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# Safe Disposition of Retired LANA.75 Hydride Beds

Greg Staack, Mark Crowder, and Mike Tosten

*Tritium Focus Group*

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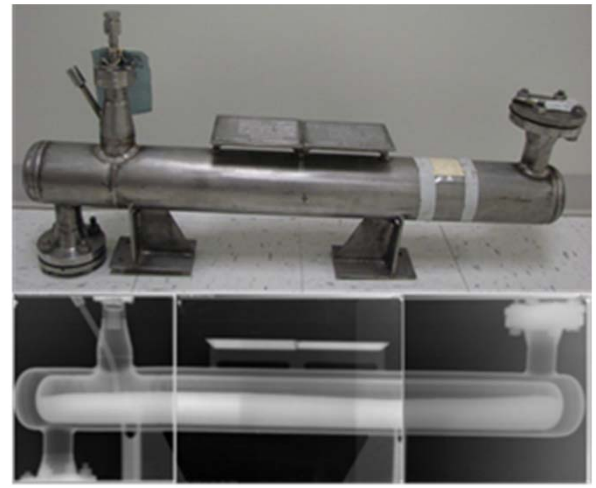
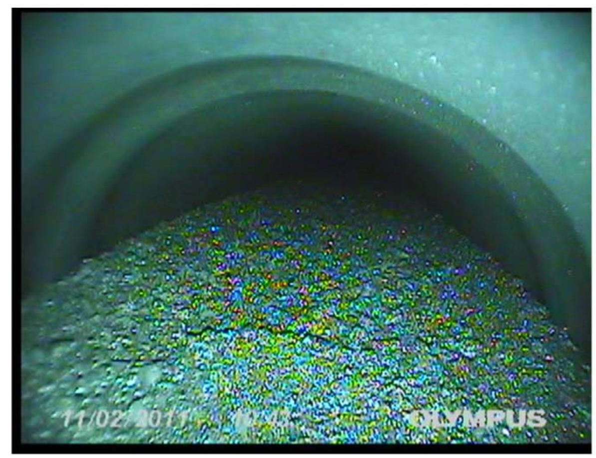
# History/Advantages of Metal Hydrides

$LaNi_{4.25}Al_{0.75}$ or LANA.75 has been used by the Savannah River Site Tritium Facilities for years to safely store hydrogen isotopes

- High molar density at moderate pressures - less glovebox space
- Can be used as a pump by varying temperature - fewer moving parts
- Can deliver He-3 free gas – fewer unit operations





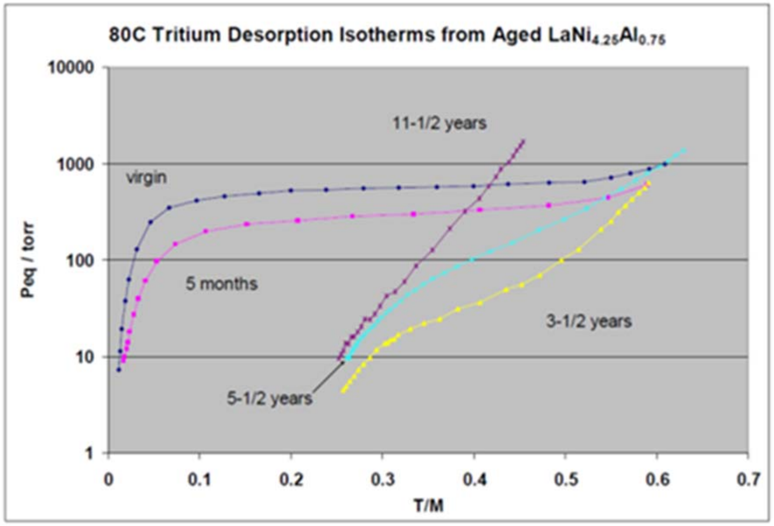
# Tritium Aging of LANA

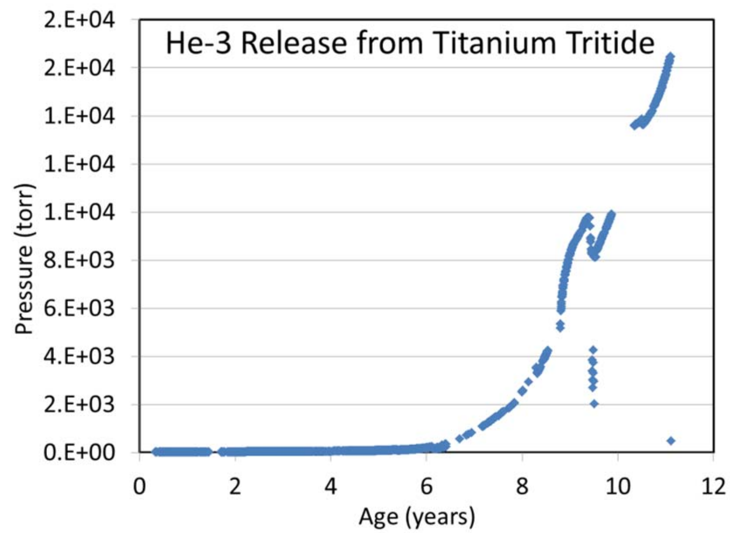
Decay of T to He-3 causes:

- Decrease in plateau pressure
- Formation of a "heel" of trapped hydrogen isotopes
- Increase in the plateau slope
- Eventual breakthrough of He-3

Beds failure modes:

- Reversible capacity adversely impacts process
- Can no longer deliver He-3 free hydrogen

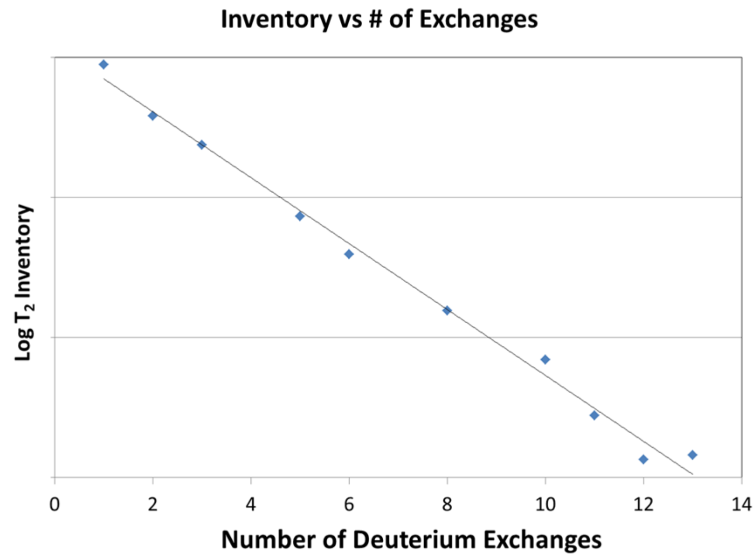


# Bed Retirement

Perform a series of isotope exchanges to remove as much tritium as practical

Backfill with inert gas and remove from the process




But.. there are disposal issues-

- Potential for pressure generation
- Concerns regarding pyrophoric metal particulate

Significant quantities of He-3 trapped in the bed = $$

- Neutron detectors
- Cryogenics
- Medical imaging

# Motivation

Over the years, many beds have been retired from the process and are accumulating in a rad storage area.

Previous testing had demonstrated gas release characteristics in an inert environment. The primary goal of this project was to determine whether the addition of oxygen could prepare the beds for disposal in a one-step process at lower temperatures.

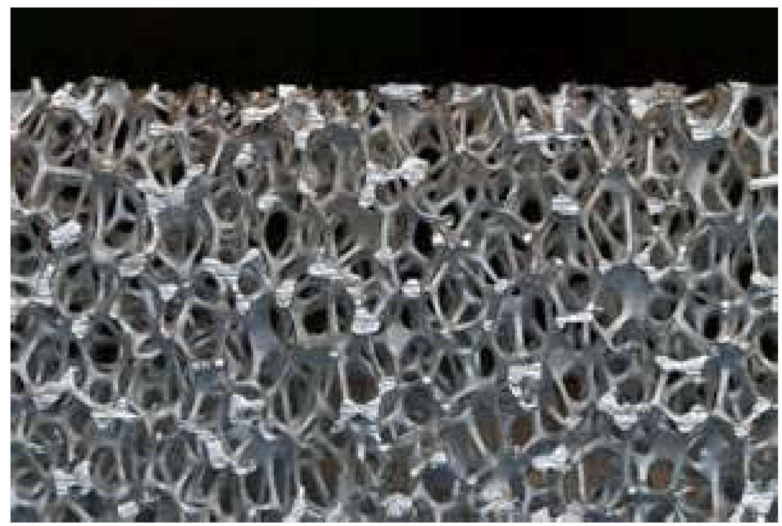
# Proposed LANA Oxidation

Heat the LANA in a dilute oxygen environment to -

- Release all trapped He-3 and hydrogen isotopes
- Render the LANA insensitive to air (passivate)

Goal was to be able to process the beds without modifications -

- Temperatures >450 °C require removal of the bed filter
- Temperatures >650 °C raise concerns related to melting Al heat tx foam



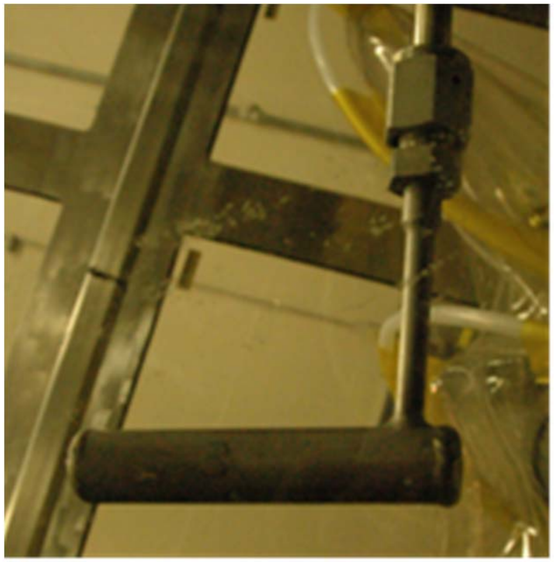
# Approach

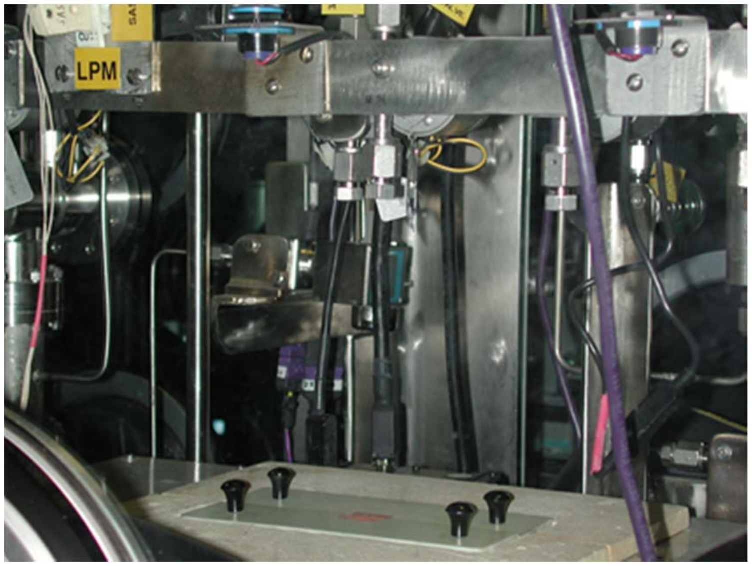
- Determine baseline gas release properties of tritium aged LANA by heating in an inert gas at temperatures up to 1000 °C with 60 minute hold points at 400, 500, 600, 700, or 1000 °C
- Repeat gas release testing using a dilute oxygen gas
- Obtain SEM, XRD, and TEM results on as-received material, material heated to 1000 °C in both inert and dilute oxygen, and selected other samples

# Sample Background

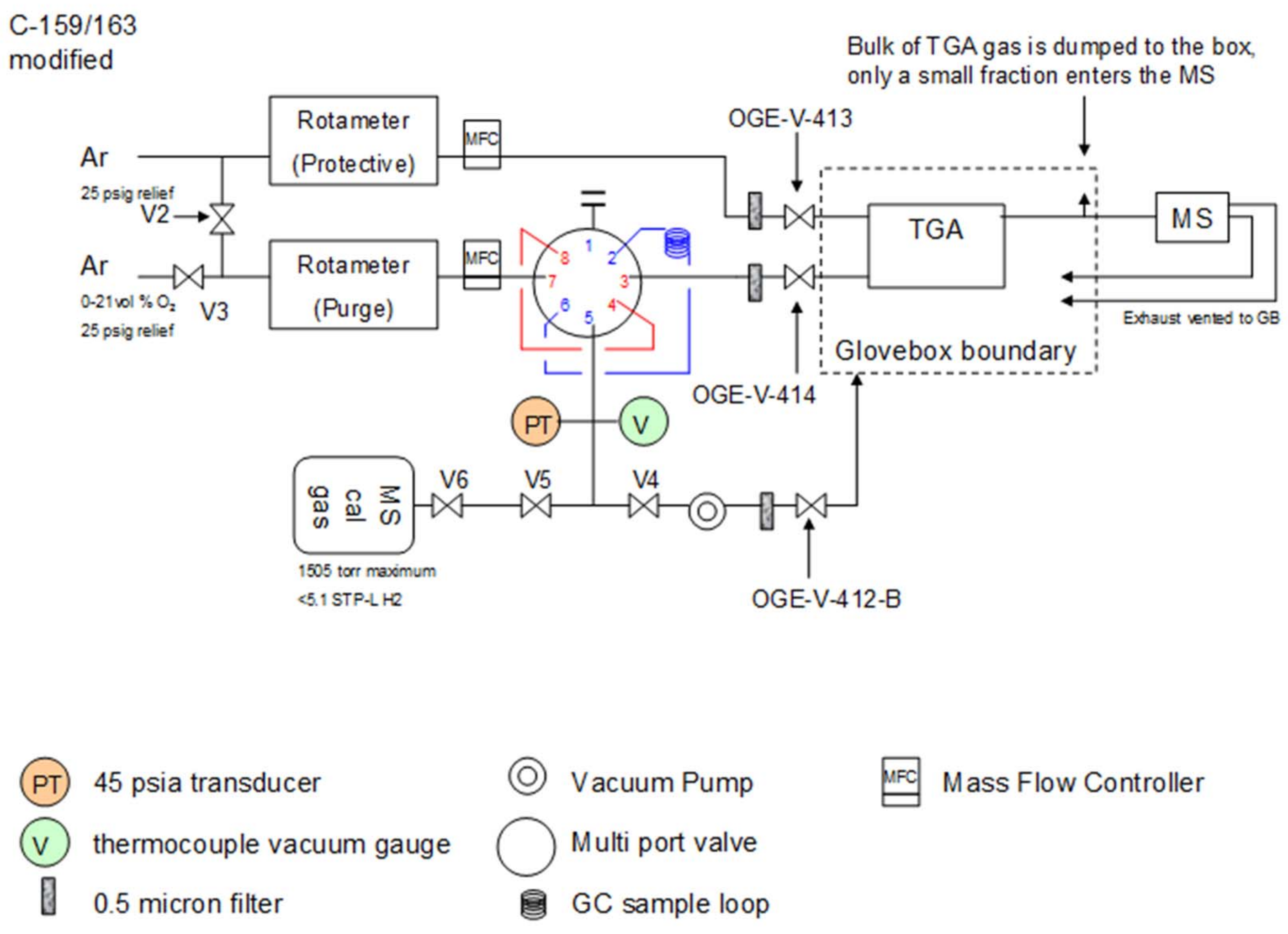
LANA.75 sample was selected from the Tritium Exposure Program

- Loaded in 1987
- Isotherm collected in 1988, reloaded
- Overpressure sampled in 1995 >99% He-3, reloaded
- Isotherm collected in 2000, not reloaded
- Overpressure sampled in 2002
- Final processing initiated in 2012
  - Isotope Exchange
  - Passivation
  - Recovery
- Transferred to SRNL

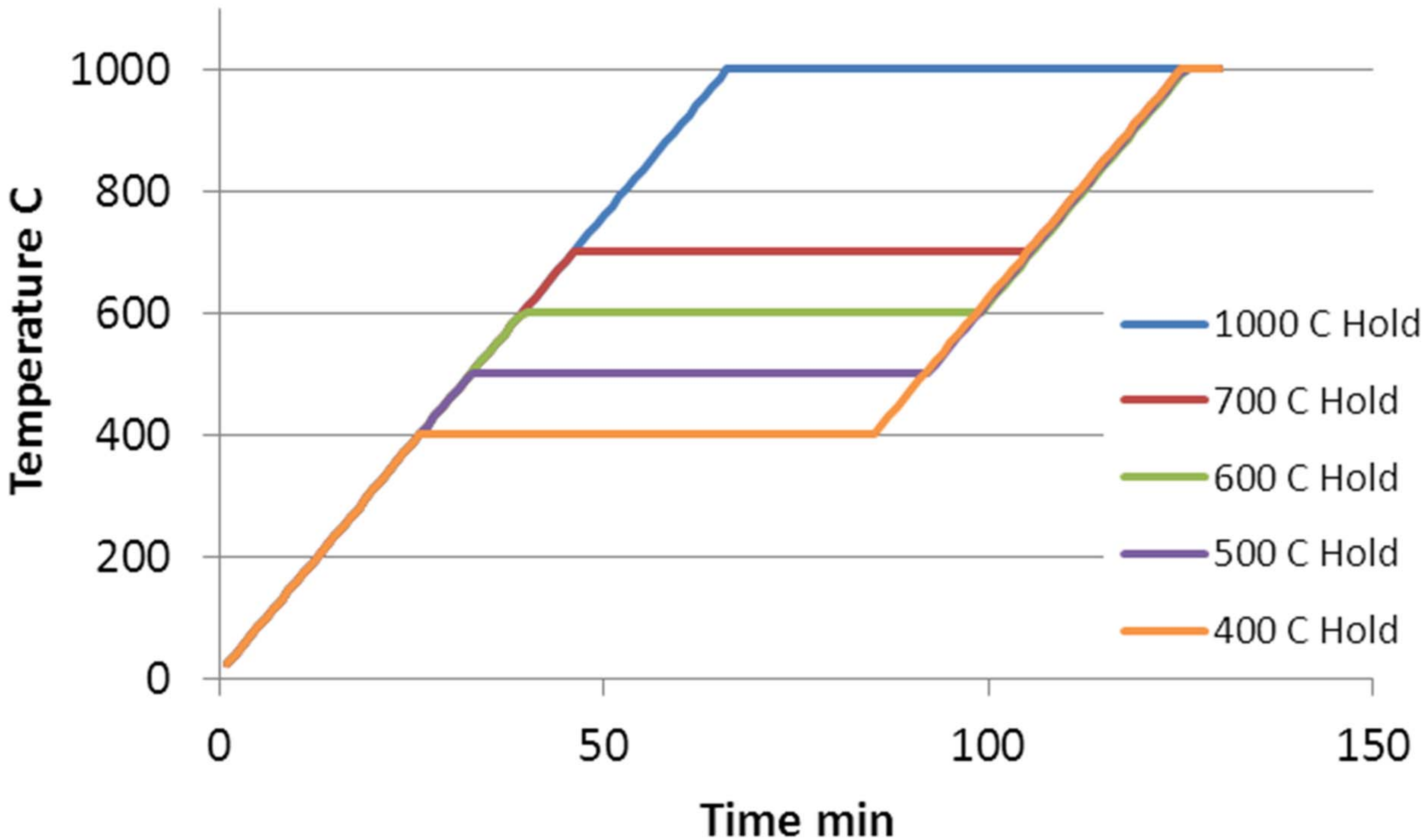




# Testing Apparatus



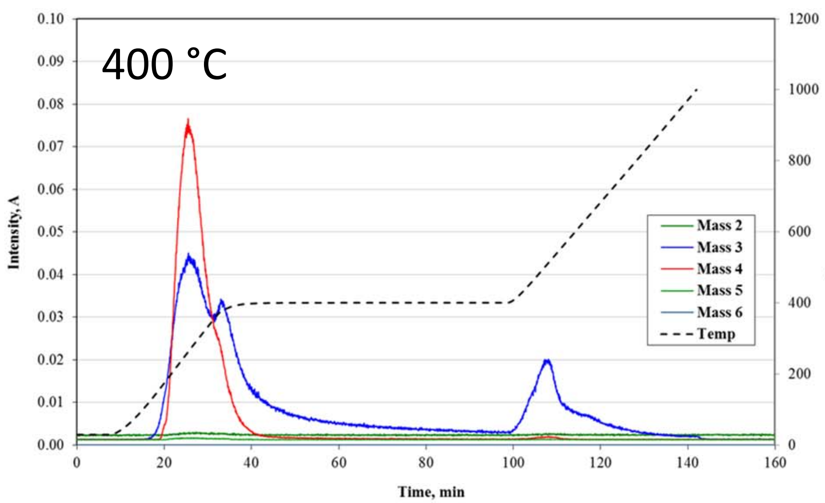
# Temperature Profiles for Tritiated LANA Testing



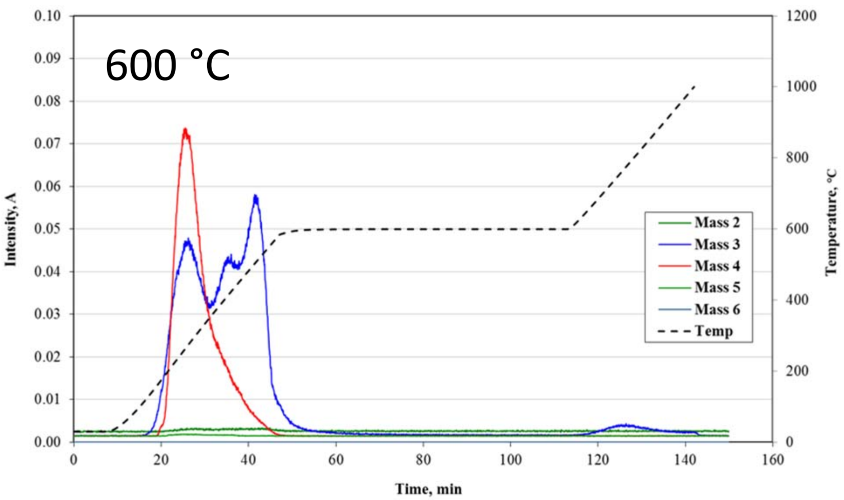
# TGA-MS Results with Argon

- Essentially all of the trapped hydrogen was released by 400 °C
- Progressively more He-3 was released as test temperatures increased

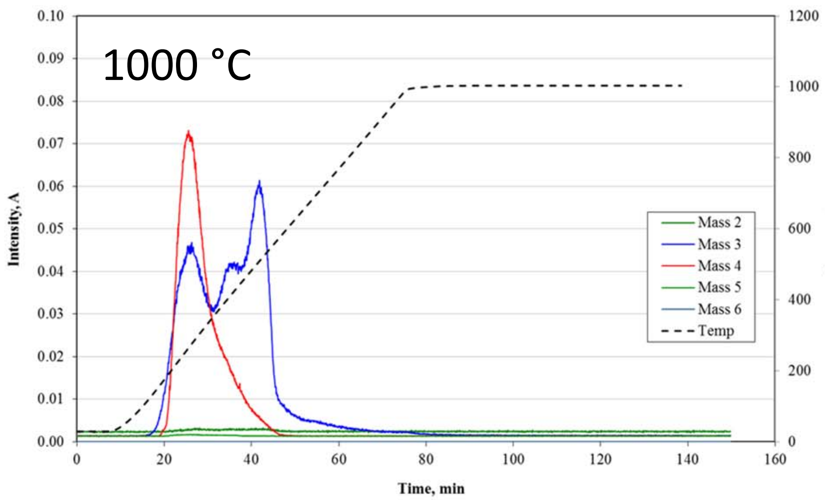
TGA-MS: Feb. 28, 2014 LANA.75 (30.372 mg in argon)




TGA-MS: Mar. 3, 2014 LANA.75 (34.582 mg in argon)

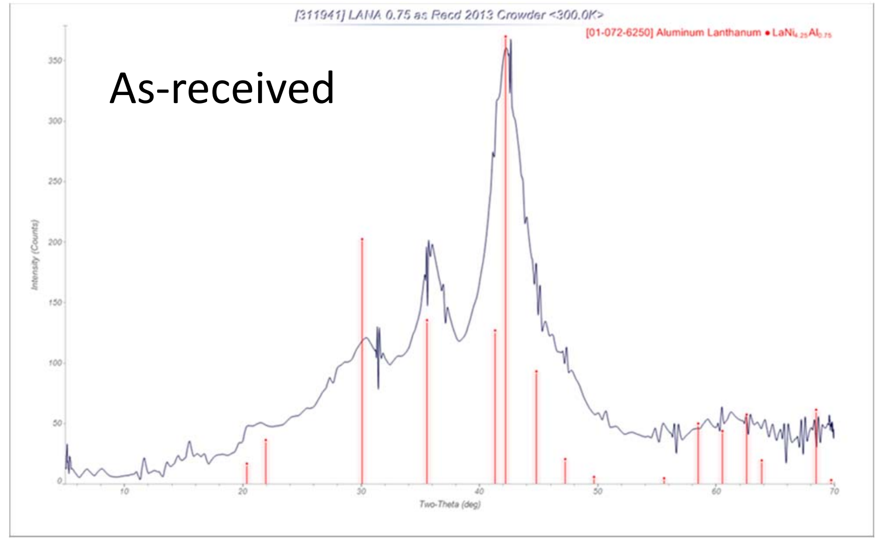


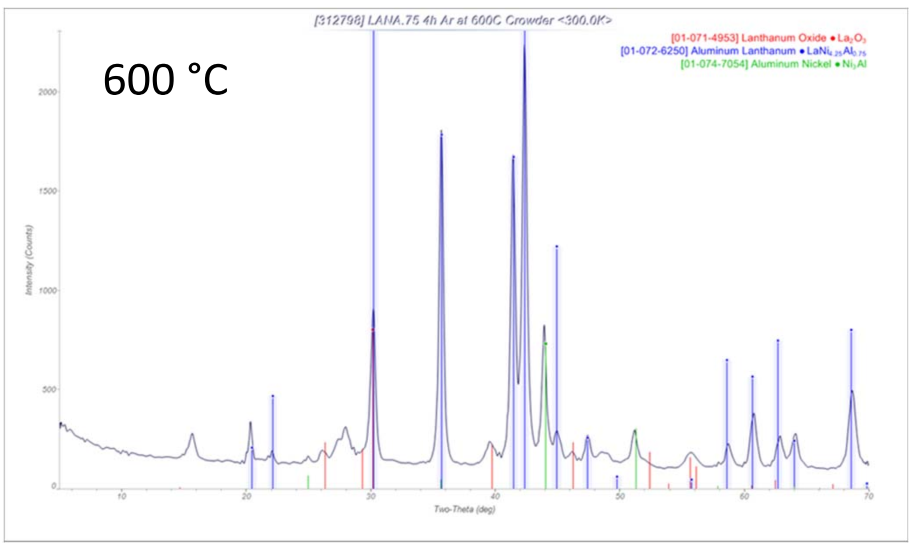

TGA-MS: Mar. 5, 2014 LANA.75 (31.938 mg in argon)

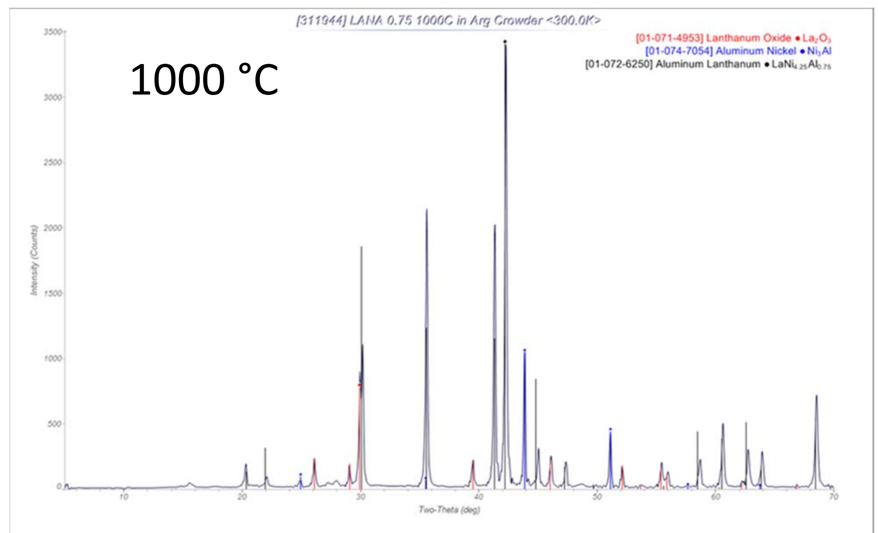


# XRD Results with Argon

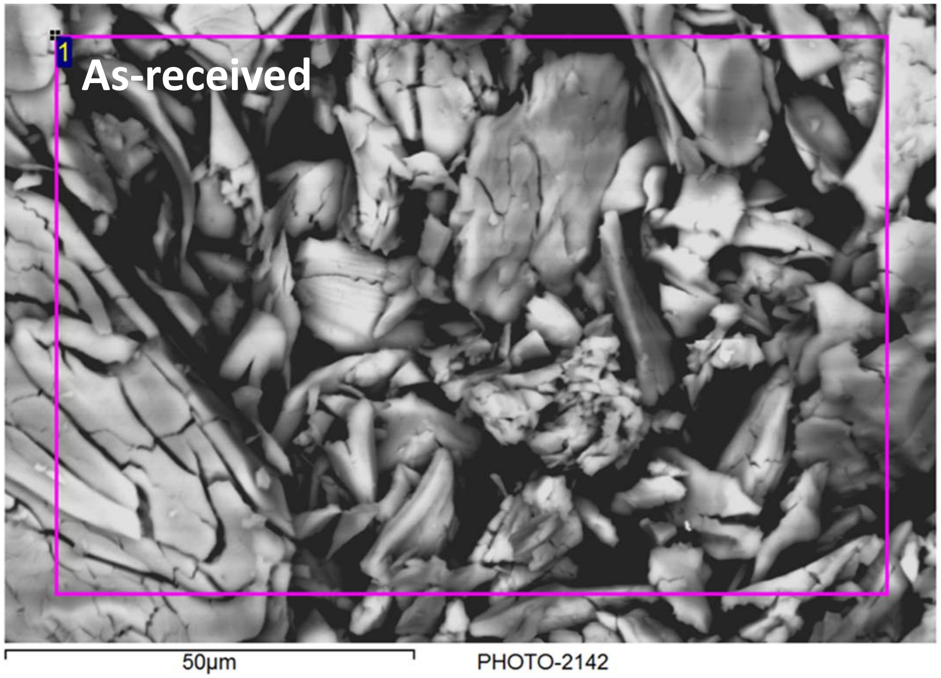
- As-received is largely amorphous
- Sample heated to 600 °C is much more crystalline
- Sample heated to 1000 °C looks essentially like virgin material

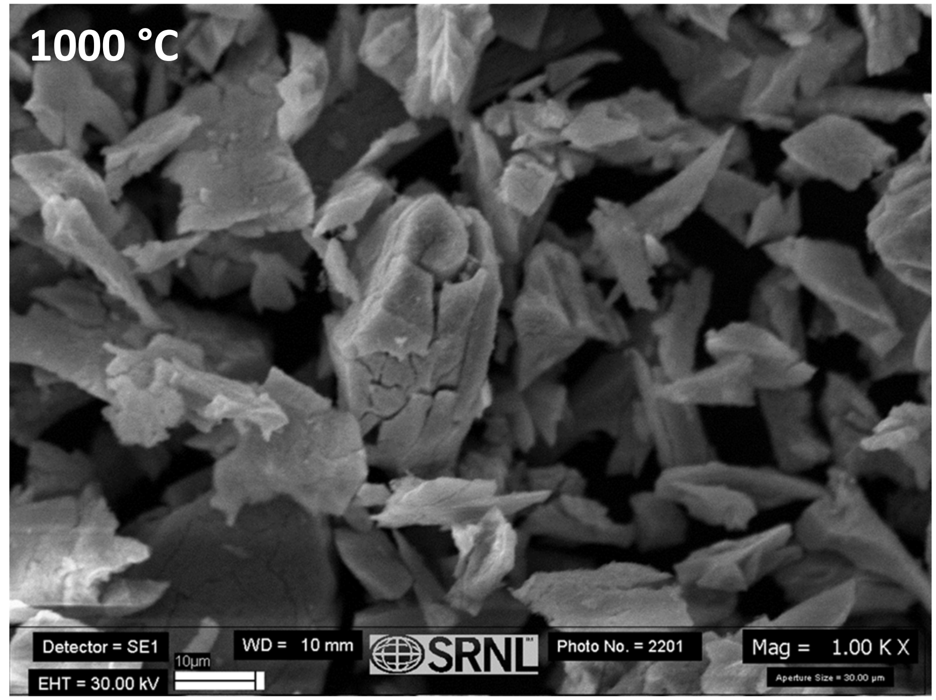


# SEM Results in Argon



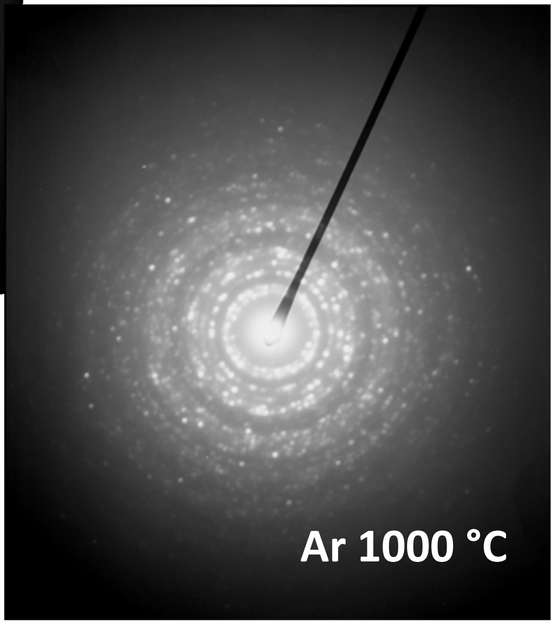




- As-received LANA shows cracked surfaces and rounded edges, probably due to abrasion during multiple isotope exchanges and sample recovery
- LANA heated to 600 °C in Argon shows cracked surfaces and sharper edges, possibly due to fragmentation during evolution of trapped gases

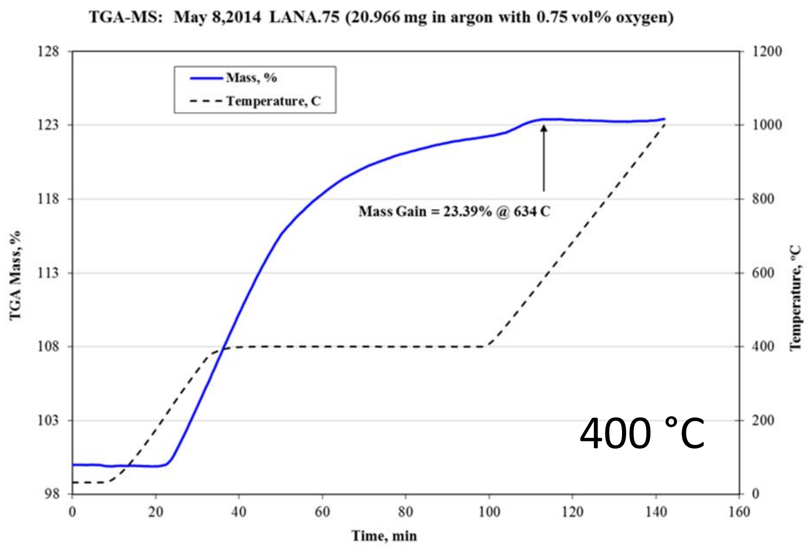
# TEM Results in Argon

- Single crystal protium cycled diffraction pattern showing single crystal reflections with diffraction rings likely due to tiny, randomly oriented lanthanum oxide particles.
- The absence of diffraction spots and the significant background intensity in the As-received TEM may indicate that the LANA.75 is, at least partially, amorphous. This is most likely due to the large number of He-3 bubbles in this material distorting the metal matrix.
- The diffraction pattern from the sample heated in Ar to 1000 °C is indicative of many small grains in a polycrystalline material. Diffraction ring d spacing correlate to LANA.75, lanthanum oxides, and additional unidentified phases/compounds.

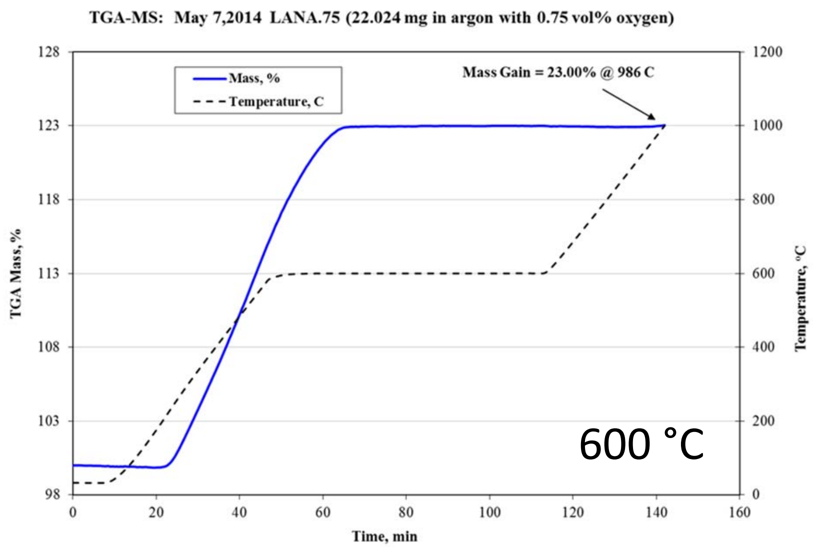


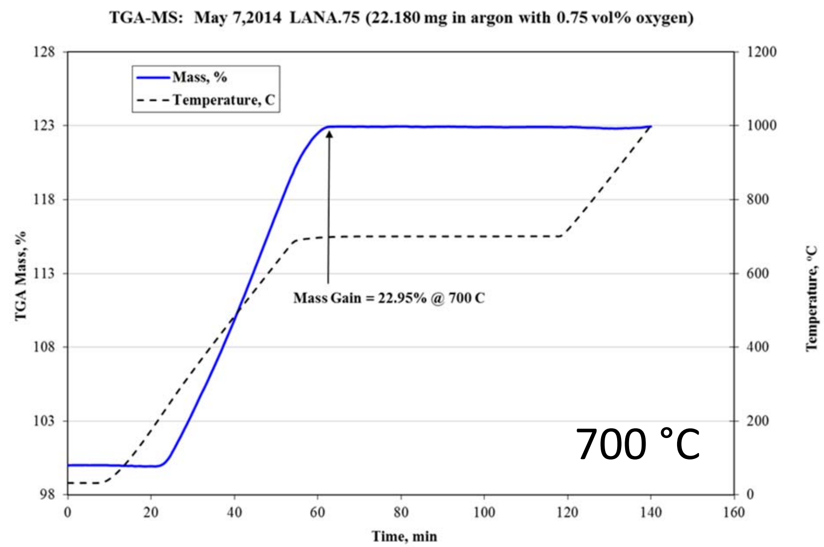


# TGA-MS Results with Argon/Oxygen – Mass Change

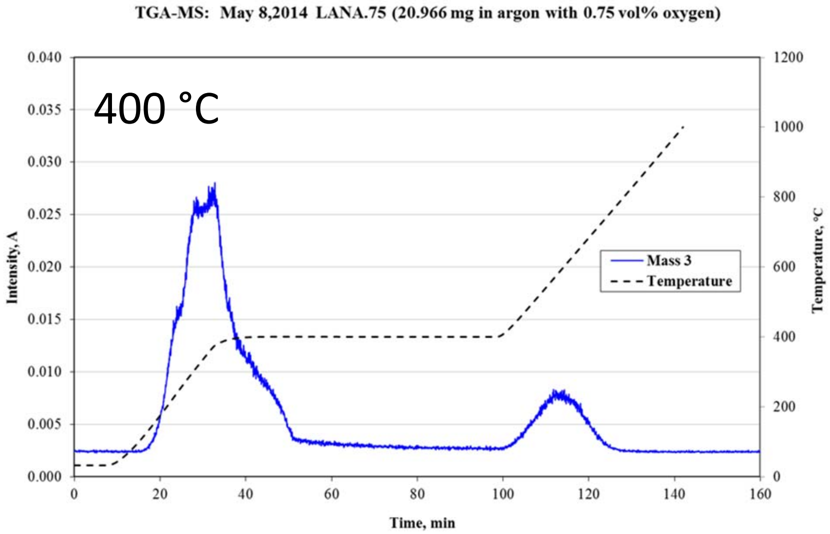



- Essentially all of the LANA sample was oxidized by the end of the 60 minute soak at 400 °C

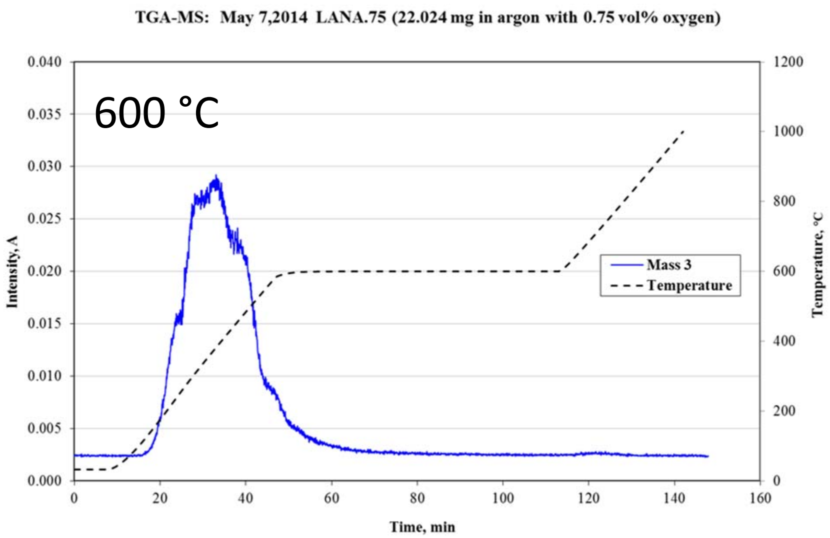


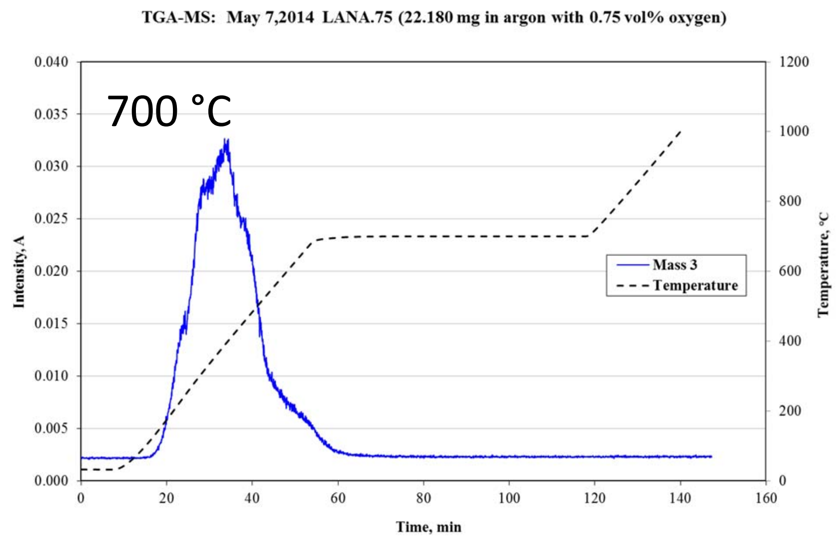



# TGA-MS Results with Argon/Oxygen – Gas Release



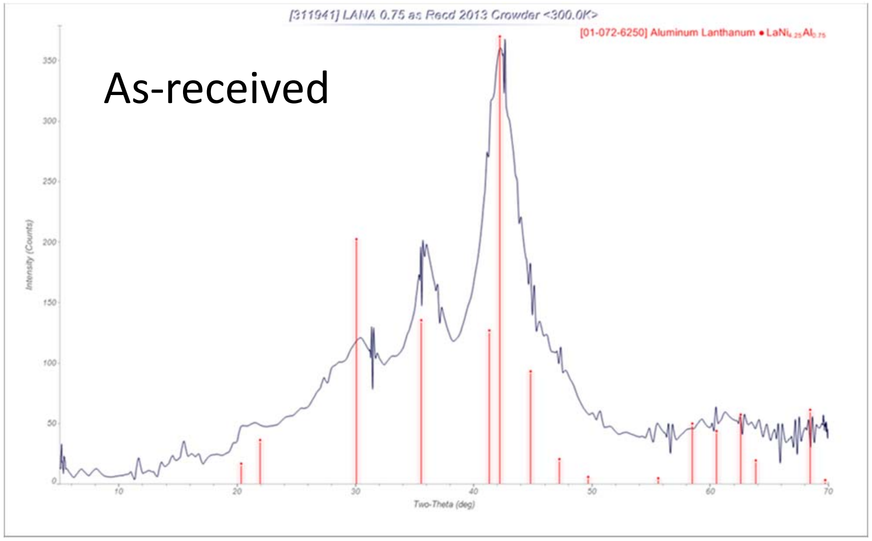

- Hydrogen releases were not quantified because an unknown portion was expected to react to form water.
- Essentially all of the trapped helium was released by 600 °C.
- Hold times above 700 °C were not performed because no additional He-3 release was observed above 700 °C.

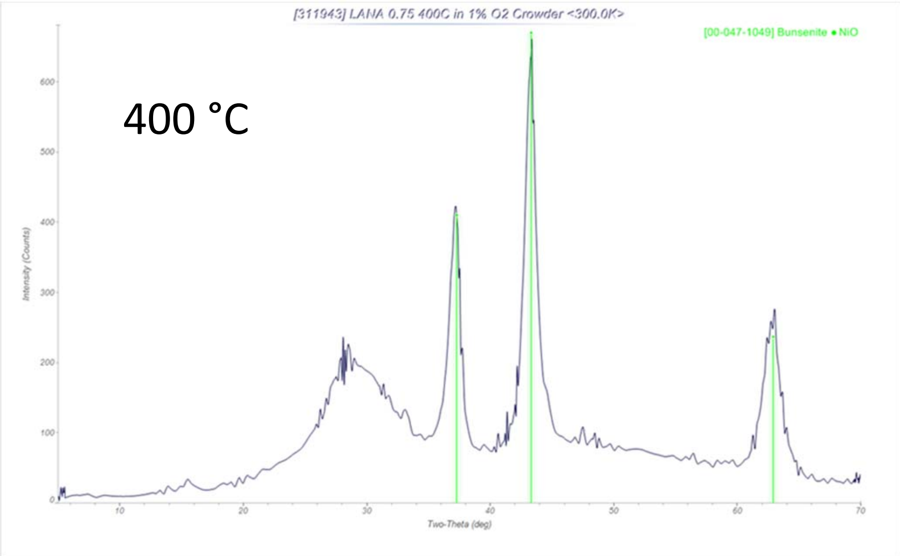


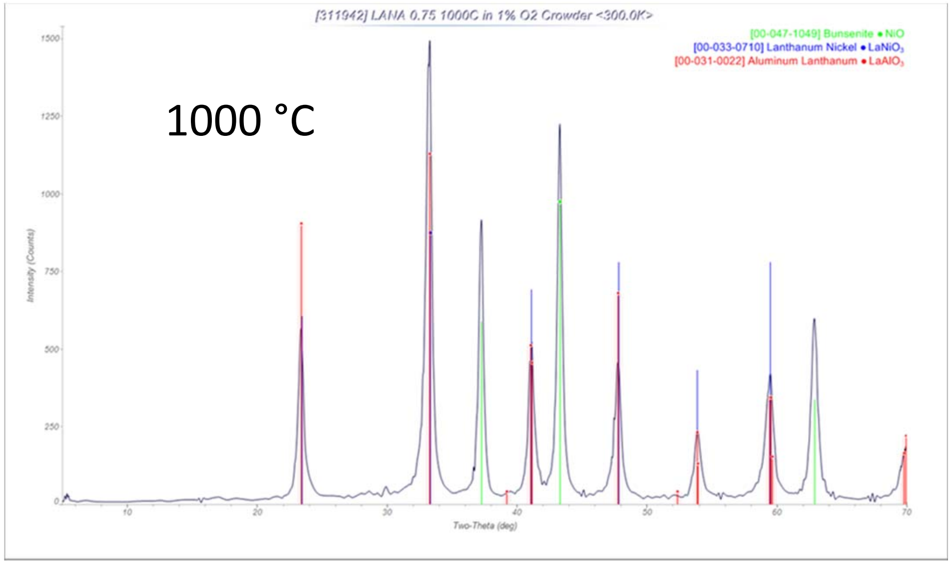



# XRD Results with Argon/Oxygen

- Sample heated to 400 °C suggests the presence of NiO. TGA results indicate nearly the entire sample has oxidized.
- Results from the sample heated to 1000 °C shows a relatively clean spectrum of NiO, $LaNiO_3$, and $LaAlO_3$.



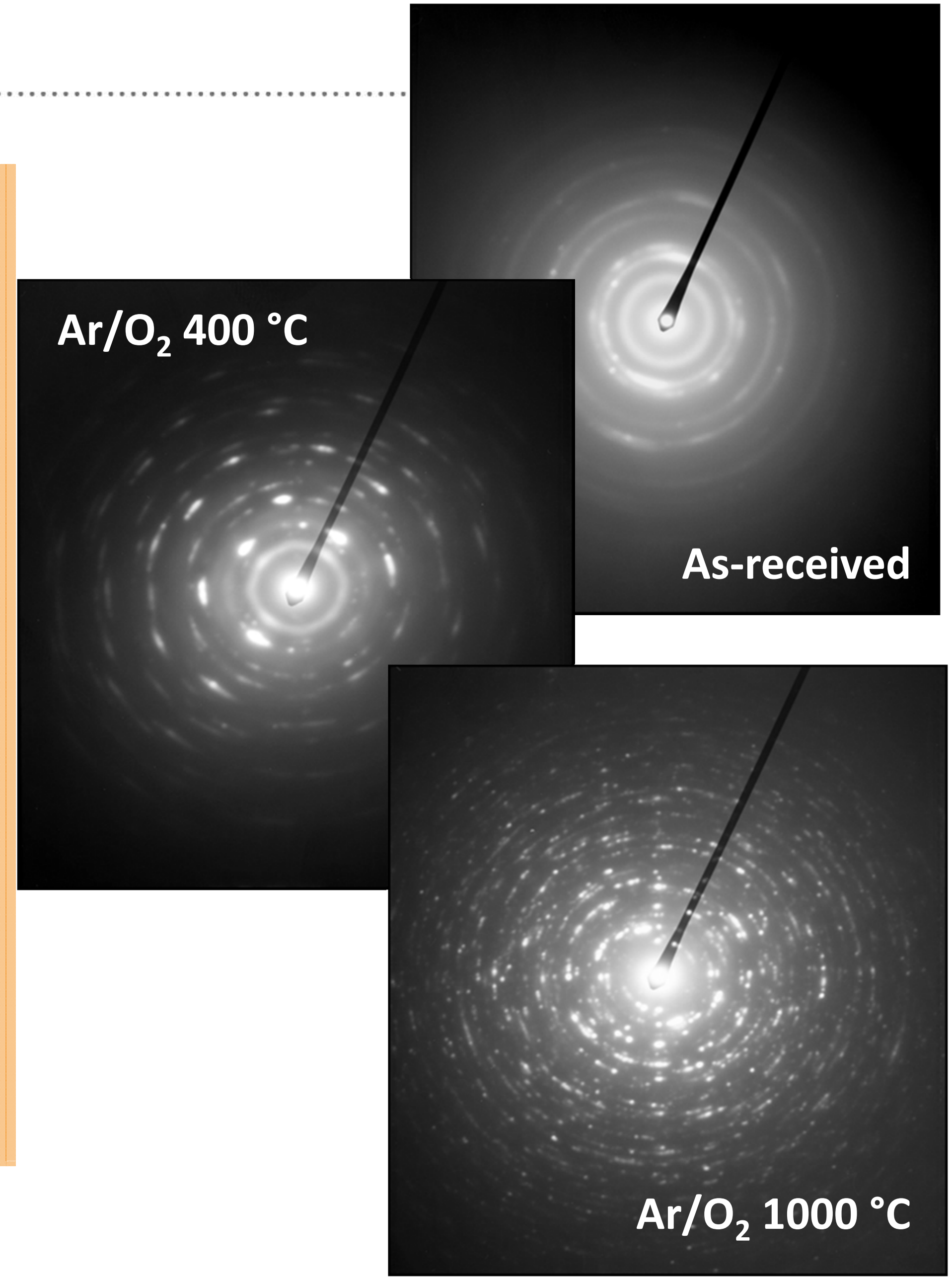



# SEM Results in Argon/Oxygen

Samples heated to 400 °C and 1000 °C in Argon/Oxygen showed a similar morphology. Significant surface cracking and jagged edges. This may have been from surface layers sloughing off during oxidation.


# TEM Results in Argon/Oxygen

- Discrete, arced reflections shown in the sample heated to 400 °C in $Ar/O_2$ can be attributed to diffraction from various oxides and indicates that the material has become more crystalline when compared to the As-received material.
- The complex diffraction pattern shown in the sample heated to 1000 °C in $Ar/O_2$ demonstrates that the material is polycrystalline and that the many small grains are randomly oriented. Diffraction ring d spacing correlate to various constituent oxides and additional unidentified phases/compounds.



# Results

## Argon Test Results

| Hold Temp (°C) | % He-3 Curve at or Below Hold Temp | He-3 (scc/g)[a] | He-3/M Ratio | % $D_2$ Curve at or Below Hold Temp | $D_2$ (scc/g)[b] | D/M Ratio |
|---|---|---|---|---|---|---|
| 400 | 78.9 | 47.0 | 0.143 | 99.3 | 16.5 | 0.100 |
| 500 | 92.9 | 46.0 | 0.140 | 100.0 | 15.2 | 0.092 |
| 600 | 96.7 | 43.3 | 0.131 | 100.0 | 14.5 | 0.088 |
| 700 | 98.4 | 46.4 | 0.141 | 100.0 | 16.0 | 0.097 |
| 1000 | 100.0 | 46.5 | 0.141 | 100.0 | 15.6 | 0.095 |
| 1200 | N/A | 44.7 | 0.136 | N/A | 15.2 | 0.092 |

[a] Assumes the entire mass 3 trace is due to He-3 (no HD)
[b] Assumes the entire mass 4 trace is due to $D_2$ (no HT)

## Argon/Oxygen Test Results

| Hold Temp (°C) | % He-3 Curve at or Below Hold Temp | He-3 (scc/g)[a] | He-3/M Ratio |
|---|---|---|---|
| 400 | 84.8 | 43.1 | 0.131 |
| 500 | 95.2 | 44.3 | 0.135 |
| 600 | 99.5 | 43.2 | 0.131 |
| 700 | 100.0 | 45.1 | 0.137 |

[a] Assumes the entire mass 3 trace is due to He-3 (no HD)

# Conclusions/Recommendations

- Nearly all of the LANA was oxidized during the heat up to 400 °C in an $Ar/O_2$ environment as shown by the TGA mass curve.
- Temperatures on the order of 425 °C are needed to “completely” desorb the trapped hydrogen heel, making passivation of the hydride easier.
- Oxidation of the LANA did not produce the desired effect of liberating all of the trapped gases – only marginally better than an inert bake-out.
- Thermal “recipe” was developed to remove gas from beds under vacuum.
- Baked out beds backfilled with argon and welded closed for final disposal.

# Acknowledgements

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