

INFRARED SPECTROSCOPIC ANALYSES OF SULFATE, NITRATE, AND CARBONATE-BEARING ATACAMA DESERT SOILS: ANALOGS FOR THE INTERPRETATION OF INFRARED SPECTRA FROM THE MARTIAN SURFACE. B. Sutter¹, J.B. Dalton¹, S.A. Ewing², R. Amundson², and C.P. McKay³, ¹SETI Institute, MS 245-3, NASA Ames Research Center, Moffett Field, CA 94035; bsutter@mail.arc.nasa.gov. ²Div. Ecosystem Sciences, 151 Hilgard Hall, U.C. Berkeley, CA 94720, ³NASA Ames Research Center, MS 245-3 Moffett Field, CA 94035.

Introduction: The Atacama Desert of northern Chile is the driest desert on Earth, receiving only a few mm of rain per decade [1]. The Mars climate may, in the past, have been punctuated by short-lived episodes of aqueous activity [2,3]. The paleo-Martian environment may have had aqueous conditions similar to the current conditions that exist in the Atacama, and Mars soils may have formed with soil chemistry and mineralogy similar to those found in the Atacama.

Remote and in-situ analysis of the Martian surface using infrared technology has a long heritage. Future investigations of the subsurface mineralogy are likely to build upon this heritage, and will benefit from real-life lessons to be learned from terrestrial analog studies. To that end, preliminary results from a near- and mid-infrared spectroscopic study of Atacama soil profiled at a range of depths are presented

Table 1 Chemical concentration of anions in the Yungay soil of the Atacama Desert.

Horizon	Depth (cm)	S wt%	CO ₃ wt%	NO ₃ wt%	Cl wt%
Y1	0-2	0.2	1.0	0.01	0.04
Y2	2-3	14.4	1.0	0.01	0.01
Y3	3-12	7.9	1.1	0.01	0.02
Y4	12-26	9.2	1.0	0.00	0.03
Y5	26-39	9.4	0.8	0.01	0.03
Y6	39-71	7.4	0.8	0.06	0.66
Y7a	71-86	4.9	0.7	0.15	0.42
Y7b	86-102	4.0	2.6	0.69	0.94
Y8	102-122	2.8	2.0	0.56	5.73
Y9	122-146	0.1	0.4	2.93	41.00

In the hyper-arid environment of the Atacama Desert, soils accumulate concentrations of sulfate (i.e., gypsum, anhydrite, Table 1) at levels similar to those found at the Meridiani landing site. High levels of nitrate and chloride also accumulate due to the lack of precipitation. Possible sources of these salts include aeolian redistribution of playa salts, marine aerosols, and/or volcanic processes. Limited precipitation in the Atacama appears to promote the formation of low con-

centrations of carbonates along soil cracks and soil aggregate faces. Sulfate tends to reside higher in the soil profile while the more soluble halite (NaCl) and nitratite (NaNO₂) are leached and concentrated lower in the soil profile during aqueous activity [4] (Table 1). The study of soil profiles containing carbonate, sulfate and nitrate provides insights applicable to the search for aqueous and biologically relevant minerals on Mars.

Methodology: Soil samples were obtained from a soil pit in the hyper-arid core of the Atacama Desert near Yungay, Chile (90km SE of Antofagasta). Soil was sampled from nine horizons (0-146 cm depth). Total chemical analyses, X-ray diffraction and infrared spectroscopy were conducted on all nine samples. A Nicolet Nexus 400 FT-IR spectrometer with a diffuse reflectance/Harrick DRIFT Praying Mantis mirror assembly was used to cover the mid-infrared region (2.5 to 25 μm , 4000 to 400 cm^{-1}) while the near-infrared region (0.4 to 2.5 μm), was analyzed using an Analytical Spectral Devices FR686-3 fiber optic spectrometer.

Results and Discussion: Table 1 lists the chemical concentration of anions at each level of the soil profile taken in the Yungay region. These are numbered consecutively Y1-9. Results of X-ray diffraction analyses are presented in Table 2. Since some IR spectra are similar, only spectra from Y1, Y3, Y6, Y7a, and Y9 are presented. Near-infrared spectra of all samples (Fig. 1) indicated trace amounts of Fe³⁺ (0.87-0.9 μm) and Fe²⁺ (1.2 μm) that likely occur in feldspar [5]. Absorptions at 1.4 and 1.9 indicate adsorbed water, possibly acquired during transport and sample preparation.

Table 2. Mineralogy of Yungay soil. Q-quartz, F-feldspar, A-anhydrite, G-gypsum, H-halite, C-Calcite, and N-nitratite (NaNO₂)

Horizon	Mineralogy
Y1	F,Q
Y2	G,A,Q,F
Y3	G,Q,F
Y4	G,Q,F
Y5	G,Q,F
Y6	Q,A,G,F
Y7a	A,F,Q
Y7b	Q,A,H,G,F,C
Y8	Q,A,H,C,F
Y9	H,Q,N

The triplet absorption features (1.45, 1.49, and 1.54 μm) associated with water of hydration in gypsum are observed in Y3 and Y6. Y7a and Y9 do not possess high concentrations of gypsum and thus the triplet water absorption features disappear and the water peaks shift from 1.45 to 1.41 and 1.94 to 1.91. The 1.75 μm absorption peak is lost when gypsum is not

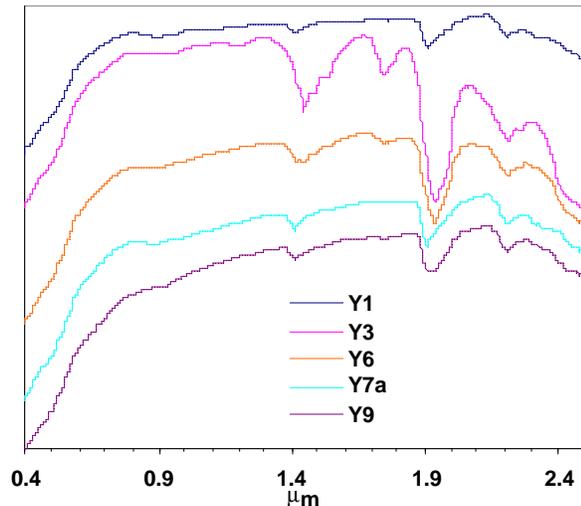


Fig.1. Near-infrared spectra of the Yungay soil surface (Y1) and at increasing depths (Y3, Y6, Y7a,

significant (Fig. 1). The less intense hydration features in the spectrum of sample Y6 indicate that gypsum and its associated water is decreasing with depth. The feature at 2.2 μm may be attributed to hydroxyl groups associated with phyllosilicates detected in these soils.

The mid-IR spectra indicate the presence of sulfate, nitrate, and carbonate. Gypsum and anhydrite sulfate are revealed by the $2\nu_3$ SO_4 overtone near 2220 cm^{-1} [6]. Sulfate as anhydrite is distinguishable from sulfate as gypsum by an absorption feature at 2235 cm^{-1} that is shallower than the absorption feature at 2130 cm^{-1} (Fig. 2, sample Y6). In gypsum the 2130 cm^{-1} absorption feature is shallower than the one at 2235 cm^{-1} [6]. There is more anhydrite than gypsum in Y6. Nitrate absorptions were detected in Y9 at 2852 , 2426 and 1394 , and 1095 cm^{-1} [5,7,8]. Solubility relationships allow nitrate to occur with chloride. Carbonate is detected in all spectra at 2512 cm^{-1} while the 1429 cm^{-1} carbonate band is strongest in Y9 which has the lowest carbonate concentration (Table 1). Carbonate concentrations are higher in the other soils but the 1429 cm^{-1} band is not observed which may be attributed grain size variations in concert with masking effects of interference by the other minerals present.

The uppermost soil sample Y1 is dominated by feldspar with a slight contribution from carbonate seen at (2512 cm^{-1}). Quartz occurs in all the soils but is most abundant and more easily detected in Y7b (1220 cm^{-1}).

Quartz was present in Y6 and its characteristic absorption feature (1220 cm^{-1}) was observed near the sulfate band (1155 cm^{-1}).

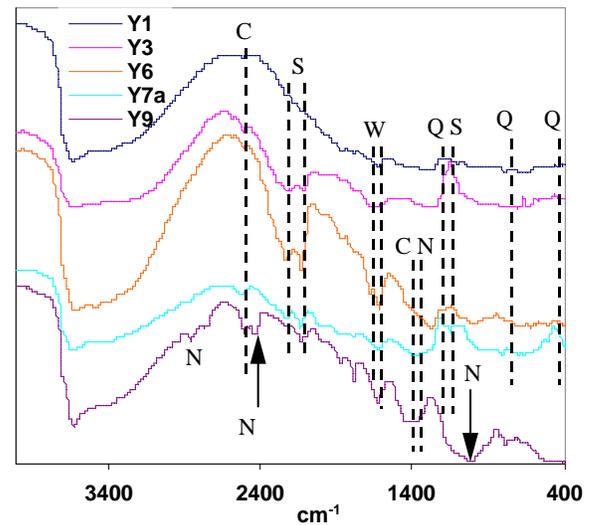


Fig. 2. Mid-infrared spectra of the Yungay soil. C-carbonate, S-sulfate, N-nitrate, Q-quartz

This work illustrates the characteristics of IR spectra of naturally occurring soils containing sulfates, carbonates, and nitrate. The carbonate band at 1429 cm^{-1} is sensitive to grain size variations and may be difficult to detect when sulfate or other minerals are present. Detecting carbonate under these circumstances may require relying on the band at 2512 cm^{-1} .

The distribution of salts at Yungay are analogous to the distributions found at the Meridiani site [4] where sulfate is concentrated higher in the soil profile and chloride is concentrated lower in the profile. Limited leaching associated with scarce precipitation has driven the distribution of salts in the Atacama. The level of aqueous activity that led to the distribution of salts in the Yungay soil may be similar to what has operated at the Meridiani site. However if the Atacama is any indicator, high levels of chloride (e.g., $>40\text{ wt.}\%$) may need to be found before nitrate can be detected by IR techniques on Mars. These results demonstrate the utility of terrestrial analog studies for anticipating issues which will affect surface and subsurface investigations of Martian mineralogy.

References:

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