

The Mineralogical and Chemical Analyses of Antarctic Dry Valley Sediments as Potential Analogs for Mars

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Abstract

Minerals such as clays, carbonates and sulfates are indicative of liquid water on Mars and provide constraints on the likely geochemical environment and can potentially be used as terrestrial analogs for Mars. The Dry Valleys of Antarctica have ice-covered lakes inhabited by microbial mats and a complex weathering system despite the cold and dry environment. This study focused on characterizing soils and sediments from the Dry Valleys region of Antarctica. The chemistry and mineralogy of the samples were analyzed in hopes of finding an analogy to the mineral alteration of Mars determined via spectral remote sensing. Sediment cores were collected from various parts of the Dry Valleys region such as the perennially ice-covered Lake Hoare in Taylor Valley and Don Juan Pond in Wright Valley. In the lab, sample sizes ranged from large gravel to sand. Elemental analyses and reflectance spectroscopy have been carried out to examine mineralogical changes along the surface layer in this region and as a function of depth. The spectroscopic analyses include determination of band centers and band depths for spectral features due to bound water (H₂O) in the mineral structure. Our results for these core samples indicate that cations and anions associated with alteration occur at elevated abundances a few cm below the surface. The information obtained from this analysis provides insights on how the water chemistry influences the types of minerals that are present in each sample. The spectral data obtained in this study will play a role in understanding the Martian surface regolith and identifying sediments on Mars. Ancient rocks on Mars enriched with clays might suggest an environment that once had liquid water and that was able to support life.

Keywords: Antarctica, sediments, mineralogy

1. Background

Lab experiments and field work are research methods to expand our knowledge about life on planet Earth. The advent of space exploration has sparked interest about life existing outside planet Earth as well. Mars has intrigued observers for many centuries because of its distinct red hue and its proximity to Earth. Martian chemistry and mineralogy have been a vast area of research for planetary scientists for decades. The fundamental question that they strive to answer is whether Mars could have harbored life sometime in its geologic history. It has been postulated that a major component required to sustaining life is liquid H₂O. There has been much discussion about the presence of H₂O on Mars, primarily in the past. There is geologic evidence of H₂O such as two shorelines²³, valley networks¹¹ and basin forming impact events¹⁰ that are regarded as evidence of the former widespread presence of liquid H₂O on Mars. Research in many disciplines has hypothesized H₂O activity on the surface of the red planet that date back to 4.1 billion years ago during the Noachian Period. This time period provides the best evidence for warm conditions, which could have been suitable for the presence of oceans¹⁰. The subsequent Hesperian and Amazonian periods have been much drier. Liquid H₂O plays a major role not only in supporting life, but also in shaping the geologic

processes such as weathering and sedimentation. Therefore, if Mars did support liquid H₂O at some point in its history, there should be some evidence of this in the chemistry and mineralogy on the surface or subsurface of Mars today.

In order to understand the geologic processes that occurred on Mars, a terrestrial environment on Earth similar to that of Mars was examined in the study: the Antarctic Dry Valleys. Both regions share physical characteristics such as having cold and dry sedimentary environments with mean temperatures always below freezing (-20°C), low humidity, no rainfall and a tendency toward oxidation¹⁷. The Dry Valleys have an annual mean temperature of -20°C, an average annual relative humidity of ~69% and all precipitation occurs as snow with an average rate of -10 cm/yr^{12,17,21,27}. Among all terrestrial environments, the Dry Valley characteristics most closely approximate those of Mars. The ground temperatures on the red planet are lower than those of the Dry Valleys, but these differences are negligible with respect to the style of weathering present on both environments. On Mars, summer equatorial temperatures can reach 0°C or a few degrees above zero. Although there are variations in the amount of humidity with latitude and season on Mars, the H₂O vapor amounts over the equatorial latitudes remain relatively constant throughout the year with the maximum value for the equatorial average of 12 pr μm (precipitable micrometers)¹⁵. Moreover, Mars is dryer with ~0 mm mean annual precipitation²¹. In the current study, reflectance spectra of the Dry Valleys sediment cores were compared to laboratory spectra of pure minerals as well as concentrations of water-soluble cations (Na⁺ and Ca²⁺) and anions (Cl⁻) to study the influence of H₂O chemistry on mineral alteration and chemical alteration. Reflectance spectroscopy in the visible/near-infrared region measures absorption bands due to electronic excitations, and combinations and overtones of molecular vibrations. Clays and sulfates were studied as they are products of chemical weathering due to interactions with H₂O molecules and they have been found on Mars²⁴. H₂O absorption bands can be seen in reflectance spectra of these samples. The presence of clays and sulfates on the surface of Mars supports the hypothesis of liquid H₂O's presence on the surface of Mars. Most importantly, the verification of H₂O on the Martian surface may indicate that conditions on Mars may have been able to support life.

2. Methods

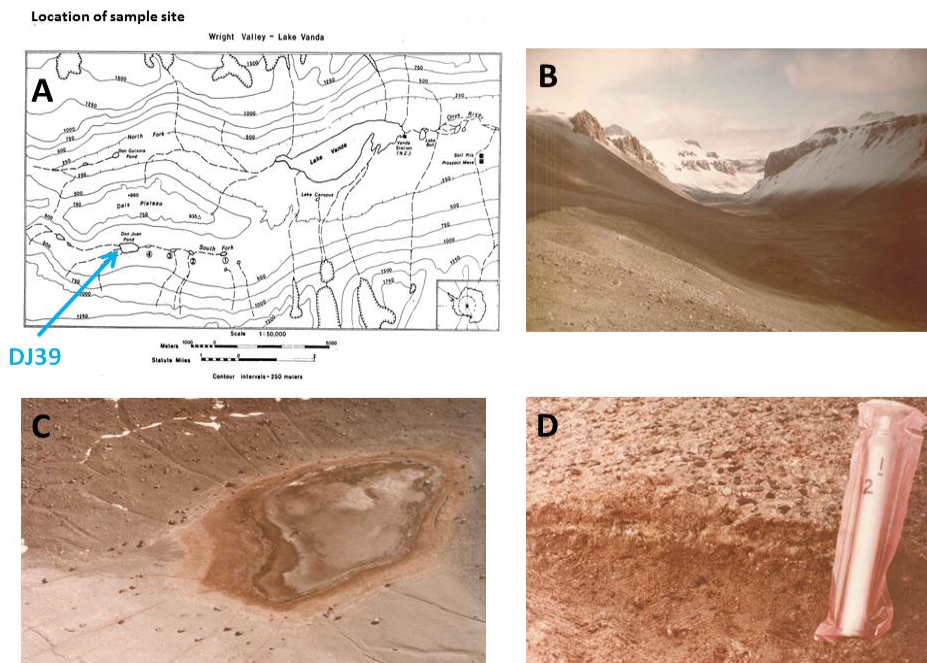


Figure 1. A. Contour map of Wright Valley showing approximately the location of sample core DJ39. B. Photograph of Wright Valley showing Don Juan Pond in the center. C. A close-up photo of Don Juan Pond where the core sample was collected. The pond is roughly 300 m along its length. D. Photograph of the 25 cm plastic tube pushed into the ground in order to collect a core or column of sediment.

The samples studied here were sediments from a 25 cm-deep core (DJ39) that was collected about 0.25 km West of Don Juan Pond (Figure 1C). A plastic tube as shown in Figure 1D was pressed into the ground, frozen and returned to the lab. The core was thawed in the lab to preserve the core and sediments were separated at 1-2 cm intervals along the core for chemical and mineralogical analyses¹⁷. The study site is located at the lowest point in the Southern Fork of Upper Wright Valley (Figure 1A). The region is characterized by past volcanic activity in an extreme aqueous environment. Similarly, the Martian surface is considered to be mainly covered with volcanic material^{20,26,29}. Previous experiments focused on lake bottom sediments in the Dry Valleys (Figure 1B) to gain insight into the biogeochemical processes and the mineralogy that could be found in the paleolakes on Mars⁴.

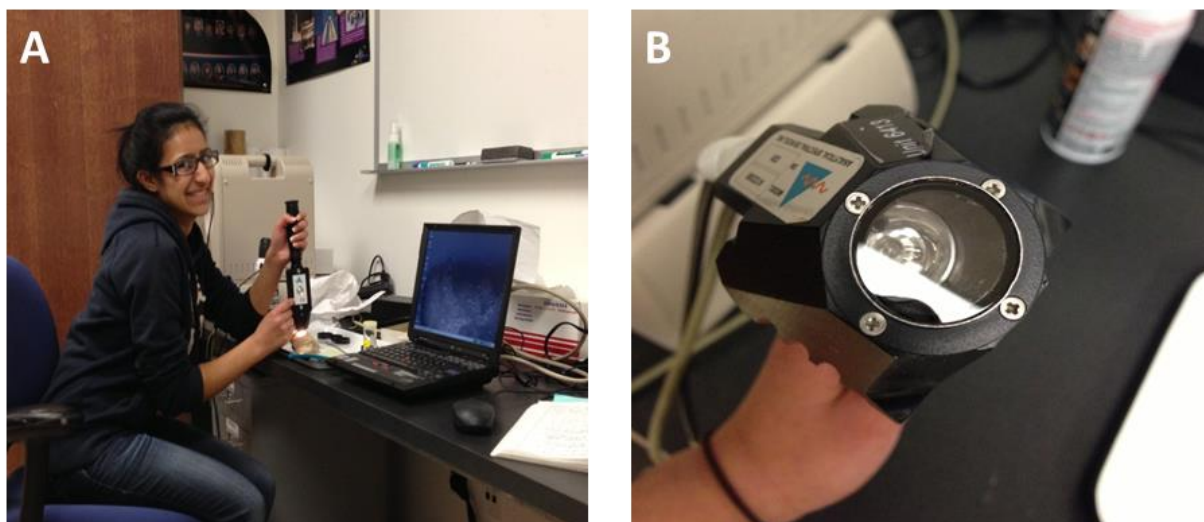


Figure 2: Reflectance Spectroscopy Apparatus

Figure 2. A. Shital N. Patel measuring reflectance spectra. B. Image of the reflectance spectrometer probe that was used to examine mineralogy of the samples.

In the laboratory, the analytical technique that was employed to study mineralogy along the core depth was visible/near-infrared spectroscopy (Figure 2). Each sample was assigned a sample number that began with JB. In this study, the samples that were analyzed were JB1349-JB1364. The samples were placed in non-reflecting black Teflon dishes and spectra were measured relative to a smooth, white calibration surface called Spectralon (trademark of Labsphere, Inc.). If a particular sample was a mixture of gravel, sand and rocks, then separate measurements were taken of the different components to account for the different grain sizes and compositions. Gravels show mineral crystals on a fractured surface and are much smaller than rocks, typically ranging from 2-4 mm across. Small rocks several mm across were also present in some samples. Sand is a type of sedimentary material that is finer than a granule and ranges from 1/16 to 2 mm in diameter. Furthermore, two-three spectra were measured and averaged for each particulate sample in order to ensure that the spectra were representative of the entire sample. The number of measurements recorded for a sample depended on the variable granularity and texture of each sample. If the first two spectra measured of the sand were similar, that was deemed sufficient. If visual differences were observed, then a third spectrum was also recorded. If a sample contained a mixture of rock and sandy material, then separate measurements were taken for that sample. Absorption bands occur in the reflectance spectra corresponding to electronic excitations of Fe in minerals such as pyroxene and iron oxides⁸. Combinations and overtones of vibrations due to H₂O, OH, CO₃ and SO₄ molecules also produce spectral features¹⁶. Band centers and band depths were determined and analyzed for characterizing features due to hydroxide and H₂O in the mineral structures based on previous studies where the band depth is the normalized distance from the spectral continuum to the bottom of the band⁹. A typical representation of a H₂O band center and band depth is shown in Figure 3 using sample JB1353 as an example. Calculations pertaining to the band depth and band center helped determine H₂O

absorption qualitatively. We used H₂O soluble cation and anion abundances from Gibson et al (1983) to evaluate chemical activity as a function of depth¹⁷.

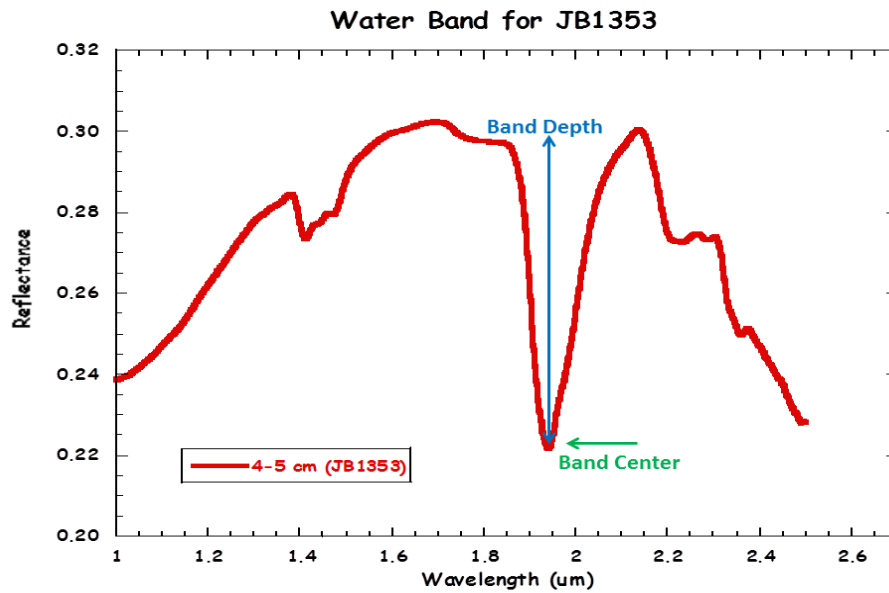


Figure 3. A graphical representation of band depth and band center for a water band in a reflectance spectrum.

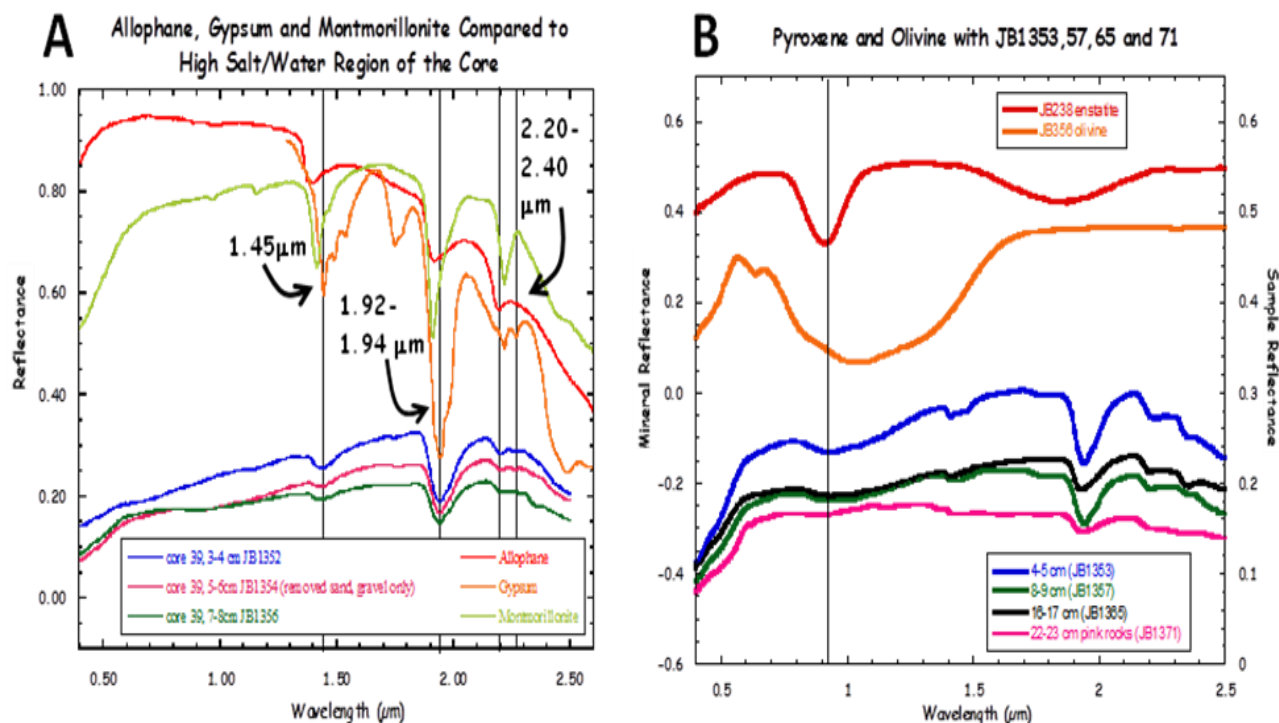
3. Results and Conclusions

The spectra for each sample contained a band centered near 1.89-1.94 µm due to a combination of H₂O stretching and bending vibrations¹ and also bands in the 2.1-2.4 µm region due to OH combination vibrations marked by the two right most vertical lines in Figure 4A. The strengths of these bands were measured for all samples and then band depth was displayed as a function of distance along the core. However, there was a specific region along the core that contained an increased abundance of H₂O. Visible and near-infrared (VNIR) spectra are shown in Figure 4B for three samples that are representative of the high salt/high H₂O absorption region of the whole core in comparison to mineral samples such as allophane [(Al₂O₃)(SiO₂)_{1.3-2}·2.5-3H₂O], gypsum (CaSO₄·2H₂O) and montmorillonite [(Na,Ca)_{0.33}(Al,Mg)₂(Si₄O₁₀)(OH)₂·nH₂O)]. These samples were JB1352, JB1354 (gravel only) and JB1356 which pertained to depths of 3-4, 5-6 and 7-8 cm below the surface. According to band center calculations, the samples corresponding to 3-9 cm below the surface had a normalized absorption ranging from 0.07-0.04. The depth of the H₂O absorption band was calculated by taking the difference in reflectance at the maximum and minimum wavelengths. In other words, the greater the depth a band has, the greater the absorption of H₂O in the sample. Bands are frequently used in reflectance spectroscopy to determine the relative abundance of mineral^{2,9}. The majority of the remaining samples showed a much lower level of H₂O content, measured as band depths well below 0.02.

Variations in spectral features are due to differences in mineralogy and grain size. The hydration bands helped us determine whether the samples contained sulfates or clays because their H₂O bands occur at different wavelengths. Some of the peaks in the samples were characteristic of minerals such as clays and sulfates. In order to determine which minerals are likely present we compared our Antarctic sediment spectra to library spectra of several sulfates and clays. These hydrated minerals are the products of alteration of the surface material. Clay minerals exhibit a hydration band at a narrow wavelength range of 1.91-1.92 µm and hydroxide band near 2.2 µm (for AlOH and SiOH) and near 2.3 µm (for FeOH and MgOH). Sulfate minerals absorb H₂O at a broader wavelength ranging from 1.94-1.98 µm, may also contain OH bands near 2.3 µm and often have a decrease in reflectance near 2.4-2.5 µm. The spectra in the high H₂O content region of the core, which had absorption values ranging from 0.7544-0.11168,

showed features characteristic of gypsum and allophane. Allophane is a proto-clay, which is a nanophase aluminosilicate clay precursor material.

The sample spectra coincided well with gypsum, especially JB1356 as shown in Figure 4A. The spectrum of JB1356 contains a triplet at 1.45-1.54 μm due to stretching overtones of OH and H₂O, a band near 1.94 μm due to the combination of stretching plus bending band of H₂O, and a doublet near 2.23 and 2.27 μm due to the combination of stretching plus bending band mode of OH^{5,16}. However, the bands in JB1356 are consistent with gypsum, which is a sulfate, as opposed to other sulfates such as rozenite, voltaite and copiapite. In addition, there may also be some allophane found in other Antarctic sediments⁶. One characteristic feature of allophane is the OH stretching and bending combination band near 2.19 μm . We plotted montmorillonite for comparison as well because it is common Al-rich clay and its spectrum includes hydration and hydroxide bands absorbing at different wavelengths from the allophane spectrum. However, its spectrum does not match as well as that of allophane. The spectra in Figure 4B show variability in the amount of olivine and pyroxene present in the sample spectra. These minerals are primary silicates that contain the elements oxygen and silicon and are susceptible to chemical weathering. These minerals were shown because they are some of the primary silicates that have been found in Antarctic soils based on previous studies^{17,4}. In terms of spectral analysis, olivine and pyroxene show a broad band near 0.8-1.0 μm region, which is due to excitations of iron to an elevated electronic state⁸. The weak iron bands present in the sample spectra indicate minor abundances of these primary silicates due to Fe electronic excitations. We did not find a correlation with depth for the iron band as we did for the H₂O bands.



Don Juan Core 39 sample analysis

Figure 4. A. The JB1352, 54 and 56 spectra reveal characteristic features of gypsum and allophane. B. Spectral comparisons of several samples along the core to show minor abundances of olivine and pyroxene.

H₂O soluble cation and anion abundances for Na⁺, Ca²⁺ and Cl⁻ were measured for a previous study¹⁷. Elevated abundances of these salts were found 3-8 cm below the surface (Figure 5B) and decreased with depth to, most likely, the permanently frozen zone, which probably began at the bottom of the image in Figure 5. This indicates that there is little exchange or ionic migration of these cations or anions in the soil below 8 cm where H₂O is really scarce based on the decreased H₂O absorptivity in Figure 5A. Therefore, it is likely that chemical weathering is occurring in the high salt region due to the presence of H₂O.

The high salinity/absorptivity region is shown in Figure 5 relative to the core sample as a whole. The bar graphs represent abundance down the core and the photograph is that of the entire core sample. The bright sediment material in the core, which is indicated by arrows, is correlated to elevated hydrous minerals and elevated salt content from the chemistry.

The purpose of this study was to investigate the mineralogy and chemistry of Antarctic Dry Valley soils as analogs for Mars primarily due to the cold and arid conditions. The mineralogy of other parts of the Dry Valleys such as sediments from Lake Hoare, Taylor Valley, have been studied in the past and it was found that the primary minerals consist of quartz (resistant to weathering), feldspar and pyroxene^{2,3,4,6}. The focus of the present study was on sulfates (gypsum) and clays (allophane) identified in the sample spectra. The region of the core with the highest H₂O absorption bands in the spectra correlates well with high sulfate abundance. Both H₂O and salt were elevated from 3-8 cm with the highest abundance near 6 cm as indicated by Figure 5, which is located a few cm below the surface. The presence of gypsum suggests that the most active chemical alteration is happening below the surface. Analyses of elemental trends for sediments and most rocks in the Antarctic Dry Valleys also indicate that physical weathering is a more important process than chemical weathering in the region^{13,14}. Allophane occurs as an alteration product under chemical weathering conditions. Furthermore, allophane indicates there is only limited soil maturity occurring, which means the mineral experiences more physical weathering as opposed to chemical weathering. The mineral converts to Al-rich clays as more chemical weathering takes place^{7,25}.

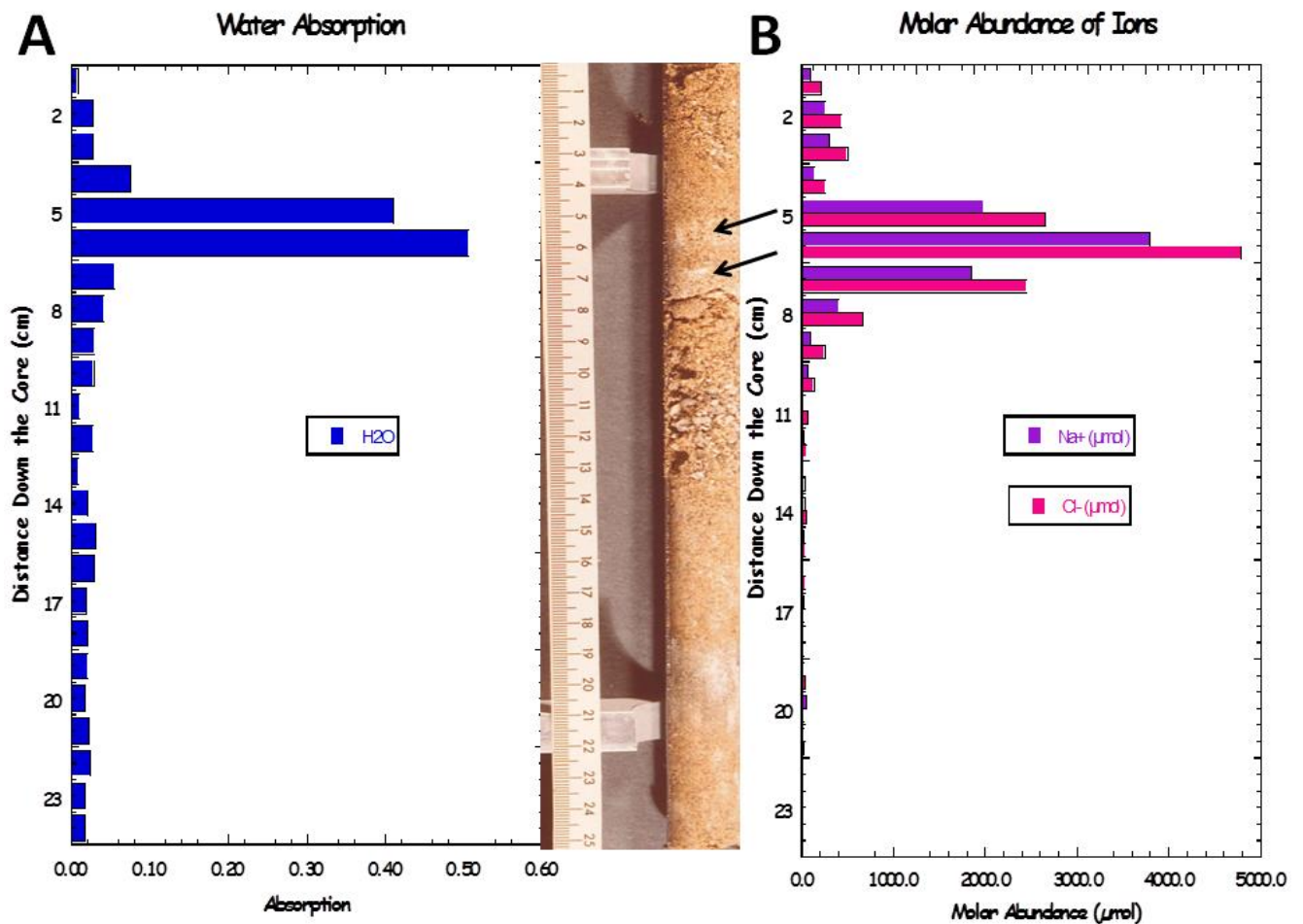


Figure 5. A. This bar graph shows the highest water absorption occurring in the 3-8 cm region. B. The latter graph shows elevated salt content in the same region as the water. Both bar graphs are aligned next to a photograph of the core sample to illustrate the relationship between the chemistry and the thin film of bright sediment (as indicated by the two arrows).

In summary, there is evidence of chemical weathering in the Dry Valley soils due to H₂O and the presence of alteration minerals as products of H₂O interaction.

4. Applications to Mineralogy on Mars

The Antarctic Dry Valleys provide insights on where to look and what to look for in terms of life detection on Mars. Hydration minerals such as phyllosilicates and sulfates have been recognized in Martian meteorites^{18,19,22,28}. In order to better understand the processes that take place in the formation of such minerals, it is key to study an environment that is physically accessible and is similar to the Martian surface. The presence of hydrated minerals can provide information about the aqueous history of the planet. The spectral data generated from this study can be compared to spectra taken using CRISM (Compact Reconnaissance Imaging Spectrometer for Mars). CRISM is an important tool for mapping clays and hydrated minerals on the surface of Mars²⁴. Alterations minerals can play a role in determining where liquid H₂O was once present and where conditions may have been possible for life.

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