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Decomposition of aqueous organic compounds in the Atacama Desert and in Martian soils

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[1] Carbon-13 labeled formate, alanine, and glucose decompose when added in aqueous solution to soils collected from the "Mars-like" Yungay region (S 24° 4′ 9.6″, W 69° 51′) of the Atacama Desert. During the first 5 d of incubation, alanine (5 mM) and glucose (5 mM) solutions decomposed at rates of 0.1 to 0.2 μmol/d, and formate solution (50 mM) decomposed at rates of 0.4 to 1.6 μmol/d. The observation of approximately equal $^{13}CO_2$ initial production rates by soils treated with D-glucose and L-alanine, compared to soils treated with L-glucose and D-alanine, indicates the presence of one or more nonbiological chemical decomposition mechanisms. An increase in the decomposition rates of D-glucose and L-alanine, compared to L-glucose and D-alanine ~5 d after the addition of these organics, demonstrates that the soils are also biologically active. When treated with sodium formate solution, tested soils released $^{13}CO_2$ gas in a manner that reproduces the initial gas release observed in the Mars Viking Labeled Release (LR) experiment. Our results indicate that the $^{13}CO_2$ produced in Yungay soils is consistent with an initial phase of nonbiological decomposition followed by biological decomposition of added organics. Heat treatment of Yungay soils eliminated all CO_2 production, while in the Viking LR experiment, the initial rapid CO_2 release was eliminated by heat treatment, but a slower secondary CO_2 production was not. Our results indicate that the mechanism for the decomposition of organics in Yungay soils is different from the processes observed in the Viking LR experiment.

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1. Introduction

[2] It has been reported that soils from the Yungay area of the Chilean Atacama Desert have some characteristics that are similar to the Martian surface samples analyzed by instruments on the two Viking Landers [*Navarro-González et al.*, 2003]. *Navarro-González et al.* [2003] described soils from Yungay as "Mars-like" based on three main criteria: low-to-undetectable levels of organic compounds in soil analyzed with a pyrolysis gas chromatograph mass spectrometer (GCMS), levels of soil microorganisms below the detection limits of dilution plating, and equal decomposition levels of both a "biotic" organic mixture (L-alanine and D-glucose) and an "abiotic" mixture (D-alanine and L-glucose) that was added to soil samples.

[3] The primary instruments on the Viking Landers consisted of a pyrolysis-GCMS to search for organic compounds and three biology experiments designed to test Martian surface samples for the presence of life by measuring metabolic activity and distinguishing it from physical or chemical activity. The Viking GCMS failed to detect organic compounds in the surface materials revealing that organics, if present, were below the levels expected due to meteoritic input [*Biemann and Lavoie*, 1979]. In one of the Viking biology experiments, the Labeled Release (LR) experiment, radioactive gas evolution was monitored after the addition of a ^{14}C-labeled aqueous organic substrate into a sealed test cell that contained a Martian surface sample [*Levin and Straat*, 1976a, 1976b, 1977]. After the first addition of LR substrate to the Martian sample, two distinct $^{14}CO_2$ evolution patterns were observed. First, a rapid release of $^{14}CO_2$ occurred over the first 24–48 h of the experiment, which has been attributed to a thermally labile oxidant [*Klein et al.*, 1976]. The initial CO_2 release was equivalent to approximately 4 to 6% of the total labeled carbon added to the soil and has been interpreted as possibly consistent with the decomposition a single component (formate) of the LR substrate [*Klein et al.*, 1976; *Levin and Straat*, 1976a, 1976b; *Ponnamperuma et al.*, 1977; *Oyama et al.*, 1976]. This initial rapid release was eliminated by heating the

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surface sample to ~160°C (and reduced by heating the sample to ~50°C) in the sealed sample cell prior to introducing the labeled organics. A subsequent pattern of a slower continual $^{14}CO_2$ evolution was observed after the first oxidative reaction ceased. This secondary $^{14}CO_2$ evolution persisted after the heat treatment (~50°C and ~160°C). The soils from both Viking sites, including a sample collected from beneath a rock, gave the same response when tested in the LR experiment [*Levin and Straat*, 1976a, 1976b, 1977]. Upon a second injection of additional LR substrate, 30% of the labeled CO_2 present in the cell headspace went into solution [*Klein et al.*, 1976]. The generally accepted interpretation of the Viking results is that the tested soils were chemically reactive and not biologically active [e.g., *Klein*, 1978; *Zent and McKay*, 1994]. Additionally, at least two oxidative reactions with different kinetics are required to explain the observed decomposition of organics in the LR [*Klein*, 1978, 1979].

[4] The Yungay region of the Atacama Desert is extremely arid; its total rainfall of only a few millimeters over decades [*McKay et al.*, 2003] makes it one of the driest places on Earth. *Navarro-González et al.* [2003] demonstrated that the quantity and diversity of heterotrophic bacteria increase as a function of local water availability in the Atacama Desert and that levels of culturable bacteria in the Yungay area (S 24° 4′ 9.6″, W 69° 51′) are below the detection limits of dilution plating. While *Skelley et al.* [2005], using the Mars Organic Analyzer, found extremely low levels of amino acids (~10 ppb) in soils collected from the Yungay region, *Navarro-González et al.* [2006] have claimed that the organic content (20–40 μg/g total organic matter) of Yungay soils would not be detected by the Viking GCMS [*Navarro-González et al.*, 2006]. However, the validity of the comparison by *Navarro-González et al.* [2006] of Yungay soil measurements to the findings of the Viking GCMS results has been disputed [*Biemann*, 2007]. Additionally, *Navarro-González et al.* [2003] reported the observation of active decomposition of organics by soils in incubation experiments patterned after the LR experiment. In these experiments, equal amounts of both a "biotic" organic mixture (L-alanine and D-glucose) and an "abiotic" mixture (D-alanine and L-glucose) were decomposed when added to Yungay soil samples.

[5] The methods used by *Navarro-González et al.* [2003] differed from the LR experiment in two important ways. First, the labeled CO_2 levels were measured only once, 3 to 5 d after soil injection. Second, the quantity of each organic substrate added to the soil was 2 to 3 orders greater than the amounts added in the Viking LR experiment [*Navarro-González et al.*, 2003]. Because of these differences, the kinetics of the LR CO_2 release cannot be compared to the results of *Navarro-González et al.* [2003]. In this paper, we describe experiments designed to determine the extent to which Yungay soils are "Mars-like" under the conditions of the LR experiment. The results of these experiments allow the decomposition kinetics of organic compounds added to Yungay soils to be compared with the Viking LR results. Reproduction of the rate of CO_2 release observed in the LR is a key parameter needed to establish if oxidative processes that occur in Yungay soils are similar to processes that occurred when Martian surface materials were tested by the Viking Landers.

2. Methods and Materials

2.1. Atacama Samples

[6] Soil samples were collected from hilltops near S 24° 4′9.6″, W 69°51′58.1″, in the Yungay region of the Atacama Desert (Figure 1). The collection locations correspond roughly to the collection site for sample AT02-03 in the *Navarro-González et al.* [2003] study. Samples were collected from the top 4 cm of soil. The samples are dominated by gypsum and anhydrite. The soil was characterized for soluble anions and cations (2:1 water-to-soil by volume extract) by ion chromatography at the NASA Ames Analytical Laboratory. Soil pH was measured in a 2:1 (water-to-soil by volume) mixing ratio using a Corning pH meter (model 125) and an Orion 911500 pH probe.

[7] After collection, the soils were transferred into sterile glass sample vials and crimp-sealed with sterile septa. Two types of control samples were used. One set of control soils was collected from the field site and baked out at 160°C for 3 h in an oven located at the University of Antofagasta Desert Field Station in Yungay. After baking, the control soils were returned to the field site and transferred into sterile glass vials and sealed using the same handling procedures used for the noncontrol samples. These controls served to verify that no microbial contamination was introduced during sample handling. The second set of controls was utilized as a test to establish the possible presence of indigenous microorganisms in the soil samples. These controls were collected along with the other samples and baked out at 160°C for 3 h (the Viking LR protocol) in the lab prior to the addition of organic substrates. If soil samples have an experimental response that is positive for the presence of life, this control set should show an attenuated response resulting from heat treatment.

2.2. Aqueous Organic Substrates

[8] Five different types of ^{13}C-labeled organic compounds were used: sodium formate, L-alanine, D-glucose, D-alanine, and L-glucose. The different enantiomers were used to help distinguish biotic from abiotic responses, with the assumption that biological activity would preferentially utilize L-alanine and D-glucose over D-alanine and L-glucose. All organics were 99+ atom % ^{13}C-labeled and were obtained from IsoTec Inc., except for the L-glucose, which was obtained from Cambridge Isotope Laboratories. The labeled organic solutions were prepared in a laminar-flow hood using autoclaved utensils and glassware. Autoclaved 18 MΩ Millipore® water that was passed through a sterile 0.2 μm filter was used to prepare the solutions. The aqueous organic solutions were introduced into the sample vial using a sterile syringe and needle. In each experiment, the organic solution was added in a quick (~10 second) injection. Syringe-extracted headspace samples were analyzed for the production of $^{13}CO_2$ using an HP 5890 gas chromatograph with a 5971 mass selective detector. Measured levels of $^{12}CO_2$ were used to correct for the natural abundance of $^{13}CO_2$ present in the sample cells.

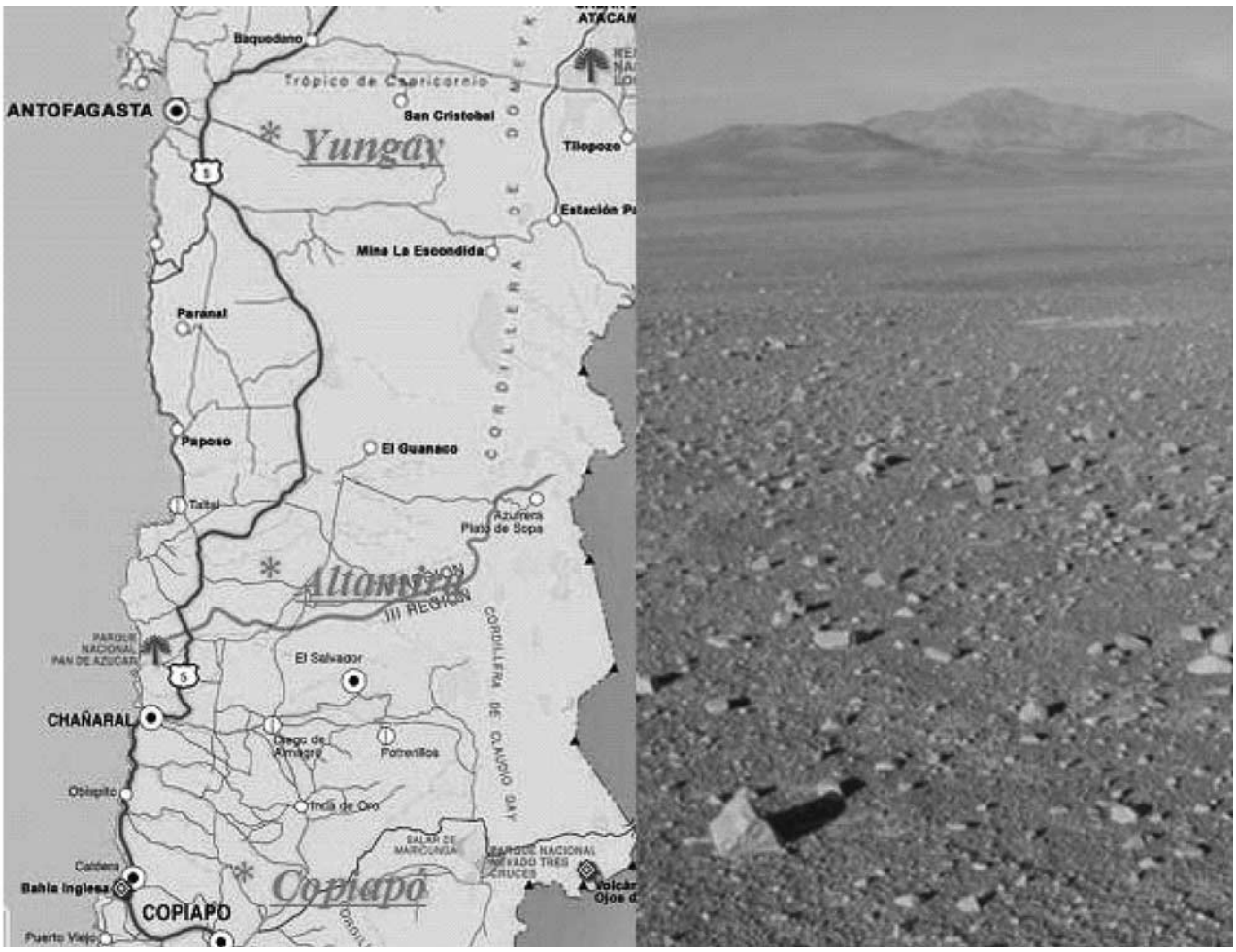

Figure 1. A map of the Chilean Pacific coast showing the Atacama Desert. The photo shows the local geology at the Yungay field site (S 24°4′9.6″, W 69°51′58.1″).

2.3. Viking Labeled Release Simulations

[9] To determine if Atacama soils can reproduce the pattern of the initial CO_2 release observed when Viking soils were tested in the LR experiment, experiments were performed using Yungay soils with 0.25 mM ^{13}C-labeled formate solution. The formate solution was added to the soils in the approximate volumetric ratio used by Viking (0.5 cm^3 soil to 0.115 cc LR solution), although, to increase sensitivity, larger sample sizes were used in the laboratory experiments (3 and 5 cm^3 of soil). The LR substrate used in the Viking experiments was a mixture of seven labeled organic components, each at 0.25 mM concentration: sodium formate, D-alanine, L-alanine, sodium D-lactate, sodium L-lactate, glycine, and calcium glycolate [*Levin and Straat*, 1976a, 1976b]. However, it has been suggested that the initial CO_2 release in the LR experiment resulted from the decomposition of the formate component of the LR solution [*Ponnamperuma et al.*, 1977; *Oyama et al.*, 1977].

[10] For comparison to the Viking and Yungay experimental results, peroxide-modified titanium dioxide was used to simulate a nonbiological LR response. The TiO_2 was synthesized and modified by vapor phase H_2O_2 adsorption at room temperature as described by *Quinn and Zent* [1999].

2.4. Viking Data Sets

[11] Viking LR data for the first cycle of the Viking 1 LR experiment was obtained from the NASA Planetary Data System. The data sets contain the counts recorded by a solid-state beta detector as a function of time resulting from the presence of $^{14}CO_2$ gas in the sample cell headspace. A conversion factor of 517 counts $nmol^{-1}$ of labeled carbon [*Levin and Straat*, 1977] was used to calculate the total nanomoles of $^{14}CO_2$ present in the LR sample cell headspace. The release of CO_2 by Viking samples is compared to the Yungay soil results as nanomoles of CO_2 produced per gram of sample. To estimate the weight of the Viking samples (0.5 cm^3), a bulk density of 1.3 g cm^{-3} was used [*Oyama et al.*, 1977].

3. Results

[12] In this section the results of new experiments on Atacama soils are presented along with the relevant results from the Viking mission obtained in 1976. However, as a starting point for our investigation, we verified that we

Table 1. Average Quantity of Organic Substrate Decomposed by Yungay Soils Using the Protocol of *Navarro-González et al.* [2003]

	Formate, μmol	D-Alanine L-Glucose, μmol	L-Alanine D-Glucose, μmol
Location B Day 3	4.5	0.6	
Location B Day 5	7.8	0.7	
Location A Day 3	1.1	0.2	0.4
Location A Day 5	2.4	0.95	1.1
Navarro Day 3–5	3–12	~0.4	~0.4

could reproduce the organic substrate decomposition results using Yungay soils as reported by *Navarro-González et al.* [2003]. The average total measured $^{13}CO_2$ present in the headspace 3 and 5 d after wetting 1 cc of soil with 1 cc of organic substrate is shown in Table 1. The total number of moles of $^{13}CO_2$ produced by the samples is consistent with the values reported by *Navarro-González et al.* [2003] for single-sample measurements taken 3 to 5 d after substrate injection. The rate of labeled-CO_2 production for the samples treated with formate solution (50 mM) is shown in Figure 2. The cause of the variability in $^{13}CO_2$ levels in the location A sample cell headspace is uncertain. However, a corresponding variability was seen in the $^{12}CO_2$ levels in these samples. This may indicate that the CO_2 variability is due to sorption of CO_2, possibly a result of temperature and/or pH shifts in the sample soil/solution.

3.1. Labeled Release First Injection

[13] The rate of change in headspace $^{13}CO_2$ levels after the addition of ^{13}C-labeled formate solution (0.25 mM) to Yungay soils collected from three nearby locations can be seen in Figure 3. Also shown in Figure 3 are the responses of the Viking Lander 1 cycle 1 LR sample along with the response of a control (heat-treated at 160°C for 3 h). The initial pattern of CO_2 released due to decomposition of formate by Yungay samples generally matches that of the Martian surface samples tested in the Viking LR experiment. The magnitude of $^{13}CO_2$ released by samples collected from location D were lower than the release from samples collected from locations B and C (Figures 3b and 3c). All of the tested control samples from locations A, B, C and D tested negative. In some Yungay samples (location B) there was a decrease in headspace CO_2 levels after the initial increase. This decrease, discussed below, may be explained by an uptake of CO_2 into solution due to a shift in soil/solution pH.

[14] For comparison, the kinetics of $^{13}CO_2$ release due to formate decomposition by peroxide-modified TiO_2 is shown in Figure 4. The pattern of CO_2 release for this nonbiological process is consistent with the LR results; the likely mechanism for this response (discussed in more detail below) is the reaction of formate with OH radicals generated upon wetting the TiO_2, not direct reaction of formate with H_2O_2.

3.2. LR Simulation Second Injection

[15] The headspace $^{13}CO_2$ changes for two Yungay samples collected from location C (pH 7.6 and pH 6.8) upon a second injection of formate solution are shown in Figure 5. The decrease in CO_2 observed after the second substrate injection in the LR experiment is consistent with an overall alkaline pH for the Viking soil. This trend is replicated by the slightly alkaline Yungay sample. In both the acid and basic Yungay samples, upon injection of additional formate, CO_2 production resumed at a rate that exceeds the rate observed after the second injection of organic substrate in the Viking experiments.

3.3. Experiments Using D- and L-enantiomers

[16] To help establish whether the formate decomposition caused by Yungay soils was due to biological activity or to nonbiological oxidation, experiments were performed using organic substrates with D- and L-enantiomers of glucose and alanine. Generally, over the first 4–5 d of reaction, both the D- and L- form of glucose and alanine decomposed at approximately equal linear rates (Figure 6), indicating nonbiological decomposition of the organic compounds. However, as can be seen in Figure 6, after 4 to 5 d, an increase in $^{13}CO_2$ production in the D-glucose and L-Alanine samples compared to the L-glucose and D-Alanine samples was observed. This response, a lag period followed by an increase in CO_2 production, is a clear indicator of biological activity in the soil. Heating the soil significantly attenuated all CO_2 release. Additionally, as shown in Figures 6a and 6b, reactivity levels were variable and, in some cases, no $^{13}CO_2$ production was observed.

4. Discussion

[17] The sequence of events in an LR experiment that would constitute a positive signal for metabolism has been outlined by *Levin and Straat* [1976a, 1976b]. The sequence involves the accumulation of labeled gas until available organics are exhausted, which is indicated by a plateau in labeled gas levels. The second criteria in the sequence is the resumption of labeled gas production after additional or-

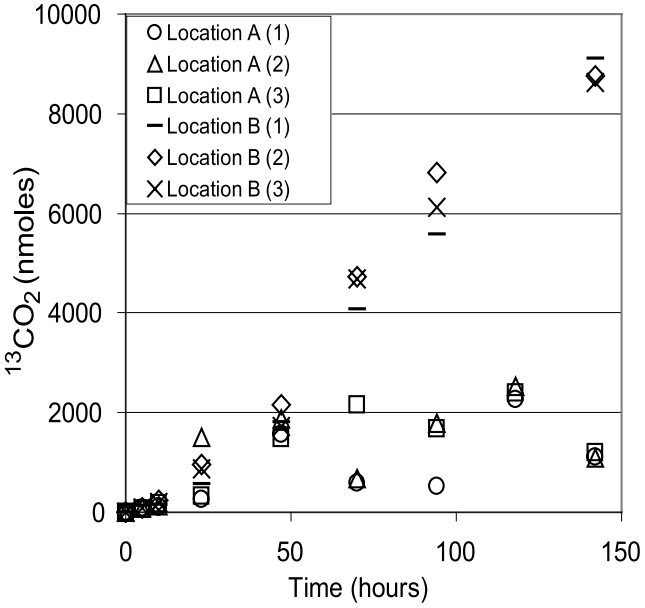

Figure 2. Changes in headspace levels of $^{13}CO_2$ due to decomposition of aqueous formate for samples collected at Yungay locations A and B. The protocol of *Navarro-González et al.* [2003] was used to obtain the data shown.

ganic substrates are added to the test cell. A positive response is confirmed by comparison to a control that has been heat treated at 160°C for 3 h. Both Viking and Yungay soils heated to 160°C for 3 h had significantly attenuated responses, which would be expected for soils that contain microorganisms. However, nonbiological explanations for the observation of an attenuated response in heat-treated samples are also possible, and several have been proposed to explain the Viking LR results [e.g., *Klein*, 1978; *Zent and McKay*, 1994]. Additionally, several parameters observed in the LR experiment point to a nonbiological explanation for the Viking results. These observations include the cessation of CO_2 release after only 10–14% of the added organic substrate decomposed and the uptake of CO_2 gas when additional organic substrate was added [*Klein*, 1978, 1979]. In the LR experiment, when organic substrate is available, biological processes would be expected to result in the continual production of CO_2 due to microbial respiration. However, after the initial CO_2 release, the failure of the Viking soils to generate an increased rate of CO_2 production upon introduction of additional organic substrate is consistent with a limiting or unstable reactant in the soil and not with biological activity.

[18] There are also several other lines of evidence that have been discussed extensively in the literature that lead to the conclusion that Viking soils were chemically reactive and not biologically active. Among these are the failure of the Viking GCMS to detect organic compounds [*Biemann and Lavoie*, 1979; *Biemann*, 1979]; the failure of the other two biology experiments, the Pyrolitic Release (PR) [*Horowitz et al.*, 1977] and Gas Exchange (GEx) experiment, to detect evidence of life [*Klein*, 1978; *Oyama and Berdahl*, 1977]; and evidence for the presence of a strong oxidant in the soil [*Oyama and Berdahl*, 1977].

[19] Since the return of the Viking data, a number of hypotheses have been presented to explain the results of the Viking biology experiments. *Klein* [1978, 1979] proposed that the presence of at least three soil oxidants is required to explain all of the Viking results. Hydrogen peroxide is frequently evoked as a probable oxidant in the Martian surface environment [e.g., *Hunten*, 1979; *Huguenin et al.*, 1979; *Huguenin*, 1982; *Bullock et al.*, 1994; *McDonald et al.*, 1998; *Benner et al.*, 2000; *Encrenaz et al.*, 2004] and as an explanation for the initial CO_2 release observed in the LR [e.g., *Ponnamperuma et al.*, 1977; *Oyama and Berdahl*, 1979].

[20] *Oyama and Berdahl* [1979] proposed a mechanism to explain the peroxide-induced decomposition of formate in the LR experiment. This hypothetical mechanism involves the formation of an iron peroxy acid derivative by HOO^- that then reacts with available formate to produce H_2O and CO_2. *Levin and Straat* [1981] investigated possible nonbiological explanations for the LR results and concluded that hydrogen peroxide could be responsible for the initial CO_2 release only if a peroxide stabilization mechanism was present in the soil. *Quinn and Zent* [1999]

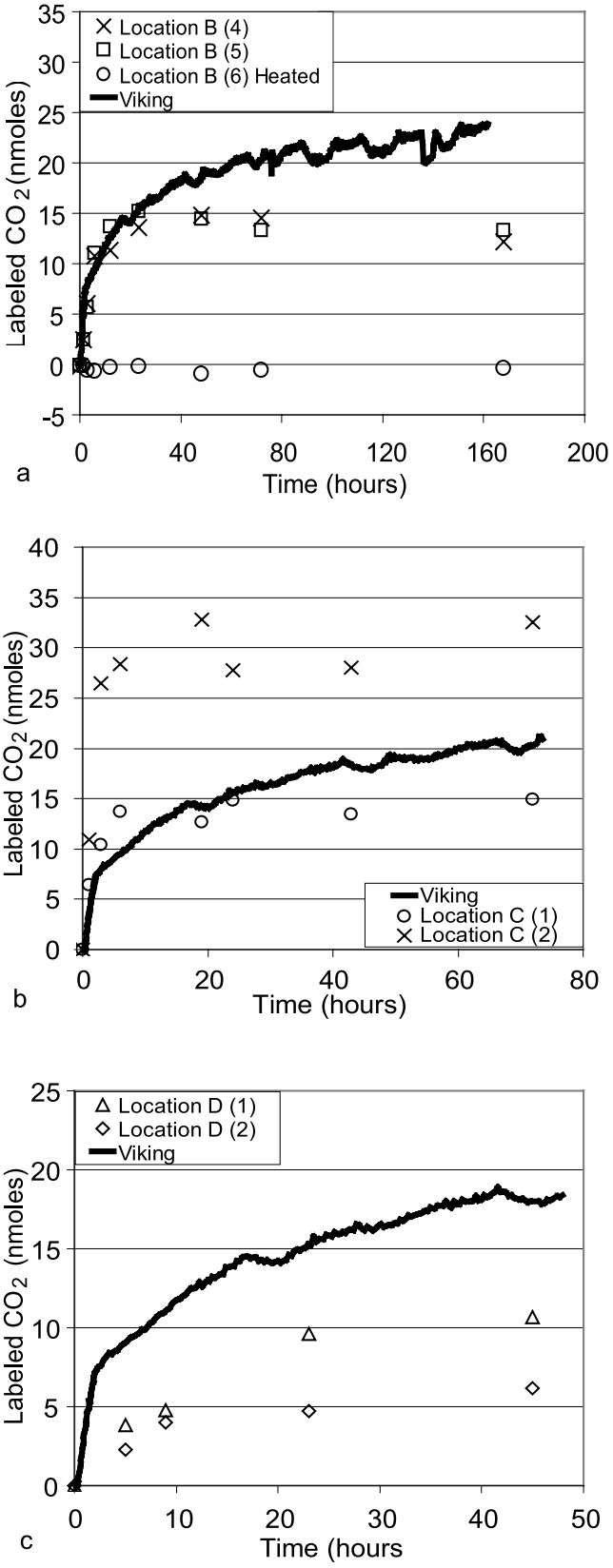

Figure 3. A comparison of the Viking 1 Labeled Release Experiment (cycle 1) CO_2 release with Yungay soil samples (collected from three nearby locations) wetted with 0.25 mM sodium formate solution. The release of CO_2 by Viking samples is compared to the Yungay soil results as nanomoles of CO_2 produced per gram of sample. To estimate the weight of the Viking samples (0.5 cm^3), a bulk density of 1.3 g cm^{-3} was used [*Oyama et al.*, 1977].

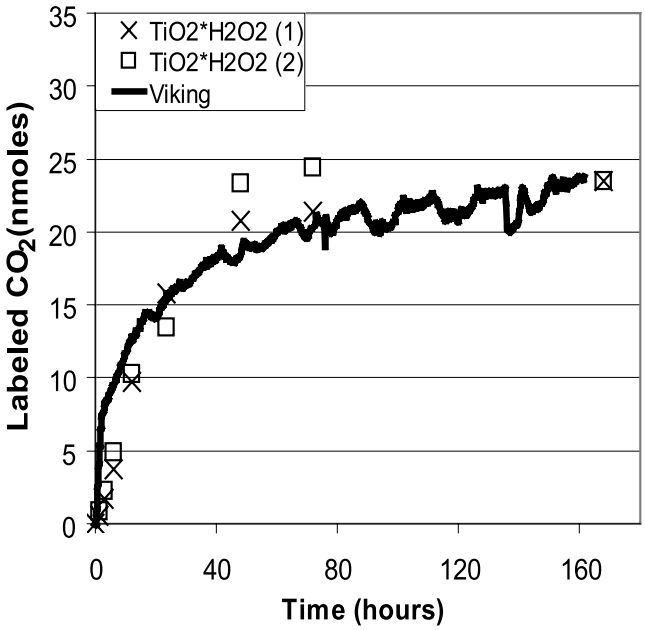

Figure 4. A comparison of the Viking 1 Labeled Release Experiment (cycle 1) CO_2 release with peroxide-modified TiO_2 wetted with sodium formate solution. To account for the difference between the laboratory and Viking sample sizes, the nanomoles of CO_2 released by peroxide-modified TiO_2 was normalized to the Viking data.

proposed that peroxide complexation with titanium in Martian soil could stabilize peroxide and produce the results of both the LR CO_2 release and the O_2 release observed in the Gas Exchange Experiment [*Oyama et al.*, 1977; *Oyama and Berdahl*, 1977]. The pattern of CO_2 release by peroxide-modified titanium dioxide is consistent with the LR results (Figure 4); the likely mechanism for this response is the reaction of formate with OH radicals generated upon wetting the TiO_2. Sodium formate has been used as a probe molecule to measure production of OH radicals in soil systems on earth [*Kwan and Voelker*, 2002; *Southworth and Voelker*, 2003]. In the presence of formate, wetting the soil can result in the destabilization of adsorbed peroxides and the generation of OH radicals, which would rapidly decompose formate and release carbon dioxide.

[21] In the LR experiment, the decomposition of organics by Martain soils was observed in the absence of light. However, on Mars and in the Atacama, photochemical processes are likely to be the most active pathway for the (nonbiological) decomposition of organics. The Yungay region is characterized by large amounts of deposited nitrate, apparently of atmospheric origin [*Bohlke et al.*, 1997], that have not been biologically decomposed. These salt deposits are also known to contain highly oxidizing species, including iodates (IO_3^-), chromates (CrO_4^{-2}), and the only known naturally occurring deposits of perchlorate (ClO_4^-) [*Ericksen*, 1981, 1983]. Nitrate and metal oxides in soils can adsorb radiation; this process initiates free radical reactions that generate OH radicals and that can chemically alter organic compounds. Multiple contributing mechanistic pathways are likely in soil systems; three of the most common involve nitrate photochemical reactions, fenton and photo-fenton reactions, and metal oxide photochemistry. The key radical precursors and radicals in these reaction mechanisms are superoxide, hydrogen peroxide, and the OH radical [*Zhou and Mopper*, 1990; *Zepp et al.*, 1992; *Kwan and Voelker*, 2002; *Southworth and Voelker*, 2003]. Superoxide has been suggested as an explanation for the Viking Biology Gas Exchange experiment results [*Chun et al.*, 1978; *Yen et al.*, 2000], while the OH radical, as shown in this work and suggested by others, is capable of oxidizing organic compounds on Mars [*Benner et al.*, 2000]. In the Atacama, nitrate photochemistry is likely to play an important role in the desert's carbon cycle (Table 2). While on Mars, Fenton reactions and metal-oxide photochemistry are likely to be important processes. Additional pathways exist for the generation of reactive species in soils, including the production of singlet oxygen through the creation of excited states in soil humic acids [*Zepp et al.*, 1992]. Singlet oxygen reacts at significant rates with several types of furans, sulfides, amines, polynuclear aromatics, hydrocarbons, and other electron-rich compounds. These reactions are highly efficient in decomposing organic compounds.

[22] Yungay soils meet the three criteria established for a positive detection of life in the LR experiment: decomposition of organics until the added organic substrate is exhausted, the resumption of CO_2 production after additional nutrient is added, and an attenuated control response (heated 3 hrs at 160°C). The resumption of CO_2 after the second injection of organic substrate indicates that the response is not due to the presence of peroxide or other unstable soil oxidants (e.g. superoxide), which would be expected to rapidly react and decompose after the initial injection of aqueous organics. Biological activity in Yungay soils was confirmed by the different decomposition rates observed for D- and L- forms of glucose and alanine (Figure 6). The positive response of Yungay soils in LR simulations is consistent with the presence of low levels of

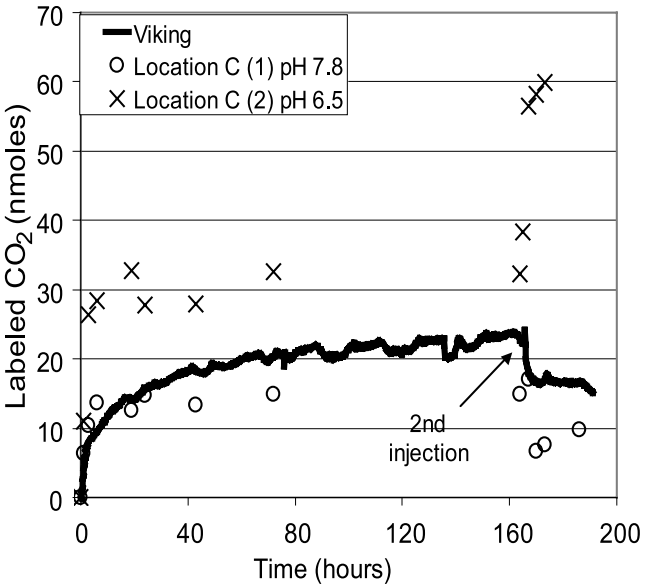

Figure 5. A comparison of the Viking 1 Labeled Release Experiment (cycle 1) CO_2 release with an alkaline Yungay soil (pH ~ 7.8) and a slightly acidic Yungay soil (pH ~ 6.5) wetted with 0.25 mM sodium formate solution.

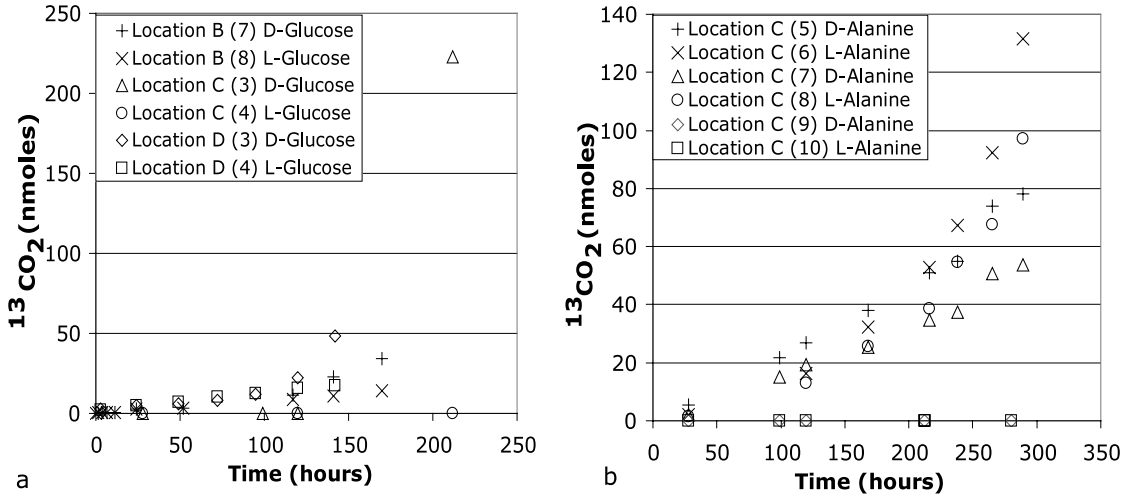

Figure 6. Differences in $^{13}CO_2$ production by individual D- and L-enantiomers added to Yungay surface soils. Each of the four organic compounds, (a) D-glucose, L-glucose, (b) L-alanine, and D-alanine were added individually to independent soil samples.

microorganisms in the Yungay region that has been reported by *Lester et al.* [2007] and *Conelley et al.* [2006].

[23] The levels of organic chemical decomposition seen with L-glucose and D-alanine confirm the coexistence of nonbiological oxidative processes in Yungay soils. Heating the Yungay samples to 160°C for 3 h eliminates the decomposition of both the L- and D-glucose. In the Viking LR, after the initial CO_2 release, a slower, continuous CO_2 release was observed, even in the heat-treated control samples. This apparently catalytic decomposition of organics in the LR has been attributed to the presence of hematite in the Mars surface sample. 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. These catalytic species are frequently used in low-temperature, wet-air oxidation processes for the conversion of organic compounds into CO_2 and H_2O [*Lin et al.*, 2002]. Determination of the activity of these species is difficult due to the high ionic strength and complex nature of Yungay soil solutions, but they may play a role in the apparent instability of organic compounds in these soils. In contrast to the Viking samples, if the chemical decomposition of organics is due to the presence of a soil catalyst, it is deactivated by heat.

[24] *Oyama et al.* [1977] concluded that the surface material at the Viking site contained an acidic component. The experimental evidence that lead to this conclusion was the release of CO_2 from the soil during the humid mode in the Gas Exchange Experiment (GEx); an initial small CO_2 peak in the Pyrolytic Release Experiment (PR) [*Horowitz et al.*, 1977]; and the release of $^{14}CO_2$ from the heat-treated VL 1 cycle 2 sample (injection 1). The observation of higher background counts in the LR experiment after the heat treatment led *Oyama et al.* [1977] to suggest that the acidic component may be $H_2SO_4 \bullet 2H_2O$, and that it is semi-volatile when heated. However, the magnitude of CO_2 uptake subsequent to any initial CO_2 release during the GEx and LR experiments indicates that the acid component is neutralized upon wetting.

[25] In the LR experiment, upon the second injection of additional LR substrate, 30% of the labeled CO_2 present in the cell headspace went into solution. *Oyama et al.* [1977] attributed resorption of headspace CO_2 in the GEx to the generation of hydroxyl ions from the reaction of soil superoxides with water. Simulations of the GEx have indicated that although acidic components may be present in Martian soils, the aqueous soil mixtures tested by Viking equilibrated to a slightly basic pH [*Quinn and Orenberg*, 1993]. When wetted, the behavior of Atacama soils with an alkaline soil pH appears to be similar to Viking soils (Figure 5). Yungay soils typically have a near neutral or slightly alkaline pH, although they may also contain acids that are neutralized when wetted [*Quinn et al.*, 2005].

5. Conclusions

[26] We have performed experiments using soils collected from the Yungay region of the Atacama Desert and compared the results to the results of the Viking LR experiment. Based on this comparison we draw the following conclusions:

[27] 1. Comparison of the decomposition rates of D-glucose and L-alanine (biologically favored enantiomers) to L-glucose and D-alanine when added in aqueous solution to soils collected from the Yungay region of the Atacama Desert provide evidence for the presence of one or more

Table 2. Soluble Cations and Anions Extracted From Yungay Soil (Location A)

Soluble Cations		Soluble Anions	
F	56.3 ppm	Na	391 ppm
CI	26.2 ppm	K	262 ppm
NO_3	82.1 ppm	Mg	106 ppm
PO_4	10.9 ppm	Ca	2.94%
SO_4	6.35%	Fe	0.4 ppm
		Ba	1.2 ppm
		Sr	102 ppm

nonbiological chemical decomposition mechanisms in these soils.

[28] 2. An increase in the decomposition rates of D-glucose and L-alanine compared to the rates of L-glucose and D-alanine decomposition was observed, indicating the presence of microorganisms in these soils.

[29] 3. When treated with an aqueous sodium formate solution, soils tested released CO_2 gas in a manner that reproduces kinetics of the gas release observed in the Viking LR experiment.

[30] 4. A second rapid CO_2 release by Yungay soils, when additional formate was injected into the sample cell, is consistent with biological processes. In contrast, a second rapid release of CO_2 was not observed in the Viking LR experiment after a second injection of organic solution, which is not consistent with a typical biological response.

[31] 5. Although other explanations have been suggested for the Viking LR results, our results are consistent with the decomposition of added formate by OH radicals as the primary mechanism for the decomposition of organics.

[32] 6. Heating the Yungay soil to 160°C for 3 h eliminated both the biological and nonbiological decomposition of glucose and alanine, as well as the decomposition of formate. Catalytic decomposition of organics was also observed in the Viking biology experiments, but it was not the dominant mechanism. Only the initial rapid CO_2 release was eliminated by heating in the Viking LR experiment; the secondary, apparently catalytic, CO_2 release was thermally stable.

[33] 7. Our results indicate that the mechanisms for the decomposition of organics added (in aqueous solution) to Yungay soils is different from the processes observed in the Viking LR experiment. However, photochemical processes are likely to provide active pathways of organic chemical decomposition in the Atacama and on Mars. In an LR experiment, the soil is decoupled from the dynamic photochemical processes that likely determine the overall rate and extent of organic chemical oxidation occurring in situ in these soils.

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