

**DECOMPOSITION OF ORGANIC COMPOUNDS IN AQUEOUS CONDITIONS IN THE CHILEAN ATACAMA DESERT AND ON MARS.** R. C. Quinn<sup>1</sup>, P. Ehrenfreund<sup>2</sup>, F. J. Grunthner<sup>3</sup>, C. L. Taylor<sup>1</sup>, A. P. Zent<sup>4</sup>, <sup>1</sup>SETI Institute, NASA Ames Research Center, MS 239-12 Moffett Field, CA 94035, rquinn@mail.arc.nasa.gov, <sup>2</sup>Astrobiology Group, Leiden Institute of Chemistry, NL, <sup>3</sup>NASA Jet Propulsion Laboratory, Pasadena, CA, <sup>4</sup>Planetary Science Branch, NASA Ames Research Center, Moffett Field, CA.

**Introduction:** While there is abundant evidence that liquid water was present on the surface of Mars at some point in its history, this is not the case for organic compounds. Aside from trace amounts of atmospheric methane [1], no other organic chemicals have been detected on the surface or in the atmosphere of Mars. The most comprehensive search for organic compounds on Mars, which was carried out using the Viking Gas Chromatograph Mass Spectrometer (GCMS), revealed that the surface material was depleted of organic compounds [2]. Data returned from the Opportunity payload confirmed a history of aqueous processes at the landing site including deposition of sulfur-rich sedimentary rocks [3]. However, Sumner [4] pointed out that organics would be expected to be unstable in the types of aqueous environments in which the sedimentary rocks observed by Opportunity typically form. This conclusion is based on the expected thermodynamic stability of organic compounds at the MER site and does not comprehensively address the kinetics of aqueous systems on Mars. In this paper, we report the results of experiments that examine the degradation kinetics of organic substrates using Atacama soils as Mars analogs and compare these results to organic chemical decomposition rates observed with Mars soils during the Viking biology experiments. The choice of Atacama soils as Mars analogs was based on the research of Navarro-González et al. [5].

**Methods and Materials:** Samples were collected from hilltops near S 24° 4' 9.6", W 69° 51' 58.1" which is located in the Yungay region of the Atacama desert. This location corresponds to the collection site for sample AT02-03 in the Navarro-Gonzalez et al. study [5]. The samples were taken from a fluffy particulate layer dominated by gypsum and anhydrite, 3-4 cm thick, directly beneath the crust.

Three different sets of organic substrates were used: a 50 mM <sup>13</sup>C-labeled sodium formate solution; a 5 mM L-alanine and 5 mM D-glucose solution (biotic substrate); and a 5 mM D-alanine and 5 mM L-glucose solution (abiotic substrate). The different combinations of enantiomers were used to distinguish biotic from abiotic responses. All organics were 99+% <sup>13</sup>C labeled. The organic substrate (either 1 or

0.2 cc) was introduced into a sample vial containing soil using a 1 cc sterile syringe with a sterile 0.2 µm filter. Extracted headspace samples were analyzed for the production of <sup>13</sup>CO<sub>2</sub> using an HP 5900 gas chromatograph with a 5972 mass selective detector. Measured levels of <sup>12</sup>CO<sub>2</sub> were used to correct for the natural abundance of <sup>13</sup>CO<sub>2</sub> present in the sample cells.

**Results and Discussion:** Insights into the extent to which the oxidative behavior of Atacama soils in aqueous systems may be analogous to martian surface materials can be obtained by comparing the substrate-induced production of <sup>13</sup>CO<sub>2</sub> in the Yungay samples to Viking LR results. In the Viking LR experiment, radioactive gas evolution was monitored after the addition of a <sup>14</sup>C-labeled aqueous organic substrate into a sealed test cell that contained a martian surface sample [6]. Two distinct <sup>14</sup>CO<sub>2</sub> evolution patterns were observed. First, a rapid release of <sup>14</sup>CO<sub>2</sub> occurred over the first 24-48 hours of the experiment and has been attributed to a thermally labile oxidant. The second pattern of <sup>14</sup>CO<sub>2</sub> evolution was a slower log-linear release observed after the first oxidative reaction ceased.

The responses of the Viking lander 1 cycle 1 sample and Yungay samples (after sodium formate addition) is shown in figure 1. The initial rapid <sup>14</sup>CO<sub>2</sub> release pattern in the Viking LR has been interpreted as the complete decomposition of the sodium formate (30 nmoles) component of the substrate. This was followed by the slower decomposition of other substrate organics. This slower release has been attributed to substrate decomposition by hematite in the martian surface sample while the initial rapid release has been attributed to H<sub>2</sub>O<sub>2</sub> in the presence of hematite [7].

As can be seen in figure 1, the kinetics of formate decomposition by the Yungay samples differ from the Viking LR results. Although a number of explanations for the LR results have been proposed [8], H<sub>2</sub>O<sub>2</sub> together with hematite reproduces the kinetics of the LR experiment and is used as a model system here for comparisons with Atacama soils. An Fe(III)-initiated chain reaction involving hydrogen peroxide (fenton reaction) results in decomposition of formate by OH radicals.

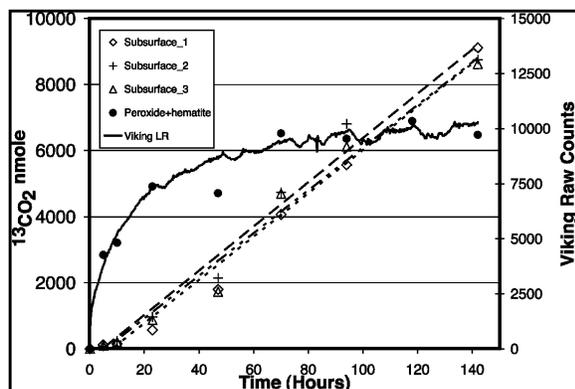


Figure 1. The responses of the Viking lander 1 cycle 1 sample and Atacama samples (after sodium formate addition). The initial rapid  $^{14}\text{CO}_2$  release pattern in the Viking LR has been interpreted as the complete decomposition of the sodium formate (30 nmoles) component of the substrate. This was followed by the slower decomposition of other substrate components. Hydrogen peroxide in the presence of hematite mimics the LR response.

The kinetics of this reaction, which closely mimic the LR results, is shown in figure 1. The kinetics of formate decomposition by the Yungay soil samples in the laboratory experiments is not consistent with the LR results or an OH radical decomposition mechanism. However, overtime the overall rate of formate decomposition by the Yungay soil exceeds the rate of decomposition by the peroxide-hematite system.

The ability of the Yungay soil and the peroxide-hematite system to decompose organics that are more complex than formate can be seen in figure 2. In the first 48 hours, the total  $^{13}\text{CO}_2$  produced by the peroxide-hematite system is approximately equal to the amount produced by the Yungay sample. This was not the case when formate was the added substrate (figure 1) and is due to the slower reaction kinetics of OH radicals with glucose and alanine than with formate.

These results suggest that when wetted, the Yungay soil samples are a more active catalyst for organic chemical decomposition than the Viking soil samples. Yungay soil deposits can contain highly oxidizing species, including iodates, chromates, and perchlorate [9]. These oxidizing compounds are likely formed by photochemical reactions at the soil/atmosphere interface, analogous to the possible photochemical origin of martian oxidants. Due to differences in water availability, solar flux, soil composition, and atmospheric composition, specific

mechanisms and reaction products may differ, but it appears that similar photochemical processes may be occurring both in the Atacama and on Mars. Bulk chemical analysis of Yungay soils show that significant quantities of redox active transition metals including manganese, cesium, and copper are present at ppm levels. Determination of the activity of these species in Yungay soils is difficult due to the high ionic strength and complex nature of the soil solutions. However, we are further analyzing these soils and performing electrochemical studies to determine the dominate redox couples and catalytic pathways in these aqueous systems.

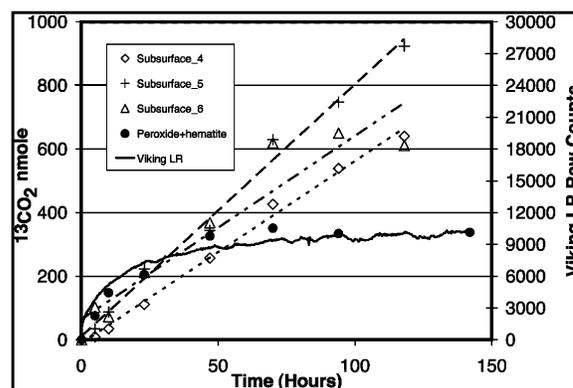


Figure 2. The response of D-alanine and L-glucose added to the Atacama samples. The total  $^{13}\text{CO}_2$  produced by the Atacama soils exceeds the production by the peroxide-hematite sample. This suggests that even in the absence of OH radicals, when wetted, the Atacama sample is a more active catalyst for organic chemical decomposition than the Viking soil samples.

**Acknowledgements:** This work was supported by the NASA Mars Fundamental Research program, the NASA Astrobiology Science and Technology for Exploring Planets program, and NASA Ames/SETI Institute cooperative agreement NCC2-1408. P. Ehrenfreund acknowledges grant NWO VI 016.023.003.

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