

# VNIR spectroscopy of the Atacama salars: An analogue study for Mars evaporate deposits

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## Abstract

A high priority for determining the past habitability of Mars includes identification and characterization of hydrated minerals within ancient Martian aqueous environments. Sulfates, found in a variety of hydrous environments on Earth, can aide our understanding of past Martian environments if their context can be constrained. In the present study, we combine both spaceborne (Landsat, Hyperion) and field (ASDinc FieldSpec) VNIR observations to study the mineralogy of various sulfate-rich salt flats (salar) in the Atacama desert region of Chile as an analogue for Martian evaporites. There is good agreement between remote sensing and field observations on the major classes of minerals present in the salars and their spatial distribution, that are easily identified from VNIR spectroscopic data.

## 1. Introduction

Sulfates, on the surface of Mars, were first detected by the spectral imager OMEGA (on-board the Mars Express Mission) [1, 2]. They are often associated with 100's km wide, thick, sedimentary deposits and sometimes mixed with clays [1-6]. On Earth, sulfates form in a wide range of conditions including: shallow lakes, deep marine basins, periglacial environments, hydrothermal systems, and acidic rainfalls (e.g. [7]). The geological context of Martian sulfates is, however, poorly understood.

We propose to study sulfate-rich deposits in the Chilean Atacama Desert found in a similar context to those found on Mars. The Atacama is a hyper-arid desert spread across the Andes long volcanic ridge. In the Atacama region, meteoric water infiltrates from elevated areas in the Andes Mountains, dissolving salts from volcanic-origin soil and transporting them towards lower areas. In these lower areas, the dissolved salts are concentrated due to evaporation forming shallow lagoons and salt flats

which are filled with mixed clays and sulfates [8]. The geological context and composition of this site, plus its proximity to a volcanic mountain range, make it an ideal Martian analogue site. In addition, this site is well-known to host extremophile microbial life, providing links to astrobiology (ongoing joint study with Leiden University, NL).

## 2. Datasets

High-resolution remote sensing data from hyperspectral (Hyperion) and multispectral (ALI, Landsat) imaging instruments were used to characterize, and map, the mineralogy of the Atacama salars from space. Landsat 8 reflectance data provide a full coverage of the area, whereas Hyperion data are only available at selected locations, including the Cordillera de la Sal (Figure 1). Landsat imagery has previously been demonstrated to be efficient at mapping salar zonation [9] and was, therefore, used to select field sites within a diverse range of terrains.

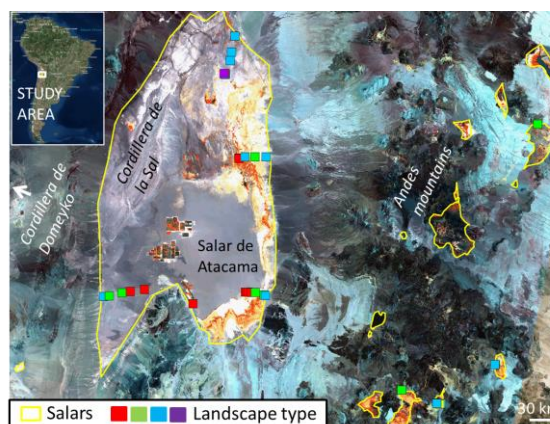


Figure 1: The location of the salars (as mapped from space, yellow outlines) and landscape types (as observed on the field, colored squares) are reported on these Landsat 8 color composites of reflectance bands 7-6-5. Cf. text for more details.

A field campaign was carried out in February 2015. VNIR reflectance values were measured in the field at selected sites (squares on Figure 1), and samples were collected to be further analyzed by Raman spectroscopy and XRD at the VU University Amsterdam. The aim of the field survey was to quantitatively constrain the mineralogy and provide ground-truth to the remote sensing analyses.

### 3. Results

Core (grey tones) and marginal (orange to white) zones within the salars are easily distinguished on the Landsat 8 7-6-5 band color composite (Figure 1). Each colored zone was visited in the field. Outcrops were classified into multiple types based on their morphology. The main categories include (1) sharp, blocky thick halite crust (red squares on Figure 1), (2) smooth, indurated, undulated surface (green squares), (3) muddy surface with polygonal cracks, and a thin salt layer in depressions (blue squares). To the first order these morphologies correlate to mineralogy, according to field spectra. The mineralogic assemblages were dominated by; halite (1), clays (3), or gypsum and other sulfates (2) (Figure 2). More diversity in terms of morphologies and mineralogies is observed locally, and additional categories were made. Ongoing lab analysis should provide more constraints on those additional categories by the conference time.

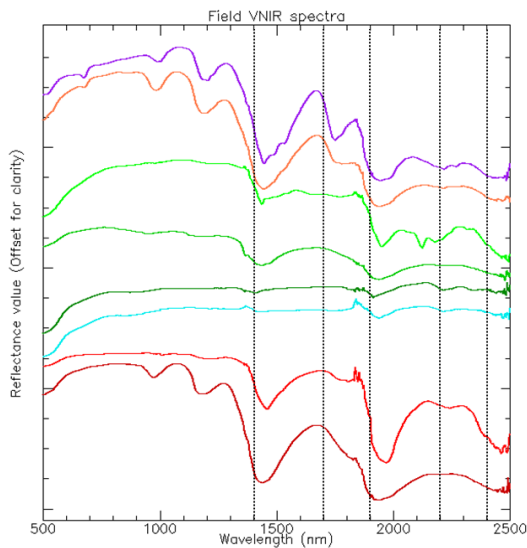


Figure 2: VNIR reflectance spectra of field outcrops at various sites. Colors correspond to the morphologic types mapped on Figure 1.

### 4. Discussion and Further Work

VNIR spectra can easily discriminate between clay-dominated and salt-dominated sediments; as well as different types of salt crusts. Mineral zonation is observed within the salars on a scale of dozen of meters, and appears to be a function of the distance to the (ground)water sources. An example is given in the Salar de Atacama, where clays and gypsum are observed in the salar margins, whereas halite dominates the mineralogy of the rocks at its center, further away from the discharge zone. Distinct mineral assemblages appear to be present in the various salars. The relationship with the bedrock composition and geographic location is being investigated. Space and field VNIR spectra will be compared to Raman and XRD analyses of collected field samples. This step will allow us to discuss the benefits and limitations of VNIR spectroscopy when applied to evaporites deposits on both Earth and Mars.

### Acknowledgements

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## Oxidation (or not) of Hot Rocks in a Laboratory Vacuum

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### Abstract

To assess the effects of high temperature on ultraviolet through infrared reflectance spectra, we heat-treated olivines and pyroxenes in mid to high vacuum using temperatures analogous to Mercury surface conditions. Samples darkened and changed absorption band properties with increasing temperature. Some samples returned to pre-heated reflectance values when cooled back to standard temperatures. Others, when heated beyond 500-525 K developed darkening that remained after cooling. Whether this darkening is the result of oxidation, surface flaw annealing, or some other process is still under investigation.

### 1. Introduction

Reflectance properties of silicate minerals change with temperature and pressure as predicted by theory [1] and experiments [2,3]. Positions and intensities of crystal field bands in the visible region are affected, and reflectance spectra show changes in band shape resulting from thermal population of vibrational levels within crystal field states [1,2]. These effects have been demonstrated for near-Earth objects [3, 4], and may be most pronounced at the hottest surface temperatures of the inner solar system planets. In addition to band shifts and shape changes, increased temperature generally results in broadening and/or shallowing of the 1  $\mu\text{m}$  Fe absorption band in olivines and pyroxenes (Figure 1). The change of reflectance with temperature is referred to as a thermospectrum [5].

The day-side surface of Mercury can achieve temperatures as high as 700K. Rocks and regolith are exposed at these temperatures in vacuum, so creating a proper analog environment in the laboratory requires a high vacuum as well as high temperature. The Applied Physics Laboratory Optical Lab chamber can achieve vacuums as high as  $10^{-9}$  torr at cryogenic to room temperatures, and  $10^{-6}$  to  $10^{-7}$  torr at temperatures up to 650-675K. For this project, we heated olivines and pyroxenes to a range of temperatures up to >600K; “permanent” darkening

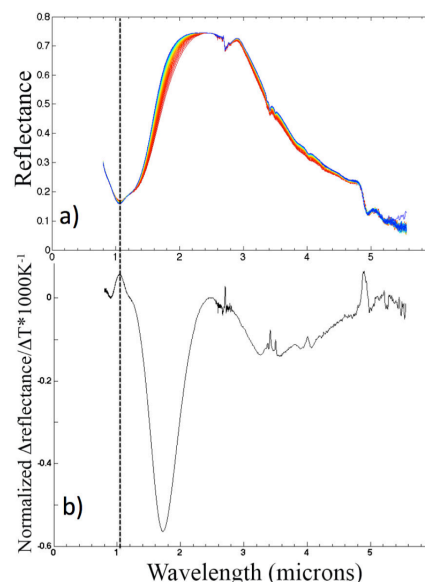


Figure 1: a) Temperature series of Globe Olivine reflectance spectra heated from 333K (blue) to 550K (red). b) Derived thermospectrum.

appeared that did not disappear upon cooling, similar to results of other TEM [6] and spectral studies [7, 8].

### 2. Assessing Causes of Darkening

Permanent darkening of samples may have several causes, including breakdown into other phases, annealing of crystalline flaws, destruction of color centers [9], and oxidation. The latter possibility would inhibit the ability of laboratory analog observations to properly address the properties of materials in the vacuum of space and was further investigated.

Mössbauer analyses of heated and unheated olivine and pyroxene samples from our experiments were undertaken to determine if the darkening could be due to oxidation, even at a vacuum  $\sim 10^{-7}$  torr. Figure 2 shows an example of San Carlos olivine before and

after heating to 630K and 647K. In both cases, the sample underwent permanent darkening, and in both cases an  $\text{Fe}^{3+}$  component (2 and 3% of Fe in the sample, respectively) was present only post-heating. This demonstrates slight but conspicuous oxidation in the sample. The Mössbauer parameters of the newly-formed doublet in the heat-treated olivine are characteristic of 4-coordinated  $\text{Fe}^{3+}$ . Because olivine contains only 6-fold sites, this suggests that olivine is breaking down to another phase as seen in [6]. In contrast, a second olivine sample from Globe AZ heated to similar temperatures under the same vacuum conditions yielded no oxidation product. The two olivines have the same composition ( $\text{Fo}_{91}$ ) so the difference in oxidation may result from varying H contents [10] or different defect populations relating to eruptive history. Finally, heating also induced oxidation in a diopside sample similarly heated (from 18 to 20%  $\text{Fe}^{3+}$ ). Because the unannealed diopside already contained  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  oxidation likely occurred *in situ* within the pyroxene structure and would not require formation of a second phase as was the case for olivine. These results show that the reaction of mineral structures to high temperatures is difficult to generalize given the diversity of possible causes.

### 3. Conclusions and Next Steps

Our results suggest that laboratory conditions, even with high vacuum, cannot prevent oxidation of samples, either from monolayers of oxygen in the system, or possibly from breakdown of samples themselves due to heating. We can at present neither confirm nor rule out non-oxidation causes for permanent sample darkening at high temperatures.

We are currently conducting a systematic set of experiments heating samples incrementally, at three vacuum levels, and obtaining Mossbauer spectra for each stage and will present the results.

### Acknowledgements

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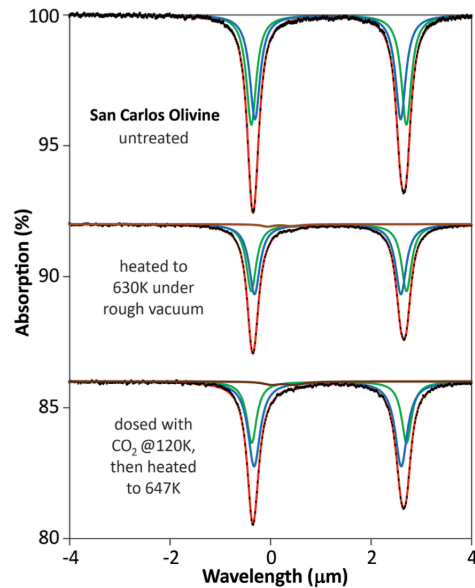


Figure 2: Mössbauer spectra of unheated and heated San Carlos olivine.

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## VNIR spectral analyses of powdered mixtures with ExoMars-Ma\_Miss instrument

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### Introduction

Ma\_Miss (Mars Multispectral Imager for Subsurface Studies) experiment onboard of ExoMars 2018 mission to Mars will study the Martian subsurface down to a depth of 2 meters [1]. Ma\_Miss is a miniaturized spectrometer, integrated within the drilling system of the ExoMars rover; it will perform visible and near infrared spectroscopy in the 0.4 – 2.2  $\mu\text{m}$  range, acquiring signal from the excavated borehole wall. The spectroscopic characterization of the subsurface rocks will give us important information about mineralogy, petrology and geological processes; moreover it will give insights about materials that have not been altered by surface processes such as erosion, weathering or oxidation. Spectroscopic measurements have been performed on different types of rock/mineral mixtures with the Ma\_Miss laboratory model (*breadboard*).

### 1. The Ma\_Miss instrument

The miniaturized spectrometer will be integrated within the rover drill [2]. A 5W lamp and an optical fiber bundle provide the illumination of the target; the Optical Head focuses the light on the target (1 mm spot) and collects the scattered light from the target (about 100  $\mu\text{m}$  spot, spatial resolution). An optical fiber carries the light to the spectrometer. The optical fibers system is hosted within the driller; a depth of 2 meters can be reached using four 50-cm extension rods. A sapphire window is the interface between the Optical Head and the target. This window is characterized by a high transparency and hardness. The focal distance, between the window and the subsurface wall, is less than 1 mm. The breadboard (BB) consists of the optical main subsystems (Optical Head, Sapphire Window) and the illumination system (illumination bundle and signal fiber). In the laboratory it must be coupled with another spectrometer: here we used the FieldSpec Pro spectrophotometer [3]. Details on the instrument and on the laboratory BB setup are in [4].

### 2. Spectral measurements of rock mixtures

A set of powdered rock/mineral mixtures have been analyzed with the Ma\_Miss breadboard instrument. Here we report about the results obtained on two different powder samples: (i) granite, and (ii) a mixture composed of alunite and a basaltic rock. The first mixture was produced starting from a granite piece: granite was composed by millimeter-sized crystals. The second mixture was produced starting from alunite crystals on a rock. Both powders have been grinded and sieved in four different grain sizes:  $d < 100 \mu\text{m}$ , 100-200, 200-500 and 500-800  $\mu\text{m}$ . Spectra have been acquired in several positions on each of the different samples. The high Ma\_Miss spatial resolution (100  $\mu\text{m}$  spot) will allow to obtaining spectra from different minerals, when measuring coarser grains: thus it allows to investigating in detail mineral mixtures with grain size exceeding about 100  $\mu\text{m}$ .

#### *Granite.*

The spectra relative to the smallest grain size ( $d < 100 \mu\text{m}$ , fig.1A) have been acquired on four different positions. They are very similar: the spectral shape is characterized by a red slope, typical of fine powder, and lacks remarkable absorptions except the one of  $\text{H}_2\text{O}$  at 1.9  $\mu\text{m}$ . The spectral behavior is dominated by quartz. Increasing the grain size of the powder with respect to the instrument spot, the spectral (and mineralogical) diversity becomes more evident (fig.1, panel B to D); the spectral slope also begins to vary among redder and bluer values, as the particle size increases. In fig.1 panel C, the spectrum of biotite appears (blue curve). In panel D the spectrum of feldspar (microcline) appears, characterized by blue slope (cyan curve). Other spectra are indicative of quartz; spectra blue and red in fig.1D could be attributed to biotite.



### Alunite – rock mixture.

In the case of the mixture alunite/basaltic rock, the effects of spectral and mineralogical diversification become more evident as the grain size increases (fig.2). While spectra in fig.2A are very similar and with little shift in reflectance, spectra in fig.2D are characterized by different spectral shapes and reflectance values. Black, green and yellow curves (panel D) are indicative of the basaltic rock. Blue spectrum is characterized by Al-OH absorptions near 1.75-1.8, 2.2  $\mu\text{m}$ , OH features near 1.3-1.5  $\mu\text{m}$  and H<sub>2</sub>O near 1.9  $\mu\text{m}$ .

In this case the effect of the presence of dark volcanic rock is to lower the overall reflectance, and to smooth the spectral features due to alunite. In some spots, only alunite grains can be present (fig.2D, blue spectrum), while in other spots a mixture of mineral and basalt can be observed: in this case there are no additional spectral features, but only a flattening of the spectrum.

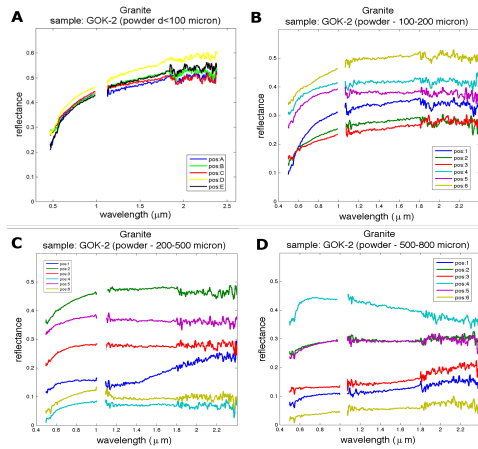


Figure 1: spectra of powdered granite, at four different grain sizes. Spectra in panels B,C,D are shifted in reflectance for clarity.

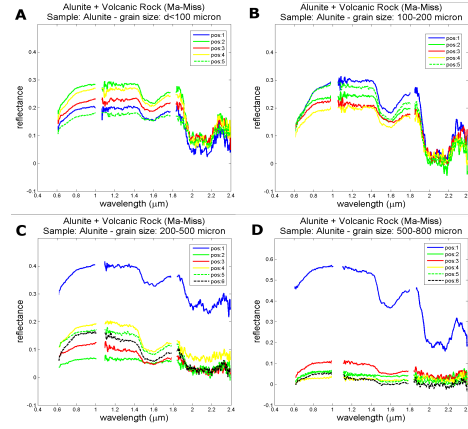


Figure 2: spectra of a powder mixture of alunite and basaltic rock, obtained at four different grain sizes.

### 3. Summary and Conclusions

The ExoMars/Ma\_Miss miniaturized spectrometer will be integrated within the Rover Drill, and will perform VNIR spectroscopy of the subsurface rocks. Two different types of mineral/rock mixtures have been analyzed with the breadboard at INAF-IAPS laboratory. In both analyzed mixtures the spectral diversity gradually increases as the grain size exceeds the instrument spot of 100  $\mu\text{m}$  (spatial resolution). The overall spectral slope also starts to become bluer as the dimension of grains increases. Thus it will be possible to investigate in detail mineral/rock mixtures with grain size (or texture) exceeding 100  $\mu\text{m}$ .

### Acknowledgements

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# Investigation of the solar influence on clean and dusty CO<sub>2</sub>-ice under Martian conditions

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## Abstract

CO<sub>2</sub> is the main component of the Martian atmosphere. Therefore the polar caps are – depending on hemisphere and season - partially or totally covered with CO<sub>2</sub>-ice. In contrast to rock and soil surface layers, which absorb and reflect incoming solar radiation immediately at the surface, ices are partially transparent in the visible spectral range, while they are opaque in the infrared. These properties are responsible for the so-called “Solid-State Greenhouse Effect” (SSGE). The SSGE may have a major influence on the sublimation and re-condensation of CO<sub>2</sub> and its circulation in the Martian atmosphere. Our work will concentrate on the influence of the SSGE on CO<sub>2</sub>-ice under Martian like conditions.

## 1. Introduction

The planetary atmospheric greenhouse effect and the temperature increase connected to it is a well-known phenomenon. Less known is that a similar effect takes place in solid translucent objects like ice. The solid-state greenhouse effect can lead to an increase in subsurface temperatures because low-albedo particles embedded in the ice absorb energy across the entire solar spectrum and radiate in the infrared. The SSGE has implications for many planetary processes. For example, a subsurface temperature increase is a possible scenario for the formation of the so-called Martian spiders [1]. One hypothesis regarding the formation of these spiders is that they form through the channelling of CO<sub>2</sub> gas sublimed from beneath the transparent seasonal ice [2]. The subsurface temperature evolution leading to the temperature maximum below the surface as described above is not limited to CO<sub>2</sub>; over different spatial scales, it can be observed in all transparent or translucent ices and may result in cavities being filled with liquid or gas.

Our experiments at The Open University’s Planetary Ices Laboratory focus on the SSGE in CO<sub>2</sub> ice where we are building on past experiments performed at the Space Research Institute in Graz with the main focus on layered samples with a covering coat consisting of pure H<sub>2</sub>O-ice (see [3]). The first results of measurements in CO<sub>2</sub>-ice will be shown and possible implications for the understanding of various phenomena observed in the Mars polar areas will be discussed.

## 2. Laboratory experiments

The experiments were conducted in an environmental chamber that can be evacuated to a pressure of  $<10^{-5}$  mbar and cooled down to 80 K. Radiation intensities corresponding to solar distances from 1 to 2 AU can be achieved with a solar-simulator. Our experiments have included measurements of the temperature profile in CO<sub>2</sub> snow, in transparent CO<sub>2</sub> ice and in transparent CO<sub>2</sub> ice with a layer of JSC MARS-1A dust.



Figure 1: Laboratory set-up: Solar simulator (left), vacuum chamber (right), LN<sub>2</sub> dewar (front).

### 3. First results

The series of test was started with several runs using CO<sub>2</sub> snow as sample material. During each test the temperature profile inside the block was measured with PT100 sensors while the sample was irradiated with artificial solar light with a power of about 650 Wm<sup>-2</sup> at a pressure of 5.7 mbar ± 0.25 mbar. The measured temperature profile of the snow samples, as shown in Figure 2, showed no clear sign of an internal temperature maximum – a result that was not unexpected since snow has a very high albedo and only a small part of the irradiation is absorbed by the sample. Furthermore, one has to bear in mind that there is a volume loss during the irradiation phase and therefore not all sensors show the temperature inside the sample for the entire duration of the test.

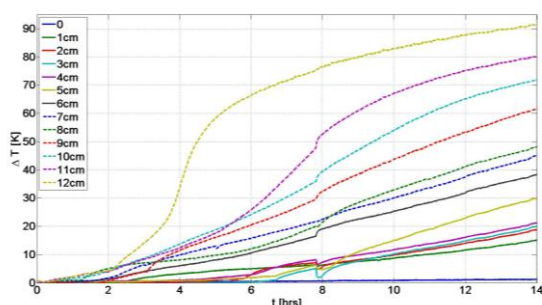


Figure 2: Temperature profile of a CO<sub>2</sub> snow sample at Martian pressure irradiated with 650 Wm<sup>-2</sup>.

First tests with blocks of clear CO<sub>2</sub>-ice show - in some cases - higher temperatures deeper inside the block than closer to the surface. Moreover, first tests with a block of CO<sub>2</sub>-ice that included a dust layer were carried out. We found that temperature increases inside the sample were linked to the ambient pressure.

### 4. Summary

We could not find any experimental evidence for the relevance of the SSGE in pure CO<sub>2</sub> snow/ice. However, our experiments show an influence on the temperature profile if the ice includes a dust layer. In order to obtain reproducible results, further tests with an improved set-up are required.

### Acknowledgements

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## Seismometer Signature of Dust Devils : Implication for InSight

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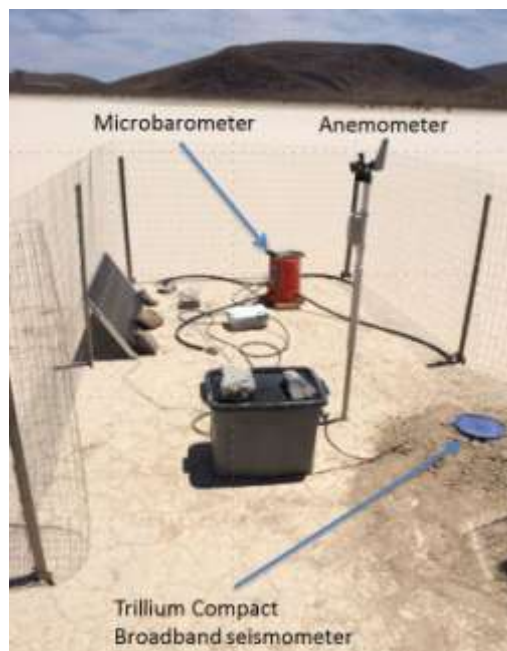
### Abstract

As well as Marsquakes, the sensitive InSight SEIS instrument will detect ground deformations caused by atmospheric effects. In order to validate the models used to validate the models used to study the environment impact on a seismometer deployed on the field, a station with a configuration similar to the one deployed on Mars has been set-up at a playa near the Goldstone DSN station. Among the most locally-intense of these are dust devils, which act as a negative load on the surface. We have identified the tilt of the ground caused by dust devils in field measurements with a seismometer on a with the vortex encounters documented by an array of pressure loggers. One devil had a signature consistent with a simple point-load model, but the signature of a larger vortex had a more complicated structure requiring wind effects to be considered. There is evidence that dust devils may be detectable at longer ranges by seismic means than by in-situ meteorological measurements.

### 1. Introduction

Seismic stations for geological studies are typically installed in concrete vaults, ideally deep underground. While burial suppresses direct wind effects (a noted problem on the Viking seismometer) and reduces temperature fluctuations, shallow installations are somewhat susceptible to tilts caused by the elastic response of the ground to the atmospheric pressure and wind fields. While InSight's SEIS instrument has a wind and thermal shield (WTS) to improve its noise performance considerably over Viking, it is expected to measure atmospheric effects, which can be partly decorrelated from the signal by meteorology measurements.

In order to gain an understanding of seismometer response to field conditions and to explore atmospherically-excited seismic noise, a field experiment [1] was conducted in summer 2014 in Goldstone. This experiment (figure 1) featured a seismometer buried at very shallow depth in the soft playa sediment, together with meteorological instrumentation which included an array of pressure loggers (used previously in dust devil surveys [2]) dispersed around the seismic station. This configuration allowed to identify when atmospheric event. Dust devils encounters were therefore recorded, and the vortex size and trajectory could be derived from the measurement setup. In typical summer conditions, a few encounters a day may be seen.



## 2. Event

A pair of dust devils was identified, about 10 minutes apart (a typical interval, likely related to be advection of the planetary boundary layer convection pattern) which made it easy to recognize the event in all datasets (not all were recorded on the same time reference). A first vortex had an irregular maximum pressure drop of  $\sim 1$  mbar and a duration of about 1 minute, and appeared similar in all loggers (spanning a distance of  $\sim 120$  m, indicating a vortex at least this large). The second had a pressure dip of  $\sim 0.6$  mbar and was somewhat shorter in duration: the pressure loggers suggest it moved in a ENE direction, passing about 45 m to the south. Seismic signals are clearly seen (figure 2) for both events.

## Conclusions

We have searched for and found a seismic signature of dust devils, and find the characteristics can be effectively modeled, in some cases by a simple point load on an elastic half-space, but in some cases demanding a more sophisticated approach. The

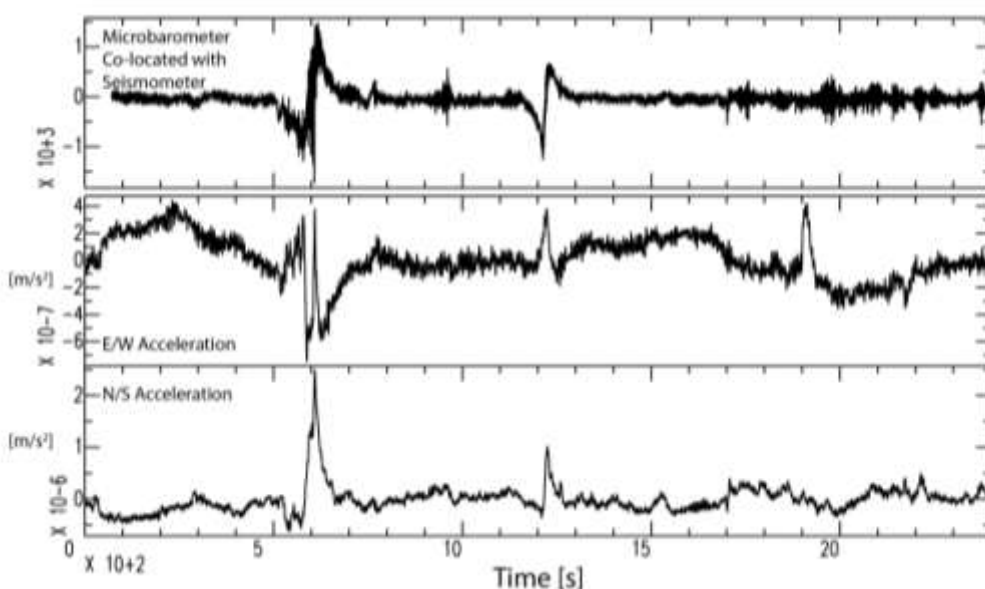
migration of devils can in fact be tracked, the tilt azimuth indicating the direction to the dust devil, and it may be that dust devils can be detected better with seismic data than in-situ meteorological measurements. By acquiring both types of data, InSight should prove interesting for boundary layer convection studies. Dust devils may also serve as useful 'calibration' loads to assess the regolith elastic properties.

## Acknowledgements

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*Figure 3. Record of the seismometer output showing tilts of tens to hundreds of nanoradians, coincident with pressure excursions (the microbarometer is co-located with the seismometer, but differentiates the pressure time series). Three events are seen – the first, largest has a somewhat complex structure (which can be largely reproduced using the theory of Sorrells [2]). The second event is smaller and simpler, and can be essentially reproduced with a point-load model, with the vortex moving eastwards to the south of the station. A third event, equispaced from the first two, is seen in the E/W data alone, suggesting an additional encounter that was not detectable in the pressure signal.*

## Electron irradiation and thermal driven chemistry on $\text{H}_2\text{S}-\text{CH}_3\text{OH}-\text{NH}_3-\text{H}_2\text{O}$ and

### $\text{CH}_3\text{OH}-\text{NH}_3-\text{H}_2\text{O}$ ices: application to Jupiter Trojans

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#### Abstract

In this work we investigate chemical reactions driven by irradiation and thermal processing of outer solar system simulants and the resultant products. The main goal of this laboratory simulation work is testing migration hypotheses predicted by solar system formation models [1]. The ice samples are chosen to simulate the differences between chemistry in objects initially located inside and outside the stability line of  $\text{H}_2\text{S}$ .  $\text{CH}_3\text{OH}-\text{NH}_3-\text{H}_2\text{O}$  (3-ice) and  $\text{H}_2\text{S}-\text{CH}_3\text{OH}-\text{NH}_3-\text{H}_2\text{O}$  (4-ice) ice films was irradiated under ultrahigh vacuum conditions. Mid-IR analysis of the ice composition and mass spectrometry monitoring of the released volatiles during the heating of the irradiated mixtures show a rich chemistry for both mixtures. Our experimental work suggests that S-bearing molecules like OCS and  $\text{SO}_2$  could be formed under conditions expected for objects that initially contained near-surface frozen  $\text{H}_2\text{S}$  and were then exposed to space weathering, particularly heating and irradiation while migrating to a position close to Jupiter's orbit.

#### 1. Introduction

Jupiter Trojan asteroids are a population of small bodies captured around the L4 and L5 Lagrangian points of the Sun-Jupiter system. This family of asteroids can be categorized into two classes according to their Visible and Near-IR spectra: red Trojans and less red Trojans. The issue of how objects belonging to the same dynamical group have such diversity in their Vis-NIR spectra is tentatively linked to the origin and evolution of the Trojans asteroids. One hypothesis postulates that these objects were formed in the Kuiper Belt region and then migrated to their present position [1,2]. Space weathering factors, such as energetic particles and photon irradiation, are believed to be responsible for the growth of an organic refractory mantle covering the surfaces of these icy, airless objects. Energy

released by irradiation of the organic ices drives a complex chemistry leading to the production of red crust. The surface chemical composition of icy bodies between 5 and 20 A.U. is expected to be dependent on their orbital distance as well as their size. A strong gradient in starting surface composition, followed by UV and particle irradiation, would lead to bimodal surface colors as seen today [3]. Space weathering alteration of the surface and the chemistry engaged in the development of such an organic layer has been investigated by very few laboratory simulation studies. While one experiment [4] shows that the irradiation of carbon containing molecules leads to a reddening of the initial ice, no laboratory studies have tested whether the addition of N or S containing molecules have an effect on the observed reddening.

#### 2. Experimental Methodology

Electron irradiation experiments were carried out using the Icy World Simulation Laboratory at the Jet Propulsion Laboratory. The experimental setup used consisted of a high vacuum stainless steel chamber (base pressure  $\sim 1 \times 10^{-8}$  torr). The ices were grown on a gold coated glass substrate attached to the cold finger of a closed-cycle helium cryostat. The ice films were grown by leaking gas mixture into the chamber directly onto the 50 K gold mirror.

An electron gun is mounted on the chamber, perpendicular to the substrate. High energy electrons (10 keV) impact the sample with a typical beam current of 0.5  $\mu\text{A}$ . All studied ices were submitted to the same fluence of electron energy  $\sim 2 \times 10^{21} \text{ eV cm}^{-2}$ . After irradiation, samples were warmed to 120 K at 0.5 K/min while continuing electron irradiation. Samples were then irradiated 1 hour at 120 K, the electron beam turned off, and then warmed at 0.5 K/min to 150 K. This experimental procedure simulated the irradiation and heating history of an icy surface scattered from the Kuiper Belt region (50 K)

to Jupiter Trojans region (120 K). Chemical changes in the constituents of the ice were monitored with a Midac Fourier transform infrared spectrometer covering a wavenumber range 400-7000  $\text{cm}^{-1}$  at 2  $\text{cm}^{-1}$  resolution. A quadrupole mass spectrometer was also used to monitor the gaseous species released when the irradiated ices were warmed.

### 3. Results

Figure 1 presents mid-IR spectra of the 4-ice mixture as deposited and after electron irradiation at  $T = 50$  K. We observe a significant decrease in absorbance of the initial ice components, and new products appear in the spectrum of the irradiated sample. In the 3-ice mixture and the 4-ice mixture, we observe  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{OCN}^-$ ,  $\text{HCOOH}$ ,  $\text{CH}_2\text{OH}$  and  $\text{CH}_4$ . In the 4-ice mixture we also observe, after irradiation, an intense band at 2040  $\text{cm}^{-1}$ . This band is assigned to the  $\text{C}=\text{O}$  stretching mode of  $\text{OCS}$ .  $\text{OCS}$  can be a product of reactions between a  $\text{CO}$  (which is produced from the dissociation of methanol) and an  $\text{S}$  atom or  $\text{HS}$  radical produced by photo-dissociation of  $\text{H}_2\text{S}$ .

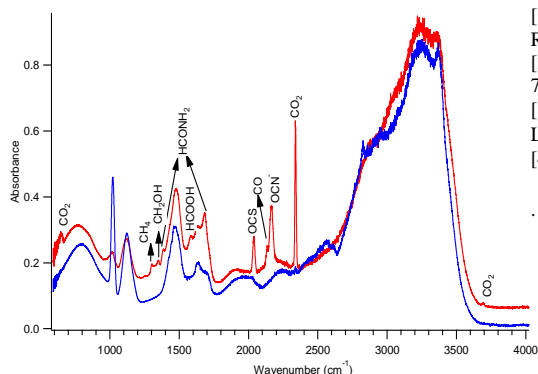


Figure 1: mid-IR spectra of  $\text{H}_2\text{S}-\text{CH}_3\text{OH}-\text{NH}_3-\text{H}_2\text{O}$  (3:3:3:1) deposited on a cold substrate (50 K) before (blue) and after (red) electron irradiation.

The heating of the irradiated 4-ice mixture to temperatures above 120 K leads to the appearance of new products. We tentatively assign these bands to  $\text{SO}_2$  and  $\text{CS}$ .

### 4. Summary and Conclusions

Irradiation and heating of laboratory analogues of the icy surface with and without  $\text{H}_2\text{S}$  results in a rich chemistry that varies, depending on whether S-bearing species are present in the initial ice mixture. The generation of molecules like  $\text{OCS}$ ,  $\text{OCN}^-$ , and  $\text{HCONH}_2$ , and their stability under irradiation and heating (simulating the migration of an object from the Kuiper belt region to Jupiter's orbital distance) can be helpful for choosing target molecules for potential future missions to the Jupiter-Trojan asteroids.

### Acknowledgements

This work has been conducted at the Jet Propulsion Laboratory, Caltech, under a contract with the National Aeronautics and Space Administration (NASA) and at the Caltech Division of Geological and Planetary Sciences. This work has been supported by the Keck Institute of Space Studies (KISS). Government sponsorship acknowledged.

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# Formation of authigenic sulfates in cold dry glaciers: terrestrial and planetary implications

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## 1. Introduction

Salts are commonly found on planetary surfaces, and sulfates have been widely observed on Earth, Mars [1] and on some of Jupiter's and Saturn's icy moons [2]. These minerals can form under a wide range of conditions, from warm environments with high water/rock ratios to cold environments with low water/rock ratios [3, 4]. The accurate determination of sulfate formation can thus provide key elements for deciphering past planetary surface conditions.

If terrestrial sulfates are mainly formed with a high water/rock ratio, this condition is rarely encountered in the solar system. A formation process involving cold and dry conditions is thus perhaps more relevant for Mars and icy moons. Sulfate formation in this kind of environment is however poorly documented on Earth. As planetary sulfates are often associated with ice deposits, this study focuses on the formation mechanism of cryogenic sulfates in extreme cold and dry environments. For that purpose, we performed a detailed analysis of sulfates found on a Chilean glacier. The obtained results are then compared to planetary data.

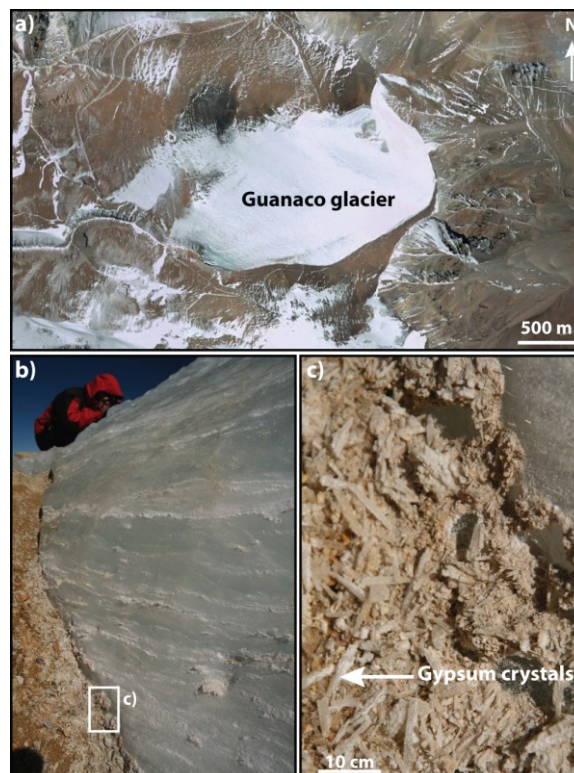
## 2. Terrestrial cryogenic sulfates

Two mechanisms of cryogenic sulfate formation have been documented so far: (1) post-depositional chemical reaction in ice [5, 6], and (2) crystallization during ice destabilization [4]. However, the first mechanism is very anecdotic and the second one has been observed only in Antarctica, where ice impurities include an important oceanic contribution.

The Guanaco glacier (29.3°S, 70.0°W) is located in the Pascua Lama region in the "South American Arid Diagonal", above an altitude of 5000m (Fig. 1a). According to the surrounding geology, the glacier ice is mostly contaminated by continental impurities and volcanic aerosols. Field analyses [7, 8, 9] reveal a cold-based glacier and a surface temperature that remains below 0°C throughout the year. The annual

mass balance is negative and ablation occurs mostly by sublimation.

Sublimation leads to the formation of ice cliffs where deep ice layers are exhumed (Fig. 1b). Field observations on the cliffs reveal the presence of gypsum crystals interstratified in dust-rich ice layers and accumulated at the foot of the cliff (Fig. 1c). The fine needle morphology of these crystals suggests that the gypsum is neoformed and has not been transported in the ice. This interpretation is supported by the absence of gypsum crystals in ice cores drilled through the glacier. Gypsum thus seems to have crystallized as the ice cliffs retreated by sublimation and by sublimation.



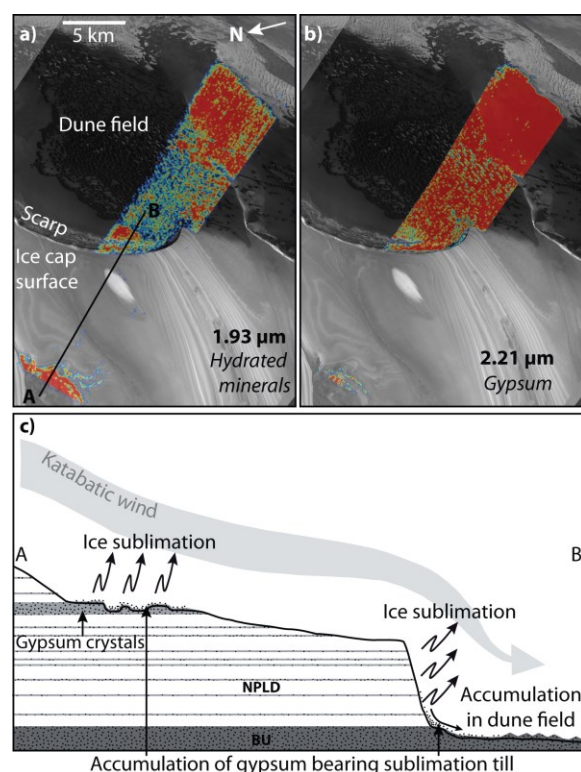
**Figure 1:** a) Landsat satellite image of Guanaco glacier, b) Sublimation cliff observed on Guanaco surface, c) Gypsum crystals released from the cliff.



### 3. Planetary implications

On Mars, sulfates have been found in two main areas: (1) in equatorial regions and (2) close to the North Polar Cap.

Conditions observed on the North Polar Cap are particularly similar to those of the Guanaco glacier with: cold and dry climate, ablation by sublimation only, and impurities coming from martian dust or volcanic aerosols. Mineralogical analyses of the North Polar Cap reveal the presence of gypsum on all superficial sediments [10] (Fig. 2a-b). These gypsum-rich sediments derive from the ice deposits and have been exhumed in ablation areas such as sublimation cliffs (Fig. 2). These sediments are then reworked and transported by katabatic winds in the circumpolar dune fields [11]. As gypsum appears on sublimation areas, we infer that the crystallization process is the same as the cryogenic process observed on the Guanaco glacier and due to sublimation.



**Figure 2:** Sublimation cliff and associated superficial sediments observed on the North Polar Cap of Mars [10, 11]. a) Detection of hydrated minerals signatures, b) Detection of gypsum signature, c) Interpretative scenario for the formation of superficial gypsum bearing sediment in the North Polar Cap.

Martian equatorial sulfates were formed in the past with a low water/rock ratio [12]. One of the last hypothesis thus suggests that these sulfate deposits may have a glacial origin, but the exact formation mechanism remains unclear [12]. This hypothesis is consistent with the presence of glacial landforms in the same areas [13]. We propose a cryogenic origin for these sulfates during sublimation, consistent with the formation of large volumes of sulfates deposits, on widespread and various terrains and at various altitudes.

Sulfates have also been detected on icy moon surfaces, particularly on Europa [2]. Liquid water can't exist on the icy satellites surface. A completely dry formation process lead by ice sublimation thus has to be considered, and is supported by the observation of sublimation processes on icy moon surfaces [14].

### 4. Conclusions

The analysis of a cold and dry glacier located in the Chilean Andes reveals that authigenic sulfate crystals can form by cryogenic processes at the surface of glaciers. The crystallization occurs during ice sublimation and does not involve liquid water. Though this original formation process is uncommon and generates minor quantities of sulfates on Earth, it may be dominant in the Solar System because sublimation is a common process at the surface of other planets. The Guanaco glacier is thus a particularly relevant analog for the Martian North Polar Cap, but sulfate formation by ice sublimation has also to be considered for the formation of sulfates in martian equatorial regions and on icy moons.

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## Mars analogue activities: the Ibn Battuta Centre and the Sahara desert

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### Abstract

The Ibn Battuta Centre for Exploration and Field Activity is a facility of the Europlanet Research Infrastructure. It was established in 2006 by the International Research School of Planetary Sciences (IRSPS) at Pescara, Italy to prepare and execute analogue science and tests of rovers, landing systems, instruments and operations related to the exploration of Mars and Moon.

### 1. Introduction

The analysis of Mars analogue environments on Earth is important for the interpretation of the data from past, present and future orbital and lander missions, as well as mission planning. Whereas testing single instruments dealing with collection and analysis of single specimens can be performed in restricted environment, the testing of instrument suites, rovers, landers and operations must be conducted in large-scale analogue environments. Therefore, analogue terrains are also of paramount importance for the robotic and human exploration of Space. Human planetary missions will face tremendous challenges that can be mitigated by a careful planning based on testing of human mission on planetary analogues. However, test for robotic and, chiefly, human missions requires environmental characteristics of the analogues different from the environments used for scientific analogue studies. Human mission testing needs broad, arid and vast landscapes. Relief must be smooth and scattered over a large area. Landmarks must be negligible or absent. Surface water must be absent as well as vegetation. The Ibn Battuta Centre ([www.ibnbattutacentre.org](http://www.ibnbattutacentre.org)) deals with both scientific and operational analogues. In both cases it takes advantage of the long geological history of Morocco and the remarkable geological

and geomorphological diversity. Quaternary environments are a host of morphologies and geological settings similar to Mars from reg surfaces to dry lakes, from aeolian dunes to bio-induced carbonates. Besides these quaternary environments, several sites of the Centre consist of ancient deposits such as the Devonian Mud Mounds of the Kess Kess or the Precambrian stromatolites.

### 2. The activities

Under the frame of the Europlanet RI, in the last 4 years, about 15 scientists have been able to obtain grants to carry on field work in Ibn Battuta field sites. In addition, other activities deal with space missions or future exploration scenarios, such as the test of Dreams, the atmosphere and dust instrument onboard ExoMars 2016. Human exploration is an important issue that takes Human exploration simulations have



Figure 1: Test of the Dreams instruments in a Moroccan Martian-like environment.

been already executed. In particular, the Centre participated to the control, organized in ESTEC by ESA, of the NASA simulation experiment Desert RATS in Utah. Moreover, with the Austrian Space Forum, a month-long simulation test was performed in two desert sites near Erfoud. The Ibn Battuta Centre deals with both scientific and operational analogues. In both case it take advantage of the long geological history of Morocco and the remarkable geological and geomorphological diversity. The Centre is both using the remarkable diversity of the Moroccan desert and also is investigating other areas such as Patagonia, the Arctic, the Mediterranean volcanic edifices, and other desert areas in Africa. of Morocco. The Sahara in South Morocco exhibits a large-scale scenario that can be similar to the broad Martian landscape. This allows the creation of large test range that can mimic the Martian surface over 100s of km. This characteristic allows the test of aerial operations like spacecraft descent, test of touch down and also of launching to mimic a sample return missions.

### 3. Why Sahara

Sahara is a continent-wide desert that replicates several large-scale processes occurring on Mars. Sahara has experienced during its long geological history a large number of climatic changes from humid conditions (with savanna-type environments) to dry conditions (with hot desert environments). Therefore since the late Miocene Sahara alternated periods with rivers, lakes, deltas swamps with periods with a strong aeolian activity and the formation of deflation surface and sand seas. The Sahara is also dominated by a cratonic landscape with a marginal mountain chain (the Atlas) and volcanic centres (Hoggar, Tibesti). The landscape is therefore broad with swells and domes resembling the Martian topography. Wind processes have reworked, during dry periods, the fluvial deposits that formed during humid period. The aeolian erosion has been extremely efficient leaving some remains of the fluvial deposits as meander belts or exhumed (inverted) channels. Deltaic deposits are strongly eroded and large inland lakes and swamp eroded and a few remains are mostly buried below dunes and sand seas. The leftover of the fluvial deposits is basically the coarse-grained component because the finer sediment has been removed by the wind. Sand to silt material accumulated (mostly by saltation) in the sand sheets and seas. The finer portion (able to enter the wind as suspended material) can be trapped

in the large- scale atmospheric circulation. The consequence is that it enter the large-scale atmospheric circulation and has been redistributed in Sahara and in other adjacent continents (mostly Europe and South America) and oceans. The results of these climatic changes are fluvial systems and lacustrine deposits interrelated with deflation surfaces and sand accumulations. This situation is similar to Mars where fluvial deposits and morphologies abound but are largely eroded. When deposits are present are basically coarse-grained (e.g. the meandering channels of the Eberswalde deltaic plain) because the long lasting aeolian. This has removed the finer portion of the sediment and accumulated the sand to silt grade portion in sand seas and sheets and the fines in a sort of draping dust. Therefore Sahara harbour a large number of sedimentary environments that dominated Mars in the mid- and low-latitude. These deposits underwent a number of climatic changes from wet to dry condition in a similar way than the climatic changes on Mars. Aeolian erosion and deposition has been similar in both Sahara and Mars in term of duration of the events, extension and efficiency. Extensive fluvial deposits have been deflated by strong wind activity.

### 4. Future work

Science is the first item of the Ibn Battuta Centre mission. In order to increase the impact in this field it is planned to increase the number of fieldwork grants to work in Morocco. Moreover, a couple of expeditions will be organised in the next 4 years in the Danakil depression or other remote Martian analogues. It would be also interesting to create science team operating a rover in Martian conditions. This experiment would allow scientists to be exposed to the planning and execution of an analogue rover missions with the identification and analysis of geological settings. Finally the Ibn Battuta Centre/IRSPS would like to increase the link with the industry under the Europlanet RI programme.

# Effects of low velocity impacts on basaltoids

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## Abstract

We study the effects of low velocity impacts on basaltoids as analogue materials to HED meteorites and V-type asteroids. The aim of this study was to investigate changes to V-type asteroid spectrum under impacts and its implications to interpretation of remotely obtained spectra. We have performed number of low velocity ( $\sim 4\text{--}7$  km/s) impacts into various basaltoids and performed reflectance spectroscopy, of the samples before and after the impact.

Low velocity impacts enhance the spectroscopic features of the studied samples. In particular, the absorption bands are deepened and broadened. Overall the spectrum is brighter as compared to the spectrum of the solid samples before impact. The after impact spectrum resembles closely the spectrum of powdered samples.

The enhancement in the spectrum is mostly due to grinding of the sample during the impact. Effects of low velocity impacts can therefore be simulated by graining the samples. Future studies are needed to check for the possible effect of different grain sizes on spectrum.

## 1. Introduction

According to Antarctic Meteorite Collection (ANS-MET program) less than 1% of collected meteorites belong to the so-called HED (howardite-eucrite-diogenite) meteorite group. Those meteorites have been identified to originate from asteroid (4) Vesta - the only currently known differentiated and intact asteroid in the Main Asteroid Belt. Few of the known HED meteorites cannot be chemically linked to Vesta, the most prominent ones include Ibitira and NWA011. Those meteorites among with other evidence suggest that additional differentiated bodies existed in the Solar System at some point during its history. The ob-

servational proofs for those bodies are however missing. This mismatch between in-situ meteoritic and observational asteroidal evidence is known as the "missing dunite" problem [1]. Several observational, dynamical, chemical and geological hypothesis were put forward to explain the mismatch. For example [1] suggested that the basaltic asteroids were "battered to bits" and are currently beyond our spectroscopic reach. More recently [2] showed that partial differentiation is possible, creating an alternative formation hypothesis for those bodies. Few of the hypothetical explanations of the missing dunite problem (such as modification of V-type spectra by space weathering or impact shocking) could be tested experimentally in laboratories. In this research we explore the possibility of using the Earth basalts and peridotites as analogues to HED meteorites. In particular we analyze the differences and similarities in chemical composition, mineralogy, reflectance spectra and material shock induced changes in the selected Earth basalts. The conclusion of this experiments may be applicable to HED meteorites and the topic of altering the surfaces of basaltoid-like planetary bodies.

## 2. Impact experiment

The basaltoids were shocked by impacting them with 1 mm stainless steel (470) projectile at a set speed between 4 and 7 km/s (Table 1) using the two stage light gas gun facilities based at the University of Kent, a detailed discussion of the methods and design can be found in [3]. The peak pressures were calculated using the Planar Impact Approximation [5]. This assumes a linear wave speed equation for both the basalt target and stainless steel projectile and that the projectile hit a solid basalt (i.e. no allowance of made for the porosity of the target). This latter assumption is considered reasonable as only a peak pressure is being found, not the full pressure history of an impact vs. time. The

required C and S values used for the calculations are  $3800 \frac{m}{s}$  and 1.58 for the steel projectile [4] and  $4960 \frac{m}{s}$  and 0.88 for the basalt [4].

Sample	Shot speed ( $\frac{km}{s}$ )	Peak Pressure Approximation (GPa)	Crater diameter (mm)
J3-2	6.42	105.4	$22.2 \pm 1.0$
KG1-3	6.35	108.9	$23 \pm 1.5$
MW3-2	4.00	59.5	$20.2 \pm 0.9$
MN5-8	3.77	56.1	$13.6 \pm 0.1$

Table 1: Impact parameters.

The powdered ejecta was removed from the sample after performing the experiment.

### 3. Spectroscopy

For each sample we obtained 4 spectra, one before the impact experiment and three after. The spectra before the experiment were taken from powdered samples, whereas the spectra after the experiment from solid samples containing impact craters. In black we denote the spectra from the powdered samples, in red spectra from the craters centers, in green spectra from the craters walls and in blue spectra outside the impact craters. In Fig. 1 we present our preliminary normalized and slope removed spectra for the sample J3-2.

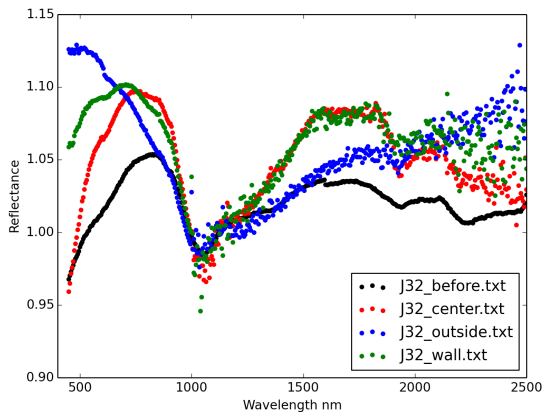


Figure 1: Slope-removed J3-2 spectra. All spectra shifted to 1.0 at 1000 nm for comparison.

### 4. Summary and Conclusions

For samples alkali basalt J3-2, basanite MW3-2, nephelinite KG1-3 rock lithology was modified to

lighter at crater centers (most likely due to mechanical damage). For peridotite-harzburgite (MN5-8) there is no visible change in the color of lithology at the crater center. The color of lithology is an important factor influencing reflectance spectroscopy. Absolute reflectance values are highest for the grinded samples before the experiment. For samples J3-2 and KG1-3 spectral slopes outside the crater are smaller than those inside, on the wall and before the impact (grinded material). This is most likely due to material roughness. Smoother samples seem to have smaller spectral slopes. samples J3-2 and KG1-3 show more pronounced and wider absorption bands in the spectra after the impact. For KG1-3, the absorption band around 1 micron was shifted towards shorter wavelengths. Preliminary measurements on the J3-2 and KG1-3 rocks also show fractionation and melts in J3-2 and KG1-3 samples.

### Acknowledgements

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