

Nano-Infrared Imaging of Amino Acids in Murchison: Sensitivity, Detection Limits, and First Results

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Introduction: While the spatial resolution of modern analytical techniques that carry-out elemental and isotopic mapping routinely achieve relatively high lateral resolutions, chemical mapping has typically lagged far-behind. This limitation is well-known to be the result of the Abbe criterion, which limits infrared imaging to resolutions comparable to the wavelength of the illumination being used ($\sim\lambda/2$).

In recent years, the development of Atomic-Force Microscope assisted infrared imaging has enable previously unattainable lateral resolutions (~ 10 nanometers) [1], opening up the possibility of understanding the heterogeneous distribution of functional groups in meteorites. This ability is particularly important for gaining insights as to the formation and alteration mechanisms of important prebiotic molecules such as amino-acids and phosphoric acids.

Here we present our first efforts at understanding the instrument response of a thermal-expansion based AFM-IR/Nano-IR instrument to amino-acids. We find that this instrumentation is sensitive to L-alanine crystals down to 7 nanometers in size, raising the possibility of doing in-situ mapping of amino-acids in planetary materials with high-sensitivity and spatial resolution.

Methods: Laboratory and natural sample preparation and measurements are described below

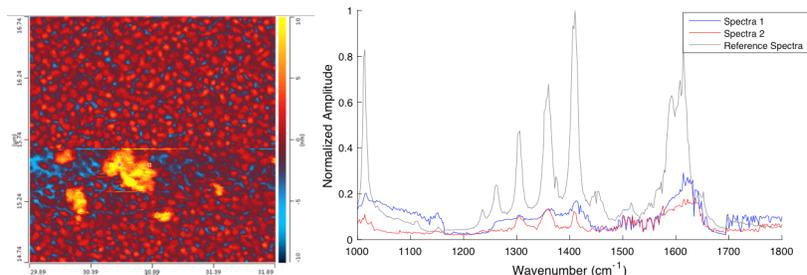
Sample Preparation. Samples of L-alanine crystals were prepared by dissolving L-alanine (>98%, Sigma Aldrich) in millipore water until solution was saturated. Drops of this solution were applied to gold covered slides and allowed to air-dry, precipitating out l-alanine crystals of various sizes.

A previously prepared and studied sample of Murchison was used to do infrared spectral hot-spot mapping. This sample's preparation history is described in ref. [1].

Nano-IR/AFM-IR: The nano-IR results reported here were taken with an Anasys AFM-IR (nanoIR-2) instrument illuminated with a broadly tunable IR Quantum Cascade Laser (QCL). Resonant absorption of IR illumination produces thermal expansion of material. Tapping mode and laser pulsing was used to enhance instrument sensitivities and thermal expansion was recorded and used to directly reconstruct FTIR equivalent spectrum [2]. Spot spectra as well as IR maps of the signal associated with a single phonon peak (fixed wavelength) were made of the l-alanine and Murchison meteorite samples.

Image Analysis: Spectra from several spots on the laboratory standard were chosen and AFM-IR spectra were taken. The simultaneously acquired topographic height information was used to determine the thickness of l-alanine and to correlate these thicknesses with AFM-IR amplitudes at various infrared wavelengths.

Results: Our nano-IR measurements indicate that AFM-IR is highly sensitive and suitable for the detection of IR spectral features associated with amino-acids. An analysis of the signal strength vs. amino acid thickness (>20 nanometers) of the laboratory amino-acid standard is consistent with the sensitivity expected with a surface sensitive technique. We were able to resolve and detect an IR signal from a ~ 9.5 nm sized L-alanine spot, indicating that the sensitivity of AFM-IR stretches down to $\sim 10^{-19}$ kilograms of material. A color mapped image of this two spectra obtained from the spot's surface are shown below.



Discussion: Applications of nano-IR techniques for the analysis of planetary materials is progressing. Previous work on amino acids in meteorites, using bulk extraction techniques are incapable of providing the contextual information that can be

provided by in-situ mapping. While our studies presented here focused on relatively easy to handle samples, applications of this technique for the analysis of returned samples from planetary missions (e.g. Stardust, Hayabusa, OSIRIS-REX) will require continued coordination and development work to be successfully implemented for the analysis of previous returned samples.

References [1] Dominguez et. al. (2014) *Nature Communications*, 10.1038/ncomms6445. [2] F. Lu, M Jin, and M.A. Belkin (2014), *Nature Photonics*, 10.1038/NPHOTON.2013.373