Supplemental Materials

Boron in Nakhla

Halite is a constituent of the secondary mineral assemblage observed in Nakhla [Bridges and Grady, 2000]. This secondary mineral assemblage is believed to be martian because veins containing these materials are truncated by fusion crust, suggesting that these veins were in place at the time of the meteorite's entry into Earth's atmosphere [*Gooding et al.*, 1991]. Boron has been detected in association with the halite and iddingsite phases seen in focused ion beam (FIB) section and analyzed by field emission scanning transmission electron microscopy, electron microprobe analysis, and nano secondary ion mass spectrometry [*Thomas-Keptra et al.*, 2015].

Methodology

Of the strongest neutral emission lines of boron [*Sansonetti and Martin*, 2005], only an unresolved doublet with peaks at 249.75 nm and 249.84 nm are observed in Mars data from the ChemCam spectrometers (Fig. S1A). These two peaks are persistent lines, the only lines observable at very low elemental abundances [see *Sansonetti and Martin*, 2005 Section 1.3] of boron, spectroscopically visible in ChemCam laboratory spectra at abundances of ≳50 ppm. However, the doublet has interference from lines of: Fe I (249.96 nm), Ca III (249.84 nm), Na III (249.77 nm), and Mn II (249.98 nm) (Fig. S2). Nominally boron-free standards from the ChemCam major element oxide standards database [*Clegg et al.*, 2017] were used to evaluate interferences with the boron peaks around 249.8 nm. For higher B abundances, singly ionized B lines are present in the ChemCam spectra at 291.89 nm and an unresolved triplet of ~703.4 nm (Fig. S1B). At 291.8 nm a set of complex B lines are very weak compared to the neutral boron lines around 249.8 nm. The B II triplet at ~703.4 nm has lines at 703.21, 703.38, and 703.45 nm (Fig. S1C), and has the strongest intensity of the B II lines in the ChemCam spectra, but is still two orders of magnitude weaker than the 249.8 nm lines. The B II triplet disappears below ~1.5 wt.% B in samples containing Al due to the presence of a strong Al II line at 704.40 nm and below ~0.08 wt.%B in Al-free spectra. The combined area of the two neutral boron lines at 249.75 and 249.84 nm in Figure S1A, corrected for interference lines of Fe II and Ca III, are used to evaluate the relative abundance of boron in Mars spectra.
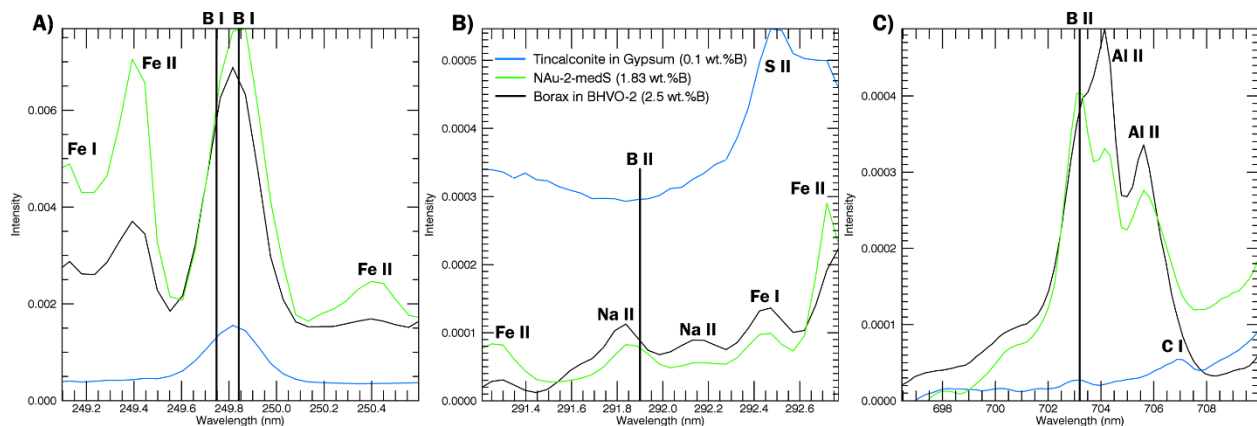
Figure S1: LIBS spectra in regions of major boron emission lines. The plots compare lab spectra of three types of boron standards: borax mixed with BHVO-2 (2.5 wt.%B), onboard standard NAu-2-medium S (1.83 wt.%B), and tincalconite mixed with gypsum (0.1 wt.%B). Lines were identified using the NIST Atomic Spectral Database. A) The region of the LIBS spectrum used for calibration with two unresolved B I lines at 249.75 and 249.84 nm. B) The region of the LIBS spectrum with three unresolved B II lines at 291.89 nm. C) The region of the LIBS spectrum with an unresolved triplet of B II lines around 703.4 nm.

After background subtraction and normalization to the spectral total in the VNIR spectrum, the spectral lines of boron and iron were fitted using an approximation of the skewed Voight function using the product of the Lorentzian and Gaussian functions [*Hesse et al.*, 2007] to extract the peak areas of the boron lines:

$$f(E) = h \left[1 + M_V \left(\frac{E - E_0}{\beta + \alpha(E - E_0)}\right)^2\right]^{-1} \times \exp\left[-(1 - M_V)\ln 2 \left[\frac{E - E_0}{\beta + \alpha(E - E_0)}\right]^2\right] \quad (1)$$

In Equation 1, the first term is the Lorentzian function and the second term is the Gaussian function, and h is the peak intensity, M_V is the mixing ratio (or the Voigt parameter), E_0 is peak position, β is half width at half maximum, and α is the skew factor. Peak fitting was performed using a custom program based on Rapin et al., [2016] method using the least squared fitting routine built into the optimization toolbox for MATLAB R2015a (Mathworks). Three lines—two boron lines and one Fe line (249.75, 249.84, 249.96 nm)—were simultaneously fitted to each spectrum (individual peaks are green and the sum is red in Figure 1G–I, while the original spectrum is black). Each peak had two free parameters (intensity and position) and the other peak parameters are fixed. Peak fits were constrained by fitting a strong Fe II line at 272.82 nm and the 249.96 nm Fe II in 47 nominally B-free standards (235 spectra) from the ChemCam spectral database that span a range of FeO compositions from 0.045–86.31 wt% FeO_T [*Clegg et al.*, 2017]. The ratio of the Fe II line intensities at 272.82 and 249.96 nm were used to constrain the intensity of the Fe II peak in Fe-bearing borate standards and Mars spectra. Fits of nominally Fe-free boron standards were used to constrain the intensity of the B I line at 249.75 nm relative to the intensity of the 249.84 nm B I line. Fixed parameter values were determined by unconstrained fitting of the Fe II lines in nominally B-free standard samples. The parameters for α, M_V, and β were fixed to the mean peak fit parameters determined by the unconstrained fits.

The boron peak area is corrected for the presence of the Ca III line from calcium sulfate by subtracting the average normalized background subtracted area of the Ca III peak for standards of pure dolomite, calcite, and 3 samples of gypsum [see *Anderson et al.*, 2017] for sample compositions. The standard deviation of the average Ca III peak area is used to calculate 2σ (1.23×10^{-5}) and 3σ (1.85×10^{-5}) dashed lines in Figure S2.

Boron-bearing standards consist of several calibration targets on the rover and 82 additional ones in the laboratory. ChemCam's onboard ceramic calibration targets contain 2–3 wt% boron [*Vaniman et al.*, 2012]. Laboratory LIBS spectra of the 82 boron-bearing and boron-free standards, corrected for instrument optical response and differences in environmental conditions between the lab and Mars [*Clegg et al.*, 2017]. Standards were placed inside a vacuum chamber containing a Mars-like atmosphere (~7 torr CO_2) and LIBS measurements were performed using

the ChemCam Engineering model at Los Alamos National Laboratory at a distance of 1.6 m. Spectra from 5-point rasters with 50 shots each were averaged. A spectrum-wide adjustment to correct for differences between ChemCam Mars spectra and terrestrial lab spectra [*Clegg et al.*, 2017] was applied in addition to the typical pre-processing [*Wiens et al.*, 2013] performed on every ChemCam spectra. We used a total of 42 boron-bearing standards. Standards included powdered terrestrial rock samples (pressed into a pellet) from the ChemCam major element oxide standards database (spectra and compositions are available from the PDS) with known concentrations of boron. Sample mixtures with proportions of sodium borate decahydrate (borax, $Na_2B_4O_7 \cdot 10H_2O$, Sigma Aldrich, 99.5% purity) ranging from 0.01–5.67 wt.% B (~0.1–50% borate) in Hawaiian basalt USGS standard BHVO-2, and 50–2000 ppm B in calcium sulfate dihydrate (Sigma Aldrich, 98–99% purity). Three mixtures each of borates provided by the Smithsonian Institution and BHVO-2 were made with compositions 0.1, 0.5, and 1.0 wt.%B with: kernite ($Na_2B_4O_6(OH)_2 \cdot 3H_2O$, NMNH 124063), ulexite ($NaCaB_5O_6(OH)_6 \cdot 5H_2O$, NMNH 124030-1), and tincalconite ($Na_2[B_4O_5(OH)_4] \cdot 3H_2O$, NMNH 124041). 10 samples of each Smithsonian borate and borax with calcium sulfate dehydrate between 100–1000 ppm B with 100 ppm B increments. Standard pellets were made by mixing materials in a mortar and pestle and then pressing them into Teflon-backed pellets using a lab press under 18 tons pressure.
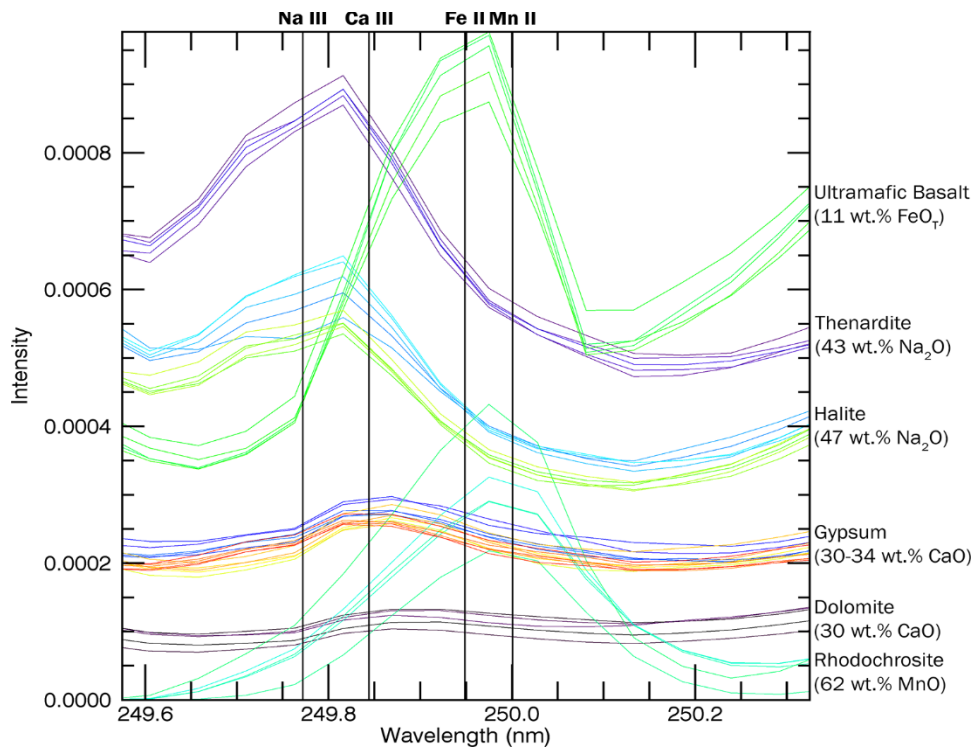

Figure S2: Normalized lab spectra showing interference lines in the region for the boron lines. Note that the normalized intensity for the 0.1 wt.% B sample mixture is ~0.0015 (Fig S1). Samples shown: ultramafic basalt [*Clegg et al.*, 2007], thenardite, halite, gypsum, dolomite [*Anderson et al.*, 2017], and rhodochrosite [*Lanza et al.*, 2017]
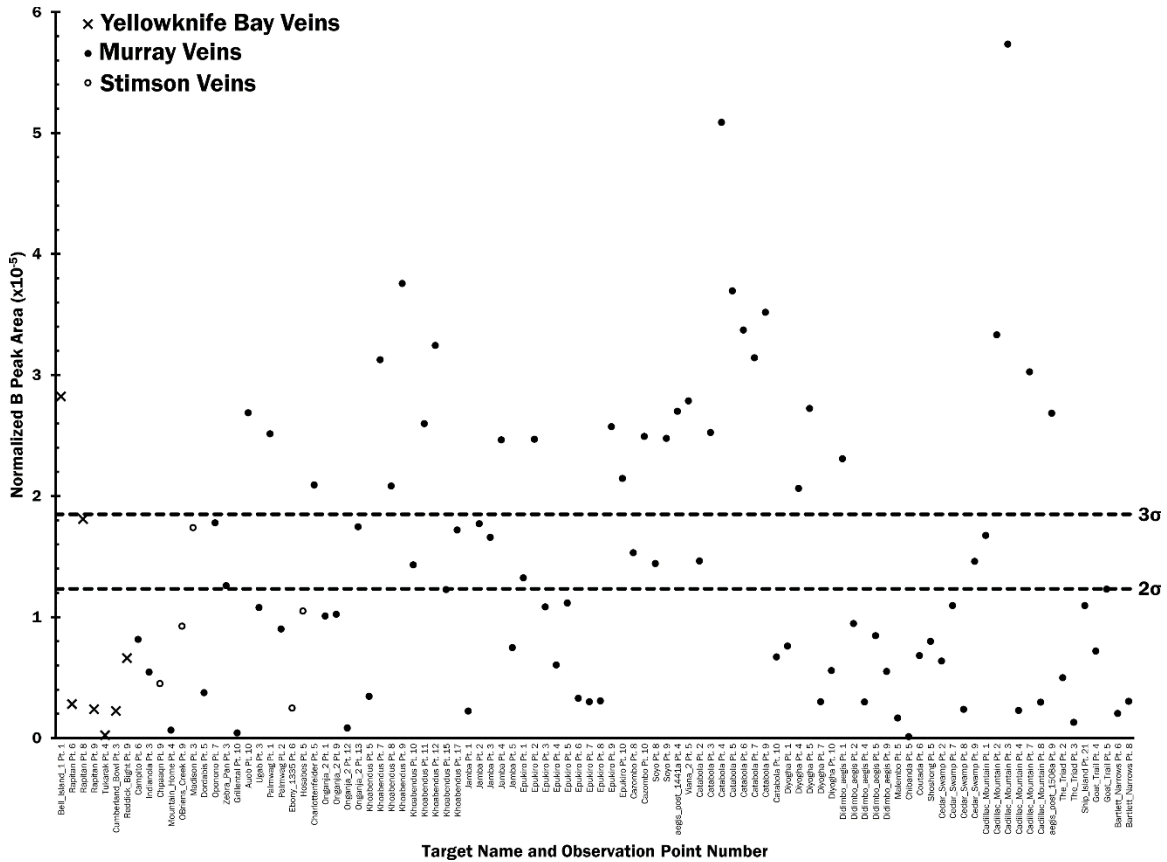
Figure S3: Normalized boron peak area of boron detections on Mars corrected for Ca III. Two and three standard deviation of the average pure Ca mineral Ca III peak area shown as dashed lines.

Table S1 (Included as a separate Excel file): Summary of boron peak area, morphology, and location of boron detections in veins.

Possible Borate Mineralogy

The abundance of boron in the veins is likely <0.05 wt.%, which is too low to determine trends with the major elements and likely below detection limits for CheMin. The most likely borate phases present in veins are the calcium-bearing borates include ulexite ($NaCaB_5O_6(OH)_6 \cdot 5H_2O$), inyoite ($CaB_3O_3(OH)_5 \cdot 4H_2O$), and colemanite ($CaB_3O_4(OH)_3 \cdot H_2O$). Colemanite precipitation is favored in warmer, more neutral conditions and might be a tracer for the initial evaporite layer; colemanite is very insoluble in water and would not be redistributed by the groundwater. If Na-rich fluids are present, the primary sodium-bearing borate, borax ($Na_2B_4O_7 \cdot 10H_2O$), would be a possible borate precipitate, and above ~35°C, dehydrated forms of borax, kernite ($Na_2B_4O_6(OH)_2 \cdot 3H_2O$) and tincalconite ($Na_2B_4O_7 \cdot 5H_2O$) would co-precipitate as well. If groundwater fluids were acidic to neutral, then borate would precipitate as sassolite (H_3BO_3) in calcium sulfate veins. More observations of vein materials are required before tight constraints on borate mineralogy can be given.