CHEMISTRY AND MINERALOGY OF MARTIAN DUST: AN EXPLORER'S PRIMER

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Introduction. A summary of chemical and mineralogical properties of Martian surface dust is offered for the benefit of engineers or mission planners who are designing hardware or strategies for Mars surface exploration. For technical details and specialized explanations, reference should be made to the literature cited. We have four sources of information about Martian dust composition:

(1) Experiments performed on the Mars surface by the Viking Landers (VL) 1 and 2 (1976-1978) and Earth-based laboratory experiments attempting to duplicate those results [1];
(2) Infrared spectrophotometry remotely performed from Mars orbit, mostly by Mariner 9 (1971-72) [2] and to be continued with Mars Observer (MO; 1992 launch);
(3) Visible and infrared spectrophotometry remotely performed from Earth [3];
(4) Laboratory studies of the shergottite-nakhlite-chassignite (SNC) clan of meteorites (since 1985) [4], for which compelling evidence suggests origin on Mars.

Source (1) is limited to fine-grained sediments at (or a few centimeters below) the surface (no rock analyses were possible) whereas (2) and (3) contain mixed information about surface dust (and associated rocks) and atmospheric dust. Source (4) has provided surprisingly detailed information but investigations are still incomplete.

Chemical Composition. Each VL carried a gas chromatograph/mass spectrometer (GCMS) and X-ray fluorescence spectrometer (XRFS) that produced information on the elemental composition of fine-grained surface sediments. The GCMS found no organic matter (for detection limits of a few parts per billion (ppb) to a few parts per million (ppm) by weight) but revealed water and adsorbed gases. Volatile inorganic compounds were not precisely measured except to bracket concentrations of 0.1-1 (and possibly as high as 3) wt. % H₂O and 50-700 ppm CO₂ in the sediments. Better measurements must be left to future experiments.

The XRFS found iron-rich sediments with surprisingly high concentrations of sulfur and chlorine (Table 1); virtually identical compositions at the two widely separated landing sites implied that the surface sediments represent homogenized, windblown dust. Unfortunately, the XRFS was not sensitive to several important chemical elements (including carbon, nitrogen, and sodium) and had comparatively large uncertainties for others. In addition, XRFS, as a method, is not capable of identifying the ways in which elements are combined as compounds. Therefore, our direct knowledge of chemical composition of sediments remains incomplete.

Precise analyses of more than 60 elements in SNC meteorites have been used to prepare detailed, if somewhat conjectural, compositional models for Martian rocks. Nonetheless, it is still not clear how these models might pertain to the dust, which is almost certainly more complex than pulverized volcanic rocks.

The MO gamma ray spectrometer (GRS) experiment will map the abundances of about 18 chemical elements from Mars orbit but its spatial resolution (footprint size) on the surface will be a few hundred kilometers. Also, the GRS emphasizes the search for variations rather than the precise numerical measurement of concentration values; GRS data will supplement but not supplant VL XRFS data.

Mineral Composition. None of the VL experiments were capable of directly identifying minerals; conclusions about minerals rest on inference only. The surface sediments apparently contain 1-7 wt. % of a strongly magnetic material which is probably a ferric (iron) oxide. Laboratory simulations of VL biology results (see below) are consistent with (but do not prove) presence of iron-rich clays of the smectite mineral family. Remote-sensing spectrophotometry favors a material denoted as "palagonite" which, on Earth, forms by natural water-driven weathering of volcanic glasses produced by basaltic (Hawaiian-type) volcanoes. Much of the favorable comparison between remotely sensed Mars spectra and laboratory spectra for palagonite is attributable to an ultrafine-grained ferric oxide known as nanophase hematite.

The Mariner 9 infrared radiometer interferometer spectrometer (IRIS) observed the Martian atmosphere during various stages of dust storm activity. No firm mineral identifications were achieved but the suspended dust was inferred to be mostly silicon-oxygen-based minerals such as clays or feldspars. Although surface dust is undoubtedly related to high-altitude atmospheric dust, the IRIS results for atmospheric dust can explain only a portion of the surface dust as characterized by the XRFS. The MO thermal emission spectrometer (TES) will map minerals from Mars orbit at a surface resolution of about 3 km/pixel but will emphasize global and regional differences rather than exact and comprehensive mineral identifications.
Weathering products in SNC meteorites might represent our current best view of minerals most likely to form Martian dust. Although SNC meteorites are volcanic products, they contain traces of minerals that clearly formed in oxidizing, watery environments of the types we might expect at the Mars surface. The minerals provisionally identified (Table 2) include iron-rich, clay-like materials and sulfur- and chlorine-bearing salts that are entirely consistent with the bulk elemental compositions of Martian sediments as measured by the VL XRFS; the carbonate minerals in SNCs would not have been detected by either the GCMS or XRFS. Precise identification of these tiny mineral grains (most < 20 μm size) remains an active area of research from which further significant conclusions are expected.

Chemical Reactivity and Corrosivity. The three different microbiological life-detection experiments on each VL produced apparently "positive" results that were eventually interpreted as the action of vigorously reactive inorganic compounds (rather than microbial life). These agents evolved oxygen when wetted with water, oxidized simple organic compounds in water-based solution, and fixed carbon dioxide into a form that was non-volatile under ambient Martian conditions. The VL experiments were incapable of identifying the reactive agents although, through Earth-based simulation experiments, they were variously inferred to be metal peroxides or superoxides, alkali peroxonitrites or catalytically active minerals (such as clays or iron oxides). Although their actions were striking, their concentrations were quite low: perhaps 1 ppb to a few tens of ppm when expressed in terms of reactivity equivalent to hydrogen peroxide. Although further analyses are important, it appears that at least one of the reactive agents can be decomposed by simple treatment with water.

Over nearly three Martian years of observations, no obvious corrosion of the VLs was observed. Mars dust wetted with water might become electrochemically corrosive toward metals if the sulfur and chlorine in the dust occur as salts (as the SNC evidence suggests) but only further experiments will constrain the possibilities.

Toxicity. None of the VL, laboratory, or remote-sensing results can be used to make blanket statements about toxicity or non-toxicity of Martian dust. Neither the VL XRFS data nor the extensive analyses of SNC meteorites has revealed unexpected concentrations of heavy-metal toxins (e.g., Cd, Hg); organic compounds, likewise, seem to be rare or absent. Although complete toxicology assessments require knowledge of how elements are combined into compounds (in addition to bulk-elemental assays), we can say that none of the minerals inferred from VL results or found in SNC meteorites presents a recognized toxic hazard. Indeed, the only significant issue surrounds interpretation of the unidentified trace-level reactants discovered by the VL biology experiments. Until the active agents are identified, however, we cannot assess their toxic potentials.


Table 1: Weight percent compositions of surface sediments (after B. C. Clark and others; summarized by [1])

<table>
<thead>
<tr>
<th></th>
<th>VL-1</th>
<th>VL-2</th>
<th>Uncertainty</th>
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<tbody>
<tr>
<td>SiO2</td>
<td>44</td>
<td>43</td>
<td>± 6</td>
</tr>
<tr>
<td>TiO2</td>
<td>0.62</td>
<td>0.54</td>
<td>± 0.25</td>
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<tr>
<td>Al2O3</td>
<td>7.3</td>
<td>n.d.</td>
<td>± 4</td>
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<tr>
<td>Fe2O3</td>
<td>17.5</td>
<td>17.3</td>
<td>-2 to +5</td>
</tr>
<tr>
<td>MgO</td>
<td>6</td>
<td>n.d.</td>
<td>-3 to +5</td>
</tr>
<tr>
<td>CaO</td>
<td>5.7</td>
<td>5.7</td>
<td>± 2</td>
</tr>
<tr>
<td>K2O</td>
<td>≤ 0.5</td>
<td>≤ 0.5</td>
<td>± 0.5</td>
</tr>
<tr>
<td>SO3</td>
<td>6.7</td>
<td>7.9</td>
<td>± 2 to +6</td>
</tr>
<tr>
<td>Cl</td>
<td>0.8</td>
<td>0.4</td>
<td>± 0.5 to +1.5</td>
</tr>
</tbody>
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Notes: Expression as oxides is by convention; minerals and compounds not identified n.d. = not determined because of instrument noise.

Table 2: Possible dust-forming minerals found as grains in SNC meteorites (J. L. Gooding and collaborators)

<table>
<thead>
<tr>
<th>Shergottite</th>
<th>EETA79001</th>
<th>Nakhla</th>
<th>Chassigny</th>
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<tbody>
<tr>
<td>CaCO3</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>CaSO4·nH2O</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>(Mg)2(PO4)y·nH2O</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Mg)2(SO4)y·nH2O</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S,CI–aluminosilicate</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Smectite (?)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Ca,K,Mg)6(Fe,Mg)2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Si,Al,Fe)4O10(OH)2·nH2O</td>
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