Altered Basaltic Glass: A Terrestrial Analog to the Soil of Mars

CARLTON C. ALLEN,* JAMES L. GOODING,† MICHAEL JERCI NOVIC,* AND KLAUS KEIL*

*Department of Geology and Institute of Meteoritics, University of New Mexico, Albuquerque, New Mexico 87131, and †Planetary Science Section, Jet Propulsion Laboratory, Pasadena, California 91109

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Analyses of Martian surface soil by Viking and Earth-based telescopes have been interpreted as indicating a regolith dominated by the weathering products of mafic or ultramafic rocks. Basaltic glass has previously been proposed as a more likely precursor than crystalline rock, given the low efficiency of surface weathering under present Martian conditions. On Earth large volumes of basaltic glass formed by quenching of magma by water. A similar interaction, between magma and ground ice, may have been a common occurrence on Mars. On the basis of this scenario palagonite, the alteration product of basaltic sideromelane glass, was studied as a possible analog to Martian soil. Samples from Iceland, Alaska, Antarctica, Hawaii, and the deserts of New Mexico and Mexico were examined by optical and scanning electron microscopy, electron microprobe analysis, X-ray diffraction, spectrophotometry, and magnetic and thermogravimetric analysis. We suggest that palagonite is a good analog to the surface soil of Mars in chemical composition, particle size, spectral signature, and magnetic properties. Our model for the formation of fine-grained Martian surface soil begins with eruptions of basaltic magma through ground ice, forming deposits of glassy tuff. Individual glass shards are then altered by low-temperature hydrothermal systems to palagonitic material. Dehydration and aeolian abrasion strip the alteration rinds from the glass, and wind storms distribute the silt-sized palagonitic fragments in a planet-wide deposit.

INTRODUCTION

Any model for the origin of the soil on Mars is constrained by a number of physical and chemical measurements made during the last decade. The bulk chemical composition of the fines at two points on the surface was measured by Viking. Mineralogical interpretation of this composition suggests that the soil is made up largely of smectite clays mixed with sulfates and chlorides (Toulmin et al., 1977). Furthermore, the particle-size distribution and bulk magnetic properties have been estimated. Spectral-reflectance measurements define the areas of the planet's surface to which the Viking data can be extrapolated, and provide further indications of the compositional nature of the surface material. The particles carried into the atmosphere by dust storms have been partially characterized. Finally, the current surface weathering environment has been monitored for more than one Martian year.

The present study attempts to shed light on the nature of weathering processes and the formation of clay-like substances on Mars by examining analogous terrestrial processes and materials. Our hypothesis, inspired by the suggestions of Toulmin et al. (1977) and Gooding and Keil (1978), is as follows: Basaltic eruptions through Martian ground ice produced glassy tuff which was later hydrothermally altered. The alteration products, widely distributed by the wind, form an identifiable and volumetrically important fraction of the surface soil, particularly in the northern hemisphere. On Earth, basaltic eruptions through ground water, rivers or lakes, shallow seas, and beneath glaciers produce large volumes of finely divided sideromelane, an orange glass. The characteristic alteration product of sideromelane is palagonite, a complex
clay-like substance. We studied sideromelane and palagonite from a wide range of weathering environments and ages in order to characterize the alteration process on Earth and understand its relevance to Mars.

MARS DATA BASE

Chemical Composition

The material analyzed by the Viking X-ray fluorescence spectrometer (XRFS; Clark et al., 1977) consists of fine particles, apparently composed largely of iron-rich silicates. In addition, significant amounts of sulfur and chlorine were detected. The analyses do not match that of any single terrestrial rock, but can be duplicated by various mixtures of materials, including some based largely on iron-rich clay minerals. The fines at the two landing sites, separated by nearly one-third of the circumference of the planet, have nearly identical chemical compositions.

Mineralogy

No experiments to determine in detail the mineralogical composition of the soil of Mars were carried aboard Viking. Thus, the mineralogy had to be deduced from XRFS data. Mineralogical interpretations of these analyses must proceed with caution, due to analytical uncertainties and limitations. Uncertainties for major element abundances, for example, range from 12–50% of their respective concentrations (Clark et al., 1977). Furthermore, no data were obtained for H, C, N, and Na. In addition, despite numerous attempts, no rock fragments were analyzed. Lastly, the fines, in all likelihood wind drift material, may not be compositionally representative of the rocks or even of the bulk regolith (Gooding, 1980).

Toulmin et al. (1977) attempted to match the oxide concentrations in Martian soil, calculated from XRFS data, to those of terrestrial, meteoritic, and lunar materials. They found no single analog that matched the Martian fines for all oxides, but proposed smectite clays mixed with sulfates and chlorides as a close compositional approximation. They further suggested that the Martian surface fines formed by weathering of basic igneous rock.

These interpretations were critically discussed by Gooding (1978), who studied the thermodynamics of weathering processes and products under present Martian conditions. He found that the production and preservation of smectite clays is generally unfavorable. Gooding and Keil (1978) suggested that basaltic glass, rather than the crystalline minerals of the rocks, would weather more readily on the dry, cold Martian surface and, hence, that the inferred clays may have been derived from widespread glass. Toulmin et al. (1977) themselves noted the nonuniqueness of the derived clay mixture and pointed out that the unlikely combination of equal parts of basalt and C1 carbonaceous chondrite material would match the Viking results almost as well.

Some support for a clay-dominated regolith came from interpretations of the Mariner 9 infrared interferometric spectrometer (IRIS) data (Hunt et al., 1973). They concluded that the material suspended in Martian dust storms could be montmorillonite. However, the results do not constitute a unique determination of mineralogy (Arons and Emslie, 1975).

An important feature of any model for the fines is total water content. While the XRFS did not measure this quantity, the deficits in the analytical totals (around 9%) provide an approximate upper limit. A more severe limit was set by semiquantitative data from the Viking gas chromatograph-mass spectrometer (GCMS) which indicated that between several tenths and several percent water was driven out below 500°C (Biemann et al., 1977).

Particle Size

The Viking landers were not equipped to make direct measurements of soil particle sizes. However, Shorthill et al. (1976),
based on highest resolution (~1 mm) images of soil clinging to the sampler arm magnets (Hargraves et al., 1976) and on physical properties of the soil, concluded that the bulk of the surface fines in the landing areas are between 10 and 100 μm in size. Pollack et al. (1979) suggested 2.5 μm as a representative particle radius for dust carried aloft during large dust storms.

Spectral Reflectance

Spectral-reflectance studies of the Martian surface, summarized by Singer et al. (1979), suggest that the Viking landers were located in "bright" areas, although telescopic spectra of the exact landing sites do not yet exist. Bright-area spectra in the range 0.30–2.50 μm possess prominent features including strong Fe3+ absorption throughout the visible range and a broad feature between 1.4 and 1.7 μm interpreted as H₂O hydrate or ice. An additional water band near 1.9 μm may be present, but is masked by Martian CO₂ absorption. Dust cloud spectra match the bright-area data closely, indicating that the bright areas contain abundant aeolian dust (McCord et al., 1977). The dark areas, which include much of the southern hemisphere, have spectral signatures indicative of rocky surfaces (Singer et al., 1979). Interpretations of surface composition derived from the Viking landing sites cannot be extended to these regions.

Magnetic Properties

Based on properties of soil attached to small permanent magnets mounted to the surface sampler arm of the Viking landers, Hargraves et al. (1979) concluded that "a limited amount of magnetic material is very homogeneously distributed in the fine-grained surface material." They estimated an absolute abundance of 1–7% for the magnetic mineral, and tentatively identified it as maghemite, γ-Fe₂O₃. If the maghemite is dispersed in material like an iron-bearing silicate, the bulk magnetic susceptibility of Martian soil is between 1–7 × 10⁻³ emu/g Oe (Hargraves and Petersen, 1972).

Weathering Conditions

An important consideration in modeling alteration at the Martian surface is the weathering environment. Meteorology experiments aboard both Viking landers operated for more than one Martian year. Thus, the weathering conditions to which the surface samples are presently exposed were measured. Relevant environmental parameters important to Martian weathering were summarized by Gooding (1978).

Present conditions on Mars may not be representative of those which prevailed at other times in the planet’s history. Some investigators concluded that certain epochs were characterized by higher temperatures, higher atmospheric pressures, and more abundant near-surface water than the present. The arguments are summarized by Mutch et al. (1976, Chap. 8). Such conditions are more amenable to the weathering of exposed rock than is the present climate, and would strengthen a weathering model for Martian soil formation.

ALTERED BASALTIC GLASS

Our terrestrial-analog study focuses on the alteration products of basaltic glass, collectively known as palagonite. The term "palagonite" has, unfortunately, been loosely used to describe various materials ranging from subaerial and submarine pyroclastic rocks to specific types of individual grains within each rock (e.g., Nayudu, 1964; Hay and Iijima 1968a). Our use of "palagonite" conforms to the general usage of these authors and of Stokes (1971) and refers to the vitreous, yellow-brown to orange-brown material that is found in association with sideromelane in certain volcanic tuffs. The parent rocks are then termed palagonite tuffs, whereas the process by which ordinary basaltic tuffs are transformed into palagonite tuffs is called palagonitization. Additional phases, besides unaltered glass and palagonite, are often reported in palagonite tuffs. These include
zeolites, carbonates, and opal (Iijima and Harada, 1969; Kristmannsdóttir, 1976). Authigenic minerals were identified in many of our samples, but appear to be totally absent in others.

Sample Descriptions and Locations

Samples of sideromelane and associated palagonite from sites throughout the world were examined. In all cases the bulk composition of the glass is basaltic. The broadest range of weathering environments, as measured by temperature and precipitation, was sought. The sample localities below are grouped by general weathering conditions as follows: cold and wet (Iceland and Alaska), cold and dry (Antarctica), warm and wet (Hawaii), warm and dry (deserts of New Mexico and Mexico). More complete sample descriptions may be obtained from the first author.


Glass Structure and Composition

Table I summarizes the analytical techniques used to study each sample. These techniques are discussed in detail below. All samples consist dominantly of shards of sideromelane glass, ranging in size from 100 to 2000 μm, and are cemented together to varying degrees by palagonite and authigenic minerals to form palagonite tuff rocks (Fig. 1). Grain shapes range from blocky to subrounded and vesicularity ranges from almost nil to extreme (Allen, 1980; Heiken, 1974). Most samples contain a scattering of plagioclase and olivine phenocrysts, but individual sideromelane grains are dominantly vitreous.

Samples were impregnated with toluene-thinned epoxy to preserve the delicate alteration products, and prepared as polished thin sections for electron microprobe analysis (EMPA) by an ARL EMX-SM instrument. The microprobe was operated at 15 kV, using an 18- to 19-nA sample current and a 2- to 3-μm diameter beam to minimize dehydration and volatization. Mineral standards were employed for calibration, and the analysis routine was verified in tests on synthetic basalt glass JB-1 (Flanagan, 1973).
ALTERED BASALTIC GLASS ON MARS

TABLE I

<table>
<thead>
<tr>
<th>Sample</th>
<th>Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OM EMPA SEM XRD VIRS MP TGA VD AE</td>
</tr>
<tr>
<td>Iceland</td>
<td></td>
</tr>
<tr>
<td>E 4</td>
<td>X X X X</td>
</tr>
<tr>
<td>EL 25</td>
<td>X X X X X X X X</td>
</tr>
<tr>
<td>EL 26</td>
<td>X X X X X X X X</td>
</tr>
<tr>
<td>G 12</td>
<td>X X X X X X X X</td>
</tr>
<tr>
<td>G 13</td>
<td>X X X X X X X X</td>
</tr>
<tr>
<td>G 14</td>
<td>X X X X X X X X</td>
</tr>
<tr>
<td>HG 1</td>
<td>X X</td>
</tr>
<tr>
<td>Alaska</td>
<td></td>
</tr>
<tr>
<td>TT 2</td>
<td>X X X X</td>
</tr>
<tr>
<td>TT 3</td>
<td>X X</td>
</tr>
<tr>
<td>W 2</td>
<td>X X</td>
</tr>
<tr>
<td>Antarctica</td>
<td></td>
</tr>
<tr>
<td>AN 1</td>
<td>X X X</td>
</tr>
<tr>
<td>AN 3</td>
<td>X X</td>
</tr>
<tr>
<td>AN 4</td>
<td>X X</td>
</tr>
<tr>
<td>Hawaii</td>
<td></td>
</tr>
<tr>
<td>HB 1</td>
<td>X X</td>
</tr>
<tr>
<td>KK 2</td>
<td>X X X</td>
</tr>
<tr>
<td>KH 1</td>
<td>X X</td>
</tr>
<tr>
<td>KL 10</td>
<td>X X</td>
</tr>
<tr>
<td>New Mexico</td>
<td></td>
</tr>
<tr>
<td>NM 1A</td>
<td>X X</td>
</tr>
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<td>NM 1B</td>
<td>X X</td>
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<td>IM 1</td>
<td>X X</td>
</tr>
<tr>
<td>Mexico</td>
<td></td>
</tr>
<tr>
<td>P 1</td>
<td>X X</td>
</tr>
</tbody>
</table>

Note. OM—optical microscopy; EMPA—electron microprobe analysis; SEM—scanning electron microscopy; XRD—X-ray diffraction; VIRS—visible/near-infrared spectroscopy; MP—magnetic properties; TGA—thermo-gravimetric analysis; VD—vacuum dehydration; AE—aolian erosion.

Representative mean glass analyses are presented in Table II. The compositions are all basaltic and closely approximate published bulk analyses of the associated crystalline rocks.

Alteration Products

Sideromelane alters to palagonite through a process which has been variously described as hydration (Peacock, 1926), diffusion-hydration (Moore, 1966), or microsolution-precipitation (Hay and Iijima, 1968a; b). While the exact mechanism is still unclear, the process evidently takes place only within a few microns of the glass-palagonite interface. The result in most cases is an unaltered sideromelane core surrounded by a distinct rind of palagonite (Fig. 2). Similar rinds line the interiors of all but the smallest vesicles in most glass grains.

Chemical Composition

Representative mean analyses for the alteration products of specific glasses are listed in Table II. The alteration of sideromelane to palagonite is compositionally complex and highly variable on a scale of microns. The distinguishing features include apparent hydration of 10-25% by
weight, coupled with a considerable loss of CaO and Na₂O. Iron is generally more abundant in the palagonite than in the glass and is reported to be almost totally in the Fe³⁺ oxidation state (Hay and Iijima, 1968a). The SiO₂ and Al₂O₃ contents do not vary greatly during alteration, although other major elements exhibit large varia-
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TABLE II
MEAN MICROPROBE ANALYSIS OF UNALTERED SIDEROMELANE GLASS AND ADJACENT PALAGONITE from PALAGONITE TUFF SAMPLES

<table>
<thead>
<tr>
<th></th>
<th>HG 1°</th>
<th>TT 2°</th>
<th>AN 3°</th>
<th>KK 2°</th>
<th>IM 1°</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S</td>
<td>P</td>
<td>S</td>
<td>P</td>
<td>S</td>
</tr>
<tr>
<td>SiO₂</td>
<td>48.1</td>
<td>50.8</td>
<td>54.5</td>
<td>48.8</td>
<td>45.1</td>
</tr>
<tr>
<td>TiO₂</td>
<td>2.75</td>
<td>0.72</td>
<td>2.34</td>
<td>4.05</td>
<td>4.01</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>12.9</td>
<td>13.8</td>
<td>15.1</td>
<td>9.4</td>
<td>15.9</td>
</tr>
<tr>
<td>FeO</td>
<td>13.7</td>
<td>15.8</td>
<td>9.6</td>
<td>16.3</td>
<td>11.5</td>
</tr>
<tr>
<td>MnO</td>
<td>0.23</td>
<td>h</td>
<td>0.14</td>
<td>0.18</td>
<td>0.20</td>
</tr>
<tr>
<td>MgO</td>
<td>6.5</td>
<td>7.7</td>
<td>5.8</td>
<td>5.6</td>
<td>4.38</td>
</tr>
<tr>
<td>CaO</td>
<td>12.0</td>
<td>2.31</td>
<td>8.8</td>
<td>4.59</td>
<td>10.2</td>
</tr>
<tr>
<td>Na₂O</td>
<td>2.49</td>
<td>0.15</td>
<td>3.64</td>
<td>0.42</td>
<td>4.49</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.36</td>
<td>0.33</td>
<td>0.68</td>
<td>0.85</td>
<td>1.92</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.36</td>
<td>0.15</td>
<td>0.37</td>
<td>0.23</td>
<td>1.05</td>
</tr>
<tr>
<td>Total</td>
<td>99.4</td>
<td>91.8</td>
<td>101.0</td>
<td>90.4</td>
<td>98.8</td>
</tr>
</tbody>
</table>

° Deviation of palagonite totals from 100% due to hydration.
Hengill, Iceland: S—Sideromelane (mean of 6); P—Palagonite (mean of 7).
Togiak Tuya, Alaska: S—Sideromelane (mean of 10); P—Palagonite (mean of 10).
Coleman Nunatak, Antarctica: S—Sideromelane (mean of 6); P—Palagonite (mean of 12).
Koko Crater, Hawaii: S—Sideromelane (mean of 11); P—Palagonite (mean of 8).
Isleta Volcano, New Mexico: S—Sideromelane (mean of 15); P—Palagonite (mean of 15).
All iron reported as FeO.
Below detection limit.

ions within the same sample and even within the same palagonite rind. Titanium and magnesium often are concentrated in distinct layers which parallel the glass-palagonite interface.

Palagonitization is not an isochemical process. A portion of the material removed from the glass may form zeolites and other authigenic minerals within the tuff deposit. However, such authigenic phases are totally absent from a number of our samples. In such cases true element loss from the glass—palagonite system apparently occurs.

Morphology

Scanning electron microscopy clearly shows the morphology of the weathering rinds and their relationships to parent glass grains. Part of the rind shown in Fig. 3 has broken away, displaying a cross section of the remaining palagonite. The rind is approximately 15 μm thick, though in other samples it varies from almost 0 to 100 μm.

The rough underlying surface is the glass—palagonite interface. The alteration rind appears to be separated from the glass by a gap of several microns. In addition, fractures normal to the interface divide the rind into distinct plates. This combination of features is characteristic of the palagonite rinds of many samples and has been previously described by Geptner (1977), who interpreted the cracking to be the result of partial dehydration of the palagonite.

Particle-Size Distribution

Although most of the samples studied required some degree of crushing in order to achieve disaggregation, G 13 was notably friable. Accordingly, a sieve analysis was performed on this sample on the presumption that its disaggregation under mechanical vibration would provide information on the particle-size distribution that might result from physical breakdown under geological conditions. The dry sieve analysis
was performed in air using an ATM L3P sonic sifter (30 min total vibration) and ASTM standard sieves.

Results of this sieving show that soil-sized (<2 mm) particles comprise only 38.7% of the sample by weight, with the remainder being coarse tephra fragments up to approximately 1 cm in size. The size

Fig. 2. Transmitted-light photomicrograph of sideromelane grains with palagonite alteration rinds (sample EL 25). Note sharp contact (arrows) between unaltered glass (centers) and palagonite (rims). Fractured white crystals between grains are chabazite (C). Scale bar equals 500 μm.
distribution of the <2 mm fraction (Fig. 4) is negatively skewed with a graphical median particle size of 0.68 mm. Furthermore, particles comparable to the apparently silt-sized (by definition <63 μm) Martian surface fines (Moore et al., 1977) comprise
only about 3% by weight of the <2-mm fraction and, hence, only about 1% of the bulk G 13 sample. Particle-size distributions of more indurated tuffs of similar macroscopic appearance could be skewed to even smaller proportions of silt.

**Spectral Reflectance**

Visible and near-infrared (VIS/NIR) reflectance spectra (0.5–2.5 μm) were obtained for selected samples using a Beckman DK-2A spectrophotometer with reflectance (integrating sphere) attachment and MgO reference. For comparison with palagonite results, parallel analyses were made on the <63-μm-sized fraction of a well-characterized nontronite (refined from bulk material SWA-1 in the University of Missouri Source Clays Repository).

VIS/NIR spectra for four Icelandic samples and the nontronite are presented in Fig. 5. Three of the palagonites and the nontronite display similar spectra, featuring bands shortward of 0.7 μm and at 0.8–0.9 μm attributable to Fe^{2+} (Singer et al., 1979). In addition, they show to varying degrees the water of hydration features at 1.4–1.5 and 1.9–2.0 μm (Hunt and Salisbury, 1970). All four also display sharp declines in reflectance longward of about 2.15 μm. Sample G 14 has a much flatter spectrum than the others, which correlates with the considerably lower degree of palagonitization in this sample.

The infrared reflectance spectra of three of the samples (EL 25, G 12 and G 13) are similar to those of Antarctic palagonite published by Soderblom and Wenner (1978), although these authors did not offer supporting mineralogical or compositional data. Over a more limited spectral range the signatures of fines from Iceland, Hawaii and Antarctica display noteworthy similarities (Fig. 6). Such results should be interpreted with caution, however. Figure 7 indicates that the spectral reflectance curve may vary considerably with particle size. In particular, the bands near 1.4 and 1.9 μm become shallower as particle size increases.

**Magnetic Properties**

Powdered bulk samples of three palagonite tuffs were studied by Dr. R. V. Morris of the Johnson Space Center using a vibrating sample magnetometer. Values of saturation magnetization (J_s), paramagnetic susceptibility (x_p) and equivalent weight percent magnetite were derived.

**Fig. 4.** Particle-size distribution of the <2-mm-sized fraction (38.7% by weight) of friable tuff sample G 13. Graphically determined value of median diameter (Md) equals 0.68 mm.

**Fig. 5.** VIS/NIR reflectance spectra of <100-μm fractions of palagonite tuffs compared with that of <63-μm nontronite SWA-1.
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FIG. 6. VIS/NIR reflectance spectra of <90-μm palagonite tuff samples. All spectra obtained at 4° phase angle from flat powder surface using the Cornell University goniometer. Reflectance is normalized relative to BaSO₄.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Jₜ (emu/g)</th>
<th>χ₀ (emu/g Oe)</th>
<th>Magnetite (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EL 25</td>
<td>0.13</td>
<td>1.81 × 10⁻⁵</td>
<td>0.14</td>
</tr>
<tr>
<td>G 12</td>
<td>0.04</td>
<td>1.73 × 10⁻⁵</td>
<td>0.04</td>
</tr>
<tr>
<td>TT 2</td>
<td>0.02</td>
<td>1.22 × 10⁻⁵</td>
<td>0.02</td>
</tr>
</tbody>
</table>

These values are typical of iron-bearing silicates (Hargraves and Petersen, 1972) and reflect the dominance of unaltered basaltic glass over palagonite in these bulk samples.

The paramagnetic susceptibility of the palagonite fraction was measured independently using a Frantz Isodynamic Magnetic Separator. A portion of sample FT 25, the most strongly palagonitized tuff in our collection, was lightly crushed with mortar and pestle and the size fraction smaller than 200 mesh (75 μm), which consisted dominantly of palagonite rinds, was isolated by sieving. The separator was adjusted to simulate the strong and weak magnets carried by the Viking landers. Repeated separations demonstrated that essentially all of the palagonitic material could have been lifted by the strong magnet against Martian gravity (i.e., the magnetic susceptibility is greater than 1.5 × 10⁻⁵ emu/g Oe). Moreover, 14% by weight has a susceptibility in excess of 1.8 × 10⁻⁴ emu/g Oe and, thus, would have adhered to the weak Viking magnet. The more susceptible fraction consists mostly of dark grains, while the remainder is composed of similar-sized orange-brown particles.

Mineralogy

X-ray-diffraction (XRD) analyses were performed using a Philips/Norelco diffractometer with Cu Kα radiation, a scintillation detector prefiltered by a curved graphite crystal monochromator and solid state electronics (single-channel analyzer, ratemeter, and scaler). Two-Θ scans at 1°/min were made with a strip-chart recorder.

Sample G 13 was dry sieved in air using a sonic sifter, as described above. Other, less friable samples were gently crushed with a mortar and pestle and sieved to obtain the <100-μm-sized fractions on which subsequent XRD work was concentrated. All samples were mounted without cement on petrographic glass slides in order to facilitate direct comparisons between dry- and wet-sedimented specimens. Isolation and analysis of the clay-sized (<2 μm) fraction of each sample was attempted by conventional methods of ultrasonic deflocculation, sedimentation, and glycolation (Brown, 1961; Carroll, 1970). Mineral identifications based on observed d-spacings were made by reference to standard files (e.g., JCPDS, 1974a; b; Brown, 1961).

FIG. 7. VIS/NIR reflectance spectra of selected size fractions of sifter-disaggregated palagonite tuff G 13 compared with that of <63-μm nontronite SWA-1.
TABLE III

Principal X-Ray Diffraction Peaks Observed for Fine (<100-μm) Fractions of Icelandic Palagonite Tuffs

<table>
<thead>
<tr>
<th>Peak number</th>
<th>(d (\text{Å}) \pm 0.01)</th>
<th>Profile</th>
<th>Mineral identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.52</td>
<td>very broad</td>
<td>smectite (060), (030)</td>
</tr>
<tr>
<td>2</td>
<td>1.62</td>
<td>sharp</td>
<td>varlamoffite (211)? or amakinite (220)?</td>
</tr>
<tr>
<td>3</td>
<td>1.73</td>
<td>very sharp</td>
<td>plagioclase (241)</td>
</tr>
<tr>
<td>4</td>
<td>1.77</td>
<td>sharp</td>
<td>olivine (112)?</td>
</tr>
<tr>
<td>5</td>
<td>1.88</td>
<td>broad</td>
<td>plagioclase (130), (200); smectite (130), (200);</td>
</tr>
<tr>
<td>6</td>
<td>2.13</td>
<td>sharp</td>
<td>varied (G 14)</td>
</tr>
<tr>
<td>7</td>
<td>2.26</td>
<td>broad</td>
<td>varied (EL 25)</td>
</tr>
<tr>
<td>8</td>
<td>2.46</td>
<td>sharp</td>
<td>calcite (104); plagioclase (131)?</td>
</tr>
<tr>
<td>9</td>
<td>2.51</td>
<td>sharp (G 14) to very broad (EL 25)</td>
<td>varied (232) (EL 25)?</td>
</tr>
<tr>
<td>10</td>
<td>2.56</td>
<td>broad</td>
<td>smectite (130), (200)?</td>
</tr>
<tr>
<td>11</td>
<td>2.82</td>
<td>sharp</td>
<td>stanfieldite (331), (008)?</td>
</tr>
<tr>
<td>12</td>
<td>2.92</td>
<td>broad</td>
<td>plagioclase (022) and chabazite (401)</td>
</tr>
<tr>
<td>13</td>
<td>3.01</td>
<td>sharp</td>
<td>calcite (104); plagioclase (131)?</td>
</tr>
<tr>
<td>14</td>
<td>3.12</td>
<td>broad</td>
<td>varied (EL 25)</td>
</tr>
<tr>
<td>15</td>
<td>3.19</td>
<td>very sharp</td>
<td>plagioclase (002)</td>
</tr>
<tr>
<td>16</td>
<td>3.35</td>
<td>sharp</td>
<td>(\alpha)-quartz (101)</td>
</tr>
<tr>
<td>17</td>
<td>3.62</td>
<td>sharp</td>
<td>serpentine (004)? and plagioclase (130)</td>
</tr>
<tr>
<td>18</td>
<td>3.75</td>
<td>sharp</td>
<td>plagioclase (130); stanfieldite (320), (411) (EL 25)?</td>
</tr>
<tr>
<td>19</td>
<td>3.90</td>
<td>sharp</td>
<td>plagioclase (111)</td>
</tr>
<tr>
<td>20</td>
<td>4.02</td>
<td>sharp</td>
<td>plagioclase (201)</td>
</tr>
<tr>
<td>21</td>
<td>4.55</td>
<td>broad</td>
<td>smectite (110), (020) or serpentine (020)</td>
</tr>
<tr>
<td>22</td>
<td>5.10</td>
<td>very sharp</td>
<td>jarosite (012)?</td>
</tr>
<tr>
<td>23</td>
<td>9.35</td>
<td>sharp</td>
<td>chabazite (101)</td>
</tr>
</tbody>
</table>

*For samples EL 25, G 12, G 13, and G 14. Limited to peaks of relative intensity >5% (see Fig. 8). Question marks indicate uncertain identifications, as discussed in text.

The only XRD peaks (Table III; Fig. 8) common to all four samples studied are numbers 6, 9, 15, and 18, indicating that plagioclase is the dominant crystalline phase, an observation verified by EMPA. In addition, hydrous phyllosilicates apparently occur in at least three of the samples since peaks 1, 10, and 21 can be attributed to smectite-group minerals, whereas 17 and 21 are suggestive of serpentine-group minerals. The 14- to 15-Å peaks characteristic of expandable clay minerals are absent, as would be expected for randomly oriented mounts having low abundances of such minerals (Brown, 1961). Although XRD analyses of glycolated bulk fines (<100 μm) separates gave only weak indications of 14- to 15-Å peaks, the generally lower intensities of peaks 1, 17, and 21 in the silty residues from clay separations (Fig. 8) are consistent with concentration of the phyllosilicates into the clay-sized fractions. Furthermore, the three samples exhibiting smectite/serpentine XRD peaks also dis-
Fig. 8. Relative intensities (100 = most intense) of X-ray diffraction peaks in <100-μm fractions of tuffs before and after deflocculation and removal of their respective clay-sized (<2 μm) components. Bulk fines are randomly oriented, whereas fines with clay fraction removed were oriented by aqueous sedimentation. Mineral identifications are given in Table III.

play IR reflectance spectra which compare favorably with those of a well-characterized ferroan smectite (Fig. 5).

Chabazite (peaks 12 and 23) appears to be an important authigenic mineral and has been documented by EMPA. However, it seems to vanish during clay removal (Fig. 8), possibly by ultrasonically induced decomposition.

At least two samples (EL 25, G 14) exhibit some XRD evidence for the presence of complex sulfates and phosphates, although identification of the responsible minerals (Table III) is highly uncertain. Peaks 9, 11, 13 and 18 in EL 25 show relative intensities and silt/clay partitioning patterns which are noticeably different from those for the same peaks in the other three samples. The near disappearance of these peaks from EL 25 after its aqueous treatment to remove the clay-sized fraction indicates that either the mineral(s) in question were highly concentrated in the clay-sized fraction or were decomposed by treatment with water. The latter interpretation would agree with the expected high solubilities of nitrates or phosphates (especially when subjected to extended ultrasonic vibration as in our procedure) and might explain the apparent absence of such minerals from our EMPA sections, most of which were prepared with water-based cutting and polishing lubricants.

XRD peaks attributable to oxides and hydrated oxides of Fe are noticeably absent from the untreated fines. Little if any evidence exists for the characteristically dominant XRD peaks of goethite (4.18 Å), lepidocrocite (6.27 Å), magnetite (2.53 Å), hematite (2.69 Å), or ilmenite (2.75 Å). Although γ-Fe₂O₃ is known to give a strong peak at 2.51 Å, the occurrence of this peak (Number 9, Fig. 8) in our samples can be adequately explained as discussed above without invoking the presence of maghemite. Nevertheless, trace amounts of maghemite or some other Fe-oxide are not excluded by our results.

We emphasize that the only crystalline phases confidently identified in the <100-μm fractions are plagioclase, chabazite, and phyllosilicates (probably smectite- or serpentine-group or mixed-layer clay minerals). The presence of phosphates, sulfates, and nitrates is strongly suspected but not confirmed. However, the bulk samples are composed predominantly of glass and poorly crystallized material.
Previous mineralogical studies of pala-
gonite tuffs from other Icelandic localities (e.g., Tómasson and Kristmannsdóttir, 1972; Kristmannsdóttir, 1976) identified nu-
merous authigenic minerals including smec-
tites, mixed layer clays, zeolites, prehnite, 
chlorite and epidote. However, the relative 
abundances of these minerals vary with 
sample locality (including drillcore depth) 
and apparent temperature of alteration in 
hydrothermal zones. Our samples, taken 
exclusively from surface material, appar-
ently do not contain many of the authigenic 
minerals which characterize subsurface 
samples in active hydrothermal areas.

Studies of submarine (Nayudu, 1964) and 
subaerial Hawaiian (Hay and Iijima, 1968a; 
b) pagonite tuffs identified smectites, zeo-
lites, calcite, and opal as authigenic phases. 
The common identification of montmoril-
nonite (rather than some other smectite or 
mixed-layer clay) as the dominant clay min-
eral has not always been rigorously demon-
strated in published accounts. In fact, Sum-
mers (1976) showed that nontronite is the 
dominant clay mineral in Columbia River 
fold basalt pagonite whereas Stokes 
(1971) correctly cautioned that many pala-
gonites contain mixed phyllosilicates which 
cannot be unambiguously identified or at-
tributed to a single clay mineral, and cited 
as evidence several key XRD peaks which 
we also found in our samples (peaks 1, 10, 
11, 13, 18, 20; Fig. 8).

Water Content

The water content of pagonite alteration 
rinds, as inferred from deficits in the 
electron microprobe analytical totals, gen-
erally ranges between 10 and 20% by 
weight, but can exceed 25%. Experiments 
on the bonding of this water were per-
formed on crushed bulk samples of several 
pagonite tuffs by Dr. R. V. Morris at the 
Johnson Space Center.

Three samples were equilibrated at room 
temperature at a relative humidity of ap-
proximately 43% and then pumped to 10 
mTorr pressure. They were held at this 
pressure for 5 hr and sample weight was 
continuously monitored. Exposure of pala-
gonite tuff samples to low pressure results 
in partial dehydration which, in these sam-


![Fig. 9. Graph of sample weight loss versus time for pagonite tuffs under vacuum. Samples were crushed, equilibrated at approximately 43% relative humidity and pumped to 10 mTorr pressure. Weight loss is essentially reversible upon reequilibration at 1 atm. Almost all weight loss represents dehydration.](image)

Conditions of Formation

The alteration of basaltic glass to pala-
gonite has been averred to take place in a 
wide range of environments. These include 
the sea floor (Bonatti, 1965), the near sur-
face in Hawaii (Hay and Iijima, 1968a), 
the soil of Iceland (Jakobsson, 1978) and
ALTERED BASALTIC GLASS ON MARS

Fig. 10. Thermogravimetric analysis (TGA) data on three crushed tuff samples. Heating was at a rate of 10°C/min in an oxygen atmosphere at 1 atm pressure. Curves are representative for samples equilibrated before heating to room temperature relative humidities of approximately 40–75%. Most weight loss represents dehydration.

the hydrothermal environment of water-saturated volcanoes (Jakobsson and Moore, 1980). Bonatti (1965) argued that palagonitization occurs at high temperature at the time the magma is quenched, and this mechanism was cited by Toulmin et al. (1977) as a possible source for the Martian soil. Such high-temperature alteration was apparently not the case for our samples, however.

The low degree of crystallinity in most of the glasses studied argues for quenching in a matter of seconds (Moore, 1976). Calculated rates of heat transfer for millimeter-scale glass particles in water yield a similar conclusion (Allen, 1979a). The time required for hydration of glass to a depth of tens of microns, even at a temperature of 500°C, is measured in hours (Bonatti, 1965), and water circulation through the parent tuff should quickly cool the deposit well below this temperature. This result is confirmed by observations at the submarine volcano Surtsey (Jakobsson, 1978). Initially the Surtsey tephra showed no signs of palagonitization, but consisted solely of pristine glass shards. Palagonite was not formed until at least 3 years after the eruption, following the commencement of near-surface hydrothermal activity. Palagonitization is most likely to take place, therefore, over long periods of time at temperatures which are low compared to magmatic temperatures.

Hay and Iijima (1968a) proposed that the infiltration of rainwater into the open structure of tuffaceous rocks in Hawaii leads to palagonitization. Iijima and Harada (1969) studied the association of palagonite with authigenic zeolites in the same area and arrived at a similar conclusion. The present EMPA study confirms several of the zeolite associations noted by these authors and supports a mechanism of low-temperature palagonitization in Hawaii.

We found evidence for hydrothermal palagonitization, on the other hand, in samples from subglacial volcanoes in Iceland, Alaska, and Antarctica. This is the mechanism cited for palagonite formation on Surtsey (Jakobsson, 1978; Jakobsson and Moore, 1980). As discussed above, the evidence is found in the authigenic minerals. Kristmannsdottir (1976), in a study of low-temperature hydrothermal fields in Iceland, showed how temperature controls zeolite formation in basaltic rocks. Below 80°C the stable assemblage is chabazite, opal, and calcite. Mesolite-sclecticite dominates from 80 to 90°C, stilbite from 100 to 120°C, and laumonite above 120°C.

Figure 2 shows the close association of chabazite with palagonite and glass in one sample from Iceland. Chabazite, analclite, calcite, and SiO₂ (possibly opal) are common in many of our subglacial eruptive samples, as shown by EMPA. Alteration of sideromelane by low-temperature (<80°C) hydrothermal systems is thus the favored mechanism for these samples. No conclusion can be drawn at present as to
the alteration mechanism for the desert samples, though all are from maar deposits and thus were in the presence of hot water during and shortly after the eruption.

**Insensitivity to Ambient Weathering Conditions**

Proponents of weathered terrestrial materials as analogs to Martian soil must face the vast differences in environment between the two planets. As noted above, present-day Mars is almost always colder and drier, and possesses a lower atmospheric pressure, than anywhere on Earth. Liquid water, the dominant agent for terrestrial weathering, is unstable at the Martian surface, so surface weathering must depend on much less efficient mechanisms such as solid–gas reactions (Gooding and Keil, 1978) or the putative warmer and wetter climates of the past.

The present study of altered basaltic glass has shown that changes in palagonite chemical composition during alteration are strikingly insensitive to the subsequent weathering environment. Support for this conclusion stems from the range of apparent gain or loss of each element in a palagonite rind relative to its parent sideromelane. Following standard practice for calculations of weathering chemistry, we normalized both glass and palagonite EMP analyses to total 100% in order to exclude water. Then, assuming that the absolute amount of Al₂O₃ in a sample remains constant across the interface, we calculated changes in the other elements relative to aluminum (Krauskopf, 1967, p. 103).

Figure 11 demonstrates that, for a given weathering environment, the range of palagonite compositions relative to sideromelane can be large for some elements. This large range is due, in part, to the microprobe’s unique ability to detect the micron-scale chemical variability (discussed above) which is a notable feature of palagonite composition. The compositional range, however, is generally replicated closely for samples from regions of grossly different air temperature and precipitation. Finally, the changes in chemical composition appear insensitive to the mechanism of alteration. As noted above, the Hawaiian samples were apparently altered by infiltration of rainwater, whereas the rocks from Iceland, Alaska, and Antarctica were probably altered in low-temperature hydrothermal systems.

We emphasize that the comparison in

![Fig. 11. Range of weight gain or loss for major element oxides in the alteration of glass to palagonite. Gain/loss calculations are based on constant Al₂O₃ and normalized (water-free) compositions. Bars represented the central 99% of the total range of values for each oxide. Samples are grouped by weathering environment, i.e., cold and wet (Iceland and Alaska—91 points) cold and dry (Antarctica—36 points), warm and wet (Hawaii—42 points) and warm and dry (deserts of New Mexico and Mexico—31 points).](image-url)
Fig. 11 is between glass and the immediately adjacent palagonite rinds. This does not imply that the bulk mineralogy of a palagonite tuff deposit is similarly insensitive to weathering conditions. In those cases where material leached during palagonitization is redeposited as authigenic minerals (zeolites, opal, etc.) within the tuff (e.g., Iijima and Harada, 1969), the compositions of the authigenic minerals, and thus the composition of the bulk sample, are apparently sensitive to temperature and pH.

**Removal of Alteration Rinds**

Figure 3 shows a sideromelane grain which has lost a portion of its palagonite rind. The remaining palagonite is dissected by deep cracks and physically separated from the underlying glass. These effects are thought to be due to shrinkage during partial dehydration after the alteration rind was formed. SEM examination of a number of altered glass grains shows that the loss of a portion of the alteration rind is a common occurrence. Optical microscopy shows that the intergranular matrix of a palagonite tuff often contains numerous fragments of palagonite not apparently associated with sideromelane grains. If the fine material on Mars is analogous to altered basaltic glass, a mechanism must exist for disaggregating masses of altered glass and removing fragments of the alteration rinds a few tens of microns in size.

We investigated the efficiency of Martian sand storms as agents of mechanical disaggregation using the aeolian erosion apparatus of Dr. R. Greeley at Arizona State University (Krinsley et al., 1979). Freshly broken samples were subjected to normal impacts by particles of quartz sand 63–125 μm in diameter at a velocity of 20 m/sec in a CO₂ atmosphere at approximately Martian surface pressure. The velocity is characteristic of Martian dust storms (Ryan and Henry, 1979).

These experiments showed that simulated aeolian abrasion under Martian conditions is sufficiently energetic to chip individual sideromelane grains and clusters of such grains from palagonite tuff samples. In addition, numerous palagonite fragments smaller than 200 mesh (75 μm) across were recovered (Fig. 12). Sand-sized material is apparently rare or absent at the Viking landing sites (Moore et al., 1977). However, abundant evidence exists for aeolian erosion and deposition of sand-sized particles in some regions of Mars (Ward, 1979; Tsoar et al., 1979).

**MATCH TO MARS DATA BASE**

The compositional resemblance of Icelandic palagonite to Martian surface fines (Fig. 13) is striking for all major oxides except Al₂O₃. This difference is real and may represent a compositional signature of the Martian source rock. Martian “basalts” may contain several percent less aluminum and potassium and somewhat more iron than their terrestrial counterparts, as suggested by Baird and Clark (1981). If alteration chemistry is insensitive to the weathering environment on Mars, the alteration products of Martian basaltic glass may be very similar to palagonite. Alternatively, chemical or mechanical fractionation during weathering could have separated aluminum-rich phases, such as feldspars, from the material measured by Viking (Gooding, 1978; 1980).

Indirect evidence from Viking shows that the fine particles in Martian soil are mostly a few tens of microns in size. We have shown that this is a characteristic scale for alteration rinds on basaltic glass. In addition, sand storms with wind velocities observed on Mars are capable of removing palagonite particles in this size range from exposed rock surfaces.

The compositional information available from visible and near-infrared spectroscopic measurements of Mars is compatible with a palagonite tuff component (Fig. 14). Both the Martian and terrestrial spectra are dominated by Fe³⁺ and water absorption bands. The depth of the water bands, as we
have shown (Fig. 7), is somewhat dependent on the size of the particles. Band depths displayed by our $<63$-μm sample seem qualitatively most like those seen in Martian spectra after removal of a model CO$_2$ atmospheric contribution (McCord et al., 1978, Fig. 4). The small percentage of water released by heating the Martian fines to 500°C, as compared to the 8–17% loss for terrestrial palagonite tuff, indicates that the
MARS SOIL FORMATION MODEL

An alteration model for Martian surface soil requires the justification of several steps. These include production of a reasonable source rock, alteration by a mechanism operable under past or present Martian conditions, separation of alteration products from starting materials and distribution of the material planet-wide.

The source material proposed for this model is basaltic glass. The composition may be somewhat lower in aluminum and potassium and higher in iron than terrestrial basalts (Baird and Clark, 1980). The presence of widespread basaltic volcanism on Mars is generally accepted, based on photogeologic evidence (Carr et al., 1977).

We propose that large volumes of basaltic magma solidified not as crystalline rock but as finely divided glass due to quenching by water (Allen, 1979b). Since liquid water cannot presently exist on the Martian surface we appeal to the widespread deposits of ground ice thought to exist at shallow depths on Mars (Soderblom and Wenner, 1978). Allen (1979a) has shown that the interaction of magma with ice in a low-
strength regolith should yield glassy tuff analogous to that produced during terrestrial subglacial eruptions. The apparent ubiquity of ground ice on Mars, as indicated by rampart craters, stream channels, and periglacial features (Allen, 1979c; Pieri, 1979; Carr and Schaber, 1977), suggests that eruptions almost anywhere on the planet could be expected to encounter near-surface water.

The only known mechanisms for the alteration of basaltic glass that could operate on present-day Mars are gas-solid weathering (Gooding and Keil, 1978) and low-temperature hydrothermal alteration. While liquid water cannot exist stably at the Martian surface, it can remain at shallow depths if kept from contact with the atmosphere by overlying regolith material (Smoluchowski, 1968). Hydrothermal palagonitization at Surtsey is presently occurring through a vertical range of 150 m in the tephra pile (Jakobsson and Moore, 1980), and alteration to similar depths should be possible on Mars, given a suitable heat source. We propose that, after initial quenching of magma by melting ground ice, further interaction of melt water with the cooling volcanic material below the surface should result in low-temperature hydrothermal conditions amenable to glass alteration.

Hydrated alteration products on Mars would be subject to loss of considerable water upon exposure to the atmosphere. Indeed, interpretation of infrared spectra of the planet favors a surface layer rich in desiccated mineral hyrates (McCord et al., 1978). By analogy to palagonite, such dehydration should lead to mechanical weakening of the alteration rinds as they shrink and crack. Such material, if exposed on the surface, would be subject to aeolian abrasion. Over long periods of time the wind should effectively strip the alteration products from the glass and separate the two phases due to their large difference in size.

The large-scale redistribution of dust-sized particles on Mars has been observed for over a century. Planet-wide dust storms occur every few years, and more-localized storms have been seen much more frequently (Ryan and Henry, 1979). The fine material at the Viking landing sites gives every impression of being composed mainly of wind-drifted or deposited material. Thus, the striking similarity of the fines at the two points measured by Viking has been consistently ascribed to homogenization in a widespread aeolian blanket (Toulmin et al., 1977).

This model addresses only the oxide components of the Martian soil, as proposed by Toulmin et al. (1977). These components can apparently be successfully explained as the alteration products of basaltic glass. The additional elements measured by Viking, namely, sulfur and chlorine, may not be derived from the same source. Settle (1979) advocated the addition of these materials to the soil via deposition of volcanic aerosols. Following deposition, the sulfur and chlorine could be mobilized by intergranular water to rise toward the surface and in some cases contribute to the Martian duricrust (Toulmin et al., 1977). Alternatively, Clark and Baird (1979) suggested that the high sulfur content may be an intrinsic property of the Martian lithosphere.

CONCLUSIONS

Altered basaltic glass, also known as palagonite, occurs over a wide range of terrestrial environments. Palagonitization is a particle surface phenomenon which yields a distinct alteration rind surrounding a pristine glass grain. Electron microprobe analysis shows that the glass-palagonite transition involves extensive hydration and highly variable gain or loss of elements. The range of gain or loss for a particular element across the glass-palagonite interface seems relatively insensitive to the ambient weathering environment and to the conditions of alteration. Palagonitization is a low-temperature phenomenon which can occur in submarine, subaerial, or near-surface hydrothermal environments.
Mineralogically, palagonite is a complex and variable material which apparently consists of poorly crystallized phyllosilicates (smectite- or serpentine-group or mixed layer clays). Zeolites are common in palagonite tuffs, and are often indicative of conditions during alteration.

Palagonite is a good analog to the soil of Mars to the level of precision available from Viking and Earth-based telescopic spectral measurements. Points of resemblance between the two materials include bulk chemical composition, particle size, reflectance spectra, and magnetic properties.

A mechanism for the formation of Martian soil, based on a palagonite model, is proposed. Basaltic eruptions through ground ice yield deposits of glassy tuff. Low-temperature hydrothermal alteration coats the glass fragments with rinds of palagonite-like material. Dehydration and aeolian abrasion break the rinds into silt-sized particles and separate them from the adjacent glass. Windstorms mix the fines and deposits them across much of the planet’s surface.

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REFERENCES


ALTERED BASALTIC GLASS ON MARS


[Abstract]


