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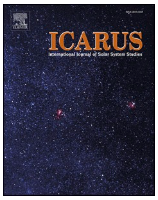

The Viking biology experiments on Mars revisited

Christopher P. McKay *, Richard C. Quinn, Carol R. Stoker

Space Science Division, NASA Ames Research Center, Moffett Field, CA 94035, USA

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ABSTRACT

The discovery of perchlorate on Mars by the Phoenix mission has provided a basis for explaining the results of the Viking Landers. Thermal decomposition of perchlorate in the ovens of the instrument can explain the lack of organics detected. Accumulation of hypochlorite in the soil from cosmic ray decomposition of perchlorate can explain the reactivity seen when nutrient solutions were added to the soil in the Viking Biology Experiments. A non-biological explanation for the Viking results does not preclude life on Mars.

1. Introduction

August 2025 will be fifty years since the first of the Viking spacecraft was launched for Mars. The two Viking landers conducted the first, and to this date only, search for biological activity on another planet. At the time the results were inconclusive and controversial with advocates arguing that Viking did detect extant Martian life and others arguing that the results were the product of some sort of chemical oxidant.

Soon after the Viking landers completed the last of the biology experiments, the Biology Team Leader, H.P. Klein, published a paper in Icarus (Klein, 1978) entitled "The Viking biology experiments on Mars". The key conclusion of this paper was that "Some of the results are consistent with a biological interpretation, although there are serious reservations in accepting this conclusion. Most of the findings, however, are inconsistent with a biological basis." The present paper is entitled "The Viking biology experiments on Mars revisited" and addresses this same question.

With Mars sample return on the horizon and the prospect of future missions to Mars, perhaps even including life detection instruments, it may be timely to revisit the results of the Viking Biology Experiments. Since Viking landed on Mars, many things have changed, and many things have not. What has not changed in the past 50 years is our understanding of the limits of life in cold and dry environments. For example, Kushner (1981) published a list of limits of life that is essentially current today in terms of comparison to Mars. The key parameter in terms of Mars is the lower limit of water activity for life. Kushner (1981) gave this as 0.6. Recently, Hallsworth et al. (2021) in a consideration of life in the clouds of Venus invoked a "0.585 limit for known extremophiles." The general understanding of the climate history of Mars has not changed: Mars had an early wet phase ending some 3.5 Gry ago, followed by cold dry desert conditions with perhaps intermittent episodes of more habitable conditions due to changes in obliquity (e.g. Mellon et al., 2024).

However, there have been two very big changes resulting from missions to Mars. The most important new data, by far, was the surprising discovery from the Phoenix Mission that the soils of Mars contain about 0.5% perchlorate (Hecht et al., 2009). A result that has subsequently been confirmed by the Curiosity Rover (Glavin et al., 2013) and orbital observations (Ojha et al., 2015). The perchlorate concentration on Mars is many orders of magnitude larger than the typical concentrations of perchlorate in desert soils on Earth (Jackson et al., 2015). This incredibly high concentration of perchlorate is still not adequately explained but the implications for the Viking results are profound. A second result from Mars was the successful detection of C_1-C_{11} organic compounds and macromolecules in ancient lakebed sediments on the surface of Mars at the many ppm (parts per million) level by the SAM (Sample Analysis on Mars) instrument on the Curiosity Rover (Eigenbrode et al., 2018). This contrasts with the report of the Viking Gas Chromatograph Mass Spectrometer (GCMS) team with organics detected on Mars at the ppb (parts per billion) level attributed to contamination (Biemann et al., 1977).

2. Viking mysteries

In addition to the GCMS (Biemann et al., 1977), the Viking Landers included two experiments to detect metabolism: the GEx (Gas Exchange) looked for gases released when liquid nutrient solution was added to the soil (Oyama and Berdahl, 1977) and the LR (Labeled Release) which

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* Corresponding author at: Mail Stop 245-3, Space Science Division, NASA Ames Research Center, Moffett Field, CA 94035, USA.
E-mail address: chris.mckay@nasa.gov (C.P. McKay).

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looked for CO_2 released when nutrient solution was added to the soil (Levin and Straat, 1977). The results of these instruments were puzzling and summarized in nine points below. Briefly

1. GCMS: no Martian organics detected. (Biemann et al., 1977).
2. GCMS: chloromethane at 15 ppb, at Viking landing site 1 and dichloromethane at 0.04–40 ppb at Viking landing site 2. Only when the samples were heated to 500 °C (Biemann et al., 1977).
3. GEx: Release of O_2 when the sample was moistened with water, 70–700 nmoles/gm (3–35 ppm) (Oyama and Berdahl, 1977).
4. GEx: ~0.5 of the original O_2 amount released after heating to 145 °C for 3.5 h (Oyama and Berdahl, 1977).
5. LR: Release of labeled CO_2 from organics (implied oxidant level ~ 1 ppm) (Levin and Straat, 1977).
6. LR: No labeled CO_2 release from organics after heating at 160 °C for 3 hours (Levin and Straat, 1977).
7. LR: Labeled CO_2 release from added organics was reduced but not eliminated after heating at ~50 °C for 3 hours (Levin and Straat, 1977).
8. LR: No labeled CO_2 release from organics after approximately 141 sols at 10–26 °C storage in the sample distribution box in the lander (Levin and Straat, 1977).
9. LR: Both GEx (at a reduced level) (Oyama and Berdahl, 1977) and LR (not reduced) (Levin and Straat, 1977) reactions were present in samples from under a rock.

The LR results (5–9 above) have been the primary basis for the claim that Viking did detect life on Mars, the GCMS results (1–2 above) notwithstanding (Levin and Straat, 1977, 2016).

The responses observed in the three Viking Biology Experiments were complex and not all aspects require evoking the presence of perchlorate as an explanation. The third Viking Biology Experiment was the Pyrolytic Release (PR) which detected low levels of CO_2 fixation in dry and moist conditions under UVA and visible light (Horowitz et al., 1977). The yield of CO_2 was highly variable and was measurable in dark controls although it was highest in the light. There was an overall reduction in fixation after exposure to high temperature but the relative thermostability was the primary reason Horowitz et al. (1977) concluded that the CO_2 fixation detected was not biological. This conclusion was supported by the Hubbard (1979) laboratory PR experiments which showed the conversion of $^{14}CO_2$ or ^{14}CO to ^{14}C-organic compounds using iron oxides. The PR results have not played a role in the chemical oxidation explanations for the LR and GEx results for several reasons. Most obviously the O_2 released by humidification of the samples (as was detected by the GEx) would not be detectable in the PR which only measured condensed organic compounds. No organic reagents were added to the PR samples, dry or wet, so there could not be any production of CO_2 as observed in the LR. In addition, the samples in the PR were not heated to temperatures high enough to decompose/activate perchlorate.

3. The perchlorate model

The detection of perchlorate on Mars by the Phoenix mission is arguably the most important result from Mars since the Viking mission, and certainly in terms of the search for life. We suggest here that the presence of perchlorate can explain all of the 9-fold mysteries of Viking on Mars and no biological component is required. Navarro-González et al. (2010) explain #1 and #2 as due to perchlorate reactions with organics in the GCMS instrument oven. Perchlorate decomposes exothermally at high temperatures – but below temperatures used in the GCMS ovens – and when it decomposes it releases reactive oxygen species. Quinn et al. (2013) explain #3 and #4, as O_2 produced when cosmic ray alteration of the perchlorates produces oxygen which is physically trapped in the soil and released when wetted or heated. Quinn et al. (2013) explain #5 and #6 as due to cosmic ray alteration of the perchlorates producing hypochlorite. This oxidizing compound added to mixtures of organics and soil in the laboratory reproduce the time dependent kinetics of the release of CO_2 seen in the LR experiment (#5) and they are destroyed by high temperatures consistent with the GEx and LR results (#4 and #6). Georgiou et al. (2017) explain #7 based on measurements of hypochlorite thermal stability. Reactivity under a rock, #9, is consistent with the LR and GEx oxidants, hypochlorite being produced by cosmic radiation.

The loss of LR activity after storage in the lander, #8, has not been duplicated in the laboratory within the perchlorate model and was highlighted by Levin and Straat (2016) as a key indicator of biological activity. The soil was stored in the sample distribution box, in the dark, open to the Martian atmosphere, but maintained at temperatures ranging between 10 °C and 26 °C for 141 sols (Levin and Straat, 2016). However, Quinn et al. (2013) showed that the primary release of $^{14}CO_2$ observed in the LR experiment can be reproduced by the decomposition of chloroalanine formed by the reaction of calcium hypochlorite (formed via calcium perchlorate radiolysis) with the ^{14}C-labeled alanine present in the LR organic medium. A reaction of chloride dioxide with the LR nutrient (including alanine) was not observed (see Fig. 2 in Quinn et al., 2013). The results of the Phoenix Wet Chemistry Laboratory indicate that perchlorate is likely present in the soil as $Ca(ClO_4)_2$ and/or $Mg(ClO_4)_2$ (Hecht et al., 2009) which supports the likely formation and presence of calcium hypochlorite. The decomposition of calcium hypochlorite is complex and, in addition to temperature, is dependent on humidity, hydration state, sample matrix details, and storage conditions, which in the case of Mars and the Viking LR experiment are poorly constrained. A reasonable explanation for #8 is that the primary LR reactant was perturbed from a metastable state in the soil and decomposed with time under the LR storage conditions. It would be reasonable to expect calcium hypochlorite to exhibit this type of behavior.

4. Discussion

The high levels of perchlorate implied in the soil of Mars have led to a focus on them, but other oxidants in addition to perchlorate and its radiolysis products may be involved in the reactivity seen in the Viking biology experiments and chemical processes occurring in the Martian soil. During the Viking Mission, H_2O_2 was proposed as a possible explanation for the LR results (Oyama et al. 1977) and photochemical models predict its formation in the Martian atmosphere (Hunten, 1979, 1987). Triboelectric effects have also been shown to produce OH radicals and H_2O_2 by aeolian dust and basalt abrasion (eg. Delory et al., 2006, Bak et al., 2017). However, a key role for H_2O_2 was not widely accepted (Zent and McKay, 1994) because the heat of formation determined from the results of the LR experiment was not comparable to that obtained from laboratory studies of H_2O_2 decomposition (Levin and Straat, 1979). Also, both ferric and ferrous iron in the soil should rapidly catalyze the decay of H_2O_2.

Metal superoxides have been suggested (eg., Oyama et al., 1977; Zent and McKay, 1994) and superoxide can be directly produced by radiation in Mars soil analogs that do not contain perchlorate (Yen et al., 2000; Georgiou et al., 2015) and may be involved in the production of perchlorate and chloride in the soil (Carrier and Kounaves, 2015). In this regard, it is interesting to note that the Curiosity rover has found that some soils on Mars have both perchlorate and nitrate below detection limits (Stern et al., 2017; Archer et al., 2024).

The discovery of nitrates in the soil on Mars (Stern et al., 2015, 2017) opens up an additional source of oxidants. Plumb et al. (1989) suggested that the Viking oxidant is a peroxonitrite in the Martian soil. In their scenario, ultraviolet photons decompose nitrates into nitrites and oxygen. The nitrites are further photolyzed to peroxonirite. The levels of nitrate on Mars appear to be too low for this mechanism alone to explain the Viking results (Zent and McKay, 1994).

The perchlorate model, possibly with other oxidants, as described above provides a straightforward explanation for the Viking results and there is no need to postulate life forms on Mars to account for the Viking results. However, this view is not unanimous in the science community. For example, Gil Levin the PI of the LR experiments never gave up the view that his instrument detected life (Levin and Straat, 2016). Nonetheless, we would submit that any scientific explanation that is based on biology, even more so any biology that is not "life as we know it" has a very high bar to reach before it becomes competitive with the non-biological explanation based on expected consequences of the high level of perchlorate discovered in Mars soils. The perchlorate model for the Viking results does not prove that there is no life on Mars, nor does it imply that the continued search for evidence of life on Mars, past or present, is pointless. Indeed, we strongly argue for the search for evidence of extant life in future missions. Good targets are salt deposits and polar ground ice.

The perchlorate model and the resultant conclusion that Viking did not detect life in the surface soils of Mars will factor into any discussion of sample return or astronaut return from Mars. The Outer Space Treaty prohibits "adverse changes in the environment of the Earth resulting from the introduction of extraterrestrial matter." Future experiments are needed to better understand the chemistry of martian soils and the possibility of life persisting there.

CRediT authorship contribution statement

Christopher P. McKay: Writing – original draft, Conceptualization. **Richard C. Quinn:** Writing – review & editing, Conceptualization. **Carol R. Stoker:** Writing – review & editing, Conceptualization.

Declaration of competing interest

The authors declare no competing interests.

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Data availability

No data was used for the research described in the article.

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