SEASONAL CHANGES IN VNIR SPECTRA OF SALTS FROM CANADIAN HYPERSALINE LAKES WITH RELEVANCE TO MARS. E. B. Hughes[1], J. J. Buffo[2], F. Rivera Hernández[1], K. L. Lynch[3] and J. J. Wray[1], [1]Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332, [2]Thayer School of Engineering, Dartmouth College, Hanover, NH 03755, [3]Lunar and Planetary Institute/USRA, Houston, TX 77062

Introduction: Orbital and surface observations indicate the presence of lakes on early Mars [e.g., 1]; however, the environmental context of these lakes, including temperature, remains under-characterized. In particular, the extent to which lakes were open or ice-covered (made stable by dissolved gases and ions) is unknown [2]. Temperature-dependent saline mineral assemblages may distinguish between freezing and evaporative conditions, as precipitation sequence and mineralogy are affected by formation mechanism [e.g., 3]. Therefore, developing methods for differentiating between evaporative and cryogenic salt assemblages may be critical for constraining climate conditions on early Mars. Here, we discuss modeling and *in situ* spectral analysis of hypersaline lakes in British Columbia, Canada that undergo cold- and warm-temperature concentration and precipitation, with application to martian paleolakes.

Geologic Context: The British Columbia Cariboo Plateau is home to a series of endorheic lakes that evaporate in the summer and freeze over in the winter. The Basque Lakes (BL) 1 - 5 have Mg-Na-SO_4-rich waters and thus have chemistry relevant to Hesperian Mars; Last Chance Lake (LCL), located in the more northern part of this region, has Na-CO_3-SO_4 rich waters and chemistry relevant to Noachian Mars and Enceladus (**Figure 1**). These lakes are thus excellent analogues for possible open or ice-covered early martian lakes.

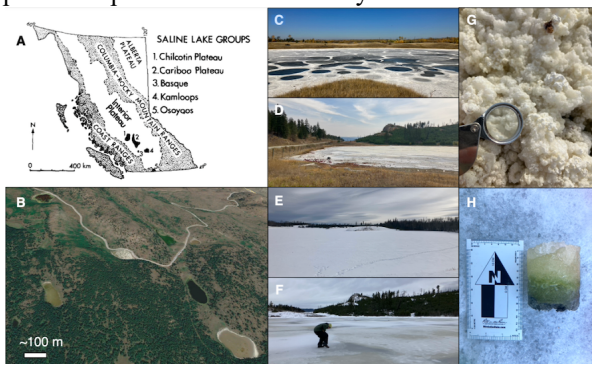

Figure 1. *The Cariboo Plateau lakes.* ***A)*** *Geographic context, from [4].* ***B)*** *Summertime aerial imagery of Basque Lakes 1 – 5.* ***C)*** *Last Chance Lake in October, 2022.* ***D)*** *Basque Lake 2 in October, 2022.* ***E)*** *Last Chance Lake in February, 2023, demonstrating ice cover.* ***F)*** *Basque Lake 2 in February, 2023.* ***G)*** *Botryoidal salt crusts from Basque Lake 2 in October, 2022.* ***H)*** *Salt core from beneath the ice in Basque Lake 2 in February, 2023.*

Methods: Here we rely on modeling and *in situ* analysis of salts and sediments from the BL and LCL to reconstruct seasonal differences in mineral formation. We use the low-temperature aqueous geochemical modeling program FREZCHEM [5], which has been extensively applied to earth and martian systems, to predict the sequence of mineral formation and their relative mass fractions under freezing (winter) and drying (summer) conditions. Geochemical and environmental data used in this model for the BL and LCL are provided in [6]. Freezing models were run from 288.15K to 250K.

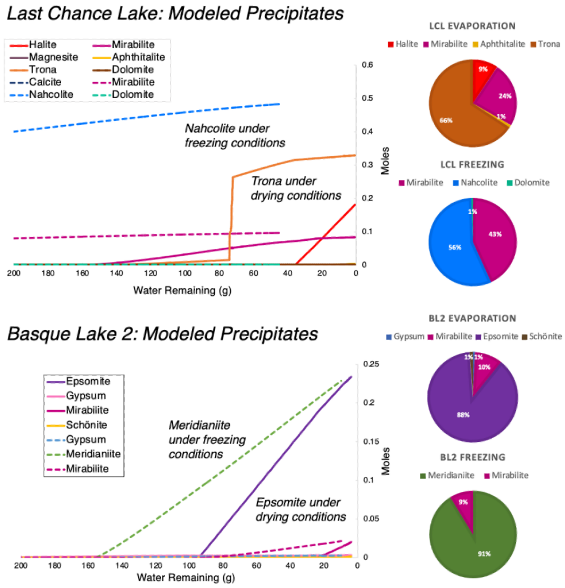

Figure 2. *Modeling of freezing and evaporation of simulated brine waters for BL2 and LCL. Winter data are the dashed lines while summer data are the solid lines.*

We visited the field sites in October 2022 and February 2023, obtaining *in situ* Visible to Near Infrared (VNIR) spectral data across the 0.5 – 2.5 µm wavelength range using a Spectral Evolution portable field spectrometer with an optical probe. We also obtained X-Ray Florescence (XRF) data during the winter season using a SciAps X-250 spectrometer with a Rh X-ray tube and 4 mm spot size. Preliminary results discussed here are focused on the VNIR data. Summer samples include salt from brine pools and salt crusts (**Figure 1.G**), while winter samples include efflorescent salt crusts and salt cores form beneath the ice-covered lakes (**Figure 1.H**). During the winter, salts were

generally present in all lakes beneath a layer of ice (~10 – 18 cm thick) and a ~2.5 – 5 cm brine layer. VNIR data are compared to USGS and Relab library spectra; the meridianiite spectrum is courtesy of Dr. Ed Cloutis.

Modeling Results: Modeling indicates the precipitation of different salts from freezing and evaporation for both LCL and BL2. Under freezing conditions, nahcolite ($NaCO_3$•$10H_2O$) and mirabilite ($NaSO_4$•$10H_2O$) are predicted in abundance for LCL, while trona (Na_2CO_3•$2NaHCO_3$•$3H_2O$) and mirabilite are predicted in the summer. Meridianiite (MgSO4•11H2O) is the stable Mg-sulfate phase in the winter for BL2 while epsomite ($MgSO_4$•$7H_2O$) and minor schönite ($K_2Mg(SO_4)_2 \cdot 6H_2O$) form in the summer. Mirabilite is predicted to be present across seasons but is modeled to precipitate earlier (with less water in solution) in the wintertime (**Figure 2**).

VNIR Results: VNIR indicates different sets of minerals form in the crusts and in the brine pools depending on season for each locality. In the summer, absorptions consistent with the possible presence of mirabilite are identifiable in some LCL crusts, based on absorptions around 1.48, 1.78, 1.96, and 2.22 µm (**Figure 3**). Additional enigmatic minerals ("LCL Summer Pool" in **Figure 3**) identified in the brine pools in the summer did not match any known library spectrum for Na-carbonates or -sulfates; we plan to do laboratory XRD analysis to identify these minerals. In the wintertime, no crusts were observed at LCL due to the presence of snow-cover and freezing over of the lake. Spectra derived from the top layer (in contact with the brine) of a core, however, match that of mirabilite. In the case of BL2, seasonal changes are also observable. Some summer crusts forming at the edges of the brine pools may be a mix of schönite and epsomite based on VNIR absorptions at 1.48, 1.63, 1.96, and 2.21 µm ("BL2 Summer Crust" in **Figure 3**). The winter crust, alternatively, appears to be consistent with mirabilite ("BL2 Winter Crust" in **Figure 3**). The winter core may be consistent either with "wet" epsomite or meridianiite based on absorptions at 1.22, 1.48, and 1.98 µm as well as general structure; we suggest meridianiite is more likely based on the location of the core at the brine interface and the season.

Discussion: Notable differences in seasonal salt include the presence of mirabilite in crusts during the wintertime in BL2, as well as a putative layer of mirabilite precipitation in the wintertime within the brine column of LCL that was not present in the summer. This may be because mirabilite is an early crystallizing salt under freezing conditions and therefore forms out of solution as a cryogenic salt. The double salt schönite, if present (based on 1.63 µm absorption) may be stable only seasonally given its lack of detection during the wintertime for BL2. The putative schönite and epsomite mixture may serve as a good analogue for warm-temperature salt assemblages on Mars. Efflorescent crusts of mirabilite and interior pools of meridianiite appear to compose a winter saline succession, consistent with FREZCHEM modeling for BL2. Na-carbonates appear generally difficult to spectrally detect for LCL in both seasons, possibly indicating if present on Mars in mixtures, they may be spectrally overwhelmed by the presence of other salts.

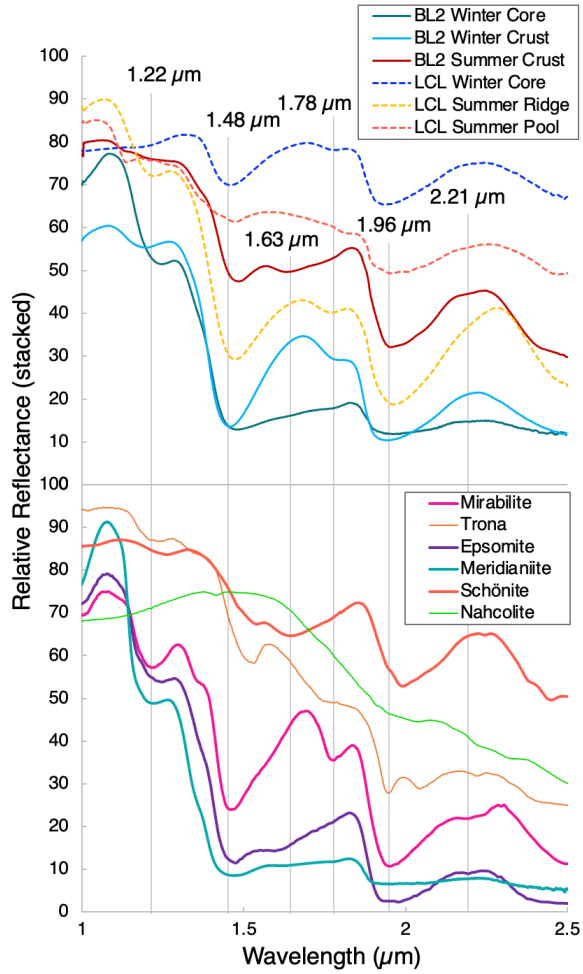

Figure 3. *Spectra of samples from LCL and BL2 compared with modeled reference spectra. LCL spectra appear as dotted lines while BL2 spectra are solid.*

References: [1] Fassett C. I. and Head J. W. (2008) *Icarus, 191*, 37–56 [2] McKay C. P. and Davis, W. L. et al. (1991) *Icarus, 90*, 214–221. [3] Herrero M. J. et al. (2015) *Clim. Of the Past, 11*, 1–13 [4] Renault R. and Long P. (1989) *Sed Geo., 64*, 239–264 [5] Marion G. M. and Kargel J. S. (2008) *Cold Aqueous Planetary Geochemistry with FREZCHEM*. Springer. [6] Buffo J. J. et al. (2021) *Astrobio., 22*, 962–980.