

NITROGEN – NOBLE GAS STATIC MASS SPECTROMETRY of GENESIS COLLECTOR MATERIALS.

Bernard MARTY^{1,2}, Pete BURNARD¹, Laurent ZIMMERMANN¹ and Pascal ROBERT¹, ¹CRPG-CNRS, 15 rue Notre Dame des Pauvres, BP20, 54501 Vandoeuvre-lès-Nancy, France. ²bmarty@crpg.cnrs-nancy.fr

Introduction. A new system for analysis of N and noble gases in GENESIS collector materials has been constructed at the Centre de Recherches Pétrographiques et Géochimiques (CRPG), Nancy, France. The new extraction and purification system, constructed specifically for analysis of GENESIS target material has, at its' core, a similar design to that developed by Marty et al at CRPG^[1] and, for example, used by Hashizume et al^[2] for N and Ar analyses of lunar soil fines.

In the Hashizume et al study^[2], extraction of N and noble gases was achieved by fusing the sample *in vacuo* using a CO₂ laser ($\lambda = 10.6 \mu\text{m}$) as a "micro-furnace" in order to melt small (10 μg) grains of lunar soil. Once extracted, the gas was purified in two aliquots, one ($\approx 20\%$) for Ar analysis, and the remainder for N analysis. Purification of the Ar aliquot was achieved using Ti sponge getters (cycled between ambient temperature and 600 °C) and a liquid N₂-cooled trap. Purification of the N portion was achieved by first oxidizing all N-bearing and C-bearing species released by the laser to NO₂ and CO₂, respectively. A CuO furnace is heated (in the presence of a Pt catalyst) to 720 °C in order to produce the O₂ required for oxidation. CO₂ was then separated from NO₂ at -170°C before reducing NO₂ back to N₂ after re-absorbing the remaining O₂ on the CuO furnace at 450 °C. The isotopes of N₂ were measured using a VG5400 static noble gas mass spectrometer by peak jumping between $m/z = 28, 29,$ and 30 (corresponding to ¹⁴N-¹⁴N, ¹⁴N-¹⁵N, and ¹⁵N-¹⁵N dimers respectively).

Description of new extraction and analysis system. The newly constructed GENESIS extraction system utilizes the same laser extraction, O₂ purification and static mass spectrometry methodology of the system used by Hashizume et al^[2] but includes three important modifications:

1. extraction of N and noble gases is by *in vacuo* ablation using a UV laser (F2 excimer);
2. a redesigned CuO furnace;
3. addition of a multicollector, high resolution static gas mass spectrometer.

F2 excimer laser

The shorter wavelength excimer laser was specifically chosen for analysis of the GENESIS collector material due to its' ability to ablate thin layers of material without heating the underlying material: in contrast, CO₂ or Nd-YAG lasers heat (and eventually melt) significant volumes of sample. The excimer laser can selectively sample a thin layer of target material, reducing the volume of collector material degassed during analysis. This therefore reduces the contribution of blank N from the collector substrate added to each analysis. This is particularly relevant for N as one of the principal GENESIS collectors designed for N isotopic analysis is diamond-like carbon deposited on silicon ("SandiaC" material), which poses two potential problems: (i). the annealing steps between deposition of layers of diamond-like C during fabrication of the collector material led to some atmospheric N contamination between layers^[3], therefore it is highly

desirable to selectively sample the layer containing implanted solar-wind N and (ii). volatilization of the Si substrate of the SandiaC collectors could produce SiN: SiN is not oxidized by O₂ during purification and therefore will not be analyzed. Furthermore, the CO₂ laser used by Hashizume et al does not couple well with the highly reflective surfaces of most GENESIS collector materials. Consequently, a micro-sampling UV laser is more appropriate for analysis of GENESIS collector materials.

In theory, for a given fluence, shorter wavelength photons will ablate target material more efficiently, thereby heating the sample less compared to a longer wavelength laser^[4]. In order to minimize sample heating, the shortest wavelength practical was selected and a LambdaPhysik OptexPro F2 excimer laser was purchased with a wavelength of 157nm. Using a simple demagnification system consisting of a 4x2 mm mask, 200 cm of beam dilation, a compound 50mm dia objective at $f = 45\text{mm}$ (at 157 nm), we are readily able to ablate 100 x 50 μm pits in SandiaC and AuOS collector materials (Fig 1). Due to the strong absorption of 157nm photons by oxygen and water molecules in ambient atmosphere, care must be taken to purge the beam path from the output of the laser to the sample with argon or nitrogen.

New CuO furnace. In order to reduce N blanks, N purification is performed in a glass section of the extraction system (the remainder being constructed from stainless steel). One of the major sources of blank N results from degassing of the quartz glass furnace when at 720 °C, required in order to liberate O₂ from CuO during N purification. The new N purification system comprises a CuO furnace contained within a double vacuum envelope, the outer portion of this envelope being independently pumped to 10⁻² mbar, while the inner portion at UHV contains CuO. This significantly reduces N blank resulting from increased N porosity across the hot quartz glass. In addition, in the new system, the CuO is not heated by an external resistance furnace, rather by two light bulbs (with silvered reflectors that focus the light bulb's output onto the CuO); two 250W light bulbs are sufficient to maintain the temperature of the CuO at 720 °C. In this way, the temperature of the glass does not exceed 100 °C, reducing N blanks due to glass degassing and due to the increased porosity of the glass. The light bulb-based furnace also rapidly increases the CuO cycling rate, reducing the purification time required during analysis.

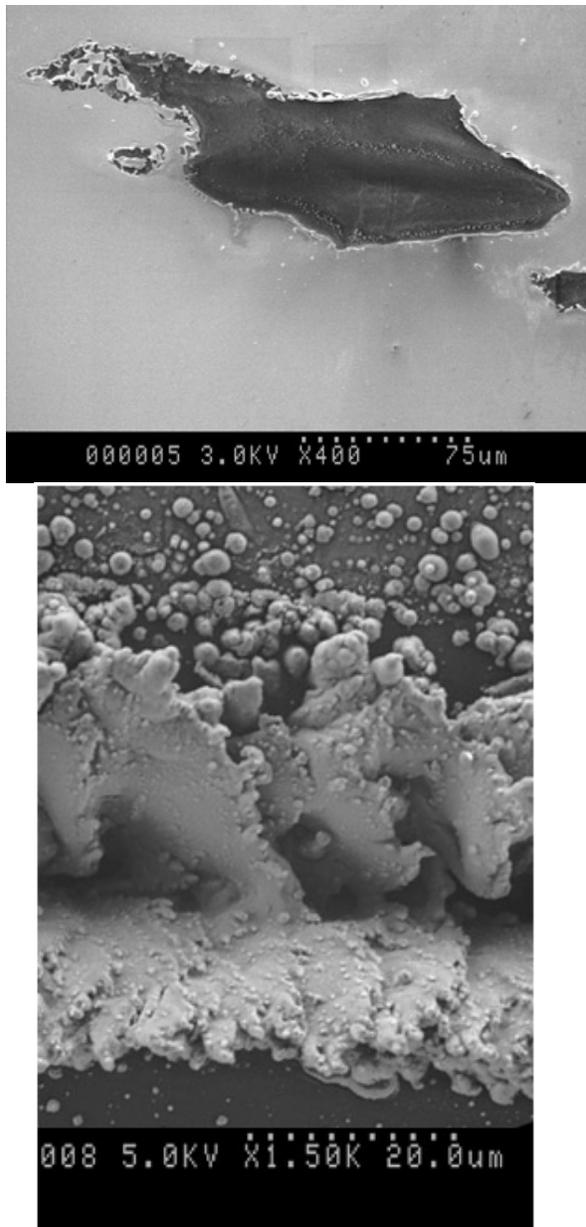


Figure 1. SEM images of a) laser ablation pit created by 10 laser pulses into AuOS. B) 50 μm wide ablation "trench" in SandiaC. Laser excimer beam profiles are typically rectangular; optics for creating homogenous, circular beams do not exist for 157nm laser beams. Large, rectangular pits will be ideal for rastering the beam over a large area: N_2 needs to be extracted from several mm^2 for each analysis. At present, each pulse extracts material to a depth of ≈ 100 nm of AuOS material and possibly more of the SandiaC; however, the laser power can be reduced in order to reduce the depth of each pit. The inhomogeneity of the laser beam, seen here as irregular shaped pits, results largely from non-normal beam incidence and can be corrected using the compound objective.

Typically, N and Ar blanks of the extraction system will reduce over time as continuous pumping at $< 2 \times 10^{-9}$ mbar by several turbo molecular pumps removes adsorbed N and Ar. Despite the new system having been under vacuum for no more than two months, Ar blanks are $\approx 8 \times 10^{-18}$ mol ^{36}Ar (2×10^{-13} cc STP) and $< 6 \times 10^{-13}$ mol N (1.3×10^{-8} cc STP), already considerably better than most established extraction systems, and these blanks continue to fall by the day. Successful analyses of N liberated from AuOS collector material irradiated with ^{15}N have been carried out using the new extraction system.

Multicollector static mass spectrometer. Significant complexity in the analysis of purified N_2 results from isobaric interferences at $m/z = 28$ and 29 from the isotopologs of CO, $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O} + ^{12}\text{C}^{17}\text{O}$: the VG5400 used previously is unable to resolve these species from the $^{14}\text{N}^{14}\text{N}$ and $^{15}\text{N}^{14}\text{N}$ peaks. A new mass spectrometer, a GV instruments Helix MC, is under construction (delivery anticipated 02/05) with a resolution of ≈ 1800 $m/\Delta m$ that should be sufficient to partially resolve N dimers from the isotopologs of CO. In addition, the Helix MC will be equipped with 5 collectors enabling simultaneous collection of all three N isotope signals. These two improvements will significantly improve precision and accuracy of N isotope measurements over that possible on the present 5400-based system ($\approx 1\%$).

Conclusion. In our poster, we demonstrate the superior ability of the new system by analyzing non-flight fragments of SandiaC and AuOS (gold on sapphire) that have been implanted with ^{15}N at Los Alamos national Labs using the new extraction system attached to the VG5400 while awaiting delivery of the new GV instruments mass spectrometer. We discuss the optimization of the laser and extraction system for recovery efficiency and blank reduction.

References 1. Marty, B., Lenoble, M. & Vassard, N. Nitrogen, helium and argon in basalt: a static mass spectrometry study. *Chemical Geology* **120**, 183-195 (1995). 2. Hashizume, K., Marty, B. & Wieler, R. Analyses of nitrogen and argon in single lunar grains; towards a quantification of the asteroidal contribution to planetary surfaces. *Earth and Planetary Science Letters* **202**, 201-216 (2002). 3. Jurewicz, A., Burnett, D. & others, a. The Genesis Solar-Wind Collector Materials. *Space Science Reviews* **105**, 535-560 (2003). 4. Telouk, P., Rose-Koga, E. F. & Albarede, F. Preliminary results from a new 157 nm laser ablation ICP-MS instrument; new opportunities in the analysis of solid samples. *Geostandards Newsletter* **27**, 5-11 (2003).