SPOTTED LAKE: MINERALOGICAL CLUES FOR THE FORMATION OF AUTHIGENIC SULFATES IN ANCIENT LAKES ON MARS. K. M. Cannon[1], L. A. Fenwick[1] and R. C. Peterson[1], [1]Department of Geological Sciences and Geological Engineering, Queen's University, 99 University Avenue, Kingston, Ontario, Canada, K7L 3N6 (cannon@geol.queensu.ca).

Introduction: Sulfate minerals have been identified on various planetary bodies [1,2,3] but on Mars in particular, it is a continuing challenge to assess whether they have been transported or have formed in place (i.e., authigenically). Gypsum and polyhydrated Mg/Fe sulfates were recently identified in a putative paleolake inside Columbus crater in Terra Sirenum [4]. *Wray et al.* [4] hypothesize these deposits may represent dried up brine pools formed during the final stages of lake evaporation. Spotted Lake in British Columbia has some of the highest sulfate concentrations in the world, and the lake water evaporates each summer to form an array of hyperconcentrated brine pools separated by efflorescent salt crusts (Fig. 1). Sulfate mineral facies relationships in Spotted Lake at different times of year can be used to infer formation processes on Mars, as has been applied to clay minerals [5]. Observed mineral assemblages can also validate geochemical models for the evolution of a sulfate brine on Earth and Mars.

Figure 1. Oblique aerial view of Spotted Lake in Osoyoos, BC on July 30, 2008. Photo used with permission of Douglas Carlson. The two-lane highway in the upper left gives approximate scale.

Spotted Lake: Spotted Lake is situated 10 km northwest of Osoyoos, BC (49°04'N, 119°34' W) in a semi-arid climate [6]. The slightly alkaline (pH = 7.2) lake is inside a closed basin with no inflow or outflow. Dominant ions are SO_4 (314150 mg/L), Na (51524 mg/L), Mg (46565 mg/L), K (11375 mg/L), Cl (3420 mg/L), and Ca (0.9 mg/L) [7].

Materials and Methods: Multiple visits were made to Spotted Lake over the course of a year to collect mineral samples, water samples and conduct *in-situ* mineral characterization with an inXitu Terra X-ray Diffraction/X-ray Fluorescence (XRD/XRF) instrument, based on the Mars Science Laboratory (MSL) CheMin design. *In-situ* analysis is crucial to studying hydrated sulfates [8] which are labile and subject to dehydration and melting upon transport.

Mineral samples were also characterized in the laboratory with a PANalytical X'Pert Pro θ-θ X-ray diffractometer. Minor phases were identified using energy-dispersive X-ray spectroscopy on an FEI™ Quanta™ environmental scanning electron microscope. Visible and Near-Infrared (VNIR) spectra of the mineral samples were collected using an ASD TerraSpec Explorer® spectrometer at wavelengths of 350-2500 nm.

The FREZCHEM computer model [9] was used to simulate the evolution of an Mg-Na-SO_4 brine under freezing and evaporating conditions. A brine with the Spotted Lake water chemistry was modeled freezing to the eutectic as well as evaporating under terrestrial (25°C) and colder martian (0°C) conditions.

Results: Distinct mineral assemblages were found at Spotted Lake due to the dominance of crystallization from freezing or evaporation during different times of the year. FREZCHEM models using Spotted Lake water chemistry predict that evaporation at 25°C will produce a mineral suite dominated by $Na_2Mg(SO_4)_2{\cdot}nH_2O$ phases, as has been previously anticipated with simulated martian brines [10]. With freezing only simple highly hydrated Mg- or Na-sulfate minerals should form. Evaporation at Mars conditions (0°C) produces a mixture of the two assemblages (Fig. 2).

A diverse suite of minerals was identified in the samples collected in August 2011. Dominant minerals included blöedite $Na_2Mg(SO_4)_2{\cdot}4H_2O$, konyaite $Na_2Mg(SO_4)_2{\cdot}5H_2O$, epsomite $MgSO_4{\cdot}7H_2O$, and gypsum $CaSO_4{\cdot}2H_2O$, with minor eugsterite, picromerite, syngenite, halite, and sylvite. This assemblage supports the FREZCHEM model in which evaporation processes are predicted to produce multicationic sulfates. The spatial distribution of these minerals between, on the edge of, and within the evaporating brine pools suggests a crystallization sequence of gypsum → blöedite

→ epsomite. A more restricted set of monocationic, highly hydrated sulfates was found in freezing conditions at Spotted Lake in December 2011. Meridianiite

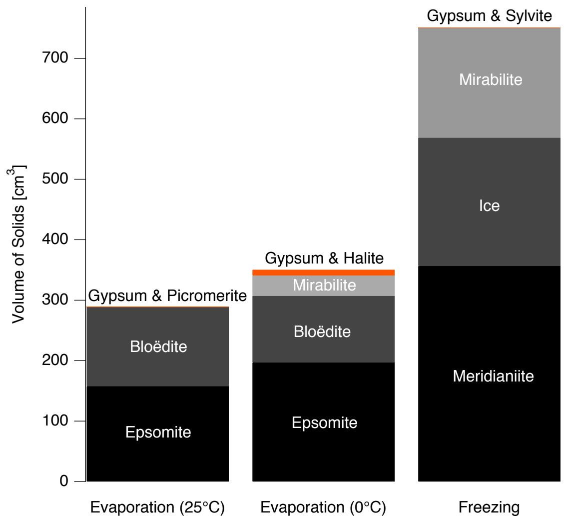

Figure 2. FREZCHEM resulting mineral assemblages and volumes for simulated evaporation of 1L of Spotted Lake brine on Earth (left), on Mars (middle), and simulated freezing (right).

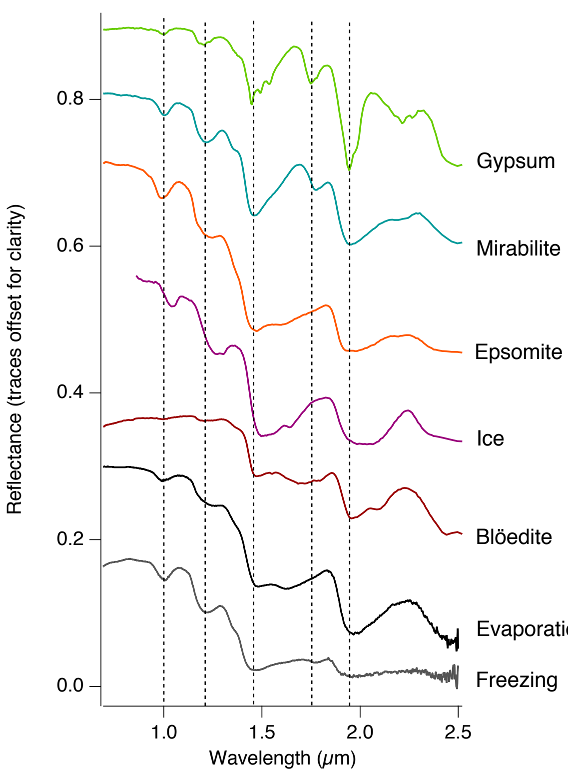

Figure 3. Sulfate mineral VNIR spectra from the USGS spectral library [11] (top 5) compared to laboratory spectra for Spotted Lake samples (bottom 2).

$MgSO_4 \cdot 11H_2O$, water ice, mirabilite $Na_2SO_4 \cdot 10H_2O$, and gypsum were the dominant minerals present. Absorption features in the VNIR spectra of the two seasonal mineral suites can be used to distinguish between them. Fig. 3 compares spectra of the two mineral suites with various individual sulfates. Work is underway to correlate these laboratory spectra with data from the Compact Reconnaissance Imaging Spectrometer for Mars instrument to determine if these assemblages could be distinguished from orbit.

Implications for Mars: Two potentially useful trends are observed in the mineral assemblages found in the field under evaporating and freezing conditions from the same initial brine chemistry: (1) A tendency for monocationic highly hydrated sulfates formed by freezing, and (2) the predominance of multicationic sulfates in evaporating conditions. This work represents the first time this latter trend has been verified in the field. The occurrence of these mineral assemblages could be used to infer depositional conditions of sulfates on Mars, and the observed crystallization sequences can offer mineralogical evidence for locations of dried out paleolakes. Such sulfate minerals are subject to post-depositional changes in hydration state, but the multi vs. monocationic trend offers unique insight. The CheMin instrument on MSL has the ability to distinguish between Na-, Mg-, and NaMg sulfates and therefore the plausible conditions of crystallization.

The abundance of algae and bacteria in Spotted Lake [12] supports the idea that life can thrive in these desiccating hypersaline conditions [13]. Films of water adsorbed onto the surfaces of hygroscopic salts represent a plausible ancient habitable environment on Mars [14]. Paleolakes such as those in Columbus crater should be targeted for future exploration, as their deposits can offer clues into the hydrologic history of Mars, and have important astrobiological implications.

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