EVAPORITES IN SOUTHERN CALIFORNIA: PRELIMINARY RESULTS FROM ANALOGS OF BORON-RICH CALCIUM SULFATE VEINS IN GALE CRATER, MARS D. Das[1], P. J. Gasda[2], R. C. Wiens[2], R. J. Leveille[1], K. Berlo[1], R. Kronyak[3], [1]Department of Earth and Planetary Sciences, McGill University, Quebec, Canada H3A 0E8 (debarati.das@mail.mcgill.ca), [2]Los Alamos National Laboratory, New Mexico, USA. [3]Department of Earth and Planetary Sciences, University of Tennessee, Knoxville, TN USA.

Introduction: Boron is a highly water-soluble element that was detected within calcium-sulfate-filled fractures of Gale crater, Mars, using the Laser Induced Breakdown Spectroscopy (LIBS) instrument on board the ChemCam suite of the NASA *Curiosity* rover [1,2]. These Ca-sulfate features are hosted by phyllosilicate-rich rocks that are interpreted as having formed in a lacustrine environment [3]; the veins are a result of late-stage groundwater circulation [4,5]. The discovery of B in Ca-sulfate veins sheds light on surface & subsurface aqueous processes on Mars. Although the boron-containing phase in Ca-sulfate veins of Gale crater is inferred to be a borate, no direct observation of its host using the instruments onboard the Curiosity rover has been made [2]. In this study we investigate if Ca-sulfate veins on Earth contain B. Boron-containing sulfates can be used as an analog to understand the geochemical process(es) that enriched B in Ca-sulfate veins of Mars. For this analogy, Death Valley in southern California was chosen because both sulfates and borates are reported together [6]. One of the most pertinent sites is Gower Gulch in Furnace Creek (Fig. 1), because this area acted as a basin for an ancient lake at the base of Death Valley's alluvial fans [7].

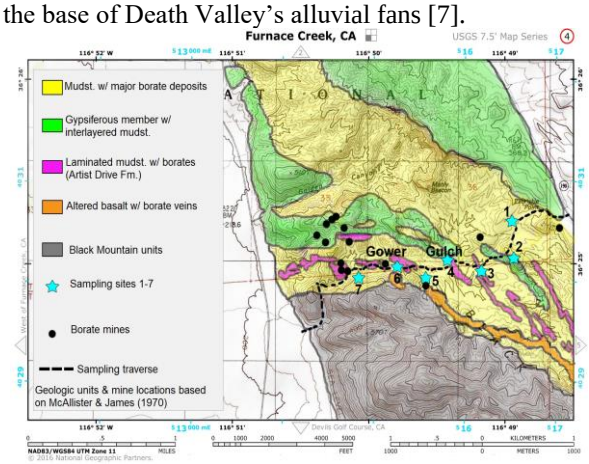

Figure 1. Geologic map of Furnace Creek, CA, indicating the geologic units and sampling sites in the Gower Gulch area. Geologic units, mine locations and elevations based on maps compiled by USGS [8,9].

Due to evaporation during episodic wet-to-dry periods, borate minerals were deposited along with Ca sulfate and clay minerals in Furnace Creek [10]. The evaporite deposits are estimated to be Neogene to Quaternary in age [6]. Alternating evaporite-mudstone in the playa setting also shows evidence (e.g., B isotopes) of interaction with groundwater [7]. This interaction may have redistributed the B from borates into Ca sulfates.

We present this study of evaporites from southern California as a progress report on furthering understanding of boron geochemistry in Gale crater using terrestrial analogue samples. We will investigate the chemical and morphological similarities between the evaporite veins in Southern California and Gale crater.

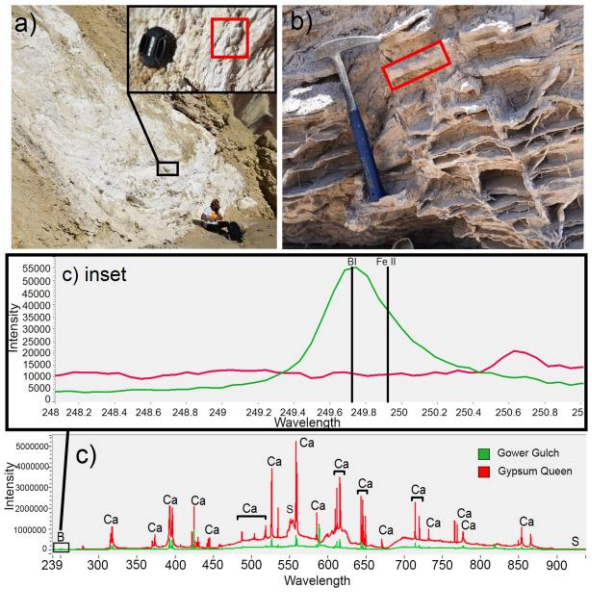

Figure 2. Samples collected from a) Gower Gulch and b) Gypsum Queen. Inset image in a) shows closeup of the samples from Gower Gulch that is used for analysis. Red box in a) and b) indicates samples that are used for analysis. c) shows the LIBS spectra for Ca sulphate from Gower Gulch (green) and Gypsum Queen (red). c) inset: Gower Gulch sample shows a boron peak at 249.75 nm while no peak is observed for the sample from Gypsum queen.

Methodology: Evaporite and bedrock samples were collected from 25 locations in southern California. The 25 locations consisted of areas in and near Gower Gulch, Cottonball Basin, Harmony Borax Works, Ryan, dry lakebeds near Searles Valley, Rio Tinto Mine, and Shoshone. Sampling sites were chosen based on the presence of layered evaporite deposits such that we could collect vein samples cross-cutting

multiple lithological layers (e.g. laminated mudstone and gypsiferous members next to altered basalts with borate veins as shown in Fig 1) in addition to surrounding clay-rich bedrock samples. Out of the 25 locations, only one area (Gower Gulch in the Furnace Creek region, shown in Fig. 1) reported both borate and Ca sulfate deposits close to each other.

In the Gower Gulch area, 21 fragments were sampled from seven sites for detailed laboratory investigation (Fig. 1). From sites 1-2 and sites 4-7, mudstones and evaporite veins were collected. At site 3, samples of altered basalts [8] containing evaporite veins were collected in addition to mudstones and evaporites. Fig. 2a shows evaporite samples collected from site 3. Ca sulfates were also collected from an abandoned gypsum mine called Gypsum Queen in Shoshone, California (Fig. 2b) which is ~60 km away from nearest borate deposit. The gypsum deposit is Shoshone is Pliocene in age and is reported to have formed due to re-working of lacustrine deposits [11]. Although samples from 25 locations were collected, analytical results for samples from Gower Gulch in Furnace Creek and from Gypsum Queen in Shoshone are focused on in this abstract. We compared likely boron-bearing Ca-sulfate veins from Gower Gulch, to baseline boron-free veins from Gypsum Queen in Shoshone.

Chemical investigation of two samples was carried out by LIBS (J200, Applied Spectra) at the Earth and Planetary Sciences department of McGill University. This instrument consist of a Q-switched, 213-nm Nd:YAG laser with < 4.5 mJ/pulse. Analysis was done using a 6 channel broad-spectrum CCD detector (190-1040 nm), at a laser delay of 0.3 ms, and an analysis gate width of 1.05 ms. The spot size was set to 80 µm. Intensities for 30 shots were accumulated in order to check for B peaks.

Results: Evaporite materials, that are found as both large patches (Fig 2a) and veins (Fig 2b) in southern California show a resemblance to light-toned veins observed in Gale crater. The veins range from a few millimeters to centimeters in width and appear to be fracture fills cutting bedding planes and alluvial fans. In some cases the veins cross each other indicating multiple generations of vein formation. Preliminary LIBS analysis of the evaporites show that Ca sulfates from Gower Gulch contain B (Fig. 2c green). A boron peak was observed at 249.75 nm in the LIBS data (the highest intensity peak and the same peak used for identifying B in ChemCam LIBS spectra) in samples from Gower Gulch. No B peaks were observed in Ca sulfates from the Gypsum Queen mine in Shoshone (Fig. 1c red). The evaporite samples from Gower Gulch and the Gypsum queen mine are inferred to be Ca sulfates based on the presence of strong Ca lines (393.37 and 396.96 nm), and S lines (550.73 and 921.49 nm). The phase responsible for the B peak in the Ca sulfates is inferred to be a borate based on the reported borate deposits in the sampling area.

Discussion: This preliminary study illustrates how the Gower Gulch locality in Death Valley is an appropriate terrestrial analog for boron-containing Ca-sulfate veins in Gale crater. These results can be applied to boron-containing Ca-sulfate veins in Gale crater and can provide insights on geochemical processes. As the *Curiosity* rover traverses higher up in the sulfate unit [12,13], this analog will help us understand more about the evaporative sequence during precipitation of diagenetic materials and climate change in Gale crater.

Conclusion: Observation of B in terrestrial Ca sulfate minerals provide a suitable analog for understanding geochemical processes that led to enrichment of B in Ca-sulfate veins in Gale crater, Mars.

Future work: Phase(s) and chemistry responsible for the boron enrichment in Ca sulfate samples as well as their distribution will be further investigated using LIBS, XRD and Raman instruments at McGill University and Los Alamos National Laboratory. Future analysis will be also be targeted at understanding the B concentration process and source body through comprehensive characterization of samples major, minor, and trace chemistry, and mineralogy from surrounding bedrocks and veins.

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