

THE COPRECIPITATION OF AKAGANEITE AND K-JAROSITE AND IMPLICATIONS FOR THEIR FORMATION IN GALE CRATER, MARS. Lingxi Zhang¹, Xiaohui Fu^{1*}, Zongcheng Ling¹ ¹Shandong Provincial Key Laboratory of Optical Astronomy and Solar-Terrestrial Environment, Institute of Space Sciences, Shandong University, Weihai, Shandong, 264209, China. (fuxh@sdu.edu.cn).

Introduction: Akaganeite, a metastable phase of Fe(III) (hydr)oxide, is rare on Earth. It forms in an acidic, highly saline, Cl-rich environment, and reveals the existence of water [1]. Akaganeite has been definitely identified on Mars by in situ detection, orbital remote sensing and martian meteorite analyses [1-3]. It has been observed by remote sensing imaging spectrometer from the CRISM instrument on MRO at Robert Sharp and Antoniadi craters on Mars [1]. Minor components of akaganeite (1.1 and 1.7 wt.%) have been identified in the drill samples from the Sheepbed mudstones of Yellowknife Bay by X-ray diffraction (XRD) analysis [2]. About 0.3 wt.% of akaganeite was also detected in Windjana sandstone drill sample by CheMin XRD in the MSL Curiosity rover [3].

On Vera Rubin Ridge, Rampe et al. (2020) reported the co-occurrence of akaganeite and jarosite in two drill mudstone [4]. Akaganeite was in trace amount (~1.2 wt.% of the bulk) in Stoer while Rock Hall sample contains the most abundant iron oxide/oxyhydroxide (~6 wt.% of the bulk) among all drill samples so far. Jarosite is present in trace amounts in both Stoer and Rock Hall, about 2.0 and 2.3 wt.% of the bulk respectively. The coprecipitation of akaganeite and jarosite was only reported in acid sulfate soil wetlands of the Murray-Darling Basin, New South Wales, Australia [5]. They suggested that akaganeite and jarosite in the wetlands formed through oxidation of sulfide-rich sediments in extreme acidic pH 2 solution containing 4.6 M chloride and 0.04 M sulfate [5].

Peretyazhko et al. (2016) have performed an experiment to explore the mechanism and conditions of akaganeite formation in the presence of sulfate in the Yellowknife Bay mudstone [6]. They synthesized akaganeite in the presence of 0-0.2 M sulfate and different pH. It was found that when a certain amount sulfate (~0.1 M at pH 1.5, ~0.2 M at pH 2) was added to the solution, natro-jarosite precipitated.

As a common sulfate on Mars, jarosite forms from the hydrolysis of Fe³⁺ in SO₄²⁻ bearing solutions at a pH of ~1.5-4 [7]. Jarosite has three endmembers: K-jarosite, Na-jarosite and H₃O-jarosite, and their crystal structure and spectral features have been extensively investigated [7]. K-bearing jarosite was discovered in the north of Mawrth Vallis by CRISM on MRO [8].

In order to constrain the aqueous environment on Mars, we synthesized akaganeite and K-jarosite, explored the upper and lower limits of SO₄²⁻

concentration for the intergrowth of akaganeite and jarosite.

Materials and Methods: We used hydrothermal method to synthesize akaganeite and jarosite. 100 mL, 0.2 M FeCl₃ solution was prepared by adding FeCl₃·6H₂O (s) to deionized water. Dissolve 0-0.2 M of K₂SO₄ to the prepared FeCl₃ solution, respectively. The reaction solution was then transferred into a teflon beaker, sealed, and reacted in an incubator at 90 °C for 5 h. After hydrolysis, the beaker was cooled to room temperature. The precipitates were centrifugally washed with deionized water for three times, and the final products were dried in an oven at 50 °C.

X-ray diffraction (XRD) patterns of the synthesized products were measured using Rigaku Ultima IV X-ray diffractometer with Cu-K α radiation at Shandong University. Powder samples were analyzed at 40 kV and 40 mA with a 0.02 ° 2 θ step size and the counting rate was 6 °/min. The instrument was operated under ambient conditions and the data were processed using MDI Jade software.

Analytical Spectral Devices (ASD) FieldSpec 4 spectrometer was used to collect visible and near-infrared spectra of samples in the range of 350 nm to 2500 nm. Its spectral resolution is 3 nm in the visible spectrum (350-1000 nm) and 8 nm in the near-infrared spectrum (1000-2500 nm).

Result: Akaganeite and/or jarosite were synthesized in the series of the mixed solutions with variable initial SO₄²⁻ concentration. The final products obtained by XRD analysis are listed in Table 1. Akaganeite precipitated alone with none SO₄²⁻ or in the presence of 0.01 M SO₄²⁻ in the reaction solution (Figure 1). The akaganeite peaks can also be found in the samples with 0.011-0.028 M SO₄²⁻. However, it is clear that the crystallinity of akaganeite decreased with the accession of SO₄²⁻, comparing the XRD patterns of 0 and 0.01 M SO₄²⁻, as indicated by the broadening of akaganeite diffraction peaks and the decrease of the peaks intensity.

Our experiments revealed that jarosite was coprecipitated with akaganeite in the 0.011~0.028 M samples (Table 1 and Figure 1). The jarosite proportion in the final products raise with increasing SO₄²⁻ concentration on the basis of the increasing XRD peak intensity of jarosite. In the solution with \geq 0.029 M SO₄²⁻, jarosite was the only phase in the final product. The sulfate content (\geq 0.029 M) in the mixed solution clearly inhibit akaganeite formation.

Table 1 The concentration of SO_4^{2-} added to the reaction solution and the final product. (A=Akaganeite, J=Jarosite)

SO_4^{2-} concentration	Products	SO_4^{2-} concentration	Products
0	A	0.025	A+J
0.01	A	0.027	A+J
0.011	A+J	0.028	A+J
0.012	A+J	0.029	J
0.013	A+J	0.03	J
0.014	A+J	0.05	J
0.015	A+J	0.1	J
0.02	A+J	0.2	J

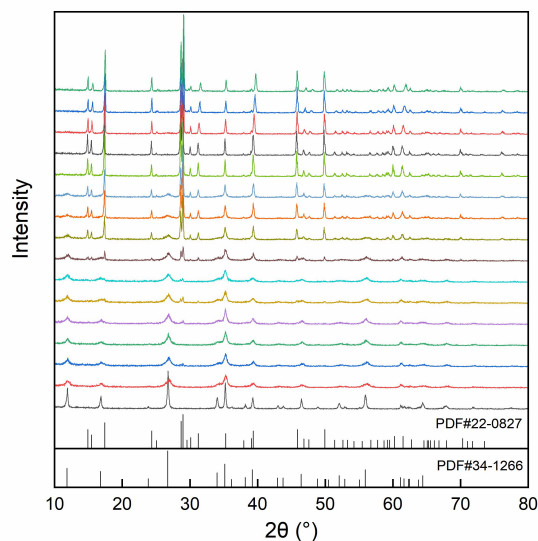


Figure 1 XRD patterns of the experimental products. Synthetic akaganeite matches well with the PDS card NO. 34 -1266, and jarosite peaks are consistent with PDS card NO. 22 -0827.

Among all solutions, akaganeite and jarosite were the only two phases in the final products. No other iron oxide/oxyhydroxide (e.g. hematite, goethite or ferrihydrite) was found.

VIS-NIR spectra of the final products are shown in Figure 2. The pure akaganeite and K-jarosite are consistent with previous studies [7,9]. For akaganeite, The 2.46 μm band is the characteristic NIR absorption of akaganeite minerals. The band is usually present as a sharp asymmetrical V-shaped band (Figure 2). The absorption band near 2.266 μm of jarosite is the diagnostic adsorption feature of this phase, which is due to the combination mode of stretching (ν) and bending (δ) vibration of OH. Its spectral shape and strength gradually increase with the addition of SO_4^{2-} , fitting well with the XRD results.

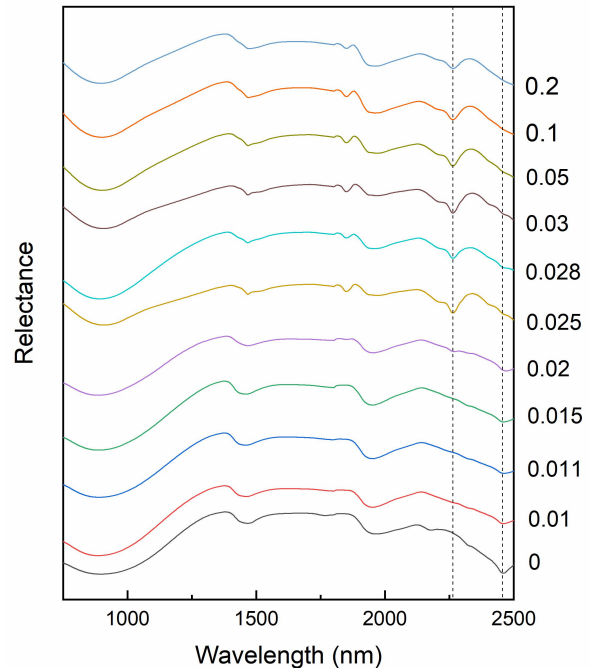


Figure 2 VIS-NIR patterns of partial samples.

Summary: The presence of minor SO_4^{2-} in the solution obviously decreased the crystallinity of akaganeite. But with more SO_4^{2-} added to the reaction solution, the intergrowth of akaganeite and jarosite appeared. We found out the lower and upper SO_4^{2-} limits to the co-occurrence of akaganeite and jarosite in the same solution were 0.011 and 0.028 M, we propose that the SO_4^{2-} concentration at Vera Rubin Ridge is in this range. This would help us better constrain the aqueous environment on Mars and a further understanding of intergrowth minerals.

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