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# The Implications and Limitations of the Findings of the Viking Organic Analysis Experiment

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**Summary.** The gas chromatograph mass spectrometer instrument of the Viking mission has demonstrated the absence of organic compounds in the immediate surface layer of the two landing sites. The demonstration of the successful operation of the instrument (comparison of ground-based test data with those obtained during interplanetary flight and the data from the surface of the planet) and its limitations (e.g., the detection of highly cross-linked polymers or polymeric carbon suboxide) are reviewed. The measurements for bound water are based on indirect data, the detectability of evolved carbon dioxide and ammonia is poor, and oxygen, liberated from the soil samples, can not be detected.

**Key words:** Viking organic analysis – Inorganic volatiles on Mars

## Introduction

Almost three years have passed since the primary phase of the Viking mission and we can now appraise its results with more perspective. Most of the data have been interpreted comprehensively by the experimenters and presented to the scientific community which was then able to expand on them in the light of their own point of view or interests. As a result of these activities a number of conclusions were drawn, comments made, and questions asked about the various experiments. It is therefore worthwhile to present a summary of the conclusions that can be drawn from the data which the molecular analysis experiment generated from the soil samples by the gas chromatograph-mass spectrometer (GCMS).

First of all, it should be reiterated that the purpose of this experiment was first and foremost to answer the question whether or not there are any organic compounds present at the surface of Mars. The answer to this question, which is a simple 'yes' or 'no' (within the detection limits of the instrument) has a vast impact on our knowledge about the environment presently existing on the planet, on the probability of past, present, or future existence of living systems on the planet or of the occurrence of nonbiological chemical synthesis. If the answer were 'yes' then it would become of interest to identify the compounds and deduce their origin.

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As has been reported, the result of the molecular analysis experiment of four samples of martian surface material, two from the Viking 1 site and two from Viking 2 (one of them from underneath a rock), was a resounding 'no' (Biemann et al., 1976; 1977). At the detection limit, which was in the parts per billion range for compounds containing more than two carbon atoms and the parts per million range for compounds containing one or two carbon atoms, no organic material could be detected other than the traces of terrestrial contaminants known to be present in the two instruments.

## Performance of the Instrument

Before discussing the ramifications and explanations of this result, one may wish to review the reliability of this negative answer. First, the question arises, whether the instruments indeed worked properly. Fortunately, experimental data exists which demonstrates this proper function beyond any doubt. During the final testing of the flight instruments, just before they were incorporated into the Lander, it was found that the cleaning procedure developed for the instruments and their parts, although performed as rigorously as possible, did not remove all traces of some of the organic materials which had to be used in the manufacture of the instrument. This was particularly difficult because great efforts had been made to make the instrument as sensitive as possible. In order to obtain base line data for these contaminants, each instrument performed a complete organic analysis cycle on an empty oven during interplanetary flight thus providing the necessary background data above which any material indigenous to Mars would have to appear. The instrument on Viking 1 turned out to be much cleaner than that traveling on Viking 2 but both gave good gas chromatographic resolution and excellent mass spectra for these contaminants both during the test run in interplanetary flight and on the surface of Mars. Thus the undesirable but unavoidable presence of contaminants was indeed a fortunate circumstance as it demonstrated that the instruments worked well, in fact better than expected, before and after landing on the surface of the planet. Fortunately, the level of the contaminants was sufficiently low as not to interfere appreciably with the detection limits for the compounds of interest.

In an effort to assess the performance and sensitivity of the GCMS, test samples had been analyzed on an instrument that was identical for all practical purposes with the flight configuration. Meteorites and antarctic soils were thought to represent the best possible analogs to the material one might encounter on Mars. The resulting data demonstrated the capability of the sample ovens to force organic materials out of the sample on to the gas chromatographic column, the ability of the latter to resolve even complex mixtures of the compounds produced, and showed that the mass spectrometer generates well resolved, interpretable mass spectra of these components. The data from the Murchison meteorite and from an antarctic soil sample which had a very low content of microorganisms was used for these tests (Biemann et al., 1977). When comparing the signal generated during the experiments performed on Mars with that obtained from those two terrestrial and extraterrestrial analogs, one can conclude that the instrument would have detected the presence of 100 to 1000 times less organic materials if they were present on the Viking 1 or Viking 2 sites. Since then three more sterile soil samples from antarctic valleys (Cameron, 1971) have been analyzed on the test instrument on Earth and in all of them organic material could be detected. Only in one sample, collected at a mountain top in the antarctic, were no organics found (Lavoie, 1979).

All these data demonstrate that the samples collected on the Viking 1 and Viking 2 sites did not contain organic material at the part per billion level containing more than two carbon atoms or at the part per million level for $C_1$ or $C_2$ compounds.

## Limitations of the Detectability of Organic Compounds

While it can be unambiguously stated that the samples that were transferred into the sample ovens did not contain organic materials at the detection limit stated above, this does not necessarily prove that there are no organic compounds anywhere on the entire planet. For example, the organic material may be inaccessible to the sampler: the results do not exclude that organic compounds may be present a meter below the surface of any of the landing sites since only material within the top 10 cm were sampled (it should be kept in mind that both GCMS instruments had used up all operative sample ovens and in fact were shut down at the time when the 'deep hole' was excavated by the surface sampler during the extended mission). Similarly, organic material existing in the interior of a rock would not have been accessible to the experiment since no drilling equipment was on board. In this context it should be recalled that I. Friedman discovered layers of blue-green algae a few millimeters below the surface of rocks found in the Antarctic (Friedman and Ocampo, 1976).

Finally, certain types of organic material can not be detected by the molecular analysis experiment which consisted of heating the sample to 500°C in several steps followed by the analysis of organic compounds evolved by volatilization or pyrolysis. Any compound that would be stable at 500°C, such as highly cross-linked polymers, would probably not produce detectable material. Certain kerogens are terrestrial examples of this type. However, one has to keep in mind that such polymers are always accompanied by comparatively low molecular weight substances and materials that are thermally degradable, and that these would have been detected. Thus, the presence of such thermally stable polymers can be ruled out unless there operates a process on Mars which removes these degradable materials selectively while leaving the stable polymer intact.

Compounds of the opposite behavior, namely one that decomposes upon heating into certain molecules which the Viking GCMS can not detect, would also remain unnoticed. The only material of that kind which has been postulated to exist on Mars is carbon suboxide (Plummer and Carson, 1969; Oyama and Berdahl, 1979). In its polymeric form it decomposes upon heating either into the very reactive monomer, which probably would not pass the gas chromatographic column, or to carbon monoxide and carbon dioxide which would not be detectable in the presence of the relatively large amount of atmospheric carbon dioxide included with the sample. Again, it is difficult to conceive of the formation and presence of carbon suboxide without the simultaneous formation of related compounds that would be detectable by the GCMS.

## Possible Destruction of Organic Compounds on Mars

The lack of organic compounds was somewhat unexpected because one would have thought to find at least the remnants of the organic material brought to the planet by impacting meteorites, such as carbonaceous chondrites. Thus there must be processes occurring on the planet which efficiently destroy or bury organic compounds. Burial by the 'gardening effect' of meteoritic impact is a possibility, but unlikely because it would require mixing the meteoritic material within a regolith layer hundreds of meters deep (Biemann et al., 1977). A number of the destructive processes have been postulated ever since the first martian sample was analyzed (Biemann et al., 1977). The relatively high flux of ultraviolet radiation would efficiently destroy organic compounds exposed to it, either directly (Oro and Holzer, 1978) or via titanium oxide catalyzed photooxidation (Chun et al., 1978); chemical oxidation by the suspected oxidizing agents in the surface detected by one of the biology experiments (Oyama and Berdahl, 1977) and other more exotic processes like glow discharge generated by friction between dust particles and the atmosphere at the low martian pressures (Mills, 1977). All these processes have been shown to destroy organic materials more or less efficiently and it is therefore difficult to decide whether there never were any organic compounds produced on the planet, whether they were produced in the past but have been destroyed since or whether they are continuously produced at the present time but destroyed at a rate which prevents their accumulating to even the extremely low level which could be detected by the GCMS. Obviously, if these processes have been operative since the accretion of the planet, no organic compounds would exist there. On the other hand, if at earlier times the conditions were much milder and more conducive to the production of organic compounds they may still be preserved at varying depth below the surface.

## Limitations on the Detection of Inorganic Volatiles

Although the experiment was aimed at the detection of volatile or volatilizable organic compounds, it is, in principle, capable of providing also some information about inorganic volatiles. It should be kept in mind, however, that this is much more difficult and in some cases impossible due to the design of the instrument or its mode of operation which did not favor the detection of inorganic gases like $H_2O$, $CO_2$, $O_2$, and $NH_3$ because of the effort to maximize the detectability of the more complex organic molecules. Of these four substances, *water* always represented a special case because it was hoped to learn something about the level of hydration of the minerals in the soil matrix. Due to the relatively large amount of water evolved upon heating of the martian samples and the operation and flow dynamics of the 'effluent divider' which protects the mass spectrometer from overloading its pumping capacity (Rushneck et al., 1978) it was not possible to determine the amount of water evolved in the same way as organic materials are measured. During most of the time when the water peak emerged from the gas chromatograph the main valve to the mass spectrometer remained closed, thus venting the water to the atmosphere. Since the behavior of the effluent divider is related to the concentration of material eluting in the carrier gas it was possible to match it in laboratory experiments by injecting various amounts of water into the test instrument (Biemann et al., 1977; Lavoie, 1979). It is for this reason that all the values reported for soil water (rate of hydration of the minerals present) are indirect data, reliable probably only to within a factor of ± 5. Caution has to be exercised when using them as absolute values. Relative ratios are more dependable.

*Ammonia* represents a similar problem, but it is aggravated by the fact that its mass spectrum is easily obscured by that of water, which shows an ion at m/e 17 about one quarter as abundant as m/e 18 and ammonia thus can not be detected with the Viking GCMS unless it is present at a concentration of about 20% with respect to water.

The quantitation of *carbon dioxide* evolved upon heating the soil sample is made difficult because some atmospheric $CO_2$ is included in the oven with the sample and the amount depends on the extent to which the oven is filled (there is no measurement of this quantity). Very approximate estimates of the quantities of $CO_2$ evolved upon heating of the sample were made for the Viking 2 experiments which were conducted in the 'hydrogen mode' (Biemann et al., 1977).

The measurement of *oxygen* evolved from soil samples would have been desirable in view of the evolution of oxygen detected by one of the biology experiments (Oyama and Berdahl, 1977). However, this is impossible because of one particular feature of the Viking GCMS which employs hydrogen as the carrier gas and a palladium separator to prevent its entering the mass spectrometer (Rushneck et al., 1978). Any oxygen expelled from the sample when it is heated in the oven is mixed with a large excess of hydrogen while it travels through the gas chromatograph. Upon entering the palladium separator all oxygen is catalytically converted into water and becomes indistinguishable from the original water expelled from the sample. Even though very little water is evolved at low temperatures, the amount of oxygen observed in the GEX experiment (Oyama and Berdahl, 1977) is minute in comparison (1 $\mu$mole/cm$^3$ of soil). A recent proposal (Nussinov et al., 1978) argues that the oxygen evolution observed in the GEX experiment was adsorbed in the microporous structure of the soil grains rather than due to the reaction of water vapor with an oxidant and cites the 'absence of $O_2$ evolution in this [the GCMS] experiment' as evidence. The above discussion makes it clear that the GCMS can not detect oxygen in the soil analysis mode, particularly not at low levels and at least this part of the argument of the Russian authors is thus unfounded.

## Conclusion

The above discussion clearly demonstrates that the molecular analysis experiment has successfully achieved its major goal as it has demonstrated the absence of organic compounds in the surface material at two Viking sites. This fact has had a very important impact on the interpretation of the data received from the biology experiments (Klein, 1977; Klein et al., 1976) and put some boundaries on the chemical and physical environment at the surface.

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