First nitrogen infusion runs at IPN Osay

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1. Conditions for successful Nitrogen doping or infusion
2. IPNO Nitrogen Infusion process
3. Cleaning, baking of N2 line and RGA test
4. First qualification run with test samples and 1.3 GHz cavity
5. Involved physico-chemical process and theoretical expectations
6. Analysis of Nitrogen infusion failure and next plan

Conditions for successful Nitrogen doping or infusion

To be performed in very clean conditions

- High purity Nitrogen
- Dry pumping
- Avoid any uncontrolled pollution

ALPHAGAZ™ 2 (N60) grade N2
Purity: 99.9999 %

Molecule	Concentration (molar ppm)
H_2O	< 0.5
O_2	< 0.1
C_nH_m	< 0.1
CO	< 0.1
CO_2	< 0.1
H_2	< 0.1

Ndoping valve

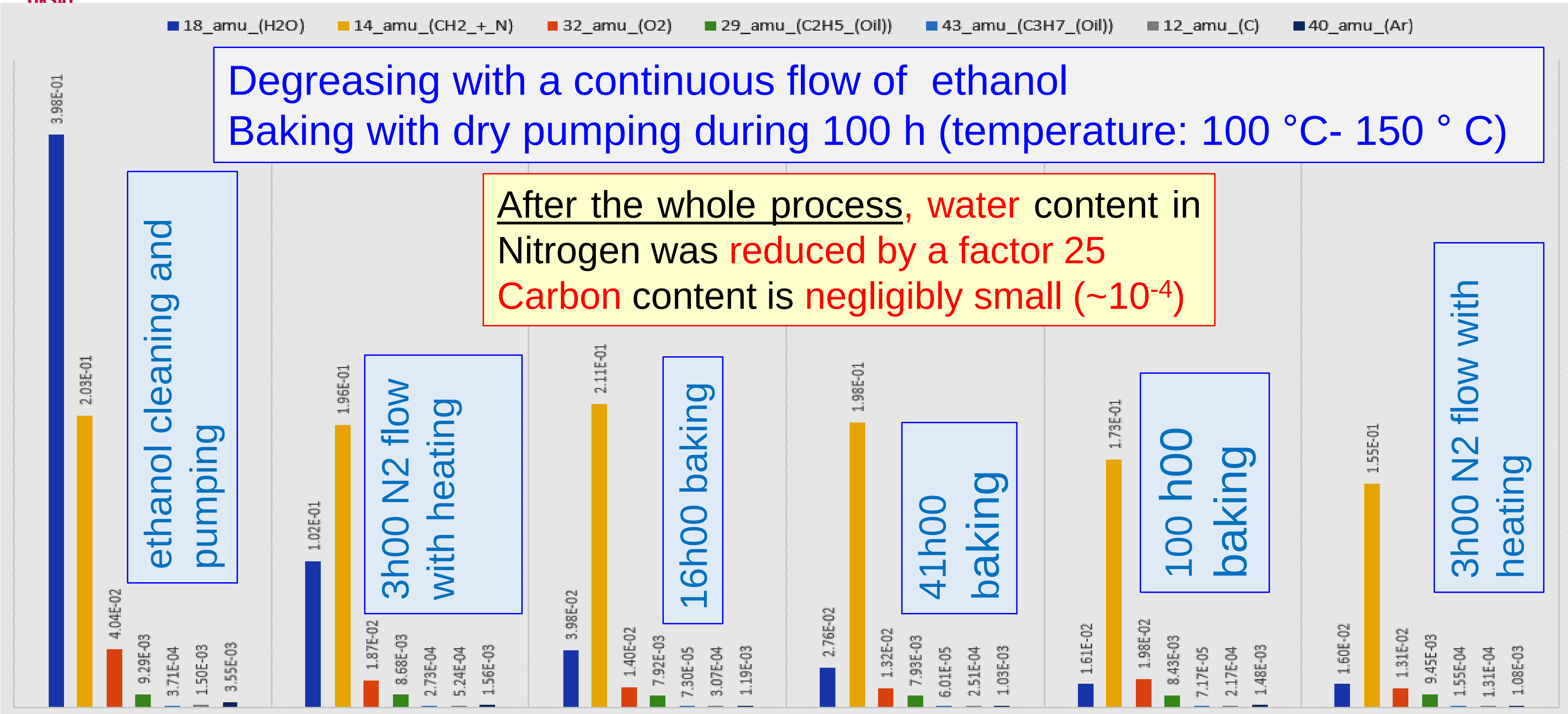
Gas flow @300K:
10^{-10} et 500 mbar.l. s^{-1}

Reliable and controlled process need virgin surface
→ remove oxides from subsurface

IPNO Nitrogen Infusion process

1. Purge N2 line (0.1 mbar, 30 min.)
2. Cryogenic Pumping
3. Heating up to 300°C @ 5°C/min - Hold @ 300 °C - dwell time : 0h30
4. Heating up to 600 °C @ 10°C/min - Annealing @à 650 °C, dwell time 0h30
5. Heating up to 800 °C @ 5°C/min - Annealing @à 650 °C, dwell time 2h00
6. Radiative cooling under vacuum down to 150 °C
7. Temperature regulation @160 °C
8. Nitrogen Doping @160 °C (0.025 mbar)
9. Cryogenic Pumping
10. Radiative cooling under vacuum down to 40 °C
11. Pressurize thermal chamber with Ar up to 900 mbar then to 1013 mbar (filtered air)
12. Cool down to 20 °C

Cleaning, baking of N2 line and RGA test

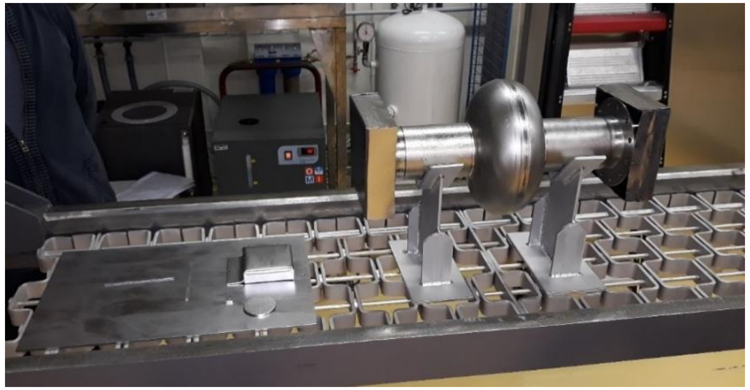


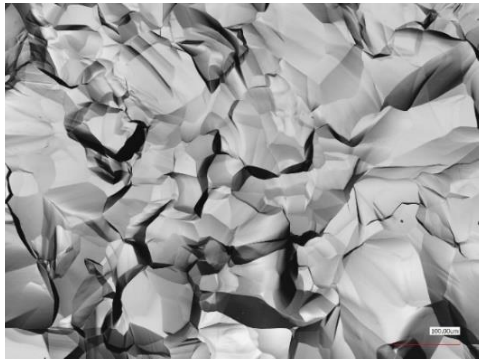
Degreasing with a continuous flow of ethanol
Baking with dry pumping during 100 h (temperature: 100 °C- 150 ° C)

After the whole process, water content in Nitrogen was reduced by a factor 25
Carbon content is negligibly small (~10^{-4})

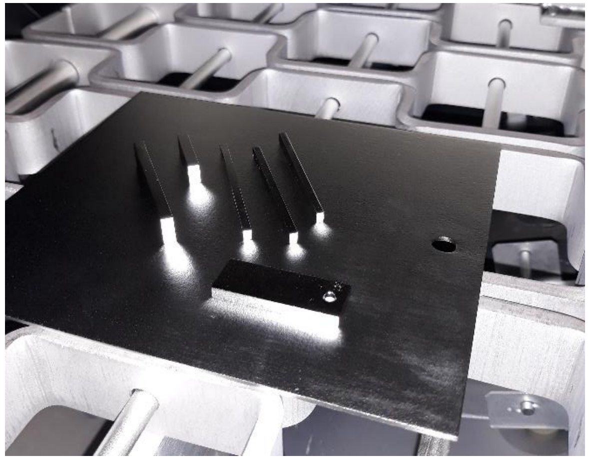
Set the furnace pressure at $P_{N2}=10^{-4}$ mbar and PID regulate P by means of the micrometric nitrogen injection valve while the furnace is pumped (screw pump and roots).

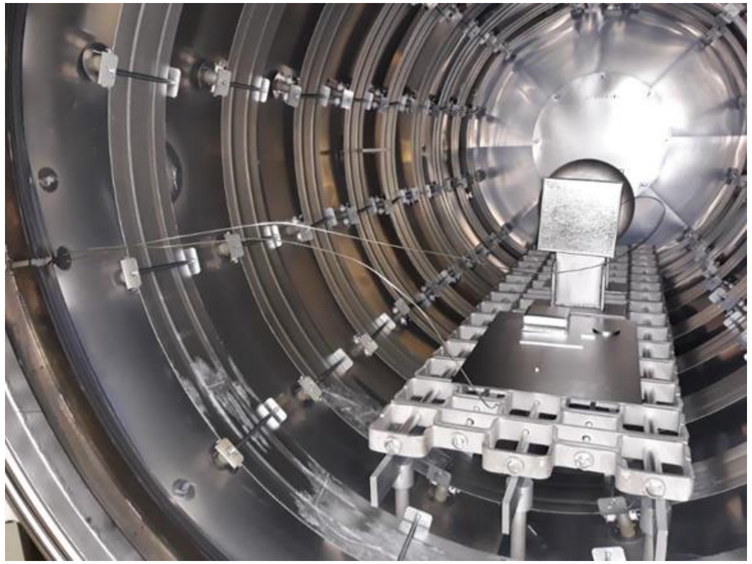
First qualification run with 1.3 GHz cavity





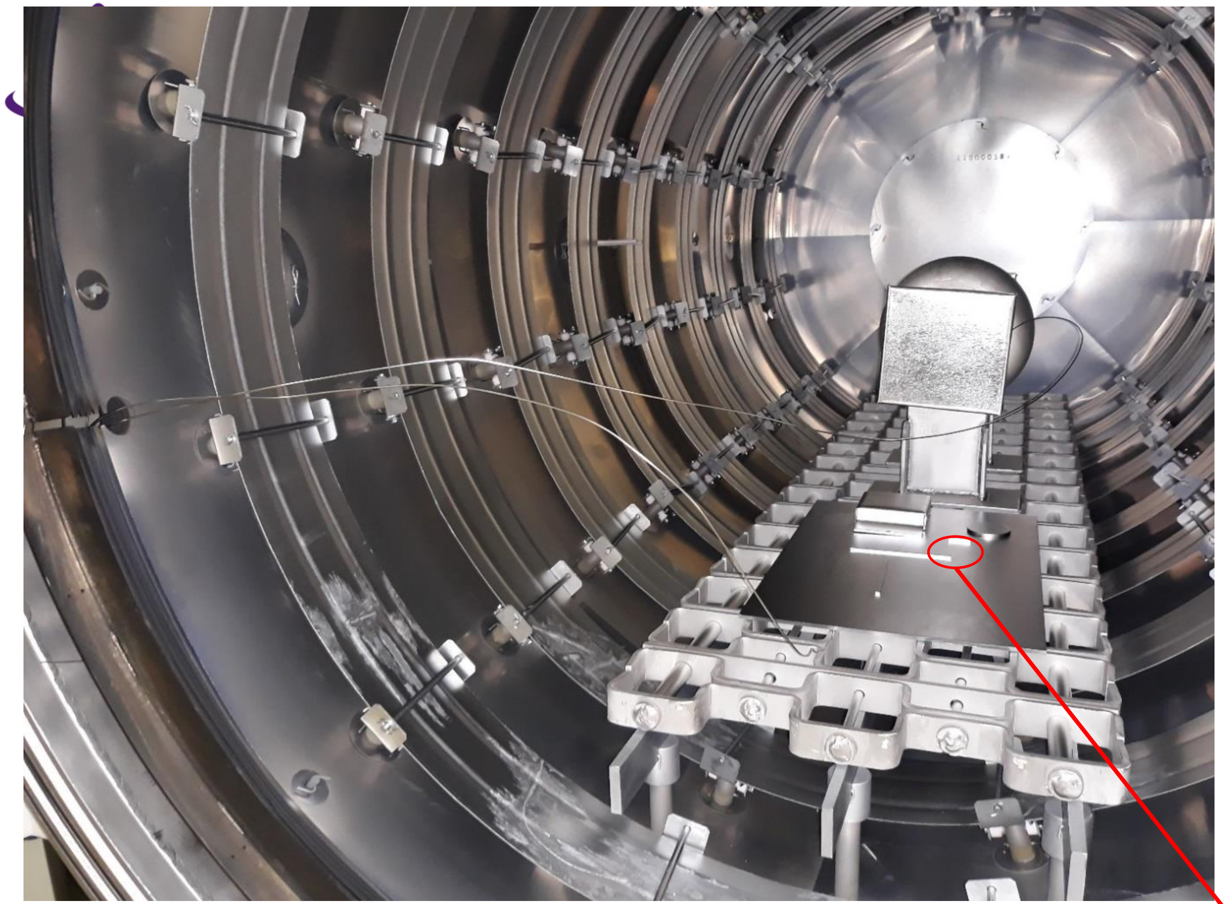
Confocal microscope micrograph





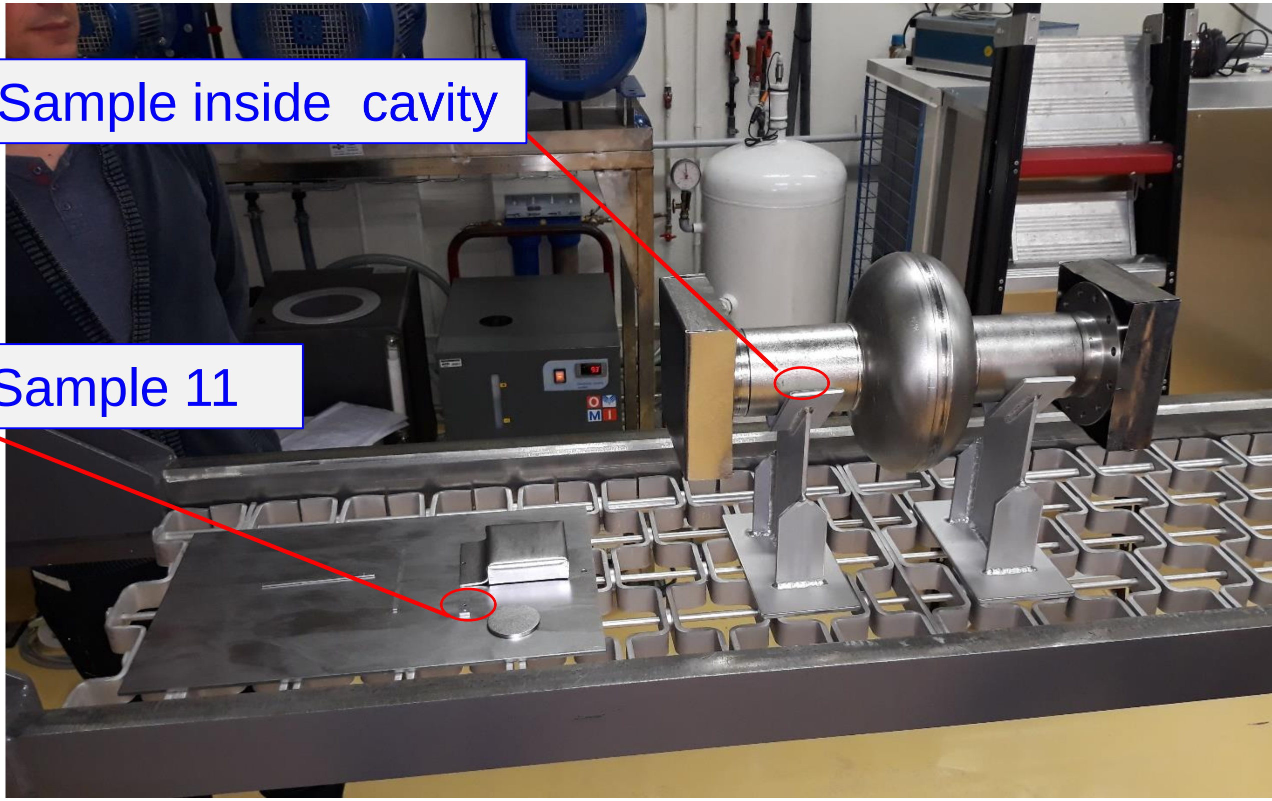
Samples (SIMS, SIMS-TOF, RRR, T_C, k)

Samples description & location



Three samples

- A reference sample not infused
- One sample inside cavity (Infused)
- One sample (#11) outside cavity (Infused))

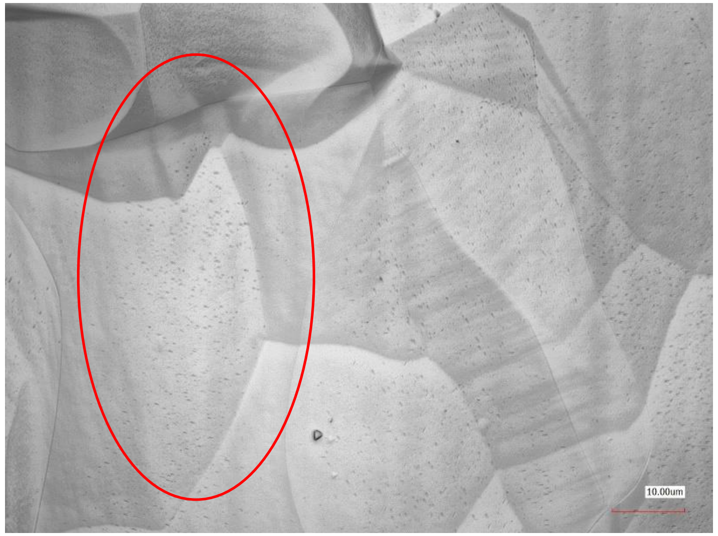


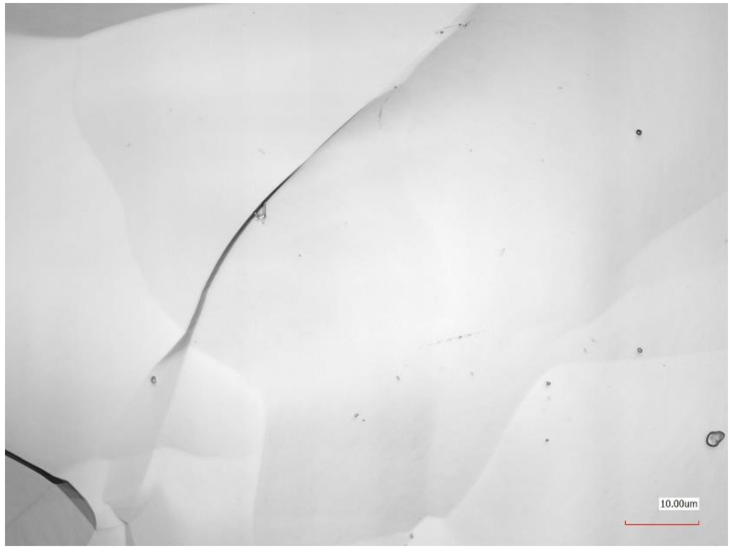
Sample already used for mechnical polishing tests
BCP 50 µm of the 3 samples
Thermal cycle :
800°C 2h
48h @ 150°C

Confocal microscope : laser image

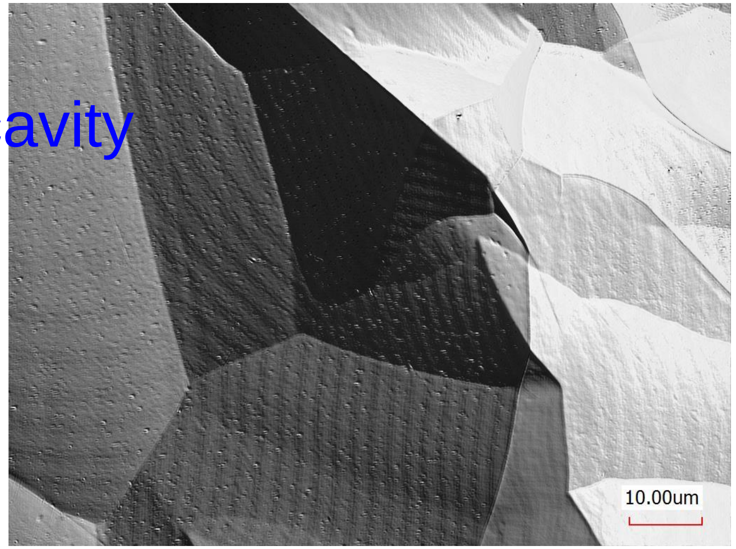
Sample 11: infused outside cavity

Reference sample: not infused

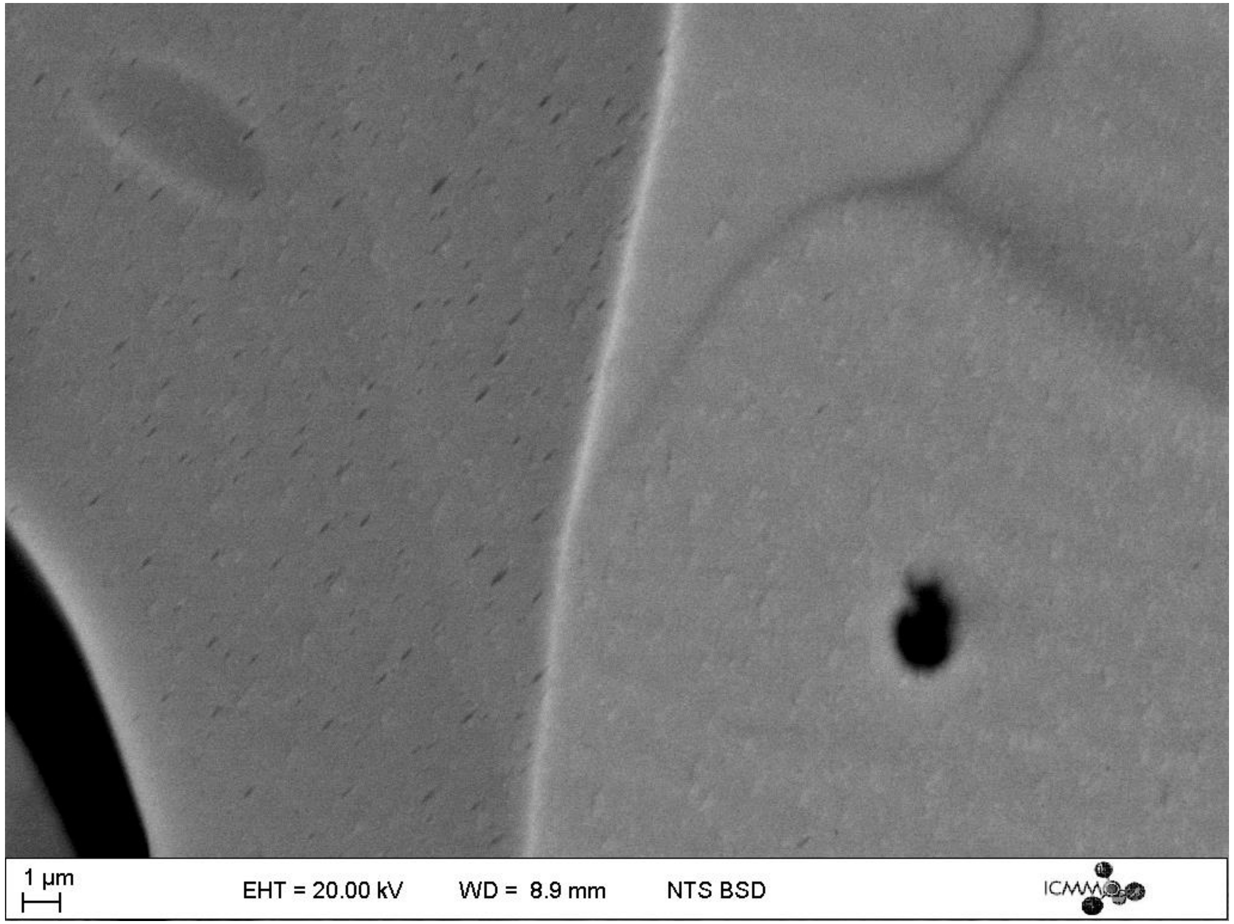


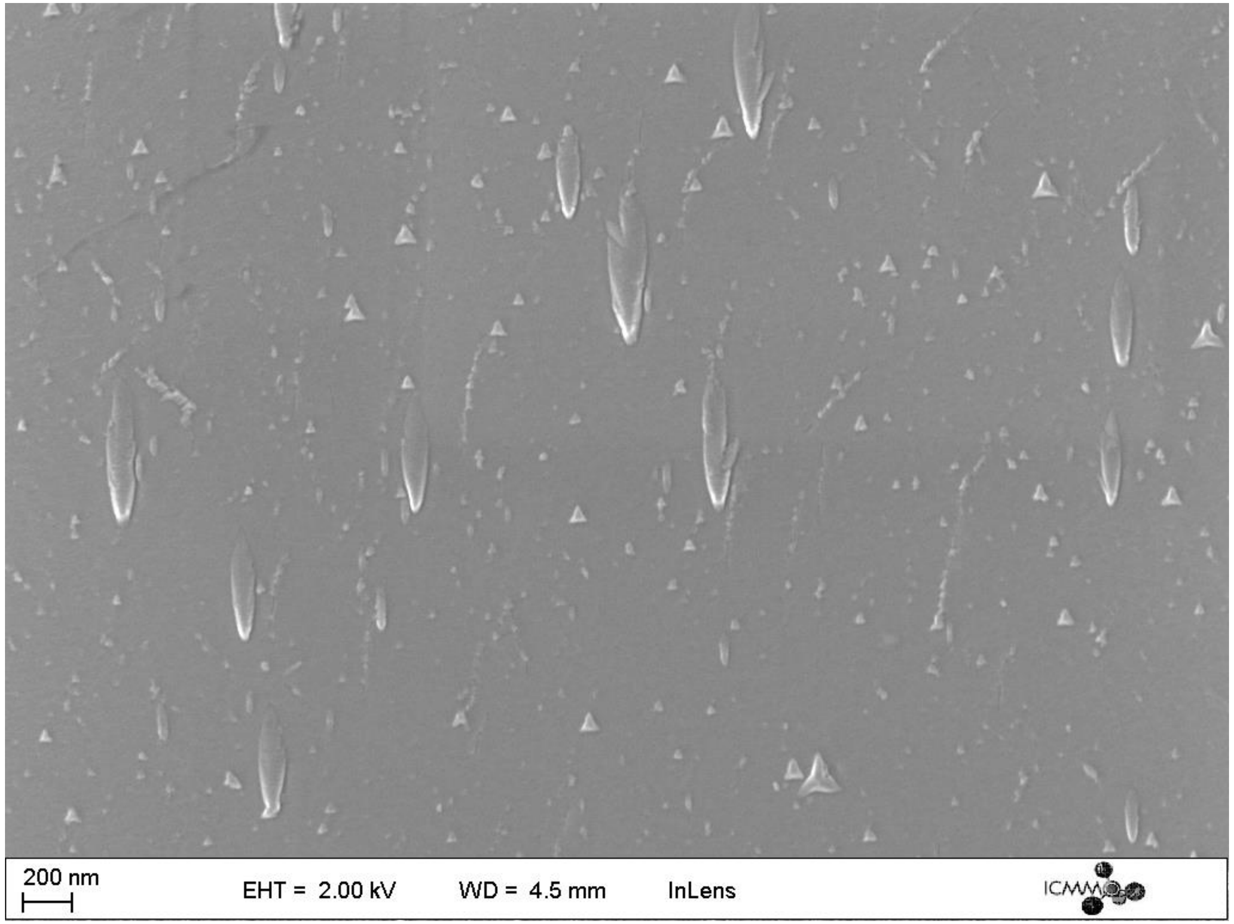


Sample infused inside cavity



SEM micrographs and EDX





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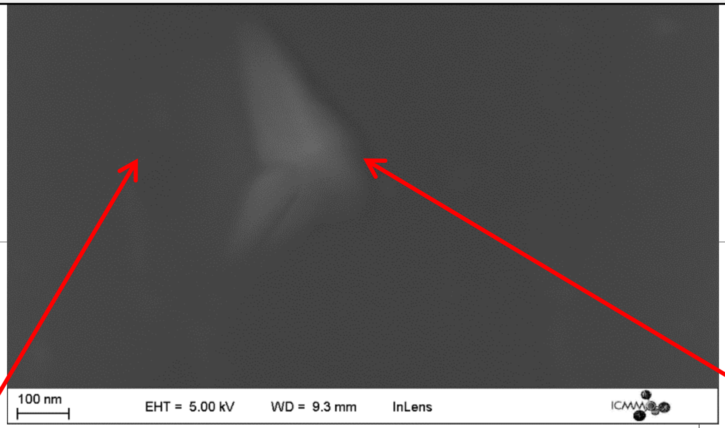
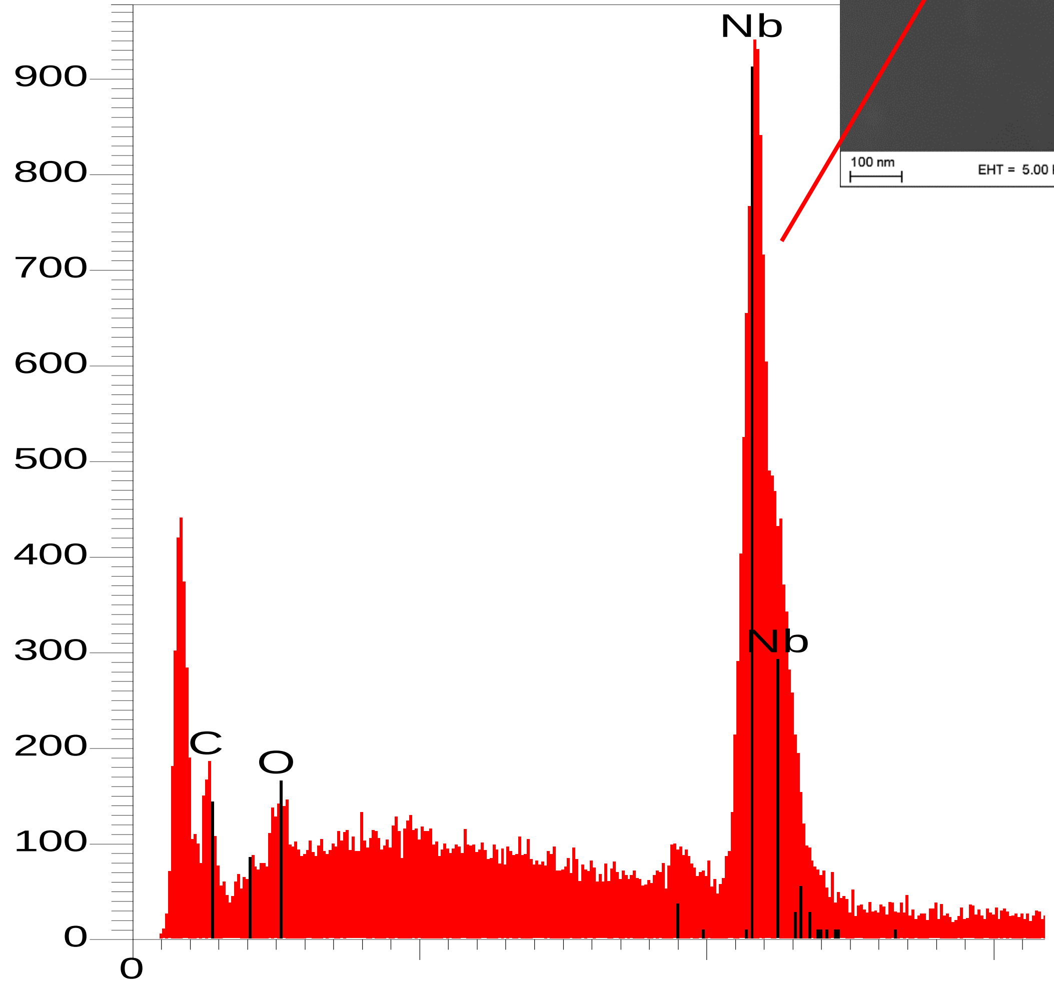
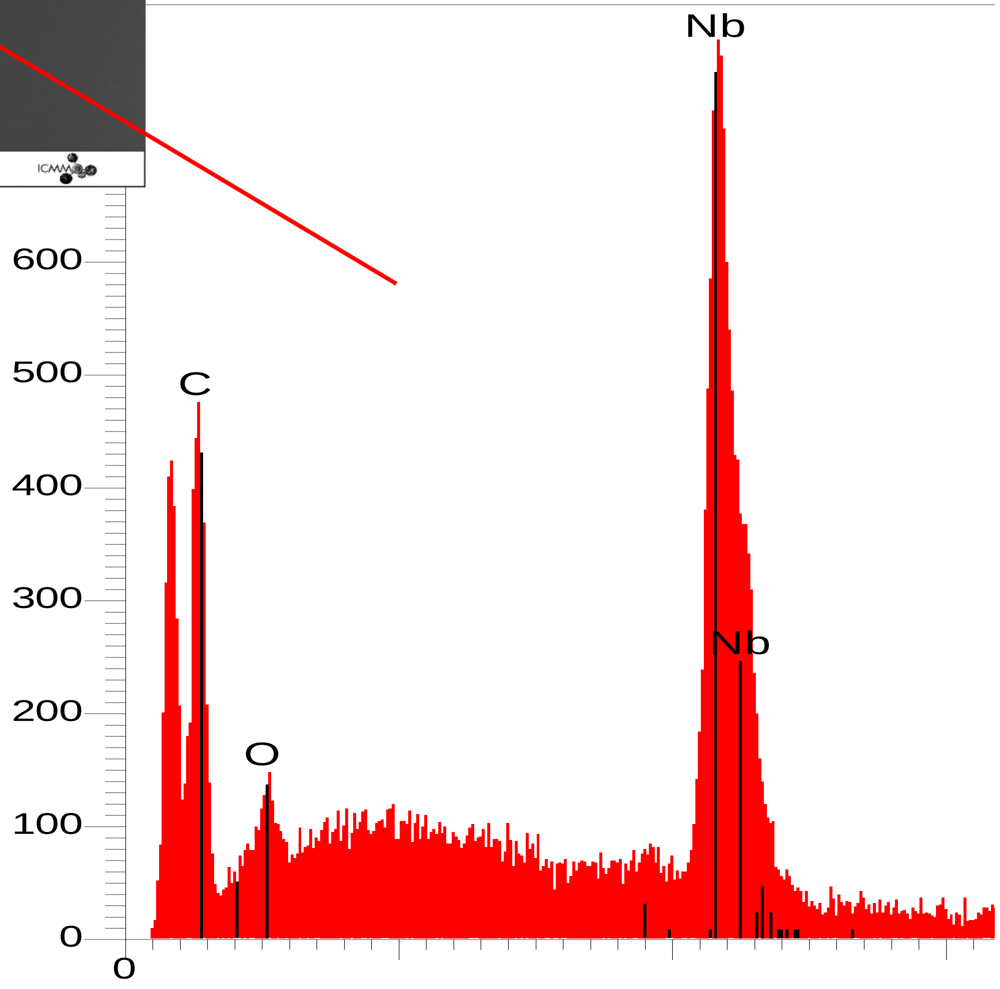
SEM micrographs and EDX



beta-Nb2C





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Comparison with Desy results

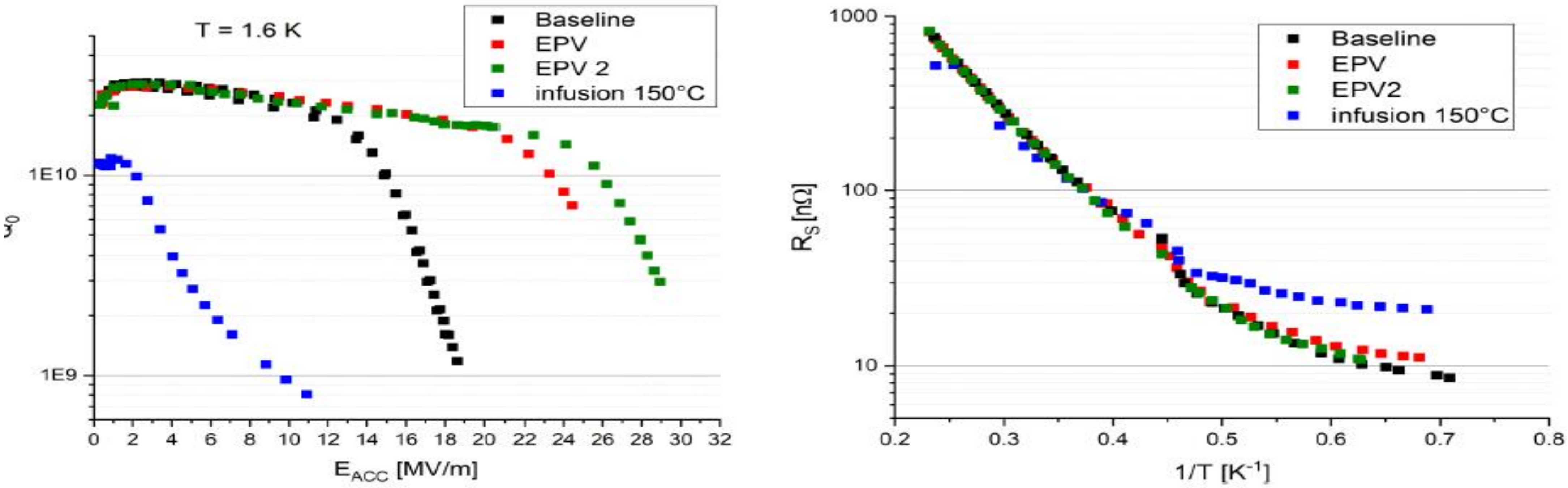
- ✓ Results very similar to the cavity tests performed at DESY after infusion
- ✓ Observed features: star-like precipitates during infusion identified as **beta-Nb_2C**
- ✓ We expect probably **a pollution or contamination due to impurities** that might be present in the nitrogen.
- ✓ We use high purity ALPHAGAZ2 grade Nitrogen: the initial purity of this nitrogen from the gas cylinde is sufficient but **it is probably polluted during the transport from the cylinder to the micrometric injectio valve.**

Detailed description of Desy nitrogen injection line:

- ✓ The nitrogen is boiled of from a N-reservoir and has a high purity (described in one paper). We use metallic injection line (stainless steel - up to the furnace, then a small piece is made out of copper). The overall length of the line is ~50m (estimated). Our valves are from Swagelok. We have a warm hand valve, electric regulating valve (open/close), a needle valve and again a hand valve. Is there anything specific you are interested in?

Saclay cavity 1AC03 results

Cavité 1AC03



- Baseline: BCP
- EPV=Electro-polissage vertical 50 µm
- EPV2=Electro-polissage vertical 50 µm
- Infusion: T_{sp} = 120°C, $T_{réelle\ cavité}$ = 147°C

P_{N2} = 2.10^{-2} mbar ; N_2 alphagaz 2

- Capots Nb: BCP ~ 100 µm + rinçage UHP

Phenomena involved in N-Doping, and N-Infusion

H. Padamsee SRF84-21 The technology of Nb production and purification

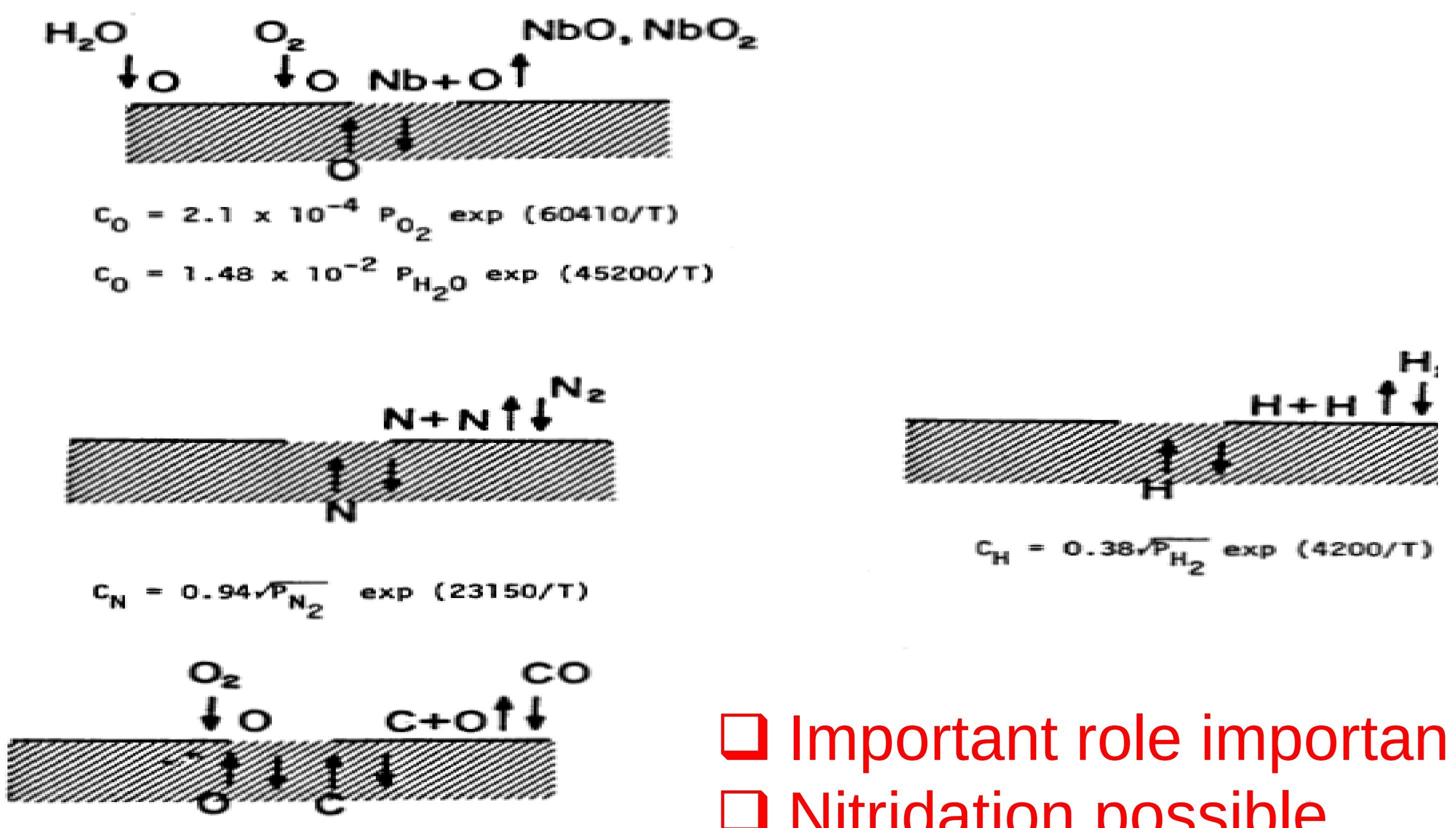


Table 4 - Outgassing reactions and equations for Nb.

$C_O = 2.1 \times 10^{-4}\, P_{O_2} \exp(60410/T)$

$C_O = 1.48 \times 10^{-2}\, P_{H_2O} \exp(45200/T)$

$C_N = 0.94\sqrt{P_{N_2}} \exp(23150/T)$

$C_H = 0.38\sqrt{P_{H_2}} \exp(4200/T)$

$C_C = 1.07 \frac{P_{CO}}{C_O} \exp(33600/T)$

$P_{O_2}, P_{N_2}, P_{CO}, P_{H_2O}$ in torr

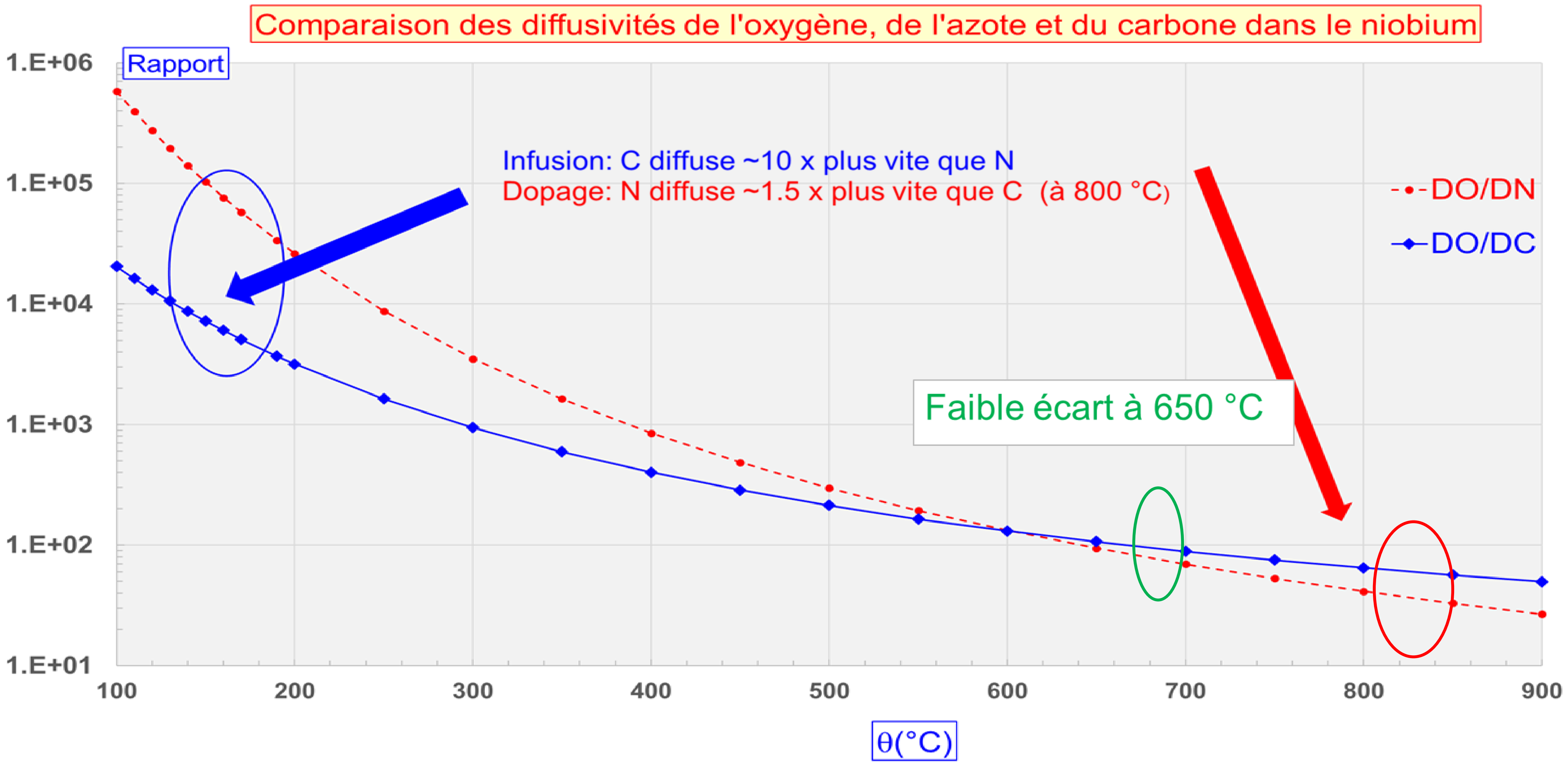
T in ° Kelvin

C_H, C_O, C_N, and C_C in wt ppm

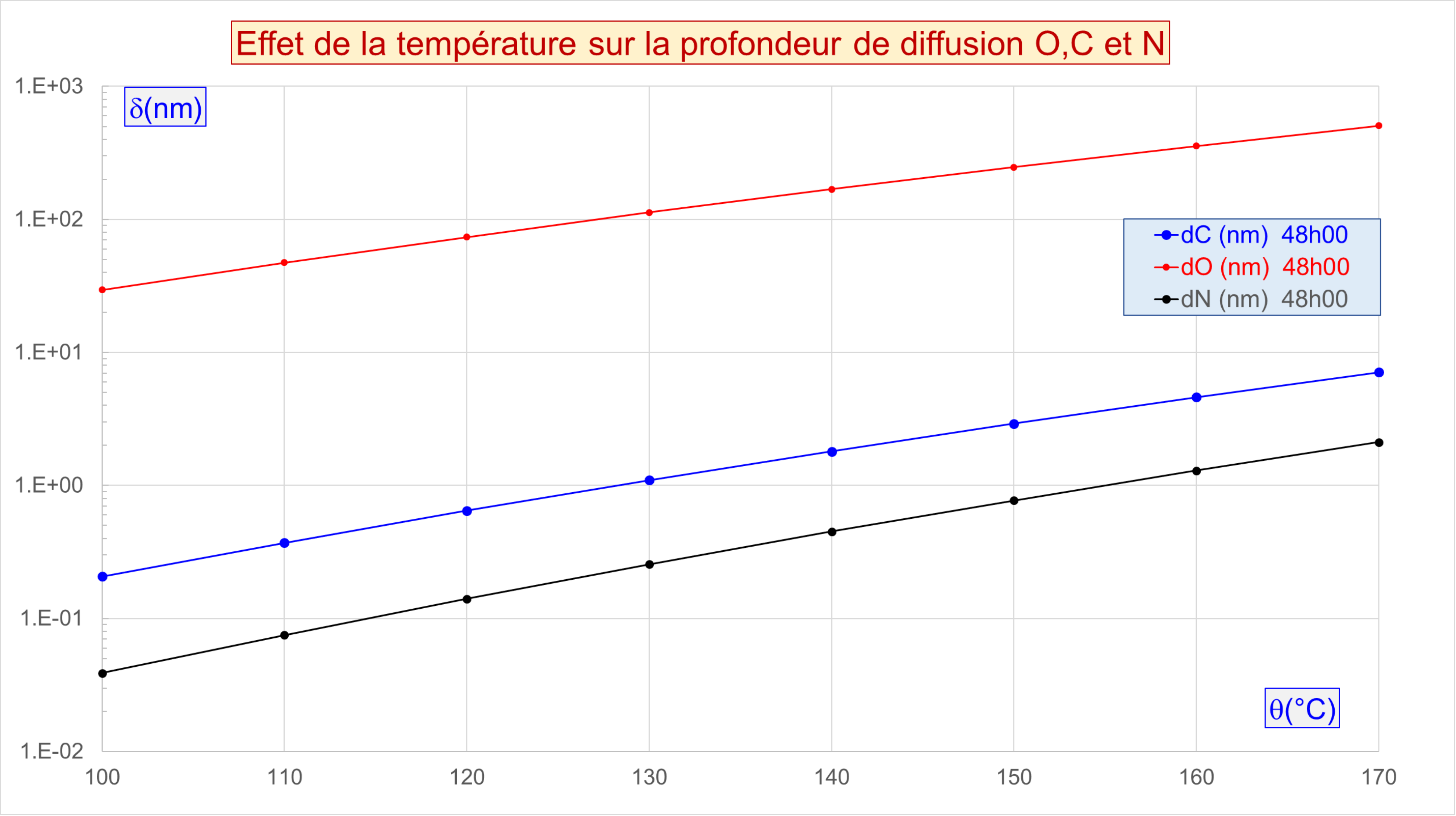
- ✓ Complex Phenomena
- ✓ Chemical recations
- ✓ Physical processes (Adsorption/desorption, diffusion,…)
- ✓ Depend strongly on operating conditions (pressure, temperature, impurities…..)

- ❑ Important role important of oxydes and water (O sources)
- ❑ Nitridation possible

Diffusion of O,N, C in niobium



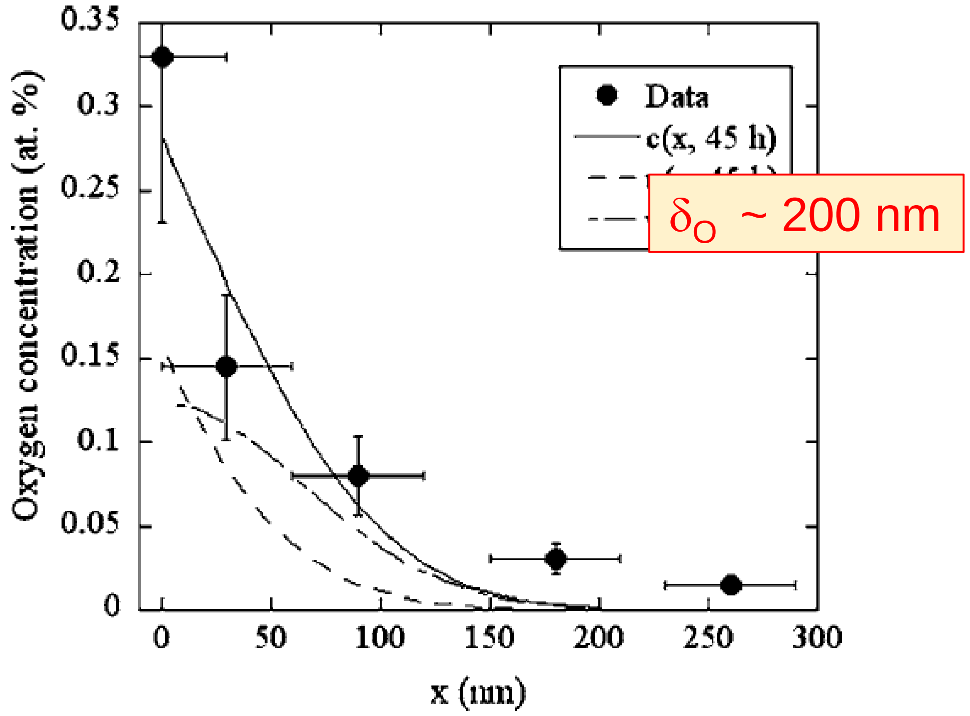
Infusion process : strong Temperature impact on diffusion



Strong temperature dependence of O, N and C diffusion in Niobium

θ(°C)	δ_O (nm)	δ_N (nm)	δ_C (nm)
120	74	0.14	0.65
140	169	0.45	1.8
150	248	0.8	2.9
160	357	1.3	4.6

Diffusion length during 48h00
Strong temperature dependence
Factor 5 -10 between120 °C and 160 °C



Oxygen Concentration Profile (deduced from RBCS)

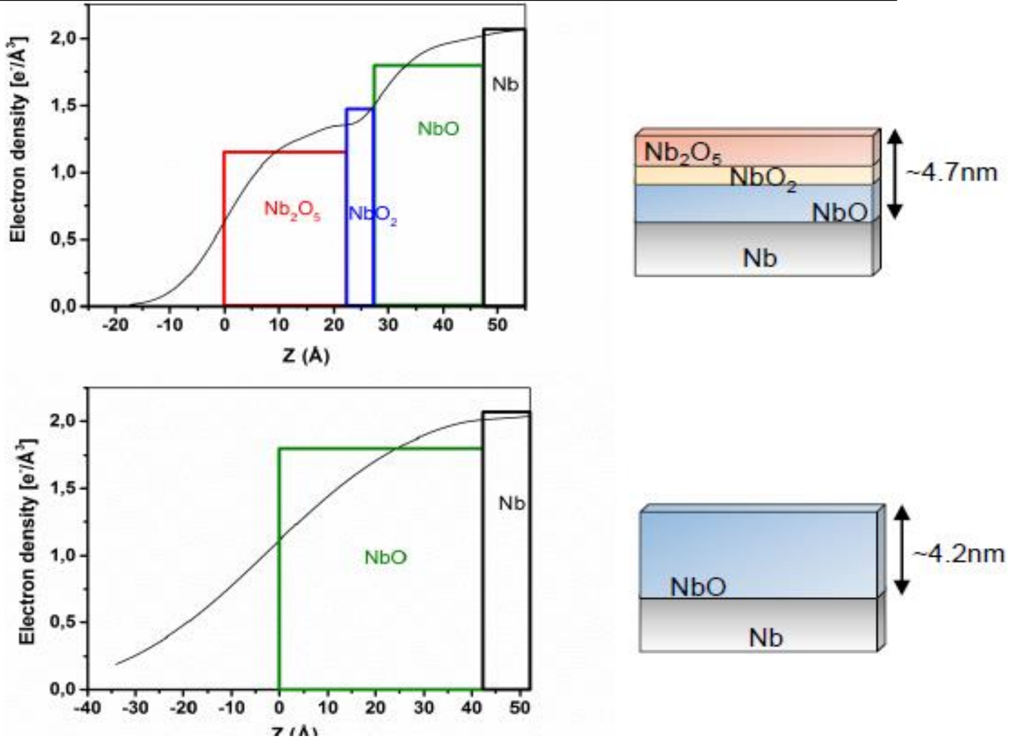
Improved oxygen diffusion model to explain the effect of low-temperature baking on high field losses in niobium superconducting cavities

G. Ciovati APL 89, 022507 (2006)

Oxydes, oxygen and High temperature annealing

Oxygen diffusion @ 650 °C
→ slight RRR reduction

Sample#	Initial O cont (µg/g)	After HT O cont. (µg/g)
4287-2	3.9	43.2
4288-1	3.9	45
4289-2	3.9	36.3
4290-2	3.9	31.9



- ✓ Diffusivity of O in Nb > 100 Diffusivity of N @ 650 °C
- ✓ Sensitivity of electrical resistivity to C_O et C_N are close
- ✓ Niobium : internal source of oxygen
- ✓ **Oxydes and chemical processes should be taken into account**

Diffusion of oxygen during heat treatment at 650 °C

D_O,Nb: diffusivity of oxygen in Nb

D_O,Nb=6.410^{-13} m²/s δ_O ~150 µm

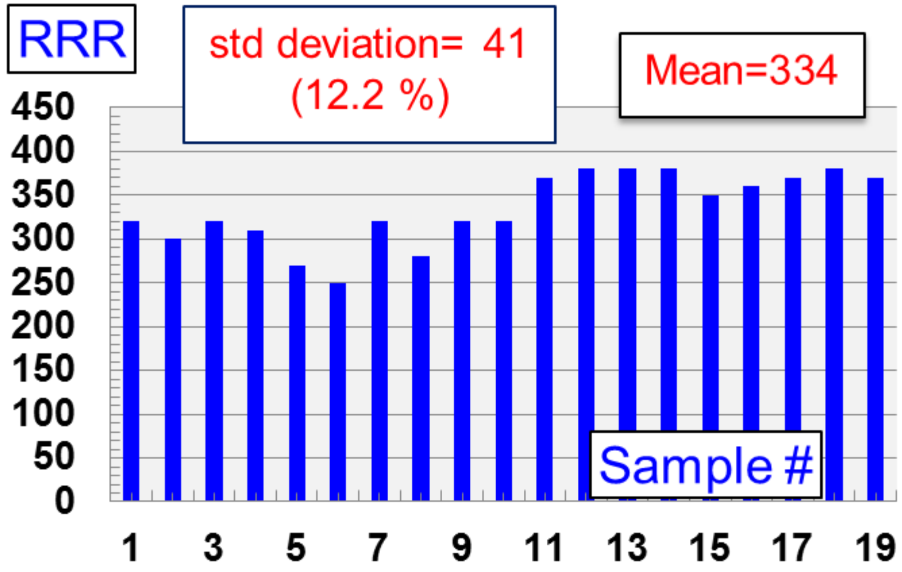
In Nb O diffusion > 100x N, C diffusion

Initial oxgen concentration ~ 4 µg/g

Initial oxgen concentration ~ 40µg/g

Consistent with measured O profile

Sample	RRR@10K As received	RRR@10K After HT @ 650 °C	ρ @ 10 K (Ω.m) As received	ρ @ 10 K(Ω.m) After HT
4287-2	320	292	4.50E-10	4.93E-10
4288-1	300	275	4.80E-10	5.24E-10
4289-2	342	315	4.21E-10	4.57E-10
4290-2	305	291	4.72E-10	4.95E-10



Slight RRR degradation is due to oxygen diffusion in Nb
Could reduce maximum E_{acc} if cavity is lmited by a quench (defect)

Effect of N-doping on Nb superconducting parameters and transport properties

Investigations tools

Conductivity

- Avoid significant degradation of bulk Nb purity
  - Absorption O, N, C
  - Diffusion of impurities or dopant (T_c ↓, Enlarged transition δT_c ↑, **k(T)** ↓

σ ↓ RRR ↓ → Elect. Resistivity & T_c

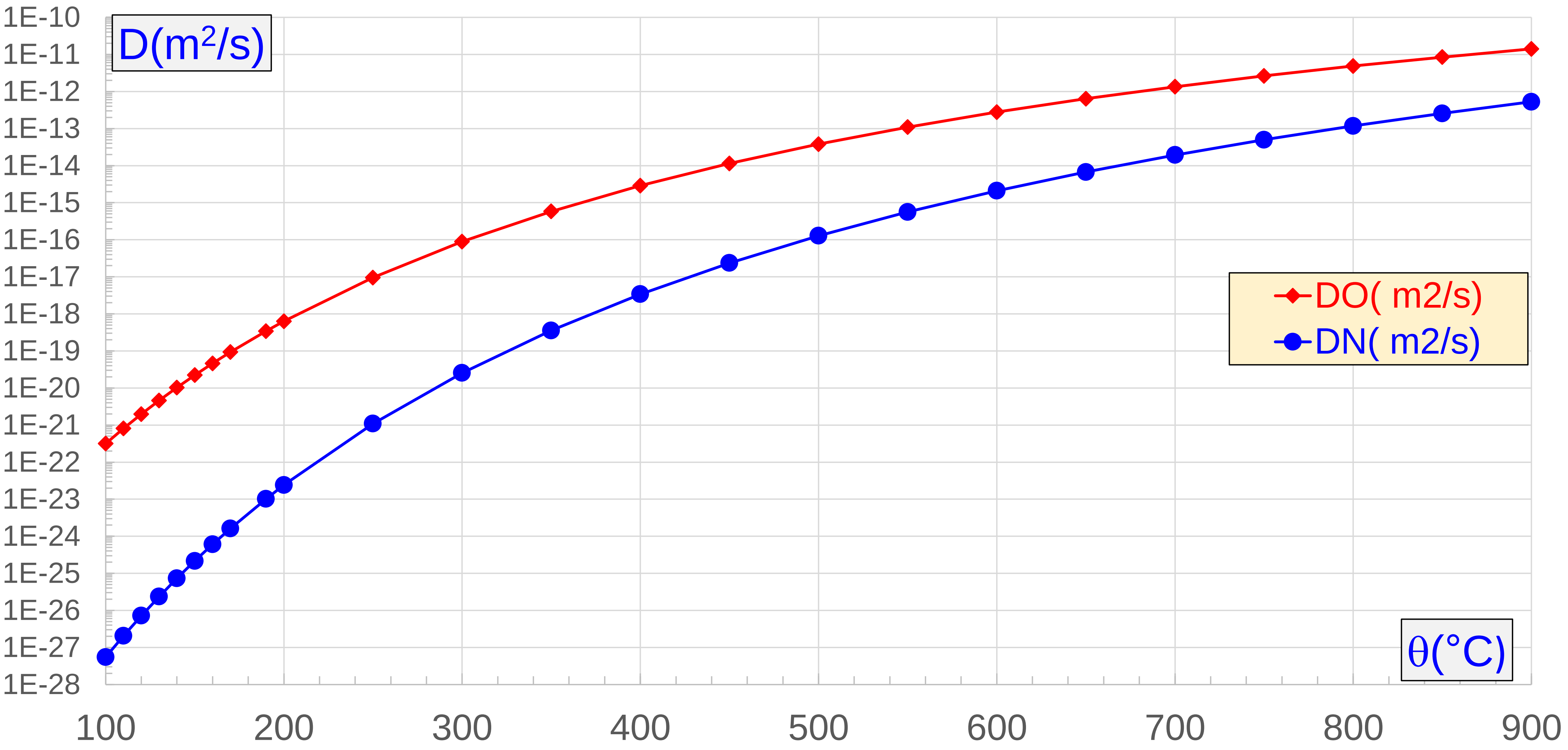
electrons mean path l ↓, ξ_P ↓, λ_P ↑ → $\Delta\lambda$ for T=4.2 K-9.26 K

- Hydrogen concentration ↓
- Reduced residual stresses → XRD
- Recristallization of Nb and restoration of RRR (hardening) → cristallography
- RF performances (Q_0 ↑, Eacc stable if quench due to defect Eaccmax ↓)

These Effect to be investigated on samples and cavities

BACK-UP SLIDES

Effet de la température sur diffusion d'oxygène de d'azote dans le niobium



Nitrogen infusion FNAL recipe

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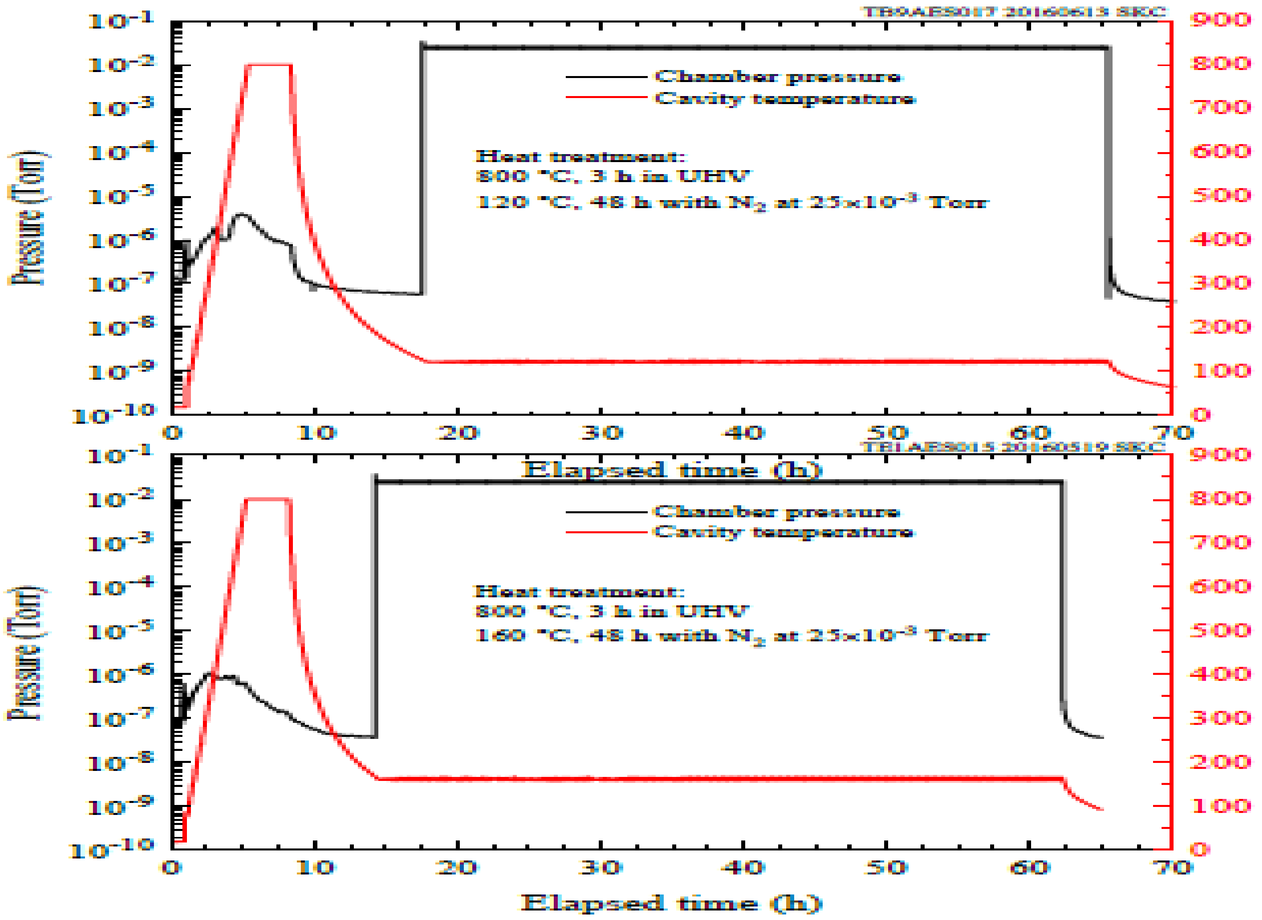
Unprecedented Quality Factors at Accelerating Gradients up to 45 MV/m in Niobium Superconducting Resonators via Low Temperature Nitrogen Infusion

A. Gasssellino et al.



θ(°C)

1- Soak at 800°C – 3h00

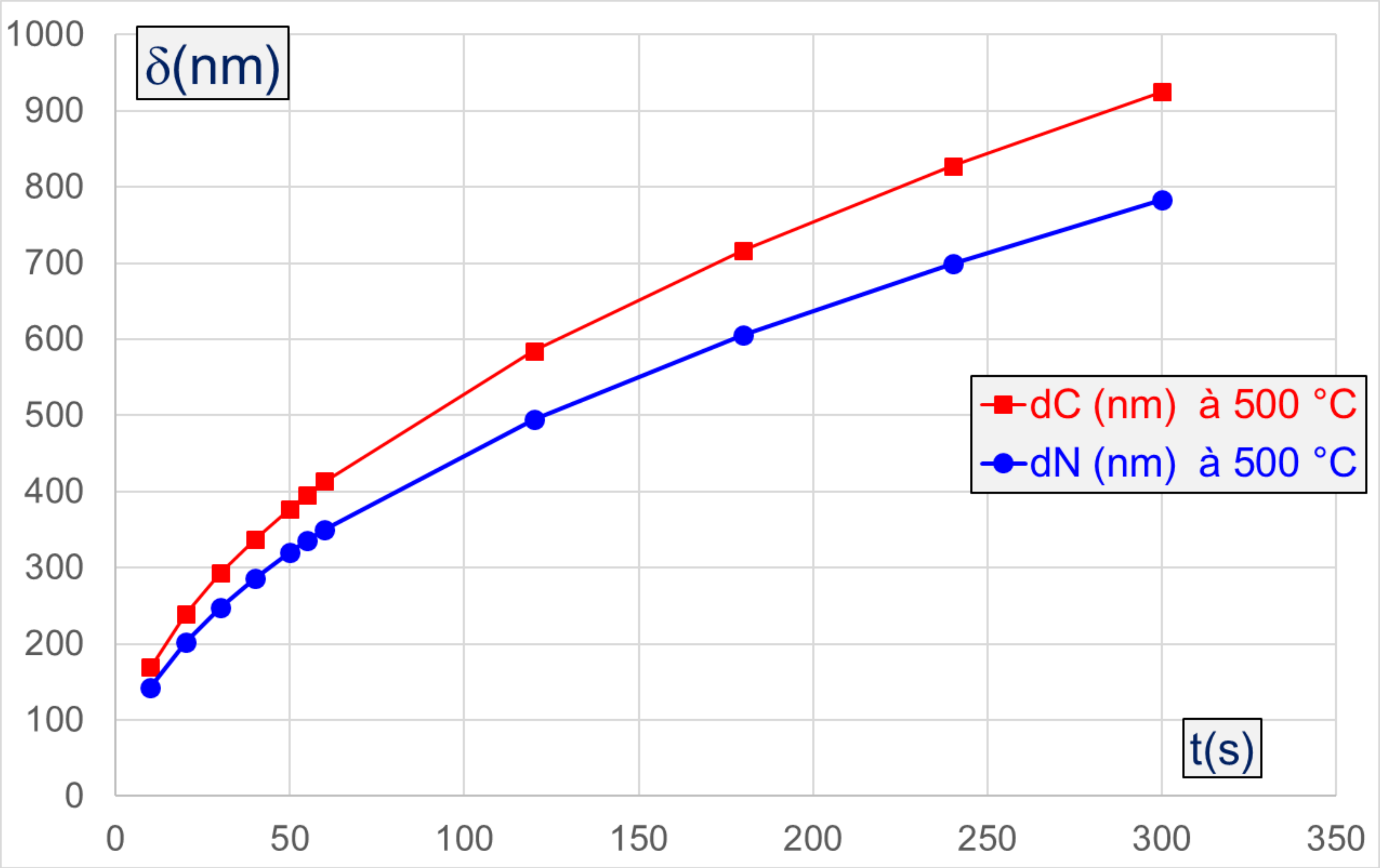
2- Radaitive cooling down to 160 °C

3- N_2 Injection N_2: P_N= 25 mTorr P_N regulation during 48h00

4- Pumping and radiative cooling.

La température d’infusion est très importante

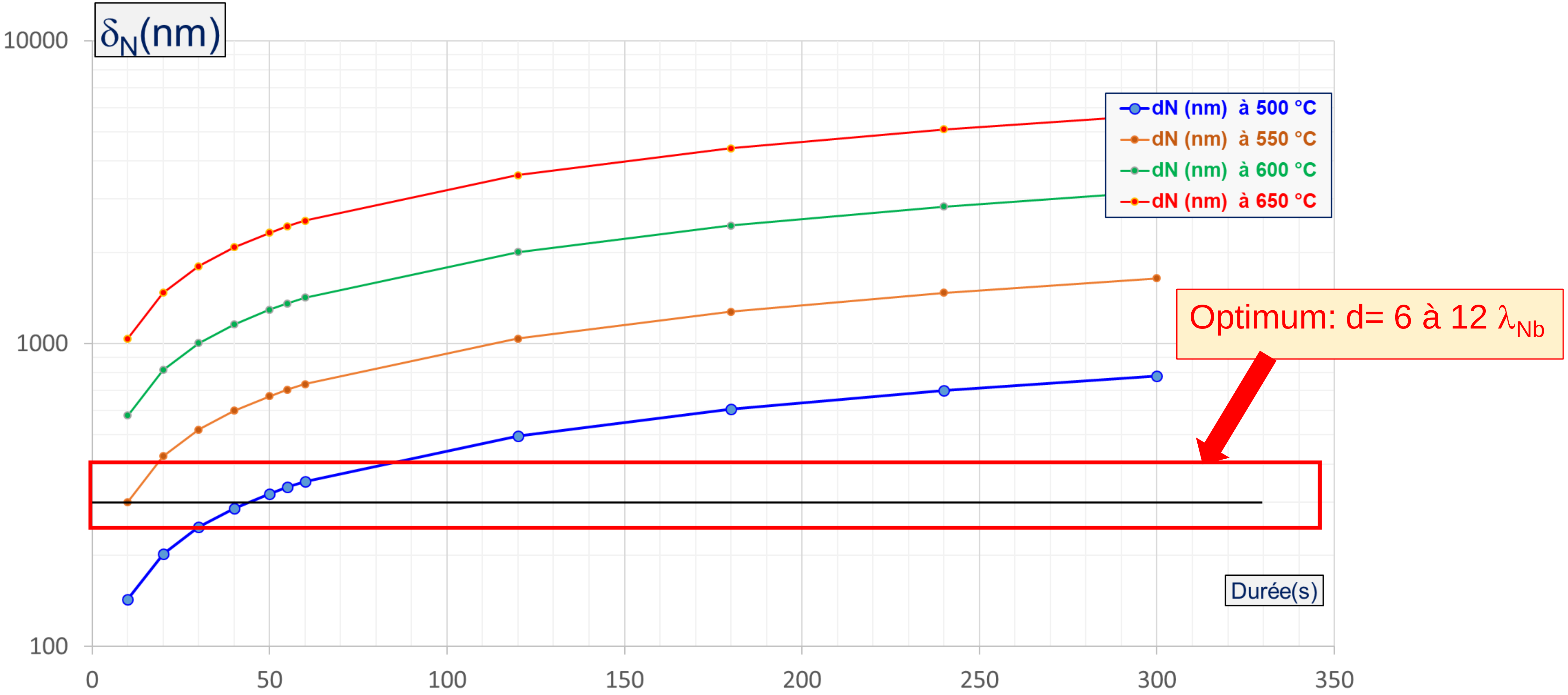
Profondeur de diffusion N et C versus temps



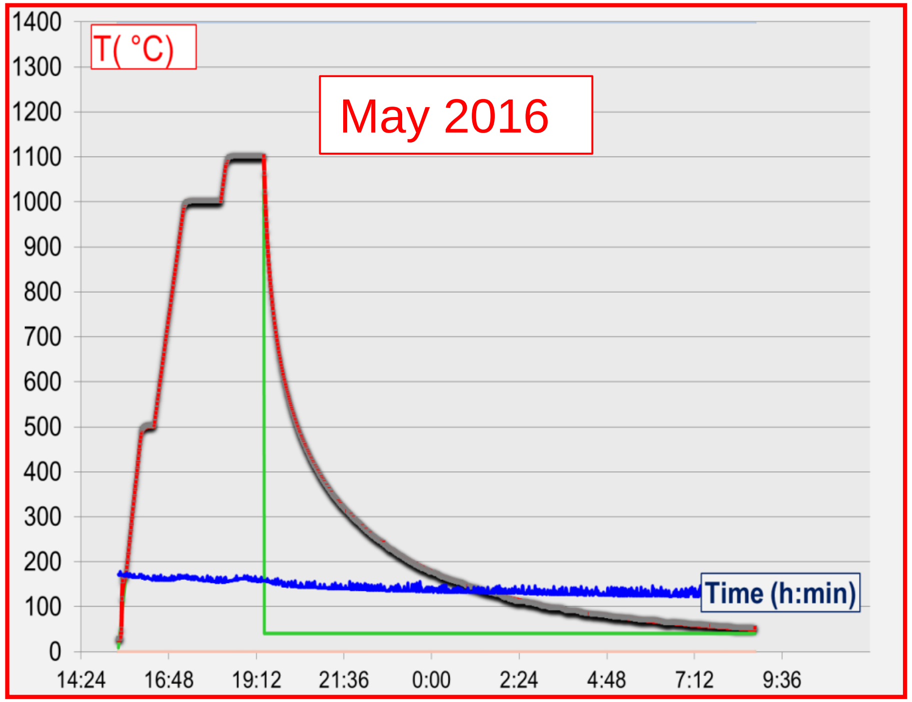
$$\delta(t) = 4\sqrt{Dt}$$

Oxygène ~ 10 à 20 fois plus entre 500°C et 650 °C

Dopage: profondeur de diffusion N optimum



Le four de l'IPNO



4.5 m^3 thermal chamber
Max Cavity Φ: 700 mm
Max lenght: 1600 mm
Molybdenum Heaters
5 Mo radiation shields

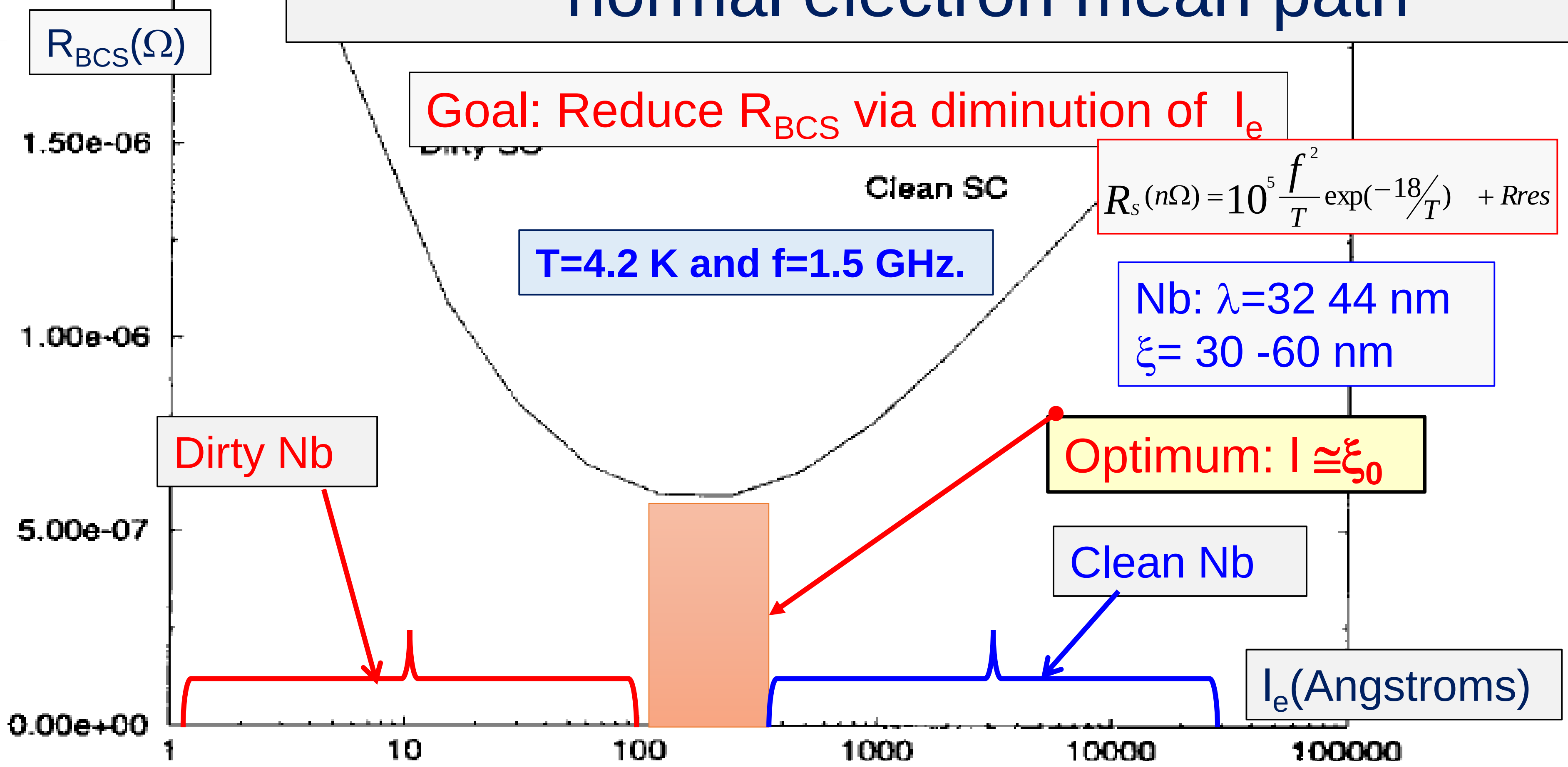
Ndoping valve-Gas flow @300K:
10^{-10} et 500 mbar.l.s^{-1}

- *3 heating zones*
- Heating rate: 1-10 °C/min
- *Max. temperature: 1400°C*
- Zone # 1 and #3: Temp. uniform (+/- 0.4 °C)
- Zone # 2: Temp. regulation $T_R = T_{set}$ +/-2 °C
- Stability in time : <+/-0.3 °C
- Pressure: 5.10^{-7} mbar- 10^{-6} mbar

Pumping

Cryo. pump (14000l/s – Hydrogen)
Roots pump (2050 std m^3/h)
Screw pump (650 std m^3/h)

Motivations for reducing the RF surface normal electron mean path



BCS surface resistance vs mean free path of normal electrons

How? Controlled pollution of Nb cavity RF surface: depth ~ 5 λ –10 λ

➡ **Nitrogen doping or infusion**

Confocal microscope : laser image

Sample infused inside cavity