NEW APPROACHES TO INTERPRETING THE GEOCHEMISTRY OF THE COLUMBIA HILLS ROCKS, GUSEV CRATER, MARS. P. L. King[1] and H. Y. McSween Jr.[2], [1] Dept. Earth Sciences, University of Western Ontario, London, ON, N6A 5B7 Canada, [2] Dept. Earth and Planetary Sciences, University of Tennessee, Knoxville, TN 37996 USA.

Introduction: The martian surface is dominated by basaltic rocks, but commonly these rocks are obscured by coatings of dust, soil, and Mg-Na-SO_4-Cl-(Br)-rich rinds, cements, veins, and mineral casts. The chemistry of the martian surface has been explained as a mixture between basalt and secondary minerals that formed due to acid fog and/or impact processes and/or precipitated from acidic water-bearing solutions [1, 2]. Mineral mixing in aeolian/impact events and weathering in acidic solution [2] may also play a role.

To test which hypothesis adequately explains the chemical and mineralogical data for Mars, we examine the bulk chemical (Alpha Particle X-ray spectrometer; APXS) data [3] from the Columbia Hills, within the Noachian Gusev Crater. We also examine the hypothesis that acidic solutions were not necessary on the martian surface.

Rock Types & Previous Interpretations: The *Gusev basalts* (Adirondack, Mazatzal, and Humphrey) are picritic basalts that contain olivine, pyroxenes, plagioclase, Fe-Ti-Cr-oxides and phosphates [4]. Compared to the Gusev basalts, all samples from the Columbia Hills are considerably enriched (>2x rel.) in S, Cl and Br suggesting the presence of salts [3]. There are significant variations in composition with surface treatment [3]; thus, we only discuss samples that have been abraded with the rock abrasion tool (RAT).

The West Spur *Clovis* samples are granular, matrix-rich, volcanic- or impact-derived rocks [5] that are significantly enriched in K and Ni, and depleted in Ca, Mn and Cr [3]. These rocks were proposed to result from weathering of pyroxene or glass in acidic solutions [2]. Compared to the Gusev basalts, the Husband Hill *Wishstone* samples (Wishtone, Champagne and Wishingwell) are significantly enriched in P, Na, K and Ti, and depleted in Fe, Mg, Mn and Ni [3]. The Husband Hill *Watchtower* samples (Watchtower and Methusela) are similar to Wishstone samples except they have Mg and Na similar to the Gusev basalts. Both groups are clastic basalts that formed through either volcanism or impact processes [5], and contain vugs or veins of bright material in PanCam images. They have been interpreted to form through Ca-phosphate weathering in acidic waters [2]. The Husband Hill (Cumberland Ridge) *Peace* samples (Peace and Alligator) are cemented clastic rocks [5] with high Mg and Ni with significantly low Na and Al, and slightly low Ca and Si compared to the Gusev basalts.

Methods: In this abstract, we emphasize the importance of examining anion mole proportions (% PO_4, SO_4, Cl , Br) to evaluate salt abundances, as has been successfully employed on Earth (see [6]). To produce a ternary diagram, we combined Cl+Br because they are geochemically similar and are generally correlated [3].

Another significant difference in our approach is that we examine the mole proportions of the cations in parallel with the anions. We use a ternary diagram of molar Al_2O_3 (A), $CaO+Na_2O+K_2O$ (CNK) and FeO+ MgO (FM), similar to [2]. We use these diagrams to evaluate: acid fog addition (Fig. 2A), mineral mixing (Fig. 2B), acidic or neutral-basic aqueous weathering (Fig. 2C), and addition of components through precipitation from a brine (Fig. 2D).

Results: The *Clovis* samples have PO_4/(Cl+Br+SO_4) similar or lower than the Gusev basalts. The (Cl+Br)/(Cl+Br+SO_4) is similar or higher than the Gusev basalts and FM/(FM+CNK) is higher (Fig. 1).

The *Wishstone* and *Watchtower* samples have PO_4/(Cl+Br+SO_4) much higher than the Gusev basalts and (Cl+Br)/(Cl+Br+SO_4) is within the range of the Gusev basalts (Fig. 1A). Overall, the Husband Hills samples define a trend (R^2=0.96) that intercepts A/(A+CNK)=40% (Fig. 1B). This trend is more CNK-rich than the plagioclase-mafic mineral join where we used the average plagioclase rim composition, $Ab_{46}An_{53}Or_1$, from the martian meteorites [7]. The other end of the line intercepts the CNK-FM join at ~97% FM/(FM+CNK) which defines a mixture of mafic minerals: clinopyroxenes (pyroxene rims; [7]) and Fe-Mg-rich phases.

Relative to the Gusev basalts, the *Peace* samples have much lower PO_4/(Cl+Br+SO_4) and (Cl+Br)/(Cl+ Br+SO_4) (Fig. 1A). They are extremely FM-rich and plot between mafic mineral compositions (Fig. 1B).

Interpretations: *Clovis* Both absolute and relative Cl, Br and SO_4 increase in the Clovis rocks suggesting addition of these components. Addition of an acid fog component alone does not provide the appropriate cations (Figs. 1B, 2A). Instead, the bulk chemistry may be explained by adding minerals (Fig. 2B), weathering (Fig. 2C), or adding brine (Fig. 2D). Minerals added to the initial starting basalt could include olivine, pyroxene, and CNK-FM-halides and/or sulfates (Fig. 2B). Minerals may be added through aeolian, impact or igneous processes. Weathering in an acid solution of pyroxene or glass [2] requires addition of the necessary anions (Fig. 2C) and it is therefore not a simple explanation. But weathering of salts and silicates in a neutral-basic solution may form the appropriate compositions (Fig. 2C). Alternately, salts may be added by precipitation from a brine (Fig. 2D). This case differs from mineral addition/weathering in that silicate minerals need not be involved and an individual brine should precipitate minerals in sequence from least to most soluble minerals, dependent on the bulk composition: Ca-Mg-phosphates (if PO_4-saturated brine), Ca-sulfates (if a Ca-rich brine), Mg-Na+K-sulfates, and Na+K-Mg chlorides [8]. In the Clovis samples, any likely brine was somewhat moderately evolved based on the high Cl+Br+SO_4 (Fig. 1A, 2D) and Mg>Na+K>Ca (Fig. 3). Thus, the most likely salts lie in the Mg-Na+K-Gusev basalt subtriangle in Figure 3 (Fe-sulfates were ignored in this figure for brevity, but may be present; see discussion in [9]). Such a salt assemblage likely precipitated near the epsomite-bloedite-halite eutectic [8].

Wishstone and *Watchtower* samples must contain CNK-rich alteration phases because they form a trend more CNK-rich than the plagioclase-mafic mineral join (Fig. 1B). The compositions may not be derived simply from an acid fog process because PO_4 and cation concentrations are incorrect (Fig. 2A). Acid weathering of phosphates is possible [2], although high Cl+Br+SO_4 contents require that halides and sulfates must have been added also. This could be achieved through addition of either those salts (Fig. 2B) or a primitive to moderately evolved brine (Fig. 2D). The most likely salts present are those in the Ca-Na+K-Gusev basalt subtriangle in Figure 3 and include phosphates and CNK-Mg sulfates and Na-K-halides.

The *Peace* samples have extremely high Mg and SO_4 and the easiest way to explain this composition is addition of Mg-SO_4-rich minerals or a primitive Mg-SO_4-brine (Fig. 2B, 2D), as discussed by [3 and 8]. MiniTES observations of bound H_2O [reported in 5] could indicate presence of hydrous salts. Other possible minerals lie in the Ca-Mg-Gusev basalt subtriangle (Fig. 3) and include Ca sulfate (gypsum).

Conclusions: Combined use of anion and cation ternary diagrams provide important insights into the possible mechanisms for changing rock compositions on Mars. The Clovis samples may form by adding minerals, weathering at neutral-basic conditions, or adding an evolved brine; acidic conditions are not necessary. The Wishstone and Watchtower samples may be explained by acid weathering of phosphates [2]. However, a simper hypothesis is that compositions result from mineral addition or precipitation from a primitive to moderately evolved brine (not necessarily acidic). The Peace samples may form by addition of Mg-SO_4 minerals or a primitive brine. To distinguish between mineral addition and brine precipitation processes it is necessary to examine textural evidence for the salt precipitation sequence *in situ* on the martian surface. Textural relations of salts in the martian meteorites are most consistent with precipitation of salt minerals from a brine [8].

References: [1] Bullock M. A. (2005) *Nature*, *438*, 1087-1088. [2] Hurowitz J. A. (2006) *JGR*, *111*, doi:10.1029/2005JE002515. [3] Gellert R. et al. (2006) *JGR.*, *111*, doi:10.1029/2005JE002555. [4] McSween H. Y. et al. (2006) *JGR*, *111*, doi:10.1029/2005 JE002477. [5] Arvidson R. V. (2006) *JGR*, *111*, doi:10.1029/2005JE002499. [6] Hardie L. A. and Eugster H. P. (1970) *Min. Soc. Am. Sp. Pap.*, *3*, 273-290. [7] McSween H. Y. and Treiman, A. H. (1998) *Rev. Mineral.*, *36*, 6-1-53. [8] King P. L. et al. (2004) *GCA*, *68*, 4993-5008. [9] King P. L. and McSween H. Y. (2005) *JGR*, *110*, doi:10.1029/2005JE002482.

Fig. 1: Ternary diagrams showing the Columbia Hills rocks.

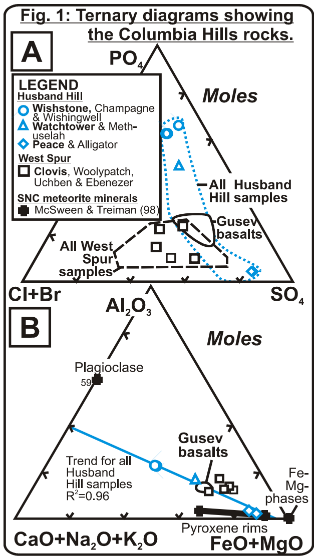

Fig. 2: Schematic changes in bulk composition from Gusev basalt due to:

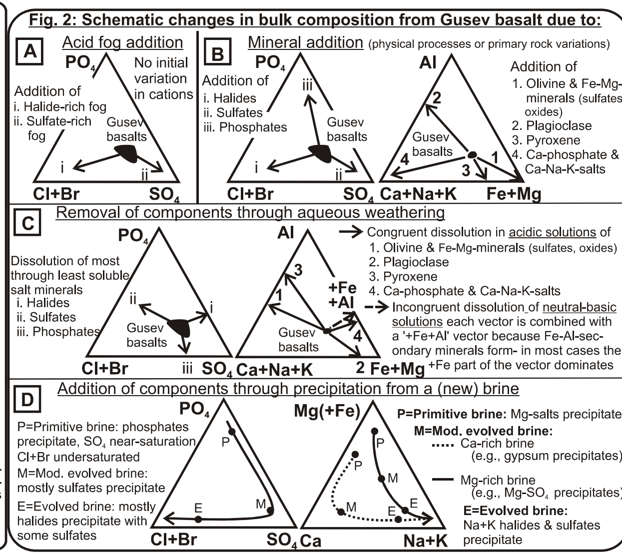

Fig. 3: Possible salts in the Columbia Hills rocks