BORON ADSORPTION ONTO CLAY MINERALS: INSIGHT INTO MARTIAN GROUNDWATER GEOCHEMISTRY M. A. Nellessen[1], L. Crossey[1], P. Gasda[2], E. Peterson[1], N. Lanza[2], A. Reyes-Newell[2], D. Delapp[2], C. Yeager[2], A. Labouriau[2], R. C. Wiens[2], S. Clegg[2], S. Legett[2], D. Das[3], [1]University of New Mexico, [2]Los Alamos National Laboratory, [3]McGill University.

Introduction: It has been hypothesized that the presence of boron may be essential for prebiotic processes to occur on Earth and possibly on Mars [1]. Borate-ribose complexes are relatively stable in water; without borate, ribose quickly breaks down in solution [2]. The formation of boron-ribose complexes [2] may thus be necessary for the formation of RNA.

Boron has been detected in calcium sulfate veins by ChemCam on the NASA *Curiosity* rover [1, 3, 4]. The discovery of boron on Mars opens the possibility for RNA-based life to have developed independently on Mars [3]. This study hopes to understand borate behavior in the martian groundwater by determining how Mars-like clays and boron interact.

Background: In water, boron appears as either borate or boric acid, and its speciation depends on pH. In alkaline water, boron comes in the form of a borate and will adsorb to 2:1 phyllosilicates [5]. On Earth, borate adsorption to clay minerals strongly depends on water pH conditions; a pH range of 8-9 [6] providing the most adsorption, yielding abundances up to 300 ppm [6] with some variance depending on the exact type of clay used.

Methods: We generated boron-enriched clay minerals in the lab. The relationship between boron adsorption and pH was studied in both Mars-like and common terrestrial clay minerals including Martian clay mineral analogs saponite, nontronite, and a clay-bearing griffithite rock [7]. Terrestrial clays, such as two montmorillonites (referred to later as A and B), a talc, and an unknown clay from the Rio Tinto borax mine were used to validate our procedures and results.

Using methods described in [6], we mixed a 200 ppm B solution made from boric acid to each clay sample and shook for 10 hr. Samples were centrifuged at 2600 rpm for 1 hr, mixed, centrifuged again, and supernatant was removed. The remaining boron-enriched clay was rinsed with a pH-similar fluid. We varied pH from to 6 to 11 in increments of 1 for each clay type to determine the relationship between pH and boron adsorption. We also varied the concentration of the boric acid fluid at pH 8 from 200, 100, 50, 25, to 10 ppm B to determine if concentration affected boron sorption.

Clay samples were 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 X-Ray Diffraction (XRD). 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 provides mineralogical analysis. In addition to comparing to *Curiosity* data, the results will be compared to the future Mars 2020 rover datasets.

Results: XRD analysis included oriented mounts of the clays to determine pre-adsorption structure (**Figure 1**), which will be followed by more x-ray scans after adsorption to see the change in structure to accommodate boron. The pre-adsorption XRD patterns all displayed expected clay signatures, with the montmorillonites and the talc being correctly identified by their respective mineral pattern. While the other species were unable to be correctly identified due to database limitations, they still exemplified their predominant clay-mineral nature.

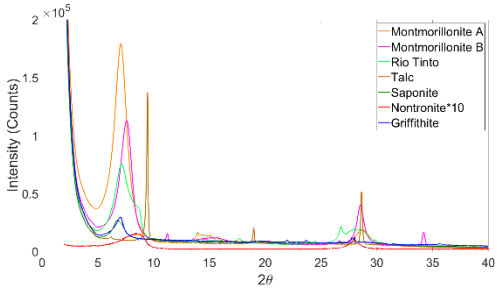

Fig. 1. XRD analysis of oriented mounts of all 7 clay species.

Adsorption analysis were run on the seven clay species. At 200 ppm B concentration, all seven clays saw varying degrees of adsorption from low adsorption (100 ppm B) in the talc to high adsorption (>2000 ppm B) in the two montmorillonites (**Figure 2**). The two montmorillonites saw the greatest degree of adsorption at over 150 µmol B/g clay (>2000 ppm B). The griffithite showed peak sorption around pH 9.5 at ~60 µmol B/g clay (~750 ppm B). The

saponite and nontronite both showed peak adsorptions at pH 10 at ~30 µmol B/g clay (~300 ppm B). The talc showed lowest degree of sorption, ~10 µmol B/g clay (~100 ppm B). The Rio Tinto clay sample indicated leaching of boron from the sample into the fluid and therefore gave the negative pattern as seen in Figure 2 (green curve).

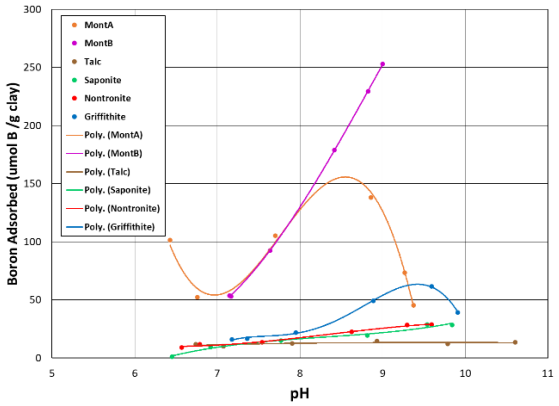

Fig. 2. Preliminary ICP-OES clay analysis.

Discussion: The XRD analysis of the clays prior to adsorption indicated the predominant clay mineral abundance in the samples. The nontronite analysis resulted in very low intensity and had to be amplified in order to observe its x-ray pattern. This analysis forms the first phase of the x-ray analysis as the clays will be re-analyzed after being adsorption with boron to see how the x-ray patterns change to accommodate the boron.

The adsorption curves for montmorillonite B, talc, saponite, and nontronite did not resemble the curves seen in previous literature [6], while the curves for montmorillonite A, griffithite, and the Rio Tinto sample (albeit negative) did reflect the expected curve seen from the literature. This may be due to the variability of clay species and their varying potential for adsorbtion [6]. In [6], the three species of clays had different sorption peaks ranging from pH 7 to 9, as well as different sorption potential, with bentonite and sepiolite sorbing 3-4 times as much boron as illite. Similarly, the different clays used in this study may have high variance in their adsorption potential and adsorption patterns.

The terrestrial clays included the montmorillonites, the talc, and the Rio Tinto sample. The montmorillonites adsorbed abundant boron as expected. The talc adsorbed very little and was near background detection limits. The Rio Tinto clay which contained boron prior to the treatment, indicated a loss of boron from the clay minerals to the solution. These results matched the terrestrial sample data as expected. The talc was expected to adsorb very little, forming a background baseline and the montmorillonites would provide a comparison for strong adsorption. The Rio Tinto was run as an unknown variable. The Mars analog clays consisted of the saponite, nontronite, and griffithite clays, being the Fe- and Mg-rich clays as seen on Mars. These analog clays adsorbed notably less boron than their montmorillonite counterparts, but a significant degree of adsorption still occured. Both the saponite and nontronite adsorbed a peak of ~300 ppm B, which compares to values of boron detected in calcium-sulfate veins in Gale crater [3]. The griffithite even reached peak adsorption values of ~750 ppm B, indicating that the Mars-like clays could have high potential for containing a high amount of boron, especially when considering these samples are impure with secondary minerals which would not adsorb boron, suggesting a pure clay would adsorb even more than indicated.

Summary: In this investigation, we found that while the different clay species used in this study did not always follow the expected trends of the literature, they still indicated highest sorption in more alkaline pH conditions. The Mars analog clays, while adsorbing notably less boron than the terrestrial montmorillonites, still adsorbed a significant quantity of boron that correlates well with values detected on Mars.

Future Work: Future work includes XRD oriented analysis of the clays after exposure to boron to compare with the pre-adsorption patterns. This is to capture the change in structure due to the accommodation of boron onto the clay. Further studies may include TEM and XPS analysis as well to get finer scale analysis of the adsorption mechanisms. Furthermore, these samples will be used for ChemCam analysis and calibrations at a later date.

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