

SALT AND SECONDARY SILICATE MINERALOGY IN ANTARCTIC SOIL PROFILES:

IMPLICATIONS FOR MARTIAN SOILS. A. C. McAdam¹, C. A. Knudson^{1,2}, S. Andrejkovičová^{1,2}, J. C. Stern¹, S. T. Wieman^{1,3}, A. Fox⁴, J. L. Eigenbrode¹, I. L. ten Kate⁵, R. P. Harvey⁶, P. R. Mahaffy¹. ¹NASA GSFC, Greenbelt, MD 20771, Amy.McAdam@nasa.gov, ²CRESST, Univ. of Maryland, College Park, MD, 20742, ³CRESST II, Univ. of Maryland, Baltimore, MD 21250, ⁴Penn. State Univ., University Park, PA 16802, ⁵Utrecht Univ. Budapestlaan 4, 3584 CD Utrecht, The Netherlands, ⁶Case Western Reserve Univ., Cleveland, OH 44106.

Introduction: Oxychlorine minerals (e.g., perchlorates, chlorates) have been detected by the Mars Science Laboratory (MSL) Sample Analysis at Mars (SAM) instrument suite in most Gale crater samples [e.g., 1], and detected at other sites on Mars [2,3]. Nitrates were also detected by SAM [4], and the ratio of nitrate to oxychlorine abundances in samples shows a trend that may result from a combination of factors including rates of input (e.g., from atmospheric sources) and aqueous redistribution of these soluble salts [5]. These salts co-occur in some semiarid and arid settings on Earth, such as Antarctic Mars analog environments, though generally there are more nitrate and less oxychlorine compounds than in martian materials [5,6]. Antarctica hosts key hyperarid Mars analog environments that bear these salts. These environments are commonly used to study a variety of Mars-relevant alteration processes, as they can provide some of the coldest and driest environments on Earth. We studied soils developed from basaltic materials in the Davis-Ward region of the Central Transantarctic Mountains. These soil environments are farther from open ocean and at higher elevation than Dry Valley soils. Samples were collected from surfaces of different apparent ages. Here we focus on the chemistry and mineralogy of a soil that developed three horizons including a duricrust horizon a few cm below the surface.

Methods: Powder patterns acquired with a Bruker D8 Discover x-ray diffractometer (XRD, Cu K α) were used to study the bulk mineralogy of each soil horizon. Near infrared (NIR) spectra were acquired using a Thermo Scientific (Nicolet iS50) FT-IR spectrometer with an integrating sphere NIR module. SAM-like evolved gas analysis mass spectrometry (EGA-MS) used a Pfeiffer HiQuad QMS coupled to a custom SAM-like oven heated to $\sim 860^\circ\text{C}$ at $35^\circ\text{C}/\text{min}$. Evolved gases were carried by an He carrier gas to the MS where they were detected by their mass-to-charge ratio (m/z). Bulk $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ and total C and N were measured on a Costech Elemental Analyzer (EA) connected to a Thermo Scientific Delta V isotope ratio mass spectrometer (IRMS). Ion chromatography mass spectrometry, used to estimate perchlorate abundances, was performed on water soil extracts using U.S. EPA Method 314.1 on a Thermo ICS-2100-MSQ.

Results: The soil was covered by a desert pavement of interlocking cobbles. This soil sat atop, and is

primarily derived from, Ferrar dolerite (diabase) exposures. Rocks show fracturing, likely due to ice and/or salt wedging, and possibly thermal expansion/contraction, as observed elsewhere in Antarctica [e.g., 7]. Some rocks exhibited discontinuous reddish weathering rinds/coatings which were exfoliating. These processes may help to produce soil materials.

All horizons contain clay minerals, though they are most abundant in the bottom layer. Analysis of separated clay size fractions is currently underway, but preliminary work suggests the horizons contain chlorite-smectite minerals that are broadly similar except for some differences in octahedral cations indicated by NIR spectra (Fig. 1). The bottom layer shows a ~ 2.3 μm band not observed in the other layers, indicating more octahedral Mg. EGA-MS H₂O evolution trends were similar for top and bottom layers (Fig. 2a). Peaks at 200 and $\sim 300^\circ\text{C}$ are likely due to dehydration of

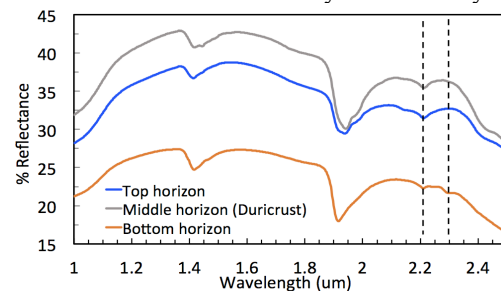


Fig. 1. NIR spectra from soil horizons show some differences in smectite clay mineral octahedral cations.

hydrated salts (nitrate, sulfates) and goethite-like phases, respectively. Peaks near $\sim 530^\circ\text{C}$ are likely from clay mineral dehydroxylation; this temperature is consistent with a chlorite-smectite phase as well as some dioctahedral smectites. The similarity of dehydroxylation temperatures implies that the differences in octahedral cations were not large enough to impact dehydroxylation temperature.

Significant nitrates were detected in all layers, both by XRD and EA total N values (NO_3 contents: $\sim 5 \times 10^4$ to $\sim 1.6 \times 10^5$ mg/kg). The lowest abundances were in the top horizon, while the middle and bottom horizons had similar abundances with slightly more in the middle (duricrust) layer. EGA NO evolution temperatures indicate that the top horizon is dominated by Ca nitrate ($\sim 620^\circ\text{C}$ peak), the middle has Ca and Na nitrate, and the lower has Na nitrate ($\sim 730^\circ\text{C}$ peak) (Fig. 2b). The

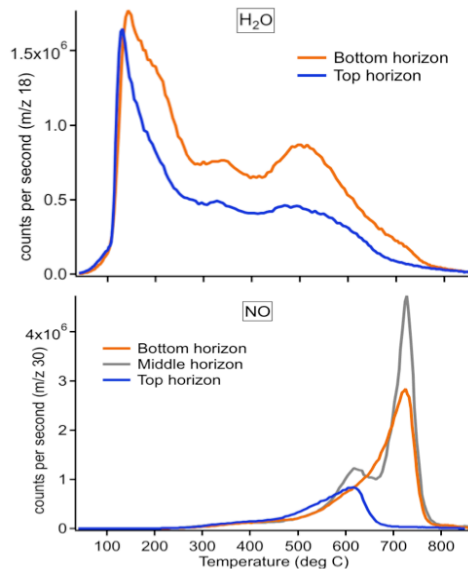


Fig. 2. a) SAM-like EGA H₂O traces (top) and b) NO traces (bottom) from soil horizon samples.

data also suggest minor Mg nitrate in all samples. XRD and evolved SO₂ in EGA indicate sulfates are also present in all samples, with abundant Mg and Ca sulfates in the duricrust and lesser amounts in the top layer. The bottom layer shows only Ca sulfates. Perchlorate abundances range from 1 to 10s of ppb ClO₄ with the highest amounts observed in the bottom layer.

Discussion: Overall, nitrate and perchlorate abundances are higher and lower, respectively, than in several other Antarctic soils from hyperarid environments [e.g., 6], though they are within an order of magnitude. The dominant sources of perchlorate and nitrate anions to inland, hyperarid regions of Antarctica are thought to be atmospheric [e.g., 8,9]. While we did not assess soil biological activity, we hypothesize that it is minimal, as in other Antarctic hyperarid soils [e.g., 6]. This is also supported by low soil total carbon (0.01-0.06 %). Soil subsamples were collected using organically clean methods; future work on any soil organic compounds may inform on levels of biological activity.

The soil's significant sulfate content is another similarity to other Antarctic analog soils. As with nitrates and perchlorates, atmospheric sources are thought to contribute sulfate anions [e.g., 8]. Analyses of the oxygen isotopic composition of soil sulfates, and nitrates, would enable atmospheric contributions to be assessed [e.g., 10,11], and we will pursue this in the near term.

Differences in salt abundances and cation compositions in our soil profile are likely due to a combination of salt solubility differences and the ion composition of weathering solutions as they move within the profile. The very soluble nitrate and perchlorate salts are most abundant in the bottom layer, whereas sulfates are

most abundant in the middle duricrust layer. These trends probably result mainly from differences in solubility, with less soluble sulfates precipitating out before perchlorate and nitrate as weathering solutions move downward. Nitrate, perchlorate, and sulfate remaining in the top layer, together with a dominantly atmospheric origin for those ions, suggests that the rate of downward aqueous redistribution of the salts is slower than the input of atmospheric aerosols to the top of the soil, or that there is also occasional upward movement of solutions.

Implications: Soil crusts were observed at the Viking landing sites [12], Mars Exploration Rover sites [13], possibly at the MSL Rocknest site [14], and are potentially widespread on Mars [e.g., 15]. Martian soils, and duricrusts, are enriched in S and Cl, and a significant atmospheric contribution (e.g., volcanic aerosols) is often hypothesized [e.g., 16,17]. These elements are thought to be largely in potentially mobile salts, as are atmospheric salt ions in Antarctic analogs. Although martian, and hyperarid Antarctic, sites, have very little water, work on Antarctic soils has shown that very low water-to-rock (W/R) (e.g., thin water film) processes in stable surfaces can move salts within soil profiles [e.g., 7].

Analog work suggests that martian S and Cl-rich soil crusts may also have associated nitrate salts and that Cl in or below crusts may be in both soluble chloride salts and more soluble oxychlorine phases (which have solubilities closer to those of nitrates). Detecting nitrate salts in potentially fine-scale soil layers with in situ techniques can be more difficult than sulfate salts because N is a light element, but techniques such as LIBS could enable N detection if present above detection limits [18]. Abundances and cation compositions of these salts in martian soil profiles could enable constraints on potential ion sources and redistribution fluids. Analog work also suggests that low W/R conditions that move soil salts can alter silicate materials to produce secondary minerals such as phyllosilicates.

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