LABORATORY INVESTIGATIONS OF MARS: CHEMICAL AND SPECTROSCOPIC CHARACTERISTICS OF A SUITE OF CLAYS AS MARS SOIL ANALOGS

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Abstract. Two major questions have been raised by prior explorations of Mars. Has there ever been abundant water on Mars? Why is the iron found in the Martian soil not readily seen in the reflectance spectra of the surface? The work reported here describes a model soil system of Mars Soil Analog Materials, MarSAM, with attributes which could help resolve both of these dilemmas. The first set of MarSAM consisted of a suite of variably iron/calcium-exchanged montmorillonite clays. Several properties, including chemical composition, surface-ion composition, water adsorption isotherms, and reflectance spectra, of these clays have been examined. Also, simulations of the Viking Labeled Release Experiment using the MarSAM were performed. The results of these studies show that surface iron and adsorbed water are important determinants of clay behavior as evidenced by changes in reflectance, water absorption, and clay surface reactions. Thus, these materials provide a model soil system which reasonably satisfies the constraints imposed by the Viking analyses and remote spectral observations of the Martian surface, and which offers a sink for significant amounts of water. Finally, our initial results may provide insights into the mechanisms of reactions that occur on clay surfaces as well as a more specific approach to determining the mineralogy of Martian soils.

1. Introduction

Exobiology draws from diverse disciplines in its attempts to understand how cosmic, solar system and planetary evolution have influenced the origin, evolution and distribution of life in the universe. Both laboratory modeling and extraterrestrial explorations are required to achieve this goal. Increasingly, exobiologists are seeking congruence between conditions necessary for the occurrence of organic chemistry involved in producing protocellular material and the geological history in which this organic chemistry must have occurred. In this context Mars is still an exceedingly important and interesting planet to search for signs of extant or extinct life, or evidence that life never existed, should this be the case. Additionally, studies of Mars, as an inner solar system planet that had an early atmosphere resembling some models of the primitive Earth's, might be expected to offer insights as to why planetary evolution of Mars diverged from that of Earth.

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Current exobiological interest in Mars differs fundamentally from that of the Viking era, when the search for extant biology and associated organic chemistry provided the major focus. New missions being planned for Mars (SSEC Reports, 1983, 1986) have as the principal exploration foci the surface geochemistry, the clues it contains to the geochemical history of liquid water on the planet (see, for example, Squyres, 1984), and its overall relationship to the distribution, sources, sinks and cycles of volatile elements and compounds. These issues are central to understanding the link between planetary evolution and the development of living systems (Chang et al., 1983). On Earth the evolution of advanced life was supported by planetary conditions whereas on Mars it was not.

The experiments conducted in 1976 by the Viking landers on the surface of Mars contributed greatly to current knowledge of Mars' surface chemistry. The data from these experiments provide important constraints on candidate compositions of surface soils of the Viking sites and, by extension, of Mars as a whole. Among the viable model minerals are the iron-containing smectite clays (Baird et al., 1977; Clark et al., 1977; Toulmin et al., 1977; Banin and Rishpon, 1979a, b; Clark et al., 1982; Banin and Margulies, 1983; Banin, 1986).

Clays and other hydrous minerals are of particular interest because confirmation of their presence on Mars would clearly establish that the geochemistry of Mars, like that of Earth, had been strongly influenced by liquid water. Water is an essential ingredient for chemical evolution of living systems. Water tied up in the crystal structure of clays, or even superficially bound as solvation water of the exchangeable cations of clays, would constitute a significant sink for water which might have been only partially detected by telescopic studies and the Viking experiments. In view of the continued controversy regarding the evolutionary pathway of volatiles on Mars and the grossly divergent estimates of the water inventory of the planet (e.g. Pepin, 1986; Carr, 1987), any additional clues to the presence, amounts, and forms of water are of great importance.

The hypothesis that significant amounts of Martian iron may be associated with surface smectite clays (Banin and Rishpon, 1979a) adds further interest to the possibility of clays existing on Mars. This model provides a novel and rational alternative non-crystalline form for the abundant surface iron. Also, iron in the crystal lattice of a clay makes a disproportionately small contribution to the reflectance spectrum (Jepson, 1985).

Clays play a major role in modern theories of the origin of life. They are widely acknowledged by exobiologists to be model catalyst systems for prebiological organic chemistry. One theory (Cairns-Smith, 1982) purports that clay minerals were inorganic precursors to organic life forms. The observations that clays, like biological systems, appear to be capable of energy storage and transduction support this thesis (Coyne, 1985). It is noteworthy that the three Viking Biology Experiments exhibited biomimetic responses, that is, results which initially suggested biological activity, but which could also be interpreted as physical-chemical phenomena (Klein, 1977, 1979a, b). In this context, it would be essential to determine if the biomimetic respon-

ses were attributable to a clay mineral system or to other types of minerals. The presence of clays on Mars implies that the geochemical components of the Martian surface had progressed significantly toward protobiological systems, despite the apparent absence of organic compounds on it now (Biemann *et al.*, 1977).

The next NASA mission to Mars will be the Mars Observer Mission, now under active preparation and scheduled for launch in the early 1990's. This mission has several objectives: (1) to determine the global elemental and mineralogical character of the surface material; (2) to determine the temporal and spatial distribution, abundance, sources, and sinks of volatile materials and dust; and (3) to explore the structure and circulation of the atmosphere of Mars. These determinations will be made principally using visual and infrared mapping and gamma-ray spectrometers. In order to interpret the results of this mission from the exobiological perspective, an advance ground-based study is being conducted with a usefully limited suite of Mars Soil Analog Materials (MarSAM). Included in this project will be the determination of the spectral properties of the MarSAM in order to provide data for interpretation of remote observations of Mars, and examination of various chemical and physical properties of the clays in order to understand the chemical and photophysical behavior (past, present and future) of the Martian surface. These materials are intended to simulate the aeolian material that presumably covers much of the surface of Mars and contributes to its atmospheric dust. The selection of the MarSAM suite is based, in part, on the constraints placed on the composition of the Martian soil by the X-ray fluorescence results obtained by the Viking landers (Clark *et al.*, 1976; Baird *et al.*, 1976, Toulmin *et al.*, 1977), in part, on laboratory studies simulating the Viking Biology Labeled Release (LR) experiments (Banin and Rishpon, 1979a, b; Banin and Margulies, 1983; Banin *et al.*, 1981, 1985), and, in part, on 0.3−2.5 μm reflectance spectra of the Martian dust and bright (high albedo) areas (McCord *et al.*, 1982) and of purported Martian analog materials (Toon *et al.*, 1972, Banin *et al.*, 1985, Singer, 1985).

The results of initial studies of the MarSAM are presented in this paper. Specifically, the chemical characterization of a set of modified clays, the determination of the water adsorption isotherms of these clays, and the measurement of reflectance spectra of the clays are reported. Conclusions drawn from the results of this study and their relevance to understanding Mars surface materials will be discussed at the end of this paper.

2. Experimental Methods

2.1. CLAY PREPARATION

A smectite, SWy-1 montmorillonite, clay from Crook County, Wyoming, obtained from the Clay Minerals Society Repository, was used for the preparation of the MarSAM. The parent clay was supplied in powder form and was converted to the desired ionic composition by the 'Quantitative Ion Exchange Method' (Banin, 1973). This

method entails titrating a mixture of freshly prepared hydrogen-saturated montmorillonite and OH-saturated ion-exchange resin (R) with the chloride salt(s) of the desired exchangeable cations, specifically iron and calcium. The added cation replaces H^+ from the clay surface while the Cl^- exchanges with OH^- from the resin. The H^+ and the OH^-, of course, then combine to form water. The overall reaction can be summarized as follows:

$$H^+\text{-Clay} + ROH + MCl \rightarrow M^+\text{-Clay} + RCl + H_2O \qquad (1)$$

For the preparation of the various clays, the cations (M) in the titrating salt solution were mixed at predesigned proportions, covering the span from (0% Fe, 100% Ca) to (100% Fe, 0% Ca). The titration was completed at a pH of 5.5, or lower, in order to prevent precipitation of the cations. At this point the electrical conductivity of the suspension is at a minimum (between $10-100$ dS m^{-1}) indicating that the suspension is essentially salt-free. After titration, the clay suspensions were centrifuged and the pastes separated and freeze dried. The dried aggregates were lightly crushed to pass a mesh of 105 μm and the powders were stored under room air.

2.2. CHEMICAL COMPOSITION

Major elements: The major elements (Mn, Ca, K, Ti, P, Si, Mg, Na, Al, and Fe) were analysed using X-ray fluorescence (XRF) and inductively-coupled plasma (ICP) techniques. For the X-ray fluorescence analyses, a Diano model 8600B wavelength dispersive fluorescence spectrometer with a Cr−W dual target tube and flow proportional counter was used. A 1.250 g portion of each clay was fused with lithium tetraborate, and the fused bead was crushed with cellulose powder and pressed for analysis. For the ICP analyses, an ARL model 35000 ICP spectrometer was used. A 0.100 g sample of the clay was fused with 0.700 g of lithium metaborate, and the molten bead was poured into 100 ml of 4% (v/v) nitric acid. Further dilutions of this solution were made as necessary to provide concentrations within the range optimal for measurement. Two sets of working standards containing the seven elements (Si, Al, Fe, Mg, Ca, Ti, Mn) of interest were prepared and used as controls for the instrument and as calibration standards. The concentrations (in ppm) of these standards were: Si-1, Al-1, Fe-1, Mg-1, Ca-0.5, Ti-0.5, and Mn-0.1 for the 'low' standard and Si-20, Al-10, Fe-20, Mg-10, Ca-5, Ti-5, and Mn-1 for the 'high' standard. Standard clays (NBS 97 and 98a) were also used to calibrate the instruments. The estimated errors in the results for all elements reported are $\pm 2\%$.

Surface-ions: 1% suspensions (0.8 g of clay in 80 ml of deionized water) were prepared from the Fe/Ca montmorillonite powders. The ions adsorbed by the clays were separated into three fractions, soluble, exchangeable and acid-extractable, by the following procedure (Gerstl and Banin, 1980). A twenty five ml aliquot of each of the clay suspensions (3 replicates) was centrifuged in a 50 ml polycarbonate centrifuge tube at 10000 rpm for 45 minutes. The supernatant was then separated from the sediment and filtered through a 0.1 μm membrane filter. The ions remaining in the solu-

tion were termed the 'soluble fraction'. The sediment was then redispersed in 20 ml of 1N KCl in the centrifuge tube and shaken (vortexed) for 30 minutes. The suspension was then centrifuged and the supernatant liquid decanted and collected in 100 ml volumetric flasks. This extraction was repeated 3 more times and the supernatants were collected. The ions found in this extract were termed the 'exchangeable fraction'. The 'acid-extractable' fraction was obtained by a similar extraction but using 0.5 N HCl as the extractant. The concentrations of Fe, Ca, Mg, and Al in the solutions were determined using a Model 5000 Perkin-Elmer atomic absorption spectrophotometer. The coefficients of variation (standard deviation/average) for the replicate analyses of the metals were: Fe-0.04; Ca-0.04; Mg-0.08; and Al-0.06.

2.3. WATER ADSORPTION ISOTHERMS

Samples of 0.250 g of three of the clay powders (0,50 and 100% adsorbed iron) were weighed into glass vials. Twelve vials of each clay type were put into each of two desiccators maintained at relative humidities (RH) of 3−5% and 100%, respectively. The desiccators were kept at a temperature of 22 °C ± 1 °C. The samples were weighed several times over 32 days, and after each weighing the air in the desiccator was pumped out to less than 3 mbar. Equilibrium was reached when consecutive weighings did not show differences of more than 0.1% moisture in the clay. The samples were then placed into six desiccators, each controlled at a different relative humidity using the saturated salt solutions listed in Table I. The samples were weighed repeatedly as before, until equilibrium was reached. By this procedure complete adsorption isotherms were obtained for the three clays showing the dependence of moisture content on relative humidity. Also, hysteresis loops developed by reaching equilibrium from the wet state (desorption leg) and dry state (adsorption leg) were obtained.

TABLE I

Saturated salt solutions and desiccants used for equilibration of clays at various relative humidities

Salt	Relative Humidity (%)
$CaCl_2$ (granular)	3−5
CH_3COOK	20
$CaCl_2 \cdot 6H_2O$	32
$NaCr_2O_7 \cdot 2H_2O$	52
$NaNO_2$	66
NaCl	76
$Na_2SO_4 \cdot 10H_2O$	93
H_2O	100

2.4. REFLECTANCE SPECTROSCOPY

Spectra from 0.3 to 2.5 μm were recorded on a Perkin-Elmer Model 330 UV/VIS/NIR spectrophotometer using an Hitachi 60 mm integrating sphere accessory (Hitachi Ltd., Tokyo, Japan). Corrections for instrument background were

made using pressed Al_2O_3 pellets in both beams of the spectrometer and for reflectance of the sample holder with a high purity, fused quartz plate (obtained from Fluorcarbon, U.S. Quartz Division, Sunnyvale, CA) in the sample beam only. Samples of approximately 1.2 g were pressed into stainless steel planchettes 25.4 mm in diameter and 2.5 mm deep using an ECC (English China Clays, Ltd., London) press. This press provided a pressure of 1.2 kg cm^{-2} on the sample, resulting in a compact, but softly packed pellet. A 20 second pressing time was used for all of the samples. All spectra were digitized using Perkin-Elmer Petos software installed on a P.-E. model 3600 data station. The Savitzky/Golay smoothing function, which determines the best fit of a quadratic polynomial through successive data windows, was used to smooth the spectra.

2.5. SIMULATION OF THE VIKING LABELED RELEASE (LR) EXPERIMENT

Simulations of the LR experiment were done using the ^{14}C absorption method ('Getter Technique', Levin and Straat, 1977; Banin and Rishpon, 1979b). Samples of 0.250 g of clay powder were put into 20 ml glass vials and 0.1 ml of 2.5×10^{-4} M radioactively labeled sodium formate ($H^{14}COONa$), with an activity of 2 μCi/ml, was injected into the clay. The vials were quickly stoppered with plastic covers each of which had a stainless-steel wire supporting a circle of filter paper attached. The fiberglass filter paper, impregnated with Hyamine hydroxide (X-10, scintillation grade, 10% w/v solution in methanol) absorbed the $^{14}CO_2$ that was given off by the clay-formate mixture. The vials were kept at a temperature of 10.2 °C ± 0.2 °C. The filter paper circles were periodically removed and replaced by fresh ones. The exposed ones were transfered into a vial containing 3 ml of Packard InstaGel 2 scintillation liquid and the β particles from the $^{14}CO_2$ were counted in a Beckman Model LS 7800 scintillation counter. Curves showing the rate of decomposition of the formate were then constructed from the scintillation data.

As clays can support bacterial growth it is important to insure that the results of the simulations are due to the action of the mineral surface rather than bacterial activity. We ruled out interference from bacterial activity based on the following grounds: (a) bacterial counts in enrichment cultures of the modified clays were negative, and (b) the shape of the decomposition curves measured in the simulation experiments lacked the sigmoidal shape, including a lag period, which is generally considered to be a criterion for the presence of biological activity. The shape of the curves observed in our experiments is typical of chemical activity.

3. Results and Discussion

3.1. CHEMICAL AND ELEMENTAL COMPOSITION

Total elemental composition

The suite of clays studied here was selected to simulate the active surface ingredients of the Martian soil and to supply information on the behavior of smectite clays under

TABLE II

Chemical composition of the parent SWy-1 clay and the modified MarSAM suite of clays[a]

	Crude SWy-1 Clay		Modified (MarSAM) Clays				
	This work	Literature value[b]	0%Fe 100%Ca	20%Fe 80%Ca	50%Fe 50%Ca	80%Fe 20%Ca	100%Fe 0%Ca
Oxide				(% by weight)			
SiO_2	58.7	62.9	55.7	56.0	56.3	56.6	57.1
Al_2O_3	17.7	19.6	17.2	17.2	17.0	16.9	17.0
TiO_2	0.10	0.09	0.10	0.18	0.10	0.21	0.10
Fe_2O_3/FeO	3.61	3.71	3.62	4.09	4.99	5.67	5.89
MnO	0.01	0.006	<0.01	<0.01	<0.01	<0.01	<0.01
MgO	2.6	3.05	2.09	2.10	2.01	2.01	2.05
CaO	1.59	1.68	1.53	1.57	0.90	0.42	0.14
Na_2O[c]	1.4	1.53	≤0.2	≤0.2	≤0.2	≤0.2	≤0.2
K_2O[c]	0.5	0.53	0.10	0.21	0.33	0.31	0.32
P_2O_5[c]	0.04	0.049	<0.02	<0.02	<0.02	<0.02	<0.02
LOI[d]	13.3	6.06	19.5	19.4	18.7	18.2	17.8
TOTAL:	99.55	99.21	100.04	100.95	100.52	100.52	100.60

[a] All values, except where noted, are averages of X-ray fluorescence and inductively-coupled plasma measurements. Relative errors in the analyses are estimated to be within 2%.
[b] From Van Olpen and Fripiat (1979).
[c] X-ray fluorescence data only.
[d] LOI is loss on ignition, that is, loss in weight upon heating to 925 °C.

the unique conditions on Mars. Total reconstitution of the Martian soil composition was not sought at the present time, and will be studied in another phase of the project.

The results of the elemental analyses are given in Table II; also included in the table are the results of an independent analysis of the SWy-1clay (Van Olphen and Fripiat, 1979). As seen in the table, the modification of the clay by the Banin method resulted in an increase in the loss on ignition (LOI, the loss in weight of the clay upon heating to 925 °C) mostly due to higher content of adsorbed water in the modified clays as compared to the crude clay and, possibly, due to some increased dehydroxylation at 600–800 °C. Furthermore, the unaltered sample of SWy-1 used in our analysis had a higher LOI than the one reported by Van Olphen and Fripiat (1979). To enable more meaningful comparisons between the modified and parent clays, the values for

A. BANIN ET AL.

TABLE III

Chemical composition of the clays listed in Table II but normalized to the 'stable–matrix' basis[a]

| Oxide | Crude SWy-1 Clay | | Modified (MarSAM) Clays | | | | |
	This Work	Literature Value[b]	0%Fe 100%Ca	20%Fe 80%Ca	50%Fe 50%Ca	80%Fe 20%Ca	100%Fe 0%Ca
			(% by weight)				
SiO_2	67.7	67.0	69.2	69.5	69.2	69.2	69.5
Al_2O_3	20.4	20.9	21.4	21.3	20.9	20.7	20.7
TiO_2	0.12	0.095	0.12	0.22	0.12	0.26	0.12
Fe_2O_3/FeO	4.16	3.94	4.50	5.07	6.13	6.93	7.16
MnO	0.01	0.006	<0.01	<0.01	<0.01	<0.01	<0.01
MgO	3.0	3.25	2.60	2.61	2.47	2.46	2.49
CaO	1.83	1.79	1.90	1.95	1.11	0.51	0.17
Na_2O	1.6	1.63	<0.25	<0.25	<0.25	<0.25	<0.25
K_2O	0.58	0.56	0.12	0.26	0.40	0.38	0.39
P_2O_5	0.05	0.052	<0.02	<0.02	<0.02	<0.02	<0.02
TOTAL:	99.45	99.22	99.84	100.91	100.33	100.44	100.53

[a] Values were calculated by $C_s = C_i/(100. - LOI)$, where C_s and C_i are percent oxide in the 'thermally-stable' matrix and initial clay, respectively. C_i and LOI were taken from Table II.
[b] From Van Olphen and Fripiat (1979).

all of the oxide concentrations were converted by calculation to the 'thermally-stable matrix' basis, that is, corrected for the loss on ignition. The results of these calculations are given in Table III. On this basis, the results for the crude SWy-1 clay obtained in the present work generally agree well with those reported previously.

The modification procedure removed almost all of the sodium and phosphorous and some of the potassium and magnesium. Most of the native calcium was also removed, as can be seen by comparing the crude and 100% Fe-clays. In the crude clay these elements mostly appear as adsorbed ions, soluble salts and in minor accessory minerals such as calcium and magnesium carbonates. Magnesium, however, is also a component of the crystal lattice and cannot be completely removed during the modification.

For the major matrix elements silicon and aluminum, no changes or only slight increases in their concentrations were observed (Table III). These increases amounted to changes of 2.2–2.7% and 1.5–4.9% for SiO_2 and Al_2O_3, respectively, over those

found for the crude clay. These are most likely due to the selective removal of the non-aluminosilicate minerals during clay preparation. Manganese concentrations were decreased to below the detection limit of the analysis. This loss is also evidenced in the ESR spectra of the treated clays (Coyne and Banin, 1986). The concentration of titanium, as determined by chemical analysis, did not change during modification.

These results show that the clay preparation procedure causes little change in the crystal lattice, thus producing purified montmorillonite clays free of soluble salts and minor accessory minerals but with predesigned proportions of adsorbed iron and calcium. As expected, large relative changes for iron and calcium were seen in the suite of clays. These two elements were manipulated by the modification procedure and their concentration varies systematically and in a complementary way within the series. As discussed above, the modification process indeed removed much of the native calcium. Iron, however, was always higher in the modified clays than in the crude clay, showing that lattice iron was not removed during the modification.

Surface-ion composition

In many terrestrial soil reactions, such as adsorption-desorption of volatiles, catalytic reactivity, decomposition of organic matter and mineral weathering, which may be relevant to the Martian soil the exchangeable surface ions should play as strong, or stronger, role in determining the soil behavior than do the lattice ions. The present suite of MarSAM was carefully prepared to contain a defined, gradually changing surface composition dominated by iron and calcium, two elements that were found to be present in significant quantities in the Martian soil.

The characterization of the surface-ion composition involved the sequential separation of these ions into three fractions: soluble, exchangeable with neutral salt, and acid-extractable. It is generally presumed that ions bound electrostatically to the clay surface are released in the exchangeable fraction while those that are specifically and covalently bound to oxy and hydroxy groups on the surface are released only by acid extraction.

The surface compositions of the clays are presented in Table IV and in Figure 1. Generally, the concentration of ions in the soluble fraction was always low since the preparation method was designed to produce clays free of soluble salts. The exchangeable fraction was high for the 100% Ca clay and systematically decreased as the calcium proportion decreased, while the acid-extractable fraction concurrently increased.

Iron varied between 0.0102 and 0.3064 mmol g^{-1} of clay (Table IV) and was found mostly in the acid-extractable fractions. However, the distribution of iron between the exchangeable and acid-extractable fractions varied with the total amount added to the clay. At the lowest level of added iron (20%) only 10% of the iron was exchangeable and almost 90% was acid-extractable. At the higher iron levels (50% Fe and larger), the distribution between the exchangeable and acid-extractable fractions stabilized at 30% and 70%, respectively.

This finding agrees with, and may be at the root of, previous observations on a

A. BANIN ET AL.

TABLE IV

Distribution of selected metals between the soluble, exchangeable and acid-extractable phases of a suite of MarSAM iron-calcium montmorillonite clays

METALS \ CLAYS	Fe				Ca				Mg			
	SOLUBLE	EX-CHANGE-ABLE	ACID EXTRACT-ABLE	TOTAL	SOLUBLE	EX-CHANGE-ABLE	ACID EXTRACT-ABLE	TOTAL	SOLUBLE	EX-CHANGE-ABLE	ACID EXTRACT-ABLE	TOTAL
0% Fe/100% Ca	0.0007a / 7b	0.0016 / 16	0.0079 / 77	0.0102 / 100	0.0026 / 1	0.4319 / 98	0.0031 / 1	0.4377 / 100	0.0001 / <1	0.0338 / 94	0.0020 / 6	0.0359 / 100
20% Fe/80% Ca	0.0014 / 1	0.0086 / 10	0.0785 / 89	0.0885 / 100	0.0041 / 1	0.3751 / 97	0.0072 / 2	0.3864 / 100	0.0016 / 4	0.0372 / 88	0.0034 / 8	0.0423 / 100
50% Fe/50% Ca	0.0014 / 1	0.0559 / 30	0.1280 / 69	0.1853 / 100	0.0005 / <1	0.2542 / 98	0.0045 / 2	0.2592 / 100	0.0002 / <1	0.0292 / 92	0.0026 / 8	0.0320 / 100
80% Fe/20% Ca	0.0014 / 1	0.0750 / 30	0.1741 / 69	0.2505 / 100	0.0002 / <1	0.0916 / 88	0.0127 / 12	0.1045 / 100	0.0002 / <1	0.0351 / 91	0.0034 / 9	0.0387 / 100
100% Fe/0% Ca	0.0026 / 1	0.0934 / 30	0.2104 / 69	0.3064 / 100	0.0009 / 3	0.0215 / 76	0.0061 / 21	0.0285 / 100	0.0006 / 2	0.0358 / 90	0.0032 / 8	0.0396 / 100

METALS \ CLAYS	Al				TOTAL			
	SOLUBLE	EX-CHANGE-ABLE	ACID EXTRACT-ABLE	TOTAL	SOLUBLE	EX-CHANGE-ABLE	ACID EXTRACT-ABLE	TOTAL
0% Fe/100% Ca	0.0048 / 6	0.0333 / 43	0.0387 / 51	0.0767 / 100	0.0081 / 1	0.5001 / 90	0.0517 / 9	0.5599 / 100
20% Fe/80% Ca	0.0100 / 16	0.0521 / 84	0 / 0	0.0621 / 100	0.0171 / 3	0.4730 / 82	0.0891 / 15	0.5792 / 100
50% Fe/50% Ca	0 / 0	0 / 0	0.0246 / 100	0.0246 / 100	0.0025 / <1	0.3393 / 68	0.1597 / 32	0.5016 / 100
80% Fe/20% Ca	0.0037 / 21	0.0136 / 79	0 / 0	0.0173 / 100	0.0055 / 2	0.2153 / 52	0.1902 / 46	0.4110 / 100
100% Fe/0% Ca	0.0083 / 100	0 / 0	0 / 0	0.0083 / 100	0.0124 / 3	0.1518 / 40	0.2197 / 57	0.3839 / 100

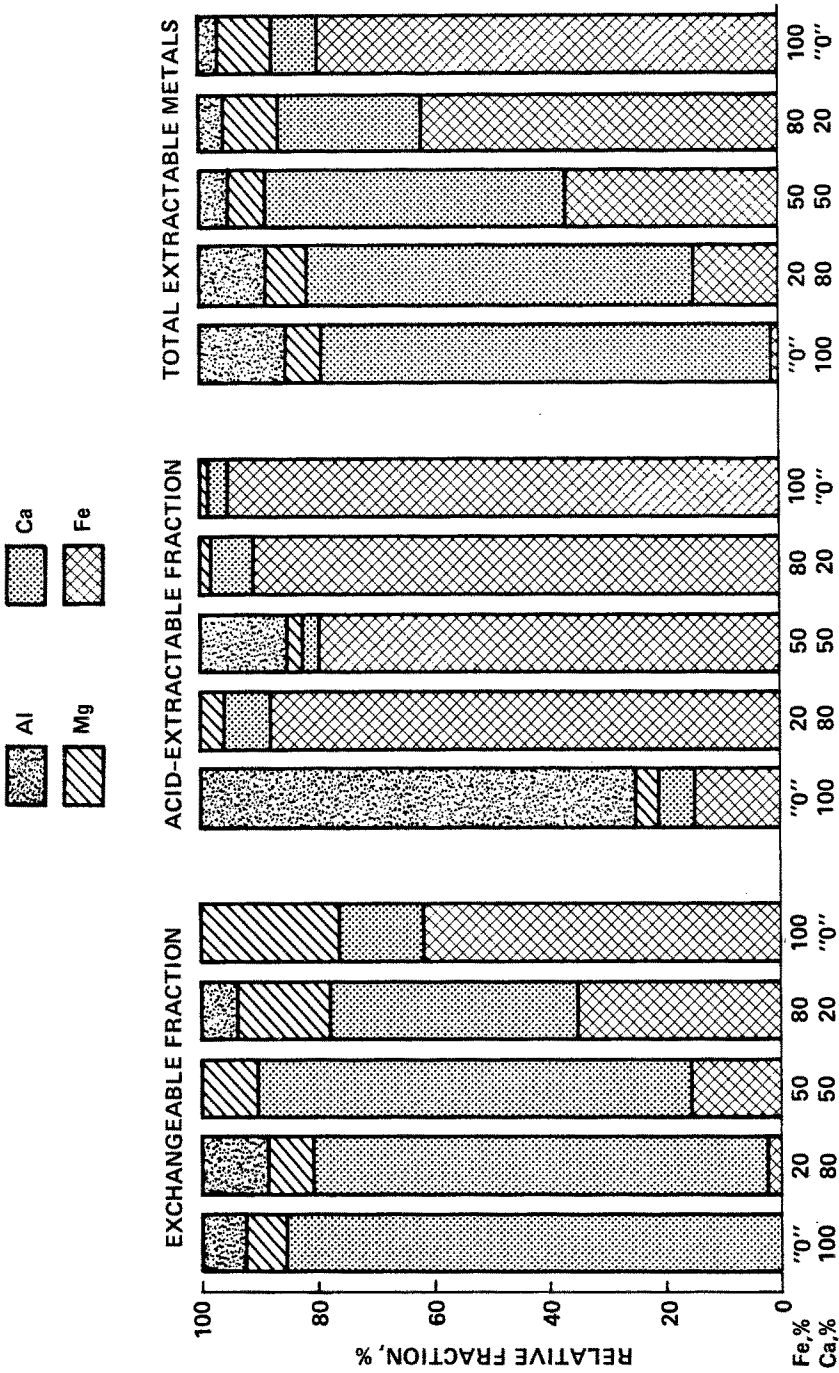[a] AMOUNT, mmol/gm of clay   [b] RELATIVE AMOUNT, %

Fig. 1. Distribution of metals in the exchangeable and acid-extractable fractions of a series of iron-calcium montmorillonite clays.

similar suite of clays that ESR and thermoluminescence (TL) signals approached saturation at the 50% Fe level (Coyne and Banin, 1986) and the observation reported later in this paper that the $t_{1/2}$ for the LR simulation reached a minimum value and did not change further as the iron content was increased above 50%. It may mean that at low total iron content most of the surface iron is in a less labile form (extractable only by acid). As iron content increases, this fraction decreases. Above a certain iron content, a constant ratio is achieved between the more labile (exchangeable) and the less labile (acid-extractable) fractions.

Calcium varied between 0.0285 and 0.4377 mmol g^{-1}. It was mostly found in the exchangeable fraction but a small (0.003−0.012 mmol g^{-1}), roughly constant amount was acid-extractable. The acid extractable calcium was equivalent to only 0.03−3.0% of the exchange capacity of the clay, and thus constituted an insignificant part of the total calcium even in the Ca clays. However, as iron replaced calcium as the exchangeable cation, the acid-extractable fraction contained an increasing percentage of the total calcium (Table IV). Also, the effect that calcium had on the chemical behavior of the clay was found to be lower than predicted by its concentration.

The total extractable magnesium, 0.03−0.04 mmol g^{-1}, was similar for all the clays, and constituted 6−10% of the total extractable metals (Figure 1). It appeared mostly in the exchangeable fraction. Magnesium was not added extraneously during the preparation of the clay. However, because Mg is a component of the crystal lattice it can be released when the clay is exposed to solutions of low pH during the clay preparation, the acid leaching, or the titration phase. It remains in the system and competes with the added cations of Fe and Ca for the binding sites, consequently occupying a constant small fraction of the exchange capacity.

The total extractable aluminum apparently varied systematically along the series, being highest in the 0% Fe/100% Ca clay and lowest in the 100% Fe/0% Ca clay. It constituted 14% to 2%, respectively, of the total extractable metals (Table IV). However, it did not systematically vary in any of the fractions, so the variation in the total quantity of extractable aluminum may not be of significance. As in the case of magnesium, aluminum was released from the crystal during acid leaching and/or titration, and also remained as part of the adsorbed complex.

Together, aluminum and magnesium constituted 10−20% of the total extractable metals, while iron and calcium constituted 90−80%. The relative concentrations of Fe and Ca were, in most cases, quite close to the desired nominal values.

The data on surface ion composition will be useful for correlating those spectral and catalytic properties of the clays which are associated with these ions, rather than with the bulk composition. Also, such data will be useful in quantitatively correlating spectral changes with ionic composition in order to improve remote determinations of the abundance of iron.

3.2. WATER ADSORPTION ISOTHERMS

The adsorption of water by Martian soil has been suggested to be an important part
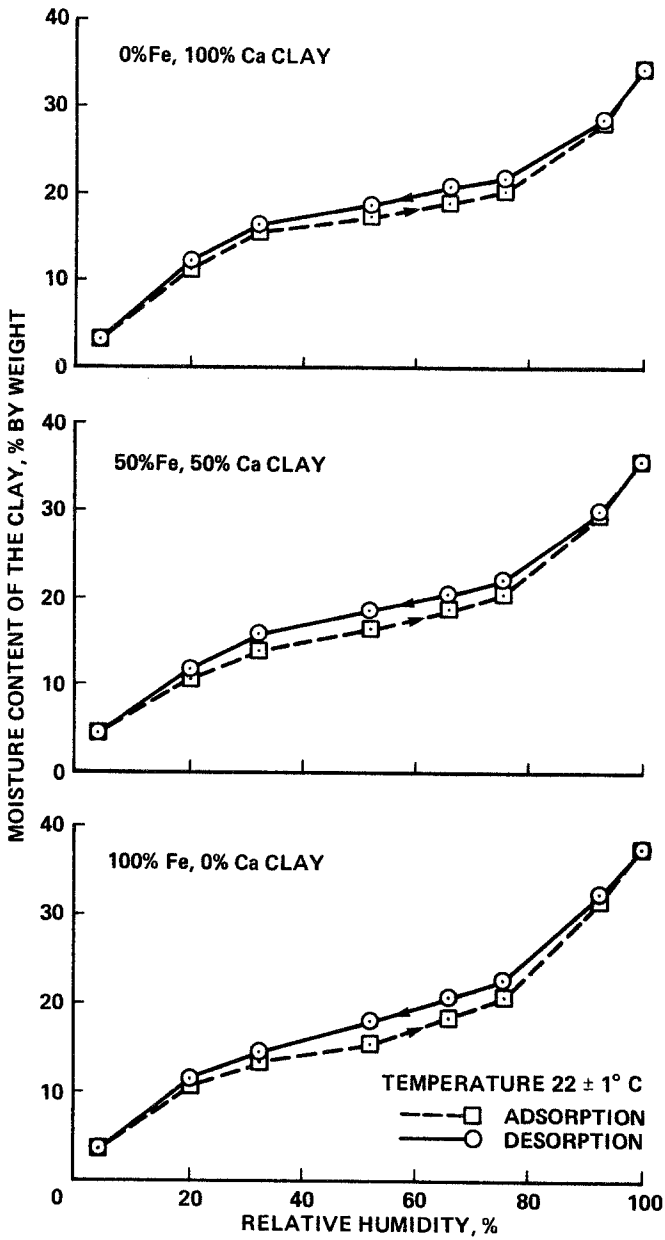
Fig. 2.   Water adsorption isotherms of three iron-calcium MarSAM clays.

of the water-cycle on Mars (Anderson and Tice, 1979). Hence, the study of adsorp-
tion of water by smectites, proposed to be major components of the Martian soils,
is important in that a significant portion of the water present on Mars may be con-
tained in such clays (as well as in other forms, such as permafrost).

The water adsorption isotherms determined for three of the clays are presented in
Figure 2. The shapes of the isotherms are typical for multilayer adsorption processes,
customarily described by the B.E.T. theory (Brunauer *et al.*, 1967). The calcium-clay
isotherm is very similar to those previously reported in the literature (*e.g.* Roderick
et al., 1969). To the best of our knowledge, water adsorption isotherms have not yet
been reported for iron-smectites.

As shown by the figure, hysteresis loops were seen for all clays. At a given relative
humidity (*i.e.* a given partial molar free energy of water), the clay contained higher
moisture on the desorption leg of the loop (starting from wet clay) than it contained
on the adsorption leg (starting from the dry clay). The widths of the hysteresis loops
were maximal in the middle of the humidity range, and it tended to increase as the
iron content in the clay was increased (Figures 2 and 3).

The surface ion composition (Fe/Ca proportion) affects the adsorption of
moisture in a complex way (Figure 3). At low relative humidities ($\leq 20\%$), the effect
of the surface composition was small, and the three clays behaved in a similar way.
Between 30% and 60% relative humidity the calcium rich clays generally adsorbed
more water than did the iron-rich clays. In the range between 60−75% relative hu-
midity, the difference between the Ca and Fe clays was again small but now the Fe
clay adsorbed more water than the Ca clay. This trend became even more prominent
at high relative humidities ($\geq 90\%$). The variation of adsorption with both humidity
and Fe/Ca ratio indicates that the energetics of adsorption of water onto the clay sur-
face depend on surface coverage with both water and iron or calcium, as will be dis-
cussed below.

Water adsorption on smectite minerals may be best described as a sequential
hydration of binding sites on both the siloxane surface and the adsorbed cations
(Sposito and Prost, 1982). NMR and IR studies have shown that a monolayer of
water molecules interspersed between two adjacent clay platelets constitutes the first
of several stable structural configurations. In this configuration four molecules of
water are bound per unit cell, resulting in a moisture content of about 10% by weight.
Some of these water molecules form ice-like structures around the adsorbed ions but
are still strongly hydrogen-bonded to each other and to the smectite surface. Some
hydrated protons are located inside the trigonal cavities of the siloxane surface,
breaking the ice-like structures to some degree. Therefore, the adsorbed water
molecules show much more orientational variability than do molecules in ice, as
shown by measurements of NMR relaxation times (Calvet, 1975). This monolayer
configuration is typical for smectites exchanged by monovalent ions, but is not readi-
ly discernible for smectites exchanged with divalent ions.

Another relatively stable configuration is formed with about 8 water molecules per
unit cell, *i.e.* at ~ 20% moisture content, forming a two-dimensional liquid layer
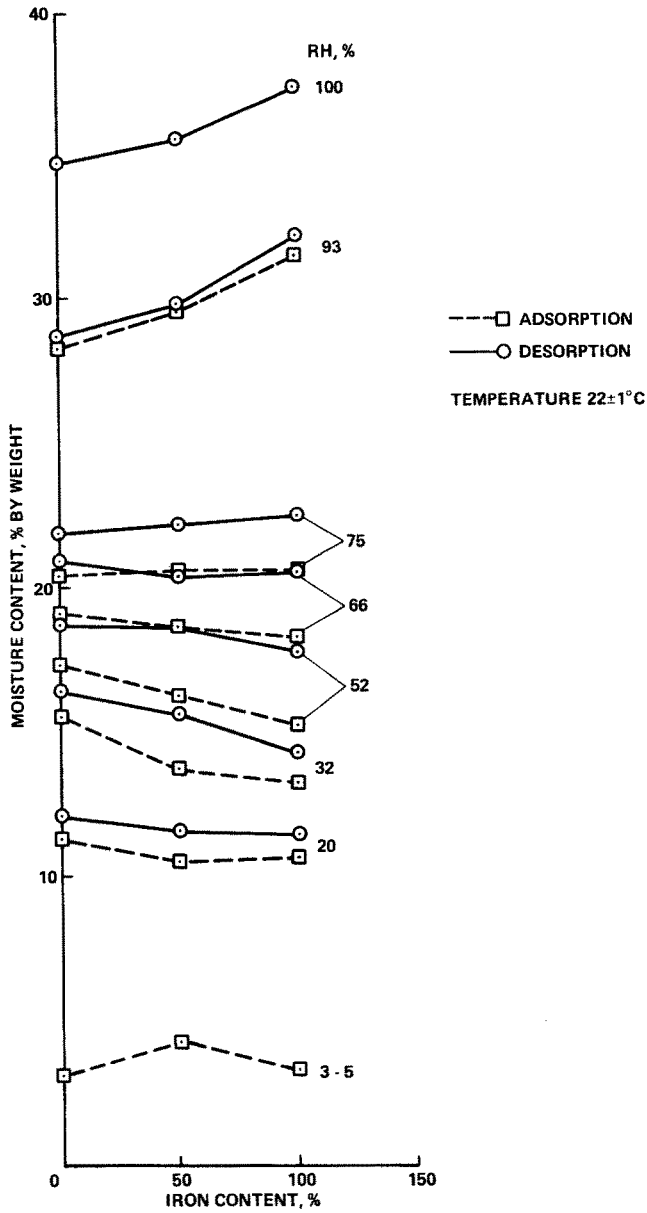
Fig. 3. Effects of composition of surface ions on the water adsorption of three MarSAM clays at various relative humidities.

with the water molecules octahedrally coordinated around the adsorbed cations and hydrogen-bonded to the siloxane surface of the clay platelets. As the water content is further increased up to and beyond 12 molecules per unit cell (~ 30% moisture content), the additional water molecules are interspersed between the cationic solva-

tion shells, showing diffusional characteristics increasingly similar to those of bulk water. On the basis of this model, we predict that the adsorption isotherms of various cationic forms of the smectite clay will be the most different at moisture contents corresponding to 4 and 8 H_2O molecules per unit cell (10–20% adsorbed moisture), where the solvation envelopes around the cations are being formed.

Returning now to the isotherm results, we observed that at very low surface coverage with water (up to 20% RH and 10% moisture content), the clay-water interactions were not very sensitive to the types of ions adsorbed (Figure 3). The B-point of the adsorption curves (the 'knee' in the isotherms), which corresponds to monolayer coverage of the water on the surface, falls for these isotherms (see Figure 2) at moisture contents of 10–15% by weight. For smectite clays having surface areas of ~ 800 m^2 g^{-1} and assuming a homogeneous distribution of adsorbed water of density of 1.0 g cm^{-3}, the calculated average thickness of the adsorbed water layers would be 0.125 nm at a moisture content of 10%. Since the clay plates are stacked parallel to each other to form tactoids, this thickness roughly corresponds to a single water layer separating two adjacent clay plates.

As predicted from the model of sequential hydration, the largest differences in adsorption between the three ion-exchanged clays were seen in the range of 10–20% moisture content (20–70% RH, Figure 3), corresponding to the swelling of the clay from a state of one layer of water between plates to two layers. At this stage, the iron clay is less adsorbing, and had the largest hysteresis loop. One reason for this behavior may be that the solvation energy of the adsorbed iron species is lower than that of Ca^{2+}. An alternative explanation is that the forces binding the clay plates together are larger when a layer of hydroxy-iron ions is interposed between them than when calcium is the sole exchangeable ion. The latter possibility has been proposed previously on the basis of Mössbauer measurements for similar iron containing clays (Diamant et al., 1982).

At higher relative humidities, when the clay plates are further separated, the iron containing clay adsorbs more water than the Ca-clay. This behavior may possibly be due to the fact that the exposed surface layer of the hydroxy iron is more polar than that of the siloxane surface exposed in the Ca-clay.

Since the surface-chemical reactivity of clays is strongly affected by the location and amount of adsorbed water, it is expected that the reactivity of Martian soil, if indeed smectite clays are major components, will be (a) modulated by the amount of adsorbed water, (b) more variable at some relative humidities than at others, depending on the stability of the molecular configuration of water, and (c) dependent, to some extent, on the surface ion distribution and water content. This latter dependence is shown in the simulations of the Viking Labeled Release experiments discussed below.

3.3. SPECTRAL AND PHOTOPHYSICAL PROPERTIES

Reflectance spectroscopy

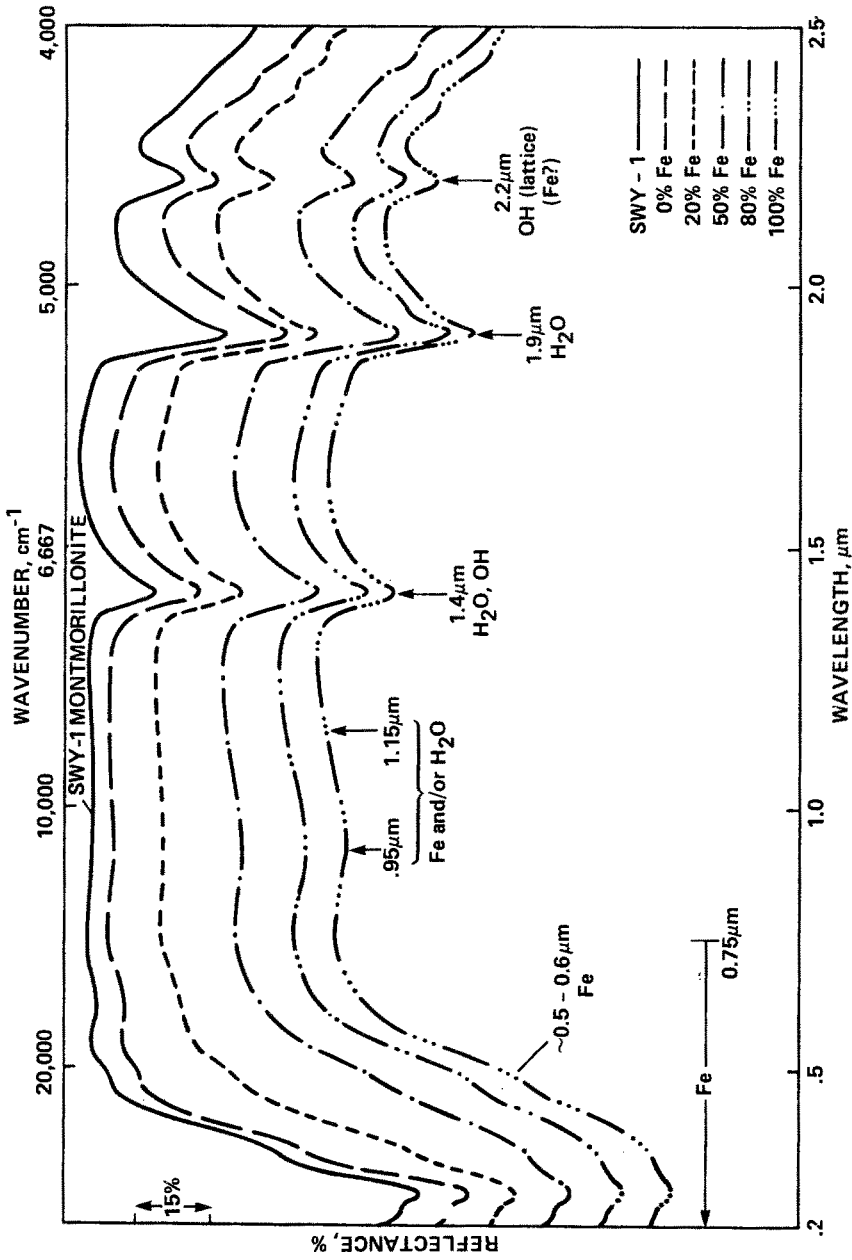The reflectance spectra in the spectral region from 0.2–2.5 μm of the MarSAM sam-

Fig. 4.   Diffuse reflectance spectra of the parent SWy-1 montmorillonite clay and clays with various levels of adsorbed iron. Reflectance is given in percent and each spectrum is offset by 10% for clarity. The assignments for various absorption features are shown.

ples are shown in Figure 4. For purposes of comparison, the spectra have been offset by increments of 10% in reflectance. The regions of spectral interest are designated in the figure. In the region from 0.20 to 0.75 μm, all peaks are attributable to $Fe-O^{2-}$ and other charge transfer bands or crystal field absorptions of iron (Karickhoff and Bailey, 1973; Chen *et al.*, 1979; Banin *et al.*, 1985; for a more general discussion of reflectance spectra in clays, see Karr, 1975). In the wavelength region from 0.8 to 1.3 μm, weak transitions are noted in the crude clay which are due to adsorbed water. However, absorptions due to iron crystal field transitions may be superimposed on the water bands (Adams, 1975) and, as expected, these absorptions become stronger with increasing iron content (Figure 4). At wavelengths longer than 1.3 μm, there are three major spectral features of interest; these occur at 1.4, 1.9, and 2.2 μm. The first two have been identified as water absorption bands due to adsorbed or interlayer water (Hunt and Salisbury, 1970). The band at 1.4 μm also contains a contribution from structural hydroxyl in the clay (Hunt and Salisbury, 1970). The third peak at about 2.2 μm is attributable to OH within the clay lattice (Hunt and Salisbury, 1970), but this peak may also have a contribution from Fe^{2+} (Adams, 1975). Also, the exact position of this peak may vary between 2.2 and 2.4 μm depending on the metal cation to which the OH is linked (Farmer, 1974; Singer, 1985). A comparison of the spectra shown in Figure 4 shows that the most readily apparent changes in the position and slope of the reflectance spectrum due to changes in iron content occur at wavelengths shorter than 1.2 μm.

Comparisons of the reflectance spectra of the 0% and 100% iron substituted clays to the reflectance spectrum of a Martian bright region, but with the spectral contribution of atmospheric CO_2 removed (McCord *et al.*, 1982), are shown in Figure 5. This Mars spectrum is a composite from telescopic observations made in Hawaii in 1973 and 1978 (McCord *et al.*, 1977; Singer *et al.*, 1979). For purposes of comparison, the MarSAM spectra have been scaled to a reflectance of 35% at 1.23 μm, a value observed in the Mars spectrum. This wavelength lies in a spectral region devoid of spectral features but is characterized by a slight upward slope. It is of interest to compare peak positions, slope changes and their magnitudes in these spectra. The Mars spectrum is characterized by strong Fe absorptions from the ultraviolet to about 0.75 μm, and these features are also evident in the spectra of the MarSAM suite. In this same spectral region, albeit not obvious from the figure, there are changes in slope in the Mars spectrum at about 0.5 to 0.6 μm as seen in more recently obtained spectra (Singer, 1985). A similar change in slope occurs in the clay spectra at about 0.5 μm. Assuming these features are due to surface iron, the differences in the observed slope changes between the Mars and MarSAM spectra may reflect differences in surface iron content (see Table II and Clark *et al.*, 1982). At 0.87 μm, a weak absorption peak that has been assigned to Fe^{3+} (Huguenin *et al.*, 1977) occurs in the Mars spectrum. Similar features are seen in the spectra of the MarSAM suite of clays, but are displaced by about 0.05 μm toward longer wavelengths. The intensities of these peaks in the MarSAM spectra increase with increasing iron substitution (see Figure 4).

The Mars spectrum (without CO_2) shows relatively intense absorption bands at 1.4 and 1.9 μm and a less intense absorption at 2.2–2.3 μm (see Figure 5), which are probably due to water ice and/or hydroxylated minerals but may contain contributions from ferrous iron. In the MarSAM suite of iron substituted clays, the bands at 1.4 and 1.9 μm are qualitatively similar to those of the Mars spectrum (without CO_2) and are attributable to adsorbed water and structural hydroxyls for the 1.4 μm band and water for the 1.9 μm band, while the absorption at 2.2 μm is attributable to clay lattice hydroxyls, with a possible contribution from iron. In Figure 5, the reflectance bands at 1.4 and 1.9 μm in the MarSAM suite are still more intense than the corresponding bands in the Mars spectrum. The greater intensities of these peaks in the MarSAM spectra are expected since the MarSAM clays, which were measured in ambient room air, should contain more water than is known to exist in the Mars soil and atmosphere. In future environmental studies, the MarSAM clays will be subjected to atmospheric conditions that mimic the water and CO_2 conditions known on Mars, and the reflectance spectra will be recorded under these conditions.
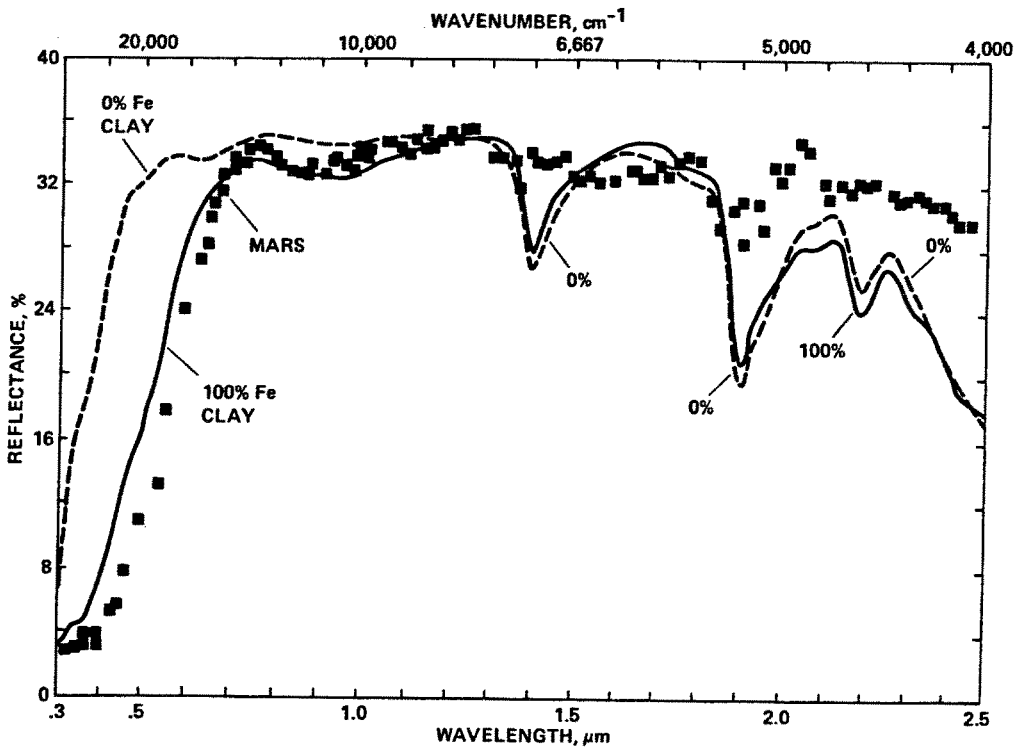

Fig. 5.   Diffuse reflectance spectra of the '0'% and 100% iron substituted MarSAM clays and of a bright region of Mars, with features of atmospheric CO_2 removed for clarity (McCord *et al.*, 1982). For purposes of comparison, the MarSAM spectra are scaled to a reflectance of 35% at 1.23 μm, corresponding to that observed in the Mars spectrum.

From Figure 5, it can be concluded that the Mars and MarSAM reflectance spectra are qualitatively similar. As the amount of surface iron in the clay is increased, a better match of the MarSAM spectrum to the Mars spectrum is obtained, especially in the important wavelength region below 1.2 μm where iron absorption occurs. There are a number of plausible explanations for the shifts of features in the Mars spectrum to the red of those in the MarSAM spectra and for the variation with iron of the intensities of the water bands in the clay spectra. The definitive interpretation of these phenomena, however, will depend upon further study.

Photophysical properties

Using a suite of iron/calcium clays similar to the ones studied in this paper, Coyne and Banin (1986) examined the relationship between the energy stored by clays, as indicated by thermoluminescence before and after gamma-irradiation, and the amount of surface iron, as determined by chemical analysis and electron spin resonance (ESR). Their findings show that ESR spectra are affected by the type and amount of iron in clays and that certain features show the same dependence on iron as do the properties of clays examined in this paper.

There are three regions of the ESR spectra of montmorillonite clays that are relevant to the study of iron. The low field ($g = 4$) signal in the clay spectra has been attributed to structural iron, whereas the broad component of the high field ($g = 2$) signal is characteristic of surface iron (Goodman, 1978; Craciun and Meghea, 1985; and Coyne and Banin, 1986). The sharp component of the high-field signal has been attributed to electronic energy that is stored as O^- centers (Hall, 1980). The results of Coyne and Banin were consistent with these interpretations, showing an insignificant change in the intensity of the $g = 4$ component of the ESR spectrum but an increasing intensity with increasing surface iron of the broad component at $g = 2$. The sharp component of the $g = 2$ signal was not quantitated in this study.

The intensity of thermoluminescence (TL) exhibited by the clays decreased with increasing surface iron concentration but, like the increase in the ESR intensity discussed above, this decrease was non-linear. The decrease in TL leveled off when the surface iron exceeded 50%. This plateau was seen in both the residual stored energy detected prior to gamma irradiation and that remaining one month after irradiation with 1 Mrad of gamma rays. The loci of the stored electronic energy have not been definitively assigned to any particular atomic centers, but are generally considered to be in the bulk crystal structure.

The results of the experiments detailed in Coyne and Banin (1986) indicate that the glow curve intensity and the ESR signal strength are both correlated with the concentration of surface iron in that both signals exhibited a pronounced diminution in the changes in their strengths as the iron content exceeded 50%. This mutual dependence of signal strengths on phenomena associated with both bulk and surface sites was interpreted as being indicative of interactions between these bulk and surface sites (Coyne and Banin, 1986). From these data, Coyne and Banin tentatively proposed

that the surface iron may affect the storage and release of energy, and, hence, the chemical reactivity of this material in a significant manner.

It has been hypothesized that bulk energy storage may affect surface reactivity of minerals (Coyne, 1985). In this regard, it is of interest to note that the labeled release studies discussed below also show a plateau of surface reactivity (decomposition of sodium formate) at concentrations of surface iron exceeding 50%. As was discussed above, at this iron content the amount of the more labile, exchangeable surface iron reaches its maximum value. Whether the similarities in the behavior of the ESR, thermoluminescence, and LR results are related, or whether they are circumstantial, has not yet been established. However, that the same iron concentration is a turning point for three different phenomena certainly is intriguing.

3.4. SIMULATION OF THE VIKING LABELED RELEASE EXPERIMENTS

In the biology experiments conducted by the Viking landers on Mars, direct 'wet chemical' studies of the interaction of the Martian soil with water, salts, gases, and organic compounds were performed. The results of these experiments have proved to be an unique and important source of chemical information on the Martian soil. Although no clear evidence for life was found, these experiments showed that the soil was chemically reactive and capable of decomposing various organic acids, catalyzing photochemical fixation of CO_2/CO, and releasing oxygen upon wetting (Klein, 1977, 1979a, b).

Specifically, the Viking Labeled Release (LR) experiments (Levin and Straat, 1976, 1977) have proven to be useful as a screening tool for identifying the mineral components of the Martian soil. Many features of the Viking LR results were reproduced in simulation experiments using smectite clays, particularly the iron and the hydrogen forms (Banin and Rishpon, 1979a, b; Banin et al., 1981). In these simulation experiments, labeled carbon was released when the same medium solution used in the Viking LR experiments was reacted with the clays. The rates and quantities released were similar to those measured by Viking on Mars. The extent and rate of the reaction were affected by the pH, by the type of exchangeable ion, by salt additives, and by preheating of the mineral catalyst. It was proposed (Banin and Rishpon, 1979b; Banin et al., 1981; Banin and Margulies, 1983) that the surface activity of the clay could be responsible for decarboxylation and/or oxidation of organic acids that results in the release of $^{14}CO_2$ in the LR experiment. The catalytic activity is modulated and affected by the surface properties of the soil, that is, the rate is dependent on an optimal combination of pH, adsorbed ions, water content, and substrate availability.

A detailed study was conducted in the context of the present work to characterize the LR activity of the suite of MarSAM. Specifically, the combined effects of surface-ion composition and moisture content on the decomposition of ^{14}C labelled sodium formate were measured in simulations of the Viking Labeled Release experiment. The results of the simulation experiments with three clays (0%, 50%, and 100% adsorbed Fe), each at two widely different adsorbed water contents, are shown in Figure 6. The clays were preconditioned by equilibration at 3–5% ('dry' series,
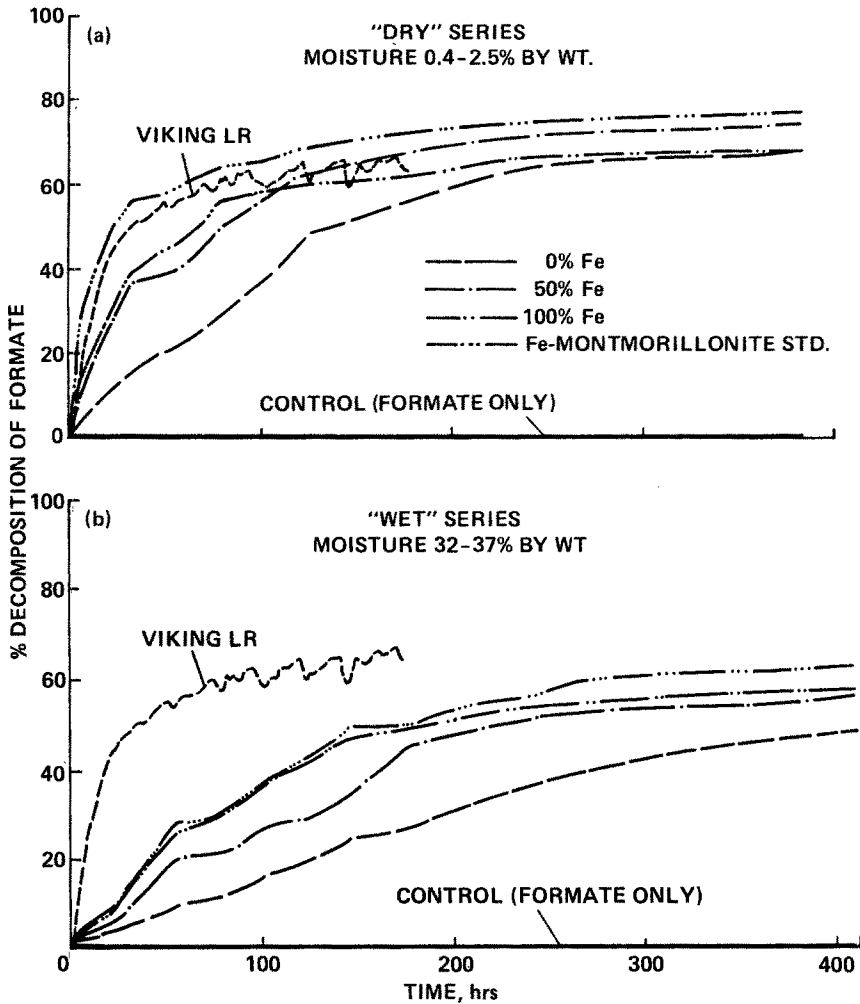
Fig. 6. Decomposition of sodium formate by Martian soil in the Viking Labeled Release Experiment and by three iron-calcium montmorillonite clays and a 'standard' iron-montmorillonite clay in simulation experiments. The simulation experiments were done using clays with two different ranges of water content achieved by pre-equilibration at different relative humidities: a) 'dry' series, clays with 0.4–2.5% moisture content; b) 'wet' series, clays with 32–37% moisture.

Figure 6a) and 100% ('wet' series, Figure 6b) relative humidity. For comparison, the decomposition curve measured in one of the Viking LR experiments employing Martian soil ('Viking LR') and the curve measured in a LR simulation using a Fe-montmorillonite prepared previously and used as a standard in past experiments ('Fe-montmorillonite Std.') are also shown.

In Figure 7, the time $(t_{1/2})$ for decomposition of 50% of the added $Na^{14}COOH$ is plotted against the nominal surface iron content. The initial rate of decomposition increased considerably as the iron content was increased and moisture content
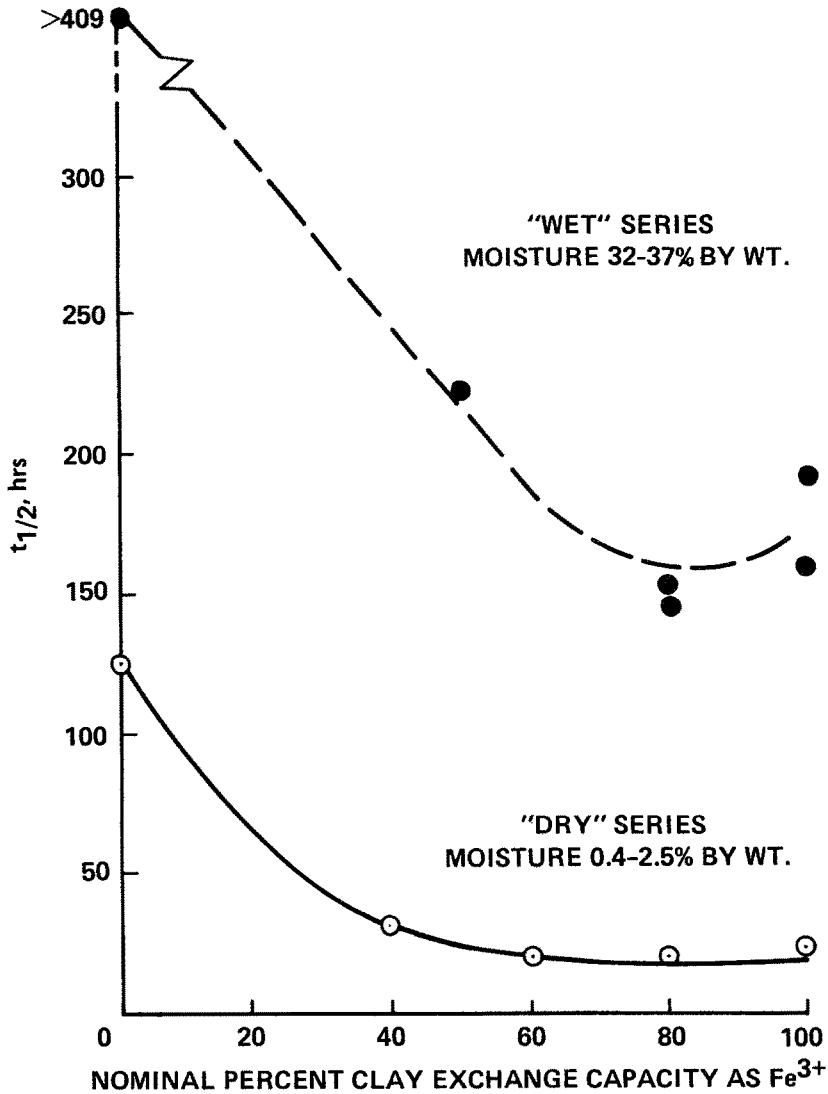
Fig. 7. Variation of the time ($t_{1/2}$) for 50% decomposition of the labeled sodium formate with percentage of iron adsorbed on a suite of MarSAM clays in a simulation of the Viking Labeled Release Experiment.

decreased (Figure 6). Correspondence with the behavior of the Martian soil was best for the 'dry' 100% Fe MarSAM (Figure 6a). The least decomposition and poorest agreement with the Martian soil was observed in the Ca-clay for each moisture series. Increasing the adsorbed iron content up to ~ 50% of the exchange capacity increased the decomposition rate, which was then unaffected by further increases in iron content. As discussed previously, similar saturation effects were observed in phenomena

(ESR and thermoluminescence) related to energy storage in these clays. These results are intriguing in that they may indicate a correlation between crystal properties and surface reactivity of the clays. Detailed analysis of the mechanisms of such a connection will have to await further experimentation.

The relative decrease in the clay reactivity as moisture content increases may be explained by the competition between water and formate for the reactive sites involving the adsorbed iron. As discussed above in relation to the water adsorption isotherms, at a moisture content of $2-3\%$ by weight, less than one water molecule per clay unit-cell is adsorbed and the surface ions are essentially without hydration envelopes, fully exposing them to the formate. Under the cold and arid Martian conditions, the top soil is probably extremely desiccated. Limited data available from the pyrolysis of the soil during the GC/MS experiment on Mars show a loss of about 1% of H_2O during rapid heating (Biemann $et\ al.$, 1977). Thus, it is not surprising that the best correspondence between the MarSAM clays and the Martian soil was with the driest, iron-rich clay.

4. Summary

Among the numerous candidates proposed since 1976 as Mars soil analogs, smectite montmorillonite clays containing adsorbed iron appear to satisfy the largest number of qualitative constraints known at present. The presence of clays on Mars may strongly affect its climatological cycles, land forming and shaping processes, and volatile cycles. Furthermore, establishing the presence of clays as a major and active component of the Martian soil and dust will be a clue to an evolutionary step on Mars when liquid water was present. Potentially the presence of significant amounts of water may have made possible primitive abiotic or biotic evolution, whose organic remnants may still be found in buried sediments. To these ends we have carried out a number of experiments studying various properties of a suite of iron-calcium montmorillonite clays as a model for the Martian soil. In summary, we have:

(1) Prepared a monomineralic model for Mars aeolian material in which:

a) the parent material is a natural montmorillonite clay, and

b) several properties, including surface iron, adsorbed water, and stored electronic energy, known or hypothesized to be key factors in influencing the reflectance signature can be systematically varied.

(2) Measured the reflectance spectra of the above clays from $0.2-2.5\ \mu m$ and found:

a) two absorption features (at $0.5-0.6$ and $0.95\ \mu m$) that increase with increasing surface iron,

b) good qualitative agreement between the spectra of our clays and of Mars, and

c) that the correspondence between the MarSAM and Martian surface spectra improved as the iron contents of the MarSAM were made increasingly similar to that found in the Martian soil.

(3) Measured water adsorption isotherms (at 22 °C) of the MarSAM and found them to:

a) be generally characteristic of multilayer adsorption processes,

b) show cation-dependent hysteresis, *i.e.* to be dependent on surface coverage of both water and exchangeable cations,

c) show three regions corresponding to ≤ 1 adsorbed monolayer of water (at 20% R.H.), 1-2 monolayers (20−70% R.H.), and ≥ 2 monolayers (> 70% R.H.),

d) exhibit maximum sensitivity to the cation type in the range of 20−70% relative humidity, as would be expected for sequential hydration, and

e) predict that for the anticipated humidity of Mars that the dependence of the isotherms on cation type would be minimal, as the water is strongly bonded to the silicate layer as well as to the cations.

4. Measured the rate of decomposition of sodium formate, as evidenced by the release of labeled CO_2, by the clays as functions of iron content and relative humidity in simulations of the Viking LR experiment and found that:

a) the rate of decomposition increased with increasing iron content and with decreasing water content, and

b) the decomposition profiles of the MarSAM were similar to those of the Martian soil and that the clay with the highest iron and lowest water gave the best match.

(5) Compared the dependence on surface iron of the amount of stored energy, as measured by thermoluminescence, with the dependence on iron of the $g = 2$ E.S.R. signal (from surface iron), the half-life of sodium formate in the Viking LR simulations, and the exchangeable iron of the MarSAM, and found that all of these parameters tended toward a plateau for surface iron > 50%. From consideration of these mutual dependences, we have concluded that:

a) iron as an exchangeable cation on a clay has particular potence for initiating chemical reactions, and

b) stored energy may also be a factor in initiating and influencing the rates of reactions on clays, and by implication, on the surface of Mars.

Acknowledgements

References

Adams, J. B.: 1975, 'Interpretation of Visible and Near Infrared Diffuse Reflectance Spectra of Pyroxenes and Other Rock Forming Minerals', in C. Karr, Jr. (ed.), *Infrared and Raman Spectroscopy of Lunar and Terrestrial Materials*, Academic Press, New York, p. 104.

Anderson, D. M. and Tice, A. R.: 1979, *J. Mol. Evol.* **14**, 33.

Baird, A. K., Castro, A. J., Clark, B. C., Toulmin III, P., Rose, Jr., H., Keil, K., and Gooding, J. L.: 1977, *J. Geophys. Res.* **82**, 4595.

Baird, A. K., Toulmin III, P., Clark, B. C., Rose, Jr., H. J., Keil, K., Christian, R. P., and Gooding, J. L.: 1976, *Science* **194**, 1288.

Banin, A.: 1973, 'Quantitative Ion Exchange Process for Clays'. U.S. Patent No. 3,725,528.

Banin, A.: 1986, 'Clays on Mars', in H. Hartman and A. G. Cairns-Smith (eds.), *Clays and the Origin of Life*, Cambridge University Press, Cambridge, p. 106.

Banin, A. and Margulies, L.: 1983, *Nature* **305**, 523.

Banin, A., Margulies, L., and Chen, Y.: 1985, *J. Geophys. Res. Suppl.* **90(C)**, 771.

Banin, A. and Rishpon, J.: 1979a, *Life Science and Space Research* **XVII**, 59.

Banin, A. and Rishpon, J.: 1979b, *J. Mol. Evol.* **14**, 133.

Banin, A., Rishpon, J., and Margulies, L.: 1981, *Third Internat. Coll. on Mars*, Publ. 441, Lunar Planet. Inst., Houston, TX, p. 16.

Biemann, K., Oro, J., Toulmin III, P., Orgel, L. E., Nier, A. O., Anderson, D. M., Simmonds, P. G., Flory, D., Diaz, A. V., Rushneck, D. R., Biller, J. E., and Lafleur, A. L.: 1977, *J. Geophys. Res.* **82**, 4641.

Brunauer, S., Copeland, L. E., and Kantro, D. L.: 1967, 'The Langmuir and BET Theories', in E. A. Flood (ed.), *The Solid-Gas Interface*, Vol. 1, Dekker, New York.

Cairns-Smith, A. G.: 1982, *The Genetic Takeover and the Mineral Origins of Life*, Cambridge Univ. Press, Cambridge.

Calvet, R.: 1975, *Clays and Clay Minerals* **23**, 257.

Carr, M. H.: 1987, *Nature* **326**, 30.

Chang, S., Des Marais, D., Mack, R., Miller, S. L., and Strathearn, G. E.: 1983, 'Prebiotic Organic Syntheses and The Origin of Life', in J. W. Schopf (ed.), *Earth's Earliest Biosphere*, Princeton Univ. Press, Princeton, New Jersey.

Chen, Y., Shaked, D., and Banin, A.: 1979, *Clay Miner.* **14**, 93.

Clark, B. C., Baird, A. K., Rose, Jr., H. J., Toulmin III, P., Christian, R. P., Kelliher, W. C., Castro, A. J., Rowe, C. D., Keil, K., and Huss, G. R.: 1977, *J. Geophys. Res.* **82**, 4577.

Clark, B. C., Baird, A. K., Rose, Jr., H. J., Toulmin III, P., Keil, K., Castro, A. J., Kelliher, W. C., Rowe, C. D., and Evans, P. H.: 1976, *Science* **194**, 1283.

Clark, B. C., Baird, A. K., Weldon, R. J., Tsusaki, D. M., Schnabel, L., and Candelaria, M. P.: 1982, *J. Geophys. Res.* **87**, 10059.

Coyne, L. M.: 1985, *Origins of Life* **15**, 161.

Coyne, L. M. and Banin, A.: 1986, *Clays and Clay Minerals* **34**, 645.

Craciun, C. and Meghea, A.: 1985, *Clay Miner.* **20**, 281.

Diamant, A., Pasternak, M., and Banin, A.: 1982, *Clays and Clay Minerals* **30**, 63.

Farmer, V. C.: 1974, 'The Layer Silicates', in *The Infrared Spectra of Minerals, Mineralogical Society Monograph 4*, Mineralogical Society, London.

Gerstl, Z. and Banin, A.: 1980, *Clays and Clay Minerals* **28**, 335.

Goodman, B. A.: 1978, *Clay Miner.* **13**, 351.

Hall, P. L.: 1980, *Ibid.* **15**, 321.

Huguenin, R. L., Adams, J. B., and McCord, T. B.: 1977, *Lunar Science* **VIII**, 478.

Hunt, G. R. and Salisbury, J. W.: 1970, *Mod. Geol.* **1**, 283.

Jepson, W. B.: 1988, 'Structural Iron in Kaolinites and in Associated Ancillary Minerals', in J. W. Stucki, B. A. Goodman, and U. Schwertmann (eds.), *Iron in Soil and Clay Minerals*, NATO Advanced Study Institute, Series C, **217**, D. Reidel, Dordrecht, p. 467.

Karickhoff, S. W. and Bailey, G. W.: 1973, *Clays and Clay Minerals* **21**, 59.

Karr, Jr., C.: 1975, *Infrared and Raman Spectroscopy of Lunar and Terrestrial Materials*, Academic Press, New York.

Klein, H. P.: 1977, *J. Geophys. Res.* **82**, 4677.

Klein, H. P.: 1979a, *J. Mol. Evol.* **14**, 161.

Klein, H. P.: 1979b, *Rev. Geophys. Space Phys.* **17**, 1655.

Levin, G. V. and Straat, P. A.: 1976, *Origins of Life* **7**, 293.

Levin, G. V. and Straat, P. A.: 1977, *BioSystems* **9**, 165.

McCord, T. B., Clark, R. N., and Singer, R. B.: 1982, *J. Geophys. Res.* **87**, 3021.

McCord, T. B., Huguenin, R. L., Mink, D., and Pieters, C. M.: 1977, *Icarus* **31**, 25.

Pepin, R.: 1986, 17th Lunar Planetary Sci. Conf., 656.

Roderick, G. L., Senich, D., and Demirel, T.: 1969, *Internat. Clay Conf.*, Vol. I, Tokyo, Japan, p. 659.

Singer, R. B.: 1985, *Advances in Space Res.* **V**(8), 59.

Singer, R. B., McCord, T. B., and Clark, R. N.: 1979, *J. Geophys. Res.* **84**, 8415.

Solar System Exploration Committee: 1983, *Planetary Exploration Through the Year 2000-A Core Program*, NASA.

Solar System Exploration Committee: 1986, *Planetary Exploration Through the Year 2000-An Augmented Program*, NASA.

Sposito, G. and Prost, R.: 1982, *Chem. Rev.* **82**, 553.

Squyres, S. W.: 1984, *Ann. Rev. Earth Planet Sci.* **12**, 83.

Toon, O. B., Pollack, J. B., and Sagan, C.: 1977, *Icarus* **30**, 663.

Toulmin III, P., Baird, A. K., Clark, B. C., Keil, K., Rose, Jr., H. J., Christian, R. P., Evans, P. H., and Kelliher, W. C.: 1977, *J. Geophys. Res.* **82**, 4625.

Van Olphen, H. and Fripiat, J. J.: 1979, *Data Handbook for Clay Materials and other Non-metallic Minerals*, Pergamon Press, London.