Raman Detection Threshold Measurements for Acetic Acid in Martian Regolith Simulant
JSC-1 in the Presence of Hydrated Metallic Sulfates

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Abstract
Several measurements, including the data from the laser spectrometer in the Sample Analysis at Mars instrument suite on the Curiosity Rover in Gale crater, have measured seasonal variations in atmospheric methane at the 0.7 ppbv (parts per billion volume) level. As a result, models have been proposed to understand the methane production including novel chemical, geological, meteorological, and biological mechanisms. Biological models often rely on methanogenic extremophile archaea which might be similar to some Earth based organisms which can be studied exhaustively in a laboratory setting. Such organisms might thrive in a subsurface ecosystem involving water and methane and as such could leave a unique biosignature in the Martian regolith that could be preserved over extended periods of time. The resulting mixture of carboxyl, acetyl and hydroxyl groups blended with the metallic sulfates and regolith constituents could produce a Raman signature detectable on the next rover mission if the concentration is high enough. Here we measure the 532 nm and the 780 nm Raman spectra of a variety of molar concentrations of several hydrated metallic sulfates mixed with JSC-1 Martian regolith simulant to identify the signature concentration thresholds for the isolated C=O Raman peak from acetic acid. We find a Raman peak removed from most fragmented molecular Raman bands near 1608 cm\textsuperscript{-1} using the 532 nm laser for the Fe and Mg sulfates to yield a threshold in the 120 - 160 ppmv range for a cutoff S/N of 2.

I. Introduction
The early detection of periodic releases of methane as atmospheric plumes at select latitudes in the northern hemisphere of Mars in 2003, as seen from both Earth based observations\textsuperscript{1,2} and from orbiting sensors,\textsuperscript{3,4} indicating that single plume masses on the order of 19 metric ktons of methane had been generated has produced a considerable amount of excitement and research. Estimates of concentrations as high as 30 ppbv (parts per billion volume), even when distributed uniformly throughout the atmosphere, required unusual decay and source channels to match the low abundances found elsewhere. Sources for methanogenesis can be geochemical- most notably low temperature geothermal serpentinization\textsuperscript{5}, can be from meteoric or cometary atmospheric infall, or can be biogenic in origin. However, detailed modeling\textsuperscript{6} and an examination of the telluric lines\textsuperscript{7} that interfere with the possible methane production lines indicate that these observations of large amounts of methane in the Martian atmosphere are overestimates. In 2015 data from the tunable laser spectrometer of the Sample Analysis at Mars (SAM) instrument suite on Curiosity Rover at Gale crater, after a twenty-month collection window, indicated the presence of varying
methane quantities lower than the original estimates to be about $0.69 \pm 0.25$ ppbv with some periods of higher production near $7.2 \pm 2.1$ ppbv. By 2017 the SAM suite team had conducted a complete methane isotopologue study including foreign broadening- from carbon dioxide and He, along with molecular rotational and vibrational analysis from the Curiosity tunable laser system that continued to support the observation of these methane levels. Methane has also been measured in six of the Martian meteorites that have been found on Earth by using a Crush Fast Scan Mass Spectrometer whereby gasses in the meteorites were released and measured and compared to Earth based and carbonaceous chondrite concentrations. Rover measurements show that the Martian surface contains more olivine and pyroxene than found on Earth and in a low temperature aqueous environment can experience serpentization to produce hydrogen and methane in combined processes such as:

$$18\text{Mg}_2\text{SiO}_4 + 6\text{Fe}_2\text{SiO}_4 + 26\text{H}_2\text{O} + \text{CO}_2 \rightarrow 12\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 4\text{Fe}_3\text{O}_4 + \text{CH}_4 \quad (1)$$

providing an abiotic origin for methane and a mechanism for the creation of a subsurface methane rich habitat. The presence of hydrated olivine rocks provides a natural pathway to methane production via serpentization, that could be catalyzed by volcanic outgassing, that could have been very active during the Noachian period and resulted in underground pockets of stored methane. Both the low temperatures and pressures at the surface would have been favorable for methane production that could then be released through surface via geothermal activity.

In addition to the direct atmospheric studies data from the Spirit rover in Gusev crater, the Opportunity rover in Meridian Planum and Curiosity rover in Gale crater determined the mineralogical composition of the Martian regolith. The dominant minerals are olivine, pyroxene, plagioclase and magnetite with admixtures of monohydrated and polyhydrated sulfates, most notably with Ca, Ni, Mg and Fe. In addition, chlorates and perchlorates have been found indicating a harsh environment for any organic compounds or potential extremophile archaea. The surface minerals experience a significant amount of UV flux on Mars, mainly at the shorter wavelengths of UVC (100-280 nm) and of UVB (280-315 nm). Various works on the biological effects of UV radiation have established that even the present-day instantaneous Martian UV flux would not in itself prevent the existence of life on Mars. However, it has been found that UV initiated photochemical reactions involving perchlorates, peroxides and iron oxides enhance the cell death rate of Bacillus subtilis by a factor of 10.8 for a sixty second exposure leading to nearly complete bactericide. Thus, the current surface environment is photo-chemically uninhabitable to many known species and would work to eradicate contaminating species from landing vehicles from Earth thereby significantly lowering contamination probability as described by the Coleman-Sagan equation. As such, the preservation of a biosignature on the surface of Mars might focus on the subsurface ecosystem. More recent data from perchlorate, oxide, and sulfate measurements has been used to produce Martian simulants for active study on various mechanical and geochemical properties possessed by the surface materials. In addition, significant amounts of frozen water have been found in exposed scarps 1-2 meters below the surface at the mid-latitude regions. The ice cliffs extend for more than 100 m below the surface and may be indicative of a long period of successive snow deposits during a high obliquity period. Both geochemical and biochemical processes could take advantage of these long-lived ice sheets.
To prepare for future spectral measurements on the surface of Mars researchers are expanding their analysis to include the advantages of Raman spectroscopy with lab based tests on Martian simulants to identify threshold identification values for various molecules. Studies have been done on the sensitivity of the Raman signal for samples in Martian simulant with hydrated salts, chlorates and perchlorates, and organic molecules such as chlorophyll, carotene, and a host of reasonable methanogenic based organic molecules, as indicated by high resolution chromatographic analysis of the Murchison meteorite and other carbonaceous chondrites, which contain numerous organic molecules, including acetic acid and amino acids such as glycine, D-Alanine and L-Alanine, it is clear that many interesting molecules can have a non-biotic Martian origin. Careful modeling of Fickian and Knudsen diffusion at depths beyond 1.0 km indicate that diffusive mechanisms alone cannot account for all of the methane production. Recently an, in principle, testable mass conservation column flux model to describe the sub-annual Gale crater variation of methane production has provided insight on developing some novel approaches to the observed time variations in atmospheric methane concertation on Mars. The authors examine three near surface interaction scenarios for methane production: in the first case the surface adsorbs methane when dry and then releases it upon deliquescence with surface water diffusion and a concentration near 4x10^6 kg/m^3, in the second microorganisms produce the methane, and in the third they examine possible deep subsurface aquifers to produce methane outgassing. They consider the conservation equation with relevant sources where we have added the UV-regolith interaction surface term to account for buildup from Interplanetary Dust Particles, IDP, with photolytic release mechanisms, a serpentinization thermal outgassing term effective to depths of up to z meters where subsurface studies and analysis has been done up to 6 km, we use these two terms as potential background methane production terms without adding an explicit relaxation term and we include a volcanic outgassing term for release through porous solidified crustal magma giving a production equation of the form:

\[ \frac{dM_{CH_4}}{dt} = F_{\text{serpentinization}} + F_{\text{Deliquescence}} + F_{\text{Methanogenic}} + F_{\text{UV}} + F_{\text{VolGr}} \]

where the total serpentinization process up to 10 km below the surface can be represented by a weakly coupled Langmuir interacting product term ξTot with indexed equilibrium constants for each interaction and associated number densities ni for each activation energy Ea, the chemical kinetics can be altered to include strongly interacting BET or Freundlich interactions to accommodate potential multilayering and surface roughness factors, the first deliquescence term corresponds to a Langmuir isotherm adsorption reaction in the soil, the second term corresponds to the production by methanogenic species where, ρs is the soil density, γ is the monolayer coverage of methane per unit surface area, As is the specific surface area, θ is the fractional coverage ratio by methane or species j, Kq is the chemical reaction equilibrium constant for methane or species j, nx is the number density of chemical species x, vth is the thermal velocity of the chemical species, Ea is the adsorption energy, Cali is the soil content of aliphatic...
hydrocarbons expressed as a dimensionless ratio in kg/kg of soil, \( t_0 \) is the baseline soil residence time for carbon at 273 K, \( Q \) is a constant chosen to be indicative of typical biological methane emission where they find the value near 2 is consistent with terrestrial studies, \( h \) is the Planck constant, \( R \) is the gas constant, \( k_b \) is the Boltzmann constant, where each term is integrated to a depth \( z \). The surface adsorption interaction is treated as a Langmuir interaction with a deliquescent interaction with water and would generally require more energy than has been seen in the lab environment, near 36 kJ mole\(^{-1}\), the methanogenic model requires microorganisms to produce the methane, and their final model examines the existence of deep subsurface aquifers as a source of methane. The \( F_{vol} \) term accounts for the solar ultraviolet surface release of methane related to sedimenting interplanetary dust particles, IDP, measured by the Rover Environmental Monitoring Station on the Mars Science laboratory\(^47\). Production rates for these interactions are measured to be about 8 x 10\(^{-4}\) ppbv sol\(^{-1}\) and depend upon the radiant UV intensity, averaged over 200-400 nm, the mass fraction of carbon in the regolith \( \chi \), surface roughness characterized by the diameter of the regolith grain \( D \), the fraction of in-falling carbon that is accreted \( f \), the molecular weight of the carbon containing molecule \( m_w \), and the overall quantum efficiency of the photolytic conversion process as a function of temperature expressed as \( aT \) - \( b \) where \( a = 2.76 \times 10^{-15} \) mole/JK and \( b = 1.54 \times 10^{-13} \) mole/J, integrated over the total the total surface area exposed. For well mixed fine-grained regolith this last term produces up to 11 ppbv with variations that depend on latitude and seasonal temperatures, grain size and weather distributions and expected fractional conversion rates. The \( F_{VolGas} \) term is for methane produced by volcanic outgassing\(^48\) on Mars. The Martian magma production rate\(^49\) is given by \( R_{Magma} \), for \( M_{crit} \) which is the mass of extracted liquid magma, \( X_{melt}(z) \) is the melt concentration\(^50\) of the extracted species in the melt which depends upon the depth below the surface, and \( \eta \) is the overall efficiency of the process where values are estimated from the Antarctic Mars meteorites and the Martian surface magnetic fields with magnitudes near 4 nT. For the currently solidified upper crust where up to 25% of the surface is covered by volcanic magma predominately\(^51\) in the Tharsis and Syrtis regions and a volume on the order of 12 x 10\(^6\) km\(^3\) with an internal geothermally active model\(^52\) of the core outgassing can continue at rates that are dependent upon the porosity, depth of the crust and includes CO\(_2\) and H\(_2\)O components which contribute to significant atmospheric gas production, can stably be productive since the Noachian period and can be deeper than 1 km below the surface, where these gasses can serve as precursors to later time serpentization. The parametrization of Eq. (2) is such that there are many solutions that yield reasonable methane values without need for extraordinary events or circumstances, better measurements will produce more robust constraints allowing for the determination of the dominant terms responsible for producing the observed methane on Mars. A number of time scales arise in this model: the volcanic outgassing through porosity and the associated production of CO\(_2\) and H\(_2\)O that can participate in serpentization can occur over time scales on the order of 100 million Earth years, the serpentization and aquifer formation can be tens of millions of years, the methanogenic production of methane can have a daily, annual, decadal or longer timeframe, the surface deliquescent interactions and production can occur on a daily and seasonal time scale and the in-fall of IPD occurs over the entire age of the planet and the pyrolysis surface UV reaction occurs in less than a second.

Initial data and boundary conditions for implementing a column model can be extracted from the rover/satellite database and from General Circulation Models such as the open source Mars Climate Database v5.3, MCD\(^53,54\). In this case the column model serves as a high-resolution test
of local conditions with inputs from the global circulation model. The MCD is a database of meteorological fields derived from General Circulation Model (GCM) numerical simulations of the Martian atmosphere and validated using available observational data. The MCD includes complementary post-processing schemes such as high spatial resolution interpolation of environmental data and means of reconstructing the variability thereof. Global maps can be constructed that include variables such as temperature, pressure, water content, dust content\textsuperscript{55}, wind speed, fractional gas content\textsuperscript{56} such as CO or CO\textsubscript{2}, surface ice, etc. In Fig. (1) we show a sample run for surface pressure in Pascals, and temperature in Kelvins, water vapor for a column in kg/m\textsuperscript{2}, solar flux at surface in W/m\textsuperscript{2}, water vapor volume mixing ratio in mol/mol and water vapor column in kg/m\textsuperscript{2}. 

Fig. 1 Mars Climate Database v5.3 output for a Global Circulation Model showing (a) surface pressure in Pascals with vectorize wind speeds at a height of 2.0 m, (b) surface temperature in
Kelvins with vectorized wind speeds at a height of 2.0 m, (c) variations in water vapor column values in kg/m², (d) variations in solar flux to the surface in W/m² with the sun centered at noon in middle of the map, (e) the global water vapor mixing ratio in mol/mol, and (f) the water ice mixing ratio mol/mol.

Each of the global maps can be displayed for altitudes near the surface, at the troposphere, at the boundary layer, at the mesosphere, or at the thermosphere and can highlight phenomena most related to the winds, weather, atmosphere, water cycle, chemistry, glaciology, landing engineering, surface meteorology and radiative balance. Data can also be collected for a fixed location, such as the Curiosity region in Gale crater. For a fixed latitude and longitude, the local variation of these parameters can be determined as functions of time or altitude as shown in Fig. (2).

Figure (2) Gale crater location showing changes in: (a) surface pressure on Pascals over one sol, (b) surface temperature in Kelvins for one sol, (c) atmospheric temperature as a function of altitude up to 250 km and (d) variation in Ozone volume mixing ratio as a function of altitude.

The range of parameters from the GCM provide a significant base for modeling and as input values for Eq. (2). The associated ice, depth, radiation, dust and estimated magma flow regions and layering provide a reasonable set of values to initiate a general study of the model.

Another approach to investigating potential organic molecules is to identify those that might be similar to Earth based methanogenic extremophiles that take advantage of the observed methane signature at Mars. The metabolic requirements of methanogenic archaea are in principle compatible with these extreme environmental conditions especially the methanogenic
permafrost and ice related psychrophiles in the cryobiosphere\textsuperscript{64}. Several common extremophiles and their average ecosystem parameters are listed below in Table 1.

### Parameters for Methanogenic Extremophiles

| Methanogenic Archa\textsuperscript{65} | M. formicicum\textsuperscript{66} | M. bryantii\textsuperscript{67} | M. ivanovii\textsuperscript{68} | M. alcaliphilum\textsuperscript{69} | M. espanolae\textsuperscript{70} | M. palustre\textsuperscript{71} | M. uliginosum\textsuperscript{72} | M. subterraneum\textsuperscript{73} |
|--------------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Morphology and structure             | Rod: (0.4-0.8) x (2-15), filaments, clumps | Rod: (0.5-1)x(1.5) filaments, clumps | Rod: 0.5-0.6 x 2-5 Filaments | Rod: 0.8 x 3-22 Filaments | Rod: 0.5 x 3-5, Filaments | Rod: 0.2-0.6 x 2-4 Filaments | Short rod: 0.1-0.15 x 0.6-1.2, Aggregates |
| Potential temperature range °C       | 25-50           | 37-39           | 15-55           | 25-45           | 15-50           | 20-45           | 15-45           | 30-45           |
| M salinity                           | 0.25            | 0.26            | 0.19            | 0.012           | n.a.            | 0.3             | n.a.            | 0.14            |
| pH range                             | 6.6-6.8         | 6.9-7.2         | 6.5-8.5         | 7.0-9.9         | 4.6-7.0         | 7               | 6.0-8.5         | 6.5-9.2         |

Table 1. General parameters associated with typical methanogenic species. As an example of a species adapted to the extreme cold, the species \textit{Planococcus halocryophilus Ori}\textsuperscript{74} survives and is metabolically active in temperatures as low as -15 °C.

The methane production rates for several methanogens have been determined from direct solid and ice samples in permafrost and glaciers. The range of CH\textsubscript{4} production varies from near 4.8 nmol/g-d to an estimated 850 nmol/g-d\textsuperscript{75}. Typical metabolic pathways\textsuperscript{76} that would involve carbon dioxide reduction and acetate fermentation often include reactions of the form:

\[
CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad \text{and} \quad CH_3COO^- + H^+ \rightarrow CH_4 + CO_2 .
\] (3)

In general, there may be several low molecular weight carboxylic acids from methanogenic extremophiles. The existence of acetate ions in the presence of water can lead to the formation of many associated acetic acid groupings involving hydrogen bonds yielding dimers\textsuperscript{77} and hydroxyl groups\textsuperscript{78} or cluster formations between the acetic acid subgroups\textsuperscript{79}. These molecules have a rich vibrational spectrum that has been well studied using Raman spectroscopic techniques. Of particular interest here are the unique Raman lines for methanogenic subsurface acetic acid that can be in dry or moist Martian regolith in the presence of metallic sulfate concentrations similar to those found by the Curiosity rover. The sulfate group produces strong symmetric stretching Raman lines near 1000 cm\textsuperscript{-1} which overlap and obscure a strong acetic acid line, however a secondary acetic acid line near 1605 cm\textsuperscript{-1} is apparent at high enough concentrations. Here we explore the threshold Raman\textsuperscript{80} signal at 532 nm and 780 nm for acetic acid as a methanogenic byproduct mixed in JSC-1 Martian Regolith simulant with hydrated metallic sulfates blended in at ratios indicated from Curiosity rover measurements and studied by Wang\textsuperscript{81} that would have been protected from radiation by being part of a subsurface environment.
II. Sample Preparation and Procedure

We mixed reagent grade hydrated iron and magnesium sulfates prepared with seven different concentration levels of glacial acetic acid in ambient conditions as shown in Table 2, leading to concentrations ranging from 52 ppm-m to 653 ppm-m. Samples were mixed with JSC-1 Martian regolith simulant, with grain size distribution given in Table 3 with an optical image of the 25 mm capsule and grain distribution and whose contents are as indicated in the first column in Table 4. Each mixture was placed into a capsule and compressed to 5 MPa and dried for one week. Samples were tested at two different wavelengths to secure Raman Spectra: an inVia confocal Renishaw 532 nm, 50mW, FSR operating from 300-3500 cm\(^{-1}\) and a Thermo-Scientific confocal DXR2 780 nm, 80mW, FSR from 200-3500 cm\(^{-1}\) Raman Spectrometer with contact spot size of 8 microns. Sample pH measurements were done using a Jenway 3510 pH meter with an Orion 910003 calibration sample at 22.3° C.

Table 2. Composition of both the Fe and Mg based samples, prepared with glacial acetic acid and JSC-1 Mars simulant to give parts per million by mass.

| Sulfates     | Sulfate | Mass Fraction | Acetic Acid 60.05 g/mol Concentration ppm by mass |
|--------------|---------|---------------|-------------------------------------------------|
| JSC-1 86.72 g/mole | | | |
| MgSO\(_4\) | 14.97 | 0.05 | 0.53 | 9.62 | 3.88E+21 | 63 | 152 | 217 | 273 | 326 | 472 | 7.03 |
| MgSO\(_4\)-3H\(_2\)O | 174.41 | 0.07 | 0.75 | 9.73 | 3.46E+21 | 52 | 163 | 241 | 296 | 383 | 547 | 7.51 |
| MgSO\(_4\)-6H\(_2\)O | 210.44 | 0.07 | 0.73 | 9.86 | 2.77E+21 | 64 | 186 | 225 | 308 | 425 | 584 | 7.45 |
| MgSO\(_4\)-7H\(_2\)O | 246.49 | 0.07 | 0.74 | 10.08 | 3.25E+21 | 73 | 148 | 216 | 283 | 397 | 563 | 7.73 |
| FeSO\(_4\) | 151.90 | 0.05 | 0.53 | 9.62 | 3.88E+21 | 59 | 137 | 275 | 329 | 381 | 498 | 7.81 |
| FeSO\(_4\)-5H\(_2\)O | 241.97 | 0.05 | 0.54 | 9.63 | 3.88E+21 | 63 | 152 | 217 | 273 | 326 | 472 | 7.03 |
| FeSO\(_4\)-7H\(_2\)O | 278.00 | 0.05 | 0.52 | 10.19 | 3.72E+21 | 84 | 165 | 283 | 352 | 412 | 485 | 7.14 |

Table 3. Image of Regolith capsule about 25 mm in diameter and 3 mm deep, 10 X Nikon Microscope optical image of granularity structure of a sample Grain size distribution of JSC-1 Martian simulant as reported by Allen, et al.\(^\text{82}\).

The JSC-1 Mars Regolith simulant was designed by NASA Johnson Spaceflight Center to help support scientific, engineering and research labs investigate and characterize materials that can mimic as closely as possible the features of Martian regolith. Table 4 gives a comparison of JSC-1 Martian Regolith to sample sites on Mars where data was available.
Comparison of Bulk Martian Regolith Samples

| Chemical          | wt %       | Chryse Planitia | Utopia Planitia | Ares Vallis | Gusev Crater | Meridiani Planum | Gale Crater |
|-------------------|------------|----------------|-----------------|-------------|--------------|------------------|-------------|
| SiO₂              | 34         | 43             | 43              | 44          | 46.1 ± 0.9   | 45.7 ± 1.3       | 42.88 ± 0.47 |
| Al₂O₃             | 18         | 7              | 7               | 7.5         | 10.19 ± 0.69 | 9.25 ± 0.50      | 9.43 ± 0.14  |
| TiO₂              | 3          | 0.66           | 0.56            | 1.1         | 0.88 ± 0.19  | 1.03 ± 0.12      | 1.19 ± 0.03  |
| Fe₂O₃ + FeO       | 12         | 18.5           | 17.8            | 16.5        | 16.3 ± 1.1   | 18.8 ± 1.2       | 19.19 ± 0.12 |
| MnO               | 0.2        | n.a.           | n.a.            | n.a.        | 0.32 ± 0.03  | 0.37 ± 0.02      | 0.41 ± 0.01  |
| CaO               | 4.9        | 5.9            | 5.7             | 5.6         | 6.3 ± 0.29   | 6.93 ± 0.32      | 7.28 ± 0.07  |
| MgO               | 2.7        | 6              | 6               | 7           | 8.67 ± 0.60  | 7.38 ± 0.29      | 8.69 ± 0.14  |
| K₂O               | 0.5        | <0.15          | <0.15           | 0.3         | 0.44 ± 0.07  | 0.48 ± 0.05      | 0.49 ± 0.01  |
| Na₂O              | 1.9        | n.a.           | n.a.            | 2.1         | 3.01 ± 0.30  | 2.21 ± 0.18      | 2.72 ± 0.10  |
| P₂O₅              | 0.7        | n.a.           | n.a.            | n.a.        | 0.91 ± 0.31  | 0.84 ± 0.06      | 0.94 ± 0.03  |
| SO₃               | n.a.       | 6.6            | 8.1             | 4.9         | 5.78 ± 1.25  | 5.83 ± 1.04      | 5.45 ± 0.10  |
| Cl                 | n.a.       | 0.7            | 0.5             | 0.5         | 0.70 ± 0.16  | 0.65 ± 0.09      | 0.69 ± 0.02  |
| Cr₂O₃             | n.a.       | n.a.           | n.a.            | n.a.        | 0.33 ± 0.07  | 0.41 ± 0.06      | 0.49 ± 0.02  |
| Ni μg/g           | n.a.       | n.a.           | n.a.            | n.a.        | 476 ± 142    | 457 ± 97         | 446 ± 29     |
| Zn μg/g           | n.a.       | n.a.           | n.a.            | n.a.        | 270 ± 90     | 309 ± 87         | 337 ± 17     |
| Br μg/g           | n.a.       | n.a.           | n.a.            | n.a.        | 53 ± 46      | 100 ± 111        | 26 ± 6       |

Table 4. Composition of the raw JSC-1 Martian Regolith from JPL compared to Viking Landers 1 and 2 from XRF, Pathfinder from APXF, Spirit from APXS, Opportunity from APXS and Curiosity from APXS. Errors for Gusev Crater and Gale Crater, in the Rocknest site, represent average values plus or minus one standard deviation, errors for the Meridiani measurements represent analytical uncertainties. The Curiosity ChemCam identified two different soil types: a fine grained mafic similar to the Martian dust and a locally derived coarse grained felsic with typical 8% one sigma average deviations. The oxychlorine compounds, soluble sulfates and ground ices were discovered by the Phoenix lander in 2008 at Vastitas Borealis and include the chlorates, perchlorates and chlorites using the Mars Environmental Compatibility Assessment (MECA) Wet Chemistry Lab and Sample Analysis on Mars (SAM) instrument.
The Raman spectra with the sulfates exhibit the strong SO$_4$ peak which splits and overall broadening dependent upon hydration states and complexity of the water interaction seen in Fig. 3 (a), as noted by Sharma$^{106}$ and Wang$^{13,20,107}$ The sulfates show the expected decrease in intensity as concentration is changed as shown in Fig. 3 (b) and (c) with the primary peak at 1006 cm$^{-1}$ with concentrations by mass percent changing as 20%, 15%, 10%,7%, 3% and 0% to approximately match amounts observed on the surface of Mars. In addition to the Raman spectra from the standard capsules with varying sulfate, acetic acid and hydration levels we considered the estimated potential Raman signals from fragmented molecular combinations that might interfere with or obscure the threshold signals of interest. We examined fragmented components that include alkanes, peroxides, dimer pairings, sulfate groupings and alcohols that can produce background signals, several of these are shown as broadband background signals in Fig. (3). For the observed acetic acid threshold, the line near 1608 cm$^{-1}$ was most often not significantly impacted by the fragmented molecular Raman lines.

### Table 5. Raman Lines for Acetic Acid$^{102,103}$ and potential hydrated sulfates$^{104,105}$ combined with the JSC -1 Martian simulant.

| Raman Lines | Units | Vibrational Mode |
|-------------|-------|------------------|
| Acetic Acid | cm$^{-1}$ |                  |
| C-H         | 3020  | sp$^3$ C-H, stretch CH$_3$:H-C-H asymmetric stretch |
| C-H         | 2985  | C-H asymmetric stretch |
| C-H         | 2940  | sp$^3$ C-H, stretch CH$_3$:CH$_3$ stretching |
| C=O dimer   | 1668  | O-H hydrogen bonded dimer |
| C=O         | 1630  | C=O stretching |
| CH$_2$      | 1428  | H-C-H asymmetric swing |
|            | 1366  | H-C-H bending |
|            | 1280  | O-H swing, C-C swing |
| CH$_2$      | 1014  | O-C-C asymmetric stretch, H-C-H symmetric swing |
|            | 982-1052 | for Mg as N=0,1,…11 |
| SO$_4$      | 1010  | for SO$_4$ symmetric stretching mode |
| H$_2$O      | 3380  | Mg stretching vibrational modes |
| X=Ca,Fe,Mg | 3300  | 3200-3480 for H$_2$O, broad line stretching mode |

| Sulfates    | Units | Vibrational Mode |
|-------------|-------|------------------|
| XSO$_4$-N H$_2$O | 1006 | 982-1052 for Mg as N=0,1,…11 |
| SO$_4$      | 1010  | for SO$_4$ symmetric stretching mode |
| H$_2$O      | 3300  | 3200-3480 for H$_2$O, broad line stretching mode |
Mars Regolith-Acetic Acid Raman Spectra and Select Group Resonances

a. [Image of Raman spectra showing peaks for different substances]

b. [Image of Raman spectra of JSC-1 MS with five levels of acetic acid and FeSO₄ ⋅ 7H₂O]

c. [Image of MgSO₄ ⋅ H₂O Raman spectra in JSC-1 regolith]

d. [Image of baseline corrected Raman spectra with iron sulfate heptahydrate data]

e. [Image of acetic acid Raman weak bond dimer resonances with FeSO₄ heptahydrate data]

f. [Image of MgSO₄ ⋅ 2H₂O Raman data with alcohol Raman group]

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Mars Regolith-Acetic Acid Raman Spectra and Select Group Resonances

Fig. 3. (a) Analytical map of Raman excitation bands due to the sulfate group combined with Fe and Mg atoms analyzed in Bio-Rad KonwItAll Raman Software\(^{108}\) with fragment resonances from H\(_3\)O, OH and SO. (b) Hydrated FeSO\(_4\) with decreasing sulfate concentrations indicated by A, B, C, D, and E, imaged using SpectraGryph\(^{109}\), (c) Decrease in hydrated Mg sulfate concentrations and decrease of the 1006 cm\(^{-1}\) peak, (d) analytical hydroxyl group Raman excitations in acetic acid with fragments from OH, CH\(_3\), C-O-H, and C-C-O, (e) weak acetic acid dimer excitations with CH\(_3\) alkanes and peroxides, (f) MgSO\(_4\) 2H\(_2\)O with alcohol group excitations from C-CH\(_2\)-OH, OH, C-O-H, and C-C-O, (g) methyl group Raman excitations in acetic acid with symmetric and antisymmetric excitations present and carboxylic-acid resonances from R-COOH, (h) four levels of acetic acid concentrations showing two above threshold and two below threshold in the hydrated Fe and Mg sulfate JSC-1 Martian regolith simulant mixture.

III. Results and Conclusions

In conclusion, we have recorded the decrease in the acetic acid hydroxyl Raman line for the 532 nm laser as the concentration was reduced when mixed with Fe and Mg sulfates from 0\% to 20\% by mass in the JSC-1 Martian regolith simulant. The Raman 780 nm line was not as pronounced for the same concentrations. Generally, the Raman peaks shift to longer wavelengths as the hydration is increased, approximately 6.2 cm\(^{-1}\) for Mg and 5.7 cm\(^{-1}\) for Fe per hydration state.
We find that the minimal one sigma signal occurs near the 141-ppmv level for the Martian simulant containing the iron based sulfates and near 116-ppmv for the Mg based sulfates as shown in Fig. (4). These values are not near the ppbv level that might be required as indicated by NASA Ames\(^\text{110}\) and Blanco\(^\text{111}\) who demonstrate that moving to a fluorescent free Raman methodology, which has the capabilities to go below the ppm level, would be a valuable addition to the study of Martian organics\(^\text{112}\).

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