

**PHASE TRANSFORMATIONS OF GREEN RUST: LASER RAMAN CHARACTERIZATION WITH IMPLICATIONS FOR ORIGIN OF LIFE AND MARS ASTROBIOLOGY.** L. M. Barge<sup>1</sup>, P. Sobron<sup>2</sup>, E. Flores<sup>1</sup>, M. J. Russell<sup>1</sup>, A. Wang<sup>3</sup>, I. Kanik<sup>1</sup>, <sup>1</sup>NASA Jet Propulsion Laboratory, California Institute of Technology (4800 Oak Grove Dr, Pasadena, CA, laura.m.barge@jpl.nasa.gov), <sup>2</sup>SETI Institute (189 Bernardo Ave, Mountain View, CA), <sup>3</sup>Washington University St. Louis (St. Louis, MO)

**Introduction:** One mineral that may be particularly relevant to prebiotic chemistry and Mars habitability is Green Rust (GR), a double layered Fe(II,III) oxyhydroxide with a hydroxylated brucite structure. GR has many astrobiologically relevant properties: it concentrates organic species in its interlayers, preserving them against degradation, and it is a versatile redox catalyst for reactions that might drive the emergence of life; e.g., the reduction of nitrate to ammonium [1]. GR would be an interesting candidate for *in situ* analysis on Mars and possibly a sample cache; however, GR is metastable to oxidation and difficult to analyze. Laser Raman spectroscopy (LRS) is best suited for GR analysis due to its ability to detect Fe oxidation states and determine interlayer anions (including organics) in near real-time, thus facilitating precise, time-resolved analysis of the transformation of GR upon exposure to oxidants. We simulated GR formation in ancient hydrothermal systems and performed, for the first time, a spectral characterization and kinetic investigation of GR phase transformations using LRS instrumentation similar to that onboard ExoMars 2018 and Mars 2020.

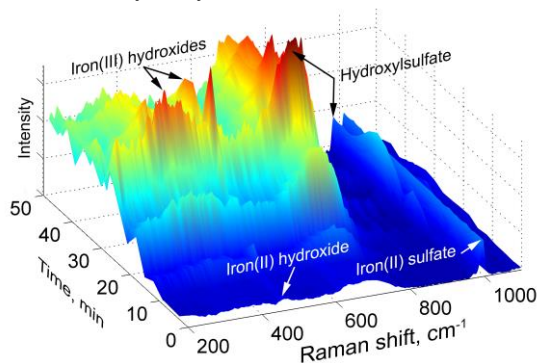
**Experimental:** GR(SO<sub>4</sub><sup>2-</sup>) (FeII:FeIII = 2:1) was synthesized by coprecipitation in anaerobic laboratory systems [2] and aged for two days at room temperature. The precipitate was treated in various ways for LRS analysis: 1) GR in aqueous suspension in an anoxic quartz cuvette; 2) GR was dehydrated under N<sub>2</sub> to produce a mud-like sample; 3) GR was dessicated under vacuum for 30 minutes to produce a dried sample.



**Fig. 1:** GR(SO<sub>4</sub><sup>2-</sup>) samples for LRS analysis: A) anoxic suspension; B) concentrated mud; C) dessication.

The resulting samples were analyzed with LRS. The laser power at the sample surface was kept below <0.3mW in order to prevent thermally-induced oxidation. GR typically shows two Raman peaks around 420-435 cm<sup>-1</sup> (Fe<sup>2+</sup>-OH) and 495-520 cm<sup>-1</sup> (Fe<sup>3+</sup>-OH) [3]. In the aqueous sample, sulfate was detectable, but the precipitate was still amorphous and the two GR peaks were merged. The concentrated mud sample, though most geologically realistic, was difficult to ana-

lyze due to the dark color of the precipitate and rapid surface dehydration. In the dessicated sample, time-resolved LRS analysis was possible for ~ one hour before the sample oxidized completely. Fig 2 shows a spectral time-series of 25 LRS spectra of the dessicated GR sample recorded at 2-min intervals. The spectra are normalized to the intensity of the 995 cm<sup>-1</sup> Fe(II)-sulfate band for comparison purposes. This Fe(II)-sulfate and the 460 cm<sup>-1</sup> Fe(II)-oxide (white crust—see Fig 1C) bands dominate the spectra early in the experiment (t < 10). As Fe(II) oxidizes, these two bands decrease in intensity relative to the spectral envelope around 300 cm<sup>-1</sup> and the sharp band at 471 cm<sup>-1</sup>—both associated to Fe(III)-hydroxides, and the 700 cm<sup>-1</sup> envelope and the sharp band at 970 cm<sup>-1</sup>—both assigned to unidentified hydroxylsulfate clusters.



**Fig. 2:** LRS time-series of GR oxidation processes

Quantitative analysis of the spectral time-series allowed us to evaluate the kinetics of green rust oxidation and determine intermediate oxidation products. This is important because it constrains the survivability of GR under oxidizing conditions, and paves the way for: (i) the design of GR phase transformation investigations under Martian environmental conditions through to akaganeite [4, 5]; (ii) the development of analytical approaches to characterizing GR in the field (including Mars) before and during transformation; and (iii) enhancing mission operation readiness for the characterization of GR during the upcoming ExoMars 2018 and Mars 2020 missions.

**References:** [1] Russell M. J. et al. (2014) *Astrobiology*, 14:308-4. [2] Gehin J.-M. et al. (2002) *Solid State Sci.* 7:545-572. [3] Pineau S. et al. (2008) *Corrosion Sci.* 50:1099-1111. [4] Vaniman, D. T. et al. (2014) *Science*, 343:1243480. [5] Refait P. and Génin J.-M. R. (1997) *Corrosion Sci.* 39:539-553.