

Chapter 23: Aqueous Alteration on Mars

Douglas W. Ming, Richard V. Morris
NASA Johnson Space Center

and

Benton C. Clark
Lockheed Martin

Abstract

Aqueous alteration is the change in composition of a rock, produced in response to interactions with H₂O-bearing ices, liquids, and vapors by chemical weathering. A variety of mineralogical and geochemical indicators for aqueous alteration on Mars have been identified by a combination of surface and orbital robotic missions, telescopic observations, characterization of Martian meteorites, and laboratory and terrestrial analog studies. Mineralogical indicators for aqueous alteration include goethite (lander), jarosite (lander), kieserite (orbiter), gypsum (orbiter) and other Fe-, Mg-, and Ca-sulfates (landers), halides (meteorites, lander), phyllosilicates (orbiter, meteorites), hematite and nanophase iron oxides (telescopic, orbiter, lander), and Fe-, Mg-, and Ca-carbonates (meteorites). Geochemical indicators (landers only) for aqueous alteration include Mg-, Ca-, and Fe-sulfates, halides, and secondary aluminosilicates such as smectite. Based upon these indicators, several styles of aqueous alteration have been suggested on Mars. Acid-sulfate weathering (*e.g.*, formation of jarosite, gypsum, hematite, and goethite), may occur during (1) the oxidative weathering of ultramafic igneous rocks containing sulfides, (2) sulfuric acid weathering of basaltic materials, and (3) acid fog (*i.e.*, vapors rich in H₂SO₄) weathering of basaltic or basaltic-derived materials. Near-neutral or alkaline alteration occurs when solutions with pH near or above 7 move through basaltic materials and form phases such as phyllosilicates and carbonates. Very low water:rock ratios appear to have been prominent at most of the sites visited by landed missions because there is very little alteration (leaching) of the original basaltic composition (*i.e.*, the alteration is isochemical or in a closed hydrologic system). Most of the aqueous alteration appears to have occurred early in the history of the planet (3 to 4.5 billion years ago); however, minor aqueous alteration may be occurring at the surface even today (*e.g.*, in thin films of water or by acid fog).

1. Introduction

The geologic processes responsible for aqueous alteration on Mars are modeled beginning with our knowledge of analog processes on Earth; *i.e.*, characterization of elemental and mineralogical composition of terrestrial environments where the alteration and weathering pathways related to aqueous activity are better understood. A key ingredient to successful modeling of aqueous processes on Mars is identification of phases that have formed by those processes. The purpose of this chapter is to describe what is known about the elemental and mineralogical composition of products of aqueous weathering and alteration on Mars and their implications for specific aqueous environments. The environmental conditions for aqueous alteration and the epoch in which they occurred are critical for assessing the extent and the timing for possible life on Mars.

2. Definitions and Terminology

2.1 Aqueous Alteration

Aqueous alteration is the change in chemical and/or mineralogical composition of a rock, produced in response to interactions with H₂O-bearing ices, liquids, and vapors by chemical weathering at ambient or hydrothermal (above ambient) temperatures. In general, weathering is the chemical and physical breakdown of rocks upon exposure to atmospheric agents under ambient temperatures at or near the surface (*e.g.*, Gooding *et al.*, 1992).

Chemical alteration is the process by which chemical reactions (*e.g.*, hydrolysis, hydration, oxidation, carbonation, ion exchange, and solution) transform rocks into new chemical combinations. Hydrolysis is a decomposition reaction involving water and the subsequent formation of metal-hydroxyl ion pairs and metal polynuclear complexes (*e.g.*, iron oxyhydroxides). Hydration is the chemical combination of water with another substance. Oxidation is a reaction where an ion or molecule loses one or more electrons, and the process can happen in aqueous and non-aqueous systems (*e.g.*, thermal oxidation). Carbonation is a reaction that transforms minerals or phases containing Ca, Mg, Fe, K, Na, etc. into carbonates or bicarbonates of these metals by CO₂-containing (or CO₃-containing) water. Ion exchange is a reversible processes where ions in a crystal are exchanged with ions in solution (*e.g.*, ion exchange in the interlayers of smectites). Solution chemical weathering is a process where a mineral or phase is removed into solution (*e.g.*, salts dissolving in passing waters). In contrast to these chemical processes, physical weathering occurs when mechanical processes (*e.g.*, abrasion, freeze-thaw, and salt-crystal growth) fragment a rock without a chemical change.

Aqueous alteration without subsequent removal of elements from the precursor rock is referred to as isochemical (or closed system) aqueous alteration. In the strictest sense, only energy (and not matter) is exchanged with its surroundings in a closed system; however, a system may be closed (*i.e.*, no removal of the original elements during alteration) but open with respect to the addition of acidic, neutral, or basic water and gases (*e.g.*, O₂, CO₂, Cl₂, and SO_x). Aqueous alteration with subsequent removal of elements from the precursor rock (*e.g.*, by leaching) is referred to as open-system aqueous alteration. In an open system both energy and matter are exchanged with the surroundings. The style and extent of aqueous alteration on Mars can vary in time and/or location in response to changes in local conditions (*e.g.*, meteoritic impact into volatile-rich material or invasion by hydrothermal fluids associated with volcanism)

and/or global conditions (*e.g.*, climate change). Diagenesis is the change in physical and chemical properties of a sediment after its initial deposition. Diagenetic processes are those that occur under conditions of pressure and temperature in the outer part of the crust, including processes such as cementation, replacement, and compaction. Aqueous processes may be key factors in the diagenetic alteration of a sedimentary deposit.

2.2 Style of Aqueous Alteration

The style of aqueous alteration depends on the chemical composition of the H₂O-bearing fluids or gasses that interact with the host rock or material. For example, hydrolytic, acid-sulfate, and acid-chloride aqueous alterations cause the breaking of chemical bonds in solid materials and adding of the elements of H₂O (H⁺ and OH⁻), H₂SO₄ (H⁺ and SO₄⁻²), and HCl (H⁺ and Cl⁻), respectively, to the weathering products (*e.g.*, Morris *et al.*, 2000). The breaking of bonds most commonly involves H⁺ reacting with and breaking M-O-Si bonds (where M = Si, Al, Mg, Ca, Fe, etc.). These three styles of alteration have been suggested as generating aqueous solutions that have interacted with martian host rocks, most likely basaltic in composition (see discussion in Section 6 below).

2.3 Extent of Aqueous Alteration

The extent of aqueous alteration is governed by many factors, including temperature, time, alteration style, parent rock mineralogy, H₂O to rock ratio, and rock permeability. Two indices have been used to evaluate the extent of alteration/weathering based upon measurements made at Mars. The Mineralogical Alteration Index (MAI) is based upon the percentage of total Fe (Fe_T) present as Fe³⁺ in alteration products (Morris *et al.*, 2006; Klingelhoefer and Morris, 2007) (see Fig 1a). However, magnetite, which contains Fe³⁺, is considered to be a product of igneous activity and not an alteration product. Unaltered to weakly altered rocks have values of MAI in the range 0 to 20%, and pervasively altered rocks have values in the range of 80 to 100%. Although the MAI indicates the extent of alteration, it does not distinguish between aqueous and non-aqueous processes. For example, it is possible that primary magnetite in the host basalt can be converted to hematite by dry, thermal processes (possibly associated with igneous or impact processes) and not aqueous processes.

In contrast, the Chemical Index of Alteration is based upon the chemical composition of the basaltic material that has been weathered (Nesbitt and Young, 1982, 1984, 1989; Nesbitt and Wilson, 1992). The Chemical Index of Alteration provides information on the extent to which elements have been removed from the host rock and the likely formation of secondary phases (see Nesbitt and Young, 1982, 1984, 1989, for details). For the purposes of this chapter, we have adopted the ternary diagrams used by Nesbitt and Wilson (1992) to evaluate the extent that elements are removed or leached away from the reaction front (see Hurowitz *et al.*, 2006, for examples of this method used for Mars). Basaltic compositions lie along the olivine to feldspar join (Figure 1b). As weathering of bulk rock proceeds, the primary minerals are destroyed and secondary minerals (such as smectite) form and the composition of the resulting secondary phases are more aluminum rich than the original basalt. Care must be taken, however, when interpreting such plots because small changes in composition resulting from weathering or leaching are not necessarily apparent. In such cases, additional techniques such as basalt normative calculations (standard CIPW normative calculations for rocks and soils on a S-, Cl-,

and Br-free basis with an assumed $\text{Fe}^{3+}/\text{Fe}_T$) may add information on the extent that a material has been altered from the original basaltic composition (*e.g.*, Ming *et al.*, 2006). For example, corundum normative mineralogies (*i.e.*, enriched in Al compared to that accommodated by feldspar) can indicate weathering and removal of mobile elements during aqueous alteration (see Section 5.2.2 below).

2.4 Nomenclature for H₂O and OH Speciation in Solid Phases

For purposes of discussion, it is useful to have specific working definitions for the ways the H₂O molecule is incorporated into solid geologic materials. We will use the following nomenclature: adsorbed H₂O, trapped H₂O, solvation H₂O, and crystal H₂O. Adsorbed H₂O is physically held to surfaces by either weak Van der Waals type forces because of the dipolar nature of the water molecule or by hydrogen bonding to acid sites on mineral surfaces. Adsorbed H₂O can usually be removed by decreasing pressure or heating the material to about 110°C under ambient pressures. Trapped H₂O is a general term we use for H₂O physically confined into interstices, pore space, fluid/vapor inclusions, and/or grain boundaries during or subsequent to rock formation. Solvation H₂O (sometimes referred to as exchange cation water or zeolitic water) is H₂O that is coordinated with a cation on the exchange sites in the interlayers of phyllosilicates and within the cages of zeolites. Crystal H₂O is part of the unit cell and cannot be removed without changing the structure (although the dehydration of exchangeable or extraframework cations in zeolites and smectites may cause only very slight changes to unit cell parameters; *e.g.*, Bish and Carey, 2001; Bish *et al.*, 2003; Brown and Brindley, 1980). In some cases (*e.g.*, in the sulfate hexahydrate-epsomite system), the rehydration of these phases is reversible and results in reconstituting the mineral. Phases with solvation and crystal H₂O are collectively referred to as either “hydrous minerals” or “hydrated minerals”. However, the phrase “waters of hydration” refers only to crystal water. The removal of adsorbed H₂O is called desorption, and the removal of trapped, solvated, and crystal H₂O is dehydration. Minerals that contain only OH⁻ (hydroxide anion) in their structures are, technically, anhydrous minerals containing hydroxyls (Dana’s New Mineralogy; Gaines *et al.*, 1997), although they are formed as a product of aqueous activity and will decompose with evolution of H₂O when heated (*i.e.*, dehydroxylation).

3. Pre-MER Mineralogical and Geochemical Indicators for Aqueous Alteration

A thorough characterization of the elemental and mineralogical composition of alteration phases and their precursors is required in order to fully evaluate the style and extent of aqueous alteration. Our knowledge of the occurrence of aqueously altered materials on Mars is limited to in-situ and remote sensing data returned by robotic missions (orbiters and landers/rovers), remote sensing data by Earth-based telescopes, and laboratory analyses of the small number of Martian meteorites that have been discovered on Earth. The style and extent of aqueous alteration can be addressed by comparing the Martian materials to terrestrial analogs that have similar phases of alteration. For purposes of discussion, we divide data for martian surface materials into pre-MER orbital and lander missions (Telescopic, Mariner, Viking, Phobos, Pathfinder, and Mars Global Surveyor), martian meteorites, and MER-era orbital and lander missions (MER, Mars Odyssey, and Mars Express).

3.1 Telescopic, Mariner, Viking, Phobos 2, and MGS Orbiters: “Bound” Water, Hematite, and Ice

Results from these earlier observations are discussed in detail elsewhere in this book (see, *e.g.*, Chapters 2, 7, 8, and 9). The intent of this section is to briefly point out major scientific findings that have suggested materials that might have formed on Mars by aqueous processes. IR spectrometry from telescopes and instruments onboard Mariner spacecrafts detected possible water-bearing phases including frost, ice or hydrated minerals such as montmorillonite along with mixtures of silicate minerals (*e.g.*, Houck *et al.*, 1973; Clark and McCord, 1982; Bell and Crisp, 1993; Pimental *et al.*, 1974; Calvin, 1997; Hunt *et al.*, 1972; Hanel *et al.*, 1977; Toon *et al.*, 1977). Visible multispectral imaging onboard the Viking orbiters suggested the presence of amorphous Fe oxides (Evans and Adams, 1980). The presence of these hydrated phases and amorphous Fe oxides established that Mars has likely seen some extent of aqueous processes during its history. A distinct 3 μm water band was detected by the ISM instrument onboard the Phobos-2 orbiter (Murchie *et al.*, 2000), confirming the presence of water-bearing phases as indicated on earlier orbiting missions and telescopic observations.

The next major step forward in understanding alteration materials on the surface was the discovery of coarse-grained "gray" hematite by the Thermal Emission Spectrometer (TES) onboard the Mars Global Surveyor (Christensen *et al.*, 2000, 2001a,b). Several hypotheses were put forth for the formation of the gray hematite (Christensen *et al.*, 2001b). One was hematite formation via precipitation of ferric iron oxides (*e.g.*, ferrihydrite and goethite) from water on early Mars, followed by subsequent burial and recrystallization to platy hematite particles and later re-exposure at the surface (Lane *et al.*, 2002). Since that time, the MER rovers have shown that water was indeed involved in the formation of the hematite and the sulfate-rich siliciclastic sediments at Meridiani Planum, and that the hematite is associated with a lag deposit of iron-rich spherules (see Chapter 25 by McLennan and Grotzinger). Other minor abundances of secondary phases have been suggested based upon TES spectral data, including carbonates (*e.g.*, Bandfield *et al.*, 2003) and zeolites (Ruff, 2004). However, with the exception of the discovery of gray hematite by the MGS TES, our knowledge of the specific elemental and mineralogical composition of the phases that might have formed by aqueous processes is extremely limited from these earlier telescopic observations and orbiting missions.

3.2 Viking and Pathfinder Landers: Sulfates? Clays?

The Viking Lander missions significantly improved our understanding of the chemical composition of the martian surface. The data returned by the X-ray Fluorescence Spectrometers (XRFS) provided the first geochemical information on surface materials (Clark *et al.*, 1977, 1982). However, the mineralogy of these phases was not determined by any definitive mineralogical method (*e.g.*, X-ray Diffraction, Raman, or Mössbauer). Comparing explicit models with chemical data via multiple variation diagrams, it was inferred that Viking soils can be explained by two chemical components, one of which is restricted to contain S, Cl and most of the Mg (Clark, 1993). The high Mg-S component occurs in what appeared to be duricrusted samples, suggesting cementation by Mg-sulfates. The Alpha Proton X-ray Spectrometer (APXS) on the Mars Pathfinder Sojourner microrover also found systematic variation between Mg and S (See Chapter 3 by Foley *et al.*). However, that trend is evident mainly in diagrams which include both soils and rocks, and could also be explained as a correlation simply resulting from Mg-S

rich soil coating Mg-S poor rock surfaces to varying degrees (Pathfinder had no capability to clean or grind the rock targets, and Viking was unsuccessful in finding small rocks which could be delivered to the analytical instruments). The martian soils analyzed by Viking and Pathfinder did not show positive correlations between Ca and S, in agreement with all later MER results. Using an X-ray backscatter standard, it was deduced that the Viking samples contained an additional 9 to 10 wt.% of undetectable components, which could include Na₂O, carbonates, and H₂O. Applying the typical Na₂O value of 3 wt.% for martian soils (Yen *et al.*, 2005) and allowing for zero to 2 wt.% of CO₂ (as carbonate), these results indicate a possible H₂O content of 4 to 7 wt.%.

Pathfinder analyses using the Rutherford scattering alpha backscatter technique placed the strongest upper limit on carbon in the soils and rocks, at a value corresponding to less than 2.5% by wt. of CO₂ equivalent (Brückner *et al.*, 1999). These measurements also indicate some H₂O content in some of the local K-rich rocks but less in soils (see Chapter 3 by Foley *et al.*).

4. Martian Meteorites: Sulfates, Halides, Carbonates, Oxides, and “Clay Minerals”

Laboratory analyses of martian meteorites have greatly improved our knowledge of the geochemical, mineralogical, and chronological characteristics of materials from the martian crust (see Chapter 17 by McSween). Although these meteorites exhibit primary lithologies, several contain minerals strongly indicating indigenous aqueous processes on Mars, showing that water did at least have some influence on martian crustal materials. The lack of evidence for extensive alteration in the martian subsurface as represented by the martian meteorites suggests that acidic weathering on Mars is restricted to the surface or uppermost crust (*e.g.*, Newsom, 2005). The intent of this section is to survey the phases that likely formed by aqueous processes in the martian meteorites; a detailed review of the alteration assemblages in martian meteorites is provided by Bridges *et al.* (2001).

The secondary phases that have been identified in martian meteorites includes sulfates, carbonates, iron oxides, sulfides, and poorly crystalline silicates/aluminosilicates (Table 1). The ALH84001 martian meteorite, which is the oldest and is also known for the possibility that it harbors relicts of life (McKay *et al.*, 1996), contains mixed Fe-Mg-Ca carbonates, magnetite, and Fe sulfides (Mittlefeldt, 1994). A plausible model for the formation of this secondary mineral suite was that carbonate globules in ALH84001 first formed as a hydrothermal precipitation product from CO₂-rich fluids whose composition changed with time and temperature, producing globules with ankeritic (Fe-Mg-Ca-carbonate) cores and concentric zones of Fe-rich carbonate (siderite) plus Fe disulfide (pyrite), magnesite (Mg-carbonate), and another Fe-rich carbonate plus Fe sulfide outer zone. During a subsequent thermal event initiated by impact or volcanic events, the ALH84001 globules were sufficiently heated to form magnetite and pyrrhotite as decomposition products of siderite and pyrite, respectively (Golden *et al.*, 2001, 2004).

Minor amounts of Ca-rich sulfate (and other sulfates), halite (and other chlorides), and possibly phyllosilicates are present in Shergotty meteorite (Table 1). Solutions may have passed through the Shergotty precursor, periodically resulting in episodic alteration (Wentworth and Gooding, 2000). The Nakhrites (Lafayette, Governador Valadares, Nakhla) contain a variety of secondary phases, including Fe-rich carbonates, Ca-sulfates, poorly crystalline aluminosilicates and iron oxides (*e.g.*, iddingsite in Lafayette), and halite (see Table 1). The recently discovered Nakhlite MIL 03346 has jarosite veins running through the meteorite's mesostasis (glassy and/or microcrystalline interstitial material); however, it is not clear whether the jarosite is indigenous

to Mars or formed as the meteorite was weathered on Earth (Herd, 2006). Water appears to have reacted with the Nakhrites' host rocks (probably at low temperature), releasing ions into solution; the secondary phases likely formed during the evaporation of the solutions (Bridges and Grady, 1999, 2000). Chassigny contains minor amounts of Ca- and Mg-rich carbonates and Ca-rich sulfates. One possible scenario for their formation is percolation of briny water through the host rock and subsequent precipitation during evaporation of solutions (Wentworth and Gooding, 1994).

In summary, aqueous fluids have interacted with the host rocks of the martian meteorites, and the interaction has resulted in low levels of alteration. No known Martian meteorite has been pervasively altered. It appears that in most instances briny waters have passed through the host rock and the secondary phases (salts) formed during evaporation of the solutions. With the exception of ALH84001, these host materials are relatively young (by martian standards); hence, these solutions must have interacted with the host rock during the late stages of the Amazonian period (recent to 1.8 Ga). The oldest martian meteorite (ALH84001), however, may have experienced hydrothermal fluids moving through its host rock during the Noachian period (3.5 Ga to around 4.54 Ga).

5. MER-era Mineralogical and Geochemical Indicators for Aqueous Alteration

The four most recent spacecraft to arrive at Mars (the MER rovers Spirit and Opportunity, and the Mars Odyssey and Mars Express orbiters) have provided several positive mineralogical identifications of phases that formed as products of aqueous alteration. The most important mineralogical and geochemical markers for aqueous processes by the four spacecraft are briefly summarized below. The recent arrival of the Mars Reconnaissance Orbiter (MRO) will provide additional information on the mineralogical composition of the martian surface.

5.1 Mineralogical Markers

5.1.1 Mars Odyssey: Water Ice, Hydrated Minerals, Adsorbed Water, OH-bearing Phases

One of the most significant discoveries by the Mars Odyssey Gamma Ray Spectrometer (GRS) and Neutron Spectrometers is the occurrence of near surface H that is thought to be in the form of water ice, water associated with solid phases (*i.e.*, crystal, solvation, trapped, and adsorbed water) and/or OH-bearing phases. Surface and subsurface ice is the most probable candidate for the high H signatures observed by GRS at high latitudes and near the polar regions (Boynton *et al.*, 2002; see Chapter 5 by Boynton *et al.*). The Neutron Spectrometer also indicated H enrichments in low to middle latitude areas that may indicate chemically and/or physically bound water and/or OH (Feldman *et al.*, 2002; see Chapter 6 by Feldman *et al.*). Water ice indicates that liquid water was available to play a significant role in surface processes (*e.g.*, diffusion of water into regolith materials, atmospheric exchange, thin water films, and adsorbed water). The H signals in areas where ice is not thermodynamically favored, *i.e.*, at low to mid latitudes, suggest that earlier aqueous processes once interacted with solid materials to form hydrated and OH-bearing phases.

5.1.2 MER: Goethite, Jarosite, Hematite, Hydrated Fe-sulfates, and NpOx

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,b). Aqueous alteration in Gusev crater ranges from minor alteration on the surfaces and interiors of rocks and within the regolith on the basaltic plains, to highly altered outcrops and rocks in the Columbia Hills (*e.g.*, Morris *et al.*, 2006a; Ming *et al.*, 2006; McSween *et al.*, 2004; Haskin *et al.*, 2005; Hurowitz *et al.*, 2006; Wang *et al.*, 2006a). Some outcrops (layered and massive) and rocks on the Columbia Hills appear to be extensively altered as suggested by their relative “softness” as compared to crater floor basalts, high $\text{Fe}^{3+}/\text{Fe}_T$ ratios, iron mineralogy dominated by nanophase Fe^{3+} oxides, hematite, and goethite, and high Br, S, and Cl concentrations in rock interiors exposed by grinding with the Rock Abrasion Tool (RAT) (Squyres *et al.* 2006; Morris *et al.*, 2006a; Ming *et al.*, 2006, Gellert *et al.*, 2006; see Chapters 4 and 15). The discovery of goethite in Columbia Hills rocks is very important to understanding the history of water in Gusev crater, because this mineral can only form in the presence of water, in contrast to hematite that can form by either aqueous or non-aqueous processes (Morris *et al.*, 2006a). Mössbauer measurements also detected the presence of a ferric-sulfate in a surface soil named Paso Robles (Morris *et al.*, 2006a). Observations by Mini-TES suggest that the sulfate is hydrated (Ruff *et al.*, 2007; see Chapter 14). The extreme mineralogical and chemical compositions of Paso Robles soil very strongly implicate aqueous processes that involved the movement of liquid water (highly acidic) through the host material (Ming *et al.*, 2006). Nanophase Fe-oxides (npOx) are also detected by the MB in soils and rocks at Gusev crater (Morris *et al.*, 2004, 2006; see Chapter 15); these npOx phases may include one or more superparamagnetic forms of hematite and goethite, lepidocrocite, akaganéite, schwertmannite, hydronium jarosite, ferrihydrite, iddingsite, and the Fe^{3+} pigment similar to that found in palagonitic tephra (Morris *et al.*, 1989, 2000, 2004, 2006; Bishop and Murad, 1996). Some of these phases contain H_2O and/or OH, but we do not have independent observational evidence that martian npOx contains $\text{H}_2\text{O}/\text{OH}$. However, the concentration of Fe associated with npOx increases as the concentration of S+Cl increases, showing that npOx is an alteration product (Yen *et al.*, 2005; Morris *et al.*, 2006a; see Chapter 15).

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; Morris *et al.* 2006b; Christensen *et al.*, 2004a; see Chapters 15 and 24). Jarosite can only form by aqueous processes under very acidic conditions (van Breeman, 1980; Bigham and Nordstrom, 2000); *e.g.*, acid-sulfate weathering conditions resulting from the aqueous oxidation of Fe sulfides (*e.g.*, Fernández-Remolar *et al.*, 2005) or by sulfuric acid alteration of basalts by solutions associated with SO_2 -rich volcanic gases (*e.g.*, Morris *et al.*, 1996). Hematite occurs as small particles (below MI resolution of $\sim 30 \mu\text{m}/\text{pixel}$) embedded within the outcrop, as spherules imbedded in the Meridiani outcrop, and a lag deposit where the hematite has physically weathered out of the outcrop and concentrated at the surface. The hematite-rich spherules have been interpreted to be concretions that have formed in the outcrop during a complex diagenetic history, as suggested by episodes of cementation and recrystallization, formation of the hematite-rich spherules, and dissolution and formation of crystal mold vugs in outcrops (McLennan *et al.*, 2005, see Chapter 24).

The identification of jarosite and goethite was made on the basis of Mössbauer data along with supportive elemental data by the APXS. Hematite in the lag deposits was identified by both the Mössbauer Spectrometer and the Mini-TES. Details on the identification of these phases by Mössbauer and Mini-TES are presented in Chapters 14 and 15 (Morris and Klingelhofer, 2007; Ruff *et al.*, 2007).

5.1.3 Mars Express OMEGA: Kieserite, Gypsum, M-OH (Possible Phyllosilicates)

The Observatoire pour la Mineralogie, l'Eau, les Glaces et l'Activité (OMEGA) instrument onboard the Mars Express orbiter has returned visible/near IR hyperspectral reflectance image data suggesting a diverse and complex surface mineralogy on Mars (see Chapter 7; Bibring *et al.*, 2007). Hydrated sulfates have been identified in some layered terrains on Mars. Kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) has been mapped at Candor, Melas, and Terra Meridiani and a few other locations; gypsum has been mapped in locations such as Iani Chaos and the northern polar dune regions; and a polyhydrated sulfate of unknown mineralogy has been identified in such locations such as Candor, Melas, and Terra Meridiani (Bibring *et al.*, 2005, Gendrin *et al.*, 2005, Lagevin *et al.*, 2005). One of the most exciting discoveries by the OMEGA instrument is the occurrence of phyllosilicate or phyllosilicate-like phases (based on metal-OH vibrations) associated with some Noachian outcrops. These iron-rich (possibly nontronite), Fe-, Mg-rich (possibly chamosite) and Al-rich (possibly montmorillonite) phyllosilicates appear to be associated with older terrains, suggesting that they formed by more neutral-pH aqueous processes during the very early history of the planet (Poulet *et al.*, 2005; Bibring *et al.*, 2006).

5.2. Geochemical Inferences: Element Correlations and Mineralogical Mixing Models

Except for Fe-bearing sulfates, hematite, and goethite identified by the MER Mössbauer instrument and hematite and sulfates suggested in Mini-TES spectra, there have been no other alteration phases such as halides, secondary aluminosilicates, and amorphous silica unambiguously detected by *in situ* instruments that are sensitive to mineralogical composition. The abundances of various phases have been estimated using elemental associations obtained from analysis of XRFS (Viking) and APXS (MER and Pathfinder) elemental data. Only MER chemical datasets are discussed here; XRFS and Pathfinder APXS data are discussed and reviewed by Clark *et al.* (1977, 1982), and in Chapter 3 by Foley *et al.*

The mineralogical modeling of chemical data can vary significantly depending on the assumptions made in the mixing models. For example, S is assumed to be present in the form of a sulfate because of the highly oxidized nature of the martian surface materials. The mineralogical composition of Columbia Hills outcrops, rocks, and soils was estimated from Fe mineralogy established by MB and mass balance calculations based upon APXS (Table 2, Ming *et al.*, 2006). Somewhat arbitrary chemical compositions must sometimes be chosen for the Fe-bearing phases (*e.g.*, the Fe/Mg ratio for olivine and pyroxene, the K/Na ratio for jarosite, npOx, etc.). Two extreme alteration cases (pervasive vs. minimal) are presented to constrain the possible degrees of alteration among these materials. On the basis of these calculations, a variety of alteration phases were modeled in rocks and outcrops, including npOx, goethite, hematite, Ca- and Mg-sulfates, halides, and secondary aluminosilicates. The altered aluminosilicate phases are grouped into a generic “secondary aluminosilicates” category because there is no direct

mineralogical evidence for phases like phyllosilicates, allophane, zeolites, or other poorly crystalline phases.

Another example of an inferred mineralogy from geochemical data is the possible occurrence of montmorillonite or a montmorillonite-like phase in the Independence Class outcrops on the upper slopes of Husband Hill in Gusev crater (Clark *et al.*, 2007). Compared to other martian rocks and soils, these materials are characterized by their very low Fe content and high Al abundances as measured by their Al/Si ratios. Their major component (80 wt.%), after allowing for minor but significant levels of MgSO₄, Ca-phosphate, and ilmenite, is quartz normative (*i.e.*, excess Si, suggesting quartz in an idealized mineral abundance calculation from a bulk chemical analysis of a rock). Associated with several of these samples are trace elements at elevated concentrations, including Cu, Sr, Y and Cr. The elemental profile of the major component is well within the range of terrestrial montmorillonites or possibly a fortuitous mixture of certain zeolites. There is no indication of smectite phyllosilicates or zeolites from the IR spectra taken by the Mini-TES instrument, however (see Chapter 14 by Ruff *et al.*). This major component therefore may be amorphous, resulting from an incomplete formation process or a structural degradation process acting on the material.

Only part of the sulfate occurring in the outcrops at Meridiani Planum is in the form of the Fe-rich sulfate jarosite. Other sulfates (Mg- and Ca-bearing) are inferred from the geochemical data obtained by the APXS on numerous holes ground by the RAT on Opportunity (Table 3, Clark *et al.*, 2005; see also Chapter 4 by Brückner *et al.*) and mini-TES spectra suggested the possibility of Mg- and Ca-bearing sulfates (Christensen *et al.*, 2004a; see also Chapter 14 by Ruff *et al.*). Over a significant portion of the outcrop sequence, MgO correlates stoichiometrically with SO₃ (for MgSO₄) while CaO has no clear correlation with SO₃; this correlation suggests the presence of Mg sulfates in the outcrop. However, to balance cations with sulfate anions, a portion of the Ca in these samples can be assigned to sulfate, after apportioning Ca also to phosphate and pyroxene. No definitive evidence is available to indicate the presence of carbonates in these samples, but a small amount could be present if the pH conditions at the time of formation or emplacement were much higher than that required for the initial jarosite formation. Multiple episodes of diagenetic modification have overprinted an earlier mineral assemblage (McLennan *et al.*, 2005). Chlorides are present, but at a low abundance relative to sulfate salts, and the predominant cation(s) could be Mg or Na. The element assemblage also is consistent with excess Si (one-fifth to one-fourth of the sample by weight as SiO₂), so that one or more of the likely weathering forms of silica and/or an aluminosilicate such as allophane may be present.

5.2.1 Upper Limits for Crystal Water

The crystal water content of a bulk material (such as the Meridiani outcrop) can be estimated from its mineralogical composition. The water content cannot be determined from MER APXS data because the element totals are normalized on a water-free basis (Gellert *et al.*, 2004, 2006; Reider *et al.*, 2004). The content of H₂O (as OH) associated with jarosite and goethite is known by stoichiometry, but the number of crystal waters associated with other Fe-bearing sulfates and the Ca- and Mg-sulfates at the MER landing sites is not well constrained. For example, the binary Fe-sulfate, Fe₂(SO₄)₃ • *n*H₂O, has values of *n* ranging from 1 to 9. Because the mineralogical composition of secondary phases is poorly constrained, only ranges of

the amount of crystal water can be derived for surface materials by assuming limiting cases for crystal water contents.

Jarosite, along with Ca- and Mg-sulfates, have been suggested as the sulfur-bearing phases in Meridiani Planum outcrop (Klingelhofer *et al.*, 2004; Morris *et al.*, 2006b; Clark *et al.*, 2005). A survey of common evaporites, including mixed salt compounds with more than one cation, shows that about one-half of all candidate salts for Meridiani outcrops can be hydrated. Magnesium sulfate is particularly versatile, with minerals ranging from one water of hydration (*i.e.*, kieserite) up through 2, 4, 6 (hexahydrate) and even 7 (epsomite) water molecules per unit cell. Calcium sulfate occurs commonly as gypsum, bassanite, or anhydrite, only the last of which is not hydrated. Hydrated sulfates are expected in Meridiani Planum outcrops as modeled during the evaporation of sulfate-rich chloride brines (Tosca *et al.*, 2005). Based upon these models, the possible hydration levels for the outcrop in Meridiani Planum are shown in Table 4 (hydroxides in oxyhydroxides and hydration in possible phyllosilicates, allophane or silica are not included in this analysis). These models reveal that from 6 to 22 wt.% of the outcrop may occur as crystal H₂O and/or OH. The estimate of water in Meridiani outcrop is consistent with measurements from the Odyssey orbiter, where the GRS has detected an average concentration of 7% H₂O-equivalent H down to a depth of approximately 1 m for the Meridiani Planum region (Feldman *et al.*, 2004).

Another example of the crystal H₂O and OH content of a rock material is shown in Table 5 for rocks (Clovis, Ebenezer, Wishstone, Watchtower, and Peace) and a soil (Paso Robles) from West Spur and the northwest slope of Husband Hill in Gusev crater. A range of water content is estimated from the least and most hydrated sulfate, phosphate, and halide phases that may be present in these materials. Unfortunately, the mineralogical composition of the secondary aluminosilicate phases and npOx is unknown, and thus the crystal water content contributed by these phases cannot be included in this estimate. A variety of secondary aluminosilicates may be present in these materials, including phyllosilicates, allophane, amorphous silica, and other poorly crystalline aluminosilicate phases. It is highly likely that the ranges listed in Table 5 are higher than indicated because of contributions of hydrated aluminosilicates to the bulk water contents of these materials. Nonetheless, the Peace outcrop materials exhibited the highest water content (1.2 to 6.9 wt.% H₂O) of the rocks and outcrops encountered on Husband Hill. Mini-TES spectra for Peace outcrop have a pronounced emissivity peak at ~1630 cm⁻¹ that typically is attributed to the bending mode of molecular bound water (Ruff *et al.*, 2007). Peace outcrop appears to be composed of basaltic sands that have been cemented by Mg- and Ca-sulfates and possibly amorphous silica (Ming *et al.*, 2006), and the high water content results from the hydrated Mg- and Ca-sulfates.

The derived water content of the unique Paso Robles soil ranges from 2.4 to 16.9 wt.%. Paso Robles soil is extensively altered. The most notable characteristic of Paso Robles light-colored material is its high concentration of S, one of the highest contents measured on Mars at any location (Gellert *et al.*, 2006). Paso Robles consists of Fe³⁺-, Mg-, Ca-bearing and other sulfates, Ca-phosphates, hematite, halite, allophane, and amorphous silica (Ming *et al.*, 2006). The hydration state of the ferric sulfate is not currently constrained by Mössbauer parameters, but if the sulfate is a simple ferric sulfate (Fe₂(SO₄)₃ • nH₂O), the hydration state (*n*) is between 1 and 9. Thus, the majority of the water in Paso Robles is likely tied up in hydrated Fe³⁺- and Mg-sulfates and perhaps hydrous forms of silica.

5.2.2 Normative Versus Actual Mineralogical Composition (Norm Calculations on a S-, Cl-, and Br-free Basis)

Normative mineral calculations based upon the MER APXS elemental composition for relatively unaltered basaltic rocks in Gusev crater compare very well with the mineralogy indicated by the Mössbauer and Mini-TES instruments (McSween *et al.*, 2004, 2006). These same calculations on a S-, Cl-, and Br-free basis, with an assumed $\text{Fe}^{3+}/\text{Fe}_T$ (see Section 2), performed on altered materials may be used to evaluate the hydrologic system in which they were altered (*i.e.*, closed or isochemical vs. open). The Wishstone, Watchtower, and Independence class rocks in the Columbia Hills have corundum normative mineralogies (*i.e.*, excess Al suggesting corundum in an idealized mineral abundance calculation from a bulk chemical analysis of a rock), although the Wishstone and Watchtower rocks are only slightly corundum normative (Ming *et al.*, 2006, Clark *et al.*, 2007). Terrestrial igneous rocks are rarely corundum normative. Therefore, the corundum normative rocks in the Columbia Hills have likely had their original igneous compositions changed by an alteration processes under an open hydrologic system where some of the original basaltic elements were removed from the system. However, with the exception of Independence, the elemental compositions of these rocks have not been substantially changed, suggesting minimal leaching from the system (see Section 6.1).

6. Models for aqueous alteration processes

Our knowledge of the types of aqueous alteration that are or have been active on Mars is limited by the small number of sites examined and by the small number of phases definitively identified to date that have formed by aqueous processes. The previous sections of this chapter focused on summarizing what is known about the mineralogical composition of secondary phases on Mars. In this section, styles of aqueous alteration are described based upon our current best estimates of the alteration mineralogy at the surface.

6.1. Isochemical vs. Open-System Alteration

Mars is a basaltic planet and the surface is dominated by basaltic elemental and mineralogical compositions (Christensen *et al.*, 2000; McSween *et al.*, 2004; 2006; Reider *et al.*, 2004; see also Chapters 3, 4, 9, 10, 14, 15, 22, and 24). Weathering or the removal of soluble species from the reaction front is expected if water freely moved on the surface of Mars similar to the way it moves in open hydrologic systems on Earth. For example, elements such as the alkali and alkaline earth cations and Si are removed from reaction fronts under near-neutral pH conditions; altered or precipitated phases that remain behind after weathering of basaltic materials are enriched in Al (see Figure 1; Nesbitt and Wilson, 1992). The MER mission has significantly enhanced our understanding of the extent of alteration and weathering because of the mobility of the rovers, the resulting ability to characterize the geochemistry of rocks, outcrops, and soils at numerous locations, and the ability to identify minerals by the MB and Mini-TES instruments. The geochemistry of the major rock classes encountered in Gusev crater is illustrated on the ternary diagram in Figure 2a. Four of the major rock classes (Adirondack, Clovis, Wishstone, and Watchtower) fall along the olivine-feldspar join. The geochemistry of these four rock classes suggests that they have not been extensively altered by open system aqueous processes; *i.e.*, they have not been extensively leached of mobile elements.

Independence class rocks, on the other hand, show trends towards Al-enrichments, suggesting that this material has undergone weathering with leaching and may contain a smectite-like phase or its compositional equivalent (Clark *et al.*, 2007).

Although leaching is not prominent in most Gusev crater rocks and outcrops (Figure 2a), the iron mineralogy suggests that some materials have been extensively altered by aqueous processes (Figure 2b). Adirondack class basalt has undergone minimal alteration according to the MAI discussed above; however, the weathering trend in Figure 2b suggests that Clovis and Watchtower Class rocks range from moderately to pervasively altered materials (*i.e.*, highest $\text{Fe}^{3+}/\text{Fe}_T$). The more altered outcrops and rocks on the West Spur of Husband Hill contain goethite (Ming *et al.*, 2006; Morris *et al.*, 2006a). Although the Watchtower outcrop has several compositional similarities to Wishstone Class rock targets (Wishstone and Champagne), it is highly altered compared to the other targets. Interestingly, Independence Class rocks appear to be among the least altered rock in the classes shown on Figure 2b. One reason for its moderate to low mineralogical alteration index is that most of the iron has been weathered or removed from the material, except that fraction most resistant to weathering (*e.g.*, chromite; Clark *et al.*, 2007). It is therefore likely that the MAI does not adequately represent the actual degree of alteration in Independence Class rocks because of the low iron content and the likely removal of Fe-bearing phases by alteration.

The combination of the two alteration/weathering indices presented here (Chemical Alteration Index and MAI) suggest that most rocks and outcrops in the Columbia Hills have not undergone extensive leaching in an open hydrolytic system. The extensively altered rocks (*e.g.*, Watchtower and Clovis Class), with the exception of Independence Class rocks as discussed above, appear to have undergone alteration under isochemical or nearly isochemical conditions. Most likely they have been altered by water, where the water to rock ratio is very low. Because these extensively altered materials contain sulfates (possibly hydrated as illustrated earlier) these systems are likely open in the sense that they received additions of S, Cl, and water, but they are closed in the sense that there is very little or no leaching of major elements away from reaction fronts. With the exception of Independence and Peace class rocks, aqueous alteration in the Columbia Hills appears to be isochemical, with only the addition of the volatile phases most likely from volcanic emissions.

Jarosite, hematite, and other sulfates (*e.g.*, Mg-bearing sulfates) occur along with siliciclastic sediments in outcrops at Meridiani Planum. A leading candidate for the formation of these sediments is the evaporation of acid fluids that have interacted with and altered olivine-bearing basaltic materials (Tosca *et al.*, 2005). A key but reasonable assumption is that waters rich in sulfuric acid interacted with precursor basaltic sediments in Meridiani Planum. Alternatively, sulfuric acid waters could form by the interaction of volcanic emissions (*i.e.*, SO_2 , Cl, Br) with water vapor or liquid or by reaction of H_2O and sulfides under oxidizing conditions. Key questions on the formation of these sulfate-rich sediments are how much acidic water interacted with the basaltic sediments and whether solutions moved through these sediments and removed soluble constituents (*i.e.*, open hydrologic system) or if these sediments were altered under isochemical conditions (*i.e.*, closed hydrologic system with the additions of water, S, Cl and other volatiles from volcanic emissions). The bulk chemical composition of the Meridiani outcrop materials does not deviate substantially from what would be expected for basalt weathered under isochemical conditions (Figure 3). It thus appears that there was very little movement of soluble components out of the Meridiani "basin" during the formation of the bedrock. Although the alteration of the original basaltic sediments is extensive, the weathering or

leaching of soluble components out of the system was minimal. An alternative hypothesis is that the sulfates, chlorides, and possibly other phases were brought into Meridiani as sediments by water and then precipitated to form the sulfate-rich siliciclastic sediments (*e.g.*, Newsom *et al.*, 2003). For example, the composition of the siliciclastic component begins to trend toward a smectite-like composition if the composition of the sulfates and halides are extracted from the average composition of the Meridiani bedrock (Figure 3). However, this hypothesis is somewhat suspect if the compositional sums of the siliciclastic sediments and sulfates resemble a basaltic composition similar to basaltic sands in the Meridiani area.

Several hypotheses on the formation processes for Meridiani outcrop materials have been put forth, including aqueous, volcanic and impact processes. Squyres *et al.* (2006) suggested that the outcrops formed when ancient Meridiani once had abundant acidic groundwater, arid and oxidizing surface conditions, and occasional liquid flow on the surface. Another hypothesis is that regional heating caused a release of sulfide-rich hydrothermal waters that formed pyrite-rich deposits, and the subsequent aqueous oxidation of these deposits formed the sulfates and hematite in Meridiani outcrops (Zolotov and Shock, 2005). On the other hand, McCollum and Hynke (2005) and Knauth *et al.* (2005) have suggested that the aqueous alteration occurred during flows induced by volcanic and impact base surges, respectively.

6.2. Acid-Sulfate Alteration

The high elemental abundance of S in surface materials is obvious evidence that sulfate has played a major role in aqueous processes at all landing sites on Mars. The sulfate-rich outcrop at Meridiani Planum contains jarosite and Ca-Mg-sulfates and has an SO₃ content of up to 25 wt.% (Rieder *et al.*, 2004; Clark *et al.*, 2005). The interiors of rocks and outcrops on the Columbia Hills have up to 8 wt.% SO₃ (Ming *et al.*, 2006). Soils at both sites generally have between 5 to 14 wt.% SO₃ (Gellert *et al.*, 2006; Haskin *et al.*, 2005) and one soil (Paso Robles) on Husband Hill contains around 31 wt.% SO₃ (Gellert *et al.*, 2006). After normalization of major element compositions to a SO₃-free basis, the bulk compositions of these materials are basaltic, with a few exceptions in the Columbia Hills (*e.g.*, Watchtower and Independence class rocks, along with certain other outcrops such as Woolly Patch; Ming *et al.*, 2006). These observations suggest that the surface materials were derived from basaltic precursors by acid sulfate alteration under nearly isochemical conditions and/or very low water:rock ratios with minimal leaching.

Several hypotheses have been suggested for the aqueous formation of sulfate-bearing phases on the surface of Mars including (1) Oxidative weathering of ultramafic igneous rocks containing sulfides (Burns, 1988; Burns and Fisher, 1990); (2) Sulfuric acid weathering of basaltic materials (Morris *et al.*, 1996, 2000); and (3) Acid fog (*i.e.*, vapors rich in H₂SO₄) weathering of basaltic or basaltic-derived materials (Clark and Baird, 1979; Banin *et al.*, 1997). All three processes involve acid-sulfate alteration environments. Other candidate processes not involving acid sulfate conditions might include the dissolution and movement of soluble components by water (*e.g.*, ground water, water in thin films, flowing or standing water) and the subsequent formation of evaporitic mineral deposits (*e.g.*, Mg- and Ca-sulfates and chlorides; Moore *et al.*, 1978, 1987; Clark *et al.*, 1982).

6.2.1 Sulfuric Acid Solutions from Volcanic Processes

The formation of jarosite in Meridiani Planum outcrops is strong evidence for the aqueous alteration of basaltic materials under acid sulfate conditions and may be analogous to the formation of jarosite in basaltic materials on Mauna Kea volcano in Hawaii under oxidizing, hydrothermal conditions (Morris *et al.*, 1996, 2000). The Mauna Kea sulfuric acid solutions are the result of interactions of SO₂-rich volcanic gases with water. Acid sulfate solutions percolated up through the basaltic tephra, dissolved Fe and other cations, and precipitated jarosite when environmental conditions permitted its formation (see Golden *et al.*, (2005) for detailed discussion on environmental conditions necessary for formation of jarosite). The pH of the system plays a major role in defining the stability field between jarosite and hematite (or goethite) formation. Jarosite is stable in the pH range ~0.75 to 3.5; below this range jarosite dissolves and above this range it hydrolyzes to form hematite and/or goethite (*e.g.*, see the stability diagram in Burns and Fisher, 1990). The sulfuric acid solutions in Meridiani were apparently not sufficiently “neutralized” by the basaltic sediments, and thus the pH was low enough to favor precipitation of jarosite.

Although jarosite was not identified in the rocks and soils of the Columbia Hills of Gusev crater, the mineralogy and chemistry of ferric sulfates in Paso Robles soil are still very strong indicators of aqueous processes. Ming *et al.* (2006) suggested that Paso Robles is an evaporite deposit that formed from solutions rich in Fe, Mg, Ca, S, P, and Si. The occurrence of ferric sulfates and not jarosite constrains the solution Eh and pH to a highly oxidized, extremely low pH solution. Support for this scenario comes from the high Fe³⁺/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 (Madden *et al.*, 2004; Burns and Fisher, 1990; Bigham and Nordstrom, 2000). As noted above, the stability field for jarosite is between pH ~0.75 and 3.5, and Fe-oxides/oxyhydroxides form in acid-sulfate solutions with pH >3.5 (*e.g.*, Nordstrom, 1982; Tosca *et al.*, 2005). Golden *et al.* (2005) showed 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 level of water activity. The high Mg, 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 that the high Fe and Mg are the result of sulfuric-acid solutions reacting with the source materials of the Peace basalt source and the P and Ca are the result of these caustic solutions reacting with a Wishstone-like source material (Ming *et al.*, 2006). Paso Robles soil appears to be localized in a small area. This may indicate that volcanic vents with SO₂-rich vapors were present in the Husband Hill area, similar to alteration vents seen on cinder cones on Mauna Kea (*e.g.*, Morris *et al.*, 2000). Other soils similar to Paso Robles have been located elsewhere on Husband Hill and in the Inner Basin (Yen *et al.*, 2007). The possibility that Paso Robles materials are more widespread cannot be ruled out because of its occurrence in the subsurface (only exposed in certain places by the action of the rover wheels). Another confounding problem with unraveling the genesis of this material 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 material into a stratigraphic sequence.

6.2.2 Sulfuric Acid Solutions from Sulfides

Acid-sulfate weathering on Earth, in general, results from processes that release sulfuric acid into a soil or sediment. Nearly all of the occurrences of acid sulfate soils and sediments on Earth have resulted from the oxidative weathering of sulphidic materials (*i.e.*, materials containing sulfides such as pyrite) and are often the culmination of complex biogeochemical processes (Nordstrom, 1982). Acid-sulfate minerals (*e.g.*, jarosite) form during the oxidation of sulfides (*e.g.*, pyrite) when the quantity of sulfuric acid exceeds the acid neutralizing capacity of adsorbed bases and weatherable minerals to the extent that the solution pH drops below 3.5 (Pons *et al.*, 1982). Under terrestrial conditions, acid-sulfate production is generally observed in freshly exposed sediments that contain sulphidic materials (*e.g.*, mine spoils) and in sediments that undergo a change in hydrology that produces oxidizing conditions (*e.g.*, drying of a lake bed, sea line regression, draining of lagoons). Major products of acid-sulfate weathering include jarosite, barite, and gypsum (Carson *et al.*, 1982); hydrated ferrous sulfates (melanterite, rozenite, szomolnokite) and copiapite (hydrated ferrous/ferric sulfate) in coal deposits (Nuhfer, 1967); oxyhydroxysulfates like schwertmannite and ferrihydrite (Bigham *et al.*, 1990); goethite (van Breeman, 1982); hematite (Kevie and Yenmanas, 1972); nontronite (van Breeman, 1982); amorphous silica (van Breeman, 1982), and ferric sulfates (copiapite, coquimbite, jarosite, schwertmannite) in acid river sediments (Hudson-Edwards *et al.*, 1999; Buckby *et al.*, 2003).

Burns (1988) suggested that oxidative weathering of sulfides might be a significant process on the surface of Mars. In his model, iron-rich ultramafic igneous rocks containing pyrrhotite-pentlandite contacted aerated groundwater, generating strongly acidic, sulfate-rich solutions. In the oxidized section above the groundwater table, sulfates (*e.g.*, jarosite) and hydrated ferric oxides are precipitated from solution by the oxidation of the sulfide and dissolution of Fe. In a follow-up study, Burns and Fisher (1990) proposed that massive and disseminated iron sulfide mineralization might have occurred near the Martian surface based upon the probable presence of komatiitic igneous rocks, as suggested by geochemical evidence from SNC meteorites and the Viking XRFS analyses (Baird and Clark, 1984). As described above, these deposits would then postulated to have undergone oxidative weathering near the martian surface and result in the formation of Fe-rich sulfates and hydrated Fe-oxides.

Perhaps the basaltic sediments at Meridiani Planum initially contained sulfides (*e.g.*, pyrite) as a major component; however, there are no indicators (*e.g.*, framboidal growth and/or cubic morphology of jarosite) that suggest a sulfide precursor.

6.2.3 Acid fog on Rock/Soil Surfaces

Acid fog alteration on rock and soil surfaces has been suggested as an acid sulfate weathering process for surface materials (Clark and Baird, 1979; Banin *et al.*, 1997; Tosca *et al.*, 2004; Golden *et al.*, 2005; Hurowitz *et al.*, 2006). The acid sulfate reactions are driven by acidic volatiles (*e.g.*, SO₂, HCl, H₂O) deposited from the atmosphere and then reacted with the mineral surfaces in the dry Mars environment. Laboratory simulated acid weathering of palagonitic tephra by Banin *et al.* (1997) resulted in the formation of gypsum and alunogen; those authors hypothesized that the top layer of Mars “soil” may have formed by extremely slow ongoing weathering interactions at the atmosphere-rock interfaces. Tosca *et al.* (2004) subjected synthetic basaltic analogs derived from Mars Pathfinder soil and rock compositions to various acidic solutions and subsequent evaporation. Crystalline Mg, Fe, Ca, and Al sulfates (but not jarosite)

were identified as reaction products, along with secondary ferric oxide phases, which formed via rapid Fe oxidation under relatively high pH levels buffered by basalt dissolution. Amorphous silica was also identified as a ubiquitous product on particle surfaces. Golden *et al.* (2005) subjected basaltic tephra materials to acid fog conditions in the laboratory and found that Al, Fe, and Ca sulfates and amorphous silica formed from plagioclase-rich tephra, and Mg and Ca sulfates and amorphous silica formed from the olivine-rich sand.

Hurowitz *et al.* (2005) have presented evidence for very low pH (pH = 0 to 1) alteration at rock and outcrop surfaces in Gusev crater based upon laboratory experiments. They suggest that there is a leached layer where, for example, Clovis outcrops and rocks are depleted in Mg and Fe at their surfaces compared to their interiors (*i.e.*, holes created by grinding with the RAT), probably as a result of pyroxene and/or basaltic glass dissolution by acidic fluids (*e.g.*, sulfuric acid fog). Under this process, acidic vapors reacted only at the surfaces of rocks and outcrops, leaching some elements (*i.e.*, Fe and Mg) and resulting in the observed depletion trends of Mg and Fe from the rock's interior.

6.3 Neutral and Alkaline pH Hydrolytic Alteration

The geochemistry and mineralogy of surface materials analyzed by MER instruments are consistent with aqueous alteration under acid sulfate conditions, with the possible exception of the Independence Class rocks. However, recent near IR spectral data returned by the OMEGA instrument on Mars Express suggests the presence of phyllosilicates such as smectites that potentially formed under near neutral or even slightly basic conditions (Bibring *et al.*, 2006).

The formation of smectites in the terrestrial environment requires aqueous environments where solutions have high Si and Mg activity and neutral to alkaline pH conditions (Jackson, 1965, Kittrick, 1971, Weaver *et al.*, 1971, Klopogge *et al.*, 1999). Although smectites can form under low-temperature and hydrothermal conditions, smectite formation in laboratory experiments has been most successful under hydrothermal conditions (see review by Klopogge *et al.*, 1999). The OMEGA instrument detected IR spectral features from Fe-OH, Fe/Mg-OH, and Al-OH functional groups that may suggest a range of smectite compositions from nontronite (Fe-rich) to montmorillonite (Al-rich). Numerous starting materials may result in the formation of smectites and other phyllosilicates (including volcanic materials; Klogrogge *et al.*, 1999), so it is reasonable to expect smectite formation by aqueous alteration of basaltic materials especially under neutral to alkaline pH, hydrothermal conditions.

A potential terrestrial analog for the formation of smectites and other phyllosilicates on Mars are several altered cinder cones (Puu Poliahu and Puu Waiiau) near the summit of Mauna Kea volcano in Hawaii. Deposits on these cones have been significantly altered under hydrothermal conditions to produce well-developed crystalline sulfates (alunite and jarosite), phyllosilicates (smectites and kaolinite), and zeolites (Ugolini, 1974; Golden *et al.*, 1993; Morris *et al.*, 1996, 2000; Wolfe, *et al.*, 1997). Visible and near infrared spectra suggest that the smectite endmembers are montmorillonite and saponite (Guinness *et al.*, 2007). The mineralogy of Puu Poliahu is dominated by four types of alteration processes: (1) Hydrolytic, low temperature alteration of basaltic tephra to form palagonite and nanophase Fe-oxides; (2) Hydrothermal, sulfatetic/hydrochloric acid alterations of basaltic tephra to form sulfates (jarosite, alunite) and kaolinite; (3) Hydrothermal neutral to alkaline pH alterations of basaltic tephra to smectites (saponite and montmorillonite) and zeolites; and (4) Thermal, oxidative alteration of fresh basaltic tephra to form concentrically zoned hematite units on cinder cones (Morris *et al.*, 2000;

Guinness *et al.*, 2007). The processes observed and described on Mauna Kea may not only be analogs for smectite formation on Mars, but also analog processes for the formation of sulfates, Fe-oxides, and other poorly crystalline phases on Mars in general.

Another potential aqueous process that may form smectites and other secondary phases under neutral or alkaline conditions is hydrothermal aqueous alteration associated with an impact event (*e.g.*, Newsom, 1980; Newsom *et al.*, 1999, 2001; Allen *et al.*, 1982; Morris *et al.*, 1995; Naumov, 2002). Large impacts will generate a thermal pulse through the host material. Hydrothermal aqueous alteration can thus occur in these large impact events if the host materials contain water and/or other volatile phases.

6.4. Style and Timing of Aqueous Alteration

The existence of sulfates and probably phyllosilicates on the martian surface suggests that it has experienced very different aqueous conditions over time. Although carbonates are not thought to persist at the surface (Clark and Baird, 1979), their presence in martian meteorites suggests that crustal materials have been influenced by aqueous processes that favored carbonate formation in some epoch. The general conditions and possible styles of alteration on Mars are shown in Figure 4. Fe-sulfates detected by the MER rovers suggest that acid sulfate weathering has played a major role in the alteration process on Mars as discussed in Section 6.2 above. Other sulfates that are common products during acid sulfate alteration (*e.g.*, Ca- and Mg-bearing sulfates) are also being detected in large areas by Mars Express (see Section 5.1.3 and also Chapter 7 by Bibring and Langevin). The OMEGA instrument on Mars Express is also detecting possible phyllosilicates that most likely formed under neutral to more alkaline hydrolytic conditions (see Sections 5.1.3 and 6.3, as well as Chapter 7). The occurrence of apparently secondary carbonates in the martian meteorites also suggests alteration and precipitation in neutral to alkaline conditions in crustal materials.

The occurrence of phyllosilicates suggests the presence of neutral to slightly alkaline hydrolytic conditions very early in the planet's history (Noachian) and that the sulfates may have formed later under acid sulfate conditions during the Hesperian (Bibring *et al.*, 2006). Also during the Noachian, alkaline conditions in crustal waters would have to have been favorable, at least locally, for the formation of carbonates as suggested by the 3.9 billion year old carbonates in the ALH84001 martian meteorite (Golden *et al.*, 2001). Conditions at the surface were either unfavorable for the formation of carbonates, or the carbonates have since been destroyed (Clark *et al.*, 1979), because there is only minor orbital or *in situ* evidence for their existence on the surface and in the airborne dust (*e.g.*, Bandfield *et al.*, 2003; see also Chapter 9 by Christensen *et al.*). Thus, most of the aqueous alteration appears to have occurred early in the history of the planet (3 to 4.5 billion years ago). While aqueous alteration may still be occurring at the surface today (*e.g.*, thin films of water, acid fog, etc.), no evidence has yet been found of substantial alteration at the surface for the past 3 billion years.

Some of the Martian meteorites are relatively young (*e.g.*, 1.26 to 1.38 Ga for Nakhilites) and have evidence for minor secondary phases such as carbonates. Although the alteration of these crustal materials is minor, it does suggest that solutions have moved through these materials in Amazonian times and that aqueous processes may indeed still be active in the subsurface on Mars.

7. Science Needs and Future Missions

Our understanding of aqueous processes on Mars will be significantly enhanced by additional definitive mineralogical identification of phases that form by one or a limited number of pathways. Mars Reconnaissance Orbiter data will enhance our understanding of the occurrence and distribution of sulfates and secondary aluminosilicates on the surface, but it may not be able to provide definitive mineralogy of those phases. The next landed mission on Mars is the 2007 Mars Phoenix Scout Mission, which does not have instruments onboard that will provide definitive mineralogical identifications. However, the Phoenix payload will provide unique new information on the volatile-bearing content of regolith materials (Thermal Evolved Gas Analyzer, TEGA) and the chemistry of soluble components (Microscopy, Electrochemistry, Conductivity Analyzer, MECA) (Smith, 2006). The 2009 Mars Science Laboratory (MSL) will provide an instrument suite that should significantly improve our understanding of the mineralogical composition of secondary phases (Blaney, 2006). For example, the CheMin instrument is primarily an X-Ray diffraction instrument that should provide definitive mineralogical data. The Sample Analysis at Mars (SAM) instrument should provide chemistry of the volatile-bearing phases (*i.e.*, carbonates, sulfates, hydrated minerals). Along with the APXS and ChemCam element analyzers on the MSL payload, our new knowledge about the secondary phases on Mars should allow significant enhancements in our understanding of the aqueous processes at work there. Ultimately, sample return missions will provide suites of samples from specific locations with known geologic context.

The continuation of both laboratory experimental and terrestrial analog studies will also be needed to understand and interpret the data returned by the missions described above. Aqueous processes on Mars can only be understood to the degree that we understand those processes on Earth.

8. Summary

Aqueous alteration has substantially shaped the geologic history of Mars. A key requirement to model aqueous alteration is the identification of phases that have formed by these processes. Our knowledge on the style and extent of aqueous alteration on Mars is based upon our understanding of terrestrial environments where these phases have formed.

A variety of mineralogical and chemical indicators for aqueous alteration on Mars have been identified by a combination of surface and orbital robotic missions, telescopic observations, characterization of Martian meteorites, and laboratory and terrestrial analog studies. Phases that have formed by aqueous alteration such as sulfates (poly-hydrated sulfates, kieserite, and gypsum), phyllosilicates (smectites), hematite, and nanophase iron oxides (*e.g.*, palagonite) have been identified by Earth-based telescopic and Mars orbital observations. Jarosite, Fe-Mg-Ca-bearing sulfates, goethite, hematite, nanophase iron oxides, halides, and possibly secondary aluminosilicates have been identified by landers and rovers. Analyses of martian meteorites in terrestrial laboratories have led to the identification of minor amounts of phases that have formed by aqueous alteration, such as Fe-Ca-Mg-bearing carbonates, Ca-bearing sulfates, goethite, iddingsite, halite, and pyrrhotite.

Based upon these phases, several styles of alteration have been proposed for the surface of Mars. Mars is a basaltic planet, so most of the styles involve the alteration of basaltic precursors. The high sulfur content and the occurrence of jarosite suggest that one style of

aqueous alteration on Mars (especially at Meridiani Planum) is acid sulfate alteration. There may be several pathways for materials to be altered in acid sulfate environments including: (1) Oxidative aqueous alteration of ultramafic igneous rocks containing sulfides; (2) Sulfuric acid alteration of basaltic materials; and (3) Acid fog (*i.e.*, vapors rich in H₂SO₄) alteration of basaltic or basaltic-derived materials. Another possible style is the alteration of basaltic materials by near-neutral or alkaline pH solutions. This type of alteration may result in the formation of smectites like those observed by the Mars Express OMEGA instrument.

The extent of alteration will depend on whether the material is altered in a closed or open hydrologic system and the rock:water ratio. Reactants are not displaced from the reaction front in a closed system (*i.e.*, isochemical alteration) whereas in an open system soluble phases are removed as water moves through the host material. The Mössbauer spectrometer onboard the MER rovers indicated that the extent of alteration varies substantially from rocks that are relatively unaltered to rocks and outcrops that appear to be pervasively altered. In most cases, the pervasively altered materials still had essentially basaltic compositions, suggesting that the alteration was isochemical (*i.e.*, closed hydrologic system) and/or low rock:water ratios. On the other hand, in several instances the altered materials were enriched in Al (*e.g.*, Independence outcrop on the Columbia Hills), suggesting that alteration occurred in an open hydrologic system where soluble phases were removed from the host rock.

Future missions, observations, and laboratory and terrestrial analog studies will no doubt advance our understanding of the phases, styles, and extent of aqueous alteration on Mars.

Acknowledgements

DWM and RVM acknowledge support of the NASA Mars Exploration Rover Project, NASA Mars Fundamental Research Program, and the NASA Johnson Space Center. We thank H. Newsom, D.C. Golden, and J.F., Bell, III for their insightful reviews of this chapter.

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Table 1. Aqueous Alteration Phases in Martian Materials.

Mineralogy	Location/Material	Mission/Method	References
Sulfates			
Mg-rich sulfates	CP & UP duricrusts#	Viking XRFs	Clark (1993)
	GC soils, GC & MP outcrops#	MER APXS	Haskin et al. (2005); Wang et al. (2006a); Clark et al. (2005); Ming et al. (2006)
	MM (Nakhla, Chassigny)	laboratory analysis	Gooding et al. (1991); Wentworth and Gooding (1994)
kieserite	layered terrans	MEx OMEGA	Gendrin et al. (2005)
Ca-rich sulfates	GC & MP outcrops; GC rocks#	MER APXS	Clark et al. (2005); Ming et al. (2006)
	MM (Chassigny, Nakhla, Shergotty, Governador Valadares, Lafayette)	laboratory analysis	Bridges and Grady (2000); Wentworth and Gooding (1994); Wentworth et al. (2005)
gypsum	layered terrans, North Polar region	MEx OMEGA	Gendrin et al. (2005); Langevin et al. (2005)
anhydrite	MM (Nakhla)	laboratory analysis	Bridges and Grady (2000)
Fe-rich sulfates	MP outcrops	MER MB	Klingelhofer et al. (2004)
jarosite	MM (MH103346 NakhlaHite&)	laboratory analysis	Herd (2006); Fries et al. (2006)
	GC soils	MER MB	Morris et al. (2006)
Carbonates			
Fe-rich carbonates	MM (Lafayette, Governador Valadares, Nakhla)	laboratory analysis	Bridges and Grady (1999, 2000)
Mg-rich carbonates	MM (ALH84001, Chassigny)	laboratory analysis	Mittlefehdt (1994); Wentworth and Gooding (1994)
	martian dust (minor (?))	MGS TES	Bandfield et al. (2003)
Mg-Ca-Fe carbonates	GC dust & surface soils (minor (?))	MER Mini-TES	Christensen et al. (2004)
Ca-rich carbonates	MM (ALH84001)	laboratory analysis	Romanek et al. (1994); Dreibus et al. (1994); Harvey and McSween (1996)
	MM (Chassigny, EETA79001, ALH84001)	laboratory analysis	Gooding et al. (1988); Wentworth and Gooding (1994); Harvey and McSween (1996)
Oxides/Oxyhydroxides			
goethite	GC outcrops & rocks	MER MB	Morris et al. (2006)
	MM (Nakhla, Lafayette, Governador Valadares)	laboratory analysis	Bridges and Grady (2000)
hematite	MP soils	MGS TES	Christensen et al. (2001a,b)
npOx	GC outcrops & rocks, MP outcrops & soils	MER MB & Mini-TES	Klingelhofer et al. (2004); Morris et al. (2006); Christensen et al. (2004a,b)
iddingsite ferrhydroxide	GC soils, outcrops, & rocks	MER MB	Morris et al. (2004); Morris et al. (2006)
magnetite\$	Mars bright and dark regions	Telesopic	Singer (1982); Morris et al. (2000); Bell et al., (1990)
	MM (Lafayette)	laboratory analysis	Treiman et al. (1993)
	GC rocks, outcrops and soils	MER MB	Morris et al. (2004); Morris et al. (2006)
	MM (ALH84001)	laboratory analysis	McKay et al. (1996)
	GC outcrop	MER MB and APXS	Morris et al. (2006); Clark et al. (2007)
Silicates			
amorphous silica	GC soils#	MER APXS	Ming et al. (2006); Haskin et al. (2005)
phyllosilicates			
smectite			
montmorillonite-like (?)	GC outcrops#	MER APXS	Clark et al. (2006)
Al-rich montmorillonite (?)	Mawrth Vallis	MEx OMEGA	Poulet et al. (2005)
Fe-rich (montmorillonite (?))	Nili Syrtis Mensae	MEx OMEGA	Poulet et al. (2005)
Fe-rich (montmorillonite (?))	CP & UP	Viking Labeled Release	Bain and Margulies (1983)
iddingsite (smectite (?))	MM (Lafayette)	laboratory analysis	Gooding et al. (1991); Treiman et al. (1993)
chlorite (?)	northern Syrtis Major	MEx OMEGA	Poulet et al. (2005)
mica (phlogopite)	MM (ALH84001)	laboratory analysis	Brearely (1998, 2000)
kaolinite/serpentine/1:1 phyllosilicate (?)	GC outcrop#	MER APXS	Wang et al. (2006b)
zeolites (?)	martian dust	MGS TES	Ruff (2004)
Salts of Cl and Br			
Cl salts	GC & MP soils, rocks, and outcrops#	MER APXS	Reider et al. (2004); Gellert et al. (2004, 2006); Clark et al. (2005); Ming et al. (2006)
halite	MM (Nakhla, Shergotty)&	laboratory analysis	Gooding et al. (1991); Wentworth and Gooding (2000)
	MP outcrop	MER APXS	Yen et al. (2006)
Br salts#	GC & MP soils, rocks, and outcrops#	MER APXS	Reider et al. (2004); Gellert et al. (2004, 2006); Clark et al. (2005); Ming et al. (2006)
Phosphates			
brushite (?)	GC outcrops, rocks, and soils	MER APXS	Ming et al. (2006)
Others			
pyrite\$	MM (ALH84001)	laboratory analysis	Mittlefehdt (1994)
pyrrhotite	MM (ALH84001)	laboratory analysis	Weiss et al. (2002)

Key: CP = Chryse Planitia; UP = Utopia Planitia; MPF = Mars Pathfinder; MER = Mars Exploration Rover; MGS = Mars Global Surveyor; MEX = Mars Express; GC = Gusev crater; MP = Meridiani Planum; XRFs = X-ray Fluorescence Spectrometer; APXS = Alpha Particle X-ray Spectrometer; MB = Mossbauer Spectrometer; Mini-TES = Miniature Thermal Emission Spectrometer; TES = Thermal Emission Spectrometer; OMEGA = Observatoire pour la Mineralogie, l'Eau, les Glaces et l'Activité; MM = Martian meteorite

= implied phase from elemental chemistry measurements on the surface of Mars
 \$ = primary or secondary phase
 & = possible terrestrial contamination
 (?) = questionable phase
 % = residual primary phase after aqueous alteration

Table 2. 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 upon APXS compositions (see Ming *et al.*, 2006). 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.

Mineralogy	Clovis Class						Rock Classes						Soil Class				
	Clovis Outcrop		Ebenezer Rock		Wishstone Class		Wishstone Rock		Watchtower Class		Peace Class		Paso Robles Class		Case 1	Case 2	Case 1
	Case 1	Case 2	Case 1	Case 2	Case 1	Case 2	Case 1	Case 2	Case 1	Case 2	Case 1	Case 2	Case 1	Case 2			
%																	
Primary Phases																	
Olivine	tr	tr	tr	tr	tr	7	6	4	4	4	15	14	c	c	c	c	c
Pyrroxene	12	33	9	42	11	12	5	22	5	22	24	48	c	c	c	c	c
Feldspar	0	34	0	21	13	52	0	30	0	30	0	7	c	c	c	c	c
Apatite	0	2	0	2	11	11	7	10	7	10	1	1	c	c	c	c	c
TiO ₂	1	1	tr	tr	1	1	1	1	1	1	tr	tr	c	c	1 ^c	c	c
Other Metal Oxides	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	1	1	c	c	c	c	c
Magnetite ^d	tr	tr	2	2	1	1	1	tr	tr	tr	5	5	c	c	c	c	c
Ilmenite	0	0	0	0	1	1	1	1	1	1	0	0	0	0	0	0	0
Secondary Phases																	
NpOx	3	3	4	4	1	1	4	4	4	4	2	2	c	c	c	c	c
Hematite	2	2	2	2	1	1	3	3	3	3	0	0	4	1	1	1	1
Goethite	5	5	2	2	0	0	1	1	1	1	0	0	0	0	0	0	0
Ferric Sulfate	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Mg-Sulfate	tr	1	0	tr	2	1	5	5	5	5	9	10	10	10	10	10	10
Ca-Sulfate	11	10	5	4	1	2	0	0	0	0	6	6	3	4	4	4	4
Other Sulfates	0	0	0	0	0	0	0	0	0	0	0	0	2	5	5	5	5
Brushite (CaH(PO ₄) · 2H ₂ O)	2	0	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Halides	2	2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Secondary Aluminosilicates ^e	62	-	71	-	47	-	67	-	67	-	35	-	-	-	-	-	-
Allophane ^e	-	7	-	12	-	8	-	13	-	13	-	tr	tr	7	7	7	7
Amorph. SiO ₂ ^e	-	0	-	5	-	0	-	5	-	5	-	4	4	10	10	10	10
Soil Component ^f	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA

^aFeature/Target = Pasadena/Paso Robles.

^bFeature/Target = Paso Robles2/Light Soil.

^cPhase is calculated as part of the soil component listed below.

^dMagnetite may be secondary phase.

^eSecondary aluminosilicates include allophane and amorphous SiO₂ 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.

^fNA = not applicable. Soil component is the average composition of Gusev surface soils that has been mixed with the Paso Robles materials.

Table 3. Mineralogical composition of Meridiani Planum outcrop inferred by modeling of geochemical data (Clark *et al.*, 2005). An aluminosilicate is advocated as feldspar in Case 1. A basaltic rock composition similar to Bounce Rock is used for the rock component in Case 2. The principle difference between the two cases is that alkali elements and Al are modeled in the feldspar for Case 1 and these elements are modeled as alteration phases in Case 2.

	Case 1 (SO ₃ =20%) Wt%	Case 2 (average) Wt%
<i>Rock Component</i>		
Basaltic Rock	0.0	16.2
Pyroxene ^a	4.5	0.0
Feldspar (Ab=79 wt.%, Or=21%, An=0%) ^b	16.4	0.0
Sum rock component	20.9	16.2
<i>Oxide Components</i>		
Hematite, Fe ₂ O ₃	5.9	5.9
Anatase, TiO ₂	0.7	0.6
Pyrolusite, MnO ₂	0.3	0.3
Iron Oxide, (Fe _{0.94} Cr _{0.06}) ₂ O ₃	3.7	2.7
Sum Oxide components	10.6	9.5
<i>Sulfate Components</i>		
Jarosite, (K _{0.51} Na _{0.49})(Fe _{0.91} Al _{0.09}) ₃ S ₂ O ₁₁ (H ₂ O) ₃	0.0	10.0
H-Jarosite, (H ₃ O) ₃ S ₂ O ₁₁ (H ₂ O) ₃	9.7	0.0
Schwertmannite, (Fe _{0.94} Cr _{0.06}) ₃₂ O ₆₉ S ₇ (H ₂ O) ₉	0.0	1.0
Kieserite, (Mg _{0.99} Ni _{0.01})SO ₄ (H ₂ O)	17.0	17.6
Bassanite, Ca(SO ₄)(H ₂ O) _{0.5}	8.6	7.4
Thenardite, Na ₂ SO ₄	0.0	0.5
Sum Sulfate Components	35.3	36.5
<i>Chloride Components</i>		
Bischofite (MgCl ₂)(H ₂ O) ₆	2.4	0.0
Halite (NaCl)	0.0	1.9
<i>Phosphate Component</i>		
Ca-phosphate	2.4	0.0
Variscite, (Al _{0.90} Fe _{0.10})PO ₄ (H ₂ O) ₂	0.0	1.2
<i>Aluminosilicate Components</i>		
Allophane, halloysite, and/or kaolinite, Al ₂ Si ₂ O ₇ (H ₂ O) ₂	7.3	8.9
Opalline Silica, SiO ₂ (H ₂ O) _{0.2}	21.1	25.8
Sum Aluminosilicate Component	28.4	34.7
<i>Carbonate Component</i>		
CaCO ₃	0.2	0.0

^a Tentatively identified as pyroxene by the Mossbauer spectrometer.

^b Ab = albite; Or = orthoclase, An = anorthite.

Table 4. Inferred salt hydration content for the average composition of Meridiani Planum outcrop material for Case 1 mineralogy listed in Table 3 (Clark *et al.*, 2005). Minimum (Min) and maximum (Max) water contents are provided to bracket the possible water content. The estimate for the minimum and maximum H₂O contents used minerals that would satisfy the composition with the lowest and highest possible water contents in their structures, respectively.

Salt	Min H ₂ O	Max H ₂ O
	wt. %	wt. %
MgSO ₄ ·7H ₂ O (epsomite)	-	14.5
MgSO ₄ ·H ₂ O (kieserite)	2.8	-
^a MgSO ₄ adsorbed	2.2	-
CaSO ₄ (bassanite)	0.0	-
CaSO ₄ ·2H ₂ O (gypsum)	0.0	
MgCl ₂ ·6H ₂ O	-	2.2
Na-jarosite	0.9	-
H ₃ O-jarosite	-	1.3
Hydroxylapatite	-	0.04
Chloroapatite	0.0	-
Total H₂O	5.9	22.2

^aMgSO₄ adsorbed is the amount of water assumed to be adsorbed on the surfaces of the sulfate.

Table 5. Inferred water content (wt.%) of several outcrops, rocks, and soils in the Columbia Hills, Gusev crater. Minimum (Min) and maximum (Max) water contents are provided to bracket the possible water content. The estimate for the minimum and maximum H₂O contents used minerals that would satisfy the elemental composition with the lowest and highest, respectively, water contents in their structures (data taken from Ming *et al.*, 2006).

Mineralogy	Clovis outcrop		Ebenezer rock		Wishstone rock		Watchtower outcrop		Peace outcrop		Paso Robles soil	
	Min. H ₂ O	Max. H ₂ O	Min. H ₂ O	Max. H ₂ O	Min. H ₂ O	Max. H ₂ O	Min. H ₂ O	Max. H ₂ O	Min. H ₂ O	Max. H ₂ O	Min. H ₂ O	Max. H ₂ O
NpOx	?	?	?	?	?	?	?	?	?	?	?	?
Hematite Fe ₂ O ₃	0	0	0	0	0	0	0	0	0	0	0	0
Goethite FeOOH	0.5	0.5	0.2	0.2	0	0	0.1	0.1	0	0	0	0
Ferric Sulfate												
Fe ₂ (SO ₄) ₃ · H ₂ O	0	0	0	0	0	0	0	0	0	0	1.1	0
Fe ₂ (SO ₄) ₃ · 9H ₂ O	0	0	0	0	0	0	0	0	0	0	0	8.4
Mg-Sulfate												
MgSO ₄ · H ₂ O	0.1	0	0	0	0.2	0	0.7	0	1.2	0	1.3	0
MgSO ₄ · 7H ₂ O	0	0.5	0	0	0	1.0	0	2.6	0	5.1	0	5.1
Ca-Sulfate												
CaSO ₄	0	0	0	0	0	0	0	0	0	0	0	0
CaSO ₄ · 2H ₂ O	0	2.1	0	1.0	0	0.4	0	0	0	1.3	0	0.8
Other Sulfates	0	0	0	0	0	0	0	0	0	0	?	?
Ca-phosphate												
chloroapatite (or fluoro) ^a	0	0	0	0	0	0	0	0	0	0	0	0
Hydroxyapatite Ca ₅ (PO ₄) ₃ OH ^a	0	tr	0	tr	0	0.2	0	0.2	0	tr	NM	NM
brushite CaH(PO ₄) · 2H ₂ O	NM	?	2.1									
Halides												
Halite NaCl	0	0	0	0	0	0	0	0	0	0	0	0
Mirabalite MgCl ₂ · 6H ₂ O	0	1.1	0	0.5	0	0.5	0	0.5	0	0.5	0	0.5
Secondary Aluminosilicates ^b	?	?	?	?	?	?	?	?	?	?	?	?
Soil Component ^c	NM	?	?									
Total H₂O	0.6	4.2	0.2	1.7	0.2	2.1	0.8	3.4	1.2	6.9	2.4	16.9

? = H₂O content unknown and not modeled (i.e., H₂O content is assumed to be 0). NpOx may include nanophases of goethite and other iron oxyhydroxides.

NM = phase not modeled for this case.

^aPrimary phase.

^bSecondary aluminosilicates may include phyllosilicates, allophone, amorphous SiO₂, or other poorly crystalline aluminosilicates.

^cGusev basaltic soil component mixed in with Paso Robles light-toned soil. Water content of Gusev basaltic soils is unknown.

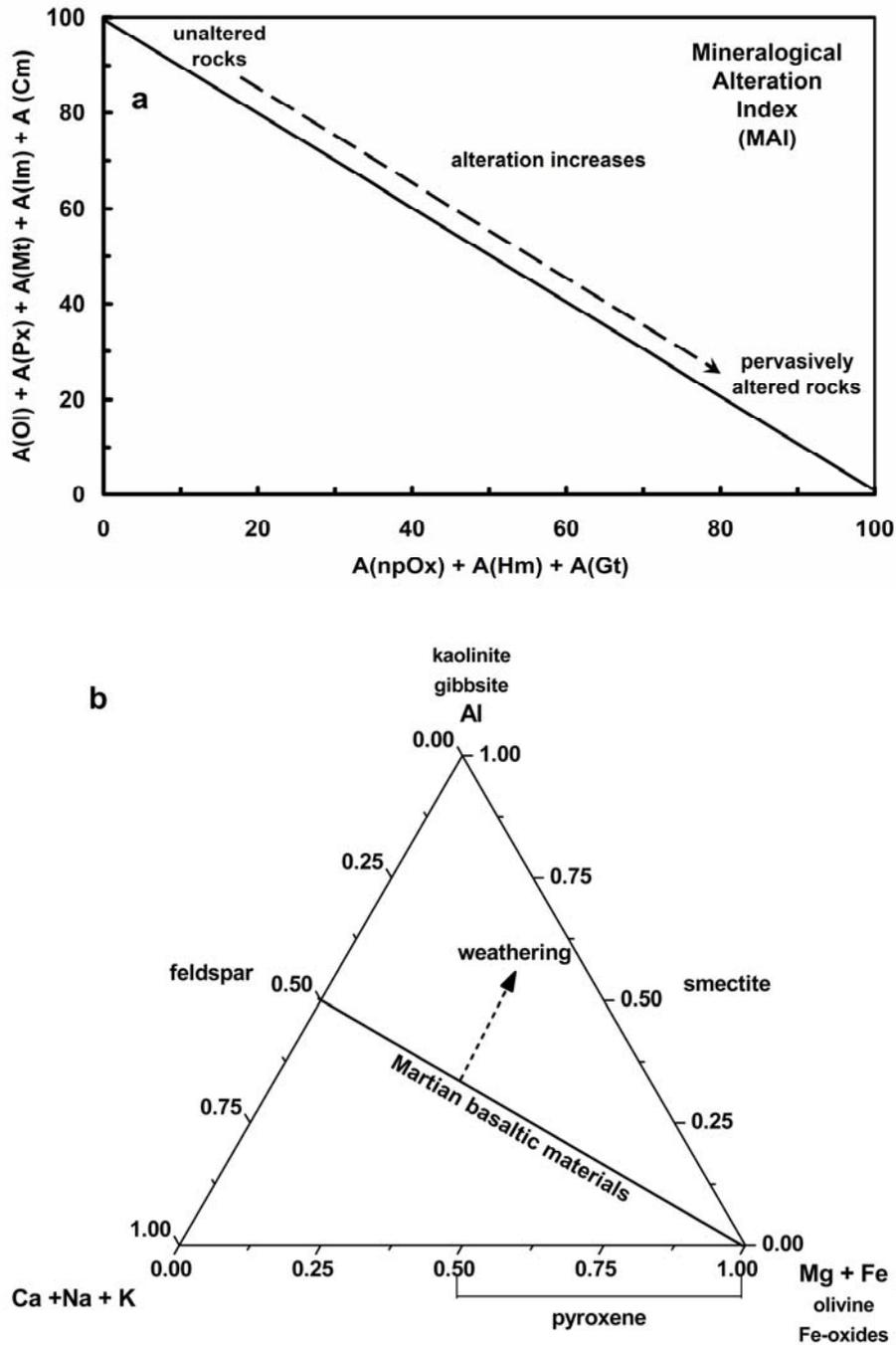


Figure 1. Chemical and mineralogical indices to evaluate alteration on Mars. a) Mineralogical Alteration Index (MAI) established by the mineralogy of iron-bearing phases (Morris *et al.*, 2006). Alteration trends are based on the area (spectral area (A) of each phase determined by Mossbauer spectroscopy) of primary phases (olivine (Ol), pyroxene (Px), magnetite (Mt), ilmenite (Im), chromite (Cm)) compared to the area of the secondary phases (nanophase oxide (npOx), hematite (Hm), and goethite (Gt)). b) Compositional trends for basaltic materials (molar %). Unaltered basaltic materials will lie along the olivine-feldspar join. Weathered basaltic materials where leaching has taken place will fall away from the olivine-feldspar join to more Al-rich composition (after Nesbitt and Wilson, 1992).

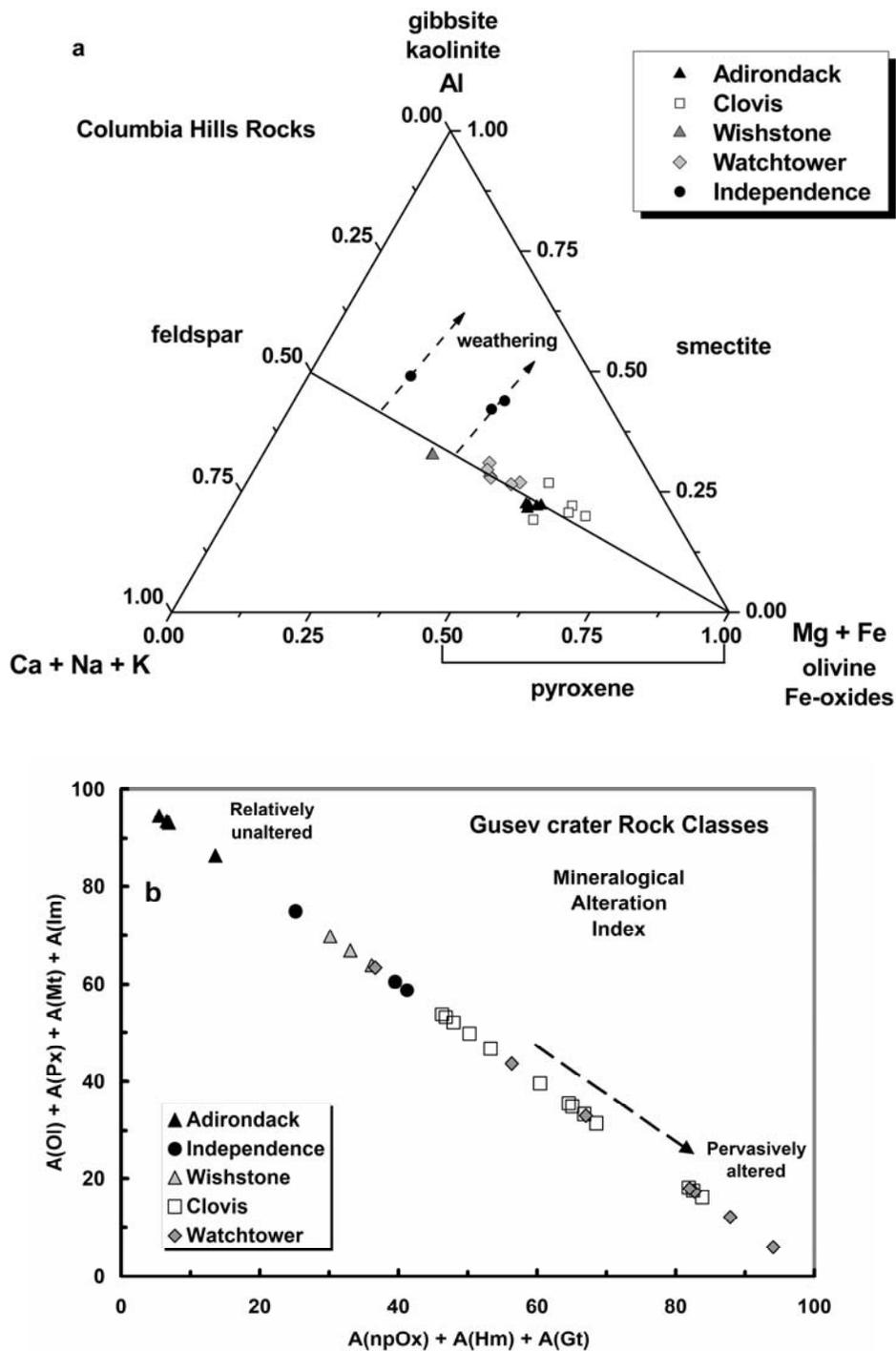


Figure 2. Chemical and mineralogical alteration indices for rock classes in the Columbia Hills, Gusev crater. a) Mineralogical Alteration Index (MAI). b) Compositional trends [see Fig. caption 1 for definition of terms].

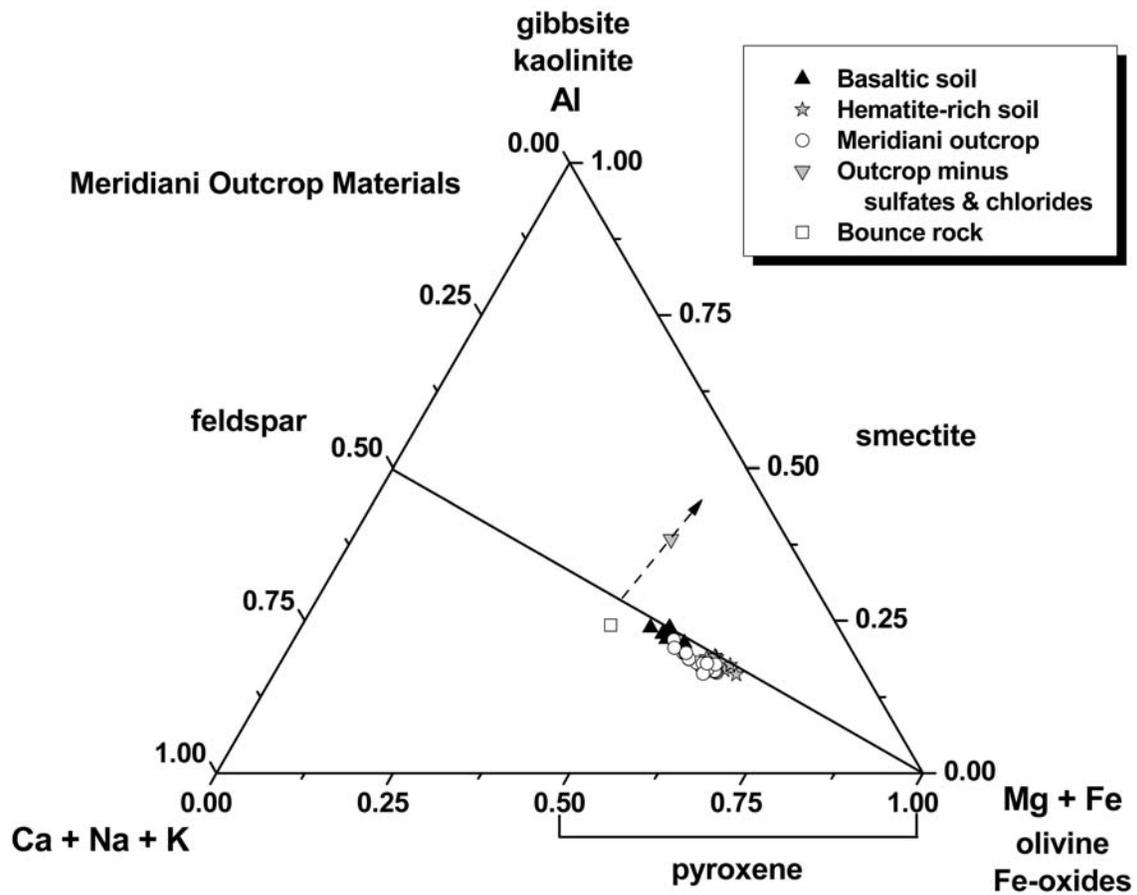


Figure 3. Compositional trends for Meridiani Planum outcrop materials. The composition for the point marked Outcrop minus sulfates & chlorides has been corrected for Fe, Mg, and Ca sulfates and chlorides (data from Clark *et al.*, 2005).

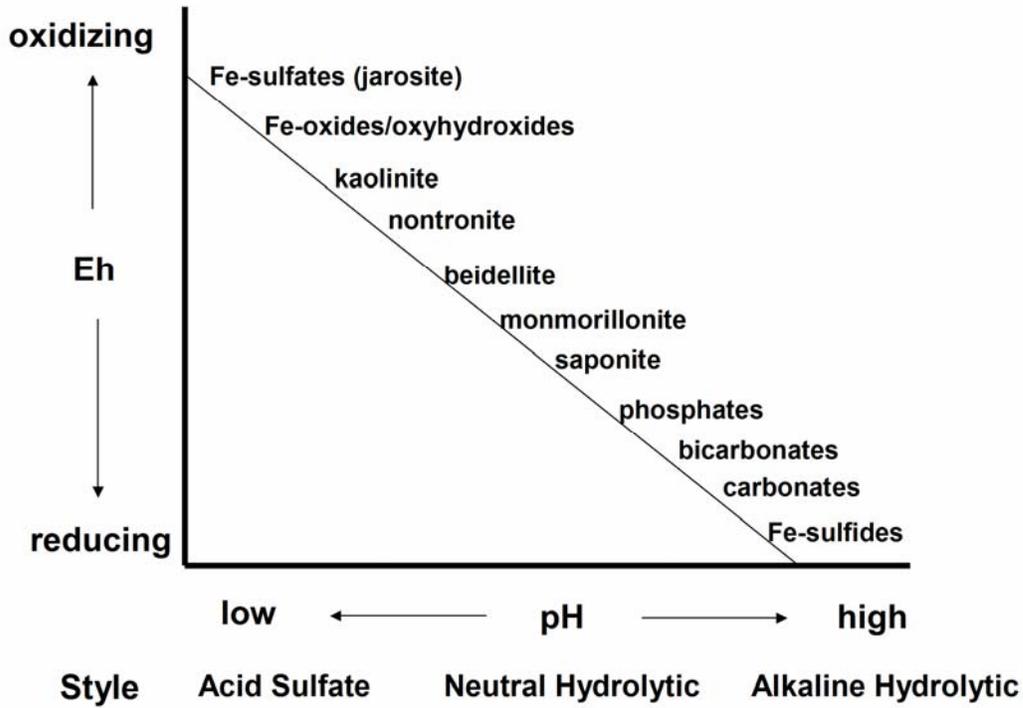


Figure 4. General environmental conditions and styles of weathering for the formation of secondary phases that might be present on Mars [note: These are conditions are provided only in a general sense. Formation conditions vary substantially for these phases].