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CHEMICAL WEATHERING
ON MARS

MSATT

Mars Surface and Atmosphere Through Time

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WORKSHOP ON

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Edited by

Roger Burns and Amos Banin

Held at
Cocoa Beach, Florida

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PREFACE

This volume contains papers that have been accepted for the Workshop on Chemical Weathering on Mars, September 10–12, 1992, in Cocoa Beach, Florida. The Program Committee consisted of Roger Burns (Massachusetts Institute of Technology) and Amos Banin (Hebrew University and NRC/NASA Ames Research Center).

Logistics and administrative support were provided by the Program Services Department staff at the Lunar and Planetary Institute. This volume was prepared by the Publications Services Department staff at the Lunar and Planetary Institute.

CONTENTS

THE MINERALOGY AND FORMATION PROCESSES OF MARS SOIL.

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The mineralogical nature of Mars soil is far from being understood, nor are the formation time and weathering processes known. Quantitatively, the two major mineral-forming elements in Mars soil are silicon and iron, constituting 44% and 19% of the soil as SiO_4 and Fe_2O_3 respectively [1]. The silicate phases have been studied only briefly, mostly because of their limited spectral fingerprinting in the VIS and NIR. Much attention was given to the iron minerals in the soil, due to their pronounced absorption in the VIS and NIR, making them easily detectable by telescopic observations [2,3]. In the following, the available information on Mars soil mineralogy, mostly obtained by remote sensing, will be reviewed and it will be hypothesized that it leads to the suggestion that nanophase short-range-ordered ("amorphous") phases of the silicates and iron oxides abound in the soil. This then raises several questions: Why are the major minerals in Mars soil poorly crystalline? What are the weathering pathways? Why did the secondary silicate and iron oxides in Mars soil not "ripen" and develop into well-crystallized phases despite the long period of time since aqueous weathering took place? Is it the kinetics? Antarctic weathering analogues do not support this. Alternatively, is it possible that the minerals in the thin top layer of Mars soil, which is what we have sampled and analyzed up to now, represent a relatively fresh and recent product of slow weathering processes of volcanic materials proceeding on the surface of Mars over hundreds of millions of years?

Earlier studies [4] have identified 60% "silicate" in the soil, using the Mariner 9 IRTM data. Montmorillonite (a smectitic aluminosilicate clay mineral) was suggested as a major component of the dust and soil on Mars, on the basis of more detailed analysis of the IRTM (Mariner 9) data [5]. Nonweathered basalt was rejected as it did not fit the spectral features. Nontronite and montmorillonite were initially suggested as the major silicate components on the basis of the elemental analyses of the soil [6]. This was supported by successful simulations of the Viking Labeled Release (LR) experiment using iron-enriched montmorillonite [7] and the similarity of this clay's reflectance spectra in the visible range to those of Mars soil [8]. Another candidate was suggested, primarily on the basis of spectral telescopic data, to be palagonite, a weathering product of volcanic glass [9–12]. However, several palagonites tested did not simulate the reactivity of Mars soil as observed in the LR experiment [13]. A magnesium containing silicate (saponite?) was detected in the analyses of the NIR spectra at 2.2 μm [2]. However, the typical doublet of wellcrystalized standard montmorillonite at 10 μm was not observed in the IR spectra of Mars, leading to the conclusion that no crystalline smectite is present in the soil [3] or, alternatively, that it constitutes less than 15–20% of the soil [14]. If these observations are further corroborated, they suggest that most of the weathered silicates in Mars soil are of the low-crystallinity or amorphous varieties. No definitive identification of this phase was given until now. It is interesting to note in this context that a poorly crystalline silicate-alumininum mineraloid was detected in nonmetamorphosed inclusions in EETA 79001, one of the SNC meteorites [15]. Furthermore, the possibility that the silicate "rust" (iddingsite) found in the interior of Nakhla is of preterrestrial origin has not been completely ruled out, since this SNC meteorite is a fall with very limited terrestrial weathering. The "rust" is a silicate alteration product produced perhaps by the action of fluids enriched in halides on olivine. The very limited data are consistent with di- or trioctahedral phyllosilicates with excess Fe and Si [16].

Iron, the second most abundant element in Mars soil, appears to be primarily present in its oxidized form (ferric), strongly suggesting chemical weathering of the basaltic parent material. The typical reflectance spectrum of Mars in the visible/short-wave NIR range [12,17,18] bears the strong fingerprinting of oxidized iron and has been reproduced more or less faithfully in laboratory measurements of many different iron-containing phases They include "amorphous" iron oxides [19], palagonite [9,10], nanophase hematite deposited in silica matrix [11], and iron-enriched smectites [8,13]. One conclusion from the abundance of spectral analogues is that unambiguous identification of the iron mineral(s) in Mars soil, on the basis of reflectance only, is not possible at present. A more important conclusion is that the accumulating evidence shows that iron in the weathered component of Mars soil is mostly present in poorly crystallized clusters of oxyhydroxy ferric iron, or as crystalline minerals but in extremely small particle size ranges ("nanophases" or "nanocrystals"). Recent telescopic observations have detected typical hematite features at 860 nm, and possibly other crystallized iron oxides [12,20]. However, these features are very weak and estimates of the content of hematite and/or other crystalline phases are in the range of 1–3% or less. The content of the magnetic mineral in the soil is also estimated to be in the range of 1–3%. It may be maghemite, magnetite, or nanophase hematite that is typically superparamagnetic. However, the bulk of the iron oxide-oxyhydroxide in the soil is amorphous or short-range ordered and is characterized by extremely small particle sizes.

As a whole, the evidence now leads to the suggestion that much of the silicon- and iron-containing phases in Mars soil are short-range-ordered or "amorphous," i.e., do not have well-developed crystallinity. This hypothesis is based on accumulating excellent telescopic observations during the late 1980s (1988–1990 Mars-Earth oppositions) and detailed laboratory studies on soil analogues. It opens a new and intriguing question—what is the peculiar mode of weathering that has produced these amorphous silicates and iron oxides? More specifically, what is the cause of the limited growth of crystals of secondary silicate and iron oxide minerals in the weathered soil on Mars. Given that currently the most accepted model for the soil formation is during earlier epochs (~3.5 b.y. ago) when Mars was "warm and wet" [e.g., 21,22], it is puzzling that only a minor portion of the silicates and iron oxides have crystallized and developed a more thermodynamically stable mineralogical composition and particle size distribution.

Similar silicate and iron oxide entities are found on Earth only as transitory phases that "ripen" rapidly (geologically speaking) to more stable minerals. Palagonites represent such a transitory assemblage of minerals produced as the initial weathering product of volcanic glass. The maximal age of palagonite deposits on Earth is in the range of $1–10 \times 10^6$ yr.

Is it possible then that the peculiar nature of the martian dust and soil is due to a relatively "young" weathering product that has formed, and continues to form at an extremely slow rate, over the last several hundred million to a billion years? It is then plausible that this "recent" (in Mars timescale of changes) and nonevolved weathering product is coating or burying ancient, more-evolved weathered mineral assemblages that formed in the earlier "warm and wet" epochs of Mars. This suggestion apparently goes against the "common wisdom" on weathering. The low-temperature and arid conditions on Mars seem to preclude hydrolytic weathering as a significant process on its surface [22]. However, "surface weathering," involv-

ing gas phase-solid phase reactions taking place at the atmosphere-rock microscopic interface, may proceed, albeit at a very slow rate, even there. Such surface weathering may involve just the unfrozen water layers (1–3 molecular layers [24]), sorbed on the surface of any rock or solid phase by virtue of the surface potential exerted by the solid. These weathering reactions are, generally speaking, driven by the same chemical driving forces that act on rocks in the more humid environments on Earth with which we are familiar. Overall, these processes can be viewed as reequilibration of minerals formed under magmatic conditions of high temperature and low redox, with their new conditions of lower temperature, higher redox potential, higher water activity, and, frequently under soil conditions, more varied and less fractionated ionic environment. So it is expected that the end products of these weathering processes may be similar to those found in the more water-rich environments of Earth. A major difference in rate is expected, however. The lack of excess liquid water on Mars may cause chemical saturation of the aqueous phase thus slowing down the overall rate of dissolution. Furthermore, the low temperature prevailing in these extremely cold environments may slow down the intrinsic rate of the reactions, causing the processes to proceed at a very slow pace. Still, in Mars-like environments on Earth (e.g., Dry Valleys, Antarctica), where the weathering processes involving excess water are limited or nonexistent, the products of the surface weathering mechanisms become quantitatively important, given enough time to proceed [25]. The data available for Antarctic soils cover a period of ~3 m.y. only [25]. Mars surface may be of much older age, perhaps up to 1 b.y. old. The global surface stability (lack of plate tectonics) facilitates the accumulation of weathering products over long periods. Even at an extremely slow linear rate of rock-surface weathering of 0.3 nm/yr (approximately one molecular layer per year) an average layer of 30 cm could be weathered on Mars over the last 10^9 years. Wind abrasion rates on Mars are estimated at 1 μm/yr [27], i.e., 3–4 orders of magnitude faster than the assumed hydration front penetration rate, thus the assumption of a linear-rate of advancement of the weathering front (rather than a square-root-of-time dependence), is warranted. This leads to higher overall rate of weathering than arrived at under diffusion-limited conditions [22]. Particularly susceptible to such weathering are the more recently erupted volcanic materials. Estimated at 26.4×10^6 km^3 during Amazonian [27], these materials may have supplied the highly unstable minerals that weathered and produced the thin recent coating remotely sensed on much of the planet's surface.

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MARTIAN WEATHERING/ALTERATION SCENARIOS FROM SPECTRAL STUDIES OF FERRIC AND FERROUS MINERALS.

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In this abstract we review the major aspects of our current knowledge of martian ferric and ferrous mineralogy based on the available groundbased telescopic and spacecraft data. What we know and what we don't know are used to constrain various weathering/alteration models and to identify key future measurements and techniques that can distinguish between these models.

What We Know: *Ferric mineralogy.* There is obvious and abundant evidence that oxidized Fe^{3+}-bearing minerals exist on Mars. Spectroscopic observations and Viking data over the past 20 years have revealed that the ferric mineralogy occurs in two distinct styles: (1) poorly crystalline or even amorphous Fe^{3+}-bearing materials that spectrally resemble certain terrestrial palagonites [e.g., 1–3]; and (2) well-crystalline ferric oxides like hematite (α-Fe_2O_3) or maghemite (γ-Fe_2O_3) [e.g., 4–6]. The available data indicate that the palagonitelike phases are spectrally dominant, and that the well-crystalline ferric oxides cannot constitute more than about 4–6 wt% abundance (if intimately mixed) [7]. All the noncondensate surface regions have a ferric spectral signature; however, the classical bright regions are distinctly "redder" than the classical dark regions and recent data have shown that the bright regions have generally enhanced crystalline ferric oxide absorption features [7]. Higher spatial resolution telescopic imaging and Viking Orbiter color data [e.g., 8] have revealed several small dark regions with increased crystalline ferric absorptions, though, and thus the albedo-crystallinity correlation is not globally uniform. Viking Lander color imaging reveals that the apparently unaltered rocks are covered to varying degrees by ferric-rich dust at the two locations studied [e.g., 9].

Ferrous mineralogy. There is much more debate and uncertainty about the occurrence and distribution of martian Fe^{2+}-bearing minerals. Certain telescopic [1,10] and spacecraft [11,12] datasets have shown evidence for weak 1-μm and 2-μm Fe^{2+} absorption bands that preferentially occur in the dark regions, but other observations have either not clearly revealed such features [5] or have not seen a correlation between albedo and Fe^{2+} band depth [13]. In data where the band has been observed, it has been interpreted as evidence of low-Ca, high-Fe clinopyroxene, indicating (in agreement with Viking Lander compositional results) that the martian "basement" rocks are mafic in composition.

Summary and other minerals. The only mineral definitively identified on the martian surface is hematite [4,5,7]. A possibly different poorly crystalline ferric-bearing phase(s) is present, but it is not at all well characterized in the currently available data. The highly magnetic component measured by Viking may be maghemite [6], magnetite (Fe_3O_4) [14], or even the poorly crystalline ferric

phase itself. Pyroxene in some form probably exists [1,10], but conclusive mineralogic identification is still forthcoming [e.g., 12]. Data at longer near-IR wavelengths and simulations of Viking experiments have been used to claim the existence of iron-rich clay minerals [e.g., 15] and carbonate-bearing minerals like scapolite [16]. Confirmation of these mineralogic identifications by other researchers and other techniques has not yet been provided, though.

What We Don't Know: The presence of hematite masks the spectral identification of many other crystalline ferric oxide phases, like goethite (α-FeOOH), at telescopic spatial scales [7,17]. This provides a severe constraint on our current ability to identify almost all the ferric oxyhydroxides and iron-rich smectites in the currently available spectral data. Terrestrial analog studies have shown that several different extremely fine-grained ("nanophase") ferric oxides are spectrally consistent with the Mars data. These include nanophase hematite [3,4] and lepidocrocite [18]. In addition, the poorly crystalline mineral ferrihydrite (a hematite precursor in many terrestrial weathering environments) is also spectrally consistent [7]. Thus, there is no current consensus on the mineralogy of the poorly crystalline ferric phase.

The identification of the ferrous mineralogy is clouded somewhat by the presence of abundant and spectrally dominating ferric minerals. For example, there are several ferric oxyhydroxide minerals with weak absorption features in the 0.90–1.05-μm region [e.g., goethite, akaganeite (β-FeOOH)]. Hematite masks the shorter wavelength absorption features of such minerals, and thus it is not readily clear to what extent the surface ferric mineralogy may be enhancing the features from (or be mistaken for features due to) the surface ferrous minerals. In addition, the distinction in the data between well-crystalline ferrous minerals like pyroxenes and ferrous glasses and tephra (which also can exhibit a 1-μm absorption feature) has not been examined in detail.

Possible Weathering Scenarios Consistent with Available Data: Here, we define "weathering" as the steady-state oxidation and/or hydration of exposed surface materials, specifically leading to the conversion $Fe^{2+} \rightarrow Fe^{3+}$. This is to be distinguished from "alteration," which we define as a more forced process resulting from, for example, hydrothermal circulation, impact into ground ice, etc. The available data are consistent with two primary models for the weathering of martian surface materials.

Model 1. The exposed bedrock and surface rocks never have been weathered and are simply covered by and/or mechanically mixed with variable amounts of mobile Fe^{3+}-bearing materials. This implies that these unweathered rocks are not the source of the global dust, and that the dust was formed in the past under different conditions. The currently exposed unweathered rocks could have escaped weathering by not being exposed during previous weathering events, or these rocks may postdate weathering conditions (e.g., later eruptions of basalt). The original source materials for the dust may currently be either buried or completely eroded. This model implies that there may be areas of oxidized (older) and unoxidized (postdust formation) bedrock materials on Mars.

Model 2. Exposed bedrock and surface rocks have been weathered in the past or are actively weathering, resulting in the creation of Fe^{3+}-rich weathering rinds or cracks, and spallation or mechanical breakdown then frees the weathered materials. This implies that the dust is a direct product of the weathering of bedrock and/or tephra by surface reactions.

There are important climatic and mineralogic implications for each of these scenarios. If the exposed rocks are not actively weathering and producing the ubiquitous ferric-rich dust and soil (model 1), then the question must be asked, where did the weathering products come from? Two possibilities are immediately obvious: (1a) Current reaction rates are exceedingly slow [21], leaving the exposed rocks in metastable thermodynamic disequilibrium, but reaction rates at some point(s) in the past were substantially higher, allowing oxidative weathering of bedrock/tephra to occur and to generate globally significant amounts of ferric material (i.e., model 2 was dominant in the past); or (1b) A single event or series of events (e.g., impacts, intrusions, etc.) has produced all the observed weathering products over the course of martian geologic history [see 3]. Model 1a requires substantial climatic variations (increased T, P, RH) at some point(s) in the past. Model 1b could operate either in the current climatic regime or under warmer, wetter conditions. In either case, model 1 argues that the present inventory of surface weathering products is a fossil remnant from the past and thus the distribution of Fe^{3+}-bearing phases may have little or no genetic relationship to the locally underlying bedrock.

If well-defined pyroxene absorption features occur in telescopic and/or spacecraft spectral data on 10–250-km spatial scales, then there must be exposures, at some subpixel scale, of relatively pure, unaltered pyroxene. Viking Lander images at Chryse and Utopia did not show any evidence that the ferric-rich soils and dust were genetically related to the abundant local rocks [9]. These arguments favor model 1. If, however, only weak, broad Fe^{2+} spectral features are observed, then it may be possible that the pyroxene (or other basaltic glass or minerals) are coated by a thin ferric weathering layer [19,20]. Telescopic and Viking observations of apparently ferric-rich dark regions (e.g., parts of Erythraeum [7,8]) provide some data that are more consistent with such an active weathering scheme (model 2).

What Needs To Be Done To Narrow The Possibilities: The key to understanding both the current and past martian weathering/alteration environment lies in being able to accurately measure the spectra of the rock "end member." If the spectral signature of the ferric-rich surface soil and dust (and of the intervening atmospheric dust) can be properly removed, then it will be possible to determine whether the underlying basalt is "lunar" (not at all oxidized) or "terrestrial" (actively oxidizing). This is an extremely difficult task in practice, because it requires simultaneous knowledge of the surface spectral reflectance (or albedo) and the airborne dust opacity, as well as various assumptions about (or direct measurements of) the dust composition and scattering properties. This is certainly hard to do at groundbased telescopic spatial resolution, but is much more possible and practical using a Mars-orbiting platform.

Our understanding of the currently available spectral data can be substantially enhanced by additional experimental and theoretical work on mixtures of basalts and tephras, poorly crystalline ferric materials, and well-crystalline ferric oxides and oxyhydroxides. For example, as mentioned above, the identification of band centers and absorption band depths of Fe^{2+}-bearing minerals in the 1-μm region may be influenced by the presence of certain crystalline ferric oxides/oxyhydroxides. Both intimate and areal mixture studies of the detectability of various ferrous minerals, including glasses, within a ferric background (and vice versa) are needed. We also need more experimental and theoretical data on the variability of spectral parameters such as band depth, width, and center position given different systematic mixtures of potential Mars materials under varying degrees of atmospheric dust and condensate opacity. Finally, it may be possible to compare the results of other age-dating techniques (craters, superposition) with UV-visible spectral slope or "redness" derived from Mars Observer and/or groundbased telescopic measurements to determine whether or not the less-oxidized rocks are younger than the more oxidized rocks, dust, and soils.

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EFFECTS OF THE CHEMICAL ENVIRONMENT ON THE SPECTROSCOPIC PROPERTIES OF CLAYS: APPLICATIONS FOR MARS.

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Introduction: Laboratory studies of Mars soil analogs pose unique problems, since soils interact readily with their environment and exhibit variable characteristics depending on the environment. We have performed a series of experiments focusing on the spectral properties of clays and how they vary as a function of composition and environment, including examination of fundamental as well as overtone absorptions, that occur in the mid- and near-IR respectively. Smectite clays have been selected in our laboratory experiments as a primary surface analog for Mars because of their compatibility with results of the Viking biology experiments [1], their stability under current martian conditions, and their compatibility with reflectance spectra of Mars [2]. We prepared a number of monoionic montmorillonites in order to examine the influence of

cations on the water molecules in the clay interlayer region. Mössbauer spectra of several montmorillonites with variable amounts of interlayer iron confirm the presence of ferrihydrite [3].

General Character of Clay Absorption Bands: Montmorillonite exhibits several strong features due to interlayer water, structural OH, and the silicate layers as shown by the composite RELAB spectrum in Fig. 1. Fundamental molecular water vibrations occur at ~3 μm (v_w) and 6 μm (δ_w), which have combination bands at 1.45 μm and 1.95 μm. Interlayer cation-bound molecular water has a stretching vibration (v_w') at a lower wavelength than that of the extensively H-bonded interlayer water (v_w), resulting in combination bands at ~1.41 μm and ~1.91 μm. Structural OH has fundamental vibrations at 2.75 μm (v_{OH}) and ~11 μm (δ_{M-OH}, M = Al, Fe, Mg), a combination at 2.2 μm, and an overtone at 1.41 μm. Both the strength and energy of these absorptions are sensitive to the chemical environment of the OH and H_2O molecules. For instance, the polarizability of the octahedral and interlayer cations influences the OH and H_2O stretching and bending vibrational energies. One phase of our initial experiments has focused on the influence of interlayer cations on the character of near-infrared hydration bands [4]. Spectral characterization of clays and hydrated minerals is based on the H_2O and OH vibrational energies, which are dependent on the chemical environment of the bonds. The nature of interlayer water is affected by the interlayer cations and the degree of H-bonding.

Interlayer Cation-Water Interactions: *Exchange experiments.* In our laboratory experiments Fe^{3+}, Mg^{2+}, Ca^{2+}, Na^+, and H^+ are exchanged for the naturally occurring mixture of Na and Ca interlayer cations in SWy-1 montmorillonite (obtained from the Clay Mineral Society, Source Clays Repository) using a procedure similar to that of Banin [2]. The amount of exchanged cation added was calibrated for 100% cation exchange capacity (CEC), which is the amount of interlayer cations required to compensate the charge deficit from octahedral layer substitutions. Fe^{3+}-rich montmorillonites were prepared in a similar manner with up to 600% CEC.

Water analyses. The nature of interlayer water molecules in smectite clays is known to be quite complex [5]. Some H_2O is readily removable by mild heating and drying, while more resilient H_2O remains in the clay to above 300°C. Spectroscopic studies [4,6] suggest that water molecules can be present in many forms in the

Fig. 1. Reflectance spectrum of SWy montmorillonite: (a) 0.3–3.6 μm, (b) 3.3–25 μm.

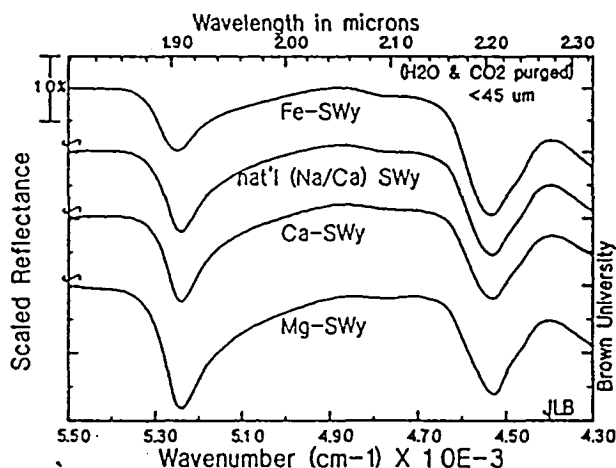Fig. 2. Reflectance spectra of homoionic montmorillonites (1.8– 2.3 μm (note relative strength of 1.9- and 2.2-μm absorption).

interlayer regions: (1) strongly cation-bound, inner sphere H_2O, (2) strongly surface-bound H_2O, and (3) strongly H-bonded, liquidlike water. We have obtained chemical information about the form of water present in several homoionic clays through infrared spectroscopy and digital thermal analysis. We attribute the low temperature (<200°C) water loss to the liquidlike interlayer water, the water loss in the 350° to 550°C range to inner sphere cation-bound water, and the water loss at 600°C to the structural OH. We have found for both dry and moist relative humidity environments that the amount of removable water in the montmorillonite samples varied depending on the interlayer cation ($Na < Fe^{3+} < Ca < Mg$). This trend corresponds to adsorption isotherms for Na-, Ca-, and Mg-smectites [7].

Strength of bands. We found that the amounts of removable water in our suite of cation-exchanged clays correlates with the 1.9-μm and 6-μm band depths. The strengths of the 1.9-μm and 6-μm hydration features thus depend on the kind of interlayer cation, as well as on the relative humidity of the environment, whereas the strength of the 2.2-μm feature is primarily due to structural OH and octahedral cations. Reflectance spectra of natural (Na/Ca), Fe^{3+}-, Ca-, and Mg-montmorillonite showing the relative strengths of the 1.9-μm and 2.2-μm hydration features are presented in Fig. 2.

The interpretation of Mars spectra serves as an example of the need for an improved understanding of the relationships between chemical environment, fundamental vibrations, and overtones of hydration features in clays. Some confusion over the presence of molecular water and structural OH in Mars surface material exists because a strong band has been observed at 2.7–3.0 μm (attributed to fundamental molecular water) and weak features have been suggested at 2.2–2.35 μm, but the characteristic water combinations and overtones at 1.4 μm and 1.9 μm are difficult to confirm. These features at 1.4 μm and 1.9 μm are composed of multiple overlapping peaks that vary as a function of octahedral cation, interlayer cation, and amount of interlayer water molecules [4]. An important application to Mars from our recent work is that a ferric montmorillonite in a dry environment would have a 1.9-μm absorption that is weaker than the 2.2-μm absorption, and thus the 1.9-μm absorption would be difficult to observe in Mars spectra.

Fe^{3+}-rich Clays and Ferrihydrite Formation: Smectite clays readily incorporate aqueous ions and chemical complexes into their interlaminar regions. Clays are therefore highly sensitive to their chemical environment and clays on Mars should reflect the martian

environment in the nature of their interlayer regions. In addition, smectite clays are able to serve as a template for chemical reactions in the interlayer regions [8], and interlayer expansion would physically allow production of nanophase products, but would restrict long-range order.

Several Fe^{3+}-rich montmorillonite samples were prepared containing 2–10 wt% (as Fe_2O_3) interlayer iron, in addition to the 4 wt% (as Fe_2O_3) structural iron already present in our Wyoming montmorillonite samples. During the exchange process Fe^{3+} ions are added to the clay solution at pH 2, then the pH is increased to 7, causing the $Fe(H_2O)_6^{3+}$ complexes to polymerize to $Fe_2(H_2O)_8(OH)_2^{4+}$ and $Fe_2(H_2O)_8(OH)(O)^{3+}$, losing H_2Os and Hs as bridges are formed [9]. Concentrated Fe^{3+} complexes react further, forming double chains of $[Fe(O,OH,H_2O)_n]$ units and eventually ferrihydrite [10,11]. Ferrihydrite is thus predicted as an important step in weathering processes of ferric materials.

We have evaluated several of our montmorillonite samples using Mössbauer spectroscopy in a cryogenic facility at MIT in collaboration with R. Burns. Mössbauer studies of our Fe^{3+}-rich montmorillonites have produced magnetic hyperfine splitting patterns that confirm the presence of ferrihydrite in these Fe^{3+}-rich clays [3]. Room-temperature spectra of all our montmorillonites showed a quadrupole doublet, characteristic of the structural iron in montmorillonite. At 4.2 K a sextet indicating magnetic ordering was observed for the Fe^{3+}-rich montmorillonites, but not the Na and Ca montmorillonites. This sextet was significantly stronger in the samples containing higher quantities of Fe_2O_3, and is characteristic of crystalline ferric oxides. The magnetic splitting in the Mössbauer spectra of our Fe^{3+}-rich clays is 48.5 T, which is within the range of 48.2–50.5 T for ferrihydrite [12]. The magnetic splitting of other ferric oxides is measurably different, for example, hematite: 54.6 T; goethite: 50.6 T; and lepidocrocite: 45.8 T [10].

Furthermore, visible reflectance spectra of this Fe^{3+}-rich, ferrihydrite-bearing montmorillonite are characterized by a weak, broad absorption at ~0.9 μm, a reflectance maxima at ~0.75 μm, an inflection point at ~0.6 μm, and a steep falloff toward ultraviolet wavelengths (Fig. 3). These features are not observed in natural (Na/Ca)-, H-, Na-, Ca-, or Mg-exchanged SWy montmorillonites. As shown in Fig. 3, reflectance spectra of the Fe^{3+}-rich montmorillonites correspond remarkably well to telescopic data of several bright areas of Mars [3]. The Syria Planum spectrum was measured by Bell [13] and the Lunae Planum spectrum was measured by McCord [14].

Continuing Experiments: Although infrared reflectance spectroscopy is routinely used to study planetary surfaces and atmo-
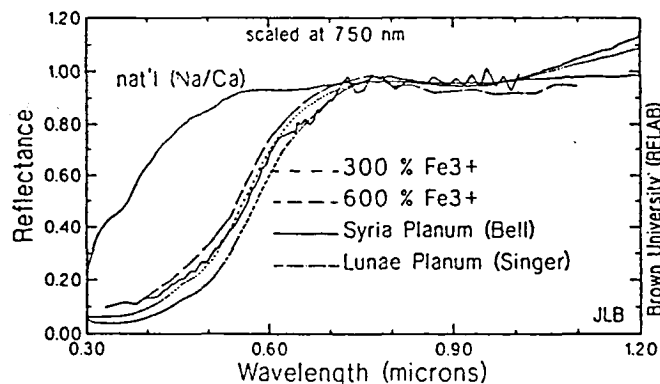

Fig. 3. Reflectance spectra of natural (Na/Cl) and Fe^{3+}-rich montmorillonites and telescopic spectra of Mars (0.3–1.2 μm).

spheres, very little infrared research has been performed on the interactions between these surfaces and their atmospheres. We plan to use an environmental chamber to explore surface-atmosphere interactions that will provide information relevant to Mars. In order to better understand the nature of interlayer water in smectite clays and the cation-water interactions, we are planning spectral experiments for our homoionic (Na, Ca, Mg, Fe^{3+}) montmorillonites that will (1) measure shifts in vibrational energy at 1.9 μm, 3 μm, and 6 μm at 25°C while varying the relative humidity of the sample chamber and (2) measure variations in the spectral character of these features as the temperature is elevated from 25°C to 300°C to study the clay hydration features in an ultradry environment. We are also designing experiments to measure spectra of the Fe^{3+}-rich montmorillonites at low temperatures (100–250 K), which will allow us to study the hydration bands in clay-ice systems.

In order to evaluate the behavior of clay systems under both current and more clement possible past environments on Mars, we are currently planning aqueous and anhydrous reactions with sulfates, carbonates, and chlorides in Fe^{3+}-rich montmorillonites. Spectra will be measured for these samples with a focus on the development of absorptions relating to Fe^{3+}-sulfate, Fe^{3+}-carbonate, and Fe^{3+}-chloride bonds. We plan to measure spectra of these new and complex Fe^{3+}-rich montmorillonites at cool temperatures (100–250 K) to study clay-anion-ices. Perhaps these experiments will lead to novel ideas for duricrust models. The nature of selected iron oxides and iron material formed in the interlayer region of these Fe^{3+}-rich samples will be characterized using Mössbauer spectroscopy at room temperature and 4.2 K.

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DEHYDROXYLATED CLAY SILICATES ON MARS: RIDDLES ABOUT THE MARTIAN REGOLITH SOLVED WITH FERRIAN SAPONITES.

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Introduction: Clay silicates, resulting from the chemical weathering of volcanic glasses and basaltic rocks of Mars, are generally believed to be major constituents of the martian regolith [1] and atmospheric dust [2]. However, the occurrence of smectite clays

such as montmorillonite and nontronite on Mars presents several dilemmas. First, hydroxylated minerals are considered to be thermodynamically unstable on the arid outermost surface on Mars [3]. Second, diagnostic infrared spectral features of clay silicates, most notably peaks in the 2.2–2.4-μm region, are much weaker in remote-sensed reflectance spectra than expected for the inferred abundance of clay silicates on Mars [4,5]. Third, crystal field spectra of Fe^{3+} in nontronite are not good matches of visible-region reflectance spectral profiles of Mars [6]. On the other hand, Fe^{3+}-exchanged montmorillonites yield comparable spectra to Mars in the UV-visible region, as well as simulating reactions in the Viking biology experiments [7–9]. Clay silicates have also been identified as accessory minerals in SNC meteorites [10,11] believed to have originated from Mars.

Because little attention has been given to the role, if any, of Mg-bearing clay silicates on the martian surface, the crystal chemistry, stability, and reactivity of Mg-Fe smectites are examined here. Partially dehydroxylated ferrian saponites are suggested to be major constituents of the surface of Mars, regulating several properties of the regolith.

Crystal Chemistry of Iron Saponites: Trioctahedral ferromagnesian smectites may be formulated as $(Na, 0.5Ca)_x(Mg, Fe)_3$ $(Si_{4-x}Al_xO_{10})(OH)_2$, with $x \leq 0.6$, indicating solid-solution between Mg (saponite) and Fe endmember compositions, substitution of Al for Si in the $[SiO_4]$ tetrahedra, and some exchangeable cations such as Na^+ and Ca^{2+} [12]. The OH^- ions belong to coordination polyhedra about Mg and Fe cations located in octahedral sites in the crystal structure, giving rise to cis- and transconfigurations. Alternatively, each OH^- ion is coordinated to three cations, two occurring in cisoctahedra and one in transoctahedra, giving trioctahedral smectites. Note that in corresponding Al^{3+} (montmorillonite) and Fe^{3+} (nontronite) smectites, cisoctahedra are occupied by Al^{3+} and Fe^{3+} while transoctahedra are mostly vacant, leading to dioctahedral structures. In Mg-Fe^{2+} saponites, cation clusters such as MgMgMg, $MgMgFe^{2+}$, $MgFe^{2+}Fe^{2+}$, and $Fe^{2+}Fe^{2+}Fe^{2+}$ exist in the octahedral sites coordinated to each OH^- ion. However, some OH^- ions may be associated with vacancies (V), usually in transoctahedra, resulting in cation clusters such as $MgFe^{2+}(V)$, $Fe^{2+}Fe^{2+}(V)$, etc.

Experimental Studies of Mg-Fe Smectites: Ferromagnesian saponites are readily synthesized at low temperatures in reducing environments by stoichiometric mixing of appropriate solutions of Na_2SiO_3 and Mg(II) and Fe(II) salts in HCl or H_2SO_4 solutions [13,14]. On Earth, Fe^{2+} saponites are unstable under atmospheric conditions and are oxidized rapidly to Fe^{3+}-bearing assemblages, often obscuring evidence for initial Fe^{2+} saponite formation. The oxidation reaction can be simply written as

$$3 Fe^{2+}_{clay} + 1/2 O_2 (+ 1/2H_2O) = \\ 2 Fe^{3+}_{clay} + 1/2 Fe_2O_3 \text{ (or FeOOH)} \quad (1)$$
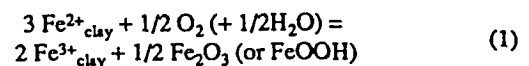
resulting in the formation of a dioctahedral smectite intimately associated with the ferric oxide phase [12,15]. However, intracrystalline redox reactions involving the oxidation of Fe^{2+} to Fe^{3+} ions within the clay silicate structure is also possible, by analogy with processes leading to the formation of oxyamphiboles and oxybiotites [16–18]. Two different oxidation mechanisms exist [19]. First, dehydroxylation by oxygenation may occur when the clay silicate is exposed to atmospheric oxygen or is heated in air (reaction (2))

$$Fe^{2+} + OH^- + 1/2 O_2 \rightarrow Fe^{3+} + O^{2-} + 1/2 H_2O \quad (2)$$
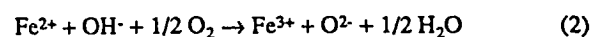
Second, dehydroxylation by dehydrogenation may occur when the clay silicate exists in a vacuum or is heated in an inert gas or vacuum (reaction (3))

$$Fe^{2+} + OH^- \rightarrow Fe^{3+} + O^{2-} + 1/2 \, H_2 \qquad (3)$$
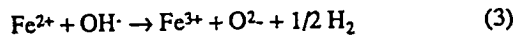
In both cases, the crystal structure remains intact (i.e., the mineral has not decomposed), but the OH groups have been replaced by O^{2-} ions.

Spectroscopic studies of phyllosilicates including saponites, based on changes of peaks in the 3600–3700 cm^{-1} region [e.g., 18,20–22], indicate that hydroxyl groups close to three Mg^{2+} in the two cis- and one transoctahedral sites are relatively stable. However, cation clusters such as $MgMgFe^{2+}$ and $MgFe^{2+}Fe^{2+}$ in these octahedral sites are vulnerable to dehydrogenation and oxygenation resulting from oxidation of structural Fe^{2+} ions to Fe^{3+} (reactions (2) and (3)). Hydroxyl groups associated with vacancies, corresponding to cation clusters such as $MgFe^{2+}(V)$ and $Fe^{2+}Fe^{2+}(V)$, are particularly vulnerable to conversion to O^{2-} ions. Extensive intracrystalline oxidation of Fe^{2+} to Fe^{3+} produces additional spectral features attributable to hydroxyl groups adjacent to cation clusters such as $MgFe^{2+}Fe^{3+}$, $MgFe^{3+}(V)$, etc. These clusters contribute weak peaks to poorly defined spectra in the fundamental ($\approx$2.75 μm) and first overtone ($\approx$1.41 μm) hydroxyl stretching regions. Similar effects may produce additional peaks in the 2.2–2.4-μm region in infrared spectra of partially dehydroxylated Fe^{2+}-Fe^{3+} silicates, but these effects have not yet been studied in detail [23,24]. However, they could be contributing shoulders to bands measured around 2.35 μm in remote-sensed reflectance spectra of the martian regolith [5,25,26].

Terrestrial Occurrences of Ferromagnesian Smectites: On Earth, Fe^{2+} saponites have been identified in several environments, including weathered ultramafic rocks [27], gabbros [28], vitric tuffs [29], oceanic and continental basalts [30–32], and submarine depressions associated with brines and metalliferous sediments [15]. These ferroan saponites rapidly oxidize to mixed-smectite assemblages containing ferrian saponites, Fe^{3+}-montmorillonite, and nontronite, which are often intimately intergrown with ferrihydrite, nanophase Fe_2O_3, or FeOOH. Some ferromagnesian smectites occurring in alteration products of oceanic and continental basalts appear to have compositions intermediate between di- and trioctahedral smectites. For example, a smectite from oceanic basalts [31], originally formulated as

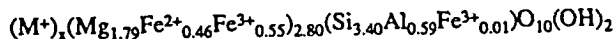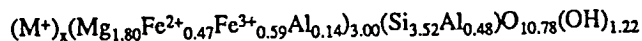$$(M^+)_x(Mg_{1.79}Fe^{2+}_{0.46}Fe^{3+}_{0.55})_{2.80}(Si_{3.40}Al_{0.59}Fe^{3+}_{0.01})O_{10}(OH)_2$$
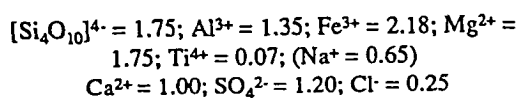
has a total octahedral occupancy of only 2.80. Mössbauer spectral data suggesting that this smectite is partially dehydroxylated, were confirmed by chemical analysis that indicated a deficiency of OH$^-$ ions. Recalculation of the formula yielded [12]

$$(M^+)_x(Mg_{1.80}Fe^{2+}_{0.47}Fe^{3+}_{0.59}Al_{0.14})_{3.00}(Si_{3.52}Al_{0.48})O_{10.78}(OH)_{1.22}$$

in which the dehydroxylated smectite is perfectly trioctahedral with a total octahedral occupancy of 3.00. Similar dehydroxylated ferrian saponites might have formed on Mars.

Dehydroxylated Mg–Fe Smectites on Mars: The Viking XRF analyses [1], when expressed as modal proportions of ionic species [33], yield the following formula units (g.ion/kg soil)

$$[Si_4O_{10}]^{4-} = 1.75; \; Al^{3+} = 1.35; \; Fe^{3+} = 2.18; \; Mg^{2+} = 1.75; \; Ti^{4+} = 0.07; \; (Na^+ = 0.65)$$
$$Ca^{2+} = 1.00; \; SO_4^{2-} = 1.20; \; Cl^- = 0.25$$

Although the Mg and Ca are traditionally associated with SO_4^{2-} in evaporite minerals on Mars [34], the majority of the Mg may be partitioned as trioctahedral (Mg-Fe saponite) coexisting with dioctahedral (Al-Fe montmorillonite), with each dehydroxylated smectite accommodating ferric iron.

Terrestrial environments producing ferromagnesian smectites, such as low-temperature alteration of basaltic rocks and hydrothermal reactions involving brine-saturated metalliferous sediments, also probably exist on Mars. Upon exposure to the martian atmosphere, the ferroan saponites would undergo aerial oxidation by reactions (1) and (2), with dehydroxylated smectites being formed by reaction (2). Restoration of OH$^-$ by propotonation of the O^{2-} is known to cause some of the Fe^{3+} ions to be expelled from the octahedral sites in the clay silicates [12], thereby creating vacancies in the phyllosilicate structure and the precipitation of ferrihydrite between the layers. Such a mechanism accounts for the suggested occurrence of ferrihydrite associated with clay silicates on Mars [35]. On the other hand, reversal of reaction (2) would liberate oxygen from the regolith, accounting for results obtained in the Viking gas exchange experiments [36].

Spectral features originating from MgMgMg, $MgMgFe^{3+}$, $MgFe^{3+}(V)$, etc., cation clusters, as well as AlAl(V) and $AlFe^{3+}(V)$, are likely to contribute fine structure to peaks in the fundamental and first-overtone hydroxyl stretching frequencies at 2.75 μm and 1.41 μm, as well as in the 2.2–2.4-μm region. Thus, features attributed to HSO^{4-} or HCO^{3-} in scapolite in remote-sensed reflectance spectra of Mars [26] may originate, instead, from partially dehydroxylated ferrian saponites in the regolith.

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THE FATE OF IRON ON MARS: MECHANISM OF OXIDA-
TION OF BASALTIC MINERALS TO FERRIC-BEARING
ASSEMBLAGES.   Roger G. Burns, Department of Earth,
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Introduction: Perhaps the most conspicuous indication that
chemical weathering has occurred on the surface of Mars is the
overall color of the Red Planet and the spectroscopic features that
identify ferric-bearing assemblages in the martian regolith [1,2].
Apparently, Fe^{2+} ions in primary minerals in parent igneous rocks on
the martian surface have been oxidized to ferric iron, which occurs
in degradation products that now constitute the regolith. The miner-
alogy of the unweathered igneous rocks prior to weathering on the
martian surface is reasonably well constrained, mainly as a result of
petrographic studies of the SNC meteorites [3]. However, the
alteration products resulting from oxidative weathering of these
rocks are less well-constrained. Thus, a variety of candidate ferric-
bearing materials have been suggested, ranging from poorly crystal-
line ferric oxides [4], such as nanophase hematite [5], to altered
volcanic glass or palagonite [6,7], various clay silicates [8,9], and
gossaniferous ferrihydrite-jarosite-clay silicate assemblages [10].
Moreover, the mechanism and rate of oxidative weathering of
surface rocks on Mars are poorly understood [11], raising numerous
questions of chemical kinetics about the nature and extent of
chemical weathering processes on Mars.\For example, when did
oxidative weathering reactions take place on Mars? Were reaction
rates faster in the past and did they necessitate an aqueous phase? Is
the oxidized regolith a fossilized remnant of past weathering pro-
cesses, or are chemical weathering reactions still occurring in the
frozen regolith? If so, are they seasonal? Are the ferric-bearing
assemblages metastable and can they be characterized more rigor-
ously? Some of these questions are addressed here by examining
experimental data bearing on the mechanism of oxidation of ferro-
magnesian silicates to insoluble ferric-bearing phases, which include
pathways of dissolution, ferrolysis, and hydrolysis reactions that
may be appropriate to conditions on the surface of Mars.

Primary Rocks Subjected to Chemical Weathering: Mineral
assemblages in SNC meteorites [3,12], particularly the shergottites
(Shergotty, Zagami, EETA 79001, ALHA 77005), indicate that
olivine ($\approx Fa_{30}Fo_{70}$), low-Ca pyroxene (pigeonite, $\approx Fs_{25}En_{65}Wo_{10}$),
and high-Ca pyroxene (augite, $\approx Fs_{15}En_{50}Wo_{35}$) are probably the
predominant ferromagnesian silicates in basaltic rocks that were
subjected to chemical weathering on Mars. Lower Fe^{2+} concentra-
tions occur also in plagioclase feldspar and accessory sulfide and
oxide minerals [12], although local bodies of massive iron sulfide
deposits may be present near the surface of Mars [13]. These basaltic
sulfide, olivine, and pyroxene minerals are particularly vulnerable to
chemical weathering reactions, which in aqueous solutions proceed
through dissolution, oxidation, and hydrolysis stages that are strongly
pH dependent [14]. The eventual hydrolysis products of dissolved
ferric iron also depend on the type of anions present in the solutions
[15,16]. Thus, Fe(III) phases precipitated from SO_4^{2-} and Cl^--
bearing solutions are most relevant to Mars if brines have existed
there [17].

Dissolution Processes: Dissolution of ferromagnesian sili-
cates is generally congruent under anoxic conditions, indicating that
soluble Fe^{2+}, Mg^{2+}, Ca^{2+}, and silica dissolve from olivines and
pyroxenes at rates proportional to their concentrations in the silicate
minerals [14]. Incongruent solubility of pyroxenes may occur ini-
tially, however, both as a result of preferential release of cations in

M2 sites and armoring of crystal surfaces by protective layers of
insoluble ferric oxides when dissolution occurs under oxidiz-
ing conditions. Solubility rates of Fe^{2+} ions decrease in the order
olivine $\geq$ pyroxene M2 > pyroxene M1 >> feldspars [11,14]. Disso-
lution rates of these minerals are highest in acidic solutions, decrease
with rising pH, are least at near-neutral pH, and increase when the pH
is in the alkaline range. Rates of dissolution are slow near freezing
temperatures and in solutions of high ionic strength. Since low
temperatures and, perhaps, brines may currently exist on Mars,
dissolution rates of basaltic minerals are probably extremely slow on
the present-day martian surface, but may have been much faster in
the past when warmer climates prevailed, particularly if acid rain and
acidic groundwater conditions prevailed [10,18].

Oxidation of Dissolved Fe^{2+}: Ferrous iron released during
chemical weathering of ferromagnesian silicate and sulfide minerals
is metastable with respect to ferric iron when aerated groundwater
exceeds pH 3.5 [10]. In near-neutral and alkaline solutions, dissolved
Fe^{3+} ions formed from Fe^{2+} ions are removed almost immediately;
the rates of precipitation of ferric oxide and oxyhydroxide phases are
then controlled by the supply of Fe^{2+} ions by dissolution processes.
Reaction rates for the oxidation of dissolved Fe^{2+} ions are strongly
pH dependent [19,20] and are very slow in acidic solutions. There is
a 10-fold decrease in oxidation rate for each temperature-interval
decrease of 15°C. Rates also decrease with increasing ionic strength,
and are slower in sulfate-bearing solutions than in chloride-bearing
solutions. Therefore, in brine eutectics proposed for Mars [17]
(which are themselves slightly acidic due to hydrolysis reactions)
that have equilibrated with oxygen in the current martian atmosphere
(at $P_{O2} = 10^{-5}$ bar), rates of oxidation of Fe^{2+} ions are estimated to be
at least 10^6 times slower than in laboratory experiments performed
at room temperature on Earth [11].

Mechanism of Polymerization of Hydrous Ferric Oxides:
Once Fe^{3+} ions are produced in solution, they are highly vulnerable
to hydrolysis to poorly crystalline ferric hydrous gels or ferrihydrite,
which age to different crystalline phases, depending on the rate of
oxidation of dissolved Fe^{2+} to Fe^{3+}, the concentration of Fe^{3+} ions, the
nature of anions present, pH, temperature, and time of aging [15,16].
For example, rapid oxidation of dissolved Fe^{2+} at near-neutral pH
produces lepidocrocite (γ-FeOOH) [21], which may revert to
maghemite (γ-Fe_2O_3) by dehydration [22]. Such maghemite is one of

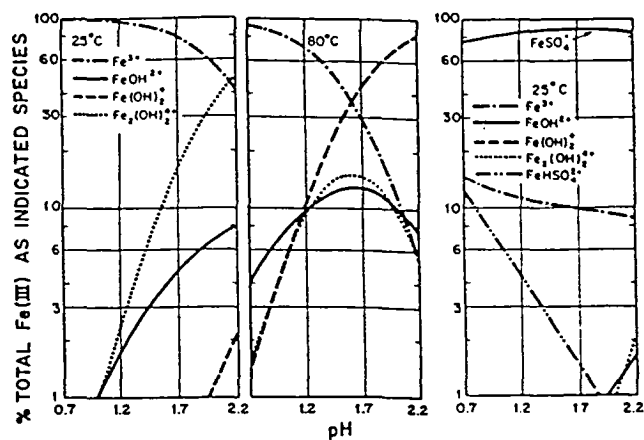**Fig. 1.** Species distribution diagrams as a function of pH for ferric hydroxo
and sulfato complexes. In all cases, $[Fe^{3+}]_{tot} = 0.18$ M and ionic strength = 2.67
M; in (c), $[SO_4]^{2-} = 0.53$ M (modified from [26]).

the candidate magnetic phases in the martian regolith [22,23]. Fast oxidation of Fe^{2+} in strongly alkaline solutions, on the other hand, produces δ-FeOOH or feroxyhyte (δ'-FeOOH), the magnetic properties of which also make it a candidate magnetic phase if peralkaline phases exist on the martian surface [24].

Hydrolysis of $FeCl_3$ solutions initially yields akaganeite (β-FeOOH), which may subsequently transform to goethite or hematite [25]. However, ferrihydrite that forms in the presence of NO_3^- or ClO_4^- anions ages to goethite (α-FeOOH), hematite (α-Fe_2O_3), or a mixture of the two, depending on the pH and temperature. Hematite is favored at elevated temperatures, low water activity, and neutral pH, whereas goethite formation predominates at both low and high pH. The mechanism of precipitation and aging of ferrihydrite are controlled by the types of the complex ferric ions in solution [26], which are influenced by temperature and pH, as illustrated in Fig. 1. Thus, monatomic Fe^{3+} ions predominate only in highly acidic solutions and some monomeric complex ions (e.g., $\{FeOH^{2+}\}$ and $\{Fe(OH)_2^+\}$) are also present. However, it is polymerization of dimeric complex ions (e.g., linear $\{Fe_2(OH)_2^{4+}\}$ and cyclic $\{Fe_3(OH)_4^{5+}\}$ clusters [27], which are the major species in solution above pH 2, that generates goethite, the crystal structure that consists of double chains of edge-shared $[FeO_4(OH)_2]$ octahedra. The $\{Fe(OH)_2^+\}$ species prevails at higher pH and elevated temperatures (Fig.1) and facilitates polymerization of faceshared octahedra, the key feature of the hematite structure, by deprotonation-oxalation reactions [28]. Such a mechanism leading to the production of nanophase hematite would occur on Mars when permafrost sublimed, brine eutectics evaporated, and clay silicates were desiccated on the arid martian surface.

Another important polymerization mechanism relevant to sulfate brine eutectics on Mars involves hydrolysis products of ferric iron in H_2SO_4 solutions, which are distinctly different from those of other inorganic acids [16,29]. At low pH, the $\{FeSO_4^+\}$ complex ion predominates (Fig. 1c) [26], so that in strongly acidic solutions hydronium jarosite, $(H_3O)Fe_3(SO_4)_2(OH)_6$, may be precipitated [31], particularly in the presence of Na^+ and K^+ ions. By analogy with terrestrial gossans, jarosite formed during sublimation or evaporation of sulfate-bearing groundwater could have persisted on the arid surface of Mars [10].

Applications to Mars: Chemical weathering on Mars appears to have occurred when acidic groundwater interacted with surface basalts. In anoxic conditions in the deep-weathering environment, dissolution rates of silicate and sulfide minerals were fast, yielding high concentrations of Fe^{2+}, Mg^{2+}, silica, etc., in the acidic groundwater [10,18]. Soluble Fe^{2+} ions could persist indefinitely in cold, subsurface water and be transported around the planet, provided anoxic conditions prevailed. When exposed to the oxygenated martian atmosphere, slow oxidation of dissolved Fe^{2+} ions to Fe^{3+} ions would occur and the ferric iron, too, would remain in solution indefinitely provided the groundwater remained acidic. Eventually, hydrolysis of dissolved ferric ions to hydrous ferric oxide occurred. Incomplete aging of the ferrihydrite to Fe_2O_3, which is retarded by dissolved silica [31], provided a mechanism for producing nanophase hematite, which is believed to occur on Mars [5]. Carbonate mineralization was not possible on Mars while acidic groundwater prevailed. Such conditions have probably persisted by the condensation of volcanic gases, through oxidative weathering of sulfide minerals, and during oxidation of dissolved Fe^{2+} ions.

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N93-31939

IMPLICATIONS FOR VOLCANOGENIC VOLATILE RELEASE ON THE WEATHERING OF MARS. Benton C. Clark, Planetary Sciences Lab (B0560), Martin Marietta, Denver CO 80201, USA.

Volcanism on Mars has been widespread in both space and time [1]. Notwithstanding important specific differences between the mantles of Earth and Mars, the similarities are such that the suite of gases emitted from martian volcanic activity surely includes gases such as H_2O, CO_2, S-containing gases (H_2S, SO_3, or SO_2), and Cl-containing gases (e.g., Cl_2 or HCl). Both H_2O and CO_2 are present in the atmosphere of Mars; both are also present as surface condensates. Spectroscopic observations of the martian atmosphere clearly show that the S- and Cl-containing gases are severely depleted [2,3]. Likewise, there is no evidence of surface condensates of compounds of these elements. Within the soil, there is direct evidence of incorporation of H_2O [4] and some compounds of sulfur and chlorine [5]. None of the resultant weathering products have been directly identified, but both clays and salts have been indirectly implicated.

Estimates for the total magma generated after initial crustal formation and the terminal stages of heavy bombardment have recently been updated. Although some 60 times lower than the current areal rate of extrusive lava resurfacing on Earth [1], the martian total is nonetheless equivalent to the release of ≥ 500 g/cm^2 of volatile averaged over the planet for every 0.1% wt/wt of volatile species released from magma. Quantitatively, this is sufficient to comprise as much as 5% of fine-grained regolith weathering product to a mean depth of 100 m. A reservoir of extremely fine-grained weathering product can be readily mobilized globally by the episodic dust storm activity. The relative absence of soil-consolidation factors, such as reworking by liquid water, tectonically driven metamorphism, and ubiquitous burial processes on Earth may permit survival of some material over significant portions of geologic time on Mars. As fines are repeatedly transported over the surface, they sample weathering regimes from various geologic settings and epochs.

These fines therefore could represent an undecipherable melange of past weathering processes, but also a planetwide sampling of the physical and chemical products from various surface materials. Excess acidity in the fines can occur due to the preponderance of acidic volcanic emissions. Some minerals will be more susceptible to attack than others [6]. The degree to which initial weathering reactions form barriers to further conversion of source material will be functionally dependent upon martian ambient conditions. Considerable interest would then center on the potential for comparisons between secondary products found as weathering rinds, vugs, or veins in their source rock and this eolian-transportable weathering product, presumably older and more reworked.

Resistant units such as large rocks and bedrock outcrops would be subjected to a balance between surficial chemical weathering and physical removal by eolian abrasion. Because of saltation heights and wind shadowing effects, important three-dimensional geochemical gradients of secondary alteration products could be present in weathering rinds on large boulders such as those observed at the Viking 1 lander site.

Although carbonates and nitrates are widely expected in the martian regolith by many planetary geologists, current evidence is lacking or weak. Reworked fines may be scrubbed of any weathering product of either class of compounds since it has been demonstrated experimentally that volcanogenic SO_2 gas can undergo rapid heterogeneous phase displacement reactions with susceptible solid substrates even under simulated dry, cold martian conditions, releasing CO_2 and NO_2 respectively. The problem requires detailed modeling of functional relationships between quantities for each species released, reaction rates, and availability of labile substrates.

On the other hand, magmas release additional volatiles, many of higher atomic weight. Although it is experimentally difficult to identify and quantify all such emissions, a variety of data relevant to volatility would imply that weathering products may be highly enriched in elements such as Na, Cu, Zn, As, Se, Br, Rb, Cd, In, Sn, Sb, Hg, Yl, Pb, and Bi compared to rock compositions [7]. Many of the compounds formed by these elements may be soluble in H_2O, as data indicate for the S- and Cl-bearing compounds in martian fines, and hence be subject to transport processes that create duricrust and soil peds.

Where weathering products have been exposed to bulk liquid water, chemical sediment deposits with complex evaporite sequences should be found on Mars. Quasistable liquid brine pools might also have resulted. However, if the dominant soluble anion on Mars is SO_4^{2-}, then most strong freezing-point depressant salts would not be available for contemporaneous brine.

Although it is widely believed that the missing H_2O is buried in the regolith as physical deposits of permafrost ice, it cannot be ruled out that significant quantities, perhaps most, of this inventory have been incorporated into secondary minerals. The extent to which a pervasive drawdown of atmospheric volatiles has been mediated by chemical reaction with surface materials is important to understanding the past climatological history of Mars.

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CALCULATED MINERAL PRECIPITATION UPON EVAPORATION OF A MODEL MARTIAN GROUNDWATER NEAR

0°C. J. D. DeBraal[1], M. H. Reed[1], and G. S. Plumlee[2], [1]Department of Geological Sciences, University of Oregon, Eugene OR 97403, USA, [2]U.S. Geological Survey, Box 25046, Mail Stop 973, Denver Federal Center, Denver CO 80225, USA.

Previously we calculated [1] the effect of weathering a basalt of Shergotty meteorite composition [2] with pure water buffered at martian atmospheric values of CO_2 and O_2, to place constraints upon the composition of martian groundwater, and to determine possible equilibrium mineral assemblages. Figure 1 shows a revised calculation of the composition of the aqueous phase in the weathering reaction as a function of the amount of basalt titrated into the solution. The concentrations of sulfate and chloride ions increase in the solution from high water/rock ratios (w/r) on the left to low water/rock ratios on the right, until at w/r = 1, where 1 kg of basalt has been titrated, sulfate concentration is 1564 ppm and chloride is 104 ppm. This resulting fluid is dominated by sulfate and sodium, with bicarbonate and chloride at about the same concentration. We have evaporated this solution in an attempt to determine if the resulting evaporite can explain the Viking XRF data.

We used the program CHILLER [3] to evaporate this solution at 0.1°C. The solution was buffered at martian atmospheric values of CO_2 and O_2 (fCO_2 = $10^{-2.2}$ bar, fO_2 = 10^{-5} bar). Prior to evaporating the fluid, it was fractionated from its host rock to prevent back-reaction, under the assumption that the kinetics of evaporite precipitation are faster than those for solution reequilibration with its host rock. Evaporation was simulated by removing pure water from the
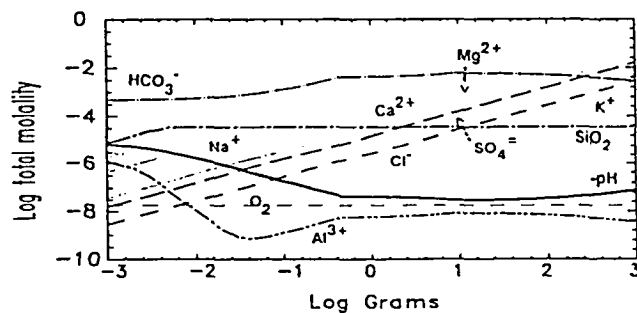
Fig. 1. pH and total modalities of aqueous components plotted vs. log grams of basalt added to pure water buffered by the martian atmosphere. Notice the accumulation of aqueous sulfate by oxidation of sulfide from the rock.
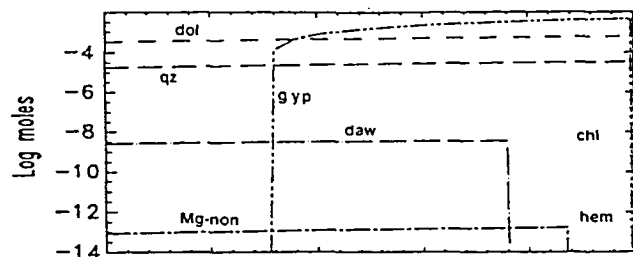
Fig. 2. Mineral abundance diagram that shows the presence and absolute abundance (in moles) of the evaporite minerals produced as 1 kg of martian groundwater is evaporated (see Fig. 3 for scale). Mineral abbreviations: dol - dolomite; qz - quartz; gyp - gypsum; daw - dawsonite; chl - chlorite; hem - hematite; non - nontronite.
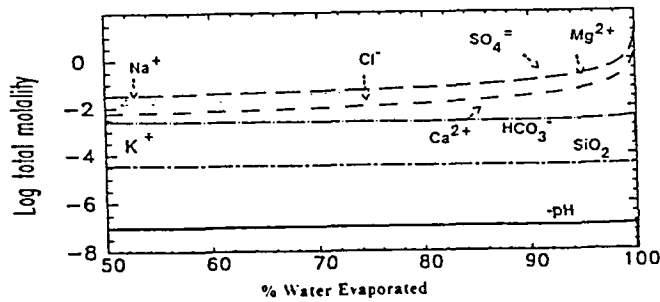
Fig. 3. The pH and total modalities of aqueous components vs. percent martian groundwater evaporated.

% Water Evaporated
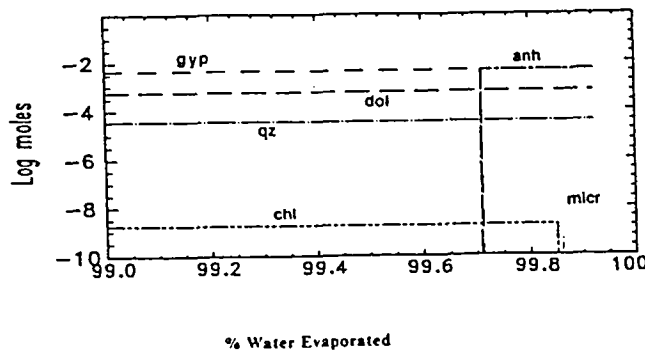
Fig. 4. Detailed mineral abundance diagram for the last 1% of evaporation. The transition from gypsum to anhydrite occurs just after 98.7% evaporation. Mineral abbreviations: gyp - gypsum; anh - anhydrite; dol - dolomite; qz - quartz; chl - chlorite; micr - microcline .

system until activity coefficients could no longer be reliably calculated (after 99.8% evaporation). These results are plotted in Figs. 2 and 3.

Dolomite, quartz, dawsonite ($NaAlCO_3OH_2$), and nontronite saturate at the beginning of the evaporation and little change occurs in either the solution or the initial mineral assemblage until just after 65% of the water has been evaporated. At this point gypsum precipitates from the solution and becomes the dominant mineral in the assemblage. Gypsum is replaced by anhydrite once 99.8% of the water has been evaporated (Fig. 4), at which point the mineral assemblage is 84.7 wt% anhydrite, 15.1 wt% dolomite, with small amounts of quartz, chlorite, and hematite making up the difference. This assemblage is sulfur-rich (19.9 wt%), and if appropriately mixed with rock fragments from other sources, is consistent with the 3–4 wt% sulfur detected by the Viking XRF [4].

No chloride minerals precipitate in the evaporation of this fluid. At the point of anhydrite saturation, saturation indices (log Q/K) for halite and sylvite are −1.65 and −2.20, indicating that they were still significantly undersaturated. The Viking XRF data indicate that up to 0.7 wt% chloride is present in martian fines. Our results suggest that chloride may not reside in alkali halides, unless soil waters evaporate to dryness. An alternative residence for chloride may be in phosphates [5].

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ON THE WEATHERING OF MARTIAN IGNEOUS ROCKS. G. Dreibus and H. Wänke, Max-Planck-Institut für Chemie, Saarstrasse 23, D-6500 Mainz, Germany.

Besides the young crystallization age, one of the first arguments for the martian origin of SNC meteorites came from the chemical similarity of the meteorite Shergotty and the martian soil as measured by Viking XRF analyses [1]. In the meantime, the discovery of trapped rare gas and nitrogen components with element and isotope ratios closely matching the highly characteristic ratios of the Mars atmosphere in the shock glasses of shergottite EETA 79001 [2,3] was further striking evidence that the SNCs are martian surface rocks.

The martian soil composition as derived from the Viking mission, with its extremely high S and Cl concentrations, was interpreted as weathering products of mafic igneous rocks. The low SiO_2 content and the low abundance of K and other trace elements in the martian soils point to a mafic crust with a considerably smaller degree of fractionation compared to the terrestrial crust. However, the chemical evolution of the martian regolith and soil in respect to surface reaction with the planetary atmosphere or hydrosphere is poorly understood. A critical point in this respect is that the geochemical evidence as derived from the SNC meteorites suggests that Mars is a very dry planet that should have lost almost all its initially large water inventory during its accretion.

In Shergotty, a H_2O content of 180 ppm was measured, compared to the about 2000 ppm H_2O in ocean ridge basalts. These 180 ppm H_2O correspond to 36 ppm H_2O for the martian mantle [4]. A mantle concentration of 36 ppm water would correspond to an ocean covering the whole planet to a depth of 130 m. According to all estimates, the degassing efficiency on Mars is thought to be small and outgassing of the interior is likely to have provided no more than about 10 m of water to the surface. These estimates are in conflict with the geological evidence for large amounts of water at the martian surface as derived from the large flood features and the valley networks [5].

The contradictory evidence of a dry martian mantle and the erosional martian surface features has been discussed by Carr and Wänke [6,7]. Recently, it has been found that part of the water present in SNC meteorites differs drastically in their oxygen isotopes from the oxygen bound in silicates [8]. This indicates that the martian surface water of today cannot be derived from the martian mantle in a direct way.

We do not have a definitive answer about the amount of water at the surface, but we have good reasons to assume that this water was very salty. The halogen content of the martian mantle as estimated from the chemistry of shergottites must be a factor of 3 higher compared to the Earth [4]. On today's Earth most of the total water content is in the oceans, which have an average NaCl concentration of 3.1%. Hence, we should expect that the small amount of water on Mars was saturated with NaCl [9] at least at the time close to the final disappearance of liquid water on the martian surface. In addition to NaCl, $MgSO_4$ and $MgCO_3$ [10] are also expected to be present in the martian water. Recently, Wänke et al. [11] emphasized the importance of SO_2 on Mars. If we take 180 ppm H_2O in Shergotty at face value and compare it with the 1330 ppm S and 620 ppm C in Shergotty, it is evident that sulphur and carbon, respectively SO_2 and CO_2, are the most abundant volatiles in the Shergotty magma. Under martian surface conditions, SO_2 will be transformed quickly to SO_3, which in turn will react with H_2O to form sulfuric acid. Hence, it seems likely that in addition surface water became acidified.

To study the interaction between a fluid phase and martian surface samples we carried out leaching experiments with water and acids on the basaltic meteorite Shergotty, the komatiitic shergottite ALHA 77005, and the augite-olivine cumulate Nakhla. Leaching experiments on shergottites with brine water are in progress.

Nakhla contains alteration products of probably extraterrestrial origin that may be produced by the action of fluids rich in halides [12]. This "rust" contains high amount of Cl and K. The leaching experiment on Nakhla showed that of the very high concentration of Cl (1145 ppm) and Br (4.1 ppm) 96% resp. 50% are water-leachable, together with about 16% of the bulk Na and K, corresponding exactly to the leachable Cl as NaCl and KCl. Also sulphur is in Nakhla to 77% water-leachable. The water-leach was followed by an acid-leach (1n HNO_3). The treatment with this acid dissolved 80% of La, but only 16% Dy, 50% U, and 26% K. The La/Dy ratio of the leach is with 9.2 a factor of 3 higher as the La/Dy ratio in the bulk sample, but matches exactly the La/Dy ratio of the low-density fraction separated by Nakamura et al. [13]. However, these authors could not precisely identify this low-density fraction.

The leach experiments on the two shergottites show other features. In Shergotty only 19% of the Cl and 15% of the Br was found to be water-leachable. At the following acid leach (1n HCl) the residual halogens were completely dissolved together with the whole phosphate-phase, whereas the treatment of ALHA 77005 with 1n HNO_3 leached halogens and phosphates from the bulk sample to only 70% [14]. This could mean that the sample was not sufficiently fine-ground or that part of P and the halogens are in insoluble phases, most likely glasses.

We observed that in all acid-leach experiments of Nakhla and the two shergottites LREE as well as U are considerably more leachable than K. The K/U ratio in Nakhla leach was 5400 compared to the residue ratio of 42,000. In Shergotty leach a K/U ratio of 780 was found compared to a ratio of 37,000 in the residue. The reason for the difference of the behavior of K and U during weathering of martian rocks clearly lies in the fact that U as well as many other LIL elements, but not K, reside in the phosphates (apatite and whitlockite), which dissolve easily in dilute acids. The observation that acid weathering of igneous martian rocks yields drastically different K/U between leach and residue phases might be highly significant in respect to the interpretation of the K/U ratios derived from γ ray experiments by Phobos 2 and Mars 5 [15].

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AN UNUSUAL SPECTRAL UNIT IN WEST CANDOR CHASMA: EVIDENCE FOR HYDROTHERMAL OR AQUEOUS ALTERATION?

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A spectrally distinctive unit on the floor of W. Candor Chasma (6°S, 76°W) in the central Valles Marineris may be a likely candidate for hydrothermal or aqueous alteration. This unusual material is noticeably redder than nearby plains and canyon floor-covering deposits of similar brightness in several Viking Orbiter color-composite images calibrated using PICS Level 1 procedures [1]. The surrounding plains and canyon floor units have colors that are typical for much of the weathered soil on Mars. Relative to adjacent materials, the West Candor unit has lower green-filter reflectance and higher red-filter reflectance (Fig. 1). While subtle, these spectral characteristics have been observed for this unit in a number of multispectral images acquired at different seasons and phase angles. When the color image data are transformed to hue, saturation, and value coordinates, the West Candor material stands out prominently among the rocks and soils of Coprates Quadrangle as a spatially coherent unit with a unique hue (Fig. 2). Physically, this means that the unit is compositionally distinct (unlike most of the bright materials in the region), since its spectral reflectance cannot be obtained through simple multiplicative scaling of the reflectance of the surrounding bright materials or by altering the spectral reflectance of the surrounding materials with an additive constant that is independent of wavelength. Recent studies of the directional reflectance properties of the surface in this region [2] indicate that the photometric phase function of the unit is similar to that of surrounding bright materials (isotropic to slightly backscattering).

In Viking high-resolution images (e.g., Fig. 3) the anomalous unit can be seen to correspond to two topographic depressions in heavily eroded floor-covering deposits in West Candor. Its restricted spatial distribution suggests that the unit may be genetically associated with the depressions. It is not clear whether we are seeing exposed underlying deposits distinct in composition, or later material deposited in preexisting depressions. Within these depressions are fine horizontal laminations possibly due to layering. However, Komatsu et al. [3] make a case that many of the apparent layers in the Valles

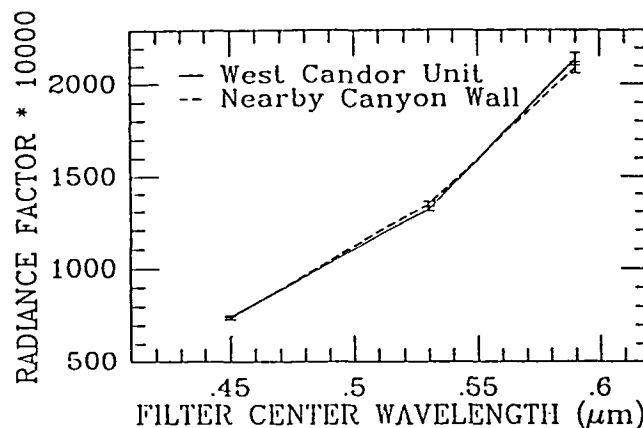**Fig. 1.** Comparison of West Candor Unit 3-point spectrum (solid line; 25 pixel avg.) with spectrum of nearby canyon wall rock of similar brightness (dashed line; 36 pixel avg.). Data from calibrated image composite, Viking Orbiter 1, orbit 583.
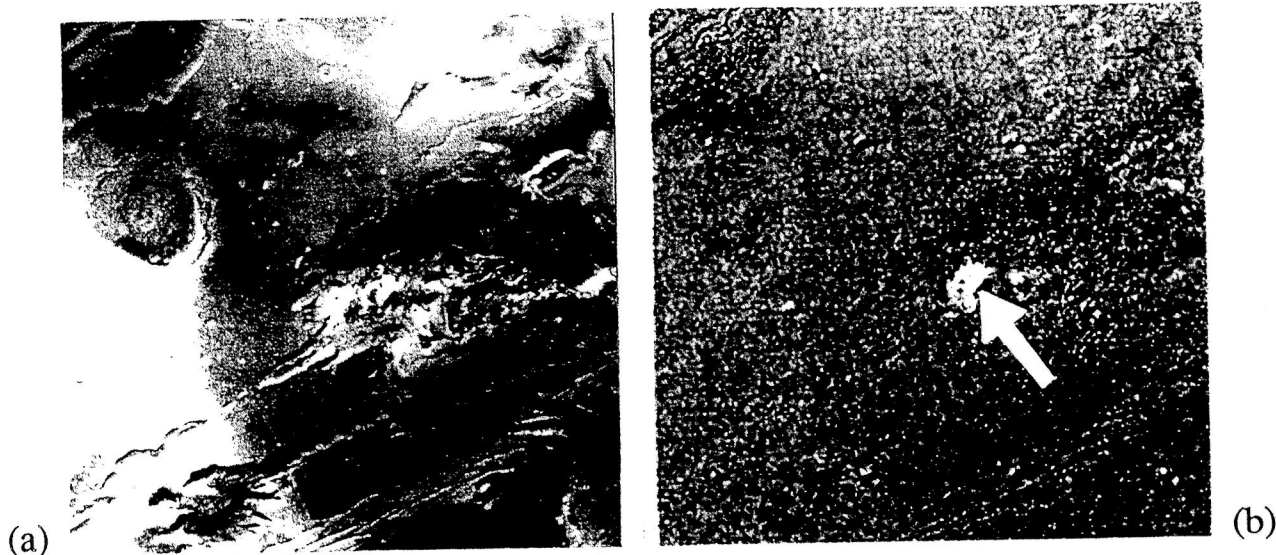
Fig. 2. (a) Location of anomalous spectral unit in West Candor Chasma. Portion of 583A40, 400 km in width; north is toward the top left. (b) Hue image from color coordinate transformation. The West Candor unit (arrow) is prominent as a spatially coherent region of unique hue.

Marineris interior deposits, including these, resemble erosional terraces and wave-cut platforms of terrestrial lakes and playas. Such erosion could have produced the morphology seen in West Candor even in unstratified, homogenous materials. In any case, this unit is apparently compositionally unique. The absence of similar material in depressions elsewhere in the canyon system seems to require a local mechanism for formation and/or alteration.

The Viking Orbiter bandpasses do not provide enough spectral information to generally allow unique mineralogic interpretations. Nevertheless, we think that the observed spectral reflectance characteristics of the West Candor unit are most readily explained by a composition somewhat richer in bulk crystalline hematite than typical for weathered or altered soils on Mars [e.g., 4,5]. Crystalline hematite, which is visually red, displays a strong and diagnostic crystal-field absorption near 0.53 µm [e.g., 4,6] to which the Viking green bandpass is quite sensitive despite that filter's width. While crystalline hematite is not the primary coloring agent for typical soils on Mars there have been a number of observations consistent with its occurrence on the planet [4,7–10]. We interpret the Candor units to have a greater hematite content than typical martian soils, but to also contain the ubiquitous poorly crystalline or nanophase ferric oxide phase that gives Mars its characteristic orange-brown color.

Hematite is the most thermodynamically stable ferric oxide mineral under current martian surface conditions [11,12]. Crystalline hematite on Earth forms in a variety of environments through a number of mechanisms, including subaerial weathering of soils, hydrothermal alteration associated with volcanism or circulating mineralized fluids, and conversion of other previously formed hydrated ferric oxide minerals such as ferrihydrite and goethite. All these mechanisms might be viable on Mars as well, making it difficult to pinpoint the genesis of hematite in this Candor unit. The most common characteristic of hematite formation, relative to other ferric oxides, is heat. Increased temperature favors hematite, as does decreased water content and relatively neutral pH [e.g., 11,13]. The Candor units may have formed by primary volcanic oxidation, or through the action of circulating hydrothermal fluids. They might also have formed through aqueous precipitation of ferrihydrite in

receding lakes, consistent with the localized nature of these deposits and the possibility of wave-cut terraces. This ferrihydrite could have subsequently converted to hematite through drying and application of heat. Whatever the origin, this unit is apparently unique, and required a geologically localized source of heat greater than current surface conditions, and greater than that to which surrounding weathered soils have been exposed. Localized volcanism, in one form or another, is a plausible source of that heat (cf. [14]).

We recommend that this region in Candor Chasma be observed carefully with upcoming missions to Mars. From Mars Observer, high-resolution images with the MOC should help resolve details of geologic relationships, including the question of layering vs. terracing. Data from the TES infrared spectrometer will be useful to search for possible clay minerals and/or evaporite salts. Unfortunately,

Fig. 3. Morphology of the spectrally anomalous region in West Candor. In high resolution, the unit can be seen to correspond to two topographic depressions in heavily eroded canyon floor-covering sediments. Layering or wave-cut terraces can be seen within the depressions. Picture width is 50 km.

there is no visible-region spectral capability on Mars Observer to help refine our understanding of the ferric-oxide mineralogy. Mars 94 will carry two such instruments, the Omega visible and near-IR imaging spectrometer, and the Svet visible and near-IR imaging spectrophotometer. While we have not found other similar color units in the Valles Marineris region, they may exist elsewhere on Mars. Searches for such units throughout the large Viking Orbiter multispectral dataset will continue to be important.

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N93-31943

LOCATION OF NANOPHASE Fe-OXIDES IN PALAGONITIC SOILS: IMPLICATION FOR MARTIAN PIGMENTS.

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Introduction: Palagonitic materials from Mauna Kea, Hawaii, have been identified as Mars analogues based on their spectral and magnetic properties. These materials probably resulted from hydrothermal alteration during eruption of the volcano and/or from weathering under ambient conditions. The reflectance spectra of the Mars surface obtained by Earth-based telescopes and the reflectance spectra of analogues obtained in the laboratory show features due to electronic transitions of Fe(III) in oxide particles that range in size from nanometer (nanophase) to micrometer sized or larger. The presence of Fe(III) suggests oxidizing conditions during the alteration process in Mars that may have occurred in the past or during a slow ongoing process. In this study we examined two naturally altered basaltic samples from Hawaii (HWMK12 and HWMK13) and a laboratory-altered (PH-13-DCGT2) basaltic glass similar in elemental composition to the above two samples. All three samples exhibited spectral characteristics similar to martian bright-region spectra. Chemical and mineralogical changes occurring at the surface of these basalts were studied in order to understand the basis for their Mars-like properties. The spectral properties of the three samples were examined after the removal of Fe oxides by chemical extractants.

Materials and Methods: *Samples.* Palagonitic soils HWMK12 and HWMK13 were collected from near the summit of Mauna Kea, Hawaii [1]. The <20-μm fraction of the HWMK12 and HWMK13 samples was used for all the investigations reported here. Sample PH-13, which is a black, relatively unaltered material, was obtained from the Puu Huluhulu cinder cone ~15 km due south of the Mauna Kea summit by J. Bell. A 1-g sample of the <1-mm fraction of PH13 sample was heated in a teflon-lined vessel in the presence of 7 ml of H_2O_2, 4 ml of 1 M NaOH, and 5 ml of water for seven days

TABLE 1.   Fe-removal by oxalate and DCB extractions as a percent of the total Fe.

Sample	Oxalate-Fe	DCB-Fe
	%	
HWMK12	12	16
HWMK13	9	17
PH-13-DCG-T2	ND	17

at 200°C. The product (PH13-DCG-T2) was washed four times with deionized water, freeze dried, and stored in an air-tight bottle for further use.

Chemical extractions [2]. Acidified ammonium oxalate (pH = 3) (hereafter referred to as oxalate) was used to extract poorly crystalline Fe-oxides. A 0.3-M solution of ammonium oxalate was adjusted to pH 3 using 0.3-M oxalic acid solution. Extraction was performed by shaking 0.5 g of soil with 200 ml of the reagent in a polypropylene tube in the dark. A citrate-dithionite-bicarbonate (DCB) method was used to extract free Fe(III)-oxide. A solution of 0.3 M sodium citrate was mixed with 1 M $NaHCO_3$ solution in the ratio 8:1. The pH was adjusted to 7.3 by adding 0.3 M citric acid. Extraction was performed by adding 25 ml of the reagent to 200 mg of the sample in a polypropylene tube at 75°C in a water bath followed by 1-g additions of sodium dithionite powder at 5-min intervals as necessary.

Untreated and extracted samples were analyzed by Mössbauer spectroscopy, reflectance spectroscopy, electron microscopy (SEM and TEM), and electron probe microanalysis.

Results and Discussion: The spectral data for natural samples HWMK12 and HWMK13 (<20 μm) are both characterized by relatively featureless absorption edges (Fig. 1). Compared to martian bright region spectra, the edges occur at somewhat shorter wavelengths. The bands near 1.4 and 1.9 μm are due to absorbed water on phyllosilicate surfaces or in zeolite structures. Both samples behaved in a similar fashion with respect to their reflectance spectra upon oxalate and DCB treatment. Upon oxalate treatment there is a slight shift of the absorption edge toward the shorter wavelengths and also a slight decrease in reflectance at longer wavelengths. The DCB treatment, however, had an appreciable effect (Fig. 1). The strength of the ferric absorption is reduced and there is a relative reflectivity maximum near 0.8 μm. The reflectivity maximum is the region between ferrous bands near 1.0 μm and ferrous-ferric charge transfer bands near 0.65 μm. The bands near 1 μm are also evident in the untreated samples.

The Mössbauer spectra of all three untreated samples are dominated by a ferric doublet that we have attributed to nanophase oxide (np-Ox) particles. The absolute intensity of the doublet did not decrease *as much as expected on the amount of Fe extracted* (Table 1). Apparently Fe and other elements were removed by the extraction procedures in a way such that the Fe content remained nearly constant.

Transmission electron microscopy of palagonitic soil sample HWMK12 before chemical treatment (Fig. 2a) shows the weathering basaltic glass matrix. The hydrated glass shows signs of polymerization of [$Si(OH)_4$] increasing the porosity of the glass. Fe(II) in the original glass structure is oxidized and hydrolyzed as channels are formed during hydration and repolymerization of silica. Once a nucleus of Fe(OH)_3 is formed more Fe(II) diffuses in that direction and the iron oxide particle grows perhaps by surface catalyzed oxidation of Fe(II) near the original nucleus. As weathering proceeds, soluble cations and Si move away from the weathering front
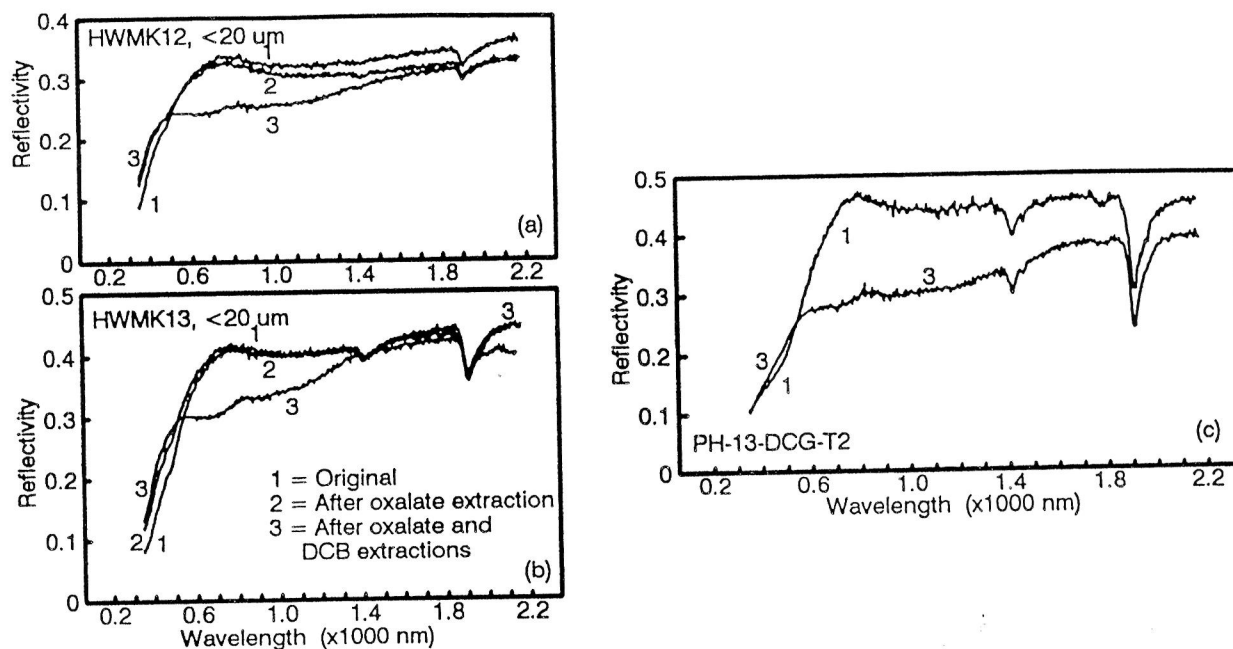
Fig. 1. The reflectance spectra of Mars analogue samples: (a) HWMK12, (b) HWMK13, and (c) PH-13-DCGT2. Numbers 1 through 3 represent curves corresponding to untreated, oxalate-treated, and oxalate-DCB-treated samples respectively.
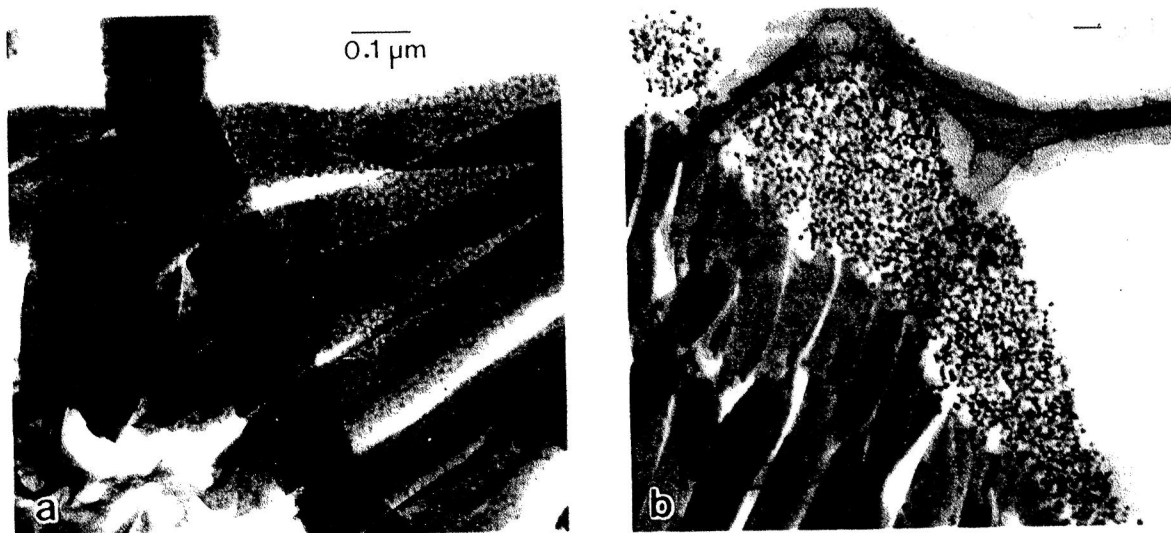
Fig. 2. Transmission electron micrographs of microtomed thin sections of HWMK12 sample mounted on holey carbon substrate showing two different weathering stages of basaltic glass: (a) initial glass repolymerization and Fe oxide nucleation, and (b) the accumulation of nanophase Fe oxide particles near the glass weathering front.

while leaving a residue of Fe oxides (the np-Ox particles). These cations and the silica precipitate as smectite or zeolite near the weathering front. Fe concentrations during hydration and oxidation of the glass can be seen as electron dense (dark) spots in the weathered zone (Fig. 2b). As the weathering advances, more ordered Fe oxide minerals are formed. Most of these oxides are still surrounded by the silica derived from weathered glass, which protects the Fe oxides from reducing agents like DCB. Therefore most of the np-Ox particles are not dissolved by oxalate or DCB treatment. Only the np-Ox particles on the surfaces are removed. The mineralogy of the hydrothermally altered PH-13 sample consisted of smectite, zeolite, and Fe-oxides as inferred from TEM, SEM, and X-ray diffraction.

Hydrothermal alteration in the laboratory of basaltic glass (PH-13-DCG-T2), similar in elemental composition to HWMK12 and HWMK13, produced a martian spectral analog similar to natural palagonites. The alteration products of the synthetic sample consisted of smectite, zeolite, and Fe oxides. Fe oxides were poorly

crystalline and were not completely extracted by DCB. Acidified ammonium oxalate is used to extract poorly crystalline Fe oxides in soils, while citrate-bicarbonate-dithionite (DCB) is used to extract more crystalline Fe oxides [2]. These reagents work well in soils where particles can be easily disaggregated. Palagonites, however, are not completely weathered and some of the products are still embedded in the silica-rich matrix, which prevents access to oxalate or DCB. Structure of a typical palagonite particle consists of a thin outer rind (1–5 μm) of a loose-textured mineral assemblage consisting of smectite, zeolite, and fine Fe oxides. Fe oxide in this layer can be removed using DCB. Underneath this layer is a thin, leached glass layer, where hydration and polymerization of silica and oxidation of Fe(II) take place. This layer contains nanometer-sized Fe oxide particles in various stages of formation. Although the extensively hydrated glass consists of submicroscopic pores in this layer, oxalate and DCB reagents cannot react with the Fe oxides still embedded in the silica-rich matrix. The reflectance spectra that are surface dependent change after the DCB treatment, indicating the removal of Fe(III) oxides from the surface layer. The extractants oxalate and DCB are useful in detecting the surface Fe(III) oxides and understanding the weathering process. It is very likely that the weathering on Mars is similar to that of palagonitic martian analogues, although there can be several mechanisms to yield materials with martian spectral characteristics.

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AQUEOUS GEOCHEMISTRY ON MARS: POSSIBLE CLUES FROM SALTS AND CLAYS IN SNC METEORITES. James L. Gooding, Code SN2, Office of the Curator, NASA Johnson Space Center, Houston TX 77058-3696, USA.

Salts and Clays in SNCs: All subgroups of the shergottite, nakhlite, and chassignite (SNC) meteorites contain traces of water-precipitated minerals that include various combinations of carbonates, sulfates, halides, ferric oxides, and aluminosilicate clays of preterrestrial origin (Table 1) [1–8]. Oxygen three-isotope analysis of thermally extracted bulk water has confirmed that at least some of the water in SNCs is, indeed, extraterrestrial [9]. A mixture of aqueous precipitates found in the SNCs, comprising smectite, illite, and gypsum (with minor halite ± calcite and hematite), provides a self-consistent, though not unique, model for the bulk elemental composition of surface sediments at the Viking Lander sites (Fig. 1). Therefore, if the salts and clays in SNCs are truly linked to aqueous alteration and soil formation on Mars, then the suite of SNC secondary minerals might provide the best currently available insight into near-surface martian chemistry.

Implications for Water-based Chemistry on Mars: It is not clear whether the aqueous precipitates in SNCs represent products of surface weathering (i.e., actual rock-atmosphere reactions) or subsurface alteration (i.e., pedogenic weathering, groundwater infiltration, or deuteric alteration by residual magmatic volatiles); contributions by different water-rich environments cannot be excluded. As lavas, shergottites are the SNCs most likely to have experienced surface weathering; as deeper-seated rocks, nakhlites and chassignites may be the best candidates for deuteric or groundwater interactions. Further detailed microchemical, microstructural, and isotopic studies are needed to decipher the precise conditions under which the SNC salts and clays formed, but a few first-order conclusions about

TABLE 1. Products of aqueous alteration in SNC meteorites*.

	Shergottite EETA79001	Nakhla	Chassigny
CaCO₃	[1]	[3]	[5,6]
Mg-bearing CaCO₃	[8]		
MgCO₃			[6]
(Fe,Mn)CO₃		[7]	
CaSO₄·nH₂O	[1]	[3]	[5,6]
(Mg)ₓ(PO₄)ᵧ·nH₂O	[1]		
(Mg)ₓ(SO₄)ᵧ·nH₂O		[3]	
(Na,K)Cl		[3,4]	
"Illite" (K,Na,Ca₀.₅,H₃O)(Al,Mg,Fe)₂(Si,Al)₄ O₁₀[(OH)₂,H₂O]	[2]		
S,Cl-bearing "micabole"	[2]		
Smectite (Na,Ca₀.₅)₀.₃(Al,Mg,Fe)₂₋₃(Si,Al)₄ O₁₀(OH)₂·nH₂O		[3,4]	
Fe₂O₃·nH₂O		[4]	

* x, y, and n are generalized coefficients where stoichiometry is variable or uncertain.

paragenesis are already possible. These inferences bear on possible geochemical reaction pathways for hydrothermal alteration, surface weathering, and soil-forming processes on Mars.

First, precipitation of the SNC secondary minerals occurred from saline liquid water. The vein-forming textures of the various hydrous and water-soluble phases are unmistakable evidence for aqueous solutions. Furthermore, on chemical-thermodynamic grounds, liquid water would be required to stabilize Fe-rich and Al-poor, smectite-type clay minerals under martian surface conditions [10]. Persistent traces of Cl and P (probably as PO_4^{3-}) in Nakhla clays and Chassigny carbonates show that the solutions contained significant concentrations of dissolved anions.

Second, the solutions were oxidizing and alkaline. Among the SNC secondary minerals, carbonate and sulfate are the dominant forms of carbon and sulfur, respectively, and much of the total iron is in the ferric state. In terms of aqueous geochemistry, the calcite-gypsum-hematite assemblage in Nakhla (with no evidence for secondary sulfides) implies Eh > –0.2 and pH > 8 [11, p. 396]. Smectites also require pH > 6 for precipitation [12] although such conditions can be achieved by the reaction of acidic hydrothermal solutions with silicate minerals, as occurs on Earth where midocean hot springs encounter seafloor sediments [13]. Pure water in equilibrium with the Mars atmosphere should definitely be acidic so that formation of an alkaline solution on Mars would require either protracted disequilibrium with the atmosphere or extensive hydrolysis of silicates [10]; the latter process dominates chemical weathering on Earth [14].

The temperatures and pressures of the solutions from which the SNC clays and salts precipitated are not well constrained by current knowledge except that extreme hydrothermal conditions are probably excluded. If, as indicated in Nakhla, the original Ca-sulfate among the SNC precipitates was gypsum rather than anhydrite, arguments based on equilibrium relationships among water-precipitated phases in the $CaSO_4$-H_2O system [15] would argue for formational temperatures <70°C. Although anhydrite is stable to much higher temperatures compared with gypsum, occurrence of anhydrite as the principal Ca-sulfate would not necessarily require extraordinarily high formational temperatures. Anhydrite can be precipitated directly from terrestrial seawater, for example, at tem-
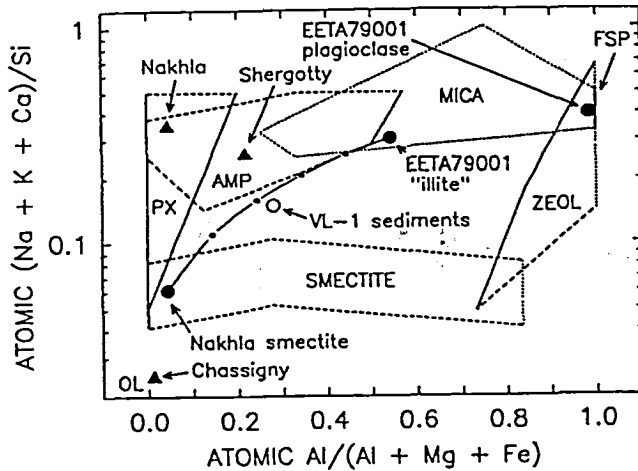
Fig. 1. Bulk elemental composition of martian surface sediments at the Viking Lander 1 site (open circle [20]) compared with whole-rock compositions of representative SNC meteorites (filled triangles), individual clays found in SNCs (filled circles and curved mixing line), and compositional fields of common aluminosilicate minerals. Note that the VL-1 composition should be expected to plot higher along the y-axis if its Na and K concentrations were known (i.e., Viking did not measure Na and set only an upper limit for K). By adding Na or K, the VL-1 point can be moved vertically upward onto the mixing line defined by the SNC clays; by subtracting Ca as CaSO$_4$, it can be moved vertically downward through the smectite field. AMP = amphibole; FSP = feldspar; OL = olivine; PX = pyroxene; ZEOL = zeolite.

peratures of only about 150°C [16]. In addition, stabilization of ferrihydrite requires temperatures <100°C [17]. At present, no lower limit can be set for the temperature at which the SNC aqueous precipitates formed and solutions at or near freezing cannot be excluded. The ^{18}O enrichment in calcite from EETA79001,239 is most reasonably attributed to reactions within the CO$_2$-H$_2$O system at low temperatures (where isotopic fractionations are greatest), perhaps as low as 0°C [18]. Because carbonates in EETA79001,239 have generally the same isotopic compositions as those in Nakhla, a low-temperature origin is also implied for the Nakhla carbonates. If the solutions were cold, however, the moderate crystallinity of the clays would suggest that the fluids were long-lived in order to explain the partial ripening of colloidal gels into ordered phyllosilicate phases. Ordinarily, ripening times of at least a few weeks are required to experimentally synthesize crystalline clays at <200°C [19, p. 479–490]. Better thermometric constraints will require more detailed mineralogical studies and, ideally, separate oxygen-isotopic analyses of coexisting precipitates.

If the SNC parent planet is Mars, as previously inferred from independent evidence, the aqueous precipitates indicate that oxidizing, water-based solutions probably have been chemically active on Mars for at least the time interval represented by the radiometric ages of the meteorites, namely, the past 200–1300 m.y.

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(1965) *Solutions, Minerals, and Equilibria*, Freeman, Cooper, San Francisco, 450. [12] Kittrick J. A. (1977) In *Minerals in Soil Environments* (J. B. Dixon and S. B. Weed, eds.), 1–25, Soil Science Society of America, Madison. [13] Bowers T. S. et al. (1985) *GCA, 49*, 2239–2252. [14] Schott J. and Berner R. A. (1985) In *The Chemistry of Weathering* (J. I. Drever, ed.), 35–53, Reidel, Dordrecht. [15] Blount C. W. and Dickson F. W. (1973) *Am. Mineral., 58*, 323–331. [16] Bischoff J. L. and Seyfried W. E. (1978) *AJS, 278*, 838–860. [17] Johnston J. H. and Lewis D. G. (1983) *GCA, 47*, 1823–1831. [18] Clayton R. N. and Mayeda T. K. *(1988) GCA, 52*, 925–927. [19] Grim R. E. (1968) *Clay Mineralogy, 2nd edition*, McGraw-Hill, New York, 596. [20] Clark B. C. et al. (1982) *JGR, 87*, 10059–10067.

N93-31945

EFFECT OF PURITY ON ADSORPTION CAPACITIES OF A MARS-LIKE CLAY MINERAL AT DIFFERENT PRESSURES.

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Introduction: There has been considerable interest in adsorption of carbon dioxide on Marslike clay minerals. Some estimates of the carbon dioxide reservoir capacity of the martian regolith were calculated from the amount of carbon dioxide adsorbed on the iron-rich smectite nontronite under martian conditions [1,2]. The adsorption capacity of pure nontronite could place upper limits on the regolith carbon dioxide reservoir, both at present martian atmospheric pressure and at the postulated higher pressures required to permit liquid water on the surface. In this study, adsorption of carbon dioxide on a Clay Mineral Society standard containing nontronite was studied over a wide range of pressures in the absence of water. Similar experiments were conducted on the pure nontronite extracted from the natural sample. Heating curves were obtained to help characterize and determine the purity of the clay sample.

Experimental Procedure: The Clay Mineral Society standard used was SWa-1, a ferruginous smectite from Grant County, Washington. Except for routine crushing, the unpurified samples were not treated prior to use.

The natural sample was crushed and suspended in water via disaggregation by sonification. Particles <2 μm were isolated by filtration and centrifugation. The final SWa-1 product was flocculated with MgCl$_2$. Excess salt was removed from the clay using
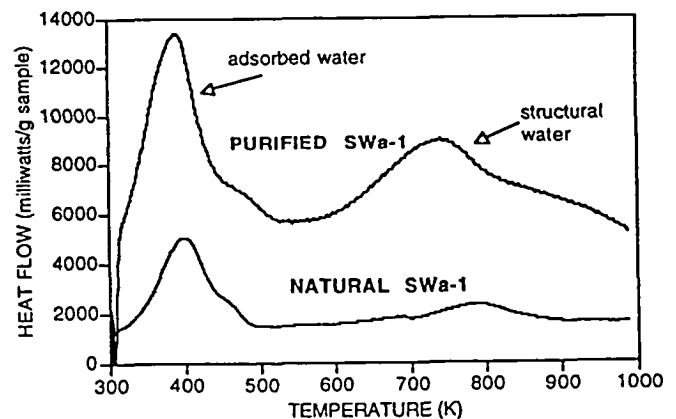

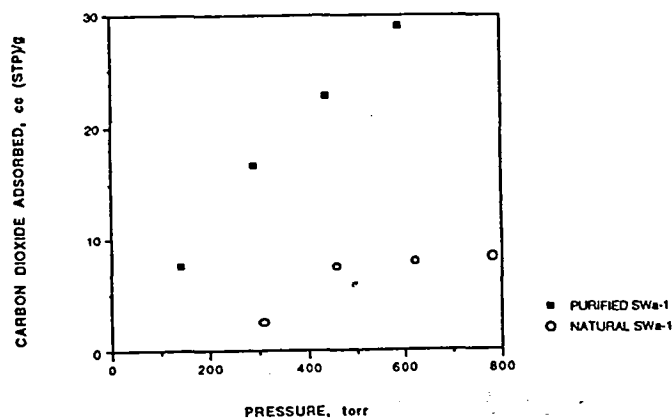Fig. 1. Heat flow curves for natural and purified SWa-1.

Fig. 2. Comparison of carbon dioxide adsorption capacity for natural vs. purified samples.

dialysis. Water was removed by freeze drying. The resulting sample was a fluffy yellow solid. For the adsorption studies, the samples were placed in a Waring blender on the low power setting for 15 s in order to provide uniformity in the samples. Sample sizes of 0.25 g were used in each trial.

The apparatus used in the adsorption studies consisted of a stainless steel vacuum rack with a removable glass sample holder. The volume of the entire system was 90.0 cm³, and the volume of the sample flask was 60.5 cm³. The volume occupied by the sample was considered in the calculation of gas adsorbed.

A sample was placed in the flask, and the entire system was evacuated to a pressure of about 10 μm. To remove any residual gases, the stainless steel line was heated with a heat gun and the sample flask was warmed to 343 K (70°C) in a heating mantle during evacuation. When a constant pressure of about 10 μm was obtained, the sample chamber was brought to the desired temperature, and the valve to the vacuum pump and the stopcock to the sample flask were both closed. The sampling line (of predetermined volume) was then filled with carbon dioxide, and the pressure was measured with an electronic manometer. The stopcock to the sample flask was slowly opened, the final pressure was measured, and the amount of carbon dioxide adsorbed by the sample was calculated.

Heating curves were obtained with a Perkin-Elmer DSC-7 Differential Scanning Calorimeter (DSC) using a scan rate of 20 K/min under argon gas purge of 18.5 cm³/min.

Results and Discussion: In the purification step, the yield of pure product was 36% by weight. Nontronite content of the natural clay, measured by differential scanning calorimetry, was 30% (Fig. 1). With increasing temperature, changes in heat flow indicate the release of adsorbed and interlayer water under 500 K and release of structural (hydroxyl) water between 600 and 900 K.

The adsorption capacity for the purified sample was significantly greater than for the natural smectite. Figure 2 shows carbon dioxide adsorption for natural and purified SWa-1 samples. Adsorption was three times greater on the purified sample. As expected, adsorption increased with increasing pressure for all samples studied.

Conclusion: Significantly greater carbon dioxide adsorption occurred on the purified sample. Thus, when using terrestrial clay samples as analogs for martian soils, especially when making comparisons between studies, the purity of the clay mineral sample should be considered.

Studies at lower temperatures and on an additional CMS standard (NG1) are in progress. Although these studies were initiated to determine head-space pressures in sealed containers of martian soils upon heating, the adsorption data may also be useful in estimating the magnitude of the regolith carbon dioxide reservoir.

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N93-31946

LOW-TEMPERATURE FORMATION OF MAGNETIC IRON OXIDES.

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Elemental analysis and magnetic measurements of the surface of Mars have indicated the presence of an iron oxide with a considerable magnetic moment [1]. Identification of the oxide phase(s) is an important subject as this may be used to identify the process of weathering on the martian surface as well as the composition of the Mars regolith itself. Consequently, we have been interested in evidence of new formation of strongly magnetic phases (e.g., magnetite, maghemite, feroxyhyte) in terrestrially derived Mars sample analogues. Within the group of Mars sample analogues derived from low-temperature weathering of basalts in Arctic regions we have never observed evidence of magnetic oxides formed at the outermost weathering rind. However, in one instance where we investigated the weathering products accumulating in a crack of a basaltic stone we have found evidence of magnetite. Below we present the experimental details.
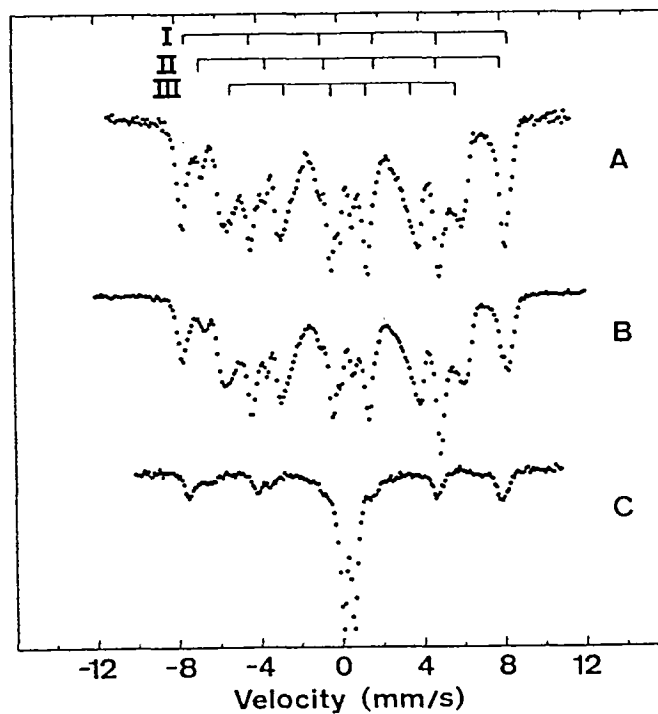

Fig. 1. Mössbauer spectra of the magnetic fraction obtained at 298 K (a, b) and 368 K (c). Spectrum B was obtained in a magnetic field of 0.6 T applied perpendicular to the γ rays. I, II, and III: see text.

TABLE 1. Mössbauer parameters of components I and II at 368 K.

Component	$B_{hf}(T)$	σ(mm s^{-1})	ϵ(mm s^{-1})	A_{rel}(%)
I	47.4 ± 0.5	0.23 ± 0.05	-0.05 ± 0.10	26 ± 2
II	45.2 ± 0.5	0.71 ± 0.05	0.08 ± 0.10	14 ± 3

The sample was collected as a loose powder from a crack in a basaltic stone that was exposed upon splitting the stone. A magnetic fraction was obtained using a ferrite magnet and studied by Mössbauer spectroscopy. All the oxide components found in the magnetic fraction were also observed in the spectra of the nonfractionated powder; however, here the relative intensity was slightly lower.

Figure 1 shows the Mössbauer spectra of the magnetic fraction obtained using different experimental conditions. The room-temperature spectra may be considered to consist of three magnetically split sextets and one ferric doublet. Roman I, II, and III denote the three sextets. The strong polarizing effect of the magnetic field on components I and II indicates the presence of at least one strongly magnetic (ferrimagnetic) oxide in the sample. Component III is due to goethite and in order to minimize overlap of component III, particularly with component II, we have obtained a spectrum at a temperature close to the Néel temperature of goethite (see Fig. 1c). Table 1 gives the parameters of components I and II at 368 K.

The Mössbauer parameters of components I and II are similar to those of magnetite (Fe_3O_4) although they do not exactly match literature values for pure stoichiometric magnetite [2].

This study has demonstrated that magnetic iron oxide (nonstoichiometric magnetite) has formed during low-temperature terrestrial weathering. The details of the formation of magnetite is not known.

In relation to conditions of weathering on Mars it is notable that the formation of the magnetite has included precipitation from solution in a restricted microenvironment (crack) and not on the exposed surface of the rock.

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N93-31947

IMPLICATIONS OF ISOTOPIC COMPOSITIONS OF N AND Ne IN THE MARTIAN ATMOSPHERE TO TEMPORAL EVOLUTION OF ITS ATMOSPHERE AND REGOLITH. D. Lal, Scripps Institution of Oceanography, Geological Research Division, La Jolla CA 92093, USA.

The isotopic compositions of N and Ne in the martian atmosphere are governed by several factors, principal among which are the temporal evolution in (1) the absolute surface pressure of oxygen, (2) the physicochemical characteristics of the regolith, and finally (3) the ^{15}N enrichment expected due to preferential hydrodynamical escape of ^{14}N (due to solar wind bombardment). Each of these factors is unique to Mars. In fact, no other planet offers the uniquely favorable situations for ^{15}N and ^{21}Ne enrichments. The cosmogenic production of ^{15}N is, in particular, unique. It promises to provide very valuable constraints on the temporal evolution of the martian CO_2 and H_2O, both in the atmosphere and regolith.

The rate of production of cosmogenic (spallation) ^{15}N is dependent on the surface pressure of oxygen, the principal target element

for formation of ^{15}N. In view of the relatively high O/N ratio in the martian atmosphere, relatively high $^{15}N/N$ ratio are expected to arise from cosmogenic reactions. The added bonus comes from the fact that an appreciable production of ^{15}N is expected in the martian regolith because of its thin atmosphere.

We show from model calculations that if accurate isotopic composition data become available for N and Ne, it should be possible to put robust constraints on the time averages martian oxygen surface pressure and subsurface water in the upper layers. Cosmogenic N and Ne isotopes formed in the martian rocks would not be expected to be released to the atmosphere; however, those formed in surface and subsurface water reservoirs, as well as in any amorphous weathering products, would be released to the atmosphere. An interesting fact is that whereas the atmospheric ^{15}N production is linear with the surface pressure of oxygen, the regolith production of ^{15}N is not, due to atmospheric absorption of cosmic ray energy. Furthermore, cosmogenic Ne isotopes are expected to be produced primarily in the regolith. Hence, it is possible, given accurate isotopic data on N and Ne isotopic compositions in the martian atmosphere, to delineate possible temporal changes in the martian oxygen surface pressure and its regolith. Should a martian surface sample become available, the conclusions can be made very robust.

We present model calculations of expected N and Ne isotopic compositions in the martian atmosphere for a number of hypothetical models, based on scenarios for the martian regolith from Viking Lander experiments, together with Earth-based observations of Mars and studies of SNC meteorites.

N93-31948

PRELIMINARY RESULTS OF AN EXPERIMENTAL STUDY OF THE INTERACTIONS OF BASALT GLASS AND A WATER VAPOR ATMOSPHERE: IMPLICATIONS FOR WEATHERING ON MARS. J. J. Mazer, J. K. Bates, and C. R. Bradley, Chemical Technology Division, Argonne National Laboratory, Argonne IL 60439, USA.

Models of weathering processes on the surface of Mars invoke hydrothermal alteration as the primary mechanism responsible for clay formation. Previous experimental studies of basalt glass interactions with water under hydrothermal conditions (i.e., high dilution; glass-surface-area-to-solution-volume ratio (SA/V) is small) demonstrate that phyllosilicates and zeolites are the primary alteration minerals [1-3]. Gas-solid weathering is thought to be less thermodynamically favorable and relatively unimportant [4,5]; however, the experimental alteration of basalt glass under vapor hydration conditions (large SA/V) can result in the formation of clay minerals, zeolites, and hydrated calcium silicates [1].

We have undertaken a study of the reacted layers formed on basalt glasses experimentally altered under vapor hydration conditions to resolve this issue. High SA/V ratios promote reaction product build-up in solution and promote alteration mineral formation. It has previously been shown that these reaction conditions promote weathering processes similar to those found in nature for tektite glasses [6], rhyolitic glasses [7,8], and basalt glasses [1]. The hydration of basalt glass is described for 100% relative humidity experiments at temperatures at 150°C, 175°C, and 200°C for up to 400 days. Preliminary characterization of the alteration layers with analytical electron and scanning microscopy suggest that the reaction mechanism includes precipitation of a smectite clay on the outermost surface of the glass. Between the clay and the unreacted glass is an amorphous gel-like phase (palagonite). Our results provide an experimental basis for

proposing that basalt glass interactions with vapor atmospheres can be an important source of clay minerals. Therefore, the process of weathering igneous rocks on the surface of Mars by contact with the atmosphere may be more important than previously thought.

Extrapolating the results of experiments performed at high temperatures (>100°C) to conditions relevant to the surface of Mars is only meaningful if the glass weathering processes are the same in both systems. Assuming identical processes are occurring on the surface of Mars and in our experiments, direct extrapolation of the results to 0°C results in a alteration rate of approximately 0.05 μm/yr. A significant effect of relative humidity on alteration rates in vapor hydration experiments has been demonstrated for rhyolitic glasses [9]. Thus, the limited amount of water in the martian atmosphere probably means that the actual weathering rate may be significantly lower.

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N93-31949

MARS BRINE FORMATION EXPERIMENT. Jeffrey M.
Moore[1], Mark A. Bullock[2], and Carol R. Stoker[1], [1]Space Sciences Division, NASA Ames Research Center, Moffett Field CA 94035, USA, [2]Department of Astrophysical, Planetary, and Atmospheric Sciences, University of Colorado, Boulder CO 80309, USA.

Evaporites, particularly carbonates, nitrates, and sulfates, may be major sinks of volatiles (e.g., CO_2, N_2) scavenged from the martian atmosphere [1–3]. Mars is thought to have once had a denser, warmer atmosphere that permitted the presence of liquid surface water. The conversion of atmospheric CO_2 into carbonate is hypothesized to have degraded the martian climate to its present state of a generally subfreezing, desiccated dessert (see review in [4]). The rate for such a conversion under martian conditions is poorly known, so the timescale of climate degradation by this process cannot be easily evaluated. If some models are correct [e.g., 1,2,5,6], carbonate formation may have been fast at geological timescales. The experiments of Booth and Kieffer [7] also imply fast (10^6–10^7 yr) removal of the missing CO_2 inventory, estimated to be 1–5 bar [2], by means of carbonate formation. The timing of formation of many of the fluvial features observed on Mars is, in large part, dependent on when and how fast the atmosphere changed. A knowledge of the rate at which carbonates and nitrates formed is also essential to assessing the probability that life, or its chemical precursors, could have developed on Mars [4]. No previous experiments have quantitatively evaluated the rate of solution for a suite of mobile anions and cations from unaltered minerals and atmospheric gases into liquid water under Mars-like conditions. Such experiments are the focus of this task.

The presence of water-soluble cations and anions in the martian regolith has been the subject of speculation for some time [e.g., 8]. Viking lander data provided evidence for salt-cemented crusts on the martian surface. This evidence is in the form of lander imagery of friable soil layers and planar fragments of disturbed soil [e.g., 9,10], and the detection of abundant sulfur and some evidence for chlorine

in the soil [e.g., 11]. Martian sulfur is very likely to exist in the form of sulfate, and chlorine in the form of chlorides [11], chlorates, or perchlorates [12]. Following the Viking landings, there was considerable discussion of other salt-forming materials that "should" exist on the martian surface, including carbonates [e.g., 13] and nitrates [e.g., 3,14]. Very recently, Earth-based IR spectroscopic evidence has been obtained indicating the presence of carbonates as well as sulfates and other hydrates on the martian surface [15]. Carbonates have been detected in the SNC meteorites that are commonly believed to have a martian origin [16]. If the crusts observed at the two Viking landing sites are, in fact, cemented by salts, and these crusts are globally widespread, as IRTM-derived thermal inertia studies of the martian surface seem to suggest [e.g., 17], then evaporite deposits, probably at least in part derived from brines, are a major component of the martian regolith. The composition of liquid brines in the subsurface, which not only may be major agents of physical weathering [8] but may also presently constitute a major deep subsurface liquid reservoir [18], is currently unconstrained by experimental work.

A knowledge of the chemical identity and rate of production of martian brines is a critical first-order step toward understanding the nature of both these fluids and their precipitated evaporites. Laboratory experiments are being conducted to determine the identity and production rate of water-soluble ions that form in initially pure liquid water in contact with Mars-mixture gases and unaltered Mars-analog minerals. The main components of the experiment apparatus consist of 10 identical, hermetically sealable sample containers made of Teflon. The interior volume of the containers is 250 ml. The lids of each container have two ports to which are fixed stopcocks to provide gas flow access to the head space when needed. Above one of the stopcocks a stainless steel vacuum/gas line fitting was mounted. Eight of the containers will be kept within a large (and heavy) bell jar. The bell jar's mouth is sealed to its base plate with vacuum grease. The bell jar base contains two gas ports. Each port has a stainless steel gas line running from the exterior of the base. One line is attached to a cylinder of gas with the same mixture as that of the martian atmosphere. The entire assembly of bell jar and enclosed sample containers set within a large refrigerator whose interior can be maintained at 20° ± 0.5°C. The other two sample containers also reside within the refrigerator.

The experiment pilot run set consists of 10 samples. Individual pristine minerals to be used to simulate martian rocks were chosen on the basis of SNC meteorite mineralogy. Six of the samples are composed of 50 g of sorted and mixed minerals (57.2% augite, 25.26% forsterite, 13.14% anorthoclase, 3.14% ilmenite, 0.78% pyrite, and 0.48% chloroapatite) acting as unaltered Mars rock analogs immersed in 100 ml of deoxygenated, doubly distilled liquid H_2O, and above which the head space is filled with a martian gas mixture (CO_2 95.50%, N_2 2.70%, Ar 1.60%, O_2 0.13%, CO 0.07%). These six containers will be the source of the principle data to be obtained by this pilot run set. Two other sample containers are filled with the same materials as those just discussed but with terrestrial gas in their head space. The results of the analysis of their fluids will provide some ability to compare the "martian" vs. terrestrial environmental influence, which in this case is only the difference between the two atmospheric compositions. Two other sample containers hold 100 ml of deoxygenated, doubly distilled H_2O and martian gas mixture in the head space (no rock particles). These serve as controls. The rock/gas/water or gas/water mixtures are allowed to interact with one another for specific time durations, then the reactions are stopped by the removal of the fluid, which is stored under argon in the transfer containers. The individual run durations

were chosen on the basis that most chemical reaction rates (including those that are grain-rind diffusion limited) decay exponentially with time.

The experimental matrix is as follows:

Sample Number	Run Duration (in days)	Sample Composition
1	1	Water/Mars Gas
2	1	Water/Rock/Mars Gas
3	42	Water/Rock/Mars Gas
4	84	Water/Rock/Mars Gas
5	84	Water/Rock/Earth Gas
6	168	Water/Rock/Mars Gas
7	336	Water/Rock/Mars Gas
8	336	Water/Rock/Earth Gas
9	672	Water/Rock/Mars Gas
10	672	Water/Mars Gas

The eight Mars gas-containing containers were placed within the bell jar. The bell jar is flushed with Mars gas. The bell jar and the two containers with Earth gas in their head space reside within a refrigerator, whose temperature is maintained at a constant 20° ± 0.5°C. The temperature is periodically monitored with an analog (Hg-containing) thermometer that sits within a depression on the bell jar base (exterior to the bell jar). The gas pressure within the sample containers is 1 bar.

When sample interaction is terminated, the container is removed from the bell jar. The fluids of the samples are analyzed for their pH and for a number of cations and anions. The cations to be searched for are Fe, Mg, Al, K, Na, Ca, Ti, Mn, and Ba with minimum quantity detection limit of 1 ppm. The anions to be examined are Cl^-, F^-, SO_4^-, SO_3^-, NO_3^-, NO_2^-, and CO_3^- with minimum detection limits of 10 ppm.

The results of the pilot run set will provide the first experimental determination of the rates of formation and relative abundances of the common water-soluble cations and anions that form in liquid water in contact with initially unaltered "martian" rocks and the gases of the present martian atmosphere for up to two years after initial contact. If an equilibrium composition is recognized or can be extrapolated from trends in the production rates, then a model martian brine composition will be established. Such a brine can then be synthesized in any lab. The dehydration of the model brine could be used to create a model martian evaporite.

The presence of brines on Mars has been hypothesized, both as a crustal store of H_2O-rich liquid and as an agent of chemical rock weathering. The physical properties of martian brine can be evaluated by making solutions of brine at various concentrations, guided by the results of this experiment, and then measuring such parameters as density and freezing point. The model martian brine can also be used in rock weathering experiments or calculations. An extension of this work would be to investigate the effect of brine/evaporite composition on clay mineral chemistry. The spectral signature of the model evaporite can be compared with spectral data to be obtained from past, present, or forthcoming missions and observations.

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N93-31950

EFFECT OF DCB EXTRACTION ON MÖSSBAUER AND SPECTRAL DATA FOR A HAWAIIAN PALAGONITIC SOIL (PN-9): IDENTIFICATION OF PIGMENTARY PHASES.   Richard V. Morris[1], D. C. Golden[1], J. F. Bell III[2], H. V. Lauer Jr.[3], and J. B. Adams[4], [1]Code SN4, NASA Johnson Space Center, Houston TX 77058, USA, [2]NASA Ames Research Center, Moffett Field CA 94035, USA, [3]Lockheed ESC, Houston TX 77058, USA, [4]University of Washington, Seattle WA 98195, USA.

Introduction: The study of palagonitic soils is an active area of research in martian geoscience because the spectral and magnetic properties of a subset are spectral and/or magnetic analogues of martian bright regions [e.g., 1–6]. An understanding of the composition, distribution, and mineralogy of ferric-bearing phases for palagonitic soils forms, through spectral and magnetic data, a basis for inferring the nature of ferric-bearing phases on Mars. Progress has been made in this area, but the dataset is incomplete, especially with respect to the nature of pigmenting phases. The purpose of this study is to identify the nature of the pigment for Hawaiian palagonitic soil PN-9 by using extraction procedures to selectively remove iron oxide phases. This soil was collected at the same locale as samples Hawaii 34 [1,2] and VOL02 [4]. All three soils are good spectral analogues for martian bright regions.

Sample and Methods: The <1-mm size fraction (obtained by wet sieving with Freon) of bulk PN-9 soil was used for this study. A citrate-dithionite-bicarbonate (DCB) method was used to extract free ferric oxides as described by [7]. Untreated and DCB-extracted samples of PN-9 were studied by diffuse reflectance spectroscopy, Mössbauer spectroscopy, and scanning electron microscopy.

Mössbauer Mineralogy: Mössbauer spectra (293 K) of PN-9 before and after DCB extraction are shown in Fig. 1. Both spectra are characterized by a ferrous doublet with quadrupole splitting (QS) of ~3.0 mm/s, a weak ferrous doublet with QS of ~2.1 mm/s, a ferric doublet with QS of ~0.70 mm/s, and a magnetic sextet with a hyperfine field (B_{hf}) of ~51.0 T and QS of ~−0.17 mm/s. The ferric doublet with QS ~3.0 mm/s most likely results from unweathered olivine. The assignment for the other ferrous doublet is pyroxene and/or glass.

Of the common ferric oxide/oxyhydroxide phases, hematite (Hm) is the most reasonable assignment for the sextet. The values of B_{hf} and QS for PN-9 are in good agreement with the corresponding values of 51.2 T and −0.22 mm/s for bulk-Hm [e.g., 8]. Maghemite, goethite, and lepidocrocite are not reasonable assignments because at 293 K their bulk forms are characterized by QS = 0.0 mm/s, B_{hf} = 38.0 T, and B_{hf} = 0.0 T respectively [e.g., 8]. The skewed shape of the lines could result from a second magnetic phase, a range in the composition of the hematites resulting from Ti substitution, and/or hematite particles in the diameter range ~20–140 nm.

The ferric doublet most likely results from nanophase ferric oxide particles (np-Ox). Np-Hm (hematite particles having diameters less than ~10 nm) is characterized by the same Mössbauer parameters [9], but unique assignment to this or any specific np-Ox is not possible
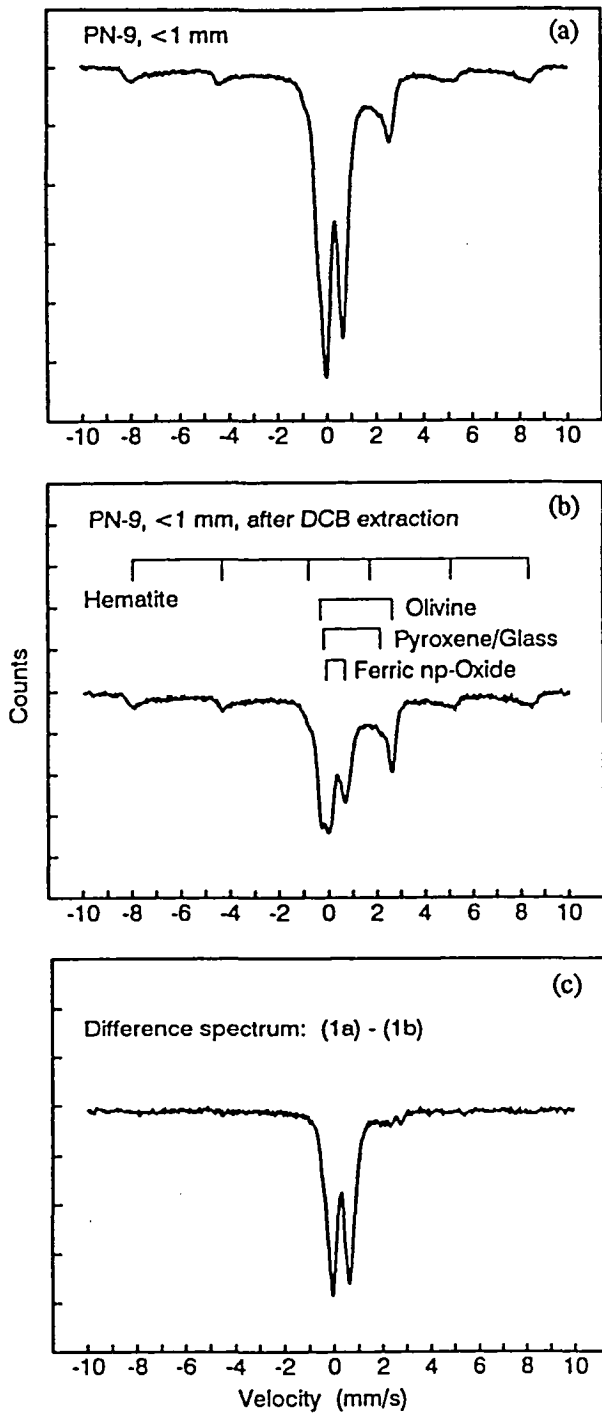
Fig. 1. Mössbauer spectra (293 K) for the <1-mm size fraction of PN-9.

based on Mössbauer data. Direct observation of np-Ox particles in palagonitic soils has been made by [7] using transmission electron microscopy. They found Fe-rich regions ~10 nm in diameter within the glass matrix of palagonitic soil particles that were obtained from a sample whose Mössbauer spectrum was dominated by a ferric doublet.

Effect of DCB Extraction: Comparison of the Mössbauer spectra of PN-9 before (Fig. 1a) and after (Fig. 1b) DCB extraction shows the procedure preferentially removed the np-Ox. This is shown directly in Fig. 1c, which is the spectrum obtained by

subtraction of spectrum 1b from 1a under the constraint that the resulting spectrum has no positive peaks. Note that the ferric doublet resulting from np-Ox is present. The presence of a residual ferric doublet in the DCB-extracted sample implies some of the np-Ox was protected from the reagent, probably by being imbedded within a glass matrix as observed by [7]. The np-Ox extracted by DCB was probably derived from porous surface rinds where they are readily accessible to the reagent. This view is supported by SEM results that show that DCB treatment removed Fe-rich surface regions. Chemical analysis showed ~38% of the total Fe was removed by DCB extraction.

The effect of DCB extraction on the reflectivity spectra of PN-9 is shown in Fig. 2. The untreated PN-9 sample shows a ferric absorption edge through the visible that gives the sample its characteristic brown color. There is a pronounced inflection near 480 nm, a relative reflectivity maximum near 750 nm, and a shallow band near 850–900 nm. After DCB extraction, the sample is grey because the ferric absorption edge is at shorter wavelengths. The spectral slope in the near-IR is negative and the 750-nm feature is the reflectivity maximum. A shallow band centered near 900 nm is also present. The reflectivity data clearly establish that the pigmentary phase for PN-9 is DCB extractable. The Mössbauer data identify the pigmentary phase as predominantly np-Ox particles. The position of the band at 850–900 nm and Mössbauer data are both consistent with
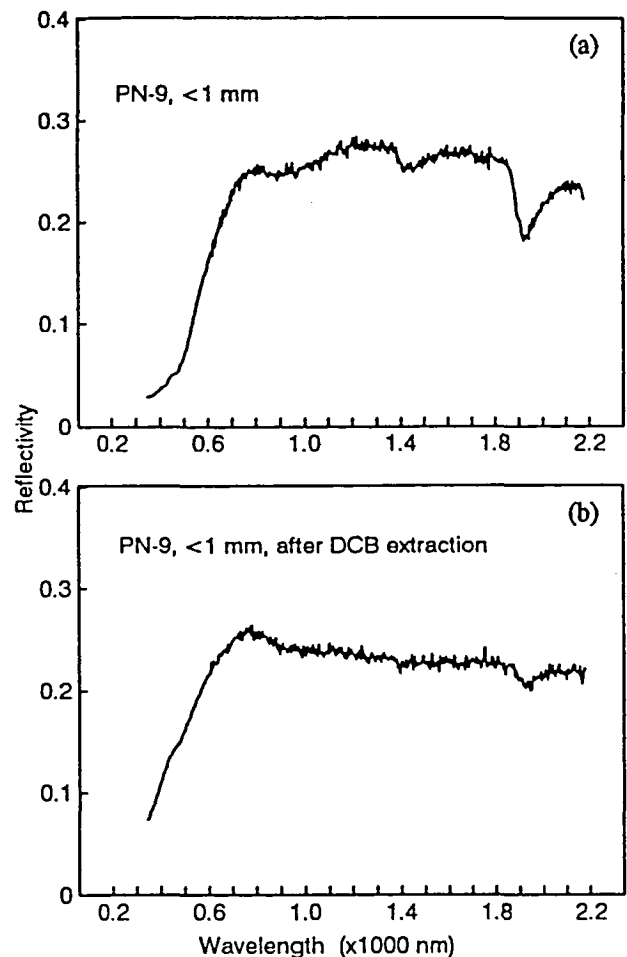

Fig. 2. Diffuse reflectivity spectra (293 K) for the <1-mm size fraction of PN-9.

the presence of well-crystalline (bulk) hematite in PN-9. However, evidence for bulk-Hm is not indicated in the reflectivity data after DCB extraction even though Mössbauer data show it is still present. A possible explanation is that the bulk Hm remaining after DCB extraction is located in particle interiors and is thus observable by Mössbauer spectroscopy but not reflectance spectroscopy.

Summary: The correspondence in spectral properties between palagonitic soil PN-9 and martian bright regions implies the nature of the pigmenting phases also corresponds. Mössbauer and reflectivity data obtained before and after DCB treatment of palagonitic soil PN-9 show that DCB removed the pigmentary phases and identify them as ferric np-Ox particles together with minor bulk Hm. The presence of bulk Hm on Mars has been inferred in other studies [e.g., 6,9–11]. The main contribution of this study and that of [7] is identification of np-Ox particles as a pigmenting agent for palagonites and, by inference, for Mars.

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N93-31951

SYSTEMATIC VARIATIONS IN THE SPECTRAL PROP-ERTIES OF BRIGHT REGIONS ON MARS.   Scott Murchie[1], John Mustard[1], Janice Bishop[1], James Head[1], Carle Pieters[1], and Stephane Erard[2], [1]Brown University, Providence RI 02912, USA, [2]University of Paris, Orsay, France.

Introduction: Color and albedo of the martian surface define two basic surface units, dark gray material interpreted as relatively unaltered "rock" and bright reddish material interpreted as weathered "soil" [1,2]. Understanding the processes contributing to soil formation first requires assessment of the soil's composition and compositional diversity. In this abstract, we report first results of an investigation of the character and variability of Fe- and water-bearing phases in bright reddish materials using ISM data. Based on previous information on martian surface chemistry, we also explore implications of these results for chemical evolution of martian soil.

Information on the composition and distribution of bright reddish material comes from three major sources: Viking images, measurements by the XRF and GCMS instruments on the Viking Landers, and spectroscopic data. The XRF experiment found nearly identical, Fe-rich major-element compositions comparable to weathered basalt [3]. Soil water, amounting to ~1–3 wt% as measured by the GCMS, was liberated mostly by heating to $\geq 350°C$, suggesting that it is present in a chemically bound form [4]. Spectroscopic studies have detected ferric oxide, probably hematite [1,5,6], as well as molecular water [7]. However, the identities of major silicate phases have been controversial, with conflicting evidence regarding phyllosilicates [8,9]. Two main interpretations of this evidence have been proposed: (1) Weathering of basaltic glasses by H_2O and CO_2 formed a mixture of oxides, salts, and metastable phyllosilicates such as montmorillonite [10] and (2) "palagonite" formed when basaltic melt contacted ground ice or water [11,12]. Palagonite is a hydrated basaltic glass containing dispersed ferric oxide, recrystallized in varying degrees to phyllosilicates [11,13]. Typically it is aphanitic, although some examples contain phenocrysts [14]. In either case, eolian redistribution is thought to have resulted in the material's global homogenization.

Imaging spectroscopic data returned by the ISM instrument on Phobos 2 provide a powerful new basis for evaluating the composition and origin of martian soil because they are indicative of the presence and distribution of water- and Fe-bearing phases whose mineralogy is sensitive to the history of chemical weathering. ISM returned 9 images approximately 24 × 120 pixels in size, with 22-km spatial resolution and 128 spectral channels covering the wavelength range 0.76–3.16 μm [15]. Water- and Fe-related absorptions in this range include H_2O at ~1.9 and ~3.0 μm; H_2O and OH at ~1.4 μm; OH at ~2.78 μm; metal-OH at 2.2–2.3 μm; ferric oxides and oxyhydroxides near 0.9 μm; and pyroxene near 1 μm and 2 μm. Initial calibration of these data and atmosphere removal were described by Erard et al. [16]; calibration refinements are described elsewhere [17]. The high signal-to-noise ratio within each image (up to 500:1) results in high sensitivity to the presence of weak absorptions.

Procedure: We are using Viking Orbiter images and ISM data to investigate the presence, distribution, and relation to surface geology of water- and Fe-bearing phases in bright reddish materials. Our initial investigations have covered Valles Marineris, the surrounding Tharsis plateau, and Arabia, which exhibit a variety of
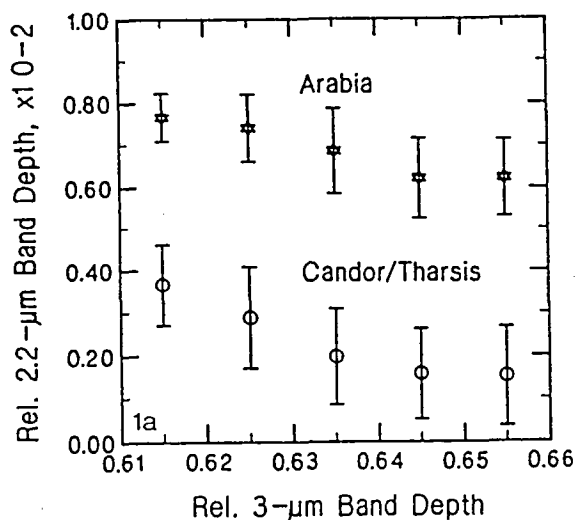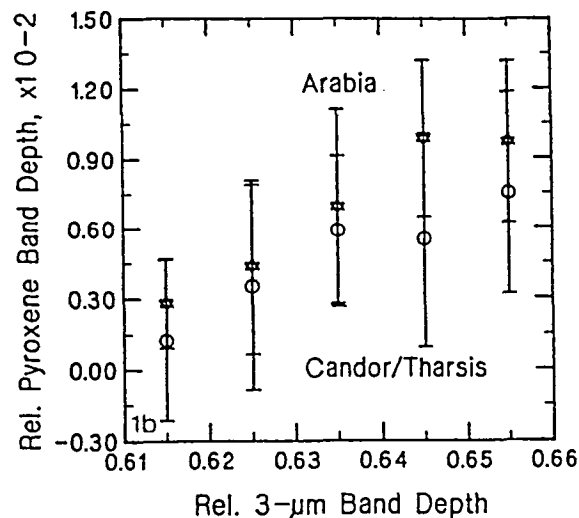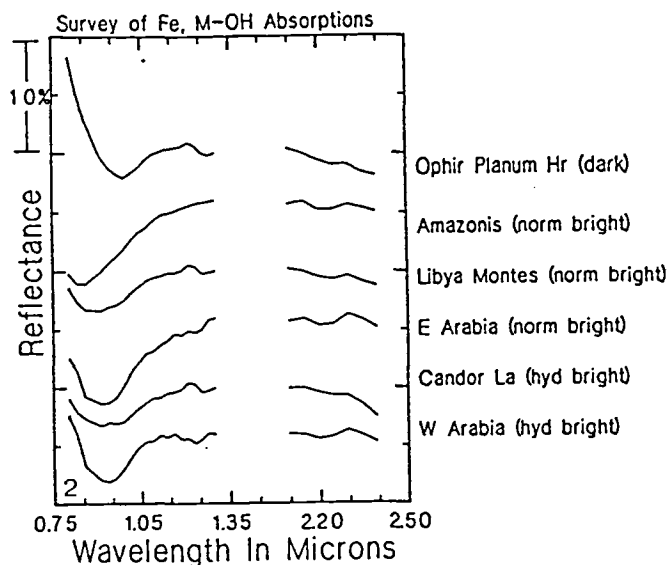
Fig. 1a.

Fig. 1b.

Fig. 2.

geologic units. Surficial geology of each area was mapped using Viking images. ISM data were analyzed initially by reconnaissance of spectra from different regions. Parameterized images of strengths of absorptions due to water- and Fe-bearing phases were then calculated. Regions recognized as spectrally heterogeneous were examined in detail by extracting and analyzing representative spectra. Identification of absorptions and variations in their strengths were constrained to meet the criteria of presence of a distinct absorption, exhibition of spatially coherent variations, and occurrence outside major atmospheric absorptions where calibration artifacts are most likely. The last criterion is best satisfied by the absorptions expected for Fe-bearing phases, the 3-μm H_2O absorption, and 2.2- to 2.3-μm metal-OH absorptions.

In parallel work, laboratory measurements of Mars analogues are being used to assess possible soil compositions. The analogues include a suite of Icelandic and Hawaiian palagonites, plus SWy montmorillonite clays with different exchanged ions in interlayer sites. Reflectance spectra were measured at 0.3–3.2 μm, at 25°C with ~50% relative humidity and after heating to 175°C and 275°C to simulate the dehydrated state of martian soil found by the GCMS experiment. Water contents at each temperature were estimated using thermogravimetric analysis of duplicate aliquots.

Modes of Occurrence of Bright Reddish Material: Surface deposits of bright reddish material occupy two basic geologic settings in the study regions. First, they occur on cratered, ridged, and volcanic plains, as a surface layer thin enough not to obscure hundreds-of-meters-scale topography. This mode of occurrence at the Viking Lander sites is characterized by discontinuous coverage of rocky surfaces by unconsolidated sediment [18]. The second mode of occurrence is as kilometers-thick deposits in Candor Chasma and western Arabia, which are overlain unconformably on older, eroded surfaces. Bright materials in this mode obscure up to even kilometers-scale topography of the underlying terrain. The deposits in Candor Chasma consist of "layered materials," whose lower-albedo morphologic equivalents elsewhere in Valles Marineris exhibit pyroxene absorptions interpreted to indicate a basaltic lithology [19]. The deposits in Arabia consist of a Hesperian-aged mantling partly stripped away by eolian processes [20].

Spectral Heterogeneities in Bright Reddish Materials: The strength of the 3-μm H_2O absorption exhibits lateral variations of several percent within bright reddish materials (Fig. 1). The variations are spatially coherent and independent of albedo and atmospheric path length, thus representing physical variations rather than calibration or optical artifacts. In fact, the variations are correlated with surface geology. "Normal" bright areas, with less strong absorptions, correspond to surface morphologies indicative of only a thin cover of dust and soil (e.g., cratered plains). In contrast, "hydrated" bright regions with stronger absorptions correspond to unconformable deposits in Candor Chasma and western Arabia. Both exhibit stronger 3-μm H_2O absorptions than do dark gray regions.

Representative spectra synoptically illustrate the "normal" and "hydrated" regions' spectral systematics (Fig. 2). The H_2O absorption at 1.9 μm is too weak ($\leq$0.3–0.5%) to observe. However, there is a weak, narrow absorption at 2.2 μm with a depth of up to 1.5%, which meets the above criteria for validity. This absorption is attributed to AlOH bonds in a phyllosilicate. It is present in "normal" bright regions, but weaker or absent in the two "hydrated" regions as well as most or all dark gray regions. Within and around each "hydrated" region, strengths of the 2.2-μm and 3-μm absorptions are inversely correlated (r,~–0.7) (Fig. 1a). This relationship substantiates identification of the 2.2-μm absorption, and provides information on local variations in the chemical form of water: If strength of the 3-μm absorption is indicative of water content, then more water-rich bright materials are also less hydroxylated.

"Normal" bright regions exhibit absorptions consistent with one or more ferric-bearing minerals. Most have an absorption ~3–4% deep with a band minimum near ~0.86 μm, consistent with hematite. Eastern Arabia is distinct, with a stronger (~5–6%) absorption having a band minimum near ~0.93 μm. In contrast, "hydrated" regions' Fe absorptions are broadened toward longer wavelengths: Candor Chasma exhibits two minima, at ~0.86 and ~0.96 μm, and western Arabia exhibits a minimum at ~0.95 μm. Both "hydrated" regions also exhibit a broad, weak absorption centered at ~2.1 μm that is weaker or absent in "normal" bright regions (Fig. 1b). These observations suggest that the "hydrated" regions also contain ferric iron plus pyroxene as an additional Fe-containing phase.

Water-related Absorptions in Laboratory Analogs: At room temperature, Fe-montmorillonites contained ~7–11% H_2O and palagonites 13–24%, with the large water contents producing nearly saturated 3-μm absorptions. All samples exhibited significant 1.4-, 1.9-, and 2.2-μm absorptions, which were stronger in the clays, presumably due to their greater crystallinity [cf. 10]. The 2.2-μm absorption was consistently the weakest water-related absorption. After heating to ~275°C, the analogues acquired more Mars-like
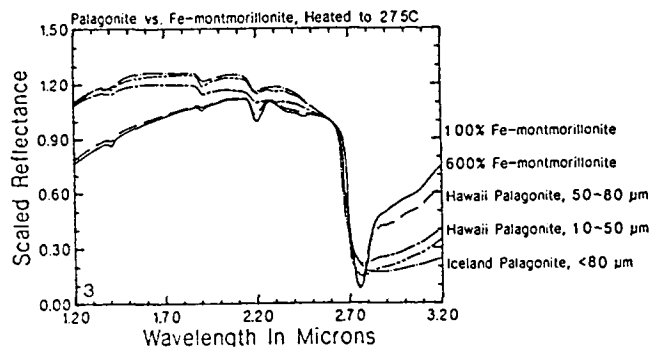

Fig. 3.

water contents and spectral properties. H₂O content dropped to ≤1% for the clays and 3–4% for the palagonites. Three-micrometer band strengths decreased in all cases, but by the largest amounts in the clays (Fig. 3). Strengths of the 1.4- and 1.9-μm absorptions decreased to less than that of the 2.2-μm absorption; the clays retained a stronger 2.2-μm absorption than in the palagonites. These and similar results reported by Bruckenthal [21] are understandable in terms of crystallinities of the analogues: H₂O incorporated in the glassy structure of palagonites is held more tightly than electrostatically bonded water in crystalline clay. As a result, under dehydrating conditions palagonites exhibit greater water contents and stronger 3-μm absorptions than clay. Conversely, the less crystalline palagonite exhibits a weaker 2.2-μm absorption.

Possible Compositional Interpretations: In light of Viking Lander elemental abundances and the experiments with laboratory analogues, the 2.2-μm absorption in "normal" bright reddish material is interpreted to indicate presence of dehydrated, iron-rich montmorillonite. This interpretation is supported by 0.4–1.1-μm reflectance spectra of the laboratory analogues, which demonstrate that montmorillonite saturated with ferric iron reproduces Mars' characteristic spectrum in that wavelength range [22]. However, regional variations in the 0.9-μm Fe absorption imply a degree of chemical heterogeneity inconsistent with global homogenization.

The relationship of "normal" and "hydrated" bright materials is constrained by the stronger 3-μm absorption, weaker 2.2-μm absorption, and stronger 2-μm pyroxene absorption in the "hydrated" regions. The "hydrated" regions' weaker 2.2-μm absorption and stronger 2-μm pyroxene absorption cannot be explained simply by mixing of dark gray and "normal" bright materials because of the weak 3-μm H₂O absorption in dark gray material. However, at least two models can explain spectral differences between the two types of bright reddish material as resulting from soil-forming processes.

Model 1. "Hydrated" materials consist of "normal" bright material and basalt fragments, cemented by hydrated salts and perhaps ferric oxyhydroxides into a "duricrust" like that at the Viking Lander sites [18]. The intergranular cement masks the 2.2-μm absorption.

Model 2. "Hydrated" materials are deposits of palagonitized basaltic glass containing pyroxene phenocrysts, from which a glassy fine-grained fraction has been partly removed and redistributed regionally by wind. Reaction of the fines with H₂O and CO₂ formed montmorillonite [cf. 10], which became dehydrated to form "normal" bright material.

We are currently expanding our studies to additional bright reddish regions, to further determine the character of spectral heterogeneities and to evaluate models for their origin.

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COMPOSITION OF WEAKLY ALTERED MARTIAN CRUST: CLUES FROM IMAGING SPECTROSCOPY.

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Introduction: Two of the fundamental questions regarding chemical weathering on Mars are the chemical pathways by which pristine crustal rocks are altered to produce observed ferric iron-bearing assemblages and inferred clay silicate, sulfate, and magnetic oxide phases, and the timing of the oxidative weathering. High-spatial- and -spectral-resolution imaging spectrometer data provide a tool to investigate aspects of these questions for material exposed on the surface of Mars. In this study, ISM imaging spectrometer data [1,2] are used (1) to develop an inventory of least-altered crustal materials and (2) to quantitatively model the mineralogic composition of the weakly altered crustal rocks.

Spectral Data: High-spatial-resolution (22 km/pixel) imaging spectrometer data were acquired in 1989 by the ISM instrument on board the Phobos II spacecraft for nine different areas near the equatorial regions on Mars [1,2]. The data windows are 300 km wide and 2000 km long and sample a wide variety of terrain and surface morphologies. In particular, the geologic units in the Tharsis plateau and Valles Marineris were well sampled with additional coverage in the Arabia and the Syrtis Major-Isidis regions. A 128-channel reflectance spectrum from 0.76 to 3.16 μm was obtained for each surface element of which 64 are used in these analyses. The signal to noise ratio is >300:1 across most of the detector elements and the absolute radiometric accuracy is ≈10%. Details of data reduction and calibration are presented elsewhere [2,3].

Composition of "Fresh Crustal Materials": Studies of the reflectance properties of Mars suggest that most regions at the scale of an ISM pixel show evidence of ferric material being present, which suggests that altered materials are widespread. Small amounts of ferric oxide can dominate the visible spectral properties, but have relatively little effect at longer wavelengths. Surfaces that are weakly altered, or relatively "fresh," can be identified based on several spectral properties. First, studies of Viking lander and orbiter images demonstrate that, in general, low-albedo materials exhibit the least effects of alteration [4,5]. Second, substantial amounts of ferric oxides would be indicated by an absorption centered near 0.85 μm or a broadening of ferrous absorptions in this wavelength area. Finally, flat continuum slopes are generally thought to indicate an absence of coating of rock surfaces by ferric oxides, although a negative continuum slope does not uniquely confirm an altered surface. Initial investigations of the ISM windows have identified many spectra that meet one or more of these criteria. A subset is shown in Fig. 1.

These spectra represent a broad sample of plains-forming geologic units of different age and surface morphology and all show a strong, well-defined absorption near 1.0 μm and an absorption of variable strength and definition near 2.1 μm. In the spectra that exhibit the strongest absorptions (Nili Patera, Melas Chasma, Eos Chasma), both the 1.0- and 2.1-μm absorptions are very symmetric and they all exhibit a shoulder on the long wavelength side of the 1.0-μm absorption near 1.15 μm. The shape, position, and strength of these absorptions are typical of calcic pyroxene [6,7] and unambiguously confirm tentative identification of this mineral phase on the martian surface made by previous workers [8,9]. The other spectra show diversity in the shape, position, and relative strengths of these two dominant absorptions, suggesting additional mineral phases or compositions are present. In particular, there is great diversity in all
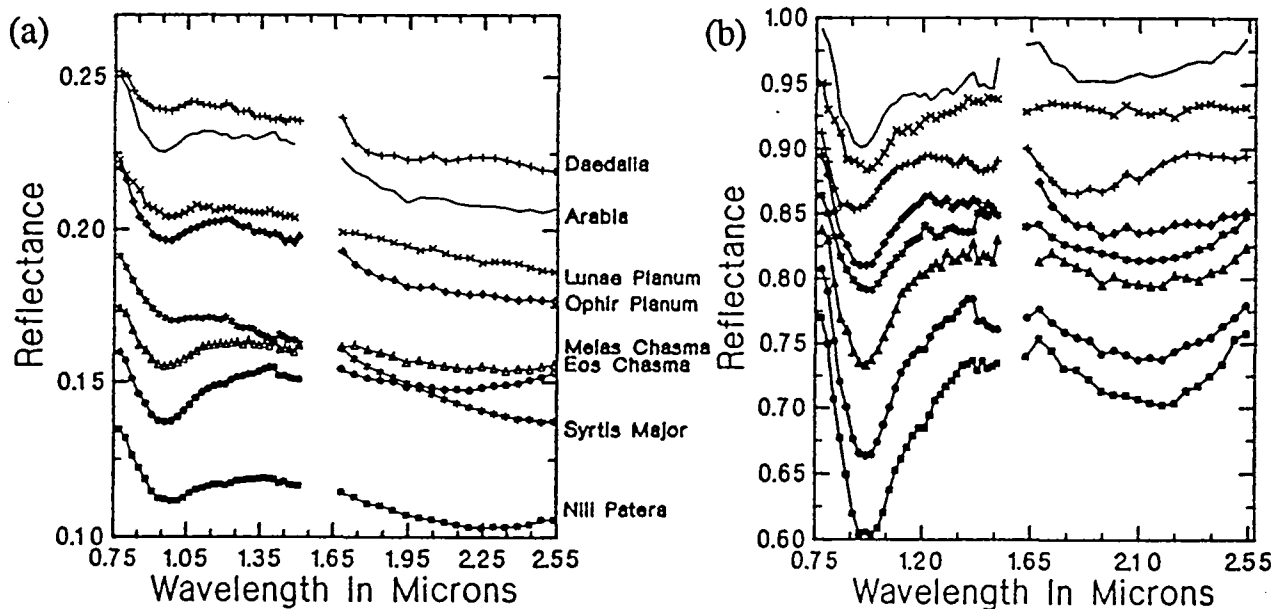
Fig. 1. (a) Representative spectra of low-albedo terrains on Mars interpreted to be of weakly altered crustal materials; labels along the right side give the geographic location from where they were collected. (b) The same spectra as in (a), but with a straight-line continuum removed to emphasize the absorption features. The same symbols are used in both plots. Note the very diagnostic, broad pyroxene absorptions near 1.0 and 2.0 μm.

these spectra in the existence, position, and character of the shoulder between 1.1 and 1.3 μm. This feature can be due to many factors including Fe site populations in pyroxene and the presence of such mineral phases as feldspar, olivine, and glass.

The dominant mineral phase spectroscopically is pyroxene. Reflectance spectra of pyroxenes exhibit variations in the wavelength position of the absorption band minima centered near 1.0 and 2.0 μm that are systematic with composition [6,7,10]. This provides a framework for deriving estimates of the pyroxene chemistry for the surface of mafic-rich regions containing pyroxene. Spectra from Nili Patera on Syrtis Major have been modeled with the Modified Gaussian Model (MGM) [11] to derive quantitative absorption parameters to compare to the results of [7] and derive initial estimates of pyroxene chemistry [3,12]. An MGM solution to the spectrum from Nili Patera is shown in Fig. 2. The data appear to be well fit by a complement of bands for a single pyroxene, although there are very small, systematic errors in the fit to the 2.0-μm band that may indicate an additional pyroxene mineral is present [13]. The band minima determined from this analysis are compared to generalized band minima chemical composition diagrams of [7] from which a Ca/(Ca + Fe + Mg) ratio of 0.275 ± 0.075 and a Fe/(Fe + Ca + Mg) ratio of 0.3 ± 0.1 are derived. The general pyroxene field that these chemical ratios correlate to is shown in Fig. 3.

Discussion: The basic results determined above indicate a basaltic composition for weakly altered crustal materials sampled by ISM. The estimate of bulk pyroxene composition determined above for Nili Patera lies between the pyroxenes augite and pigeonite. Since pyroxenes of such a composition are unusual, this may indicate a mixture of augite and pigeonite, or it may indicate a chemically zoned pyroxene with a similar bulk composition. Such zoned pyroxenes are typical in lunar basalts, which also happen to have very similar spectral properties to the low-albedo regions of Syrtis Major [3]. The strongly zoned pyroxenes in lunar basalts are considered to have resulted from rapid, nonequilibrium cooling during eruption and emplacement of the basalts. A similar set of conditions is likely

for volcanics on the Syrtis Major plateau and elsewhere. Evidence for mineral phases in addition to pyroxene is subtle and the focus of continuing analysis. However, our expectations are that plagioclase will be common, as well as opaque phases and perhaps olivine. We will be continuing detail mineralogic modeling of the low-albedo regions on Mars and extend the analysis performed at Nili Patera to the other regions identified above. This will quantify the diversity of weakly altered crust, and therefore the starting materials for models of chemical weathering on Mars.

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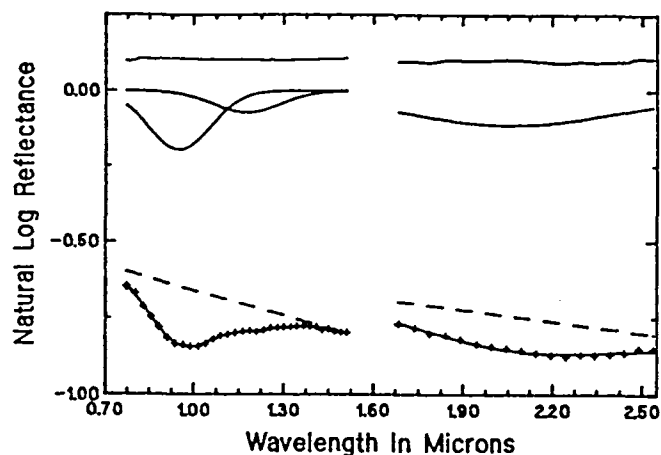

Fig. 2. Fit of the Modified Gaussian Model [11] to the reflectance spectrum of Nili Patera. The actual data are shown by the crosses, the fit by the solid line superimposed on the crosses, the continuum by the dashed line, the model absorptions by the solid curves near the zero reference, and the error of the fit by the solid lines near the top of the plot.
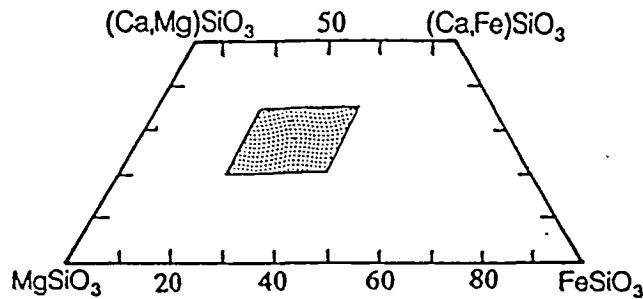
Fig.3. Estimate of pyroxene composition plotted on the pyroxene quadrilateral, based on the results on the MGM model shown in Fig. 2 and comparison to the work of [7] showing the relationship between pyroxene chemistry and reflectance spectra.

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CHEMICAL TRANSPORT DURING FORMATION AND ALTERATION OF MARTIAN IMPACT AND VOLCANIC DEPOSITS. H. E. Newsom, Institute of Meteoritics and Department of Geology, University of New Mexico, Albuquerque NM 87131, USA.

Much of the surface of Mars, including volcanic and cratered terrains, probably experienced alteration and degassing processes. These processes may have depleted or enriched many important elements in surface materials, including bedrock, dust, and soils. The composition of the martian soil may represent the best estimate, for some elements, of the average composition of the martian crust, similar to the composition of loess created by glacial action on the Earth [1,2]. The martian soil may represent the only convenient, globally or regionally averaged sample of the martian crust. In order to understand the composition of the source material for the soil, however, we need to understand the contributions of volcanic vs. impact sources for this material and the chemical fractionations involved in its production. The processes to be addressed include (1) degassing of volcanic deposits, as observed in the Valley of Ten Thousand Smokes at Katmai, Alaska [3,4]; and degassing of melt-bearing impact ejecta as inferred for suevite ejecta sheets at the Ries Crater [5,6]; and (2) alteration or palagonitization of volcanic deposits, as documented for volcanos in British Columbia [7] and many other volcanic terrains, and impact crater deposits [5,6,8]. The process of palagonitization has been the subject of several studies with reference to Mars and palagonite is a good analogue for the spectroscopic properties of the martian dust. The role of impact cratering has not been as well studied, although Allen et al. [8] and Newsom et al. [5,6] have established that both degassing and alteration are common features of impact crater deposits. Other relevant sources of experimental data include the extensive literature on the corrosion of nuclear waste glass [9] and leaching of shocked materials [10].

Chemical Transport in Martian Analogue Systems: There are at least two processes that may result in significant chemical transport in volcanic and impact deposits. The first process is the initial degassing, including the release of volatiles from molten or partially molten fragments. The second process is the release and transport of mobile elements by hydrothermal alteration.

1. Degassing of volcanic deposits and impact-melt-bearing deposits. In studies of the fumaroles at the Valley of Ten Thousand Smokes in Katmai, Alaska, Papike et al. [3,4] have demonstrated that vapor-phase transport of both major and trace elements has occurred. They have studied fumarole deposits located in proximal (dacite) and distal (rhyolite) portions of the 1912 eruptive sequence. Significant enrichments are observed for SO_3, F, H_2O, Zn, As, Cu, Pb, Br, Sn, Sb, and Au with minor enrichments for Ni and Cr. In the rhyolite portions the same elements are observed to be enriched, along with Fe, Mg, Ca, Sr, V, and Sc. Although such enrichments are undoubtedly small volumetrically, some of the fractionations are so large that a general enrichment of broad surface areas of volcanic terrains on Mars are possible. For example, enrichment factors of nearly 50 or greater have been observed for F, V, Sn, Br, As, and Pb in Katmai fumaroles. Equally important is the information that many elements are not observed to be significantly fractionated by the fumarole activity in the dacite, including Si, Ti, Al, Fe, Mg, Mn, Ca, Na, K, Ba, Sr, Ga, Y, and Sc. Some minor depletions of the REE were observed in the altered dacite. In the rhyolite portion, one fumarole that was not subjected to acid alteration showed little fractionation of the REE, while another fumarole affected by acid alteration showed mobilization of all the REE.

Chemical transport within impact crater deposits has not been extensively studied. Transport of volatile elements such as K, Mn, and Br has been reported in impact melt deposits from the East Clearwater Crater [11] and at Brent Crater [12]. These studies were of impact melt deposits located within the impact crater itself, although the impact-melt-bearing ejecta is the material that will be most subject to erosion on Mars. A characteristic of the impact-melt-bearing breccia (suevite) at the Ries Crater in Southern Germany, which is analogous to some fumaroles in ignimbrites, is the presence of degassing pipes. These pipes may represent important conduits for chemical transport. Newsom et al. [5] discussed the possible origin of these pipes by fluidization, and chemical studies will also contribute to understanding the origin of these pipes. They observed the presence of vertical degassing pipes at most of the available outcrops of suevite at the Ries, but the pipes are best exposed at the Otting quarry.

2. Hydrothermal alteration and palgonitization of volcanic and impact deposits. A likely analogue for the martian soil is the alteration product of basaltic glass called palagonite [13,14]. Palagonite is an amorphous or microcrystalline gel-like product formed by a hydrolytic dissolution/precipitation mechanism that results in the formation of well-defined surface layers [15–17]. Work on the formation of palagonite has been stimulated by the similarity of basaltic glass to the types of borosilicate glass proposed for high-level nuclear waste disposal. The rate of formation of palagonite depends on the environment, especially the amount of silica in the fluids. Palagonitization is rapid (3–20 µm/1000 yr) on the seafloor in the presence of silica-undersaturated conditions, but is 2–3 orders of magnitude slower in the silica-saturated conditions often found in drill cores [9]. The palagonite is initially amorphous, but becomes microcrystalline with age and, in the case of freshwater and shallow seawater, palagonite is commonly replaced with authigenic clays and zeolites, usually chabazite ($CaAl_2Si_4O_{12}.6H_2O$). Zeolites are indicators of high reaction progress and are associated with relatively thick palagonite rinds, aluminum loss during palagonitization, and closed-system (low flow rate) conditions during alteration [7].

Chemical fractionations involving major elements during the formation of palagonite have been the subject of several studies, mainly using microprobe techniques [e.g., 18–22]. In general, Si, Mg, and Ca are depleted in the palagonite, while Fe, Ti, and Al are generally unfractionated. In addition, with freshwater exposure, Na and K are generally depleted, while these elements are not depleted during palagonite formation in seawater. Similar results have been obtained in experimental alteration of basaltic glasses [e.g., 17,23]. Trace-element data are available from the freshwater alteration of basaltic glasses from British Columbia [7]. The palagonites for all samples from this study are enriched relative to fresh basalt for Cs, Ba, Hf, Ta, Th, U, and REE. Other elements, including Sr, Rb, Cr, Co, and Ni, are variably enriched or depleted in different samples, with a tendency for Co, Ni, and Cr to be more highly concentrated in high-Al palagonites, and depleted in low-Al palagonites. Other studies of trace-element fractionations during palagonitization have been reported by Staudigel and Hart [18] indicating, for example, that the REE are depleted in marine palagonites, and by Furnes [24] of subglacial hyaloclastite from Iceland, who found that the elements least affected by alteration are Zn, Ni, Y, Ba, and Nb.

Hydrothermal alteration of impact melt sheets and impact-melt-bearing ejecta may have implications for the evolution of the surface of Mars [5,6,8,25–27]. Current estimates suggest a minimum global thickness of impact melt on Mars of 110 m [28]. Evidence of hydrothermal alteration of impact melt deposits on the Earth is ubiquitous [e.g., 8,29]. At the Ries Crater, Newsom et al. [5] showed that the mineralogy of the clays in the suevite at the Otting quarry is consistent with a relatively low-temperature formation, presumably after liquid water had become stable near 100°C. This led to the problem of establishing that the alteration was connected with the thermal event. A paleomagnetic and rock magnetic study [6] provided evidence for hydrothermal alteration occurring immediately following deposition of the impact-melt-bearing breccias (suevite). They found evidence for the formation of maghemite during low-temperature oxidation of titanomagnetite. The maghemite, however, records the same magnetization direction as Ti-magnetite, which recorded the magnetic direction when the suevite was at high temperature. These observations suggest that the low-temperature alteration of the suevite, including clay formation, occurred during hydrothermal alteration shortly after emplacement of the suevite, and not in response to weathering under ambient conditions since crater formation, 15 m.y. ago. Now that the existence of low-temperature hydrothermal alteration of impact-melt-bearing deposits has been established, further work is needed to understand the chemical fractionation that occurs during the formation of the alteration phases. Ries et al. [29] report major-element analyses for the <2-µm size fraction, which can be compared with the composition of the impact melt glass from the same outcrops. They found that Al, Mg, and Fe are usually enriched in the fine-grained fraction, Ti is usually conserved, Si and Ca show minor depletions, and Na and K are usually highly depleted.

Given that the mechanisms for alteration are similar, assuming similar types of parent material, the chemical fractionations observed in impact deposits could be similar to those observed in volcanic deposits. Several aspects of impact deposits on Mars, however, may produce different results from alteration of mafic volcanic material. The alteration of experimentally shocked mineral grains has been shown to be significantly enhanced compared to unshocked mineral grains [10]. The alteration of impact melt glasses may also be enhanced due to the formation of metastable glasses [30]. In addition, impact-melt-bearing deposits on Mars may have much larger fractions of impactor material (up to 40%) compared to

terrestrial impacts (8%). Therefore, if shock-activated weathering of impact-produced glass is a primary source of soils on Mars, then those weathered martian surface materials should be greatly enriched in meteoritic material, which is consistent with the Viking XRF analyses [30].

3. Chemical transport and soil formation: Volcanic processes vs. cratering processes on Mars. The martian dust may be derived from a mixture of altered material at ancient impact sites and altered volcanic material [31]. For example, Squyres et al. [32] have suggested the possibility of large-scale volcano-ground ice interactions on Mars to produce palagonite. Additional investigation of chemical fractionation and transport within impact-melt-bearing deposits is needed to find elements that may discriminate among the alteration mechanisms, including alteration under ambient conditions. From the limited data discussed above, there is little difference in the major-element fractionations observed in suevite and the formation of freshwater palagonite, with the only difference being a slight enrichment of Fe and Al in the altered impact material, which is not present in the palagonite. Compared to the freshwater alteration, however, deep-sea palagonite does not show the pronounced Na and K depletions seen in the altered suevite and the freshwater palagonite. There may also be a distinction in the transport of elements by fumarole-type activity, because transport of the volatile elements K and Mn has been reported in impact melt deposits from the East Clearwater Crater [11] and at Brent Crater [12]. These elements, however, were not enriched in the altered fumarole material in the dacite Drotolith at Katmai.

Conclusions: Understanding the chemical processes involved in the formation of the martian soil may be critical to interpreting chemical data obtained from orbital instruments, landers, and sample return missions in order to determine the bulk composition of the planet. Chemical clues may also be important in sorting out the relative importance of volcanic vs. impact crater sources of the martian soil and the alteration mechanisms, including alteration under ambient conditions vs. hydrothermal conditions. The abundance and distribution of water on Mars is another problem that also concerns issues such as the origin of life and the density of the early martian atmosphere [32,33]. The chemical fractionations associated with hydrothermal alteration such as palagonitization of volcanic terrains or alteration of impact deposits, if they can be observed by remote sensing, could provide clues to the distribution of water on Mars.

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N93-31954

REFLECTANCE SPECTROSCOPY AND GEX SIMULATION OF PALAGONITE AND IRON-RICH MONTMORILLONITE CLAY MIXTURES: IMPLICATIONS FOR THE SURFACE COMPOSITION OF MARS.   J. B. Orenberg, J. Handy, and R. Quinn, Department of Chemistry and Biochemistry, San Francisco State University, San Francisco CA 94132, USA.

Because of the power of remote sensing reflectance spectroscopy in determining mineralogy, it has been used as the major method of identifying a possible mineral analogue of the martian surface. A summary of proposed martian surface compositions from reflectance spectroscopy before 1979 was presented by Singer et al. [1,2]. Since that time, iron-rich montmorillonite clay [3,4], nanocrystalline or nanophase hematite [5], and palagonite [6–8] have been suggested as Mars soil analogue materials.

Palagonite in petrological terms is best described, perhaps, as an amorphous, hydrated, ferric iron, silica gel. Montmorillonite is a member of the smectite clay group and its structure is characterized by an octahedral sheet in coordination with two tetrahedral sheets in which oxygen atoms are shared. The crystallinity of montmorillonite

is well defined in contrast to palagonite where it is considered amorphous or poorly crystalline at best.

Because of the absence of the diagnostic strong 2.2-μm reflectance band characteristic of clays in the near-infrared (NIR) spectrum of Mars and palagonite, and based upon a consideration of wide wavelength coverage (0.3–50 μm), Roush et al. [9] concluded that palagonite is a more likely Mars surface analogue. In spite of the spectral agreement of palagonite and the Mars reflectance spectrum in the 2.2-μm region, palagonite shows poor correspondence with the results of the Viking LR experiment [10,11]. In contrast, iron-rich montmorillonite clays show relatively good agreement with the results of the Viking LR experiment [3,10,12].

This spectral study was undertaken to evaluate the spectral properties of mixtures of palagonite and Mars analogue iron-rich montmorillonite clay (16–18 wt% Fe as Fe_2O_3) as a Mars surface mineralogical model. Mixtures of minerals as Mars surface analogue materials have been studied before [2,8], but the mixtures were restricted to crystalline clays and iron oxides.

Reflectance spectra from 0.3 to 2.5 μm were recorded on a Perkin Elmer Lambda 9 spectrophotometer (Norwalk, CT) using a Labsphere DRTA-9A Diffuse Reflectance and Transmittance Accessory (North Sutton, NH). Reflectance data presented below thus represent hemispherical reflectance. The spectral bandpass was set between 1/5 and 1/10 of the widths at half height of the spectral features of interest by setting the slits to 2.0 nm in the UV/VIS. This allowed for a constant spectral resolution (±10%) in the UV/VIS. In the NIR, an automatic slit program was used to maintain a constant energy level during spectral scanning (120 nm/min).

Mixtures (% by wt) of palagonite with the iron-rich Mars analogue montmorillonite (15.8 ± 0.8 wt% Fe as Fe_2O_3—a full Mars iron analogue) are shown in Fig. 1. In the very important 2.2-μm region, the band due to clay lattice structure becomes noticeable in mixtures at the 10–20 wt% Fe-montmorillonite level. In order to evaluate this observation more quantitatively, a rigorous band depth analysis was carried out [12]. The results indicated that band depth at 2.2 μm is insensitive to the presence of up to 15 wt% Fe-
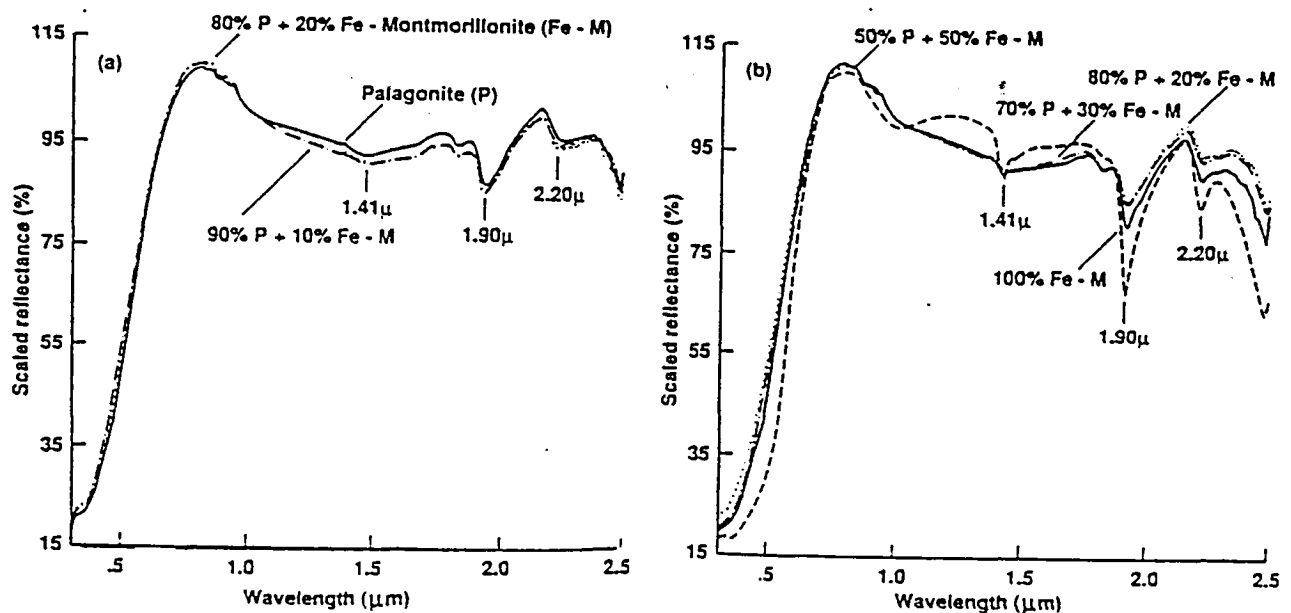

Fig. 1.   A comparison of the diffuse reflectance spectra of different wt% mixtures of palagonite and Fe-montmorillonite (15.8 ± 0.8 wt% Fe as Fe_2O_3). All spectra are scaled to unity at 1.02 μm.

montmorillonite. Above these concentrations, there is an increase in band depth with increasing wt% Fe-montmorillonite (decreasing palagonite), which is attributable to the 2.20-μm absorption feature characteristic of smectite clays. If one accepts the premise that palagonite is a "good" spectral analogue of the Mars surface material, up to 15 wt% of Fe-montmorillonite can be present on the surface of Mars and remain undetected. In spite of the fact that the most recent telescopic observations of Mars do not show evidence of a 2.20-μm band [13], the absence of the 2.20-μm band cannot be used to eliminate less than 15 wt% iron-enriched montmorillonite. The conclusion follows that a Mars analogue, iron-rich, montmorillonite clay can be present on the surface of Mars as a major component (up to 15 wt%) of the Mars soil even if the 2.20-μm band is absent from remotely sensed spectra.

Simulations of the Gas Exchange Experiment (GEX), one of the Viking Lander Biology experiments [14,15], were run using palagonite and iron-enriched montmorillonite. Periodic sampling of the headspace gases above the mineral samples and analysis using gas chromatography was carried out with mineral samples in dry, humid, or wet conditions using a nutrient solution of the same composition as used in the Viking Lander experiments. Interpretation of the data shows that a correspondence to the Viking results occurs with palagonite-iron montmorillonite mixtures. The results will be discussed with reference to the conclusion of the reflectance spectroscopic measurements and previous results of the Labeled Release Viking Biology experiment [3,10].

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N93-31955 $\emptyset \mathcal{F}$

USING THE VIKING BIOLOGY EXPERIMENTAL RESULTS TO OBTAIN CHEMICAL INFORMATION ABOUT MARTIAN REGOLITH.

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Although initially formulated as biology experiments, most of the results produced by the Viking Labeled Release (LR), Gas Exchange (GEX), and Pyrolytic Release (PR) experiments have been reproduced by chemical means [1]. The experiments do not need more study as "biological" phenomena, but they do deserve much more careful consideration from a chemical viewpoint. They are the only "wet-chemical" experiments that scientists have performed on another planet, but they have not found very general use as sources of scientific information. There is a large set of potentially useful chemical observations, e.g., the three resolvable and precisely measured kinetic components of the release of ^{14}C-labeled gases, the thermal sensitivity and magnitudes of the oxidation reaction(s) of the LR experiments, the kinetics and magnitude of the O_2 and CO_2 release of the GEX experiments, the thermal sensitivity of the GEX

results, the differences between the thermal sensitivity of the GEX and the thermal sensitivity of the LR responses, and the kinetics and magnitudes of the LR successive injection reabsorption effect. It should be possible to test many chemical aspects of hypothetical martian phenomena in experiments using the biology experimental configurations and derive much valuable information by comparisons to the Viking observations.

To a considerable extent the underutilization has resulted from the fact that the methods of scientific logic tend to become tailored to specific fields of study [2]. The methods by which information can be derived from the Viking biology experiments do not match well with the currently popular logic methodologies used by chemists and other scientists: The experiments were not designed by chemists; they were biology experiments. However, the necessary methods of chemical logic do exist.

It is suggested that the scientific community would benefit and obtain more information from the Viking results if we were to resurrect a mode of thinking that was widely used in the nineteenth century. It isn't a standard deductive or inductive process, but is a method of reasoning specifically developed to take advantage of observations of chemical reactions. Scientists need to understand the chemical subtleties in this method if they are to effectively judge arguments that invoke the Viking biology results. A superb explanation of this chemical logic was provided by Michael Faraday in his lecture series to groups of young people ca. 1850 entitled "Chemical History of a Candle" [3]. In those lectures Faraday showed how comparisons of the chemical reactions of products formed when a candle burns in air with those reactions occurring with products formed when carbon and hydrogen are burned in air can be used to prove that the wax of a candle is composed of carbon and hydrogen. A similar logical method has been used (with decreasing frequency in recent years) in high school and college qualitative analysis courses where the similarity of precipitates and colors produced by reactions of unknowns and knowns with various reagents has been used to determine what cations and anions are present in an unknown salt. Nowadays basing a proof upon observations of chemical reactions has fallen into disuse and the power of the method is not generally appreciated. Today's scientists do not resort to the these "old-fashioned" proofs; they pride themselves on state-of-the-art apparatus. They would send such samples to the analytical lab for mass spectrometry or atomic absorption tests and draw conclusions by "deductive" arguments based on such physical measurements.

Several aspects of Faraday's logical process must be given careful consideration in designing laboratory studies of the Viking biology results and in drawing conclusions from the experiments. Chemical reaction rates and magnitudes of reactions at equilibrium are usually very sensitive to physical parameters such as temperature, pressure, methods of product detection, and reactor vessel geometry. Unless the correct physical parameters, including the trapped atmosphere of Mars, are built into the simulations, the results can lead to erroneous conclusions [4]. Even such seemingly minor matters as the conditions of storage after sample acquisition and before testing can impact the results, it having been demonstrated that adsorbed H_2O_2, often suggested to explain the LR and GEX results, does not survive the conditions of storage [5].

After establishing that the experimental conditions of the test satisfactorily mimic the actual Viking biology experiments one needs to consider the "resolution" of the tests, i.e., could more than one chemical model produce the same quality of simulation? The resolution, and hence the quality of proof for a particular model, increases greatly with the number of independent observations being replicated. Much of the power of this approach to determining the

chemistry of Mars stems from the fact that so many parameters were measured in the biology tests. It must also be recognized that more than one chemical process may have occurred, but multiple processes are constrained by the fact that those processes must take place simultaneously. Another important constraint is that the conditions required to form the chemical reactant(s) must be consistent with other physical and chemical information about Mars.

A satisfactory chemical model should, with a single assembly of reagents, provide the correct amounts of oxidant and oxygen gas, have the same thermal labilities as those observed on Mars, produce the correct chemical reaction kinetics, and reproduce the LR reabsorption effect. The model should also incorporate the possibility of independently varying the relative magnitudes of the oxidation and oxygen-release reactions, as these were observed to differ at different sample acquisition sites.

To this date only one chemical model for the reactivity of the regolith has met the requirements of this logical process [1]. According to that model the regolith contains peroxonitrite and trapped oxygen gas. Both are generated by UV photolysis of nitrate salts. Also, the carbonate present with the largest k_{sp} is $CaCO_3$, and the pH of the regolith in contact with the atmosphere is about 7.6 [6]. These chemical conditions are expected to have a significant effect upon Mars' surface and atmosphere interactions. The model disagrees in important respects with some ideas being advocated by others [4]. It seems appropriate to offer Viking biology test simulations to any of you interested in using this method to evaluate your chemical models.

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CHEMICAL MODELING CONSTRAINTS ON MARTIAN SURFACE MINERALOGIES FORMED IN AN EARLY, WARM, WET CLIMATE, AND SPECULATIONS ON THE OCCURRENCE OF PHOSPHATE MINERALS IN THE MARTIAN REGOLITH.   Geoffrey S. Plumlee[1], W. Ian Ridley[1], and Jeffrey D. DeBraal[2], [1]U.S. Geological Survey, MS 973, Denver Federal Center, Denver CO 80225, USA, [2]Department of Geological Sciences, University of Oregon, Eugene OR 97403, USA.

This is one in a series of reports summarizing our chemical modeling studies of water-rock-gas interactions at the martian surface through time. The purpose of these studies is to place constraints on possible mineralogies formed at the martian surface and to model the geochemical implications of martian surficial processes proposed by previous researchers. Plumlee and Ridley [1] summarize geochemical processes that may have occurred as a result of inferred volcano- and impact-driven hydrothermal activity on Mars. De Braal et al. [2,3] model the geochemical aspects of water-rock interactions and water evaporation near 0°C, as a prelude to future calculations that will model sub-0°C brine-rock-clathrate interactions under the current martian climate.

In this report, we discuss reaction path calculations that model chemical processes that may have occurred at the martian surface in a postulated early, warm, wet climate [4]. We assume a temperature of 25°C in all our calculations. Processes we model here include (1) the reaction of rainwater under various ambient CO_2 and O_2

pressures with basaltic rocks at the martian surface, (2) the formation of acid rain by volcanic gases such as HCl and SO_2, (3) the reactions of acid rain with basaltic surficial materials, and (4) evaporation of waters resulting from rainwater-basalt interactions. —

Theory of Chemical Reaction Path Modeling: Computer-based chemical reaction path calculations determine heterogeneous chemical equilibrium conditions among minerals, gases, and/or aqueous solutions along an incremental series of specified temperature, pressure, and/or bulk composition changes [5]. Based upon measured or estimated thermodynamic data, reaction path modeling predicts the changes in aqueous solution composition and the resulting amounts of minerals precipitated during specific chemical processes. Because they are computer-based, large numbers of reaction path calculations can be carried out to address the full range of factors influencing a particular chemical process. The chemical speciation and reaction path programs SOLVEQ and CHILLER [5,6] were used in this study.

It should be noted that minerals predicted by the modeling to be stable thermodynamically for a given set of chemical conditions may not actually precipitate in nature due to kinetic factors. For example, Nordstrom et al. [7] note that quartz, illites, smectites, and other aluminosilicates are not likely to precipitate at 25°C except under quite saline conditions; instead, minerals such as chalcedony, kaolinite, and aluminum hydroxides are kinetically stable. Also, ferrihydrite (rather than goethite or hematite) probably controls iron solubility under oxygenated conditions. We have addressed such considerations in the modeling by carrying out both runs in which kinetically inhibited minerals were allowed to precipitate, and runs in which precipitation of these minerals were suppressed, thereby allowing the precipitation of thermodynamically less-stable minerals.

Constraints on the Chemistry of Martian Rainwater: The initial chemistry of rainwater strongly affects the minerals formed during rock weathering. It is thus necessary to constrain the chemistry of martian rainwaters in a warm, wet climate. Lacking detailed information in this regard, we have used in our calculations a range of water compositions reflecting (1) reasonable variations in ambient partial pressures of atmospheric CO_2 and O_2 and (2) possible variations in the input of acidic volcanic gases such as SO_2 and HCl. For example, under current Earth conditions, rainwater in equilibrium with atmospheric O_2 ($pO_2 = 0.2$ bar) and CO_2 ($pCO_2 = 0.033$ bar) has calculated pH = 5.66, dissolved O_2 = 2.5×10^{-4} m/kg, and dissolved CO_2 = 1.3×10^{-5} m/kg. In contrast, martian rainwaters in a postulated warm, wet climate with $pCO_2 = 2.2$ bar [4] and $pO_2 = 10^{-5}$ bar (approximately the same as that for present-day Mars) are calculated to have lower pH (4.08), greater dissolved CO_2 (7.5×10^{-2} m/kg), and lower dissolved O_2 (1.3×10^{-8} m/kg). Our modeling predicts, as expected, that addition of volcanic gases to these waters results in decreased pH and increased levels of sulfate and chloride in solution; the volcanic gas composition used in these calculations is a restored gas analysis from Kilauea, Hawaii [8], that we modified to contain slightly higher concentrations of HCl than those actually measured.

Chemical Modeling of Rainwater-Basalt Interactions: We modeled the interactions of rainwater and basalts by theoretically titrating increments of an assumed martian basalt composition into the various calculated rainwater compositions. To represent martian basalt, we used the composition inferred by Longhi and Pan [9] for the Chassigny parental magma; lacking reported S, Cl, and P, we assumed for our calculations that this basalt composition contains an additional 165 ppm NaCl and 1375 ppm FeS (the median for terrestrial basalts [4,10]) and 0.8 wt% P_2O_5 (the value inferred for the parent magma of another SNC meteorite [9]).

Modeled reactions of the basalt with acid rainwaters (those acidified by volcanic gases and those under high atmospheric pCO_2) initially produce ferric and manganese hydroxides, kaolinite, smectites, chalcedony, and apatite [$Ca_5(PO_4)_3(OH, Cl, F)$] at high water/rock ratios (>100) and low pH values (<5); the greater the initial acidity, the greater the amounts of basalt converted to these minerals. As progressive rock additions cause the pH to rise to near 8 (at water/rock ratios <10), dolomite and calcite are also predicted to form. Reactions of the basalt with less acidic rainwaters are predicted to form mixtures of ferric hydroxides, apatite, carbonates, and smectites. Ferric hydroxides and ferric smectites are predicted to form under all but the most reducing conditions; such conditions probably existed only very early in martian history [4].

Chemical Modeling of Evaporation: Results of paths modeling the evaporation of rainwaters after reaction with basalts varied according to the initial sulfate, chloride, and carbonate content of the waters. Those waters acidified by volcanic SO_2 prior to reactions with basalt produce gypsum as the dominant sulfate mineral with relatively small degrees of evaporation (less than 0.1 wt% H_2O removed); waters that obtain their sulfate solely from dissolution of the basalt precipitate gypsum only after extensive evaporation. Other minerals predicted to form by limited evaporation include dolomite, calcite, potassium feldspar, and sodium feldspar. We are currently modeling the more extreme evaporation conditions needed to produce NaCl, $MgSO_4$, and other soluble salts.

Phosphates in the Martian Regolith: An interesting prediction of our calculations is the formation of apatite during the weathering of basalts containing phosphorus. If aqueous chloride is present in high enough concentrations, the modeling predicts that chlorapatite will form. Our modeling is thus permissive that apatite (or other phosphate phases such as crandallite) could have formed in the martian regolith (1) as an alteration product of basalt and (2) possibly as an evaporation product of phosphate-bearing waters; the extent of phosphate enrichment in the regolith would depend on the primary phosphate content of the basalts, the concentration of phosphate in the waters, and the water/regolith ratio. It is possible that phosphate could partly make up the low totals measured in the Viking analyses [11]. Furthermore, chlorapatite could, if present, serve as a mineralogical host for some of the chloride measured in the regolith.

Summary: Our chemical modeling predicts that weathering of martian basalts in an early, warm, wet climate (with at least some free atmospheric oxygen) would have produced ferric and manganese hydroxides, chalcedony, kaolinite, apatite (or other phosphate minerals), dolomite, and calcite; smectite clays may have also been produced if kinetic barriers to their nucleation were overcome. Acid rain would have enhanced these weathering reactions, and may have provided a source for the high Cl measured in the regolith. Limited evaporation of waters that had previously reacted with basalt leads to formation of gypsum, calcite, dolomite, sodium and potassium feldspars, and some phosphate minerals. Waters initially high in dissolved sulfate and chloride (such as acid rain) require substantially less evaporation to reach saturation with gypsum (and other readily soluble salts) than waters that obtain their sulfate and chloride solely from the rocks. Our modeling also indicates that apatite or other phosphate minerals are likely products of basalt weathering, and should therefore be considered both as possible components of the martian regolith and as possible mineralogical residences for regolith Cl.

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N93-31957

INFRARED OPTICAL PROPERTIES OF MARS SOIL ANALOG MATERIALS: PALAGONITES.   Ted L. Roush, Department of Geosciences, San Francisco State University, San Francisco CA 94132, USA (also an associate at NASA Ames Research Center, Space Sciences Division, Mail Stop 245-3, Moffett Field CA 94035–1000, USA).

The globally distributed bright soils on Mars represent products of chemical alteration of primary igneous materials. As such, understanding the chemistry and mineralogy of these soils provides clues about the nature of the parent materials and the type, duration, and extent of the chemical weathering environments on Mars. Such clues are key in developing an understanding of the interior and surficial processes that have operated throughout Mars' history to yield the surface as it is currently observed. The generally homogeneous nature of these soils is illustrated by a variety of observational data. These data include (1) direct determination of elemental abundances by the X-ray fluorescence instruments on both Viking Landers [e.g., 1–4], (2) Earth-based telescopic observations [e.g., 5–7], and (3) space-based observations [e.g., 8,9].

Based on their spectral properties in the visible and near-infrared, terrestrial palagonitic soils have been suggested as analogs for the bright regions on Mars [10–12]. Palagonites represent the weathering products of basaltic glass and as such are composed of a variety of minerals/materials. In order to gain an understanding regarding the chemical, mineralogical, and spectral properties of a broad suite of palagonites, several samples were collected from the eastern and central regions of the island of Hawaii. The underlying collection strategy was to select samples from a variety of current climatic environments. As a result, samples were collected from regions that have a wide range in the annual amount of precipitation. Additionally, samples were collected from regions that have similar amounts of annual precipitation. For example, the summit region of Mauna
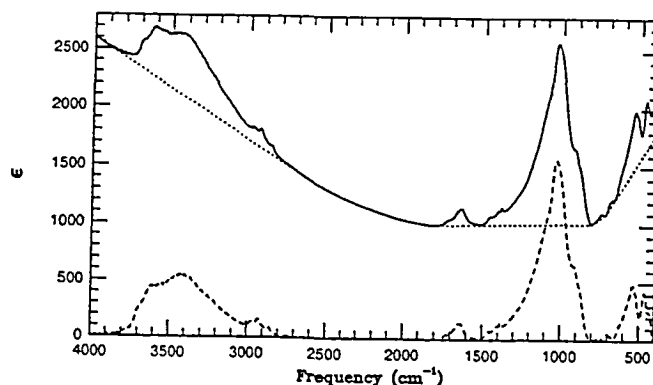

Fig. 1.   Solid line is the initial calculated mass extinction coefficient (ε) of one palagonite sample. The dotted line is the straight line continuum and the dashed line is the difference between ε and the continuum.
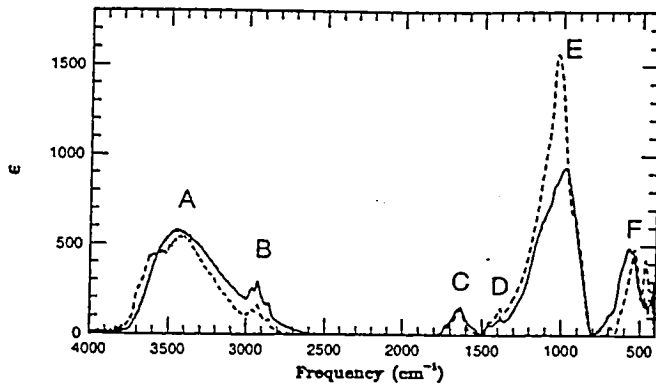
Fig. 2. Continuum-removed ε for two palagonite samples. These curves illustrate the two general classes of spectral behavior. See the text for a discussion of the labeled features.

Kea and the south Point peninsula receive 38 cm and 51 cm of annual rainfall respectively. Because of the proximity of the Pacific Ocean, the south Point region is continuously influenced by spray due to wave action, and additionally is likely to have a higher relative humidity compared to the summit region of Mauna Kea.

Each palagonite sample was dry sieved to the <38-μm grain size fraction. Approximately 0.9–1.3 mg of a palagonite sample was thoroughly mixed with 400 mg of spectroscopic grade KBr in a methanol-powder slurry. After evaporation of the methanol, 200 mg of this mixture was pressed into a pellet using a 12-mm-diameter die at a pressure of 6.89 Kbar for 5 min. Each pellet was placed in the sample beam of a Nicolet 7199 model spectrometer and the transmission was measured at 4 cm^{-1} spectral resolution over the 400–4000 cm^{-1} frequency range. This transmission was divided by the transmission of a pure KBr pellet. The thickness of each pellet was measured with a vernier micrometer after data acquisition. To facilitate a comparison of the spectral behavior of these different samples a parameter is required that describes the intrinsic absorptive properties of the materials. One such parameter is the mass extinction coefficient (ε), which is defined as the extinction per centimeter of a gram of material per gram of KBr. From each ratio spectrum ε was calculated via

$$\varepsilon = \frac{-\log_{10}(T)}{ct}$$

where c is the concentration of the sample in g of palagonite per g of KBr, t is the measured thickness of the pellet in cm, and T is the ratio of the transmission of the palagonite pellet to that of the KBr pellet. Because the scattering properties of the individual pellets can vary substantially, a straight line continuum was fit using the minima points of the ε curves and then subtracted to yield a corrected ε. An example is shown for one sample in Fig. 1. The solid curve is the initially calculated ε, the dashed line is the straight line continuum, and the dotted line is the final ε.

Figure 2 shows ε as a function of frequency for two of the palagonite samples and several extinction maxima are labeled. The broad maxima labeled A and centered between 3400 and 3500 cm^{-1} is due to the O-H stretching fundamentals of molecular water. The triplet feature labeled B located between 2850 and 3000 cm^{-1} occurs in the region of the C-H stretching fundamental, although overtone and/or combination modes of a carbonate group may also yield features at these frequencies. Feature C near 1650 cm^{-1} is due to the H-O-H bending fundamental of molecular water. The feature labeled

D, occurring between 1360 and 1490 cm^{-1}, may be due to either C-H stretching modes or the presence of carbonate groups. The two broad remaining features labeled E and F, occurring in the 1300–800 cm^{-1} and 700–500 cm^{-1} regions, are both due to Si-O vibrations. The higher frequency feature, E, corresponds to the stretching mode while the lower frequency feature, F, corresponds to the bending mode.

Figure 2 also illustrates the major differences observed in the ε of these palagonite samples. There are two classes of spectra. Class A exhibits a single SiO ε peak at frequencies slightly higher than 1000 cm^{-1} with an associated ε doublet located between 400 and 600 cm^{-1}. Class B exhibits a single SiO peak at frequencies lower than 1000 cm^{-1} and an associated singlet near 600 cm^{-1}. It also appears that Class B has a higher ε due to molecular water. Some class A εs also exhibit an indication of structural OH as evidenced by distinctive inflections near 3600 cm^{-1} and between 870 and 940 cm^{-1}.

The identity of the sources of the major, and less distinctive, differences observed in the ε of these samples awaits independent determinations of the chemistry and mineralogy of these samples. Nevertheless, the results from the current study lead to the conclusion that the infrared properties of palagonitic soils from a wide variety of environments generally fall into two categories. The implication for interpretation of Mars thermal infrared data is that perhaps only a limited number of terrestrial analogs need be considered.

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N93-**31958**

THE MARTIAN OCEAN: FIRST ACID, THEN ALKALINE.

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In Mars' distant past, carbon dioxide and water may have been plentiful. Values of total outgassed CO_2 from several to about 10 bar are consistent with present knowledge [1], and this amount of CO_2 implies an amount of water outgassed equal to an equivalent depth of 500 to 1000 m [2]. It is quite reasonable, therefore, to envision an early Mars in which there was a body or bodies of liquid water, perhaps in the northern plains, and a dense carbon dioxide atmosphere.

Under such conditions, the pH of the water will be low, due to the dissolution of carbon dioxide in the water to form carbonic acid [3]. This acidic water is capable of weathering the available rock quite intensely, particularly because this rock is likely to be heavily fractured (from meteorite bombardment) or even consist of fine particles (such as pyroclastic deposits).

As time goes on, however, the carbon dioxide atmosphere will rapidly pass through the ocean to form carbonate deposits. As the density of the atmosphere decreases, so will the flux of carbonic acid into the ocean. Without this input of carbonic acid, the effect of the dissolved weathering products will be to increase the pH of the water. The ocean will then become alkaline. This alkalinity could be even
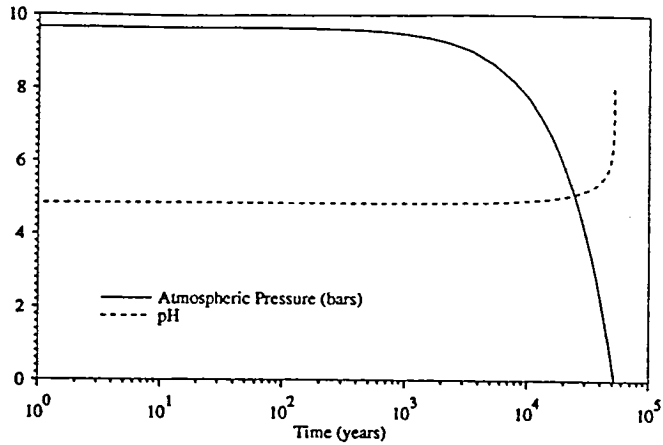
Fig. 1. Plot of the disappearance of a CO_2 atmosphere, and associated increasing alkalinity of the ocean, with time. These results assume no recycling of carbonates back to the atmosphere and no change in salinity.

more enhanced by the evaporation of the water. Such saline bodies of water are resistant to freezing, and this ocean could persist as a liquid body on the surface for an extended period of time. There is at present a hypersaline lake in Antarctica (Deep Lake) that never freezes, even though the average temperature there is well below the freezing point of pure water [4].

To study this process, I have developed a geochemical cycle model for the atmosphere-hydrosphere-regolith system of Mars. The treatment of geochemical cycles as complex kinetic chemical reactions has been undertaken for terrestrial systems in recent years with much success [5–8]. This method is capable of elegantly handling the interactions between the simultaneous chemical reactions needed to understand such a system. Geochemical cycles may be represented mathematically by systems of nonlinear differential equations. These systems, which include equations with timescales of widely differing lengths, are considered "stiff." Such systems require care in the method of integrations, so that a stable solution may be found within a reasonably small time. The present model uses the reverse Euler method, with the computer algorithm based on those presented by Walker [9].

A plot of the decrease in the atmospheric pressure, and subsequent increase in salinity of the ocean, is shown in Fig. 1. Secondary effects of the decrease in water volume, and of the increase in salinity itself, are not included.

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EXPERIMENTAL INVESTIGATION OF CARBONATE FORMATION ON MARS. Stuart K. Stephens[1], David J. Stevenson[1], and Leon F. Keyser[2], [1]Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena CA 91125, USA, [2]Mail Stop 183-901, Jet Propulsion Laboratory, Pasadena CA 91109, USA.

Introduction: If Mars had an early dense CO_2 atmosphere (>1 bar), then the transition to the present low pressure (7 mbar) may require carbonate formation without liquid water (e.g., [1], although [2] questions the early greenhouse on the basis that modeled CO_2 condensation prevents buildup of such a pressure). Our experiments

Fig. 1.

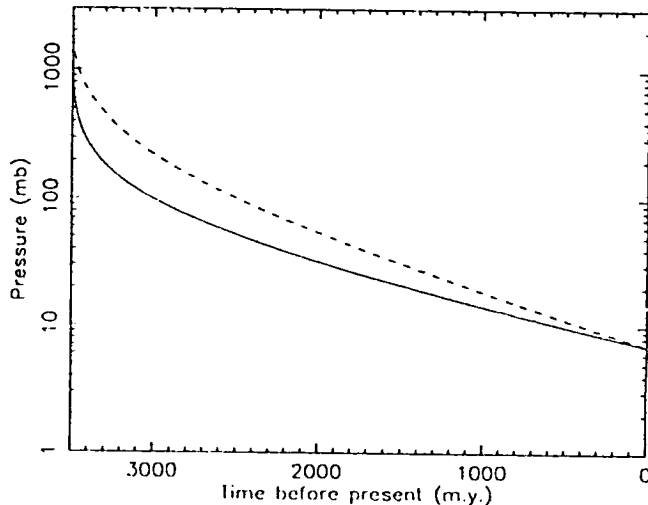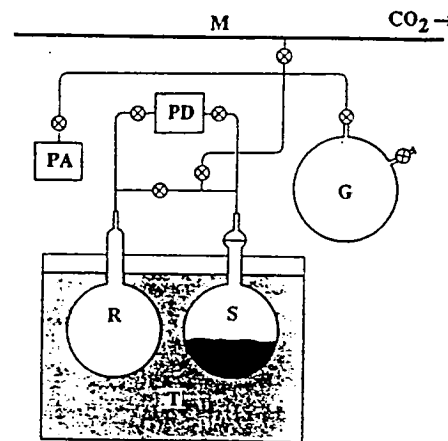M = manifold for gas and vacuum
PD = high precision differential manometer (100 torr F.S., 10^{-5} resolution)
PA = general purpose absolute manometer (1000 torr F.S., 10^{-4} resolution)
G = volume (5 liters) for pre-mixing $CO_2 \pm H_2O$
R = reference volume (≈65 ml)
S = sample container (≈65 ml), with O-ring seal
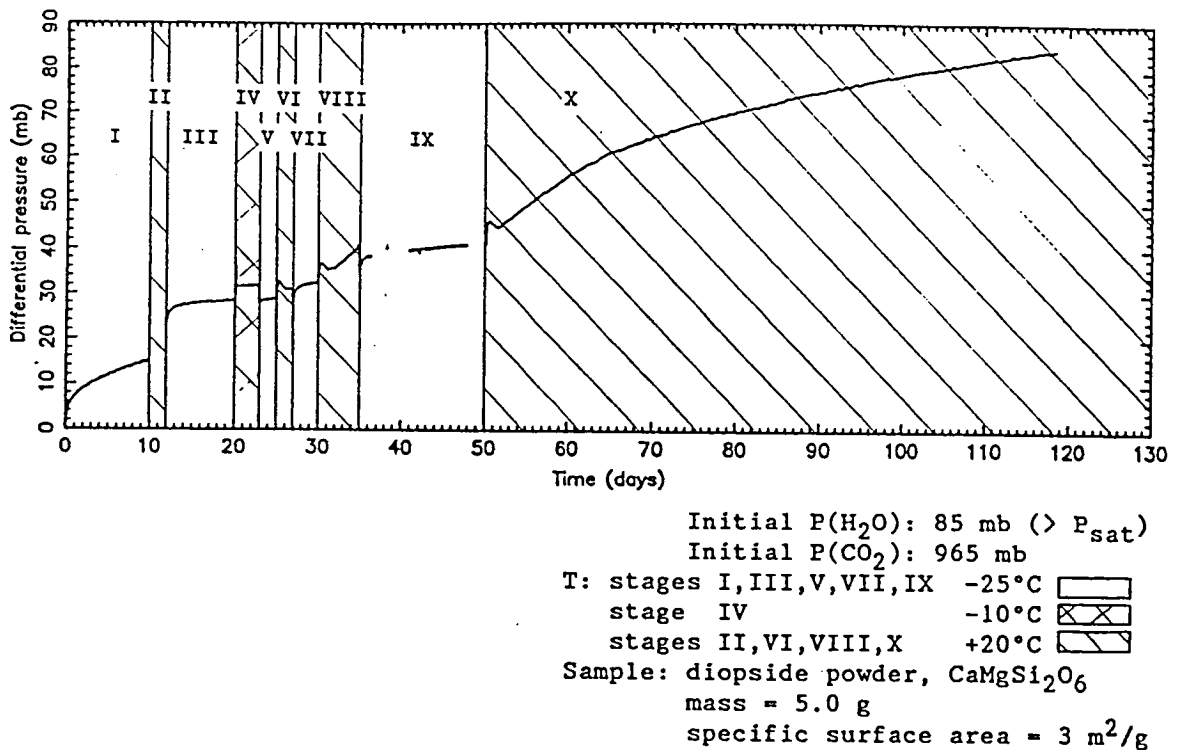T = refrigerated circulating bath (-30°C to +100°C, stability < 0.1°C)

Fig. 2.

Initial $P(H_2O)$: 85 mb $(> P_{sat})$
Initial $P(CO_2)$: 965 mb
T: stages I,III,V,VII,IX   -25°C
    stage   IV   -10°C
    stages II,VI,VIII,X   +20°C
Sample: diopside powder, $CaMgSi_2O_6$
        mass = 5.0 g
        specific surface area = 3 m^2/g

Fig. 3.

[3] have focused on the kinetics of such "dry" reactions. Booth and Kieffer [4,5] suggested rates consistent with removal of >1 bar of CO_2 over geologic time, but their results were questionable since their reactions did not proceed beyond one monolayer of carbonate formed on powdered silicate under martian conditions. Theoretical considerations [1] implied that if nonporous rinds formed, then the rate of carbonate formation would be limited by diffusion, not reaction. Therefore, our experiments optimize reaction conditions to test for continued carbonate production, as well as to verify previous conclusions for initial growth of carbonate.

Models of Diffusion-limited Carbonate Formation: Our previous models [3] envisioned carbonate formation at the CO_2-silicate interface in the presence of carbonate or bicarbonate ions formed by the interaction of gaseous CO_2 with a thin film (monolayer?) of adsorbed OH^- [5]. Considering a tarnishing reaction where the build-up of product is limited not by reaction rate but by diffusion rate, and using reasonable extrapolations from experimentally measured diffusivities, we derived an equation ($dP/dt = f(P)$) describing the history of the CO_2 atmosphere.

Results of this model (Fig. 1, for two diffusivities) show that the CO_2 pressure decays very rapidly in the first few 100 m.y. as a result of higher temperatures and therefore higher diffusivities. More recently than ~2 b.y. ago, the pressure declines gradually—roughly exponentially with a 1–2-b.y. time constant. Buffering effects of CO_2 storage in the regolith and polar ice caps [6] are not modeled and would modify our results slightly.

Present Experiments: *Setup.* Our design (Fig. 2) detects reaction of CO_2 (premixed with H_2O vapor) with powdered diopside to form carbonate, via careful monitoring of pressure changes in a temperature-regulated environment. Booth and Kieffer [4,5] relied on low-P/T simulations of Mars, whereas we optimize experimental conditions for measurement of a reaction rate that will allow us to

extrapolate to martian conditions. (Calculations by Gooding [7] suggest that we are still operating in a thermodynamically favorable regime for the diopside → carbonate reaction.) Also, we use differential pressure measurement in a small volume of atmosphere, instead of relying on acid to dissolve carbonate and infer a reaction [5].

Results. Data from an ongoing (6/92) experiment are shown in Fig. 3. Differential pressure (PD) > 0 corresponds to pressure loss in the sample volume (see Fig. 2). At –25°C, most of the water will be adsorbed or condensed as solid (its vapor pressure will have negligible effect on the pressure change). Note the initial effect of CO_2 adsorption, and the longer-term rate (stage IX), PD ~ 0.2 mbar/day,
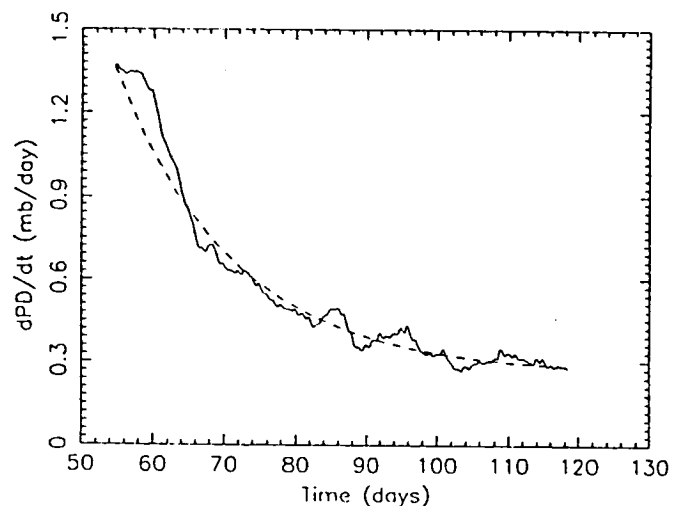

Fig. 4.

of CO_2 loss measured in the sample volume. If this is not a leak or a long-timescale adsorption effect, then it represents a carbonate reaction in the presence of (presumably vapor-phase) water. Since there was a possibility that this $-25°C$ signal represented continued adsorption, we attempted to test this by raising T briefly to $-10°C$ (stage IV), but dPD/dt did not change enough to distinguish adsorption from reaction.

Periods of warmer, wetter conditions ($+20°C$, liquid water possible) occur in stages II (power out → no data), VI, VIII, and X. The initial rise and fall of PD over 1-2 days is due mainly to the competing effects of (1) PD ~ T in the two volumes and (2) desorption of CO_2. The subsequent rapid rise of PD in stages VIII and X is very interesting. Since long-timescale adsorption of CO_2 should be more vigorous at low temperatures, the most likely explanation for our signal is a chemical reaction that takes CO_2 out of the sample volume.

Discussion. Clearly, something is going on in stage X of this experiment. The role of water is not clear: The amount of H_2O introduced is comparable to the total change in pressure, and that suggests the possibility that water is somehow "used up" (one-on-one with CO_2) in a reaction. However, arguing against that, (1) we do not expect water to be destroyed in a carbonate reaction and (2) the total change in pressure is also comparable to that expected due to formation of a monolayer of carbonate (again, assuming one-on-one with CO_2). We have not yet addressed whether any reaction proceeds beyond one monolayer.

In Fig. 4, we plot dPD/dt vs. t, and find that a model of the form PD = a + bt + c exp(-dt), fits well, especially beyond t ~ 65 days. An exponential form is consistent with a process in which something runs out (e.g., water or available surface area). The fact that we achieve a better fit using values of b > 0 suggests that a roughly linear effect contributes to—but is not responsible for all of—our signal. This effect may represent a leak, or it may represent reaction (possibly involving diffusion through a product layer) beyond the surface reaction that takes place as a monolayer of carbonate is formed. A speculative upper limit can be placed on the diffusivity through this monolayer ($D < 10^{-19}$ cm^2/s).

A rate of b ~ 0.25 mbar/day would correspond to CO_2 storage on Mars rapid enough to get rid of 1 bar in 10^4 to 10^5 years (assuming an available specific surface area equivalent to that in a 1-m powdered regolith). This rate is similar to that reported by Booth [5], and is consistent with the diffusion-limited scenario we initially proposed for continued reaction beyond a monolayer [1,3].

Continuing Work: *Analysis.* If a monolayer of carbonate has formed in the experiment described above, then it represents ~0.3 wt% of our sample, which is barely detectable with reflection IR spectroscopy. We therefore intend to analyze the sample at the end of the current experiment. We also have designed an experiment to subject a fresh surface of diopside (crystal) to similar environmental conditions, and analyze the surface composition with X-ray photoelectron spectroscopy (XPS). Any reaction product should be distinguishable from the surface of a control crystal kept in an inert atmosphere. Finally, we intend to better monitor the composition of the atmosphere in our experimental apparatus.

Further experiments and modeling. Aside from focusing on T < 273 K and varying water content, we intend to try other sample compositions (e.g., forsterite—Mg_2SiO_4), greater sample mass, and lower initial $P(CO_2)$. Eventually, we plan to apply experimentally derived reaction rates to models of the past and present CO_2 cycle on Mars (e.g., [8]), which would include the effects of diffusion through a rind, as well as other sources and sinks.

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N93-31960

WEATHERING PROCESSES IMPLIED FROM ANALYSIS OF SMALL MARTIAN AVALANCHE CHUTES. R. Sullivan, Department of Geology, Arizona State University, Tempe AZ 85287, USA.

It has been proposed that the smaller features of martian spur and gully slope morphology, located along the upper walls of Valles Marineris, are avalanche chutes [1]. A three-dimensional stability back-analysis technique was developed and applied to these small avalanche chutes, yielding average values of cohesion and angle of internal friction for the mobile layer materials on these slopes at time of each slope failure [2]. Generally, the analysis showed that at the time of each slope failure material strengths had been reduced to those of moderately cohesive debris down through depths of tens of meters. These results have implications and possible constraints for the nature and rate of martian weathering processes. —

Dry mass-wasting has long been considered responsible for the recession of the walls of Valles Marineris [1,3,4], but no explanation has been offered as to why steep martian slopes have receded, and may still be receding, forming avalanche chutes, talus, and larger spurs and gullies. This is an important issue, because seemingly older, yet well-preserved features (for example, fluidized ejecta impact craters) are prominent on plateaus adjacent to receding/receded scarps. If older topographic features exist on adjacent plateaus in a relatively fresh state, then the clear evidence of slope recession in the intervening time, including prominent talus production, seems paradoxical. The key question is, after all, why should martian steep slopes recede at all? Recession of such prominent slopes represents profound physical change to the martian landscape. Why should a combination of degradational processes affect one set of features—the steep slopes—and not older features nearby?

One possibility is that weathering (and associated weakening) of martian surface materials occurs broadly across the martian surface—not just on steep, receding slopes—but this process or suite of processes is revealed especially on steep, receding slopes by the periodic removal of weathered layers under the influence of gravity. Debris or soils generally have significantly lower strengths than the
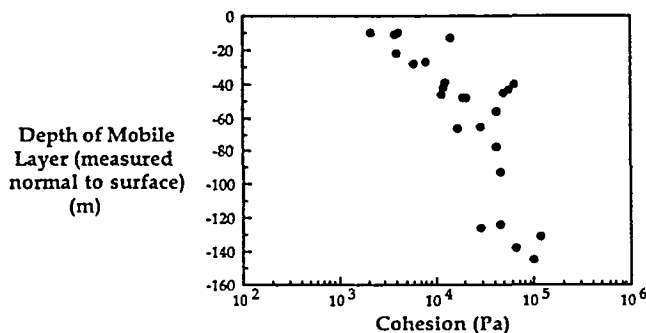

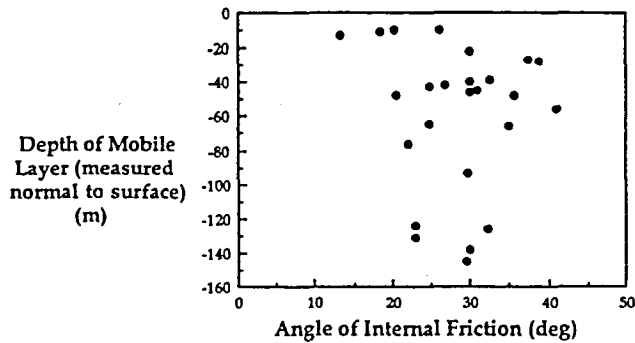Fig. 1.   Cohesion vs. depth for 25 martian avalanche chutes.

Fig. 2.   Angle of internal friction vs. depth for 25 martian avalanche chutes.

rocks they are derived from. Periodic catastrophic mass movement of a weathered, weakened top layer seems inevitable if (1) the weathered material is weak enough, (2) surface sloughing of the top of the weathered layer is minor, and (3) the slope upon which the weathered layer forms is steep enough. The mass-wasting cycle begins with a weak debris layer developing and thickening through a weathering process or suite of weathering processes at the expense of the underlying sloping rock, until the debris layer fails catastrophically under its own weight along the debris/rock interface. Less weathered, more pristine material is exposed by this mass movement, and the cycle repeats. Steep slopes (with correspondingly steep debris/rock interfaces) should develop relatively thin debris layers before layer failure occurs. Gentler slopes will require more extensive weathering and thicker debris development for failure to occur, resulting in avalanche chute floors that are deeper and wider, and have greater longitudinal curvature. The gentlest slopes may never be subject to failure no matter how deeply beneath the surface weathering, weakening, and debris development proceeds.

These ideas, and the results of the three-dimensional stability back-analysis performed previously, build upon civil engineering and geomorphological work by other workers and do not require relatively extended, speculative inferences to be made from the fundamental geomorphological observations. A surface environment other than the current one, or geomorphological processes that current surface conditions do not support (such as running water), have not been called upon to explain the primary observations. However, it is required that a weathering process or suite of processes be capable of weakening martian slope materials to depths of tens of meters. No recourse can be made to slope base removal or other oversteepening mechanisms because no evidence exists for such mechanisms for the small avalanche chutes under consideration in this work. Internal changes within these slopes must have occurred, reducing their stability to the point of failure. Within the original standing slopes, the strength of the materials located along what eventually became failure scars must have decreased.

Considering that the current presence of a mobile liquid solvent in the near subsurface is problematic, the depth range of the indicated weathering activity implies that subsurface materials in the study areas are either drastically out of equilibrium with the martian surface environment, or the state of disequilibrium is less, but that some influential aspect of the surface environment is capable of penetrating the surface to depths of tens of meters. One hypothesis that combines aspects of both of these possibilities is that the subsurface materials originally owe some of their strength to binding of a solid volatile such as some form of ice, and that the low martian atmospheric pressure acts as a penetrating "solvent" that, through

sublimation, carries the binding agent (ice) away into the atmosphere. The sublimation of subsurface ice is an appealing hypothesis in some respects, but the recent presence of subsurface ice in equatorial latitudes is an unsettled question [5] and direct evidence for the existence or nonexistence of subsurface ice (at depths appropriate to this issue) will probably be a long time in coming.

As an alternative to invoking the unproven presence of a volatile ice in the martian near-subsurface, how could our present knowledge of the current surface and near-subsurface environment and its suite of weathering processes explain the geomorphological observations and stability analysis results? This is a difficult task because our knowledge of possible chemical weathering reactions, reaction efficiencies, and products is relatively unconstrained. As yet unmeasured or unimagined characteristics of the martian subsurface environment and its weathering reactions may be responsible. The results of stability back-analysis may offer some useful constraints in addressing this question in the future, however. Figures 1 and 2 represent avalanche chute analysis results plotted such that the average indicated cohesion and angle of internal friction for each avalanche chute mobile layer is plotted vs. the depth (normal to the surface) of each chute floor. A crude "soil profile" of cohesion and angle of internal friction results, and is presented here as a possible constraint for the future analysis of martian weathering processes and products. It should be emphasized that Figs. 1 and 2 are only suggestive and should be used with caution, for together they do not represent a true soil profile from a single location, but are composed of results from 25 different locations and slope angles, and only where slope failure has occurred. For instance, it is not implied here that the stronger materials at the deeper points weather upward to the weaker materials at the points nearer the surface; initial strength variations of pristine parent material from one location to another could account for much of the variation in strength of these presumably weathered products. Nevertheless, these results should be suggestive of the range of cohesion and angle of internal friction values of martian subsurface materials to be found in the study areas. Figure 1 shows that where these avalanche chutes have formed, cohesion increases gradually with depth. Figure 2 shows that angle of internal friction does not vary strongly with depth for the analyzed chutes (as might be expected, for angle of internal friction is not diagnostic for most classes of geological materials). The slight increasing trend with depth in Fig. 2 is probably an artifact; the shallowest chutes were only visible because their average slope angles were shallow, making their headscarps more prominent, and shallow slope angles lead to smaller indicated angles of internal friction in the calculations.

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N93-31961

GEOCHEMISTRY AND SETTING OF MARTIAN(?) "WEATHERING": THE LAFAYETTE METEORITE.   A. H. Treiman[1], R. A. Barrett[2], and J. L. Gooding[1], [1]Code SN2, NASA Johnson Space Center, Houston, TX 77058, USA, [2]Lockheed Engineering and Sciences Co., Houston TX 77058, USA.

Lafayette, one of the SNC (martian) meteorites, contains preterrestrial alteration materials rich in smectite and ferric oxides. The compositions and textures of the veinlets suggest that they were formed in episodic alteration events by waters that contained a relatively small load of dissolved salts.
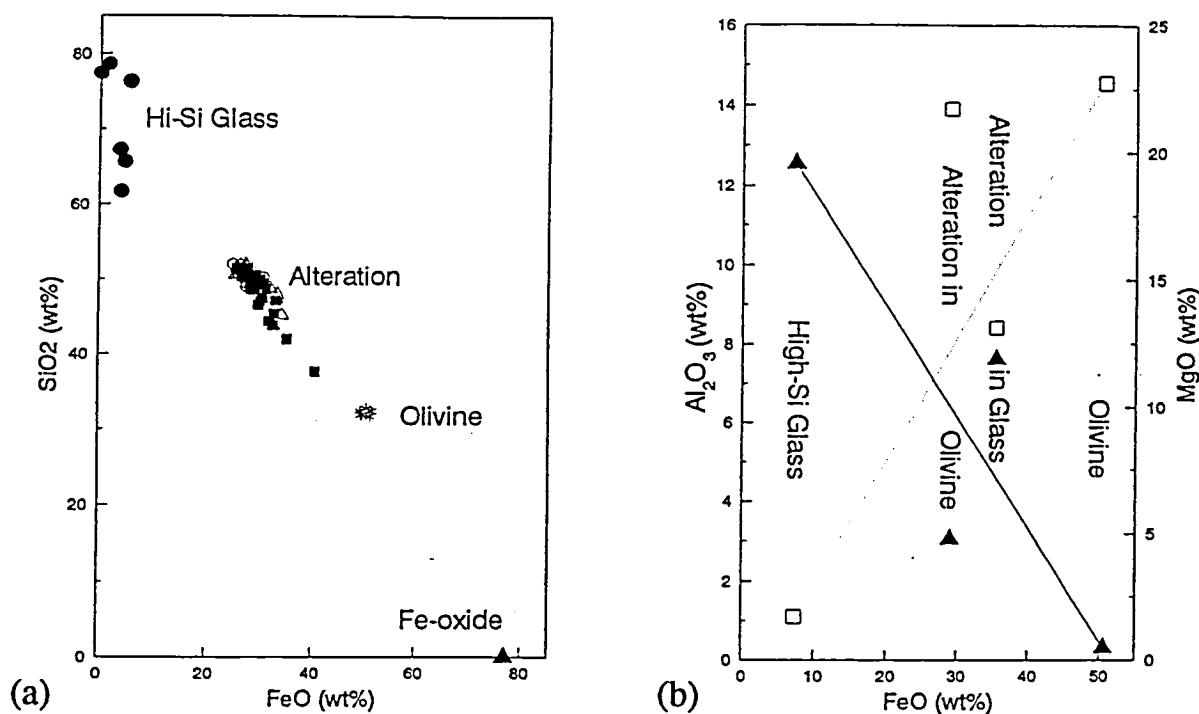
Fig. 1. Chemical relationships among Lafayette's alteration (SEM/EDS analyses). (a) FeO-SiO$_2$. Note that alteration materials are collinear with olivine and high-Si glass. (b) MgO- and Al$_2$O$_3$-FeO. Average compositions of materials in Lafayette: MgO, squares; Al$_2$O$_3$, triangles. Note that alteration materials in a phase are enriched in the essential constituents of that phase (Mg in olivine; Al in glass). Note also that the average composition of all alteration materials is closely approximated by a mixture, the lines, of olivine and high-Si glass (+ water).

The Lafayette achondrite, one of the nakhlites of probable martian origin, is an igneous rock consisting mostly of augite and olivine, with interstitial feldspar, sulfides (pyrite), high-Si glass, and other phases [1–3]. Like Nakhla itself, Lafayette contains veinlets of hydrous alteration materials [1–7].

Sample and Methods: We studied thin sections of sample ME2116 (Field Museum, Chicago), using scanning and transmission electron microscopy (SEM and TEM) with energy dispersive X-ray spectrometry (EDS) as in [4,8]. SEM elemental analyses were done in spot mode (1 μm) and in rastered selected area mode (to 10 μm); TEM elemental analyses were for areas from 100 to <10 nm diameter. Standards were well-characterized minerals; Na abundances in SEM/EDS were corrected for interference from FeL X-rays [7]. SEM/EDS analyses of olivine in Lafayette are nearly identical to EMP analyses from [1–3].

Petrography: Rusty veinlets of aqueous alteration material replace olivine, pyroxene, and high-Si glass, and occur as intergranular films. Olivine is replaced by veinlets and spikes of rhombic cross sections [7]. The veinlets commonly have exterior zones of 3–5-μm phyllosilicate grains, cut by veinlets of <100-nm material ± 100-nm grains of high secondary electron (SEI) brightness. These fine-grained veinlets may cross-cut each other, and commonly have cores with higher SEI brightness than the rims. By TEM, the veinlets consist of felted masses of smectite (platy or fibrous grains, 1.0-nm lattice fringes, composition consistent with trioctahedral clay) and iron oxides, probably hematite and ferrihydrite. These materials are cut by later veinlets consisting of magnetite and void space.

Preterrestrial Origin: These aqueous alteration materials are preterrestrial, as shown by changes in the alteration veinlets as they approach the fusion crust [6,7]. More than 0.5 mm from the fusion crust, veinlets are as above. Between 0.5 mm and 0.3 mm, the

veinlets are as above, and become depleted in volatile elements. Within 0.3 mm of the crust, the veinlets are melted to uniform vesicular glass and lose almost all volatiles. The melted veinlets are cross-cut by the fusion crust. These data suggest that the veinlets existed before Lafayette entered the Earth's atmosphere, and that the veinlets were heated, devolatilized and melted by passage through the Earth's atmosphere [3]. These inferences are consistent with the oxygen isotope data of Karlsson et al. [9].

Composition: The compositions of the alteration materials are consistent with their mineralogy as inferred from SEM and TEM [6,7]. The rough correlation of K and Al is consistent with smectite. Abundances of Cl and S are correlated for analyses with less than 1% SO$_3$ and 0.5% Cl; the remaining analyses are richer in SO$_3$ or Cl. The latter analyses suggest discrete S-rich (sulfate) and chloride phases similar to those in Nakhla [4,5]. Correlation of S and Cl at lower abundance levels suggests a single carrier phase, perhaps ferrihydrite acting as an ionic sorbent.

Among the analyses, abundances of Fe and Si are inversely correlated, and are collinear with the compositions of the olivine and high-Si glass (Fig. 1a). A similar collinearity is seen for Mn and Fe. Imperfect collinearities are seen for abundances of Mg, Al, and Fe (Fig. 1b).

Geochemistry: The alteration veinlets here and in the other SNC meteorites are the only available traces of the hydrosphere on their parent planet, presumably Mars. As such, they may have significant implications for the origins, cycling, and availability of water on Mars. Detailed studies are in progress, and we can here point out a few features of the geochemistry of Lafayette's alteration.

Temperature. Lafayette was altered at low temperatures, almost certainly below 100°C. This limit comes from the presence of ferrihydrite in the alteration materials. Ferrihydrite dehydrates read-

ily to hematite or goethite at temperatures above 100°C [10,11]. On Earth, ferrihydrite and ferroan smectite are most commonly produced during the weathering or low-temperature alteration of basaltic rocks [12–14], notably weathering in the dry valleys of Antarctica [15,16]. The porous oxide alteration materials must also have formed at low temperature; otherwise, ferrihydrite in the other alteration materials would have been converted to other minerals. At such temperatures, the altering phase was almost certainly liquid water.

Oxidation state. The oxidation state of Lafayette's alteration was near or below that of the magnetite-hematite oxygen buffer, distinctly more reducing than the alteration of Nakhla [4,5] or the martian atmosphere. This estimate of oxygen fugacity comes from the presence of magnetite (or maghemite) and ferrihydrite in the alteration materials. Because the assemblage magnetite-hematite-ferrihydrite-water is invariant in Fe-O-H_2O (constant p,T), the oxygen fugacity buffered by magnetite-ferrihydrite-water must be below that of magnetite-hematite, but probably not by much.

Fluid composition and transport. The compositions of the altering fluids are poorly constrained so far. The fluids did contain some dissolved salts, as shown by the moderate abundances of S, Cl, and P in the alteration materials. The S and Cl may be present in part as minute grains of discrete phases (see above), not only as adsorbed anions. Note that the Lafayette's magmatic sulfides and phosphates could be the sources of the S and P in the alteration materials.

In a similar vein, it appears that the altering solutions transported little into or out of Lafayette. Figure 1 shows the collinearity of FeO vs. SiO_2 for the alteration materials, olivine, and high-Si glass. The collinearity suggests that the Fe-Si-"others except water" abundances of the alteration material can be explained merely by mixing of Lafayette olivine and high-Si glass (± iron oxides). Limited chemical transport *within* Lafayette is suggested by MgO and Al_2O_3 concentrations in the alteration materials from different settings. In Fig. 1b, note that alteration materials in olivine are relatively rich in MgO, just as is the olivine, and that alteration materials in mesostasis glass are relatively rich in Al_2O_3, just as is the glass. This chemical similarity between host and alteration product suggests that Mg and Al were not completely mobile during Lafayette's alteration. For both elements, the average composition of all alteration materials lies close to the line between olivine and the mesostasis glass.

So there is no evidence that major elements in the alteration materials have been transported into or out of Lafayette during alteration (Fig. 1). In effect, alteration of Lafayette was a water-mediated reaction between its own olivine, Si-rich glass, and possibly other (S-, Cl-bearing) phases. The altering solutions need have transported little except water, Cl, and possibly S. Lacking evidence for extensive chemical transport, it seems likely that water-rock ratios during alteration were low.

Geological Setting: From the limited data available, Lafayette probably was altered in a geological setting of episodic water flow or injection. Long-term saturation with aqueous fluid, as beneath a water table, does not seem consistent with available data as we understand them.

First, it seems unlikely that Lafayette was saturated with aqueous solutions for long times, because such soaking ought to produce alteration materials on all surfaces and cracks that expose olivine or high-Si glass [17]. In fact, the alteration materials are present only along some cracks and some grain boundaries, and *not* pervading the rock.

Direct evidence for episodic alteration comes from the presence of different varieties of alteration materials in cross-cutting relationships, and from the cross-cutting relationships between different veinlets of fine-grained alteration materials. Episodic alteration is also consistent with the presence of alteration materials only adjacent to cracks, which (as above) suggest fluid flow through the rock and not stagnant fluid in the rock.

Setting on Mars. We cannot specify a geological environment for the aqueous alteration of Lafayette. Possible martian causes for episodic, limited alteration of basaltic rocks may include melting of permafrost by magma injection [18], hydrothermal convection cells (distal only) [19], and thermal transients associated with meteorite impacts [20]. Given the limited data on the martian hydrosphere, this list is likely not exhaustive.

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ATTEMPTS TO COMPREHEND MARTIAN SURFACE PROCESSES THROUGH INTERPRETATION OF THE OXYGEN ISOTOPIC COMPOSITIONS OF CARBONATES IN SNC METEORITES.

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The SNC meteorites are known to contain trace quantities of a variety of secondary minerals such as carbonates [e.g., 1,2], sulfates [e.g., 3,4], and aluminosilicates [e.g., 4]. Since these constituents are thought to be mostly preterrestrial in origin, their study has the potential to provide rigorous constraints on the nature of martian weathering processes. However, this line of investigation is potentially complicated by the presence within the meteorite samples of any additional weathering products produced by terrestrial processes. Examination of such terrestrial components is important since weathering processes that affect meteorite samples following their fall to Earth might have some bearing on the nature of analogous processes at the surface of Mars. It is obviously necessary to try and distinguish which secondary components in SNC meteorites are terrestrial in origin from those that are preterrestrial. Herein consideration is made of the stable isotopic compositions of weathering products in two SNC meteorites: EET A79001 (a sample collected from Antarctica) and Nakhla (a fall from Egypt, 1911).

Carbonate minerals in EET A79001 and Nakhla have similar carbon and oxygen stable isotopic compositions [1,5,6], suggestive of a common (martian) origin. Nonetheless, it has recently been

reported that carbonates in EET A79001 contain high levels of [14]C [7], 57–95% of what might be expected if the minerals were of modern terrestrial origin. In contrast, the carbonates in Nakhla contain very little [14]C [8], which endorses a preterrestrial origin for these minerals. It has previously been pointed out that the stable isotopic data for the carbonates in EET A79001 ($\delta^{13}C + 7$ to $+ 10\%_o$, $\delta^{18}O + 21\%_o$) and Nakhla ($\delta^{13}C + 6$ to $+ 9\%_o$, $\delta^{18}O + 23$ to $+ 26\%_o$) are somewhat unusual compared to common terrestrial occurrences of these minerals [5], although it is now clear that there is a similarity with Antarctic weathering products [7,9,10]. While an origin in the Antarctic is clearly possible for the carbonates in EET A79001 this is not the case for Nakhla. It could be argued that in light of the possibilities that EET A79001 has been altered on Earth, the study of this meteorite is ill-advised. However, EET A79001 is an important sample for many reasons—for instance, this sample contains trapped martian atmospheric gases [e.g., 11,12] including CO_2 [1,13]. Furthermore, EET A79001 is a fairly large find and is therefore readily available for study. Rather than simply discounting the EET A79001 sample, several in-depth investigations have been carried out in order to try and understand the nature of the carbon compounds in this meteorite [e.g., 5,14].

It remains to be explained why EET A79001 and Nakhla contain carbonate minerals with similar stable isotopic compositions, but which apparently formed on different planets (Earth and Mars respectively). There are a number of possible explanations—for example, EET A79001 could contain (1) martian carbonates similar to those in Nakhla, but with the high levels of ^{14}C incorporated as a result of poorly understood exchange process(es) acting on Earth; (2) secondary minerals produced in the Antarctic, with $\delta^{13}C$ and $\delta^{18}O$ not dissimilar to the carbonates in Nakhla, in addition to martian carbonates; (3) only terrestrially produced carbonates, the similarity in stable isotopic compositions to Nakhla being due to the operation of similar processes at the surface of Earth (i.e., in Antarctica) and Mars.

Point (1) has been addressed briefly by Jull et al. [7]—the carbonates in EET A79001 may originally have been preterrestrial, but their isotopic compositions could have subsequently been reset by fluid-related processes in Antarctica. This hypothesis can only be assessed by further studies. The notion that EET A79001 contains two different sorts of carbonate, option (2), is demonstrably true [2] and attempts have been made to determine the carbon isotopic compositions of the different varieties [14,15]. In regard of point (3), the martian surface environment can undoubtedly be considered similar in some respects to Antarctica. As such it is instructive to know more about how Antarctic weathering products may be formed.

When meteorites are subjected to weathering processes in Antarctica, a fluid phase, which derives from the ice, is involved. For illustrative purposes it can be assumed that Antarctic ice has a $\delta^{18}O$ value of about –40‰ (compared to 0‰ for terrestrial ocean water)—the depletion in [18]O is a reflection of the temperature of precipitation of snow, etc., that compacts to form the ice sheets. An assessment of the oxygen isotopic compositions of Antarctic weathering products is obtained from measurements of carbonates associated with a variety of ordinary chondrites collected from Antarctica. The carbonates are found to have $\delta^{18}O$ in the range –5 to +25‰ [16,17]. One particular Antarctic meteorite (LEW 85320) has been studied in detail due to the extensive deposits of weathering products that cover the sample's exterior surface—these have $\delta^{18}O$ values between +9 and +22‰ [9,10]. Although Antarctic weathering products can take on many different forms, since the carbonates in SNC meteorites can be ascribed to calcite [2,18], it is convenient to consider only this mineral in the following discussion. As noted

above, carbonates in EET A79001 have $\delta^{18}O$ of +21‰, while those in Nakhla have $\delta^{18}O$ of +23 to +26‰. At 0°C, $\delta^{18}O$ of calcite produced in isotopic equilibrium with Antarctic melt water would be about –5‰; in order to obtain a $\delta^{18}O$ of +25‰, carbonate would have to be precipitated at an unrealistic temperature of –70°C. Thus, while it may be possible, in theory, to derive some of the Antarctic weathering products observed in meteorites by exchange with, or formation from, Antarctic melt water, it is not possible to explain the oxygen isotopic data for carbonates in EET A79001 entirely by this mechanism. It may therefore be argued that the oxygen isotopic composition of the melt water has become enriched in [18]O by exchange with either the silicates of the meteorite ($\delta^{18}O \sim +4\%_o$) or atmospheric CO_2 ($\delta^{18}O = +41\%_o$). Isotopic exchange with the meteorite itself is unlikely in this instance since this would depress the $\delta^{18}O$ of the silicates [e.g., 19], a feature not observed in the case of EET A79001, which has $\delta^{18}O$ similar to all other SNC meteorites [20,21]. Calcite grown in isotopic equilibrium with atmospheric CO_2 would have $\delta^{18}O$ of +29‰. It is apparent that the range of $\delta^{18}O$ values displayed by Antarctic weathering products (–5 to +25‰) demands the involvement of melt water and atmospheric CO_2. If the carbonates in EET A79001 are also Antarctic weathering products then these too must have been formed by a similar process.

It is now possible to equate what is observed on Antarctica to potential processes on Mars. In simplistic terms, if the temperature of carbonate formation is similar to that in operation in Antarctica, then the isotopic constraints can theoretically be satisfied by a martian water phase that has $\delta^{18}O$ of –40‰ and atmospheric CO_2 with $\delta^{18}O$ of +41‰. However, the situation is a little more complicated and notice needs to be taken of the magnitude of the CO_2/H_2O ratio [22]. The effects of martian weathering can be explored further if the $\delta^{18}O$ values of the surface volatiles on Mars are known. This subject has been dealt with extensively by Jakosky [23]—in brief, the $\delta^{18}O$ of atmospheric CO_2 has been measured at $0 \pm 50\%_o$, while $\delta^{18}O$ of atmospheric water vapor is $-100 \pm 60\%_o$. Unfortunately these measurements are not particularly useful for constraining the operation of martian surface weathering processes because of their large associated uncertainties. A recent study of water liberated from SNC meteorites by heating [24] has shown coupled variations in $\delta^{18}O$ and $\delta^{17}O$ that indicate that at least some of the SNC meteorites (Nakhla included) contain water of preterrestrial origin. The exact form of this water is unknown, but SNC meteorites are known to contain hydrated minerals of both high temperature [e.g., 25] and secondary origin [e.g., 18]. Since variations in $\delta^{17}O/\delta^{18}O$ indicate that the hydrated phases of SNC meteorites are not in isotopic equilibrium with the silicates, it seems logical to conclude that the majority of the water in SNC meteorites arises from secondary weathering products. Water released from Nakhla was about 10‰ enriched in [18]O compared to a "terrestrial control sample"; on the other hand, water from EET A79001 had a similar $\delta^{18}O$ to the control [24]. Unfortunately the $\delta^{18}O$ of the control is not given in [24], but if it is assumed that it was a rock of Antarctic affinities then it is possible to accept that the water in EET A79001 was imparted by terrestrial weathering processes. In other words, the water in EET A79001 arises from minerals produced in equilibrium with Antarctic melt water ($\delta^{18}O = -40\%_o$) and as such would have $\delta^{18}O$ values of about –10‰ (there being an ~30‰ oxygen isotopic fractionation at 0°C for a number of common hydrated minerals). Taking this further, it is apparent that $\delta^{18}O$ of hydrated minerals in Nakhla would be about 0‰; if these were formed in isotopic equilibrium with water at 0°C, the $\delta^{18}O$ of this water would be –30‰, which is outside the range of possible values for mean atmospheric water vapor (i.e., $\delta^{18}O = -100 \pm 60\%_o$). If, as seems more likely, the $\delta^{18}O$ of the control used in [24] was

somewhere in the range +10 ± 5‰, the hydrous phases of Nakhla would have $\delta^{18}O$ of ~+20‰ and the water from which they were produced would have $\delta^{18}O$ of –10‰.

Intuitively, since there is an effective cycling of water vapor through the atmosphere and regolith on Mars, it would be anticipated that any surface fluids (which could induce weathering) would be isotopically similar to the atmospheric water vapor. As such, the disparity noted here is somewhat surprising. However, it has been proposed that the $\delta^{17}O/\delta^{18}O$ values of water released from SNC meteorites were established as a result of isotopic disequilibrium between the lithosphere and hydrosphere of Mars [24]. Perhaps we should conclude that this disequilibrium extends to the near-surface fluids and atmospheric gases on Mars. On the basis of the (admittedly meagre and somewhat incomplete) SNC data it would seem unlikely that surface water on Mars could have $\delta^{18}O$ of –40‰. In contrast, if the water has $\delta^{18}O$ of –10‰ then carbonates that precipitate in equilibrium with this will have, at 0°C, $\delta^{18}O$ of +25‰, a value commensurate with what is observed in SNC meteorites.

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N93-31963

CHEMICAL REACTIVITY OF THE MARTIAN SOIL. A. P. Zent[1] and C. P. McKay[2], SETI Institute and NASA Ames Research Center, Moffett Field CA 94035, USA, [2]NASA Ames Research Center, Moffett Field CA 94035, USA.

Introduction: The Viking life sciences experimental packages detected extraordinary chemical activity in the martian soil, probably the result of soil-surface chemistry. At least one very strong oxidant may exist in the martian soil.
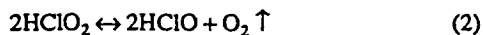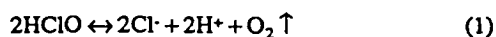
The electrochemical nature of the martian soil has figured prominently in discussions of future life sciences research on Mars. Putative oxidants in the martian soil may be responsible for the destruction of organic material to considerable depth, precluding the recovery of reducing material that may be relic of early biological forms. Also, there have been serious expressions of concern regarding the effect that soil oxidants may have on human health and safety. The concern here has centered on the possible irritation of the respiratory system due to dust carried into the martian habitat through the air locks. —

Viking Results: The results of the Viking biology experiments have led to the widespread belief that there are oxidants in the martian soil: (1) The Gas Chromatograph Mass Spectrometer (GCMS) failed to detect organics in surface samples or from samples below the surface (maximum depth sampled was about 10 cm) [1]. (2) The soil released O_2 upon humidification of the headspace gas in the Gas Exchange experiment (GEx) [2,3] in amounts ranging from 70–770 nmoles cm^{-3}. (3) The labeled release experiment indicated the rapid release of CO_2, followed by a prolonged slow release of CO_2, from radioactively labeled C in a nutrient solution.

Models of the Soil: The nature of the putative oxidants is unknown. A wide variety of explanations have been offered in the literature (see Table 1).

Klein [17,18] suggested that there were at least three different oxidants in the martian soil: a strong, thermally stable oxidant (GEx results), a second strong, thermally labile oxidant required to explain the LR results, and a weak oxidant required to explain the slow continued release of O_2 in the LR. The standard mechanism to explain the chemical reactivity of the Mars soil is the presence of oxidants, such as H_2O_2, produced by an external energy source interacting with atmospheric gases and/or the soil [19]. In addition to peroxide, alkali and alkaline Earth superoxides and ozonides could be produced by a variety of energetic processes.

Another possible series of oxidants that previously received little attention are oxidized halides. Many forms of Cl and Br can oxidize water to O_2, and both Cl and Br are detected in the martian regolith at levels well above those required to explain the GEx results. (If each mole of oxidant released approximately one mole of O_2, and assuming a soil density of 1.5 g cm^{-3}, then the concentration of oxidant would be about 2–25 ppm by mass.) There is a wide variety of compounds that are unstable in the presence of water and that may occur simply as activated sites on evaporite crystals and not as discrete phases; some examples of plausible redox reactions include

TABLE 1. Explanations for Viking results from the literature.

• GEX release of O_2 upon humidification.	
KO_2	[4]*
ZnO_2	
CaO_2 in soil	[5]
MnO_2	[6]
O_2 trapped in micropores	[7]
	[8]
Frost on olivine/pyroxene	[9]
Amboy Soil under plasma	[5]
Oxidized halides	[21]

• LR decomposition of added nutrient.	
H_2O_2	[10]
	[11]
	[4]
Peroxonitrite (NOO_2)	[8]
Smectite clays	[12]

• Lack of organic in martian soil.	
$UV + TiO_2$	[13]
	[14]
Dust electrostatics	[15]
Feroxyhyte (δ-FeOOH)	[16]

*See references.

$$2HClO \leftrightarrow 2Cl^- + 2H^+ + O_2 \uparrow \qquad (1)$$

$$2HClO_2 \leftrightarrow 2HClO + O_2 \uparrow \qquad (2)$$

Although H_2O does not appear on the lefthand side of these equations because there is a net production of H_2O in the reaction, it is a necessary catalyst to rapid decomposition reactions. In addition, acids of Br and I can be identified that may play a role in H_2O decomposition, although their stability under GEx sterilization conditions has not yet been determined.

A possible compound for the LR oxidant is H_2O_2, catalyzed by the presence of iron in the soil. The concentration of H_2O_2 required to explain the LR results is about 1 ppm by mass.

Measurement on Future Missions: An *in situ* investigation of the putative regolith oxidant is indicated for precursor missions leading to human exploration.

The traditional variable for characterizing the oxidation state of terrestrial soils is Eh. Eh is inappropriate to characterization of the martian regolith for a variety of reasons. For example, Eh is used to determine aqueous speciation and saturation levels for terrestrial soil solutions. In cases where a soil solution exists, successful measurements of Eh can be made if it can be established that the solution is truly in equilibrium with the soil [20]. These techniques are applied with great success in saturated soils, such as rice paddies or long-lived bodies of soil solution. However, in cases where there is no soil solution, the technique is highly suspect.

There are two requirements for successful characterization of the oxidation potential of a soil solution via this method that apply to terrestrial soils, and a third requirement that applies rather uniquely to Mars. First, there must be dissolution equilibrium between the soil and the solution. This ensures that the potential developed at the electrode-solution interface reflects the properties of the soil. In dry terrestrial soils, it is often impossible to determine whether dissolution equilibrium exists, except by maintaining the sample in contact with the solvent/electrolyte for extended periods of time. Even more stringent is the requirement that electrochemical equilibrium between all redox couples exposed to the solution exist. This includes species that may not be soluble in the solution but may exist on the surfaces of the soil grains. Electrochemical equilibration is notoriously slow in terrestrial soils, in spite of the fact that most electro-

chemical reactions are catalyzed by microorganisms in the soil. In sterile soils, equilibration may be expected to take months; this requirement severely complicates implementation of an Eh measurement on a landed experiment. Even more problematic is the requirement that, if no soil solution is present, a solvent must be added in order to make the Eh measurements. In terrestrial soils, H_2O is the solvent of choice because of its ubiquity. However, it is implicit that the solvent/electrolyte must be electrochemically neutral with respect to the soil sample. There is abundant evidence, as described above, that the putative oxidant has an electrode potential greater than that of the H_2O-O_2 couple, and reacts vigorously with H_2O. Therefore, H_2O is an inappropriate solvent/electrolyte. Addition of H_2O to the soil is likely to destroy the species that we are most interested in measuring. It is possible to substitute another electrolyte with an oxidation potential greater than that of the H_2O-O_2 couple. Although the putative oxidant may be electrochemically inert with respect to such a solvent, acetonitrile for example, the dissolution equilibrium requirement then becomes problematic.

A possible approach to measurement of the putative LR oxidant is a specific search for H_2O_2 in the martian soil. We have proposed a H_2O_2 fluorometer, in which an organic acid dimerizes in the presence of H_2O_2. The dimer can be excited by UV radiation, and fluoresces at 400 mn. The fluorescence is directly proportional to the catalytic activity of the H_2O_2 on the acid monomer.

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