Introduction: Transmission electron microscopy (TEM) studies of sub-μm presolar SiC grains showed that 3C-SiC is the dominant polytype (~80%) [1]. Although TEM is the most effective technique to determine the crystal structure and disorder, TEM is destructive and time-consuming, and may not be representative of the bulk sample. On the other hand, Raman spectrometry investigates matter at the scale of chemical bonds, and automatic Raman mapping allows a very representative view of a sample surface.

Previous Raman studies, however, mainly focused on SiC grains of usually large size (>3 μm) and did not study Raman peak shifts in detail [2,3] due to limited spatial and spectral resolutions (~1 μm and ~5 cm⁻¹, respectively). We previously reported use of a confocal imaging Raman microscope with much improved spatial and spectral resolutions (~400 nm and ~0.1 cm⁻¹, respectively) to investigate Raman spectral characteristics of μm to sub-μm sized presolar SiC grains [4]. However, our initial results were subsequently found to be severely affected by instrument calibration problems. Here, we have quantified the precision of our Raman measurements by bracketing presolar SiC grain measurements with an external Ne lamp. In addition, we report crystal structures and Raman peak shifts of presolar SiC grains that are classified by correlated C, N, and Si isotopic data.

Experimental Methods: The SiC grains in this study were extracted from the Murchison meteorite using the isolation method described in [5] and dispersed on two high purity Au mounts (mounts #1 and #3). Presolar SiC grains on mount #3 were first measured with the Carnegie NanoSIMS 50L ion microprobe for C, N, and Si isotopic compositions using a Cs⁺ beam and standard methods. Raman spectra were acquired later from the SiC grains with a WiTeC multifunction scanning probe microscope with a spatial resolution of ~400 nm, which includes near-field optical microscopy and confocal imaging Raman microscopy (532 nm frequency-doubled Nd:YAG laser). Spectral images were obtained in 13 ~60×80 μm areas on the mount #3, where each pixel contains a full Raman spectrum with ~0.1 Å cm⁻¹ spectral resolution. For mount #1, Raman spectra were acquired prior to the NanoSIMS analysis in 10 areas.

Results: We obtained correlated Raman and isotopic data on 48 SiC grains. One SiC grain that was analyzed with the Raman microscope could not be located during the NanoSIMS analysis and is therefore unidentified. The 49 grains range from 0.5 to 2 μm, so they are larger than the grains (Murchison KJB residue with mean diameter of 0.49 μm) analyzed by TEM [1].

Isotope Data: 35 of the measured grains were isotopically anomalous, indicating a presolar origin, while the remaining 13 grains had normal isotopic compositions, e.g., terrestrial δ⁴⁰N/³⁵N ratio. Two of the anomalous grains were determined to be of type Z, three to be of type AB, two to be of type X [e.g., 6]. As shown in Fig. 1, the C, N and Si isotopic compositions of the 48 presolar SiC grains agree well with the literature data [6], e.g., the 28 mainstream grains fall on a line of 

\[
\delta^{28}\text{Si} = (1.47±0.23)\times\delta^{29}\text{Si}+(-16±12)\ 
\]

in the Si three isotope plot.

Raman Data: Raman spectra were acquired on the 49 SiC grains over a period of one week. Although the Raman microscope itself is equipped with an internal Ne lamp to calibrate the multichannel Raman spectrometer, an external Ne lamp was used in our study to
monitor the long-term stability of the spectrometer. Surprisingly, we found that (1) the measured Raman peak positions of the Ne lamp differ from the reference values from ~1700 to ~3600 cm⁻¹ and the higher the wavelength, the smaller the offset; (2) the peak of the Nd:YAG laser beam is shifted to higher wavelength (~10 cm⁻¹). Thus, based on the Ne Raman spectral data, we recalibrated the multichannel spectrometer using the method given in [7] and found that the offset is a nonlinear function of wavelength, e.g., ~3 cm⁻¹ at 1700 cm⁻¹ and 2 cm⁻¹ at 800 cm⁻¹. The average of 23 Ne Raman spectra during the whole analysis period yields a spectral precision ranging from ±0.5 cm⁻¹ (strongest peak) to ±1.1 cm⁻¹ (weakest peak).

Raman TO peak positions of the 49 SiC grains are shown in Fig. 2. The Raman TO peak positions of 3C, 2H, 4H, and 6H SiC are at 797, 764, 776, and 789 cm⁻¹, respectively [8]. The average TO peak position of the 3C-SiC grains is 798.9 ± 1.3 cm⁻¹, and that of the 6H-SiC grains is 790.9 ± 1.3 cm⁻¹. The average values of both 3C and 6H TO peaks are therefore higher than the reference values, consistent with the offset (2 cm⁻¹) indicated by our recalibration using the Ne lamp.

Discussion: Figure 2 shows that with the exception of one mainstream and one unidentified grain, 6H-SiC grains all have terrestrial isotopic compositions, indicating that they are contamination. This agrees with the fact that 6H-SiC is the most common polytype for synthetic SiC grains in laboratory, and also that [1] did not observe any 6H grains in their study of presolar SiC [1]. Also, another three terrestrial SiC grains have TO peaks at much lower wavelengths, 779 and 782 cm⁻¹, indicating the 4H SiC structure.

In contrast, with one exception, all the other mainstream grains are 3C-SiC. The TO peaks of seven 3C-SiC grains are shifted ≥3σ away from the average, which are larger shifts than are seen for the Ne lamp and terrestrial SiC spectral data. In addition, the TO peak of the AB grain with the lowest ¹²C/¹³C ratio is among the highest (799 cm⁻¹). Therefore, in contrast to our preliminary study, C isotopic composition is not the dominant factor in causing such Raman peak shifts. A downshift of the phonon Raman bands was observed in disordered and amorphous SiC grains, e.g., ion-implanted SiC [9]. Moreover, [1] found that 1% of the KJB grains are highly disordered. Thus, crystal disorder is the most likely explanation for the downshift of the TO peak in some of the mainstream SiC grains. In addition, Raman images of several grains show that the TO peak at the edge is downshifted relative to the center, indicating amorphization or crystal disorder due to e.g., ion implantation [9]. Also, none of the TO peaks of our grains is lower than 770 cm⁻¹, indicating that the 2H-SiC abundance is less than 2% for 0.5–2 μm presolar SiC, ten times lower than the 2H fraction of smaller grains studied previously by [1].

Interestingly, one of the mainstream grains (A8-G26) has a needle-like shape, similar to the one reported in Fig. 12 of [10], which was determined to be of type 2H. However, A8-G26 peaks at 786 ± 3 cm⁻¹, and is therefore more likely to be 6H or 15R. We only measured half of the grain during the NanoSIMS analysis, and the other half is intact for TEM analysis, which will allow for a better characterization of its crystal structure.

Conclusions: We have demonstrated the high spectral resolution and long-term stability of the Raman microscope used in this study. It can be concluded that (1) SiC grains with terrestrial isotopic compositions have 6H and 4H hexagonal crystal structures, indicating terrestrial contamination; (2) most of the mainstream, Z, and AB grains have 3C cubic crystal structure; (3) peak shifts are found in some of the 3C-SiC grains, which are likely caused by crystal disorder and amorphization; (4) The TO peaks of both X grains in our study are shifted to much lower wavelengths, and are likely to be hexagonal polytypes. TEM analysis of both grains is needed to definitively determine their structures [10].