

ABUNDANCE AND SPECIATION OF WATER AND SULFATE AT GUSEV CRATER AND MERIDIANI PLANUM. Richard V. Morris (richard.v.morris@nasa.gov)¹, D. W. Ming¹, B. C. Clark², G. Klingelhofer³, R. Gellert⁴, D. Rodionov³, C. Schroeder³, P. de Souza⁵, A. Yen⁶, and the Athena Science Team. ¹NASA Johnson Space Center, Houston, TX 77058; ²Lockheed Martin Corporation, Littleton, CO; ³J. Gutenberg-Universität, Mainz, Germany; ⁴Max-Planck-Institut für Chemie, Mainz, Germany; ⁵CVRD Group, Vitoria, Brazil; ⁶JPL, Pasadena, CA.

Introduction: A major science goal of the Mars Exploration Rover (MER) mission is to search for evidence of water activity, and direct mineralogical evidence for aqueous activity has been reported for Meridiani Planum in the form of the iron sulfate hydroxide mineral jarosite and at Gusev crater in the form of goethite. The Spirit and Opportunity rovers have each collected 110+ Mössbauer (MB) and 75+ Alpha Particle X-Ray Spectrometer (APXS) spectra from Gusev crater and Meridiani Planum [1 - 4]. In this abstract, we use mineralogical and elemental data, primarily from the Mössbauer and APXS instruments, to infer the speciation and estimate the abundance of sulfate and water (as either the H₂O molecule or the hydroxyl anion) at Gusev crater and Meridiani Planum.

Throughout the abstract, we adopt a format for mineral formulas that shows water explicitly rather than the usual practice of structure-based formulas (e.g., for goethite we write Fe₂O₃•H₂O instead of FeOOH).

Gusev crater: The primary weathering product identified in the Gusev plains is nanophase ferric oxide (np-Ox) [1]. The concentration of iron associated with this phase has a positive correlation with S (slope = Fe/S = 0.57), implying a sulfate or formation in direct proportion to sulfates [5]. This ratio is quite low for iron sulfates [6, 7], although the 0.5 value for rhomboclase (H₃O)Fe(SO₄)₂•2H₂O is essentially the same. Schwertmannite, an acid-sulfate alteration product, has values that range from 8 to 4.6 [6]. If the np-Ox is modeled as np-goethite, ferrihydrite (Fe₂O₃•9/5H₂O), low-S schwertmannite (Fe₈SO₁₅•3H₂O), or rhomboclase, then the Gusev plains basaltic soils have the equivalent of up to ~1 wt% H₂O based on the maximum value of np-Ox (~30% of the total Fe).

Rocks on the Columbia Hills are more altered than those on the Gusev plains. Goethite is identified in "Clovis" by Mössbauer spectroscopy. On the basis of the goethite content from MB and total Fe content from APXS, this rock has the equivalent of ~1 wt% H₂O.

Meridiani Planum: We focus here on the sulfate-bearing outcrop. MB results constrain average outcrop to have Fe distributed among hematite, jarosite, Fe₃D₃, pyroxene, and olivine in the proportion 39:28:21:11:1 [2]. Fe₃D₃ is an unidentified phase constrained only to have a MB spectrum with a doublet from octahedrally coordinated Fe³⁺. We find no distinct units or layers in the outcrop on the basis of outcrop MB data from Eagle, Fram, and Endurance craters. The presence of magnesium and calcium sulfates is indicated by analysis of mini-TES data [8].

APXS data from Endurance crater, however, show the presence of a unit that has a distinctly lower Mg content compared to the rest of the outcrop. We calculated the average composition of the two outcrop targets with the lowest Mg concentration and the four outcrop targets with the highest Mg+S concentrations as the major outcrop chemical endmembers. All 6 targets are from subsurface exposed by the Rock Abrasion Tool (RAT). Because the APXS does not detect hydrogen, all the compositions are with respect to a water-free basis.

Using the elemental abundances and inter-element correlations [9], the mineralogical constraints discussed above, and a variety of studies dealing with terrestrial weathering (particularly those focused on acid sulfate weathering) [10-14], we calculated a suite of minerals that plausibly constitute the outcrop matrix. These calculations at present do not have provisions for specific chemical adsorption (e.g., phosphate adsorption on Fe-oxides). Elements present in small concentrations and for which a specific phase was not warranted (Ni and Cr), were incorporated as substitutional impurities. The component elemental compositions also had to be calculated to a water-free basis. Thus hematite (Fe₂O₃) and ferrihydrite (Fe₂O₃•9/5H₂O) are indistinguishable in this calculation because both are Fe₂O₃. The results of the calculations are given in Tables 1 and 2.

In each table, column 1 lists the mineral name along with its formula; omit any "(H₂O)" for the formula on a water-free basis. Columns 2 and 3 are the mole% and wt% of each component on a water-free basis, respectively. Calculation to a water-free basis has the advantage of dramatically reducing the number of possible components (e.g., the 7 hydrated Mg-sulfates, are all MgSO₄), but it has the disadvantage of removing information about the water content. Column 4 represents an effort to introduce water into the calculations, and doing so necessarily involves assumptions. Jarosite is the only component whose water content is fixed, because of its identification by MB. For the Mg and Fe sulfates, the lowest hydration state was chosen, to give a lower limit for the calculated water content. For allophane and halloysite, (H₂O)₂ was chosen because Al₂Si₂O₇(H₂O)₂ is also the formula for kaolinite. For opaline SiO₂, (H₂O)_{0.2} was selected because it corresponds to water concentrations measured in laboratory samples (unpublished results). The most sulfate-rich composition for schwertmannite was used (Fe/S = 4.6), which fixed its water content. For phosphates, we chose relatively insoluble variscite. However, phosphates have strong specific chemical

adsorption on the surfaces of ferric oxide particles, so that variscite may be an inadequate representation for phosphate.

Table 1. Calculated components for average low-Mg outcrop (average of targets MacKenzie_Campbell_RAT and Inuvik_Toruyuktuk_RAT). Moles calculated with respect to 24(O+Cl).

| | Anhydrous | | Hydrous H ₂ O | |
|---|-----------|--------|--------------------------|------|
| | Mole% | Wt% | Wt% | Wt% |
| <i>Rock Component</i> | | | | |
| Basaltic Rock | 16.88 | 17.10 | 15.93 | 0.00 |
| <i>Oxide Components</i> | | | | |
| Hematite, Fe ₂ O ₃ | 4.72 | 6.79 | 6.32 | 0.00 |
| Anatase, TiO ₂ | 0.63 | 0.76 | 0.71 | 0.00 |
| Pyrolusite, MnO ₂ | 0.28 | 0.37 | 0.34 | 0.00 |
| Np-Ox, (Fe _{0.94} Cr _{0.06}) ₂ O ₃ | 0.14 | 0.20 | 0.18 | 0.00 |
| <i>Sulfate Components</i> | | | | |
| Jarosite, (K _{0.57} Na _{0.43})(Fe _{0.99} Al _{0.01}) ₃ S ₂ O ₁₁ (H ₂ O) ₃ | 8.95 | 10.41 | 10.87 | 1.19 |
| Schwertmannite, (Fe _{0.94} Cr _{0.06}) ₃₂ O ₆₉ S ₇ (H ₂ O) ₉ | 3.49 | 4.52 | 4.42 | 0.22 |
| Rhombochase, Fe ₂ S ₄ O ₁₅ (H ₂ O) ₇ | 0.00 | 0.00 | 0.00 | 0.00 |
| Kieserite, (Mg _{0.99} Ni _{0.01})SO ₄ (H ₂ O) | 12.78 | 11.52 | 12.31 | 1.60 |
| Bassanite, Ca(SO ₄)(H ₂ O) _{0.5} | 7.64 | 7.81 | 7.75 | 0.48 |
| Thenardite, Na ₂ SO ₄ | 0.00 | 0.00 | 0.00 | 0.00 |
| <i>Chloride Components</i> | | | | |
| Hydromolysite, FeCl ₃ (H ₂ O) ₆ | 0.16 | 0.29 | 0.44 | 0.18 |
| Halite (NaCl) | 1.22 | 1.60 | 1.49 | 0.00 |
| <i>Phosphate Component</i> | | | | |
| Variscite, (Al _{0.91} Fe _{0.09})PO ₄ (H ₂ O) ₂ | 1.83 | 1.29 | 1.54 | 0.35 |
| <i>Aluminosilicate Components</i> | | | | |
| Allophane, Halloysite, and/or Kaolinite, Al ₂ Si ₂ O ₇ (H ₂ O) ₂ | 11.06 | 10.06 | 10.87 | 1.52 |
| Opaline Silica, SiO ₂ (H ₂ O) _{0.2} | 30.23 | 27.27 | 26.87 | 1.52 |
| Sum | 100.00 | 100.00 | 100.00 | 7.05 |

Column 4 is the calculated concentration (in wt%) of the water-bearing component as listed in column 1. Again, we emphasize that mode of occurrence of water in the structure is not indicated by the formula. H₂O is incorporated as molecular water in kieserite and as hydroxide anion (Si-OH) in kaolinite, for example. For both outcrop bulk chemical compositions, we calculate ~7 wt% equivalent H₂O. Column 5 gives the concentration of equivalent H₂O associated with each component in the outcrop. For the low-Mg outcrop, the source of the H₂O is approximately equally divided among jarosite, kieserite, aluminosilicate polymorphs, and opaline silica. For high S+Mg outcrop, ~40 wt% water equivalent is associated with kieserite and ~20 wt% from jarosite and opaline silica. The primary difference between outcrop units is the abundance of kieserite, which is a factor of 2 more abundant in high-Mg+S outcrop. Schwertmannite is the most abundant iron sulfate after jarosite, and its MB spectrum is consistent with the Fe3D3 component.

Conclusions: Basaltic soils and rock at Gusev crater contain ~1-2 wt% equivalent H₂O as either molecular

water in their structure or as hydroxide. It, and possibly sulfate, are associated with the np-Qx component. The Meridian Planum outcrop contains ~7 wt% equivalent H₂O, again as hydrates and/or hydroxide. Fe³⁺ sulfates are jarosite and schwertmannite. Mg- and Ca-sulfates are the most abundant sulfates, and, depending on their actual degree of hydration and that for opaline silica (as hydroxide), the major water-carrying components. The major SiO₂-bearing components are amorphous, unless kaolinite is present. Contributions from adsorbed H₂O, which were not modeled, will increase the calculated H₂O content of surface materials.

Table 2. Calculated components for average high-Mg and high-S outcrop (average of Guadalupe_RAT, Golf_RAT, Tennessee_RAT, and Kentucky_Cobble_Hill2_RAT). Moles calculated with respect to 24(O+Cl)

| | Anhydrous | | Hydrous H ₂ O | |
|---|-----------|--------|--------------------------|------|
| | Mole% | Wt% | Wt% | Wt% |
| <i>Rock Component</i> | | | | |
| Basaltic Rock | 13.05 | 13.38 | 12.41 | 0.00 |
| <i>Oxide Components</i> | | | | |
| Hematite, Fe ₂ O ₃ | 4.64 | 6.75 | 6.27 | 0.00 |
| Anatase, TiO ₂ | 0.53 | 0.64 | 0.59 | 0.00 |
| Pyrolusite, MnO ₂ | 0.26 | 0.35 | 0.32 | 0.00 |
| Np-Ox, (Fe _{0.94} Cr _{0.06}) ₂ O ₃ | 0.00 | 0.01 | 0.01 | 0.00 |
| <i>Sulfate Components</i> | | | | |
| Jarosite, (K _{0.46} Na _{0.54})(Fe _{0.91} Al _{0.09}) ₃ S ₂ O ₁₁ (H ₂ O) ₃ | 8.90 | 10.27 | 10.73 | 1.20 |
| Schwertmannite, (Fe _{0.94} Cr _{0.06}) ₃₂ O ₆₉ S ₇ (H ₂ O) ₉ | 3.38 | 4.44 | 4.34 | 0.21 |
| Rhombochase, Fe ₂ S ₄ O ₁₅ (H ₂ O) ₇ | 0.28 | 0.30 | 0.35 | 0.07 |
| Kieserite, (Mg _{0.995} Ni _{0.005})SO ₄ (H ₂ O) | 23.37 | 21.35 | 22.77 | 2.96 |
| Bassanite, Ca(SO ₄)(H ₂ O) _{0.5} | 8.02 | 8.30 | 8.21 | 0.51 |
| Thenardite, Na ₂ SO ₄ | 0.22 | 0.20 | 0.19 | 0.00 |
| <i>Chloride Components</i> | | | | |
| Hydromolysite, FeCl ₃ (H ₂ O) ₆ | 0.00 | 0.00 | 0.00 | 0.00 |
| Halite (NaCl) | 0.44 | 0.59 | 0.55 | 0.00 |
| <i>Phosphate Component</i> | | | | |
| Variscite, (Al _{0.90} Fe _{0.10})PO ₄ (H ₂ O) ₂ | 1.64 | 1.17 | 1.40 | 0.31 |
| <i>Aluminosilicate Components</i> | | | | |
| Allophane, Halloysite, and/or Kaolinite, Al ₂ Si ₂ O ₇ (H ₂ O) ₂ | 8.14 | 7.49 | 7.51 | 0.56 |
| Opaline Silica, SiO ₂ (H ₂ O) _{0.2} | 27.12 | 24.76 | 24.36 | 1.38 |
| Sum | 100.00 | 100.00 | 100.00 | 7.21 |

References: [1] Morris *et al.*, *Science*, 305, 833, 2004; [2] Klingelhoefer *et al.*, *Science*, 306, 1740, 2004; [3] Gellert *et al.*, *Science*, 305, 829, 2004; [4] Rieder *et al.*, *Science*, 306, 1746, 2004; [5] Yen *et al.*, *Nature*, submitted, 2005; [6] Bigham and Nordstrom, *Sulfate Minerals, Rev. Min. Geochem*, 40, 351, 2000; [7] Jambor *et al.*, *Sulfate Minerals, Rev. Min. Geochem*, 40, 303, 2000; [8] Christensen *et al.*, *Science*, 306, 1733, 2004; [9] Clark, this volume; [10] Johnson, *GCA*, 41, 539, 1977; [11] Dixon and Weed (ed), *Minerals in Soil Environments*, SSSA, Madison, 1977; [12] Bishop and Murad, in *Mineral Spectroscopy*, SP Geochem. Soc. #5, 337, 1996; [13] Morris *et al.*, in *Mineral Spectroscopy*, SP Geochem. Soc. #5, 327, 1996; [14] Morris *et al.*, *JGR*, 105, 1757, 2000.