

DISSOLUTION RATES OF ALLOPHANE, FE-CONTAINING ALLOPHANE, AND HISINGERITE AND IMPLICATIONS FOR GALE CRATER, MARS. S. J. Ralston¹, E. M. Hausrath¹, O. Tschauner¹, E. B. Rampe², R. Christoffersen³, ¹University of Nevada, Las Vegas (ralsts1@unlv.nevada.edu), Las Vegas, NV 89154, ²NASA/JSC, Houston, TX 77058, ³Jacobs, NASA Johnson Space Center, Mail Code XI3, Houston, TX 77058, USA.

Introduction: Investigations with the CheMin X-ray Diffractometer (XRD) onboard the *Curiosity* rover in Gale Crater demonstrate that all rock and soil samples measured to date contain ~15-70 wt% X-ray amorphous materials [e.g., 1-4]. The diffuse scattering hump from the X-ray amorphous materials in CheMin XRD patterns can be fit with a combination of allophane, ferrihydrite, and rhyolitic and basaltic glass [1]. Because of the iron-rich nature of Mars' surface, Fe-rich poorly-crystalline phases, such as hisingerite, may be present in addition to allophane [1].

Allophane is a poorly-crystalline aluminosilicate commonly found in terrestrial volcanic soils [5]. Its structure consists of a gibbsite sheet rolled into hollow spheres about 5 nm in diameter, with multiple pores perforating the sphere walls [6]. If the environment is slightly more Fe-rich, Fe-substituted allophane can be produced, where some of the Al is substituted with Fe [7]. If a large amount of Fe is available, hisingerite can be produced. All of these materials share the same hollow, porous nano-ball structure [7].

The prevalence of X-ray amorphous materials in martian samples provides an opportunity to characterize ancient surface and groundwater chemistry and longevity in Gale Crater by investigating the dissolution properties of various amorphous phases.

For our experiments, allophane, Fe-substituted allophane, and hisingerite were synthesized and then characterized in order to determine their viability as analogs for the Mars amorphous soil component. Dissolution experiments were conducted in order to derive rate laws for the dissolution of all three materials under acidic to alkaline pH conditions.

Methods: *Synthesis:* Allophane, Fe-substituted allophane, and hisingerite were synthesized following the methods of [8], which are a modification of the methods of [9]. The synthetic products were washed with 18.2 MΩ deionized water until the conductivity of the supernatant was <20 μmhos. The resultant solids were frozen for more than 24 hours and then freeze-dried for further analysis.

Characterization: A suite of analyses were conducted in order to ensure that 1. the intended materials had been synthesized, and 2. our synthetic allophane, Fe-allophane, and hisingerite were appropriate Mars soil analogs. The analyses included Fourier-transform infrared (FTIR) spectroscopy, XRD analysis, field-emission scanning electron microscopy (FE-SEM),

BET specific surface area (SSA), and transmission electron microscopy (TEM). Both unreacted materials and materials reacted in dissolution experiments were analyzed with TEM. Evolved Gas Analysis (EGA) was also conducted in order to compare EGA measurements of our samples with EGA measurements of martian soils conducted by the Sample Analysis at Mars (SAM) instrument [10]. FT-IR and FE-SEM analyses were conducted at UNLV, while XRD, TEM, EGA, and BET analyses were conducted at NASA Johnson Space Center.

Experimental design: Dissolution experiments were carried out in batch reactor format following the methods of [11]. 0.15 g of allophane, Fe-allophane, or hisingerite was dissolved in 180 mL of 0.01 M NaCl solution made with 18.2 MΩ deionized water at pH 3, 5, 8, and 10. A blank was run with each experiment. 8 mL solution aliquots were taken at regular intervals based on the expected dissolution rate. These aliquots were filtered through a 0.2 μm nylon filter, then acidified with 1% v/v high purity HNO₃. The concentrations of Fe and Si in solution were measured at each time point using a Thermo Scientific iCE 3000 series Atomic Absorption Spectrometer. The measured concentrations were converted to moles of Fe or Si released using the following equation from [12]:

$$m_{(t)} = m_{(t-1)} + (c_{(t)} - c_{(t-1)})V_{(t-1)} \quad (\text{Eq. 1})$$

where $m_{(t)}$ and $m_{(t-1)}$ are the moles Fe or Si released at times t and $t-1$, $c_{(t)}$ and $c_{(t-1)}$ are the corresponding concentrations, and $V_{(t-1)}$ is the volume of solution remaining in the reactor at time $t-1$. The apparent dissolution rate constant was calculated using the method from [13], which accounts for re-precipitation of species.

In preliminary experiments, salinity was also varied for hisingerite and Fe-allophane dissolution.

Results: In all dissolution experiments, the solution pH trended towards neutral, with the pH of the acidic experiments (pH 3 and 5) increasing with time, and the pH of the alkaline experiments (pH 8 and 10) decreasing with time.

For all but one dissolution experiment, Fe concentrations remained below the practical quantitation limit of 0.2 ppm throughout the experiment run. The single exception was hisingerite dissolved at pH 3, which showed an initial Fe release, followed by a decrease in concentration of Fe in solution that may represent re-precipitation of an Fe-rich phase.

Silica concentrations in all experiments first increased, then leveled off to a steady concentration.

The apparent dissolution rate constants for allophane, Fe-allophane, and hisingerite are an order of magnitude faster than dissolution rates of well-crystalline clay minerals of similar composition (**Figure 1**).

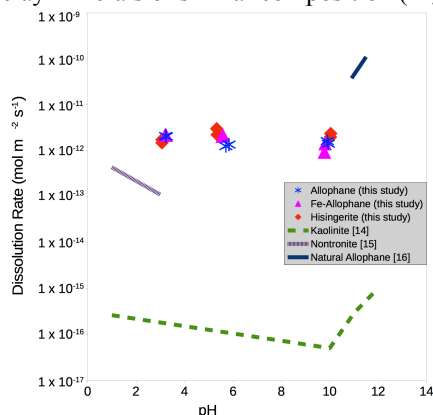


Fig. 1: Dissolution of allophane, Fe-allophane, and hisingerite compared to other phases important on Mars.

TEM analyses of materials reacted at pH 10 for between one and six months demonstrated that structural changes occurred due to dissolution. Thin linear features (indicated by arrows), interpreted as the rolled edges of silicate sheets, were observed in reacted hisingerite and allophane, shown in **Figure 2**. These features were not observed in the unreacted materials, although more thorough examinations are necessary in order to confirm that they were not present.

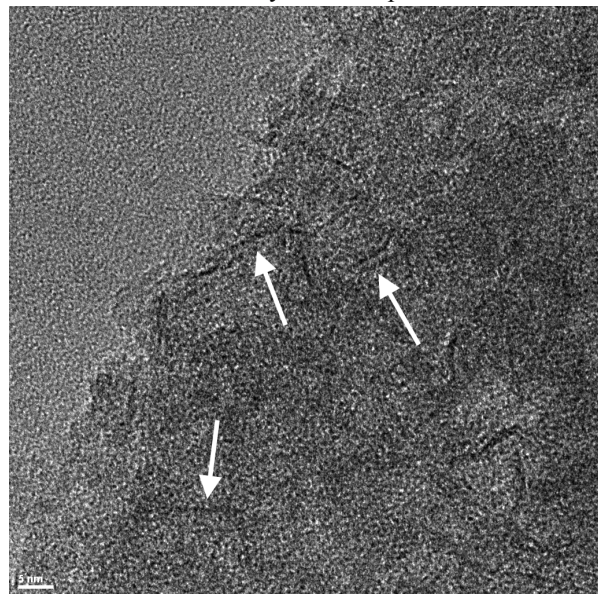


Fig. 2: TEM image of synthetic hisingerite reacted at pH 10 for 2 months.

Discussion: The release of silica into solution without accompanying Fe concentration increases may

be due to several factors, including precipitation of secondary Fe-rich phases; the formation of silica leached-layers; or some combination of both.

The apparent dissolution rate constants presented here represent fundamental data that can be used for extrapolations to Mars-relevant conditions. For example, lower temperatures would tend to decrease the dissolution rate, while a slightly higher salinity (0.1 M NaCl instead of 0.01 M NaCl) was shown to increase hisingerite dissolution at pH 3, although it had no apparent effect on Fe-allophane dissolution.

Further work is necessary to understand how Mars-like conditions affect the dissolution of poorly-crystalline silicate materials. Our dissolution experiments showing rapid dissolution of these X-ray amorphous phases and their prevalence in all samples measured by CheMin to date, however, suggest that liquid water was limited after deposition of the X-ray amorphous materials.

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