



## On the *in situ* aqueous alteration of soils on Mars

Ronald Amundson<sup>a,\*</sup>, Stephanie Ewing<sup>a</sup>, William Dietrich<sup>b</sup>, Brad Sutter<sup>c</sup>,  
Justine Owen<sup>a</sup>, Oliver Chadwick<sup>d</sup>, Kunihiro Nishiizumi<sup>e</sup>, Michelle Walvoord<sup>f</sup>,  
Christopher McKay<sup>g</sup>

<sup>a</sup> Division of Ecosystem Sciences, 137 Mulford Hall, University of California, Berkeley, CA 94720, USA

<sup>b</sup> Department of Earth and Planetary Science, McCone Hall, University of California, Berkeley, CA 94720, USA

<sup>c</sup> Jacobs NASA/Johnson Space Center, MC JE23, 2224 Bay Area Blvd., Houston, TX 77058, USA

<sup>d</sup> Department of Geography, University of California, Santa Barbara, CA 93106, USA

<sup>e</sup> Space Sciences Laboratory, 7 Gauss Way, University of California, Berkeley, CA 94720, USA

<sup>f</sup> U.S. Geological Survey, Denver Federal Center, Box 25046, MS-413, Lakewood, CO 80225-0046, USA

<sup>g</sup> NASA-Ames Research Center, Building 245, Room 212, MS 245-3, Moffett Field, CA 94035, USA

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### Abstract

Early (>3 Gy) wetter climate conditions on Mars have been proposed, and it is thus likely that pedogenic processes have occurred there at some point in the past. Soil and rock chemistry of the Martian landing sites were evaluated to test the hypothesis that *in situ* aqueous alteration and downward movement of solutes have been among the processes that have transformed these portions of the Mars regolith. A geochemical mass balance shows that Martian soils at three landing sites have lost significant quantities of major rock-forming elements and have gained elements that are likely present as soluble ions. The loss of elements is interpreted to have occurred during an earlier stage(s) of weathering that may have been accompanied by the downward transport of weathering products, and the salts are interpreted to be emplaced later in a drier Mars history. Chemical differences exist among the sites, indicating regional differences in soil composition. Shallow soil profile excavations at Gusev crater are consistent with late stage downward migration of salts, implying the presence of small amounts of liquid water even in relatively recent Martian history. While the mechanisms for chemical weathering and salt additions on Mars remain unclear, the soil chemistry appears to record a decline in leaching efficiency. A deep sedimentary exposure at Endurance crater contains complex depth profiles of SO<sub>4</sub>, Cl, and Br, trends generally consistent with downward aqueous transport accompanied by drying. While no model for the origin of Martian soils can be fully constrained with the currently available data, a pedogenic origin is consistent with observed Martian geology and geochemistry, and provides a testable hypothesis that can be evaluated with present and future data from the Mars surface.

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### 1. INTRODUCTION

Growing evidence indicates that Mars possesses a complex climatic history, and that the waxing and waning of surficial water availability is etched in the planet's physical and chemical features. Remotely sensed data reveal the

presence of significant smectite deposits on portions of ancient (Noachian) Martian surfaces (Poulet et al., 2005; Chevrier et al., 2007). The formation of smectite requires significant aqueous alteration of parent rock, with at least a partial physical removal of various reaction products (Allen and Hajek, 1989), a process accepted as a plausible mechanism for the origin of Martian smectites (Chevrier et al., 2007). In contrast with the ancient smectite-rich landscapes, SO<sub>4</sub> accumulations are widespread on younger (Hesperian and Amazonian) Martian surfaces (Arvidson

\* Corresponding author. Fax: +1 510 643 5098.  
E-mail address: [earthy@nature.berkeley.edu](mailto:earthy@nature.berkeley.edu) (R. Amundson).

et al., 2005; Bibring et al., 2005). The accumulation and retention of highly soluble sulfates (and chlorides) on terrestrial surfaces occurs only under arid conditions (Phillips, 1994). These seemingly contradictory chemical signatures from remotely sensed data have been reconciled as reflecting profound aridification over time (Bibring et al., 2006).

While this first-order view of Mars climate history is consistent with the remotely sensed mineralogical data, there is a growing body of geomorphic evidence for aqueous physical alteration of the Martian surface late in Martian history (Baker, 2001), and evidence of current activity in some of the young gullies on Mars suggests that liquid water may be actively influencing contemporary processes (Malin et al., 2006). Were any of these later episodes sufficiently widespread and long-lived to cause *in situ* chemical alteration of the Martian soils as suggested by Baker (2001), and if so, can any details of these events be deciphered? Five missions to the Mars surface provide abundant information to begin to test this question, and to determine if a complex hydrological history is recorded in post-Noachian landscapes. Here we reexamine published soil data from several of these missions using a mass balance model common to Earth surface geochemical studies (e.g. Brimhall et al., 1992). These Mars results are compared to ancient Earth soils formed in ~0 to 4 m of mean annual precipitation, and show that widely spaced Martian soils exhibit evidence of complex weathering histories, consistent with oscillations (and a general decline) in the availability of liquid water from atmospheric sources over geological time.

## 2. GEOMORPHOLOGY AND CHEMISTRY OF MARS LANDING SITES

The locations of the Mars lander sites are shown in Fig. 1. Data from four missions (Viking 1 and 2, Pathfinder,

Spirit) reveal that soils are a loose silicate matrix enriched with variable quantities of S (as  $\text{SO}_4$ ), Cl, and Br (Clark et al., 1982; Wänke et al., 2001; Gellert et al., 2004; Rieder et al., 2004). Comparisons of the elemental abundances at these widely separated sites have revealed many similarities, leading to the suggestion of a global soil unit reflecting a mixture between relatively unaltered basalts and dust/aerosols (Clark et al., 1982; Yen et al., 2005; Nelson et al., 2005). Additionally, the consistently high Ni content of Mars soils is attributed to meteoritic inputs that have been estimated to make up about 3% of the total soil (Yen et al., 2006).

Several observations are inconsistent with a “global” soil unit on Mars. First, in terms of global variability, there are spatial variations in remotely sensed smectite (Bibring et al., 2006), sulfate (Arvidson et al., 2005), and an array of chemical parameters, including K/Th ratios, which may indicate at least subtle regional differences in weathering histories (Taylor et al., 2006). Second, geomorphological and sedimentological analyses of individual landing sites suggest a local origin for the bulk of the soil volume in at least several locations. The Viking 1 landing site is located on Chryse Planitia at the end of outflow channels from the southern highlands. The local geology is interpreted to be basaltic bedrock, altered by chemical, physical and fluvial processes (Binder et al., 1977), and the surface consists of boulders and sediment derived from possible impact events and wind (Binder et al., 1977). Viking 2, located in the northern Utopia Planitia, landed on a plain of fine-grained sediment overlain by a bouldery layer of possible ejecta (Mutch et al., 1977). This region also contains extensive polygonal cracking that may have been formed by ice-wedging. The surficial geology at the Pathfinder landing site is a catastrophic fluvial deposit, possibly overprinted with impact ejecta that has experienced minor erosion (McSween et al., 1999) and is in an outflow region similar to that of Viking 1. The surficial geology at the Spirit landing site

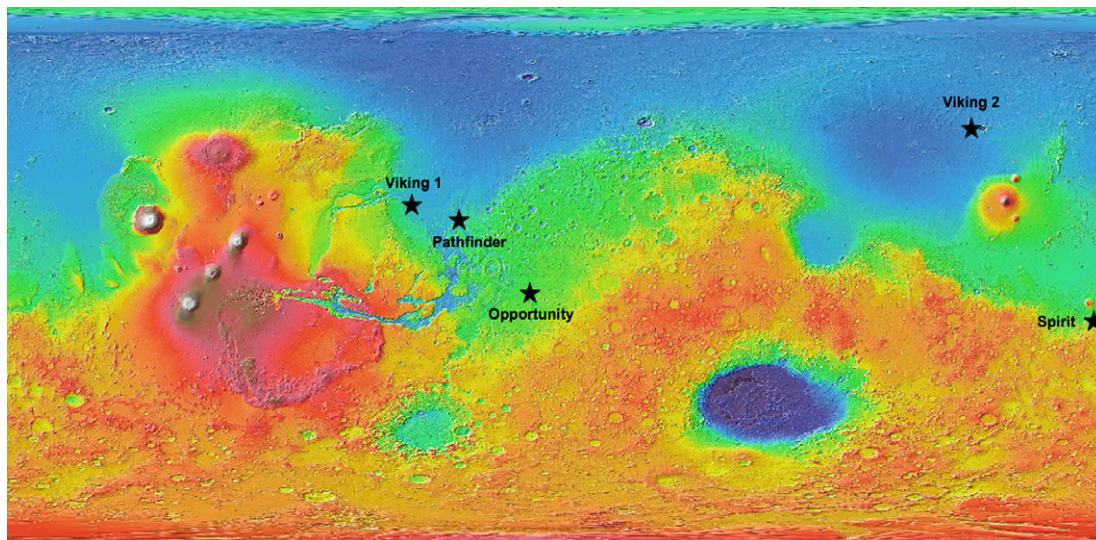


Fig. 1. A topographic map of the Mars surface, centered at 0° latitude and longitude, showing the approximate locations of the five Mars landers. Data and images from the Arizona State University Odyssey web page, and Google Mars.

(Gusev crater) is interpreted as being “an impact-generated regolith that likely formed in basalt lava flows” with a thin, possibly micron thick, surface dust layer (Golombek et al., 2006). Additionally, the general features at Gusev crater suggest a slight net deflation or exhumation of rocks, rather than a net deposition of dust, over geologic time (Golombek et al., 2006). While there is indeed a surficial layer of dust at these sites, the geomorphic evidence (and published interpretations) supports the contention that a significant portion of the soil may be locally derived.

In contrast to the first four landers on Mars, the Mars Exploration Rovers (MER) Opportunity at Meridiani Planum landed on a broad plain comprised of a thick sequence of sedimentary rock interpreted to include both eolian and subaqueous depositional facies (Squyres and Knoll, 2005; Squyres et al., 2006). This sedimentary sequence is overlain by a mobile silicate and hematite dominated layer that is sculpted by wind. A detailed analysis of the geochemistry of the sediment suggests significant pre-weathering of the basalt-derived silicate components (Squyres et al., 2006) with an accumulation of large quantities of S (as various forms of sulfate) during the depositional events. A thick exposure (~5 m) of these sediments within the Endurance crater potentially provides data on the first complete “soil” or sediment profile on Mars, and in that vein, depth trends of S in this exposure have been interpreted to reflect the upward movement of salts due to the presence of evaporating ground water (Squyres et al., 2006).

### 3. MODEL OF MARTIAN PEDOGENESIS

#### 3.1. Present concepts

Soils on Mars are defined by the Mars Rover Exploration (MER) team as “denot(ing) any loose, unconsolidated materials that can be distinguished from rocks, bedrock, or strongly cohesive sediments. No implication of the presence or absence of organic materials or living matter is intended” (Squyres et al., 2004; Gellert et al., 2004). The formation of Mars soils has been the focus of numerous studies and approaches, but the interpretations have commonly concluded or assumed that little or no *in situ* weathering (soil development) has occurred and that the soil chemistry can best be explained by a physical or chemical mixing of aerosols, dust, meteoritic components, and eolian material with basaltic sands, gravels, and boulders in a “closed” physical system (additions, but no losses, of mass) (McSween et al., 1999; McLennan, 2000; Nelson et al., 2005; Yen et al., 2006). Aqueous alteration, if present, is assumed to have occurred at extremely low water/rock ratios with a general retention of weathering products. Because the soil chemistry at some sites is interpreted by some to reflect evidence of chemical alteration and element depletion (Nelson et al., 2005), it has been assumed that a pre-weathered eolian material, altered earlier in some unknown geological setting, has been added to the soil (Nelson et al., 2005). Some have argued that no Earth-based analogue can explain Martian soil chemistry (e.g. McSween et al., 1999; McLennan et al., 2006), though presently, no true consensus exists as to the origin of these soils (Banin, 2005).

#### 3.2. Proposed model of pedogenesis

In this paper, we suggest that soils and soil-forming processes on Mars may be (or may have been) akin to soil formation on Earth, and that this process may provide insights into at least some of the chemical properties of the Martian regolith. This distinction is far more than a semantic issue, for its acceptance allows avenues of investigation and interpretation not possible under the more restrictive concepts presently being considered for Mars. Soils, in a scientific sense, are defined in relation to theory. Soils are physical systems that exchange matter and energy with their surroundings, and the rates and direction of the exchanges are controlled by “state factors” that commonly include parent material, topography, climate, biota, and time (Jenny, 1941; Soil Science Society of America, 1997). Most importantly, while biota is one of a number of variables that control rates of soil processes, its presence is not required. The absence of biota simply causes the biotic term to reduce to 0.

The issue of whether soils “exist” without life is not entirely restricted to Mars, and is thus important in this paper. The hyperarid Atacama Desert of northern Chile is likely the most abiotic environment possible on Earth. But the region and its exceedingly mature *soils* (Ewing et al., 2006) are by no means uninterpretable using pedological models. The region lies at the dry end of a nearly continuous decline in rainfall with latitude (Houston and Hartley, 2003), and the chemical properties of the soils are understandable, though sometimes unanticipated, from pedological and geochemical models (Ewing et al., 2006, 2007). The same argument is relevant to the Dry Valleys of Antarctica (Mahaney et al., 2001), which contain soils formed at the cold end of the Earth’s temperature continuum. With respect to these later two regions, the USDA Soil Taxonomy, the internationally recognized system of soil classification, defines soil as “horizons, or layers, that are distinguishable from the initial material as a result of additions, losses, transfers, and transformations of energy and matter. . . (which) is to include soils in areas of Antarctica where pedogenesis occurs but where the climate is too harsh to support the higher plant forms” (Soil Survey Staff, 1999). This definition thereby fully includes generally abiotic soils within a standard pedological framework. Thus, it is a small conceptual step to extend the scientific concept of soils, and pedogenesis (the combined suite of geophysical processes that form soils), from these regions to the Martian surface. It is an equally small physical step because Mars is also composed of silicate rock with all the weathering products found in these extremes of the Earth’s climate spectrum.

Chemical changes during pedogenesis are due to mass exchanges between soils and their surroundings. These fluxes can occur in any direction but the most common avenue on Earth is the addition of water and dust/solutes from the atmosphere, *in situ* chemical reactions within the soil system, and net aqueous transport downward into the lithosphere. Removal of weathering products is determined by rainfall amount and the solubility of the dissolved species (Amundson, 2004; Ewing et al., 2006). The rates of these processes can also vary enormously over time in response

to climatic change, causing unique chemical signatures partially reflecting each weathering stage. The resulting integrated chemical signatures of soils thus can also record evidence of environmental changes, which is important because Martian landscapes have experienced significant climatic changes (and water availability) over billions of years. The fact that Mars geomorphic surfaces are orders of magnitude older ( $10^9$  vs.  $10^6$  y) than the oldest surfaces found on the tectonically active Earth only adds to the need to consider Martian soil formation from multiple geochemical perspectives. To our knowledge, pedogenesis has not been seriously considered as a process responsible for Mars soil chemistry.

Given the early climate history of Mars (and presence of secondary silicates), it is almost certain that pedogenic processes have occurred. Thus, we hypothesize that on certain landscapes, existing Martian soils reflect pedogenic alteration relative to their geological substrates and that the source of solutes (and water) was/is of atmospheric origin. This hypothesis results in the following (potentially) testable predictions:

1. Aqueous alteration of soil from atmospheric sources of water/solutes results in chemical weathering of silicates and the subsequent transport of weathering products to lower depths, with associated chemical depletions of the remaining surficial soil matrix.
2. Pedogenesis during arid or hyperarid periods (but with some liquid water) involves little chemical weathering of the soil matrix but involves an accumulation and a vertical partitioning of atmospheric solutes, based on their solubility and molecular diffusivities, to greater depths (Walvoord et al., 2002a,b, 2003; Ewing et al., 2006). On Mars, a caveat to this scenario is that acidic deposition may have accompanied small aqueous inputs, causing chemical weathering to occur along with incomplete leaching of acidic anions.

First, is there evidence that water and solutes have an atmospheric origin on Mars? While the hydrological history remains a highly debated subject (Baker, 2001), there is ample evidence for both ancient and recent hydrological activity on the planet (Baker, 2005). It is also widely accepted that solutes in the soils may have been derived from atmospheric sources. Clark and Van Hart (1981) discuss the possibility of volcanic origins for the  $\text{SO}_3$  and Cl found ubiquitously in Mars soils, presumably originally in the form of sulfuric and hydrochloric acid. These acids, combined with even limited amounts of liquid water, could cause measurable weathering and chemical fractionation. An atmospheric origin of at least a fraction of the Mars soil sulfates is convincingly demonstrated by triple S and O isotope analysis of sulfate in Martian meteorites, which reveals the formation of this sulfate with atmospheric oxidants (Farquhar and Thiemens, 2000; Farquhar et al., 2000). Thus, the presence of this atmospherically derived  $\text{SO}_4$  in Martian meteorites ejected from near-surface Mars settings is certainly highly suggestive, by itself, of downward aqueous transport of atmospherically produced anions in some locations.

### 3.3. Detection of chemical gains or losses in soils

If soils have been chemically weathered and leached by water, they will exhibit elemental changes or fractionation (e.g. Chevrier et al., 2007) relative to their starting chemistry. How can these possible changes be detected from available Mars soil and rock chemistry? Here, we show how elemental gains or losses in Mars soils can be calculated with a mass balance model that uses an immobile index element (Brimhall et al., 1992). The gain or loss of an element relative to its amount in the parent material is described by the following expression:

$$\frac{V_p \rho_p C_{j,p}}{100} + m_{j,\text{flux}} = \frac{V_w \rho_w C_{j,s}}{100} \quad (1)$$

where  $V$  = volume of original parent material (p) and soil (s), respectively;  $\rho$  = bulk density of parent material and soil;  $C$  = concentration of mobile element  $j$  in parent material or soil, and  $m_{j,\text{flux}}$  = mass gain or loss of element  $j$  during soil formation. Strain ( $\epsilon$ ), the volumetric change of soil during weathering, is determined by:

$$\epsilon_{i,s} = \frac{\Delta V}{V_p} = \left( \frac{\rho_p C_{i,p}}{\rho_s C_{i,s}} - 1 \right) \quad (2)$$

where  $C_i$  = concentration of an immobile element  $i$ . Through rearrangement and substitution, the fractional gains or losses of an element  $j$  relative to the parent material, defined as the tau value ( $\tau$ ), can be calculated by the following relationship:

$$\tau = \frac{R_s}{R_p} - 1 \quad (3)$$

where  $R_s = C_{j,s}/C_{i,s}$  and  $R_p = C_{j,p}/C_{i,p}$ . Positive tau values represent elemental gains, negative values represent loss. Tau values, if multiplied by 100, equal % changes relative to the parent material. Elements commonly chosen as index elements include Ti or Zr, though elements from nearby positions on the periodic table, such as Hf or Nb, have also been used. Immobile element-normalized gains/losses eliminate the ambiguity of direct soil to bedrock ratios. For example, un-normalized soil/parent elemental ratios on Earth may suggest apparent gains of Si due to the residual accumulation of quartz during weathering, even though large net mass losses of Si have occurred. Similar ambiguities can also arise in the interpretation of un-normalized Mars soil data.

The use of the mass balance model requires certain geochemical conditions in order for the interpretations to be quantitative: (1) the soils must be physically derived from the reference rock or sediment, and (2) the index element must be immobile, or the least mobile element considered. These requirements with respect to our analysis of Martian soil geochemistry are addressed below.

As discussed above, the bulk of the soil mass at Spirit and Pathfinder landing sites appears to be physically mixed with rocks deposited at the time the surfaces formed (no rock was analyzed by the Viking landers). At the Endurance crater (Opportunity), we use both Gusev basalt (as done also by Squyres et al., 2006) and the base of the deep exposure as the reference materials. Dust and aerosols com-

prise a second important “parent material” to soils on both Earth and Mars. Dust and aerosols add mass to soils, but on Earth dust is commonly depleted in Ti and Zr relative to soil (Reheis, 1990) and therefore causes a dilution of Ti or Zr and an underestimation of chemical losses rather than an overestimation.

The dust chemistry on Mars, however, is poorly known. Some of the studies on potential dust chemistry include: (1) direct Alpha Proton X-ray Spectrometry (APXS) analyses of dust on the magnet aluminum surfaces on the Spirit and Opportunity Rovers which show Ti concentrations roughly similar to local soils (Goetz et al., 2005), (2) Yen et al. (2005) report that the bright dust at the Spirit location is more enriched in Ti (0.8–1.0%) than dark soil, (3) deflation and winnowing have been speculated to physically concentrate Ti in soil (McLennan, 2000), but this implies the accumulation of Ti-depleted dust or sediment somewhere on the planet, and finally, (4) Morris et al. (2006) recently assumed that the chemistry of dust is the same as undisturbed soil at Gusev. Here, we follow the interpretation from Miniature Thermal Emission Spectrometer (MINITES) data which suggests that Spirit rock surfaces have a coating comprised of ~50% dust (Christiansen et al., 2004). A two component mixing model (unbrushed vs. brushed surface or RATED surfaces (Adirondak)) analysis shows that Spirit dust has a TiO<sub>2</sub> content of 0.7–0.8% (Table 1). These values are used later, along with all proposed soil component endmembers, to determine if soils are weathered relative to all proposed source materials.

Finally, Martian soils almost always contain more Ni than pristine basalt, and this has been interpreted to be due to the addition of up to several wt % of meteoritic components to the soils (Yen et al., 2006). However, Ni is also commonly concentrated in soils due to chemical weathering on Earth (Railsback, 2003), and many Ni ore bodies on Earth are formed via chemical weathering and residual

accumulations with Fe and silicates (e.g. Brimhall and Dietrich, 1987). As we will suggest, some of the apparent extraneous Ni in Martian soils can therefore alternatively be explained by a residual concentration during weathering. However, assuming a meteoritic input of mass into Martian soils, it is important to note that chondritic meteorites (the assumed source of extraneous Ni) are lower in TiO<sub>2</sub> than Martian basalts (Fig. 4 in Yen et al., 2006), and the additions of meteoritic mass would therefore cause a dilution of the soil TiO<sub>2</sub> concentration, yielding (as discussed below) minimum estimates of the loss of more soluble constituents.

If dust is an important chemical component of Mars soils, it is important to have definitive evidence of its incorporation. Thus, the known physical effects of dust influx into soils must be used to determine if the observations of Mars soil exposures are consistent with predicted features of this process. On Earth, the incorporation of dust into the surface of arid and hyperarid soils results in unique and distinctive textural profiles (McFadden et al., 1988). As dust (silt and fine sand are particularly important on Earth) enters a gravelly matrix, the downward movement of the dust by physical processes lofts gravel upward creating, over long periods of time, an interlocking gravelly desert pavement (derived from uplifted gravels) that immediately overlies a relatively gravel-free, dust-rich, matrix (McFadden et al., 1988). Below this layer, gravel increases and dust decreases, with depth. This is observed to occur both in the nearly abiotic Atacama (Ewing et al., 2006) and equally abiotic Antarctic Deserts (Ugolini and Anderson, 1973).

While a gravelly surface is observable at several Mars locations, certainly not all sites have interlocking pavements, nor do the few shallow depth profiles observed at Gusev crater show that gravels have been completely expelled by infiltrating dust (Wang et al., 2006) to the degree that might be expected for this process on Earth. The Vik-

Table 1

Calculated dust chemical composition at Gusev crater, based on a two component mixing model, and Gusev disturbed soil (samples 43, 74, 122, 135, 158, Gellert et al., 2006) tau values relative to the dust values and basalt (average RATED rock data (Humphrey, Adirondak, and Mazatal) from Gellert et al., 2006)

Element or oxide % (except Ni, Zn, Br = ppm)	Calculated dust		Tau values (disturbed soil at Gusev relative to indicated reference)		
	Dust (Brushed rock surface endmember)	Dust (RATED rock surface endmember)	Soil vs. dust (brush)	Soil vs. dust (RATED)	Soil vs. basalt
Na <sub>2</sub> O	2.70	2.87	-0.06	-0.40	-0.22
MgO	8.64	7.27	-0.17	-0.17	-0.38
Al <sub>2</sub> O <sub>3</sub>	10.23	9.94	-0.14	-0.04	-0.29
SiO <sub>2</sub>	44.97	44.48	-0.13	-0.04	-0.27
P <sub>2</sub> O <sub>5</sub>	0.78	0.97	-0.16	-0.26	-0.15
SO <sub>3</sub>	5.56	8.09	-0.29	-0.47	0.30
Cl	0.65	1.07	-0.28	-0.52	-0.01
K <sub>2</sub> O	0.26	0.40	0.40	-0.02	0.69
CaO	6.82	6.38	-0.22	-0.09	-0.41
TiO <sub>2</sub>	0.71	0.78	0.00	0.00	0.00
Cr <sub>2</sub> O <sub>3</sub>	0.54	0.46	-0.39	-0.22	-0.50
MnO	0.38	0.34	-0.28	-0.11	-0.41
FeO	17.73	16.95	-0.25	-0.14	-0.39
Ni	318.67	410.33	0.17	-0.01	0.39
Zn	351.00	447.00	-0.43	-0.52	0.08
Br	16.00	<0.00	1.03	-7.61	-0.56

ing 2 landing site, at Utopia Planitia, contains evidence of polygonal cracking suggestive of freeze–thaw processes on Earth. If true, then these soils may indeed have undergone both extensive physical mixing and incorporation of dust, at some point in the past (Mutch et al., 1977). In terms of surficial dust incorporation, while it may be argued that this ubiquitous Earth process is not applicable to Mars (an argument that, without evidence, remains to be proven), an alternative set of processes and mechanisms still must be developed to explain how dust can infiltrate into the surficial materials of Mars and yet leave no peculiar physical evidence as a result. Even without these considerations, geological observations have been used to interpret that the net impact of dust on total soil mass may be modest or minor at Gusev crater (Golombek et al., 2006) as well as at the Pathfinder site (Ward et al., 1999), and that net deflation, rather than inflation, is the main land surface change over time.

The second geochemical requirement is that the index element must be immobile or, at a minimum, the least mobile element considered. Of the suite of elements measured by Mars landers, only Ti is commonly used as an immobile element in terrestrial geochemical studies. Titanium typically occurs in ilmenite in basalt where Ti has been shown to remain immobile between pH 1 and 7 (White et al., 1994) (pH <1 was not examined). Ilmenite has been detected in Gusev crater but not at Meridiani (Morris et al., 2006). Titanium release at pHs <1 have been demonstrated for synthetic basalts where the Ti source was titanomagnetite (Tosca et al., 2004; Hurowitz et al., 2005). Extreme terrestrial acid environments, (e.g., next to sulfuric-acid volcanic vents), dissolve titanomagnetite and ilmenite causing Ti release. However, Ti tends to re-precipitate as anatase or rutile so that the overall result is Ti immobility even under the most acid conditions (Milnes and Fitzpatrick, 1989; Li et al., 2007).

The detection of jarosite at Meridiani and goethite in the Columbia Hills (Morris et al., 2006) indicates that pHs in Mars soils tend to be pH >1; therefore, Ti may not be released from Ti phases in Mars materials. Special case soils like Paso Robles in the Columbia Hills have a Fe-mineralogy suggestive of pH <1 (Ming et al., 2006) which could cause Ti release. As discussed above, any Ti released should not travel far due to anatase or rutile precipitation. These results suggest to first-order approximation that Ti is chemically immobile in Mars soils. Even if Ti is partially soluble, or diluted by meteorites, then tau values represent *minimum* weathering losses, and they are thus conservative, while apparent mass gains are over-estimates.

### 3.4. Water and solute transport in unsaturated soils and sediments

Pedogenesis is driven by a downward movement of water. How can the direction of water and solute movement on planetary surfaces be determined? Solute profiles are one indicator available to determine the direction and rate of water flow in soils and sediments in dry environments. Unsaturated water (liquid and vapor) flow dominates Earth

soils in semiarid to hyperarid climates. Because of the low water contents and small water fluxes, vadose zones in dry climates seldom achieve a hydrologic steady state as they slowly equilibrate to arid surface boundary conditions (Walvoord et al., 2002a). Precipitation events enable water and solutes to percolate into the soil. On Earth, the near-surface environment (root zone) undergoes large temporal changes in water content (and matric potentials), but supports a gravity-driven downward water flux when soils are sufficiently moist. Desert plants are very efficient at water uptake and maintain very low (negative) matric potentials at the base of their root zone which may persist for thousands of years unaffected by precipitation events (Walvoord et al., 2002a,b) (On Mars, which lacks plants, any surficial water addition should be thus able to penetrate to greater depths than on Earth). Under these conditions, an upward matric potential gradient exceeds the downward gravitational gradient below the root zone and drives a very small upward flux of water, mostly as water vapor, from the deeper vadose zone. This reversal in water flux in the shallow vadose zone, and the absence of a downward water (and solute) flux below the root zone, facilitates the continued accumulation of solutes at the root zone base. Below the root zone, solutes, driven by concentration diffusion, move downward very slowly against an even smaller net upward flux of liquid water, thus producing a net downward migration of salts. Deeper in the vadose zone, gravitational gradients may again dominate as residual water and solutes (from a past wetter climate) drain towards the water table. In widely spaced arid and semiarid locations on Earth, observed vadose zone Cl and NO<sub>3</sub> profiles show distinctive “bulges” below the rooting zone (Phillips, 1994; Walvoord et al., 2003). In the most extreme environments, with essentially a no-flux water and solute boundary at the base of the soil due to extreme hyperaridity, these solute accumulations occur in the upper few meters (Ewing et al., 2006; Fig. 2c). In these situations, a very negative surface matric potential creates an upward driving force for water. However, under these extremely dry conditions, most of this water flux is in the vapor phase, leaving unaffected the solute profiles created by rare precipitation events.

Water vapor transport in arid soils is an important means of redistributing water. This water flux excludes solutes. In deep vadose zones, water vapor fluxes are driven by geothermal and matric potential gradients (both upward), whereas in near-surface environments, the direction of vapor transport varies as a result of diurnal and seasonal temperature oscillations, and by fluctuations in wetting and drying. Vapor transport can, in certain cases, result in condensation and subsequent accumulation of liquid water near the soil surface (Jury and Bellantuoni, 1976). As deep vadose zones in dry climates approach hydrologic equilibrium (which theoretically may be on the order of 10<sup>4</sup>–10<sup>5</sup> yr), geothermally driven upward vapor flow from the water table condenses nearer the surface (lower temperatures) due to decreased vapor pressure gradients and decreased thermal diffusivities, and the resulting condensation returns a very small downward flux of liquid water as the vapor cools and condenses (Walvoord et al., 2002a).

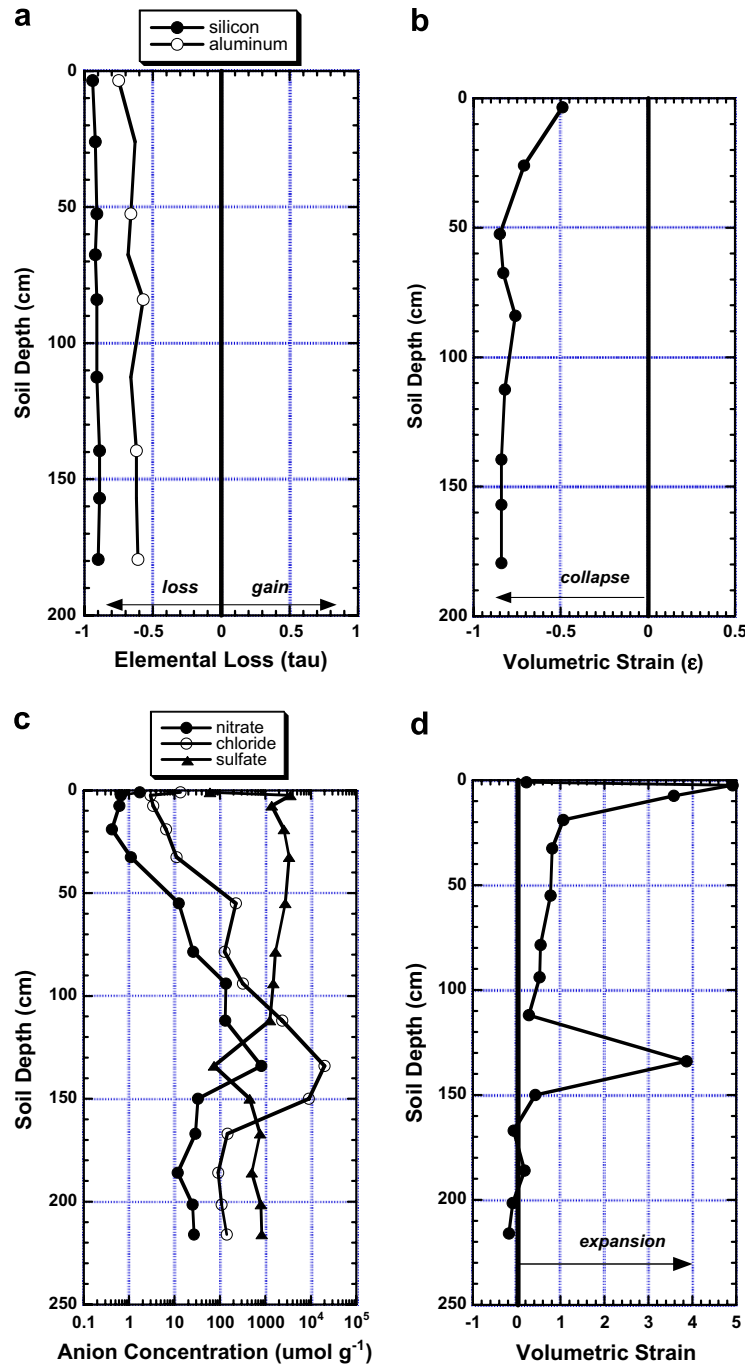


Fig. 2. (a) Fractional losses ( $\tau$  values) of Si and Al and (b) volumetric collapse for 4100 Ma soils under 4100 mm annual precipitation in Hawaii (Chadwick and Goldstein, 2004). (c) Concentrations of water soluble nitrate, chloride and sulfate and (d) volumetric expansion for a 2.1 Myr soil in the hyperarid Atacama Desert, Chile (Ewing et al., 2006).

Despite the physical complexity of unsaturated water and solute transport, current physically based models have been developed that reproduce measured matric potential and chloride profiles in thick vadose zones by specifying important boundary conditions and physical parameters and incorporating vapor transport (Walvoord et al., 2002a,b). The hydrological model presented above is relevant to temperate hydrological conditions on Earth. On Mars, gravity is about 1/3 that of Earth. Also, in cold

regions, water and solute flow respond to additional factors. Differential freezing point depressions of saturated solutions of salts have long been proposed to cause salt mobility (Clark and Van Hart, 1981). The direction of salt movement in polar soils can be both upward and downward due to seasonal temperature gradients (Ugolini and Anderson, 1973). However, the presence of  $\text{SO}_4$  (Boa et al., 2000) and  $\text{NO}_3$  (Michalski et al., 2005) of atmospheric origin at depths of up to 2 m in soils of the

Dry Valley, Antarctica, clearly illustrates that atmospherically derived salts migrate in a net downward direction in Earth environments that approach the temperature conditions of Mars.

#### 4. DATA USED IN ANALYSIS

In order to demonstrate the utility of our pedogenic model, and to reveal the chemical fingerprint of precipitation on soil chemistry, a suite of Earth soils are examined where soil-forming factors other than mean annual precipitation (MAP) are relatively constant (Table 2). The sites chosen represent the oldest ( $\sim 10^6$  y) soils found in their respective climates, and thus likely reflect the maximum degree of alteration found in those regions on Earth. The even greater antiquity of much of the Mars surface ( $10^9$  y) should only enhance the imprint of chemical weathering processes and their variation over time if these processes have been active. Earth and Mars are compared by reporting the mean chemical composition of the upper 20 cm of Earth soils (Fig. 3), a depth interval approximately equivalent to the maximum depths excavated by the Mars rovers ( $\sim 10$  cm) (e.g. Wang et al., 2006) or Viking landers ( $\sim 20$  cm) (Clark et al., 1982). Additionally, for the extreme endmembers of the climate spectrum, we examine depth profiles of soil chemistry.

The chemical composition of soils and soil-free rock for the Pathfinder mission is from Taylor et al., 2006. Data for soils and rocks at Gusev crater that have been analyzed by Spirit are from Gellert et al. (2006) and Wang et al. (2006), which are similar except that Wang et al. (2006) report Zn and Ni as oxide percents, and report both FeO and Fe<sub>2</sub>O<sub>3</sub> abundances for shallow trenches at Gusev crater. The chemical composition of the vertical exposure at Endurance crater, measured by Opportunity, is from data available on the NASA web page: <http://pds-geosciences.wustl.edu/>.

The accuracy of the alpha particle X-ray spectrometer (APXS) aboard the Spirit and Opportunity Rovers is dependent on analysis conditions and duration, sample matrices, etc. (Gellert et al., 2006). The standard deviation of analytical results, based on about 60 samples of widely varying composition, were reported in Gellert et al. (2004): Na (8.5%), Mg (17.3%), Al (7.2%), Si (3.5%), P (16.8%), S (14.1%), Cl (12.5%), K (14.4%), Ca (7.7%), Ti (20.4%), Cr (20%), Mn (7.9%), Fe (5.8%), Ni (10.1%), Zn (11.7%), and Br (10%). Analytical precision (repeated analyses on similar materials) is considered high, and thus small chemical differences between similar samples are reported as being significant (Gellert et al., 2004).

#### 5. RESULTS AND DISCUSSION

##### 5.1. Earth soils

We begin by demonstrating how soil chemistry on Earth varies with changes in MAP. Above 300–500 mm MAP on Earth, the upper 20 cm of soils experience losses of every major element, with  $\tau$  values of nearly  $-1$  (100% loss) in the most humid regions (Fig. 3). Of particular importance to Mars, we note that the basalt soils of Hawaii have lost large fractions of their total Fe and Al, as revealed through normalization to Zr. Terrestrial weathering of basalts has been asserted to conserve these elements, and it has been assumed that weathering on Mars that causes losses of Fe and Al thus has no terrestrial analogue (Hurowitz et al., 2006). While Al and Fe may indeed accumulate as weathering residues, this is because they are only less mobile than other elements. Only in the most hyperarid regions (Atacama Desert,  $<20$  mm rain yr<sup>-1</sup>) are Si and other major rock-forming elements retained or gained, along with large accumulations of sulfates (as gypsum and anhydrite) and other soluble salts from the deposition of dust and aerosols (Rech

Table 2  
Summary of the location and site characteristics of Earth soils used in this paper

Site	Lat/long	MAP (mm)	MAT (°C)	Parent material	Age (Ma)	Soil classification	References
Yungay, Chile	24°06.102'S, 70°01.097'W	~1	~16	Granitic alluvium, fan	2.12 ± 0.05	Thermic petrogypsic haplosalid	Ewing et al. (2006)
Altamira, Chile	25°45.587'S, 70°11.797'W	~12	~16	Granitic alluvium, terrace	3.95 ± 0.14	Thermic typic petrogypsid	Ewing et al. (2006)
Copiapo, Chile	27°01.279'S, 70°17.672'W	~20	~15	Granitic alluvium, fan	2.31 ± 0.41	Thermic typic petrocalcic	Ewing et al. (2006)
Las Cruces, NM	32.28°N, 106.75°W	242	16	Granitic and volcanic alluvium	2.0	Petrocalcic paleargid	Capo and Chadwick (1999)
Merced, CA	37.28°N, 120.50°W	310	16	Granitic alluvium, terrace	2-4	Fine, mixed, active, thermic typic palexeralf	Harden (1987)
Hawaii	20°5'25"N, 155°52'6"W	500	26	Basalt lava flow	0.350	Haplocambid	Chadwick and Goldstein (2004)
Mattole River, CA	40°15'N, 124°15'W	1000	13	Beach sand/gravel from greywacke	0.24	Udult	Brimhall et al. (1992)
Hawaii	22°8'22"N, 159°37'12"W	2500	16	Basalt lava flow	4.1	Kandiudox	Chadwick and Goldstein (2004)
Hawaii	22°8'40"N, 159°34'8"W	4500	16	Basalt lava flow	4.1	Haplosaprist	Chadwick and Goldstein (2004)

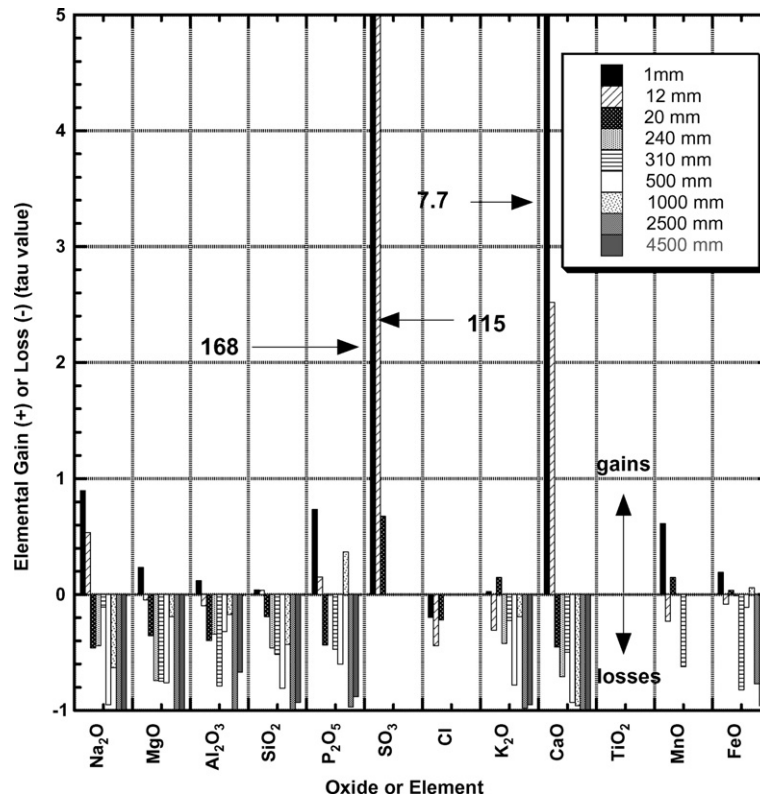


Fig. 3. Fractional elemental gains (positive  $\tau$ ) or losses (negative  $\tau$ ) of elements in upper 20 cm of ancient Earth soils, relative to their parent materials, as a function of mean annual precipitation.

et al., 2003; Ewing et al., 2006). Additionally, easily weatherable primary minerals such as plagioclase are largely preserved despite the great age of these soils (Ewing et al., 2006).

Ancient soils in the humid extremes on Earth are severely depleted in Si, with losses of  $\sim 2000 \text{ kg m}^{-2}$  of Si and Al and other major elements in the upper 1 m (Fig. 2a). This occurs through chemical weathering and leaching, which causes a corresponding volumetric collapse (Fig. 2b). Atmospheric deposition of Si (Kurtz et al., 2001) and P (Hedin et al., 2003) in these soils maintains a quasi steady state of these elements, balancing the losses by chemical erosion. Dust and aerosol deposition is globally pervasive on Earth (Jickells et al., 2005), and is intimately linked to soil formation (Jackson et al., 1971; Chadwick et al., 1999; Amundson, 2004). The impact of dust is particularly evident, however, in desert soils on Earth—soils most similar to those on Mars. Enormous gains of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Na}^+$ , and  $\text{Ca}^{+2}$  ( $800 \text{ kg m}^{-2}$  total) occur at the hyperarid extreme on Earth (Ewing et al., 2006). These gains arrive in both solid and solute form from dry and wet deposition. Chemical variation with depth in hyperarid soils records rare vertical infiltration events during which relative mineral solubility dictates aqueous chemical fractionation with depth. The maximum transport depth is  $\text{NaNO}_3 = \text{NaCl} > \text{CaSO}_4 > \text{CaCO}_3$  in the driest portion of the Atacama Desert, with decreasing transport depth clearly related to decreasing mineral solubility (Fig. 2c). As a consequence of mass gains, soils exhibit volumetric expansion

of up to 500% (Fig. 2d). However, despite the large quantities of  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  in the profile (Fig. 2c), the surface 20 cm is depleted of nearly all  $\text{Cl}^-$  and 45% of the  $\text{SO}_4^{2-}$  relative to the in-coming dust and aerosols. This is the result of rare rainfall events that move salts downward according to solubility, to depths well below the soil surface (Fig. 2d). Atacama fog, which is relatively frequent, may serve to move highly soluble salts downward from the surface on shorter time scales. Thus, even the driest and most abiotic (Navarro-González et al., 2003) region on Earth has sufficient moisture to drive salts to lower depths, in part by solute diffusion, and partially by leaching the surface. These pedogenic accumulations of  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  on Earth are exceedingly rare due the planet's relatively humid state, but would be expected to be more common on Mars where extreme aridity is or was coupled with atmospheric deposition of S and Cl (Banin et al., 1997).

The Atacama Desert soil at 20 mm MAP contains the geochemical fingerprint of climate change. This site lies at the broad rainfall boundary between net losses via chemical weathering and net gains due to atmospheric deposition. The upper 20 cm of the soil exhibits small losses of Si, Al and some other major elements (Na, Mg; although not Fe), but gains of S relative to the parent sediment. These patterns, taken together, are an example of the geochemical evidence of polygenesis, i.e. material chemically weathered in a wetter climate in which highly soluble salts then accumulate during a more recent, drier period. This pattern of both loss and gain is weakly expressed at  $12 \text{ mm yr}^{-1}$  and

absent at  $240 \text{ mm yr}^{-1}$  (Fig. 3). At the  $20 \text{ mm yr}^{-1}$  site, variations in rainfall have occurred due to oscillations in the northerly excursion of Pacific westerlies (Lamy et al., 2000), and more pluvial periods in the past are likely responsible for the surface elemental losses. The present hyperarid climate has facilitated the accumulation of soluble salts and dust within the previously leached and weathered soil. Desert soils of Pleistocene age on Earth commonly contain a variety of features indicative of polygenesis, including late stage carbonate overlain on previously weathered and clay-rich horizons (Birkeland, 1999; McFadden, 1988) and changes in the depth of water penetration and depth of carbonate accumulation (Wang et al., 1996). Thus, the polygenetic chemical features of the Atacama soil are consistent with other locations on Earth found at the climatic boundary between net elemental gains and losses.

We conclude by emphasizing that Earth soils clearly reflect the geochemical fingerprint of rainfall in spite of the many processes that mix and add/remove mass at the land surface. Physical and biological mixing (Yoo et al., 2005), dust additions (discussed above), and erosion all impact soils to varying degrees. That all these processes occur, and that soils yet retain a chemical imprint reflecting climate, is important to consider on Mars where some of these processes have and continue to occur, but likely at rates considerably lower than on Earth.

## 5.2. Mars surficial soil chemistry

Mars soil chemical patterns at the Spirit and Pathfinder landing sites bear some striking similarities to both semiarid and hyperarid soils on Earth. The normalized Martian soil chemistry reveals previously unrecognized losses of up to 50% (tau values of  $-0.5$ ) for major elements except those likely to be atmospheric (S, Cl), which instead show gains of 300–1200% (tau values of 3–12) (Fig. 4). These patterns are striking because they occur consistently at widely separated landing sites. Because APXS analyzers are capable of detecting the geochemistry of the upper few microns of exposed soil, we binned “undisturbed” and “disturbed” soils at Spirit (soils crushed and compacted by rover wheels) separately to determine if the apparent losses at Gusev are due entirely to the presence of the thin, bright (and weathered) surface dust. The comparisons in Fig. 4 show large similarities, relative to basalt, for both materials (additionally, deeper trenches discussed below reveal similar trends). These apparent losses have not been reported in previous analyses of the data (e.g. Yen et al., 2005) because Ti normalization has not been used. When normalized to Ti, Spirit soils exhibit Ni tau values of 0.5 or less, greatly reducing the apparent increase in Ni relative to rock. Elemental losses of this magnitude on Earth require MAP of 300 to 500 mm (Fig. 3) though the possible presence of strong acids (McLennan et al., 2006) on the Martian surface makes any direct correlation to Earth rainfall “fingerprints” somewhat tenuous.

The Mars soil chemistry, from a pedogenic perspective, suggests *in situ* weathering and downward losses of weathering products. A key alternate explanation is one com-

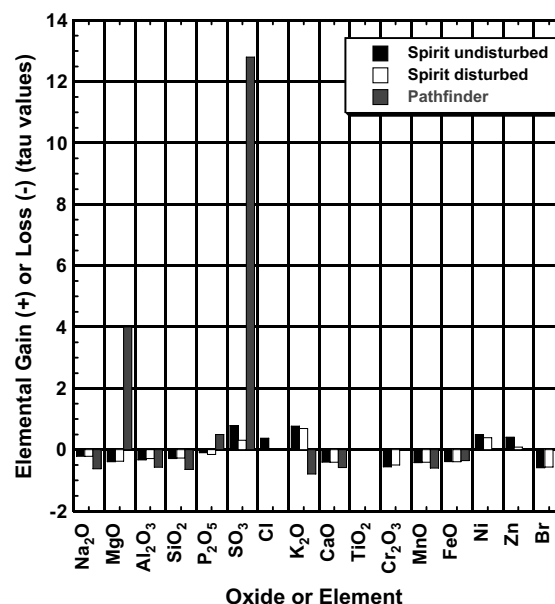


Fig. 4. Fractional elemental mass gains (positive  $\tau$ ) or losses (negative  $\tau$ ) of soils at Mars lander sites relative to local rock. Spirit undisturbed soils = sample #14, 41, 45, 47, 52, 65, 71, 105, 113, 126 and Spirit disturbed soils = 43, 74, 122, 135, 158 (Gellert et al., 2006), and Pathfinder soils = samples A4, A5, A9, A10, A15 (Foley et al., 2003). Tau values for Spirit mission is calculated relative to Gusev basalt (all RAT'd Adirondak, Humphrey, and Mazatal samples (Gellert et al., 2006)), while Pathfinder soil tau values are calculated relative to soil-free rock at the Pathfinder site (Foley et al., 2003).

monly considered for Martian soils: additions of pre-weathered dust or eolian materials to a basaltic matrix. We recognize that chemically mature global dust (Yen et al., 2005) may contribute to the apparent weathering losses, and that Mars soils appear to contain residual weatherable primary minerals (e.g. Morris et al., 2004), suggestive of mixing. However, as noted above, the globally distributed bright dust forms a thin surficial layer at the landing sites, and disturbed and trenched samples at Gusev crater (Spirit) also show similar chemical trends (see below) lending support to *in situ* alteration. These trenches reveal that the soil is “poorly sorted sand, granules, pebbles, and cobbles. . . rather than an aeolian origin, this characteristic suggests that impact mixing processes dominated the formation of the subsurface regolith at these two trenches” (Wang et al., 2006). Thus, if eolian additions are indeed small, the apparent weathering either occurred *in situ*, or alternatively, occurred in a previous landsurface that was subsequently bombarded and which supplied the impact-generated sediments now at Gusev.

Chemical similarities exist among sites; however, the lander sites also exhibit their own unique signatures and histories. Apparent gains of Mg occur only at the Pathfinder site, and gains of K at Spirit. Thus, while similarities in chemical alteration do exist among sites, differences also possibly exist due to local differences in geology, chemical inputs, climatic conditions, and weathering histories.

If dust or eolian inputs, rather than Martian basalt, is the major parent material for Mars soils (e.g. the source of the “weathered” soil material), the apparent soil elemental changes may differ, and even be of a different sign, indicating that no chemical losses have occurred. Hypothesized contributors to soil mass (discussed below) are based on direct measurements of various surficial sediments that have been suggested to have mixed with the Martian soil. Dust chemistry estimates assume that the pure “non-dust” endmember can be either a brushed rock surface or a RATED surface (ground), which suggests the pure “dust” endmember to be chemically intermediate in value between RATED rock and soil at Gusev crater. Thus, soils are generally enriched/depleted in rock-forming elements, relative to this calculated dust, with the same sign as they are relative to rock, but the values are generally smaller (Table 1).

Alternatively, we have assembled a suite of proposed “soil components” for Gusev crater as classified by Yen et al. (2005): (1) fine-grained, “bright dust”, (2) “dark soil” with a maximum particle size of 100  $\mu\text{m}$ , (3) eolian “bed-form armour”, and (4) “lithic fragments” embedded in the soils. We also, for direct comparison, include (5) basalt (Table 3). Using the published chemical composition of these proposed endmembers, and the chemistry of Gusev trench soils (discussed in greater detail below), we show using Al and Si for illustrative purposes, that the Gusev soil is, relative to any of the measured eolian endmembers, generally depleted in these two elements following Ti normalization. The apparent depletion increases as particle size of the substrate increases. Thus, while we believe it is impossible to entirely reject external inputs as the sole source for the “weathered” Mars soil based strictly on available landscape features and soil profile morphology, the chemical data leave few other plausible alternatives to post-depositional, *in situ* pedogenesis, regardless of starting parent material (dust or basalt). The only other reasonable alternative, which is impossible to verify, is that dust chemistry has changed over Martian geological time.

The apparent loss of rock-forming elements in the soil surface of the Pathfinder or Spirit landing sites, if caused by pedogenesis, requires that the weathering products are concentrated at lower depths. Deep exposures are not present at any of these sites, although the Spirit rover excavated trenches to  $\sim 10$  cm in two locations on geomorphologically mature landsurfaces: Big Hole and The Boroughs (Wang et al., 2006), and thus a comparison of surface and subsurface chemistry is possible. First, the tau values with depth (relative to basalt) (Fig. 5a) reveal generally similar overall chemical gain/loss patterns for both trenches at all depths (an exception being Br in Boroughs trench) indicating that apparent mass losses are not due entirely to surficial dust, but subtle differences with depth suggest downward aqueous transport of the most soluble components.

In order to illuminate the subtle chemical trends with depth in the shallow Gusev trenches, we have compared the Ti-normalized subsurface samples to similarly normalized ratios of the surface samples (e.g. the surface serves as the “parent material”) (Fig. 5b), the results clearly show gains of Cl,  $\text{SO}_3$ , MgO,  $\text{Fe}_2\text{O}_3$ , Zn, and Cr with depth. Decreased Fe(II) and increased Mg with depth are

Table 3  
Calculated elemental gains (+) or losses (–) (tau values) for Big Hole and Boroughs trenches at Gusev crater, using the soil component classification of Yen et al. (2005)

Gusev crater trench samples	Depth (cm)	Bright dust		Dark soil		Bedform armour		Lithic fragments		Basalt	
		Gobi parent material (bright avg. Gusev dust) <sup>a</sup>		Low-S global dark soil Panda subclass <sup>a</sup>		Arena (morning crest) basalt sand <sup>b</sup>		Ramp flats <sup>b</sup>		Adirondack parent material (rock) <sup>b</sup>	
		$\text{Al}_2\text{O}_3$ Tau	$\text{SiO}_2$ Tau	$\text{Al}_2\text{O}_3$ Tau	$\text{SiO}_2$ Tau	$\text{Al}_2\text{O}_3$ Tau	$\text{SiO}_2$ Tau	$\text{Al}_2\text{O}_3$ Tau	$\text{SiO}_2$ Tau	$\text{Al}_2\text{O}_3$ Tau	$\text{SiO}_2$ Tau
Bighole_Mayfly_surface	0	-0.08	-0.09	-0.17	-0.14	-0.29	-0.28	-0.25	-0.23	-0.56	-0.52
Bighole_RS2	10	-0.03	-0.01	-0.13	-0.06	-0.25	-0.21	-0.22	-0.16	-0.54	-0.47
Bighole_Trico	10	-0.05	-0.02	-0.15	-0.07	-0.27	-0.22	-0.23	-0.17	-0.55	-0.48
Boroughs_Hellskitchen_side	5	-0.14	-0.09	-0.23	-0.14	-0.34	-0.28	-0.30	-0.23	-0.59	-0.52
Boroughs_Mills_bottom	10	-0.12	-0.09	-0.22	-0.14	-0.32	-0.28	-0.29	-0.23	-0.58	-0.52

The source of the soil component chemical composition, and the samples used, are given below the class.

<sup>a</sup> Morris et al. (2006).

<sup>b</sup> Gellert et al. (2006).

consistent with the high solubility of  $\text{MgSO}_4$  and the published interpretation that these salts have been concentrated

in the trench substratum (Wang et al., 2006). The Big Hole trench shows small increases in Si and Al relative to the

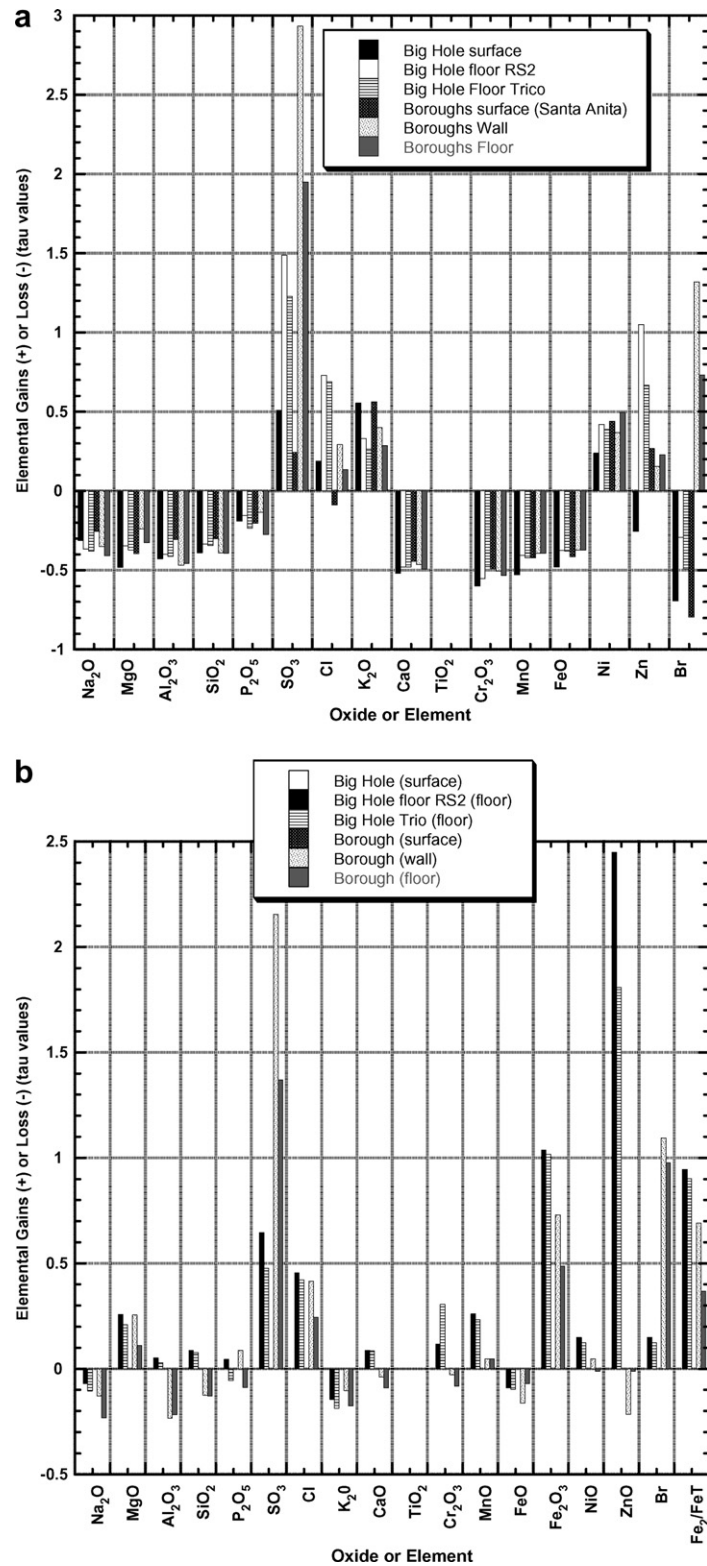


Fig. 5. (a) Fractional elemental mass gains (positive  $\tau$ ) or losses (negative  $\tau$ ) of trenches on Gusev crater (Gellert et al., 2006) vs. rock chemistry (average of RAT'd Adirondak, Humphrey, and Mazatal boulders) (Gellert et al., 2006) (b) Fractional elemental gains (positive  $\tau$ ) or losses (negative  $\tau$ ) of subsurface horizons relative to surface values, all normalized to Ti (Wang et al., 2006). Surface =  $\sim 0$  cm, wall =  $\sim 5$  cm, floor =  $\sim 10$  cm (Wang et al., 2006). Surface values, because they are the reference points, have values of 0.

surface, consistent with the interpretations of Wang et al. (2006). The Boroughs trench indicates that the maximum SO<sub>3</sub> and Cl enrichment occurs at approximately 5 cm in depth, and that these elements decline with depth to 10 cm, though they remain well above surficial levels.

The results above, taken together, suggest a significant decline in weathering and solute flux over time, with a late stage accumulation of exceedingly soluble salts over a modestly (to moderately) pre-weathered soil. The apparent pedogenic loss of rock-forming elements (common in Earth soils) would be unambiguously supported if these weathering products were found at greater depths. Unfortunately, the data (depth profiles) to test this hypothesis do not exist. There is some evidence of subsurface accumulation of Al and Si in the Big Hole Trench (Fig. 5b), though the increases are small. The shallow nature of the exposure, while valuable for studying late stage soluble anion chemistry, is inadequate for fully accepting or rejecting the interpretation that open system chemical alteration, and downward transport of rock-forming elements, occurred earlier in Gusev history. However, the apparent depth trends in SO<sub>3</sub> and Cl (and other elements) suggest modest aqueous transport even in the late stages of soil formation, though the full depth of the salt enrichment is unknown.

What was/is the direction of the aqueous flow? Wang et al. (2006) concluded that in “an open hydrologic system characterized by ion transportation in the fluid, subsequent evaporation of the fluid and salt deposition” is the model that best describes the profiles, and they assumed that the flow was either upward (from some groundwater source) or lateral. Downward transport from above was not explicitly considered. Yet, these depth trends are more consistent with downward aqueous transport and subsequent water loss due to evaporation in hyperarid conditions on Earth. We argue this from several perspectives. First, the chemical loss of rock-forming elements is problematic for upward rising waters: where have these leached elements gone? Downward migrating fluids, on the other hand, could carry these elements to depths well below the current exposed trenches. Second, the soluble anion profiles (increasing concentration with depth) are consistent with salt profiles formed in hyperarid soils on Earth (Fig. 2c). In general, the concentration of Cl (and other soluble anions) in unsaturated soils increases with depth as the downward liquid water flux decreases and water is removed via evaporation (Phillips, 1994). The observed profiles from Mars (albeit very shallow) are inconsistent with upward moving water. The water holding capacity of the upper 5 cm of the Mars surface, based on average water holding capacities of soil materials (Arkley, 1963), may be about 5 mm. Liquid water of this quantity or more would be needed for simple piston flow displacement of surficial salts, though much lower amounts of water would be needed for unsaturated processes such as salt diffusion. The presence of significant salts below 10 cm presumably requires pulses of even more water during the salt accumulation phase. The source of acidity that may have driven the initial chemical weathering is poorly known, but the soils have apparently been stripped of their weathering products (Figs. 4 and 5) and have been

oxidized (Wang et al., 2006), suggesting much more aqueous movement earlier in the soil’s history. The accumulation of up to 14 wt % SO<sub>3</sub> over this chemically altered/depleted matrix is incompatible with the chemical losses, and thus requires a change in leaching/weathering regimes.

In addition to the missing rock-forming elements, there are other reasons to question the proposal that the chemical signature reflects upward flow from groundwater. First, on Earth, a literal “water planet”, soils impacted by groundwater are rare, and are found only in restricted geomorphic settings (basin rims, localized groundwater discharge areas, floodplains, coastal margins). In particular, the predominance of secondary carbonates (Quade et al., 1989), sulfates (Rech et al., 2003; Ewing et al., 2006) and nitrates and chlorides (Walvoord et al., 2003; Ewing et al., 2006) in arid soils on Earth are due to precipitation events that have mobilized solutes downward followed by evapotranspiration (Phillips, 1994) rather than upward from groundwater sources. Second, at the Gusev landing site, despite an earlier interpretation that the crater was once occupied by standing water, after landing the site was found to be a modified basalt plain. This suggests that water tables may not have been high here. Third, near surface sulfate and chloride “crusts” or accumulations occur at all landing sites (in vastly different geologies and geographic settings), making a planetary shallow groundwater necessary, which seems improbable. Thus, the most parsimonious explanation for the near-surface salt accumulations at these sites on Mars is atmospherically derived solutes/acids transported downward by small quantities of liquid water followed by subsequent evaporation.

### 5.3. Mars soil chemical profiles

The deep exposure of the sedimentary section of the Burns formation in Endurance crater offers a unique opportunity to examine chemical changes with depth, and thus evidence for weathering and solute transport. Briefly, the present interpretation of the section is that it consists of three sedimentary units: Upper = sub aqueous deposition, Middle = eolian sand, Lower = eolian sand (e.g. Grotzinger et al., 2005). The sediment is comprised of a mix of sulfates (including jarosite) and weathered basaltic silicates. Squyres et al. (2006) compared the silicate chemistry to unweathered basalt at Gusev crater, and concluded that the silicate material has lost about 55% of its cations (based on [Al/Fe + Mg + Ca] ratios). *In situ* formation of hematite nodules has apparently occurred following deposition, and recrystallization of sulfates has occurred in the middle and upper units following the accumulation of the hematite nodules. SO<sub>3</sub> (and Br) declines with increasing depth, and Cl increases with depth (Fig. 6a). Based on these and other data (see references for more details), McLennan et al. (2005) have interpreted these solute profiles to have accumulated by evaporation of water from a near-surface water table (e.g. a phreatic zone). In contrast to the reported data, solute profiles produced by water and solute flux from a water-table source and driven by evaporation at the surface would have an exponential shape, with highest concentrations of the most soluble salts immediately below the soil

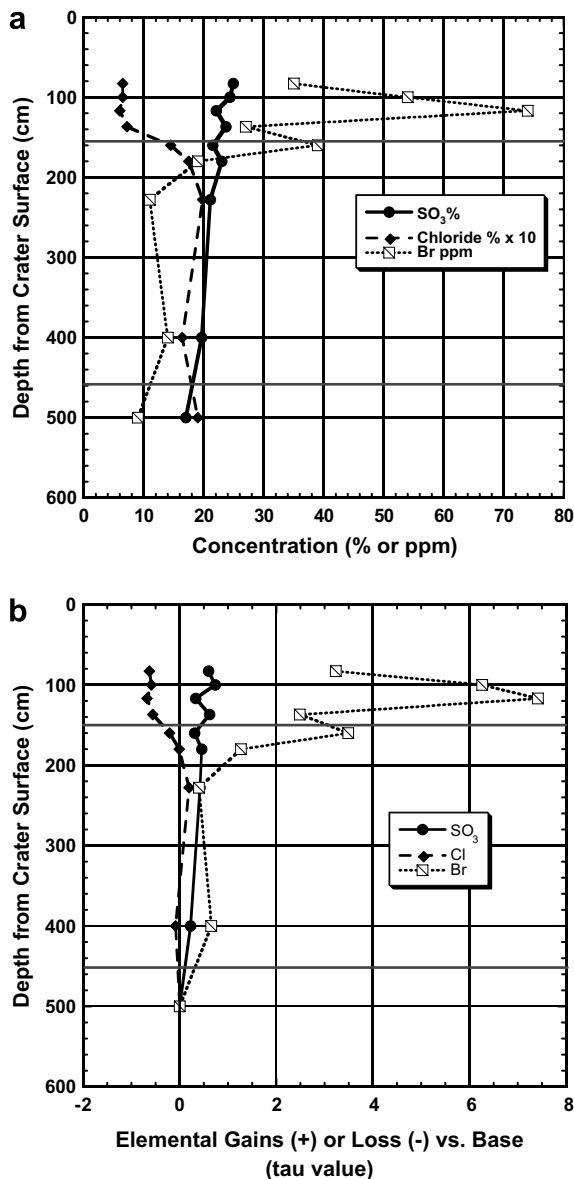


Fig. 6. (a) Concentration of anions in a depth profile of the Burns formation, Endurance crater. (b) Tau values of the anions, relative to the basal unit (Gm). Horizontal lines indicate approximate location of boundaries between sedimentary units. Samples used are listed in Tables 4 and 5.

surface (Allison and Barnes, 1985). Observed profiles from the Endurance do not display this characteristic.

Following Squyres et al. (2006), we compared the chemistry of the Endurance profile to Gusev basalt—but using Ti-normalized data (Table 4). This approach suggests an apparent loss of Mg, Ca, and Fe of approximately 50%, but also reveals an apparent loss of significant quantities Al and Si (and other elements) as well. Apparent gains of P, S, Cl, K, Ni, and Zn occur, elements presumably associated with the sulfate cement in the profile. A small apparent addition of Ni is still in evidence after Ti normalization. Yen et al. (2006) assert that “little research has been carried out on the aqueous geochemistry of Ni, especially under

Table 4

The fractional gains (+) or losses (-) (tau values) of elements in the Endurance crater profile relative to Gusev basalt (all RAT's Adirondak, Humphrey, and Mazatal samples) (Gellert et al., 2006)

Sample name	Unit	Approximate depth (cm)	Elemental gains (+) or losses (-) (tau values)															
			Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	SiO <sub>2</sub>	SO <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	Cl	K <sub>2</sub> O	CaO	Cr <sub>2</sub> O <sub>3</sub>	MnO	FeO	Ni	Zn
Tennessee_RAT	A	83	-0.62	-0.34	-0.57	-0.41	-0.41	0.20	6.48	0.24	1.43	-0.50	-0.73	-0.38	-0.36	1.28	1.62	-0.57
Kentucky_Cubble_Hill2_RAT	B	100	-0.52	-0.20	-0.52	-0.33	0.36	7.14	0.38	1.66	-0.47	-0.73	-0.29	-0.33	1.31	1.03	1.03	-0.27
Virginia_RAT	C	117	-0.52	-0.34	-0.57	-0.42	0.17	5.23	0.08	1.36	-0.58	-0.73	-0.29	-0.40	1.10	0.76	0.76	-0.15
Ontario_London_RAT	D	137	-0.51	-0.24	-0.53	-0.35	0.38	6.59	0.46	1.55	-0.48	-0.71	-0.36	-0.37	1.29	0.87	0.87	-0.65
Grindstone_RAT	E1	160	-0.55	-0.38	-0.56	-0.39	0.19	5.14	1.63	1.31	-0.56	-0.75	-0.40	-0.42	0.93	0.49	0.49	-0.55
Kettlestone_RAT	E2	180	-0.60	-0.33	-0.58	-0.40	0.19	5.82	2.29	1.27	-0.52	-0.73	-0.37	-0.39	1.18	0.68	0.68	-0.77
millstone_Dramensford_RAT	F	228	-0.53	-0.39	-0.52	-0.34	0.44	5.67	2.97	1.60	-0.46	-0.70	-0.37	-0.32	1.00	1.26	1.26	-0.86
Diamon_Jenness_Holman3_RAT2	Gd	400	-0.53	-0.50	-0.52	-0.34	0.20	4.75	2.05	1.57	-0.51	-0.71	-0.42	-0.38	0.69	1.33	1.33	-0.83
MacKenzie_Campell_RAT	Gm	500	-0.50	-0.61	-0.51	-0.34	0.23	3.69	2.33	1.65	-0.58	-0.75	-0.43	-0.41	0.87	1.02	1.02	-0.90

conditions relevant to Mars where acid–sulfate weathering may be dominant”. However, the chemistry of Ni in weathering profiles is indeed a well studied phenomenon on Earth because of the economic importance of Ni-rich laterites which are formed by the residual accumulation of Ni, Fe, and secondary silicates during deep, tropical weathering of mafic igneous rocks (Brimhall and Dietrich, 1987; Gleeson et al., 2004). While Ni may not be as immobile as Ti in aqueous environments, it is highly conserved relative to Si and other elements (Brimhall and Dietrich, 1987), and can ultimately form Ni/Fe-rich ores. Thus, an alternative origin of the Ni concentrations, is that Ni was even less mobile than Ti in the weathering regime that originally altered the sediment that fills Endurance crater, and thus it represents a residual accumulation. This hypothesis, along with the others previously proposed (Yen et al., 2006), are difficult to test with the information available, but should be included among the suite of possible mechanisms for the Ni accumulation.

Squyres et al. (2006) have argued that for the Endurance crater samples (and Meridiani in general), a plot of the molar concentrations of  $\text{Al}_2\text{O}_3/(\text{FeO} + \text{MgO} + \text{CaO})$  vs. the molar fraction of  $\text{SO}_3$  in soil and sediment samples is a reliable means of revealing a silicate/sulfate mixing relationship, and that the  $y$ -intercept provides the chemistry of the silicate endmember. The underlying assumption of this approach is that Al in the starting silicate matrix is immobile during weathering while cations are leached. Using this approach, they interpreted that the silicate component of the Endurance crater samples had lost up to 55% of its cations (relative to Gusev basalt) before being mixed with the sulfates. We also plotted the  $\text{Al}_2\text{O}_3/(\text{FeO} + \text{MgO} + \text{CaO})$  vs.  $\text{SO}_3$  for soils measured by both Spirit and Pathfinder, and found mixing relationships that suggest these soils are also composed of S-free silicate materials depleted in cations relative to Gusev basalt (data not shown). Additionally, we plotted the  $\text{Al}_2\text{O}_3/(\text{FeO} + \text{MgO} + \text{CaO})$  for soils and outcrops examined by Spirit, Opportunity and Pathfinder rovers vs. the Ti content of the sample relative to the local rock (Fig. 7). As the  $\text{Al}_2\text{O}_3/(\text{FeO} + \text{MgO} + \text{CaO})$  increases (indicating increased weathering and loss of rock-derived cations (Squyres et al., 2006)), the  $[\text{TiO}_2(\text{rock})/\text{TiO}_2(\text{soil})]-1$  (a quantitative measure of total mass loss if Ti is an immobile element during weathering (Ewing et al., 2006)) decreases (also indicating increased weathering losses). Clearly, both indices of weathering indicate that the silicate component of the soils/sediments at these three sites are chemically altered and fractionated. However, since Al is likely to be more mobile than Ti (see Table 4), we view the Ti normalization to be the much more quantitative of the two measures. Additionally, the good correlation between the two measures is also strongly supportive of the notion that Ti is enriched in soils relative to rock via weathering processes, as opposed to other alternatives such as meteoric additions.

To test whether the Endurance crater section reflects late stage, post-depositional movement of solutes from surface derived moisture, we used the base of the Endurance crater section (sample Gm, MacKenzie-Campbell RAT) as a geochemical reference, and examined the fractional gains or

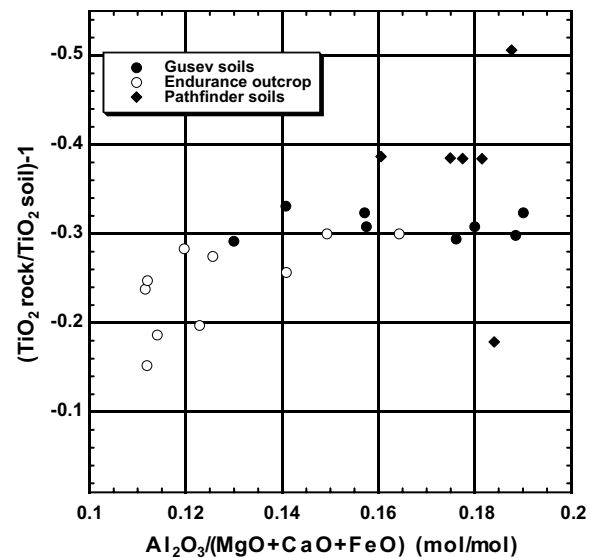


Fig. 7. A plot of  $\text{TiO}_2$  in rock vs.  $\text{TiO}_2$  in soils vs. Al/cation ratios. Gusev soils = Big Hole and Burrough Trench surface and subsurface samples and average disturbed soil; and Gusev rock = RAT'd Adirondak, Humphrey and Mazatal samples (Gellert et al., 2006). Pathfinder soil = A4, A5, A10, A15, mean soils and soil-free rock (Foley et al., 2003). The Endurance crater samples are listed in Table 4.

losses of elements in overlying layers (Table 5; Fig. 6b). The analysis reveals small apparent depletions of Si and Al in the upper layers relative to Gm, and gains in Fe (consistent with the accumulation of jarosite). Because these trends for Si and Al are small, and encompass three temporally distinct sedimentary units, it is speculative to interpret this as a post-depositional signal. However, the very large depth trends in  $\text{SO}_3$ , Cl, and Br likely do suggest post-depositional alteration and transport (Grotzinger et al., 2005; Squyres et al., 2006). Here we consider the profiles in light of the probable mineralogy and solubility, and in light of aqueous and solute transport in arid environments on Earth.

Chloride is a widely used tracer of unsaturated water flow in arid zone environments (Phillips, 1994; Wood, 1999; Walvoord et al., 2002a,b). Small quantities of precipitation, coupled with wet and dry deposition of chloride, are slowly transported downward within sediments by gravitation potential gradients. In the simplest case on Earth, “an idealized chloride profile under steady-state piston flow conditions with extraction of water by roots would be characterized by concentrations increasing with depth through the root zone to uniform values below the root zone” (Walvoord et al., 2002a). However, in most arid environments, the transport processes are more complicated. In particular, climate change from more humid to arid conditions results in a major reduction or elimination of percolation past the root zone, thereby initiating transient drying over multi-thousand year time scales (Walvoord et al., 2002b). As a result, chloride (and nitrate) profiles reveal a subsurface “bulge” caused by declines in recharge during the Holocene (Walvoord et al., 2002a,b, 2003).

Table 5  
The fractional gains (+) or losses (-) (tau values) of elements in the Endurance crater profile relative to unit Gm

Sample name	Unit	Approximate depth (cm)	Elemental gains (+) or losses (-) (tau values)															
			Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	Cl	K <sub>2</sub> O	CaO	Cr <sub>2</sub> O <sub>3</sub>	MnO	FeO	Ni	Zn	Br	
Tennessee_RAT	A	83	-0.23	0.68	-0.12	-0.11	-0.02	0.60	-0.63	-0.08	0.19	0.09	0.09	0.10	0.35	0.30	3.23	
Kentucky_Cubble_Hill2_RAT	B	100	-0.03	1.05	-0.02	0.01	0.11	0.74	-0.59	0.00	0.24	0.09	0.25	0.14	0.37	0.01	6.27	
Virginia_RAT	C	117	-0.03	0.70	-0.11	-0.12	-0.05	0.33	-0.68	-0.11	-0.01	0.08	0.25	0.02	0.25	-0.13	7.42	
Ontario_London_RAT	D	137	-0.01	0.96	-0.04	-0.02	0.12	0.62	-0.56	-0.04	0.23	0.16	0.13	0.08	0.36	-0.07	2.49	
Grindstone_RAT	E1	160	-0.09	0.60	-0.09	-0.08	-0.04	0.31	-0.21	-0.13	0.05	-0.02	0.07	-0.02	0.15	-0.26	3.49	
Kettlestone_RAT	E2	180	-0.19	0.71	-0.13	-0.10	-0.04	0.46	-0.01	-0.14	0.13	0.08	0.11	0.05	0.27	-0.17	1.27	
Millstone_Dramensford_RAT	F	228	-0.06	0.56	-0.02	0.00	0.17	0.42	0.19	-0.02	0.27	0.20	0.11	0.16	0.29	0.12	0.40	
Diamon_Jenness_Holman3_RAT2	Gd	400	-0.06	0.27	-0.02	-0.01	-0.02	0.23	-0.08	-0.03	0.16	0.17	0.03	0.05	0.19	0.15	0.65	
MacKenzie_Campell_RAT	Gm	500	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	

The Endurance crater profiles of Cl, S, and Br are, from a first-order perspective, consistent with observed depth trends in ancient soils of the Atacama Desert (Fig. 2c) and with observed vadose zone chloride profiles in other arid regions (Phillips, 1994; Walvoord et al., 2003). However, from a more critical and detailed perspective, the profile is complex and likely records large changes in the efficacy of aqueous transport over time due to increasingly drier (and colder) conditions. In addition to jarosite, the near-surface salts at Endurance are a mix of Ca (solubility in cold water =  $<0.1 \text{ mol l}^{-1}$ ) and Mg ( $2.2 \text{ mol l}^{-1}$ ) sulfates, Mg (and possibly Na and Ca) chlorides ( $4.6\text{--}6.1 \text{ mol l}^{-1}$ ) and  $\text{MgBr}_2$  ( $18.1 \text{ mol l}^{-1}$ ) (minerals from Clark et al., 2005; solubility data from Weast et al., 1984). The mixture, and vertical differences, of these vastly different salts (in terms of aqueous solubility) is suggestive of changing transport efficiencies over time. A simple interpretation, but one consistent with the data, is that Ca sulfate (whose presence is based on interpretations by Clark et al. (2005) and on Ca-tau values relative to the basal layer (Table 5)), which declines discontinuously with depth, was first accumulated near the surface under a relatively more humid condition due to its low solubility. More soluble anions/salts were transported to greater depths. With declining aqueous activity, the effectiveness of  $\text{MgCl}_2$  and  $\text{MgSO}_4$  removal decreased and their depth of accumulation shifted closer to the surface, although they were still separated vertically because of their relative solubility differences ( $\text{MgCl}_2$  more soluble than  $\text{MgSO}_4$ ). Finally, as liquid water fluxes declined to exceedingly restricted levels, where vapor transport may have dominated, only the highly soluble  $\text{MgBr}_2$  (possibly facilitated by freezing point depression in residual brines) was transported downward, possibly by diffusive processes. The “bulge” in the Br profiles is at least qualitatively consistent with Cl profiles on Earth that have undergone pluvial/interpluvial hydrological declines. Finally, the fact that post-impact chemical alteration of the crater profile appears to be almost negligible (Clark et al., 2005), with the exception of thin weathering rinds on exposed sediment (Squyres et al., 2006), is indicative of a nearly continuous period, of unknown duration, of post-impact aqueous inactivity. Taken together, the chemical profiles and exposure chemistry signal a protracted decline in the availability of surface water, and its downward transport. This interpretation is consistent with the data and with hydrological modeling of arid environments on Earth. The total quantities apparently involved must be recognized as being modest (Fig. 6a), and thus post-depositional redistribution is potentially consistent with the largely preserved sedimentary textures in these sediments. The proposed alternative (Grotzinger et al., 2005 and Squyres et al., 2006), where these patterns are attributed to ground water interactions, fails to account for the apparent need for a subsequent downward chemical re-sorting of the accumulated salts by soil water. However, the late stage chemical alteration, possibly from downward moving waters, does not preclude earlier stage groundwaters which likely would have occurred in due subaqueous deposition of the upper units. For both the upward and downward water flow hypotheses during late phase diagenesis, textural and permeability dif-

ferences through the various sections of the profile may also have impacted solute transport, though the remarkably constant chemistry throughout the profile (except for the soluble salts) suggests that these physical differences may be modest.

In summary, the chemical profiles are likely a complex record of water movement and climate history. Because the boundary conditions are unknown, unambiguous interpretations of physical processes are not possible. However, the observed data along with pedogenic and hydrological concepts can help reject hypotheses inconsistent with the observations. Given the importance of the aqueous history of Mars, future missions should consider alternative analyses that can provide more definitive information about solute flux. One approach involves the measurement of the S and O isotope composition of the sulfates. Downward transport of sulfates in hyperarid soils on Earth causes large S and O isotope fractionations (and thus depth profiles) due to dissolution/precipitation coupled with vertical advective/diffusive transport (Ewing et al., 2008). Thus, in addition to the need for the examination of both soil cores and further crater exposures on Mars, future payloads may consider instrumentation capable of isotopic measurements in order to ultimately test whether atmospherically derived waters have chemically interacted with, and passed through, Mars soils. This information could reveal interesting chemical information relevant to Mars climate, and the potential geographical distribution of life, earlier in Martian history.

## 6. CONCLUSIONS

Soils, produced by near-surface chemical and physical alteration of *in situ* materials due to downward penetration of waters, likely formed on Mars at some point in its history. The origin of the acids, the amounts of water, and the duration of the pedogenic processes remain obscure, and the question of whether pedogenic processes are detectable in the present surface deposits has not been advanced. In this paper we applied pedological concepts to the interpretation of the origin of some Martian soils. In general, the hypothesis that Mars soils (at least partially) reflect reactions with atmospherically derived water and salts/acids is both geologically reasonable and is parsimonious with the data. Using a chemical mass balance model, we find that widely spaced Martian soils have evidence of *both* losses of rock-forming elements (not widely noted before) and large gains of highly soluble anions (widely discussed) that suggest a long-term (but not necessarily monotonic) decline in surficial inputs of water over time. Chemical weathering of soils has clearly occurred on Mars, and the likelihood that it also occurred *in situ* via pedogenesis remains a viable hypothesis. However, the acceptance or rejection of this hypothesis will ultimately rely on deeper soil analyses.

It is even clearer that additions and vertical transport of sulfate, chloride, and bromide occurred later in Martian history. The widely spaced Viking, Pathfinder, and MER landing sites all have surficial accumulations of these salts that support a regional to global atmospheric deposition and contradict a groundwater source for their origin. The

deep geological exposure at Endurance crater, with complex depth trends in sulfate, chloride, and bromide minerals, is most simply explained by downward transport of atmospherically derived salts under conditions of slowly declining water availability, and this profile has many similarities to anion profiles in hyperarid soils on Earth. The redistribution of salts in frozen soils may also have played a role in these profiles, though it is clear that any solute redistribution has been minimal since the impact that excavated Endurance crater.

The interpretation of Mars chemical data must encompass multiple perspectives and models. Mars is a silicate planet that possesses a surface that has been physically and chemically etched by liquid water. Because of these conditions, any interpretation of Martian surficial chemistry should include a consideration of pedogenesis, which is the most prevalent geochemical process on the surface of the Earth. Ultimately, any viable model of Mars surface chemistry must be based on a sound understanding of how open system chemical, physical, and hydrological processes behave at planetary surfaces, and the lessons we have learned about them from our own planet Earth.

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