

TITANIUM AND OXYGEN ISOTOPIC COMPOSITIONS OF SUB-MICROMETER TiC CRYSTALS WITHIN PRESOLAR GRAPHITE. F. J. Stadermann, T. Bernatowicz, T. K. Croat, E. Zinner, S. Messenger and S. Amari, Laboratory for Space Sciences and Department of Physics, CB 1105, Washington University, 1 Brookings Drive, St. Louis, MO 63130-4899, USA (fjs@wuphys.wustl.edu)

Introduction: Low-density presolar graphite spherules from the Murchison (CM2) density separate KE3 were found to contain large numbers of internal TiC crystals which range in size from 30 to 500 nm [1]. We have studied one such graphite grain in great detail by successive analyses with SEM, ims3f SIMS, TEM and NanoSIMS [1 - 3]. The NanoSIMS measurements indicated C and O isotopic gradients from center to rim of the grain and showed variations of O isotopic compositions among the internal TiC crystals that are distinct from those of the surrounding graphite matrix. The results of the O isotopic measurements are summarized in Figure 1. We have now extended this NanoSIMS study to the measurement of all 5 Ti isotopes in individual TiC subgrains.

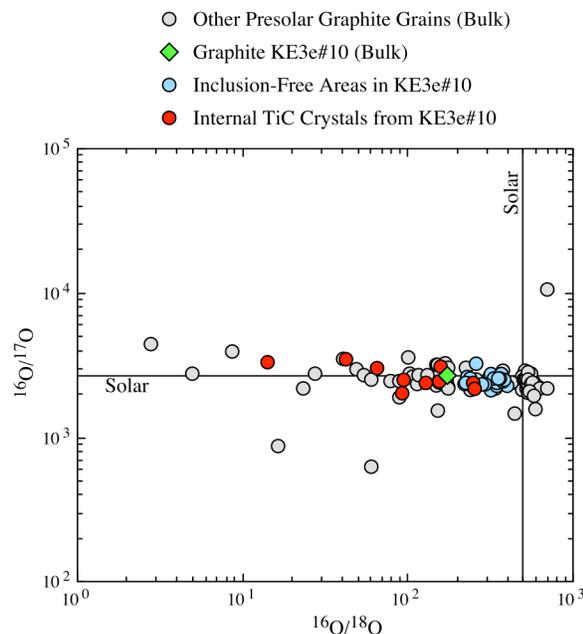


Figure 1. Three-isotope plot of the oxygen isotopic compositions of components of KE3e#10 and of other presolar graphite grains for comparison. The bulk value for KE3e#10 falls right in the middle of the distribution measured in other presolar graphites, making it a 'typical' graphite spherule with respect to its oxygen isotopic composition. A closer look at the isotopic compositions of the subcomponents reveals that the inclusion-free areas of the graphite are closer to the solar value while the internal TiC crystals have much larger ^{18}O excesses.

Experimental: All data presented here are from the large (12 μm) presolar graphite spherule KE3e#10. The supernova origin of this particle has been estab-

lished by its bulk isotopic composition, which was measured with the ims3f ion microprobe [4]. The graphite grain was then embedded in resin and sliced with the ultramicrotome into 70 nm thick slices. The ensuing TEM study of 37 slices found many internal TiC grains with an average diameter of 200 nm [1]. For NanoSIMS analysis, the TEM grids containing the slices were mounted on a flat surface, without any further modifications. The isotopic ratios of C and O were measured with a Cs^+ primary ion beam in multi-collection raster imaging mode [2, 3]. The lateral resolution of the Cs^+ beam during these measurements was around 100 nm, which is routinely achieved in the NanoSIMS.

We selected two previously analyzed TEM sections containing a total of three TiC crystals for complementary Ti measurements. To measure Ti isotopes, O^- primary ions and positive secondary ions have to be used. In the NanoSIMS the lateral resolution of the O^- beam is generally inferior to that of Cs^+ and primary beam tune-up is more difficult. However, since virtually all Ti in these sections comes from the TiC subgrains, the lateral resolution is not critical in this case (see Fig. 2). Since secondary electron images [2] are not available for the O^- primary beam mode, sample navigation below the scale of the optical camera is much more challenging than with Cs^+ . However, we could obtain an intense signal from the previously imaged squares around the graphite slices when we used the (non-mass-filtered) total ion signal of the NanoSIMS for imaging. Most of this secondary ion signal appears to come from previously implanted Cs, which is now extracted as Cs^+ . With these total ion images it was straightforward to locate the previously studied areas on the TEM grids.

Although the NanoSIMS has six electron multipliers (EMs) which can be used for parallel detection of different masses, adjacent masses (*i.e.* $\Delta m = 1$ amu) can be measured in multicollection mode only up to mass 30 (*e.g.* ^{28}Si , ^{29}Si , ^{30}Si), due to the size of the EMs. Therefore, the most efficient way to measure all 5 Ti isotopes (^{46}Ti to ^{50}Ti) is to use the 'combined analysis' (CA) mode of the NanoSIMS. This mode combines multicollection with magnetic peak jumping. It is thus possible to measure the Ti isotopes at odd and even masses in two separate steps while automatically cycling the mass spectrometer through two different magnetic field values. Since only few detectors are

needed for Ti isotopes in this CA setup, we added several Ca isotopes in the other detectors. In step one ^{40}Ca , ^{43}Ca , ^{46}Ti , ^{48}Ti , and ^{50}Ti were measured in EMS 1 – 5 and in step two ^{44}Ca , ^{47}Ti , and ^{49}Ti in detectors 2, 3, and 4. Since the mechanical positions of the detectors cannot be changed during a CA measurement, exact centering of the position of different mass lines is achieved with appropriate settings of the deflectors in front of the exit slits for both steps. Measurements were done at high mass resolution and peak positions were checked on a perovskite (CaTiO_3) standard before each analysis. This standard was also used for external correction of the isotopic ratios.

After a TiC crystal was localized by Ti elemental imaging in 256^2 pixels (see bottom image in Fig. 2), the primary ion beam was rastered over a small 5^2 pixels area for the CA mode measurement.

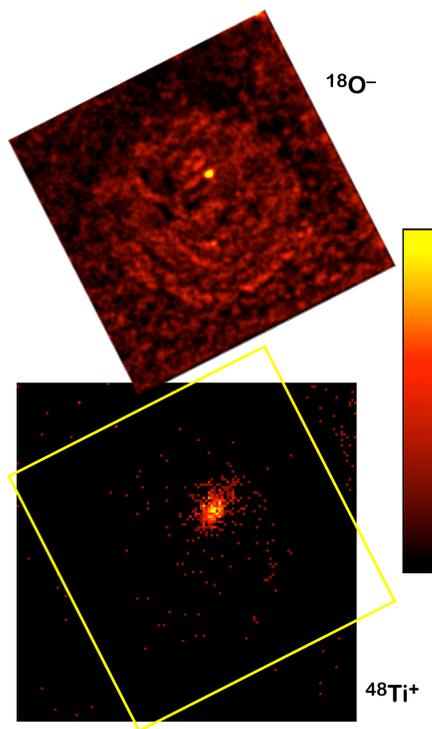


Figure 2. Secondary ion raster images of the ^{18}O and ^{48}Ti distributions in a TEM slice of presolar graphite KE3e#10. The sample was rotated between measurements and the ^{18}O raster area is indicated by the yellow square in the ^{48}Ti image. One TiC grain can clearly be seen in both images, although the lateral resolution is much better with the Cs^+ primary beam (top) than with the non-optimized O^- beam (bottom). The diameter of the graphite grain (see top image) is 12 μm .

Results and Conclusion: The Ti isotopic compositions of the three TiC crystals are shown in Figure 3 in comparison with the previously measured bulk composition [4] of the same graphite spherule. There

are no large differences between the Ti isotopic compositions of the different TiC grains and they are also very similar to the bulk composition. The O isotopic compositions of these three TiC crystals, however, vary significantly, by a factor of 3, in their $^{16}\text{O}/^{18}\text{O}$ ratio. It is not clear in what form the O is associated with the TiC grain and whether it is cogenetic or the result of surface reaction of the TiC grains before they were embedded into the growing graphite spherule. The latter case would imply that individual TiC grains were formed in an environment with uniform Ti isotopic composition in the envelope of the supernova, were then separated and exposed to a gas with variable $^{18}\text{O}/^{16}\text{O}$ ratios, and were finally incorporated into the same graphite sphere. More detailed studies of a larger number of TiC subgrains, also from other presolar graphites, will be needed to find a conclusive explanation of their isotopic compositions.

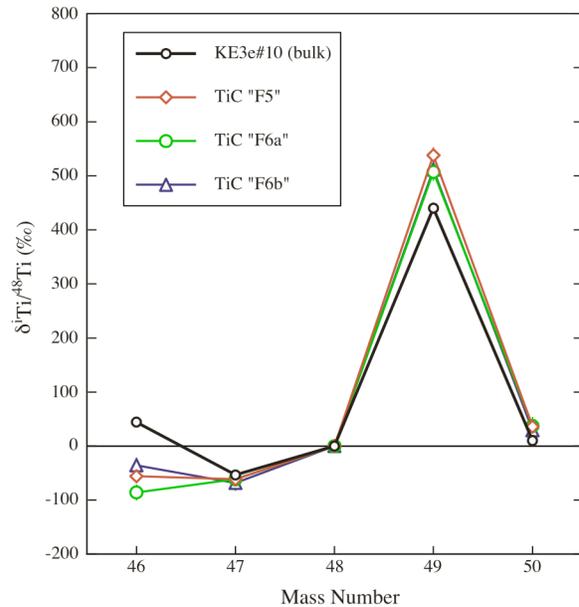


Figure 3. Plot of the titanium isotopic compositions of presolar graphite spherule KE3e#10 and its TiC subgrains. The bulk value was measured with the *ims3f* ion microprobe and the composition of three individual TiC subgrains was determined with the NanoSIMS. The results are expressed as delta values, deviations from the 'normal' isotopic ratios relative to ^{48}Ti in per mil. Note that the curve for "F6b" is partially obscured because the compositions of "F6a" and "F6b" are virtually identical for masses 49 and 50.

References: [1] Croat K. et al. (2002) *LPS XXXIII*, Abstract #1315. [2] Stadermann F. J. et al. (2002) *LPS XXXIII*, Abstract #1796. [3] Stadermann F. J. et al. (2002) *Meteoritics & Planet. Sci.*, 37, A136. [4] Travaglio et al. (1999) *ApJ* 510, 325.