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TERRESTRIAL SULFATES IN AN EXTREME ACID MINE DRAINAGE ENVIRONMENT: THE RICHMOND MINE AT IRON MOUNTAIN, CALIFORNIA. Charles N. Alpers¹, U.S. Geological Survey, California Water Science Center, 6000 J St., Placer Hall, Sacramento, CA 95819-6129, cnalpers@usgs.gov

Introduction: The Iron Mountain mining district, in the Klamath Mountains of northern California, is host to some of the most extremely acid mine waters ever documented and a spectacular array of associated iron-sulfate minerals [1, 2, 3]. Oxidation of massive sulfide deposits consisting of > 95 % pyrite in rhyolitic host rocks with minimal acid-neutralization potential has led to mine waters with pH values as low as -3.5 and concentrations of dissolved iron and sulfate of several molar [1]. The underground tunnels and stopes of the Richmond mine at Iron Mountain have provided a useful laboratory for improving the understanding of hydrogeochemical, mineralogical, and microbiological processes associated with sulfide mineral oxidation and the formation of iron-sulfate minerals. Some of the hydrogeochemical and mineralogical characteristics observed on a large scale within the Richmond mine may occur on a smaller scale in other settings, such as other mine drainage and mine-waste environments. Because jarosite and other iron-sulfate minerals likely occur on the surface of Mars [4, and references therein] it is useful to describe the mineralogy and geochemistry of the sulfate minerals and associated water chemistry as a possible analog to conditions that may have occurred during Martian history.

Mineralogy and Water Chemistry: Table 1 lists idealized formulas for the principal iron-sulfate minerals found in the Richmond mine in their general sequence of formation. The oxidation of pyrite proceeds by a reaction in which ferric iron (Fe³⁺) is the oxidant and ferrous iron (Fe²⁺) is a product. As long as an acid mine water is in contact with pyrite, the dissolved Fe will remain predominantly in the ferrous state because of the strong reducing capacity of the pyrite. Rapidly flowing mine water will still maintain a high proportion of Fe²⁺ because the oxidation rate typically is slow relative to the flow rate of the water. Within the Richmond mine, Fe-sulfate salts containing exclusively Fe²⁺ (melantherite, rozenite, and szomolnokite) are found close to pyrite sources and associated with the more rapidly flowing waters. Fe³⁺-bearing sulfate minerals were observed to form in more stagnant conditions, spatially removed from pyrite mineral surfaces [3].

The Fe-S molar ratio (Fe/S) is an important factor in determining both the acidity of weathering solutions and the mineralogy of iron-sulfate weathering products. The excess of S in the stoichiometry of pyrite (Fe/S = 0.5) leads to abundant sulfuric acid upon oxidation. A systematic relation was found between the

pH of the mine water and the Fe/S of Fe³⁺-sulfate weathering products. Rhomboclase (Fe/S = 0.5) is associated with waters of pH less than -3. Copiapite group minerals, coquimbite, römerite, and voltaite (Fe/S between 0.67 and 1.0) are associated with waters of pH between -0.9 and -2.6 [5]. Jarosite group minerals (Fe/S = 1.5) are associated with water in the pH range 1.5 to 3 [6]. In other settings, schwertmannite [Fe₈O₈(OH)_{8-2x}(SO₄)_x, Fe/S = 5 to 8] is associated with weathering solutions in the pH range of 3 to 5 [7].

Conclusions: Some insights into the systematics of iron-sulfate mineral formation have been gained from initial studies of the mineralogy and geochemistry of weathering products at Iron Mountain, California. Additional work on mineral solid solutions and thermodynamic properties of minerals and aqueous solutions are needed to develop predictive models that would be helpful in understanding mineral formation in mine drainage settings and in other environments such as the surface of Mars.

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TABLE 1. IDEALIZED FORMULAS OF THE IRON-SULFATE MINERALS THAT OCCUR IN THE RICHMOND MINE, IRON MTN., CA

<u>Mineral</u>	<u>Idealized Formula</u>
Melantherite	Fe ²⁺ SO ₄ ·7H ₂ O
Rozenite	Fe ²⁺ SO ₄ ·4H ₂ O
Szomolnokite	Fe ²⁺ SO ₄ ·H ₂ O
Magnesiocopiapite	MgFe ³⁺ ₄ (SO ₄) ₆ (OH) ₂ ·20H ₂ O
Römerite	Fe ²⁺ Fe ³⁺ ₂ (SO ₄) ₄ ·14H ₂ O
Coquimbite	Fe ³⁺ ₂ (SO ₄) ₃ ·9H ₂ O
Kornelite	Fe ³⁺ ₂ (SO ₄) ₃ ·7H ₂ O
Rhomboclase	(H ₃ O)Fe ³⁺ (SO ₄) ₂ ·3H ₂ O
Voltaite	K ₂ Fe ²⁺ ₅ Fe ³⁺ ₄ (SO ₄) ₁₂ ·18H ₂ O
Halotrichite-	Fe ²⁺ Al ₂ (SO ₄) ₄ ·22H ₂ O -
Bilinite	Fe ²⁺ Fe ³⁺ ₂ (SO ₄) ₄ ·22H ₂ O
Jarosite	(K,H ₃ O,Na)Fe ₃ (SO ₄) ₂ (OH) ₆

THE SEDIMENTARY ROCKS EXPOSED IN TERRA MERIDIANI. R. E. Arvidson¹, ¹Washington University, St. Louis, MO 63130, arvidson@wunder.wustl.edu.

Introduction: In this abstract the observations acquired by the Mars Exploration Rover, Opportunity [1], and the orbital data acquired by the Mars Express OMEGA hyperspectral imager for the sedimentary rocks in Terra Meridiani [2-5] are jointly analyzed, and a model is presented for the formation and modification of the deposits.

Observations: The traverses and observations completed by Opportunity show that the Meridiani plains consist of sulfate-rich sedimentary rocks that are covered by poorly-sorted basaltic aeolian sands and a lag of granule-sized hematitic concretions. Orbital spectra obtained by OMEGA over this region are dominated by pyroxene, plagioclase feldspar, crystalline hematite (i.e., concretions), and nano-phase iron oxide dust signatures, consistent with Pancam and Mini-TES observations. Mössbauer Spectrometer observations indicate more olivine than observed with the other instruments, consistent with preferential optical obscuration of olivine features in mixtures with pyroxene and dust.

A ~1 km vertical section of etched terrain and hematite-bearing plains materials and nearby cratered terrain surfaces was mapped in the northern portion of Meridiani Planum (~390 km to the northeast of Opportunity) using OMEGA data. The oldest materials are the cratered plains, which are dominated by a mix of low and high calcium pyroxenes. Etched plains materials overlie this unit and are exposed within a 120 km NW-SE trending valley to the south of the cratered plains. Lower etched plains materials exhibit a kieserite-like signature on a plateau-forming horizon and polyhydrated sulfate-like signatures on the main valley floor. The upper etched plains unit exhibits signatures consistent with hydrated iron oxides and is covered by a relatively thin layer of basaltic sand and hematitic concretions. The youngest unit consists of ejecta deposits from a cluster of six craters that mantle the eastern portion of the study area.

Model: The most plausible regional-scale model for formation of the Meridiani deposits is one in which the water table rose relative to the dissected cratered terrain surfaces, resulting from tectonic subsidence and/or enhanced recharge of the cratered terrain highlands to the southwest. A regime of relative uplift and dissection switched to one of relative subsidence and sedimentary accumulation onto the cratered terrains. The several kilometers of relief between the cratered highlands to the northwest and the dissected cratered terrains to the southeast would have produced the hydrostatic head necessary for regional-scale ground

water flow. In fact, regional scale modeling of ground water flow indicates that the Meridiani area would be one where ground water would upwell toward the surface [6]. Sulfur and other volatile species were introduced to the hydrologic system as a consequence of extensive volcanism from Tharsis (and other) volcanoes and/or by weathering of pre-existing sulfur-bearing deposits and would have produced an acid-sulfate ground water system.

Relative rise of the groundwater table resulted in the development of springs and playa lakes of high ionic strength within local topographic depressions. Desiccation of these local, shallow water bodies would have provided a ready source of "dirty evaporite" deposits dominated by sulfates and weathered siliciclastic components. Evaporation of pore fluids within the capillary fringe, or surface water within playa lakes, would have precipitated evaporite minerals as cements that bound siliciclastic grains together [7,8]. During dry periods, erosion and redistribution of these cemented mudstones would have occurred by aeolian processes and during wetter periods by water flow. Preservation would have been assured as the ground water table continued to rise, with associated diagenetic processes and cementation of deposits within the capillary fringe. New evaporite and related deposits would have continued to accumulate at the depositional surface as the water table continued to rise, and rose to form shallow pools that became evaporitic playas.

After the Meridiani hydrologic system ceased operating, aeolian processes would have taken over as the dominant process. The modern Meridiani plains formed via wind erosion of the sulfate-dominated sedimentary deposits, and accumulation of a thin veneer of aeolian basaltic sand advected into the region. Hematitic concretions formed as lag deposits as the softer sulfate rocks were eroded by wind. Occasional sulfate outcrops were exposed via cratering and in-between aeolian ripples, where the basaltic sand cover is thinnest.

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Detection of the Hydration Phase of Martian Sulfates Using Emission Spectroscopy of Magnesium and Calcium Sulfates. A. M. Baldridge¹ and P. R. Christensen¹, ¹School of Earth and Space Exploration, Arizona State University, M.C. 6305, Tempe, AZ, 85287-6305 alice.baldridge@asu.edu.

Introduction: Orbital data at Mars suggest the occurrence of near surface water [1-3]. The hydration may be associated with hydrated sulfate species observed *in situ* and by orbital measurements. OMEGA data as well as modeling of APXS chemistry [4], and linear unmixing of the mini-TES data [5] from the Mars Exploration Rovers at Meridiani, suggest both calcium and magnesium sulfates are present. Detailed analysis of the outcrop spectra at Meridiani [6] suggest the presence of gypsum and kieserite. However, the libraries for deconvolution of mini-TES include only a few hydration states of magnesium and calcium sulfates. We have added to the library a complete suite of hydration states for both of these sulfate groups. We have applied these new spectral data to the deconvolution of the martian outcrop spectra to better understand the sulfate chemistry and hydration state

Methods: Magnesium sulfate powders were prepared by S. Chipera for this study using techniques described in [7, 8]. The minerals were analyzed with XRD at both ASU and LANL to verify chemistry, structure and hydration state. Powders were pressed into pellets to decrease scattering and thermal infrared spectra were acquired at Arizona State University's Thermal Emission Spectroscopy Laboratory at ambient pressure. Mineralogical analysis was performed using the linear deconvolution method of [9]. A library of endmembers was selected following [6] and adding the full suite of Mg-sulfates.

Results: Emissivity spectra for the sulfate samples are shown in Figure 1. The position of the absorption corresponding to the ν_3 S-O asymmetric stretch shifts to higher energy with decreasing number of bound waters. This shift has been noted by [10] in emissivity studies as well as by [11, 12] in Raman spectral studies. Variations in water content give rise to changes in the crystal structure of sulfates [13] as well as change in energy of the bonds between water and the SO_4 tetrahedra groups and between SO_4 and the $\text{MgO}_n(\text{OH}_2)_{6-n}$ octahedral resulting in the shift of absorption features with mineral hydration.

The deconvolution results using the library and constraints of [6] and the library that includes the full suite of sulfates are shown in Figure 2. The differences between this study and [6] include the increased abundance of jarosite and the lack of nontronite. The detection of multiple hydration states of both Mg- and Ca-sulfates is not unexpected [8, 14-16]. Use of the sulfates improves both the fit and the RMS error previously derived by [6].

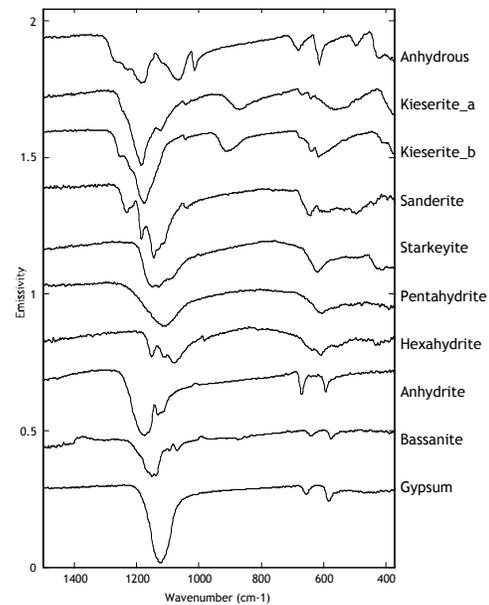


Figure 1.

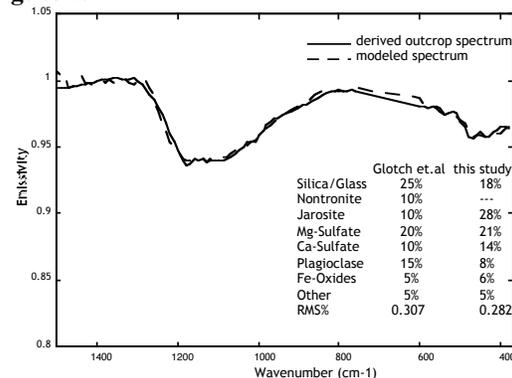


Figure 2.

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TRANSFORMATION OF JAROSITE TO HEMATITE IN SIMULATED MARTIAN BRINES. V. Barrón¹, J. Torrent¹, and J. P. Greenwood², ¹ Universidad de Córdoba, Edificio C4, Campus de Rabanales, Córdoba, Spain, ²Dept. of Earth & Environmental Sciences, Wesleyan University, Middletown, CT 06459.

Jarosite [KFe₃(OH)₆(SO₄)₂], a pale yellow mineral, is a common product of the oxidation of iron sulfides in acidic environments, such as sulfuric soil horizons and acid mine drainage. Jarosite has recently attracted much attention because it has also been identified in the evaporitic deposits of Mars. Here, we report the hydrolysis products of synthetic K-jarosite at different pH, temperature, and phosphate and salt concentrations by X ray diffraction, diffuse reflectance spectroscopy, scanning and transmission electron microscopy, and chemical analysis. We synthesized jarosite by first dissolving 0.1 mol of Fe₂(SO₄)₃, 0.4 mol MgSO₄, 0.04 mol of AlCl₃, 0.06 mol of Na₂SO₄, 0.002 mol of CaCl₂, 0.004 mol of MnSO₄ and variable amounts of KH₂(PO₄) in 160 mL of de-ionized water. A concentrated solution of KOH was then added to reach a pH of 2 and a volume of 220 mL before shaking the resulting suspension at room temperature for two weeks. At this time, the solids in the suspension consisted exclusively of jarosite. In a factorial experiment, portions of the suspension were then mixed with saline solutions of the same ionic composition as the one used in the synthesis [except for Fe(III) and PO₄] and water at different proportions so that the resulting electrical conductivity (EC) of the suspension (first factor) was either 60, 20 or 1 mS/cm. The pH (second

factor) was raised to 4, 6 or 8. Finally, the suspensions were aged for 6 months at a temperature (third factor) of either 303 or 333 K. During aging, pH and salt concentration were periodically adjusted to the target values. High salt concentration inhibited the transformation of jarosite except at pH 8 (Figure 1), suggesting that jarosite is stable even at circum-neutral pH if water activity is sufficiently low. Nanophase hematite was the most common product of the transformation of jarosite, particularly when salt and phosphate concentrations were high. Nanogoethite was formed only when salt concentration was low (i.e., at high water activity) and pH was 6, and was never an intermediate phase in the transformation from jarosite into hematite. At pH 8 jarosite was converted rapidly (<7 days) to 2-line ferrihydrite then evolved, with time, to hematite or to a mixture of 2-line ferrihydrite and nanolepidocrocite.

Implications for Meridiani: Direct transformation of jarosite to hematite is possible without intermediate formation of goethite or poorly crystalline iron oxyhydroxide phases at low pH in short time. With high PO₄, the jarosite-goethite transformation at circum-neutral pH is suppressed and jarosite can transform directly to hematite as well. This implies a very transient fluid system after jarosite formation at Meridiani.

	303 K						333 K					
	pH4		pH6		pH8		pH4		pH6		pH8	
	P0	P2	P0	P2	P0	P2	P0	P2	P0	P2	P0	P2
1 mS/cm	J(99.5)	J(100)	G(47)	J(95)	F(80)	F(100)	J(65)	J(95)	G(5)	H(100)	H(100)	F(100)
	H(0.5)		H(53)	H(5)	H(20)		H(35)	H(5)	H(95)			
20 mS/cm	J(100)	J(100)	J(98)	J(98)	F(85)	F(50)	J(97)	J(98.5)	J(76)	J(78)	F(60)	F(50)
			H(2)	H(2)	H(15)	L(50)	H(3)	H(1.5)	H(24)	H(22)	H(40)	L(50)
60 mS/cm	J(100)	J(100)	J(100)	J(100)	F(100)	F(100)	J(100)	J(100)	J(100)	J(100)	F(90)	F(100)
											H(10)	

Figure 1. Alteration products of jarosite after 6 months of aging (J, jarosite; H, hematite; G, goethite; L, lepidocrocite; F, ferrihydrite; percentages in parenthesis).

DIFFERENTIAL MOBILITY OF URANIUM AND THORIUM IN AQUEOUS SOLUTIONS AS POTENTIAL INDICATOR OF PAST GEOCHEMICAL ENVIRONMENT ON MARS. A. T. Basilevsky, B. N. Ryzhenko, and A. M. Abdrakhimov. Vernadsky Institute of Geochemistry and Analytical Chemistry, RAS, Moscow 119991 Russia (atbas@geokhi.ru).

Introduction: Recent orbital (1, 2) and on-surface (3, 4) studies of Mars accompanied by thermodynamical calculations (e.g., 5) provided evidence that in Late Noachian-Hesperian time the surface environment on Mars allowed to form Mg, Ca and Fe+3 (jarosite) sulfates as well as “grey” hematite suggesting deposition in acidic water of shallow lakes under oxidizing conditions. The Opportunity observations showed that aqueous environment was alternating in time with aeolian one probably suggesting wetter and dryer periods [3]. The gamma-ray mapping by the Mars Odyssey orbiter [6, 7] has provided data on contents of thorium (and a number of other elements) in the surface materials of this planet and will expectedly provide the data on uranium contents as well. In this work we explore possibility of differential mobility of uranium and thorium in aqueous solutions under different pH and Eh conditions during the sulfate-formation period of the geologic history of Mars that may provide additional information on exogenic geochemical processes of that time.

The calculations results: We have done the multi-component thermodynamic modeling using the GIBBS computer code (8, 9) calculating Th and U contents in the aqueous solution resulting from interaction of water with different additions of H₂SO₄ with Th-U-bearing rock (average mafic [10]) containing thorianite and uranium minerals (chosen depending on Eh). The modeling was done for T = 25°C, P = 1 bar and oxygen fugacity from 1 to 10 exp -60 (g = 0 to -60) (Figure 1).

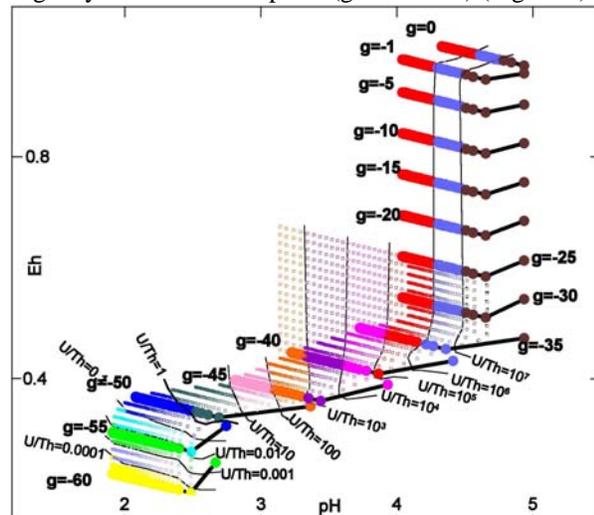


Figure 1. Diagram showing changes in U/Th ratio in the model solutions as a function of pH and Eh.

It can be seen from Figure 1 that with increasing acidity of the reacting solution and decreasing oxygen

fugacity the U/Th ratio in the resulting solution changes: At pH = 4 to 5 and Eh = 0.5 to 1, U is more soluble and the resulting solutions are highly U-enriched. Further addition of H₂SO₄ leads to decrease in pH and Eh and the uranium prevalence in the solution decreases. At pH being in between 2 and 3 and Eh close to 0.35-0.4 the resulting U/Th ratio is close to 1. Further addition of H₂SO₄ leads to decrease in pH and Eh making Th to be more soluble and prevailing in the solution.

Discussion and conclusion: The modeling results suggest that most of the explored pH/Eh combinations have to lead to noticeable deviations from U/Th ≈ 0.3 ratio, which is typical for majority of igneous rocks and meteorites [11]. In the modeled sulfate era surface environment three alternatives could be: 1) The resulted solutions could migrate downward leaving behind the leached residuals like it happens in podzol environment of Earth; 2) The resulted solutions could migrate upward bringing the dissolved material closer to the surface like it happens in salinization of soils in arid environments of Earth; and 3) The resulted solutions stay stagnant intimately mixed with the altered rock. In the cases 1 and 2, surface material should have a U/Th ratio changed comparing to the initial rock. In the case 3, the U/Th ratio stays unchanged. It also has to stay unchanged if the rock-water chemical interaction is not effective. We believe that the U/Th ratios provided by the Mars Odyssey gamma-ray survey [6, 7] will show whether the U/Th ratio in different areas of the planet deviates from canonical ~0.3 or not. This in turn could be analyzed in terms of geochemical processes in different surface environments.

We are working now on modeling of interaction of water with Th-U-bearing rock at neutral (pH = 7) environment, which probably took place in the earlier “phyllosilicate” era [1, 2].

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MINERALOGIC DIVERSITY OF MARS AND DISCOVERY OF SULFATE DEPOSITS FROM THE OMEGA/MARS EXPRESS INVESTIGATION. J-P. Bibring¹ on behalf of the entire OMEGA team, ¹Institut d'Astrophysique Spatiale (IAS), Orsay, France, bibring@ias.fr

Introduction: OMEGA is the VIS/NIR hyperspectral imager operating on board the ESA Mars Express mission since January 2004 [1], [2]. It maps the surface and atmosphere of Mars with a footprint varying from 300m to 5 km depending on the observation altitude. To date, most of the surface has been mapped once at a 2-5 km resolution, while selected areas amounting to 5% have been covered at < 450m. OMEGA acquires the spectrum of each resolved pixel in 352 contiguous spectral channels from 0.35 to 5.1 μm . The spectral domain chosen is dominated by solar reflectance (with minor contribution from thermal emission up to 3.5 μm) and contains diagnostic signatures of a variety of atmospheric and surface species.

Detected constituents: Atmospheric gases (CO_2 , CO and H_2O primarily, O_2 and O_3 marginally) [3], [4], clouds (CO_2 , H_2O), and aerosols have been detected and mapped as a function of time. Frosts and ices (CO_2 , H_2O) [5], [6], [7], have been detected and their extension monitored over a complete Martian year. OMEGA has identified both mafic and altered surface minerals [8]. More specifically, pyroxene (orthopyroxene and clinopyroxene) and olivine (forsterite to fayalite) have been discriminated [9], as well as: anhydrous ferric oxides [10], hydrated phyllosilicates [11] and hydrated sulfates [12], [13], [14].

The majority of phyllosilicates are Mg/Fe smectites; some Al-rich ones have also been identified. Among the hydrated sulfates, kieserite (MgSO_4 , H_2O) and gypsum (CaSO_4 , $2\text{H}_2\text{O}$) have been detected, as well as other polyhydrated ones, for which a more specific composition could not be assessed yet.

It is important to note that a number of minerals cannot be unambiguously identified by OMEGA, such as the non Fe-bearing silicates (e.g. feldspar), and anhydrous sulfates. On the other hand, OMEGA could detect carbonates, if present at levels down to a few wt%; so far OMEGA did not detect carbonates.

Mapping of surface minerals: Some of the detected minerals are spread over wide units: pyroxene are present in the ancient cratered terrains, in contrast with the more recent Northern lowlands in which anhydrous (nanophase) ferric oxides dominate. Most other altered minerals, including hydrated phyllosilicates and sulfates, have been detected in a restricted number of localized areas only. The geomorphological context of these sites, when studied through optical (MOC, HRSC) and thermal IR (TES, THEMIS) data, shows systematic trends for the emplacement of the

various minerals. Phyllosilicates are found in the most ancient terrains, exposed by either impact or erosion; the two main areas are located within i) the Nili Fossae region and ii) the Marwth Vallis. Hydrated sulfates have been found primarily in three units: within ILDs of Valles Marineris, within Terra Meridiani, and within the dark dunes of the Northern polar cap. Sulfates in Terra Meridiani and Valles Marineris are often coupled to ferric oxides (although not always at a pixel size).

Implication for Mars History: Phyllosilicates record an early era during which liquid water was likely present and stable over geological timescales, either at the surface or in the subsurface. The large occurrence of Mg/Fe smectites indicates a non acidic environment, as one would expect from an aqueous alteration of basaltic rocks. Sulfates are found in terrains formed later, some of which requiring much more acidic fluids to precipitate. On the other hand, sulfate formation does not require liquid water to remain stable over long durations. The Mars global environment seems to have drastically changed between the era when phyllosilicates could form (phyllosian) and that of sulfate formation (theikian) [10]: in the latter, the atmosphere could no longer sustain surface liquid water at a global scale. Sulfates would record the areas where surface water was supplied, possibly along sequences of transient episodes, following the Valles Marineris opening and the tilt of Terra Meridiani, both triggered by the building of Tharsis. The coupled outgassing provided massive amounts of sulfur all over the planet, ending with a reduced surface pH. Study of Martian sulfates (composition, hydration level, formation, context), have thus a huge potential to contribute to deciphering the early History of Mars and the role water might have played.

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SULFATE MINERAL ANALYSIS BY THE CHEMIN XRD/XRF INSTRUMENT ON MSL. D. L. Bish¹, P. Sarrazin², D. Blake³, D. Vaniman⁴, and S. Chipera⁴, ¹Dept. of Geol. Sci., Indiana Univ., 1001 E. 10th St., Bloomington, IN 47405-1405, bish@indiana.edu; ²inXitu, Mountain View, CA 94042; ³NASA Ames Research Center, Moffett Field, CA 94035; ⁴Los Alamos Nat. Lab., Los Alamos, NM 87545.

Introduction: The presence of sulfate minerals on Mars has been inferred since the discovery of an Mg-S correlation in Viking X-ray fluorescence data [1]. The existence of Mg-sulfates on Mars was bolstered by Pathfinder [2,3] and by MER chemical, thermal emission spectroscopy, and Mössbauer data [4,5,6]. Recent OMEGA hyperspectral images have identified hydrated sulfates, including gypsum or bassanite, “polyhydrated sulfates,” and kieserite [7]. Of these minerals, with the exception of jarosite, identified by Mössbauer spectroscopy [6], and the OMEGA kieserite identification [7], mineral identifications are typically somewhat ambiguous and alternate identifications are usually possible. Inferences about past conditions can be made from the presence of specific minerals [8], and accurate mineralogic data are particularly crucial to constrain stability and genesis. Diffraction data typically provide unambiguous mineral identification, even in mixtures or for compositionally very similar materials such as gypsum and bassanite (Fig. 1).

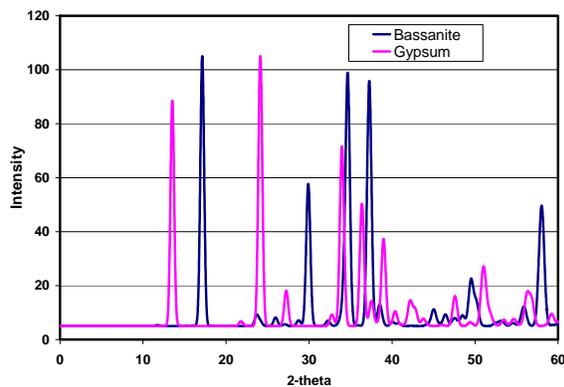


Figure 1. Calculated XRD patterns for bassanite ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) (Co $\text{K}\alpha$).

Methods: CheMin is a miniaturized X-ray diffraction/X-ray fluorescence (XRD/XRF) instrument that is part of the MSL payload. It uses a Co X-ray source with an angular range of ~ 2 to 60° 2θ and operates in transmission mode with a vibrated specimen, yielding partial to full Debye rings. These features compensate for poor particle statistics and preferred orientation.

Specimen Transparency: Total diffracted intensity for a beam perpendicular to a specimen is $I_D = [a*b*t*I_0/(\cos\theta)] e^{-\mu t/\cos\theta}$, where a = volume fraction of the specimen oriented for diffraction; b = fraction of the incident energy diffracted, t = specimen thickness, and μ = linear absorption coefficient. With this equa-

tion, we see that I_d is a maximum when $t = 1/\mu$, so it is important to minimize μ . Fe-bearing minerals are problematic with Cu radiation because of their high values of μ , and CheMin’s use of a Co X-ray tube increases transmission for Fe-minerals by at least a factor of two [e.g., μ values for hematite, Fe_2O_3 , are 1150.2 cm^{-1} (Cu) vs. 222.2 cm^{-1} (Co)]. For Co radiation, the transmission factor for 100- μm thick jarosite ($\text{KFe}^{+3}(\text{SO}_4)_2(\text{OH})_6$) is 0.15 and the intensity falls off to $1/e$ at 53 μm (compared with 25 μm for Cu radiation). The transmission factor for 100- μm thick botryogen ($\text{MgFe}^{+3}(\text{SO}_4)_2(\text{OH}) \cdot 7\text{H}_2\text{O}$) is ~ 0.4 and the intensity falls off to $1/e$ at 110 μm . The transmission factor for 100- μm thick gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is ~ 0.11 , and the intensity falls off to $1/e$ at 45 μm . These values are for theoretical densities, and powder specimens in CheMin will have fractions of these values, yielding much more transparent powders. A sample cell thickness for CheMin of 175 μm allows acceptable transmission values for all expected minerals; Figure 2 illustrates a CheMin-measured XRD pattern of a mixture of three sulfate minerals.

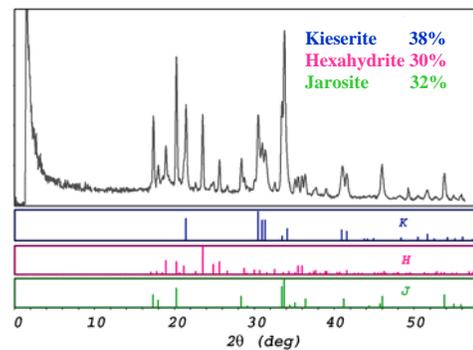


Figure 2. CheMin III diffractogram of a jarosite-kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$)-hexahydrite ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$) mixture. Colored bars show maxima for each mineral (inset: quantitative Rietveld analysis, nominally 33% of each mineral).

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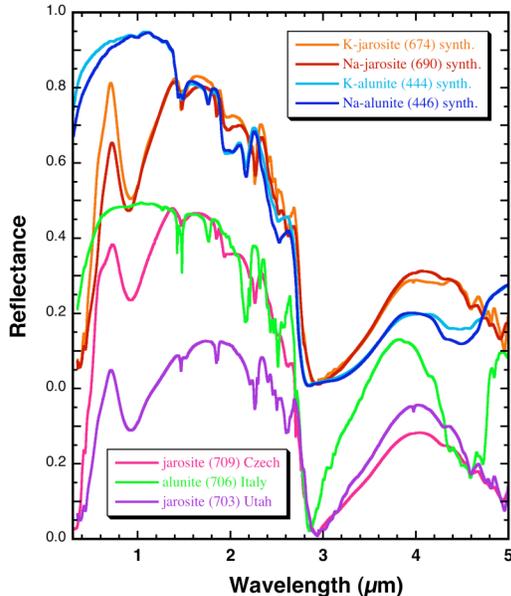
VNIR SPECTRA OF SULFATES FORMED IN SOLFATARIC AND AQUEOUS ACID SULFATE ENVIRONMENTS AND APPLICATIONS TO MARS. J. L. Bishop¹, A. J. Brown¹, M. Parente², M. D. Lane³, M. D. Dyar⁴, P. Schiffman⁵, E. Murad⁶ and E. Cloutis⁷. ¹SETI Institute/NASA-Ames Research Center, Mountain View, CA, ²Stanford University, Packard Engineering Building, Stanford CA, ³Planetary Science Institute, Tucson, AZ, ⁴Mount Holyoke College, South Hadley, MA, ⁵Dept. of Geology, Univ. of Calif., Davis, CA, ⁶Bayerisches Landesamt, Marktredwitz, Germany, ⁷Univ. of Winnipeg, Canada. (jbishop@arc.nasa.gov)

Sulfates formed in solfataric and aqueous acid sulfate environments on Earth can provide information about current and former environments on Mars. VNIR lab spectra of sulfate minerals and sulfate-bearing rocks and soils are being compared with current Mars spectral datasets. New tools currently being finalized for processing and identification of Pancam, OMEGA (and CRISM) images enable global mapping of sulfates in these Martian image cubes.

Lab Spectra of Sulfates from Mars Analog Sites:

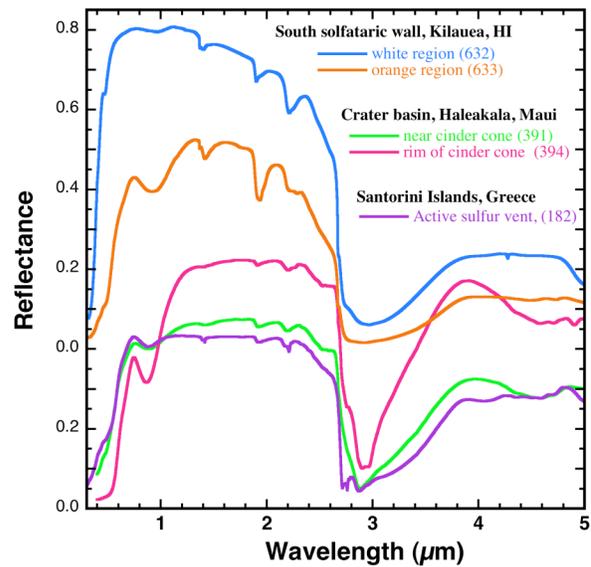
We have been collecting and measuring spectra of a variety of sulfate minerals and sulfate-bearing samples from solfataric and aqueous acid sulfate environments in order to provide compositional information on the jarosite and other sulfates observed in Martian spectra.

Jarosite Family. One project involves a collection of jarosite and alunite samples from many locations plus several synthetic ones and builds on a recent study [1]. These together span a range of Fe and Al values and K, Na and H₂O abundances.

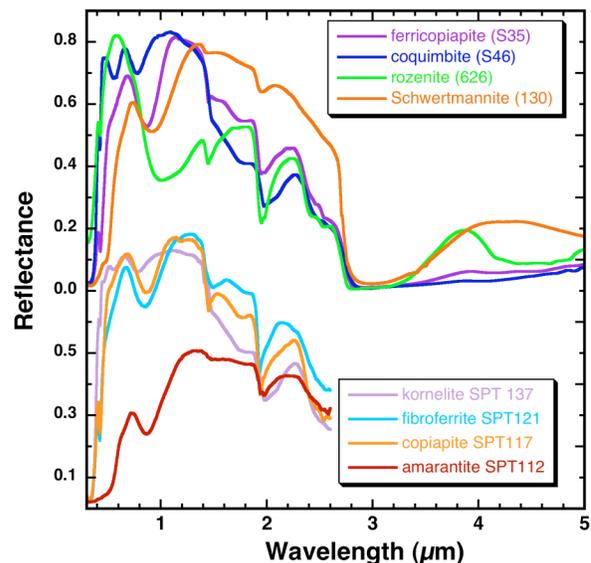


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Solfataric Sites. Samples from an acid-fog type weathering environment in Kilauea contain jarosite (orange layer) and gypsum (white layer) [2]; samples collected near a cinder cone at Haleakala contain alunite and jarosite [3]; a sample from an active vent at Santorini contains alunite and alunogen [4].



Aqueous Acid Sulfate Sites. Low pH environments, such as acid rock drainage sites, produce a variety of sulfate minerals: e.g. schwertmannite [5] and rozenite [6], ferricopiapite [7] and coquimbite [7] and others [8].



The Mars Science Laboratory (MSL) Mission. D. L. Blaney, NASA Jet Propulsion Laboratory, California Institute of Technology, MS 183-501, 4800 Oak Grove Drive, Pasadena, CA 91109, email: Diana.Blaney@jpl.nasa.gov.

Introduction: The MSL mission will be the first chance to follow up *in situ* on the wealth of new information on Martian sulfates that has emerged over the last several years. MSL will bring to bear a powerful suite of analytical, remote sensing, and environmental instrumentation on a capable, long-lived rover with a flexible sample acquisition and processing capability. This talk will provide an overview of the MSL mission and how it might answer key questions about Martian sulfates. An emphasis will be placed on the payload and how the various instruments work together with the rover to accomplish the MSL science objectives.

Mission Overview: MSL launches in Sept 2009 and arrives on Mars between July and October 2010. The MSL rover can land at elevations up to +1.0 km (Mars Orbiter Laser Altimeter [MOLA]) with a landing accuracy of 10 km (radial) between $\pm 45^\circ$ latitude. MSL will operate on the Martian surface for 1 Mars year (669 sols/687 days). The rover is capable of traveling up to 20 km distance and collecting 74 samples of rock and regolith.

Science Objective: The primary scientific goal of the MSL project will be to deploy to the surface of Mars a mission equipped with the capability to assess the present and past habitability of the Martian environments. An assessment of present habitability requires an evaluation of the characteristics of the environment and the processes that influence it from microscopic to regional scales and a comparison of these characteristics with what is known about the capacity of life as we know it to exist in such environments. The determination of past habitability has the added requirement of inferring environments and processes in the past from observation in the present. Such assessments require integration of a wide variety of chemical, physical, and geological observations with the full range of instruments that comprise the MSL payload. These goals are very compatible with investigating sulfates on Mars due to the pervasiveness of sulfates as an indicator of aqueous processes on Mars.

Payload: The MSL Science Payload consists of 10 instruments that are provided by a combination of U.S. and international Principal Investigators (PI).

- Mast Camera (MastCam), PI M. Malin, MSSS: Color stereo and multispectral imaging for geomorphology and atmospheric opacity.
- Mars Hand Lens Imager (MAHLI), PI K. Edgett, MSSS: Color hand lens imaging for rock and soil texture.

- Mars Descent Imager (MARDI), PI M. Malin, MSSS: Imaging during descent.
- Alpha Particle X-Ray Spectrometer (APXS), PI R. Gellert, U of Guelph (Canada): Chemical composition of contact surface.
- Chemistry & Camera (ChemCam), PI R. Wiens, LANL: Remote chemical composition and imaging.
- Chemistry & Mineralogy X-Ray Diffraction/X-Ray Fluorescence Instrument (CheMin), PI D. Blake, NASA ARC, Mineralogy and chemical composition of samples.
- Sample Analysis at Mars Instrument Suite with Gas Chromatograph, Mass Spectrometer, and Tunable Laser Spectrometer (SAM), PI P. Mahaffy, NASA GSFC: Chemical and isotopic composition (incl. organic molecules) of samples and atmospheric gas.
- Radiation Assessment Detector (RAD), PI D. Hassler, SwRI: High-energy radiation.
- Dynamic of Albedo Neutrons (DAN), PI I. Mitrofanov, IKI (Russia): Subsurface hydrogen abundance / distribution.
- Rover Environmental Monitoring Station (REMS), L. Vazquez, CAB / CRISA (Spain): Meteorology / UV radiation

Rover Capabilities: The MSL rover will be able to drive up to 20 km which will provide it the capability to drive up to landforms on the edge of the 10 km landing ellipse. This will allow access to material that is too rough to land in but is of high scientific interest. The rover also can abrade and/or brush surfaces and place and hold contact instruments (MAHLI and APXS) on rocks and soils. Samples of rock or regolith can be acquired via coring device or scoop. Once acquired, rock cores, small pebbles, or regolith into are processed into smaller particles and deliver the processed material to the analytical lab instruments (SAM and CheMin).

Landing Site: Landing site selection will also play a vital role in the success of MSL mission. MSL landing site selection involves inputs from the entire Mars community. The first workshop was held May 31-June 2, 2006. At this workshop a wide range of landing sites were discussed and prioritized. Sulfate rich sites were widely recognized as important and were prioritized as high priority for added study and information.

Martian Sulfate Mineralogy from Spectroscopy: Ground-Based, Orbital, and In Situ Perspectives. D. L. Blaney¹, D. Glenar², W. Maguire², G. Bjoraker². ¹NASA Jet Propulsion Laboratory, California Institute of Technology, MS 183-501, 4800 Oak Grove Drive, Pasadena, CA 91109, email: Diana.Blaney@jpl.nasa.gov. ²NASA Goddard Space Flight Center, Solar System Exploration Division, Code 693, Bldg 2, Rm S107.

Overview: New ground based data can be used to determine sulfate mineralogy in the 4-5 μ m region. This data complements existing orbital and *in situ* data and can be used to investigate the origin of sulfates in the bright soils of Mars.

Prespectives from *In Situ* and Orbital Data: Recent results from NASA's Mars Exploration Rovers (MER) and the ESA Mars Express OMEGA investigation have demonstrated the widespread role of sulfate minerals as the key marker in aqueous / chemical processes on Mars. The Spirit rover confirmed earlier discoveries by Viking and Pathfinder that sulfates are generally enriched in the Martian crust (e.g. Squyres et al. 2004a, Reider et al. 1997, Clark et al. 1982) with sulfate abundances ranging from 5-15%. Meanwhile, the Opportunity rover found extensive magnesium sulfate rich deposits associated with aqueous sediments (e.g. Squyres et al. 2004b).

Orbital remote sensing of sulfates has provided a new perspective on the surface sulfate distribution but has also left major unanswered questions. Recently, OMEGA has detected large localized deposits of several hydrous sulfate mineral deposits (gypsum, kieserite, hydromagnesite) in the 1-2.5 μ m region (e.g. Bibring et al. 2005, Langevin et al. 2005, Gendrin et al. 2005). These sulfates have been mapped and are clearly associated with specific geologic locations (e.g. intercrater layer deposits in Valles Marineris and other locations, the North polar sand sea gypsum deposit) and are not the sulfates associated with bright soils and duracrust formation. The sulfate bands mapped by OMEGA are due to water in sulfate minerals but these sulfates also have features at longer wavelengths.

The sulfur content of Martian bright soils at the Viking I, II, and Pathfinder sites is higher than the sulfur content of basaltic rocks which provide the original starting material for Martian soils. Thus sulfur (and other salts) must be incorporated into the soils by chemical processes.

Two types of processes have been proposed for the incorporation of sulfates into Martian soils: aqueous and atmospheric. Determination of the mineralogy of the sulfates in martian bright soils and maps of the regional distribution of sulfates may allow us to distinguish between potential sources of sulfates and their mode of origin.

Background: In Blaney and McCord, (1995) it was shown that the rise out of the 4.2 μ m - 4.4 μ m CO₂

band on Mars cannot be matched solely by atmospheric gas constituents. An absorption must be added at roughly 4.5 μ m in order to decrease the reflectance rise and produce the 4.5 μ m inflection present in the data. The location of this feature at the 2 ν_3 overtone of the SO₄⁻² anion indicated that the surface absorption is caused by sulfates on the Martian surface and/or in atmospheric dust. An exact match to a terrestrial sulfate mineral was not made but it was suggested that the mineral has very weak structure and thus a high degree of symmetry.

The shape of the surface sulfate feature should be sensitive to both sulfate species and concentration, but this information is suppressed by interference from the overlying atmosphere. The 4.5-5 μ m wavelength region on Mars is spectrally very complex. In addition to surface absorptions, the Martian atmosphere between 4.4 - 5.1 μ m contains numerous absorption bands from CO₂, CO, and O₃. Both reflected solar and thermal emission from surface and atmosphere contribute significantly at these wavelengths. Kirchoff's law (emissivity = 1-reflectance) can provide pathologic cases where (depending on the surface temperature) mineralogical absorption features can be filled in by thermal emission. Thus Mars spectra in this region will require careful modeling to interpret successfully.

New Ground Based Data: On Oct 25, 2005 we obtained multiple spectral image cubes spanning this wavelength range using SPEX at the NASA Infrared Telescope Facility. This high quality data set permits us to explore sulfate mineralogy globally and regionally via a combination of forward modeling and least-squares retrievals, utilizing new laboratory measurements of sulfate minerals. Additional constraints are imposed by existing compositional data sets (orbital, *in situ*, and ground-based). We summarize the results of our ongoing analysis of this data set.

This work is being carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract to NASA.

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EXTREMOPHILE MICROORGANISM TRANSFORMATIONS OF SULFATES AND OTHER SULFUR MINERALS IN SURFACE AND SUBSURFACE ENVIRONMENTS. P.J. Boston¹, M.N. Spilde², and D.E. Northup³, ¹Dept. Earth & Environmental Sci., New Mexico Tech., 801 Leroy Place, Socorro, NM 87801, pboston@nmt.edu, ²Inst. Meteoritics, Univ. New Mexico, Albuquerque, NM 87131, mspilde@unm.edu, ³Biol. Dept., Univ. New Mexico, Albuquerque, NM 87131, dnorthup@unm.edu

Introduction: Numerous active sulfur transforming organisms live in sulfur rich environments in both Earth's surface and subsurface. Amongst those that our team has studied are organisms in a sulfuric acid dominated cave system that aid in precipitation of sulfates [1] (Fig. 1), microbial communities in a briny sulfur-rich iron mine environment that appear to be mediating the deposit of microcrystalline jarosite (Fig. 2), and organisms that utilize copper sulfides producing copper oxides and sulfates as byproducts of that transformation (Fig. 3).

The association of sulfate minerals with microbial communities can be seen in the physical proximity of organism with mineral grains, and in the gradual transformation from amorphous to crystalline phases in the living materials. No such transformations occur in killed controls. Such microbial communities are of relevance to potential biology and mineralogy of Mars.

Methods: We analyze isotopic signatures of C, S, O, and H/D in both mineral and biological components. We assess other geochemical biosignatures and bulk chemistry. To study the association of various elements with organisms, we construct elemental maps via electron microprobe of C, S, and other relevant elements. Organisms that are growable are maintained in culture and subjected to an array of experiments including those aimed at inducing the same or similar precipitation of minerals that we see in nature. Lastly, we analyze the DNA of both environmental and cultured samples to determine organism identities, or their closest relatives if they are unknown strains.

Conclusion: Numerous microorganisms are involved in processes that either degrade or precipitate sulfates. The biology of these communities can serve as a comparison model for similar Martian minerals and environments.

References:

[1] Boston, P.J. et al. (2006) *GSA Sp. Pap.* 404, 331-344.

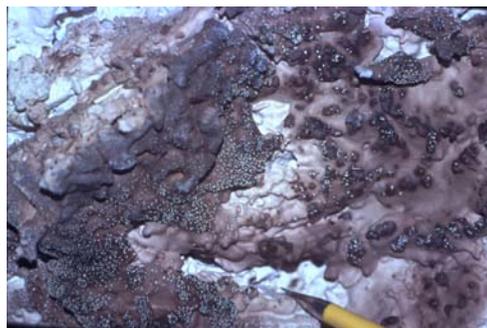


Figure 1: Gypsum paste soaked with sulfuric acid in Cueva de Villa Luz, an active sulfuric acid cave in Tabasco, Mexico. White dots on dark material are microbial colonies growing at pH 1.-2.5. Image courtesy of Kenneth Ingham.

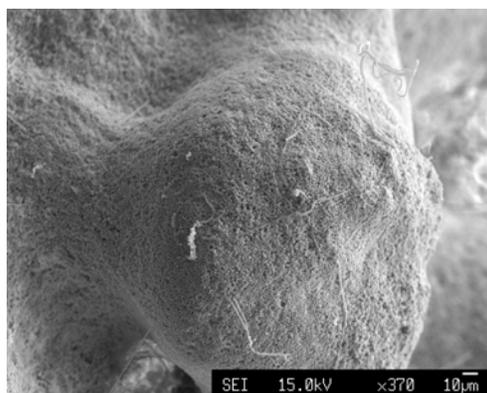


Figure 2: Jarosite and microbial filaments and cell bodies mound up in briny samples from the Soudan Iron Mine in northern Minnesota. SEM by Spilde and Boston.

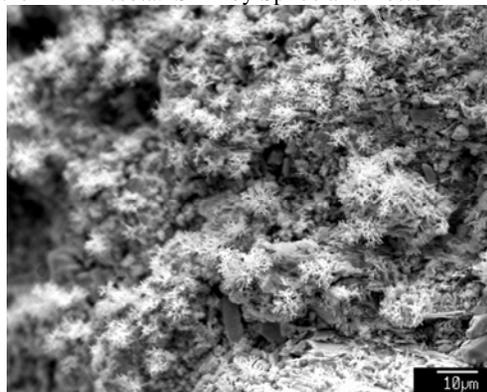


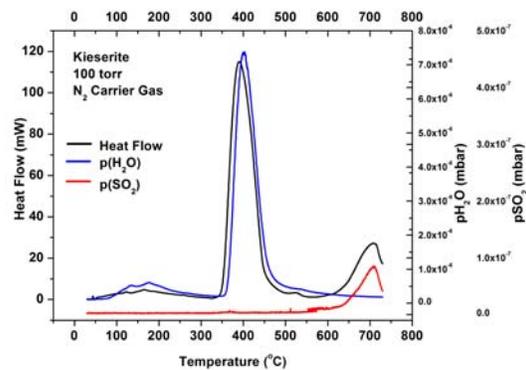
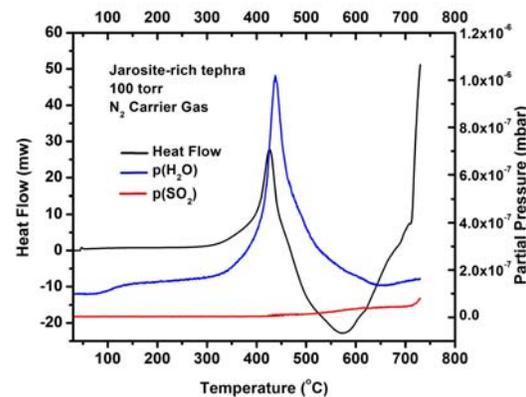
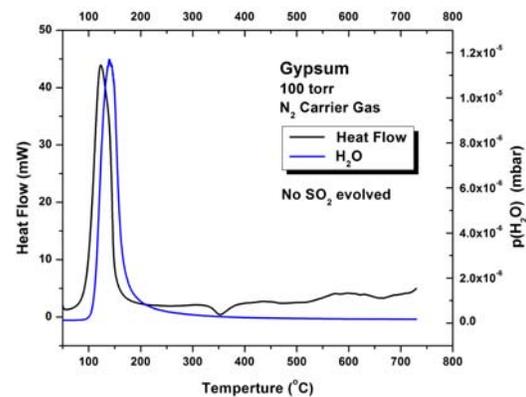
Figure 3: Cellular "bushes" coated with copper oxides derived from copper sulfides. SEM by Spilde and Boston.

USE OF THE THERMAL AND EVOLVED-GAS ANALYZER (TEGA) ON THE PHOENIX LANDER TO DETECT SULFATES ON MARS. W.V. Boynton¹ and D.W. Ming², ¹Department of Planetary Sciences, University of Arizona, Tucson AZ 85721 (wboynton@LPL.Arizona.edu), ²ARES, NASA Johnson Space Center, Houston TX 77058 (douglas.w.ming@nasa.gov)

Introduction: TEGA is one of several instruments on the Phoenix Lander. This lander will launch in August of 2007 and land in the north polar region of Mars. TEGA is similar to the instrument that originally was provided for the Mars Polar Lander mission of 1999, which failed during descent. It consists of eight small ovens, each of which can hold a 0.030 ml sample of Mars regolith. The samples will be delivered to the instrument via a robotic arm that digs or grinds the sample from the martian surface. The samples are heated at a programmed ramp rate (typically 5 to 20 K/min) up to 1000° C. As the sample is being heated, the required heat input is monitored to provide calorimetric data on any phase transitions (This is the thermal analyzer). In addition, the evolved gases that are generated during the heating are analyzed with the evolved-gas analyzer (a magnetic sector mass spectrometer) to determine the composition of the gases released as a function of temperature.

Expected Results: Iron, Ca, and Mg sulfates have distinct thermal and evolved gas behaviors. We show here the thermal and evolved gas analysis (TA/EGA) using a laboratory based instrument for three candidate Martian sulfates. Ca-sulfates, such as gypsum, do not evolve SO₂ in the operational temperature range of TEGA. Gypsum may be identified by a very distinct evolution (endoenthalpic transition) of H₂O with an onset of around 100-120°C under the operation conditions of TEGA. TA/EGA for the jarositic tephra indicates a strong endoenthalpic transition near 420°C, which marks the dehydroxylation of the ferric-OH bonds in jarosite and the evolution of water (e.g., $2\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6 \rightarrow \text{K}_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 + 2\text{Fe}_2\text{O}_3 + 6\text{H}_2\text{O}$). A second endoenthalpic transition near 580°C represents the breakdown of sulfate in jarosite. During this transformation, K₂SO₄ (and Na₂SO₄) and Fe₂O₃ form as SO₂ is evolved (e.g., $\text{K}_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{K}_2\text{SO}_4 + \text{Fe}_2\text{O}_3 + 3\text{SO}_2 + 3/2\text{O}_2$). Mg sulfates have a variety of hydration states that can be characterized by TA/EGA. Kieserite (MgSO₄H₂O) has been suggested as being stable at the surface of Mars [1] and has a similar TA/EGA as jarosite. We are currently characterizing the thermal and evolved gas behaviors for a variety of sulfates under conditions that TEGA will operate on Mars such that we will be able to differentiate between the sulfates, particularly kieserite from jarosite and other Fe sulfates.

References: [1] Vaniman et al., Nature. Vol. 431, 2004.



REMOTE SENSING OF WESTERN AUSTRALIAN SULFATE DEPOSITS AND APPLICATIONS FOR MARS. A. J. Brown¹, ¹SETI Institute, 515 N. Whisman Rd, Mountain View, CA 94043, <http://abrown.seti.org>

Introduction: The European hyperspectral imaging instrument *Observatoire pour la Minéralogie, l'Eau, la Glace et l'Activité* (OMEGA) has been in operation around Mars since early 2004. OMEGA has constructed imaging maps covering almost the entire Martian surface. OMEGA has returned evidence of surficial sulfate deposits at several locations around the Martian globe [1]. The presence of sulfates on the Martian surface has important links with past water and possible life on Mars.

On Earth, sulfates most commonly form in dry lake evaporite basins, many examples of this type of deposit are in evidence in arid Western Australia. A number of these dry lakes criss-cross the ancient (late Archean) Yilgarn Craton. The ultramafic-mafic volcanic flows in this region make the Yilgarn a good analog for the volcanic flood basalts of Mars.

In 2004, a hyperspectral imaging survey of the Yilgarn Craton was carried out using the airborne HyMap instrument. We have analysed this hyperspectral coverage of the evaporite deposits of the Yilgarn GGT and found large deposits of gypsum in evidence. We intend to use an analysis method based on curve fitting of individual spectra in the dataset, to compare the results for the Martian North Polar region with the arid Western Australian evaporite deposits [2].

Hyperspectral Dataset: The airborne dataset was collected by the CSIRO Division of Exploration and Mining in 2004 as part of a field mapping for the Next Generation Maps project [3]. The data was obtained using the Australian built HyMap hyperspectral spectrometer, operated by HyVista Corporation (www.hyvista.com). HyMap is a VNIR (0.4-2.5 micron) spectrometer, and was configured to obtain spectels 5m a side on the ground. This dataset has been complemented by ASTER imagery of the region (Figure 1).

Results: Using standard multispectral analysis techniques, mineral maps have been obtained of gypsum abundance in the dry lakes near Kalgoorlie (Figure 1). These show the central regions of dry lakes to be high in gypsum abundance – as measured by the depths of their absorption bands. In the future, the hyperspectral dataset will be analyzed completely using the absorption band modeling technique in order to measure such parameters as wavelength center, absorption band width and asymmetry.

Fieldwork: Colleagues working on the airborne hyperspectral survey collected several samples of gypsum near Kalgoorlie. We have collected a wide range of library spectra from the literature covering the Ca

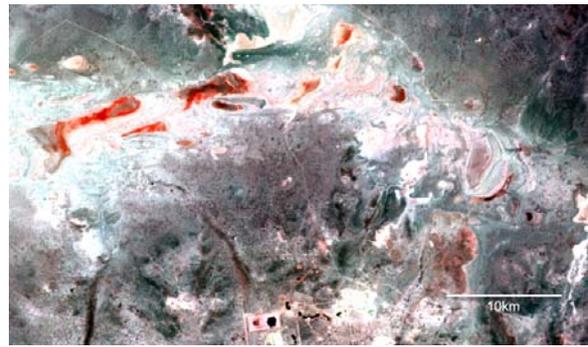


Figure 1 – Gypsum abundance mapped using ASTER false color R4(1.65) B5 (2.16) G6 (2.2) image showing sulfates in red.

and Mg sulfates that we wish to study. These spectra currently form the basis of discriminating these materials in the field (and on Mars). It is our intention to further refine the locations of the absorption bands of these spectra so that the cause for each band can be well understood, and also attempt to find additional diagnostic absorption bands for other minerals in an acid sulfate weathering environment. This work has recently been funded [4]. It is critical we identify what the most likely minerals (down to the specific species of sulfate) are in a basaltic acid weathered region and what the implications are for detecting these minerals from airborne and satellite survey.

Future work: This project has started to collect the necessary data for identifying sulfates and determining hydration state and cation type using hyperspectral data. Future work is intended to use an absorption band modeling approach to interpret reflectance spectra of sulfates with variable cation and hydration state. The results will be a guide to the features in IR spectra that are indicative of cation type and hydration state, linking molecular cause to spectral effect.

Conclusion: Understanding of sulfate distribution, species and hydration state in the Martian regolith will lead to greater understanding of the Martian hydrological cycle. In the forthcoming year, with the addition of CRISM data, sites where sulfates have been discovered will be analyzed with absorption band modeling techniques and the knowledge gained by this project will be used to attempt to determine sulfate hydration states and distributions all over the Red Planet.

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SULFUR ON THE MARTIAN SURFACE: IN-SITU DATA FROM ALL LANDING SITES. J. Brückner¹ and APXS Team², ¹Max-Planck-Institut für Chemie, J. J. Becher Weg 27, D-55128 Mainz, Germany, brueckner@mpch-mainz.mpg.de, ²NASA Mars Exploration Rovers Mission.

Introduction: On all landing sites high concentrations of sulfur in soils and rocks were determined by instruments onboard the landers Viking 1 and 2, Mars Pathfinder Rover Sojourner, Mars Exploration Rovers Spirit and Opportunity. Measurements were carried out by X-Ray Fluorescence Spectrometers on the Viking landers or Alpha Particle X-Ray Spectrometers (APXS) onboard of all three rovers.

Viking Sites: The surface sampler could not catch any rock piece at either Chryse or Utopia Planitia. However, several soil samples (surface fines or protected fines) could be analyzed. In spite the fact that both landing sites were more than 6000 kilometers apart, the soil compositions were very similar; S contents varied between 3.2 weight-percent at Utopia and 2.6 wt.% at Chryse [1]. Soils were characterized to contain mafic material; however, high S (and Cl) contents could result from volcanic exhalations [2]. As further landing sites revealed, the soil compositions were very similar suggesting a global homogenization mechanism, such as large dust storms.

Mars Pathfinder Site: In Ares Vallis, soil sites several meters apart were measured by the APXS. The mean S content was 2.7 ± 0.3 wt.% (standard deviation), which is comparable to both Viking sites [3]. A cemented soil did not show any different concentrations for S and Cl. Again the mafic nature of the soils could be confirmed. For the first time, several rocks on the martian surface were measured and a soil-free rock composition could be derived [4]. Since sulfur was used as a tracer for the amount of adhering soil, no intrinsic S contents of the rocks could be obtained [3]. Nevertheless, the Pathfinder rocks seemed to have S contents compatible with those of martian meteorites. In particular, basaltic Shergottites show a mean S content of 0.21 ± 0.08 wt.% [5]. This level of S contents could be indigenous to most martian basaltic rocks.

Gusev Crater sites: The soils encountered at the Plains have a rather similar composition with a few exceptions. The mean S contents of the top soil layer (APXS radiation penetrates about 10 μm) is 2.59 ± 0.33 wt.% [6]. Three so-called undisturbed soils were discovered that had S contents below 2 wt.%. The rover wheels did scuff a few soils, so-called disturbed soils, whose mean S content is 2.21 ± 0.43 wt.%. In the Columbia Hills, three disturbed soils were discovered that had S contents between 13 and 14 wt.% [6]. Here, the soils were enriched with sulfur-bearing compounds probably due to aqueous processes. Trenches, which

were dug by the Rover Spirit, disclosed varying S contents ranging from normal soil contents to enrichments of up to 5.6 wt.% [6]. At the Plains, primitive basaltic rocks were encountered that had a mean S content of 0.53 ± 0.05 wt.% (abraded surface) somewhat higher than the Shergottites. In the Columbia Hills, several new rock classes were discovered, floats and outcrops; all showing strong indications of alteration. S concentrations of up to 5.2 wt.% were found [6]. Gusev crater revealed that within several kilometers the chemical composition can vary distinctively, probably depending on their geological history. The Hills, which seem to be older than the Plains, had seen aqueous activities in the past, while the Plains represent the dryer more recent (2 to 3 billion years) environment. Independent of the location, abraded rocks contained at least 0.5 wt.% sulfur, which makes an indigenous S content of the Pathfinder rocks very likely. The assumption of at least 0.3 wt.% S seems therefore to be justified.

Meridiani Planum Sites: The soils at Meridiani Planum vary somewhat in composition depending on how many spherules, which contain high contents of hematite (Fe_2O_3), are covering the soils. Spherule-free top-most soils have a mean S content of 2.23 ± 0.46 wt.% [7,8] and the spherule-covered soils have a similar mean of 2.1 ± 0.2 wt.%. However, spherule-rich soils show a mean Fe content of 23.0 ± 1.7 wt.% (which causes dilution of other major elements) compared to 14.0 ± 0.7 wt.% of spherule-free soils [7,8]. All rocks occur as outcrops (except some unusual rocks). Just the abraded rocks have very high sulfur concentrations: mean of 9.1 ± 1.1 wt.% with a maximum of 11.5 wt.% [7,8]. These sulfur-rich outcrops occur along a traverse of at least 8 kilometers, where they typically seem to be covered by the ubiquitous soil except for certain locations. The formation of these outcrops could be explained by a mixture of siliciclastic material with brines containing high amounts of salts [7]. Sulfur, a very mobile element, influenced geological processes everywhere on Mars.

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ATMOSPHERIC CONDITIONS ON EARLY MARS AND THE MISSING LAYERED CARBONATES.

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Introduction: Massive layered sediments investigated by the Opportunity rover at Meridiani Planum leave little doubt that liquid water has chemically altered the surface of Mars [1]. Stacks of mixed sulfate-siliciclastic layers, 7 m of which are exposed near the rim of Endurance crater, most likely were laid down in a lacustrine environment as evaporitic sediments [2]. MOC and Themis images show that the exposed outcrops at Meridiani are merely a portion of light-toned sediments that are up to 800 m thick and several hundred thousand km² in extent [3]. The OMEGA instrument on board the Mars Express spacecraft has identified at least some of these layers as evaporitic salts [4].

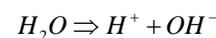
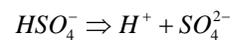
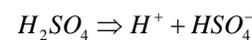
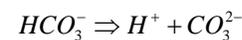
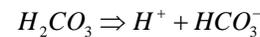
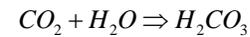
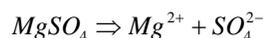
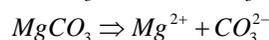
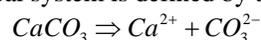
Aqueous Geochemical Model: We present a simple aqueous chemical model of the formation of the Meridiani sediments, and offer an explanation for why extensive layered carbonates are not found there or elsewhere on Mars [5].

In order to gain insight into how early martian waters could have formed the chemical sediments found at Meridiani, we consider a simplified geochemical system. A body of water is in equilibrium with carbon dioxide at the top and carbonates and sulfates at the bottom. Sulfur is added at the top in the form of sulfuric acid. Carbon dioxide partial pressure and sulfuric acid concentration define the stability fields for carbonate and sulfate.

Based on what was measured by APXS, mini-TES, and the Mossbauer spectrometer on the Opportunity rover at Endurance and Eagle craters, the two most prominent sulfate cations are Mg²⁺ and Ca²⁺. [6] We assume that the water was in contact with CO₂ at a partial pressure between 0.1 and 3000 mbar and therefore H₂CO₃, H₂CO₃⁻ and CO₃²⁺ were also in the water. Since we are investigating the precipitation of CO₃²⁺ and SO₄²⁻ this will happen with the available cations, mostly Mg²⁺ and Ca²⁺.

Thus, the initial model system consists of water in equilibrium with CO₂ of some amount, and also Mg²⁺, Ca²⁺, CO₃²⁻, and SO₄²⁻. This is equivalently a system with water in equilibrium with CO₂ (at some pressure), CaCO₃, MgCO₃, CaSO₄, and MgSO₄.

The chemical system is defined by the reactions:



Acid Rain: During the late Noachian, widespread volcanism, such as that associated with the formation of Tharsis [7], very likely injected large amounts of SO₂ into the atmosphere of Mars. Efficient photochemical conversion of SO₂ to H₂SO₄ [8] would have caused widespread atmospheric precipitation and the acidification of standing bodies of water. Based on the total amount of igneous activity during the Noachian [7], and on estimates of the S composition of Mars magmas [8], there should be enough sulfate to cover Mars in a global layer 100 m thick. Much of this may be in the fines, but massive layered deposits also exist in areas other than Meridiani.

Conclusions: The results of our simple model show that acidic waters in equilibrium with a more massive CO₂ atmosphere would precipitate Mg and Ca sulfates but not carbonates. Mars may have sustained a thick CO₂ atmosphere, and thus supported liquid water, as long as atmospheric CO₂ was precluded from forming carbonates by constantly resupplying volcanic gases such as SO₂ to the atmosphere. The dissolved acidic gases would rapidly combine with altered basaltic minerals to form layered water-lain deposits such as those seen at Meridiani. Once acidic gas production dropped and the waters become pH-neutral, the CO₂ atmosphere collapsed to form non-massive, non-layered, poorly consolidated carbonate patinas. Among other things, such patinas were probably susceptible to being transformed into Martian atmospheric dust, further diminishing their detectability.

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THE ROLE OF FLUID CHEMISTRY AND CRYSTALLIZATION KINETICS IN Na AND K ZONING IN JAROSITE. P.V. Burger, J.J. Papike, C.K. Shearer and J.M. Karner. Astromaterials Institute, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131.

As jarosite is known to be a prominent phase on the martian surface, zoning in jarosite crystals likely contains important information about martian surface conditions at the time of deposition [1,2,3]. Here we document several striking examples of Na-K zoning in a suite of terrestrial samples in order to place constraints on the conditions of jarosite growth. The study was carried out using a combination of electron microprobe (EMP), back-scattered imaging (BSE) and energy-dispersive (EDS) mapping techniques.

BSE imaging of a suite of 14 jarosite samples from various terrestrial environments (both supergene and hydrothermal) reveal a range in zoning development, from samples with no zoning to those with spectacular oscillatory bands (Fig. 1,2,3). Differences in zoning among samples is likely due to both crystallization kinetics and fluid chemistry. In these samples, jarosite growth begins with multiple nucleation sites, leading to the growth of numerous euhedral crystals (Fig. 1), possibly when an oxidant is introduced into the system [2,3]. EDS maps and microprobe analyses confirm that these bands are defined by fluctuations in Na and K, while Al and Fe show no variation. Na-K zoning is likely caused by changes in Na and K concentration in the fluid immediately adjacent to zones of crystal growth. In the case of sample AA01AZ (Fig. 1,2), later precipitation/crystal growth is characterized by a higher concentration of Na and lower concentration of K, suggesting the overall fluid composition has become more sodic. Further growth likely results in the coalescing of various crystals, as voids are filled in. Sample GH01UT (Fig. 3) may represent this later stage of crystal growth; while it would appear that there were once numerous crystals, one large grain has developed, and subsequent crystal growth is characterized by zoning along the periphery of the large grain, the area to which fluids were likely sequestered once voids between crystals had been filled in. While zoning is quite dramatic, electron microprobe analyses [4] suggest that the overall Na/(Na+K) of these two samples are quite low when compared to the samples discussed in [3], and zones are the result of changes in fluid Na and K concentration in a very limited Eh/pH range.

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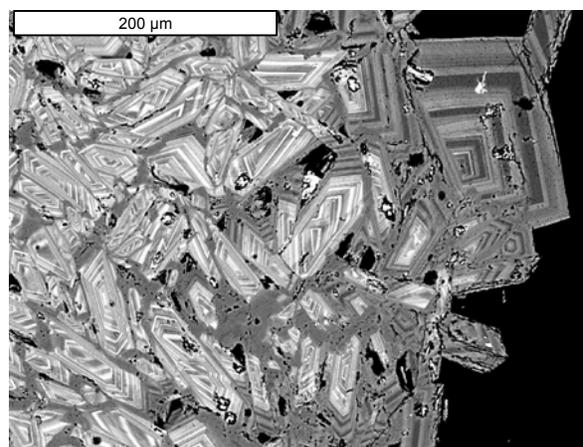


Figure 1. Jarosite crystals with prominent oscillatory zoning in sample AA01AZ. Darker regions are more sodic.

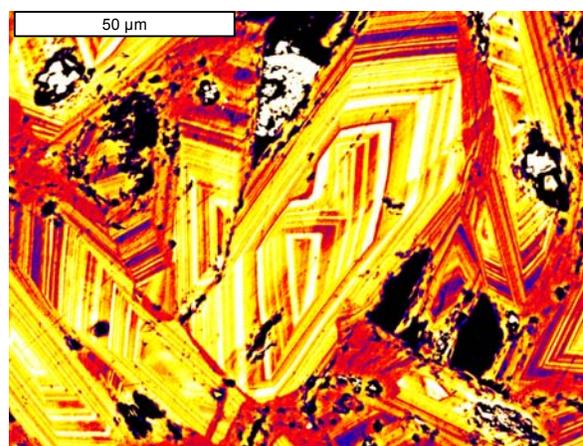


Figure 2. False-color BSE image of a jarosite crystal in sample AA01AZ. Cooler regions are more sodic.

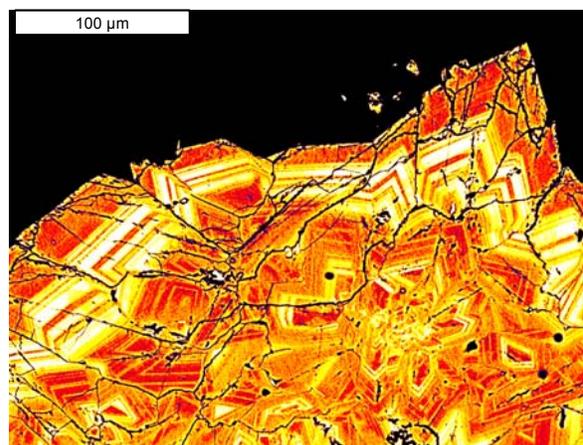


Figure 3. False-color BSE image of jarosite in sample GH01UT.

INTRINSIC ACIDITY OF JAROSITE AND OTHER FERRIC SULFATES AS AN INDICATOR OF HOW THEY FORM. D. M. Burt¹ School of Earth and Space Exploration, Arizona State University, Box 871404, Tempe, AZ 85287-1404 (dmburt@asu.edu).

Introduction: The sulfate-rich (or at least S-rich) nature of the martian surface was indicated by analyses performed by the Viking landers, and was attributed to some sort of planet-wide volcanogenic “acid mist” process [e.g., 1]. More recently, acid sulfates (jarosite group) were indicated by the Mossbauer spectrometer on the Mars Exploration Rover Opportunity at Meridiani Planum [2], and were attributed initially to deposition by evaporating acid seas or lakes [3], and later, to deposition by rising sulfuric acid groundwaters [4]. All of the hydroxyls in the jarosite formula, as normally written, apparently were taken to indicate that it must have formed in an extremely water-rich environment (i.e., under water). Another hypothesis for sulfate formation at Meridiani involved hot acid steam in a giant solfatera system [5]. Independently, the Spirit rover discovered isolated areas of extreme subsurface enrichment in ferric sulfate salts at Gusev Crater [6]. Most recently, OMEGA remote sensing data indicated abundant sulfates in layered rocks and fines in many areas of Mars [7]; sulfate formation was attributed to a volcanic acid mist episode that postdated the “warm wet” formation of surficial clays in the most heavily cratered areas. As a suitability test for Mars, do any of these conflicting hypotheses reflect how jarosite and other ferric sulfates typically form on Earth? No!

Jarosite as Acid: If the K-jarosite formula is doubled to $K_2Fe^{3+}_6(SO_4)_4(OH)_{12}$, it would appear to contain 12 hydroxyls, in support of an “abundant water” hypothesis. However, this formula can alternatively be written as $6FeO(OH) + K_2SO_4 + 3H_2SO_4$. In other words, it can be written as a combination of goethite (or hematite + H_2O) with $\frac{1}{4}$ neutral salt (arcanite) and $\frac{3}{4}$ sulfuric acid. Jarosite can thus be considered a crystalline form of sulfuric acid (analogous to crystalline sodium bisulfate that is added to plumbing fixtures to remove hard water deposits). The jarosite end-member hydronium jarosite, with H_3O^+ in place of K^+ , is entirely ferric oxide plus acid. Contrary to what has been claimed for Meridiani, such jarosite-group minerals don’t form in the presence of abundant liquid water (except fairly concentrated sulfuric acid), and, in fact, are stable in the presence of very little water [8], as on the present martian surface (or on an Arizona mine dump in June).

Other Ferric Sulfates as Acids: Jarosite (hydronium jarosite) is only one of many iron sulfates. Others (neglecting ferrous phases and polymorphs) include mikasaite, lausenite, kornelite, coquimbite,

quenstedtite, butlerite, fibroferrite, amarantite, hohmannite, rhomboclase, ferricopiapite, and schwertmannite. All can be considered as a combination of ferric oxide, water, and sulfuric acid (i.e., as crystalline forms of sulfuric acid). Of these, the most acid is possibly rhomboclase, $HFe^{3+}(SO_4)_2 \cdot 4H_2O$, sometimes seen on mine waste as a blue efflorescence. Owing to compositional degeneracies, one can write ferricopiapite (bright yellow) + $H_2SO_4 \implies$ coquimbite (gray) + $H_2SO_4 \implies$ rhomboclase (blue). In other words, these three colored minerals are potential indicators (or buffers) of sulfuric acid activity. They can occur together as layered efflorescent crusts, with the “more acid” (gray or blue) phase on top. A process of “damp” (but not overly wet) sulfide weathering is how such ferric sulfates typically form in terrestrial mine waste [e.g., 9], and could well be how they formed on Mars [10,11], perhaps after the surface had become too dry and cold to form abundant clays [7]. This hypothesis (minus the impact mining part) originated with Roger Burns [11,12]. No life-hostile, sulfuric acid atmosphere or hydrosphere (or steam) is indicated or required. Just moisture, dispersed sulfides, and an oxidizing environment.

Summary: Jarosite and other ferric sulfates typically form as coatings and efflorescences on and in mine waste, via moist weathering of contained iron sulfides. They can be thought of as ephemeral crystalline forms of sulfuric acid. Add too much water (as when it rains), and they dissolve incongruently, acidifying the water and leaving ferric oxide (goethite or hematite) behind. The originally sulfidic surface of Mars may not have experienced rain for about 4 billion years, if ever, accounting for the preservation of acid sulfates there.

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IMPACT EXCAVATION OF SULFIDES THAT THEN WEATHER INTO SULFATES: AN ASTROBIOLOGY-FRIENDLY EXPLANATION FOR ACID SULFATE FORMATION ON MARS. D. M. Burt¹, L. P. Knauth¹ and K. H. Wohletz², ¹School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287-1404 (dmburt@asu.edu; knauth@asu.edu), ²Earth and Environmental Sciences, Los Alamos National Lab, Los Alamos, NM 87545-1663 (wohletz@lanl.gov).

Introduction: Based on recent orbital and all lander/rover observations to date, much of the surface of Mars appears to be highly enriched in sulfate minerals; much also is heavily cratered. We suggest that these two observations can be correlated, especially as regards the origin of the acid sulfate-rich, cross-bedded sediments discovered by the Opportunity Rover in Meridiani Planum [1], and local Fe-sulfate enrichments discovered by the Spirit Rover in Gusev Crater. Our impact excavation hypothesis [1] represents a modification (updated for cratering) of the gossan hypothesis of the late Prof. Roger Burns of MIT.

Gossan Hypothesis: Burns [2-6] hypothesized that the surface mineralogy and color of Mars could, at least in part, be caused by the weathering of sulfide minerals in martian igneous rocks. Based on the observation that martian mafic rocks appear to be at least twice as rich in Fe as terrestrial equivalents, he concluded that they should also be richer in reduced S and in cumulate Fe,Ni-sulfides (dense immiscible droplets that “rain out” of the liquid magma). Weathering of sulfide deposits on Earth typically produces Mars-colored, acid-sulfate bearing deposits called gossans (rusty areas long sought by metal prospectors). Burns simply proposed the same process of gossan formation could have occurred on Mars. In his multiple discussions of Mars gossans and weathering, Burns never mentioned impact cratering and its associated comminution (rock breakage) and sulfide dispersal.

Open-Pit Mines as Mars Analogs: Rather than gossans as Mars analogs, we suggest Arizona-style open-pit sulfide mines as better analogs for acid sulfate formation during weathering. Open-pit sulfide mines are analogous to large impact craters that intersected subsurface magmatic sulfide deposits (common on Mars, according to Burns [2-6]). Surrounding rock-strewn mine dumps are then analogous to impact-excavated breccias. Finally, associated sandy, layered, mill tailings (the result of fine comminution during ore separation in a milling operation) are analogous to distal sandy layered impact surge and fall deposits. In contrast to their apparent absence on the Moon, such non-ballistic layered deposits are presumed to be widespread on Mars [1] owing to its atmosphere and subsurface volatiles. In this regard, we note that sulfide minerals, compared to silicates, tend to be soft and extremely brittle, greatly facilitating shattering and

dispersal during impacting, and greatly speeding up weathering afterwards. We further note that many sulfate minerals are extremely hygroscopic (able to extract moisture even from dry air), so that subsurface moisture should be readily available to promote sulfide weathering, once the process has begun (i.e., owing to positive feedback, it should go to completion).

Discussion: This explanation for the formation of jarosite and other acid sulfates on Mars (impact excavation of sulfides, followed by their *in situ* oxidation to acid sulfates) provides a simple alternative to far more complex hypotheses involving planet-wide, volcanically-derived sulfuric acid mists, sulfuric acid lakes and streams, or sulfuric acid groundwaters, such as have been proposed by other authors [e.g., 7,8,9]. These hypotheses suffer numerous contradictions, not the least of which is the fact that acids in contact with brecciated mafic rocks should be neutralized almost immediately, with formation of abundant clays. By our alternative impact hypothesis, the surface of early “warm, wet” Mars dried up and froze down while impacting still continued. Impacts into a partly frozen, salty/briny, locally sulfide-rich regolith, followed by moist weathering, produced all of the sedimentary and geochemical features seen at Meridiani Planum and probably in many other layered deposits on Mars [1]. Martian breccias and layered sediments are then analogous to weathered sulfide mine wastes, but with the mining and milling having been done by impacts. Planet-wide sulfuric acid mists and liquids are not particularly friendly to life [10]. In contrast, sulfide weathering in terrestrial mine waste is commonly accompanied by intense microbial activity. Did such activity accompany sulfide oxidation on Mars? If so, acid sulfate-bearing areas might provide good targets for future astrobiologic investigations.

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MAPPING SULFATES IN NEVADA USING REFLECTED, EMITTED, MULTI-SPECTRAL AND HYPERSPECTRAL SYSTEMS. W. M. Calvin¹, R.G. Vaughan², C. Kratt³, and J. D. Shoffner¹, ¹Geological Sciences, MS172, University of Nevada – Reno, NV 89557, wcalvin@unr.edu; ²Jet Propulsion Lab, greg.vaughan@jpl.nasa.gov; ³Desert Research Institute, christopher.kratt@dri.edu.

Overview: The remote sensing group of the Arthur Brant Laboratory for Exploration Geophysics at UNR has used a wide variety of airborne and spaceborne sensors to map the occurrence of sulfates using both reflected solar wavelengths (0.4 to 2.5 μm) and emitted thermal wavelengths (7 to 14 μm). Data sets range in spatial resolution from 2m/pixel to 30m/pixel and spectral fidelity varies from hyperspectral systems (hundreds of channels) to multi-channel systems. Data sets have been acquired over geothermal systems and old mine districts. New work on an acid producing system in an historic California mining district is just beginning. Here we summarize the results of these efforts [1-5] and make recommendations for the exploration of Mars, based on our terrestrial experience.

Geologic terrains: We have mapped sulfates in Nevada in association with current geothermal systems at Steamboat Springs [1,2], Brady's Hot Springs [3], in regions of geothermal development potential on Pyramid Lake Paiute Tribal Lands [4], over the historic mining district of Virginia City [5], and are beginning to examine Leviathan Mine, CA.

Geothermal Systems. Geothermal systems in Nevada are concentrated in regions of extensional tectonics, rather than active volcanism as seen in the Pacific "ring of fire". These systems are typified by active fumaroles and mud pots, large expanses of steaming ground, recent and ancient siliceous sinter and structurally controlled tufa (carbonate), and of course, sulfates. Sulfates tend to concentrate near old vent structures or around current fumaroles (Fig 1). Yellow and white crusts are common, and iron alteration is also sometimes seen. At Pyramid Lake sulfates are seen in playa evaporites and in seeps where geothermal ground water reaches the surface.

Mining Districts. Historic mining districts in the state tend to occur in areas of intrusive volcanics with substantial hydrothermal alteration with varying levels of sulfur. Virginia City economic mineralization appeared during a low-sulfidation hydrothermal phase, but many sub-economic minerals contain sulfides that weather in mine tailing piles to form hydrated sulfate minerals. At Leviathan, the region is hosted by intrusive volcanics with former open pit mining of elemental sulfur – presumably a capped vent.

Sensors and Data Sets: We have used a variety of airborne hyperspectral systems: AVIRIS, HyMAP, HyperSpecTIR, all measuring the optical and short-wave infrared, and SEBASS, measuring the thermal

infrared. Multi-channel spaceborne data from ASTER and airborne data from MASTER have also been used to map mineralogy at varying spatial scales. We perform extensive field validation of remotely mapped mineralogy using portable field spectrometers (ASD, D&P) and collect samples for laboratory measurements and XRD corroboration of mineral species.

Mapping Results: We have mapped common sulfate species at these locations, including alunite, gypsum, and jarosite. In many regions hydrated sulfates were mapped remotely and later XRD characterized them as hexahydrite, alunogen, tamarugite, or kieserite. In all cases the most diagnostic spectral features were identified using hyperspectral airborne data at high spatial resolution corroborated with field measurements. Coarse spatial resolution and low spectral fidelity can broadly identify alteration zones, but are not capable of uniquely identifying specific sulfate minerals. In many instances, mixed sulfates were identified in remote data sets, but field and laboratory measurements were needed to confirm individual species. Sulfates are identified in both shortwave and thermal infrared data and using measurements from both spectral regions allows greater mineral identification ability.

Recommendations: Laboratory measurements of more exotic sulfate species are needed. Our experience shows that both high spatial and spectral resolution are needed to map these minerals remotely. Spectral identifications benefit from complementary XRD.



Figure 1: Vent structure at Brady's with sulfur/sulfate crusts and iron alteration.

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Cracks and Fins as Evidence for Water Evaporation and Condensation Associated with Temperature Changes in Hydrous Sulfate Sands G. V. Chavdarian and D. Y. Sumner, Geology Department, University of California-Davis, Davis, CA 95616, chavdarian@geology.ucdavis.edu, sumner@geology.ucdavis.edu

Introduction: The Mars Exploration Rover Opportunity, on Meridiani Planum, is documenting sulfate-rich sedimentary rocks that formed in eolian environments with some evidence for overland water flow [1], [2]. Contractural cracks on outcrop surfaces define centimeter to decimeter scale polygons that cross-cut bedding in Endurance Crater and on the plains of Meridiani. The perpendicular-to-outcrop surface orientation of the cracks is inconsistent with synsedimentary contraction [3]. Some cracks in Endurance Crater are associated with fins, which are mm-thick, platy features that protrude a few centimeters above outcrops. Fin geometry is consistent with differential cementation along cracks, followed by differential weathering. Frost observed on Opportunity demonstrates modern atmospheric water cycling. We use observations from an analog site at White Sands National Monument, New Mexico, to provide insights into processes forming cracks and fins.

Cracks and Fins in Gypsum Sand: Dunes and playas at White Sands National Monument provide excellent analogs for sedimentary structures in Meridiani outcrops because of the ubiquitous hydrous sulfate (gypsum) sand and the similarity of depositional environments. Fieldwork at White Sands has demonstrated that cracks and fins form seasonally in the gypsum sand [4]. Unfilled polygonal cracks were actively forming in January 2005 in the moist and cohesive sand (Figure 1A); the moisture was due to frost. At all other times, including in dry January 2006, cracks on dune slopes were covered and dry, and not actively forming. However, cracks did form after one significant rainstorm in June 2005. Cracks on dune slopes crosscut bedding as do Meridiani cracks.

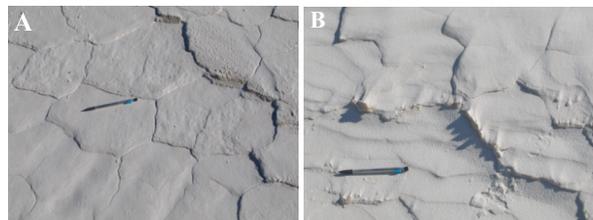


Figure 1: A: Cracks on a dune slope in gypsum sand in January 2005 at White Sands National Monument. B: Tan fins along a crack edge that stand up to a centimeter above the surface.

Fins are also present at White Sands [4]. Slightly cemented tan colored fins were only present in January 2005 when abundant frost was present (Figure 2B).

Tan fins are thin, platy, preferentially cemented features that protrude a few centimeters out of the dune sand along crack edges. Tan fin surfaces always face into the wind and are composed of finer grains than the surrounding sediment.

Results: Temperature and humidity loggers monitoring subsurface conditions at 10 minute intervals since January 2006 show that the air between sand grains retains 100% humidity with daily temperature fluctuations. Temperature varies with depth; at the surface, daily fluctuations are up to 30°C, whereas at 45 cm daily fluctuations are ~1°C. The constant humidity with temperature changes requires water to evaporate and condense on a daily cycle, possibly inducing precipitation of sulfate cements. Summer temperature changes may also promote cementation as the sand grains skirt across the gypsum-anhydrite transition range of 42-60°C depending on water activity [5]. Cracks may form as the grains contract during dehydration. Hydrous Mg-sulfates break down into water plus less hydrous Mg-sulfates at temperatures near 0°C [6]. Therefore, a similar volume-loss process may produce cracks on Meridiani when surface sediment temperatures cycle above and below 0°C. Thus, atmospheric water cycling with the evaporation (or sublimation) and condensation of water associated with hydrous sulfates may promote crack formation in sulfate sand both at White Sands and on Mars, implying an active water vapor cycle on Mars in recent history.

Field observations of variable cementation along crack edges and adhesion structures suggest that tan fins at White Sands form from 1) preferential cementation along cracks and 2) adhesion of fine-grained particles to structures above the sediment surface. Near-surface water cycling may also play a role as tan fins were only present when there was abundant frost. Laboratory experiments are currently underway to understand crack and fin formation. These or similar processes may provide a testable model for crack and fin formation in Meridiani Planum outcrops

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WATER CONTENT AND DEHYDRATION BEHAVIOR OF Mg-SULFATE HYDRATES. S. J. Chipera, D. T. Vaniman, and J. W. Carey, Earth and Environmental Sciences, Los Alamos National Laboratory, MS D469, Los Alamos, NM 87545 (chipera@lanl.gov)

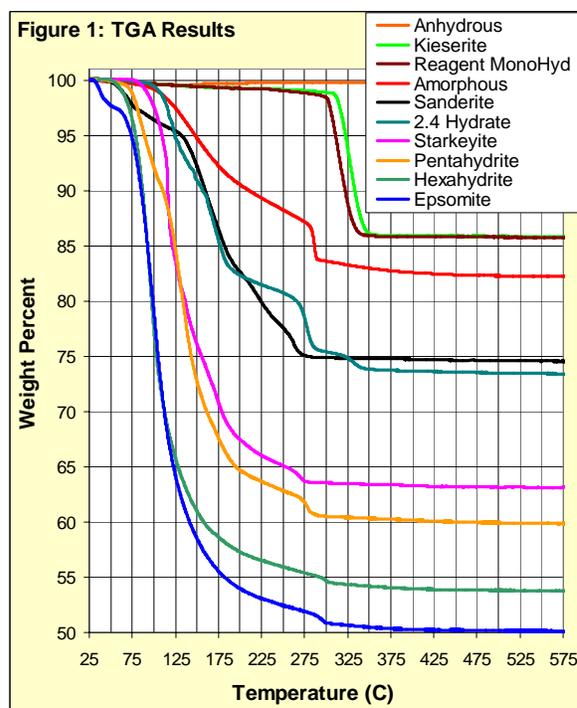
Introduction: Recent studies have been undertaken to characterize stability relationships between the various MgSO_4 hydrates [1,2,3]. These studies have found, however, that the MgSO_4 hydrate system is extremely complicated, with numerous unexpected results. In addition to the known 1, 2, 4, 5, 6, and 7 hydrates found in nature, numerous MgSO_4 hydrates have been synthesized including several phases in these studies which have not been previously described. Thermogravimetric analyses were conducted on the various MgSO_4 hydrates to characterize water content and thermal evolution in an attempt to gain a better understanding of the relationships between these phases.

Methods: Thermogravimetric analyses (TGA) were conducted using a DuPont 951 thermogravimetric analyzer operated with Omnitherm Corporation hardware and software. Typically, ~15 mg samples were analyzed from ambient temperature to 600°C at 10°C/min, using 50cc/min dry N_2 as a purge gas.

Results: TGA is a powerful method that measures both the amount of water and dehydration behavior in hydrous phases. Figure 1 shows the TGA results for various MgSO_4 hydrates plotted as sample weight vs. temperature upon heating. A trend is seen in the data with water release occurring earliest in the most hydrated phases (e.g. epsomite) and later in the least hydrated phases (mono-hydrates) where the water is more tightly bound in the crystal structure.

The more hydrous phases (epsomite-7 H_2O , hexahydrate-6 H_2O , pentahydrate-5 H_2O , starkeyite-4 H_2O) have similar dehydration patterns, where water is evolved in a rather continuous fashion with temperature. Epsomite shows an initial weight loss that corresponds to loss of the single non-octahedrally bound water to form hexahydrate. The intermediate hydrates (2.4-hydrate and sanderite-2 H_2O) have distinctive weight loss curves with several inflections, which are normally indicative of multiple structural sites containing water. However, available data suggest that these hydrates are reacting to form monohydrates which then dehydrate to anhydrous MgSO_4 .

Water content in the amorphous phases can be quite variable, with water contents from 2 to 0.6 H_2O per MgSO_4 . Their weight loss patterns resemble those of the hydrated crystalline phases (epsomite, hexahydrate, starkeyite) that they are made from, even though



they do not retain the crystal structure or water content. The reagent monohydrate and kieserite-1 H_2O both show gradual weight loss until the single distinct weight-loss event occurring at about 300 to 325°C.

Of interest in the TGA data, water content in the Mg-sulfate system is not always integral (e.g., 2, 3, 4, 5, 6, 7). Also of interest is the final distinct weight-loss event that occurs at approximately 280-300°C in the more hydrated phases. The exact cause for this event is uncertain. Ultra-pure MgSO_4 was used to ensure that it was not due to a minor gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) impurity. The amount of water evolving during this event is also variable as can be seen by comparing the weight-loss patterns of the amorphous phase with the hexahydrate from which it was made. It appears to represent a final terminus of water evolution from either the starting product or from the final dehydration of an intermediate reaction product that formed during the heating/dehydration.

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DIRECT CHEMICAL ANALYSIS ON THE MARTIAN SURFACE: A REVIEW OF SULFUR OCCURRENCE AND INTERPRETATION FROM VIKING TO MER

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With five sites on Mars that have been explored in situ, and an equivalent number of orbital mapping missions, Mars emerges as a planet with a sulfate-rich surface, a S-rich mantle, and a probable high S content in its core. Sulfur at the surface of Mars should be in the fully oxidized form because of photochemical oxidants in the atmosphere and in martian soils. Martian meteorites contain ~ 10x higher S than their igneous analogs on Earth. Some rocks on Mars contain even more S, probably due to perfusion by sulfate brines and possibly implying that martian meteorites may be a biased sample of less altered, highly competent launchable rocks. Globally-distributed martian soils contain 4 to 7 wt % SO₃, with a nearly uniform molar S:Cl ratio of ~4:1. Soil trends with anionic salt components are indeterminate with respect to cations despite an extensive high-precision data set, consistent with incorporation of volcanic volatiles containing S and Cl. Condensed SO_x gases and H₂SO₄ cannot be ubiquitous on Mars, however, because atmospheric concentrations are well below their equilibrium vapor pressures. MgSO₄ enrichments have been detected in some indurated soils (duricrust) and trenches. Thermal cycling of H₂O frosts to provide moderate ion mobility may favor formation of weak duricrusts. Non-systematic Br enrichments may result from similar mobilizations.

High concentrations of kieserite, polyhydrated MgSO₄ and gypsum on the ~10 km scale occur in some regions. Sedimentary outcrops at Meridiani Planum are composed of up to one-half salts, including Mg, Ca and Fe (jarosite) sulfates cementing silicate and Fe oxide grains. A low-pH range of 3 to 5 is indicated for formation and preservation of jarosite. Opposite distributions of MgSO₄ and chlorides in outcrop sequences may be explained as solubility in aqueous brines governed by freezing-point depression.

CaSO₄ enrichments have been detected in two sets of altered rocks in the Columbia Hills of Gusev crater. Whitish powder churned from shallow depths (~ 10 cm) at multiple locations in Columbia Hills is almost pure ferric sulfate with silica and sometimes MgSO₄. Low-Fe "Independence class" material may be a source of this Fe.

No conclusive detections have been made of Na or Al sulfate salts, in spite of important occurrences in terrestrial settings. Both Na and Al tend to correlate well with Si content, indicating their preservation as primary plagioclase. In spite of the widespread sulfate, there are significant concentrations of olivine in soils and some basalts. Soils are at approximately one-fourth of saturation for SO₃ with respect to modeled original olivine and pyroxene. Inferred content of highly soluble MgSO₄ in sedimentary outcrop and soils provides a tracer indicating a lack of exposure to significant quantities of meteoric H₂O or groundwater since formation of craters at Meridiani or emplacement of soils at other sites. Shallow soluble ferric sulfates in Columbia Hills could indicate emplacement by upward evaporation, but the inferred water table would need to vary greatly in altitude over a relatively short distance.

The sulfur cycle on Mars presumably lacks the terrestrial complications of subduction, mid-ocean ridge recirculation, and extensive biological processing. Carbonate deposits on Mars may be generally encrusted with sulfate-rich weathering rinds, rendering their detection much more difficult. Impact cratering is a relatively more important process on Mars, however, providing a mechanism for re-introducing S-gases into the atmosphere.

LASER INDUCED BREAKDOWN SPECTROSCOPY (LIBS) REMOTE DETECTION OF SULFATES ON MARS SCIENCE LABORATORY ROVER. S.M. Clegg¹, R.C. Wiens², M.D. Dyar³, D.T. Vaniman⁴, J.R. Thompson², E.C. Sklute³, J.E. Barefield¹, and S. Maurice⁵ ¹Advanced Diagnostics and Instrumentation Group, Los Alamos National Laboratory, Los Alamos, NM 87545, sclegg@lanl.gov, ²Space Sciences and Applications Group, Los Alamos National Laboratory, Los Alamos, NM 87545, ³Earth and Environment Department, Mount Holyoke College, South Hadley, MA 01075, ⁴Hydrology and Geochemistry Group, Los Alamos National Laboratory, Los Alamos, NM 87545, ⁵Centre d'Etude Spatiale des Rayonnements, Toulouse France.

Introduction: The mineralogy and chemical characteristics of Martian surface sulfate deposits can provide key information about aqueous processes, hydrogeologic cycling, and the history of atmosphere/soil interactions. In this paper, we show that the ChemCam Laser Induced Breakdown Spectrometer selected for the Mars Science Laboratory (MSL) Rover can remotely probe and distinguish among various sulfur-containing minerals. Working with a laboratory LIBS instrument similar to ChemCam, we probed and characterized various sulfur-containing minerals including jarosite, pyrite, gypsum and anhydrite. Analysis of the elements in each sample observed with LIBS is used to reconstruct the composition of the sample probed.

Experimental: LIBS involved ablating a small amount of material from the surface of the sample with a focused Nd:YAG laser (20mJ/pulse, <1GW/cm²). The samples were placed 5.4 meters away from the LIBS instrument in a vacuum chamber filled with 7 Torr CO₂ to simulate the Martian atmosphere. This produced a plasma containing electronically excited atoms, ions and small molecules that expand from the surface. As these excited species relaxed back to the ground electronic state, they emitted light characteristic of the identity of the elements present in the sample. Some of this emission was directed into Ocean Optics HR2000 dispersive spectrometers and detected with a CCD camera. Thompson et al. [1] contains a detailed description of the experimental setup.

Figure 1 is an example of the structurally rich LIBS spectrum obtained from a jarosite-containing rock. The sample, from the Apex Mine in Arizona, has coatings of essentially pure jarosite (mineral identification by X-ray diffraction). The top spectrum depicts the emission from a portion of the visible region in which some of the more prominent peaks are annotated. The bottom spectrum covers the region of the visible spectrum in which three emission lines from sulfur are observed.

Results: There are two significant challenges to detecting S with LIBS. First, the strongest S LIBS emission lines are found in the vacuum UV (180.73nm) and in the NIR (>900nm)[2,3]. The ChemCam instrument's spectral range is 240 – 800nm and consequently, S can only be detected by the weaker emission lines in the 400 – 600nm region.

Secondly, Dudragne et al. [2] demonstrated that electronically excited S readily reacts with oxygen. While the reduced Martian atmosphere produces much stronger LIBS signals, LIBS will still break down the atmospheric CO₂ and produce excited oxygen.

Despite these challenges, observations from an instrument similar to ChemCam were used to characterize emission from several sulfur-containing minerals. Spectra similar to those in Figure 1 were collected for each sample. Major elemental composition as well as the lighter elements present in functional groups containing sulfur and carbon were extracted from each sample. These observations demonstrate ChemCam's ability to distinguish between various sulfate assemblages likely to be found on the Martian surface.

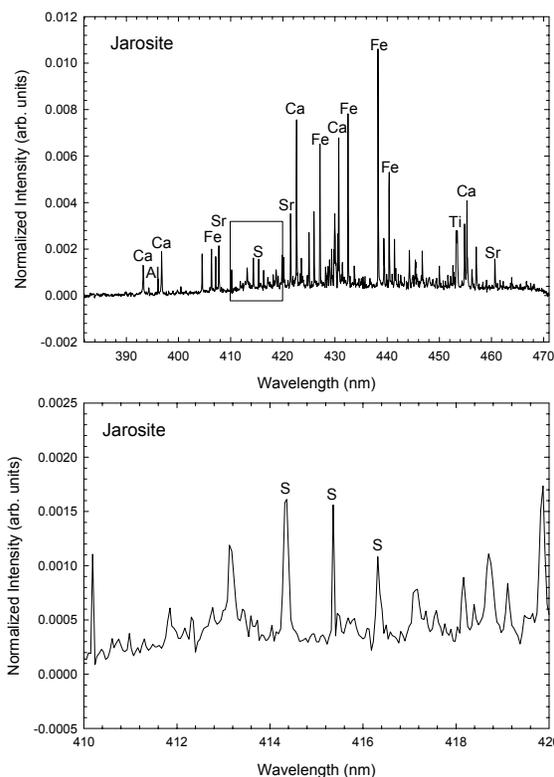


Figure 1

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Estimating minimum volumes of water involved in formation of sulfate evaporite deposits. Max Coleman¹ and Diana Blaney¹, ¹Jet Propulsion Laboratory, California Institute of Technology (4800 Oak Grove Drive, Pasadena, CA 91109. max.coleman@jpl.nasa.gov).

Introduction: The description of the Burns Formation, Meridiani Planum, as an eolian sulfate evaporite deposit [1] raises the question of how much water was involved in its deposition. Sedimentary basin volumes can give estimates of the maximum water volume previously present [2] but are not appropriate for evaporite basins. The complexity of water volume estimation is exacerbated by: the eolian transport of the sulfate grains from the evaporitic basin and whether it was from a single body of water or if the same water was recycled during evaporation.

We propose a geochemical approach to estimate the minimum volume of water involved in the process by in situ analysis of relatively few evaporite crystals.

Geochemical approach: Crystals grow radially by successive episodes of precipitation forming layers around the nucleus. Analysis of successive growth zones in minerals can reveal the history of changing environmental conditions during crystal growth [3], but has not been applied to monitor changes during evaporation. An isotopic phenomenon allows the opportunity to interrogate individual grains in which internal composition variations record the history of formation (including amount of water involved) and any possible subsequent alteration. Growth of a mineral in an aqueous system causes a shift of the relative abundances of stable isotopes ($^{34}\text{S}/^{32}\text{S}$ and $^{18}\text{O}/^{16}\text{O}$) and an opposite shift in the material remaining in solution.

Mineral compositions of Burns Formation sulfates have not been determined. Although not a likely candidate we use the example of calcium sulfate (gypsum) crystallization because it is one of the few salts for which the isotopic shift has been measured (+1.65‰) [4]. Changes in isotopic composition follow a form of the Rayleigh fractionation equation: for the reaction, $\text{sulfate}_{\text{solution}} \rightarrow \text{sulfate}_{\text{solid}}$, $R/R_0 = f^{(\alpha-1)}$, where $R = ^{34}\text{S}/^{32}\text{S}$ of the solid at any time, R_0 = initial value of R , f = the fraction of sulfate left in solution, $\alpha = R_{\text{solid}} / R_{\text{solution}}$ (the isotopic fractionation factor). In

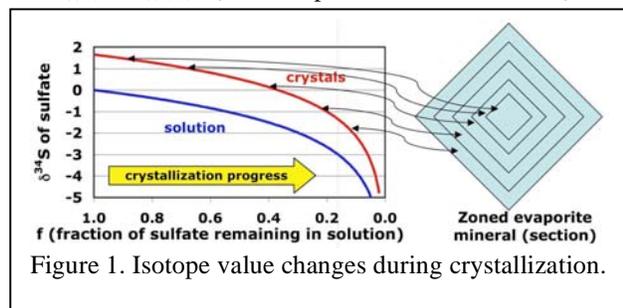


Fig 1, the values for both solution (lower line) and crystals (upper line) show parallel trends and relatively large and nonlinear changes in isotopic composition, despite the small, initial isotope effect.

Isotopic analysis of successive zones in evaporite mineral crystals, and estimating their relative volumes will determine where in the evolution trend the zones grew, a nonlinear evolution. Thus we can extrapolate back to the initial condition ($f=1$) and the original mass of gypsum in solution, even if examples of the first-formed crystals are not analyzed or not even preserved. Zonal analysis of a few crystals will show if they are part of the same evaporitic system and together with outcrop data allow estimation of bulk isotopic masses and what fraction of the total evaporation record it represents. Gypsum solubility is relatively independent of temperature, 2.42 – 2.79 g/L between 0° and 50°C [6] and thus the minimum water volume involved can be calculated. Equally, changes in sulfate sources could be identified by step changes in isotopic composition. A further advantage is that sulfur and oxygen in sulfate, even in solution, are resistant to isotopic exchange and will preserve their original signature [8].

Validation: Data on crystallization of sodium chloride and chlorate samples during the manufacturing process [5] give isotopic trends that conform qualitatively to the Rayleigh fractionation model. A similar effect has been observed qualitatively on a much larger scale in successive, massive evaporite salt beds [6].

Conclusions: This approach could add valuable information about evaporite deposits. Its use for Mars exploration could be applied to almost any evaporites and would not require sampling from large volumes or over large areas. It would, however, need further calibration of isotope effects for potentially relevant minerals and development of in situ instruments from the current generation of laboratory devices.

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Stable isotope characterization of microbially produced sulfate: field data validation at Río Tinto of new laboratory culture experiments. Max L. Coleman¹, Stuart Black², Benjamin Brunner¹, Christopher G. Hubbard², Terry J. McGenity³, Randall E. Mielke¹ and Jae-Young Yu⁴, ¹Jet Propulsion Laboratory, California Institute of Technology (4800 Oak Grove Drive, Pasadena, CA 91109, max.coleman@jpl.nasa.gov), ²School of Human and Environmental Sciences, The University of Reading (Reading RG6 6AB, UK), ³Department of Biological Sciences, University of Essex (Wivenhoe Park, Colchester, Essex, CO4 3SQ, UK), ⁴Department of Geology, Kangwon National University (Chuncheon, Kangwon-Do 200-701, Republic of Korea).

Introduction: The sources of sulfate on Mars described recently [1-3] have not been determined but one possibility is pyrite oxidation [4]. This exposes another possibility that the oxidation process was microbial. There are many reported stable isotope fractionation values associated with microbial oxidation of pyrite for both sulfur [5] and oxygen [6-8]. The oxygen isotope fractionation is large and variable but different results are reported from the various experiments reported and explained by differences in experimental conditions [5, 7]. Our experiments on microbial growth of *Acidithiobacillus ferrooxidans* oxidizing pyrite have identified isotopic fractionation of sulfur, apparent during lag phase of microbial growth. In the same experiments two processes can be identified by their sulfate oxygen isotope values, one of which predominates during lag phase growth. Despite the transience of the lag phase growth period we have detected these isotope signatures in the waters produced by pyrite oxidation in the Río Tinto system, southern Spain.

Lab oxidation of pyrite: We measured sulfur and oxygen isotope compositions of sulfate from pyrite oxidation, compared with those of pyrite and water, respectively. The samples used were those for which we had identified different chemical compositions of solutions during lag and exponential growth phase, the former characterized by having almost all iron present as Fe^{2+} [9]. Significant isotope fractionation occurs only in the lag phase of microbial growth where the predominant oxidation pathway is represented by $\text{FeS}_2 + 3.5\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+$. Abiotic pyrite oxidation, catalyzed by ferric ion, $\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + \text{SO}_4^{2-} + 16\text{H}^+$, is the dominant pathway in the exponential growth phase and gives negligible sulfur and oxygen isotope fractionation while the microbes oxidize Fe^{2+} to Fe^{3+} . The sulfur isotope fractionation during the lag phase may result from disproportion of sulfoxyanion after dissolution of pyrite. $\delta^{34}\text{S}$ in sulfate is $+4.3 \pm 0.6\%$ relative to the pyrite. Oxygen isotope fractionation during lag phase growth is estimated as a maximum of approximately $+13\%$, $\delta^{18}\text{O}$ sulfate relative to water. Our simple mass balance calculations show that at least two mechanisms are operating and contributing in different proportions during

the lag and exponential growth phases. The variations in previously published values are indeed most likely produced by differences in experimental conditions that could control the relative contributions of the two oxidation pathways. Thus, lag phase microbial oxidation of pyrite is characterized by presence of Fe^{2+} and relatively positive $\delta^{18}\text{O}$ values.

Río Tinto area field studies: Extensive analysis of chemical and isotopic compositions of waters of the Río Tinto basin has identified a multicomponent mixing system. Two main sources predominate. The first is typified by the headwaters at Peña del Hierro: a small volume of red, concentrated (Fe, 10-23 g/L), nearly fully oxidized ($\text{Fe}^{2+} \leq 3\%$ of Fe_{total}), low pH (1.6-1.7) water. Iron speciation and microbial assays [10] imply pyrite oxidation by ferric iron with the released Fe^{2+} being rapidly oxidized by *L. ferriphilum* and *A. ferrooxidans*. Our data show a fractionation of $+4.0\%$ in $\delta^{18}\text{O}\text{-SO}_4$ relative to water and suggest that water is the primary source of oxygen. The other main component is a green, lower pH (0.87 – 1.1), more concentrated (Fe, 8.1-46 g/L), reduced (Fe^{2+} , 72-97 %) solution sampled at Zarandas Naya. $\delta^{18}\text{O}\text{-SO}_4$ is $+11.2\text{-}13.0\%$, relative to the water and implies a major contribution from atmospheric oxygen, similar to that in lag phase growth. Since these solutions form Fe^{2+} sulfate evaporite minerals microbial oxidation biosignatures may occur and be preserved.

Conclusions: Paradoxically, solutions like those from lag phase oxidation are produced persistently at Río Tinto. Their preservation as sulfate evaporites can offer an insight into past microbial processes.

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SULFATE STABILITY UNDER SIMULATED MARTIAN CONDITIONS. M. Craig, E. A. Cloutis, Department of Geography, University of Winnipeg, 515 Portage Avenue, Winnipeg, Manitoba, Canada R3B 2E9 (m.craig@uwinnipeg.ca, e.cloutis@uwinnipeg.ca).

Introduction: Spectral properties of a number of sulfate samples, 450 to 2500 nanometers, have been investigated under simulated Mars surface conditions of atmospheric pressure and composition, ultraviolet light regime and limited temperature regulation in the Planetary Spectrometer Facility at the University of Winnipeg.

Experimental Procedure: Reflectance spectra of the $45\ \mu\text{m}$ samples were acquired with an ASD Field-Spec Pro HR from 450-2500 nm with between 2 and 7 nm spectral resolution via bifurcated fibre optic probe $i=0^\circ$, $e=0^\circ$ relative to halon. Two thousand spectra were averaged to increase signal-to-noise ratio. Reflectance spectra from 2-4.3 μm were measured with a Designs and Prototypes Model 102F FTIR spectrometer with $i=35^\circ$, $e=0^\circ$ and 6 wavenumber resolution, relative to brushed gold. One hundred spectra were averaged to reduce signal-to-noise ratio. Reference spectra were measured in air, without the sapphire window of the environment chamber, then with window prior to and immediately following pump down to 5 torr CO_2 (0.2 inHg, 6.7 Mb). Spectra were collected approximately every two days thereafter as well as before and after each change in experimental conditions. Standard procedure has been a run of 10 days at 5 torr, 10 days at 5 torr plus irradiation by ultraviolet light (1 day = 1 decade on Mars) and 10 days at lower pressure, 2×10^{-2} to 8×10^{-3} torr CO_2 ; excepting samples from the first run which spent 14, 9 and 24 days at equivalent conditions, respectively. The samples were kept between 12° and 26°C throughout.

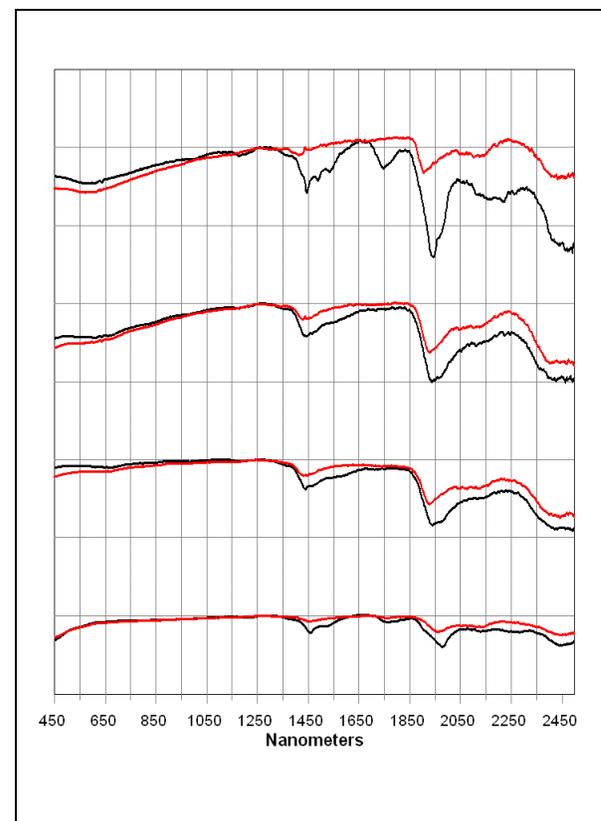
Results: Presented in figure 1 are the reflectance spectra of four samples (normalized to 1 at $1.25\ \mu\text{m}$), from top to bottom: gypsum (run 1), hexahydrite 1 (run 1), hexahydrite 2 (run 3) and kieserite (run 2). Not shown are corresponding spectra from 2-4.3 μm and spectra from samples that evidenced little or no changes: jarosite (run 1), anhydrite, alunite, szomolnokite, fibroferrite, paracoquimbite, copiapite and rhomboclase (run 2) and gypsum (run 3). What differed between runs other than overall duration was vacuum level of the lower pressure portion. Ultimate vacuum achieved for runs 1 thru 3 was 8×10^{-3} , 1×10^{-2} and 2×10^{-2} torr, respectively.

Discussion: The results of exposure to current Martian surface conditions have been vastly different on the series of sulfates studied. The H_2O bearing members have experienced the most spectral changes due to dehydration with both decreases in hydration

feature band depth, and subtle shifting to lower wavelengths of some band centers. The OH and $\text{H}_2\text{O}/\text{OH}$ free samples evidenced no changes with exposure to 5 torr and 5 torr with UV. Dehydration did not occur in any samples until the pressure was lowered below 5 torr and preceded very rapidly thereafter if a particular sample's vacuum threshold was crossed. This effect is most evident in the two identical gypsum samples. The sample from the first run dehydrated very rapidly at 8×10^{-3} torr but did not dehydrate at all at 2×10^{-2} torr.

Conclusions: This study raises several questions, some of which we cannot yet answer. Exposure to 5 torr of such short duration has no discernable effect on the sulfates studied thus far; as such, does exposure to lower pressures approximate a vastly longer time span at 5 torr? Additionally, what are the effects of the diurnal/seasonal temperature swings on Mars?

Figure 1: From top to bottom: gypsum, hexahydrite 1, hexahydrite 2 and kieserite. **Black**, first spectra acquired in air with window, **red**, last spectra acquired with window at 8×10^{-3} , 8×10^{-3} , 2×10^{-2} and 1×10^{-2} respectively. Only first and last spectra shown for clarity.



MIXING AND RE-SOLUTION PROCESSES AFFECTING EVAPORITE MINERAL DISTRIBUTIONS ON EARTH AND MARS. J. K. Crowley¹, J. S. Kargel², G. M. Marion³, S. J. Hook⁴, N. T. Bridges⁴, A. J. Brown⁵ and C. R. de Souza Filho⁶

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Introduction: Near-surface groundwaters that freeze or evaporate produce saline mineral assemblages that are generally related to the initial dissolved solute compositions [1]. Such assemblages formed by the fractional crystallization of evaporating brines are composed mainly of phases that represent major chemical divides, and these assemblages can be readily predicted by chemical modeling [2], [3]. Here we highlight several additional processes that can markedly increase evaporite assemblage complexity on Earth and likely also on Mars. Temporal oscillations in these processes can produce evaporite laminations and beds.

Dilute Inflow Additions to Brine: During the course of groundwater evolution certain solutes are typically depleted. A classic terrestrial example is potassium, which is removed from groundwaters by clay mineral adsorption. Even major solutes such as calcium may be depleted via the action of chemical divides. However, playa-margin springs and ephemeral streams provide inflow sources of dilute, unevolved waters that may discharge directly into more concentrated brines. A similar source function may be served on Mars by permafrost melting during warm climatic shifts or by impact heating or hydrothermal activity. These sources "short-circuit" the normal course of brine evolution and produce mineral assemblages containing "unexpected" solute components.

Volcanic Exhalative and Hydrothermal Additions to Brine: In terrestrial playa settings, and hypothetically also on Mars, some springs have water sources and solute compositions that are very different from typical basinal groundwaters. For example, spring waters enriched in borate produce distinctive evaporite mineral assemblages and at the same time signal the existence of deeper circulating, perhaps hydrothermal, water sources.

Zone Refining: Another way that unusual brine compositions are produced is by passage of concentrated brines through thick sequences of evaporitic materials; already saturated major mineral species remain stable, but minor and trace species are progressively leached and fractionated into the brine until they too, saturate. Salts enriched in K, Rb, Sr, Br, I, B, and other elements can be produced this way. On Mars, where rainfall washing and re-solution of precipitated

salts has been minimal or absent through much of geologic time, zone refining in subsurface saline groundwater/evaporite systems or in surficial duricrusts may have produced long-lasting deposits of exotic salt compositions.

Re-cycling of Evaporite Crusts: Partial re-solution of evaporite crusts-- a process that includes zone refining but includes other processes, too-- also can lead to increased mineral diversity. For example, Mg is present in many terrestrial salt crusts as highly soluble chloride phases that are easily leached and redistributed. However, in sulfate-rich brines, perhaps akin to those on Mars, Mg is more resistant under some circumstances. On Mars, we expect that incongruent dissolution-- peritectic melting of hydrates with partial dehydration of residual salts-- is apt to be even more important than on Earth, because the higher hydration states are expected to be more common. In fact, crustal re-cycling outcomes are complexly dependent on parent brine compositions.

Redox and pH Cycling: Special types of geochemical divides are represented by the buffering of pH and redox state by major mineral or dissolved species. When acid/base or reductant/oxidant titration occurs, buffers eventually can be overwhelmed and brine equilibria can suddenly shift, additional species can be solubilized or precipitated out of solution, and mineral stability completely altered. This type of behavior can occur in response to oscillations in brine sources and brine mixing, episodes of igneous rock emplacement in the catchment basin, volcanic exhalative activity, erosional exhumation and weathering of different rock types, or shifts in atmospheric composition.

Terrestrial acid evaporite mineral deposits are one of several Mars-analog environments being studied by the authors in the field and through chemical modeling.

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