

**GEOCHEMISTRY, MINERALOGY AND DIAGENESIS OF THE BURNS FORMATION AT MERIDIANI PLANUM: INSIGHTS INTO THE SEDIMENTARY ROCK CYCLE ON MARS.** Scott M. McLennan<sup>1</sup>, R. E. Arvidson<sup>2</sup>, B. C. Clark<sup>3</sup>, M. P. Golombek<sup>4</sup>, J. P. Grotzinger<sup>5</sup>, B. L. Jolliff<sup>2</sup>, A. H. Knoll<sup>6</sup>, S. W. Squyres<sup>7</sup>, N. J. Tosca<sup>1</sup> and the Athena Science Team. <sup>1</sup>Dept. Geosciences, State University of New York, Stony Brook, NY, 11794-2100 ([Scott.McLennan@sunysb.edu](mailto:Scott.McLennan@sunysb.edu)); <sup>2</sup>Dept. Earth & Planetary Sciences, Washington University, St. Louis, MO, 63130; <sup>3</sup>Lockheed Martin Corporation, Littleton, CO, 80127; <sup>4</sup>Jet Propulsion Lab, California Institute of Technology, Pasadena, CA; <sup>5</sup>Div. Geological & Planetary Sciences, California Institute of Technology, Pasadena, CA, 91125; <sup>6</sup>Dept. Organismic & Evolutionary Biology, Harvard University, Cambridge, MA, 02138; <sup>7</sup>Dept. Astronomy, Cornell University, Ithaca, NY, 14852.

**Introduction:** The *Opportunity* rover discovered outcrops of ancient sedimentary rocks at Meridiani Planum. Intense study of these deposits over some three and a half years has resulted in significant insight into the operations of surficial processes on Mars, especially during the early history of that planet. These deposits, informally named the Burns formation, include evaporitic sandstones that were deposited by eolian and locally subaqueous processes and that have a diagenetic overprint resulting from interaction with a dynamic groundwater system. Accordingly, they demonstrate the activity of liquid water at and near the martian surface during the Late Noachian to Early Hesperian.

As with any coherent sedimentary deposit on Earth, the Burns formation holds great potential for revealing far more about Mars than the few meters of stratigraphic section studied so far might first imply [1]. For example, such detailed studies give confidence in placing orbital images and spectroscopy into a global stratigraphic reference and provide a far more constrained framework within which to design laboratory experiments and theoretical modeling exercises. Chemical sediments, such as evaporites, are especially valuable sedimentary deposits for evaluating surficial processes because they provide a direct link to the fluids that have interacted with the near surface environment and from which the saline minerals were precipitated [2]. The highly reactive nature of evaporites also provides a very sensitive index to any post-depositional interaction with aqueous fluids and thus constrains the compositions and volumes of such fluids.

Accordingly, the purposes of this paper are to review the most recent findings and understanding of the mineralogy, geochemistry and diagenetic history of the Burns formation at Meridiani Planum. Armed with this information, we will then discuss the implications of the Burns formation for understanding some of the broader questions relevant to the nature of the martian sedimentary rock cycle.

**Sedimentology and Stratigraphy:** The physical sedimentology, stratigraphy and regional geological

setting of the Burns formation will be described in detail elsewhere at this conference. In summary, the Burns formation, examined to date, consists of a sequence of well-sorted fine- to medium-grained evaporitic sandstones. The rocks were deposited in a “wetting upwards” eolian sand dune – sand sheet – interdune environment possessing a dynamic groundwater system that periodically breached the martian surface to produce shallow subaqueous depositional environments. Individual sand grains are composed of fine-grained siliciclastic material produced by chemical alteration of basalt and cemented by sulfate salts and possibly silica prior to eolian and subaqueous reworking [3-5]. In effect, sand grains are intrabasally recycled sedimentary lithic fragments. Within arid eolian environments on Earth, such grains are common products of desiccating playa lakes. The grains are mineralogically highly labile as is clearly shown by the observation that grain boundaries commonly are entirely obliterated during formation of diagenetic sulfate cements around hematitic spherules.

**Diagenetic History:** Textural evidence indicates that the Burns formation was strongly influenced by several, temporally distinct, groundwater-mediated diagenetic processes including (from oldest to youngest) [3, 5, 6]:

1. syndepositional precipitation of cross-cutting “poikilitic” mm-scale highly soluble evaporite minerals with solubility comparable to Mg-sulfates, preserved as molds. Mold shapes suggest minerals with monoclinic and rarely cubic crystal habits, the latter possibly being halite.
2. syn- to post-depositional crystallization of pore-filling evaporitic sulfate cements;
3. crystallization of mm-scale highly spherical hematitic concretions;
4. formation of two distinct types of secondary porosity (crystal molds, elongate vugs) due to dissolution of highly soluble sulfate salts and constituting up to ~35% of the rocks by volume;
5. formation of isopachous cements and zones of pervasive recrystallization surrounding hematitic concretions and other nodules composed of cemented

sandstone. At about the same time, decimeter-scale stratigraphically controlled diagenetic zones of enhanced secondary porosity and recrystallization formed, notably at the Whatanga contact.

At least four distinct groundwater (brine) recharge events, at least on the scale of the 7 m of stratigraphic section preserved in Endurance crater, can be documented or inferred from this sequence of diagenetic events.

**Geochemistry:** The geochemistry of the Burns formation is characterized by very high sulfur content, with  $\text{SO}_3$  in the range of 17-27 wt%, suggesting >35-40% sulfate mineralogy in the non-porous fraction of the rocks by volume (depending on hydration states). On a S- and Cl-free basis, the rocks have a broadly basaltic composition consistent with non-sulfate components being composed of altered basaltic debris. This bulk basaltic composition has given rise to suggestions that these deposits were originally volcanoclastic sediments pervasively altered in place by acidic vapors and fluids [7]. However, on Earth, mixed siliciclastic – chemical sediments also can have compositions that broadly overlap the composition of granitic rocks characteristic of the upper continental crust [e.g., 8] and so a mixed sediment on Mars could be expected to have a bulk composition approximating basalt. In any case, detailed chemical relationships are inconsistent with simple sulfur addition to explain the geochemistry of the Burns formation (Fig. 1).

At the stratigraphic section studied within Endurance crater, the Burns formation exhibits stratigraphic variations in chemical composition that are dominated by increases in Mg and S abundances and decreases in Si, Al and Cl with stratigraphic height. These variations are consistent with vertical diagenetic redistribution of small amounts of sulfates and chlorides [9].

The Burns formation is also characterized by elevated Ni contents, on the order of 400-1,000 ppm. These values are at the high end of, but overlap with, what has been so far observed in martian basalts and ultramafic igneous rocks. Using the same field experiments employed to constrain the hematitic mineralogy of spherules (see below), the Ni content of spherules can be estimated to be in the range of 1,000-1,800 ppm. It has been suggested that these concentrations are inconsistent with formation of hematitic spherules as concretions because  $\text{Ni}^{2+}$  will not substitute for  $\text{Fe}^{3+}$  in hematite [10,11]. These workers further suggest that the Burns formation is an impact surge deposit with the spherules better explained as iron condensation spherules derived from iron meteorites and subsequently oxidized to hematite.

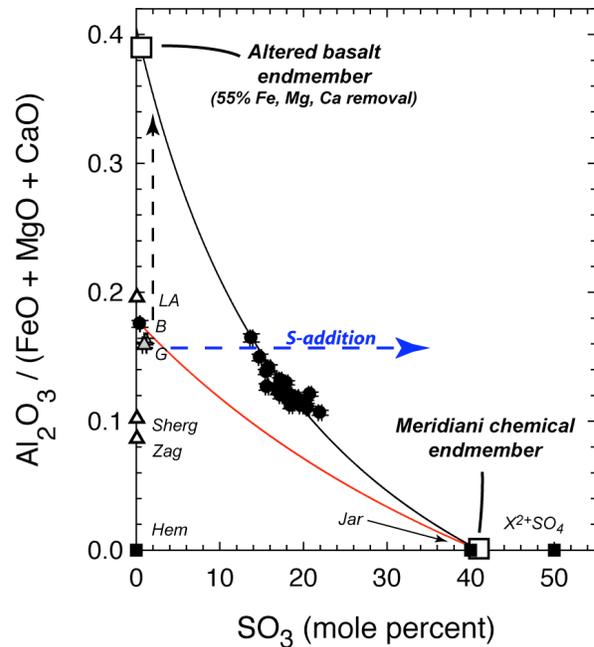


Fig. 1. Plot of mole ratio  $\text{Al}_2\text{O}_3/(\text{FeO}+\text{MgO}+\text{CaO})$  versus mole percent  $\text{SO}_3$  for Burns formation and basalts from Mars. Three mixing lines are shown: (1) between unaltered basalt and Meridiani sulfates (solid red), altered basalt and sulfates (solid black) and simple sulfur addition to basalt (dashed blue). The composition and variation of the Burns formation is consistent with a mixture between altered basalt and sulfates but inconsistent with in situ alteration of basalt by addition of sulfuric acid. Adapted from [5].

This interpretation fails on several counts. Where they occur, hematitic spherules are evenly dispersed throughout the Burns formation in spite of numerous erosional surfaces. Several workers [e.g., 3-6] have pointed out that such a distribution pattern cannot be produced by depositing mm-size dense spherules at the same time as sub-mm-scale sand grains and then reworking the sediment without producing concentrations of spherules at erosional surfaces. Accordingly, the spherules are best interpreted as forming post-depositionally.

The geochemistry is also inconsistent with a spherule origin from iron meteorites. Fig. 2 plots Fe against Ni and it is clear that the composition of spherules cannot be explained by any reasonable mixture between iron meteorites and any potential basalt-ultramafic target rocks. The suggestion that an iron meteorite impacted into massive sulfide deposits [11] is both *ad hoc* and extraordinarily unlikely.

Although Ni abundances in the spherules are moderately high, the Fe/Ni ratio, on average, is about a factor of two lower than the surrounding Burns formation and so Ni has likely behaved as an incompatible

element in the crystallization of the concretions, as expected (Fig. 2). In any case, these levels of Ni (<2,000 ppm) in fact are not especially high (per cent levels of Ni have been recorded in hematite) and  $\text{Ni}^{2+}$  can readily substitute for  $\text{Fe}^{3+}$  as long as it is accompanied by a site vacancy or a coupled substitution such as with  $\text{H}^+$  to maintain charge balance [e.g., 12,13]. The hematitic concretions may also have had a goethite precursor [14] and goethite can accommodate even higher Ni contents [15].

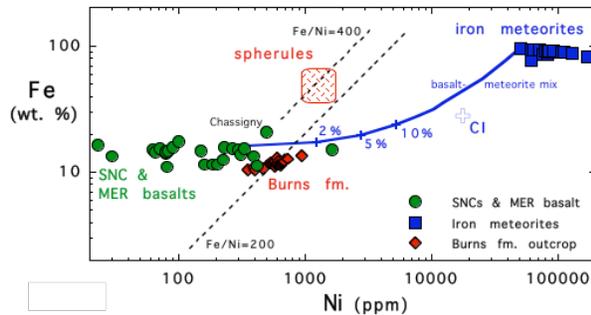


Fig. 2. Plot of Fe vs. Ni for the Burns formation, martian basalts, iron meteorites and inferred composition of hematitic spherules. Also shown is a mixing line between a low-Ni iron meteorite and high-Fe martian basalt.

**Mineralogy:** Several analytical tools on the Opportunity rover can be used to constrain mineralogy, including Pancam, Mini-TES, Mössbauer and APXS. However, with only one exception, it has not been possible to tie mineralogy directly to the various sedimentary microtextures (e.g., grains, cements) that have been observed. The exception is that with careful sample selection and multiple analyses, it has been possible to constrain the spherules to be composed largely of hematite although even with such careful analysis, the exact amount of hematite can only be constrained confidently to within about a factor of 2 (i.e., 50-100%).

The current best estimate of Burns formation mineralogy is that it consists, on an anhydrous basis, of:

1.  $60 \pm 10\%$  of chemical constituents, comprising approximately 15-25% amorphous silica, 15-20% Mg-sulfate, 10% jarosite, 5-10% other sulfates, likely dominated by Ca-sulfates (total sulfate mineralogy is 35-40%), 6% hematite and <2% chlorides. Many of these chemical constituents are likely hydrated and the proportion of chemical constituents on a volumetric basis could be as high at 80% of these sedimentary rocks. Recent experimental studies [16] have demonstrated that instead of pure end-member sulfates, a variety of Fe-Mg

sulfate solid solutions (e.g., Mg-copiapite) may precipitate during evaporation.

2.  $40 \pm 10\%$  siliciclastic constituents, comprising about 5-15% plagioclase, 3-9% pyroxene, 15-25% other altered igneous components and perhaps a trace of olivine.

Iron is mostly oxidized, with  $\text{Fe}^{3+}/\text{Fe}_T \sim 0.9$  [17], suggesting that most iron-bearing igneous components have been altered.

The sand grains make up well in excess of 40% of the solid (i.e., non-porosity) volume of the rocks and accordingly sand grains must be composed of a significant component of chemical constituents. Accordingly the grains have been interpreted as evaporite-cemented altered fine-grained basaltic debris, possibly derived from contemporaneous desiccating playa lakes [e.g., 4-6].

**Chemical Diagenesis:** An important but not fully resolved question is to what degree diagenesis affects the mineralogy and geochemistry of the Burns formation. Some diagenetic mineral reactions are reasonably well constrained. For example, the formation of hematitic concretions has been explained by diagenetic transformations during groundwater recharge either by increasing pH and transforming ferric sulfate (e.g., jarosite) to hematite or by oxidation of ferrous sulfates (e.g., melanterite) to hematite [14]. As pointed out above, there are also stratigraphic variations in chemical composition that could be the result of post-depositional redistribution of highly soluble salts [9]. Nevertheless, the general textural integrity of the Burns formation suggests that the amount of fluid that has interacted with these rocks after deposition of diagenetic cements has likely been very small (Fig. 3).

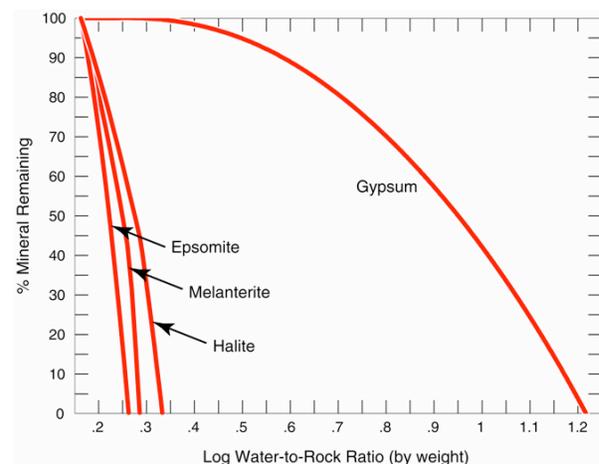


Fig. 3. Model showing the expected strong fractionation between Mg- and Fe-sulfates and Ca-sulfate during water-rock interaction of a hypothetical martian evaporite assemblage.

The origin of the ferric sulfate jarosite is also uncertain. Modeling of evaporation processes of low pH, S- and Fe-bearing brines [14] has demonstrated that jarosite is a highly plausible evaporite mineral. However, ferrous sulfates, such as melanterite, are also predicted to precipitate with the ratio of ferric/ferrous sulfates depending on the oxidation state of the initial brine [14]. An alternative petrogenetic pathway is that ferrous sulfates precipitated during evaporation and were subsequently oxidized to ferric sulfates and then to ferric oxides [16].

**The Burns Formation and the Sedimentary Rock Cycle on Mars:** When combined with recent orbital spectroscopic data that suggest sulfate salts may be common on the martian surface but that the identification of carbonates continues to be elusive, the chemistry, mineralogy and inferred diagenetic history of the Burns formation provides considerable insight into the sedimentary rock cycle of Mars [1].

Widespread occurrence of sulfates and dearth of carbonates suggests that the sulfur cycle, rather than the carbon cycle, dominates surficial processes on Mars. Unlike weak carbon-based acids (i.e., carbonic acid, organic acids) sulfuric acid is very strong and even small amounts will result in highly acidic waters. Interaction with the martian basaltic upper crust will result in brines enriched in Fe and Mg but depleted in K and Na compared to terrestrial seawater. Evaporite assemblages will thus be dominated by Mg-, Fe- and Ca-sulfates with carbonates possibly being restricted to sub-surface environments where acidity is buffered by water-rock interaction, leading to increased alkalinity [18].

Under such conditions, Al is also highly soluble and thus might be expected to produce Al-sulfates, such as alunite, during evaporation. To date, no evidence for Al-sulfates has been observed on Mars. Indeed martian alteration processes do not appear to result in substantial Al fractionation, which is in stark contrast to the Earth where Al fractionation during weathering and alteration is typical [19]. Hurowitz and McLennan [19] suggested that if alteration proceeds under very low water/rock ratio conditions, plagioclase, the dominant Al-bearing mineral in the martian crust, may be relatively stable and unaffected by alteration. Natural waters would then be dominated by the dissolution of minerals such as olivine, Fe-Ti oxides, phosphates and possibly pyroxene.

The occurrence of ancient (Noachian) widespread sulfate deposits would also have implications for the subsequent geological history of Mars. Just as carbonate deposits are major sinks for acidity on Earth, sulfates may provide the same role on Mars, at least in near-surface environments. Thus recycling of sulfate

deposits are likely to have an ongoing influence on surficial processes.

Rocks on Mars commonly exhibit mm-scale alteration surfaces [20]. Volcanic acid fogs have often been proposed as a mechanism for such alteration but impacts into sulfate deposits are also capable of dissociating sulfate minerals and producing SO<sub>2</sub> [21] which when combined with even small amounts of water could distribute significant amounts of acid over the martian surface.

Even very low fluid/rock ratio aqueous interaction with sulfate deposits will likely strongly influence the mineralogy (Fig. 3) thus providing a possible mechanism for strongly fractionating sulfate mineralogy on the martian surface [e.g., 22].

**References:** [1] McLennan, S. M. and Grotzinger, J. P. (in press) in J. B. Bell, ed., *The Martian Surface: Composition, Mineralogy, and Physical Properties*, CUP. [2] Hardie, L. A. (1991) *Ann. Rev. Earth Planet. Sci.*, 19, 131-168. [3] Squyres, S. W. et al. (2004) *Science*, 306, 1709-1714. [4] Grotzinger, J. P. et al. (2005) *EPSL*, 240, 11-72. [5] Squyres, S. W. et al. (2006) *Science*, 313, 1403-1407. [6] McLennan, S. M. et al. (2005) *EPSL*, 240, 95-121. [7] McCollom, T. M. and Hynek, B. M. (2006) *Nature*, 438, 1129-1131. [8] McLennan, S. M. (1995) *AGU Ref. Shelf* 3, 8-19. [9] Clark, B. C. et al. (2005) *EPSL*, 240, 73-94. [10] Knauth, L. P. et al. (2006) *Nature*, 438, 1123-1128. [11] Burt, D. M. et al., *EOS*, 87, 549-552. [12] Singh, B. et al. (2000) *Clay Clay Mineral.*, 48, 521-527. [13] Saragovi, C. et al. (2004) *Phys. Chem. Mineral.*, 31, 625-632. [14] Tosca, N. J. et al. (2005) *EPSL*, 240, 122-148. [15] Carvalho-e-Silva, M. L. (2003) *Am. Mineral.*, 88, 876-882. [16] Tosca, N. J. and McLennan, S. M. (2007) *this conference*. [17] Morris, R. V. et al. (2006) *JGR*, 111 (E12), E12S15. [18] Tosca, N. J. and McLennan, S. M. (2006) *EPSL*, 241, 21-31. [19] Hurowitz, J. A. and McLennan, S. M. (2007) *EPSL*, in press. [20] Hurowitz, J. A. et al. (2006) *JGR*, 111 (E02), E02S19. [21] Pierazzo, E. (1998) *JGR*, 103, 28607-28625. [22] Bibring, J.-P. et al. (2005) *Science*, 307, 1576-1581.