Title

Poor preservation potential of organics in Meridiani Planum hematite-bearing sedimentary rocks

Journal

Journal of Geophysical Research-Planets, 109(E12)

ISSN

0148-0227

Author

Sumner, Dawn Y.

Publication Date

2004-12-01

DOI

10.1029/2004JE002321

Peer reviewed

Poor Preservation Potential of Organics in Meridiani Planum Hematite-Bearing Sedimentary Rocks

Dawn Y. Sumner
Geology Department, University of California, Davis, CA 95616, sumner@geology.ucdavis.edu

Citation: Sumner, D. Y. (2004), Poor preservation potential of organics in Meridiani Planum hematite-bearing sedimentary rocks, J. Geophys. Res., 109, E12007, doi:10.1029/2004JE002321.

Abstract

Life is composed of organic compounds, and characterizing preserved compounds provides insights into the presence of specific types of life, including early life on Earth. With growing evidence for a wet early Mars, excitement over the potential of an early Martian biosphere strongly motivates Mars exploration. However, the preservation potential of organic compounds in rocks on either Earth or Mars depends critically on mineralogy. Results from elemental, mineralogical, and morphological characterization of sedimentary rocks by the Opportunity rover team in the vicinity of the Challenger Memorial Station, Meridiani Planum, demonstrate an abundance of Fe(III) and sulfate minerals that formed from liquid water. The composition of these sedimentary rocks suggests that organic compounds are unlikely to be preserved within them, even if present when the rocks were deposited, based on comparisons with iron-formation, acid lake deposits, and iron-containing concretions from Earth. No evidence consistent with the presence of organic compounds, such as the presence of Fe(II) minerals, has been reported from Meridiani Planum to date. Thus, these Martian sedimentary rocks are not a good target to explore for organic compounds on Mars.

1. Introduction

The identification and characterization of organic compounds is one of the most popular approaches to looking for evidence of fossil life. Although abiotic synthesis of organics occurs [see *Simoneit*, 2004, and references therein], many compounds reflect specific biological processes. These "biomarkers" can be preserved for billions of years under the right circumstances, and they provide very important insights into the early evolution of life on Earth [e.g. *Brocks et al.*, 1999; *Summons et al.*, 1999; *Brocks et al.*, 2003]. If life was once present on Mars, biomarkers may still be present. Even if Martian life was never present, organic matter might still exist on Mars due to inputs of meteoritic organic compounds that may be preserved [e.g. *Benner*, 2000], although these would not be biomarkers. The discovery and characterization of the distribution and composition of any organic compounds on Mars would provide valuable insights into either abiotic organic reactions or the evolution of life on a second planet.

Evidence for persistent water flow on the surface of Mars has increased substantially due to high resolution imaging [e.g. *Malin and Edgett,* 2003; *Newsom et al.*, 2003; *Williams and Malin*, 2004], observations of neutron flux patterns [*Boynton et al.*, 2002; *Feldman et al.,* 2002; *Mitrofanov et al.*, 2002; *Tokar et al.*, 2002; *Prettyman et al.*, 2004], and the discovery of abundant evaporites in the area of the Challenger Memorial Station, Meridiani Planum [*Arvidson et al.*, 2004; *Brueckner*, 2004; *Johnson*, 2004; *Morris et al.*, 2004; *Squyres and the Athena Science Team*, 2004; see http://marsrovers.nasa.gov/home]. The high bromine, chlorine, and sulfur concentrations in the sedimentary rocks, as measured by instruments on the rover Opportunity, suggest extensive aqueous weathering, a substantial volume of liquid water, and sustained water flows across the surface of early Mars [see http://marsrovers.nasa.gov/home]. Geochemical results, coupled to strong morphological evidence for flowing water, demonstrate that water played an important role in shaping the surface of early Mars. Aqueously influenced rocks, particularly when associated with mineral precipitation, are excellent sites to look for evidence of possible life on Mars, and they are a specific target of exploration as articulated in the Mars Exploration Program goal to "Determine if Life Ever Arose on Mars" [*MEPAG*, 2004]. Thus, identification of sedimentary rocks composed at least in part of evaporite minerals is a substantial advance along the path towards determining if life ever arose on Mars. Mission plans to continue the search for evidence of life need to use the wealth of data provided by Opportunity. Specifically, we can use this data to predict characteristics of the rocks that we can not measure directly. These predictions should guide the design of future missions to this or similar sites to maximize scientific returns. Characterizing the preservation potential of organic compounds provides predictions of particular interest due to the importance of organics as potential biomarkers.

Complex organic compounds are unstable or metastable in most natural surface environments on Earth and Mars. Their abiotic synthesis requires complex catalytic processes under very specific conditions in which the compounds are rarely stable [e.g. *McCollom and Seewald*, 2003; *Simoneit*, 2004, and references therein]. Primary production of organics by biology represents a sophisticated use of thermodynamically favorable reactions to produce compounds that are inherently unstable in the larger environment. Photosynthetic oxidation of water is the prime example; it uses the energy in light to reduce carbon and oxidize water. The resulting organics and O_2 would back react to form water and CO_2 if allowed to remain in contact. The rest of the biosphere, with the exception of some very important chemoautotrophic processes, uses the reduced carbon as an energy source either by reacting it with more oxidized compounds or by breaking C-C bonds through fermentation. The thermodynamic instability of the vast majority of organic compounds makes these reactions energetically useful [see *Nealson*, 1997]. This instability also makes organics difficult to preserve; decay continues even in the absence of microbial processes as long as oxidants remain present. Thus, the preservation of organics in the rock record of Earth is sparse compared to the volumes of organic carbon buried with the original sediments.

Fortunately, there are specific rock types that lend themselves to better preservation of organics by limiting redox equilibration. Shales are excellent at preserving organics due to their low permeability; the ability of many clay minerals to bind organics, preventing their decay; and the buffering of interstitial water redox conditions to very reducing by the organics [e.g. *Kennedy et al.*, 2002; *Schultz,* 2004]. Chert (amorphous SiO_2 that recrystallizes to fine-grained quartz) is also excellent due to its low permeability and very low reactivity; most well preserved microfossils on Earth are found in chert that formed penecontemporaneously with death of the precursor organism [e.g. *Knoll*, 1992; *Bartley*, 1996; *House et al.*, 2002]. If post-depositional fluids flowing through sedimentary rocks are sufficiently reducing, organics can be preserved, due to the lack of reactivity between organics and reduced ions in water [e.g. *Spangenberg et al.*, 1999]. In contrast, organics are rarely preserved in sedimentary rocks composed of highly oxidized minerals or ones that have had oxidized fluids flow through them.

The mineralogy of the Challenger Memorial Station area, specifically the abundance of Fe(III) minerals and apparent lack of Fe(II) minerals, does not support expectations that organic compounds deposited with the original sediments would be well preserved. This paper places the mineralogy of these sediments into the context of the thermodynamics of organic compound preservation and similar sedimentary rocks on Earth. Geochemical considerations suggest that organic compounds have a poor preservation potential in hematite-bearing sedimentary rocks, such as those characterized by the Opportunity rover science team.

2. Meridiani Planum Unit P2 Geology

The Meridiani Planum sedimentary rocks studied by Opportunity are part of a >600 m thick sedimentary sequence deposited about 4 billion years ago and exhumed about 10 million years ago [*Hartmann et al.*, 2001; *Hynek et al.*, 2002; *Lane et al.,* 2003]. The hematite-rich unit is regional [*Christensen et al*., 2001] and forms layer P2 as mapped by Hynek et al. [2002]. Unit P2 was buried by at least the 200 m thickness of the overlying unit. Minerals identified within the evaporitic sedimentary rocks in the Challenger Memorial Station area include hematite (Fe_2O_3), jarosite ($KFe_3(SO_4)_2(OH)_6$), magnesium and calcium sulfates, chlorides, and bromides based on spectroscopic signatures and modal mineral calculations from *in situ* elemental analyses [*Arvidson et al.*, 2004; *Brueckner*, 2004; *Johnson*, 2004; *Morris et al.*, 2004; *Squyres et al.*, 2004; see http://marsrovers.nasa.gov/home]. Chlorides and bromides do not play a significant role in oxidation-reduction reactions with organic compounds because their components are present in a single oxidation state under reasonable Martian surface conditions. Thus, they will not be considered here beyond demonstrating that evaporation led to high ionic strength fluids. Sulfates are very important to organic geochemistry, and particularly to microbial reduction of aqueous SO_4^{2-} coupled to the oxidation of organic compounds [e.g., *Nealson*, 1997]. However, the specific mineralogy of the magnesium and calcium sulfates is not critical to first-order evaluations of organic preservation; rather the behavior of SO_4^{2-} in solution will be considered. The presence of small amounts of jarosite provides the constraint that acidic waters, probably pH<6, either deposited the sediments or flowed through them at a later date [Figure 1; *Baron and Palmer*, 1996]. This pH constraint is very important because neither carbonates nor magnetite are stable under acidic conditions [Figure 1], making it very unlikely that either will be found in association with jarosite; neither carbonates nor magnetite have been reported to date [see http://marsrovers.nasa.gov/home]. Additional minerals, probably silicates, are required by elemental analyses to account for observed Si, Al, Ti, and other metal concentrations [see http://marsrovers.nasa.gov/home]. However, the lack of instrumentation capable of unambiguously identifying minerals lacking iron results in an inability to identify these silicates or other potential minerals of interest.

3. Oxidation of Organics

Thermodynamically, almost all organic compounds should react with SO_4^{2-} and Fe^{3+} in solution to form simpler compounds or CO_2 and more reducing forms of sulfur, such as H_2S, HS^-, S^0, SO_3^{2-}, or $S_2O_3^{2-}$, and Fe^{2+} [Figure 1; *Stumm and Morgan,* 1996]. However, reaction rates can limit the extent to which thermodynamic equilibration is reached in sedimentary rocks. The kinetics of abiotic SO_4^{2-} reduction are extremely slow at temperatures <200°C [*Ohmoto* and *Lasaga*, 1982 and references therein; *Zolotov* and *Shock*, 2002], in part because reduction of $S(VI)O_4^{2-}$ to $H_2S(-II)$ requires the transfer of 8 electrons. As a general rule, only one electron is transferred at a time during redox reactions, making the stability of intermediate species a critical control on reduction rate [e.g. *Stumm* and *Morgan*, 1996; *Nordstrom*, 2000]. Ohmoto and Lasaga [1982] calculated isotopic equilibration times between SO_4^{2-} and H_2S as on the order of 1-10 billion years at pH 4-7, although the time for equilibration decreases to only ~5,000 years at pH 2. Their analysis of experimental rate constants for abiotic SO_4^{2-} reduction to H_2S suggests that roughly similar lengths of time are necessary for significant abiotic SO_4^{2-} reduction [*Ohmoto and Lasaga*, 1982]. Thus, reaction between sulfates and organic compounds are possible over geological time scales at very low pH [Figure 1], but are otherwise not likely to lead to the decay of organics in the absence of a biological sulfate reduction metabolism.

In contrast, the reduction of Fe(III) to Fe(II) requires the transfer of only a single electron and is strongly coupled to the oxidation of organic carbon in sediments both due to microbial activity and abiotic reactions [e.g., *LaKind* and *Stone*, 1989; *Stumm* and *Morgan*, 1996; *Lovley et al.*, 1991; *Benner et al.*, 2000]. The reactivity of various compounds depends on their structure and oxidation state [e.g., *Stumm* and *Morgan*, 1996; *Lovley et al.*, 1991]. However, oxidized carbon in the form of CO_2 is the only thermodynamically stable phase at low pH with an electron potential above 0; Fe(III)-bearing minerals are not stable at the low electron potentials necessary for organic carbon stability [Figure 1; *Stumm* and *Morgan*, 1996]. The kinetics of organic carbon oxidation in the presence of iron are also rapid, in large part due to the generation of free radicals and H_2O_2 on the surface of iron-containing minerals [e.g., *Fubini et al.*, 1995; *Stumm* and *Morgan*, 1996; *Benner et al.*, 2000; *Borda et al.*, 2003]. Hydrogen peroxide can also be produced by O_2 reduction and photochemical reactions in the atmosphere and surface waters [e.g., *Stumm* and *Morgan*, 1996]. Organics are commonly abiotically oxidized by free radicals in solution, particularly $^{\bullet}OH$, and the presence of iron in solution catalyzes the production of $^{\bullet}OH$ from H_2O_2 via the well known Fenton reaction [e.g. *Stumm* and *Morgan*, 1996; *Perez-Benito*, 2004]. The production of H_2O_2, $^{\bullet}OH$, and other free radicals is critical to Martian organics preservation. Benner et al. [2000] calculated oxidation rates for meteoritic carbon delivered to the Martian surface assuming production of $^{\bullet}HO$ and H_2O_2 via UV dissociation of H_2O on a dry surface. They concluded that alkanes, alkylbenzenes, naphthalene and larger polycyclic aromatic hydrocarbons, kerogen, and amino acids and hydroxyacids decay to produce carboxylic acids, which could be preserved and detectable in the Martian regolith once it was relatively dry [*Benner et al.*, 2000]. However, in the presence of water and iron, degradation of organics is accelerated by the iron-catalyzed production of $^{\bullet}HO$, which oxidizes the carbon skeleton of otherwise metastable organic compounds [*Benner et al.*, 2000]. Although depositional and diagenetic conditions for the Meridiani Planum unit P2 sedimentary rocks are poorly constrained, the abundance of evidence for interactions with water in the presence of Fe(III) minerals makes preservation of organic compounds from early Mars unlikely in these rocks.

Evidence of the oxidation of organic compounds can be preserved in minerals if iron or sulfur species were reduced. Iron sulfides, such as pyrite (FeS_2), are extremely common in sedimentary rocks with microbial carbon oxidation [Figure 2]. These minerals require microbial mediation of SO_4^{2-} reduction to overcome kinetic barriers to sulfur reduction in most sedimentary environments on Earth. Other reduced iron phases, such as siderite ($FeCO_3$) or magnetite (Fe_3O_4), are not expected in Meridiani Planum unit P2 rocks, due to the low pH values implied by the presence of jarosite [Figure 1]. Thus, the only mineral signature of carbon oxidation reasonably likely to be present in Meridiani Planum sediments would be iron sulfides, which are kinetically difficult to form without microbial activity. Identification of pyrite via Mössbauer spectroscopy would be a truly exciting find by Opportunity!

4. Fe-S-C Sedimentary Rocks on Earth

Iron and sulfur compounds of diverse oxidation states are found in association with organics in modern sedimentary environments on Earth. These systems are dominated by biological activity, including the biological oxidation and reduction of iron and sulfur species for metabolic purposes. This biological activity results in complex profiles of aqueous species with depth in sediments [e.g. *Nealson*, 1997]. However, progressive burial of these sediments results in the equilibration of the diverse oxidation states with time and progressively elevated temperatures; sediments approach thermodynamic equilibrium during lithification into rocks. The distances over which oxidation states equilibrate over millions to billions of years vary with metamorphic temperature and the extent of water-rock reactions after deposition; distances retaining disequilibrium species range from less than millimeters to kilometers. Disequilibrium between successive sedimentary laminae is promoted by rapid lithification that limits subsequent water flow and restricts reactions between reduced and oxidized phases. Equilibration over very large scales is promoted by substantial water flow through permeable rocks. Chert can maintain small-scale disequilibrium conditions when it contains inclusions of both organic compounds and oxidized iron [e.g., *Kaufman et al.*, 1990; *Tazaki et al.*, 1992; *Allen et al.,* 2001]. In contrast, porous sandstones commonly have a uniform redox chemistry along groundwater flow paths [e.g., *Parry et al.*, 2004]. Thus, permeability and the history of lithification are essential to predicting the oxidative equilibration expected for various sedimentary rocks. Three types of iron-sulfur-carbon sedimentary rocks provide insights into the redox behavior of these elements in sediments: banded iron-formations, acid lake deposits, and hematite concretions.

4.1 Banded Iron-Formation

Latest Archean and Paleoproterozoic banded iron-formations provide a good analog for iron-sulfur-carbon systems with fine-scale disequilibrium sometimes preserved. Most iron-formations consist of combinations of iron oxides, iron silicates, siderite ($FeCO_3$), chert, and organic-rich shales, with rare to common sulfides [Figure 2]. Sulfates usually are absent due to the reducing depositional environments for iron-formation and the presence of sulfate reducing bacteria. A general model of iron-formation deposition includes the precipitation of iron oxyhydroxides due to: 1) oxidation of Fe^{2+} by O_2 [e.g. *Cloud*, 1973]; 2) direct microbial oxidation of Fe^{2+} [e.g. *Konhauser et al.*, 2002; *Kappler and Newman,* 2004]; or 3) UV oxidation of Fe^{2+} in shallow water [e.g. *Anbar and Holland*, 1992]. These oxyhydroxides settle out of suspension into reduced depositional environments, typically quite deep [e.g. *Beukes*, 1984; *Simonson and Hassler*, 1996] along with suspended clay minerals and organic compounds produced by pelagic organisms or by *in situ* growth of microbial communities. Silica gels form at or near the sedimentary surface; these convert to chert with progressive dehydration. Immediately below the surface, organic compounds react with iron oxyhydroxides to form siderite [e.g. *Beukes et al.*, 1990; *Kaufman et al.*, 1990; *Tsikos et al.*, 2003]. Depending on the volume of organics versus iron oxyhydroxides, the resulting sedimentary rock is composed of organic compounds, siderite and chert when the reducing power of organics exceeds the oxidizing power of iron oxyhydroxides, or hematite and chert with trace reduced iron minerals when the oxidizing power of iron oxyhydroxides exceeds the reducing power of organics [Figure 2]. Organic compounds are well known to be sparse in oxide-facies iron-formation [e.g. *Kaufman et al.*, 1990]. In the absence of iron oxyhydroxide accumulation, organics, silica, and clay minerals accumulate, forming cherts and shales that sometimes also contain calcium and magnesium carbonates. The resulting sedimentary rocks consist of bands rich in dominantly oxidized iron minerals, mixed oxidized and reduced iron minerals, predominantly reduced iron minerals with minor organic compounds, or abundant organic compounds in shale. Usually, layers abundant in oxidized iron minerals are not directly interbedded with organic-rich shales [e.g. *Beukes et al.*, 1990; *Kaufman et al.*, 1990].

Some chert in the 1,878±1 Ma Gunflint Iron Formation [*Fralick et al.*, 2002] contains inclusions of both organic compounds and iron oxides [*Tazaki et al.*, 1992; *Allen et al.*, 2001; *Schelble et al.*, 2004]. Iron oxides outline the shapes of filaments and chains of spheres, which are very similar to microfossils preserved as organic inclusions in chert [e.g. *Awramik and Barghoorn*, 1977]. These iron oxide microfossils are associated with traces of carbon with C-C bonds implying the presence of organic carbon rather than carbonate minerals [*Tazaki et al.*, 1992]. When Tazaki et al., [1992] extracted carbonaceous microfossils from the chert, they found an electron diffraction pattern characteristic of graphite, which may be the phase containing the C-C bonds. The association of carbon with iron oxides, as measured qualitatively by EDX on an SEM [*Allen et al.*, 2001; *Schelble et al.*, 2004], raises the possibility that neutral carbon may be preserved in association with iron oxides. The early chert precipitation in the Gunflint Iron Formation [e.g. *Winter and Knauth*, 1992], may have limited redox equilibration by limiting diagenetic fluid flow and slowing the kinetics of carbon-iron redox reactions. Additional investigation of these relationships and careful analyses of other iron-formations may provide very important insights into preservation of organics in the presence of iron oxides; co-preservation may occur under circumstances that have yet to be characterized.

4.2 Acid Lake Deposits

Acid lake deposits also provide a good analog for Meridiani Planum unit P2 sedimentary rocks [e.g. *Benison and LaClair*, 2003], although few have been recognized in the rock record on Earth. One excellent example is mid-Permian acid lake deposits of the Nippewalla Group, Kansas, USA [*Benison et al.*, 1998; *Benison and Goldstein*, 2001]. They contain siliciclastic sediments of various grain size interbedded with evaporites, including anhydrite ($CaSO_4$) and halite (NaCl). Hematite is present as coatings on sand grains in fully oxidized facies. In contrast, organic matter is associated with grey mudstone laminae in non-evaporitic facies; the grey color indicates generally reducing conditions within the laminae. In oxidized red sedimentary rocks, grey reduction spots formed around organic fragments [*Benison and Goldstein*, 2001]. These color relationships suggest an inverse correlation between organic preservation and sedimentary rocks containing oxidized iron; in overall oxidized sedimentary rocks, reduced zones are associated with decay of deposited organic compounds. Detailed mineralogical and geochemical studies of these Permian lake deposits are likely to shed important insights into interpretations of Meridiani Planum unit P2 sedimentary rocks and interactions among iron, sulfur, and carbon in an acid environment. Reported results to date indicate that organics are correlated with an absence of hematite.

4.3 Hematite Concretions

Iron mineral concretions make up a third comparison rock type for Meridiani Planum unit P2 sedimentary rocks, specifically for the spherical concretions containing abundant hematite called “blueberries” [e.g. *Chan et al.*, 2004; *Catling*, 2004]. Many iron concretions found in sedimentary rocks on Earth nucleated around fragments of organic matter, and geochemical gradients produced during (microbial) degradation of organics led to concretion growth [e.g. *Coleman and Raiswell,* 1993]. Iron-containing concretions associated with organic compounds contain almost exclusively reduced iron minerals such as siderite and pyrite [e.g. *Coleman and Raiswell*, 1993; *Duan et al.*, 1996; *Schieber*, 2002]. Hematite concretions, such as those in the Jurassic Navajo Sandstone, U.S., formed either around *oxidized* nuclei or as a self organizational process during mixing of oxidizing and reducing fluids [*Chan et al.*, 2000; *Chan et al.*, 2004]. They are associated with neither organic remains nor reduced iron minerals. Rather, they reflect oscillating oxidation conditions: deposited sand grains had hematite coatings; the flow of a reducing, probably hydrocarbon-rich, fluid through sandstones reduced that hematite, providing a source of iron; and the reduced water mixed with oxidized ground water to form the concretions [*Chan et al.*, 2000; *Beitler et al.*, 2003; *Chan et al.*, 2004; *Parry et al.*, 2004].

5. P2 Sedimentary Rocks and Preservation of Organic Compounds

Meridiani Planum unit P2 sedimentary rocks have interacted with water extensively. Aqueous deposition of the sediments, formation of evaporite casts, and the growth of hematite concretions demonstrate that multiple stages of water-rock interactions are likely in their >3 billion year history [Figure 3]. Water-rock interactions during evaporation and subsequent diagenesis would have allowed at least partial redox equilibration among minerals, aqueous solutions, and any organics present. Thus, ancient sedimentary rocks on Earth that experienced similar water-rock interactions form a better analog for P2 rocks than modern sediments or significantly less permeable rocks from Earth. Specifically, approaches in the search for organic compounds in the rocks composing Meridiani Planum unit P2 need to be modeled after expected preservation of organics in rocks of appropriate compositions, rather than on modern sediments with similar dominant mineralogy.

The most significant problem with preservation of organic compounds in sedimentary rocks observed by Opportunity is the instability of most organics in the presence of Fe(III), as discussed above. Abundant Fe(III) indicates that even if organic compounds were deposited with the sediment, they are likely to have been oxidized soon after deposition, during lithification, or as a result of subsequent diagenesis. The presence of the hematite concretions demonstrates that iron was mobilized by acid or reducing waters and a subsequent pH increase or mixing with oxidizing fluids resulted in hematite precipitation. During this stage, any organics probably oxidized producing Fe(II). No reduced iron minerals have been identified in these sedimentary rocks to date. Thus, if any organics were present, they were not abundant enough to produce reduced iron minerals at the detection limit of the Mössbauer spectrometer or reduced iron minerals were reoxidized during subsequent diagenesis. In either case, organic compounds deposited with the sediments are unlikely to be preserved in the hematite-rich region of Meridiani Planum.

Although very unlikely, it is possible that some early Mars organic compounds or their decay products may be present. The full mineralogy of sedimentary rocks observed by Opportunity is unknown, and small concentrations of non-reactive minerals may shelter organic inclusions from degradation. For example, minor chert may encase organic matter, such as that found in the Gunflint Iron Formation. Unfortunately, the very small excesses of silica in some elemental analyses does not suggest significant concentrations of chert [data from http://marsrovers.nasa.gov/home]. Alternatively, magnesium or calcium sulfates may host metastable organics as inclusions if they did not recrystallize during oxidizing fluid flow. Rigorous studies of organic preservation in analog rocks from Earth are essential to evaluating the sparse preservation potential of organics in Meridiani Planum unit P2 sedimentary rocks. On Earth, if organics are not present in ancient sedimentary rocks, it is an indication that they were not preserved; on Mars, if organics are absent, we can not yet tell if they were not present or just not preserved.

6. Implications for Mars Exploration

Exploring for complex organic compounds with an *in situ* mission to Meridiani Planum unit P2 sedimentary rocks is not likely to produce positive results given the absence of mineralogical evidence for good organic preservation and the abundance of evidence for minerals inimical to long-term preservation. At best, organics will be difficult to find and, if not found, their absence can be attributed to the low preservation potential of the host rocks. Results will not allow us to distinguish between an initial absence of organics and an absence due to poor preservation. Thus, *in situ* organic compound characterization of these rocks is unlikely to contribute to the goal to “Determine if Life Ever Arose on Mars.” Sample return of sedimentary rocks from this unit, on the other hand, is more likely to produce useful results, because analytical approaches can respond to initial observations. The choice of the types of organic analyses one intends to do does not have to be made prior to the detection of organic compounds. Sample return would allow characterization of the full range of oxidation states present, detailed studies of the relationships between phases, and use of advanced carbon characterization tools that can not be flown on missions.

Better targets for the *in situ* search for ancient organic compounds on Mars include clay-rich deposits, due to the ability of many clay minerals to sequester organics inhibiting their decay, and carbonates and cherts which are less reactive with respect to organic carbon. Hopefully, clay, carbonate, or chert deposits will be identified and can be targeted in the search for organics on Mars with the new analytical capabilities of instruments on Mars Express, particularly the OMEGA Visible and Infrared Mineralogical Mapping Spectrometer [see http://www.esa.int/SPECIALS/Mars_Express] and on the Mars Reconnaissance Orbiter, particularly the Compact Reconnaissance Imaging Spectrometer for Mars [http://mars.jpl.nasa.gov/mro].

Acknowledgements

I would like to thank B. Jakosky for prompting me to write this paper, and D. DesMarais for helpful comments on the manuscript. The ideas presented here are assembled from decades of research by many excellent scientists working in diverse fields; I deeply appreciate the availability of this wealth of data. Finally, the Mars Exploration Rover teams have worked for years to make this mission a tremendous success; thank you!

References

Allen, C.C., F.W. Westall, and R.T. Schelble (2001), Importance of a Martian hematite site for astrobiology, *Astrobiology, 1(1),* 111-123.

Anbar, A.D., and H.D. Holland (1992), The photochemistry of manganese and the origin of banded iron formations, *Geochimica et Cosmochimica Acta, 56(7)*, 2595-2603.

Arvidson, R.E. and the Athena Science Team (2004), Geology of Meridiani Planum as inferred from Mars Exploration Rover observations, Lunar Planet. Sci. Conf. XXXV Abstr. 2161, http://www.lpi.usra.edu/

Awramik, S.M., and E.S. Barghoorn, E.S. (1977) The Gunflint microbiota, *Precambrian Res. 5*, 121–442.

Baron, D. and C.D. Palmer (1996), Stability of jarosite at 4-35°C, *Geochimica et Cosmochimica Acta*, *60*, 185-195.

Bartley, J.K. (1996), Actualistic taphonomy of cyanobacteria: Implications for the Precambrian fossil record, *Palaios, 11(6),* 571-586.

Beitler, B., and M.A. Chan, and W.T. Parry (2003), Bleaching of Jurassic Navajo Sandstone on Colorado Plateau Laramide highs: Evidence of exhumed hydrocarbon supergiants? *Geology, 31(12),* 1041-1044.

Benison, K.C., and R.H. Goldstein (2001), Evaporites and siliciclastics of the Permian Nippewalla Group of Kansas, USA: A case for non-marine deposition in saline lakes and saline pans, *Sedimentology, 48*, 165-188.

Benison, K.C., and D.A. LaClair (2003), Modern and ancient extremely acid saline deposits: Terrestrial analogs for Martian environments? *Astrobiology, 3(3)*, 609-618.

Benison, K.C., R.H. Goldstein, B. Wopenka, R.C. Burruss, and J.D. Pasteris (1998), Extremely acid Permian lakes and ground waters in North America, *Nature, 392(),* 911-914.

Benner, S.A., K.G. Devine, L.N. Matveeva, and D.H. Powell (2000), The missing organic molecules on Mars, *Proceedings of the National Academy of Science, 97(6)*, 2425-2430.

Beukes, N.J, (1984), Sedimentology of the Kuruman and Griquatown iron-formations, Transvaal Supergroup, Griqualand West, South Africa, *Precambrian Research, 24(1)*, 47-84.

Beukes, N.J., C. Klein, A.J. Kaufman, and J.M. Hayes (1990), Carbonate petrography, kerogen distribution, and carbon and oxygen isotope variations in an Early Proterozoic transition from limestone to iron-formation deposition, Transvaal Supergroup, South Africa, *Economic Geology, 85(4)*, 663-690.

Borda, M.J., A.R. Elsetinow, D.R. Strongin, and M.A. Schoonen (2003), A mechanism for the production of hydroxyl radical at surface defect sites on pyrite, *Geochimica et Cosmochimica Acta, 67(5),* 935–939.

Boynton, W.V., W.C. Feldman, S.W. Squyres, T.H. Prettyman, J. Brückner, L.G. Evans, R.C. Reedy, R. Starr, J.R. Arnold, D.M. Drake, P.A.J. Englert, A.E. Metzger, I. Mitrofanov, J.I. Trombka, C. d'Uston, H. Wänke, O. Gasnault, D.K. Hamara, D.M. Janes, R.L. Marcialis, S. Maurice, I. Mikheeva, G.J. Taylor, R. Tokar, and C. Shinohara (2002), Distribution of hydrogen in the near surface of Mars: Evidence for subsurface ice deposits, *Science, 297(5578)*, 81– 85.

Brocks, J.J., G.A. Logan, R. Buick, and R.E. Summons (1999), Archean molecular fossils and the early rise of eukaryotes, *Science, 285*, 1033-1036.

Brocks, J.J., R. Buick, G.A. Logan, and R.E. Summons (2003), Composition and syngeneity of molecular fossils from the 2.78 to 2.45 billion-year-old Mount Bruce Supergroup, Pilbara Craton, Western Australia, *Geochimica et Cosmochimica Acta, 67*, 4289–4319.

Brückner, J. (2004), Determination of chemical composition of soils and rocks at the MER landing sites Gusev crater and Meridiani Planum using the APXS, Eos Trans. AGU, 85(17), Jt. Assem. Suppl., Abstract V11A-05

Catling, D.C., (2004), On Earth, as it is on Mars? *Nature, 429,* 707-708.

Chan, M.A., B. Beitler, W.T. Parry, J. Ormo, and G. Komatsu (2004), A possible terrestrial analogue for haematite concretions on Mars, *Nature, 429,* 731-734.

Chan, M.A., W.T. Parry, and J.R. Bowman (2000), Diagenetic hematite and manganese oxides and fault related fluid flow in Jurassic sandstones, southeastern Utah, *Am. Assoc. Petrol. Geol. Bull.*, *84*,1281–1310.

Christensen, P.R., R.V. Morris, M.D. Lane, J.L. Bandfield, and M.C. Malin (2001), Global mapping of Martian hematite mineral deposits: Remnants of water-driven processes on early Mars, *J. Geophys. Res., 106(E10),* 23,873-23,885.

Cloud, P., (1973), Paleoecological significance of the banded iron-formation, *Econ. Geol., 68*, 1135-1143.

Coleman, M.L., and R. Raiswell (1993), Microbial mineralization of organic matter: Mechanisms of self-organization and inferred rates of precipitation of diagenetic minerals, *Phil. Trans. R. Soc. Lond. A, 344,* 69-87.

Duan, W.M., D.B. Hedrick, K. Pye, M.L. Coleman, and D.C. White (1996), A preliminary study of the geochemical and microbiological characteristics of modern sedimentary concretions, L*imnol. Oceanogr, 41(7),* 1404-1414.

Feldman, W.C., W.V. Boynton, R.L. Tokar, T.H. Prettyman, O. Gasnault, S.W. Squyres, R.C. Elphic, D.J. Lawrence, S.L. Lawson, S. Maurice, G.W. McKinney, K.R. Moore, and R.C. Reedy (2002), Global distribution of neutrons from Mars: Results from Mars Odyssey, *Science, 297(5578)*, 75– 78.

Fralick, P., D.W. Davis, and S.A. Kissin (2002), The age of the Gunflint Formation, Ontario, Canada: single zircon U–Pb age determinations from reworked volcanic ash, *Can. J. Earth Sci., 39*, 1085–1091, DOI: 10.1139/E02-028.

Fubini, B., L. Mollo, and E. Giamello (1995), Free-radical generation at the solid/liquid interface in iron-containing minerals, *Free Radical Research, 23(6),* 593-614.

Hartmann, W.K., J. Anguita, M.A. de la Casa, D.C. Berman and E.V. Ryan (2001), Martian cratering 7: The role of impact gardening, *Icarus, 149*, 37-53.

House, C.H., J.W. Schopf, K.D. McKeegan, C.D. Coath, T.M. Harrison, and K.O. Stetter (2000), Carbon isotopic composition of individual Precambrian microfossils, *Geology, 28(8),* 707-710.

Hynek, B.M., R.E. Arvidson, and R.J. Phillips (2002), Geologic setting and origin of Terra Meridiani hematite deposit on Mars, *J. Geophys. Res., 107(E10)*, doi:10.1029/2002JE001891.

Johnson, J.R. (2004), Mineralogy and geochemistry at the Meridiani Landing Site, Mars, Eos Trans. AGU, 85(17), Jt. Assem. Suppl., Abstract U44A-03

Kappler, A. and D.K. Newman (2004), Formation of Fe(III)-minerals by Fe(II)-oxidizing photoautotrophic bacteria, *Geochimica et Cosmochimica Acta, 68(6)*, 1217–1226, doi:10.1016/j.gca.2003.09.006

Kaufman, A.J., J.M. Hayes, and C. Klein (1990), Primary and diagenetic controls of isotopic compositions of iron-formation carbonates, *Geochimica et Cosmochimica Acta, 54,* 3461-3473.

Kennedy, M.J., D.R. Pevear, and R.J. Hill (2002), Mineral surface control of organic carbon in black shale, *Science, 295(5555)*, 657-660.

Knoll, A.H. (1992), Vendian microfossils in metasedimentary cherts of the Scotia Group, Prins Karls Forland, Svalbard, *Paleontology, 35*, 751-774.

Konhauser, K.O., T. Hamade, R. Raiswell, R.C. Morris, F.G. Ferris, G. Southam and D.E. Canfield (2002), Could bacteria have formed the Precambrian banded iron formations? *Geology, 30 (12)*, 1079-1082.

LaKind, J.S., and A.T. Stone (1989), Reductive dissolution of goethite by phenolic reductants, *Geochimica et Cosmochimica Acta***, 53,** 961-971.

Lane, M.D., P.R. Christensen, W.K. Hartmann, and the THEMIS Science Team (2003), A study of Meridiani Planum, Mars, using THEMIS data, *Sixth International Conference on Mars*, abstract 3122, http://www.lpi.usra.edu/meetings/sixthmars2003/

Lovely, D.R., E.J.P. Phillips, and D.J. Lonergan (1991), Enzymatic versus nonenzymatic mechanisms for Fe(III) reduction in aquatic sediments, *Environmental Science and Technology, 25(6),* 1062-1067.

Malin M.C., and K.S. Edgett (2003), Evidence for persistent flow and aqueous sedimentation on early Mars, *Science, 302(5652)*, 1931-1934.

McCollom, T.M. and J.S. Seewald (2003), Experimental constraints on the hydrothermal reactivity of organic acids and acid anions: I. Formic acid and formate, *Geochimica et Cosmochimica Acta, 67(19)*, 3625–3644, doi:10.1016/S0016-7037(03)00136-4

MEPAG (2004), Scientific Goals, Objectives, Investigations, and Priorities: 2003. Unpublished document, http://mepag.jpl.nasa.gov/reports/index.html.

MER-B Rover Team (2004), Opportunity rover finds strong evidence Meridiani Planum was wet, press release, March 2, 2004, http://origin.mars5.jpl.nasa.gov/gallery/press/opportunity/20040302a.html

Mitrofanov, I., D. Anfimov, A. Kozyrev, M. Litvak, A. Sanin, V. Tret'yakov, A. Krylov, V. Shvetsov, W. Boynton, C. Shinohara, D. Hamara, and R.S. Saunders (2002), Maps of subsurface hydrogen from the high energy neutron detector, Mars Odyssey, *Science, 297(5578)*, 78–81.

Morris, R.V., S. Squyres, R.E. Arvidson, J.F. Bell III, P.C. Christensen, S. Gorevan, K. Herkenhoff, G. Klingelhöfer, R. Rieder, W. Farrand, A. Ghosh, T. Glotch, J.R. Johnson, M. Lemmon, H.Y. McSween, D.W. Ming, C. Schroeder, P. de Souza, M. Wyatt, and the Athena Science Team (2004), A first look at the mineralogy and geochemistry of the MER-B landing site in Meridiani Planum, Lunar Planet. Sci. Conf. XXXV Abstr. 2179, http://www.lpi.usra.edu/

NASA Jet Propulsion Laboratory. Mars Exploration Rover Mission (February-July, 2004), http://origin.mars5.jpl.nasa.gov/home/.

Nealson, K.H. (1997), Sediment bacteria: Who's there, what are they doing, and what's new? *Annu. Rev. Earth Planet. Sci*., *25*, 403–34

Newsom, H.E., C.A. Barber, T.M. Hare, R.T. Schelble, V.A. Sutherland, and W.C. Feldman (2003), Paleolakes and impact basins in southern Arabia Terra, including Meridiani Planum: Implications for the formation of hematite deposits on Mars, *J. Geophys. Res., 108,* E8075 doi: 10.1029/2002JE001993.

Nordstrom, D.K. (2000), Aqueous redox chemistry and the behavior of iron in acid mine waters, *Proceedings of the Workshop on Monitoring Oxidation-Reduction Processes for Ground-water Restoration*, Dallas, Texas, April 25-27, Cincinnati, OH, U.S. Environmental Protection Agency, EPA/600/R-02/002, edited by R.T. Wilkin, R.D. Ludwig, and R.G. Ford, p. 43-47.

Ohmoto, H. and A.C. Lasaga (1982), Kinetics of reactions between aqueous sulfates and sulfides in hydrothermal systems, *Geochimica et Cosmochimica Acta, 46,* 1727- 1745.

Parry, W.T., M.A. Chan, and B. Beitler (2004), Chemical bleaching indicates episodes of fluid flow in deformation bands in sandstone, AAPG Bulletin, *88(2)*, 175-191.

Perez-Benito, J.F. (2004), Iron(III)-hydrogen peroxide reaction: Kinetic evidence of a hydroxyl-mediated chain mechanism, *J. Phys. Chem. A* 2004, *108,* 4853-4858.

Prettyman, T.H., W.C. Feldman, M.T. Mellon, G.W. McKinney, W.V. Boynton, S. Karunatillake, D.J. Lawrence, S. Maurice, A.E. Metzger, J.R. Murphy, S.W. Squyres, R.D. Starr, and R.L. Toka (2004), Composition and structure of the Martian surface at high southern latitudes from neutron spectroscopy, *J. Geophys. Res., 109*, E05001, doi:10.1029/2003JE002139.

Schelble, R.T., F. Westall, and C.C. Allen (2004), ~1.8 Ga iron-mineralized microbiota from the Gunflint Iron Formation, Ontario, Canada: Implications for Mars, *Advances in Space Research, 33,* 1268–1273.

Schieber, J. (2002), The role of an organic slime matrix in the formation of pyritized burrow trails and pyrite concretions, *Palaios, 17,* 104-109.

Schultz, R.B. (2004), Geochemical relationships of Late Paleozoic carbon-rich shales of the Midcontinent, USA: A compendium of results advocating changeable geochemical conditions, *Chemical Geology, 206 (3-4)*, 347-372.

Simoneit, R.B.T. (2004), Prebiotic organic synthesis under hydrothermal conditions: An overview, *Advances in Space Research, 33*, 88-94.

Simonson, B.M., and S.W. Hassler (1996), Was the deposition of large Precambrian iron formations linked to major marine transgressions? *J. Geol, 104(6),* 665-676.

Spangenberg, J.E., L. Fontbote, and S.A. Macko (1999), An evaluation of the inorganic and organic geochemistry of the San Vicente Mississippi Valley-type zinc-lead district, central Peru: Implications for ore fluid composition, mixing processes, and sulfate reduction, *Economic Geology*, *94(7),* 1067-1092.

Squyres, S.W. and the Athena Science Team (2004), Initial results from the MER Athena Science investigation at Gusev Crater and Meridiani Planum, Lunar Planet. Sci. Conf. XXXV Abstr. 2187, http://www.lpi.usra.edu/

Stumm, W. and J.J. Morgan (1996), *Aquatic Chemistry*, 1022 pp., Wiley & Sons, Inc., New York.

Summons, R.E., L.L. Jahnke, J.M. Hope, and G.A. Logan (1999), 2-Methylhopanoids as biomarkers for cyanobacterial oxygenic photosynthesis, *Nature, 400*, 554-557.

Sumner, D.Y. and S.A. Bowring (1996), U-Pb geochronologic constraints on deposition of the Campbellrand Subgroup, Transvaal Supergroup, South Africa, *Precambrian Research, 78*, 25-35.

Tazaki, K., F.G. Ferris, R.G. Wiese, and W.S. Fyfe (1992), Iron and graphite associated with fossil bacteria in chert, *Chem. Geol., 95*, 313-325.

Tokar, R.L., W.C. Feldman, T.H. Prettyman, K.R. Moore, D.J. Lawrence, R.C. Elphic, M.A. Kreslavsky, J.W. Head III, J.F. Mustard, and W.V. Boynton (2002), Ice concentration and distribution near the south pole of Mars: Synthesis of Odyssey and Global Surveyor analyses, *Geophys. Res. Lett., 29*, 1904, doi:10.1029/2002GL015691.

Tsikos, H., J.M. Moore, and C. Harris (2001), Geochemistry of the Palaeoproterozoic Mooidraai Formation: Fe-rich limestone as end member of iron formation deposition, Kalahari Manganese Field, Transvaal Supergroup, South Africa, *J. African Earth Sciences, 32(1),* 19-27.

Williams, R.M.E., and M.C. Malin (2004), Evidence for late stage fluvial activity in Kasei Valles, Mars, *J. Geophys. Res., 109*, E06001, doi:10.1029/2003JE002178.

Winter, B.L. and L.P. Knauth (1992), Stable isotope geochemistry of cherts and carbonates from the 2.0 Ga Gunflint Iron Formation: Implications for the depositional setting, and the effects of diagenesis and metamorphism, *Precambrian Research,* 59 283-313.

Zolotov M.Y., and E.L. Shock (2003), Energy for biologic sulfate reduction in a hydrothermally formed ocean on Europa, *J. Geophys. Res., 108(E4)*, 5022, doi:10.1029/2002JE001966.

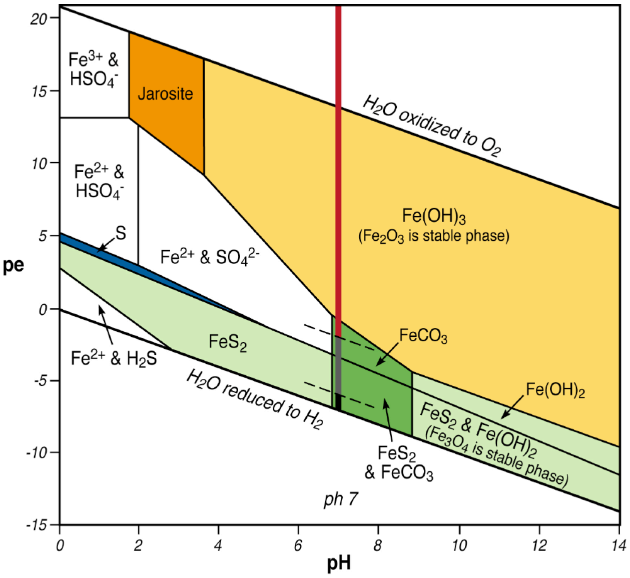

Figure 1. Fe-S-C geochemistry. Various aqueous species and minerals are stable at different pH and pe values. (pe is defined as log$_{10}$(activity$_{e-}$) and is a measure of the potential for electron transfer. Low pe values promote reduction and are dominated by reduced chemical forms, whereas high pe values promote oxidation and are dominated by oxidized chemical forms.) Hematite (Fe$_2$O$_3$) is the stable iron oxide for most oxidizing conditions, but is more soluble at lower pH. Pyrite (FS$_2$) is stable at low pe across all pH values. Magnetite (F$_3$O$_4$) and siderite (FeCO$_3$) are stable at high pH and low pe. Siderite also requires a substantial carbonate ion activity to form and remain stable; under some conditions, it decomposes into magnetite and carbon dioxide or graphite. Various hydrated iron oxides form from water, rather than the thermodynamically stable hematite and magnetite. They are metastable and convert to hematite and magnetite with time and higher temperatures. Jarosite (KFe$_3$(SO$_4$)$_2$(OH)$_6$) is metastable at high pe and low pH values and can decompose into hematite. Few minerals are stable at pe's between jarosite and pyrite under the conditions calculated here. The black vertical line at pH=7 and low pe represents conditions under which many organics are stable; the grey line indicates a zone of stability for some organics such as carboxylic acids; and the red line marks areas where organic carbon compounds are not stable [*Stumm and Morgan*, 1996]. Note that in the presence of hematite and jarosite, organics are not thermodynamically stable.

This diagram was calculated for a dilute solution with total dissolved inorganic carbon 10^{-3} M, aqueous iron species with activities of 10^{-4} M, aqueous sulfur species with activities of 10^{-3} M, and potassium activity of 10^{-10} M. The abundance of evaporite minerals in Meridiani Planum unit P2 sedimentary rocks demonstrates that the relevant solutions had a high ionic strength. Mineral stability fields vary substantially with ion pairing in solution, which depends critically on brine compositions. Thus, mineral stability fields should be regarded as guidelines for expected conditions until a much more complete compositional and mineralogical analysis is available. For example, one can compare this diagram to Catling's [2004] example of mineral stability for slightly different conditions.

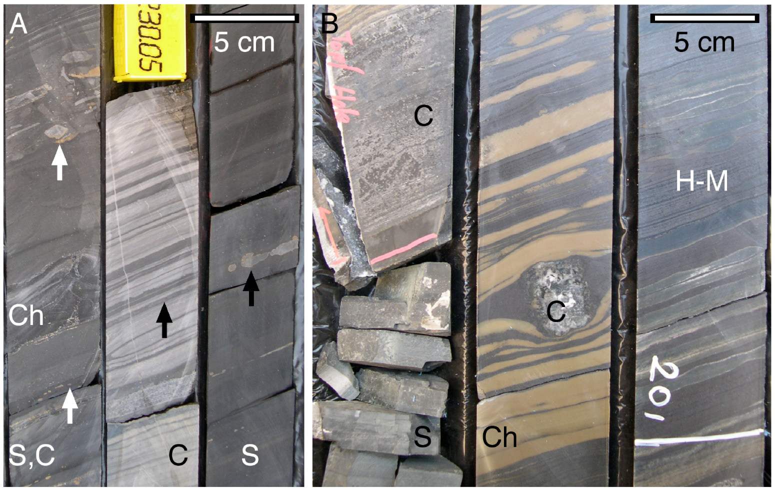

Figure 2. Iron-formation in Agouron core GKP-1 from the base of the Kuruman Iron Formation, South Africa, deposited about 2,520 million years ago [*Sumner and Bowring*, 1996]. These rocks were deposited in a deep water slope environment during a transition from calcium carbonate to iron-formation deposition [*Beukes,* 1984]. They have experienced very little metamorphism. Core in B has a larger diameter than core in A. A) Interbedded carbonaceous shales (S) and carbonate-chert iron-formation (C, Ch). Carbonates consist of siderite, ankerite (MgFe(CO$_3$)$_2$), dolomite, and calcite. Pyrite (white arrows) is abundant as nodules and clasts. The dark shale contains abundant organic compounds, whereas the carbonate-chert layers contain very few. B) Hematite-magnetite-chert iron-formation, with iron-rich areas appearing darker (H-M). The lighter chert (Ch) is yellowish due to traces of various iron minerals. Interbedded shale layers (S) tend to be grey, dolomitic, and organic carbon poor. Minor carbonates (C) are present as nodules and secondary mineral growth.

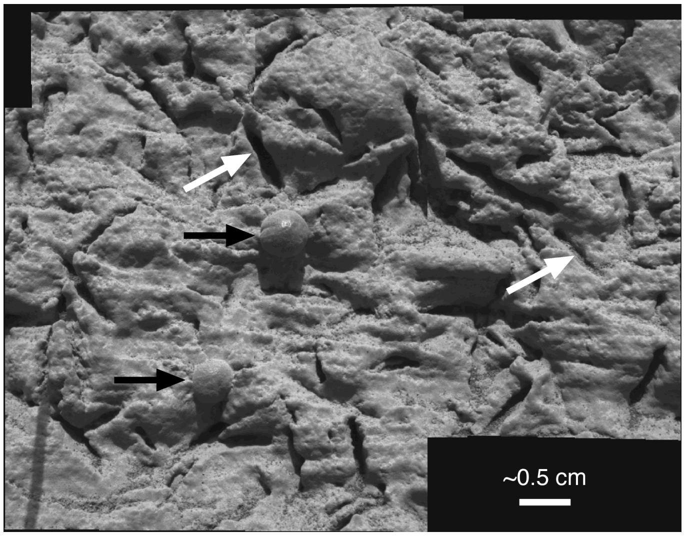

Figure 3. Evaporite casts (white arrows) and hematite concretions (black arrows) from “Guadalupe” in Eagle Crater, Challenger Memorial Station, in a photo take by the Microscopic Imager on MER rover Opportunity. The sedimentary rocks are well lithified, a result of substantial water-rock interactions. Image 16-jg-02-mi1-B035R1.jpg courtesy of NASA/JPL-Caltech [MER-B Rover Team, 2004].