GEOCHEMISTRY AND ASTROBIOLOGY SCIENCE PAYOFF USING LASER DESORPTION FOURIER TRANSFORM MASS SPECTROMETRY (LD-FTMS) TECHNIQUES FOR MARS SAMPLE RETURN.

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Introduction: To maximize science payoff, samples returned from Mars need to be analyzed by techniques that will provide inorganic, organic and isotopic chemical information. This will provide planetary scientists the opportunity to understand the evolution of Mars from a geochemical and possibly biochemical perspective. Previous missions have indicated that a variety of geological environments exist on Mars, and sampling strategies should be used that will yield a wide range of geomaterials. Laser desorption Fourier transform mass spectrometry (LD-FTMS) has been used to detect inorganic, biological, and organic chemical signatures associated with different geomaterials. LD-FTMS requires no sample preparation and offers high sensitivity allowing acquisition of spectra with a single laser shot for heterogeneously distributed chemical signatures. Some organic compounds (i.e., polyaromatic hydrocarbons or PAHs) self-ionize and are easily detected[1], but most organic compounds require ionization assistance. Therefore, we are exploring how different minerals assist in ionization, a process called geomatrix-assisted laser desorption/ionization (GALDI)[2]. We have used synthetic, biologically induced, and natural mineral samples to evaluate GALDI using LD-FTMS.

Our focus has been on sulfate minerals, such as jarosite and Na/Mg-sulfate salts, both of which have been found on Mars.[3,4] Jarosite forms from aqueous solutions and is a biologically induced mineral on Earth[5]. Herein we present results of our characterization of these minerals using GALDI-FTMS.

Results: GALDI-FTMS has revealed the presence of organic matter, including the amino acid glycine, in several jarosite samples from various worldwide locations[6]. Complex cluster ions can form in the gas phase during analysis and systematic studies of isotopic distributions using synthetic jarosites and glycine mixtures (Fig. 1) help identify the original molecules present in the samples[6]. Stearic acid with thenardite (sodium sulfate) used to ascertain the limit of detection (LOD) for GALDI-FTMS. The LOD was estimated to be 3 parts per trillion based on bulk concentrations, corresponding to approximately 7 zeptomoles (10^{-21}) per laser shot. Determining the LOD is complicated by the heterogeneity of the sample (Fig. 2) and evidence that the signal-to-noise ratio (S/N) tends to increase as the concentration of bio/organic compounds decreases relative to the mineral host.

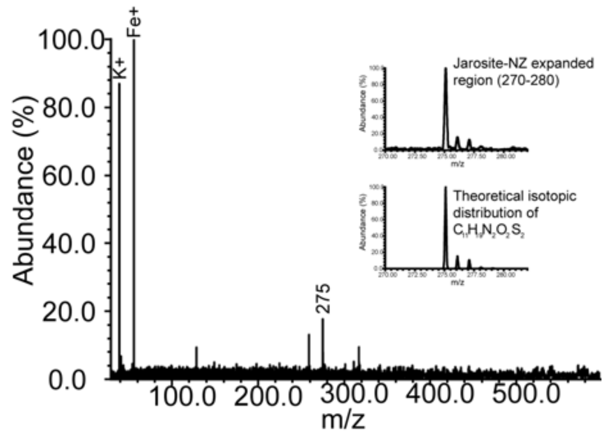

Fig. 1. LD-FTMS spectra of natural jarosite from New Zealand (NZ) and expanded region 270–280 m/z for glycine related ion isotopes.

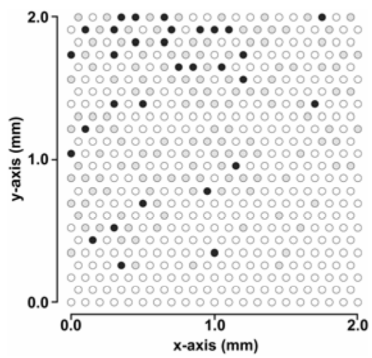

Fig. 2. Two-dimensional map showing heterogeneity of distribution of stearic acid biosignature in thenardite. Gray spots have m/z 390 peaks with S/N of 3 to 10 and black spots have S/N 10 or greater.

Conclusions: GALDI-FTMS offers the opportunity to obtain both geological and biological information simultaneously from a sample with minimal sample disturbance. Future improvements to the instrumentation should be able to provide more accurate isotope ratios, which would be a great asset for acquiring data from heterogeneous samples.

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