ATOM-PROBE TOMOGRAPHIC ANALYSES OF NIOBIUM SUPERCONDUCTING RF CAVITY MATERIALS

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**Now at Imago Scientific Instruments, Madison, Wisconsin*

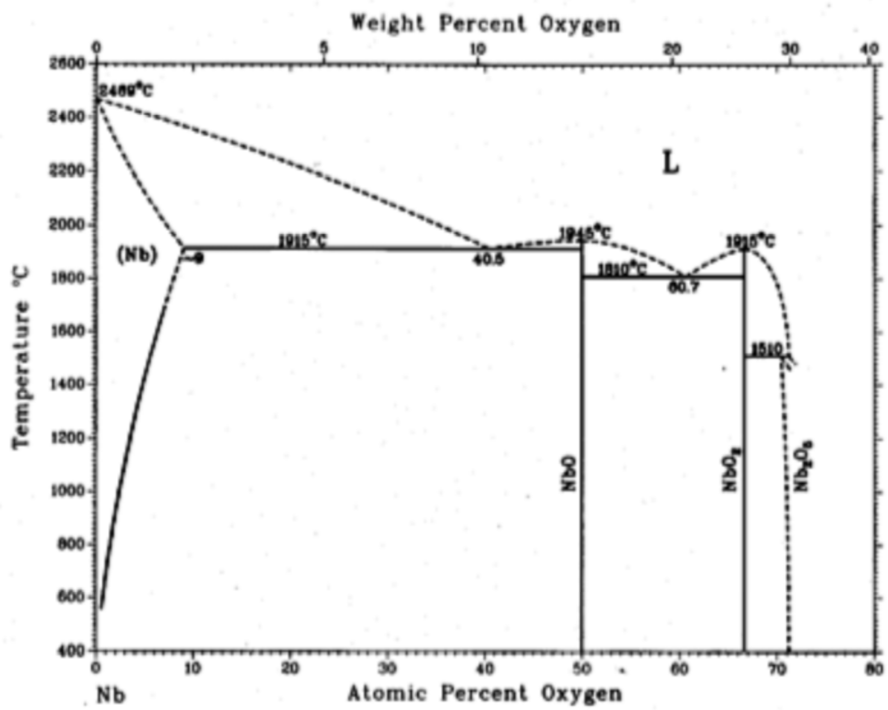
Agenda

- Background
  - Superconducting Nb rf cavities
  - Atom-Probe Tomography (APT)
- Specimen preparation
- Preliminary APT results
  - Three analyses (separate tips)
- Conclusions and next steps

The Nb-O phase diagram - a variety of different oxide phases can form

- NbO, NbO_2, and Nb_2O_5 are the thermodynamic equilibrium phases
- Other phases (e.g., Nb_2O_3 and Nb_2O) also reported
- Kinetic effects must also be considered

From Binary Alloy Phase Diagrams (2nd Ed.), ASM (1990)



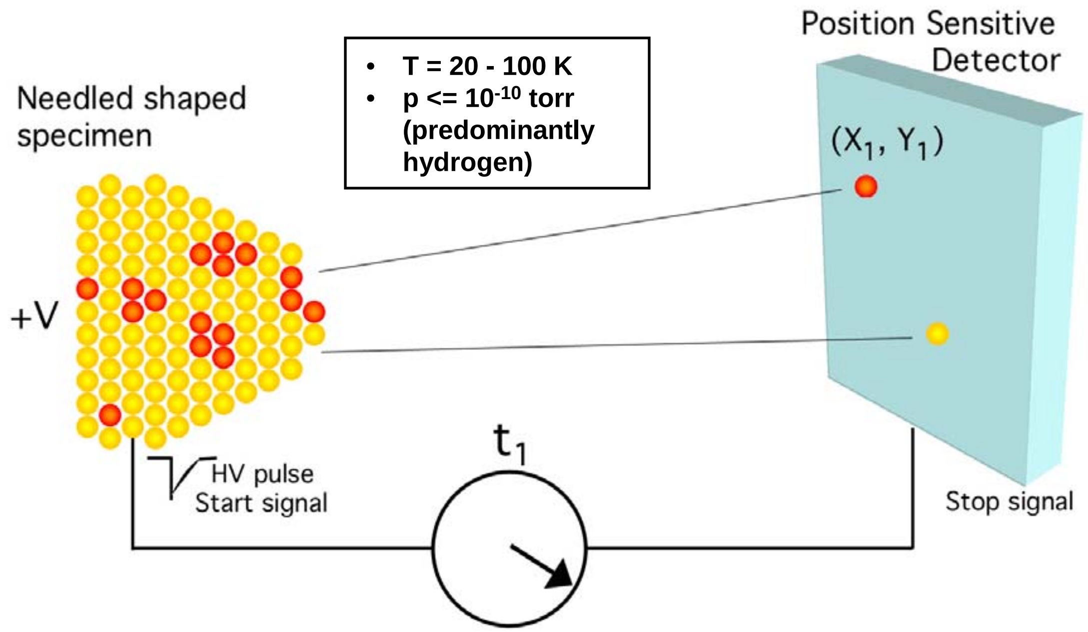
Phase	Composition (at. % O)	Pearson symbol	Space group	Prototype
(Nb)	0 to ~9	cI2(bar)	Im3(bar)m	W
NbO	50	cP6	Pm3(bar)m	NbO
NbO_2	66.7	tI96	I41/a	
Nb_2O_5	~71.4	mP99	P2/m	

Atom-probe tomography (APT) - schematic

The time-of-flight (TOF) of each field-evaporated ion is measured simultaneously with the position of the impact on the 2D detector

$E = V / (k\, r)$
[field enhancement]

- **T = 20 - 100 K**
- **p <= 10^{-10} torr (predominantly hydrogen)**



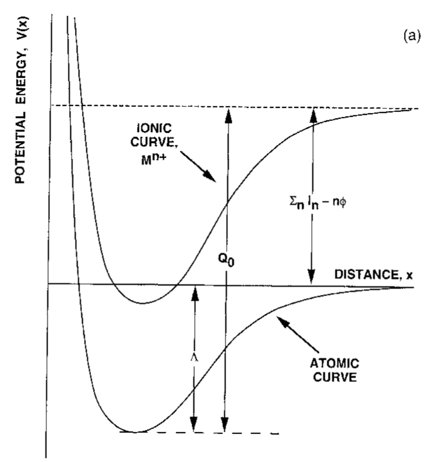
$$\frac{m}{n} = k\alpha(V_{dc} + \beta V_{pulse})\left(\frac{t + t_o}{d}\right)^2$$

- **Time of flight** → **Chemical nature**
- **Impact Position** → **Atom position on tip surface (projection microscope)**

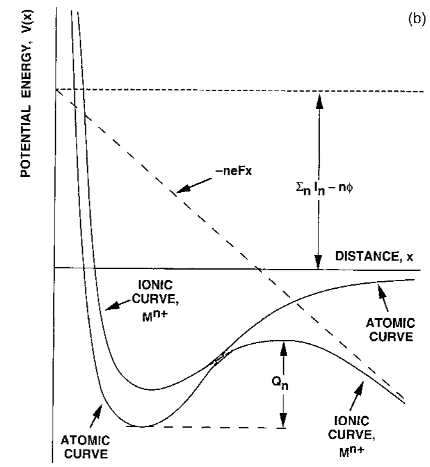
Field evaporation - schematic

- **A thermally-activated process involving the excitation of a surface atom over a Schottky hump in the presence of an electric field**
  - **In an atom probe, evaporation is controlled via the use of a high-voltage pulser, or high frequency (femtosecond) pulsing laser**

Without electric field



With electric field



In the presence of an, electric field, the ionic state is energetically favorable to the atomic state at distances away from the tip surface

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NUCAPT's new local electrode atom-probe (LEAP) tomograph takes atom-probe microscopy to a new level

- Increased data collection rate (up to 72 million ions hr^{-1})
- Expanded specimen geometry capabilities
- Analysis volumes of, for example, 50 nm x 50 nm x 400 nm (= 10^6 nm^3 = 10^{-3} μm^3)

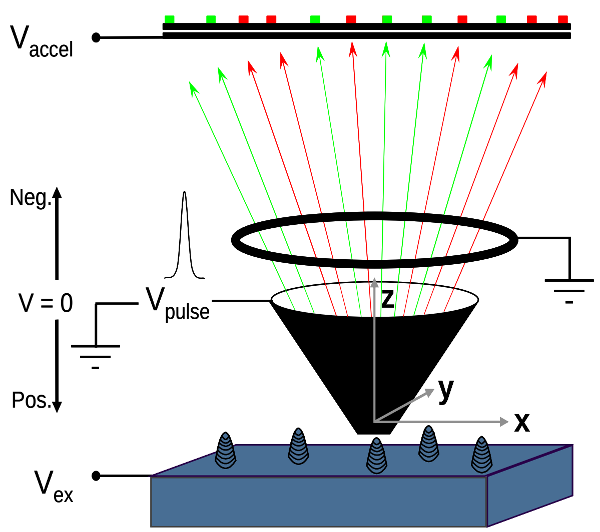
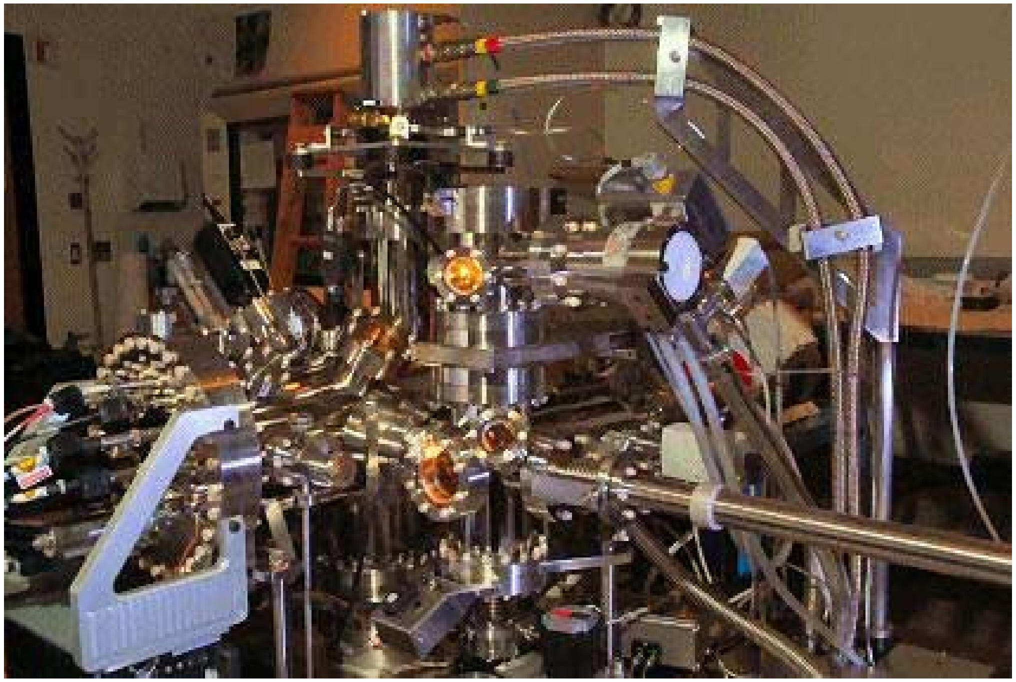


Figure courtesy of Imago Scientific Instruments



NUCAPT's LEAP Tomograph

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Specimen preparation

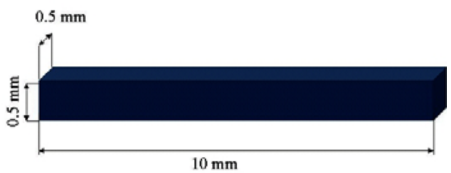
1. Electropolishing
   - 10% HF (48%) in 90% HNO_3 (68%)
   - DC voltage
   - "Drop off" technique
   - Keep things as clean as possible
     - Rinsing (UHP water)
     - Minimal time in air (stored in desiccator under dry N_2)

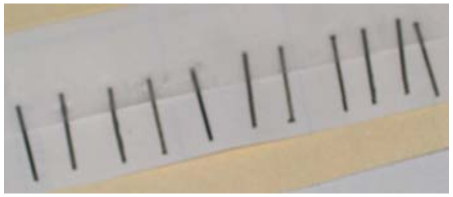
2. Buffered Chemical Polishing (BCP)
   - 1 : 1 : 2
     HF (49%) : HNO_3 (68%) : H_3PO_4 (85%)
   - No voltage
   - Replicating the setup at FNAL

3. Focused ion beam (FIB) milling at ANL to be done soon
   - "Site-specific" specimen preparation

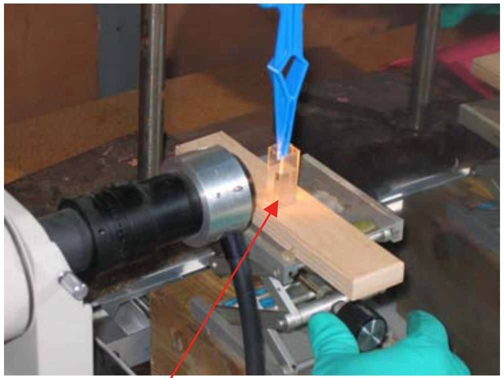
Specimen preparation - electropolishing and buffered chemical polishing

Step 1 - Machining Blanks (EDM at FNAL from Nb cavity material)

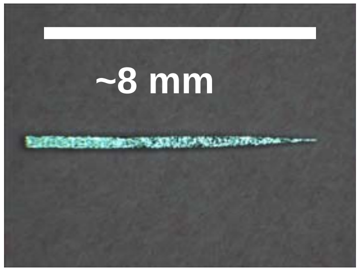




Step 2 - Polishing at FNAL



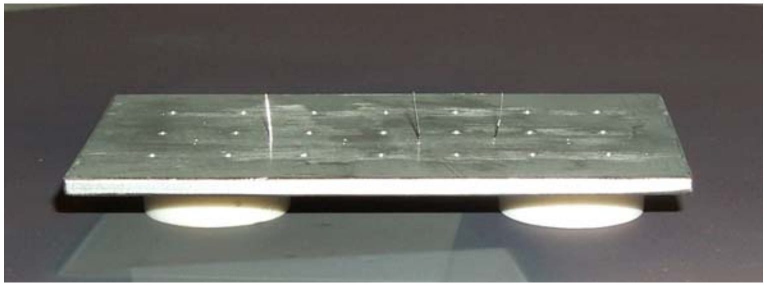
Rectangular cuvette with polishing solution (BCP)



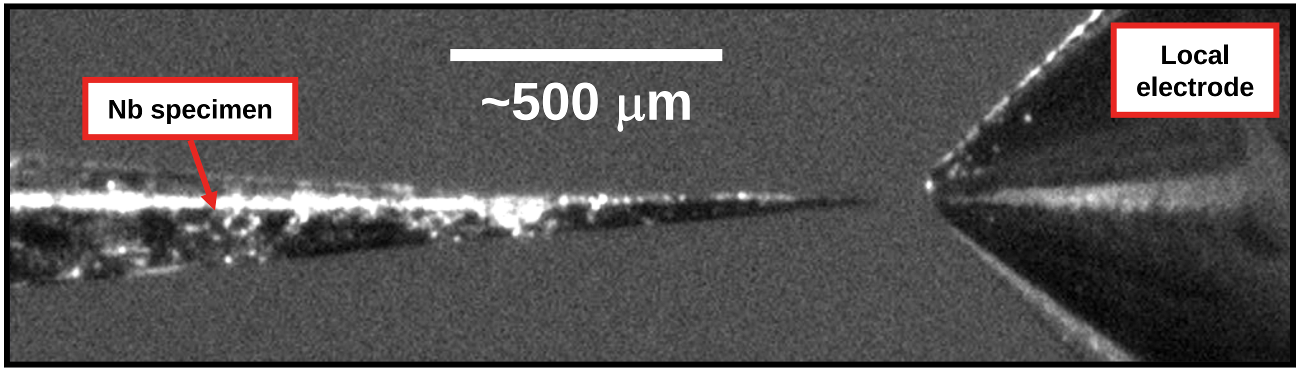
Stereo-microscope

Specimen preparation - electropolishing and buffered chemical polishing

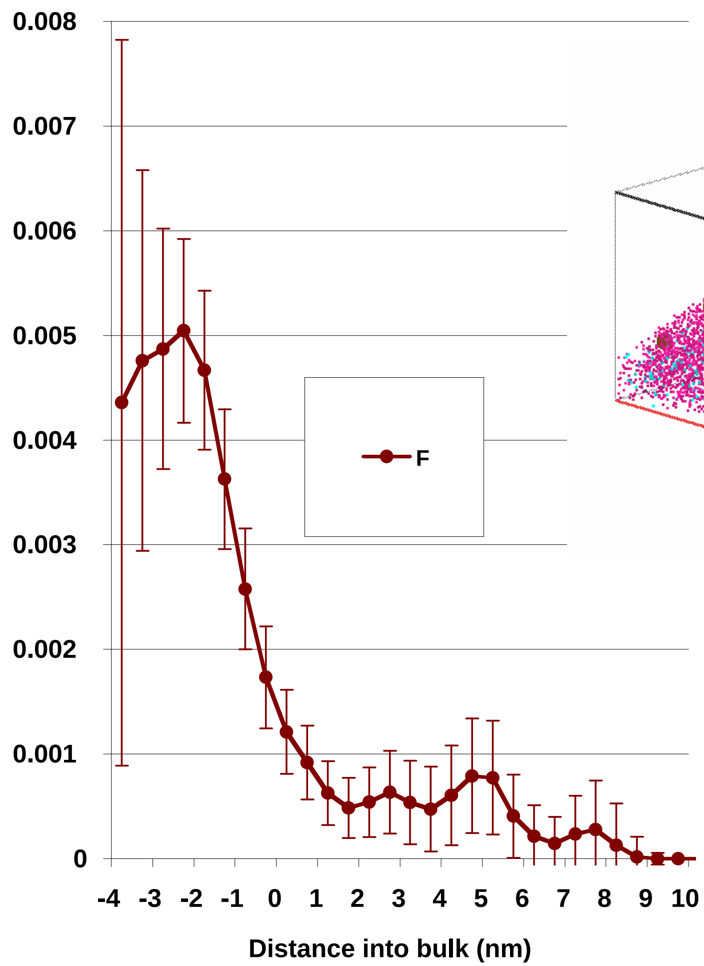
Step 3 - Heat treatment at FNAL

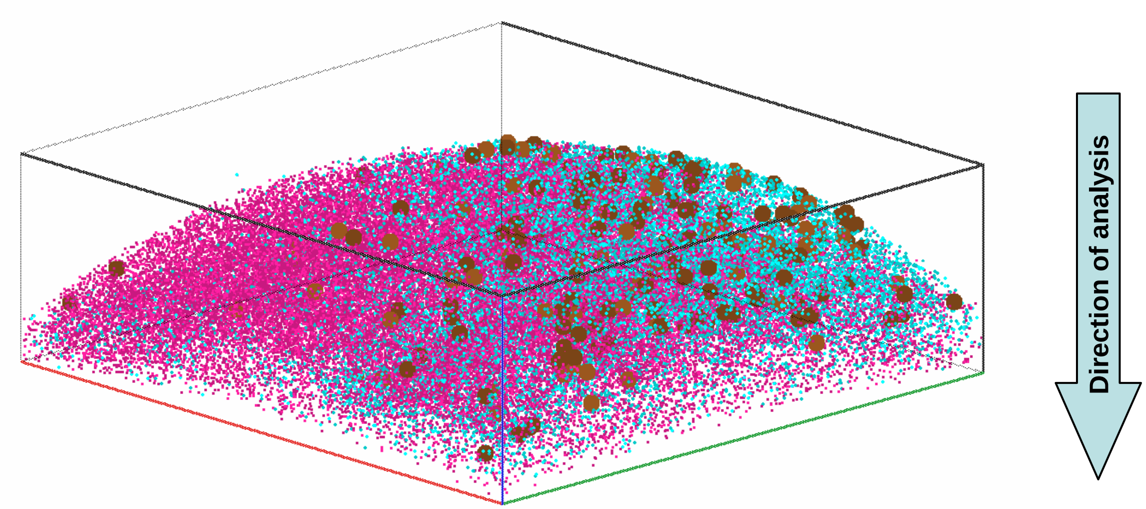


Step 4 - Alignment in the LEAP tomograph



Atomic sensitivity of the technique - individual fluorine atoms on and near the surface (propensity for the oxide)





27 x 26 x 9 nm^3
~95 k atoms

Oxygen

Niobium

Fluorine

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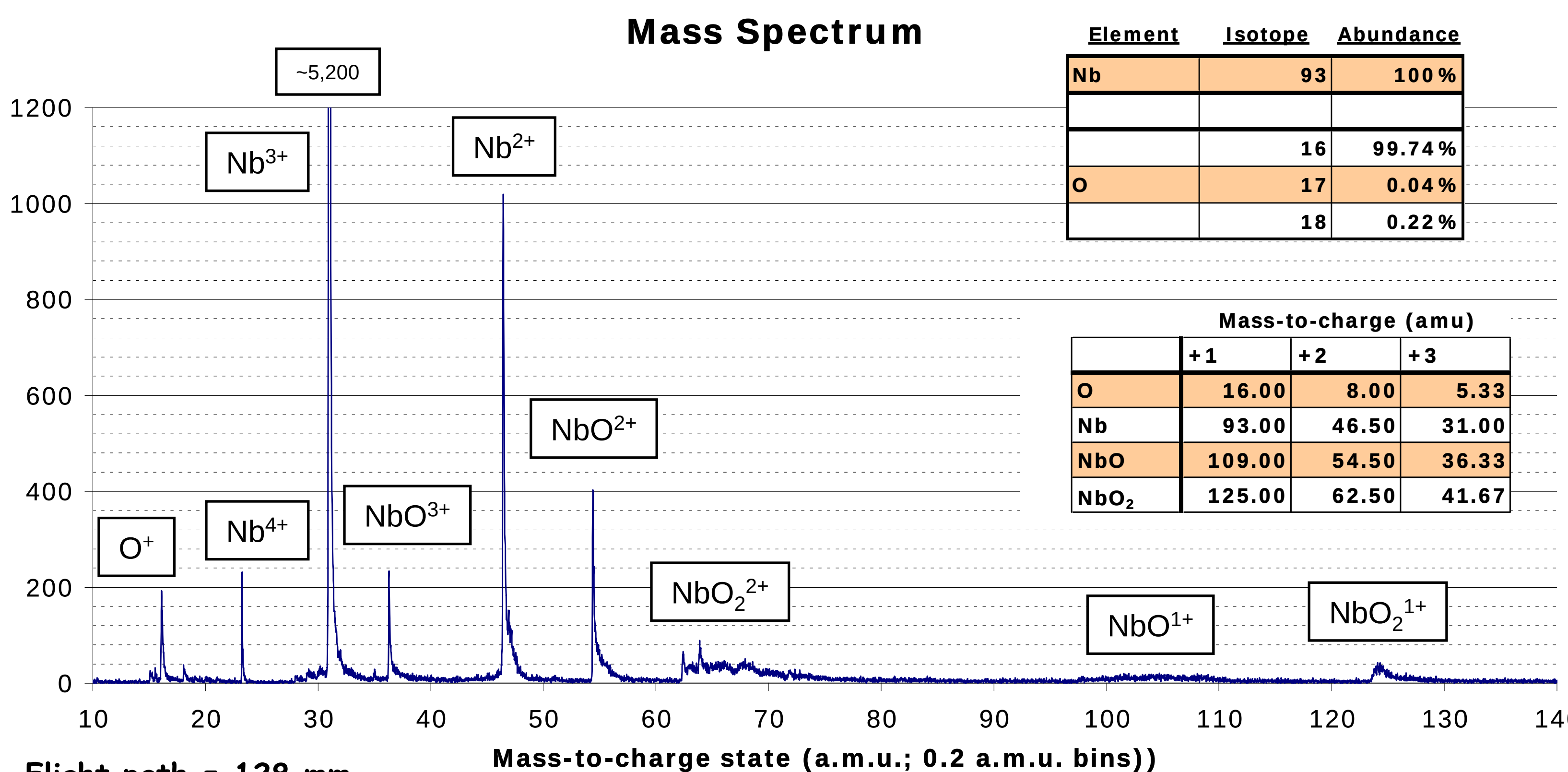
Complex mass spectrum - lots of complex ions



Element	Isotope	Abundance
Nb	93	100%
	16	99.74%
O	17	0.04%
	18	0.22%

Mass-to-charge (amu)

	+1	+2	+3
O	16.00	8.00	5.33
Nb	93.00	46.50	31.00
NbO	109.00	54.50	36.33
NbO_2	125.00	62.50	41.67

- Flight path = 128 mm
- Resolution ≈ 1/250 (FWHM)
- T = 50K
- f = 15%
- p ≈ 8 x 10^{-11} torr

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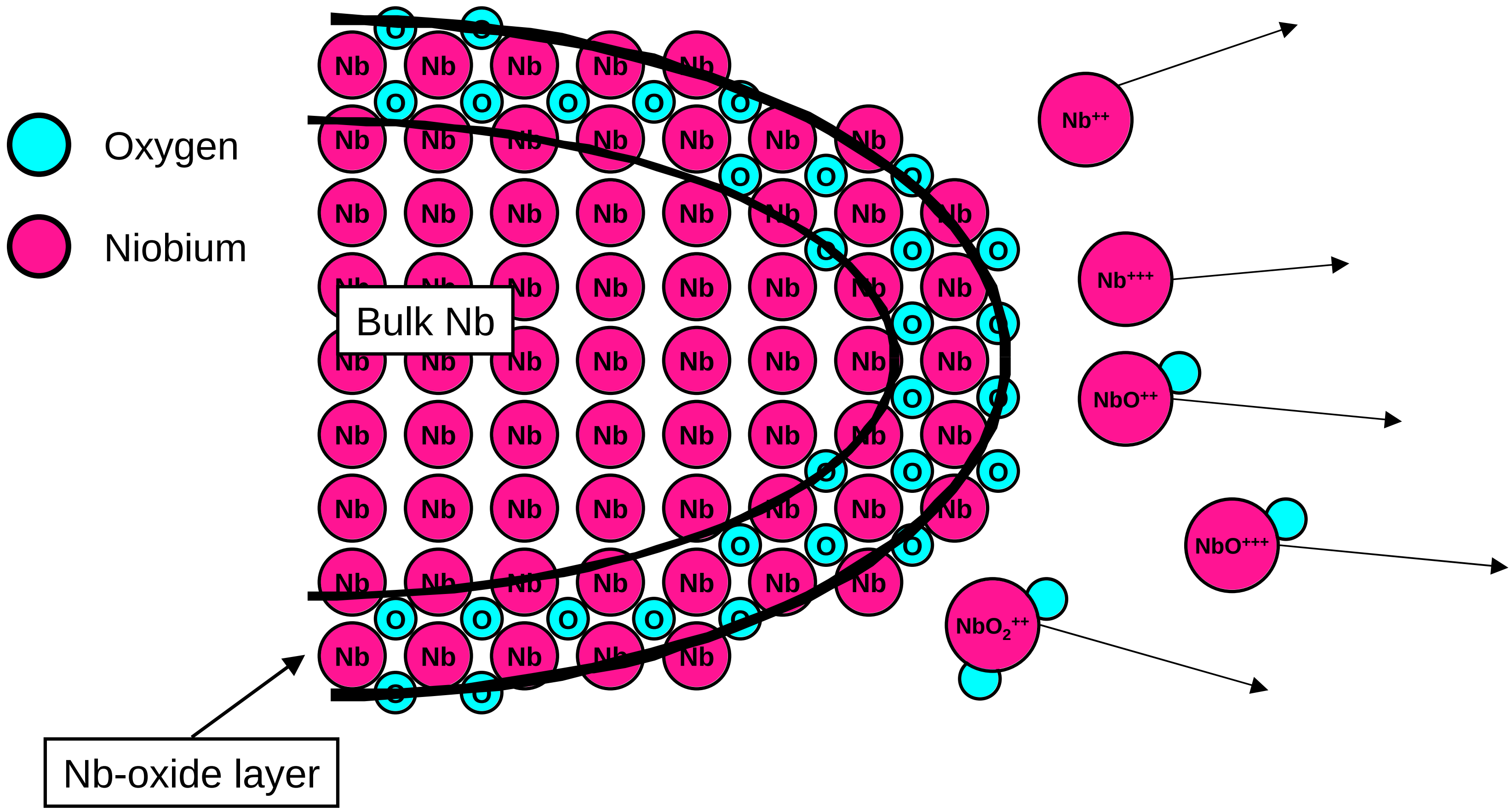
Evaporation of complex ions (*very* schematic) - many different complex ions are field evaporated from the oxide layer of the tip



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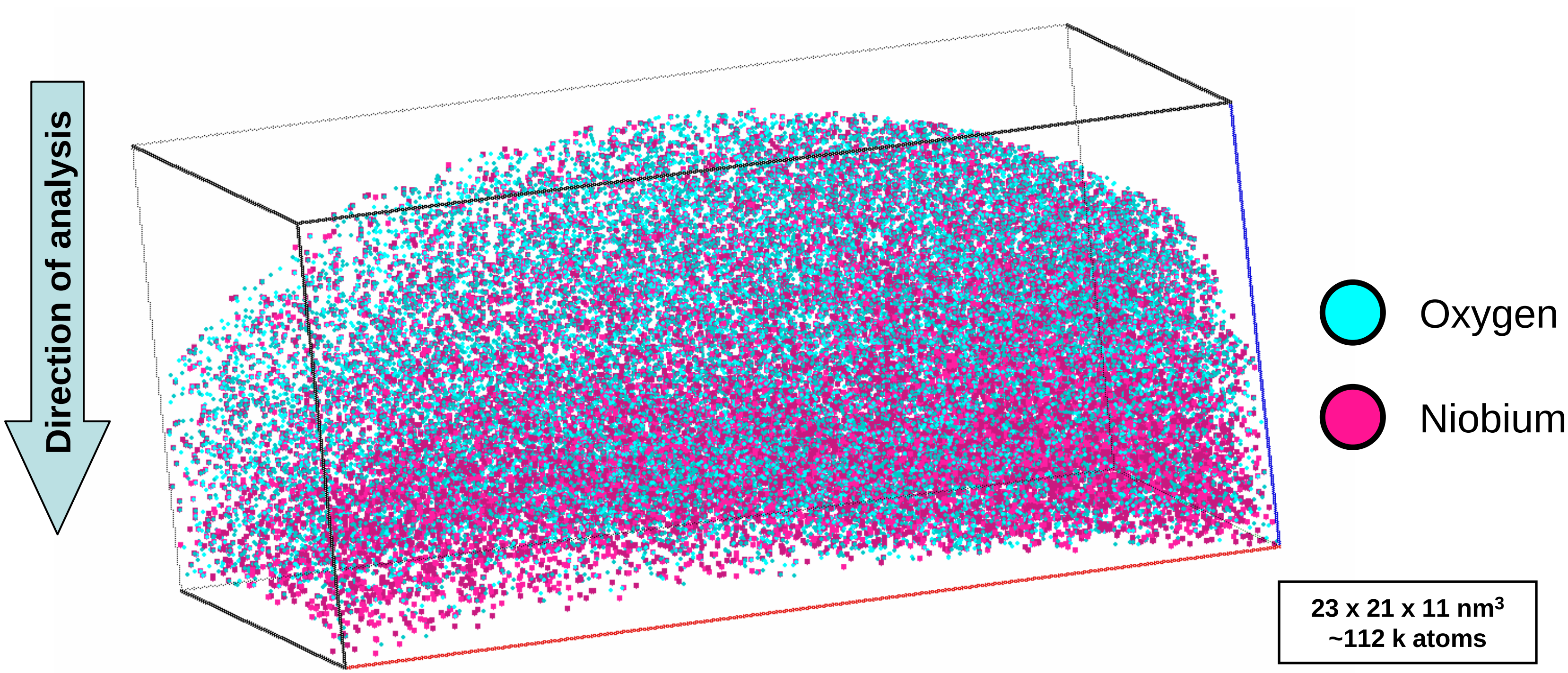
Atomic reconstruction of the transition through the oxide layer

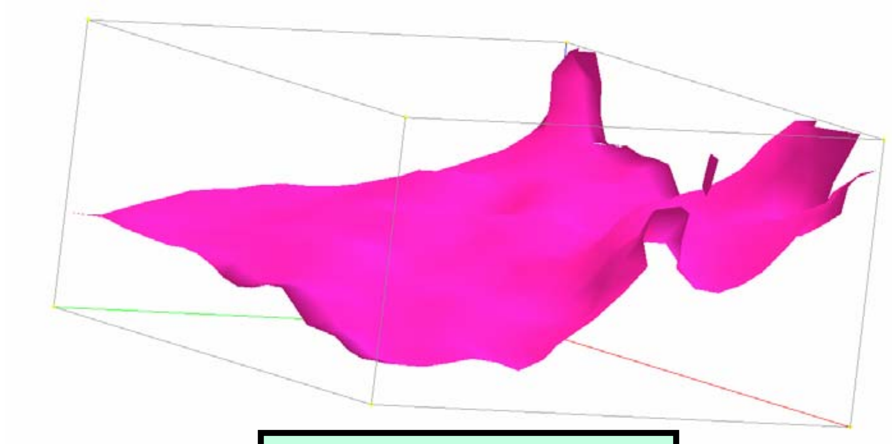


We see a clear transition from oxygen (cyan) to niobium (magenta) as we move along the analysis direction

A 30 atomic percent Nb isosurface gives a better representation of the spatial gradients in atomic concentration

Oxygen

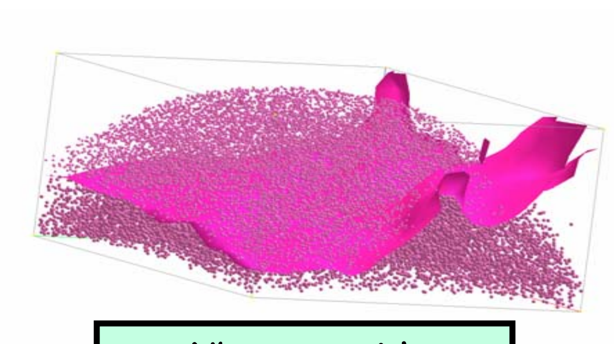
Niobium



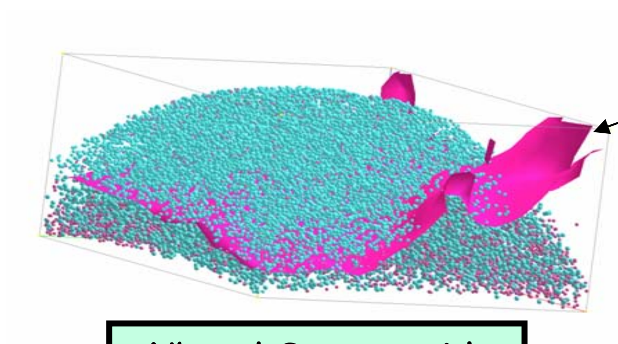
23 x 21 x 11 nm^3
~112 k atoms

30 at. % Nb isosurface

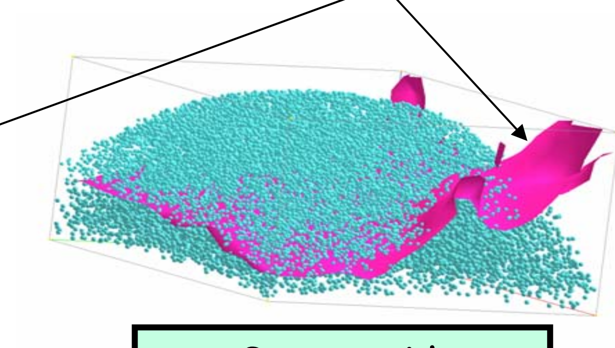
Extraneous surfaces (not important)



Nb atoms with 30 at. % Nb isosurface



Nb and O atoms with 30 at. % Nb isosurface



O atoms with 30 at. % Nb isosurface

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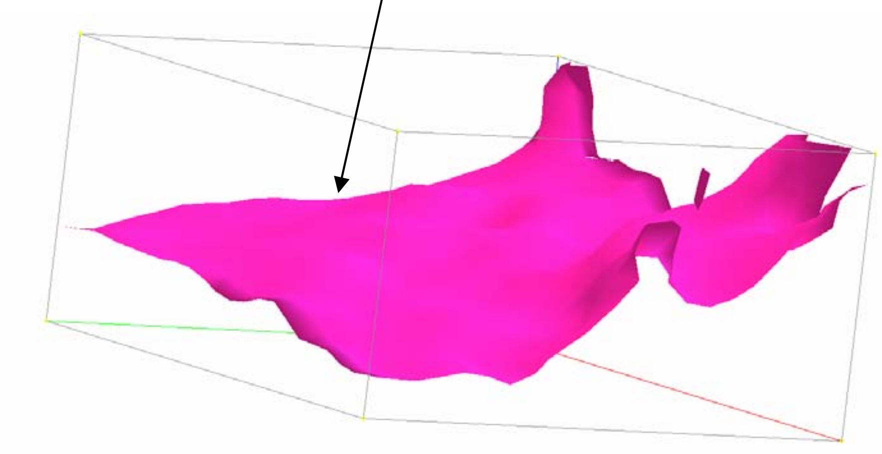
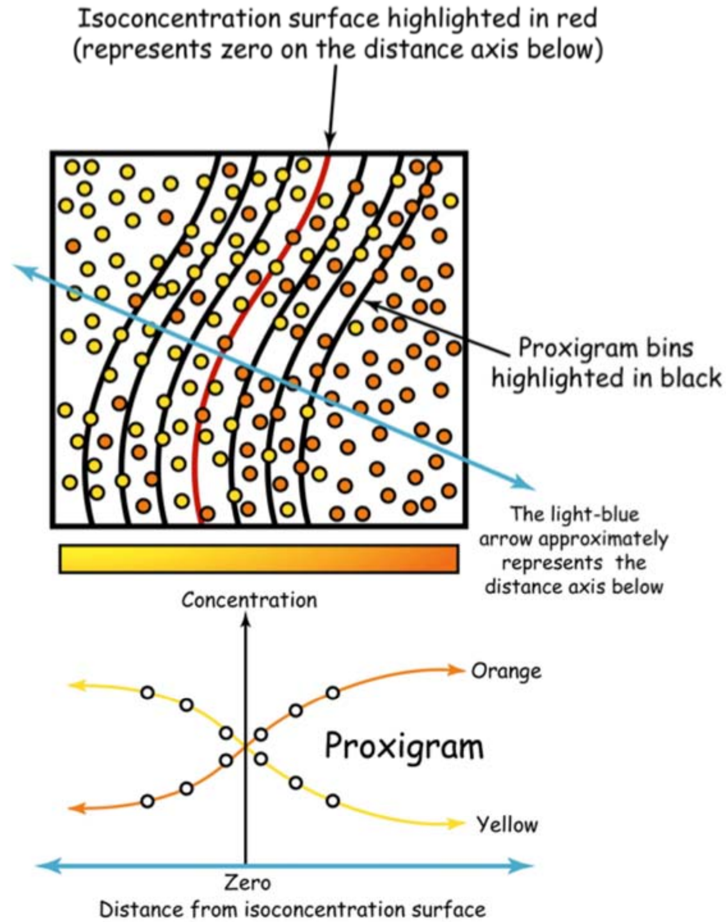
The proximity histogram (proxigram) allows for the determination of quantitative concentration profiles relative to the position of an irregularly-shaped interface

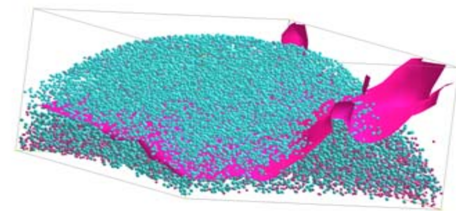
30 at. % Nb isosurface

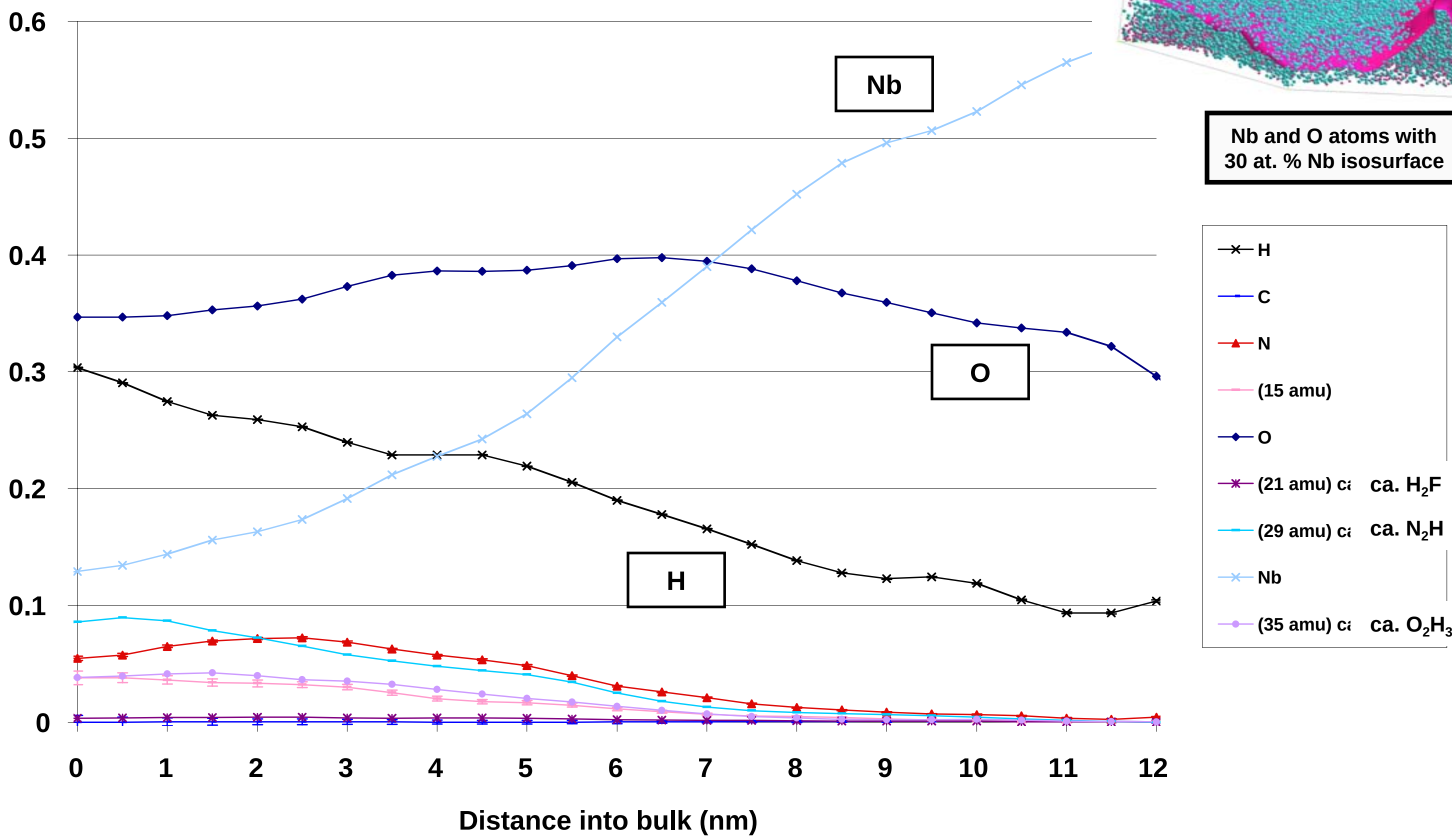


23 x 21 x 11 nm^3



30 atomic percent Nb proxigram - we see the transition from oxygen to niobium





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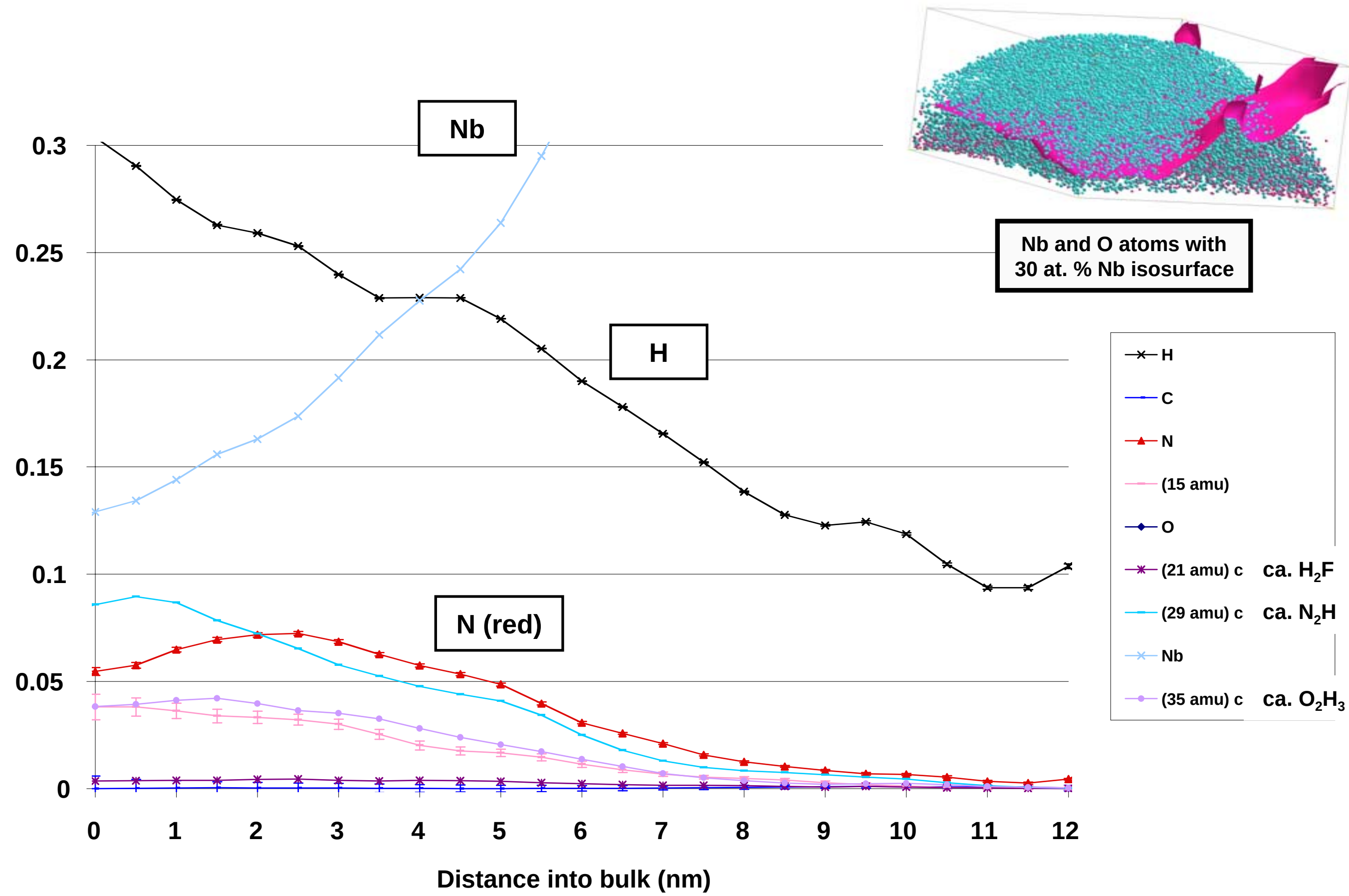
Hydrogen, residual gas atoms, and other "UFO" peaks make up nearly 50% of the ions collected



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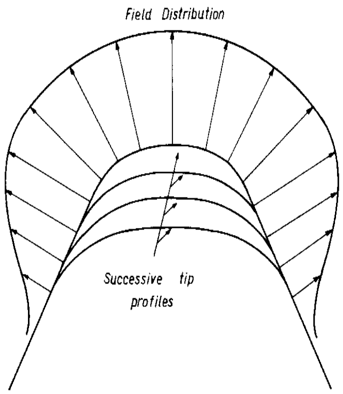
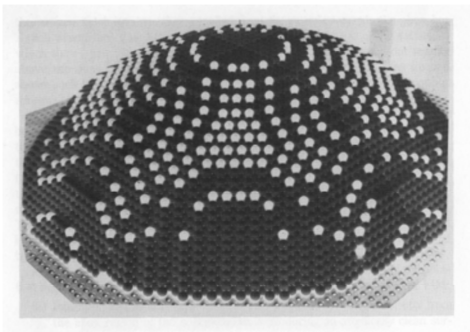
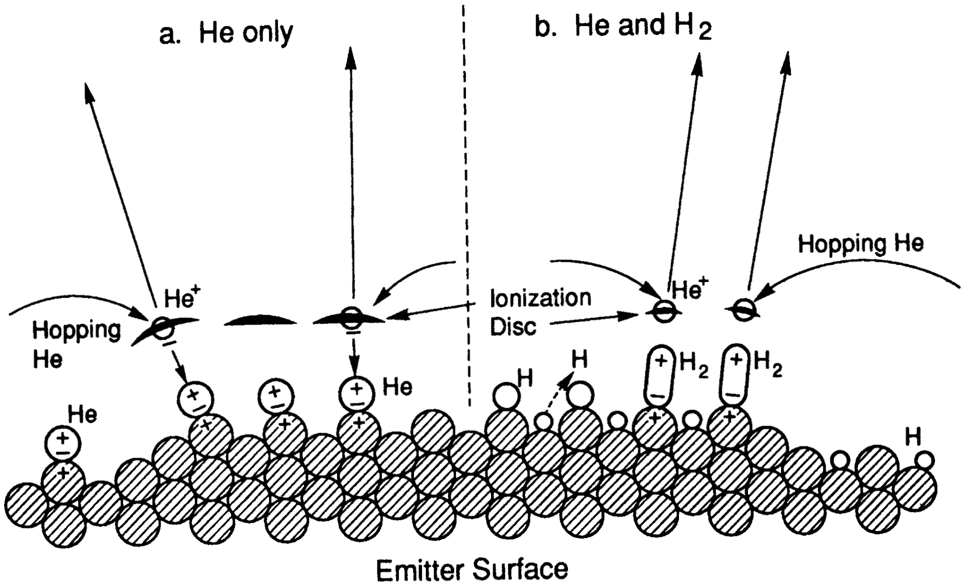
Hydrogen and residual gas atoms can come from "outside the specimen"



Electric field distribution on a atom-probe specimen (schematic)



Ball model of an atom-probe tip surface (schematic)



Field-ionization of gas atoms on an atom-probe tip surface

From Miller et al., (1996)

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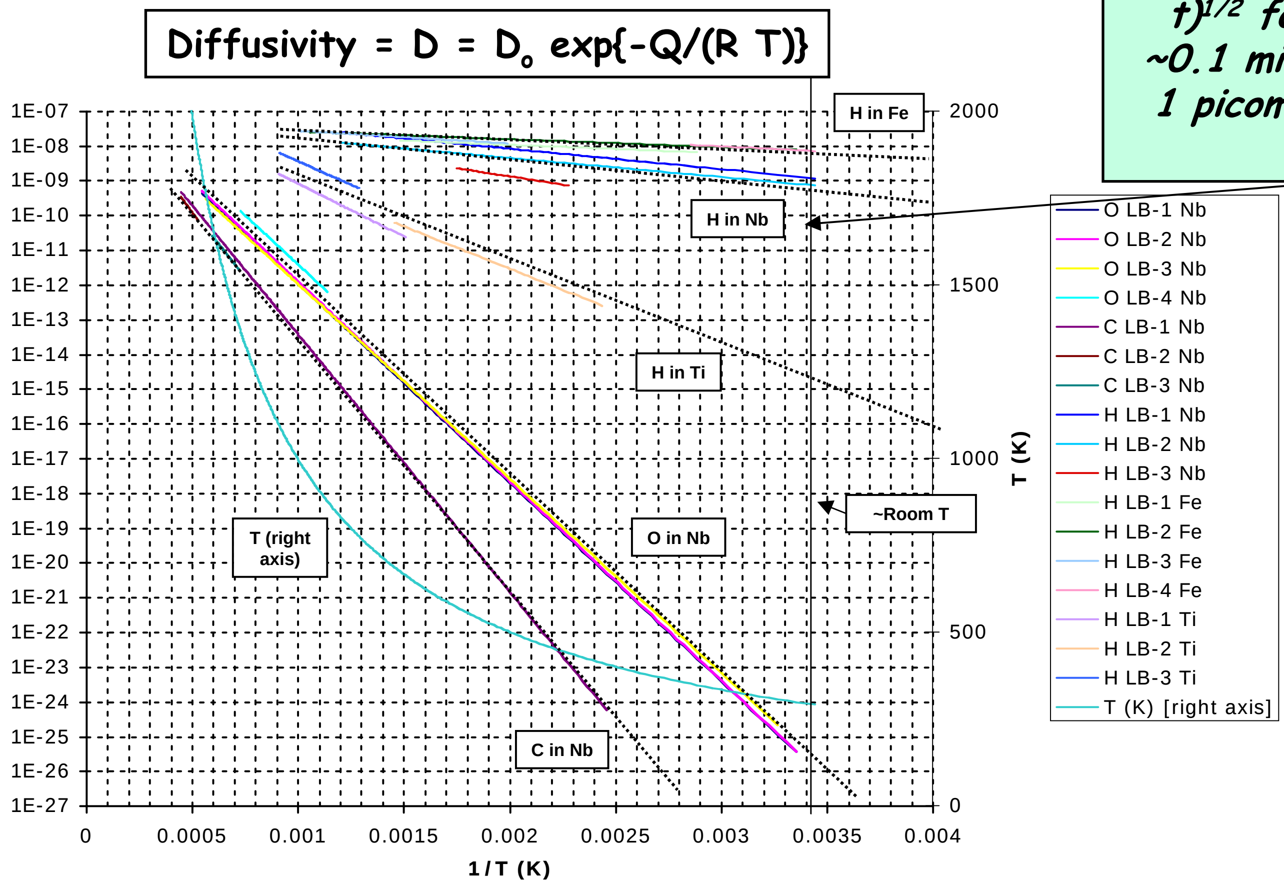
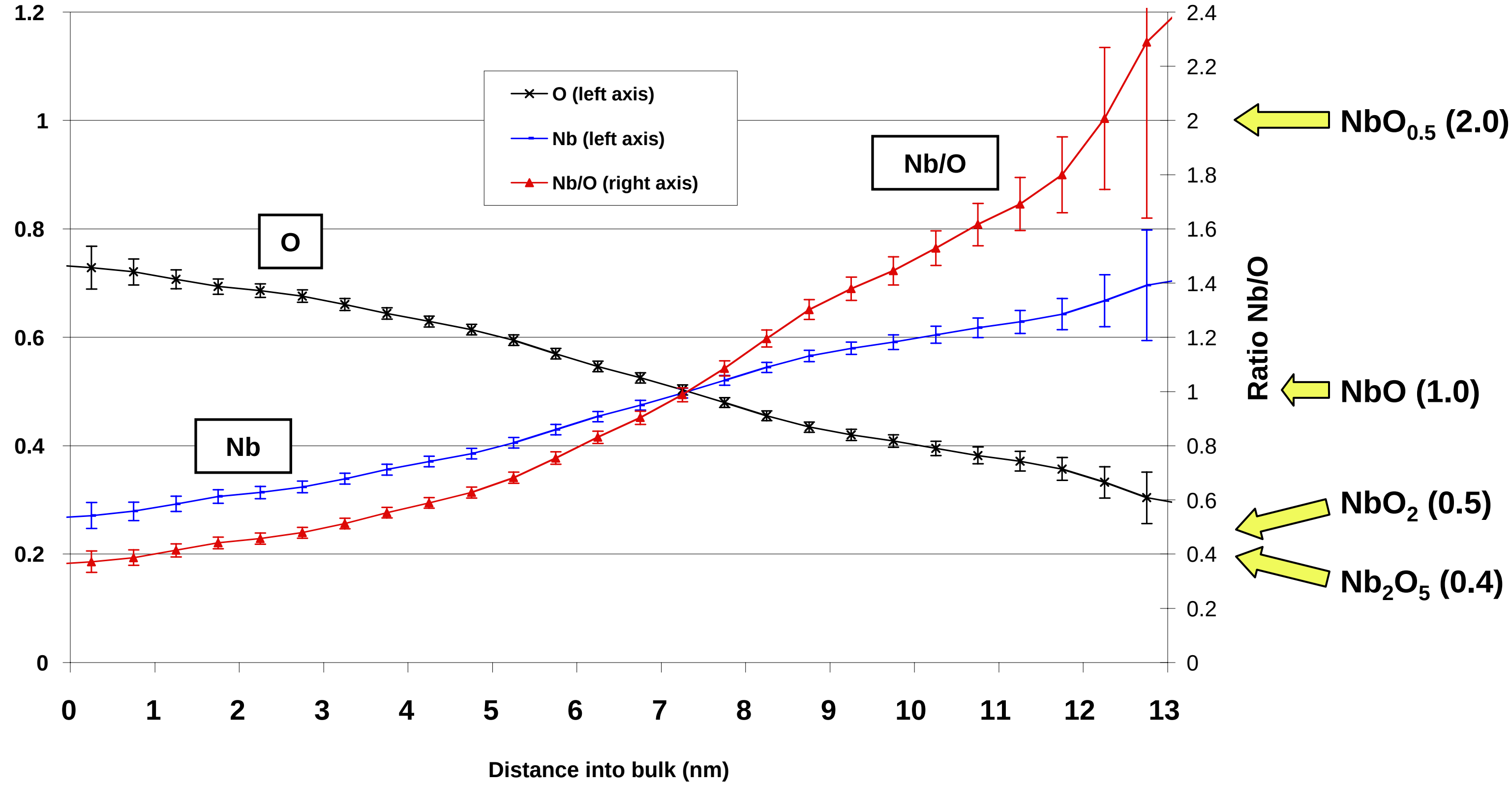
Hydrogen is extremely mobile in niobium (even at room temperature)



At room temperature, after ten seconds, $(6D\ t)^{1/2}$ for H in Nb is ~0.1 millimeter (cf. ~ 1 picometer for O in Nb)

Removal of the hydrogen and residual gas atoms from the concentration gives a better picture of the transition through the oxide layer



We see a clear and smooth transition from Nb_2O_5 to $NbO_{0.5}$ (= Nb_2O)

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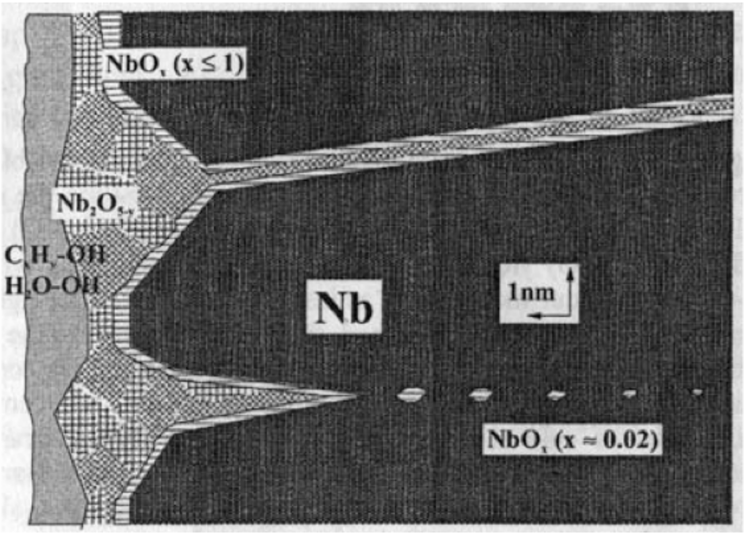
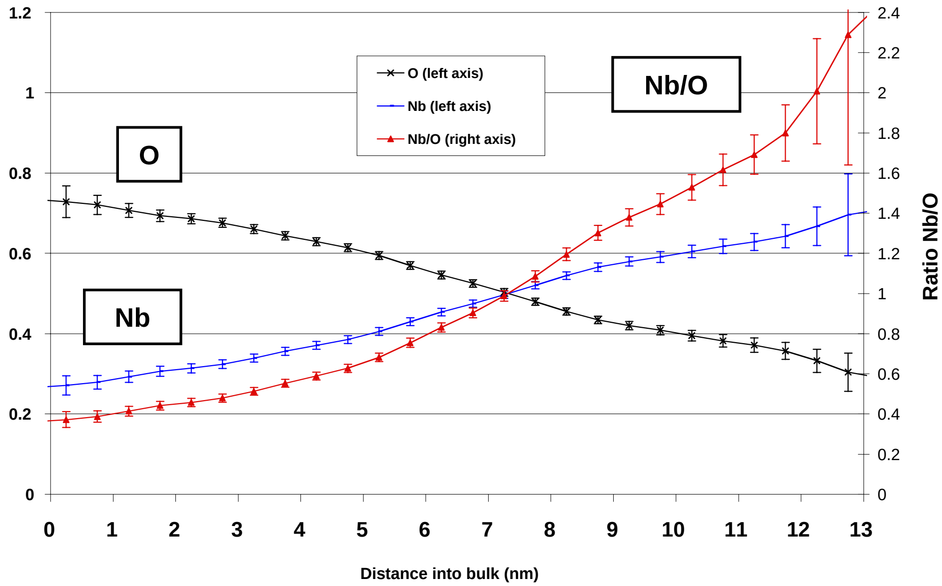
The profile corresponds, to first order, to the current models of oxide and suboxide formation on Nb





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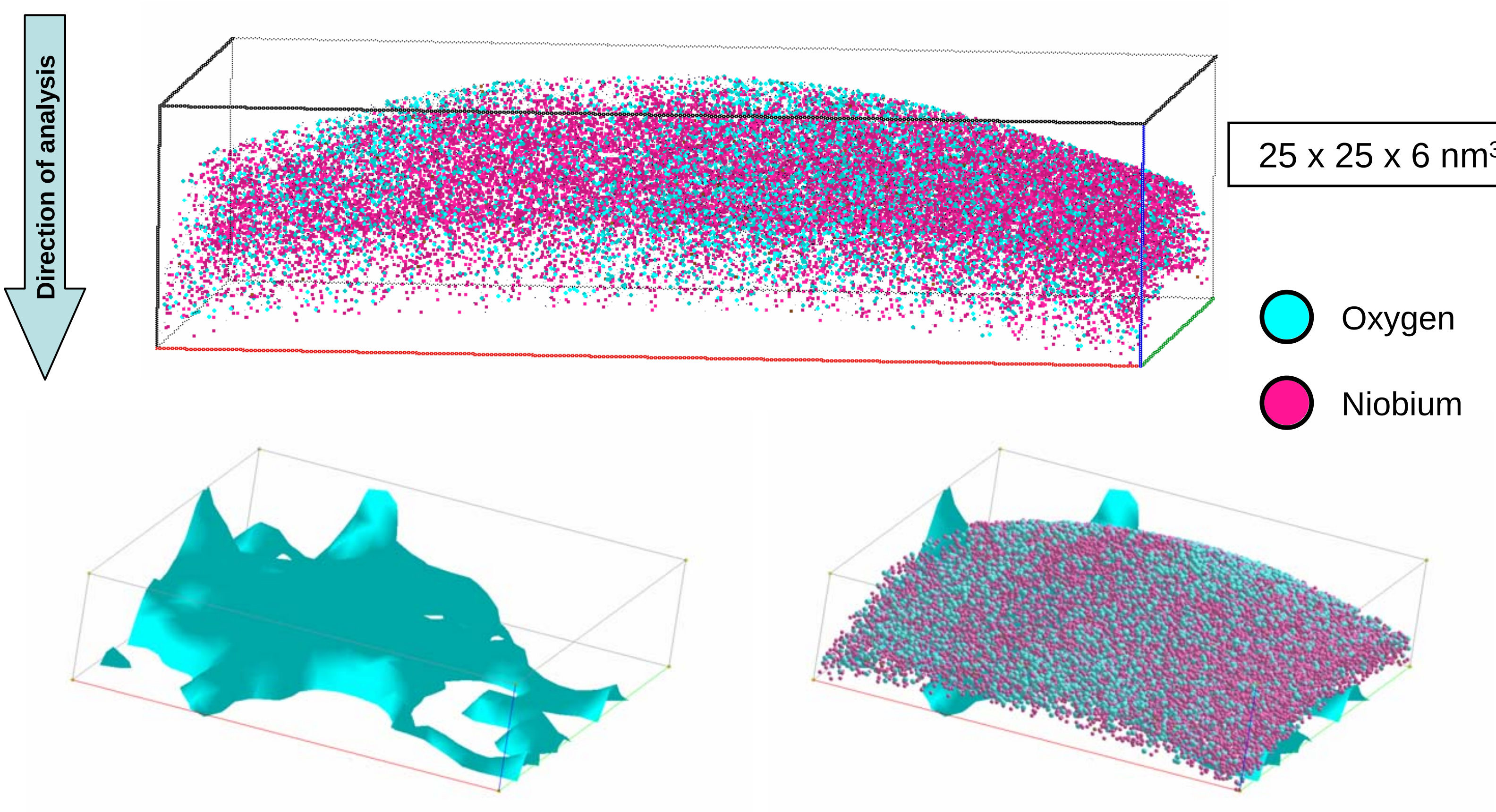
Second Nb analysis - more Nb-rich



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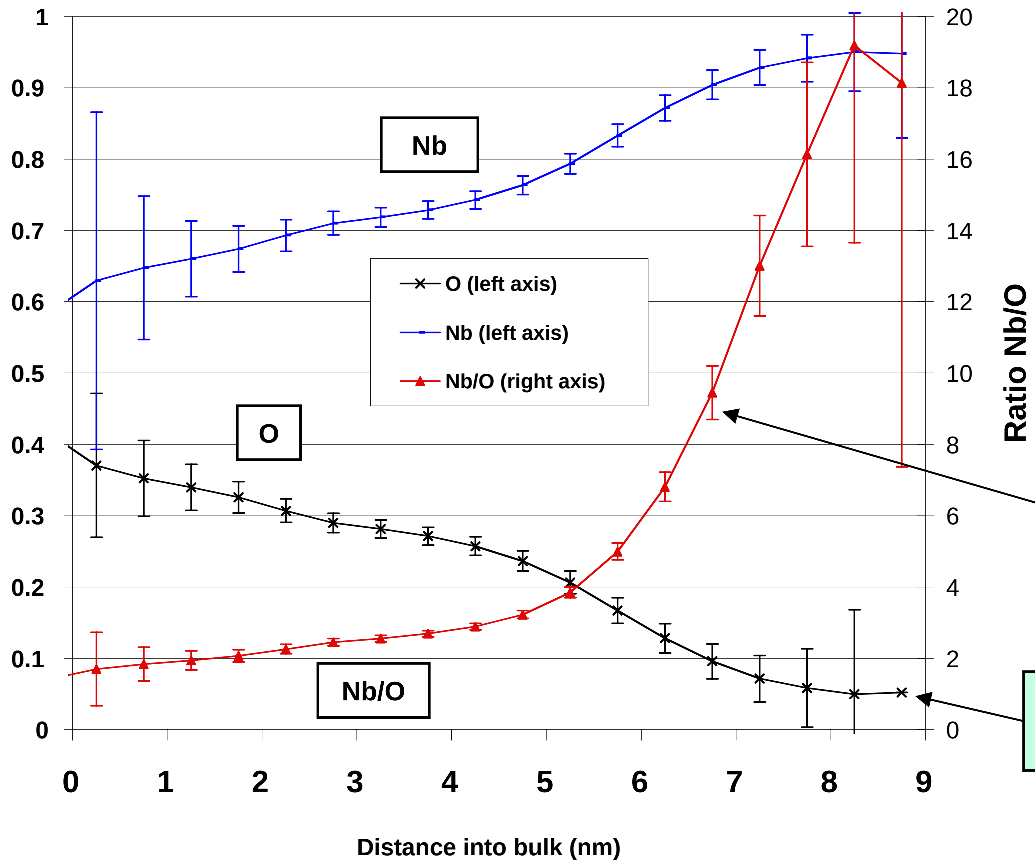
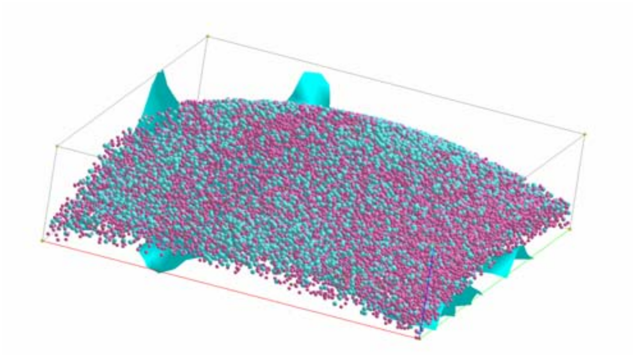
Second Nb analysis proxigram - a glimpse at the transition from oxide to Nb metal (?)

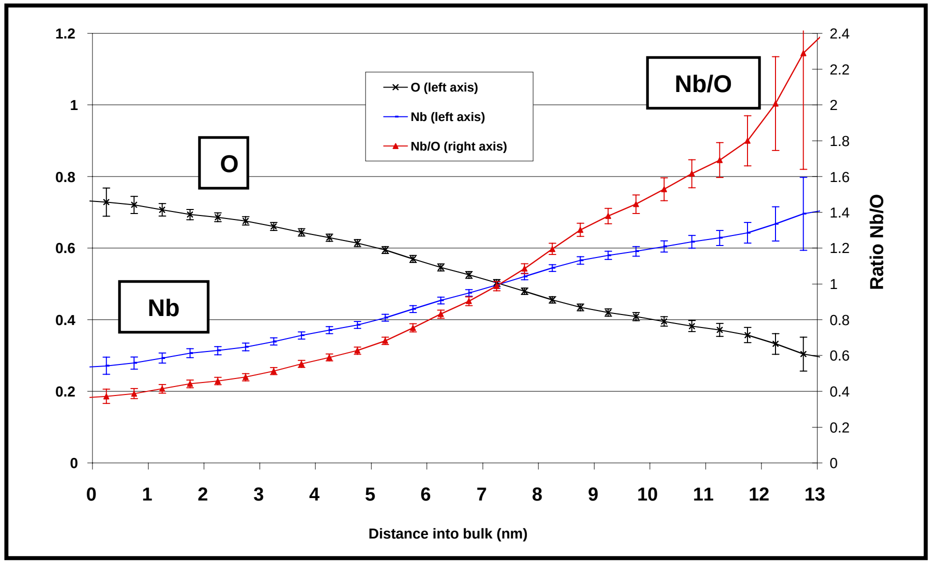


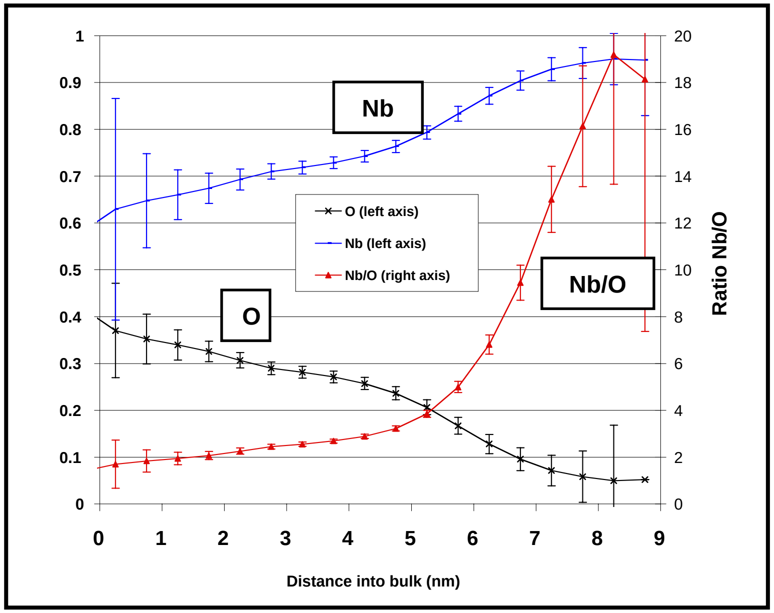


The transition from oxide to metal may be marked by a rapid increase in the ratio of Nb and O concentrations

Dissolved atomic oxygen in Nb metal (~5-10 at. %)

Second analysis … a "continuation" of the first analysis





First analysis (Nb_2O_5 to Nb_2O)

Second analysis (Nb_2O to Nb metal [?])

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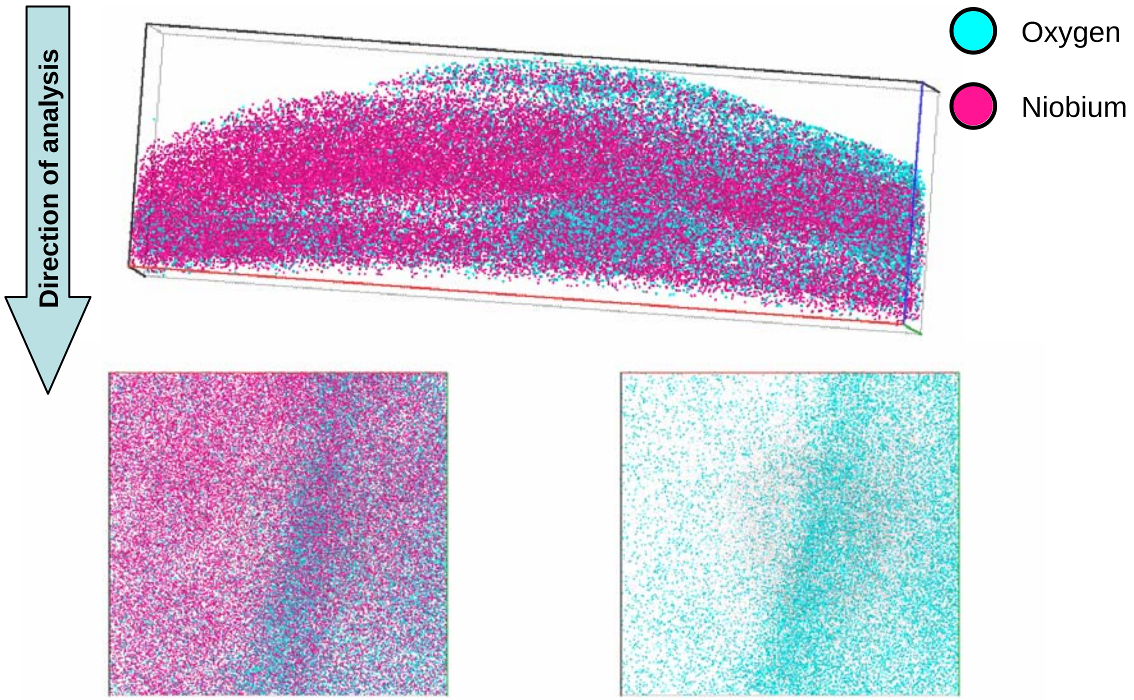
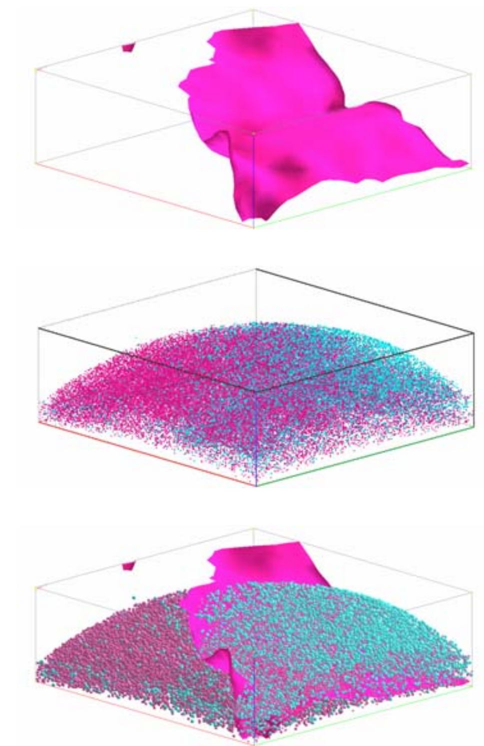
Third Nb analysis - an oxide metal interface

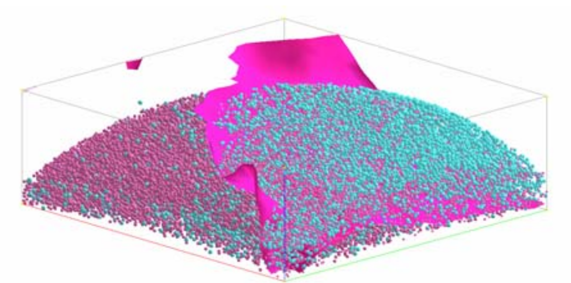


27 x 26 x 9 nm^3
~95 k atoms



55 at. % Nb isosurface

55% Nb isosurface and proxigram



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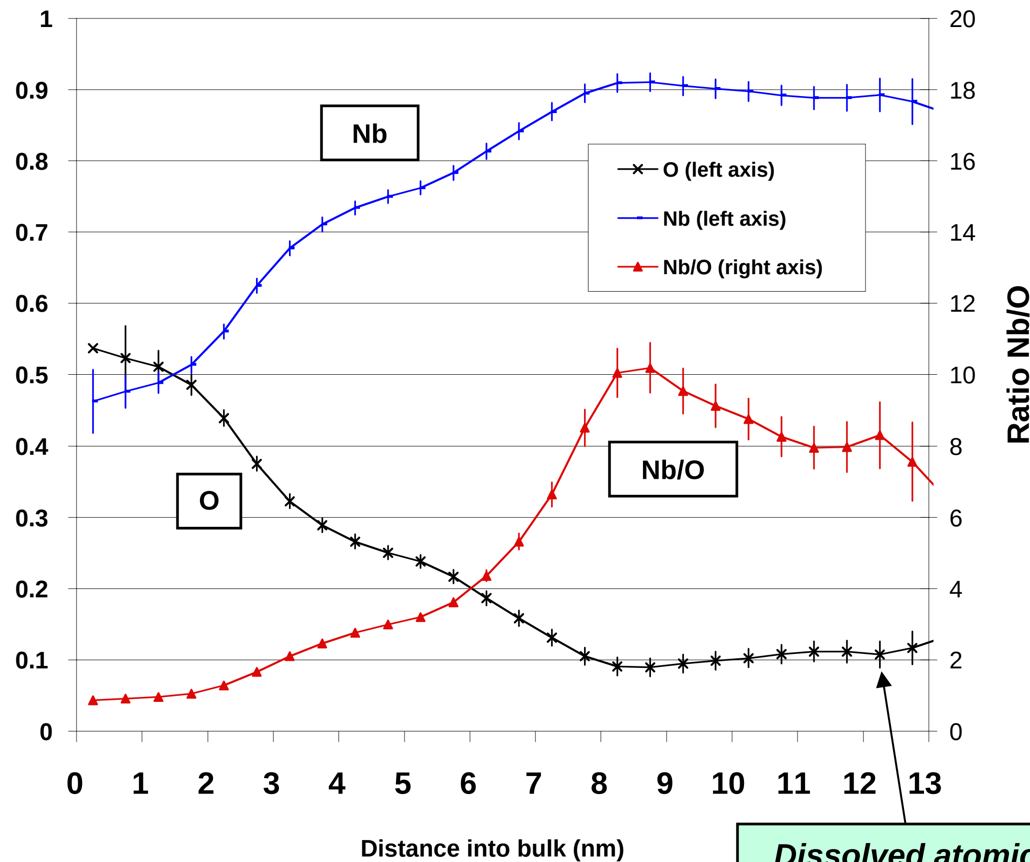

Dissolved atomic oxygen in Nb metal (~10 at. %)

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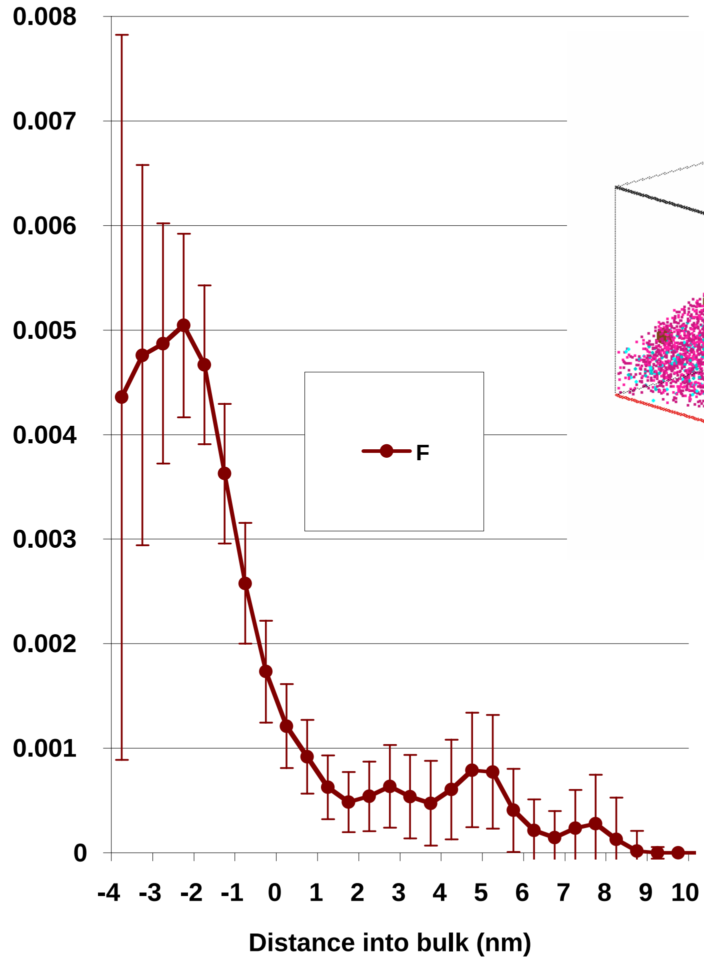
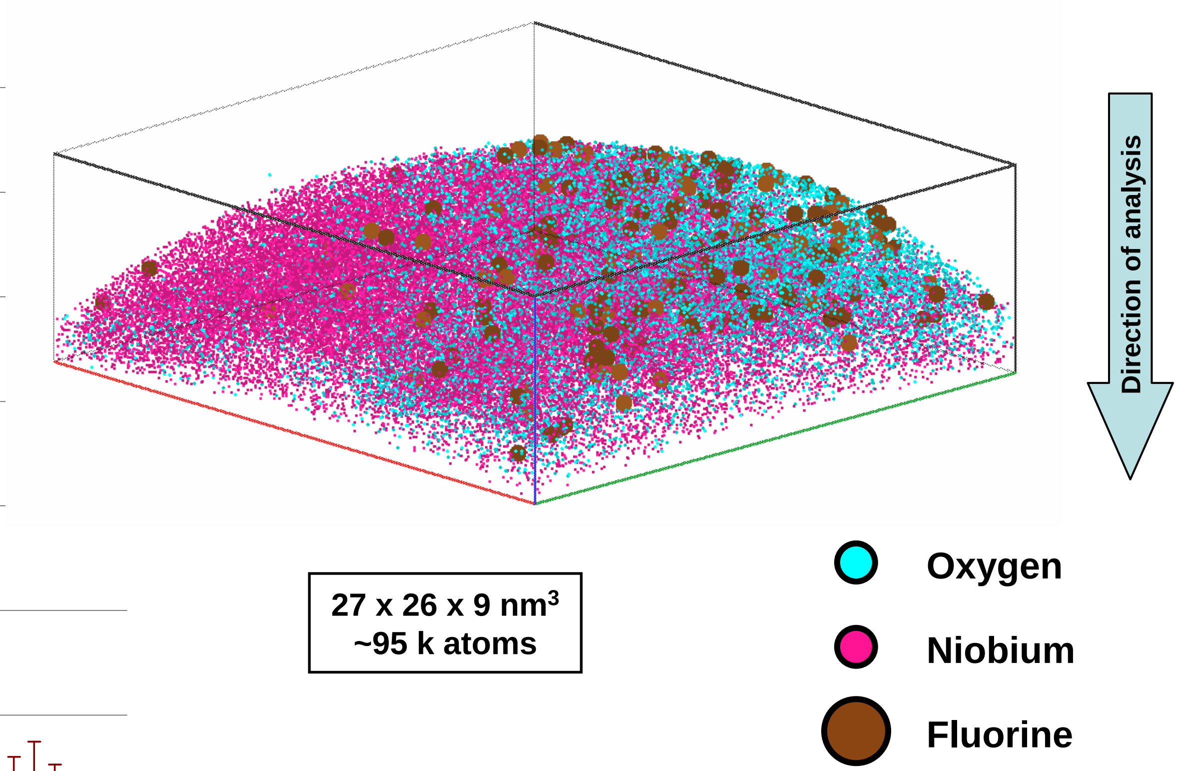
Atomic sensitivity of the technique - individual fluorine atoms on and near the surface (propensity for the oxide)





27 x 26 x 9 nm^3
~95 k atoms

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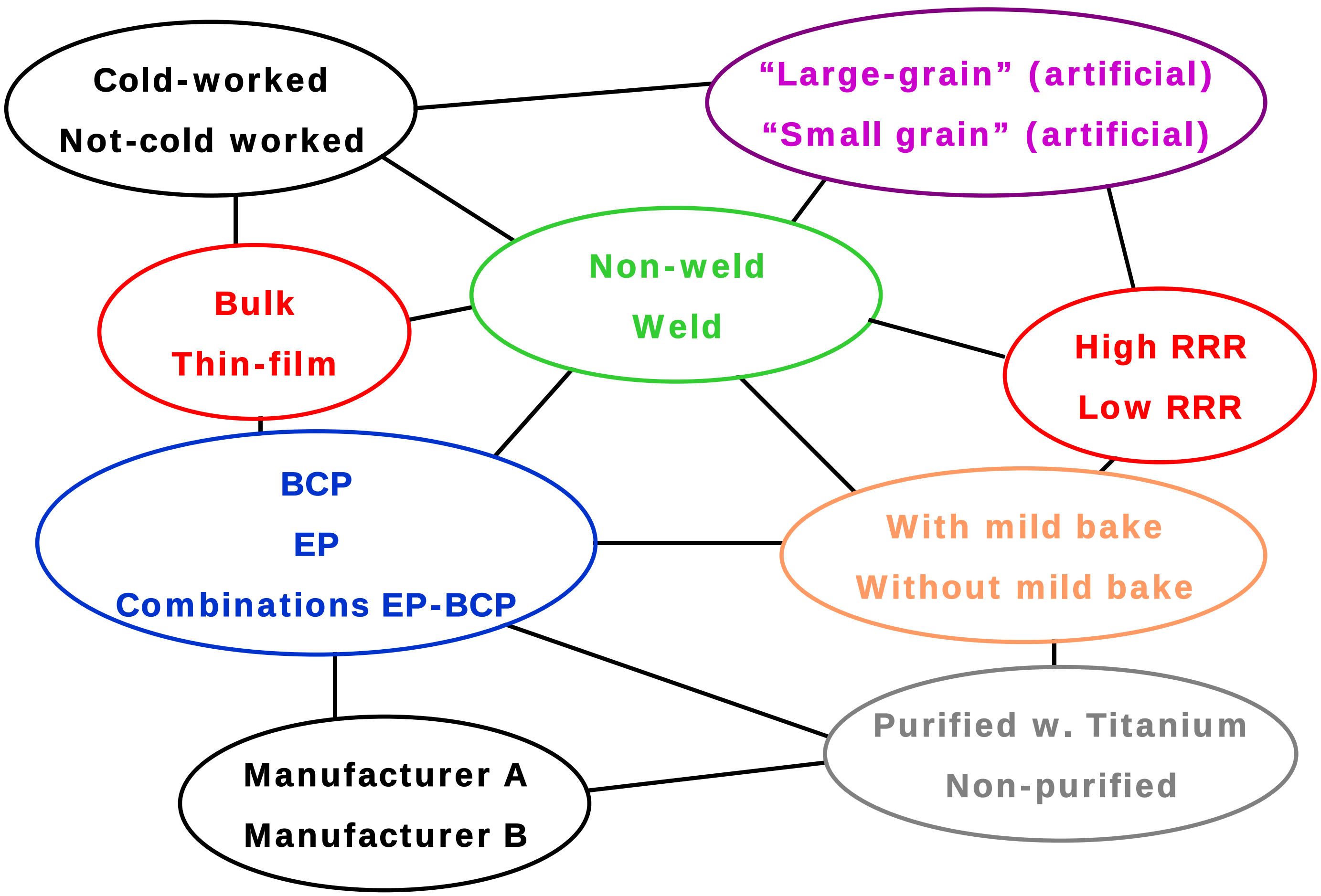
Conclusions and next steps

- Nanochemical, atomic scale analyses of the oxide surface and of the near-surface bulk niobium are being performed
  - "Smooth" transition from surface Nb_2O_5 to Nb_2O (and into the bulk Nb)
  - Ability to detect small number of contaminant atoms in the oxide surface and in the near-surface bulk niobium
  - Levels of oxygen in the near-surface bulk niobium (metal) of 5-10 atomic percent, which is consistent with bulk Nb-O phase diagram

- More analysis to come
  - Interpretation of mass spectra
    - Improved analysis conditions
  - Improved specimen preparation techniques (reliability and repeatability)
    - Focused ion beam (FIB) milling and/or femtosecond laser ablation
  - Many classes of samples

Classes of samples - effects of many, many variables on the atomic chemistry



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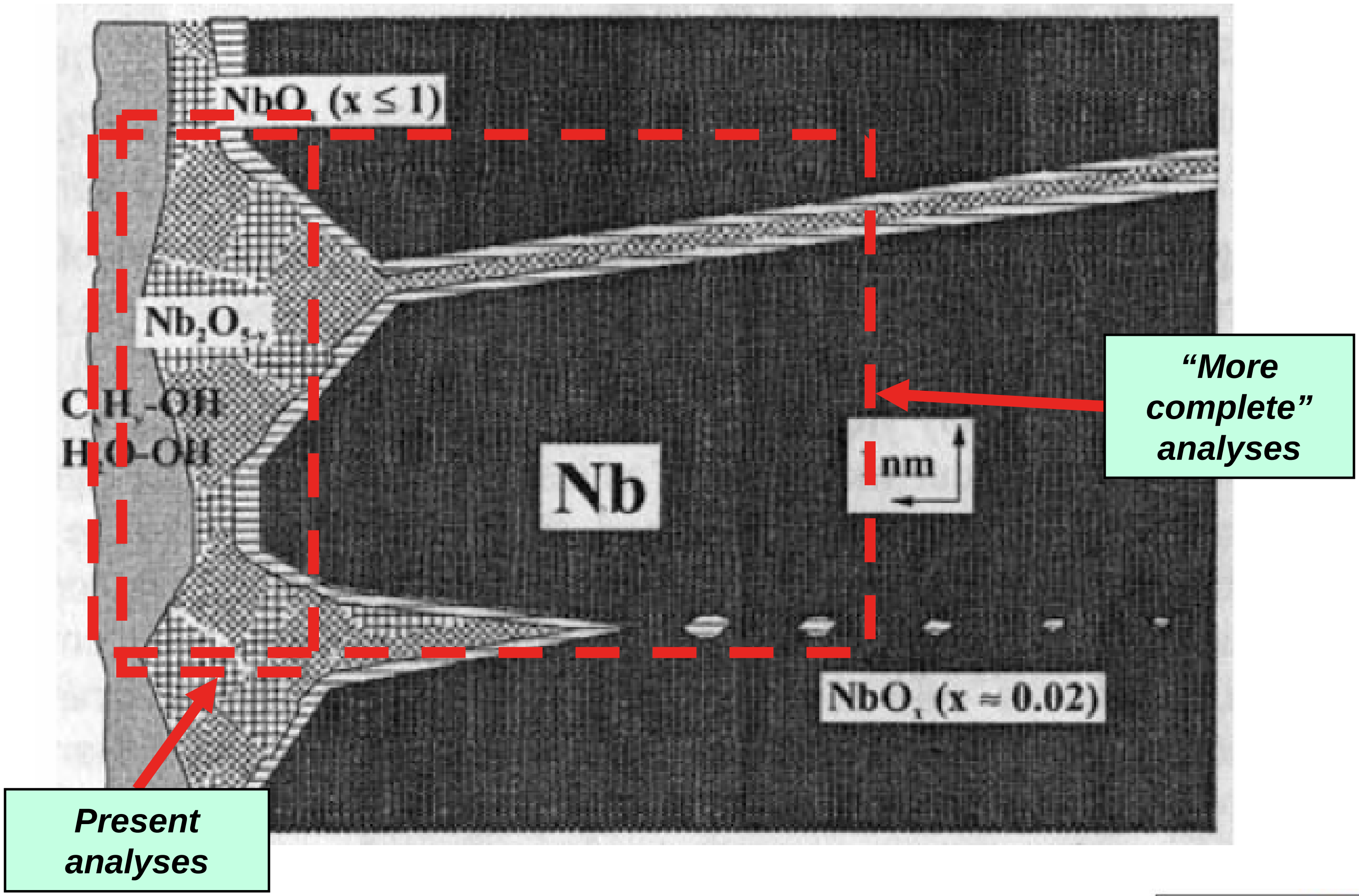
A "more complete" run would capture much more of the atomic chemistry of the oxide surface and of the near-surface bulk niobium



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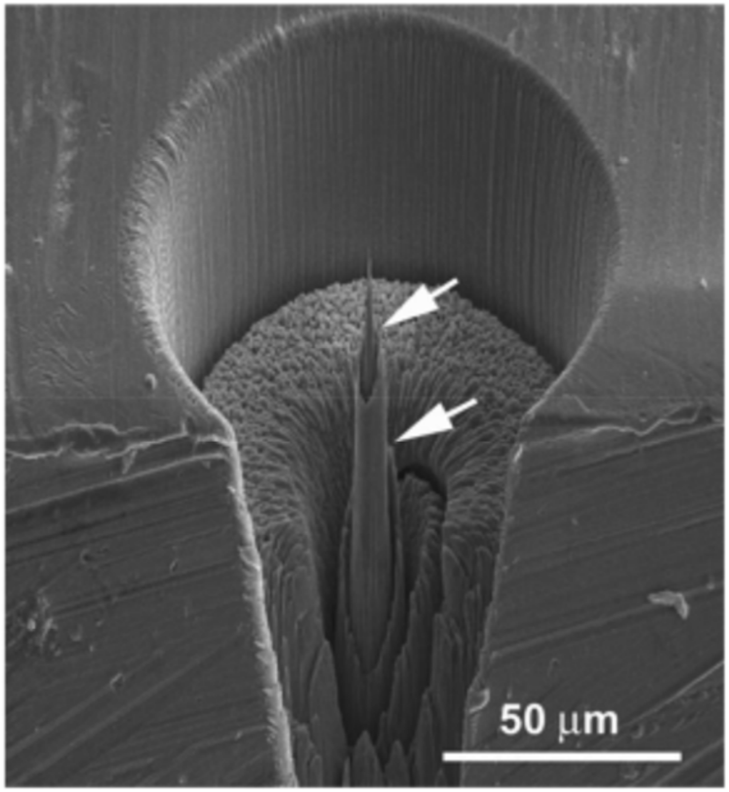
Specimen preparation - focused ion beam (FIB) milling of "site-specific" LEAP specimens from niobium cavity materials



Possibility of centering a specimen on a region of interest (e.g., a grain boundary)

We will use the ANL Zeiss 1540XB dual-beam FIB to attempt "site-specific" specimen preparation

REFERENCE
Strategies for Fabricating Atom Probe Specimens with a Dual Beam FIB,
M.K. Miller, K.F. Russell and G.B. Thompson
Ultramicroscopy, 102 (2005) 287-298.

Studies of Nb cavity materials

- SEM micrographs from P. Bauer et al.