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Evidence for montmorillonite or its compositional equivalent in Columbia Hills, Mars

B. C. Clark III,[1] R. E. Arvidson,[2] R. Gellert,[3] R. V. Morris,[4] D. W. Ming,[4] L. Richter,[5]
S. W. Ruff,[6] J. R. Michalski,[6] W. H. Farrand,[7] A. Yen,[8] K. E. Herkenhoff,[9] R. Li,[10]
S. W. Squyres,[11] C. Schröder,[12] G. Klingelhöfer,[12] and J. F. Bell III[11]

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[1] During its exploration of the Columbia Hills, the Mars Exploration Rover "Spirit" encountered several similar samples that are distinctly different from Martian meteorites and known Gusev crater soils, rocks, and sediments. Occurring in a variety of contexts and locations, these "Independence class" samples are rough-textured, iron-poor (equivalent FeO $\sim$ 4 wt%), have high Al/Si ratios, and often contain unexpectedly high concentrations of one or more minor or trace elements (including Cr, Ni, Cu, Sr, and Y). Apart from accessory minerals, the major component common to these samples has a compositional profile of major and minor elements which is similar to the smectite montmorillonite, implicating this mineral, or its compositional equivalent. Infrared thermal emission spectra do not indicate the presence of crystalline smectite. One of these samples was found spatially associated with a ferric sulfate-enriched soil horizon, possibly indicating a genetic relationship between these disparate types of materials. Compared to the nearby Wishstone and Watchtower class rocks, major aqueous alteration involving mineral dissolution and mobilization with consequent depletions of certain elements is implied for this setting and may be undetectable by remote sensing from orbit because of the small scale of the occurrences and obscuration by mantling with soil and dust.

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1. Introduction

[2] The Martian surface is richly populated by basaltic and ultramafic source material, as revealed by 31 Martian meteorites (C. Meyer, Mars Meteorite Compendium, 2005, http://www-curator.jsc.nasa.gov/antmet/mmc/index.cfm), numerous in situ analyses of rocks [*McSween et al.*, 2004] and soils [*Morris et al.*, 2006], and remote sensing by infrared reflectance and thermal emission spectroscopy from orbit [e.g., *Soderblom*, 1992; *Christensen et al.*, 2000a; *Wyatt and McSween*, 2002; *Bibring et al.*, 2005]. (Andesites or altered basalt may also be present [*Hamilton et al.*, 2001]. For purposes of this and other MER project publications, "soil" is used here to denote any loose, unconsolidated materials that can be distinguished from rocks, bedrock, or strongly cohesive sediments, without implications of the presence or absence of organic materials or living matter.) Because the clay mineral montmorillonite (a smectite group phyllosilicate) is a typical alteration product of basalt mediated by aqueous processing, its presence on Mars could be a key indicator for past climate conditions and activities. Previous searches for phyllosilicates by remote sensing have not been as definitive as is now achievable with the more recent orbiting instrumentation. In the Mars Global Surveyor (MGS) Thermal Emission Spectrometer (TES) data set, *Bandfield* [2002] found evidence of sheet-silicates (or high-Si glass), especially in northern hemisphere low-albedo regions, although it has been suggested that these are likely poorly crystalline aluminosilicates such as Al- or Fe-bearing silica and phyllosilicate precursors, or certain zeolites [*Michalski et al.*, 2004, 2006; *Ruff*, 2004]. *Wyatt and McSween* [2002] proposed that Type 2 materials identified by TES could be weathered basalt with clay mineral components. The OMEGA instrument on Mars Express has detected rare

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[1] Lockheed Martin Corporation, Littleton, Colorado, USA.
[2] Department of Earth and Planetary Sciences, Washington University, St. Louis, Missouri, USA.
[3] Department of Physics, University of Guelph, Guelph, Ontario, Canada.
[4] NASA Johnson Space Center, Houston, Texas, USA.
[5] DLR Institut fur Raumsimulation, Linder Hoehe, Cologne, Germany.
[6] Department of Geological Sciences, Arizona State University, Tempe, Arizona, USA.
[7] Space Science Institute, Boulder, Colorado, USA.
[8] Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, USA.
[9] U.S. Geological Survey, Flagstaff, Arizona, USA.
[10] Department of Civil and Environmental Engineering and Geodetic Science, Ohio State University, Columbus, Ohio, USA.
[11] Department of Astronomy, Cornell University, Ithaca, New York, USA.
[12] Institut für Anorganische und Analytische Chemie, Johannes Gutenberg-Universität, Mainz, Germany.

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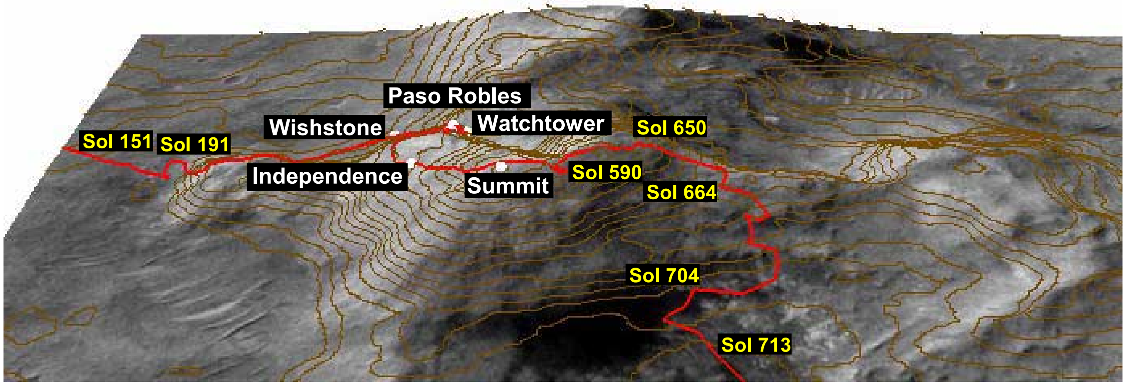

Figure 1. Topographic relationships with Independence class samples.

occurrences of nontronite [*Bibring et al.*, 2005] as well as Fe/Mg-smectites and montmorillonite-rich areas on Mars [*Poulet et al.*, 2005]. From the ongoing Mars Exploration Rover (MER) mission in Columbia Hills [*Arvidson et al.*, 2006], we report the first in situ detection of various local occurrences of low-iron geologic materials whose major, minor and trace elements are consistent with the elemental composition of montmorillonites.

2. Geologic Setting

[3] The Columbia Hills are a set of coalescing constructs reaching up to ~120 m in elevation above the surrounding plains in Gusev crater. Orbital observations show that the Hills rocks are clearly embayed by the olivine-bearing basaltic plains materials and thus represent the oldest geologic unit encountered by the Spirit rover during its mission [*Arvidson et al.*, 2006]. The first portion of the Hills encountered by Spirit was West Spur. Ascent onto the western slopes of the spur showed that outcrops dip conformably with topography, including Clovis, the site of an extensive remote sensing and in-situ science measurement campaign [*Squyres et al.*, 2006].

[4] Following West Spur, Spirit continued its ascent onto the northwestern flank of Husband Hill (Figure 1) encountering Wishstone class float rocks and salt deposits at Paso Robles [*Ming et al.*, 2006]. The first major outcrops explored by Spirit on Husband Hill were the Peace/Alligator and the Methuselah (Watchtower class) complex. Both outcrops were found to be dipping conformably with topography. Methuselah, in particular, dips at a greater angle than the topographic slope [*Squyres et al.*, 2006]. As Spirit continued its ascent beyond the Methuselah and Backstay areas it next encountered the Independence outcrops, followed by the Voltaire outcrops. The Independence outcrop dips northwest conformably with topography. On the other hand, the Voltaire outcrops dip to the southwest, even though the topography slopes toward the northwest. The Voltaire outcrops consist of approximately a half dozen layers, each ~20 cm in thickness. At the top of the Voltaire section a more irregular outcrop can be found, including the rock Assemblee. After conducting an extensive measurement campaign on the Voltaire outcrop, Spirit left the site and continued its ascent to the summit of Husband Hill. Measurements on the summit and during its descent to the south show that rocks dip toward the southwest [*Squyres and Arvidson*, 2006]. Thus, between Independence and Voltaire, the rover may have crossed the apex of an anticline. However, detailed reconstruction of the stratigraphic column and structural patterns has not yet been accomplished.

3. Samples: Context, Preparation, and Analysis

[5] On sol 528, the Spirit rover encountered the approximately one meter diameter, flat lying outcrop of light toned, rough material (Figure 2) which we called "Independence."

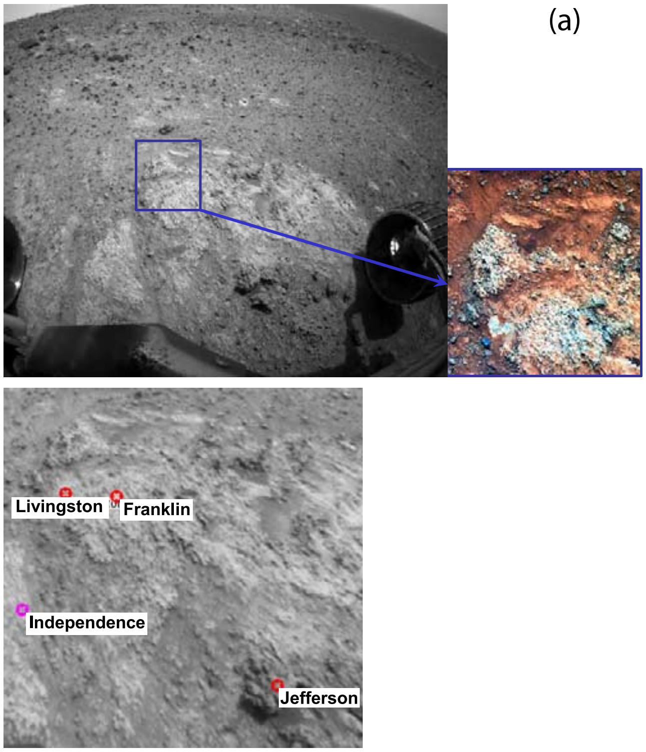

Figure 2. The Independence outcrop. (a) Independence outcrop as viewed in HazCam monochromatic camera, with false color PanCam where scuff was performed. (b) Approximate true color image of the Independence sample site (sol 536A_P2540). (c) Location of APXS analyses on scuffed portion, sample Independence_Penn2. The field of view (FOV) of the Mini-TES analysis is larger than this image, so the scuff portion occupied only a portion of the Mini-TES FOV.

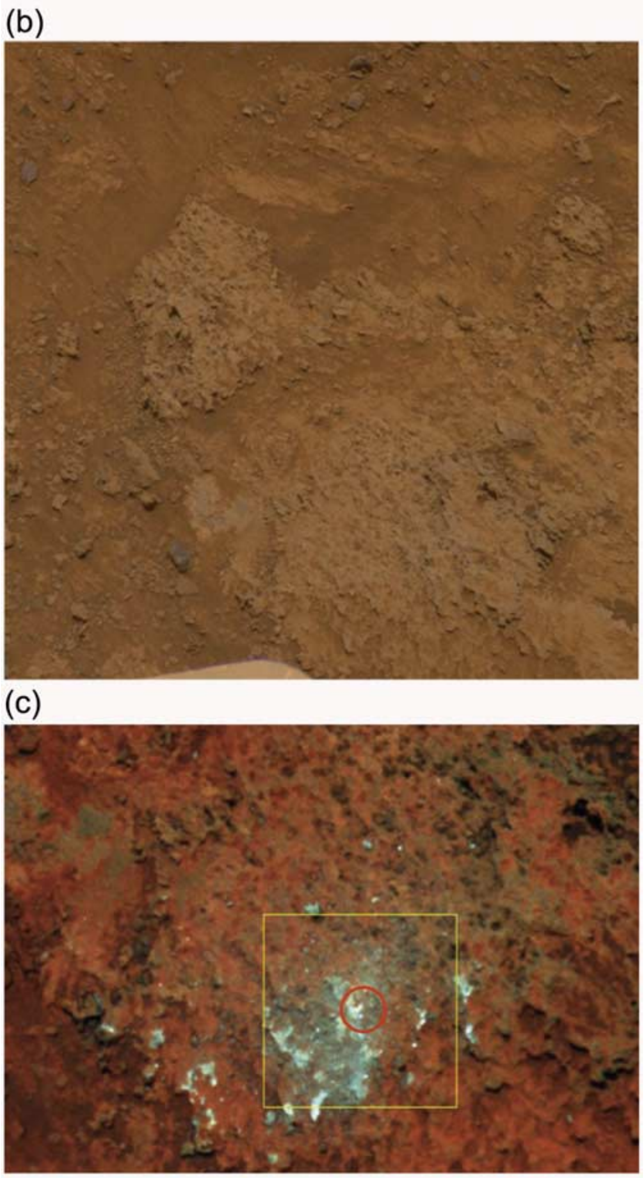

Figure 2. (continued)

This rough material resembled clods found at a previous location called Paso Robles. Using the MER instrument suite [see *Squyres et al.*, 2003], this outcrop was imaged by the Panoramic Camera (Pancam), the Microscopic Imager (MI), and the Miniature Thermal Emission Spectrometer (Mini-TES). In situ analyses were conducted by Mössbauer spectroscopy (MB) and alpha particle X-ray spectrometry (APXS). Portions of the outcrop were viewed and analyzed in both the undisturbed state and after brushing with the Rock Abrasion Tool (RAT) to clear off as much contaminating dust and soil as possible.

[6] Results of APXS analyses indicate that brushing alone may not remove all extraneous particulate contamination on rough or involuted surfaces. The cutting head of the RAT on Spirit rover was worn out and no longer available for grinding into Independence, so it was decided to attempt to dig into the outcrop using a wheel "scuff" to expose a fresh surface. The scuff was accomplished by rotating the left front wheel for three successive cycles of 2 radians forward then 1 radian backward while the other wheels remained stationary. This scuff operation was followed by a brush operation. Although the wheel paddle cleats did not dig deeply into the outcrop, demonstrating that its strength is high, subsequent APXS analyses showed an additional decrease in Fe, S and other elements, indicating successful removal of some, and perhaps most of the surface contamination.

[7] An earlier occurrence of similar material was at Paso Robles (sol 401), some 150 meters to the north-northeast and 12 meters lower in elevation [*Li et al.*, 2006]. This general location has received considerable attention ever since it was discovered accidentally when wheel slippage in loose material churned up whitish sub-surface material whose major component was found to be ferric sulfate salt [*Ming et al.*, 2006; *Morris et al.*, 2006]. The data from analysis of this bright material was not received on Earth until the rover had moved on to a new location. Because of the unique composition, the decision was made to return to this site to conduct further studies. New bright material was exposed at Paso Robles II, using a programmed wheel scuff digging maneuver. Several light-toned, rough-textured clods were observed next to the bright material (Figure 3b). A RAT brushing of a selected clod (Ben's_Clod) was made and an APXS analysis was performed [*Gellert et al.*, 2006]. No Mössbauer analysis was obtained. Although we have named these discrete objects "clods" because of their morphology and the possibility that they were created by the actions of the rover, subsequent analysis indicates that they were preexisting at the Paso Robles (PR) site, and in fact must be highly indurated because the rover wheels passed over some of them without causing their disintegration. Nonetheless, the chemical analysis of the clod is not consistent with igneous rocks. We believe that these objects are peds, i.e., naturally occurring aggregates of fine-grained material that may underlie significant portions of Columbia Hills surface but are only occasionally evident, e.g., when exposed by deflation. ("Ped" is used to denote a naturally formed object constructed of soil or sedimentary grains, including some finer than sand. "Clod" is used to denote a similar object, but formed by artificial means, such as rover activities.) No disaggregated version of this low-Fe material has yet been found, but we believe its composition is clearly that of a chemical sediment, apparently produced by the strong aqueous alteration of igneous minerals.

[8] We use chemical compositional profiles to argue that these peds, the Independence outcrop, and a half-meter sized object called Assemblee (part of Voltaire outcrop, Figure 4) are a similar compositional type which we call Independence class material (APXS calibration and analytical uncertainties are discussed by *Gellert et al.* [2006] and *Rieder et al.* [2003]).

4. Results

4.1. Elemental Composition of Major and Minor Components

[9] Element compositions of the Independence class materials as measured by APXS are given in Table 1. The low content of iron in these samples (<4 wt% FeO-equivalent for Independence_Penn2) compared to the

average of Husband Hills rocks and soils of 13.5% (range, 10–21%) [*Gellert et al.*, 2006], is their most characteristic elemental signature. All have Fe concentrations lower than other known Martian materials, including Martian meteorites and numerous in situ measurements of rocks and soils at five distinct landing sites. The lowest Fe, S, and Cl concentrations occur in sample Independence_Penn2, which is evidence that the wheel scuff was effective at removing much or most of the air fall dust and soil contaminants from the proximate surface. The remaining S can be explained as $MgSO_4$ (see below). For this reason, we choose this sample as the closest available approximation to the true end-member of this class of materials.

[10] Independence class materials have among the highest Al_2O_3/SiO_2 ratio of known Martian meteorites and samples analyzed on Mars, being equaled only by two Wishstone class rocks. Figure 5 compares this ratio for Martian meteorites, Gusev samples, and some likely igneous and sedimentary minerals. Siliceous, differentiated igneous rocks typically contain higher concentrations of K_2O, at least on Earth, and also have Al_2O_3/SiO_2 ratios that are well below 0.25 for siliceous samples ($SiO_2 > 60\%$) compared to the values of 0.30–0.36 (or somewhat higher, when corrected for residual dust contamination) observed in these samples. Independence is clearly in the compositional range for montmorillonite, and well below the Al/Si ratio for anorthite, allophane and kaolinite. It is also in the range for illite, but this phyllosilicate is ruled out because of the very low K_2O content of these materials.

[11] The low Fe concentration and high Al/Si ratio therefore directs our attention to the possibility of the smectite mineral montmorillonite. By considering other chemical components, we can mathematically remove accessory minerals from the bulk composition to isolate the major component. Because Mössbauer spectroscopy measurements, discussed below, shows a strong presence of ilmenite in the outcrop sample we therefore remove all Ti as stoichiometric ilmenite. As seen in Figure 6, the Mg and S in various Independence class samples generally show a strong correlation corresponding to $MgSO_4$, which has been found as a chemical component in numerous Martian materials [*Clark and van Hart*, 1981; *Clark*, 1993; *Brückner et al.*, 2003; *Yen et al.*, 2005; *Clark et al.*, 2005; *Ming et al.*, 2006; *Haskin et al.*, 2005]. Because of the fidelity of this correlation, and the lack of definitive evidence of Fe-sulfate from MB measurements (section 4.3), we remove S as stoichiometric $MgSO_4$. Although some S may be in the form of $CaSO_4$, the relative abundances demand that this would be minor, or absent, compared to $MgSO_4$ (see below, regarding Ca correlation with P).

[12] Rock materials found in these upper portions of Husband Hill, with the exception of Peace class, have concentrations of P and Ti in samples that are much higher than in other Martian rocks, sediments or soils, while the Cr concentrations are extraordinarily low [*Ming et al.*, 2006; *Squyres et al.*, 2006; *Gellert et al.*, 2006]. This P-Ti-Cr fingerprint is subdued but persists in the Independence class

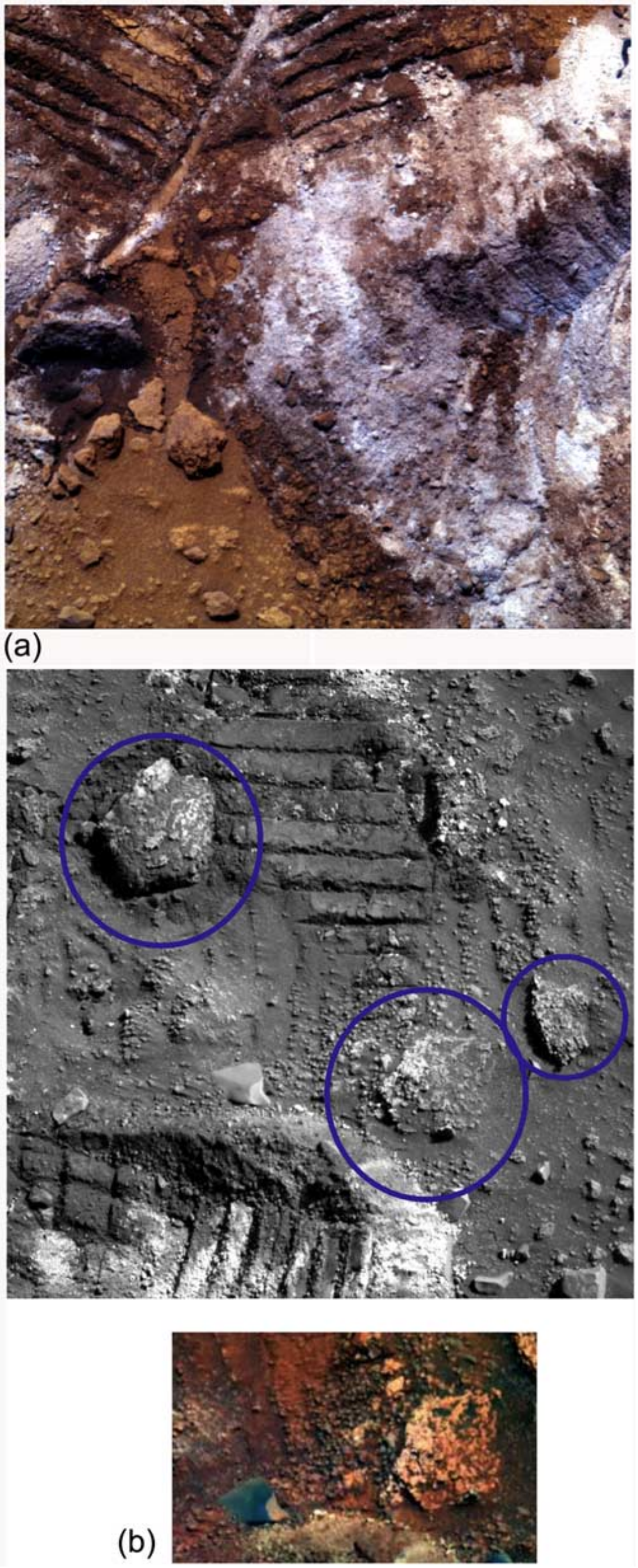

Figure 3. Peds at Paso Robles. (a) Paso Robles I. Several peds (cloddy in appearance) are seen in the lower left quadrant of this image, on top of a portion of soil that does not appear to have been greatly disturbed by the wheel interactions with the local soil. (b) Paso Robles II. Several peds are also observed at this nearby site, and it appears that the rover drove over some of them without destroying their structure. The object in the middle circle, and shown in PanCam color below, is the analyzed Ben's_Clod.

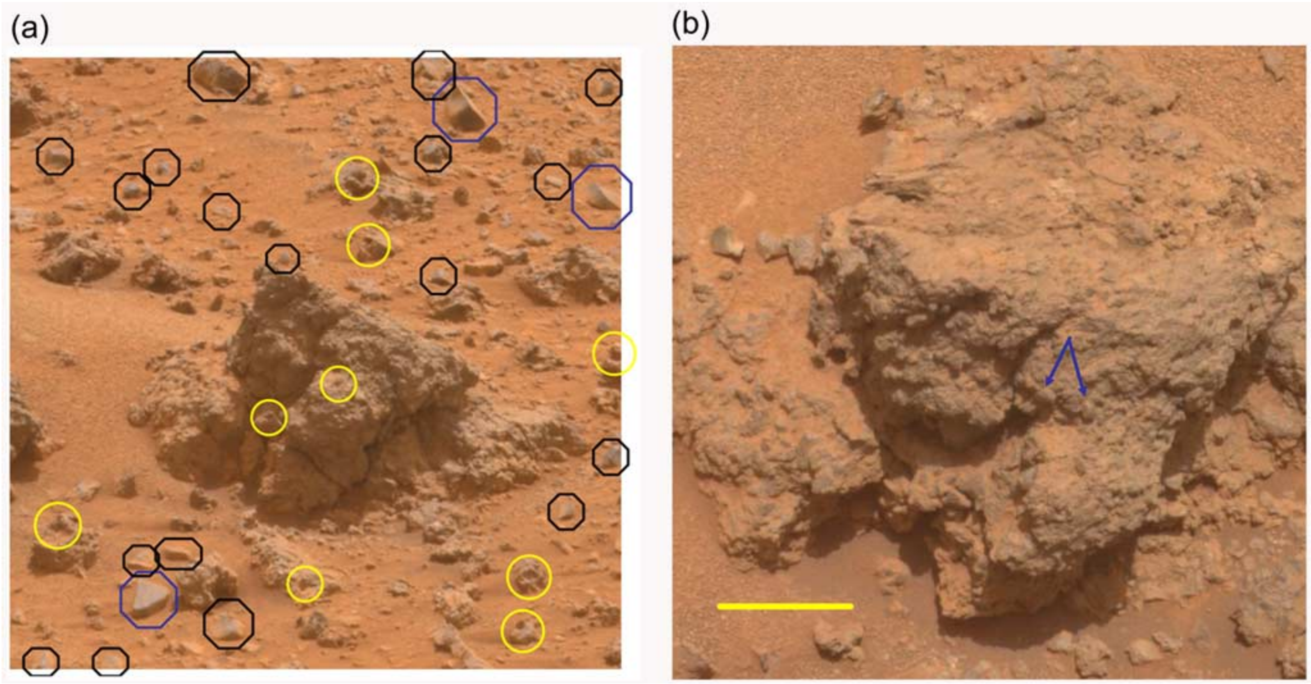

Figure 4. Assemblee. (a) Assemblee and environs. Black octagons circumscribe dark, smooth, often ventifacted rocks of probable igneous origin. Most other objects in the image are rough and appear to be spalled portions of Assemblee, which itself shows evidence of many fractures. To the right and left of the peak of Assemblee are pedestals indicating this is an outcrop. Yellow circles show possible vugs due to reentrant morphology or from removal of clasts such as those in Figure 4b. (b) Assemblee in close-up prior to sampling, taken with PanCam filters 3, 5, and 7. Two rounded, gravel-sized clasts are designated by arrows. Scale bar is 5 cm.

materials, except the Cr concentration in the ped at Paso Robles is not low and Cr in Assemblee is in fact extraordinarily high.

[13] In many samples at Husband Hill, the high P content covaries well with Ca [*Ming et al.*, 2006], with stoichiometric trends that could imply apatite, whitlockite, merrillite, or brushite. In Shergotty meteorite, the phosphorus component is acid-extractable and exhibits a stoichiometry with Ca close to the whitlockite found in those meteorites [*Dreibus et al.*, 1996]. As evident in Figure 7, within the Independence class samples, correlation between Ca and P is positive, but not with a unique slope. This could indicate that P is in the form of apatite, but with excess Ca in all samples, more in some than in others. This is not surprising in view of the mineralogic versatility of Ca, and it cannot be excluded for these samples that some Ca is in the form of carbonate, sulfate, pyroxene, and/or feldspar. In addition, Ca^{2+} ion is also often found as an adsorbate in geologic materials with cation exchange capacity.

[14] After mathematically removing Mg-sulfate, phosphate (as apatite), and Fe minerals determined by Mössbauer analysis (see section 4.3 below), the mineralogy inferred from the elemental composition of the residual major component (“MC”, amounting to ~80% of each Independence class sample) does not correspond with well-known igneous rocks. A standard normative mineralogy calculation (“norm”) is given in Table 2 for the major component (MC) in the Independence outcrop without (column A) and

Table 1. Composition of Independence Class Samples[a]

Sample	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	Cr_2O_3	FeO	Fe_2O_3	Other[b]
Soil (Whymper, A587)	3.2	8.6	9.7	45.1	0.9	7.4	0.5	6.0	0.9	0.3	9.9	6.4	1.1
BensClod_brushed	3.3	5.1	15.1	49.7	4.6	5.0	0.6	7.6	1.4	0.5	3.4	2.5	1.0
Independence_Jefferson	2.6	5.2	13.3	53.3	3.2	5.1	1.0	5.6	1.2	0.1	4.9	3.6	0.9
Independence Brushed	3.0	5.6	12.9	52.4	2.3	6.1	0.6	6.6	1.6	0.2	3.7	3.9	0.7
Independence_Penn2	3.2	3.4	18.7	54.8	3.5	2.2	0.5	7.3	1.9	0.04	2.4	1.6	0.4
Independence_Penn2[c]	3.2	3.4	17.1	55.4	3.5	2.2	0.5	7.3	1.9	0.04	2.4	1.6	0.4
Assemblee_Gruyere	1.7	8.2	17.3	50.9	1.6	4.0	0.9	3.8	0.8	2.8	3.7	3.0	1.1
Assemblee_APXS	1.9	7.5	16.6	50.3	1.8	4.2	1.0	4.7	1.0	2.7	4.0	3.0	1.1
MC-Independence	3.6	2.1	20.9	65.7	0.0	0.0	0.6	3.3	0.6	0.05	0.0	1.9	0.1
MC-Assemblee	0.9	7.0	23.2	61.9	0.0	0.0	1.3	1.7	1.0	0.0	0.0	2.4	0.2

[a] Values are in wt% equivalent oxide. MC, major component, with composition derived as described in the text.

[b] Other is Cl + MnO.

[c] Corrected for Al_2O_3 contamination from wheel scuff.

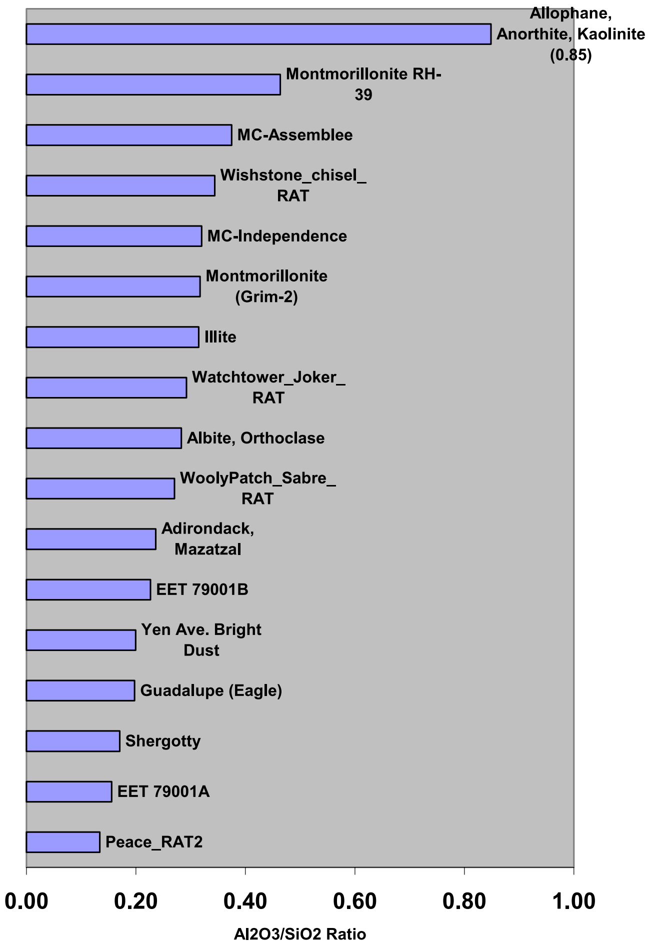

Figure 5. Al_2O_3/SiO_2 ratio for Independence class sample, selected minerals, Martian meteorites, and Martian rocks and soils. The Independence_Penn2 and other samples occupy the range common to a wide variety of montmorillonites but differ from most Martian geologic materials.

with (column B) correction for possible Al contamination from the wheel scuff (see below). As with Wishstone and Watchtower rock samples [*Ming et al.*, 2006], this analysis is strongly corundum normative, indicating that insufficient cations are present to account for all Al_2O_3 as feldspars. By terrestrial analogy, the excess silica and alumina are highly suggestive of alteration of plausible igneous source materials by aqueous-mediated geochemical separations.

[15] The element compositional profile of this major component does, in fact, correspond closely to the montmorillonite compositions encountered in a wide range of terrestrial settings, as shown in Figure 8. Not only are the SiO_2 and Al_2O_3 values within typical ranges of these compositions (H_2O-free), but all the major cations (Na, Mg, K, Ca) are present and at requisite low levels. Smectites like montmorillonite are well known for their high cation exchange capacities (CEC), which can incorporate some level of one or more of these cations [*Grim*, 1968].

[16] The Mg enrichment in Assemblee compared to the other Independence samples is still within the range for natural terrestrial montmorillonites, as seen in Figure 9. Interestingly, Dana's Mineralogy [*Gaines et al.*, 1997] distinguishes between low-Mg and high-Mg montmorillonite. The type montmorillonites for these, from Wyoming ("wyo") and Arizona ("cheto"), have been studied extensively by *Grim and Kulbicki* [1961]. They exhibit characteristically different aggregation morphologies on the microscale as well as different thermal phase transition profiles and cation exchange capacity. These low- and high-Mg montmorillonites are good matches in elemental composition to the Independence and Assemblee samples, respectively. The availability of magnesium has often been cited as favorable to the formation of montmorillonites [*Grim and Güven*, 1978; *Buol et al.*, 1980; *Ross and Hendricks*, 1945].

4.2. Anomalous Elements

[17] In Figure 10, the raw X-ray fluorescence emission spectra are shown for samples in the current Independence class. Compared to most other samples analyzed on the MER missions at Gusev crater and Meridiani Planum, these samples exhibit several anomalies in minor and trace elements. Although not uniformly present in all samples, there are anomalously high occurrences of Cr, Ni, Cu, Sr and Y (Table 3). Highlighted values are cases where the concentration measured is at or among the highest in more than 140 samples analyzed for trace elements by the Spirit rover through sol 809.

[18] In some samples, especially the clod, there is an anomalous occurrence corresponding to the X-ray K-shell alpha line for Y, equivalent to ~100 ppm concentration. This peak could actually be the smaller beta emission of Rb (the more intense Rb alpha line at 13.39 keV is overlain by the Pu L-alpha incoherent backscatter peak), but the Rb concentration would have to reach ~1,000 ppm to produce this beta peak. Considering the low potassium content of these samples and the low Rb concentrations in Martian meteorites (<7 ppm [*Lodders*, 1998]), Rb is not likely to be so highly enriched as to reach these levels.

[19] We considered several sources of contamination that might be responsible for the anomalous readings. The brush

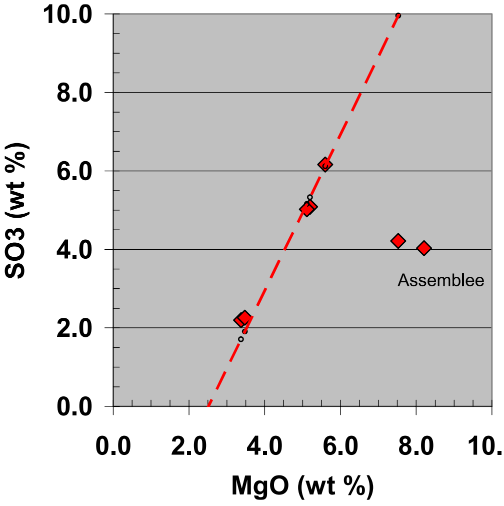

Figure 6. Independence class data for MgO and SO_3, showing strong correlation. Dashed line is stoichiometry for $MgSO_4$. Assemblee samples are MgO-rich (see text).

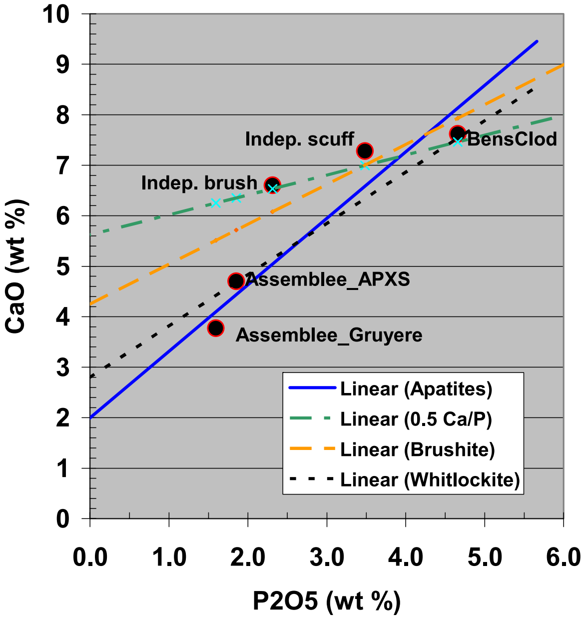

Figure 7. Ca and P data for Independence class materials (round dots). Although there is clearly a positive correlation, the stoichiometry is not well constrained, as shown by four possible trend lines for Ca/P atom ratios of 1.66:1 (e.g., apatites), 1.33:1 (whitlockite), 1:1 (e.g., brushite), and 1:2 (e.g., canaphite).

wires of the RAT are composed of stainless steel (alloy 302) which contains both Cr and Ni. Although excessive wear is not expected, a wire might detach and lay in the area analyzed. If the anomalously high Ni in the Independence_Livingston (brushed sample) were from a wire, the sample would also exhibit 0.65% Cr_2O_3, which is three times higher than the observed amount.

[20] The high Zn and Cu in the Independence_Penn2 scuff sample are suspect because they could include scrapings from the wheel paddles, which are made from an aluminum alloy (7075) containing significant levels of Zn, Cu and Mg in addition to Al, with possible Zn/Cu ratios of 2.5 to 5.0. Filings of paddle wheel material, below the anodize coating, have been taken from the Egress Test Rover and measured by laboratory X-ray fluorescence and electron beam X-ray emission. The Zn/Cu ratio found for the actual paddle material is 3.60 ± 0.18. The measured ratio for the Penn2 sample is 3.11 ± 0.36, which is indistinguishable within error bars. On the other hand, the Cu content of the Independence_Livingston brushed sample is the highest found, at 230 ppm, and shows no enhancement of Zn.

[21] Lead (Pb) has been detected in the sample Wishstone from two energy peaks (L alpha and beta X-ray emissions) which clearly distinguishes it from arsenic (with its single major emission at the same location as the Pb L alpha peak). Wishstone is a rock with Fe present in the forms of pyroxene, olivine, Fe^{3+} oxide, and ilmenite [*Morris et al.*, 2006], but apparently is partially altered, as discussed by *Ming et al.* [2006]. For the Independence_Jefferson sample, at the location marked "As?" in Figure 10, the emission is too small for a second peak to be detected. This peak, which is near the statistical limit of detection, could indicate either Pb or As.

[22] In addition, analyses of APXS raw spectra for trace elements not yet rooted to a quantitative concentration scale indicate apparent enrichments in barium for Independence and Ben's_Clod and a possible cobalt enrichment in Assemblee.

4.3. Mössbauer Mineralogy

[23] Four analyses were made on Independence class rocks by the MIMOS II Mössbauer (MB) spectrometer on Spirit (cf. *Klingelhöfer et al.* [2003] and *Morris et al.* [2006] for instrument description, operation, and data analysis procedures). Mössbauer mineralogy at Gusev crater through sol 510 is reported by *Morris et al.* [2004, 2006]. Between sols 530 and 573, four analyses were made on Independence class rocks. Three were on the outcrop rock Independence (undisturbed surface Independence_Franklin, RAT-brushed surface Independence_Livingston, and RAT-brushed and rover-scuff surface Independence_Penn2), and one was on the outcrop rock Assemblee (undisturbed surface Assemblee_Gruyere).

[24] MB spectra for Independence class rocks are shown in Figure 11. Five doublet subspectra (Fe2D2 assigned to pyroxene (Px), Fe2D3 assigned to ilmenite (Ilm), Fe2D4 and Fe3D5 assigned to chromite (Chr), Fe3D1 assigned to nanophase ferric oxide (npOx)) were fit to the spectra. Sextet subspectra were not detected. Least squares fitting procedures and assignments for Px, Ilm, and npOx are discussed by *Morris et al.* [2006]. The line width for Px in Independence_Penn2 (0.90 mm/s) is significantly larger than observed previously for rocks at Gusev crater (Ave ± 2σ = 0.51 ± 17 mm/s [*Morris et al.*, 2006]). This suggests that our physical model (one Px doublet) is oversimplified and that multiple octahedral Fe^{2+} sites are likely present. The chromite assignment is discussed below. The MB parameters center shift (δ), quadrupole splitting (ΔE_Q), and full widths at half maximum intensity (Γ) are compiled in Table 4, and MB areas for component subspectra (A) are in Table 5. The parameter δ is relative to metallic Fe foil at nominally the same temperature as the Martian surface target.

[25] The elemental and MB mineralogical compositions of Independence and Assemblee are distinctly different from the compositions of other rocks at Gusev crater [*Gellert et al.*, 2006; *Morris et al.*, 2006]. Both rocks have very low total Fe contents and Assemblee has a Cr concentration much higher than any other Martian sample to sol 833. The low Fe contents account for the low maximum values of signal-to-baseline for Independence samples (~0.02–0.05, Figure 11) compared to typical basalts on

Table 2. Normative Mineralogy Calculation for the Major Component-I of Independence_Penn2[a]

	A	B
Quartz	30.6	31.2
Corundum	7.6	5.0
Orthoclase	3.6	3.6
Albite	20.5	21.0
Anorthite	26.4	26.9
Hypersthene	11.1	11.3

[a] A, as measured; B, corrected for wheel contamination of Al.

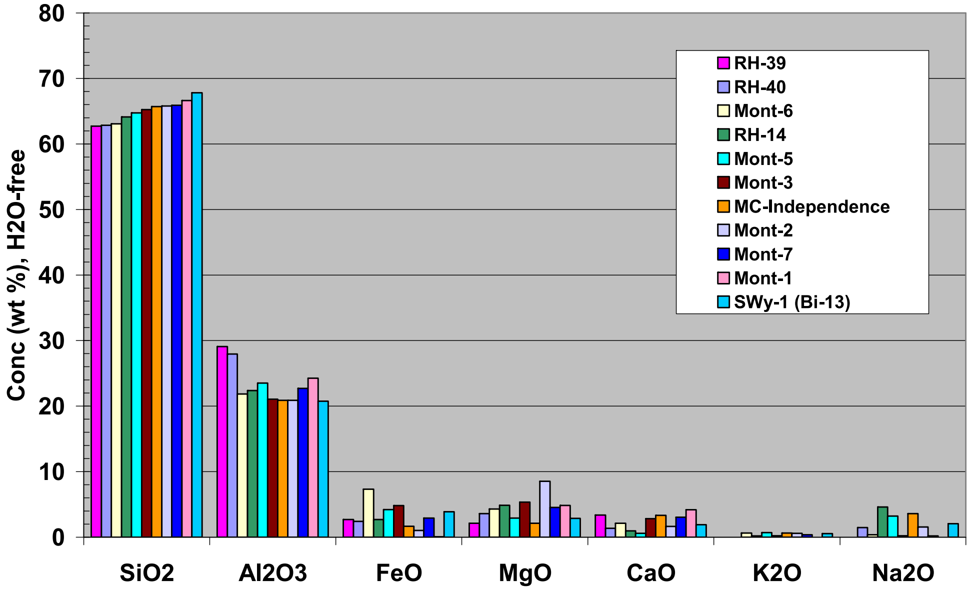

Figure 8. Comparison of terrestrial montmorillonites with sample Independence_Penn2 after removal of accessory minerals ($MgSO_4$, Ca phosphate, ilmenite) to determine the major component (MC). Data from *Grim* [1968] and *Ross and Hendricks* [1945].

the Gusev plains (~0.09) and consequently to the relatively poor counting statistics within allocated integration times.

[26] Independence MB spectra indicate 24–33% of its total iron from ilmenite ($FeTiO_3$). This high proportion of Fe from ilmenite corresponds to the high Ti/(Ti + Fe) molar ratios (0.12–0.31) as calculated from APXS data. For comparison, Adirondack class rocks have Ti/(Ti + Fe) ~ 0.02–0.04 and no detectable Ilm. Watchtower and Wishstone class rocks have comparable Ti/(Ti + Fe) molar ratios (0.12–0.18) but significantly less Fe from Ilm (<8%), implying a higher proportion of Ti is associated with phases other than Ilm for Watchtower and Wishstone class rocks relative to Independence. The values of Ti/(Ti + Fe) and total Fe for Independence Penn2 are the highest (0.31) and lowest (3.7 wt.% as FeO) values, respectively, reported to date for the Martian surface. Ilm was not detected in Assemblee (Ti/(Ti + Fe) ~ 0.10).

[27] We now focus on the identification of chromite, $Fe^{2+}(Cr,Fe^{3+})_2O_4$, in Assemblee. During least squares fitting of the Assemblee_Gruyere spectrum (Figure 11), we anticipated that the peak centered near 1.55 mm/s was the high-velocity peak of the ilmenite doublet, which we found near 1.54 mm/s in other Gusev samples. However, ilmenite did not give a physically acceptable solution during fitting procedures (negative subspectral area, which means negative concentration) when the low-velocity peak of the ilmenite doublet was used as a fitting constraint. Because of the high Cr concentration in Assemblee, we selected the values of δ and ΔE_Q for chromite as constraints in the fitting procedures. The values we used are listed in Table 4, and they were obtained from a transmission MB spectrum of a terrestrial chromite sample we obtained at 293 K. The spectrum and parameters are similar to those reported by *Chen et al.* [1992] for chromite spinels. These parameters worked well in the fitting procedures, giving both the chromite Fe^{2+} and Fe^{3+} subspectra (Figure 11); the relative subspectral areas of the two doublets was not constrained. The chromite accounts for about 23% of total Fe. Because the elemental concentrations of Cr in all other Gusev crater samples are much lower, we would not expect detection of chromite by MB in any other sample.

[28] The disproportionately high abundance of ilmenite in Independence, a relatively high abundance of npOx (Figure 11) and the low elemental concentration of Fe for both Independence and Assemblee are not consistent with

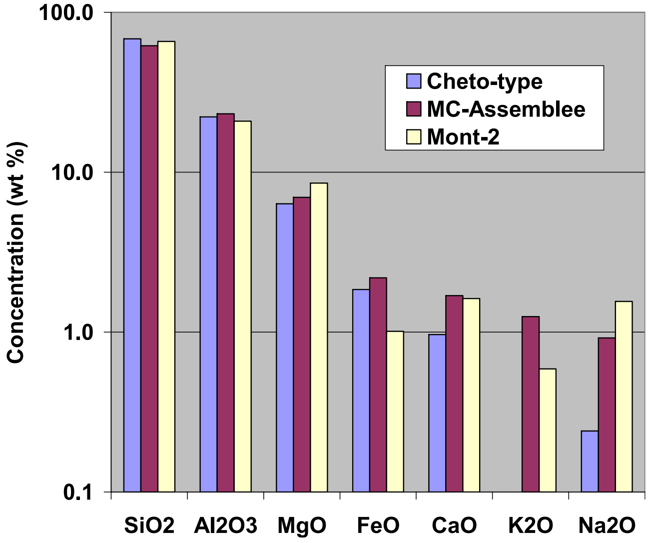

Figure 9. Comparison of MC-Assemblee (major component in Assemblee_Gruyere) with high-Mg montmorillonites, demonstrating correspondence in MgO and other cation concentrations. Chromite and 10% soil (Whymper) also have been removed from Assemblee. Cheto from *Grim and Kulbicki* [1961]; Mont-2 from *Grim* [1968].

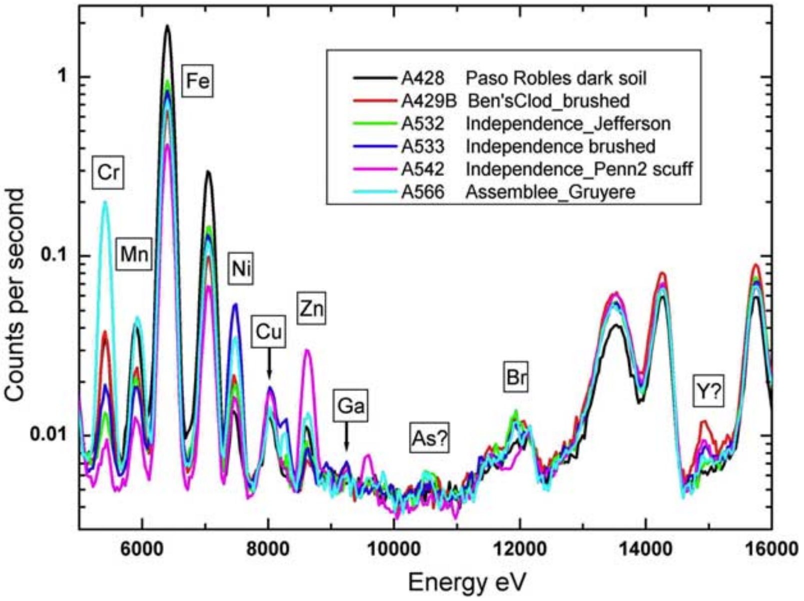

Figure 10. APXS X-ray fluorescence spectra for Independence class materials, with the exception of the dark soil (A428). "Y?" is yttrium (see text). "As?" could be arsenic but also is the location of one of the two Pb peaks.

igneous assemblages. We also note that the values of ΔE_Q for Px for Independence_Franklin, Independence_Penn2, and Assemblee (2.39–2.45 mm/s) are larger than all other values reported for Px at Gusev crater (2.00–2.25 mm/s [*Morris et al.*, 2006]) with the exception of analyses for Clovis class rocks. Clovis itself is a heavily altered rock (Fe^{3+}/Fe_T = 0.84) that has the highest reported goethite (α-FeOOH) content (37% of total Fe from Gt). Aqueous processes are implied by the presence of goethite. The observed assemblage for Independence and Assemblee implies alteration under aqueous conditions such that some elements are leached (e.g., Fe from olivine) and less soluble Fe-bearing phases remain (e.g., ilmenite and chromite). It is possible that Fe2D2 doublets with ΔE_Q in the range ~2.25–2.50 mm/s are Fe^{2+} products of alteration and not primary pyroxene.

4.4. Physical Characteristics

[29] The rough texture on the large scale occurs also on a smaller scale, as shown in the MI images of Figure 12. However, the characteristics of each sample are somewhat different, as is the nature of the roughness.

[30] Both Independence and the peds at Paso Robles II are apparently quite competent, as are many terrestrial peds when dried and when salt cementation (e.g., $MgSO_4$) is present. This competence is demonstrated by (1) the shallow dig of the scuff at Independence_Penn2, (2) the apparent abrasion of the wheel paddles during the scuff, and (3) the survival of peds at Paso Robles after being driven over by the rover wheels. Other than MB and MI instrument placements, no significant physical contact was made with Assemblee, although this object appears to be in a state of intermediate disintegration, with parting cracks in the main body and a halo of nearby peds (Figure 4).

4.5. Multispectral Imaging

[31] Pancam multispectral observations of Independence class materials are shown in Figure 13. Neither the main part of Assemblee (Figure 13a) nor the Independence_Penn2 surface post-scuff (Figure 13b) show the shallow minimum centered at 900 nm that is characteristic of soils observed by Spirit. Some spectra show a weak absorption trend over 860–930 nm that is characteristic of Fe^{3+} oxides in Martian soils and dust [*Bell et al.*, 2004], but without greater spectral coverage it cannot be stated with certainty

Table 3. Anomalous Elements for Independence Class Materials[a]

			% by wt			ppm				
Sol	Sample	State	Cr_2O_3	P_2O_5	K_2O	Ni	Cu	Zn	Sr	Y
A532	Independence_Jefferson	natural	0.09	3.2	**0.97**	600	0	120	140	<30
A533	Independence_Livingston	brushed	0.19	2.3	0.60	**2100**	**230**	100	160	50
A542	Independence_Penn2	scuff + brush	0.04	3.5	0.51	450	220[b]	670[b]	170	70
A429B	PR BensClod_brushed	brushed	0.47	**4.6**	0.65	600	<100	60	**340**	**110**
A566	Assemblee_Gruyere	natural	**2.85**	1.6	0.93	1300	<100	240	130	<30
A571	Assemblee_APXS	natural	**2.68**	1.8	**0.99**	1200	<100	250	180	<30

[a] Results for trace elements Sr and Y are preliminary, pending further APXS instrument calibration, but indicate relative abundances between samples.
[b] Primarily due to contamination from wheel scuff.

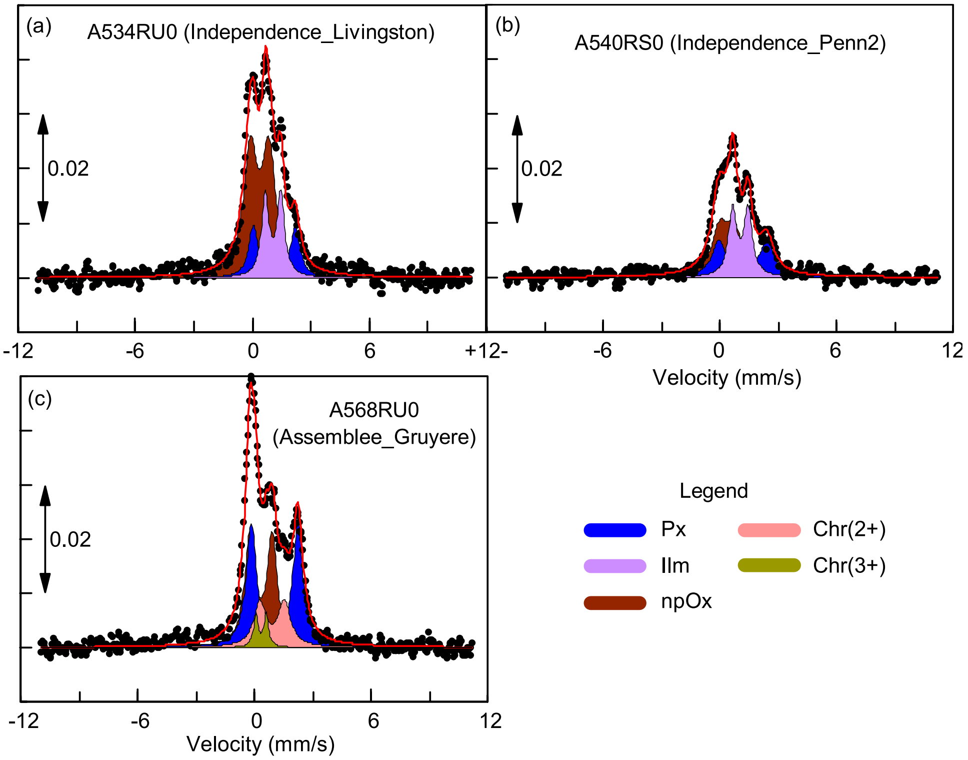

Figure 11. Mössbauer spectra and component subspectra from least squares fits for Independence class rocks (a) A534RU0 (Independence_Livingston), (b) A540RS0 (Independence_Penn2), and (c) A568RU0 (Assemblee_Gruyere). The spectrum of A530RU0 (Independence_Franklin) is similar to that for Independence_Penn2. The parameter TC/BC - 1.0 is the ratio of total counts to baseline counts (obtained from the least squares fitting procedure) minus 1.0.

whether the same mineral phases in Martian soil are responsible for the weak absorption feature seen, for example, in Bruce rock and Ben's_Clod.

4.6. IR Spectroscopic Mineralogy

[32] Mini-TES measured two 200-scan spectral stares on Independence, one targeting the scuff and a second away from the scuff. No significant differences are apparent in the spectra (Figure 14) although the scuffed portion of the target is small. Other examples of Independence-like rocks occur nearby based on their similar texture and relatively light tone, two of which were observed by Mini-TES. All appear to be contaminated by varying amounts of dust and soil. The rocks Abigail and Whistler are included to demonstrate some of these variations. Two 200-scan stares were acquired of the same spot on Assemblee but from two different sols, resulting in nearly identical spectra. Spectral data were calibrated and corrected for dust on the pointing mirror according to the provisional methodology of *Ruff et al.* [2006]. As shown by Figure 14, the Independence rocks and

Table 4. Mössbauer Parameters δ, ΔE_Q, and Γ for Fe2D2 (Px), Fe2D3 (Ilm), Fe2D4 (Chr), Fe3D5 (Chr), and Fe3D1 (npOx) Doublet Subspectra for Independence Class Rocks[a]

	Fe2D2[b] (Px)			Fe2D3 (Ilm)			Fe2D4 (Chr)			Fe3D5 (Chr)			Fe3D1 (npOx)			
Generic Name (Assignment)	δ, mm/s	ΔE_Q, mm/s	Γ, mm/s	δ, mm/s	ΔE_Q, mm/s	Γ, mm/s	δ, mm/s	ΔE_Q, mm/s	Γ, mm/s	δ, mm/s	ΔE_Q, mm/s	Γ, mm/s	δ, mm/s	ΔE_Q, mm/s	Γ, mm/s	T, K
A530RU0 (Independence_Franklin)[c]	[1.19][d]	[2.45]	[0.90]	[1.07]	[0.80]	[0.51]	–	–	–	–	–	–	[0.38]	[0.76]	[0.96]	210–290
A534RB0 (Independence_Livingston)	[1.13]	[2.14]	[0.59]	[1.07]	[0.80]	[0.45]	–	–	–	–	–	–	0.38[e]	0.95	0.86	210–290
A540RS0 (Independence_Penn2)	1.19	2.45	0.90	[1.07]	[0.80]	[0.51]	–	–	–	–	–	–	0.38	0.76	0.96	210–290
A568RU0 (Assemblee_Gruyere)	1.05[f]	2.39[f]	0.64[f]	–	–	–	[0.92]	[1.26]	[0.76]	[0.35]	[0.53]	[0.28]	0.34[f]	1.16[f]	0.63[f]	200–280

[a] Parameters were calculated from spectra summed over the temperature interval given in the last column. The values of δ are referenced to metallic iron foil at the same temperature as the sample.

[b] Doublet naming convention: FexDy; x = is Fe oxidation state; y = sequential number.

[c] Target naming convention: Awwwxyz (Feature-name_Target-name); A = MER-A (Gusev Crater); www = Gusev Crater sol number that data product was returned to Earth; x = R (rock); y = U (undisturbed), B (RAT-brushed surface), or S (rover wheel scuff surface); z = 0 by default. Alphanumeric strings before parentheses are unique target identifiers. For integrations covering multiple sols, the sol of the first returned data product is used.

[d] MB parameters in brackets are constraints used in the fitting procedure.

[e] Unless otherwise stated, MB parameter uncertainty is ±0.02 mm/s.

[f] MB parameter uncertainty is ±0.04 mm/s.

Table 5. Mössbauer Areas for Component Subspectra, Fe^{3+}/Fe_T, and Temperature Measurement Interval for Mössbauer Spectra for Independence Class Rocks at Gusev Crater[a]

Generic Name Phase Assignment	Fe2D2 Px, %	Fe2D3 Ilm, %	Fe2D4 Chr, %	Fe3D4 Chr, %	Fe3D1 npOx, %	Sum, %	Fe^{3+}/Fe_T	T, K
A530RU0 (Constitution_Franklin)	35[b]	26	0	0	39	100	0.39[c]	210–290
A534RB0 (Independence_Livingston)	20	24	0	0	56	100	0.57	210–290
A540RS0 (Independence_Penn2)	32	33	0	0	35	100	0.35	210–290
A568RU0 (Assemblee_Gruyere)	44	0	19	4	32	100	0.37	200–280

[a] A, Mössbauer areas. Component subspectra are (f-factor corrected).
[b] Uncertainty in subspectral area is ±3% absolute unless otherwise stated.
[c] Uncertainty in Fe^{3+}/Fe_T is ±0.03.

Assemblee are spectrally dissimilar from one another despite certain chemical similarities. This is most evident and most compellingly displayed in the low wave number range (<600) where Assemblee shows a deep, relatively narrow absorption feature compared to the much shallower absorption and fine structure of the Independence spectra in this range. Although differences in surface dust accumulation could account for some of the spectral differences [*Graff*, 2003], it is not possible to combine the spectral features of surface dust and those of Assemblee to produce the Independence spectra. We conclude then that there are mineralogical differences between the two.

[33] The emissivity spectra of Independence rocks and Assemblee do not contain the features obviously attributable to montmorillonite, or any aluminous, dioctahedral phyllosilicates as outlined by *Michalski et al.* [2006] and shown in Figure 14. A broad absorption between 900 and 1250 cm^{-1} indicates that the rocks contain multiple aluminosilicate components, but the absence of a doublet in the low wave number range (<600) significantly diminishes the potential for a substantial dioctahedral phyllosilicate component. The relatively low spectral contrast of the Independence rocks could be an indication of a porous surface texture that contributes a blackbody-like component to the emission spectrum, but again, this is insufficient to fully mask the spectral features of the rocks.

[34] We used a linear-least squares spectral deconvolution algorithm to quantitatively model the mineralogy of Independence and Assemblee [*Ramsey and Christensen*, 1998]. The two Independence spectra along with the two similar rocks were averaged together for the deconvolution in an effort to minimize the effects of dust and soil contamination. We included a mix of primary igneous minerals, crystalline phyllosilicates, amorphous silicates, and sulfates in the spectral end-member library. Various combinations of this library were used in multiple runs of the deconvolution algorithm. The best fit results are dominated by amorphous aluminosilicate phases with lesser primary igneous and sulfate phases. No combination of end-member spectra yielded any phyllosilicate phases in the modeled result. One way to judge the goodness of fit of the spectral model is by visibly comparing the measured and modeled spectra. In the best fit case, the spectral match is still relatively poor (Figure 15). There are clear mismatches throughout the full spectral range suggesting that the modeled mineralogy should be interpreted cautiously. Possible causes for the poor fit and the apparent absence of clay minerals include: dust and soil contaminants that are not properly modeled; the presence of allophane or other phases that are not included in our current spectral library; the possibility that clay-sized particles dispersed throughout a matrix of other grains may be difficult to detect [*Michalski et al.*, 2006]; and possible inaccuracies in the mirror-dust correction [*Ruff et al.*, 2006].

[35] Deconvolution of the Assemblee spectrum yielded a much better fit than that achieved with Independence (Figure 15). The quality of the fit suggests that the spectral end-members used in the deconvolution were sufficient to model this spectrum. Amorphous aluminosilicate components dominate the modeled results with lesser sulfate, and only minor primary igneous components. Clay minerals

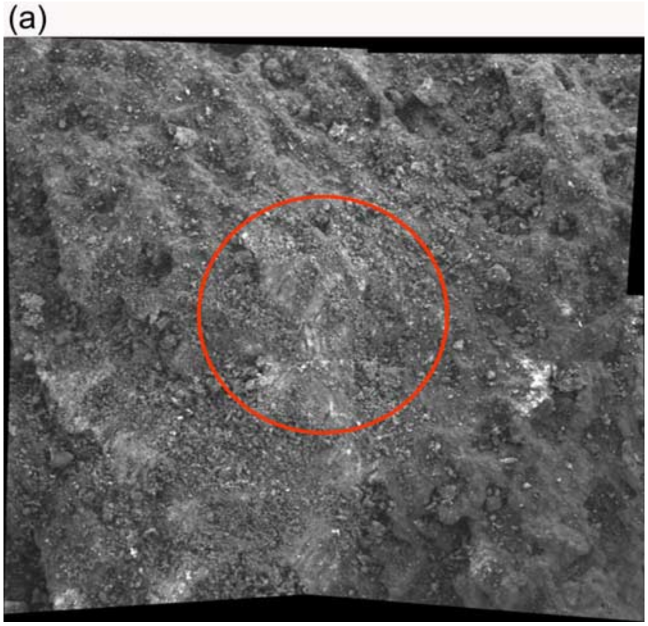

Figure 12. (a) Mosaic of MI images of Independence_ Penn2 after target was scuffed by a rover wheel and brushed by the RAT. The RAT brushing operation did not remove all of the fine grains on the surface of the target, which partly fill pits in the rock surface. The mosaic is 5 cm across. The target was completely shadowed when the images were acquired. (b) MI of Ben's_Clod, on the portion analyzed by APXS (no MB was performed on this target). (c) Radiometrically calibrated MI image 2M177053218 of Assemblee acquired on Sol 571. Illumination is from the top; image is 3 cm across. This clastic rock is poorly sorted, with subrounded grains in a fine-grained matrix. Note specular reflections from many parts of the target, suggesting perhaps a coating, in contrast with the rough surface of the overall object.

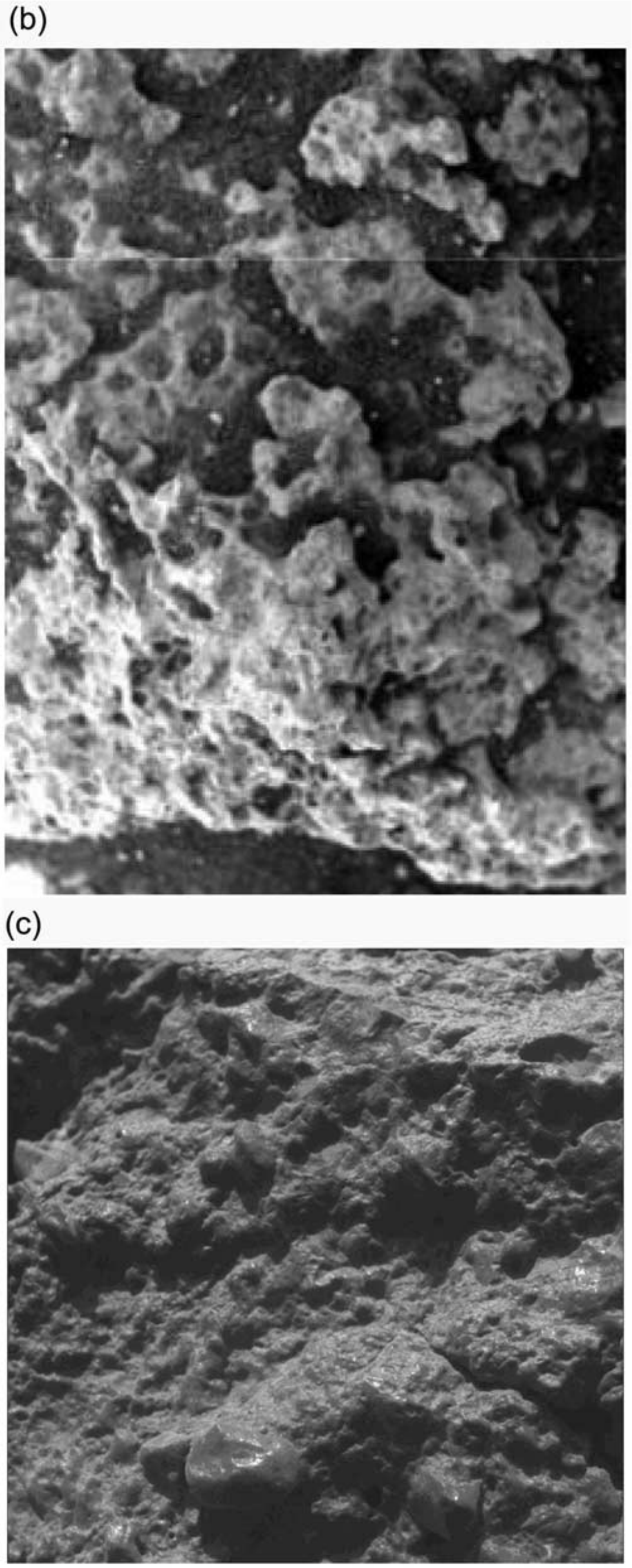

Figure 12. (continued)

appear as only trace components (<5%). It is noteworthy that maskelynite is one of the modeled amorphous components at ~15–20% abundance following normalization for dust and the slope component used to account for temperature error [*Ruff et al.*, 2006]. This suggests the possibility of impact processes in the formation of Assemblee.

[36] Several important conclusions can be drawn from the Mini-TES analysis of Independence and Assemblee. The results do not demonstrate a large component of crystalline clay minerals, including montmorillonite. However, the spectral character and modeled components of both rocks are distinct from typical basaltic materials and the results are consistent with an interpretation of Independence and Assemblee as altered rocks. Modeled aluminous silica could correspond to (1) pure aluminous silica (with structural Al^{3+}), (2) an intimate mixture of pure opal with an aluminous phase like allophane, or (3) primary felsic glass of similar composition [*Michalski et al.*, 2004]. The modeled sulfate abundances are consistent with inferred abundances from APXS data. The modeled basaltic glass component could correspond to primary glass, or possibly to an amorphous secondary phase(s) of similar composition that is not represented in our library. Mini-TES observations of Independence and Assemblee favor an interpretation of amorphous mineralogy over crystalline clay mineralogy.

5. Discussion

5.1. Surficial Versus Bulk Alteration

[37] Although the APXS instrument senses material only within the upper tens of micrometers of typical geologic specimens, it is likely that the Independence class analyses reflect a deeply altered material rather than a weathering

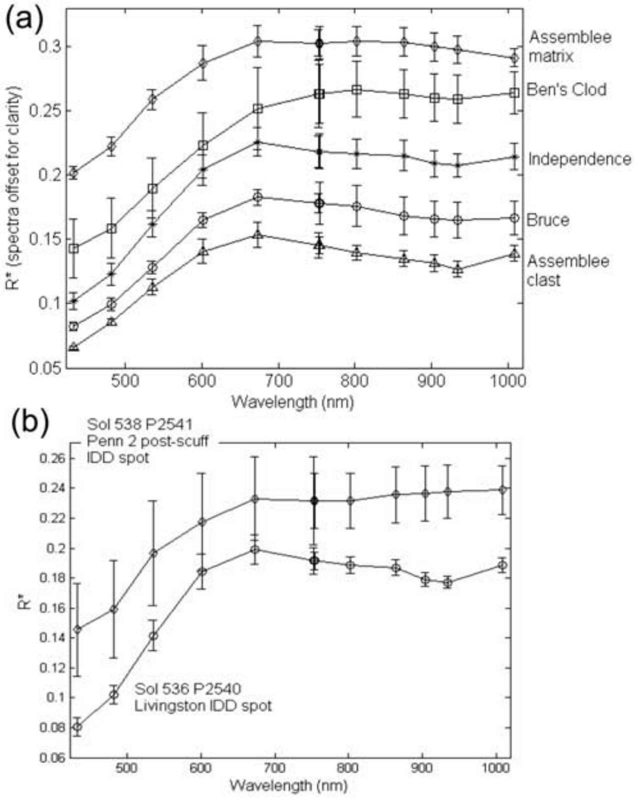

Figure 13. Pancam spectra of Independence_Penn2 and other Independence class samples (all spectra have separate vertical offsets for clarity).

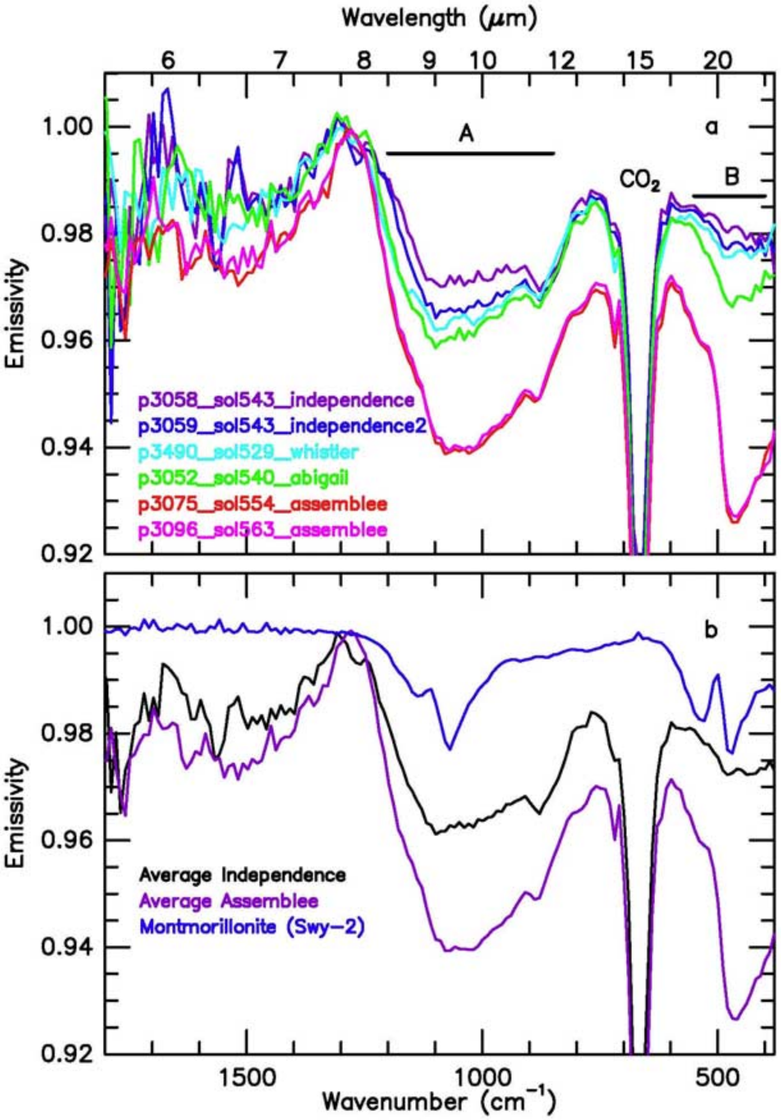

Figure 14. Calibrated, mirror dust-corrected Mini-TES infrared spectra of outcrop target Independence, two rocks near Independence, and Assemblee. (a) The Independence-area spectra share similar features but are dissimilar to Assemblee. All display features attributable to aluminosilicate stretching absorptions (A) and aluminosilicate bending absorptions (B) as well as CO_2 absorption due to the atmospheric path between the surface target and the instrument. (b) The average Independence and Assemblee spectra compared to a montmorillonite spectrum (SWy-2) scaled to the equivalent of 20% abundance. The Martian rock spectra lack the distinctive low wave number doublet (<600) of dioctahedral clays like montmorillonite.

rind. First, brushing the outcrop resulted in markedly lower measurements of Fe and Mg and a higher Al/Si ratio than the unbrushed surface. Second, the rugged surface and cracks of Assemblee, the nearby peds, and the peds at Paso Robles II are consistent with a pervasive alteration. Third, the weathering rinds of basalts under common terrestrial weathering conditions are typically enriched in Fe and depleted in Si, opposite the Independence class trends, and do not contain phyllosilicate minerals [*Colman*, 1982].

5.2. Geologic Occurrences of Independence Materials

[38] Independence class materials may arise from bedded or lenticular deposits. Certainly the type-sample after which the class is named is an outcrop (Figure 2). Assemblee does not have the appearance of a free-standing block (Figure 4a) and may also be an outcrop, as suggested by its flanking pedestals, apparent partial submergence, and halo of smaller objects of similar morphology. The apparent collection of similar peds at Paso Robles II, taken together with the texture of the surrounding undisturbed surface, likewise argues for a more extended substrate of the material that only locally protrudes when loose fines are stripped away by deflation. Candidate natural mechanisms for formation of surrounding fragments from a more massive deposit are many, including fracturing by stresses from freeze/thaw cycles, repeated extreme thermal excursions, recurring wind

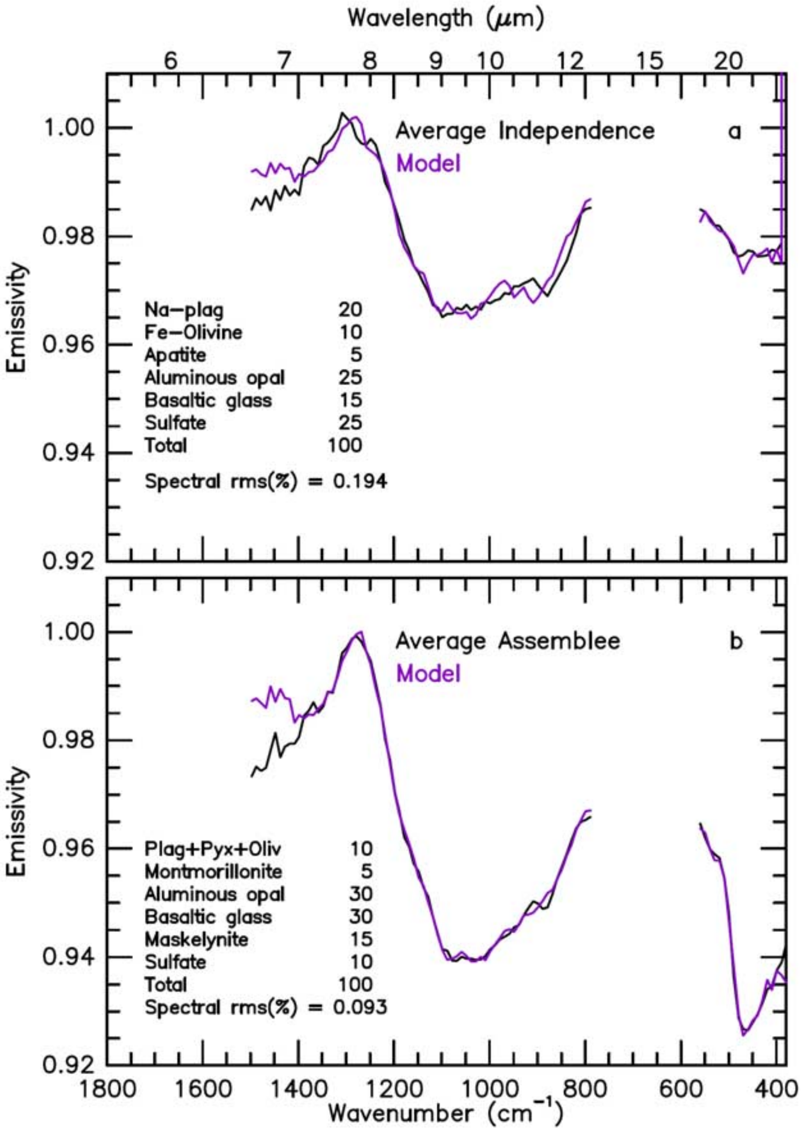

Figure 15. Deconvolution of Independence and Assemblee spectra. (a) The deconvolution of the average Independence spectrum yields a relatively poor model fit, an indication that the modeled components may have some significant errors. (b) The modeled fit of Assemblee is very good, an indication that the deconvolution results are robust. See text for a discussion of possible interpretations of the various components.

gusts, or mild impact by small secondary ejecta. If this material indeed contains $MgSO_4$ salts and/or an expansive smectite, such as montmorillonite, formation of peds could also be facilitated by hydration/dehydration cycles under fluctuating levels of ambient humidity or wetting by melting of transient frost.

[39] The three locations of Paso Robles, Independence and Assemblee are relatively distant from one another. From Paso Robles II to Assemblee encompasses 27 m in increased elevation and nearly 200 m in surface separation [*Li et al.*, 2006]. Assemblee rock was found at an altitude only 13 m below Husband Hill's summit, which itself is more than 106 m above the Gusev plains. The downhill location of the Paso Robles peds could be consistent with translocation by mass wasting. The Independence occurrence manifests itself as an outcrop, but is topographically some 15 m lower than the Assemblee object at the Voltaire outcrop.

[40] Wishstone rocks have been found both below and above Independence class materials [*Ruff et al.*, 2006], while the entire sequence of Watchtower class rocks and outcrop were encountered above Paso Robles and below Independence outcrop.

[41] Other candidate Independence class materials have been seen but not analyzed by the in situ instruments. An earlier set of peds and very light-toned material, seen at "Hank's Hollow" at the foot of Husband Hill (sols 158–165) [*Arvidson et al.*, 2006], has been suggested by one of us (LR) to have interesting similarities to the Paso Robles setting. Multispectral Pancam imaging a distant light patch on a small hill east of Haskin Ridge was inconclusive. A rough object heavily draped by aeolian material was imaged on sol 619. Pancam imaging on sol 673 while approaching the Seminole target showed the rover crossed over light-toned materials reminiscent of Independence. A rough clod

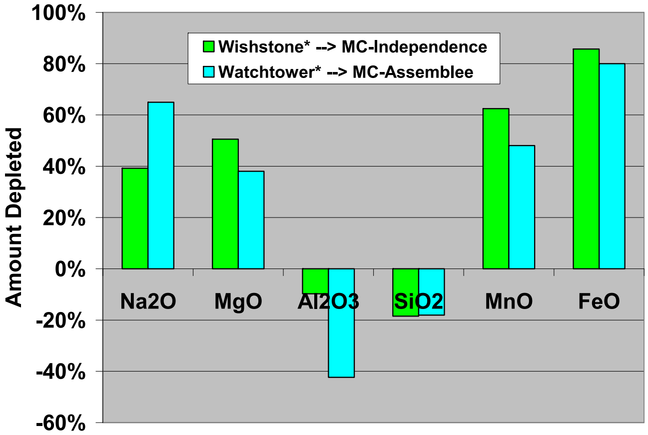

Figure 16. Depletion factors for key elements, comparing samples after removing putative accessory minerals of $MgSO_4$, Ca-phosphate, ilmenite, and chromite (factors are calculated for residual whole-rock compositions normalized to 100 wt%).

or ped proximate to the Arad Dead Sea ferric sulfate-rich material of sol 724 is similar in appearance to the Independence class ped at the Paso Robles II ferric sulfate occurrence.

5.3. Genetic Relationships

[42] The provenance of these presumed altered outcrops is unclear because of our as-yet incomplete understanding of the stratigraphy of Husband Hill [*Squyres et al.*, 2006], but chemical relationships may offer a clue. The commonality of the P-Ti-Cr fingerprint indicates a possible genetic relationship among three classes of materials, i.e., Independence, Wishstone and Watchtower classes. Intriguingly, the Na is lower but Mg is significantly higher in Assemblee compared to Independence outcrop, while the same is true for Watchtower compared to Wishstone, and by about the same degree. Furthermore, the Cl/SO_3 ratio for Assemblee is about 50% higher than in Independence, and the same is also true for Watchtower compared to Wishstone. Finally, the Zn is elevated in both Assemblee and Watchtower (element compositions for Wishstone_chisel_RAT and Watchtower_Joker_RAT are from *Gellert et al.* [2006]).

[43] If Independence_Penn2 is an alteration product of Wishstone class rocks, a certain extent of mobilization of major cations would be required. If Assemble were also derived from Wishstone, different degrees of mobilization would be required, especially for Na and Mg. If, however, Assemblee were instead derived from some Watchtower class material, we found that the degree of mobilization, expressed as depletion/enrichment factors in Figure 16, is highly similar. This surprising relationship could result if similar environmental conditions and processes controlled the alterations in both cases. Anomalous concentrations of certain minor or trace elements, most notably Cr, may be due to separate enrichment processes.

5.4. Anomalous Element Concentrations

[44] Montmorillonites often contain enrichments of minor or trace elements. In the tetrahedral coordination layer of the mineral, Si may be substituted by P. In the octahedral coordination layer, Al may be substituted by Li, Cr, Zn, or Ni (as well as by Mg or Fe). Furthermore, the extensive CEC of montmorillonites can be accommodated by a variety of cations, from H^+ to heavy metals. Monovalent cations, such as Na^+ or K^+, are often more readily replaced by the more favorable divalent cations, such as Ca^{2+} and Mg^{2+}, which in turn can be displaced by trivalent ions such as Al^{3+} or Fe^{3+}. A large radius for the hydrated ion favors displacement [*Grim*, 1968]. For these reasons, certain metals are often found in smectites. Common trace elements enriched to ppm levels in montmorillonite and bentonite analyses are cations such as B, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Ba, REE (rare earth elements) and Pb [e.g., *Jenkyns*, 1986; *Ruffell et al.*, 2002; *Taylor and McLennan*, 1985]. Trace element abundances in phyllosilicates are a combination of the above physicochemical affinities, as well as their available concentrations and susceptibilities to mobilization, especially by aqueous leaching.

[45] As tracers of hydrothermal alteration versus volatile release (magmatic degassing), *Newsom and Hagerty* [1997, 1999] ascribe Pb enrichments to both processes, but Pb also has affinity to minerals with ion exchange. Florida phosphatic clay, a mixture of apatite and phyllosilicates (montmorillonite and kaolinite), exhibits enhanced sorption affinity and fixation capability for Pb, compared to Cd and Zn [*Singh et al.*, 2001]. Interestingly, Wishstone rock exhibits not only the striking Pb component, but also the highest P and Ca of rocks in Columbia Hills.

[46] It should be noted that APXS analyses are outside the energy range of low-Z elements, such as B and Li. Furthermore, the x ray emissions from elements such as V, Co, Ba, Cd and Ce are overlain by interfering lines from more common elements and might not be detectable unless at unusually high values, while U is overlain by backscatter peaks.

[47] Tracers of hydrothermal alteration include several of the clay-affinity elements, but also Li, F, Rb, Ag, Sb, Cs and Au, according to the synthesis of *Newsom and Hagerty* [1997]. Most of these are beyond APXS analysis capability except potentially the difficult cases of Rb, Cs and Au. The same authors also point out the value of Zn as a tracer for magmatic volatile release. Martian soils are rich in Zn [*Yen et al.*, 2005], but are not significantly enhanced in Independence class materials (except for the scuff sample, which appears to result from contamination by wheel Zn, Cu and Al). Elements which are found in some Independence samples at levels considerably higher than for other samples in Gusev crater include Cr, Ni, Cu, Sr, Y and K.

5.4.1. Chromium

[48] Typically, Cr appears in igneous rocks as chromite and as a minor constituent of pyroxenes; in sediments and soils, Cr is concentrated in the clay size mineral fraction of the weathering products [*Ilton*, 1999; *Marshall and Fairbridge*, 1999]. In the highly oxidizing environment of Mars [*Hunten*, 1979], there is the potential that the rarer Cr^{6+} may be produced, which is of geochemical interest because of enhanced solubility, and of special concern for the future because it is toxic and a known carcinogen. Wishstone, Watchtower, and several of the Independence class materials are strikingly deficient in Cr, with values below the minimum detection limit of APXS of about

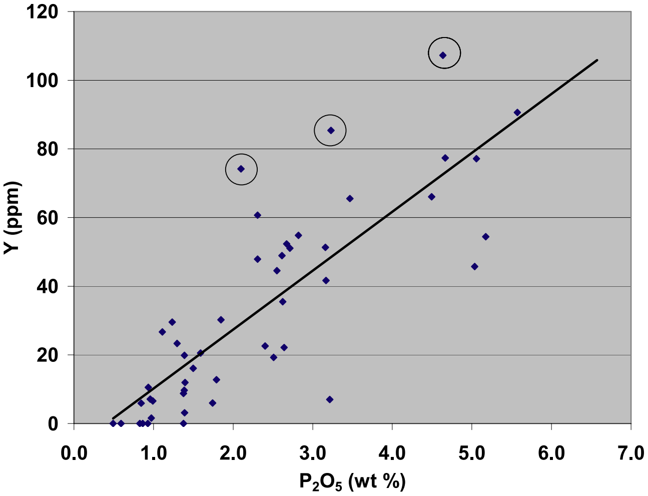

Figure 17. Yttrium trends with phosphorus content. Line is a linear least squares fit ($R^2 = 0.67$), including all plotted data. Circled samples anomalously high in Y are (from highest to lowest) Ben's_Clod, Bourgeosie_Chic clast, and HangTwo soil (see text).

0.03 wt%. In contrast, values of Cr are in the range of 0.1 to 0.7% for Martian meteorites [*Lodders*, 1998], which is also true for Gusev plains rocks [*McSween et al.*, 2004] and soils, and Meridiani samples. However, the Assemblee samples are anomalously high in Cr_2O_3, at 2.8 wt%. If resulting from chromite grains, they could account for 1.3 wt% of FeO, or one-fifth of the Fe in those samples. If present as a cation, exchangeable Cr could account for 1.0% Cr_2O_3 by weight of the sample if occupying one-half the available CEC sites of a typical montmorillonite (1 mEq/g). Cr-rich clays, up to 15%, have been reported by several authors [*Weaver and Pollard*, 1973]. As a trivalent cation, Cr can also readily substitute for Fe^{3+} and Al^{3+} in many minerals, and for Ca in diopside.

5.4.2. Nickel

[49] Ni in Martian soils has been investigated by *Yen et al.* [2005], but concentrations are generally limited to the range of 500–700 ppm, with the exception of some rocks and nearby soils along West Spur in which Ni reaches almost 900 ppm. One portion of Independence outcrop (brushed) contains 2000 ppm Ni, and the Assemblee samples assay at 1200 ppm. Numerous igneous minerals, especially olivines, provide Ni, which is easily mobilized during weathering and often enriched in weathering products, including silico-ferric gels such as iddingsite [*Galoisy*, 1999; *Martini and Chesworth*, 1992]. Ni^{2+} is an exchangeable cation, but can also be structurally incorporated into nickeliferous smectites to reach values up to 22% Ni [*Martini and Chesworth*, 1992]. Alternatively, Assemblee could be a breccia incorporating Ni-rich meteoritic infall material.

5.4.3. Copper

[50] Readily entering solution during weathering, especially enhanced by acidic Fe-sulfate solutions, Cu is subject to immobilization by adsorption as well as by precipitation [*Williamson*, 1999]. Cu enrichment up to 200 ppm occurs in the one Independence site (brushed), and Cu is also present in the scuff but is questionable because of probable contamination by abrasion of the wheel.

5.4.4. Strontium

[51] Alteration of feldspars or clinopyroxene liberates Sr, and it is strongly absorbed by clay minerals or taken up in carbonates [*Simmons*, 1999]. The Sr content of Martian meteorites (SNCs) ranges from 7 to 75 ppm [*Lodders*, 1998], much lower than in Independence class samples in Columbia Hills (Table 3).

5.4.5. Yttrium

[52] In chloride or sulfate form, Y is quite soluble [*Vickery*, 1960]. Y is significantly mobilized, especially relative to Ti and Nb, in the early stages of weathering during the growth of clay minerals [*Hill et al.*, 2000]. Yttrium and the rare earths are enriched in many smectites, including the Shanklin bentonite [*Ruffell et al.*, 2002]. Montmorillonite can have selectivity for adsorption of trivalent yttrium, compared to a univalent ion, at moderate to low temperatures and across a wide range of pH [*Frysinger and Thomas*, 1960]. The highest concentrations of Y are typically found in phosphate minerals and substituting for Ca [*Vickery*, 1960]. APXS results reveal a correlation between Y and P, Figure 17.

[53] The concentration of Y is 2 to 3 times higher in Watchtower class rocks than in Shergottites, but Independence class and the Paso Robles materials contain more Y, with the clod at approximately 100 ppm (compared to 6 – 31 ppm for shergottites [*Lodders*, 1998]). Hence the inferred Ca phosphate that is nearly ubiquitous in upper Husband Hill may be an important source of Y, but the enrichments observed may also result from adsorption by mobile alteration products of aluminosilicates. Another interesting deviation is the ~85 ppm Y in sample Bourgeosie_Chic, a large clast at Voltaire which exhibits some characteristics of both Wishstone and Watchtower, and has the highest K_2O content of all samples analyzed during the ascent of Husband Hill (Backstay, Assemblee and one Independence sample have the next highest K_2O) and the lowest Fe except for the Independence class samples themselves. Summit soil HangTwo also has an uncharacteristically high Y/P ratio (Figure 17).

5.4.6. Potassium

[54] In Viking soils, Meridiani soils and sediments, Martian meteorites, and in most Gusev samples, K_2O is significantly less than 1% by wt (0.03 to 0.3%, typical; 0.8% maximum). Only at the Pathfinder site does K_2O range up to 1.3% [*Brückner et al.*, 2003; *Foley et al.*, 2003]. However, Assemblee contains about 1%, and nearby Bourgeousie_Chic contains about 1.5% (note: these are unbrushed samples, and the K_2O could be higher in the bulk material). In montmorillonites and some other phyllosilicates, potassium can be "fixed" so that it is no longer exchangeable, especially if they have experienced strong drying [*Grim*, 1968] and have a high interlayer charge.

5.5. Mineralogic Alternatives to Montmorillonites

[55] There is no confirmation of montmorillonite at this site by the Mini-TES thermal IR spectrometer. With Independence, this could be partially due to overrepresentation by surface dust or soil contamination because the field-of-view of the instrument is significantly larger than the

cleaner, scuffed portion of the outcrop. Alternatively, the rough texture of this material could be providing a "stealthy" IR signature which is not totally representative of composition [*Kirkland et al.*, 2003]. It is also possible that Independence materials contain poorly crystallized forms of the mineral [*Michalski et al.*, 2006] or simply precursor gels. This latter explanation can be applied to Assemblee as well, but given the good quality of its spectrum and deconvolution results, contamination and/or texture likely are not masking a montmorillonite signature.

[56] Palagonite formed from mafic glasses of compositions like Wishstone or Watchtower class rocks is not indicated. Independence materials do not show the palagonitization trends of enrichment in Ti, Fe, Al and minor P, accompanied by depletions in Ca [*Bouska et al.*, 1993; *Staudigel and Hart*, 1983; *Morris et al.*, 2000]. All trends are opposite.

[57] Zeolites have been suggested as weathering products on Mars [*Ruff*, 2004], and are a candidate here because of their low Fe content. Most zeolites, such as clinoptilolite and erionite, have a lower Al_2O_3/SiO_2 ratio (0.2) than the major components of Independence samples (0.32 and 0.38 for Independence MC and Assemblee MC, respectively), and contain very minor or no MgO. Most with $Al_2O_3/SiO_2 > 0.3$, have too high CaO or NaO content, with the exception of some varieties of faujasite [*Ming and Mumpton*, 1989]. However, faujasite is rare in terrestrial settings [*Wise*, 1982], and the Mg-enriched variety that best matches the Assemblee major component is even more rare. Although the overall elemental composition does not favor the presence of zeolites, multicomponent mixtures of zeolites potentially could have such a composition.

[58] As an alternative to smectites, the compatible Al/Si ratio could be explained by fortuitous proportions of silica (52%–60%) mixed with allophane or imogolite. Allophane is also a well-known alteration product of basalt and can have relatively high CEC, but exhibits this property only under high pH conditions [*Wada*, 1989; *Weaver and Pollard*, 1973].

[59] Furthermore, montmorillonite may have formed, then been altered by strong-acid hydrolysis, burial diagenesis, contact metamorphism or some other degradation mechanism that was relatively isochemical in its process. In all cases, significant CEC and H_2O-uptake properties are usually present in amorphous material, although not so pronounced as in a mature smectite.

6. Implications for Aqueous Processes on Mars

6.1. Mode of Origin

[60] On Earth, montmorillonites result from aqueous alteration of igneous rocks by a variety of pathways. The most common origin of bedded quantities of montmorillonite is from in situ alteration of volcanic ash or tuff deposits under poorly drained, alkaline conditions with availability of Mg [*Gaines et al.*, 1997; *Grim and Güven*, 1978; *Ross and Hendricks*, 1945]. Eluviation from the original deposit can translocate the material to form a separate bed.

[61] Hydrothermal alteration of basaltic glass or other igneous materials is a well-known method of producing smectites, and even deuteric alteration by entrained volatiles following volcanic emplacement can produce smectites along joints or in amygdules [*Grim and Güven*, 1978].

[62] The occurrence of rounded clasts in Assemblee (Figure 4b) and the high-Cr content may also be indications that this material has been subjected to significant aqueous processing.

6.2. Detection of Alteration Zones by Orbital Remote Sensing

[63] Many, perhaps most rocks in Columbia Hills have been subjected to intermediate levels of aqueous alteration [*Ming et al.*, 2006; *Morris et al.*, 2006], and it is concluded here also that Independence class samples experienced major aqueous alteration. However, the optical signatures and morphologies of these materials do not clearly reveal these degrees of alteration in most cases. Furthermore, their areal extent, compared to the pervasive soils, is relatively small. Spectral remote sensing from orbit, with ground tracks on the order of km per pixel, will not necessarily reveal these chemical and mineralogical signatures of past episodes of aqueous activity. Only where such products are highly concentrated, such as the hematite spherules at Meridiani (sensed by TES [*Christensen et al.*, 2000b]) and major deposits of salts or smectites (sensed by OMEGA [*Bibring et al.*, 2005]) will the occurrences be detected. Aeolian activity on Mars redistributes large quantities of dust and even sand-sized grains, resulting in widespread masking of the intrinsic bedrock and sedimentary bed forms. For these reasons, it cannot be excluded that far larger portions of the Martian surface of a variety of geologic ages have undergone aqueous processing than would otherwise be concluded from orbital observations.

6.3. Water Cycle on Mars

[64] About 5% by mass of montmorillonite is structural OH. Because of its high effective surface area, it can reversibly adsorb an additional 2 to 17 wt% of water even in the cold climate of Mars [*Clark*, 1978]. Under terrestrial conditions, palagonites also can take up as much as 10% or even 20% of their mass in H_2O [*Morris et al.*, 2000], as can other amorphous products. Some fraction of the 7–10% H_2O-equivalent H detected within one meter of the surface by Mars Odyssey [*Feldman et al.*, 2004] in the general region of Gusev crater could be accounted for by smectites or highly absorptive secondary minerals, if widespread at shallow depths. Experimental results show that large amounts of hydrated minerals are needed in order to account for the GRS water signature (upwards of 40% if a phyllosilicates phase) [*Bish et al.*, 2003]. Sulfate and phosphate salts add additional H_2O, and *Foley et al.* [2003] analyze up to 4 wt% H_2O in Pathfinder "soil free rock", which they interpret as evidence for aqueous alteration of those rocks.

6.4. Astrobiological Relevance

[65] As discussed above, we have chemical but not definitive mineralogical evidence for montmorillonite. If the phyllosilicate is in fact present, there are important astrobiological implications.

[66] The high CEC capacity of montmorillonites allows them to accumulate cations which are then bioavailable as nutrients for life forms. At low H_2O/rock ratios, smectites and many other alteration minerals bind H_2O so strongly,

however, that it is no longer useful to organisms (low water activity). Under contemporary ambient conditions, scarce H_2O might be locked into adsorbed, bio-unavailable forms on montmorillonites in the local environment. Water vapor from the atmosphere will be taken up by these minerals in preference over formation of free ice.

[67] Montmorillonite is also known for its ability to take up and bind certain organic molecules. This characteristic contributes to montmorillonite serving as a versatile catalyst for prebiotic reactions, such as proto-protein synthesis via the polymerization of adenylated amino acids to polypeptides [*Paecht-Horowitz and Eirich*, 1988] and the synthesis of RNA oligomers from activated mononucleotides, sufficiently competent to serve as templates for enzymatic RNA replication [*Miyakawa and Ferris*, 2003].

[68] Montmorillonite can provide special protection of organics captivated in the crystal interlayer structure. Consolidated units may provide a refuge for organics on Mars. Alteration products may trap not only organic biomarkers, but can potentially preserve microfossils of ancient life forms.

7. Conclusions

[69] There are three possible mineralogical explanations for the elemental data of Independence class samples: (1) smectite is actually present but its mineralogical structure has been masked from detection by the MER instrument suite (in particular, Mini-TES); (2) an adventitious matching of elemental composition by a more complex assemblage of alteration products; and (3) an amorphous form of pre- or post-montmorillonite, implying either that the smectite formation process could not go to completion, perhaps because of a low pH environment, or that the smectite was formed then structurally destroyed in a process that was approximately isochemical with respect to the elements measured. In any case, important element mobility and concentration changes have occurred from the plausible igneous starting materials. These changes are strong indications of aqueous alteration processes. The original motivation for exploring Gusev crater was the geomorphologic evidence that it was at one time flooded by water from Ma'adim Vallis [*Squyres et al.*, 2004]. Present limitations on understanding the geology of Columbia Hills preclude a firm conclusion whether Independence outcrop materials may represent a remnant of sedimentary deposits that were formed during this putative former lacustrine environment or were formed by some more localized process.

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References

Arvidson, R. E., et al. (2006), Overview of the Spirit Mars Exploration Rover Mission to Gusev Crater: Landing site to Backstay Rock in the Columbia Hills, *J. Geophys. Res.*, *111*, E02S01, doi:10.1029/2005JE002499.

Bandfield, J. L. (2002), Global mineral distributions on Mars, *J. Geophys. Res.*, *107*(E6), 5042, doi:10.1029/2001JE001510.

Bell, J. F., et al. (2004), Pancam multispectral imaging results from the Spirit rover at Gusev Crater, *Science*, *305*(5685), 800–806, doi:10.1126/science.1100175.

Bibring, J.-P., et al. (2005), Mars surface diversity as revealed by the OMEGA/Mars Express observations, *Science*, *307*, 1576–1581.

Bish, D. L., J. W. Carey, D. T. Vaniman, and S. J. Chipera (2003), Stability of hydrous minerals on the Martian surface, *Icarus*, *164*, 96–103.

Bouska, V., Z. Borovec, A. Cimbalnikova, I. Kraus, A. Lajcakova, and M. Pacesova (1993), *Natural Glasses*, Ellis Horwood, New York.

Brückner, J., G. Dreibus, R. Rieder, and H. Wänke (2003), Refined data of Alpha Proton X-ray Spectrometer analyses of soils and rocks at the Mars Pathfinder site: Implications for surface chemistry, *J. Geophys. Res.*, *108*(E12), 8094, doi:10.1029/2003JE002060.

Buol, S. W., F. D. Hole, and R. J. McCracken (1980), *Soil Genesis and Classification*, 2nd ed., Iowa State Univ. Press, Ames.

Chen, Y. L., B. F. Xu, J. G. Chen, J. G. Chen, and Y. Y. (1992), Ge, Fe^{2+}-Fe^{3+} ordered distribution in chromite spinels, *Phys. Chem. Miner.*, *19*, 255–259.

Christensen, P. R., J. L. Bandfield, M. D. Smith, V. E. Hamilton, and R. N. Clark (2000a), Identification of a basaltic component on the Martian surface from Thermal Emission Spectrometer data, *J. Geophys. Res.*, *105*, 9609–9621.

Christensen, P. R., et al. (2000b), Detection of crystalline hematite mineralization on Mars by the TES: Evidence for near-surface water, *J. Geophys. Res.*, *105*, 9623–9642.

Clark, B. C. (1978), Implications of abundant hygroscopic minerals in the Martian regolith, *Icarus*, *34*, 645–665.

Clark, B. C. (1993), Geochemical components in Martian soil, *Geochem. Cosmochem. Acta*, *57*, 4575–4581.

Clark, B. C., and D. Van Hart (1981), The salts of Mars, *Icarus*, *45*, 370–378.

Clark, B. C., et al. (2005), Chemistry and mineralogy of outcrops at Meridiani Planum, *Earth Planet. Sci. Lett.*, *240*, 73–94.

Colman, S. M. (1982), Chemical weathering of basalts and andesites: Evidence from weathering rinds, *U. S. Geol. Surv. Prof. Pap.*, *1246*.

Dreibus, G., E. Jagoutz, B. Spettel, and H. Wänke (1996), Phosphate-mobilization on Mars? Implications from leach experiments on SNCs (extended abstract), *Lunar Planet. Sci.*, *XXVII*, 323.

Feldman, W. C., et al. (2004), Global distribution of near-surface hydrogen on Mars, *J. Geophys. Res.*, *109*, E09006, doi:10.1029/2003JE002160.

Foley, C. N., T. Economou, and R. N. Clayton (2003), Final chemical results from the Mars Pathfinder alpha proton X-ray spectrometer, *J. Geophys. Res.*, *108*(E12), 8096, doi:10.1029/2002JE002019.

Frysinger, G. R., and H. C. Thomas (1960), Adsorption studies on clay minerals. VII. Yttrium-cesium and cerium (III)–cesium on montmorillonite, *J. Phys. Chem.*, *64*(1960), 224–228.

Gaines, R. V., H. C. W. Skinner, E. E. Foord, B. Mason, and A. Rosenzweig (1997), *Dana's New Mineralogy*, John Wiley, Hoboken, N. J.

Galoisy, L. (1999), Nickel, in *Encyclopedia of Geochemistry*, edited by C. P. Marshall and R. W. Fairbridge, p. 425, Springer, New York.

Gellert, R., et al. (2006), Alpha Particle X-Ray Spectrometer (APXS): Results from Gusev crater and calibration report, *J. Geophys. Res.*, *111*, E02S05, doi:10.1029/2005JE002555.

Graff, T. G. (2003), Effects of dust coatings on visible, near-infrared, thermal emission, and Mossbauer spectra: Implications for mineralogical remote sensing of Mars, M. S. thesis, Ariz. State Univ., Tempe.

Grim, R. E. (1968), *Clay Mineralogy*, 2nd ed., McGraw-Hill, New York.

Grim, R. E., and N. Güven (1978), *Bentonites: Geology, Mineralogy, Properties and Uses*, Elsevier, New York.

Grim, R. E., and G. Kulbicki (1961), Montmorillonite: High temperature reactions and classification, *Am. Mineral.*, *46*, 1329–1369.

Hamilton, V. E., M. B. Wyatt, H. Y. McSween Jr., and P. R. Christensen (2001), Analysis of terrestrial and Martian volcanic compositions using thermal emission spectroscopy: 2. Application to Martian surface spectra from the Mars Global Surveyor Thermal Emission Spectrometer, *J. Geophys. Res.*, *106*(E7), 14,733–14,746.

Haskin, L., et al. (2005), Water alteration of rocks and soils from the Spirit rover site, Gusev Crater, Mars, *Nature*, *436*, 66–69, doi:10.1038/nature03640.

Hill, I. G., R. H. Worden, and I. G. Meighan (2000), Yttrium: The immobility-mobility transition during basaltic weathering, *Geology*, *28*, 923–926.

Hunten, D. M. (1979), Possible oxidant sources in the atmosphere and surface of Mars, *J. Mol. Evol.*, *14*, 71–78.

Ilton, E. S. (1999), Chromium, in *Encyclopedia of Geochemistry*, edited by C. P. Marshall and R. W. Fairbridge, p. 81, Springer, New York.

Jenkyns, H. C. (1986), Pelagic environments, in *Sedimentary Environments and Facies*, edited by H. G. Reading, Blackwell Sci., Malden, Mass.

Kirkland, L. E., K. C. Herr, and P. M. Adams (2003), Infrared stealthy surfaces: Why TES and THEMIS may miss some substantial mineral deposits on Mars and implications for remote sensing of planetary surfaces, *J. Geophys. Res.*, *108*(E12), 5137, doi:10.1029/2003JE002105.

Klingelhöfer, G., et al. (2003), Athena MIMOS II Mössbauer spectrometer investigation, *J. Geophys. Res.*, *108*(E12), 8067, doi:10.1029/2003JE002138.

Li, R., et al. (2006), Spirit rover localization and topographic mapping at the landing site of Gusev crater, Mars, *J. Geophys. Res.*, *111*, E02S06, doi:10.1029/2005JE002483.

Lodders, K. (1998), A survey of shergottite, nakhlite and chassigny meteorites whole-rock compositions, *Meteorit. Planet. Sci.*, *33*, A183–A190.

Marshall, C. P., and R. W. Fairbridge (Eds.) (1999), *Encyclopedia of Geochemistry*, Springer, New York.

Martini, I. P., and W. Chesworth (1992), *Weathering, Soils and Paleosols*, Elsevier, New York.

McSween, H. Y., et al. (2004), Basaltic rocks analyzed by the Spirit rover in Gusev Crater, *Science*, *305*(5685), 842–845, doi:10.1126/science.1099851.

Michalski, J. R., M. D. Kraft, T. G. Sharp, L. B. Williams, and P. R. Christensen (2004), Mineralogical constraints on the high-silica Martian surface component observed by TES, *Icarus*, *174*, 161–177.

Michalski, J. R., M. D. Kraft, T. G. Sharp, L. B. Williams, and P. R. Christensen (2006), Emission spectroscopy of clay minerals and evidence for poorly crystalline aluminosilicates on Mars from Thermal Emission Spectrometer data, *J. Geophys. Res.*, *111*, E03004, doi:10.1029/2005JE002438.

Ming, D. W., and F. A. Mumpton (1989), Zeolites in soils, in *Minerals in Soil Environments*, 2nd ed., edited by J. B. Dixon and S. B. Weed, pp. 873–911, Soil Sci. Soc. of Am., Madison, Wis.

Ming, D. W., et al. (2006), Geochemical and mineralogical indicators for aqueous processes in the Columbia Hills of Gusev crater, Mars, *J. Geophys. Res.*, *111*, E02S12, doi:10.1029/2005JE002560.

Miyakawa, S., and J. P. Ferris (2003), Sequence- and region-selectivity in the montmorillonite-catalyzed synthesis of RNA, *J. Am. Chem. Soc.*, *125*, 8202–8208.

Morris, R. V., et al. (2000), Mineralogy, composition, and alteration of Mars Pathfinder rocks and soils: Evidence from multispectral, elemental, and magnetic data on terrestrial analogue, SNC meteorite, and Pathfinder samples, *J. Geophys. Res.*, *105*, 1757–1817.

Morris, R. V., et al. (2004), Mineralogy at Gusev Crater from the Mössbauer Spectrometer on the Spirit Rover, *Science*, *305*(5685), 833–836, doi:10.1126/science.1100020.

Morris, R. V., et al. (2006), Mössbauer mineralogy of rock, soil, and dust at Gusev crater, Mars: Spirit's journey through weakly altered olivine basalt on the plains and pervasively altered basalt in the Columbia Hills, *J. Geophys. Res.*, *111*, E02S13, doi:10.1029/2005JE002584.

Newsom, H. E., and J. J. Hagerty (1997), Chemical components of the Martian soil: Melt degassing, hydrothermal alteration, and chondritic debris, *J. Geophys. Res.*, *102*, 19,345–19,355.

Newsom, H. E., and J. J. Hagerty (1999), Mixed hydrothermal fluids and the origin of the Martian soil, *J. Geophys. Res.*, *104*, 8717–8728.

Paecht-Horowitz, M., and F. R. Eirich (1988), The polymerization of amino acid adenylates on Na-montmorillonite with preadsorbed peptides, *Origin Life Evol. Biosphere*, *18*, 359–387.

Poulet, F., J.-P. Bibring, J. F. Mustard, A. Gendrin, N. Mangold, Y. Langevin, R. E. Arvidson, B. Gondet, and C. Gomez (2005), Phyllosilicates on Mars and implications for the early Mars history, *Nature*, *438*, 623–627, doi:10.1038/nature04274.

Ramsey, M. S., and P. R. Christensen (1998), Mineral abundance determination: Quantitative deconvolution of thermal emission spectra, *J. Geophys. Res.*, *103*, 577–596.

Rieder, R., R. Gellert, J. Brückner, G. Klingelhöfer, G. Dreibus, A. Yen, and S. W. Squyres (2003), The new Athena alpha particle X-ray spectrometer for the Mars Exploration Rovers, *J. Geophys. Res.*, *108*(E12), 8066, doi:10.1029/2003JE002150.

Ross, C. S., and S. B. Hendricks (1945), Minerals of the montmorillonite group: Their origin and relation to soils and clays, *U. S. Geol. Surv. Prof. Pap.*, *205B*.

Ruff, S. W. (2004), Evidence for zeolites in the dust on Mars, *Icarus*, *168*, 131–143.

Ruff, S. W., P. R. Christensen, D. L. Blaney, W. H. Farrand, J. R. Johnson, J. R. Michalski, J. E. Moersch, S. P. Wright, and S. W. Squyres (2006), The rocks of Gusev Crater as viewed by the Mini-TES instrument, *J. Geophys. Res.*, *111*, E12S18, doi:10.1029/2006JE002747.

Ruffell, A. H., S. P. Hesselbo, G. D. Wach, M. I. Simpson, and D. S. Wray (2002), Fuller's earth (bentonite) in the lower cretaceous of Shanklin (Isle of Wight), *Proc. Geol. Assoc.*, *113*, 281–290.

Simmons, E. C. (1999), Strontium, in *Encyclopedia of Geochemistry*, edited by C. P. Marshall and R. W. Fairbridge, p. 598, Springer, New York.

Singh, S. P., L. Q. Ma, and W. G. Harris (2001), Heavy metal interactions with phosphatic clay, *J. Environ. Qual.*, *30*, 1961–1968.

Soderblom, L. A. (1992), The composition and mineralogy of the Martian surface from spectroscopic observations, in *Mars*, edited by H. H. Kieffer et al., pp. 557–593, Univ. of Ariz. Press, Tucson.

Squyres, S. W., and R. E. Arvidson (2006), Recent results from the Spirit rover at Gusev Crater, *Lunar Planet. Sci.*, *XXXVII*, Abstract 1472.

Squyres, S. W., et al. (2003), Athena Mars rover science investigation, *J. Geophys. Res.*, *108*(E12), 8062, doi:10.1029/2003JE002121.

Squyres, S. W., et al. (2004), The Spirit Rover's Athena Science Investigation at Gusev Crater, Mars, *Science*, *305*, 794–799.

Squyres, S. W., et al. (2006), Rocks of the Columbia Hills, *J. Geophys. Res.*, *111*, E02S11, doi:10.1029/2005JE002562.

Staudigel, H., and S. R. Hart (1983), Alteration of basaltic glass: Mechanisms and significance for the oceanic crust-seawater budget, *Geochim. Cosmochim. Acta*, *47*, 337–350.

Taylor, S. R., and S. M. McLennan (1985), *The Continental Crust: Its Composition and Evolution*, Blackwell, Malden, Mass.

Vickery, R. C. (1960), *The Chemistry of Yttrium and Scandium*, Elsevier Press, New York.

Wada, K. (1989), Allophane and imogolite, in *Minerals in Soil Environments*, *SSSA Book Ser.*, vol. 1, 2nd ed., edited by J. B. Dixon and S. B. Weed, pp. 1051–1087, Soil Sci. Soc. of Am, Madison, Wis.

Weaver, C. E., and L. D. Pollard (1973), *The Chemistry of Clay Minerals*, *Dev. Sedimentol.*, vol. 15, Elsevier, New York.

Williamson, M. A. (1999), Copper, in *Encyclopedia of Geochemistry*, edited by C. P. Marshall and R. W. Fairbridge, p. 101, Springer, New York.

Wise, W. S. (1982), New occurrence of faujasite in southeastern California, *Am. Mineral.*, *76*, 794–798.

Wyatt, M. B., and H. Y. McSween (2002), Spectral evidence for weathered basalt as an alternative to andesite in the northern lowlands of Mars, *Nature*, *417*, 263–266.

Yen, A., et al. (2005), An integrated view of the chemistry and mineralogy of Martian soil, *Nature*, *436*, 49–53, doi:10.1038/nature03637.

R. E. Arvidson, Department Earth and Planetary Sciences, Washington University, St. Louis, MO 63130, USA.

J. F. Bell III and S. W. Squyres, Department of Astronomy, Cornell University, 428 Space Sciences Building, Ithaca, NY 14853, USA.

B. C. Clark III, Lockheed Martin Corporation, Littleton, CO 80127, USA. (benton.c.clark@lmco.com)

W. H. Farrand, Space Science Institute, Boulder, CO 80301, USA.

R. Gellert, Department of Physics, University of Guelph, Guelph, ON, Canada N1G 2W1.

K. E. Herkenhoff, U.S. Geological Survey, Flagstaff, AZ 86001, USA.

G. Klingelhöfer and C. Schröder, Institut für Anorganische und Analytische Chemie, Johannes Gutenberg-Universität, D-55099 Mainz, Germany.

R. Li, Department of Civil and Environmental Engineering and Geodetic Science, Ohio State University, Columbus, OH 43210, USA.

J. R. Michalski and S. W. Ruff, Department of Geological Sciences, Arizona State University, Tempe, AZ 85287, USA.

D. W. Ming and R. V. Morris, NASA Johnson Space Center, Houston, TX 77058, USA.

L. Richter, DLR Institute of Space Simulation, D-51170 Cologne, Germany.

A. Yen, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA.