Pergamon

Geochimica et Cosmochimica Acta, Vol. 64, No. 12, pp. 2155–2166, 2000

0016-7037/00 $20.00 + .00

PII S0016-7037(99)00401-9

# Mixing relationships in the Martian regolith and the composition of globally homogeneous dust

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(*Received July* 21, 1999; *accepted in revised form October* 20, 1999)

**Abstract**—Comparison of the chemical compositions of Martian soils reveals distinct mixing trends, resulting from admixture of variable amounts of sulfate/chloride cement at Viking landing sites and of the local andesitic rock fragments at the Mars Pathfinder site. These trends, most easily visualized in plots of oxides versus $SO_3$, intersect approximately at a common composition, thought to represent a global dust that has been homogenized by pervasive aeolian activity. The source rocks that were weathered to produce the global dust are inferred to have been basalts rather than felsic rocks, based on the observation that the dust lies along well-established chemical weathering trends for terrestrial basalts. The basaltic protolith was chemically similar (e.g., high Fe/Mg, low $Al_2O_3$) to basaltic shergottite meteorites. Chemical changes during the weathering of Martian basaltic rocks are apparently not as drastic as in terrestrial weathering, perhaps because of evaporation of hydrous fluids that leave soluble components behind in the residue. Comparison with chemical trends for previously proposed Martian soil-formation mechanisms suggests that palagonitization of basalts more readily explains the dust composition than do hydrothermal alteration at higher temperatures or reactions of rocks with an acid fog produced by volcanic exhalations. Local or temporal processing of dust into soil involves not only cementation by salts and mixing with rock fragments, but also chemical fractionations of $Fe_2O_3/TiO_2$ presumably resulting from aeolian sorting by grain size and density. If the global dust represents a broad average of the Martian surficial or upper crustal composition, the planet's surface geology is dominated by basaltic volcanic rocks and evaporitic salts. *Copyright © 2000 Elsevier Science Ltd*

## 1. INTRODUCTION

The Martian regolith, consisting of drifts and dunes of fine dust and sand atop variably indurated soil and rock fragments, has defied attempts to determine its nature and origin. (Note: Here we use the term *soil* in the planetary sense to identify the uppermost, unconsolidated, weathered portion of the regolith, in contrast to the terrestrial useage that also specifies that soil must have an organic component.) The importance of Martian soil derives from the recognition that it is the only accessible planetary regolith, besides Earth's, that has been exposed to hydrolytic, atmospheric, and possibly even biologic (?) weathering processes. Also, terrestrial studies document that fine-grained sediments can provide an effective means of estimating the composition of the crust (e.g., McLennan and Taylor, 1984). Major and some minor element abundances in soils have now been analyzed by Viking 1, Viking 2, and Mars Pathfinder landers at three locations on the planet. Mineralogic information is almost completely absent, because of spectral masking by fine-grained ferric oxides. (There is even disagreement about the identities of the ferric oxide minerals themselves, based on ambiguities in the interpretation of available spectroscopic and magnetic susceptibility data.) In the absence of other measurements, we must rely on soil chemistry alone to infer how this dynamic geologic unit formed and what processes might have caused spatial and temporal changes in its composition.

It seems almost impertinent to attempt to understand a planetary regolith that has been analyzed at only three locations, albeit separated by thousands of kilometers. However, the soils at all these sites are broadly similar in composition (Clark et al., 1982; Rieder et al., 1997), leading to speculation that planetwide processes have homogenized parts of the regolith. Spectroscopic studies have demonstrated that airborne dust is nearly indistinguishable from pervasive, bright red regions of the Martian surface (e.g., Wolff et al., 1997), and several decades ago it was postulated that wind had distributed and deposited a global blanket of dust having uniform composition over the entire planet (Toulmin et al., 1977; Singer et al., 1979; McCord et al., 1982). In this article, we discuss how the chemical composition of the homogenized dust might be determined from mixing relationships in Viking and Pathfinder soil analyses, and speculate about the origin of the dust and its local processing into soils.

## 2. DATA SELECTION AND NORMALIZATION

Preliminary Mars Pathfinder APXS soil analyses (A-2, A-4, A-5, A-8, A-10, A-15) were reported by Rieder et al. (1997). Sample A-8 is "rock" Scooby Doo, which is compositionally indistinguishable from soil and is considered to be an indurated hardpan (Bell et al., 1999; McSween et al., 1999), and so is included as soil. Sample A-15 represents an analysis of a duneform. Sample A-2 has a low original oxide sum (Rieder et al., 1997), possibly because of a complicated viewing geometry. Soil analyses (Table 1) report all Fe as $Fe_2O_3$, in accordance with evidence that the Martian surface is highly oxidized (e.g., Burns, 1993; Bell, 1996). Initial, unpublished reports

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Table 1. Chemical analyses of Martian soils (wt.% oxides).

| Sample | $Na_2O$ | MgO | $A1_2O_3$ | $SiO_2$ | $SO_3$ | C1 | $K_2O$[a] | CaO[a] | $TiO_2$[a] | $Fe_2O_3$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Pathfinder soils: APXS analyses[b] (Rieder et al., 1997) | | | | | | | | | | |
| After deployment | | | | | | | | | | |
| A-2 | 2.2 ± 0.9 | 7.7 ± 1.2 | 7.2 ± 0.7 | 49.5 ± 2.5 | 3.9 ± 0.8 | 0.5 ± 0.1 | 0.2 ± 0.1 | 6.7 ± 1.0 | 1.2 ± 0.2 | 17.9 ± 1.8 |
| Next to Yogi | | | | | | | | | | |
| A-4 | 3.7 ± 1.5 | 8.1 ± 1.2 | 8.9 ± 0.9 | 46.8 ± 2.4 | 6.3 ± 1.3 | 0.6 ± 0.2 | 0.2 ± 0.1 | 5.5 ± 0.8 | 1.4 ± 0.2 | 15.6 ± 1.5 |
| Dark soil next to Yogi | | | | | | | | | | |
| A-5 | 2.7 ± 1.1 | 7.3 ± 1.1 | 8.4 ± 0.9 | 46.5 ± 2.4 | 5.4 ± 1.1 | 0.6 ± 0.2 | 0.3 ± 0.1 | 6.3 ± 1.0 | 0.9 ± 0.1 | 18.6 ± 1.8 |
| Scooby Doo | | | | | | | | | | |
| A-8 | 1.9 ± 0.8 | 6.9 ± 1.1 | 8.9 ± 0.9 | 50.3 ± 2.6 | 5.2 ± 1.1 | 0.7 ± 0.2 | 0.5 ± 0.1 | 7.1 ± 1.1 | 1.1 ± 0.2 | 14.5 ± 1.4 |
| Lamb soil | | | | | | | | | | |
| A-10 | 1.5 ± 0.6 | 7.7 ± 1.2 | 8.1 ± 0.8 | 46.8 ± 2.4 | 6.0 ± 1.2 | 0.7 ± 0.2 | 0.2 ± 0.1 | 6.2 ± 1.0 | 1.1 ± 0.2 | 18.8 ± 1.8 |
| Mermaid Dune | | | | | | | | | | |
| A-15 | 1.3 ± 0.7 | 7.1 ± 1.1 | 8.2 ± 0.8 | 48.8 ± 2.5 | 5.1 ± 1.0 | 0.6 ± 0.2 | 0.5 ± 0.1 | 5.8 ± 0.9 | 1.3 ± 0.2 | 18.5 ± 1.8 |
| Viking 1 soils: XRF analyses[c] (Clark et al., 1982) | | | | | | | | | | |
| Fines, Sandy Flats | | | | | | | | | | |
| C-1 | | 6.4 | 8.4 | 46.0 | 7.5 | 0.8 | | 6.4 | 0.7 | 18.9 |
| Crusty, Rocky Flats | | | | | | | | | | |
| C-5 | | 7.4 | 7.2 | 44.1 | 10.0 | 0.9 | | 5.9 | 0.6 | 18.3 |
| Deep fines, Sandy Flats | | | | | | | | | | |
| C-6 | | 6.4 | 7.8 | 47.1 | 7.2 | 0.9 | | 6.4 | 0.7 | 18.5 |
| Fines, Jonesville | | | | | | | | | | |
| C-7 | | 5.3 | 7.8 | 46.6 | 7.2 | 0.6 | | 6.4 | 0.7 | 20.1 |
| Fines, Rocky Flats | | | | | | | | | | |
| C-8 | | 6.5 | 7.7 | 46.4 | 6.4 | 0.7 | | 6.3 | 0.8 | 20.3 |
| Bulk soil, near Bashful rock | | | | | | | | | | |
| C-9 | | 5.2 | 7.8 | 46.8 | 7.5 | 0.8 | | 6.2 | 0.7 | 19.7 |
| Crust, Deep Hole 2 tailings | | | | | | | | | | |
| C-13 | | 7.3 | 7.3 | 44.7 | 9.4 | 0.9 | | 5.6 | 0.6 | 18.9 |
| Uncertainty | | −3 to +5 | ±4 | ±6 | −2 to +6 | −0.5 to +1.5 | | ±2 | ±0.25 | −2 to +5 |

[a] Corrected values in average Pathfinder soil were given by Dreibus et al. (1999), but are not included here (see text).
[b] Normalized to 97% oxides, to allow for unreported components ($P_2O_5$, $H_2O$, C, $Cr_2O_3$, MnO, and corrected $K_2O$; see text).
[c] Normalized to 94.6% (97% minus sum of average Pathfinder $Na_2O + K_2O$ abundances, which were below detection limits).

during the Pathfinder mission indicated $P_2O_5$ values of 2.0–3.4 wt.% in soils, but a newer calibration suggests values near 1 wt.% (Dreibus et al., 2000). Alteration models for Martian soils suggest that water of hydration is present (Bell, 1996) and the response of Viking fines to heating (Biemann et al., 1977) is consistent with dehydroxylation of an amount equivalent to $<2\%$ $H_2O$, although values of adsorbed and bound water varying between $<0.5\%$ and 4% have been suggested (Yen et al., 1998). Carbon in Pathfinder soils is below the detection limit (0.8 wt.%) (Brückner et al., 1999). Brückner et al. (1999) and Dreibus et al. (1999) reported that the average Pathfinder soil contains 0.7 wt.% $Cr_2O_3$ and 0.5% MnO, and that recalibration of the X-ray detector indicates an average of 0.6% $K_2O$ for soils (approximately twice that reported by Rieder et al., 1997). Because there was no in-flight APXS calibration, Pathfinder chemical data must be normalized. Accordingly, Pathfinder soils in this study were normalized to 100% −1.5% for $P_2O_5$, $H_2O$, C, −0.7% for $Cr_2O_3$, −0.5% for MnO, −0.2% for $K_2O$ correction = 97%. (Previously, analyses of Pathfinder rocks and soils were normalized to 98%, with all Fe reported as FeO [McSween et al., 1999; Rieder et al., 1997].) Error bars were also normalized to 97% totals. These error bars include all uncertainties, but uncertainties in the points relative to each other may be significantly less (McSween et al., 1999). Thus, error bars shown in the figures may be misleadingly large when comparisons among rock or soil compositions are involved.

Several other corrections to published Pathfinder soil data, based on on-going recalibration of the X-ray detector, have been reported in abstract form. Dreibus et al. (1999) indicated revised abundances of CaO (5.5% rather than 6.0%) and $TiO_2$ (0.9% rather than 1.2%) for the average of four soil analyses (A-4, A-5, A-10, A-15; normalized to 97% with Fe as $Fe_2O_3$). We have not included these corrected values in Table 1 because no revised data for other soil analyses (A-2, A-8) were given, but we have used them to adjust the preferred global dust composition for Pathfinder in Table 2.

Unlike Pathfinder soil analyses, which represent the compositions of the uppermost few tens or hundreds of microns of mostly undisturbed surface samples, Viking analyses are bulk soils collected from up to several centimeters depth. Because of the high rate of dust accumulation on the surface (e.g., Rover Team, 1997), we expect the proportion of dust in soil analyses to be greater for Pathfinder than for Viking.

Viking XRF data were taken from Table 2 of Clark et al. (1982). Because Utopia (Viking landing site 2) data are missing some elements, only Chryse (Viking 1 landing site) analyses (C-1, C-5, C-6, C-7, C-8, C-9, C-13) were used in calibrating regressions, although Utopia data are included in many plots. Chryse samples C-2 and C-11 were also omitted from regressions because of missing elements in the analyses.

In principle, the Viking analyses may be absolute measurements because they used a backscatter reference on the landers to calibrate the total X-ray interaction of the target. However, because that peak is a scattering peak and the element peaks are

Table 2. Estimated chemical composition of Martian fines (wt.% oxides).

| $Na_2O$ | MgO | $A1_2O_3$ | $SiO_2$ | $SO_3$ | C1 | $K_2O$ | CaO | $TiO_2$ | $Fe_2O_3$ | MnO |
|---|---|---|---|---|---|---|---|---|---|---|
| Pathfinder high-sulfur end member: Average of APXS analyses A-4 and A-10 | | | | | | | | | | |
| 2.6 ± 1.0 | 7.9 ± 1.2 | 8.5 ± 0.9 | 46.8 ± 2.4 | 6.3 ± 1.3 | 0.7 ± 0.2 | 0.6 ± 0.1[a] | 5.5 ± 0.7* | 0.9 ± 0.1* | 17.2 ± 1.6 | 0.5 ± 0.1 |
| Viking 1 low-sulfur end member: XRF analysis of fines sample C-8 | | | | | | | | | | |
| | 6.5 −3 to +5 | 7.7 ± 4 | 46.4 ± 6 | 6.4 −2 to +6 | 0.7 −0.5 to +1.5 | | 6.3 ± 2 | 0.8 ± 0.25 | 20.3 −2 to +5 | |
| Intersection of Pathfinder and Viking 1 regression lines | | | | | | | | | | |
| | | 7.7 | 47.5 | 6.2[b] | | | 6.4 | 0.8 | 19.2 | |

[a] $K_2O$ adjusted from 0.2 ± 0.1, CaO from 5.9 ± 0.9, and $TiO_2$ from 1.3 ± 0.2 (Table 1), and new MnO analysis, based on recalibration of average soil composition reported by Dreibus et al. (1999).

[b] $SO_3$ based on overlap of Pathfinder and Viking soil ranges; omitted elements are considered unreliable.

emission signals, it is possible that various matrix effects and heterogeneities could bias the calibrations and lead to absorption or enhancement effects (Clark et al., 1982). Viking analyses did not include data for $Na_2O$, and $K_2O$ values were reported to be below the detection limit (0.15–0.25%) (Clark et al., 1982). For purposes of normalization, we have assumed that the abundances of alkalis in Viking soils are the same as the average values in Pathfinder soils (2.1% $Na_2O$, 0.6% $K_2O$). It is debatable whether or not Viking soils have alkali contents this high. Soil analyses for an equatorial area to the southwest of the Viking 1 and Pathfinder sites, performed by gamma-ray spectroscopy on the Phobos orbiting spacecraft (Trombka et al., 1992), indicate $K_2O$ values of 0.2–0.5%, intermediate between the Viking detection limit and revised Pathfinder analyses. For purposes of comparison with Pathfinder soil analyses, we have normalized Viking analyses to 100% −1.5% for $P_2O_5$, $H_2O$, C, −0.7% for $Cr_2O_5$, −0.5% for MnO, −2.7% for $Na_2O$, $K_2O$ correction = 94.6%. One representative error bar, normalized to this total, is illustrated on plots. As for Pathfinder errors, this error bar may be misleadingly large when comparing Viking points to each other.

The sum of oxide equivalents in the original Viking data is ≈90% (Clark et al., 1982); therefore, this normalization increases these abundances by <5%. The reason for the low totals is unknown. One possibility is that S and Cl abundances were underestimated due to matrix particle coating effects. Another possibility is that extremely fine-grained materials may cause skewing of the ratio of scattering to fluorescence, although laboratory simulations of this effect were inconclusive (B. C. Clark, personal communication, 1999).

## 3. EVIDENCE FOR MIXING

### 3.1. Imaging and Spectral Observations of Physical Mixing

Many spectral studies suggest that the Martian surface is characterized by mixtures of mafic igneous rocks and highly altered dust and soil on a broad scale (e.g., Mustard et al., 1993), and intimate mixing of rock and dust may also occur at small scales. Viking 1 observations indicated that some Chryse soils are blocky, containing centimeter-sized red clods and a few dark fragments (Arvidson et al., 1989). Dale-Bannister et al. (1988) compared the radiance factors for the dark fragments on the XRF experiment funnel with those of the local rocks and concluded that the dark chips were lithic fragments. However, repeated attempts to sieve out rock fragments at the Viking 1 site did not recover significant amounts of these materials. Soils at the Viking 2 landing site were cloddy but contained no obvious dark lithic fragments. Soil mechanics experiments by the Sojourner rover indicated that most soils at the Pathfinder site are cloddy, with dust- to granule-sized mineral or rock fragments (Moore et al., 1999), and the abundance of dark granules is greater than at the Viking 1 site (Larsen et al., 1999). Of the soil sites analyzed by APXS, A-15 appears to contain the highest proportion of lithic fragments (Rover Team, 1997). The spectra of darker Pathfinder soil units suggest admixture of ferrous minerals, such as clinopyroxene and olivine (presumably particles of, or derived from, igneous rocks), relative to bright red soils spectrally dominated by nanophase ferric oxides (Bell et al., 2000).

All the chemically analyzed Pathfinder soils were cloddy; although drifts were present at the site, they were not analyzed. Moore et al. (1999) and Bell et al. (2000) describe the physical characteristics of each APXS soil analysis location. Viking 1 soils analyzed by XRF include both fines and clods separated from fines, with specific characteristics as described by Baird et al. (1977) and Clark et al. (1982).

### 3.2. Chemical Mixing

Several geochemical components, identified generically as "silicates" and "sulfate/chloride salts," were recognized in the original analyses of Viking soils (Baird et al., 1976; Clark et al., 1982), and interelement correlations in them were quantified by Clark (1993). However, there have been no published attempts to explain Viking soil chemical data as mixtures of rock fragments and dust, probably because of the general absence of lithic fragments in sieved Chryse soils.

The compositions of Pathfinder rock samples tend to form nearly linear arrays when plotted as oxides versus $SO_3$, with soils clustering at the $SO_3$-rich ends of the arrays (Rieder et al., 1997). These arrays have been interpreted as mixing lines, composed of andesitic rock (termed sulfur-free rock) plus adhering surficial dust or soil, a conclusion supported by a correlation between $SO_3$ content and spectral properties (McSween et al., 1999). Because $SO_3$ appears to be an excellent discrimintor for Martian soils, we will graphically examine possible sulfate mixing relationships in both Pathfinder and Viking soil data. Other attempts to deconvolve rock and dust components from the chemistry of Pathfinder soils have been

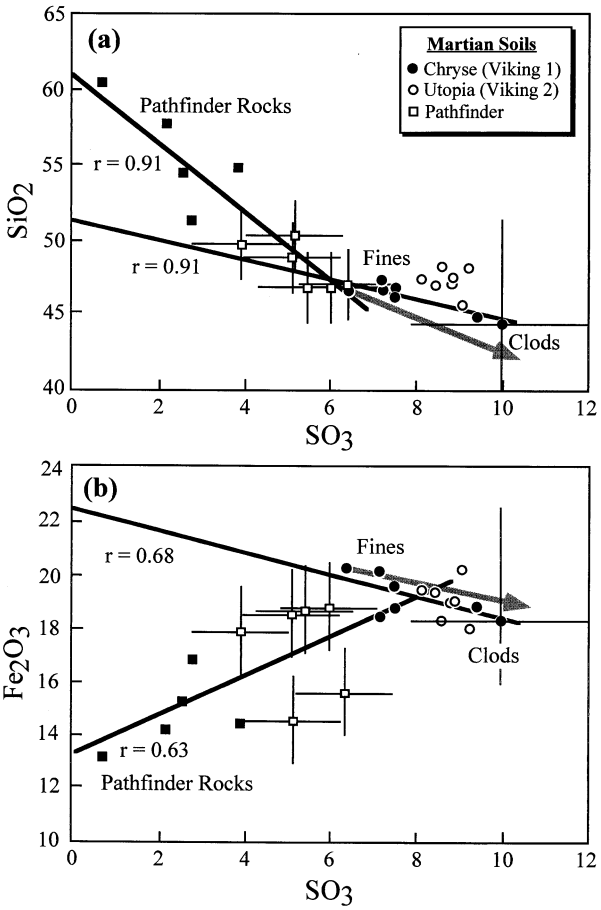

Fig. 1. Comparison of wt.% $SO_3$ versus (a) $SiO_2$ and (b) $Fe_2O_3$ in analyzed soils from the Viking 1 (both fines and dirt clods) and Mars Pathfinder landing sites (normalized data from Table 1), with regression lines and coefficients. Figures also include data for Pathfinder rocks (Rieder et al., 1997) and Viking 2 soils (Clark et al., 1982, renormalized as in Table 1). Pathfinder regressions include rocks plus soils; Viking regressions include only Chryse data. These regressions intersect at high angles. One representative error bar for Viking analyses is shown. Arrows are vectors illustrating the effect of adding 7% $MgSO_4$ to the lowest $SO_3$ Chryse soil.

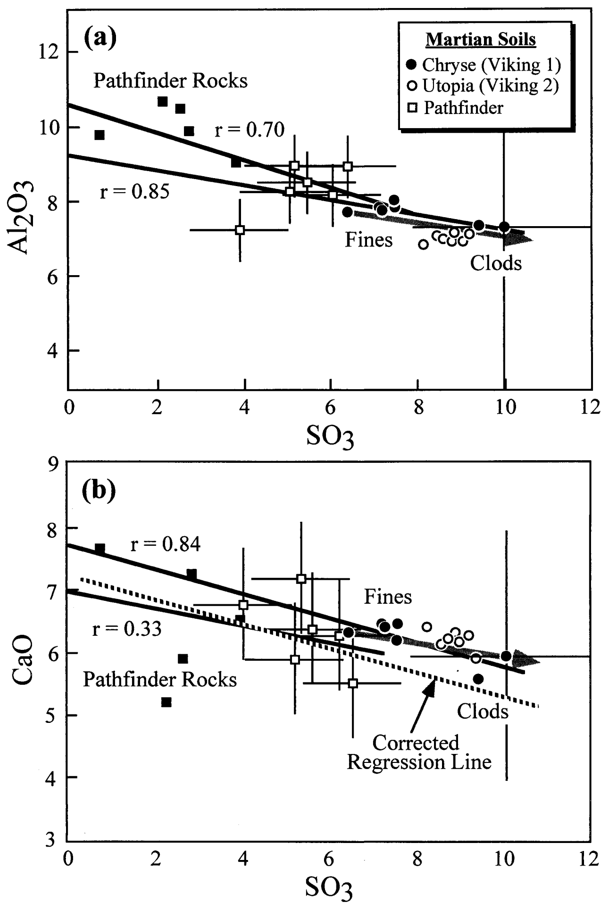

Fig. 2. Comparison of wt.% $SO_3$ versus (a) $Al_2O_3$ and (b) CaO in analyzed Martian soils and rocks Data sources and description of regressions and vectors are as in Fig. 1. The corrected regression line in (b) is based on recalibration of the X-ray detector (see text). These regression lines intersect at very low angles.

presented in abstract form (Bridges and Crisp, 1999; Brückner et al., 1999; Larsen et al., 1999; McLennan, 1999; McSween and Ghosh, 1999; Morris, 1999; Wänke et al., 1999), with conclusions that may differ from those derived in this article.

In the following oxide or element versus $SO_3$ plots, regression lines and coefficients are illustrated for Pathfinder soils plus rocks and for Chryse soils. We argue that including Pathfinder rocks and soils in the same data set is justified because soils contain admixed rock fragments and rocks are partly covered by soils (McSween et al., 1999). Figure 1 shows two oxides ($SiO_2$ and $Fe_2O_3$) that form Pathfinder and Viking arrays having distinct slopes. In contrast, $Al_2O_3$ and CaO (Fig. 2) produce Pathfinder and Viking arrays that are virtually indistinguishable. $TiO_2$ and MgO (Fig. 3) also define distinct arrays, and Cl (Fig. 4) arrays have virtually the same slope but Viking data extend the Pathfinder trend to higher concentrations.

In all these figures, the Pathfinder soil data are somewhat “noisy” but appear to be roughly distributed along the rock plus soil regression lines. It seems plausible, then, to attribute this compositional variation to admixture of small fragments of the local andesitic rock in the soil. The scatter might arise from inclusion of some rock fragments of other compositions as well, possibly conglomerates that have been suggested to occur at the site (Rover Team, 1997). It is tempting to infer that compositional variations in Viking soils arise from a similar mixing process, and to derive the local rock composition by extrapolation of the regression line to zero sulfur. This extrapolated composition is very similar to that of basaltic shergottites (meteorites thought to be derived from Mars; McSween, 1994, and references therein). However, we do not believe that the Chryse soil arrays result from admixture of basaltic rock fragments. The cloddy soils, which contain the greatest abundance of recognizable dark lithic fragments (Dale-Bannister et al., 1988), plot farthest from the extrapolated rock composition, and the fines, which likely contain little or no locally derived materials, plot closest. Instead, we suggest that the shallow negative slopes of all the Chryse arrays (except MgO) simply reflect the addition of sulfate, probably as a cement that produces the cloddy texture at higher concentrations. The cement is probably dominated by magnesium sulfates (with unknown

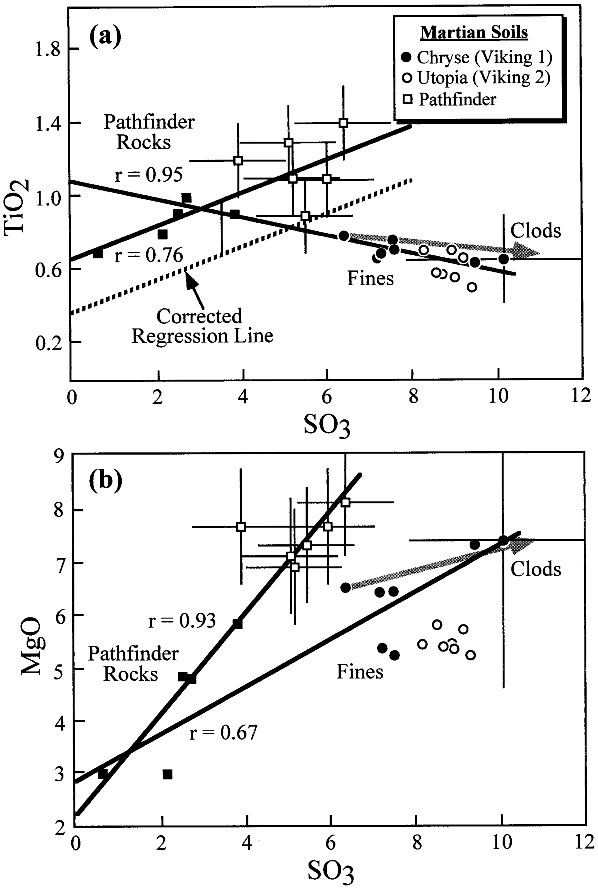

Fig. 3. Comparison of wt.% $SO_3$ versus (a) $TiO_2$ and (b) MgO in analyzed Martian soils and rocks. Data sources and description of regressions and vectors are as in Fig. 1. The corrected regression line in (a) is based on recalibration of the X-ray detector (see text).

hydration state), because MgO correlates positively with $SO_3$ in Viking soils (Clark, 1993) and Pathfinder soils (Fig. 3b) and magnesium sulfates have been predicted to be stable in the Martian regolith on theoretical grounds (Clark and Van Hart, 1981). The gray arrows in each diagram (Figs. 1, 2, and 3) illustrate the effect of adding 7% $MgSO_4$ to the most $SO_3$-poor Chryse soil. These arrows correspond approximately to the observed Chryse arrays. The fact that Cl correlates positively with $SO_3$ (Fig. 4) suggests that the cement also includes chlorides, possibly halite.

Our preferred model, then, is that the Pathfinder and Viking arrays arise from distinct processes: admixture of local, mostly andesitic rock fragments to dust deposits in the case of Pathfinder soils, and introduction of sulfate/chloride (salts) cement into dust deposits in the case of Chryse soils. If this model is correct, the high $SO_3$ end-member of the Pathfinder arrays (which contains the least lithic fragments) and the low $SO_3$ end-member of the Chryse arrays (which contains the least cement) might represent the global dust composition. These compositions are compared in Table 2; we have averaged Pathfinder soils A-4 and A-10 to derive the Pathfinder end-member, because these soils have similar $SO_3$ contents. This model predicts that the respective end-members should have very similar compositions (as they do). Appropriately, the low $SO_3$ Chryse soils are fines; however, the high $SO_3$ Pathfinder end-members are cloddy materials (Moore et al., 1999).

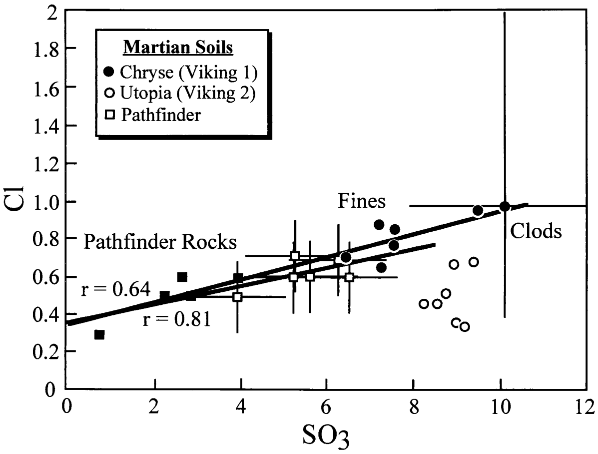

Fig. 4. Comparison of wt.% $SO_3$ versus Cl in analyzed Martian soils and rocks. Data sources and description of regressions are as in Fig. 1.

A graphic way to estimate the global dust composition is to determine the intersections of the regression lines, which should converge at or near these end-member compositions (as most do, see Figs. 1 and 2a). However, the CaO (Fig. 2b) regression lines are nearly parallel, and the $TiO_2$ and MgO (Fig. 3) regressions intersect at the wrong ends of the Pathfinder soil arrays. The Pathfinder CaO and $TiO_2$ regression lines are likely to be in error. On the basis of recalibration of the X-ray detector, Brückner et al. (1999) revised the CaO and $TiO_2$ abundances in average Pathfinder soil downward by 0.5% and 0.3%, respectively. If the Pathfinder regression lines in Figures 2b and 3a are shifted downward by these amounts, as shown by the hatched lines, they intersect the Chryse regression lines at appropriate points. The intersections of all the regression lines are summarized in Figure 5. The arrays for all the "silicate" components intersect at approximately the same $SO_3$ value, that is, within analytical error, corresponding to the overlap in $SO_3$ concentrations for Pathfinder and Viking 1 soils. The global dust composition estimated in this way is given in Table 2.

The arrays for the "salt" or "cement" components MgO and Cl intersect at lower $SO_3$ values (Fig. 5). The Cl arrays merge at 0.35% Cl and 0% $SO_3$, but the slopes are so similar that the intersection probably has little significance. The MgO intersection also occurs fairly close to 0% $SO_3$, as appropriate if this is a salt component. However, the higher MgO and lower $SO_3$ abundances in Pathfinder soils and the differences in the slopes of the regression lines (Fig. 3b) are difficult to explain. Analysis of Mg was especially difficult for both instruments, and we suggest that the absolute amounts of MgO in one or both of the data sets may be in error.

### 3.3. Chemistry and Spectra Combined

The relative rock fractions in Pathfinder soils might be estimated from their $SO_3$ contents, assuming that the admixed rock fragments are sulfur-free volcanic rocks (McSween et al., 1999) and that the highest $SO_3$ soil (A-4) represents the soil end-member. This parameter for Pathfinder rocks represents the

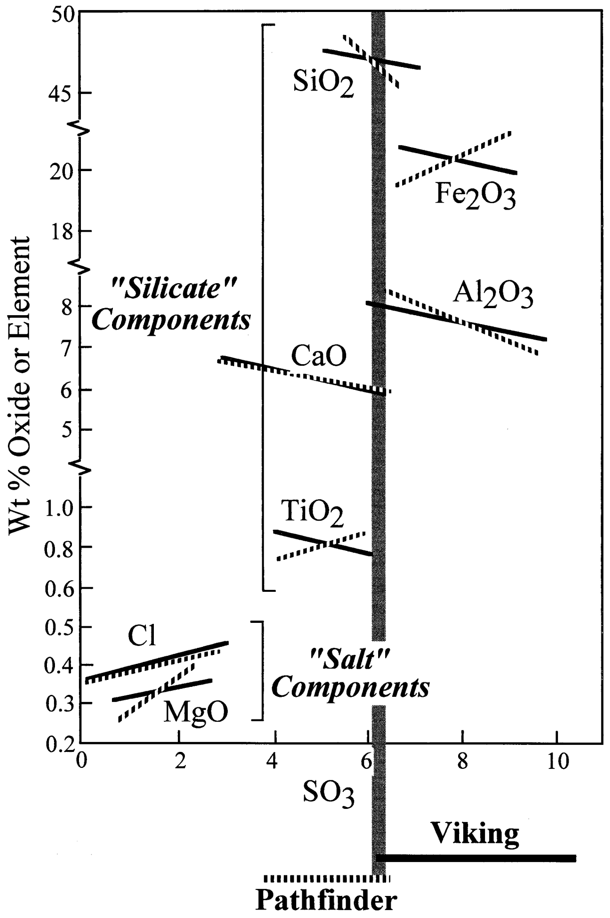

Fig. 5. Summary of the intersections of regression lines for Pathfinder and Viking arrays shown in Figs. 1–4. Components inferred to reside in "silicate" phases all have intersections near $SO_3$ = 6.2%, the approximate value where Pathfinder and Viking $SO_3$ values overlap. This conformity supports the hypothesis that the intersection defines the composition of a common dust component at both sites, presumably the global dust. The "salt" components do not intersect at this point, because the Pathfinder and Viking soils apparently have different amounts of sulfate/chloride cement.

relative contribution of rock, as opposed to adhering dust, to the APXS analysis of rock surfaces. Calculated rock fractions for the soils and rock surfaces are presented in Table 3, along with spectral data for each APXS analysis point (soil spectra from Bell et al., 1999, and rock spectra from McSween et al., 1999). The 750 nm/440 nm (red/blue) spectra ratio increases with the proportion of dust, because drift deposits are red and gray rocks are spectrally blue.

Table 3. Estimated mixing ratios and spectra of Pathfinder soils and rocks.

| Sample | Rock fraction[a] | Red/blue ratio[b] |
|---|---|---|
| Soil samples | | |
| A-2 | 0.28 | 4.7 |
| A-4 | 0 | 4.6 |
| A-5 | 0.14 | 5.2 |
| A-8 | 0.17 | 5.6 |
| A-10 | 0.05 | 5.5 |
| A-15 | 0.19 | 3.9 |
| Rock samples | | |
| A-3 | 0.65 | 2.7 |
| A-7 | 0.38 | 4.1 |
| A-16 | 0.56 | 3.1 |
| A-17 | 0.89 | 2.4 |
| A-18 | 0.59 | 2.7 |

[a] Rock fractions, relative to soil A-4 as pure soil, estimated from $SO_3$ abundance; rock fractions for rocks refer to contribution of rock relative to adhering dust in APXS analysis.

[b] Reflectance at 750 nm/440 nm, soil data from Bell et al. (2000) and rock data from McSween et al. (1999).

The relationship between estimated rock fractions and red/blue spectra ratio is shown in Figure 6 (this figure is similar to Figure 18 of McSween et al., 1999, but recast in terms of rock fraction rather than $SO_3$). The correlation is better for rock surfaces than for soils, possibly because tiny rock fragments in soils may be more easily coated with dust than are large rocks. Also, visible light reflectance derives from a significantly thinner coating than fluorescent X-rays, and hence is more susceptible to dust coating effects. We would also expect the $SiO_2$ content of soils to be a sensitive measure of the proportion of admixed rock, as the local Pathfinder rocks are silica-rich (estimated at 62.0% by McSween et al., 1999). The silica contents for each soil are given in Figure 6. The expected relationship holds, except for one sample (A-8, the indurated hardpan Scooby Doo, with $SiO_2$ = 50.3%). Lithification of this soil may have altered its spectral properties and perhaps its silica content.

## 4. GLOBAL DUST AND LOCAL SOILS

### 4.1. Source Rocks for the Global Dust

Similarity in the compositions of Martian soil (corrected for excess S and Cl, possibly added by volcanic exhalations; Baird and Clark, 1981) and basaltic shergottites led to an early hypothesis that the soil was derived from basalts by nearly

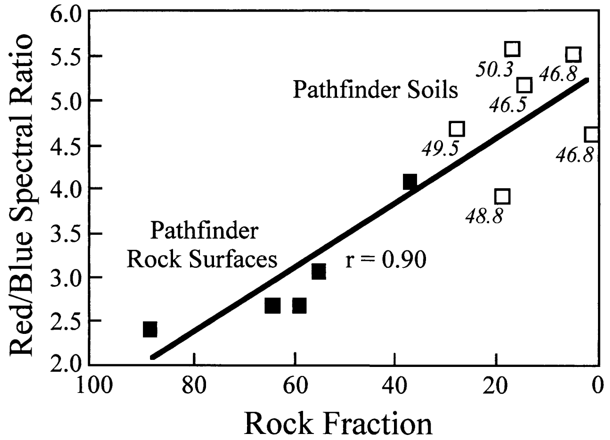

Fig. 6. Red/blue (750 nm/440 nm) reflectivity ratio versus estimated rock fraction for Pathfinder rocks and soils. Spectral data sources are given in Table 3. Pathfinder rock surfaces were variably coated with dust, and the rock fraction refers to the relative weight proportion of rock in APXS analyses of $SO_3$. Rock fraction of soils is the proportion by weight of admixed andesitic fragments, based on $SO_3$ analyses and referenced to the highest $SO_3$ soil as zero. Numbers in italics are $SiO_2$ contents of soils, which are expected to increase with rock fraction.

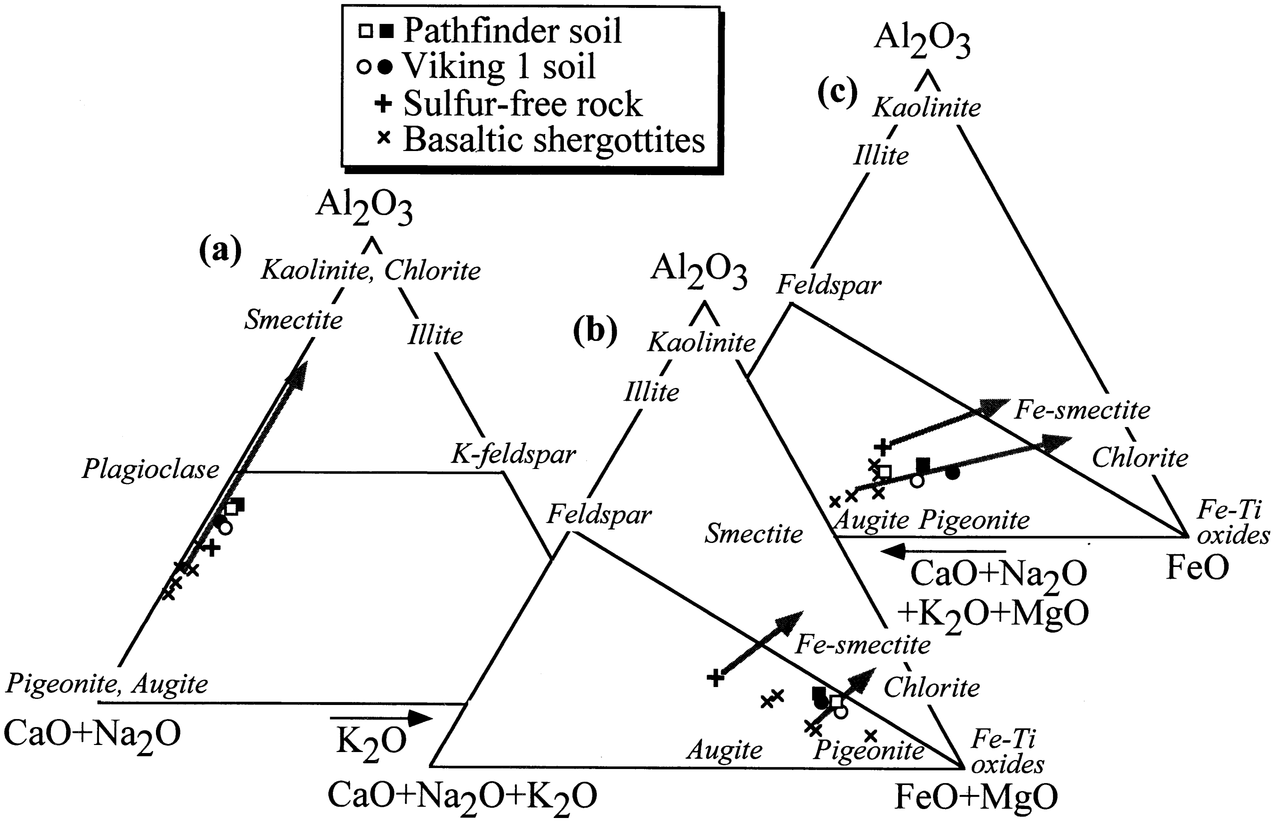

Fig. 7. Molar ternary diagrams illustrating chemical weathering trends (arrows) in volcanic rocks, after Nesbitt and Wilson (1992). Compositions of global dust derived from Pathfinder and Viking 1 mixing relationships (Table 2) are plotted as open symbols, and the same compositions corrected for salts [$MgSO_4$ and (Na,K)Cl] are shown as filled symbols. Also shown are compositions of the Pathfinder sulfur-free andesitic rock (Rieder et al., 1997) and the basaltic shergottites Shergotty (Laul et al., 1985), Zagami and EET79001A and B (Smith et al., 1984), and QUE94201 (Warren and Kallemeyn, 1997).

isochemical weathering (McSween and Stolper, 1980; Baird and Clark, 1981). These soil compositions, plus spectral similarlities between basaltic shergottites or other basalts and dark regions of the Martian surface (Singer and McSween, 1993; Mustard and Sunshine, 1995; Moersch et al., 1997; Mustard et al., 1997; Christensen et al., 2000), suggest a pervasive basaltic source. However, the discovery of silica-rich rocks at the Pathfinder site (Rieder et al., 1997) allows the possibility that the protoliths for soils could have varied compositionally. McSween et al. (1999) emphasized that the Pathfinder andesitic rock composition was plausibly derived locally by fractionation of basaltic magma, which may imply that andesitic rocks might not be volumetrically important lithologic units in the planet's crust. However, other workers have devised mixing models that explain the Martian soil as combinations of basalt with signficant amounts of ancient crust having andesitic composition (Brückner et al., 1999; Morris, 1999; Wänke et al., 1999).

Because of possible differences in weathering conditions and lava compositions on Earth and Mars, it may be misleading to use terrestrial sediments derived from volcanic rocks as an analogy for Martian soil. However, Nesbitt and Wilson (1992) reported that relative bulk leaching of major elements from weathered basalts is not greatly influenced by primary mineralogy, bulk chemical composition, or climatic conditions. We will use molar ternary diagrams devised by Nesbitt and Young (1984) to illustrate the effects of weathering of basaltic shergottites and the Pathfinder sulfur-free (andesitic) rock and compare these trends with our derived global dust composition. The trends depicted on these diagrams have been confirmed from studies of other volcanic weathering profiles (Nesbitt and Wilson, 1992) and by thermodynamic calculations (Nesbitt and Young, 1984), although the kinetics of weathering reactions involving mafic minerals are not well understood and may influence these trends. It is sometimes necessary to make a correction to $Na_2O$ for NaCl in unconsolidated sediments (McLennan et al., 1990); accordingly, we will plot our raw dust compositions as well as dust corrected for the addition of salts [both $MgSO_4$ and (Na,K)Cl].

In Figure 7a, shergottites plot as mixtures of clinopyroxenes and plagioclase, and the Pathfinder andesite plots at slightly higher $Al_2O_3$ and $K_2O$ values. Weathering of basalts leaches CaO, $Na_2O$, and sometimes $K_2O$, producing a trend directed toward the $Al_2O_3$ apex (Nesbitt and Wilson, 1992). Martian dust is displaced toward $Al_2O_3$, as appropriate for weathered materials, but it is not obvious from this diagram whether basalt or andesite was its protolith.

Progressively more weathered materials in Figure 7b define trends directed toward the $Al_2O_3$ to FeO + MgO boundary

(Nesbitt and Wilson, 1992). From this diagram, it appears that basaltic shergottites are appropriate protoliths for Martian dust but the Pathfinder andesite composition is not.

In Figure 7c, the labile oxides $CaO + Na_2O + K_2O + MgO$ are combined, and phases containing $Al_2O_3$ and FeO ($Fe_2O_3$ in the case of Martian soil) have low solubilities compared to labile oxide phases. Weathering trends are thus directed away from the labile oxide apex (Nesbitt and Wilson, 1992). Again, this diagram suggests that basalt is a more appropriate source rock for the global dust composition than is andesite.

### 4.2. Alteration Mechanisms for Producing the Global Dust

Although the global dust composition in each diagram in Figure 7 is displaced in a direction appropriate for chemical weathering of basalt (and the chemical separation that accompanies it), the displacement is small relative to terrestrial basalt weathering products (indicated by the lengths of the vectors). It is unlikely that the small displacement is an artifact of the addition of salts. The effects of adding $MgSO_4$ and NaCl, in proportions corresponding to the amounts of $SO_3$ and Cl in the dust, can be seen by comparing the open and filled (salt-corrected) soil symbols in Figure 7. Admixture of salts does not signficantly or consistently pull the dust composition back toward basalt. A more plausible explanation may be related to the fate of water at the end of the alteration process. If a hydrous fluid on Mars simply evaporated at the completion of the weathering cycle, all the dissolved components would be left behind so that chemical separations would be minimal. This is potentially a very different situation from Earth, where the stability of surface water allows dissolved constituents to be more efficiently removed from the weathered residue.

Numerous alteration mechanisms for producing Martian soil have been proposed (summarized by Bell et al., 2000), and three of these have found fairly wide acceptance. Palagonitization of volcanic or impact glasses (Gooding and Keil, 1978) produces poorly crystalline or amorphous materials that provide the best spectral analogs for Martian soils (e.g., Morris et al., 1993). Alteration of rocks and glasses by hydrothermal fluids heated by magmatism or impact (Newsom, 1980; Griffith and Shock, 1997) is a conceptually similar process but usually produces well crystalline minerals. Volcanic exhalations of S and Cl species reacting with atmospheric water vapor may produce an acid fog, which reacts in turn with basaltic rocks (Clark and Baird, 1979; Banin et al., 1997). The chemical effects of all these processes have been studied in natural and laboratory systems. Palagonites have been analyzed extensively (e.g., Staudigel and Hart, 1983; Jercinovic et al., 1990). We can use the compositions of natural palagonites and their basaltic protoliths in assessing chemical changes, although we recognize that palagonitization represents a varying assortment of processes and is thus geochemically undefined. Hydrothermal alteration of seafloor basalts has been well documented (e.g., Alt and Honnorez, 1984). Although it might be argued that hydrothermal alteration by salty seawater at mid-ocean ridges is a uniquely terrestrial process, brines have been implicated in Martian soil formation (Newsom et al., 1999) and in the alteration of Martian meteorites (Treiman et al., 1993; McSween and Harvey, 1998; Bridges and Grady, 1999). In an attempt to model acid fog reactions, Banin et al. (1997) reported the results of acidification experiments on tephra.

The chemical trends defined by the studies cited above are shown in molar variation diagrams (Fig. 8). All the trends in Figure 8a are roughly similar and not diagnostic. However, Figures 8b,c appear to discriminate between these processes. Only the palagonitization vectors (J and SH) resemble the weathering trends illustrated in Figure 7, and the hydrothermal alteration (AH) and acid fog reaction (B) trends do not pass through the compositions of the dust. These diagrams suggest that palagonitization of basalt may best explain the Martian dust composition, although the parameters affecting the alteration trends for other weathering processes are probably not well understood.

### 4.3. Local Geologic Processing of Dust Into Soil

Despite concensus that a globally homogenized dust unit exists on Mars, studies of bright, presumably dust-covered regions of Mars at increasing spatial resolution have detected spectral heterogeneities and evidence of soil mobility (e.g., Singer et al., 1979; Murchie et al., 1993; Bell et al., 1997; Lane et al., 1999). Spectrally distinctive and mobile sedimentary units are recognizable even at specific landing sites (Arvidson et al., 1989; Bell et al., 1999; Greeley et al., 1999). Thus, it seems obvious that some local and temporal processing of dust must have occurred and may be on-going, a conclusion also reached by McLennan (2000).

We have already identified several mixing processes by which global dust has been locally processed to make distinctive soils. At the Pathfinder site, dust has been mixed with fragments of the local rocks, commonly up to 20% by weight. This is consistent with observations of the mechanical breakdown of rocks such as Barnacle Bill (McSween et al., 1999). Observations of a few dark lithic fragments in some Viking soils (Dale-Bannister et al., 1988) suggest that a similar process occurred at the Viking 1 landing site, although its effect is not resolvable in soil chemistry (although Morris, 1999, suggested that the Viking soil array was due to admixture of basaltic shergottite). The processes that lead to rock comminution (a prerequisite for admixture into soil) on Mars are not well understood, but may include exfoliation (McSween et al., 1999), wind abrasion (Greeley et al., 1999), etching of softer minerals (Carr, 1981), and small impacts (Hörz and Cintala, 1999).

Soils at the Viking sites exhibit varying amounts of cementation, presumably by sulfate/chloride salts. The origin of the salt components and their introduction into the soil is a subject with a long and contentious history. Possible sources of salt components include volcanic aerosols (Clark and Baird, 1979; Banin et al., 1997), hydrothermal fluids (Newsom et al., 1999), massive sulfide deposits (Burns, 1988), and evaporating surface waters (McSween and Harvey, 1998; Warren, 1998). Cementation requires that salts were introduced by and precipitated from fluids, although the salts could have been reworked from older deposits formed from volcanic exhalations, gossans, or evaporites. The cloddy nature of Pathfinder soils suggests that they also experienced some addition of salts. Although this process is not resolvable in Pathfinder soil chemistry, the APXS

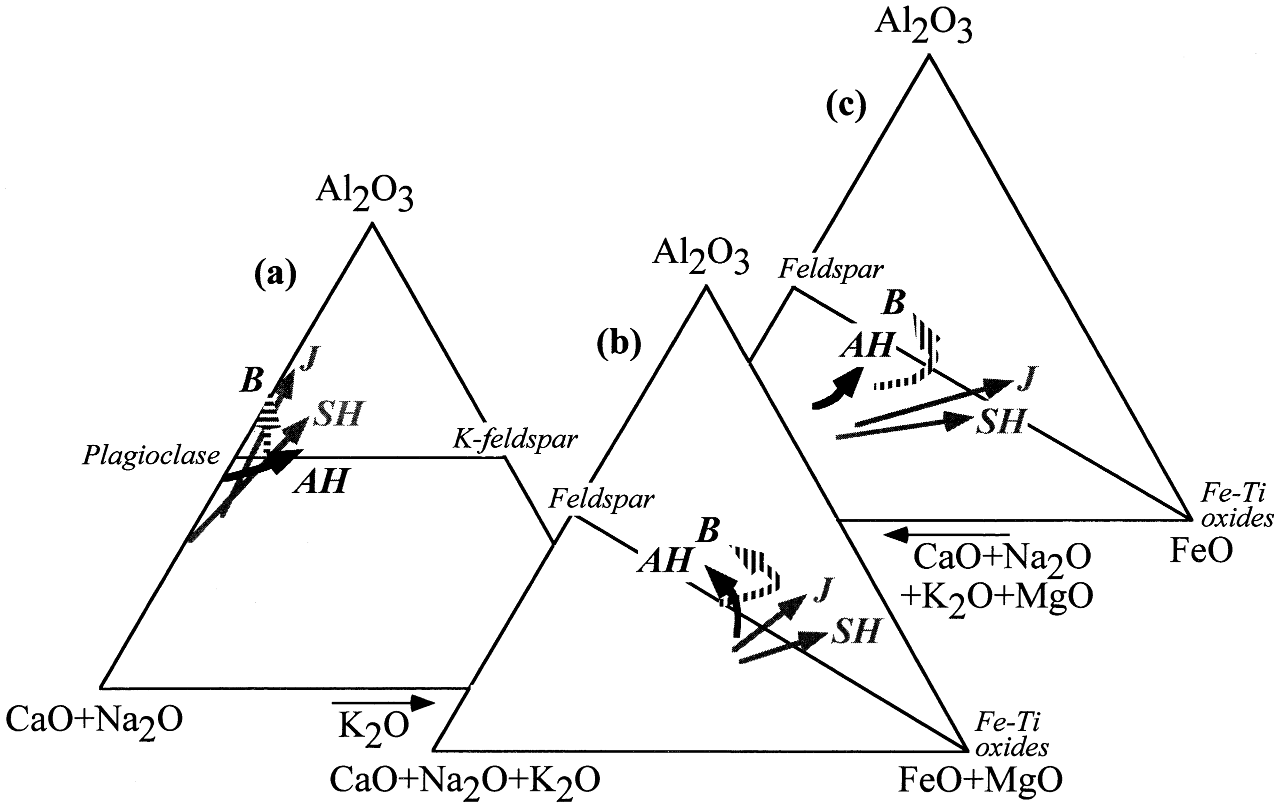

Fig. 8. Molar ternary diagrams illustrating alteration trends resulting from proposed Martian soil formation mechanisms (palagonitization, acid-fog reactions, and hydrothermal alteration). Arrows show palagonitization of basaltic glasses (SH = Staudigel and Hart, 1983, based on glass in Table 1 and percentage gain or loss in their Table 2; J = Jercinovic et al., 1990, averages of all glass and palagonite analyses in their Table 4), the results of acid leaching experiments (2 and 6 mEq/g added acidity) on tephra (B = Banin et al., 1997, calculated from data in their Figure 9), and hydrothermal alteration of ocean floor basalts (AH = Alt and Honnorez, 1984, based on unaltered basalt in their Table 5 and altered basalt from the brown zone 417A 28-1-1 and zeolite zone 417A 29-3-8 in their Table 4). Palagonitization trends are very similar to basalt weathering trends shown in Fig. 7. Trends of acid-fog reactions and hydrothermal alteration differ, and appear to be incompatible with derivation of Martian soils from either basalt or andesite.

only analyzed soil surfaces as opposed to bulk soils analyzed by Viking.

The most noticeable temporal changes at the Viking and Pathfinder sites were wind erosion and deposition. Viking time-series image data monitored two global dust storms, and surface brightening resulted from dust accumulation even during quiet periods (Arvidson et al., 1989). Wind tails, drift deposits, dunes, and ventifacts were observed at the Pathfinder site (Greeley et al., 1999), and numerous dust devils were documented (Schofield et al., 1997). With all this aeolian activity, it is very likely that sorting of sedimentary particles of different sizes and densities is a pervasive, on-going process on the Martian surface. If clay minerals are present, they would be sequestered into the finest grain-size fractions, which may lead to significant chemical fractionations (Nesbitt et al., 1996). Basaltic shergottites contain significant amounts of titanomagnetite and ilmenite (McSween, 1994). These Fe–Ti oxides have the highest densities among the rocks' constituents, and they tend to resist abrasion and weathering (Nesbitt and Wilson, 1992). The mineralogic identity of the magnetic phase in Martian dust is disputed (both maghemite and titanomagnetite appear to satisfy the magnetic susceptibility constraints; Hargraves et al., 1977; Madsen et al., 1999; Morris et al., 1999). Even if the primary igneous oxides have been comminuted into minute particles or otherwise altered and combined with silicates to form composite particles in the dust (Madsen et al., 1999), aeolian processes might still fractionate particles with different proportions of Fe–Ti oxides. Thus, $Fe_2O_3$ and $TiO_2$ are most likely to reveal any chemical effects of aeolian sorting.

Figure 9 shows the relationship between $Fe_2O_3$ and $TiO_2$ in Viking 1 and Pathfinder soils and rocks. Viking soils exhibit a positive correlation between these components (the correlation is stronger than illustrated in Figure 9, when all Viking soil analyses are considered; see Clark et al., 1982). There appears to be a slight difference in the slopes of the trends for Chryse and Utopia data, corresponding to molar Ti/Fe ratios of 0.04 and 0.07, respectively (Clark, 1993). The Pathfinder rocks show an excellent correlation between these components, but the soils do not (Fig. 9). This is perplexing, as the rock trend is thought to represent a mixing line between andesitic rock and adhering dust; if the soil is varying in composition, the rock mixing line should be scattered as well. However, our estimate of the Pathfinder dust composition does lie at the end of this trend. This scatter in soil composition may reflect aeolian

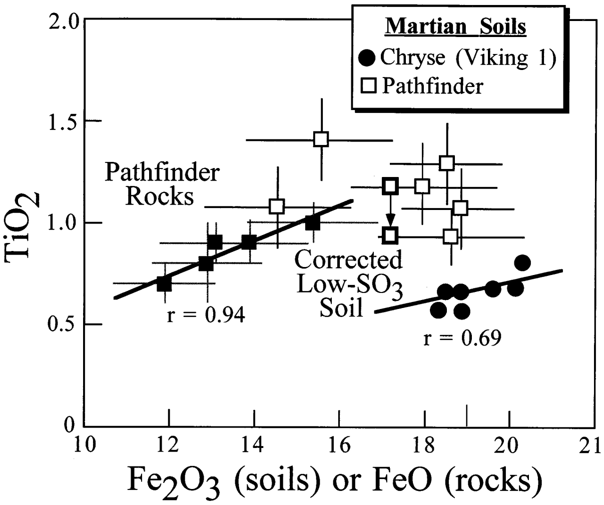

Fig. 9. Plot of $TiO_2$ versus $Fe_2O_3$ in Viking 1 and Pathfinder soils and rocks (after Rieder et al., 1997, Fe in rocks is plotted as FeO). The low $SO_3$ Pathfinder soil composition, with corrected $TiO_2$ abundance (Table 2), is also shown. Lack of coherence in Pathfinder soils may signal aeolian fractionation of dense Fe–Ti oxide grains.

sorting of Fe–Ti oxides from silicates (the latter presumably also contain FeO, but not $TiO_2$). To compare the Pathfinder and Viking 1 soils, we must adjust the Pathfinder $TiO_2$ abundances downward by 0.3% (Dreibus et al., 1999), as illustrated by the corrected low $SO_3$ soil composition in Figure 9. Most Pathfinder soils still have higher $TiO_2$ abundances than Viking soils, which may also suggest differing degrees of aeolian fractionation between sites. McLennan (2000) also argued for heavy mineral fractionation during transport, based on variations of $TiO_2$ and $Fe_2O_3$ with $SiO_2/SO_3$.

### 4.4. Does the Dust Composition Reflect Crustal Elemental Abundances?

Because sediments usually sample broad areas and large volumes of exposed crust, terrestrial sediment compositions are commonly used to identify source terrane types (McLennan et al., 1993), and they provide an effective way to estimate the bulk composition of the upper crust (McLennan and Taylor, 1984). Trace element ratios and radiogenic isotope systematics provide the most important discriminants, but major and minor element abundances in the crust may also be estimated if compensation is made for fractionations during weathering, transport, and deposition. The nearly uniform composition of dust at the Viking and Pathfinder sites suggests that sedimentary fractionations may have been relatively minor.

Estimated erosion rates at spacecraft landing sites on Mars are very low (Arvidson et al., 1989), suggesting that the dust may have been derived mainly from weathering of surficial units. As a consequence, the dust composition might provide a better estimate of the surface area of source lithologies than of their crustal volumes. Another possibility is that injection of magmas into permafrost (Gooding and Keil, 1978) could produce palagonites that would be excavated later by large impacts. Dust derived from such subsurface deposits might constitute volumetrically significant parts of the upper crust. Alternatively, the dust source regions might not be global in extent, but may be confined to "active" regions that are particularly susceptible to erosion.

In any case, the data clearly argue for pervasive source rocks with basaltic compositions, having chemical properties (e.g., high Fe/Mg, low $Al_2O_3$) like those of basaltic shergottites (McSween, 1994). Crystallization ages determined from radiogenic isotopes indicate that eruptions or near-surface intrusions of basaltic shergottites probably occurred during the last 330 m.yr. (McSween, 1994), although similar magmas may have erupted earlier. If the composition of the global dust evolves with time, as new source rocks are added to the planet's surface by volcanism or exposed by large impacts or other processes, then the present dust composition might reflect the dominance of relatively young basalts. Dust derived from older geologic units having different compositions may form stratigraphically lower deposits, perhaps producing the layering phenomena that appear to be common in near-surface units on Mars (Malin and Edgett, 1999). Felsic igneous source rocks, such as the Pathfinder andesites, should be readily identifiable as a dust component if present, but apparently are absent, possibly because they represent relatively small localized occurrences. Although we cannot rule out the presence of some carbonates in the dust, it also seems likely that their surface abundances must be minor. However, evaporites in the form of sulfate and chloride salts must be common (Clark and Van Hart, 1981). Warren (1998) has proposed a mechanism to account for the separation of evaporitic carbonates and sulfate/chloride salts in the regolith.

## 5. CONCLUSIONS

Chemical compositions of soils at the Viking 1 and Mars Pathfinder landing sites show different effects of mixing. Viking soils contain varying amounts of sulfate and chloride salts, probably as cements. In contrast, compositional variations in Pathfinder soils arise from admixture of small fragments of the local andesitic rock, possibly with smaller amounts of other lithologies. The two mixing trends intersect approximately at a common composition, which probably represents a globally homogeneous dust.

The composition of the dust lies along weathering trends for terrestrial basaltic rocks. Thus, basalt rather than andesite or other felsic lithologies appears to be the most plausible source rock for the dust. Limited chemical changes during alteration may suggest that most soluble components were not transported away but remained in the soil when an altering hydrous fluid evaporated. An assessment of chemical trends resulting from palagonitization, hydrothermal alteration, and acid fog reactions suggests that palagonite may be the best analogy for Martian soils.

Local processes have also influenced the compositions of soils. Besides admixture of rock fragments and cements to dust deposits, aeolian fractionation of denser Fe–Ti oxides appears to have occurred, as judged from changes in $Fe_2O_3/TiO_2$ ratios in soils.

The composition of global dust may either reflect the surface abundance of source rocks or their volumes within the upper crust. The dust composition implies that basalts, with similar chemical characteristics to basaltic shergottites, and evaporitic salts (sulfates and chlorides) dominate the planet's surface geology. If the global dust composition evolves with time, the present dust might be derived from source rocks dominated by relatively young volcanic materials.

*Acknowledgments*—We have benefited from discussions with Ben Clark, Rodey Batiza, Scott McLennan, Jeff Taylor, and Dan Britt, and from thoughtful anonymous reviews. This is Hawaii Institute of Geophysics and Planetology publication #1081 and School of Ocean and Earth Science and Technology publication #4895. This work was supported in part by NASA/JPL Mars Mission Data Analysis grant 1204905 to H. Y. M., and NASA Cosmochemistry grant NAG 5-4212 to K. K.

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