

# OZONE PROCESSING

Reducing field emission in superconducting cavities with ozone

JLab Seminar 6 March 2025

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# Ozone

- **Ozone, or trioxygen  $O_3$ , is a powerful oxidant**

- colourless or pale blue gas, slightly soluble in water
- distinctive pungent smell

- <https://en.wikipedia.org/wiki/Ozone>

- **$O_3$  is formed from  $O_2$  by ultra-violet (UV) light or electric discharge**

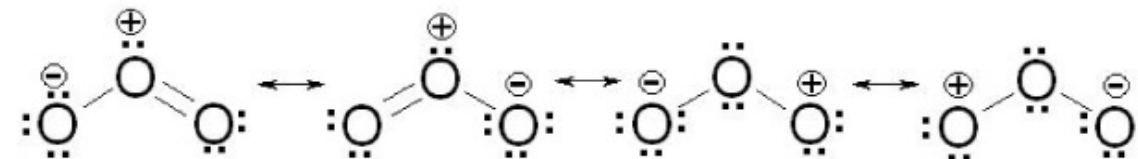
- ozone production at 185 nm
- ozone break down at 254 nm
- much less stable than the diatomic  $O_2$ 
  - half-life varies with environmental conditions
  - ~25 h at room temperature, zero humidity
  - ~3 h at 80 °C

- **a potent respiratory hazard**

- lethal dose ~50 ppm over 30 minutes

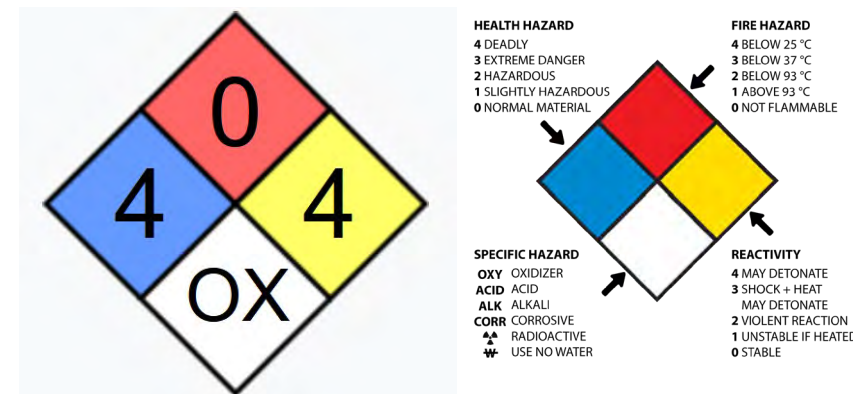
- **Widely used** for

- water treatment and food processing
- semiconductor industry



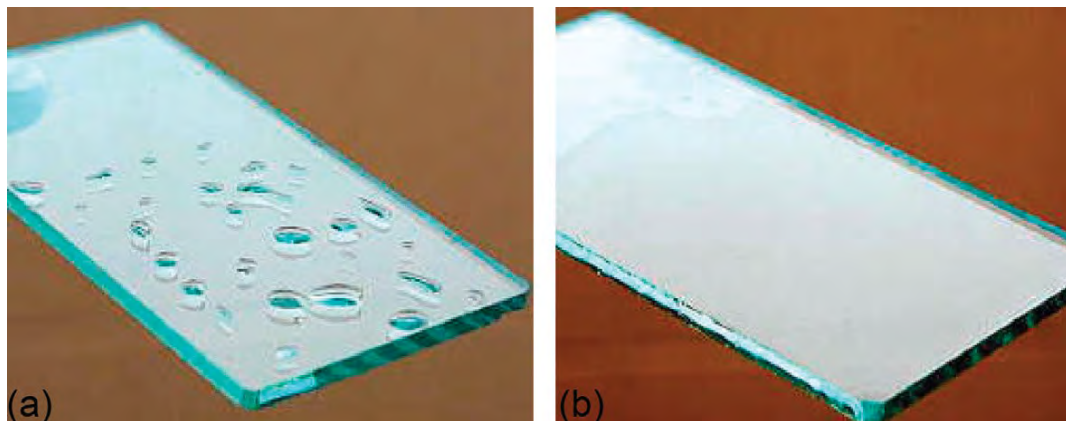
D. Klausson, Physical and Chemical Properties of Ozone, UNESCO-EOLSS E6-192-03

Ozone resonance structures



# Ozone Cleaning

- **Well-established technique** to use ozone for removing biological material, hydrocarbons
- **UV/ozone cleaning of surfaces** mentioned in the 1970's
  - using UV radiation in air or low-pressure oxygen (<mTorr)
  - R.R. Sowell et al., *Surface cleaning by ultraviolet radiation*, J. Vac. Sci. Technol. 11, 474 (1974)
  - during cleaning, the partial pressure of O<sub>2</sub> decreased, while that of CO<sub>2</sub> and H<sub>2</sub>O increased.
  - UV also desorbed gases from the vacuum chamber walls
    - J. Vig, *UV/ozone cleaning of surfaces*, J. Vac. Sci. Technol. A3, 1027 (1985)
- **Ozonized water cleaning** used in semiconductor industry since 1990's
  - remove organic impurities from the wafer surface, 1–2 ppm O<sub>3</sub> concentration
    - T. Ohmi et al., *Native oxide growth and organic impurity removal on Si surface with ozone-injected ultrapure water*, J. Electrochem. Soc. 140, 804 (1993)

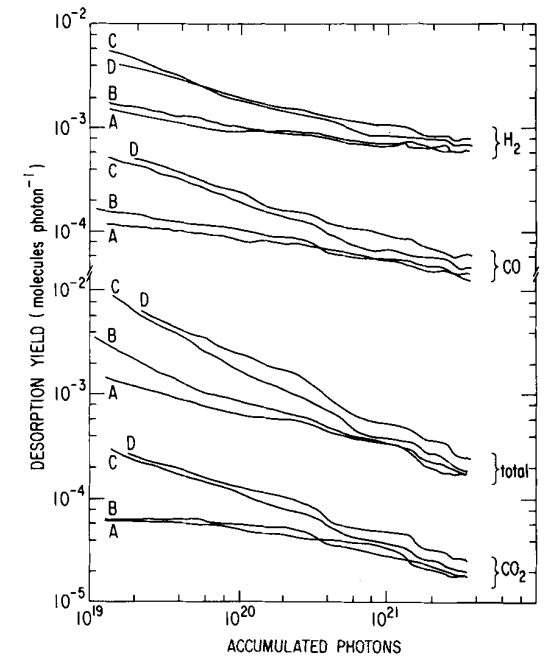


Glass plate before (a) and after (b) UV-ozone cleaning for 1 min. No water beads on cleaned surface.

R. Kohli, *UV-Ozone Cleaning for Removal of Surface Contaminants*, In *Developments in Surface Contamination and Cleaning*, Vol. 8 (2015).

# Vacuum System Cleaning with Ozone

- **Bake out** at elevated temperatures  $>300\text{ }^{\circ}\text{C}$  was the first method
  - however often not possible in situ
- Ion bombardment cleaning in **glow discharge** (GDC),
  - using argon or  $\text{Ar}/10\%\text{O}_2$  mixture
    - R.S. Calder, *Ion induced gas desorption problems in the ISR*, Vacuum 24, 437 (1974).
    - H. Hseuh et al., *Glow discharge cleaning of stainless steel accelerator beam tubes*, J. Vac. Sci. Technol. A3, 518 (1985).
- **Nitric oxide** (NO), abandoned due to safety concerns
  - H. Hseuh and X. Cui, *Outgassing and desorption of the stainless-steel beam tubes after different degassing treatments*, J. Vac. Sci. Technol. A7, 2418 (1989)
- **Ozone**
  - used at Brookhaven Nat. Lab for NSLS-2
    - H. Hseuh, private communication; K. Wilson, private communication.
- **Ozonized water**
  - cleaning of vacuum chambers for Taiwan Photon Source
    - C. Chan et al., *Cleaning of aluminium alloy chambers with ozonized water*, J. Phys. Conf. Ser. 100, 092025 (2008)



A: chemical, vacuum fired, GDC;  
B: chemical, vacuum fired, NO;  
C: chemical, vacuum fired;  
D: chemical cleaned.

H. Hseuh and X. Cui, *Outgassing and desorption of the stainless-steel beam tubes after different degassing treatments*, J. Vac. Sci. Technol. A7, 2418 (1989).



# H<sub>2</sub>O<sub>2</sub> and Ozonized Water Cleaning at KEK

- Mid 1990's, Asano et al. at KEK **copy technique from semiconductor industry**
  - experimenting first with H<sub>2</sub>O<sub>2</sub> later also test O<sub>3</sub> rinsing
- Superconducting niobium single cell 508 MHz for KEK-B, electro-polished
  - **rinse with H<sub>2</sub>O<sub>2</sub> or ozonized water**: fill cavity and empty after 10, 20 or 30 minutes
  - **observed reduced field emission and improved accelerating gradient**
  - O<sub>3</sub> rinsing has stronger effect than H<sub>2</sub>O<sub>2</sub> rinsing

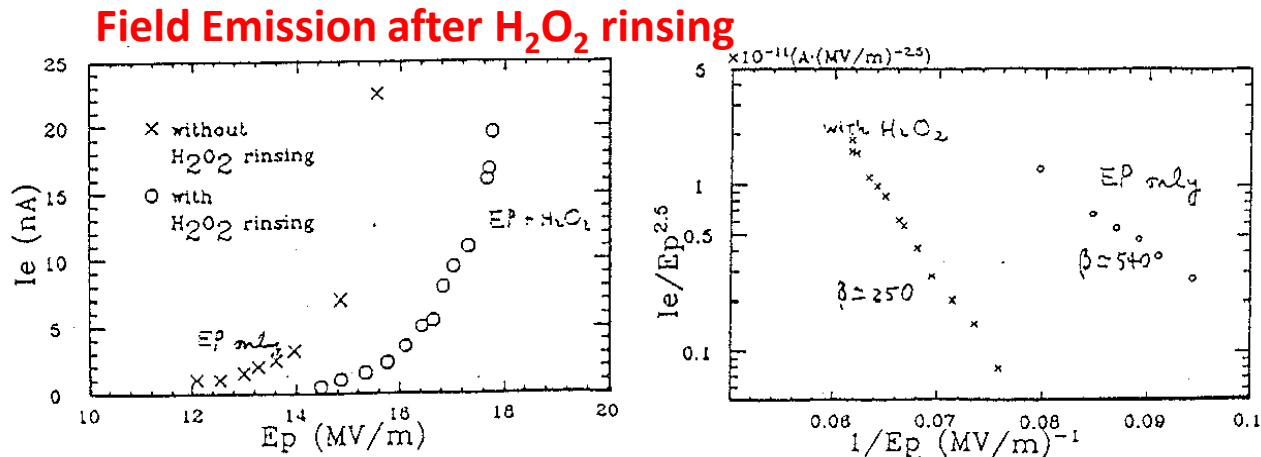


Fig.3 Field emissions for 508 MHz single cell Nb cavities with and without H<sub>2</sub>O<sub>2</sub> rinsing after EP.

K. Asano, *Ozonized Ultrapure Water Treatment of Nb Surfaces for Superconducting RF Cavities*, KEK Preprint 93-216 (1993).

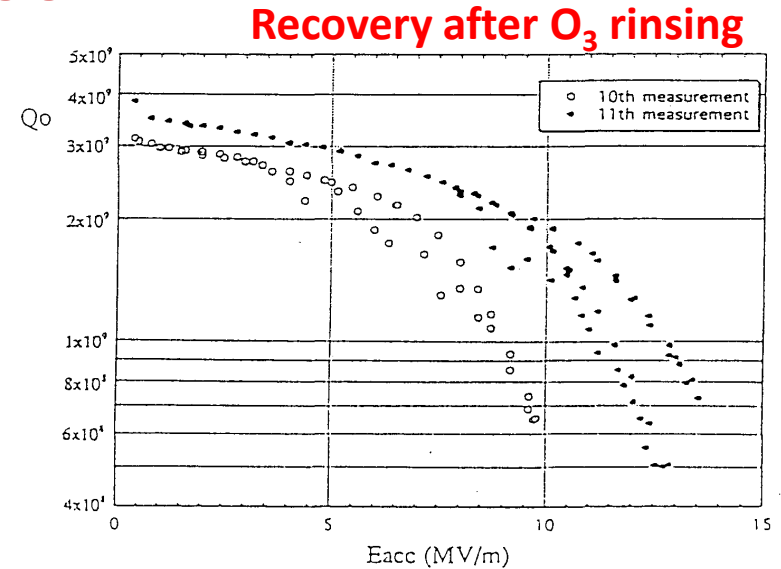


Fig. 4 Performance recovery of the 508 MHz Nb cavity with Cu plated SUS extended beam pipes, SUS flanges sealed by In ribbons and Al<sub>2</sub>O<sub>3</sub> ceramics. 10th and 11th measurements show before and after ozonized ultrapure water rinsing, respectively.

K. Asano et al., *Stable Performance of 508 MHz Superconducting RF Cavities for KEKB*, Proc. 1995 Workshop on SRF (1995) 419.

# Surface Characteristics Measurements at KEK (1/2)

After ozonized water rinsing

- Superconducting niobium cavity
  - **The carbon contamination on the electropolished Nb surfaces, ... , was removed completely by this ozone treatment**
- Aluminium and copper samples
  - The ozonized surface was exposed to synchrotron radiation with a critical energy ( $e_c$ ) of 26 keV.
    - **photo-desorption coefficient was two orders of magnitude lower than non-treated and oxygen-plasma treated samples**
    - suggests low desorption coefficient of the ozonized surface.

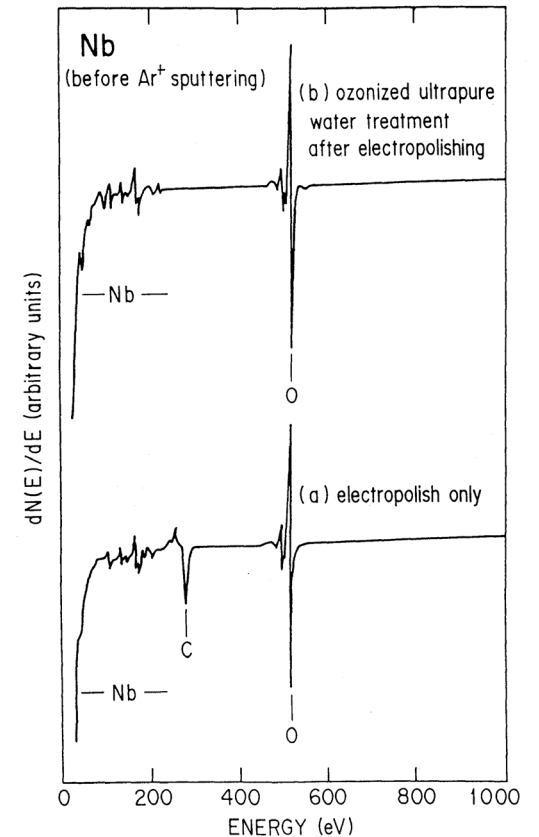
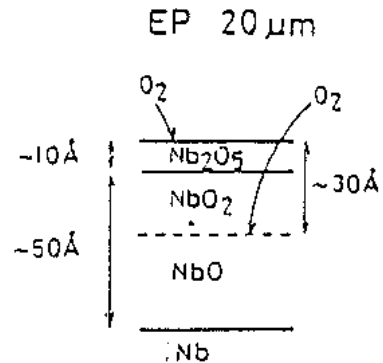


Fig. 5 Auger spectrum of Nb surfaces (a) electropolish only (b) ozonized ultrapure water treatment after electropolishing .

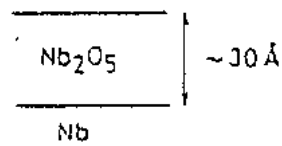
S. Mitsunobu et al., *Activities of Superconducting Cavity for KEK-B Factory*, Proc. SRF (1993) J05.  
T. Momose et al., *Surface characteristics of aluminium and of several metals from view point to reduce dynamic gas desorption*, Vacuum 47(4) (1996) 319.  
N. Ota et al., *Reduction of photodesorption yield by oxygen discharge cleaning*, J. Vac. Sci. Technol. A12(3) (1994) 826.

# Surface Characteristics Measurements at KEK (2/2)



Additional adsorptions are detected to about 30 Å after exposing to the air for 24 hours at room temperature.

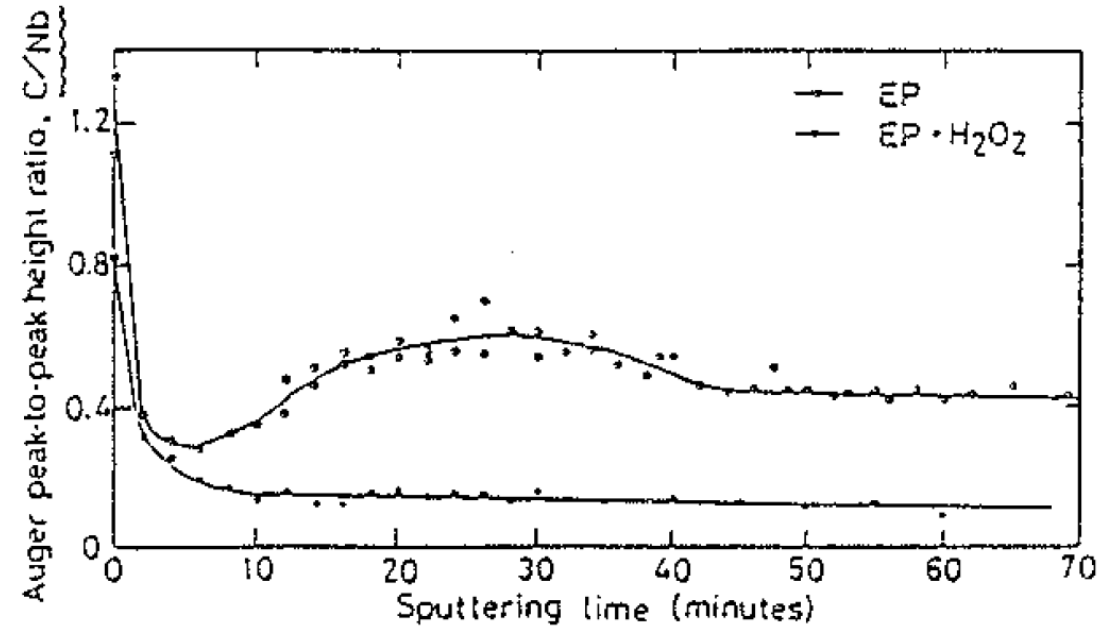
EP 20  $\mu\text{m}$  + H<sub>2</sub>O<sub>2</sub> rinsing



A stable and dense Nb<sub>2</sub>O<sub>5</sub> layer of about 30 Å is formed by H<sub>2</sub>O<sub>2</sub> rinsing after electropolishing.

Nb oxide layers for electropolished (left) and electropolished plus H<sub>2</sub>O<sub>2</sub> rinsed (right) niobium, identified by XPS spectra.

*K. Asano, Ozonized Ultrapure Water Treatment of Nb Surfaces for Superconducting RF Cavities, KEK Preprint 93-216 (1994).*



Auger peak height ratios for C/Nb as function of sputtering time ( $\sim 1 \text{ \AA}/\text{min}$ ) for Nb surface with and without H<sub>2</sub>O<sub>2</sub> rinsing after EP.

*K. Asano, Ozonized Ultrapure Water Treatment of Nb Surfaces for Superconducting RF Cavities, KEK Preprint 93-216 (1994).*

*K. Asano, Ozonized Ultrapure Water Treatment of Nb Surfaces for Superconducting RF Cavities, KEK Preprint 93-216 (1994).*

# Air Exposure after Ozonized Rinse at KEK

- Asano et al. report **relatively stable performance after ozonized water rinsing and subsequent exposure to air**
- Successfully applied to 508 MHz KEK-B niobium cavities
  - 3 ppm ozone in water at 5 l/min for 20 min
  - O<sub>3</sub> rinsing has stronger and cleaner effect than H<sub>2</sub>O<sub>2</sub> rinsing
  - **cavity performance was not degraded by air exposure for 4 days**
    - attributed to formation of a stable and clean Nb<sub>2</sub>O<sub>5</sub> layer
    - Nb<sub>2</sub>O<sub>5</sub> formed acts passively and is not able to absorb water or hydrocarbons

## Q<sub>0</sub> vs. E<sub>acc</sub> after air exposure

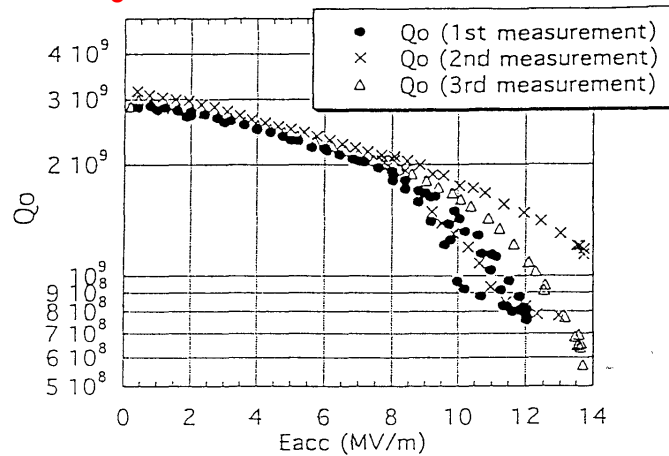


Fig. 1 Stable performance of the 508 MHz Nb cavity rinsed by ozonized ultrapure water. The 2nd and 3rd tests were measured after 1 atm air exposures for 23 hours and 69 hours, respectively.

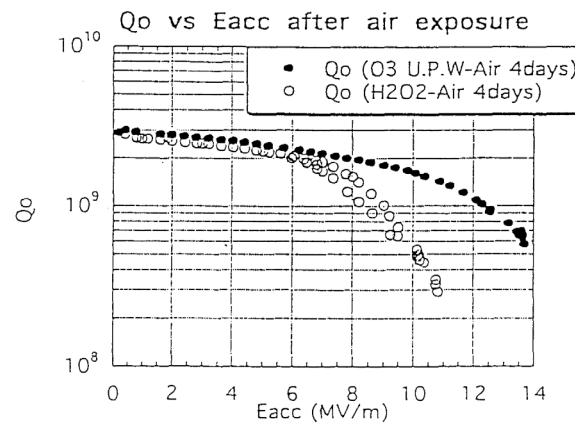


Fig. 2 The comparison of the effect of air exposures on cavity performance rinsed by ozonized water and H<sub>2</sub>O<sub>2</sub>. The clean and stable oxide layers on Nb surfaces formed by ozonized water can keep the cavity performance after air exposures.

Table] The comparison of weak superconductors (NbO<sub>x</sub>+NbO<sub>2</sub>) and hydrides of Nb for ozonized ultrapure water rinsed and H<sub>2</sub>O<sub>2</sub> rinsed Nb surfaces after electropolishing

	NbO <sub>x</sub> Nb + NbO <sub>x</sub>	Nb(OH) <sub>x</sub> Nb <sub>x</sub> O <sub>y</sub> + Nb(OH) <sub>x</sub>
EP + O <sub>3</sub>	0.9 %	24 %
EP + H <sub>2</sub> O <sub>2</sub>	4.0 %	53 %

K. Asano et al., *Stable Performance of 508 MHz Superconducting RF Cavities for KEKB*, Proc. 1995 Workshop on SRF (1995) 419.

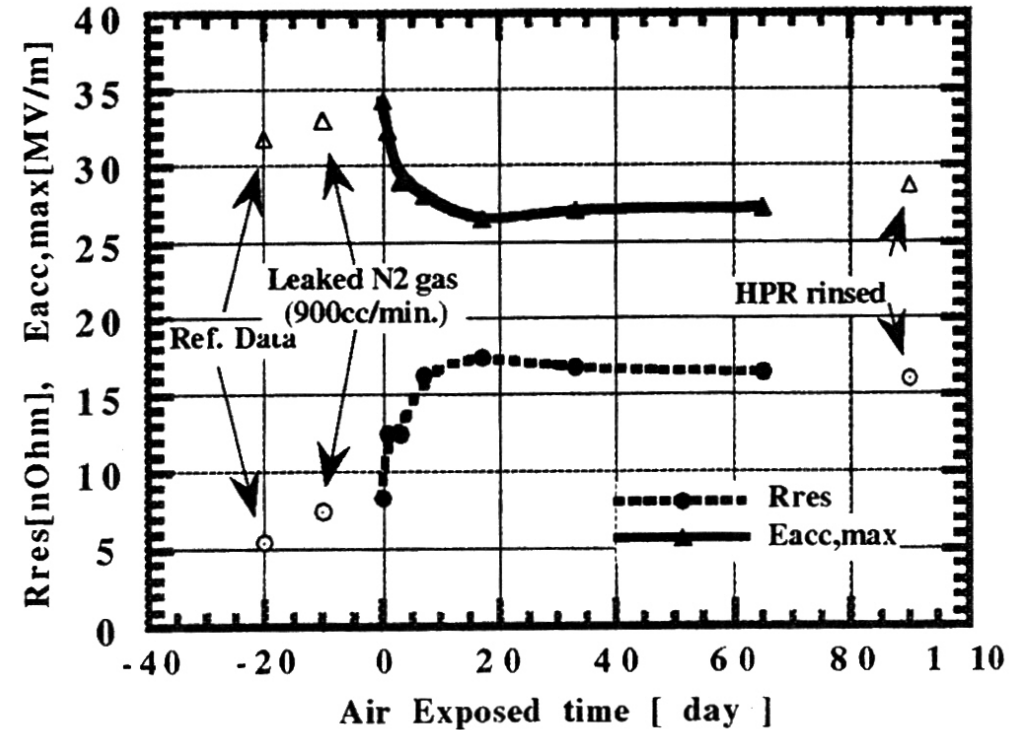


# Long Term Air Exposure Experiments at KEK

- 1.3 GHz single-cell cavity with electro-polished surface
  - RRR= 200, niobium bulk cavity
  - electro-polishing removed 30  $\mu\text{m}$
  - high-pressure rinse (HPR)
  - after baseline, vent through 0.01  $\mu\text{m}$  filter
- Air exposure up to 65 days

## • Conclusions

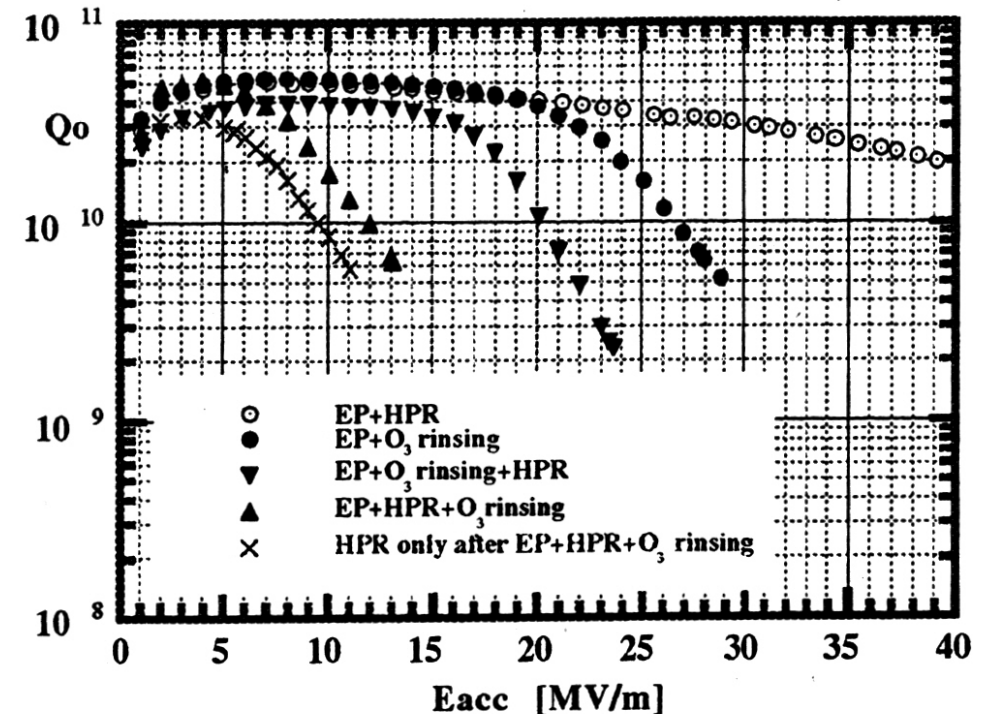
- $R_{\text{res}}$  increased  $\sim 10$  n $\Omega$  in 1 week
  - acceptable effect for Tristan 508 MHz cavity operated at 4.2 K
  - comparable or larger than  $R_{\text{BCS}}$  for cavity operated at 2 K
- Air exposure increases multipacting and limits high gradient



K. Saito, Long Term Air Exposure Effect on the Electropolished Surface of Niobium Superconducting RF Cavity, Proc. 1999 Workshop on RF Superc. (1999) 270.

# Ozonized Water Rinsing at KEK

- **Fails on high-gradient 1300 MHz single cell cavity**
  - electro-polished (EP) and high-pressure rinsed (HPR)
  - ozone ( $O_3$ ) rinsing
  - multipacting around 15 MV/m
  - field emission onset around 18 MV/m
- Method abolished
  - kept for cleaning power couplers, overflow with ozonized water for 5 minutes
- Built prototype system to produce clean ozone ice
  - can reach 150 ppm ozone in water
  - idea to use for in-situ cleaning of vacuum systems



K. Saito, *Recent Developments in SRF Cavity Cleaning Techniques at KEK*, Proc. 1999 Workshop on RF Superc. (1999) 118.

# Why try again?



# Why Not!

## Ozonized water and in situ ozone cleaning

- **Simple**
  - any shape or volume, if materials are ozone resistant
- **Cost effective**
  - no RF required
- Ozone effect seems very similar to plasma processing with oxygen mix

# In Situ Ozone Decomposition Rate

- Ozone concentration and life time depends on
  - ozone molecule diffusion in gas
  - ozone molecule collision with surface

- Ozone loss rates

- at surface

$$\frac{1}{\tau_s} = \frac{D_e}{p_0} \left\{ \left( \frac{\nu_1}{a} \right)^2 + \left( \frac{q_1}{L} \right)^2 \right\}$$

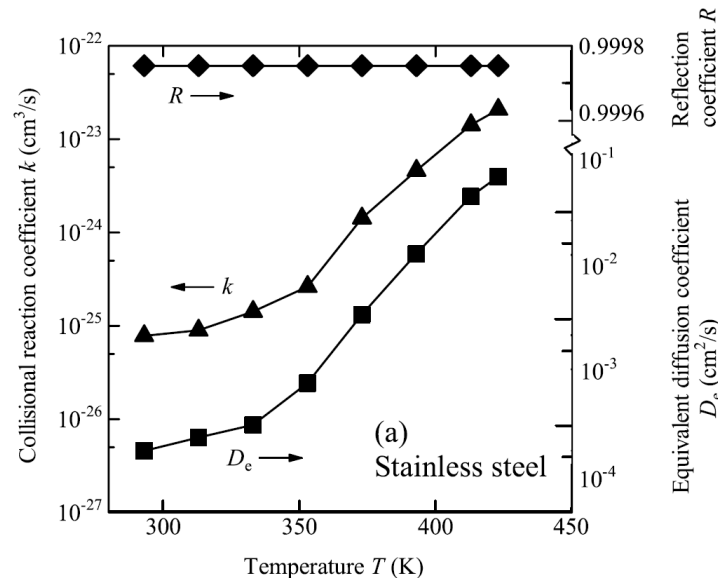
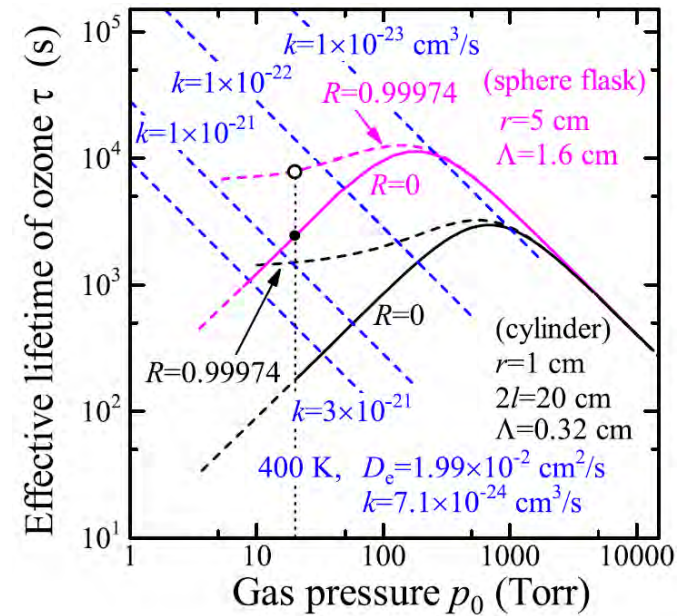
- in gas phase

$$\frac{1}{\tau_g} = G = kNp_0$$

- S. Suzuki et al., *Re-evaluation of rate coefficients for ozone decomposition by oxygen*, J. Phys. D: Appl.Phys.51 (2018) 305201.

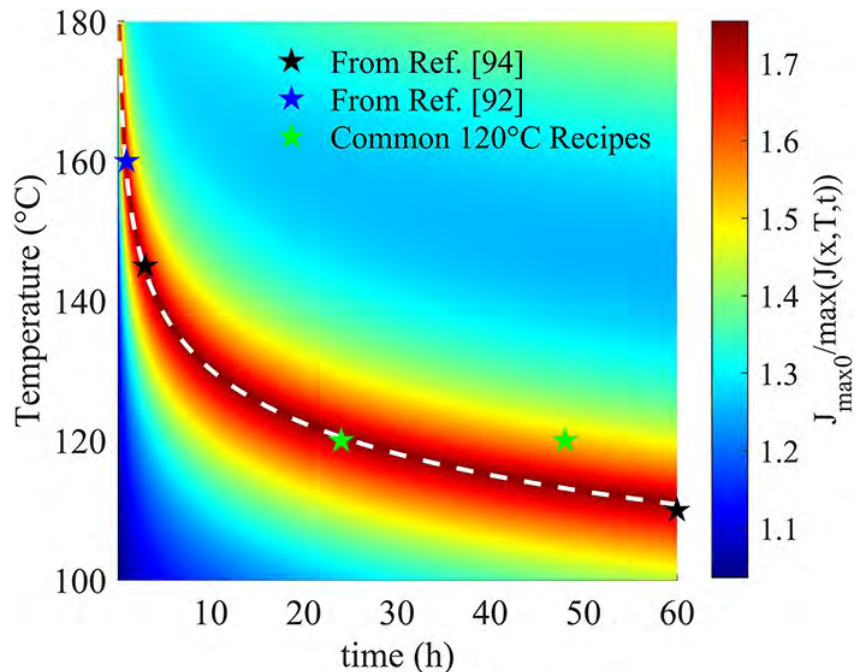
Effective lifetime curves in spherical (pink) and cylindrical (black) cell at 400 K.

S. Suzuki et al., J. Phys. D: Appl.Phys.51 (2018) 305201.

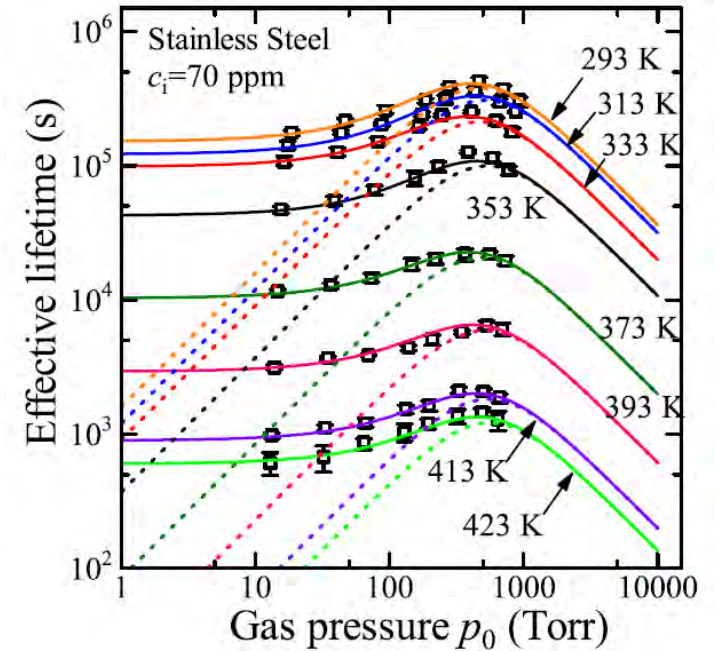


# Elevated Temperature Processing

- around 80 °C (176 F) or 353 K
- increases ozone reactivity
- increases hydrocarbon vapour pressure
- low enough to not affect cavity performance via so-called low-temperature bake
  - oxygen diffusion into the RF penetration layer



Colourmap showing the existence of a ridge of optimal baking times and temperatures to reduce the peak supercurrent compared to the clean case. The white dashed line follows the path of minimized peak supercurrent density.  
E. Lechner *et al.*, *J. Appl. Phys.* **135**, 133902 (2024).



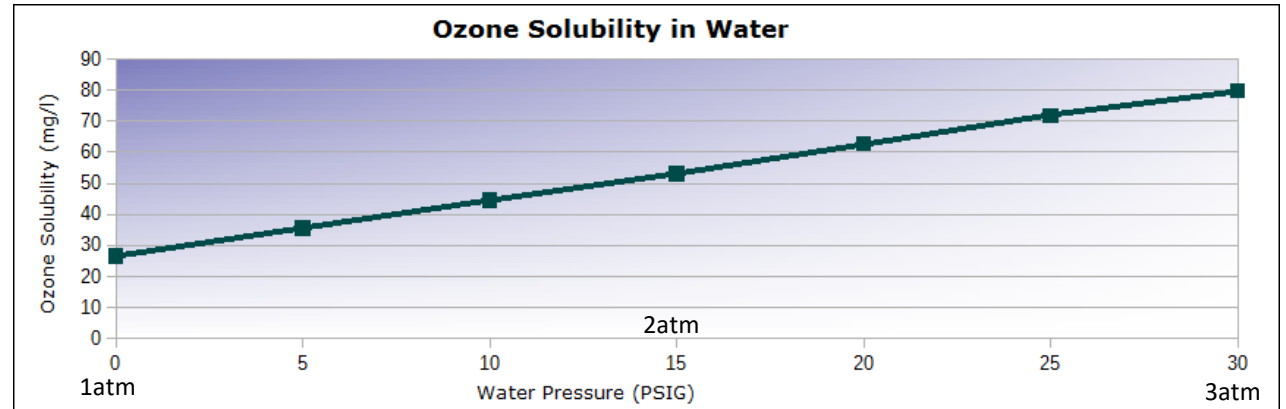
Observed effective lifetime of ozone in cell plotted against gas pressure for cell of stainless steel.  $c_i$  is the initial concentration of ozone. (Cell length  $2L = 200$  mm, inner diameter  $2a = 24$  mm)  
S. Suzuki *et al.*, *J. Phys. D: Appl. Phys.* **51** (2018) [305201](#).

# Ozone Solubility in Water

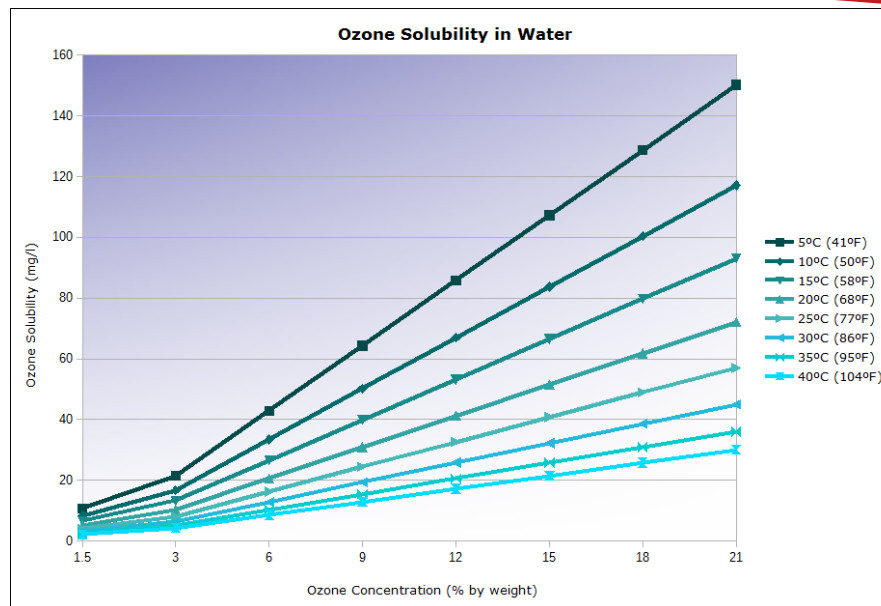
- **Ozone solubility** depends on
  - water temperature;
  - ozone concentration;
  - water pressure.

- **Solubility**

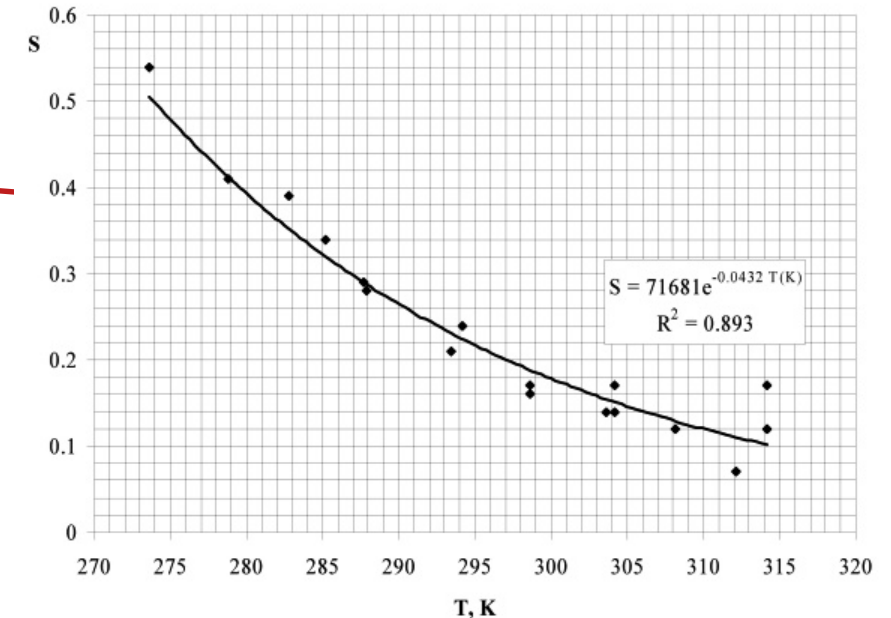
- $C_{liquid} (mg/l) = \rho_{gas} (g/m^3) \cdot S \cdot P (atm)$
- solubility ratio  $S = 71681e^{-0.0432 \cdot T(K)}$



T (°C)	S
0	0.64
10	0.39
20	0.24
30	0.15
40	0.10
50	0.06

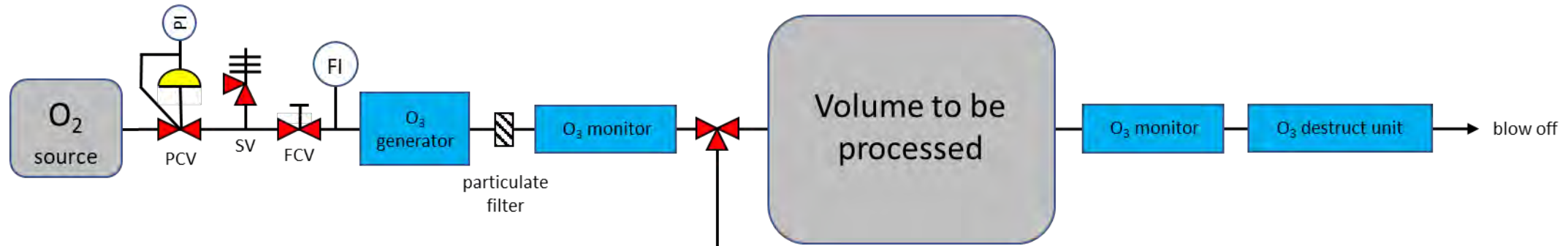


<https://www.oxidationtech.com/ozone/ozone-basics/fundamentals-of-ozone-solubility.html>

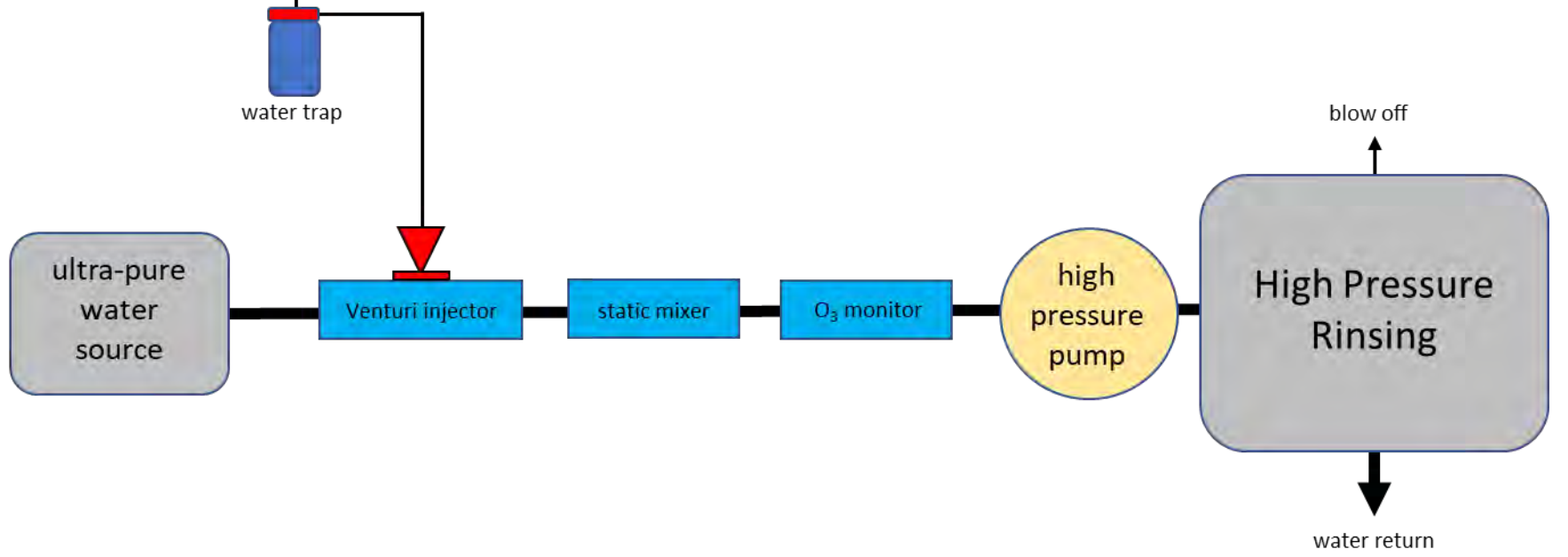


D. Klauson, *Physical and Chemical Properties of Ozone*, UNESCO – Encyclopedia of Life Support Systems, E6-192-03

# Ozone Processing Layout



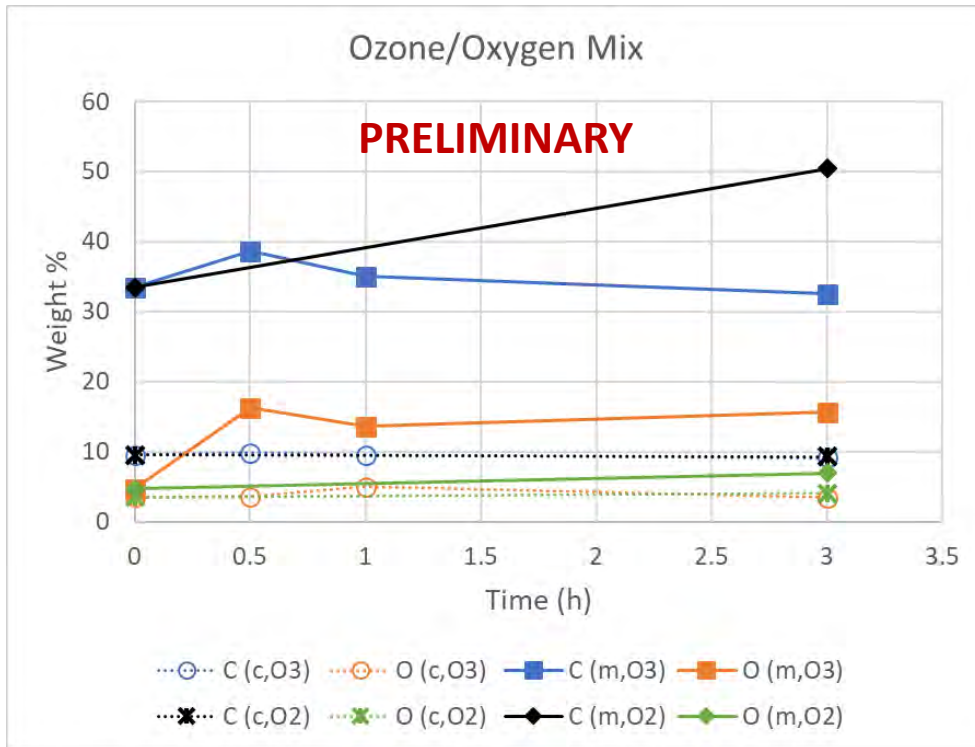
FI = flow indicator  
 FCV = flow control valve  
 NRV = non-return valve  
 PCV = pressure control valve (regulator)  
 PI = pressure indicator  
 SV = safety relief valve





# First Sample Testing

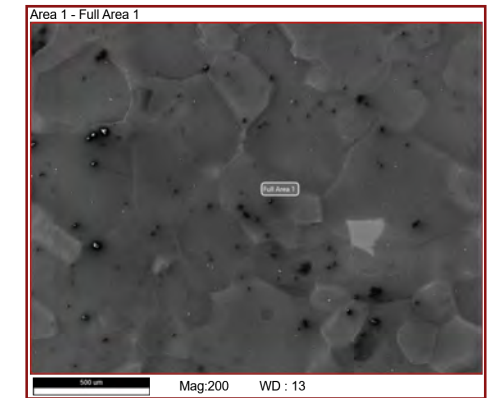
- Niobium samples contaminated with “Sharpie”
- **Visible clean after ozone treatment**
- Analysis: SEM APEX —————→



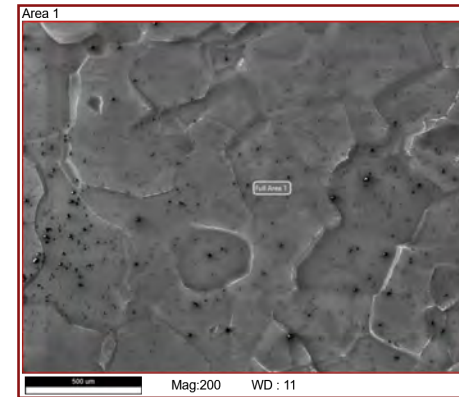
(c)=clean; (m)=contaminated



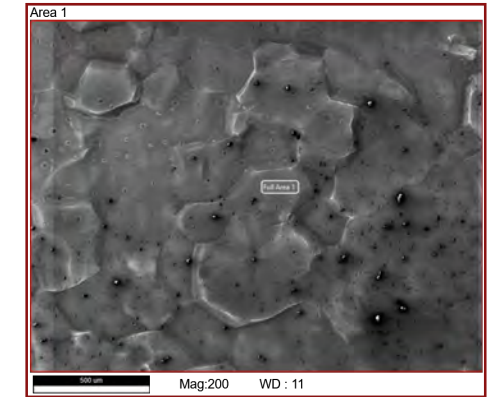
#597: sharpie / reference



#643: sharpie / 3h 100% O<sub>2</sub>



#643: sharpie / 1h 4% O<sub>3</sub>

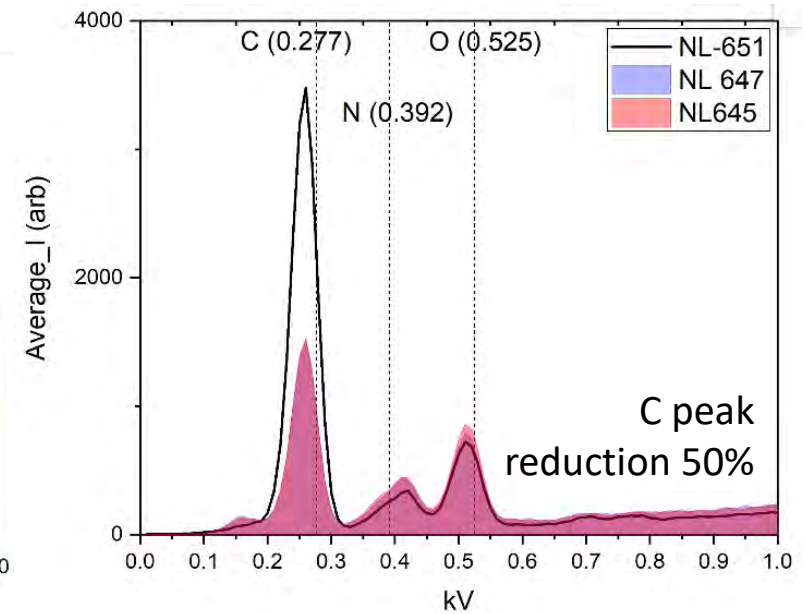
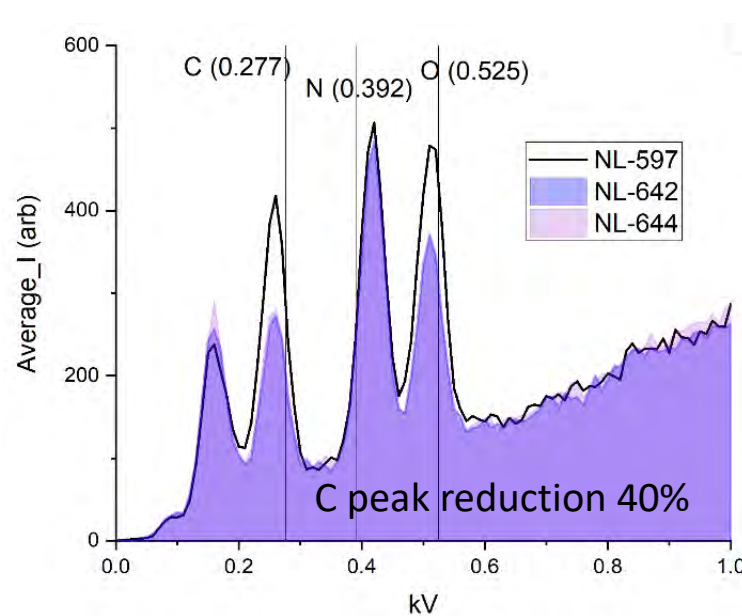
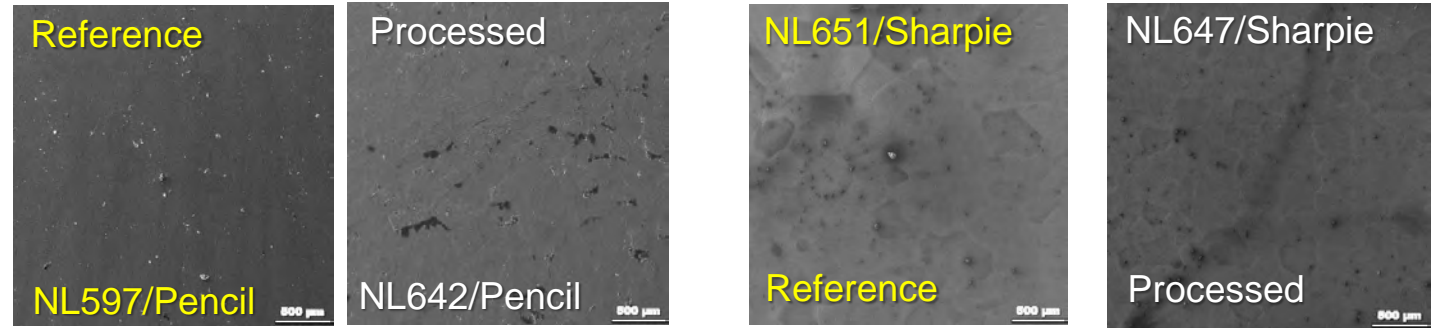


#643: sharpie / 3h 6% O<sub>3</sub>

Analysis courtesy Olga Trofimova

# More Sample Testing

- Niobium samples contaminated manually
  - with HB pencil or “Sharpie”
- Keep 42 h in 8 wt.% ozone
  - Sharpie samples visibly clean
  - Pencil samples visibly light carbon cover remaining
- Analysis
  - Automated particle analysis with EDS
  - All images were taken in SE mode
- Conclusion
  - Carbon and hydrocarbon contaminants are reduced



Analysis courtesy Shreyas Balachandran

# Ozonized High-pressure Rinsing (O3HPR)

- **First test** to verify that “no harm” is done...

- **F1F2**

- single cell 1.3 GHz cavity
  - built mid-2010's, undergone multiple tests, CBP, BCP, EP, HF rinse,...
  - [G. Ciovati et al., \*Superconducting radio-frequency cavities made from medium and low-purity niobium ingots\*, Supercond. Sci. Technol. 29, 064002 \(2016\).](#)

- **Test on production cavity**

- **C75-RI-032**

- 5-cell 1.5 GHz cavity
  - manufactured for CEBAF cryomodule rework program
  - build 2018-19, undergone EP and vacuum annealing
  - [G. Ciovati et al., \*Cavity production and testing of the first C75 cryomodule for CEBAF\*, Proc. Int. Conf. RF Superc., East Lansing, USA \(2021\) 250.](#)

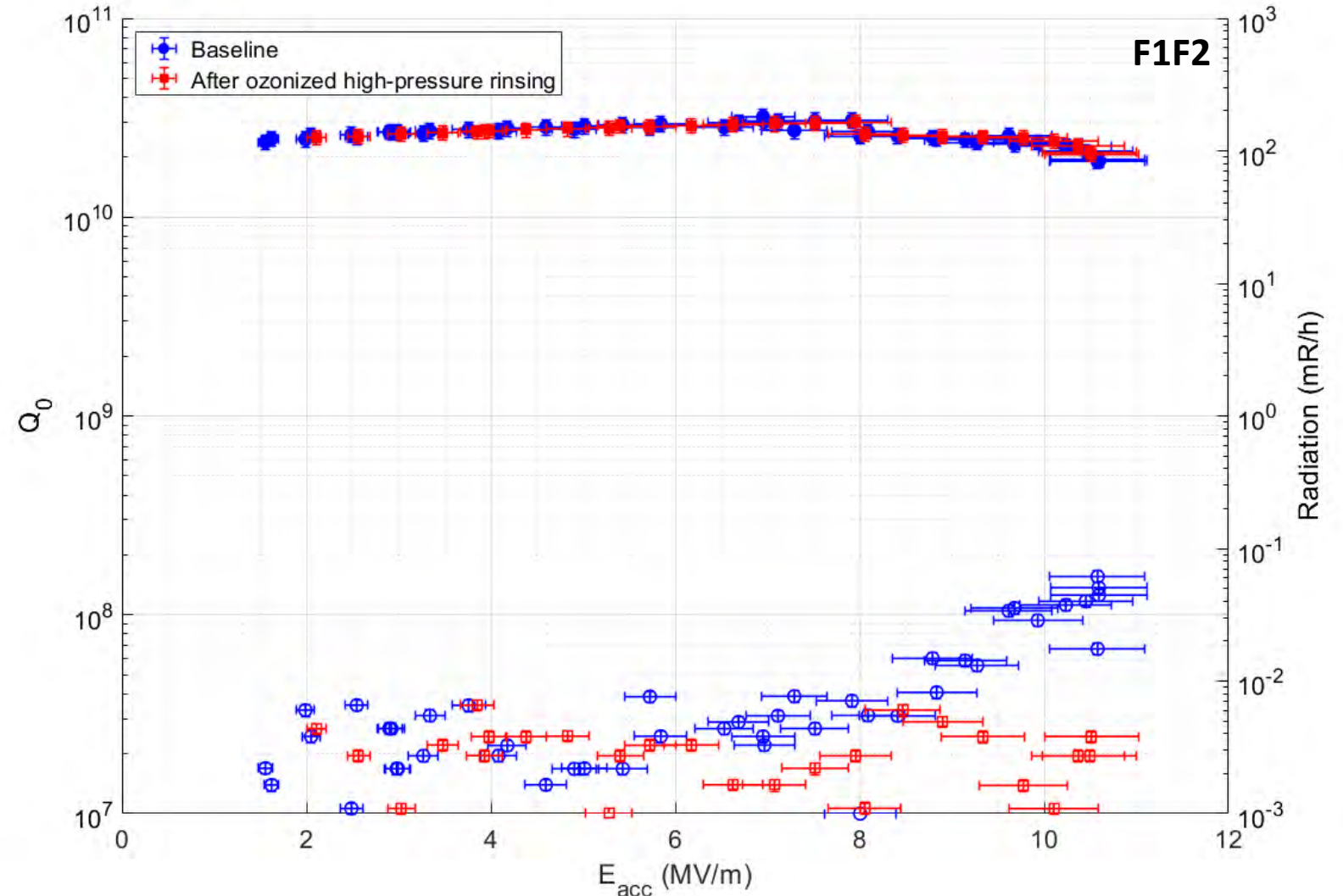
- **Experiment plan**

- prepare, assemble and baseline test cavities using same procedure
  - disassemble
  - high-pressure rinse while injecting ozone into the ultra-pure water
    - note that ozonized rinsing at KEK was done at atmospheric pressure, filling the cavity with ozonized water and then empty after 10 minutes
  - assemble and test cavity using same procedures as previously

# F1F2 Ozonized High-pressure Rinse

## 1.3 GHz single-cell elliptical

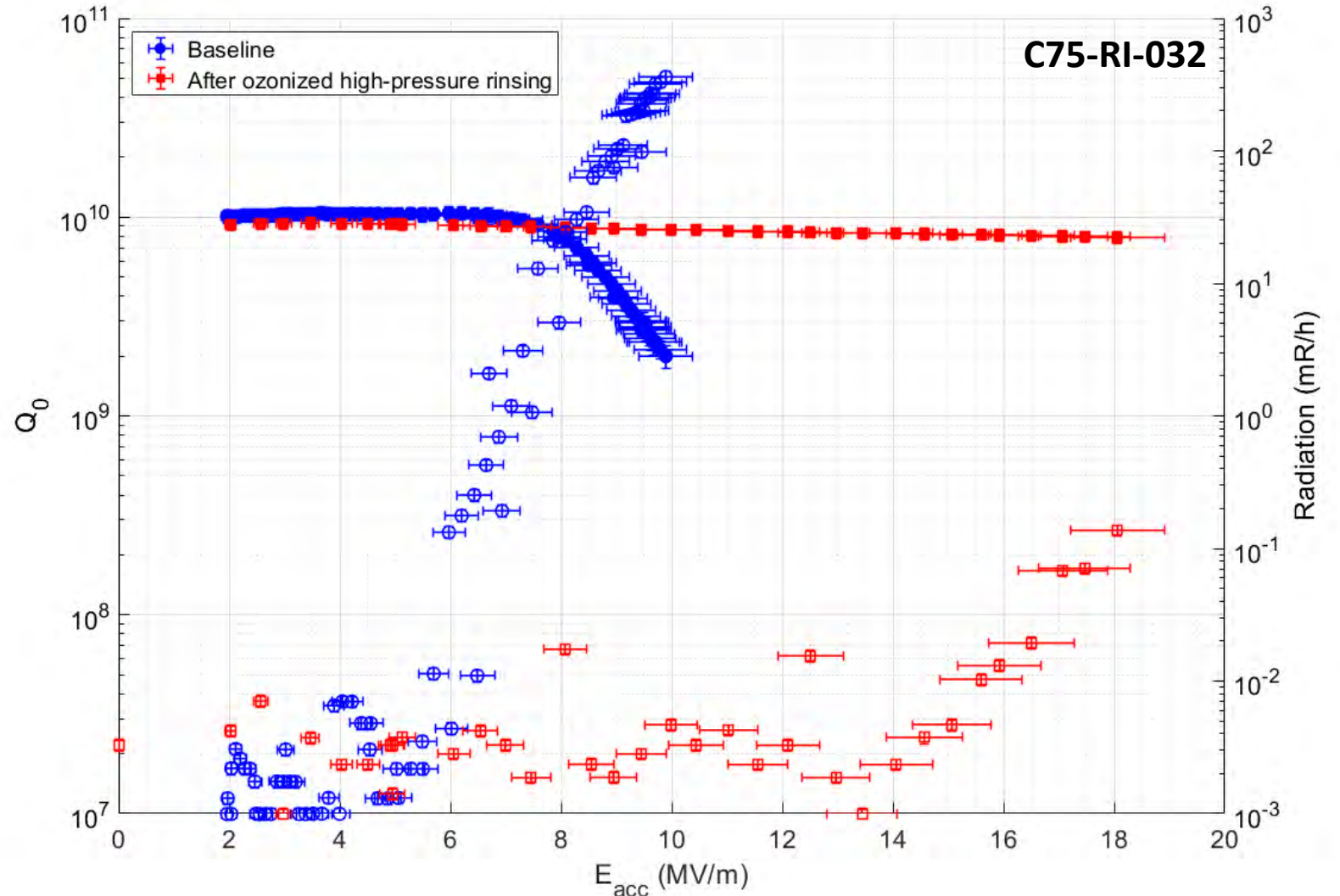
- Baseline
  - 8.5 MV/m FE onset
  - 10.5 MV/m  $E_{\max}$
- O3HPR
  - 1 h rinse
  - 22 °C
  - 1.6 ppm ozone
- RF test
  - 10.5 MV/m FE free



# C75-RI-032 Ozonized High-pressure Rinse

## 1.5 GHz 5-cell elliptical

- Baseline
  - 6 MV/m FE onset
  - 10 MV/m  $E_{\max}$
- O3HPR
  - 4 h rinse
  - 49 °C
  - 2 ppm ozone
- RF test
  - 15.5 MV/m FE onset
  - 18 MV/m  $E_{\max}$



# Ozonized High-pressure Rinsing (O3HPR) Summary

- **Ozonized HPR**

- was effective
- did not affect the cavity performance negatively

## **Postulate**

- Ozonized water enhances the HPR by removing hydrocarbons in addition to removing field emitting particulate

# In Situ Ozone Processing (O3 Cleaning)

- **Test on two production cavities**

- **C75-RI-032**

- 5-cell 1.5 GHz cavity
    - manufactured for CEBAF cryomodule rework program
    - build 2018-19, undergone EP and vacuum annealing
    - *G. Ciovati et al., Cavity production and testing of the first C75 cryomodule for CEBAF, Proc. Int. Workshop RF Superc., East Lansing, USA (2021) 250.*

- **C100-RI-086**

- 7-cell 1.5 GHz cavity
    - manufactured for CEBAF 12 GeV upgrade
    - used by Tom Powers for many plasma processing studies
    - *C. Reece et al., Optimization of the SRF cavity design for the CEBAF 12 GeV upgrade, Proc. Int. Workshop RF Superc., Beijing, China, (2007) 536.*
    - *T. Powers, N. Brock, and T. Ganey, In Situ Plasma Processing of Superconducting Cavities at JLab, Proc. NAPAC, Albuquerque, USA, (2022) 22–25.*

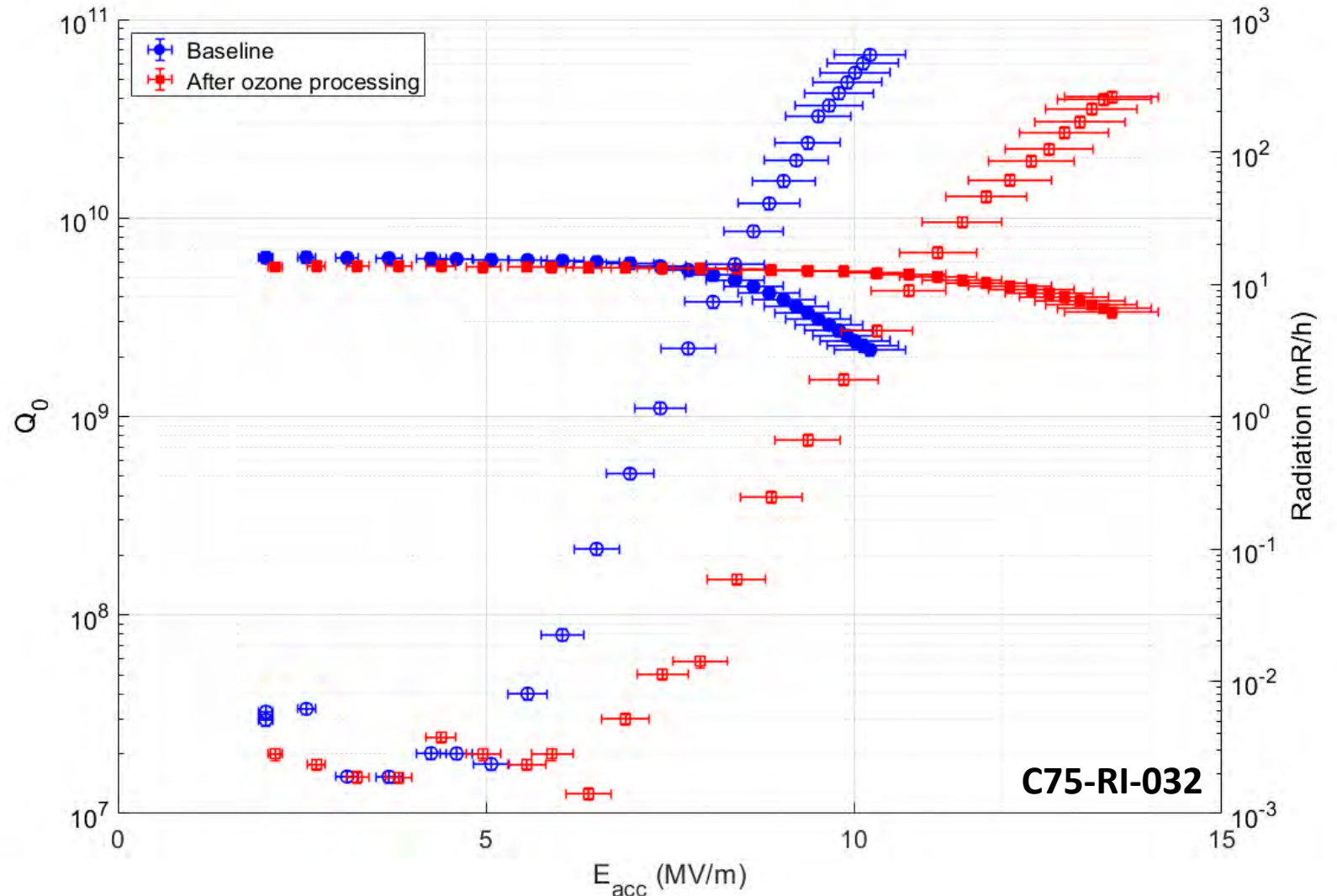
- **Experiment plan**

- prepare, assemble and baseline test cavities using same procedure
  - in situ ozone processing at room temperature
  - retest

# C75-RI-032 In Situ Ozone Processing

## 1.5 GHz 5-cell elliptical

- Baseline
  - 10 MV/m FE onset
  - 20.5 MV/m  $E_{\max}$
  - quenched
  - 6 MV/m FE onset
  - 10.5 MV/m  $E_{\max}$
- In situ  $O_3$  processing
  - 6 h: 8 wt%, 0.7 l/min, 84 °C
  - next day
  - 10 h: 7 wt%, 0.7 l/min, 83 °C
- RF test
  - 7.4 MV/m FE onset
  - 13.5 MV/m  $E_{\max}$

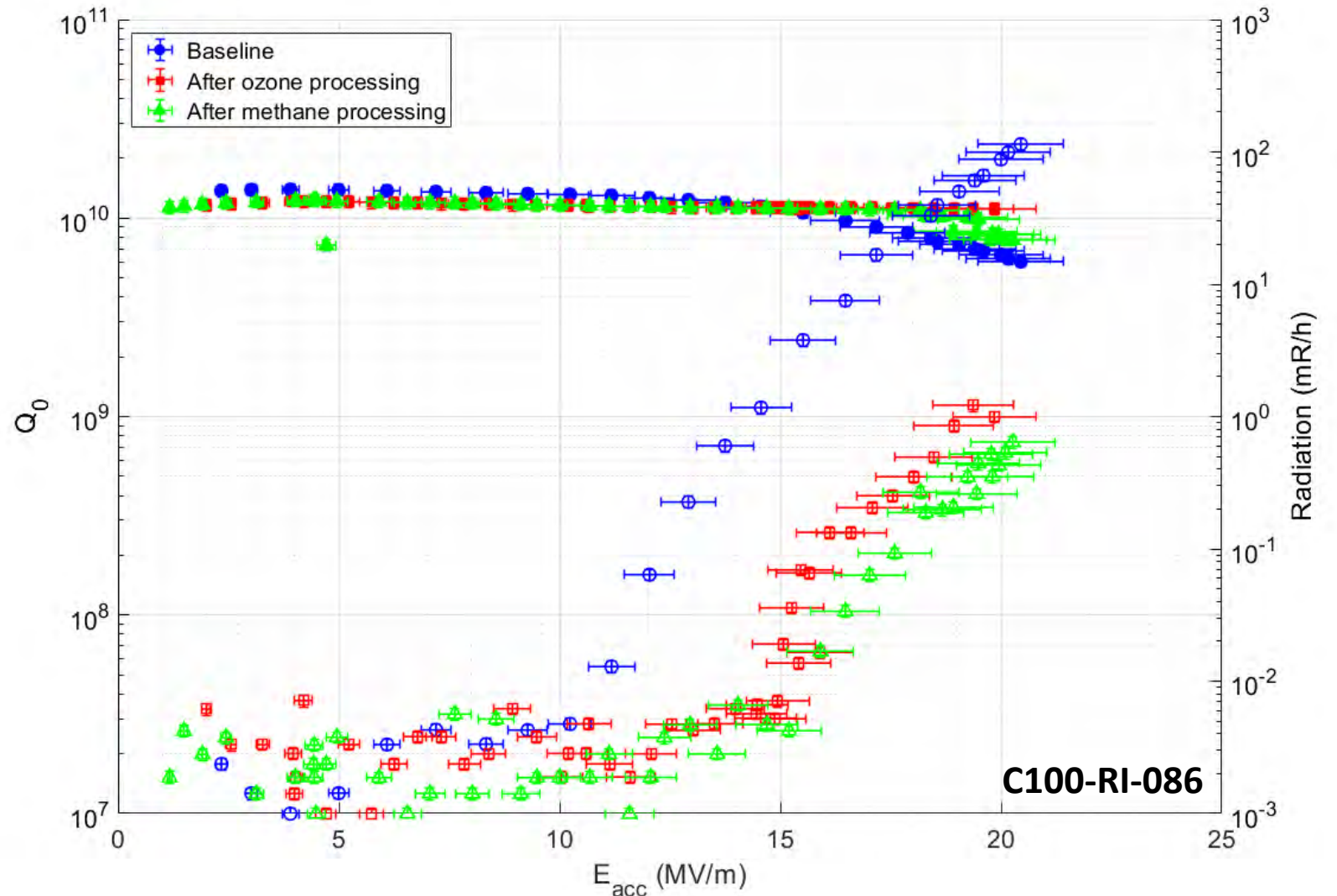




# C100-RI-086 In Situ Ozone Processing

## 1.5 GHz 7-cell elliptical

- Baseline
  - 10 MV/m FE onset
  - 20 MV/m  $E_{\max}$
- In situ  $O_3$  processing
  - 2.5 h: 6 wt%, 1 l/min, room temp.
  - repeat 2 days later
  - 3.25 h: 6 wt%, 1 l/min, room temp
- RF test
  - 14.5 MV/m FE onset
  - 20 MV/m  $E_{\max}$
- Methane processing (Ar/ $CH_4$ )
- RF test
  - same results



# In Situ Ozone Processing (O<sub>3</sub> Cleaning) Summary

- **In situ ozone processing**

- was effective
- did not affect the cavity performance negatively

- **Methane processing was not effective after ozone processing**

- used same cavity and procedure as Powers et al. used to demonstrate controlled contamination by methane processing and subsequent cleaning by plasma processing
- T. Powers, N. Brock, and T. Ganey, *In Situ Plasma Processing of Superconducting Cavities at JLab*, Proc. NAPAC, Albuquerque, USA, (2022) 22–25.

## Hypothesis

- Ozone removes hydrocarbons and reacts with NbO<sub>x</sub> to form a more stable Nb<sub>2</sub>O<sub>5</sub> surface impeding adsorption of hydrocarbons

# Field Emission (FE)

- Two basic mechanisms
  - *thermionic emission*, Richardson effect
  - *quantum mechanical tunneling*, Fowler-Nordheim
  - *joint effect* described by Murphy and Good
    - E. Murphy and R. Good, *Thermionic emission, field emission, and the transition region*, Phys. Rev. 102, 1464 (1956).
- Energy to remove electron from cavity surface determined by the **work function** value
  - C. Kittel, *Introduction to Solid State Physics*, Wiley (1986)
  - work function value depends on surface conditions including oxide states and contaminations
    - easier to emit an electron from NbC or NbN surface contamination than from Nb<sub>2</sub>O<sub>5</sub> surface
    - ozone effectiveness increases the work function and thereby decreases field emission

Workfunction	Value (eV)	
NbO	4.2	Gao (2004)
Nb	4.3	Eastman (1970)
NbC	4.85 – 4.95	Fujii (2006)
NbN	4.95	Fujii (2006)
Nb <sub>2</sub> O <sub>5</sub>	5.2	Daccà (1998)

# Secondary Electron Yield (SEY)

- $\delta$  Number of secondary electrons emitted per incident particle
  - $\delta_m$ ,  $\delta_{100}$ ,  $\delta_{1000}$  = maximum value of  $\delta$ , value of  $\delta$  at 100, 1000 eV primary electron energy
- Can cause parasitic oscillation, *multipacting*

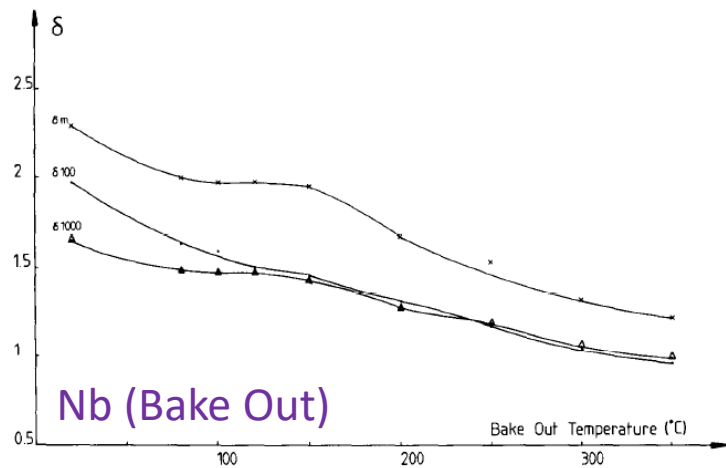


Fig. 1. Influence of bakeout temperature on  $\delta_m$ ,  $\delta_{100}$ ,  $\delta_{1000}$ .

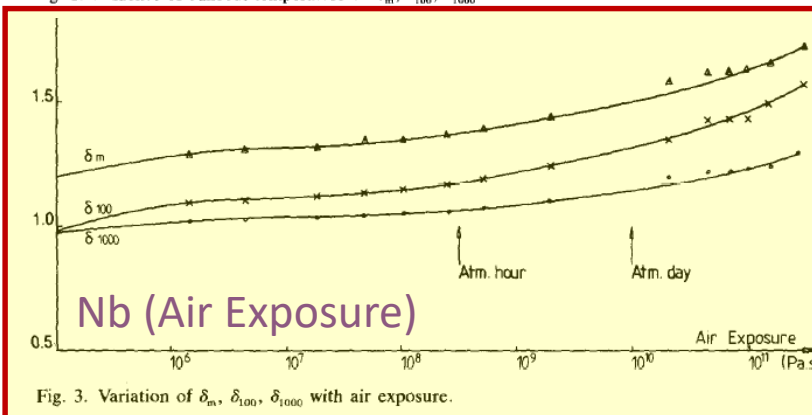


Fig. 3. Variation of  $\delta_m$ ,  $\delta_{100}$ ,  $\delta_{1000}$  with air exposure.

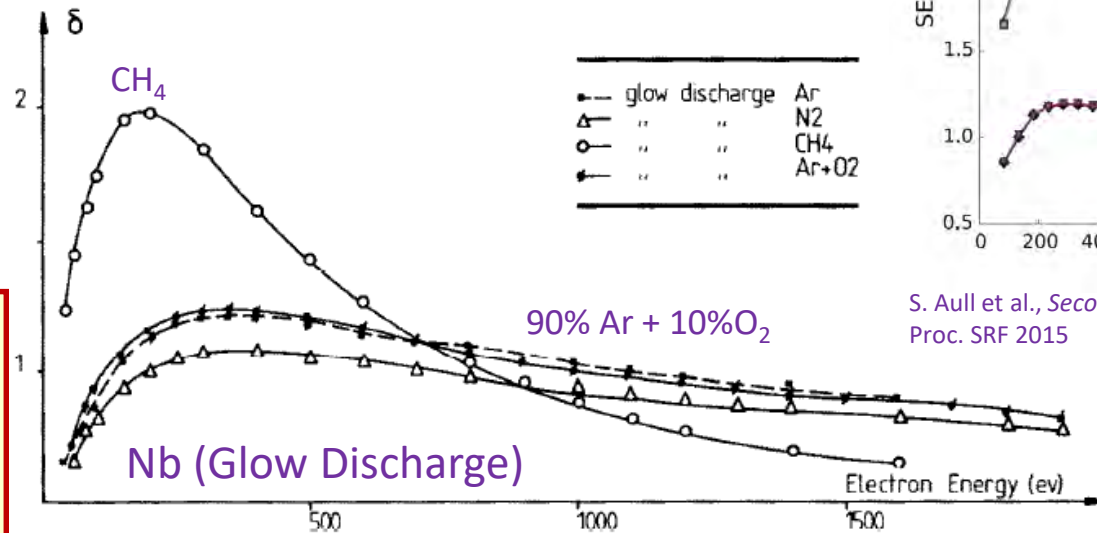
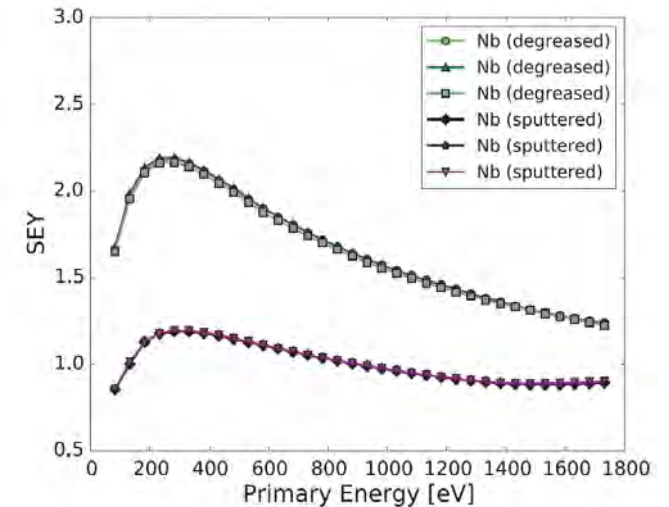


Fig. 5.  $\delta(E)$  curves after various glow discharge treatments.

R. Calder, G. Dominichini, N. Hilleret, *Influence of various vacuum surface treatments on the secondary electron yield of niobium*, NIM B13 (1986) 631.



S. Aull et al., *Secondary electron yield of SRF materials*, Proc. SRF 2015

# Effect of Glow Discharge

- The energetic ion bombardment involved in this process is able to remove completely the surface oxide layer.
  - R. Calder, G. Dominichini, N. Hilleret, *Influence of various vacuum surface treatments on the secondary electron yield of niobium*, NIM B13 (1986) 631.
- A non-reactive gas like argon creates a surface with characteristics which are very similar to those obtained after a 350 bake-out (comparable  $E_1$ ,  $E_2$ , and  $\delta_m$ ). When exposed to air this glow-discharged surface is also very reactive and, for example,  $E_1$  decreases to 38 eV, as in the case of a 350°C bake-out.
- Reactive gases, such as the argon-10% oxygen mixture or nitrogen, can provide a surface more immune to subsequent air exposure by creating a stable protective layer.

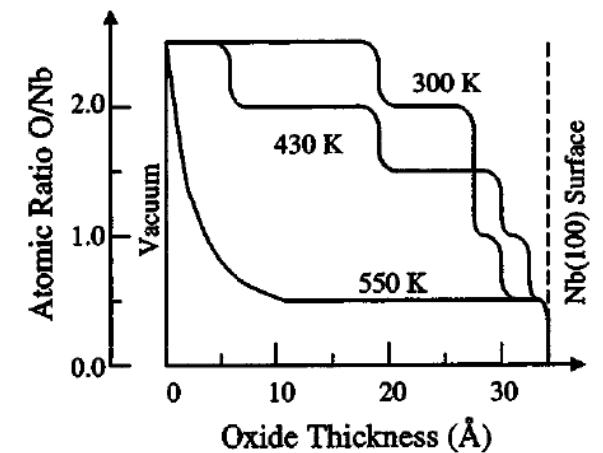
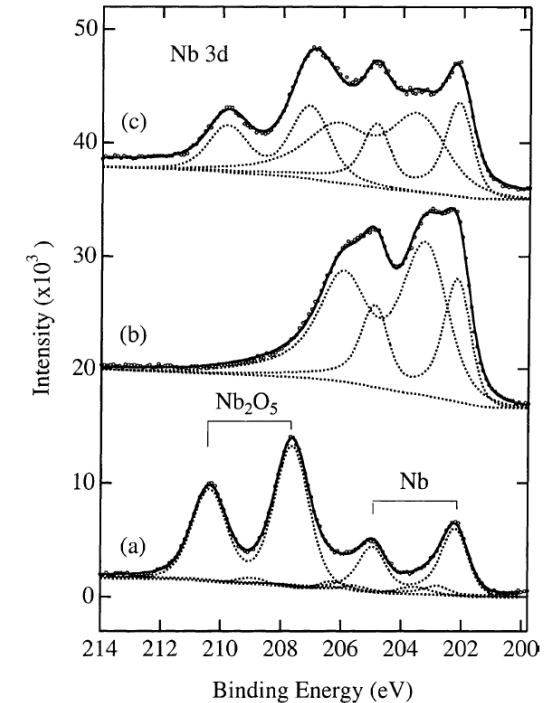
Table 2

Influence of glow discharge treatments on the characteristic values

Treatment	$\delta_{100}$	$\delta_{1000}$	$E_1$ (eV)	$E_2$ (eV)	$E_m$ (eV)	$\delta_m$
Nitrogen glow discharge						
After G.D.	0.83	0.94	150	750	400	1.09
94 h, N <sub>2</sub>	1.01	1.03	100	1100	400	1.23
Rebaked	0.9	0.99	150	950	300	1.23
48 h, air	1.07	1.13	70	1450	350	1.42
Rebaked	1.07	1.09	90	1300	300	1.37
Argon glow discharge						
After G.D.	0.87	0.98	115	980	300	1.25
8 h, air	1.5	1.4	38	–	300	1.86
Rebaked	1.03	1.05	90	1150	300	1.31
Methane glow discharge						
After G.D.	1.75	0.9	140	850	200	2
Argon + 10% oxygen glow discharge						
After G.D.	1.03	0.94	120	1100	350	1.25
66 h, N <sub>2</sub>	0.99	1.08	103	1250	350	1.32
Rebaked	0.96	1.07	105	1250	350	1.31
66 h, air	1.09	1.16	80	1570	350	1.44
Rebaked	1	1.1	100	1350	350	1.35

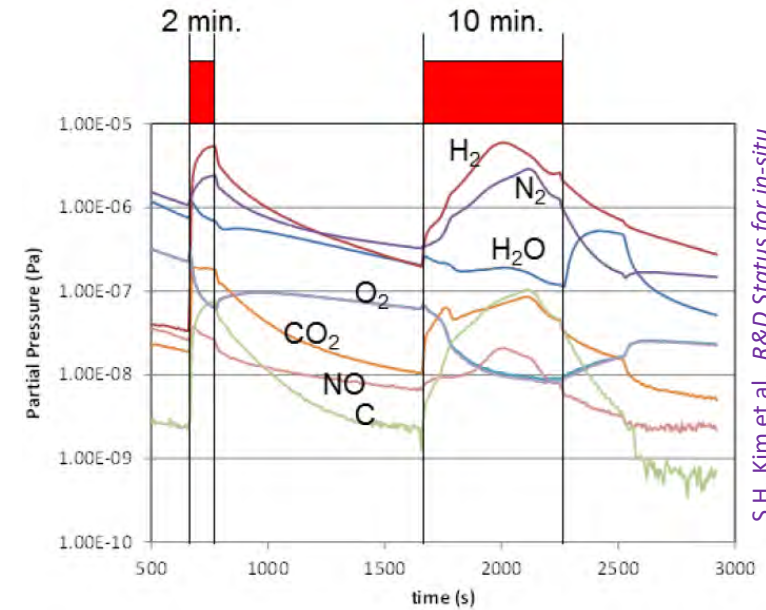
# Effect of Heat Treatment

- Heat treatment or sputtering reduces the oxide layer on the Nb surface
  - Vacuum annealing Nb at 250 °C changes the oxide composition from a Nb<sub>2</sub>O<sub>5</sub> dominated layer to a Nb<sub>2</sub>O dominated layer through oxygen diffusion.
  - Room temperature re-oxidation re-generates Nb<sub>2</sub>O<sub>5</sub> in the oxide layer.
  - Q. Ma and R.A. Rosenberg, *Angle-resolved X-ray photoelectron spectroscopy study of the oxides on Nb surfaces for superconducting r.f. cavity applications*, Appl. Surf. Sci. 206 (2003) 209–217.
  - Q. Ma et al., *Thermal effect on the oxides on Nb(100) studied by synchrotron-radiation X-ray photoelectron spectroscopy*, J. Appl. Phys. 96 (2004) 7675–7680.
- Niobium transition temperature drops by ~1 K per % O<sub>2</sub> impurity
  - C.C. Koch et al., *Effects of interstitial oxygen on the superconductivity of niobium*, Phys. Rev. B9 (1974) 888–897.
- Oxidation
  - Nb(110) and polycrystalline niobium initially NbO, then NbO<sub>2</sub>, then Nb<sub>2</sub>O<sub>5-y</sub>
  - Nb(001), both NbO<sub>2</sub> and Nb<sub>2</sub>O<sub>5-y</sub> are observed, but not NbO
  - Nb<sub>2</sub>O<sub>5</sub> is always the terminating oxide
  - Nb<sub>2</sub>O<sub>5</sub> can be reduced to NbO<sub>2</sub> at ~150 °C
  - K. Zhussupbekova, et al., *Oxidation of Nb(110): atomic structure of the NbO layer and its influence on further oxidation*, Sci Rep 10, 3794 (2020).



# Effect of Plasma Processing (1/2)

- Removes hydrocarbons
- Increases Nb work function by 0.5 to 1.0eV (Ar/O<sub>2</sub>)
  - after 15 min in vacuum,
    - hydrocarbon concentration on surface increases to initial level before processing
    - hydrocarbon concentration below top surface decreases
- Confirmed using methane plasma as artificial contamination
  - P.V. Tyagi et al., *Improving the work function of the niobium surface of SRF cavities by plasma processing*, Appl. Surf. Sci. 369 (2016) 29.
  - T. Powers, et al., *In Situ Plasma Processing of Superconducting Cavities at JLab*, Proc. NAPAC, Albuquerque, USA, (2022) 22–25.



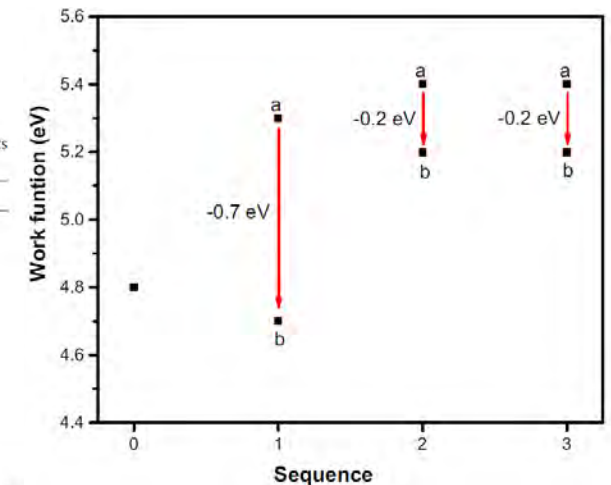
S.H. Kim et al., R&D Status for in-situ plasma surface cleaning of SRF cavities at SNS, Proc. NAPAC (2011) 2124.

## Conclusions

- hydrocarbons migrate to top surface over time
- mitigated by longer and more plasma processing cycles

**Table 1**  
Summary of the experimental conditions for work function studies experiments after subsequent cycles of plasma processing.

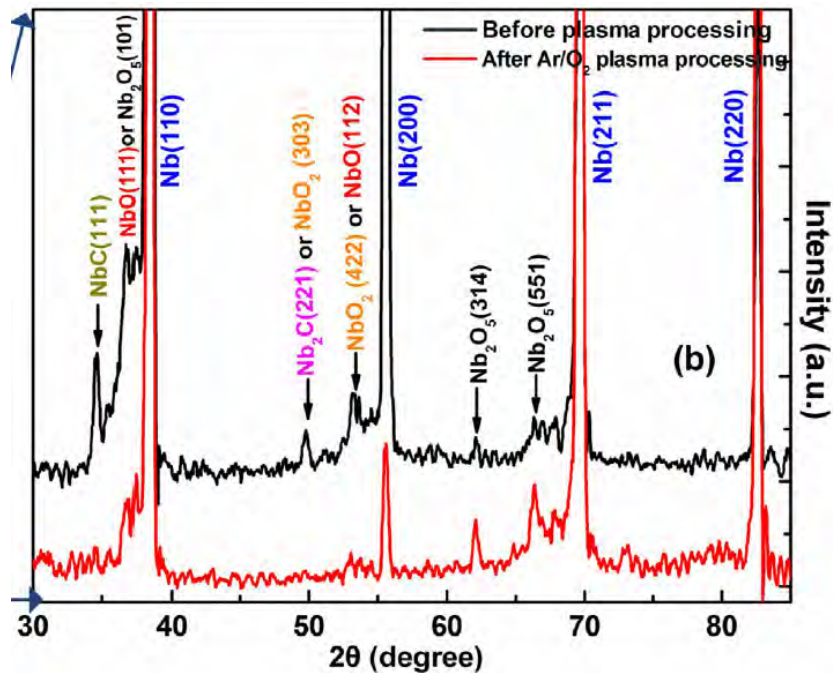
Sequence	Experimental details	Work function (eV)
0	Initial condition	4.8
1	a	5.3
	b	4.7
2	a	5.4
	b	5.2
3	a	5.4
	b	5.2



P.V. Tyagi et al., *Improving the work function of the niobium surface of SRF cavities by plasma processing*, Appl. Surf. Sci. 369 (2016) 29.

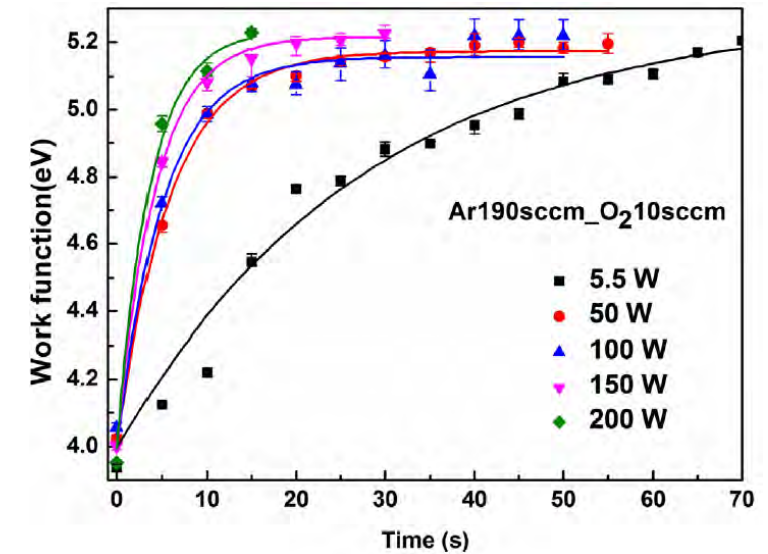
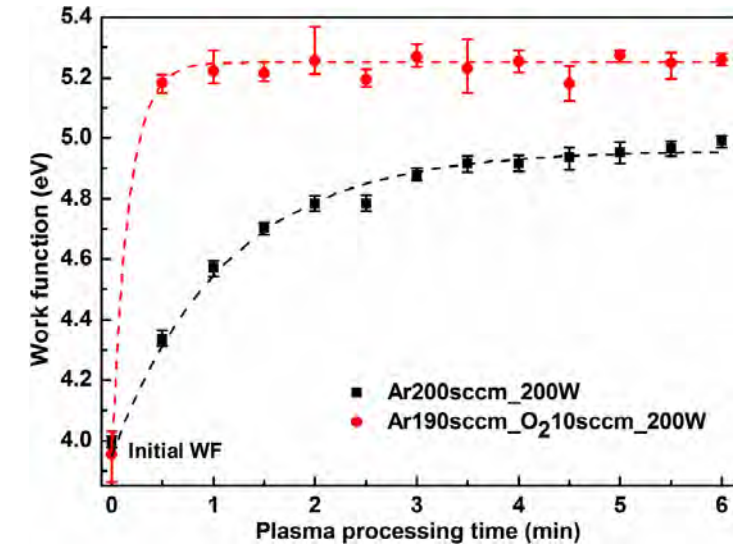
# Effect of Plasma Processing (2/2)

- Improves work function
  - from 4.0 to 5.0 with Ar only
  - up to 5.2 eV with Ar/O<sub>2</sub> mixture
- Oxidize niobium surface into Nb<sub>2</sub>O<sub>5</sub>
  - ratio increases from 25% to 79%



	Before	After
NbO	56%	21%
NbO <sub>2</sub>	12%	2%
Nb <sub>2</sub> O <sub>5</sub>	25%	79%
Nb	4%	--
NbC	3%	--

Z. Zhang et al., *The mechanism study of mixed Ar/O<sub>2</sub> plasma-cleaning treatment on niobium surface for work function improvement*, Appl. Surf. Sci. 475 (2019) 143-150.





# Immunizing the Niobium Surface

- Argon-methane mixture used for artificial contamination
- However, not successful after He/O<sub>2</sub> plasma or ozone processing
  - T. Powers, private communication.
  - R. Ruber, *Reducing field emission in superconducting cavities with ozone*, Phys. Rev. Accel. Beams 27, 122001.

## Hypothesis

- Stabilizing the upper oxide surface layer on niobium to Nb<sub>2</sub>O<sub>5</sub>
  - increases the work function energy level, and
  - immunizes the surface layer against adsorption of contaminants, and thereby
  - decreases the potential for field emission

# Ensuring a Stable Oxygen Layer

- Chemical and heat treatment reduces the oxygen surface layer
- Controlled oxidation can create a stable  $\text{Nb}_2\text{O}_5$  surface layer
  - I. Lindau and W.E. Spicer, *Oxidation of Nb as studied by the UV-photoemission technique*, J. Appl. Phys. **45** (1974) 3720–3725
  - initially NbO, then  $\text{NbO}_2$ , finally top layer  $\text{Nb}_2\text{O}_5$

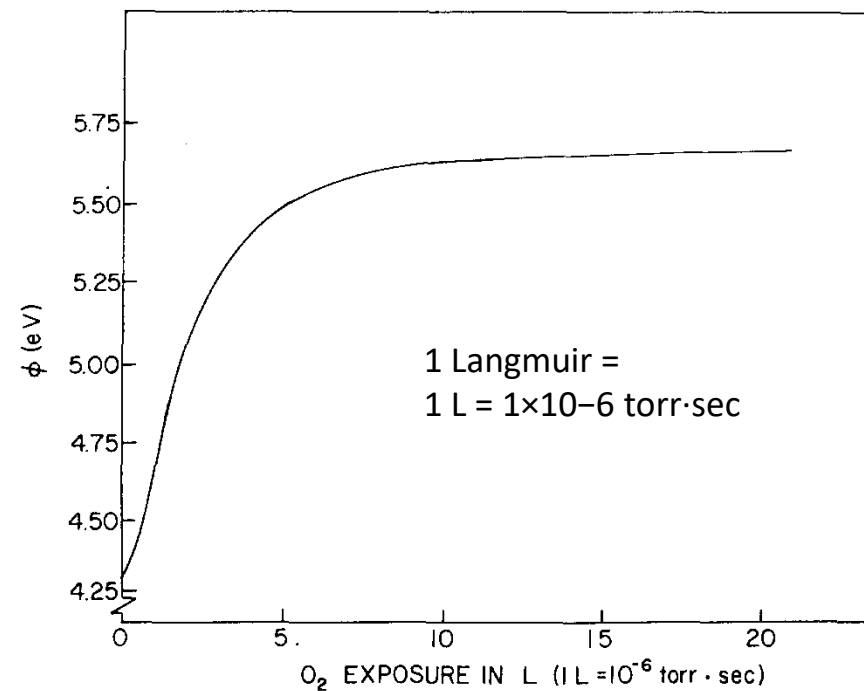
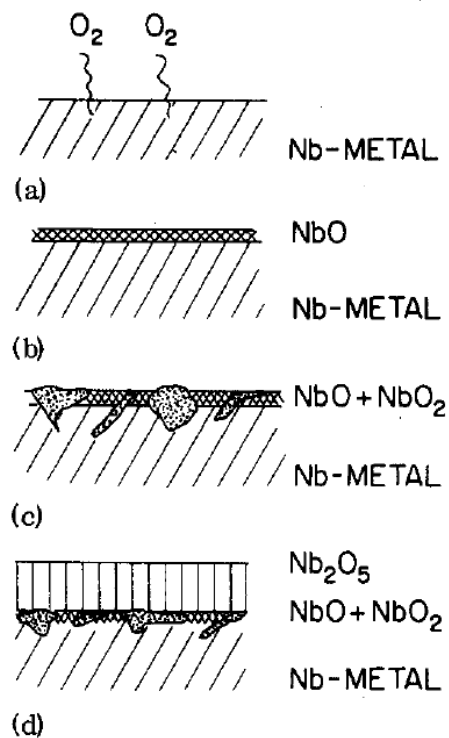


FIG. 5. The work function of the niobium sample as a function of oxygen exposure in  $L$ .

# Growth of the Oxide Layer

- Niobium always coated by niobium-oxides
  - and at least 2 to 10 monolayers adsorbates
- **Growth dynamics**
  - initial logarithmic dependence, followed by a fast rise
  - saturation around 6 nm
  - M. Grundner and J. Halbritter, *XPS and AES studies on oxide growth and oxide coatings on niobium*, J. Appl. Phys. 51, 397–405 (1980).
  - fast growth in H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> yields more inhomogeneous oxides
  - slowly grown oxides in a dry atmosphere show a fairly homogeneous oxide thickness
  - growth dynamics is given by the Cabrera-Mott process
  - M. Grundner and J. Halbritter, *On surface coatings and secondary yield of Nb<sub>3</sub>Sn and Nb*, J. Appl. Phys. 51, 5396–5405 (1980).
- **At least a day or two is required to reach a final thickness around 6–7 nm**

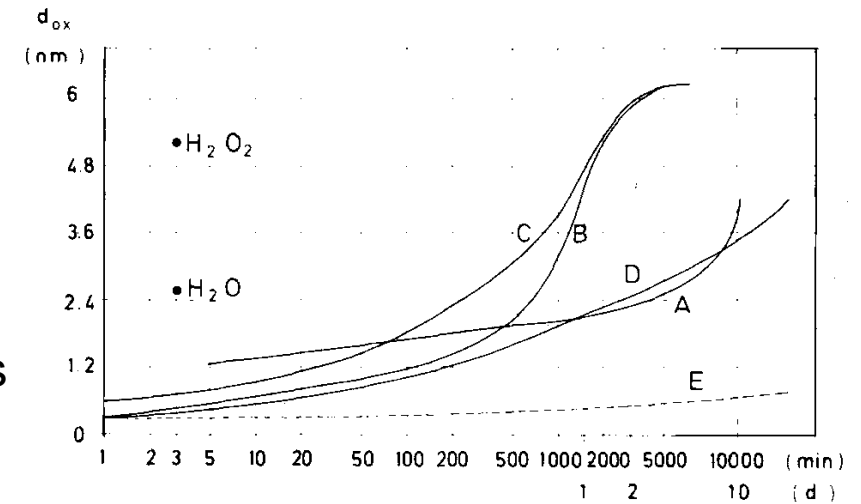


FIG. 11. Nb<sub>2</sub>O<sub>5</sub> (NbO) thicknesses on Nb. The thickness of Nb<sub>2</sub>O<sub>5</sub> after 3 min oxidation in H<sub>2</sub>O<sub>2</sub> (10% by volume) and 3 min H<sub>2</sub>O with no contact to air afterwards. The oxide growth in air at 300 K after (A) 2 h at 1850 °C and  $p < 10^{-10}$  mbar in the UHV furnace; (B) oxide stripped in HF, then heated in the XPS setup to 1700 K, and cooled down fast to 300 K (~10 min); (C) oxide stripped in HF and rinsed in CH<sub>3</sub>OH; (D) treatment similar to a Nb single crystal; (E) portion of lower oxides (~NbO), which did not depend on surface treatment.

M. Grundner and J. Halbritter, *XPS and AES studies on oxide growth and oxide coatings on niobium*, J. Appl. Phys. 51, 397–405 (1980).

# Conclusions

- **Ozone is an effective cleaning agent**
  - organic, hydrocarbons, and some inorganic, e.g. sulfur
  - improves the top Nb<sub>2</sub>O<sub>5</sub> surface layer
  - reduces adsorption of hydrocarbon contaminations
  - global effect on cavity's interior
- **Similar effectiveness as plasma processing**
- **Simple and promising cleaning method for all cavity shapes**
  - and other vacuum chambers

## Hypothesis

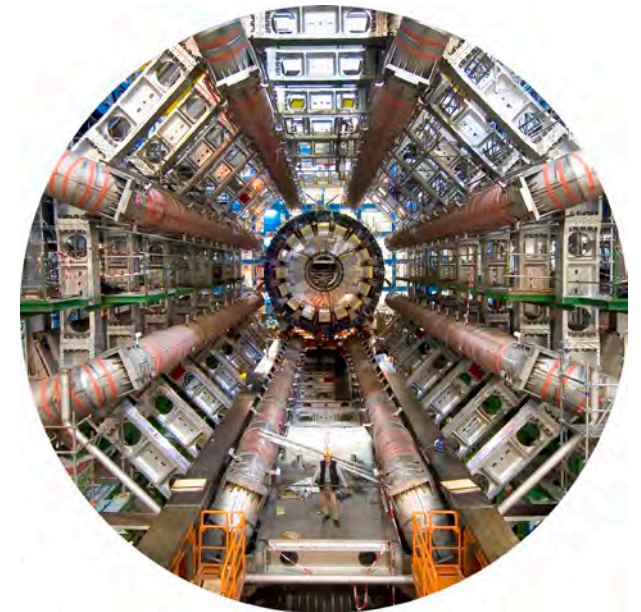
- Stabilizing the upper oxide surface layer on niobium to Nb<sub>2</sub>O<sub>5</sub>
  - increases the work function value and
  - immunizes the surface layer against adsorption of contaminants

## Acknowledgements

- JLab staff, especially SRF Ops, SRF S&T, ES&H;
- Tom Powers, Eric Lechner, Volker Ziemann, Anne-Marie Valente-Feliciano, Mauro Taborelli, Sergio Calatroni;
- Supported by US Department of Energy, Office of Science, Nuclear Physics under contracts DE-AC05-06OR23177, DE-LAB-20-2310, and DE-FOA-0002670.

## Proposal

- After heat treatment in furnace, vent (<100 °C) with dry air to build a homogeneous oxide surface layer and immunize the surface



# Backup Slides



# Ozone

- **Ozone concentration in water**

- 1 mg/l = 1 ppm = 1 g/m<sup>3</sup>

- **Ozone concentration in air**

- 1 g/m<sup>3</sup> = 467 ppm
- 1 ppm = 2.14 mg/m<sup>3</sup>
- 100 g/m<sup>3</sup> = 7.8 wt. %
- 1 wt. % = 12.8 g/m<sup>3</sup>
- 1 wt. % = 7,284 ppm

- **Ozone concentration in oxygen**

- 100 g/m<sup>3</sup> = 6.99 wt. %
- 1 wt. % = 14.3 g/m<sup>3</sup>
- 1 wt. % = 6,520 ppm
- 1 wt. % = 0.69 vol. %

- **Physical properties**

- at P = 1.013 bar; T = 273.3 K

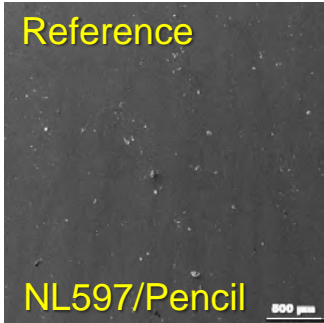
Material	Density (kg/m <sup>3</sup> )
Ozone	2.14
Oxygen	1.43
Air	1.29
Water	1.00

<https://www.oxidationtech.com/ozone/ozone-basics/fundamentals-of-ozone-solubility.html>  
<https://absoluteozone.com/ozone-library/ozone-conversions-and-equations/>

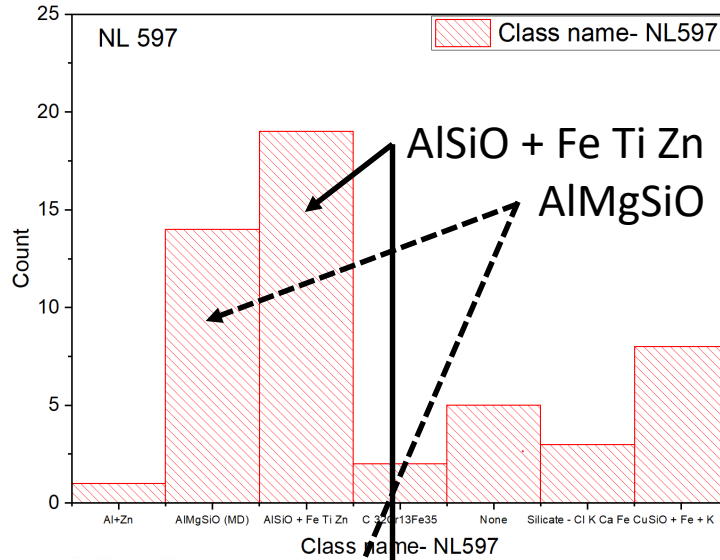
# More Sample Testing – Detailed Analysis

Analysis courtesy  
Shreyas Balachandran

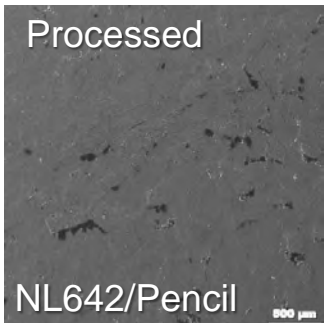
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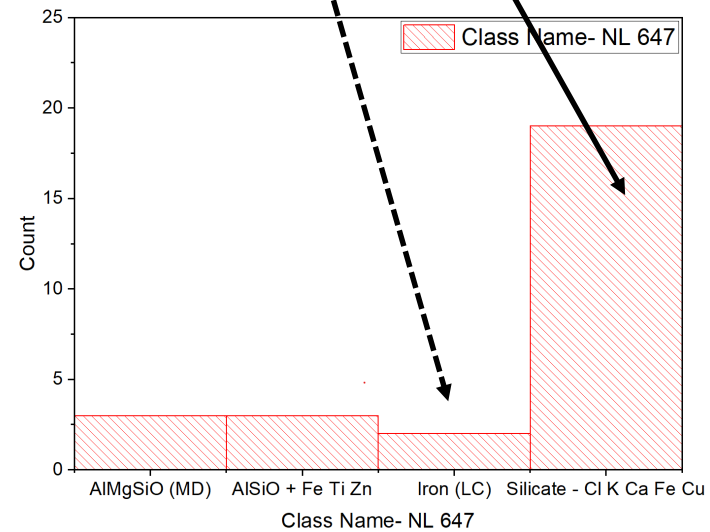
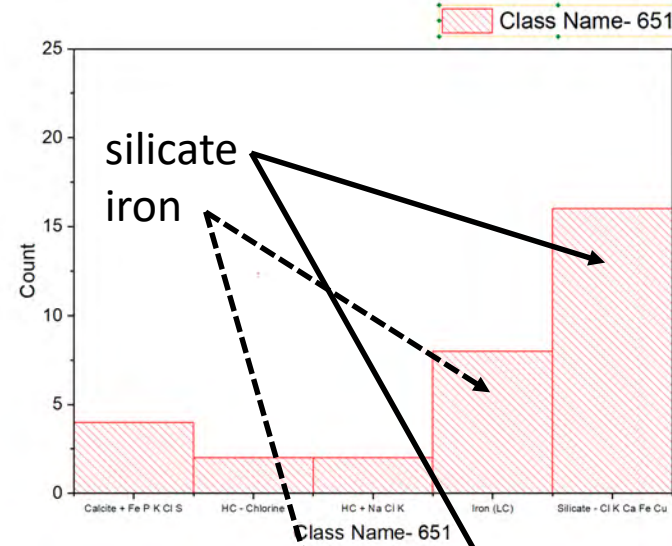
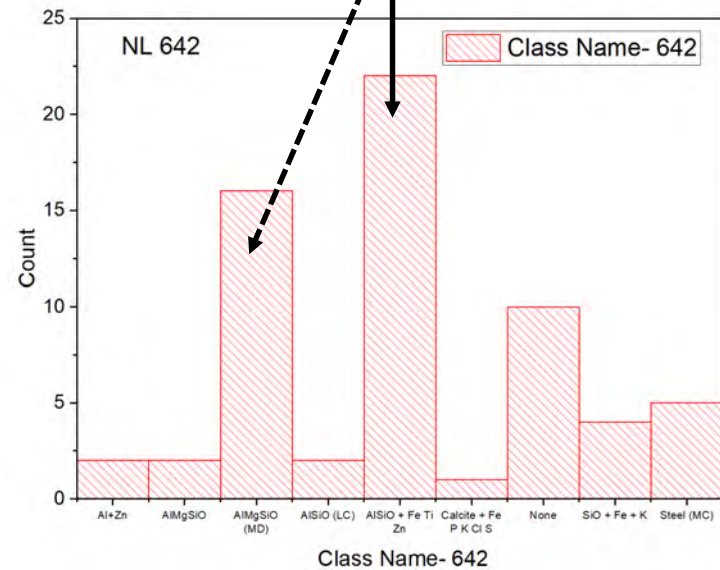
NL597/Pencil



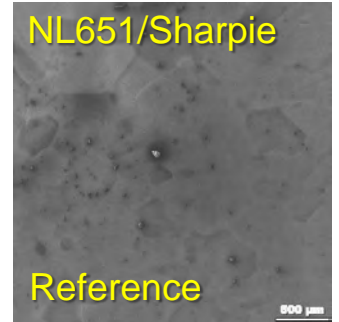
Processed



NL642/Pencil

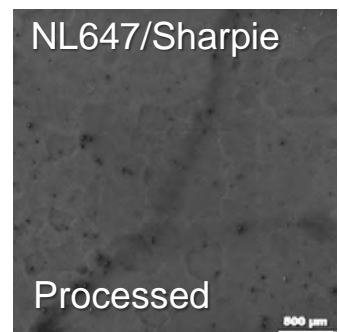


NL651/Sharpie



Reference

NL647/Sharpie



Processed