

**CORRELATION BETWEEN RAMAN PEAK SHIFTS AND ISOTOPIC COMPOSITIONS OF SUB-MICRON PRESOLAR SiC GRAINS.** N. Liu<sup>1</sup>, A. Steele<sup>2</sup>, L. R. Nittler<sup>1</sup> and C. M. O'D. Alexander<sup>1</sup> <sup>1</sup>Department of Terrestrial Magnetism, Carnegie Institution of Washington, Washington, DC 20015, USA (Email: [nliu@carnegiescience.edu](mailto:nliu@carnegiescience.edu)); <sup>2</sup>Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, USA.

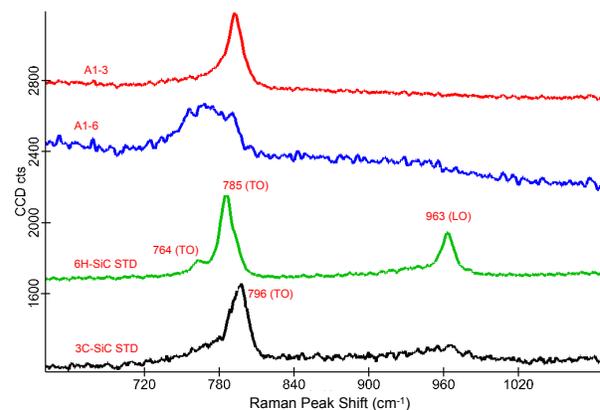
**Introduction:** Silicon carbide is a particularly interesting phase because more than a hundred different polytypes can be formed in the laboratory. The formation of these polytypes depends strongly on growth conditions (*e.g.*, temperature, pressure). Daulton et al. [1] used TEM to study the microstructures of ~500 presolar SiC grains in an acid residue of the Murchison meteorite (KJB fraction of [2], mean diameter of 0.49  $\mu\text{m}$ ). They found that cubic SiC ( $\beta$ -SiC) is the dominant polytype for presolar SiCs (~80%). Previous Raman studies of large SiC grains (>3  $\mu\text{m}$ ) showed that Raman spectra can be diagnostic for distinguishing between non-cubic (hexagonal or rhombohedral,  $\alpha$ -SiC) and cubic SiC structures [3,4]. However, the grains in the previous Raman studies were of unusually large size and it is therefore of interest to study the SiC microstructural distributions in smaller, more typical size fractions with Raman microscopy. Furthermore, Ivanov et al. [5] showed that the Raman peak positions of synthetic isotope-enriched SiCs are shifted with respect to those of the same polytype but with normal isotope ratios. It is therefore intriguing to investigate whether Raman peak positions correlate with the corresponding C and Si isotope ratios in presolar SiCs, which could potentially provide a new, non-destructive, method to find rare type SiC grains with extremely anomalous C and/or Si isotope ratios (*e.g.*, highly <sup>13</sup>C-enriched A+B grains [6]).

**Samples and Methods:** The SiC grains in this study were extracted from the Murchison meteorite using the isolation method described in [7] and dispersed on a high purity Au mount. Raman spectra were acquired first with a WiTeC multi-function scanning probe microscope, which includes near-field optical microscopy and confocal imaging Raman microscopy (532 nm frequency-doubled Nd:YAG laser). Its typical spatial resolution is ~400 nm at low power. Spectral images were obtained in four areas on the presolar SiC mount (each area ~50  $\times$  50  $\mu\text{m}$ ), where each pixel contains a full Raman spectrum (~0.1  $\Delta \text{cm}^{-1}$  spectral resolution). After Raman measurements, we further verified the chemical compositions of Raman-identified SiC grains by EDS analysis with a JEOL 6500F field-emission SEM. High-resolution Raman spectra were then acquired on single SiC grains for comparison with previous Raman scanning spectra to see if SiC Raman

peaks are shifted due to the electron beam damage. Finally, the C, N and Si isotopic compositions of these SiC grains were simultaneously measured with the Carnegie NanoSIMS 50L ion microprobe using a Cs<sup>+</sup> beam and standard methods.

**Results:** We performed Raman and isotopic measurements on 30 presolar SiC grains. The grain sizes range from 0.2 to 2.2  $\mu\text{m}$  (mean ~0.8  $\mu\text{m}$ ), which is similar to the size distribution of the KJD fraction of [2] (mean 0.81  $\mu\text{m}$ ). We succeeded in obtaining correlated data for 13 mainstream SiC grains. The C, N and Si isotopic compositions of the 30 presolar SiC grains are in good agreement with the literature data [8]. We did not see any evidence of peak shifts due to electron beam damage arising from the EDS analysis. Two of the 13 grains are hexagonal and the remainder are all cubic. This is consistent with the SiC microstructural distribution found in [1]. All the Raman and isotopic data are summarized in Table 1.

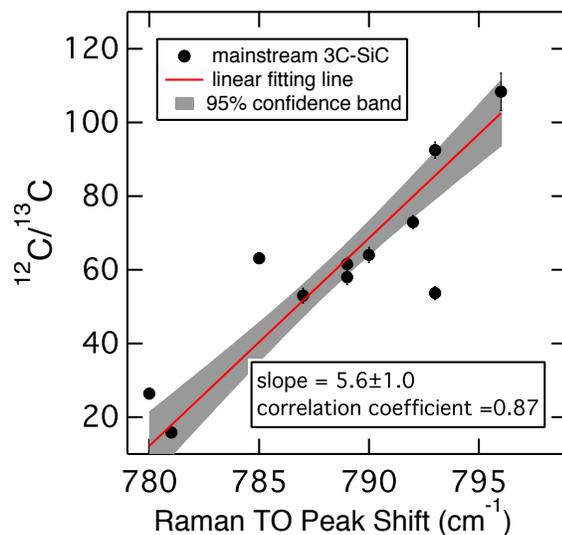
Figure 1 shows high-resolution Raman spectra of one 6H- and one 3C-SiC standard, and two presolar grains. The  $\beta$ -SiC (*e.g.*, 3C) has two first-order Raman active phonon modes, a TO mode at 796  $\text{cm}^{-1}$  and an LO mode at 972  $\text{cm}^{-1}$ . The LO mode is absent in the 3C-SiC STD spectrum, probably due to the crystal orientation. In contrast, the TO mode of the  $\alpha$ -SiC (*e.g.*, 4H, 6H) splits into several modes. For instance, in Figure 1, the 6H-SiC standard has two TO modes at 764 and 785  $\text{cm}^{-1}$  [9]. Thus, different SiC polytypes can be easily distinguished based on their Raman spectra.



**Figure 1.** Raman spectra of standards (bottom two traces) and presolar SiC grains (top two traces).

**Table 1.** Raman TO peak shifts and isotopic compositions of C, N and Si (1 $\sigma$  errors) for presolar SiC grains

Grain	Size ( $\mu\text{m}$ )	TO Peak ( $\text{cm}^{-1}$ )	Type	$^{12}\text{C}/^{13}\text{C}$	$^{14}\text{N}/^{15}\text{N}$	$\delta(^{29}\text{Si}/^{28}\text{Si})$ (‰)	$\delta(^{30}\text{Si}/^{28}\text{Si})$ (‰)
A1 1	1.0	776, 795	4H	46 $\pm$ 2	2673 $\pm$ 447	-33 $\pm$ 11	-21 $\pm$ 13
A1 2	0.2	796	3C	108 $\pm$ 5	1827 $\pm$ 457	238 $\pm$ 133	64 $\pm$ 146
A1 3	1.4	793	3C	54 $\pm$ 2	1684 $\pm$ 148	86 $\pm$ 3	93 $\pm$ 4
A1 4	0.8	793	3C	93 $\pm$ 2	913 $\pm$ 119	9 $\pm$ 25	-2.1 $\pm$ 30
A1 5	0.5	792	3C	73 $\pm$ 2	1344 $\pm$ 56	42 $\pm$ 9	66 $\pm$ 10
A1 6	0.6	766,782	6H	60 $\pm$ 2	2588 $\pm$ 199	9.3 $\pm$ 14	8.0 $\pm$ 16
A1 7	0.9	789	3C	62 $\pm$ 2	674 $\pm$ 25	23 $\pm$ 10	13 $\pm$ 12
A2 1	0.9	780	3C	26.4 $\pm$ 0.1	586 $\pm$ 14	52 $\pm$ 7	42 $\pm$ 8
A2 3	0.6	781	3C	15.8 $\pm$ 0.1	717 $\pm$ 21	1 $\pm$ 13	23 $\pm$ 16
A2 4	0.5	785	3C	63.1 $\pm$ 0.5	1579 $\pm$ 100	52 $\pm$ 8	35 $\pm$ 9
A3 2	1.2	787	3C	53 $\pm$ 2	1408 $\pm$ 100	119 $\pm$ 8	72 $\pm$ 9
A4 2	2.2	790	3C	64 $\pm$ 2.1	460 $\pm$ 9	47 $\pm$ 4	28 $\pm$ 4
A4 3	1.0	789	3C	58 $\pm$ 2	423 $\pm$ 8	21 $\pm$ 4	12 $\pm$ 5

**Figure 2.** Plot of  $^{12}\text{C}/^{13}\text{C}$  ratios versus Raman TO phonon peak shifts in 11 mainstream 3C-SiCs.

**Discussion:** Table 1 shows that the 796  $\text{cm}^{-1}$  TO phonon peak is shifted to varying degrees in the 11 3C-SiC grains. The Raman peak position is sensitive to polytype variety, disorder, stress and density of charge carriers. As C and Si are the major components of the mineral SiC, rare isotopes ( $^{13}\text{C}$ ,  $^{29}\text{Si}$ ,  $^{30}\text{Si}$ ) may be considered as isomorphous impurities to cause possible peak shifts. Ivanov et al. [5] recently reported shifts of up to 20  $\text{cm}^{-1}$  in Raman peak positions for  $^{13}\text{C}$ -enriched 4H-SiC samples ( $^{12}\text{C}/^{13}\text{C}=1$ ). Thus, we compared the TO peak shifts of the 11 3C-SiCs with their corresponding  $^{12}\text{C}/^{13}\text{C}$  ratios in Figure 2. Clearly, there exists a positive correlation between the  $^{12}\text{C}/^{13}\text{C}$  ratio and the Raman TO peak shift, with eight of the 11 grains (~70%) falling within the 95% confidence bands for the fitting line. This indicates that the Raman peak shift of main-

stream SiC grains is mainly caused by the isotope effect. However, the peak shifts of two grains with  $^{12}\text{C}/^{13}\text{C}$  ratios of ~60 do not follow the linear correlation. Their Raman shifts, therefore, could be dominantly caused by other effects, e.g., crystal impurities (varying trace element abundances).

No correlation is observed between the peak shift and the N or Si isotopic compositions because (1) N is present in presolar SiCs as a trace element, and (2) the Si isotope ratios in mainstream SiC grains are within  $\pm 200\%$ , which is two orders of magnitude lower than the corresponding C isotope variation. Therefore, in most cases, Raman peak shifts appear to be dominated by the C isotope variations in mainstream SiC grains.

**Conclusion:** This work demonstrates a clear correlation between Raman spectra and C-isotopic composition for sub- $\mu\text{m}$  to  $\mu\text{m}$ -sized presolar SiC grains, indicating that Raman microscopy should be useful for searching for rare types of grains. Raman microscopy is relatively easy and less time-consuming than NanoSIMS analysis and since it is non-destructive, it can also preserve grains for destructive analysis with other instruments (e.g., heavy element isotope measurements by CHILI [10]) to better understand their stellar origins. Additional correlated measurements will be done to better characterize the relationship between isotopic composition and Raman spectra of presolar SiC.

**References:** [1] Daulton T. L. (2003) *GCA*, 67, 4743–4767. [2] Amari et al. (1994) *GCA* 58, 459-470. [3] Virag A. et al. (1992) *GCA*, 56, 1715-1733. [4] Wopenka B. (2010) *LPS XLI*, Abstract#1390. [5] Ivanov et al. (2014) *Mater. Sci. Forum* 778-780, 471-474. [6] Amari et al. (2001) *ApJ* 559, 463-483. [7] Alexander C. M. O'D. & Nittler (1999) *ApJ* 519, 222-235. [8] Zinner (2014) *Treatise on Geochemistry I*, 181-213. [9] Zhang et al. (1992) *J. Appl. Phys.* 72, 4469-4471. [10] Stephan et al. (2014) *LPS XLV*, Abstract#2242.