

**BORON ADSORPTION IN MARTIAN CLAY ANALOGS: SIGNIFICANCE FOR MARTIAN PREBIOTIC PROCESSES AND GROUNDWATER GEOCHEMISTRY.** M. A. Nellesen<sup>1</sup>, L. Crossey<sup>1</sup>, P. J. Gasda<sup>2</sup>, E. Peterson<sup>1</sup>, N. Lanza<sup>2</sup>, C. Yeager<sup>2</sup>, A. Labouriau<sup>2</sup>, R. C. Wiens<sup>2</sup>, S. Clegg<sup>2</sup>, A. Reyes-Newell<sup>2</sup>, D. Delapp<sup>2</sup>, D. Das<sup>3</sup>, <sup>1</sup>University of New Mexico, <sup>2</sup>Los Alamos National Laboratory, <sup>3</sup>McGill University

**Introduction:** Boron is a rare water-soluble element found in organic-rich soils on Earth often in association with biologic activity [1]. Boron typically occurs as borate in water and will bind to 2:1 phyllosilicates when introduced by groundwater or other fluid process [2]. The pH of the borate fluid is integral in affecting boron sorption to these clay minerals, with a pH range of 8–9 providing the peak sorption up to ~300 ppm [1]. Martian groundwater is hypothesized to have been near-neutral to slightly alkaline [3], so martian groundwater provides an optimal pH level for boron uptake by clay minerals. Boron has been detected frequently within martian calcium sulfate veins by ChemCam on the NASA *Curiosity* rover in relatively significant quantities [4].

It has been hypothesized that boron may be a vital aspect for prebiotic processes to occur on Earth and possibly on Mars [4,5]. The formation of boron-ribose complexes [6] helps to stabilize ribose in solution, where it would normally break down rapidly in the absence of boron [6]. Ribose is integral for the formation of RNA, so its stability is integral for life to arise. With boron found on Mars, this creates the potential for life to develop independently on Mars [4].

**Methods:** We have generated boron-enriched clay minerals in the lab at a range of different pH conditions. These borate-clay samples will be used to test their interactions with ribose. The relationship between boron adsorption and pH was studied in both Mars-like clays and common terrestrial clay minerals including montmorillonite and talc, and Mars analogs such as saponite, nontronite, and griffithite [7].

Using the methods described in [1], we mix a 100-150 mg B/L solution made from boric acid ( $H_3BO_3$ ) to each clay sample and shake for 3 hr. Samples are mixed and then centrifuged at 2600 rpm for 1 hour and supernatant is removed. The remaining boron-enriched clay is rinsed with a pH-similar fluid. We will vary pH from 6 to 11 in increments of 0.5 for each clay type to determine the relationship between pH and boron adsorption.

Clay samples have been analyzed with Laser Induced Breakdown Spectroscopy (LIBS), the method used by ChemCam that detected boron, as well as with Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), a neutron activation analysis for baseline B abundance, a colorimetric method using azomethine-H, and X-Ray Diffraction (XRD). LIBS spectra collected with the ChemCam engineering unit at LANL will be directly compared with

ChemCam on *Curiosity*. ICP-OES and ICP-MS have been used for chemical analysis to determine and calibrate the LIBS chemical analysis. XRD and Raman spectroscopy provides mineralogical analysis for the samples. These methods will characterize the samples and be used for comparison with the current *Curiosity* and the future Mars 2020 rover datasets.

**Preliminary Results:** Initial analysis has included XRD, LIBS and ICP-OES of some samples to form a baseline mineralogy and chemistry. XRD results displayed the expected phyllosilicate peaks indicative of smectite clays; however, they also indicated that some samples are impure. The saponite and griffithite also contain minor amounts of plagioclase and pyroxenes, but these minerals do not adsorb borate, so they are not expected to affect the results of future analyses. The samples were also analyzed with LIBS for baseline chemistry to compare with chemical analysis via mass spectroscopy. A preliminary sample used for boron sorption tests had LIBS detect 0.67 wt% B (~5000-6000ppm) which was within range of what had been detected via ICP-OES (~3000 ppm). ICP-MS results of a clay sample from the Rio Tinto boron mine revealed a B concentration of 967 ppm, while most of the other samples contained less than 10 ppm. An understanding of the baseline mineralogy and chemistry is essential for comparing the samples before and after sorption of boron to the clays.

**Implications:** This project represents the first boron-clay adsorption experiments for Mars-like clays, which will provide new insight on the geochemical behavior of martian clays in association with boron and may allow us to infer the amount of boron present in Martian bedrock. Understanding boron-clay dynamics will allow us to relate terrestrial and Martian boron-enriched clays and also improve our boron detection techniques on Mars. Boron-clay relationships will form the basis for future work on the analysis of boron-enriched clays on prebiotic processes on Mars [8].

**Acknowledgements:** LANL LDRD-ER Program, University of New Mexico, NASA Mars Exploration Program.

**References:** [1] S. Karahan et al. 2006, Journal of Colloid and Interface Science, 293, 36-42. [2] Keren and Mezuman 1981 Clays Clay Min, 29, 198-204 [3] J. Grotzinger et al. 2014 Science 343(6169). [4] Gasda et al. 2017, Geophys. Res. Lett., 44, 8739-8748 [5] Scorei et al. 2012, Origins of Life and Evolution of Biospheres. [6] T. Georgelin et al. 2014, Carbohydrate Research. [7] D. T. Vaniman et al. 2014, Science 343(6169). [8] Ricardo et al. 2004 Science 303(5655).