NANOSIMS ISOTOPIC MEASUREMENTS OF INDIVIDUAL TiC CRYSTALS IN A SINGLE PRESOLAR GRAPHITE GRAIN. F. J. Stadermann, T. Bernatowicz, T. K. Croat, E. Zinner, S. Messenger and S. Amari, Laboratory for Space Sciences and Physics Department, Washington University, St. Louis, MO 63130-4899, USA.

A detailed TEM study of a large (12 μm) supernova graphite spherule (KE3e#10) from the Murchison (CM2) density separate KE3 found numerous internal TiC crystals [1]. These sub-grains range in diameter from 30 to 500 nm and appear to predate the formation of the graphite spherule into which they were incorporated during its growth. We previously reported on NanoSIMS measurements of the C and O isotopic gradients within this graphite spherule [2] and have now extended this study to isotopic measurements of individual internal TiC crystals.

These measurements were made directly in 70 nm thick ultramicrotome sections on TEM grids as described earlier [2]. The lateral resolution of the NanoSIMS in the acquired images is around 100 nm, which is sufficient to distinguish structures at the size range of the TiC grains whose average diameter is 200 nm. In most cases, the location of the sub-grains was first determined from the TEM images and then located in the NanoSIMS images of the same sections during data processing. Some of the NanoSIMS measurements, however, were performed on TEM sections that were directly located on top of one of the Cu bars of the TEM grid. This additional mechanical sample support allowed significantly longer isotopic measurements which resulted in improved secondary ion counting statistics. Even without the correlated TEM images, it was possible to locate individual internal TiC crystals directly in the NanoSIMS images by their high initial O secondary ion signal [2] and then to determine their isotopic compositions.

The C isotopic ratios of all the measured internal TiC grains are indistinguishable from that of the surrounding graphite. This could be due to the overwhelming C signal from the neighboring graphite which may significantly 'dilute' the C isotopic ratios of the TiC. The O isotopic compositions of the TiC crystals, however, are distinct from that of the surrounding material. The sub-grains are significantly enriched in ^{18}O but have close to terrestrial $^{16}O/^{17}O$ ratios. The most ^{18}O-enriched TiC sub-grain within this graphite spherule has a $^{16}O/^{18}O$ ratio of 14 compared to the bulk ratio of 174 in the graphite and the terrestrial ratio of 499. The O isotopic compositions of the TiC crystals from within this single presolar graphite spherule vary over a large range ($^{16}O/^{18}O$ ratios between 14 and 250), but they overlap the range observed in measurements of the bulk compositions of supernova graphites [3]. The large range of O isotopic compositions of TiC grains within a single graphite spherule confirms previous assumptions that they formed earlier than the graphite in the supernova ejecta and were mixed into the gas from which the graphite spherule formed. We are currently working on extending this isotopic study to other elements such as N and Ti.

References: [1] Croat T. K. et al (2002) *Lunar Planet Sci.* XXXIII #1315. [2] Stadermann F. J. et al. (2002) *Lunar Planet Sci.* XXXIII #1796. [3] Amari et al. (1996) *Ap. J.* 470, L101.