A GRADIENT OF CHEMICAL ALTERATION IN DON JUAN BASIN, ANTARCTICA AND APPLICATIONS TO MARS.

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Introduction: Antarctica is a barren continent, largely covered in ice. Some regions, however, such as the McMurdo Dry Valleys (MDV), offer a rare glimpse of ice-free land. Mean annual temperatures in Wright Valley range from -17 to -22 ºC, and mean annual precipitation, exclusively as snowfall, ranges from 5 to 10 cm in valley floors [1]. Despite low average temperatures, liquid water can form under special thermal and chemical conditions. The cold and arid MDV climate makes this region a good physical analog for processes taking place on modern Mars. Don Juan Pond (DJP), located in the South Fork of Wright Valley, is the second saltiest body of water on Earth and stands out as a permanently liquid pond. While physical alteration dominates near DJP [e.g., 2], chemical alteration has been found to occur.

There is evidence that DJP has been ice-free for ~2 million years [3], suggesting that standing water and related aqueous processes may have been present in the region for a similar length of time. This hypothesis is supported by the glacial history of the area, which indicates that the East Antarctic outlet glacier has not advanced into Wright Valley for at least the past 3.8 million years [4]. Instead, there has been a moderate expansion of local, cold-based alpine glaciers during the Pliocene period, along with continuous cold-desert conditions in Wright Valley [2, 3].

This study aims to determine the degree of chemical alteration occurring in and around DJP as a way of inferring the historical size of the pond. Our research will help to better understand the spatial extent of the pond over time and could serve as a model for understanding the past spatial extent of water across analogous landscapes such as Mars.

Methods: Sample cores were collected from three locations in and near DJP: the center of the pond (core #2074); 150 m southwest of DJP (#33); and 300 m southwest of DJP (#39) [5]. The core 2074 location is ~116 m above sea level, while Cores 33 and 39 are located near 116.4 m elevation. All samples investigated here were ground to size fractions <125 µm.

Major, minor, and trace element abundances were measured using X-ray fluorescence (XRF). Sulfur measurements and Loss on Ignition (LOI) at 1000 °C were also conducted using LECO combustion. Additional minor and trace element abundances, including those of the rare earth elements, were measured by instrumental neutron activation analysis (INAA) [6, 7].

Reflectance spectra were measured at the Reflectance Experiment Laboratory (RELAB) at Brown University from 0.35-2.5 µm under ambient conditions and spliced near 1.2 µm to FTIR spectra measured from 1 to 50 µm under controlled dry conditions. Mineralogical analysis was conducted with an Olympus Terra-166 X-ray Diffraction (XRD) instrument, which was designed as a field XRD unit [e.g., 7].

The Chemical Index of Alteration (CIA) is a quantitative method based on feldspar alteration (ratio of Al to the relatively mobile cations Ca, Na, K) used to measure the degree of chemical weathering having taken place during pedogenesis. The CIA is defined as CIA = $Al_2O_3/Al_2O_3 + CaO^* + Na_2O + K_2O$ (molar basis) where CaO* is the amount of CaO in the silicate fraction of the samples [8].

Results and Discussion: *Elemental Analyses:* Due to their relative immobility, primary oxides Al_2O_3, Fe_2O_3, and TiO_2 can be used to assess the degree of sample alteration in geologic samples [9]. All samples in our study exhibit comparable abundances of Fe_2O_3 between 3.34 and 5.24 wt %. However, starting from the center of DJP with core 2074, both Al_2O_3 (5.74-11.9 wt %) and TiO_2 (0.28-2.19 wt %) abundances increase on average with distance from the pond, i.e., from Core 2074 to Core 39 (Figure 1). The Th/U elemental ratio can be used to assess the degree of sample alteration as well due to the relative immobility of Th and U. Samples from the center of DJP (core 2074) have the lowest Th/U values while the Th/U ratio increases radially outwards towards cores 33 and 39 (Figure 2).

Mineralogy: Results from reflectance spectroscopy and XRD correlate well in general and both methods detect quartz, pyroxene, and silicate minerals (augite, mica, orthoclase, albite) in all samples [5]. Sulfates, including aqueously-derived anhydrite, gypsum, and thenardite support a trend of decreasing abundance of sulfate salts with distance from the center of DJP (Figure 3). This is supported by δ^{34}S values of sulfate measured near DJP (+27.1 ‰ to +32.5 ‰), and total sulfur abundance measured near DJP, compared to lower values farther uphill (eastward) along the South Fork of Wright Valley (+15.8 ‰ to +23.4 ‰) [10].

CIA: Analysis of CIA values indicates increasing alteration from the center of the pond outwards. Core 2074 samples exhibit the lowest values, ranging from 15 to 23, while core 33 and 39 samples show higher ranges of CIA values, ranging from 34 to 40 and 36 to 48, respectively. This trend is unexpected and is attributed to a salt dilution effect, where the sulfate-enriched core

2074 samples experience the highest salt dilution effect. We propose a modification to the CIA that takes into account the salt dilution effect that we believe is affecting Cores 2074 and 33 [11]. With this modification, we believe the resulting CIA values would align with the other chemical alteration indicators discussed in this study [5]. If valid, this modified CIA equation could be applied to other saline environments.

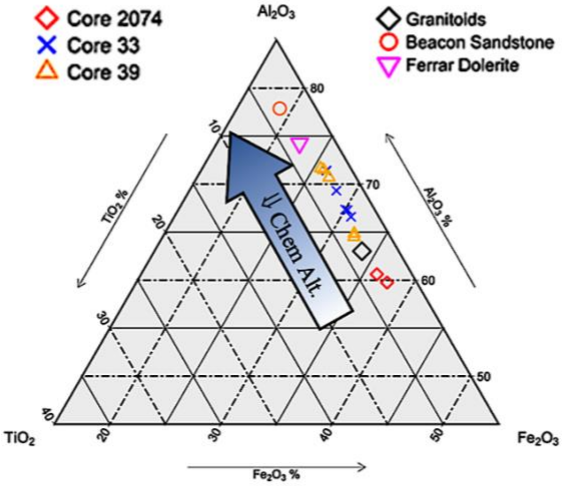

Figure 1: *Comparison of Al_2O_3, TiO_2, and Fe_2O_3 abundances of DJP cores 2074, 33, and 39. Oxide abundances have been summed and each oxide's individual abundance is plotted as a percent of the sum. Local geologic constituents "Granitoids", "Beacon Sandstone", and "Ferrar Dolerite" oxide abundances are included for comparison.*

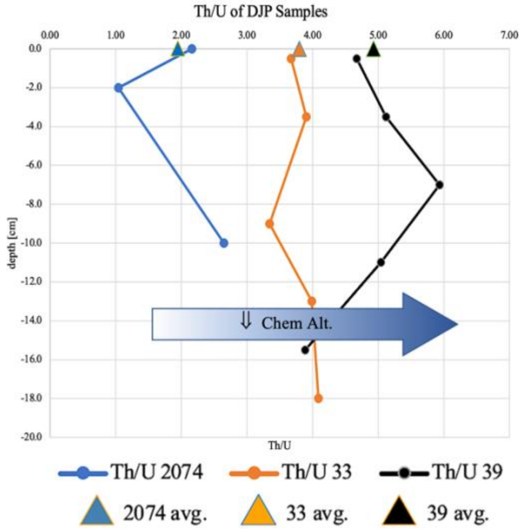

Figure 2: *Th/U of DJP cores. Th/U values in core 2074, in the center of Don Juan Pond, are the lowest. Values increase approaching cores 33 and 39, located 150 and 300 meters to the southwest, respectively.*

Chemical Alteration Gradient: Primary oxide trends shown in Figure 1, Th/U ratios shown in Figure 2, and sulfate minerals shown in Figure 3, suggest a closer relationship between cores 2074 and 33, than 39. Sediments near DJP are classified as Salic Aquorthels [12], but separate measurements of anion distributions suggest that this classification only applies to core 39, which also has a high variability of soluble ions. Cores 2074 and 33 do not have a salic horizon within 100 cm of the mineral soil surface and have constant levels of soluble ions [5, 12]. This may be due to aqueous inundation that only reached as far as core 33. Based on these findings, we propose that DJP was larger in the past and extended up to Core 33, but not as far as Core 39.

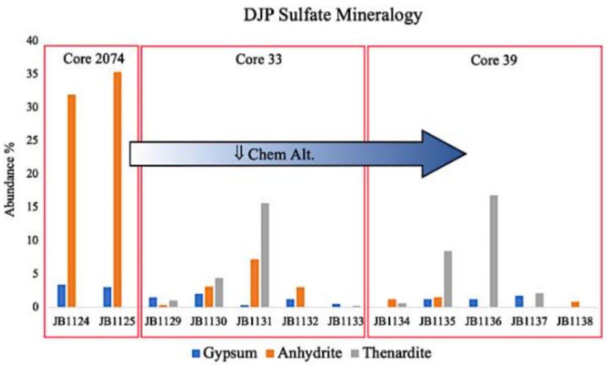

Figure 3: *Percent abundance of gypsum, anhydrite, and thenardite in DJP cores 2074, 33, and 39.*

Implications: This study used multiple techniques to investigate the degree of chemical alteration with proximity to DJP to infer the pond's historical size. Results show that chemical alteration decreases with distance from the pond, possibly due to a once larger body of water that receded over time. These methods and results can be used to gain a better understanding of the spatial extent and aqueous history in similar terrestrial and extraterrestrial environments, such as Mars, while providing a clearer picture of geochemical processes at work.

Acknowledgments: We thank the SETI Institute, The Hawai‘i Institute of Geophysics and Planetology, and the Department of Earth Science at the University of Hawai‘i at Mānoa for their support.

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