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A. Banin, Ames Research Center, Moffett Field, California
L. Margulies, Seagram Centre for Soil and Water Sciences, Hebrew University, Rehovot, Israel

National Aeronautics and
Space Administration

Ames Research Center
Moffett Field, California 94035

Smectites Versus Palagonites in Mars Soil: Evidence From Simulations of Viking Biology Labeled Release Experiments

A. Banin*†

NASA Ames Research Center, Moffett Field, California 94035 U.S.A.

and

L. Margulies

Seagram Centre for Soil and Water Sciences, Hebrew University

Rehovot, Israel

The mineralogical composition of the fine soil of Mars has not been determined and is the subject of an ongoing controversy[1]. During and immediately after the Viking Mission, smectite clays were considered as the most likely Mars soil analog material (MarSAM), but recently it has been suggested that the most likely MarSAM is palagonite, an amorphous weathering product of volcanic glass. We report here the results of an experimental comparison between palagonites and a smectite (montmorillonite) in the simulation of the Viking Biology Labeled Release (LR) experiment and draw conclusions regarding their suitability as MarSAMs. We have found that palagonites do not cause formate decomposition and ^{14}C release in their natural form or after acidification and thus cannot be a completely satisfactory analog to the Mars soil studied by Viking.

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*NRC Senior Research Associate on leave from Seagram Centre for Soil and Water Sciences, Hebrew University, Rehovot, Israel.

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The identification of the prevailing minerals in Mars soils studied by the Viking Landers remains an open and somewhat enigmatic question. Since no direct mineralogical measurement has been performed by Viking, the evidence at hand is indirect and consists mainly of the elemental chemical analyses[2]; spectroscopic measurements from Earth[3,4], from the various Mars orbiters[5], and from the Viking Lander[6,7]; and the Viking biology experimental results[8]. In the Viking biology experiments[8], the Martian soil was interacted with (a) a controlled-composition atmosphere (pyrolytic release (PR) experiment[9]), (b) solutions of various organic compounds (LR experiments[10]), and (c) a solution containing various inorganic and organic compounds (gas exchange (GEX) experiment[11]). The results of these experiments supplied information regarding the physicochemical nature of the soil material; thus, they too were used to constrain, and possibly to identify the minerals present in the soils[12-17].

Because of the elemental composition of the soil, it was originally proposed by the Viking Inorganic Chemical Analysis Team[2] that smectite minerals, mainly nontronite and montmorillonite, are the major minerals present and that they are mixed with various soluble salts. We have used the Viking biology experimental results as a reference to study these smectite minerals in simulation experiments and have obtained faithful simulations of the ^{14}C-release kinetics in the Viking Biology LR experiments and of the labeled carbon fixation in the Viking PR experiments[12-14,17]. These simulations have strengthened the case for smectites being present in the Mars soil and have offered a nonbiological, chemical explanation of the somewhat puzzling results of the Viking Biology experiments. Furthermore, this work established the technique of LR simulation as a useful tool for the physicochemical characterization of MarSAM.

Recently, several published reports have suggested that volcanic glass and especially its weathering product, the amorphous alumosilicate called palagonite, may be the major components of the Mars soil, and a geological scenario was developed[21] to account for their presence. The primary evidence leading to this suggestion was the visible (VIS) and near infrared (NIR) reflectance spectra of martian dust and the martian surface as measured from Earth[3,4,18-20]. The smectite minerals, particularly nontronite, were found not to compare well with the average Mars IR reflectance spectrum, apparently because of the high crystallinity of their Fe sites, whereas palagonites, being amorphous materials, gave a more featureless spectrum and exhibited high absorption in the NIR that better fitted the Mars spectral curve[19,20].

To further test the palagonite hypothesis, we have used several samples in LR simulation experiments. The minerals were obtained from C. C. Allen and most of them were described in detail in one of his articles[21]. According to Allen et al.[21], the samples came from cold weathering environments on Earth and represent the cold and wet (Iceland, G-13, G-14; British Columbia, Al-14) and the cold and dry (Antarctica, AN-1) environments. We also included in the study samples of a volcanic soil collected from the top 20-cm layer, 900 m west of the Halemaumau

Crater in the Kilauea Caldrea, Hawaii, and an allophane-containing rhyolitic sand from Taupo County, Japan. The montmorillonite used was of the standard Wyoming Bentonite type designated SWy-1, and obtained from the Clay Minerals Society repository. It was converted to H or Fe forms using the quantitative ion exchange method for clays[13,22].

In the LR experiment on Mars designed by Levin et al.[10], a mixture of several simple organic substrates (Na-formate, Ca-glycolate, Na-D and L-lactate, glycine, and D- and L-alanine), each labeled uniformly with ^{14}C, were added to the soil sample in a test cell. The radioactivity in the atmosphere above the soil was monitored by a β-ray detector during incubation at 10° ±2°C. The release of labeled gas was presumed to be indicative of metabolic activity of living organisms revealed by respiration.

Since in our previous work[12-14] we have found that formate was the most labile compound among those included in the LR-medium solution, we routinely used a 2.5×10^{-4} M $H^{14}COONa$ solution, labeled at a level of 2 μCi/ml, for the simulation experiments. These experiments consisted of injecting 0.1 ml of the ^{14}C-labeled formate solution into 100- to 500-mg preweighted samples of mineral powder in a stoppered vial maintained at 10.2° ±0.2°C. The ^{14}C released to the atmosphere was absorbed into hyamine hydroxide solution impregnated in a circle of fiberglass filter paper hanging from the vial's stopper. The filter paper circles were periodically replaced and the exposed ones were placed in a scintillation vial and were counted in a Tricarb scintillation counter, Packard model 3330. The counting efficiency was 75%.

In Fig. 1 we compare the Viking LR results[10] with our laboratory simulations using Fe and H montmorillonite and British Columbia palagonite. Whereas the two clays show high decomposition activity, the palagonite does not. Similar results were obtained with the other palagonites and the volcanic and allophane soils, as summarized in Table 1.

The decomposition-reaction kinetics obtained with the Fe clay is the most similar to that measured on Mars. In the past, this has led us to suggest that Fe-rich clays, particularly montmorillonite, are major components of the Mars soil[12-14]. We further suggested that the reaction would involve adsorption of formate on the clay surface, its decarboxylation due to interactions with the surface-adsorbed Fe III, and consequent release of $^{14}CO_2$ to the head space of the LR instrument[13]. A faster initial rate and a larger final percent of decomposition was measured with the H-montmorillonite than with the Fe-montmorillonite, perhaps because of the lower pH of the H-montmorillonite[13]. Although low pH is a necessary condition for the $^{14}CO_2$ release[13], it is not a sufficient condition by itself. This is shown by the behavior of the volcanic soil: it had a pH similar to the Fe-montmorillonite but released only one-tenth of the ^{14}C released by Fe-montmorillonite. Additional conditions for such decomposition and release include (refs. 13 and 14, and unpublished data): (1) a solid phase with large specific surface area, possibly typical for the smectites; (2) adsorbed ion(s) such as H and Fe, possibly Zn and Mn, but not Al, Ca, Mg, or Na; and (3) certain isomorphous substitutions in the crystal. (Our experiments indicate that the Fe and Mg replacement for Al in tetrahedra is of paramount importance for the decomposition.)

Since pH was found to be such an important factor in the simulation, we leached palagonites with HCl and studied these "acidified" minerals. The data in Fig. 1 show that the acid leaching has not increased the ability of the British Columbia palagonite to decompose. This was also true for the other palagonites and the allophane soil (see Table 1). Furthermore, the pH of the acidified palagonites was still above ~6.0 in all cases. Measurement of the pH variation of the British Columbia palagonite during acid treatment showed that the pH was 2.86 immediately after addition of 100 ml of 0.01 N HCl to 25 ml of 4% suspension and rose to 3.08 and 3.22 after 1 and 2 hr of contact, respectively. During water leaching the pH rose slightly to 3.46, 3.52, and 3.72 after the first, second, and third leachings, respectively, and after freeze-drying and redispersing to 4% suspension, the pH again rose to 8.5.

In another version of the acid leaching, we used a more concentrated HCl solution (1 N) and measured the percent dissolution of the mineral and its buffer capacity in the acid range. About one-third of the British Columbia palagonite was dissolved by the acid. The nondissolved residue was titrated with NaOH and the titration curve indicated that the remaining mineral still had a rather small buffer capacity in the acid range amounting to only 0, 0.7, and 1.9 meq/100 g mineral at pH 3.5, 4.0, and 5.5, respectively. This should be compared with the buffer capacity of acid-leached montmorillonite[23], which amounts to about 23, 42, and 57 meq/100 g mineral at the pH values listed above. This leads us to believe that (a) palagonites probably have a high buffer capacity at the more basic pH range, (b) by acidifying palagonites one causes major dissolution and obviously major chemical composition changes in them, (c) the residue after acidification still does not have a high buffer capacity in the acid range, and therefore (d) the residue could not possibly cause ^{14}C release from organics as observed in the Viking LR experiment with the Mars soil.

The present results conflict with those reported by the various groups measuring the spectroscopic properties of Mars soils[3,4,6,7,18-20]. They have concluded that smectites (particularly nontronite) are not good MarSAMs on the basis of their reflectance spectra. No completely satisfying explanation of these conflicting spectral and chemical findings is available yet. We wish, however, to offer and discuss the following two suggestions. The first suggestion involves segregation. One might visualize segregation of the fine material on Mars so that the atmosphere and the topmost thin layer of the soil contain more of the amorphous components. This top layer would affect the spectral signature of the planet, whereas the coarser material containing smectites would affect the chemical properties measured in the bulk of the soil. This explanation is supported by hints in an article by Evans and Adams[6], who found indications that "subtle but distinct compositional differences may exist between the global dust and some of the surficial deposits of the Viking-Lander 1 site." Singer[20], however, in summarizing the spectral evidence, states that ". . . evidence is good that the brightest surface units of Mars soils are composed of the same material as the homogeneous eolian dust." Obviously, these matters are not yet settled, and further spectral studies are needed.

The second suggestion involves optical properties of iron clays. There was one key observation that led to the questioning and near rejection of smectites as the most likely MarSAM: the reflectance spectrum of Mars in the VIS-NIR range is characterized by low reflectance between 0.3 μm and 0.4 μm, followed by a steep increase in reflectance between 0.5 μm and 0.8 μm, without showing any specific well-defined peak, whereas the smectites either have very pronounced spectral features from 0.5 to 0.8 μm (nontronite) or are rather transparent (montmorillonite). Singer[20], in a detailed study, has found that the mixing of minerals containing Fe in well-crystallized sites, such as hematite (α-Fe_2O_3) and goethite (α-FeOOH), with montmorillonite did not satisfy this particular combination of strong but featureless spectral opacity. The addition of just 1% hematite was enough to give the pronounced, characteristic, crystal-field absorption peak (reflectance minimum) of crystalline Fe oxides at 0.86 μm. He found, however, that the amorphous palagonites gave spectra rather similar to the Mars spectrum. We speculate here that Fe-montmorillonite has enough spectral opacity in the range of 0.5-0.8 μm, due to its adsorbed Fe. This Fe is residing on the surface of the clay particles, and not in well-crystallized sites. Thus, it may not have the crystal-field adsorption bands characterizing crystalline Fe in this spectral region. Natural montmorillonite, which has a low structural Fe content, does not have any pronounced adsorption feature in the VIS and NIR spectral ranges and its color is gray. The saturation with Fe III changes its color to light red, similar to the color of Mars soil. The amount of adsorbed Fe is about 2%-3% by weight, equivalent to about 2.8%-4.2% Fe_2O_3, and may add to the opacity of the clay, bringing its reflectance closer to that of the Mars soil. Further laboratory measurements are needed to clarify these points.

In conclusion, on the basis of the evidence presented above, we are compelled to believe that the fine soil of Mars, as now seen on the surface of the planet, cannot be fully represented by palagonites found on Earth. This does not preclude the possibility that palagonites were formed on Mars at an early evolutionary stage during volcanic eruptions and were modified by further weathering. The evidence leads us to suggest that Fe-containing smectites, particularly montmorillonite, may be important and active components of the soil, responsible for some of its chemical properties, such as ion exchange, molecular adsorption, and catalysis.

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Table 1 Kinetic parameters and pH of montmorillonites, palagonites, and volcanic soils used as possible MarSAMs in simulations of the Viking Labeled Release Experiment

Sample	Initial rate* (cpm/hr)	^{14}C released† (% ^{14}C added)	pH of slurry‡	Source
British Columbia palagonite (Al-14)	930	1.9	7.4	C. C. Allen[21]
Al-14, acid leached	370	2.0	8.5	C. C. Allen[21]
Antarctic palagonite (AN-1)	104	0.6	9.4	C. C. Allen[21]
Icelandic palagonite (G-13)	368	1.1	6.0	C. C. Allen[21]
Icelandic basaltic glass (G-14)	428	1.0	6.3	C. C. Allen[21]
G-14, acid leached	285	2.0	6.3	C. C. Allen[21]
Volcanic soil	1,905	7.8	4.5	Hawaii
Allophane, Taupo rhyolitic sand	587	3.2	7.6	Japan
Allophane, acid leached	601	4.8	7.5	Japan
Fe-montmorillonite	8,230	78.0	4.4	SWy-1 Wyoming Bentonite, CMS
H-montmorillonite	92,248	94.8	3.1	SWy-1 Wyoming Bentonite, CMS
Formate alone (control)	400	1.5	--	NA

Table 1 Concluded

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*Initial rate of ^{14}C release from the mineral sample interacting with the labeled formate solution.

†Percent of formate ^{14}C released at the end of the experiment.

‡pH measured at the end of the experiment in a 4% w/v slurry of the mineral in distilled water.

Figure Caption

Fig. 1 Kinetics of ^{14}C release caused by Mars soil in two cycles of the Viking Labeled Release Experiment (VL-1), compared with simulations using Fe- and H-montmorillonite and a palagonite from British Columbia.

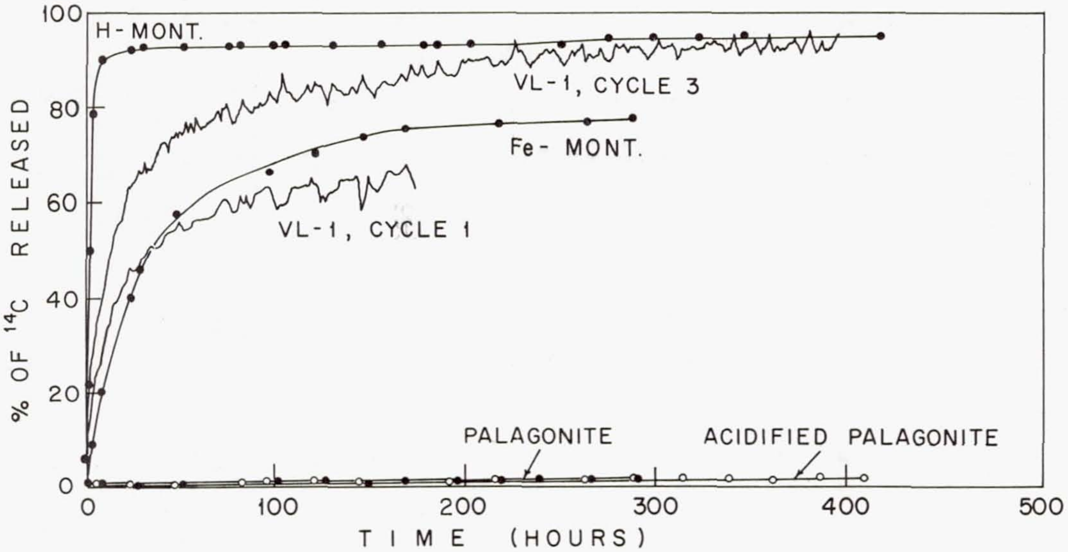
100
80
60
40
20
0
% OF ^{14}C RELEASED
0
100
200
300
400
500
TIME (HOURS)
H-MONT.
VL-1, CYCLE 3
Fe-MONT.
VL-1, CYCLE 1
PALAGONITE
ACIDIFIED PALAGONITE

Fig. 1

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Point of contact: A. Banin, MS 239-8, Ames Research Center, Moffett Field, Calif. 94035
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16. Abstract

The mineralogical composition of the fine soil of Mars has not been determined and is the subject of an ongoing controversy. During and immediately after the Viking Mission, smectite clays were considered as the most likely Mars soil analog material (MarSAM), but recently it has been suggested that the most likely MarSAM is palagonite, an amorphous weathering product of volcanic glass. We report here the results of an experimental comparison between palagonites and a smectite (montmorillonite) in the simulation of the Viking Biology Labeled Release (LR) experiment and draw conclusions regarding their suitability as MarSAMs. We have found that palagonites do not cause formate decomposition and ^{14}C release in their natural form or after acidification and thus cannot be a completely satisfactory analog to the Mars soil studied by Viking.

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