

X-RAY AMORPHOUS COMPONENTS OF ANTARCTICA DRY VALLEY SOILS: WEATHERING IMPLICATIONS FOR

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Introduction: The Antarctic Dry Valleys (ADV) comprise the largest ice-free region of Antarctica. Precipitation usually occurs as snow, relative humidity is frequently low, and mean annual temperatures are about -20°C [1]. Substantial work has focused on soil formation in the ADVs [2], 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 [3]. The occurrence of chemical weathering processes are suggested by the presence of clay minerals and iron and titanium oxides in soil. Previously we have investigated soils from two sites in the ADV's and have shown evidence of chemical weathering by the presence of clay minerals (vermiculite, smectite), short-range ordered (SRO) and/or X-ray amorphous materials, and Fe- and Ti-oxides as well as the presence of discrete calcite crystals [4, 5].

The Chemistry and Mineralogy (CheMin) instrument onboard the Mars Curiosity rover has detected abundant amounts (approx. 25-30 wt. %) of X-ray amorphous materials in a windblown deposit or "soil" (Rocknest) and in a sedimentary rocks [6,7,8]. The occurrence of large amounts of X-ray amorphous materials in Mars sediments is surprising because these materials are usually present in small quantities in terrestrial environments.

The objective of this study is to further characterize the chemistry and mineralogy, specifically the secondary alteration mineralogy and the presence of X-ray amorphous material, of soils from two sites we have previously studied, a subxerous soil in Taylor Valley, and an ultraxerous soil in University Valley. While the chemical alteration processes and mineralogy of the ADV has been documented previously, there has been limited discussion on the occurrence and formation of X-ray amorphous and SRO materials in Antarctica soils. The process of aqueous alteration in the ADVs may have implications for pedogenic processes on Mars, and may lead to a better understanding to the abundance of amorphous material found in sediments in Gale crater.

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 [9]. 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: Two different X-ray diffraction (XRD) instruments and methods were employed to characterize the mineralogy. A Panalytical X'Pert Pro MPD Diffractometer using Cu-K α 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 ground to less than 53 μ m), over a range of 2 to 70° with a 0.0167° step size.

A CheMin IV testbed instrument was used as an analog instrument for CheMin on Curiosity. CheMinIV employees Co-K α radiation, utilizing a transmission sample cell that is shaken piezoelectrically during analysis. Bulk soil samples (<2 mm) were sieved to < 150 μ m (fraction analyzed by the CheMin instrument on Mars). Data was collected from 4° to 56° 2 θ with a ~0.35° angular resolution. The CheMin instrument on the Curiosity rover discards the >150 μ m fraction prior to X-ray analysis and therefore analogous studies must be done using <150 μ m fraction. Quantitative estimates of the total crystalline and amorphous phases were determined by the FULLPAT method with no internal standard to replicate the analysis done on Martian soils [10].

Results:

Taylor Valley (TV): Table 1 provides results from XRD analysis of the soils from the permafrost layer (28+ cm depth) of the Taylor Valley pit. Panalytical XRD analyses of the bulk soils (<2mm size fraction) from TV were generally dominated by feldspar and quartz,

however X-ray amorphous materials (15 wt. %) and phyllosilicates were most abundant in the horizon near the permafrost contact. CheMin IV XRD analyses of the < 150 µm size fraction shows a substantially larger quantity of X-ray amorphous materials (42 wt. %) along with mica. The large differences in quantities of X-ray amorphous materials for the two methods is not surprising because the CheMinIV analysis is sampling a smaller particle size fraction.

Mineral	Panalytical (wt%)	CheMin (wt%)
Plag Feldspar	46	17
Quartz	8	3
Pyroxene	3	2
Mica	10	20
Amphibole	6	3
V/S/C	8	2
Aragonite	4	4
Salts	TRACE	TRACE
Amorphous	15	42

Table 1. XRD Results from permafrost horizon of Taylor Valley soil. V/S/C= Vermiculite/Smectite/Chlorite.

Transmission electron microscopy (TEM) indicated that mica was altering to vermiculite, which was subsequently altering to smectite, SRO smectite, and X-ray amorphous materials. Hence, the large X-ray amorphous component in TV soils is the aqueous alteration product of mica inherited from granitic materials during glaciation of Taylor Valley.

University Valley (UV): In general, there is a much smaller quantity of clay-size particles in UV soil compared with the TV soil, which is expected under the dryer conditions found in UV. Panalytical XRD analyses of the bulk soils from the profile in UV were generally dominated by quartz, with lesser amounts of feldspar, crystalline salts, mica, x-ray amorphous materials and chlorite.

Mineral	Panalytical (wt%)	CheMin (wt%)
Feldspar	9	9
Quartz	69	39
Pyroxene	1	ND
Mica	8	31
Chlorite	3	2
Zeolite	2	2
Gypsum	2	TRACE
Hematite	TRACE	1
Salts	TRACE	TRACE
Amorphous	5	15

Table 2. XRD Result from permafrost (34+ cm) horizon of University Valley. ND= not determined.

Table 2 shows XRD results from the permafrost layer of the UV horizon. X-ray amorphous content increases in the CheMinIV analysis similar to the analyses of TV soils. TEM analysis indicates the presence of mostly crystalline, fine-grained phyllosilicates in the clay size fraction, e.g., mica, and nanophase Fe- and Ti-oxides. The X-ray amorphous material is most likely comprised of nanophase Fe and Ti oxides. No evidence of weathering was observed on the surface of the mica or chlorite in the TEM, which suggests the alteration in UV is limited to Fe-oxidation and salt precipitation.

Implications for Mars: X-ray amorphous and secondary phyllosilicates in Taylor Valley soils are consistent with a warmer, wetter, and more dynamic chemical-weathering environment than University Valley. However, the high abundance of X-ray amorphous materials in Taylor and University Valleys is surprising for one of the coldest, driest places on Earth. These materials have been physically and chemically altered during soil formation, however, the limited interaction with water and low temperatures have resulted in the formation of “immature” X-ray amorphous or SRO materials. The kinetics are slow and insufficient to result in well-ordered secondary phases. Perhaps, a similar process contributes to the formation of the high content of X-ray amorphous materials detected on Mars. The comparison of the two X-ray diffraction methods discussed here suggests that the X-ray amorphous content measured by CheMin (i.e., < 150 µm fraction for Rocknest) is greater than what would be found in the bulk soil (defined at <2mm in size). Terrestrial soils are typically ground bulk samples, including <2mm size fraction for bulk soil mineralogy. On Mars, there is a limitation of only examining the less than <150 µm fraction, which causes a concentration of the fine particle phases. More detailed X-ray diffraction studies are required on additional soil horizons to fully understand the variation in x-ray amorphous material in the ADV and the abundance of amorphous found on Mars.

References: [1] Doran, P. *et al.* (2002) *JGR*, doi:10.1029/2001JD002045. [2] Bockheim, J. (2007) *Geografiska annaler, Series A, Physical Geography*, **89**, 153-165. [3] Gibson, E. *et al.* (1983) *JGR*, **88**, A912-A928. [4] Quinn, J.E. *et al.* (2010) *LPSC*, Abstract 2403. [5] Quinn, J.E. *et al.* (2011) *LPSC*, Abstract 2670 [6] Bish, D.L., *et al.* (2013) *Science*, **27**, 341, 1238932. [7] Vaniman, D.T. *et al.* (2014) *Science*, **343**, 1243480. [8] Rampe, E.B. *et al.* *Earth and Planetary Science Letters*, **471**, 172–185. [9] Soil Survey Staff (2006) *Keys to Soil Taxonomy*, 10th ed. USDA-NRCS, Washington, DC. [10] Chipera, S.J., Bish, D.L., 2002. *J. Appl. Crystallogr.* **35**, 744–749.