WEATHERING OF BASALTIC ROCKS FROM THE GUSEV PLAINS UP INTO THE COLUMBIA HILLS FROM THE PERSPECTIVE OF THE MER MÖSSBAUER SPECTROMETER.

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Introduction: Rocks on the ejecta blanket of Bonneville crater and along *Spirit's* traverse over the Gusev plains towards the Columbia Hills are angular and strewn across the surface. They have a basaltic composition [1,2], and their Mössbauer spectra are dominated by an olivine doublet [1]. The ubiquitous presence of abundant olivine in rocks and in surrounding soil suggests that physical rather than chemical weathering processes currently dominate the plains at Gusev crater [1]. However, MB spectra of rocks and outcrops in the Columbia Hills suggest more aggressive alteration processes have occurred. Ascending into the hills, *Spirit* encountered outcrop and rocks exhibiting layered structures. Some scattered rocks at the foot of the Columbia Hills appeared "rotten" or highly altered by physical and/or chemical processes (fig. 1). Mössbauer spectra of those rocks show a decrease in olivine accompanied by an increase in the Fe-oxides magnetite, hematite, and nanophase Fe^{3+}-oxides (fig. 2), suggesting that chemical weathering processes in the presence of water have altered these rocks and outcrops.

Figure 1. The rock "Breadbox" is an example of a "rotten" rock at the foot of the Columbia Hills (Pancam image, false color).

Results and Discussion: *Spirit's* Mössbauer spectrometer identified the Fe-bearing silicates olivine (Ol) and pyroxene/glass (Px), nanophase ferric oxides (np-Ox), and the Fe-oxides magnetite (non-stoichiometric, ns-Mt) and hematite (Hm) in rocks on the Gusev plains and at the foot of the Columbia Hills. Mössbauer spectra of different rocks have been stacked in Figure 2 in order of a possible sequence of increased weathering from top to bottom as suggested by the decreasing relative abundance of olivine and increasing relative abundance of np-Ox and Fe^{3+}-bearing oxides. Assuming approximately isochemical weathering and Fe^{3+}/Fe_{total} ~ 0.16 for the unaltered precursor, the unaltered precursor rocks are olivine basalts with respect to norm calculations done on a S- and Cl-free basis (Table 1). That is, olivine was likely a mineralogical component of these rocks when they crystalized. The observational evidence by MB suggests olivine as the primary mineral that has undergone alteration. Laboratory observations show that olivine weathers readily to form Fe-oxides under a variety of conditions [3, 4]. Similarly, the Fe^{2+} doublet attributed to pyroxene and/or glass is consistent with pyroxene alone, as Fe-bearing glass may be more susceptible to weathering and alteration than olivine.

The role of magnetite is more ambiguous, because it can be either a primary igneous mineral or a secondary weathering product. Therefore, we must consider the possibility that at least some of the magnetite observed at Gusev crater is secondary in origin.

At high pH levels (>8), magnetite can form from olivine through solubilization, partial oxidation, hydrolysis and subsequent precipitation [5] or via serpentinization:

$$6FeMgSiO_4 + 10H_2O \rightarrow 2Fe_3Si_2O_5(OH)_4 + 6Mg(OH)_2 + 2SiO_2$$

$$2Fe_3Si_2O_5(OH)_4 + 6Mg(OH)_2 \rightarrow 2Mg_3Si_2O_5(OH)_4 + 2Fe_3O_4 + 2H_2(aq) + 4H_2O$$

High pH solutions are hard to reconcile with S abundances at Gusev crater (i.e., alteration at the surface may have been under sulfur acid weathering). Furthermore, there is no observational evidence for serpentine or other phyllosilicates from *Spirit's* instruments [6]. However, magnetite formation is also possible at lower pH levels [5]. Another possible formation mechanism is that a transient heating event (e.g., associated with impact or volcanic events) may have caused the partial oxidation of Fe^{2+} silicates to magnetite prior to the start of aqueous alteration (e.g., [7]).

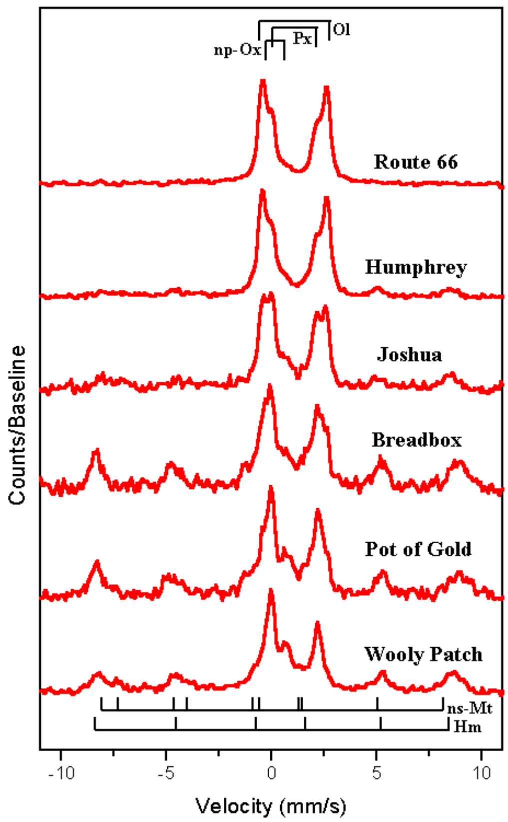

Figure 2. Mössbauer spectra of rocks (from the top) Route 66, Humphrey and Joshua in the Gusev plains, and Breadbox, Pot of Gold and Wooly Patch at the foot of the Columbia Hills.

The magnetite identified in the Mössbauer spectra is non-stoichiometric. Compared to stoichiometric magnetite, the sextet resulting from tetrahedral (Fe^{3+}) sites is enhanced relative to the sextet resulting from octahedral (Fe^{2+} + Fe^{3+}) sites [1].

This deviation from stoichiometry can result from partial oxidation of Fe^{2+} to Fe^{3+} and/or impurities, the former suggesting that the hematite identified in some rocks might be the endproduct of further oxidation and subsequent restructuring of the ns-Mt. However, the formation of hematite might also take place independent of magnetite due to variations in pH, water/rock ratio, and oxidation state.

Conclusions: Mössbauer spectra in Figure 2 have been arranged to show a possible weathering sequence of basaltic rocks at Gusev crater. The rocks with high olivine content have been found on the Gusev plains, whereas the olivine content decreases in favor of Fe^{3+}-oxides at the foot of the Columbia Hills and ascending into them. The Columbia Hills may be a domain of highly altered basaltic rocks or volcaniclastic materials and might thus be a remnant of a wetter past inside Gusev crater. It is possible that the higher levels of magnetite observed in the most olivine-poor rocks results from contributions from both igneous and weathering processes. The occurrence of olivine along with highly altered phases, e.g., hematite, might reflect the non-equilibrium nature of the current martian surface.

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Table 1. Normative mineralogy of rocks on the plains and the Columbia Hills at Gusev crater. Normative calculations were made on S-free and Cl-free APXS compositions assuming a $Fe^{3+}/Fe_{(total)}$ ratio of 0.16 (note: this mineralogy is not proposed for these rocks and outcrops; this mineralogy only illustrates the possible mineralogy prior to isochemical 'weathering" or alteration).

Sample	Feldspar	Pyroxene	Olivine	Magnetite	Ilmenite	Apatite	Nepheline	Corundum	Chromite
A060_Humphrey_Heyworth2_PostGrind	40.79	24.35	26.87	4.7	1.01	1.39	-	-	0.88
A100_Route66_Soho_PostBrush	45.1	18.42	28.12	4.58	1.08	1.88	-	-	0.8
A150a_Mojave_Joshua_Undisturbed	38.4	17.51	32.05	4.76	0.87	1.3	4.36	-	0.72
A172_PotofGold_PostGrind	46.02	13.44	31.25	4.52	1.52	2.8	-	-	0.41
A176_Breadbox_Sourdough	46.69	26.8	17.7	4.06	1.61	2.66	-	-	0.46
A197_WoolyPatch_Sabre_PostGrind	42.04	27.02	18.26	4.16	1.69	3.1	-	3.28	0.4
A199_Woolypatch_Mastodon_PostGrind	36.19	34.66	16.99	4.89	1.65	3.01	-	2.29	0.27