

PHOTO-ELECTROCHEMISTRY OF MARS, AND PROSPECTS FOR MEASUREMENTS ON THE MARS SCIENCE LABORATORY

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Abstract

Until recently, the chemistry of the atmosphere of Mars was believed to be straightforward, driven photochemically, largely by just two molecules – CO₂ and H₂O. This all changed with the detection of the first organic molecules, methane (CH₄). The existence and behavior of methane on Mars is of great significance, as methane is a potential biomarker. Where does methane come from? Where does it go? Is it transient? Although these and related questions are difficult to answer at the present considering the limitations of available data, they have opened up new vistas into the chemistry in the atmosphere and at the surface of Mars.

We recognize now that the chemistry of Mars is neither straightforward, nor is it simply the result of absorption of the solar ultraviolet photons by CO₂ and H₂O. Triboelectric processes in the Martian aeolian activity could potentially be a major player in the chemistry. Heterogeneous surface losses and surface chemistry could be important in the distribution of trace constituents. These processes may be producing oxidants that are needed to explain the mysterious absence of organics from the surface of Mars.

In this talk we will review our current understanding of (1) the conventional photochemical processes that produce, in particular, CO, O₂, O₃, and H₂O₂, (2) possible sources and sinks of methane, (3) modification of conventional photochemistry by the introduction of CH₄, and possibly SO₂, H₂S, and the halogens, (4) special role of electrostatic fields in the generation of oxidants during the Martian aeolian activity, and subsequent loss of surface organics.

For the source of methane, a number of possibilities will be examined, including the exogenous, hydrogeochemical — especially water-rock reactions — and biological sources. It is suggested that comets and meteorites are the least likely, whereas "low" temperature serpentinization is the most plausible of all candidates to explain the methane observations. Nevertheless, it is premature to rule out the role of biology in producing methane on Mars, in view of the lack of appropriate measurements at this time. The conventional mechanism for the loss of methane from the atmosphere is photochemistry, i.e. by the UV photolysis above approximately 60 km and by oxidation lower in the atmosphere. However, loss to the surface must also be factored in. Normally, ordinary heterogeneous loss process to surface tends to be very slow. On the other hand, a reactive surface

could potentially accelerate the destruction of methane. If correct, it would imply that a bigger source of methane is present than currently estimated on the basis of photochemical loss. A reactive surface can also explain why no organic material has ever been detected on the Martian surface.

The surface could become reactive if some oxidizer were present. The hydrogen peroxide generated in normal photochemistry in the atmosphere is orders of magnitude smaller (after accounting for diffusion into the regolith) than that needed to explain the surface reactivity measured by the Viking Life Sciences Experiments. Instead, we suggest that vast quantities of a powerful oxidant, hydrogen peroxide, can be produced in chemistry triggered by electrostatic fields generated in the Martian dust devils and dust storms, and in the normal saltation process close to the surface.

Finally, current observations are inadequate to prove or disprove the existence of life on Mars, now or in the past. The question of extant or extinct extraterrestrial life and of habitability, the ability of an environment to sustain life, is so fundamental that it needs to be addressed carefully on future Mars missions. The 2009 Mars Science Laboratory (MSL) is designed to substantially extend the systematic investigation of the Martian habitability with a powerful analytical laboratory capability that includes both definitive mineralogy and a comprehensive volatiles analysis. The search by the MSL for organic molecules in the atmosphere, near surface solid samples, and rocks will substantially extend the measurements of the 1976 Viking Landers. The SAM Suite of MSL, comprising a GCMS and a Tunable Laser Spectrometer, will have the capability to measure variations in both atmospheric methane and the hydrogen peroxide oxidant over the course of an entire Mars year. MSL will traverse tens of kilometers to explore a diversity of sites. If more complex organic molecules than methane are found, the MSL measurement of patterns in molecular weight, structural complexity, oxidation states, carbon isotope ratios, and possibly chirality will provide significant constraints on abiotic, prebiotic, or biotic sources and sinks for these molecules.

Bibliography

Articles from the past three years only are cited. References to previous literature may be found in these articles. Ask Sushil Atreya for preprints of unpublished material, or go to his website where pdf's of articles may be found. Webpage URL:

<http://www-personal.engin.umich.edu/~atreya/>

Atreya, S.K., Wong, A.S., Renno, N.O., Farrell, W.M., Delory, G.T., Sentman, D.D., Cummer, S.A., Marshall, J.R., Rafkin, S.C.R., Catling, D., 2005. Oxidant enhancement in Martian dust devils and storms: Implications for life and habitability. *ASTROBIOLOGY*, submitted revised version.

Atreya, S.K., Mahaffy, P.R., Wong, A.S., 2005. Methane and related trace species on Mars – origin, loss, implications for life, and habitability, Submitted to *Planet Space Sci.*

Delory, G.T., Farrell, W.M., Sentman, D.D., Renno, N.O., Atreya, S.K., Wong, A.S., Cummer, S.A., Marshall, J.R., Rafkin, S.C.R., Catling, D., 2005. Oxidant enhancement in Martian dust devils and storms: storm electric fields and electron dissociative attachment. *ASTROBIOLOGY*, submitted.

Formisano, V., Atreya, S.K., Encrenaz, T., Ignatiev, N., Giuranna, M., 2004. Detection of methane in the atmosphere of Mars. *Science* 306, 1758-1761.

Krasnopolsky, V.A., Maillard, J.P., Owen, T.C., 2004. Detection of methane in the Martian atmosphere: evidence for life? *Icarus* 172, 537-547.

Wong, A.S., Atreya, S.K., Encrenaz, Th., 2003. Chemical markers of possible hot spots on Mars, *J. Geophys. Res.*, 108, No. E4, 5026, doi:10.1029/2002JE002003. Correction and update, in *J. Geophys. Res.*, 110, E10002, 5026, doi:10.1029/2005JE002509, 2005.