

**REACTION OF AKAGANEITE WITH MARS-RELEVANT ANIONS.** M. J. Pan<sup>1</sup>, D. W. Ming<sup>2</sup>, E. B. Rampe<sup>2</sup>, T. S. Peretyazhko<sup>3</sup>. <sup>1</sup>Franklin and Marshall College, Lancaster, PA, 17603, <sup>2</sup>NASA Johnson Space Center, Houston, TX, 77058, <sup>3</sup>Jacobs, NASA Johnson Space Center, Houston, TX, 77058 (tanya.peretyazhko@nasa.gov).

**Introduction:** Akaganeite has been identified by the Chemistry and Mineralogy (CheMin) and Sample Analysis at Mars (SAM) instruments onboard the Curiosity rover in Yellowknife Bay, Gale Crater, Mars [1-2]. Akaganeite was also detected by the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) instrument on the Mars Reconnaissance Orbiter (MRO) in Robert Sharp Crater and Antoniadi basin [3]. Akaganeite is an iron(III) hydroxide with a hollandite-like tunnel structure with tunnels usually occupied by Cl<sup>-</sup> [4]. Chloride in tunnels is not immobile and can be replaced by other anions in solution [4]. Identification of tunnel composition with Mars-like instruments can help to characterize composition of ancient aqueous environments where akaganeite is present on Mars.

The objective of this work was to determine if different tunnel compositions of akaganeite can be distinguished using laboratory analogs of mission instruments. Synthetic Cl-containing akaganeite (Cl-akaganeite) was reacted with Mars-relevant anions (Br<sup>-</sup>, OH<sup>-</sup>, F<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) and the mineralogical and spectral properties of the final products were characterized by X-ray diffraction, Visible and Near-Infrared Spectroscopy, and thermal analysis.

#### Methods:

**Synthesis** Cl-akaganeite (Fe/Cl ratio = 0.5) was synthesized by forced hydrolysis of 0.2 M Fe(ClO<sub>4</sub>)<sub>3</sub> • H<sub>2</sub>O (Sigma Aldrich) and 0.4 M NaCl (Fisher Scientific). After incubation at 90°C for 24 hours, the precipitates were washed three times with Milli-Q water by centrifugation and freeze dried. For total chloride determination in the synthesized Cl-akaganeite, a 30 mg sample was digested in 20 mL of 5 M HNO<sub>3</sub> (Fisher Scientific, ultrapure) on a hot plate for one hour and diluted to 100 mL with Milli-Q water.

**Anion Exchange Experiments** Individual anion exchange experiments were conducted by incubating 200 mg of synthesized akaganeite (Cl-akaganeite) in 50 mL solution of 0.1 M NaBr (Fisher Scientific), NaOH (Sigma Aldrich), NaF (Fisher Scientific), or Na<sub>2</sub>SO<sub>4</sub> (Acros Organics, extra pure) solutions for 96 hours at 55°C. Two anion exchange experiments were performed with the same mass of akaganeite in 50 mL solutions containing a mixture of 0.05 M NaBr or NaF with 0.05 M Na<sub>2</sub>SO<sub>4</sub>. A control experiment with no anion addition was also performed (denoted as H<sub>2</sub>O-akaganeite). Aliquots (5 mL) of akaganeite suspension were collected at 0, 2, 24, 48, 72, and 96 hours using a 10 mL syringe-driven filter unit for dissolved chloride

analysis. At the end of incubation, solids were collected by centrifugation, rinsed with Milli-Q water, and freeze-dried.

**Characterization** Total chloride content in Cl-akaganeite as well as dissolved chloride at different time points were measured by ion chromatography (IC) using a Dionex ICS-2000 RFIC Ion Chromatography system. Measurements of solution pH were performed using a Thermo Scientific Orion Star Series Meter. Thermal gravimetry (TG), differential scanning calorimetry (DSC), and evolved gas analysis (EGA) were conducted using Labsys Evo Simultaneous Thermal Analysis (Setaram Instrumentation, KEP technologies) connected to a quadrupole mass spectrometer (Thermostat GSD 320, Pfeiffer Vacuum Incorporated) configured to operate similarly to the SAM instrument: ramp rate of 35°C/min, furnace pressure of 30 mbar, flow rate of 10 sscm, maximum temperature of 1000°C, and helium carrier gas. Powder X-ray diffraction (XRD) analysis patterns were collected using a Pananalytical X'Pert Pro diffractometer with Co K $\alpha$  radiation. Samples were scanned at 45 kV- 40 mA with a 0.02° 2 $\theta$  step from 4-80° 2 $\theta$ . Visible and near-infrared reflectance spectroscopy (VNIR) was conducted using an Analytical Spectral Devices FieldSpec3 fiber-optic based spectrometer.

#### Results/Discussion:

**IC and pH.** The exchange capacities of individual anions were measured by the amount of chloride released over time. Chloride release reached equilibrium in under 24 hours and increase in the total Cl<sup>-</sup> release from akaganeite followed the order: H<sub>2</sub>O < Br<sup>-</sup>  $\approx$  SO<sub>4</sub><sup>2-</sup> < F<sup>-</sup> < OH<sup>-</sup> for individual anion exchange experiments (Figure 1A). For the two anion exchange experiments, equilibrium was reached after 48 hours in the the Br<sup>-</sup>+SO<sub>4</sub><sup>2-</sup> sample, while no equilibrium was reached after 96 hours in the the F<sup>-</sup>+SO<sub>4</sub><sup>2-</sup>-sample. Chloride loss was greater for the Br<sup>-</sup>+SO<sub>4</sub><sup>2-</sup>-exchanged sample than the F<sup>-</sup>+SO<sub>4</sub><sup>2-</sup>-exchanged sample (Figure 1B). Overall chloride release for two anion exchange experiments was larger than individual anion exchange with Br<sup>-</sup>, F<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>.

pH behaved differently in exchange experiments. The value of pH decreased over time in Br<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>O, and Br<sup>-</sup>+SO<sub>4</sub><sup>2-</sup> samples to pH 3. Decrease in pH could be attributed to the deprotonation of the surface of akaganeite, accompanied by release of chloride from tunnels [4-5]. pH did not change over time and remained around 12.5 for the OH-exchanged sample and around 5.22 for the F<sup>-</sup>+SO<sub>4</sub><sup>2-</sup>-exchanged sample. Constant pH could be due to approximately equal rate of protonation and deprotonation, accompanied release and uptake of

anions, or by an excess of a strong base in solution, as in the case of incubation in akaganeite in NaOH. Finally, pH increased for the F<sup>-</sup>-exchanged sample to reach a pH of 7. Increase in the pH of the F-exchanged sample solution was likely due to incorporation of F<sup>-</sup> in tunnels, accompanied by H<sup>+</sup> uptake and, consequently, pH increase [4].

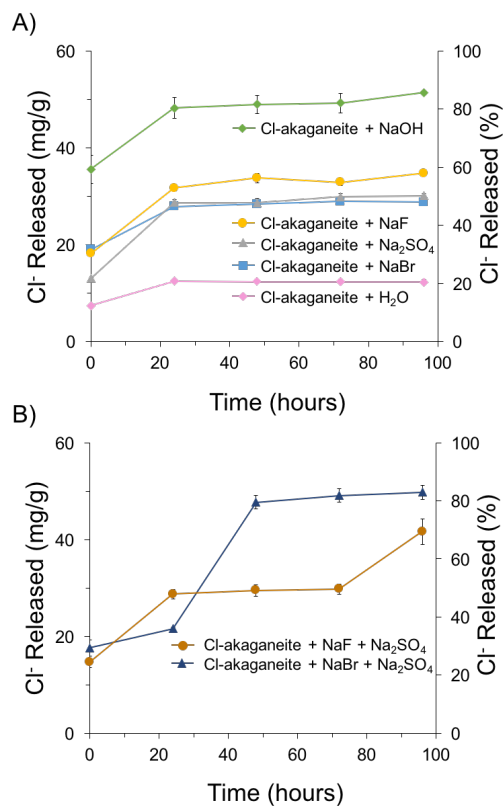


Figure 1. Time dependent release of chloride from Cl-akaganeite during incubation in A) water and solutions containing one anion (SO<sub>4</sub><sup>2-</sup>, F<sup>-</sup>, Br<sup>-</sup>, OH<sup>-</sup>) and B) two anions (F<sup>-</sup>+SO<sub>4</sub><sup>2-</sup>, Br<sup>-</sup>+SO<sub>4</sub><sup>2-</sup>).

**XRD.** X-ray diffraction analysis of the initial and anion-reacted samples revealed that akaganeite remained highly crystalline after reaction. Formation of other oxides or any mineralogical changes were not observed. Peaks in all reacted samples were shifted towards higher  $2\theta$  values relative to the starting material. For the 001 peak, the shift in peak position increased in the order of H<sub>2</sub>O < Br<sup>-</sup> ≈ SO<sub>4</sub><sup>2-</sup> < F<sup>-</sup> ≈ OH<sup>-</sup>. The peak positions for Br<sup>-</sup>+SO<sub>4</sub><sup>2-</sup> and F<sup>-</sup>+SO<sub>4</sub><sup>2-</sup>-reacted samples were in-between the positions for the constituent individual anions, indicating that peak positions were dependent on the anions in the reaction.

**VNIR.** Two akaganeite characteristic bands were detected in the samples: H<sub>2</sub>O combination band at 2.00 μm and OH combination band at 2.46 μm. Both bands were sensitive to Cl<sup>-</sup> content in akaganeite. Position of the

2.00 μm band correlated with chloride content [6]. The band at 2.46 μm, indicative of OH-Cl stretching and out-of-plane bending vibrations, was observed in all samples except the OH<sup>-</sup>-exchanged sample which had the largest release of Cl<sup>-</sup> (Figure 1A). Only a broad shoulder was observed at 2.46 μm in the OH<sup>-</sup>-reacted sample, due to vibrations of isolated OH<sup>-</sup>.

**TG/DSC/EGA.** Thermogravimetric data showed approximately 20% total weight loss across all samples. Dehydration and dihydroxylation corresponded with endotherms between 0-250 °C, and exotherms occurring concurrently with HCl<sub>(g)</sub> release between 300-400 °C. These processes were attributed to akaganeite transformation to hematite through the reaction 2FeOOH = Fe<sub>2</sub>O<sub>3</sub> + H<sub>2</sub>O [7]. The shapes of the DSC curves and specific gas releases were different for each sample with the exception of non-reacted Cl-akaganeite and H<sub>2</sub>O-reacted akaganeite. Release of SO<sub>2(g)</sub> and HF<sub>(g)</sub> were observed for the SO<sub>4</sub><sup>2-</sup> and F<sup>-</sup>-exchanged samples, respectively, and these gases released together in the the F<sup>-</sup>+SO<sub>4</sub><sup>2-</sup>-reacted sample. HBr<sub>(g)</sub> release was not observed for Br<sup>-</sup>-exchanged samples, implying possible retention of Br<sup>-</sup> in hematite.

### Conclusions:

Experimental studies of akaganeite reaction with Mars-relevant anions revealed that laboratory instruments similar to instruments onboard rovers and orbiters can differentiate between Cl<sup>-</sup>-rich and Cl<sup>-</sup>-poor akaganeite, as well as between akaganeite with different tunnel compositions. XRD peak positions can distinguish between akaganeite reacted with smaller-radii anions like F<sup>-</sup> and OH<sup>-</sup> and larger-radii anions like Br<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>. TG/DSC/EGA data shows that anion-exchanged samples display different shapes and/or positions of exotherm temperatures, implying replacement of anions in tunnels. Finally, VNIR is sensitive to loss of chloride from akaganeite as shown by shifts in band position at 2.00 μm and band shape at 2.46 μm. The obtained results indicate that the aqueous environment in akaganeite-containing deposits on Mars can be constrained using akaganeite characterization data obtained by orbital and landed missions.

**References:** [1] Vaniman et al. (2014), *Science*, 343, 6169. [2] Ming et al. (2014) *Science*, 343, 6169. [3] Carter et al. (2015), *Icarus*, 253, 296-310. [4] Cai et al. (2001), *Chem. Mater.*, 13, 4595-4602. [5] Chitrakar et al. (2009), *Ind. Eng. Chem. Res.*, 48, 2107-2112. [6] Peretyazhko et al. (2016), *Geochim. Cosmochim. Acta*, 188, 284-296. [7] Paterson et al. (1982), *Thermochim. Acta*, 54, 201-211.