

**POORLY CRYSTALLINE, IRON-BEARING ALUMINOSILICATES AND THEIR IMPORTANCE ON MARS.** L.L. Baker<sup>1</sup>, D.G. Strawn<sup>1</sup>, P.A. McDaniel<sup>1</sup>, R.D. Nickerson<sup>1</sup>, J.L. Bishop<sup>2</sup>, D.W. Ming<sup>3</sup>, and R.V. Morris<sup>3</sup>, Division of Soil and Land Resources, University of Idaho, Moscow, ID; lbaker@uidaho.edu, <sup>2</sup>SETI Institute, Mountain View, CA, <sup>3</sup>NASA-Johnson Space Center, Houston, TX.

**Introduction:** Martian rocks and sediments contain weathering products including evaporite salts and clay minerals that only form as a result of interaction between rocks and water [1-6]. These weathering products are key to studying the history of water on Mars because their type, abundance and location provide clues to past conditions on the surface of the planet, as well as to the possible location of present-day reservoirs of water.

Weathering of terrestrial volcanic rocks similar to those on Mars produces nano-sized, variably hydrated aluminosilicate and iron oxide minerals [7-10] including allophane, imogolite, halloysite, hisingerite, and ferrihydrite. The nanoaluminosilicates can contain isomorphically substituted Fe, which affects their spectral and physical properties. Detection and quantification of such minerals in natural environments on Earth is difficult due to their variable chemical composition and lack of long-range crystalline order [9, 11, 12]. Despite the difficulty in characterizing these materials, they are common on Earth, and data from orbital remote sensing and rover-based instruments suggest that they are also present on Mars [9, 10, 13-17]. Their accurate detection and quantification require a better understanding of how composition affects their spectral properties. We present here the results of XAFS spectroscopy; these results will be corroborated with planned Mössbauer and reflectance spectroscopy.

Allophanic materials take the physical form of nanospherical particles [11]. These particles are thought to consist of a gibbsite (aluminum octahedral) sheet, rolled into spherical shape, with tetrahedral silica in the interior. This structure has not yet been fully solved, however. The nanotubular aluminosilicates imogolite and halloysite [18], are thought to be constructed of rolled gibbsite and silicate sheets. These materials may be precursors to more crystalline clays, possibly transforming from rolled configurations to platy particles as crystallite size increases.

Allophanes and other nanoaluminosilicates formed from weathering of volcanic tephra may contain substituted Fe and other elements. Evidence from natural and synthesized materials suggests that Fe may isomorphically substitute for Al in the octahedral sheet, as in clay minerals. The extent of Fe substitution in allophane is not well understood, nor are its effects on the transformation of allophanic materials to clay minerals. The nanomineral hisingerite, in which the octahedral sheet may be completely occupied by Fe rather than Al, may

be a form of allophane [19] or halloysite [20], although a number of other classifications have also been proposed for this material.

**Methods:** Aluminosilicate nanoparticles of varying crystallinity were synthesized with varying amounts of isomorphically substituted Fe (Figure 2). Synthesized materials include allophanes with varying Al:Si ratio [21], imogolite, hisingerite, kaolinite, and nontronite. The proportion of Fe substitution varied from a nominal 0.1 to 10 % (as mol % of Al in the mineral) for the non-crystalline materials, and up to 50% Fe in octahedral sites in hisingerite and nontronite.

We have also collected weathered basalts and ash-influenced soils from northern Idaho and eastern Washington and isolated the clay-size fraction from these materials. The clay fraction contains nanoscale weathering products, including allophane. We have characterized the chemistry and mineralogy of these natural materials, and they will be used for comparison with laboratory-produced synthetic materials.

**Syntheses.** Allophane and clay precursor gels were prepared from tetraethyl orthosilicate, 0.1 M  $\text{Al}(\text{NO}_3)_3$ , and 0.1 M NaOH using the method described in [21] and adding 0.1 M  $\text{Fe}(\text{NO}_3)_3$  to obtain the desired Fe concentrations. Hisingerite was prepared in the same way as allophane with  $\text{Fe}(\text{NO}_3)_3$  substituted for 50 mol% of  $\text{Al}(\text{NO}_3)_3$ . The same method was used to prepare a gel precursor of kaolinite composition, which was then annealed in a Teflon-lined autoclave for 2 months at 200 °C. A nontronite precursor was prepared using the method above with  $\text{Fe}(\text{NO}_3)_2$  substituted for 50 mol% of  $\text{Al}(\text{NO}_3)_3$ . Splits of this gel were annealed at room temperature, at 95 °C, and at 150 °C to produce samples of progressively increasing crystallinity. Supernatants were collected at the end of all syntheses and analyzed for residual ion concentrations.

**XAFS analyses.** We are using the substituted Fe in the natural and synthetic aluminosilicates as a structural probe to characterize their mineral structure using Fe K-edge X-ray absorption fine structure spectroscopy (XAFS). The XAFS spectrum contains information about the immediate molecular environment surrounding the target atom, and is an ideal technique for studying poorly crystalline materials that are difficult to characterize using bulk methods such as XRD. The near-edge (XANES) and extended (EXAFS) portions of the XAFS spectrum will be used to characterize the structural environment of Fe isomorphically substituted in the synthetic aluminosilicates, as well as in

natural materials isolated from the weathering products of terrestrial volcanic materials.

The synthetic and natural materials are also being characterized using visible and infrared spectroscopy, x-ray diffractometry (XRD), Mössbauer spectroscopy, and scanning electron microscopy (SEM).

**Results:** Results from XRD, FTIR, SEM and XAFS confirm that Fe-substituted allophanes, imogolite, hisingerite, and clay minerals have been synthesized. Ferrihydrite was not detected in the synthetic materials, suggesting all Fe was incorporated into the aluminosilicate structure. Selected synthetic nanoparticles are shown in Figures 1 and 2. Figure 3 shows the Fe K-edge EXAFS spectrum for synthetic allophanes (Al:Si = 1:1, 1 and 5% of Al substituted by Fe), beidelite, and nontronite. The XAFS results suggest that Fe substituted into the allophane structure is present as ferric Fe in octahedral coordination, with some Fe-Fe next-neighbor pairing (Figure 3, boxes). This spectrum is similar to those of Fe in nontronite and ferruginous smectites, with some features being more similar to those in lower-Fe smectites [22]. XANES spectra rule out ferrihydrite in the allophane samples.

This difference may be attributable to distortion of the octahedral sites in the spherical allophane structure (Figure 1) by substitution of Fe for Al, or to more fundamental structural differences between Fe-substituted allophane and clay minerals. Additional spectroscopic analysis of Fe-allophanes and other Fe-substituted nanoaluminosilicates will help resolve this question.

**Applications to Mars:** Confirmation of the presence of allophane or other short-ordered phases on Mars will provide new constraints on the aqueous processes early in the planet's history. Allophane exhibits spectral features near 2.2  $\mu\text{m}$  similar to those of Al-smectites that have been detected on Mars. Spectra of the Fe-bearing materials in our sample suite are expected to have related bands between 2.2-2.3  $\mu\text{m}$  and are likely different from those of the ubiquitous Fe/Mg-smectite in ancient Martian rocks. Documenting the spectral properties of our samples will enable detection of these phases on Mars with orbital spectrometers.

**References:** 1. Bridges J.C. and Grady M.M. (2000) *Earth Planet Sci Lett*, 176, 267-279. 2. Gooding J.L., et al., (1991) *Meteoritics*, 26, 135-143. 3. Treiman A.H., et al. (2003) *Meteoritics*, 28, 86-97. 4. Bibring J.-P., et al., (2006) *Science*, 312, 400-404. 5. Hynek B.M. (2004) *Nature*, 431, 156-159. 6. Squyres S.W., et al. (2004) *Science*, 305, 794-799. 7. Banin A. (1996) *Adv Space Res*, 18, 233-240. 8. McDowell M.L. and Hamilton V.E. (2009) *JGR*, 114. 9. Morris R.V., et al. (2001) *JGR 106(E3)*, 5057-5083. 10. Hamilton V.E., et al. (2008) *JGR*, 113. 11. Parfitt R.L. (2009) *Clay Min*,

44, 135-155. 12. Baker L.L., et al. (2010) *Clays Clay Min*, 58, 772-782. 13. Ming D.W., et al., (2006) *JGR*, 111. 14. Morris R.V., et al. (2000) *JGR*, 105(E1), 1757-1817. 15. Morris R.V., et al. (2008) *JGR*, 113(E12), E12S42. 16. Rampe E.B., et al. (2010) *AGU Fall Meeting 2010*. San Francisco, CA. 17. Chevrier V. and Mathé P.E. (2007) *Planet Space Sci*, 55, 289-314. 18. Joussein E., et al. (2005) *Clay Min*, 40, 383-426. 19. Sudo T. and Nakamura T. (1951) *Amer Min*, 37, 618-621. 20. Eggleton R.A. and Tilley D.B. (1998) *Clays Clay Min*, 46, 400-413. 21. Montarges-Pelletier E., et al. (2005) *Coll Surf A*, 255, 1-10. 22. Vantelon D., et al. (2003) *Phys Chem Min*, 30, 44-53.

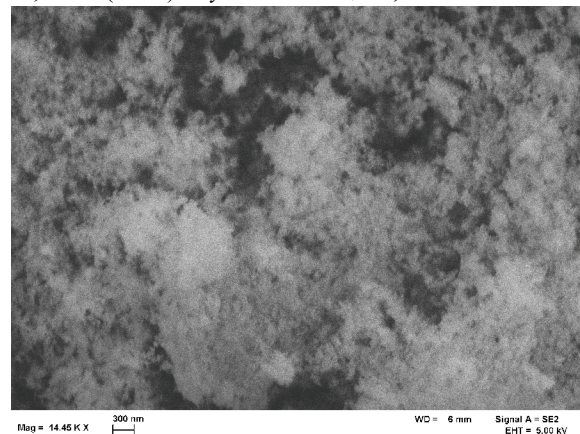


Figure 1: Synthetic Fe-substituted allophane

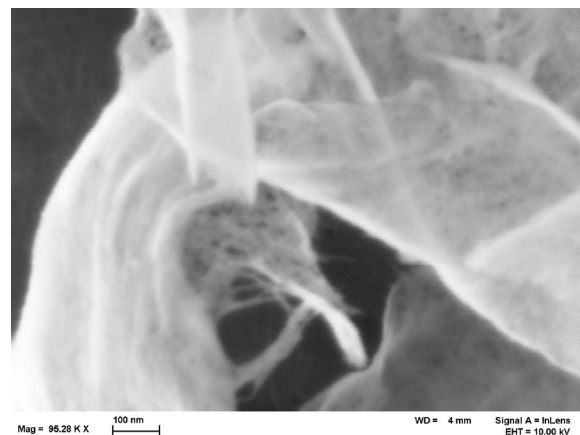


Figure 2: Synthetic Fe-substituted imogolite

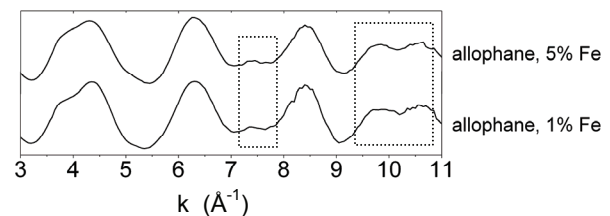


Figure 3: XAFS spectra of synthetic Fe-substituted allophanes