

ESTIMATING PAST FLUID PH AND EVAPORATIVE CONDITIONS IN GALE CRATER USING TERRESTRIAL ANALOG EVAPORITES AND CLAYS. D. Das¹, P. J. Gasda¹, K. Berlo², R. J. Leveille², M. A. Nellesen³, L. Crossey³, E. Peterson³, R. Beal¹, A. L. Reyes-Newell¹, S. M. Clegg¹, A. M. Ollila¹, N. L. Lanza¹

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Introduction: Boron and lithium have been frequently observed in Ca-sulfate veins of Gale crater. B and Li are highly water mobile elements can be used as proxies to identify aqueous processes in Gale crater's history [1,2]. B enrichments in Ca-sulfates of Gale crater likely formed due to pre-existing borate deposits that were remobilized and precipitated in close association with Ca-sulfates veins [2]. In areas where evaporative environments are not supported by the sedimentology, it is likely that B and Li are drawn out of clay minerals during acidic aqueous events [1]. Here, we test these hypotheses using samples of evaporites and sedimentary rocks from a terrestrial analog area.

In this work, we study the distribution of B and Li in various phases within samples collected from a terrestrial analog area in Southern CA where an environment similar to that estimated for ancient Gale crater is reported (i.e., multiple wet-dry events with variable aqueous conditions). The diverse geology of the terrestrial analog area in Southern CA consists of volcanics and playa-lacustrine deposits, which enables the sampling of a range of rock types and minerals that include evaporites, clay-rich sedimentary rocks, and igneous rocks from an environment that is similar to the inferred ancient Gale crater environment. We apply our findings to infer fluid pH and evaporative extent on Gale crater. In the analog area, evaporites such as borates, Ca-sulfates, halite, and carbonate are reported in addition to the presence of clay rich sedimentary rocks [3-4]. The comparison of terrestrial analogs with Gale observations enables constraining possible bounds on the relative pH, and the evaporation stages of fluids likely in Gale crater. This comparison is important for determining the range of habitable conditions possible in Gale crater during an evolving aqueous history.

Methodology: Twenty-two samples were collected from the four sites: the Gower Gulch area in the Furnace Creek (17 samples) and the Ryan region in Death Valley (1 sample), from the Searles Lake region (1 sample), and from the Kramer borate deposit region (2 samples). The specific sampling areas were selected in order to collect representative end member rocks (i.e., evaporites, clay-rich sedimentary rocks, and altered igneous rocks) and areas that show the presence of mixtures between the end members. The broader sampling sites were selected based on previously reported presence of evaporites, clay-rich sedimentary and altered igneous rocks, the specific sampling sites were selected based on

the availability of the features that visually resemble Ca-sulfate veins in Gale crater.

We used analytical techniques: Laser Induced Breakdown Spectroscopy (LIBS) instrument in the Los Alamos National Laboratory (LANL) ChemCam engineering unit [5], Fusion X-Ray Fluorescence (Fus-XRF), Fusion Laser Ablation Inductively Coupled Plasma Mass Spectrometry (Fus-LAICPMS), and Prompt Gamma Neutron Activation Analysis (PGNAA) at Activation Laboratory Ltd. (ActLabs), and X-Ray Diffraction (XRD) at University of New Mexico (UNM) to characterize the phases, in the terrestrial analog samples and determine the major and minor elements including B and Li.

Results: In the three sample groups (predominantly borate, predominantly Ca-sulfate, and neither predominantly borate or Ca-sulfate; Fig 1) high Li abundance is consistently correlated with the presence of clay minerals. Clay containing samples that do not contain any crystalline borates also show up to ~600 ppm B. Predominantly Ca-sulfate samples show B abundance up to ~3000 ppm (with majority of the Ca-sulfate samples containing up to ~500 ppm B). The sample group with no predominant borates or Ca-sulfates has up to ~1000 ppm B associated with the presence of halite. PCA identified a negative correlation between B and Li.

The A-FM-CNK ternary (Fig 2) also shows a physical mixing trend reported for Gale crater [6] in red extending from a Gale crater nontronite composition. The ternary diagram also shows reference endmember igneous samples (Death Valley plutonic and basaltic rocks) [7] and clay mineral data (illite) [8,9], and clay sampled from the Rio Tinto borax mine in Kramer, CA. These are plotted for comparison of the mixed samples with relatively unmixed reference igneous and clay mineral end members. Our samples plot closer towards the CNK corner compared to the reference end member igneous and illite samples (Fig 2).

Discussion: Based on the observations, we infer that Li enrichment is specifically associated with the presence of clay minerals while B enrichment is associated with the presence of evaporites. Although Li is enrichment is specifically associated with clay minerals, clay mineral containing samples also show the presence of ~600 ppm B in samples that are not predominantly borate or Ca-sulfate bearing. The distribution of B and Li in at least two different phases is likely indicative of fluid pH and evaporative state. In an area where there are both clay minerals with Li and borates are present in close association with each other, the following set of

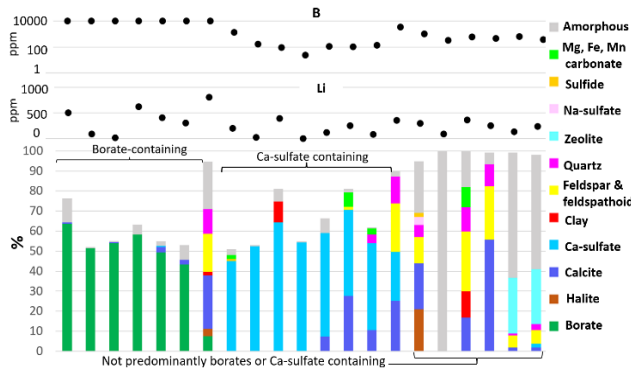


Figure 1. Crystalline and amorphous proportions in analog samples determined using XRD and full-pattern analysis techniques.

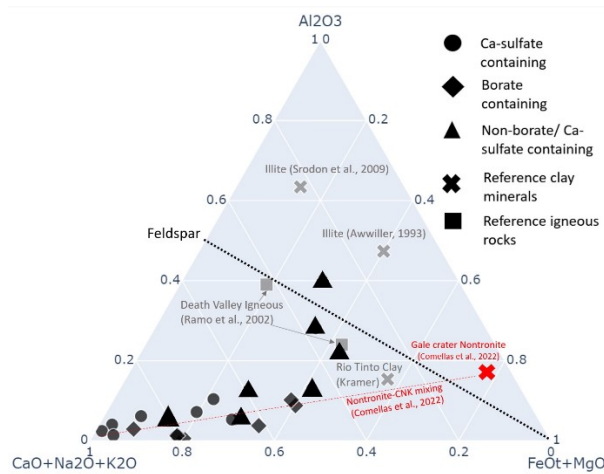


Figure 2. Ternary diagram indicating molar proportions of Al_2O_3 , $(CaO+Na_2O+K_2O)$, and (FeO_T+MgO) for terrestrial analog samples.

events are possible (based on observations made in Southern California by [10] and [11]):

- 1) Adsorption of B and Li on to the surface of clay minerals during alkaline aqueous event.
- 2) Release of B and Li into fluid during a relatively acidic aqueous event increasing B and Li concentration in the fluid.
- 3) Evaporation of fluid causing borate precipitation in close association with other evaporites such as Ca-sulfates and halite, while Li remaining in the fluid due to its higher solubility compared to B [12].
- 4) Adsorption of Li and remaining B partially dissolved B from a borate on the clay minerals back on the clay minerals in a following separate alkaline fluid event causing B-rich evaporites and B and Li clay minerals to coexist in close association.

Based on the negative correlation between B and Li in the terrestrial analog samples identified using PCA,

we also infer that the B and Li enrichment in Ca-sulfate veins formed during secondary diagenetic events due to remobilization of primary evaporites and clay minerals while preserving the negative trend between B and Li caused on their relative solubilities.

Observations in Gale crater show a mixing between evaporites and surrounding sedimentary rocks [13-15]. This mixing is inferred to be due to presence of cements or simultaneously sampling an evaporite vein and bedrock at the same time by ChemCam [15] and is represented Figure 2 as a red line. Figure 2 also illustrates that the physical mixing trend in the terrestrial samples is consistent with the trend observed in Gale crater, along with some mixing with illite.

For this work, we assume that Ca-sulfate in Gale crater was produced locally in each formation (similar to the hypothesis presented by [1, 2, 13, 16] before being remobilized by later stage diagenetic fluids. Alternatively, Ca-sulfate formation and B and Li enrichment may have been caused and modified by longer-distance fluid transportation (as discussed by [17]).

Conclusion: We established that B enrichment is linked with evaporite formation likely supported by a relatively acidic pH condition and high evaporation that enabled precipitation of evaporites while Li enrichment is linked with clay minerals through adsorption which was likely supported by a relatively high pH aqueous condition. Hence, in Gale crater, Li and B adsorption took place in clay minerals likely during alkaline aqueous conditions while primary borates, Ca-sulfates and halite likely formed in low-pH high evaporative conditions over multiple wet-dry cycles with varying fluid pH. The physical mixing trends between evaporites and sedimentary rocks are consistent with mixing trends observed in Gale crater by the rover. The inferences made for the terrestrial analog samples can be applicable to Gale crater and provide a ground truthing for the observation made using the Curiosity rover.

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References: [1] Das et al., *JGR:P* 125(8), (2020); [2] Gasda et al., *GRL* 44(17), 8739-8748, (2017); [3] Lowenstein et al., *Geology* 27, no. 1, 3-6, (1999); [4] Swihart et al., *Chemical geology*, 127(1-3), pp.241-250 (1996); [5] Clegg et al., *SCA* 129(64-85), (2017); [6] Comellas et al., *LPI*, 2678(2445), (2019); [7] Ramo et al., *CMP* 143(4), 416-437, (2002); [8] Srodon et al., *CCM*, 57(5), 649-671, (2009); [9] Awwiller, *JSR* 63(3), 501-512, (1993); [10] Karahan et al., *JCIS*, 293(1), 36-42, (2006); [11] Rohman et al., *Orient. J. Chem*, 36(2), 273-279, (2020); [12] Dalton et al., *IUPAC/NIST sol. database*, (2006); [13] L'Haridon et al., *Icarus*, 311, 69-86 (2018); [14] Hurowitz et al., *Science*, 356(6341), (2017); [15] Gasda et al., *JGR:P*, (2022); [16] Schwenzer et al. *MPS*, 51(11), 2175-2202, (2016); [17] Fraeman et al., *JGR:P*, 125(12), (2020).