

THE DISTRIBUTION OF BORON IN VEINS IN GALE CRATER WITH IMPLICATIONS FOR MARS AQUEOUS PROCESSES AND ASTROBIOLOGY.

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Introduction: The study of boron on Mars sheds light on martian aqueous and climate history. Boron has been detected in calcium sulfate veins in Gale Crater by the ChemCam instrument on board the NASA MSL rover. Possible hypotheses for boron deposition include initial enrichment in either an evaporite layer or lacustrine clays. Late-stage groundwater either dissolved the evaporites or released boron from the clays and these fluids were precipitated as fracture-filling veins in the bedrock.

Methods: ChemCam is a combined remote imager and laser-induced breakdown spectroscopy (LIBS) instrument that provides elemental emission spectra for 350–550 μm sized points on rocks from up to 7 m away from a target [1,2].

Boron has been quantified for Mars spectra using a calibration curve constructed with measurements on standards collected by the ChemCam engineering unit at LANL (Fig. 1). These spectra have been corrected for the instrument optical responses and environmental conditions [3]. Standards included powdered terrestrial rock samples and sample mixtures with various proportions of B and Fe contents: sodium borate decahydrate (borax, $\text{Na}_2\text{B}_4\text{O}_7\text{H}_2\text{O}$, Sigma Aldrich, 99.5% pure) and calcium sulfate dihydrate (Sigma Aldrich, 98% pure) or Hawaiian basalt USGS standard BHVO-2. Other mixtures of borates (Smithsonian Institution) and BHVO-2 were made with kernite ($\text{Na}_2\text{B}_4\text{O}_6(\text{OH})_2 \cdot 3\text{H}_2\text{O}$, NMNH 124063), ulexite ($\text{NaCaB}_5\text{O}_6(\text{OH})_6 \cdot 5\text{H}_2\text{O}$, NMNH 124030-1), and tinealconite ($\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 3\text{H}_2\text{O}$, NMNH 124041). Spectral lines of boron and iron (Fig. 1 left) were fitted using a Voight function to extract the peak areas of the boron emission lines.

Results: Analysis of boron-containing spectra indicate a detection limit, the lowest level of boron where a peak is still visible in the LIBS spectrum, of ~50 ppm B. Data from 0–3.0 wt% B (154 analyses) were fitted with a curve (Fig. 1). The root mean square error (RMSE), equivalent to the level of quantification, is ~0.023 wt% B for 0–0.1 wt% B. At abundances of B<0.1 wt%, predicted B abundance has a relative error of ~50% and more analyses are needed to improve accuracy of the lowest predicted values.

Up to sol 1525, Boron has been detected in 35 calcium sulfate filled fractures targets (74 ChemCam observation points), and 57 ChemCam observation points have abundances of boron above the quantification limit. Boron has only been detected in calcium sulfate

filled fractures and only fracture fills in Yellowknife Bay mudstone, Murray mudstone, and Stimson sandstone, and observed as early as martian day (sol) 113. The majority of detections have been observed since sol 1350 and at an elevation above -4435 m (Fig. 2). Relative abundances, up to ~0.08 wt% B, are indicated by the color scale in Fig. 2. The level of B detected in the veins is highly enriched compared to estimates of B in martian igneous rocks (~0.01–0.1 ppm) [4].

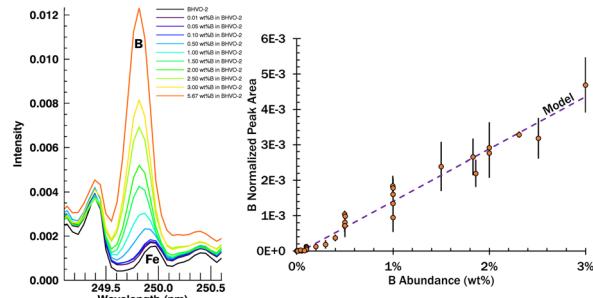


Figure 1: Left: Example lab spectra of borax diluted with BHVO-2 with various concentrations of B. Right: Calibration curve (dashed purple line) for 0–3.0 wt% B samples (orange dots) with 2σ standard error bars based on the lab spectra.

Discussion: The two major possibilities for borate enrichment in the veins, (a) and (b), have intriguing implications for Mars. Both suggest a long-lived and habitable groundwater system existed in Gale Crater after the burial of the crater and disappearance of surface water on Mars. But the competing mechanisms suggest different fluid conditions.

(a) Based on models of sulfate vein formation [5,6], groundwater may have dissolved sulfates and borates from an evaporite-rich stratigraphic layer higher in the crater, and precipitated the sulfates as veins in lower layers. These calcium sulfate veins are present in the Yellowknife Bay mudstones, the lacustrine mudstone Murray formation, and the unconformably overlying eolian sandstone Stimson formation [7]. Given the occurrence of boron in both the Murray formation (deposited during the existence of Gale Lake) and the Stimson (deposited in subsequent dry conditions), the secondary deposition of sulfates and borates in the veins occurred when Mars had already transitioned to a drier climate [8].

(b) Borates will adsorb to 2:1 phyllosilicates under certain conditions [9], and boron has been used as a

method to determine terrestrial paleosalinity [10]. The Murray bedrock in the vicinity of B detections is rich in 2:1 phyllosilicates [11]. Hence, boron may have been trapped in the clays during the initial deposition of the Murray bedrock. When groundwater later permeated the Murray and Stimson units, a change in fluid chemistry could have caused a release of the borates into the fluid, leading to precipitation in the veins.

An initial deposition of B in evaporites suggests a regional to global-scale process of drying the surface of Mars, retreat of groundwater to the subsurface, later remobilization of the soluble elements, and their precipitation in veins lower in the stratigraphic column. Models of calcium sulfate vein formation, clay hydration, and early Amazonian subsurface heat flow estimates suggest vein fluid temperatures from $\sim 0\text{--}60^\circ\text{C}$ [12–14]. ChemCam cannot determine the mineralogy of the boron present in the veins, but the common borates that form in a playa environment (e.g., Death Valley), include borax and ulexite, which typically precipitate from fluids with pH of ~ 9 .

An initial deposition of B in clays begins with an initial trapping of the borates dissolved in Gale Lake by clays and then later remobilization of those borate ions by groundwater. Boron is stable as a neutral hydroxide in water at pH < 6 and mainly as an anion at pH > 9 [15]. The borate anion is adsorbed by positively charged sites of 2:1 phyllosilicates that form in alkaline pH fluids and the optimum level of adsorption of boron by clays depends on the type of clay and fluid pH, with a pH range for terrestrial clays of $\sim 8\text{--}9$ [9]. Thus, later groundwater would likely need to be more acidic than the lake waters to free the adsorbed borate from the clays. For example, if the borate is adsorbed by the clays in water with pH of 8, then fluids of pH 6–7 would be sufficient to free the majority of the borate anions trapped in the clay, and the borate would precipitate as boric acid (sassolite) in the veins. This model leaves open the possibility of more acidic groundwater, but strongly acidic conditions are not necessary to achieve the observation of boron in the veins.

Arguments for an evaporitic model. As Gale Lake dried, conditions were ripe for the production of evaporites. Borates are very soluble in water and are typically only found in very arid environments after the evaporation of large amounts of water. Considering that Gale Crater is a topographical low, it would have acted as a closed drainage basin. Chloride deposits, which may have associated borates, have been remotely detected throughout the martian Southern Highlands and tend to be found in low-lying areas [16]. Chlorine and high sodium have been detected together by ChemCam in calcium sulfate veins in the same vicinity as the boron detections [17]. Hence, in the veins, we have observations of three major evaporite constituents, B, Cl, and S. Lastly, a thick layer of sulfates exist further up the stratigraphic column [7] that could represent the source evaporitic layer [8].

Implications for astrobiology. Borates can stabilize ribose [18], and the timing of the initial concentration of borates in sediments has important implications for possible origins of life. If the primary deposition is in an evaporite layer, the timing of the primary enrichment would post-date Mars climate change, possibly too late for the borates to be utilized for prebiotic chemistry. On the other hand, primary enrichment in the clays, while the lake was active during the late-Noachian to Hesperian, would increase the potential that borates could be used for prebiotic chemistry on Mars if the necessary organics were present.

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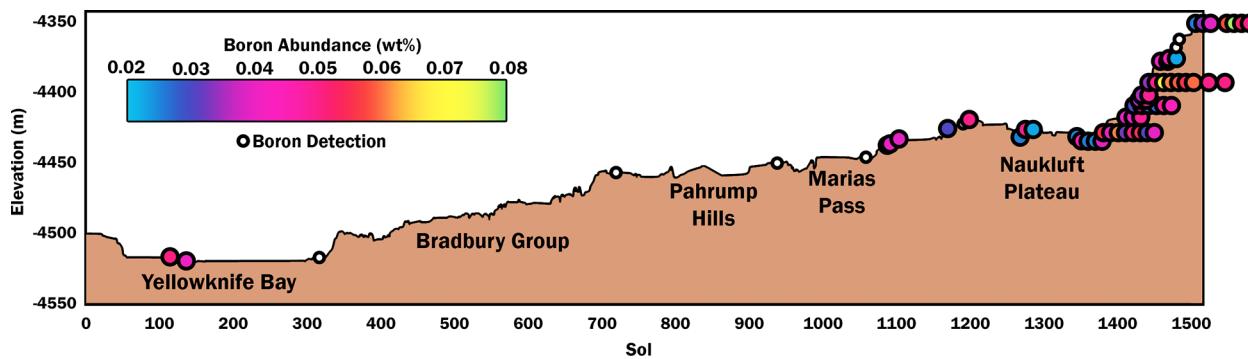


Figure 2: Boron detections observed along the traverse through sol 1504. Detections of boron above the quantification limit are colored based on the estimated boron abundance.