Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Disclaimer:

Effects of Extreme and Unusual Conditions on LANA Alloys: Year End Report, FY15

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September 30, 2015
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Savannah River National Laboratory™

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LIST OF ABBREVIATIONS

SRNL	Savannah River National Laboratory
TF	Tritium Facility
LANAxx	Where xx is a number. Lanthanum-nickel-aluminum alloy with xx being the subscript on the Al element in the alloy chemical formula, i.e. $LaNi_{4.25}Al_{0.75}$ = LANA75 or $LaNi_4Al$ = LANA100
GfE	Gesellschaft für Elektrometallurgie
TCON	Tritium Consolidation Project, aka Tritium Facility Modernization and Consolidation Project
EXOP	Extreme Operating Conditions
TTP	Technical Task Plan
Erg.	Ergenics
SEM/EDX	Scanning Electron Microscopy with Energy Dispersive X-ray Analysis
XRD	X-ray Diffraction (Powder pattern)
SCR	Specification Change Request
FY	Fiscal Year
HHT	Hydrogen and High Temperature Treatment
TCM	Toxic Chemicals Manifold
ADS	Analytical Development Section

1.0 Introduction

The Extreme Operating Conditions Project (EXOP) was initiated in FY14 based on the desire to investigate the new ability offered by new hydride bed designs to go to higher temperatures than previously possible. This was especially pertinent due to the results of a scoping study that showed significant changes in isotherms after aging at 240 °C under ~400-600 psia of hydrogen for an extended period of ~1 year. Results from that study are shown in Figure 1. A mid-year[1] and year-end report[2] were issued covering the FY14 results obtained that showed significant isotherm changes could be induced in both $LaNi_{4.25}Al_{0.75}$ (LANA75) and $LaNi_{4.15}Al_{0.85}$ (LANA85) by holding a fully-loaded hydride material at 240 °C for various periods of time. A mid-year report for FY15[3] was also issued that added more data and showed that these changes tended to be complete in ~100 days or less. This report adds new information obtained in the second half of FY15, primarily XRD results on retired samples, while retaining the information from the FY15 Mid-Year Report[3].

The EXOP studied samples were made from 4 different lots of two nominal compositions of LANA materials: two LANA85 ($LaNi_{4.15}Al_{0.85}$) materials and two LANA75 ($LaNi_{4.25}Al_{0.75}$) materials. In both types of LANA, one sample was taken from a 'recent' lot of material (the GfE LANA85 and TCON LANA75) and one was from Ergenics produced materials procured in the late 1980's or early 1990's (GfE is the official abbreviation for the company Gesellschaft für Elektrometallurgie. The GfE material was procured in 2008 for use in a R&D prototype bed. TCON designates the Tritium Facility Modernization and Consolidation Project that was also known as the Tritium Consolidation Project which acquired LANA75 for replacement beds with delivery in 2004.)

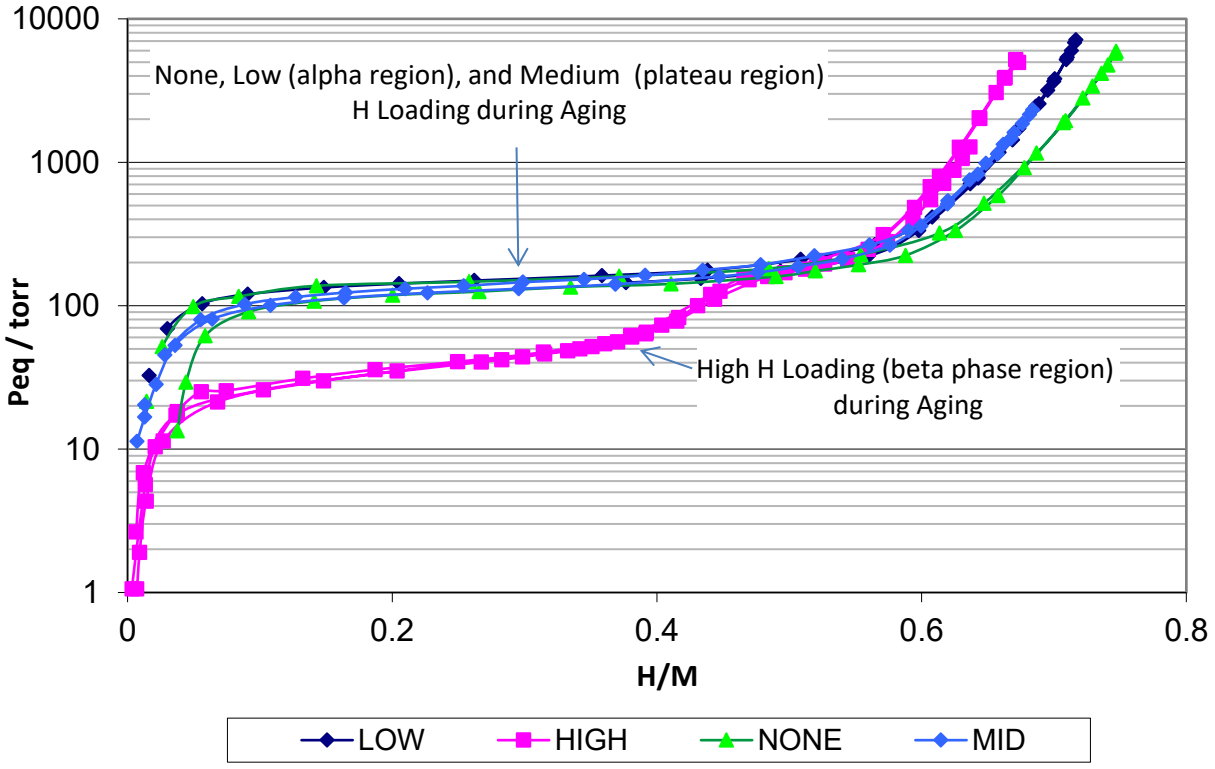
The EXOP objectives are to more fully investigate this phenomenon and determine the minimum conditions needed to induce isotherm changes. It was found that changes could be induced quickly at 240 °C, and that lesser changes could also be noted quickly with heat treatment at 150 °C. It was noted that these changes tended to be complete in ~100 days at 240 °C. It was further discovered that the LANA75 and 85 materials reacted to the high pressure hydrogen heat treatments (HHT) somewhat differently, where the LANA75 samples developed split plateaux isotherms showing plateau pressure lowering in the low H/M region initially and the high H/M region later, whereas the LANA85 materials only displayed plateau pressure lowering with no splitting observed.

In FY15, the EXOP was extended to fill in details of the rate of change of these materials. The original Technical Task Plan (TTP) had proposed the use of 3 temperatures to facilitate numerical quantification of the degradation rates. Based on an inquiry made at the oral presentation of the FY14 year-end report, the original 150 °C studies were abbreviated in favor of 300 °C treatments. In FY15, the early time period (first few weeks) of HHT have been probed for the materials, and studies of the materials' responses to HHT at 300 °C have been investigated.

In addition, the original TTP specified that the effects of poisons, such as CO and S, would also be investigated. A new manifold, designated the Toxic Chemicals Manifold (TCM), was constructed to handle the dosing gases for these studies because the gases are toxic. The pressure protection calculations required to define the needed pressure relief devices for this manifold were completed and

pressure safety devices were ordered and received. Because of timing and funding issues however, the TCM was not activated and no work on poisons was accomplished.

Figure 1. 80°C H_2 Isotherms on Four LANA85 Samples Thermally Aged for ~1 year



Since issuing the FY15 mid-year report[3], the majority of the samples have been retired, which entails passivation and disassembly of the sample. The samples were then submitted to ADS for XRD and SEM analyses. Some attempts were made to study the kinetics issue reported previously, but a software upgrade issue hampered that effort and made the data collected difficult to use (see section below). The Figures used in the Mid-year report[3] are repeated here essentially unchanged simply to consolidate all results into this summary Final Report. Except for the poisons study, the overall objectives of the FY14 TTP have been met.

2.0 Results

Table 1 provides a summary of the samples used/prepared thus far in this study, defining where the different LANA75 and 85 lots are used.. All isotherms in this report have been offset to align the β-phase sections. This is because clear changes in working Q/M capacity were noted. This may be attributed to the formation of trap sites, as noted in the literature, which should be taken as a suggestion until such time as the existence of Q in trap sites is shown in these materials.

Table 1. Sample ID and status as of FY15 year end

Sample ID	Material	HHT Protocol	Aging Periods Completed	Last Period Isotherm Complete?	Current Status
LANA85_GFE5	GfE LANA85	monthly, 240°C	12	Y	Retired
LANA85_EXOP1	Erg. Lot 1138	monthly, 240°C	3	Y	Retired
LANA75_EXOP2	Erg. Lot 1316	monthly, 240°C	3	Y	Retired
LANA75_EXOP3	TCON blend	monthly, 240°C	3	Y	Retired
LANA75_EXOP4	Erg. Lot 1316	weekly, 240°C	2	y	On hold
LANA75_EXOP5	TCON blend	weekly, 240°C	3	Y	Retired
LANA85_EXOP6	GfE LANA85	monthly, 150°C	3	Y	Retired
LANA85_EXOP7	Erg. Lot 1138	-	0	NA	Assembled
LANA75_EXOP8	TCON blend	monthly, 150°C	3	Y	Retired
LANA75_EXOP9	Erg. Lot 1316	-	0	NA	Assembled
LANA85_EXOP10	GfE LANA85	-	0	NA	Retired
LANA75_EXOP11	TCON blend	300 °C studies	2	Y	Retired
LANA75_EXOP12	TCON blend	300 °C studies	2	Y	Retired
LANA75_EXOP13	TCON blend	300 °C studies	2	Y	On hold

GfE LANA85

Two samples of GfE LANA85 material have been studied to date, not including the 4 scoping study samples. The first is LANA85_GFE5, which has seen thermal aging under high hydrogen pressure at 240 °C for approximately 380 days, and is the basis for the data points in Figure 2 (unchanged from mid-year report[3]). Figure 2 presents the 240 °C plateau pressure plot, showing that the cumulative aging time has now exceeded that of the scoping study sample. This has produced the anomalous result that the dual plateaux structure observed in the scoping study sample has not been reproduced, for reasons unknown (see the Discussion section below for some speculative reasons). In addition, the new data has demonstrated that the plateaux had actually reached a maximum lowering at ~100 days.

The second GfE material sample, LANA85_EXOP6, has undergone 3 aging periods of approximately 1 week long, the isotherms for which are presented in Figures 3a-c. These isotherms illustrate the possible 'trapping' phenomenon. Fig. 3c adds an additional decade on the pressure scale to show the α–phase behavior with H_2 in virgin material.

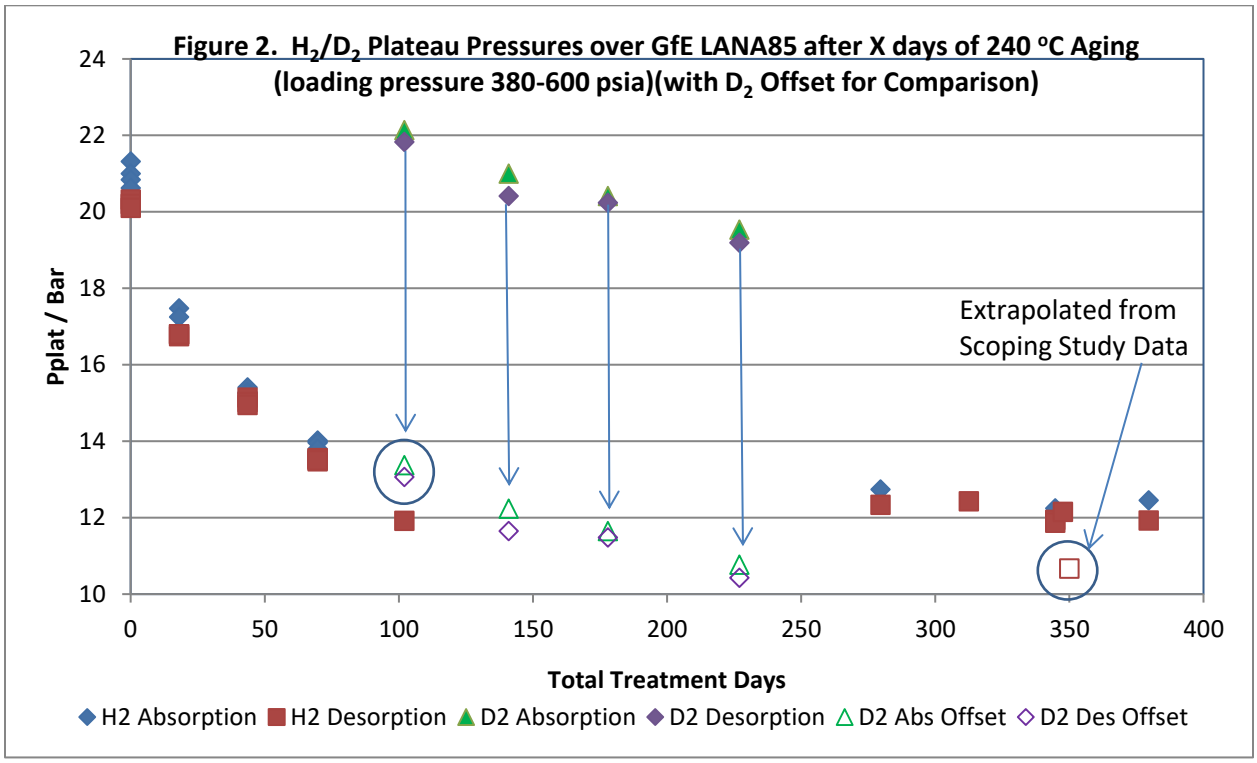


Figure 3a. 80C H2 isotherms on LANA85_EXOP6 (GfE)

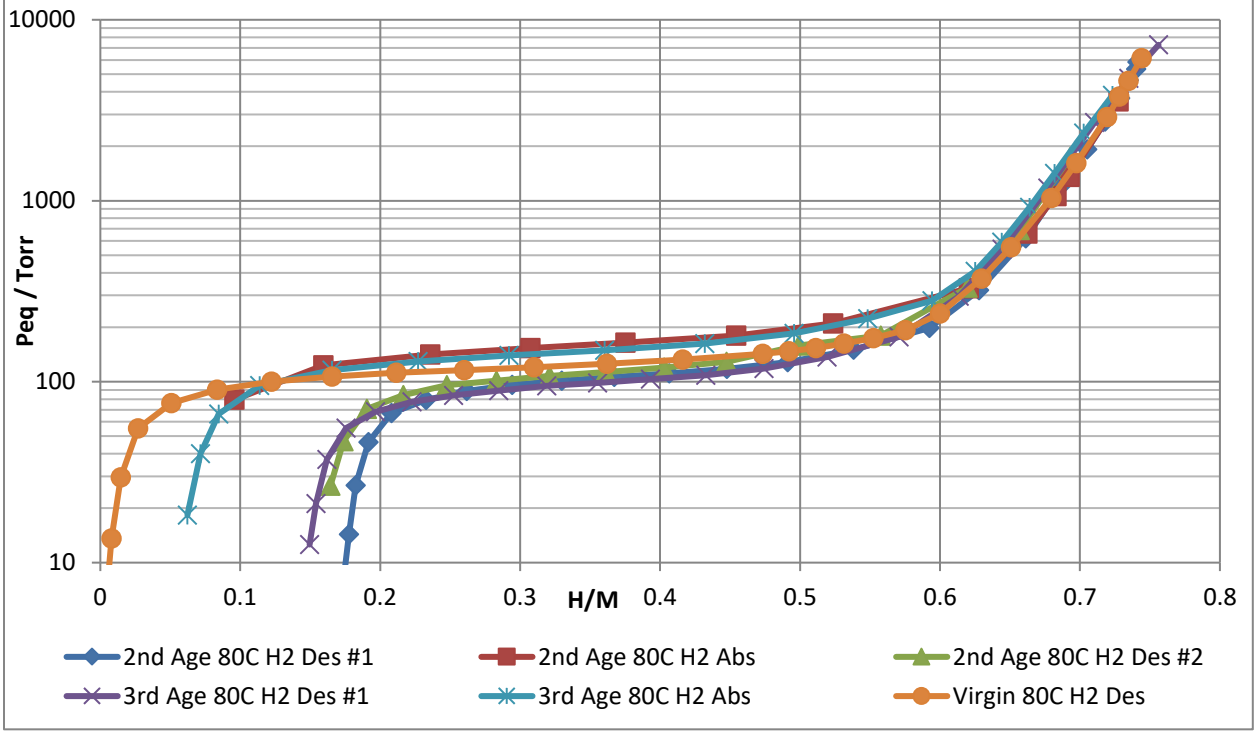
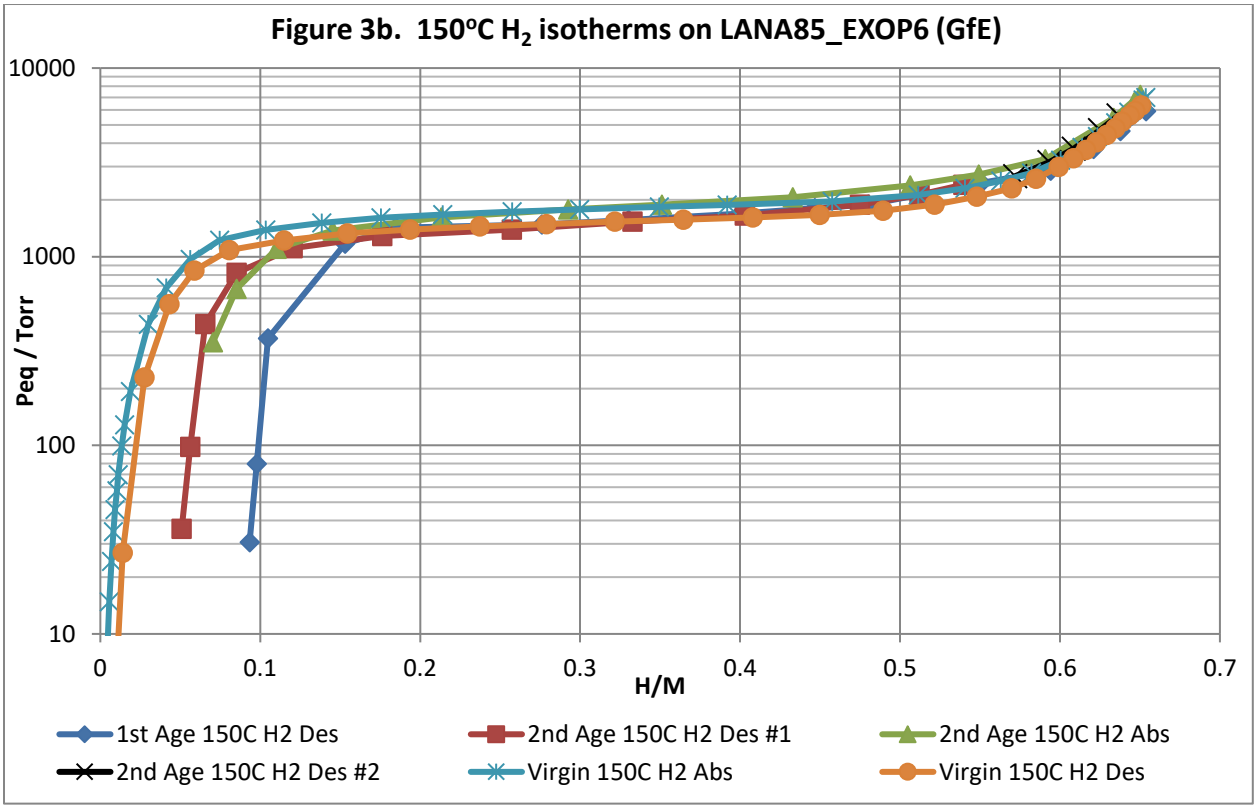
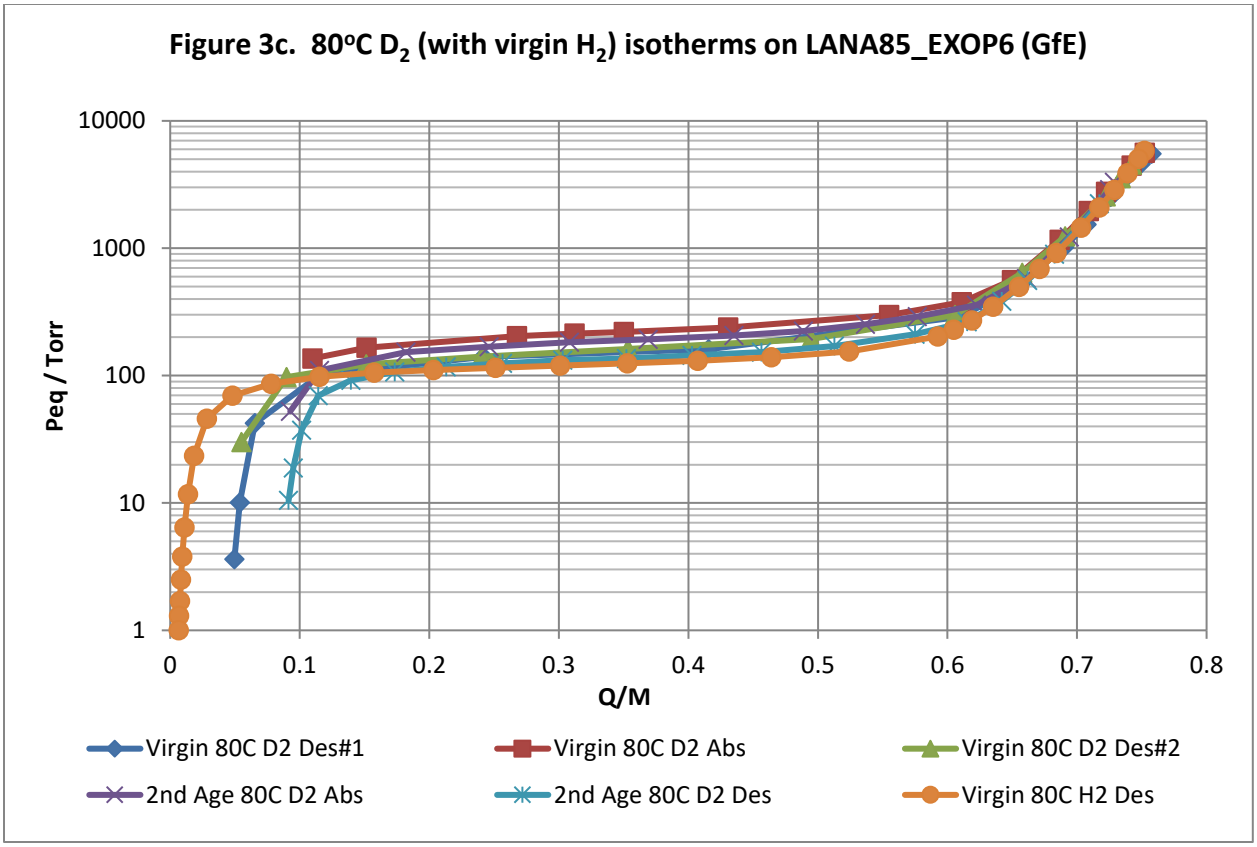


Figure 3b. 150°C H_2 isotherms on LANA85_EXOP6 (GfE)

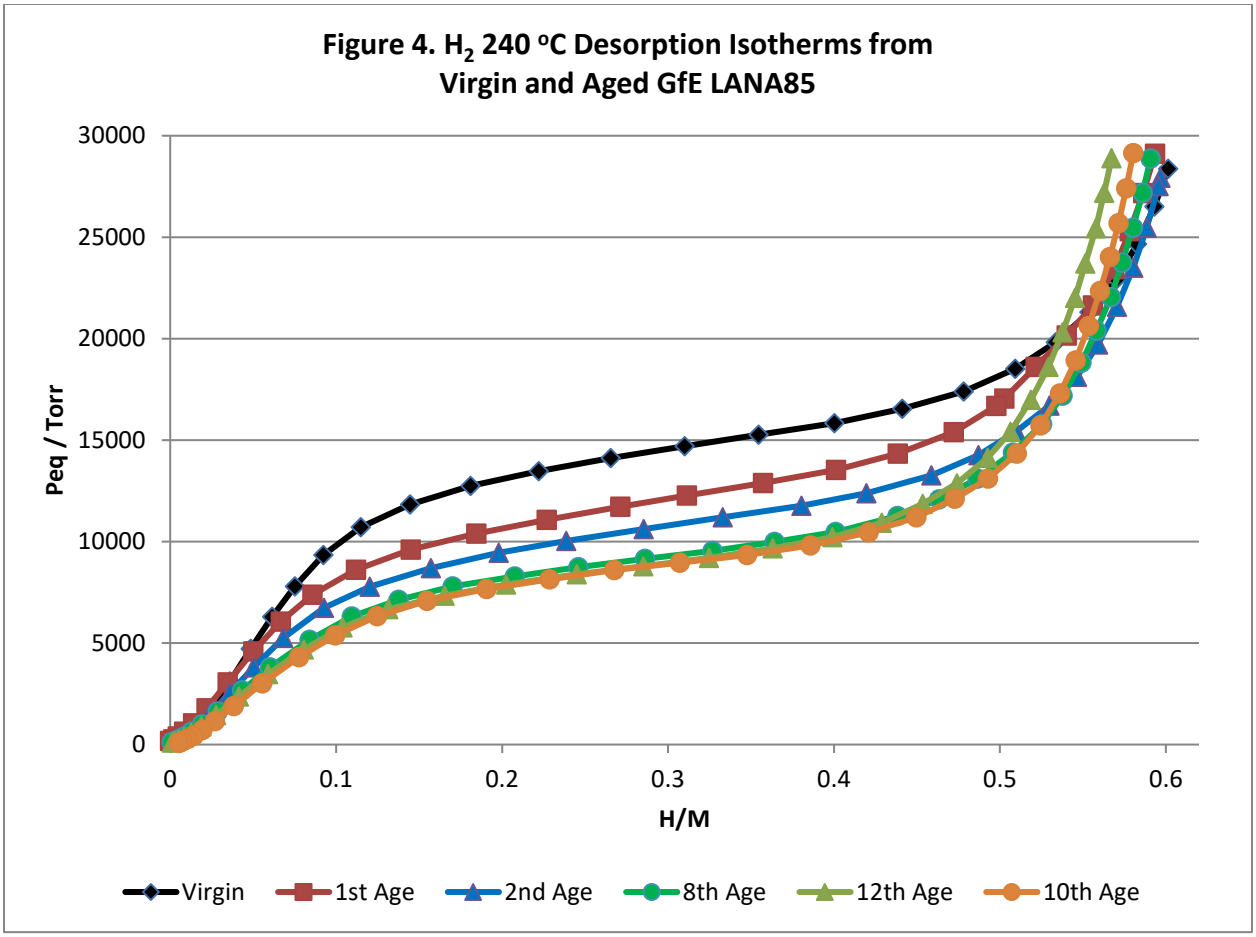




The Hydrogen and High Temperature Treatments (HHTs) have shown very little effect in this case. A possible very slight plateau pressure lowering may be present, but the observed differences might be attributable to sample-to-sample and/or run-to-run variation.

These results can be contrasted with the observed behavior in the GFE5 sample, where clear shifts in plateau pressure occur early on, but are minimal thereafter, as shown in Figure 4 . In this case, the shift between HHT #1, #2, and #3 is large and lesser thereafter, up to HHT #12. Note that in Figure 4 the isotherms have been matched to the same end point in the α–phase, with a resulting mismatch at the starting point in the β–phase. In this case, there is minimal indication that the capacity loss is due to the formation and destruction of 'trap sites'. The literature also reports capacity loss in some studies. Therefore, we believe the capacity loss indicated by the smaller maximum H/M loading seen in the 12th Aging Period sample's isotherm is real and we have plotted it as such.

The XRD data for the retired samples GFE5 and EXOP6 are shown in the XRD discussion below. The EXOP10 sample was prepared and activated but never thermally treated. This sample was subsequently retired and its XRD results are used to illustrate the changes arising from the activation process alone (see below and in Appendix B). SEM data were reported in Appendix A of the FY15 Mid-year report[3], which is retained in this report unchanged.



Lot 1138 LANA85

To date, only one sample of this material has been investigated, LANA85_EXOP1 via 240 °C HHT broken into ~month-long periods. Three aging periods have been completed and diagnostic isotherms collected for each. In Figure 5, we plot the plateau pressure determined from 80 °C isotherms collected after each aging period. The full plateau pressure lowering seems to have completed much faster than was observed with GfE LANA85, reaching the minimum in approximately 30 days. Figures 6a, b, and c show the protium and deuterium isotherms collected. Figure 6b is an enlargement of the 80 °C isotherm results, which aids in noting the slight capacity decrease and the apparent shortened isotherm obtained from the sample after its 3rd aging period (H_2 isotherms only). XRD results are included in the section below.

Figure 5. LANA85_EXOP1 80C H2 Isotherm Plateau Pressure vs. Total Treatment Days

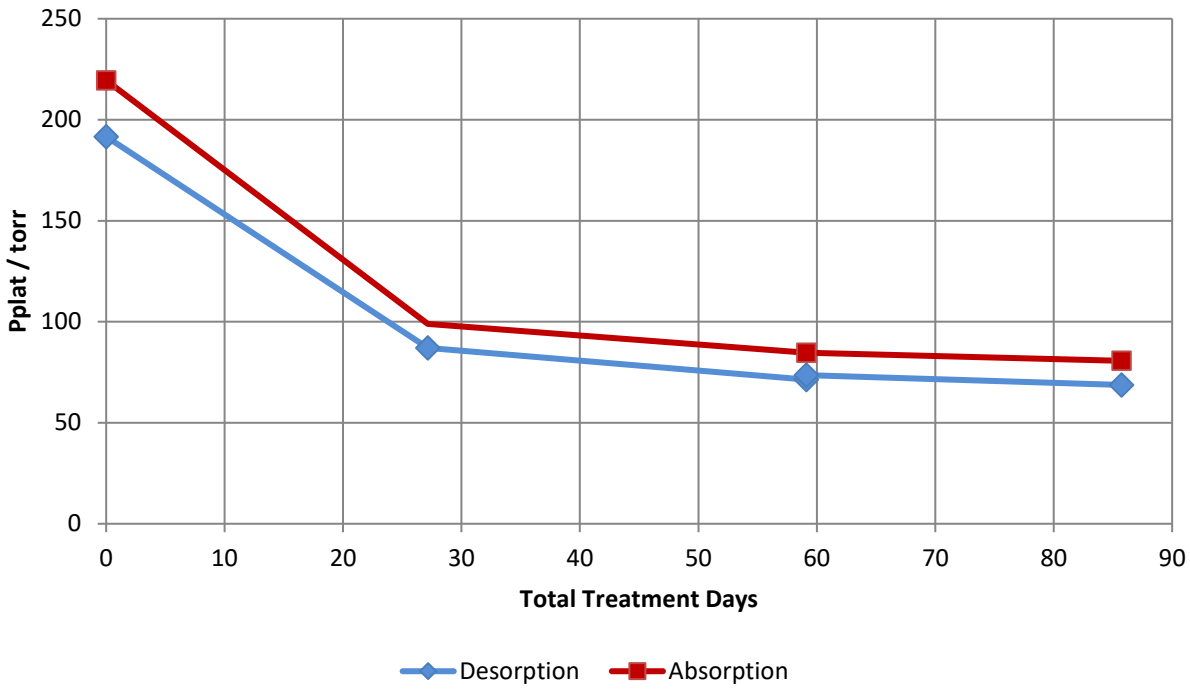


Figure 6a. H_2 Isotherms (80, 200, 240 °C) on LANA85_EXOP1

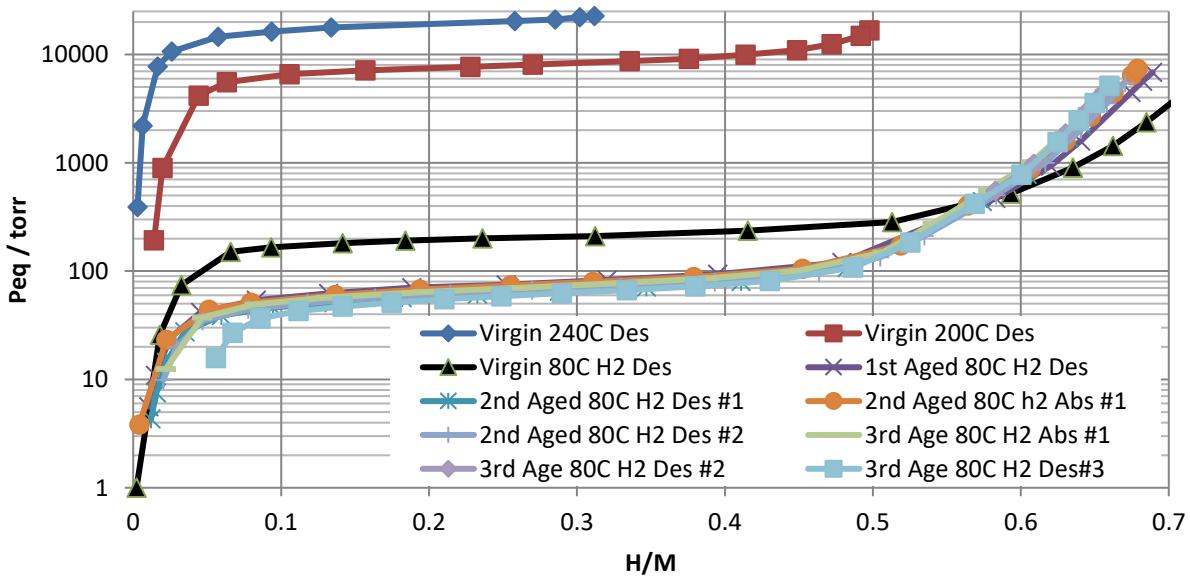


Figure 6b. Expanded 80°C H_2 Isotherms on LANA85_EXOP1

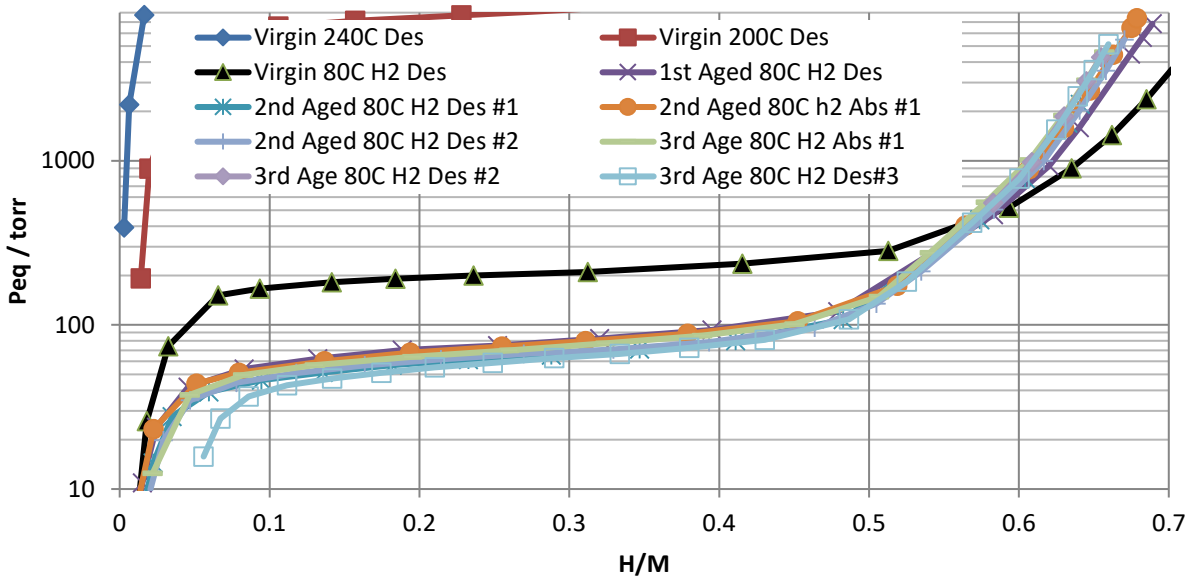
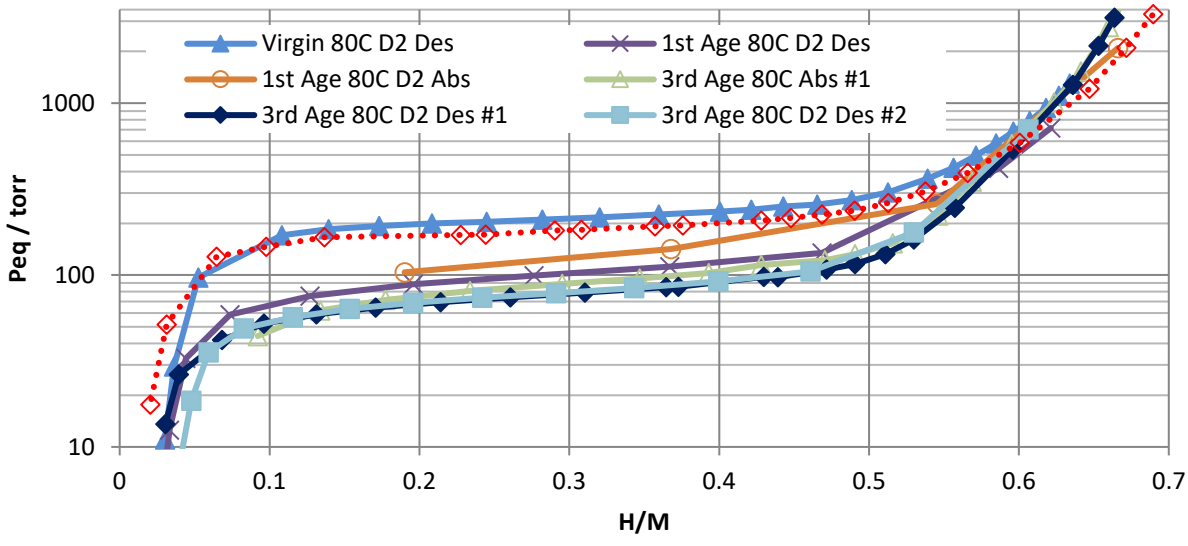


Figure 6c. 80°C D_2 Isotherms on LANA85_EXOP1 (with virgin 80C H_2 Des - (dotted line))

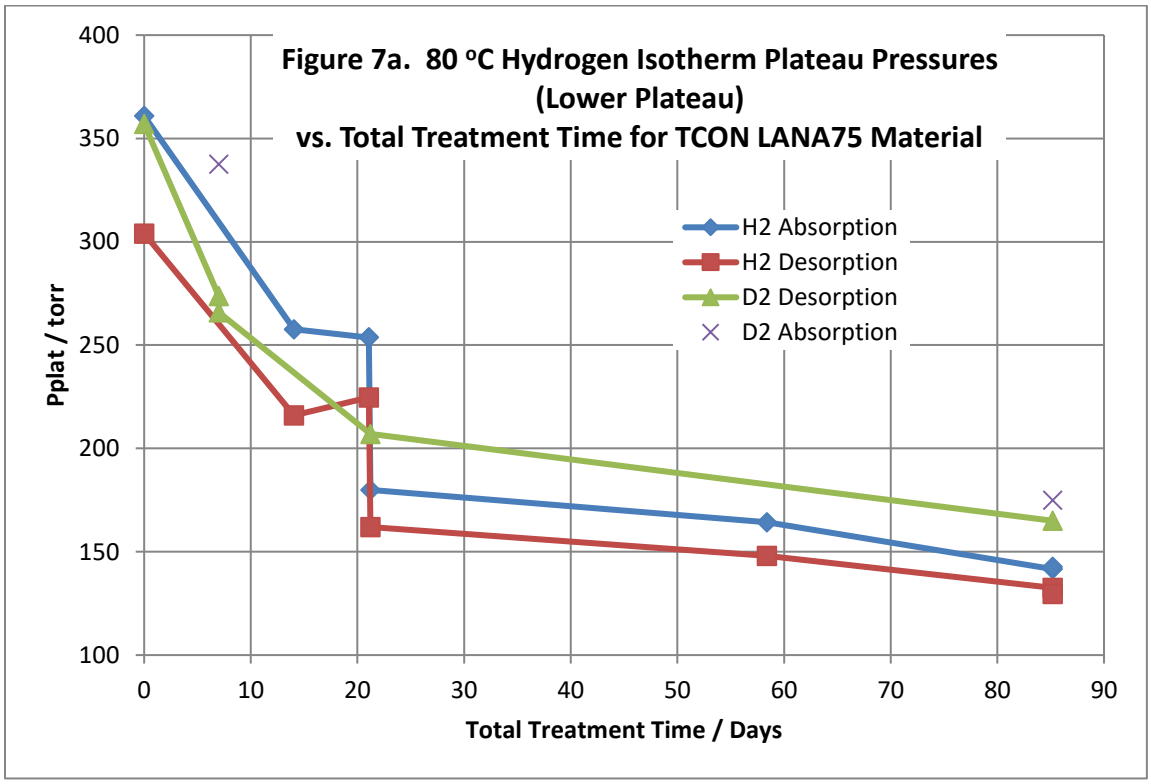


TCON LANA75

The TCON LANA75 material used in these studies was obtained from an archival 100 g sample taken at the time the material was acquired (c. 2004). The bulk of the material was used to fill replacement beds that were installed in the TF process. *Both* LANA75 materials used in these studies produced split plateau isotherms at select temperatures, in contrast to the LANA85 materials. This is unexpected as the compositional difference between LANA85 and LANA75 is relatively small.

Figure 7a shows the combined data for plateau pressure lowering of the *lower* pressure plateau observed in the isotherms of both TCON LANA75 samples aged at 240 °C. Figure 7b shows the data for LANA75_EXOP3 and Figure 7c shows the data for LANA75_EXOP5. The lowering appears to be nearly complete at 21 days for LANA75_EXOP3, but LANA75_EXOP5 seems to be complete even earlier, which leads to a difference in appearance of Figure 7a from the other materials used in this study (Figures 2, 5, and 14). This will be discussed more in the Discussion section.

Figure 8 shows the set of 80 °C isotherms acquired from sample LANA75_EXOP3, which saw ~month-long treatments, except the first treatment which was conducted for 21 days. Sample LANA75_EXOP5 was exposed to high loadings of H for 3 week-long periods at 240 °C. Figure 9 shows the deuterium isotherms for LANA75_EXOP5 acquired at several temperatures (see the Figure's key).



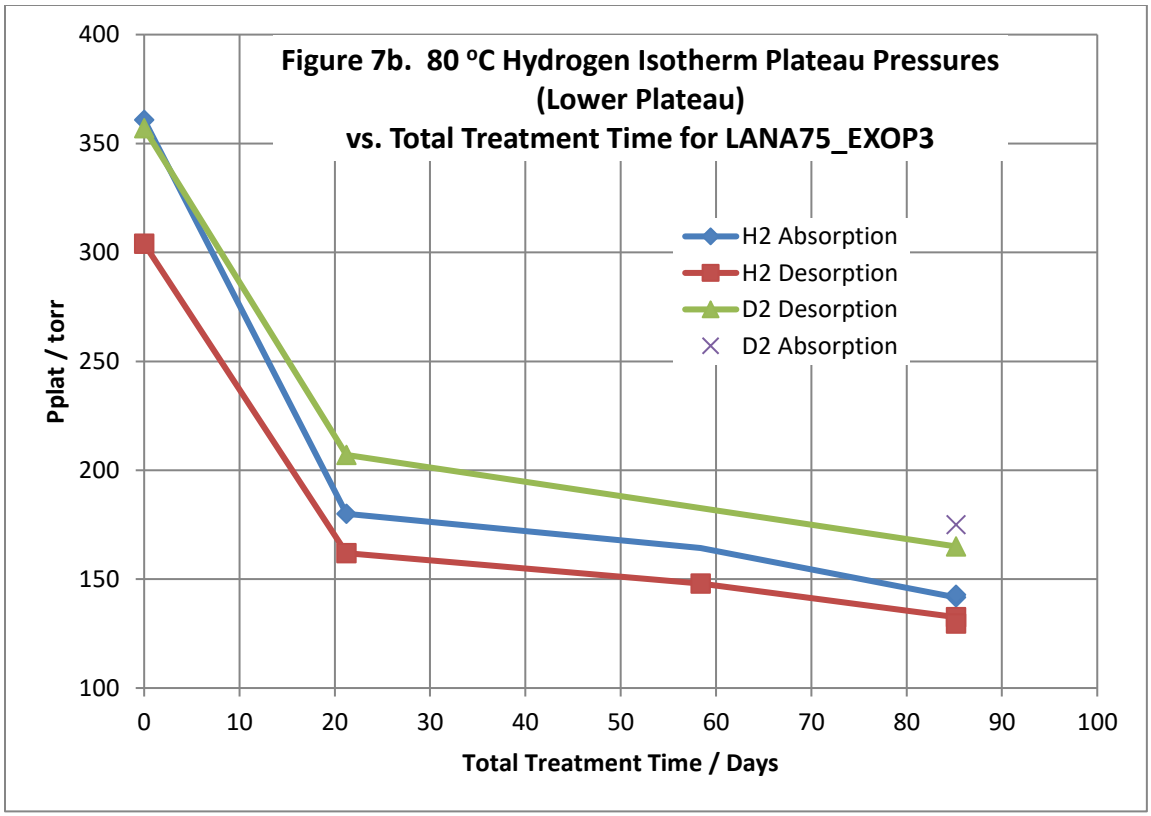


Figure 7b. 80 °C Hydrogen Isotherm Plateau Pressures
(Lower Plateau)
vs. Total Treatment Time for LANA75_EXOP3
H2 Absorption
H2 Desorption
D2 Desorption
D2 Absorption
Pplat / torr
Total Treatment Time / Days
400
350
300
250
200
150
100
0
10
20
30
40
50
60
70
80
90
100

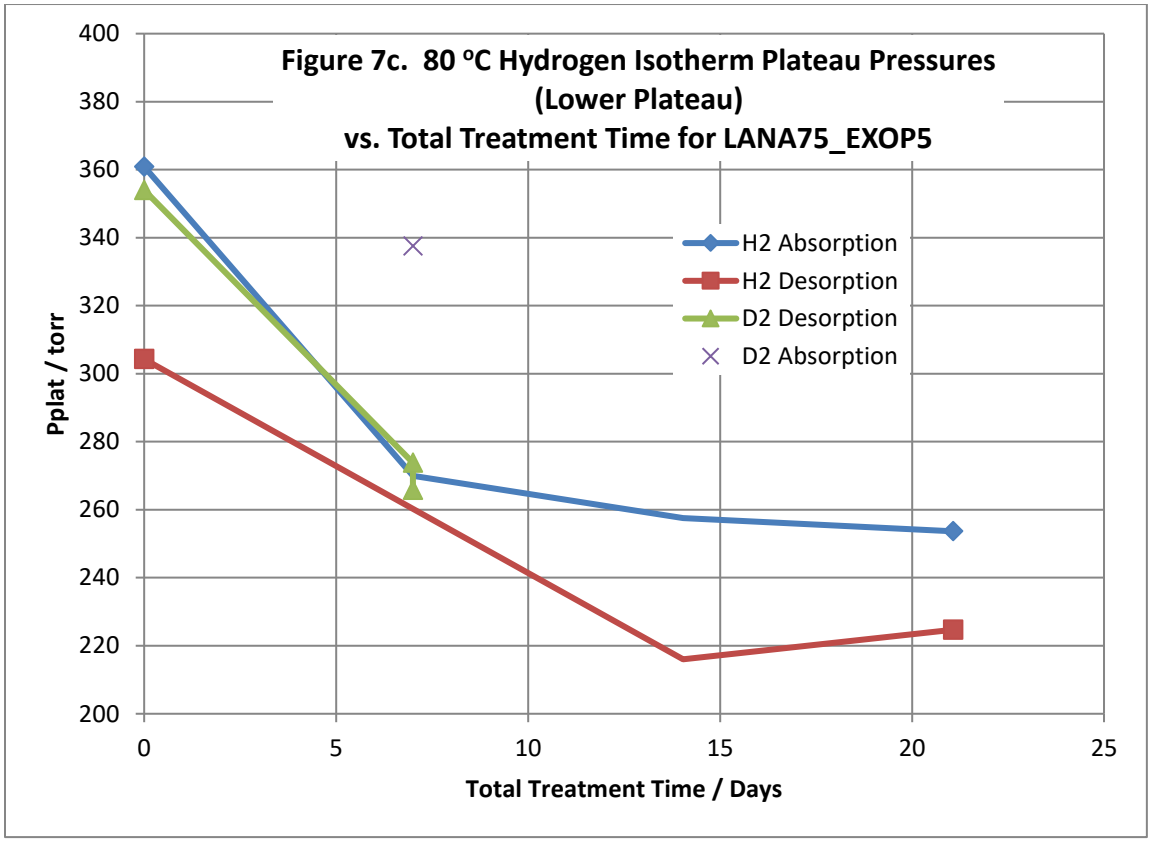


Figure 7c. 80 °C Hydrogen Isotherm Plateau Pressures
(Lower Plateau)
vs. Total Treatment Time for LANA75_EXOP5
H2 Absorption
H2 Desorption
D2 Desorption
D2 Absorption
Pplat / torr
Total Treatment Time / Days
400
380
360
340
320
300
280
260
240
220
200
0
5
10
15
20
25

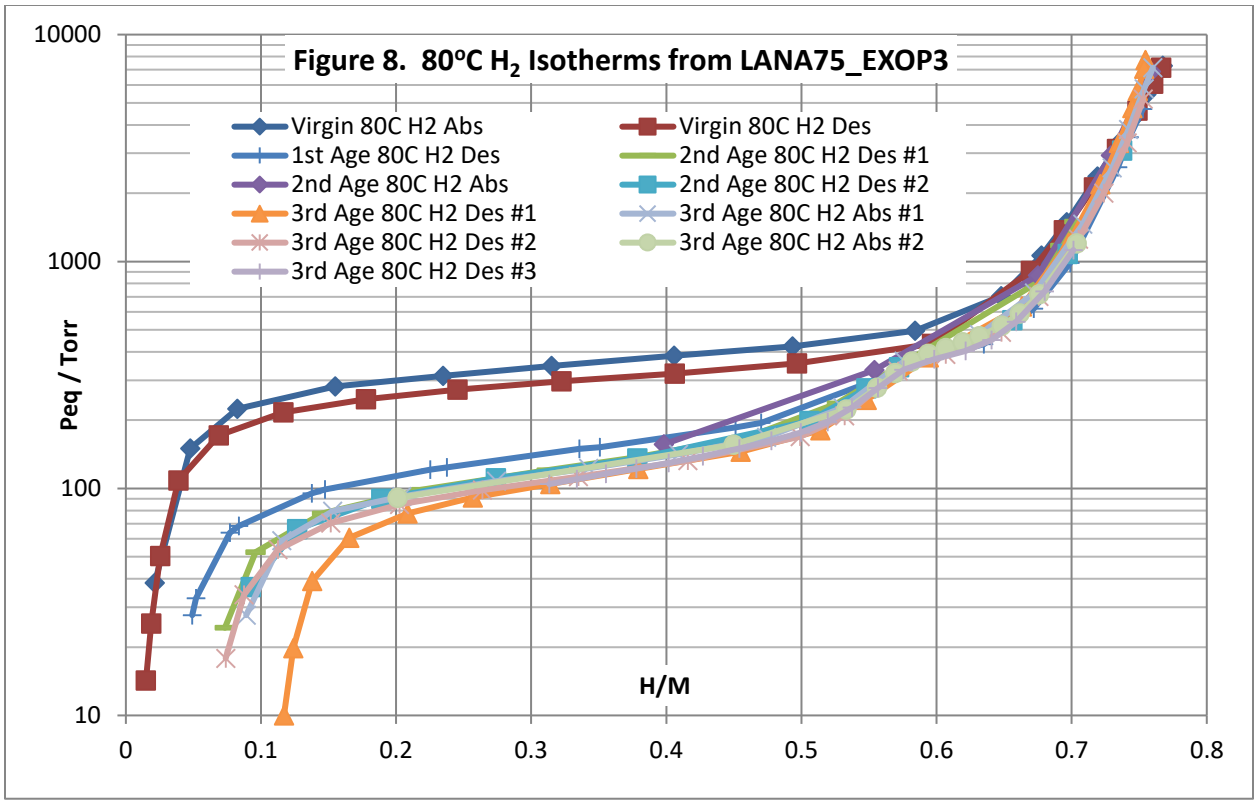


Figure 8. 80°C H_2 Isotherms from LANA75_EXOP3
Virgin 80C H2 Abs
Virgin 80C H2 Des
1st Age 80C H2 Des
2nd Age 80C H2 Des #1
2nd Age 80C H2 Abs
2nd Age 80C H2 Des #2
3rd Age 80C H2 Des #1
3rd Age 80C H2 Abs #1
3rd Age 80C H2 Des #2
3rd Age 80C H2 Abs #2
3rd Age 80C H2 Des #3
Peq / Torr
H/M
10000
1000
100
10
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8

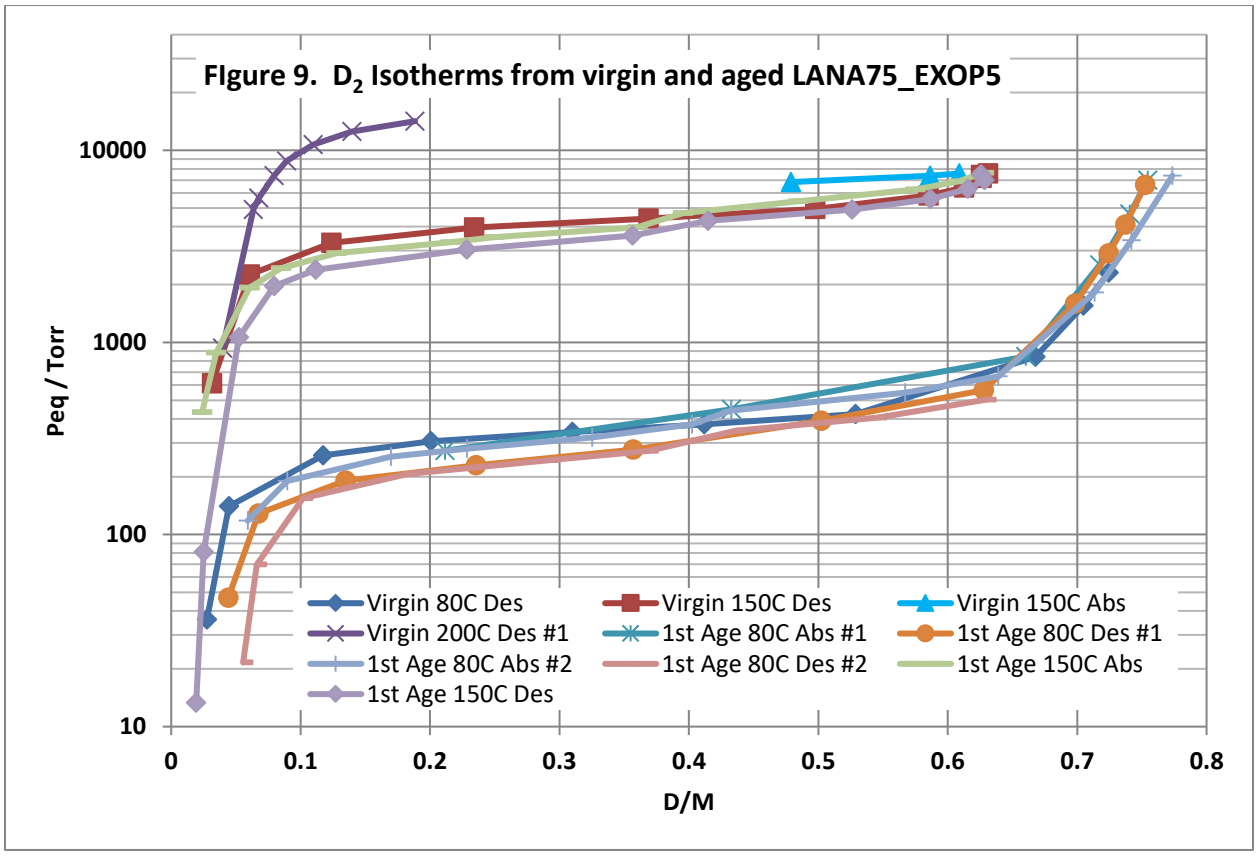
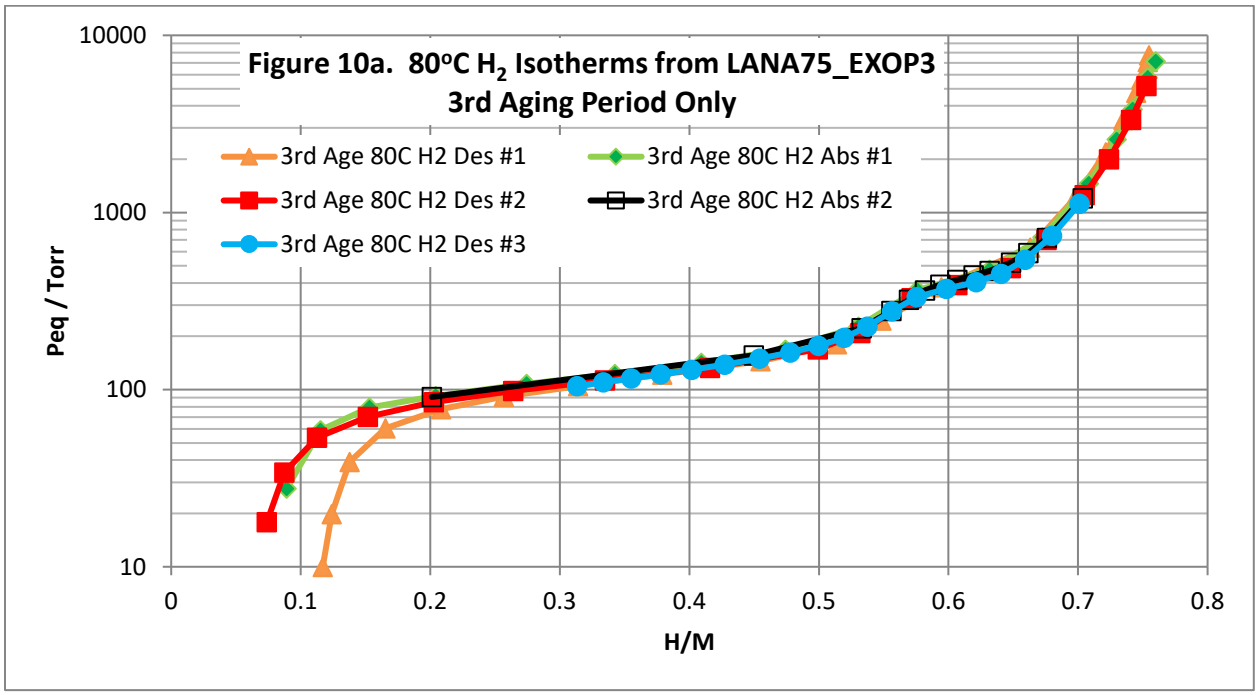
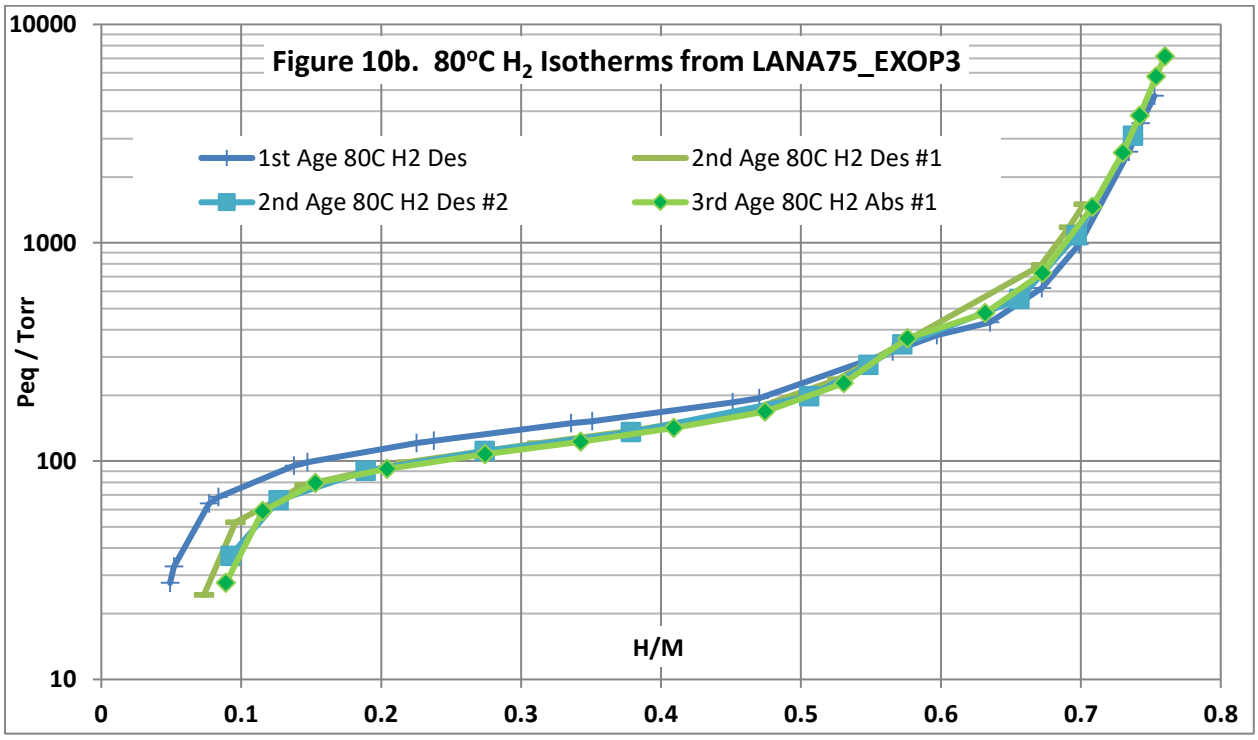


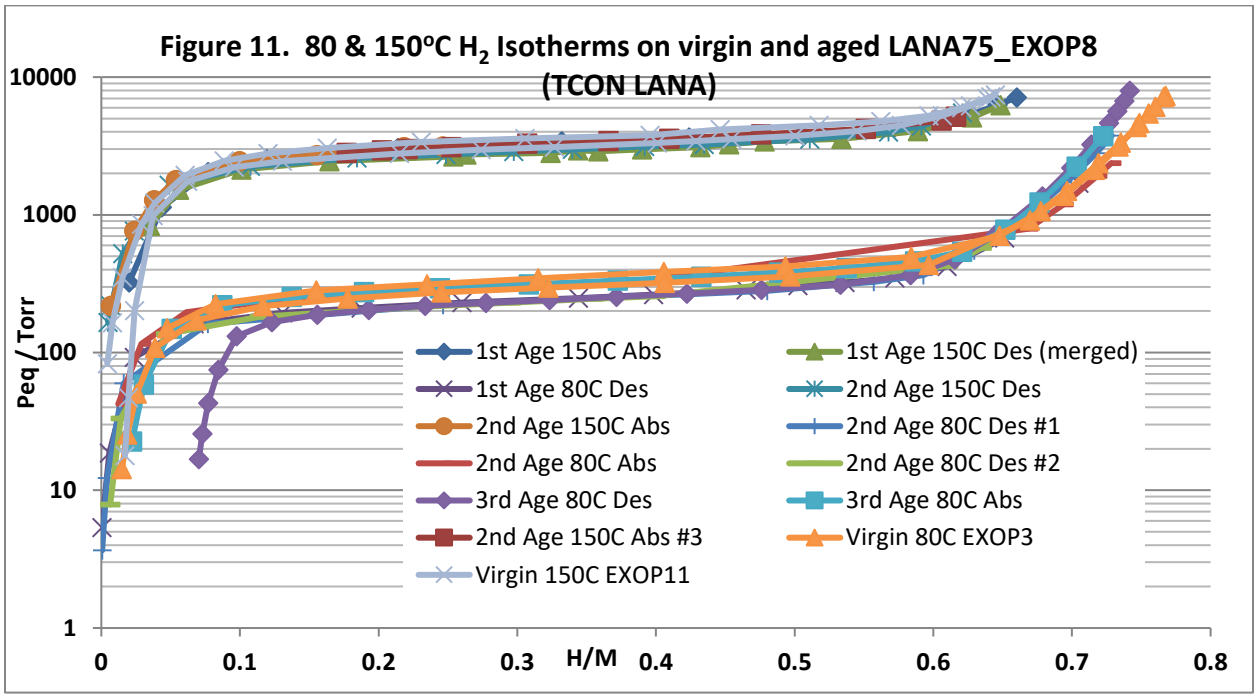
FIgure 9. D_2 Isotherms from virgin and aged LANA75_EXOP5
Virgin 80C Des
Virgin 150C Des
Virgin 150C Abs
Virgin 200C Des #1
1st Age 80C Abs #1
1st Age 80C Des #1
1st Age 80C Abs #2
1st Age 80C Des #2
1st Age 150C Abs
1st Age 150C Des
Peq / Torr
D/M
10000
1000
100
10
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8

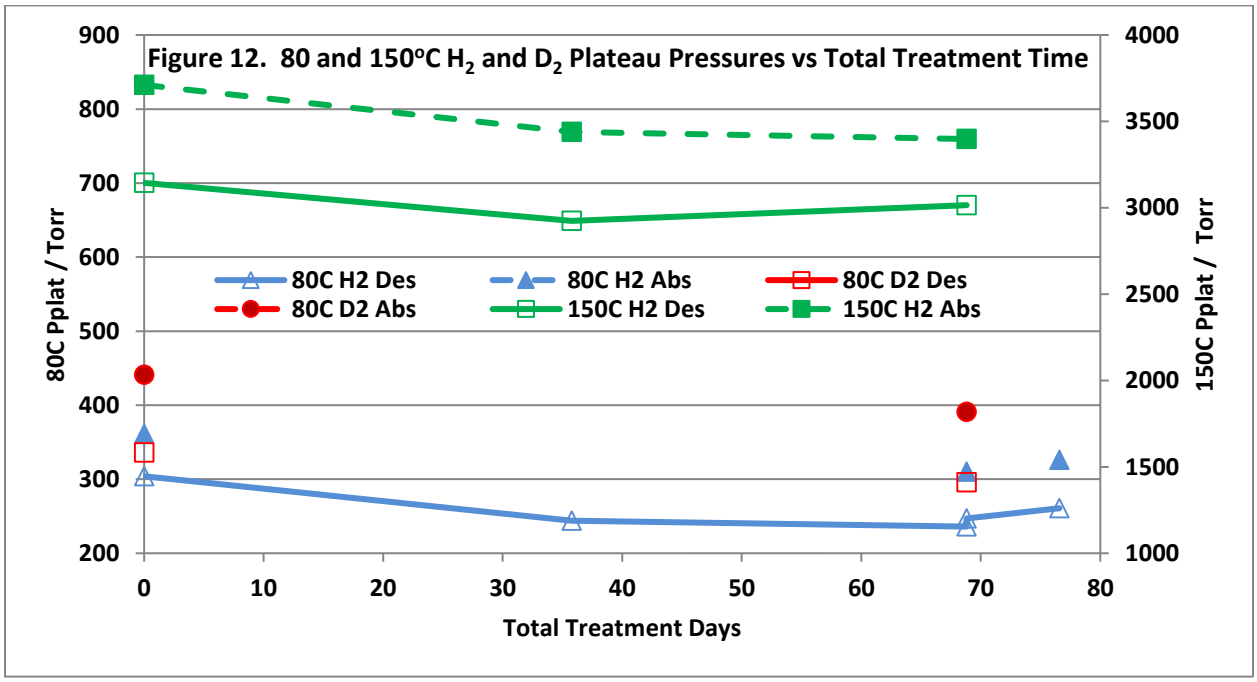
Figures 10a and b show part of the data presented in Figure 8. The main points of Figure 8 are to illustrate a) the dual plateaux structure, and b) the limited amount of change that occurs after 21 days of HHT. Figure 10a presents only the results obtained after the 3rd aging period on LANA75_EXOP3 (85.2 total days HHT), and illustrates the reproducibility of the isotherms in the H/M regions greater than ~.3 for the data taken after the second and third HHTs. Figure 10b illustrates the slight differences noted in the isotherms after the first aging period, apparently before the change process was completed.





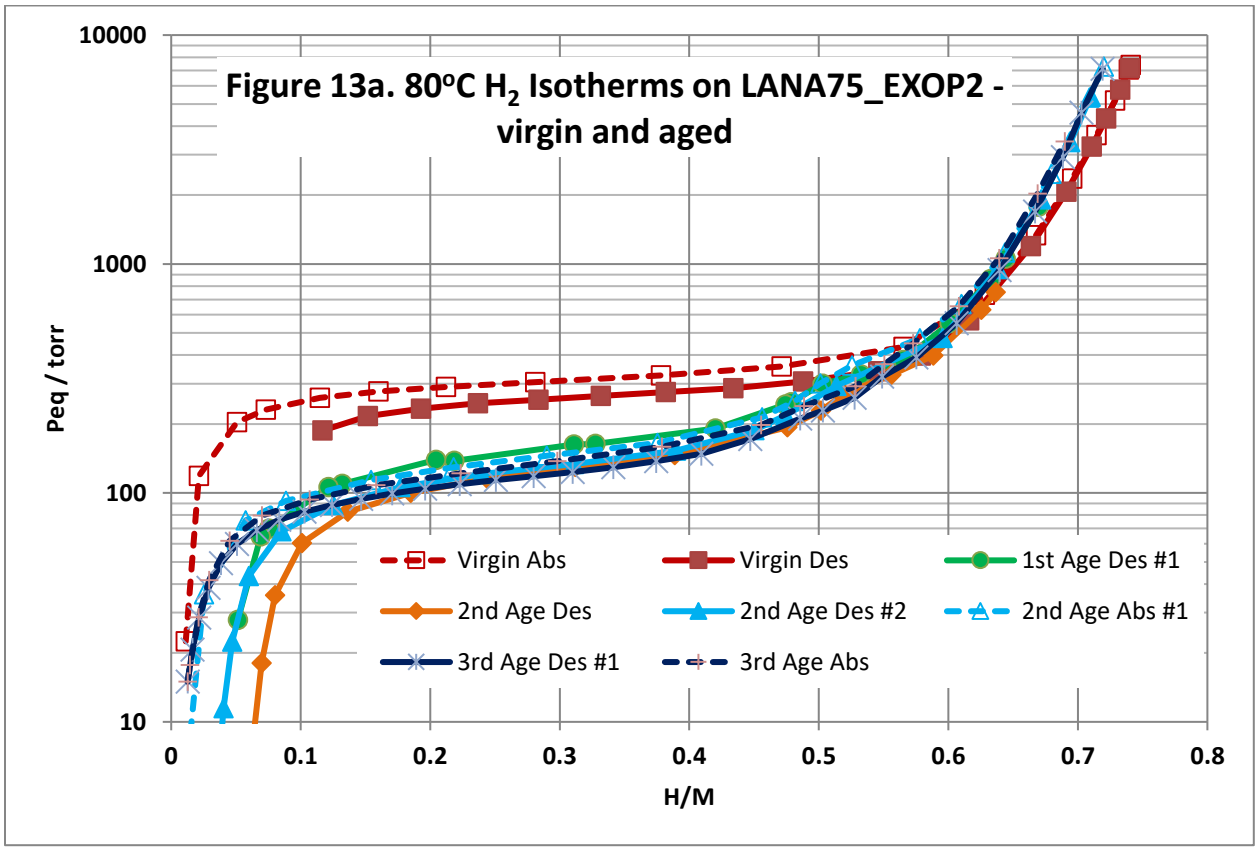
One sample, LANA75_EXOP8, was aged in 3 ~month-long periods at 150 °C, the isotherm results for which are shown in Figure 11. Of note is the loss of capacity in the "3rd Age" Desorption. See below for discussion. Figure 12 shows the plateaux pressures obtained at different total HHT times. XRD results are shown below.





Lot 1316 LANA75

Two samples of Lot 1316 LANA75 material were employed in these studies: LANA75_EXOP2, which has seen 3 ~month-long HHTs, and LANA75_EXOP4, which has seen 3 ~week-long HHTs. Figure 13a presents the 80 °C H_2 isotherms acquired from LANA75_EXOP2 before and after aging. Figure 13b is an expansion of the plateau region presented to clarify the small impact HHT had on this sample. The observed plateau pressures at 80 °C are plotted versus the total HHT time in Figure 14, including some acquired using deuterium. Figure 15 adds deuterium isotherms at both 80 and 150 °C from EXOP4, whereas Figure 16 shows 80 °C data from EXOP2. (Figures 14 and 16 have been updated with new EXOP4 data vs. the FY15 Mid-Year report[3].) Figure 17 presents virgin isotherm data from both samples using both deuterium and protium at higher temperatures with selected aged material data. Of note is the failure to close the mass balance on the 80 °C H_2 isotherm. This will be discussed further below. XRD data are also shown below.



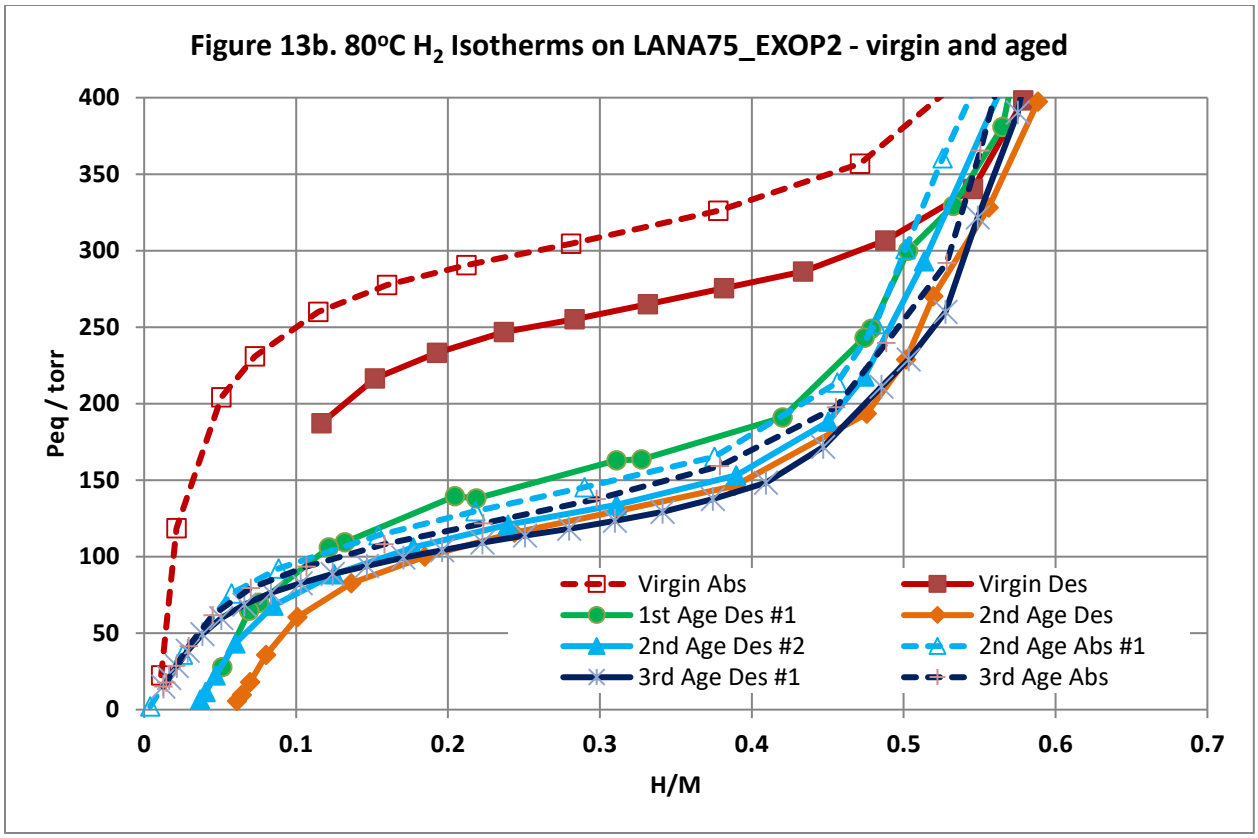


Figure 13b. 80°C H2 Isotherms on LANA75_EXOP2 - virgin and aged
Peq / torr
H/M
Virgin Abs
Virgin Des
1st Age Des #1
2nd Age Des
2nd Age Des #2
2nd Age Abs #1
3rd Age Des #1
3rd Age Abs

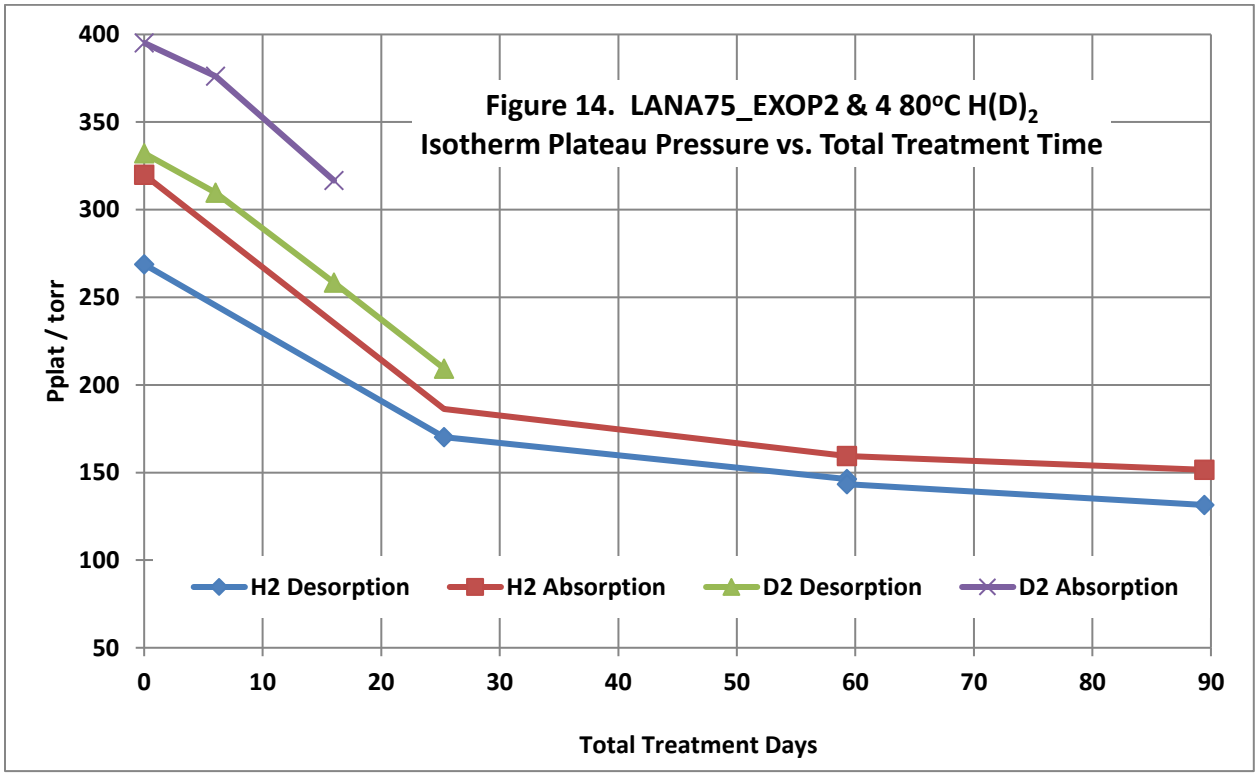


Figure 14. LANA75_EXOP2 & 4 80°C H(D)2
Isotherm Plateau Pressure vs. Total Treatment Time
Pplat / torr
Total Treatment Days
H2 Desorption
H2 Absorption
D2 Desorption
D2 Absorption

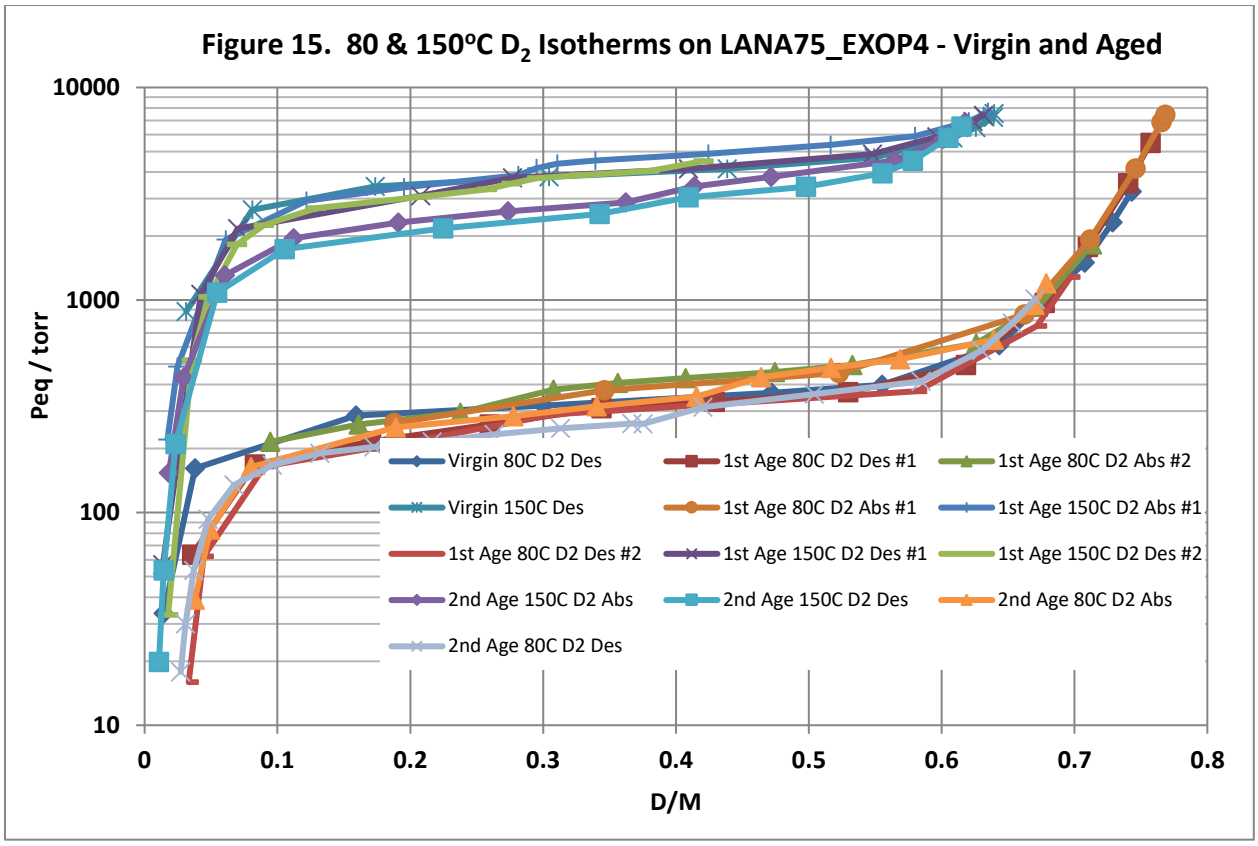


Figure 15. 80 & 150°C D2 Isotherms on LANA75_EXOP4 - Virgin and Aged
10000
1000
100
10
Peq / torr
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
D/M
Virgin 80C D2 Des
1st Age 80C D2 Des #1
1st Age 80C D2 Abs #2
Virgin 150C Des
1st Age 80C D2 Abs #1
1st Age 150C D2 Abs #1
1st Age 80C D2 Des #2
1st Age 150C D2 Des #1
1st Age 150C D2 Des #2
2nd Age 150C D2 Abs
2nd Age 150C D2 Des
2nd Age 80C D2 Abs
2nd Age 80C D2 Des

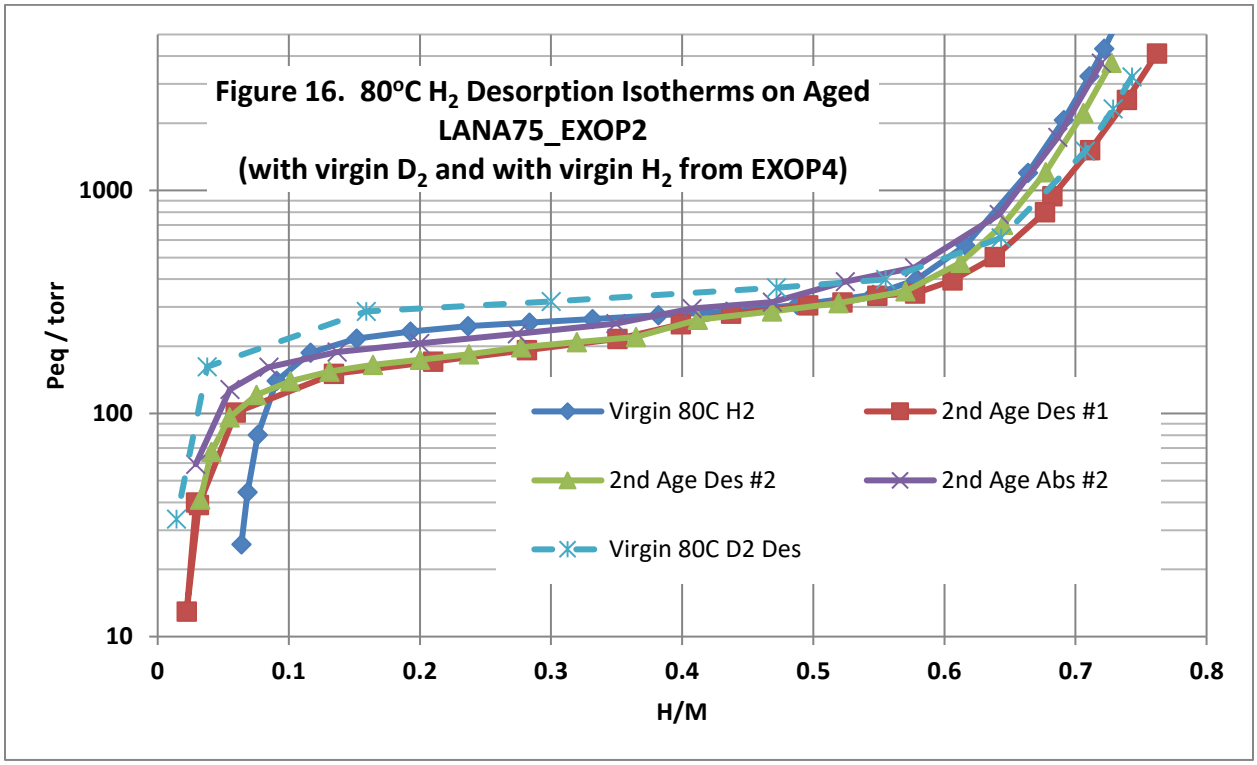
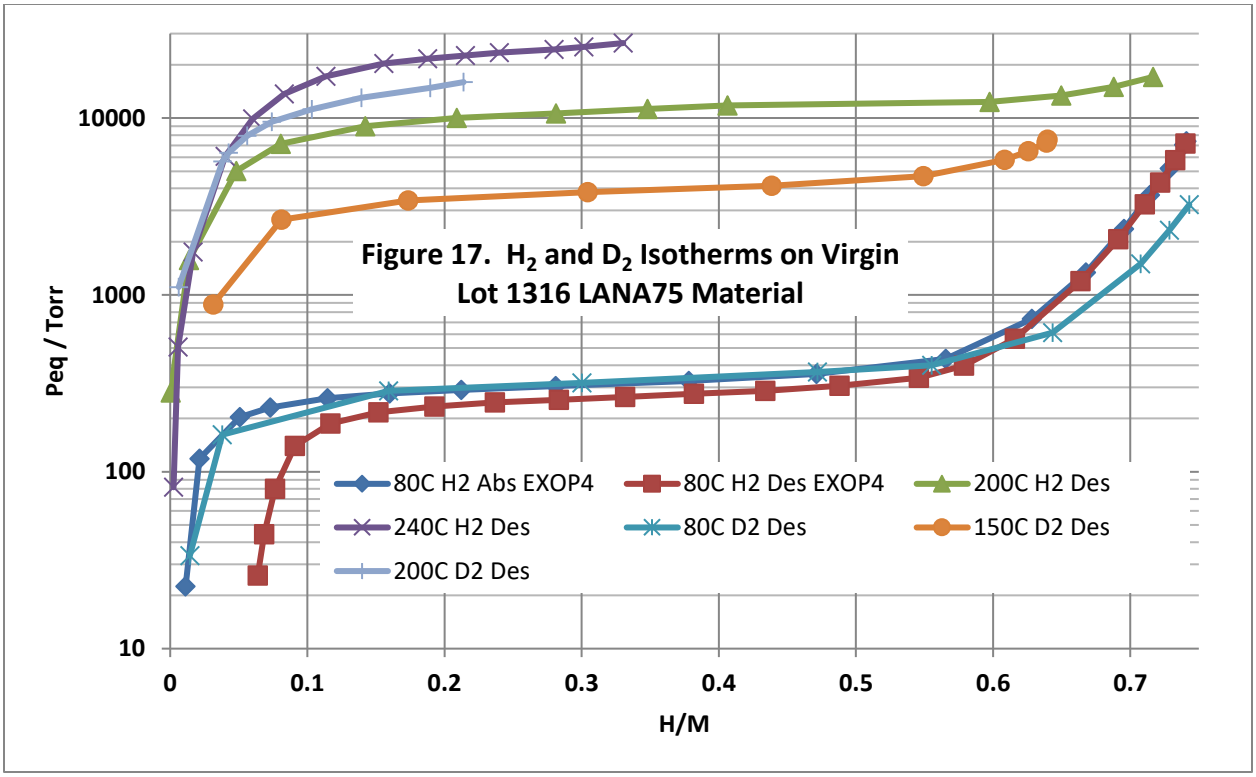


Figure 16. 80°C H2 Desorption Isotherms on Aged LANA75_EXOP2
(with virgin D2 and with virgin H2 from EXOP4)
1000
100
10
Peq / torr
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
H/M
Virgin 80C H2
2nd Age Des #1
2nd Age Des #2
2nd Age Abs #2
Virgin 80C D2 Des



300 °C studies

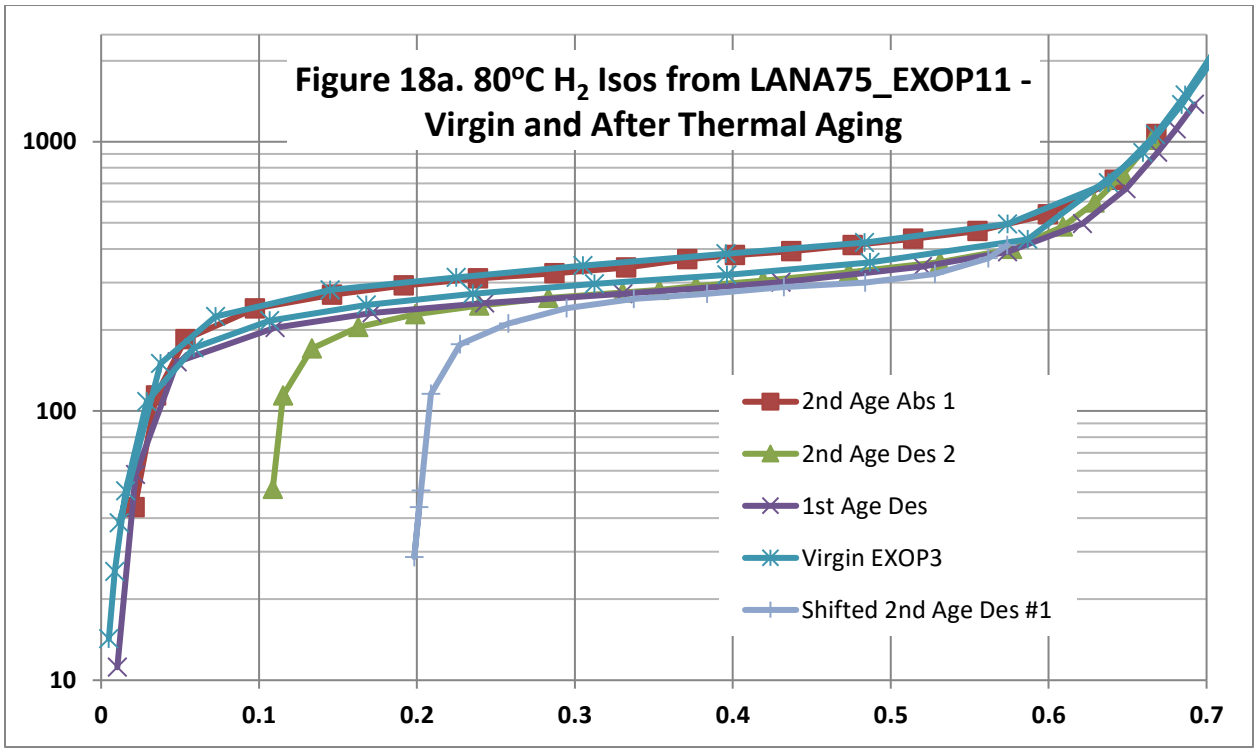
Based on input received during the oral presentation of the FY14 results obtained under the earlier part of this program, the materials' behavior at 300 °C was investigated. Only one type of LANA has been utilized at this point, the TCON LANA material. At 300 °C, the plateau pressures obtained exceed the working pressure range of the manual manifold used to obtain the bulk of the data presented so far. At 300 °C, the plateau pressure lies in the vicinity of 540 psi (~36.7 atm or ~27,900 torr) and the pressure would need to be twice that to probe the β–phase region for a 'full' isotherm.

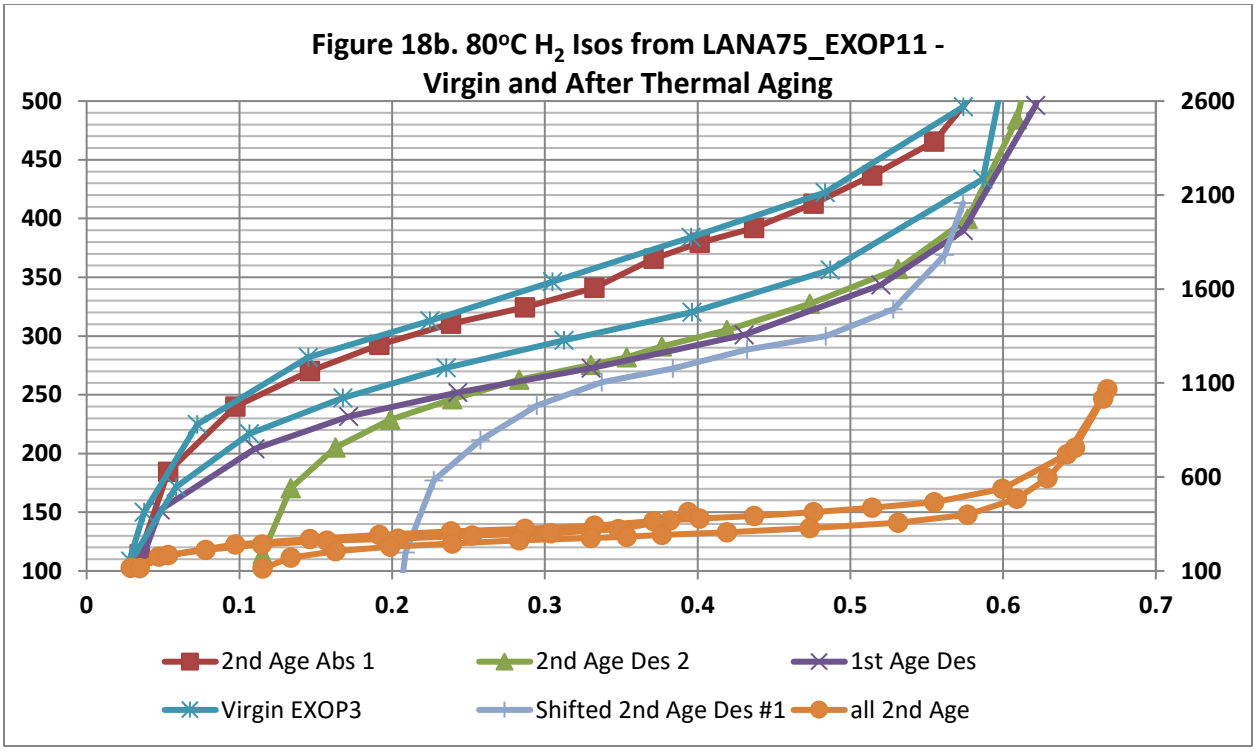
Therefore, two new samples were prepared using the sample cell of the available high pressure apparatus, a commercial instrument capable of reaching 3000 psi, the Setaram PCTPro. (Setaram bought rights to this instrument from the original manufacturer, Hy Energy, LLC.) This device uses very small volume manifolds to minimize the hazards associated with working at higher pressures. The PCTPro sample cell is thermally large and can be heated to 400 °C with the supplied heater/controller configuration.

In preparation for the HHTs, isotherm collection was attempted on sample LANA75_EXOP12 at 240 °C first, followed by attempts at 300 °C. However, it was immediately apparent that these treatments were causing isotherm shape changes just by the process of obtaining them. In addition, our first attempts were with a partially empty hydrogen cylinder as the source, which limited the maximum pressure obtained. Nevertheless, some data was acquired, and when the shape changes were noted, the sample was retired and the powder submitted to the SRNL Analytical Development Section (ADS) for XRD and SEM/EDX analysis (presented below).

Subsequent to the EXOP12 studies, another PCTPro sample was prepared and designated LANA75_EXOP13. After activation at 20-80 °C, this sample was volume calibrated at increasing temperatures up to 300 °C, whereupon 300 °C H_2 isotherms were measured. Those isotherms showed immediate changes from cycle to cycle, even though only partial isotherms were collected. The temperature was lowered and isotherms collected at 150 and 270 °C under slightly different PCTPro parameters. The 150 °C plateau pressures agreed with those obtained from the other TCON LANA samples. This sample is still available for further studies.

The original interest in 300 °C work was accompanied by the idea that it was unlikely to exceed 100 psi during any high temperature treatments. Therefore, the manual manifold sample LANA75_EXOP11 (which was also made from the TCON LANA material), which was previously used to obtain some virgin material isotherms, was loaded to 100 psi at 240 °C and allowed to age for two periods. The first period extended for ~2 days and the second for ~7 more days. The obtained results are shown in Figure 18a. From the scoping study, since the aging pressure was below the plateau pressure, the only expected change was a slight loss in capacity. However, as shown in the expanded and linear Peq axis of Figure 18b, there may have been some slight plateau lowering (~30 Torr). More importantly, there are some clear shifts in working capacity, which will be discussed in more detail in the Discussion section.





LANA75_EXOP12 XRD and SEM/EDX Results (from FY15 Mid-Year Report[3])

After LANA75_EXOP12 showed isotherm changes from 300 °C isotherm determination, the sample was retired and the powder removed from the sample cell and submitted to the SRNL Analytical Development Section for X-ray Diffraction (XRD) pattern collection and analysis, and for Scanning Electron Microscope with Energy Dispersive X-ray analysis. In addition, a virgin sample of the TCON LANA75 material was also submitted for comparison. Figure 19 shows the XRD intensity patterns for the two samples (virgin on the left Y axis) and the difference spectrum (on the right Y axis with aged sample pattern) obtained by scaling the strongest peaks to the same value and then subtracting the scaled virgin spectrum from the aged sample's spectrum. Differences in peak intensities unfortunately are not normally considered diagnostic of anything, but shifts in peak position and shape are. The comparison shows that the aged sample peaks have broadened slightly, and some loss of the fine structure is observed in the virgin sample. Because of the shape change, it appears that the peak positions have shifted slightly, but this is probably just an artifact of the broadening. Peak broadening arises from either increased strain in the sample or from decreased crystallite size. More will be said on this in the Discussion section.

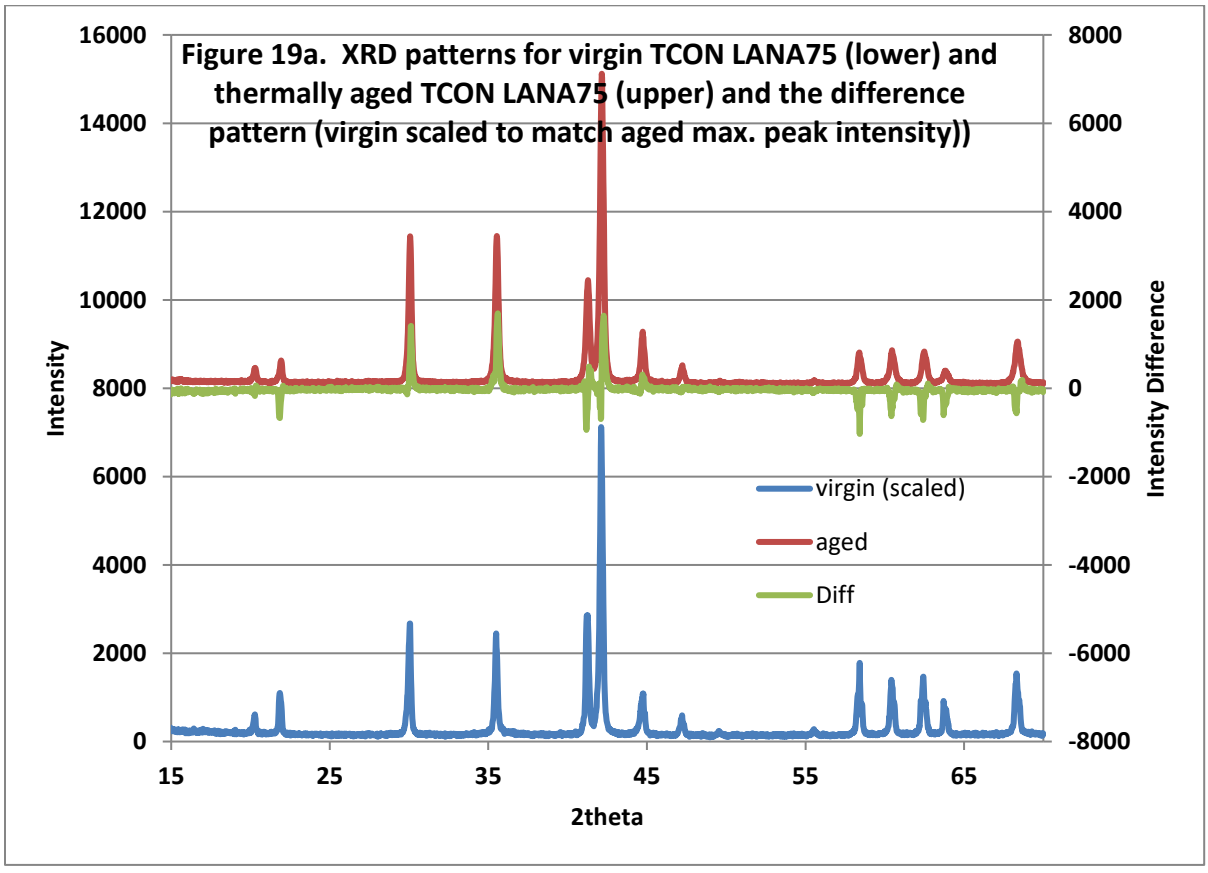
The key analysis resulting from the XRD patterns is the unit cell dimensions. Prior SRL (now SRNL) work[4] (see Figure 20) and the literature[5] (see Figure 21) have shown that these parameters are influenced by the Al content of the alloy. Both of these samples have very similar cell parameters (a,b, and c, where a=b in this crystal structure.) Cell parameters were reported as: Activated (thermally aged) Material a = b = 5.04926 Å, c = 4.04956 Å and Virgin material a = b = 5.04935 Å, c = 4.04916 Å, which indicate that the nominal LANA75 composition has been obtained. Also important is the lack of additional peaks

beyond those expected for LANA75, which indicates a high degree of crystallinity and low impurity content.

Appendix A of the FY15 Mid-Year Report[3] presented a large number of SEM photos and some associated EDX results. This Appendix is reproduced unchanged in this report. The key points noted then are:

- The 'aged' material has decrepitated, and any remaining larger particles are heavily cracked as expected from known LANA behavior
- There are symmetrical 'holes' found in both the aged and virgin material of unknown origin and impact
- There are NiAl phases, La_2O_3 crystallites and some Si, Fe, and Ti contaminants detected, which have been seen in prior studies as well

Similar to the XRD results, the SEM/EDX results gave no indication of any major change caused by the thermal aging.



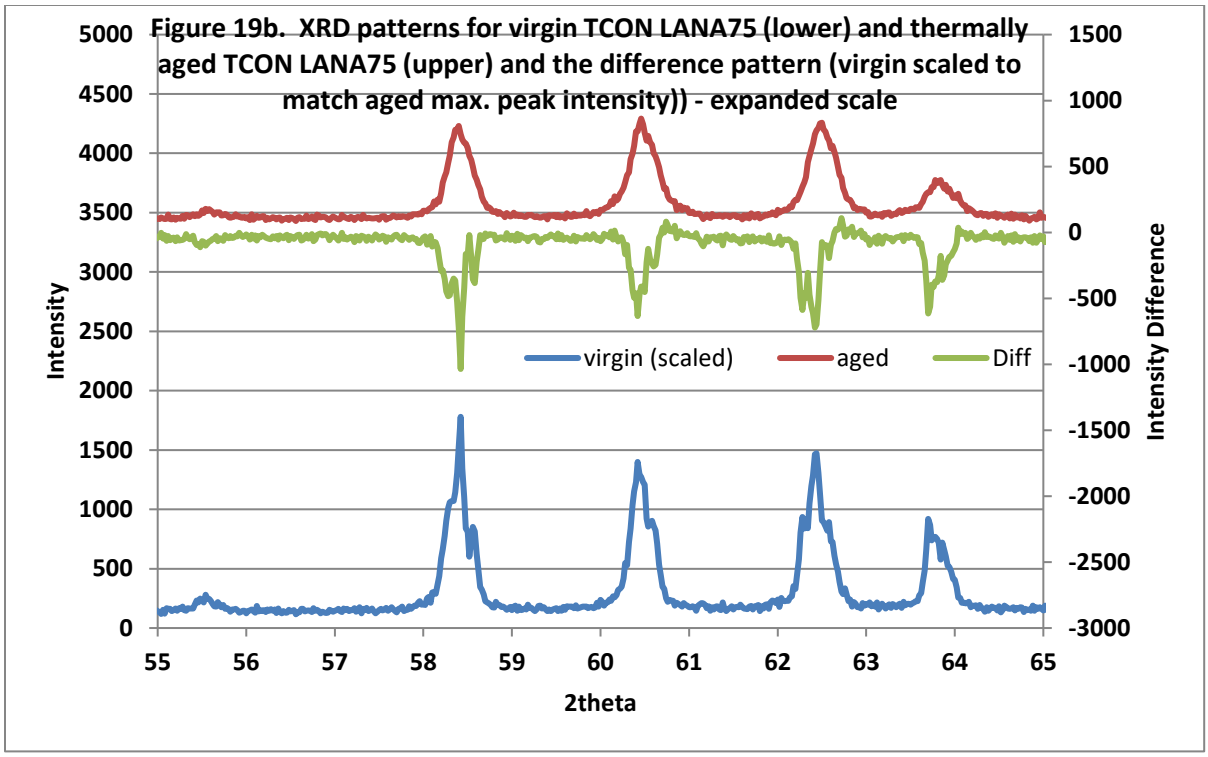


Figure 19b. XRD patterns for virgin TCON LANA75 (lower) and thermally aged TCON LANA75 (upper) and the difference pattern (virgin scaled to match aged max. peak intensity)) - expanded scale
Intensity
Intensity Difference
2theta
virgin (scaled)
aged
Diff
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
1500
1000
500
0
-500
-1000
-1500
-2000
-2500
-3000
55
56
57
58
59
60
61
62
63
64
65

Figure 20. Moseley's "Table 2" giving cell parameters for LANA compounds. (Note information on Lots 1316 and 1138 which were also used in this study.)

Table 2. X-ray Diffractometry Results for Lanthanum-Nickel-Aluminum Alloys.

HEAT NUMBER	Bulk Composition (Nominal) $La_XNi_{5-Y}Al_Y$ X	Y	Lattice Constants of Primary Phase a (Å)	c (Å)	a/c	Vol (Å^3)	Other Phases Detected By XRD	Aluminum in Primary Phase $LaNi_{5-y}Al_y$ y(calculated)
87659*	1.00	0.00	5.018	3.980	1.261	86.79	La_2Ni_7	0.00
82108C**	1.00	0.00	5.018	3.979	1.261	86.77	None	0.00
82885C	0.89	0.00	4.997	3.996	1.251	86.40	Ni	-----
82885	0.89	0.00	4.983	4.006	1.244	86.16	Ni	-----
82886C	0.71	0.00	4.987	4.002	1.246	86.17	Ni	-----
1112	1.0	0.30	5.025	4.008	1.254	87.63	c-Ni_3Al	0.26
88543	1.0	0.30	5.025	4.008	1.254	87.63	c-Ni_3Al, $La(OH)_3$	0.26
87075*	1.0	0.30	5.025	4.011	1.253	87.70	c-Ni_3Al	0.28
1323	1.09	0.30	5.038	4.009	1.256	88.02	$La_2Ni_{7-z}Al_z$	0.38
1324	1.00	0.30	5.031	4.011	1.254	87.90	$La(OH)_3$	0.34
1325	0.91	0.30	5.023	4.001	1.255	87.44	c-Ni_3Al, $La(OH)_3$	0.20
82099*	1.00	0.50	5.032	4.030	1.249	88.38	c-Ni_3Al	0.49
1126	1.00	0.50	5.039	4.024	1.252	88.50	$La(OH)_3$	0.52
1158	1.00	0.75	5.045	4.048	1.246	89.24	$La(OH)_3$	0.75
1286	1.00	0.75	5.030	4.033	1.247	88.36	t-Ni_3Al	0.48
1287	1.00	0.75	5.039	4.038	1.248	88.79	t-Ni_3Al, $La(OH)_3$	0.61
1288*	1.00	0.75	5.047	4.052	1.246	89.40	$La(OH)_3$	0.80
1294	1.00	0.75	5.052	4.054	1.246	89.60	LaNi	0.86
1295	1.00	0.75	5.042	4.041	1.248	88.97	t-Ni_3Al	0.67
1302	1.18	0.75	5.049	4.051	1.246	89.45	LaNi	0.81
1303	1.09	0.75	5.051	4.054	1.246	89.57	LaNi, $La(OH)_3$	0.85
1304	1.00	0.75	5.050	4.055	1.245	89.55	$La(OH)_3$	0.84
1305	0.91	0.75	5.045	4.043	1.248	89.12	Ni_3Al, $La(OH)_3$	0.71
1306	0.82	0.75	5.038	4.037	1.248	88.75	c-Ni_3Al, $La(OH)_3$	0.60
1312	1.00	0.75	5.051	4.052	1.247	89.54	$La(OH)_3$	0.84
1313	1.00	0.75	5.055	4.056	1.246	89.73	$La(OH)_3$	0.90
1314	1.00	0.75	5.052	4.058	1.245	89.71	$La(OH)_3$	0.89
1315	1.00	0.75	5.052	4.055	1.246	89.62	$La(OH)_3$	0.86
1316	1.00	0.75	5.052	4.055	1.246	89.60	t-Ni_3Al, $La(OH)_3$	0.86
1138	1.00	0.85	5.054	4.059	1.245	89.77	$La(OH)_3$	0.91
1250	1.00	0.85	5.054	4.057	1.246	89.74	$La(OH)_3$, Ni_3Al	0.90
1251	1.00	0.85	5.053	4.060	1.245	89.79	$La(OH)_3$	0.92
1252	1.00	0.85	5.055	4.062	1.244	89.89	$La(OH)_3$, Ni_3Al	0.95
1253*	1.00	0.85	5.055	4.059	1.245	89.83	$La(OH)_3$	0.93
87656*	1.00	1.00	5.060	4.073	1.242	90.32	X***	1.08
89174*	1.00	1.00	5.077	4.080	1.244	91.08	NiAl, X, Y***	-----

*Quantitative Analysis with Scanning Electron Microprobe
**C indicates as-cast alloy. All other alloys were annealed.
***Phases X and Y are unidentified

Taken from Moseley, WSRC-MS-92-038-Pt.1

Figure 21. Diaz, Percheron-Guegan, Achard, Chatillion, and Mathieu's "Figure 1" showing variation in cell parameters with Al content

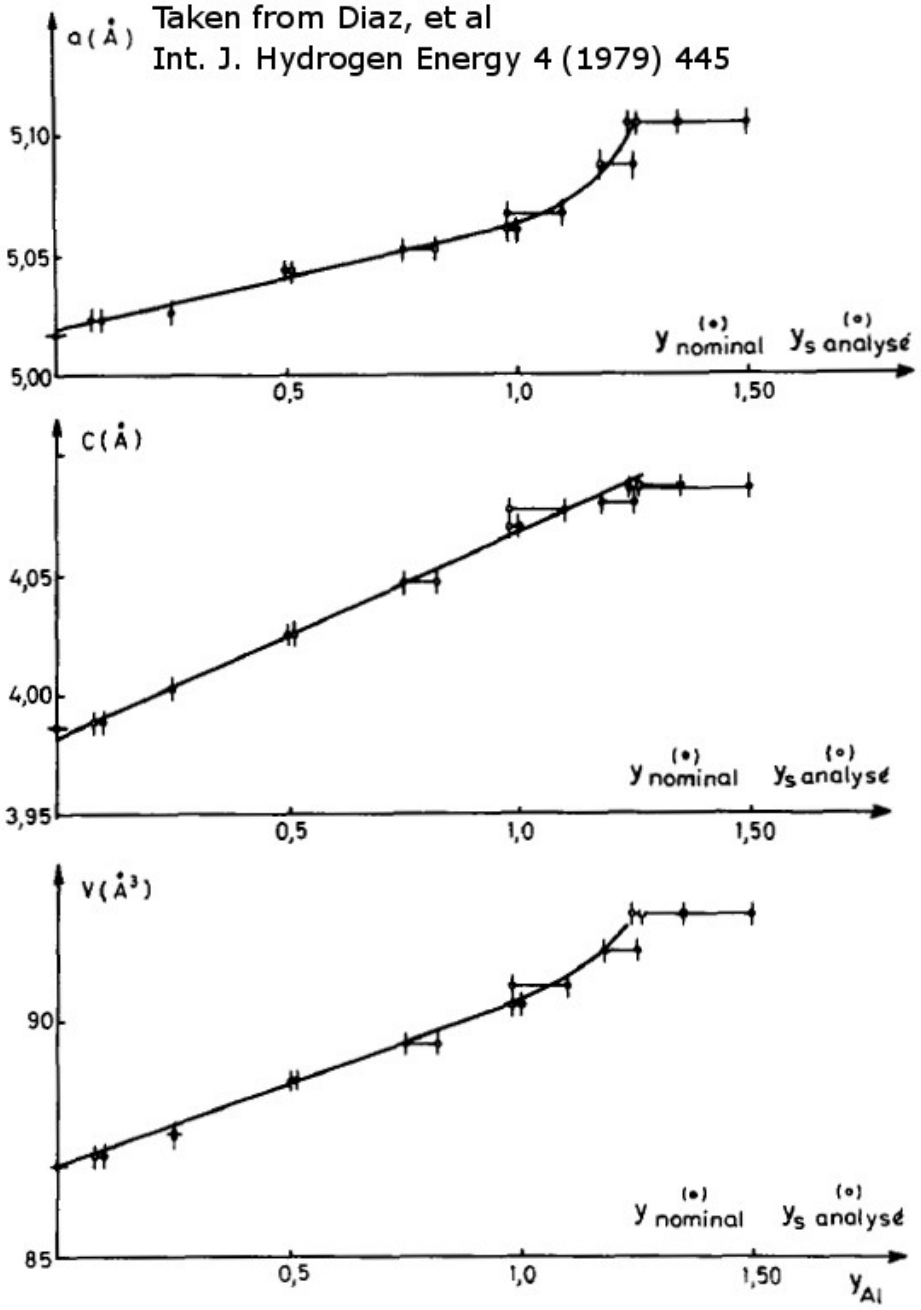


FIG. 1. Variation of the lattice parameters and of the cell volume vs the aluminium substitution rate in the intermetallic compounds.

Kinetics

No additional information related to kinetics was successfully acquired during the second half of FY15 due to a PCTPro software upgrade-induced issue with volume calibrations (see next section). Therefore, the reader is referred to the FY15 Mid-Year Report[3] for previously reported details.

The data collected under the improper volume parameters conditions are potentially correctable but will involve significant effort and was not attempted at this time. The data that were collected showed the same effects as those reported in the FY15 Mid-Year report[3], thus it was deemed to be unnecessary to recalculate the results.

Equipment Issues

The 480V-to-120V transformer was received and installed but not in time to impact data acquisition. It was reported in the FY15 Midyear report[3] that there was a volume calibration issue with the PCTPro. This issue was resolved by determining that the specific volume calibration information for our instrument had accidentally been overwritten during the software upgrade process. Once the correct parameters were reconstructed, the instrument returned the same determined volumes. Unfortunately, we did not have time or motivation to recalculate those spectra taken with the incorrect parameters, thus the FY15 year-end report does not include any additional data from the PCTPro than previously reported. This primarily impacted the kinetics section of the experimental results.

3.0 Discussion

The open literature of the period during which the TF processes were converted to metal hydride use had several examples of thermal aging effects both from a static and from cycling conditions. Shown below is Figure 1 from ref 6, which illustrates that LANA alloys were presumed to grant stability against cycling degradation vs. binary alloys such as LaNi5 or CaNi5.

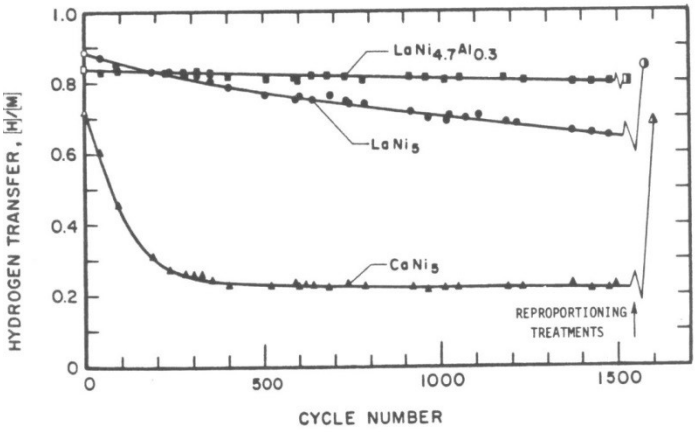


Fig. 1. Cycling response of three alloys at 85 °C and 30 min cycle period (0 - 2068 kPa (300 lbf in^{-2} absolute)).

Split plateaux have been noted as well, as seen in Figures 5 and 6 of ref. 6 (below).

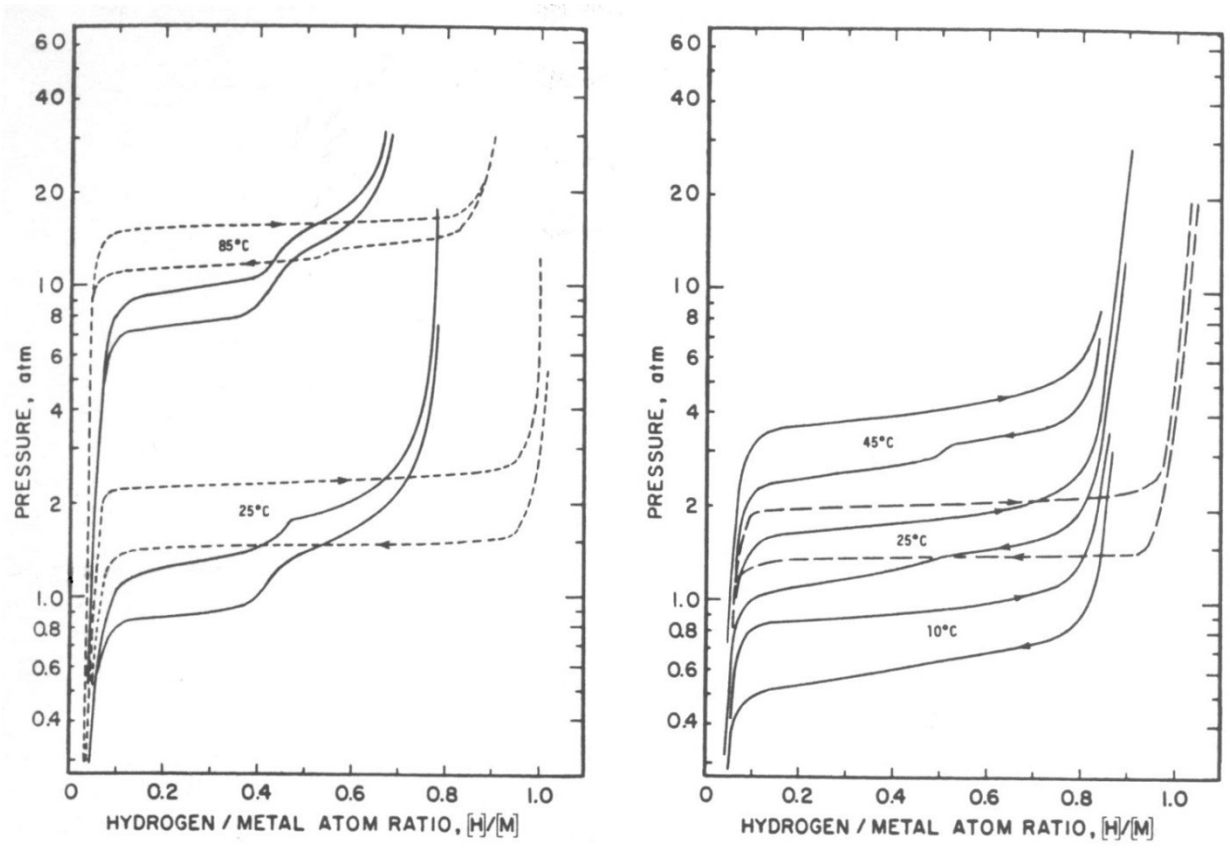


Fig. 5. Effect of 85 °C cycling on the shape of reaction isotherm plateaux of $LaNi_5$ at 85 and 25 °C: — — —, tests after 30 cycles at 25 °C (0 - 300 lbf in^{-2} absolute); ——, tests after 1500 cycles at 85 °C (0 - 300 lbf in^{-2} absolute).

Fig. 6. Effect of 25 °C cycling on the reaction isotherm plateaux of $LaNi_5$ at several temperatures: — — —, tests after 30 cycles at 25 °C (0 - 300 lbf in^{-2} absolute); ——, tests after 1400 cycles at 25 °C (0 - 300 lbf in^{-2} absolute).

In Figure 2 of ref. 7 one can see significant capacity losses and the development of a split desorption plateau with thermal cycling:

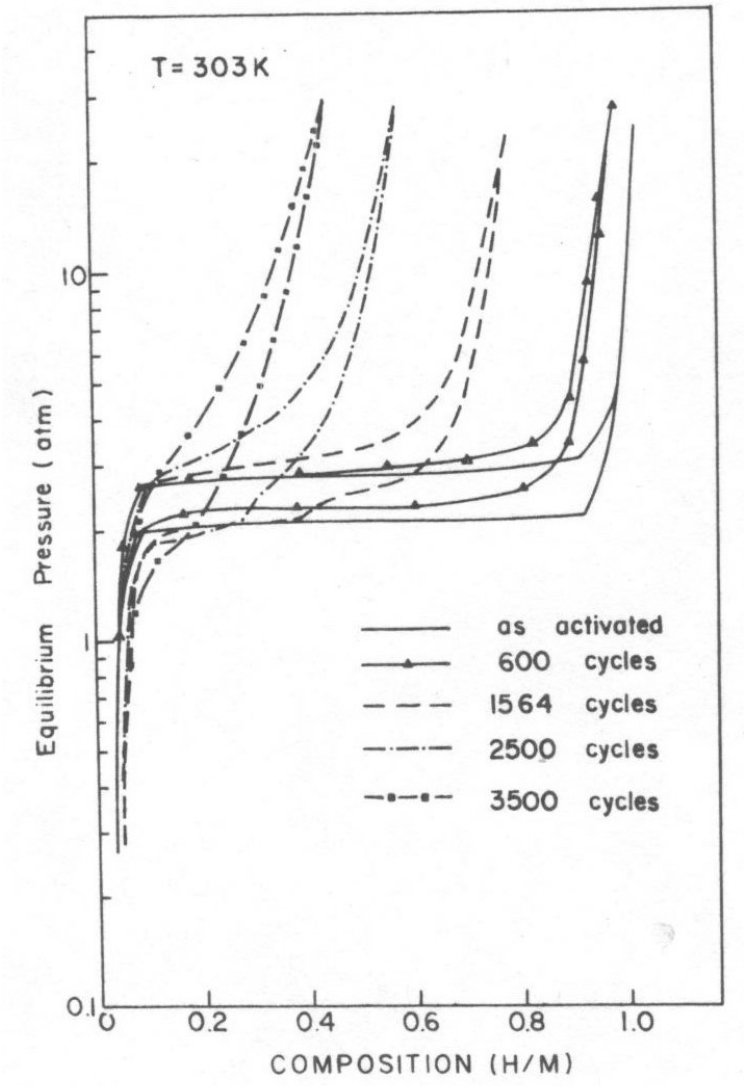


FIG. 2
Change of P-C-T curve with 203-458 K thermal cycle of $LaNi_5$.

Also, capacity changes and plateau pressure shifts have been seen specifically in LANA30, as shown in Figures 10 and 11 of ref. 7:

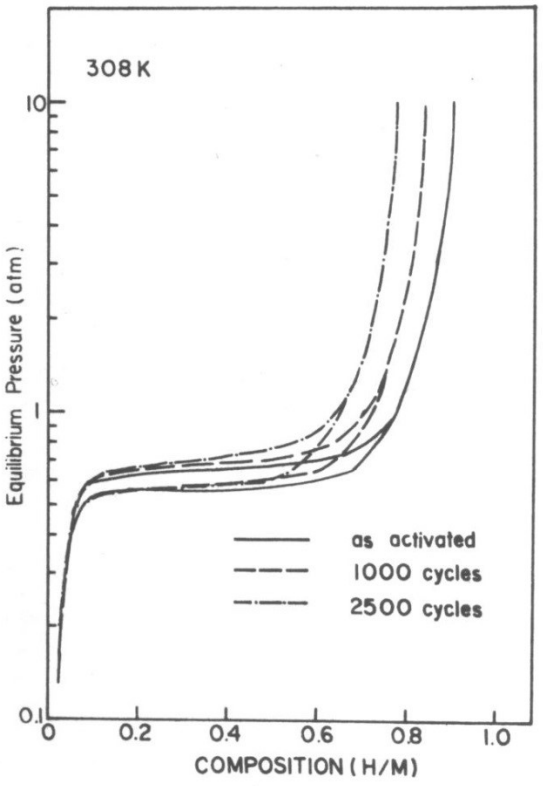


FIG. 10
Change of P-C-T curve with 303-458 K thermal cycling of $LaNi_{4.7}Al_{0.3}$

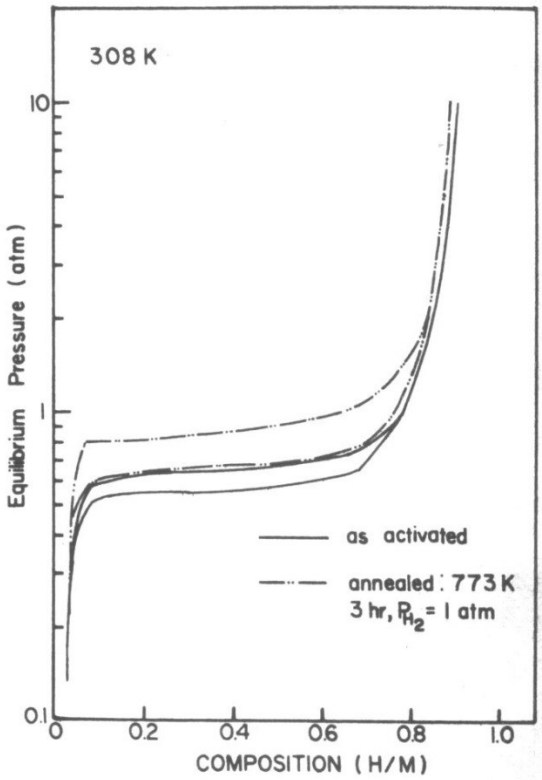


FIG. 11
Effect of annealing on the reversal of $LaNi_{4.7}Al_{0.3}$

Therefore, it was not unexpected that such effects have been seen in LANA75 and 85.

The results obtained in FY15 have supported and extended the FY14 results. In summary, all 4 types of LANA studied have shown plateau pressure depression upon thermal aging (or hydrogen-heat treatment, HHT) when hydrogen loaded to pressures exceeding the plateau pressure is applied to the sample and the sample is heated without cycling. This has been noted with 150, 240, and 300 ^{o}C HHTs, with the effects occurring more rapidly as temperature increases. In fact, the simple process of acquiring a 300 ^{o}C isotherm changes the sample.

In the LANA75 materials studied, the plateau lowering is accompanied by the development of a dual plateau isotherm, i.e. plateau splitting. The first plateau lowers significantly, whereas the second plateau does so to a lesser extent. In fact, in some of the lesser treated samples, the second plateau may actually see a slight increase in pressure.

These effects do not continue indefinitely, but rather reach a maximum level in ~30-100 days, depending on the material and temperature. However, noticeable effects can occur with ~ 1 week of HHT at 240 ^{o}C, and the effects are cumulative, meaning that even short HHTs can induce effects. In all cases, even with split plateaux, the plateau pressures were defined at Q/M = 0.35, which may be higher than usually determined on a plateau for the lower of the split plateaux.

The XRD data available at this point for the TCON LANA material heated at 300 ^{o}C suggest that no or very minimal material decomposition occurs while these changes are underway. The primary impact seems to be a broadening of the XRD peaks, which in the TCON LANA sample obscured some fine structure in the peaks. This fine structure may indicate a slight compositional inhomogeneity in the sample, which would be consistent with the fact that the material was composed of a blend of three separate heats of LANA75 (which was due to SRS accepting this procedure via an approved SCR). The unit cell parameters extracted from the XRD spectra confirm the material is nominally LANA75 based on results reported from internal studies[4] and in the open literature[5]. Likewise, SEM images showed no massive change except the anticipated decrepitation that occurs routinely in activating LANA to obtain rapid absorption/desorption kinetics (Appendix A of the FY15 Mid-Year report[3], reproduced herein).

Studies conducted at 300 ^{o}C on the TCON LANA75 material at a loading pressure of ~100 psi have not shown any effect except for a slight lowering of capacity. (The conditions of 300 ^{o}C and 100 psi were suggested at the oral presentation of the FY14 Final Report as 'maximum' exposure conditions.) This is consistent with the scoping study results, where using loading pressures at or below the plateau pressure seemed only to reduce capacity very slightly.

Behavior similar to this was noted with the materials originally proposed for the Unloading Line B Project beds[10]. Additionally, there are several open literature reports on the effects of static thermal aging of $LaNi_5$ and some LANA materials, and on the impact of thermal cycling on $LaNi_5$ and LANA materials. These studies generally agree that thermal aging causes XRD line broadening and that observing decomposition products such as Ni particles in XRD spectra is uncommon. However, Ni particles are magnetic, and magnetization of thermally aged samples has been observed, indicating the development of nickel particles that are less than 150 nm in size. In fact, these Ni particles are thought to be present to some extent even in virgin material and that they serve as the primary hydrogen

dissociation sites. Virgin (inactivated) $LaNi_5$ was recently shown to be active to hydrogen loading, albeit with very slow kinetics[11].

Plateau splitting has also been reported in the literature of $LaNi_5$ chemistry. In that case however, it is usually accompanied by an increase in plateau pressure, especially in the absorption isotherm. The desorption isotherm generally remains unaffected. This is normally discussed in terms of developing a separate plateau for the formation of the half-loaded compound $LaNi_5H_3$, which would give a plateau split at the half-loaded point, i.e. approximately at H/M = 0.3-0.4. Note that this includes the separate effect noted in the literature where freshly made $LaNi_5$ can absorb its full theoretical loading of H/M=1, which decays to a full load of H/M~=0.75-0.8 after being held in air for a short period of time. (Thus a capacity loss occurs first, separately from the thermal aging effect of plateau splitting.) However, our results show split points as high as 0.5 H/M for materials that began with the typical 0.75-0.8 maximum load. Thus, our results suggest something else may be contributing; perhaps a mixture of the effect described above and a partial conversion to a closely related but different form, which when combined produce the split at an unexpected point. HHT of Pd alloys is thought to produce 'superabundant vacancies', i.e., points where a metal atom would normally be where the metal atom has moved elsewhere, displacing atoms to the surface and leaving behind a 'hole' or vacancy in the metal atom lattice. These vacancies are thought to form ordered structures under some conditions. Something similar may be occurring in LANA but attempting to determine if this is the case is currently beyond the scope of this project.

One tantalizing observation has been made from the SEM study of the 300 ^oC aged TCON LANA75. Virgin material SEM images show occasional round 'holes' in the material of unknown origin that tend to be distributed in straight lines. Most likely they are located on grain boundaries and may have been formed by included gas bubbles formed from trapped gases during the melting and alloying process. However, in the aged sample photos these 'holes' have clustered together instead of being spread out in straight lines. This may be the result of 'vacancy ordering' or it may have been simply a fortuitous observation of an unusual formation originally present in the virgin material. Unfortunately, the SEM studies on the retired samples were not completed in FY15 for a variety of reasons.

The objective of this project was to determine the specifics of what might happen to LANA75 and 85 materials when used in the new generation of hydride beds that incorporate electric heaters. Those heaters allow the TF to reach much higher temperatures, which are required by some applications. The changes noted in this study must be examined and assessed by TF process engineers in light of process needs and applications to determine material suitability.

Anomalies

All experimental work shows evidence of anomalies, and this study is no exception. The primary anomaly was the failure to replicate the results from the GfE material scoping study sample that was heated at 240 ^oC for ~350 days under an initial load of ~380 psi of hydrogen without any intermediate studies. That sample suffered significant plateau depression, but a fraction of the capacity was retained at approximately the original plateau level. The LANA85_GFE5 sample examined in this study was

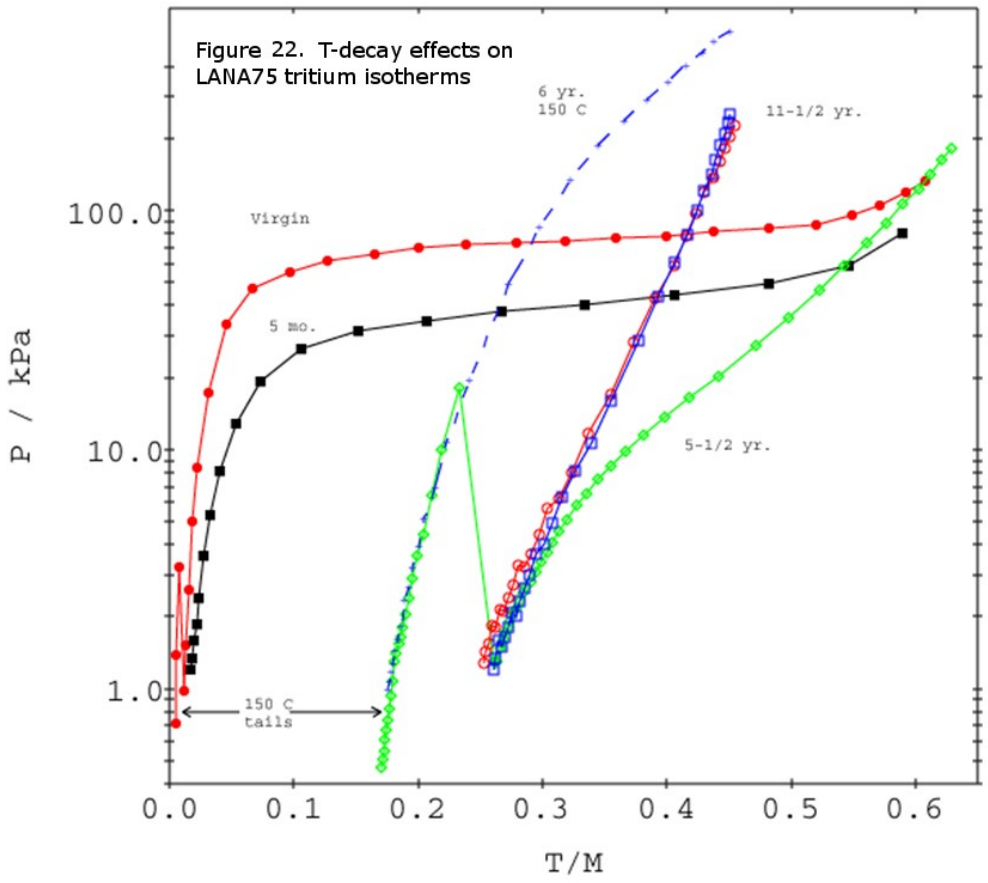
similarly treated, but was examined by acquiring isotherms on a periodic basis, and it failed to retain any of the original plateau. Instead, it showed a uniform progressive plateau pressure lowering over the entire isotherm for ~100 days, at which point it appeared to cease changing. Furthermore, the plateau pressure of the GfE samples used in this study stabilized at ~100 torr, whereas the plateau pressure of the lower (in H/M) plateau was in the vicinity of 36-40 torr. The midpoint pressure of the higher plateau region of the scoping study sample was ~150 torr, which was approximately that of the virgin material and is consistent with the plateau pressure behaviors noted initially with the LANA75 samples. It is obvious that the periodic isotherm determinations may have caused this anomaly, but the reason for this is unknown. Additional studies are required to attempt to elucidate this finding.

A second set of anomalous results were obtained from sample LANA75_EXOP5 (TCON LANA75 material). The sample was aged in ~1 week intervals at 240 ^{o}C, but there was no observed change in plateau level between the 2nd and 3rd treatment. In Figure 7a, all data from both TCON LANA samples aged at 240 ^{o}C is presented, whereas the data from each sample is split into Figures 7b and c. On their own, the samples appear to behave normally, with a very short time to final configuration obtained with EXOP5. However, the other samples in this study did not result in disagreement between the month-long and the week-long aging protocols (see Figures 2, 5, and 14). Once again, the reason for this discrepancy is unknown and requires more study to possibly resolve.

A paper published in 1988[12] reported studies on the $LaNi_5$-H system that appeared to show the existence of up to 6 distinct metal hydride phases, most of which were deemed to be metastable. Metastable phases are unstable and metastable phase formation and decomposition is highly dependent on how the sample is treated. The LANA75 and 85 materials could also potentially show multiple metastable phases if treated properly; therefore, insufficient care was used in the loading and cycling (for isotherm determination) in this study to demonstrate these possible multiple phases. Further study would be needed to potentially resolve this issue.

Comparison to T aging

It is of passing interest to note the similarity of the effects of HHT on LANA versus the effects of tritium decay. Below is a Figure (Figure 30) that has been used to illustrate the impact of T-decay (aging) on LANA75. It illustrates the plateau pressure lowering, heel growth, and slope increases observed initially, and the eventual loss of any trace of a plateau, accompanied with loss of capacity with heavily aged material.



Similar effects have been noted in $LaNi_5$ as seen in Figure 1 from ref. 8, and in Figure 2-1 of ref. 9 for La-Ni-X alloys.

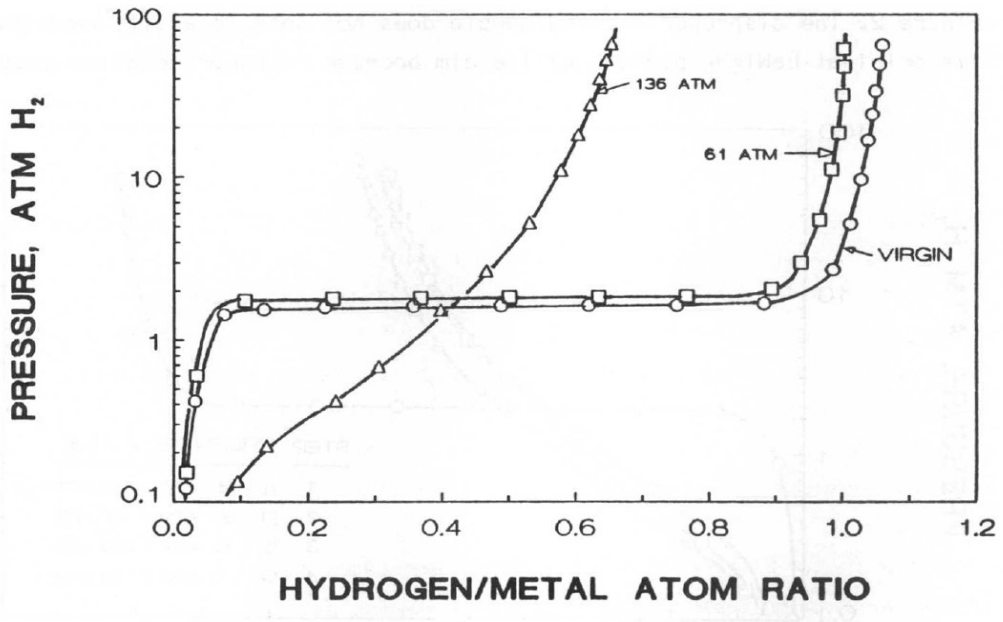


Figure 1 - Effect of H_2 pressure during 180°C/260 hr age on the 25°C desorption isotherm of $LaNi_5$.

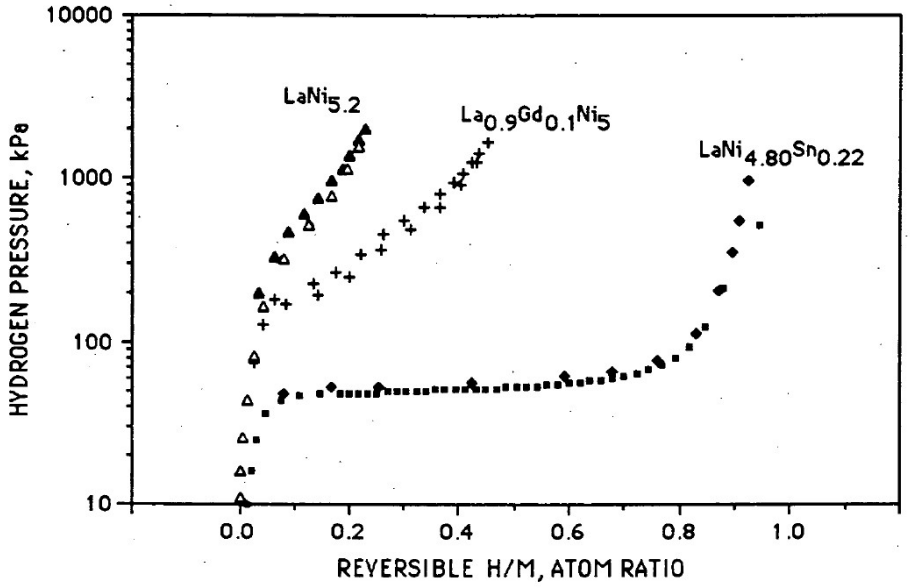


Figure 2-1. Absorption (upper) and desorption (lower) isotherms for three AB_5-type hydride alloys show significant differences in long- term performance. All three hydrides originally had flat plateaux and hydrogen capacities near H/M = 1. After 10,000 cycles only $LaNi_{4.80}Sn_{0.22}$ retained its original plateau pressure and most of its original *reversible*[6] hydrogen capacity.

The intriguing question is whether thermal aging can be used to predict tritium aging effects. Answering that question will require a significant amount of additional studies.

4.0 Summary and Path Forward

In general, no new conclusions have been generated concerning this project in FY15 and the prior conclusions have been reinforced and more thoroughly studied. The anomalous behavior of the highly loaded scoping study sample (GfE material), vis-à-vis the samples from the same base material used in this study, has been reinforced by noting the differences in plateau pressures obtained and by comparing those behaviors to the split-plateau behaviors of the LANA75 samples.

To repeat the FY14 conclusions, modified by the addition of FY15 work:

1.) LANA75 materials and other LANA85 material show HHT effects
2.) HHT effects occur differently in LANA75 than in LANA85
3.) The differences in HHT response suggest sensitivity to composition, which includes changes found from lot-to-lot in the same nominal material

Filling in the pressure depression per HHT time allows the additional conclusions:

4.) HHT effects tend to be complete within 100 days at 240 ^{o}C and higher, and are cumulative. Increased temperature induces the changes faster, with the simple process of acquiring an isotherm at 300 ^{o}C causing noticeable changes.
5.) Some anomalous behavior remains, indicating that some potentially significant variables remain unknown at this time.

No further work is currently planned on these objectives. Additional funding may be sought to pursue the poisons effect objective, which has not been addressed to date. The observation that temporary capacity loss can be observed suggests that some work aimed at defining the controlling characteristics of this phenomenon might be beneficial.

A large purchase of both LANA75 and 85 is planned in early FY16. It may be beneficial to examine some samples from these ‘fresh’ materials to assess the potential changes that occur during material storage. Literature results suggest that such changes occur rapidly in freshly prepared material.

5.0 References

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2. "Effects of Extreme and Unusual Conditions on LANA Alloys: Year-End Report, FY14 (U)", K. L. Shanahan, SRNL-STI-2014-00493, Sept. 29, 2014

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6. P. D. Goodell, J. Less Common Metals, 99 (1984) 1

7. J.-M. Park, J.-Y. Lee; Mat. Res. Bull. 22 (1987) 455

8. G. D. Sandrock, P. D. Goodell, E. L. Huston, P. M. Golben; Zeit. Phys. Chem. N.F., 164 (1989) S1285

9. F. E. Lynch, Report to NASA, NAS9-18175, p. 2-2, (1991)

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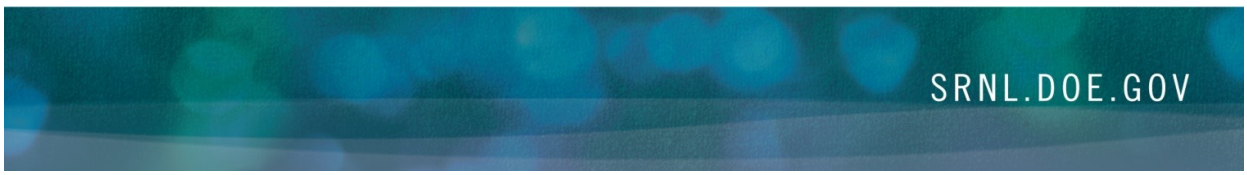
11. S. Luo, Ted B. Flanagan, Robert C. Bowman, Jr., J. of Alloys and Cmpds. 574 (2013) 443.

12. A. L. Shilov, M. E. Kost, and N. T. Kuznetsov, J. of the Less-Common Metals, 144 (1988) 23.

Appendix A: SEM/EDX results

This Appendix is retained unchanged from the FY15 Mid-Year report[3].

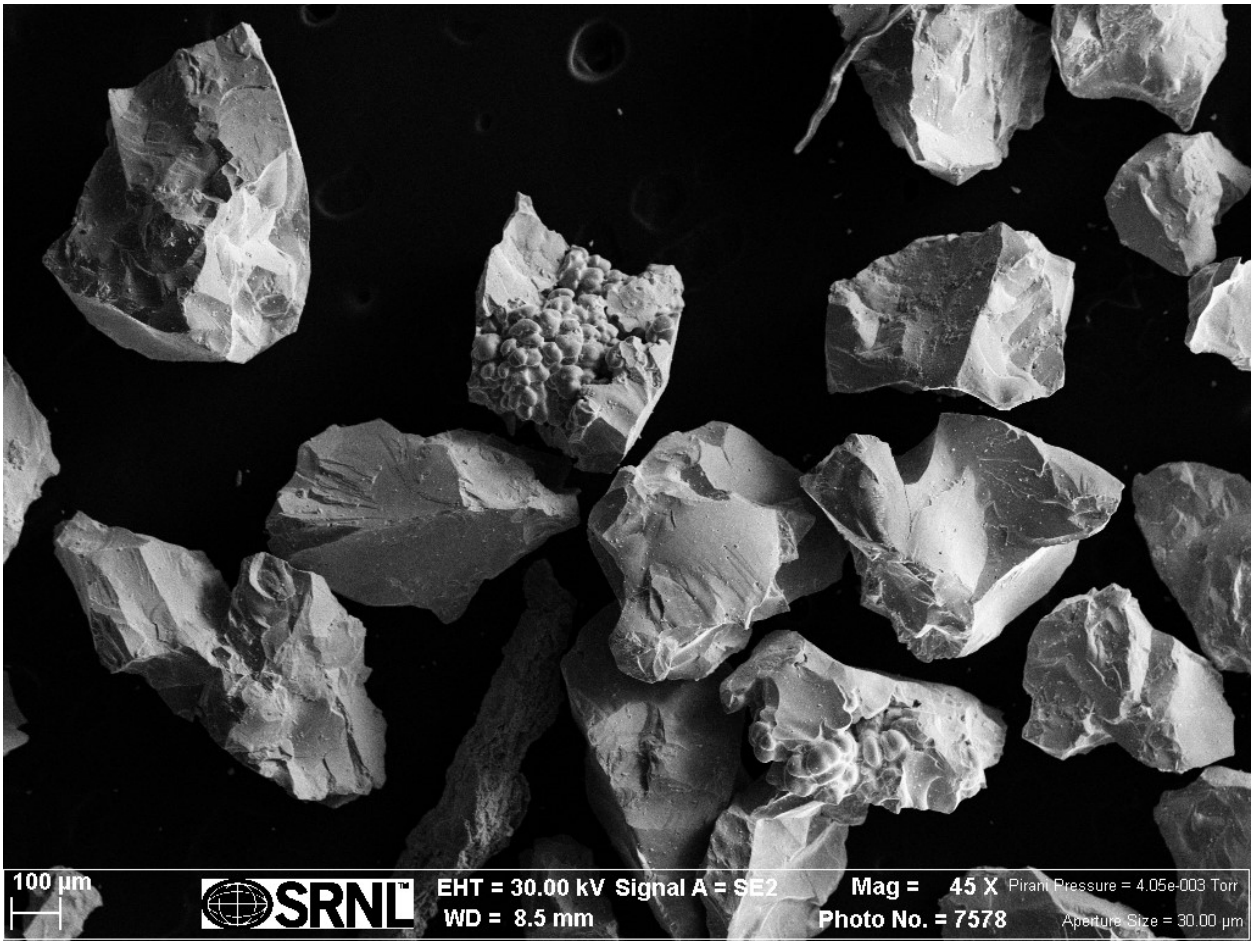
Only selected images are presented here. Many other additional SEM images were acquired and examined, and will be available in the final report. All available EDX results are included here. The results in this appendix were supplied by Henry Ajo of the Analytical Development Section of SRNL.



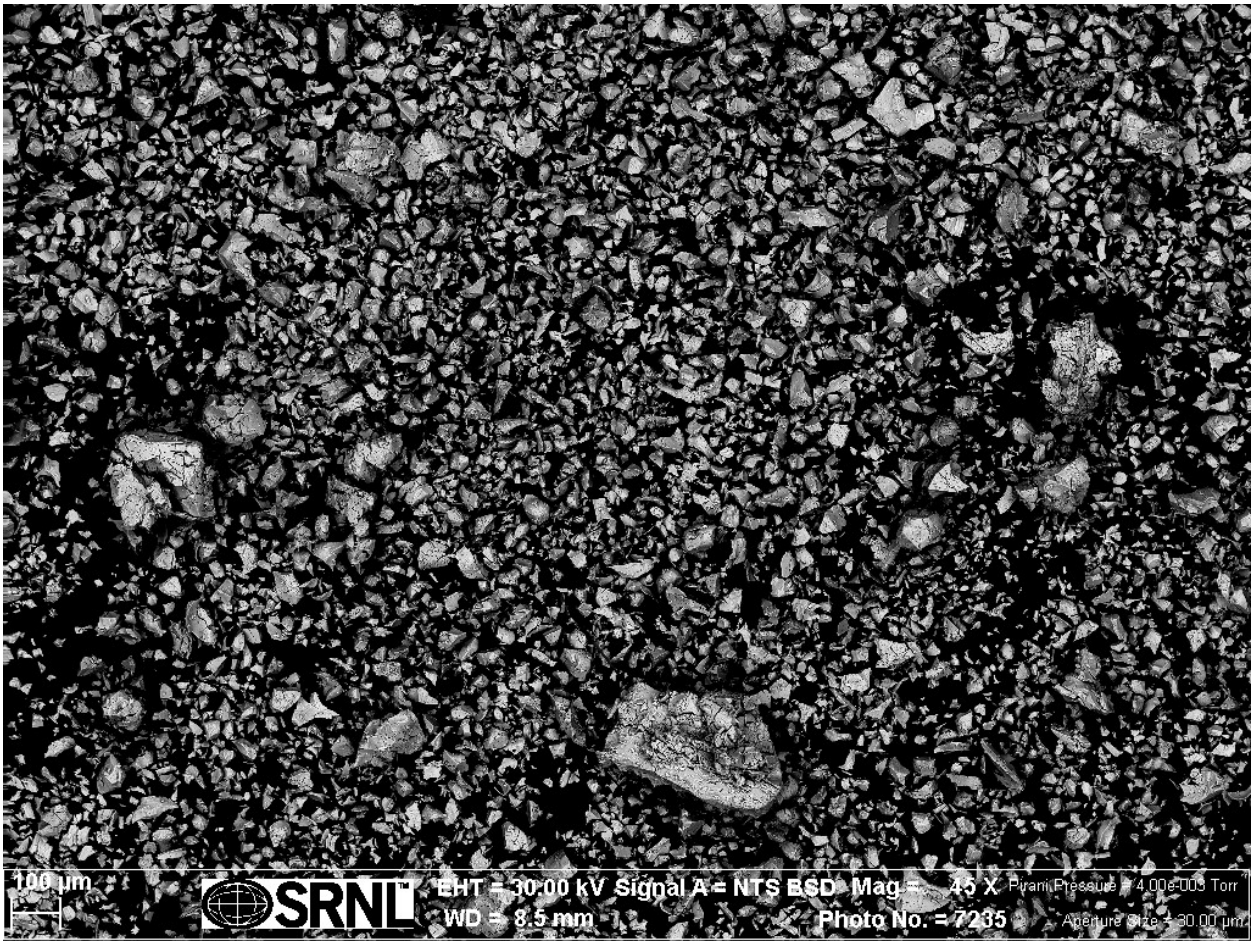
Part 1a: SEM images

Some selected comparative SEM images for Virgin and Aged TCON LANA:

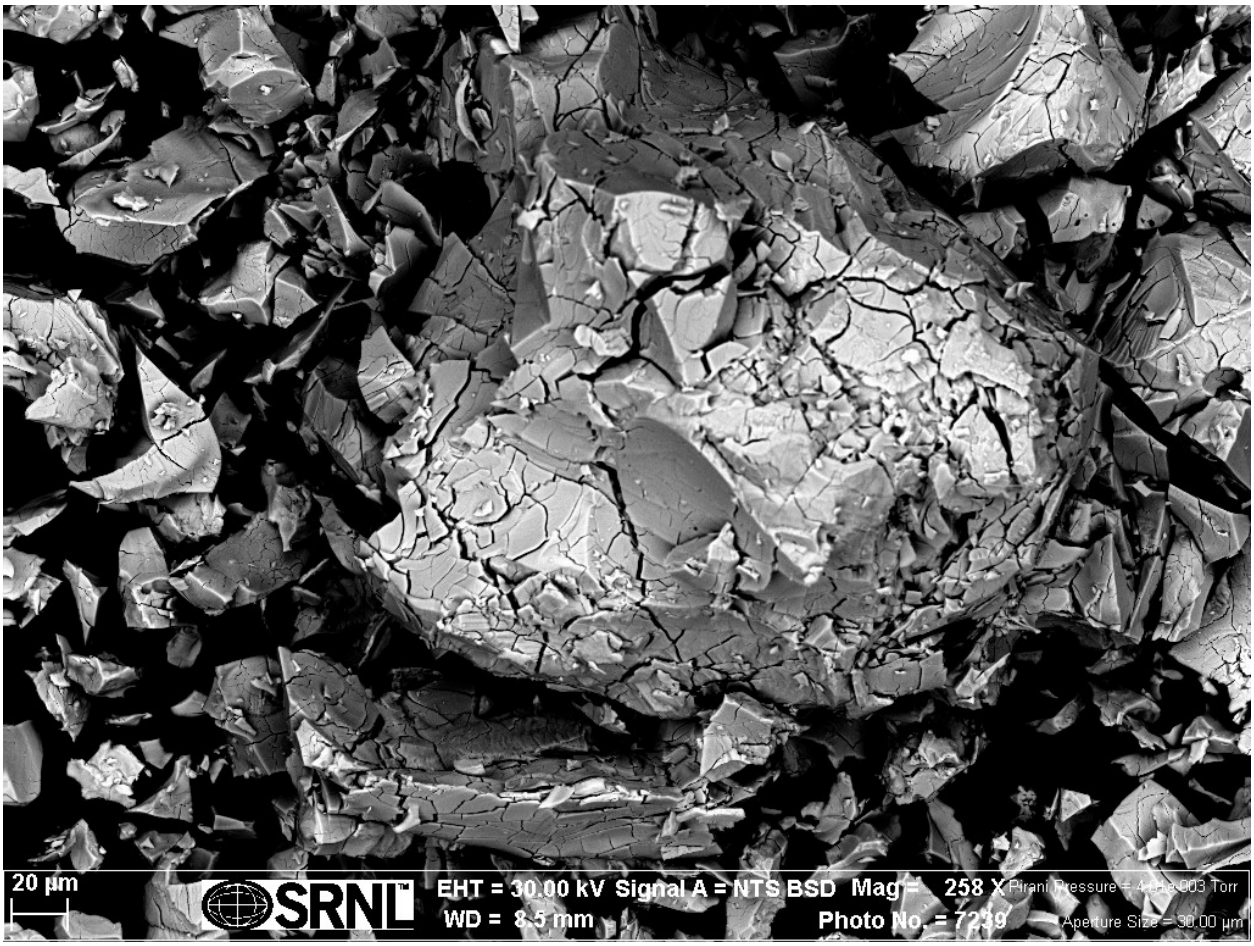
Virgin – 45X - Note the three types of surfaces: flat, fracture surfaces that comprise most of the sample's surfaces, the globular formations seen on two particles, and the highly textured surface on the one pseudo-cylindrical particle



Aged - 45X – Note the size reduction due to decrepitation

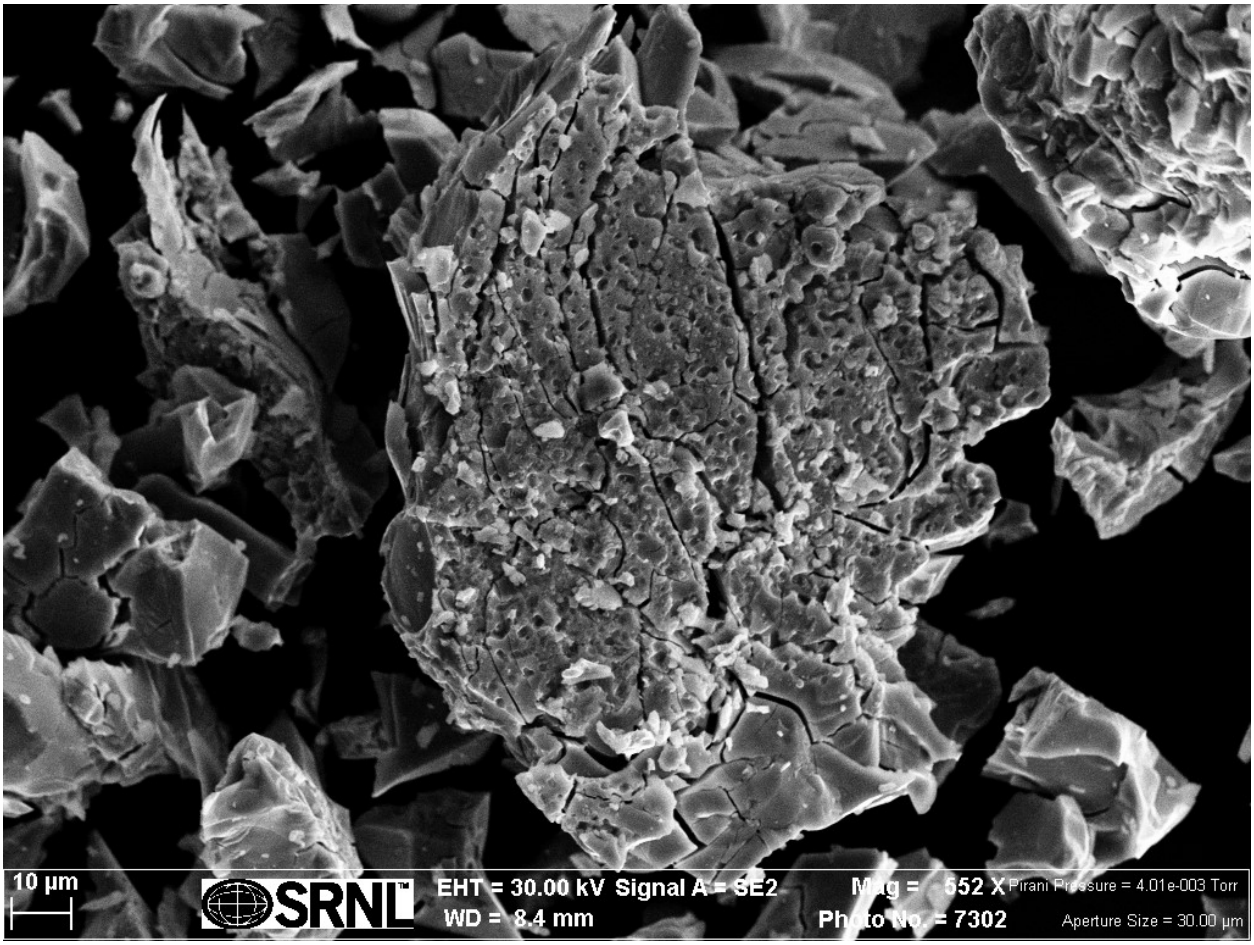


Aged – 258X – cracked larger particle



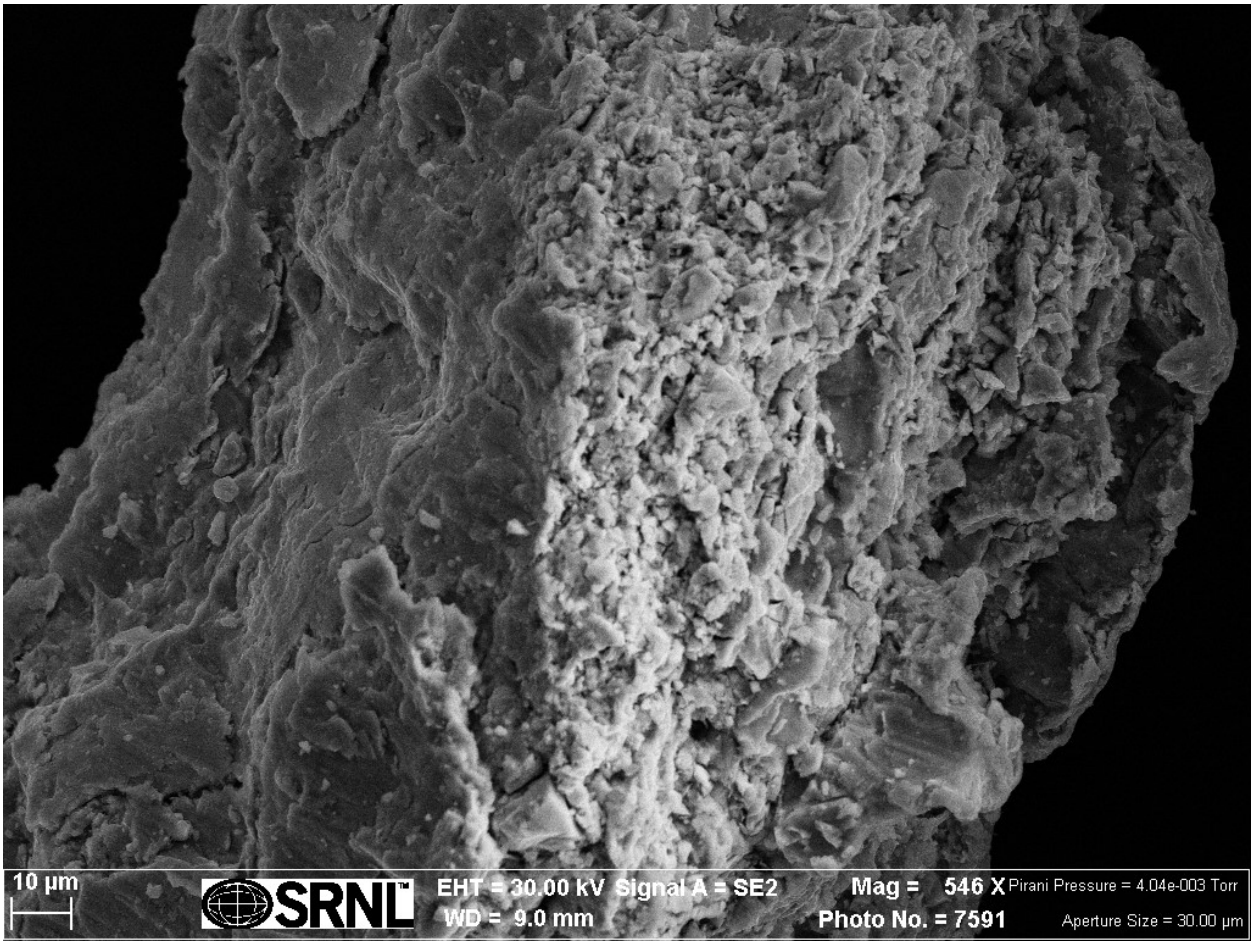
Aged – 295X - cracked larger particle

Aged – 552X – cracked with holes

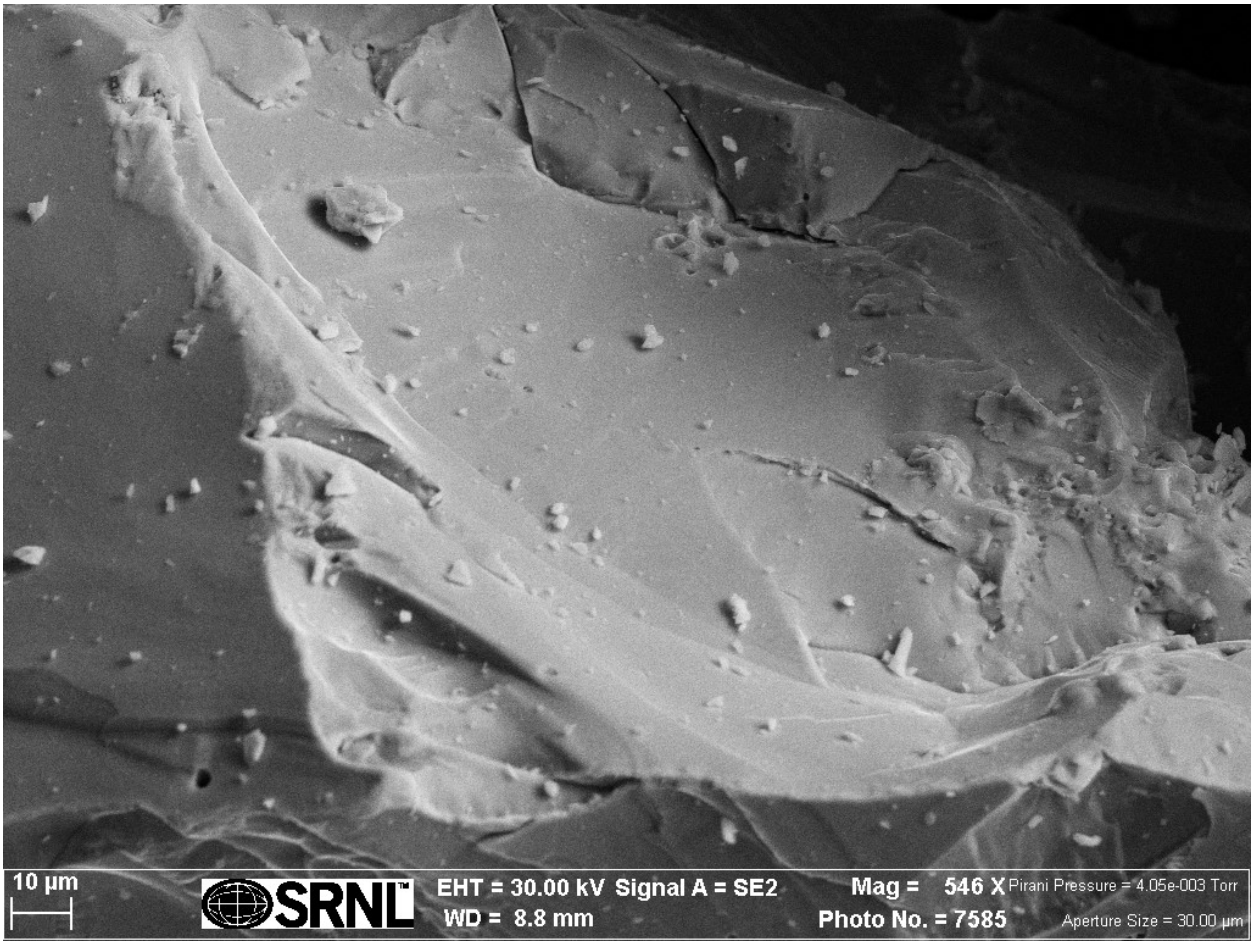


Virgin – 546X – unusual formation – ‘melted’ or ‘globular’ appearance

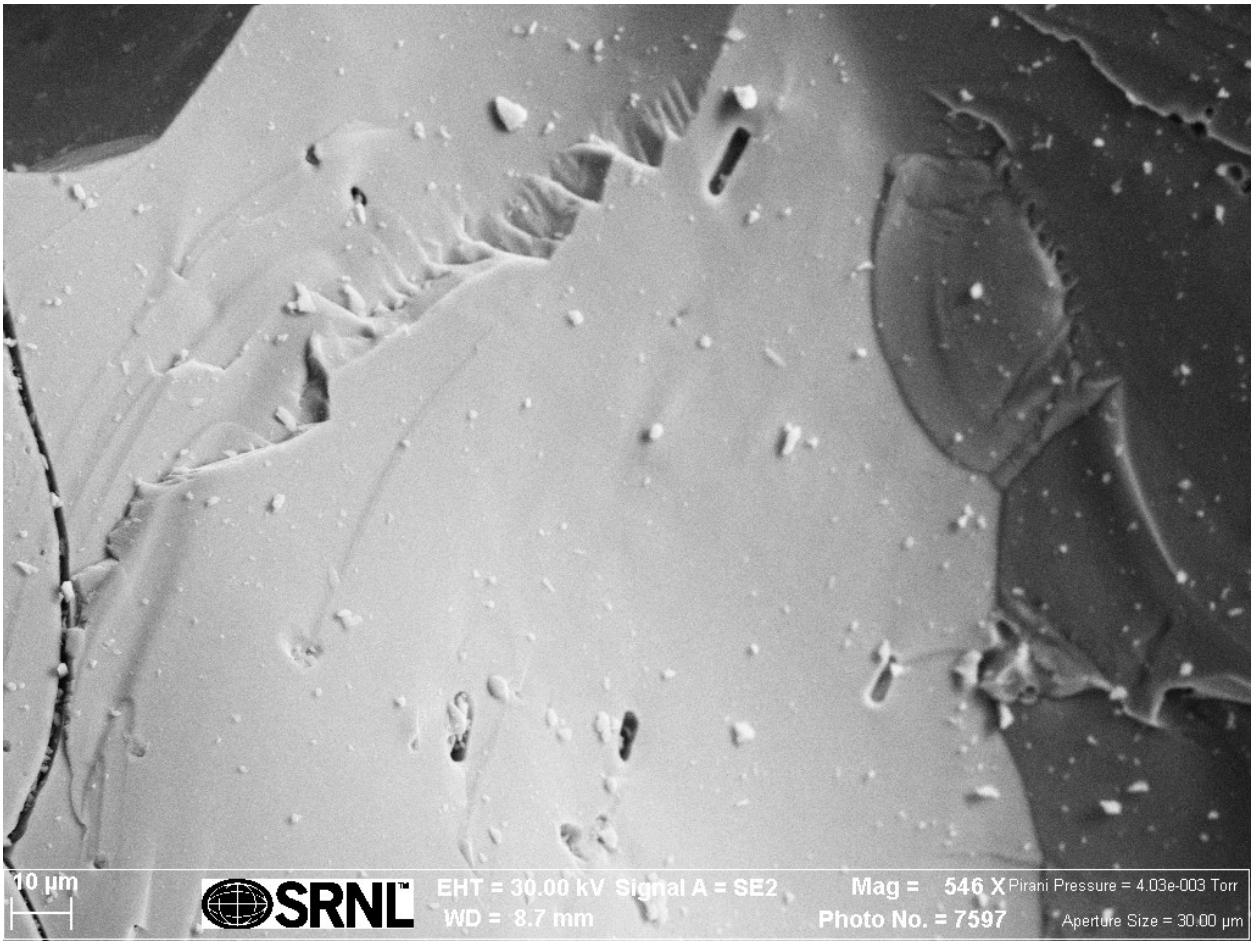
Virgin – 546X – unusual formation – ‘textured’ surface



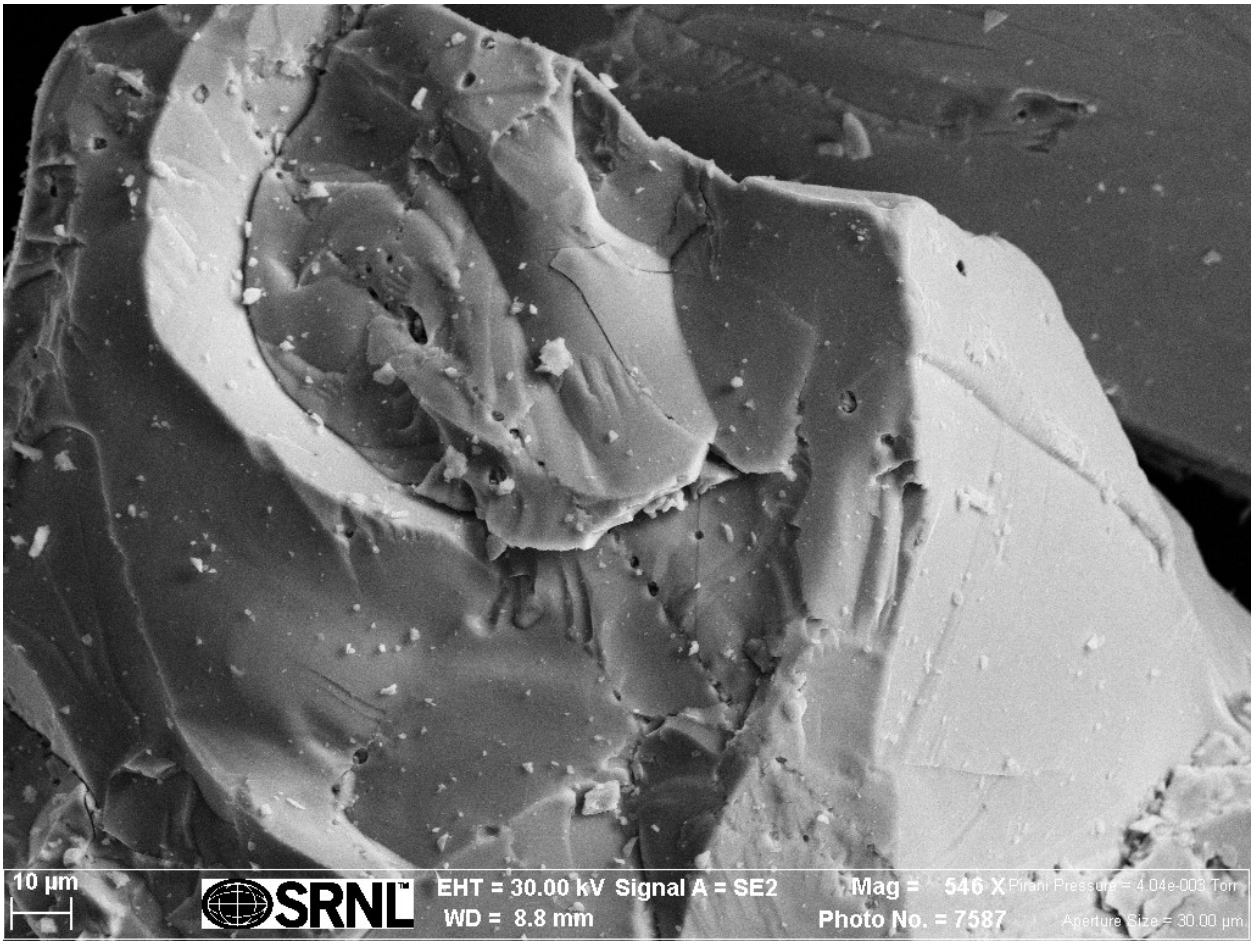
Virgin – 546X – flat surface, probably due to fracture



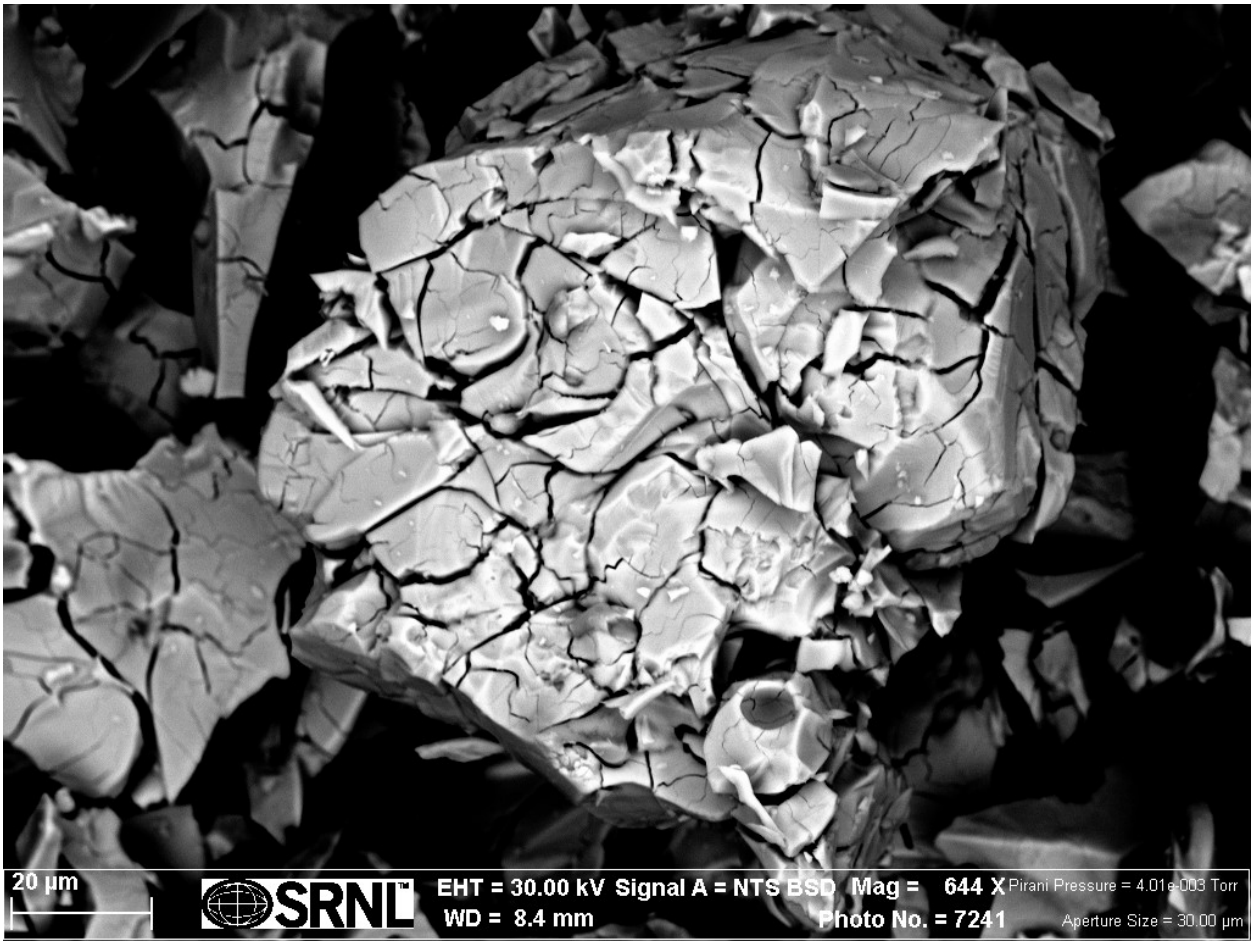
Virgin – 546X


10 µm
SRNL
EHT = 30.00 kV Signal A = SE2
WD = 8.7 mm
Mag = 546 X Pirani Pressure = 4.03e-003 Torr
Photo No. = 7597
Aperture Size = 30.00 µm

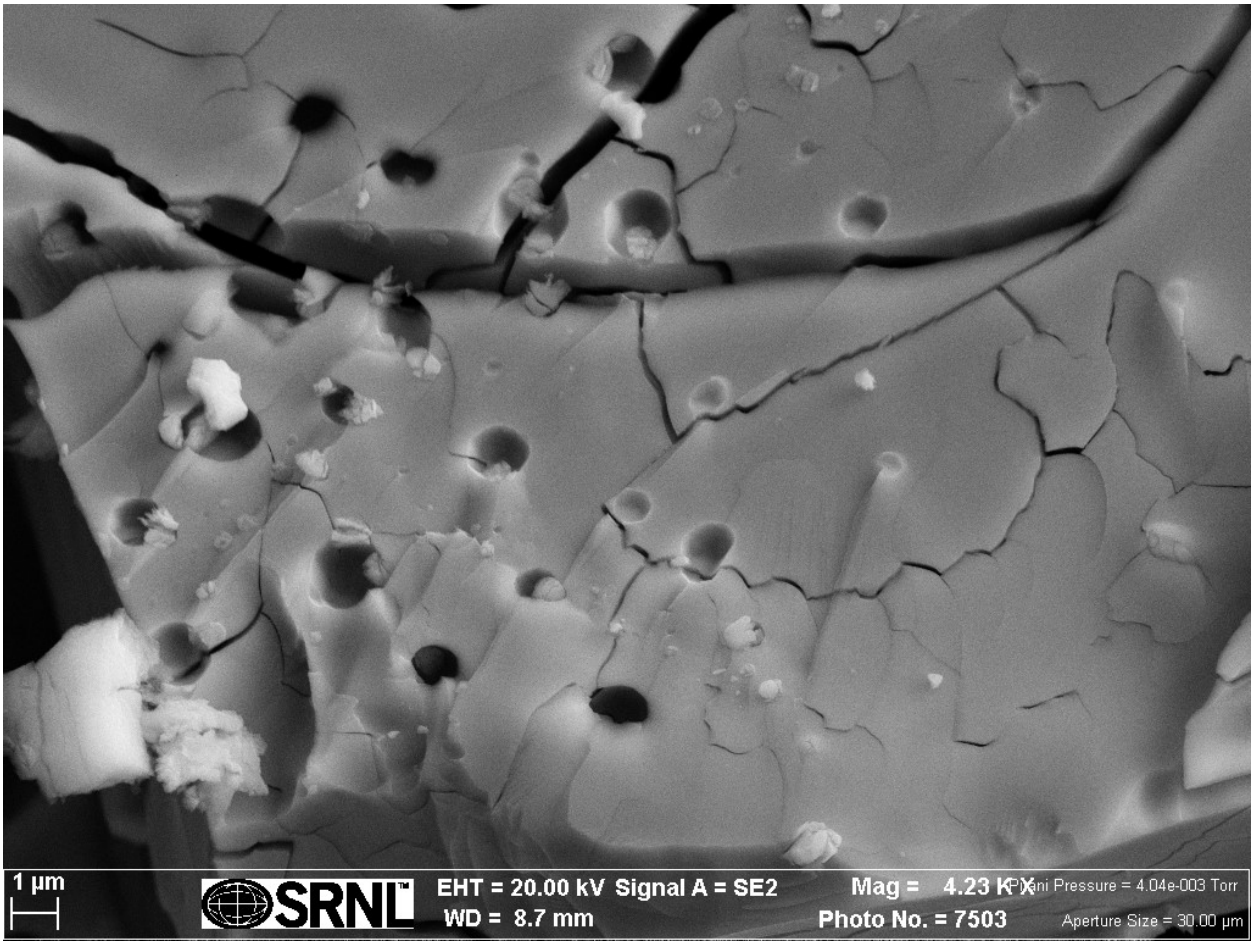
Virgin – 546X


10 µm
SRNL
EHT = 30.00 kV Signal A = SE2
WD = 8.8 mm
Mag = 546 X
Photo No. = 7587
Pirani Pressure = 4.04e-003 Torr
Aperture Size = 30.00 µm

Aged – 644X

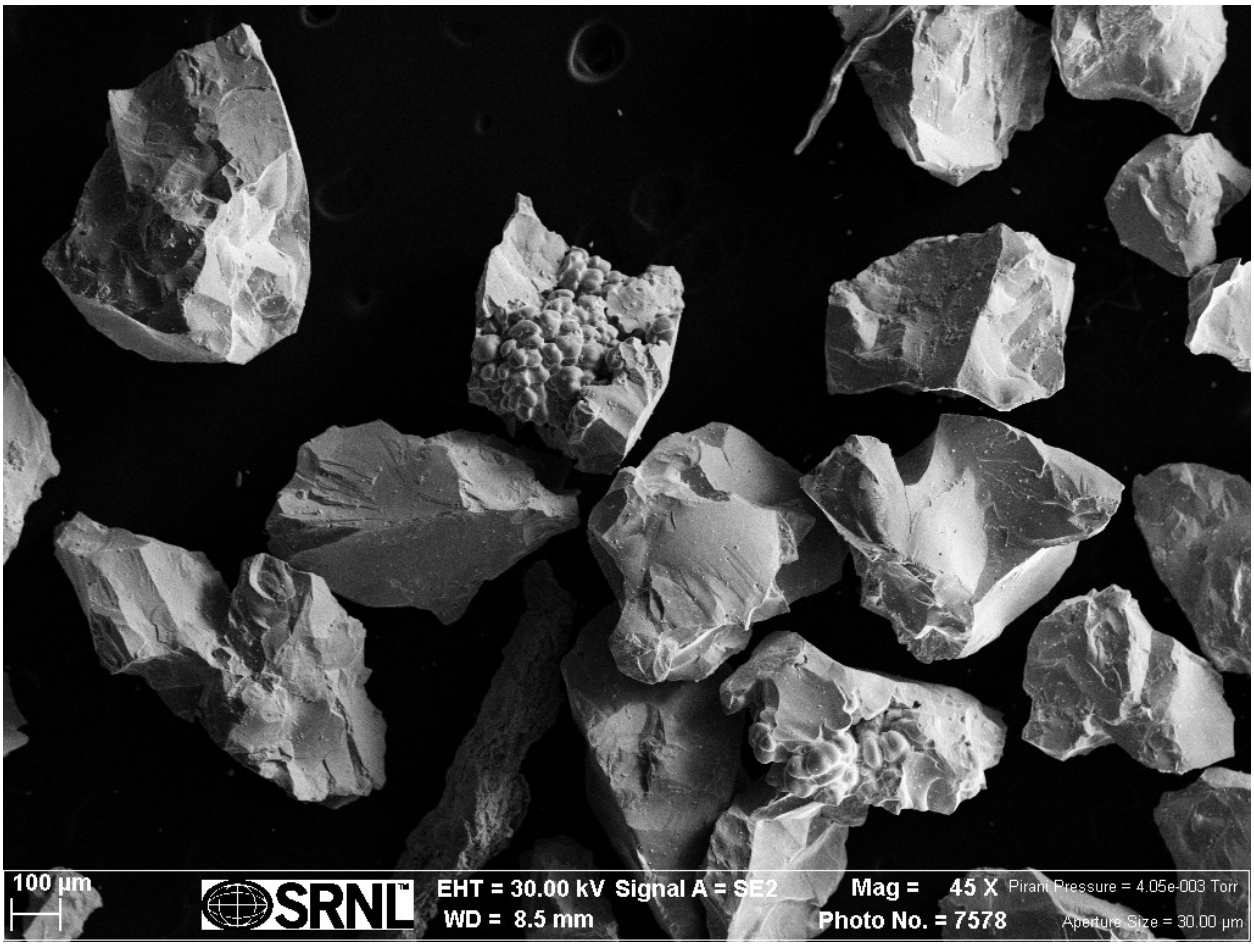

20 µm
SRNL
EHT = 30.00 kV Signal A = NTS BSD Mag = 644 X Pirani Pressure = 4.01e-003 Torr
WD = 8.4 mm Photo No. = 7241 Aperture Size = 30.00 µm

Aged - 4230X – La2O3 (bright spots) and Ni (dark spots) contaminants

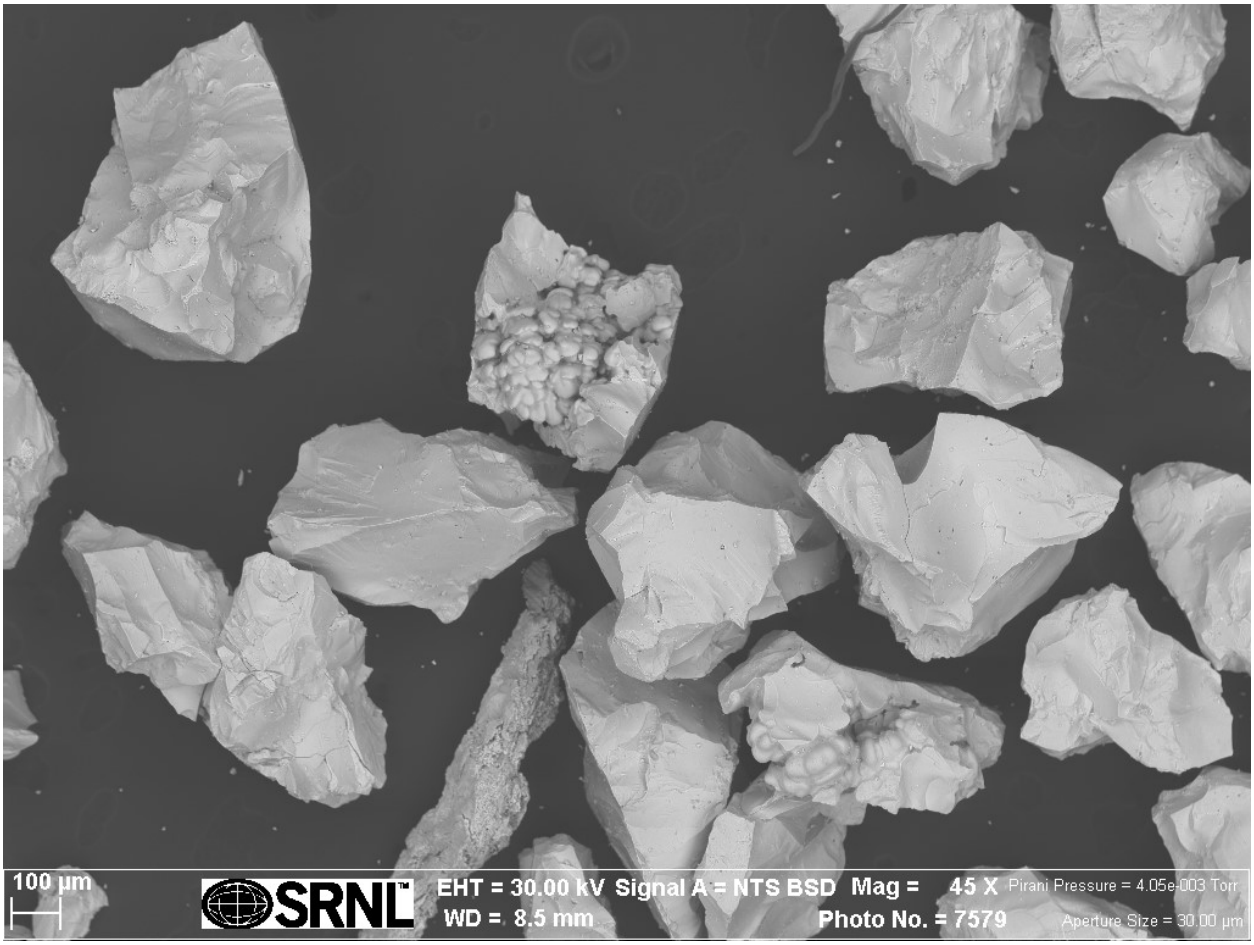


Part 1b: SEM images - Virgin material with EDX spectra

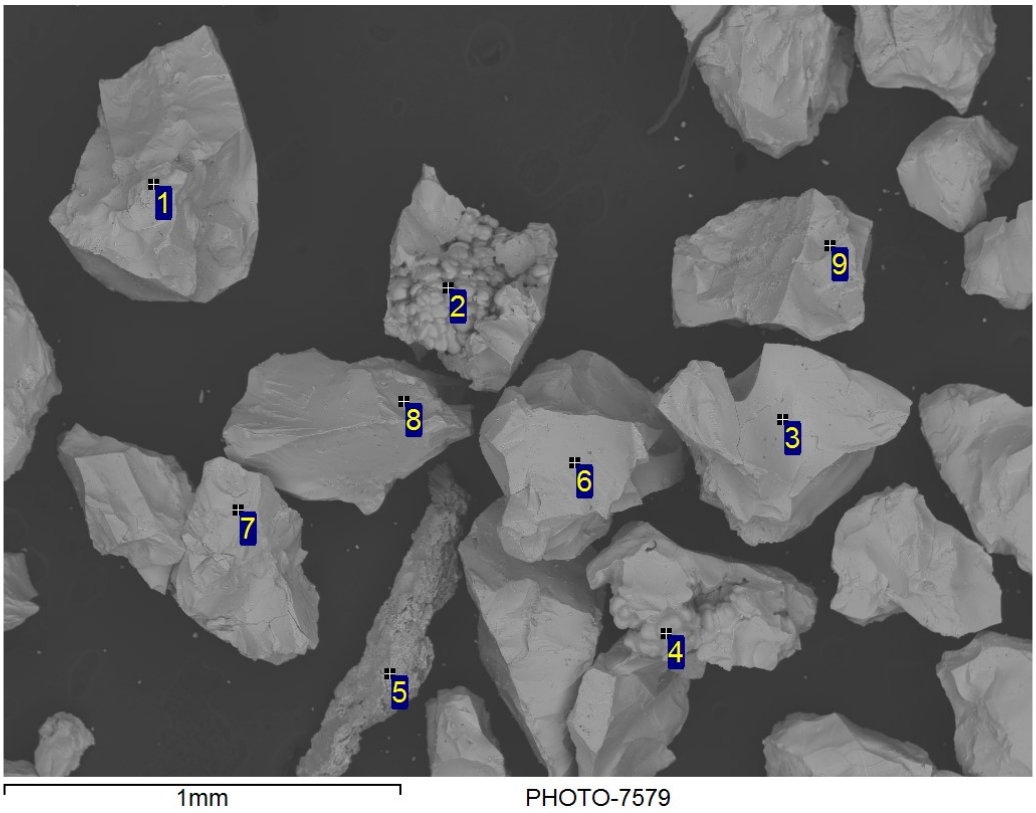
The TCON LANA75 virgin material was studied with EDX analysis. Shown below is a SEM photograph at 45X magnification. Note the three types of surfaces: flat, fracture surfaces that comprise most of the sample's surfaces, the globular formations seen on two particles, and the highly textured surface on the one pseudo-cylindrical particle. This image is obtained from secondary electrons, and shows high visual contrast.



This image shows the same view as the image above but taken with backscattered electrons.

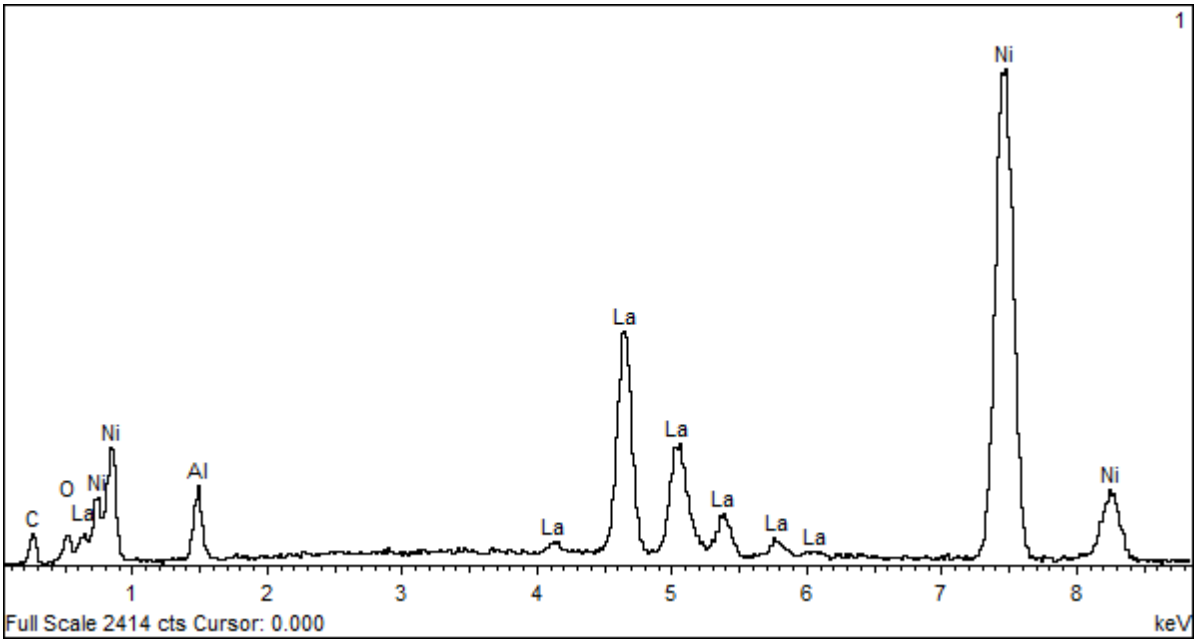


Below, numbers are superimposed on the above image, appearing in the image below to link the EDX spectra shown subsequently to a physical location in the sample/photograph. The number in the upper right-hand corner of the EDX image corresponds to the numbers superimposed on the SEM photo. This convention is used with the other following photographs as well.

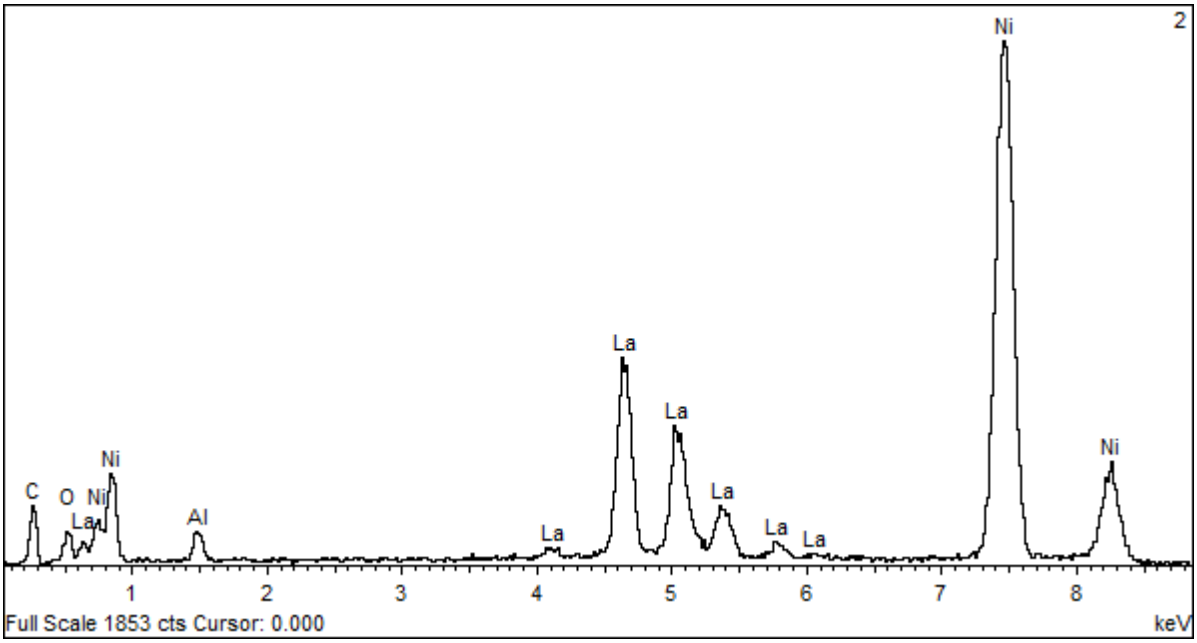


EDX Spectra

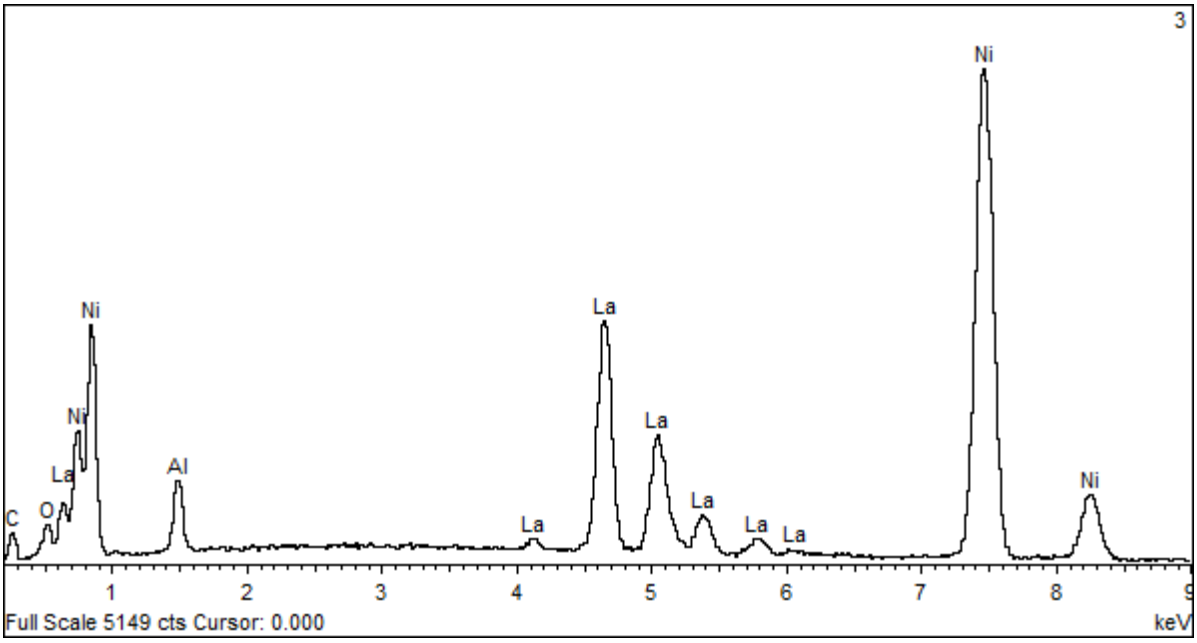
From one of the flat spots (#1), a typical LANA75 spectrum, note the La to Ni to Al peak height ratios:



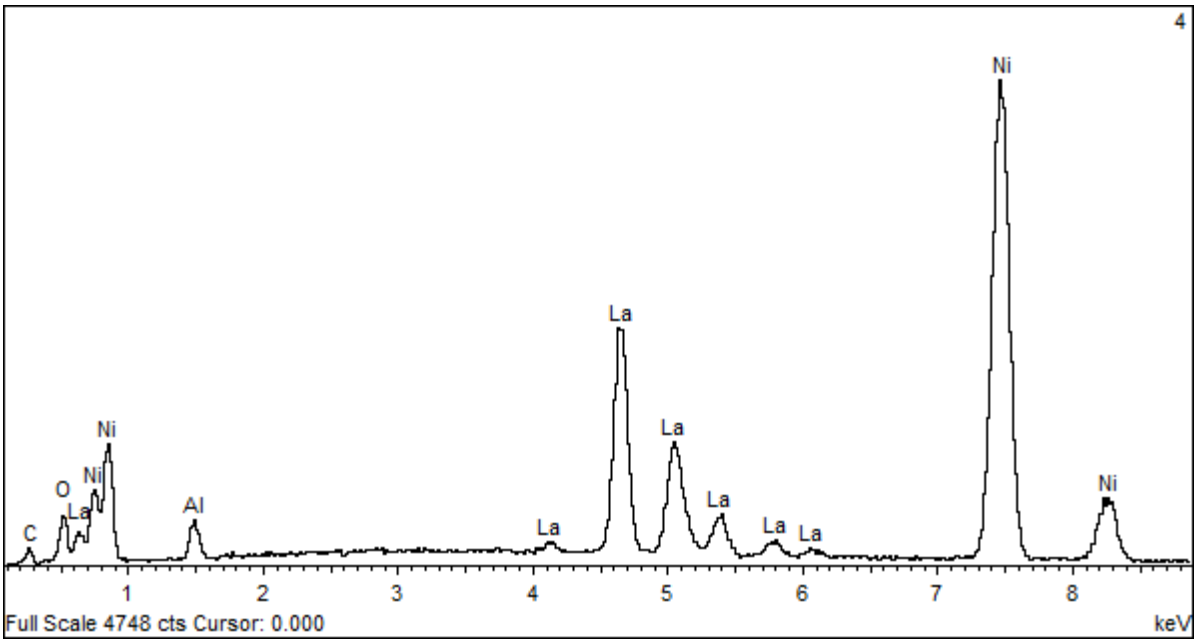
A spot on the globular formation (#2), seems to be low in Al:



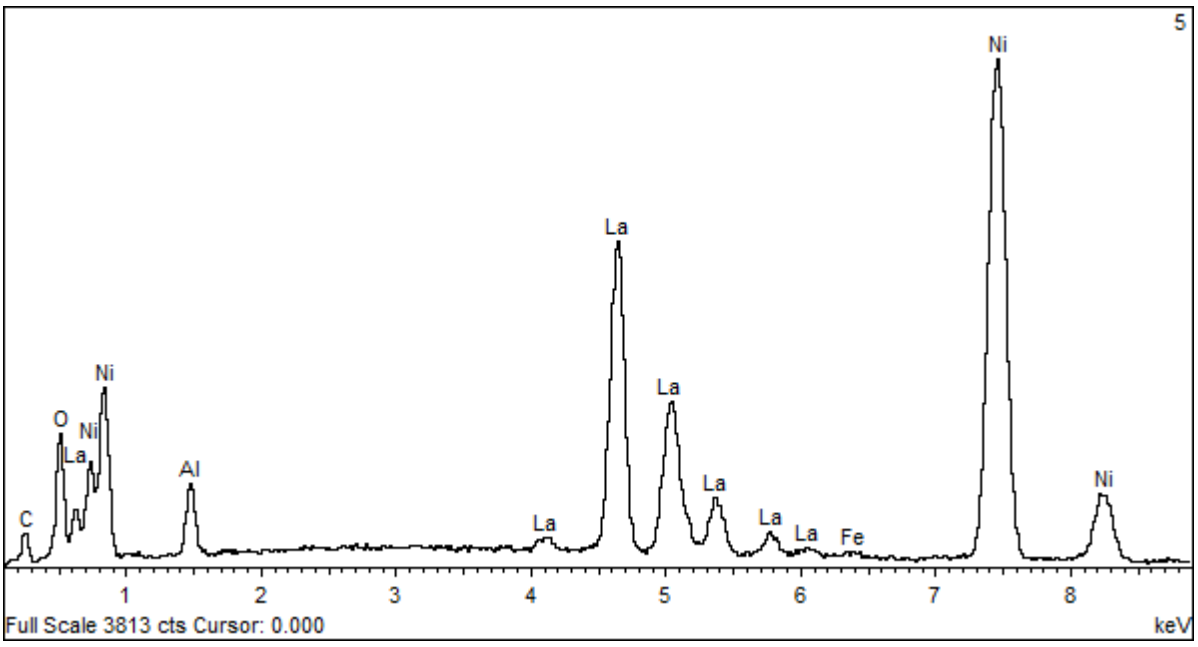
A flat area (#3):



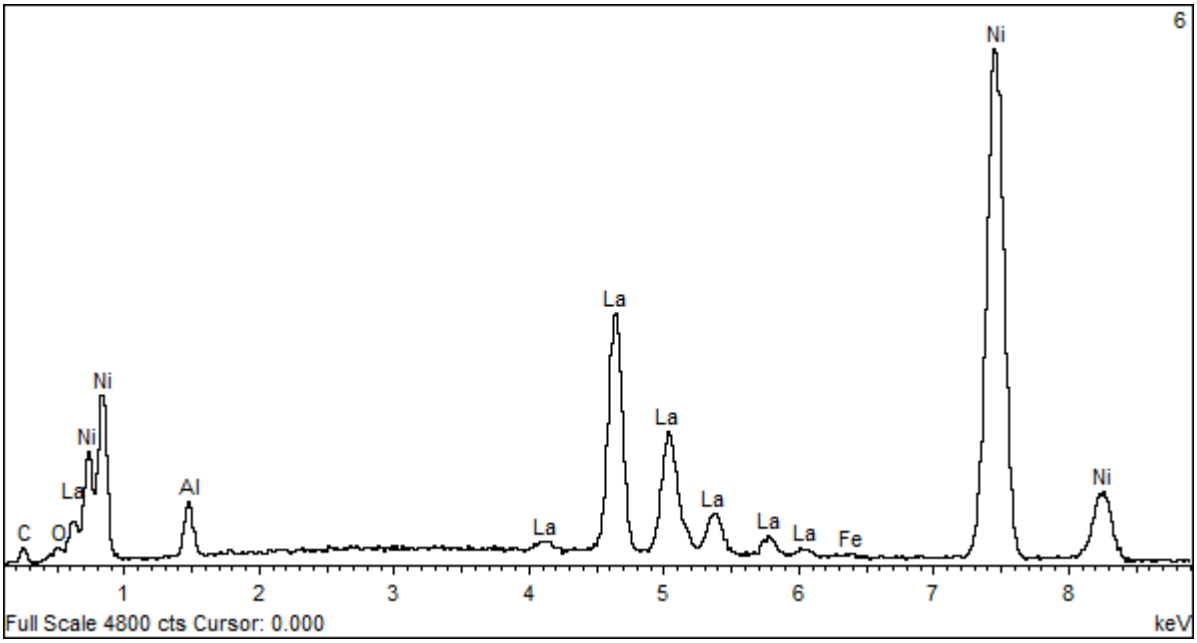
From the other globular area (#4), a little low in Al:



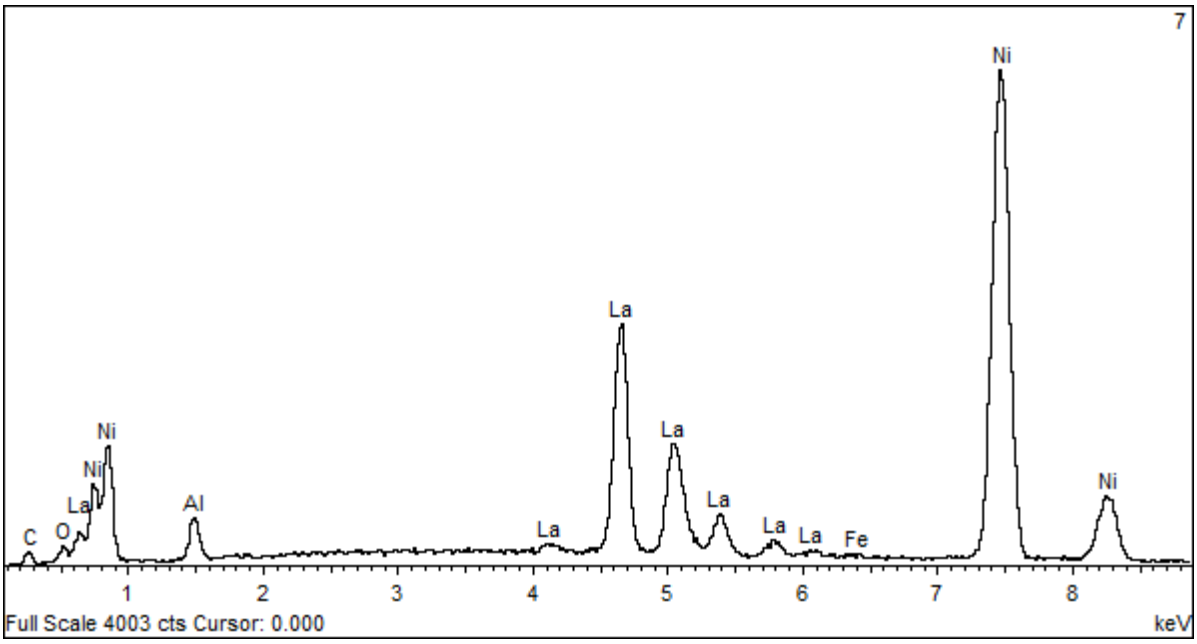
From the textured area on the pseudo-cylindrical particle (#5)



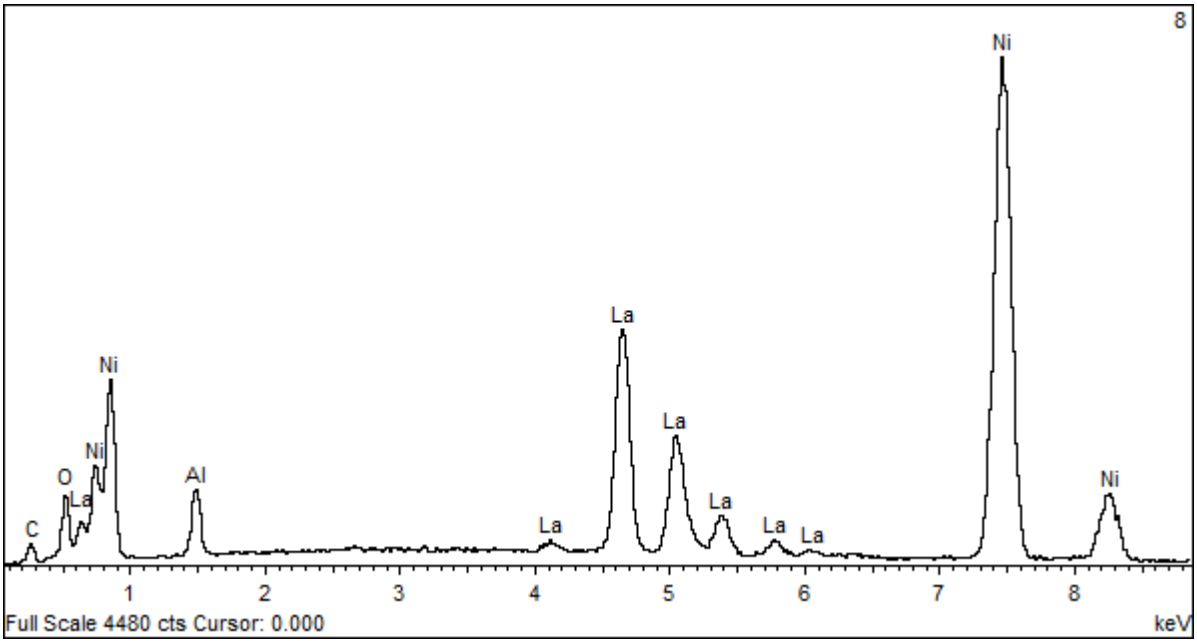
A flat area (#6), lowest O level:



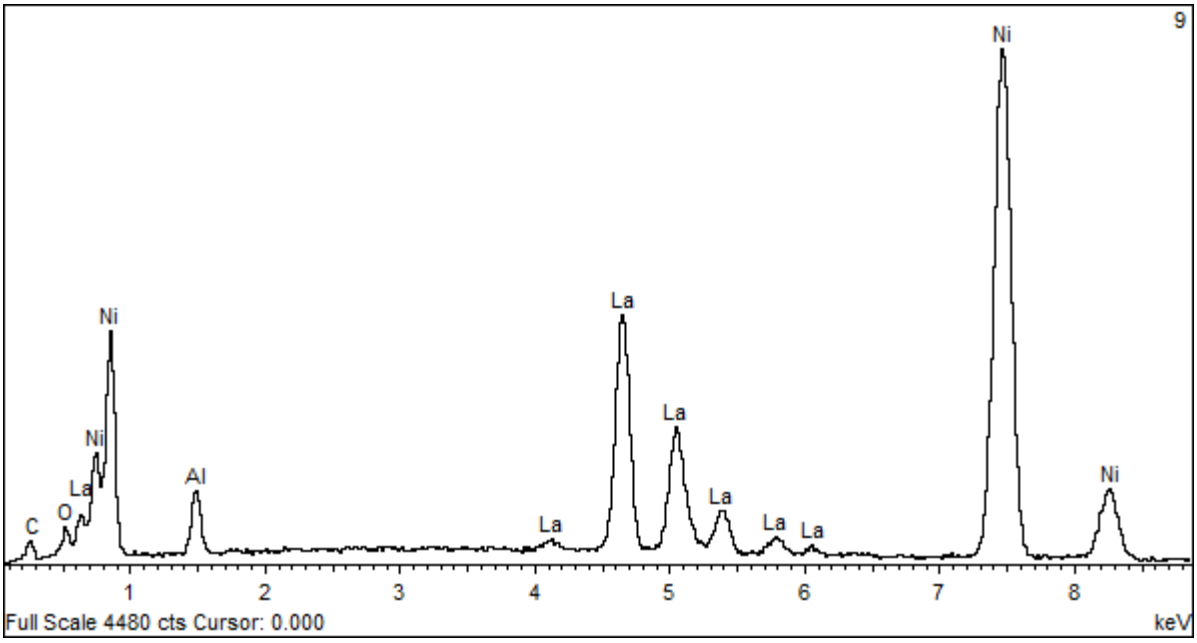
A flat area (#7):



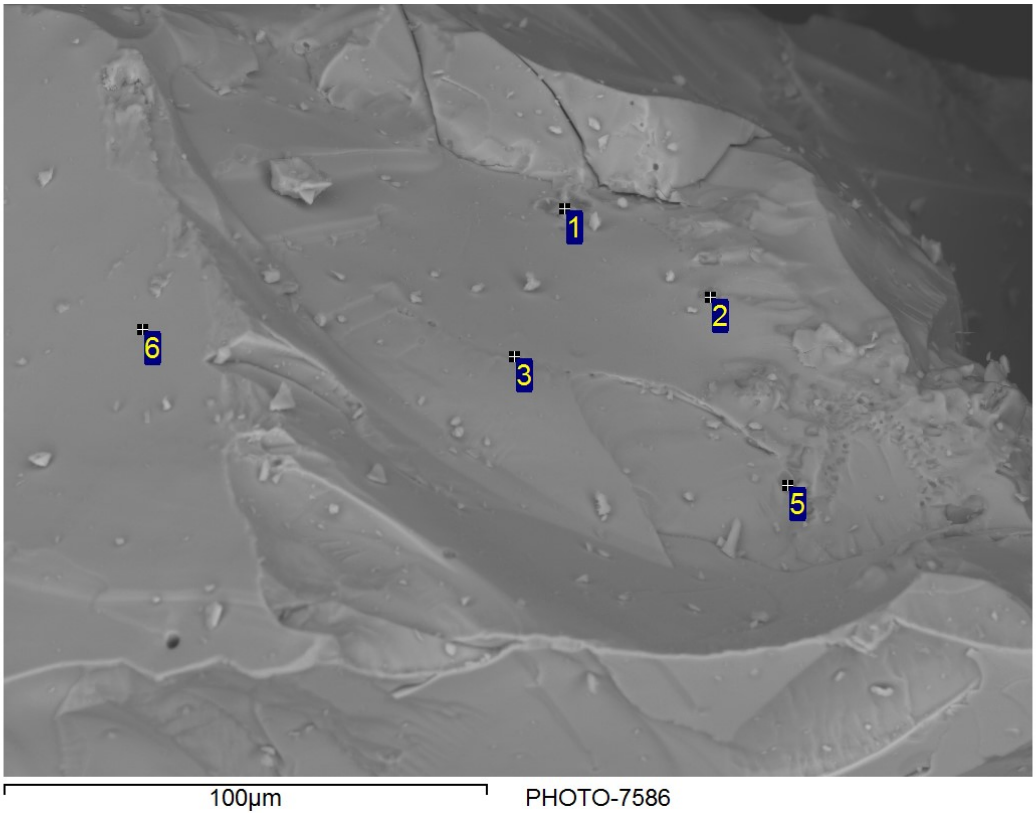
A flat area (#8), slightly high O level:



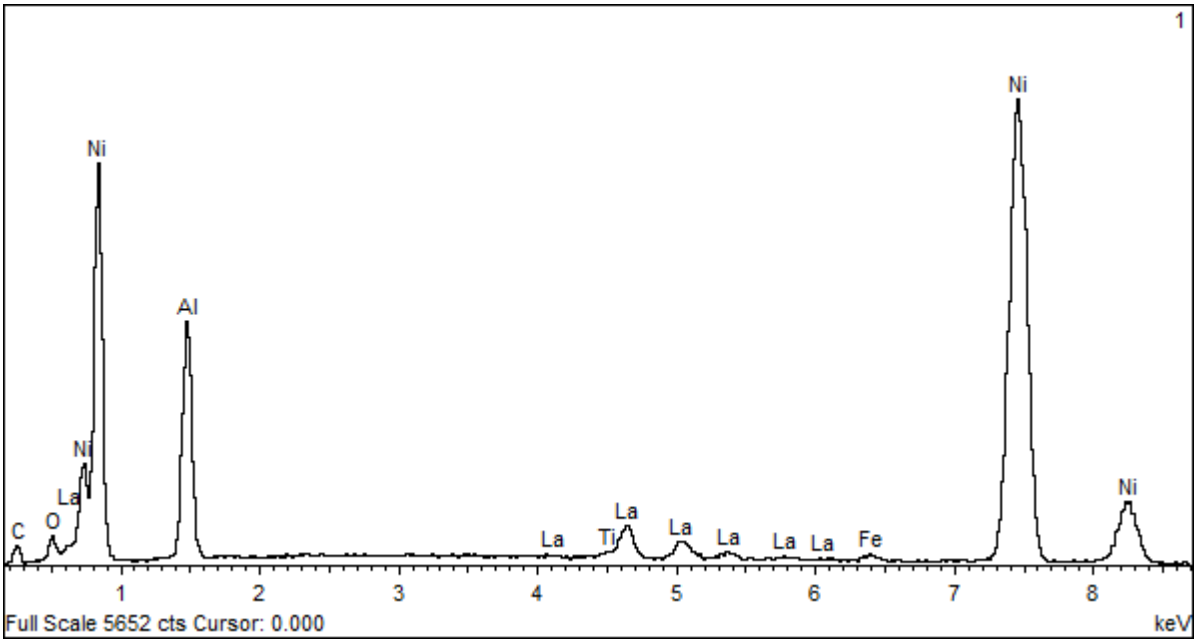
A flat area (#9):



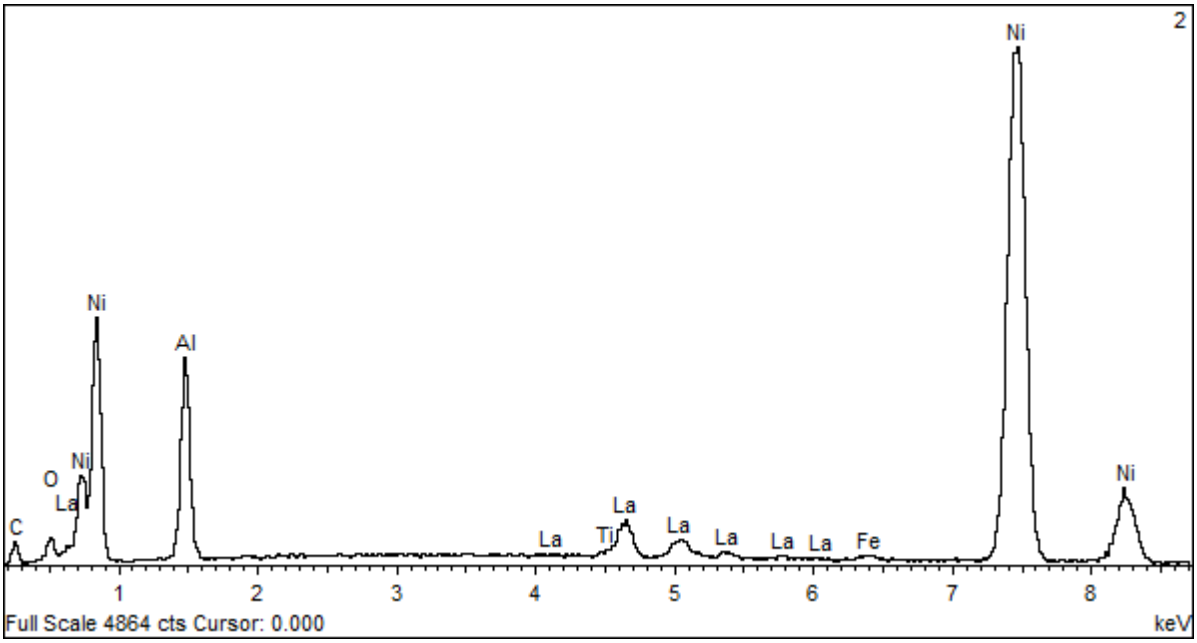
Another image: Spots 1, 2, and 5 are darker spots with trace Fe and sometimes Ti.



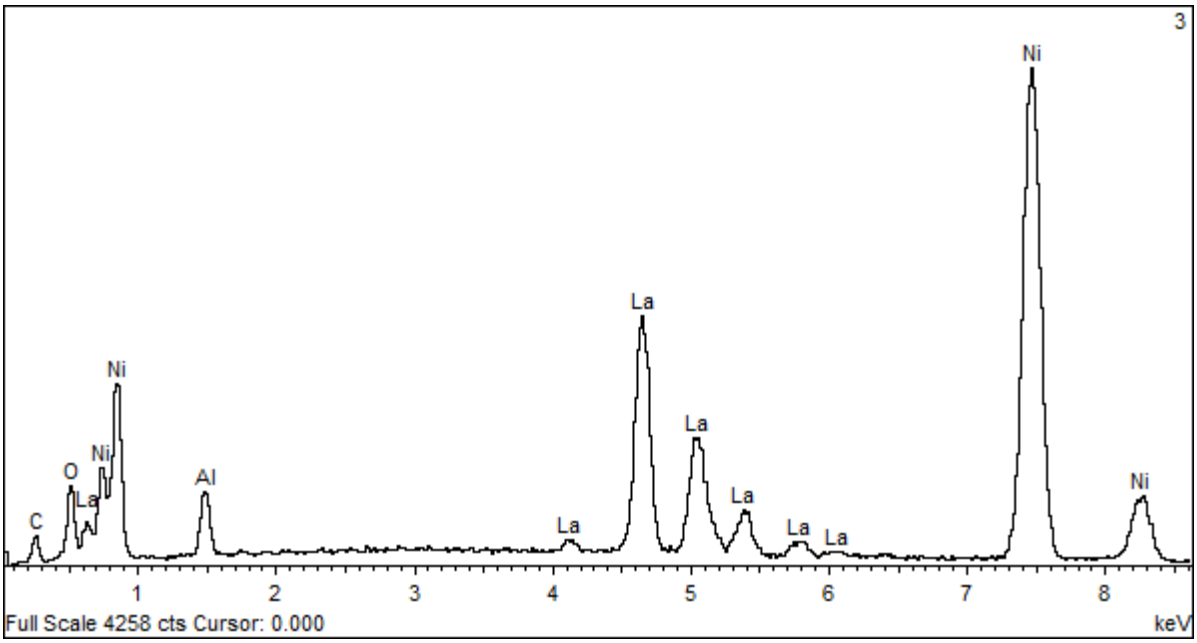
Spots 1: trace of Fe detected, depleted in La, enriched in Ni – probably a NiAl phase



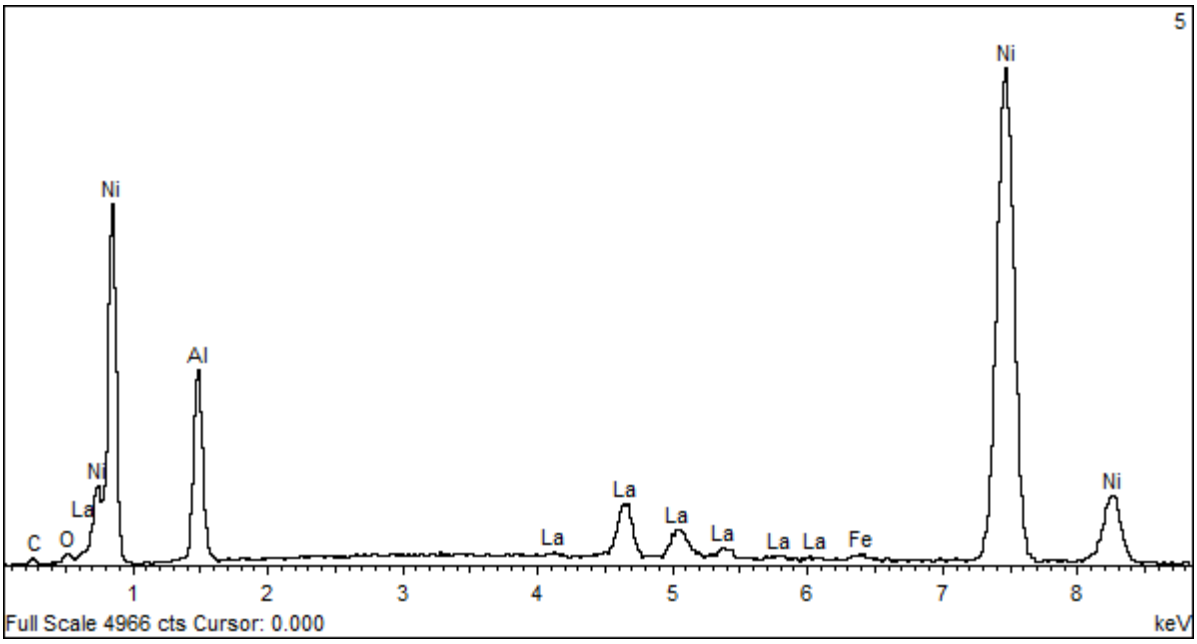
Spot 2: Depleted in La, trace Fe, Ti



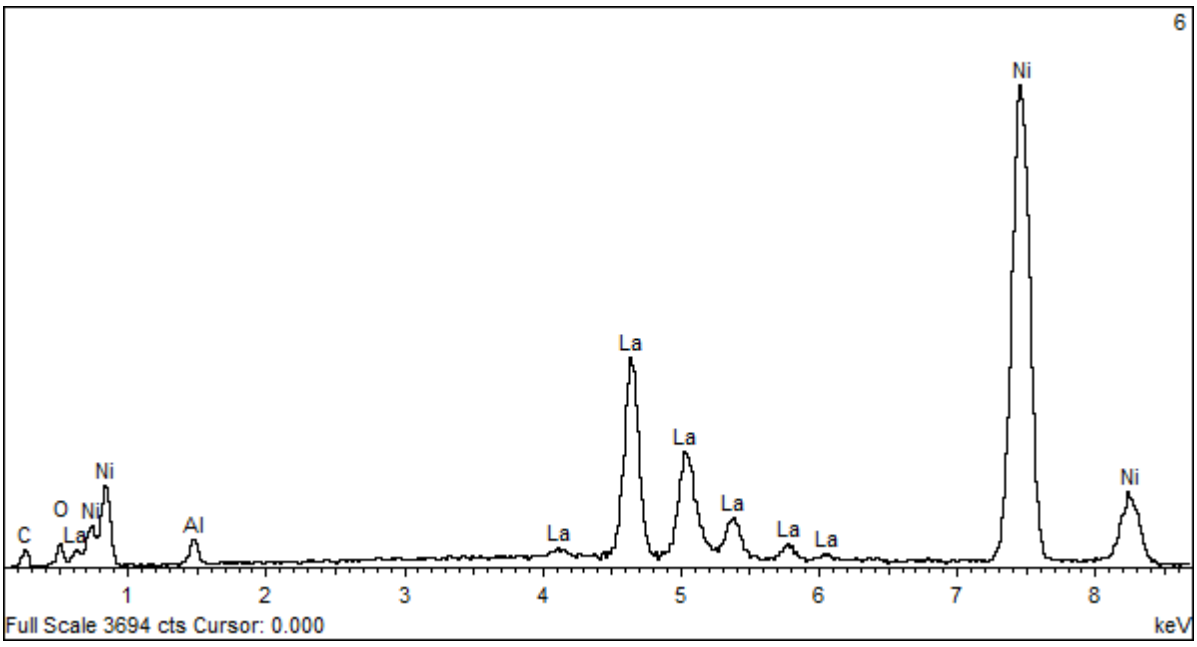
Spot 3: On the flat fracture surface, 'normal' LANA



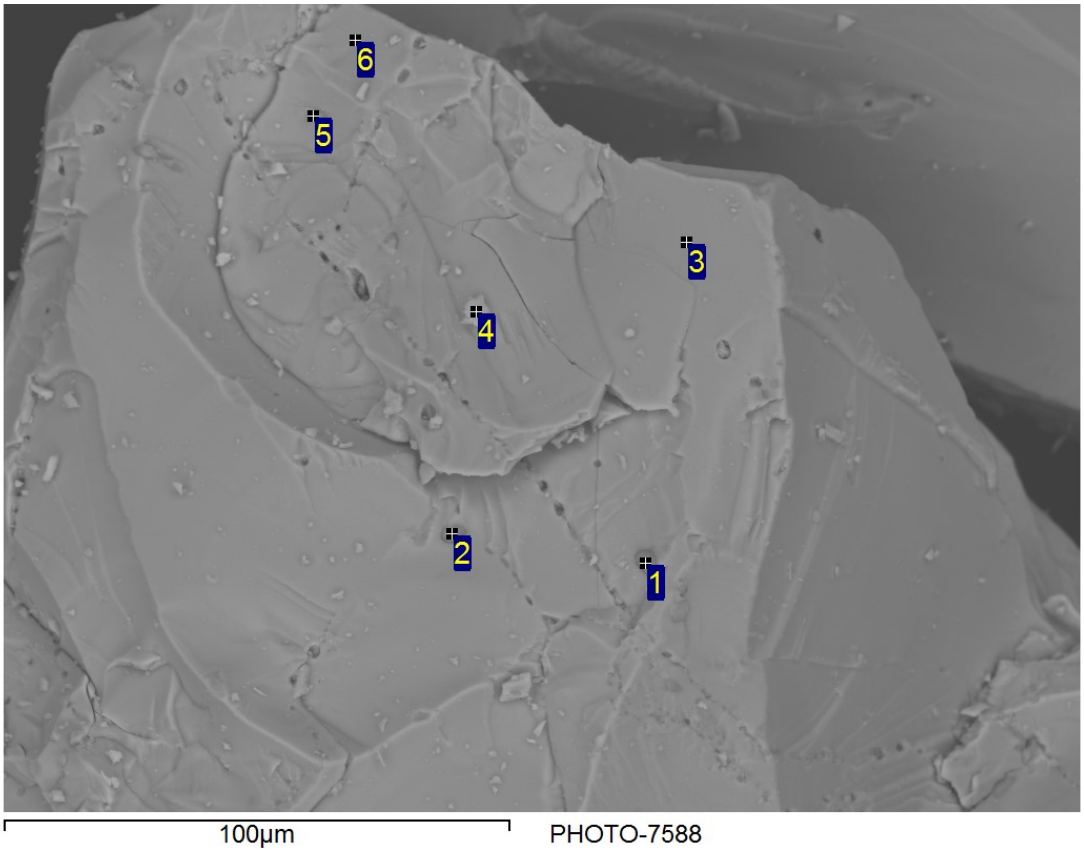
Spot 5: NiAl phase again (Spot 4 not recorded due to low counts)



Spot 6: Low Al

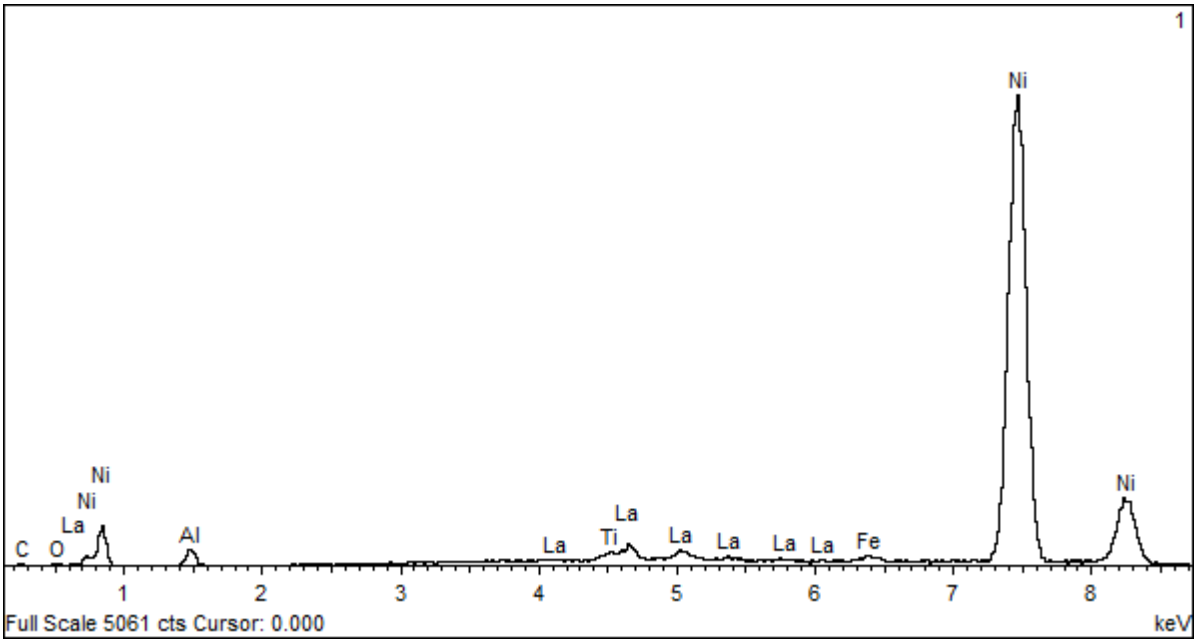


Another image. Note the chain of spots (holes?) that run in straight lines, probably at grain boundaries

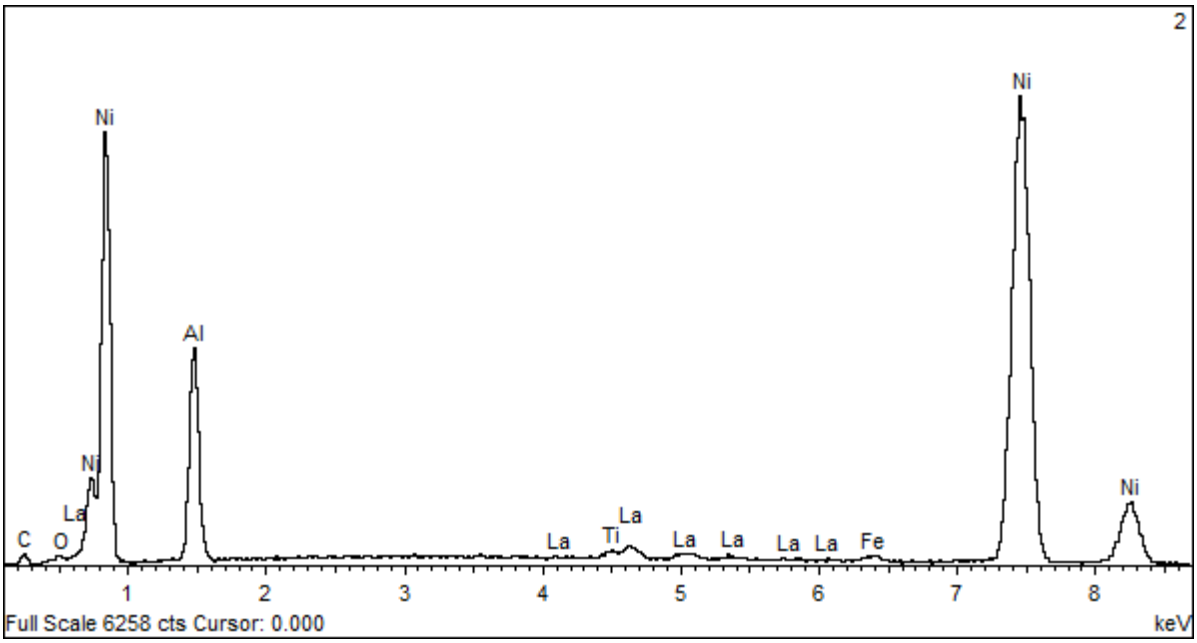


Spots 1, 2, and 5 are darker spot with trace Fe and Ti.

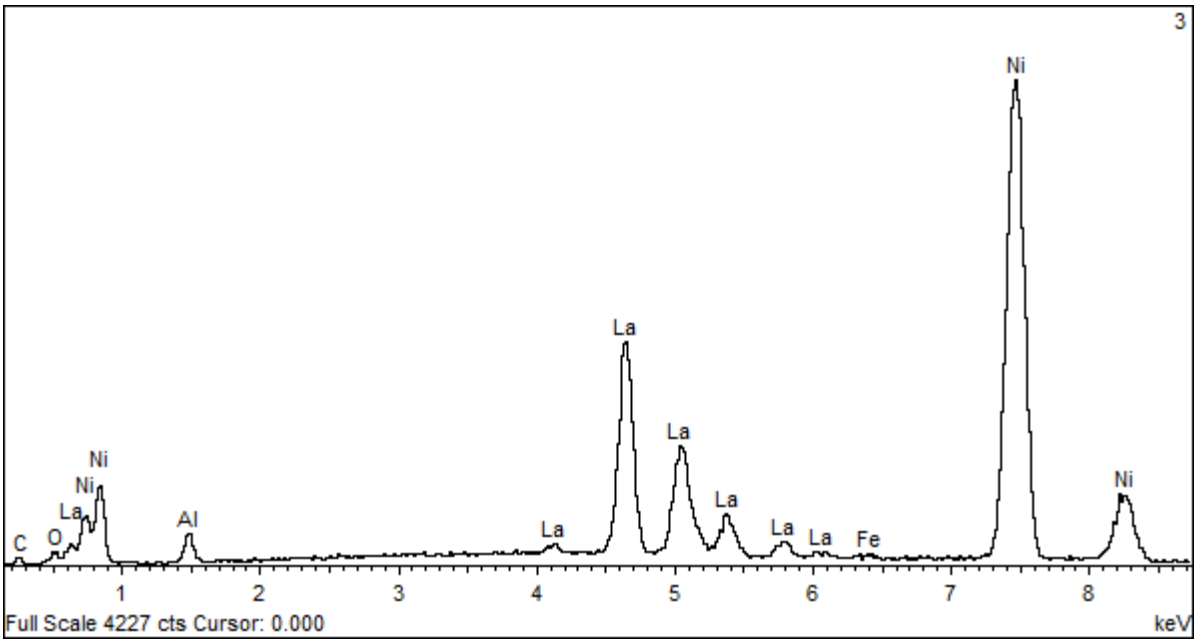
Spot 1: Highly enriched in Ni, probably a Ni particle



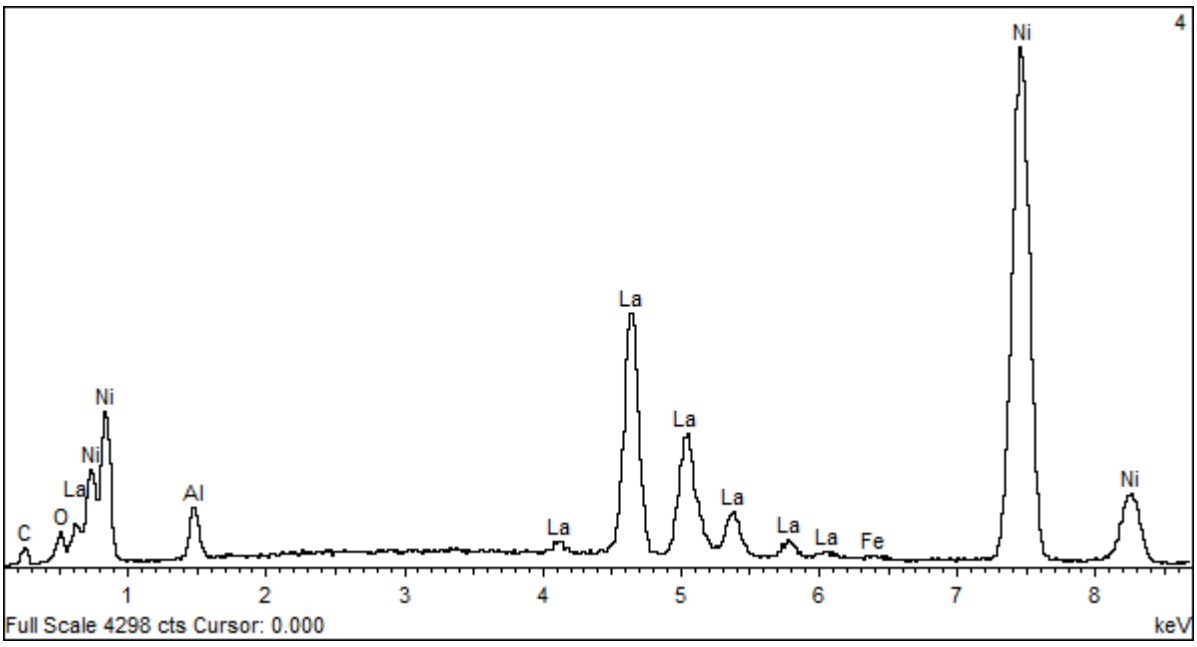
Spot 2: High Ni and Al, probably a NiAl phase



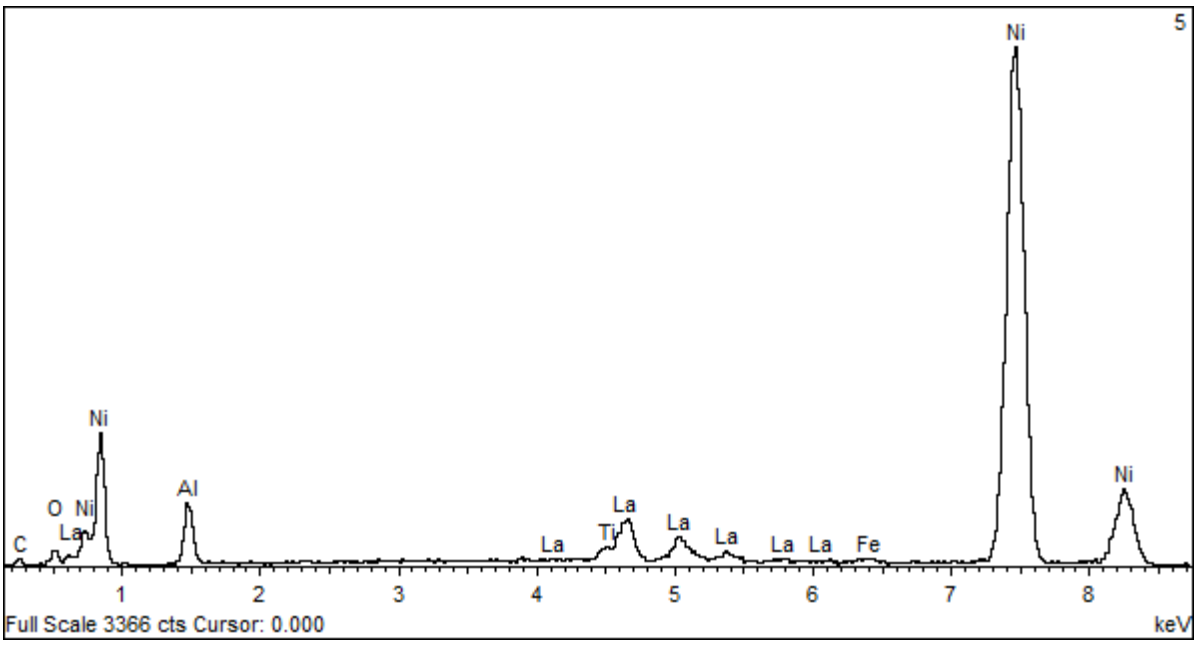
Spot 3: Depleted in Al



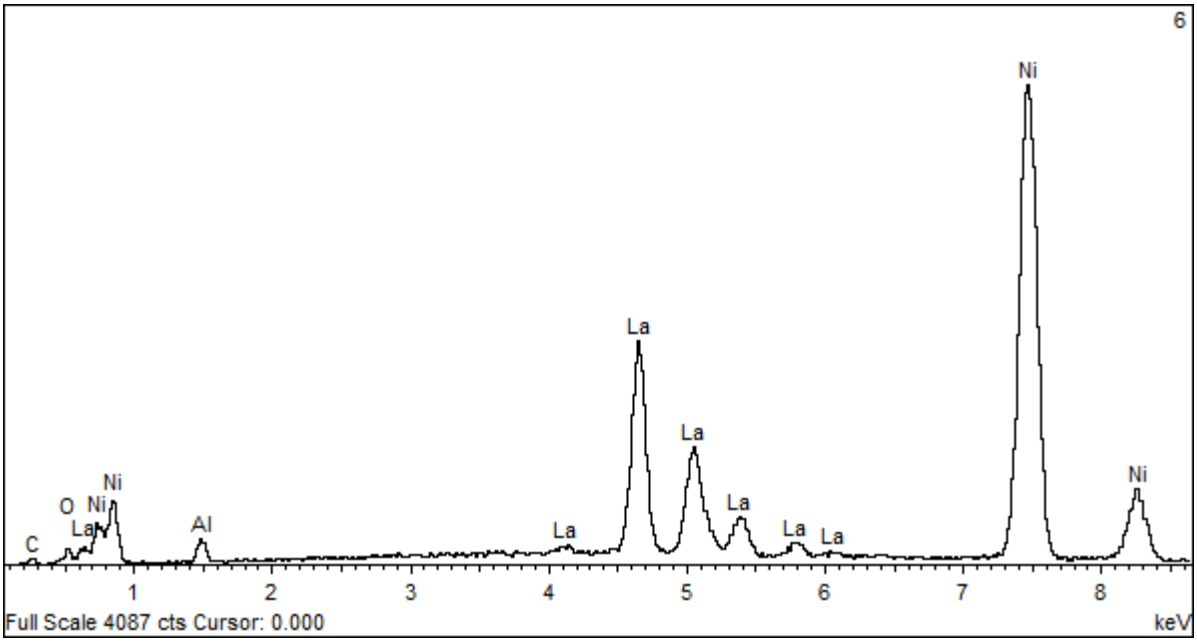
Spot 4: “Normal” LANA



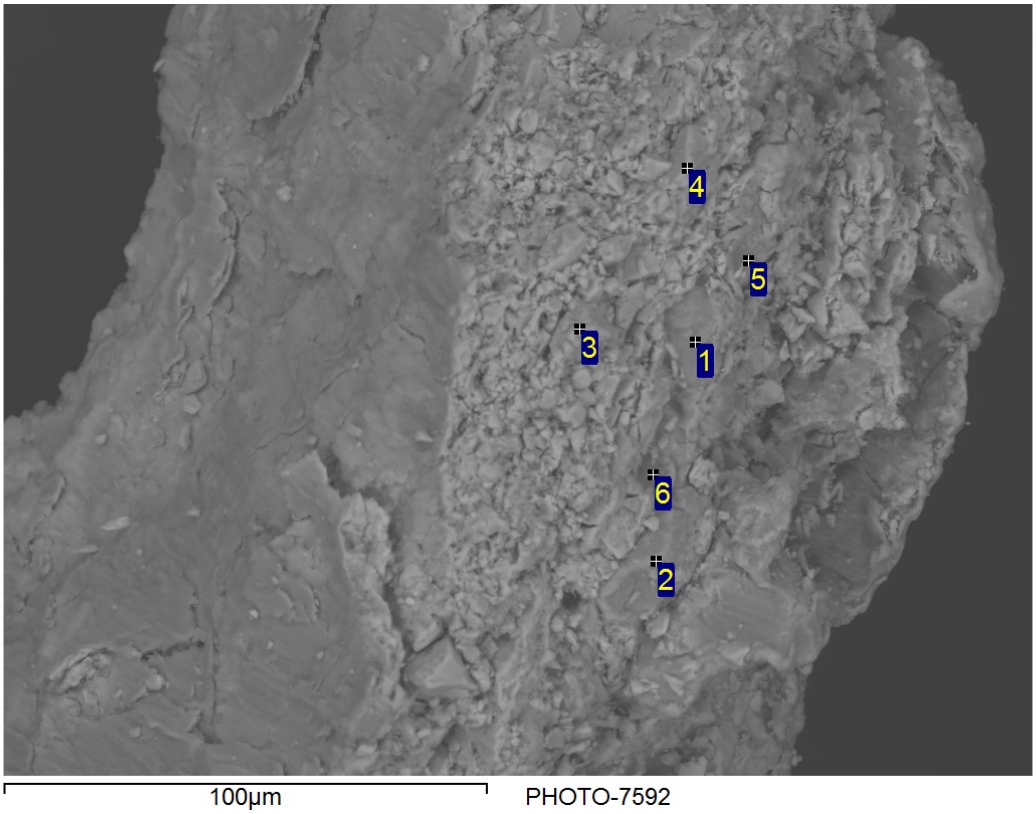
Spot 5: Ni particle again, or NiAl with low Al and some La, trace Fe and Ti, located in the middle of a flat face



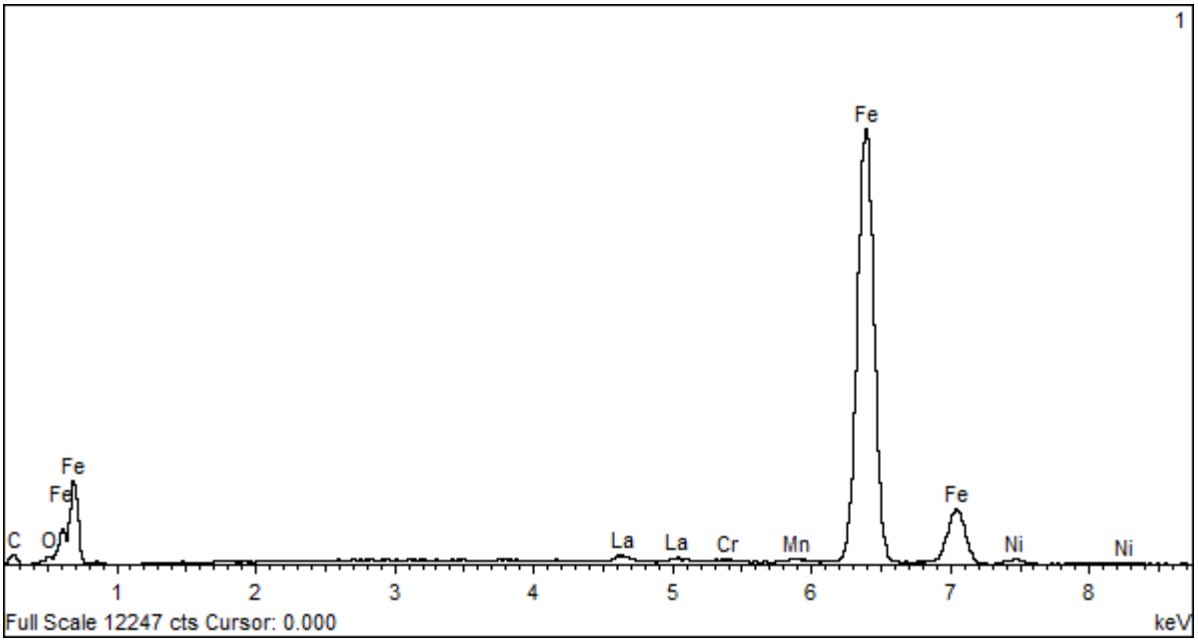
Spot 6: “Normal” LANA, on a flat face



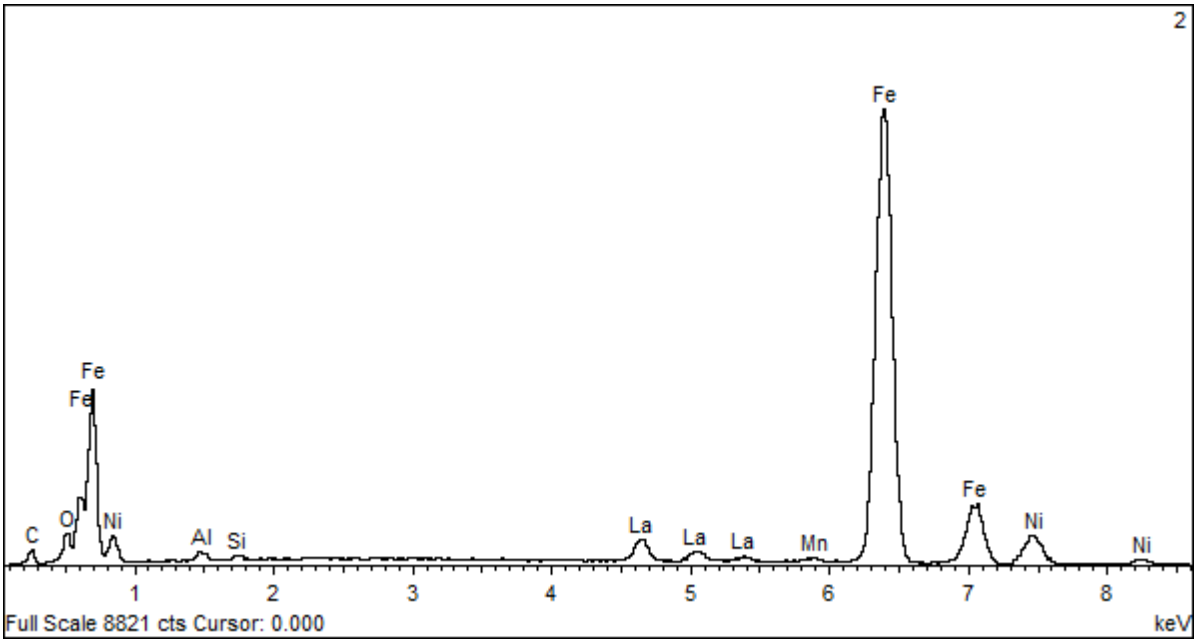
SEM image of pseudo-cylindrical particle with rough surface: Varied chemical composition from LANA75 in some spots.



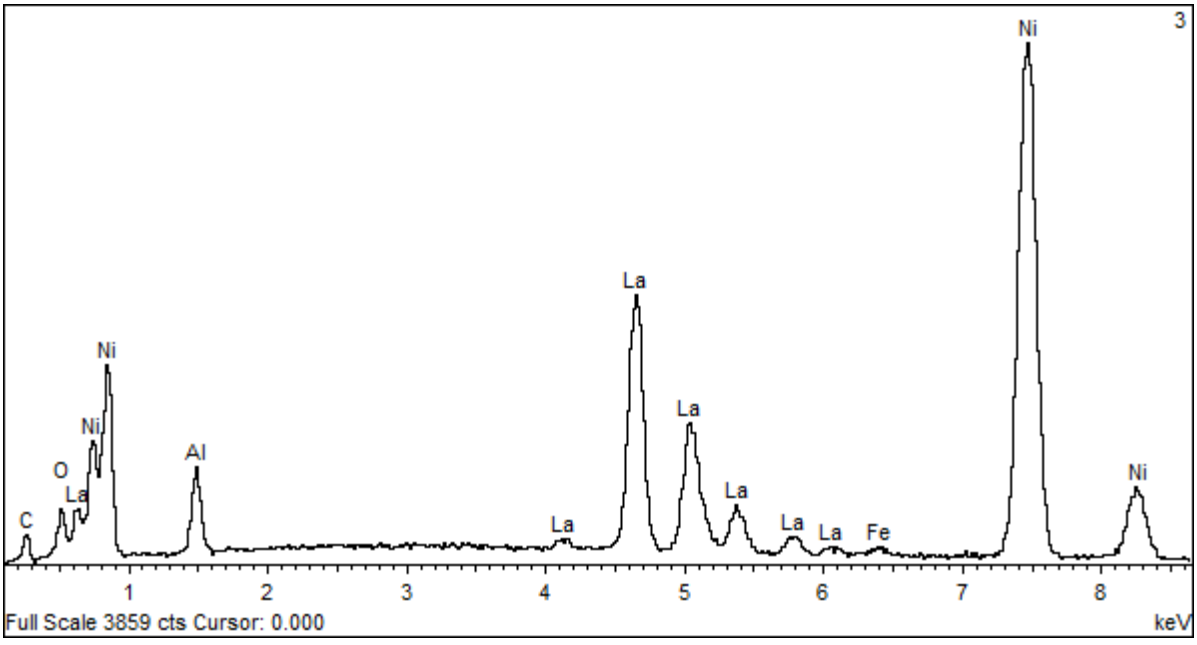
Spot 1: Almost pure Fe



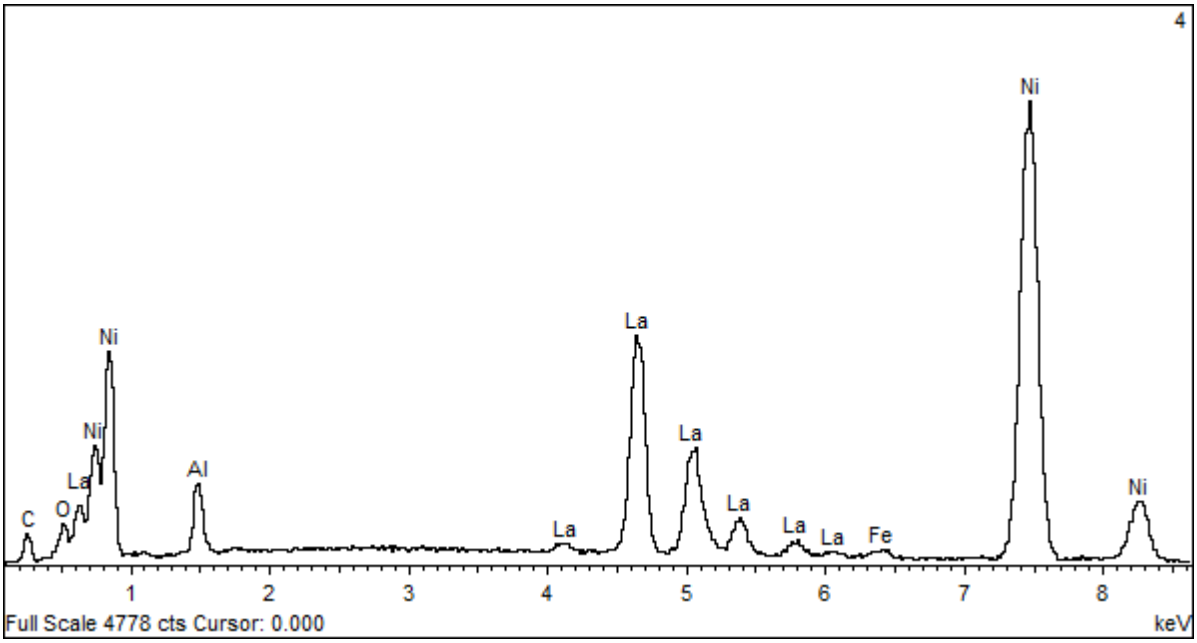
Spot 2: Again, almost pure Fe.



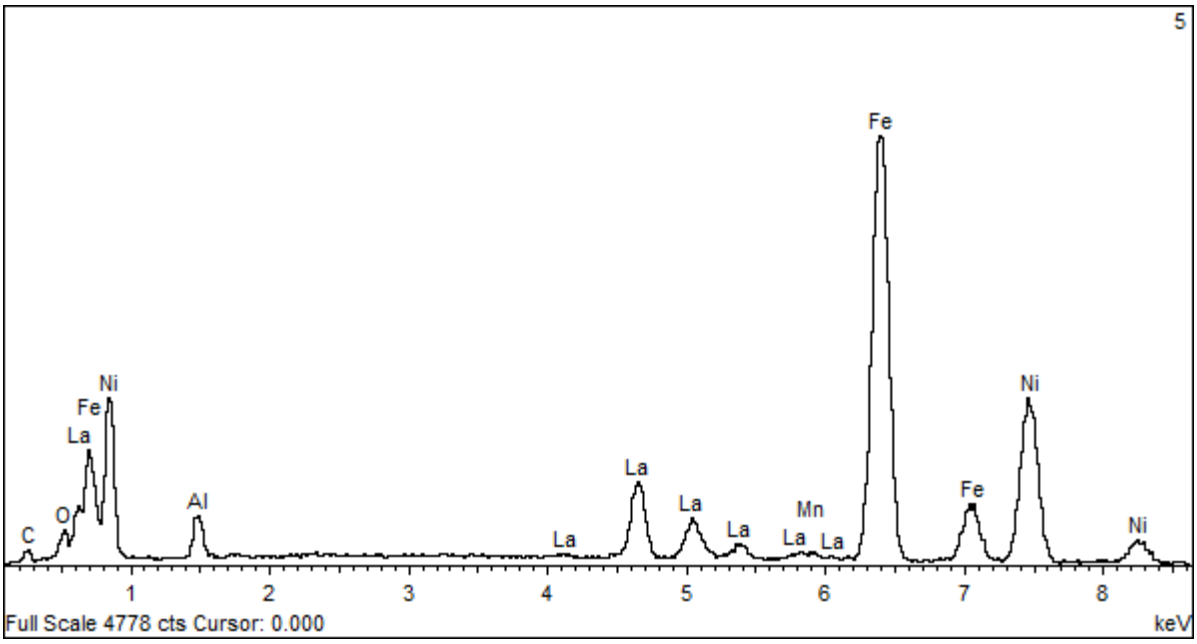
Spot 3: “Normal” LANA



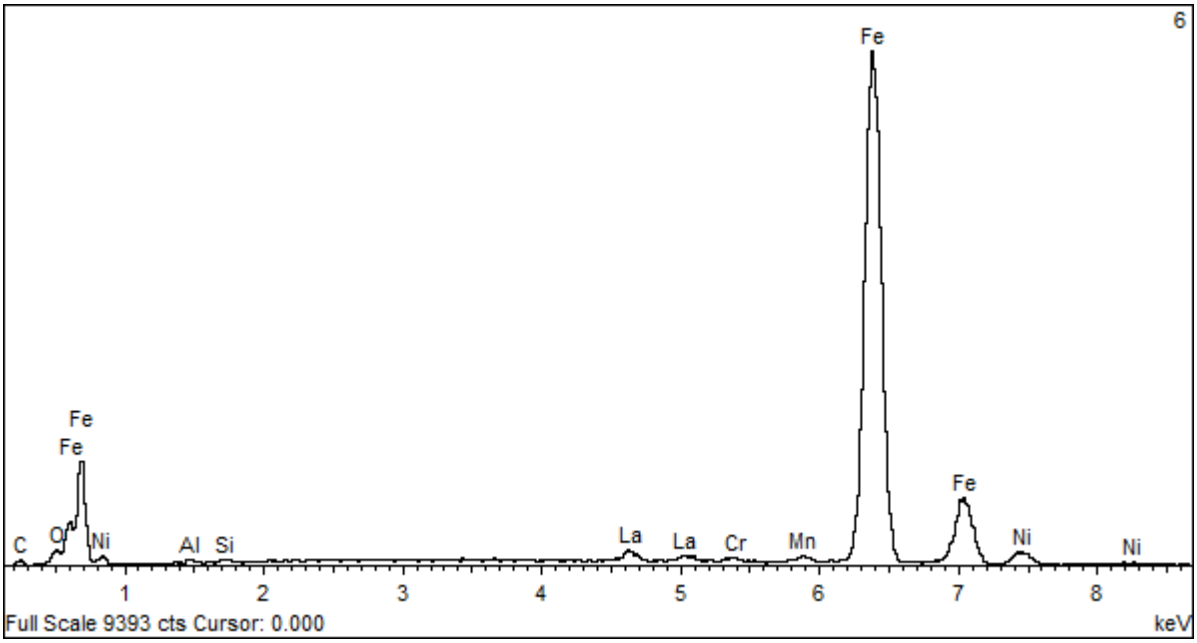
Spot 4: “Normal” LANA with trace Fe



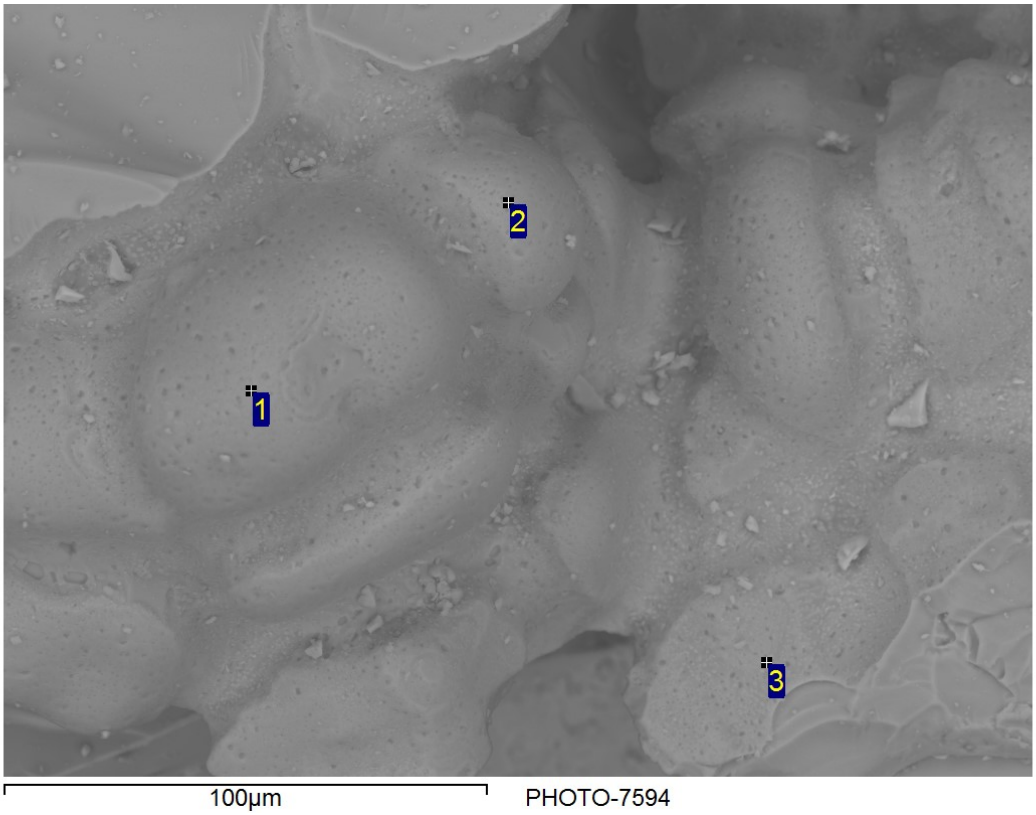
Spot 5: “Normal” LANA with very high Fe content



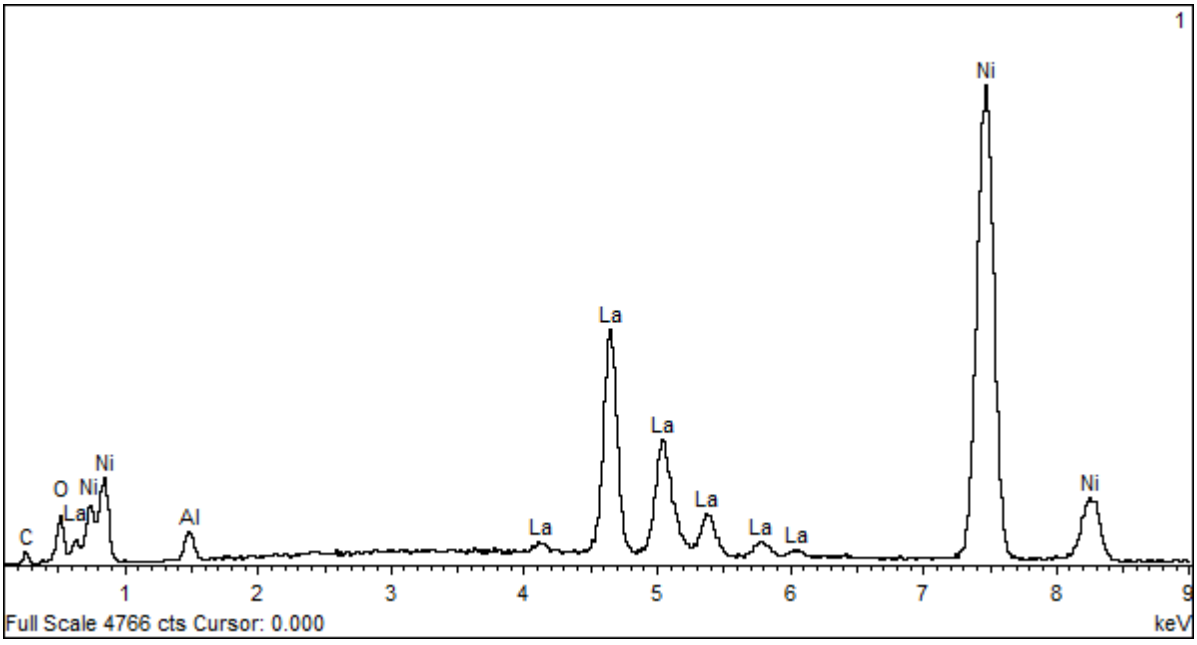
Spot 6: Almost pure Fe with low content of La and Ni. “Cr” and “Mn” are probably other La peaks



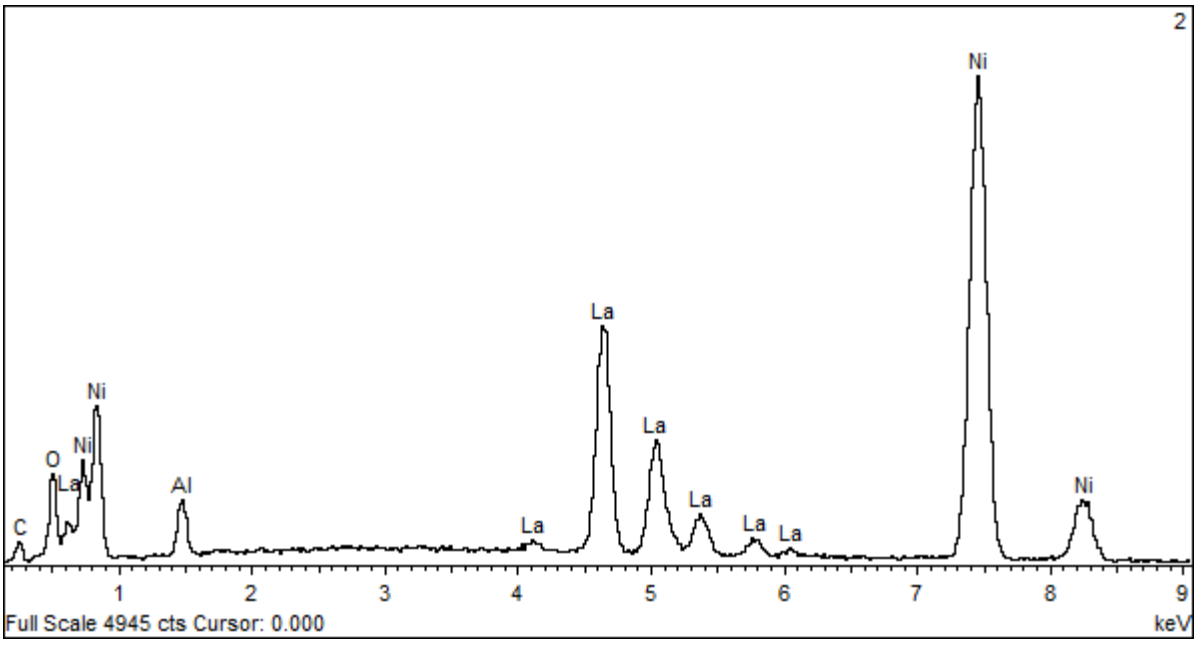
SEM image of the globular area:



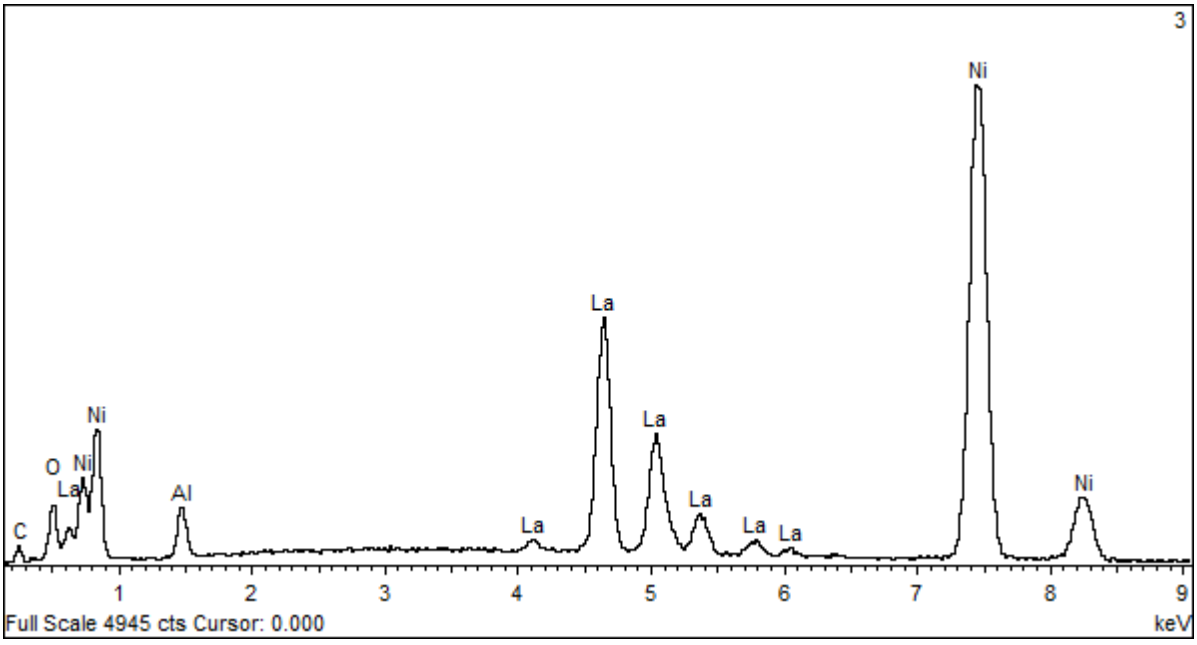
Spot 1: “Normal” LANA



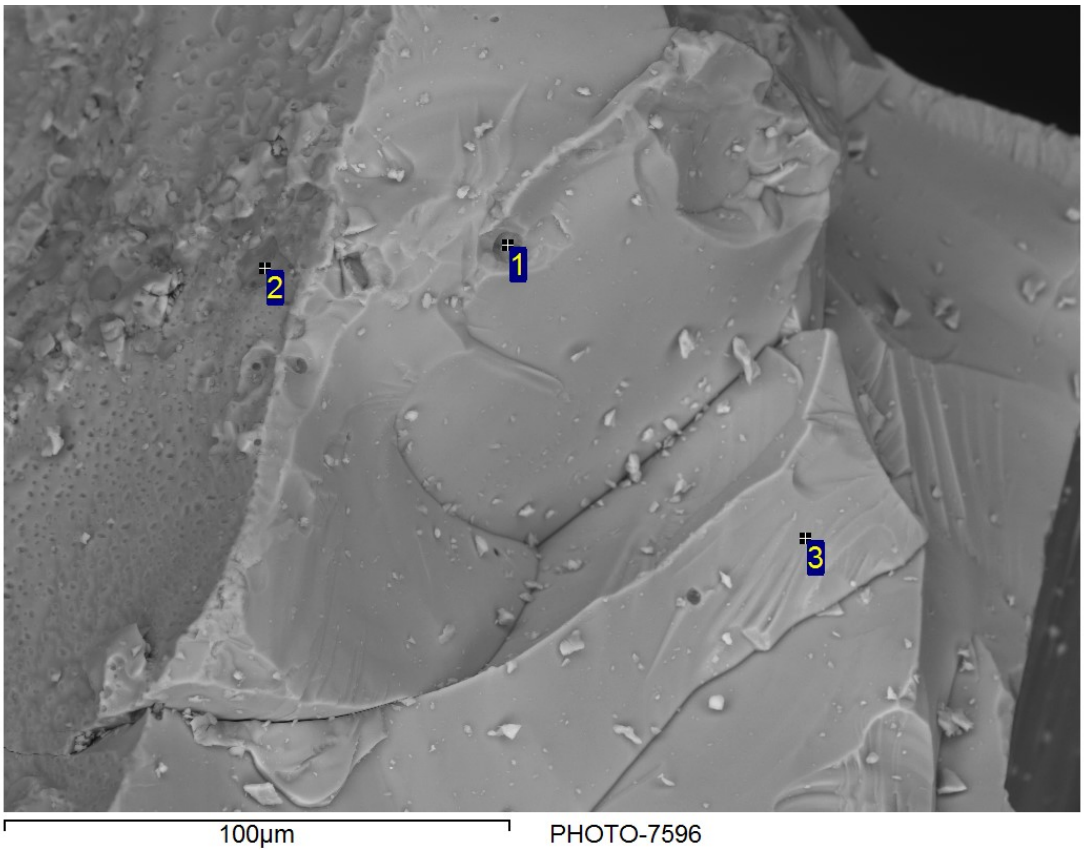
Spot 2: “Normal” LANA, possibly high O content



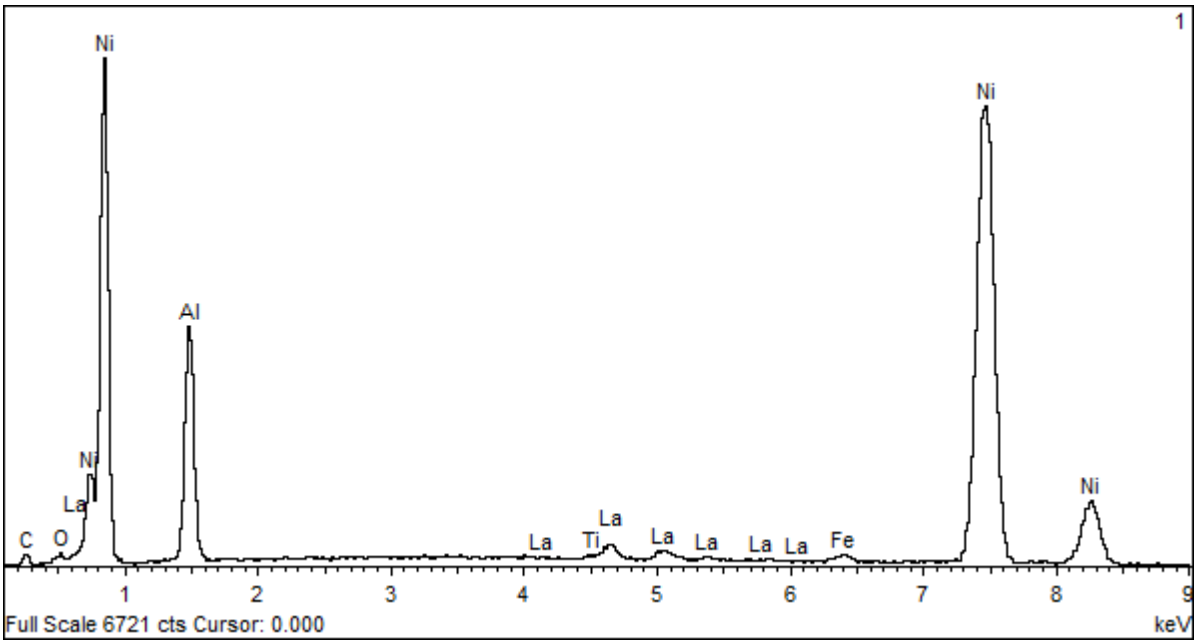
Spot 3: “Normal” LANA



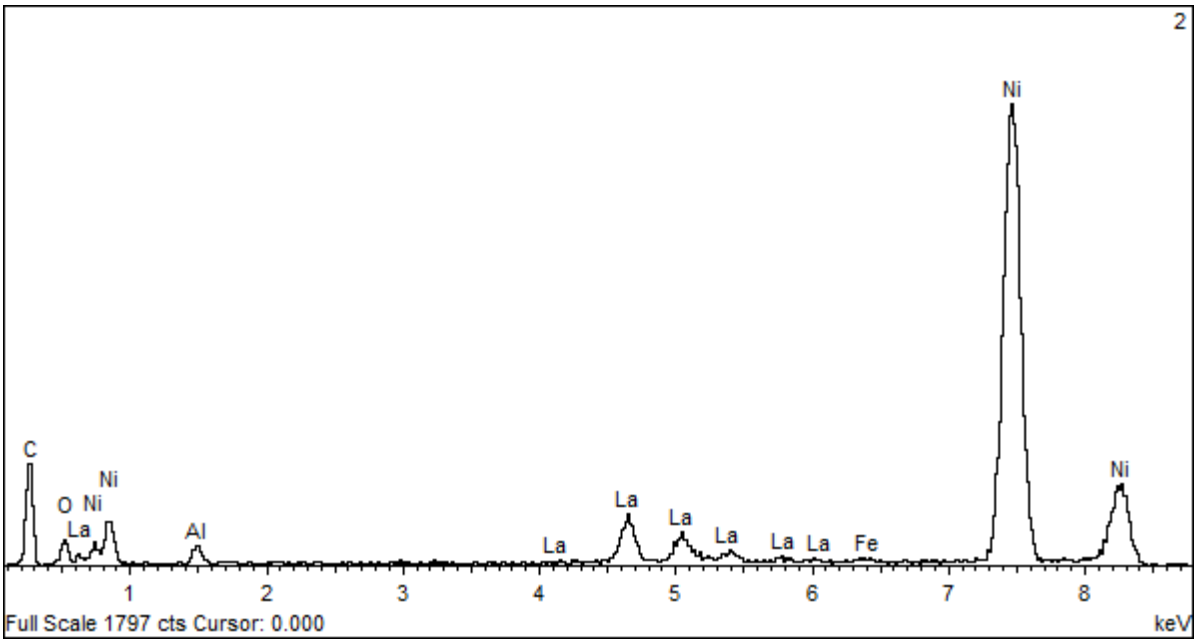
SEM image of flat fracture surface with darker areas:



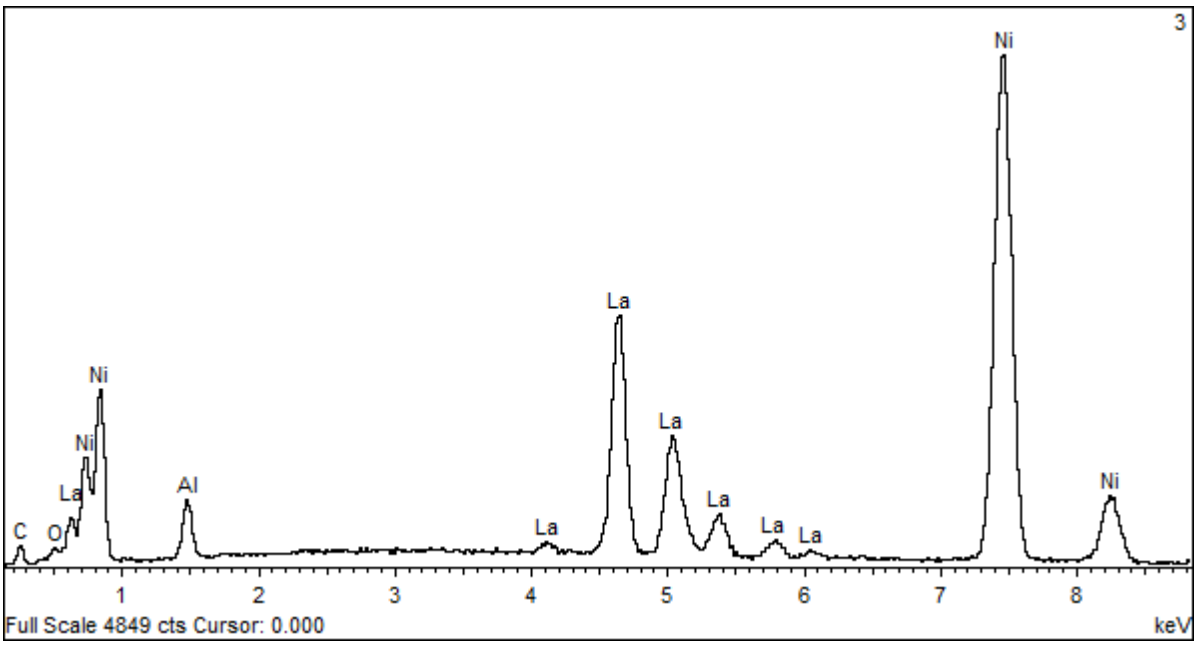
Spot 1: Low in La, probably NiAl phase, trace Fe



Spot 2: NiAl phase again



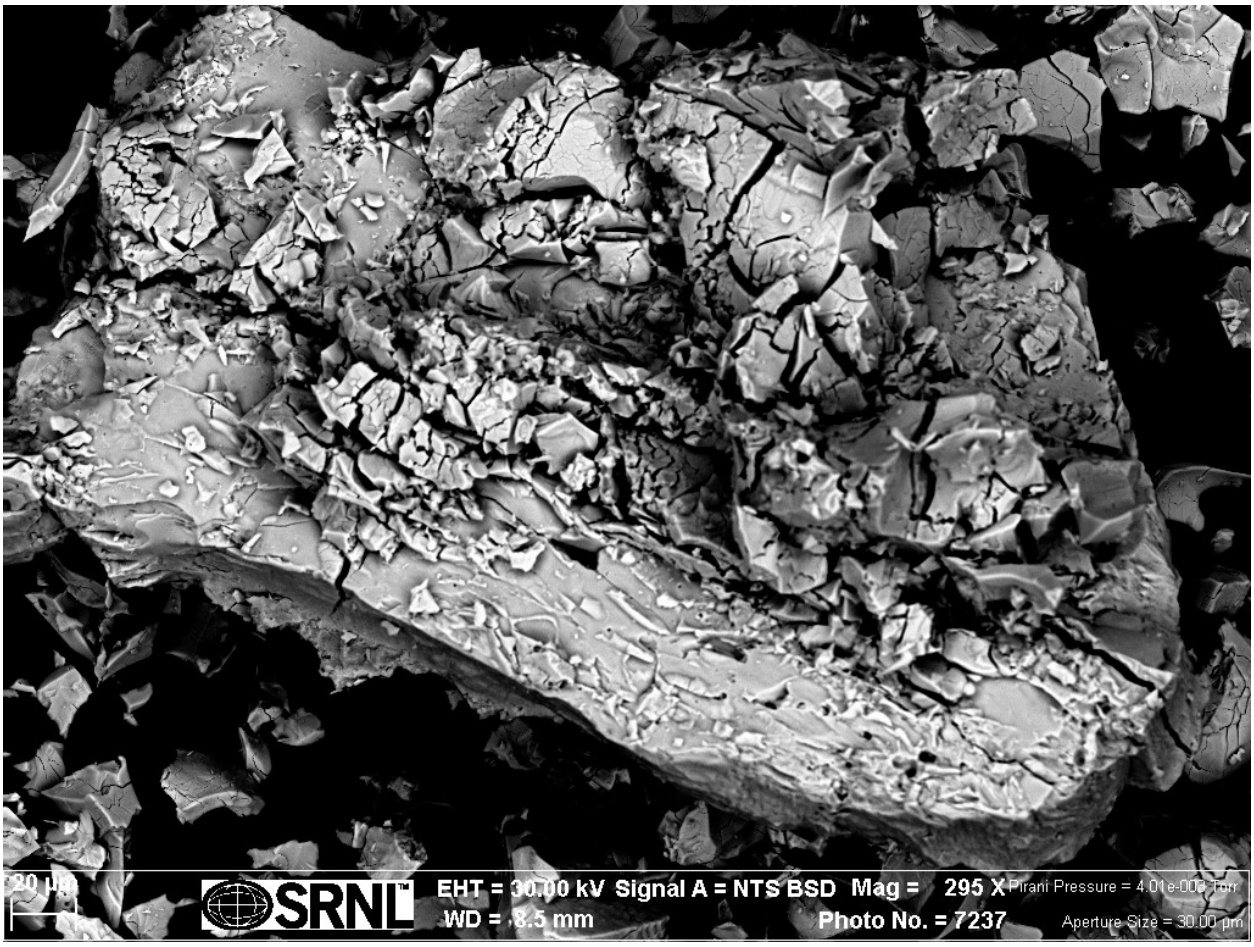
Spot 3: “Normal” LANA



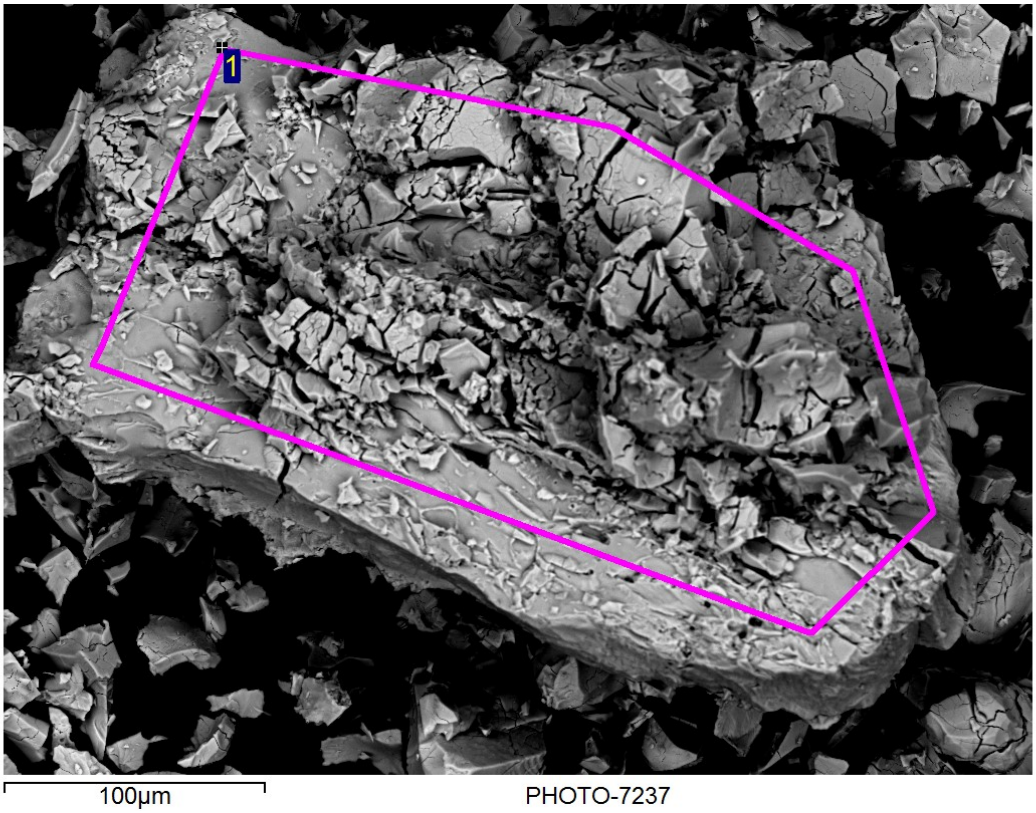
Part 2: SEM images - Thermally aged material with EDX spectra

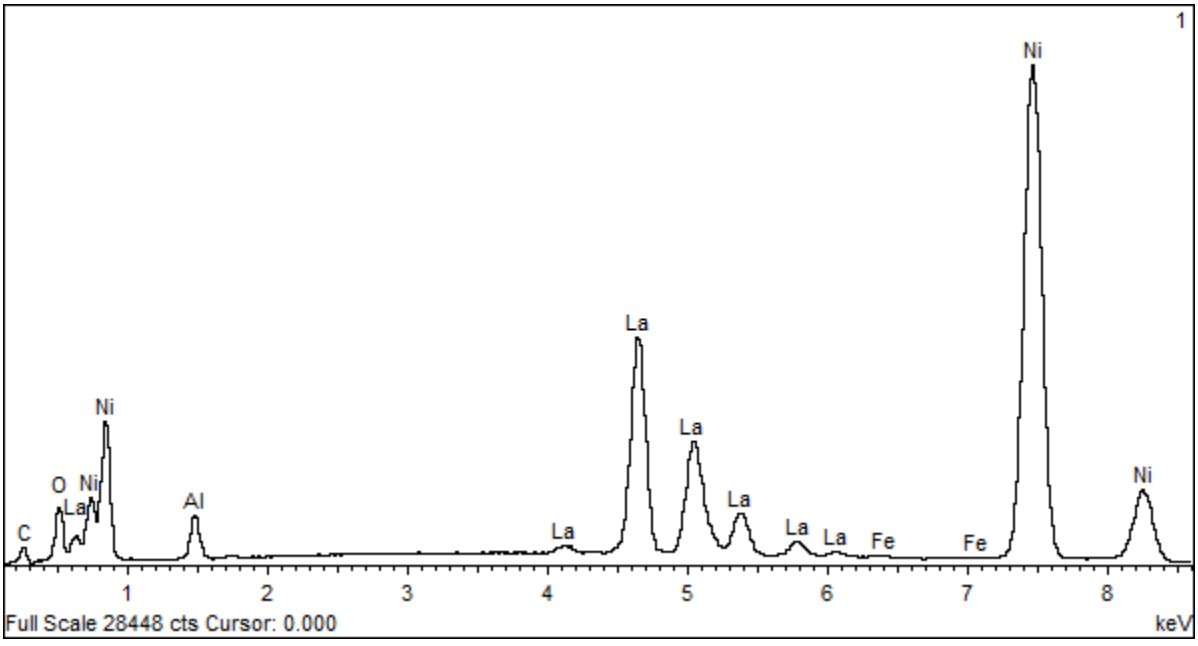
The following are images of several particles of sample LANA75_EXOP12 and thermally aged (300 °C) TCON LANA75. Because of the low number of hydrogen absorption/desorption cycles performed on this material, many of the large, original particles can still be seen, but they are heavily cracked and likely to fall apart with only a little more cycling.

Note that bright areas indicate a higher average atomic weight in that area, i.e. Al depleted, La enriched, etc.

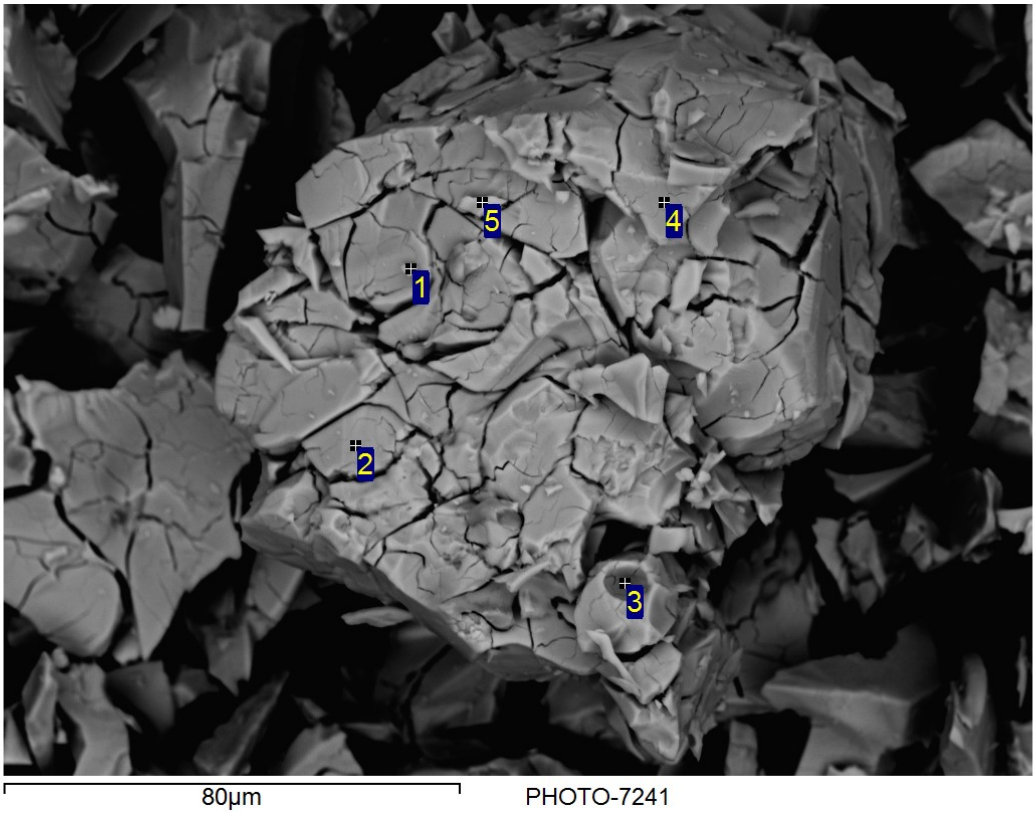


The outlined area (“1”) was used to determine the following EDX spectrum which shows “normal” LANA75 with a trace of Fe.

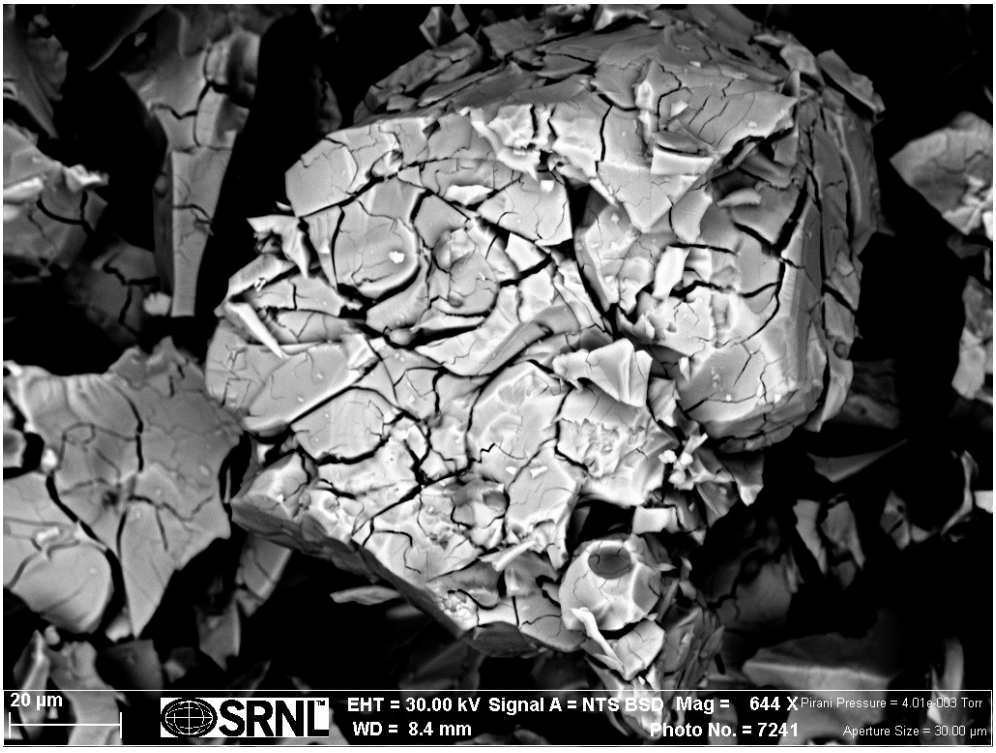




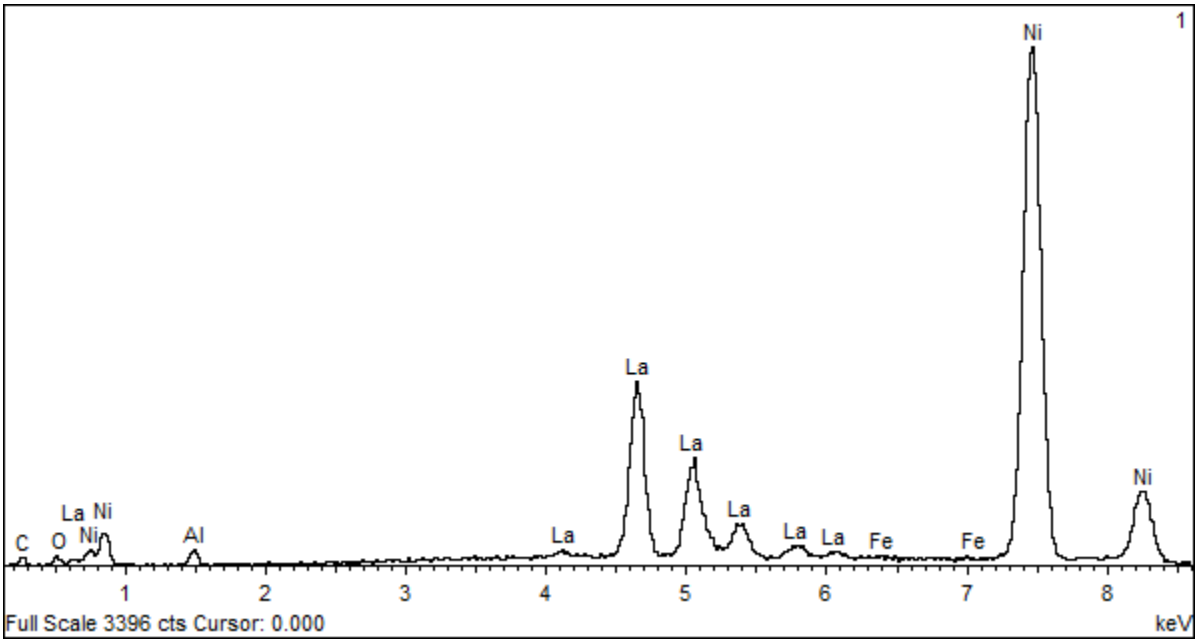
Another image, with numbers indicating EDX spot analyses, ties to following spectra as above in Part 1.



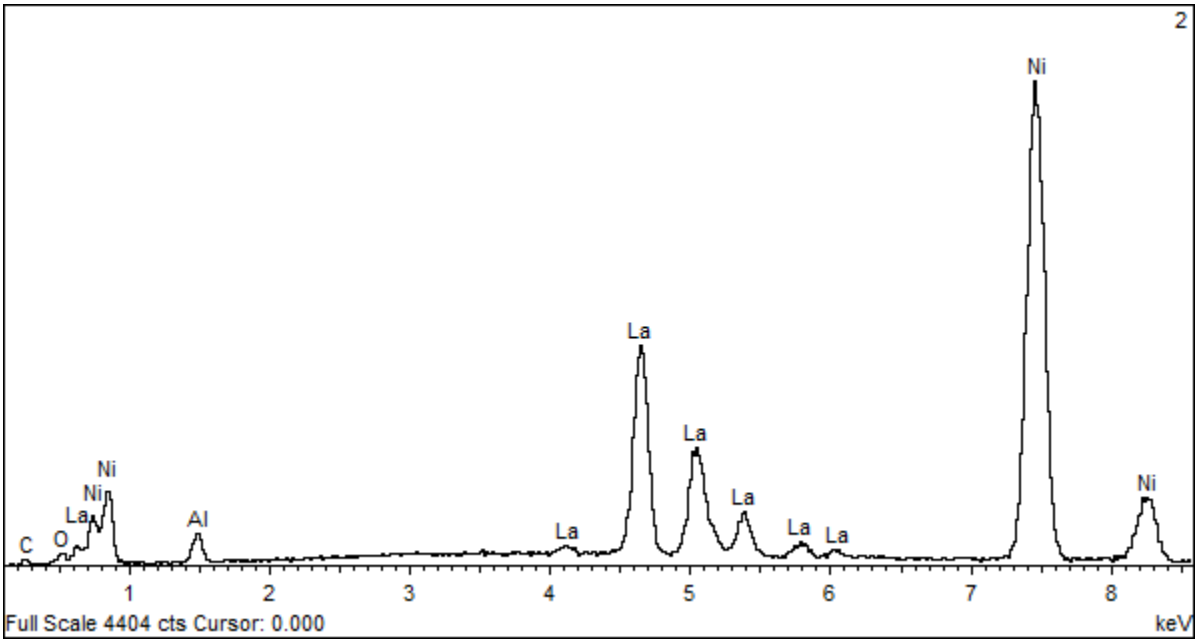
The unnumbered image to allow the spots covered by numbers in the photo above to be seen:



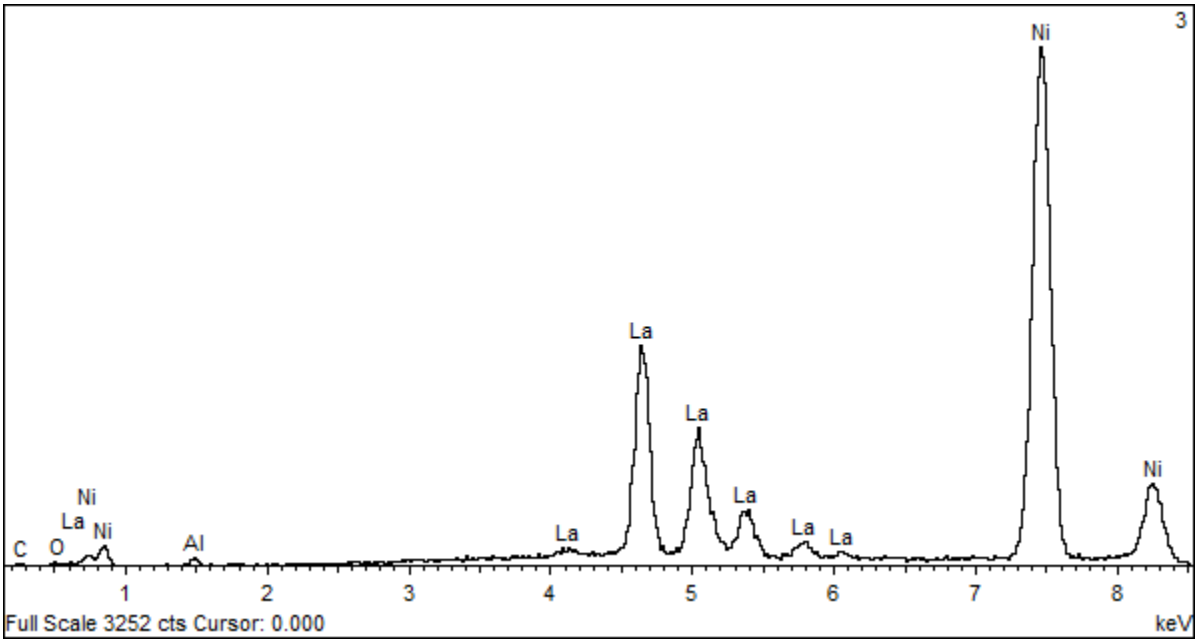
Bright spot, low Al:



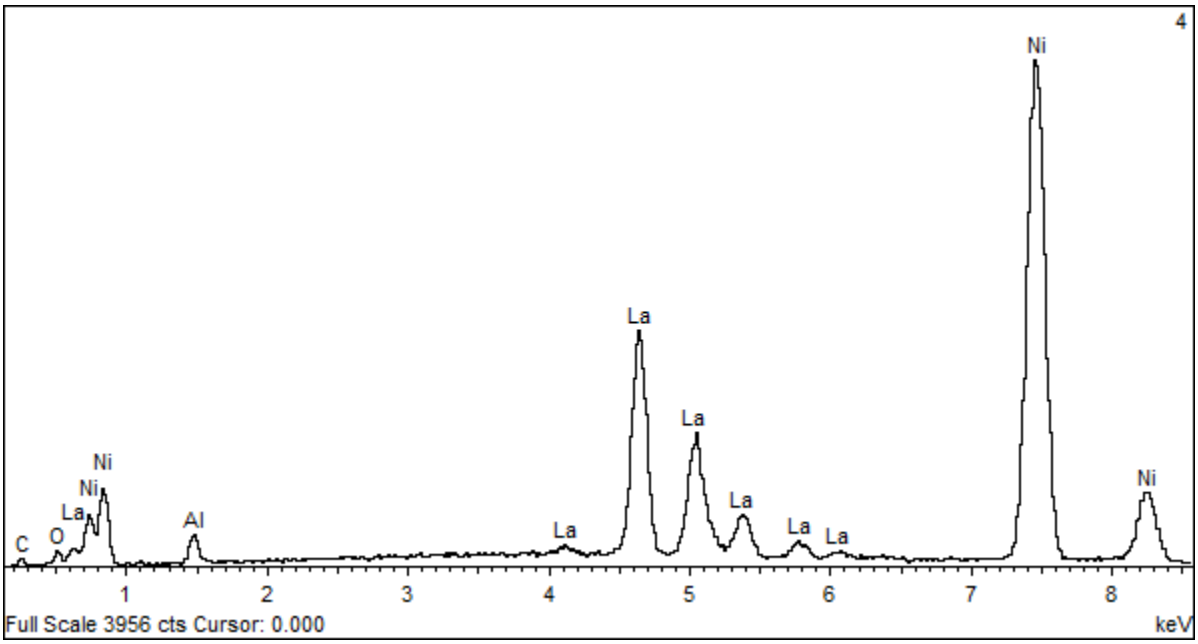
Brighter flat region, low Al:



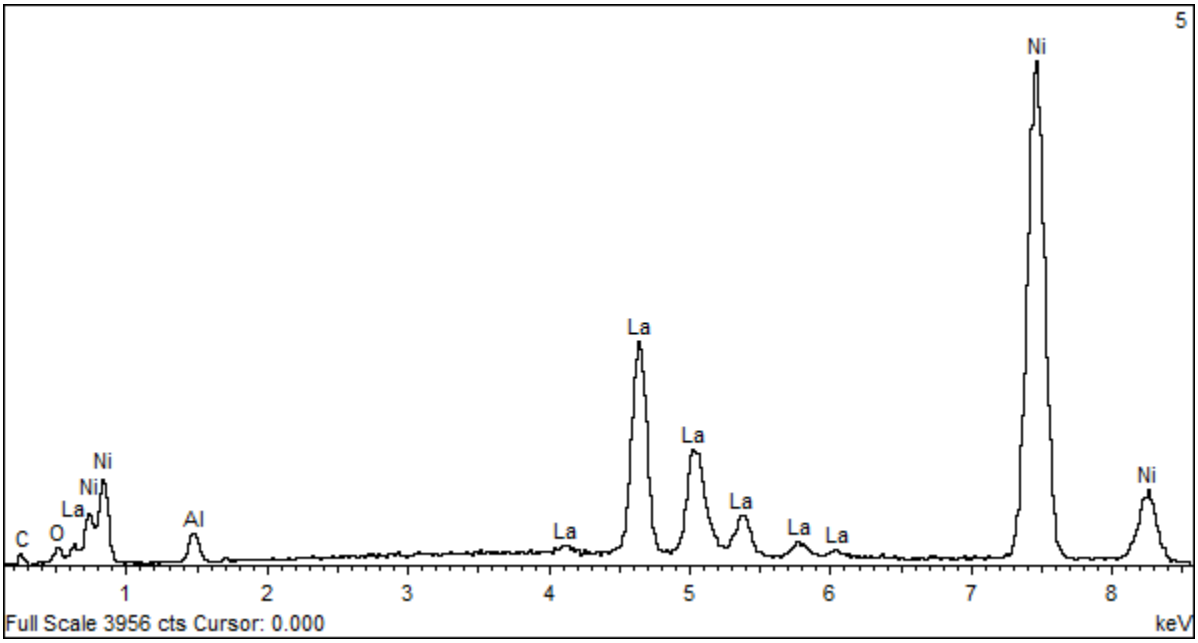
Very low Al in this dark spot:



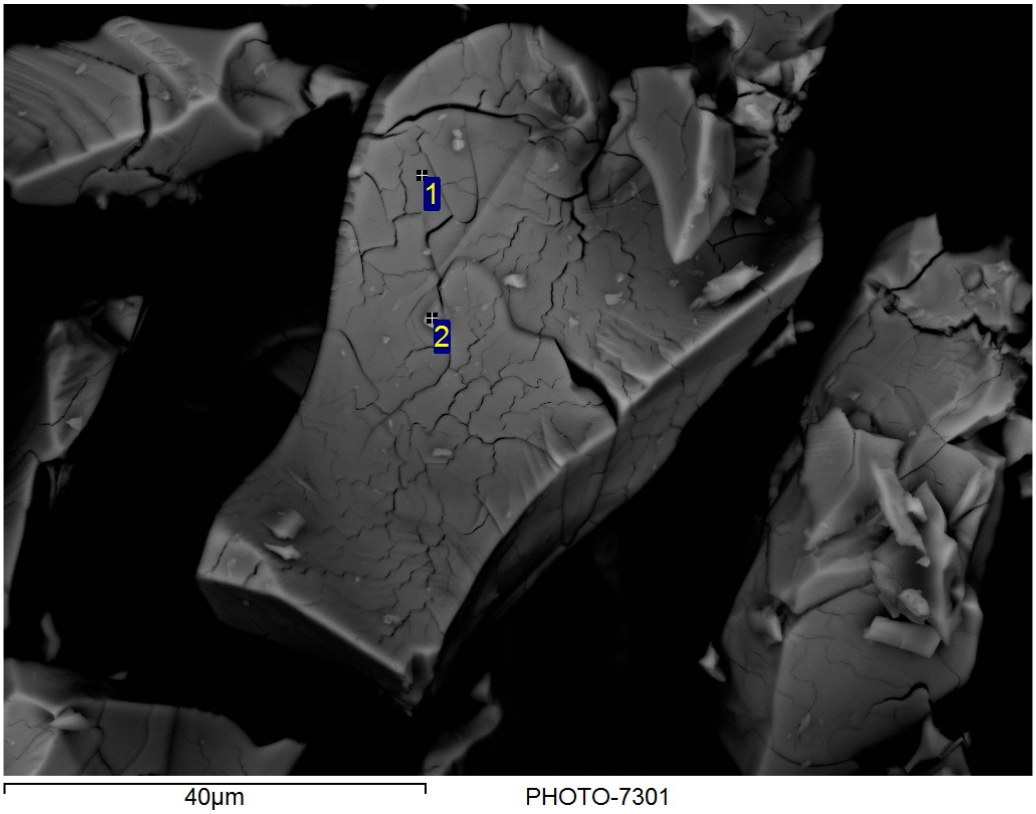
Brighter flat region, Al still low:

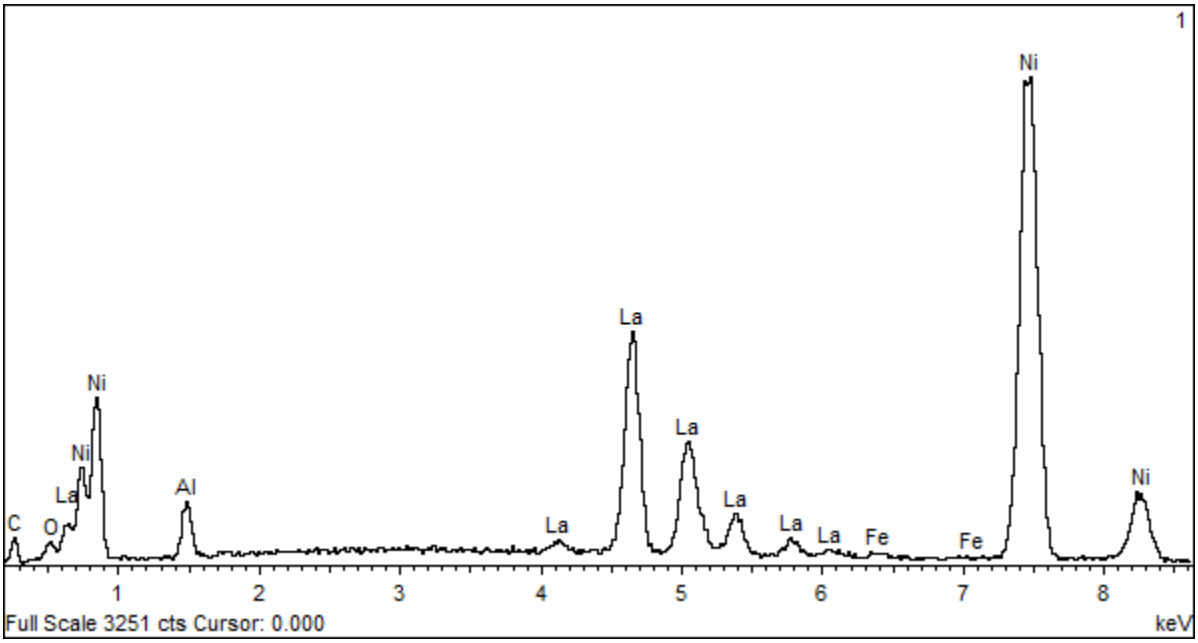


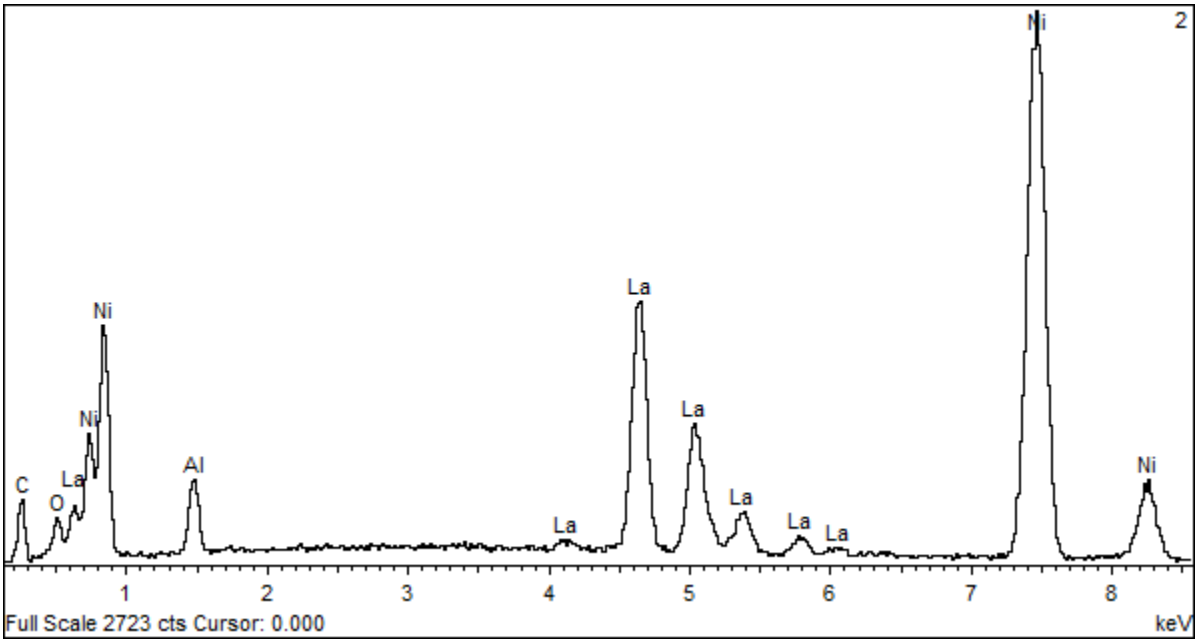
Brighter flat spot, Al still low:



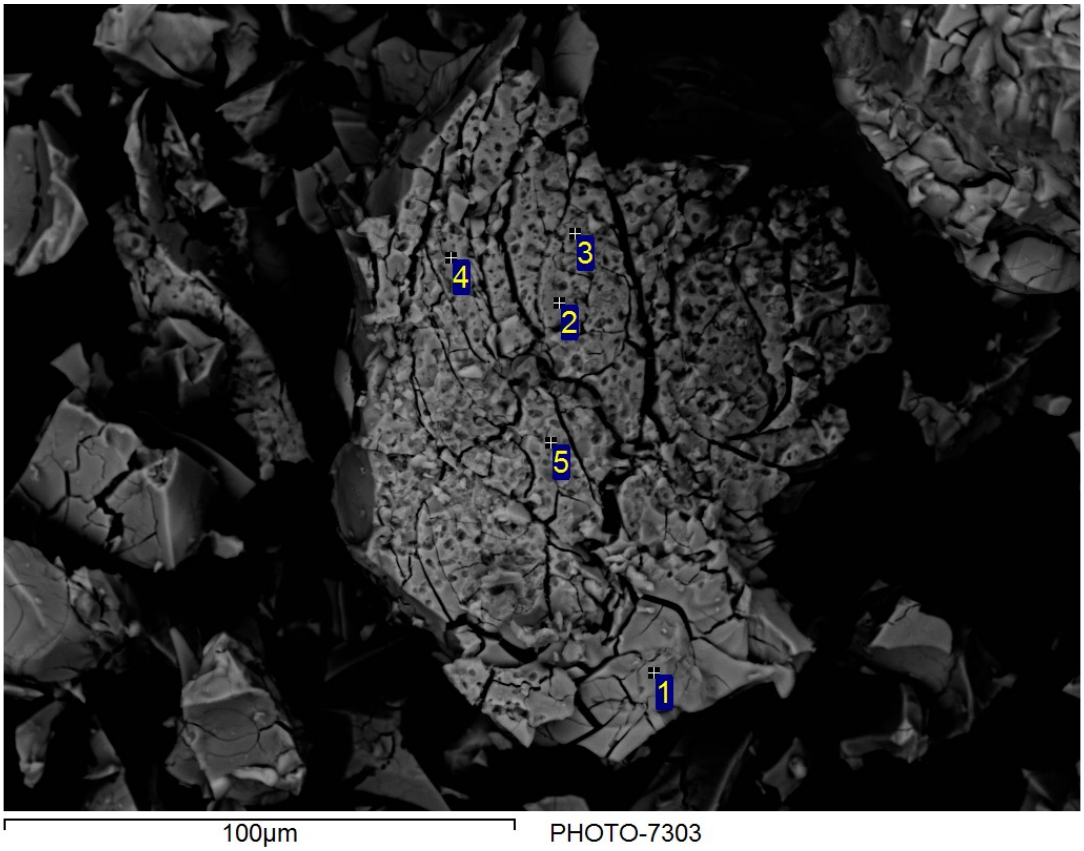
Another image, with numbers indicating EDX spot analyses, ties to following spectra as above in Part 1.

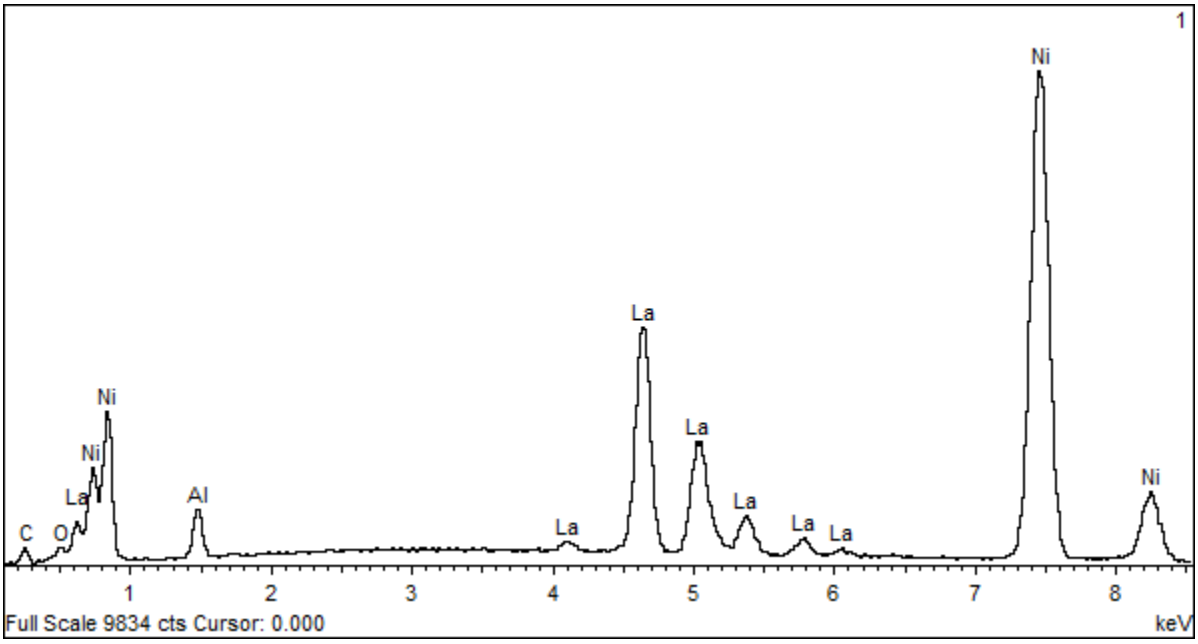


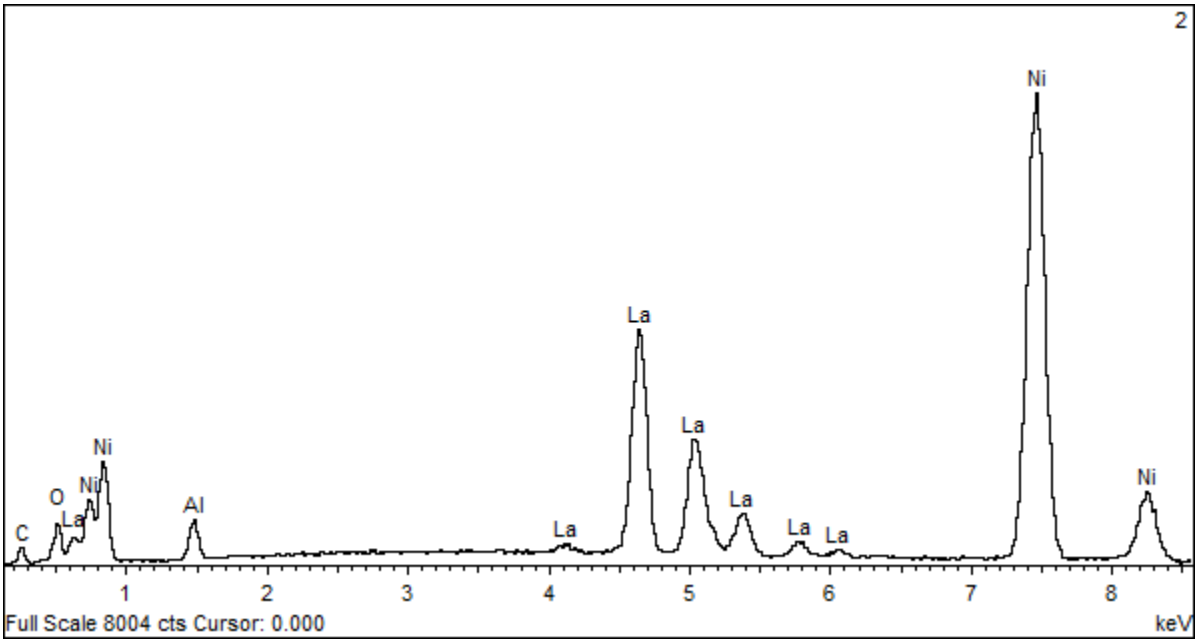


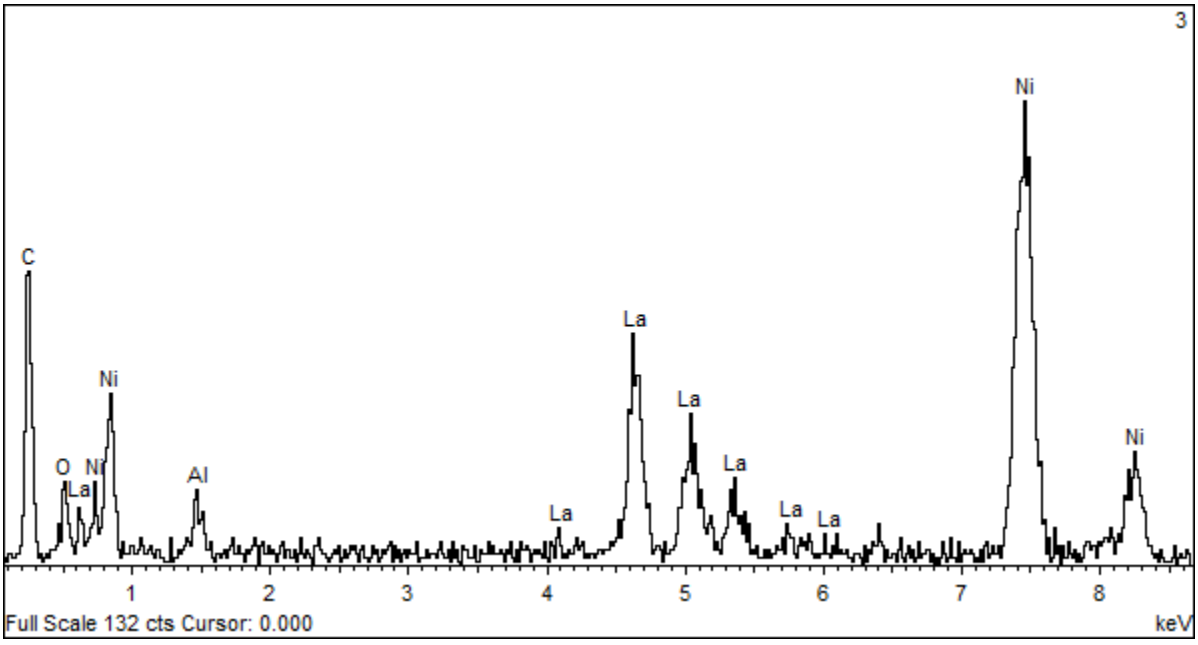

Ni
2
La
Ni
La
Ni
C
O
La
Al
La
La
La
La
La
Ni
1
2
3
4
5
6
7
8
Full Scale 2723 cts Cursor: 0.000
keV

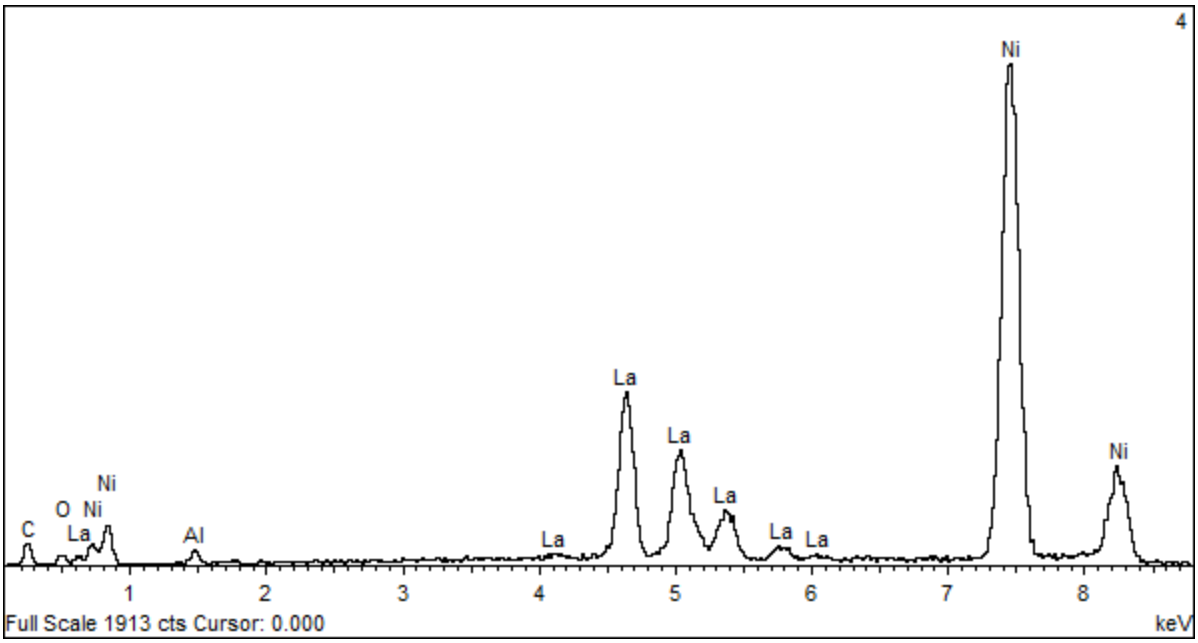
Another image, with numbers indicating EDX spot analyses

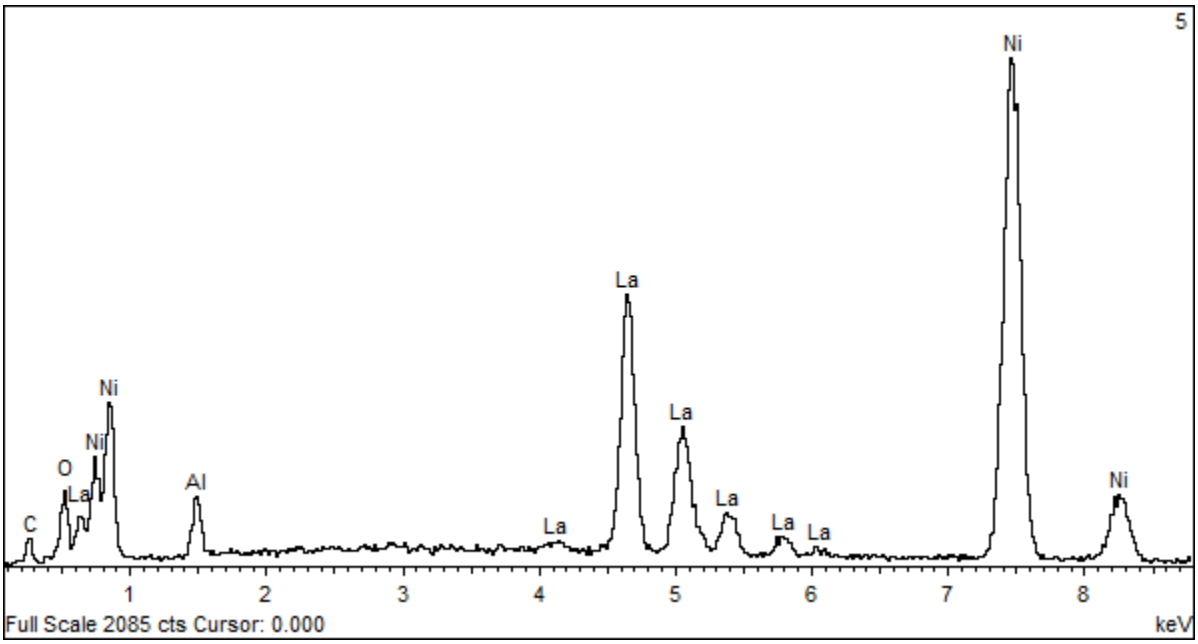




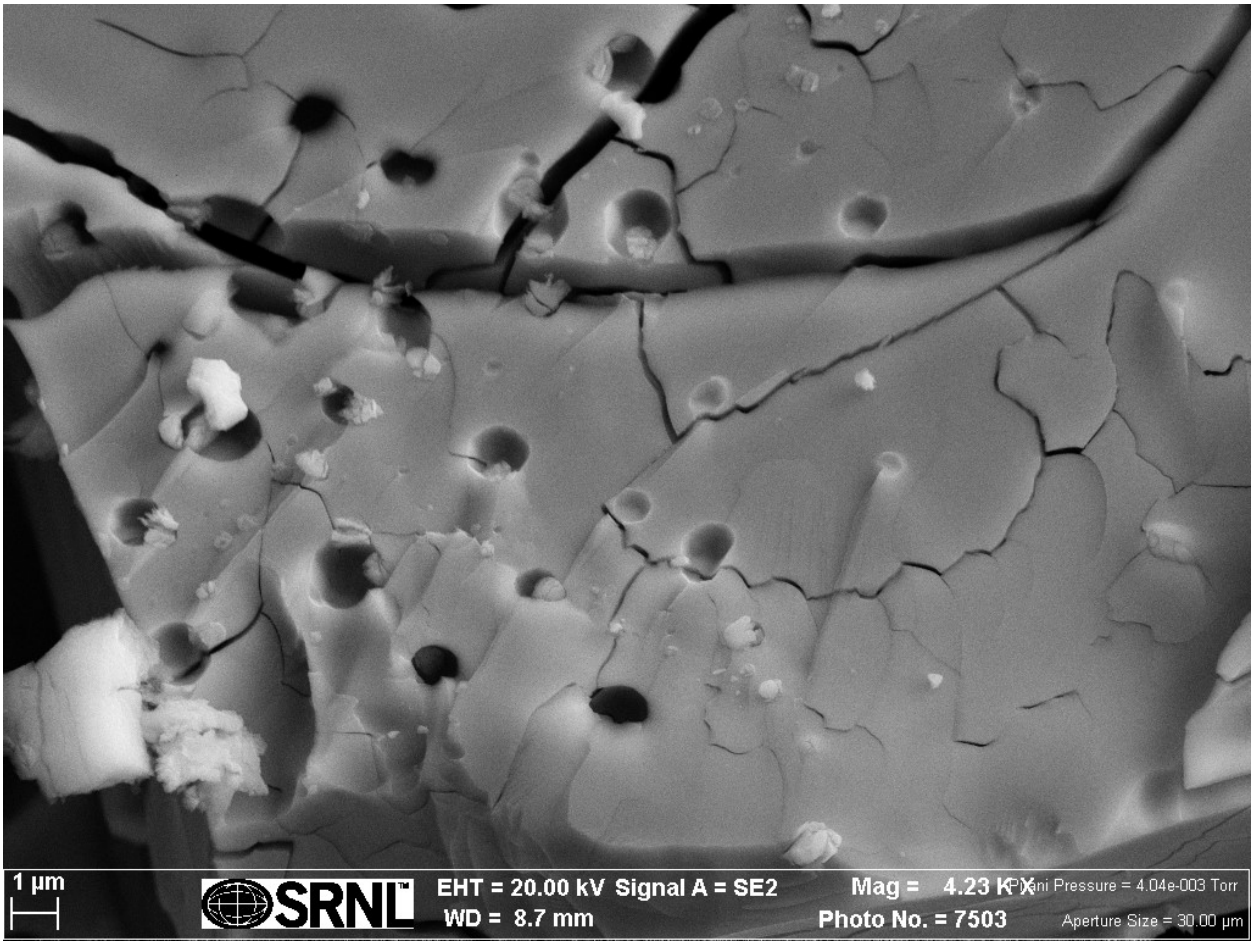

2
Ni
La
La
Ni
Ni
O
La
Al
C
La
La
La
La
La
1
2
3
4
5
6
7
8
Full Scale 8004 cts Cursor: 0.000
keV

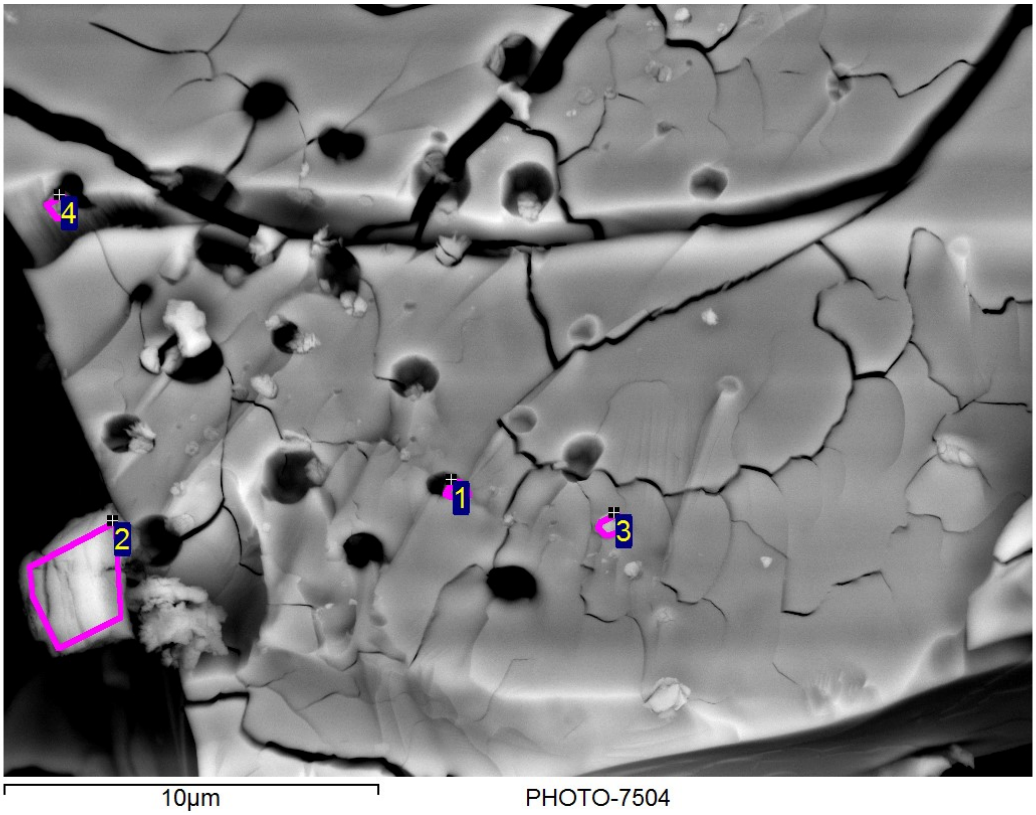

3
Ni
C
La
La
Ni
Ni
O
La
Al
La
La
La
La
La
1
2
3
4
5
6
7
8
Full Scale 132 cts Cursor: 0.000
keV


4
Ni
La
La
La
La
La
Ni
Ni
O
Ni
C
La
Al
La
1
2
3
4
5
6
7
8
Full Scale 1913 cts Cursor: 0.000
keV

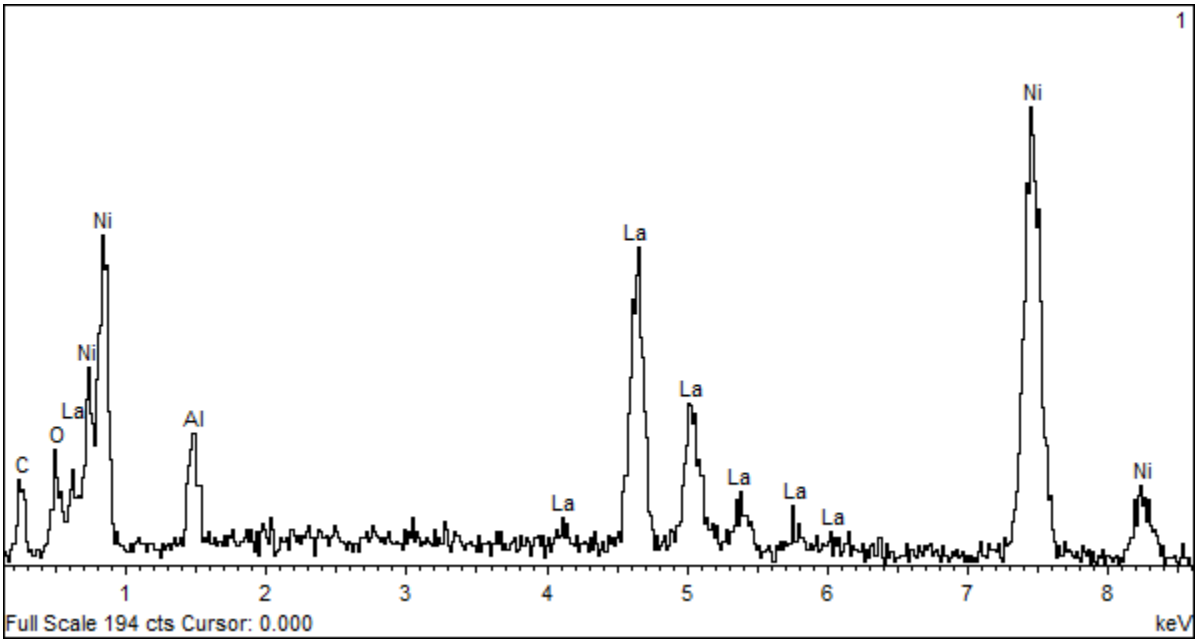

5
Ni
La
La
La
La
La
Ni
Ni
Ni
O
La
C
Al
La
1
2
3
4
5
6
7
8
Full Scale 2085 cts Cursor: 0.000
keV

Several images were observed to have highly symmetrical “spots” or “holes” in both the thermally aged and virgin material. EDX analyses were performed on some of the thermally aged material. Lanthanum oxide (La_2O_3) (indicated by enriched La and O ratios) with Ni crystallites (indicated by enriched Ni ratio) was probably present, as they have been reported in prior SRL (now SRNL) and outside reports. It is unknown why the “holes” cluster and are so symmetrical.

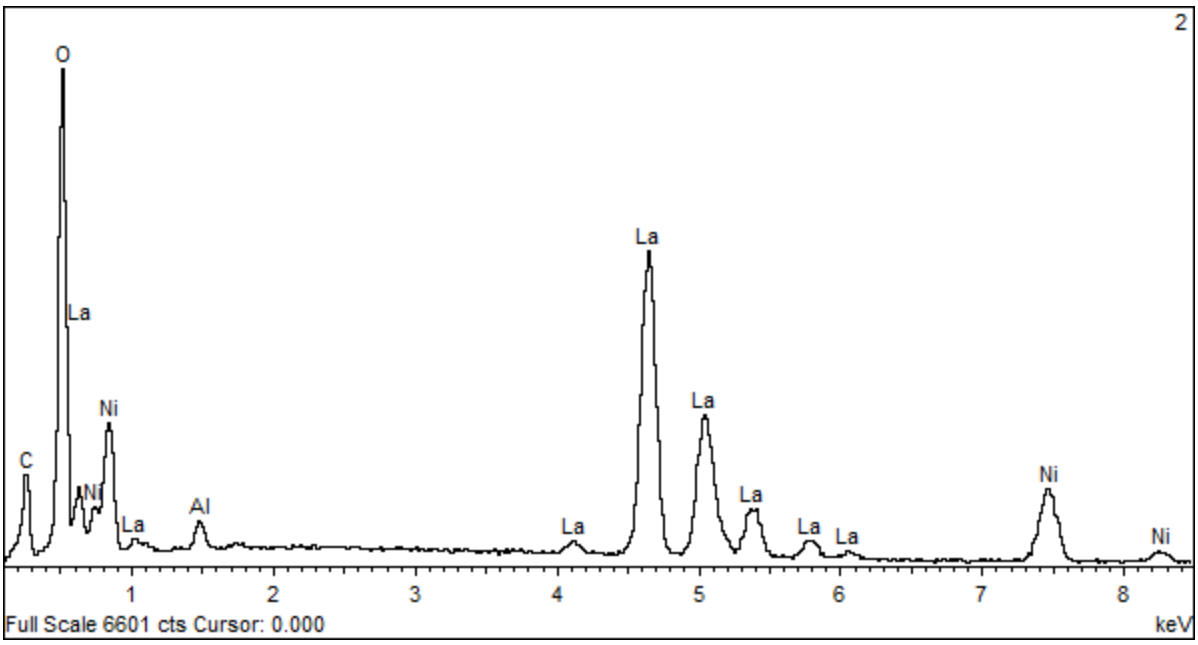




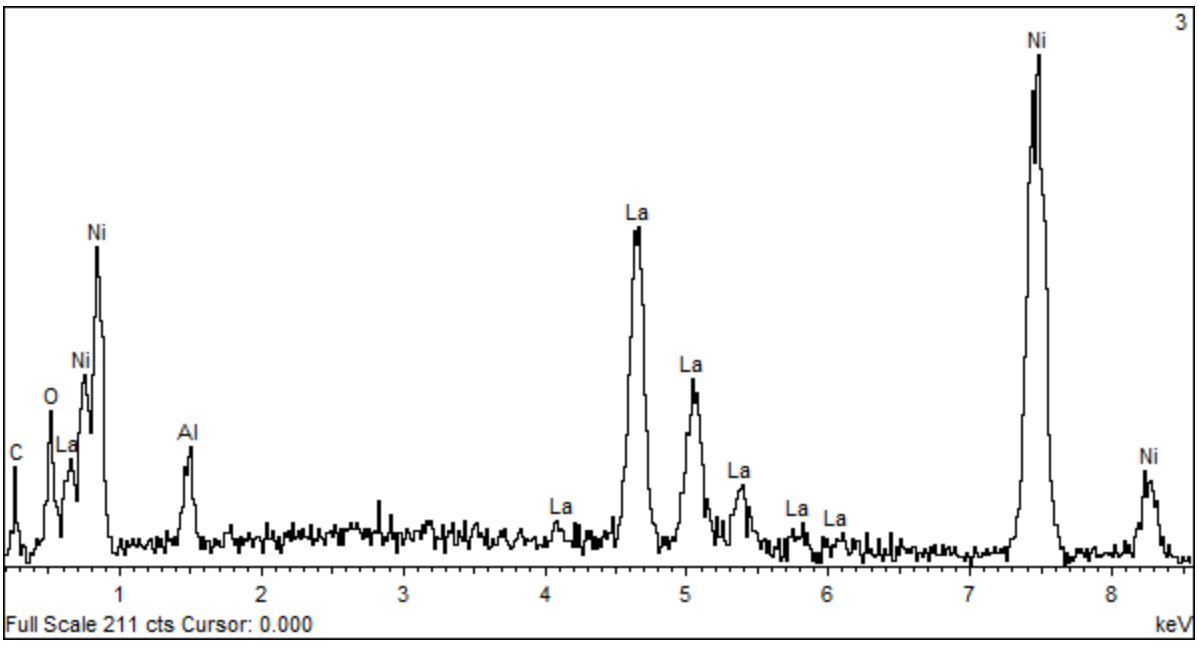
Spot 1: Low in Ni



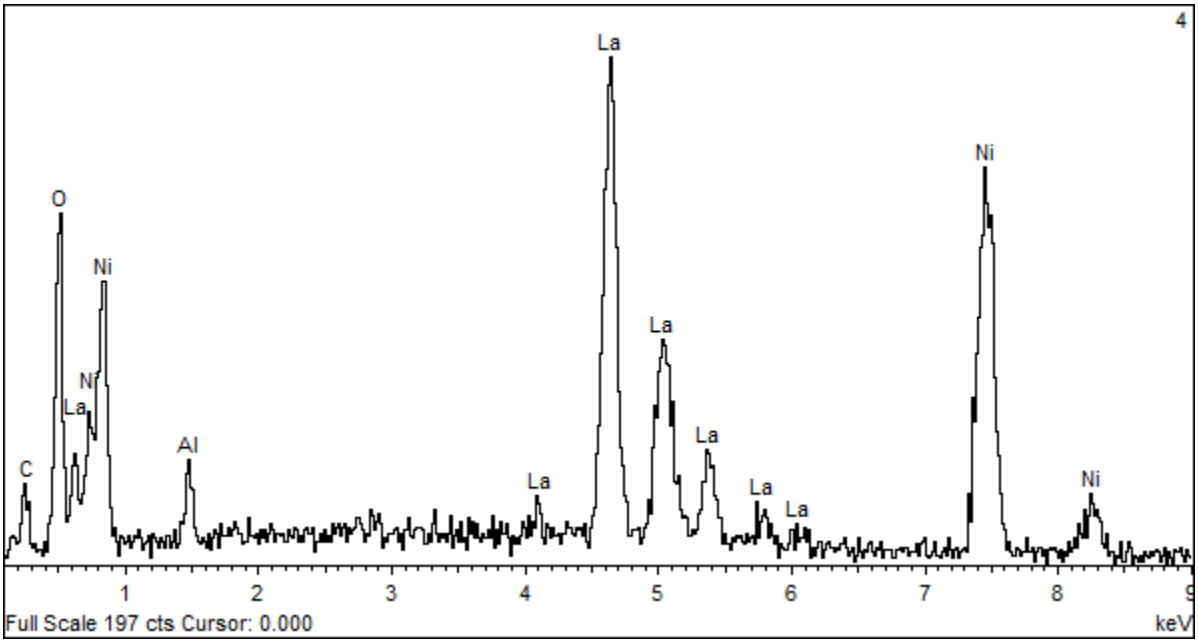
"Spot" 2 – actually a small bright particle: High O content and strong La signals probably indicates it is primarily La_2O_3 with Ni crystallites



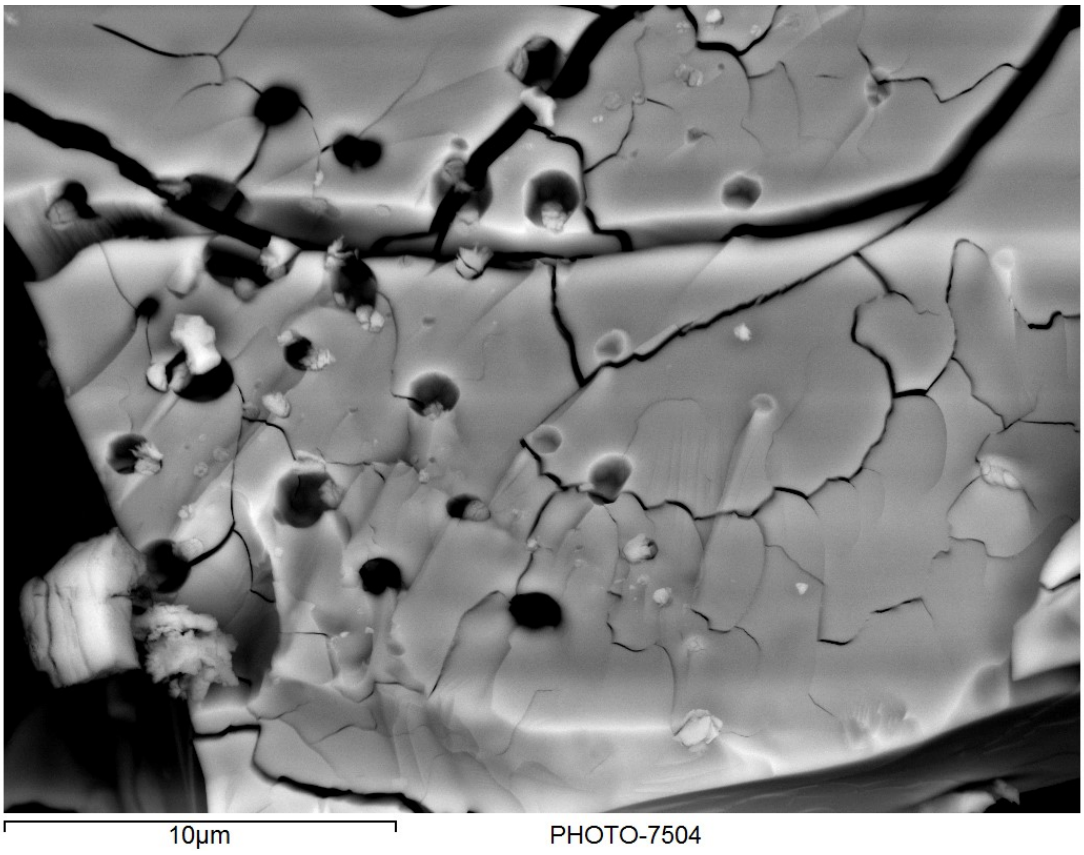
Spot 3: Ni depleted (Al is a little low for normal LANA Ni/Al peak ratio)



Spot 4: La and O enriched, mixed LANA and La_2O_3 + Ni

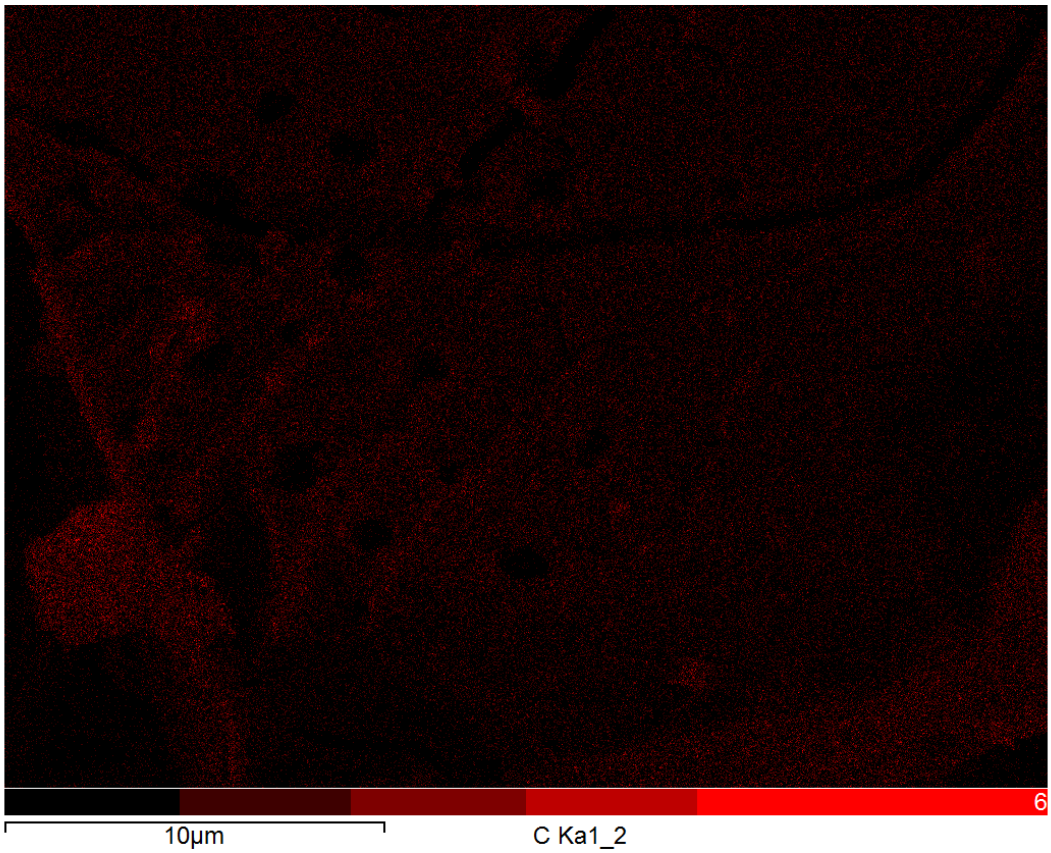


The SEM/EDX instrument is capable of element mapping, where a given area (shown in the normal image) is scanned for selected elements. The amount of that element in a given spot correlates to the apparent brightness in the colored image. This allows one to see if the elemental composition is non-uniform. Compositional inhomogeneity produces severely sloped isotherms.



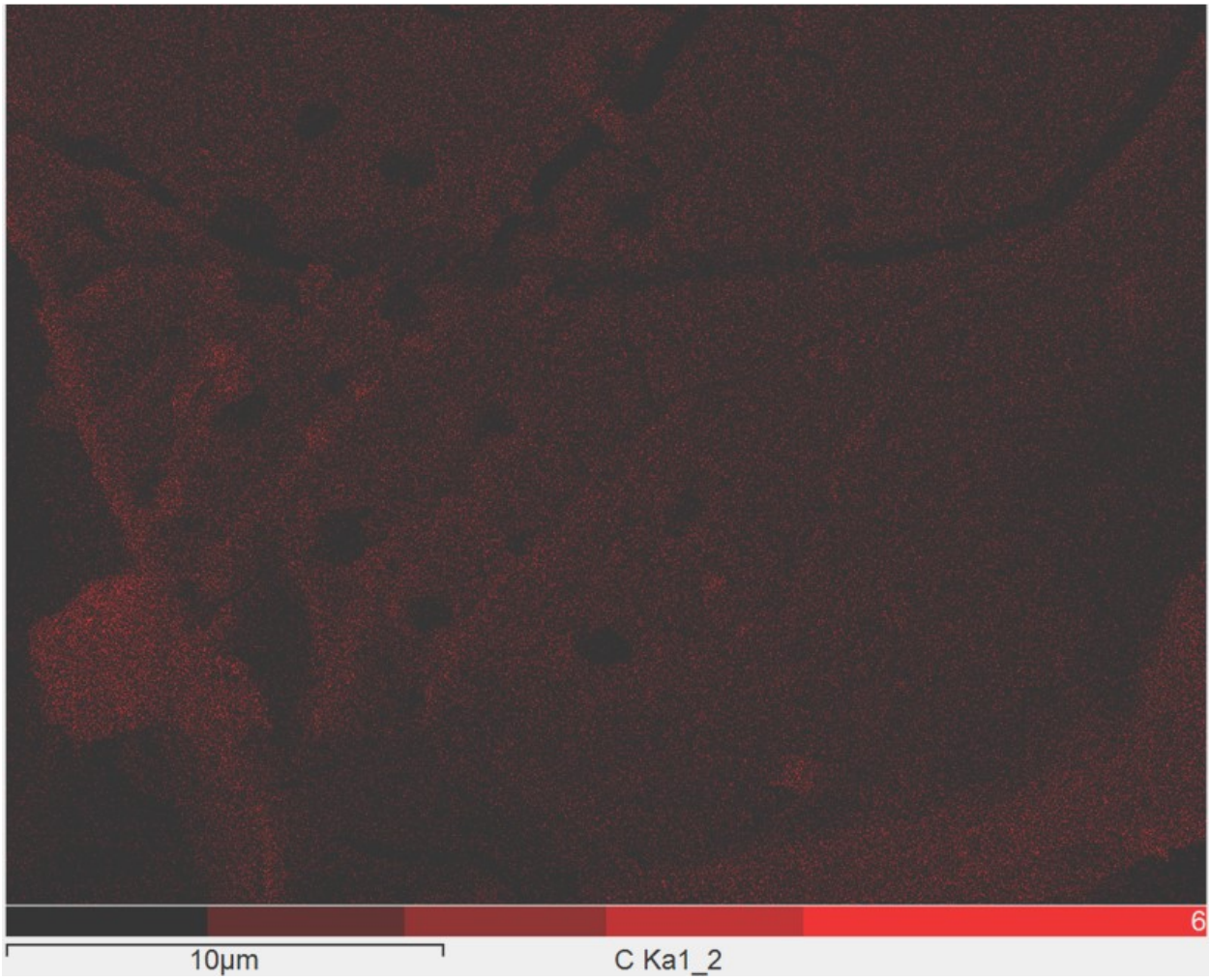
The following maps have a 10 micron bar, the element scanned for, and the x-ray line used indicated along the bottom of the image.

Carbon Map

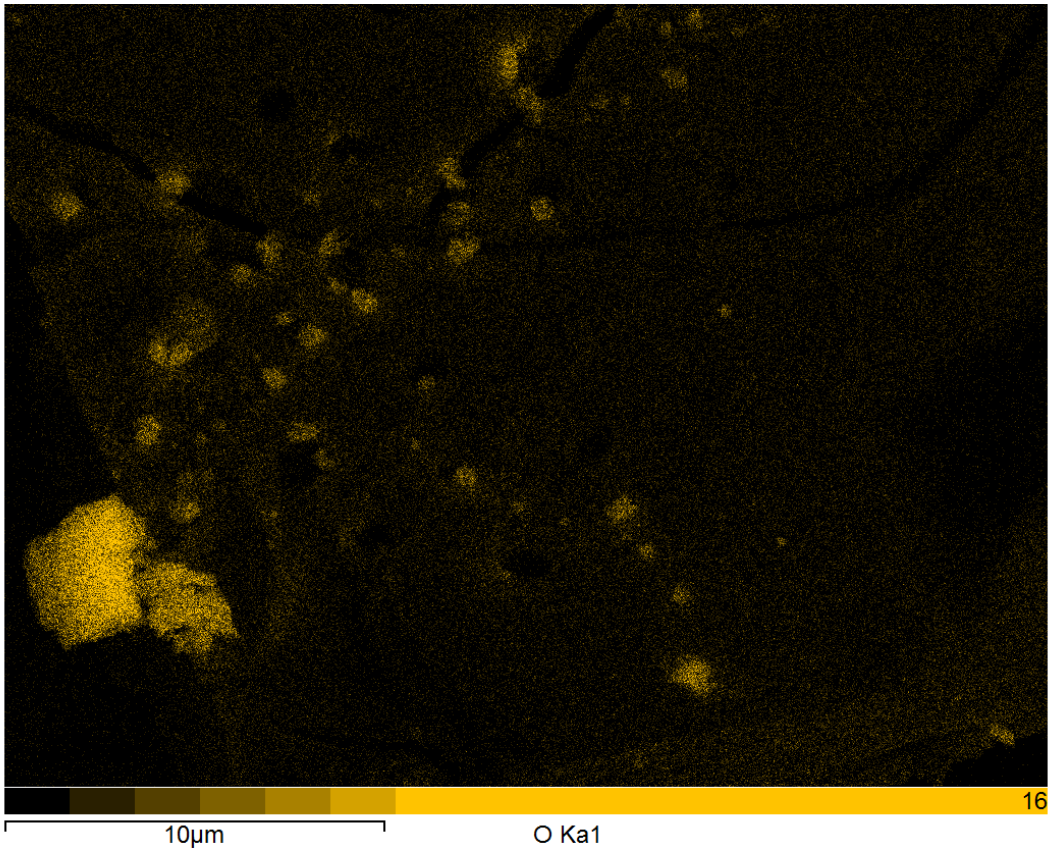


The Carbon image above was very dark. Below is a brightened image that allows one to see the image. (Software used was GIMP 2.8.4 (a freeware 'Photoshop' counterpart.))

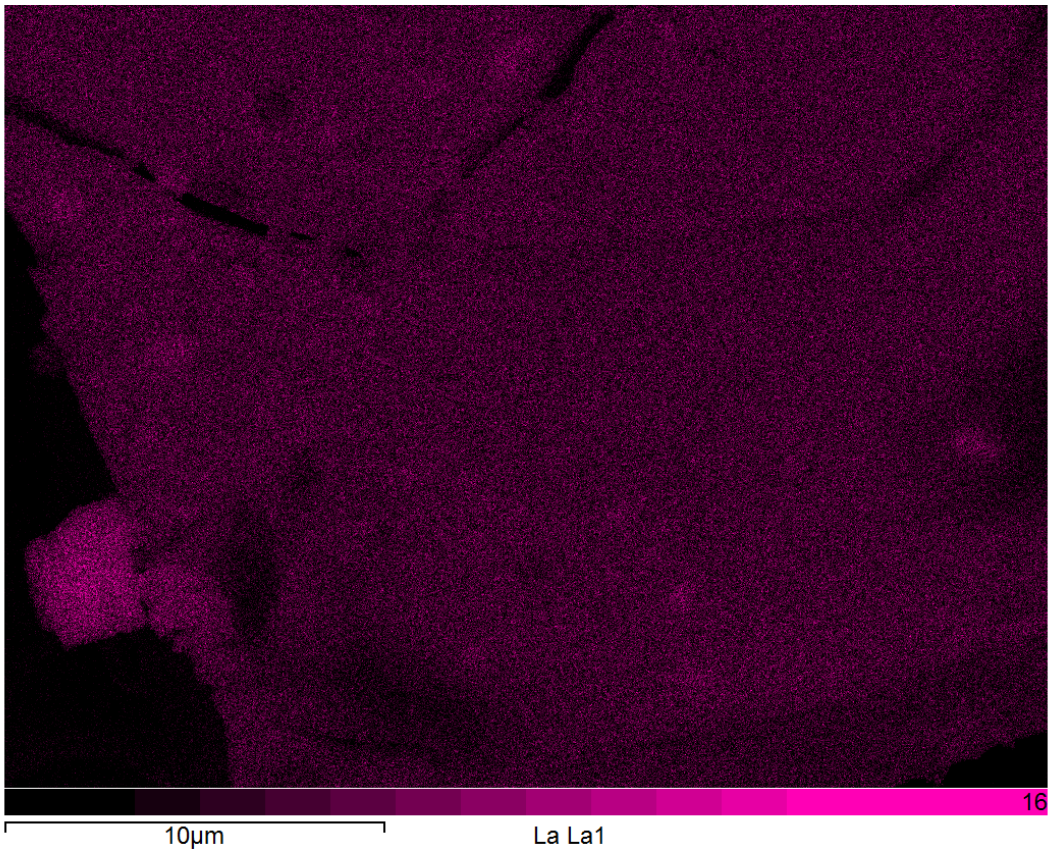
Brightened Carbon Map



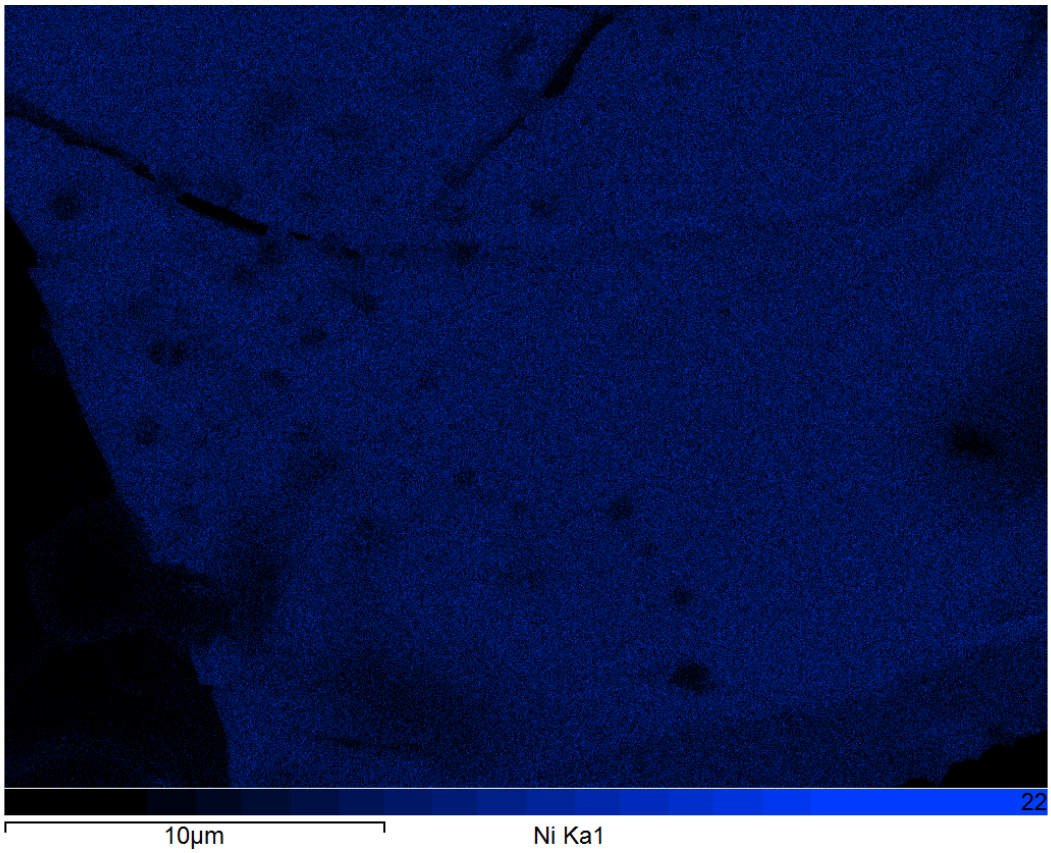
Oxygen Map: Note the strong signal from the particle in the lower left. Coupled with the O map shown below, this indicates La_2O_3 is likely present, also noted in several other spots.



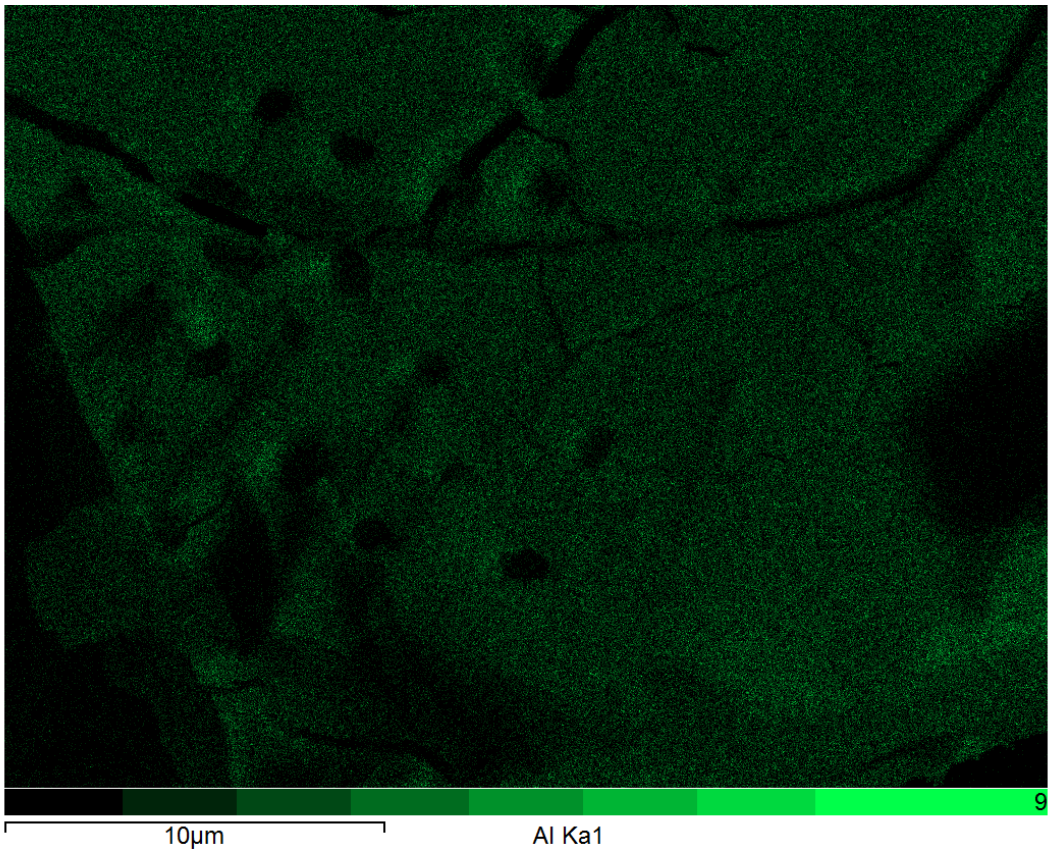
Lanthanum Map (especially note the brightness of the particle in the lower left)



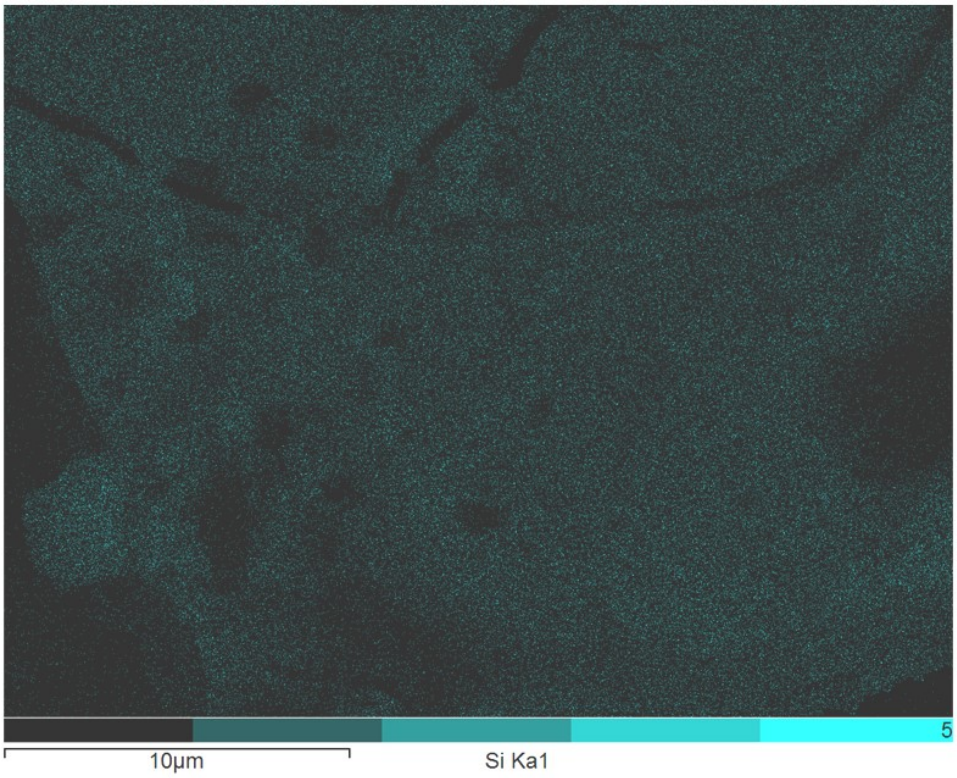
Nickel Map



Aluminum Map



Silicon Map (a contaminant detected in prior SNL studies) – this photo has also been brightened.



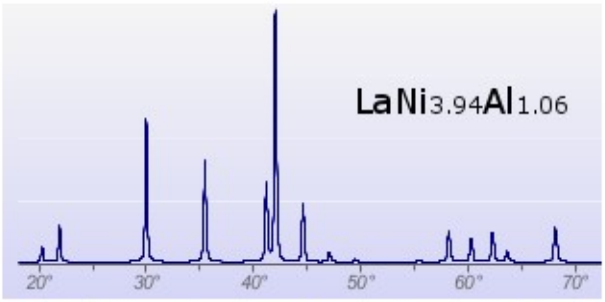
Appendix B: XRD results

The results in this appendix were supplied by David Missimer of the Analytical Development Section of SRNL.

After completing the isotherm determinations on the various samples, each was 'retired' by passivating with room air at room temperature (no significant temperature spikes were noted). The test cells were then opened and the material removed and placed in glass vials. They were then sent to ADS for further analysis, which included XRD powder pattern determination.

The lines observed in an XRD arise due to diffraction of monochromatic x-rays that occurs from the periodic structure of the solid lattice in the alloys. The XRD technique exposes a multi-particle, multicrystalline sample to a collimated beam of x-rays and the x-ray detector is then rotated around the sample to record the scattered x-ray intensity at a given angle, referred to as 2θ (2 theta). Below (Figure B-1.) is a reference library spectrum of LANA106 ($LaNi_{3.94}Al_{1.06}$)

Figure B-1. Low angle reference XRD Spectrum of LANA106 (2θ <=70°)



#	Angle	d(Å)	I%(f)	(h k l)
1	20.2395	4.38400	5.0	(1 0 0)
2	21.8575	4.06300	13.0	(0 0 1)
3	29.9608	2.98000	52.0	(1 0 1)
4	35.4374	2.53100	39.0	(1 1 0)
5	41.1474	2.19200	31.0	(2 0 0)
6	42.0093	2.14900	100.0	(1 1 1)
7	44.5768	2.03100	24.0	(0 0 2)
8	47.0459	1.93000	4.0	(2 0 1)
9	49.4114	1.84300	1.0	(1 0 2)
10	55.4004	1.65710	1.0	(2 1 0)
11	58.1789	1.58440	14.0	(1 1 2)
12	60.2584	1.53460	11.0	(2 1 1)
13	62.2593	1.49000	14.0	(2 0 2)
14	63.6186	1.46140	5.0	(3 0 0)
15	68.1187	1.37540	17.0	(3 0 1)

Each reflection is associated with a specific plane through the material's crystal structure. Thus, the most intense peak located at 2θ = 42.0093° arises from the (111) plane (2θ values listed on the Figure under 'Angle'). These numbers are known as the Miller indices and are shown in the Figure for each reflection ('(h k l)' column).

The XRD pattern of each LANA alloy shows the same general structure. As the Al content varies, the precise angle at which these reflections occur changes slightly as a result of the small difference in crystal spacings produced by varying the Al content. However, the changes are not enough to disturb the general pattern shown, thus the (111) peaks of LANA75 and 85 are expected to occur near 42°, the (101) peaks near 30°, etc.

The relative intensities of the reflections are also given in the 'I%(f)' column. From sample-to-sample these may vary slightly due to the statistical fact that a given sample may randomly have more of one plane presented to the beam than another sample.

Also indicated in the associated data of the Figure is the reflection number (sequential from low angle to high) and the 'd' value in Angstroms, which is the interplanar spacing. From these spacings, the unit cell dimensions can be calculated. The unit cell dimensions plotted as a function of Al content can be used to determine Al content of an unknown LANA alloy, as in refs. 1 and 2.

In the following sections, XRD patterns of the virgin and treated materials used in the EXOP study are presented and discussed. In all but one case, the 'treated' designator refers to the fact that the sample has been thermally aged under high hydrogen pressure, or HHT treated. The one exception is the XRD spectrum obtained from sample LANA85_EXOP10, which was only activated, i.e. cycled in hydrogen a few times. The primary purpose of the activation process is to decrepitate the material, which exposes more surface area and increases the absorption/desorption kinetics.

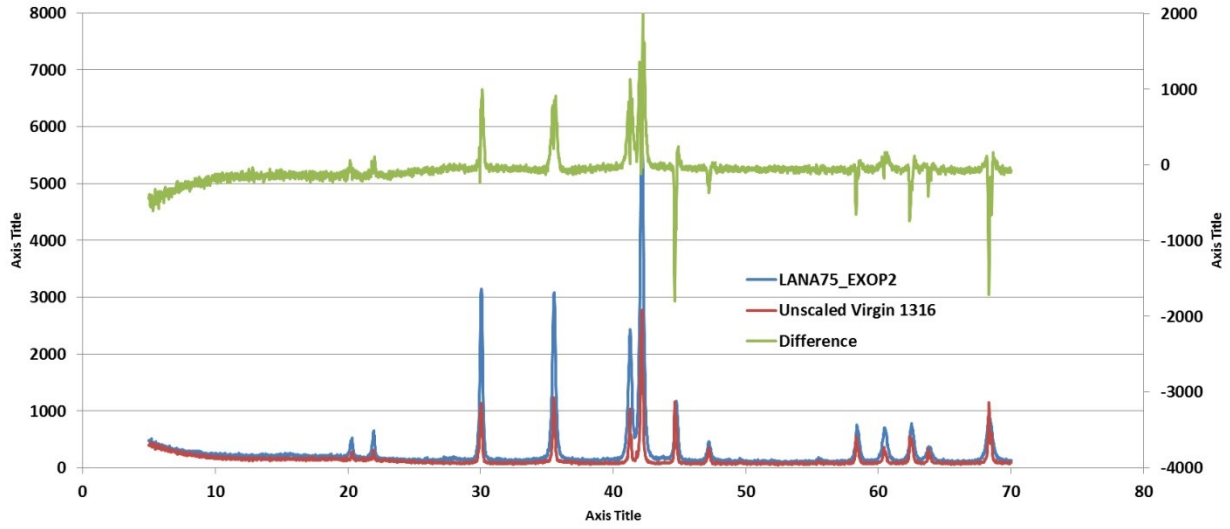
Most of these XRD spectra were not acquired using nominally identical sample masses, thus the overall intensity of one spectrum can vary significantly from others. In the following results, the virgin material spectra routinely have a lower total intensity than the treated material, primarily due to the fact that the virgin sample was not ground to the same small particle size as is naturally obtained in the decrepitation process. Thus, the virgin sample has more void volume even with identical sample weight than the decrepitated sample. However, it was observed that the relative peak intensities changed due to the HHT. This change appears to be consistent over several samples, and thus is thought to *not* be due to random effects but rather to illustrate another diffraction phenomenon, the more intense scattering of x-rays by heavier elements.

Difference spectra in which the scaled virgin spectral intensity is subtracted from the treated sample peak intensity are shown to illustrate this observation. We employed this scaling approach based on the fact that we attempted to acquire XRD patterns from identical weights of virgin and treated samples of the same material (Lot 1316 LANA75) and observed that the virgin spectrum was still less intense overall. Those XRD spectra are shown in Figure B-2. The scaling involved multiplying the virgin spectrum by a factor derived from the ratio of the peak intensities of the (111) peak (the strongest peak) in both samples. The virgin material peak was the lowest intensity of the two in all cases.

Some literature papers have suggested that there is a transfer of Ni and Al atoms in the crystal structure with the various treatments employed. We feel that may be the case here based on the fact that there is a consistent increase of intensity in the (101), (110), and (111) reflections and a slight decrease in the (001), (002), (112), (211), (202), (300), and (301) reflections. The decreases in peak intensities were smaller than the increases, and even opposite (i.e., an enhancement) in a few instances. In the TCON LANA materials case, there were multiple samples used, all of which seem to show the same enhancements. It seems highly unlikely that exactly the same changes in 'random' planes presented to the beam would occur in multiple separate samples. Thus, we conclude that the Ni-Al exchanges postulated above are indeed occurring. We do not know if this repairs compositional inhomogeneity or induces it, and we do not know if this would be harmful or helpful with respect to tritium aging effects.

Another effect observed in the literature that was reproduced here is the broadening of the peaks. This will be pointed out below when spectra for each material are presented. The peak broadening is thought to occur because of a reduction in the average crystallite size.

Figure B-2. Virgin and Treated LANA75 Lot 1316 XRD Spectra with DIfference Spectrum



GfE LANA85 XRD results

Three GfE LANA85 samples, LANA85_GFE5, LANA85_EXOP6, and LANA85_EXOP10, were submitted for XRD analysis. The raw XRD spectrum for LANA85_GFE5 is shown in Figure B-3a along with the scaled virgin GfE material XRD (Lot 60836) and the difference spectrum calculated by subtracting the scaled virgin GfE XRD from LANA85_GFE5's XRD. Expanded 2θ scale sections of Figure B-3a are shown in Figures B-3b and B-3c to illustrate the widening of the treated sample's XRD peaks. A slight peak position shift seems to accompany the broadening in some cases (~0.2°, the resolution of the 2θ scale). The equivalent data from LANA85_EXOP6 are shown in Figure B-4, where the GFE5-scaled virgin spectrum is also shown (offset for clarity) for comparison.

LANA85_EXOP10 was not HHT treated but was activated, which caused it to decrepitate, reducing the particle size substantially compared to the virgin material. The resulting XRD spectrum is presented in Figures B-5a, b, and c. The changes in the XRD spectrum are very similar to those observed for HHT samples, suggesting that the major cause of the changes are due to the stresses of hydriding/dehydriding cycles.

Figure B-3a. XRD Spectra from LANA85_GFE5 Compared to Virgin GfE Material

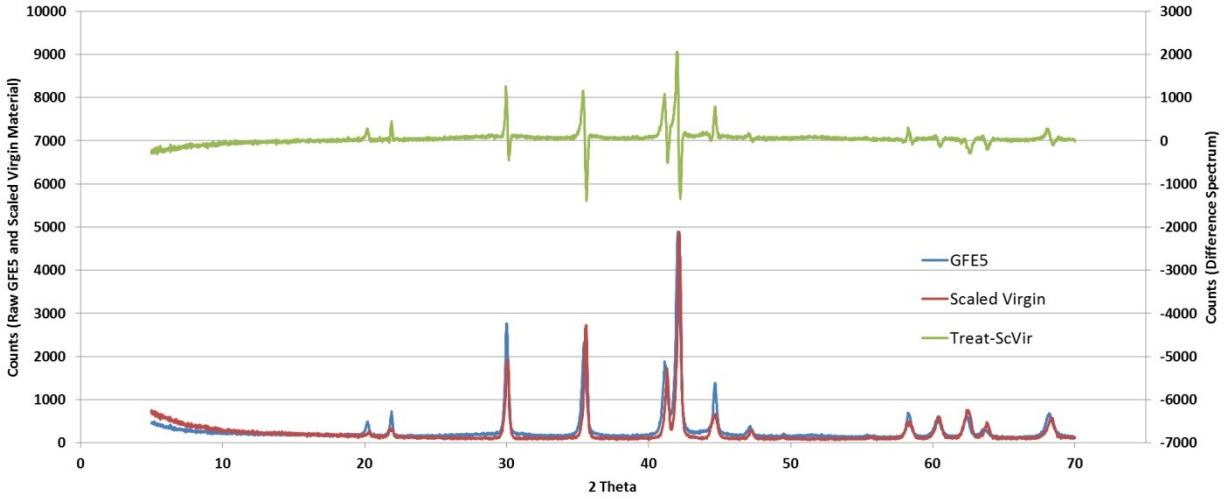


Figure B-3b. Expanded Scale XRD Spectra from LANA85_GFE5 Compared to Virgin GfE Material

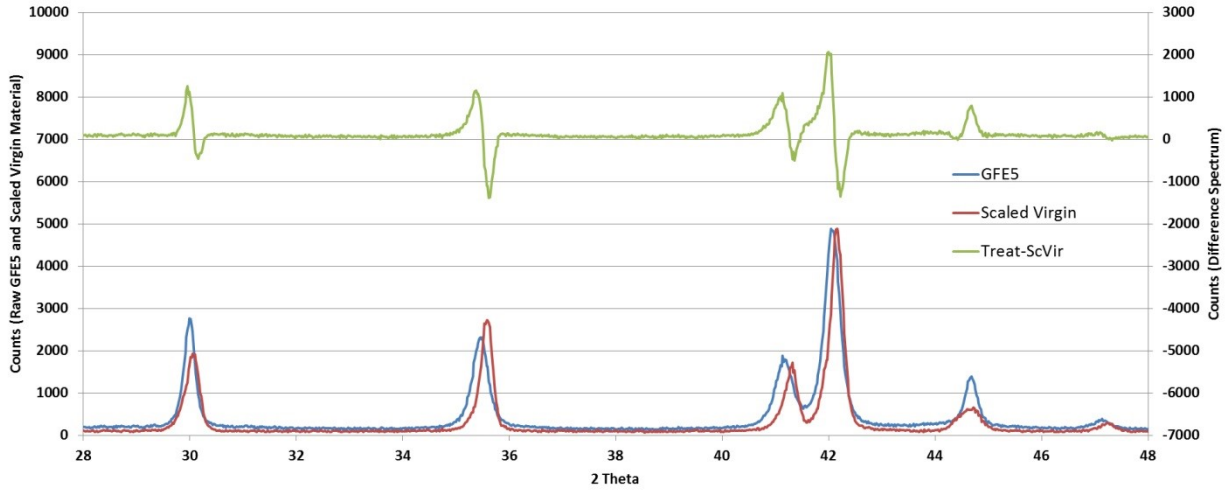


Figure B-3c. Expanded Scale XRD Spectra from LANA85_GFE5 Compared to Virgin GfE Material

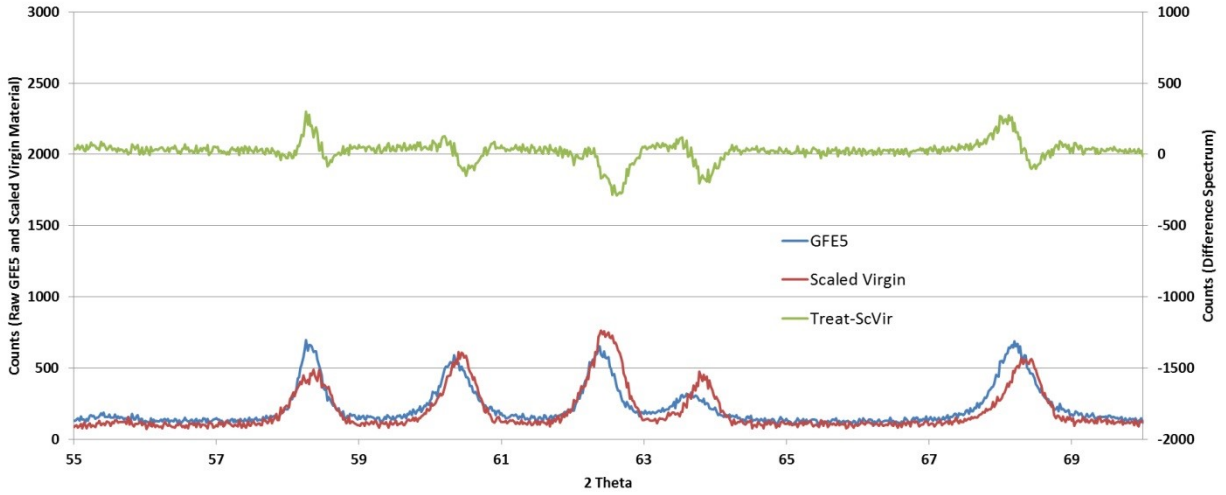
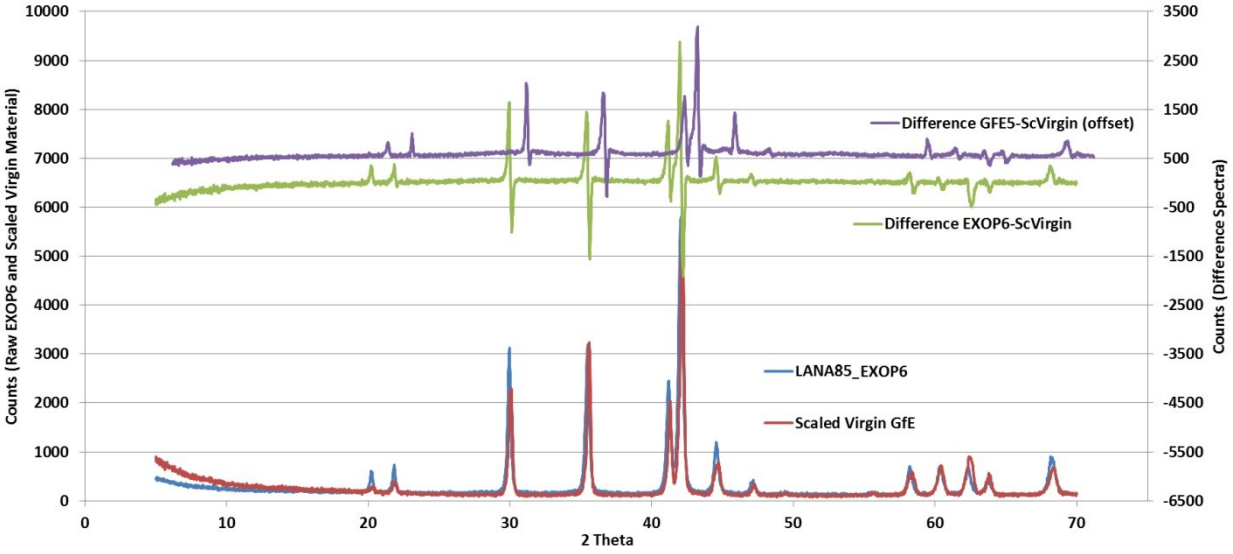
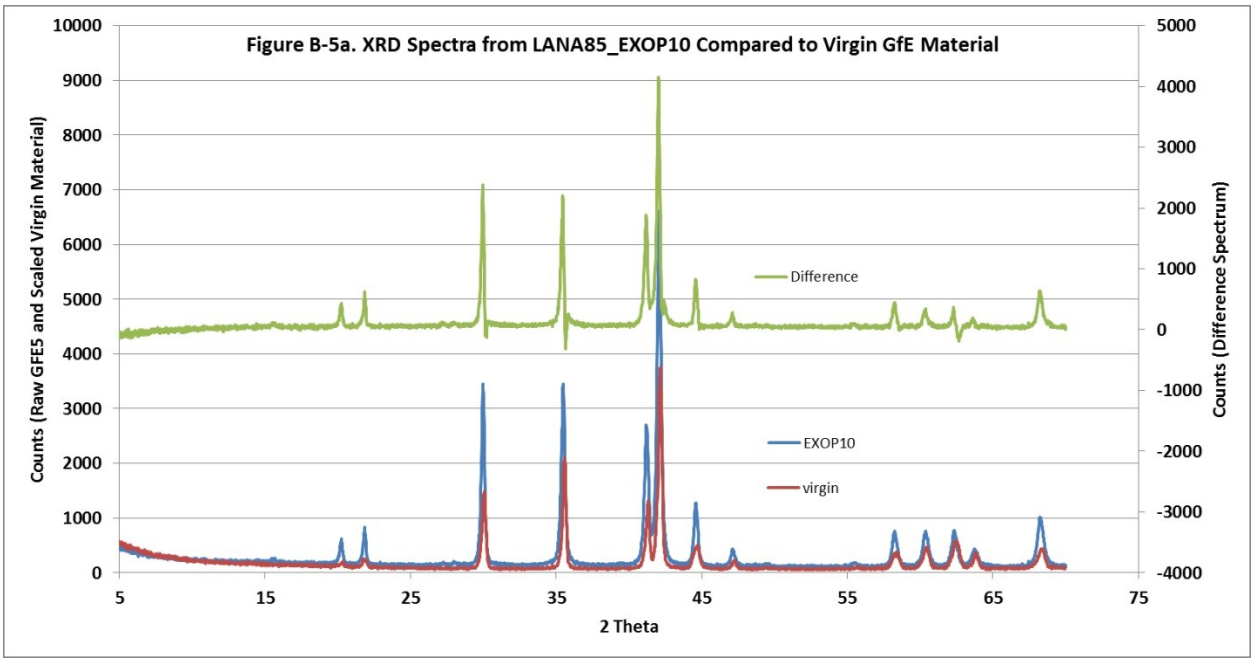


Figure B-4. XRD Spectra for LANA85_EXOP6 (and LANA85_GFE5) Compared to Virgin GfE Material





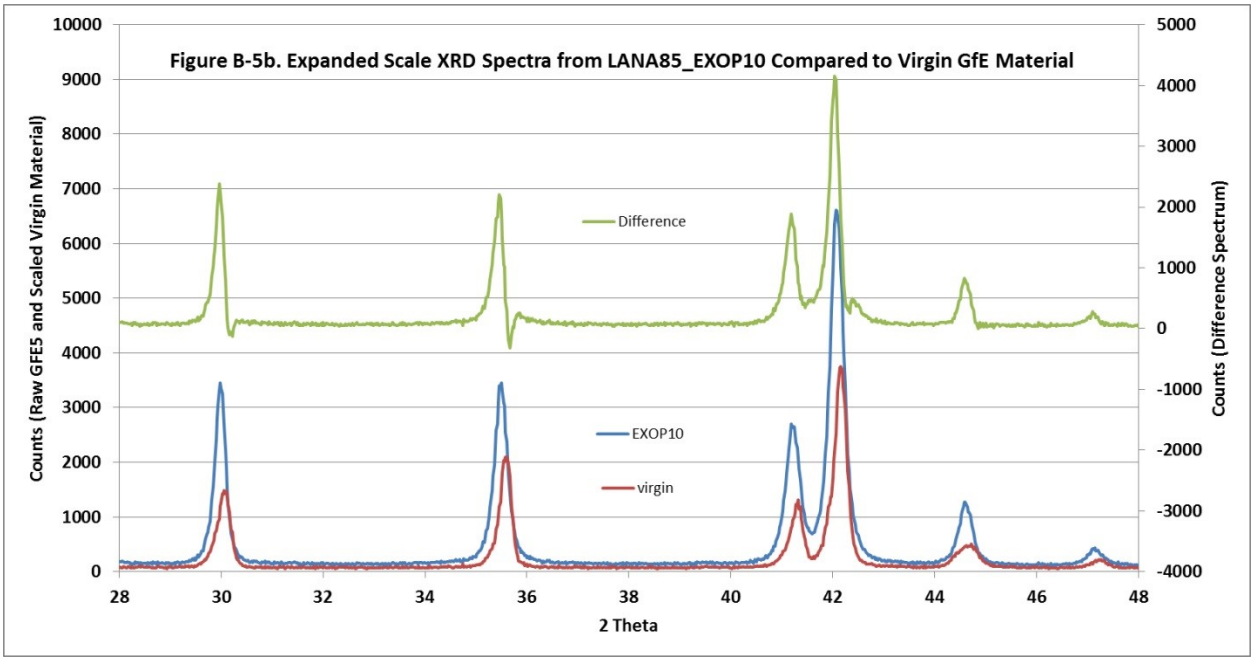


Figure B-5b. Expanded Scale XRD Spectra from LANA85_EXOP10 Compared to Virgin GfE Material
Counts (Raw GFE5 and Scaled Virgin Material)
Counts (Difference Spectrum)
2 Theta
Difference
EXOP10
virgin
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
-4000
28
30
32
34
36
38
40
42
44
46
48

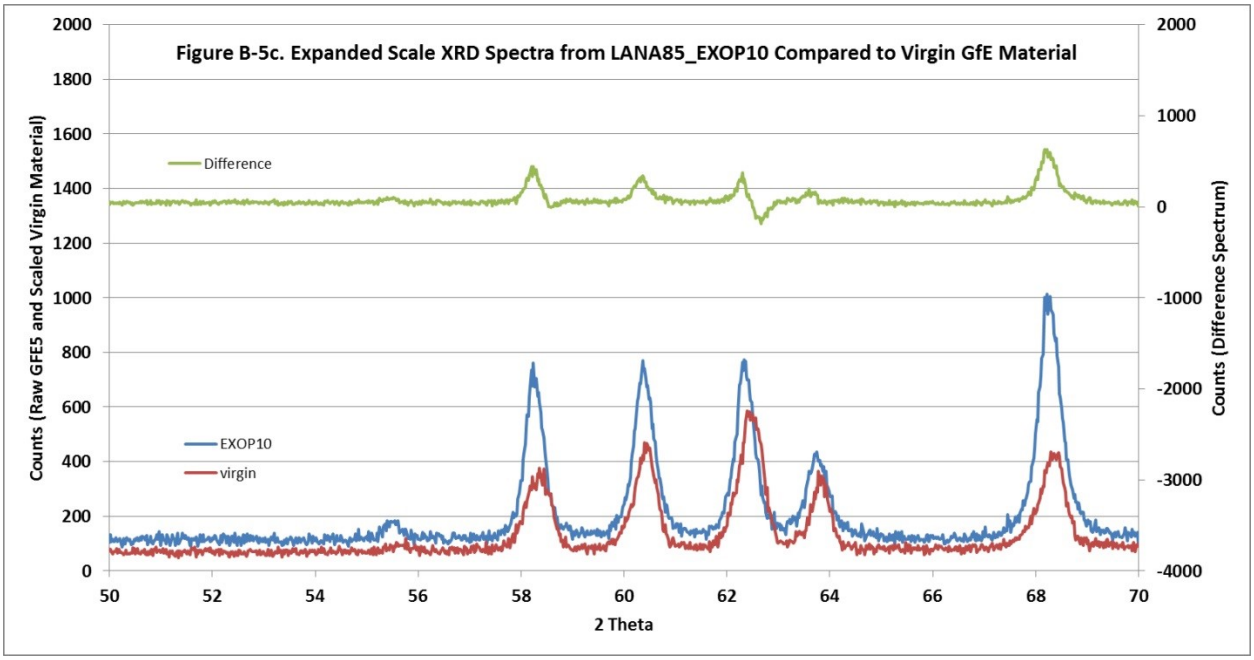
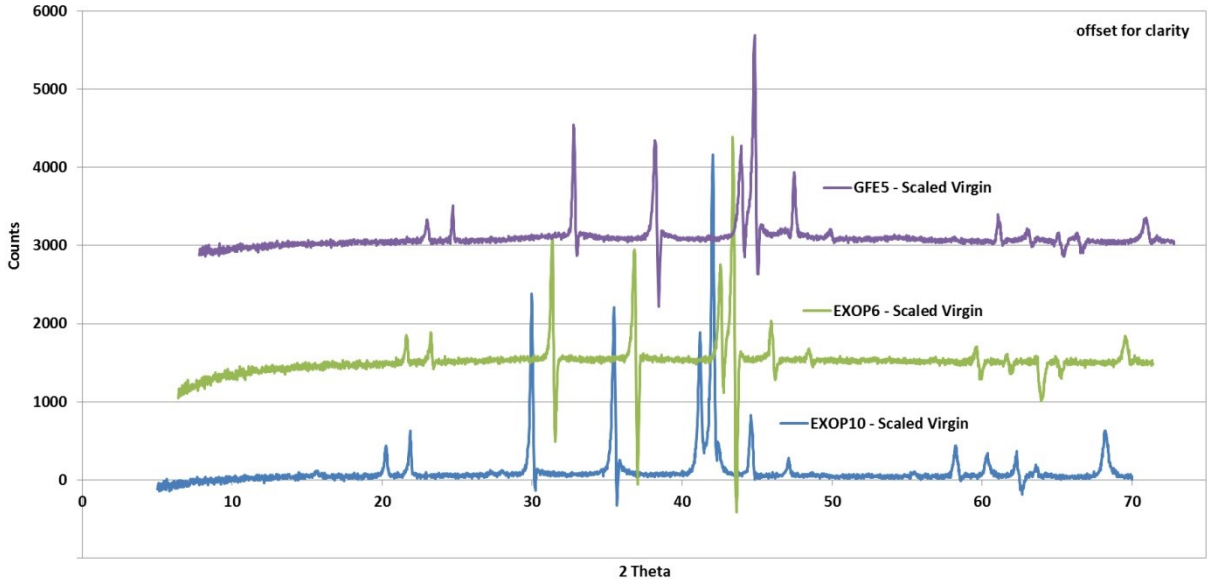


Figure B-5c. Expanded Scale XRD Spectra from LANA85_EXOP10 Compared to Virgin GfE Material
Counts (Raw GFE5 and Scaled Virgin Material)
Counts (Difference Spectrum)
2 Theta
Difference
EXOP10
virgin
2000
1800
1600
1400
1200
1000
800
600
400
200
0
2000
1000
0
-1000
-2000
-3000
-4000
50
52
54
56
58
60
62
64
66
68
70

Figure B-5d. XRD Difference Spectra for LANA85_EXOP10, LANA85_EXOP6, and LANA85_GFE5



Lot 1138 LANA85 XRD results

Only one sample, LANA85_EXOP1, was studied and submitted for XRD analysis, the results of which are presented in Figures B-6a, b, and c. The expanded scale views illustrate the line broadening noted in the treated sample. The virgin material peaks seem to be slightly asymmetric and/or split, which could arise from compositional inhomogeneity.

Figure B-6a. XRD Spectra for LANA85_EXOP1 Compared to Virgin Lot 1138 Material

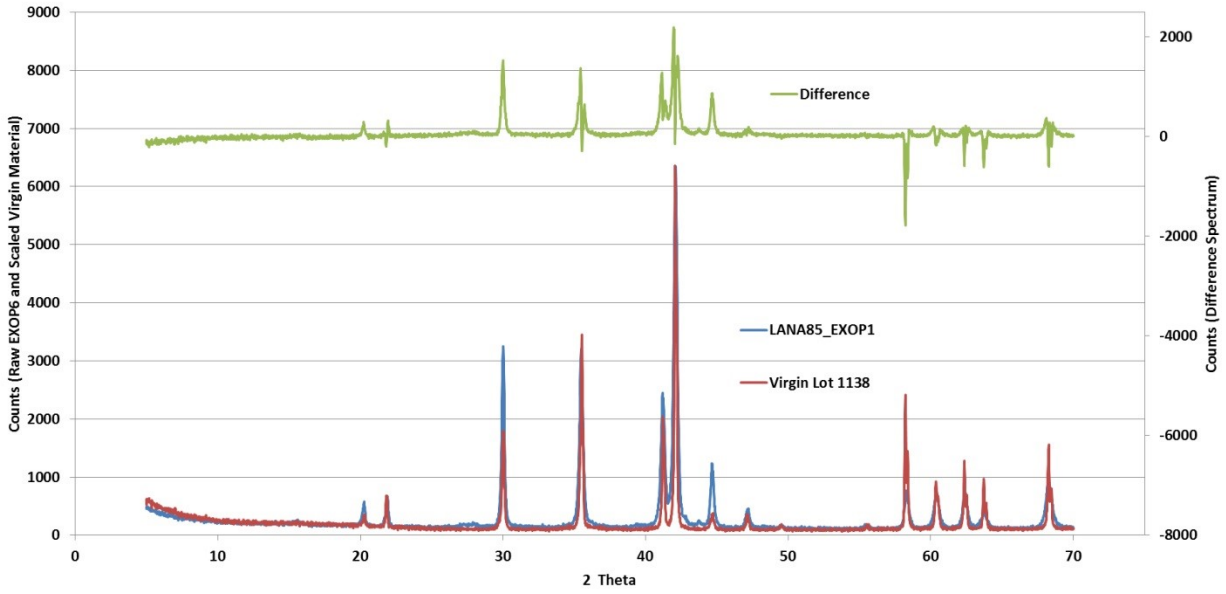


Figure B-6b. Expanded Scale XRD Spectra for LANA85_EXOP1 Compared to Virgin Lot 1138 Material

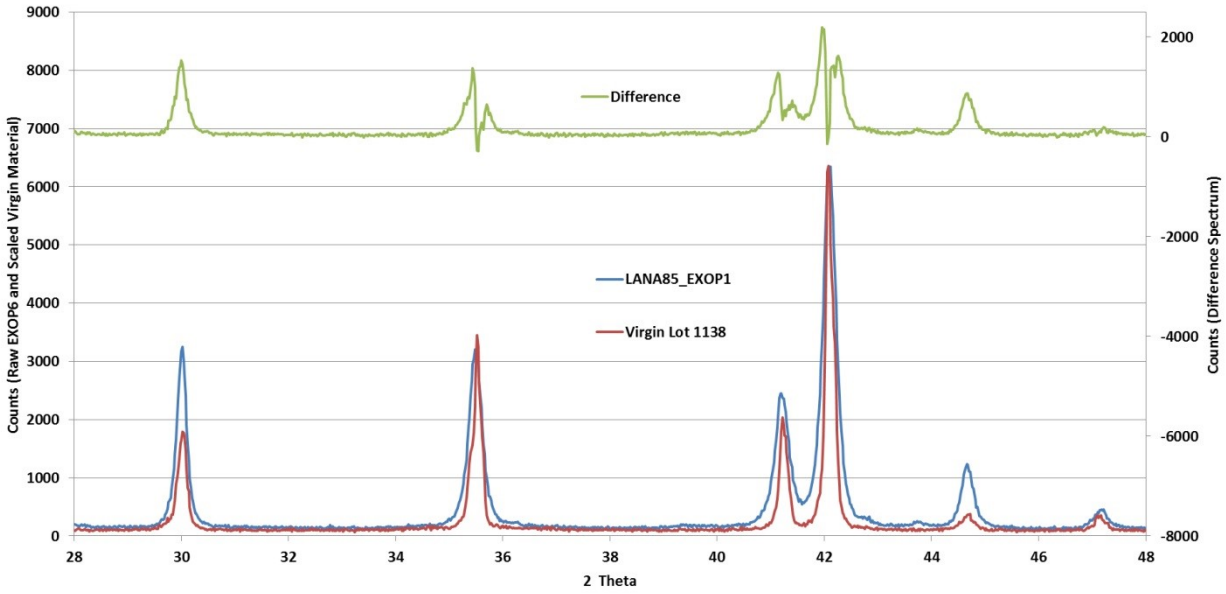
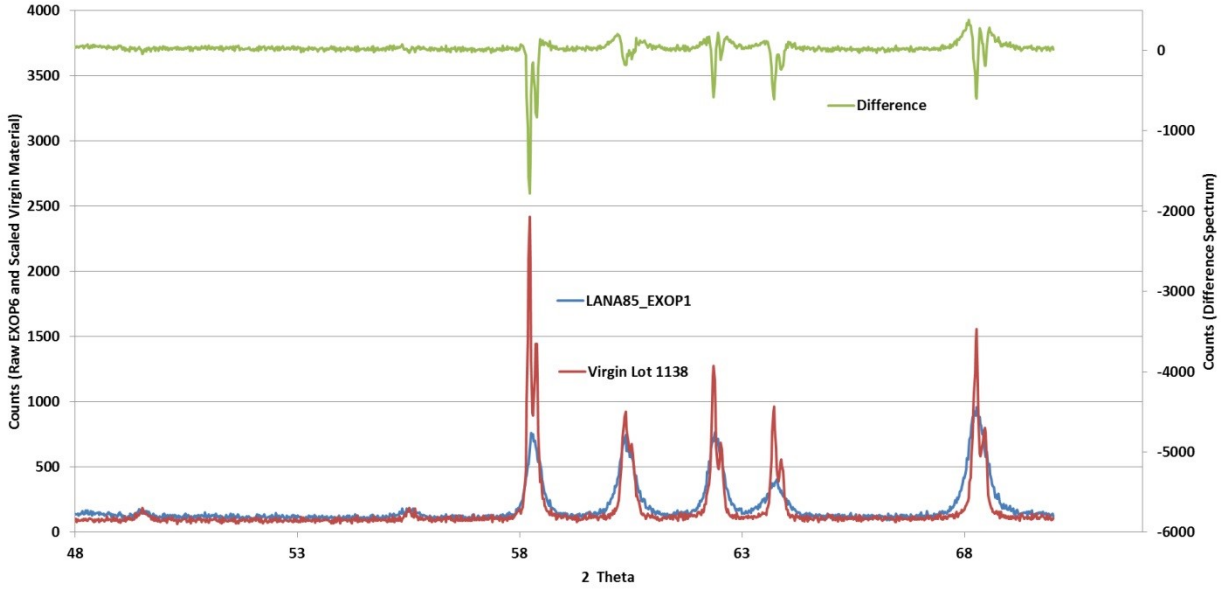


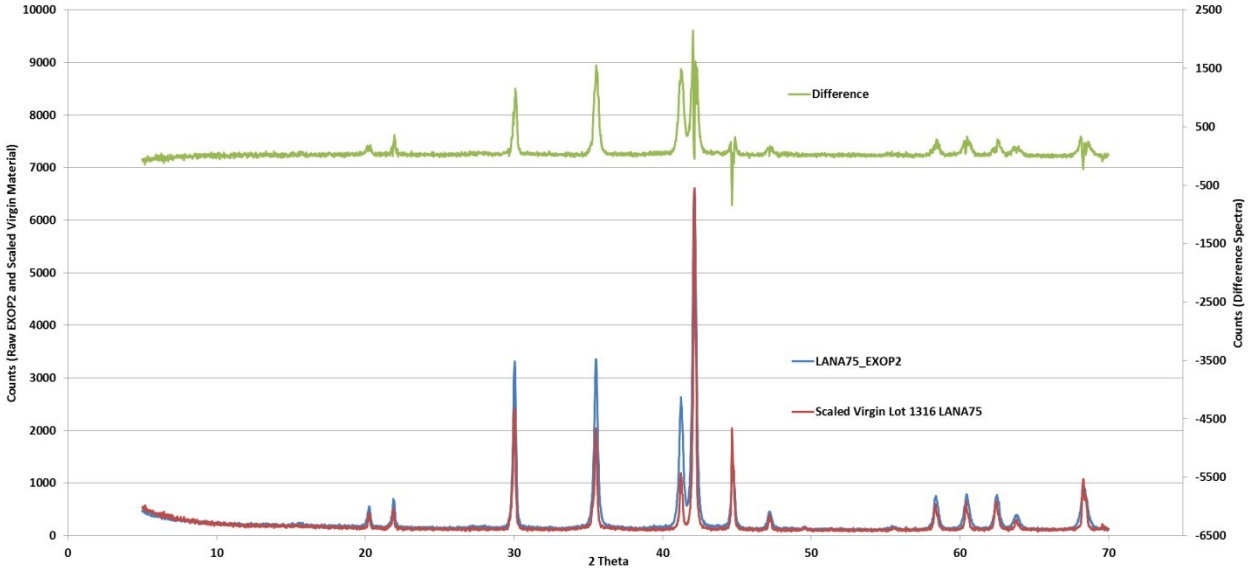
Figure B-6c. Expanded Scale XRD Spectra for LANA85_EXOP1 Compared to Virgin Lot 1138 Material



Lot 1316 LANA75 XRD results

Two samples of Lot 1316 material were studied during this research; one was still active when this report was written (LANA75_EXOP4), the other (LANA75_EXOP2) was submitted for XRD, the results of which are shown in Figures B-7a, b, and c.

Figure B-7a. XRD Spectra from LANA75_EXOP2 Compared to Virgin Lot 1316 LANA75 Material



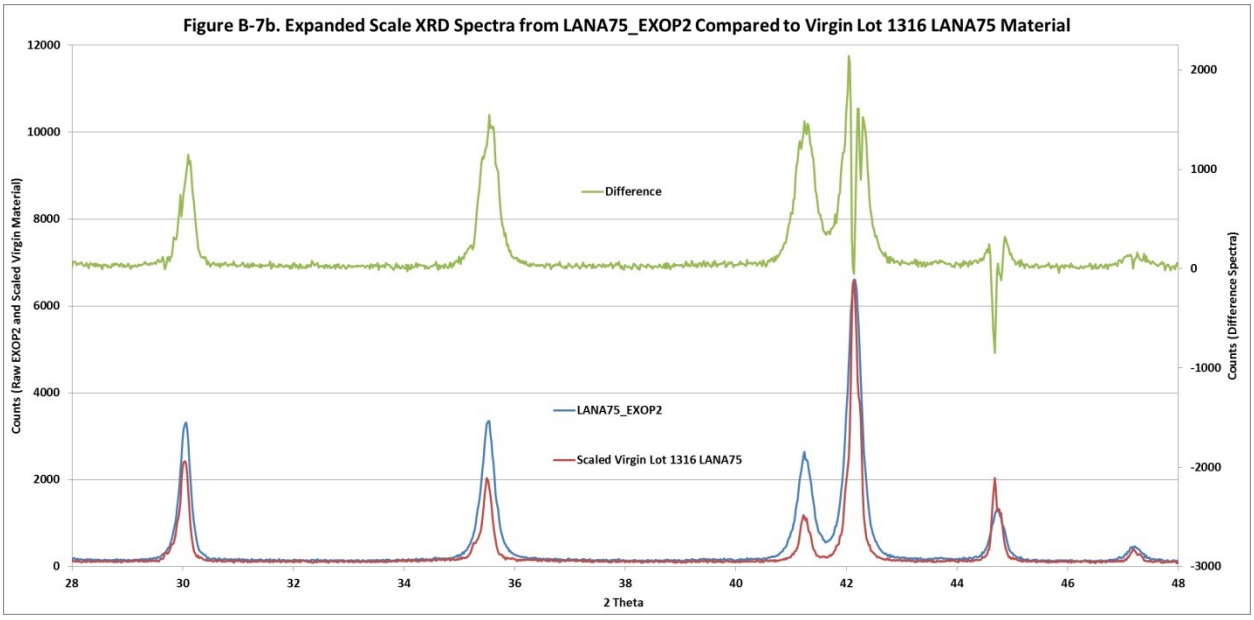


Figure B-7b. Expanded Scale XRD Spectra from LANA75_EXOP2 Compared to Virgin Lot 1316 LANA75 Material
Counts (Raw EXOP2 and Scaled Virgin Material)
Counts (Difference Spectra)
2 Theta
Difference
LANA75_EXOP2
Scaled Virgin Lot 1316 LANA75
12000
10000
8000
6000
4000
2000
0
2000
1000
0
-1000
-2000
-3000
28
30
32
34
36
38
40
42
44
46
48

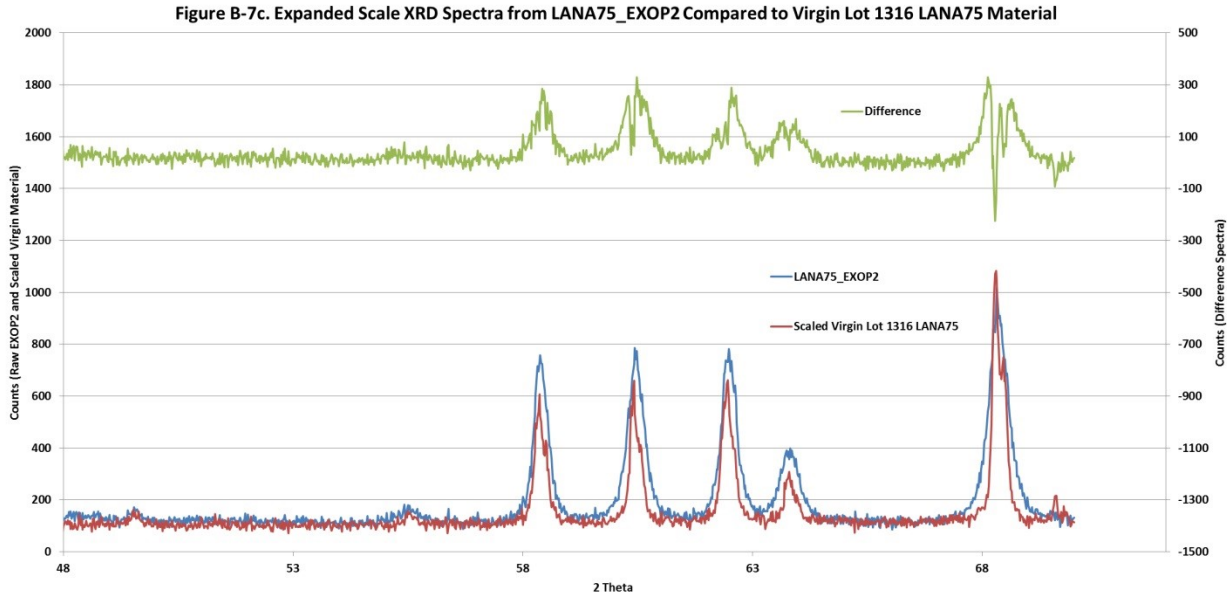


Figure B-7c. Expanded Scale XRD Spectra from LANA75_EXOP2 Compared to Virgin Lot 1316 LANA75 Material
Counts (Raw EXOP2 and Scaled Virgin Material)
Counts (Difference Spectra)
2 Theta
Difference
LANA75_EXOP2
Scaled Virgin Lot 1316 LANA75
2000
1800
1600
1400
1200
1000
800
600
400
200
0
500
300
100
-100
-300
-500
-700
-900
-1100
-1300
-1500
48
53
58
63
68

Figure B-8a. Comparison of Oxidized LANA75 Lot 1316 Sample (LANA75_JEKP) to Virgin Material

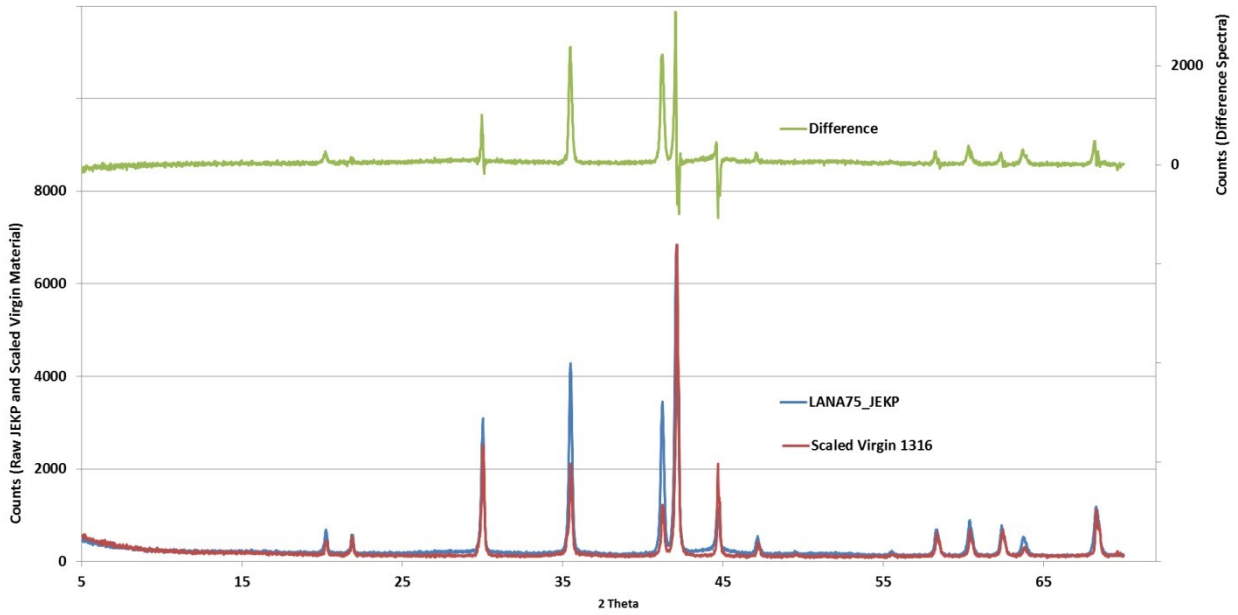


Figure B-8b. Expanded Scale of Oxidized LANA75 Lot 1316 Sample (LANA75_JEKP) vs. Virgin Material

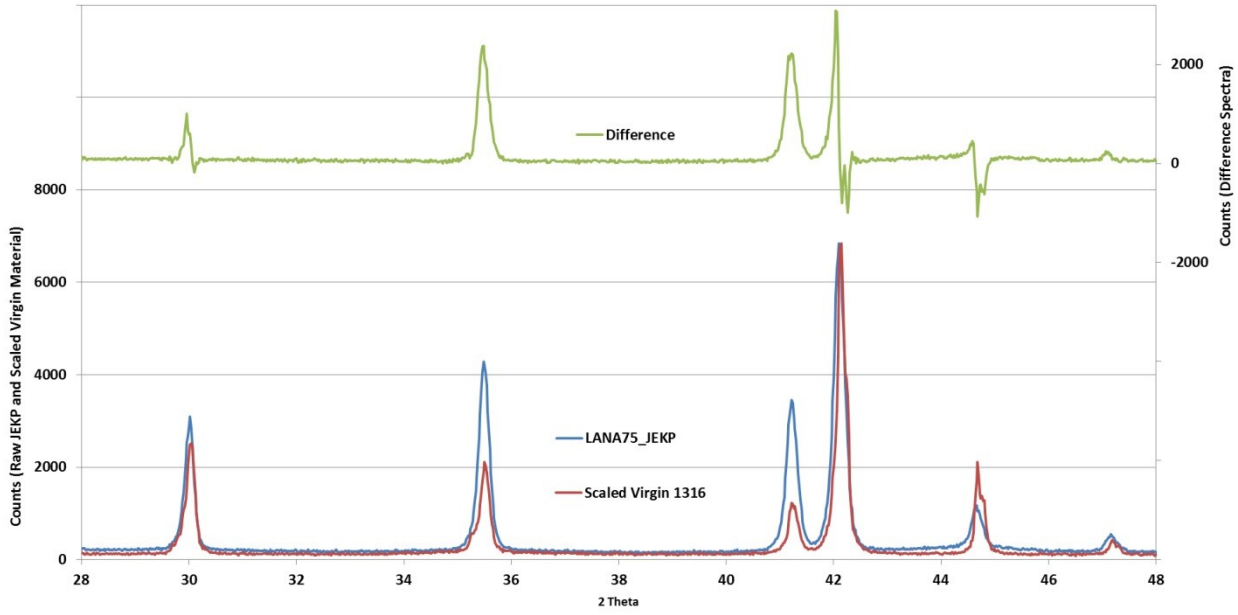
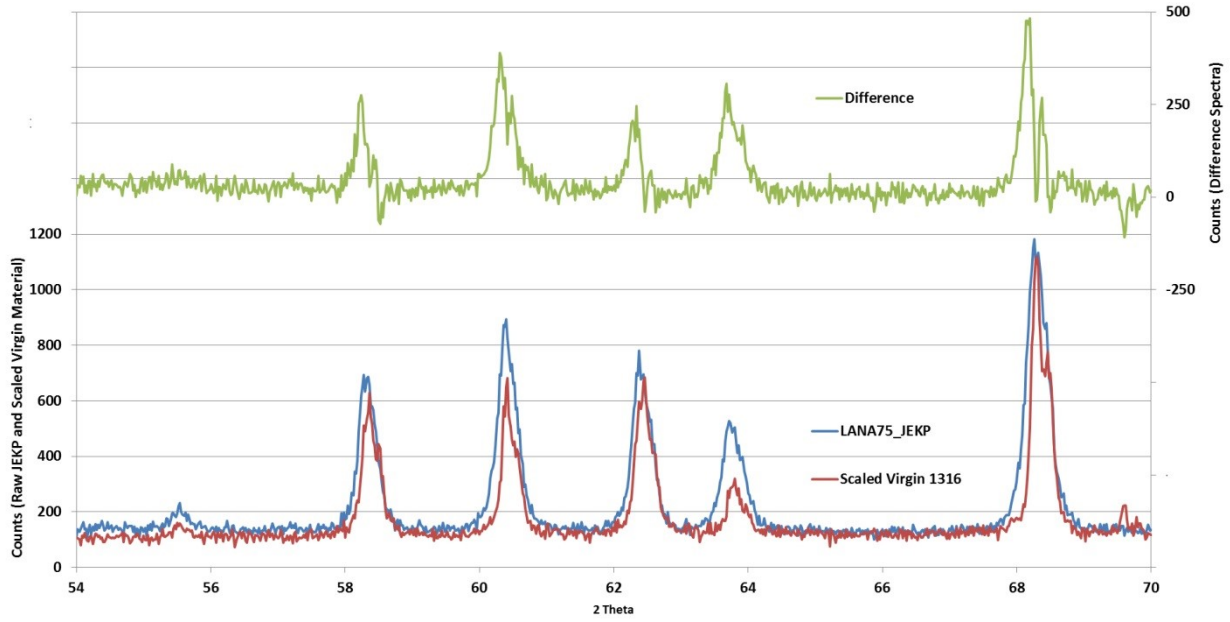


Figure B-8c. Expanded Scale of Oxidized LANA75 Lot 1316 Sample (LANA75_JEKP) vs. Virgin Material



TCON LANA75 XRD results

The TCON LANA75 material is an Ergenics-produced blend of 3 heats. The heats were blended due to one of them failing select acceptance criteria; however, the blend passed the acceptance tests (which was approved by an SDR). The XRD spectrum of the virgin material shows a triplet-like structure in many of the reflections, most likely due to the slight chemical composition differences between heats. HHT broadened the reflections such that this structure was obscured (it is unlikely that composition was homogenized since these differences would occur between particles, not within particles).

Multiple samples of the TCON LANA75 material were studied and XRD analysis was performed on LANA75_EXOP3, 5, 8, 11, and 12 (EXOP13 was still active at the time this report was written). The XRD spectra of all the submitted samples were quite similar and were similarly different from the virgin material XRD.

Figure B-9a. XRD Spectra for TCON LANA75 Samples (offset for clarity)

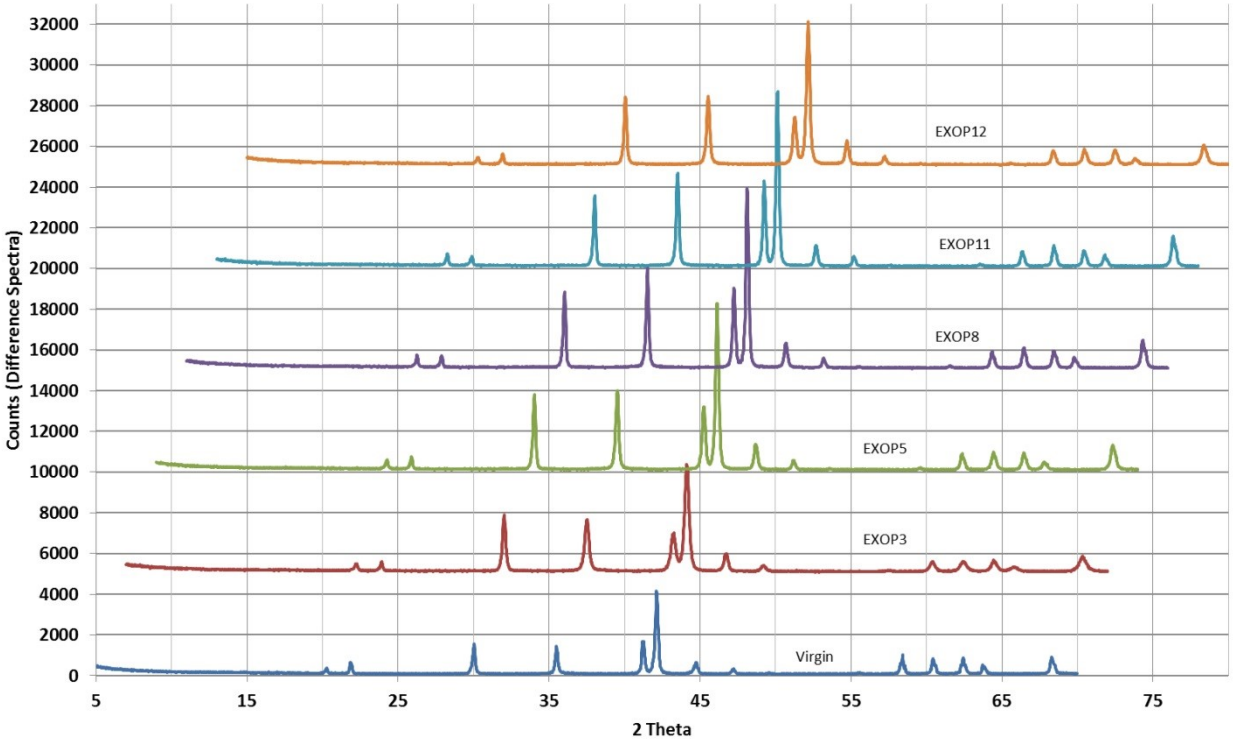


Figure B-9b. Difference Spectra for TCON LANA75 Samples (offset for clarity)