Evidence for Amazonian acidic liquid water on Mars—A reinterpretation of MER mission results

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The Mars Exploration Rover (MER) missions have confirmed aqueous activity on Mars. Here we review the analyses of the field-based MER data, and conclude that some weathering processes in Meridiani Planum and Gusev crater are better explained by late diagenetic water-rock interactions than by early diagenesis only. At Meridiani, the discovery of jarosite by MER-1 Opportunity indicates acidic aqueous activity, evaporation, and desiccation of rock materials. MER-based information, placed into the context of published data, point to local and limited aqueous activity during geologically recent times in Meridiani. Pre-Amazonian environmental changes (including important variations in the near-surface groundwater reservoirs, impact cratering, and global dust storms and other pervasive wind-related erosion) are too extreme for pulverulent jarosite to survive over extended time periods, and therefore we argue instead that jarosite deposits must have formed in a climatically more stable period. Any deposits of pre-existent concretionary jarosite surviving up to the Amazonian would not have reached completion in the highly saline and acidic brines occurring at Meridiani. MER-2 Spirit has also revealed evidence for local and limited Amazonian aqueous environmental conditions in Gusev crater, including chemical weathering leading to goethite and hematite precipitation, rock layering, and chemical enhancement of Cl, S, Br, and oxidized iron in rocks and soils. The estimated relative age of the impact crater materials in Gusev indicates that these processes have taken place during the last 2 billion years. We conclude that minor amounts of shallow acidic liquid water have been present on the surface of Mars at local scales during the Amazonian Period.

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1. Introduction

Aside from safety considerations, landing sites for the Mars Exploration Rovers (MER) Opportunity and Spirit in the Meridiani Planum and Gusev crater regions, respectively, were selected because they were previously identified as potential locations of past water and related sedimentary deposition based on distinct morphologic and mineralogic indicators (Golombek et al., 2005). Water is regarded as a key prerequisite for life on Earth, and as such, answering the question of when and where liquid water has been present on the surface of Mars is a first-order objective for astrobiology-oriented planetary exploration. If liquid water had been present during the Amazonian Period, especially the Late Amazonian epoch (see Table 1), then microbial life could have found a way to endure near the surface of Mars until recent or even present times.

The hematite signature in the Meridiani Planum region (lat. 5°S–10°N, lon. 12°W–5°E) was identified through the TES instrument (Thermal Emission Spectrometer, on the Mars Global Surveyor spacecraft, see Christensen et al., 2001). It was interpreted to consist of Noachian and possibly Early Hesperian layered hematite deposits, based on MOC and THEMIS crater retention ages (Mars Orbiter Camera, on the Mars Global Surveyor, and Thermal Emission Imaging System, on the Mars Odyssey spacecraft; see Hartmann et al., 2001; Lane et al., 2003). The deposits have a relief of ~600 m and an areal extent of about 3 × 10^5 km^2 (Hynek, 2004). This outcrop of hematite, which has been interpreted to consist of basaltic rock materials with ~10–15% crystalline grey hematite deposits (specularite, Fe_2O_3), may have been precipitated from groundwater upwelling and/or hydrothermal circulation (Christensen et al., 2001; Hynek et al., 2002; Squyres et al., 2004a,b; Hynek, 2004; Andrews-Hanna et al., 2007), among other possible mechanisms which also include a volcanic (McCollom and Hynek, 2005) or impact (Knauth et al., 2005) origin. Opportunity data has also shown the presence of hematite (confirmed by TES, Mössbauer and APXS), ferrhydrite, poorly crystalline goethite, and schwertmannite in Meridiani outcrops (Farrand et al., 2007). An extended diagenetic history in the presence of an episodic water system of high ionic strength (McLennan et al., 2005; Tosca et al., 2005) aptly explains the origin of hematite: by heating and dehydroxilation of goethite, which in turn precipitated from the breakdown of jarosite. Jarosite formed when acidic liquid water infiltrated the Meridiani ferric sulfatic soils, dissolving ancient basaltic and sulfide phases and promoting evaporitic sequences. The timing of all these events is unknown, and we argue here that, although they essentially occurred in the early times of Mars history, but also indicate the deposition of surface materials in water-enriched environments. Our conclusions indeed support very ancient weath

Table 1

<table>
<thead>
<tr>
<th>Epoch</th>
<th>Absolute age range (Ga)</th>
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<tbody>
<tr>
<td>Late Amazonian</td>
<td>0.6–0.3 to present</td>
</tr>
<tr>
<td>Middle Amazonian</td>
<td>2.1–1.4 to 0.6–0.3</td>
</tr>
<tr>
<td>Early Amazonian</td>
<td>3.1–2.9 to 2.1–1.4</td>
</tr>
<tr>
<td>Late Hesperian</td>
<td>3.6 to 3.1–2.9</td>
</tr>
<tr>
<td>Early Hesperian</td>
<td>3.7 to 3.6</td>
</tr>
<tr>
<td>Late Noachian</td>
<td>3.82 to 3.7</td>
</tr>
<tr>
<td>Middle Noachian</td>
<td>3.95 to 3.82</td>
</tr>
<tr>
<td>Early Noachian</td>
<td>&gt; 3.95</td>
</tr>
</tbody>
</table>

Condensed from Fig. 14 of Hartmann and Neukum (2001).

2. Jarosite dates Amazonian liquid water at Meridiani Planum

The only place where jarosite has been found on Mars is in bedrock outcrops in Meridiani Planum, where up to 28% of the Fe is in the form of this hydrated ferric sulfate mineral (Klingelhöfer et al., 2004), as revealed by the exploration rover Opportunity along the traverses to Eagle and Victoria craters (Fig. 1). Jarosite has a rather distinctive Mössbauer signature, so it is easy to detect and to place an upper limit on its abundance. But Mössbauer spectroscopy is not sensitive to Fe-free sulfate minerals, so the detected jarosite is possibly a mixture of sulfates and mafic siliciclastic grains (debris). This mineralogical assemblage is indicative of a complex diagenetic history in the Meridiani plains, which are Noachian in origin, but also record modification
processes which have been dated as Amazonian in age (Grant et al., 2006). After jarosite precipitation, an arid environment must have prevailed, as jarosite becomes unstable and rapidly decomposes to ferric oxyhydroxides in humid climates. However, it still remains an open question (Elwood Madden et al., 2004; S奎res et al., 2004b) whether jarosite was formed in ancient times, with no subsequent aqueous alteration for billions of years, or in a more recent period of local liquid water stability embedded in the long-term dry Amazonian climate. Several factors, listed below, illustrate problems with the consideration that Meridiani jarosite is an ancient mineral assemblage.

On Mars, where aqueous acidic conditions may have existed and have been widespread (Fairien et al., 2004), at least during some periods (Bibring et al., 2006), jarosite could have had a global distribution as a common evaporitic and/or diagenetic mineral (Tosca et al., 2005). On Earth, under the oxidizing and near neutral conditions of the surface, and because of the lack of iron and sulfur compared to other elements, jarosite is by necessity of limited distribution in typical weathering environments. It is usually found in the oxidized zones of sulfide deposits, and forms through the reaction of dilute sulfuric acid derived from the oxidation of pyrite. The oxidation of pyrite (Burns and Fisher, 1990, 1993) and pyrrhotite (the usual primary sulfide in basaltic rocks, e.g. Lorand et al., 2005) lead to jarosite, as shown by experimental weathering in simulated Martian environment (Chevrier et al., 2004, 2006).

Jarosite is a brittle secondary mineral, with a Mohs’ hardness of 2.5 to 3.5, and is usually found as amber-yellow to brown crusts or coatings of minute crystals, as larger crystals are rather rare. Natural jarosite occurs in two different morphologies: (1) pulverulent, in nodules or fibrous masses, earthy, including granular crusts where indistinguishable crystals are made up of fibers and form uniformly large masses, best exemplified in mine drainage waters, such as in Rio Tinto (Amils et al., 2007; see Fig. 2); or (2) concretionary, as distinct fine-grained crystals, first described in 1852 in El Jaroso Hydrothermal System, which is the world locality of jarosite (Martinez-Frias et al., 2007; see Fig. 2).

The aqueous alteration of sulfides also leads to nanocrystalline jarosite, with crystals <500 nm in size (Chevrier et al., 2004, 2006). Interestingly, relatively large sizes and well developed crystal forms of jarosite suggest that it is abiotic in origin (Akai et al., 1999), while pulverulent jarosite can be abiotic (Chevrier et al., 2006) or have a biologically induced origin (Amils et al., 2007). To date, the morphology of Meridiani jarosite is still unknown, and thus we will consider both possibilities in our analysis.

2.1. Meridiani jarosite is pulverulent

Rio Tinto is an acid–sulfate dominated fluvial system with near constant acidic pH (about 2.3) along its 100 km long course. A variety of hydroxylated and hydrated sulfate minerals form annually in the river as evaporite and efflorescent concretions during the summer dry season, and are destroyed in the wet season due to the highly seasonal rainfall. Sulfate-bearing minerals found along the river derive from aqueous alteration of iron-rich sulfide minerals of the Iberian Pyrite Belt, the largest pyritic province in the world, and include jarosite, copiapite, coquimbite, schwertmannite, gypsum and epsomite. Similarly to Rio Tinto, if soft jarosite formed on Mars billions of years ago, during the Noachian or Hesperian time periods, not only the chemical but also the physical environmental parameters at Meridiani must have remained strictly constant, and similar to the arid current conditions, during the entire time for pulverulent jarosite to be stable. This scenario seems unlikely, as any pre-Armani assemblage of jarosite would have faced complete destruction due to continuing and powerful weathering processes of surface materials operating in Meridiani during the Noachian and the Hesperian, which include:

(a) Important changes in the near-surface water reservoirs (Boyton et al., 2002), and in atmospheric composition, pressure, and temperature due to (i) large excursions in planetary obliquity (Touma and Wisdom, 1993), (ii) continuing extensive volcanism (Dohm et al., 2001; Neukum et al., 2004), and/or (iii) impact effects (Segura et al., 2002). A large number of evidences indicates climate change on Mars over its entire geological history, including ocean-related landforms (Parker et al., 1993), massive layered outcrops (Malin and Edgett, 2000), valley networks and other valley forms (Scott et al., 1995; Mangold et al., 2004), anastomosing and meandering rivers and deltas (Malin and Edgett, 2003), and mineralogies indicating ancient aqueous environments over regional scales (Hynek, 2004). For these features to have formed, increased wetter conditions must have prevailed (e.g., Baker, 2001). Such substantial variations in atmospheric pressure, temperature and humidity would have destroyed pulverulent jarosite assemblages in relatively brief periods of time. Only if Meridiani water was in equilibrium with jarosite, it could have come into contact with the bedrock with no chemical alteration. If this was the case, water must have also been in equilibrium with Mg-sulfates, as there is very strong evidence that these minerals exist in the bedrocks (Clark et al., 2005), and this family of minerals is among the most soluble sulfates. Any aqueous solution in chemical disequilibrium with jarosite and Mg-sulfates existing in Meridiani at any time would have dissolved the hypothesized ancient jarosite right away. Even reaction with atmospheric water vapor can convert jarosite to ferric oxide when exposed at an outcrop surface. In Rio Tinto, jarosite assemblages are seasonal, forming every summer and dissolving after the first rain fall.

(b) Impact cratering, especially before the Amazonian, resulting in a number of impact craters in varying states of degradation,
including deeply modified rims and interiors through wind and mass wasting processes, as revealed by Opportunity’s traverse in Meridiani Planum. Impact cratering results in enormous transient increases in local (or even global for Noachian impacts) temperatures and pressures which affect jarosite, as it begins dehydroxylation at over 700 K. Also, excavation of target materials, bedrock deformation, exposure of fractured rocks, emplacement of fresh ejecta blankets with widely varying grain sizes, formation of perched coarser fragments, deposition of ejecta blocks on the surface, and impact-related crushed layers mantling previous deposits, are usual consequences of bolide impacts possibly affecting jarosite assemblages. Water may have also contributed to crater modification, including the local redistribution of fragments to form pavements (Fig. 3) and similar small-scale landforms.

(c) Wind activity, in this case through the entire geological history of Mars, which includes rock abrasion by saltating sand grains impacting the very soft bed rock, dust particle transport including jarosite and other sulfates in the form of very fine particles highly diluted in the global wind-transported dust (as there are no detection of jarosite in the soils), and wind streak, dune, and fine-grained dust mantle formation blanketing the soil, all reported for Meridiani: bright wind streaks seen in MGS-MOC and Opportunity descent images indicate ongoing pervasive wind erosion. Seen from orbit, Eagle, Fram and Endurance craters have bright streaks to their southeast, and surface observations confirm that the streaks derive from bright dust-sized particles, probably deposited from the air during a dust storm. In Meridiani, the major components of bright dust and dark basaltic sand are supplied by wind, and various episodes of dust deposition cover the previous soil (Yen et al., 2005). The bright local dust deposits on Mars are interpreted to be part of a global unit (Yen et al., 2005), indicating mobilization of large amounts of dust and the associated burial and/or exposure of rocky surfaces, as well as the dramatic change of the Martian landscape and albedo on decadal scales (Geissler, 2005), all of which collectively mark the significant influence of global circulating winds across the planet. The surface is thus covered by dust from annual global storms, and then deflated by winds capable of completely stripping away the dust, exposing the rock outcrop (Soderblom et al., 2004), as well as resulting in erosion of the bedrock and reorienting ubiquitous small sinuous crested eolian bedforms (Sullivan et al., 2005). These processes of sand movement and bedform development are recorded as occurring even nowadays (Bridges et al., 2007). Delicate assemblages of pulverulent jarosite embedded in very soft bedrock cannot survive wind abrasion, removal and redistribution of debris, global mixing, and other wind-related weathering processes during billions of years.

It is therefore difficult to imagine how assemblages of pulverulent jarosite formed before the Amazonian could have survived the intense weathering of the early history of Mars, leaving as the only plausible explanation for its presence in Meridiani that the synthesis of jarosite occurred during the
climatically stable Amazonian. Any alternative explanation considering these same physical weathering mechanisms as trigger agents for environmental changes leading to the exhumation of ancient (i.e., pre-Amazonian) buried assemblages of pulverulent jarosite, must convincingly resolve how this extremely delicate form of jarosite could have been first buried without being destroyed. And, when exposed, how it can resist the fundamentally perturbing processes of exhumation, which must have included at least one of the following destructive mechanisms: surface or subsurface liquid water-related chemical weathering, impact temperatures and pressures, impact mantling, or destructive global dust storms removing uppermost deposits. No other mechanisms exist on Mars to expose ancient sediments, and sandblasting and weathering would rather bury and destroy than exhume any pulverulent jarosite exposed at the surface. The same can be argued to explain the survival of any soluble salts in exposed outcrops. Therefore, pulverulent jarosite in Meridiani would likely be the result of a late (i.e., Amazonian) sequence of precipitation events in ponded brines, where jarosite would be dissolved when water is available and reprecipitated in the arid epochs, in a similar way as is recorded in Rio Tinto.

2.2. Meridiani jarosite is concretionary

We explore here the possibility that jarosite assemblages in Meridiani are concretionary, although terrestrial jarosite is most of the time pulverulent, or forming very small crystals. Terrestrial concretionary jarosite from El Jaroso is genetically linked to the calc-alkaline shoshonitic volcanism of the SE Mediterranean margin of Spain, dating from the Upper Miocene (Martinez-Frias et al., 2004, 2007), a mode of formation so far not very relevant to Mars (and especially not relevant for Meridiani) compared to other process such as aqueous weathering.

Only in the case that jarosite in Meridiani was concretionary, formed in wetter conditions during the Noachian or the Hesperian, and the mineral deposit was immediately buried after formation, jarosite would have been protected from humidity, pressure and temperature changes over time. As Meridiani has been a deflation area for quite some time, in this unlikely scenario concretionary jarosite would be currently exhumed, exposing a fresh surface of jarosite-containing rock outcrops. Such an ancient rock outcrop would not necessarily require Amazonian aqueous conditions. But the stripping of buried concretionary jarosite in Meridiani does not imply per se the absence of liquid water on the Martian surface during the Amazonian. Any solution interacting with concretionary jarosite in Meridiani during the Amazonian would likely have been in the form of episodic, highly saline and acidic brines, derived from intense evaporation and/or sublimation processes through transient migration of groundwater to the surface. In the anticipated recent aqueous phases, the hydrolization of concretionary jarosite would not have reached completion (Barron et al., 2006). Instead, concretionary jarosite assemblages would have remained stable in the bottom part of impact craters, where they may interact with these cold and acidic brines. Therefore, previous investigations that consider jarosite as an indicator of water-limited chemical weathering (Elwood Madden et al., 2004) no longer qualify as an argument to rule out the presence of water on the surface of Mars during the Amazonian. Assuming a prolonged diagenetic history in the Burns formation (Mclennan et al., 2005), at least some of the concretionary jarosite may have been a relatively late precipitate of the brines, rather than an early-forming mineral. Jarosite mineralization could even be a much later feature of the Burns formation, such as during transient aqueous activity (Barron et al., 2006).

2.3. The aqueous history of Meridiani Planum during the Amazonian

After the previous analysis of the mineralogy in Meridiani, we conclude that jarosite formed in a geologically recent, transient wet environment, as scenarios under which jarosite might persist for several billion years on Meridiani are very unlikely. Furthermore, these unlikely scenarios do not imply an absolutely dry Amazonian climate. In summary, we propose that the presence of pulverulent jarosite in Meridiani would imply the activity of
acidic liquid water during the Amazonian, while the existence of concretionary jarosite could not be used as an argument to exclude the presence of Amazonian acidic brines. The important difference is that, in such acidic brines, pulverulent jarosite would be physically dissolved and precipitated repeatedly responding to the variations in water availability, while concretionary jarosite would resist complete chemical hydrolyzation in such a variable brine regime. Therefore, ponded acidic brines may have been associated to both types of jarosite during the Amazonian.

The actual contribution of water on Meridiani during the Amazonian was not a continuous body the size of the sulfate-bearing unit that extends over regional scales (up to $3 \times 10^7$ km$^2$) (HYNEK, 2004; GENDRIN et al., 2005; ARVIDSON et al., 2005). Rather it comprised shallow and heterogeneously localized ponded brines remaining liquid at temperatures below 273 K (KUZMIN and ZABALUEVA, 1998; GENDRIN et al., 2005; FAIREN et al., 2008), in the form of an open acid–sulfate weathering regime (GOLDEN et al., 2005). The water would have been acidic and oxidizing, reacting with the basaltic surfaces to produce sulfates and iron oxides. The diageneric process likely prolonged in time during the Amazonian, including episodic inundations by shallow acidic and salty surface water followed by evaporation/sublimation, and desiccation. For example, rocks located deep within Endurance crater display a higher degree of chemical alteration when compared to the rock outcrops located at higher stratigraphic positions within the crater (Fig. 4), which could be interpreted as an indication of enhanced weathering by acidic liquid water in the past (e.g., NOACHIAN/HESPERIAN, see ARVIDSON et al., 2006) compared to more geologically recent times (Amazonian). Alternatively, we favor the idea that this vertical gradation in chemical alteration may indicate occasional acidic groundwater rising to the surface and leaving a film at the bottom of the crater in recent times. This is also supported by the erosional features described at the surface of the crater, evidencing the activity of minor amounts of post-crater formation surface water (see Fig. 3, and CHAVDARIAN and SUMNER, 2006), and suggesting that this is a recent evaporite deposit. Small-scale, shallow crack systems observed on outcrops of the Burns formation can equally be originated in the precipitation and dissolution of salts, moisture changes or partial dehydration of some minerals (CHAN et al., 2008). Also KNOLL et al. (2008) have concluded that the alteration history of Meridiani outcrop rocks did not end with the early groundwater-mediated diageneric features described in previous publications.

Meridiani outcrops show sulfur concentrations as much as a factor of 4 to 5 times higher than soil materials in the other four Martian landing sites, as well as a very high ferric to total iron ratio in excess of 0.84 (Klingelhofer et al., 2004). According to our model, modest acidic liquid water has infiltrated the Meridiani ferric sulfatic soils during the Amazonian, dissolving ancient olivine basaltic and sulfatic phases and promoting evaporitic sequences, which led to the formation of jarosite in local surficial depressions. During periods of very limited aqueous activity, the breakdown of jarosite caused goethite precipitation, and posterior heating, dehydroxilation and crystallization forming coarse-grained hematite. Alternatively, jarosite could have transformed directly to hematite (BARRON et al., 2006), as both goethite and hematite are direct products of the hydrolysis of jarosite. This extended diageneric history finally resulted in the assemblage of hematitic spherules (Squyres et al., 2004b; Zolotov and Shock, 2005). Hematite may also be an early mineral phase, due to its very low solubility, although it can dissolve quite easily in acidic conditions. Such aqueous activity appears to have been recurrent during the Amazonian, in the form of episodes of shallow surface acidic water, infiltration and subsequent desiccation. As a result of the recurrent infiltration of limited amounts of water, jarosite was formed and coexisted along with hematite and goethite, probably even forming mixtures of the three minerals. Also, hematitic spherules are located at various stratigraphic sequences in the rock outcrops, indicating that the spherules have been formed in watery environments occurring in different times prior to crater excavation, and that this diageneric process can still be active today. The most recent of such watery episodes is hypothesized here to have contributed to jarosite formation observed both in Eagle, Fram, and Endurance craters, as well as in rocks exposed at Anatolia trough. Also, various stratification styles (planar lamination, low-angle cross-stratification, cross-bedding, ripple cross-lamination, and crinkly and undulatory lamination) have been identified at Meridiani, indicating deposition from subaqueous dunes in an environment characterized by episodic inundation by surface water via the rise of an aquifer to shallow depths, followed by evaporation/sublimation, exposure and desiccation. In fact, minor amounts of water appear to have been flowing recently between rocks and ponding deep into craters in Meridiani, as suggested by the MER Opportunity investigations in Endurance crater (Fig. 3). As the outcrop was infiltrated by surface liquid H$_2$O, that water likely became hypersaline, with soluble sulfates and chlorides, or enriched in Na and Cl (KNOLL et al., 2008).

3. Amazonian water-surface interactions in the Gusev crater rocks and soils

Decades of Mars exploration and derived photogeological interpretations have illuminated an evolutionary sequence for Gusev crater, which includes Ma’adim Vallis-related flooding and associated ponding and sedimentation on at least more than one occasion during the Noachian and Hesperian (SCOTT et al., 1993; GRIN and CABROL, 1997; CABROL et al., 1998; KUZMIN et al., 2004). The multi-levelled terraces in the crater interior were interpreted to mark episodic flood-related erosional events, while the smooth surface was interpreted to be fine-grained sediments deposited into the crater by the floodwaters (CABROL et al., 1998). This proposed paleohydrologic history, revealed through geologic and geomorphic mapping, was the basis for selecting Gusev as the first of the two MER targets, with the twofold objective of (1) collecting in situ evidence to test the hypothesis of the existence of an
ancient paleolake, and (2) determining the characteristics of this putative ancient depositional environment.

3.1. Early MER investigations

Initial investigations by the rover Spirit indicated that the plains-forming materials (encountered at the landing site and along the traverse to the Columbia Hills, see Fig. 5) within the Gusev impact crater did not support the purported flood-lacustrine environment, but rather a mostly volcanic surface mainly composed of dark, fine-grained, vesicular rocks interpreted as basaltic lava flows (Squyres et al., 2004a). Furthermore, impact and eolian activity appeared to dominate the geologic history recorded in the plains-forming materials. The composition of the fine-grained component of the plains-forming materials, as revealed by Spirit, displays similar characteristics to those encountered at the Viking and Pathfinder landing sites, interpreted to be the possible result of global mixing and distribution by dust storms (Gellert et al., 2004). Thus, the elemental composition of the bright surface dust at the scale of the Gusev crater floor is remarkably uniform. Moreover, the basaltic lava flows appear to be the most pervasive of the plains-forming materials, and rocks are angular and dispersed across the surface, suggesting that they are by-products of nearby impacts (McSween et al., 2004). This led to the initial interpretation that the evolution of the crater surface was dominated by physical rather than chemical weathering processes, such as impact events followed by eolian modification (Squyres et al., 2004a; Grant et al., 2004; Morris et al., 2004) over a largely volcanic surface.

3.2. Evidence for brines on the surface of Gusev

Further along the traverse, Spirit encountered a major geologic contact near the base of the Columbia Hills that separates the plains-forming materials from the more diverse suite of rock assemblages observed in the Columbia Hills (Crumppler et al., 2005; Ming et al., 2006). Here, after some 160 Sols following touch down onto the surface of Mars, the “dry” view based largely on unequivocal evidence of limited chemical weathering in the plains-forming materials (e.g., Haskin et al., 2005) reverted back to the previously hypothesized wetter impact crater paleoenvironment, noted particularly for the West Spur area of the Columbia Hills, where the record preserved in the ancient rocks points to substantial water activity (Cabrol et al., 2006; Squyres et al., 2006a), and where the extent of alteration of rocks and soils ranges from moderate to extensive (Cabrol et al., 2006; Ming et al., 2006).

The interaction between the volcanic rocks and minor amounts of water has been highlighted by Spirit’s in situ local reconnaissance. Aqueous-related activity within Gusev impact crater is accentuated in the Columbia Hills through the identification of bedrock containing goethite and hematite, layering of rock materials, rounded blocks, rock interiors with enhanced softness, and high concentrations of sulfur, chlorine, and bromine (elements easily mobilized by water and known to form highly soluble salts) in rocks and soils (Farrand et al., 2006; Gellert et al., 2006). In addition, Haskin et al. (2005) reported high concentration of S, Cl, and Br in both multi-layered coatings and interiors of rocks. In the case of some of the rocks of the plains-forming materials, such as those provisionally dubbed “Mazatzal” and “Humphrey”, enhanced Br concentrations in their interiors (mm deep, relative to their exteriors) have been observed to be associated with alteration zones or veins, suggesting that water played a major role in Cl/Br fractionation within the crater (Gellert et al., 2004). “Mazatzal” shows high concentrations of sulfur, chlorine, and oxidized iron, and is coated by materials with an elevated concentration of sulfur, oxidized iron, chlorine, and bromine, suggesting post-crystallization interaction with acidic water and subsequent evaporation. “Humphrey” shows bright material in interior pores, crevices, and cracks that are similar to minerals crystallized out of water flowing through volcanic rocks on Earth. The identification of goethite in rocks in the Columbia Hills, such as significant concentrations in the rock “Clovis”, confirms aqueous processes in the West Spur (Morris et al., 2006; see Fig. 6), as goethite contains the hydroxide anion as an important part of its structure (~10% H₂O by weight). Hematite is also abundant in both rock outcrops and mantles of the Columbia Hills (“Pot of Gold”, “Watchtower”, and “Keel”). Jarosite along with other ferric sulfates (coquimbite and copiapite) has been detected in the regolith (Johnson et al., 2007; Lane et al., 2008).

![Fig. 5. Spirit’s traverse through Columbia Hills. To find the exact location of Spirit, see http://marsrover.nasa.gov/mission/traverse_maps.html. Image courtesy NASA/JPL/Cornell/MRO-HiRISE/New Mexico Museum of Natural History and Science.](Image)

![Fig. 6. Mössbauer spectrum (200–220 K) showing the presence of hematite and goethite in a rock called “Clovis” in the Columbia Hills. This is definitive evidence for water activity in Gusev. Image courtesy NASA/JPL/University of Mainz.](Image)
Optically thick coatings of fine-grained ferric iron-rich dust dominate most bright soil and rock surfaces at Gusev.

Subsurface materials, exposed by trenching and wheel movements of the rover, show additional evidence for aqueous processes. Spirit measured higher Mg, S, and Br concentrations in rock materials exposed in “Boroughs” trench compared to surface materials. Another example is rock materials exposed by the movement of Spirit’s wheels referred to as “Paso Robles”, where Fe is increased, SO$_3$ represents more than 30% wt, and the sulfate and phosphate contents are the highest measured so far on Mars (Gellert et al., 2006; Ming et al., 2006; Morris et al., 2006). Interestingly, Mg-sulfates in trenches appear to be in a higher hydration state than is potentially stable at the surface under current Mars atmospheric conditions (as speculated by Wang et al., 2006), suggesting that they may have formed very recently, perhaps during the most recent period of high obliquity (Head et al., 2006), an epoch during the Late Amazonian that may have provided elevated humidity and somewhat warmer temperatures. In general, salts exposed by trenching appear to have been separated according to solubility. Bromine is also observed to be elevated in materials that fill the vugs and veins of plains-forming basaltic rocks where chemical mobility and separation are indicated by decoupling of salt concentrations between rock materials exposed in the trenches and at the Martian surface. Positive correlations between salt components have also been identified in the trenches (Haskin et al., 2005). In addition, the soluble elements S and Cl are exposed at the surface, suggesting transport to the surface by liquid water. Other soluble species such as an evaporitic MgSO$_4$ phase have been mobilized and concentrated in near-surface intercrater plains-forming materials exposed by rover activities (Crumpler et al., 2005). Wang et al. (2006) concluded that the geochemical trends observed in the trenches are best explained by ion transportation via fluids, fluid evaporation, and sequential salt deposition as a result of open-system hydrologic behavior. As discussed above, the latest aqueous activity could have occurred during the Late Amazonian epoch.

3.3. The history of water at Gusev

Taken together, the geological and geochemical data collected in the field at Gusev indicate an evolutionary sequence consistent with Viking-based geological mapping (Cabrol et al., 1998; Kuzmin et al., 2004; see Fig. 7). Some of the earliest geologic and paleohydrologic activities recorded in the Gusev impact crater and surroundings include significant widespread flooding and associated ponding in topographic depressions during the Middle Noachian Period, prior to the formation of Ma’adim Vallis. Geochemical conditions during this more ancient period of Mars point to moderately to highly acidic waters, due to the CO$_2$-dominated atmosphere and the steady supply of sulfate and iron to the water accumulations (Fairen et al., 2004). Subsequently, episodic flooding ensued during the Late Noachian and into the Hesperian, resulting in the formation of Ma’adim Vallis, as well as multi-tiered terraces cut into the crater floor and rim materials; water input into the crater included relatively small flows that dissected Hesperian terrain to form a large number of small valley networks. Impact cratering and wind activity dominate the post-flood record.

Minor aqueous activity extended into the Amazonian, followed by wind-related activity prevalent at present-day, which involves mantling and etching of flood-related deposits and landforms. One of the more important processes that may suggest Amazonian acidic waters is acidic alterations on rock surfaces (Hurowitz et al., 2006). The identification of a compositional equivalent of the smectite montmorillonite (Clark et al., 2007) could argue for a higher pH; but as it seems to be an amorphous form of pre- or post-montmorillonite, we favor the interpretation that it indicates smectite formation process not going to completion in the low-pH environment that characterized water occurrences at Gusev.

Traces of water based on data from instruments onboard Spirit point to post-Noachian water events (Gellert et al., 2006), including episodic aqueous fluid movement altering multiple geologic units and resulting in the formation of surficial thin crusts through recent evaporation of brines (Herkenhoff et al., 2006). The redistribution of Cl, S, Br, and oxidized iron may have been mobilized by thin films of liquid water; these mobile phases may penetrate into fractures and cracks in rock surfaces and translocate in soils. A plausible mechanism for such transient liquid water on the surface of Mars and associated thin crusts (Herkenhoff et al., 2006) observed on the top layer of some soils and rocks may include atmosphere/surface interactions, as the atmospheric pressure at Gusev is above the triple-point pressure of water and the melting point of surficial water could be substantially depressed by the high ionic content of the surface layers (Cabrol et al., 2006). This is consistent with Spirit data showing generally enhanced concentrations of S, Mg, Br, Cl, and Fe$^{3+}$/Fe$_{total}$ in the trenched soil materials when compared to the materials observed at the upper soil layer (Haskin et al., 2005), suggesting initial aqueous alteration of volcanic rocks in an acidic environment followed by mostly physical weathering. Elevated and highly variable Br concentrations in stratigraphically young soil materials of Gusev crater argue for episodic brine deposition and evaporation (Haskin et al., 2005), even during the Amazonian Period, with the water and soil interactions occurring at unknown water/rock ratios. Alternatively, water may have been recently present in Gusev as hydrothermal and fumarolic condensates, ultimately forming the unconsolidated and near-surface soils exposed by the actions of the rover wheels (Yen et al., 2008).

The minimum exposure time of surface rocks to acidic liquid water in Gusev is 22 ky (Hausbrath et al., 2008), likely due to episodic aqueous alteration; but the age of the rocks and the total time they have been placed at their current locations is still unknown, so it is possible that some of these alteration episodes took place recently. The coating, which characterizes most rock surfaces explored by Spirit, may have been produced by varying amounts of water, though only small quantities of transient daily to seasonal acidic liquid water are necessary to explain the above mentioned geochemical signatures. Consequently, the long-term net change of the surface at Gusev at global scales has been very small (Golombek et al., 2006).

Fig. 7. Stratigraphic diagram showing the ages of five different geologic units in the Ma’adim/Gusev complex hydrologic system. Duration of the Amazonian time is well in accordance with all published Martian cratering geochronologies. After Cabrol et al. (1998).
Much of the exposed Martian rock surfaces generally consist of volcanic materials, over which chemically different waters have weathered the late-stage basaltic surfaces through time. Aside from the Meridiani plains, hydrated sulfates have been detected in extensive dune fields in the north polar regions, as well as within Valles Marineris and in Aram Chaos (Gendrin et al., 2005). This suggests that in these places acidic and oxidizing waters, provided by volcanogenic SO$_3$ and HCl and atmospheric CO$_2$ and H$_2$O, have reacted with the mafic-ultramafic surface, dissolving rocks and producing hydrated sulfates and iron oxides, while no carbonates are evident as a result of the acidity of the early water masses (Fairen et al., 2004). In fact, Meridiani-like ground water systems seem to have been widespread and representative of an extensive acid-sulfate aqueous system (Bibring et al., 2007). Also, the discovery of phyllosilicates (Poulet et al., 2005) indicates the interaction of slightly acidic to neutral liquid water with igneous minerals over geological timescales (Chevrier et al., 2007).

After an active loss of atmosphere (Melosh and Vickery, 1989; Brain and Jakosky, 1998; Lundin et al., 2004) and surface water (Clifford and Parker, 2001; Lammer et al., 2003) that occurred during the latter part of the wetter Noachian Period, the solutions became more and more evapoorconcentrated. In a later stage, a highly saline cryolithosphere derived from the disappearance of the ionic supersaturated hydrosphere, especially in the northern lowlands and in the bottom of crater lakes and depressions. Particularly, Hesperian and Amazonian plains-forming units (e.g., Tanaka et al., 2005) cover the Noachian basement of the Martian northern lowlands (Frey et al., 2002) with relatively recent secondary and water-related minerals, indicating extensive sediment deposition occurring well into the Amazonian era. Conditions on Mars must have also been wetter than today during transient episodes into geologically very recent times (Fairen et al., 2003), when minor amounts of water are likely to have covered and infiltrated individual rocks and unconsolidated rock materials, as well as ponded to form puddles within closed depressions at sub-meter scale. Some thermokarst processes, including the episodic loss of ponded water by evaporation or drainage, are noted even for the Late Amazonian (Soare et al., 2008). Also described are quite young dry lake beds and sediments, displaying features such as deltas, shorelines and terraces, which require the action of liquid water over extended periods of time (Cabrol and Grin, 2001). Diminished liquid accumulations during the Amazonian Period occurred over terrains cemented with different salts, sulfur, and iron, thereby increasing the density and acidity of the water solutions, and making the global Martian hydrologic system persisting into the Late Amazonian as a heterogeneous and chemically evolving one, with enhanced acidity through time. Thus, the Amazonian Period can be viewed as persistently cold and dry, recording small impact events and pervasive wind activity, with probable continued slow digestion of basaltic rock/regolith and silicate rocks by supercold brine films and low-pH ponds that are episodically liquid. Gas/solid reactions cannot be assumed as the sole alteration process in the Amazonian.

The above scenario for the Amazonian Period is supported by gamma ray spectrometer (GRS) and neutron spectrometer investigations showing the presence of water in equatorial regions of Mars (Boynton et al., 2002; Jakosky et al., 2005), eventually related to some hydrated sulfates (Feldman et al., 2004). In addition, the GRS identified a large anomaly in chlorine in Gusev crater, about 2–3 times the average value (Keller et al., 2006; Boynton et al., 2007; Newsom et al., 2007), which validates our hypothesis about recent brine activity in this region, since further eolian and other physical alteration would have definitively remixed the fragile sediments into the planetary homogeneous soil. GRS has also shown variations of potassium relative to thorium (Taylor et al., 2006), typical indicators of water transfer and weathering. Also the CRISM instrument onboard the Mars Reconnaissance Orbiter has revealed the presence of H$_2$O- and SiOH-bearing phases and hydrated Fe-sulfates, including jarosite, on late Hesperian to Amazonian deposits on and surrounding Valles Marineris (Milliken et al., 2008), implying extensive recent water alteration on the surface of Mars.

SNC meteorite information is also consistent with liquid water on Mars during the Amazonian: Baker et al. (2000) conclude that meteorite-sourcing Martian rocks were intermittently exposed to water, Swindle et al. (2000) argue that the Lafayette meteorite was weathered by liquid water during the past 650 million years, Borr and Drake (2005) suggest episodic flooding at the surface during almost the entire geological history of Mars, and Rao et al. (2008) found that Cl-rich fluids seem to have infiltrated into the nakhlite source region ~600 Ma ago, whereas SO$_3$-rich fluids likely percolated into the shergottite source region at ~180 Ma (or less). Taken together, these studies on meteorites provide evidence of subsurface water at very low water/rock ratios during the Amazonian period. About the surface, Haberle et al. (2001) provide a detailed examination of where and for how long liquid water may be present in contemporary times, highlighting that the regions where liquid water may remain stable for periods up to 70 Martian days cover nearly a third of the planet's surface area. This correlates remarkably well with reported Amazonian paleolakes (Scott et al., 1995; Cabrol and Grin, 2001), and include Elysium (the region that straddles the rise to near Gusev) and the plains of Arabia Terra (which includes Meridiani).

Realizing that atmospheric changes may have been regional and even global, brine evolution and subsequent evaporite assemblages in different Martian locations (i.e., Meridiani and Gusev) would have been somewhat different due to varying rock/sol composition and other local distinctions buffering water to different pH levels. Minor amounts of recent (Amazonian) liquid acidic water, transiently weathering the sulfate-rich materials in Meridiani, would have contributed to the formation of jarosite outcrops detected by Opportunity. Similarly, minor amounts of acidic water (from precipitation, condensation, or melting of ground ice; e.g., Haskin et al., 2005) on the mostly basaltic Gusev crater surface may have produced the sulfate coating of rocks and soil materials as highlighted by Spirit.

The fact that some of these geochemical signatures (jarosite on Meridiani and sulfates on Gusev, see Squyres et al., 2004b; Stockstill et al., 2005, respectively) and varying surface compositions down to the meter scale, have gone undetected in the orbital datasets because of the small scale of the occurrences and obscuration by mantling with soil and dust, and the fact that landers cannot offer a broad geomorphological perspective, both reinforce the importance of a multi-tiered reconnaissance mission architecture for future science-driven and distributed planetary surface and subsurface exploration, which includes simultaneous orbital, airborne, in situ (surface/subsurface) and sample return investigations (Fink et al., 2005). Sample return will contribute to a first approximation of real age dates for surface features or alteration, the current lack of which leads to speculation about potential ages of modification events, with error bars of a billion years or more.

5. Conclusions

The scenario of Amazonian water alterations proposed in this paper has profound implications for the ongoing debate about the age of the water-related geology at Meridiani (Squyres et al.,
2004a,b; Christensen et al., 2004) and Gusev (Haskin et al., 2005). We have argued that both the presence of jarosite deposits in Meridiani Planum and the acid alterations on rock surfaces in Gusev crater are better explained by the combination of early (Noachian–Hesperian) aqueous alteration and later (Amazonian) episodic occurrence of small quantities of liquid water on the surface of Mars, rather than by early diagenesis only. Therefore, we suggest that part of the mineralogical history of Meridiani and Gusev, as derived from data provided by the MER rovers, reflects recent supercold episodes of local acidic brines, likely extending into the Amazonian period. As episodic aqueous processes also occurred several billions of years ago at Meridiani (Fairen et al., 2004; Squyres et al., 2004a,b) and Gusev (Cabrol et al., 1998; Haskin et al., 2005), diverse amounts of acidic shallow surface water may have been recurrently present in Meridiani, Gusev, and other Martian locations during a major part of the history of Mars.

Acknowledgements

The work of A. G. F. and A. F. D. has been supported by NPP-OARU. Valuable comments and suggestions were provided by V. Chevrier and one anonymous reviewer.

References


