

SEDIMENTARY GEOCHEMISTRY OF FINE-GRAINED GLACIAL DEPOSITS: IMPLICATIONS FOR WEATHERING AND PALEOCLIMATE ON ICY PLANETARY SETTINGS. C. Demirel-Floyd¹, G.S. Soreghan¹, Y.J. Joo², N.D.S. Webb⁴, and M.E. Elwood Madden¹, ¹University of Oklahoma, School of Geosciences, Norman, OK (cansu.demirel@ou.edu), ²Korea Polar Research Institute, ⁴Impossible Sensing, St. Louis, MO.

Introduction: Silicate weathering is controlled by lithology (composition, texture), climate, and biological activity, as well as chemistry of weathering solutes. Secondary products such as clay minerals and Fe-(hydr)oxides are concentrated in fine-grained sediments and record planetary geochemistry and surface alteration conditions. In addition, chemical weathering buffers atmospheric CO₂; therefore, investigation of weathering products holds great implications for paleoclimate on Earth and other planets [1,2].

Glacial settings on Earth, including Antarctica are sensitive to global warming, serve as analogs to planetary environments [2], and also hold vast deposits of comminuted minerals susceptible to chemical weathering [3]. Although weathering is limited in extremely dry and cold conditions, numerous studies on Antarctic meltwater chemistry suggest that chemical weathering occurs in such settings [4,5]. Relatively high weathering fluxes in Antarctic McMurdo Dry Valleys (MDV) were attributed to fresh, fine-grained sediments with high surface area produced by glacial grinding [5,6,7], as well as microbial activity [8]. However, reports of high surface area of MDV sediments relative to their temperate counterparts is puzzling [9,10], as wet-based glaciers should produce more fine-grained sediment due to basal sliding [3,7], which conventionally translates into grains with higher surface area [11]. In addition, temperate settings should display higher chemical index of alteration (CIA) values and higher surface areas associated with secondary minerals, owing to higher weathering rates resulting from warmer, wetter conditions. However, previous studies show otherwise, reporting higher CIA and specific surface area values in MDV sediments as compared to temperate glacial [8] and comparable to tropical fluvial [12,13] systems. Considering that 1) fine-grained glacial sediments hold such importance for weathering and paleoclimate, and 2) the unconventional low-temperature weathering signals observed in glacial deposits, detailed characterization of fine-grained glacial sediments from various climatic regimes on Earth is necessary to draw accurate relationships between sedimentary geochemistry of glacial sediments and paleoclimate, and to apply this knowledge to surface alteration processes on glaciated planetary bodies such as Mars.

Here we report the specific surface area, grain size, mineralogy, and geochemistry of fine-grained glacial

sediments collected from drift, soil, water track, proglacial fluvial and lacustrine systems in cold-arid (Antarctica MDV), temperate-arid (Peru) and temperate-humid (Norway, Washington, Iceland) systems, as well as hot-arid (Anza Borrego) and hot-humid (Puerto Rico) non-glacial fluvial sediments and soils to investigate statistically significant relationships between BET (Brunauer-Emmett-Teller) surface area and chemical weathering history of these deposits.

Methods: We collected fine-grained sediments from slack-water deposits in fluvial systems, and from soils, and glacial drifts, then wet sieved the samples to obtain the mud-sized (<63µm) fractions, then treated with acetic acid and H₂O₂ to remove carbonate and organic constituents, respectively [14]. We measured the grain-size distribution within the mud fraction with Laser Particle Size Analysis (LPSA), after treatment with sodium hexametaphosphate. Surface area was measured using BET nitrogen adsorption method [14]. We determined the bulk mineralogy using X-Ray Diffraction (XRD) with a Cu radiation source and interpreted the data with MDI Jade software using Reitveld refinement method, in combination with ClaySIM software using RockJock method [8]. We cataloged the weathering features such as etch pits and secondary minerals [8] using scanning electron microscopy (SEM) coupled with electron dispersive spectroscopy (EDS). Bulk chemistry of the samples was determined by ALS labs, using ICP-MS by Li borate fusion and acid-digestion methods. Finally, we performed Principal Component Analysis (PCA) using Prism Graphpad, after imputing the data that were missing or below detection limit (BDL) with multiplicative replacement (multRepl function of zCompositions package) for <10% BDL, ilr-EM algorithm (impRZilr function of robCompositions package) for >10% BDL, using R software [15]. We transformed compositional data (mineralogy, geochemistry) using clr (centered log ratio) function (compositions package) [16] prior to PCA.

Results and Discussion: Though MDV glaciers produce less mud-sized material (wt%), they contain more clay-sized particles within the mud fraction as compared to other glacial sites in general. We posit that wet-based glaciation history of Taylor Valley (MDV) during LGM-aged Ross Sea ice encroachment [17] produced abundant high surface area material both via rock flour production and active chemical weathering

potentially accelerated by sea salt containing weathering fluids that are more concentrated than the MDV meltwater [5], as well as salt deposition on sediments from sea water aerosols [18]. In addition, pedogenic processes and chemical weathering aid the production of high surface area due to etch-pit formation via leaching, and secondary clay precipitation. We observed abundant etch pits on Antarctic fluvial sediments and drifts collected from MDV, in addition to physical weathering signatures resulting from glacial crushing, such as parallel ridges. We also observed abundant microbial biofilms, cell-shaped etch-pits and secondary nano-phase Fe-(hydr)oxide precipitates around microbially-influenced areas on mostly mafic grains of Taylor Valley deposits [8]. Such secondary minerals and increased etching on grains were also observed by laboratory weathering of glaciofluvial sediments by Antarctic cyanobacteria [8], which might also contribute to higher BET values observed in Taylor Valley sediments, where macro-scale microbial mats are abundant.

PCA of major oxide geochemistry and BET of different climatic regimes showed overlapping dry and wet climate PC scores, as observed by Washington and Antarctica data points (Fig.1). Note here that samples from Antarctica and Washington State overall exhibit similar chemical and mineralogical compositions, except for higher illite and pyroxene contents of Antarctic samples and higher amphibole content in Washington sediments. This indicates that the provenance signal weighs heavily on the results, which hinders climatic interpretations based on PCA of geochemical data. In addition, CIA plots showed overlapping data points and similar trends for all climatic regimes, wherein some MDV deposits displayed even higher CIA values than deposits from temperate and hot climate settings. Finally, we found that MFW plots on fine-grained material might lead to misleading interpretations wherein samples with high plagioclase contents plot on the mafic end, even though they are felsic (i.e., Puerto Rico samples), due to heavy weighting of CaO in the respective formulas.

Implications for Mars and Other Icy Planetary Bodies: Interpretation of data coming from space depends on Earth analogs. Based on the sedimentologic and geochemical data collected on terrestrial sediments of various depositional settings and climatic regimes, we conclude that physical, chemical, and biological processes all leave imprints on glacially produced sediments. However, interpreting paleoclimate for planetary regions of complicated glacial or depositional histories with mixed felsic and mafic mineralogy, such as Antarctic Taylor Valley, regions of bedrock with high plagioclase content, as well as extraterrestrial samples

of unknown provenance, using geochemical and/or bulk mineralogy data might generate misleading conclusions. Our results showed that weathering indices such as CIA and MFW that are commonly used for climatic interpretations may yield misleading results. Therefore, caution should be taken in making paleoclimatic interpretations based on regolith and sediment geochemistry and mineralogy from orbital analyses and rovers. Future work will investigate methods for removing the provenance effect in statistical analyses and geochemical analyses to highlight the climate signal in planetary data.

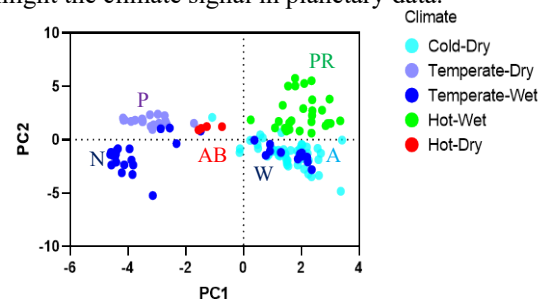


Fig.1. PCA plot principal component scores based on BET and major oxide chemistry of glacial deposits and fluvial sediments under different climatic regimes (A: Antarctica, PR: Puerto Rico, W: Washington State, P: Peru, N: Norway, AB: Anza Borrego).

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References: [1] Rutledge A. M. et al. (2018) *Geophys. Res. Lett.*, 45(15), 7371–7381. [2] Salvatore M. et al. (2019) *Icarus*, 319, 669–689. [3] Anderson S. P. (2005) *Geomorphology*, 67, 147–157. [4] Gooseff M. N. et al. (2002) *Water Resour. Res.*, 38(12), 15–1–15–17. [5] Stumpf A. et al. (2012) *Chem. Geol.*, 322–323, 79–90. [6] Marra K. R. et al. (2017) *Geomorphology*, 281, 13–30. [7] Anderson S. P. et al. (1997), *Geology*, 25(5), 399–402. [8] Demirel-Floyd et al. (2021) *Permafrost. Periglac. Process.*, <https://doi.org/10.1002/ppp.2133> [9] Marra K. R. et al. (2014) *Geomorphology*, 206, 483–491. [10] Demirel et al. (2019) *Goldschmidt Conference Abstracts*, Abstract #749. [11] Horowitz A. J. and Elrick K. A. (1987) *Appl. Geochem.*, 2(4), 437–451. [12] Joo Y. J. et al. (2018) *Geology*, 46(8), 691–694. [13] Webb N. D. S. et al. (2021) *ESSOAr*, <https://doi.org/10.1002/essoar.10508575.1> [14] Marra K. R. et al. (2015) *Appl. Geochem.*, 52, 31–42. [15] Palarea-Albaladejo J. et al. (2014) *J. Geochem. Explor.*, 141, 71–77. [16] van den Boogaart K. G. and Tolosana-Delgado R. (2008) *Comput. Geosci.*, 34(4), 320–338. [17] Hall B. L. et al. (2013) *Geol. Soc. Spec. Publ.*, 381, 167–181. [18] (Harry)Keys, J. R. and Williams, K. (1981) *Geochim. Cosmochim. Acta*, 45(12), 2299–2309.