TOF-SIMS ANALYSIS OF ISOTOPICALLY ANOMALOUS PHASES IN INTERPLANETARY DUST AND RENAZZO.

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Introduction: Deuterium and ^{15}N enrichments are widespread in interplanetary dust particles (IDPs) and primitive meteorites [1]. However, little is known about the carrier phases of these two types of anomalies, which are in general not correlated with each other. Recent developments in analytical techniques with sub-micrometer spatial resolution now give us the opportunity to investigate the lateral distribution of isotopically anomalous phases within single IDPs in order to shed light on their origins.

In a continuation of our previous work on other dust grains [2,3], we investigated 'Kipling' (L2011-R12), the particle with the highest ^{15}N enrichment ever reported in an IDP [4]. In contrast to the other IDPs, which only showed ^{15}N enrichments in distinct regions [2,3], Kipling is dominated by heavy nitrogen, but also contains two hot spots with $\delta^{15}N = +1250$ ‰ and $\delta^{15}N = +1090$ ‰, respectively, that were found with the Washington University NanoSIMS [4]. An ^{17}O-rich presolar grain has recently been found in another area of this IDP [5]. In the present study we used time-of-flight secondary ion mass spectrometry (TOF-SIMS) to identify the different carriers of these anomalies.

With the intention of comparing the results on IDPs with other primitive chondritic material, we also investigated matrix material of the CR chondrite Renazzo. This meteorite is well known for its deuterium and ^{15}N enrichments. The material we used is part of a series of matrix samples heated to various degrees in vacuum and in air [6].

The purpose of our comparative study is to investigate the origin, history, and nature of isotopically anomalous phases in primitive solar system material, how they survived in their respective parent bodies, and what they endured while they traveled to Earth, especially during atmospheric entry.

Samples and Analytical Techniques: Kipling was pressed into high-purity Au foil for Cameca ims 3f and NanoSIMS investigations. Although most of the interesting phases were sputtered away during the NanoSIMS analyses, some remnants were still available for the TOF-SIMS measurements.

From Renazzo two series of 9 residues each are available. They were heated for two hours to temperatures between 200 and 1000 °C at 100 °C intervals under vacuum or in air [6]. These 18 samples as well as an unheated sample for comparison were also pressed in Au foil and analyzed with the ims3f to examine the variations in H and N isotopic compositions with increased degree of heating [6,7]. From this sample suite we selected the material heated up to 1000 °C in air and the unheated sample for our first TOF-SIMS analyses. Previous work [6,7] showed that both H and N isotopic compositions are normal in the 1000 °C residue, in contrast to unheated Renazzo matrix, which shows high and variable enrichments of D and ^{15}N. Three different regions (150×150 µm^2 – 250×250 µm^2) from each sample, containing several individual grains, were investigated.

All samples were sputter-cleaned with a 3 keV Ar^+ ion beam prior to the TOF-SIMS analyses to remove surface contamination. Although this sputtering results in fragmentation of some of the organic molecules we are interested in, surface cleaning was necessary due to the high abundance of organic contaminants from previous sample handling.

Imaging TOF-SIMS analyses [8] were performed at high lateral resolution (beam diameter ~0.3 µm) as well as high mass resolution (up to $m/\Delta m = 10,000$ at full-width half-maximum) allowing an unambiguous identification of most ion peaks and a clear assignment to the various sample regions. Positive as well as negative secondary ions were analyzed in two subsequent measurements.

Results:

Kipling. Although most of the interesting phases were sputtered away during the NanoSIMS study, an overall enrichment, relative to CI, of the Mg/Fe-ratio could be observed for Kipling, as in ^{15}N-rich regions of other IDPs [2,3]. Kipling has a mean Mg/Fe-ratio of 2.3 (1.9×CI), whereas the two ^{15}N hot-spots have ratios of 3 and 10, respectively (all element ratios are given as atomic ratios). (Mg+Fe)/Si-ratios are below 1 (0.4–0.8) in all these regions. Although still too low, these ratios suggest the presence of Mg-rich pyroxene ((Mg+Fe)/Si = 1, Ca plays no role in this sample) rather than olivine ((Mg+Fe)/Si = 2). However, a pure forsterite grain was identified during SEM-EDS analysis that also yields a (Mg+Fe)/Si-ratio of only 0.7 in TOF-SIMS. The deviations may be due to silicone oil residues from sample collection in the stratosphere that increased the Si signal drastically. The silicone oil may also be responsible for O/Si-ratios that in most regions are lower (<3) than those for pyroxene (3) as well as for olivine (4). Finally, we note that carbon is enriched in the particle by a factor of 2.9 over CI abundances; this can only partly be explained by silicone oil.

Renazzo. Comparing the TOF-SIMS results of the two Renazzo samples elucidates some of the changes the samples experienced during heating (Fig. 1). Elements such as H, C, F, S, Br, and Pb are depleted in the heated samples relative to unheated Renazzo, whereas Li, Mg, Sc, Cr, V, and Cu are enriched. We note, in particular, elevated abundances of the major element magnesium.

Molecular species also show significant alterations during heating. Although the intensity of low-mass hydrocarbons decreases, polycyclic aromatic hydrocarbons (PAHs) show higher intensities in the heated samples. Furthermore, differences are apparent among various low-mass molecular species. CN^-, for example, decreased less than C^- or C_2^-. Therefore the CN^-/C^--ratio increased by a factor of 1.3 and CN^-/C_2^- by a factor of 1.7 in the 1000 °C residues relative to unheated Renazzo.

Although we cannot determine D/H isotopic ratios, we note that D^-/H^--ratios decreased by a factor of 2 in the heated samples, consistent with previous work [6].

Discussion:

Kipling. The results on Kipling support our earlier contention that heavy nitrogen is correlated with high Mg/Fe-ratios [2,3]. Forsterite and enstatite are the most likely phases to be present. In addition, as noted above, this IDP is enriched in C. Thus, the heavy nitrogen is probably hosted in organic material associated with the Mg-rich phases.

Renazzo. Our Renazzo measurements show an increase of the Mg/Fe-ratio by a factor of 2.8 and a decrease of C/Si and H/Si by factors of 2.8 and 1.8, respectively, after heating (Fig. 1). Hydrocarbons typically lower the secondary ion sensitivities of all elements in the SIMS process. A preferential loss of hydrocarbons from Mg-rich areas would therefore explain the observed increase of the Mg/Fe-ratio.

However, the observed changes in relative abundances of molecular ions clearly indicate that not all organic material is lost. In particular, the increase of CN^-/C^- and CN^-/C_2^- suggest that an isotopically normal N-containing phase is still present in the heated sample. PAHs also still exist after heating.

Conclusions: Organic material closely connected to Mg-rich, Fe-poor anhydrous minerals seems to be the most plausible carrier of isotopically anomalous matter in IDPs and maybe also in Renazzo. However, additional analyses are required, both on IDPs and on Renazzo material. We plan to investigate Renazzo residues heated to different, intermediate temperatures, in order to examine the exact temperature dependencies of the changes occurring during heating.

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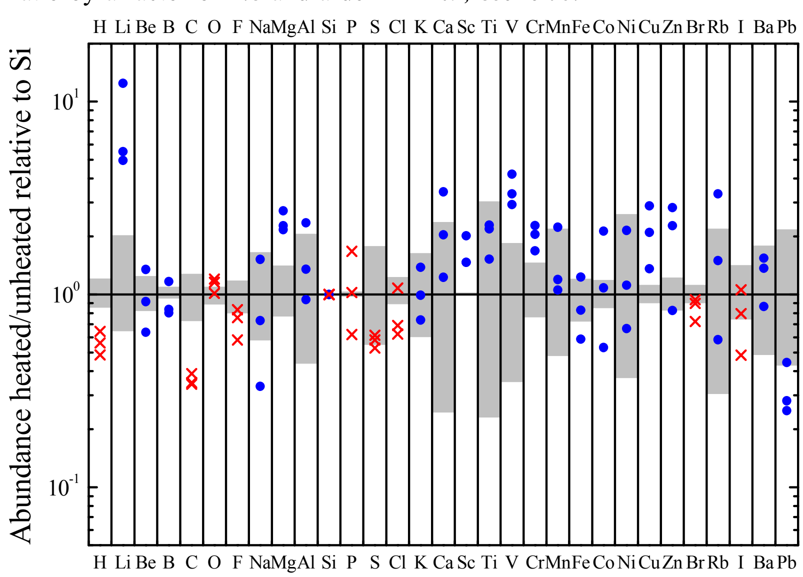

Fig. 1: Abundances of various elements in Renazzo residues heated to 1000 °C relative to unheated samples. The variation among the different unheated fragments is shown as gray areas. Results from positive secondary ions are displayed as blue circles, results from negative ions as red crosses.