

TEMPERATURE AND HUMIDITY EFFECTS ON SPECTRAL FEATURES OF AKAGANEITE AND IMPLICATIONS FOR ITS STABILITY ON MARS

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Introduction: Akaganeite has been found in the Yellowknife Bay mudstones in Gale crater by the Chemistry and Mineralogy X-ray diffraction instrument (CheMin) on the Curiosity rover [1]. This phase has also been discovered in limited locations on Mars by the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) aboard Mars Reconnaissance Orbiter [2]. As a metastable phase, akaganeite was proposed as a precursor candidate of hematite widely distributed at Meridiani Planum [3,4]. Akaganeite is an important hydrated mineral that could preserve detailed information on diagenetic and post-depositional environments of the region where it has been found [5]. In the present study, synthetic akaganeite were processed under different temperature (room temperature to 300 °C) and relative humidity conditions (7%-60%). The structures of akaganeite samples were analyzed with X-ray diffraction (XRD) while their spectral features were characterized with mid-Infrared, Raman, and VIS-NIR reflectance spectroscopy. This work could help better understand the stability and occurrence of akaganeite on the Martian surface and accurate identification of akaganeite on Mars in the coming Mars 2020 and ExoMars missions.

Experiments: Akaganeite was synthesized by forced hydrolysis of FeCl₃ solutions at 90 °C [5]. Synthetic akaganeite samples were heated in a laboratory muffle furnace to 150, 180, 220, 245, 260, 300 °C for 24 hours. We applied a humidity-buffer method to set-up a micro-environment with fixed temperature and relative humidity (RH) conditions. The humidity buffers were prepared with saturated solutions of the LiBr, LiCl, MgCl₂, and NaBr salts. The relative humidity of each buffer at 50 °C is 6 %, 11 %, 31 % and 51 %, respectively [6].

XRD patterns were collected using analyzed with a Rigaku UltimaIV diffractometer. VIS-NIR spectra (0.35-2.5 μm) was obtained with ASD FieldSpec4 spectrometer. In-situ VIS-NIR reflectance spectra of akaganeite were obtained in a Mars chamber. MIR spectra covering 400 to 4000 cm⁻¹ were collected with Bruker VERTEX 70 spectrometer. The morphology and chemistry of akaganeite samples was analyzed using a FEI Nova NanoSEM 450 equipped with an Oxford Energy Dispersive X-ray spectrometer.

Results: *X-Ray Diffraction.* Figure 1 presents the XRD patterns of synthetic akaganeite and heat-treated

products at various temperatures. XRD pattern of synthetic akaganeite matches well with that of β-FeOOH reference (JCPDS NO. 34-1266) [7]. XRD patterns of akaganeite samples heated at 260 and 300 °C, clearly indicate that the akaganeite transformed into hematite. No other phases have been identified, which indicates that there are no intermediate phases involved in the akaganeite phase transformation. The akaganeite transformation to hematite due to heating could be expressed as the following reaction formula: $8\beta\text{-FeOOH} \rightarrow 4\alpha\text{-Fe}_2\text{O}_3 + 4\text{H}_2\text{O}$.

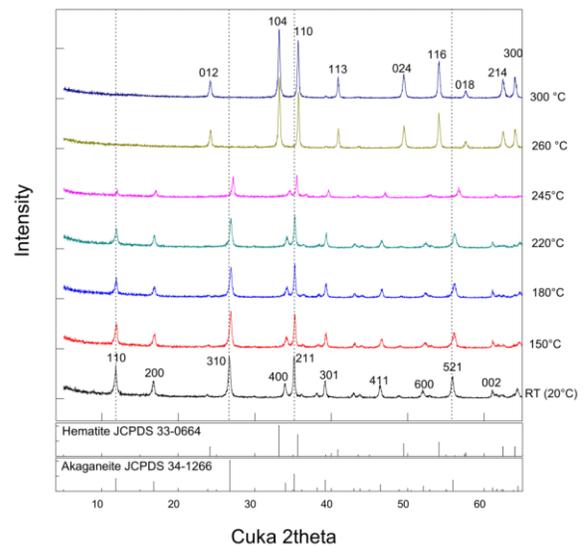


Fig. 1 X-ray diffraction patterns of akaganeite heated at various temperatures.

Chemical compositions. The chemical compositions of akaganeite samples obtained by SEM-EDS analysis (Figure 2). The loss of chloride in akaganeite with increasing heating temperature was observed. The obvious chloride loss in akaganeite started at 245 °C. According to XRD results, akaganeite all transform into hematite structure at higher temperature. This indicates that the structure changing from akaganeite to hematite is clearly associated with chloride loss in akaganeite tunnels.

MIR transmittance spectra. The OH...Cl vibrations in the region 550-1000cm⁻¹ are characteristic of chloride-containing akaganeite. Synthetic akaganeite presents strong bifurcated OH bending vibrations near 647/696cm⁻¹ (out-of-plane bending) and a relatively weak band near 850 cm⁻¹ (in-plane bending)[8]. Fe-O-

Fe vibrations are observed at 421 and 488 cm^{-1} in transmittance spectra of akaganeite. The bifurcated bands (647 and 696 cm^{-1}) are broadened and weakened with increasing temperature. The Fe-O-Fe vibration at 421 cm^{-1} could still be observed up to 245 °C. All these characteristic bands of akaganeite disappeared at 260 and 300 °C, indicating the phase transformation of akaganeite.

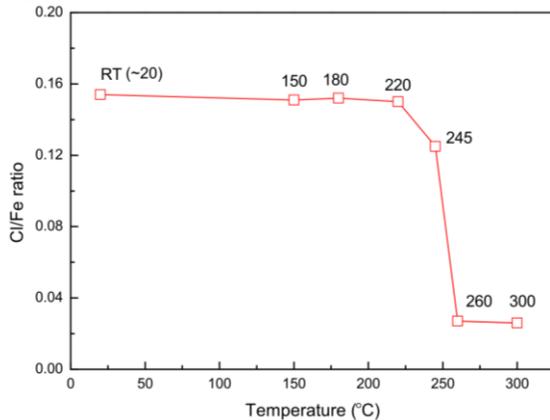


Fig. 2 Cl/Fe ratio decreasing with heating temperature

VIS-NIR reflectance spectra. Reflectance spectra of akaganeite consist of two regions: Fe (III) electronic transitions at 0.35 to 1.3 μm , Fe-OH and H_2O overtone and combination absorptions at 1.3-2.5 μm . In the NIR region, akaganeite shows combinations and overtones of OH and H_2O absorption bands near 1.4, 1.9, and 2.46 μm . We noted that the strength of 1.4, 1.9, 2.46 μm bands all decrease with reducing RH.

In-situ VIS-NIR spectra collected in a Mars chamber suggested that akaganeite experienced continuous dehydration in CO_2 atmosphere with 7 mbar pressure. When exposing to ambient lab environments (RH 65%), akaganeite started to rehydrate.

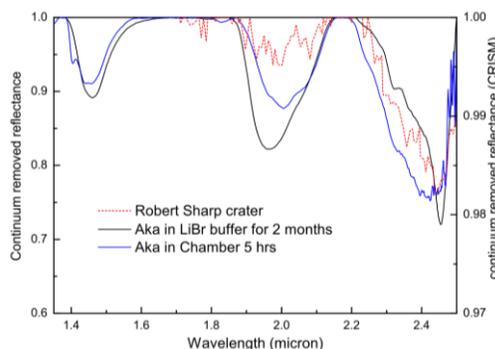


Fig. 3 CRISM spectrum of akaganeite at Robert Sharp crater plotted together with continuum removed NIR reflectance spectra for akaganeite.

Discussions: *The transformation of akaganeite to hematite.* Akaganeite structure changes with increasing temperature match with chloride loss in the structure. On the basis of EDS results, we noted that the loss of chloride started at 245 °C and mainly occurred from 245 to 260 °C. Mid-IR results demonstrate that akaganeite heated at 245 °C share the similar OH...Cl vibration features with unheated one, indicative of stable structure at temperature less than 245 °C. The 260 °C product with trace chloride content (Cl/Fe ratio = 0.026) shows typical Fe-O vibration bands at 557 and 476 cm^{-1} of hematite. These observations suggest the presence of chloride in the tunnel is not only essential for the akaganeite precipitation but also its structural stability.

Stability of akaganeite on Mars. On the basis of these results, we could assess the stability of akaganeite under current Mars surface conditions. In dry conditions, akaganeite would thermally transform to hematite above 245 °C (as observed in Fig. 1). We compared continuum-removed NIR reflectance spectra of akaganeite analogs with the CRISM spectrum of akaganeite in Robert Sharp crater (Fig. 3). The spectral features of dehydrated akaganeite, measured in simulated Mars atmosphere for 5 hours, best match with the CRISM spectra. This indicates that akaganeite on Mars surface should be highly dehydrated.

According to experimental results on akaganeite, we could make several inferences about akaganeite activities on Mars: 1) in early wet Mars, akaganeite grains could absorb water vapor on its surface and incorporated them in its tunnels, and these crystals survived in the Martian subsurface may still hold significant volumes of water so far since their formation; 2) in a diurnal cycle, akaganeite on Mars surface absorb water vapor in early morning, and desorb at noon; 3) RH variations could result in discernable band strength variations of water absorptions in NIR range, but not the phase transformation; 4) Impact events and magmatism could thermally transform akaganeite in target materials and surrounding sediments, which is a possible pathway of hematite formation on Mars.

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