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Special Paper

The *Urey* Instrument: An Advanced *In Situ* Organic and Oxidant Detector for Mars Exploration

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Harold C. Urey (1893–1981)

The organic and oxidant detector profiled herein was named in honor of Harold Clayton Urey, whose contributions to the field of isotope chemistry earned him the 1934 Nobel Prize in Chemistry. Along with his graduate student, Stanley L. Miller, he helped create a stable foundation for the study of the origin of life and paved the way for extraterrestrial exploration. We would like to recognize Urey for his vision in helping to create the field of prebiotic chemistry, which has evolved into one of the central disciplines of astrobiology. (Photograph from the Miller archives in the Mandeville Special Collection at the Geisel Library, University of California at San Diego)

Abstract

The ***Urey*** organic and oxidant detector consists of a suite of instruments designed to search for several classes of organic molecules in the martian regolith and ascertain whether these compounds were produced by biotic or abiotic processes using chirality measurements. These experiments will also determine the chemical stability of organic molecules within the host regolith based on the presence and chemical reactivity of surface

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and atmospheric oxidants. ***Urey*** has been selected for the Pasteur payload on the European Space Agency's (ESA's) upcoming 2013 ExoMars rover mission. The diverse and effective capabilities of ***Urey*** make it an integral part of the payload and will help to achieve a large portion of the mission's primary scientific objective: "to search for signs of past and present life on Mars." This instrument is named in honor of Harold Urey for his seminal contributions to the fields of cosmochemistry and the origin of life. Key Words: *In situ* measurement–Mars–Extraterrestrial life—Biosignatures—Atacama Desert. Astrobiology 8, xxx–xxx.

Introduction

Measurements performed on the martian regolith during the 1976 Viking missions revealed that the surface minerals at the landing sites were chemically reactive with respect to the degradation of organic compounds. Major experimental findings of Viking which form the basis of this conclusion were (1) the liberation of O_2 gas after soil samples were exposed to water vapor in the Gas Exchange Experiment (GEx) (Oyama and Berdahl, 1977), (2) the rapid decomposition of aqueous organic material by martian regolith samples in the Labeled Release Experiment (LR) (Levin and Straat, 1977), and (3) the absence (less than a few ppb) of detectable organic compounds in regolith samples analyzed by the Gas Chromatograph Mass Spectrometer (GCMS) (Biemann *et al.*, 1977). The most widely accepted explanation for the GEx and LR results is the presence of oxidants in the martian soil. The combined results of the Viking GEx, LR, and GCMS led to the hypothesis that the GEx and LR oxidants are the cause of the oxidative decomposition of organic compounds in the martian environment and at least 3 different oxidizing species are needed to explain all the experimental results (Klein, 1979).

Experimental laboratory simulations have recently established that the Viking GCMS would not have detected key biomolecules, such as amino acids, if the bacterial density were less than $\sim 10^7$ bacterial cells per gram (Glavin *et al.*, 2001), as originally pointed out by Klein (1978). Oxidation of organic matter on the martian surface would have likely produced non-volatile diagenetic alteration products such as mellitic acid salts (Benner *et al.*, 2000), which also would have been undetectable by Viking. Another explanation for the apparent failure of the Viking GCMS to detect organic compounds is that the compounds may have been destroyed by exposure to harsh ionizing radiation from space and endogenous radioactive elements within the top ~1 m of the martian regolith (Kminek and Bada, 2006). Therefore, although Viking clearly demonstrated that the levels of organic molecules on the near-surface of Mars are depleted even below the expected levels due to meteoritic input, the results did not conclusively demonstrate the absence of organic compounds in the near subsurface. Higher-sensitivity analyses of samples from beneath the radiolyzed zone or within minerals that offer protection from radiation and surface oxidation are necessary to allow the best chance at detecting organic molecules on Mars. Subsurface drilling capabilities are included in the current 2013 ESA ExoMars rover specifications and are compulsory for mission success.

Recent results from the NASA Mars Exploration Rovers provide compelling evidence that liquid water was once present on Mars (Squyres *et al.*, 2004). The detection of sulfate minerals and phyllosilicates by the OMEGA instrument on ESA's Mars Express (Poulet *et al.*, 2005) has yielded further evidence of near-surface evaporitic deposition and aqueous alteration. Although the timescale, duration, and frequency of martian surface water bodies are unknown, they could have provided a habitable environment, or at least a location, for prebiotic chemistry to have occurred in the past.

These combined findings indicate that one key prerequisite for life, liquid water, once existed on Mars. However, the major unknown is whether organic compounds ever existed or perhaps still persist on the surface of Mars. On the basis of what we know now, it is apparent that if there are organic compounds on Mars, they are present at low concentrations, and their detection requires extraordinary sensitivity. In addition, the role of oxidants in the preservation of organic material within the martian regolith needs careful examination. Thus, in the last decades, considerable effort has been made to develop state-of-the-art *in situ* instrumentation to search for organic compounds on Mars as well as evaluate the oxidation potential of the surface.

Urey consists of instrumentation that has been in development for over 15 years and is specifically designed to assess the possible presence of organic compounds at sensitivities several orders of magnitude greater than those of the Viking GCMS or other comparable instrumentation. The primary scientific objectives of the ***Urey*** experiments are to investigate the following questions:

- At what concentrations are organic molecules present in the martian regolith?
- Can a biotic or abiotic origin be determined from the composition and chirality of detected amino acids?
- Are organic compounds degraded in near-surface environments on Mars, and do diagenetic processes control the abundance and distribution of detected organic compounds?

The presence of organic compounds alone does not unequivocally demonstrate the existence of life on Mars because there are abiotic pathways that can generate many of these compounds (Bada, 2004). Many surficial organic compounds have undoubtedly been derived from exogenous delivery or possibly generated by endogenous prebiotic chemistry, similar to production mechanisms on early Earth (Chyba and Sagan, 1992). ***Urey's*** capacity to carry out amino acid chirality measurements can evaluate whether the detected organic compounds were derived from biological activity or abiotic formation pathways.

The ***Urey*** objectives are derived from the most accepted understanding of the Viking experiment results: levels of organic compounds in the near-surface of Mars are extremely low, and there is evidence for at least 3 different oxidants in the martian regolith (Klein, 1979). There is likely a relationship between the oxidizing characteristics of the martian regolith and the abundance and distribution of organic compounds. ***Urey*** will target several molecular classes of organic compounds at very low concentration levels and utilize chemical sensors to detect and characterize oxidants present in identical samples. These complementary analyses will ex-

amine the hypothesis that oxidants and organic matter on the surface of Mars are inversely correlated.

Urey Molecular Targets and Experiments

Urey's scientific experiments specifically address life detection and soil chemical reactivity. The life-detection strategy involves the analysis of the martian regolith for the most abundant classes of terrestrial biomolecular compounds at state-of-the-art detection limits. The presence of polycyclic aromatic hydrocarbons (PAHs) is also investigated to determine the concentrations of some of the most abundant carbon compounds in the galaxy (Ehrenfreund *et al.*, 2006) that may have been derived from exogenous delivery or diagenetic surface reactions. The second group of experiments profiles the chemical reactivity of the soil to correlate these measurements with the abundance and distribution of biomolecules or to explain their absence.

Organic compound detection and characterization

Any investigation into life detection must be focused on the major molecular classes at the core of terrestrial biology and presumably extraterrestrial biochemistry (Pace, 2001). The ***Urey*** organic detector is designed to detect trace levels of primary target compound classes, including amino acids, nucleobases, amino sugars, amines, and PAHs.

Amino acids as protein comprise approximately 55% of prokaryotic cellular mass (Neidhardt, 1996). The most abundant of these protein amino acids have been identified in meteorites (Botta and Bada, 2002) and can be readily synthesized in prebiotic chemistry experiments (Bada, 2004). It is unknown whether life on other planets is modeled after terrestrial biochemistry; however, the ubiquity of amino acids on Earth and the potentially large amount of exogenous delivery (Chyba and Sagan, 1992) suggest that they would have been available for biochemistry on other planets (Sephton and Botta, 2005).

One crucial property of amino acids other than glycine is their chirality. The α-carbon in the amino acid structure provides for 2 mirror image configurations, called enantiomers, based on the relative orientation of the side group (Fig. 1). Terrestrial protein amino acids consist of only one enantiomeric configuration (the L-form), while abiotic pathways yield equal amounts of D- and L-enantiomers, a racemic mixture. There is no biological reason why proteins in extraterrestrial life would need to be based on L-amino acids as on Earth. Proteins composed of entirely D-amino acids have been synthesized and are as catalytically active as their L-amino acid counterparts (Milton *et al.*, 1992); thus it is assumed that life elsewhere could be based on either L- or D-amino acids. The marked difference between homochiral biological and racemic abiotic composition permits ***Urey*** to discriminate the source of the detected amino acids by resolving their enantiomeric abundances.

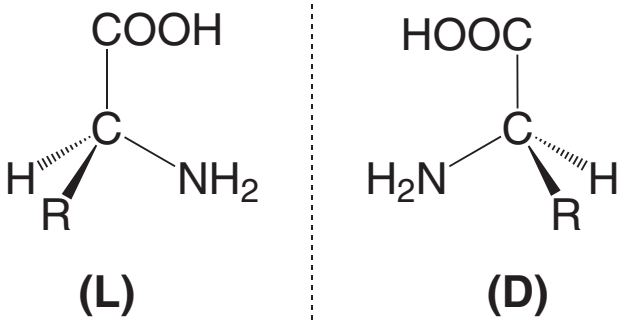

FIG. 1. Amino acid enantiomers: terrestrial proteins are composed of the L-configuration exclusively, D-enantiomers are created as a result of racemization, and abiotic synthesis generates no selectivity between the two.

The chirality of amino acids associated with deceased terrestrial life changes over time due to the interconversion of amino acids from the biological L-enantiomer to the abiotic D-enantiomer. Racemization proceeds over geological time until a D/L ratio of 1 is attained, and application of the kinetics of this reaction has proved useful in determining the geological age of terrestrial samples. On Mars, it is expected that racemization is extremely slow because of the cold, dry conditions, and any chiral signature of previous life should be preserved for billions of years (Bada and McDonald, 1995; Aubrey *et al.*, 2006). If chiral amino acid signatures were detected on Mars, the degree of racemization would allow for the determination of the ages of these extinct organisms.

Terrestrial life makes use of the canonical 5 nucleobases—adenine, guanine, cytosine, thymine, and uracil—as components of DNA and RNA. These compounds contribute almost 25% to the mass of a prokaryotic cell (Neidhardt, 1996). ***Urey*** also targets nucleobase derivatives, such as nucleotides and nucleosides, as well as nucleobase degradation products that are common components of oceanic organic matter (Benner and Kaiser, 2003).

Amino sugars and aliphatic amines are other classes of nitrogenous compounds, which have been suggested to be the most important target in the search for extraterrestrial life (Capone *et al.*, 2006). Sugars only make up approximately 2% of the total mass of a prokaryotic cell (Neidhardt, 1996), and the most common terrestrial amino sugars—glucosamine, galactosamine, and manosamine—only represent a small fraction of this reservoir. Amines such as methylamine and ethylamine are produced from the decarboxylation of the amino acids glycine and alanine, respectively, while diamines are known organic matter degradation products (Saccani *et al.*, 2005). The importance of these compounds to terrestrial biochemistry makes them high-priority targets for the search for life on Mars, and their diversity exhibits the large range of compounds detectable by ***Urey***.

Polycyclic aromatic hydrocarbons are part of the largest molecular carbon reservoir in the Universe (Ehrenfreund *et al.*, 2006) and are perhaps the most abundant class of free organic molecules in space (Botta and Bada, 2002). Because of their ubiquity and abundance in meteorites, significant amounts of PAHs were probably delivered to the surface of early planets during impact events (Ehrenfreund *et al.*, 2002). Although they have no current biological role, PAHs can be formed from biogenic precursors, such as sterols and other cyclic organic molecules (Wakeham *et al.*, 1980), and they can persist over geological timescales due to their high chemical stabilities (Neff, 1979). Thus PAHs are expected to be relatively copious on the surface of Mars due to extraterrestrial delivery, possible generation via diagenetic pathways, and their refractory nature.

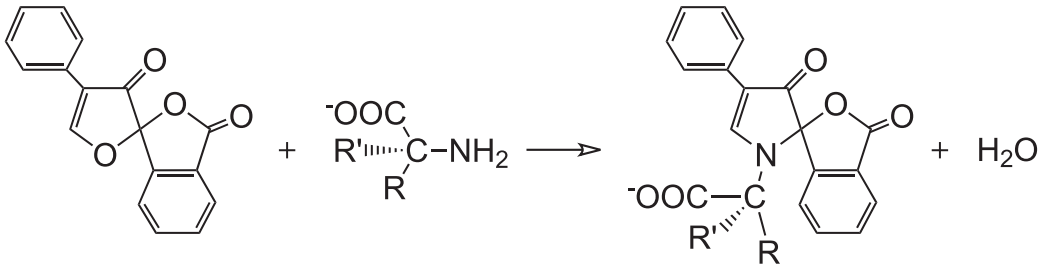

FIG. 2. Reaction of fluorescamine with an amino acid.

Fluorescence detection offers superior detection limits with high compound specificity and has the capability to identify single molecules (Moerner and Orritt, 1999). PAHs are naturally fluorescent under UV excitation and allow for direct analysis by fluorescence detection. Quantification of amines is possible after reaction with the fluorescent adduct fluorescamine (Fig. 2). This derivatization method specifically targets the amino group of primary amine compounds, including amino acids, nucleobases with exocyclic amine groups (*e.g.*, cytosine and adenine), diamines, and amino sugars. These are the primary classes of simple bioorganic compounds that are targeted with the fluorescamine reaction. Proteins from intact bacterial cells will be detected as amino acids by our methods, and nucleobases will be quantified from DNA and RNA. Resolution of these primary amine compound derivatives is possible with the microcapillary electrophoresis (μ-CE) instrument. Amino acid chirality resolution is achieved after a reaction with a chiral adduct following the fluorescamine labeling protocol. ***Urey*** utilizes the reaction with β-cyclodextrin (β-CD) in order to provide a method to resolve amino acid enantiomers (Skelley and Mathies, 2003). Because of the low aqueous solubility of β-CD, 2-hydroxypropyl-β-cyclodextrin (HPβCD) is used for derivatization before chirality determination. This extra step allows for the separation of amino acid enantiomeric pairs, which are otherwise chemically indistinguishable from one another.

The integration of ~20 α-amino acids in biological proteins as only the L-enantiomers is considered a biosignature of terrestrial life (Kvenvolden, 1973). Detection of a suite of amino acids different from those in terrestrial proteins or those generated by Miller-Urey chemistry on Mars would imply an independent biosphere and alternate origin of life or markedly different martian prebiotic chemistry. Figure 3 illustrates the stages in the origin of life from prebiotic chemistry to extinct life and the expected biosignatures of the amino acids, their chirality, and PAHs at each of these stages. Assuming they have not been degraded, PAHs and racemic amino acids should be detectable, whether from exogenous delivery or prebiotic chemistry, if it has occurred on the martian surface. The presence of a significant excess of either the L- or D-amino acid enantiomer would be compelling evidence for the existence of life on Mars (Bada, 2001), more convincingly so than the presence of these biomolecules alone (*e.g.*, nucleobases, amino sugars). Any chiral amino acid biosignature from extinct life would have been altered over time due to racemization, resulting in an increase in the enantiomeric ratio (D/L). Other diagenetic pathways, such as degradation of nucleobases and amino sugars, would also be observed along with the possible generation of PAHs as diagenetic oxidation products of organic matter. These relationships and associated biosignatures of prebiotic chemistry, extant, and extinct life can be used to determine the origins of any detected target compounds.

Establish surface and subsurface oxidation mechanisms and rates

Besides searching for *in situ* evidence of life, ***Urey*** also has the capacity to investigate the reactivity and chemistry of the surface to better assess the fate of organics on Mars. Some have suggested that the high UV-flux and ionizing radiation environment has resulted in the generation of powerful oxidants within the surface and near-surface regolith. These oxidants may have altered any evidence of life in these areas as well as any organics derived from meteoritic input. There are undoubtedly a number of complex, photochemically driven oxidative processes on Mars that involve interrelated atmospheric, aerosol, dust, soil, and organic chemical interactions. Hypotheses that attempt to explain oxidant generation on the surface of Mars in relation to the Viking results include UV generation of superoxide radicals (Yen *et al.*, 2000), triboelectric enhancement of H_2O_2 production (Atreya *et al.* 2006), and the deposition of sulfuric acid and other oxidizing acids in the martian soil (Quinn *et al.*, 2005).

The role of the interaction between Mars surface oxidants and organic compounds is unknown to a large extent. ***Urey*** will establish a correlation between the levels of organic compounds, oxidant concentration, water abundance, and UV flux at various sampling localities and as a function of depth in the subsurface. ***Urey*** measurements will help to discrim-

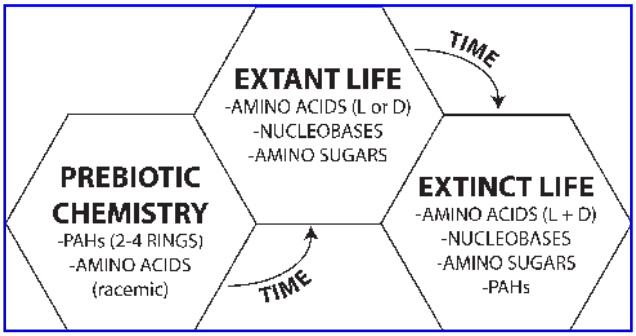

FIG. 3. Expected target compounds and amino acid chiralities associated with prebiotic chemistry and extant/extinct life.

inate between various oxidant formation mechanisms and their effect on the degradation of organics in the martian regolith. However, this is complicated by the fact that several of these processes are likely occurring simultaneously on Mars.

Component Instrumentation Overview

The ***Urey*** integrated instrument suite consists of 2 analytical systems: the first designed to determine trace organics and PAHs and the second to measure the oxidative activity of the regolith and atmosphere. The weight of the instrument payload is approximately 4.4 kg, with external dimensions of 21 × 20 × 16 cm. The ***Urey*** instrument suite consists of the following integrated subsystems:

- Subcritical Water Extractor (SCWE)
- Mars Organic Detector (MOD)
- Micro-Capillary Electrophoresis Instrument (μ-CE)
- Mars Oxidant Instrument (MOI)

Each of these systems contributes to the science output via sample processing (SCWE/MOD/μ-CE) or direct measurements (MOI/MOD/μ-CE), or both. ***Urey*** is unique in that it provides a stand-alone, end-to-end sample-processing instrument with both extraction, analytical, and sample-handling capabilities. Figure 4 shows a concept illustration of the ***Urey*** Mars organic and oxidant detector along with photographs of the individual subsystems. Presently, the component instruments are not a packaged flight-ready instrument; rather, each technology is represented by a miniature field version that together represent an inline sample-processing method for organic detection. The ***Urey*** instrument represents the integration of the field prototypes that are currently utilized for instrument development and optimiza-

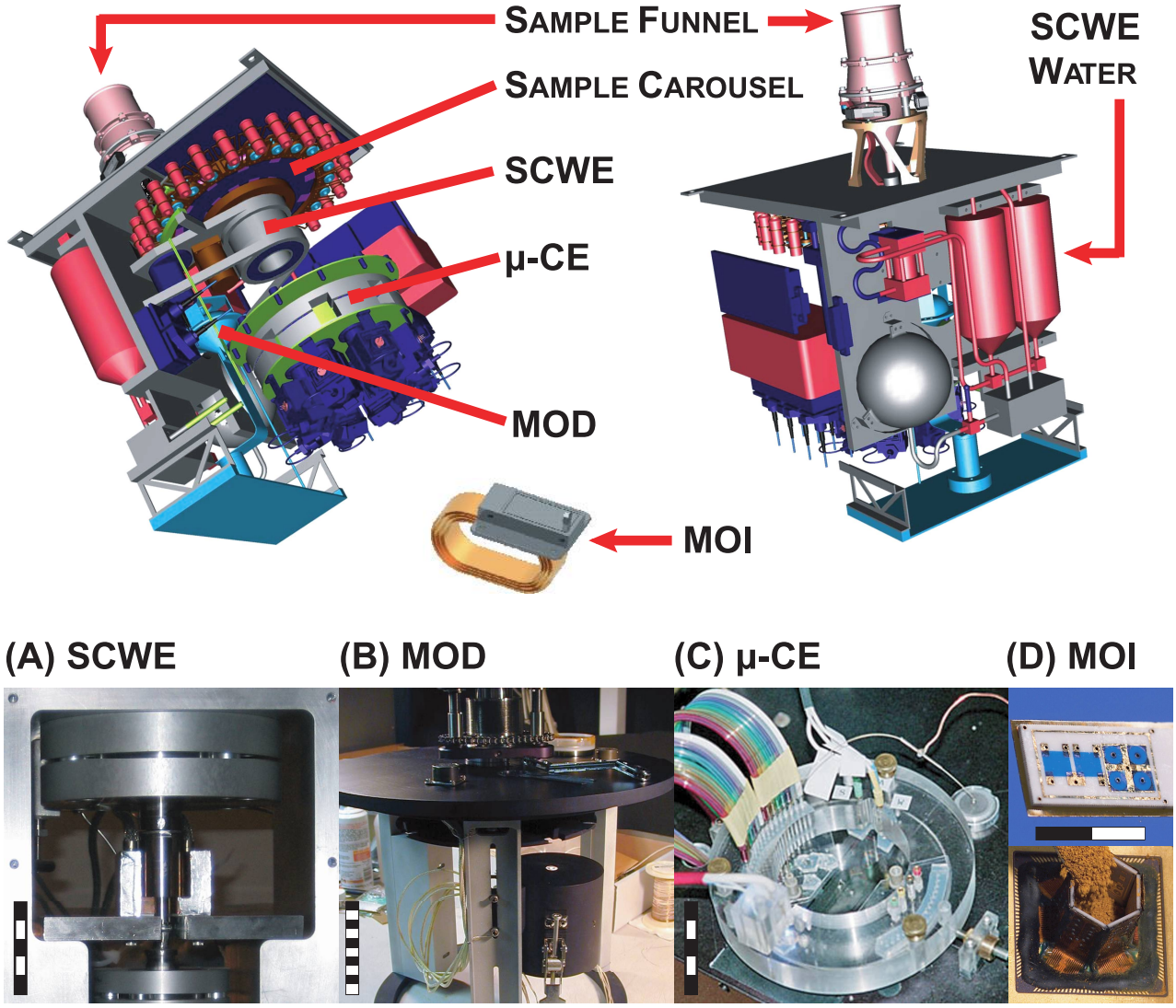

FIG. 4. Concept illustration of ***Urey***—Mars organic and oxidant detector (images courtesy NASA-JPL) and photographs of field subsystem prototypes (scale bar graduations ~1 cm): (**A**) Sub-Critical Water Extractor, (**B**) Mars Organic Detector, (**C**) μ-Capillary Electrophoresis instrument, and (**D**) Mars Oxidation Investigation deck unit (top) and internal unit (bottom).

tion. The instrument suite is currently rated at a NASA Technology Readiness Level (TRL) of 5. Further demonstration of the advanced capabilities of ***Urey*** via laboratory and field testing, and subsequent development of smaller subsystems, will increase the TRL levels over the next year. The final flight-ready instrument will be built over the next 2 years and will be the central component on the Pasteur rover payload for ExoMars 2013.

The ExoMars sample-delivery system first delivers 800 mg of pulverized regolith sample to the ***Urey*** sample funnel, which aliquots solid samples to the SCWE (600 mg) and the MOI (200 mg). Simultaneous characterization of the soil oxidants and organic constituents then begins. The ***Urey*** organic analyzer first extracts solid samples with high-temperature high-pressure water (SCWE), concentrates and labels the extract by sublimation coupled with solid-state fluorescamine labeling (MOD), and analyzes the sample via laser-induced fluorescence (LIF) and μ-capillary electrophoresis (μ-CE) with parts-per-trillion sensitivity (pptr) by fluorescence detection (LIF). Direct measurement by LIF on the sublimation extract can distinguish between naturally fluorescent PAH compounds and fluorescamine-labeled primary amine compounds, though the best separation is achieved by multiple analyses with the μ-CE instrument. After this organic characterization, the aqueous extract can be delivered to other inline instruments in the Pasteur payload. The ***Urey*** MOI soil oxidant profiling monitors the regolith's properties during the addition of water to characterize soil reactivity levels. Integrated electronics and mechanical subsystems tie the analytical components into a cohesive instrument package, and data are transferred to the team via the ExoMars satellite link. Detailed information about the component instruments is listed below.

Subcritical Water Extractor (SCWE)

A unique property of water is that its dielectric constant decreases with increasing temperature and pressure (Josephson, 1982), making it exhibit properties chemically similar to organic solvents under these conditions. It has been demonstrated that subcritical water can be used to extract organics from botanicals (Ibañez *et al.*, 2003; Ong *et al.*, 2006), fish meat (Yoshida *et al.*, 1999), and soils (Hartonen, 1997). The advantages of subcritical water extraction include the ability to extract a variety of organic compounds efficiently with a relatively benign solvent.

The SCWE has been developed for front-end soil extraction of organics from the martian regolith. The solid sample from the ***Urey*** sample funnel is first delivered into one of 24 SCWE sample carousel slots (Fig. 5). The loaded carousel cell is then filled with 30°C water from the SCWE water tanks and pressure sealed at 20 MPa with the use of a high-pressure argon supply prior to performing the organic extraction. After a short equilibration time, the water is exhausted into a waste collection tank to prevent rover cross contamination. This preliminary low-temperature sample rinse is sufficient to remove most of the soluble salts from the sample, which may otherwise interfere with the organic analyses. The second stage is the extraction of the organics at a designated temperature between 100°C and 300°C at 20 MPa for a number of minutes. The SCWE protocol may be optimized to extract any target compound from the martian regolith; however, the extraction conditions are optimized for ***Urey's*** target compounds, specifically amino acids. Utilization of the ***Urey*** SCWE not only extracts amino acids from soil and regolith samples, but it also provides necessary thermal energy for hydrolysis of any polymeric organic matter. Any partial hydrolysis during SCWE extraction is completed during the sublimation isolation procedure with the MOD instrument.

With the use of Atacama soils as a proxy, the SCWE protocol has been optimized at 200°C for 10 minutes at 20 MPa (Amashukeli *et al.*, 2007) and will likely be similar for most martian regolith terrestrial soil analogues. Because each of the 24 carousel cells is used for only one extraction, extracted samples remain inside the instrument for the duration of the mission. More details on the SCWE specifications and efficiency can be found in this issue (Amashukeli *et al.*, 2008).

Mars Organic Detector (MOD)

The MOD is an advanced sublimation apparatus developed within the last decade for the extraction and analysis of organics on Mars (Kminek *et al.*, 2000). It has been demonstrated that the MOD can effectively isolate amino acids (Glavin *et al.*, 2001) and nucleobases (Glavin *et al.*, 2002) at Mars ambient pressures (~5 torr). Microbial cell concentrations can then be estimated based on the detected amounts of nucleobases (Glavin *et al.*, 2004). Microbial cell enumeration based on amino acid recovery is also possible through these methods because microbial proteins are hydrolyzed during the MOD sublimation (Glavin *et al.*, 2001), concentrated on the cold finger, and isolated for analysis. Coupled with SCWE extraction, the degradation of amino acids to amines during sublimation is minimized, though these products are also detectable by ***Urey***. Amino acids are robust enough to survive the sublimation protocol and subsequent solid-state fluorescamine labeling. The design of the ***Urey*** MOD component includes a sublimation chamber, heated at high temperatures under reduced pressure, to sublime volatile organic compounds. It also includes a cooled sublimation collection disk on which volatile organic compounds are deposited. Twenty-four MOD collection disks are held within the sample carousel, and each has been pre-coated with fluorescamine on one half of the disk so that primary amine compounds are tagged with this fluorescent reagent.

Following the SCWE extraction, approximately 1 ml of SCWE water extract is delivered directly to MOD, where freeze drying strips water from the sample. Sublimation then begins at Mars ambient pressure on the solid sample through a temperature protocol from 125–350°C to sublime amino acids, nucleobases, and their degradation compounds, nucleotides, nucleosides, and amino sugars. The temperature is ramped up to 450°C to sublime PAHs. The volatile organics sublime and condense upon the cold collection disk, which is held at a temperature of −10°C by a cold finger. After the MOD sublimation protocol is completed, the sublimation collection disk is moved into position for the LIF system to measure the fluorescence of the uncoated side of the MOD sample disc to verify whether PAHs are present. The fluorescamine-coated portion of the disc is then targeted to determine the abundance of primary amine compounds. Depending on what section of the disk is targeted, the fluorescence will be from PAHs or fluorescamine derivatives. Analyses at multiple wavelengths can distinguish between the two. After these preliminary measurements verify the

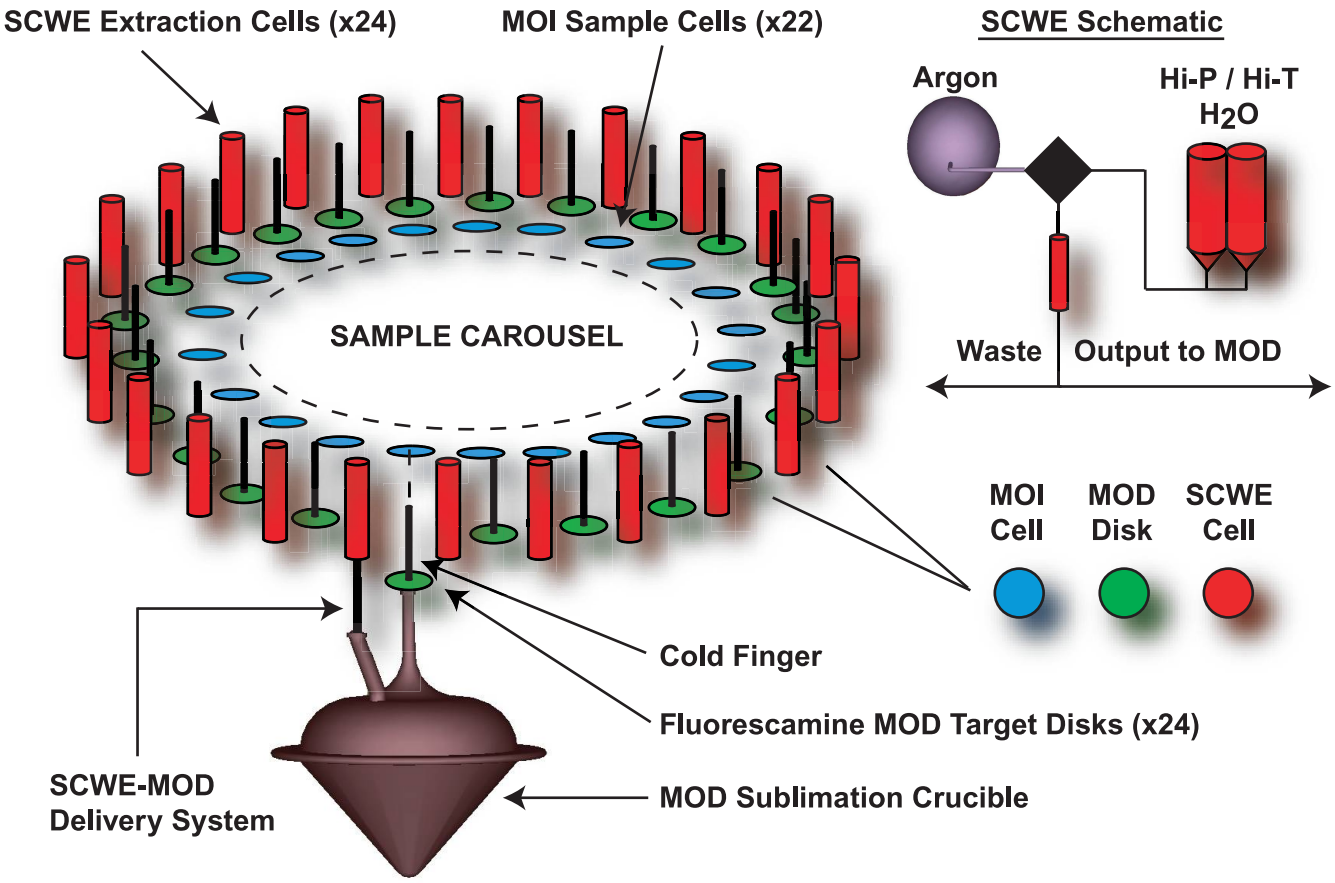

FIG. 5. ***Urey*** sample extraction system including MOD, SCWE, MOI internal unit, and sample carousel engineering designs.

presence of ***Urey's*** target organic compounds, the μ-CE instrument extracts the organic sublimate from the fluorescamine-labeled side of the collection disk with a small amount of water (~10 μl) for further analyses and separation of primary amine compounds. The labeled amines in this fraction are separated within the μ-CE analytical channel and resolved by fluorescence detection after excitation at 400 nm, similar to the methods of Skelley *et al.* (2005). PAH compounds can be further analyzed with the μ-CE system after extraction from the unlabeled half of the sublimation disk with a cyclodextrin solution (optimized to increase PAH solubility) and classified according to their emission profile and mobility.

Figure 5 illustrates the MOD design and coupling with the sample carousel and SCWE. The SCWE cells are held on the outside, and the fluorescamine-coated sublimation collection disks are held in the middle ring. The MOI soil reactivity cells are located on the inside of the sample carousel. The SCWE system and MOD sublimation collection disks are fully sealed prior to the extractions, and the MOD unit is

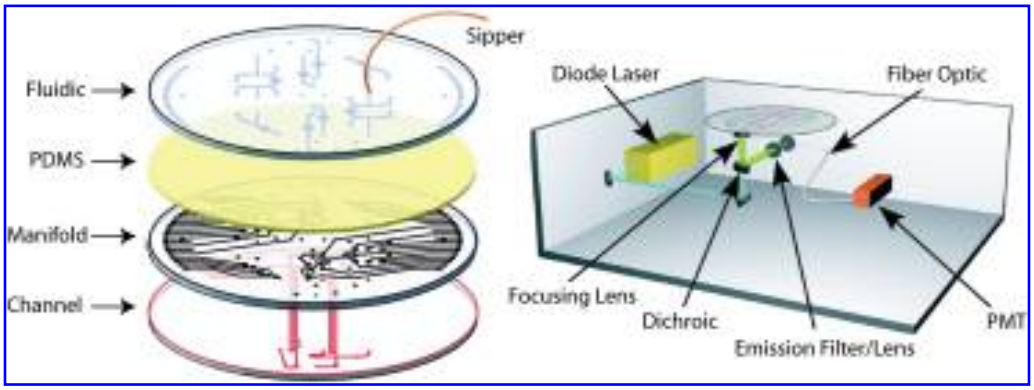

FIG. 6. μ-CE lab-on-a-chip wafer schematic and internal arrangement of the analytical unit [modified from Skelley *et al.* (2005)]. PDMS, polydimethylsiloxane; PMT, photomultiplier tube detector.

thoroughly cleaned between sublimation runs with high-temperature water to prevent any sample communication.

Micro-Capillary Electrophoresis (μ-CE)

The ***Urey*** μ-CE component consists of (1) a manifold system to bring in the sample (via the sipper) and control the ambient atmosphere over the wafer surface, (2) a laminated multilayer lab-on-a-chip wafer stack that performs fluidic manipulations and electrophoretic analysis, and (3) a confocal laser fluorescence detection system (LIF) that records fluorescence from the desired electrophoretic channel. The design of the μ-CE instrument (Skelley *et al.*, 2005) is shown in Fig. 6, and the analytical methods are detailed by Skelley and Mathies (2003). More recently, these methods have been demonstrated to detect and quantify nucleobases (adenine and cytosine), nucleobase degradation products, nucleotides and nucleosides, mono- and diaminoalkanes (Skelley *et al.*, 2006), and amino sugars (Skelley and Mathies, 2006).

The MOD LIF detector can confirm the presence of ***Urey*** target molecular compound classes (*i.e.,* PAHs and primary amines); however, μ-CE analyses can specifically characterize both primary amine compounds and PAHs present in martian regolith extracts. The MOD extract from the fluorescamine-coated half of the sublimation collection disk is dissolved by 10 μl of water from the μ-CE reservoir and routed by internal microfluidic pumps through the capillary sipper to a sample channel. Because this MOD aliquot has already undergone solid-state labeling with fluorescamine, the primary amine compounds will have been detected by LIF. An aliquot of this 10 μl aqueous extract is delivered to the sample reservoir and injected into an analytical channel filled with buffer (regular injection). Voltage is applied across the cathode and anode reservoirs (15 kV), and the fluorescence detector (LIF) records the fluorescence intensity for 120 seconds after injection. After this separation is complete, a second separation is performed on an identical aliquot with a more concentrated sample extract injection, which involves the direct injection of the sample aliquot into the column buffer for 2 seconds (2 s direct injection). The 2 s direct injection method increases the detection sensitivity at lower compound resolution between trace neutral and acidic amine-containing compounds (Skelley *et al.*, 2005). The third separation is an injection of an identical extract aliquot with a standard labeled amino acid mixture analyzed by regular injection. These injections will identify and quantify all primary amine target compounds that are present in the extract with subnanomolar sensitivity. The regular injection detection limit is 13 n*M,* the 2 s direct injection detection limit is 1.3 n*M;* and, if necessary, a 10 s direct injection method can provide up to 130 p*M* sensitivity (Skelley *et al.*, 2005).

To resolve amino acid chirality, 2 more sample aliquots are run on the μ-CE via regular injection (for increased resolution) utilizing a running buffer containing HPβCD with and without a standard. Assuming that each sample injection is 2 μl out of 10 μl total extract from 600 mg of regolith, of which only $^1/_2$ is labeled with fluorescamine, each aliquot represents ~60 mg of regolith. With the superior detection limits of the μ-CE offered by direct injection methods (~100 p*M* injected sample concentration), the amino acids from bacterial concentrations of $\sim 10^3$ cells/gram can be detected. This is equivalent to pptr sensitivity on a mass basis. If the amino acids in the martian regolith have been degraded, their decarboxylation products, such as methylamine, ethylamine, ethanolamine, isopropylamine, and isobutylamine, should be detected in the sample extracts.

Figure 7 shows electropherograms from various μ-CE analyses. These results demonstrate the successful separation of amino acids within a laboratory SCWE-extracted Atacama surface soil sample (A), the difference in sensitivity and resolution between regular injection and 2 s direct injection (B), and the analyses of identical extracts labeled with fluorescamine in regular (C) and 15 m*M* HPβCD (D) buffers. The sample analyses show positive detection and chirality resolution of amino acids within low ppb level samples from the Atacama Desert and demonstrate why multiple injection analyses of identical sample extract aliquots are necessary for detection of trace pptr amounts of organic compounds.

Analyses of the MOD extract also allow for increased sensitivity and characterization of PAH compounds. Because PAHs are relatively insoluble in water, they are extracted from the unlabeled side of the MOD sublimation disk with a cyclodextrin solution instead of water to provide greater PAH solubility. The sipper extracts the PAHs from the sample disk with the use of 10 μl of cyclodextrin solution and routes the solution to a μ-CE channel where separation and characterization of PAH components occur via fluorescence detection. Laboratory demonstration of this capillary electrophoresis application can be found elsewhere (Nie *et al.*, 1993); however, these μ-CE separations and analyses will only be necessary if large amounts of PAHs are confirmed by initial LIF analyses on the sublimation disk. Currently, the plans are to analyze the PAH extract via μ-CE regular injection for increased compound resolution.

The μ-CE separation and detection of fluorescent derivatives of primary amines allow for ultra-high resolution between these compounds with the lowest detection limits (pptr sensitivity) available for organic detection. These detection limits are several orders of magnitude lower than the Viking instruments' (~10,000×) and offer the best methodology for detecting bioorganic compounds on Mars. The application of μ-CE separation technology to resolve PAHs broadens the range of detectable target compounds to include one of the largest known carbon reservoirs in the Universe. The labeled sublimate aliquots can be routed to other ExoMars instruments after μ-CE analyses by ***Urey***.

Mars Oxidant Investigation (MOI)

The MOI is designed to establish the presence of reactive chemical species in the martian soil and dust and provide detailed reaction model system measurements to enable comprehensive Earth-based study. This approach uses chemical sensors to quantify the effective reactivity of the martian soil and dust with a set of well-characterized thin-film test compounds that exhibit different responses to oxidation, including different reactivities and reaction pathways. The different kinetics and reactivities will be used to probe the chemical properties of the unknown reactants in the soil and dust by monitoring the changes in the probe films placed in contact with the soil and dust samples as a function of time, temperature, and relative humidity, or partial pressure of water. The objectives of the MOI investigation are to (1) correlate reaction rates of experimental test

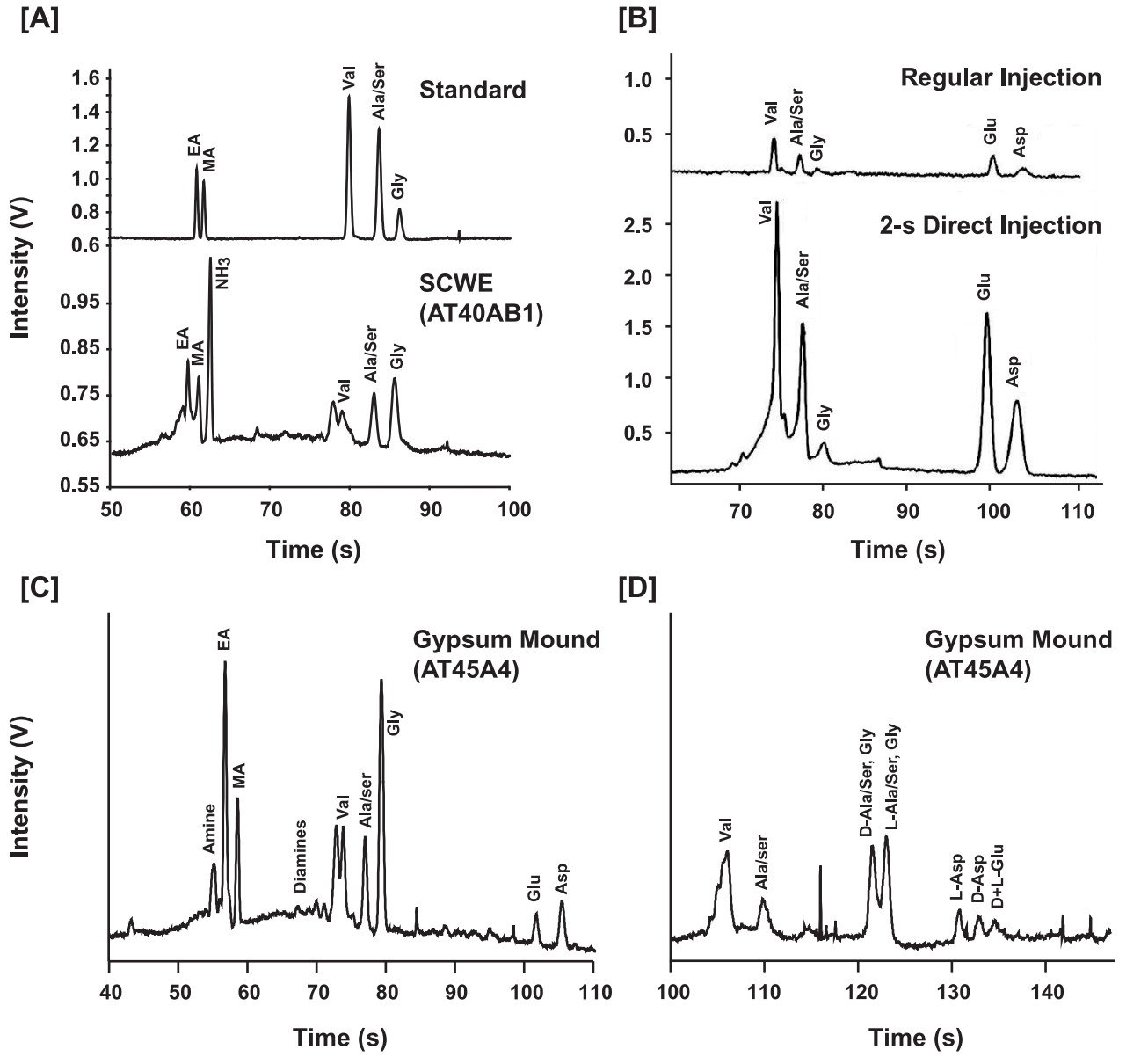

FIG. 7. μ-CE electropherograms of (**A**) fluorescamine-labeled amino acid standard ($\sim 10^{-15}$ total moles) and ppb level Atacama Desert sample AT40AB1 extracted by static laboratory SCWE at 200°C for 10 minutes, (**B**) regular injection ($\sim 10^{-16}$ total moles) and 2 s direct injection ($\sim 10^{-15}$ total moles) results from fluorescamine-derivatized amino acid equimolar standard demonstrating $\sim 10\times$ increase in sensitivity with the μ-CE direct injection technique [modified from Skelley *et al.* (2005)], (**C**) SCWE field-extracted subsurface gypsum mound sample AT45A4 from the 2004 Atacama Desert field test derivatized with fluorescamine [modified from Skelley *et al.* (2007)], and (**D**) chirality results from the identical gypsum extract quantified after reaction with fluorescamine in HPβCD buffer [modified from Skelley *et al.* (2007)]. Ala, alanine; Asp, aspartic acid; EA, ethylamine; Glu, glutamic acid; Gly, glycine; MA, methylamine; Ser, serine; Val, valine.

compounds with dust abundance, UV flux, and temperature, (2) determine the oxidation potential of the martian surface environment and the rate of oxidation, especially of organics as a function of sample collection depth, and (3) characterize the functional groups responsible for the oxidizing potential of the martian dust and atmosphere. The MOI data and the measured concentrations of organics within the regolith will allow for examination of the proposed inverse relationship between soil oxidation potential and soil organic content.

There are 2 separate units of the MOI—the deck unit and the internal unit. The deck unit is modeled after the thermoacoustic oxidant detector, TAOS (Zent *et al.*, 1998), the Mars atmospheric oxidant sensor, MAOS (Zent *et al.*, 2003), and the recently developed atmospheric oxidation sensor (Quinn *et al.*, 2006). The deck portion of the MOI operates while exposed to the atmosphere to investigate the chemical oxidation potential of dust, UV, and atmospheric gas exposure. The deck MOI characterizes the reactive nature of surface environments with a filtered sensor configuration,

which is designed to discriminate between Mars oxidant formation hypotheses based on the detected species. The internal unit is modeled after the Mars Oxidant Experiment, MOx (Grunthaner *et al.*, 1995; McKay *et al.*, 1998) and has been experimentally demonstrated on samples in the Atacama Desert (Quinn *et al.*, 2005).

The MOI internal unit is located within the sample carousel and used to characterize the chemical reactivity of the regolith samples. It has the capability to reproduce conditions similar to those of the Viking experiments with improved thermal and sampling resolution. The addition of water to the regolith sample allows for observation of a high level of chemical reactivity. The soil reactivity is determined parallel to the SCWE extraction after an aliquot of the pulverized solid sample (200 mg) is partitioned to the internal MOI unit's powerful chemi-resistors.

The fundamental component of the MOI is a "chemical pixel," an 8×2 array of gold electrodes arranged on a sapphire substrate like the one illustrated in Fig. 8. One array is used per sample, and each of the 8 electrodes is coated with a different type of reactive film. MOI monitors changes in film electrical resistance as a function of time; and, from these measurements, chemical reactivity levels and oxidation processes are derived. The array electrode gaps and configurations are chosen to maximize the sensitivity to oxidation of each film. During an experiment, 8 of the sensing films are exposed to the environment, while 8 matched sealed films are controls. Resistance corrections for temperature and physical effects are compensated by the control samples. The reactive films include highly electropositive metals, organometallic redox indicators, semiconductors, and a set of organic functional groups. MOI detection sensitivity ranges from a few tenths of a monolayer to several monolayers of reaction (Zent *et al.*, 2003).

The sensor arrays are made of a chemically inert sapphire substrate, with filter sets for isolating the effects of UV and dust on chemical reactivity, and silicon nitride (SiNx) hermetic seals for maintaining film integrity prior to deployment. The effectiveness and reproducibility of the MOI sensing films depends on the extent to which they are delivered in pristine condition to their destination. To accomplish this, the films are encapsulated in a hermetically sealed enclosure. Micromachined top seal covers and filters are bonded to the substrate immediately following sensor film deposition. The seal cover is fabricated via bulk silicon micromachining and consists of a thick frame with suspended, thick films of silicon nitride. The silicon nitride film is strong enough to withstand more than 15 psi gauge differential across the membrane and has been tested to vibration loads of more than 500 G with use of the Proton launch vibration spectrum (Manning *et al.*, 1997).

Field Tests

Aspects of ***Urey*** have been demonstrated in comprehensive field experiments over the past 5 years. The first experiment at Panoche Valley, California, demonstrated the capabilities of the MOD and μ-CE during field analyses of terrestrial deposits of gypsum and jarosite (Skelley *et al.*, 2005). In this same study, the samples were analyzed back in the laboratory after aqueous laboratory extraction, and organic concentrations were found to be well above the detection limits of the μ-CE.

Another field experiment that demonstrated the validity of ***Urey*** components was accomplished in the Atacama

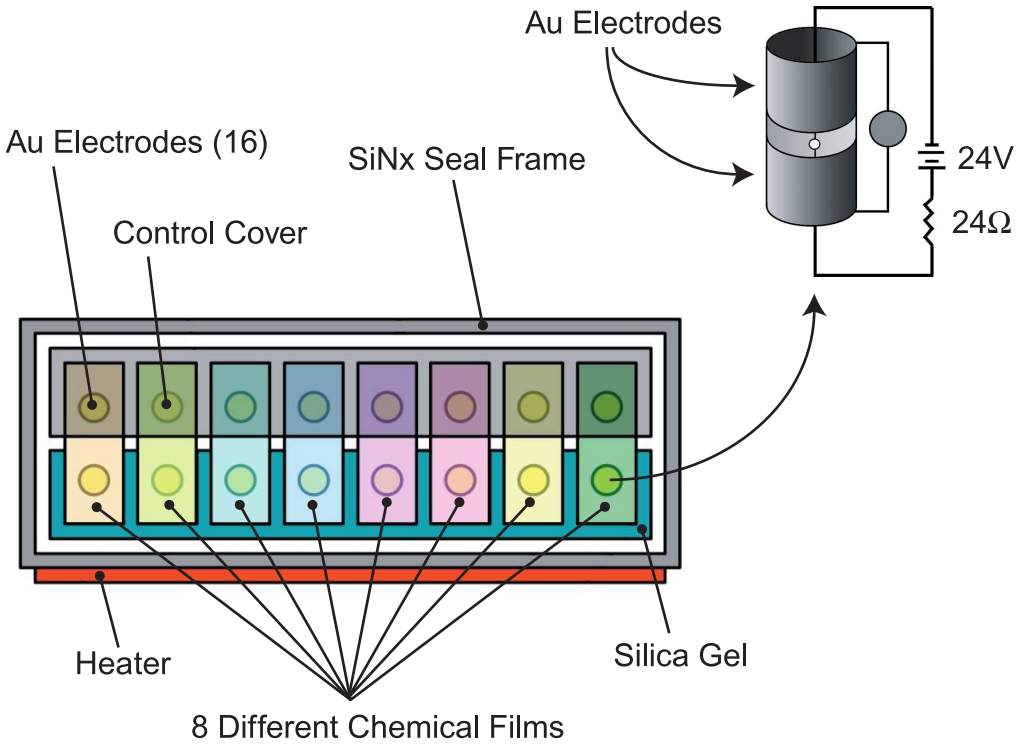

FIG. 8. MOI cell array schematic and single cell design. SiNx, silicon nitride.

Desert, Chile. The soils of the Atacama Desert have been suggested to be the best terrestrial analogue to the martian regolith (Banin, 2005) due to the region's extreme aridity, oxidizing conditions, and soil mineralogy. During this experiment, the MOD, μ-CE, SCWE, and MOI were transported to the Atacama Desert and run inline to demonstrate successful operation in a harsh terrestrial Mars analog environment on samples chemically similar to the martian regolith. The soil oxidant experiments and organic extraction field experimental results are profiled elsewhere (Quinn *et al.*, 2005; Skelley *et al.*, 2007).

These field campaigns have demonstrated the extremely high sensitivity of the μ-CE analytical instrument (pptr sensitivity) and validated the MOD and SCWE sample-extraction methods that are integrated into ***Urey***. The Atacama Desert MOI field study obtained soil oxidation measurements on regional dust and soils that are consistent with the presence of oxidizing acids, which may play a role in regulating the concentrations of organics in these surface soils. Organic matter concentrations in the Atacama Desert near-surface soils showed high spatial variability both laterally and as a function of depth. These results demonstrate that the search for life on Mars requires instrumentation with superior detection limits of important biomolecules (Bada *et al.*, 2005) as well as the scientific expertise to predict locations where viable organic matter may exist.

Field experiments of the ***Urey*** component instruments on terrestrial Mars analog samples offer the most rigorous scientific testing possible before flight to Mars on future missions. Although many aspects of martian surface organic chemistry remain unknown, the ***Urey*** methodology and protocols should be successful upon martian regolith samples with ultra-low organic concentrations. The SCWE is effective in extracting organic compounds from a wide range of soils with variable chemistries. Concentration of ***Urey*** target compounds from the bulk SCWE extract is achieved via sublimation. This procedure isolates volatile compounds at low pressure onto a collection disk coupled with fluorescamine derivatization of primary amines. There is no reason why compounds in the SCWE extract of the martian regolith should poison this reaction, because the MOD sample disks are coated with an excess of fluorescamine and it is not expected that compounds would be present that would completely inhibit this solid-state reaction. Testing on Mars analogues provides optimization of SCWE and MOD extraction conditions, which will contribute to an increased likelihood of success in organic detection on Mars.

Conclusion

The ***Urey*** instrument is an integrated suite of instruments designed to search the martian regolith for biomarkers at terrestrial laboratory state-of-the-art sensitivities and characterize soil chemistry and reactivity. ***Urey's*** capabilities of measuring amino acid chirality allow for the determination of whether the amino acids are of biological or abiotic origin. Furthermore, MOI measurements may clarify how oxidants may have affected the original suite of organic compounds over the geological history of Mars.

A positive result from ***Urey***, *i.e.*, the detection of target organic molecules, would be the first convincing demonstration that organic compounds are present on Mars. Any homochiral or excess enantiomeric signature would be strong evidence that the source of these organics is biological. A chiral L-amino acid signature would imply that martian life is similar to terrestrial life and may share a common origin. Conversely, a chiral D-amino acid signature would imply a unique martian biochemistry and possibly a biosphere whose origin and evolution were independent of Earth's.

If no organic compounds are detected above the pptr detection limits, these results may be explained by the MOI investigations. It is possible that in the near-surface of Mars, oxidizing conditions do not allow for the preservation of simple organic compounds. The correlation between the soil chemistries and the levels of detectable organic compounds will be a major accomplishment by ***Urey***.

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Abbreviations

ESA, European Space Agency; GCMS, Gas Chromatograph Mass Spectrometer; GEx, Gas Exchange Experiment; HPβCD, 2-hydroxypropyl-β-cyclodextrin; LIF, laser-induced fluorescence; LR, Labeled Release Experiment; MAOS, Mars atmospheric oxidant sensor; MOD, Mars Organic Detector; MOI, Mars Oxidant Instrument; MOx, Mars Oxidant Experiment; PAHs, polycyclic aromatic hydrocarbons; pptr, parts per trillion; SCWE, Subcritical Water Extractor; TAOS, thermoacoustic oxidant detector; TRL, Technology Readiness Level; β-CD, β-cyclodextrin; μ-CE, Micro-Capillary Electrophoresis Instrument.

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