

**CHEMISTRY AND MINERALOGY OF ANTARCTICA DRY VALLEY SOILS: IMPLICATIONS FOR MARS.** J. E. Quinn<sup>1</sup>, D. C. Golden<sup>1</sup>, T.G. Graff<sup>1</sup>, D.W. Ming<sup>2</sup>, R.V. Morris<sup>2</sup>, S. Douglas<sup>3</sup>, S.P. Kounaves<sup>4</sup>, C.P. McKay<sup>5</sup>, L.K. Tamppari<sup>3</sup>, P.H. Smith<sup>6</sup>, A.P. Zent<sup>5</sup> and P.D. Archer, Jr.<sup>2</sup>; <sup>1</sup>Jacobs Technology ESCG, Houston, TX, 77058 (julie.quinn@nasa.gov), <sup>2</sup>NASA Johnson Space Center, Houston TX, <sup>3</sup>California Institute of Technology-JPL, Pasadena, CA, <sup>4</sup>Tufts University, Medford, MA, <sup>5</sup>NASA AMES Research Center, Moffett Field, CA, <sup>6</sup>Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ.

**Introduction:** The Antarctic Dry Valleys (ADV) comprise the largest ice-free region of Antarctica. Precipitation almost always occurs as snow, relative humidity is frequently low, and mean annual temperatures are about -20°C [1]. The ADV soils have previously been categorized into three soil moisture regimes: subxerous, xerous and ultraxerous, based on elevation and climate influences [2]. The subxerous regime is predominately a coastal zone soil, and has the highest average temperature and precipitation, while the ultraxerous regime occurs at high elevation (>1000 m) and have very low temperature and precipitation. The amounts and types of salts present in the soils vary between regions. The nature, origin and significance of salts in the ADV have been previously investigated [3].

Substantial work has focused on soil formation in the ADVs [4], however, little work has focused on the mineralogy of secondary alteration phases. The dominant weathering process in the ADV region is physical weathering, however, chemical weathering has been well documented [5]. The objective of this study was to characterize the chemistry and mineralogy, including the alteration mineralogy, of soils from two sites, a subxerous soil in Taylor Valley, and an ultraxerous soil in University Valley. The style of aqueous alteration in the ADVs may have implications for pedogenic processes on Mars.

**Soil Profiles:** Representative soil profiles from subxerous and ultraxerous soil moisture regimes were selected for detailed mineralogy. A subxerous soil was sampled in the coastal region of lower Taylor Valley. The soil location was 77.60°S, 163.14°E at an elevation of 22 ± 5.5 m. The soil was covered by a desert pavement and formed in glacial till and possibly volcanic ash and lake sediments from Lake Fryxell. An ultraxerous soil was sampled in University Valley, which is a high elevation valley located above Beacon Valley. The soil location was 77.86°S, 160.71°E at an elevation of 1683 ± 5.9m. The soil formed in glacial till comprised of Beacon sandstone and Ferrar dolerite. Soils were described according to standard soil classification techniques[6]. The soil from Taylor Valley has eight horizons (0-1, 1-9, 9-12, 12-17, 17-20, 20-24, 24-28 and 28+ cm) while the University Valley soil has five horizons (0-1, 1-9, 9-20, 20-34 and 34+ cm). Representative materials from each soil horizon were returned to the laboratory in a frozen state.

**Methods:** Soil water 1:1 suspensions were prepared by standard methods [7]. Soil extracts analysis and results were recently described [8,9].

A Panalytical X'Pert Pro MPD Diffractometer using Cu-K $\alpha$  radiation operated at 45 kV and 40 mA current was used to characterize the mineralogy of random powder mounts of bulk soils (< 2 mm size fraction), over a range of 2 to 70°  $\theta$ . Bulk soils were ground by hand with an agate mortar and pestle to <53  $\mu$ m prior to XRD analysis. Quantitative estimates of the total crystalline and amorphous phases were determined by the Rietveld method [8]. The XRD analysis of the clay size fraction (<2  $\mu$ m) was described previously[10].

Silt size fractions of the soil samples were mounted on sticky tape attached to a stub and carbon-coated for morphological analysis using a JSM 5910LV scanning electron microscope equipped with an iXRF energy dispersive X-ray spectroscopy (EDS) system. The <0.2  $\mu$ m fraction of selected soils were mixed in water and dispersed onto a carbon coated copper grid and were examined without coating under a JEOL 2000FX scanning transmission electron microscope (TEM) operated at 200 kV at 10 nA beam current.

#### **Results:**

*Subxerous soil.* Soluble ions in the coastal Taylor Valley soil profile were dominated by Na<sup>+</sup> and Cl<sup>-</sup>. The 1-9 cm horizon is the most saline in the profile; all cations, as well as SO<sub>4</sub><sup>2-</sup> are most abundant here. The maximum Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> concentrations were observed in the 12-17 cm horizon. PO<sub>4</sub><sup>3-</sup> was only below 17 cm.

XRD of the bulk soils from Taylor Valley were generally dominated by feldspar (22-53%), quartz (4-16%) and x-ray amorphous materials (3-50%), and lesser pyroxene (2-8%), mica (4-10%), amphibole (2-8%), vermiculite (1-3%), and crystalline salts (3.5-9%). The amount of amorphous materials present generally increased with depth, with the exception of the 20-24 cm horizon which has a slight depletion. Trace amounts (1-3%) of olivine were identified from 12-24 cm. Gypsum was identified in the 1-9, 9-12 and 12-17 cm horizons. Nitratine was identified in the 12-17 and 24-28 cm horizons and Ca-sulfate in the 28+ cm horizon.

Pyrite framboids were identified by SEM throughout the Taylor Valley profile. Ca-phosphate was identified in the 1-9, 9-12 and 20-24 cm horizons by SEM, and needle-like crystals that contain Ca (assumed to be

CaCO<sub>3</sub>) were observed by SEM in the 24-28 cm and 28+ cm horizons, which are the two horizons with the most alkaline pHs (8.5-8.7). TEM (Figure 1a) of the clay size fraction from the 0-1 cm horizon shows the weathering of a mica particle from the outside inward with a pristine core intact. (b) TEM of clay fraction from the 20-34 cm horizon of the University Valley site. Image shows fine grained, crystalline mica particles (EDS analysis: Si>Al>Mg-Fe>K), scale bar reads 0.2 μm.

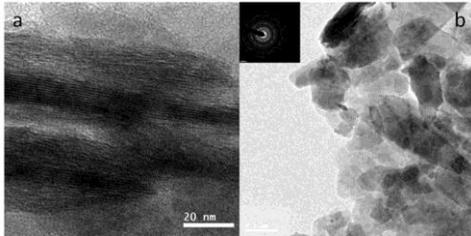


Figure 1. (a) TEM of clay fraction from the 0-1 cm horizon of the Taylor Valley site. Image shows the weathering of a mica particle from the outside inward with a pristine core intact. (b) TEM of clay fraction from the 20-34 cm horizon of the University Valley site. Image shows fine grained, crystalline mica particles (EDS analysis: Si>Al>Mg-Fe>K), scale bar reads 0.2 μm.

**Ultraxerous soil.** Soluble ions in the University Valley profile were dominated by Na<sup>+</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>. The top two horizons are particularly saline, with the maximum for all soluble ions occurring here. No PO<sub>4</sub><sup>3-</sup> was observed in this soil profile. The pH values for the entire profile are near neutral (6.9-7.3).

XRD of the bulk soils from the profile in University Valley were generally dominated by quartz (> 55%), with lesser amounts of feldspar (11-14%), crystalline salts (7-10%), mica (6-9%), laumontite (1-3%), pyrophyllite (2-3%), x-ray amorphous materials (4-9%) and chlorite (1-2%). X-ray amorphous materials were concentrated below 20 cm, though small amounts were found in the upper two horizons. Gypsum and nitrate were found throughout the profile, with the maximum concentration observed in the 9-20 cm horizon.

Gypsum crystals observed in the SEM (Figure 2) of the 34+ cm horizon have a uhedral shape, while the gypsum identified in the higher horizons have a rounded shape. SEM also identified the presence of iron oxide particles in the 34+ cm horizon. TEM indicates the presence of mostly crystalline, fine-grained phyllosilicates in the clay size fraction, e.g., mica, of the 9-20 cm horizon. The TEM of the 20-34 cm layer shows the presence of sub-micron quartz crystals, fine particles of mica (Figure 1b) and nanophase Ti-oxides. Preliminary Mössbauer data suggests the presence of iron oxides throughout the profile. It is possible that the small amounts X-ray amorphous material identified in the XRD is comprised of nanophase Fe and Ti oxides. No evidence of weathering has been seen on the surface of the mica or chlorite in the TEM, which then suggests the alteration in University Valley is limited to Fe-oxidation and salt precipitation.

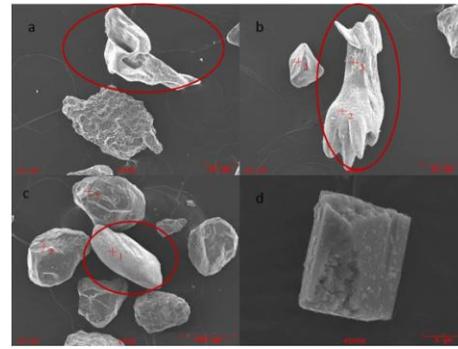


Figure 2. SEM images of gypsum crystals from University Valley at depths of (a) 1-9 cm, (b) 9-20 cm, (c) 20-34 cm and (d) 34+ cm.

**Implications for Mars:** In Taylor Valley, our mineralogical results are consistent with a warmer, wetter, and more dynamic environment than University Valley. Fe-oxidation and salt formation in University Valley dry-permafrost soils suggest oxidative, aqueous alteration under very dry and cold conditions. We hypothesize that the aqueous alteration is due to thin films of water on particle surfaces similar to the hypothesis recently suggested for the formation of aqueous phases in Mars Phoenix soils [11]. Aqueous alteration and oxidation of upper soil horizons in University Valley soils provide a mechanism for the formation of Fe-oxides and possibly poorly crystalline aluminosilicates on Mars. Atmospheric water vapor transport into Martian soils interacts at surfaces of basalt particles (i.e., thin films) resulting in aqueous alteration and Fe oxidation. University Valley soils are excellent terrestrial analogs to characterize “pedogenic” processes that may be occurring in Martian soils.

**References:** [1] Doran, P. *et al.* (2002) *JGR*, doi:10.1029/2001JD002045. [2] Campbell and Claridge (1981) *JRSNZ*, **11**, 401-410. [3] Keys and Williams (1981) *Geo. Cosmo. Acta.*, **45**, 2299-2309. [4] Bockheim, J. (2007) *Geografiska annaler, Series A, Physical Geography*, **89**, 153-165. [5] Gibson, E. *et al.* (1983) *JGR*, **88**, A912-A928. [6] Soil Survey Staff (2006) *Keys to Soil Taxonomy*, 10<sup>th</sup> ed. USDA-NRCS, Washington, DC. [7] Rhoades, J.D. (1982) *Methods of Soil Analysis. Part 2: Chemical and Microbiological Properties*, p. 167-180. Soil Science Society of America, Inc., Madison, WI. [8] Tamppari, L., *et al.* (2011) *Submitted to Antarctic Science*. [9] Kounaves, S. P. *et al.* 2010, *Environ. Sci. Technol.*, **44**, 2360-2364. [10] Quinn, R. *et al.* (2010) *LPSC*, Abstract 2403. [11] Boynton, W.V. *et al.* (2009) *Science*, 325: 61-64.