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**EVOLVED GAS ANALYSIS ON THE 2009 MARS SCIENCE LABORATORY.** P. R. Mahaffy<sup>1</sup> and H. B. Franz<sup>2</sup>, <sup>1</sup>NASA Goddard Space Flight Center, Code 699, Greenbelt, MD 20771 ([Paul.R.Mahaffy@nasa.gov](mailto:Paul.R.Mahaffy@nasa.gov)), <sup>2</sup>Department of Geology, University of Maryland, College Park, MD 20742 ([hfranz@geol.umd.edu](mailto:hfranz@geol.umd.edu)).

**Introduction:** Sulfates on Mars have been directly studied or inferred from a variety of experiments. These include the in situ Viking Lander XRS experiments [1] and laboratory chemical analyses of martian meteorites [2, 3]. Mars Pathfinder [4] and more recently the MER rovers have measured sulfur with the alpha particle backscatter experiment. The sulfate-containing rocks at Meridiani [5] have been found to contain the mineral jarosite, which can be uniquely identified with the Mossbauer instrument. The identification of jarosite at Meridiani was one of the early indicators of aqueous processes at that site [6]. Various Fe, Ca, and Mg sulfates have also been identified in the rocks of Columbia Hills [7], with varying degrees of aqueous alteration inferred in several different rock classes. Recent maps of hydrated and sulfate mineral distributions on Mars have been obtained from the Mars Express OMEGA experiment [8], and these together with additional data expected soon from the Mars Reconnaissance Orbiter will significantly enhance the site selection process for future surface landers, for either in situ exploration or sample return.

The 2009 Mars Science Laboratory (MSL) [9] is designed to greatly expand our ability to identify minerals on Mars as well as associated organic or inorganic volatiles. Samples screened by MSL remote sensing and contact instruments can be processed and delivered to one of two locations in the MSL Analytical Laboratory (AL): the MSL CheMin (XRD/XRF) experiment will provide definitive mineralogy, while the Sample Analysis at Mars (SAM) instrument suite will measure the chemical and isotopic composition of volatile species.

**Evolved gas analysis by SAM:** The Mars Science Laboratory utilizes a highly mobile rover and a sophisticated set of sample acquisition, screening, and processing tools. Selected samples will be examined with advanced laboratory-like analytical instruments to assess sites on Mars as potential habitats for past or present life, through the most comprehensive geological and chemical analysis possible within the constraints of in situ robotic investigation. The SAM instrument suite includes an evolved gas analysis (EGA) measurement mode in which volatiles released from rocks and fines are continuously sampled by a quadrupole mass spectrometer or a tunable laser spectrometer as sample temperature is raised from ambient to 1100 °C.

Although the Viking landers heated sampled fines in several experiments on each lander and detected evolved CO<sub>2</sub> and H<sub>2</sub>O [10], these experiments were primarily designed to search for organic molecules and did not continuously sample gases evolved in a controlled temperature ramp. As previously demonstrated [11] in laboratory experiments designed to support first the Mars Polar Lander and later the Phoenix TEGA and MSL/SAM experiments, the rich EGA spectra of sulfate compounds are quite informative, as they can reveal the degree of weathering based on the water structurally incorporated into these materials. As the temperature of the sample is increased, the water of hydration is released first, followed by eventual breakdown of the sulfate to produce SO<sub>2</sub>. The degree of incorporation of water into the mineral structure is revealed in the temperature of its release for each sulfate type.

Our EGA experiments are presently being implemented on a breadboard of the SAM suite to allow optimization of experimental parameters. Sulfate analogs include jarositic tephros from Hawaii with different degrees of aqueous alteration.

**Preservation environments for organic molecules:** One of the primary goals of SAM is to search for reduced carbon compounds and, if these are found, to understand their source and their transformation processes in the martian chemical environment. Terrestrial microbes often thrive in sulfate-rich environments and an improved understanding of the long-term preservation potential of residue organics in Mars analog sulfate environments is critical in this regard [12, 13].

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**SULFATE DEPOSITS AND GEOLOGY OF WEST CANDOR CHASMA, A CASE STUDY.** N. Mangold<sup>1</sup>, A. Gendrin<sup>2</sup>, C. Quantin<sup>1,3</sup>, B. Gondet<sup>2</sup> and J.-P. Bibring<sup>2</sup> and the OMEGA Co-Investigator Team (1) IDES-Orsay, UMR 8148, CNRS and Université Paris-Sud, Bat. 509, 91405 ORSAY Cedex, France, mangold@geol.u-psud.fr (2) IAS, Université Paris-Sud, France, (3) CEPS, Smithsonian Institute, Washington DC.

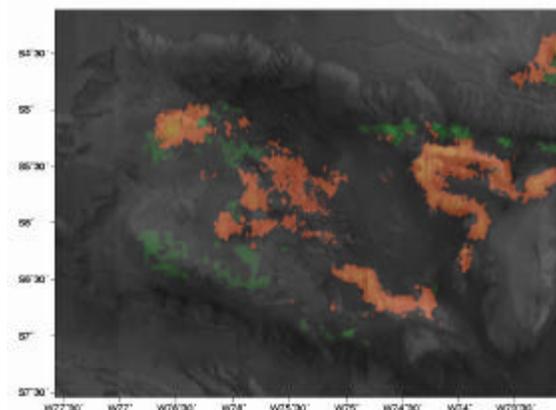
**OMEGA Analysis:** Sulfates are identified on many areas of the Valles Marineris region, with broad outcrops in the Candor Chasma region [1]. The match between the spectra and the spectrum of kieserite is excellent between 1.4 and 2.5  $\mu\text{m}$ , with three main absorption bands at 1.6, 2.1 and 2.4  $\mu\text{m}$ . These bands are due, in monohydrated sulfates, to the single, strongly hydrogen bonded, water molecule. A second group of minerals is detected in West Candor with absorption bands at 1.4 and 1.9  $\mu\text{m}$  and a drop at 2.4  $\mu\text{m}$ . Such associations are observed in spectra of polyhydrated sulfate minerals. Additionally, a drop between 1 and 1.3 micron suggests the frequent occurrence of iron oxides close to the locations where sulfates are detected. Notice also that sulfates might not be the only minerals present, especially if the rocks contain minerals that are spectrally neutral in the NIR wavelengths (halite salt or silica for example). On the other hand, darker parts and canyon floor mainly correspond to eolian mantling do not show any sulfates but most often pyroxenes signatures.

**Comparison with geology:** The most striking result of the identification of sulfates is their systematic correlation with interior layered deposits (ILD) which cover more than half of the West Candor Chasma surface (Fig. 1) [1,2]. At MOC scale, the surface texture of bright deposits displays flutes and yardangs typical of eolian erosion in weakly consolidated material. They are also devoid of small impact craters (< 100 m), which does not mean that the layers formed recently, but that they were exhumed recently. When compared to albedo and thermal inertia, sulfates are detected over terrains significantly bright (albedo :0.15-0.25) and with thermal inertia of 250-450 usi showing the lack of dust and a relative induration of the material.

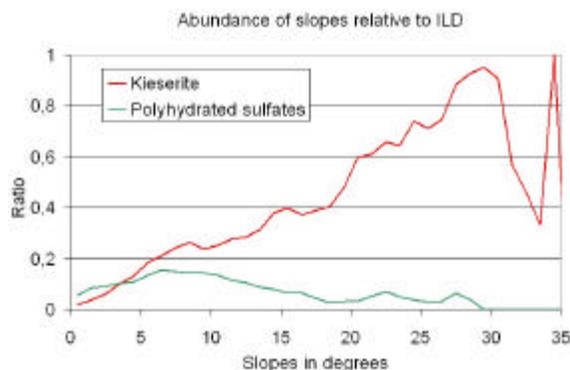
A detailed look to the eastern mesa shows a pile of layers reaching more than 3 km over which sulfates are present. We observe that deep band depths of kieserite are present on steep slopes (> 15°). In order to quantify this observation we compared the relative proportion of kieserite-rich areas relative to ILD mapped from images. This histogram shows a continuous increase in the relative proportion of kieserite with the increase of the slope. At 20 to 25° of slope, kieserite cover 60 to 80% of the ILD unit whereas only 20% at 5°. This effect is not observed for the polyhydrated sulfates showing this is not a statistical bias. The effect of steep slopes is mainly to provide more freshly eroded material at outcrops. The increasing presence of kieserite there is thus an evidence that kieserite is

directly present in the bedrock and does not come from surface interactions.

**Conclusion:** The detailed study of West Candor Chasma shows that sulfates are in the bedrock of interior layered deposits with kieserite more frequent on freshly eroded bright scarps.



**Fig. 1:** Identification of kieserite (red) and polyhydrated sulfates (green) by OMEGA/MEX in West Candor Chasma. The brighter red corresponds to deeper depth of the main absorption band at 2.1 micron for kieserite.



**Fig. 2:** Proportion of each sulfates ratioed by the total proportion of ILD versus slope (1 means kieserite on all ILD outcrops mapped from geology). Kieserite becomes more and more frequent as the slope increases. Strong variations for slopes >30° are due to statistical unsampling of slopes of such steepness.

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**SULFATE GEOCHEMISTRY AND THE SEDIMENTARY ROCK RECORD OF MARS** S. M. McLennan<sup>1</sup>, J. P. Grotzinger<sup>2</sup>, J. A. Hurowitz<sup>1</sup> and N. J. Tosca<sup>1</sup>; <sup>1</sup>Department of Geosciences, SUNY at Stony Brook, Stony Brook, NY, 11794-2100, USA ([Scott.McLennan@sunysb.edu](mailto:Scott.McLennan@sunysb.edu); [joel.hurowitz@stonybrook.edu](mailto:joel.hurowitz@stonybrook.edu); [ntosca@ic.sunysb.edu](mailto:ntosca@ic.sunysb.edu)); <sup>2</sup>Division of Geological & Planetary Sciences, California Institute of Technology, Pasadena, CA, 91125, USA ([grotz@gps.caltech.edu](mailto:grotz@gps.caltech.edu)).

**Carbonate Earth vs. Sulfate Mars?:** Terrestrial surficial processes are controlled by the carbon cycle. Early in Earth history, the bulk of Earth's carbon was sequestered into carbonate rocks and reduced carbon-bearing sediments. CO<sub>2</sub> derived from volcanism and recycling of carbon-bearing sedimentary rocks dissolves in water to produce weak carbonic and organic acids that are the primary agents of rock weathering. Carbonate equilibria buffers the pH of the marine system to about 8.2 and the overall effect is that the pH of most terrestrial aqueous systems is in the narrow moderate range of 5-9. Low pH settings are restricted mostly to environments where sulfur cycling locally dominates (e.g., acid mine drainage, acid lakes, crater lakes). Another effect is that the chemical sedimentary rock record is dominated by carbonates (limestones, dolostones) with sulfates, mostly evaporites, being an order of magnitude less abundant.

Apart from minor occurrences in SNC meteorites, no carbonates have been unambiguously identified on Mars. Instead, spectral and geochemical evidence points to a variety of Mg-, Ca- and Fe-sulfates of evaporitic origin on the surface of Mars throughout its history. This fundamental contrast with the terrestrial situation suggests that the sulfur cycle rather than the carbon cycle dominates surficial processes on Mars and that sulfates may dominate the chemical sedimentary record. Even in the presence of a CO<sub>2</sub>-bearing atmosphere small amounts of SO<sub>2</sub> would lead to very low pH aqueous conditions. For example, pure water in equilibrium with an atmosphere containing 10<sup>-5</sup> atm SO<sub>2</sub> (~10 ppm) has a pH of 2.9.

**Acid Sulfate Alteration on a Basaltic Planet and the Martian Sedimentary Rock Record:** Chemical weathering of the terrestrial granodioritic upper crust at modest pH results in abundant siliciclastic sediment composed of quartz, residual clays and oxides and K-feldspar. Chemical constituents (carbonate, evaporite, chert) compose only 15-20% of the sedimentary record. In contrast, the martian exposed crust is basaltic in character with relatively labile olivine, Fe-Ti oxides, plagioclase and pyroxene being abundant and chemically resistant quartz and K-feldspar being absent. Dissolution rates of most basaltic minerals are orders of magnitude greater than quartz and K-feldspar. Accordingly, for a given amount of water that interacts with martian crust, chemical weathering, under low pH

conditions, coupled with a primary basalt lithology, should be fundamentally more efficient than on Earth.

The fate of dissolved constituents by deposition of Mg-, Fe- and Ca-sulfate evaporites appears well documented. (One caveat is that freezing can also produce brines from which evaporite minerals could precipitate.) Another abundant product of chemical weathering of basalt is amorphous silica and there is growing evidence that such deposits exist. Accordingly, the chemical sedimentary record likely includes both evaporites and secondary silica as major constituents.

The nature of the martian siliciclastic rock record is less clear. At low pH, Al and Fe are soluble and formation of residual aluminous clays and secondary oxides should be inhibited. There is growing evidence for clay minerals on at least local scales but large scale chemical fractionation of Al during sedimentary processes appears to be absent. Accordingly, the siliciclastic component of the martian sedimentary record may be characterized by a dearth of secondary and resistate minerals and thus dominated by relatively unweathered basaltic material.

**Amazonian Acid Sulfate Alteration and Sulfate Recycling Processes:** Wherever examined, rocks on the present martian surface have thin mm-scale alteration rinds characterized by elevated S and Cl. Geochemical differences between brushed and abraded igneous rock surfaces are consistent with alteration dominated by very low fluid/rock ratio and low pH followed by evaporation, physical erosion and soil adhesion. The origin of fluids that give rise to this relatively young alteration is not known but most workers appeal to SO<sub>2</sub> volcanic emissions, analogous to acid sulfate alteration observed on young Hawaiian volcanoes and elsewhere. There is geomorphological evidence for young volcanism on Mars and isotopic systematics of shergottites are interpreted by most to indicate young crystallization ages, thus adding plausibility to the occurrence of young volcanic gases in the martian atmosphere. An alternative (or additional) source for young widely dispersed acidic fluids is recycling of ancient sulfate deposits by impact processes. Sedimentary sulfates, especially Fe-sulfates, release considerable amounts of acidity when dissolved in water. Such a process would be limited by the availability of water, which could come from hydrated evaporite minerals ( $M^{2+}SO_4 \cdot nH_2O$ ) or from subsurface water.

**EXTRA-MARTIAN ORIGINS OF C, FE, NI, S and CL ELEMENTS TO FORM DEPOSITS AS LOCAL CYCLE SYSTEM ON MARS.** Yasunori Miura, Inst. Earth Sciences, Graduate School of Science & Engineering, Yamaguchi University, Yoshida 1677-1, Yamaguchi, 753-8512, Japan, [yasmiura@yamaguchi-u.ac.jp](mailto:yasmiura@yamaguchi-u.ac.jp)

**Introduction:** There are many Fe-rich minerals including sulfate mineral of jarosite [1] found on Martian surface by previous robotic explorations. Simple interpretation of sulfate minerals on Mars, compared with Earth, will discuss sources of these elements of Fe, Ni, S and Cl to Mars. The purpose of this paper is to elucidate extra-Martian sources of Fe, Ni, S and Cl elements to form sulfate minerals as comparison with various terrestrial minerals.

**Present special carbon cycle of Martian system:** On present Mars without wide sea water, major two (large and small) carbon cycle systems on Earth [2-7] cannot be expected to find except Polar Regions of Mars as special carbon cycle system (C-O) between air (carbon oxides) and Polar ices (solid carbon dioxides).

**Carbon from cycle system on Mars:** As there are few oxygen and nitrogen on Mars in large cycle system, there is no active living species of plants with photosynthesis to produce oxygen on Mars. This is mainly because carbon-bearing carbonate rocks of limestone blocks formed in wide sea water (as in active plate crust of Earth) cannot be found so far on Martian surface. Size of bio-minerals formation from cycle system is considered to be 1) local formation at deeper mantle rocks (mainly by local water or fluid carbon dioxides), or 2) wide formation of carbonate minerals with Fe-rich surface.

**Extra-Martian sources of C on primordial Mars:** From large carbon cycle system of Mars in the Solar System, C and H elements of Mars are considered to be supplied originally from 1) older rocks of Mars to evaporate to form gas (CO, CO<sub>2</sub>, H<sub>2</sub>O etc.) and fall as rain water to deposit as bio-minerals on Martian surface, and 2) impact explosions with Mars of C-H-O-rich gas collided with carbonaceous meteorites from asteroids and comets, together with breaking blocks before impacts. As there are few relict rocks of pure carbonate minerals (except spherules of ALH84001 meteorite [8]), extra-Martian sources of C element by carbonaceous meteorites and comets are explained to start active reaction among gas, liquid and solid states during shock wave impact event at local range (including local fluid formation).

**Elements of Fe, Ni, S and Cl rich in meteorite compared with the terrestrial crust:** Apollo lunar samples indicate extra-lunar elements of Pt-group elements and so on from meteorites are found in breccias samples [9]. From elemental abundances of carbonaceous meteorite and terrestrial crusts [10] which will be applied to Martian surface. Fe is 3 times higher (than terrestrial crust), S is 82 times higher, Cl

is 1.5 times higher, C is 5.8 times higher, and Ni is 138 times higher than crust of Earth. In fact, sulfate minerals [11] found at impact crater sites by instruments on current rovers and orbiter spacecraft (NASA-JPL).

**Formation of sulfate minerals in fluid conditions on Mars:** Sulfate minerals on Mars are considered to be formed from impact-induced elements of meteorites with fluid conditions before or after initial impact events. Fluid conditions on Mars are proposed by an impact condition including comets with C, H and O.

**Resources of elements and living species on Mars:** Impact process is cycle system on planet without active volcano [12]. Mars is not active planet, except relicts of old volcanism. Numerous impact events on Mars are considered to be formed concentration of elements (i.e. Fe oxides and sulfate minerals). Living species at primordial stage are formed as local reaction and area on Mars.

**Summary:** The present results are summarized as follows: 1) Extra-Martian sources of carbon by carbonaceous meteorites and comets are considered to be during shock wave impact event at local range. 2) Elements of Fe, S and Cl are rich in carbonaceous meteorite than terrestrial crusts, which is applied to Martian surface to form sulfate minerals. 3) Sulfate minerals on Mars are considered to be formed from impact-induced elements of meteorites with fluid conditions before or after initial impact events including comets.

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**MARS-ANALOG BRINES AND EVAPORITE EXPERIMENTS: IMPLICATIONS FOR SULFATES.** J. M. Moore<sup>1</sup> and M. A. Bullock<sup>2</sup>, <sup>1</sup>NASA Ames Research Center, M/S 245, Moffett Field, CA 94035; jeff.moore@nasa.gov, <sup>2</sup>Southwest Research Institute, 1050 Walnut St., Suite 400, Boulder CO 80302; bullock@boulder.swri.edu.

**Introduction:** For the past 7 years we have been producing Mars-analog brines and evaporites in the laboratory under strictly-controlled Mars simulated conditions. We generated Mars-analog brines by allowing a mixture of minerals derived from SNC mineralogy [1] to soak in pure water under a synthetic current-Mars atmosphere [2] and under a gas similar to the present Mars atmosphere but with added acidic gases [3]. We then produced evaporitic assemblages by allowing these brines (or synthetic versions of them) to dry out under both kinds of atmosphere, either by direct evaporation or by freezing followed by sublimation.

**Laboratory Mars Brines:** In our first set of laboratory experiments we allowed an SNC-derived mineral mix to react with pure water under a simulated Mars atmosphere of modern composition for 7 months. These experiments were performed at one bar and at three different temperatures in order to simulate the subsurface conditions that most likely exist where liquid water and rock interact on Mars today. The dominant cations dissolved in the solutions we produced, which may be characterized as dilute brines, are  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Na}^{+}$ , while the major anions are dissolved C, F,  $\text{SO}_4^{2-}$  and Cl. Typical solution pH was in the range of 4.2-6.0. Abundance patterns of elements in our synthetic sulfate-chloride brines are distinctly unlike those of terrestrial ocean water or continental waters, however, they are quite similar to those measured in the martian fines at the Mars Pathfinder and Viking 1 and 2 Landing sites. This suggests that salts present in the martian soils may have formed over time as a result of the interaction of surface or subsurface liquid water with basalts in the presence of a martian atmosphere similar in composition to that of today. If most of the mobile surface layer was formed during the Noachian when erosion rates were much higher than at present, and if this layer is roughly homogeneous in salt composition, the total amount of salt in the martian fines is approximately the same as in the Earth's oceans.

In a second set of laboratory experiments we allowed an SNC-derived mineral mix to react with pure water under a simulated Mars atmosphere containing the added gases  $\text{SO}_2$ , HCl and  $\text{NO}_2$ . The addition of acidic gases was designed to mimic the effects of volcanic gases that may have been present in the martian atmosphere during periods of increased volcanic activ-

ity. The experiments were performed at one bar and at two different temperatures. The dominant cations dissolved in the solutions we produced were  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Na}^{+}$ , while the major anions are dissolved C, F,  $\text{SO}_4^{2-}$  and Cl. Typical solution pH was in the range of 3.6-5.0. Abundance patterns of elements in these enhanced sulfate-chloride brines were also unlike those of terrestrial ocean water, terrestrial continental waters, but also unlike those measured in the martian fines at the Mars Pathfinder and Viking 1 and 2 Landing sites. In particular, the S/Cl ratio in our experiments was about 200, compared with an average value of approximately 5 in martian fines.

The results of these two sets of laboratory Mars-brines experiments provide evidence that salts seen on much of the planet were created under atmospheric conditions similar to today. This suggests that salts present in the martian soils, such as those seen by MER *Spirit* may have formed over time as a result of the interaction of surface or subsurface liquid water with basalts in the presence of a martian atmosphere similar in composition to that of today, rather than with an atmosphere higher in acidic volatiles. This environment is distinctly different than the acid-rich environment which we hypothesize [4, 5] existed when the massive layered evaporates observed by MER *Opportunity* and the *Mars Express* Omega spectrometer were formed.

**Laboratory Mars Evaporites:** Our initial evaporates experiments involved the rapid evaporation of synthetic brines formed under simulated present-day atmosphere of Mars [2]. The precipitate was analyzed using X-Ray Diffraction. The predominant phase is gypsum, which occurs with a mixture of hydrous sulfates such as hexahydrate ( $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ ), and possibly mirabilite ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ), and starkeyite ( $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ ). Calcite is probably present in very small amounts and magnesian calcite, sylvite and halite were found in very small amounts. Ongoing experiments are investigating the relative stability of sulfate and carbonates under simulated Mars conditions.

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**IRON SULFATES AT GUSEV CRATER AND MERIDIANI PLANUM, MARS.** Richard V. Morris<sup>1</sup> and Athena Science Team, <sup>1</sup>ARES NASA Johnson Space Center, Houston, TX 77058 (richard.v.morris@nasa.gov).

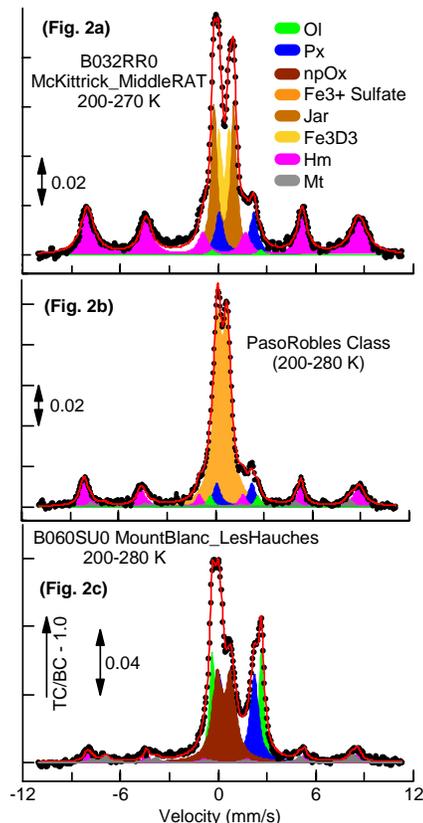
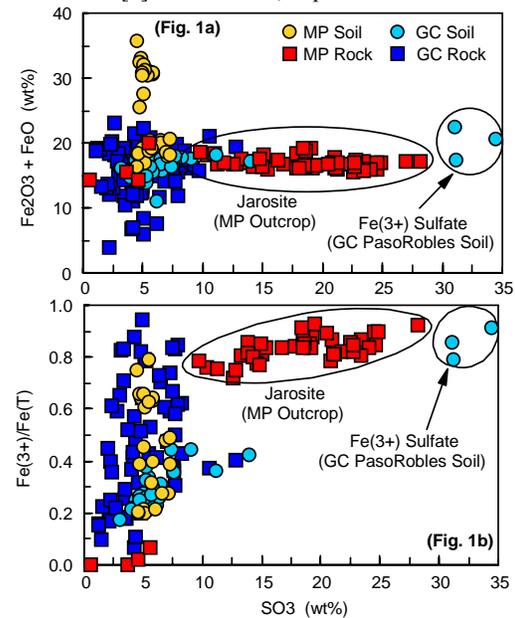
**Introduction:** The abundance and speciation (oxidation and coordination state and mineralogical composition) of both Fe and S are parameters that characterize the formation conditions of primary rock lithologies and the style, extent, and timing of weathering and alteration. The parameters directly address a major scientific objective of the Mars Exploration Rover (MER) mission, which was to characterize the atmosphere and surface of Mars, searching for evidence of aqueous activity [1,2]. The MER rovers Spirit (Gusev crater (GC)) and Opportunity (Meridiani Planum (MP)) carried Alpha Particle X-Ray (APXS) and Mössbauer (MB) spectrometers for elemental analysis and Fe speciation, respectively [1,2]. Summarized here is evidence largely from [3-7] for the presence of Fe-bearing sulfates at the GC and MP landing sites through sols 723 and 560, respectively.

**Discussion:** Total Fe concentration and Fe-oxidation state are shown as a function of SO<sub>3</sub> concentration in Fig. 1. The Burns formation outcrop at MP and the PasoRobles class soils at GC have exceptionally high SO<sub>3</sub> concentrations (up to ~28 and 34 % SO<sub>3</sub>, respectively). The high Fe-oxidation state (Fe<sup>3+</sup>/Fe<sub>T</sub> ~0.7-0.9) implies that sulfur is present as the sulfate anion ((SO<sub>4</sub>)<sup>-2</sup>). Their MB spectra (Fig. 2a and 2b) and characterizing MB parameters (isomer shift  $\delta$  and quadrupole splitting  $\Delta E_Q$ ) are also distinctive. The MB parameters for MP ( $\delta$  ~0.38 mm/s and  $\Delta E_Q$  ~1.22 mm/s) are consistent with the presence of jarosite ((K,Na,H<sub>3</sub>O)(Fe,Al)<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>) with Fe>>Al, and those for GC ( $\delta$  ~0.42 mm/s and  $\Delta E_Q$  ~0.60 mm/s) are consistent with octahedrally-coordinated Fe<sup>3+</sup> in a sulfate. The mineralogical composition of the GC Fe<sup>3+</sup>-sulfate is not constrained, but available MB evidence [8,9] is not consistent with the simple anhydrous sulfate Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. Jarosite (and probably the GC Fe<sup>3+</sup>-sulfate) are evidence for aqueous alteration, probably under acid-sulfate conditions.

Basaltic soils at GC and MP (Laguna class soil) have ~2 – 15% SO<sub>3</sub>. The concentration of Fe associated with the nanophase ferric oxide doublet ( $\delta$  ~0.38 mm/s and  $\Delta E_Q$  ~0.6 - 1.0 mm/s; Fig. 2c) increases with the SO<sub>3</sub> concentration (see [5,7]), suggesting that npOx is also a sulfate-bearing phase. The unidentified ferric doublet Fe3D3 at MP may also be sulfate-bearing.

**References:** [1] Squyres S. W. et al. (2004) *Science*, 305, 794. [2] Squyres S. W. et al. (2004) *Science*, 306, 1698. [3] Morris R. V. et al. (2004) *Science*, 305, 833-836. [4] Klingelhöfer G. et al. (2004) *Science*, 306, 1740-1745. [5] Morris R. V. et al. (2006) *JGR*, 111, E02S13,

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**LOOKING FORWARD TO CRISM.** S. Murchie<sup>1</sup>, R. Arvidson<sup>2</sup>, P. Bedini<sup>1</sup>, J.-P. Bibring<sup>3</sup>, J. Bishop<sup>4</sup>, P. Cavender<sup>1</sup>, T. Choo<sup>1</sup>, R.T. Clancy<sup>5</sup>, D. Des Marais<sup>4</sup>, R. Espiritu<sup>6</sup>, R. Green<sup>7</sup>, E. Guinness<sup>2</sup>, J. Hayes<sup>1</sup>, C. Hash<sup>6</sup>, K. Hefferman<sup>1</sup>, D. Humm<sup>1</sup>, J. Hutcheson<sup>1</sup>, N. Izenberg<sup>1</sup>, E. Malaret<sup>6</sup>, T. Martin<sup>7</sup>, J.A. McGovern<sup>1</sup>, P. McGuire<sup>2</sup>, R. Morris<sup>8</sup>, J. Mustard<sup>9</sup>, S. Pelkey<sup>9</sup>, M. Robinson<sup>10</sup>, T. Roush<sup>4</sup>, F. Seelos<sup>1</sup>, S. Slavney<sup>2</sup>, M. Smith<sup>11</sup>, W.-J. Shyong<sup>1</sup>, K. Strohhbehn<sup>1</sup>, H. Taylor<sup>1</sup>, M. Wirzburger<sup>1</sup>, and M. Wolff<sup>5</sup>, <sup>1</sup>Applied Physics Laboratory, Laurel, MD, 20723, scot.murchie@jhuapl.edu; <sup>2</sup>Washington University, St. Louis, MO; <sup>3</sup>Institut d'Astrophysique Spatiale, Orsay, France; <sup>4</sup>NASA/ARC, Moffett Field, CA; <sup>5</sup>Space Science Institute, Boulder, CO; <sup>6</sup>Applied Coherent Technology, Herndon, VA; <sup>8</sup>NASA/JSC, Houston, TX; <sup>9</sup>Brown University, Providence, RI; <sup>10</sup>Northwestern University, Evanston, IL; <sup>11</sup>NASA/GSFC, Greenbelt, MD; <sup>7</sup>NASA/JPL, Pasadena, CA.

**Instrument:** The Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) [1] is a hyperspectral imager on the MRO spacecraft. CRISM consists of three subassemblies, a gimbaled Optical Sensor Unit (OSU), a Data Processing Unit (DPU), and the Gimbal Motor Electronics (GME). Spectral coverage is 362-3920 nm with sampling at 6.55 nm/channel. Spatial sampling is 15-19 m/pixel.

**Measurements:** CRISM's objectives are (1) to map the entire surface using a subset of bands to characterize crustal mineralogy, (2) to map the mineralogy of key areas at high spectral and spatial resolution, and (3) to measure spatial and seasonal variations in the atmosphere. These objectives are addressed using three major types of observations. In multispectral survey mode, with the OSU pointed at planet nadir, data are collected at a subset of 73 channels covering key mineralogic absorptions, and binned to pixel footprints of 100 or 200 m/pixel. Nearly the entire planet can be mapped in this fashion. In targeted mode, the OSU is scanned to remove most along-track motion, and a region of interest is mapped at full spatial and spectral resolution (545 channels). Ten additional abbreviated, spatially-binned images are taken before and after the main image, providing an emission phase function

(EPF) of the site for atmospheric study and correction of surface spectra for atmospheric effects (Figure 1). In atmospheric mode, only the EPF is acquired. Global grids of the resulting lower data volume observations are taken repeatedly throughout the Martian year to measure seasonal variations in atmospheric properties.

**Hydrated Minerals:** Detection of sulfates and phyllosilicates by OMEGA [2] drove both the selection of wavelengths in the multispectral survey and the selection of preliminary sites for targeted observations. Pelkey et al. [3] used OMEGA data to refine the initial selection of multispectral wavelengths to adequately sample these minerals' diagnostic absorptions (Figure 2), and formulated a set of standard parameters to represent occurrences of these minerals in map form. From those maps, thousands of targets have been identified for targeted observation at CRISM's full spatial resolution. In the 99% of the planet not targeted, occurrence of sulfates and phyllosilicates will be mapped at 2-20 times the resolution of OMEGA. These data will provide improved understanding of distributions and spatial relations of Martian aqueous minerals.

**References:** [1] Murchie S. et al. (2006) *JGR*, in press. [2] Bibring J.-P. et al. (2005) *Science*, 307, 1576-1581. [3] Pelkey S. et al. (2006) *JGR*, in press.

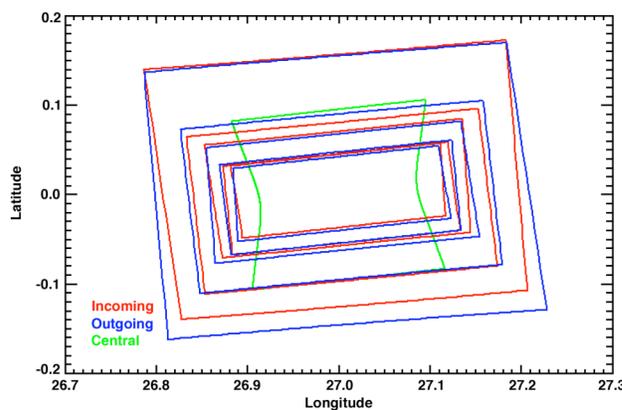


Figure 1. During overflight of a target, five short incoming (red) and outgoing (blue) scans across the target are performed during which data are taken spatially binned. At the time of target closest approach, a slow scan is performed at full spatial resolution (green).

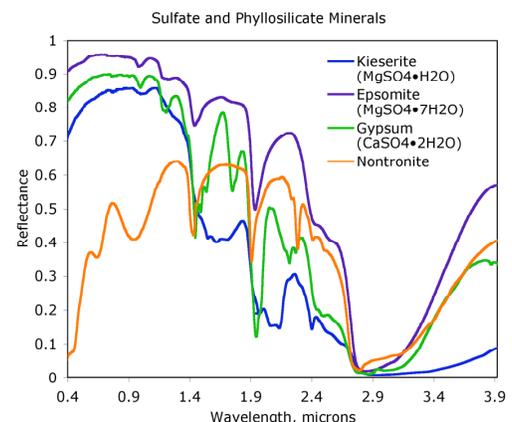


Figure 2. Reflectance spectra of sulfate and phyllosilicate minerals over CRISM's spectral range.

**MULTI-INSTRUMENT SULFATE DETECTION AND MINERAL STABILITY ON MARS.** J. F. Mustard<sup>2</sup>,  
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**Introduction:** While sulfate minerals have been long been predicted to be present in martian surface materials, it has only been in the last five years that sulfate minerals have been unambiguously detected. Importantly, these detections have been achieved using a variety of instruments including orbital data spanning the electromagnetic spectrum (thermal IR, [1]; visible-near infrared (VNIR), [2] [3]) and instruments on landed science packages (Mössbauer, [4]; APXS [5], Mini-TES [6]). These results provide multiple lines of evidence for the presence of sulfate, as well as defining which sulfate minerals are stable on the surface of Mars. In this abstract I consider the range of sulfate minerals detected from remotely sensed and other instruments in the context of remotely sensed detectability, uniqueness, and stability.

**Sulfate Detected:** The OMEGA instrument on the Mars Express spacecraft has detected sulfate minerals on the basis of absorption bands in the VNIR wavelength region [2]. These data uniquely identify the Mg-sulfate kieserite [3] which contains 1-H<sub>2</sub>O and the Ca-sulfate gypsum [7] which contains 2-H<sub>2</sub>O. Another class of sulfate is identified that is referred to as polyhydrated sulfate for which neither the degree of hydration nor coordinating cation can be uniquely resolved with existing data [3]. Thermal infrared data from TES provide evidence for sulfate in mineral deconvolutions. For these orbital observations the model abundances are at the detection limit of the instrument and method [1]. Mini-TES data show clear signatures of sulfate based on a distinct shoulder in the spectra near 8 μm and show model abundances up to 35% [6]. Thermal IR analyses are not as specific as to the type of sulfate present though Mg and Ca sulfate minerals are typically identified.

Interestingly, Mössbauer spectroscopy has identified jarosite on the basis of the iron mineralogy in the sediments in Meridiani [4]. Mössbauer spectroscopy is not sensitive to Fe-free sulfate minerals such as kieserite and gypsum and the amount of jarosite present is not precisely known. However, the amount of sulfur detected with the APXS instrument requires abundant sulfate to accommodate the detected sulfur levels [5] and Mg- and Ca-sulfates are expected on the basis of the APXS measurements.

**Detectability:** The ability to detect the presence of sulfate varies among these instruments. Instrumental and observational effects (e.g. signal to noise, atmospheric dust or ice clouds) will affect observations. For the VNIR, only water- or hydroxyl-bearing sulfates

exhibit absorptions and thus sulfate minerals such as anhydrite would not be detected. Thermal IR is sensitive to hydrous and anhydrous sulfates, but absorption features are strongly affected to surface texture and particle size. Mössbauer is only sensitive to Fe-bearing sulfate minerals. Nevertheless, the remote sensed instruments do present a consistent set of results indicating the presence of sulfates in the Meridian region from the outcrop to orbital scale.

**Stability:** Many water-bearing sulfates are in dynamic equilibrium with their environment, particularly affected by the relative humidity. On the martian surface, relative humidity can cycle between 1% and 100% on time scales as short as a day as well as on orbital time scales [8]. [9] showed that hydrated sulfates will readily dehydrate under martian low humidity conditions, often becoming amorphous. Upon rehydration under high humidity conditions, the amorphous state is maintained.

**Discussion and Conclusions:** The detection of sulfate minerals by orbital and landed science instruments are in general agreement. Gypsum and kieserite are clearly identified from orbit and jarosite from the Opportunity rover. The VNIR spectrum of polyhydrated sulfate is consistent with a range of sulfate chemistry and hydration states including the amorphous forms of hydrated sulfate that might result from the cycling of humidity on the martian surface. The clear presence of kieserite and gypsum indicate that some well crystalline phases are stable on the surface. However, the polyhydrated sulfate minerals may be indicative of regions where amorphous hydrous sulfates are present perhaps formed through humidity variations on geologic time scales. It is interesting to note that kieserite deposits are typically observed on fresh appearing outcrops, perhaps recently exposed by erosion while polyhydrated sulfates are on apparently more mature surfaces [10].

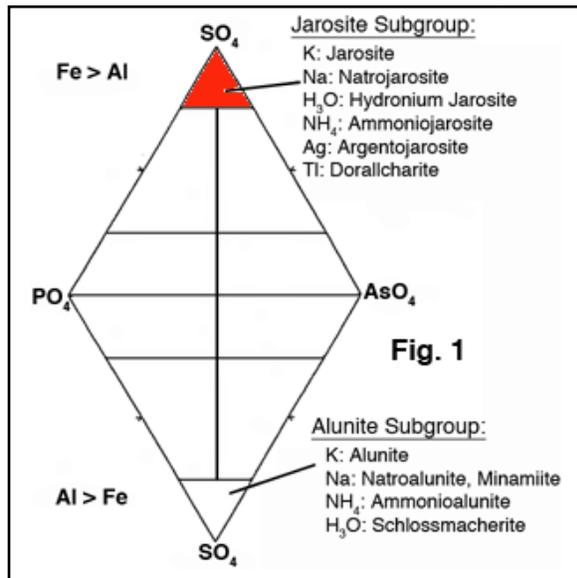
**References:** [1] Bandfield J. L. (2002) *JGR* 107, 5042, doi:10.1029/2001JE001510. [2] Bibring J.-P. et al. (2005) *Science* 307, 1576-1581. [3] Gendrin A. et al. (2005) *Science* 307, 1587-1591. [4] Klingelhöffer G. et al. (2004) *Science* 306, 1740-1745. [5] Rieder R. et al. (2004) *Science* 306, 1746-1749. [6] Christensen P. R. et al. (2004) *Science* 306, 1733-1739. [7] Langevin Y. et al. (2005) *Science* 307, 1584-1586. [8] Mellon M. T. and B. M. Jakosky (1995) *JGR* 100, 11781-11799. [9] Vaniman D. T. et al. (2005) *LPSC* 36, 1489. [10] Mangold N. et al. (2006) this volume.

**THE CHALLENGE OF RETURNING HYDRATED SULFATES FROM THE SURFACE OF MARS TO EARTH.** C. R. Neal<sup>1</sup>, <sup>1</sup>Dept. of Civil Eng. & Geological Sciences, University of Notre Dame, Notre Dame, IN 46556, USA, neal.1@nd.edu.

**Introduction:** The identification of Jarosite by the MER rovers produced intense excitement regarding the evolution of the Martian surface and the fluid-rock interactions that occurred to produce the sequence on Meridiani Planum [1]. This mineral and those associated with the Alunite Supergroup can contain important trace elements useful for isotopes studies (e.g., Sm-Nd) as well as useful chronometers (e.g., K-Ar and Ar-Ar). While advances have been made in robotic surface instrumentation, it is inevitable that in order to discern the potential information contained in these sulfates, analyses using terrestrial laboratories will be required in order to produce high precision and accuracy for the results. This requires sample return and raises the question: How will we know that Martian samples returned to Earth are still in their pristine (i.e., Martian surface) condition? This presentation is a continuation of the CAPTEM-initiated paper regarding Mars Sample Return [2]. It focuses on the issues of sampling caching, and return of sulfate samples.

**Minerals of the Jarosite-Alunite Subgroups:**

The alunite supergroup contains over 40 minerals with the general formula  $DG_3(TO_4)_2(OH,H_2O)_6$ , where  $D$  = mono- (K, Na,  $NH_4$ , Ag, Tl,  $H_3O$ ), di- (Ca, Sr, Ba, Pb), tri- (Bi, REE);  $G$  = usually Al or  $Fe^{3+}$ ;  $T$  =  $S^{6+}$ ,  $As^{5+}$ , or  $P^{5+}$ , with subordinate amounts of  $Cr^{6+}$ , or  $Si^{4+}$  [3]. The



Al:Fe<sup>3+</sup> ratio determines whether minerals are in the jarosite or alunite families ([4 Dut]; Fig. 1). Jarosite has trigonal symmetry [5] and its structure allows the substitution of many elements [6].

**Challenges:** Several papers written since the discovery of Jarosite (and potentially other hydrated sulfates) on Mars have noted that this mineral can be used to obtain age data using argon methods (e.g., [6]). Data indicate little to no Ar loss at 90°C for 12-14 hours [7]. Dehydration of Jarosite from the hydronium site occurs at 260°C and dehydroxylation occurs between 450-480°C [8]. For other hydrated sulfates, the situation is radically different. Hexahydrite ( $MgSO_4 \cdot 6H_2O$ ) forms from Epsomite ( $MgSO_4 \cdot 7H_2O$ ) at 16-20°C at relative humidities <60%. Kieserite ( $MgSO_4 \cdot H_2O$ ) forms from Hexahydrite as relative humidity drops below 20-45% [9,10]. Hexahydrite dehydrates rapidly ( $\leq 24$  hours) to a variety of secondary products (Starkeyite: 4  $H_2O$ ; Sanderite: 2  $H_2O$ ; Kieserite: 1  $H_2O$ ) at 75°C [11]. Such changes would radically affect H and O isotope compositions especially if the sample cache was not sealed.

These examples demonstrate the need to understand mineral stability in order to maintain their pristinity once they have left the Martian surface. While Jarosite appears to be quite robust, it is likely that the samples will be in transit for at least 6 months, so we need to know the kinetics of the dehydration/dehydroxylation reactions and the closing temperature for Ar in the mineral structure.

**Sample Return Environment:** Maintaining samples returned from the Martian surface in their pristine state is essential. By understanding the types of materials that are present on Mars is vital for engineering the sample return capsule. For the examples given above, the ideal situation would be to not allow the capsule to exceed the maximum surface temperature known on Mars. Also, once the sample canister has been filled, it needs to be sealed thus including Martian atmosphere at the time of caching so the environment can be kept buffered. Finally, monitoring the environment with the sample cache will be needed from the time it leaves Mars until the time they arrive on Earth.

**References:** [1] Klingelhofer G. et al. (2004) *Science* 306, 1740-1745. [2] Neal C.R. (2000) *JGR* 105, 22487-22506. [3] Stoffregen R.E. (1993) *GCA* 57, 2417-2429. [4] Dutirzac J.B. & Jambor J.L. (2000) *Rev. Min. Geochem.* 40, 405-452. [5] Stoffregen R.E. et al. (2002) *Rev. Min. Geochem.* 40, 453-479. [6] Papike J.J. et al. (2006) *GCA* 70, 1309-1321. [7] Vasconcelos P.M. et al. (1994) *GCA* 58, 401-420. [8] Alpers C.N. et al. (1992) *Chem. Geol.* 96, 203-226. [9] Vaniman D.T. et al. (2004) *Nature* 431, 663-665. [10] Chipera S.J. et al. (2005) *LPSC XXXVI*, #1497. [11] Chipera S.J. et al. (2005) *LPSC XXXVII*, #1457.

## CORRELATIONS BETWEEN SULFATE AND HEMATITE DEPOSITS AS OBSERVED BY OMEGA AND TES. E. Z. Noe Dobrea<sup>1</sup>, <sup>1</sup>Malin Space Science Systems (edobrea@msss.com).

**Introduction:** Although crystalline grey hematite has been detected in many of locations of the Valles Marineris system and adjacent chaotic terrain [1,2], its nature remains unknown to this day. Recent detections of sulfate-bearing minerals by the OMEGA spectrometer [3] have been found in some cases to correlate spatially with the TES hematite detections [4]. In such cases, they are associated with and with either layered outcrops or dark mantles at MOC resolution[4,5]. Here, we investigate the spatial extent of the correlation between TES hematite detections and OMEGA sulfate detections.

**Methods and tools:** We have used TES to generate hematite index maps of the regions where [1] and [2] have reported the detection of crystalline grey hematite using TES. We then studied the same areas using available OMEGA data and compared our mapping result to the TES hematite index maps.

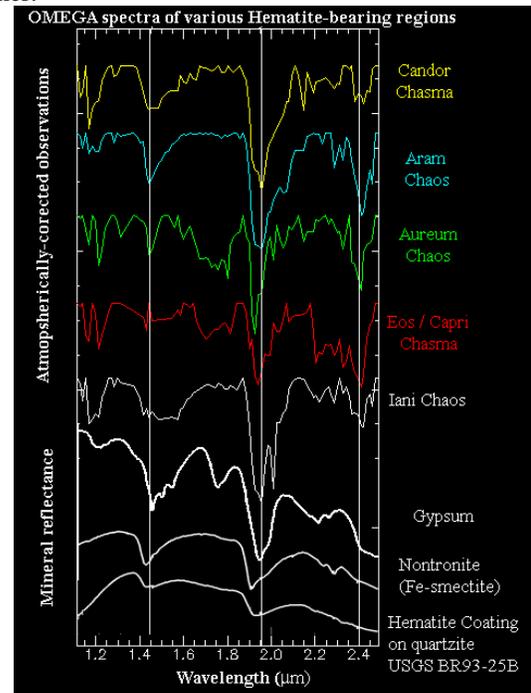
**Results:** Our analysis suggests a strong correlation between TES hematite concentration and OMEGA sulfate mineralogy. All the high-resolution OMEGA observations of hematite-bearing regions have been found to also contain an enhanced sulfate signature, characterized by  $\sim 1.95\text{-}\mu\text{m}$  and a  $2.4\text{-}\mu\text{m}$  bands (Fig. 1). The regions that do not show a signature correspond to lower resolution OMEGA observations, making comparisons difficult.

These deposits are associated to two types of terrains as observed by MGS/MOC: 1) a dark-toned mantling material that is usually found in proximity to light-toned outcrops, and 2) an intermediate-toned outcrop that forms either stair-stepped or finely layered outcrops at MOC resolutions. It is not clear whether the outcrops are intrinsically intermediate in tone or whether they are lighter-toned outcrops that are sprinkled with a venner of darker material, but their proximity to dark mantling material in MOC images suggest the latter.

**Mineralogy:** The NIR spectra of the hematite-bearing regions is very similar from region to region (Fig. 1). Comparisons to spectral libraries shows that their signature is at least in part consistent with that of gypsum ( $\text{CaSO}_4\cdot\text{H}_2\text{O}$ ).

**Stratigraphy:** MOC data of these regions indicates that the hematite-bearing outcrops are not the only outcrops in the region. Instead, they are usually found in association to other outcrops, some of which display the near-infrared signature of other sulfates. The specific stratigraphic relationships between these outcrop units are complicated and are being studied.

Preliminary topographic analysis of their locations indicates that they are found at different elevations, suggesting that they formed independently from each other.



**Figure 1.** Continuum-removed spectra of hematite bearing regions in Valles Marineris and nearby chaotic terrains (top 5), and spectral library mineral reflectance for comparison (bottom 3). All spectra have been shifted for clarity.

**Discussion:** On Earth, gypsum is a very common mineral, typically formed as an evaporite deposit in association with sedimentary rock. It can be deposited in lake and sea water, in veins, from volcanic outgassing, and in hot springs. The morphology and thickness of the gypsum- and hematite-bearing outcrops is consistent with the repeated deposition of several layers material, making it likely that it is part of a sedimentary deposit. We therefore speculate a formative regime similar to that hypothesized for the outcrops at the Opportunity landing site.

**References:** [1] Christensen, P.R. *et al.* (2001), *J. Geophys. Res* 106; [2] Glotch, T.D. *et al.* (2005), *AGU Fall*, abstract # P21C-0160; [3] Gendrin, A. *et al.* (2005) *Science* 307; [4] Noe Dobrea, E.Z. *et al* (2006) *LPS XXXVII*, Abstract #2068; [5] Knudson and Christensen (2005) *AGU Fall*, abstract #P21C-0162.

**TERRESTRIAL ANALOGS OF MARTIAN SULFATES: MAJOR AND MINOR ELEMENT SYSTEMATICS OF SELECTED JAROSITE SAMPLES.** J.J. Papike<sup>1</sup>, P.V. Burger<sup>1</sup>, J.M. Karner<sup>1</sup>, C.K. Shearer<sup>1</sup>, and V.W. Lueth<sup>2</sup>. <sup>1</sup>Astromaterials Institute, Dept. of Earth and Planetary Sciences, Univ. of New Mexico, Albuquerque, NM, 87131. <sup>2</sup>New Mexico Bureau of Geology and Mineral Resources, New Mexico Tech., Socorro, NM, 87801.

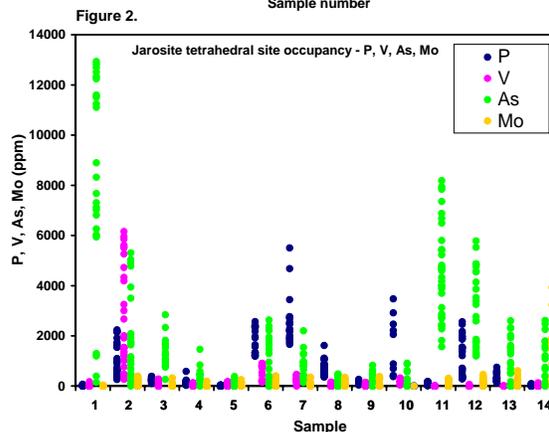
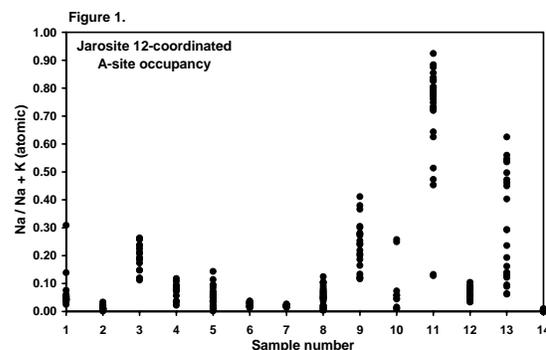
Jarosite has been found to be an important phase at the Meridiani locality on Mars [1]. Papike et al. [2, 3] reviewed the potential of martian jarosite as a recorder of rock-fluid interactions by using terrestrial examples. Here we continue that research by discussing electron microprobe (EMP) analyses for 14 selected sample localities (Table 1). Another important use for jarosite is as a “Canary in a Mine” to detect potential toxins on the martian surface. An element of interest is arsenic and jarosite is a good recorder of the arsenic in the fluids from which it formed. We used a relatively broad beam for these analyses, between 10 and 30 microns (depending on grain sizes and texture), to avoid volatile loss of S, Na, and K. Thus the analyses average over most zoning features. EMP analyses show that these jarosites are mainly solid solutions between jarosite,  $\text{KFe}_3^+(\text{SO}_4)_2(\text{OH})_6$ , and natrojarosite,  $\text{NaFe}_3^+(\text{SO}_4)_2(\text{OH})_6$ . Minor elements include Pb

in the 12-coordinated A-site, Al in the octahedral B-site, and P, As, Mo, and V in the tetrahedral T-site. Figures 1 and 2 show the variations of  $\text{Na}/(\text{Na}+\text{K})$  atomic, and the range of P, As, Mo, and V in the T-sites, respectively. The tetrahedral site is an important player in these samples. Very high abundances of arsenic are detected in some samples, especially sample 1. In a companion abstract, Burger et al. [4] discuss oscillatory zoning of Na and K in a subset of these samples. This zoning was also documented by [3]. However, it should be noted [5] that 32 natural hydrothermal and supergene K- and Na- jarosites analyzed with XRD show <5% solid solution between the end-members. This indicates a very wide solvus (miscibility gap) and kinetics that allow phase separation on a submicron scale, even in samples that are still optically zoned and show chemical zoning by EMP with a 1 micron beam (EDS).

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**Table 1. Jarosite sample information.**

NO.	SAMPLE	LOCALITY
1	8977	Mina la Mojina, Chih., Mexico
2	PP01NV	Post Pit, 5320 bench, NV
3	AA01AZ	AZ Apex Mine, AZ
4	GH01UT	Gold Hill -middle pit, UT
5	AL01SP	Almeiria, Spain
6	H1	Gumma Fe Mine, Japan
7	L1	Gumma Fe Mine, Japan
8	MO01AZ	Morenci Mine, AZ
9	98417129	Copiapo Mine, NM
10	9841416	Sunshine #1, Bingham, NM
11	SM01NM	Sandia Crest, NM
12	BC97-011	Bluestar Mine, NM
13	GF-1	Goldfield, NV
14	PB-1	Pena Blanca, Mexico



**JAROSITE-ALUNITE CRYSTAL CHEMISTRY.** J.J. Papike ([jpapike@unm.edu](mailto:jpapike@unm.edu)), J.M. Karner, and C.K. Shearer, Institute of Meteoritics, University of New Mexico, Albuquerque, New Mexico 87131-1126.

**CRYSTAL CHEMISTRY.** Although there are more than 40 mineral species with basically the alunite crystal structure [1], we emphasize alunite,  $KAl_3(SO_4)_2(OH)_6$ , natroalunite,  $NaAl_3(SO_4)_2(OH)_6$ , jarosite,  $KFe^{3+}_3(SO_4)_2(OH)_6$ , and natrojarosite,  $NaFe^{3+}_3(SO_4)_2(OH)_6$ . We use the general formula  $AB_3(XO_4)_2(OH)_6$  [2] where A is a 12-fold coordinated site that can contain monovalent cations K, Na, Rb etc., divalent cations Ca, Pb, Ba, Sr, etc., and trivalent cations, REE, etc. The B position represents an octahedral site that usually contains trivalent Fe and Al but can include  $Zn^{2+}$ ,  $Mg^{2+}$ , etc. The X position represents the tetrahedral site and contains S, P, As, Sb, etc.

Our discussion of the crystal structure is derived from the discussions of Menchetti and Sabelli (1976) [3]. The structure drawing (Figure 1) projected down c, was kindly provided by Dr. Eric Dowty. The alunite-jarosite crystal structure is represented by space group  $R\bar{3}m$ , with  $Z = 3$ . For alunite there are 3 K, 9 Al, 18 (OH) groups, 24 O, and 6 S atoms per unit cell. The unit cell parameters [3] are alunite,  $a = 7.020 \text{ \AA}$ ,  $c = 17.223 \text{ \AA}$ ; Na-alunite,  $a = 7.010 \text{ \AA}$ ,  $c = 16.748 \text{ \AA}$ ; jarosite,  $a = 7.315 \text{ \AA}$ ,  $c = 17.224 \text{ \AA}$ ; Na-jarosite,  $a = 7.327 \text{ \AA}$ ,  $C = 16.634 \text{ \AA}$ . The

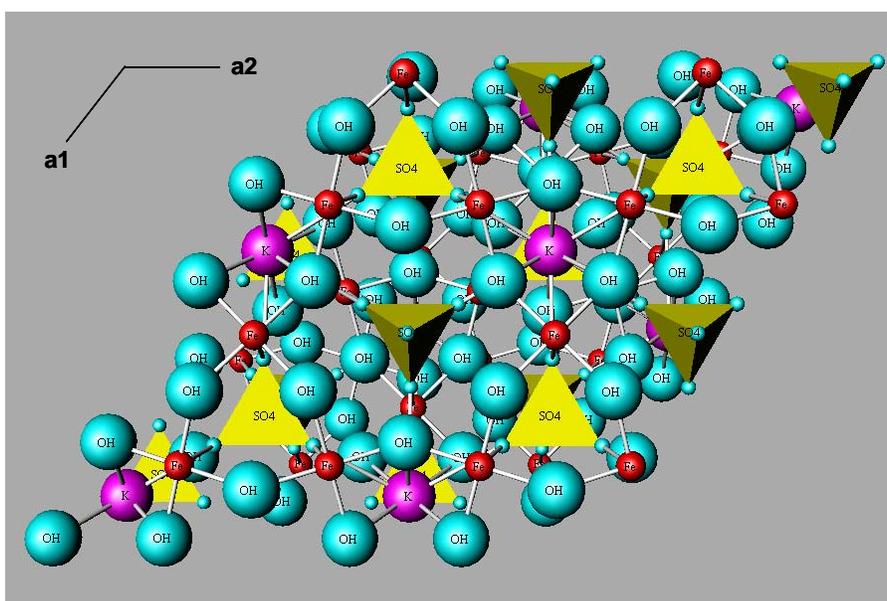
a-axis increases with the substitution of  $Fe^{3+}$  for Al in the octahedral site, and the c-axis decreases with the substitution of Na for K in the 12-coordinated site. Thus, these unit cell variations can be used for estimating the Na/K and Al/ $Fe^{3+}$  ratios in solid solution among the end-members alunite-natroalunite-jarosite-natrojarosite.

The jarosite-alunite crystal structure is beautiful in its simplicity and truly remarkable (Figure 1) in that it can accommodate many elements in the periodic table. Figure 1 shows the jarosite structure projected down the c-axis. The K atom sits in a 12-coordinated site and is coordinated by 6 oxygen ligands and 6 OH ligands. All 6 oxygen ligands and all 6 OH groups are symmetrically identical. Thus the A-site has a highly symmetrical coordination with 6 identical K-OH bonds and 6 identical K-O bonds.

For a more complete discussion of jarosite-alunite crystal chemistry see Papike et al. [4].

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**Figure 1.**



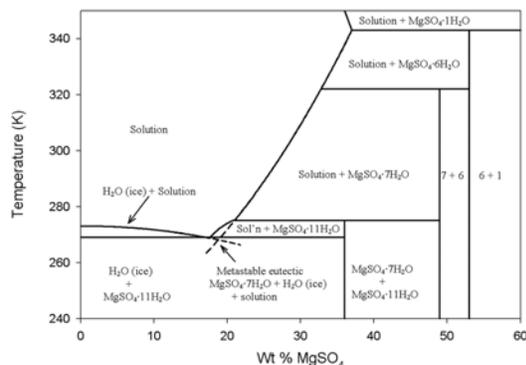
## Crystal Molds On Mars:

### Melting of a possible new mineral species to create martian chaotic terrain

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Images sent back by the Mars Exploration Rover Opportunity from the Meridiani Planum show sulfate-rich rocks containing plate-shaped voids with tapered edges that are interpreted as crystal molds formed after a late-stage evaporite mineral has been removed (Herkenhoff et al., 2004, 2006). Experimental studies of the  $\text{MgSO}_4$  -  $\text{H}_2\text{O}$  system at low temperatures reveal that the triclinic phase  $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$  exhibits a crystal morphology that matches the shapes of these molds.  $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$  melts incongruently above  $2^\circ\text{C}$  to a mixture of 70% epsomite ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) and 30%  $\text{H}_2\text{O}$  by volume. The latent heat of fusion is much lower than ice

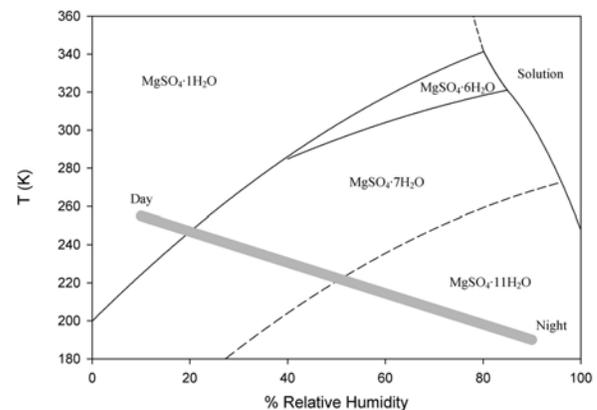


Phase diagram for the  $\text{MgSO}_4$  -  $\text{H}_2\text{O}$  system (after Hogenboom et al. 1995) The field of  $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$  in the original reference has been relabeled as  $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$  based on this work.  $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$  melts incongruently to epsomite and a saturated solution at  $2^\circ\text{C}$  (275 K) in this binary system.

When this occurs while crystals are encased in sediment, plate-shaped voids would remain. The existence of ice, low surface temperatures and the high sulfate content of surface rocks and soil on Mars makes  $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$  a possible mineral species

near the surface at high latitudes or elsewhere in the sub-surface. If an evaporite layer contained a significant amount of this phase, incongruent melting would result in a rapid release of a large volume of water and could explain some of the landform features on Mars that are interpreted as outflow channels.

$\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$  would not survive a sample return mission unless extraordinary precautions were taken.



Phase diagram illustrating the hydration/dehydration relationships of  $\text{MgSO}_4$  as a function of temperature and relative humidity (Chou and Seal 2003) The gray line indicates the conditions at the Viking Lander 1 site in summer (Savijarvi, 1995). A possible boundary for the epsomite -  $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$  as a function of relative humidity is given as a dashed line by assuming it to be parallel to the kieserite - epsomite dehydration boundary. Dehydration / hydration rates are slow at these temperatures. Reactions would not reverse on a daily basis but in general temperature and relative humidity conditions, at or below the surface at the Viking site, are such that either epsomite or  $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$  will be the stable phase.

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**GEOLOGY OF SULFATE DEPOSITS IN VALLES MARINERIS** C. Quantin<sup>1,3</sup>, A. Gendrin<sup>2</sup>, N. Mangold<sup>3</sup>, J-P. Bibring<sup>2</sup>, E. Hauber<sup>4</sup> and the OMEGA Team, <sup>1</sup>Center of Earth and Planetary studies, National Air & Space Museum, Smithsonian Institution, Washington, D.C. 20013-7012, USA, <sup>2</sup>IAS, Orsay, France, <sup>3</sup>IDES, Orsay, France, <sup>4</sup>DLR, Berlin, Germany, [quantinc@si.edu](mailto:quantinc@si.edu)

**Introduction:** Valles Marineris exposes thick central layered deposits named “Interior Layered Deposits” (ILD). The origin and nature of the ILD of Valles Marineris is one of the key issues of the canyon’s evolution. First, from a geological point of view, there is no consensus in their interpretation. The ILDs have been interpreted as lacustrine deposits [i.e. 1,2], as volcanic deposits [i.e. 3,4], or as aeolian deposits [i.e.5]. Secondly, also in terms of their age, there is no consensus. They are interpreted to be the Noachian basement of Valles Marineris by some authors [6] or to be subsequent to the opening of Valles Marineris and thus Hesperian [i.e. 7].

OMEGA, the spectrometer onboard Mars Express, has revealed sulfate signatures in association to these layer deposits in Valles Marineris [8,9]. OMEGA detects absorption bands typical of the monohydrated sulfate Kieserite at 1.6, 2.1 and 2.4  $\mu\text{m}$  and of polyhydrated sulfates, with absorption bands at 1.4 and 1.9  $\mu\text{m}$  and a drop at 2.4  $\mu\text{m}$  [8].

We focused on the geological context of the sulfate signatures within Valles Marineris with respect to their morphology, stratigraphy and also to their elevation distribution. The objective is to understand the origin of the sulfates in this part of Mars, as well as their relationship with the ILD and the origin of the ILD.

**Data set and method:** Our present work is based on multiple remote sensing data from the MGS, Mars Odyssey and Mars Express missions. The different data sets have been imported and integrated into a Geographic Information System (GIS). Our GIS superimposes for the entire Valles Marineris area: (1) MOLA DEM, (2) the TES thermal inertia map, (3) a mosaic of day-time THEMIS infrared, (4) a mosaic of night-time THEMIS infrared images, (5) a mosaic of HRSC images covering Valles Marineris, (6) the available THEMIS visible images (7) all available MOC images and (8) the mineralogy from OMEGA.

The mapping of sulfate spectral signatures has been performed by [9] from OMEGA data. Although the different observations are of different quality (atmospheric conditions, observation time...) as detailed in [9], the current updated OMEGA mineralogical map gives us a good idea of the sulfate distribution throughout the canyon system.

**Results:** Sulfates have been detected in all the canyons of Valles Marineris, where sulfate signatures are correlated to layered deposits [8,9]. The sulfates are mainly located on the flanks of massive deposits and on several isolated ILDs. Most of the OMEGA sulfate signatures correspond to high thermal inertia areas ( $>250$  usi), and this is confirmed by morphology: the sulfates detected by OMEGA correspond to outcrops which are typically cliffs, with almost no impact craters suggesting that they are extremely freshly exposed.

The observation of MOC or HRSC images corresponding to kieserite detections shows that the kieserite mineral is correlated to massive light toned material with yardang erosional features. The polyhydrated sulfates are usually correlated to slightly darker units. Kieserite and polyhydrated sulfates correspond either to distinct lithologies or to distinct degree of hydration or of freshness of the outcrops.

In case of obvious flat layers at canyon’s scale like in Melas Chasma or Gangis Chasma, the sulfates are observed in same range of elevation, over typically 1 km of thickness, in all parts of the canyon. The sulfates follow the ILD stratigraphy and certain kinds of layers. In case of more deformed layers like in Candor Chasma [10] or in Ophir Chasma, the sulfates still seem to follow the more complex stratigraphy. Comparing the different canyons in term of vertical location of the sulfates, we found no relationship between the canyons even neighboring and currently joined canyons. This might be explained either if the sulfates units were formed previously to the coalescence of canyons and/or if sulfates formed by groundwater connections. Ages of layered deposits are currently under study and will be reviewed at the time of the meeting.

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**MÖSSBAUER SPECTRA OF SULFATES AND APPLICATIONS TO MARS.** E.C. Sklute<sup>1</sup>, M.D. Dyar<sup>1</sup>, J.L. Bishop<sup>2</sup>, M.D. Lane<sup>3</sup>, P.L. King<sup>4</sup>, and E. Cloutis<sup>5</sup>. <sup>1</sup>Dept. of Astronomy, Mount Holyoke College, South Hadley, MA, 01075; mdyar@mtholyoke.edu. <sup>2</sup>SETI Institute/NASA-Ames Research Center, Mountain View, CA, <sup>3</sup>Planetary Science Institute, Tucson, AZ, <sup>4</sup>Univ. of Western Ontario, Canada, <sup>5</sup>Univ. of Winnipeg, Canada.

**Introduction:** Given the increasingly-apparent importance of sulfate minerals on Mars, it has become critical to collect analog Mössbauer spectra of the many different mineral species (and intermediate compositions) in the sulfate minerals groups. Because Mössbauer spectra are quite temperature-dependent, these must be collected at Mars analog temperatures. Unfortunately, almost no comparative data exist in the literature for these mineral groups. Furthermore, Mössbauer spectra of sulfates (and especially, silicate-sulfate mixtures) may be significantly affected by differential recoil-free fraction ( $f$ ) effects. Here we report progress on collection of 4-293K Mössbauer spectra of a broad selection of minerals in the various sulfate groups. Our goal is to characterize their Mössbauer parameters, isomer shift (IS) and quadrupole splitting (QS) over a broad temperature range, and to determine  $f$  values that will facilitate correct interpretation of area ratios in Mossbauer spectra of sulfate minerals. All spectra and data files collected to date may be viewed at <http://www.mtholyoke.edu/courses/mdyar/database/>. These samples are also part of a larger study of visible-IR reflectance and mid-IR emittance spectra.

**Samples:** Minerals for this study were chosen from Dana groups 2, 6, 12, 28-32 and 76, and acquired from the NMNH, HMM, and mineral dealers. Minerals were carefully handpicked to permit analyses of

single phases, and XRD was used to confirm phase identifications immediately prior to acquisition of reflectance spectra. Although monitored, humidity was not controlled during our Mössbauer experiments, and we expect that phase changes may have occurred in some phases, particularly those with varying hydration states. Work is in progress to evaluate those changes.

**Methods:** Mössbauer spectra were collected at Mount Holyoke College over the temperature range from 4-293K using a closed-cycle helium cryostat.

**Results:** Mössbauer spectra of sulfates follow different rules than those for silicates and oxides, but display consistent parameters representing varying permutations on the steric configurations of SO<sub>4</sub> tetrahedra. Most of the laboratory spectra contain multiple doublets or quadrupole splitting distributions reflecting multiple populations of site geometries, though it is doubtful that these could be resolved in MER data.

**Implications for Mars Mössbauer spectroscopy:** Comparison of data acquired *in situ* on Mars to terrestrial laboratory spectra requires use of 293K isomer shift and Mars surface temperature quadrupole splitting data, as well as simplified fits (e.g. only doublets rather than multiple components). More data on additional sulfates at variable temperatures are needed before mineral identifications based on Mössbauer parameters in MER results can be properly interpreted.

**Table 1. Room temperature Mössbauer parameters for paramagnetic doublets in selected sulfates (in mm/s)**

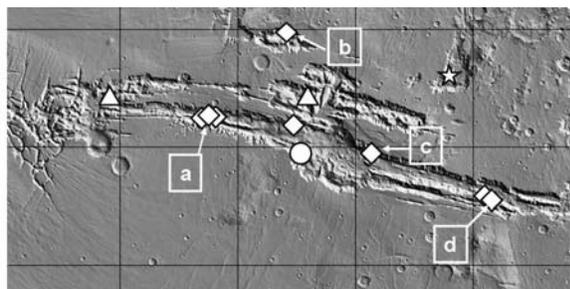
	oct Fe <sup>2+</sup>		oct Fe <sup>2+</sup>		oct Fe <sup>2+</sup>		oct Fe <sup>2+</sup> or		oct Fe <sup>3+</sup>		tet Fe <sup>2+</sup>	
	IS	QS	IS	QS	IS	QS	IS	QS	IS	QS	IS	QS
tochilinite			1.17	2.78					0.45	0.50	0.19	0.36
mackinawite*							0.48	1.28			0.20	0.50
yavapaiite									0.48	0.31		
römerite	1.29	3.31	1.29	2.78					0.44	0.33	0.16	0.60
szomolnokite			1.29	2.74					0.55	0.38	0.23	0.69
rozenite			1.27	3.33			0.37	1.15			0.20	0.48
chalcantite			1.30	2.88	1.26	2.32			0.26	0.76	0.10	0.51
halotrichite	1.30	3.31	1.28	2.77					0.46	0.37	0.13	0.50
kornelite					1.32	1.62	1.18	1.57	0.47	0.45	0.21	0.67
coquimbite									0.45	0.08	0.16	0.66
voltaite					1.34	1.62	1.20	1.58	0.47	0.37	0.14	0.61
jarosite							0.38	1.23				
ferricopiapite							0.38	1.18	0.42	0.40	0.43	0.77
sideronatrite							0.42	1.15				
fibroferrite							0.42	0.96	0.41	0.52		
botryogen					1.30	1.74	0.42	1.18	0.40	1.64	0.08	0.52

\*spectrum also contains sextets

**PHOTOGRAPHIC EVIDENCE FOR EXHUMATION OF LIGHT-TONED DEPOSITS FROM THE WALLS OF VALLES MARINERIS.** M. R. Smith, D. R. Montgomery, A. R. Gillespie, S. E. Wood and H. M. Greenberg. Department of Earth and Space Sciences, University of Washington, Box 351310, Seattle, WA 98195

The origin, age, and method of deposition of the light-toned layered deposits (LLD) found within Valles Marineris have been debated since their discovery by the Viking spacecraft in the late 1970's. Some have argued that the deposits lie unconformably on the existing topography within the pre-existing chasmata and post-date their formation [1,2], while others found that evidence shows light-toned material being exhumed from the chasmata walls, suggesting that the light-toned deposits pre-date the chasmata formation [3-5]. In this study, we find significant visual evidence, as determined from analysis of high-resolution (~3 m/pixel) narrow-angle MOC images (Fig. 2) that exhibit exhumation of light-toned deposits from beneath darker-toned, blocky material, which has been interpreted to be basalt flows of Hesperian Age [6]. This implies that the LLDs would be dated to Noachian age, far older than previously thought. As shown in Fig. 1, we see widespread evidence of such exhumation throughout the extent of the valley system. Our work, combined with prior work of others [3-5], suggest widespread burial of the LLDs beneath the surrounding lava flows.

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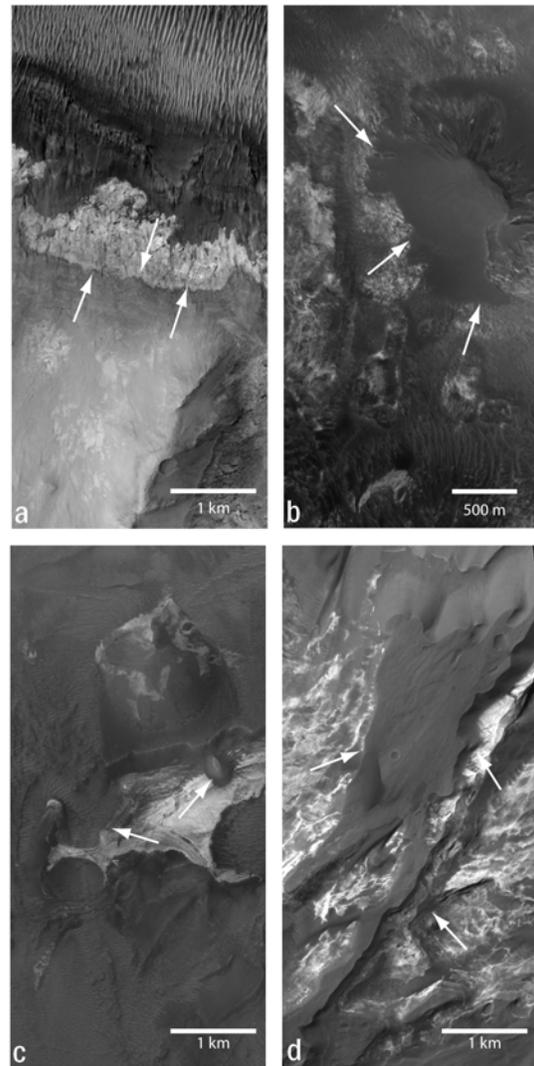
△ Malin & Edgett, 2000

☆ Catling et al., 2006

○ Montgomery & Gillespie, 2005

◇ Smith et al., in preparation

**Figure 1.** Context image for Fig. 2 along with locations of other contacts in this study and those found by additional researchers. Shows the regional extent of evidence for exhumation of LLDs from beneath younger basalt flows.



**Figure 2.** Portions of narrow-angle MOC images showing dark-toned materials (interpreted as basalt flows) covering light-toned material. White arrows indicate contacts between dark and light material. (a) E1700753, (b) R1101206, (c) R1103842, (d) E2001074.

**OVERVIEW OF THE PHOENIX MARS LANDER MISSION.** P. H. Smith<sup>1</sup>, <sup>1</sup>Lunar and Planetary Lab, University of Arizona, Tucson, AZ 85721, psmith@lpl.arizona.edu.

**Introduction:** The Phoenix lander is the next mission to study the surface of Mars in situ. By studying the active water cycles in the polar region, it complements the Mars Exploration Rovers that look at the ancient history of Mars contained in the solid rocks. Lacking mobility, Phoenix explores the subsurface to the north of the lander, studying the mineralogy and chemistry of the soils and ice.

**Scientific Objectives, Phoenix Follows the Water:** The Phoenix mission targets the northern plains between 65 and 72 N. High-resolution images from the Mars Orbiter Camera on the Mars Global Surveyor spacecraft show a “basketball-like” texture on the surface with low hummocks spaced 10’s of meters apart; polygonal terrain, or patterned ground, is also common. These geologic features may indicate the expansion and contraction of the permafrost [1].

*Science goal #1: Study the history of water in all its phases.* The circumpolar plains are active and hold clues to the cycle of water transport on Mars. Orbiter measurements show large seasonal variations in the atmospheric humidity and CO<sub>2</sub> frost blanketing the winter surface.

Quantifying the volatile inventory locked into the arctic soils and the water chemistry of wet soils, even at one location, is a giant step toward modeling the weather processes and climate history of Mars [2].

Liquid water changes the soil chemistry in characteristic ways. Obliquity wander and precession are known to strongly influence the climate on time scales of 50,000 years or more. Does the water ice melt and wet the overlying soil on cycles commensurate with orbital dynamics?

*Science goal #2: Search for evidence of a habitable zone.* Microbial colonies can survive in a dormant state for extremely long periods of time. Recent work [3] shows that as water ice melts onto soil crystals at temperatures as cold as -20 C microbes are activated and are able to search for food. As temperatures increase, growth and reproduction begin. Instruments on the Phoenix lander receive sam-

ples of this biological paydirt and test for signatures related to biology.

**Baseline Mission:** After the initial assessment of the landing site by the science team, the primary science phase of the mission begins with the collection of surface samples. Two major science instruments receive and analyze the samples. The first is the thermal evolved gas analyzer (TEGA). A sample is delivered to a hopper that feeds a small amount of soil into a tiny oven, which is sealed and heated slowly to temperatures approaching 1000 C. The heater power profile necessary to maintain a constant temperature gradient contains peaks and valleys that indicate phase transitions. For instance, ice will show a feature at its melting point of 0 C and jarosite has strong endoenthalpic transitions at 670 and 950K [4].

Gases driven from the sample are combined with a carrier gas and piped to a mass spectrometer. The spectra of the gases change as a function of release temperature. Isotope ratios for H, O, C, and N as well as heavier gases like Ar and Xe provide scientific clues to the origin of the volatiles.

The second instrument provides a microscopic, electro-chemical, and conductivity assessment (MECA) of the soils. Microscopic examination of tiny grains (less than 200 microns diameter) gives clues to the emplacement process: aeolian, lacustrine, or fluvial. A probe on the RA scoop measures the electrical and thermal conductivity of the soil.

The MECA wet chemistry laboratory accepts small samples into a warm beaker, and water is added to the soil while stirring. Special chemical sensors return data concerning the water chemistry including: the salt content and its composition, the acidity, and the trace mineral concentration.

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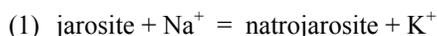
## EXPERIMENTAL STUDIES OF JAROSITE AND ALUNITE AT HYDROTHERMAL CONDITIONS.

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**Introduction:** The minerals jarosite ( $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ ), alunite ( $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ ) and their sodium analogs have been studied in a variety of hydrothermal experiments over a temperature range of 100 to 450°C. Due to mineral stability and reaction rate considerations, experiments on jarosite were conducted mainly in the temperature range of 100-250°C, and those for alunite from 250-450°C. These experiments have defined the stability field of jarosite relative to hematite [1]; determined mineral-fluid Na-K distribution coefficients and provided constraints on the mixing behavior along the jarosite-natrojarosite [1] and alunite-natroalunite [2] binaries; measured the fractionation of oxygen isotopes between water and the sulfate and hydroxyl sites in alunite, and the D-H fractionation between water and alunite [3]; and provided reconnaissance information on these mineral-water isotope fractionation factors for jarosite [4]. In addition, the experiments provide rates of alkali and isotope exchange between these minerals and co-existing aqueous solutions that can be extrapolated to lower temperatures with some confidence [1,5].

**Jarosite Stability:** Jarosite is stable relative to hematite below a  $\log m \text{H}_2\text{SO}_4$  of  $-0.35 \pm 0.5$  at 250°C and  $-0.58 \pm 0.12$  at 200°C (corresponding to  $m \text{H}_2\text{SO}_4$  of 0.45 and 0.26). Natrojarosite could not be produced from hematite at 250°C, but was stable below a  $\log m \text{H}_2\text{SO}_4$  of  $-0.17 \pm 0.08$  at 200°C (corresponding to a  $m \text{H}_2\text{SO}_4$  of 0.68). These extreme sulfuric acid concentrations required for jarosite stability are consistent with the rarity of jarosite in hydrothermal environments on earth. Decreasing temperature increases the jarosite stability field, consistent with the common occurrence of jarosite in terrestrial surface environments where pyrite serves as a source of sulfuric acid during weathering.

**Alkali Exchange and Mixing:** The distribution coefficient for the exchange reaction



is -4.9 at 150°C, -3.7 at 200°C, and -3.1 at 250°C, and values for the analogous alunite-natroalunite reaction are: -2.56 at 250°C, -1.73 at 350°C and -0.99 at 450°C. These values indicate that partitioning of alkalis is similar for jarosite and alunite, and that increasing temperature favors the sodium end-member for both phases.

Experimental results suggest that jarosite-natrojarosite can be modeled as an ideal solid solution at 200°C. Increasing departures from ideality with decreasing temperature are not precluded by the experimental data, but a solvus in the system jarosite-natrojarosite is considered unlikely. In contrast, the alunite-natroalunite binary shows a substantial departure from ideality that increases with decreasing temperature from 450 to 250°C. An asymmetric solvus is considered likely with decreasing temperature.

**Isotope Exchange:** Alunite-water oxygen and hydrogen isotope fractionations were determined in couple alkali and isotope exchange experiments. Results were used to develop an intra-mineral geothermometer based on oxygen isotope fractionation between the alunite sulfate and hydroxyl sites. Reconnaissance jarosite-water isotope fractionation experiments were also conducted, but their interpretation was complicated by apparent non-equilibrium effects.

**Reaction rates:** The experimentally determined rate of jarosite-fluid alkali exchange over the temperature range of 200-108°C was

$$\log t_{1/2} = -14.38 + 6.28 (1000/T \text{ (K)}),$$

where  $t_{1/2}$  is equal to the time required for 50% exchange, in days. When extrapolated to 25°C, this equation suggests that jarosite will rapidly equilibrate (at geologic times scales) with co-existing fluids even at earth-surface conditions. This should be taken into consideration when studying the stable isotope systematics of jarosite, or using it for K-Ar dating. Experimentally determined alunite-fluid exchange rates are roughly three orders of magnitude slower than those for jarosite, which suggests that alunite, unless it is fine-grained, will not re-equilibrate at surface conditions.

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**DETECTION OF JAROSITE AND ALUNITE WITH HYPERSPECTRAL IMAGING: PROSPECTS FOR DETERMINING THEIR ORIGIN ON MARS USING ORBITAL SENSORS.** G. A. Swayze<sup>1</sup>, G. A. Desborough<sup>1</sup>, R. N. Clark<sup>1</sup>, R. O. Rye<sup>2</sup>, R. E. Stoffregen<sup>3</sup>, K. S. Smith<sup>1</sup>, and H. A. Lowers<sup>1</sup>, <sup>1</sup> U.S. Geological Survey, MS964, Box 25046 DFC, Denver, CO 80225, [gswayze@usgs.gov](mailto:gswayze@usgs.gov), <sup>2</sup> U.S. Geological Survey, MS963, Box 25046 DFC, Denver, CO 80225, <sup>3</sup> AWK Consulting Engineers, Inc., 10 Duff Rd., Suite 304, Pittsburgh, PA, 15218.

Recent identification of jarosite at Meridiani Planum [1] has generated intense interest because its mode of formation may constrain past conditions on the planet. The small footprint (18 m) of the Mars Reconnaissance Orbiter CRISM spectrometer may allow recognition and mapping of jarosite and other sulfate minerals from orbit in the coming months on a planetary scale. Alunite is commonly associated with jarosite in terrestrial deposits [2, 3] and has been recognized in Hawaiian basalts [4] used as analogs for Martian volcanic rocks. Given this, it is likely that CRISM scientists will eventually find alunite on the Martian surface. Alunite, like jarosite, may potentially form on Mars in a number of modes ranging from high-temperature environments associated with magmatic fluids, to lacustrine or supergene environments (formed possibly from CO<sub>2</sub>-facilitated oxidation [5] of Fe<sup>2+</sup> in sulfides and H<sub>2</sub>S in aqueous fluids).

Determining the origin of alunite and jarosite in terrestrial environments can be accomplished using stable isotopes; however, this method requires laboratory analyses [2, 3]. A spectroscopic tool that could be used from orbit to distinguish between such environments may prove valuable in selecting future landing sites with the highest potential for preserving evidence of past life.

Jarosite and alunite have detectable spectral features in the 1.3 to 2.5 micron region that can be used to determine their Na and K composition in the laboratory [6]. Reflectance spectra of jarosites and alunites synthesized at different temperatures (95 to 200C and 150 to 450C respectively) show OH-related vibrational absorptions that become narrow and more intense in the higher-temperature samples. A possible explanation for this behavior is the protonation of hydroxyls that charge balance Fe and Al deficiencies in low-temperature synthetic jarosite and alunite. Replacement by H<sub>2</sub>O of one or more of the three hydroxyls, which are each hydrogen bonded to an apical sulfate oxygen, disrupts strong vibrational coupling, thereby weakening the spectral absorptions. When these samples are heated, the protonated hydroxyls are liberated as "excess water," and recrystallization produces fully hydroxylated crystals with intense spectral features that resemble those of natural high-temperature jarosite and alunite. Synthetic hydronium jarosite and alunite spectrally resemble low-temperature synthetic Fe-deficient jarosite and Al-deficient alunite, respectively. Proton transfer from the H<sub>3</sub>O<sup>+</sup> ion to the OH site in synthetic hydronium jarosite increases chemical disorder on its OH sites [7], also resulting in muted spectral features. This also applies to hydronium alunite.

Temperature-dependent spectral variations have been observed for 70 natural alunite samples formed at temperatures ranging from 20 to 400C. Spectral observations of 19 natural jarosite samples showed only a temperature dependency for a recently formed stalactitic hydronium-bearing jarosite from Iron Mountain, California. This jarosite had broad, weak absorptions characteristic of the low-temperature synthetic jarosites. All the other jarosite samples, including those formed in supergene environments (<80C), have narrow, intense absorptions similar to high-temperature synthetic jarosites. A likely explanation for the spectral similarity of all aged jarosites is the tendency for them to recrystallize into alkali endmembers over time. XRD analysis of 32 natural hydrothermal and supergene K- and Na-jarosites determined that intermediate compositions are absent, and instead, mixtures of discrete K and Na endmembers typify most samples [8]. The recrystallization likely results in loss of protonated hydroxyls in the lattice that are diagnostic of formation temperatures. This is not the case for natural alunite, which apparently does not undergo extensive recrystallization over time.

If alunite is exposed on the surface of Mars over a sufficiently large area, then the CRISM spectrometer should detect it and determine its K and Na composition as has been shown using AVIRIS spectra collected over Cuprite, Nevada [9]. This spectrophotometer also could be used to differentiate between alunite in high-temperature, relict, acid-sulfate hydrothermal systems and low-temperature, acid-saline lacustrine sediments. Selection of Martian landing sites to seek evidence of past life could be guided by sulfate alteration minerals. Which has the greatest probability of preserving evidence of life, alunite-bearing, low-temperature supergene and lacustrine rocks or alunite-bearing, hydrothermally-altered rocks? This spectrophotometer and others like it may be useful tools for selecting interesting landing sites from Mars orbit.

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**CHEMICAL DIVIDES AND VARIATION IN MARTIAN SALINE MINERALOGY.** N. J. Tosca<sup>1</sup> and S. M. McLennan<sup>1</sup>, <sup>1</sup>Department of Geosciences, SUNY at Stony Brook, Stony Brook, NY 11794-2100 (ntosca@ic.sunysb.edu)

**Introduction:** Characterization of evaporitic environments at the martian surface remains a priority for Mars exploration. Saline mineral assemblages, now identified and characterized by missions such as MER and MEx, can retain detailed chemical characteristics about their parent fluids, potentially yielding properties such as pH, oxidation state, anion content (and hence atmospheric volatile input), and dominant weathering processes. The interplay of this information is complex, but on Earth, the “chemical divide” concept has been used with much success in unraveling these properties. However, the fundamental differences in surface geochemistry between Earth and Mars prevent the direct use of the terrestrial chemical divide system and its predictive capabilities. Accordingly, we have suggested a new chemical divide system for the martian surface that predicts evaporite assemblages identified in SNC-meteorites, ancient evaporites identified by the MER mission, as well as Mars Express OMEGA [1].

**Dilute fluid chemistry and chemical divides at the martian surface:** The mineralogy of a saline assemblage is already pre-determined at the time the dilute fluid has acquired solute and evaporation has begun. Indeed, understanding possible variation in martian fluid chemistry translates to understanding variation in saline minerals across the planet, the frequency of their occurrence, and modes and timing of their formation.

During evaporation, the precipitation of each saline mineral will create a turning point in the outcome of the entire saline assemblage. This turning point can be referred to as a chemical divide – it occurs when the precipitating mineral consumes two chemical components in a different ratio than their abundance in the fluid.

One of the most important controls on solute acquisition of any surficial fluid is the chemical weathering of crustal materials. On Mars, where the crust is almost entirely basaltic in composition, fluids weathering the crust will be dominated by Mg, SiO<sub>2</sub>(aq), Ca and, under acidic conditions, Fe. At the martian surface, chemical weathering reactions will be driven by acid input and the consumption of acidity by mineral dissolution will compete with this process to increase pH levels. The variation in pH will in turn control the anion balance, which may be imposed on the system by the atmosphere. For Mars, SO<sub>4</sub>, HCO<sub>3</sub> and Cl are the most important anions to the system, controlled mainly by volcanic input and a high pCO<sub>2</sub> atmosphere.

Taken together, the cation ratio present in surficial fluids will be determined by basaltic weathering and

the inter-dependence of pH, HCO<sub>3</sub>, SO<sub>4</sub> and Cl content serves as the major source of variation in anion composition of martian surface waters.

Geochemical modeling of varying solution compositions according to the model above permits us to identify the major saline precipitates and resulting assemblages. By constructing a detailed chemical divide scheme for this system, the possible products and their modes of formation under acidic conditions are identified and can be used for predictive capabilities.

**Application to current and future mineralogical data:** The chemical divide system described above predicts the occurrence of the saline assemblages identified in the SNC meteorites, and specifically, in the Nakhla meteorite (representing the most advanced stage of evaporation). The distinct chemistry of these parent fluids corresponds to a mixed, sulfate-carbonate geochemical environment. The implications of the SNC mineralogy and their formation pathways points to slow Fe oxidation, only mildly acidic pH and HCO<sub>3</sub> input, possibly confined to the subsurface where atmospheric cutoff allows pH to increase.

The geochemical environment giving rise to the saline minerals identified by the MER rover resides on the opposite end of the spectrum from the SNC mixed carbonate-sulfate environment. Acidity in the parent fluids need only to overcome carbonate alkalinity to result in an entirely sulfate-dominated mineral assemblage. Low pH may have been attained by any combination of acid volatile input, evaporation, Fe oxidation and hydrolysis, or sulfate-mineral recycling. This chemistry may have been attained by constant exposure to the atmosphere and high acidic-volatile input. Such a geochemical environment is also consistent with OMEGA-derived sulfate mineralogy. In comparing these two environments, it is clear from the system of chemical divides that a common fluid type simply buffered to varying degrees by chemical weathering can explain the variation observed in martian saline assemblages.

Perhaps more importantly, our chemical divide system shows that at least three factors are responsible for the unique saline mineralogy observed at the surface of Mars: (1) acidic environments controlled by SO<sub>4</sub>, HCO<sub>3</sub> and Cl input, (2) increased mobility and concentration of Fe in aqueous systems, and (3) dilute water chemistry dominated by the weathering of a basaltic regolith.

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**SULFATE-BEARING MINERALS IN THE MARTIAN METEORITES.** A. H. Treiman, Lunar & Planetary Institute, 3600 Bay Area Blvd., Houston TX 77058 <treiman{at}lpi.usra.edu>.

**Introduction:** The Martian meteorites contain Martian, water-deposited sulfate-bearing materials [1,2] – direct positive evidence of sulfate and other volatiles in the Martian hydrosphere. These materials are invaluable for understanding Martian chemical hydrology, as they can be characterized for structure, chemistry, and isotope ratios using the most sophisticated instruments on Earth. Commonly, Martian sulfatic materials are difficult to distinguish from terrestrial deposits and alterations. In addition, the environments and processes of terrestrial alteration are under active study [3,4], and alteration features at the sub-micron level can be ambiguous [5,6]. Despite these issues, interest in sulfates in Martian meteorites is strong, benefiting from new instrumental methods, and synergy with results from spacecraft at Mars.

**Nakhlites:** The nakhlites are augite-rich cumulate igneous rocks, which contain clay-rich alteration material (iddingsite), Fe-Mn carbonate, halite, and Ca sulfate (anhydrite and/or gypsum) [2]. Several apparently contain jarosite (by EMP analyses [7,8,9]). These materials were deposited by aqueous solutions in void-space produced by dissolution of olivine. Deposition of carbonate and sulfate may precede, and overlap with, deposition of clay [10]. Nakhla also contains Mg-sulfate along cracks [11].

Stable isotopic data show that these minerals are Martian, and that their source was in chemical communication with the Martian atmosphere.  $\delta D$  of the iddingsite ranges up to  $\sim +750\%$  [12], consistent with admixture of atmospheric H.  $\Delta^{17}O$  of the iddingsite, carbonate, sulfate are  $+0.6 - +1.4\%$  [13-15], much higher than the anhydrous silicates, and ascribed to the Martian atmosphere. Sulfur from the sulfates shows strong non-mass-dependent fractionations suggestive of atmospheric photochemical reactions [16]. These isotope data suggest that the water and solutes involved in nakhlite alteration were derived from (and processed through) the Martian atmosphere, and had limited prior interactions with Martian igneous rocks.

**EETA79001:** Shergottite EETA 79001 contains the purest known samples of Martian atmosphere gases [17], and has a rich assemblage of alteration salts: Ca-sulfate, S-Cl-bearing aluminosilicate (poorly defined), calcite, Mg-phosphate, and a Pb-S-Cr mineral [18,19]. The last may be  $Pb_2O(SO_4, CrO_4)$  [20]. The origin of these salts is not clear. Some of the carbonate is terrestrial by  $^{14}C$  [21], while  $\delta^{13}C$  and  $\delta^{18}O$  suggest an extraterrestrial source [22]. The textures are (to me) not conclusive of a Martian origin [18,19].

**Other Martians:** Little is known about Martian sulfate alteration materials in other meteorites. ALH 84001 contains abundant carbonate minerals, but little or no sulfate [23]. Chassigny contains Ca-sulfate and Ca-Mg carbonates (with traces of Cl and P), along grain boundaries [24]. Shergotty contains Ca sulfate, halite, an Mg sulfate, and phyllosilicates along fractures [25]. Shergottite QUE 94201 contains a rich assemblage of Ca-sulfate, Fe-sulfate, K-Fe sulfate (jarosite?), Mg-phosphate, silica, and S-Cl-bearing aluminosilicate. Their textures, however, are consistent with a terrestrial origin [26]. ALH77005 contains aqueous replacements of olivine and chromite [27]; the latter are rich in K, S, and P and may include jarosite ([28], K. Kuebler, pers. comm.).

**Conclusion:** Aqueous alteration materials in the Martian meteorites contain sulfate minerals: anhydrite and/or gypsum, Mg-sulfate, jarosite (?), and S-bearing aluminosilicates (clays?). These minerals can provide crucial information on Martian aqueous processes and chemistry, if they can be proven to be Martian.

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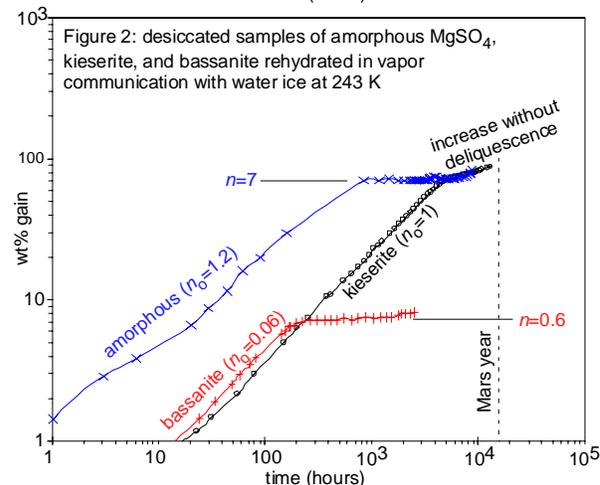
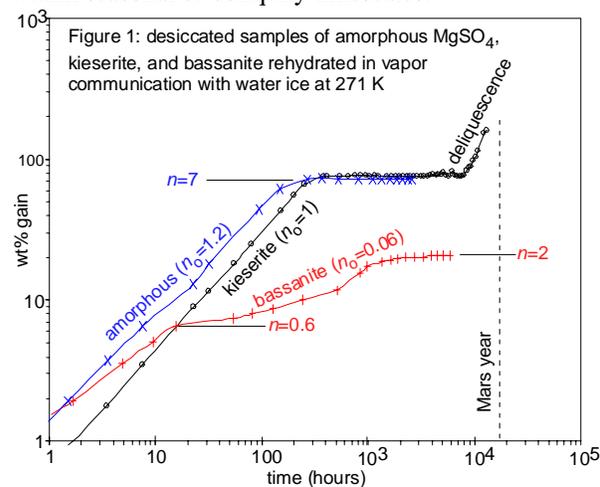
**RATES AND MODES OF HYDRATION IN Mg- AND Ca-SULFATES ON MARS.** D. T. Vaniman and S. J. Chipera, Hydrology, Geology and Geochemistry, Group EES-6, MS D462, Los Alamos National Laboratory, Los Alamos NM, 87545 (vaniman@lanl.gov).

**Introduction:** Many salts and salt hydrates may be present on Mars. Here we consider the simple sulfate salts  $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$  ( $n=1$  to 7, but  $n$  of 11 or 12 may be possible) and  $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$  ( $n=0$  to 2). Experiments at low  $p\text{H}_2\text{O}$  indicate that if derived from forms with higher values of  $n$ , at least some Mg-sulfates with low values of  $n$  are amorphous [1]. However, more hydrous forms such as epsomite ( $n=7$ ) may be stable at higher latitudes where near-surface water ice persists [2]. Spectral data indicate that near-equatorial Ca-sulfate forms are hydrated, but do not constrain the value of  $n$  [3]. Gypsum may be common at all latitudes, but high-temperature events (volcanism, impact, metamorphism) may produce less hydrated forms such as bassanite ( $n \sim 0.5$ ) or anhydrite ( $n=0$ ). Even at modestly elevated temperature (297 K), bassanite forms from gypsum with prolonged exposure to Mars-like  $p\text{H}_2\text{O}$  ( $\sim 100$  hours at  $p\text{H}_2\text{O}$  of  $\sim 0.7$  Pa; [4]). Impact distribution or eolian transport can move sulfates from zones with one persistent hydration state to zones where they may either desiccate or hydrate.

**Hydration Rates and Products:** Figure 1 compares hydration of three salts at 271 K – kieserite ( $n_0=1$ ), amorphous Mg-sulfate ( $n_0=1.2$ ), and desiccated bassanite ( $n_0=0.06$ ). Hydration was at 100% RH controlled by water ice. Kieserite and the amorphous Mg-sulfate pass through states of hydration equivalent to several different phases (e.g., sanderite, starkeyite, pentahydrate, hexahydrate), but the hydration curves show no inflection at these hydration states, indicating that intermediate phases either do not form or they present no energy barriers to further hydration. The curves do however have pronounced inflection where epsomite is fully formed ( $n=7$ ); epsomite persists for  $\sim 7,000$  hours before deliquescence begins. In contrast, the desiccated bassanite hydrates rapidly to  $n \sim 0.6$ , where the hydration rate slows before accelerating again to the point where gypsum is fully formed ( $n=2$ ).

Figure 2 shows hydration of the same three desiccated salts at 243 K with RH controlled at 100% by water ice. There are no significant inflections in the Mg-sulfate hydration curves up to  $n=7$ . X-ray diffraction shows early formation of hexahydrate with in-growth of epsomite; less hydrous forms do not appear. Hydration of amorphous starting material is significantly more rapid than kieserite. The kieserite starting material shows a strong decrease in hydration rate at  $n=7$  but does not plateau at  $n=7$ . Beyond  $\sim 4000$  hours both Mg-sulfates show a slow increase in weight; it is

yet to be determined whether these second-stage hydration curves will lead to crystalline forms of higher hydration ( $n=11$  or  $12$ ); at this low temperature (27 degrees below the freezing point of saturated Mg-sulfate solution) deliquescence will not occur. Desiccated bassanite hydrates to  $n \sim 0.6$  within 200 hours, but at 3,000 hours there is yet no indication of further hydration toward gypsum (experiment in progress). At 243 K hydration can occur in less than one Mars year, but preliminary data indicate that this is not the case at 190 K. Further studies will evaluate whether desiccated forms migrated to higher latitudes can rehydrate within seasonal or obliquity timescales.



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**OLIVINE AND SECONDARY SULFATE MINERALS IN CHASSIGNY AND OTHER MARS METEORITES: COMPARISON WITH INCIPIENT WEATHERING OF TERRESTRIAL DUNITIC AND BASALTIC OLIVINE.** M. A. Velbel<sup>1</sup>, S. J. Wentworth<sup>2</sup>, and J. M. Ranck<sup>3</sup>, <sup>1</sup>Department of Geological Sciences, 206 Natural Science Building, Michigan State University, East Lansing, MI 48824-1115 (velbel@msu.edu), <sup>2</sup>ESCG, Mail Code JE23, Johnson Space Center, Houston, TX 77058 (susan.j.wentworth@nasa.gov), <sup>3</sup>Affiliation URS Corporation-North Carolina, 1600 Perimeter Park Drive, Morrisville, NC 27560 (mike\_ranck@urscorp.com).

**Introduction:** Sulfates have been reported from several Mars meteorite falls [1] encompassing a variety of igneous rock types, including Chassigny (dunite) [1,2], Nakhla (clinopyroxenite) [1,3], and Shergotty (basalt) [1], as well as in a number of Mars meteorite finds [1,4,5]. The Mars Exploration Rovers have revealed the importance of sulfates in Mars' surface materials. This contribution describes the occurrence of sulfate minerals in Chassigny and several olivine-rich terrestrial rocks that might serve as analogs for the onset of aqueous alteration in Chassigny.

**Previous work:** *Olivine and sulfates in dunite: Chassigny.* Wentworth and others [1] reported various Ca-sulfates on exposed olivine grain-boundary fracture surfaces in the Martian dunite Chassigny. In addition to occurrences of individual evaporite minerals, some disk-shaped masses occur with non-porous Ca-sulfate in the center, surrounded by microgranular/porous (devolatilized?) Ca-carbonate [1].

*Silicates and sulfates in Nakhla and Shergotty.* Wentworth et al. [1] reported striated (corroded) Ca-sulfate in Nakhla, superposed in some instances by halite [6]. They also reported several occurrences of evaporites in Shergotty [1,6], in which corroded Ca-sulfate occurs on an unmodified silicate surfaces.

**Methods:** Samples of Chassigny and several terrestrial olivine-rich rocks were fragmented exposing natural fracture surfaces, coated with Au or Au-Pd, and examined by conventional and field-emission-gun (FEG-) scanning electron microscopy (SEM).

**Results:** SEM images reveal local, fracture-filling disk-shaped patches of microgranular or porous material similar to the porous carbonate/sulfate patches previously reported from Mars meteorites, in ostensibly "fresh" (mineral-teaching-collection) dunite from North Carolina. Olivine in the terrestrial dunite is locally corroded by typical anhedral, funnel-shaped etch pits identical to those observed elsewhere [7,8]. In some instances, the etch pits are directly associated with small amounts of cornflake-textured clay-like material; much similar material occurs unrelated to etch pits in this and other samples. In neither Martian nor terrestrial dunite observed to date are secondary non-clay products (sulfates or carbonates) associated with olivine etching/corrosion features (e.g., etch pits, mammillary surfaces). Furthermore, while possible

corrosion textures have been observed in other Mars meteorites [1], such corrosion features have not been observed to date in Chassigny. Anhedral olivine etch pits like those common on terrestrially weathered olivines [7,8] are observed in other parts of the "fresh" teaching-collection terrestrial dunite, but not in direct association with fracture-filling products.

**Discussion:** Olivine etch pits on the "fresh" terrestrial dunite indicate either pre-weathering aqueous alteration of olivine, or that small amounts of weathering affected the sample despite its fresh appearance. Sulfate is likely not the original form of S in dunite. Any sulfates in dunite may have formed by oxidation of primary sulfide minerals. However, sulfide oxidation in the presence of water usually forms sulfuric acid, suggesting that sulfate formation by this process should be accompanied by corrosion features typical of acid dissolution of olivine. The lack of direct association of secondary evaporites with corrosion features on primary olivine in the terrestrial analog dunite suggests that, in these cases, olivine exposed at grain-boundary and grain-traversing fractures was a passive substrate for the deposition of the evaporites, and that the olivine did not react directly or locally with the solutions from which the evaporites precipitated. It remains to be established whether sulfate introduced into olivine fractures is indigenous to the parent rock or transported into the fractures from other regolith materials. The lack of association between olivine corrosion and secondary sulfates favors the latter. If so, occurrences of sulfate minerals in Mars meteorites may be related to sulfate-bearing surface- and groundwaters inferred to have been important in Mars' surface and near-surface aqueous environments.

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**HYDRATION STATE OF MAGNESIUM SULFATES ON MARS.** Alian Wang, John J. Freeman, Bradley L. Jolliff, Department of Earth & Planetary Sciences and McDonnell Center for the Space Sciences, Washington University, St. Louis, MO, 63130 ([alianw@levee.wustl.edu](mailto:alianw@levee.wustl.edu))

**Introduction:** Mg-sulfate has been found on Mars by the Mars Exploration Rovers (MER) <sup>[1,2,3]</sup> and by OMEGA/Mars Express <sup>[4,5,6]</sup>. The MER data do not directly measure the hydration state of these Mg-sulfates; however, OMEGA spectra suggest kieserite ( $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ) and “Polyhydrated sulfates.” Knowledge of the hydration state of Mg-sulfates currently at or near the surface of Mars is important to tie these evaporate minerals with the hydrogen detected by the Neutron Spectrometer on the Mars Odyssey orbiter <sup>[7]</sup>. More importantly, their structural character (e.g., crystallinity) and hydration states could be crucial indicators for short-term and long-term hydrologic evolution on Mars. The specific mineralogy of sulfur is also significant in martian  $\text{H}_2\text{O}$  and S cycles, and may play key roles in the potential for habitability.

**Experiments:** We have studied the stability field and phase transition pathways of hydrous Mg-sulfates

using Raman spectroscopy as the major analytical method, accompanied by mass-loss measurements, XRD, and IR spectroscopy. Eighty six samples of pure Mg-sulfates and mixtures of Mg- and Ca-sulfates were studied over 1000 hours at 10 different relative humidities and two temperatures, with 4 different hydration states as starting phases.

**Results:** Four major results were obtained from these experiments. Figure 1 shows the Raman spectra from this study <sup>[8,9,10]</sup>, with hydration states ranging from anhydrous through 12  $\text{H}_2\text{O}$ , and  $\text{MgSO}_4$  in solution. Fig. 2a shows Raman spectra from mixed hydrous Mg-sulfates, which represent experimental products.

(1) Amorphous Mg-sulfate can be formed readily from epsomite and hexahydrate, but not from starkeyite or kieserite, through fast vacuum dehydration or slow dehydration under dry condition (5.5% RH). An amorphous

structure can hold up to 3  $\text{H}_2\text{O}$  per  $\text{MgSO}_4$  molecule at  $50^\circ\text{C}$ , and is stable under extremely dry (5.5% RH) conditions.

(2) Starkeyite is stable at extremely dry conditions (5.5% RH) at  $21^\circ\text{C} \leq T \leq 50^\circ\text{C}$ . The NIR spectral patterns of starkeyite and amorphous Mg-sulfates match the OMEGA spectrum of “Polyhydrated sulfates”.

(3) At  $T \leq 50^\circ\text{C}$ , kieserite is not formed by either fast or slow dehydration of epsomite, hexahydrate, or starkeyite, but can be formed from slow dehydration of amorphous Mg-sulfates and from a mixture of hexahydrate and Ca-sulfate (Fig.2b).

(4) The dehydration rate of hexahydrate can be greatly reduced (over 10 times) when it is first mixed with Ca-sulfates of all hydration states.

**References:** [1]. Klingelhoefer et al., 2004, Science; [2] Haskin et al., 2005, Nature; [3] Wang et al., 2006a, JGR; [4] Bibring et al., 2005 Science; [5] Gendrin et al., 2005, Science; [6] Arvidson et al., 2005 Science, [7] Feldman et al., 2006 JGR., [8] Wang et al., 2006b, 37<sup>th</sup> LPSC; [9] Wang et al., 2006c, 37<sup>th</sup> LPSC; [10] Wang et al., GCA, in press.

Figure 1. Raman spectra of hydrous & anhydrous, crystalline and amorphous Mg-sulfates as the basis of the current study<sup>8,9,10</sup>

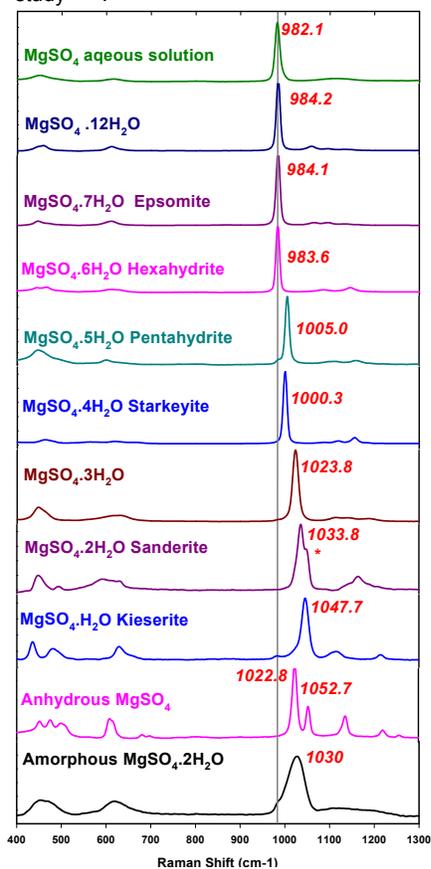
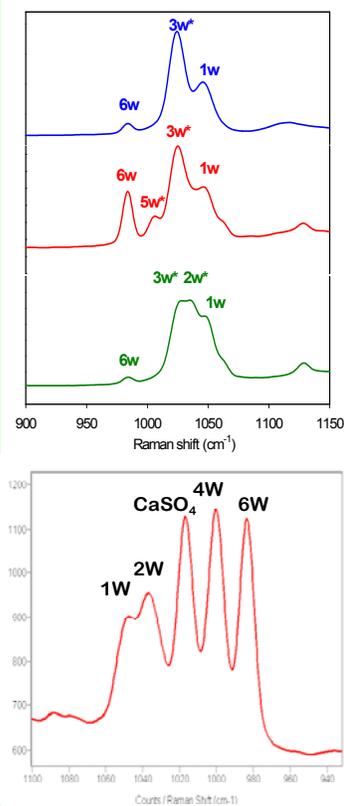


Figure 2. (a) Raman spectra of Mg-sulfate mixtures; (b) 1w- & 2w- (in addition to 4w-)  $\text{MgSO}_4$  can be produced from the dehydration of hexahydrate, when it is first mixed with Ca-sulfates.



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**Introduction:** Sulfates appear to be abundant on Mars. The ultimate source of the sulfate was probably volcanic gases [1], much as it would have been on Earth before the advent of atmospheric oxygen [2]. Isotopically fractionated S found in martian meteorites confirm that at least some martian sulfate had its origin in photochemically processed atmospheric gases [3].

The chief volcanic sulfur gas on Earth is SO<sub>2</sub>. If anything, SO<sub>2</sub> would be more dominant for Mars, whose basalts are much drier than Earth's and hence less capable of emitting H<sub>2</sub>S. We might expect other reduced volcanic gases –H<sub>2</sub> and CO – to be less important on Mars as well.

Ancient volcanic SO<sub>2</sub> fluxes are estimated presuming that the global mean sulfate cover is 100 m thick, and that the volcanoes erupted for 0.5 Gyrs. This gives an average SO<sub>2</sub> injection rate of 4e9 molecules/cm<sup>2</sup>/s. This is about twice the current terrestrial average.

In an oxidized atmosphere SO<sub>2</sub> is invariably oxidized to SO<sub>3</sub>, which quickly hydrates to make sulfuric acid. This is SO<sub>2</sub>'s fate on Earth, and it is SO<sub>2</sub>'s fate on Mars if the volcanoes are extinct enough. But in a neutral or reduced atmosphere the source of oxygen to make SO<sub>3</sub> from SO<sub>2</sub> becomes an issue.

For ancient Mars, the thriving volcanoes needed to generate 100 m of sulfate greatly exceed the capacity of hydrogen escape to oxidize the atmosphere. The only real alternative is for SO<sub>2</sub> to disproportionate, so that as some SO<sub>2</sub> is oxidized to SO<sub>3</sub>, other SO<sub>2</sub> is reduced to elemental sulfur. In the limit one expects 24SO<sub>2</sub> + photons → 16SO<sub>3</sub> + S<sub>8</sub>. We therefore expect that elemental sulfur would have been a significant product of atmospheric photochemistry.

Here Earth provides a reality check. Terrestrial sediments older than 2.46 Ga preserve strong signatures of distinctively mass fractionated sulfur [4]. The fractionations undoubtedly took place in the atmosphere. The tricky bit is how they reached the sediments with fractionations intact. The best answer is that particles of elemental sulfur fell from the sky [5]. Elemental sulfur is insoluble in water and thus, while all other sulfur species dissolve together in vast salty seas, elemental sulfur does not. It makes its own way by its own path into the geologic record.

**The photochemistry model:** In order to make quantitative predictions we developed a 1D photochemical model.

The central fact of martian photochemistry is the O<sub>2</sub>/CO ratio. In steady state, the O<sub>2</sub>/CO ratio is determined by how much O<sub>2</sub> needs to build up in the atmosphere to make the oxygen sink big enough to balance hydrogen loss to space. This means that the key question is to identify the oxygen sink. To apply a photochemical model to the redox state of ancient martian atmospheres (those with more SO<sub>2</sub>, those with more CO<sub>2</sub>, or both) requires specifying the processes that govern H escape and O loss.

Our model does a good job with O<sub>2</sub>, CO, and H<sub>2</sub>O<sub>2</sub>, it underpredicts O<sub>3</sub>, and it overpredicts H<sub>2</sub> for the current best estimates of the rate of H escape to space. In short it closely resembles all other 1D photochemical models [6-8]. The distinctive feature of our model is that it works by chemical reactions at the surface; i.e., our model presumes that hydrogen escape is directly balanced by soil oxidation. We implement this by assuming a single deposition velocity for all reactive gases. Currently H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> are the most important.

Our model features an extensive sulfur photochemistry that includes H<sub>2</sub>SO<sub>4</sub>, SO<sub>3</sub>, SO<sub>2</sub>, SO, S, S<sub>2</sub>, S<sub>3</sub>, S<sub>4</sub>, S<sub>8</sub>, OCS, HS, and H<sub>2</sub>S, and also H<sub>2</sub>SO<sub>4</sub> and S<sub>8</sub> aerosols. Both kinds of aerosols can precipitate.

Preliminary results indicate that the transition between oxidized and reduced 6.3 mbar martian atmospheres begins when the SO<sub>2</sub> source reaches 2e8 molecules/cm<sup>2</sup>/s (~10% of modern terrestrial levels). The onset of elemental sulfur precipitation occurs at 2e9 molecules/cm<sup>2</sup>/s, and at 1e10 (exuberant volcanoes) more than 20% of the sulfur precipitates as the element. The model also predicts that reduced sulfur gases, especially SO and SO<sub>2</sub>, would be likely to react directly with the soils at significant rates.

Preliminary results indicate that the redox state of the martian atmosphere is sensitive to pCO<sub>2</sub>, with higher pCO<sub>2</sub> levels producing more reduced atmospheres. CO becomes a major gas for pCO<sub>2</sub> > 200 mbars.

**References:** [1] Settle M. and Greeley R. (1979) *JGR* 84, 8343–8354. [2] Walker J. C. G. and Brimblecombe P. (1985) *Precambrian Res.* 28, 205-222. [3] Farquhar J. et al. (2000) *Nature* 404, 50–52. [4] Farquhar J. and Wing B. (2003) *E.P.S.L.* 213, 1–13. [5] Ono S. et al. (2003) *E.P.S.L.* 213, 15-30. [6] Nair H. et al. (1994) *Icarus* 111, 124-150. [7] Atreya S. and Gu H. (1994) *JGR* 99, 13133-13145. [8] Krasnopolsky V. A. (1993) *Icarus* 101, 313-332.