

HETEROGENEOUS DISTRIBUTIONS OF C, N, AND O ISOTOPES AND RAMAN SIGNATURES IN LOW-DENSITY SUPERNOVA GRAPHITE GRAINS FROM ORGUEIL. E. Groopman¹, B. Wopenka², T. Bernatowicz¹, and E. Zinner¹, ¹Physics Dept. and ²Earth and Planetary Sciences, Washington University in Saint Louis. eegroopm@physics.wustl.edu

Introduction: We report on ongoing correlated NanoSIMS, TEM, Raman, and XANES studies of low-density presolar graphites. Three low-density graphite grains (G17, G18, G24) from the Orgueil OR1d size/density fraction ($\rho=1.75\text{-}1.92\text{ g cm}^{-3}$, $>1\mu\text{m}$) [1] were selected based upon their isotopic and Raman signatures [2,3]. The grains range in size from 12 to $18\mu\text{m}$. The grains' isotopic compositions, with excesses in ^{18}O , ^{15}N , and ^{28}Si and the inferred presence of ^{26}Al and ^{44}Ti indicate supernova [SN] origins. Grains G17 and G18 have high $^{12}\text{C}/^{13}\text{C}$ ratios of 306 and 121, while G24 has a low ratio of 13 (solar = 89). Isotopic imaging on the whole grains indicated heterogeneities in the C, N, and O isotopic ratios. These grains were embedded in LR white hard resin and ultramicrotomed into 70nm -thick sections. Slices of each grain were deposited on Si wafers and Cu TEM grids, both SiO and holey-C coated. For the slices on Si wafers, Raman microprobe spectra with 532nm excitation and $\sim 1\mu\text{m}$ resolution were obtained on 12 sections of two of the grains (G17, G18). Isotope images in $^{12,13}\text{C}$, $^{14,15}\text{N}$, $^{16,18}\text{O}$, and $^{28,29,30}\text{Si}$ were obtained with the NanoSIMS, with the resin and Si wafer as standards. Due to the large size of the grains, many of the slices contain holes from microtoming; in Figs. 1-3 these areas are colored dark grey.

Results: Multiple slices of grains G17 and G18 contain highly anomalous and spatially correlated hotspots in both $\delta^{18}\text{O}/^{16}\text{O}$ and $\delta^{15}\text{N}/^{14}\text{N}$ [Fig. 1c,d]. Deviations from solar values in the hotspots range up to 5200% in ^{18}O and 2090% in ^{15}N , 4-24 times higher than in the rest of the grain. No corresponding increases in $^{16}\text{O}^-$ and $^{12}\text{C}^{14}\text{N}^-$ intensities at these

hotspots were seen. This is the first observation of spatially correlated hotspots of ^{18}O and ^{15}N without corresponding increases in $^{16}\text{O}^-$ and $^{12}\text{C}^{14}\text{N}^-$.

These grains were also found to have heterogeneously distributed C isotopic ratios, with their centers being more anomalous than their outer regions. G24 and G18 exhibit smooth gradients in $^{12}\text{C}/^{13}\text{C}$ from their centers to edges with ratios ranging from 8.5 to 14 and 125 to 132, respectively [Fig. 2]. G17 is more heterogeneous, containing much larger variations in $^{12}\text{C}/^{13}\text{C}$, from 450 to 1291, with the largest anomalies occurring in hotspots close to the center of the grain [Fig. 3].

Raman spectra obtained on μm -sized spots of all analyzed sections show intense narrow first- and second-order peaks, characteristic for crystalline and/or glassy sp^2 -bonded carbon. From the Raman perspective, G18 appears quite homogenous, with most of the spots having the same type of spectrum that has been found on the surface of the whole grain ($D>G$); only the center of each G18 section has a different Raman signature with $D<G$, an indication of better crystallinity/order of the sp^2 -bonded carbon. G17, however, appears to be much more inhomogeneous, because D/G band intensity ratios from different areas of the sections show distinct differences. Whereas most of the spots in the inner regions of the analyzed sections have spectra similar to what is referred to as "glassy carbon" in the Raman literature with $D>G$, an area that appears as a "black knob" in the reflected light images (and is at the same location as the $^{18}\text{O}/^{16}\text{O}$ hotspot found in the sections [Fig. 1c]) has spectra with $D<G$ [Fig. 4], similar to those found on the surface of the whole grain.

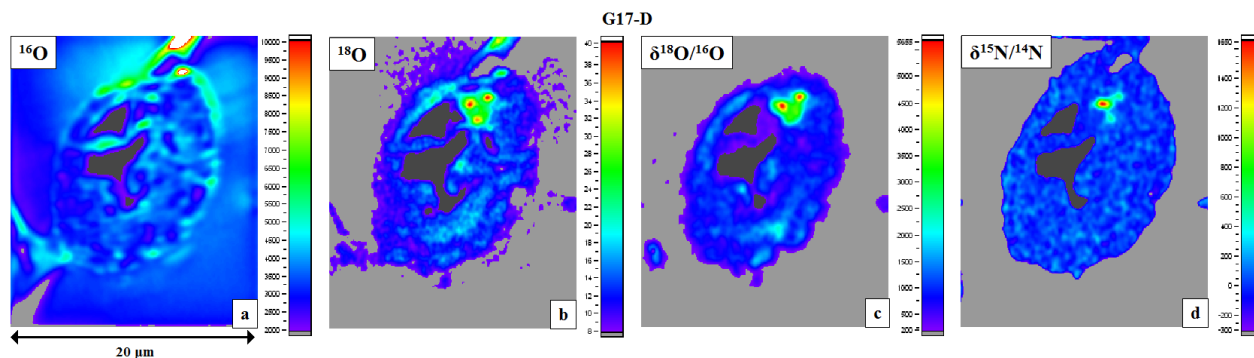


Figure 1: Isotopic images and derived ratio images obtained on microtome slice D of grains G17. δ -values in permil.

Discussion: We have found evidence for heterogeneities in the C, N, and O isotopic compositions of three low-density graphite grains. These grains contain excesses of ^{18}O and ^{15}N , evidence of SN origins; however they also contain hotspots that are much more anomalous. Subgrains provide one possible explanation for the heterogeneity; preliminary TEM/EDXS studies on other slices of G17 and G18 have confirmed the presence of Ti-rich subgrains. Previous NanoSIMS studies of microtomed slices of a SN graphite found that internal TiC subgrains have much larger ^{18}O excesses than the parent grain [4]. However, $^{16}\text{O}^-$ signals associated with these internal TiCs are much higher than those in the parent grain, though it has not been clear whether this is due to higher O content or whether TiC causes a higher yield of O^- . In the present study, we do not observe corresponding increases in $^{16}\text{O}^-$ in the anomalous hotspots. Combined with the spatially correlated presence of excess ^{15}N without $^{12}\text{C}^{14}\text{N}^-$ increases, these data suggest that the grains may have occluded small pieces from the He/C zone that have large ^{18}O and ^{15}N excesses, while the bulk of the grain formed from material that was mixed with other zones, yielding more modest ^{18}O and ^{15}N excesses. The high $^{12}\text{C}/^{13}\text{C}$ ratios of G17 and G18 also indicate contribution from the He/C zone, which has a C isotopic composition that is nearly pure ^{12}C . We plan to use the Auger Nanoprobe to obtain elemental maps of these hotspots to determine whether subgrains are the carriers of these anomalies.

Previous studies have also found radial gradients in the C and O isotopic compositions of graphites and have suggested isotopic equilibration with the environment as a possible explanation [4]. However, it is hard to justify such an explanation for the C isotopic gradients and heterogeneities that we observe, because the grains consist primarily of C. More likely are isotopic changes in the grains' formation environments during grain condensation, although these changes and mixing would have to occur on the time-scale of the grains' formation.

The relative ratios of the D and G band intensities from numerous areas of the slices show small variations across the interiors of the grains, indicating variations in the crystallinity of the grains, with G18 being more homogeneous than G17. Most spectra of low density grains have $\text{D}>\text{G}$ (a distinctive Raman feature of "glassy carbon"), while most high density grains have $\text{D}<\text{G}$, i.e., they are more crystalline and are considered graphitic from the Raman point of view [5]. Future TEM work will allow us to directly determine the average size of nanocrystalline regions

within the grains and to use this information to obtain a quantitative understanding of the Raman D/G band intensity ratios.

References: [1] Jadhav, M. et al. (2006) *New Astron. Rev.*, 50, 591-595. [2] Groopman, E. et al. (2011) *Meteorit. Planet. Sci.* 46, A82. [3] Wopenka, B. et al. (2011) *Meteorit. Planet. Sci.* 46, A252 [4] Stadermann, F.J. et al. (2005) *Geochimica et Cosmochimica Acta*, 69, 177-188. [5] Wopenka, B. et al. (2011) *Lunar Planet. Sci. XLII*, Abstract #1162.

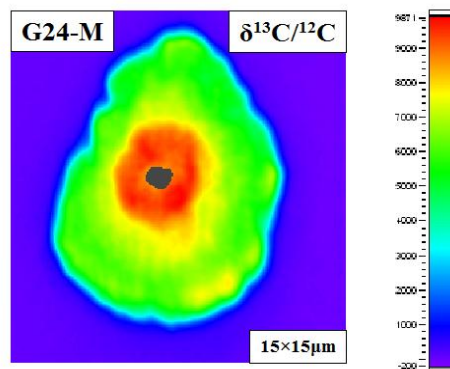


Figure 2: Isotope delta image showing radial gradient in C isotopic composition in slice G24-M.

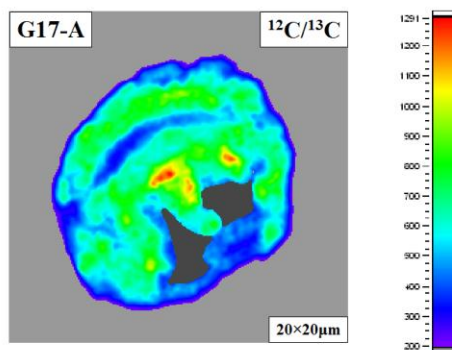


Figure 3: Isotope ratio image showing heterogeneous distribution of C isotopic hotspots from slice G17-A.

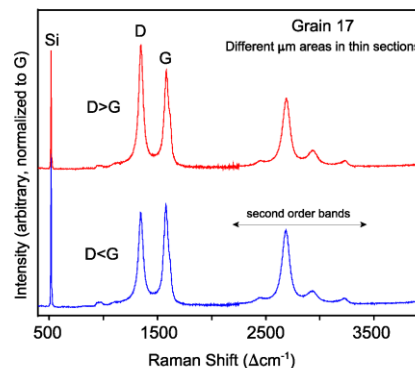


Figure 4: Examples of Raman spectra of grain G17 demonstrating heterogeneity in sp^2 carbon bonding.