

HYDROGEN, CARBON, AND NITROGEN ISOTOPIC IMAGING OF SUB-MICRON COMPONENTS FROM INTERPLANETARY DUST PARTICLES. F. J. Stadermann, Laboratory for Space Sciences, Physics Department, Campus Box 1105, Washington University, St. Louis MO 63130, USA (fjs@wuphys.wustl.edu).

Introduction: The new Washington University NanoSIMS makes it possible to image a sample's isotopic structure at a sub-micrometer scale. Since this can be done at high mass resolution without significant loss of sensitivity, it can be used for a wide variety of isotopic systems in very small samples [1-3]. Here, this new capability is applied to the study of the internal H, C, and N isotopic compositions of 7 chondritic IDPs (interplanetary dust particles). These particles and their isotopic compositions have been studied before [4, 5] by 'conventional' -i.e. ims3f- secondary ion mass spectrometry (SIMS). While most of the basic results from those earlier measurements were confirmed, there are several new observations that could not have been made without the analytical capabilities of the NanoSIMS. The most interesting result is the discovery of a discrete, 400 nm sub-grain with a ^{15}N enrichment of $\delta^{15}\text{N} = +813\text{‰}$.

Samples and Analytical Details: The analyzed IDPs are from stratospheric collectors U2-044 and U2-047 that were mounted on high-purity Au foil together with various isotopic standards as part of a previous study [4, 5]. During the mounting procedure, the particles were crushed between quartz plates and then pressed into the Au substrate, resulting in flattened IDP fragments that cover areas on the Au much larger than the particles' original size of typically 10 – 20 μm . Although most information on the internal correlation of sub-components is lost this way, this mounting technique makes it possible to analyze the different phases directly with SIMS.

Previous Analyses. There are 7 IDPs in this study, all of which are classified as 'chondritic' based on their major element composition. The H, C, and N isotopic compositions of fragments of all of these particles have been measured with the ims3f ion microprobe as part of the earlier study [4, 5]. Those analyses were made in the point-mode with a Cs^+ beam diameter of 5 μm or more, meaning that (a) there is no information on the lateral distribution of the isotopic composition and (b) every result represents the 'average' isotopic composition of a 5 μm (or larger) area. Large isotopic anomalies were found in fragments of the particles 'Aurelian' (δD up to +771 ‰) and 'Florianus' (δD up to +1120 ‰ and $\delta^{15}\text{N}$ up to +411 ‰). All other measurements of H and N, as well as all C measurements of fragments from these 7 particles yielded isotopically normal or close to normal results.

New NanoSIMS Analyses. For the new measurements, the same sample mount was used as for the earlier study. Since SIMS is a destructive measurement technique, much of sample material was already sputtered away, leaving only small remnants available on the Au substrate. However, because the sensitivity of the NanoSIMS at high mass resolution is almost a factor of 100 higher than that of the ims3f instrument, the same kind of analysis can be made with much smaller sample amounts [1]. It was thus possible to perform additional measurements on fragments of the same IDPs that had been studied before. The new measurements were performed in a raster-imaging mode where the ~ 100 nm Cs^+ beam is scanned over the sample surface. The resulting secondary ion images cover areas of 5 $\mu\text{m} \times 5 \mu\text{m}$ to 40 $\mu\text{m} \times 40 \mu\text{m}$ which are represented variably by 128^2 , 256^2 , and 512^2 pixels. In each measurement, secondary ions of 4 different masses were detected simultaneously: H^- , D^- , $^{12}\text{C}^-$, and $^{13}\text{C}^-$ in a first set of 14 measurements and $^{12}\text{C}^-$, $^{13}\text{C}^-$, $^{12}\text{C}^{14}\text{N}^-$, and $^{12}\text{C}^{15}\text{N}^-$ in a second set of 9 measurements. The detection of $^{12}\text{C}^{14}\text{N}^-$ and $^{12}\text{C}^{15}\text{N}^-$ is a typical way to measure N isotopic ratios in C-bearing phases, since N^- ions are not efficiently formed. The measurements of both C and N isotopic ratios require high mass resolution to eliminate possible interferences from neighboring mass peaks and the exit slits for the detectors involved were set accordingly. Before the measurement, it was verified that there is no overlap between the neighboring peaks of $^{13}\text{C} - ^{12}\text{CH}$, $^{12}\text{C}^{14}\text{N} - ^{10}\text{B}^{16}\text{O}$, and $^{12}\text{C}^{15}\text{N} - ^{11}\text{B}^{16}\text{O}$. All results were calibrated relative to the known composition of isotopic standards which were measured along with the IDPs on the same sample mount.

Before each measurement, the analysis area was sputter-cleaned with a rastered high-current Cs^+ beam to remove surface contaminants. At a pressure of $2.9 \cdot 10^{-9}$ torr in the analysis chamber, the redeposition rate of contaminants appeared tolerable. This is mostly a problem for the D/H measurements, where surface H deposits could lead to 'more normal' isotopic results. Note that an isotopic anomaly can never be caused by the deposition of the isotopically normal contaminants.

Many of the measurements were made in a single, slow scan across the analysis area. In some cases, this led to problems with 'saturated pixels': Since all masses are counted simultaneously for the same amount of time, masses with higher count rates could exceed the 2^{16} limit, resulting in data loss. For this rea-

son, the measurement routine was modified in several cases: Instead of one single, slow scan across the analysis area, a series of 10 faster scans was performed. These 10 scans represent individual measurements which could then be added into a single measurement without being affected by the counting system's 2^{16} counts/pixel limit. Since the sample is slowly sputtered away during a SIMS measurement, the results from consecutive scans can also be seen as 'layers' of the sample.

During data processing, the isotopic composition of an individual grain can be determined by adding the counts from all pixels belonging to the grain for each mass and then calculating the isotopic ratios. Since different masses are measured simultaneously in the NanoSIMS, it is not necessary to perform image-shift or measurement-time corrections, even in cases where a particle is sputtered away during the analysis.

The low abundance of D made it necessary to combine the pixel counts from a larger area into a single 'measurement spot' to get enough D counts for meaningful isotopic ratio statistics. The lateral resolution of the D/H measurement was thereby reduced to around 500 nm, while the lateral resolution of $^{13}\text{C}/^{12}\text{C}$ and $^{15}\text{N}/^{14}\text{N}$ was limited only by the size of the primary beam diameter (100 nm).

Results and Discussion: Normal isotopic compositions (within 2σ of the terrestrial range of variation) were found for most of the analyzed fragments, as was expected from the original *ims3f* measurements. The exceptions are:

Hydrogen. Several IDPs showed slightly increased D/H ratios. A sub-micrometer sized D-hotspot with $\delta\text{D} = +1200\%$ was found in a fragment from the particle 'Jovian'. A hotspot of this size, embedded in other H-bearing phases could not have been identified in the earlier *ims3f* study, even if exactly the same spot had been analyzed. There is no correlated isotopic effect in C at the site of this D-hotspot.

Carbon. Although there are variations in the $^{13}\text{C}/^{12}\text{C}$ ratio images in some particles, it is not clear whether they are statistically significant. In addition, there seems to be some indication that 'preferential sputtering' may have led to some of the small variations observed. Until this has been studied in more detail, it seems safer to assume that there is no clear evidence for anomalous C in these IDPs.

Nitrogen. In one IDP ('Florianus') the earlier *ims3f* study had found heavy N. In a fragment of the same particle, significant ^{15}N enrichments were again found, confirming previous observations. In addition, one of the most interesting results of this study comes from another IDP, 'Aurelian'. Although most fragments of this particle show normal to only slightly increased

$^{15}\text{N}/^{14}\text{N}$ ratios, one well-defined and isolated 400 nm sub-grain has a composition of $\delta^{15}\text{N} = +813\%$. This is the largest ^{15}N enrichment found in any IDP to date. Since this hotspot was measured in 10 scans with the Cs^+ beam, it was possible to verify that the anomaly was present in all analyzed layers. A comparison with the C isotopic image of the same area showed no anomalies in this sub-grain. Interestingly, however, the C to N ratio in the hotspot appeared to be significantly lower than in other fragments of the same IDP. Since the location of the highly ^{15}N enriched sub-grain is well known, it may be possible to identify the carrier phase of the heavy N. It has been suggested that N in IDPs is sited in an organic phase [6, 7] and this study may give new clues on the carrier of the heavy N.

Conclusions: It is clear that valuable new information can be obtained by re-examining old samples with improved analytical capabilities for isotope analysis. The NanoSIMS is basically taking a 'closer look' at the distribution of isotopic anomalies in sub-components of IDPs.

Since the NanoSIMS can also be used to measure TEM slices directly [1], it is now possible to determine the isotopic compositions of IDP sub-components after they have been mineralogically characterized in the TEM. The most intriguing question, of course, is the isotopic makeup of GEMS [8] and their possible correlation to the observed anomalies.

References: [1] Stadermann F. J. et al. (1999) *LPS XXX*, #1407. [2] Stadermann F. J. et al. (1999), *Meteoritics & Planet. Sci.* 34, A111. [3] Hillion F. et al. (1999) *Proc. SIMS XII*, 209. [4] Stadermann F. J. et al. (1989) *Meteoritics* 24, 327. [5] Stadermann F. J. et al. (1990) *LPS XXI*, 1190. [6] Messenger S. et al. (1996) *Meteoritics & Planet. Sci.* 31, A88. [7] Messenger S. (2000) *Nature* 404, 968. [8] Bradley J. P. (1994) *Science* 265, 925.

Notes and Acknowledgements: These measurements were performed with the Washington University NanoSIMS at CAMECA's factory a few days before the instrument was shipped. This first commercial NanoSIMS is now installed at the Laboratory for Space Sciences in St. Louis. Visit the website <http://presolar.wustl.edu/nanosims/> for a detailed description of the new instrument. I would like to thank François Hillion of CAMECA for his help with the measurements.