

Investigating the Surface Chemistry of Mars

One of the primary objectives of the Viking missions to Mars in the 1970s was to search for life. The landing crafts, or landers, detected extraordinary reactivity in the Martian soil, but no organic material (1). Numerous theories were put forth to explain the Viking data, most of which involved an oxidizing species in the Martian surface material. In December 1992, the Mars Oxidant Experiment (MOx) was selected as the U.S. contribution to the Russian Mars '96 mission. Two landers are scheduled for launch in November 1996 and should arrive at Mars in September 1997. This is the first mission in 20 years to conduct experiments on and near the surface of Mars.

The MOx instrument, shown on the Russian lander in Figure 1, is designed to

The Mars Oxidant Experiment Team

The unusual conditions found on the Martian surface 20 years ago prompt the Mars Oxidant Experiment

investigate the chemical nature of the Martian surface material, with particular emphasis on its oxidative character. The instrument uses fiber-optic technology to monitor real-time physicochemical changes in a suite of chemically sensitive thin-film materials, some in contact with the Martian surface, others exposed only to the atmosphere.

Designing MOx was extremely challenging. The entire instrument had to fit

within a very small volume in the Russian lander, could not exceed 850 g, and could consume no more than 25–50 mW of the lander's power for very short periods of time. It had to survive landing shocks with a force 250 times that of Earth's gravity and diurnal temperature variations of $\sim 100^\circ\text{C}$, and it had to have its own central processor, command set, and memory. This report describes the scientific rationale and basis for the MOx instrument, along with details of its design and construction.

Background

The objective of MOx is to examine broad and important questions in Martian exobiology (nonterrestrial biology) and geochemistry. These include heterogeneous geochemical weathering of the surface and the hypothesis that one or more inorganic oxidants is responsible for the unexpected results obtained by the Viking biology experiments. The Martian

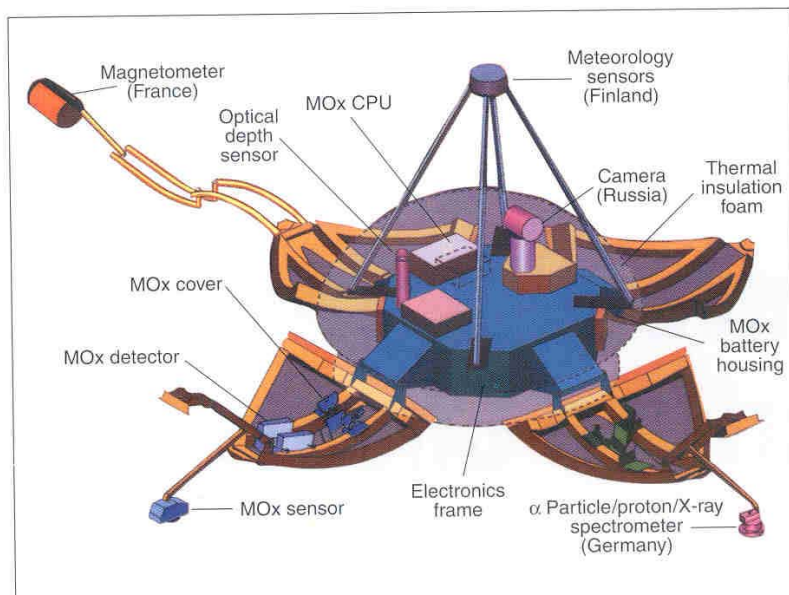


Figure 1. Russian lander showing the MOx sensor and its components.

surface material was found to be uniquely reactive, an observation that provoked a host of explanations (2, 3), but the mechanisms involved remain open to interpretation. Identification of reaction mechanisms in the soil could, however, explain why no organics were found in the Martian surface material and could assist in predicting the depth to which future missions must penetrate to possibly recover organic materials that may be "leftovers" from a period of organic and chemical evolution. The absence of organic material is surprising, because organics are believed to be almost ubiquitous throughout the solar system as a result of the accumulation of carbonaceous meteoritic material. If the Martian surface is an exception, an explanation is required.

If primitive organic materials exist in the Martian surface material, they will provide the best-preserved record of the chemical evolution of early Mars. On Earth, organics recovered from the stratigraphic column have yielded preserved cellular materials, morphological microstructures (4), and chemical discontinuities associated with the appearance of life (5–7). Finding geographic or stratigraphic domains on Mars from which primitive, unoxidized material might be recovered is a fundamental objective of the exobiology community.

Given the absence of liquid water, the interaction between the Martian atmosphere and the surface may be the most active and important geochemical process. The thin films that will be exposed to the Martian environment were selected to span a wide range of chemical activity. The cumulative response of the films will indicate whether oxidizing species are produced in the atmosphere and soil and will help identify the species by bracketing the strength of any oxidant(s). (The Martian atmosphere is 95.3% CO₂; a few percent nitrogen and argon; and trace amounts of oxygen, carbon monoxide, water, and ozone [8].) In addition, specific minerals in the Martian surface material may be identified if their pattern of reactivity is sufficiently distinct.

A final environmental consideration that could be a driving factor in the chemical state and reactivity of the Martian surface is the influence of solar radiation. The thin Martian atmosphere provides minimal shielding from solar UV radiation. Compared with the spectrum of the solar radiation found at the top of the Earth's atmosphere, the solar radiation reaching Mars' atmosphere has the same spectral distribution and about 43% of the intensity. The UV cutoff at the Martian surface is about 190 nm because of absorption by CO₂.

The chemical micromirror array approach

In its most general form, a chemical microsensor combines a physical transduction platform with a chemically sensitive layer or interface (9). Mechanical, electrical, electrochemical, thermal, and optical means of transduction have all been examined in detail, as have a wide range of chemically sensitive interface materials (10, 11). With the appropriate choice of physical platform, chemical microsensors can be small and compact. Optical sensors are particularly promising in this regard, because a single light source and one detector array can be combined with hundreds of optical fibers to create a suite of chemical microsensors.

In general, the key to devising an array of chemically sensitive interfaces that produces a unique response pattern for each analyte is the "chemical orthogonality" of the sensitive interfaces: If the responses of one of the interfaces can be expressed as a linear combination of the responses of the other members of the array, then it has little added value. This particular requirement means that chemically sensitive interfaces must have a degree of selectivity, although the selectivity need not be as perfect as in the one-film/one-analyte approach.

For chemical detection using nonbiological interfaces, the partial selectivity that works best with pattern recognition allows for the consideration of many more candidate chemically sensitive interface materials than would a requirement for perfect selectivity. For the MOx experiment the relatively unknown nature of the Martian surface means that a wide variety of sensitive coatings, some with very high reactivity, are needed.

The MOx instrument uses micromirror chemical sensor technology developed at Sandia National Laboratories (12). The end of an optical fiber is coated with a material that acts as a chemical transducer through changes in its optical properties that result from exposure to the chemical to be detected (13). These changes alter the reflectivity at the end of the fiber. This instrument takes advantage of components developed for optical communications using silica-clad-silica communications fibers, an LED as the source, and a conventional photodiode as the detector.

Sensitivity to different chemicals is achieved by selecting the appropriate coating material for the end of the fiber. The overall reflectivity of the coated optical fiber tip depends on both its Fresnel reflectivity (front-surface reflectivity) and its integrated optical thickness. Thus, for metal films, which have large indices of refraction, very small effective changes in the film thickness, as little as 0.01 nm, can be measured. Metal films must be thin enough to be optically semitransparent, and so are typically in the 5- to 15-nm thickness range. When the reflective element is a film with a predominantly real refractive index, such as a polymer or inorganic dielectric layer, thickness changes of a few tenths of a nanometer (equivalent to a fraction of a percent of the wavelength of light) are necessary for detection; these films must be several wavelengths thick, so they are typically a few micrometers thick.

The MOx instrument was designed to include as many as 256 integrated micromirror chemical sensors, one for each pixel of the linear diode array detector. Sets of 12 micromirrors are grouped in micromachined silicon structures called cells. A number of these 12-micromirror cells, along with a precision optical reflectometer that includes light source, distribution system, detector, and minimal analog conditioning electronics, are housed in the sensor head.

Several factors were taken into account in designing the optical measurement system, or reflectometer. Reflectivity measurements are made at 590 nm (amber) and 870 nm (near-IR) with two illumination intensities for each wavelength. The dual-wavelength feature is especially helpful for some organic coatings, such as pH indicators, that change absorbance (hence reflectivity) at only a single wavelength in response to a change in concentration of a particular chemical species; the unaffected wavelength is used as a reference. High-intensity illumination is used to provide a stronger signal to probe poorly reflective materials, and low-intensity illumination avoids the problem of detector saturation for highly reflective materials.

Bringing the micromirror coatings into contact with the Martian surface material is a primary concern, so each cell was designed using a passive pivoting system for

mounting. Optical fibers were chosen as a means of delivering and collecting light, as opposed to rigid, integrated-optics construction. The optical layout of the reflectometer is shown in Figure 2. The "light table" (upper left of Figure 2) provides multiple sources of light that can be conveniently coupled into a large number of fiber bundles. After passing a collimating lens, the light from both LEDs is folded into a single beam using a dichroic mirror. This illuminates the input of the optical fiber distribution system, which starts with a set of rigid light pipes or guides that dispense light into several fiber bundles. The function of the "harness" is to deliver light from the light table to the sampled films, collect the reflected light, and deliver it to the detector, a 256-pixel linear diode array.

Each pixel is used to detect the light intensity from one fiber. Coupling the fibers

into the detector pixels was accomplished by mounting the fibers in "plugs" in groups of 12, with each plug butting the fibers against the detector surface. The spacing between the fibers, the depth of the fiber-retaining groove, and the thickness of the plug are chosen such that, by placing the plug at an angle of 8° from the vertical pixel dimension of the detector, each fiber is aligned with one detector pixel. Cross-talk between pixels is controlled by a metal mask deposited on the surface of the protective oxide covering the face of the detector.

The chemical sensor cell (Figure 3) consists of four parts. The silicon retaining sleeve assembly aligns the fiber guides with the set of micromirrors. The etched "egg crate" assembly, made from a 250- μm -thick silicon wafer fusion bonded to a 50- μm -thick fused-silica wafer, divides the

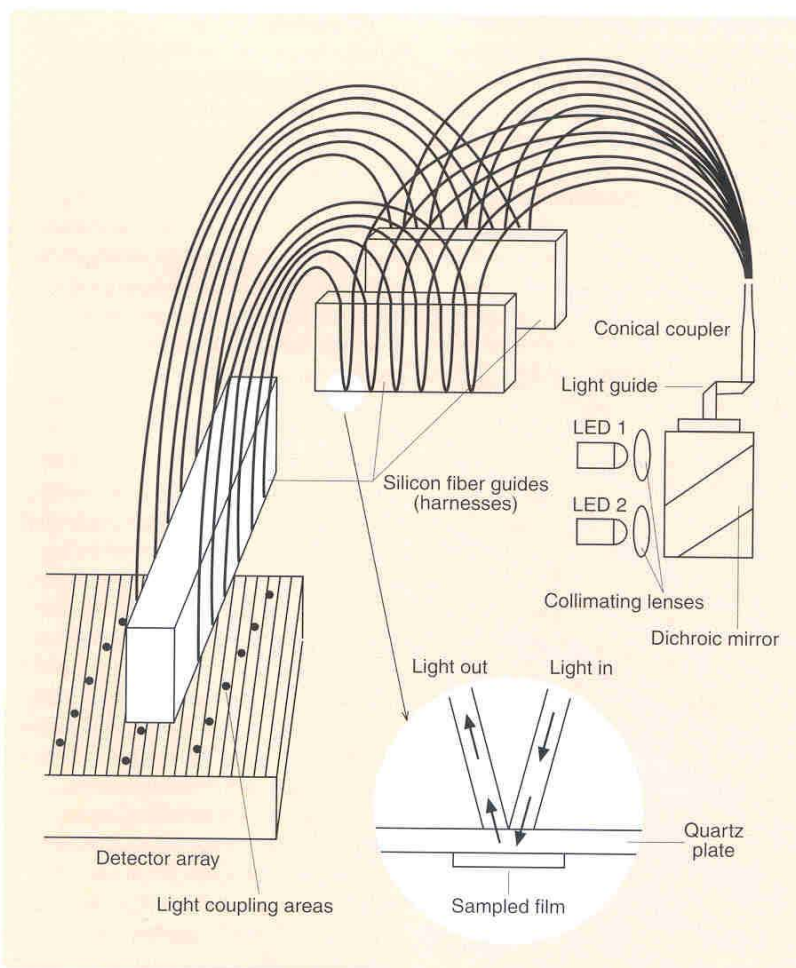


Figure 2. Optical layout of the reflectometer.

fused-silica surface into 12 distinct micromirrors. The chemically sensitive films are deposited on the front face of the fused silica through the egg crate assembly. A membrane-based silicon nitride hermetic seal is applied over the egg crate assembly to minimize contamination.

Thin films

Twenty-one chemically diverse coatings were chosen for use on the cells. These coatings had to be highly reactive because of the anticipated low temperatures (~80 to -20 °C) and short measurement period (40–100 days). Permanent hermetically sealed cells serve as controls, experiencing the same temperature fluctuations and mechanical perturbations but having no contact with chemical species. Three of every 12 micromirrors are reference films: optically thick Au/Pt/Ti to provide a constant-reflectivity film, unperturbed by chemical reaction, as a check on LED illumination levels; bare SiO₂ to monitor ambient light levels and scattering of light by dust; and a thick Au/Pt/Ti/Si composite to monitor ambient temperature by variations in the bandgap and refractive index of the Si film.

The seven metal films listed in Table 1 have a range of electrochemical potentials and oxidation chemistries. These metals are listed in the approximate order of increas-

ing reactivity. Learning which metals do and do not oxidize will give a first-order estimate of the approximate "oxidizing power" of the Martian surface and atmosphere, and some specific reactions may be detected by particular metal films. (The Au/Pt/Ti film in Table 1 is not as thick as the film used for the reference.)

The other films were selected for their characteristic reactivities. Two kerogen-like films, with ratios of hydrogen to carbon of 0.5 and 1.2 that approximate some of the carbonaceous species thought to be deposited on Mars by meteorites, will be monitored for oxidation to CO₂. A polybutadiene film will be used to check for traces of ozone (14) present in the Martian atmosphere. L- and D-Cysteine are used to monitor the rate of degradation of simple amino acids and to ascertain whether any chiral species, such as a transition metal complex, are in the Martian dust and involved in the degradation of organics.

The pH indicators thymol blue, bromothymol blue, and 2,6-dichloroindophenol will be used to characterize proton activity of the surface material and of gaseous species, including water, that may adsorb from the atmosphere onto the surfaces of the films. We attempted to choose indicators with a pH-sensitive absorbance maximum overlapping the wavelength of one of the LEDs used to measure reflectivity but without significant absorbance at the second LED wavelength so that non-specific changes in the film, such as oxidative degradation, can be separated from proton activity effects.

Methylene blue is sensitive to reducing agents, and fluorescein could provide additional information regarding proton activity. In its long-lived excited electronic state, fluorescein is both a stronger reducing agent and a stronger oxidizer than the ground-state molecule, which means that solar UV light can be used to convert a fairly unreactive material into a high-reactivity coating. Like the pH indicators, hematin has an absorbance maximum near one of the two LED wavelengths and can change reflectivity depending on whether it binds O₂ or CO. Whether such binding can occur in the solid state under anticipated Martian conditions is unclear; during the Martian day, the atmospheric cells will be exposed to solar UV radiation, which could affect both the

Table 1. Metal micromirror coatings

Coating	Purpose
Au/Pt/Ti	Indicates frost and organic adsorption; reacts with sulfur compounds
Pd	Sensitive to H ₂ , H ₂ S, and unsaturated hydrocarbons
Ag	Extremely reactive to O [·] and O ₃
V	Moderately to highly reactive to oxidants
Ti	Highly reactive to oxidants
Al	Highly reactive to oxidants
Mg	Very highly reactive to oxidants; reactive to CO ₂ if film is clean enough

kinetics and equilibrium concentration of bound O₂ and CO.

Cells are located in two places on the sensor head: Eight cells face downward to contact the surface material, and four face upward for exposure to the atmosphere and solar irradiation. To distinguish photo-assisted from unassisted chemical reactions, some atmosphere-probing cells will use dust filters that have a thin layer of metal deposited onto the surface, eliminating about 95% of light transmission without hindering gas permeation. Any photo-assisted deposition of organic materials will be indicated by a difference between the response of the solar-exposed and solar-unexposed bare SiO₂ micromirrors.

Preliminary results

From the reflectivity-versus-thickness curves for deposited metals and organics, and assuming reflectivity can be measured to within 0.3% accuracy over a 40-day experiment lifetime, it is possible to estimate minimum changes in material thickness, and thus minimum reaction rates, that can be detected by the instrument. (Laboratory measurements are significantly more stable and accurate, but 0.3% is consistent with the capabilities of the MOx instrument). For metal films the minimum detectable thickness change is 0.1 nm; therefore, the minimum detectable reaction rate is 3×10^{-8} nm/s. For organic films the corresponding values are 10 nm and 3×10^{-6} nm/s.

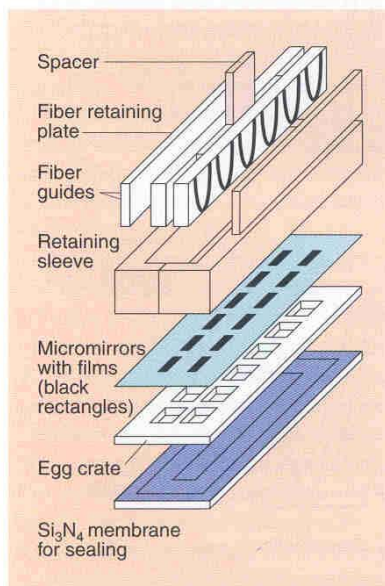


Figure 3. Exploded view of an optical sensor cell.

From these numbers and reaction rates for various chemical species, the minimum detectable average concentration of such species can be estimated. For example, to study possible degradation of organic compounds, a clean fiber end was monitored during plasma deposition of hydrogenated carbon films. Figure 4 shows deposition of a kerogen film $\sim 1 \mu\text{m}$ thick. As the thickness of the film grows to one, two, or more half-multiples of the wavelength of the illuminating light in the film material, reflections from the front and rear interfaces of the layer alternately add and cancel, producing the interference fringes. This film was subsequently exposed to atomic oxygen, a strong oxidant produced in an oxygen plasma, resulting in the removal of the film, as indicated by the second set of interference fringes. The oxygen concentration was estimated to be 10^{13} – 10^{14} atoms/cm³.

Assuming impact rate-limited kinetics and a chemical reaction that is first order in atomic oxygen, the measured rate of reaction of 1 nm/s for removal of the hydrocarbon film, together with the minimum detectable reaction rate of 10^{13} – 10^{14} atoms/cm³, yields a minimum average concentration of atomic oxygen of 3×10^7 to 10^8 atoms/cm³, which corresponds to 0.5 ppb by volume in the 5.6-Torr Martian atmosphere. The detection limit for oxidants that have a lower relative rate of removal of the film (i.e., weaker/less active oxidants) is higher. This estimate gives an idea of the sensitivity of the micromirror technique for detection of oxidants at room temperature. The lower Martian temperatures would result in slower reaction rates and therefore higher minimum detectable limits for equivalent reactive species for a given exposure period.

The micromirror approach (13, 15) has largely been applied to the measurement of reactions between gases and the micromirror. To study the Martian surface material, the micromirror must be brought into contact with a granular surface. However, chemical reactivity at a dry, solid–solid interface could be orders of magnitude slower than at a gas–solid interface. Scanning electron microscopic images of films placed in varying degrees of contact with 1.0- and 0.1- μm particle-size powders suggest a strong bonding of powder to film by an electrostatic mecha-

nism. This particle pickup also suggests that intimate contact with Martian surface material may not be necessary, although electrostatic pickup will undoubtedly oversample the fine-grained fraction of the surface material. Laboratory studies of micromirror materials indicate that a pure superoxidant material such as KO_2 can react at -30°C with several metallic films, providing about a 0.3% relative change in optical reflectivity in a 5- to 15-day period.

The lander and MOx components

Each craft lands on an airbag cushion after a parachute descent. Approximately 10 min after landing, the lander separates from the airbag, dropping 30–50 cm to the surface. The instrument begins its internal calibration and measurement sequence, which continues through petal opening. Some 3–5 min later, the petals of the lander open, providing an upright

Each craft lands on an airbag after a parachute descent.

configuration for the station. About a minute later, a 150-g Russian-designed and built boom, which holds the MOx sensor head on the inside of one petal, is activated and the sensor head descends to the surface in 3–5 s. As the sensor head extends away from the lander, the protective membranes over the reaction cells are pulled and shattered. The electronics are checked to determine whether they withstood landing and any subsequent bouncing. The estimated lifetime for the lander is ~ 1 Mars year or ~ 2 Earth years.

The basic long-duration measurements begin ~ 28 s after boom deployment and continue until the memory buffer is filled. For the first 40 days measurements are made at a logarithmically decreasing rate to maximize the range of chemical reaction rates that can be detected. After 40 days, additional measurements are made every third day, but only if there is any re-

maining memory into which data can be placed. The instrument should provide active measurements for at least 50 days.

Because the lander cannot provide power or accept data for transmission until 20–40 days after landing (and then only at data rates sufficient for slower-than-normal operation of the MOx instrument), the instrument requires batteries and memory to enable stand-alone operation during the active chemical measurement portion of the instrument's activity. The MOx data system will retain data in memory, sustained by a long-lived battery, and will provide several repeated transmissions of data acquired early and any subsequent data, assuming the lander-orbiter pair lifetime exceeds 70 days.

The design of the mechanical aspects of the instrument was driven by having to fit pieces wherever room could be found in the lander. To minimize mass and cost and to maintain instrument integrity, enclosures were made from aluminum or magnesium. The MOx sensor head had to be similar in mass and size to the German α particle/proton/X-ray (APX) sensor, for which the boom was originally designed. The analog and sequencer electronics box is located on the lander petal, close to the sensor head. A temperature sensor is located near the A/D converter to monitor that critical area's temperature swings for calibrating the data. The central processing unit is located between the APX instrument electronics and the top of the instrumentation frame within the lander.

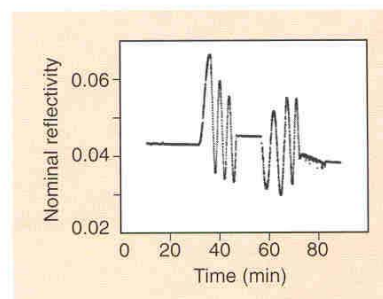


Figure 4. Response during the deposition and subsequent removal of a $\sim 1\text{-}\mu\text{m}$ kerogen film on the tip of an optical fiber.

The first three interference fringes correspond to film deposition from a hydrocarbon plasma that was extinguished at ~ 48 min. An oxygen plasma was ignited 10 min later, which removed the film as indicated by the final three interference fringes.

The battery box, containing sets of primary power cells that drive the experiment and a single memory backup power cell, is located external to the instrumentation frame, inside insulating foam that fills much of the empty space in the lander. Lithium/thionyl chloride batteries were selected because of their ability to deliver power at temperatures below -30°C once properly conditioned. Three sets of these batteries should be sufficient to provide power to operate MOx for 50–70 days. Two internal radioactive heater units in the lander should provide enough heat to prevent the CPU and battery box from being exposed to the extremes of the Martian day. The late summer/early fall landing at latitudes $25\text{--}40^{\circ}\text{N}$ means a peak day temperature around -20 to -30°C and a dawn temperature of around -95 to -105°C . The electronics in the petal box and sensor head were designed and tested to operate in these temperature extremes.

Final words

Many exciting prospects exist for using fiber optic-based sensors in future planetary missions. The MOx experiment is a nearly unprecedented combination of translating advanced laboratory technology into a foreign spacecraft, doing retrofits and, of course, trying to follow a compressed schedule. Data from these experiments, conducted over a few tens of days,

will give us insight into the chemistry that has defined the Martian surface over the course of eons.

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