Geochemical and mineralogical indicators for aqueous processes in the Columbia Hills of Gusev crater, Mars

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[1]   Water played a major role in the formation and alteration of rocks and soils in the Columbia Hills. The extent of alteration ranges from moderate to extensive. Five distinct rock compositional classes were identified; the order for degree of alteration is Watchtower $\cong$ Clovis > Wishstone $\cong$ Peace > Backstay. The rover's wheels uncovered one unusual soil (Paso Robles) that is the most S-rich material encountered. Clovis class rocks have compositions similar to Gusev plains soil but with higher Mg, Cl, and Br and lower Ca and Zn; Watchtower and Wishstone classes have high Al, Ti, and P and low Cr and Ni; Peace has high Mg and S and low Al, Na, and K; Backstay basalts have high Na and K compared to plains Adirondack basalts; and Paso Robles soil has high S and P. Some rocks are corundum-normative, indicating that their primary compositions were changed by loss and/or gain of rock-forming elements. Clovis materials consist of magnetite, nanophase ferric-oxides (npOx), hematite, goethite, Ca-phosphates, Ca- and Mg-sulfates, pyroxene, and secondary aluminosilicates. Wishstone and Watchtower rocks consist of Fe-oxides/oxyhydroxides, ilmenite, Ca-phosphate, pyroxene, feldspar, Mg-sulfates, and secondary aluminosilicates. Peace consists of magnetite, npOx, Mg- and Ca-sulfates, pyroxene, olivine, feldspar, apatite, halides, and secondary aluminosilicates. Paso Robles consists of Fe^{3+}-, Mg-, Ca-, and other sulfates, Ca-phosphates, hematite, halite, allophane, and amorphous silica. Columbia Hills outcrops and rocks may have formed by the aqueous alteration of basaltic rocks, volcaniclastic materials, and/or impact ejecta by solutions that were rich in acid-volatile elements.

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1.   Introduction

[2]   The Athena science payload onboard the Mars Exploration Rovers (MER) Spirit and Opportunity has provided new insights into the aqueous history at their respective landing sites in Gusev crater and Meridiani Planum [*Squyres et al.*, 2004a, 2004b]. The occurrence of jarosite, other sulfates (e.g., Mg- and Ca-sulfates), and hematite along with siliciclastic materials in outcrops of sedimentary materials at Meridiani Planum are strong indicators of aqueous processes [*Squyres et al.*, 2004c; *Klingelhöfer et al.*, 2004; *Clark et al.*, 2005; *McLennan et al.*, 2005]. Aqueous alteration in Gusev crater ranges from minor alterations on the surfaces of rocks and within the regolith on the basaltic plains [*McSween et al.*, 2004; *Haskin et al.*, 2005; *Hurowitz et al.*, 2006; *Wang et al.*, 2006a] to highly altered outcrops and rocks in the Columbia Hills [e.g., *Morris et al.*, 2006]. The high abundance of S is evidence that sulfate has played a major role in aqueous processes in the Columbia Hills. We advocate that sulfates in rocks, outcrops, and soils are the result of acid-sulfate weathering environments (see *Golden et al.* [2005] for discussion on
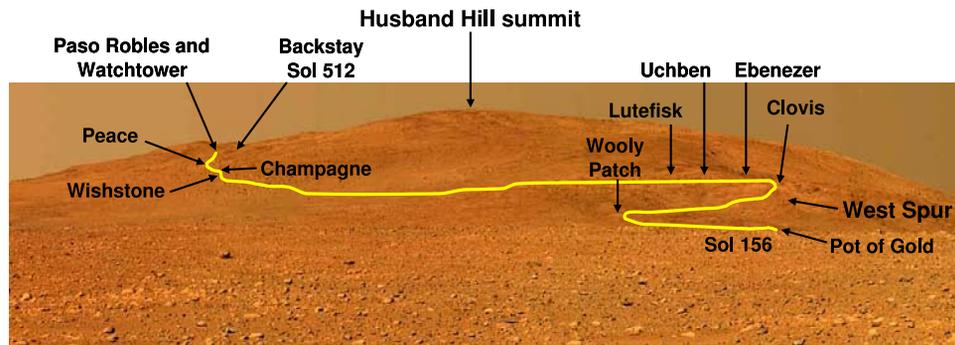
Figure 1. Pancam image (approximate true color) of the Columbia Hills from the Gusev "plains." Several outcrop and rock targets examined by the Athena science payload are shown along Spirit's traverse over the West Spur and up the slopes of Husband Hill. Spirit's instruments were analyzing a float rock dubbed Backstay on Sol 512.

acid-sulfate environments on Mars). Recent Mars Express OMEGA observations provide further support for sulfates on the surface of Mars [*Bibring et al.*, 2005].

[3] The objectives of this paper are to characterize the elemental and mineralogical compositions of outcrops, rocks, and soils in the Columbia Hills, to determine the extent these compositions reflect alteration by aqueous processes, and to constrain the nature of the aqueous processes. On Earth, life is dependent on aqueous media, and there is speculation that aqueous environments suitable for life may have existed on Mars. Thus a better understanding of aqueous processes in the Columbia Hills will aid in evaluating potential habitats for life that may have existed on Mars. To achieve our objectives, we have asked the following questions. Are the compositions of rock and soil in the Columbia Hills different from one another, and from the basaltic rocks on the Gusev plains? What are the source materials of the Columbia Hills? What evidence is there that these materials have been altered by aqueous processes? What are the alteration phases and extent of alteration? Is there evidence that suggests the presence of Fe-free alteration phases? (Iron alteration phases are discussed in detail by *Morris et al.* [2006]). What are the types and conditions of aqueous alteration?

[4] The focus of this paper is the geochemical and mineralogical properties of rocks, outcrops and soils in the Columbia Hills, which rise above the surrounding volcanic plains about 2.6 km to the southeast of Spirit's landing site. We divide the eastward traverse of Spirit in the Columbia Hills into two segments: West Spur and Husband Hill. West Spur is a hill that rises ~20 meters above the adjacent plains. Spirit examined several outcrops and float rocks on West Spur from sols 156–315. Between sols 315–512, Spirit climbed up the northwest flank of Husband Hill. Locations of float rocks, outcrops, and soils analyzed by the Athena payload in the Columbia Hills are shown in Figure 1. Details of Spirit's trek over West Spur and Husband Hill, and measurements made by the Athena Payload are described by *Arvidson et al.* [2006].

2. Methods and Data Analysis

2.1. Athena Science Payload

[5] The Athena Science instrument package consists of the Panoramic Camera (Pancam), Miniature Thermal Emis-

sion Spectrometer (MiniTES), Mössbauer Spectrometer (MB), Alpha Particle X-ray Spectrometer (APXS), Microscopic Imager (MI), Magnetic Properties Experiments, and the Rock Abrasion Tool (RAT) [*Squyres et al.*, 2003]. The analyses presented in this paper focus primarily on elemental compositions from APXS [*Gellert et al.*, 2006] (auxiliary material[1] Table S1) and mineralogical compositions from MB [*Morris et al.*, 2006].

2.2. Rock Classes

[6] Rock classes in the Columbia Hills were established by grouping rocks with similar APXS chemical compositions. Except for Backstay, only analyses from fresh surfaces exposed by grinding with the RAT were used for classification. For Backstay, a RAT-brushed surface was used because the grinding bit was worn beyond use by that time. Classes were named by a representative rock or feature within each measured group [*Squyres et al.*, 2006]. Several targets on the plains of Gusev crater around the landing site were used for comparison to the Columbia Hills classes. These plains classes include Adirondack (RAT grind analyses of the basaltic rocks Adirondack, Humphrey, and Mazatzal) and undisturbed surfaces of plains soils encountered during the first 150 sols.

[7] Analysis of variance (ANOVA) was used to determine whether significant differences exist between classes on the basis of composition. ANOVA was significant for the five rock classes in the Columbia Hills (Clovis, Wishstone, Watchtower, Peace, and Backstay) plus Adirondack basalts on the plains and two soil classes (Plains Soil Surfaces, Paso Robles soil). For example, for Si, $F = 195.05$, $p < 0.0001$, where F is equal to the ratio of variance σ_v/σ_u (where σ_v is between class variance and σ_u is within class variance). The p of <0.0001 indicates that the probability of the two variances being equal when F is 195.05, is <1 in 10,000. Therefore our null hypothesis ($\sigma_u = \sigma_v$) is rejected in this instance. Tukey-Kramer multiple comparison tests [*Hochberg and Tamhane*, 1987] were then performed to test the significance for all possible pairs of classes. (A significant F test is a prerequisite for the Tukey-Kramer multiple comparison.) The null hypothesis for the Tukey-Kramer test is that $\mu_i = \mu_j$, where μ_i is the mean of the ith class and

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Table 1. Diagnostic Elemental and Fe-Mineralogy Characteristics for Columbia Hills Rock and Soil Classes

Class	Location	Representative Rocks Within Class	Diagnostic Elemental Characteristics[a]	Diagnostic Fe Mineralogy Characteristics[b]	Average Fe^{3+}/Fe_T[b]
		Rocks			
Clovis	• West Spur	• Wooly Patch • Clovis • Ebenezer • Uchben • Lutefisk	• Similar to Gusev plains soil but enriched in Mg, Cl, and Br and depleted in Ca, Mn, and Zn	• Goethite • Hematite • NpOx[d] • Pyroxene • Magnetite	0.72 (0.56–0.84)[c]
Wishstone	• NW Flank, Husband Hill	• Wishstone • Champagne • Wishingwell	• Enriched in Al, Ti, P and Na and depleted in Cr compared to plains Adirondack basalts	• Olivine • Pyroxene • Magnetite • Hematite • NpOx • Ilmenite	0.43 (0.40–0.47)[c]
Watchtower	• Cumberland Ridge, Husband Hill	• Watchtower • Keystone • Keel • Larry's Lookout • Pequod	• Enriched in Al, Ti, and P and depleted in Cr compared to plains Adirondack basalts • Enriched in Mg compared to Wishstone	• NpOx • Hematite • Goethite • Ilmentie	0.74 (0.43–0.94)[c]
Peace	• NW Flank, Husband Hill	• Peace • Alligator	• Enriched in Mg and S and depleted in Al, Na, and K compared to plains Adirondack basalts	• Olivine • Pyroxene • Magnetite	0.35 (0.31–0.39)[c]
Backstay	• Cumberland Ridge, Husband Hill	• Backstay	• Enriched in Na, K, and Al and depleted in Fe, Mn, and Cr compared to plains Adirondack basalts	• Olivine • Pyroxene • Magnetite	0.23 (0.03)[e]
		Soils			
Paso Robles	• NW Flank, Husband Hill	-	• Strongly enriched in Fe, S, P, and Ca and depleted in Si and Al compared to Gusev plains soils	• Ferric sulfate	0.83 (0.05)[e]

[a]Elemental characteristics based on Tukey Kramer test (see text).
[b]From *Morris et al.* [2006]. Trace Fe phases not reported here.
[c]Number in parentheses represents the range within class.
[d]NpOx = nanophase Fe oxides.
[e]Number in parentheses represents std. dev. of class members.

μ_j the mean of the jth class; the probability p is fixed at 5% and is valid for unequal sample sizes such as ours. These statistical comparisons were performed on whole sample chemical compositions both with and without S, Cl, and Br (normalized to 100 wt.%).

2.3. Precursor Rock Composition

[8] We evaluated potential igneous mineralogical compositions of unaltered precursor rocks using standard CIPW normative calculations for rocks and soils on a S-, Cl-, and Br-free basis with an assumed Fe^{3+}/Fe_T from the Martian meteorites. (We assumed these volatile elements were added and the oxidation state was changed by alteration, but that all other elements were unchanged.) Diagnostic elemental associations were graphically compared to chemical data from Martian meteorites to constrain primary rock chemistry and alteration of rocks and outcrops in the Columbia Hills. On the basis of these calculations and comparisons, we were able to differentiate materials where isochemical alteration (except for addition of water and salt anions such as S, Cl, and Br)

is indicated from those where alteration probably took place in an open hydrologic system.

2.4. Mineralogical Compositions of Alteration Phases

[9] Mineralogical compositions are constrained by MB data for Fe-bearing phases [*Morris et al.*, 2006] and by MiniTES data (S. W. Ruff et al., The rocks of Gusev Crater as viewed by the Mini-TES instrument, manuscript in preparation, 2006; hereinafter referred to as Ruff et al., manuscript in preparation, 2006). It was difficult to derive representative mineralogical compositions from MiniTES because the RAT hole is smaller than the MiniTES field of view. In some cases, however, measurements of dust-free surfaces were possible. Pancam provided multispectral information which lacked the detailed spectral resolution and wide range necessary for the confident identification of all but a handful of the most distinctive Fe^{2+}- and Fe^{3+}-bearing minerals [*Farrand et al.*, 2006]. Alteration phases such as sulfates (excluding Fe-sulfates) and aluminosilicates were not directly detected by the Athena instrument suite. The abundances of these phases were estimated using

Table 2. Average Compositions of Columbia Hills and Gusev Plains Classes[a]

Location	West Spur		Husband Hill										Plains			
Class	Clovis		Wishstone		Watchtower		Peace		Backstay		Paso Robles		Adirondack		Soil Surfaces	
	Ave.	Std Err.	Ave.	Std. Err.	Ave.	Std Err	Ave.	Std. Err.	Ave.	Std. Err.	Ave.	Std. Err.	Ave.	Std. Err.	Ave.	Std. Err.
								wt %								
Si	21.4	0.2	20.3	0.3	19.8	0.5	17.4	0.4	23.1	0.4	10.9	0.4	21.5	0.2	21.5	0.2
Ti	0.51	0.03	1.71	0.04	1.33	0.06	0.26	0.05	0.56	0.05	0.45	0.05	0.35	0.03	0.51	0.02
Al	5.4	0.2	7.9	0.2	6.5	0.4	1.3	0.3	6.9	0.3	2.7	0.3	5.6	0.2	5.2	0.1
Fe	12.5	0.4	9.5	0.5	10.3	0.9	15.2	0.6	10.3	0.6	14.4	0.6	14.5	0.4	12.6	0.3
Mn	0.14	0.01	0.19	0.02	0.17	0.03	0.34	0.02	0.19	0.02	0.21	0.02	0.32	0.01	0.25	0.01
Mg	7.6	0.3	2.5	0.3	6.0	0.5	12.5	0.4	5.0	0.4	3.2	0.4	6.0	0.3	5.1	0.2
Ca	3.0	0.2	6.3	0.2	5.3	0.4	3.7	0.3	4.3	0.3	4.9	0.3	5.6	0.2	4.6	0.1
Na	2.2	0.1	3.7	0.1	2.0	0.2	0.1	0.2	3.0	0.2	1.1	0.2	2.0	0.1	2.2	0.1
K	0.19	0.03	0.45	0.04	0.62	0.07	0.01	0.05	0.85	0.05	0.25	0.05	0.13	0.03	0.38	0.02
P	0.47	0.03	2.23	0.04	1.97	0.07	0.24	0.05	0.59	0.05	2.25	0.05	0.27	0.03	0.37	0.03
Cr	0.13	0.02	0.00	0.03	0.00	0.05	0.46	0.04	0.11	0.04	0.14	0.04	0.40	0.02	0.22	0.02
Cl	1.4	0.1	0.5	0.1	0.8	0.2	0.8	0.1	0.4	0.1	0.6	0.1	0.3	0.1	0.8	0.1
S	1.7	0.2	0.8	0.3	1.4	0.4	4.7	0.3	0.7	0.3	12.7	0.3	0.7	0.2	2.6	0.1
								mg/kg								
Ni	600	-	50	-	70	-	660	-	210	-	340	-	200	-	480	-
Zn	100	-	70	-	140	-	80	-	270	-	110	-	120	-	300	-
Br	390	-	50	-	250	-	130	-	20	-	490	-	80	-	30	-

[a]Standard error uses a pooled estimate of error variance. Rock and outcrop average compositions were obtained by averaging APXS measurements in holes created by grinding with the Rock Abrasion Tool, except for the Backstay class (see text). For Ni, Zn, and Br, variation is large and standard errors are not meaningful.

apparent elemental associations obtained from APXS chemical compositions for multiple targets. The mineralogic modeling can vary significantly depending on the assumptions made in the mixing models. We have chosen two extreme cases to constrain possible degrees of alteration. Case 1 is modeled for pervasively altered materials assuming that secondary phases (i.e., sulfates, aluminosilicates) are present. Case 2 is for minimally altered materials where primary phases are assumed present. For both cases, elements associated with the Fe mineralogy were first backed out of the total APXS composition using MB data. Somewhat arbitrary compositions were used for olivine and pyroxene detected by MB depending on the Mg and Fe present in the rock or outcrop. Elements associated with the other MB-detected iron minerals were subtracted from the remaining chemical composition until no Fe was left. Iron-bearing phases included in the models were nanophase Fe-oxides (npOx, which can include the superparamagnetic forms of hematite and goethite, lepidocrocite, akaganéite, schwertmannite, hydronium jarosite, ferrihydrite, iddingsite, and the Fe^{3+} pigment in palagonitic tephra [*Morris et al.*, 1989, 2000, 2004, 2006; *Bishop and Murad*, 1996], magnetite (Fe_3O_4), hematite (Fe_2O_3), goethite (FeOOH), ilmenite ($FeTiO_3$), and a unidentified octahedrally coordinated ferric MB doublet that likely corresponds to a Fe^{3+}-bearing sulfate [*Morris et al.*, 2006]. We next used elemental abundances and a variety of studies dealing with terrestrial weathering (particularly those focused on acid-sulfate (sulfatetic) and hydrolytic weathering of basaltic materials [e.g., *Dixon and Weed*, 1989; *Morris et al.*, 1996, 2000; *Golden et al.*, 1993]) to constrain mineralogy. Phosphorous was assumed to be in the Ca-phosphates apatite or brushite unless otherwise stated, and we ignored the possibility of specific chemical adsorption (e.g., phosphate adsorption on Fe-oxides). Elements present in trace concentrations (Ni, Zn, Cr, Mn) were calculated as separate oxides; however, they are likely incorporated into primary and secondary phases as substitutional impurities. Titanium not incorpo-

rated in ilmenite was calculated as TiO_2. Sulfur, Cl, and Br were assumed to be in various sulfates and halides depending on the target's composition.

[10] The percentages and types of Fe-, S-, Cl-, and Br-bearing phases did not vary much for Case 1 and Case 2 estimates. The remaining chemistry is composed of Si, Al, Mg, Ca, K, and Na. MiniTES measurements helped constrain Al-Si phases (e.g., feldspar). On the basis of our experiences with sulfatetic and hydrolytic alteration of basalts in terrestrial environments [e.g., *Morris et al.*, 2000; *Golden et al.*, 1993], we chose feldspar (alkali and plagioclase feldspars), pyroxene (hypersthene, enstatite), and olivine to model the primary mineralogy. No specific secondary aluminosilicates were detected, although weathering trends and corundum-normative mineralogies (see below) suggested they are likely present in several of the Columbia Hills rocks and outcrops. We group these phases together as "secondary aluminosilicates." A variety of aluminosilicate phases can form via the hydrolytic or sulfatetic alteration of basaltic materials including amorphous or short-order phases such as palagonite, allophane, and amorphous silica, and crystalline aluminosilicates such as smectites, kaolinite, and zeolites [e.g., *Morris et al.*, 2000; *Golden et al.*, 1993; *Wolfe et al.*, 1997]. All estimates were derived by making mass balance calculations for these phases. For Case 1 examples, we modeled secondary aluminosilicates first and then primary phases. For Case 2 examples, we fit Al and Si with primary phases and what could not be charge balanced as primary was modeled as secondary phases. These two cases are provided to bracket the possible degree of alteration for each rock or outcrop. Example calculations are provided in auxiliary material Table S2.

3. Columbia Hills Classes: Definitions and Characteristics

[11] Outcrops and float rocks in the Columbia Hills are grouped into five classes established by differences in
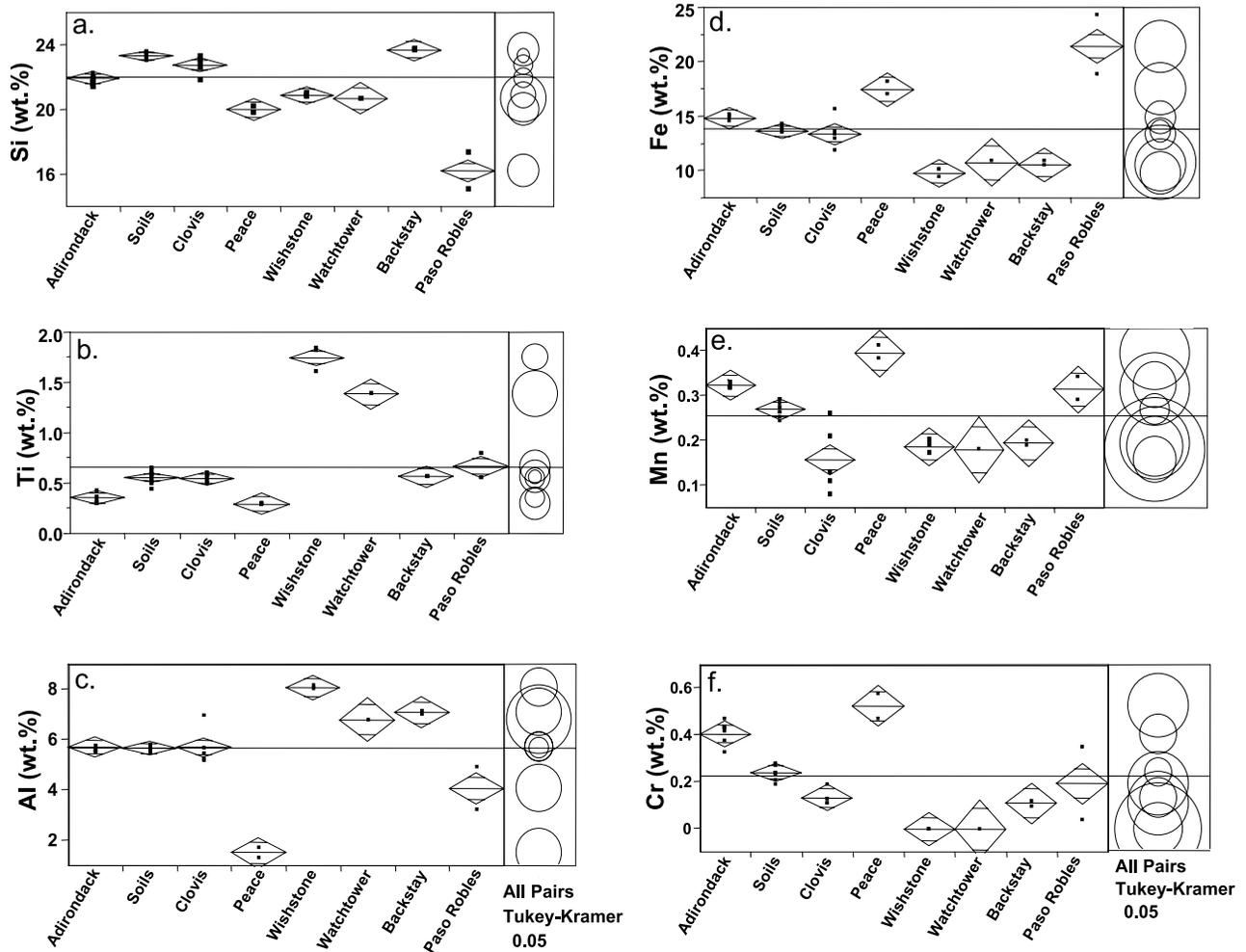
Figure 2. Elemental comparisons of Columbia Hills classes for several of the rock-forming elements on a S-, Cl-, and Br-free basis. The Adirondack basalt class and undisturbed soil surfaces (designated "Soils") on the Gusev plains are shown for comparison. The elemental compositions of individual measurements for outcrop, rock, or soil target are shown as black squares to illustrate the variation within each class. Compositions are expressed in elemental wt.%. Classes are designated as being significantly different by Tukey-Kramer tests (p = 0.05 level) for all pairs; groupings that are significantly different from each other lie outside their circles, which are drawn on the right side of the figure.

chemical compositions presented here, and by stratigraphic, mineralogic, petrologic, and physical properties [*Squyres et al.*, 2006; *Morris et al.*, 2006; *Arvidson et al.*, 2006]. The classes are Clovis, Wishstone, Peace, Watchtower and Backstay (Table 1). One soil called Paso Robles is also described here because of its importance to the aqueous history of the Columbia Hills (see below). The rocks are located on two geographic locations: West Spur and Husband Hill (Table 1). There is another geographical grouping of rocks in Hank's Hollow at the base of the West Spur that we will briefly describe.

[12] Iron mineralogy and elemental characteristics, and average compositions of the Columbia Hills classes are listed in Tables 1 and 2. Comparisons for several of the rock-forming elements on a S-, Cl-, and Br-free basis are shown in Figure 2. The Adirondack class and undisturbed plains soil surfaces are shown for comparison. Adirondack basalts have compositions consistent with picritic basalts, containing normative olivine, pyroxenes, plagioclase, and

accessory Fe-Ti oxides [*McSween et al.*, 2004]. Elemental compositions of each target are shown in Figure 2 (black squares) along with the mean (horizontal black line in diamond) to illustrate the variation within each class. Element contents between classes are significantly different when the null hypothesis of the Tukey-Kramer test fails at the 95% confidence level; groupings that are significantly different from one another have non-intersecting circles.

[13] Silicon, Ti, Al, and Fe in Clovis class rocks are not significantly different from plains soil surfaces and Adirondack basalts, although Fe is lower in Clovis. Another exception is a higher Al content in the Wooly Patch Sabre target. There is also a larger range of variation in the Fe and Al compositions for Clovis materials than in Adirondack basalts. Manganese and Cr are significantly different for Clovis and Adirondack classes (Figure 2). Wishstone, Watchtower, Peace, Backstay and Paso Robles have very different Si, Al, and Fe compositions as compared to Adirondack and Clovis classes, and there are significant
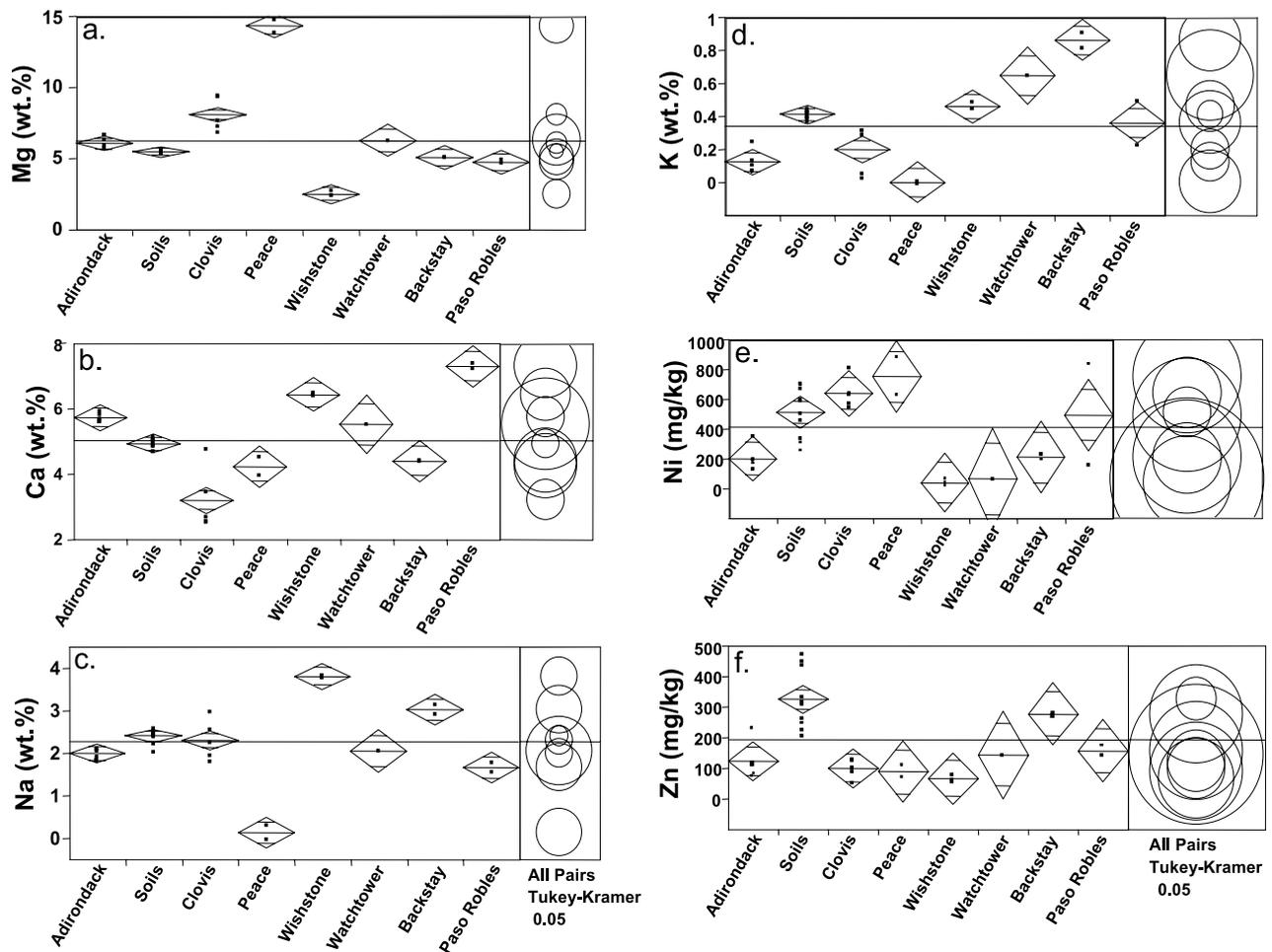
Figure 3. Elemental comparisons of Columbia Hills classes for alkali and alkaline earth cations, Ni and Zn on a S-, Cl-, and Br-free basis. See Figure 2 caption for additional information. Nickel and Zn compositions are expressed in mg/kg.

differences for these elements among the five Husband Hill classes. These compositional variations may result from differences in primary rock and/or alteration processes (see discussion below).

[14] Differences exist for the alkali and alkaline earth cations in Clovis compared to plains soil surfaces and Adirondack basalts (Figure 3). The most significant differences are higher Mg and lower Ca in Clovis. With the exception of Peace, Mg is lower in Husband Hill materials than in West Spur outcrops and rocks. Backstay, Wishstone, and Watchtower have high Na and K concentrations, with Backstay having the highest K content.

[15] Paso Robles soil has the highest S concentration (Figure 4) (31.7 wt.% SO_3), exceeding even sulfate-rich outcrop rocks in Meridiani Planum [*Rieder et al.*, 2004]. Peace class has higher S than Clovis, whereas Wishstone class is not different from Adirondack in S. Clovis and Watchtower classes have slightly higher S than Adirondack and nearly the same S as plains soils. Chlorine is higher in Clovis class rocks compared to the other classes and there is a large range in Cl within the class. Bromine is higher in Clovis and Paso Robles compared to the other classes. Phosphorus is high in Wishstone and Watchtower class rocks and in Paso Robles soil.

[16] The surfaces of three rocks in Hank's Hollow, located at the boundary of the Gusev plains and West Spur, were analyzed. Only the rock Pot of Gold will be briefly described. A RAT grind operation was only partially successful because of the small size of the rock. Pot of Gold is similar in composition to the Clovis class rocks and outcrops except that Ca, S, and Ni are higher and Mg, K, Cl, and Br are lower in Pot of Gold (Figure 5). Details on the Fe mineralogy of Pot of Gold are described by *Morris et al.* [2006].

4. Evidence of Aqueous Alteration in the Columbia Hills

4.1. CIPW Normative Mineralogy

[17] On the basis of normative mineralogy, we divide Columbia Hills rocks into two groups; the high diopside group has >7% normative diopside, and the low-diopside group has <7% normative diopside or normative corundum (Figure 6). For comparison, all Gusev plains analyses have >11% normative diopside. Husband Hill and West Spur each have members in the high and low diopside groups. Considering only the RAT post-grind APXS analyses, rocks in the low normative diopside group include Champagne, Watchtower and Wishstone from Husband Hill, and Ebe-
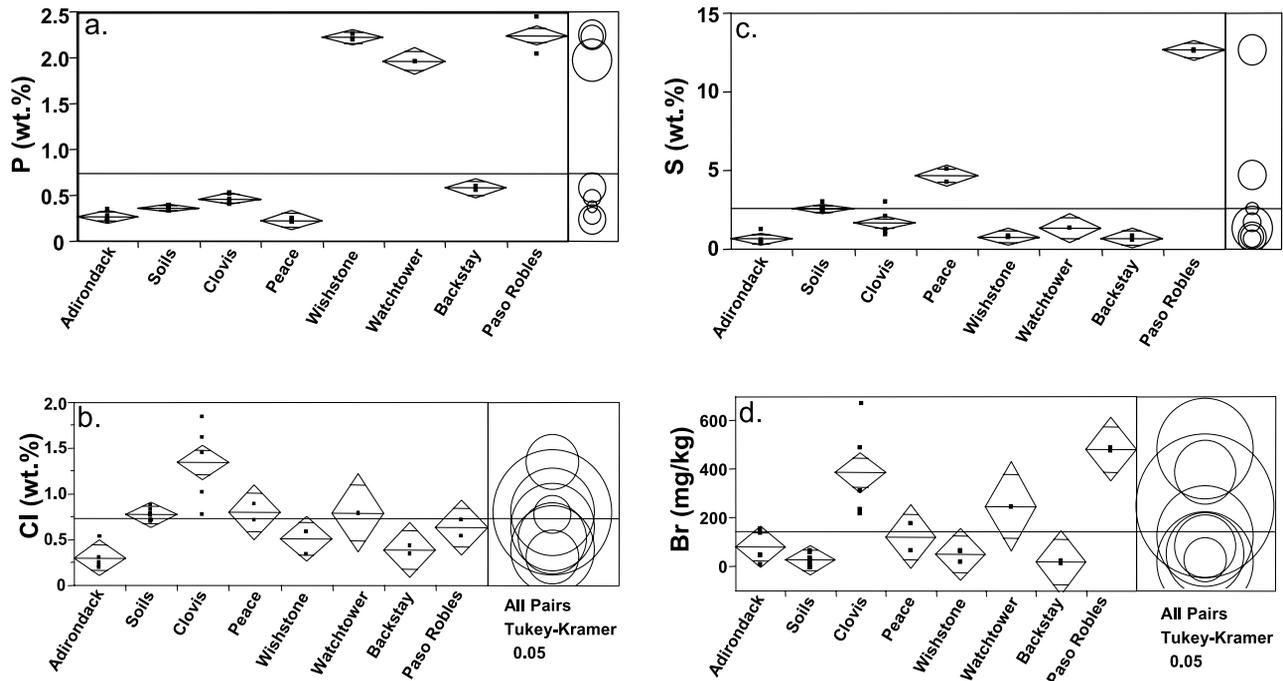
Figure 4. Elemental comparisons of Columbia Hills classes for S, Cl, Br, and P on a whole rock basis. See Figure 2 caption for additional information. Bromine compositions are expressed in mg/kg.

nezer, Uchben, and Wooly Patch from West Spur. Rocks within the high normative diopside group include Peace from Husband Hill and Clovis from West Spur. Clovis is nepheline normative, the only such rock from Columbia Hills. The CIPW norms are given in Table 3.

[18] Terrestrial igneous rocks are rarely corundum normative. The most common types of corundum-normative igneous rocks are peraluminous granites and rhyolites. The Columbia Hills outcrops and rocks are low in Si and olivine normative, and therefore are not granitic. We conclude that the outcrop and rock analyses that are corundum normative

must have had their original, igneous compositions changed by an alteration processes. Those with low normative diopside may also have had their compositions altered, but the case is not as compelling. The high diopside group may have been altered isochemically (other than S, Cl and Br addition), but this cannot be verified.

4.2. Weathering Trends

[19] We consider here several chemical trends that can be used to examine the degree of weathering of materials in the Columbia Hills. The degree of weathering in a sample can
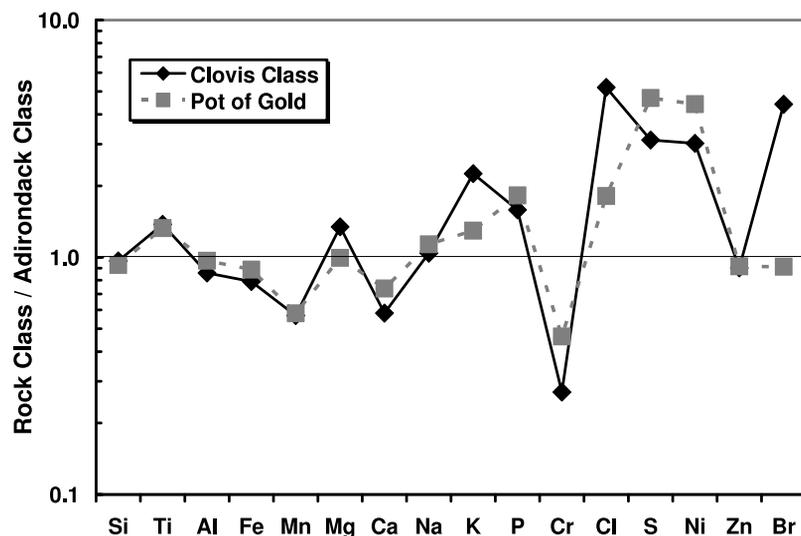

Figure 5. Elemental comparisons of a rock dubbed Pot of Gold and the average composition of Clovis class rocks on West Spur. Pot of Gold is a float rock located in a small depression called Hank's Hollow at the boundary between the Gusev plains and West Spur of the Columbia Hills. The data are normalized to the average composition of the Gusev plains Adirondack basalt class.
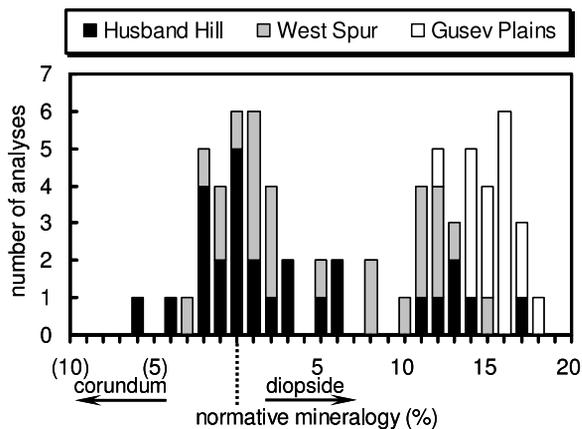
Figure 6. Histogram of CIPW normative diopside and corundum in Columbia Hills outcrops and rocks. Diopside and corundum are mutually exclusive normative minerals; a diopside-normative rock cannot have normative corundum. Normative corundum is highly unlikely for pristine Martian crustal rocks and demonstrates non-isochemical alteration of some of the rocks. Gusev plains rocks are also shown for comparison to the Columbia Hills materials. All normative calculations are for compositions on a S-, Cl-, and Br-free basis.

be estimated from Fe^{3+}/Fe_T and Fe^{2+} in olivine and pyroxene assuming that weathering occurred under oxidizing conditions [Banin et al., 1992]. Iron mineralogy and the Fe^{3+}/Fe_T ratios for key targets in each class (mostly MB of RAT grind holes) are listed in Table 4 [Morris et al., 2006]. We have plotted the area of Fe^{2+} in olivine and pyroxene (A(ol) + A(px)) versus Fe^{3+}/Fe_T of these targets in Figure 7a along with Adirondack basalt class and undisturbed soil surfaces. The Adirondack basalts appear to have minor amounts of weathering near rock surfaces [McSween et al., 2004; Haskin et al., 2005] and the soil surfaces on the plains have weathered phases in the form of npOx [Morris et al., 2004].

[20] This weathering trend suggests that Clovis class rocks range from moderately to pervasively altered materials (i.e., highest Fe^{3+}/Fe_T). The Wooly Patch outcrop is the least altered while the Clovis outcrop is the most altered (Table 4). The more altered outcrops and rocks on West Spur contain goethite. Although the Watchtower outcrop has a composition similar to Wishstone class rock targets (Wishstone and Champagne), it is highly altered compared to the other targets. Backstay is the least altered rock in the Columbia Hills and has a degree of alteration comparable to Adirondack basalts. Peace is only slightly more altered than Backstay despite its much higher S content. The most altered material according to this trend is the Paso Robles soil. The relative degree of alteration of Columbia Hills classes is Backstay < Peace ≅ Wishstone < Clovis < Watchtower ≅ Paso Robles.

[21] A second weathering trend was derived from the sum of S + Cl + Br plotted against Fe^{3+}/Fe_T (Figure 7b). Higher concentrations of these volatiles reflect materials that have been pervasively altered by solutions or vapors (discussed below). On the basis of this weathering trend, Paso Robles soil is the most altered material encountered by Spirit.

Table 3. CIPW Normative Mineralogy for Rock Classes From the Gusev Plains and Columbia Hills[a]

Region-class	Gusev Plains-Adirondack				West Spur-Other Rocks				West Spur-Clovis
Feature	Adirondack	Humphrey	Mazatzal		Pot of Gold		Breadbox	String of Pearls	Wooly Patch
Target	Prospect	Heyworth	New York	Brooklyn	Fools Gold		Sourdough	Pearl	Sabre
Type	float rock	float rock	float rock	float rock	float rock	float rock	float rock	float rock	outcrop
Preparation	post-grind	post-grind	post-grind	post-grind	undisturbed	post-grind	undisturbed	post-brush	undisturbed
C	-	-	-	-	-	-	-	-	-
Or	0.43	0.57	1.78	1.00	1.21	1.28	2.56	2.21	2.56
Ab	20.63	21.76	24.17	23.92	24.87	27.95	27.72	27.03	31.47
An	18.88	17.74	14.43	16.47	19.25	15.32	14.13	14.20	10.84
Ne	-	-	-	-	-	-	-	-	-
Di	13.85	14.96	15.95	16.36	0.62	7.21	9.10	10.59	10.62
Hy	11.50	10.69	12.45	5.80	33.77	10.30	25.32	13.07	12.52
Ol	29.82	29.16	25.35	31.10	14.09	31.37	14.64	26.41	25.56
Mt	1.85	1.85	1.85	1.85	1.62	1.77	1.61	1.77	1.76
Il	0.92	1.04	1.36	1.14	1.27	1.62	1.77	1.58	1.84
Cm	0.90	0.90	0.69	0.82	0.32	0.43	0.50	0.39	0.39
Ap	1.22	1.33	1.96	1.54	2.97	2.76	2.65	2.76	2.44

Table 3. (continued)

Region-class	West Spur-Clovis									
Feature	Wooly Patch		Clovis			Cratchit	Ebenezer	Ratchit	Temples	Tetl
Target	Sabre	Mastodon	Plano			Cratchit	Ebenezer	Ratchit	Dwarf	Clump
Type	outcrop	outcrop	outcrop	outcrop	outcrop	outcrop	outcrop	outcrop	float rock	outcrop
Preparation	undisturbed	post-grind	undisturbed	post-brush	post-grind	undisturbed	post-brush	post-grind	undisturbed	undisturbed
C	3.52	2.18	2.78	2.35	2.28	2.21	1.12	1.21	2.70	2.78
Or	0.43	0.21	-	-	-	-	1.99	2.06	-	-
Ab	29.20	25.54	32.17	33.30	27.03	28.97	23.15	20.53	30.33	30.45
An	10.36	9.61	10.53	9.46	7.75	13.84	12.28	11.32	10.91	12.41
Ne	-	-	-	-	3.71	-	-	-	-	-
Di	-	-	13.00	12.00	14.48	1.67	-	-	11.09	7.49
Hy	35.13	38.34	10.15	1.00	-	28.08	41.64	43.83	16.65	22.48
Ol	14.49	17.26	25.11	35.56	38.33	19.31	14.14	15.31	22.12	18.47
Mt	1.63	1.92	1.60	1.53	1.67	1.58	1.53	1.58	1.64	1.55
Il	1.87	1.80	1.77	1.58	1.77	1.58	1.52	1.58	1.77	1.77
Cm	0.41	0.26	0.30	0.30	0.28	0.26	0.24	0.24	0.30	0.32
Ap	2.97	2.86	2.60	2.92	2.71	2.49	2.39	2.33	2.49	2.28

Note: Or row values — Sabre 0.43, Mastodon 0.21, Plano undisturbed 2.78, Plano post-brush 2.35, Plano post-grind 2.28, Cratchit 2.21, Ebenezer 1.99, Ratchit 2.06, Dwarf 2.70, Clump 2.78. (C row: Sabre 3.52, Mastodon 2.18, remaining "-" except Ebenezer 1.12, Ratchit 1.21.)

Table 3. (continued)

Region-class	West Spur-Clovis					Husband Hill-Wishstone				
Feature	Koolik	Uchban	Chikbes	Flatfish	Lutefisk	Wishstone		Wishingwell	Champagne	
Target	Koolik	Uchban	Chikbes	Flatfish	Roe	Chisel	Chisel	Dreaming	Lip	Lip
Type	outcrop	outcrop	outcrop	outcrop	outcrop	float rock	float rock	float rock	float rock	float rock
Preparation	undisturbed	post-grind	post-brush	post-brush	post-brush	post-brush	post-grind	undisturbed	undisturbed	post-brush
C	-	-	-	-	-	0.44	2.52	-	-	0.86
Or	2.78	2.28	2.56	1.85	1.49	3.34	3.49	3.49	3.27	3.13
Ab	29.77	22.24	26.12	22.92	22.01	44.66	43.31	39.78	37.49	44.39
An	11.95	15.01	14.61	16.61	16.96	17.64	10.43	19.20	17.21	15.91
Ne	-	-	-	-	-	0.26	-	-	-	1.02
Di	10.85	1.92	1.40	0.72	0.06	-	-	2.82	4.38	-
Hy	16.04	30.27	28.83	27.60	27.04	-	5.08	6.61	8.95	-
Ol	22.43	22.62	20.44	24.64	26.62	21.88	16.59	18.88	18.94	21.56
Mt	1.62	1.45	1.47	1.45	1.44	1.16	1.15	1.24	1.36	1.26
Il	1.77	1.65	1.65	1.62	1.58	4.27	5.06	3.70	3.92	5.57
Cm	0.30	0.24	0.26	0.26	0.24	0.02	-	0.04	0.06	-
Ap	2.49	2.33	2.65	2.33	2.55	6.31	12.35	4.24	4.40	6.31

Table 3. (continued)

	Husband Hill-Wishstone		Husband Hill-Peace				Husband Hill-Watchtower			Keystone
Region-class										
Feature	Champagne		Peace				Alligator	Watchtower		Keystone
Target	Lip	RAT2	Justice	Justice	Peace	APXS target	Jambalaya	Joker	Joker	Center Mosaic
Type	float rock	float rock	outcrop	outcrop	outcrop	outcrop	outcrop	outcrop	outcrop	outcrop
Preparation	post-brush	post-grind	post-brush	post-grind	post-grind	undisturbed	post-brush	post-brush	post-grind	undisturbed
C	2.22	2.22	-	-	-	-	-	2.46	4.57	-
Or	3.20	3.20	1.07	0.07	-	1.78	1.21	4.77	4.55	3.20
Ab	43.76	43.65	21.09	3.65	-	27.93	14.94	24.97	23.60	29.87
An	10.71	10.72	7.09	6.89	6.90	7.69	8.07	13.06	7.83	18.63
Ne	-	-	-	-	-	-	-	-	-	-
Di	-	-	10.08	16.22	13.78	11.05	12.93	30.59	35.01	2.60
Hy	3.66	3.78	15.22	21.55	25.14	8.27	21.08	12.31	7.82	27.23
Ol	17.36	17.45	38.53	46.04	48.45	36.76	36.94	1.36	1.34	9.51
Mt	1.24	1.24	2.02	2.09	2.23	2.00	1.96	3.80	4.40	1.31
Il	5.82	5.76	1.49	0.89	0.98	1.42	1.11	-	-	4.46
Cm	-	-	0.92	1.01	1.25	0.92	1.03	-	-	0.17
Ap	12.03	11.98	2.49	1.59	1.27	2.17	0.74	6.68	10.87	3.02

Table 3. (continued)

	Husband Hill-Watchtower								Husband Hill-Backstay	
Region-class										
Feature	Keystone	Pennsylvania	Keel	Davis	Larry's Lookout				Backstay	Scurvy
Target	Haunch	Pittsburgh	Reef	Davis	Paros	Ahab	Pequod	Moby Dick	Scuppers	Scurvy
Type	outcrop	outcrop	outcrop	outcrop	outcrop	outcrop	outcrop	outcrop	float rock	float rock
Preparation	post-brush	post-brush	undisturbed	post-brush	undisturbed	undisturbed	post-brush	undisturbed	post-brush	undisturbed
C	1.59	0.72	-	-	1.57	0.74	0.78	-	-	-
Or	3.56	2.85	2.49	2.42	2.35	2.42	2.42	2.70	6.47	5.83
Ab	30.79	29.98	31.35	33.05	30.78	30.56	31.13	31.01	35.80	33.28
An	16.76	16.98	18.46	16.96	18.05	19.06	17.88	18.73	14.57	15.50
Ne	-	-	-	-	-	-	-	-	-	-
Di	-	-	0.28	1.07	-	-	-	0.42	5.53	5.43
Hy	31.92	25.80	27.80	22.75	33.29	31.10	28.02	25.49	7.86	14.70
Ol	4.42	10.68	8.68	12.24	4.30	4.37	7.82	10.27	23.18	18.79
Mt	1.07	1.23	1.18	1.14	1.17	1.14	1.13	1.24	1.28	1.33
Il	3.93	3.83	3.07	3.99	2.79	3.99	3.86	3.70	1.80	1.80
Cm	0.06	0.09	0.22	0.06	0.02	0.09	0.06	0.13	0.22	0.26
Ap	5.89	7.85	6.47	6.31	5.67	6.53	6.90	6.31	3.29	3.08

[a]The norms were calculated on a S- and Cl-free basis, with molar Fe^{3+}/Fe^{2+} set to 0.06, approximately the average measured for Martian meteorites. The intent of these norms is to capture an ''igneous'' mineralogy for the materials, assuming isochemical alteration of primary crustal rocks with the exception of S and Cl addition (Q, quartz; C, corundum; Or, orthoclase; Ab, albite; An, anorthite; Ne, nepheline; Di, diopside; Hy, hypersthene; Ol, olivine; Mt, magnetite; Il, ilmenite; Cm, chromite; Ap, apatite).

Table 4. Mössbauer Fe Mineralogy and Fe^{3+}/Fe_{total} for Selected Columbia Hills Outcrops, Rocks, and Soils[a]

Sol_Feature_Target_Treatment	Ol	Px	npOx	Sulfate	Mt	Hm	Ilm	Gt	Fe^{3+}/Fe_T
			West Spur Rocks						
Clovis Class									
A198_WoolyPatch_Sabre_PostGrind	2[b]	34	25	0	15[c]	19[d]	0	3	0.59[e]
A200_WoolyPatch_Mastodon_PostGrind	1	33	29	0	16	13	0	8	0.61
A218_Clovis_Plano_PostGrind	1	14	25[c]	0	2	18	0	40[c]	0.84
A233_Ebenezer_Ratchit2_PostGrind	1	11	35	0	19	14	0	20	0.83
A288_Uchben_Koolik2_PostGrind	2	16	38	0	14	8	0	22	0.79
A302_Lutefisk_FlatFish_PostBrush	2	23	24	0	15	18	0	19	0.71
A303_Lutefisk_Roe_PostBrush	2	28	20	0	20	12	0	19	0.65
Other West Spur Rocks									
A171_PotoofGold_FoolsGold_PostGrind	10	38	15	0	5	32	0	0	0.51
			Husband Hill Rocks						
Wishstone Class									
A336_Wishstone_Chisel_PostGrind	20	29	16	0	12	14	8	0	0.40
A358_Champagne_RAT2_PostGrind2	20	27	12	0	9	11	7	13	0.45
Watchtower Class									
A418_WatchTower_Joker_PostGrind	7	7	39	0	1	31	3	12	0.83
A472_Keystone_Haunch_PostBrush	0	47	17	0	10	15	6	4	0.43
A483_Keel_Reef_Undisturbed	15	18	25	0	10	31	1	0	0.64
A486_Keel_Davis_PostBrush	4	13	27	0	9	40	8	0	0.73
A493_LarrysLookout_Paros_PostBrush	3	1	66	0	0	18	2	11	0.94
A498_Pequod_Ahab_Undisturbed	4	2	62	0	0	14	6	12	0.88
A501_Pequod_MobyDick_Undisturbed	7	5	55[c]	0	0	18[c]	6	9	0.82
Peace Class									
A376_Peace_Justice_PostGrind1	21	28	16	0	35	0	0	0	0.40
A379_Peace_Justice_PostGrind2	24	29	14	0	33	0	0	0	0.37
A385_Alligator_Jambalaya_PostBrush	32	31	14	0	23	0	0	0	0.31
Backstay Class									
A510_Backstay_Scuppler_PostBrush	35	37	13	0	11	2	3	0	0.23
			Paso Robles Soil						
A401_Pasadena_PasoRobles	3	10	0	62	5	20	0	0	0.86
A426_PasoRobles2_Dark	30	40	19	0	10	2	0	0	0.27
A429_PasoRobles2_Light1	10	8	0	69	6	7	0	0	0.79

[a]Values are percent. Ol, olivine; Px, pyroxene; npOx, nanophase Fe-oxides; sulfate, ferric-sulfate; Mt, magnetite; Hm, hematite; Gt, goethite. Data extracted from *Morris et al.* [2006].

[b]Uncertainty in subspectrum area is ±2% absolute unless otherwise stated.

[c]Uncertainty in subspectrum area is ±3% absolute.

[d]Uncertainty in subspectrum area is ±4% absolute.

[e]Uncertainty in Fe^{3+}/Fe_T is ±0.03.

Clovis and Watchtower have similar degrees of alteration except for the Wooly Patch outcrop that has lower Fe^{3+}/Fe_T and volatile element sum. Although Peace has a similar Fe^{3+}/Fe_T to Wishstone class rocks, the high S content in Peace suggests a greater degree of alteration based on volatile element content. This issue is discussed in detail in section 6.3. Backstay plots very near the Adirondack basalts and appears to have been minimally altered. The relative degree of alteration from this index is Backstay < Wishstone < Peace < Clovis ≅ Watchtower < Paso Robles. We cannot place a quantitative measure on the degree of alteration of the classes.

4.3. Precursor Materials (Protoliths)

[22] Plots of Ca versus S and Mg versus S for West Spur and Husband Hill rocks and Martian meteorites are shown in Figure 8. All rocks from the Columbia Hills have excess S compared to Martian meteorites. A distinction between West Spur and Husband Hill is that the former show a positive Ca-S correlation but no Mg-S correlation, while at Husband Hill there is a negative Ca-S correlation and a strong positive Mg-S correlation. This demonstrates a difference in alteration style between two locations that are only 200–300 meters apart. There is yet no clear

understanding of the type of alteration that has taken place. The hypothesized "acid fog" process [*Banin et al.*, 1997] ought to be relatively uniform over an area of the scale of the Columbia Hills because acid volatiles in the atmosphere should be well-mixed; variations in alteration should then depend mostly on the nature of the protolith. Thus the difference in Ca-S and Mg-S trends for outcrops and rocks on Husband Hill suggests distinct protoliths if acid fog were the dominant alteration process. As shown in section 4.1, many rocks both at West Spur and on Husband hill are corundum-normative, and hence unlikely to have been altered by an isochemical (excluding anions) process like acid fog weathering. If the alteration was caused by more localized media, for example meteoric water at one location and hydrothermal water at the other, then identical protoliths could yield different altered rock compositions.

[23] Alternatively, the observed variations in weathering trends could result from non-isochemical weathering processes operating on different protoliths. The geologic structure of the Columbia Hills is complex, potentially reflecting a mixture of impact, volcanic and tectonic processes. It would not be unexpected for materials of differing provenance and initial lithology to be separated by hundreds of meters. If the protoliths in the West Spur and Husband Hill
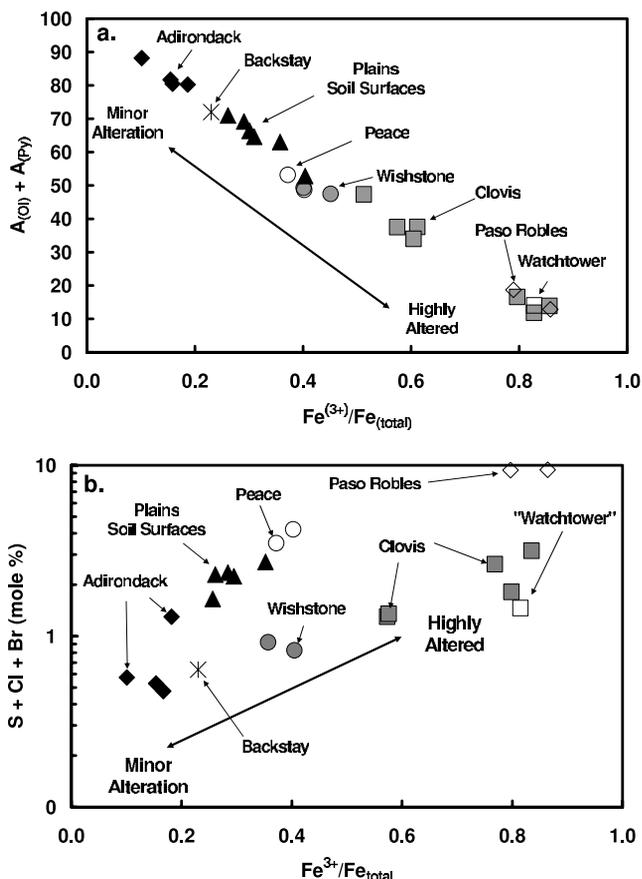
Figure 7. Chemical alteration trends. (a) Alteration or weathering trends based on a comparison of the area of olivine plus pyroxene (A(ol) + A(py); determined by the spectral area of each phase by MB) as a function of Fe^{3+}/Fe_{TI} for the major classes in the Columbia Hills. (b) Alteration trend based on the sum of S, Cl, and Br compositions as a function of Fe^{3+}/Fe_T for the major Columbia Hills classes. Gusev plains Adirondack class rocks and the Gusev plains undisturbed soil surface class are also shown for comparison with the Columbia Hill materials. Only data acquired in RAT grind holes were used for rocks, except for Backstay (see text).

are different, then the distinct alkaline-earth − S correlations may have been inherited from the materials deposited at each location; these may have been altered at different times under different conditions. The trends shown in Figure 8 suggest that alteration was not isochemical; positive Ca-S and Mg-S correlations imply increasing $CaSO_4$ or $MgSO_4$. However, it is also possible that the extent of sulfate alteration in the outcrops and rocks was controlled by the abundances in the protoliths of Ca- and Mg-bearing phases susceptible to sulfatetic weathering (see discussion below).

[24] In Martian meteorites, Ti and Cr are mostly contained in ilmenite, titanomagnetite, ulvöspinel, and chromite. These phases are relatively robust during terrestrial weathering processes as evidenced by chromite, ilmenite and magnetite being common accessory heavy minerals in beach sands. These phases are insoluble or very slightly soluble in various mineral acids; they may stand up well

against low-pH weathering process. Thus, even for highly altered rock, Ti and Cr may contain a memory of primary rock compositions. Figure 9a is a plot of Cr versus Ti for the Columbia Hills analyses compared to Martian meteorites and a field for Gusev plains rocks. The Columbia Hills rocks are consistent with the igneous fractionation trend exhibited by Martian meteorites. Chromium is a compatible element in ultramafic-mafic igneous systems, and decreases during fractionation. Titanium is an incompatible element and increases. Six analyses from Husband Hill, all of Peace class rocks, have moderate Cr (0.4–0.6 wt%) and moderate Ti (0.3–0.5 wt%). The Martian meteorites closest to these samples in Cr-Ti are olivine-phyric basalts such as Dar al Gani 476. The Clovis class analyses are tightly clustered on this diagram at low Cr (0.1–0.2 wt%) and moderate Ti contents (0.4–0.6 wt%), and are similar to the quartz-normative Martian basaltic meteorites Shergotty and Zagami. The majority of Husband Hill outcrops and rocks (Wishstone and Watchtower classes) have high Ti (>1 wt%) and very low Cr contents (less than the 0.02 wt% detection limit). Quartz-normative basalt QUE 94201 is closest to these analyses, but has lower Ti than any of the rocks in this
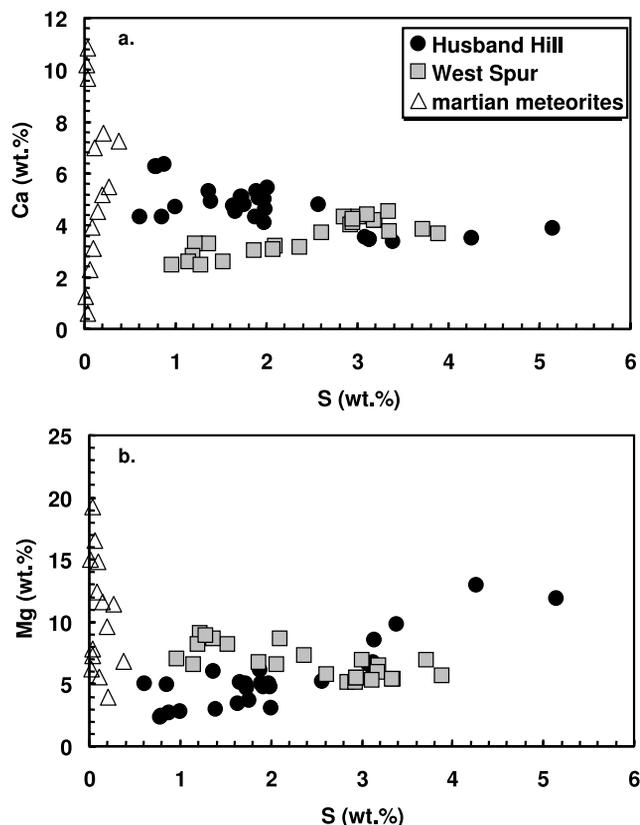
Figure 8. Calcium and Mg versus S elemental plots for Columbia Hills outcrops and rocks compared to the suite of Martian meteorites. Targets in the Columbia Hills are grouped together into two broad geographical areas: West Spur and Husband Hill. Husband Hill and West Spur compositions show distinct trends, and all analyses have higher S than do Martian meteorites. Martian meteorite data are averages of all available data in a database developed by Mittlefehldt.
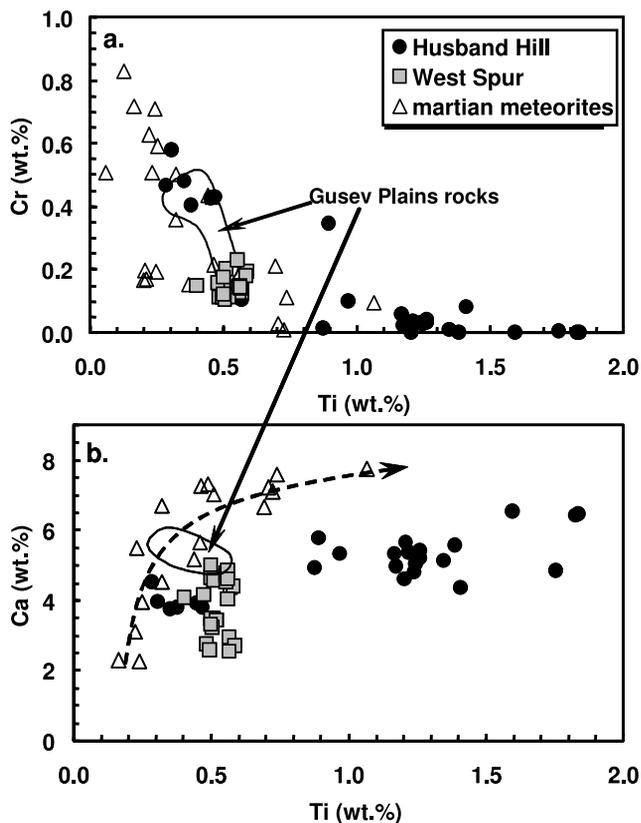
Figure 9. Chromium versus Ti and Ca versus Ti for Columbia Hills outcrops and rocks compared to Martian meteorites and a field for Gusev plains rocks. Chromium and Ti should be robust against most alteration processes. The Columbia Hills rocks plot on the trend of Martian meteorites, suggesting similar igneous protoliths. However, they are generally depleted in Ca compared to the Martian meteorite igneous trend (dashed arrow), most probably attesting to Ca depletion by alteration.

group. The very high Ti and very low Cr contents of these Husband Hill rocks suggest highly fractionated protoliths.

[25] The Cr-Ti data appear to make petrological sense, on the basis of comparison with the Martian meteorite data. This suggests that these elements can be used to make inferences regarding the natures of the protoliths for the outcrops and rocks. However, the Columbia Hills are Hesperian age [*Martínez-Alonso et al.*, 2005; *Milam et al.*, 2003], and therefore >2000 Ma old using a recent crater-based chronology [*Hartmann*, 2005], while the Martian meteorites with similar Cr-Ti contents are all <600 Ma old [*Nyquist et al.*, 2001]. We cannot know whether young Martian volcanism was compositionally similar to old Martian volcanism.

[26] Figure 9b is a plot of Ca versus Ti for the Columbia Hills outcrops and rocks, Martian meteorites, and Gusev plains rocks. Calcium is an incompatible element in ultra-mafic-mafic systems unless augite and/or plagioclase are crystallizing in sufficient amounts to deplete the melt in Ca. If Ca is incompatible, it will increase with increasing Ti, and this is what is observed for Martian meteorites. The change in slope of the Ca-Ti trend in Martian meteorites does suggest that Ca was approaching compatibility in Martian

magma systems for the most Ti-rich meteorites. The field for Gusev plains rocks overlaps the trend for Martian meteorites. The majority of Columbia Hills rocks plot below this trend. This suggests loss of Ca from their protoliths, and is consistent with the low normative diopside and corundum-normative rocks in the Columbia Hills. Note that even the high normative diopside rocks in Columbia Hills have lower normative diopside on average than do the Gusev plains rocks (Figure 6).

[27] Figure 10 contains plots of Ni versus Ti and Ni versus Mg for the Columbia Hills rocks, Martian meteorites, Gusev plains rocks and soils, and ancient and modern terrestrial mafic-ultramafic volcanics. The low-Ti outcrops and rocks have much higher Ni contents than are observed for Martian meteorites, or the majority of Gusev plains rocks (Figure 10a). (Four of 17 Gusev plains rocks plot far from the Martian meteorite data; these are not included in the field.) On the other hand, the Gusev plains soils are generally similar to the moderate-Ti Columbia Hills outcrops and rocks in Ni content. Martian meteorites show a strong trend of decreasing Ni with decreasing Mg (solid curved arrow, Figure 10b). This is expected because Ni and Mg are compatible elements in mafic igneous systems, both being strongly partitioned into olivine and orthopyroxene [e.g., *Jones*, 1995]. The Ni-poor end of the Gusev plains rocks overlaps the Martian meteorite trend, but most data plot above the trend. A few Husband Hill rocks plot along the Martian meteorite trend. All West Spur rocks plot well above the Martian meteorite trend, at Ni contents as high as or higher than Gusev plains soils.

[28] We find two possible explanation for the Ni-Mg distribution of Spirit's data compared to the Martian meteorite trend: (1) the Gusev Crater rocks represent an older, Ni-Mg trend that approximately parallels that of the Martian meteorites (dotted arrow, Figure 10b), or (2) alteration has changed the Ni and/or Mg contents of the rocks. Case 1 could explain some of the Gusev plains rocks, many of the Husband Hill rocks, and a few of the West Spur rocks. It would leave unexplained why some Gusev plains and Husband Hill rocks follow the Martian meteorite trend. As mentioned, Ni and Mg are compatible elements in ultramafic-mafic igneous systems, and do not strongly fractionate from each other. Therefore it is not obvious why ancient Martian magmatism would follow a Ni-Mg trend distinct from that of the younger Martian meteorites. Such a difference is not observed when comparing ~2700 Ma komatiites and basalts with modern MORBs and ocean island tholeiites (Figure 10c). Case 2 would suggest that most of the rocks analyzed by Spirit have had their Ni increased and/or their Mg decreased.

[29] The high Ni contents of Gusev plains soils compared to rocks have been explained as resulting from meteoritic contamination [*Yen et al.*, 2005]. Only 1–5% CI chondritic debris in the Martian soils would be enough to elevate their Ni contents to the highest of those observed. The moderate Ti rocks at the Columbia Hills (all rocks except the Wishstone and Watchtower classes) contain similar or higher Ni contents. The rocks from West Spur are considered to be either volcanogenic deposits or impact deposits [*Arvidson et al.*, 2006; *Squyres et al.*, 2006; *Morris et al.*, 2006]. The high Ni contents present a problem for these interpretations. Volcanogenic deposits should have low Ni contents, similar
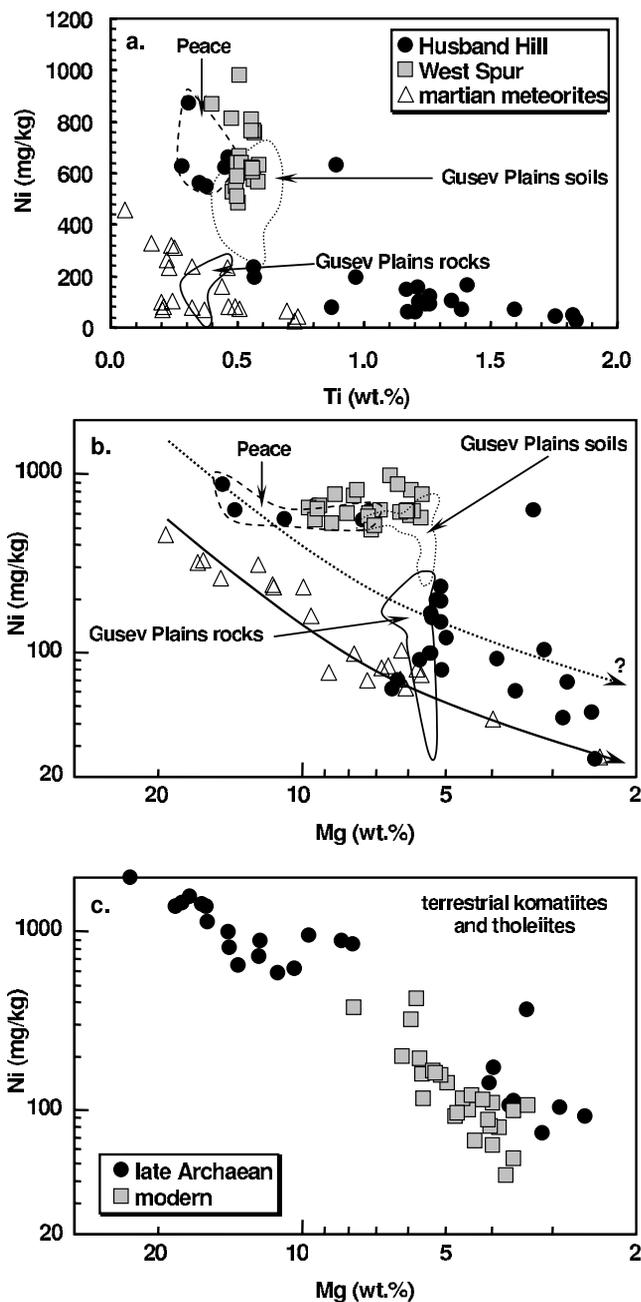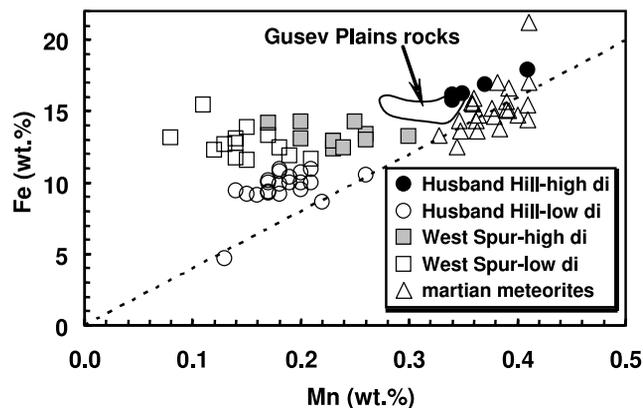
Figure 11. Iron versus Mn for Columbia Hills outcrops and rocks compared to Martian meteorites and a field for Gusev plains rocks. The Husband Hill rocks with low normative diopside or corundum may have lost both Fe and Mn compared to the high normative diopside group. At West Spur, only Mn may have been lost.

to the Gusev plains rocks and Martian meteorites. Because of their high Ni contents, it seems unlikely that the West Spur rocks are ash fall deposits. Impacts dredge up materials from the entire crater depth, and deposit them in inverse stratigraphy on the rim [*Melosh*, 1989]. Thus most of the material in these putative impact deposits would be low-Ni crustal rocks. The impact process does not distribute much projectile material into the breccias deposited outside the crater. At Meteor Crater, rocks from the overturned flap have <0.01% meteoritic material [*Morgan et al.*, 1975]. Thus, unless Ni was mobilized during alteration and enriched in these rocks by chemical weathering, the high Ni contents of Columbia Hills outcrops and rocks argues against formation as either volcanogenic or impact deposits of primary crustal rocks. Taken at face value, the Ni contents would rather support an origin as reworked soils containing 1–5% meteoritic debris. Hence the West Spur rocks and outcrops may represent soil materials that have been deposited, possibly during impact events or by wind, and subsequently altered and/or indurated by aqueous processes.

[30] An alternative is to posit that the floor of Gusev Crater contained a well-gardened regolith layer prior to formation of the Columbia Hills. Lunar soils and regolith breccias can contain Ni contents like those of the West Spur rocks [*Haskin and Warren*, 1991]. Impact into this deep regolith could then form high-Ni impact deposits that were lithified by either the impact or later alteration to form the West Spur rocks. In this case, the West Spur rocks would be physical mixtures of all the source rocks that were present in the deep regolith, rather than distinct primary crustal units.

[31] The high-Ti, low-Mg Columbia Hills outcrops and rocks (Wishstone and Watchtower classes) are low in Ni. These could be altered volcanic deposits of fractionated magmas. All of these high-Ti outcrops and rocks are corundum normative or have low normative diopside. Thus their compositions have been substantially changed, and leaching of Ni cannot be excluded.

[32] Leaching of other transition elements is suggested by Fe-Mn systematics. Figure 11 shows Fe versus Mn for the

Figure 10. (a) Nickel versus Ti and (b) Ni versus Mg for the Columbia Hills outcrops and rocks compared to Martian meteorites and fields for Gusev plains rocks and soils, and (c) Ni versus Mg for ancient (late Archaean) and modern terrestrial volcanics. In Figure 10b, one possible explanation for the higher Ni-Mg trend for Mars surface rocks (dotted arrow) compared to Martian meteorites (solid arrow) is distinct Ni-Mg fractionation trends for ancient versus young volcanism. However, this is not observed in terrestrial systems (Figure 10c). The high Ni contents of Gusev plains soils have been ascribed to meteoritic contamination. The low Ti Columbia Hills outcrops and rocks are similarly enriched in Ni, suggesting that they are likely reworked soils, rather than first generation volcanic deposits. Terrestrial data taken from *Fan and Kerrich* [1997], *Frey et al.* [1974], *Roden et al.* [1984], and *Schilling et al.* [1983].

rocks highlighting the differences between those in the high normative diopside group compared to the low normative diopside group. The Husband Hill data show two distinct groupings, but this is in part an artifact of the sampling. All members of the high diopside group are analyses taken from Peace outcrop. All analyses of low diopside group rocks have lower Mn and Fe, suggesting (but not requiring) that these elements may have been leached from the rocks. Note that the high diopside group analyses plot near the Gusev plains rocks and the Martian meteorites. For West Spur rocks, members of the low diopside group have systematically lower Mn contents, but similar Fe contents (Figure 11). This suggests Mn, but not Fe, may have been lost from these rocks during alteration. There is no good evidence for gain of Mn or Fe, and thus there is no reason to suspect that Mn may have been added to the rocks by alteration processes. This is only a qualitative argument that needs to be substantiated.

[33] Further evidence on the alteration process of the source materials is shown by comparing Mg/Si versus Al/Si for the Columbia Hills rocks (Figure 12). The West Spur analyses (Clovis class) are relatively uniform in Mg/Si and Al/Si ratios, and there is no systematic distinction between those of the high diopside and low diopside groups. Thus Al mobility is not the cause of normative corundum in these rocks. West Spur Clovis class is similar to the Gusev plains Adirondack class in Mg/Si and Al/Si. In contrast, the Husband Hill analyses show wide ranges in both Mg/Si and Al/Si. The negative correlation is consistent with igneous fractionation; compatible Mg decreases as incompatible Al increases during igneous fractionation. Those Husband Hill samples with high Mg/Si ratios are also those with the highest S contents (Figure 8). Simple addition of $MgSO_4$ to a rock will not cause a correlation between Mg/Si and Al/Si (Figure 12). This lends support to the notion that the Mg-S correlation may reflect enhanced sulfatetic weathering of rocks with more abundant primary magnesian phases such as olivine.

5. Clovis Class

5.1. Alteration Mineralogy of Clovis Outcrop

[34] Clovis outcrop is the most altered outcrop encountered as suggested by the high Fe^{3+}/Fe_T ratio and low Fe^{2+} silicate contents (Table 4). On the basis of the MB Fe mineralogy and the elemental abundance of Fe from APXS, Clovis outcrop has about 10 mole% Fe-oxides/oxyhydroxides (Table 5). We assumed that P in this system is primarily associated with Ca. This may be incorrect because there is not a good association between Ca and P. If these materials are pervasively altered (Case 1), then the P may be present in part as an adsorption phase on iron oxide/oxyhydroxide surfaces or as Fe- and Al-phosphate precipitates [*Lindsay and Stephenson*, 1959; *Lindsay et al.*, 1989; *Tisdale et al.*, 1985]. However, we will associate the P with Ca in the form of brushite ($CaHPO_4H_2O$) that can form in acid systems [*Golden et al.*, 1991]. We have modeled the S-bearing phase in Clovis as mainly Ca-sulfate on the basis of the very good correlation between Ca and S ($R^2 = 0.96$ for RAT-grind targets); however, there is not enough Ca in the rock for charge balance with S if we assume brushite is present. The remainder of the S was associated with Mg. The total sulfate
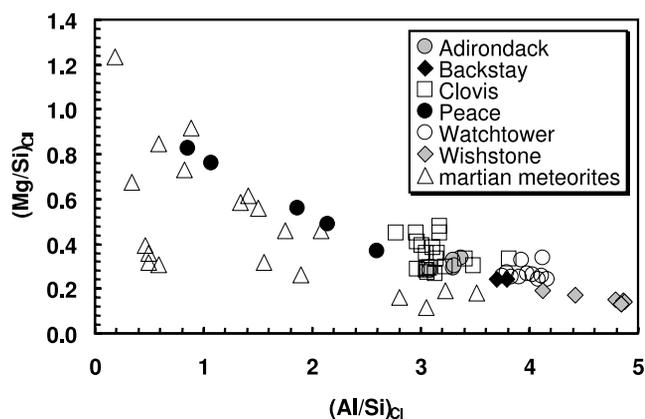

Figure 12. CI-normalized Mg/Si versus Al/Si for the Columbia Hills outcrop and rock classes compared to Martian meteorites. The Husband Hill rocks show a negative correlation, which is consistent with igneous fractionation. Low diopside group analyses have systematically lower Mg/Si and higher Al/Si. If this is an alteration feature, then coupled Al-Si or Mg-Al mobility occurred. The West Spur rocks are relatively uniform in these ratios.

content of Clovis is around 11%. The metal oxides (Mn, Cr, Ni, Zn) in nearly all cases account for less than 1% of the total mineral content. Titanium was modeled as ~1% TiO_2. The Cl content of Clovis class is higher than in classes encountered on Husband Hill. There is a good elemental association between K and Cl ($R^2 = 0.85$ for RAT grind targets), but there is insufficient K to charge balance Cl. We modeled Cl and Br as K- and Mg-halides (approx. 1%); bromides account for <0.03% of the outcrop. The phases described so far account for about 25% of the outcrop and are alteration phases, with the exception of metal oxides and possibly magnetite that account for less than 1%. MB mineralogy suggests the presence of a pyroxene-like phase. The pyroxene content of Clovis is about 12% if we assume a composition of $(Mg_{0.6}Fe_{0.4})SiO_3$, which is reasonable because of the high Mg content. The Fe^{2+} phase in these calculations has been based on pyroxene; however, *Morris et al.* [2006] suggest that the Fe^{2+} phase detected by MB could be a Fe^{2+} alteration phase. Those types of phases were not used in the calculations discussed here.

[35] The mineralogical assumptions for the Fe-oxide/oxyhydroxide, sulfate, chloride, and phosphate are fairly straightforward. Modeling of the remaining Mg, Na, K, Al, and Si has few constraints. Zeolites, smectites, kaolinite, allophane-like glass, palagonitic glass, and amorphous silica are just a few of the phases that can be modeled for pervasively altered Case 1 on the basis of charge balances and chemical compositions. These phases are common products of hydrolytic and sulfatetic alteration of basaltic materials, generally under hydrothermal conditions such as the alteration of basaltic tephra on Mauna Kea Volcano [*Golden et al.*, 1993; *Wolfe et al.*, 1997; *Morris et al.*, 2000]. We favor sulfatetic conditions for alteration on West Spur because MiniTES did not detect crystalline phyllosilicates or zeolites (Ruff et al., manuscript in preparation, 2006). We have modeled the aluminosilicate phase in Clovis as "generic secondary aluminosilicates" because there is no direct

Table 5. Mineralogy of Columbia Hills Outcrops, Rocks, and Soils Estimated From Fe Mineralogy Established by MB, Whole Rock Mineralogy by Mini-TES, and Mass Balance Calculations Based on APXS Compositions[a]

	Rock Classes										Soil Class	
	Clovis Class				Wishstone Class		Watchtower Class		Peace Class		Paso Robles Class	
	Clovis Outcrop		Ebenezer Rock		Wishstone Rock		Watchtower Outcrop		Peace Outcrop		Paso Robles[b]	Paso Robles2[c]
Mineralogy	Case 1	Case 2	Case 1	Case 2	Case 1	Case 2	Case 1	Case 2	Case 1	Case 2	Case 1	Case 1
	Primary Phases											
Olivine	tr	tr	tr	tr	7	6	4	4	15	14	[d]	[d]
Pryoxene	12	33	9	42	11	12	5	22	24	48	[d]	[d]
Feldspar	0	34	0	21	13	52	0	30	0	7	[d]	[d]
Apatite	0	2	0	2	11	11	7	10	1	1	[d]	[d]
TiO_2	1	1	tr	tr	1	1	1	1	tr	tr	[d]	1[d]
Other metal oxides	tr	tr	tr	tr	tr	tr	tr	tr	1	1	[d]	[d]
Magnetite[e]	tr	tr	2	2	1	1	tr	tr	5	5	[d]	[d]
Ilmenite	0	0	0	0	1	1	1	1	0	0	0	0
	Secondary Phases											
NpOx	3	3	4	4	1	1	4	4	2	2	[d]	[d]
Hematite	2	2	2	2	1	1	3	3	0	0	4	1
Goethite	5	5	2	2	0	0	1	1	0	0	0	0
Ferric sulfate	0	0	0	0	0	0	0	0	0	0	29	25
Mg-sulfate	tr	1	0	tr	2	1	5	5	9	10	10	10
Ca-sulfate	11	10	5	4	1	2	0	0	6	6	3	4
Other sulfates	0	0	0	0	0	0	0	0	0	0	2	5
Brushite	2	0	2	0	0	0	0	0	0	0	10	8
Halides	2	2	1	1	1	1	1	1	1	1	1	1
Secondary aluminosilicates[f]	62	-	71	-	47	-	67	-	35	-	-	-
Allophane[f]	-	7	-	12	-	8	-	13	-	tr	5	7
Amorph. SiO_2[f]	-	0	-	5	-	0	-	5	-	4	10	11
Soil component[g]	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	27	27

[a]Values are in percent (tr = trace). The mineralogic modeling of these rocks and outcrops can vary significantly depending on the assumptions made for minerals used in the mixing models. Two extreme cases (Case 1 and Case 2) are provided to constrain the possible degree of alteration. Case 1 is modeled for pervasively altered materials assuming secondary phases (i.e., sulfates, aluminosilicates) are present. Case 2 is for least altered materials where primary phases are assumed present. Representative calculations are presented in auxiliary material Table S2.

[b]Feature/Target = Pasadena/Paso Robles.

[c]Feature/Target = Paso Robles2/Light Soil.

[d]Phase is calculated as part of the soil component listed below.

[e]Magnetite may be secondary phase.

[f]Secondary aluminosilicates include allophane and amorphous SiO_2 for the pervasive alteration case. Allophane and amorphous Si are listed for the minimal alteration case. The dash mark (-) indicates that these phases were not modeled for that case.

[g]NA, not applicable. Soil component only estimated for the Paso Robles soil targets.

evidence for specific phases. We do not rule out the possibility of the presence of phyllosilicates. Zeolites are unlikely because they require alkaline conditions for their formation [*Ming and Mumpton*, 1989]. Up to 62% secondary aluminosilicates can be modeled in Clovis for the pervasively altered case and secondary phases account for nearly 85% of all phases.

[36] In Case 2, the aluminosilicates in Clovis are modeled for minimal alteration (Table 5). Potassium and Na in Clovis are modeled as alkali feldspars. MB indicates the possible occurrence of Fe^{2+} silicate (pyroxene), and much of the Mg in Clovis was modeled as Mg-rich pyroxene (i.e., enstatite). Regardless of how the Case 2 example is modeled, excess Al and Si are present after establishing charge balances between the alkali and alkaline earth cations and Al and Si in primary phases. The excess Al and Si were modeled as an allophanic-like phase (assumed Si:Al ratio of 1:1), although, other 1:1 Al:Si phases could be modeled (e.g., kaolinite, halloysite). The sum of the phases formed by aqueous processes in the Case 2 example is about 30% with pyroxene and feldspar making up the remainder.

[37] The two cases presented here for Clovis suggest that the outcrop can contain between 30 and 85% alteration

phases. MiniTES observations did not identify primary basalt phases (e.g., feldspar) in Clovis, but there was a strong spectral signature for a phase interpreted as basaltic glass (Ruff et al., manuscript in preparation, 2006). It is not clear how to reconcile this observation, unless the glass has a low Fe^{2+} content and is thus not detected by MB and/or the aluminosilicate alteration products have glass-like MiniTES signatures. Therefore, on the basis of the high degree of weathering as suggested by weathering trends (section 4.2) and the lack of primary phases, we suggest that Clovis is pervasively altered and contains mainly secondary phases. Olivine and pyroxene are the probable sources of Mg and Fe alteration phases. Regardless of the total content of the altered phases, aqueous processes have played a major role in the formation of the Clovis outcrop.

5.2. Alteration Mineralogy of Ebenezer Rock

[38] The degree of weathering (Fe^{3+}/Fe_T and Fe^{2+} silicate mineralogy) in Ebenezer is similar to Clovis outcrop. Ebenezer has about 10 mole% Fe-oxides/oxyhydroxides, and a trace of ilmenite (Table 5). Brushite, Ca-sulfate, halides, and Ti and other metal oxides constitute about 9% of the rock. Ebenezer must have some type of alumi-

nosilicate alteration phase(s) on the basis of its corundum-normative mineralogy. Aluminosilicate phases in Ebenezer were modeled similar to Clovis. About 71% of the rock is modeled as secondary aluminosilicates for the Case 1 example (Table 5). Only about 9% of the rock was modeled as pyroxene.

[39] For Case 2, pyroxene and alkali feldspars account for about 63% of the rock and allophane-like and amorphous silica phases accounted for about 19%. The range of alteration phases in Ebenezer for Case 1 to Case 2 examples is about 87% to 30% of the rock. The high Fe^{3+}/Fe_{total} suggests a high degree of alteration, and hence Case 1 may be closer to the truth.

5.3. Aqueous Processes in Clovis Class Materials

[40] Mössbauer and APXS data sets suggest that npOx, goethite, hematite, Ca- and Mg-sulfates, and halides are phases that have formed by aqueous processes in most Clovis outcrops and rocks. Corundum-normative mineralogies of most West Spur outcrops and rocks suggest the presence of secondary aluminosilicates. Aluminosilicates such as allophane, amorphous silica, phyllosilicates, and zeolites are all grouped into this category. Phyllosilicates were not detected directly in Clovis; however, Wang et al. [2006b] suggest that they might be present. Because Mini-TES did detect the presence of glass but not phyllosilicates and zeolites in Clovis materials (Ruff et al., manuscript in preparation, 2006), we suggest that the aluminosilicate alteration phases are either amorphous or short order materials such as an allophane-like material.

[41] The high S and Cl (and sometimes Br) compositions in surfaces created by the RAT indicate that these elements played an important role in the alteration of Clovis materials. The low levels of primary minerals such as olivine suggest that these phases have undergone alteration if they were present in the protolith. West Spur outcrops and rocks may have formed by the alteration of volcaniclastic materials, and/or impact ejecta of basaltic composition by solutions that were rich in volatile elements (i.e., Br, Cl, and S). However, it is difficult to determine whether aqueous alteration occurred by hydrothermal solutions, by aqueous vapors from volcanic emanations, or by low-temperature solutions moving through the West Spur materials. The layered rocks and outcrops on the West Spur (e.g., Uchben) appear to be clastic in nature and deposited in a fluid, e.g., air fall deposits from volcanic ash or impact materials [Squyres et al., 2006]. The high Ni content in West Spur materials argues against a volcanogenic origin but it is difficult to interpret the Ni content because of the highly altered nature of these materials. However, the Ni content in West Spur might be explained if the precursor of these materials were an impact-generated megaregolith or breccia containing 1–5% meteoritic debris. We therefore favor the hypothesis that the West Spur rocks are ejecta deposits formed by impact into such a Ni-rich material.

[42] Solutions that have been enriched by S-bearing volcanic gases are acidic and generally result in sulfuric acid weathering [e.g., Morris et al., 2000]. One scenario for aqueous alteration on the West Spur is that vapors and fluids rich in SO_2, HCl, HBr, other acids, and water interacted with rocks and outcrops, which may have been basaltic in bulk composition and were presumably impact deposits.

Acidic solutions diffused into the rocks and outcrops and reacted with the primary phases. Soluble ions from the host rock reacted with S, Cl and Br to form Ca-, Mg- and other sulfates, halides, iron oxides/oxyhydroxides, and secondary aluminosilicates. The occurrence of goethite and hematite and not jarosite (or other ferric-sulfates) in most Clovis outcrops and rocks suggests that the acidic solutions were substantially neutralized by basalt dissolution; although the npOx in West Spur rocks could be schwertmannite or another iron sulfate phase because of the correlation between npOx and S [Morris et al., 2006]. The pH of the system plays a major role in defining the stability field between jarosite, schwertmannite, and hematite (or goethite). Jarosite is stable in the pH range 0.75–3.5; below this range jarosite dissolves and above this range it hydrolyzes to form hematite and/or goethite (e.g., stability diagram of Burns and Fisher [1990]). In West Spur outcrops and rocks, pH values were high enough to initiate hydrolysis of Fe to form Fe-oxides or oxyhydroxides. Calcium- and Mg-sulfates precipitated from solutions enriched in these elements as their activities exceeded their solubility products.

[43] Hurowitz et al. [2006] have presented evidence for very low pH (pH = 0–1) alterations at rock and outcrop surfaces. They suggest that there is a leached layer where Clovis outcrops and rocks are depleted in Mg and Fe at their surfaces compared to their interiors (i.e., holes created by RAT grinds), probably as a result of pyroxene and/or basaltic glass dissolution by acidic fluids (e.g., sulfuric acid fog [Banin et al., 1997; Tosca et al., 2004]). It is likely that initially acidic solutions moved through the West Spur materials and pervasively altered the basaltic materials in an open hydrologic system resulting in corundum normative mineralogies. Then, acidic vapors reacted at the surfaces of rocks and outcrops leaching some elements (e.g., Fe and Mg) as postulated by Hurowitz et al. [2006].

6. Husband Hill Classes

6.1. Wishstone Class

6.1.1. Alteration Mineralogy

[44] Wishstone class rocks are all float rocks and have the highest Ti contents (3.0 wt.% TiO_2 in the rock Champagne) of all rocks analyzed in Gusev crater. Another unique chemical signature of this class is high P concentrations (up to 5.2 wt.% P_2O_5). Wishstone class rocks Wishstone and Champagne have very similar chemistry and Fe mineralogy. The most notable difference is the presence of goethite in Champagne but not in Wishstone (Table 4). The presence of goethite in Champagne may represent a slightly different alteration process; however, Champagne and Wishstone have essentially the same Fe^{3+}/Fe_T indicating that they have about the same degree of alteration.

[45] Wishstone has a relatively low degree of alteration compared to other Husband Hill rocks. Iron oxides/oxyhydroxides account for about 3% of the rock (Table 5). About 1% ilmenite was identified in this rock by MB. The high P content in Wishstone was modeled as apatite and not brushite for the Case 1 example on the basis of the observation that this rock appears to be less altered than other Columbia Hills materials. Whitlockite and merrillite are also viable phosphate candidates [see Hurowitz et al., 2006]. Sulfur was assigned as Mg- and Ca-sulfates.
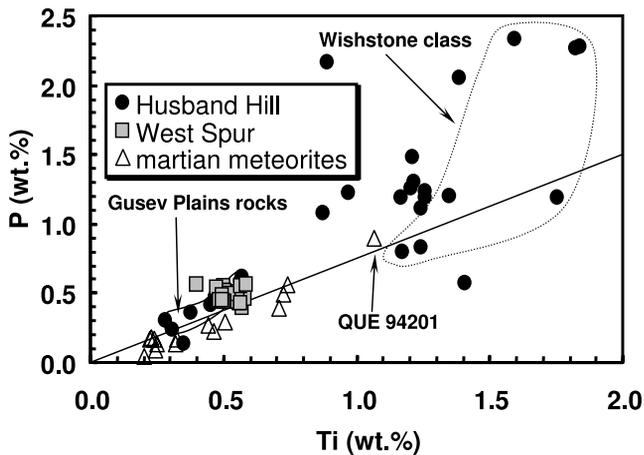
Figure 13. Phosphorus versus Ti for the Columbia Hills outcrops and rocks compared to Martian meteorites and a field for Gusev plains rocks. The slope of the line is the estimated P/Ti ratio for Mars [*Longhi et al.*, 1992]. Some of the Ti-rich Husband Hill rocks have P/Ti as estimated for Mars and are consistent with igneous fractionation. Some have P contents that are far too high to be explained by Martian igneous processes. The dotted field encloses the Wishstone class rocks.

[46] The olivine and pyroxene, identified by MB, total about 18% (Table 5) for assumed compositions of Fo_{60} and $(Mg_{0.5}Fe_{0.5})SiO_3$. MiniTES observations of Wishstone-type rocks in the vicinity suggest a plagioclase feldspar (labradorite) component is also present (Ruff et al., manuscript in preparation, 2006). Hence we modeled plagioclase feldspar, olivine, and pyroxene for Case 1 and Case 2 examples. The amounts of plagioclase in Case 1 and Case 2 were 13 and 52%, respectively. The difference between Case 1 and 2 is arbitrary and the amount of plagioclase in Wishstone likely falls somewhere between these two. There are no mineralogical measurements that suggest a possible secondary aluminosilicate phase. Hence we have modeled generic secondary aluminosilicate phases for the Case 1 example. This may include allophanic-like phases and amorphous silica. We do not rule out the possibility of the presence of phyllosilicates or zeolites. Texturally this rock is clastic and has features of a tuff-like material [*Arvidson et al.*, 2006; *Squyres et al.*, 2006].

[47] The two cases presented here for Wishstone suggest that the rock may contain between 14 and 53% alteration phases. These mineral calculations also support the notion that Wishstone and Champagne are less altered than West Spur outcrops and rocks.

6.1.2. Aqueous Processes

[48] Backing out the possible modes of formation for Wishstone materials is challenging because of the unusually high P contents. The P content of Wishstone is too high for known igneous systems [*Piccoli and Candela*, 2002], with the exception of phoscorites. These are extremely rare on Earth [*Krasnova et al.*, 2004] and unlikely on Mars. The P-Ti correlation for Spirit analyses and Martian meteorites also suggests that those Wishstone rocks with the highest P contents do not represent igneous compositions (Figure 13). Martian meteorites, West Spur, Gusev plains and many Husband Hill rocks plot along a line with the estimated

Martian P/Ti ratio [*Longhi et al.*, 1992]. Titanium and P are incompatible elements in ultramafic-mafic igneous systems, and igneous fractionation will not greatly change the P/Ti ratio of rocks. Some high-Ti Wishstone rocks have P contents consistent with evolved Martian igneous rocks (e.g., QUE 94201; Figure 13). However, many have P contents roughly twice what would be expected on the basis of their Ti contents. Therefore the high P in some Wishstone rocks suggests P-enrichment alteration processes affected this material. There are several possibilities for enrichments, such as metasomatism of silicate materials by hydrothermal solutions rich in P [e.g., *Wheat et al.*, 1996] or acidic solutions dissolving P from source material and precipitating it in Wishstone materials [e.g., *Deevey*, 1970].

[49] Wishstone and Champagne have textures similar to terrestrial volcanic ash deposits or possibly tuffs [*Squyres et al.*, 2006]. The Ni content of Wishstone materials supports a volcanogenic origin. Their Ni contents are the lowest for Columbia Hills rocks and comparable to those in Martian meteorites (Figure 10). The possibility that Ni was weathered out of this material cannot be discarded. The weathering trends indicate a moderate amount of alteration in Wishstone and Champagne, which suggests that Ni was not removed during alteration. However, these rocks are also corundum normative, which indicates non-isochemical weathering. The normative corundum is a consequence of the high P content of these rocks, which results in a high apatite content in the norm. If the phosphate is instead assumed to be brushite (lower Ca/P), normative corundum is still calculated for some of these rocks. Thus, while they are relatively unaltered based on the various weathering trends we examined, they are nevertheless altered materials. The low sulfate contents suggest that these materials were subjected to sulfatetic alteration processes, but alteration was not pervasive. Above we suggested that chromite and ilmenite should be more resistant to alteration. The Wishstone class has the highest Ti and lowest Cr of any of the Columbia Hills rocks, supporting a more evolved composition.

6.2. Watchtower Class
6.2.1. Alteration Mineralogy

[50] Watchtower class rocks have many of the same elemental characteristics as the Wishstone class rocks (Table 1). The most notable chemical difference between Watchtower and Wishstone class rocks is the high Mg in Watchtower outcrop, roughly twice that in Wishstone or Champagne rocks. Although Watchtower otherwise has similar chemical characteristic to Wishstone and Champagne, it is extensively altered. Watchtower outcrop contains slightly higher amounts of Fe-oxides/oxyhydroxides and Mg-sulfates, and less Ca-phosphate than in Wishstone (Table 5). Ilmenite and magnetite contents of Watchtower are similar to those of Wishstone. Olivine and pyroxene total 9% of Watchtower for the Case 1 example. The remaining Mg, Na, K, Al, and Si have been modeled as secondary aluminosilicates similar to what was modeled for the West Spur rocks and outcrops. About 90% of the sample is an alteration phase in the Case 1 example if we assume the Ca-phosphate is also a secondary product.

[51] Feldspar, pyroxene, and olivine are modeled as the primary silicates in the Case 2 example where they account for about 56% (Table 5). Excess Al and Si that could not be

balanced by alkali and alkaline earth cations in primary phases were assigned to allophanic-like phase and amorphous silica. The sum of the alteration phases in the Case 2 example is about 32%.

[52] The two cases presented here for Watchtower suggest that the outcrop may contain between 32 and 88% alteration phases. This range of alteration is very similar to the range for Clovis rocks suggesting that these materials may have been altered under similar conditions.

6.2.2. Aqueous Processes

[53] Wishstone and Watchtower class rocks appear to have had the same source materials, but Watchtower has undergone much more extensive alteration than Wishstone. Watchtower consists of goethite, hematite, Mg-sulfates, Ca-phosphates, secondary aluminosilicates, some olivine and pyroxene, and trace amounts of ilmenite and magnetite. The addition of volatile elements (S, Cl, and Br) to Watchtower suggests that it has been altered by solutions enriched in these elements, but the water to rock ratio must have been low to prevent leaching or removal of soluble elements from the outcrop. Acid-sulfate weathering similar to the process described above for West Spur Clovis class materials may have altered Watchtower.

6.3. Peace Class
6.3.1. Alteration Mineralogy

[54] Peace outcrops have the lowest Al/Si molar ratio (Figure 12) and the lowest Al content of all materials analyzed in Gusev crater. One interesting feature of Peace is the very low content of alkali elements ($Na_2O + K_2O \cong 0$) in the interior of the outcrop. To some extent, Peace shows chemical similarities to the partial cumulate Martian lherzolites such as ALHA77005, LEW 88516 and Yamato 793605. These rocks are low in Al_2O_3 and Na_2O and thus plagioclase-poor [e.g., *Ikeda*, 1997; *Mittlefehldt et al.*, 1997; *Treiman et al.*, 1994].

[55] Peace has a high S content, yet there is apparently little alteration of primary silicates according to MB Fe^{2+} silicate mineralogy. The only Fe-oxides identified in Peace are minor npOx and magnetite (Table 5). High Ca, Mg, and S contents suggest that the S-bearing phases in Peace are Mg- and Ca-sulfates, which account for about 15–16% of the outcrop. The P content is low and was modeled as apatite.

[56] The remaining Mg in Peace is likely associated with olivine and pyroxene. We have modeled the pyroxene phase as $(Mg_{0.6}Fe_{0.4})SiO_3$ and olivine as Fo_{60}. About 39% of Peace is modeled as olivine and pyroxene for the Case 1 example. About 35% is assigned as secondary aluminosilicates (Table 5) and the total amount of alteration phases is about 52%.

[57] The sum of K, Na, and Ca is low and the amount of feldspar modeled for the Case 2 example is therefore low. Olivine and pyroxene totaled about 68% for Case 2 (Table 5). Alteration products for Case 2 totaled about 22% assuming magnetite is not an alteration phase. We calculate a small amount of amorphous silica for Case 2. The range of possible amounts of alteration phases in Peace is thus 22–52%. We favor the least altered case for Peace because of the abundant olivine and pyroxene determined by MB (Table 4).

6.3.2. Aqueous Processes

[58] Peace outcrop appears to be basaltic grains that have been cemented by Mg- and Ca-sulfates and possibly amorphous silica. Solutions rich in Ca^{2+}, Mg^{2+}, SO_4^{2-} and H_4SiO_4 apparently moved through clastic material of basaltic composition and formed sulfate-indurated layers as the solutions evaporated. The basaltic materials in these layers appear to be relatively unaltered, which suggests that the Mg and Ca solutions were not strongly acidic, i.e., slightly acidic to alkaline solutions. We propose that sulfuric acid solutions produced by volcanic activity reacted with basaltic materials in an open hydrologic system and these caustic solutions became neutralized as they passed progressively through basaltic sediments. The sulfates and amorphous silica formed when the activities of dissolved species exceeded their solubility products; possibly by evaporation of solutions near the surface.

[59] The presence of Mg- and Ca-sulfate cements is a very strong indicator that aqueous processes were instrumental in forming the Peace class. The most important aspect of these cements is that they suggest the movement of solutions through Columbia Hills materials. Because of the nature of the unaltered basaltic materials in the outcrop, we propose that the cementation process occurred in an open hydrologic system in which Ca, Mg, S, and Si (and possibly Fe to form npOx) were added to the basaltic sediments. We have attempted to arrive at a possible composition of the basaltic materials prior to sulfate cementation by subtracting the content of Mg- and Ca-sulfates, halides, Fe-oxides, and amorphous silica from the total chemical composition. The proposed chemical and mineralogical compositions of the Peace protolith are listed in Table 6; the Peace protolith is very similar to Martian meteorite ALHA77005. This rock is a partial cumulate composed of cumulus olivine and chromite±pigeonite, with intercumulus pigeonite, plagioclase and augite [e.g., *McSween et al.*, 1979]. If we are correct that the Peace class is a basaltic sediment cemented by sulfates, then one possibility is that it is a physical mixture of olivine, orthopyroxene and chromite grains with basaltic material (sands) that results in an ultramafic composition that mimics partial cumulates in major element composition. Alternatively, Peace could simply be a disaggregated and cemented version of partial cumulates similar to ALHA77005. Peace has a high magnetite content, which is not found in ALHA77005. We do not know whether the magnetite is primary or secondary. Because of its higher density and lower susceptibility to destruction by alteration, magnetite (and chromite) could have been concentrated by aeolian processes relative to olivine, pyroxene and basaltic sand. Thus the high magnetite content could support a physical mixture of materials as the mechanism forming Peace class rocks.

6.4. Backstay Class
6.4.1. Mineralogy

[60] Backstay is the least altered rock encountered in Columbia Hills on the basis of its low Fe^{3+}/Fe_T (Table 1) and contains the highest K content measured in Gusev crater. Only surface APXS measurements were made on Backstay. Backstay has minor amounts of alteration phases as suggested by the presence of about 1–2% npOx and minor hematite. The amount of npOx on Backstay is slightly higher than the plains basaltic rocks Adirondack and Humphrey but less than the surface of Mazatzal [*Morris*

Table 6. Compositions and Normative Mineralogies of Basaltic Materials in Peace Outcrop and Backstay Rock[a]

	Peace	ALHA77005	Backstay	QUE 94201
		Compositions: Oxides		
SiO_2, wt.%	44.5	42.8	52.0	47.0
TiO_2, wt.%	0.57	0.40	0.98	1.78
Al_2O_3, wt.%	3.6	2.7	13.9	11.6
Fe_2O_3, wt.%	3.5	-	0.9	-
FeO, wt.%	19.4	20.0	10.8	18.4
MnO, wt.%	0.58	0.46	0.26	0.45
MgO, wt.%	23.6	27.5	7.9	5.9
Na_2O, wt.%	0	0.44	4.04	1.68
K_2O, wt.%	0	0.03	1.12	0.06
P_2O_5, wt.%	0.7	0.4	1.5	2.0
Cr_2O_3, wt.%	0.9	1.0	0.2	0.1
Ni, mg/kg	650	320	140	140
Zn, mg/kg	80	71	200	85
		CIPW Normative Calculations: Minerals, %		
Quartz	-	-	-	1.14
Orthoclase	-	-	6.62	0.36
Plagioclase	9.74	9.24	50.76	38.25
Diopside	-	6.83	4.45	13.85
Hypersthene	55.74	23.82	20.21	36.32
Olivine	25.42	56.95	11.2	-
Magnetite	5.08	-	1.32	1.78
Ilmenite	1.08	0.77	1.86	3.39
Apatite	1.62	0.86	3.38	4.72
Chromite	1.32	1.54	0.24	0.19

[a]Compositions of basalts were estimated by subtracting sulfates, halides, and nanophase Fe-oxides from the bulk APXS chemical compositions of Peace and Backstay. An average of literature compositional data for Martian meteorite ALHA77005 is shown for comparison with Peace, and QUE 94201 for Backstay.

et al., 2004, 2006]. Sulfur was calculated as Mg-sulfate and Cl was modeled as halite. At the surface, about 4% of the rock is alteration phases; the remainder appears to consist of primary minerals.

6.4.2. Aqueous Processes

[61] Backstay is a relatively unaltered basalt. There appears to be minor amounts of alteration phases at the rock's surface, which may be primarily associated with dust and soil adhering to the rock's surface. We have attempted to arrive at a possible composition of the basalt by subtracting the content of sulfates, halides, and Fe-oxides from the total chemical composition. The proposed chemical and mineralogical compositions of Backstay are listed in Table 6. In terrestrial igneous parlance, Backstay would be classified as a sodic series alkalic basalt [*Irvine and Baragar*, 1971]. On the total alkali-silica classification diagram [*Le Bas et al.*, 1986], Backstay plots near the trachybasalt-basaltic trachyandesite boundary, and thus is best classified as a Martian equivalent of hawaiite-mugearite. However, the CIPW normative mineralogy of Backstay contains substantial hypersthene (Table 6), which is incompatible with assignment to an alkali basalt series; augite is the dominate pyroxene in terrestrial alkali basalts. Backstay plots near the tholeiitic-alkalic series boundary of *Irvine and Baragar* [1971] and errors in the analysis and in our attempts to calculate an alteration-phase-free composition thus make assignment as a Martian alkalic basalt problematical. Regardless, the relatively high Si content does suggest that Backstay is a more evolved, intermediate composition rock.

[62] Backstay is compared to QUE 94201, the Martian meteorite with the highest Ti and P content, and thus is an evolved basalt (Table 6). Backstay has lower Ti and P and higher Mg than QUE 94201, indicating it is a less evolved composition, yet has higher alkalis, Al and Si suggesting the opposite. The same disparity applies to comparison of Backstay with Martian meteorite Los Angeles (not listed in Table 6). If Backstay represents a Martian magmatic composition, then clearly it was formed as part of an igneous fractionation series quite distinct from that shown by the Martian meteorites.

6.5. Paso Robles Soil

6.5.1. Alteration Mineralogy

[63] Paso Robles soil is extensively altered. The most notable characteristic of Paso Robles light-colored material is S, the highest content measured on Mars at any location. Because it is highly altered, we only did a Case 1 calculation. Two different light-toned soil targets were measured by APXS and MB (targets Pasadena_PasoRobles and Paso-Robles2_LightSoil). A dark disturbed soil adjacent to the high albedo material was analyzed to provide compositional data on the local soil that may have been mixed with light-toned material by the rover's wheels. We have used the MB Fe^{2+} silicate and oxide compositions to provide estimates on the amount of dark soil mixed with the high albedo Paso Robles soil. The dark soil component is about 27% (Table 5). The two Paso Robles targets have relatively low Fe-oxides contents, about 4 and 1% hematite. MB measurements also suggested the presence of a ferric-sulfate [*Morris et al.*, 2006]. It is likely that S exists in sulfate form because the soil is highly oxidized as shown by the high Fe^{3+}/Fe_T (0.80–0.86). Ferric-sulfates account for about 25–29% of the Paso Robles composition. The additional S was assigned to Mg-, Ca-, Na-, K-, Al-, Mn-, Ni-, and Zn-sulfates. The total amount of sulfates for the Paso Robles and Light Soil targets is about 44% (Table 5), excluding about 1% sulfate added by the dark soil contaminant. Paso Robles also has a high P content. The P was modeled as brushite; although Fe-phosphate (e.g., strengite) cannot be ruled out. Iron phosphates are more thermodynamically stable than Ca-phosphates in most weathered systems [e.g., *Lindsay et al.*, 1989]. Regardless of whether we model the phosphate as Fe-or Ca-phosphate, the total phosphate composition in Paso Robles is 8–10%.

[64] Nearly all cations detected by APXS in Paso Robles were required to satisfy the charge balance with S and P assuming both are present as anions. Aluminum and Si remaining after we extracted the SO_4- and PO_4-bearing phases and dark soil contamination were assigned to an allophane-like phase and amorphous silica. These two phases accounted for 14–18% of Paso Robles.

6.5.2. Aqueous Processes

[65] The mineralogy and chemistry of Paso Robles soil very strongly indicate aqueous processes that involved the movement of liquid water within the host material. We suggest that Paso Robles is an evaporite deposit that formed from solutions rich in Fe, Mg, Ca, S, P, and Si. The probable identification of a Fe^{3+}-sulfate by the MB spectrometer [*Morris et al.*, 2006] presents unusual formation conditions for this locality. Fe-oxides and Fe-oxyhydroxides (with the exception of about 4% hematite) and Fe^{3+}-bearing sulfates

such as jarosite do not occur in Paso Robles; this may constrain the solution Eh and pH to a highly oxidized, extremely low pH solution. The support for this scenario is the high Fe^{3+}/Fe_T and the lack of goethite, jarosite, and abundant hematite. Ferric-sulfates are predicted in acid-sulfate weathering environments when solution pH is <1 [*Elwood Madden et al.*, 2004; *Burns and Fisher*, 1990; *Bigham and Nordstrom*, 2000]; the stability field for jarosite is between pH 1 and 3, and Fe-oxides/oxyhydroxides form in acid-sulfate solutions pH > 3 [e.g., *Nordstrom*, 1982; *Tosca et al.*, 2005]. *Golden et al.* [2005] show that Ca-, Mg- and Al-sulfates form by the alteration of olivine-rich and plagioclase-rich basaltic materials in very-acidic (sulfuric acid), oxidizing solutions (pH < 1) with a very-low water activity. The high Fe and P in Paso Robles may reflect the nature of the host material that was altered by sulfuric acid. For example, it is reasonable to assume the Fe and Mg are the result of sulfuric-acid solutions reacting with the source materials of the Peace basalt (Table 6) and the P and Ca are the result of these corrosive solutions reacting with a Wishstone-like source material.

[66] Paso Robles soil appears to be localized. This may indicate that a volcanic vent with SO_2-rich vapors was present within Husband Hill, similar to alteration vents seen on cinder cones on Mauna Kea [*Morris et al.*, 2000], but we cannot rule out the possibility that Paso Robles materials are more widespread. Another confounding problem with unraveling the genesis of this soil is the impact history of the Columbia Hills. Materials may have been reworked and possibly overturned by impact [*Arvidson et al.*, 2006], so it is difficult to place this soil in a stratigraphic sequence.

7. Summary

[67] Water and acid volatiles have played a major role in the alteration and formation of rocks, outcrops, and one unusual soil in the Columbia Hills. The degree of alteration ranges from moderately altered to materials that appear to be completely altered as suggested by their high Fe^{3+}/Fe_T, lack of Fe^{2+} in primary phases, and corundum normative mineralogies. These materials are substantially more altered than the basaltic rocks Spirit encountered on the plains of Gusev crater. The most important geochemical and mineralogical properties of rocks, outcrops, and one soil in the Columbia Hills are briefly summarized below.

[68] On the basis of elemental chemistry, there are five rock classes and one unique soil in the Columbia Hills: rock classes Clovis, Wishstone, Watchtower, Peace, and Backstay, and the soil Paso Robles. Clovis class rocks have compositions similar to basaltic soils on the Gusev plains with the exception of higher Mg, Cl, and Br and lower Ca and Zn; Wishstone and Watchtower have high Al, Ti and P and low Cr and Ni; Peace has high Mg and S and low Al, Na, and K; Backstay has high Si, Na and K; Paso Robles soil has high S and P.

[69] Clovis class rocks on West Spur exhibit a range of alteration, from moderately altered materials such as Wooly Patch outcrop to extensively altered materials such as Clovis outcrop. Wishstone class rocks are moderately altered and Watchtower appears to be a highly altered outcrop on Husband Hill. Backstay and the basaltic component of Peace are relatively unaltered materials. Peace, however, is composed of relatively unaltered mafic sands or pebbles cemented by Mg-rich sulfate salts. Some rocks and outcrops are corundum-normative suggesting that their original, primary compositions have been changed by loss and/or gain of rock-forming elements; i.e., alteration was not isochemical.

[70] The mineralogical composition varies substantially between classes. Clovis class consists of Fe-oxides/oxyhydroxides (magnetite, npOx, hematite, goethite), Ca-phosphates, Ca-sulfates, pyroxene and secondary aluminosilicates (e.g., allophane, amorphous silica). Wishstone class consists of Fe-oxides/oxyhydroxides (magnetite, npOx, hematite, goethite), ilmenite, Ca-phosphate (e.g., merrillite, whitlockite, apatite), pyroxene, feldspar, Mg-sulfates, and secondary aluminosilicates. Watchtower consists of Fe-oxides/oxyhydroxides (npOx, hematite, goethite, magnetite), ilmenite, Ca-phosphates (e.g., brushite), Mg-sulfates, secondary aluminosilicates, olivine, and pyroxene. Peace outcrop consists of magnetite, npOx, Mg- and Ca-sulfates, pyroxene, olivine, feldspar, apatite, halides, secondary aluminosilicates, and amorphous silica. Backstay consists of minor npOx, trace hematite, Mg-sulfates, and feldspars, pyroxenes, olivine, magnetite, and ilmenite. The light-toned soil Paso Robles consists of ferric-sulfates, Mg-, Ca-, and other sulfates, Ca-phosphates (e.g., brushite), hematite, halite, allophane, and amorphous silica.

[71] The Columbia Hills have experienced a very complex depositional, alteration, and impact history, which complicates deriving protoliths or source materials for the various outcrops and rocks. The high Ni contents of Clovis materials, similar to those of Gusev plains soils, suggest that they may have been derived from meteorite-contaminated soils. This may have been an impact-deposited older regolith that was subsequently altered by aqueous processes. Wishstone and Watchtower materials appear to have been derived from protoliths that were high in Ti and P, and low in Cr and Ni. These materials are consistent with volcanic deposits from fractioned magmas. Peace rocks appear to be sediments composed of igneous materials with ultramafic compositions indurated by Mg- and Ca-sulfate cements. Backstay has a trachybasalt composition with a high alkali content.

[72] Clovis, Wishstone, and Watchtower source materials were altered by fluids rich in the volatile elements S, Cl, and Br. However, it is not clear whether aqueous alteration occurred by hydrothermal solutions, by aqueous vapors from volcanic emanations, or by low-temperature solutions moving through the source materials. Outcrops and rocks such as Clovis, Ebenezer, and Watchtower appear to have been more extensively altered by solutions than other materials in the Clovis and Wishstone classes. Peace appears to have formed when basaltic sands or perhaps cobbles were deposited in layers by air-fall (e.g., volcanic ash, impact, or aeolian materials) or fluvial materials that were weakly cemented by Mg- and Ca-sulfates and silica when solutions rich in Ca^{2+}, Mg^{2+}, SO_4^{2-} and H_4SiO_4 moved through these layers. The mineralogy and chemistry of Paso Robles high albedo soil very strongly indicate aqueous processes that involved the movement of liquid water within the host material. Paso Robles appears to be an evaporite deposit that formed via the evaporation of solutions rich in Fe, Mg, Ca, S, P, and Si. The presence of

ferric-sulfates suggested it precipitated from highly oxidized, low-pH solutions.

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