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MARTIAN OXIDATION PROCESSES AND SELECTION OF ANCIENT SEDIMENTARY SAMPLES FOR BIO-ORGANIC ANALYSIS; J. Oro´, Department of Biochemical and Biophysical Sciences, University of Houston, Houston, TX 77004

We summarize here the results obtained by the Viking Missions concerning organic and biological analysis and indicate that these results do not preclude the existence in buried or protected regions of the planet or organic molecules or fossil life. Then we suggest the use of an automated instrument for the analysis of samples obtained from certain regions of the Planet, as a preliminary step before they are selected, retrieved, and returned to Earth for more complete analysis.

1. Viking organic and biological analysis. Samples from the surface of Mars were analyzed by the two Viking landers, at two different sites, Chryse and Utopia regions. Being the first two soft landing missions, the sites were selected for the safety of landing, not their biopotential. No organic matter was found at either site by the pyrolysis-gas chromatograph-mass spectrometer (GC-MS) at detection limits of the order of parts per billion and for a few substances closer to parts per million. On the other hand, two of the biological experiments, the Labelled Release (LR) and the Gas Exchange (GEX) experiments gave quite positive results. Two alternative possible interpretations were advanced for the positive results: Either very active biological processes or chemical processes brought about by a chemically active Martian soil. The latter view advanced by the author has been found to account for most of the observations (1).

2. The positive biological results. Chemical oxidation as an explanation. It was proposed that hydrogen peroxide or other oxygen-bearing species in the Martian soil caused the oxygen to be released in the GEX experiment. The peroxide, in conjunction with the iron oxides of the Martian soil would also cause the oxidation of the carbon -14 formate in the LR experiment. In support of this proposal were several facts: (a) Upon a second injection of nutrient solution containing the labelled substrates into the chamber of the LR experiment no more labelled carbon dioxide release was observed, but rather a reabsorption of some of the previously generated carbon dioxide took place. (b) The amount of labelled carbon dioxide (in equivalents) generated, was always below that corresponding to the number of equivalents of formate present in the sample, even though the sample contained many more equivalents of other labelled substrates. (c) It is known that formate is readily oxidized by hydrogen peroxide in the presence of certain iron oxides. (d) These inorganic oxides are present in the Martian soil. (e) The amount of oxygen released by the independent GEX experiment was of the same order of magnitude as that required for the oxidation of formate to carbon dioxide.

3. The negative organic analysis results. Photo-oxidation as an explanation. The observations which provided the most conclusive evidence for the absence of terrestrial-type life on Chryse and Utopia regions were the negative results obtained by the Viking GC-MS instrument on a number of surface and subsurface samples. These two sites of Mars contain no traces of organic compounds. This was in contrast to the results obtained from the Moon, since a few parts per million of carbon compounds were found in most lunar soil samples analyzed. This result was also surprising because, in addition to any organic compounds which may have been formed in earlier times, Mars has supposedly received during its geological history carbon compounds from cometary and meteoritic influx. How can this apparent paradox be explained? By photo-oxidation. There is a significant flux of ultraviolet radiation (200 to 300nm) reaching continuously the planet's surface, which in the presence of oxygen and other oxidizing species in the Martian atmosphere and regolith is capable of destroying by photochemical oxidation most of the organic compounds in relatively short periods of time in a geological scale. Laboratory experiments under simulated Martian conditions have confirmed the efficiency of these photo-oxidation processes.

4. Earlier Mars conditions. All of the above facts about the lack of evidence for life and organic matter at the two Viking sites do not rule out the possibility that organic compounds, and

perhaps also life, may have been generated shortly after the planet was formed. One would expect more favorable conditions for the generation of organic matter and life during the first 1 billion years as a consequence of a more benign climate and the contribution by late accretion processes of water, as well as, organic compounds from comets and other sources. Indeed, the extensive data obtained by the Mariner 9 and the Viking orbiters, and recent interpretations of the data, suggest that during the first two billion years substantial amounts of liquid water were present on Mars, which caused the formation of Martian channels, valleys, and river basins, as well as other sedimentary layered terrains.

5. Criteria for the selection of Martian samples. It is important to realize the significance of the above oxidative processes in any plans for the retrieval of any samples containing prebiologically synthesized organic matter or remains of microfossil life. This means that only those sites which have remained buried or protected from UV-induced photochemical oxidation processes since the organic material was laid down can be expected to contain organic matter. These considerations provide a basis for simple criteria to select Martian samples for bioorganic analysis. Obviously, they should not be surface or subsurface samples of regolith which has had a significant turnover rate. They should be preferably solid or compacted sedimentary rocks (e.g. cherts, stromatolitic type rocks), or alternatively they should be ancient subsurface sediments which have not been exposed to the surface during the last two thirds of the planet's history.

In line with other criteria for a Mars-Rover Sample Return Mission, samples should be collected from different Martian areas or sites such as the following (a) Valles Marineris' subsurface samples from the bottom or the slopes of the layered terrains. (b) Subsurface samples from other presumed fluvial areas, including "river basins", "lake shores", "channels" and delta zones. (c) An effort should be made to determine the possible presence on Mars of areas where dark outcrop rocks of sedimentary origin may be found. In addition to the stromatolitic rocks from the Warawoona formation (in Australia) some of the oldest microfossils on Earth have been found in black cherts and other outcrop rocks exposed to the surface. (d) The significance of other areas such as the circumpolar regions and the circumvolcanic zones (e.g. base of Olympus Mons) should be also assessed. (e) At any rate a flexible strategy for the Rover exploration of Mars should be followed so that samples could be retrieved from any alternative sites indicating the current or past presence of ice, permafrost or transient liquid (aquifer) forms of water.

Whether any microorganisms similar to the endolithic microbiota found in Antarctica may have evolved on Mars and disappeared since then is not known. Although it is highly unlikely that they exist today these organisms offer a model for the adaptation on a harsh climate where photochemical carbon dioxide fixation could be performed within an internal microenvironment which would protect the organisms from the photodestructive UV-flux on Mars. It may be of interest to determine the possible existence in the past on Mars of similar habitats to those of Antarctica

6. Implementation of Mars Rover strategy for preliminary sample analysis, collection, and return to Earth. The implementation of a successful Mars-Rover Sample Return Mission will require, among other things, the resolution of a number of questions concerning instruments, methods, strategies, etc. such as: (a) Screening and preselection of biopotential habitats. (b) Rover strategy for sample location, collection and preliminary in situ examination. (c) Building a simplified Viking GC-MS instrument and possibly a Mars optical electron microscope for automatic bio-organic and microfossil analysis. (d) Sample preparation analysis and data transmittal. (e) Sample retrieval and protection for return to Earth. All these matters are very tentative and need to be fully discussed by all the interdisciplinary scientists at the Workshop who are interested in bioorganic analysis. A substantial amount of pertinent information is available from the organic analysis of meteorites, as well as lunar and terrestrial samples.

1. Oro´, J., 1979 (editor). The Viking Mission and the Question of Life on Mars, Springer-Verlag KG, Heidelberg, pp. 321. (Special issue of Journal of Molecular Evolution, 1979, Vol. 14, Nos. 1-3).