

ASTROBIOLAB: A MOBILE BIOTIC AND SOIL ANALYSIS LABORATORY. J. L. Bada¹, A. P. Zent², F. J. Grunthaner³, R. C. Quinn⁴, R. Navarro-Gonzalez⁵, B. Gomez-Silva⁶, and C. P. McKay², ¹University of California at San Diego (Scripps Institution of Oceanography, La Jolla, CA 92093-0212, jbada@ucsd.edu), ²NASA Ames Research Center, ³NASA Jet Propulsion Laboratory, ⁴SETI Institute, ⁵Universidad Nacional Autonoma de Mexico, ⁶Universidad de Antofagasta, Chile.

Introduction: The Jet Propulsion Laboratory, Scripps Institution of Oceanography, and NASA Ames Research Center are currently developing a mobile Astrobiology Laboratory (AstroBioLab) for a series of field campaigns using the Chilean Atacama Desert as a Martian surface analog site. The Astrobiology Science and Technology for Exploring Planets (ASTEP) program funded AstroBioLab is designed around the Mars Organic Detector (MOD) instrument and the Mars Oxidant Instrument (MOI) which provide complementary data sets. Using this suite of Mars Instrument Development Program (MIDP) and Planetary Instrument Definition and Development Program (PIDDP) derived *in situ* instruments, which provide state-of-the-art organic compound detection (attomolar sensitivity) and depth profiling of oxidation chemistry, we measure and correlate the interplay of organic compounds, inorganic oxidants, UV irradiation and water abundance. This mobile laboratory studies the proposition that intense UV irradiation coupled with low levels of liquid water generates metastable oxidizing species that can consume moderate amounts of seeded organic compounds. Results from the initial spring 2003 field campaign will be presented.

Viking Results: Today, nearly three decades after the mission, the results of the Viking biology experiments remain to be fully explained. These experiments revealed properties of the Martian surface material that are puzzling in three respects: (1) the release of O₂ gas (70–770 nanomoles g⁻¹) when soil samples were exposed to water vapor in the Gas Exchange Experiment (GEx) [1]; (2) the ability of the surface material to rapidly decompose aqueous organic material that was intended to culture microbial life in the Labeled Release Experiment (LR) [2]; and (3) the apparent absence of organics in samples analyzed by gas chromatography and mass spectroscopy (GCMS)[3].

Oxidants on Mars: The most widely accepted explanation for the results of the GEx and LR experiments is the presence of oxidants in the Martian soil. Differences in stability of the active agents in the two experiments suggest that the GEx and LR oxidants are different species and that at least three different oxidizing species are needed to explain all of the experimental results [4]. However, since the publication of the Viking results, no chemical model has been presented which can explain all the important details of both the GEx and the LR results [5] and, although numerous hypotheses have been presented, the chemical nature and identity of the soil oxidants remain unknown.

Atmospheric Water: While there is general agreement about the importance of UV irradiation in the generation mechanism of Martian oxidants and the decomposition of organic compounds, the role of water is more problematic. In the course of our development of *in situ* reactivity monitoring instrumentation (the Mars Oxidant Experiment (MOx) and the Mars Atmospheric Oxidant Sensor (MAOS)) we have found that many of the more virulent superoxide compounds react strongly with water vapor. The first reaction product of water with the inorganic oxidant is the generation of a strong base that rapidly accelerates reactions (by orders of magnitude) with both organic and inorganic materials. These reactions modify the surface chemistry of the fine grained solids or soils in ways that could seriously affect residual organic compounds that might be trapped and preserved in the medium. A critical reassessment of the Viking results by Benner [6], has suggested that the diagenesis of meteoritic or biotic organic material in an oxidizing environment could have lead to carboxylic acid intermediates. These salts would have had low volatility and consequently not have been detected by the Viking GCMS experimental protocol. One key component of this argument lies in the critical role of water in the known oxidation mechanisms of complex organic molecules. Low levels of water could stabilize highly reactive metastable oxidants, but could also give rise to kinetically-stabilized and partially-oxidized organic materials. Higher levels of water could react with photochemically generated strong oxidants lowering their net concentration. This could shift the steady state balance of organic influx and environmentally induced oxidation leading to higher levels of organics. Still higher abundances of water could enable the development of more complex organic molecules that might prove more resistant to photochemically enhanced oxidation.

Atacama Test Sites: AstroBioLab field experiments are being performed in the Atacama Desert, which is located along the northern Chilean pacific coast from 30° S to 20° S latitude (figure 1). The part of this region between 22° S and 26° S is extremely arid; its total rainfall is only a few millimeters over decades [7] making it one of the driest deserts in the world. These conditions have existed in the region for 10-15 Myrs [8], making it one of the best analogs on Earth for the present dry conditions on Mars. The driest parts of the region appear to be depleted in, and in some cases essentially devoid of, life, including hy-

polithic algae that are found in other arid deserts on Earth.

Studies of the presence of culturable bacteria in the Atacama region from 24° S to 28° S indicate that the quantity and diversity of heterotrophic bacteria increase as a function of local water availability. In the driest regions (24° S) there are sites where no bacteria could be isolated. The driest, apparently sterile, regions also are extremely depleted of carbon in the soil. Soils collected from these regions were reported to be essentially free of organic matter based on a flash pyrolysis GCMS analysis protocol similar to the Viking GCMS experiment [9]. The causes of the depletion of organics in some regions have not yet been established.

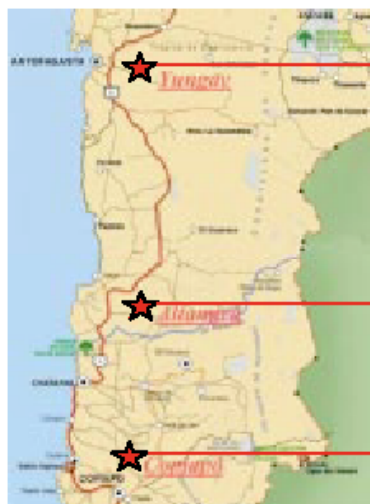


Figure 1. AstroBioLab targets the three starred sites in the Atacama Desert for field campaigns.

These deposits are known to contain highly oxidized salts, including iodates (IO_3^-), chromates (CrO_4^{2-}), and the only known naturally occurring deposits of perchlorate (ClO_4^-) [11]. The oxidized inorganic salts are postulated to be formed by UV irradiation without the presence of water at levels that would reduce the material.

The field campaign includes collaborative efforts that will acquire correlative measurements, including soil wet chemistry, mineralogical characterization, UV flux and humidity time series, nitrogen cycle chemistry, and organic infall measurements. The results of these investigations will provide additional constraints on the Atacama carbon cycle model.

AstroBioLab In Situ Instrumentation: *Mars Organic Detector (MOD)*. MOD is an miniaturized in situ instrument that has been developed to search for traces of the key organic compounds, amino acids/amines and PAHs, directly on the Martian surface [12]. It is based on the following concepts: (a) Amino acids and PAHs can be directly sublimed from natural samples by heating to 450°C under partial vacuum, thus eliminating the use of the aqueous reagents and organic solvents used in benchtop analyses; (b) sublimed amino

The existence of organic-depleted, apparently sterile soil is a remarkable Earth analog of the martian surface material.

Another striking feature of the Atacama are the large nitrate deposits, probably of atmospheric origin [10], that have not been biologically decomposed. These deposits are known to contain highly oxidized salts, including iodates (IO_3^-),

acids condensed on a cold finger coated with a reagent specific for amino acids can be detected at very high sensitivities using UV-induced fluorescence; and (c) sublimed PAHs can be directly detected on the cold finger because they are naturally fluorescent when exposed to UV light. In our characterization experiments, natural samples including crushed fossil shells, carbonaceous deep ocean sediments and crushed samples of the Murchison meteorite, have been analyzed using a sublimation apparatus evacuated to 5–6 torr to approximate Martian atmospheric pressure [13]. Primary amines were found to react with the reagent fluorescamine coated on the cold-finger surface to yield intensely fluorescent derivatives. Experiments indicate that the fluorescamine reaction proceeds in the dry state; no solvent is necessary. Amino acid/amine detection limits with this method are in the 10^{-13} mole range. Thus, amino acids, present in a Martian sample at a level of a few parts per trillion, would be detectable by this fluorescamine-based method. The detection of sublimed PAHs can be carried out directly on the cold finger under identical conditions without derivatization reagents because these compounds are extremely fluorescent when irradiated with near UV light. Detection limits are in the 10 to 100 femtomole (10^{-14} to 10^{-15} mole) range. This work resulted in the MIDP funded development of the MOD survey instrument to the brassboard level. This instrument (figure 2) consists of a high purity pyrolytic boron nitride crucible

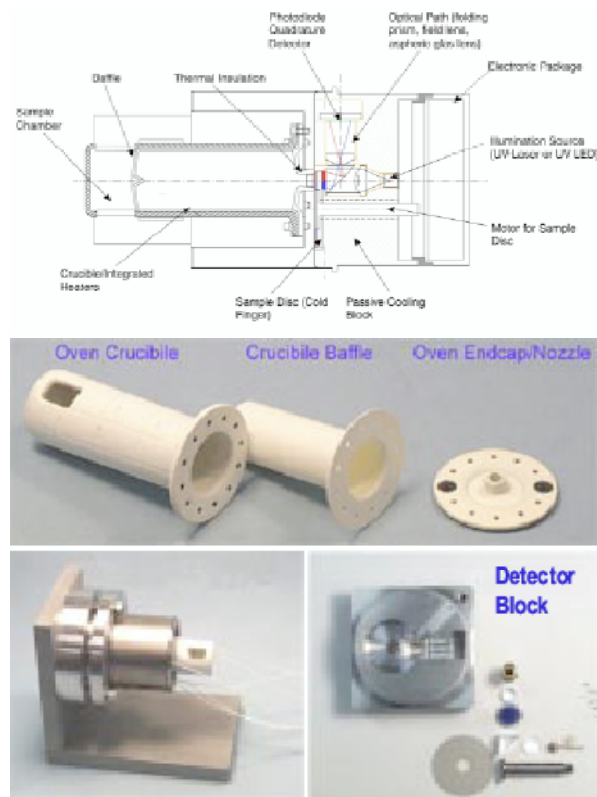


Figure 2. MOD prototype design and hardware components.

with imbedded and encapsulated pyrolytic graphite heaters used to heat a powdered sample to 175 to 450 °C, thereby developing a low level flux of volatile PAHs, amino acids and amines. The sample chamber uses gate valves at the top and bottom of the assembly to control specimen introduction and ejection. The evolved flux is passed into the “oven assembly area” and focused on a transparent cold finger (diamond-like carbon), which has been coated with the fluorescamine reagent. The PAHs, amines and amino acids condense on the cold finger (temperatures from -200 °C to 25 °C, background pressures of microns to 10 torr) and are detected by UV excitation at 375 to 405 nm of the fluorescamine/ amino acid adduct with an avalanche photodiode. The method is particularly sensitive because only the amine adduct (not the unreacted reagent) fluoresces.

A second version of the instrument (MOD II) is currently under development by ASTID funding to use subcritical water extraction to remove low level amines, amino acids, carboxylic acids and PAHs from powder samples and to integrate a capillary electrophoresis (CE) analyzer with the detection cold finger. The integrated MOD II CE system will provide separation, detection and identification of these compounds along with chiral resolution and measurement of enantiomeric ratios for assessment of biotic or abiotic sources.

Mars Oxidant Instrument (MOI). MOI is the result of an extended development of in situ instrumentation designed to probe the reactivity of Martian soil and solid samples to validate the oxidant hypothesis and determine the chemistry and chemical mechanisms of the process. The first of these miniature chemical laboratories was the Mars Oxidation Experiment (MOx) which flew as part of the ill-fated Mars 96 mission. The basic principle [14] is to expose a set of reference reactants, each with a different oxidation potential, to a powdered sample.

The extent of reaction is carefully monitored by following the change in either refractive index or resistivity of the thin film sensor, as a function of time, temperature and water abundance. Multiple films are exposed simultaneously, and the collective response is analyzed using a chemometric approach. The MOx instrument used a fiberoptic detection scheme, and more recent implementations have used chemiresistors as the sensors.

The MOI instrument was developed through MIDP funding to measure the reactivity of powdered solids and to provide for activation of oxidation chemistry through controlled addition of water vapor. The MOI instrument was brought to the brassboard level and a photograph of the sensor package mounted on the supporting electronics board is given in figure 3, along with a data plot showing the interaction of a 150 Å film with dilute potassium superoxide in palagonite.

Note that the reaction rate is a strong function of the water vapor level. The sensitivity of the approach is limited by the exposure time/ temperature/ water profile and measurement of 0.001 monolayers of reaction is a typical limit. The MOI cell is a single use measurement where powdered sample is added to the sensor cup that is then hermetically sealed for the duration of the experiment (days to months). In the field implementation of MOI for this experiment, 24 test cells will be provided on the sample deck for each campaign site with the ability to replenish cell packages as needed. The technology of MOI is based on a number of advances in semiconductor processing. The sensor units are produced in 64 unit batches. Highly reactive films are deposited on the sensor substrate in the laboratory, then sealed with a thin membrane of silicon nitride and stored until use. Just before sample introduction, the seal membranes are removed electrically, providing pristine material for the experiment.

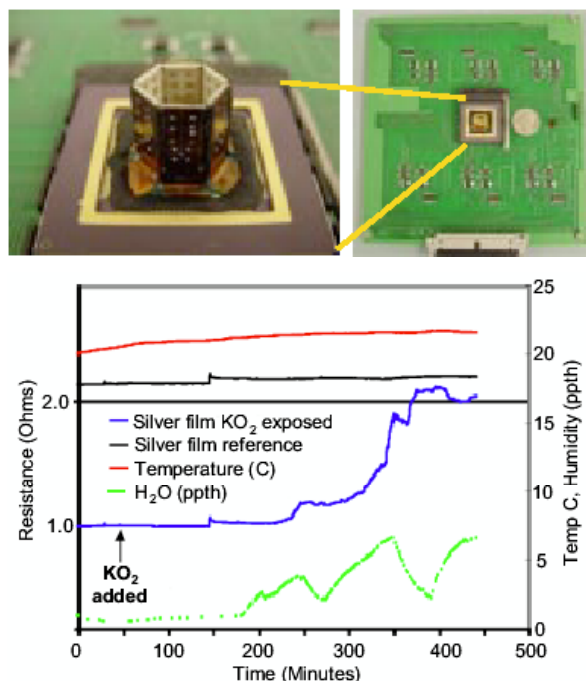


Figure 3. The MOI prototype to measure the reactivity of powdered samples was developed under MIPP funding. The spectrum shows the MOI response of a silver film to ppm levels of the oxidant KO_2 mixed with palagonite.

Conclusions: The AstroBioLab conducts a set of carefully controlled field experiments to ascertain the chemical interrelationship between low surface water concentrations, UV excitation, possible mineral surface catalysis and the diagenesis of atmospherically transported organic infall. The comparison of three field sites ranging from sterile (virtually carbon free) to biologically colonized with identical geology and with

major differences in water abundance provides a unique system to study the role of water and UV radiation in organic compound degradation. The use of in situ instruments on a sterilized platform optimizes the ability to study metastable oxidation chemistry and uncontaminated low level organic residues. The results of the study and field campaign will demonstrate the efficacy of integrated in situ astrobiology instrumentation focusing on organic compound detection and oxidation chemistry. Finally, the field campaign and experimental results will measurably enhance our understanding of the limits and constraints of life in extreme environments.

References: [1] Oyama V. I. and Berdahl B. J. (1977) *JGR*, 82, 4669–4676. [2] Levin G. V. and Straat P.A. (1977) *JGR*, 82, 4663 - 4667. [3] Biemann K. et al. (1997) *JGR*, 82, 4641-4658. [4] Klein H. P. (1978) *Icarus* 34, 666–674. [5] Zent A. P. and McKay C. P. (1994) *Icarus*, 10, 8 146–157. [6] Benner S.A. et al. (2000) *Proc. Natl. Acad. Sci., USA*, 97, 2425-2430. [7] McKay C.P. et al. (2003) *J. Arid Environ.*, Submitted. [8] Ericksen G.E. (1983) *Amer. Sci.*, 71, 366-374. [9] Navarro-Gonzalez R. (2003) *Science*, In review. [10] Bohlke J.K. et al. (1997) *Chemical Geology*, 136, 135-152. [11] Ericksen G.E. (1981) *US Geological Survey Professional Paper* 1188. [12] Glavin D.P. and Bada J.L. (1999) *Proc. Natl. Acad. Sci. USA*, 96, 8835-8838. [13] Kminek G. et al. (2000) *Planetary Space Sci.*, 48, 1087-1091. [14] Grunthaner F. J. et al. (1995) *Anal Chem.*, 67, 605A-610A.