

**UNDERSTANDING THE FORMATION STAGES OF EVAPORITES IN GALE CRATER USING THERMOCHEMICAL MODELING.** D. Das<sup>1</sup>, S. M. R. Turner<sup>2</sup>, P. J. Gasda<sup>3</sup>, S. P. Schwenzer<sup>2</sup>, J. Palandri<sup>4</sup>, M.H. Reed<sup>4</sup>, L. Crossey<sup>5</sup>, R. J. Leveille<sup>1</sup>, K. Berlo<sup>1</sup>, J. Frydenvang<sup>5</sup> <sup>1</sup>McGill University (debarati.das@mail.mcgill.ca), <sup>2</sup>As-trobiologyOU, <sup>3</sup>LANL, <sup>4</sup>UO, <sup>5</sup>UNM, <sup>5</sup>Globe Institute.

**Introduction:** The *Curiosity* rover's ChemCam instrument suite has frequently detected water-soluble elements B and Li in Ca-sulfate veins of Gale crater [1,2]. Ca-sulfates of Gale crater contain relatively high amounts of B and Li compared to Ca-sulfates or basalts on Earth (Table 1). In Table 1 basalts from Iceland are chosen for the comparison due to large geochemical dataset available for multiple suites of basaltic samples including weathered basalts.

**Table 1.** Relative abundances of B and Li in Gale crater Ca-sulfates, Earth Ca-sulfates, and Icelandic basalts.

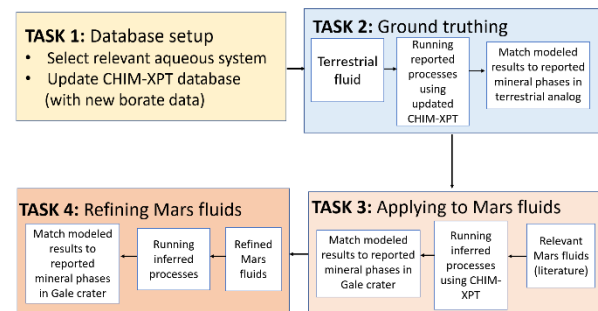
Location	B (ppm)	Li (ppm)
Gale crater Ca-sulfates [2]	~300	~65
Earth Ca-sulfates [3]	< 20	< 7
Icelandic basalts [4,5]	< 20	< 30

The B and Li abundances in Ca-sulfate veins of Gale crater also show a broad inverse correlation between them [2]. In the clay-rich Murray formation, the enrichment of B in Ca-sulfate veins is attributed to remobilization of pre-existing evaporites [1]. However, the Ca-sulfate veins in Vera Rubin Ridge (VRR) indicate that B and Li may have been sourced out of surrounding clay-rich rocks after interaction with acidic fluids [2]. The presence of B and Li and the correlation between the two elements are attributed to a combination of dehydration, sequential precipitation, multiple generations of dilution and remobilization, and mixing with trace elements drawn out of clays during late-stage alteration [2]. The relationship between B and Li abundances in Gale Ca-sulfates is not an perfect correlation as not all targets show this trend. This implies that multiple processes contributed to the formation of the evaporites in Gale crater [2]. We aim to use modeling to deconvolute the various geochemical processes to understand how to produce the observed B and Li in Gale crater and use the results for better understanding of evaporite phases in the sulfate unit [6].

The goal of this work is to determine which Li and B containing phases could be present in the sulfate unit of Gale crater, understand the conditions under which these phases could form, and create testable hypotheses based on those constraints. We do this by using a combination of analog sample investigations for ground truthing our model [7] and reaction-pathway modeling of Gale aqueous conditions (e.g., <100°C) in an evaporative setting to understand the possibility of formation of minerals such as borates and halite [8]. Although we have not detected B or Li phases in the sulfate unit, Mg

sulfates and halite have been tentatively detected by ChemCam [9-11]. Mg sulfates have very high solubility [12] and boric acid and LiCl have 0.17x and 2.4x solubility relative to Mg sulfate. Hence, we may expect B and Li phases, e.g., LiCl to occur in the sulfate unit, if there is enough B and Li in the fluids. Moreover, ChemMin has observed a reduction of clay mineral abundance along the rover traverse [13]. Lithium has been used as a proxy for clay mineral content in the past [14], but Li has remained steady or has increased over the elevations where clay mineral content has decreased [15]. Hence, the elevated Li may be an indication that Li salts, especially in targets that coincide with Cl detections [16], are present in the sulfate unit.

**Methodology:** The workflow is shown in Figure 1. As the thermochemical constants of selected B phases observed in terrestrial analogs were not included in modeling software, we start by expanding the thermochemical database from the literature [17,18]. Three new borate minerals (borax, kernite, and tinalconite) were added to the CHIM-XPT [19] from [20]. Using CHIM-XPT we aim to emulate the processes that may have taken place in a late-stage diagenetic environment using our understanding of terrestrial dry lakes.



**Figure 1.** Methodology flow chart.

The extent of comparison between the results from Earth and Mars are limited due to the differences in extent of alteration, host rock composition, availability of water, presence of life, and difference in atmospheric conditions on the two planets. We start with evaporating modified Gale Portage Water (GPW; Table 2) [21] to understand whether an evaporative enrichment process can explain the evaporite suite observed in Gale crater. GPW composition does not contain any Li or B ions and was modified to include Li and B ions based on natural Icelandic thermal waters [22,23]. SiO<sub>2</sub> was also omitted from the composition after making the assumption that SiO<sub>2</sub> has precipitated. This composition was enriched

up to 2000 times and evaporated (water content was systematically removed from the system) at 10°C, 30°C and 60°C to check if evaporites relevant to Gale crater form in this iteration of run. We also ground-truthed the model using a terrestrial analog (Searles Lake).

**Table 2.** Starting fluid composition (moles) for modified GPW and Searles Lake fluid.

Ions	Mod. GPW (moles)	Searles Lake (moles)
Cl <sup>-</sup>	5.76 E-03	5.41
SO <sub>4</sub> <sup>2-</sup>	3.97 E-03	0.75
HCO <sub>3</sub> <sup>-</sup>	1.68 E-04	1.04
Ca <sup>2+</sup>	1.401 E-05	0.141
Mg <sup>2+</sup>	1.27 E-08	0.127 E-05
Fe <sup>2+</sup>	-	-
K <sup>+</sup>	5.02 E-04	1.01
Na <sup>+</sup>	9.20 E-03	7.45
Mn <sup>2+</sup>	4.36 E-08	0.436 E-07
Li <sup>+</sup>	1.15 E-04	0.46
H <sub>3</sub> BO <sub>3</sub>	8.39 E-04	2.60

We used brine geochemical data from Searles Lake in Southern CA to test our model and check whether we can precipitate the new borate minerals using CHIM-XPT that occur in Searles Lake [24] (Table 2).

**Results:** The Searles Lake ground-truthing exercise resulted in forming all the evaporites for which thermochemical data in the CHIM-XPT database is available. We confirmed that the updated database functions as expected. The resultant phases using the Searles Lake brine are: halite (NaCl), anhydrite (CaSO<sub>4</sub>), borax (Na<sub>2</sub>[B<sub>4</sub>O<sub>5</sub>(OH)<sub>4</sub>] • 8H<sub>2</sub>O), kernite Na<sub>2</sub>[B<sub>4</sub>O<sub>6</sub>(OH)<sub>2</sub>]•3H<sub>2</sub>O, sylvite (KCl), and calcite (CaCO<sub>3</sub>).

**Table 3.** Resultant precipitate minerals formed when modified GPW concentrations (1x-2000x) were evaporated using CHIM-XPT with an updated database.

Mod. GPW	10°C	30°C	60°C
1x	-	-	-
100x	Anhydrite, borax, kernite	Borax, kernite	Anhydrite, kernite
1000x	Anhydrite, kernite	Anhydrite, kernite	Anhydrite, kernite
1500x	Anhydrite, kernite	Anhydrite, kernite	Anhydrite, kernite
2000x	Anhydrite, kernite	Anhydrite, kernite	Anhydrite, kernite

In the case of the modified GPW composition (Table 3), the resultant phases formed for the various enrichment concentrations from 1-2000x (anhydrite, borax, and kernite). No halites were formed using the enriched compositions by only invoking evaporation.

**Discussion:** This current model invoking precipitation through only evaporation does not explain the formation of evaporites such as halites that are observed in Gale crater. The formation of halites in this model likely

requires a higher concentration of Na and Cl. Although the Searles Lake fluid is not an exact analog for Gale crater fluids (as Searles Lake shows the presence of a large amount of borates that are not observed in Gale crater), constrain the fluid composition required to form evaporites such as halites. Searles lake likely needed multiple generations of evaporative precipitation and dilution that lead to selective enrichments of elements in the lake deposits [25]. Obtaining a fluid composition that represents cyclic precipitation and dilution is key for modeling the late stage diagenetic processes that may have been in play in Gale crater; Gale diagenesis includes reworked primary evaporites resulting in Ca-sulfate veins [1] and evidence that the fluids that formed the Ca-sulfate veins leached Li and B from surrounding clays [2]. While we start with relatively simple modeling parameters, the increased complexity in terms of fluid composition, evaporative and dilutive processes, fluid and surrounding rock amounts, and the degree to which each parameter affects the system will help us determine the diagenetic processes Gale crater.

**Conclusion and Future Work:** CHIM-XPT database was updated to include borates. Updated software was successfully ground-truthed using Searles Lake fluid composition. Modified Gale crater relevant fluid composition was concentrated through evaporation using CHIM-XPT to simulate processes that formed evaporites in Gale crater. Evaporation-only does not explain the formation of minerals such as halite in Gale crater and may require cyclic dissolution and enrichment similar to Earth caused by seasonal changes. Future model runs will take in to consideration realistic fluid volumes for Gale [26], geological processes that cause selective enrichment of elements such as leaching, phase separation during multiple generations of dilution and precipitation to simulate formation of evaporites.

**Acknowledgements:** NSERC Discovery program, CSA support for NASA MSL Participating Scientists, NASA Mars Exploration program.

**References:** [1] Gasda et al., (2017) *GRL* 44(17), 8739-8748; [2] Das et al., (2020) *JGR:P* 125(8); [3] Ma et al., (2017) *Tlnta*. 175, 250-255; [4] Dutrizac et al., (2017) *Hydromet* 174, 38-46; [5] Lacasse et al., (2006) *BOV* 64.4, 373; [6] Gasda et al., (2021) *LPI* 2548; [7] Das et al., this meeting; [8] Thomas et al., (2019) *GRL* 4 (10754-10763); [9] Rapin et al., (2019) *NatGeo* 12(11), 889-895; [10] Clegg et al., (2020) *LPI* 2561; [11] Meslin et al., this meeting; [12] Dalton et al., (2016) *NIST*; [13] Rampe et al., this meeting [14] Frydenvang et al., (2020) *JGR:P*; [15] Frydenvang et al., *AGU Fall Meeting* 2021; [16] Rapin et al., this meeting; [17] Anovitz et al., (1996) *RIM* 33, 181-222; [18] Monnin et al., (2002) *JCED* 47.6, 1331-1336; [19] Ruhl (2008) UoF Thesis; [20] Reed et al., (2010) *U.Oregon*; [21] Bridges et al., (2014) *JGR:P* 120(1) 1-19; [22] Ólafsson et al., (1978) *Chem. Geo* 21.3, 4; [23] Arnórsson et al., (1995) *GCA* 59.20 (4125-4146); [24] Felmy and Weare., (1986) *GCA* 50 (2771-2783); [25] Kristian and Lowenstein (2021), *GSA Bulletin*; [26] Siebach et al., (2014) *JGR:P* 119.1(189-198)