

The Mars Oxidant experiment (MOx) for Mars '96

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Abstract. The MOx instrument was developed to characterize the reactive nature of the martian soil. The objectives of MOx were: (1) to measure the rate of degradation of organics in the martian environment; (2) to determine if the reactions seen by the Viking biology experiments were caused by a soil oxidant and measure the reactivity of the soil and atmosphere; (3) to monitor the degradation, when exposed to the martian environment, of materials of potential use in future missions; and, finally, (4) to develop technologies and approaches that can be part of future soil analysis instrumentation. The basic approach taken in the MOx instrument was to place a variety of materials composed as thin films in contact with the soil and monitor the physical and chemical changes that result. The optical reflectance of the thin films was the primary sensing mode. Thin films of organic materials, metals, and semiconductors were prepared. Laboratory simulations demonstrated the response of thin films to active oxidants. © 1998 Elsevier Science Ltd. All rights reserved

1. Background: the Viking results

The Mars Oxidant Experiment (MOx) was built for the Russian Mars '96 mission (which failed after launch) to study the chemistry of the martian soil. To understand the context of the MOx instrument it is necessary to con-

sider the results of the soil analyses conducted on the Viking mission to Mars.

The primary objective of the Viking mission to Mars was the search for extant life in the soil of Mars. Accordingly, samples of the martian soil were incubated in the three biology experiments and other samples were analyzed for organic matter in a combined gas chromatograph and mass spectrometer (GCMS). The results were puzzling in three respects. First, and most surprising, was the absence of organics as measured by the GCMS (Biemann *et al.*, 1977; Biemann, 1979)—this absence was clearly unexpected or a GCMS would not have been flown. The second unexpected result was the rapid release of O₂ at levels of 70–770 nanomoles gm⁻¹, when soil samples were exposed to water vapor in the Gas Exchange Experiment (GEx) (Oyama and Berdahl, 1977). The third puzzling result was that organic material in the Labeled Release Experiment (LR) was consumed as would have been expected if life was present (Levin and Straat, 1977). However, the presence of life was in apparent contradiction with the results from the GCMS.

Currently, the most widely held explanation for the reactivity of the martian soil is the presence of one or more inorganic oxidants (Klein, 1978; 1979; Zent and McKay, 1994). Table 1, adapted from Klein (1978), summarizes the GEx and LR results and the inferred level of oxidants implied. Table 2, modified and updated from Zent and McKay (1994), is a summary list of the models published to explain the release of O₂ in the GEx, the decomposition of added nutrient in the LR, and the absence of organics in the GCMS. In general the release of O₂ observed in the GEx is explained by the presence of an oxidant able to oxidize water (oxidizing potential over 1.23 volts) or by the presence of O₂ mechanically trapped in the interstitial spaces of the soil. The decomposition of

Table 1. A comparison of GEx O₂ LR ¹⁴C results (after Klein, 1978)

Sample	GEx O ₂ (nanomoles cm ⁻³)	Oxidant ¹ (KO ₂ → O ₂)	LR CO ₂ (nanomoles cm ⁻³)	Oxidant ¹ (H ₂ O ₂ → O)
Viking 1 (surface)	770	35 ppm/m	~ 30	1 ppm/m
Viking 2 (surface)	194	10	~ 30	1
Viking 2 (sub-rock)	70	3	~ 30	1

¹ Assuming a soil density of 1.5 g cm⁻³.

Table 2. Published non-biological explanations for the Viking results

● GEx release of O ₂ upon humidification	
KO ₂	Ponnamperuma <i>et al.</i> , 1977
ZnO ₂	
CaO ₂	Ballou <i>et al.</i> , 1978
MnO ₂	Blackburn <i>et al.</i> , 1979
O ₂ trapped in micropores	Nussinov <i>et al.</i> , 1978 Plumb <i>et al.</i> , 1989
Chemisorbed H ₂ O ₂	Huguenin <i>et al.</i> , 1978
O plasma	Ballou <i>et al.</i> , 1978
Activated halides	Zent and McKay, 1994
● LR decomposition of added nutrient	
H ₂ O ₂	Hunten, 1974 Oró and Holzer, 1979 but cf. Levin and Straat, 1981 Ponnamperuma <i>et al.</i> , 1977
Peroxonitrite (NOO ₂ ⁻)	Plumb <i>et al.</i> , 1989
Fe-rich smectite clays	Banin and Margulies, 1983
● Lack of organics in martian soil	
UV + TiO ₂	Chun <i>et al.</i> , 1978 Pang <i>et al.</i> , 1982
Dust electrostatics	Mills, 1977
Feroxyhyte (δ-FeOOH)	Burns, 1980
UV alone	Bullock and Stoker, 1997

organics in the LR experiment is also held to be due to an oxidant. However, because the LR activity was removed by heating but the GEx activity was not, the oxidants responsible for them must be different. The lack of organics can be explained by the presence of oxidants or UV light. Despite the many hypotheses listed in Table 1, no chemical (or mixed chemical and biological) model has been presented that can adequately and self-consistently explain the important details of both the GEx and the LR results and is also consistent with the known elemental composition and lack of organics (Zent and McKay, 1994).

If the gases released in the GEx and the LR experiments are assumed to be due to a specified oxidant then it is possible to use the measured amounts of these gases to determine the probable concentration of the oxidant in the soil. Such an analysis is shown in Table 1 for typical examples of the oxidants suggested in Table 2. The likely concentrations of reactive species in the martian soil can be of order ppm and still account for the reactivity seen by Viking. Zent and McKay (1994) have argued that the amount of oxidant required would cover less than 1% of the surface area of grains that compose martian soil. Bal-

lou *et al.* (1978) determined that the specific surface area of the martian soil was 17 m² g⁻¹.

1.1. Organic stability and oxidant models

A key science question that must be addressed in future Mars missions is the distribution and stability of organics on Mars. Organic material may provide the best evidence that life existed on Mars during an early wetter epoch (McKay, 1997). There are at least three possible sources for organics on Mars: meteoritic infall, *in situ* abiotic production, and remnants of biological material. Unfortunately, the Viking landers could not sample soils below about 10 cm and so the depth of the organic-free, apparently oxidizing, soil is unknown. As discussed above the distribution of organics is intimately related to the presence of oxidants on the surface. For this reason we briefly review the questions of organics on Mars.

The absence of organics is a puzzle because it is expected that, even in the absence of an *in situ* source of organics on the martian surface, meteoritic infall would carry organics to Mars. Flynn (1996) estimates that the present accretion rate of unaltered meteoritic carbon onto Mars is 2.4×10^8 g yr⁻¹, which, for a specific density of one, is equal to a layer of 10⁻¹⁰ cm yr⁻¹. Presumably the oxidant responsible for the GEx and LR results would be actively destroying these incoming organics. Solar UV could also account for the absence of organics (Oró and Holzer, 1979; Bullock and Stoker, 1997).

Gooding (1992) has pointed out that the SNC meteorites are also oxidized with the dominant forms of carbon, sulfur, iron, being carbonate, sulfate, and ferric iron, respectively. These meteorites date back from 200 to 1300 million years suggesting oxidizing conditions on the near surface of Mars at least that long ago (Gooding, 1992). However, there have been reports of organic material in the young SNC meteorites (Wright *et al.*, 1992). Furthermore, one of the lines of evidence from the martian meteorite ALH84001 consistent with evidence of life was the presence of organic material (McKay *et al.*, 1996). Thus, it is likely that some organic material could be preserved on Mars from an early biotic period. The key question is where, or how deep must one look to find this organic material.

Fundamentally photochemical production of oxidants occurs due to the photolysis of H₂O and the subsequent loss of H₂ to space. Clearly photochemical oxidant production is occurring on Mars and it has been suggested that atmospheric photochemistry is producing H₂O₂ in the martian atmosphere and that the deposition of these

molecules onto the soil is a source of oxidizing power (Hunten, 1979; Bullock *et al.*, 1994). The standard model used to explain the Viking Biology Experiment results invokes the existence of at least two oxidants in the martian soil, a thermally stable oxidant such as KO_2 or CaO_2 as well as a thermally labile oxidant such as H_2O_2 (Klein, 1978; Zent and McKay, 1994), presumably both are derived from atmospheric oxidants.

It is important to note here that the production of net oxidation on Mars at the present time is zero because for every H_2 molecule that escapes one O atom escapes as well (McElroy *et al.*, 1977; Liu and Donahue, 1976) thus effectively resulting in the escape of H_2O . Only if the H_2 escapes and the O is left behind is there a net source of oxidant. Presumably if there were a sink for O on the surface—such as exposed organic material—then O would be consumed and the unbalanced loss of H_2 would represent a net shift towards oxidizing conditions.

Despite uncertainties in our understanding of the redox balance of the present Mars atmosphere the photodissociation rate of H_2O is an upper limit to the photochemical production of oxidant on Mars. The present rate of oxidant production due to photolysis of water, about $6 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ (Liu and Donahue, 1976; McElroy *et al.*, 1977), would produce a layer of iron oxide about 10 m thick over 3 billion years if there were no escape of O_2 . Thus there may be a relatively thin layer of oxidizing soil, although it is possible that the escape rate was much higher in the past—this is one possible explanation for the high D/H ratio on Mars.

Recent modeling studies suggest that the depth of the penetration of H_2O_2 —a likely photochemical oxidant and certainly a mobile one—is small. Bullock *et al.* (1994) developed a coupled soil/atmosphere transport model for H_2O_2 on Mars. Their results suggest that the concentration of H_2O_2 in the soil goes to zero at a finite depth, a consequence of nonlinear diffusion in the soil. A significant result of their model is that for a wide range of H_2O_2 lifetimes (up to 10^5 years), the extinction depth was found to be less than 3 m. Thus only a fraction of the potential total photochemical oxidation is realized with the rest escaping to space as O_2 .

Biology is an alternative explanation for the source of oxidation on Mars (Hartman and McKay, 1995). In this case the oxidant at the surface would be balanced by biogenic organics buried in the sediments.

The MOx results would have allowed for better determination of the life time and reaction kinetics of the oxidant(s) and possibly even their chemical identification. This information would have been used to develop coupled soil-atmosphere models similar to that of Bullock *et al.* (1994). From these models we could determine the depth below which organic materials might remain. We could also determine if latitudinal effects (e.g. the presence of ground ice inhibiting diffusion) could be reflected in the distribution of organics.

Understanding the nature and concentration of any reactive component of the martian soil is important for both science and engineering reasons. Scientifically one of the key questions about Mars is the possibility that there was life at some time in the past. Clearly, if an oxidant has been destroying the organic remains of past life then understanding the nature, sources, and concentration of

this oxidant will be vital to determining at what locations and depths organics might have been preserved.

In addition to destroying organic material the reactivity of the martian surface could be an important geological agent of weathering. Furthermore, the reactivity of the martian soil may pose a hazard to equipment and humans on the surface. While the concentrations are so low that there is likely to be no threat, it would be prudent to determine the nature of the compounds in question.

2. The MOx instrument

As discussed by Zent and McKay (1994) it is likely that investigations into the nature of the oxidant in the martian soil require *in situ* analysis and cannot be done on a sample returned to Earth. Fundamentally this is because the oxidants are unstable and are composed of common elements. The instability of the oxidants was observed by the Viking LR experiment. Samples stored in the spacecraft for long periods of time showed considerably reduced activity. Presumably, the oxidants are present due to continual production in the martian environment. If the oxidants were to decompose enroute to Earth, their expected low concentrations (ppm as listed in Table 1) and the common elements into which they decomposed would not be detectable against the background level of these same elements not in the form of oxidants. For example K may be present as an oxidant (KO_2) at the ppm level but the concentration of K as K_2O (not an oxidant) in the soil is likely to be 0.2% (Banin *et al.*, 1992). Thus MOx and other instruments to characterize the soil oxidant on Mars are designed as *in situ* investigations.

2.1. Objectives

The overall goal of MOx was to provide further information on the nature of the reactivity of the martian soil seen by Viking and to determine if organics are unstable at the surface. The specific objectives of MOx were:

- Measure the rate of degradation of organics in the martian environment (soil and atmosphere) to a level of less than 10 nm thickness in 30 days.
- Determine if the reactions seen by the Viking biology experiments were caused by a soil oxidant and measure the oxidative reactivity of the soil and atmosphere at levels corresponding to less than 1 ppm of H_2O_2 and/or metal superoxides. We are not identifying the oxidant.
- Expose materials that are of interest to human exploration (such as space suit fabrics, coatings for electronics, plastics and building materials) and monitor degradation of these materials at a level of 10 nm thickness over 30 days.
- Develop technologies and approaches that can be part of future soil analysis instrumentation.

It is important to note that the investigation of the stability of organics on the surface of Mars is not logically dependent on the hypothesis of oxidants causing the reactivity observed in the GEx and LR results. By exposing organics to the martian environment their stability can be measured directly. If chemical, biological, or physical processes

heretofore not considered are responsible for the removal of organics on Mars the effect of these would still be detected.

2.2. Design

The basic approach taken in the MOx instrument to investigating the reactivity of the martian surface is to place a variety of materials in contact with the soil and monitor the physical and chemical changes that result. To provide a comparison to the soil cells, an identical set of materials are exposed only to the atmosphere and sunlight. Controls are provided in both the air and soil cells with identical coatings that remain sealed.

Table 3 is a listing of the coatings used in MOx. For each coating the thickness of the coating in nm is given as well as a brief description of the expected reactivity or scientific rationale for inclusion of that coating. The coatings on MOx were selected to best achieve the science objectives stated earlier although the choice of materials was constrained to those materials that could be deposited in an optically uniform layer.

The amorphous hydrocarbon coatings were chosen to directly investigate the fate of refractory meteoric organic material (kerogen-like material) in the martian environment. These coatings were produced by a plasma polymerization process from CH₄ and C₄H₈ monomers to form films of different H : C ratios. The CH₄ produces the higher hydrogen content film. We chose a range of H : C that would be representative of kerogens in meteorites. Presumably the coating with the higher H : C value would be more susceptible to attack by oxidants. The C₆₀ coating

was chosen partly to address the issue of organic decomposition and partly because it provided a well characterised and easily deposited form of carbon. In addition to the refractory organics we were interested in the decomposition rate of biogenic organic compounds such as amino acids. Along with kerogens, amino acids are found in carbonaceous meteorites and thus would be expected to be a component of the meteoritic infall on Mars discussed above. The results of the LR experiment suggested that such compounds would be oxidized when exposed to martian soil.

Cysteine was the lightest amino acid that allowed for adequate coating. In addition its chemical bonding with the thin Au film, via the thiol (SH) group, causes it to (1) stay immobile and (2) respond to any change in its oxidation state by a change in the electron density at the Au surface. To investigate possible exobiological as well as chemical selectivity, the L and D forms of cysteine were coated separately. (We note that since the sample would be exposed to ambient martian conditions in which no terrestrial microorganisms could metabolize we were not concerned with false signals arising from contamination.) Other organics were added on a space available basis based on the following criteria: (1) they could be deposited in acceptable form; (2) they would provide information on the stability of organics by their degradation; (3) they might undergo a chemical change that could be indicative of the conditions (pH, eH, etc.) in the environment. It was recognized that many of these chemical indicators could be expected to function only in solution but it was thought that their inclusion in MOx might provide information depending on the mobility of absorbed water on Mars.

Table 3. MOx coatings

Coating		Purpose
		Controls
Bare Si _x N _y	No-film control	
40 nm Cr, 150 nm Au	High reflectivity inert control	
		Non-metals
< 500 nm Amorphous hydrocarbon; H : C = 1.2		Degradation rate of meteoritic organics on Mars
< 500 nm Amorphous hydrocarbon; H : C = 0.5		Degradation rate of meteoritic organics on Mars
2 nm Ti, 10 nm Au, L-cysteine (1 monolayer)		Organic degradation rate and enantiomer selectivity
2 nm Ti, 10 nm Au, D-cysteine (1 monolayer)		Organic degradation rate and enantiomer selectivity
7.5 nm Ni, 120 nm C ₆₀		Sensitive to combination of UV and oxidant(s)
7.5 nm Ni, 100 nm Bromocresol Purple		pH indicator dye: $pK = 6.3$
7.5 nm Ni, 100 nm Bromophenol Blue		pH indicator dye: $pK = 4.0$
7.5 nm Ni, 100 nm Thymol Blue		pH indicator dye: $pK_1 = 2.0, pK_2 = 8.8$
7.5 nm Ni, 100 nm Fluorescein		Fluoresces only at neutral or basic pH
7.5 nm Ni, 100 nm Fe Tetrphenyl Porphyrin		May bind CO with color change
7.5 nm Ni, 250 nm Copper Phthalocyanine		Well-characterized sensor material for oxidants
7.5 nm Ni, 100 nm Chlorophyllin		Ozone detection via ozonolysis of C=C double bonds
90–100 nm PbS		Reactions with hydrogen peroxide giving large color change
		Metals
20 nm Ti	Moderately high reactivity to oxidants; oxide is permeable allowing intrafilm reaction	
15 nm Pd	Low reactivity but sensitive to hydrogen, sulfides, unsaturated hydrocarbons	
10 nm Ag	Low reactivity, but extremely reactive to ozone, oxygen radicals, sulfur compounds	
25 nm V	Moderate-to-high reactivity to oxidants; rich and variable oxide chemistry	
2 nm Cr, 10 nm Au	Frost indicator; reactive to sulfur compounds; organic absorption indicator	
7.5 nm Mg	Very high reactivity to oxidants	
7.5 nm Al	High reactivity to oxidants; oxide is permeable, allowing intrafilm reaction	

The logic of the metallic and semiconductor coatings was more straightforward than for the organics. For these materials deposition methodologies are well established and coatings were selected to cover a range of reactivities. These range from relatively inert gold coatings to highly reactive Al coatings.

The soil cells come in contact with the soil directly. The air cells are exposed to the atmosphere as well as to UV containing sunlight. This comparison is important for several reasons. First, as discussed above, it is plausible that the soil oxidants derive from atmospheric oxidants such as H_2O_2 and O_3 . The ultimate source of these oxidants is UV light. The air cells therefore would allow for a direct investigation of both of these effects.

To protect the coatings from the very reactive and oxidizing environment on Earth prior to launch, each coating intended for deployment on Mars was covered with a hermetic seal which is broken only as the instrument is deployed on Mars. Duplicate reference coatings remained hermetically sealed throughout the experiment.

The physical and chemical state of the coatings is determined by measuring changes in their optical reflectance. MOx senses these chemical changes by monitoring the optical properties of the chemical films. This approach is known as the micromirror sensor (Hughes *et al.*, 1991) and is shown schematically in Fig. 1. In the MOx instrument light is emitted from two LEDs (light emitting diodes) at wavelengths of 590 and 870 nm and is carried to and from the films with a fiber optic system. The light signal reflected from the films is sensed by the detector. The electronics module processes this data and they are relayed to Earth. On Earth the data are "inverted" using the MOx instrument characteristics and the martian environmental data to determine the actual pattern of reactions on Mars. From this one, or more, hypotheses as to the nature of the martian oxidant(s) can be developed. Both the steps of data inversion and hypothesis formation would rely on laboratory simulations of specific compounds under a range of conditions.

To test the Mars oxidant hypothesis would require an accurate simulation of the martian environment and the exposure of faithful duplicates of the MOx coatings to this environment. The MOx project produced 20 complete

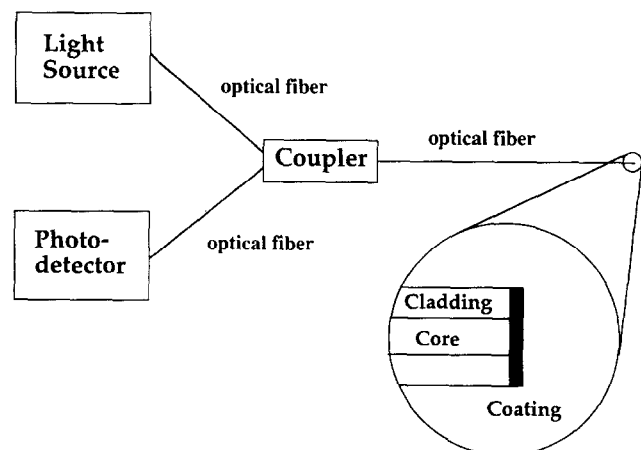


Fig. 1. Schematic of the micromirror chemical thin-film sensor that formed the basis of the MOx instrument

Table 4. Minimum detectable thickness changes and reaction

Coating type	Detectable thickness change nm	Detectable reaction rate nms^{-1}
Metals	0.1	3×10^{-8}
Organics	10	3×10^{-6}

sets of duplicates allowing for MOx simulation with 20 oxidant combinations. Based on the results of these tests further refinements in the data analysis, and oxidant models would be developed. This "method of 20 questions" should produce an accurate model of the surface reactivity of Mars if the data analysis that feeds into the process is an accurate reflection of the processes on Mars.

The major uncertainty in the MOx design was the expected reaction rates. It was thought that, even for very reactive oxidants, the reaction rates would be quite low at the expected conditions on Mars—mean temperatures -60°C , frost points -100°C . Predesign laboratory simulations demonstrated a 0.3% change in reflectivity of the metallic coatings over 5–15 days when exposed to pure KO_2 at -30°C , with nearly saturated water vapor. Simple extrapolation to martian temperature and humidity suggests that the expected changes in the reflectivity could be lower than 0.1% and maybe as low as 0.01%. This does not account for the difference between solid oxidant and the ppm levels expected on Mars. In all cases it is likely that the reactivity on Mars would be very low and to obtain a reliable measurement would require both long time integration as well as an extremely precise characterization of the response and stability of the MOx unit.

3. Simulations

As part of the MOx development we conducted a series of simulations in which thin films were exposed to various oxidants. These results form the basis for the expected performance on the instrument on Mars. Table 4 provides a summary of the sensitivity of the metal and organic coatings.

3.1. Organics

Figure 2 from Grunthner *et al.* (1995) shows the reflectivity of a micromirror as a film of kerogen-like material is deposited on the reflection surface and then removed by reaction with atomic oxygen. As the thickness of the film grows to one, two, or more multiples of the wavelength of the illuminating light, reflections from the front and rear interfaces of the layer alternately add and cancel, producing interference fringes. After 50 min the film was 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 in Fig. 2. The O concentration was estimated to be 10^{13} to 10^{14} cm^{-3} . As discussed by Grunthner *et al.* (1995), if we assume a chemical reaction that is first order in atomic O

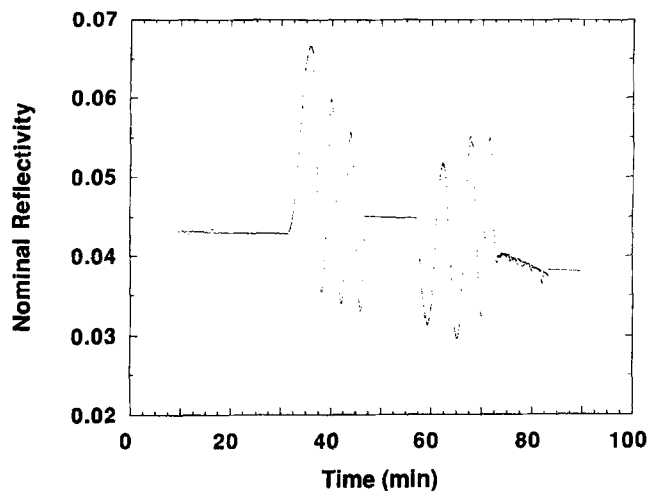


Fig. 2. Change in reflectivity of a fiber as a coating several wavelengths thick of kerogen-like organic material is deposited (20 to 50 min) and subsequently eroded (after 50 min) by atomic oxygen (from Grunthaler *et al.*, 1991)

and impact rate-limited kinetics, the measured rate of reaction for removal of the hydrocarbon film of 1 nm s^{-1} , together with the minimum detectable reaction rate given above, we can determine that the minimum average concentration of atomic oxygen that can be detected is 3×10^7 to 10^8 O cm^{-3} (at 0°C , $10^8 \text{ atoms cm}^{-3}$ 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) would of course be higher (poorer).

3.2. Inorganics

Figure 3 shows the reduction in reflectivity of a thin Al film when exposed to BaO_2 powder, a solid oxidant. From the measured reaction rate, in this case $10^{-6} \text{ nm s}^{-1}$, as well as the exposure period, system stability, and minimum detectable reaction rate for metals given in Table 4 above, the minimum detectable concentration of BaO_2 in a solid mixture is estimated to be 30,000 ppm. The above esti-

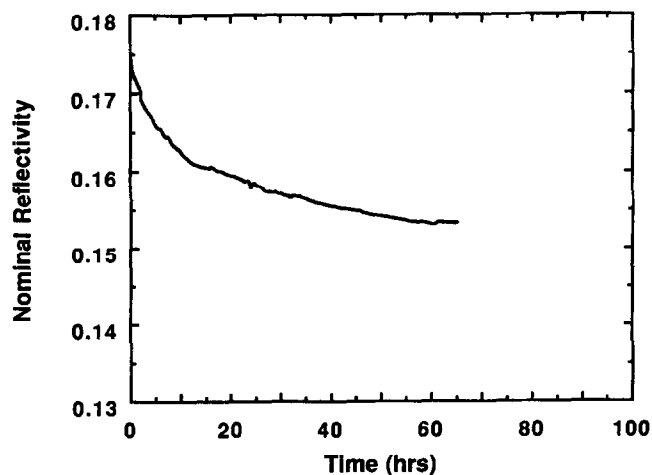


Fig. 3. Decrease in reflectivity as a function of time for a fiber-tip thin Al film immersed in pure BaO_2 powder at 25°C

mates assume first-order kinetics and give 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, hence higher minimum detectable limits for equivalent reactive species for a given exposure period.

The change in reflectivity versus time for a 6 nm Ti micromirror immersed in solid KO_2 at 25°C is shown in Fig. 4. A 3–6% relative reflectivity change is found after a two-day exposure. Assuming a uniform surface reaction, this corresponds to about a 0.1 nm increase in oxide thickness.

Verification that the measured change in reflectivity was due to an increase in oxide thickness was done using X-ray photoelectron spectroscopy (XPS). In XPS, the kinetic energy of electrons emitted due to absorption of X-ray photons by an atom is measured and used to calculate the binding energy of the electron. Binding energy, which is unique for each electron of each element, varies as a function of oxidation state as well as the type and number of elements with which it is combined. Thus, an increase in the net counting rate of emitted electrons (as seen in Fig. 5 and described below) corresponds to an increase in oxide thickness, while a shift in binding energy (as seen in Fig. 7 and described below) corresponds to a change in neighboring elements.

The XPS Ti 2p spectrum (where 2p refers to the orbital form which the electron is ejected) for the micromirror surface shows a small corresponding increase in thickness of a complex, TiO_2 -like oxide (Fig. 5, top). The O 1s spectrum of the Ti micromirror film exposed to both BaO_2 and KO_2 is shown in Fig. 5, bottom. Note that the control film, which was not exposed to the solid oxidant, nevertheless has a substantial (about 2 nm) passivating oxide layer, a result of its exposure to oxidative impurities in the N_2 during the transport process. Thus, reaction with the solid oxidant(s) requires diffusion through this TiO_2 -like overlayer. Laboratory studies of such micromirror materials indicate that a pure superoxidant material (KO_2) can react at $\sim 30^\circ\text{C}$ with several metallic films, providing about a 0.3% relative change in optical reflectivity in a 5 to 15 day period. Thus, our best current estimate is that the ability to measure a 0.3% change

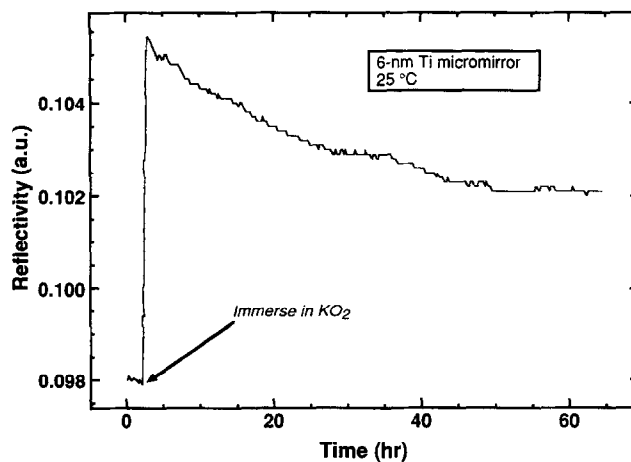


Fig. 4. Reflectivity versus time for a 6 nm Ti fiber tip micromirror immersed in solid KO_2 at 25°C

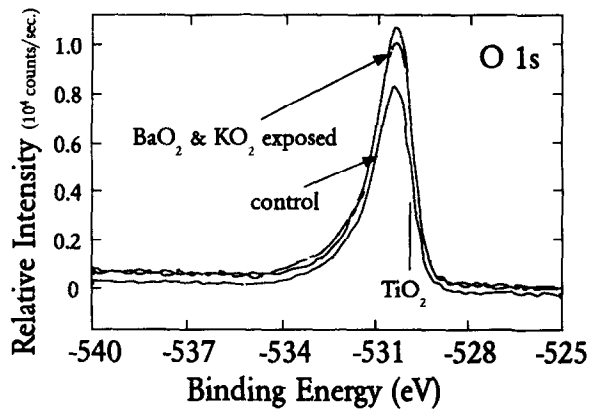
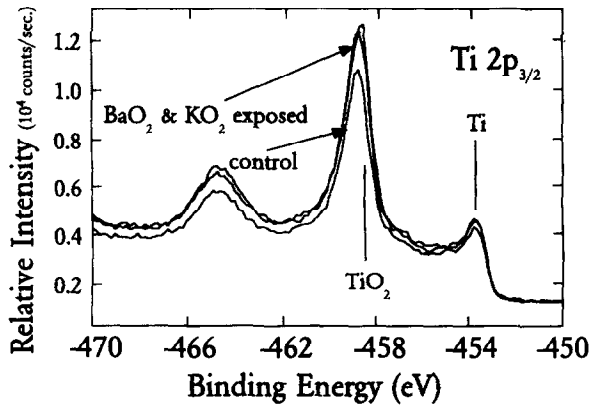


Fig. 5. Comparison of X-ray photoelectron spectra of the Ti 2p region (top) for micromirrors before (labeled “control”) and after exposure to oxidants (BaO₂ and KO₂) reveals a small increase in the thickness of a complex, TiO₂-like oxide. The O 1s spectra of Ti micromirror films exposed to BaO₂ and KO₂ are shown at bottom, along with a control spectrum

in relative film reflectivity is absolutely necessary; this requires exceptional photometric stability under extremely challenging environmental conditions.

The results for a 4-nm Cr film are somewhat different. The reflectivity change after immersion into KO₂ is shown in Fig. 6 (~3% relative reflectivity change over 12 h). The XPS data for the Cr 2p and O 1s regions of the Cr

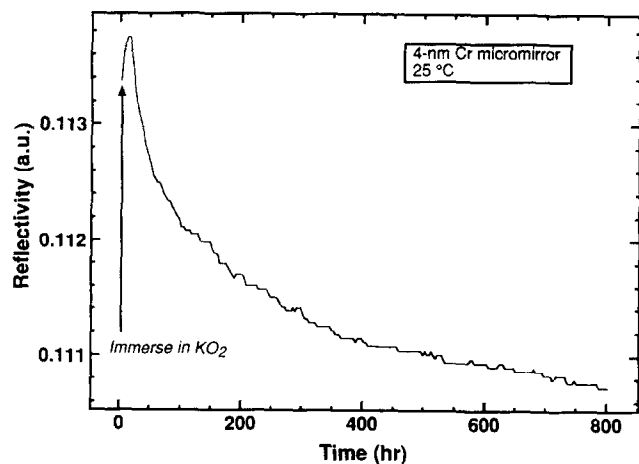


Fig. 6. Reflectivity versus time for a 4 nm Cr fiber tip micromirror immersed in solid KO₂ at 25°C

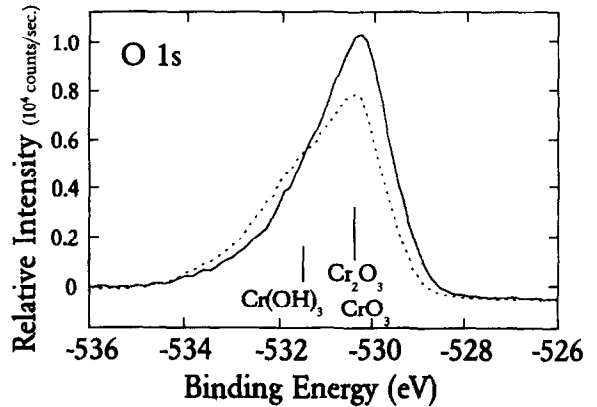
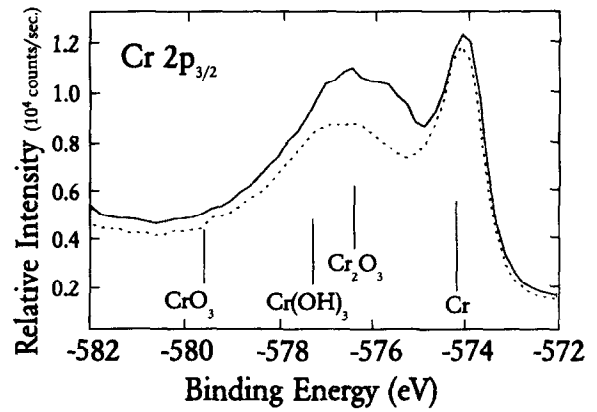


Fig. 7. XPS data for the Cr 2p (top) and O 1s (bottom) regions from a KO₂-immersed Cr film. Dashed curves are the spectra before immersion in the KO₂, solid curves are after immersion for 12 h

micromirror are shown in Fig. 7 at the top and bottom, respectively. Dashed curves are the spectra before immersion in the KO₂, solid curves are after immersion for 12 h. Note that the major change for the Cr film is the conversion of the part of the heavily hydroxylated surface (Cr(OH)₃) formed during exposure to impurities in the N₂ to Cr₂O₃; this change represents not an oxidation, but a dehydration of the film. From XPS, the net change in oxide overlayer thickness corresponds to 0.2 to 0.3 nm, in modest agreement with the reflectivity data. In both the Ti and the Cr control samples (unexposed to solid oxidant), more than a monolayer of carbon-based contamination is revealed by XPS. The amount of carbon decreases by a factor of 3 to 8 in samples exposed to the solid-phase oxidant(s). Figure 8 shows the reflectivity of the semiconductor PbS when exposed to KO₂ at 25°C. In this case a 3% increase in reflectivity is seen over a period of 200 min.

3.3. Effect of relative humidity

In the course of the solid-oxidant experiments measuring reflectivity changes for Ti micromirrors, considerable variability was encountered in the results. Suspecting a variation in the relative humidity of the reaction chamber, we performed a number of experiments in which the Ti/fiber system was exposed to nitrogen with different

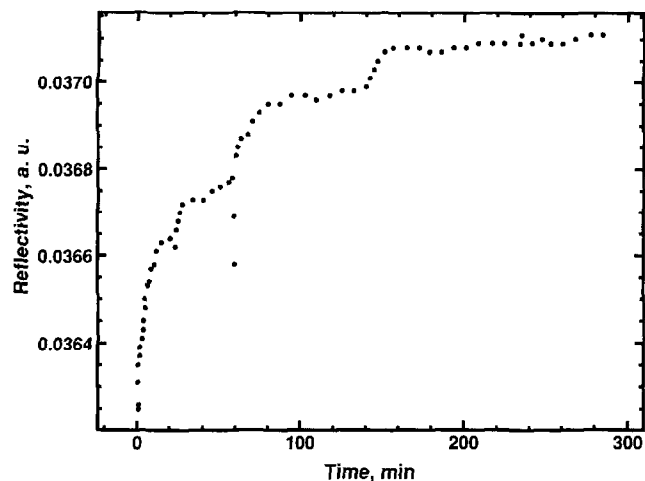


Fig. 8. Reflectivity change as a function of time for a PbS film exposed to KO_2 at 25°C

partial pressures of water vapor. All Ti-coated fiber tips (except for the control) were first immersed in KO_2 powder, then removed and exposed to humid nitrogen. Small amounts of KO_2 powder remained on the fiber tips following emersion from the powder; all measurements were made at room temperature. The results are shown in Fig. 9. Curve (a) is for the 6-nm Ti control film, never exposed to KO_2 , but exposed to approximately 1 Torr of water vapor in atmospheric-pressure nitrogen for 100 h; the relative reflectivity changes by less than 2%. Curve (b) corresponds to a KO_2 -reacted Ti-coated fiber exposed to ~ 0.2 Torr of water vapor in nitrogen for 100 h; the Ti film is mostly converted to oxide in about 7 h, with further decrease in film reflectivity occurring until about 70 h. Curve (c) corresponds to a KO_2 -reacted Ti-coated fiber exposed to ~ 1 Torr of water vapor in nitrogen; this film is completely converted to oxide in about 2 min.

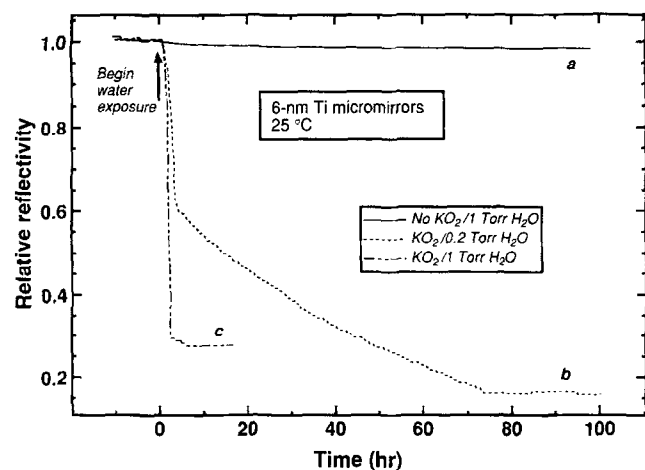


Fig. 9. Reflectivity versus time for experiments in which Ti fiber tip micromirrors were exposed to N_2 streams containing various partial pressures of H_2O : curve (a) is for a 6 nm Ti control film, never exposed to KO_2 , but exposed to ~ 1 Torr of H_2O in 1 atm of N_2 ; curve (b) corresponds to a KO_2 -reacted, Ti-coated fiber exposed to ~ 0.2 Torr of H_2O in N_2 ; curve (c) corresponds to a KO_2 -reacted, Ti-coated fiber exposed to ~ 1 Torr of H_2O in N_2 ; this film completely converted to oxide in about 2 min

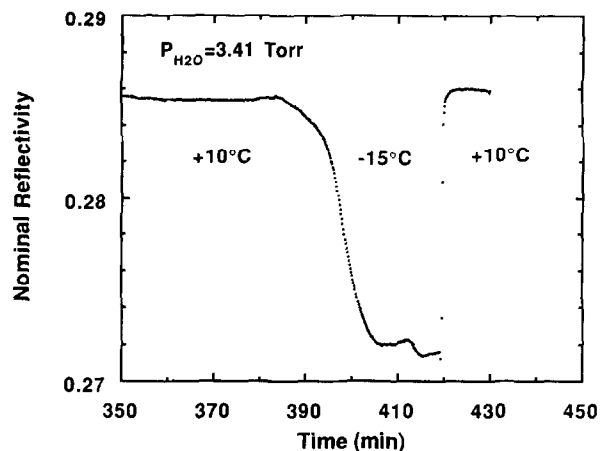


Fig. 10. Reflectivity versus time for an optical fiber with a semi-transparent tip coating of gold. As the temperature drops to -15°C condensation occurs in the moist air. This results in a reversible and measurable change in the reflectivity

Acceleration of the Ti oxidation by water is not unanticipated and may be a particular problem with ionic superoxide model systems. The conclusion from these experiments is that absolutely dry KO_2 shows little oxidative reactivity, most likely due to the highly ionic nature of this compound, a consequence of which is that the absence of water inhibits both transport and reactivity. The partial pressure of water is low by terrestrial standards but can be saturated at the low nighttime temperatures on Mars.

The reflectivity of the micromirrors in the air cell would also be used to detect frost on Mars. This is illustrated in Fig. 10. Fibers with semi-transparent coatings of gold in humid air show a decrease in reflectivity due to frost formation on the gold surface when the temperature is lowered through the dew point.

4. Conclusions

The MOx instrument for the ill fated Russian Mars '96 mission was designed to investigate the chemical reactivity of the martian soil. Thin metallic and organic films formed the basis for the chemical sensors on MOx. In the course of the design and construction of the MOx instrument we reached the following conclusions.

1. The *in situ* investigation of reactive chemistry on Mars can be accomplished by exposure of a varied set of materials to the martian environment.
2. At martian temperatures and humidity levels the reaction rates are expected to be exceedingly slow. To generate a measurable reaction requires either that the samples and sensors be warmed or that long integration times be employed. For MOx we allowed for integration of reactivity for over 1 year.

Although the MOx instrument was destroyed along with the Mars '96 spacecraft we anticipate that the technology and sensor approaches developed could be used to investigate the martian soil on future missions.

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