

Martian basalts-Planetary analogue of terrestrial MORBs?

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Abstract

Geochemical comparison between Martian and terrestrial basalts suggest that the Martian samples are similar in bulk composition to the terrestrial MORBs. However, disparity in composition exists between Martian meteorite and *in-situ* Martian surface chemistry. In this work, we use the extended geochemical data sets of the Martian basalts including the *in-situ* X-ray measurements of Martian surface and Martian meteorites to evaluate their geochemical similarity/ dissimilarity with the terrestrial analogs.

1. Introduction

A common geological feature of our inner Solar system planetary bodies is that the outermost crusts of these bodies are generally composed of basalts [1]. The only exception is the Moon, which comprises significant proportion ($3.8 \times 10^7 \text{ km}^2$) of anorthositic crust [2]. In terms of trace elements geochemistry, the basaltic rocks occurring within the mare impact basin have compositions ranges between terrestrial E-MORB (Enriched Mid-Ocean Ridge Basalt) and OIB (Ocean Island Basalt), however, some important compositional differences exist [3]. Therefore, one of the best ways in evaluating the Precambrian plate tectonics on Earth is perhaps a detailed comparative study among the terrestrial and planetary basalts, because the Earth-like plate tectonic signatures is not known for the Moon and Mars [4]. In this study, we present our preliminary observation on the comparative geochemistry between the Martian basalts, and the terrestrial MORBs and Continental Flood Basalts (CFBs) of the Phanerozoic age.

2. Data Source

The Martian basaltic meteorite data were compiled from the Mars Meteorite Compendium [5] and some recent publications [6-9]. *In-situ* APXS data of

Martian surface were collated from literature [10,11]. Apart from Global MORB compilation, CFB data include only the least (crustally) contaminated members of Deccan Traps and Karoo basalts, respectively [12,13,14].

3. Geochemistry

In the TAS diagram, the majority of the *in-situ* analyses of the Martian basalts form a cluster at SiO_2 and $(\text{Na}_2\text{O}+\text{K}_2\text{O})$ around 46 and 3.3 wt% respectively. In contrast, Martian basaltic meteorites have variable SiO_2 ranging 45 and 51 wt% with typically low alkali ($\text{Na}_2\text{O}+\text{K}_2\text{O} \leq 2 \text{ wt}\%$) content (Fig. 1). The clusters of the Martian basalts partly overlap with the terrestrial MORBs but exclude the field of terrestrial CFBs. Even, the Martian basaltic meteorite compositions also mismatch with terrestrial MORBs or CFBs. The only exception perhaps is NWA 7034 ($\text{Na}_2\text{O}+\text{K}_2\text{O} \sim 4.08$), spuriously matches with the *in situ* Martian data.

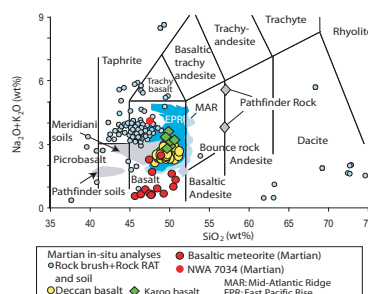


Fig. 1. TAS diagram for Martian *in-situ* basalts, basaltic meteorites and terrestrial MORBs and CFBs.

In MgO versus $\text{Al}_2\text{O}_3/\text{TiO}_2$ plot [15], the *in-situ* analyses of Martian surface show significant overlap in composition with that of the terrestrial MORBs, although these basalts show tight cluster with $\text{Al}_2\text{O}_3/\text{TiO}_2$ values less than ~ 15 (Fig. 2). The Martian

basalts show minimum overlap with the fields of terrestrial CFBs and they occupy a distinct field. However, the Martian basaltic meteorites show different composition in comparison to the Martian basalts and vary over the fields of basalt-komatiitic basalt-low Mg komatiite.

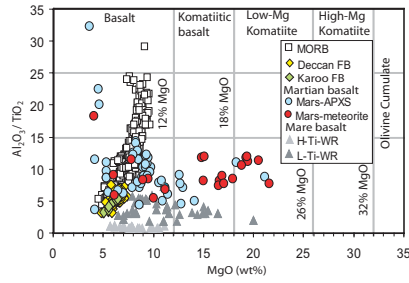


Fig. 2. $\text{Al}_2\text{O}_3/\text{TiO}_2$ versus MgO plot showing the fields of Martian basalts, meteorite and terrestrial MORBs and CFBs.

In $\text{Al}_2\text{O}_3/\text{TiO}_2$ versus $\text{CaO}/\text{Al}_2\text{O}_3$ plot, the examples of terrestrial MORBs and CFBs show a restricted $\text{CaO}/\text{Al}_2\text{O}_3$ ratio close to an average 0.8 (Fig. 3). The *in-situ* Martian basalts have $\text{CaO}/\text{Al}_2\text{O}_3$ range between ~ 0.4 and 0.8 and overlap in majority with the field of terrestrial MORBs. In contrast, the Martian basaltic meteorites have higher values between ~ 1 and 2 . The mare basalts, however, are different in composition to those of terrestrial and Martian basalts since the former have relatively low $\text{Al}_2\text{O}_3/\text{TiO}_2$ (≤ 5) and high $\text{CaO}/\text{Al}_2\text{O}_3 \sim 1.1$.

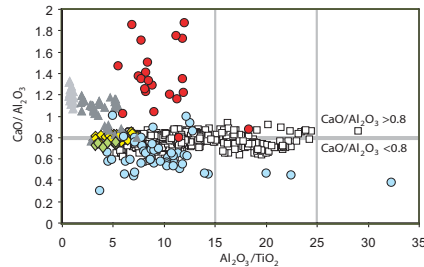


Fig. 3 $\text{Al}_2\text{O}_3/\text{TiO}_2$ versus $\text{CaO}/\text{Al}_2\text{O}_3$ plot showing the fields of planetary basalts.

In Nb/Yb versus Th/Yb plot [16], the Martian meteorites show wide variation in Nb/Yb ratio between 0.1 to 10, and fall in a similar trend to the

terrestrial MORBs (Fig. 4). Similar behaviour is also observed in Nb/Yb versus Ti/Nb and Zr/Nb plots.

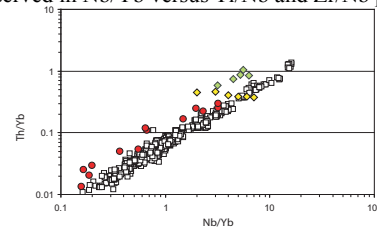


Fig. 4 Nb/Yb versus Th/Yb plot showing terrestrial MORBs, CFBs and Martian basaltic meteorite.

4. Summary and Conclusion

Our present observation suggests that the *in-situ* Martian basalts resemble with the terrestrial MORBs, however, the Martian basaltic meteorites vary within the entire spectrum of basalt- komatiitic basalt and low-Mg komatiite (Fig. 2,3). Martian meteorites are also found similar to the terrestrial MORBs in terms of both conservative and non-conservative trace element ratios (Fig. 4). Although $\text{Al}_2\text{O}_3/\text{TiO}_2$ versus $\text{CaO}/\text{Al}_2\text{O}_3$ plot is commonly used for Komatiitic rocks [17], we found the same can be very useful in the classification of planetary basalts (Fig. 2, 3).

Both Moon and Mars lack the evidences of plate tectonics, therefore, a plate tectonic like set up might not be a prerequisite for generation of terrestrial MORBs-like basalt. Hence, the wide application of plate tectonic concept in explaining terrestrial basaltic rocks of Archaean age needs further attention.

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Field and spectral investigation of gypsum deposit, Tamil Nadu, India: A martian analogue site

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Abstract

Investigations on the rim of a large ancient impact crater, called Endeavour Crater on Mars, have revealed gypsum rich veins cutting through the sedimentary rocks. This vein called as 'Homestake' in the area adjacent to rim of the Endeavour Crater, played a major role in deciphering the early wet history of Mars. The width of the vein is around 0.4 to 0.8 inch with 16 to 20 inches length, and protrudes slightly higher than the bedrock on either side of it. Similar type of geomorphic feature has been observed in Karai Formation, Tiruchirappalli, Tamil Nadu, India, where gypsum veins are observed cutting through the phyllosilicate rich ground mass. These gypsum veins are precipitated from the aqueous fluids rich in Ca and SO_4^{2-} ions moving upwards through the fractures in the ground mass. Although the genesis of Calcium Sulphate rich vein has been hypothesized, it is yet to be validated from terrestrial environment. This proposed site, therefore present a potential example of similar genetic environment in terrestrial conditions. Hyperspectral analysis of the gypsum samples collected from this terrestrial site can be used for ground truth validations and also as the optimum bands to locate similar type of deposits on Mars.

1. Introduction

Endeavour Crater represent an ancient epoch (Noachian) in Martian history and have the rich record of the phyllosilicate minerals in the parts of the crater rim [1]. Exposure of light coloured mineral vein 'Homestake' in the area adjacent to Endeavour Crater rim put an example that liquid water has flowed through the fractures in the rock [2]. The Karai Formation is mainly composed of veined to disseminated gypsum deposits on or within the groundmass of sediments rich in phyllosilicates in a badland topographic setting [3]. The major geomorphological features involve mounds of

phyllosilicate rich sediments, disseminated and veined gypsum, mud cracks and stream deposits of buff coloured grits with the varying proportion of calcareous rounded grains. Here we are presenting the geomorphic investigations and the spectral characterization of collected veined gypsum deposit samples in the laboratory conditions. Having compositional and geomorphic similarities with the gypsum vein of Endeavour Crater on Mars, proposed site could serve as a potential analogue and provide significant insights into the genesis history of the region.

2. Geological background

The study area lies in the Cretaceous of Tiruchirappalli of Cauvery Basin, located in Indian peninsular shield (Fig.1a and b). It contains thick sedimentary sequences of around 6 km, which were deposited over the Archaean granitic gneiss basement [4]. This thick sedimentary rock sequence comprises Karai Formation. Lithology of the formation constitutes grey-brown, gypsiferous, glauconitic mudstone and marl which is black and gypsum free when fresh [5], with sporadic thin, interbeds of siltstone, calcareous sandstone.

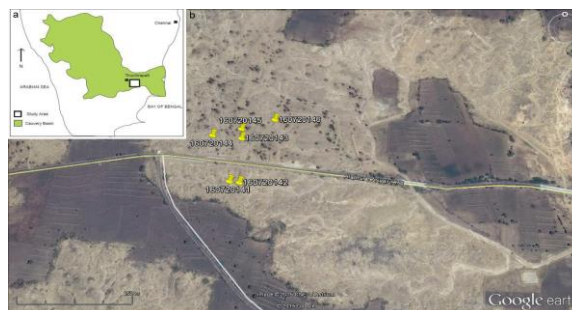


Figure 1: (a) Location of Cauvery Basin in the map of India, (b) Google Earth Images of the study area along with the locations of collected samples.

3. Methods and Results

Extensive field studies have revealed the distribution of gypsum veins throughout the area of almost same thickness (2 cm). The groundmass is mainly made up

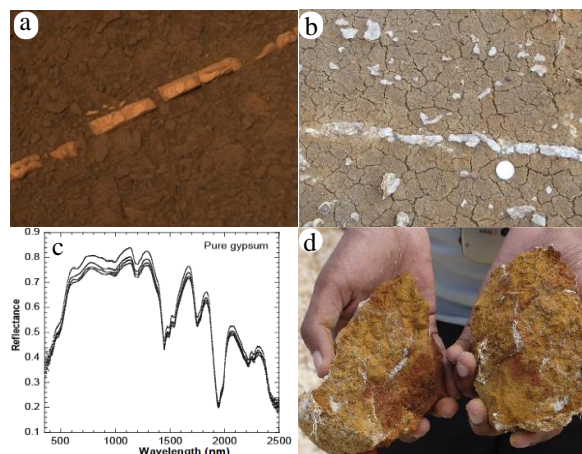


Figure 2: (a) Panoramic camera (Pancam) image of mineral vein called 'Homestake' taken by NASA's Mars Exploration Rover Opportunity (source: NASA/JPL-Caltech/Cornell/ASU), (b) Photograph of hydrous sulphate vein running through the phyllosilicate ground mass, (c) Spectra of Gypsum and (d) Gypsum veins running through the phyllosilicate sample.

of clay and marl rich sediments. Gypsum vein of Endeavour Crater (Fig. 2a) is having geomorphologic similarity to veined gypsum of Karai Formation (Fig. 2b). Spectral analysis has been done by ASD spectrometer in the wavelength range of 350-2500 nm. The spectral characterization of gypsum revealed the optimum absorption bands at 650 nm, 1450 nm, 1900 nm and 2200 nm represent ferric iron absorption, OH crystal transition, H₂O and OH absorption respectively, which matches well with the gypsum spectra of USGS spectral library (2c). Within the phyllosilicates, gypsum veins are distributed unevenly at places with varying thickness (Fig. 2d).

6. Summary and Conclusions

Spectral and geomorphologic investigations of the proposed analogue site suggest the formation of gypsum through the fractures in the clayey groundmass is similar to the model proposed by [1] for the formation of light coloured veins (gypsum veins) through the fractures in the sedimentary

sequence at the western flank of Cape York, Endeavour Crater on Mars. The sedimentary sequence in Endeavour crater near to western flank of Cape York mainly include Shoemaker formation breccias, Deadwood and sulphate rich sandstones of the Burns formation from bottom to top [1], is having sandstone as a major entity of sedimentary deposit in relation to the formation of veined gypsum deposit. Therefore, in spite of having slight variations in lithological assemblage (clear from the results), it seems that the mechanism involved in the formation of the veins is same and both of the regions are well comparable. Apart from this, Karai formation gypsum deposit has been marked with the presence of fluid inclusions, which could be probed in gypsum of Endeavour Crater for the investigations related to the paleo water chemistry and geochemical evolution of the whole deposit.

Acknowledgements

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ChemCam analyses of the Pahrump Hills sediments in the context of other sediments analysed by the Curiosity Rover

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Abstract

We report the results of ChemCam observations at the location of Pahrump Hills, analysed by the rover during the end of 2014 and beginning of 2015. Although Pahrump Hills sediment compositions are overall close to that of the coarser conglomerates analysed earlier by the rover, these observations show a strong variability in texture and composition, suggesting variations in source material and a complex aqueous history.

Chemistry of sediments analysed by ChemCam before Pahrump

The Curiosity rover has encountered a diversity of sedimentary rocks, which have displayed significant variations in both texture and composition. Early observations by the Curiosity rover in Gale crater revealed isolated outcrops of cemented pebbles and sand grains with textures typical of fluvial sedimentary conglomerates [1]. Conglomerates observed by Curiosity contain clasts with a strong diversity in albedo and textures indicating multiple sources on the Gale crater rims. Sandstones and mudstones observed at Yellowknife Bay

were interpreted as having been deposited in a fluvio-lacustrine environment [2]. More stratified sandstones have been observed in the second and third terrestrial years of investigation in the outcrops named Cooperstown and Kimberley. These outcrops show a different composition than those previously analysed, with enhanced K interpreted as being due to the presence of alkali feldspars, also correlated to high proportions of fluorine and lithium [3, 4].

The chemistry of Pahrump Hills

Pahrump Hills likely correspond to the lower part of Mt Sharp/Aeolis Mons based on orbital images. Their facies is interpreted as fluvio-lacustrine sediments [5]. The Pahrump Hills sediments have major element chemistry close to that of the conglomerates, suggesting a genetic relationship through the deposition of fluvial sediments from a similar source, likely the Gale crater rim. Nevertheless, Pahrump sediments display subtle variations in major elements connected to variations in facies. There is an enhanced Mg content in resistant layers, which is correlated with a depletion

in Fe and enhanced Al/Si ratios as well as enhanced hydrogen emission.

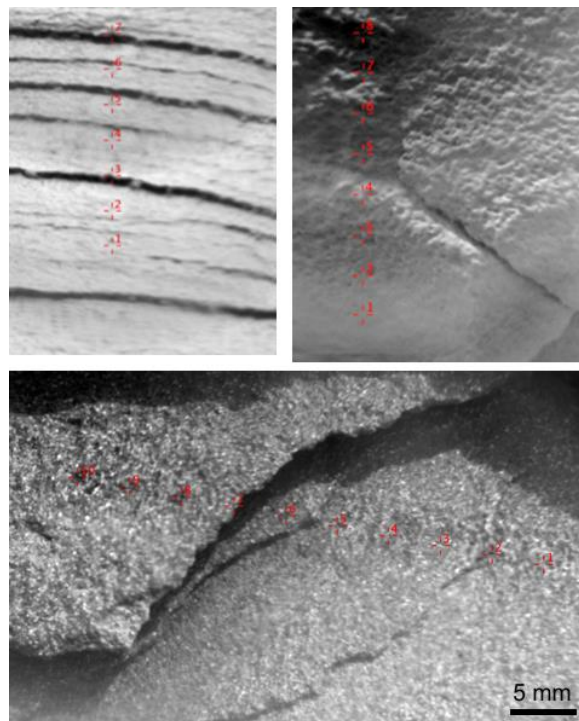


Fig. 1: Various sedimentary facies observed by ChemCam RMI images. Top left: Laminated facies. Top right: Resistant facies with lamination barely visible. Bottom: Upper unit with light-toned minerals inside darker-toned matrix.

These resistant layers have also a higher CIA (Chemical Index of Alteration) compared to the sediments previously encountered, suggesting alteration occurred. Laminated facies transitioning laterally into indurated facies suggest the role of cementation, in an early diagenetic phase (Fig. 1). Diagenetic features include concretions with enhanced sulfur and nickel, and calcium sulfate veins crossing all layers late [5]. The upper layers show deposits with high calcium and titanium with interesting light-toned mineral pseudomorphs (Fig. 1). These observations

point towards a complex setting with deposition in an aqueous context and alteration during deposition and/or diagenesis during cementation in these sediments.

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Classification Scheme for Diverse Sedimentary and Igneous Rocks encountered by the Curiosity Rover

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Abstract

The Curiosity Rover landed in a lithologically and geochemically diverse region of Mars [e.g., 1, 2, 3]. We present a recommended rock classification framework based on terrestrial schemes, and adapted for the imaging and analytical capabilities of MSL as well as for rock types distinctive to Mars (e.g., high Fe sediments, presence of sulphur, etc.).

1. Chemistry

Designed as a robotic geologist, the Curiosity rover is outfitted with imaging, geochemical, and mineralogical instruments for rock characterization. MSL cameras acquire grain size and shape information at a range of scales. The overall classification procedure involves: (1) the characterization of rock type according to grain size and texture; (2) the assignment of geochemical modifiers according to Figs 3 and 4, and if applicable, in depth study of (3) mineralogy and (4) geologic/stratigraphic context.

2. Texture classification

Sedimentary rock types are assigned by measuring grains in the best available resolution image and classifying as conglomerate/breccia, (coarse, medium, or fine) sandstone, siltstone, or mudstone [4]. If grains are not resolvable in MAHLI images, grains in the rock are assumed to be silt sized or smaller than surface dust particles. Rocks with low colour contrast between grains are classified according to minimum size of apparent grains from surface

roughness or shadows outlining apparent grains. Igneous rocks are described as intrusive or extrusive depending on crystal size and fabric. Igneous textures may be described as granular, porphyritic, phaneritic, aphyric, or glassy depending on crystal size. Further descriptors may include terms such as vesicular or cumulate textures.

Table 1. Imaging grain size capabilities [5, 6]

Image	Min detectable grain size
MAHLI (2 cm stand-off)	45-60 µm (fine silt)
Mastcam M100 (3 m dist)	~500 µm (coarse sand)
ChemCam RMI (3 m dist)	~200µm (med sand)

3. Chemistry classification

Geochemical analytical instruments include the Alpha Particle X-ray Spectrometer (APXS) for bulk compositions [2], which examines 1.8 cm spots on rock surfaces, and the ChemCam, which utilizes Laser Induced Breakdown Spectroscopy (LIBS) to examine 200-500 µm spots and is best for understanding grain compositions and rock heterogeneity. While mineralogy is fundamental for the classification of terrestrial rocks, the CheMin instrument (X-Ray Diffractometer) was not used frequently during the traverse to Mount Sharp and is applied to in depth studies.

Geochemistry is commonly applied to the classification of igneous rocks on Earth, but it is much less commonly applied to sedimentary rocks. Although we would like to adhere to conventional practice as much as possible, and have a scheme that is applicable beyond Gale Crater, we are limited to the data in hand. We take a simplified approach in

order to be more flexible to the discovery of possible new rock types (e.g., carbonates). Our recommendations for geochemical classification of APXS rock targets are: (1) unless S and Cl are a major component (>10%), all analyses should be volatile-free to compensate for variable surface dust coverage; (2) use the total alkali vs. silica diagram [7] for igneous rocks; and (3) use elemental enrichment and/or depletion modifiers relative to Mars crust [8] for sedimentary rock names (Table 2).

Table 2. Geochemical Modifiers Relative to Average Mars Crust for Sedimentary Rocks

Oxide	Value ¹	Modifier	Notes
FeO* ¹	>23%	Fe-rich	5% above Mars crust
	<13%	Fe-poor	5% below Mars crust
SO ₃	>10% ³	Sulfur-rich	> very dusty soil
K ₂ O	>1%	Potassic ⁴	~2× Mars crust
	<0.2%	K-poor ⁵	~50% Mars crust
Na ₂ O	>5%	Sodic ⁴	natural break in data
	<1.5%	Na-poor ⁵	~50% Mars crust

¹In weight percent. ²Total Fe as FeO. ³No veins or white blebs obvious in MAHLI images. ⁴**Alkaline** is both sodic and potassic. ⁵**Alkali-poor** if both K- and Na-poor.

In order to maintain flexibility over the course of the mission, the exact values defining “rich” and “poor” could change later if data warranted. We may also add modifiers (e.g., Si-rich) as new rock types are discovered along Curiosity’s traverse.

4. Conclusion

This classification scheme is envisaged for the duration of the MSL mission, but is subject to revision as new rock types are discovered. Note that instrument-specific rock classes (e.g., [10]) are also in use among the science team and this scheme is meant not as a replacement, but as a standardization of general terminology.

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Field investigation and spectral characterization of Banded Iron Formation, Odisha, India: Implications to hydration processes on Mars

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Abstract

Banded iron formations are major rock units having hematite layers intermittent with silica rich layers and formed mainly by the sedimentary processes during Late-Archaean to Mid-Proterozoic time period. They found their significance as a major iron-ore deposits and the first terrestrial rock bodies with existing life signatures on Earth. Here, we propose Odisha BIFs as a probable analogue site to the martian layered hematite deposit and its implications in inferring the sedimentary processes, hydration and astrobiological activities on Mars. Hyperspectral analysis identifies the optimum bands for the identification of similar type of deposits on Mars. Odisha BIFs have been found well comparable with the existing analogue sites of Lake Superior and Carajas Formation, Brazil.

1. Introduction

Banded Iron Formations (BIFs) are Fe-oxide- and silica-rich chemical sedimentary rocks, most of which were deposited during Late-Archaean to Mid-Proterozoic. BIFs are good cradles for extensive hematite deposits on earth. Earth's atmosphere was in transition phase from early anoxic conditions to a more oxygenated state during this period [1]. The Mars and Earth atmosphere were more similar during this time period, with both planets initially being blanketed by thick reducing atmospheres [2]. Hence, BIFs are thought to be potential candidates to understand the redox transitions and their possible relations to hydration processes and early life [3, 4]. Therefore, BIFs are also ideal targets for astrobiological explorations.

Mars surface has marked with the widespread layered hematite deposits and other FeO-OH polymorphs (Fe-oxides and Fe-(oxy-) hydroxides). Hematite layered deposits have been found in regions like

Meridiani Planum, Aram Chaos, and Valles Marineris on Mars [5]. Layered hematite deposits confirmed in Meridiani Planum and other regions of Mars are proposed to be of sedimentary origin due to absence of volcanogenic geomorphic features such as lava flows and fissures. [6] proposed that where spectra indicate bands of hematite and jaspilitic quartz, without discernable clays, and where this pattern extends from the millimeter to meter scale and is laterally continuous, it is highly likely BIFs are present. The layered hematite deposits therefore, could be treated as potential target rocks for probing ancient microbial and hydration processes.

2. Regional geology

Banded Iron Formation is present in the Archean Supracrustal belts in the region and is called as Iron Ore Group [7] (Fig. 1a). This supracrustal sequence starts from the base with sandstone-conglomerate overlain by ferruginous shales (with some manganiferous horizons), tuffs, lavas and BIF [8]. The mining activity in the area has exposed the major spatial features of the areas (Fig. 1b and c).

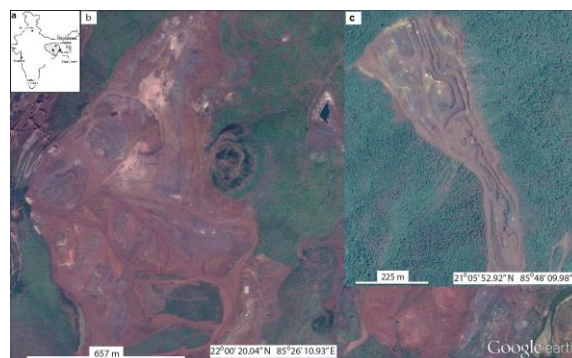


Figure 1: (a) Location of Singhbhum craton in Indian map. Google earth images of study areas (b) Joda (c) Daitari, located in Singhbhum craton.

3. Methods and Results

The results of this study are based on the fieldwork conducted in the regions of Joda and Daitari in Singhbhum craton, Odisha, India followed by the hyperspectral analysis of the samples. The collected sample shows alternate bands of hematite rich layer and quartz rich layer (Fig. 2a). Deformational structures such as faulting etc. have also been observed in the field and even, it is observable in the specimen scale (Fig. 2b).

Hyperspectral analysis has been done by ASD spectrometer in the wavelength range of 350-2500 nm. The spectral signatures identified are presented in the Fig. 2c and d. the optimum bands for the samples mainly fall into the region of 600-800 nm, 1850-1950 nm and 2200 nm. It has been observed that the spectra of the samples from the study area are found to match with the spectra of hematite, and goethite minerals of USGS spectral library. The absorption band present at 1900 nm, characteristic absorption feature for H₂O is also present indicating the hematite composition shift to the goethite.



Figure 1: (a) Field photo depicting the Banded Iron Formation. (b) BIF with fault structure through which quartz vein is observed. (c) Reflectance spectra of hematite and goethite samples with characteristic absorption bands.

6. Summary and Conclusions

With reference to Lake Superior and Carajas, Barazil BIF [6, 9], Odisha BIF could also be considered as a potential analogue to sedimentary layered deposits of Meridiani Planum and the aqueous environment, in which they would have generated. This study of spectral parameters in the context of BIFs may help to better understand the early environments of distinguished regions of Mars. Combined hyperspectral results from this study and [10] could work as reference in differentiating the types of iron deposits on Mars and also help in relative measurement of Fe content in different deposits.

Acknowledgements

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Diagenetic features analysed by ChemCam/Curiosity at Pahrump Hills, Gale crater, Mars

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Abstract

At Pahrump Hills, the ChemCam instrument observed unique chemical signatures on a diversity of diagenetic features.

1. Introduction

Onboard the Mars Science Laboratory (MSL) Curiosity rover, the ChemCam instrument suite consists of : (1) the first Laser-Induced Breakdown Spectrometer (LIBS) flown on a planetary mission, which provides elemental composition of targets up to 7 m from the rover [1;2] and (2) a Remote Micro-Imager (RMI) for grayscale imaging context of the small (350-550 μm diameter) LIBS points [3]. Within Gale crater, Curiosity traveled from Bradbury Landing toward the base of Mount Sharp, reaching the Pahrump Hills outcrop circa sol 750. This area, as seen from orbit, seems to represent the first exposures of lower Mount Sharp [4].

2. Observations

Here we report analyses on features present at Pahrump Hills outcrop : (1) cluster-like/dendritic features and (2) light-toned veins.

2.1 Cluster-like/dendritic features

At Pahrump, Curiosity observed a type of cluster-like (sometimes ramified/dendritic) feature, protruding several millimeters from the country rock, but appearing to be embedded in it [4;5]. They are the same color as the surrounding sediment (confirmed by MastCam and MAHLI imagers) and display a very fine-grained texture. ChemCam analysed four of these millimeter-to-centimeter-long features (Figure 1a,b). The typical ChemCam analysis of ~30 laser

shots at the same point allows dust removal and provides “depth-profile” analysis of the underlying target composition. As compared to the surrounding sediments, these cluster-like features display a clear enhancement in Mg that does not appear to correlate with Fe content, nor with Si. They display sulfur peaks (Figure 2), and nickel may be above the usual level of detection, though this is still under investigation.

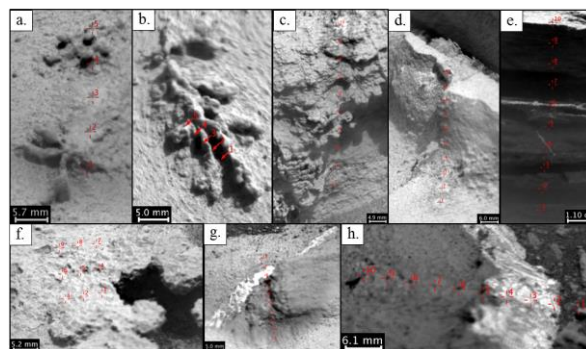


Figure 1 : ChemCam/RMI images of different types of diagenetic features observed at Pahrump and analyzed by ChemCam/LIBS (red locations).

2.2 Other diagenetic features

Other types of features embedded in the local host rock were analysed by ChemCam : (a) Nodular/globular surface exposure (b) A raised feature (Figure 1c) that shows Fe-enhancement. (c) Resistant structures (Figure 1d) that could represent fracture fills. (d) An aggregate feature (Figure 1f) which displays one point with significant Fe-enrichment compared to the other points and to the country rock, as well as weaker Si, Mg, Ti ; the presence of S and Na suggests Na-jarosite, or Fe-sulfates mixed with a Na phase.

2.3 Light-toned veins

At Pahrump Hills, multiple light-toned veins, usually millimeter to centimeter in width (Figure 1e,g,h) and cm to decimeter long, were observed. Their compositional analysis by ChemCam shows a clear detection of sulfur (Figure 2) as well as enhanced calcium, compared to the host rock.

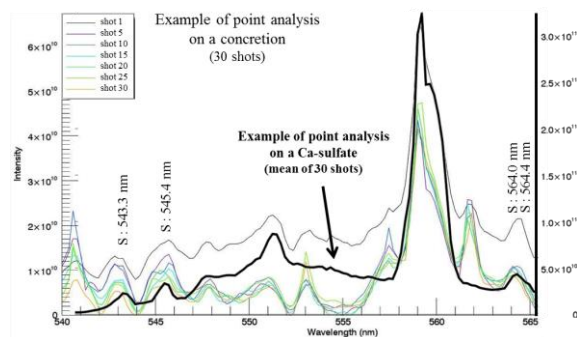


Figure 2: Sulfur detection within the shots of a ChemCam point analysis on a cluster-like resistant feature at Pahrump. The mean spectra (30 shots) of a local light-toned vein is also displayed (with its intensity scale on the right).

One Ca-rich vein (Figure 1h) displays a « fibrous » (rectilinear) texture in the upper portion of the RMI image, and more “chicken wire like” (circular) texture on the bottom. One analysis on a vein displays low Si, clear S peaks, stronger Ca and Mg signal, as well as strong H signal, suggesting the presence of both Mg- and Ca-sulfates.

2.4 Localization and geological settings

The basal fractured platy unit on which Curiosity drove at Pahrump Hills’ entrance displays light-toned veins that crisscross the mudstones in a variety of orientations ; cluster-like concretions are also present [4;5]. An example target imaged by MAHLI displays a fine light-toned vein clearly criss-crossing a cluster-like resistant feature, suggesting (at least in this particular case) that the veins were emplaced after the cluster-like features formed.

Laminated faciès located in one of the higher stratigraphic units of Pahrump Hills also present light-toned material, in the form of fine veins cutting the stratification, and sometimes present inter-layers. Cluster-like concretions mentioned above were not observed up at this location, but more nodular-like

features were present, on the top and at the edges of the laminations.

3. Discussion

In terms of diagenetic features, the most detailed observations previously reported at Gale correspond to nodules, hollow nodules [6], raised-ridges [7], and light-toned veins [8], all at Yellowknife Bay [9]. The raised ridges had enhancements in Mg, but sulfur was not detected; this was interpreted to be related to a smectite-clay deposit [7].

At Pahrump Hills, within the cluster-like features, the S-detection related to the enhanced Mg and associated with the Ni-detection could be related to sulfates or sulfides. Given the diversity of other diagenetic features (nodular/globular, aggregates) analysed by ChemCam through the Pahrump Hills stratigraphy, and given their distinct compositions, the precise mechanism(s) that led to their formation is still under investigation.

Along Curiosity’s ~10 km traverse from Bradbury Landing towards Yellowknife Bay [8] and up to Pahrump Hills, ChemCam has analysed more than 50 light-toned veins. All display calcium enhancement and sulfur, leading to the interpretation that all of them contain a (more or less pure) calcium sulfate phase. Their more detailed compositional variation is still under investigation. Light-toned veins appear to record a later event of fluid circulation.

Acknowledgements

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Search for organic matter at Mars with combined measurements of the SAM and ChemCam instruments onboard the Curiosity rover

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Abstract

Since 2012, the Curiosity rover on Mars seeks clues of habitability in Gale crater. One of these clues is the presence of organic matter. For the moment, only a few traces of organic matter were recently found with the SAM experiment. We propose here to evaluate the capabilities for the ChemCam experiment to detect organic molecules from its elemental analysis of the Mars regolith or rocks. The first results obtained in laboratory with the ChemCam spare model and different samples show that it is possible to detect organic signatures with LIBS, focusing on atomic carbon, hydrogen and nitrogen peaks, and on a C-N molecular peak when the samples are enriched in organic molecules (100-10 wt%). We currently work with Mars representative samples to determine the instrument detection limit for organics, in order to determine if it can be used to guide Curiosity towards interesting outcrops.

1. Introductions

One of the priorities of the Mars Science Laboratory mission is the search for a past or present prebiotic chemistry. Among the possible indicators of such a chemistry, the **organic molecules** are key entities linked to the emergence and the development of life, as we know it on Earth. However, only rare evidences of the presence of such molecules (chlorobenzene and other chlorinated hydrocarbons) in the Mars sedimentary rocks^[1] and regolith^[2] were recently found^[1] and at a very low concentration (150-300 ppm in the Cumberland mudstone). Thus, one of the most pressing questions is to follow the search and identification of molecules currently present at Mars, and their concentration. Onboard the NASA Curiosity rover currently operating on Mars in Gale crater, the **ChemCam instrument**^[3] (*Chemistry and Camera*) performs quasi-systematic analyses of the elementary composition of rocks and soils of the Mars surface

instrument is precious to determine the targets of interest to perform contact science and drills from a mineralogical point of view, it also gives chemical information that could be used to look for organics present in the soil.

2. Objectives

Curiosity has recently reached the base of Mount Sharp, a 5-km thick sedimentary formation where **phyllosilicates** were detected from the orbit by OMEGA and CRISM hyperspectral imagers^[4]. Phyllosilicates are minerals known on Earth to concentrate organic molecules. We propose to determine the ChemCam instrument capabilities to detect organic molecules in the Martian rocks by evaluating the nature of the elemental signatures produced by the presence of organic in mineral samples, and the organic concentration detection threshold. If this work done at the laboratory with the ChemCam testbed reveals that ChemCam is able to detect organic matter at concentrations relevant to Mars, then Curiosity could be guided towards interesting outcrops potentially containing some organic matter to assess their presence. If a positive signature is obtained, then, the sample would have to be analyzed by the **SAM instrument**^[5] (*Sample Analysis at Mars*) to identify and quantify the present organic species.^[6]

3. Method

Figure 1a shows the **ChemCam testbed** used to analyse various samples, using its infrared laser (1067 nm). The interaction between the laser and the target generates a plasma, which is analysed by three dispersive spectrometers to cover the ultraviolet (240-342 nm), purple (382-469 nm) and visible/near-infrared (479-906 nm) wavelength regions. These test samples are composed of organic molecules and synthesized mineral mixtures. The first tests are realized on clay minerals like nontronite, which are formed in the presence of liquid water, and known to be present at the Mars surface and on Mount Sharp^[7].

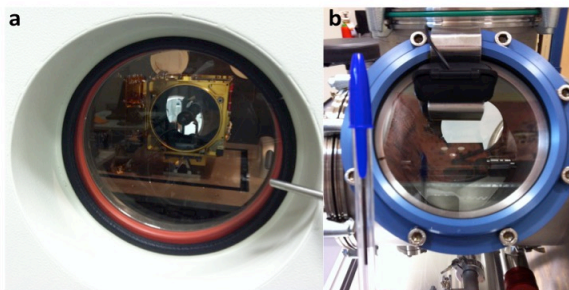


Figure 1: Close-up view of the ChemCam testbed located at IRAP (Toulouse) used for laboratory simulations of detection of organic matter in mineral matrixes (a). Low pressure chamber where the samples are placed. This system runs at Martian pressure (6 mbar) and Martian atmosphere analog composition (b).

The purpose is to determine the organic concentration threshold that ChemCam can detect in a sample. We selected glycine and adenine as the first test organic molecules because they are found in some micrometeorites and they are potentially present on Mars. These samples are placed in a low pressure chamber (**figure 1b**), reproducing the Martian environment (6 mbar of pressure and CO₂-rich atmospheric composition), to reproduce as closely as possible the spectra acquisition conditions encountered by ChemCam at Mars.

This first measurement campaign in the LIBS mode is aimed at determining if it is possible to detect organic matter through the elemental analysis and to proceed to a molecular identification.

Currently, samples of nontronite with different adenine concentrations are synthesized and they will be analysed to determine at best the concentration threshold in organic matter.

4. First Results

First tests were focused on reference samples (organic matter alone and mineral alone) in order to determine the characteristic emission lines of the different materials and to know if we are able to distinguish an organic molecule from inorganic ones

With these preliminary tests, we were able to highlight an enhancement of the carbon and hydrogen spectral signature, when the sample is enriched in organic matter. We also identified atomic nitrogen and a C-N vibrational molecular peak when introducing a nitrogen bearing molecules in the samples.

5. Present and future work

After the accurate characterization of the spectra of reference materials, samples will be synthesized with a gradually reduction of their organic content to determine the threshold below it appears impossible to trace the organics influence in the sample spectral signature. This study will be done with different “organic-clay” samples in an intimate mixing more representative of what it could be found on Mars, to see the influence of the nature of the samples on this detection threshold.

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***In situ* analysis of Mars soil and rocks samples with the SAM experiment: laboratory measurements supporting treatment and interpretation of the detection of organics**

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Abstract

The Sample Analysis at Mars (SAM) experiment onboard the Curiosity rover detected numerous organic compounds when analyzing the solid samples collected on the way to Mount Sharp. But MTBSTFA, the chemical reactant for the chemical treatment of the refractory molecules present in the solid samples and present in cups of SAM, was shown to be unfortunately present in the Sample Manipulation System (SMS). During the sample analysis, this chemical species reacts with the organic and inorganic molecules present in the samples. This reaction leads to the production and subsequent detection of numerous MTBSTFA derivatives which makes the treatment and the interpretation of the SAM data complex. Moreover, for the first time on Mars, the wet chemistry method was used on a Cumberland sample to help the GC separation and the MS identification of non volatile compounds. To ensure the identification of the organic molecules and try to discriminate organics generated internally to SAM from those present in the samples analyzed, it is mandatory to perform laboratory experimental calibrations under martian operating conditions.

1. Introduction

The rover Curiosity of the Mars Science Laboratory (MSL) mission, landed on Mars the August 6th of 2012 at Gale crater to provide clues of its past and/or present habitability. The SAM experiment is partly devoted to the *in situ* molecular analysis of gases evolving from solid samples collected by the rover on Mars surface/sub-surface. SAM is composed of a pyrolysis oven coupled to a gas-chromatograph mass spectrometer (GC-QMS) [1]. The GC-QMS is dedicated to the separation and the identification of organic and inorganic material evolved from the

samples by the derivatization method. The GC is especially devoted to the separation of organic molecules. A thermal conductivity detector (TCD) and a quadrupole mass spectrometer (QMS) allow the detection and identification of the molecules (Figure 1). The GC analytical channel which has been used to do almost all the measurements of the martian samples to date is composed of a MXT-CLP chromatographic column coupled with a Tenax GR thermal desorption trap.

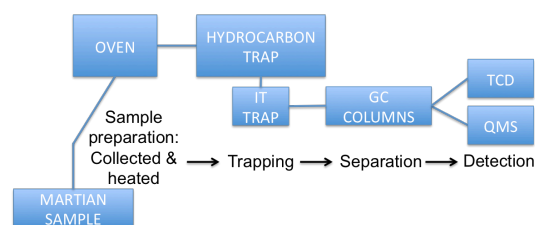


Figure 1: simplified analytical channel from samples collection to the detection and the identification of the organic molecules.

During the 900 first sols, Curiosity collected one sand sample at the Rocknest site, two rock samples at the Yellowknife Bay site (John Klein and Cumberland) and one rock sample at the Pahrump Hills site (Confidence Hills). They have been successfully analysed by the SAM experiment and provided an extended set of data. The chemical reactant carried within SAM and used for derivatization on the Cumberland sample is the *N*-methyl-*N*-*tert*-butyldimethylsilyl-trifluoroacetamide (MTBSTFA). It is present into seven of the SMS cups but is known to be leaking from cups, so its amount has been maximized to react with the molecules present in the Cumberland solid sample. To support the treatment and the interpretation of the data provided by the SAM instrument, it is of primary importance to perform laboratory experiments using SAM like apparatus and the same

sample wet chemistry treatment under simulated martian operating conditions.

2. SAM GCMS data treatment: comparison of organic molecules retention times between laboratory experiments and FM data

Organic compounds, mostly chlorinated, have been clearly detected by SAM [2]. Indeed, chlorobenzene and 3 chlorinated alkanes have been shown to be indigenous to Mars [6]. Thanks to laboratory experiments, it is known that chlorohydrocarbons are also produced by the reaction of perchlorates, globally distributed in Martian soil [2,4], with organic matter, during the pyrolysis. This organic matter can be present in the experiment and some chlorinated compounds have been identified as reaction products of the MTBSTFA and/or the Tenax TA porous polymer adsorbent used to concentrate organic molecules on the SAM hydrocarbon traps. The last GC-MS analysis: the opportunistic derivatization (OD) consisted in the application of the chemical reagent, the MTBSTFA, to the Cumberland solid sample. It reacts with polar organic molecules containing a labile hydrogen atom, to improve their volatilisation and their separation and detection by the SAM GCMS system. In the SAM chromatogram of the OD analysis, several chromatographic peaks were interpreted, thanks to the identification by the mass spectrometer, as long chains of alcohols and/or carboxylic acid derivatized. The aim of this work is to discuss the organic molecules detections done by SAM and to predict the relevant retention times. For laboratory experiments, a GC-MS apparatus including a SAM-like MXT CLP capillary column was used. A 20 cm capillary tube was coupled to the column to reproduce the carrier gas flow of the SAM experiment. A set of organic compounds, identified with MS or potentially present in SAM chromatograms, have been selected for this study.

3. Results

The laboratory studies using the GC5 spare column under martian operating conditions allowed to remove ambiguities on the identification of the organic components detected by SAM (Figure 2). It also allowed to disprove the presence of derivatized alcohols and carboxylic acids, suspected to be present in the OD analysis using the chemical

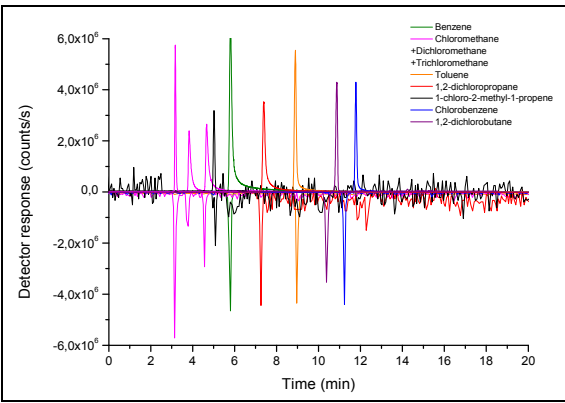


Figure 2: GC-MS analysis of organic compounds detected by SAM: comparison between the laboratory gas chromatogram and the reconstructed ion chromatogram.

Column	Laboratory	SAM
Suspected compounds	T _R (min)	T _R (min)
Carboxylic Acid	28	14.31
1-undecanol	26.7	17.15

Table 1: Example of suspected organic components disconfirmed by GC-MS laboratory analysis.

4. Summary and conclusions

The SAM experiment is a powerful tool to detect, separate and identify the organics on Mars. The retention times obtained in laboratory martian operating conditions, with those obtained in SAM chromatograms, is a strong method to strictly identify the molecules present in Mars surface/sub-surface solid samples, when the QMS signature is not sufficiently clear. This work is still under progress to identify the molecules present in the last OD analysis, essentially to identify the molecules such the retention times has not been confirmed by the laboratory measurements.

Acknowledgements

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Evaluating the homogeneity of the X-ray amorphous component along the *Curiosity* rover traverse

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Abstract

Mass balance calculations are used to evaluate the chemical homogeneity of the X-ray amorphous component among the soil and rocks samples collected by the *Curiosity* rover at Gale crater, Mars.

1. Introduction

Since its landing in Gale crater in August 2012, the Mars Science Laboratory (MSL) rover *Curiosity* has collected several soil and rock samples along its traverse. X-ray diffraction (XRD) patterns of the <150- μ m fraction of these samples have been acquired by the Chemistry and Mineralogy (CheMin) instrument [1] and have revealed a significant amorphous component of unclear origin [2-5]. Efforts to characterize the amorphous component so far have included estimates of its composition and abundance through mass balance calculations [6,7], and comparisons with XRD patterns of laboratory analogs [8,9]. Here, we report the results of preliminary mass balance calculations for the Windjana sandstone and compare the estimated composition of the amorphous component of this sample with the ones of the Rocknest soil and Sheepbed mudstone.

2. Methods

Following an approach similar to [3,4,6], we have based our calculations on bulk chemical compositions measured by the APXS instrument, and on phase abundances and structural formulas derived from the CheMin XRD patterns by [2-4]. We have developed a Scilab program that calculates all the possible chemical compositions of the crystalline component – and thus of the complementary amorphous component – of each sample, taking into account the uncertainties on the phase abundances derived from CheMin data [2,4]. Taking into account these uncertainties allow us to more rigorously compare the similarities and differences between two individual samples analyzed by *Curiosity*'s payload.

We have explored a range of values between 10 and 50 wt% of amorphous component but, for more detailed analyses, we have focused on 30 wt%, a value close to the XRD-based estimates for Rocknest and Sheepbed [2,4]. In some cases, the calculated amorphous component may have one or more oxides with concentrations below 0 wt%; the combination is then “chemically unrealistic” and thus rejected by the program. Therefore, this constraint can be used to determine a lower limit to the overall abundance of the amorphous component, i.e., the minimum amount required to have all oxides ≥ 0 wt%.

3. Results

3.1 Rocknest sand and Sheepbed mudstone

Detailed results of mass balance calculations performed with data from the Rocknest sand and the Sheepbed mudstone are reported in [7]. Despite obvious differences (in nature and age) between the two samples, their amorphous components were found to be chemically very similar to each other, having comparable estimated concentrations of SiO₂, TiO₂, Al₂O₃, Cr₂O₃, FeO_T, CaO, Na₂O, K₂O, and P₂O₅ (Table 1). MgO tends to be lower in Rocknest, although it may also be comparable between the two samples depending on the exact composition of the smectite clay in Sheepbed. The only unambiguous difference is the SO₃ content, which is always higher in Rocknest, suggesting the presence of amorphous sulfates or adsorbed SO₄²⁻ in the soil. Estimated minimum abundances are 21–22 wt% for Rocknest and 15–20 wt% for Sheepbed, in good agreement with estimates derived from the XRD patterns [2,4].

3.2 Windjana sandstone

Preliminary mass balance calculations have been performed using the mineralogy of the Windjana sandstone reported by [5]. Future adjustments are expected as the structural formulas of primary silicate minerals are further refined. In addition, the nature of the phyllosilicate component is not yet definitely

established: a ferromagnesian smectite analogous to the one of the Sheepbed mudstone is favored [5], but other species such as illite cannot be ruled out. Thus, we have considered the two possibilities here.

Compared to Rocknest and Sheepbed, the amorphous component of Windjana has comparable ranges for SiO_2 , Al_2O_3 , FeO_T and CaO (Table 1). Na_2O is lower, which directly reflects the much lower Na content of the bulk sample as measured by APXS [5]. The fate of K_2O is highly dependent on the nature of the phyllosilicate. SO_3 is lower than in Rocknest and comparable to Sheepbed. Finally, the range of MgO concentrations is clearly shifted to higher values, especially when compared to Rocknest. Estimated minimum abundances are <10 wt% with illite and ~10-15 wt% with saponite.

4. Discussion and future work

Despite the caveats mentioned above, early results indicate that the amorphous component of Windjana share some similarities with the ones found at Rocknest and Sheepbed (high Si and Fe, low Al and Ca). S-rich amorphous component seems to be characteristic of the soil, which could be consistent with adsorbed SO_4^{2-} . Finally, Mg appears to be the most variable element between the amorphous components investigated so far.

Future work will include refinements of the calculations as more information on the samples are derived from the CheMin XRD patterns. Additional calculations will also be performed for the samples collected by *Curiosity* at Pahrump Hills.

Table 1: Comparison of the estimated composition of the amorphous component of the Rocknest soil (RN), Sheepbed mudstone (Cumberland drill, CB) [7], and Windjana sandstone (WJ), assuming an abundance of 30 wt%. G = Griffith saponite. I = illite.

(wt%)	RN	CB-G	WJ-I	WJ-G
SiO_2	25.6-38.7	28.8-44.4	19.7-40.5	24.6-42.4
Al_2O_3	0.0-6.7	0.0-5.4	0.0-8.3	3.6-9.6
FeO_T	21.2-34.6	13.7-33.6	8.2-33.5	6.3-28.3
MgO	0.0-4.9	3.4-15.0	19.8-27.4	15.3-24.6
CaO	0.6-6.5	2.6-10.0	0.1-6.2	0.0-5.4
Na_2O	3.8-5.1	3.7-6.1	0.7-1.1	0.7-1.0
K_2O	0.5-1.6	0.2-1.1	0.0-4.8	1.7-6.4
SO_3	14.7-17.2	0.0-5.9	2.1-7.0	2.1-7.0

Acknowledgements

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Redox conditions and alteration pathways on early Mars

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Abstract

Laboratory experiments under CO₂ atmospheres show that strong oxidants would have inhibited the formation of Fe/Mg-smectites on early Mars.

1. Introduction: oxidation on Mars

Sulfates and Fe-oxides detected by orbital and in situ missions [e.g., 1,2] indicate that oxidizing conditions existed on early Mars, at least locally and/or episodically. In the context of rock alteration and weathering, redox conditions are especially critical for the behavior of iron, which is soluble in his divalent state but insoluble in his trivalent state. Abiotic oxidation of ferrous iron under a primitive, CO₂-rich atmosphere can take place through different mechanisms: (1) alteration of Fe²⁺-bearing minerals into Fe³⁺-bearing products by reduction of H₂O during rock-water interactions (e.g., serpentinization); (2) direct photo-oxidation of aqueous Fe²⁺ by ultraviolet irradiation; or (3) chemical oxidation by reaction between Fe²⁺-bearing minerals or aqueous Fe²⁺ and an oxidant produced by the UV photolysis of H₂O (e.g., O₂, H₂O₂). All these mechanisms involve directly or indirectly the reduction of H₂O to H₂, and therefore require H₂ loss into space to prevent back reactions and obtain net oxidation at a global scale.

Among these three mechanisms, oxidation by photolysis-derived oxidants is the most efficient in low-temperature, surficial conditions, because: (1) it is very rapid and thus overcomes gel/mineral precipitation [3] and (2) it has the potential to create oxidizing conditions in environments protected from direct UV exposure, through diffusion or percolation.

2. Effects of redox conditions on alteration pathways

In the past years, we have reported in several publications [4-7] the results of laboratory experiments studying the alteration of various primary

materials in conditions relevant for early Mars (Table 1). Among other parameters, these experiments tested the influence of highly-oxidizing (H₂O₂-bearing) vs poorly-oxidizing (H₂O₂-free) conditions on the secondary mineralogy of early Mars.

2.1 Sulfides and silicate+sulfide mixtures

Results from [4-6] show that the alteration of Fe-sulfides (pyrrhotite) and silicate+sulfide mixtures under H₂O₂-bearing and H₂O₂-free conditions produce assemblages similar in nature (elemental sulfur, sulfates and Fe-oxides). However, in silicate+sulfide mixtures, the relative abundances of Mg- and Ca-sulfates were controlled by the composition of the silicate component, demonstrating that the acidification induced by the alteration of pyrrhotite promoted the alteration of silicates in both conditions. In addition, H₂O₂ do favor the formation of sulfates (especially jarosite) at the expense of elemental sulfur.

2.2 Primary silicates

Here we present new analyses of samples of olivine and orthopyroxene (“Ol1” and “OPx” in [6]) weathered for 4 years under CO₂. Although these samples were much less modified than the corresponding mixtures with pyrrhotite, a careful study of their near-infrared spectra reveals absorption bands at 2.31 and 2.39 μm associated with Mg-rich smectite clays (Fig. 1). In the case of olivine, these bands are present for the sample weathered in poorly-oxidizing conditions (i.e., without H₂O₂, named “H₂O” in Fig. 1), while they are absent for the initial sample and for the sample weathered with H₂O₂. In the case of orthopyroxene, the initial sample displays shallow bands at these positions due to pre-experiment alteration. However, the band depths clearly increased for the sample weathered without H₂O₂, whereas they remained stable for the one weathered with H₂O₂.

The formation of smectite clays (or precursors) is further confirmed in the Ol1-H₂O and OPx-H₂O samples by the observation by SEM of “filaments”

similar in size and morphology to those observed in [7]. These filaments are absent from the initial samples and from the samples weathered with H₂O₂.

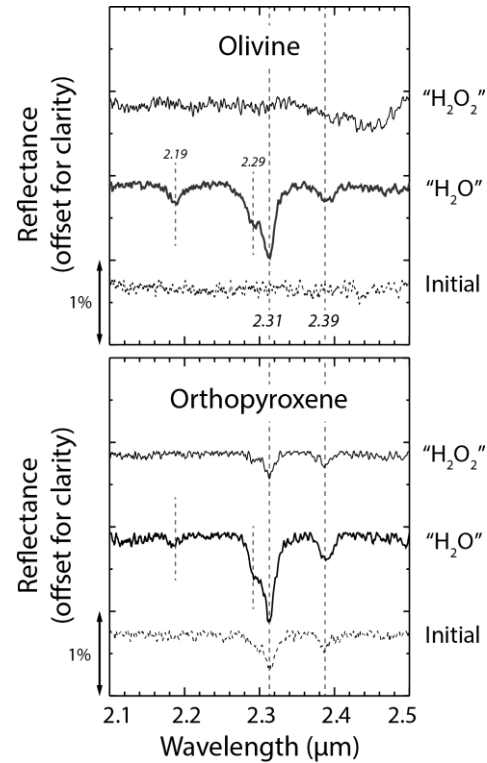
3. Implications

Our experimental results show that highly-oxidizing conditions on early Mars (e.g., due to H₂O₂ deposition on the surface) would have strongly inhibited the formation of Fe/Mg-smectites from alteration of igneous ferromagnesian minerals. This is due to the fact that purely Mg-smectites are not stable at the relatively low pH associated with a CO₂ atmosphere, and thus that Fe²⁺ is required, at least transiently, to form the smectites [7]. In turn, this suggests that volcanic release of reduced gases was high enough to overcome photochemical production of oxidants and thus prevent effective oxidation of the surface during the Noachian era. Nonetheless, strong oxidants were found to enhance the production of sulfates – especially jarosite – during alteration of Fe-sulfides and silicate+sulfide mixtures, which suggests that their influence on the secondary mineralogy may have progressively increased later in Mars history.

Table 1: Summary of primary materials studied in our alteration experiments under simulated early Mars conditions. Po = pyrrhotite; L/R = liquid-to-rock ratio.

Primary materials	Magnetite α-Fe Pyrrhotite	Olivine OPx CPx Ol+Po OPx+Po CPx+Po	Olivine
Atmospheres and oxidants	CO ₂ CO ₂ +H ₂ O ₂	CO ₂ CO ₂ +H ₂ O ₂	CO ₂ CO ₂ +H ₂ O ₂ Air Air+H ₂ O ₂
Experimental parameters	T=15-20°C P=0.8 bar Low L/R	T=15-20°C P=0.8 bar Low L/R	T=45°C P=1.5 bar L/R=10
Duration	1.4 year	4 years	3 months
References	[3,4]	[6], this study	[7]

Figure 1: Continuum-removed spectra of olivine and orthopyroxene samples before and after alteration under CO₂ atmospheres. Absorptions bands at 2.31 and 2.39 μm are typical of Mg-rich smectites.



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Influence of the sample mineralogy on the nature of the organic compounds detected by the SAM experiment analysis condition at Gale Crater.

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1 Introduction

1.1 Structure and aim of SAM

Sample Analysis at Mars (SAM) is one of the instruments of the MSL mission. It is devoted to analyze the composition in volatile species contained in solid samples collected by the Curiosity rover. To do it, it is composed of 3 complementary analyzers : the Tunable Laser Spectrometer (TLS), the Gas Chromatography (GC) and the Mass Spectrometer (MS) (Mahaffy et al., 2012).

Solid samples can be treated by different ways to extract the volatile compounds and inject them in the analyzers : (a) a pyrolysis system, (b) wet chemistry: MTBSTFA and TMAH (c) the hydrocarbon trap (silica beads, Tenax® TA and Carbosieve G) and the injector trap (Tenax® GR) (Mahaffy et al., 2012).

1.2 Definition of pyrolysis and derivatization

Pyrolysis is the thermal degradation of chemical compounds with the aim is to reduce the sizes of molecules to increase their volatilities to analyze them by GC-MS and those in the absence of oxidant like oxygen (Stauffer, 2003).

Pyrolysis has the advantage of being easily implemented because it does not require the use of solvent contrary to thermochemolysis and pyrolysis. However, this technique has the inconvenience to bring about a large number of products (pyrolysats). The molecules produced by pyrolysis are function of the pyrolysis conditions (Moldoveanu, 1998, 2010).

Derivatization replaces labile hydrogens (e.g. present in a group -OH, -COOH, =NH, -NH₂) with apolar groups. Polarity of the targeted molecule decrease and the volatility is increased (Orata, 2007). On SAM wet chemistry unit, the N-tert-Butyldimethylsilyl-N-methyltrifluoroacetamide (MTBSTFA) is used as derivatization agent (Mahaffy et al., 2012).

1.3 Interaction of organic matter with minerals during pyrolysis - Generalities

During pyrolysis, minerals may have several effects on the organic material: degradation, transformation or preservation (François, 2014).

Degradation of organic matter can be catalyzed by solid phase minerals or be triggered by the formation of secondary products coming from the thermal degradation of minerals such as oxygen.

Pyrolysis of mineral may also transform the organic material such as sulfuration caused by sulfates.

Some minerals have the ability to maintain organic matter in specific conditions. During the pyrolysis, the minerals will degrade at various temperatures. Thus, the thermal degradation of a mineral does not affect the organic material enclosed in another mineral which have a higher thermal decomposition temperature.

1.4 Interaction of organic matter with minerals during pyrolysis – Example of perchlorates

The measurements done with the SAM experiment on Mars have already proved the impact of minerals on the molecules detected. Indeed, the presence of perchlorates has been demonstrated. When this salt is exposed to a thermal energy, it is decomposed and leads to the production of oxygen O₂, hydrogen chloride Cl₂ (Kirillov & Svyanko, 1988) or chlorine HCl when water is present.

Thermal degradation products of perchlorates react with organic molecules and the products of this reaction have been highlighted by SAM: some aliphatic chlorinated species have been detected. In fact, these chlorinated aliphatic compounds are produced by the reaction between perchlorates and degradation products of the derivatizing agent (MTBSTFA) by the reactions of chlorination, hydrochlorination and oxychlorination (Glavin et al., 2013; Ming et al., 2014).

In conclusion, the mineralogy is an essential parameter to be taken into account in the interpretation of GC-MS analysis.

1.1 Mineralogy on Gale Crater and result of pyrolysis of organic compound with kieserite in SAM condition

Gale Crater contains a wide variety of minerals which are divided into strata and whose evolution of composition is influenced by the deposition environment. Among these minerals, we can cite silicates, clays, sulfates, iron oxides and perchlorates (Ming et al., 2014; Vaniman et al., 2014) .

Kieserite is a hydrated sulfate ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$). When it is thermally decomposed, kieserite generates sulfur dioxide (SO_2) and dioxygen (O_2) which could interact with organic matter by oxidation and sulfidation (addition of sulfur) (Lau, Cubicciotti, & Hildenbrand, 1977). When the kieserite is pure, the thermal decomposition of kieserite occurs around 1000°C (Scheidema & Taskinen, 2011) but in the presence of reducing species, this temperature may decrease.

From the work of François et al. (2014) we know that the degradation of kieserite impacts the organic matter. Indeed, two molecules were tested: phthalic acid and alanine. The production of a large number of aliphatic and aromatic compound has been observed, and those either in the presence of phthalic acid and alanine. Among pyrolysates, we can cite phenol, benzofuran and octathiocane for phthalic acid and pyridine and benzonitrile for alanine. Then, during the SAM pyrolysis of sample containing kieserite, the thermal degradation products of kieserite and MTBTFA will likely initiate the formation of various compounds.

1.5 Objectives

The objective of our study is to identify and list all the compounds that can be produced by the interaction of MTBSTFA and kieserite at high temperature to help for the interpretation of SAM results.

2 Experiments and methods

Upstream of the GC-MS (thermo ISQ) is placed a pyrolyzer (CDS Pyroprobe 5150) able to reproduce the SAM conditions.

Pyr-GC-MS. GC-MS is equipped with a Rtx-5Sil MS column ($30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$) with a helium flow in the column of 1.1 ml/min with a split of 15 mL/min . The sample placed in the pyrolyzer is heated to 35°C/min from 40°C to 850°C . During pyrolysis, the compounds are trapped in the injector

by cryogenic trap at -30°C . The transfer line between the pyrolyzer and GC-MS is heated to 250°C .

Three samples are analyzed under pyrGCMS conditions of SAM: MTSBTFA, kieserite and the mixture of the two.

Table 1: Samples analysed by pyr-GC-MS reproducing the SAM GC-MS analysis

N°	Name	Composition
1	WCM	0.2mg MTBSTFA
2	MgS	20mg of $\text{MgSO}_4 \cdot \text{H}_2\text{O}$
3	WCM_MgS	20mg of $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ + 1%wt of MTBSTFA

3 Results and interpretation

All the aliphatic and aromatic molecules detected will be presented and the phenomenon involved on the pyrolysis of samples will be shown. From these results we will be able to better understand the origin of the organic molecules detected with SAM.

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Chemo-stratigraphy at the Pahrump outcrop and Garden City Vein Complex in Gale Crater using ChemCam.

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Abstract

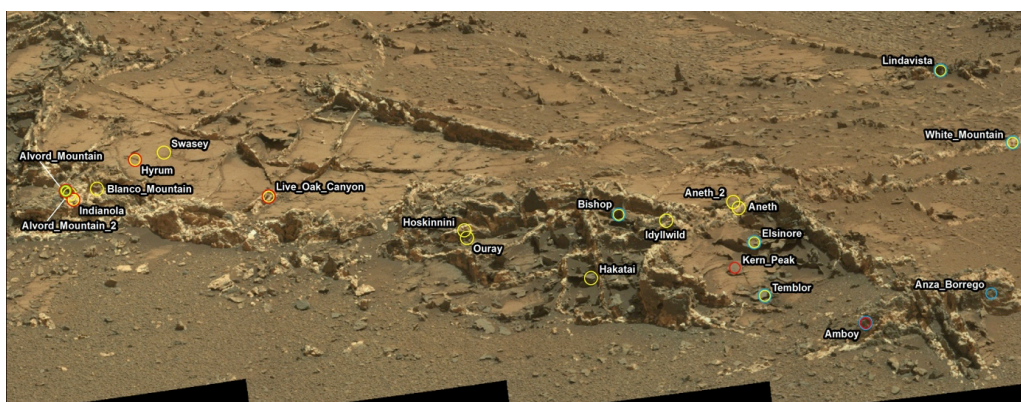
Curiosity has completed a detailed chemo-stratigraphy analysis at the Pahrump outcrop in Gale Crater. Data from the nearby “Garden City” vein complex can be used to provide insight into the fluids that may have migrated through the section and evolved locally from water-rock interactions. From these data emerges a complex aqueous history where sediments have interacted with fluids with variable chemistry in distinct episodes.

1. Introduction

From September 2014 through April 2015 Curiosity explored the unit informally known as the “Pahrump” which has been identified based on orbital data as

part of the lowermost strata of Mount Sharp (1). During this period, ChemCam systematically targeted bedrock and diagenetic features to study the chemo-stratigraphy of exposure and investigate its aqueous history and evolution. In total >540 chemical measurements at distinct locations were collected. Previous results from these data include the identification and investigation of a wide range of diagenetic features (2); average compositions of the units have variable chemical alteration indexes (e.g. 3,4) indicating variable mineralogy. Additional elemental trends also support variations in mineralogy (e.g. Al_2O_3 vs TiO_2 , FeO) (e.g. 5, 6). More recent ChemCam data collected at the “Garden City” vein complex (Figure 1) can be used to provide additional constraints on the chemical evolution of the Pahrump section.

Figure 1: ChemCam measurement targets in the “Garden City” vein complex are shown in yellow. Background mosaic sol 925 Garden City Mosaic (mcam04072, credit NASA/JPL/MSSS)



2. Garden City

The “Garden City” vein complex consists of a mass of interconnected veins that are resistant to erosion compared to local bedrock. Garden City is thought to be stratigraphically above the Pahrump outcrop. Thus the fluids producing the veins likely also migrated through the Pahrump sediments. The Garden City veins have distinct chemical signatures that are different from both the local bedrock and each other. Linear chemical mixing models also cannot be used to link the chemical end members measured. This implies distinct fluids forming the veins. Figure 2 shows example chemical trends in this data set using Independent Component Analysis (ICA)(7). Different subsets of analyses are grouped by color symbols. The high-albedo veins (labeled “CaSO₄Vein, green”) are dominated by CaSO₄ (e.g. White Mountain, Indianola, Hoskinnin). The gold “Flourine” observations (e.g. Alvord_Mt2) are distinctive due to extremely high (e.g., several to > 10 wt %) fluorine concentrations and abundant Ca (8). A subset of the dark veins (labeled “Dark Vein Lower Fe, pink”) has relatively low iron and high Mg suggesting a Mg-rich fluid is involved in their formation. Relatively high iron observations are seen in a subset of the dark veins (e.g., Ouray, orange) and in the resistant fins (magenta) (Hakatai, Bishop, Elsinor, Temblor). While morphologically similar to the other fins, Elsinor has lower potassium. This may indicate that the erosion resistant morphology of these features is the result of excess iron phases present.

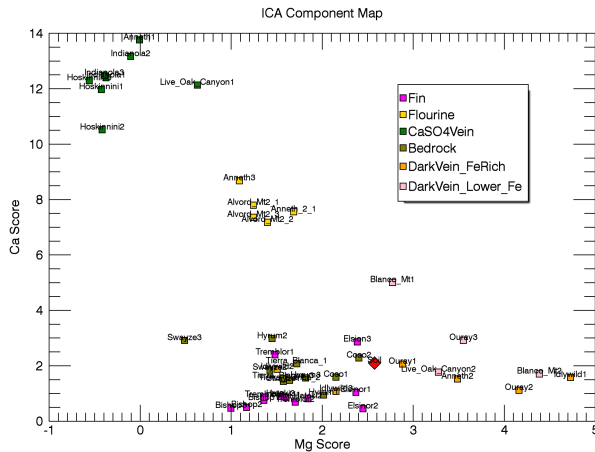
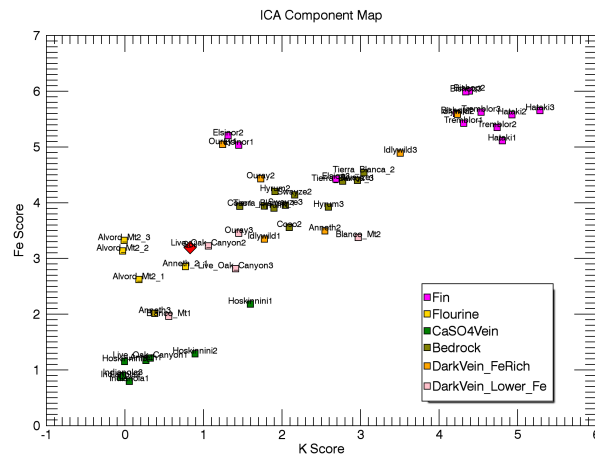
3. Conclusions.

Given the distinct fluid chemistry at Garden City, it is likely that multiple fluid compositions interacted with the sediments at Pahrump. The vein compositions at Garden City can be used to develop insight into the overall variability of the chemistry within the Pahrump section and its aqueous evolution. The fluids can be used as end members to assess how the sediments interacted with the fluids producing the veins. These different fluid chemistries at Garden City could be the result of distinct fluids migrating through the section from a

distance with a pre-established chemical signature, fluids locally evolved from water rock interactions, or both. Thus the chemical relationships between the Pahrump bedrock and the veins’ chemistry can be used to constrain the origin of the fluids.

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Figure 2: ICA analysis of ChemCam Garden City bedrock, veins, and resistant fins.



Detection of Zn with ChemCam on Mars

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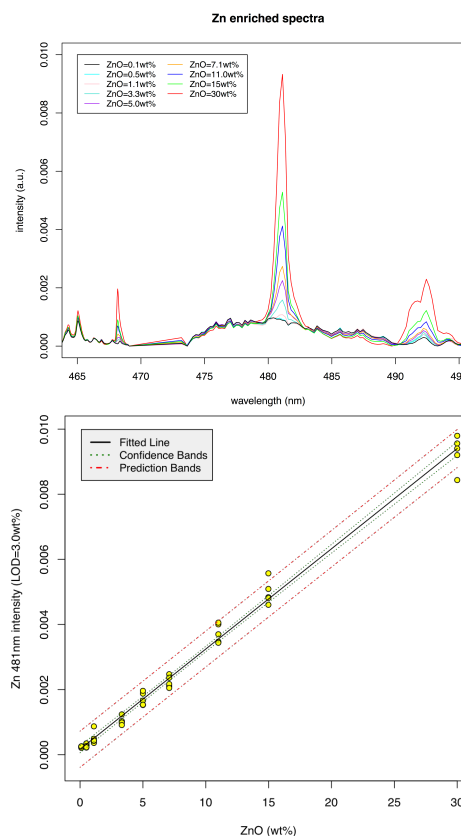
Abstract

ChemCam is a Laser-Induced Breakdown Spectroscopy (LIBS) instrument on-board the NASA Curiosity rover currently exploring Mars. ChemCam can analyze the chemical composition of geological samples without preparation and at a distance by detecting the laser induced atomic emission lines from elements present [1, 2]. ChemCam is sensitive to most chemical elements. In addition to the major elements, ChemCam can be used to detect and quantify a set of minor and trace elements such as Li, Sr, Ba, and Rb using univariate and multivariate regression techniques [3]. Mn has also been detected and quantified with ChemCam at high concentrations indicating that highly oxidizing conditions must have occurred on the surface of Mars [4]. We report here the detection of high Zn content targets with ChemCam at the Kimberley location at Gale Crater that are linked to high-Mn concentrations.

1. Zn detection and quantification

ChemCam was not initially designed to detect Zn which has a relatively high ionization energy of 9.39eV [5], higher than typical elements detected by LIBS, meaning that we expect to detect it only at the wt.% level [6]. The clear detection of Zn lines for Yarrada (sol 628) indicating strong enrichment of this element at the Kimberley outcrop triggered the need to develop a specific database to detect and quantify Zn enrichments on Mars.

The database for Zn quantification was developed at LANL by producing pressed pellets from ZnO powder intimately mixed with powdered Brammer geological standard basalt BHVO-2. Using this procedure we generated calibrated standards with 10 ZnO fractions ranging from 0.1 wt.% to 100 wt.% in a matrix that is close to the average martian basaltic composition. After pre-processing of the spectra and normalization [7], comparison of the spectra is used to define the best Zn lines for Zn detection and quantification. Some Zn emission lines are weak, while others interfere with the emission lines of major elements and cannot be used for calibration.



Figures 1 and 2: ChemCam Zn emission line at 481.2nm shown for different ZnO contents, and the resulting linear regression model.

The best Zn emission lines for quantification purposes with ChemCam are located around 330nm, 480nm and 760nm. Figure 1 shows the effect of increasing Zn content on the emission lines located around 480nm. A Lorentzian fit of the emission lines is used to calculate their area, and generate a univariate regression model for Zn. Such a procedure has been used to generate univariate models for quantification of other elements [8]. Figure 2 presents the regression model for the Zn emission line at 481.2 nm with 95% confidence bands for the linear fit in green and 95% prediction bands in red, giving a limit of quantification (LOQ) of 3 wt.%.

The Zn emission lines of the standard containing pure ZnO behave non-linearly and were not used to generate the model, as no pure ZnO has been found on Mars. The LOQ gives the limit of quantification with ChemCam at the 95% confidence level. The limit of detection of the Zn line at 481.2 nm is lower than this limit as can be seen on Figure 1. If defined as the level at which an emission line can be detected above 3 sigma of the background noise level of the spectrum, then it is about 0.5 wt.%. The model can also be improved by using multiple line detection and multivariate regression instead of relying on a single emission line [3].

2. Zn-rich targets

We have applied the Zn detection and quantification model on all data taken by ChemCam until sol 800. First, the Zn lines intensities 3 sigma above the background noise level of the spectrum are detected. Then the univariate regression model for the emission line at 481.2 nm is applied to quantify the Zn content. The highest predicted content is obtained for target Yarrada (location 5 sol 628) with ZnO=7.0 wt.%. When considering the number of detections and the predicted ZnO content of the targets as a function of time, there is a clear enhancement in Zn content around the Kimberley outcrop (analyses done from sol 580 to sol 630).

Yarrada #5 clearly stands out as the ChemCam target with the highest content in ZnO. From the RMI context image (Figure 3), Yarrada #5 is located above the rock strata, on the flat overlying surface. Shot-to-shot analysis of the ChemCam data indicates that the first two shots are contaminated by overlaying dust cover. Below the dust, the rock is slightly hydrated, and Zn content is about constant over all the remaining 28 shots taken at that location.

3. Discussion of the results

The fact that Zn does not vary with depth suggests it is not linked to a thin weathering coating of the rock. There is no clear detection of S, indicating that Zn is unlikely to be present in the form of Zn-sulfide, sphalerite, which is its most common form on Earth. The APXS measurements at Kimberley also indicate strong enrichment in Zn on Windjana drill fines (3430-4680 ppm Zn) and Stephen (~8150 ppm Zn) on which MnO-rich coating has been detected [9].

The enrichment of Zn in Yarrada seems also linked with an increase in Mn and Na content. Overall, Kimberley is an outcrop that presents strong enrichments in alkali and especially Mn content. The strong Mn signatures detected are interpreted as oxide coatings, suggesting the presence of Mn-oxides possibly formed at a time when Mars surficial

conditions involved abundant water and were more strongly oxidizing than today [10]. The Zn enrichment in Kimberley is probably also in the form of oxides and would support the conclusions derived from the presence of Mn-oxide veins in the outcrop.

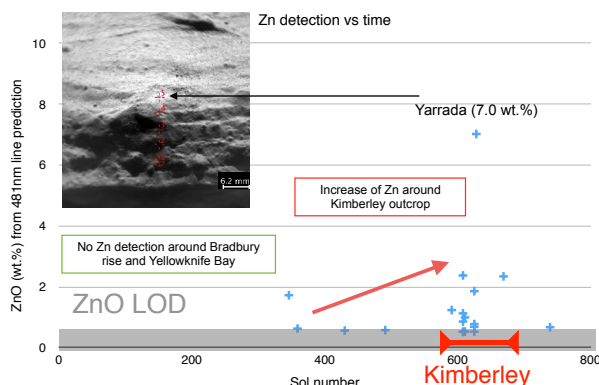


Figure 3: ChemCam Zn detection as a function of time during the first 800 sols on Mars.

6. Summary and Conclusions

High Zn content targets have been detected on Mars using the ChemCam instrument at the Kimberley outcrop. These targets are linked to a location where high Mn content was also detected. These enrichments can be interpreted as oxides deposited during previously highly oxidizing conditions on the surface of Mars. Improvements of the technique and application to the detection of Zn-enrichments in the Pahrump stratigraphy at the base of Mount Sharp will be presented.

Acknowledgements

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Carbonation and Serpentinization of the Martian Crust inputs from by Geochemical Modelling

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Abstract

The investigation of the CRISM data indicates that the serpentinization and the carbonation have to be considered as significant processes of alteration of the early Mars. We report here a tentative of characterization of these processes by geochemical modelling with EQ3/6 programs.

1. Introduction

Carbonates are described in Martian meteorites as minor phases [1]. In situ analysis of the Martian dust also reveals carbonates as a minor component [2]. Only orbital detections allow the analysis of the geological context of the formation of the Martian carbonates. Crustal outcrops have revealed carbonates and serpentine: in an olivine rich layers linked with the ejectas of Isidis basin, or in crustal outcrops such as deep canyon or central peak of large impact crater that may have exhumed crust from depth [3], [4], [5], [6] and [7]. A systematic analysis of the alteration minerals in these central peaks of impact craters on the Noachian crust has been conducted by [4]. They demonstrate that the typical mineralogical assemblage observed in central peak of impact crater between Isidis and Hellas Basins are chlorites, Fe-Mg smectites, serpentine and carbonates. The most abundant phases in term of detection are chlorite and smectite while serpentine and carbonate are rarer. A geological analysis of these detections suggests that these minerals are exhumed from depth rather than being formed at time of the impact.

2. Geochemical Model

Our model use the software code EQ3/6, version 8.0 [8] and [9] and a customized database for 0-400°C and 50MPa [10].

We use different $p\text{CO}_2$ from 6mbar to 1 bar in a closed system and heat the fluid at different temperature (400°C and 200°C). Then, the system is studied during a cooling from 400° (or 200°) to 25°C with two endmember of W/R (1 and 10) to simulate rock- vs fluid-dominated environments. We used three different rock compositions (mafic, basaltic and anorthositic). We used different fluids from pure water to typical terrestrial seawater enriched in sodium and potassium and a typical water of serpentinization systems describe by [11] and also used in [12].

3. Results

Our results show that the hydration and carbonation of the martian crust lead to minor presence of serpentine and carbonates along with Mg-smectite, chlorite and talc under certain conditions. This study shows that it should be a fluid dominated system, with a partial pressure of CO_2 ($p\text{CO}_2$) of 1 bar and high amount of olivine should be present in the protolith (~30%) [13]. Moreover, we show that the serpentinization is favoured by a fluid influenced by an ultramafic system and that the carbonation is favoured by a fluid influenced by a mafic system [14].

4. Discussion

Our modelling success to reproduce most of the Martian minerals association found with serpentine and carbonates. We will present the possible scenarios for the formation of these mineral associations.

Our results demonstrate that the hydration and carbonation can lead to a production of H_2 and CH_4 what are key parameter for the construction of more complex organics matters and therefor the emergence of life. We will detail which mineral associations should or should not be seen as life

friendly. These results will help to determine the potential of habitability of future landing sites.

Acknowledgements

The research leading to these results has received funding from the European Research Council under the European Union's Seventh Framework Program (FP7/2007-2013)/ERC Grant agreement n° 280168.

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Detections of carbonates in Valles Marineris

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Abstract

Valles Marineris is a unique place on Mars where deep crust is exposed at its original place [1]. The primitive crust is observed at the base of Coprates Chasma as well as in the eastern parts of Valles Marineris [1]. Elsewhere on Mars, several authors [2 and references therein] reported key observation of the martian primitive crust being altered thanks to CRISM (Compact Reconnaissance Imaging Spectrometer for Mars) data. Coprates Chasma is a proposed landing site for Mars 2020 mission and is so intensely covered by CRISM data. It allows us to investigate the alteration signs of the primitive crust. We describe here the study of 3 CRISM FRT observations on the wall of Valles Marineris in Coprates Chasma and on a remnant horst in middle of the canyon seeking for alteration minerals.

1. Geological context

According to [1 and 3], the walls of Coprates Chasma exposes both the primitive Low Calcium Pyroxene rich crust and the Noachian Tharsis lava stack [1 and 3]. The sharp crustal boundary between the two types of crust would occur around our study area [1, 3]. A part of the observation on the southern wall is a 24 km crater lying down the floor of the canyon. Another observation is on the central horst (maximum of elevation around -2400m) of the canyon (Figure 1).

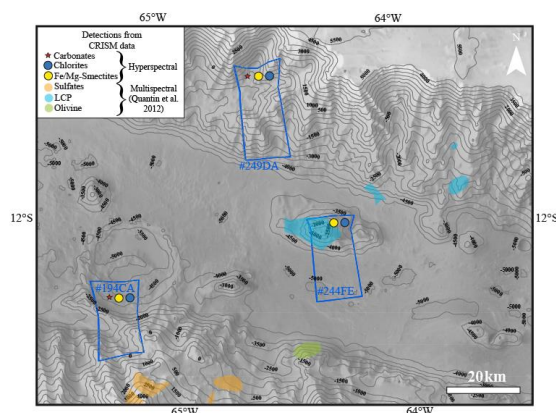


Figure 1: Geological context. CRISM observations footprints are shown in blue. The Detected mineralogy from CRISM study is reported with the following symbol: blue for chlorite, yellow for smectite, red star for carbonates, orange for sulfates, light blue for LCP and green for olivine.

2. Spectroscopic investigation

We use CRISM data that we pre-process with CAT [4]. Because the signal to noise ratio in CRISM data is low, we use CoTCAT, a personal noise removal pipeline describe in [5]. The ratio used is the median by column ratio describe in [5]. We discriminate our detections by the study of the combination of the position of centre of absorption near 2.3 and 2.5 μm after continuum removal [6 and 7]. Our results highlight the presence of carbonates. The carbonates are detected by these combinations of absorption in addition to a strong absorption before 3.45 μm and to the presence of the drop near 3.8 μm . All the carbonates signatures reported here present the characteristic of a mixture with a hydrated phase or a weathering of the carbonates (presence of absorptions near 1.4 and/or 1.9 μm , shoulder near 2.27 μm and drop of the reflectance after 2.2 μm) [8]. We detected the carbonates signatures on the two CRISM observations on the walls of Coprates

Chasma while similar signature are absent of the CRISM observation on the floor of the chasma studied here.

We observe absorptions of the Fe/Mg-rich phyllosilicates on the horst that are close to 2.3 μ m rather than 2.33-2.35 μ m as for the observations on the walls. This suggests a better match with chlorite for the observations on the walls and a better match with smectite for the observation on the horst.

3. Discussion

Carbonates are so observed in the crater walls at the level of the southern wall as well as in the north wall (at the north at around 500m and at the south at around -3000m). The central horst shows only phyllosilicates. A relationship between the presence of the crater and the presence of carbonates is likely to be exclude because of the same detections made on the facing side of the wall of the chasma. This may suggest an extended layer of carbonated crust The absence of carbonates signature on the central horst of the chasma can be explained either because the carbonated layer is not exposed in the central horst or that the carbonation process is a spatially localized process.

4. Conclusion

Hydrothermal signatures have already been reported in this area [i. e.: 3 and 9] suggesting hydrothermal processes at a large scale in the region of Valles Marineris. Our detections of carbonates associated to phyllosilicates imply carbonation and hydration process of the crust exposed in the deepest part of Valles Marineris. Implication for exobiological perspectives will be presented by comparing the mineral assemblages detected here and geochemical modelling and the potential efficiency of H₂ and CH₄ production.

Acknowledgements

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Valles Marineris ILDs: updated mapping of sulfates from the whole OMEGA dataset

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Abstract

We present an updated regional mapping of monohydrated and polyhydrated sulfates in Valles Marineris ILDs. Using spectra of actual mixtures of a sulfate with unaltered basalt we infer the amount of sulfur in the ILDs and discuss implications.

1. Introduction

Knowledge of the mineralogy of the Interior Layered Deposits (ILD) of Valles Marineris (VM) can help distinguishing between various hypotheses of their formation (lacustrine, volcanoclastic, etc.). Hyperspectral data acquired by OMEGA (Observatoire pour la Minéralogie, l'Eau, les Glaces et l'Activité) have provided new insights on the composition of the ILDs, revealing monohydrated and polyhydrated sulfates [1, 2].

2. VM ILDs at various scales

Most studies made since the earliest detections of sulfates in VM ILD have focused on areas of relatively small extent. Notably, high spatial resolution (tens of m scale) data from CRISM (Compact Reconnaissance Imaging Spectrometer for Mars) have revealed a large diversity of minerals in VM, including various sulfates (kieserite, szomolnokite, polyhydrated Fe-sulfates, jarosite), Fe-oxides, Fe/Mg and Al clays [eg. 3], and a hydrated phase which nature is still debated [eg. 4].

While assessing the mineralogical diversity at local scale can give more insight on the chemistry and formation processes of the ILDs, it should be joined with a more synthetic regional scale view, has yet to have been updated since the first detections from OMEGA data.

We therefore used the whole archive of OMEGA data acquired since late 2004 to map monohydrated

and polyhydrated sulfates in VM. We then deployed an original empirical strategy to try and quantify those sulfates in VM ILDs. Our results allow discussing various hypotheses of sulfates formation.

3. Analysis of OMEGA data

OMEGA, operating in the near infrared (NIR), allows distinguishing between two spectral classes of sulfates, based on their absorption bands in the 1.7-2.5 μm range: monohydrated and polyhydrated [5]. After applying routine spectral calibration and atmospheric correction on OMEGA data, we computed respective proxies for monohydrated and polyhydrated sulfates based on absorption band depths at 2.1 μm (BD21) and 1.9 μm (BD19).

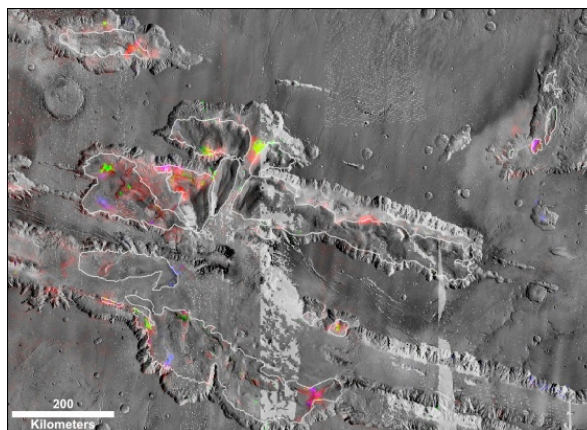


Figure 1: Composite RGB mapping of a Fe-oxide index, BD21 and BD19 in central VM from OMEGA (on Themis day IR).

We mitigated problems arising from variable observation geometry, dust and ice atmospheric opacity, and OMEGA instrument evolution over the course of the mission, through a series of steps. We filtered out observations with unfavorable incidence and emergence angles, high dust or ice opacity as determined from Themis observations [6], and

corrected for the progressive loss of spectral channels. We then built mosaics of OMEGA observations using higher spatial resolution on top. The results are regional scale maps of BD21 and BD19 (Figure 1).

3. Empirical quantification strategy

We decided to tackle the issue of the quantification of sulfates from an original angle, based on preparing, in the laboratory, binary mixtures of a sulfate intimately mixed with an unaltered basalt.

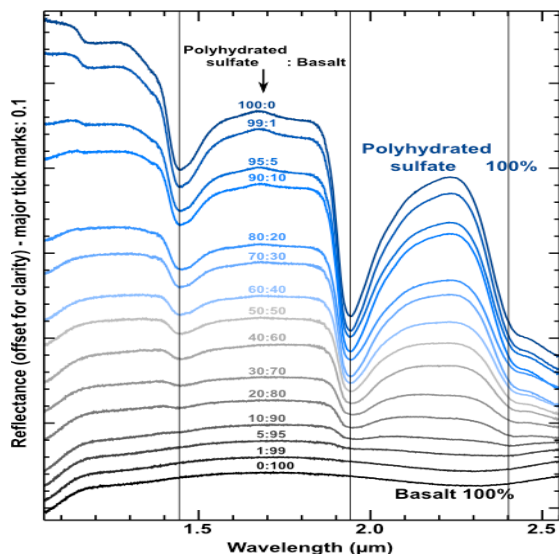


Figure 2: Laboratory spectra of actual mixtures of basalt and polyhydrated sulfate

We manually prepared series of 15 mixtures of two endmember materials from 100%-wt basalt to 100%-wt sulfate. Endmembers were first verified for purity, crushed in a mortar and passed through a 63μm sieve. We then acquired NIR spectra of the whole mixture series. Figure 2 shows the spectral series for polyhydrated sulfate. We found a linear relation between sulfate weight abundance and BD19 or BD21 for polyhydrated and monohydrated sulfates, respectively, for <30%-wt sulfate. We then inverted these relations to produce maps of sulfates weight abundances in VM and MP.

Sulfate abundances retrieved by this method must be interpreted with caution. Indeed, among other assumptions, it assumes that the sulfate-bearing material on the surface of Mars behaves similarly as a 2-endmember mixture of materials with similar fine grain size and that the material is homogeneous,

which may well be untrue. Nonetheless, it allows for tentative first order interpretations.

4. Geological interpretations and discussion

Averaging the abundance of sulfates from OMEGA data over the volume of all ILDs, as mapped using MOLA, Themis, CTX and OMEGA data ($\sim 0.5 \times 10^6$ km³), we propose within the ILDs a total sulfur mass of $\sim 5 \times 10^{16}$ kg, equivalent to a global layer (GEL) of ~ 0.75 m of sulfates (and with a water content of ~ 0.4 m GEL). If all this sulfur were in SO₂ form it would account for ~ 4 times the current Mars atmospheric pressure (~ 25 mbar).

The formation of major sulfate deposits on Mars seems to have been restricted in space and time. Most large sulfate-rich deposits are Hesperian in age while Noachian sulfates are lacking, despite a probable sustained magmatic activity. Our estimates show that Hesperian sulfates in VM ILDs could have resulted from groundwater alteration of sulfide-rich earlier (Noachian) rocks [eg. 7] as well as from uptake of atmospheric sulfur outgassed by volcanism during the Hesperian. In the latter case, our quantitative analysis suggests that VM and other equatorial sulfates could only account for a small fraction of what all of the Hesperian volcanism could have outgassed, questioning either one or both of processes of magmatic outgassing or sulfate precipitation in sediments on Mars.

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Regional hydrothermal alteration in Noctis Labyrinthus: scattered, yet pervasive.

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Abstract

We analyzed 113 CRISM cubes in Noctis Labyrinthus. We found 10 classes of alteration minerals including clays and sulfates, sometimes associated in the same setting. Fe and Al sulfates argue for acidic hydrothermal alteration.

1. Introduction

The Valles Marineris (VM) region of Mars bears various alteration minerals, as initially revealed by km-scale data from OMEGA (Observatoire pour la Minéralogie, l'Eau, les Glaces et l'Activité) [1,2], and which diversity has been assessed by numerous local studies using finer resolution (tens of m) data from CRISM (Compact Reconnaissance Imaging Spectrometer for Mars). These minerals include Fe-oxides and sulfates in the chasmata and hydrated silica or phyllosilicates on the surrounding plateaus [3].

Noctis Labyrinthus (NL) is an ensemble of depressions located at the western extremity of Valles Marineris, where an unexpected diversity of minerals, including phyllosilicates, sulfates and silica, has been recently reported [4], and its geological context discussed [5]. Expanding on these findings, we surveyed this region using 113 targeted CRISM near-infrared cubes (footprints shown in Figure 1) to assess the region-wide diversity of alteration minerals.

2. Data analysis showing a larger diversity of alteration minerals than for contemporaneous terrains

A custom batch processing pipeline was developed to rapidly process a list of CRISM observations, based on calibration and correction routines of the CAT, as well as a custom spectral ratioing procedure to filter out column-dependant artifacts and improve signal-

to-noise. Custom spectral criteria, based on the shape and combination of absorption bands, were then computed to look for various alteration minerals.

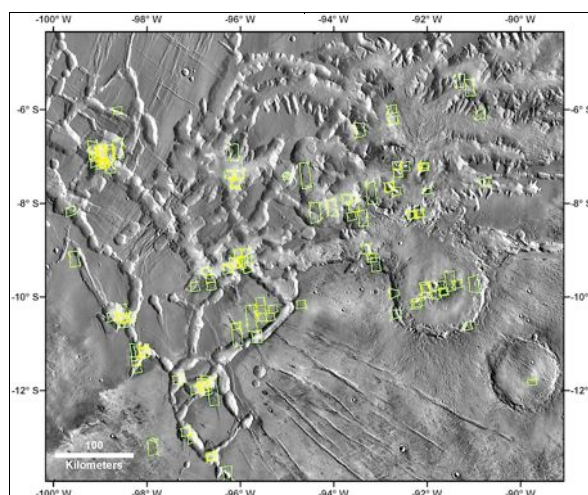


Figure 1: Extent of the area of study with CRISM footprints in yellow.

We found widespread occurrences of outcrops of ~10 classes of different hydrated minerals. These include Fe/Mg-phyllosilicates, Kaolinite-group minerals, silica, Ca, Mg and Fe-bearing polyhydrated sulfates (gypsum, copiapite, hexahydrite), kieserite, jarosite (Figure 2), alunite, and a so-called “doublet”-bearing phase.

3. Discussion

Both clays and sulfates are pervasive in Noctis Labyrinthus depressions. This region shows the most widespread occurrence of jarosite-bearing materials yet reported on Mars (see spectra in Figure 2). The association of jarosite with silica, gypsum, and, in at least one location, the rare Al-sulfate alunite argues strongly for acidic alteration. Indeed, acidic waters greatly enhance the mobility of the elements Fe and Al.

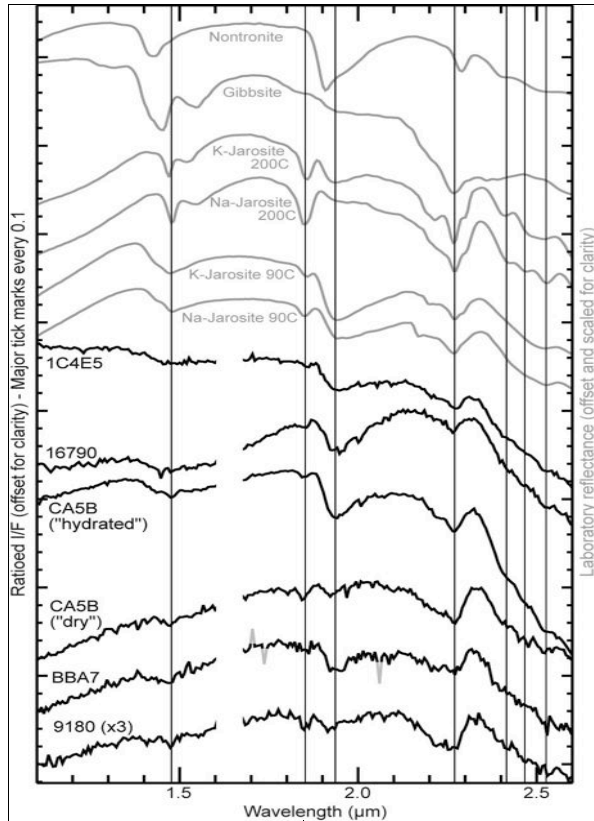


Figure 2: CRISM ratioed spectra of jarosite in NL (black) with library spectra (grey) for comparison.

A morphological study of the region using CTX (ConTeXt imager) and HiRISE (High Resolution Imaging Science Experiment) data is revealing several clues (ash layers, volcanic vents, lava flows) that point to volcanic activity in at least parts of NL. Coupled with the peculiar mineralogy associating silicates with sulfates, including jarosite and alunite, the morphological evidences argue for hydrothermal alteration, as proposed locally by [5] for one depression of NL, but as a major regional occurrence, over as much as several hundreds of km squared.

On a global scale on Mars, the mineralogical diversity is somewhat higher in older terrains than in younger terrains. NL, being one of the latter, appears to stand at odds with this global trend, which may be related with the long-lived magmatic activity of the Tharsis province.

NL alteration minerals formed more recently than most hydrous phases elsewhere on Mars, after the late Hesperian (age of the plateau cross-cut by NL

depressions), when Mars climate is believed to have been cold and dry. Yet, the mineralogical diversity is as important as it ever gets on Mars.

This study shows that despite a changing, drying, surface environment, there were regional locations on Mars possibly hosting habitable conditions, in hydrothermal settings, further down the history of the planet.

This work also gives insights, by analogy, on the possible role of hydrothermal processes in the formation of sulfates and other alteration minerals found in VM Interior Layered Deposits.

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Martian Chemical Weathering at Hematite Ridge, Gale Crater

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Abstract

A likely origin of Hematite Ridge, Gale Crater is from the in-situ weathering of precursor silicates under oxidizing conditions: it might represent an ancient sub aerially exposed horizon. High W/R associated with FeMg mineral alteration and hematite enrichment is envisaged within a near surface aquifer.

1. Introduction

Secondary minerals identified by Mars Science Laboratory (MSL), together with their sedimentological context, provide an unprecedented opportunity to constrain the nature of martian fluids and habitability. One of the main targets for MSL Mission is the Hematite Ridge on the north, lower slopes of Mt. Sharp (Aeolis Mons). Hematite Ridge is a 200 m wide protruding feature extending 6.5 km northeast-southwest [3], identified by CRISM as having a hematite-rich signature, contrasting with clay- and sulfate-rich mineralogy dominating other parts of Mt. Sharp [1,2].

After landing in August 2012, Curiosity has identified clay and Fe oxides within sediments along the traverse to Hematite Ridge. ChemCam analyses show the overall basaltic composition of the sediments (Fig. 1). The Sheepbed member is a mudstone of basaltic chemical composition with ~15% smectite, ~50% igneous minerals, and ~35% amorphous material [4]. The observed magnetite is considered to be authigenic [5]. In previous work we showed that dissolution of approximately 70:20:10 % amorphous material, olivine, and basaltic material in an open system within the Sheepbed Member mudstone can explain the smectite and magnetite abundances identified by CheMin XRD at the John Klein and Cumberland sites [6]. More recently, at

the Kimberley drill site, CheMin has identified ~10% magnetite with some hematite [7].

Here we show thermochemical models for the formation of Fe oxide enrichments, and the ferric oxide hematite in particular, within Gale sediments. This provides an insight into the formation conditions of the Hematite Ridge layer during diagenesis or other alteration stages. An alternative model has been suggested by [3] who suggested exposure of a Fe²⁺ rich groundwater to an oxidizing environment, leading to precipitation of hematite or its precursors. These models will be tested once we have a full mineral assemblage from Hematite Ridge.

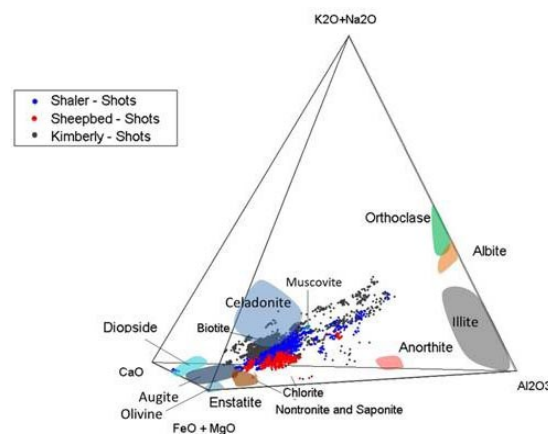


Figure 1: ChemCam LIBS data (PLS1) of the Sheepbed Member mudstones. The sedimentary horizons show an overall basaltic mixing trend between pyroxene and feldspar. The more alkali-rich Kimberley and Shaler units are shown for comparison.

2. Methods

We use ChemCam (PLS1), APXS and CheMin analyses and sedimentological observations of the

Gale sediments [4,8,9] to guide the input parameters of our thermochemical model. We have used CHIM-XPT [10] to perform the model runs for a variety of compositional, T, W/R values and initial fluid compositions. The bulk composition is assumed to be basaltic (Fig. 1). Here Water/Rock ratio W/R is the ratio of incoming fluid to reacted rock.

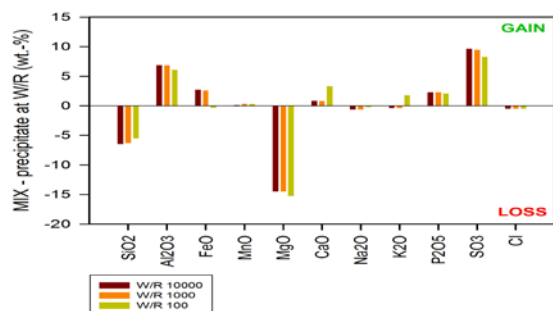


Figure 2: Element gain/loss in precipitate relative to the dissolving host rock (incongruent dissolution of Portage soil, see [6])

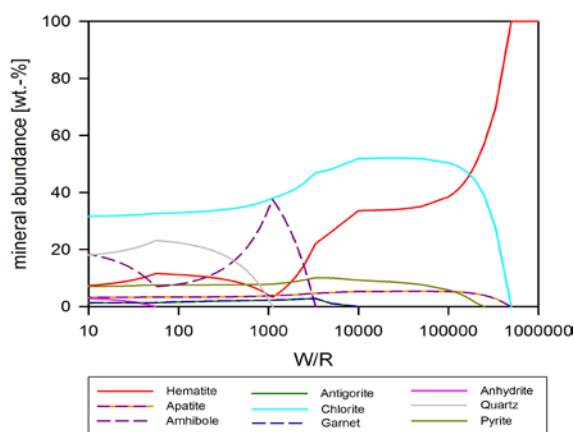


Figure 3: The effect of temperature on ferric oxide abundance. Higher T, here 150 °C, is associated with more hematite relative to magnetite and other oxides; particularly at the very highest W/R [6].

3. Results

In general, the model based on dissolution of 70% amorphous phase, 20 % olivine and 10 % whole rock [6], produces precipitates that are enriched in Fe, Al, and S compared to the original rock. This effect can be more pronounced at higher W/R (Fig. 2). High W/R runs, e.g. >1000, and higher temperature (Fig. 4) also predict the precipitation of ferric oxide at the

expense of ferric silicates or other Fe oxides. Repeated weathering/leaching cycles such as can occur at the surface or along fluid conduits, will increase the effect. For example, if the alteration assemblage formed by incongruent dissolution of Portage soil (with 70 % amorphous phase, 20 % olivine and 10 % whole rock), is subject to another fluid event, the newly precipitated assemblage (at W/R 1000) contains 27 % goethite, 44 % serpentine, and 22 % clay with minor pyrite and apatite (Fig. 4).

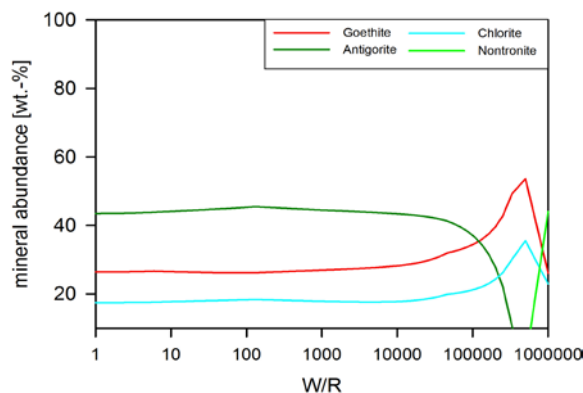


Figure 4: Re-dissolution of an alteration mineral assemblage at W/R 100 from the model runs for the 70:20:10 amorphous:olivine:bulk rock mixture. The original weathering products were dissolved in a new batch of the dilute diagenetic brine (see [6]). This shows that repeated weathering cycles will lead to enrichment of ferric oxide (goethite here, though this can readily transition to hematite).

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Chemostratigraphy of potassic sedimentary rocks in Gale crater, Mars, as seen by ChemCam onboard Curiosity

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Abstract

The analysis of the sedimentary record on Aeolis Palus reveals the occurrence of rocks showing a significantly enhanced K content at Cooperstown and Kimberley. Ranging between massive and cross-bedded fine to very coarse sandstones, and conglomerates, those rocks are inferred to represent fluvial or fluvio-deltaic depositional environments and derive from basalt and potassic sources, essentially unweathered.

1. Introduction

The Mars Science Laboratory (MSL) rover Curiosity encountered potassic sedimentary rocks along its traverse to Mount Sharp. Those rocks have been analyzed by the ChemCam instrument that combines a Laser-Induced Breakdown Spectroscopy (LIBS) instrument [1, 2] and a Remote Micro-Imager (RMI) [3] at two waypoints informally named Cooperstown

(sols 438 to 453) and Kimberley (sols 576 to 632). Here, we report a synthesis of the chemical composition of the potassic rocks as seen by ChemCam according to their stratigraphic unit and facies at Cooperstown and Kimberley.

2. Stratigraphy and rock facies

The potassic rocks are primarily associated with two geomorphological units defined from orbit: a light-toned topographically variable, or “Rugged Unit”; and overlying light-toned striated rocks forming a “Striated Unit” [4] (*Fig. 1*). Cooperstown (-4.62°N, 137.42°E) is associated with the Rugged Unit and is topographically above the Yellowknife Bay Formation (YKB) investigated during the first phase of the mission [4]. Two members of the Cooperstown formation have been investigated by ChemCam and correspond to massive fine and coarse sandstones (*Fig. 1A*). The Kimberley formation (-4.64°N, 137.4°E) is associated with both the Rugged Unit and

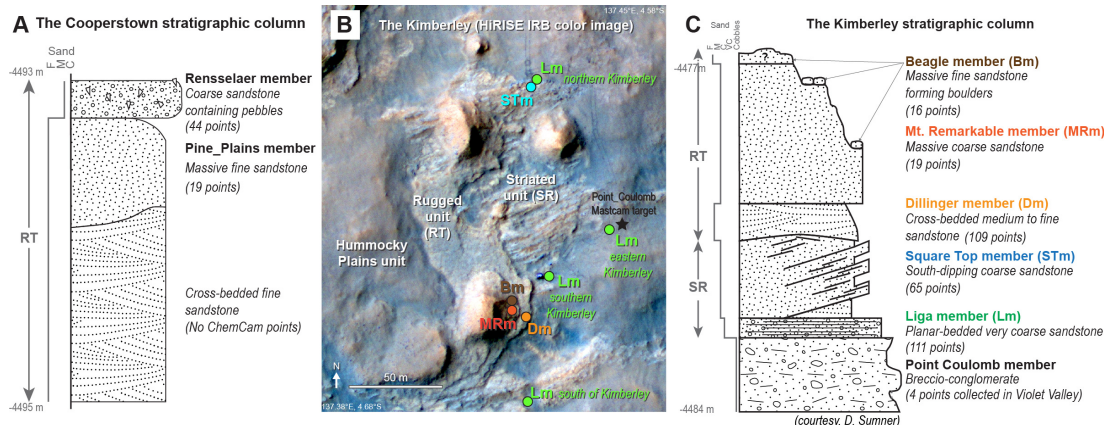


Fig. 1: Stratigraphy and facies of the potassic sedimentary rocks. Thicknesses of the stratigraphic columns are not to scale. Elevations have been estimated by K. Stack [5]. The number of points indicated refers to the number of ChemCam points collected for each member and located in Fig. 1B for the Kimberley formation.

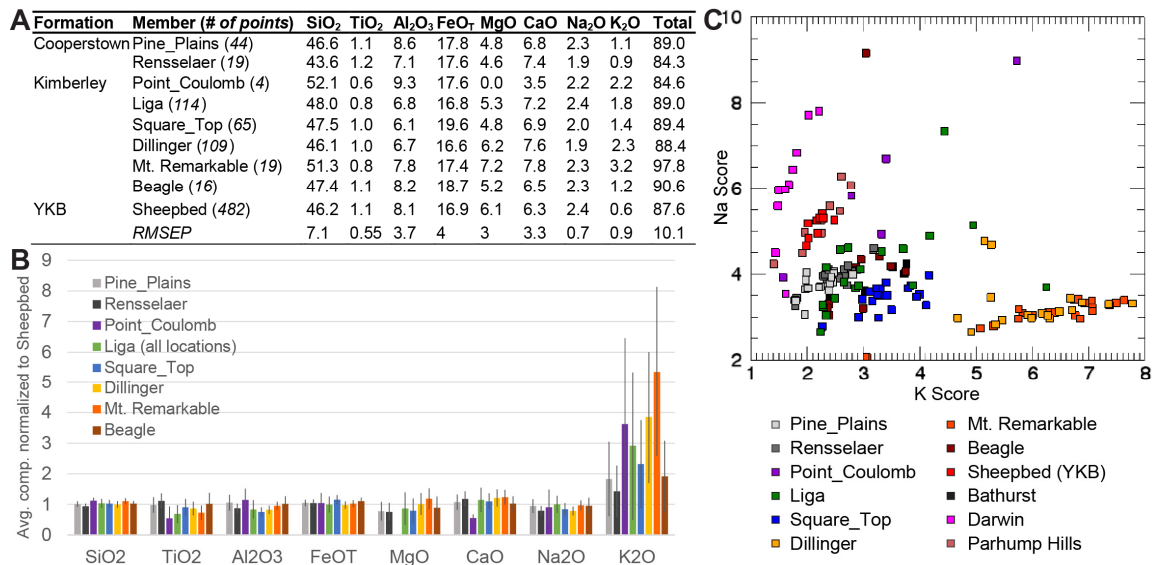


Fig. 2: Major-element composition of the potassic sedimentary rocks analyzed by ChemCam. (A) Average composition (wt%) of each member determined by PLS. Drill tailings, soils and Mn-rich targets are not taken into account in the average composition of the Dillinger member. (B) Average composition of the potassic rocks normalized to Sheepbed (YKB). Error bars are standard deviation of the compositions and primarily reflect heterogeneity within each member. (C) ICA score plot of K component versus Na component. Sheepbed, Bathurst, Darwin and Parhump Hills targets are indicated for reference.

the Striated unit, and it can be subdivided into seven members corresponding to massive and cross-bedded fine to very coarse sandstones, and conglomerates (Fig. 1B-C). These rock facies point to fluvial or fluvio-deltaic depositional environments [5-7].

3. Chemical composition

The sedimentary rocks of the Cooperstown and Kimberley formations have a basaltic-like composition according to Partial Least Squares (PLS), a multivariate regression method [8] (Fig. 2A). Those sedimentary rocks primarily differ in composition from the previously encountered sedimentary rocks in YKB or the conglomerates in Darwin [9] by their significantly higher content in K₂O (Fig. 2B). The Dillinger and Mt. Remarkable members (Kimberley) in particular display the strongest enrichments in K (Fig. 2A). An Independent Component Analysis (ICA) [10] reveals that the Na/K ratio of the Dillinger and the Mt. Remarkable members is much lower than for the other members (Fig. 2C). The K-feldspar and phyllosilicates (illite and/or smectite) identified in the Dillinger member by CheMin [11-12] are consistent with this enrichment in K. Overall the K abundance gradually increases between the Cooperstown and the Kimberley formations and between the Striated Unit and the Rugged Unit in the Kimberley Formation, which suggests an increasing contribution of a potassic source rock. ChemCam analyses also reveal

high contents in F, Li [13], Zn [14] in the bulk rock of the Kimberley Formation, and in Mn-rich fracture fills [15] suggesting that alteration processes, possibly pre- and post-depositional, may have contributed to the enrichment in K. However, all of these rocks display a low CIA (Chemical Index of Alteration) with CIA ≤ 46, except for Point_Coulomb. It indicates a rather limited chemical weathering prior to deposition and supports a primarily detrital origin for the enhancement in K.

Acknowledgements

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Mineralogic context of the final four, circum-Chryse candidate landing sites for the ExoMars rover

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Abstract

The ExoMars rover mission [1] will sample ancient, aqueously altered terrains to search for traces of extinct life and characterize the water history of Early Mars. These objectives translate into site-specific constraints in order to maximize the opportunity to access morphological and/or chemical markers for past aqueous environments and possibly life [2]. Currently, four candidate landing sites are being considered, all located on or near the margin the Chryse Planitia impact basin and all exhibiting hydrous clays within or near the ellipse: Mawrth Vallis [3], Oxia Planum [4], Aram Dorsum [5] and Hypanis Vallis [6]. Assessing the composition and morphologic/stratigraphic context of these clays is necessary to narrow down possible formation scenarios and help rank the sites according to their relevance to the science goals. This work investigates the aqueous mineralogy of the circum-Chryse region -where the LS are proposed-, in order to provide a framework for future in-depth investigations.

Regional mapping of the clay mineralogy was performed using the OMEGA and CRISM NIR imaging spectrometers [7,8] (figure 1). Global coverage of the circum-Chryse margin was achieved with OMEGA while detailed mapping was carried out locally with OMEGA and CRISM. Over 250 observations with pixel scales ranging 20 m - 4 km were investigated. Additionally, detailed analysis of the clay chemical composition was carried out using linear unmixing which provided the relative abundances of several Fe/Mg-rich phyllosilicate endmembers in the region.

The analysis revealed large exposures of dominantly Fe/Mg-rich phyllosilicates over most of the preserved Noachian-aged margins of Chryse Planitia. These minerals have spectral features which are generally similar to what is found elsewhere on Mars [9],

consistent with either vermiculites or smectite-bearing mixed-layered clays [10,11].

A regional outlier exists at and around the Mawrth Vallis LS: the most common clay there is likely Fe-rich nontronite associated with Al-rich phyllosilicates within layered deposits [12,13], indicating a different alteration setting. This site may however have shared a common aqueous history with the other circum-Chryse clays and then diverged to form Al/Fe-rich clays; alternatively their detection may be the result of specific mantling/re-surfacing processes. Two other sites may have undergone the same pedogenic type of alteration as Mawrth.

A number of similarities in composition and surface morphology have been detected between clay deposits in the Oxia Planum, Hypanis Vallis and possibly Aram Dorsum regions. These similarities and their regional distribution may hint at a common formation setting for most clays found circum-Chryse, in what may be the remnant of an extensive clay-rich horizon spanning an arc of at least 2500 km. Their mineralogy and context are also highly relevant to what is known of Mars alteration at a global scale [9]. Future work will be carried out to test this hypothesis by investigating their stratigraphy and unit ages, as well as the transitional regions with the Mawrth-like deposits.

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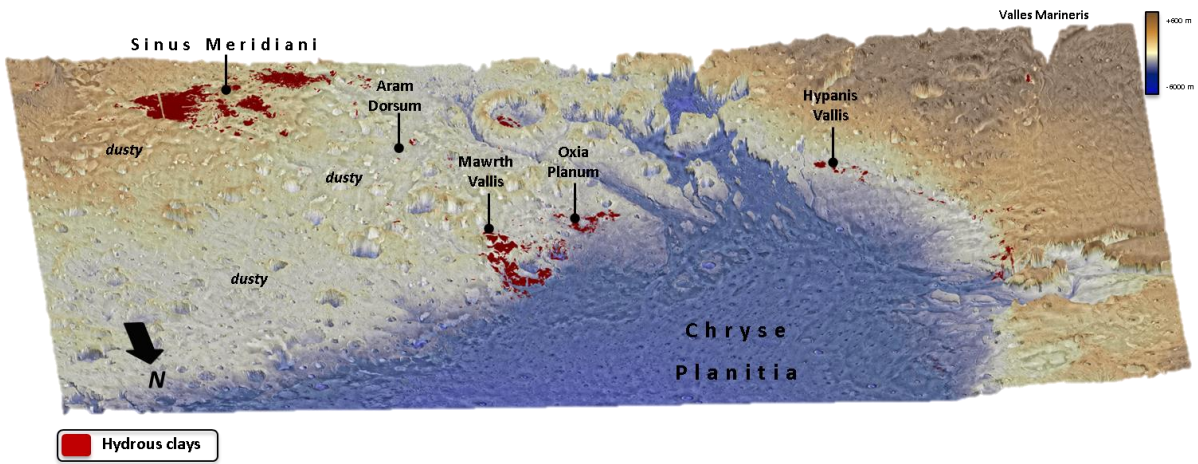


Figure 1: Perspective view of the circum Chryse Planitia hydrous clay detections (red) with candidate landing site locations.

Oxia Planum: a suitable landing site for ExoMars 2018 Rover

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Abstract

We suggest the landing of ExoMars in Oxia Planum between 16° and 19° of latitude north and -23° to -28° of eastern longitude, and below -2 km of MOLA elevation. This region exhibits one of the widest Mg/Fe phyllosilicates exposures as mapped globally with OMEGA and with CRISM multispectral data. The outcrop of Mg/Fe phyllosilicates is so wide that several potential landing ellipses (19 x 110 km) fitting the engineering constraints is possible. The exposed terrains are 4 Ga old (Hartmann's age system) and have undergone intense erosional processes until 3.6 Ga. The region also reveals fluvial related morphologies such as valleys and a delta fan attesting the water-related history of this region. Moreover, the region is current under erosion so that the exposition age of the fresher phyllosilicate rich surfaces is younger than 100 My attesting the potential preservation of putative biosignature. This proposed site fulfills ExoMars objectives.

1. Introduction

The ExoMars 2018 mission (ESA) has for scientific objectives to search for signs of past and present life on Mars, to investigate the water/geochemical environment as a function of

depth in the shallow subsurface, to study the Martian atmospheric trace gases and to characterize the surface environment [1]. The Exomars rover will carry a suite of instruments dedicated to geology and exobiology and will be able to travel few kilometers searching for past and present traces of life while its landing ellipse is 19 km by 104 km. The Rover will collect and analyze samples from outcrops and from subsurface drills down to 2 m depth to look for well preserved organic molecules [1]. The landing site has to be relevant as regards of these objectives while fitting the restrictive engineering constraints. From the scientific point of view, the site must be ancient, from the Early Mars period, for which many scientific evidences favor the existence of water-related cycle. The site must bears abundant morphological and mineralogical evidence of long-lived aqueous activity, the site must expose sedimentary rocks that are good candidate for organic matter preservation and more important the relevant outcrops must be distributed over the landing ellipse to ensure that the rover will catch one of them while the rover traverse range is restricted to few kilometer [1]. In this paper, we present the unique place Oxia Planum, a wide clay bearing plain located between 16° and 19° of latitude north and -23° to -28° of eastern longitude. We will discuss the geological context of these clay-bearing deposits, their mineralogy at both global and local scale, the age of the deposits and the water-related morphologies observed in the unit. We will finally discuss the results in term of implications for ancient Mars

history as well as recommendations for ExoMars 2018 landing.

2. Site description

Oxia Planum is located on the south west margin of Arabia Terra and exhibits Noachian terrains that become increasingly eroded towards the crustal dichotomy [2]. The region is located just between Marwth Vallis and Ares Vallis (Figure 1). This margin is dissected by outflows and diverse channels converging toward Chryse Planitia. Several alluvial fans or deltas have been preserved at the outlets of those valleys into hundred kilometer scale basins.

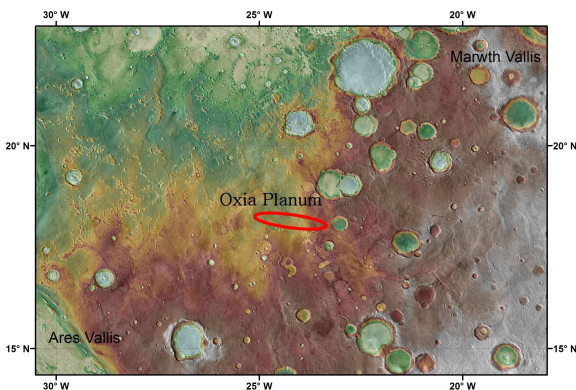


Figure 1: Regional context of Oxia Planum and potential landing ellipse for ExoMars 2018 (red ellipse is 19*104 km). Background is MOLA topography.

Regional compositional mapping of Oxia planum is achieved based on near-infrared, nadir-pointed OMEGA data at a 2.5 km pixel scale as well as CRISM multispectral data at 200 m/pix. Mg/Fe phyllosilicates are identified and mapped based on their diagnostic absorptions at ~1.4, ~1.9 and ~2.3 μm [3]. Phyllosilicate coverage is about 80% of the ellipses based on conservative mapping at low resolution. Several hyperspectral targeted CRISM cubes at full (~20m/pixel) and half (~40m/pixel) resolution are also available over the Oxia Planum region and confirm widespread occurrence of Mg/Fe phyllosilicates in association with layered light toned unit similar to Marwth Vallis.

The entire unit composed of phyllosilicates corresponds to a light toned layered unit that is observed over a large range of elevations while the layered formation is about 100 m thick. This may

suggest that like in Marwth Vallis region, the layered formation overlaps a pre-existing topography [4]. The layered formation displays lot of fluvial features such as former valleys and channels that are some time inverted. Rarely the unit is capped sporadically by a scattered unit, several meters thick, with no phyllosilicate signature. On the edge of this capping unit, we find the youngest exposures of the underlying phyllosilicate rich unit, which is as young as 100 My based on crater retention age assessment. This may suggest that putative biosignature may have been preserved by the capping unit from the cosmic ray exposure during the past 4 Gy, which is the estimated age of the phyllosilicate bearing unit.

3. Conclusion

Oxia Planum exhibits outcrops of Noachian phyllosilicates over hundreds of kilometers of terrain that has been affected by subsequent and/or contemporaneous sedimentary and fluvial activity. Hence, this site is extremely relevant to fulfill the ExoMars objectives. Deciphering the formation environment for such an extensive deposit would in particular provide constraints on the paleo-climate and habitability of Mars during the Noachian.

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Granodiorite and alkaline suite at Gale crater: continental crust on early Mars

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Abstract

The Curiosity rover landed at Gale, an early Hesperian age crater formed within Noachian terrains on Mars. The rover encountered a great variety of felsic igneous float rocks ranging from granodiorite to trachy andesite and trachyte during the first part of the traverse up to sol 550. They are the first in-situ evidence of low density early Noachian crust on Mars, sampled by Peace Vallis river cross-cutting the crater wall over a 2-3km thick vertical section, below the basaltic regolite.

1. Introduction

Fifty three igneous float rocks were identified along the Curiosity's traverse at Gale crater between sol 13 and 550 [1-3]. Textural and compositional analyses using MastCam, ChemCam Remote Micro Imager (RMI) and Laser Induced Breakdown Spectroscopy (LIBS) allow recognition of 29 mafic and 24 felsic igneous targets (over 95 locations totaling 2850 laser shots). At Bradbury rise (sol 13 to 45), located at a distal portion of the alluvial fan derived from Peace Vallis, a fluvial channel cutting through the northern rim of Gale crater, 3 light-toned rocks were initially observed (Blanchet, Stark and Thor Lake) [1]. Since the rover left the fluvio lacustrine deposit of Yellow Knife Bay on sol 326, 21 additional feldspar-rich rocks were recognized within Hummocky plains and Rugged Units on our way to Aeolis Mons up to sol 550.

2. Methodology

Grain size, shape and distribution were first assessed using MastCam (450 and 150 μm /pixel) and RMI cameras (14 μm /pixel). The smallest visible grain with RMI is 95 μm at 2.4m, and 140 μm at 3.6m.

Moreover, ChemCam LIBS offers the first opportunity to assess mineralogical diversity at grain-scales with its $\sim 300\text{-}500\mu\text{m}$ laser spot and, from this, lithological diversity. Key element ratios (Al/Si, (Fe+Mg)/Si) and oxide concentrations are derived from the spectra using univariate analysis [4], a method that quantifies the peak areas of well-chosen LIBS lines that are related to concentration thanks to calibration curves using on-board calibration targets (CCCTs: 3 basaltic glasses 1 felsic macusanite glass and 4 ceramics). Whole rock estimates are obtained by averaging large rasters (> 9 points) on fine-grained homogenous targets. For heterogeneous targets such as phenocrysts in fine-grained mesostasis, whole rock compositions are calculated using modal proportions of felsic and mafic phases and their respective molecular compositions.

3. Rock morphology and texture

Felsic rock are mainly float faceted by wind erosion (Fig.1). Some targets form 8-10 cm clasts in polymict conglomerates (Fig.1D) associated with the Peace Vallis alluvial fan system. From morphology, color, grain size, and patina, 3 different classes of rocks have been identified: (1) Class 1 (9 targets) are light-toned coarse granular rocks dominated by leucocratic minerals ($\approx 80\%$ of the rock volume). Pearly coarse crystals ($>5\text{mm}$) are locally intergrown with finer (1mm) rectangular translucent gray grains in a graphic texture (Fig. 1A, C). Some of these targets are chunky when weathered (Fig.1B); (2) Class 2 (6 targets) are aphyric leucocratic rocks with no visible grains (less than 100 μm at 2.5 meters, Fig.1F). They sometimes have shiny scoriaceous surfaces; (3) Class 3 (11 targets) are porphyritic with light-toned, euhedral white crystals 1-20 mm in length (48 to 65% of the rock volume) set in a dark gray

mesostasis (Fig. 1D,E). Porphyritic targets of class 3 and aphanitic to glassy rocks of class 2 are effusive whilst class 1 has granoblastic textures corresponding to intrusive rocks.

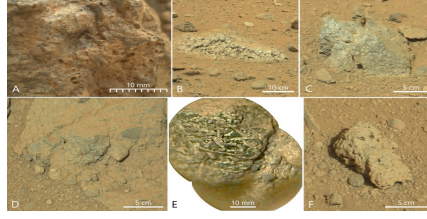


Figure 1: Rock texture from MastCam, MAHLI and RMI: A) coarse intrusive: Clinton (MAHLI); B) chunky weathered Little Wind River (MAHLI); C) coarse intrusive Sparkle; D) porphyritic clast Harrison of porphyritic class in a polythic conglomerate (MastCam); E) Harrison; F) vesiculated: Becraft (RMI).

4. Chemical composition and mineral inference

The 24 anhydrous targets have been plotted in Al/Si vs. (Fe+Mg)/Si (mole %) diagrams (Fig. 2). For the light-toned rocks such as Clinton (Class 1: red symbols), 80% of the points plot on a mixing line between oligoclase-albite (Al/Si: 0.48-0.30; An30-0) and a silica-rich component and less than 20% correspond to mafic composition. Vesiculated light-toned rocks such as Becraft (Class 2: brown symbols) have compositions close to the macusanite CCCT, a rhyolitic glass (Al/Si < 0.33), indicative of silica saturated rocks mixed with alkali-feldspar needle including more than 1500ppm Ba. Porphyritic class such as Harrison (Class 3: green symbols) plot on a basaltic mixing line between oligoclase (Al/Si 0.38-0.44; An 10-28) and augitic composition [2].

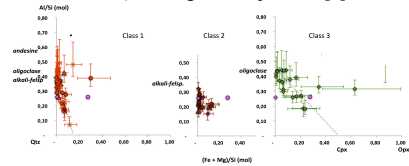
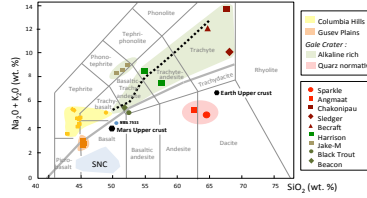


Figure 2: Al/Si vs. (Fe+Mg)/Si Purple symbols are the CCCTs

Whole rock estimations distinguish quartz-normative intrusive rocks of class1 (red symbols, Fig.3) with

dioritic to granodioritic composition, from effusive rocks (class 2- 3) that plot in the alkali domain. Porphyritic effusive (class 3) rocks plot in the trachyandesitic field (Fig. 3) whilst felsic targets of class 2 with $\text{SiO}_2 > 64\%$ and $\text{Na}_2\text{O} + \text{K}_2\text{O} > 10\%$ are consistent with trachytic composition. These liquids could be related to basanites [2] and trachyandesites of class 3 along liquid line of descent from 1-bar primary basalt produced by 6% melting of the mantle at 1GPa



5. Summary and Conclusions

This work provides the first in situ detection of low density leucocratic igneous rocks on Mars. They comprise two distinct geochemical series: (i) alkali-K-feldspar bearing effusive suite including porphyritic and aphyric members; (ii) quartz-normative intrusives close to granodioritic composition. The former looks like felsic clasts recently described in two SNC meteorites (NWA 7034/7533 [5-6] the first Noachian breccia sampling the martian regolite. The latter rock-type is unlike anything proposed in the literature for Mars but resembles Archean TTG's encountered on Earth related to the building of continental crust. Our finding would be consistent with quartz-feldspathic material detected locally from orbit in the southern thus felsic material should be widespread in Early Noachian terrains

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Compositions of sedimentary strata, nodular features and veins at the base of Mount Sharp, Gale crater, Mars: an APXS perspective

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Abstract

Since the MSL Curiosity rover arrived at the lower most slopes of Mount Sharp, the APXS instrument has encountered four distinct bedrock compositions, two of which have not previously been encountered on the mission, indicating different source regions and/or post-depositional alteration/diagenetic histories. Raised, resistant nodular features are interpreted as diagenetic and exhibit elevated, and positively correlated Mg, S and Ni. Late vein networks and associated resistant fins reveal a complex texture and chemistry, recording multiple fluid flow events.

1. Introduction

The MSL Curiosity rover has arrived at the base of Mount Sharp after driving ~9 km since landing within Gale crater in August 2012. Curiosity's APXS instrument has acquired 138 analyses en route to Mount Sharp, recording a diversity of rock chemistries, facilitating the development of an APXS compositional classification scheme [1] [2].

Since arriving at the base of Mount Sharp, the rover has completed a detailed investigation of the Pahrump Hills stratigraphic section. This work describes the results from 26 distinct APXS targets in this section, as well as several target locations examined along the traverse route since commencing the ascent of Mount Sharp. The compositions determined by APXS are compared to targets encountered along the transit route and are placed in a regional context within Gale Crater. Compositional variations within the Pahrump section are highlighted. Specifically, differences in chemistry between raised, resistant features and the surrounding bedrock, and what this reveals about the diagenetic history of these rocks are explored. The extensive vein network encountered at Garden City is also examined in detail.

2. Pahrump Hills to Kanosh

The strata at Pahrump Hills is light-toned and appears softer than many previously encountered units, which retain craters more effectively. The rocks comprise interbedded recessive and resistant, fine to medium grained sedimentary strata that can be laminated or more massive, and which can exhibit cross stratification. Brushing has revealed interesting textures on many of the bedrock surfaces; from light-toned, lozenge shape crystals to more irregular shaped, light- and dark-toned inclusions.

The uppermost section is characterized by more resistant, massive, sandstone (Whale Rock). Distinctive features of the Pahrump rocks are raised, resistant, irregularly shaped nodular concretions. They can be isolated or form part of a more extensive cluster [3].

Bedrock encountered since driving away from Pahrump is similar to the uppermost recessive units at Pahrump. However, the boulder Kanosh is interpreted to represent a fragment of a more resistant, crater-retaining cap rock unit exposed in the Salsberry Peak area. Vein networks and associated resistant "fins" at Garden City reveal complex textures of light- and dark-toned materials that cross-cut the bedrock.

3. APXS Results

Pahrump Bedrock: APXS analyses of the various Pahrump bedrock targets reveal three different compositions: 1) The majority define a new and distinct compositional class at Gale crater (Fig. 1), characterized by relatively high Si, Ni and Zn, and low Mg, Ca and Cl, as well as a relatively high CIA index (i.e., high $Al/(Al+Ca+Na+K)$).

2) The recessive bedrock encountered at the top of the Pahrump section, and since leaving Pahrump (Santa Ana and Telegraph Peak), is characterized by elevated Na, Si, Fe and K, and lower Mg, Al, S, Ca, Mn, Ni, Zn and Se compared to the majority of Pahrump bedrock (Fig. 1). 3) In contrast, the resistant, cross laminated sandstone ledge exposed at Whale

Rock is characterized by low Ni, Zn, Si, Al, Cr, K, P and Ti, and high Mn, Fe, S, Br, Mg, Ca and Cl compared to the majority of Pahrump bedrock (Fig. 1).

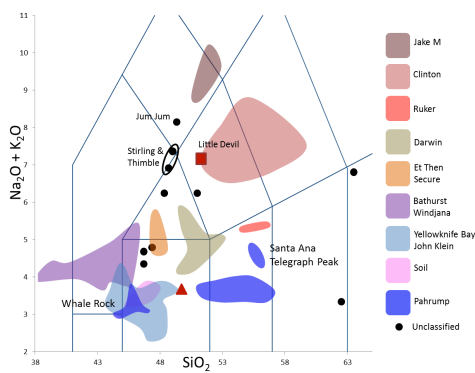


Fig. 1: Total alkalis versus SiO_2 for all rocks and soils analyzed by APXS at Gale. Pahrump rocks are royal blue.

Pahrump Raised, Nodular Features: The isolated, raised, resistant nodular concretions ubiquitous throughout the basal Pahrump section [3], are compositionally distinct from the bedrock. They exhibit characteristically high Mg, S and Ni contents, as well as elevated Cl and Br relative to nearby bedrock. The Ni contents are the highest so far recorded on Mars, with the exception of meteorite samples. The Zn contents are higher than for most rocks at Gale, but similar to the bedrock. The strong positive correlations of Mg, S, Ni and Cl from bedrock to raised feature are consistent with an increase of up to 12 wt% MgSO_4 (Fig. 2).

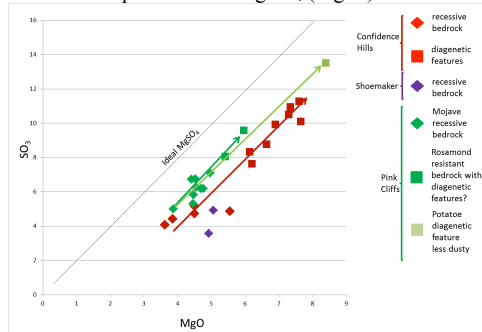


Fig. 2: SO_3 versus MgO of raised, nodular concretions (squares) and associated bedrock (diamonds).

Garden City Veins: At least four distinct compositional phases are identified associated with

the vein system at Garden City: 1) white, CaSO_4 -bearing veins, 2) dark, Ca-enriched (little to no associated S) material (high Mn, Zn and Ni), which is intimately associated with the white vein material, 3) dark, Mg-rich material (high Ge), also associated with the white veins, and 4) resistant dark “fins”/plates with characteristically high Na, K, Fe and P, as well as elevated Ga, Sr, Ge and Pb.

Kanosh – Little Devil Cap Rock: APXS analysis reveals a similar composition to other targets thought to represent cap rock (Stirling and Thimble) (Fig. 1). These rocks are characterized by relatively high Na, and K, and moderate Si and Fe.

4. Discussion

The APXS instrument has encountered four distinct bedrock compositions at the base of Mount Sharp, two of which have not previously been encountered on the mission, indicating different source regions and/or post-depositional alteration/diagenetic histories.

Raised, resistant nodular features within the Pahrump section are interpreted as diagenetic and exhibit elevated, and positively correlated Mg, S and Ni consistent with ~12% of a MgSO_4 phase.

Late vein networks and associated resistant “fins” reveal a complex texture and chemistry, apparently recording multiple fluid flow events.

The cap rock exposed in the area has a similar composition to other cap rock targets previously analyzed by APXS along the route to Mount Sharp, possibly indicating the presence of a once continuous layer of cap rock.

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Spectral Evidence for Hydrated Salts in Seasonal Brine Flows on Mars

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Abstract

Recurring Slope Lineae (RSL) are seasonal flows on warm Martian slopes initially proposed, but not confirmed, to be caused by briny water seeps. Here we report spectral evidence for hydrated salts on RSL slopes from four different RSL locations from the Compact Reconnaissance Imaging Spectrometer for Mars on board Mars Reconnaissance Orbiter. These results confirm the hypothesis that RSL are due to present-day activity of briny water.

1. Introduction

Pure water would rapidly evaporate and/or freeze on the present-day surface of Mars at most times and places; however brines are far less volatile compared to pure water due to their lower freezing points and evaporation rates [1-2]. Various salts (e.g. sulfates, chlorides and perchlorates) have been detected on the surface of Mars from remote and in situ investigations [e.g. 3-5]. These salts can lower the freezing point of water by up to 80 K, lower the evaporation rate of water by an order of magnitude, and can be hygroscopic (i.e. able to easily absorb atmospheric moisture) [e.g. 6-8], thus increasing the possibility of forming and stabilizing liquid water on the surface of present day Mars [e.g. 9].

Recurring Slope Lineae (RSL) are narrow, low-reflectance features forming on present-day Mars that have been hypothesized to be due to the transient flow of liquid water. RSL extend incrementally downslope on steep, warm slopes, fade when inactive, and reappear annually over multiple Mars years as monitored by the HiRISE camera on board the Mars Reconnaissance Orbiter (MRO) [e.g. 10-12]. In the southern mid-latitudes of Mars, RSL are observed to form most commonly on equator facing slopes, but in equatorial regions RSL often “follow the sun”,

forming and growing on slopes that receive the greatest insolation during a particular season [10]. The temperature on slopes where RSL are active typically exceeds 250 K and often but not always exceeds 273 K, although sub-surface temperatures would be colder. These characteristics suggest a possible role of salts in lowering the freezing point of water, allowing briny solutions to flow [10-12]. Confirmation of this wet origin hypothesis for RSL would require either (i) detection of liquid water absorptions on the surface, or (ii) detection of hydrated salts precipitated from that water. The mineralogical composition of RSL and their surroundings can be investigated using orbital data acquired by the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) also on board MRO, which acquires spectral cubes with 544 spectral channels in the visible to near-infrared range of $\sim 0.36 \mu\text{m}$ to $3.92 \mu\text{m}$ [13], within which both liquid water and hydrated salts have diagnostic absorption bands at $\sim 1.4 \mu\text{m}$, $\sim 1.9 \mu\text{m}$, $\sim 3.0 \mu\text{m}$. Additionally, hydrated salts may have combination of overtones at other wavelengths from $1.7 \mu\text{m}$ to $2.4 \mu\text{m}$. We present results from examination of individual pixels containing RSL at four different sites.

2. Results

We found hydration absorption bands at four different RSL locations (Table 1). All the HiRISE/CRISM observations reported here of the southern mid-latitude RSL sites were acquired during the late southern-summer ($340^\circ < L_s < 360^\circ$, where L_s is the areocentric longitude of the Sun), when the RSL had reached their maximum extent for the year and were fading.

Palikir crater: The CRISM pixels closest to wide RSL in Palikir exhibited absorption features at wavelengths near $1.48 \mu\text{m}$, $1.91 \mu\text{m}$, $2.15 \mu\text{m}$ and $3.0 \mu\text{m}$. Although liquid water has absorptions at most of

these wavelengths, the absorptions observed in CRISM images are too narrow to be explained by liquid water. Alternatively, they are consistent with hydrated salts; a linear spectral mixture of Martian soil, Mg-perchlorate and Mg-chlorate provided the closest match to the observed spectrum from Palikir. The observed hydration bands were also transient: present in images that had extensive RSL in late summer and absent in those that had short/narrow RSL. This confirmed that hydration features observed at Palikir were due to areally extensive presence of RSL, and perhaps due to greater stability of hydrated salts in late summer when temperatures drop.

Table 1: List of locations inspected and summary of hydration bands observed.

Site	Geological Setting	Hydration bands (μm)	Metal-OH bands (μm)
Palikir crater (-41.6°N, 202.3°E)	Crater wall	1.4, 1.9, 3.0	2.15
Horowitz crater (-32.0°N, 140.8°E)	Central peak	1.9, 3.0	2.15, 2.42, 2.52
Hale crater (-35.7°N, 323.5°E)	Central peak	1.4, 1.9, 3.0	None
Coprates Chasm (-14.7°N, 304.6°E)	Canyon wall	1.9	None

Horowitz crater: At two of the central peaks in Horowitz, we observe absorptions at 1.9 μm , 2.15 μm and 2.52 μm . A linear spectral mixture of Martian soil and Na-perchlorate provided the best match to the observed spectra. We could not confirm the transient nature of the spectral absorption bands at this site because of lack of repeat CRISM coverage.

Hale crater: Some of the most intense RSL activity in the southern mid-latitudes occurs on the central peak structures of Hale crater. Analysis of the CRISM data shows strong ~1.46 and 1.9 μm absorption features in the location where dense RSL activity is observed in the HiRISE image. A linear spectral mixture of Mg-perchlorate and Martian soil provided the best match to the observed spectra.

Coprates Chasma: In equatorial Coprates, RSL are abundant and in some cases entire fans

associated with RSL are observed to change their reflectance [10]. Spectra of RSL fans in Coprates were analyzed and were found to show transient, and we found multiple places in the CRISM images with 1.9 μm absorptions. Without detection of other absorptions, assignment to a particular salt mineralogy is not possible, but it does suggest precipitation of salts and related wetting and/or modification of grain sizes as a viable mechanism for the change in albedo of the fans, possibly explaining VIS-NIR spectral changes previously reported in RSL fans [14].

3. Discussion

The origin of water forming the RSL is not understood [10-12], given the extreme aridity of Mars' surface environment. Water could form by the surface/sub-surface melting of ice, but the presence of near-surface equatorial ice is highly unlikely. Water could also form via deliquescence by hygroscopic salts, although it is unclear how the Martian atmosphere can sufficiently supply water vapor every year to create RSL [10, 15]. The absence of concentrated deliquescent salts would rule out this hypothesis. Another hypothesis is seasonal discharge of a local aquifer, which concentrates salt deposits as the brine evaporates, but then lineae emulating from the tops of local peaks [10] are difficult to explain. It is conceivable that RSL are forming in different parts of Mars via different formation mechanisms. The new compositional insights reported here from widely separated sites provide essential new clues.

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