Radiation chemistry in exploration of Mars

Zbigniew P. Zagórski

Abstract Problems of exploration of Mars are seldom connected with radiation research. Improvements in such approach, more and more visible, are reported in this paper, written by the present author working on prebiotic chemistry and origins of life on Earth. Objects on Mars subjected to radiation are very different from those on Earth. Density of the Martian atmosphere is by two orders smaller than over Earth and does not protect the surface of Mars from ionizing radiations, contrary to the case of Earth, shielded by the equivalent of *ca*. 3 meters of concrete. High energy protons from the Sun are diverted magnetically around Earth, and Mars is deprived of that protection. The radiolysis of martian "air" (95.3% of carbon dioxide) starts with the formation of CO_2^+, whereas the primary product over Earth is N_2^+ ion-radical. The lack of water vapor over Mars prevents the formation of many secondary products. The important feature of Martian regolith is the possibility of the presence of hydrated minerals, which could have been formed milliards years ago, when (probably) water was present on Mars. The interface of the atmosphere and the regolith can be the site of many chemical reactions, induced also by intensive UV, which includes part of the vacuum UV. Minerals like sodalite, discovered on Mars can contribute as reagents in many reactions. Conclusions are dedicated to questions of the live organisms connected with exploration of Mars; from microorganisms, comparatively resistant to ionizing radiation, to human beings, considered not to be fit to manned flight, survival on Mars and return to Earth. Pharmaceuticals proposed as radiobiological protection cannot improve the situation. Exploration over the distance of millions of kilometers performed successfully without presence of man, withstands more easily the presence of ionizing radiation.

Key words carbon dioxide chemistry • cosmic rays • ionization spurs • Martian regolith • origins of life • planetary system exploration • radiation chemistry

Z. P. Zagórski
Department of Radiation Chemistry and Technology,
Institute of Nuclear Chemistry and Technology,
16 Dorodna Str., 03-195 Warszawa, Poland,
Tel.: +48 22-8112347, Fax: +48 22-8111917,
E-mail: zagorski@ichtj.waw.pl

Received: 30 November 2004
Accepted: 30 April 2005

Introduction

Present day approaches to the exploration of Mars seldom involve consideration of chemical effects caused by ionizing radiation and UV light, reaching the planet. Ionizing radiation emitted by minerals on Mars does not seem to have substantial influence. However, external radiation cannot be neglected. Consideration of the ionizing background is specially important, if manned missions to Mars are expected. Relatively high doses of ionizing radiation can be tolerated by inorganics present on, and above Mars surface. More sensitive are organics, e.g. polymers brought to Mars by exploratory missions [15]. Moreover, living structures like bacteria present (perhaps) there, or brought on missions not carefully sterilized [29] are influenced by radiation. The most sensitive to ionizing radiation creature is human being. The scale of sensitivity of objects on Mars, towards ionizing radiation is several orders of magnitude wide.

The attitude of world researchers to the question of the role of ionizing radiation in the exploration of Mars is different. The most popular, extended to the majority of mass media and popular science writers, does not take this factor into account. The serious researchers are aware of ionizing radiation; e.g. Zeitlin *et al.* [38]

writes: "Space radiation presents a hazard to astronauts, particularly those journeying outside the protective influence of the geomangnetosphere. Crews on future missions to Mars will be exposed to the harsh radiation environment of deep space during the transit between Earth and Mars. Once on Mars, they will encounter radiation that is only slightly reduced, compared to free space, by the thin Martian atmosphere". As few radiation chemists only are engaged in exploration of Mars, the present paper will address these points more closely.

Information about radiation environment of Mars is gained from experiments MARIE (Martian Radiation Environment Experiment) [1]. Data are collected from three apparatuses working on station Mars Odyssey orbiting around Mars. Results are processed in NASA laboratories in Houston. The leading one is the National Space Biomedical Research Institute, other belong to Lockheed-Martin, Boeing, Lawrence Berkeley National Laboratory and the University of Houston. The orbit of the station is circular, stable, 400 km above the Mars surface.

Ionizing radiations reaching Mars are similar to those well outside Earth, before reaching magnetic field present around Earth: deep space radiation has two components, GCR (Galactic Cosmic Radiation) and SEP (Solar Energetic Particles). The MARIE with its detectors measures all radiations, with particular attention paid to particles of energy above 30 MeV, as able to penetrate walls of space stations. GCR is composed of nuclides of all known elements, but without orbital electrons. These ions attack our Solar System with the rate of one particle per cm^2 and second. The origin of GCR is unknown; the energy spectrum covers 10 to 10^{14} eV. The flux is dominated by H (87%) and He (11%), the rest are heavy nuclides, but those above iron are rare. They are symbolized as HZE (High Z Elements). In spite of low contribution expressed as number of particles, the chemical effects are substantial, because they carry large energies, dissipated in cascades. E.g., iron ($Z = 26$) brings the energy 676 times higher than proton of the same speed [20]. The HZEs do not reach the surface of Earth, because of the atmosphere and magnetic field but they reach the surface of Mars easily. Specific ionizing radiation reaching Mars, i.e. protons, is emitted irregularly by the Sun [7] in connection with the CME (Coronal Mass Ejection). These events are reaching Mars without modifications, observed on Earth due to its magnetic field. The magnetic field is diverting protons, other radiations are attenuated mainly by mass absorption of the atmosphere.

The quality and intensity of radiation reaching the surface of Mars is, therefore, different in comparison to Earth. The latter is shielded by the atmosphere which is equivalent to 3 meters of concrete, as concerns the absorption ability. The Mars atmosphere is 120 times thinner than around the Earth and so are its shielding capabilities, which are very poor.

Radiation chemistry of the atmosphere of Mars

The first encounter of ionizing particles and quanta reaching Mars from the space is the atmosphere, totally different in composition and density from that around Earth. The composition of the gas phase around Mars has been determined from data gained during two Viking missions and described by Owen [22]. This composition is created in experiments on Earth, in which, e.g., the behavior of known bacteria is investigated [27]. The composition is carbon dioxide 95.3%, nitrogen 2.7%, argon 2.7%, oxygen 0.2%, water 0.03%. The content of water vapor can fluctuate, but there is little hope that it may fluctuate upwards, because the most of it has already escaped [18]. With improvement and refinement of analytical methods, the list of determined components is enlarged, recently by traces of hydrogen, ammonia and methane. Especially the presence of CH_4 provoked hopes that its presence can be connected with volcanic activity, comets impact [17], or even the presence of primitive forms of life. In the opinion of the present author there are other ways for methane formation, from the materials present on Mars and with the participation of available sources of energy. Origin of methane on Mars from life-processes is unlikely.

Partial pressure of the main constituent of Martian atmosphere, carbon dioxide is very low (8 mb), therefore the total pressure of the atmosphere is by two orders of magnitude lower than on the surface of Earth! The next factor is the low temperature of the gas, –10°C on the average. All simulations of Martian conditions start at –80°C and machines expected to work on the surface of March are adapted to do so, starting with –120°C. Oscillations of temperatures can produce mechanical-chemical effects on inorganics.

Poor shielding properties of Martian atmosphere leave small hopes, as concerns the preservation of life, if it has been formed and developed in caves. Also the lack of protective ozon layer, like above Earth, speaks out against of survival of life exposed to short wave UV [16].

Radiation chemistry of Martian atmosphere is completely different to radiolysis of ours atmosphere above us. Radiolysis starts always from the compound to which most electrons belong; in the case of Earth it is nitrogen. The first major ionization leads to relatively long-lived N_2^+ which undergoes different reactions with other constituents of the air. In the case of Mars, the main primary product is CO_2^+, which has few opportunities for interesting gas phase reactions, except with solids on the surface of regolith.

Radiation induced reactions in Martian atmosphere cannot make it more friendly for life. On the contrary, they can increase aggressive actions, also against inorganic materials, e.g. towards devices generating electric current and to all products imported from Earth. They worsen also the possibilities of survival of living systems brought to Mars.

Radiation chemistry of the surface of Mars and the interface atmosphere/regolith

Radiaton chemistry of the regolith on Mars cannot be understood fully yet, because composition of minerals is known only partially. Solids covering the planet are probably similar to minerals which compose other planets [23]. Only acquisition of minerals from the surface of Mars will help to recognize the situation, not mentioning the exploration of deeper layers. In the mean time, speculations are the only possibility, basing on intelligent guess [9]. Too much attention is paid to meteorites found on Earth, but supposed to be from Mars. The probability, that they really have originated there, is very low [6].

The most interesting question is the relation of Martian minerals to water. The experience of geology shows that many clays can contain water in the structure. Also the technological experience of our civilization shows that many aluminosilicates can easily incorporate water molecules in the process of their formation and keep it for ages, as it is the case with concrete, which contains up to 20% water. These structural water molecules are difficult to recover, e.g. during supposed exploration by human crew. Before realizing projects like this, one has to prove existence of hydrated salts. Important study of this effect has been done [21]. The best opportunity shows IR spectroscopy, realized with the help of Near Infrared Camera Multi Object Spectrograph, working at the Hubble Space Telescope. Results are not ready in full, for the time being. Another research [25] with the help of Thermal Emission Spectrometer indicates the presence of minerals similar to zeolithes known from Earth. Bish [3] discusses the stability of other hydrated minerals. Indirect indications, that water was present at the beginnings on Mars, is the presence of hematite [5]. This mineral does not contain water, but its formation is connected with water. It does not, by no means, support the notion of such large amounts of H_2O, as on Earth at the beginnings and now [19].

Detection of water is based also on neutron absorbtion. Neutrons are absorbed by hydrogen and its presence is most probably connected with water. This method does not distinguish between free water (liquid or ice) and bound crystallochemically. Amounts of either form are modest and do not promise any help in exploration, even if recognized in specific "oasis". The inventory of more or less accessible water is in progress with application of different methods. Both the atmosphere and regolith of Mars show deficit of hydrogen. The lack of remaining debris of life, so plentiful on Earth, which was shaped by live creatures is convincing that water on Mars was always in short supply.

Radiation chemistry of concrete indicates [33] that water absorbs ionizing radiation in proportion to the content of electrons in the system, but behaves like pure water, i.e. molecular products of radiolysis are decomposed by the radical ones. The most interesting feature of Martian regolith is the possibility of the presence of hydrated minerals, which could have been formed milliards years ago, when (probably) water was present on Mars. Water present in the crystalline lattice undergoes only limited radiolysis, as it is known from the case of concrete, produced as biological shield build on Earth, around the sources of ionizing radiation. Absorbed energy is transformed into heat. Therefore, hydrated minerals are not decomposed by absorption of ionizing radiation lasting for millions of years. Formation of natural hydrated silicates on Mars was possible, therefore survival of traces of H_2O on Mars is possible. However, this kind of water cannot be recovered easily, to be used by Mars explorers. Starting amount of water on Mars could have been much smaller than on Earth at the beginnings. Mysterious origin of plenty of water on Earth was not necessarily repeated on Mars [24]. Even if some water appeared on the surface of Mars, at time when it has cooled down sufficiently, different mechanisms were working on disappearance of water. There is a slight hope that some water was continuously supplied by comets [8], and it has survived until now in specific deep caves, rather absent in volcanic formations.

Radiation chemistry on the boundary of Mars atmosphere and the regolith can be partly modified by photochemistry [31]. The range of UV light in minerals is very shallow in comparison to ionizing radiation, but substantial areas of Mars are covered with fine dust. The grains are time and now turned around by intensive winds, therefore they can be illuminated effectively from all sides. The nature and properties of dust on the surface of Mars are considered very seriously and proper devices for investigations are proposed [2].

Radiobiology and Mars, as the special case of radiation chemistry

The most significant radiation effects connected with the exploration of Mars are of radiobiological nature, because of enormous radiation yields of such effects. They are caused by biological enhancement of primary chemical effects. These are not amplified in the case of simple inorganics, like sodium chloride crystals. Sometimes they are amplified in the system itself, like in the case of chemical chain reactions, e.g. in oxidation processes [37]. Biological systems are easily inactivated by ionizing radiation; already few ionization spurs can cause disruption of critical reactions in the cell, e.g. by irreversible detachment of hydrogen. This radiation induced reaction is under study in the author's Laboratory [10, 36] also in relation to biosystems.

Analysis of relations of ionizing radiation on the planet of Mars to any forms of life on it are worth of consideration in view of the same problems connected with the origin and survival of any forms of life on Earth [4, 32, 34, 35] including human being.

Exposure of a person in the space suit on Mars can be similar to the exposure during EVA (Extra Vehicular Activity), or during the walk on the Moon. It is tolerable, if the stay is not longer than few months and exposure to proton burst events from the Sun are avoided. Longer stays in the background of galactic cosmic rays and occasional, unavoidable extra doses of radiation brings the exposure easily to levels above 1 Sv. Five sieverts mean the LD_{50}, i.e. the death of 50% of irradiated population, after the whole body exposure in the short period of time.

There are many radiobiological studies dealing with possible pharmaceuticals which could diminish the action of ionizing radiation on human organism. They were developed for the purpose of cancer therapy with ionizing radiation, with the hope that they will diminish the destruction of normal tissue close to the tumor.

Another reason was represented by military medicine, with the intention to increase the radiation resistance of soldiers entering the site of explosion of nuclear device. As an example, paper by Kennedy *et al*. [14] is promoting the use of seleno-methionine as a compound protecting against adverse biological effects by space radiation. Weiss and Landauer [30] recommend protection against ionizing radiation by antioxidant nutrients and phytochemicals. However, it is doubtful, if an introduction of additional compounds into a diet, already carefully composed to prevent the decalcification of bones, will not complicate further conditions of Marsonauts.

There are some approaches to create in humans conditions similar to known in some animals as hibernation, applied for the time of travel to and back from Mars. Marsonauts kept in such state would save food and oxygen and the response to ionizing radiation would be more tolerable. However, these are projects of doubtful realization.

Much more resistant to ionizing radiation are primitive organisms like bacteria, which have some chance to survive on Mars, when brought with poorly sterilized devices installed there [11–13]. The possibility to survive for years has nothing to do with panspermia. Some dry spores, still able to recover when wetted, found several hundred kilometers from Earth, originate from the waste, disposed from orbiting space stations. Thus, in search for extra-terrestrial life, the correction has to be taken in future for possible biological noise, created by human activity in space [26]. The harsh conditions for life in space are worse than encountered by microorganisms living on Earth in strange, not-friendly surroundings [28]. Using such findings as the argument for possible life on Mars makes no sense. Evidently all "extremophiles" were formed in proper conditions in specific places on Earth. They were brought by accident to harsher places on Earth later, e.g. falling on oceans floor, acquiring there increased resistance by the process of mutations.

Final conclusions

Conclusions are dedicated to questions of the fate of the live organisms connected with exploration of Mars; from microorganisms, comparatively resistant to ionizing radiation, to human beings, considered not to be fit to manned flight, survival on Mars and return to Earth. The genius of mankind which is able to create effective means of exploration over the distance of millions of kilometers, should create a satisfaction more important than the extremely expensive and not necessary for exploration, the presence of man or woman on Mars. Such a way of thinking is represented by the American Physical Society, which criticizes administrations decision to support manned expeditions to Mars, being one hundred times more expensive than by instruments.

All the references in the present paper are made to papers in peer reviewed journals. As many ideas presented there can be controversial, there is at least assurance that the text has been accepted by a scientific body. The important topic of exploration of Mars is also very often treated by scientifically irresponsible authors and organizations, presenting their views in the Internet and in popular science journals and even in tabloids. As concerns Mars exploration, a typical misinformation consists in publishing future designs of houses for people on Mars, which do not take into consideration the ionizing radiation, the very low outside pressure, which resembles industrial liofilization chambers etc. Even worse are concepts of changing Mars atmosphere into similar to that around the Earth. That is also fiction without science. Such fantasies published in papers, books, cinema and TV pictures, were not mentioned in the present paper, as the discussion with such views is useless.

Note added in proof: The author has participated in 14th International Conference on the Origin of Life on June 19–24, 2005, this time in Beijing, as the only delegate from Poland. He presented the paper on the case against panspermia, supported by radiation chemistry, also important in exploration of Mars. He initiated the discussion on water on Mars, and the one of best experts of the subject, Benton C. Clark expressed the view, that all H_2O, assumed from indirect measurements, e.g. from absorbtion of neutrons, occurs on Mars exclusively as water bound chemically. It is the view expressed by the author of the present paper.

Acknowledgments The study was supported by the Polish Ministry of Scientific Research and Information Technology, Grant No. 619/E-76/SPB/COST/T-09/DWM 641/2003–2006. The European support and sponsorship concerted by COST Action D27 "Prebiotic Chemistry and Early Evolution" are also kindly acknowledged.

References

1. Atwell W, Saganti P, Cucinotta FA *et al.* (2004) A space radiation shielding model of the Martian Radiation Environment Experiment (MARIE). Adv Space Res 33:2219–2221
2. Battaglia R, Palomba E, Palumbo P *et al.* (2004) Development of a micro-balance system for dust and water vapour detection in the Mars atmosphere. Adv Space Res 33:2258–2262
3. Bish DL, Carey JW, Vaniman DT *et al.* (2003) Stability of hydrous minerals on the martian surface. Icarus 164:96–103
4. Cabane M, Coll P, Szopa C *et al.* (2004) Did life exist on Mars? Search for organic and inorganic signatures, one of the goals for "SAM" (sample analysis at Mars). Adv Space Res 33:2240–2245
5. Catling DC, Moore JM (2003)The nature of coarse-grained crystalline hematite and its implications for the early environment of Mars. Icarus 165:277–300
6. Clark BC (2001) Planetary interchange of bioactive material: Probability factors and implications. Origins Life Evol Biosph 31:185–197
7. Cleghorn TF, Saganti PB, Zeitlin CJ *et al.* (2004) Solar particle events observed at Mars: dosimetry measurements and model calculations. Adv Space Res 33:2215–2218
8. Ehrenfreud P, Charnley SB (2000) Organic molecules in the interstellar medium comets and meteorites: A voyage

from dark clouds to the early Earth. Ann Rev Astronom Astrophys 38:427–483
9. Fairen AG (2004) Age and origin of the lowlands of Mars. Icarus 168:277–284
10. Głuszewski W, Zagórski ZP (2005) Determination of radiolytic molecular hydrogen on line with EB irradiation. J Radioanal Nucl Chem (in print)
11. Horneck G (1993) Response of *Bacillus subtilis* spores to space environment: results from experiments in space. Origins Life Evol Biosph 23:37–52
12. Horneck G, Bucker H, Reitz G (1994) Long term survival of bacterial spores in space. Adv Space Res 14:41–45
13. Horneck G, Rettberg P, Reitz G *et al.* (2001) Protection of bacterial spores in space: a contribution to the discussion of panspermia. Origins Life Evol Biosph 31:527–547
14. Kennedy AR, Ware JH, Guan J *et al.* (2004) Selenomethionine protects against adverse biological effects induced by space radiation. Free Radic Biol Med 36:259–266
15. Kim M-H, Thibeault SA, Wilson JW *et al.* (2000) Development and testing of *in situ* materials for human exploration of Mars. High Perform Polym12:13–26
16. Krasnopolsky VA, Feldman PD (2002) Far ultraviolet spectrum of Mars. Icarus 160:86–94
17. Kress ME, McKay CP (2004) Formation of methane in comet impacts: Implications for Earth, Mars and Titan. Icarus 168:475–483
18. Lammer H, Lichtenegger HIM, Kolb C *et al.* (2003) Loss of water from Mars: Implications for the oxidation of the soil. Icarus 165:9–25
19. Lathe R (2004) Fast tidal cycling and origin of life. Icarus 168:18–22
20. Lee KT, Cleghorn T, Cucinotta F *et al.* (2004) Heavy ion observations by MARIE in cruise phase and Mars orbit. Adv Space Res 33:2211–2214
21. Noe Dobrea EZ, Bell III JF, Wolff MJ *et al.*(2003) H_2O- and OH-bearing minerals in the martian regolith: analysis of 1997 observations from HST/NICMOS. Icarus 166:1–20
22. Owen T (1992) The composition and early history of the atmosphere of Mars. In: Kieffer HH, Jakosky BM, Snyder CW, Mathews MS (eds) Mars. University of Arizona Press, Tucson, AZ, pp 818–834
23. Palme H, Jones A (2003) Chapter 1.03: Solar system abundances of the elements. In: Treatise on geochemistry, vol. 1. Meteorites, comets and planets. Elsevier, New York, pp 41–61
24. Raymond SN, Quinn T, Lunine JI (2004) Making other earth: dynamical simulations of terrestrial planet formation and water delivery. Icarus 168:1–17
25. Ruff SW (2004) Spectral evidence for zeolite in the dust on Mars. Icarus 168:131–143
26. Rummel JD (2001) Planetary exploration in the time of astrobiology: protecting against biological contamination. Proc Natl Acad Sci 98:2128–2131
27. Schuerger AC, Mancinelli RL, Kern RG *et al.*(2003) Survival of endospores of *Bacillus subtilis* on spacecraft surfaces under simulated martian environments: implications for the forward contamination of Mars. Icarus 165:253–276
28. Tehei M, Franzetti B, Maurel M-C *et al.* (2002) The search for traces of life: the protective effect of salt on biological macromolecules. Extremophiles 6:427–430
29. Venkatesvaran K, Satomi M, Chung S *et al.* (2001) Molecular microbial diversity of a spacecraft assembly facility. System Appl Microbiol 24:311–320
30. Weiss JF, Landauer MR (2003) Protection against ionizing radiation by antioxidant nutrients and phytochemicals. Toxicology 189:1–20
31. Wong AS, Atreya SK, Formisano V *et al.* (2004) Atmospheric photochemistry above possible martian hot spots. Adv Space Res 33:2236–2239
32. Zagórski ZP (2001) Radiation chemistry and origins of life on Earth. Wiadomości Chemiczne 55:965–985 (in Polish)
33. Zagórski ZP (2001) Radiation resistance of concrete. INCT Annual Report 2000:39–40
34. Zagórski ZP (2003) Radiation chemistry and origins of life on Earth. Radiat Phys Chem 66:329–334
35. Zagórski ZP (2003a) Panspermia. Postępy Techniki Jądrowej 46;2:42–52 (in Polish)
36. Zagórski ZP, Głuszewski W (2004) Irreversible radiolytic dehydrogenation of polymers: the key to recognition of mechanisms. INCT Annual Report 2003:40–42
37. Zagórski ZP, Sehested K, Nielsen SO (1971) Pulse radiolysis of aqueous alkaline sulfite solutions. J Phys Chem 75:3510–3517
38. Zeitlin C, Cleghorn T, Cucinotta F *et al*. (2004) Overview of the Martian radiation environment experiment. Adv Space Res 33:2204–2210