Infrared Spectroscopy for the Non-Destructive Identification of Presolar Grains

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Introduction

- Presolar grains can by *crystalline* or *amorphous* and are identified by large isotope anomalies compared to Solar System materials
- Presolar supernova silica discovered in chondrites by Haenecour et al. 2013 and has been observed to form in supernova remnants (Rho et al. 2008)
- Identification of presolar grains by SIMS is complicated, expensive, and *destructive*
- SiC presolar grains can be identified using a combination of Raman spectroscopy and SEM-EDX (Liu et al. 2016)

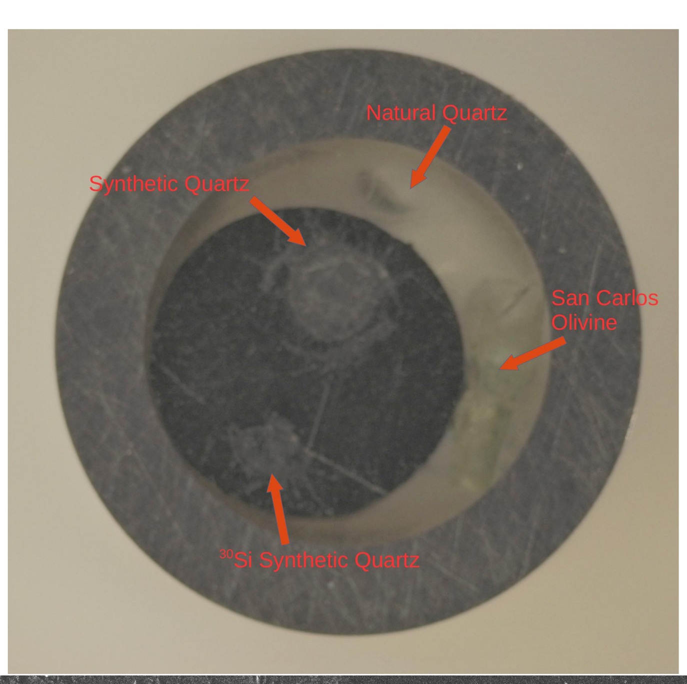
Here we demonstrate the use of infrared (IR) spectroscopy, both far-field and near-field, to identify large isotope anomalies in quartz (SiO_2).

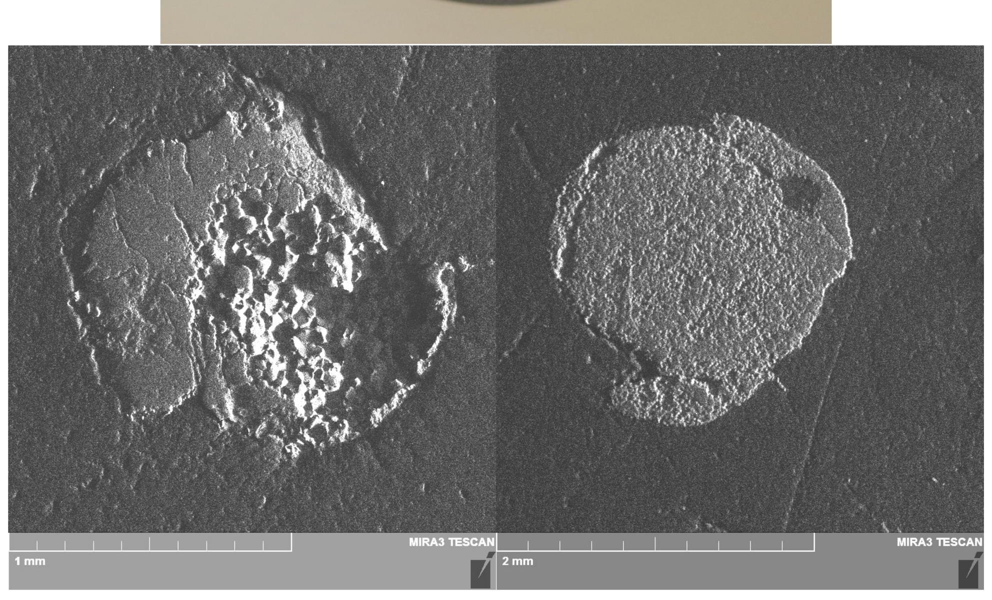
Methods

To ensure any observed spectral shift was due to isotope substitution, we synthesized three different types of quartz under identical conditions.

A graphite capsule containing amorphous silica powders (isotopically doped from Cambridge Isotope Labs, and undoped) was heated in a 150-ton piston cylinder (Experimental Studies of Planetary Materials lab at Wash U) at a temperature of 1160° C and a pressure of 1 GPa for 24 hours. Then the experimental charge was quenched, which resulted in the formation of α-quartz. We synthesized:

1. Quartz of nearly pure ^{28}Si
2. Quartz of terrestrial isotopic composition (92% ^{28}Si, 5% ^{29}Si, 3% ^{30}Si)
3. Quartz of nearly pure ^{30}Si





Top) Experimental capsule mounted in a 1 cm Al annulus with epoxy and natural quartz and olivine standards. Bottom) BSE images of ^{28}Si (left) and terrestrial (right) synthesized quartz.

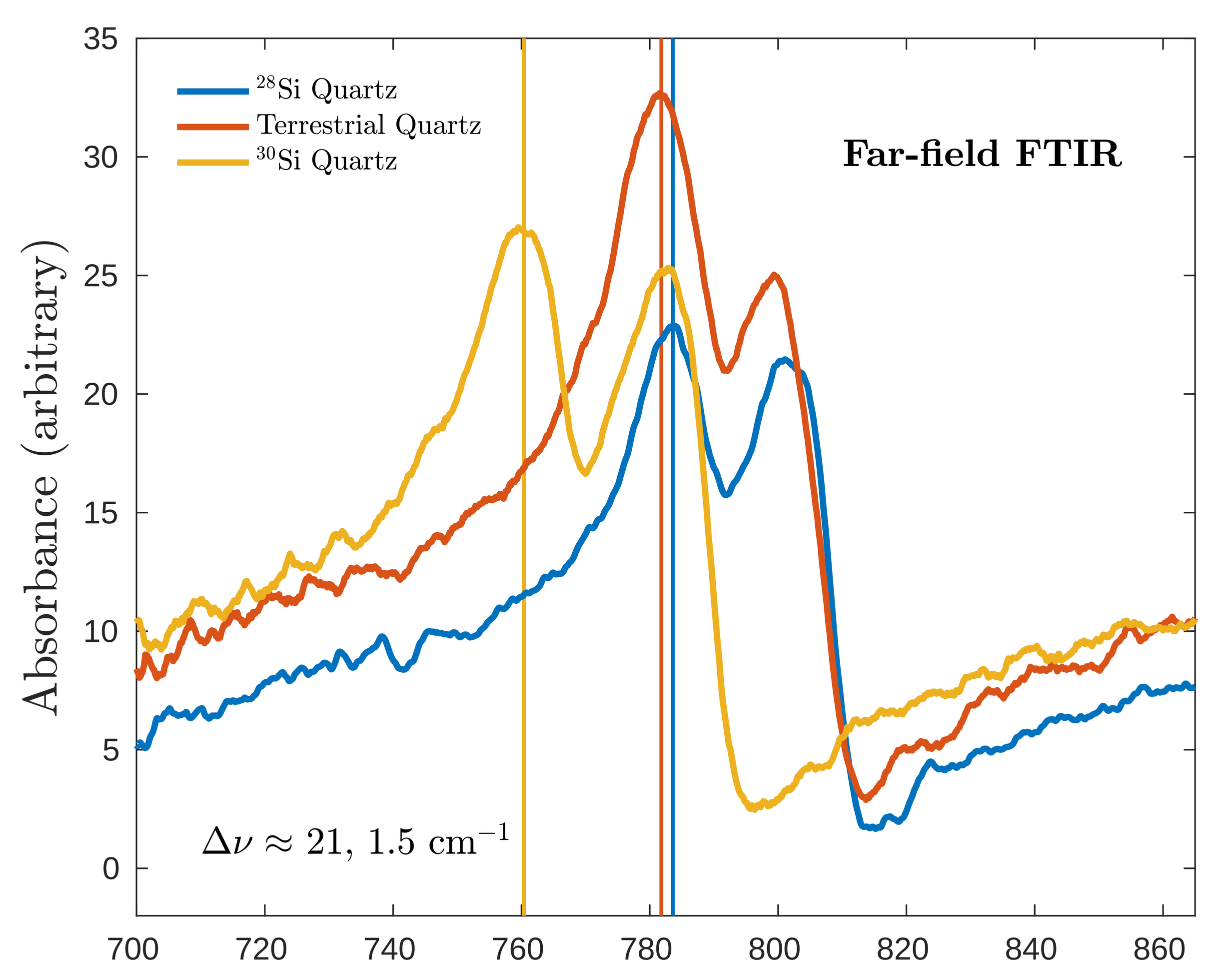
FTIR Spectroscopy

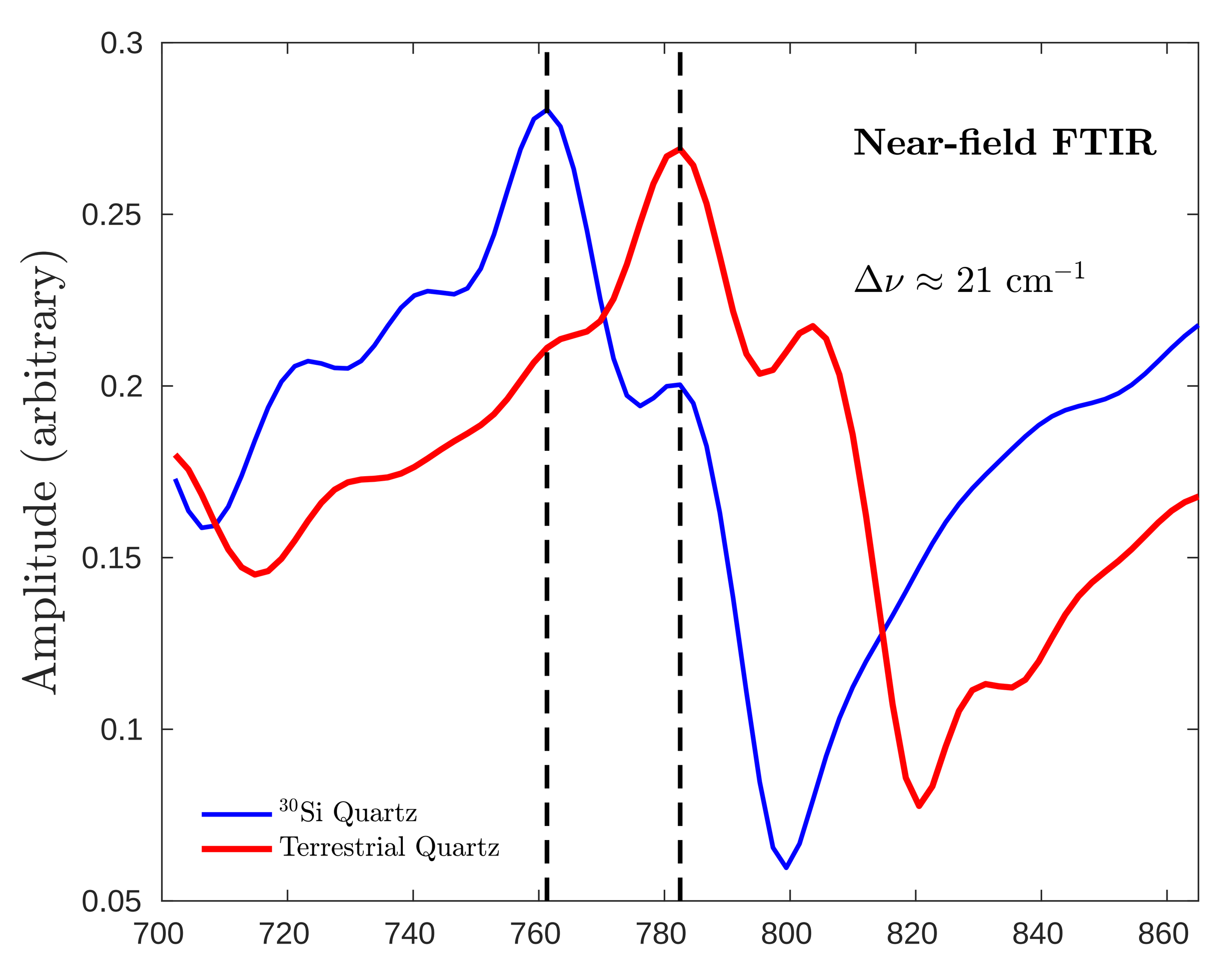
We measured the infrared reflectance spectra of the doped and undoped synthesized quartz using traditional (far-field) and near-field FTIR spectroscopy:

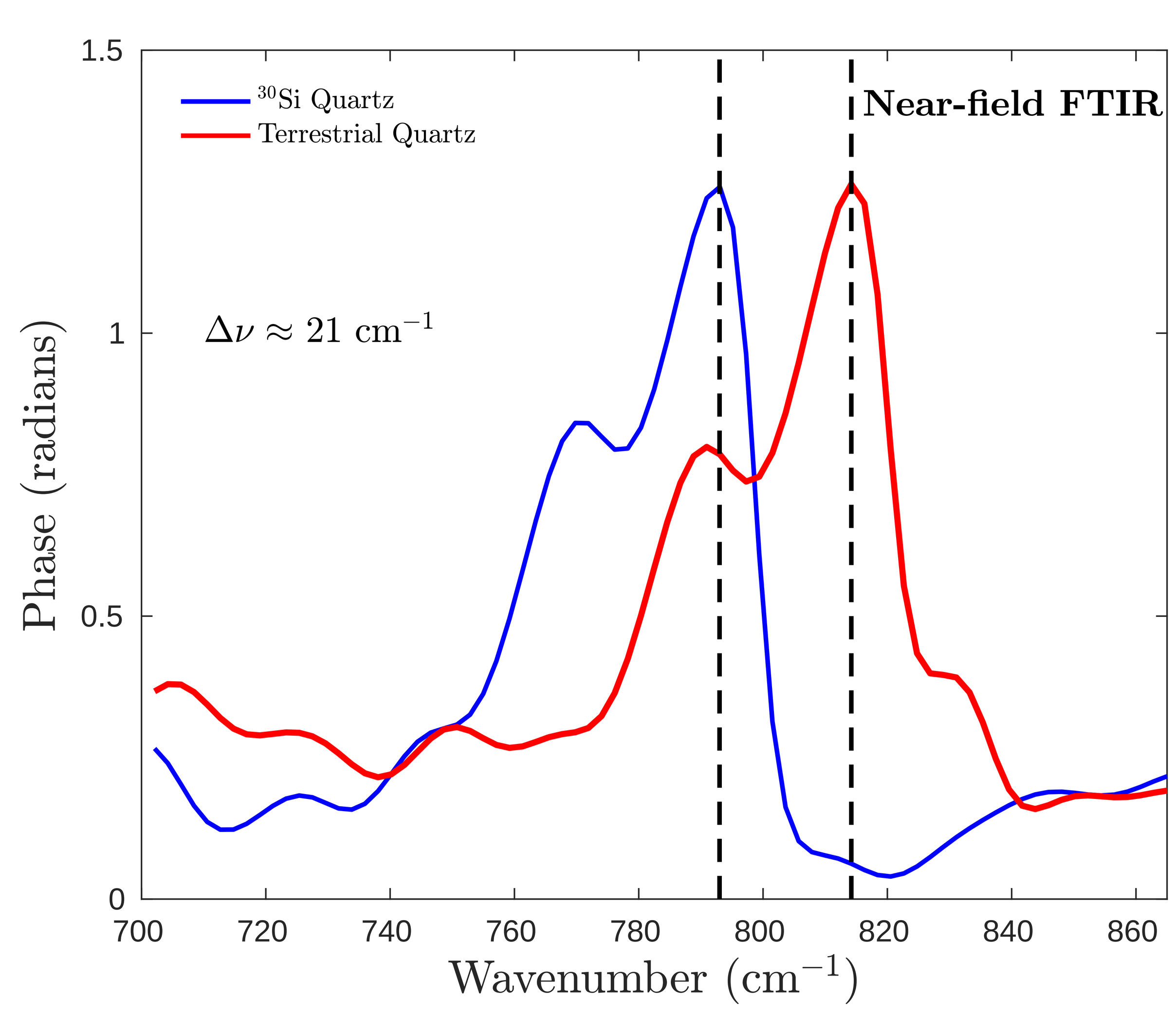
Far-field FTIR: Acquired with a Nicolet iS50 FT-IR (wit Nicolet continuum microscope attachment) at Southern Illinois University. The spectral range was 500–1500 cm^{-1} and spectra were collected for ∼10 minutes. Spot size diffraction limited to ∼10 μm.

Near-field FTIR: Acquired with a NeaSpec nano-FTIR from 700–1500 cm^{-1} for ∼10 minutes using a high-brightness laser light source. Spot size as small as AFM tip: 30 nm.

Results

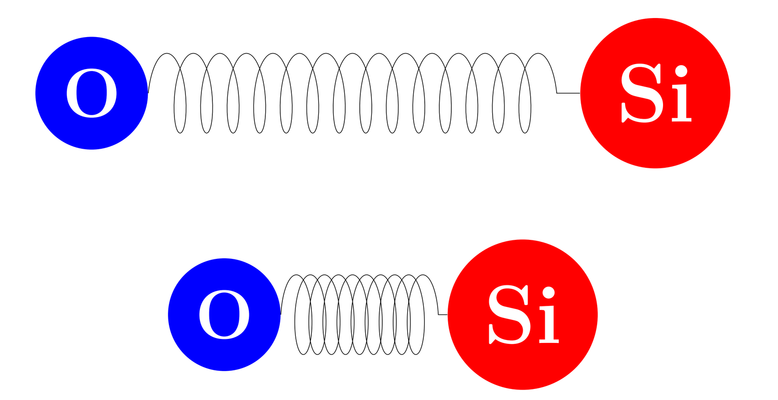






Discussion

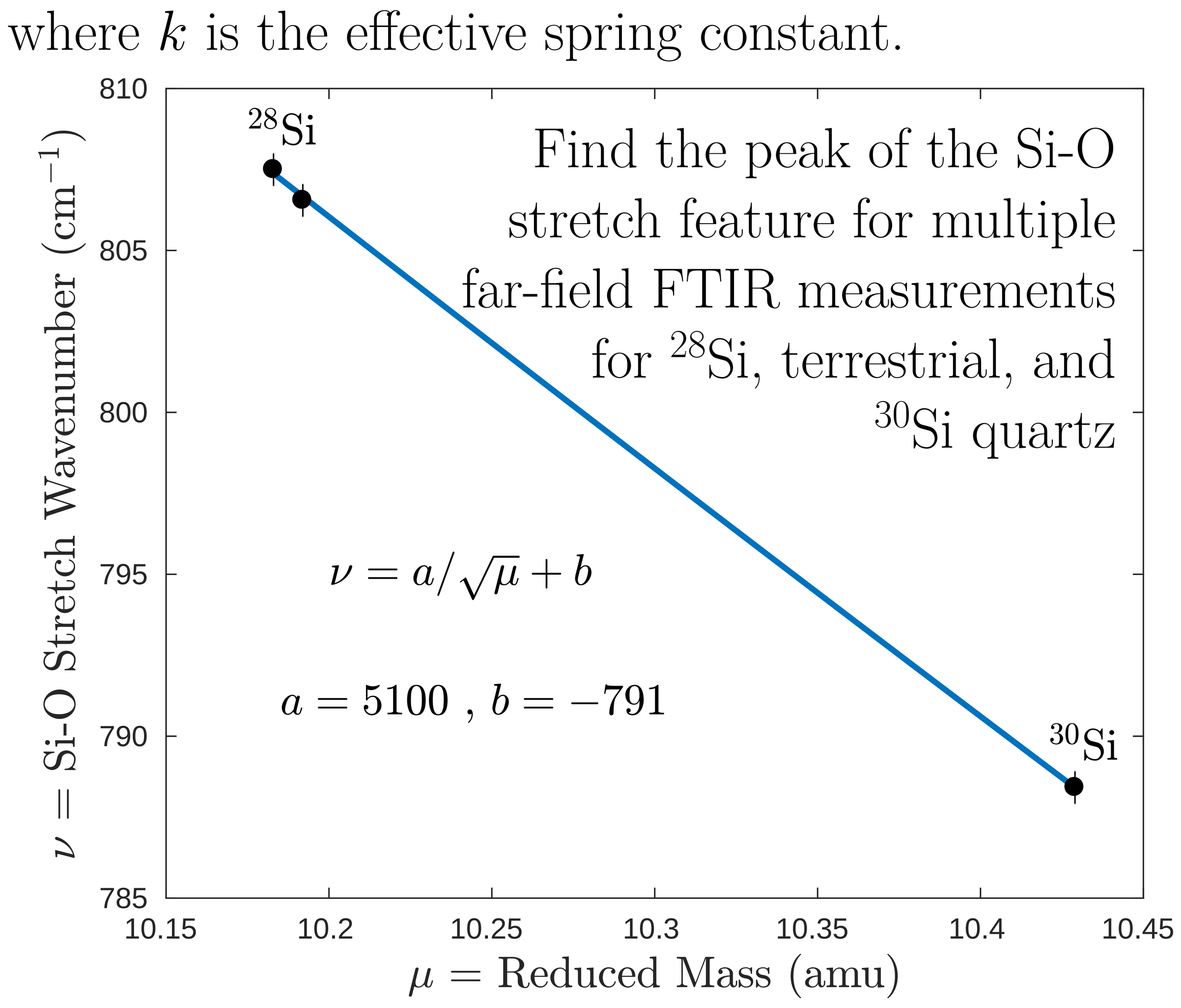
The vibrational frequency of an Si-O stretch feature in the IR spectrum of quartz can be modeled simply as two masses attached by a spring:



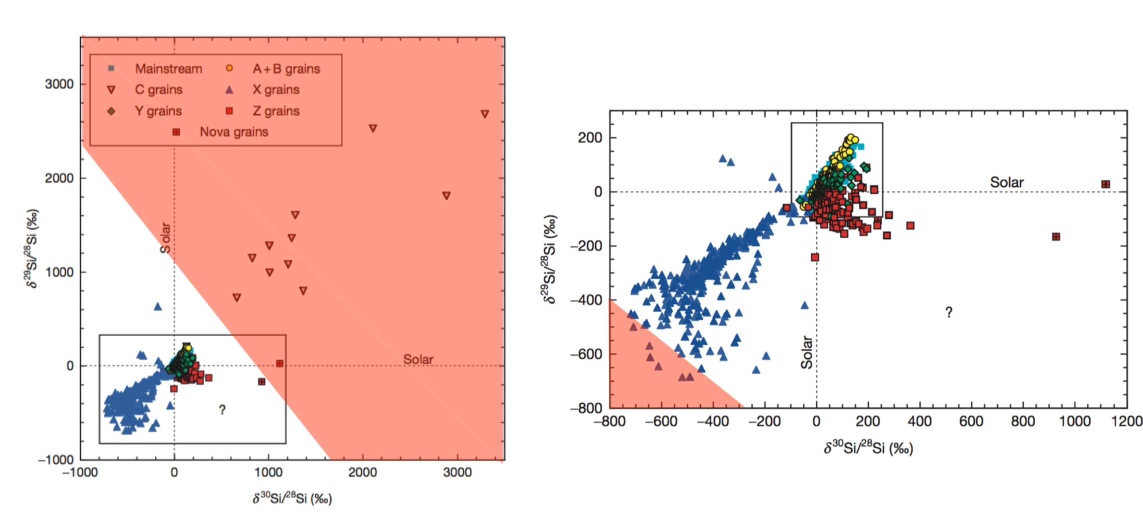
The separation between the two atoms undergoes oscillatory motion, with angular frequency ω given by:

$$\omega = \sqrt{\frac{k}{\mu}} \qquad \mu = \frac{m_{\mathrm{Si}} m_{\mathrm{O}}}{m_{\mathrm{Si}} + m_{\mathrm{O}}}$$

where k is the effective spring constant.



Conclusions



- Identifiable 2σ isotope anomalies in Si are shown above using our data from far-field FTIR, in context of presolar SiC grains
- Uncertainty in μ determination from FTIR is from determination of peak location of Si-O stretch feature (∼0.5 wavenumbers)
- Near-field spectra are (surprisingly!) less noisy, likely because of the extremely bright light source
- Additionally, the NeaSpec nano-FTIR collects phase information, which can *also* be leveraged to identify Si-O shifts due to isotope substitution
- Therefore, near-field FTIR detectable anomalies will be smaller than what is shown above!
- **The NeaSpec nano-FTIR has the potential to non-destructively identify crystalline presolar grains with a spot size of ∼30 nm**