

SIMULATING EVAPORATIVE WET AND DRY CYCLES IN GALE CRATER, MARS USING THERMOCHEMICAL MODELING TECHNIQUES. D. Das¹, S. M. R. Turner², P. J. Gasda¹, S. P. Schwenger², J. Palandri³, M.H. Reed³, L. Crossey⁴, R. J. Leveille⁵, K. Berlo⁵, N. L. Lanza¹, ¹LANL (debaratidas@lanl.gov), ²Open Univ., ³UO, ⁴UNM, ⁵McGill University.

Introduction: In terrestrial settings, primary borates and Ca-sulfates can crystallize in brine pool beds as bottom-growth crusts in dry lakes that have experienced multiple wet-dry cycles [1-3]. The *Curiosity* rover's ChemCam instrument suite has detected B and Li in secondary diagenetic Ca-sulfate veins in the Murray Formation of Gale crater, Mars [4,5]. The Murray formation consists of fine-grained lake sediments and contains a topographic feature, Vera Rubin Ridge (VRR) which formed during diagenesis within the Murray formation [6]. In the Murray formation, the enrichment of B in secondary Ca-sulfate veins is attributed to remobilization of pre-existing primary evaporites such as borates and Ca-sulfates [4]. However, based on the lack of inferred lake margin environments in the VRR region, the B and Li in Ca-sulfate veins of VRR are hypothesized to have been sourced out of surrounding clay-rich rocks after interaction with acidic fluids [5,7]. Here we determine the potential minimum number of wet and dry cycles and placing them in the context of the broader Gale crater timeline established using sedimentological observations made by the *Curiosity* rover enables a better understanding of the window of habitability within Gale.

Methodology: We use thermochemical modeling, code CHIM-XPT [8] to simulate the conditions required to form primary borates and Ca-sulfates using a Gale relevant fluid while monitoring the corresponding Li concentration of the fluid during fluid-rock equilibration, fluid-fluid mixing, and evaporation. Prior to executing the simulation steps, we updated the thermochemical database of CHIM-XPT to include relevant B-phases based on thermal parameters measured by [9] and tested the updated database using a terrestrial analog fluid composition from Searles lake, CA [10]. We simulated four cycles of wet and dry periods and, based on the composition of the resultant phases, extrapolated brine compositions for up to 250 wet and dry cycles to test the minimum number of cycles required to form Ca-sulfates and borates in an early Gale lake environment. In this study, we limit our simulation to primary evaporite formation and do not simulate the secondary processes (e.g., [11]) or the Li or B adsorption process to clay minerals inferred for Gale crater [4,12]. This allows us to focus on establishing a minimum time constraint to form borates and Ca-sulfates. Gale is a closed basin which enables the modeling of primary evaporite formation upon saturation within the lake, for which we start with a local Gale lake fluid by equilibrating a local

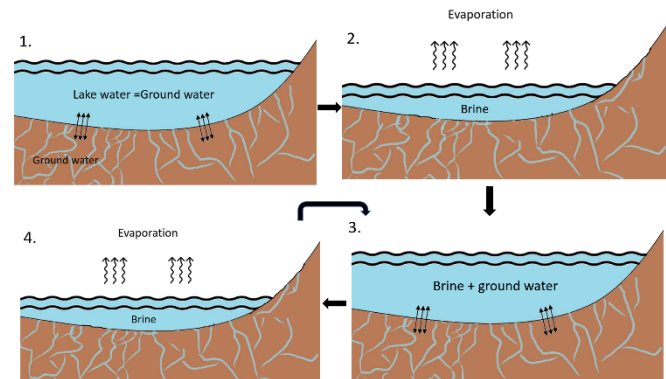


Figure 1. Illustration of the hypothesized sequence of events occurring in Gale crater

Gale rock composition with modified Gale Portage Water fluid composition [13] as shown in Figure 1, stage 1. We hypothesize that multiple wet and dry cycles consisting of evaporation (as shown in Figure 1, stage 2) followed by dilution (Figure 1, stage 3) are required to form a part of the primary evaporitic assemblage. We use thermochemical modeling to test this hypothesis as a continuation of previous and current models established for Gale aqueous fluids [11, 13, 14, 15]. Next, we use average time periods recorded for wet-dry cycles for terrestrial lakes and the interpreted sedimentological facies in Gale crater to establish a minimum time constraint for formation of primary borates and Ca-sulfates in Gale crater.

For the global Mars relevant fluid, we chose Gale Portage Water (GPW) [13], however, it does not contain B and Li; therefore, we modified the composition of GPW (modGPW) to include B and Li based on observed Icelandic stream compositions [16]. For the rock, we use the mean Hartmann's Valley (HV) composition; a unit within the Murray formation characterized by cross-stratified fine sediments [17]. We selected the mean bedrock composition of HV, obtained by the ChemCam instrument, that is calculated from a dataset where points with obvious diagenetic materials, soils, and out of focus points, have been removed [12].

Following this step, we used time constraints established for terrestrial closed lakes [18-20] to estimate a minimum time constraint for the number of wet and dry cycles required to form Ca-sulfates and borates for a Gale relevant scenario.

Results: We identify that it takes a minimum of 250 cycles to form primary Ca-sulfates and borates. We also

find that 1270 ppm Li⁺ would be in the resultant brine after 250 wet-dry cycles.

Discussion: On Earth lakes are categorized into three types based on the ratio of the lake's water content. These three types are 1) perennial lakes (high water content), ephemeral lakes (lower water content compared to perennial lakes with low water levels during dry seasons enabling evaporite formation), and dry lakes (predominantly dry with sporadic water content) [18-20]. The average wet-dry cycling time is approximately 1.5 year for dry lakes with sporadic water presence, 9 years for ephemeral lakes, and 65 years for perennial lakes [18-20]. We apply the knowledge from terrestrial analogues to estimate possible water levels in Gale crater based on the sedimentological observations

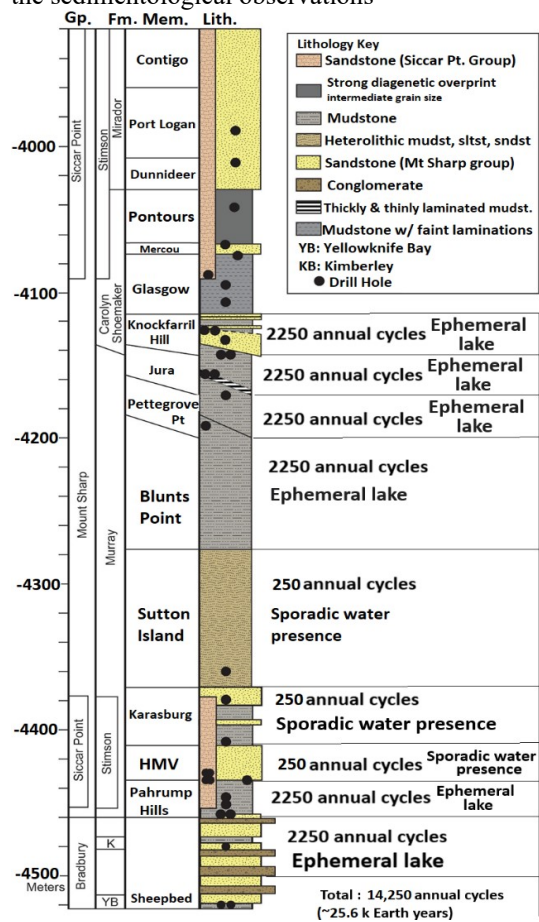


Figure 2. Gale crater stratigraphic column with estimated minimum annual cycles per member.

made by the Curiosity rover and establish the possible minimum time constraint of 14250 wet-dry cycles to form primary Ca-sulfates and borates based on the modeling results (Figure 2). 14250 cycles are the minimum time needed to form the first sulfates in the sequence and approximately 10^6 cycles ($\sim 10^7$ Earth years) are likely required to accumulate enough Ca in the fluid to account for all of the Ca sulfate (e.g., 1% of the volume

of the lake sediments, assuming an ephemeral lake) that formed in Gale crater. This value is consistent with timescale of valley and lake formation on Mars [21].

The saturation point of Li⁺ to form LiCl at 25°C and 1 bar pressure in 1 kg of water is 1.36×10^5 ppm [22]. Compared to this value, the concentration of Li⁺ in the Gale brine of is 10^5 times lower than required to start forming LiCl. However, after 14250 wet dry cycles the Li⁺ concentration of the resultant brine would be ~ 6000 ppm with precipitation of borates. In Gale crater, the average concentration of Li in veins and sedimentary rocks measured using the Curiosity rover does not exceed ~ 50 ppm and no major borate deposits are observed thus far in the mission [5,12]. Based on the large difference between the observed Li concentration in Gale crater rocks and Ca-sulfate veins and calculated Li in the remnant brine and precipitated borates after simulating wet-dry cycles in a Gale relevant scenario, we infer that B and Li rich brines may have formed and remained underground long after Gale lake disappeared.

Conclusion: A minimum of 250 wet-dry cycles are required to start forming Ca sulfates and borates from a Gale-relevant fluid. Comparing this result to terrestrial closed lake systems and placing the established time constraint in a broader context of Gale's timeline for aqueous activity, a minimum of 14,250 Mars annual cycles (or 25, 600 Earth years) is established for the start of formation of primary Ca-sulfates and borates. $\sim 10^6$ cycles ($\sim 10^7$ years) would be required to account for Ca-sulfate equivalent to 1% of the volume of the lake sediments. Based on the difference between the calculated Li⁺ in the leftover brine and observed Li concentration in sedimentary rocks and Ca-sulfates of Gale crater in addition to a lack of observation of major borate deposits, we infer the possibility that an underground B and Li-rich brine formed.

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