

Urey: Mars Organic and Oxidant Detector

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Abstract One of the fundamental challenges facing the scientific community as we enter this new century of Mars research is to understand, in a rigorous manner, the biotic potential both past and present of this outermost terrestrial-like planet in our solar system. Urey:

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Mars Organic and Oxidant Detector has been selected for the Pasteur payload of the European Space Agency's (ESA's) ExoMars rover mission and is considered a fundamental instrument to achieve the mission's scientific objectives. The instrument is named Urey in recognition of Harold Clayton Urey's seminal contributions to cosmochemistry, geochemistry, and the study of the origin of life. The overall goal of Urey is to search for organic compounds directly in the regolith of Mars and to assess their origin. Urey will perform a groundbreaking investigation of the Martian environment that will involve searching for organic compounds indicative of life and prebiotic chemistry at a sensitivity many orders of magnitude greater than Viking or other in situ organic detection systems. Urey will perform the first in situ search for key classes of organic molecules using state-of-the-art analytical methods that provide part-per-trillion sensitivity. It will ascertain whether any of these molecules are abiotic or biotic in origin and will evaluate the survival potential of organic compounds in the environment using state-of-the-art chemoresistor oxidant sensors.

Keywords Mars · Life detection instrumentation · Space research

1 Introduction

Based on results from the NASA Mars Exploration Rovers and the ESA Mars Express mission, there is compelling and accumulating evidence that liquid water bodies were once present on Mars. Although it is unknown how long these watery environments existed, they could potentially have provided a milieu capable of supporting life or its precursor, prebiotic chemistry. The detection of phyllosilicates and sulfate minerals indicates that Mars has had a complex aqueous history with chemical processing giving rise to sedimentary deposits that could preserve organic material (e.g. Poulet et al. 2005; Bibring et al. 2006; Bishop et al. 2005; Thomas et al. 2005).

All known life is based on organic carbon. The 1976 Viking missions detected no organic compounds above a threshold level of a few parts per billion (ppb) in near-surface samples (Biemann et al. 1976). However, experimental testing has now established that the Viking Gas Chromatography/Mass Spectrometry (GCMS) would not have detected key biomolecules, such as amino acids, even if several million bacterial cells per gram were present (Glavin et al. 2001). In addition, oxidation reactions involving organic compounds on the Martian surface would likely produce nonvolatile products such as mellitic acid salts that would have also precluded detection by the Viking instruments (Benner et al. 2000). Thus,

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although Viking clearly demonstrated that the levels of organics at the Viking sites are depleted below the expected levels due to meteoritic input, the results did not conclusively demonstrate the absence of organic compounds on the surface of Mars. An additional consideration is that Viking only sampled the first tens of centimeters of the Martian regolith. It is now thought that ionizing radiation and oxidants formed in the surface and/or near-surface atmosphere have largely destroyed any organic compounds within the upper meter of the Martian surface (Kminek and Bada 2006). Thus, drilling to a depth deeper than this zone of radiolysis is required to obtain samples with the best prospect of containing organic molecules (Dartnell et al. 2007). This is one of the primary goals of the Pasteur rover on ExoMars.

2 The Urey Instrument Experiments

The primary scientific objectives of the experiments to be conducted by Urey are to investigate the following questions:

- Are organic compounds with a primary amino group (amino acids, amines, nucleobases, amino sugars) and polycyclic aromatic hydrocarbons (PAHs)—our target compounds—derived from either extinct or extant life and/or abiotic sources, detectable in the regolith of Mars?
- Using compositional and chirality characteristics of detected amino acids, can we determine whether they are of biotic or abiotic origin?
- Are organic compounds degraded in near surface environments on Mars via an array of photolytic and heterogeneous chemical processes, and are these processes a central factor in determining the abundance and type of our target compounds in the Mars regolith?

Figure 1 graphically illustrates the target organic compounds for Urey and the relationships between the amino acids, their chirality, and PAHs. These relationships can be used to determine the origins of any target compounds that are detected. The Urey objectives focus on the search for evidence of extant or extinct life on Mars and derive from the most accepted understanding of the results of the Viking experiments: levels of organic compounds in the near-surface region are extremely low (part per billion or less); there is evidence for at least three different oxidants in the Martian regolith at the Viking sites (Klein 1979); and the surprisingly low levels of organic compounds may be related to the long-term interaction

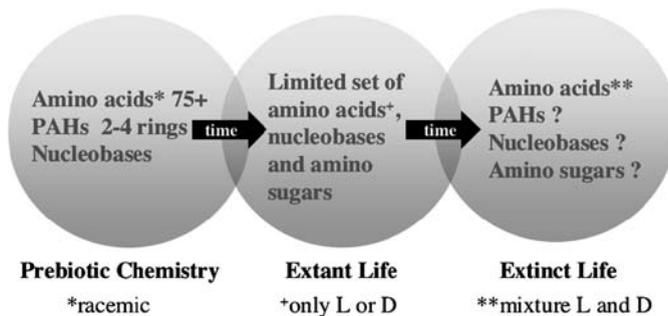


Fig. 1 The target organic compounds for *Urey* and the relationships between the amino acids, their chirality, and PAHs. Although terrestrial life uses 20 distinct amino acids and 5 nucleobases, life elsewhere could be based on a different ensemble of these compounds, which *Urey* will be able to detect and characterize

with these oxidants or the oxidizing conditions of the Martian surface. Urey will target several key organic molecules at very low concentration levels (1,000 times better than Viking) and use sensors to detect and characterize oxidants present in the same samples. These complementary analyses will examine the hypothesis that oxidants and organic matter on the surface of Mars are inversely correlated.

3 Organic Compound Detection and Characterization

In any investigation of organic compounds possibly derived from life, it is important to search for molecules at the core of terrestrial (and presumably extraterrestrial) biochemistry (Pace 2001). Primary examples of such molecules include amino acids and nucleobases. However, abiogenic occurrences of these compounds do exist. More than 70 different amino acids and several amines and nucleobases have been identified in carbonaceous meteorites (Botta and Bada 2002). These compounds can also be readily synthesized in laboratory simulation experiments (Bada 2004). Biological occurrences of these organic compounds exhibit selected characteristic structural forms that facilitate their biochemical roles. Both abiogenic and biogenic organic structures can be detected and differentiated by Urey.

Searching for amino acids and nucleobases is of fundamental importance with respect to assessing the biopotential of Mars. In bacterial cells, amino acids (in the form of proteins) and nucleobases (in the form of nucleic acids) constitute nearly 75% by dry weight of the total organic material. Although it is not certain that an extraterrestrial biology would use the same set of amino acids as on Earth, their presence in certain types of meteorites indicates they were constituents of organic material in the early solar system and thus available for incorporation in living entities elsewhere (Sephton and Botta 2005). In addition, amino acids are robust compounds and would be expected to survive for billions of years in the Martian regolith (Aubrey et al. 2006).

In terrestrial biology, 20 different amino acids are incorporated into proteins and 5 different nucleobases into nucleic acids. Compositional analyses provide important information with respect to whether any of these compounds detected on Mars consist of a limited set of compounds such as found in biology or the more diverse set found in meteorites and prebiotic experiments. One of the most distinctive features of amino acids is their molecular architecture, which gives rise to the property of handedness or chirality. Most amino acids contain asymmetrically substituted carbon atoms that result in left-handed and right-handed versions (enantiomers). Abiotic chemical reactions (in the absence of artificial asymmetry-inducing compounds) always produce a 1 : 1 (racemic) mixture of the two enantiomers. Thus, equal (or nearly equal) amounts of left and right amino acids are found in carbonaceous chondrites that are free of terrestrial contaminants. Likewise, prebiotic amino acid synthesis yields racemic mixtures in absence of an asymmetric source in the system. In contrast, terrestrial biology uses almost totally left-handed (L-enantiomer) amino acids as building blocks for proteins and enzymes. Although some D-amino acids are found in the cellular membranes of some bacteria, L-amino acids are far more abundant in the total cell and in Earth regolith.

On Earth, racemization can slowly convert biological amino acids in geologic samples into a racemic mixture. However, the D/L amino acid ratio in geologic samples has never been found to exceed 1.0. Racemization may be very slow because of the cold, dry environmental conditions and thus homochiral amino acids even in deposits billions of years old would still be preserved today (Bada and McDonald 1995). Urey can “look back in time” at amino acids and use their D/L ratio as a window into when past life may have existed on Mars. Amino acid homochirality is found only in biology and is considered to be

an inevitable characteristic of any biochemistry, terrestrial or alien. It is likely a universal biomarker signature of molecule-based life (de Duve 2005). Biochemical reactions require exclusively one chiral form of amino acids, although either form could be used. Thus, life elsewhere could be based on either L- or D-amino acids. The detection of homochiral amino acids, whether all L- or all D-amino acids, would provide evidence for the existence of life on Mars (Bada 2001).

Aromatic macromolecules are the dominant organic material in space (Ehrenfreund et al. 2006). Aromatic material is extremely stable and quite versatile and PAHs are some of the most ubiquitous molecules in the solar system and universe. PAHs and aromatic macromolecular carbon were among the most abundant materials delivered to the early planets (Ehrenfreund et al. 2002) by meteoritic infall. Thus, PAHs are excellent target molecules in the search for organic material that may have originated elsewhere in the solar system and was subsequently delivered intact to the surface of Mars.

Laser-induced fluorescence is one of the most sensitive organic compound detection techniques. It is far more sensitive than other techniques, such as charged particle detection used in gas chromatography/mass spectrometry (GCMS). Fluorescence methods have the capacity to detect single molecules (Moerner and Orritt 1999), and this is now routinely practiced. One of the most exhaustively characterized fluorescent analytical detection chemistries that has been developed is for the detection of primary amines, in particular those compounds associated with biology as we know it: amino acids (the components of proteins) and nucleobases (the components of RNA and DNA). Reagents such as fluorescamine provide sub-ppb sensitivity for organic compounds with a primary amino group. PAHs are by themselves naturally fluorescent when stimulated with near-UV light and thus can be directly detected at ppb levels.

4 Establish Surface and Subsurface Oxidation Mechanisms and Rates

The search for organic compounds on the surface of Mars has proven to be a difficult task. In the Martian atmosphere several trace gases have been detected including hydrogen peroxide (Encrenaz et al. 2004) and methane (CH₄, Krasnopolsky et al. 2004; Formisano et al. 2004).

The Viking landers performed an in situ search on the surface of Mars for both life and organic compounds. However, soil measurements revealed that the surface materials at the landing sites were chemically but not biologically active under the conditions of the Viking life-detection experiments. Three of the major experimental results of Viking were: (1) the release of O₂ gas when soil samples were exposed to water vapor in the Gas Exchange Experiment (GEx) (Oyama and Berdahl 1977); (2) the ability of the surface material to rapidly decompose aqueous organic material that was intended to culture microbial life in the Labeled Release Experiment (LR) (Levin and Straat 1977); and (3) the apparent absence of organics in samples analyzed by gas chromatography and mass spectroscopy (GCMS) (Biemann et al. 1977). Today, 30 years later, these results remain to be fully explained. The most widely accepted explanation for the GEx and LR results is the presence of oxidants in the Martian soil (Klein, 1978, 1979). Differences in stability of the active agents in the two experiments suggest that the GEx and LR oxidants are different species and that at least three different oxidizing species are needed to explain all of the experimental results (Klein 1979). The combined results of the Viking GEx, LR, and GCMS led to the hypothesis that the GEx and LR oxidants are evidence of the oxidative decomposition of organic compounds in the Martian environment (Klein 1978, 1979).

A key to understanding carbon chemistry on Mars lies not only in identifying soil oxidants, but also in characterizing the dominant reaction mechanisms and kinetics of oxidative

processes that are occurring on the planet. These processes may have decomposed or substantially modified any organic material that might have survived from an early biotic period. There are currently a number of hypotheses to explain oxidant formation on Mars and the roles of oxidants in both the Viking biology experiments and the decomposition of organics on the planet's surface. These hypotheses include: UV generation of superoxide radicals (Yen et al. 2000), triboelectric enhancement of H₂O₂ production (Atreya et al. 2006), and the deposition of oxidizing acids in the Martian soil (Quinn et al. 2005), to name just a few (for a review, see Zent and McKay 1994). Urey will investigate a broad range of Mars oxidant hypotheses, because it is likely that, to a greater or lesser degree, several of the processes that have been hypothesized are occurring on Mars simultaneously (Bullock et al. 1994). There are undoubtedly a number of complex, photochemically driven oxidative processes on Mars involving interrelated atmospheric, aerosol, dust, soil, and organic chemical interactions.

To a large extent, the role these processes play in the carbon chemistry on Mars is unknown. Urey will establish the correlation between the levels of organic compounds, oxidant concentration, water abundance, and UV flux levels, at the various sampling localities, as well as a function of depth in the subsurface. Urey measurements will also discriminate between different oxidant formation and organic decomposition mechanisms that may be occurring.

5 Field Tests

The value of the Urey investigation has been demonstrated in a series of comprehensive field tests conducted in the Panoche Desert Valley (California) and in the Atacama Desert (Chile) (Quinn et al. 2005; Skelley et al. 2005). These sites are among the best Martian regolith analog sites on Earth for studying organic survival and degradation, owing to their uniquely arid and oxidizing environment, the presence of sulfate mineral deposits and low levels of indigenous living organisms and detectable organic compounds (Navarro-Gonzales et al. 2003). The analytical integration of portable versions of Urey's components was demonstrated in analyses at both sites and produced high-quality data now published in the peer-reviewed literature (see Fig. 2). The MOI tests carried out simultaneously at the field sites showed how the characterization of oxidants is critical in the evaluation of the results obtained in the organic compound analyses (Quinn et al. 2005).

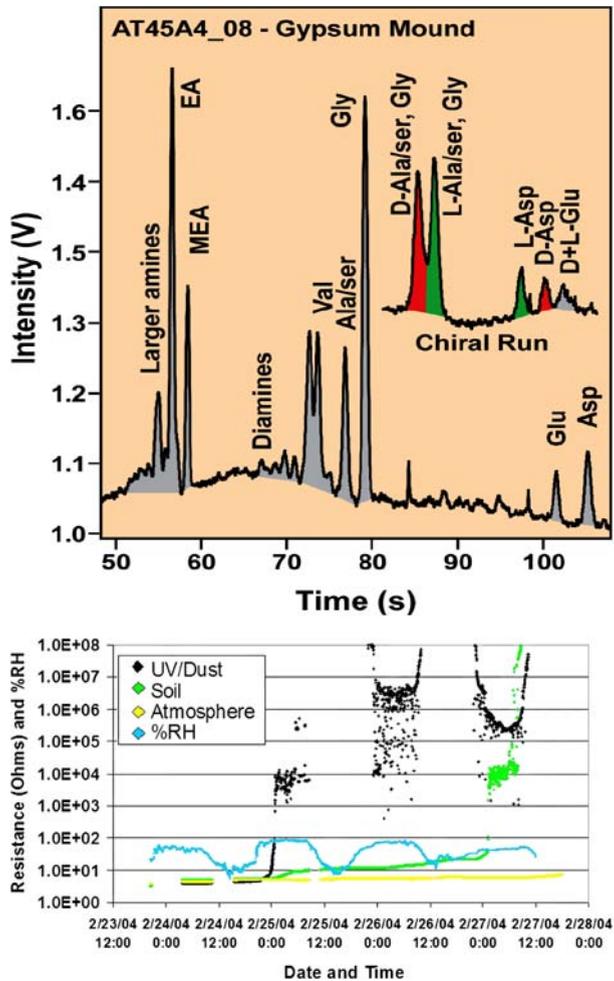
6 Instrumentation Overview

The overall Urey instrument design is shown in Figs. 3 and 4 and consists of four major subsystems:

- Sub-Critical Water Extractor (SCWE)
- Mars Organic Detector (MOD)
- Micro-Capillary Electrophoresis Unit (μ CE)
- Mars Oxidant Instrument (MOI).

Mass properties, power, and energy budgets of subsystems are listed in Tables 1 and 2. The total return data (without Exomars-based compression) is <40 Mbits/EC for a full data set that can be returned over several sols. For a quick turnaround product, returned on the next available pass and appropriate to make a drive-away decision, <1 Mbit total is appropriate.

Fig. 2 (Top) μ CE electropherogram showing amino acids and amines detected in an Atacama sample (from Skelley et al. 2005). Nucleobases were determined to be below the detection limit (<1 ppb) in this sample. (Bottom) MOI sensor responses showing the detection of trace levels of oxidizing acids in Atacama dust using the MOI (from Quinn et al. 2005)



Each of these systems contributes to the overall science output either with analytical processing steps (SCWE/MOD) and/or direct measurements (MOD/ μ CE/MOI). In addition, integrated electronics and mechanical subsystems tie the analytical components into a cohesive instrument package. The design of Urey is organized around the flow of sample material through the instrument in its various states of analytical processing. Figure 4 illustrates this flow at a conceptual level. The sample to be delivered to the instruments is pulverized prior to delivery. Urey accepts samples of 800 mg. The sample is parsed by the ExoMars sample distribution system into 200 mg for the MOI unit and 600 mg for the SCWE. Solid sample provided to Urey remains inside of the instrument for the duration of the mission.

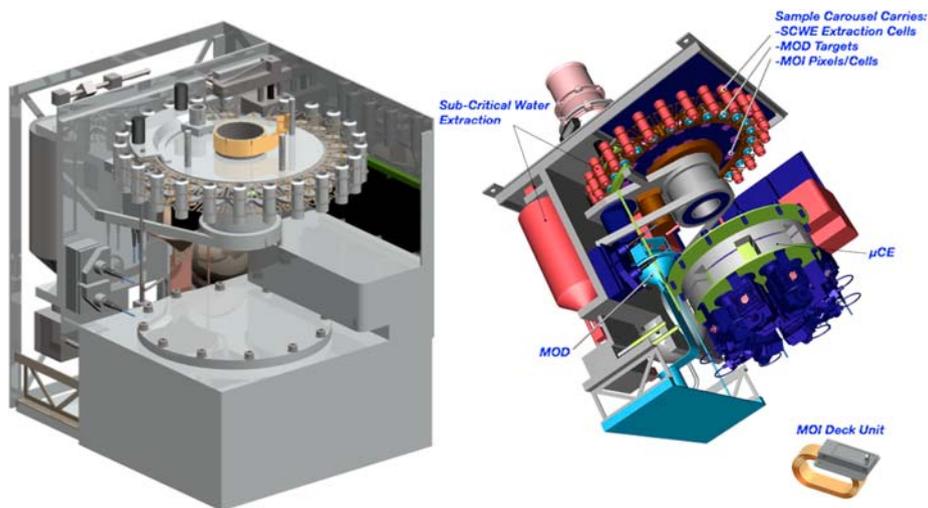
The SCWE uses subcritical water (20 MPa at 150–325°C) producing a low-dielectric constant solvent that extracts organic compounds from the sample much in the manner of making espresso (Yoshida et al. 1999). Prior to performing the organics extraction, the SCWE flushes salts from the sample with a 30°C “rinse”. This flush water is exhausted into a waste collection tank to prevent rover cross-contamination.

Table 1 Mass properties of the *Urey* instrument

| Component | Mass (g) |
|---------------------------|----------|
| MOI (including deck unit) | 315 |
| SCWE (wet) | 1972 |
| MOD | 269 |
| μ CE | 1423 |
| Sample handling | 443 |
| Total | 4422 |

Table 2 Power and energy budgets of MOD/ μ CE and MOI subsystems

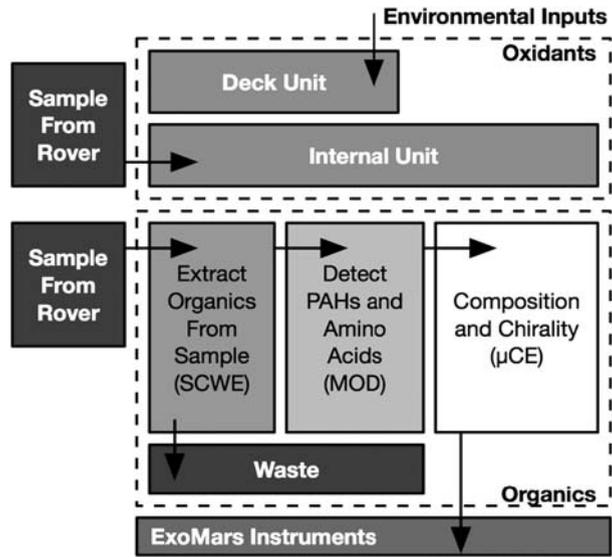
| Subsystems | Power | |
|---------------------------|-------|--|
| MOD/ μ CE Peak Power: | 36 W | during SCWE heater or sublimation crucible operation |
| MOD/ μ CE Peak Power: | 6 W | detection readout, standby modes |
| MOD/ μ CE Energy: | TBD | sequence dependent, not more than 100 W h |
| MOI Peak Power: | 8 W | continuous |
| MOI Energy: | 8 W h | per hour while measuring |

**Fig. 3** Concept drawing of *Urey*: Mars organic and Oxidant Detector

The MOD takes the liquid extract from the SCWE and removes the water by freeze drying and then slowly sublimates the volatile organic compounds to a fluorescamine-coated target “puck” held at -10°C by a cold-finger. Using laser-induced fluorescence, it then can excite PAHs or amino acids (bound to the fluorescamine) and detect their presence.

The μ CE component sends a small amount of liquid to the sublimate on the puck and dissolves some of the sample returning the aliquot to the capillary electrophoresis component

Fig. 4 Overall sample flow through *Urey*



for characterization of composition. Using buffers and other reagents, the μ CE component can also detect the chirality of amino acids. The μ CE component can also output a small amount of the processed aliquot to other ExoMars instruments for confirming analysis.

MOI is deployed in two separate units. The deck unit uses a filtered sensor configuration to characterize the reactive nature of surface environments and oxidant formation mechanisms by isolating the chemical effects of exposure to dust, UV, and atmospheric gases. This configuration will discriminate between current Mars oxidant hypotheses and measure in situ the effects of UV, dust, and trace gases on the degradation rates of organic compounds. An internal MOI unit is used to bracket the redox potential of the regolith and to characterize oxidative processes that affect the concentration and distribution of organic chemicals in the regolith. The MOI internal unit is configured to examine a split of each regolith sample analyzed by the organics experiment. This configuration will allow the distribution of soil oxidants and oxidative processes to be mapped and correlated with soil organic content. By controlling experimental humidity levels, the MOI internal unit will be able to reproduce (with improved thermal and temporal resolution) the conditions that triggered the high levels of chemical reactivity observed in the Viking experiments.

The fundamental unit of MOI is the “chemical pixel”, an 8×2 array of high-purity gold electrodes patterned on a sapphire substrate. Each electrode is coated with a different film type as specified for each MOI experiment. The electrode gaps and spatial configurations on the array are chosen to maximize the sensitivity of each film type to oxidation. During an experiment, the eight different sensing films are exposed to the environment and eight matched, sealed films serve as controls. The approach is derived from the classical, field-proven “spot test” method of chemical analysis, wherein the identity of unknowns is elucidated through the reaction pattern of the sample with well-characterized test compounds. In the MOI implementation, chemical reactivity levels and oxidation processes are characterized by measuring changes in film electrical resistance as a function of time. A differential measurement approach is used and changes in a sensing film’s paired seal reference are used to correct for temperature and other physical effects due to the details of the contact of the thin film to the noble metal of the electrode array.

7 Significance of Urey Experiments

The Urey Instrument is an integrated suite which is designed to search the Martian regolith for chiral biomarkers at terrestrial laboratory state-of-the-art detection levels. Urey will search for organic compounds, characterize the biotic composition of discovered organics, and determine chirality. Furthermore, it can explain how oxidants may have affected the original suite of organic compounds and describe how they may have been altered over the geological history of Mars.

A positive result from the Urey investigation, i.e., the detection of our target organic molecules, could be the first convincing demonstration that organic compounds are present on Mars. This would be a major advance in our understanding of the Martian environment and its potential to harbor life. If a convincing signal for the presence of homochiral D-amino acids were found, this would provide the first evidence for the possible presence of unique life that is not related to terrestrial biology. The detection of a homochiral L-amino acid (if different from terrestrial L-amino acids) would provide the same evidence. This result would be of enormous significance to not only NASA and the science community, but to the general public as well. The presence of homochiral L-amino acids would imply that life on Mars and Earth may be related by a common genesis (if these L-amino acids are the terrestrial proteinaceous ones). The alternative possibility, that the amino acids are derived from forward terrestrial contamination, will be quantitatively assessed through controls that determine the degree and composition of residual terrestrial spacecraft contamination. Compositional analyses thus play a pivotal role in the search for life on Mars.

A result indicating no organic target compounds are detectable above the parts-per-trillion detection level will be investigated by the oxidant instrument to establish if the sample environment was capable of preserving organic compounds. This analysis will provide further understanding of the potential for organic compounds to survive the harsh conditions presently found on Mars.

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