ADSORPTION OF BORON 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, e.g., Ca-rich montmorillonite (bentonite) 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 10 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 at 200, 100, 50, 25, and 10 ppm B to determine if concentration has an effect on 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 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 provide mineralogical analysis, NMR provides organic structural analysis, and GCMS provides the organic concentration and identification analysis and organic chemical fraction analysis [8]. In addition to comparing to *Curiosity* data, the results will be compared to the future Mars 2020 rover datasets.

Results: Preliminary tests were run on two montmorillonite clays (A & B) [6]. At 200 ppm B concentration, all samples for both A and B at all pH values saw some degree of sorption, though the pH's of 8 and 9 did not see the greatest sorption as expected. Instead montmorillonite A saw greatest sorption at pH 10, with a steady decrease with decreasing pH. Montmorillonite B displayed a similar trend but saw an additional peak around pH 7, but this was likely an outlier.

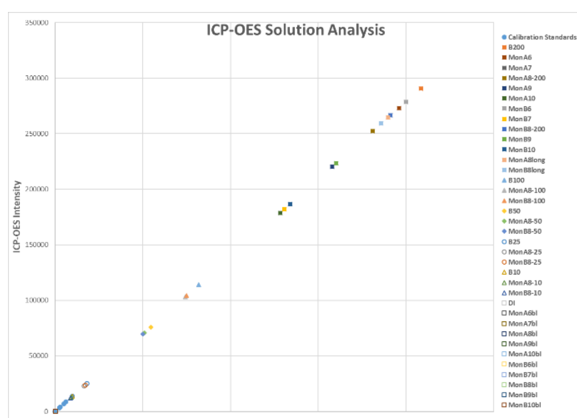

Fig. 1 Preliminary ICP-OES analysis on all samples.

Discussion: The adsorption curves from [6] were not recreated in this analysis (Fig 2). This may be due to using slightly different clays and different concentrations of borate fluid. Different clays have different potential for adsorbing clays so some variance can come from that [6]. In [6], the three species of clays used 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.

Figure 3 shows how increasing the concentration of B in solution increases the amount of sorbed borate. The initial borate concentration was much greater in our experiments as compared to the literature procedure because we are trying to making a gram's worth of -enriched clay material. The literature uses concentrations between 4–50 mg B/L on 0.1 g of clay, while we used a concentration of 40 g B/L on 1 g.

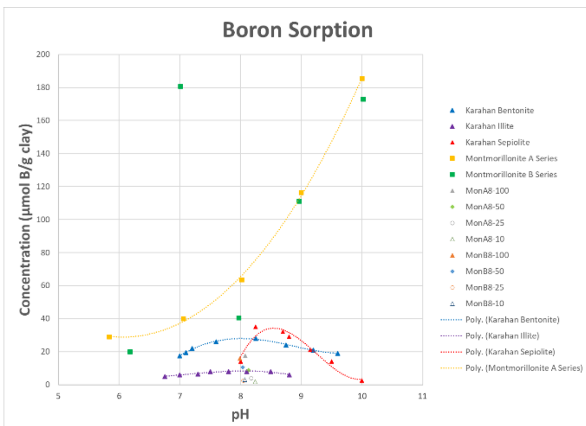

Fig. 2 Sorption curves for montmorillonite samples compared to the clays from [6].

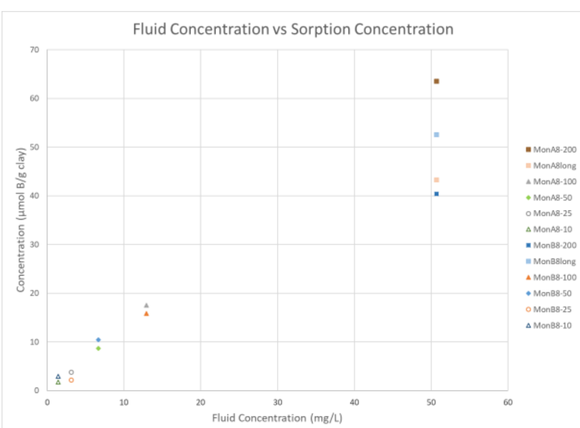

Fig. 3 Comparison between concentration of the borate fluid and the concentration of boron sorbed to the clays.

Figure 3 shows that the samples at 100, 50, 25, and 10 ppm B saw decreasingly less sorption than the samples mixed with 200 ppm B. There is a clear relative linear trend between boron fluid concentration and adsorption. This indicates that the degree of boron sorption depends on the concentration of the borate-carrying fluid. This is important because it means that if a given composition of boron is detected within the clay, the original fluid composition can therefore be predicted, assuming alkaline pH conditions. This will be vitally important for looking at boron Mars in being able to understand the groundwater geochemistry conditions present in Gale Crater at the time. There did not appear to be a significant difference in sorption when the solution was allowed to sit for 10 hours compared to 20 hours.

Summary: The key results of this research have found that while the two montmorillonite samples used in analysis did not follow the expected trends of the literature, they did still see the most sorption in more alkaline pH conditions. It was also determined that the amount of boron sorption to the clay is determined by the original concentration of boron in the fluid. Extended time of sorption did not seem to increase sorption, likely indicating that most of the sorption happens relatively quickly.

Future Work: 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. Using the data in figures 2 and 3, if the borate fluid concentration is reduced to roughly 7-15 mg B/L, the pH vs sorption relationship for these clays would suggest values similar to those seen in [6], and allow us to better replicate the literature results.

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