THE MINERALOGY AND CATION EXCHANGE OF SEDIMENTS IN DON JUAN POND, ANTARCTICA DRY VALLEY: IMPLICATIONS FOR MARS. V. M. Tu[1], D. W. Ming[2], and R. S. Sletten[3]
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Introduction: Located in the McMurdo Dry Valleys of Antarctica (MDV) is among of the saltiest bodies of water of Earth, Don Juan Pond (DJP) [1]. DJP pond waters are unique in that they contain nearly 40% salt by weight including 95% $CaCl_2$ [1-5] and they never evaporate or freeze entirely due to the high hygroscopicity and low eutectic temperature of the $CaCl_2$ brine (-52˚C) [6]. The source of DJP water is suggested to be due to groundwater upwelling through a weathered dolerite aquifer and/or near-surface runoff, including salt deliquescence in the pond's watershed [7,8], however the source of water is still a topic of study.

During the 2017-2018 field season, we collected soil samples and altered sediments on hillslopes and drainage basins near the pond (Fig. 1). Two drill bores were also acquired in Don Juan Pond sediments in a episodically flooded area of the pond basin. This study's objectives were to characterize the mineralogy of these soils and sediments to determine if there are mineralogical indicators and/or controls for the delivery of salts to DJP and understand the role of salts on Mars on these analog studies.

Materials and Methods:

Study Site. DJP resides within a salt pan DJP approximately 800m long (E-W) and 250m wide (N-S), with a pond depth of ~10-30cm (Fig. 1) [9,10], bound by a rock glacier to the west, small basins to the east, and steep colluvial slopes to the north and south [8]. The mineralogy of the DJP reflects the granitic basement material and the surrounding mountains of Beacon sandstone and Ferrar dolerite (Jurassic-aged dolerite sills) [11]. Two boreholes approximately 1.5 meters deep were extracted from near the water line in DJP sediments (Fig.1), and sampled loose fines were collected at 10 cm intervals. Soil pits were excavated, described, and sampled in the drainage basins that flow into DJP. Several small streams flow out of a rock glacier into the pond and a drainage basin with a small stream channel (dry surface but evidence of subsurface water flow) is evident in the eastern watershed.

Sediments were sampled from several euphemeral lakes in the eastern watershed towards a ridge that separates the DJP and Lake Vida drainage basins. Visual observations suggest that most of the water in the eastern watershed is supplied by snowmelt from the Asgard Mountains. Mineralogy of the core and soil samples was characterized by XRD. Samples were analyzed in the field with a Terra XRD instrument and in the laboratory with a PANalytical XRD.

Results and Discussion: Mineralogy of pond sediments indicates that salt formation and concentrations are due to evaporation wicking of salts towards the surface. Smectite is common in lake sediments and may provide cation exchange control for salts in DJP.

Salt Mineralogy. Core 1, sampled outside of the "wet" zone, contains higher abundances of gypsum than core 2. Halite abundance are relatively similar between the two boreholes and is concentrated near the surface of the DJP sediments (Fig. 2). Gypsum is also abundant near the surface and decreases with depth until encountering the water table, and then abundances significantly increase (Fig. 2). The concentration of more soluble salts near the surface in DJP sediments indicates that water movement was upwards, most likely by pond water evaporation.

Clay Mineralogy. All borehole sediment samples contained about 5 wt. % smectite (Fig. 3) and abundant smectite (20- 35 wt. %) was present in sediments from ephemeral lakes in the eastern watershed towards the ridge that separates the DJP and Lake Vida drainage basins. No smectite was observed in the soil samples around the pond.

Smectite tends to be the most common authigenic clay mineral and can form at low temperatures and low pressures [12]. We hypothesis that smectite formed insitu as an alteration product of granitic mica in the glacial till, or weathering of Ferrar dolerite sills and dikes that intrudes the valley walls to the south and north of the pond. The high salt contents of DJP and other pond basins in the vicinity may aid in providing aqueous conditions that enhance the formation of smectite. Generally, synthesis of smectite requires the presence of Mg in solution [12], hence, smectite formation in DJP and other lake sediments with high Ca^{2+} water concentrations may be the result of the alteration of mica under sustained aqueous conditions due to the lowering of the freezing point of H_2O [13].

Antarcticite. An extremely hygroscopic and cryogenic mineral, Antarcticite ($CaCl_2.6H_2O$), was observed in field XRD measurements at DJP. Antarcticite readily precipitates and dissolves with diurnal changes; evaporation of the pond causes precipitation and then dissolves during freshwater input during the "hotter" times of the day. Deep groundwater models yielded early precipitation of antarcticite, which were hypothesized to limit the concentration of Ca^{2+} [8] however this is inconsistent with the high Ca^{2+} concentrations (5.6mol kg^{-1}) measured in DJP. Antarcticite may play a role in influencing the concentrations of Ca^{2+}, but further investigation is required.

Cation Exchange. Smectite in DJP and adjacent lake sediments may selectively remove Na^{+} from the solution and provide a mechanism for enhancing Ca^{2+} in lake waters. [14] reported temperate climate soils showed an affinity for Na^{+} with an increase in ionic strength. Salts affect the surface charges of clay particles, and an increase in ionic strength can increase the surface charge of clays, which can act as temporary ion repositories for cation exchange [15]. Also, interlayer charge in smectite and ionic strength of solutions will have a role in the selectivity of Na^{+} and Ca^{2+} on exchange sites.

Previous studies have suggested salts were introduced into the pond by groundwater upwelling through a weathered dolerite aquifer and/or via near-surface run-off, including salt deliquescence in the pond's watershed. Here we hypothesis that cation exchange with smectite affects the type of ions delivered to DJP brines. Smectite formation in streams and lakebeds provides an avenue to exchange Ca^{2+} for Na^{+}, thereby providing a mechanism to "concentrate" Ca^{2+} in DJP water. Clay mineral ion selectivity experiments by [16] demonstrated that the selectivity of divalent ions over monovalent cations varies considerably with changes to ionic strength, and an increase ionic strength and entropy cause a preference for Ca^{2+} over Na^{+}. [17] indicated an increase in the surface concentration of high-charge ions generally increases up to a maximum, and then decreases beyond that. This may be one mechanism responsible for Ca^{2+} in DJP, however, more research is required to determine critical variables such as interlayer charge density, cation exchange capacity, and cation selectivity under various ionic strength systems.

Implications for Mars: DJP is a unique analog site for Mars (chloride deposits) to understand the habitability potential on Mars in these types of environments [2,3]. Mars is a cold, dry environment, and aqueous flows on Mars may be enhanced by CaCl2-rich brines [3,18,19].

Cation exchange may have played a role early in Mars history in concentrating and removing salt cations in clay minerals. Smectite and chlorite are the most abundant phyllosilicates on Mars [20], and partial chloritization has been hypothesized as a mechanism for expanded smectite in Gale crater [21, 22] due to cation exchange. High ionic-strength water similar to DJP brines may provide a low-temperature aqueous environment for forming clay minerals on Mars.

Figure 1. Core samples and water drainage into Don Juan Pond.

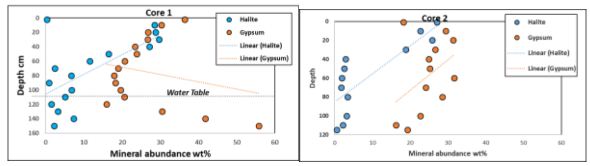

Figure 2. Halite and gypsum mineral abundance trends for DJP core sediments. Halite is concentrated near the surface and decreases with depth. Gypsum decreases with depth to the water table and then increases with depth below the water table.

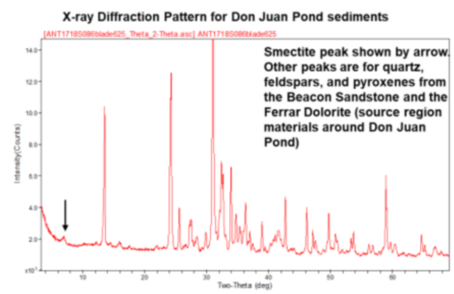

Figure 3. X-ray diffraction pattern for the 80-90cm DJP core sample. The black arrow indicates the 001 basal peak for smectite (~15Å). Other major peaks are quartz, feldspar, and pyroxenes from the Beacon Sandstone and the Ferrar Dolerite from the source region materials around DJP.

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