

**TIME-COURSE MINERALOGY AND TEXTURE OF NANOSCALE JAROSITE DISSOLUTION PRODUCTS.** A.S. Madden<sup>1</sup>, M.E. Elwood Madden<sup>1</sup>, J.D. Rimstidt<sup>2</sup>, and M.R. Kendall<sup>1</sup>, <sup>1</sup>University of Oklahoma, School of Geology and Geophysics, <sup>2</sup>Virginia Tech, Dept. of Geological Sciences.

**Introduction:** In acid environments, ferric oxides and ferric sulfates form depending on the iron/sulfate ratio, pH, temperature, water-to-rock ratio, etc. Incongruent dissolution of iron-bearing sulfate minerals by episodic or continuous wetting serves as a source of nanophase iron oxides. Aqueous transport of ferric iron on Earth is limited by the insolubility of ferric oxides. Thus, the mineralogy and textures of ferric sulfate reaction products in association with the primary grains provides clues to the conditions during their formation (e.g., [1]). Additionally, nanoparticulate minerals can be transported for hundreds of kilometers in stream systems as colloids [2] or globally as wind-borne dust [3,4]. Thus ferric sulfate-bearing units exposed to aqueous solutions could serve as sources of nanophase iron oxides to sediments either located hydrologically down-gradient or when receiving inputs from atmospheric dust deposition. Relationships between the ferric sulfate jarosite, observed on Mars [5], and its reaction products by aqueous dissolution in laboratory experiments are reported here.

**Methods:** Synthetic jarosite was prepared and characterized by Atomic Force Microscopy (AFM), powder X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy (TEM) before and after dissolution reactions. Jarosite was added to batch reactors at temperatures of 277 K, 298 K, 313 K, or 323 K containing solutions adjusted to pH 2 with sulfuric acid, with ultrapure water only, solutions buffered to near-neutral pH with MES, or solutions adjusted to basic pH values with NaOH. Most experiments were conducted for approximately one month, although durations were in some cases as long as 14 months.

**Results:** *Jarosite grain textures.* Under acidic conditions, circular pitting dominated over uniform grain boundary retreat. This effect was emphasized by higher temperatures, in which skeletal grains preserve nearly intact grain boundaries. Particle size distributions by grain counting did not appear to measurably change over the course of one month. Jarosite grains were too thick to obtain electron diffraction patterns from particle interiors. However, selected samples were embedded in resin and sectioned, demonstrating that particle interiors were single-crystal jarosite. Although dissolution was incongruent, accumulation of Fe-oxides in particle interiors was not observed.

Higher-pH dissolution led to unique textures. Accumulations of ferrihydrite often led to preservation of

the grain boundaries, while the particle interiors were completely dissolved.

*Reaction product mineralogy and textures.* The phase distribution, textures, and time-course evolution of reaction products depended strongly on pH and temperature. In all cases, reaction products were nanoparticulate. Schwertmannite-like crystallites were found only at the lowest temperature investigated. Maghemite formed initially for all room-temperature experiments. At pH 2, no reaction products were observed past 10 days. Above initial pH values of 6.2, ferrihydrite was the predominant additional reaction product and no goethite/hematite was observed. Between initial pH values of 4.4 and 6.2, the mineralogy was initially dominated by maghemite but over weeks became dominated by hematite. Minor goethite was observed in experiments with initial pH of 6.2. Coarsening of hematite and goethite was observed over 14 months at room temperature; however, crystallites remained nanoparticulate.

**Discussion:** Jarosite grain textures themselves give very little information about dissolution conditions below neutral pH, but were in some cases significantly different under basic conditions. Dissolution of jarosite can serve as both a source of nanoparticulate maghemite, known to be present in Mars dust [6], and hematite. However, maghemite converts to hematite as the contact time with solution or water-to-rock ratio increases.

The influence of sulfate was seen in reaction product mineralogy and morphology, favoring hematite over goethite in the short-term. After 14 months at room temperature in ultrapure water, both goethite and hematite coarsened, but goethite dominated by powder XRD. The lack of goethite on Mars suggests low water-to-rock ratios predominated in the past. Additionally, associations of sulfates with hematite and maghemite are suggestive of acidic paleo-solutions.

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**References:** [1] Murad E. and Rojik P. (2005) *Clay Mins.*, 40, 420–444. [2] Moore J. N. and Louma S.N. (1980) *Environ. Sci. Tech.*, 24, 1278–1285. [3] Yen A. S. et al. (2005) *Nature*, 436, 49–54. [4] Moore J. N. and Louma S.N. (1980) *Environ. Sci. Tech.*, 24, 1278–1285. [5] Klingelhöfer, G., et al. (2004) *Science*, 306 1740–1745. [6] Bishop J.L. et al. (2002) *JGR*, 107(E11), 5097.