teraction with the ribose ring of the nucleotide. When the $(\beta\alpha\beta)_2$ fold in DHFR is rotated onto the $(\beta\alpha\beta)_2$ fold in LDH, Gly-96 in DHFR lies within 3 Å of the conserved glycine residue. A second conserved residue among all NAD$^+$-dependent dehydrogenases is an aspartate that forms a hydrogen bond with the 2′-hydroxyl of the ribose. The superposition described above places Arg-44 of DHFR within 3 Å of the conserved aspartate residue. This is precisely what would be expected for interaction between the enzyme and the 2′-phosphate in NADPH. Moreover, sequence alignments suggested by Freisheim (*10*) show that the glycine and arginine residues under consideration are conserved in the other two DHFR's for which sequence information is complete.

A comparison of the geometries of LDH and DHFR shows that the spatial arrangement, but not the connectivity, of the $(\beta\alpha\beta)_2$ structure is nearly the same for the two enzymes, and that this $(\beta\alpha\beta)_2$ structure is also the nucleotide binding site in DHFR. Thus, DHFR cannot have evolved from the common ancestral $\beta\alpha\beta$ mononucleotide-binding protein postulated by Rossmann *et al.* (*6*). We suggest that a better explanation for the existence of a pair of $\beta\alpha\beta$ structures in DHFR which are geometrically similar to those in LDH but have different connectivities is that such a structure represents a preferred and perhaps unique way of binding mononucleotides which has been arrived at in these two cases by convergent evolution.

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1. Abbreviations used in this report: NADPH, reduced nicotinamide-adenine dinucleotide phosphate; NADH, reduced nicotinamide-adenine dinucleotide; Ile, isoleucine; Ala, alanine; Leu, leucine; Phe, phenylalanine; Asp, aspartic acid; Arg, arginine; Lys, lysine; Gly, glycine; and Ser, serine.
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22 February 1977; revised 5 April 1977

Possible Surface Reactions on Mars: Implications for Viking Biology Results

Abstract. *The results of two of the three biology experiments carried out on the Viking Mars landers have been simulated. The mixture of organic compounds labeled with carbon-14 used on Mars released carbon dioxide containing carbon-14 when reacted with a simulated martian surface and atmosphere exposed to ultraviolet light (labeled release experiment). Oxygen was released when metal peroxides or superoxides were treated with water (gas exchange experiment). The simulations suggest that the results of these two Viking experiments can be explained on the basis of reactions of the martian surface and atmosphere.*

One of the principal objectives of the Viking mission was the search for life on Mars. The biological investigation designed to detect microorganisms in the martian soil—the labeled release (LR), the gas exchange (GEX), and the pyrolytic release (PR) experiments—provided positive responses (*1, 2*). On the other hand, the analysis of martian soil by pyrolysis gas chromatography–mass spectrometry showed no organic compounds at concentrations as low as 10 parts per billion (*3*) at either Viking landing site (*4*). Although such a low concentration of organic carbon compounds is not, in itself, synonymous with the absence of life, this apparently anomalous observation led us to look for possible nonbiological explanations for the results of the biology experiments. The findings of our simulation studies may be relevant to the interpretation of the data from the Viking mission.

In the Viking LR experiment, when an equimolar mixture (total, $17.5 \times 10^{-4}M$) of glycine, DL-alanine, DL-sodium lactate, sodium formate, and calcium glycolate uniformly labeled with ^{14}C and adjusted to pH 7 with KOH was injected onto the surface of 0.5 ml of martian soil in the test chamber, $^{14}CO_2$ was released (*1, 2*). In attempting to simulate this result in the laboratory by purely chemical means, we searched for possible conditions for the release of CO_2. In one procedure 3 ml of 30 percent H_2O_2 was placed in a glass tube, and 2 ml of $0.1M$ formic acid, adjusted to pH 7 with KOH, was introduced through a stopcock; the formic acid solution was degassed before being introduced into the glass tube. Upon mixing these two solutions, CO_2, at a concentration significantly above background, was detected by mass spectrometry. However, CO_2 release was not detected as a result of the interaction of the same proportions of 30 percent H_2O_2 and $2 \times 10^{-4}M$ formic acid, probably because of the low sensitivity of the mass spectrometer.

Table 1. Peroxides and superoxides release CO_2 from $0.1M$ $H^{13}COONa$ (pH 7).

Oxide	$^{13}CO_2/^{12}CO_2$
H_2O_2	0.49
Na_2O_2	0.11*
CaO_2	0.14*
KO_2	0.78*

*After addition of HCl.

In order to ensure that atmospheric CO_2 did not interfere with our reaction, we carried out a series of experiments in which ^{13}C-labeled formate ($0.1M$ $H^{13}COONa$ at pH 7) was used in place of formic acid. The interaction of the formate with the H_2O_2 solution showed a new peak at a mass-to-charge ratio (m/e) of 45, which can be attributed to $^{13}CO_2$. The ratio of $^{13}CO_2$ to $^{12}CO_2$ equals 0.49, as measured by their peak heights (Table 1). This ratio is in marked contrast to the $^{13}C/^{12}C$ ratio of 0.01 from natural abundances. Although there is no evidence from the Viking experiments to suggest that concentrated H_2O_2 is present in significant abundance on the martian soil, these results demonstrated that a peroxide could decarboxylate formate.

In our next experiment, we assumed that solid peroxides could exist in the martian soils. Metal peroxides and superoxides (about 0.5 g) from our laboratory were reacted with the $0.1M$ labeled formate solution (about 3 ml), and the $^{13}CO_2$ release was examined with the mass spectrometer in a manner similar to the experiments with H_2O_2. These results are shown in Table 1.

The results were surprising, since $^{13}CO_2$ was not detected. The $^{13}CO_2$ released by the reaction of Na_2O_2, CaO_2, or KO_2 with the labeled formate may have subsequently reacted with the NaOH, $Ca(OH)_2$, or KOH also produced in the reaction to form the corresponding carbonates. A pH measurement of the mixed formate-peroxide or formate-superoxide solutions showed a highly alkaline condition ($p\mathrm{H} > 12$), an indication of possible carbonate formation. When a small volume of concentrated HCl solution was added to each of these solutions, $^{13}CO_2$ was immediately released (*5*). Thus, the CO_2 release in the Viking LR experiment may be attributed to the reaction of metal peroxides or superoxides.

We then attempted a more realistic simulation of the surface of Mars. A gas mixture consisting of 97 percent CO_2, 2 percent N_2, and 1 percent Ar (total pressure, 0.5 atm) and 1.5 g of powdered hematite (Fe_2O_3) were sealed in a glass tube (about 100 ml) with a Suprasil window [a form of isotropic silica, which transmits ultraviolet (UV) light down to a wavelength of 160 nm]. A trace of water was also introduced into the reaction tube. To eliminate any free O_2, the tube containing the hematite and water was first evacuated to a pressure of less than 10^{-1} torr before the gas mixture was introduced. The tube was irradiated with UV light from a water-cooled H_2 discharge tube through a LiF window. In the absence of precise data on the UV flux near the martian surface, our martian soil may be considered an approximate simulation. The Suprasil window and the CO_2 in the reaction vessel may have a filtering effect qualitatively equal to that of the atmospheric column above the martian surface; quantitatively, we may have reproduced in a few fours what may take place on Mars over a period a thousand times longer.

In the simulated soil experiment we used the same ^{14}C-labeled organic mixture that was used in the Viking experiments (*6*). One hundred microliters of the original solution diluted to 1 ml was introduced onto the simulated martian surface, and the $^{14}CO_2$ released was trapped in a NaOH solution. The radioactivity was determined by means of a liquid scintillation counter. As in the Viking 1 lander control experiments, we also conducted an inactivation experiment by heating the irradiated reaction tube at 160°C for 3 hours before introducing the labeled mixture. These results (Table 2), obtained by a radiometric method with the ^{14}C-labeled "soup," confirm that CO_2 is released by the interaction of the organic mixture with the simulated martian surface. The UV photodissociation of CO_2 is known to give rise to reactive oxygen. In our reaction tube, the dissociated oxygen might have attached to the hematite crystallites, making the hematite more oxidized (Fe_2O_3O). If this is the case, the CO_2 release here may be similar to the reactions of the metal peroxides or superoxides with labeled formate. The mechanism of $^{14}CO_2$ release may be through H_2O_2 formation:

$$CO_2 + Fe_2O_3 \overset{h\nu}{\rightarrow} Fe_2O_3O + CO$$

$$Fe_2O_3O + 4H_2O \rightarrow 2Fe(OH)_3 + H_2O_2$$

$$H_2O_2 + H^{14}COONa \rightarrow NaOH + H_2O + {}^{14}CO_2$$

We recognize that in our experiment absorption by CO_2 took place in the range of 160 to 180 nm.

Table 2. A simulated martian surface releases CO_2 from ^{14}C-labeled mixture of biochemicals. The counts per minute (cpm) listed are the averages of at least three separate determinations; the range is shown in parentheses. One hundred microliters of the ^{14}C mixture gave a reading of 6×10^6 cpm.

Radiation period* (hours)	Radioactivity (cpm)	
	$^{14}CO_2$	Background
17.6†	2489 (2465–2531)	150 (142–165)
10.6† (heated to 160°C for 3 hours)	308 (302–315)	107 (99–112)
10‡	10140 (10103–10200)	207 (203–211)

*These periods were chosen for convenience. †The irradiation was carried out with the Suprasil window of the reaction tube in contact with the LiF window of the source. ‡The irradiation was carried out in N_2 in order to cut off the UV absorption by any air between the two windows.

Table 3. Release of O_2 in a simulated GEX experiment.

m/e	Peak intensity* (%)	
	Background	Measured after 10 minutes
	$KO_2 \pm H_2{}^{18}O$	
32	19	>130
34	1.8	13.8
36	1.4	1.2
	$ZnO_2 \pm H_2{}^{18}O$	
32	13	86
34	3.7	3.2
36	2.0	2.5

*Relative to m/e 28.

Our inactivation experiment (Table 2) suggests that the dissociated oxygen could be released from the hematite crystallites and recombined to an inactive O_2 by the heating at 160°C. This result appears to mimic the "biological sterilization" used as a control for the Viking experiments.

It has been suggested that iron oxide minerals may be present on the martian surface (*7*). The results of the Viking LR experiment may be due to surface chemistry reactions as demonstrated in our simulation experiment. The possibility of H_2O_2 on the surface of Mars should not be discounted.

In the Viking GEX experiment, O_2 was released when the gas over the martian soil in the test chamber was analyzed in the humid mode (*1*). We have explored the possibility of whether the results of the GEX experiment may be due to surface chemistry.

The release of O_2 produced by the interaction of water with a metal superoxide (KO_2) or a peroxide (ZnO_2) was examined to obtain information on whether O_2 could be generated by chemical reactions of the martian soil. To minimize contamination by atmospheric components, the KO_2 or ZnO_2 (0.1 g) was placed in a glass tube and evacuated to 10^{-1} torr. Then, 0.2 ml of 50 percent $H_2{}^{18}O$ was introduced into the tube. The use of ^{18}O-labeled water would also enable us to find the sources of O_2 generated by the interaction. Peaks at m/e 32 ($^{16}O_2$), 34 ($^{16}O^{18}O$), and 36 ($^{18}O_2$) were investigated by mass spectrometry. Relative peak intensities are listed in Table 3, with the background reading given before the reading for O_2 generated. The striking increase in the peak intensity at m/e 32 indicates that KO_2 and ZnO_2 easily release O_2 upon reaction with water. In the case of the interaction of KO_2 with water, the increase in the peak intensity at m/e 34 indicates that O_2 is also generated from the water. The formation of $^{16}O^{18}O$ may be explained as follows:

$$2K^{16}O_2 + H_2{}^{18}O \rightarrow 2K^{16}OH + 2^{16}O + {}^{18}O$$

$$^{16}O + {}^{18}O \rightarrow {}^{16}O^{18}O$$

These observations, although preliminary, strongly suggest that the results of the Viking GEX experiments may have been due to surface chemical reactions on Mars (*8*).

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29 December 1976; revised 25 February 1977

Shock-Produced Olivine Glass: First Observation

Abstract. *Transmission electron microscope (TEM) observations of an experimentally shock-deformed single crystal of natural peridot,* $(Mg_{0.88}Fe_{0.12})_2SiO_4$, *recovered from peak pressures of about* 56×10^9 *pascals revealed the presence of amorphous zones located within crystalline regions with a high density of tangled dislocations. This is the first reported observation of olivine glass. The shocked sample exhibits a wide variation in the degree of shock deformation on a small scale, and the glass appears to be intimately associated with the highest density of dislocations. This study suggests that olivine glass may be formed as a result of shock at pressures above about 50 to 55* $\times 10^9$ *pascals and that further TEM observations of naturally shocked olivines may demonstrate the presence of glass.*

We know of no case in which olivine liquid (Mg_2SiO_4 to Fe_2SiO_4 in composition) has been quenched to a glass. Numerous studies of the liquidus of olivine (*1–3*) and corresponding compositions in analogs of the system (Mg,Fe)O-SiO_2 [for example, LiF-BeF_2 (*4*)] have never resulted in the unequivocal quench of such a glass. Furthermore, attempts to produce olivine glass by means of rapid fusion and quench techniques have also been unsuccessful (*5*). Similarly, the presence of olivine glass has never been unambiguously demonstrated in the extensive studies of naturally and (a few) experimentally shocked olivines (*6, 7*), although it is known that most silicates that have been studied become amorphous when subjected to shock of high enough intensity (*7*).

We report the first observation of olivine glass and its synthesis by means of shock. A disk, cut from a crystal of San Carlos, Arizona, peridot, $(Mg_{0.88}Fe_{0.12})_2$-SiO_4, was shocked along [010] (propagation direction of the shock wave) (*8*). A peak pressure of 56×10^9 pascals (560 kbar) was achieved by the "multiple-reverberation" technique for a period of approximately 0.5 μsec (*9*).

Transmission electron microscope (TEM) observations (*10*) on ion-thinned slices of the shocked olivine revealed patchy, nondiffracting zones of no contrast within crystalline and diffracting sample material (Fig. 1, a and c). The lack of diffraction contrast implies that the zones consist of material lacking crystalline order down to a scale of several nanometers. These zones grade into the surrounding crystalline olivine, and diffracting fragments within the amorphous material indicate remnants of crystalline material. There is no evidence for phase separation or other heterogeneities within the glass. Marked, spotty asterism in the diffraction pattern indicates misorientation of fragments and bending of the olivine (Fig. 1d). Although the amorphous zones attain maximum dimensions of 10 μm and more (representing approximately 1 to 2 percent of the sample by volume), they were not evident during optical microscopic examination carried out on the shocked olivine prior to the TEM analysis.

Regions of low dislocation density (Fig. 1b), as well as the high-density tangles (Fig. 1, a and c), can be found in the shocked sample, an indication of wide variations in shock-induced deformation on an extremely small scale. Significantly, the glassy zones are located within the regions of highest dislocation density. This result may indicate that a threshold stress for the production of diaplectic glass exists, which was only achieved locally in the present experiments.

Estimates of the average temperature of the sample at peak pressure are between 740 and 1000 K, based on the equation-of-state properties of the sample container (*11, 12*) and a model presented in (*13*). The temperature attained immediately upon the release of pressure is poorly constrained as a result of its strong dependence on the details of the irreversible thermodynamic path followed by the sample on compression and decompression (*14, 15*). Nevertheless, a temperature well below the melting point of olivine [above 2000 K at 1 atm and presumably much higher at 56×10^9 pascals (*1, 3, 16*)] is indicated at peak pressure and probably on pressure release (*13, 14*).

These results suggest that the shocked olivine contains diaplectic glass [glass apparently formed in the solid state by shock (*7, 17*)]. The fact that the glassy zones are associated with the regions of the sample showing the highest amount of crystalline deformation suggests that they possibly represent portions of the sample quenched from material which at one point was in a high-pressure phase or phases. Although no microtextural evidence for the formation of any high-pressure phases was seen in the TEM studies, Hugoniot equation-of-state data for olivine indicate partial transformation to one or more high-density phases at 56×10^9 pascals [transformation is apparently