TOF-SIMS ANALYSIS OF SiC GRAINS WITH HIGH LATERAL RESOLUTION. T. Stephan[1], D. Rost[1], E. K. Jessberger[1], R. Budell[1], A. Greshake[1], E. K. Zinner[2], S. Amari[2], P. Hoppe[3], and R. S. Lewis[4], [1]Institut für Planetologie, Wilhelm-Klemm-Str. 10, D-48149 Münster, Germany, stephan@nwz.uni-muenster.de, [2]McDonnell Center for the Space Sciences and the Physics Department, Washington University, One Brookings Drive, St. Louis MO 63130-4899, USA, [3]Physikalisches Institut, Universität Bern, Sidlerstr. 5, 3012 CH-Bern, Switzerland, [4]Enrico Fermi Institute, University of Chicago, 5630 Ellis Ave., Chicago IL 60637-1433, USA.

Introduction. In addition to the ten interstellar SiC grains analyzed previously [1] we investigated nine more grains from the Murchison separate KJG with TOF-SIMS (time-of-flight secondary-ion-mass-spectrometry) at high lateral resolution using a gallium liquid metal ion source. A minimum beam diameter of ~ 0.2 µm allows the investigation of lateral element distributions within small SiC grains having typical diameters of < 6 µm [2]. Carbon isotope analysis is limited by the insufficient mass resolution resulting from the Ga primary ion source. Nevertheless, grains enriched in ^{13}C were isotopically analyzed with sufficient precision by employing new peak separation techniques [1].

Isotope Analysis. The major problem for carbon isotope analysis in SiC grains with TOF-SIMS is the separation of $^{13}C^-$ at mass 13.0039 amu from $^{12}C^1H^-$ at mass 13.0084 amu. Due to the required high lateral resolution, an increase in mass resolution is not feasible without a substantial loss in sensitivity. In TOF-SIMS spectra $^{12}C^1H^-$ is always present due to adsorption of atmospheric hydrocarbons or, after sputtering, surface reactions with the remaining hydrogen gas in the vacuum system even at typical pressures of $2–5 \times 10^{-10}$ mbar. In contrast to conventional ion microprobes using double focusing mass spectrometers (DF-SIMS) the information depth with TOF-SIMS is in the order of a few atomic monolayers resulting in little sample destruction as well as high sensitivity for surface contamination. CH^-/C^- ratios are typically in the order of 1–2 but may be reduced by sputtering to 0.1–0.5. But even then a separation of $^{13}C^-$ from $^{12}C^1H^-$ is still not possible for samples with solar carbon isotope ratio ($^{12}C/^{13}C = 89.9$ [3]) with sufficient precision. Figure 1 shows the relatively good agreement of the results from TOF-SIMS analysis with the results obtained with DF-SIMS [2] for 13 SiC grains where the peak separation was possible. In cases with $^{12}C/^{13}C$ near or above 60 the obtained error does not allow a clear identification of interstellar carbon isotope ratios.

Element Analysis. The main advantage of TOF-SIMS above conventional SIMS techniques is the parallel detection of **all** secondary ions with the same polarity in conjunction with the imaging capability at high lateral resolution allowing the investigation of element distributions even in small samples like interstellar SiC grains. Figure 2 shows the distribution of Al, Si, Ca, and Ti positive secondary ions for grain KJG2–0411, ~ 4 × 6 µm^2 in size. These images were obtained after extensive sputtering in order to remove adsorbed contaminants like hydrocarbons. The images clearly indicate that these elements are not distributed uniformly within the sample.

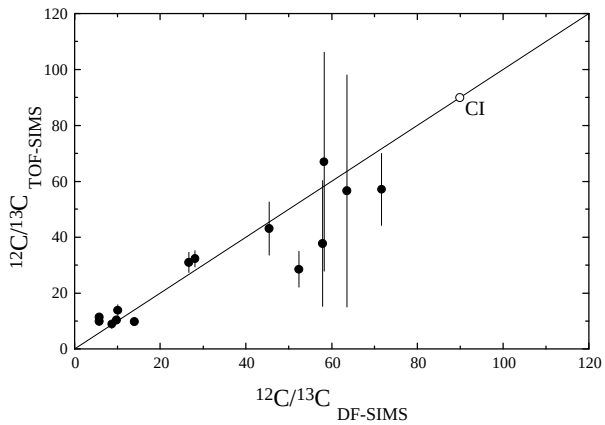

Fig. 1. Comparison of $^{12}C/^{13}C$ ratios from DF-SIMS [2] and TOF-SIMS analyses. 1σ statistical errors are shown for the TOF-SIMS results.

Table 1. Ratios for major elements relative to silicon in Si-, Al-, and Ti-rich areas of KJG2–0411 (A, B, C, c.f. Fig. 2). Errors mentioned derive only from the counting statistic and do not include the uncertainties of the used elemental SIMS sensitivities.

	A	B	C
Al	0.341 ± 0.004	1.436 ± 0.012	1.491 ± 0.008
Si	1	1	1
Ca	0.021 ± 0.001	0.037 ± 0.002	0.050 ± 0.002
Ti	0.017 ± 0.001	0.020 ± 0.002	0.043 ± 0.002

Table 1 comprises the element ratios obtained from TOF-SIMS spectra taken from three different areas, ~ 1 × 1 µm^2 each, of the same grain, corresponding to the Si, Al, and Ti maxima in the secondary ion images, respectively. The high Al abundance appeared only after sputtering. From earlier measurements there are indications for SiC enclosing Al-rich material. During subsequent sputtering the Al/Si ratio increased from 0.05 to 0.7 in average for the whole analyzed section and > 1.4 in Al-rich spots. Due to so far unknown ma-

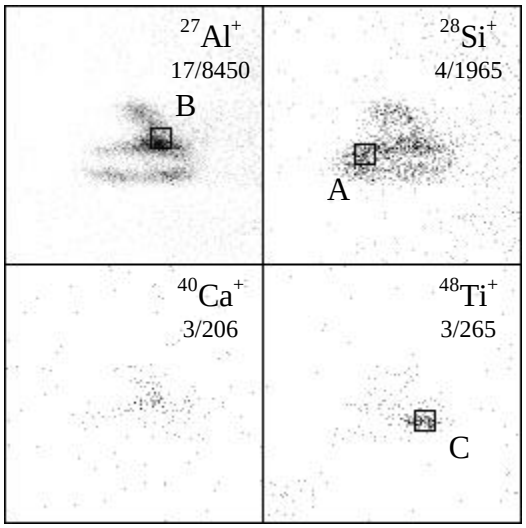

Fig. 2. TOF-SIMS images of SiC grain KJG2–0411 showing the lateral distribution of ^{27}Al, ^{28}Si, ^{40}Ca, and ^{48}Ti positive secondary ions. The sample was analyzed with 800 primary ion shots per pixel, 128 × 128 pixel, and a field of view of 12 × 12 µm^2. The intensity of the most intense pixel (e.g., 17 for $^{27}Al^+$), shown as black, and the integrated intensity for the total image (e.g., 8450), respectively, are given for each ion species.

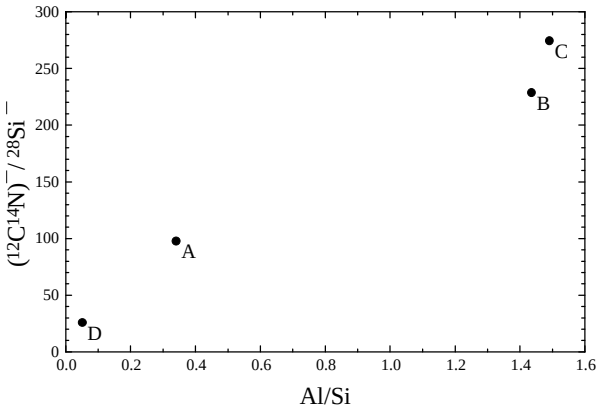

Fig. 3. $(^{12}C^{14}N)^-/^{28}Si^-$ secondary ion ratios in three different areas in KJG2–0411 (A, B, C, c.f. Table 1) and of the total section before sputtering (D) show a correlation with Al/Si element ratios.

trix effects of SiC there is still a relatively high uncertainty up to a factor of two for these absolute numbers but the general trend is obvious. The determined Al/Si ratio before sputtering corresponds to a slightly lower Al abundance than 5.2 wt.-% determined with DF-SIMS. Therefore, an overestimate of the Al/Si ratios seems unlikely. Since most of the material is now sputtered away, a subsequent SEM-EDX analysis of the remaining grain failed. Due to an observed correlation between Al/Si ratios and CN/Si negative secondary ion ratios (Fig. 3), AlN seems to be the dominant Al bearing phase. Since the DF-SIMS analysis used an O primary ion beam, the TOF-SIMS results on oxygen are ambiguous and the presence of corundum [4, 5] cannot be excluded.

Conclusions. Besides limited abilities in carbon isotope measurements, only ^{13}C-rich samples can be analyzed with sufficient precision, TOF-SIMS has its main advantage in the analysis of element distributions at high lateral resolution. Our results demonstrate that especially with its imaging capabilities this technique can deliver a wealth of information about the chemical composition of SiC grains. Aluminum and nitrogen, the most abundant elements besides Si and C in SiC grains [2], show an excellent correlation within KJG2–0411, an indication for the presence of AlN. The increase of the Al/Si ratios towards the center of the grain might be due to destruction of AlN on or near the grain's surface during chemical processing. Calcium, generally depleted in SiC grains [6], is also correlated with Al and N. In the same grain a titanium rich region was found (Fig. 2). This might be due to the presence of small TiC grains like observed in a TEM study of one other silicon carbide grain [7].

References:

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