Article

The Case of the Lacking Carbonates and the Emergence of Early Life on Mars

David Carlos Fernández-Remolar [1],*, Mónica Sánchez-Román [1] and Ricardo Amils [1,2]

[1] Centro de Astrobiología (INTA-CSIC), Instituto Nacional de Técnica Aeroespacial (INTA), Ctra Ajalvir km 4, Torrejón de Ardoz, 28850 Madrid, Spain; E-Mail: msanz78@gmail.com

[2] Centro de Biología Molecular, CSIC, Universidad Autónoma de Madrid, 28049 Cantoblanco, Madrid, Spain; E-Mail: ramils@cbm.uam.es

* Author to whom correspondence should be addressed: E-Mail: fernandezrd@inta.es; Tel.: +34-915206429; Fax: +34-915201074.

Abstract: The mineralogical characterization of Mars by different exploration missions, provides a new image of the earliest conditions that prevailed on the planet surface. The detection of extensive deposits of phyllosillicates has been considered to be as a result of the production of hydrated silicates through alteration and precipitation under neutral to sub-alkaline conditions. Although extensive deposits of carbonates should precipitate beneath a thick CO_2-bearing atmosphere, only a few outcrops of Mg-rich carbonates have been detected on Mars. Paradoxically those carbonates occur in association with geological units exposed to acidic paleoenvironments. Given such geochemical conditions on Earth, the carbon cycle is intimately associated with life, then, we can assume that the presence or absence of microbial communities should have impacted the distribution of those carbonate compounds on Mars. In this paper, we suggest three potential geobiological scenarios to explain how the emergence of life on Mars would have impacted the carbon cycle and, hence, the formation of carbonates on a planetary scale.

1. Introduction

The latter missions to Mars have provided outstanding information about the earliest conditions that governed the primordial Martial surface environments. Mars Express and Mars Reconnaissance Orbiter (MRO), as well as the grounded Mars Exploration Rovers (MERs), have recovered essential mineralogical and geochemical information to reconstruct past conditions on Mars surface [1-3]. Interpretation of some planetary data suggest three distinctive periods during which various sedimentary materials and geomorphical structures were formed. The two first great episodes ranging from Early Noachian to Hesperian (4.5 to 3.4 Ga) were associated to very distinctive mineralogies like phyllosilicates and sulfates, respectively [4,5]. Whereas the sulfates have mostly been detected in terrains as old as Middle to Late Noachian (<4.0 Ga) in close association with ferric oxides like hematite, the phyllosilicate-rich deposits crop out topping the oldest basement ever found on Mars [6,7]. The formation of such an extensive set of materials has been explained by a strong hydrous alteration of the primary crystalline basement which induced the production of clays on a global scale, but other formative mechanisms like hydrothermal or weathering precipitation are also likely mineral forming processes which contributed to the phyllosilicate inventory.

Although the weathering of a silicate crust produce on Earth great quantities of carbonates as by-products of the chemical neutralization of the solutions [8,9], on Mars few carbonate evidences have been found associated to the phyllosilicate deposits. Some scarce outcrops of carbonates have been reported in co-occurrence with phyllosilicates [10] which appear in Late Noachian terrains much younger and currently exposed to acidic conditions. The lack of carbonates in the early Noachian record have been explained as the result of weathering and chemical precipitation under a CO_2-depleted atmosphere which promoted neutral to alkaline surface solutions [5]. However, recent modeling on the mantle oxidation state for early Mars suggests that CO_2 was likely an abundant volatile in the Mars atmosphere [11]. Moreover, the detection of nontronites, a Fe^{3+}-bearing clay, would suggest that some regions of the crust of Mars was also exposed to oxidizing conditions.

One alternative explanation to the missing carbonates on the Mars surface could be the acidifying effect (see Table 1 for thermodynamical constraints) produced in the solutions by oversaturation of the carbon dioxide, which could occur through atmospheric overload during the Early Noachian times [11,12]. Under these conditions, dissolution of CO_2 [13] would favor global acidification and promote carbonate inhibition in the surface regions of the red planet. The same mechanism could operate as an incipient process that induces moderate acidification of modern oceans as a consequence of anthropogenic CO_2 emissions [14]. However, carbonate precipitation would be favored in those regions of the Mars crust where the surface solutions were isolated from the atmospheric input of volatiles. Such regions would be fractured basalts, Mars regolith, alteration units and fine-grained sedimentary deposits. In these geological settings, carbonate crystals could precipitate as a consequence of simple chemical neutralization of the surrounding waters (precipitating solutions) resulting in sedimentary bodies that, with time, would increase their size and volume.

In this paper, we evaluate how the carbon cycle could operate on early Mars (~4.5 Ga) under the control of an emerging biosphere exposed to a global acidification maintained by CO_2 emissions. The high concentration of CO_2 interacting with an incipient biosphere, which did not take control in the geochemical cycling of carbon, would explain the absence of carbonates on the Mars surface, and

would explain the possible occurrence of those mineralogies in cryptic areas of the planet. Although, this model contemplates the presence of microbial life, we also consider a potential scenario where the carbon cycle would operate in a sterile planet. In this context, those mineralogies should have formed in the subsurface areas of Mars and would escape from the detection capabilities of the grounded and orbiter missions, they would be undetectable for the probes scrutinizing the Mars surface. The possible scenarios are built up on the basis of different environmental constraints which are supported by recent reports dealing with the early environmental conditions of Mars and based on geochemical data such as: (1) the surface of early Mars was exposed to an atmospheric overload exceeding 20 bar [11-13]; (2) the mantle composition of Mars promoted partial pressures for CO_2 higher than 5 bar [11,15,16]; (3) the high geothermal gradient of the planet maintained surface temperatures well above 298 K [17,18]; (4) the low volatile accretion of Early Mars induced shallow continental water bodies [19] subjected to slightly oxidizing conditions (Eh > 0) [5]. Under these conditions, the production of phyllosilicates occurred in acidic and slightly oxidizing environments, which thermally favored weathering of the Martian crust.

Table 1. Thermodynamical calculations to calculate the saturation index for carbonate minerals for a solution bearing SiO_2 and equilibrated with an atmosphere enriched on CO_2 with 5 bar that would induce solutions with a pH of 3.5. The resulting solution does not favor the precipitation for any of the carbonate mineralogies that might be potentially formed.

Aqueous species	log activity
CO_2 (aq)	−0.77
SiO_2 (aq)	−2.83
Mg^{2+}	−3.13
Ca^{2+}	−3.14
Fe^{2+}	−3.18
HCO_3^-	−3.61
$FeHCO_3^+$	−4.07
$CaHCO_3^+$	−5.71
$MgHCO_3^+$	−5.71
Mineral saturation	**log Q/K**
Siderite	−3.1
Calcite	−5.1
Aragonite	−5.2
Magnesite	−5.5

2. Carbonate Precipitation on Earth

2.1. Geological and Biological Aspects of the Carbon Cycle on Earth

CO_2 is a greenhouse gas that plays an important role on the Earth's climate. The concentration of CO_2 in the atmosphere is controlled by the balance between gains and losses occurring during the transfer of carbon between air and other reservoirs such as the biosphere, the ocean and the Earth's interior. The primary source of carbon/CO_2 is outgassing from the Earth's interior at mid ocean ridges, hotspot volcanoes, and subduction-related volcanic arcs. Much of the CO_2 released at subduction zones

is derived from the metamorphism of carbonate rocks subducting with the ocean crust. Some of the outgassed carbon remains as CO_2 in the atmosphere, some is dissolved in the oceans, some carbon is held as biomass in living or dead and decaying organisms, and some is bound in carbonate rocks. Carbon is removed into long term storage by burial of sedimentary strata, especially coal and black shales that store organic carbon from undecayed biomass and carbonate rocks like limestone (calcium carbonate). Plants, photosynthetic algae and bacteria use energy from sunlight to combine CO_2 from the atmosphere with H_2O to form carbohydrates (CH_2O). These carbohydrates store energy. Oxygen (O_2) is a byproduct that is released into the atmosphere. This process is known as photosynthesis (Reaction 1).

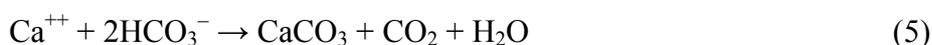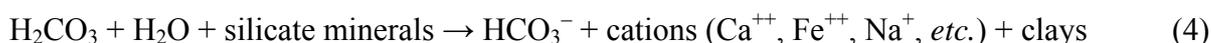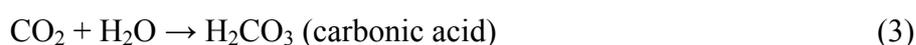$$CO_2 + H_2O + sunlight \rightarrow CH_2O + O_2 \tag{1}$$

Plants (and photosynthetic algae and bacteria) then use some of the stored carbohydrates as an energy source to carry out their life functions. Some of the carbohydrates remain as biomass. Consumers such as animals, fungi, and bacteria get their energy from this excess biomass either while living or dead and decaying. Oxygen from the atmosphere is combined with carbohydrates to liberate the stored energy. Water and carbon dioxide are byproducts (Reaction 2).

$$O_2 + CH_2O \rightarrow energy + H_2O + CO_2 \tag{2}$$

2.2. Carbonate Formation on Earth

Carbon dioxide is removed from the atmosphere by dissolving in water and forming carbonic acid (Reaction 3) which is used to weather rocks, yielding bicarbonate ions, other ions, and clays (Reaction 4). Then, calcium carbonate is precipitated from calcium and bicarbonate ions in seawater by marine organisms like coral (Reaction 5). Finally, the carbon is stored on the seafloor in layers of limestone.

$$CO_2 + H_2O \rightarrow H_2CO_3 \text{ (carbonic acid)} \tag{3}$$

$$H_2CO_3 + H_2O + silicate\ minerals \rightarrow HCO_3^- + cations\ (Ca^{++}, Fe^{++}, Na^+, etc.) + clays \tag{4}$$

$$Ca^{++} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O \tag{5}$$

Almost all deep-sea carbonate-rich sediments are composed of calcite low in magnesium (99% $CaCO_3$), which is primarily derived from pelagic skeletal organisms [20,21]. Indeed, carbonates in ancient sedimentary rocks are dominantly calcite ($CaCO_3$) and dolomite [$CaMg(CO_3)_2$] predicted by equilibrium thermodynamics. This is reflected by the observation that about 20% by volume of Phanerozoic (0–547 Ma) sedimentary rock is made up of the carbonate minerals calcite and dolomite [20]. Over the history of Earth, the primary source of marine carbonate minerals has shifted from abiotic precipitation to biogenic sources [21]. Dolostone (sedimentary carbonate rock that contains a high percentage of the mineral dolomite), a very common carbonate sedimentary rock, is ubiquitous in the geologic record from the Precambrian to the Pleistocene. The rare occurrence of dolomite in modern environments constitutes the base of the Dolomite Problem [22,23]. McKenzie [22] suggested that the combination of models together with laboratory experiments could explain

diverse factors related with formation, such as a kinetic inhibition, and greatly increase our understanding of the different mechanisms of carbonates formation on the Earth surface. The variables that affect the rate of a chemical reaction are commonly referred to as kinetic factors [24] such as: (1) the Mg/Ca ratio [25]; (2) the carbonate ion concentration [26]; (3) the ionic strength of the solution [27]; (4) or the sulfate concentration of the solution [28].

Obviously, a large number of geochemical factors (e.g., thermodynamics, chemical kinetics, hydrology, host-rock mineralogy and texture) interact to form carbonate minerals. Recent studies consider a microbial factor in addition to the chemical requirements for the formation of carbonates and other authigenic minerals [29-31]. Most of these studies are based on field observations and validated by laboratory experiments. The role of microbes in mineral formation has been emphasized because inorganic changes in the conditions alone, could not induce mineral precipitation. The ability of living organisms to control and direct the precipitation of minerals is an important geo-biological process. In any event, a diverse microbial population is generally involved in carbonate precipitation in natural environments, including photoautotrophic cyanobacteria, bacteria producing ammonia from the oxidation of the organic compounds and hydrogen-oxidizing methanogenic archaea [32-36]. We should also note the formation of carbonates in extreme hydrocarbon-bearing submarine ecosystems [37,38] and in environments associated to hydrothermal systems as has been recently documented for Mars [39]. Interestingly, some hydrothermal carbonates have been found associated to some acidic mineralogies like jarosite [40,41], which illustrate how variable the geochemical conditions can be that drive the mineral precipitation in a limited area.

3. Control of pH in Surface Waters by Microbial Uptake of CO_2

Carbonate precipitation in surface waters is a common geochemical process that is actively mediated by different geobiological processes. Plants and microorganisms are effective geochemical pumps extracting CO_2 from waters in the form of organic compounds or carbonate mineralogies [25,42,43]. In this context, the oceanic CO_2 content sourced on the atmosphere and submarine hydrothermal centers [44] is efficiently removed by biological activity that, together with the crustal neutralization, increase and maintain the pH between 7.5 and 8.1 [45]. On the other hand, the pH would decrease to acidic ranges if all the CO_2 integrated in both organic and inorganic compounds were released to the surface solutions. Therefore, in a sterile Earth, where the biogeochemical extraction of CO_2 would be inactive, the open water bodies would equilibrate at 293 K to a pH below 4 subjected to an atmospheric concentration of CO_2 about 10 bar. In this situation, the carbonate formation would be restricted to marginal areas where CO_2 is eventually pumped out by reaction in subsurface regions or marginal water bodies partially closed to the CO_2 sources. Therefore, both pressure and temperature are two essential parameters that control the dissolution rate of CO_2. In deep oceanic areas, characterized by high pressure and low temperature conditions, the CO_2 solubility would be much greater than in shallow waters [13] which are directly exposed to the atmosphere. As a consequence, it is very likely that an Earth deprived of life would host acidic oceans that would prevent the formation of carbonates [46].

Venus is an extreme, but interesting comparison, where a great part of the volatile inventory in the planet has been relocated to the atmosphere as a consequence of its extreme thermal conditions. In this

planet, the atmosphere accommodates about 90 bar of CO_2 [47] which roughly doubles the total carbon content estimated for the hydrosphere, biosphere and upper crust on Earth [42]. Such overconcentration of CO_2 would equilibrate the chemistry of a terrestrial-sized hydrosphere with a meteoric pH lower than 3 at 293 K. Assuming the same proportion of carbon removal through microbial and geological activity in Earth, the CO_2 concentration in Venus atmosphere would have roughly 510 ppm [48] which would average the pH meteoric and seawater solutions around 4.8 and 8 respectively (Figure 1).

Figure 1. Expected ocean pH at 298 K calculated on the basis of atmospheric CO_2 equilibrated with calcite using the polynomial equation shown by Loáciga [48].
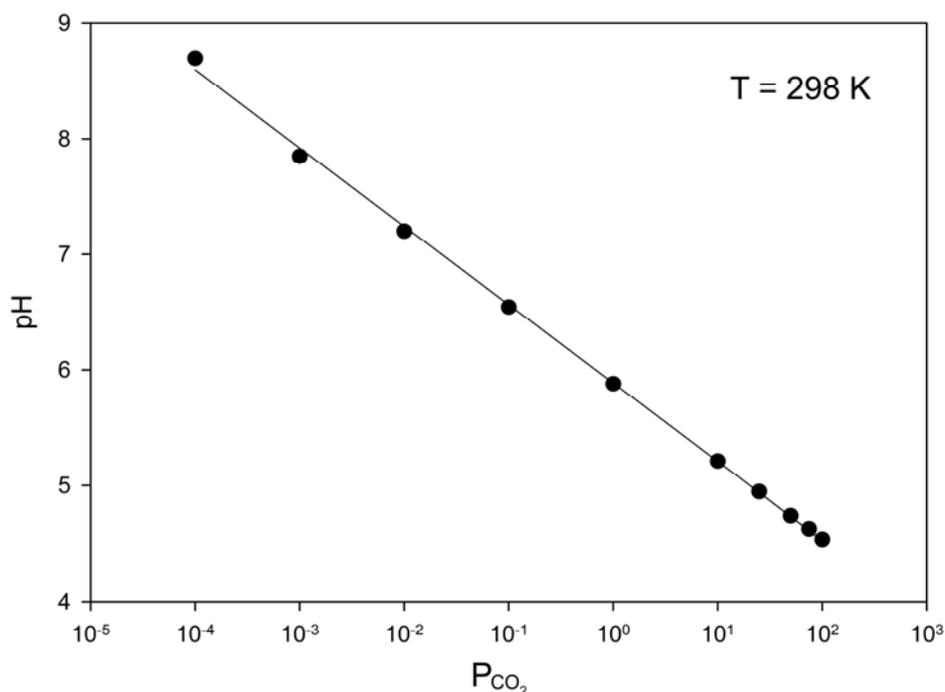
4. Carbonate Distribution on Mars

By considering the premise that Early Mars (~4.5 Ga) likely had an atmosphere enriched in CO_2 and a crust subjected to a high geothermal gradient [11,12], the production of phyllosilicates by weathering, apart from hydrothermalism and volcanism, would be the primary geochemical process that would greatly change the geochemistry of the basaltic primordial crust. The acidic leaching promoted by warm temperatures (~323 K) and CO_2-rich meteoric waters (pH < 3.5) exposed to a dense atmosphere (>20 bar) [15] would prevent carbonate formation on the surface, but the precipitation of carbonates in CO_2-depleted underground environments. Although this CO_2 consumption can have occurred through abiotic pathways, microbes are excellent catalysts that accelerate, by several orders of magnitude, the chemical reaction rates. In this sense, the microbial metabolism creates pH and Eh strong gradients which favors the carbonate precipitation in those geological scenarios subjected to geochemical undersaturation in carbonates. As a consequence, the formation of carbonate minerals and other mineralogies in an early terrestrial planet exposed to acidification would be far different whether life emerges or not. Moreover, assuming that life emerged on Early Mars, the carbonate factory may

have been far different depending both on the microbial metabolism plus surface waters *versus* underground colonization of Mars.

Having all the previously expounded context in mind, the apparent lack of carbonates on Mars can be understood in terms of different geobiological scenarios where carbonate mineralogies were inhibited on the surface or formed in cryptic areas which are restricted to the detection instruments onboard the Mars missions. As a result, three different geobiological scenarios in Mars where carbonates might have formed can be postulated, these scenarios are discussed in the following sections.

4.1. Carbonates in a Sterile Mars

In a sterile world, the main loss of CO_2 would be the weathering of the primordial crust in which kinetics depend on the temperature of the planet surface. Given that surface carbonates should form once the CO_2 consumption increases the pH of the surface waters to the chemical threshold of carbonate precipitation. The inhibition of carbonates suggest that the crust alteration ceased or never compensated the acidic conditions of the meteoric solutions to reach mildly acidic-neutral conditions which are necessary to form extensive deposits of these mineralogies. Assuming that surface waters of Mars never neutralized completely over the first millions of years, it can be concluded that precipitation of carbonates would be possible in those crustal areas under CO_2 reaction with the crust in some areas. In this case, different subsurface and cryptic areas would be plausible locations to neutralize incoming surface solutions. The lower part of the alteration deposits would be a potential place for carbonate formation after the neutralization of the acidic surface waters (Figure 2a). They would occur below the oxide minerals and phyllosilicates which are formed through the alteration of the primary siliceous crust.

Moreover, the CO_2 could also be removed by reacting with the Mars aquifers which are emplaced in fractured basaltic materials [49]. However, the alkalinization of solutions can also be promoted in the internal fluids trapped in the extensive sedimentary bodies of clay that were formed by strong alteration of the early crust of Mars. Inside these deposits, the internal solutions, initially enriched in CO_2, would gradually be neutralized through the formation of bicarbonate ions until a compensation depth allowing solutions to be oversaturated in carbonates.

4.2. Carbonates on Mars Inhabited with both Surface and Subsurface Life

The emergence of life on Mars should have impacted the carbon cycle during the earliest planetary development to create a new global carbon reservoir. Assuming that Mars life inhabited the surface, the only way to explain the apparent lack of carbonates would be the formation of these mineralogies in very shallow underground regions of the planet (Figure 2b). Although carbonates would form in the same areas as in a planet depleted of life, these mineralogies might occur in shallower areas of the crust depending on the predominant metabolism of the microbial communities. A faster CO_2 removal by microbial uptake would favor a higher alkalinization of the incoming waters which would raise the compensation depth for the carbonate oversaturation and, therefore, its precipitation at higher locations of the crust. As a result, carbonate formation would occur extensively in those three different locations like alteration deposits, aquifer of fractured rocks and sedimentary bodies, at shallower depths than those expected for a sterile planet. Despite the fact that autotrophic microbes would remove great

quantities of CO_2 favoring the neutralization of the surface solutions, the activity of heterotrophs would promote a local increase of CO_2 and carbonate undersaturation. This effect together with the regional increment in the rate of volatile production through volcanic centers might locally modify the distribution of alkaline mineralogies in the subsurface areas subjected to greater influx of CO_2 to the atmosphere.

Figure 2. Different geobiological scenarios for carbonate formation on early Mars assuming acidic conditions for the first millions of years under an atmospheric pressure of 20 bar where 5 bar corresponds to CO_2. (a) Carbonate formation in a sterile planet. (b) Carbonate precipitation through microbial activity inhibited by destruction of early habitats; in this case an incipient of pH increase should be expected for surface water bodies. (c) Development of the carbonate factory in the subsurface through combined heterotophic and chemolithoautotrophic regulation of the carbon cycle.
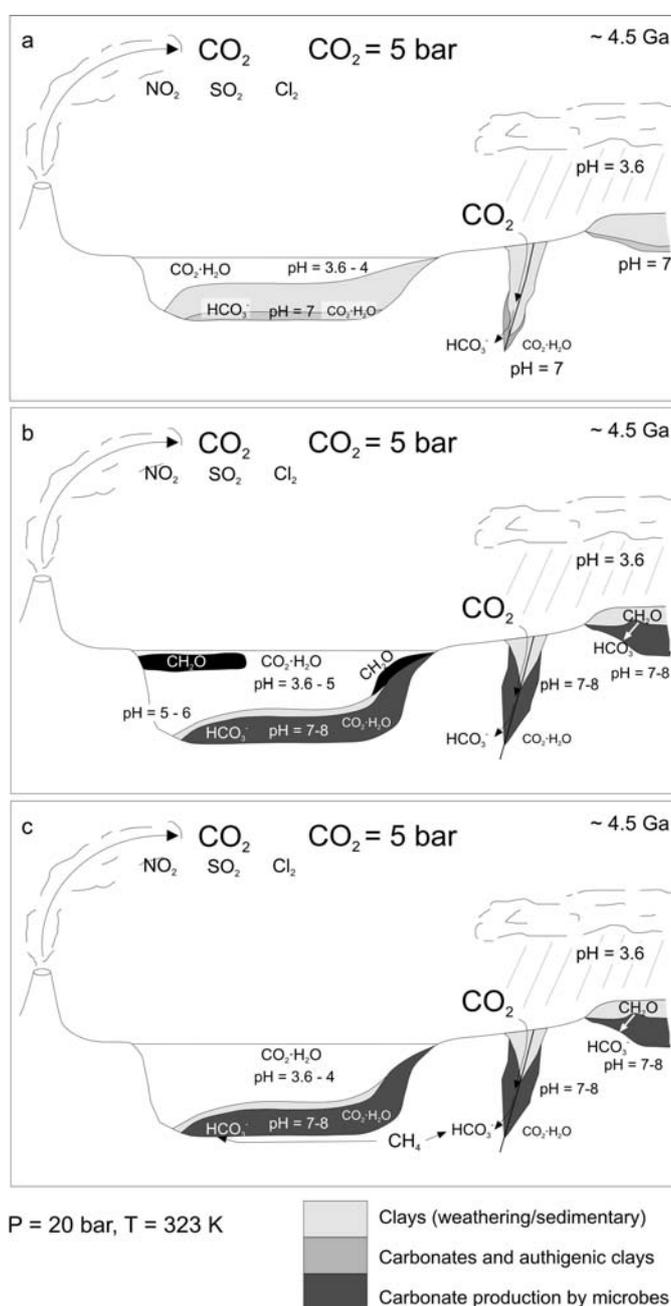
The colonization of surface habitats by microbial communities would maintain a new carbon reservoir which would sequester CO_2 stored in the atmosphere and hydrosphere in the form of biomass. As a consequence, the emergence of a biosphere on the Mars surface habitats would increase the pH in the water bodies and would provide organics to the fine-grained sediments that were formed in weathering and sedimentary systems. Existence of surface bacteria would favor a faster neutralization of waters which should have impact on the mineralogy which likely would favor the emergence of space limited oasis were the precipitation of small-sized carbonate patches, undetectable by remote sensing, could be possible. Moreover, in this context, it is very likely that, even under acidic conditions, the microbial activity can induce the production of small-sized dispersed carbonates in the clayey sedimentary matrix through strong pH and Eh microgradients. As these mineralogies can hardly be detected by remote sensing, the presence of carbonates biotically and/or abiotically mediated can be missed and the paleoenvironments of Mars incorrectly interpreted. Although very recently, Mg-Fe carbonates have been identified using the Mars Exploration Rover (MER) Spirit in the Columbia Hills of Gusev crater [39], these carbonates probably precipitated from carbonate-bearing solutions under hydrothermal conditions at near-neutral pH in association with volcanic activity during the Noachian era [41].

4.3. Carbonates on Mars Inhabited with Subsurface Life

An extreme, but also feasible possibility, is the emergence of a cryptic biosphere [50] whose activity would activate the carbonate factory in cryptic areas of the Martian crust (Figure 2c). Although heterotrophic life has been described as the main biological agent to form carbonates in the subsurface, chemolithoautotroph organisms would release components like methane and ethane providing organic compounds to the heterotrophic organisms and, thus, favoring the formation of carbonates. Methane and ethane consumers, which drive the anaerobic oxidation of methane (AOM) [51,52] through the reduction of SO_4^{2-}, currently form carbonates in deep and cryptic regions of ocean and crust. Similar biogeochemical processes are mediated by heterotrophic bacteria which have been associated to carbonate formation [14,34]. In this case, the microbial activity favors the neutralization of the precipitating solutions through complex biogeochemical pathways which involve autotrophic CO_2 uptake, organic compounds degradation and heterotrophic release of CO_2 through the reduction of iron and/or or sulfur [52] By means of an intricate biogeochemistry, the potential subsurface life may have induced the massive production of carbonates that have been accumulated over the first millions of years in the cryptic regions of Mars. Although the same process could occur abiotically under neutralization of meteoric solutions, the extension and distribution of the subsurface carbonates produced by microbes would be much higher than those deposits formed by simple geochemical mechanisms. This is the case of some carbonates microbially mediated that have been observed in cryptic areas of the Río Tinto acidic environment [53] where carbonates occur in subsurface sites exposed to acidic oxidation [54].

5. Carbonates and the Emergence of Life on Mars

Whether or not life arose on Mars, has likely been associated, as on Earth, to the formation of carbonates in surface and/or subsurface regions. However, the lack of extensive carbonate deposits

originated in surface water bodies suggests that they were inhibited through different geochemical factors. One of the reasons could be the acidification of surface waters by a CO_2 overconcentration in the atmosphere that can be expected in young planetary bodies [11,12]. However, under these conditions microbial activity can uptake and store huge quantities of CO_2 in the form of organic carbon, neutralizing the solutions and generating carbonates. Therefore, the lack of extensive carbonates should be associated to the clayey deposits of the Early Noachian and those carbonates may not have formed due to three different reasons: (1) Life never arose on Mars and abiotic carbonates were inhibited by a peculiar geochemistry; (2) Microbial life colonized the surface waters but did not take the chemical control necessary to produce extensive carbonates; (3) Life inhabited the cryptic habitats of Mars depositing carbonates in the subsurface.

These three different scenarios would be plausible under the great paleoenvironmental changes that forced Mars to have a transient hydrosphere over the first billion of years of planetary evolution [55]. During the same span of time, life on Earth initiated the chemical control of the carbon cycle to neutral conditions through a continuous CO_2 uptake assisted by the meteoric weathering of the terrestrial crust. Under these conditions, the first microbial communities formed carbonates in the shallower regions of the oceans which were recorded as silicified deposits associated to extensive volcanosedimentary systems [56]. In this way, Earth was provided with a stable hydrosphere which favored the formation and coupling of the different biogeochemical cycles. On the contrary, the missing carbonate on Mars suggests that its hydrosphere did not likely have enough time to acquire a geochemical mature stage to stabilize the geochemical cycling of carbon. Whether this effect was a product of the atmospheric chemistry, the climatic change, the inhibition of a biosphere or a simple artifact, is an essential question that the exploration of Mars has to face as key elements to understand how to operate the carbon cycle in early times, critical for the understanding the distribution of life in the Universe.

Acknowledgements

References and Notes

1. Bibring, J.P.; Langevin, Y.; Mustard, J.F.; Poulet, F.; Arvidson, R.; Gendrin, A.; Gondet, B.; Mangold, N.; Pinet, P.; Forget, F.; The OMEGA Team; Berthe, M.; Gomez, C.; Jouglet, D.; Soufflot, A.; Vincendon, M.; Combes, M.; Drossart, P.; Encrenaz, T.; Fouchet, T.; Merchiorri, R.; Belluci, G.; Altieri, F.; Formisano, V.; Capaccioni, F.; Cerroni, P.; Coradini, A.; Fonti, S.; Korablev, O.; Kottsov, V.; Ignatiev, N.; Moroz, V.; Titov, D.; Zasova, L.; Loiseau, D.; Pinet, P.; Doute, S.; Schmitt, B.; Sotin, C.; Hauber, E.; Hoffmann, H.; Jaumann, R.; Keller, U.; Arvidson, R.; Duxbury, T.; Forget, F.; Neukum, G. Global mineralogical and aqueous Mars history derived from OMEGA/Mars express data. *Science* **2006**, *312*, 400–404.

2. Squyres, S.W.; Arvidson, R.E.; Bell, J.F.; Bruckner, J.; Cabrol, N.A.; Calvin, W.; Carr, M.H.; Christensen, P.R.; Clark, B.C.; Crumpler, L.; Des Marais, D.J.; d'Uston, C.; Economou, T.; Farmer, J.; Farrand, W.; Folkner, W.; Golombek, M.; Gorevan, S.; Grant, J. A.; Greeley, R.; Grotzinger, J.; Haskin, L.; Herkenhoff, K.E.; Hviid, S.; Johnson, J.; Klingelhofer, G.; Knoll, A.; Landis, G.; Lemmon, M.; Li, R.; Madsen, M.B.; Malin, M.C.; McLennan, S.M.; McSween, H.Y.; Ming, D.W.; Moersch, J.; Morris, R.V.; Parker, T.; Rice, J.W.; Richter, L.; Rieder, R.; Sims, M.; Smith, M.; Smith, P.; Soderblom, L.A.; Sullivan, R.; Wanke, H.; Wdowiak, T.; Wolff, M.; Yen, A. The Spirit Rover's Athena science investigation at Gusev Crater, Mars. *Science* **2004**, *305*, 794–799.

3. Murchie, S.L.; Mustard, J.F.; Ehlmann, B.L.; Miliken, R.E.; Bishop, J.L.; McKeown, N.K.; Noe Dobrea, E.Z.; Seelos, F.P.; Buczkowski, D.L.; Wiseman, S.M.; Arvidson, R.E.; Wray, J.J.; Swayze, G.; Clark, R.N.; Des Marais, D.J.; McEwen, A.S.; Bibring, J.P. A synthesis of Martian aqueous mineralogy after one Mars year of observations from the Mars Reconnaissance Orbiter. *J. Geophys. Res.* **2009**, *114*, E00D06.

4. Wiseman, S.M.; Arvidson, R.A.; Andrews-Hanna, J.C.; Clark, R.N.; Lanza, N.L., Des Marais, D.; Marzo, G.A.; Morris, R.V.; Murchie, S.L.; Newsom, H.E.; Noe Dobrea, E.Z.; Ollila, A.M.; Poulet, R.; Roush, T.L.; Seelos, F.P.; Swayze, G.A. Phyllosilicate and sulfate-hematite deposits within Miyamoto crater in southern Sinus Meridiani, Mars. *Geophys. Res. Let.* **2009**, *35*, L19204.

5. Chevrier, V.; Poulet, F.; Bibring, J.P. Early geochemical environment of Mars as determined from thermodynamics of phyllosilicates. *Nature* **2007**, *448*, 60–63.

6. Skok, J.R.; Mustard, J.F.; Murchie, S.L. Identification of primary Noachian crustal blocks on Mars with CRISM observations. In *Proceedings of the 40th Lunar and Planetary Science Conference*, The Woodlands, TX, USA, 23–27 March 2009.

7. Bibring, J.P.; Ardvison, R.E.; Gendrin, A.; Gondet, B.; Langevin, Y.; Le Mouelic, S.; Mangold, N.; Morris, R.V.; Mustard, J.F.; Poulet, F.; Quantin, C.; Sotin, C. Coupled ferric oxides and sulfates on the Martian surface. *Science* **2007**, *317*, 1206–1210.

8. Sherlock, E.J.; Lawrence, R.W.; Poulin, R. On the neutralization of acid rock drainage by carbonate and silicates minerals. *Environ. Geol.* **1995**, *25*, 43–45.

9. Lackner, K.S. Carbonate chemistry for sequestering fossil carbon. *Annu. Rev. Energ. Environ.* **2002**, *27*, 197–232.

10. Ehlmann, B.L.; Mustard, J.F.; Murchie, S.L.; Poulet, F.; Bishop, J.L.; Brown, A.J.; Calvin, W.M.; Clark, R.N.; Des Marais, D.; Milliken, R.E.; Roach, L.H.; Roush, T.L.; Swayze, G.A.; Wray, J.J. Orbital identification of carbonate-bearing rocks on Mars. *Science* **2008**, *322*, 1828–1832.

11. Gaillard, F.; Scaillet, B. The sulfur content of volcanic gases on Mars. *Earth Planet. Sci. Let.* **2009**, *279*, 34–43.

12. Elkins-Tanton, L.T. Linked magma ocean solidification and atmospheric growth for Earth and Mars. *Earth Planet. Sci. Let.* **2008**, *271*, 181–191.

13. Duan, Z.; Sun, R.; Zhu, C.; Chou, I.M. An improved model for the calculation of CO2 solubility in aqueous solutions containing Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, and SO_4^{2-}. *Mar. Chem.* **2006**, *98*, 131–139.

14. Orr, J.C.; Fabry, V.J.; Aumont, O.; Bopp, L.; Doney, S.C.; Feely, R.A.; Gnanadesikan, A.; Gruber, N.; Ishida, A.; Joos, F.; Key, R.M.; Lindsay, K.; Maier-Reimer, E.; Matear, R.; Monfray, P.; Mouchet, A.; Najjar, R.G.; Plattner, G.K.; Rodgers, K.B.; Sabine, C.L.; Sarmiento, J.L.; Schlitzer, R.; Slater, R.D.; Totterdell, I.J.; Weirig, M.F.; Yamanaka, Y.; Yool, A. Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. *Nature* **2005**, *437*, 681–686.

15. Squyres, S.W.; Kasting, J.F. Early Mars: How warm and how wet? *Science* **1994**, *265*, 744–749.

16. Hirschmann, M.M.; Withers, A.C. Ventilation of CO_2 from a reduced mantle and consequences for the early Martian greenhouse. *Earth Planet. Sci. Let.* **2008**, *270*, 147–155.

17. Robert, F.; Chaussidon, M. A palaeotemperature curve for the Precambrian oceans based on silicon isotopes in cherts. *Nature* **2006**, *443*, 969–972.

18. Carr, M.H. Retention of an atmosphere on Early Mars. *J. Geophys. Res.* **1999**, *104*, 21897–21909.

19. Albarède, F. Volatile accretion history of the terrestrial planets and dynamic implications. *Nature* **2009**, *461*, 1227–1233.

20. Morse, J.W.; Mackenzie, F.T. Geochemistry of sedimentary carbonates. In *Developments in Sedimentology*; Elsevier: Amsterdam, The Netherlands, 1990.

21. Morse, J.W.; Arvidson, R.S.; Lüttge, A. Calcium carbonate formation and dissolution. *Chem. Rev.* **2007**, *107*, 342–381.

22. McKenzie, J.A. The dolomite problem: An outstanding controversy. In *Controversies in Modern Geology: Evolution of Geochemical Theories in Sedimentology, Earth History and Tectonics*; Müller D.W., McKenzie, J.A., Weissert, H., Eds.; Academic Press: London, UK, 1991; pp. 37–54.

23. Sánchez-Román, M.; Vasconcelos, C.; Schmid, T.; Dittrich, M.; McKenzie, J.A.; Zenobi, R.; Rivadeneyra, M.A. Aerobic microbial dolomite at the nanometer scale: Implications for the geologic record. *Geology* **2008**, *36*, 879–882.

24. Morrows, D.W.; Rickets, B.D. Experimental investigation of sulphate inhibition of dolomite and its mineral analogues. In *Sedimentology and Geochemistry of Dolostones*; Shukla, V., Baker, P.A., Eds.; SEPM: Tulsa, OK, USA, 1988; Volume 43, pp. 25–38.

25. Gaines, A.M. Dolomiotization kinetics: Recent experimental studies. In *Concepts and Models of Dolomitization*; Zenger, D.H., Dunhan, J.B., Ethington, R.L., Eds.; SEPM: Tulsa, OK, USA, 1980; Volume 28, pp. 81–86.

26. Lippman, F. *Sedimentary Carbonate Minerals*; Springer-Verlag: New York, NY, USA, 1973; p. 228.

27. Folk, R.L.; Land, L.S. Mg/Ca ratio and salinity: Two controls over crystallization of dolomite. *AAPGB* **1975**, *59*, 60–68.

28. Baker P.A.; Kastner, M. Constraints on the formation of sedimentary dolomite. *Science* **1981**, *213*, 214–216.

29. Vasconcelos, C.; McKenzie, J.A.; Bernasconi, S.; Grujic, D.; Tien, A.J. Microbial mediation as a possible mechanism for natural dolomite formation at low temperatures. *Nature* **1995**, *377*, 220–222.

30. Knorre, H.; Krumbein, W.E. Bacterial calcification. In *Microbial Sediments*; Riding, R.E., Awramik, S.M., Eds.; Springer: Berlin, Germany, 2000; pp. 25–31.

31. Thompson, J.B.; Ferris, F.G. Cyanobacterial precipitation of gypsum, calcite, and magnesite from natural alkaline lake water. *Geology* **1990**, *18*, 995–998.

32. Roberts, J.A.; Bennett, P.C.; Gonzalez, L.A.; Macpherson, G.L.; Miliken, K.L. Microbial precipitation of dolomite in methanogenic groundwater. *Geology* **2004**, *32*, 277–280.

33. Warthmann, R.; van Lith, Y.; Vasconcelos, C.; McKenzie, J.A.; Karpoff, A.M. Bacterially induced dolomite precipitation in anoxic culture experiments. *Geology* **2000**, *28*, 1991–1094.

34. Ehrlich, H.L. *Geomicrobiology*, 4th ed.; Marcel Dekker: New York, NY, USA, 2002; p. 768.

35. Schultze-Lam, S.; Beveridge, T.J. Nucleation of celestite and strontianite on a cyanobacterial S-layer. *Appl. Environ. Microbiol.* **1994**, *60*, 447–453.

36. Sánchez-Román, M.; Rivadeneyra, M.; Vasconcelos, C.; McKenzie, J.A. Biomineralization of carbonate and phosphate by halophilic bacteria: Influence of Ca^{2+} and Mg^{2+} ions. *FEMS Microbiol. Ecol.* **2007**, *61*, 273–284.

37. Díaz-del-Río, V.; Somoza, L.; Martínez-Frías, J.; Mata, M.P.; Delgado, A.; Hernandez-Molina, F.J.; Lunar, R.; Martín-Rubí, J.A.; Maestro, A.; Fernández-Puga, M.C.; León, R.; Llave, E.; Medialdea, T.; Vázquez, J.T. Vast fields of hydrocarbon-derived carbonate chimneys related to the accretionary wedge/olistostrome of the Gulf of Cádiz. *Mar. Geol.* **2003**, *195*, 177–200.

38. Merinero, R.; Lunar, R.; Martínez-Frías, J.; Somoza, L.; Díaz-del-Río, V. Iron oxyhydroxide and sulphide mineralization in hydrocarbon seep-related carbonate submarine chimneys, Gulf of Cadiz (SW Iberian Peninsula). *Mar. Petrol. Geol.* **2008**, *25*, 706–713.

39. Morris, R.V.; Ruff, S.W.; Gellert, R.; Ming, D.W.; Arvidson, R.E.; Clark, B.C.; Golden, D.C.; Siebach, K.; Klingelhöfer, G.; Schröder, C.; Fleischer, I.; Yen, A.S.; Squyres, S.W. Identification of carbonate-rich outcrops on Mars by the Spirit Rover. *Science* **2010**, *329*, 421–424.

40. Martinez-Frias, J.; Delgado-Huertas, A.; García-Moreno, F.; Reyes, E.; Lunar, R; Rull, F. Oxygen and carbon isotopic signatures of extinct low-temperature hydrothermal chimneys in the Jaroso Mars analog. *Planet. Space Sci.* **2007**, *55*, 441–448.

41. Martínez-Frías, J.; Lunar, R.; Rodríguez-Losada, J.A.; Delgado, A. The volcanism-related multistage hydrothermal system of El Jaroso (SE Spain): Implications for the exploration of Mars Earth. *Planet. Space* **2004**, *56*, 5–8.

42. Sundquist, E.T.; Visser, K. The geologic history of the carbon cycle. In *Treatise on Geochemistry*; Holland, H.D., Turekian, K.K., Eds.; Elsevier: Amsterdam, The Netherlands, 2003; Volume 8, pp. 425–472.

43. Morse, J.W. *Sediments, Diagenesis and Sedimentary Rocks*; Mackenzie, F.T., Ed.; Elsevier: Amsterdam, The Netherlands, 2005; Volume 7, pp. 67–85.

44. Shitashima, K. CO_2 supply from deep-sea hydrothermal systems. *Waste Manag.* **1998**, *17*, 385–390.

45. Millero, F.J. The Marine inorganic carbon cycle. *Chem. Rev.* **2007**, *107*, 308–341.

46. Krumbein, W.E. How and where on Earth were and are carbonate minerals formed? *Geochim. Cosmochim. Acta* **2009**, *73*, A699.

47. Lodders, K.; Feggley, B., Jr. *The Planetary Scientist's Companion*; Oxford University Press: New York, NY, USA, 1998.

48. Loáiciga, H.A. Modern-age buildup of CO_2 and its effects on seawater acidity and salinity. *Geophys. Res. Let.* **2006**, *33*, L10605.

49. Schultz, R.; Lin, J. Three-dimensional normal faulting models of the Valles Marineris, Mars, and geodynamic implications. *J. Geophys. Res.* **2001**, *106*, 16549–16566.

50. McKay, C.P. The deep biosphere: Lessons for planetary exploration. In *Subsurface Microbiology and Biogeochemistry*; Fredickson, J.K., Fletcher, M., Eds.; Wiley-Liss: New York, NY, USA, 2001; pp. 315–328.

51. Reeburgh, W.S. Methane consumption in Cariaco Trench waters and sediments. *Earth Planet. Sci. Let.* **1976**, *28*, 337–344.

52. Konhauser, K. *Introduction to Geomicrobiology*; Blackwell Publishing: Malden, MA, USA, 2007; Chapter 2.

53. Fernández-Remolar, D.C.; Prieto-Ballesteros, O.; Rodríguez, N.; Gómez, F.; Amils, R.; Gómez-Elvira, J.; Stoker, C.R. Underground habitats in the Río Tinto Basin: A model for subsurface life habitats on Mars. *Astrobiology* **2008**, *8*, 1023–1047.

54. Fernández-Remolar, D.C.; Sánchez-Román, M.; Rodríguez, N., Amils, R.; Romanek, C.S. The association of carbonate minerals to acidic environments: A possible biosignature for Mars 2009. In *Proceedings of the 40th Lunar and Planetary Science Conference*, The Woodlands, TX, USA, 23–27 March 2009.

55. Tosca, N.J.; Knoll, A.H. Juvenile chemical sediments and the long term persistence of water at the surface of Mars. *Earth Planet. Sci. Let.* **2009**, *286*, 379–386.

56. Allwood, A.C.; Walter, M.R.; Kamber, B.S.; Marshall, C.P.; Burch, I.W. Stromatolite reef from the Early Archaean era of Australia. **2006**, *441*, 714–718.