EFFECT OF SULFUR CONCENTRATION AND pH CONDITIONS ON AKAGANEITE FORMATION: UNDERSTANDING AKAGANEITE FORMATION CONDITIONS IN YELLOWKNIFE BAY, GALE CRATER, MARS.

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Introduction: The Chemistry and Mineralogy Instrument (CHEMIN) on board the Mars Science Laboratory (MSL) Curiosity Rover identified minor amounts of akaganeite (β-FeOOH) at Yellowknife Bay, Mars [1]. There is also evidence for akaganeite at other localities on Mars from the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) [2]. Akaganeite is an iron(III) hydroxide with a hollandite-like structure and Cl in its tunnels [3]. Terrestrial akaganeite usually forms in Cl-rich environments under acidic, oxidizing conditions [4]. Previous studies of akaganeite have revealed that akaganeite formation is affected by the presence of sulfate (hereafter denoted as S [5, 6]). The prediction of circumneutral pH coupled with the detection of S at Yellowknife Bay [7] dictate that work is needed to determine how S and pH together affect akaganeite formation. The goal of this work is to study how changes in both S concentration and pH influence akaganeite precipitation. Akaganeite formation was investigated at S/Cl molar ratios of 0, 0.017, 0.083, 0.17 and 0.33 at pH 1.5, 2, and 4. Results are anticipated to provide combined S concentration and pH constraints on akaganeite formation in Yellowknife Bay and elsewhere on Mars. Knowledge of solution pH and S concentrations can be utilized in understanding microbial habitability potential on the Martian surface.

Materials and Methods: *Synthesis* Iron (III) precipitates were prepared by hydrolysis of 0.2M $FeCl_3 \cdot 6H_2O$ (Sigma Aldrich. Reagent $\geq$99%). $Na_2SO_4 \cdot 10H_2O$ (Acros Organics, extra pure) was added to obtain S/Cl molar ratios of 0, 0.017, 0.083, 0.17, and 0.33. Three series of akaganeite syntheses were performed. Series 1 was not pH adjusted and had pH 1.5, series 2 was adjusted to pH 2$\pm$0.2 using 8M NaOH (ChemPure), and series 3 was adjusted to pH 4$\pm$0.3 using 16M NaOH solution (Table 1). The samples were heated at 90°C for 5 hours, then cooled to room temperature. The precipitates were washed 3x with water by centrifugation and dried for 24 hours at 70°C.

Characterization Powder XRD data were collected on a Panaylitical X'Pert Pro diffractometer with Co Kα radiation. All samples were scanned from 4-80°2Θ, with a step size of 0.02. Weight percents were determined using the Rietveld refinement method and the amount of amorphous material was determined by the internal standard method (sample mixed with 20 wt. % corundum).

Total chlorine in each synthesized material (Table 1) was measured by ion chromatography (IC) after dissolution of 50 mg sample in 5M HNO_3 (Fisher Chemical) at 80°C for 1 hour. Milli-Q water was added to

Table 1: Summary of experimental results including: pH conditions, phases identified and total chlorine. AK-akaganeite, NJ-natrojarosite, GO- goethite, HE-hematite, HA-halite, A-amorphous material. Samples are identified as S/Cl ratio-pH condition, for example, a sample with an S/Cl=0.017 and an initial pH of 1.5 is represented as S0.017-1.5. Estimated errors are ~10% of the amounts shown.

Sample	pH Before Heating	pH After Heating	Phases Present (wt. %)						Total Chlorine (mg/g)
			AK	NJ	GO	HE	HA	A	
S0-1.5	1.577	1.005	100	-	-	-	-	-	7.24±0.02
S0.017-1.5	1.557	1.072	100	-	-	-	-	-	37.6±0.5
S0.083-1.5	1.506	1.231	98.4	1.6	-	-	-	-	29.5±0.3
S0.17-1.5	1.488	1.435	40.2	59.8	-	-	-	-	20.5±0.2
S0.33-1.5	1.504	1.38	-	100	-	-	-	-	1.4±0.1
S0-2	1.882	1.012	100	-	-	-	-	-	86±2
S0.017-2	1.9	1.114	87.2	-	12.8	-	-	-	53±3
S0.083-2	1.903	1.223	74.2	5.7	20.1	-	-	-	68.0±0.7
S0.17-2	1.97	1.322	67.3	3.2	29.5	-	-	-	26±1
S0.33-2	1.952	1.3575	11	80.9	8.1	-	-	-	5.9±0.2
S0-4	4.115	2.556	-	-	-	68.5	6.2	25.3	86±2
S0.017-4	4.139	2.622	-	-	-	78.6	4.1	17.4	65.6±0.5
S0.083-4	3.909	2.124	-	-	71.5	-	1.6	26.9	38.5±0.4
S0.17-4	3.817	2.109	-	-	78.6	-	4.6	16.8	42.4±0.6
S0.33-4	4.24	2.291	-	-	69.8	-	6.5	23.7	43.6±0.6

bring the volume to 100 mL. Chlorine concentration was determined by a Dionex ICS-2000 RFIC Ion Chromatography System.

Results and Discussion: *Fe(III) precipitates.* XRD analyses of the samples prepared at pH 1.5 revealed formation of akaganeite at S/Cl = 0, 0.017, 0.083, and 0.17 and natrojarosite $((Na_{0.67}(H_3O)_{0.33}Fe_3(SO_4)_2(OH)_6)$ at S/Cl = 0.083, 0.17, and 0.33 (Table 1). Akaganeite was found at all S/Cl ratios in samples prepared at pH 2. Natrojarosite was identified at S/Cl = 0.083, 0.17, and 0.33 and goethite (α-FeOOH) was found at S/Cl $\geq$0 (Table 1). Goethite in pH 2 samples could be formed through Fe (III) hydrolysis and/or transformation of less stable akaganeite to goethite [8].

Samples prepared at pH 4 did not yield akaganeite. Our results agree with previous work that constrained akaganeite synthesis to pH $\leq$2 [5]. All samples appeared to contain a disordered material characterized by the broad X-ray peaks. Hematite (α-Fe_2O_3) and halite (NaCl) were formed at S/Cl = 0 and 0.017 and goethite and halite were obtained at S/Cl = 0.083, 0.17 and 0.33 (Table 1).

Crystallinity and Crystallite size. Samples prepared at pH 1.5 and 2 had broadening and intensity loss of akaganeite peaks as S concentration and pH increases. Peak broadening is a consequence of small crystallite size and/or strain in the crystal structure [9]. . Addition of S reduces the crystallinity of akaganeite and as S concentration increases, particle size decreases and the crystals become irregularly shaped [6]. Cai et al demonstrated that pH increase accelerated Fe (III) hydrolysis leading to formation of less crystalline akaganeite [5].

Chlorine Content. Chlorine can occupy either sites in the tunnels within the akaganeite structure or surface sites. [10]. Samples prepared at initial pH 1.5 had between 6 and 40 mg/g Cl (Table 1). This is slightly lower than the reported concentrations, which fall between 10 and 70 mg/g Cl [7]. With the exception of S0-1.5, Cl content decreased as S concentration increased. The decrease correlates with a decreased amount of akaganeite being produced. The low Cl content of S0-1.5 is likely the result of formation of highly crystalline akaganeite with low surface area and consequently less surface sites available for Cl complextion [6].

Samples prepared at pH 2 had between 6 and 87 mg/g Cl (Table 1). The higher Cl content than the samples prepared at pH 1.5 is likely due to crystallinity and size decrease and consequently surface area increase as initial pH changes from 1.5 to 2. Ishikawa et al. observed an increase in surface area as crystallinity decreased in akaganeite [6]. An increase in surface

area would allow for more Cl adsorption. Samples prepared at pH 2 also showed a decrease in Cl as S concentrations increased due to smaller akaganeite amount in the samples, except S0.083-2, whose low Cl content cannot be explained.

Samples prepared at pH 4 have between 38 and 86 mg/g Cl (Table 1). These samples do not contain akaganeite nor enough halite to explain the high amounts of Cl. Therefore the majority of the Cl is likely contained in the amorphous material. The amorphous material is possibly an akaganeite-like phase [4] but further analysis would be needed to ascertain the nature of Cl in that material.

Conclusions: Both pH and S/Cl molar ratios were found to affect mineralogy, crystallinity, and Cl content. Total Cl content of akaganeite was observed to increase as crystallinity decreased, likely due to increased surface area allowing more Cl adsorption. Akaganeite did not form above pH 2, in agreement with previous work [5]. At S/Cl ratios below 0.017 akaganeite is the only product at pH 1.5 and 2. Akaganeite and other products form at S/Cl=0.083 and 0.17 at pH 1.5 and S/Cl=0.083, 0.17, and 0.33 at pH 2.

Conditions at Yellowknife Bay do not appear to have been suitable for akaganeite formation. The Cumberland (CB) S/Cl is 0.52 (correcting for pyrrohotite, FeS) and pH estimates for Yellowknife Bay are near neutral [7], which are both too high for akaganeite formation according to our experiments. This assumes that all CB sulfur, excluding FeS sulfur, would have been available in solution at the time of CB emplacement. Akaganeite, once formed, is stable at near neutral pH conditions [10], so it is possible Yellowknife Bay akaganeite is detrital and was transported from a distal location where a more acidic and Cl-rich environment allowed for its formation. Akaganeite may have alternatively formed in Yellowknife Bay during a separate event when geochemical conditions were more acidic and Cl rich than the conditions that allowed for other CB minerals to form that require neutral pH conditions or higher S concentrations.

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