

NanoFTIR for the Analysis of Planetary Materials Alex S. McLeod¹, Gerardo Dominguez^{2,1}, Zack Gainsforth³, Andrew Westphal³, Fritz Keilmann⁴, Dimitri Basov¹, Mark Thiemens¹, ¹University of California, San Diego, San Diego, La Jolla, CA 92093, USA, ²California State University, San Marcos, San Marcos, CA 92096-0001, USA, ³Space Sciences Laboratory, University of California, Berkeley, Berkeley, CA 94720, USA, ⁴LASNIX, Sonnenweg 32, 82152 Berg, Germany

Introduction and Motivation: Planetary materials such as meteorites and returned samples from asteroids and comets may display chemical and isotopic heterogeneity at sub-micron spatial scales. Fortunately, there now exist a variety of analytical methods extract and maximize the scientific return provided by these samples. Secondary ionization mass spectrometric techniques such as NanoSIMS can be used to provide elemental and isotopic mapping of a sample with sub-micron lateral resolutions and has been used, for example, to identify presolar dust grains found within primitive meteorites by using extreme isotopic anomalies as a marker of extrasolar provenance [1]. Synchrotron-based techniques such as XANES, on the other hand, can resolve functional groups such as C-H, C-N and provide functional group mapping for spatial scales from 30 nm to microns. Raman spectroscopy may achieve spatial resolutions $\sim 1\mu\text{m}$, but typically requires high intensity visible radiation often resulting in sample alteration. Conventional infrared (IR) spectroscopy, well known as the chemical “fingerprinting” technique, is excellent for bulk analysis and spatial average characterization of planetary materials [2], but is unable to provide detailed chemical information at the sub-micron level. This presents a major challenge for analysis of samples with sub-micron spatial heterogeneity.

Scanning Near Field Infrared Microscopy (SNIM) has recently matured as a non-perturbative technique capable of providing infrared spectral maps of samples and has found applications in the study of surface phonons and graphene plasmons. The application of SNIM for the analysis of planetary materials has been limited and, until now, has not achieved spatial resolutions less than 1 micron [3]. Here we present infrared sub-micron spectral maps acquired using a broad-band NanoFTIR system recently developed at UC San Diego.

Principle, Operation and Implementation of NanoFTIR: NanoFTIR builds upon a conventional SNIM system, in which the back-scattered light from an illuminated atomic force microscope tip is modulated by nano-scale variations in a sample’s optical properties while scanning, conferring sub-diffractive optical contrast with resolutions down to the tip apex size (typically 20 nm) [6]. The difference-frequency combination of two near-infrared lasers provides broadband illumination ($3\mu\text{W}/\text{cm}^2$), which when combined with an asymmetric Michelson interferometer optical setup enables conventional FTIR spectroscopy at the nano-scale, resolving both the frequency-dependent amplitude and phase of back-scattered radiation with 3cm^{-1} spectral resolution (Fig. 1) [7], [8]. Quantitative spectroscopy is possible through normalization to a reference sample (e.g. Au).

NanoFTIR of Murchison: A piece of the CM carbonaceous chondrite Murchison was embedded in resin (EPO-

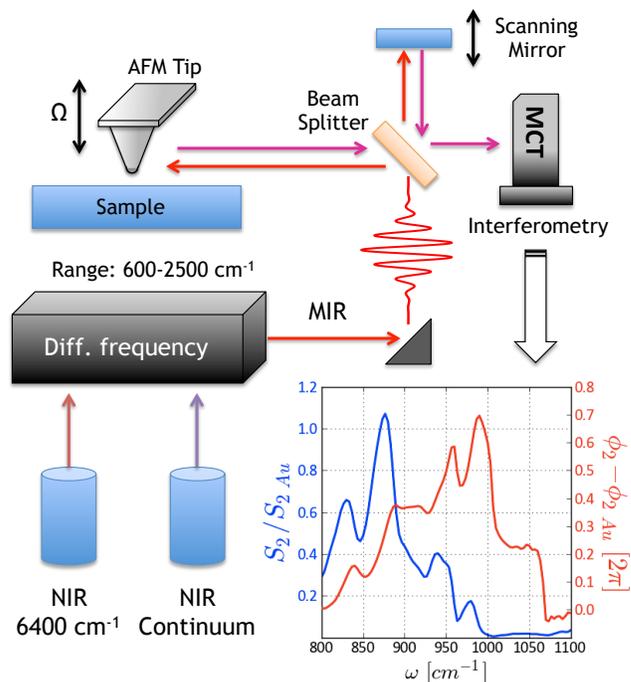


Figure 1: Schematic depiction of the nanoFTIR system described in the text. A typical spectrum of the amplitude and phase of the back-scattered electric field is shown for illustration, in this case revealing phonon modes of an olivine crystal in the Murchison meteorite.

FIX) and hardened overnight into a cylindrical epoxy puck. A region of the meteorite was then exposed and simultaneously flattened using an optical polisher. We conducted large-area $30\times 30\mu\text{m}$ near-field imaging and nanoFTIR studies with 30-100 nm resolution at two representative regions. In the first, white-light imaging at $800\text{-}1100\text{cm}^{-1}$ located olivine in a chondrule by comparison of nanoFTIR spectra (e.g. Fig. 1) against a forsterite standard. Micron-scale pyroxene crystals and metallic inclusions were also spectroscopically identified by nanoFTIR.

The second study examined a carbonaceous inclusion over the spectral range $850\text{-}1400\text{cm}^{-1}$. Fig. 2 displays the white beam infrared contrast of fine 200 nm-wide acicular inclusions resonant at 1100cm^{-1} . The shape of the 1100cm^{-1} peak is consistent with quartz. Additionally, infrared imaging and nanoFTIR spectroscopy above 1100cm^{-1} reveal spatially associated distributions of organic materials, whose distinct vibrational modes may enable chemical fingerprinting.

NanoFTIR of Stardust Cometary Dust Grains: Mineral assemblages returned from Comet Wild-2 by NASA’s Stardust mission contain very fine grained material. We have

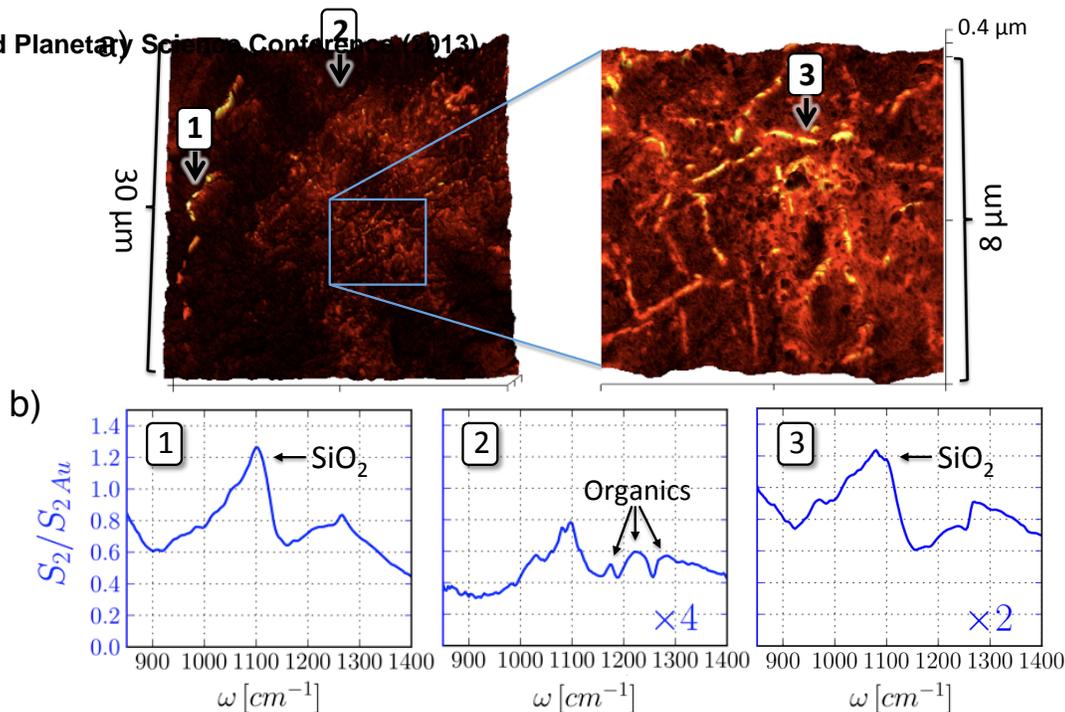


Figure 2: a) Mid-infrared scans of a carbonaceous matrix region of the Murchison meteorite (Left: 100 nm/pixel, Right: 27 nm/pixel). b) NanoFTIR spectra acquired at select image positions indicate a network of bright acicular structures whose spectral signature is consistent with quartz, with evident traces of organic vibrational modes.

demonstrated the ability to acquire infrared spectroscopy on two such Stardust grains. Iris, a terminal particle from track C2052,12,74,2, contains crystalline plagioclase and an amorphous phase of nearly the same composition as determined by TEM and SEM [4]. We imaged this particle near the 10 μm silicate stretch and found a significant variation in the infrared spectral characteristics over the transition from crystalline plagioclase to amorphous material. Figure 3 shows a white light infrared image with its associated line scan over 8 μm of the sample and over the spectral range of 850 - 1150 cm^{-1} . The line scan overlapped with the neighboring olivines on each end by a bit more than a μm . In the image, the star shaped object is mostly crystalline plagioclase, but the bottom portion circled in yellow is determined to be amorphous. This manifests in a diminution of the two phonon peaks at 907 and 970 cm^{-1} , and a shift of the 1110 cm^{-1} peak to 1070 cm^{-1} . Caligula, a particle from track C2035,5,10, shows variation within a silicate-sulfide assemblage and is reported in a related abstract [5].

Future Work: NanoFTIR exhibits sufficient sensitivity and reproducibility to enable quantitative interpretation of near-field spectra via derivation of material optical constants at measured (<100 nm square) sample regions. We will verify this capability by building a standards library of nanoFTIR spectra acquired on relevant crystalline and organic materials of known optical constants (e.g. olivines, pyroxenes, thermoplastics) and comparing with theoretical models of the near-field contrast mechanism. Improvements to the broadband laser should enable spectroscopy of O-H functional groups and aromatic stretch modes up to 3500 cm^{-1} .

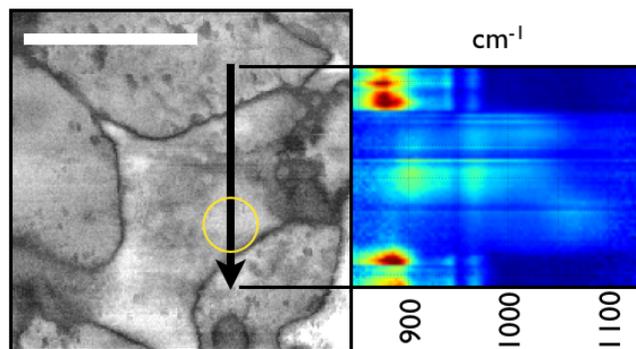


Figure 3: NanoFTIR image and line-spectrum of the Stardust grain named Iris. (Left) White light infrared image showing mineral phases present in the sample. The center star is crystalline/amorphous plagioclase surrounded by olivine crystals. (Right) Line spectrum across the transition from crystalline to amorphous material (latter circled in yellow) as discussed in the text. Scalebar is 5 μm .

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