PEROXIDE-MODIFIED TITANIUM DIOXIDE: A CHEMICAL ANALOG OF PUTATIVE MARTIAN SOIL OXIDANTS

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Abstract. Hydrogen peroxide chemisorbed on titanium dioxide (peroxide-modified titanium dioxide) is investigated as a chemical analog to the putative soil oxidants responsible for the chemical reactivity seen in the Viking biology experiments. When peroxide-modified titanium dioxide (anatase) was exposed to a solution similar to the Viking labeled release (LR) experiment organic medium, CO_2 gas was released into the sample cell headspace. Storage of these samples at 10 °C for 48 hr prior to exposure to organics resulted in a positive response while storage for 7 days did not. In the Viking LR experiment, storage of the Martian surface samples for 2 sols (∼49 hr) resulted in a positive response while storage for 141 sols essentially eliminated the initial rapid release of CO_2. Heating the peroxide-modified titanium dioxide to 50 °C prior to exposure to organics resulted in a negative response. This is similar to, but not identical to, the Viking samples where heating to approximately 46 °C diminished the response by 54–80% and heating to 51.5 apparently eliminated the response. When exposed to water vapor, the peroxide-modified titanium dioxide samples release O_2 in a manner similar to the release seen in the Viking gas exchange experiment (GEx). Reactivity is retained upon heating at 50 °C for three hours, distinguishing this active agent from the one responsible for the release of CO_2 from aqueous organics. The release of CO_2 by the peroxide-modified titanium dioxide is attributed to the decomposition of organics by outer-sphere peroxide complexes associated with surface hydroxyl groups, while the release of O_2 upon humidification is attributed to more stable inner-sphere peroxide complexes associated with Ti^{4+} cations. Heating the peroxide-modified titanium dioxide to 145 °C inhibited the release of O_2, while in the Viking experiments heating to this temperature diminished but did not eliminated the response. Although the thermal stability of the titanium-peroxide complexes in this work is lower than the stability seen in the Viking experiments, it is expected that similar types of complexes will form in titanium containing minerals other than anatase and the stability of these complexes will vary with surface hydroxylation and mineralogy.

1. Introduction

Since the return of data from the Viking Landers in 1977, numerous hypotheses have been presented to explain the results of the Labeled Release (LR) and Gas Exchange (GEx) Experiments. These biology experiments were designed to test Martian surface samples for the presence of life by measuring metabolic activity and distinguishing it from physical or chemical activity (Oyama *et al*., 1976; Levin and Straat, 1976). In the Viking Gas Exchange Experiment (GEx), an attempt was made to identify microbial activity by using gas chromatography to measure the

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Table I
Explanations for the Viking Results

GEx oxygen release	
KO_2, ZnO_2	Ponnamperuma *et al*., 1977
MnO_2, irradiated	Blackburn *et al*., 1978
O_2 trapped in micropores	Nussinov *et al*., 1978
O plasma	Ballou *et al*., 1978
Activated halides	Zent and McKay, 1994
H_2O_2 formed on olivine and pyroxene	Huguenin *et al*., 1978
H_2O_2 adsorbed on Titanium dioxide	This Work
LR CO_2 release	
H_2O_2	Oro, 1979; Levin and Straat 1981
H_2O_2 adsorbed on Titanium dioxide	This Work
Peroxonitrate (NOO_2^-)	Pumb *et al*., 1989
Fe-rich smectite clays	Banin and Margulies, 1983

gas changes in the headspace above a soil sample after the addition of a aqueous nutrient medium designed to promote microbial growth. The primary result of this experiment was the release of oxygen in amounts ranging from 70 to 700 nmole cm^{-3} by the Martian surface samples upon introduction of water vapor into the sample cell. Heating the sample to 145 °C was found to diminish but not eliminate the release of oxygen. The Labeled Release Experiment (LR) (Levin and Straat, 1976) attempted to detect metabolism or growth of microorganisms through radiorespirometry. In the LR experiment, a liquid medium containing several organic substrates labeled with ^{14}C was introduced to the Martian surface sample. The major results of the LR were: ^{14}C-labeled CO_2 was rapidly released upon contact of the surface material with the solution; the reaction slowed down after only a small fraction of the added organic medium decomposed; preheating the samples to 160 °C for three hours completely inhibited the release of $^{14}CO_2$ (Levin and Straat, 1977).

These results, combined with the failure of the Viking GCMS to detect organic compounds in tested surface samples, have generally lead investigators to the conclusion that the surface material was not biologically active under the experimental conditions, but was chemically reactive (for reviews see Klein, 1978; 1979; Zent

and McKay, 1994). In a review article, Zent and McKay (1994) examined a suite of GEx and LR hypotheses (Table I) and concluded that the simplest and most consistent explanation involves a photochemically-produced oxidant which originates in the atmosphere and diffuses into the regolith in very small quantities. Heterogeneous chemical reactions between these photochemically-produced oxidants and the regolith then create surface complexes responsible for the results seen in the Viking biology experiments. The most likely candidate for the oxidant species are the various forms of odd-oxygen and odd-hydrogen expected to be photochemically produced in the Martian atmosphere.

For instance, Hunten (1979) calculated the H_2O_2 flux to the surface of Mars to be 2×10^9 molecules cm^{-2} s^{-1} and suggested that this may be the source of the oxidant detected by the Viking biology experiments. Huguenin *et al*. (1979) and Huguenin (1982) suggested that surface peroxides formed from the process of water frost dissociating into OH^- and H^+ on the surface of olivine and basalt could be responsible for both the LR and GEx results. In this model the protons from the dissociated water frost migrate into the mineral lattices leaving the OH^- radicals on the surface to recombine into surface peroxides. Unfortunately, the experiments described by Huguenin failed to demonstrate the thermal stability of these surface peroxide groups, although allowing the frost to melt on the mineral surfaces did produce an oxygen release. Other interpretations of the LR results have also invoked hydrogen peroxide. Levin and Straat (1979; 1981) performed LR simulations using aqueous hydrogen peroxide mixed with Mars soil analogs and concluded that some of the tested mixtures can reproduce the kinetics and thermal information contained in the LR data, however, if H_2O_2 is responsible for the LR results, it would have to be complexed in an unknown way with the Martian surface material.

It is the objective of this study to investigate the complexation of hydrogen peroxide with titanium dioxide to determine if these complexes exhibit stability and reactivity that is similar to what was seen in the Viking biology experiments. Elemental analysis of the Martian surface by the Viking XRF determined that the Martian surface material contains approximately 1% Ti, reported as TiO_2 (Clark *et al*., 1977). However, while the XRF analysis provided elemental abundance, no mineralogical characterization of the surface material was carried out. On earth, titanium is widely distributed in igneous rocks, with rutile being the most common form of naturally occurring TiO_2. Anatase, a low temperature form of TiO_2, is often formed as an alteration product of ilmenite ($FeTiO_3$) which is a common accessory mineral in igneous rocks. Another widespread accessory mineral containing titanium that is found in igneous rocks is sphene $CaTi[SiO_4](O,OH,F)$. For this work, we chose to use synthetic titanium dioxide (anatase) as the substrate for complexation with peroxide. Although the use of natural titanium containing samples would be preferable over synthetic samples, natural samples were avoided for several reasons. Through careful synthesis of samples, the microbial and organic contaminants that are commonly found in natural samples can be avoided. Organic

compounds and microbes will not only react with hydrogen peroxide, they also can lead to false interpretations of any GEx or LR like activity. Additionally, through careful selection of the synthesis conditions the chemical state of the titanium dioxide surface can be controlled, leading to a better understanding of the chemical nature of the complexes that form. Since we are not using a mineral likely to be abundant on Mars, we are proposing a chemical analog for possible stabilization mechanisms of hydrogen peroxide on Mars, we are not proposing a mineralogical model. Of primary interest in this study is the chemical interaction of hydrogen peroxide with the Ti^{4+} cations that are present in the TiO_2 samples, and would also be expected be to present in titanium-containing minerals on Mars.

2. Experimental

2.1. Synthesis of titanium dioxide (Anatase)

Samples of titanium dioxide (anatase) were prepared by hydrolysis of reagent grade titanium tetrachloride (Aldrich Chemical). 5.5 mL of $TiCl_4$ was slowly added to 100 cc of doubly-distilled water cooled in an ice bath. The pH of the resulting mixture was adjusted to 9 by the addition of ammonium hydroxide, and the solution was boiled for one hour. The resulting precipitate was washed with doubly-distilled water by filtering on a sintered glass funnel until free of chloride ions as determined by spot tests of acidified effluent with 0.1 N silver nitrate. The sample was then calcined at either 200 or 350 °C for four hours. Calcination at 200 °C removes molecular water from the sample, but leaves the majority of surface hydroxyl groups intact (creating a hydroxylated sample), while heating to 350 °C removes molecular water as well as a large number of surface hydroxyl groups (creating a partially dehydroxylated sample). Munuera *et al*. (1978) determined that heat treatment of anatase at 350 °C yields a surface with 2.8 OH groups per nm^2, while anatase heat-treated at 150 and 250 °C contain 8.2 and 6.5 OH groups per nm^2 respectively. Analysis of samples prepared in this manner have been determined to be predominately anatase type TiO_2 (Funaki and Saeki, 1956; Bauer 1963). The surface area of the partially dehydroxylated samples used in this work was determined to be 208 $m^2\ g^{-1}$ from N_2 adsorption isotherms measured at 77 K.

2.2. Decomposition of aqueous organics

The fundamental result of the Viking LR experiment was the decomposition of aqueous organic compounds. Samples of peroxide-modified titanium dioxide were prepared and tested to see if sufficient reactivity was retained by the peroxide complexes to decompose the organics that were used in the LR experiment. Because of the difficulty in working with radioisotopes in the laboratory, the LR radioscopic technique was not used, and as such actual simulations of the LR experiment were not performed. Instead the decomposition of LR organics by the peroxide-modified

TiO_2 was monitored by measuring CO_2 in the sample cell headspace using gas chromatography. Details of sample preparation and analysis are discussed below, while a discussion on how CO_2 release measured by GC compares to the LR technique is included in Section 3 (Results and Discussion).

Samples of TiO_2 (1.0 g) were suspended in freshly prepared 1% H_2O_2 solutions (prepared by dilution of Aldrich Chemical 30% H_2O_2) for 20–30 min. The samples were then filtered on sintered glass filters and washed with distilled water to remove excess H_2O_2. The total peroxide coverage was determined to be 7.2×10^{17} molecules m^{-2} from the difference in concentration (determined by titration with potassium permanganate) of the effluent and the original solution.

To prevent microbial contamination of the samples, all glassware was cleaned with Micro cleaning solution (International Products Inc.), rinsed with doubly-distilled water, and dried under vacuum at 160 °C. Additionally, glassware was covered or sealed to prevent spore or microbe contamination during the synthesis. After synthesis, all samples were immediately transferred to a clean box with a continuous purge He atmosphere. Once transferred into the box, 0.1 g samples were placed into 8.6 cc glass sample vials and crimp sealed with rubber septa. The samples were stored in the dark at 10 °C between analyses.

Sample analysis of headspace gases was carried out by extracting 1.0 mL of the cell headspace with a gas-tight syringe. The gas sample was then analyzed using a Varian 3400 GC fitted with a 6ft. × 1/8 o.d. HayeSep N column (column temperature 140 °C) and thermal conductivity detector (detector 180 °C, filament 220 °C). Helium, delivered at 80 psi, was used as the carrier gas. A three-level calibration was done for CO_2 using 99.99% carbon dioxide.

Before injection of aqueous organics, the samples were incubated in the dark at 10 °C for 48 hr and an initial headspace analysis was performed to verify that no atmospheric CO_2 contamination or sample outgassing had occurred. After this initial analysis, 0.5 mL of a equal-molar solution of DL-alanine (Sigma, 99% minimum purity), formic acid (Aldrich, 99+% purity), glycine (Sigma, 99+% purity), glycolic acid (Sigma, 98% minimum purity) and DL-lactic acid (Sigma, sodium salt 60% (w/w) syrup 98%) was added to the test cells (total molarity 0.25, pH adjusted to 8.0 with KOH). After injection of the organic medium, the CO_2 level in the headspace was monitored for a period of 72 hr.

In this work, both the sample size and the concentration of the organic solution was increased compared to the Viking experiments (0.1 g vs. 6.5 mg as TiO_2 and 0.25 m vs. 0.25 mm) to compensate for the lower sensitivity of the GC analysis relative to the LR radioisotopic technique. Later interpretations of the LR experiment indicate that the soil oxidant, not the nutrient, was the limiting reagent in the LR reaction (Levin and Straat, 1981). Since the total load of active hydrogen peroxide adsorbed on the TiO_2 samples was not known, the relative amount of nutrient used in this work was increased over the Viking LR to insure that the nutrient did not become the limiting reagent. Therefore, results are scaled based on the weight of TiO_2 used since the total amount of CO_2 released by the samples is related to the

availability chemisorbed peroxide and not the amount of nutrient injected. This scaling is discussed further in Section 3 (Results and Discussion).

The thermal stability of the peroxide complexes was tested by heating samples (sealed in a helium atmosphere) at 50 °C for three hours prior to addition of the organic solution and testing of headspace gases. Blank samples of titanium dioxide that had not been exposed to hydrogen peroxide, were analyzed in the same manner as the peroxide-modified samples.

2.3. Oxygen release upon humidification

The primary result of the Viking GEx was the rapid release of O_2 gas upon humidification of the Martian surface samples. In both the Viking GEx and this work changes in sample cell headspace composition were monitored using gas chromatography.

Samples of TiO_2 (1.0 g) were suspended in approximately 30 mL of 3% H_2O_2 (Aldrich, stabilized, A.C.S. reagent grade) for 30 min, filtered on a covered sintered glass crucible in air and transferred into a 35 cc stainless steel sample cell. To prevent atmospheric oxygen from leaking into the cell, all seals were metal gasket compression type (conflat, Varian). The cell was equipped with two Nupro SS-4BK bellow-sealed valves. One valve allowed for the evacuation and sampling of cell gases, the other was used to introduce water vapor into the cell via a glass reservoir connected to the cell with a glass-to-metal transition tube. Doubly-distilled water de-gassed by at least 3 freeze-pump-thaw cycles was used for all experiments.

After transferring the sample into the cell, the cell was attached to a vacuum manifold and pumped to a pressure of 10^{-4} torr at room temperature for 16–20 hr. Samples were then heated to approximately 50 °C under vacuum for an additional three hours to remove water from the sample and to test the thermal stability of the peroxide complexes. The samples were then cooled to 10 °C (the temperature of the Viking GEx test cell) and, as was done in the Viking GEx, the sample cell was filled to 200 torr with He. After filling with He, the samples were equilibrated for 16 hr before testing.

The gases in the headspace were separated, identified and quantified using a Varian 3400 GC gas chromatograph. A poropak Q 100/120 mesh 7.6m $\times$ 1 mm i.d. column (column temperature 25 °C) capable of separating N_2, O_2, Ar/CO, and CO_2 was used to insure that air contamination in the cell could be recognized. Helium carrier gas was delivered at a pressure of 80 psi with a flow rate of 30 cc min^{-1}. A thermal conductivity detector was used for detecting gases eluted from the column. A three-level calibration was done for O_2 using 99.9% pure oxygen.

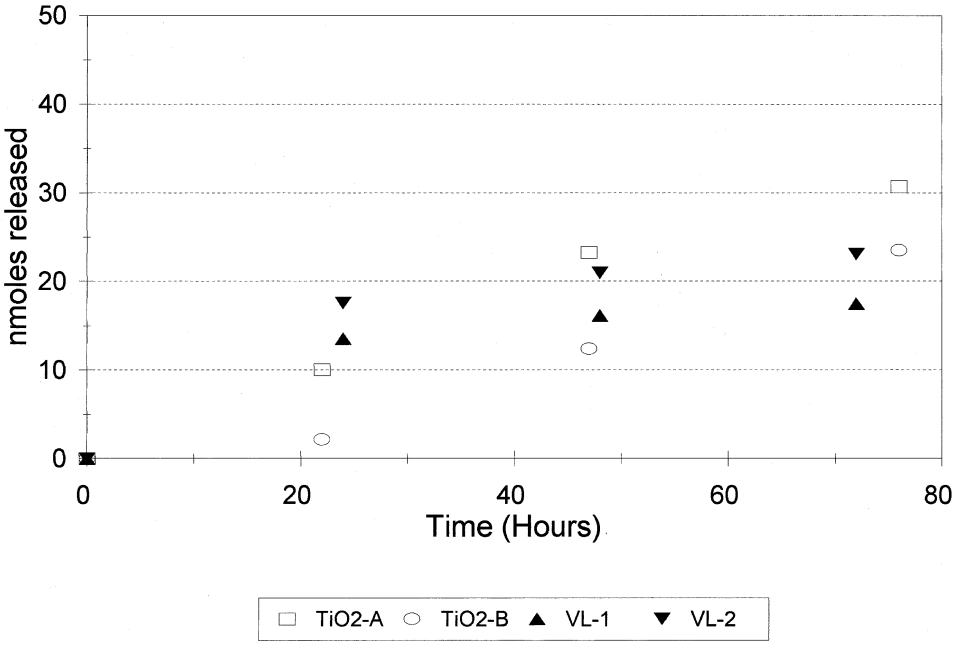

Figure 1. Carbon dioxide changes upon introduction of organic nutrient medium to the peroxide-modified titanium dioxide (partially dehydroxylated anatase) containing sample cell compared to the results of the Viking LR-1 cycle one and VL-2 cycle one samples.

3. Results and Discussion

3.1. Carbon dioxide release

Figure 1 compares the carbon dioxide released from the organic nutrient by two replicate samples of partially dehydroxylated (350 °C synthesis) peroxide-modified titanium dioxide with the results of the Viking LR VL-1 cycle one and VL-2 cycle one samples (Levin and Straat, 1979). To facilitate comparison, the release of CO_2 by the peroxide-modified TiO_2 is reported as nmoles of CO_2 released per 0.0065 g of titanium dioxide. The Viking LR utilized 0.5 cm^3 of Martian surface material, which corresponds to 0.0065 g of titanium (as TiO_2) in each sample, assuming a density of 1.3 g cm^{-3} (Oyama *et al.*, 1977) and a 1% titanium content by weight (Clark *et al.*, 1977).

The use of GC instead of the LR radioisotopic technique to monitor the release of CO_2 affects the interpretation and comparison of results. Analysis by GC required extraction of headspace gas at periodic intervals and continuous measurement of the release of CO_2 was not possible as it was with the LR experiment. Therefore, no comparison between the kinetics of CO_2 release by the peroxide-modified TiO_2 with the kinetics observed in the first few hours of the LR experi-

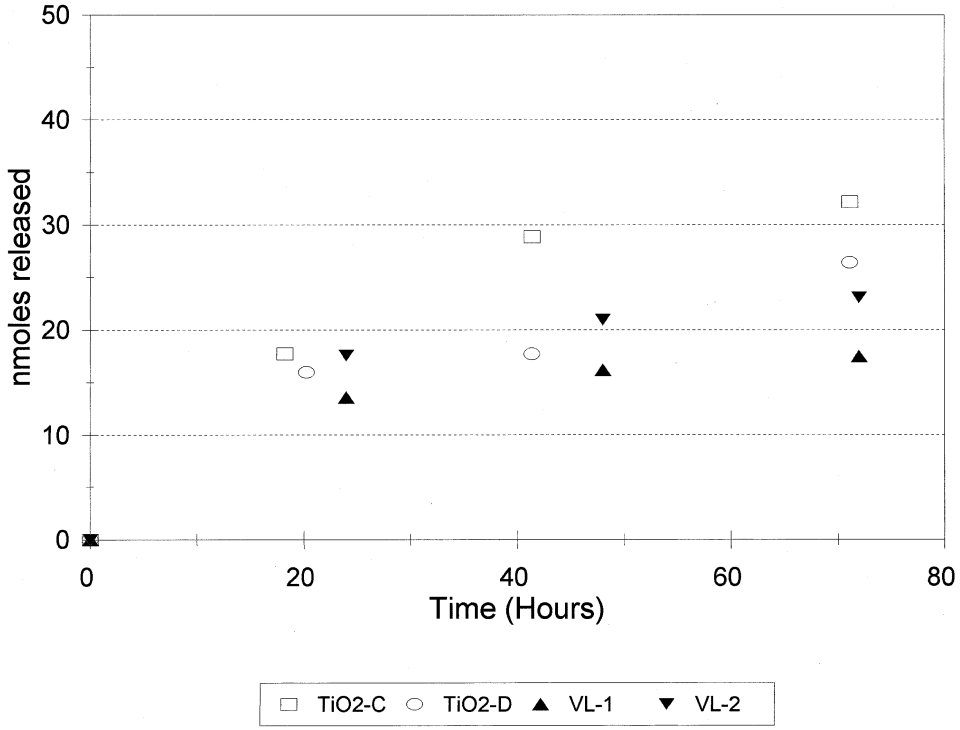

Figure 2. Carbon dioxide changes upon introduction of organic nutrient medium to the peroxide-modified titanium dioxide (hydroxylated anatase) containing sample cell compared to the results of the Viking LR-1 cycle one and VL-2 cycle one samples.

ment can be made. However, general trends occurring over the first 72 hr can be compared.

The Viking LR experiments were characterized by a rapid release of CO_2 from the nutrient medium during the first 24 hr followed by a slower prolonged increase over the next few sols. As can be seen in Figure 1, during the first 24 hr of the Viking experiments the VL-1 sample decomposed approximately 14 nmoles of nutrient while the VL-2 sample decomposed approximately 18 nmoles. In contrast, for the peroxide-modified TiO_2 (partially dehydroxylated), a smaller amount of CO_2 was released into the headspace (when scaled by weight as describe above), during the first 24 hr, 10 nmoles of CO_2 from sample TiO_2-A and 2 nmoles from sample TiO_2-B. In addition, after the first 24 hr, the rate of CO_2 released by the Viking samples decreased, while the rate of release by these TiO_2 samples did not. Although partially dehydroxylated samples do result in the release of CO_2 into the cell headspace, the initial rate of release appears to be some what slower and the release fails to level off at the same rate seen in Viking LR results.

In the case of hydroxylated samples, the rate of CO_2 release differed slightly from the partially dehydroxylated samples. Figure 2 compares the carbon dioxide

released by hydroxylated samples of peroxide-modified titanium dioxide with the results of the VL-1 cycle one and the VL-2 cycle one. During the first 24 hr, sample TiO_2-C released (scaled by relative weight as described above) approximately 18 nmoles of CO_2 while sample D released 16 nmoles. This compares to approximately 14 nmole for VL-1 cycle one and approximately 18 for nmoles VL-2 cycle one. Additionally, unlike the partially dehydroxylated samples, the release from the hydroxylated samples starts to decrease after the first 24 hr as is seen in the Viking results. No CO_2 was released by titanium dioxide samples that were exposed to the organic solution (and stored in the dark) but not exposed to hydrogen peroxide, indicating that the decomposition of the organic medium is due to the presence of H_2O_2 complexes and not due to the inherent catalytic activity of TiO_2 or microbial contamination.

The ability of peroxide-modified titanium dioxide to reproduce the Viking LR results is apparently influenced by the hydroxylation state of the sample. This is indicative of different types of peroxide complexes forming on the surface titanium dioxide, which is consistent with other studies of peroxide-modified titanium dioxide (Boonstra and Mutsaers, 1975; Munuera *et al.*, 1980; Klissurski *et al.*, 1990). It has also been found that the same types of complexes form from exposure of TiO_2 to vapor phase or aqueous hydrogen peroxide (Boonstra and Mutsaers, 1975). This is important since on Mars the source of soil peroxide-complexes would likely be from hydrogen peroxide that is photochemically produced in the atmosphere and diffuses into the soil where complexation then occurs.

When exposed to either vapor phase or aqueous hydrogen peroxide, different types of peroxide complexes form on the surface of titanium dioxide. One of these types is inner-sphere peroxo-complexes of Ti^{4+} ions, where the H_2O_2 molecules act as bidentate ligands saturating the coordinative capacity of the Ti^{4+} ions originally in a 4-fold coordination scheme (Munuera *et al.*, 1980). The bonding in these complexes is coordinative in nature and gives peroxide-modified titanium a characteristic bright yellow color. Another type of complex that forms is outer-sphere complexes associated with surface hydroxyl groups. These complexes are tightly bonded to the surface through hydrogen bonding (Munuera *et al.*, 1980). The number and type of complexes that form depends on the hydroxylation state of the titanium dioxide, with the hydroxylated samples containing a greater number of surface hydroxyl groups and therefore more outer-sphere complexes than the partially dehydroxylated samples. Likewise, the partially dehydroxylated samples have a greater number of inner-sphere complexes than the hydroxylated sample. It is likely that the less tightly bonded, outer-sphere peroxide complexes on the surface of the titanium dioxide are responsible for the initial rapid release of CO_2 by the hydroxylated samples.

In the Viking LR experiment, three samples were heat-treated for three hours prior to injection of the nutrient medium. Sample VL-2 cycle four was heated at approximately 46 °C (accurate to within only a few degrees), and exhibited a 54–80% decrease in CO_2 release compared to the unheated Viking samples (Levin and

Straat, 1977, 1979). Sample VL-2 cycle two was heated at 51.5 °C for three hours, (again accurate to within a few degrees) and in this case, the release of CO_2 was essentially eliminated. In addition, unusual kinetics which could not be traced to instrument anomalies were seen for the very small amounts of CO_2 detected in the cell (Levin and Straat, 1977). The third sterilized sample VL-1, cycle two, which was heated to 160 °C, exhibited essentially no initial release of CO_2 when exposed to the nutrient medium.

Given the uncertainty in the accuracy of the Viking temperature measurements, it can be said that the LR oxidant decomposes at about 50 °C. In this study, samples heated to 50 °C for three hours released no detectable amount of CO_2. This is consistent with the direct measurement of the thermal stability of outer-sphere peroxide complexes on titanium dioxide which are completely desorbed at about 50 °C (Boonstra and Mutsaers, 1975; Munuera *et al.*, 1980; Klissurski *et al.*, 1990).

The lifetime of the peroxide complex at 10 °C was also investigated. In the Viking LR experiments, samples stored for 2 sols (∼49 hr) at 10 °C in the dark produced positive responses while the initial rapid release of CO_2 was essentially eliminated after storage for 141 sols. In this work, the responses reported are for samples stored for 48 hr in a He atmosphere at 10 °C in the dark before introduction of the nutrient medium. Samples that were stored for 7 days exhibited a negative response consistent with the Viking results.

3.2. Oxygen Release

Figure 3 shows oxygen released upon humidification by peroxide-modified titanium dioxide samples compared to the results of the Viking GEx VL-1 Sandy Flats and VL-2 Beta samples (Oyama and Berdahl, 1977). For comparison the amount O_2 released by the peroxide-modified titanium dioxide is scaled by weight and reported as nmoles released per 0.013 g of TiO_2. The Viking GEx utilized 1.0 cm^3 of Martian surface material, which corresponds to 0.013 g of titanium (as TiO_2) in each sample, assuming a density of 1.3 g cm^{-3} (Oyama *et al.*, 1977) and a 1% titanium content by weight (Clark *et al.*, 1977).

Upon humidification of the peroxide-modified anatase samples in the simulated GEx experiments, the O_2 level in the headspace rapidly increased. Control samples of TiO_2 not exposed to peroxide did not exhibit any release of oxygen. The general trend for O_2 changes in the headspace of the peroxide-modified titanium dioxide samples in this work is similar to the increase in oxygen seen in the Viking VL-1 cycle one and VL-2 cycle one data where an initial rapid release of O_2 gas was seen during the first 24 hr after exposure to water vapor (Figure 3).

The decomposition of organics in this work has been attributed to outer-sphere peroxide groups on the surface of a hydroxylated anatase sample. This is based on the thermal stability of these complexes reported in the literature (Boonstra and Mutsaers, 1975; Munuera *et al.*, 1980; Klissurski *et al.*, 1990) and the negative result obtained with these samples after heating at 50 °C for three hours. In the case

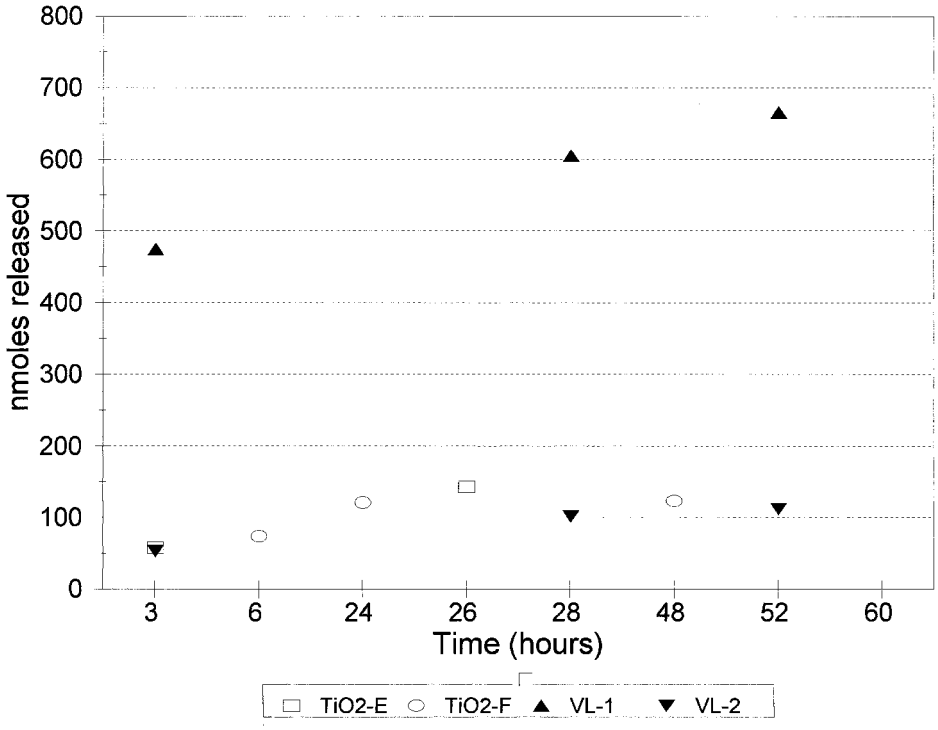

Figure 3. Oxygen release from peroxide-modified titanium dioxide upon humidification compared to the Viking VL-1 Sandy Flats and VL-2 Beta samples.

of the humidification experiments, all samples were heated under vacuum at 50 °C for three hours prior to use. This heat treatment was done to remove physically adsorbed water from the surface of the sample. Since samples of peroxide-modified titanium dioxide heated to 50 °C released O_2 upon humidification, but did not decompose organics, it appears that different species are responsible for these two responses although their origin is the same (complexed hydrogen peroxide). This is consistent with conclusions drawn from the results of the Viking Biology experiments (Klein, 1977; 1979). It should be noted however, that in both the Viking LR experiments and the CO_2 release experiments in this work, the sample cell was sealed during the heating procedure. Thus, the stability of the oxidant may have been affected by exposure to high water vapor concentrations during the heating process (Horowitz, 1986).

An average of 120 nmoles of O_2 (scaled by relative wt. of TiO_2) were released by the peroxide-modified titanium dioxide in this work which is consistent with the VL2 GEx results. Table II compares values reported in the literature for the temperature stability of inner-sphere peroxide complexes on anatase with the samples used in this work. In this work, all the peroxide complexes desorbed at temperatures below 120 °C, and not surprisingly samples heated to 145 °C did not release O_2

Table II
Stability of inner-sphere peroxide complexes on TiO_2

	Surface coverage	Desorption range
Klissurski *et al*., 1990	1.5×10^{13} molecules cm^{-2}	75–170 °C
Boonstra and Mutsaers, 1975	1.7×10^{14} molecules cm^{-2}	50–150 °C
Munuera *et al*., 1980	1.0×10^{14} molecules cm^{-2}	150–200 °C
This work	7.2×10^{13} molecules cm^{-2}	50–120 °C

upon humidification. However, peroxide desorption occurs over a broad temperature range with variations in the upper and lower temperature limits that depend on mineralogy and hydroxylation state (Boonstra and Mutsaers, 1975; Munuera *et al*., 1980; Klissurski *et al*., 1990).

The total amount of O_2 released by the TiO_2 represents a fraction of the total chemisorbed peroxide. The number of inner-sphere peroxide groups present on the surface of the anatase is approximately 7×10^{17} molecules m^{-2}, which corresponds to a release of 1572 nmoles of O_2 for a 0.013 g sample if all groups decompose to form water and O_2. Furthermore, the TiO_2 samples retained their bright yellow color after humidification, which indicated that at least some of the inner-sphere peroxide groups remained. One possible explanation for the release of O_2 in amounts that correspond to only approximately 10% of the chemisorbed hydrogen peroxide, is that during the sample dehydration process, some of peroxide groups may partially decompose or migrate to sites previously occupied by water molecules. Upon re-hydration of the anatase sample, water displaces the peroxide and it decomposes into H_2O and O_2. On Mars, the surface coverage of physically adsorbed water is only a fraction of a monolayer (Zent and Quinn, 1995). Under these conditions, it is possible that peroxide may adsorb onto sites that would be occupied by molecular water at higher temperatures and higher water vapor abundance. When the dry Martian surface sample is exposed to 100% humidity at 10 °C in the gas exchange experiment, several monolayers of physically-adsorbed water form on the surface, displacing peroxide. Once desorbed from the surface, the peroxide decomposes (catalyzed by iron oxide and other components of the surface material) and releases oxygen into the headspace.

4. Conclusions

Levin and Straat (1981) demonstrated that hydrogen peroxide could reproduce the results of the Viking LR experiment, although they concluded the peroxide would have to be complexed with the surface material in some unidentified manner. We have demonstrated that hydrogen peroxide complexes with titanium dioxide and re-

tains the ability to decomposed the same organics used in the Viking LR experiment and release O_2 when humidified as was seen in the Viking GEx. This complexation of peroxide with titanium dioxide imparts stability which is similar, although not identical, to that seen in the Viking samples. The outer-sphere peroxide complexes on titanium dioxide which are most probably responsible for the release of CO_2 in this work decompose at approximately 50 °C. In the Viking LR experiments, heating to 46 °C (plus or minus several degrees) decreased the signal by as much as 80%, and heating to 51.5 °C (plus or minus several degrees) may have eliminated the response altogether (Levin and Straat, 1977). Storage of the peroxide modified-titanium dioxide samples at 10 °C for 48 hr prior to exposure to organics resulted in a positive response while storage for 7 days did not. In the Viking LR experiment, storage of the Martian surface samples for 2 sols (∼49 hr) resulted in a positive response while storage for 141 sols essentially eliminated the initial rapid release of CO_2.

Oxygen release by the peroxide-modified titanium dioxide apparently is related to the presence of the more stable inner-sphere peroxo-complexes. The ability of these samples to release O_2 upon humidification was seen in samples that were heated at 50 °C for three hours, distinguishing these complexes from the complexes responsible for the release of CO_2 which was eliminated by prolonged heating at 50 °C. This somewhat consistent with the findings of the Viking experiment where activity was diminished but not eliminated in samples heated to 145 °C. Although the samples used in this work heated to 145 ° C did not exhibit a release of O_2 upon humidification as seen in the Viking samples, other researchers have demonstrated that chemisorbed hydrogen peroxide in some case is stable above 145 °C (Table II). Since the chemisorption occurs at Ti^{4+} sites it is reasonable to expect that the same type of chemisorption will occur on titanium containing minerals other that anatase such as rutile, ilmenite and sphene, although the stability and surface coverage of the peroxide groups is expected to differ some what with variations in hydroxylation state and mineralogy.

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