

**FE-CONTAINING ALLOPHANE AND HISINGERITE DISSOLUTION AND IMPLICATIONS FOR GALE CRATER, MARS.** S. J. Ralston<sup>1</sup>, E. M. Hausrath<sup>1</sup>, O. Tschauner<sup>1</sup>, E. B. Rampe<sup>2</sup>, J. V. (Clark)-Hogancamp<sup>2,3,4</sup>, R. Christoffersen<sup>4</sup>, <sup>1</sup>University of Nevada, Las Vegas (ralstsl@unlv.nevada.edu), <sup>2</sup>NASA/JSC, Houston, TX 77058, <sup>3</sup>Jacobs, NASA Johnson Space Center, Mail Code XI3, Houston, TX 77058, USA, <sup>4</sup>Geocontrols Systems Inc, Houston, TX.

**Introduction:** Understanding the aqueous history of Mars is essential to understanding its potential habitability. Materials formed by aqueous alteration of primary minerals, such as secondary amorphous silicates, are useful tools for understanding the characteristics of ancient water. The *Curiosity* rover discovered an amorphous component of the martian soil in Gale Crater, which possessed an x-ray diffraction (XRD) pattern that could be fit with allophane and basaltic glass [1] as well as water release patterns consistent with allophane [2]. We may be able to utilize the dissolution kinetics of these Mars-relevant amorphous materials to constrain the characteristics and longevity of the liquid water that was present in Gale Crater.

Allophane is an aluminosilicate found terrestrially as a weathering product in volcanic soils [3]. It forms hollow, porous nanoballs ~5 nm in diameter that aggregate into clumps [4]. In Fe-rich environments, Fe can substitute for Al in allophane [5]. Although there is extensive soil science research on allophane, e.g. [3], its dissolution kinetics are not well-studied. Abidin et al. [4] provided dissolution rates for allophane at high pH, however its overall behavior remains poorly understood, and to the best of our knowledge there are no rate laws for allophane dissolution in the literature.

Although the XRD patterns of a portion of the amorphous component of the soil at Gale Crater, Mars can be fit with allophane, the chemical data suggest that an Fe-rich phase such as hisingerite is also possible [1] [7]. Hisingerite is an Fe-silicate generally found terrestrially in iron-rich soils [8] or as a hydrothermal alteration product [9]. It shares the chemical structure of allophane [8], but much less research has been dedicated to it. To our knowledge, no dissolution data for hisingerite exist.

Constructing dissolution rate laws for allophane and hisingerite will provide insight into the timescales over which liquid water was present on Mars while secondary precipitates can give clues to the water's pH.

**Methods:** 18.2 MΩ deionized water was used for all syntheses and dissolution experiments.

**Synthesis:** Fe-allophane and hisingerite were synthesized using the methods of Baker et al. [10], which are a modification of those used by Montarges-Pelletier et al. [11]. Millimolar solutions of AlCl<sub>3</sub>·6H<sub>2</sub>O and FeCl<sub>3</sub>·6H<sub>2</sub>O were mixed with tetraethyl orthosili-

cate (TEOS). For Fe-allophane, an Al/Fe/Si ratio of 0.99:0.01:1 was used; for hisingerite, the ratio was 0.5:0.5:1. 50 mL of 1M NaOH was added at 25 mL/hr to hydrolyze TEOS while preventing formation of silica monomers. The suspension was stirred for an hour, allowed to sit overnight to enhance colloid formation, and then incubated at 95°C for seven days. The incubated suspension was washed with deionized water until the conductivity of the supernatant was <20 μmhos. The synthetic material was frozen for at least 24 hours and then freeze-dried for analysis and dissolution.

**Characterization:** Freeze-dried samples of Fe-allophane and hisingerite were analyzed to confirm their identities and suitability as martian analogues. Analyses included XRD, Fourier-transform infrared spectroscopy (FT-IR), field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), and evolved gas analysis (EGA). EGA, XRD, and TEM were performed at NASA Johnson Space Center. All other analyses were performed at UNLV.

**Dissolution:** Dissolution of hisingerite and Fe-allophane was carried out in batch reactor format following the methods of Steiner et al. [12].

For each experiment, 180 mL of 0.1M NaCl solution, adjusted to pH 3 with concentrated HNO<sub>3</sub>, was added to 0.15 g of either hisingerite or Fe-allophane in acid-washed LDPE bottles. The bottles were capped and placed in a shaker bath at 25°C and 50 rpm. Each experiment was performed in duplicate with a blank. 10 mL aliquot samples were taken every hour for the first six hours to measure elemental release into solution over time. Solution pH was measured on a separate unfiltered aliquot of each solution over time. The remainder was filtered through a 0.2 μm polypropylene filter and acidified to 1% v/v with high purity HNO<sub>3</sub>. Fe and Si were measured on a Thermo Scientific iCE 3000 Series Atomic Absorption Spectrometer at UNLV.

The moles Si measured in solution were corrected to moles Si released using the equation:

$$m(t) = m(t-1) + (c(t) - c(t-1))V(t-1) \quad (Eq. 1)$$

where  $m(t)$  and  $m(t-1)$  are the moles 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 at time  $t-1$ . The moles Si released were then plotted against time. The slope of this line is the dissolution rate.

**Results and Discussion:** Characterization of the synthetic materials was conducted prior to dissolution experiments to ensure that the results of those experiments would be meaningful.

XRD data confirmed that the products were poorly-crystalline, and therefore these materials were appropriate analogues for the Mars amorphous soil component. Additionally, features at small wavenumbers in the FT-IR data were compared to those presented by Wada [3] for allophane, and by Milliken et al. [13] for hisingerite, and were judged to be comparable. FE-SEM and TEM analyses revealed nanoball structures indicative of hisingerite and allophane. EGA data, shown in Fig. 1, were compared with those obtained by Leshin et al. [2]. The water release attributed to allophane in their data corresponds closely to our observed water release for hisingerite.

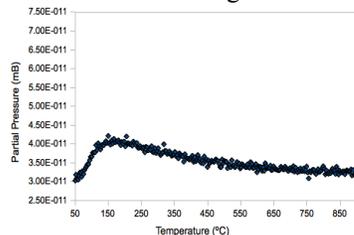


Fig. 1: Mass 18 water releases from synthetic hisingerite.

Over the course of each experiment, solution pH was variable between duplicates and increased within each duplicate, aqueous Si concentration increased, and aqueous Fe concentration decreased over time. The variability of pH is likely due to the heterogeneity of samples. Increasing silica concentration indicates dissolution of a silica-containing phase. Decreasing Fe concentration with time suggests re-precipitation of an Fe-rich phase, e.g., ferrihydrite.

Using the data from the first six hours, dissolution rates were calculated for hisingerite and Fe-allophane, attributing all of the silica release to dissolution of these phases. Because the pH was variable, we used the first measured pH as the representative pH. Fig. 2 shows the average mass-normalized dissolution rates of the hisingerite and Fe-allophane duplicates on a graph comparing them to the dissolution rates of kaolinite and nontronite, which are crystalline phyllosilicates with similar composition to allophane and hisingerite. The mass-normalized dissolution rates of Fe-allophane and hisingerite are much higher than those of the more crystalline phyllosilicates.

Future work will include measuring BET surface areas and particle sizes for hisingerite and allophane for estimations of geometric surface area, and a comparison of these rates as well as the mass-normalized rates.

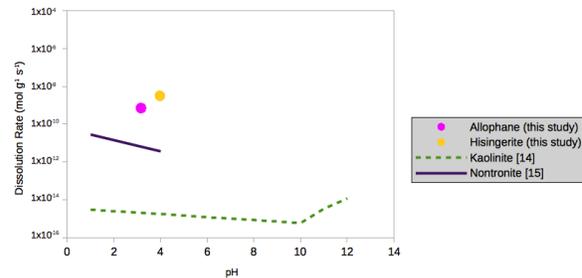


Fig. 2: Mass-normalized dissolution rates of Fe-allophane and hisingerite compared to other phases important on Mars.

**Conclusions:** The mass-normalized dissolution rates measured in this study demonstrate that hisingerite and Fe-substituted allophane dissolve rapidly, much faster than crystalline phyllosilicates such as nontronite and kaolinite that have similar compositions. In addition, hisingerite dissolves more rapidly than allophane.

Future work will focus on measuring dissolution rates at other pH values, so that dissolution rate laws for allophane and hisingerite can be derived. Results will be used to interpret data from Gale Crater.

These initial experiments suggest that, if the liquid water present in Gale Crater was highly acidic, it was likely present for only a short time, allowing some amorphous soil-material similar to allophane to persist. Further experiments will enable us to constrain the timescales over which liquid water was present in Gale Crater and provide insight into its pH. This information is essential to assessing the potential habitability of ancient Mars.

**References:** [1] Bish D. L. et al. (2013) *Science*, 341, 1238932. [2] Leshin L. A. et al. (2013) *Science*, 341, 1238937. [3] Wada K. (1989) *SSSA*, 1051-1087. [4] Iyoda F. (2012) *Appl Clay Sci*, 56, 77-83. [5] Baker L. L. et al. (2014) *Clays Clay Min*, 62, 20-34. [6] Abidin Z. et al. (2004) *Clay Sci*, 12, 213-222. [7] Dehouck E. et al. (2014) *JGRP*, 119, 2640-2657. [8] Ingles O. G. and Willoughby D. R. (1967) *Soil Sci*, 104, 383-385. [9] Eggleton R. A. and Tilley D. B. (1998) *Clays Clay Min*, 46, 400-413. [10] Baker L. L. et al. (2011) *LPS XXXII*, 1939. [11] Montarges-Pelletier E. et al. (2005) *Colloid Surface A*, 255, 1-10. [12] Steiner M. H. et al. (2014) *LPS XXXV*, Abstract #1510. [13] Milliken R. E. and Bish D. L. (2014) *LPS XXXV*, 2251. [14] Carroll S. A. and Walther J. V. (1990) *Am J Sci*, 290, 797-810. [15] Gainey, S. R. et al. (2014) *Geochim Cosmochim Ac*, 126, 192-211.