

INFRARED SPECTROSCOPY FOR THE NON-DESTRUCTIVE IDENTIFICATION OF PRESOLAR GRAINS

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Introduction: Presolar grains can be crystalline or amorphous and are identified by their large isotope anomalies, often tens of percent different from isotope ratios in grains that formed in the Solar System. Supernova silica was recently discovered in meteorites [1] and has been observed to form in supernova remnants [2]. SiC presolar grains can be identified using a combination of Raman spectroscopy and SEM-EDX [3]. Here we demonstrate the use of infrared (IR) spectroscopy, both far-field and near-field, to identify isotope anomalies in quartz (SiO₂).

Experimental Methods: The goal of this study is to determine the minimum detectable Si isotope anomaly in quartz. We synthesized: 1) quartz of terrestrial isotopic composition using normal amorphous silica powder, and 2) quartz of nearly pure ³⁰Si using doped silica powder from Cambridge Isotope Laboratories.

We synthesized the isotopically doped and undoped quartz using a piston cylinder apparatus at the Experimental Studies of Planetary Materials lab at Wash U. To ensure that both the doped and undoped quartz crystals were created under identical conditions, we created an experimental graphite capsule with two cylindrical holes to hold the two different silica powders simultaneously without mixing (Figure 1).

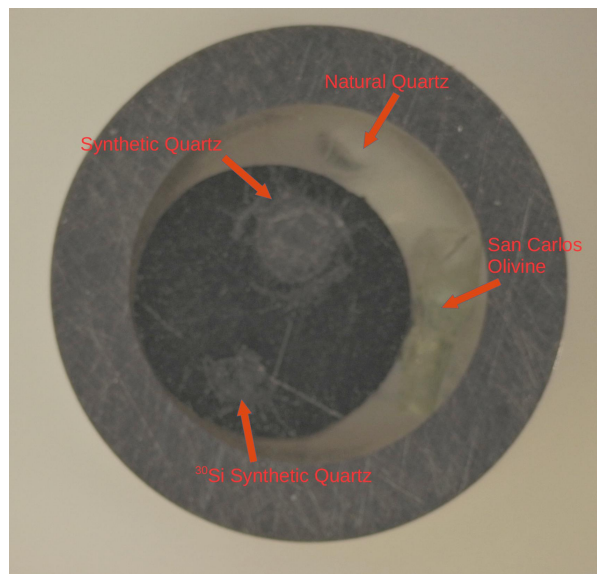


Figure 1: Experimental capsule mounted in a 1 cm Al annulus with epoxy and natural quartz and olivine standards.

The capsule with undoped and doped silica powders was heated in a 150-ton piston cylinder 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.

The sample was mounted in an Al annulus with epoxy and natural quartz and olivine, and then polished (Figure 1).

Analytical Methods: We acquired infrared spectra of the isotopically doped and undoped quartz grains by far-field micro-reflectance FTIR and also by near-field FTIR [4] with ~ 30 nm spatial resolution.

The far-field IR spectra were acquired with a Nicolet iS50 FT-IR (with a Nicolet continuum microscope attachment) at Southern Illinois University. The spectral range was 500–1500 cm⁻¹ and spectra were collected for ~ 10 minutes. Near-field IR spectra were acquired with a NeaSpec nano-FTIR from 700–1500 cm⁻¹.

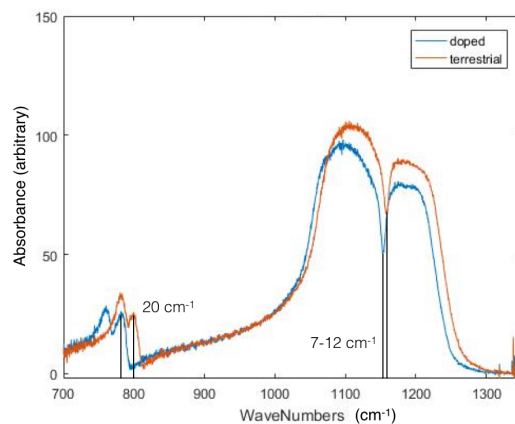


Figure 2: Far-field infrared reflectance spectra of doped (blue) and undoped (red) synthetic quartz grains using a Nicolet iS50 FT-IR.

Results: The far-field FTIR spectra showed significant differences between the doped and undoped quartz in the Si-O stretch features at ~ 780 cm⁻¹ and ~ 1160 cm⁻¹ (Figure 2). The undoped (terrestrial Si isotopic composition) quartz had a peak that was consistently 20 cm⁻¹ higher than the ³⁰Si-doped quartz for the ~ 780 cm⁻¹ Si-O stretch. The undoped quartz had a peak that was 7–12 cm⁻¹ higher, but more variable, than the ³⁰Si-doped quartz for the ~ 1160 cm⁻¹ Si-O stretch.

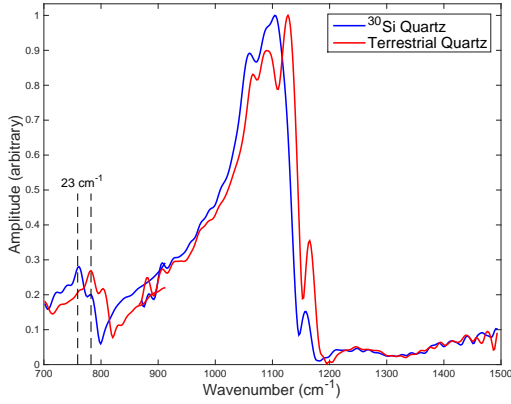


Figure 3: Near-field infrared reflectance spectra of doped (blue) and undoped (red) synthetic quartz using a NeaSpec nano-FTIR.

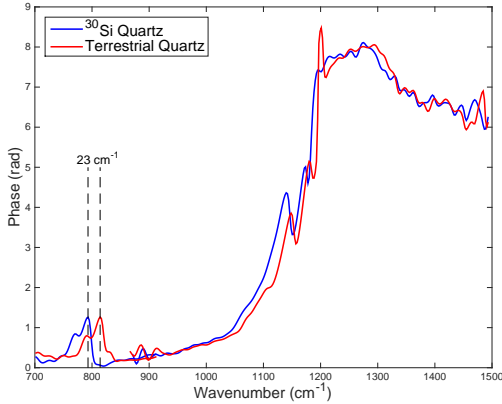


Figure 4: Near-field infrared phase spectra of doped (blue) and undoped (red) synthetic quartz using a NeaSpec nano-FTIR.

The near-field FTIR spectra showed a 23 cm^{-1} difference for the smaller wavenumber Si-O stretch in the reflectance spectrum, the larger wavenumber stretch was variable (Figure 3). The reflection spectrum is a measure of the imaginary component of the sample's complex refractive index. The NeaSpec nano-FTIR also (indirectly) measures the real component of the refractive index of the sample, the phase (Figure 4). The phase spectrum also showed a 23 cm^{-1} shift between the doped and undoped synthetic quartz.

Discussion: The vibrational frequency of the Si-O stretch is approximately equal to:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \mu = \frac{m_{\text{Si}}m_{\text{O}}}{m_{\text{Si}} + m_{\text{O}}} \quad (1)$$

where k is the effective spring constant of the Si-O bond and μ is the reduced mass of the the Si and O atoms. Changing the mass of the Si atom from 28.0855 amu to 30 amu changes the reduced mass, which changes the vibrational frequency of the Si-O stretch. We measured $\Delta\nu$: the change in vibrational frequency between $m_{\text{Si}} = 28.0855$ and $m_{\text{Si}} = 30$, and the uncertainty in $\Delta\nu$: $\sigma_{\Delta\nu}$, which we estimate from the standard deviation of repeated measurements of $\Delta\nu$ on different synthesized crystals. The magnitude of $\sigma_{\Delta\nu}$ depends on the uncertainty of finding the peak of the Si-O stretch feature and real variability of $\Delta\nu$ between measurements of different crystals (possibly due to crystal orientation, crystal defects, or instrumental artifacts).

From our estimate of $\sigma_{\Delta\nu}$ and Equation 1, we calculate σ_{μ} . Converting this value to δ units yields the minimum detectable $\delta^{30,29}\text{Si}$ anomaly using IR spectroscopy.

For the far-field FTIR measurements, we calculate a 1σ minimum detectable $\delta^{30,29}\text{Si}$ anomaly of $\sim 600\%$. This sensitivity is sufficient to detect the Si isotope anomalies seen in SiC grains of type C and some of the more isotopically anomalous SiC grains of type X [5]. The Si isotopic compositions of presolar silica grains from supernovae have not yet been measured.

The near-field FTIR spectra acquired with the NeaSpec nanoFTIR (Figures 3 and 4) show very low noise and may possibly yield a lower minimum detectable anomaly than the far-field measurements. More measurements must be acquired to estimate $\sigma_{\Delta\nu}$ from multiple near-field IR spectra of different crystals.

Conclusions: We have demonstrated that infrared spectroscopy can be used to non-destructively identify presolar grains. The traditional method of identifying presolar grains by secondary ion mass spectrometry consumes part of the grains and creates an ion-damaged layer that compromises structural analyses.

Presolar grains are present in meteorite matrices at the part-per-million levels, so it is not feasible to acquire 10-minute analyses on millions of sub- μm grains to identify supernova grains. A better approach would be to acquire point spectra at wavenumbers near the major Si-O stretch feature at $\sim 1100 \text{ cm}^{-1}$ (mineral identification) and also at a few wavenumbers around 800 cm^{-1} (to identify the isotope anomaly). This could be done with tunable quantum cascade lasers in the appropriate frequency range, which can be attached as modules on the NeaSpec nano-FTIR system.

References: [1] P. Haenecour, et al. (2013) *The Astrophysical Journal Letters* 768(1):L17. [2] J. Rho, et al. (2008) *The Astrophysical Journal* 673(1):271. [3] N. Liu, et al. (2016) *LPI Contributions* 1921:6094. [4] G. Dominguez, et al. (2014) *Nature Communications* 5:5445. [5] E. Zinner (2003) *Treatise on Geochemistry* 1:711.