BORON ADSORPTION IN CLAY MINERALS: IMPLICATIONS FOR MARTIAN GROUND-WATER CHEMISTRY AND PREBIOTIC PROCESSES. M. A. Nellessen[1], L. Crossey[1], E. Peterson[1], P. Gasda[2], N. Lanza[2], C. Yeager[2], B. Parsons[2], A. Labouriau[2], R. C. Wiens[2], S. Clegg[2], D. Das[3], [1]University of New Mexico, [2]Los Alamos National Laboratory, [3]McGill University.

Introduction: Boron has been detected in calcium sulfate veins by ChemCam on the NASA *Curiosity* rover [1;2;3]. In water, boron is a borate, and its speciation depends on pH. In alkaline water, borates will adsorb to 2:1 phyllosilicates [4]. Borate adsorption to clay minerals strongly depends on water pH conditions; a pH range of 8-9 [5] providing the most adsorption, yielding abundances up to 300 ppm [5] with some variance depending on the exact type of clay used. *Curiosity* has traversed through Gale crater, which has been interpreted as a fluvial lacustrine system with near neutral surface water [6]; this study hopes to understand borate behavior in the martian groundwater, assuming neutral to alkaline pH conditions [6].

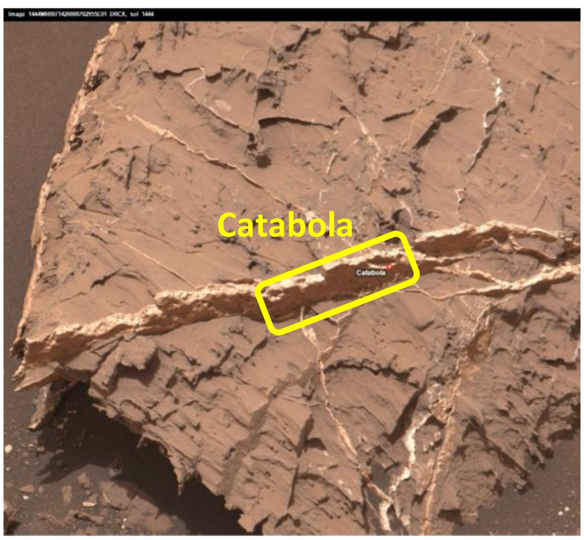

Fig. 1 Mastcam image of the Catabola target in Gale crater, Mars [4]. Bedrock can be seen with abundant light-toned, calcium sulfate veins, within which boron has been detected. This vein contains one of the highest relative concentrations of boron detected so far in Gale crater [1]. Photo: JPL-Caltech/MSSS.

It has been hypothesized that boron may be a vital aspect for prebiotic processes to occur on Earth and possibly on Mars [2]. The formation of boron-ribose complexes [7] might allow the formation of RNA. Borate-ribose complexes are relatively stable in water; without borate, ribose quickly breaks down in solution [7]. The discovery of boron on Mars opens the possibility for RNA-based life to have developed independently on Mars [1].

Methods: We will generate boron-enriched clay minerals in the lab. The relationship between boron adsorption and pH will be studied in both Mars-like and common terrestrial clay minerals including martian clay mineral analogs saponite, nontronite, and a clay-bearing griffithite rock [8]. Terrestrial clays, e.g., Ca-rich montmorillonite (bentonite) will be used to validate our procedures and results.

Using methods described in [5], we mix a 150 mg B/L solution made from boric acid to each clay sample and shake for 3 hr. Samples are centrifuged at 2600 rpm for 1 hr, mixed, centrifuged again, and supernatant is removed. The remaining boron-enriched clay is rinsed with a pH-similar fluid. We will vary pH from to 6 to 11 in increments of 0.5 for each clay type to determine the relationship between pH and boron adsorption.

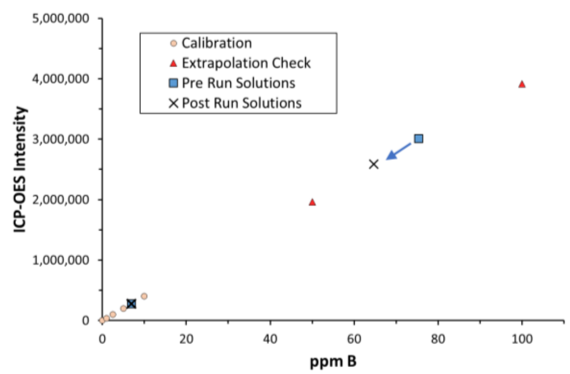

Fig. 2 Above depicts the preliminary data run on the Ward's bentonite when mixed with a low concentration and high concentration borate solution. In the low concentration, there was not detectable change between the borate solution and the supernatents, indicating the boron was below detection limits. In the higher concentration, there was a significant loss of boron from solution (106.1 ppm B) indicating sorption by the clay.

Clay samples will be analyzed with Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES), Laser Induced Breakdown Spectroscopy (LIBS), the method used by ChemCam that detected boron, as well as with Raman spectroscopy, X-Ray Diffraction (XRD), Nuclear Magnetic Resonance (NMR) spectroscopy, and

Gas Chromatography-Mass Spectrometry (GCMS). LIBS spectra collected with the ChemCam laboratory unit at LANL can be directly compared with ChemCam on *Curiosity*. These spectra can also be added to the set of standard boron calibration spectra to improve the quantification of boron in ChemCam Mars data. XRD and Raman will provide mineralogical analysis, NMR will provide organic structural analysis, and GCMS will provide the organic concentration and identification analysis. The organic chemical fraction of these clays will also be analyzed with GCMS [9]. In addition to comparing to *Curiosity* data, the results will be compared to the future Mars 2020 rover datasets.

Preliminary Results: Preliminary tests have been run on a Ward's Bentonite (46 E 0435) to get an initial idea of recreating the results seen in [5]. At the lower concentration of ~70 ppm B at a pH of ~9, we used ICP-OES to determine if there was a loss in boron concentration between the original borate solution and the subsequent supernatent after it had been mixed with the clay sample. There was not a significant decrease in boron detected at this level (see Figure 2). This indicates that this low concentration is below the limits of detection for B on ICP-OES. We then increased the borate solution concentration to around ~750 ppm B and ran the same ICP-OES test and were able to detect a decrease in the boron concentration from ~750 ppm B in the original solution down to ~650 ppm B in the supernatent.

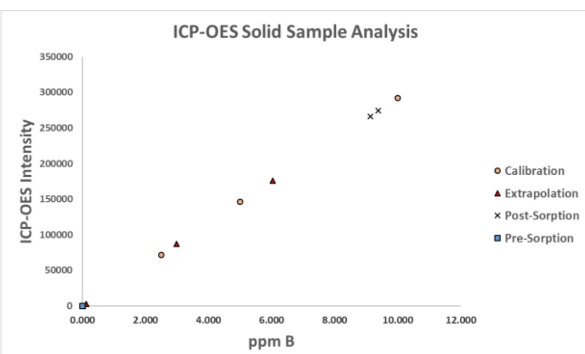

Fig. 3 Preliminary data for the solid samples when run through ICP-OES analysis. As can be seen the two samples with sorbed boron, in red, show detectable boron in the range of ~90 ppm B/ g clay (1:10 dilution shown in plot) or ~220 μmol B/g clay.

ICP-OES analysis of the solid samples involved runnning the solid samples through acid digestion to separate the sorbed boron into solution to be detected by ICP-OES. Two samples of the high B concentration clay were run alongside a sample fo the clay without B and a clay standard containing ~72 ppm B. The ICP-OES analysis (see Figure 3) indicated that the original clay and the standard contained no boron or were below the detection limits for B. The two samples with sorbed B were seen to have ~90 ppm B detected, indicating that these samples did sorb B from solution efficiently.

Further experimental analysis will include repeating the procedure on the previously mentioned Mars-analog clays at varying pH to determine how well Mars-like clays sorb boron given varying groundwater conditions.

Implications: Our project represents the first boron-clay adsorption experiments for Mars-like clays, which will provide new insight on the geochemical behavior of borate in Martian groundwater, and allow us to infer the amount of boron that could be present in Martian bedrock. Understanding boron-clay relationships will allow us to make some clear comparisons between terrestrial and Martian boron-enriched clays and improve our techniques for boron detection on Mars. Boron-clay relationships will form the basis for later work on the impact of boron-enriched clays on prebiotic processes that could have occurred on Mars [10].

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