisms, have been observed in Gale Crater (Joseph *et al.* 2019, 2020a,c) in the same areas where Trainer *et al.* (2019) documented seasonal variations in oxygen. Levels of oxygen in the soil, oceans, and atmosphere of Earth, also vary according to the season and increase during the Spring and Summer due to fluctuations in the biological activity of photosynthesizing

organisms (Keeling and Shertz 1992; Kim et al. 2019) and as related to increases in temperature and the availability of water and water vapor condensation and precipitation (Buenning et al. 2012; Keeling and Shertz 1992). These seasonal fluctuations on Earth parallel the Spring/Summer increases in oxygen, temperature and water availability on Mars (Fedorova et al. 2020; Read and Lewis 2004; Smith 2004; Todd et al. 2017; Trainer et al. 2019); and these variations on Mars parallel seasonable increases in biological activity and the respiration of oxygen on Earth.

DE GRUYTER

9 Photosynthesis and the Biology of Oxygen

Oxygen is the third most common chemical element in the cosmos and the most abundant chemical in Earth's oceans, seas, soil and atmosphere by mass (Canfield 2014; Emsley 2001). However, it is well established that the primary source of free oxygen, on Earth, is via the photosynthetic activity of algae, cyanobacteria (blue-green algae) and water living and land-based plants (Canfield 2014; Hall and Rao 1986) including lichens (Vinyard et al. 2018; Ten Veldhuis et al. 2020) which are fungal-algae composite organisms. On Earth, water and land-dwelling algae, cyanobacteria, and trees and plants, inspire and break down carbon dioxide, utilize the oxygen for energy, and release excess oxygen, thereby oxygenating the water, soil and atmosphere—a process that may be occurring on Mars: "The process is general and should apply to all habitable planets of all sizes and types throughout the universe" (Zahnle et al. 2013).

10 Carbon Dioxide, Photosynthesis, and Oxygen

The Martian atmosphere, as measured in Gale crater, is 95.1% carbon dioxide (Trainer et al. 2019). Carbon dioxide consists of a carbon atom covalently double bonded to two oxygen atoms and is the primary carbon source for life on Earth. Algae, cyanobacteria, and lichens photosynthesize carbohydrate from carbon dioxide and water to produce glucose, polysaccharides, proteins and other energy rich molecules (Canfield 2014; Graham et al. 2016). Sunlight and photosynthesis, therefore, enables these organisms to split these CO₂ molecules and utilize oxygen as an energy source to create their own food; and excess oxygen is released as a waste product. In fact, CO₂ enhances photosynthetic activity (Ainsworth 2008; Long et al. 2006) and

reduces the organism's reliance on water (Drake et al. 1997) thus making Mars with its CO₂ enriched atmosphere, an ideal environment for photosynthesizing organisms. Conversely, CO₂ is also produced as a waste product by aerobic organisms when they use oxygen to produce energy which enables them to metabolize carbohydrates and lipids (Butler 2018; Canfield 2014). Carbon dioxide, like methane is also produced via the decay of organics; whereas Fairén (2020) has argued that organic matter has been processed in a liquid-rich environment consistent with habitability.

Concentration of carbon dioxide in the atmosphere of Mars also varies according to the season, with significant reductions in the winter (Tillman et al. 1993), and these variations have also been documented within Gale Crater (Haberle et al. 2014; Harri et al. 2014a,b). It has been hypothesized that this is due to "the condensation and sublimation of CO₂ in the polar regions during winter and spring, respectively (Trainer et al. 2019). However, on Earth these same seasonal variations in CO2 have been documented as a function of biological, photosynthetic activity (Conway et al. 1994; Keeling et al. 1996; Sawa et al. 2012).

On Earth, photosynthesis and breakdown of CO₂ releases oxygen which provides energy, and excess oxygen is released into the atmosphere, while respiration, decay, and combustion remove it from the atmosphere, creating a seasonally variable equilibrium (Greenwood and Earnshaw 1997). Therefore, it is probable that the seasonal changes in Martian atmospheric CO₂ may be related, at least in part, to biological activity.

11 Algae / Cyanobacteria and Water on Mars

In 1978, after examining specimens photographed during the 1976 Viking Missions, Levin, Straat and Benton published evidence of changing patterns on "greenish rock patches" which were "green relative to the surrounding area." Levin et al. (1978) speculated that these greenish areas may represent "algae" growing on Mars. Ice-filled clouds were also observed overhead, and condensation and sublimation of ground frost (Wall 1981) and water within regolith was also detected via the Viking's suite of instruments (Biemann et al. 1977). Utopia and Chryse Planitia, therefore, has sunlight, water, and what looked like green algae was growing on rocks. DiGregorio (2002) also examined these Viking images, and reported what he interpreted to be "rock varnish" which is typically produced by "epilithic and edolithic cyanobacteria" i.e., blue-green photosynthesizing algae.

Joseph *et al.* (2020a) also observed what appeared to be green algae growing on rocks, sands, and mudstone in Gale Crater; in the same general area that was later found to be a major source of oxygen, particularly during the spring and summer (Trainer *et al.* 2019). As described by these investigators, these Gale Crater algae-like specimens, appear as spherules, green clumps, cake-like layers, thin sheet-like layers, and thick layered leafy vegetative masses which partially cover Martian rocks, sand, and fungi-like surface features. Many specimens appeared to be moist or covered by a thin layer of ice or adjacent to moist soil (Figure 3). The author's stressed, however, that it was impossible to precisely determine if these surface features were in fact living organisms without direct physical examination and extraction.

Gale Crater appears to be a series of ancient lakes that have periodically filled with water (Martínez *et al.* 2017a; Rampe *et al.* 2020), in a cycle that may have lasted billions of years into the near present (Frydenvang *et al.* 2017; Yen *et al.* 2017; Hausrath *et al.* 2018; Jaumann *et al.* 2014). As summed up by Rampe *et al.* (2020): "Evidence for a long-lived lake or lake system in Gale crater is compelling...." possibly "up to the present day."

It also appears that moisture may be available on a daily basis during the summer months (Castro et al. 2015; Martín-Torres et al. 2015; Steele et al. 2017). Clouds have been observed above Gale Crater (Moores et al. 2015), whereas on Earth, clouds consist of water with saturation ranging from 81% to 100% (Pruppacher and Klett 2010; Hu et al. 2010). Columns of water vapors have also been observed every spring and summer (Smith 2004; Read and Lewis 2004), and which drift toward Gale Crater (Harri et al. 2014a,b). Moreover, these vapors have a precipitable water content of at least 10-15 pr um (Smith 2004). In addition, Steele et al. (2017) have argued that during "the evening and night, local downslope flows transport water vapour down the walls of Gale crater. Upslope winds during the day transport vapour desorbing and mixing out of the regolith up crater walls, where it can then be transported a few hundred metres into the atmosphere." Martín-Torres et al. (2015), have also reported the possible "formation of night-time transient liquid brines in the uppermost 5 cm of the subsurface that then evaporate after sunrise." Therefore, it appears that there is sufficient moisture available, at least during the summer, to sustain the metabolic activity of algae and other oxygen-producing species, thus accounting for the significant increases in Martian atmospheric oxygen within and above Gale Crater (Trainer et al. 2019).

Gusev Crater, like Gale Crater is also believed to have been an ancient paleolake and is marked by obvious evidence of silt deposits, deltas, and water erosion (Haskin *et* *al.* 2005; Hurowitz *et al.* 2006; Wang *et al.* 2006; Morris *et al.* 2006a,b). It is believed that the surface of Gusev Crater may have been and may still be supplied with moisture via precipitation and condensation from the atmosphere and the melting of frost, snow, and water-ice above and below ground thereby providing water to the surface (Barnhart *et*



Figure 3. Sol 871. Green sphericals upon Martian sand, soil, rocks and pinnicle-columnar structures resembling terrestrial stromatolites and thrombolites and algae growing in shallow water. On Earth, the greenish-coloration of sand and rock is due to green cryptoendolithic cyanobacteria. The darkening in soil coloration may indicate moisture. These sphericals are similar to algae growing in shallow water, but may be frozen – the arrangement of sandy substance in between rocks is the typical nature of shallow rocky pools.



Figure 4. Sol 298: Algae and lichen-like-mushroom-shaped specimens atop what appears to be microbial mats and, surrounded by ovoid and tubular specimens.

al. 2009; Herkenhoff *et al.* 2004; Ruff *et al.* 2014; Richardson and Mischna 2005; Arvidson *et al.* 2006).

Thus, Gusev Crater may also experience sufficient moisture to sustain oxygen-producing species. In support of this hypothesis: Krupa (2017) upon closely examining soil surface features, discovered evidence of what appear to be green photosynthetic organisms growing in Gusev Crater, adjacent to water pathways which appear to have intermittently filled with water. He noted that "the hillside…is covered by a very thin layer of green material" and "green spherules" which resembles algae in the soil.

Therefore, numerous investigators have observed specimens which resemble algae growing in various locations on Mars. Algae produce oxygen via photosynthesis, and if these are in fact living organisms, they may be contribut-

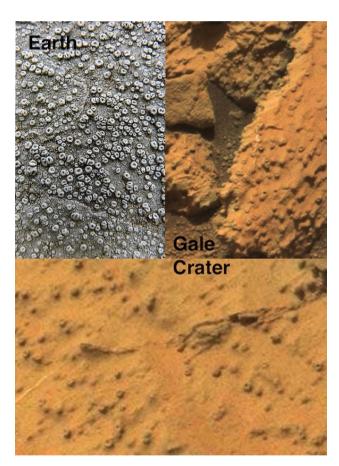


Figure 5. (Top Left): Earth. Lichens growing on the west coast Ireland cliffs of Moher. Photographed by Dr. Jessica Winder, https://natureinfocus.blog. and reproduced with permission. Gale Crater Sol 298: Specimens resembling dimpled lichens with what may be hyphae along the surface/subsurface. Note hollow apertures in the upper right corner and lower center of photo, and which resembles an oxygen-gas vents typically produced by photosynthesizing organisms.

ing to the production and the continual replenishment of oxygen, on Mars.

12 Photosynthesizing Lichens and Oxygen Gas Vents on Mars?

Lichens are photosynthesizing organisms which respire oxygen (Ten Veldhuis *et al.* 2020).)—activity associated with its photobiont; respiration being dominated by fungi and bacteria in the consortium. Numerous studies have demonstrated that lichens remain viable and maintain photosynthetic activity when exposed to simulated Martian temperatures, atmosphere, humidity, and UV radiation (De Vera 2012; De Vera *et al.* 2019; De la Torre Noetzel *et al.* 2017, 2020).

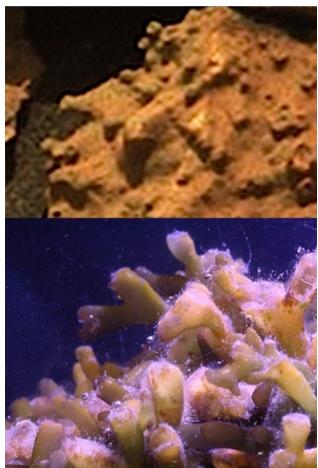


Figure 6. Sol 232 (Top): Specimens similar to gas-vent apertures for the release of oxygen secondary to photosynthesis, photographed in Gale Crater. (Bottom) Cone-like tubes for the venting of oxygen produced by photosyntheizing algae (reproduced with permission from Freeman *et al.* 2018).

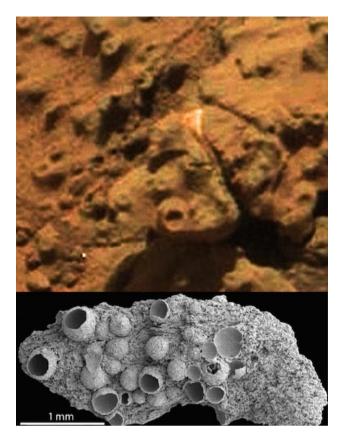


Figure 7. Sol 232 (Top): Specimens similar to gas-vent apertures for the release of oxygen secondary to photosynthesis. Photosynthesizing organisms respire oxygen and release gas bubbles via the surrounding matrix (most noticeable in water). (Bottom) Open globular structures, interpreted as formed by gas bubbles via cyanobacteria oxygen respiration within microbial mats (from Bengtson *et al.* 2009, reproduced with permission).

Hundreds of Martian surface features which resemble agaric (Lichenomphalia umbellifera) and dimpled lichens (Figure 5) have been observed in Gale Crater (Joseph *et al.* 2020a,c). These were often photographed in association with specimens resembling green algae and open-cone apertures the latter of which were either bubble-like or elongated with an open aperture at one end, similar to those produced by living algae/cynaobacteria during oxygen production (Figures 6, 7). As is well established, when photosynthesizing organisms respire oxygen they may release gas bubbles in the surrounding matrix (Freeman et al. 2018), which, over time, may become mineralized and fossilized (Bengtson et al. 2009; Sallstedt et al. 2018). Joseph et al. (2020a) hypothesized that the open-cone apertures observed in Gale Crater are evidence of photosynthesis oxygen release on Mars, thereby accounting for the seasonal waxing and waning of oxygen in the Martian atmosphere as measured in Gale Crater.

Vast clusters of thousands of lichen-like formations, with thin stems and top heavy with bulbous mushroom-shaped caps, have also been observed in Eagle Crater, Meridiani Planum (Joseph *et al.* 2020b,d). These lichen-mushroom-shaped formations are attached by thin stalks to the sides and tops of rocks, and those top-side are often collectively oriented in a similar upward-angled direction, jutting above these rocks, as might be expected of colonies of organisms engaged in photosynthesis (Figures 8-12).

Although it has been reported that the soil of Eagle Crater may contain hematite, and there has been speculation that the numerous spheres upon the top soil may consist of hematite (Christensen *et al.* 2004; Squyres *et al.* 2004), these latter claims have been disputed (Burt *et al.*





Figure 8. Sol 88 (left) and Sol 37 (right). Lichen-like specimens photographed in Eagle Crater.



Figure 9. Sol 88 (left), Sol 85 (right) Lichen-like specimens photographed in Eagle Crater.

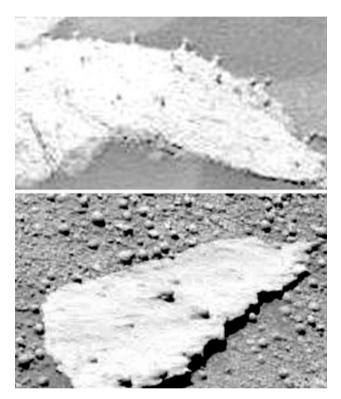


Figure 10. Sol 85: Lichen-like specimens photographed in Eagle Crater.

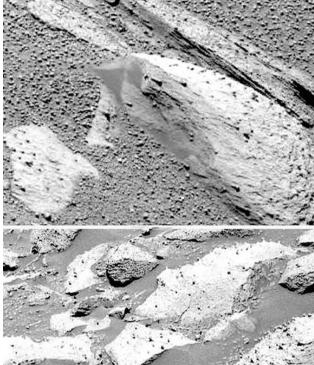


Figure 11. Sol 85: Lichen-like specimens photographed in Eagle Crater.

2005; Dass 2017; Joseph *et al.* 2020b; Knauth *et al.* 2005) and the data was often found to be a "poor fit" for hematite (Glotch and Bandfield 2006).

The lichen-mushroom shaped specimens attached by stems to rocks were never examined for evidence of hematite (Joseph *et al.* 2020b). And hematite does not sprout from rocks and mudstone via long stems topped by bulbous mushroom-shaped caps. These lichen-like formations have absolutely no resemblance to hematite or any other abiotic rocks or substances on Earth; and, typical of many species of plant and lichen, the stems were hollow,

thus (presumably) serving to draw up and distribute water throughout the organism (Joseph *et al.* 2020b).

The hematite claims are also refuted by subsequent studies conducted by the rover Curiosity and which detected only "minor" amounts of hematite in samples obtained from multiple locations (Treiman *et al.* 2016; Rampe *et al.* 2017; Yen *et al.* 2017). By contrast, upward-oriented mushroom-shaped lichen-like formations have also been observed in Gale Crater (Joseph *et al.* 2020a, see Figure 8



Figure 12. Sol: 85. Photographed in Eagle Crater. Colonies of lichenlike specimens approximately 2 to 8 mm in length. Note similar orientation of specimens on tops of rocks and which may be affected by gravity due to the top-heavy bulbous caps.

in) similar to those observed in Eagle Crater (Joseph *et al.* 2020b).

Thousands of lichen-like specimens were observed in Eagle crater, forming clusters, all of which are characterized by stalks attached to rocks and oriented upward (or upward then downward depending as if pulled by gravity) and topped by bulbous caps (Joseph et al. 2020b). An extensive abiotic image search was also conducted and these investigators were unable to find any terrestrial analogs or abiogenic similarities or evidence of weathering processes which can sculpt high density masses of mushroomshapes with thin stalks and bulbous caps out of rock, salt, or sand, and which orient skyward, above their substrates, in the same or similar upward angled direction (Joseph et al. 2020b). As also pointed out by these authors, if consisting of sand, minerals or salt, then powerful winds, Mars-quakes, meteor strikes, or the turbulence created by Opportunity's wheels or drill would cause these thin stalks to fracture and break and these bulbous caps to tumble to the surface. Instead, they have remained standing, and are oriented upward, which suggests they are flexible, recently developed and, perhaps, engaged in photosynthesis; or, conversely, due to the lichen-propensity to uptake high concentration of Fe, they have formed fossils with the consistency of iron.

At present, it is unknown if these vast clusters of lichenlike formations are fossils, living organisms, or were fashioned by some abiotic process that is completely alien to that of Earth. If alive, however, they would require water, and significant amounts of water appear to be available, particularly in the summer months. In addition to providing oxygen via photosynthesis, this same water might also be subject to abiogenic photosynthesis.

13 Subglacial Lakes, Oceans, Oxygen and Abiotic Photosynthesis

The splitting of atmospheric water molecules is yet another possible abiogenic source for Martian oxygen (Franz *et al.* 2020). For example, it has been hypothesized that water in the atmosphere or upon the surface may be split by UV radiation, thereby resulting in hydrogen escape into space and the release of oxygen, which, being heavier, would remain in the lower atmosphere (Davankov 2020). As argued by Franz *et al.* (2020), H_2O photolysis and the photolysis of CO_2 and ozone could generate O atoms, thereby providing Mars with the oxygen in its atmosphere.

Therefore, hypothetically, oxygen may be produced via abiogenic photosynthesis of water molecules; a view endorsed by a number of investigators (Davankov 2020; Guo *et al.* 2009; Luger and Barnes 2015; Wordsworth and Pierrehumbert 2014) who have proposed that the detection of oxygen in the atmosphere of any planet orbiting within a habitable zone, may be completely abiogenic in origin thereby giving the false impression of life.

What most of these theories have in common is the requirement of oceans of water. Therefore, according to these scenarios, completely abiotic oxygen atmospheres can be sustained so long as there is a substantial reservoir of water in the atmosphere, oceans of water flow upon the surface, and the planet is irradiated by UV rays (Davankov 2020; Guo et al. 2009; Luger and Barnes 2015). Eventually, however, and due to the splitting of water molecules coupled with hydrogen escape, water levels would also diminish on these abiotic worlds. Guo et al. (2009) and Luger and Barnes (2015) have argued-depending on a planet's mass, climate, temperature, and gravity—that due to the photolysis of water vapor coupled with hydrogen escape, that oceans of water would eventually disappear from the surface of an uninhabited planet. According to these scenarios, atmospheric oxygen-alone- is not proof of life.

Davankov (2020) has also proposed that a significant proportion of Earth's oxygen atmosphere is likewise abiogenic, its source the oceans of Earth. He points out that molecular weight of water is only 18 g/mol, and water

molecules migrate to the upper atmosphere and are subject to irradiation thus resulting in hydrogen escape and with the heavier oxygen left drifting back toward the surface. In consequence, he argues, oceans of water have been depleted. Pope et al. (2012) estimate that 26% of Earth's early ocean has been lost due to hydrogen escape. Hence, based on these scenarios, the oceans of Earth should continue to diminish in volume and the same may be true of any inhabited or uninhabited water-rich planet.

Many investigators believe that ancient Mars was wet and habitable (Ehlmann et al. 2011; Fairén 2020; Squyres and Knoll 2006; McKay 2010; Vago and Westall 2017; Grotzinger et al. 2014; Jaumann et al. 2014), and that in addition to thousands of lakes, oceans of water were at least temporarily present (Duxbury 2000; Fawdon et al. 2018; Parker 1986; Head et al. 1999; Ivanov et al. 2014; Dickeson and Davis 2020; Fairén et al. 2003). However, if ancient Mars had a stable, long-duration Earth-like ocean is subject to considerable debate and no clear consensus has emerged, except in regard to the generally agreed belief that oceans of water may have flowed across the surface of the northern hemisphere (Ramirez et al. 2020; Carr and Head 2019; Dickeson and Davis 2020)

What became of the Martian lakes and its oceans of water is also subject to much debate; though one contributing possibility may be abiotic photosynthesis. If over the course of the last 4 billion years the production of atmospheric oxygen has been completely abiotic, then this would have resulted in the complete evaporation of a planet-wide ocean of water with an initial depth of 50 to 80 meters (Barth 1974; Zhang et al. 2012). If, however, the original volume of water on Mars was much greater than 80 meters, then the remnants of these lakes and oceans of water should still be present, most likely frozen within or beneath the surface; and, depending on heat or sublimation, providing water molecules that can be split and transformed into atmospheric oxygen.

An increasing body of evidence indicates that massive bodies of Martian water may have become frozen in the distant past (Duxbury et al. 1999; Fairén 2010; Head et al. 1999; Woodworth-Lynas and Guigné 2003); forming dust covered glaciers and ice sheets beneath the surface and deep within the crust (Holt et al. 2008; Head et al. 1999; Barkerand and Bhattacharya 2018; Janhunen 2002). Putzig et al. (2014), employing the Shallow Radar on the Mars Reconnaissance Orbiter reported clear evidence of 2900 km² of ground ice in a depression at the Phoenix landing site, and extending from the near surface to ~15-66 m below ground. Conway and Balme (2014) detected 30-meters thick layers of dust-covered ice and extending from the poles to the midlatitudes, covering at least 23% of the surface, containing between 46% and 95% ice by volume and accounting for ~104 km³ of near-surface ice.

Using ground-penetrating reflecting radar, a mixture of ice, air, and dust, and up to 14,300 km³ of water-ice has been reported by Stuurman et al. (2016) in the Utopia Planitia region, whereas Bramson et al. (2015), reports a widespread, decameters-thick layer of water-ice in this same area, ~104 km³ in volume. Sublimation-thermokarst landforms with scales of decameters to kilometers have been observed in the midlatitudes which likely resulted from surface collapse when ice was lost from the subsurface due to sublimation over tens of thousands of Mars vears (Dundas et al. 2015). It was estimated that meteor impact craters also increased in size due to subsurface ice sublimation thereby collapsing the surface (Dundas et al. 2015).

Dust covered glaciers beneath layers of surface debris have also been detected in the Hellas region of Mars by the Shallow Radar on the Mars Reconnaissance Orbiter (Holt et al. 2008), whereas cliffs composed primarily of layered sheets of water ice over 100 meters thick, extending 1-2 meters beneath the surface have been reported by Dundas et al. (2018). These massive ice sheets were exposed due to weathering and erosion and appear to be melting and actively retreating because of sublimation.

The south polar caps also consist of thick deposits of water ice (Byrne 2009) beneath which substantial amounts of ice-water and layers of ice sheets have also been detected by the Mars Advanced Radar aboard the Mars Express space craft (Orosei et al. 2018, 2020; Lauro et al. 2020). As detected by neutron spectroscopy these ice sheets extend from the south pole into the lower latitudes (Feldman et al. 2002). The Dorsa Argentea Formation in particular appears to consist of a large body of ice water which may be the remnants of a much larger ice sheet or glacier that has been melting (Fastook et al. 2012). Moreover, there appears to be a large volume of liquid water beneath the surface, i.e. melt water due to some unknown thermal anomaly (Arnold et al. 2019; Sori and Bramson 2019); and there is evidence of multiple subglacial lakes that may contain liquid water as well as water-ice (Lauro et al. 2020; Picardi et al. 2005).

Therefore, massive amounts of water, in discrete and widespread locations, have become frozen. And over time they have become smaller in size due to sublimation and heat-generated melting, most likely during the summer months and afternoons when surface temperatures rise. This melt-water, in turn, might pool upon the surface only to evaporate during the Martian summer. In consequence, this moisture would provide liquid water for photosynthesizingoxygen producing organisms, and that which evaporates might also be transformed into oxygen via abiotic photosynthesis. Hence, the correlation between atmospheric oxygen levels and increases in ground temperature reported by Livengood et al. (2020) and the presumed association with water vapors beginning back in the 1970s (Barth 1974; Strickland et al. 1973).

Based on data provided by orbital observations and the Mars Science Laboratory and its Environmental Monitoring Station, four major reservoirs of Martian water have been identified, i.e. in the northern and south poles (Kieffer et al. 1992; Farmer et al. 1977; Orosei et al. 2018, 2020; Lauro et al. 2020), in the upper atmosphere which is subject to "large, rapid seasonal intrusions of water" with large portions of the atmosphere becoming supersaturated during the Spring and Summer (Fedorova et al. 2020), and within atmospheric vapors every spring and summer (Farmer et al. 1977; Korablev et al. 2001; Smith et al. 2001; Read and Lewis 2004; Smith 2004; Todd et al. 2017). These columns of water vapor may also contribute to the formation of Martian clouds observed by several investigators (Kahn 1984; Whiteway et al. 2009; Moores et al. 2015); and which, like the clouds of Earth, probably contain high concentrations of water.

These water molecules might also be cleaved by powerful UV rays thereby resulting in hydrogen escape and the release of free oxygen thus contributing to the diurnal and summertime increases in atmospheric oxygen. If this scenario is correct, and if oxygen is being produced via abiogenic photosynthesis, then in consequence, the total volume of water should have declined significantly from its original levels, and should continue to diminish.

As based on measured D/H ratios in surface rocks vs the atmosphere, Villanueva et al. (2015) have estimated that the global volume of Martian water was initially at least 137 meters deep, and over the last 4.5 billion years there has been "great water loss" such that initially there was 6 to 7 times more water on Mars. Jakosky et al. (2018) and Dong et al. (2018) concur and also postulate that a significant amount of water has been lost to space. These D/H ratios, therefore, supports the abiogenic photosynthesis hypothesis, and the possibility that at least 50 to 80 meters of water may have been cleaved over billions of years leaving only free oxygen in its wake (Barth 1974; Zhang et al. 2012).

This does not mean, however, that the oxygen atmosphere of Mars is completely abiotic. As pointed out by Zahnle et al. (2013): "Although it is possible to imagine atmospheres that might become oxygenated abiotically through some combination of vigorous hydrogen escape and high rates of stellar ultraviolet irradiation, to the best of our knowledge no one has vet succeeded in demonstrating this with an actual photochemical model." Oxygen atmospheres appear to be produced primarily via photosynthesizing organisms.

14 Conclusions

Free oxygen is an obvious biomarker and is produced by photosynthesizing organisms. Oxygen is reactive and on Mars may be destroyed in 10 years. Hence oxygen is continually replenished. Diurnal and seasonal fluctuations and spring/summer increases in oxygen have also been documented, and these variations parallel seasonal biologically induced fluctuations on Earth.

There is no convincing evidence that abiotic-oxygen locked within rocks, minerals, sand or soil, are somehow becoming liberated, thereby providing any significant degree of oxygen to the Martian atmosphere. By contrast, given that most scientists agree that large volumes of water once flowed across the Martian surface, and the findings of massive ice sheets, glaciers, and subglacial bodies of water-ice that appear to be melting and/or undergoing sublimation, it is probable that some of this water has been transformed into oxygen via abiotic photosynthesis, thus accounting, in part, for the loss of lakes and oceans of water over the last 4.5 billion years. This melt-water, however, would have also provided moisture to photosynthesizing organisms who would produce free oxygen.

That biological photosynthesis is also responsible for Martian atmospheric oxygen is supported by reports of sedimentary structures that clearly resemble concentric stromatolites that are pock marked with fenestra for the venting of oxygen; observations of thousands of lichenlike specimens topped with bulbous caps attached by thin stems to rock and collectively oriented skyward similar to photosynthesizing lichens; and specimens resembling algae/cyanobacteria and associated formations that resemble open-cone gas apertures for the venting of oxygen produced via photosynthesis (Figures 1-12).

If these life-like formations are biological, fossilized, or completely abiogenic, is unknown. There is in fact, no definitive, conclusive proof of life on Mars. Therefore, it is possible that most or all of the Martian oxygen atmosphere has been produced via abiotic photosynthesis. However, if these life-like specimens are biological then they and their ancestors would have significantly contributed to and would be primarily responsible for the production, replenishment, and seasonal fluctuations of Martian atmospheric oxygen via biological photosynthesis.

No Competing Interests: The authors have no competing or financial or non-financial interests and no funding to report and will not benefit financially from this article.

Author Contributions: All authors have either contributed directly to the research reviewed, and/or assisted in the analysis, writing, editing, and /in searching for and referencing the works cited.

References

- Agee CB, Wilson NV, McCubbin FM, Ziegler K, Polyak VJ, Sharp ZD, et al. 2013. Unique meteorite from Early Amazonian Mars: Water-Rich Basaltic Breccia Northwest Africa 7034. Science. 339:780-785.
- Ainsworth EA. 2008. Rice production in a changing climate: a metaanalysis of responses to elevated carbon dioxide and elevated ozone concentration. Global Change Bio. 14(7):1642-1650. DOI:10.1111/j.1365-2486.2008.01594.x.
- Alday J, Wilson CF, Irwin PGJ, Olsen KS, Baggio L, Montmessin F, et al. 2019. Oxygen isotopic ratios in Martian water vapour observed by ACS MIR on board the ExoMars Trace Gas Orbiter. A&A. 630:A91. DOI: https://doi.org/10.1051/0004-6361/ 201936234.
- Arnold NS, Conway SJ, Butcher FEG, Balme MR. 2019. Modeled Subglacial water flow routing supports localized intrusive heating as a possible cause of basal melting of Mars' South Polar Ice Cap. JGR Planets. 24:2101-2116.
- Arvidson RE, Squyres SW, Anderson RC, Bell III JF, Blaney D, Brückner J, et al. 2006. Overview of the Spirit Mars Exploration Rover mission to Gusev Crater: Landing site to Backstay Rock in the Columbia Hills. JGR. 111:E02S01.
- Ash RD, Knott SF, Turner G. 1996. A 4-Gyr shock age for a martian meteorite and implications for the cratering history of Mars. Nature. 380:57-59.
- Barker DC, Bhattacharya JP. 2018. Sequence stratigraphy on an early wet Mars. Planet. Space Sci. 151:97-108.
- Barnhart CJ, Howard AD, Moore JM. 2009. Long-term precipitation and late-stage valley network formation: landform simulations of parana basin, Mars. JGR Planets. 114:E01003.
- Barth CA. 1974. The atmosphere of Mars. Annu. Rev. Earth Planet. Sci. 2:333-367.
- Bell III JF, Squyres SW, Arvidson RE, Arneson HM, Bass D, Calvin W, et al. 2004. Pancam Multispectral Imaging Results from the Opportunity Rover at Meridiani Planum. Science. 306:1703-
- Belton MJS, Hunten DM. 1968. A search for O₂ on Mars and Venus: a possible detection of oxygen in the atmosphere of Mars. ApJ. 153:963-974.
- Bengtson S, Belivanova, V, Rasmussen, B, Whitehouse, M. 2009. The controversial "Cambrian" fossils of the Vindhyan are real but more than a billion years older. PNAS. 106(19):7729-7734.
- Bianciardi G, Miller JD, Straat PN, Levin GV. 2012. Complexity analysis of the Viking Labeled release Experiments. Int. J. of Aeronaut. Space Sci. 13(1):14-26.

- Bianciardi G, Rizzo V, Cantasano N. 2014. Opportunity Rover's image analysis: Microbialites on Mars? Int. J. Aeronaut. Space Sci. 15(4):419-433.
- Bianciardi G, Rizzo V, Farias ME, Cantasano N. 2015. Microbialites at Gusev Craters, Mars. J. Astrobiol. Outreach. 3(5): 1000143.
- Biemann K, Oro J, Toulmin III P, Orgel LE, Nier AO, Anderson DM, et al. 1977. The search for organic substances and inorganic volatile compounds in the surface of Mars. JGR. 82:4641-4658.
- Bramson AM, Byrne S, Putzig NE, Sutton S, Plaut JJ, Brothers TC, et al. 2015. Widespread excess ice in Arcadia Planitia, Mars. Geophys. Res. Lett. 42:6566-6574. DOI:doi:10.1002/2015GL064844v
- Buenning MK, Stott L, Yoshimura K, Berkelhammer M. 2012. The cause of the seasonal variation in the oxygen isotopic composition of precipitation along the western U.S. coast. JGR Atmospheres. 117:D18114. DOI: https://doi.org/10.1029/ 2012JD018050
- Buick R. 2008. When did oxygenic photosynthesis evolve? Philos. Trans. R. Soc. Lond. B Biol. Sci. 363(1504):2731-2743.
- Burt DM, Knauth LP, Woletz KH. 2005. Origin of layered rocks, salts, And spherules at the opportunity landing site on Mars: no flowing or standing water evident or required. Proceedings of the 36th Annual Lunar and Planetary Science Conference, 2005 March 14-18. League City, Texas, US. Lunar and Planetary Science XXXVI. 2005. id.1527.
- Butler JN. 2018. Carbon dioxide equilibria and their applications. CRC Press
- Byrne S. 2009. The Polar deposits of Mars. Annu. Rev. Earth Planet. Sci. 37:535-560.
- Canfield DE. 2014. Oxygen: A Four billion year history. Princeton University Press.
- Carleton NP, Traub WA, 1972, Detection of molecular oxygen on Mars. Science. 177(4053):988-992. DOI: 10.1126/science.177.4053.988.
- Carr M, Head J. 2019. Mars: Formation and fate of a frozen Hesperian Ocean. Icarus. 319:433-443.
- Castro JFB, Mier, M-PZ, Martin-Torres J. 2015. Liquid water at Crater Gale, Mars. J. Astrobiol. Outreach. 3(3):1000131.
- Christensen PR, Wyatt MB, Glotch TD, Rogers AD, Anwar S, Arvidson RE, et al. 2004. Mineralogy at Meridiani Planum from the Mini-TES Experiment on the Opportunity Rover. Science. 306:1733-
- Clayton RN, Mayeda T. 1996. Oxygen isotopes studies on achondrites. Geochim. Cosmochim. Acta. 60:19992017.
- Clayton RN, Mayeda T. 1983. Oxygen isotopes in eucrites, shergottites, nakhlites, chassignites. Earth Planet Sci. Lett. 62:115-149.
- Clement SJ, Dulay MT, Gillette JS, Chillier XD, Mahajan TB, Zare RN. 1998. Evidence for the extraterrestrial origin of polycyclic aromatic hydrocarbons in the Martian meteorite ALH84001. Faraday Discuss. 109:417-436.
- Conway TJ, Tans PP, Waterman LS, Thoning KW, Kitzis DR, Masarie KA, et al. 1994. Evidence for interannual variability of the carbon cycle from the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory global air sampling network. JGR. 99(D11):22831-22855. DOI: 10.1029/94JD01951.
- Conway SJ, Balme MR. 2014. Decameter thick remnant glacial ice deposits on Mars. Geophys. Res. Lett. 41(15):5402-5409. DOI: 10.1002/2014GL060314.

- Dass RS, 2017. The high probability of life on Mars: A brief review of the evidence. Cosmology. Vol. 27. Available from: http: //cosmology.com/LifeOnMarsReview.html.
- Davankov VA. 2020. Critical review on the origin of atmospheric oxygen: Where is organic matter? Planet. Space Sci. 190(1):105023.
- De la Torre Noetzel R, Miller B, Cubero AZ, Sancho, LG, Jordão L, Rabbow E, et al. 2017. Survival of lichens on the ISS-II: ultrastructural and morphological changes of Circinaria gyrosa after space and Mars-like conditions. Proceedings of the EANA2017: the 17th European Astrobiology Conference, 2017 August 14-17, Aarhus, Denmark.
- De la Torre Noetzel R, Ortega García MV, Miller AZ, Bassy O, Granja C, Cubero B, et al. 2020. Lichen vitality after a space flight on board the EXPOSE-R2 facility outside the International Space Station: Results of the biology and Mars Experiment. Astrobiol. 20(5):583-600.
- De Vera J-P. 2012. Lichens as survivors in space and on Mars. Fungal Ecol. 5:472-479.
- De Vera J-P, Alawi M, Backhaus T, Baqué M, Billi D, Böttger U, et al. 2019. Limits of Life and the Habitability of Mars: The ESA Space Experiment BIOMEX on the ISS. Astrobiol. 19(2):145-157.
- Dickeson ZI, Davis JM. 2020. Martian Oceans. A&G. 61:3.11-3.17. DOI: https://doi.org/10.1093/astrogeo/ataa038
- DiGregorio B. E. 2002. Rock varnish as a habitat for extant life on Mars, Proceedings Volume 4495, Instruments, Methods, and Missions for Astrobiology IV. DOI: https://doi.org/10.1117/12. 454750.
- Dong CF, Lee Y. Ma YJ, Lingam M, Bougher S, Luhmann J, et al. 2018. Modeling Martian Atmospheric losses over time: Implications for exoplanetary climate evolution and habitability. Astrophys. I. Lett. 859:L14.
- Drake BG, Gonzalez-Meler MA, Long SP. 1997. More eficient plants: A consequence of rising atmospheric CO₂? Ann. Rev. Plant. Phys. Plant. Mol. Bio. 48(1):609-639. DOI: 10.1146/annurev.arplant.48.1.609.
- Dundas CM, Byrne S, McEwen AS. 2015. Modeling the development of Martian sublimation thermokarst landforms. Icarus. 262:154-169. DOI:10.1016/j.icarus.2015.07.033.
- Dundas CM, Bramson AM, Ojha L, Wray JW, Mellon MT, Byrne S, et al. 2018. Exposed surface ice sheets in the Martian mid-latitudes. Science. 359:199-201. DOI: https://doi.org/10.1126/science.aao1619.
- Dunham T. 1952. Spectroscopic observations of the planets at Mt. Wilson. Chapter 11. In: Kuiper GP. Editor. The atmospheres of the Earth and planets. Chicago: University of Chicago Press. p. 288-305.
- Duxbury NS. 2000. Estimating the Past Martian Ocean depth. Proceedings of EGS XXV General Assembly European, Nice, France. Available from: http://hdl.handle.net/2014/18748
- Duxbury NS, Zotikov LA, Nealson KH. 1999. A Non-basal-melting origin of the possible sub-polar water on Mars as derived from Lake Vostok modeling and MOLA data. Bull. Am. Astron. Soc. 31:47.01.
- Eigenbrode JL. Summons RE, Steele A, Freissinet C, Millan M, Navarro-González R, et al. 2018. Organic matter preserved in 3-billion-year-old mudstones at Gale crater, Mars. Science. 360:1096-1101.

- Ehlmann BL, Mustard JF, Murchie SL, Bibring JP, Meunier A, Fraeman AA, et al. 2011. Subsurface water and clay mineral formation during the early history of Mars. Nature. 479:53-60.
- Emsley J. 2001. Oxygen. In: Nature's building blocks: An A-Z guide to the elements. Oxford (England): Oxford University Press. pp.
- England C. Hrubes ID. 2004. Molecular oxygen mixing ratio and its seasonal variability in the Martian atmosphere. Paper presented at Workshop on Oxygen in the Terrestrial Planets. NASA Technical Report. Available from: https://www.lpi.usra. edu/meetings/otp2004/pdf/3009.pdf.
- Fairén AG, Dohm DM, Baker VR, de Pablo MA, Ruiz J, Ferris JC, et al. 2003. Episodic flood inundations of the northern plains of Mars. Icarus. 165:53-67.
- Fairén AG. 2020. Organic chemistry on a cool and wet young Mars. Nat. Astron. 4:446-447.
- Fairén AG. 2010. A cold and wet Mars. Icarus. 208(1):165-175.
- Farmer CB, Davies DW, Holland AL, Laporte DD, Doms PE. 1977. Mars-Water vapor observations from the Viking orbiters. JGR. 82:4225-4248.
- Farquhar J, Thiemens MH, Jackson T. 1998. Atmosphere-surface Interactions on Mars: Delta170 measurements of carbonate from ALH 84001. Science. 280(5369):1580-1582.
- Farquhar J, Thiemens MH. 2000. Oxygen cycle of the Martian atmosphere-regolith system 170 of secondary phases in Nakhla and Lafavette. IGR. 105:11991-11998.
- Fastook JL, Head JW, Marchant DR, Forget F, Madeleine J.-B. 2012. Early Mars climate near the Noachian-Hesperian boundary: Independent evidence for cold conditions from basal melting of the southpolar ice sheet (Dorsa Argentea Formation) and implications for valley network formation. Icarus. 219:25-40.
- Fawdon P. Gupta S. Davis IM. Warner NH. Adler IB. Balme MR. et al. 2018. The Hypanis Valles delta: The last highstand of a sea on early Mars? Earth Planet Sci. Lett. 500:225-241.
- Fedorova AA, Montmessin F, Korablev O, Luginin M, Trokhimovskiy A, Belyaev DA, et al. 2020. Stormy water on Mars: The distribution and saturation of atmospheric water during the dusty season. Science. 367(6475):297-300.
- Feldman WC. Boynton WV, Tokar RL, Prettyman TH, Gasnault O, Squyres SW. Elphic RC, Lawrence DJ, Lawson SL, Maurice S, et al. 2002. Global distribution of neutrons from Mars: Results from Mars Odyssey. Science. 297:75-78.
- Franz HB, McAdam AC, Ming DW, Freissinet C, Mahaffy PR, Eldridge DL, et al. 2017. Large sulfur isotope fractionations in martian sediments at Gale crater. Nat Geosci. 10:658-662.
- Franz HB, Mahaffy PR, Webster CR, et al. 2020. Indigenous and exogenous organics and Surface-atmosphere cycling inferred from carbon and oxygen isotopes at Gale crater. Nat. Astron. 4:526-532.
- Freeman SE, Freeman LA, Hioroli G, Haas AF. 2018. Photosynthesis by marine algae produces sound, contributing to the daytime soundscape on coral reefs. Plos One. DOI: https://doi.org/10. 1371/105journal.pone.0201766.
- Freissinet CDP, Glavin PR, Mahaff KE, Miller JL, Eigenbrode RE, Summons AE, et al. 2015. Organic molecules in the Sheepbed mudstone, Gale Crater, Mars. J. Geophys. Res. Planets 120(3):495-514. DOI:10.1002/2014JE004737pmid:26690960.
- Frydenvang J, Gasda PJ, Hurowitz JA, Grotzinger JP, Wiens RC, Newsom HE, et al. 2017. Diagenetic silica enrichment and late-stage groundwater activity in Gale crater, Mars. Geo-

- phys. Res. Lett. 44:4716-4724. DOI: https://doi.org/10.1002/ 2017GL073323.
- Glotch TD, Bandfield JL. 2006. Determination and interpretation of surface and atmospheric Miniature Thermal Emission SpecRtrometer spectralend-members at the Meridiani Planum landing site. J. Geo. Res. 111:E12S06. DOI: 10.1029/2005IE002671.

DE GRUYTER

- Graham LE, Graham JM, Wilcox LW, Cook ME. 2016. Algae. LJLM Press, Madison.
- Greenwood NN, Earnshaw A. Editors. 1997. Chemistry of the elements. Second Edition. Butterworth-Heinemann. p. 602.
- Grotzinger JP, Sumner DY, Kah LC, Stack K, Gupta S, Edgar L, et al. 2014. A habitable fluvio-lacustrine environment at Yellowknife Bay, Gale Crater, Mars. Science. 343(6169):1242777.
- Grotzinger JP, Gupta S, Malin MC, Rubin DM, Schieber J, Siebach K, et al. 2015. Deposition, exhumation, and paleoclimate of an ancient lake deposit, Gale Crater, Mars. Science. 350(6257):aac7575.
- Guo Q, Strauss H, Kaufman AJ, Schröder S, Gutzmer J, Wing BA, et al. 2009. Reconstructing Earth's surface oxidation across the Archean-Proterozoic transition. Geology. 37(5):399-402.
- Grotzinger JP, Arvidson RE, Bell III JF, Calvind W, Clarke BC, Fike DA, et al. 2005. Stratigraphy and sedimentology of a dry to wet eolian depositional system, Burns Formation, Meridiani Planum, Mars. EPSL. 240(1):11-72.
- Haberle RM, Gómez-Elvira J, de la Torre Juárez, M, Harri AM, Hollingsworth JL, Kahanpää H, et al. 2014. Preliminary interpretation of the REMS pressure data from the first 100 sols of the MSL mission. JGR Planets. 119:440-453. DOI: https://doi.org/10.1002/2013JE004488.
- Hahn BC, McLennan SM, Klein EC. 2011. Martian surface heat production and crustal heat flow from Mars Odyssev Gamma-Ray spectrometry. Geophys. Res. Lett. 38(14):L14203.
- Halevy I, Fischer WW, Eiler JM. 2011. Carbonates in the Martian meteorite Allan Hills 84001 formed at 18±4 C in a near-surface aqueous environment, PNAS, 2011 October 11. 108(41):16895-16899. DOI: https://doi.org/10.1073/pnas.1109444108
- Hall DO, Rao JK. 1986. Photosynthesis (Studies in Biology), Hodder Arnold H&S. New York.
- Hartman H, McKay CP. 1995. Oxygenic photosynthesis and the oxidation state of Mars. Space Sci. Rev. 43:123-128.
- Harri AM, Genzer M, Kemppinen O, Kahanpää H, Gomez-Elvira J, Rodriguez-Manfredi JA, et al. 2014a. Pressure observations by the Curiosity rover: Initial results. JGR Planets. 119:82-92. DOI: https://doi.org/10.1002/2013JE004423.
- Harri A-M., Genzer M, Kemppinen O, Gomez-Elvira J, Haberle R, Polkko J, et al. 2014b. Mars Science Laboratory relative humidity observations: Initial results. JGR Planets. 119:2132-2147.
- Haskin LA, Wang A, Jolliff BL, McSween HY, Clark BC, Des Marais DJ, et al. 2005. Water alteration of rocks and soils on Mars at the Spirit rover site in Gusev crater. Nature. 436:66-69.
- Hausrath EM, Ming DW, Rampe EB. 2018. Reactive transport and mass balance modeling of the Stimson sedimentary formation and altered fracture zones constrain diagenetic conditions at Gale crater, Mars. EPSL. 491:1-10.
- Head JW, Hiesinger H, Ivanov MA, Kreslavsky MA, Pratt S, Thomson BJ. 1999. Possible ancient oceans on Mars: Evidence from Mars Orbiter Laser Altimeter Data. Science. 286(5447):2134-2137.
- Herkenhoff KE, Squyres SW, Arvidson R, Bass DS, Bell III JF, Bertelsen P, et al. 2004. Evidence from Opportunity's Microscopic

- Imager for Water on Meridiani Planum. Science. 306:1727-1730.
- Hogancamp JV, Sutter B, Morris RV, Archer PD, Ming DW, Rampe EB, et al. 2018. Chlorate/Fe-bearing phase mixtures as a possible source of oxygen and chlorine detected by the sample analysis at Mars instrument in Gale Crater, Mars. JGR Planets. 123:2920-2938.
- Holt JW, Safaeinili A, Plaut JJ, Head JW, Phillips RJ, Seu R, et al. 2008. Radar sounding evidence for buried glaciers in the southern mid-latitudes of Mars. Science 322, 1235-1238. DOI: 10.1126/science.1164246pmid:19023078
- Hu Y, Rodier S, Xu K-M, Sun W, Huang J, Lin B, Zhai P, Josset D. 2010. Occurrence, liquid water content, and fraction of supercooled water clouds from combined CALIOP/IIR/MODIS. JGR Atmospheres. 115(D4):D00H34. DOI: https://doi.org/10.1029/2009JD012384.
- Humayun M, Nemchin A, Zanda B, Hewins RH, Grange M, Kennedy A. et al. 2013. Origin and age of the earliest Martian crust from meteorite NWA 7533. Nature. 503:513-516.
- Hurowitz JA, McLennan SM, Tosca NJ, Ming DW, Schröder C. 2006. In situ and experimental evidence for acidic weathering of rocks and soils on Mars. JGR. 111:E02S19.
- Ivanov MA, Hiesinger H, Erkeling G, Reiss D. 2014. Mud volcanism and morphology of impact craters in Utopia Planitia on Mars: Evidence for the ancien ocean. Icarus. 228:121-140.
- lagoutz E. Sorowka A. Vogel ID. Wenke H. 1994. ALH 84001: Alien or progenitor of the SNC family? Meteoritics. 29:478-479.
- Jakosky BM, Brain D, Chafln M, Curry S, Deighan J, Grebowsky J, et al. 2018. Loss of the Martian atmosphere to space: Presentday loss rates determined from MAVEN observations and integrated loss through time. Icarus. 315:146-157.
- Janhunen P. 2002. Are the northern plains of Mars a frozen ocean? JGR Planets. 107(E11):13-1-13-3.
- Jaumann R, Tirsch D, Hauber E, Erkeling G, Hiesinger H, Le Deit L, et al. 2014. Water and Martian habitability: Results of an integrative study of water related processes on Mars in context with an interdisciplinary Helmholtz research alliance "Planetary Evolution and Life". Planet. Space Sci. 2014. 98:128-145.
- Jorgensen BB, Revsbech NP, Blackburn TT, Cohen Y. 1979. Diurnal cycle of oxygen and sulfide microgradients and microbial photosynthesis in a cyanobacterial mat sediment. Appl. Env. Micro. 38(1):46-58.
- Joseph RG. 2016. A High Probability of life on Mars, the consensus of 70 experts in fungi, lichens, geomorphology, mineralogy. J. Cosmol. 25:1-25.
- Joseph RG, Dass RS, Rizzo V, Cantasano N, Bianciardi G. 2019. Evidence of Life on Mars? Journal of Astrobiology and Space Science Reviews. 1:40-81. Reprinted in: Beech M, Gordon R, Seckbach J. Editors. Astrobiology Perspectives on Life of the Universe, Wiley-Scrivener, Beverly, Massachusetts, USA.
- Joseph RG, Graham L, Budel B, Jung P, Kidron GJ, Latif K, et al. 2020a. Mars: Algae, Lichens, Fossils, Minerals, Microbial Mats and Stromatolites, in Gale Crater. J. Astrobiol. Space Sci. Res. 3(1):40–111. Reprinted in: Beech M, Gordon R, Seckbach J. Editors. Astrobiology Perspectives on Life of the Universe. Wiley-Scrivener, Beverly, Massachusetts (USA).
- Joseph RG, Armstrong R, Kidron G, Gibson CH, Schild R. 2020b. Life on Mars? Colonies of mushroom-shaped specimens in Eagle Crater. J. Astrobiol. Space Sci. Res. 5:88-126.

- Joseph RG, Planchon, O, Gibson, C, Schild, R. 2020c. Seeding the Solar System with Life: Mars, Venus, Earth, Moon, Protoplanets. Open Astron. 29:124-157. DOI: 10.1515/astro-2020-0019.
- Joseph RG, Planchon O, Duxbury NS, Latif K, Kidron GJ, Consorti L, et al. 2020d. Oceans, lakes and stromatolites on Mars. Adv. Astron. 2020:6959532. DOI: https://doi.org/10.1155/2020/ 6959532.
- Kahn R. 1984. The spatial and seasonal distribution of Martian clouds and some meteorological implications. JGR: Space Physics. 89:6671-6688.
- Kaplan LD, Munch G, Spinrad, H. Analysis of the spectrum of Mars. 1964. ApJ. 139(1):1-15.
- Keeling RF, Shertz SR. 1992. Seasonal and interannual variations in atmospheric oxygen and implications for the global carbon cycle. Nature. 356:723-727.
- Keeling CD, Chin JFS, Whorf TP. 1996. Increased activity of northern vegetation inferred from atmospheric CO₂ measurements. Nature. 382:146-149. DOI: 10.1038/382146a0.
- Kieffer HH, Jakosky BM, Snyder CW. 1992. The planet Mars: From antiquity to present, in Mars. In: Kieffer HH, Jakosky B, Snyder C. Editors. Tucson (Arizona, USA): University of Arizona Press, p. 1-33.
- Kim H, Takayama K, Hirose N, Onitsuka G, Yoshida T, Yanagi T. 2019. Biological modulation in the seasonal variation of dissolved oxygen concentration in the upper Japan Sea. J Oceanogr. 75:257-271.
- Klein HP. 1978. Viking biological experiments on Mars. Icarus. 34(3):666-674. DOI: https://doi.org/10.1016/0019-1035(78)90053-2.
- Klingelhöfer G. 2004. Jarosite and Hematite at Meridiani Planum from Opportunity's Mössbauer Spectrometer. Science. 306:1740-1745.
- Knauth L, Burt D, Wohletz K. 2005. Impact origin of sediments at the Opportunity landing site on Mars. Nature. 438:1123-1128.
- Kolb CJA, Martín-Fernández R, Lammer H. 2006. The chemical variability at the surface of Mars: Implication for sediment formation and rock weathering. Icarus, 183:10-29. DOI: 10.1016/j.icarus.2006.01.020.
- Korablev OI, Baraux, J-L, Dubois J-P. 2001. Occultation of stars in the UV: Study of the atmosphere of Mars. JGR. 106:7597-7610.
- Krasnopolsky V. A. 2010. Solar activity variations of thermospheric temperatures on Mars and a problem of CO in the lower atmosphere. Icarus. 207(2):638-647. DOI: https: //doi.org/10.1016/j.icarus.2009.12.036
- Krupa TA. 2017. Flowing water with a photosynthetic life form in Gusav Crater on Mars. Proceedings of the 48th Lunar and Planetary Science Conference. 2017 March 20-24, The Woodlands, Texas. LPI Contribution No. 1964, id. 2711.
- Lane N. 2002. Oxygen: The molecule that made the world. Oxford University Press.
- Lanse J, Noblet A, Szopa C, Navarro-González R, Cabane M, Poch O, et al. 2016. Oxidants at the surface of Mars: A review in light of recent exploration results. Astrobiology. 16(12):977-996. DOI: https://doi.org/10.1089/ast.2016.1502
- Lanza NL, Wiens RC, Arvidson RE, Clark BC, Woodward W, Fischer WW, et al. 2016. Oxidation of manganese in an ancient aquifer, Kimberley formation, Gale crater, Mars. GRL. 43:7398-7407.
- Lauro SE, Pettinelli E, Caprarelli G, Guallini L, Rossi AP, Mattei E, et al. 2020. Multiple subglacial water bodies below the South

- Pole of Mars unveiled by new MARSIS data, Nat. Astron. DOI: https://doi.org/10.1038/s41550-020-1200-6.
- Lefčvre F, Krasnopolsky VA. 2017. Atmospheric photochemistry. In: Haberle R. Editor. The atmosphere and climate of Mars. Cambridge: Cambridge University Press. pp. 405-432. DOI: https://doi.org/10.1017/9781139060172.
- Leshin LA, Mahaffy PR, Webster CR, Cabane M, Coll P, Conrad PG, et al. 2013. Volatile, isotope, and organic analysis of Martian fines with the Mars Curiosity Rover. Science, 341(6153):1238937.
- Levin G, Straat PA. 1976. Viking labeled release biology experiment: Interim results. Science. 194:1322-1329.
- Levin GV, Straat PA. 1977. Life on Mars? The Viking labeled release experiment. Biosyst. 9(2-3):165-174.
- Levin GV, Straat P.A. 1981. A search for a nonbiological explanation of the Viking Labeled Release life detection experiment. Icarus. 45:494-516.
- Levin GV, Straat PA. 2016. The case for extant life on Mars and its possible detection by the Viking Labeled Release Experiment. Astrobiology. 16(10):798-810.
- Levin GV, Straat PA, Benton WD. 1978. Color and feature changes at Mars Viking Lander Site. J. Theor. Biol. 75:381-390.
- Lin CS, Chou TL, Wu JT. 2013. Biodiversity of soil algae in the farmlands of mid-Taiwan. Bot Stud. 54:41.
- Lin CS, Wu JT. 2014. Environmental factors affecting the diversity and abundance of soil photomicrobes in arid lands of subtropical Taiwan. Geomicrobiol. J. 31(4):350-359.
- Livengood TA, Kostiuk T, Hewagama T, Smith RL, Fast KE, Annen JN, et al. 2020. Evidence for diurnally varying enrichment of heavy oxygen in Mars atmosphere. Icarus. 335:113387-113392.
- Long SP, Ainsworth EA, Leakey AD, Nösberger J, Ort DR. 2006. Food for thought: lower-than-expected crop yield stimulation with rising CO₂ concentrations. Science. 312(5782):1918-1921. DOI: 10.1126/science.1114722
- Luger R, Barnes R. 2015. Extreme water loss and abiotic O₂ buildup on planets throughout the habitable zones of M dwarfs, Astrobiology. 15:14. DOI: https://doi.org/10.1089/ast.2014.1231.
- Macey MC, Fox-Powell M, Ramkissoon NK, Stephens BP, Barton T, Schwenzer SP, et al. 2020. The identification of sulfide oxidation as a potential metabolism driving primary production on late Noachian Mars. Sci Rep 10:10941. DOI: https://doi.org/ 10.1038/s41598020-67815-8
- Martínez GM, Newman CN, De Vicente-Retortillo A, Fischer E, Renno NO, Richardson MI, et al. 2017. The modern near-surface Martian climate: A Review of In-situ Meteorological Data from Viking to Curiosity. Space Sci. Rev. 212:295-338. DOI: https://doi.org/10.1007/s11214-017-0360-x
- Martín-Torres FJ, Zorzano MP, Valentín-Serrano P, Harri AM, Genzer M, Kemppinen O, et al. 2015. Transient liquid water and water activity at Gale crater on Mars. Nature. 8:357-361.
- Metting B. 1981. The systematics and ecology of soil algae. Bot. Rev. 47(110):195-312. DOI: https://doi.org/10.1007/BF02868854.
- McElroy MB, Kong TK, Yung YL, 2012. Photochemistry and evolution of Mars' atmosphere: A Viking perspective. JGR. 82(28):4379-4388. DOI: https://doi.org/10.1029/JS082i028p04379.
- McKay CP. 2010. An origin of life on Mars. Cold Spring Harbor Perspectives in Biology. DOI: 10.1101/cshperspect.a003509.
- McKay DS, Gibson EK, Thomas-Keprta KL, Vali H, Romanek CS, Clemett SJ, et al. 1996. Search for past life on Mars: possible

- relic biogenic activity in martian meteorite ALH84001. Science. 273:924-930.
- McKay DS, Thomas-Keprta KL, Clemett SJ, Gibson Jr EK, Spencer L, Wentworth SJ. 2009. Life on Mars: new evidence from martian meteorites. Instr. Meth. Astrobio. Planet. Missions. 7441.744102
- McLennan SM, Grotzinger IP, 2008. The sedimentary rock cycle of Mars. In: The martian surface - Composition, mineralogy, and physical properties. Jim Bell III J. Editor. Cambridge University Press. 541 p.
- Meteoritical Bulletin Database. 2020.
- Ming DW, Archer PD, Glavin DP, Eigenbrode JL, Franz HB, Sutter B, et al. 2014. Volatile and organic compostions of sedimentary rocks in Yellowknife Bay, Gale crater, Mars. Science Express. 343(6169): 1245267. DOI: https://doi.org/10.1126/science.1245267.
- Montgomery W, Jaramillo EA, Royle SH, Kounaves SP, Schulze-Makuch D, Sephton MA. 2019. Effects of oxygen-containing salts on the detection of organic biomarkers on Mars and in terrestrial analog soils. Astrobiology. 19(6):711-721. DOI: http://doi.org/10.1089/ast.2018.1888
- Moores JE, Lemmon MT, Rafkin SCR, Francis R, Pla-Garcia J, De La Torre Juárez M, et al. 2015. Atmospheric movies acquired at the Mars Science Laboratory landing site: Cloud morphology, frequency and significance to the Gale Crater water cycle and Phoenix mission results. Adv. Space Res. 55:2217-2238.
- Morris RV, Klingelhöfer G, Schröder C, Rodionov DS, Yen A, Ming DW, et al. 2006a. Mössbauer mineralogy of rock, soil, and dust at Gusev crater, Mars: Spirit's journey through weakly altered olivine basalt on the plains and pervasively altered basalt in the Columbia Hills. JGR. 111:E02S13.
- Morris RV, Klingelhöfer G, Schröder C, Rodionov DS, Yen A, Ming DW, et al. 2006b. Mössbauer mineralogy of rock, soil, and dust at Meridiani Planum, Mars: Opportunity's journey across sulfate-rich outcrop, basaltic sand and dust, and hematite lag deposits. JGR. 111:E12S15.
- Navarro-González RE, Vargas J, de la Rosa AC, Raga C, McKay CP. 2010. Reanalysis of the Viking results suggests perchlorate and organics at midlatitudes on Mars. JGR Planets. 115(E12):E12010. DOI:10.1029/2010JE003599.
- Noffke N. 2015. Ancient Sedimentary Structures in the < 3.7b Ga Gillespie Lake Member, Mars, That compare in macroscopic morphology, spatial associations, and temporal succession with terrestrial microbialites. Astrobiology. 15(2):1-24.
- Norlund LI, Baron C, Warren LA. 2010. Jarosite formation by an AMD sulphide-oxidizing environmental enrichment: Implications for biomarkers on Mars. Chemical. Geo. 275:235-242.
- Nyquist LE, Bansal BM, Wiesmann H, Shih C-Y. 1995. "Martians" young and old: Zagami and ALH84001. Proceedings of the Lunar Planet Science XXVI. 26:1065-1066.
- Nyquist LE, Bogard D, Shih C-Y, Greshake A, Stöffler D, Eugster O. 2001. Ages and geologic histories of martian meteorites. In: Kallenbach R, Geiss J, Hartmann WK. Editors. Chronology and Evolution of Mars. Springer, New York, p. 105–164.
- Orosei R, Ding C, Fa W, Giannopoulos A, Hérique A, Kofman W, et al. 2020. The global search for liquid water on Mars from orbit: Current and future perspectives. Life. 10:120.
- Orosei R. Lauro SE, Pettinelli E, Cicchetti A, Coradini M, Cosciotti B, et al. 2018. Radar evidence of subglacial liquid water on Mars. Science. 361:490-493.

- Oyama VI, Berdahl BJ. 1977. The Viking Gas Exchange experiment results from Chryse and Utopia surface samples. JGR. 82(28):4669-4676.
- Parker TJ, Schneeberger DM, Pieri DC, Saunders RS. 1986. Geomorphic evidence for ancient seas on Mars. In: Symposium on Mars: Evolution of its Climate and Atmosphere. Lunar & Planetary Institute, 82 p.
- Parnell J, McMahon S, Boyce A. 2018. Demonstrating deep biosphere activity in the geological record of lake sediments, on Earth and Mars. Int. J Astrobio. 17:380-385.
- Picardi G, Plaut JJ, Biccari D, Bombaci O, Calabrese D, Cartacci M, et al. 2005. Radar soundings of the subsurface of Mars. Science. 310:1925-1928.
- Plesa A-C, Grott M, Tosi N, Breuer D, Spohn T, Wieczorek MA. 2016. How large are present-day heat flux variations across the surface of Mars? JGR Planets. 121(12):2386-2403.
- Pope EC, Bird SK, Rosing MT. 2012. Isotope composition and volume of Earth's early oceans. PNAS. 109(12):4371-4376. DOI: 10.1073/pnas.1115705109
- Pruppacher H, Klett J. 2010. Microstructure of atmospheric clouds and precipitation. In: Microphysics of Clouds and Precipitation. Atmospheric and Oceanographic Sciences Library, Vol 18. Dordrecht: Springer.
- Putzig NE, Phillips RJ, Campbell BA, Mellon MT, Holt JW, Brothers TC. 2014. SHARAD soundings and surface roughness at past, present, and proposed landing sites on Mars: Reflections at Phoenix may be attributable to deep ground ice. JGR Planets. 119(8):1936-1949. DOI: 10.1002/2014JE00464.
- Quinn RC, Martucci HFH, Miller SR, Bryson CE, Grunthaner FJ, Grunthaner PJ. 2013. Perchlorate radiolysis on Mars and the origin of martian soil reactivity. Astrobiology. 13(6): 515-520. DOI: 10.1089/ast.2013.0999.
- Rahmati A, Larson DE, Cravens TE, Lillis RJ, Dunn PA, Halekas JS, et al. 2015. MAVEN insights into oxygen pickup ions at Mars. Geophys. Res. Lett. 42:8870-8876.
- Ramirez RM, Craddock RA, Usui T. 2020. Climate simulations of early Mars with estimated precipitation, runoff, and erosion rates. JGR Planets. 125(3): e2019JE006160. DOI: https://doi. org/10.1029/2019JE006160.
- Rampe EB, Blake DF, Bristow TF, Ming DW, Vaniman DT, Morris RV, et al. 2020. Mineralogy and geochemistry of sedimentary rocks and eolian sediments in Gale crater, Mars: A review after six Earth years of exploration with Curiosity. Geochemistry. 80(2):125605.
- Rampe E, Ming, D, Blake, D, Bristow, T, Chipera, S, Grotzinger, J, et al. 2017. Mineralogy of an ancient lacustrine mudstone succession from the Murray formation, Gale Crater, Mars. Earth Planet. Sci. Lett. 471:172–185. DOI: https://doi.org/10.1016/j. epsl.2017.04.021v
- Read PL, Lewis SR. 2004. The Martian Climate Revisited-Atmosphere and Environment of a desert planet, Berlin: Springer-Verlag. 326 p.
- Retallack GJ. 2014. Paleosols and paleoenvironments of early Mars. Geology. 42:755-758.
- Richardson MI, Mischna MA. 2005. Long-term evolution of transient liquid water on Mars. JGR. 110(E3):E03003. 115
- Richter SL, Johnson AH, Dranoff MM, LePage BA, Williams CJ. 2008. Oxygen isotope ratios in fossil wood cellulose: Isotopic composition of Eocene- to Holocene-aged cellulose. Geochim. Cosmochim Acta. 72:2744-2753.

- Rizzo V. 2020. Why should geological criteria used on Earthnot be valid also for Mars? Evidence of possiblemicrobialites and algae in extinct Martian lakeslakes. Int. J. Astrobiol. 19(3):283-
- Rizzo V, Cantasano, N. 2009. Possible organosedimentary structures on Mars. Int. J. Astrobiol. 8(4): 267-280.
- Rizzo V. Cantasano N. 2016. Structural parallels between terrestrial microbialites and Martian sediments: are all cases of 'Pareidolia'? Int. J. Astrobiol. 16(4):297-316.
- Romanek CS, Perry EC, Treiman AH, Socki RA, Jones JH, Gibson EK Jr. 1998. Oxygen isotopic record of silicate alteration in the SNC meteorite Lafayette. Meteorit. Planet. Sci. 33:775-784.
- Ruff SW, Farmer JD. 2016. Silica deposits on Mars with features resemblinghot spring biosignatures at El Tatio in Chile. Nat. Commun. 7:13554.
- Ruff SW, Niles PB, Alfano F, Clarke AB. 2014. Evidence for a Noachian-aged ephemeral lake in Gusev crater, Mars. Geology. 42(4):359-362. DOI: https://doi.org/10.1130/G35508.1
- Sallstedt T, Bengtson S, Broman C, Crill PM, Canfield DE. 2018. Evidence of oxygenic phototrophy in ancient phosphatic stromatolites from the Paleoproterozoic Vindhyan and Aravalli Supergroups, India. Geobiology. 16(2):139-159.
- Sanchez-Baracaldo P, Cardona T. 2019. On the origin of oxygenic photosynthesis and Cyanobacteria. New Phytol. 225(4):1440-
- Sawa Y. Machida T. Matsueda H. 2012. Aircraft observation of the seasonal variation in the transport of CO₂ in the upper atmosphere. JGR Atmosheres. 117(D):D05305.
- Shaheen Niles PB, Chong K, Corrigan C, Thiemens MH. 2015. Carbonate formation events in ALH 84001 trace the evolution of the Martian atmosphere. PNAS. 112(2):336-341.
- Smith MD. Pearl IC. Conrath BI. Christensen PR. 2001. One Martian year of atmospheric observations by the Thermal Emission Spectrometer. Geophys. Res. Lett. 28:4263-4266. DOI: 10.1029/2001GL013608.
- Smith MD. 2004. Interannual variability in TES atmospheric observations of Mars during 1999-2003. Icarus. 167:148-165.
- Sori MM, Bramson AM. 2019. Water on Mars, with a grain of salt: Local heat anomalies are required for basal melting of ice at the South Pole Today. Geophys. Res. Lett. 46:1222-1231.
- Squyres SW, Knoll AH. 2006. Sedimentary rocks at Meridiani Planum: Origin, diagenesis, and implications for life on Mars. Earth Planet. Sci. Lett. 240:1-10.
- Squyres SW, Grotzinger JP, Arvidson RE, Bell III JF, Calvin W, Christensen PR, et al. 2004. In Situ Evidence for an ancien aqueous environment at Meridiani Planum, Mars. Science. 306(5702):1709-1714.
- Steele LJ, Balme MR, Lewis SR, Spiga A. 2017. The water cycle and regolith-atmosphere interaction at Gale crater. Mars. Icarus. 289:56-79.
- Steele A, McCubbin FM, Fries M. 2012. A reduced organic carbon component in martian basalts. Science. 337:212-215.
- Strickland D, Stewart AI, Barth CA, Hord CW, Lane AL. 1973. Mariner 9 Ultraviolet Spectrometer Experiment: Mars atomic oxygen 1304-A emission. JGR. 78(22):4547-4559.
- Stuurman CM, Osinski GR, Holt JW, Levy JS, Brothers TC, Kerrigan M, Campbell BA. 2016. SHARAD detection and characterization of subsurface water ice deposits in Utopia Planitia, Mars. Geophys. Res. Lett. 43:9484-9491.

- Sutter B, Heil E, Morris R, Archer P, Ming D, Niles P, et al. 2015. The investigation of perchlorate/iron phase mixtures as a possible source of oxygen detected by the sample analysis at Mars (SAM) instrument in Gale Crater, Mars. In: 46th Lunar and Planetary Science Conference. The Woodlands, Texas, USA. id.
- Sutter B, McAdam AC, Mahaffy PR, Ming DW, Edgett KS, Rampe EB, et al. 2017. Evolved gas analyses of sedimentary rocks and eolian sediment in Gale Crater, Mars: results of the Curiosity rover's sample analysis at Mars instrument from Yellowknife Bay to the Namib Dune. JGR Planets. 122(12):2574-2609.
- Szopa C, Freissinet C, Glavin DP, Millan M, Buch A, Franz HB, et al. 2020. First Detections of dichlorobenzene isomers and trichloromethylpropane from organic matter indigenous to Mars mudstone in Gale Crater, Mars: Results from the Sample analysis at Mars instrument onboard the Curiosity Rover. Astrobiology. 20:292-306.
- ten Kate IL. 2010. Organics on Mars? Astrobiology. 10:589-603. Ten Veldhuis M, Ananyev G, Dismukes GC. 2020. Symbiosis extended: exchange of photosynthetic O2 and fungal-respired CO₂ mutually power metabolism of lichen symbionts. Photosynth. Res. 143:287-299.
- Thomas-Keprta KL, Clemett SJ, McKay DS, Gibson EK, Wentworth SJ. 2009. Origins of magnetite nanocrystals in Martian meteorite ALH84001. Geochim. Cosmochim. Acta. 73:6631-6677.
- Tillman IE, Johnson NC, Guttorp P, Percival DB, 1993. The Martian annual atmospheric pressure cycle: Years without great dust storms. JGR Planets. 84(10):963-910,971.
- Todd Clancy R, Smith MD, Lefčvre F, McConnochie TH, Sandor BJ, Wolff MJ, et al. 2017. Vertical profiles of Mars 1.27 μ m O₂ dayglow from MRO CRISM limb spectra: Seasonal/global behaviors, comparisons to LMD-GCM simulations, and a global definition for Mars water vapor profiles. Icarus. 293:132-156.
- Tosca NJ, Scott M, McLennan M, Dyar D, Sklute EC, Michel FM. 2008. Fe oxidation processes at Meridiani Planum and implications for secondary Fe mineralogy on Mars. JGR Planets. 113(E5):E05005.
- Trainer MG, Wong MH, McConnochie TH, Franz HB, Atreya SK, Conrad PG, et al. 2019. Seasonal Variations in Atmospheric Composition as Measured in Gale Crater, Mars. JGR Planets. 124:3000-3024.
- Treiman AH, Bish D, Vaniman D, Chipera S, Blake D, Ming D, et al. 2016. Mineralogy, provenance, and diagenesis of a potassic basaltic sandstone on Mars: CheMin X-ray diffraction of the Windjana sample (Kimberley area, Gale Crater. JGR Planets. 121:75-106.
- Treiman AH, Essen EJ. 2011. Chemical composition of magnetite in Martian meteorite ALH 84001: Revised appraisal from thermochemistry of phases in Fe-Mg-C-O. Geochim. Cosmochim. Acta. 75:5324-5335.
- Vago JL, Westall F, Pasteur Instrument Teams, Landing Site Selection Working Group, and Other Contributors. 2017. Habitability on Early Mars and the search for biosignatures with the Exo-Mars Rover. In: Vago JL. Editor. Special Collection of Papers: ExoMars Rover Mission. Astrobiology. 17(6-7):471-510.
- Valeille A, Combi MR, Tenishev V, Bougher SW, Nagy AF. 2010. A study of suprathermal oxygen atoms in Mars upper thermosphere and exosphere over the range of limiting conditions. Icarus. 206:18-27.

- Villanueva GL, Mumma MJ, Novak RE, Käufl HU, Hartogh P, Encrenaz T, Tokunaga A, et al. 2015. Strong water isotopic anomalies in the martian atmosphere: Probing current and ancien reservoirs. Science. 348(6231):218-221.
- Vinyard DJ, Ananyev GM, Dismukes GC. 2018. Desiccation tolerant lichens facilitate in vivo H/D isotope effect measurements in oxygenic photosynthesis. Biochim. Biophys. Acta (BBA) -Bioenergetics. 1859(10):1039-1044.
- Wadhwa M, Lugmair GW. 1996. The formation age of carbonates in ALH 84001. Meteoritics. 31:A145.
- Wall SD. 1981. Analysis of condensates formed at the Viking 2 lander site-The first winter. Icarus. 47:173-183.
- Wang A, Haskin LA, Squyres SW, Jolliff BL, Crumpler L, Gellert R, et al. 2006. Sulfate deposition in subsurface regolith in Gusev Crater, Mars. JGR. 11(E2):E02S17.
- Whiteway JA, Komguem L, Dickinson C, Cook C, Illnicki M, Seabrook J, et al. 2009. Mars water-ice clouds and precipitation. Science. 325(5936):68-70.
- Woodworth-Lynas C, Guigné JY. 2003. Ice keel scour marks on Mars: Evidence for floating and grounding ice floes in Kasei Valles. Oceanography. 16(4):90-97.

- Wordsworth R. Pierrehumbert R. 2014. Abjotic oxygen-dominated atmospheres on terrestrial habitable zone planets. Astrophys. J. Lett. 785(2):L20.
- Wright P, Grady MM, Pillinger CT. 1989. Organic materials in a martian meteorite. Nature. 340:146-157.
- Yen AS, Ming DW, Vaniman DT, Gellert R, Blake DF, Morris RV, et al. 2017. Multiple stages of aqueous alteration along fractures in mudstone and sandstone strata in Gale crater. Mars. Earth Planet. Sci. Lett. 471:186-198.
- Zahnle KJ, Catling, DC,. Claire MC. 2013. The rise of oxygen and the hydrogen hourglass. Chem. Geol. 362(20):26-34.
- Zent AP, McKay CP. 1994. The chemical reactivity of the martian soil and implications for future missions. Icarus. 108:146-157.
- Zhang MGH, Luhmann JG, Bougher SW, Nagy AF. 2012. The ancient oxygen exosphere of Mars: Implications for atmosphere evolution. JGR Planets. 98(E6):10915-10923. DOI: 10915-10923.
- Zhang X, Filser J. 2017. Suitability of contact-free oxygen optical microsensors for measuring respiration and photosynthesis in green algae. Front. Environ. Sci. 5:91. DOI: 10.3389/fenvs.2017.00091.