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Surface Characterization of Alumina: Efficacy of Various Cleaners to Select Contaminants

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Michael T. Brumbach[1], Kim Archuleta[2]
[1]Sandia National Laboratories, *Materials Characterization and Performance*
[2]Sandia National Laboratories, *Coatings and Surface Engineering*

U.S. DEPARTMENT OF ENERGY NNSA

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Outline

Alumina material

Some effects observed from cleaning

Efficacy of various cleaners on identified contaminants.

Other projects and Conclusions

NASA/TM—2004-212752

NASA

Contamination of Critical Surfaces from NVR Glove Residues Via Dry Handling and Solvent Cleaning

Marjorie F. Sovinski

Numerous instruments are available for on-site characterization of cleaning.

Alumina

94% alumina ceramic with 6% glassy phase. The glassy phase is often ill-defined, experimentally difficult to observe, and is suspected to be variable.
The alumina composition, grain structure, roughness, and surface chemistry are all believed to be important. All are suspected to be variable.

Diamonite (Cerco) expected composition.

94% amorphous Al_2O_3
Mg, Si, Ca, Cr
6% glassy phase ?

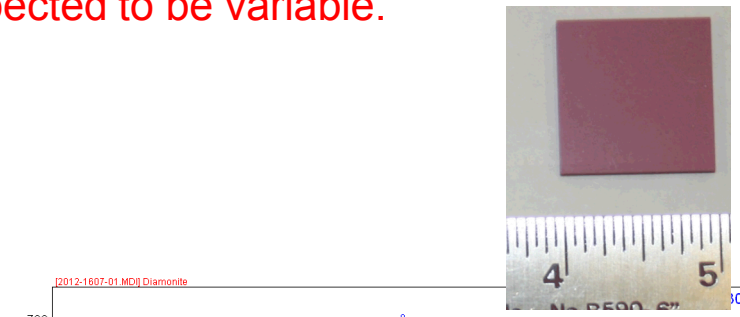
ICP-MS results

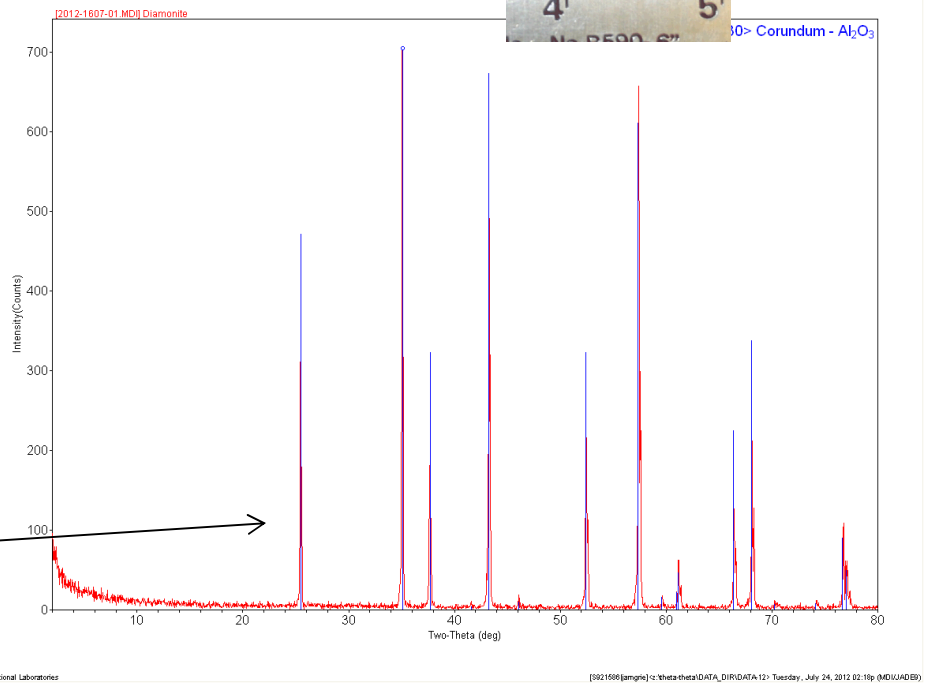
(light elements excluded):

Al	50.6 ± 0.8 wt%
Si	0.82 ± 0.13 wt%
Cr	0.66 ± 0.01 wt%
Mg	0.29 ± 0.02 wt%
Ti	0.068 ± 0.018 wt%

XRD results

Crystalline corundum Al_2O_3
No amorphous phase detectable due to sharp and intense peaks



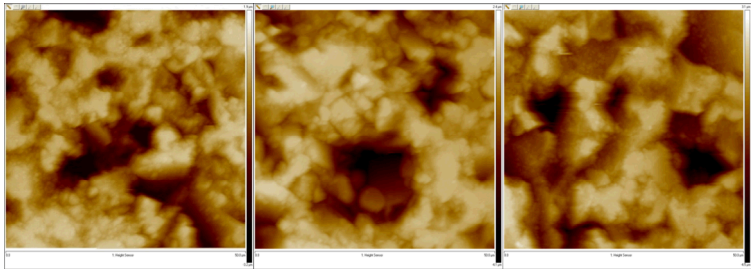


Alumina Comparison

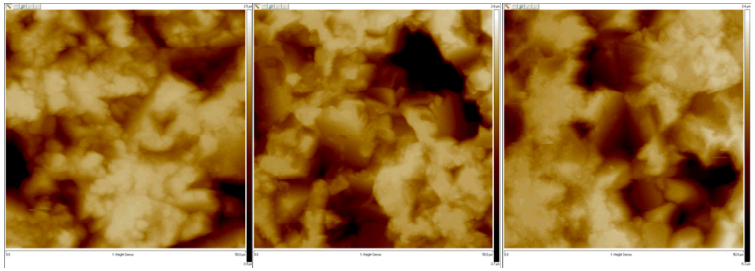
Differences in the alumina material are sometimes suggested, but the differences are not necessarily clear, nor do they necessarily relate to a known effect.

The alumina surface is rough. Various morphologies and degrees of roughness have been regarded with varying significance.

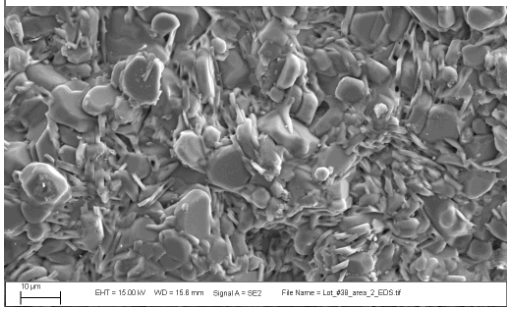
As-received Diamonite: roughness = 970 ± 180 nm



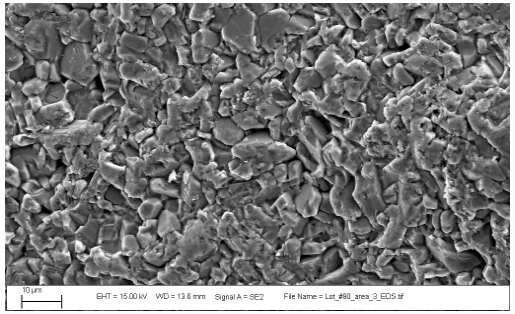
Brulin-cleaned Diamonite: roughness = 1080 ± 270 nm



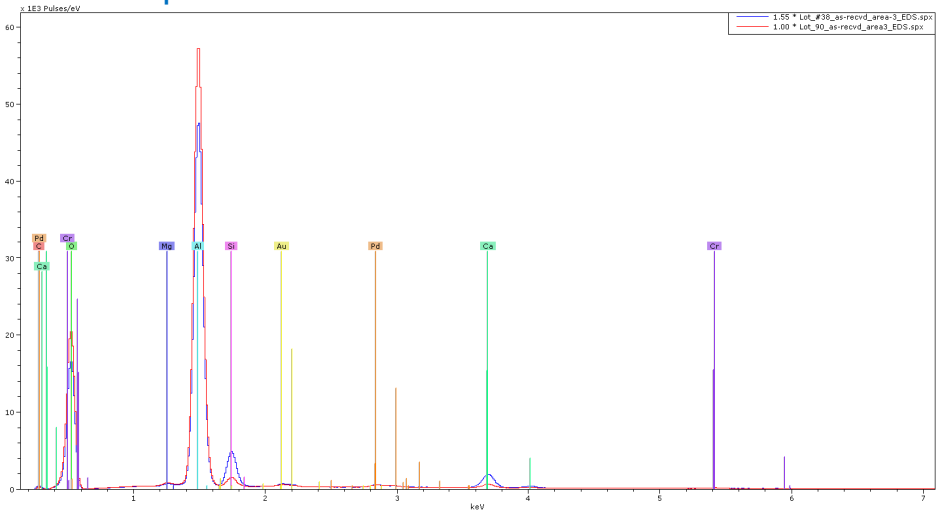
2005



2011



Substantial amounts of SEM/EDS characterization has been performed with limited definitive conclusions.



Cleaning Studies and Surface Chemistry

Alumina was used as the substrate (aluminum and alumina have yielded comparable results).
A number of cleaning solutions were tested.
Suspected contaminants were identified and simulated.

Contaminants

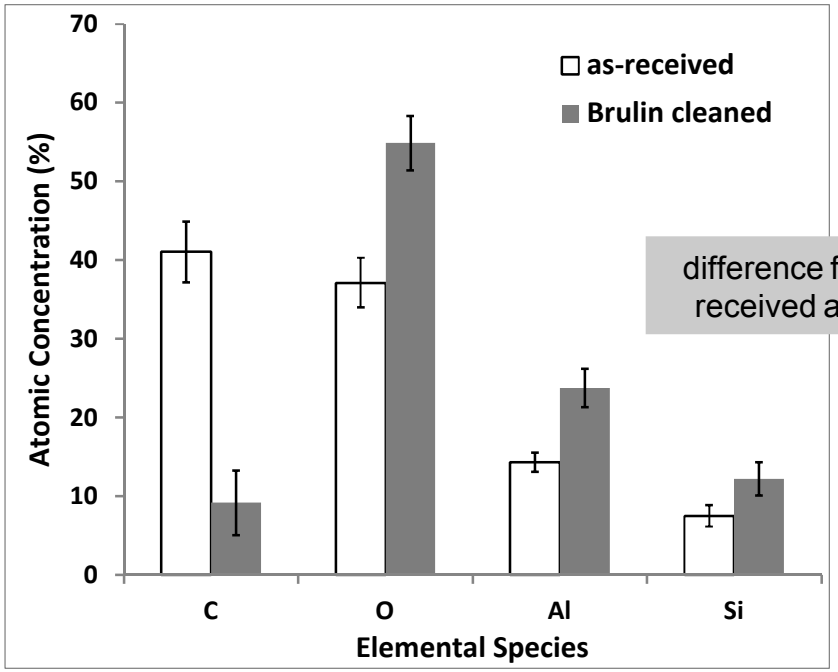
- Kester 185 Flux
- Epoxy Parfilm Ultra II Mold Release
- VWR MicroGrip 403010 Purple Nitrile gloves (poly-coated, powder-free) - ethyl alcohol exposure
- KimTech Pure G3 HC1370 Latex gloves from denatured ethyl alcohol exposure
- VWR White Nitrile (Certi-clean 40101) gloves from denatured ethyl alcohol exposure

Cleaning Solutions

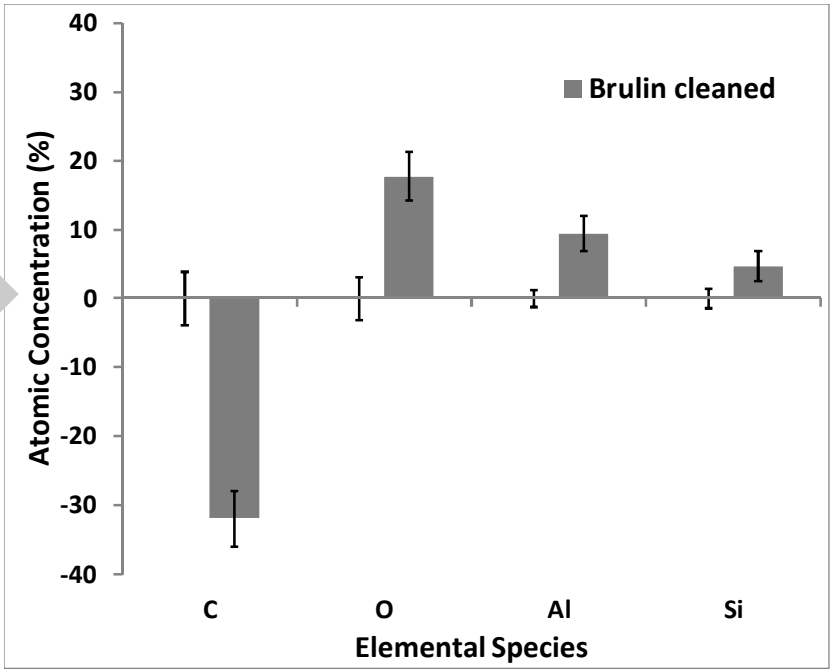
- ✓ **Brulin 815 GD, 10%** - Sodium tripolyphosphate <10%, pH=12, 1.08 g/cm^3
- ✓ **Kyzen Aquanox 4241, 20%** - 2-(2-aminoethoxy)ethanol 5-25%, pH=10.5-11.5, 0.9-1.0 g/cm^3
- ✓ **Dirl-Lum 603, 10%** - sodium metasilicate 30%, pH=12, pink powder
- ✓ **D-Limonene, 100%**, Cyclohexene (C10H16), citrus smell
- ✓ **Ethanol/Methanol,** 50/50
- ✓ **Ethanol,** denatured
- ✓ **Water,** deionized
- ✓ **KOH, H_2SO_4, NH_4OH, HCl**

Surface Carbon Content

Surface analysis gives clear chemical identifiers to evaluate the efficacy of cleaning.
The decrease in carbon after cleaning is the simplest way to evaluate the cleaning efficiency.



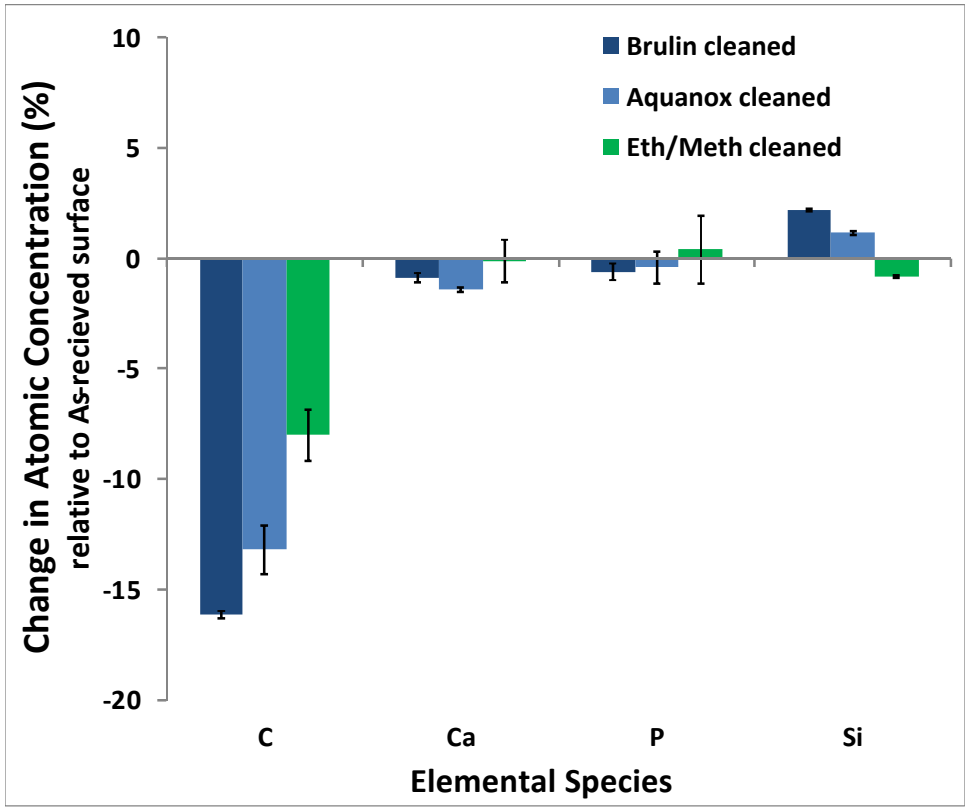
difference from as-received alumina

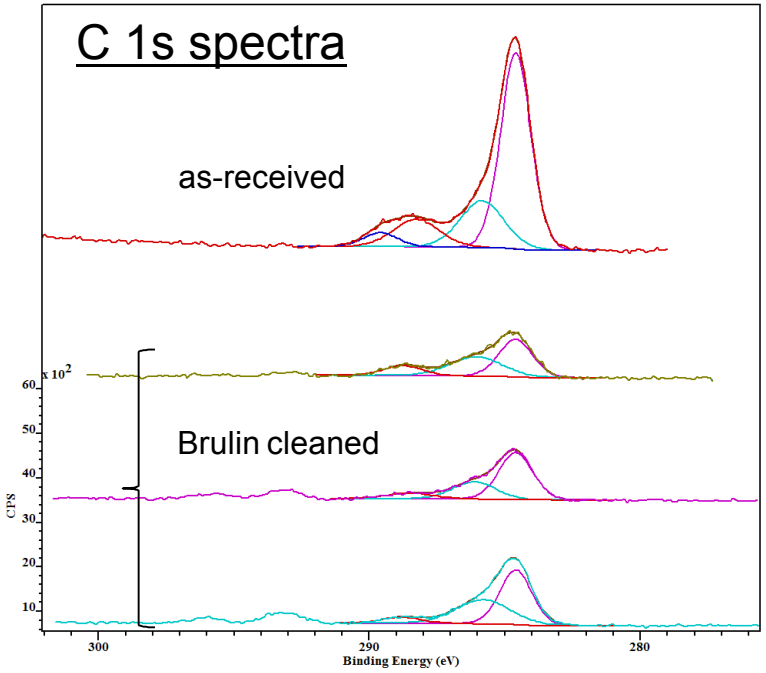


Brulin cleaning results in a significant decrease in carbon content at the surface (Auger results).

Comparison of Cleaners On Alumina

Brulin is the most effective cleaner at reducing carbon content from the surface of as-received alumina.



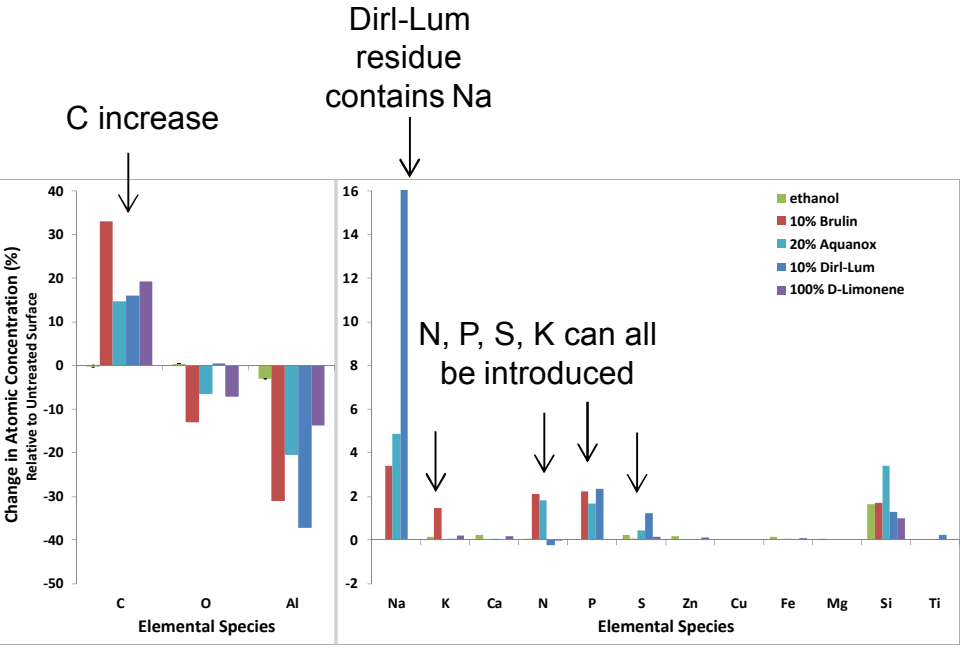


Observations:

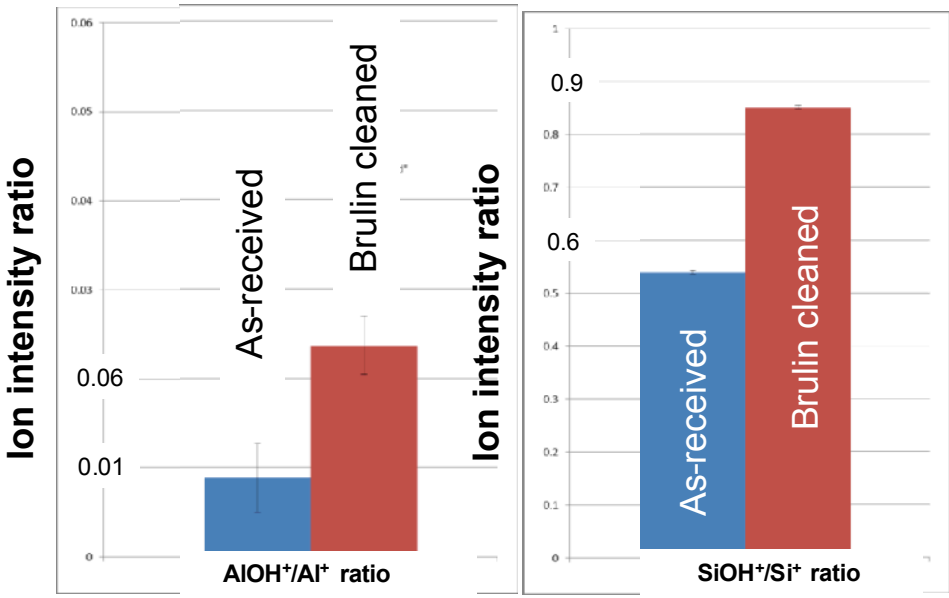
Ethanol/methanol is the least effective at removing carbon from the alumina surface.
Calcium concentration is decreased by Brulin and Aquanox.

Cleaner Residues – Not Rinsed

Cleaning solutions can leave residues.



Ion intensity ratios from ToF-SIMS suggest greater hydroxylation of the surface from Brulin cleaning.



Clean ethanol/methanol leaves no residue.

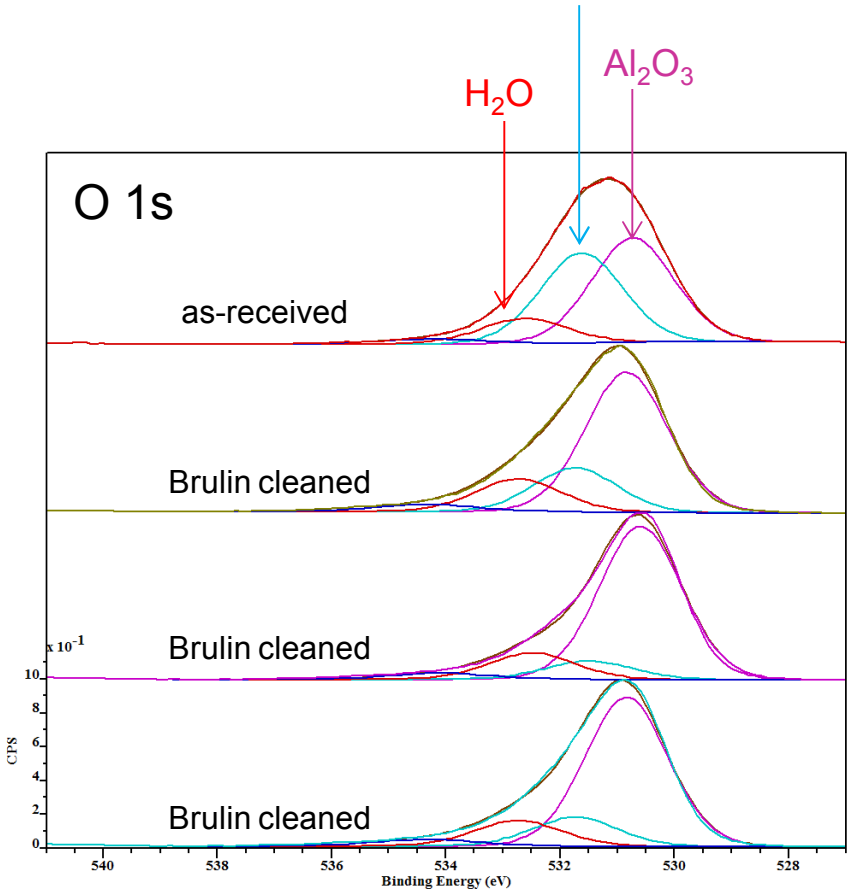
Ion intensities for Al^+, Si^+, K^+, $C_2H_3O^+$, $AlOH^+$, and amine-species increase after Brulin cleaning.

Ion intensities for Ca^+ decrease dramatically after Brulin cleaning.

Surface Hydroxylation?

Surface hydroxyls can be observed in XPS spectra, but the extent of hydroxylation from Brulin cleaning has yet to be determined.

Al-OH and C-O species



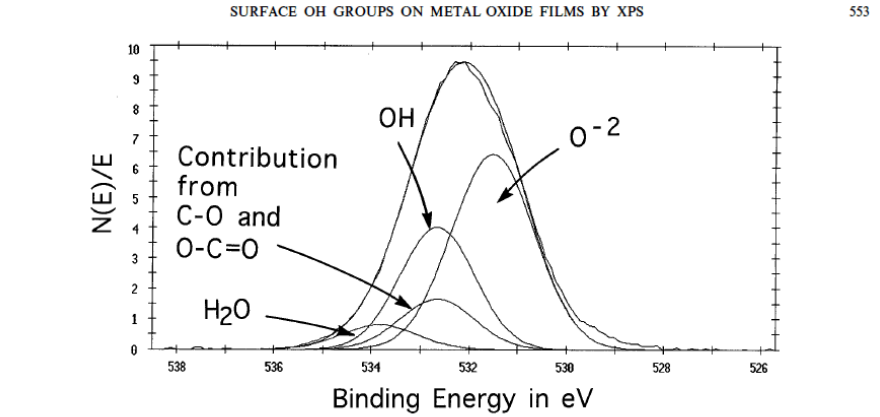
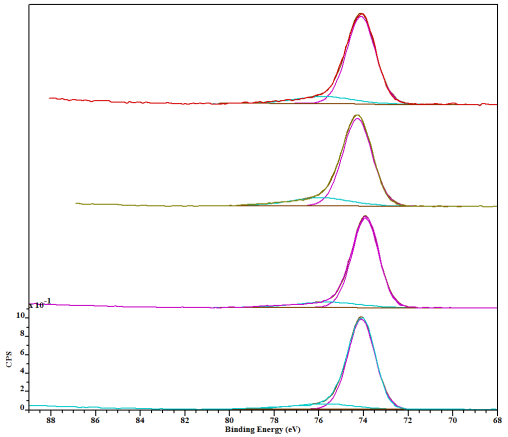


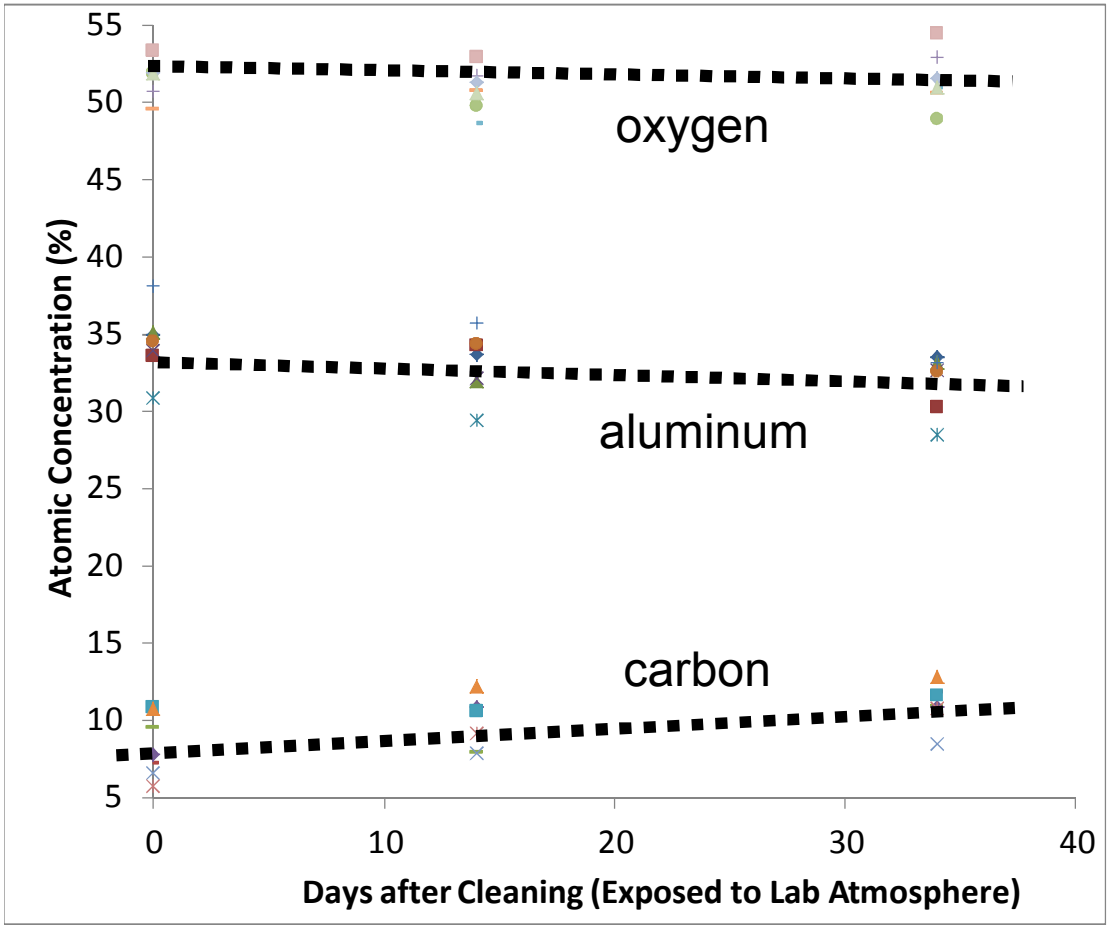
Figure 3. The XPS O 1s photopeak for an as-received aluminum sample, showing the O^{2-}, OH and H_2O components. This figure also shows the contributions to the OH subpeak from the oxygen in O–C groups and from the carbonyl oxygen in O–C=O groups residing in the organic carbon contamination layer, as is discussed later. The contributions from O–C and from the carbonyl oxygen in O–C=O are approximately equal in this case. The contribution to the H_2O peak from the ester oxygen in O–C=O (also discussed later) is ~10% of the H_2O peak and is not shown.

Al 2p cannot be used to identify hydroxylation.



Change in Surface Chemistry over Time

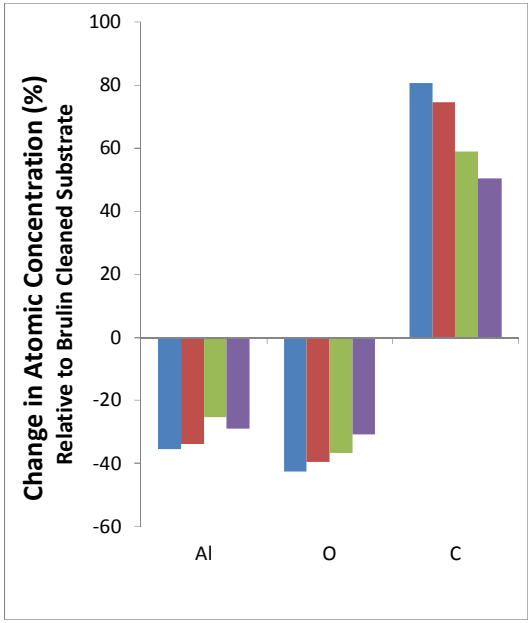
Carbon content generally increases as samples are exposed to ambient atmosphere.
This increase in carbon has been linked to a gradual decline in surface energy over time.

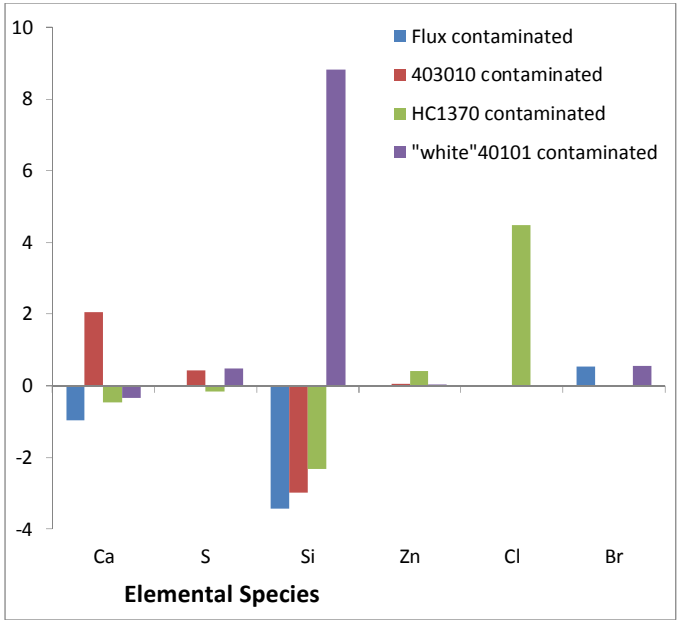


Simulated Contamination

Carbon levels are highly elevated by introducing specific contaminants on the surface.
The efficacy of various cleaners on these contaminants can be tested.
Subsequent plots will show difference in surface composition relative to contaminated surface.

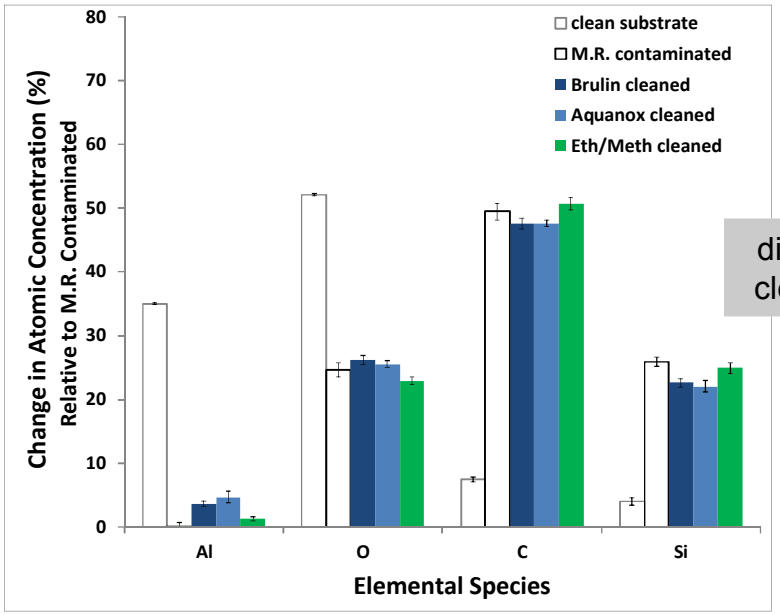
Introduced contaminant	Introduced contaminant						
Epoxy Parfilm Ultra II Mold Release	C			Si			
Kester 185 Flux	C						Br
403010 MicroGrip - Purple Nitrile gloves	C	Ca	S		Zn		
HC1370 KimTech - Latex gloves	C				Zn	Cl	
40101 - White Nitrile gloves	C		S	Si			Br





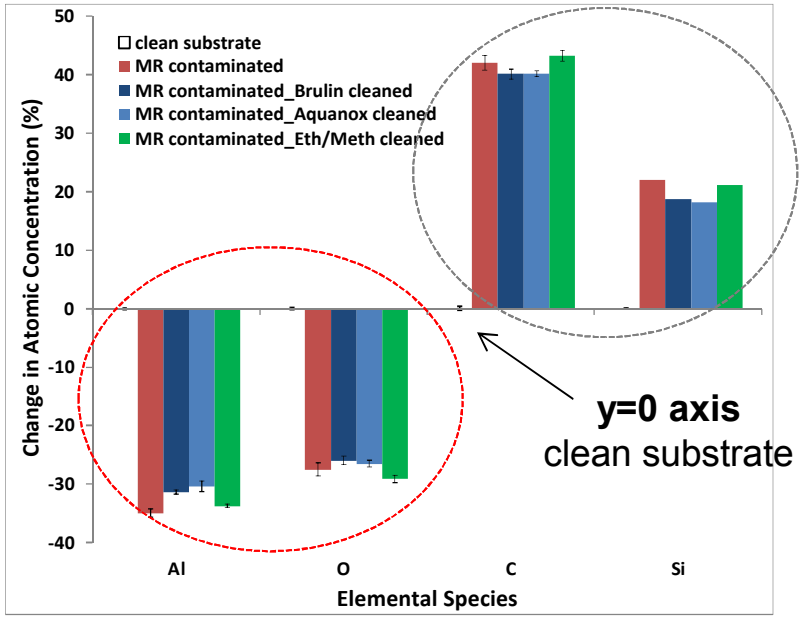
Mold Release Contamination

Cleaners are relatively ineffective at removing silicone mold release from the surface.



difference from clean substrate

Positive values → contaminants

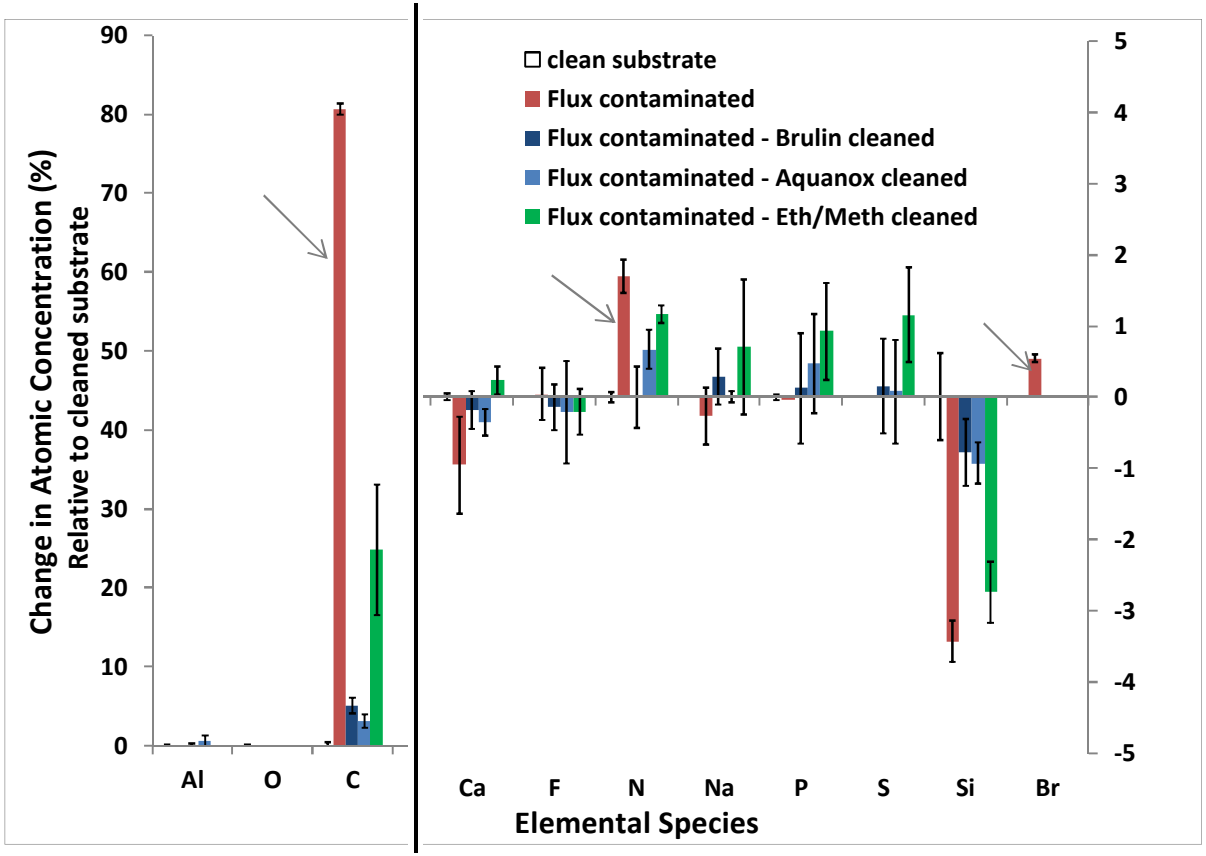


Introduced contaminant	Brulin	Aquanox	Ethanol/ Methanol
C			
Si	2nd	1st	

alues → reduction in tensities by overlying ntaminants

Flux Contamination

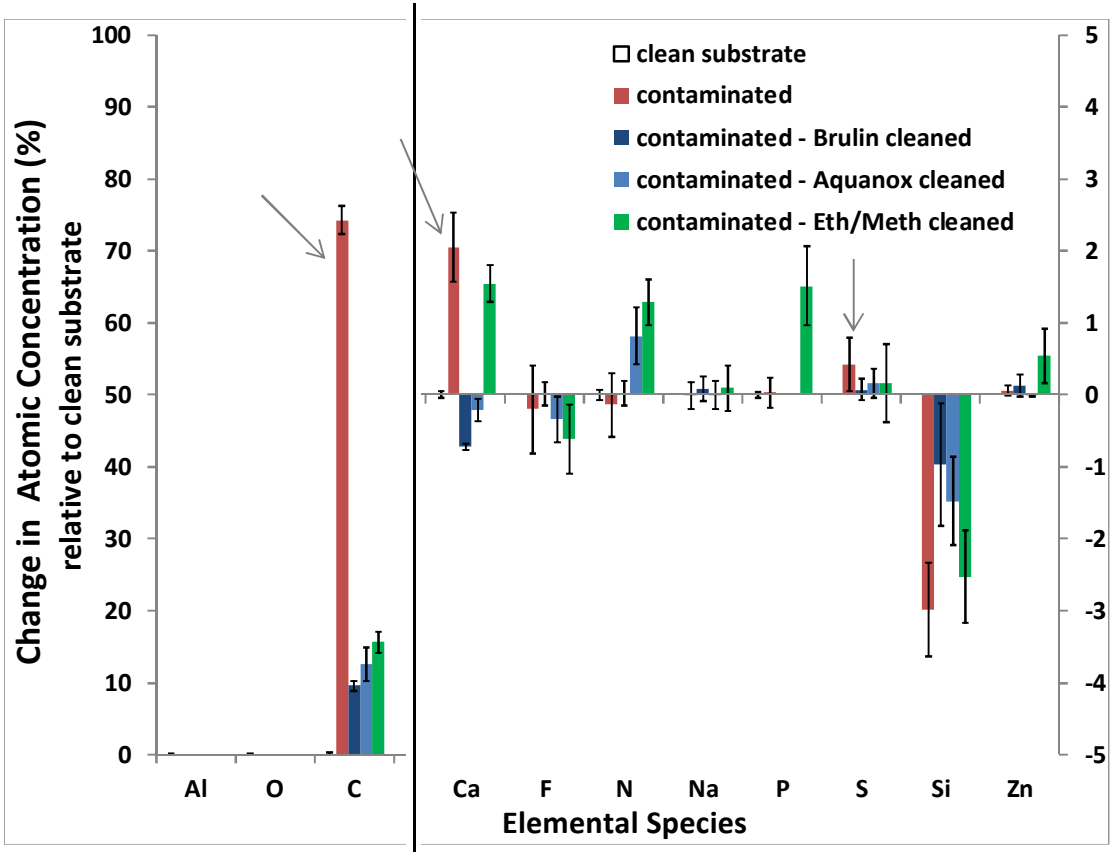
Ethanol/Methanol is the least effective at removing Flux from the surface.



Introduced contaminant	Brulin	Aquanox	Ethanol/ Methanol	Introduced by Ethanol/Methanol
C	2nd	1st	3rd	Ca, Na
N	1st	2nd	3rd	P, S
Br				

Purple Nitrile Glove Residue

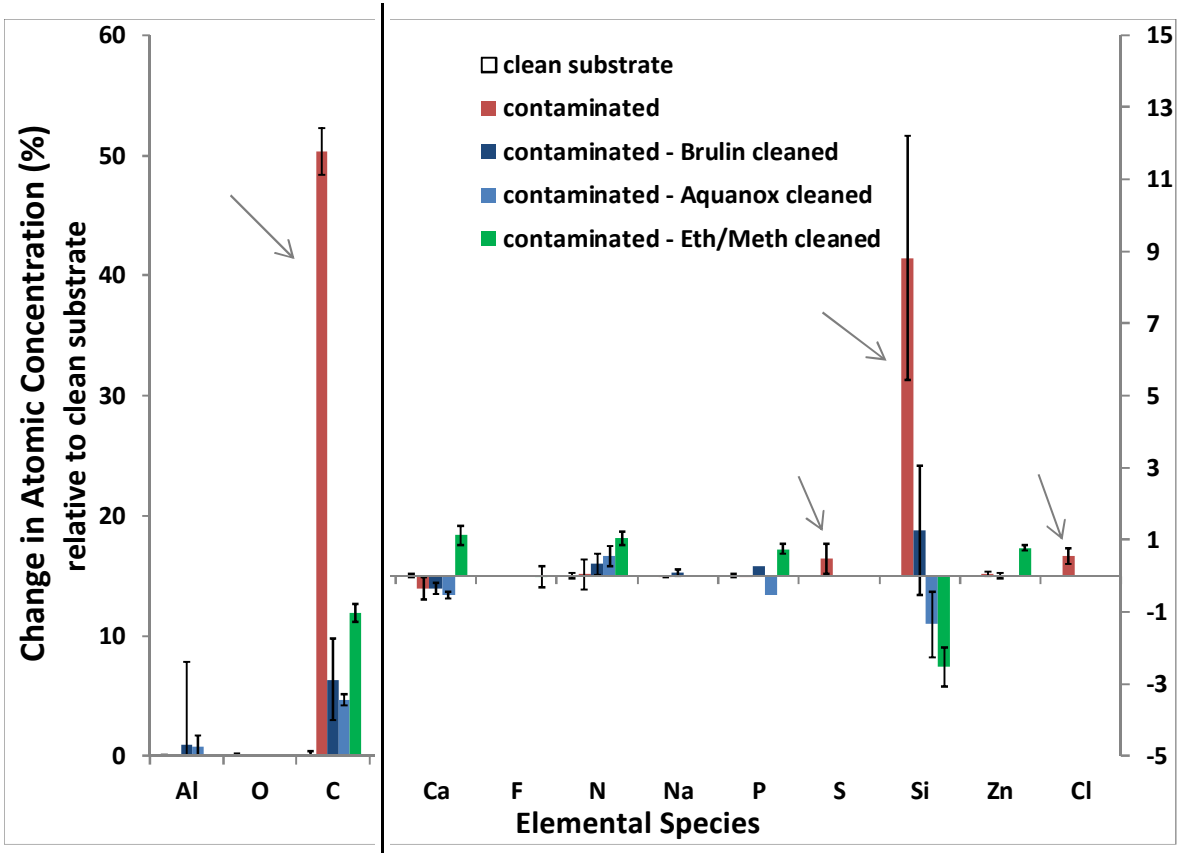
Brulin is most effective at removing nitrile glove residue from the surface.



Introduced contaminant	Brulin	Aquanox	Ethanol/ Methanol	Introduced by Ethanol/Methanol
C	1st	2nd	3rd	Ca ?
S	1st	2nd	3rd	P, N
Ca	1st ?	2nd ?		Zn

White Nitrile Glove Residue

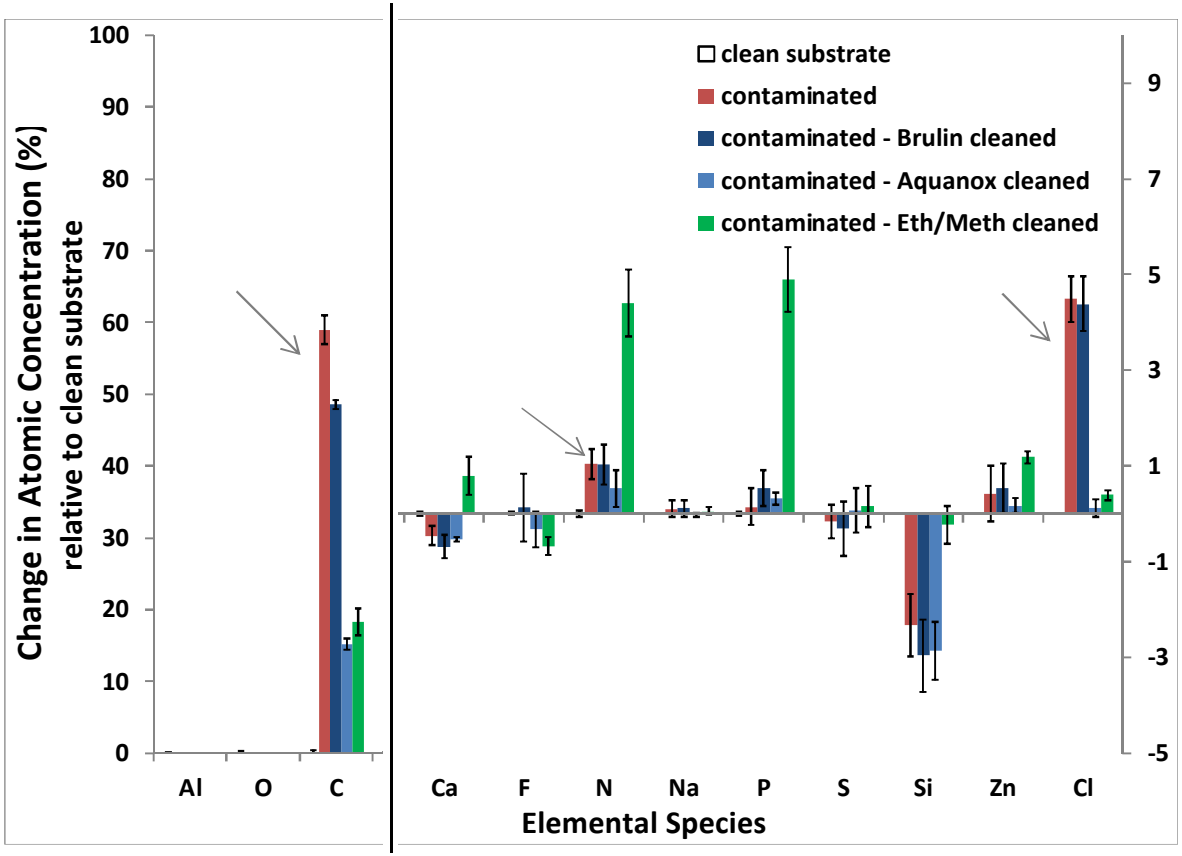
Brulin and Aquanox are effective at removing glove residue from the surface.



Introduced contaminant	Brulin	Aquanox	Ethanol/ Methanol	Introduced by Ethanol/Methanol
C	2nd	1st	3rd	Ca ?
S, Cl				P, N
Si		?	?	Zn

HC1370 Latex Glove Residue

Brulin is the least effective at removing HC1370 latex glove residue from the surface.



Introduced contaminant	Brulin	Aquanox	Ethanol/ Methanol	Introduced by Ethanol/Methanol
C		1st	2nd	Ca ?
Cl		1st	2nd	P, N
N		1st		Zn

Conclusions

- Understanding the surface composition of alumina is still an on-going effort. It is not clear how the changes in the surface affect observed properties and interactions with other materials.

- Cleaning has played an important role in solving many issues related to alumina. Cleaning has many impacts on surface compositions:
  - Reduces carbon and calcium, and increases surface energy.
  - Does not change morphology.
  - Unknown effect on glassy phase and hydroxylation.

  - Brulin is an effective cleaner for most contaminants.
  - Aquanox is also very effective.
  - Ethanol/methanol is the least effective. For some contaminants ethanol/methanol has no effect.

- Cleaning procedures usually involve multiple stages with different cleaning solutions.
- *Most* suspected contaminants can be expected to be removed.

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