

Formation of Fe(III) (hydr)oxides from Fe(II) sulfides: implications for akaganeite detection on Mars

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Introduction: Akaganeite (Cl-bearing Fe(III) (hydr)oxide) was identified by the Chemistry and Mineralogy X-ray diffraction (XRD) instrument onboard the Mars Science Laboratory (MSL) Curiosity Rover in mudstones drilled at Yellowknife Bay and Vera Rubin Ridge in Gale crater [1,2]. The mineral likely formed in chloride-bearing solutions of variable pH [3] but progenitor Fe-bearing phases for martian akaganeite are not well constrained.

Akaganeite in Gale crater has been proposed to form through oxidation of Fe(II) sulfide minerals [2,3]. The objective of this study was to constrain akaganeite formation conditions from Fe(II) sulfide pyrrhotite.

Materials and Methods: Two natural pyrrhotite samples from Santa Eulalia mining district, Chihuahua, Mexico, and Falconbridge, Canada were used in this study. Experiments were designed to investigate formation of Fe(III) (hydr)oxides by oxidative alteration of pyrrhotite and oxidation-hydrolysis of Fe(II) leached from the mineral.

For oxidative alteration experiments, 200 mg of pyrrhotite were mixed with 30 ml of 0.1 M HCl and incubated for 14 days under ambient conditions. Solutions were collected in a syringe and passed through a 0.2 μm syringe filter at the end of experiments. The separated solids were dried and stored under ambient conditions for mineralogy analysis.

For oxidation-hydrolysis experiments, the separated filtered solutions were first reacted with H_2O_2 to oxidize Fe(II), and then the pH was adjusted to initial pH (pH_0) values of either 1.5, 2, 3, or 4. All prepared samples were heated at 80 $^\circ\text{C}$ for 24 hours. Reaction precipitates were washed 3 times with ultrapure deionized water by centrifugation and then freeze-dried before mineralogical characterization.

Solution chemistry was analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Ion Chromatography and the alteration products were characterized by XRD and Mössbauer spectroscopy.

Results and discussion: Akaganeite formed via oxidative alteration of natural pyrrhotite in the presence of HCl as evident from XRD analysis performed 7d after experiment completion (Fig. 1). Mineralogical analyses of the dried HCl-reacted samples performed >100 days after completion of the experiments revealed that the formation of akaganeite continued during aging (Fig. 1). An increase in akaganeite abundance in the

aged samples was accompanied by precipitation of Fe(II) hydrated sulfates (melanterite and rosenite), Fe(III) sulfate (hydronium jarosite), and goethite (Fig. 1). Oxidative degradation of an amorphous layer formed after reaction with HCl on the surface of pyrrhotite caused the increase in akaganeite abundances and formation of goethite and Fe(II) and Fe(III) sulfates [4, 5].

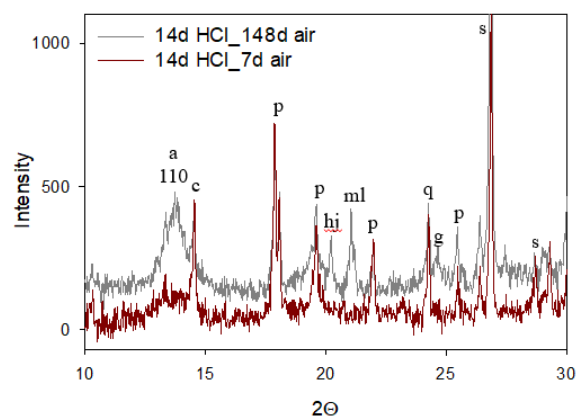


Fig. 1. XRD of the dried Falconbridge pyrrhotite sample reacted with 0.1 M HCl for 14 days and analyzed 7 and 148 days after completion of the oxidative alteration experiment. (a = akaganeite, c = clinocllore, q = quartz, p = pyrrhotite, s = sulfur, ml = melanterite, hj = hydronium jarosite, g = goethite)

Several Fe(III) (hydr)oxides were formed through oxidation-hydrolysis of Fe(II) released from the acidic weathering of the natural pyrrhotite samples. The results demonstrated that the Fe(II) oxidation-hydrolysis reaction was sensitive to the presence of dissolved Si originated from phyllosilicate dissolution present in one of the natural pyrrhotite samples and to changes in Fe(III) speciation between chloride and sulfate aqueous complexes as pH_0 increased from 1.5 to 4 [5]. Akaganeite and goethite precipitated at pH_0 1.5 and 2 (Fig. 2) with akaganeite as the dominant phase at dissolved Si/Fe ratio of 0.08 (Falconbridge sample) and goethite as the dominant phase at Si/Fe of 0.01 (Santa Eulalia sample). Akaganeite formed together with hematite, ferrihydrite, and goethite at pH_0 3, and the mineral formation was suppressed at pH_0 4 (Fig. 2). The absence of akaganeite formation at pH_0 4 could be

due to a decrease in Fe(III)-chloride and an increase in Fe(III)-sulfate aqueous complexes.

Akaganeite crystallinity varied between the samples. The well-crystallized akaganeite precipitated only at pH₀ 1.5 in the oxidation-hydrolysis experiments (Fig. 2a) while akaganeite of poorer crystallinity and/or smaller crystal domain size formed at pH₀ 2 and 3 and through oxidative alteration of pyrrhotite (Figs. 1 and 2).

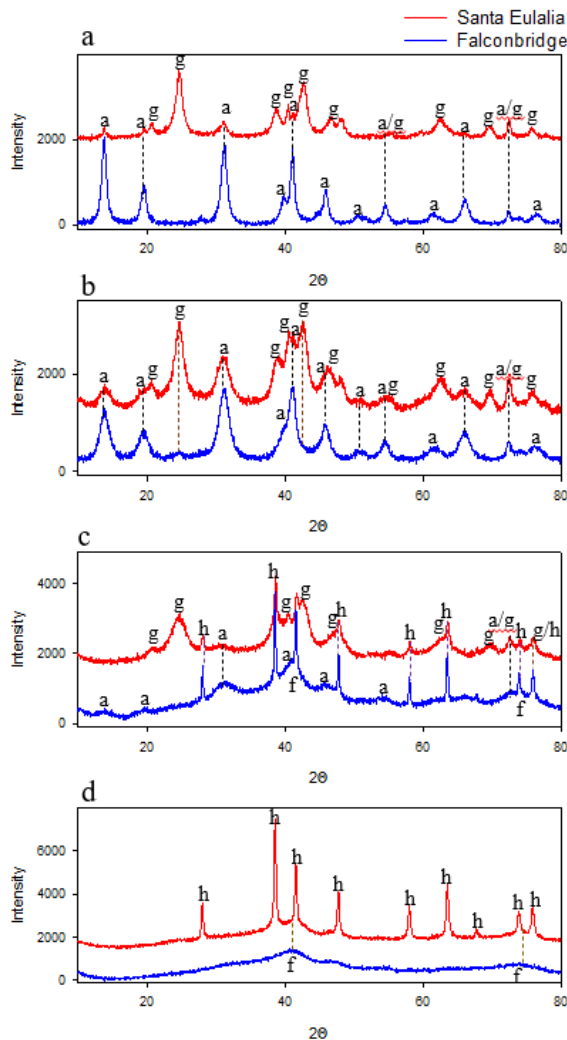


Fig. 2. XRD patterns of Fe(III) (hydr)oxides formed through oxidation-hydrolysis of Fe(II) leached from Santa Eulalia and Falconbridge pyrrhotite samples by reaction with 0.1 M HCl for 14 days. Hydrolysis reactions were performed at (a) pH₀ 1.5, (b) pH₀ 2, (c) pH₀ 3 and (d) pH₀ 4. (a = akaganeite, g = goethite, h = hematite, f = ferrihydrite)

Implication for akaganeite detection on Mars: Akaganeite in Gale crater can be a product of oxidative alteration of Fe(II) sulfides and/or oxidation-hydrolysis of leached Fe(II). The hypothesis is based upon our

experimental observations of akaganeite formation alone or together with other mineral phases and akaganeite crystallinity.

Akaganeite at Yellowknife Bay in Gale crater could form by an oxidation-hydrolysis of leached Fe(II) in acidic Cl-containing environments. Groundwater seepage at Yellowknife Bay likely delivered Fe(II) leached from Fe(II) sulfide and other Fe(II)-containing phases (ex., basaltic glass, olivine) along with other ions released through water-rock interactions, such as dissolved silica and sulfate [6]. Formation of akaganeite by oxidation-hydrolysis alone in Yellowknife Bay would have required extremely acidic conditions (pH < 2) and Si/Fe ratio > 0.01. Higher pH conditions, 2 < pH < 4 and Si/Fe > 0.01 would have led to the formation of akaganeite together with ferrihydrite and hematite.

Akaganeite could form through oxidative alteration of Fe(II) sulfides in acidic (pH 1.2 - 1.5) Cl-containing environments at Vera Rubin Ridge in Gale crater. Solution evaporation did not prevent akaganeite formation and this mineral may have continued forming through the crystallization of amorphous layers formed on the surface of Fe(II) sulfides. In addition, oxidation-hydrolysis of leached Fe(II) likely contributed to akaganeite formation in the Rock Hall drill site at Vera Rubin Ridge. Among the akaganeite-containing samples drilled in Gale crater, the Rock Hall sample was the only one that had well-resolved sharp diffraction peaks of akaganeite [2]. Such well-crystallized akaganeite could form through oxidation-hydrolysis of dissolved Fe(II) at pH < 2.

Akaganeite formation in Gale crater likely occurred after lake disappearance during the late diagenetic events characterized by low water activity [2, 7]. Influxes of acidic Cl-containing groundwater could trigger the oxidative alteration of Fe(II) sulfides under oxidizing conditions and Fe(II) leaching and migration under reducing conditions followed by oxidation and hydrolysis once oxidants were present.

References: [1] Vaniman et al et al. (2014) *Science*, [2] Rampe et al. (2020) *JGR Planets*, [3] Peretyazhko et al. (2018) *JGR Planets*, [4] Mikhlin et al. (2002) *Geochim. Cosmochim. Acta*, [5] Peretyazhko et al. (2020) *ACS Earth Space Chem*, [6] Hurowitz et al (2017) *Science*, [7] Peretyazhko et al (2016) *Geochim. Cosmochim. Acta*.