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Chemical and Physical Microenvironments at the Viking Landing Sites

Benton C. Clark

Planetary Sciences Laboratory, Martin Marietta Aerospace, Denver, CO 80201, USA

Summary. Physical and chemical considerations permit the division of the near-surface regolith on Mars into at least six zones of distinct microenvironments. The zones are euphotic, duricrust/peds, tempofrost, permafrost, endolithic, and interfacial/transitional. Microenvironments vary significantly in temperature extremes, mean temperature, salt content, relative pressure of water vapor, UV and visible light irradiance, and exposure to ionizing radiation events (100 Mrad) and oxidative molecular species. From what is known of the chemistry of the atmosphere and regolith fines (soil), limits upon the aqueous chemistry of soil pastes may be estimated. Heat of wetting could reach 45 cal/g dry soil; initial pH is indeterminate between 1 and 10; ionic strength and salinity are predicted to be extremely high; freezing point depression is inadequate to provide quantities of liquid water except in special cases. The prospects for biotic survival are grim by terrestrial standards, but the extremes of biological resiliency are inaccessible to evaluation. Second-generation in situ experiments which will better define Martian microenvironments are clearly possible. Antarctic dry valleys are approximations to Martian conditions, but deviate significantly by at least half-a-dozen criteria.

Key words: Mars – Evolution – Planetary geochemistry – Soil – Ionizing radiation – Exobiology.

Introduction

Spacecraft exploration missions and the ground-based experimental and theoretical studies they have spurred have enormously expanded our knowledge of the Martian environment. Having been placed at the atmosphere-surface interface, the Viking landers have sampled the region in which environmental gradients are the largest, the most uncertain, and from the standpoint of life, the most important. Unambiguous indications of biological activity have not been forthcoming (Klein, 1978), but the new data confirm the previous supposition that of all the planets in our solar system, Mars appears the most habitable for Earth-analogous life forms.

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Microenvironments are often inherently complex because of the multitude of interacting factors. It is the purpose here to summarize the characteristics of potential microenvironments on Mars, but much remains unknown, and the discussions below must necessarily include reasonable extrapolations while leaving undecided many critical issues.

Geologic Aspects of the Environment

Once the target latitudes had been decided upon, the final Viking landing sites (Table 1) were selected by the criteria of (a) low altitude, and (b) apparent freedom from meter-scale blocks, as judged by interpretation of orbiter photographs and earth-based radar

Table 1. Viking Landing Site Data

	VL-1	VL-2	Reference[d]
Locality Name	Chryse Planitia	Utopia Planitia	
Geologic unit	Cratered plains (Apc)	Smooth plains (Aps)	(Sc-78)
Latitude	22.49° N.	47.67° N.	(Mo-78) for VL-1
Longitude	48.04° W.	225.71° W.	(Ma-77) for VL-2
Altitude[a]	-2.5 km	-3.5 km	
Earth date of landing (Sol O)	July 20, 1976	September 3, 1976	
Seasonal Information			
At landing	98° L_s[b]	120°L_s	(He-77)
Winter solstice (L_s=270°)	Sol 307	Sol 263	
Summer solstice (L_s=90°)	Sol 654	Sol 610	
Atmospheric pressure			
At landing	7.6 mbar	7.7 mbar	(He-77)
Minimum (VL-1 Sol 100)	6.8	7.4	(He-77)
Maximum (VL-1 Sol 310)	9.0	10.1	(Ry-78)
Atmospheric water vapor			
At landing	7 pr μm	18 pr μm	(Fa-77)
Yearly minimum	5	< 1.6	c
Yearly maximum	20	30	c
Frost point (Max/min)	-78/-86°C	-75/-93°C	
Soil Temperatures			
Surface, at landing, high/low	-8°C/- 95°C	-6°C/- 92°C	(Ki-76)
Surface, yearly high/low	+4 /-103	-10 /-125	(Ki-77)
20 cm depth, at landing	-55	-51	(Ki-76)
20 cm depth, yearly high/low	-55/-68	-50/-80	(Ki-77)
30 meters depth	-58	-81	(Le-66)

[a] Below the 6.1 mbar mean reference level. Because of the large seasonal progression of pressures, the reference aeroid may be redefined in the future, which would shift the above values by some constant

[b] L_s is the planetocentric longitude of the sun

[c] Personal communication, P. Doms, 1978

[d] See Table 6 for key to references

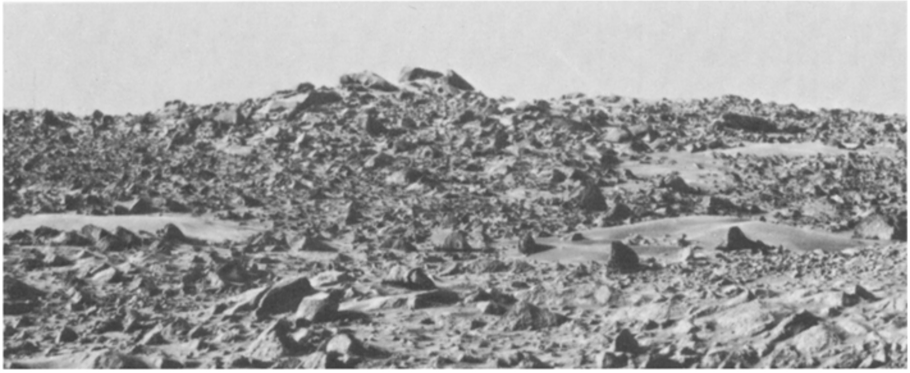

Fig. 1. A view from Viking lander-l, showing both the high density of rock cover and interspersed drifts of fine material partially burying some rocks. Lander picture 11A156.

Fig. 2. A view from lander-2, showing vesicular rocks, smooth rocks, drifts, and a trough. Shadows cast by rocks create a special low-temperature environment, where frost was observed to persist during the transition from local winter to spring. Lander picture 21A024.

echoes. Selected photographs from landers 1 and 2 are shown in Figs. 1 and 2, respectively. The general terrain type, as interpreted photogeologically, is one of volcanic plains with admixed eolian (wind-carried) material (Scott and Carr, 1978). Both landing sites are at locations intermediate between the classical bright and dark areas of Mars. A major finding of Viking has been a wealth of geologic structure on the one centimeter

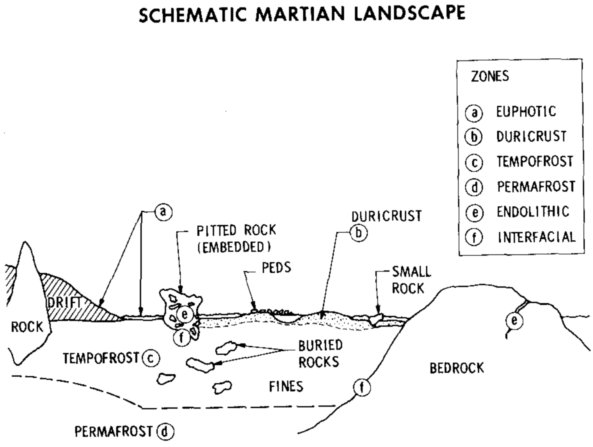

Fig. 3. Generalized schematic portrayal of the geological and pedological surrounds at the Viking landing sites. See text for definitions of units.

to one meter scale which was largely unsuspected prior to these landings. This heterogeneity, combined with thermal and other factors, leads to the definition of multiple types of microenvironment.

The general appearance of the regolith at both sites is that of a yellow-brown soil with a considerable population of rocks ranging from small to block size. A number of distinguishable rock morphologies are present. Readily identified are vesicular/pitted and smooth classes. Rocks with cracks and subtle banded structure are present. Although the vesicular rocks have all the appearance of degassed lava, alternative interpretations are possible. Cavernous weathering by wind or water can transform sedimentary material into similar form, and Fuller and Hargraves (1978) have offered the terrestrial example of ferricrete, a sandstone cemented by ferric oxyhydroxides which has morphology indistinguishable (at Viking camera resolution) from Martian "vesicular" blocks.

Observed at both locations are planar surfaces which geochemical analysis indicates are part of a layer of salt-cemented fines (Baird et al.,1976; Clark et al.,1976). A duricrust layer is particularly apparent where the descent rocket engines have blown away the surficial dust layer and in certain areas where the surface sampler has distrurbed the soil to form platy clods. This crust is probably ubiquitous at both sites, but not visible everywhere because of overcoating by soil, rocks, or fragments of itself *(peds).*

At the first site are seen large *drifts* of fine material free from rocks or peds. Microdrifts are also numerous on the lee sides of small obstacles. The terrain at lander-1 is gently undulating with bedrock exposed at several locations, while lander-2 is on a flat plain cut by several troughs typically one meter wide and several centimeters deep (Mutch et al., 1976). Fine grained material may be in the 1 to 3 μm size range (Egan et al., 1978).

Shown schematically in Fig. 3, the observed regolith provides several potential habitats with diverse microenvironments. For convenience in further analysis, six general regions will be defined which, though not perfectly mutually exclusive, do separate the regolith into distinct conceptual units with properties fundamental to each from an environmental viewpoint. These zones are

a) *Euphotic Zone.* All regions in which sufficient sunlight is available for photosynthetic metabolism. Calculations by Sagan and Pollack (1974) indicate this zone could extend to a depth of 1 cm in loose soil. The definition as used here also embraces exposed rock surfaces, and the atmosphere with its airborne particulate load.
b) *Duricrust and Peds.* The layer of indurated soil and individual aggregates therefrom.
c) *Tempofrost.* As defined by Farmer (1976), the region within the regolith which remains below the free-air frost point during the cold season only. Soil moisture in this region is effectively trapped, as ice, for the duration of the winter.
d) *Permafrost.* Region within which the temperature does not exceed the frost-point temperature for at least one Martian year. In such a region, ice is stable on a yearly basis, but on the geologic time scale is only a metastable phase because (1) any other region which can become transiently colder -- e.g., the topmost soil surface at night — will cold-pump ice from this zone, and (2) long-term climatic changes are possible (Ward et al., 1979; Sagan et al., 1973) which may warm such regions above the frost point.
e) *Endolithic.* Inside a rock vesicle, pit, crack, crevice, etc., where ultraviolet light does not penetrate, the diurnal temperature extremes are moderated by the heat capacity of the rock, moisture may be held by capillarity, and atmospheric gases are available at least by diffusion.
f) *Interfacial/Transitional.* Rock-soil interface, whether formed by bedrock underlying soil or individual rocks lying upon or buried within the soil. Also includes the layer of regolith between the euphotic zone and the tempofrost zone.

Physical Properties of the Environment

Temperature. The lack of moderating influences on Mars (e.g., oceans a dense convecting atmosphere, etc.) allows extreme daily temperature variations in the lower atmosphere and topmost layer of soil. Diurnal temperature swings are as much as 80°C, although they are considerably less during dust storms. Temperature gradients are as high as 20°C per centimeter in the euphotic, duricrust, and interfacial/transitional zones, as brought out in Fig. 4 . From the maximum and minimum water vapor abundances observed at the two landing sites, Table 1, and assuming commensurate scale heights for both CO_2 and H_2O, the derived frost point temperatures vary from -78 to -86 at lander-1, and -75 to less than -93°C at lander-2. Correlated with the thermal model of Kieffer et al. (1977), the tempofrost zone is not present at lander-1 and varies seasonally in depth from surface to many meters at lander-2. As the temperatures beneath the seasonal wave have been calculated as -58°C at 22 N. latitude, and -81°C at 48 N. latitude by Leighton and Murray (1966), a permafrost zone as defined herein also does not exist at all at lander-1, and exists only at a depth below the seasonal wave penetration thickness (~10 meters) at lander-2.

A summary of temperature extremes and average temperatures at the two landers is given in Table 1. The thermal models assume, of course, uniform horizontal surfaces. As shown by Balsamo and Salisbury, anti-solar slopes will have much lower mean temperatures , corresponding to the temperature at a latitude equivalently increased by the same number of degrees as the slope.

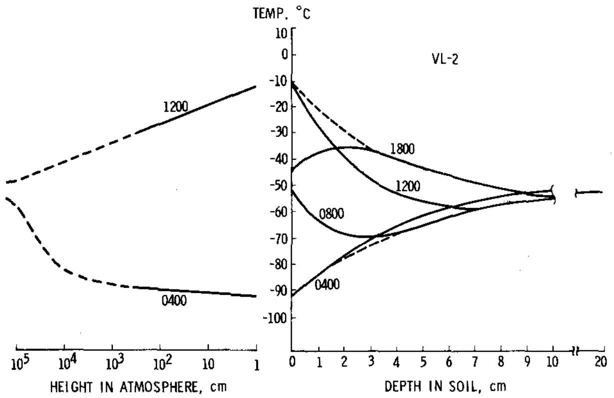

Fig. 4. Diurnal temperature profiles at the time of landing at Utopia Planitia. Note the logarithmic scale used for the atmosphere, where temperature gradients are much less extreme. The diurnal temperature wave penetrates only some 10 or 20 cm below the surface. Less extreme variations occur at the center and beneath a 10 cm rock (Data provided by B. Jakosky and H. Kieffer, 1977). Numerical labels on curves denote local time.

Pressure and Wind. Unlike the earth, the Martian atmosphere is dominated by a gas, CO_2, readily condensed on the colder portions of the planet. As the polar caps sublime, strong winds sweep equatorward, apparently carrying with them the water vapor released nearby (Farmer and Doms, 1979). At the peak of release of volatiles from the southern cap (L_s = 270°), the atmospheric pressure at the landing sites was fully 33% higher than the yearly minimum (L_s = 150°), as seen in Table 1 (Ryan et al., 1978). The water vapor abundances at the lander-1 site varied by about a factor 4 over the same period. which corresponds to a shift in the mean frost point of only a few degrees. At lander-2, a frost ground cover was present for well over 100 sols; as interpreted by Jones et al. (1979) this frost consisted mostly or totally of water ice, and was deposited by settling of ice-coated dust grains from the atmosphere.

Winds at the landing sites are highly variable, particularly with seasonal changes. At the time of landing, northern summer, the mean wind speeds were only a few meters per second for all periods of the diurnal cycle. During northern winter, also the season for dust storms, winds range considerably higher with mean winds of about 18 m/s and gusts peaking to 28 m/s (Ryan and Henry, 1979). At night, the stable inversion forms and winds die down to less than 5 m/s.

Radiation Environment. A significant proportion of the solar ultraviolet flux penetrates to the surface of Mars. This flux affects the chemical balance of the atmosphere and promotes the destruction of organic compounds in the soil (Oro et al., 1979). A discussion of the seasonal and geographical variations of the surface UV flux due to atmospheric CO_2 and O_3 absorption is given in Kuhn (1979). The carbon dioxide effectively cuts off all wave-lengths shorter than about 200 nm, while ozone absorption has primarily the effect of cutting a notch in the UV spectrum at 250 nm. Additional modifications will be caused by absorption and scattering effects of atmospheric aerosols, which include ice-grain clouds and suspended dust.

Cosmic rays will produce a higher dose-rate than on Earth since the Martian atmosperic column density at normal incidence is only 16 to 27 g/cm^2 compared to Earth's atmospheric shield of 1000 g/cm^2 (equivalent to a depth of 9 meters below ground on Mars). The Martian atmosphere stops all protons of energy less than 140 MeV; the Earth is protected from primaries up to energies of ~2 GeV (Janni, 1966). Haffner (1967) has calculated doses by galactic cosmic rays as a function of shield thickness, from which can be inferred about 36 rad/Martian year, a dose which would be deleterious to higher organisms but relatively inconsequential to microbes.

Calculation of surface doses on Mars due to solar flare proton events are in the range of a few to 10 rad for model events (Foelsche and Wilson, 1974). In an active year, the cumulative dose could reach 25 rad. More important, however, are the occasional giant outbursts capable of bathing the planets with integrated fluxes several orders of magnitude above normal. Reid et al. (1976) have suggested these rare events may be responsible for sudden, catastrophic extinctions seen in the fossil record on earth. Wdowezyk and Wolfendale (1977) calculate a proton dose event of 10^4 rad on earth every 10^6 to 10^8 years. From their flare frequency curve, and the Foelsche and Wilson data, we can estimate that events resulting in $\geqslant 10^4$ rad at the Martian surface could occur as often as every 10^3 years; 10^6 to 10^8 rad events may occur every 10^5 years. The latter dose, 100 Mrad, is the level at which even the hardiest terrestrial microbiota populations succumb. The Martian microbiota, if it exists, must cope with this periodic insult either by extraordinary resistance or by obtaining shelter at depth in the soil.

Chemical Composition of the Environment

Atmosphere. The Martian atmosphere is over 95% CO_2, with minor amounts of N_2 and Ar, and traces of O_2 and CO. It is only 1/40 as massive per unit area as the earth's atmosphere, but nonetheless is higher in its partial pressure of CO_2 than the earth's by about a factor of 20. Water vapor is present at levels variable with latitude and season, with a typical value being about 1 μb (see Clark, 1978, for discussion). Both nighttime and early morning fogs have been observed.

Photolysis of atmospheric constituents by the solar UV flux produces a number of interesting and highly reactive species in trace quantities, including molecular hydrogen, a variety of NO_x gases, the HNO_x acids, hydrogen peroxide, atomic oxygen, and the hydroxy radical (the strongest oxidizing agent known, Hunten, 1974). Present knowledge and predictions of the abundance levels of the gaseous constituents are summarized in Table 2.

Regolith. The elemental composition of the Martian soil has been measured directly at both landing sites (Clark et al., 1976), but identification of the mineral phases (i.e., chemical compounds) at present is indirect, and speculative. From infrared spectra, Hunt et al. (1973) inferred the presence of a smectite clay as a major component of the particles suspended during the dust storm of 1971. Subsequently, Baird et al. (1976) noted that the elemental analyses were consistent with up to 80% of three smectite clays in the soil: nontronite (Fe-rich), saponite (Mg-rich), and montmorillonite (Al-rich).

Table 2. Comparison of Atmospheric Constituents on Earth and Mars

	Earth	Mars		
	Partial Pressure	Partial Pressure[a]	Basis[b]	Reference[d]
CO_2	0.31 mb	5.8 mb	mi	(Ow-77)
N_2	780.8 mb	0.16 mb	mi	(Ow-77)
Ar	9.3 mb	0.10 mb	mi	(Ow-77)
O_2	209.5 mb	8 μb	mr,mi	(Ba-72,Ca-72, Ow-77)
CO	0.05 μb	5.0 μb	mr	(Yu-77)
H_2O	13 to 42,000 μb	~1.0 μb	mr	[c]
H_2	0.05 μb	0.01-0.06 μb	t	(Hu-70, Li-76, Yu-77)
CH_4	1.5 μb	<0.02 μb	mr	(Ho-72)
O_3	0-0.07 μb	0-0.001 μb	mr	(Li-76)

Gas molecules and free radicals predicted theoretically to be constituents of the Martian atmosphere (as summarized in Yu-77 and Mc-77):

NO, NO_2, HO_2, O	~part per billion each (10^{-5} μb)
H_2O_2	~10 to 100 parts per billion
H, OH, NO_3, N_2O, N_2O_5, HNO_2, HNO_3	~1 part per trillion each

Some gases not detected in the Martian atmosphere by UV spectroscopy, with approximate upper limits (Ho-72, Ow-72):

NO, C_3O_2, HCHO, COS	< 1 part per million (10^{-2} μb)
NH_3, NO_2, H_2S, SO_2, HCl	< 0.1 part per million

[a] Calculated for 6.1 mb total pressure

[b] mi = measured, in situ; mr = measured remotely (from Earth, or Mars orbit); t = theoretical

[c] For Mars value, see Clark (1978). Earth values correspond to 10% relative humidity at -40°C and 100% at 30°C

[d] See Table 6 for key to references

Lander camera six-band spectra are consistent with either nontronite or pyroxene components (Arvidson and Bragg, 1977). Recent analysis of ground-based IR spectra by Egan et al. (1978) is consistent with an average soil composition containing smectite or limonite, mixed with a basalt. Banin (1979) has reviewed a variety of evidence which suggests the presence of nontronite. Gooding (1978) has proposed that if the Martian soil has fully attained thermodynamic equilibrium with the present atmosphere, the chief mineral phases should be oxides of silicon, aluminum, ferric iron, and titanium; carbonates of magnesium and calcium; sulfates; and certain residual non-weathered igneous minerals (albite, microcline, apatite).

Other mineral phases have been suggested. The magnetic properties experiment on Viking clearly showed the presence of 1 to 7% of highly magnetic grains in the soil (Hargraves et al., 1977), most likely either magnetite (Fe_3O_4) or maghemite (γ-Fe_2O_3). Oyama et al. (1977b) have also proposed maghemite. Pollack et al. (1977) infer magnetite as a component of the airborne particulates, constituting 10 ± 5% by volume of this dust. Salts are undoubtedly present. Organic compounds are virtually absent (Biemann et al.,

Table 3. Candidate Chemical Compounds in Martian Soil

Type	Selected Candidates		
	Formula	Mineral Name	Maximum[a] Amount
a magnetic mineral	Fe_3O_4	Magnetite	1% to 7%
	γ-Fe_2O_3	Maghemite	
a S-containing mineral[b]	Na_2SO_4	Thenardite	15%
	$MgSO_4$	Kieserite (1-hydrate)	
a Cl-containing mineral	NaCl, $MgCl_2$ or $CaCl_2$	Halite, bischofite (6-hydrate), or antarcticite (6-hydrate)	1%
an aluminosilicate	$Al_2Si_4O_{10}(OH)_2$ (approx.)	Montmorillonite or Beidellite	20%
	$Al_2Si_2O_5(OH)_4$	Kaolinite	14%
	$NaAlSi_3O_8$	Albite	29%
	$CaAl_2Si_2O_8$	Anorthite	15%
other silicates	$Fe_2Si_4O_{10}(OH)_2$(approx.)	Nontronite	40% to 80%
	$Mg_3Si_4O_{10}(OH)_2$ (approx.)	Saponite	
	SiO_2	Quartz	
	Olivines, pyroxenes, talc, brucite		
carbonates	$CaCO_3$, $MgCO_3$ $CaMg(CO_3)_2$, Na_2CO_3 or $FeCO_3$	Calcite, magnesite, dolomite, soda, or siderite	~10%
miscellaneous	Fe oxides and oxyhydroxides Na, Mg, Ca, and/or Fe as exchangeable cations.		~10% to 20%

[a] The maximum amount, given in weight per cent, is that permitted by the elemental analysis of Martian soil (Clark et al., 1976) except for the magnetic component, given by Hargraves et al. (1977)

[b] More than a single sulfate may be present. In occurrences of soluble salts on earth, mixtures of several salts and even mixed-salt compounds (e.g., bloedite, $Na_2Mg(SO_4)_2 \cdot 4H_2O$) are the rule rather than the exception

1977), but Oyama et al. (1978b) have suggested the presence of polymeric carbon suboxide (C_3O_2) on the basis of its colorimetric properties (see also Plummer and Carson, 1969) and results from the pyrolytic release life-detection experiment. Carbonates have been widely predicted.

Since no instrument for mineralogic measurements was included in the Viking payload, elemental abundance data have been used to constrain the possibilities. For example, Table 3 places some limits on candidate mineral phases.

Water. The distribution and abundances of various forms of water on Mars remain largely unknown. Water has been detected as vapor and ice crystals in the atmosphere, bound water in the soil, and surface ice at the residual north polar cap. Atmospheric water vapor variations have been studied comprehensively from orbit (Farmer and Doms,1979).

Table 4. Types of water in soil

Physical		Chemical	
	(Max)		(Max)
Ice	<80%	Hydroxides and clays	
		Clays (smecite)	3.4%
		(kaolinite)	2.0%
Liquid	---	Fe oxy-	2.1%
Vapor	$\sim 10^{-7}$%	Gibbsite	2.9%
		Brucite	~10%
Adsorbed			
Basalt powder	0.6%	Hydrates	
Clay	1-20%	Sulfates (1-7)	1.7-12%
Micropores	< 1%	Chlorides (2-6)	0.3-1%
		Nitrates (1-4)	1.8-7%
Fluid Inclusions	< 1%	Carbonates (1-6)	1.8-12%
		Silica (opal)	5%
		Chemisorbed	

* Value are grams H_2O per gram soil, converted to per cent

Although the absolute value of the partial pressure of water vapor at site 1 changes by only a factor of about 4 (from 0.2 to 0.8 microbar), the wide range of temperatures at the surface and in the euphotic zone corresponds to extremes in relative pressure (i.e., humidity), varying from 0.1% in the heat of the noon-day sun to 100% at night. This cycling will lead to desiccation of the upper layers of soil (Clark, 1978).

In addition to hydrate and physically adsorbed water, the Martian soil may contain chemisorbed water, hydroxide minerals, water in capillary pores. etc. Based upon the elemental analyses and analogies with terrestrial cases, limits to regolith water abundances can be estimated. For example, the nominal aluminum concentration of about 3% limits the concentration of kaolinite in the soil to about 15% by weight, or 2% of chemically bound H_2O. Similar considerations lead to the results shown in Table 4. It is important to note that not all mineral phases listed are possible simultaneously.

Prediction of the most likely quantities of water in deep soil has been attempted in a model by Clark (1978), based upon soil mineralogy similar to that inferred by Baird et al. (1976), i.e., high clay and salt content. This model predicts bound water contents of soil at depths below a few meters (the seasonal thermal skin depth) up to about 15% for the Chryse temperature (-58°C) and 25 to 30% for the Utopia temperature at depth (-81°C). Before permafrost ice can form under such condition, the constituent salt and clay minerals must be fully hydrated.

Chemical Microenvironments in the Soil. The homogeneity of Martian regolith fines on a microscopic scale is unknown. As noted before, the bulk composition was found remarkably similar between the widely separated landing sites, presumably a consequence of the yearly duststorms.

Certain elements do show a striking concentration variablility over small sampling areas. These elements are S, Cl, and Br (Clark et al., 1978), just those implicated as water soluble salts. Duricrust is particularly enriched in these salts. Since the strong freezing-point depressors, such as $CaCl_2$, will be concentrated into the aqueous phase for any freezing event that doesn't dip below the eutectic temperature; subsequent freezing and /or freeze-drying could produce sequestered grains of the depressor salts.

The extreme aridity and active photochemistry of the contemporary environment could permit the existence of unique mineral constituents, especially at the microscale. Huguenin (1976) has emphasized the reactions occurring at mineral surfaces. In the Viking Gas Exchange experiment, Oyama et al. (1977a) detected a reaction with H_2O vapor to produce oxygen gas. The reactant, probably a superoxide or peroxide compound is a trace constituent, about 30 ppm.

Aqueous Chemistry of Martian Soil

Though normally desiccated, the question of possible wetting in the ancient past and the indications of unusual chemistry by the Viking life detection experiments emphasize the importance of characterizing the properties of Martian soil when mixed with liquid water. Direct measurements have not as yet been made.

Ionic Strength. An aqueous extraction of Martian soil is predicted to have a high ionic strength due to the putative soluble salts. For reference, a one:one extract (by weight) could contain about 90 g. of SO_4^{2-} per kg H_2O, 6 g/kg of Cl^-, 0.1 g/kg of Br^-, and 0.1 g/kg of HCO_3^- (provided carbonates are present). If the corresponding cations are divalent, the ionic strength would be 4.2 molal; if univalent, 3.0 molal. These may be compared to typical values for river, ocean, and Dead Sea water of 0.002, 0.69, and 7.2 molal, respectively.

Obviously, the Martian soil is such that only halotolerant organisms would likely survive the extremely ionic environment and the limited water activity. Note especially that a one-to-one correspondence with typical terrestrial brine environments cannot be claimed since it is not known that Na^+ is the dominant soluble cation; Mg^{2+} ion, toxic to most organisms at high concentration, is just as likely to be predominant.

Heat of Wetting. The probable presence of hydrophilic minerals in a desiccated state (in the surface layer) opens the possibility that significant heat is generated by reaction with water. Smectite clays are well-known to have high heats of wetting, amounting to 9 to 22 cal/g. for immersion of the dry clay (Grim, 1968)- -divalent exchangeable cations producing the higher values. Many salts evolve copious thermal energy upon dissolution in water. Anhydrous $MgSO_4$ yields a heat of solution of 160 cal/g., but Na_2SO_4 only 4 cal/g. All chlorides plausible for Mars have high values, except NaCl, which reacts endothermically with liquid water. The upper limit for Mars soil may be calculated by postulating a composition consisting of 80% smectite, 14% $MgSO_4$, and 1% $MgCl_2$. The net heat of reaction becomes 45 cal/g. dry soil, with the sulfate salt contributing half the total amount. A volume of soil mixed with an equal volume of water would experience a temperature rise of about 37°C (if soil wetting and consequent reactions are immediate) which could, of course drive other reactions.

An experimental test for this effect was devised during the Viking extended mission by the author in collaboration with F.S. Brown and B. J. Berdahl. The test utilized the gas exchange (GEX) module in the lander-2 biology instrument,[1] and consisted of baking out the loaded sample at +160°C for 2 hours, sealing, and after allowing cool-down time, injecting residual nutrient during a special sequence for monitoring temperature at a high rate. The results were null. However, subsequent laboratory experiments demonstrated that fine hygroscopic material can sufficiently slow the rate of wetting as the nutrient solution flows into the sample through the stainless steel fritted filter that heat evolution becomes undetectable due to thermal losses inherent in module construction. The question as to the heat of wetting of Martian soil remains, therefore, in the theoretical realm.

pH. The influence of pH on biochemical and geological systems is well known as a factor of first importance. Prediction of pH in a soil-water system requires intimate knowledge of the mineral constituents and the atmosphere they are in equilibrium with. For soils on earth, the inverse is invariably followed: the empirical pH value is used as a constraint upon the nature of the chemical phases present. The situation is especially complex for acid soils, where organic debris, amorphous and colloidal material, status of the sesquioxides, and clay cation exchangeable Al^{3+} and H^+ are of paramount importance (Jenny, 1961; Miller et al., 1965).

It has been commonly stated that water on Mars must achieve a low pH by virtue of carbonic acid formation under the atmospheric partial pressure of CO_2 more than an order of magnitude higher than on Earth. Such a statement suffers in two respects. First, in terrestrial soils, the interstitial P_{CO_2} is typically 3 to 30 times higher than that in the free atmosphere (Bower et al., 1965), i.e., it can reach levels equivalent to that on Mars. Secondly, few soils are inert. Indeed, CO_2 saturated ground-water is an effective weathering agent on Earth and the resulting reactions (carbonation, acid hydrolysis, dissolution, etc.) liberate base-forming cations which *raise* the solution pH.

If the soil were composed of a single mineral, the predicted pH would be the "abrasion pH", defined as that measured in the laboratory after grinding the mineral in pure water in air. In Table 5, the abrasion pH's of candidate minerals are tabulated. Besides the minerals listed in the table, several other compounds may exist in the soil (perchlorates, chlorates, nitrites, hydroxides, peroxides, superoxides, sulfites, and peroxydisulfates). Finally, thin films of water on mineral surfaces generally display a pH different from the bulk solution because of surface layer effects.

The primary igneous minerals produce a neutral to alkaline pH via hydrolysis reactions with water. Only after intensive weathering, with removal of cations by leaching, does the pH normally become lower (Loughnan, 1969). Smectite clays are generally considered to form under neutral to alkaline conditions (Birkeland, 1974). Even the "dry" weathering reactions proposed by Huguenin (1974) result in a hydroxide surface layer.

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[1] We are indebted to V.I. Oyama, the GEX Prinipal Investigator, for allowing such unorthodox use of this experiment during the Extended Mission of Viking.

The pH of most soils high in clay and neutral salts is within one pH unit of neutrality, and determined chiefly by the amount of exchangeable basic cations (Na, Mg, and Ca) relative to acidic ones (Al, H).

On the other hand, the high sulfate concentration in the Martian soil will have at one time caused considerable acidity to develop. If originally present as an iron sulfide, the conversion to iron sulfate produces salts whose reaction with water is strongly acidic (see Table 5). The common weathering reaction of FeS_2 on earth is (Loughnan, 1969):

$$2FeS_2 + 2H_2O + 7O_2 \rightarrow 2FeSO_4 + 2H_2SO_4$$

which produces sulfuric acid as well as the acidic salt. Even if the sulfur is initially released as a gas, the H_2S or SO_2 will readily become oxidized under current atmospheric conditions to SO_2 and SO_3 species which, in turn via reaction with H_2O molecules, will form sulfurous and sulfuric acids. Furthermore, the HCl and H_2SO_4 released during volcanic activity, as well as the photochemically produced nitrous and nitric acids (see Table 2), will react with the soil.

The pH of wetted Martian soil may have a direct bearing upon results obtained in the Viking labelled release (LR) life-detection experiment. In this experiment, the gasification of ^{14}C-labelled organic substrates following addition to Martian soil (Levin and Straat, 1977) may be due to breakdown of the formate component. Oyama et al. (1977b) have discovered a catalytic activity of artificial maghemite in the oxidation of formate by hydrogen peroxide, and proposed this as evidence for H_2O_2 and γ - Fe_2O_3 in Martian fines. Banin and Rishpon (1978) report that smectites containing Fe as the major exchangeable cation can catalyze the dehydrogenation of formate to produce $^{14}CO_2$, no participation of peroxide being required in this case. Acid conditions are necessary in both cases, and will in general cause the decomposition of formate at pH below 2.5, although the Fe-montmorillonite catalyzed reaction occurs at all pH's below 5.5 (A. Banin, personal communication, 1978). These explanations seem to require general soil acidity.

If carbonates exist within the soil, they will tend to neutralize acid components such as maghemite and the iron salts. Indeed, the *decrease* in CO_2 level following the second injection in the LR experiment may be evidence of uptake of CO_2 to form bicarbonate (the Cavendish reaction between liquid water, gaseous CO_2, and carbonates), as earlier suggested by this author. Water in equilibrium with $CaCO_3$ and 8 mb of Martian CO_2 will attain a pH of about 7.6 (Table 5). In contrast, Oyama et al. (1978b), who find an inhibitory effect of $CaCO_3$ on their γ -Fe_2O_3/H_2O_2 system (presumably due to neutralization of the surface acidity of the maghemite), propose the second-injection decrease as a high alkalinity of the solution, about $pH = 9.8$, and attribute to the Martian soil an initial high acidity upon wetting, followed by a slow transition to a strongly alkaline state as protected or slowly soluble components come into play. Weathered soils of $pH > 8.3$ almost invariably contain Na carbonate or exchangeable sodium cations (Miller et al., 1965).

Freezing-Point Depression. The freezing/melting point of water is depressed when solutes are present. Chlorides are much more effective than their analogous sulfates, carbonates,

Table 5. Abrasion pH of Candidate Mineral Components of the Martial Soil

pH	Phase Present	Atmosphere	Reference[c]
1	Ferric sulfate, $FeCl_2$	air[a]	St-48
2	Ferrous sulfate	air	St-48
3	Maghemite[b]	air	Bc-78
3	H montmorillonite	air	Lo-69
4.9	Pure water, no solutes	10 mb CO_2	Ma-64
5.2	Pure water, no solutes	3 mb CO_2	Ma-64
5.7	Pure water, no solutes	0.3 mb CO_2	Ma-64
5.3	Calcium nitrate	air	Bc-78
5 to 7	Siderite	air	Lo-69
5 to 7	Kaolinite	air	St-48
6	Hematite	air	Lo-69
6	Gypsum, Kieserite	air	Bc-78
6.7	Quartz, Na_2SO_4	air	Bc-78
6 to 7	Montmorillonite, $CaCl_2$	air	Bc-78, Lo-69
7.6	Fe_3O_4	air	Bc-78
7.5	Calcite	10 mb CO_2	Ma-64
7.8	Calcite	3 mb CO_2	Ma-64
8.5	Calcite	0.3 mb CO_2	Ma-64
8	Anorthite	air	Lo-69
9	Talc	air	Lo-69
9-10	Dolomite, Na_2CO_3	air	St-48
10-11	Magnesite, Brucite	air	St-48
10-11	Olivine, pyroxene	air	Lo-69
12	Mixed Ca-Na carbonates	air	Re-72

[a] "air" refers to the terrestrial atmosphere, under laboratory conditions

[b] Synthetic maghemite was S-300 oxide, Memorex Corp. Acidity may be due to an impurity (x-ray fluorescence studies indicate presence of sulfur-bearing compound)

[c] See Table 6 for key to references

or nitrates. Of the candidates (omitting acids), $CaCl_2$ and $FeCl_2$ are the strongest, with freezing points of respective saturated brines at about -55°C. Iron chlorides are improbable because of conversion to other forms as a result of acid attack on Ca, Na, and Mg-bearing minerals, and calcium chloride may be difficult to stabilize because of the tendency of omnipresent sulfate to tie up Ca^{2+} ions in poorly soluble forms. Even if $CaCl_2$ brine existed, evaporation rather than deliquescence would occur in the extremely dry Martian clime, as noted previously (Clark, 1978). Disequilibrium conditions, such as the injection of moisture from an external source or the trapping of buried ice from an earlier climatic regime, may produce residual brine pockets semi-isolated from the atmosphere in the endolithic zone, a cavity within a salt body, etc.

Terrestrial Analogues of the Martian Environment

The colder average temperature, paucity of water, and absence of a vigorous, environment-modifying biota on Mars thwart attempts to locate comparable regions for study on earth. However, as has been often pointed out (Cameron et al., 1970; Horowitz et al., 1972; Anderson et al., 1972), certain isolated and mostly ice-free valleys on the Antarctic subcontinent are the best approximation to contemporary Mars, particularly with respect to soil-forming processes, soil-moisture conditions, and lack of a macroflora or macrofauna. Important conditions in these dry valleys are mean temperatures always below freezing, no rain, a sparse snowfall rapidly removed by sublimation and eolian transport, abundant ahumic soils, and a landscape devoid of vegetation. Monthly mean temperatures at the ice-covered south pole range from $-30^{\circ}C$ (austral summer) to $-60^{\circ}C$; at the warmer McMurdo Sound, from $-5^{\circ}C$ to $-30^{\circ}C$ (Tedrow and Ugolini, 1966). In area, the dry valleys are $< 10^{-3}$ of the earth's surface; in bioburden, they are many orders of magnitude less important. And in spite of their similarity, there are profound discordances with Mars: (1) relative humidity even at the *coldest* times is some tens of per cent (Tedrow and Ugolini, 1966), equivalent to a water vapor partial pressure some 20 times its probable level on Mars; (2) mean temperatures are ~ 25 to $50^{\circ}C$ higher (using McMurdo Sound values); (3) soil clay content is generally minor; (4) because

Table 6. Key to References Listed in Tables 1, 2, and 5.

Code	Reference
Ba-72	Barker (1972)
Bc-78	Measurements by the author
Ca-72	Carleton and Traub (1972)
Fa-77	Farmer et al. (1977)
He-77	Hess et al. (1977)
Ho-72	Horn et al. (1972)
Hu-70	Hunten and McElroy (1970)
Ki-76	Kieffer (1976)
Ki-77	Kieffer (1977)
Le-66	Leighton and Murray (1966)
Li-76	Liu and Donahue (1976)
Lo-69	Loughnan (1969)
Ma-64	Marshall (1964)
Ma-77	Mayo et al. (1977)
Mc-77	McElroy et al. (1977)
Mo-78	Morris et al. (1978)
Ow-72	Owen and Sagan (1972)
Ow-77	Owen et al. (1977)
Re-72	Reesman (1972)
Ry-78	Ryan et al. (1978)
Sc-78	Scott and Carr (1978)
St-48	Stevens and Carron (1948)
Yu-77	Yung et al. (1977)

waterlogging and ice capping do not occur, the microenvironment is strikingly aerobic, (5) the solar ultraviolet does not penetrate deep into the atmosphere, as on Mars, and (6) the dry valleys are geologically young ($< 10^{-4}$ b.y.).

Discussion

Geologic and physical factors lead to the definition of several zones of differing environmental context. The highest temperatures reached on the surface of the planet are found in the euphotic, duricrust, and shallow endolithic zones, and are the only cases where temperatures ever penetrate the stability region of pure liquid water – except for locations near geothermal intrusions (if they exist) and the inevitably higher temperatures at considerable depths (few km). A few tens of meters below the surface, the regolith temperature remains constant, unaffected by daily and seasonal fluctuations of solar insolation. At the Viking-1 site, this temperature ($-58^{\circ}C$) is not sufficiently low to condense water vapor present at 1 μb partial pressure. The existence of permafrost ice would have to be a relic from earlier, different conditions. Ionic migration has been demonstrated to occur even in permanently frozen ground, apparently along quasiliquid interfacial films of water on mineral surfaces (Ugolini and Anderson, 1973). Gas transport is a faster process and may produce (via chemical transformation) isolated quantities of incompatible phases.

Obviously, the soil microenvironment is quite likely heterogeneous and diverse, and poised such that a large release of chemical energy occurs if liquid water is introduced. This does not bode well for a biochemistry such as that which exists on earth. In view of the oxidative pressure of the atmosphere, the solar UV, the probable desiccation of surface soil, the extremely low frost-point of atmospheric water vapor, and the infrequent but devastating fluxes of ionizing solar particles, it would seem an inescapable conclusion that any surviving organic compounds or biochemically-active assemblages must seek refuge. The logical niche is at depth in the subsurface zones (interfacial/transitional, tempofrost, permafrost) or in endolithic sites. The latter is occupied in the Antarctic environment by a blue-green algae and bacterial ecosystem which colonizes crevices within rocks, where sunlight penetrates the semi-transparent mineral grains, but plugging by eolian debris provides a porous barrier against the outside atmosphere (Friedmann and Ocampo, 1976). Neither the Viking biology experiments, nor organic experiment, analysed samples from below a few centimeters depth in the soil, although samples were obtained from beneath rocks of about 11 cm height at the lander-2 site (Moore et al., 1978). Attempts to break up rocks with the sampler arm were unsuccessful.

Even at depth, the environment must be considered hostile to the life forms we are accustomed to. Temperatures are extremely low, -60 to $-80^{\circ}C$, a good $40^{\circ}C$ lower than the empirically-demonstrated limit for terrestrial organisms. In this regime, the activity of water vapor is extremely low. Also, the ionic environment will be quite extreme if, as this author believes, the salts permeate much or all of the regolith fines. Halophilic organisms tolerate high NaCl concentrations; the likely presence of ionic forms such as Mg^{2+} or SO_4^{2-} may be more difficult to accommodate even by an active and adaptive biochemical entity. Given a sufficiently long time to bridge the transition from a favorable to unfavorable environment, remarkable evolutionary changes are possible. An example is the survival of a large fraction of floral and bacterial genera in the face of the adverse rise of a generally toxic chemical--oxygen--in the terrestrial atmosphere. Possible adaptations of Martian life forms to existing microenvironments has been the subject of a comprehensive review by Sagan and Lederberg (1976).

In the above, an attempt is made to extrapolate downward from the predominantly macroscale measurements made by Viking lander and orbiter experiments. Detailed by comparison with prior knowledge, it is nonetheless obvious that much remains speculative. An adequate understanding of microenvironments will require both additional in situ measurements and comprehensive analyses of Martian soil and rock samples here on Earth.

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