

## Effect of solution pH and chloride concentration on akaganeite precipitation: Implications for akaganeite formation on Mars

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**Introduction:** Akaganeite ( $\beta$ -FeOOH, chloride-containing Fe(III) (hydr)oxide) has been detected on the surface of Mars by the CheMin instrument onboard the Mars Science Laboratory *Curiosity* rover in Yellowknife Bay, Gale Crater, Mars [1] and from orbit by the Mars Reconnaissance Orbiter in Robert Sharp crater and Antoniadi basin [2]. However, the mechanism and aqueous environmental conditions of martian akaganeite formation (e.g., pH and chloride concentration) remain unknown.

The objective of our work was to investigate precipitation of akaganeite at variable Mars-like pH and chloride concentrations in order to assess formation conditions for akaganeite on the planet.

**Materials and Methods:** Syntheses were performed through hydrolysis of 0.1 M Fe(ClO<sub>4</sub>)<sub>3</sub> solutions with addition of 0.02, 0.05 and 0.1 M NaCl. Iron(III) hydrolysis was run at initial pH of 1.6, 4, 6 and 8 at 90 °C for 24 h. The precipitates were then washed 3x with Milli-Q water by centrifugation and freeze-dried prior to mineralogy and composition characterization.

For total chloride (Cl) analysis, freeze-dried precipitates were acid digested and analyzed by Ion Chromatography. Mineralogy of the precipitated Fe(III) phases was characterized using X-ray Diffraction (XRD), Mössbauer Spectroscopy, and Visible and Near-Infrared Spectroscopy (VNIR).

**Results:** Mineralogical analysis showed precipitation of diverse Fe(III) (hydr)oxides at variable initial Cl concentration and pH. X-ray diffraction analysis of the samples synthesized at pH 1.6 revealed precipitation of akaganeite at all Cl concentrations (Table 1). Akaganeite precipitation also occurred at pH 4, 6 and 8 and dissolved Cl concentration of 0.05 and 0.1 M. Precipitation, however, was completely suppressed at 0.02 M Cl (Table 1). Depending on initial solution pH and chloride concentration, akaganeite precipitated as a single phase or in mixture with amorphous Fe(III) oxide (mainly 2-line ferrihydrite), hematite and/or goethite (Table 1).

Table 1. Quantities of Fe(III) (hydr)oxides identified by Rietveld refinement (Akg = akaganeite, Gm = goethite, Hm = hematite, Am = amorphous Fe(III) oxide).

Sample	Fe(III) (hydr)oxide, wt%			
	Akg	Gt	Hm	Am
pH 1.6				
Cl 0.1 M	100	0	0	0
Cl 0.05 M	94	0	6	0
Cl 0.02 M	17	7	36	40
pH 4				
Cl 0.1 M	31	0	0	69
Cl 0.05 M	18	3	0	79
Cl 0.02 M	0	6	1	93
pH 6				
Cl 0.1 M	27	0	0	73
Cl 0.05 M	14	6	0	80
Cl 0.02M	0	13	3	84
pH 8				
Cl 0.1 M	28	5	5	62
Cl 0.05 M	17	7	36	40
Cl 0.02 M	0	17	31	52

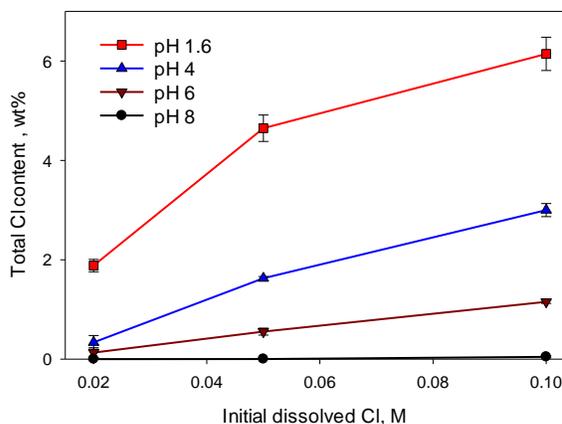


Fig. 1 Total chloride content in acid digested Fe(III) (hydr)oxides as a function of initial dissolved chloride concentration

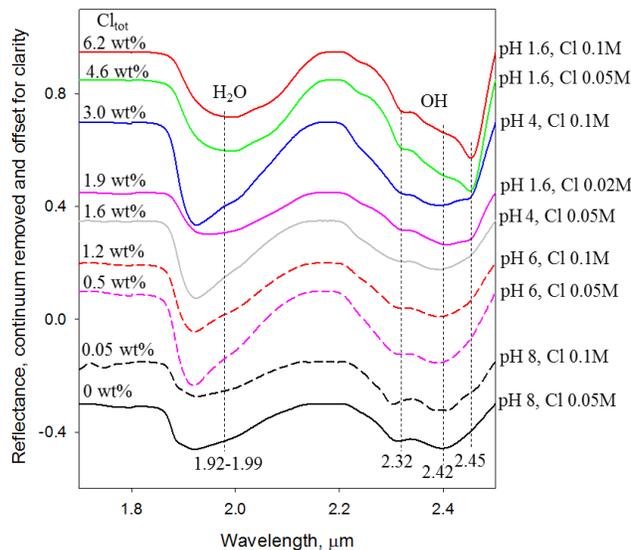


Fig. 2 Continuum removed VNIR spectra from 1.7 to 2.5  $\mu\text{m}$  of akaganeite-containing samples. Corresponding initial pH and solution Cl concentrations are shown next to each spectrum and total chloride content is shown above each spectrum. The top spectrum in red corresponds to pure akaganeite synthesized at pH 1.6 in the presence of 0.1 M Cl (Table 1). Positions of  $\text{H}_2\text{O}$  and OH combination bands in the pure akaganeite are shown with dotted lines.

Chloride detected in akaganeite-containing samples was associated with akaganeite tunnels. As pH increased from 1.6 to 8, total Cl content in akaganeite decreased and was <0.05 wt% in the samples synthesized at pH 8 and 0.05 and 0.1 M Cl and containing 17 and 28 wt% akaganeite, respectively (Fig. 1, Table 1). The result of total chloride analysis might indicate that akaganeite with little or no Cl in tunnels precipitated at pH 8.

Infrared spectroscopy revealed diagnostic akaganeite bands in the near-infrared range ( $\text{H}_2\text{O}$  combination band at  $\sim 2 \mu\text{m}$  and OH combination band at  $\sim 2.45 \mu\text{m}$ , Fig. 2) which were previously used to identify akaganeite on Mars from orbital spectrometers [2]. The akaganeite bands were sensitive to total chloride content in akaganeite. The  $\text{H}_2\text{O}$  combination band position linearly correlated with total Cl content in akaganeite [3]. Shape and intensity of the OH combination band changed as Cl content decreased from 6 to 0 wt% (Fig. 2).

**Discussion and Conclusions:** Our results demonstrate that akaganeite formation depends on initial pH and solution chloride concentration (Table 1), and they

permit constrains on ancient aqueous conditions in areas where akaganeite has been detected on Mars.

Mineralogical observations in Yellowknife Bay revealed that akaganeite was present together with hematite and Fe-rich amorphous phase that likely contained ferrihydrite [1, 4]. Comparison with XRD analysis of synthetic samples revealed that mixtures of akaganeite and ferrihydrite without hematite could form at pH range from 4 to 6 and dissolved Cl concentration > 0.05 M (Table 1). The potential mechanism of akaganeite formation in Yellowknife Bay could be basalt dissolution in acidic to neutral pH range followed by hydrolysis of dissolved Fe(III) under moderately saline conditions. The reaction can result in formation of akaganeite and ferrihydrite and further transformation of ferrihydrite to hematite leads to formation of Fe(III) (hydr)oxide mixture presently observed in Yellowknife Bay.

Similarities of spectral features of synthetic akaganeite formed at pH 1.6 (Fig. 2) and akaganeite detected in Robert Sharp crater [2] indicated that martian akaganeite likely formed under acidic pH < 4 conditions and in the presence of > 0.1 M dissolved Cl. Potential mechanisms of akaganeite formation include oxidative dissolution of Fe(II) sulfides under localized Cl-rich environments followed by hydrolysis of Fe(III) and precipitation of akaganeite.

**References:** [1] Vaniman et al. (2014) *Science*, 343, [2] Carter et al. (2015) *Icarus* 253, 296-310, [3] Peretyazhko et al. (2016) *Geochim. Cosmochim. Acta* 188, 284-296, [4] Morris et al. (2004) *Science* 305, 833-836.