A simple method for synthesizing siliceous ferrihydrite: Implication for the formation of natural ferrihydrite and Mars analogs. S. Lee[1,2,3] and H, Xu[3] [1]Lunar and Planetary Institute, USRA, Houston, TX 77058, (slee2@lpi.usra.edu), [2]ARES, NASA Johnson Space Center, Houston, TX 77058, [3]NASA Astrobiology Institute, Department of Geoscience, University of Wisconsin–Madison, Madison, WI 53706.

Introduction: Ferrihydrite is a poorly crystallized hydrous ferric oxyhydroxide nanomineral found in a wide variety of geological environments, including soils, rocks, acid mine drainage, living organisms as well as Mars surface [1,2]. The ferrihydrite plays crucial roles as an important adsorbent in abiotic and biotic processes such as global iron cycling and adsorbing of toxic metals [2]. More recently, Mars Exploration Rovers (MER) and Mars Science Laboratory (MSL) reported the presence of ferrihydrite in Martian soils and sedimentary rocks [3]. It is therefore important to understand the mechanism of formation and compositions of ferrihydrite.

The conventional method of synthesizing ferrihydrite is used by the rapid hydrolysis of ferric solutions or by slow oxidation of ferrous solutions [4]. The two-line ferrihydrite (2LFh) is synthesized by rapid hydrolysis of a $Fe(NO_3)_3{\cdot}9H_2O$ solution at neutral pH, whereas the six-line ferrihydrite (6LFh) is synthesized when a $Fe(NO_3)_3{\cdot}9H_2O$ or $Fe(ClO_4)_3$ solution is heated to 75 ºC for 10-12 minutes and then dialyzed for 2 days against distilled water to remove electrolytes after cooling it with ice water. Siliceous ferrihydrites can be synthesized by oxidizing 0.1 M $FeCl_2$ solution in Si-bearing solution (up to 73 mmol Si/L). However, these synthesis procedures have limitations on describing the ferrihydrite formation in natural environments because the synthetic conditions such as temperatures and concentrations are quite different from the natural environment. In this study, we present a method for synthesizing siliceous ferrihydrite to mimic natural ferrihydrite formation in Chocolate Pots hot spring in Yellowstone National Park. Compared to Si-free ferrihydrite, the synthetic siliceous ferrihydrite can provide the actual physical and chemical properties of ferrihydrite in natural environments because natural ferrihydrite always contains Si. The new synthetic method can provide useful information to understand the formation and properties of ferrihydrite in a wide variety of geological environments and Fe-Si amorphous phases on Mars surface.

Experimental techniques: XRD patterns were collected using a Rigaku Rapid II instrument in the Geoscience Department at the University of Wisconsin-Madison. Synchrotron radiation XRD experiments were conducted using X-rays (λ = 0.24116 Å) on beamline 17-BM at the Advanced Photon Source (APS), Argonne National Laboratory. High-resolution TEM images and selected-area electron diffraction (SAED) were carried out using a Philips CM200-UT transmission microscope operated at 200 kV in the Materials Science Center at the University of Wisconsin-Madison.

Synthetic method: Nature ferrihydrite collected from the main vent along a transect at Chocolate Pots hot spring, Yellowstone National Park (Figure. 1). The fluid chemistry of the spring water at the vent is ~5 mM Si/L and ~1mM Fe^{2+}/L with temperature 40-60 °C and ~6.1 pH. The 6LFh mixed with 2LFh is observed in a sample proximal to the vent outlet (Figure 1a). Chemistry work suggested that the increase of temperature and Fe^{2+}/Si ratio towards the vent area can promote the precipitation of siliceous 6LFh.

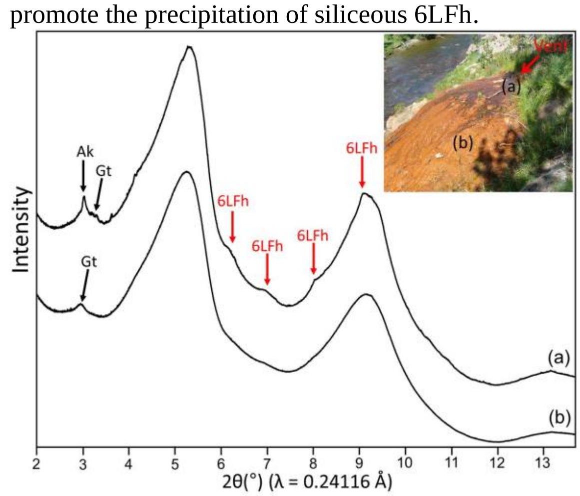

Figure 1. Synchrotron XRD patterns of ferrihydrite samples from (a) proximal (~50 °C) and (b) distal vent (~30 °C) at Chocolate Pots hot spring, Yellowstone National Park (an image of sampling site inserted). Ak: akaganéite, and Gt: goethite.

Based on the chemistry of the Chocolate Pots hot spring, the synthetic siliceous 6LFh were designed by slow oxidation of $FeCl_2{\cdot}H_2O$ in the silicate-bearing solution. First, a solution containing 28.4 mg of $Na_2SiO_3{\cdot}9H_2O$ in 50 mL of distilled water (2 mmol Si/L) was prepared in a plastic bottle. The solution preheated in the oven at 80 °C for 2 hours. The 21.7 mg of $FeCl_2{\cdot}H_2O$ (3 mmol Fe/L solution) was added to the preheated solution in the oven and then slightly covered by a cap for 2 days. The final solution had Fe/Si molar ratio of 1.5. During this time, the solution color changed from green to dark reddish brown indicating the formation of ferrihydrite Figure. 2. The solution was centrifuged and washed with distilled water to remove excessive salts and then allowed to air-dry or freeze dry. The method gives around 10 mg of siliceous 6LFh. To understand the ferrihydrite formation, we also changed the experimental conditions of Fe/Si molar ratio, temperature, and reaction times.

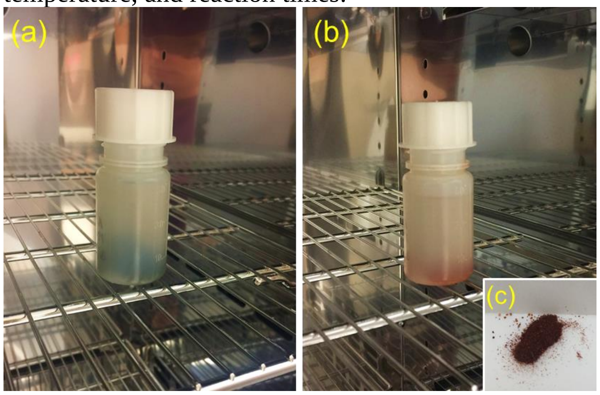

Figure. 2 Experimental images of siliceous ferrihydrite synthesis: (a) an initial solution in the presence of 2 mM Si/L and 3 mM Fe^{2+}/L; (b) ferrihydrite precipitated after 48 hours; (c) the final product of siliceous ferrihydrite.

Results and Discussion: The XRD pattern for siliceous 6LFh in this experiment is shown in Figure 3, compared with natural ferrihydrite and synthetic Si-free 6LFh. The siliceous 6LFh indicates the distinct diffractions at 2.54, 2.23, 1.96, 1.73, 1.52, and 1.47 Å, which is in agreement with 6LFh XRD pattern.

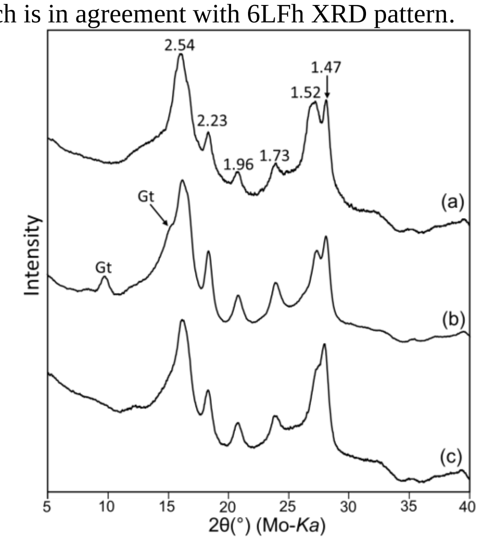

Figure. 3 XRD patterns of (a) synthetic siliceous 6-line ferrihydrite (this study), (b) natural ferrihydrite from Pennsylvania (c) Si-free 6-line ferrihydrite.

Figure 4 shows XRD patterns of siliceous ferrihydrite in different experimental conditions, such as temperature and reaction times. The synthetic experiment produced the different lines of siliceous ferrihydrite from 2-line to 6-line, indicating that these parameters influence the siliceous 6LFh formation. Without dissolved silica, only crystalline iron oxyhydroxides such as goethite and akaganéite formed in this experimental condition.

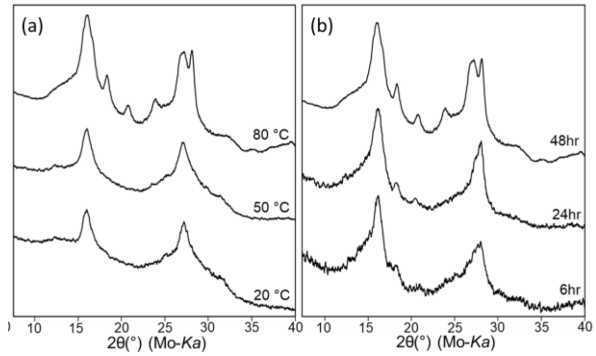

Figure. 4 XRD patterns of siliceous ferrihydrite under various experimental conditions: (A) temperature and (B) reaction times.

The representative TEM images of synthetic siliceous 6LFh shows a highly aggregated hexagonal form of ferrihydrite nanoparticles (Figure 5). Most 6LFh crystallites are 5-6 nm across, although the size of individuals ranging from ~3 to ~9 nm were observed. Overall, TEM images and the SAED pattern of synthetic 6LFh are consistent with previously reported ferrihydrite nanocrystals.

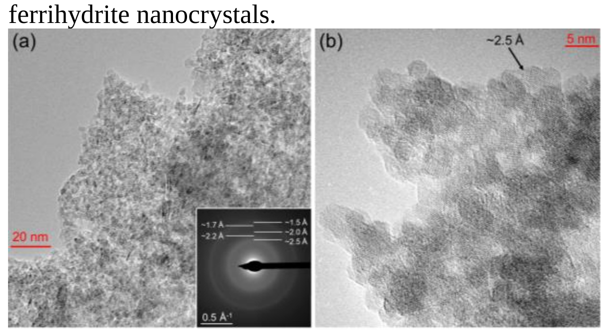

Figure. 5 Bright-field TEM image, SAED pattern, and high-resolution TEM image of synthetic siliceous six-line ferrihydrite.

Conclusions: This study presents a simple method to synthesize siliceous ferrihydrites designed to mimic their formation in the natural environment. Natural ferrihydrite always contains substantial amounts of incorporated silica. The silicate ions associated with ferrihydrite play a crucial effect on the binding of other trace elements and their transformation process. The study of siliceous ferrihydrite will be useful to understand the formation of natural ferrihydrite and provide the useful information on Mars soil analogs.

Acknowledgments: This research was funded by the National Aeronautics and Space Administration (NASA) Astrobiology Institute (NNA13AA94A).

References: [1] Lee, S. *et al.* (2016) *Am. Mineral*. 101,1986-1995. [2] Lee, S. and Xu, F. (2019) *ACS Earth Space Chem.* 3, 503-509. [3] Rampe, E. B. *et al.* (2020) *JGR:Planets*, 125, e2019JE006306. [4] Cornell, R. M. and Schwertmann, U. (2003) *The iron oxides* Wiley & Sons.