Preliminary Atom-Probe Tomographic (APT) Analyses of Nb Cavity Materials

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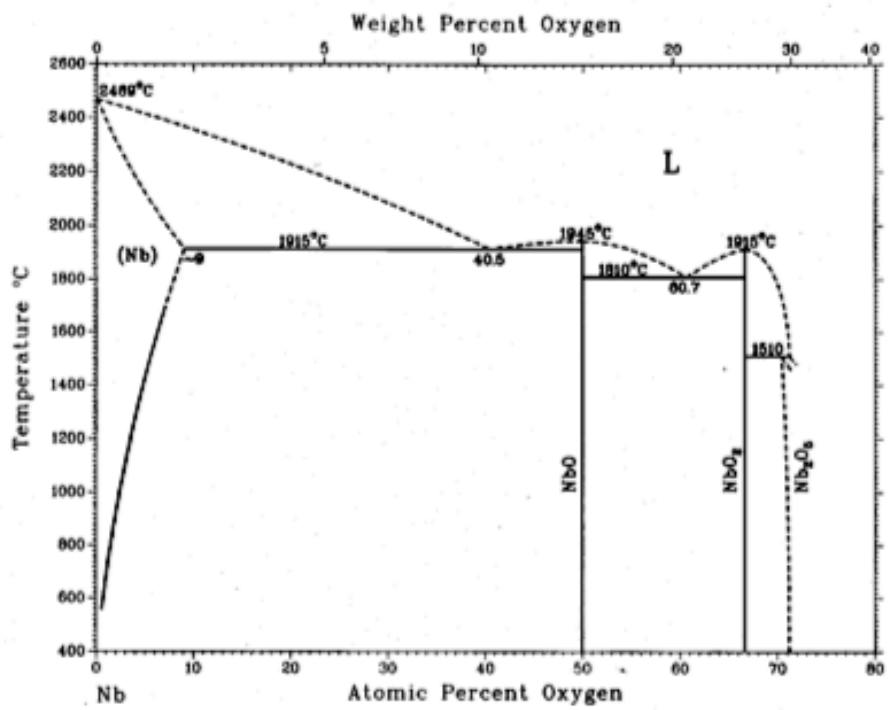
Agenda

- 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)

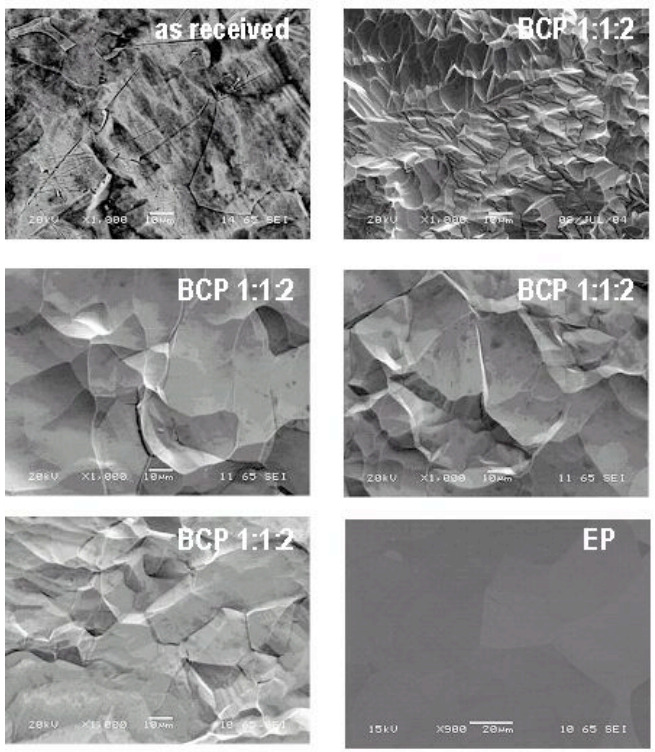


Phase	Composition (at. % O)	Pearson symbol	Space group	Prototype
(Nb)	0 to ~9	cI2(bar)	Im3(bar)m	W
NbO	50	cP6	Pm3(bar)m	NbO
NbO_2	66.7	tI96	I41/a	
Nb_2O_5	~71.4	mP99	P2/m	

Studies of Nb cavity materials

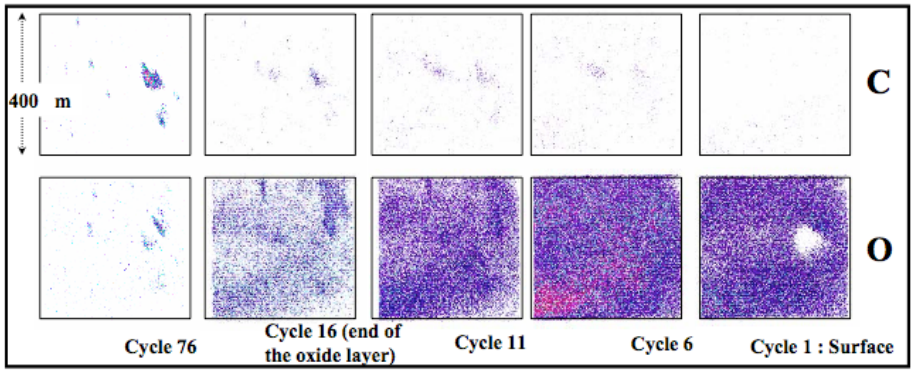
- SEM micrographs from P. Bauer (et al.)

Surfaces:



C. Chapman, D. Hicks, C. Boffo

- SIMS studies by C. Antoine



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

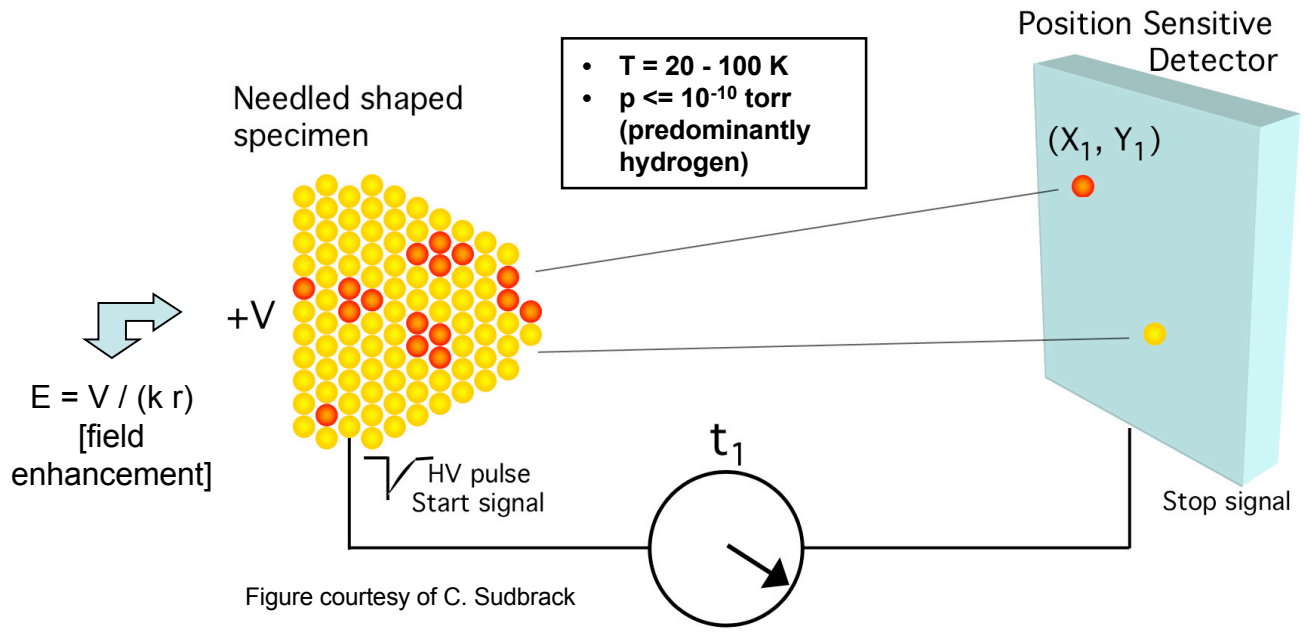


Figure courtesy of C. Sudbrack

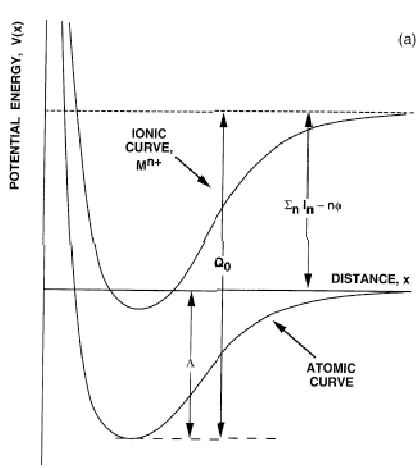
$$\frac{m}{n} = k\alpha(V_{dc} + \beta V_{pulse})\left(\frac{t + t_o}{d}\right)^2$$

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

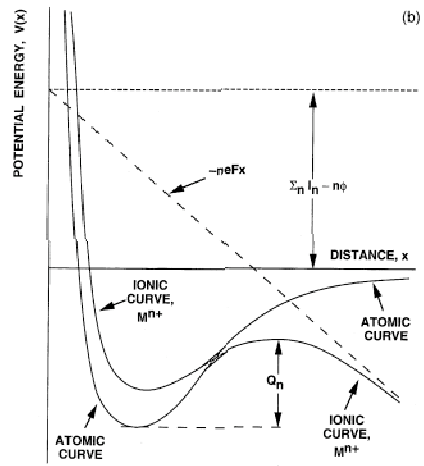
Field evaporation - schematic

- **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

From Miller et al., (1996)

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 (= 1,000,000 nm^3 = 0.001 μm^3)**

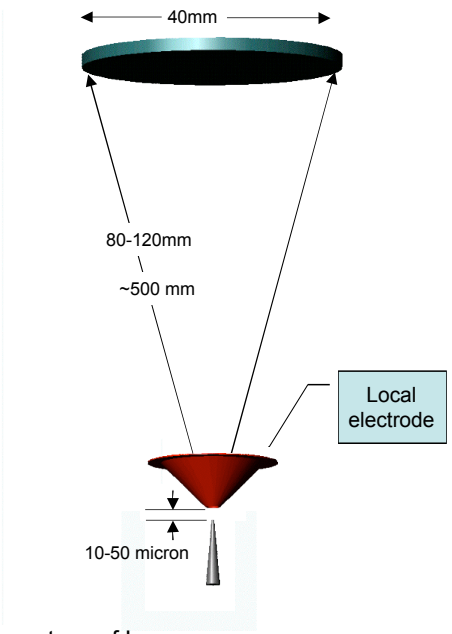
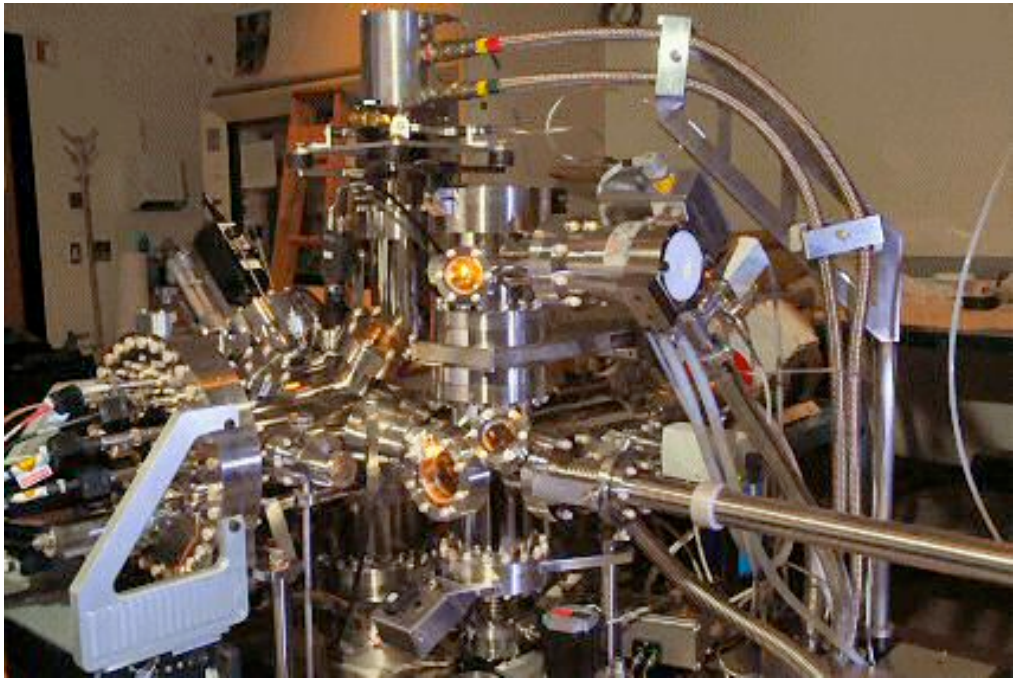


Figure courtesy of Imago Scientific Instruments



NUCAPT's LEAP Tomograph

Specimen preparation

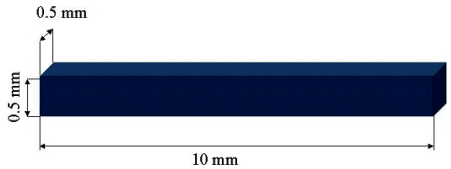
1. **Electropolishing**
   - **10% HF (48%) in 90% HNO_3 (68%)**
   - **DC voltage**
   - **"Drop off" technique**
   - **Keep things as clean as possible**
     - **Rinsing (UHP water)**
     - **Minimal time in air (stored in desiccator under dry N_2)**

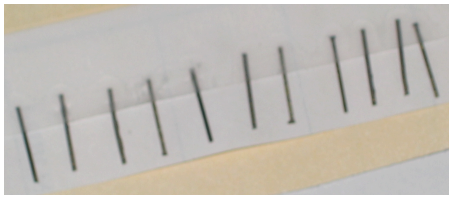
2. **Buffered Chemical Polishing (BCP)**
   - **1 : 1 : 2**
     HF (49%) : HNO_3 (68%) : H_3PO_4 (85%)
   - **No voltage**
   - **Replicating the setup at FNAL**

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

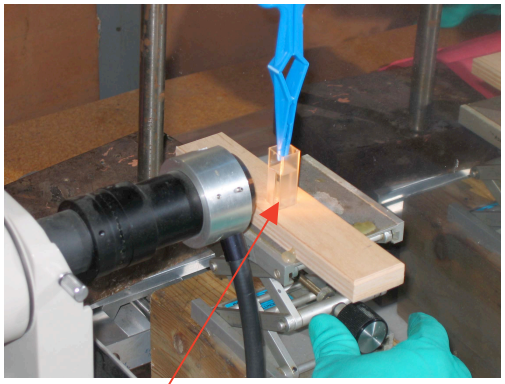
Specimen preparation - electropolishing and buffered chemical polishing

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

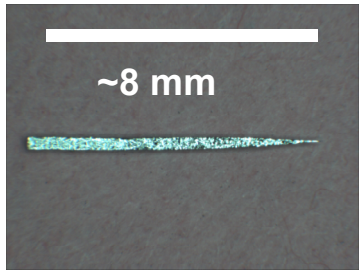




Step 2 - Polishing at FNAL



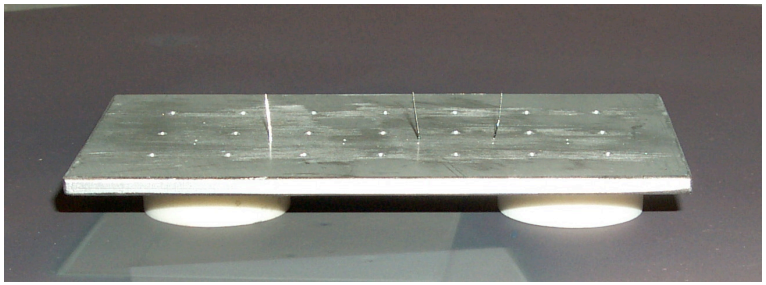
Rectangular cuvette with polishing solution (BCP)



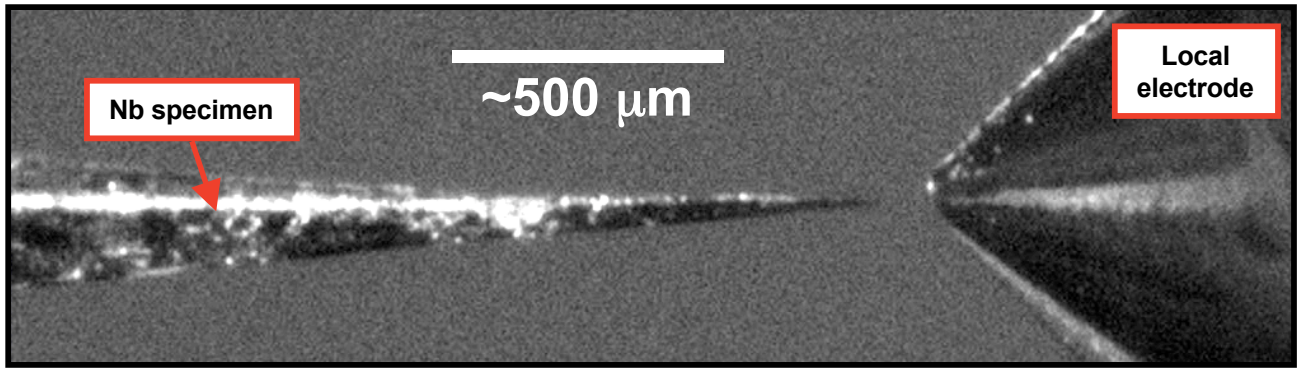
Stereo-microscope

Specimen preparation - electropolishing and buffered chemical polishing

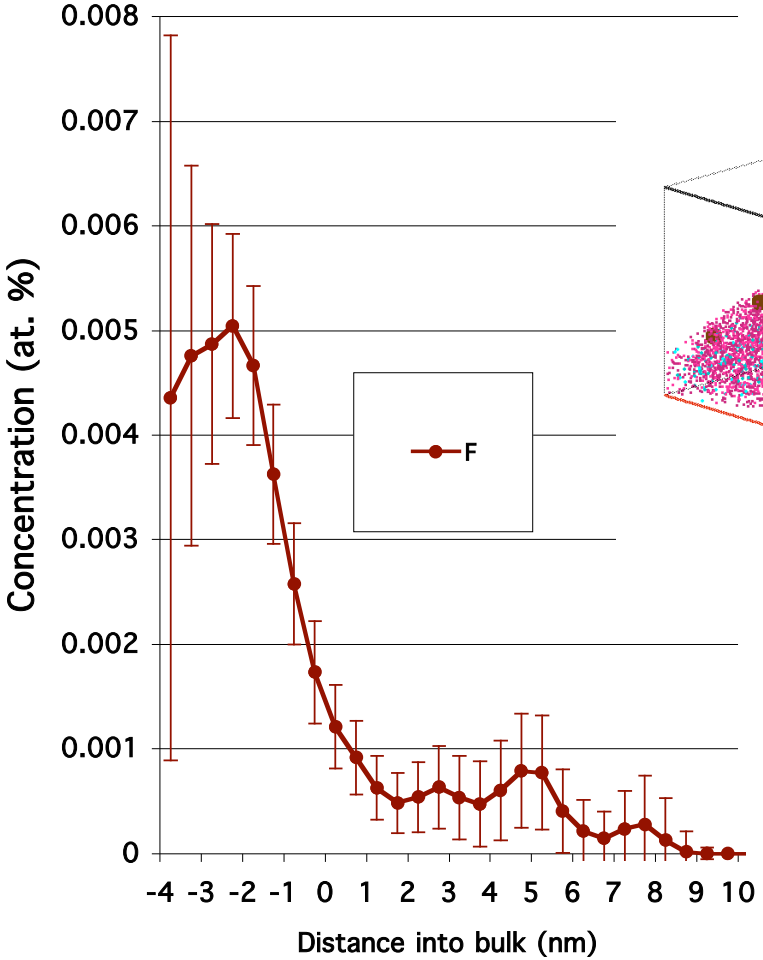
Step 3 - Heat treatment at FNAL

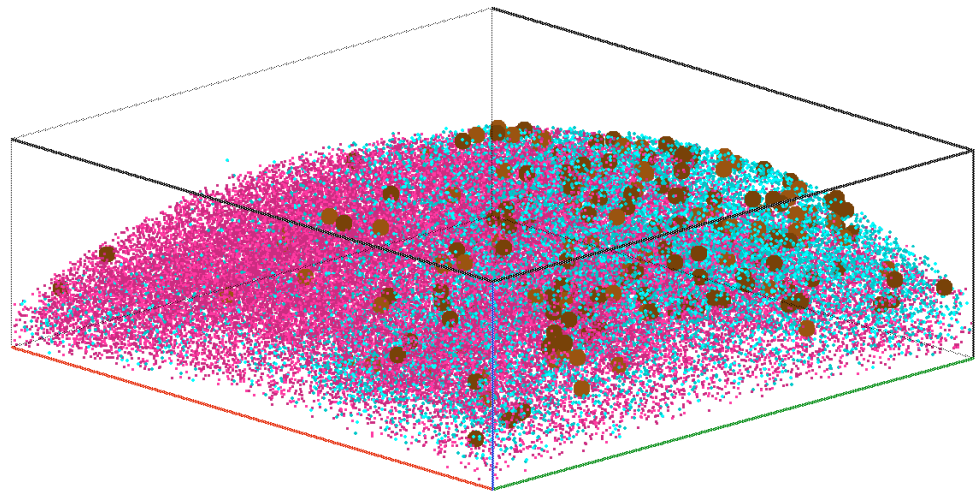


Step 4 - Alignment in the LEAP



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



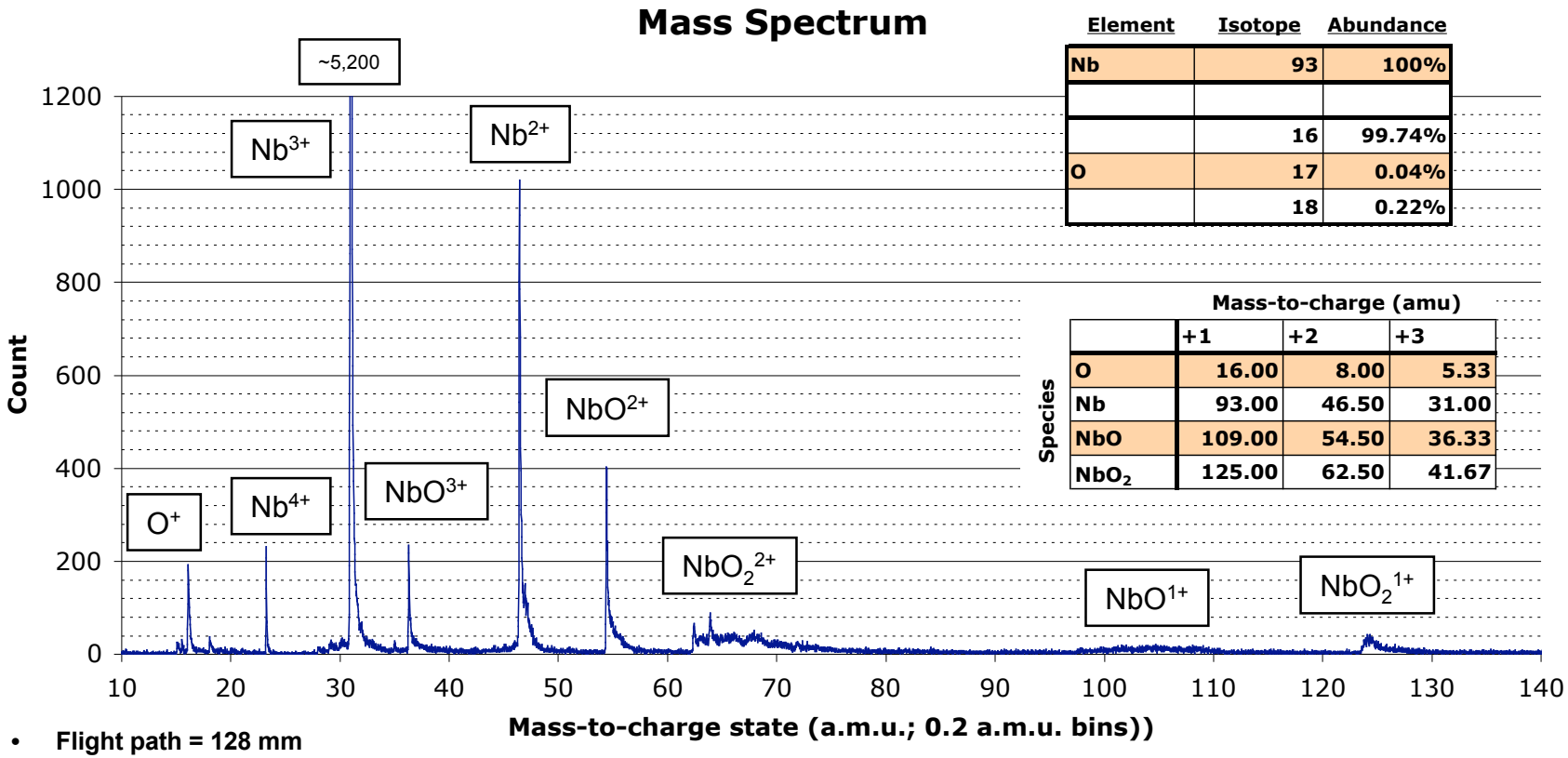


Direction of analysis

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

Oxygen
Niobium
Fluorine

Complex mass spectrum - lots of complex ions



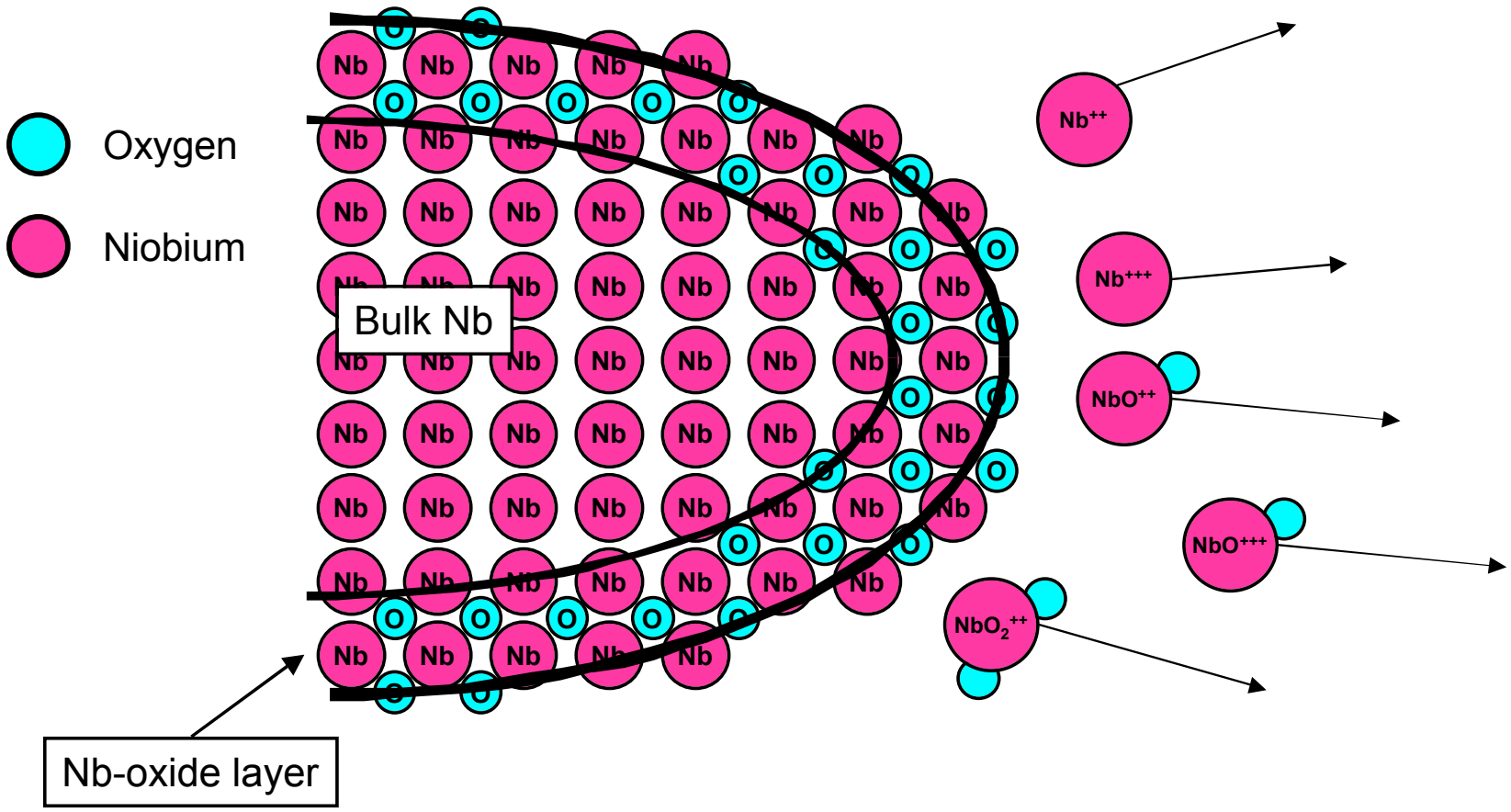
Element	Isotope	Abundance
Nb	93	100%
	16	99.74%
O	17	0.04%
	18	0.22%

Mass-to-charge (amu)

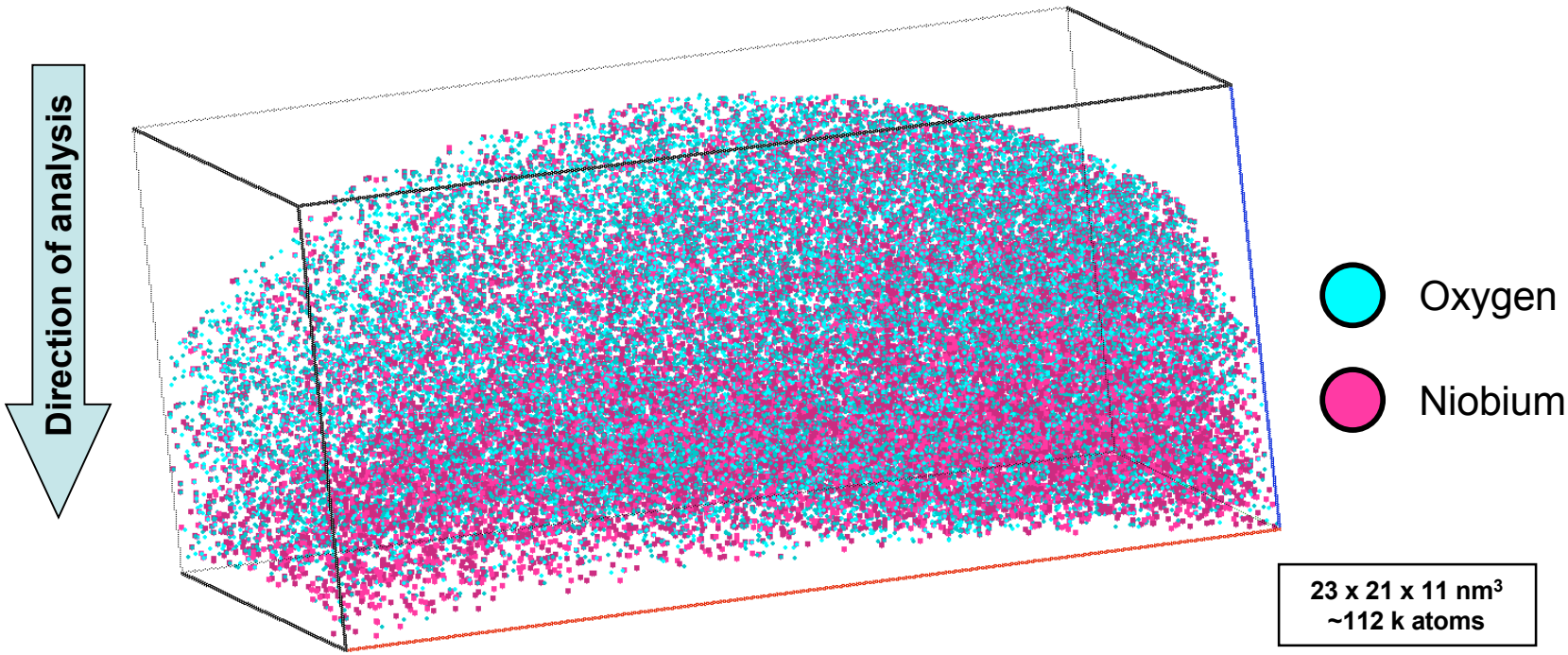
Species	+1	+2	+3
O	16.00	8.00	5.33
Nb	93.00	46.50	31.00
NbO	109.00	54.50	36.33
NbO_2	125.00	62.50	41.67

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

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



Atomic reconstruction of the transition through the oxide layer

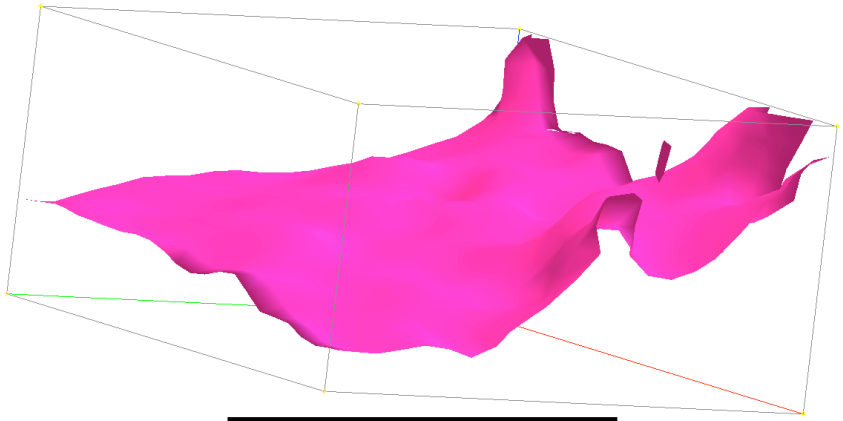


We see a clear transition from oxygen (cyan) to niobium (magenta) as we move along the analysis direction

A 30 at. % Nb isosurface gives a better representation of the spatial gradients in atomic concentration

Oxygen

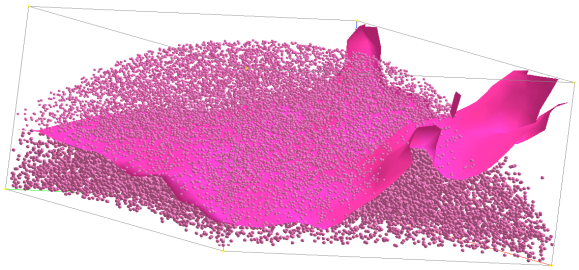
Niobium



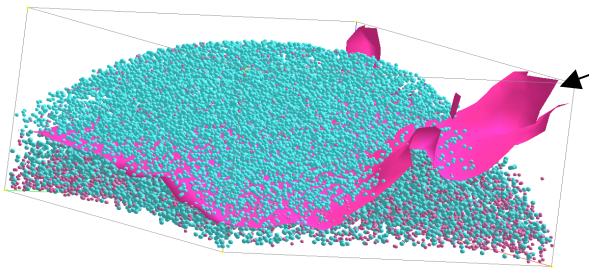
23 x 21 x 11 nm^3
~112 k atoms

30 at. % Nb isosurface

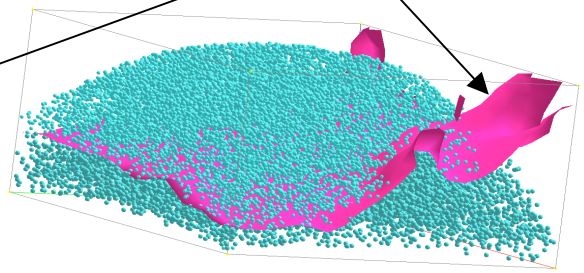
Extraneous surfaces (not important)



Nb atoms with 30 at. % Nb isosurface

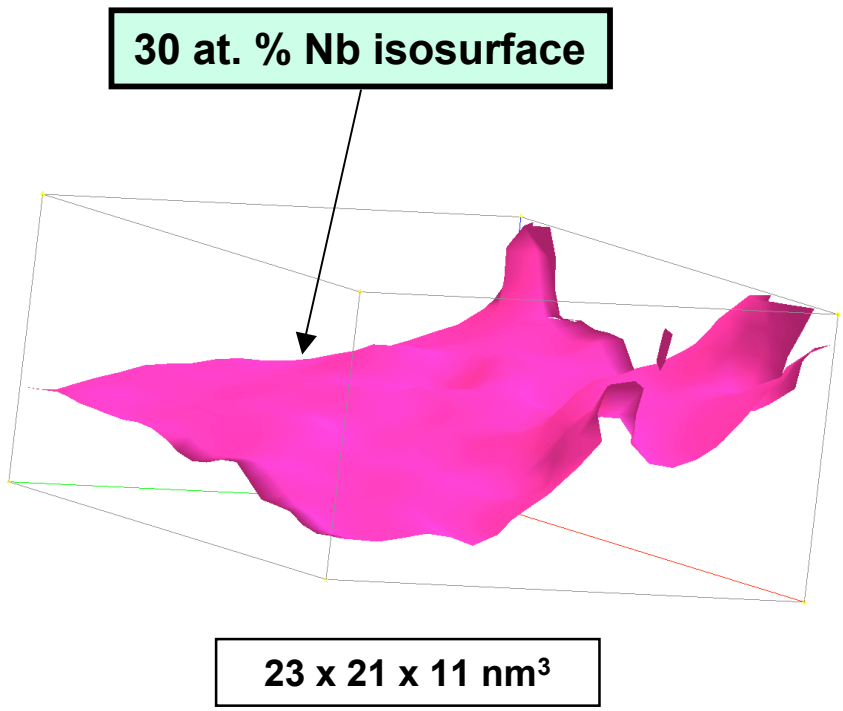


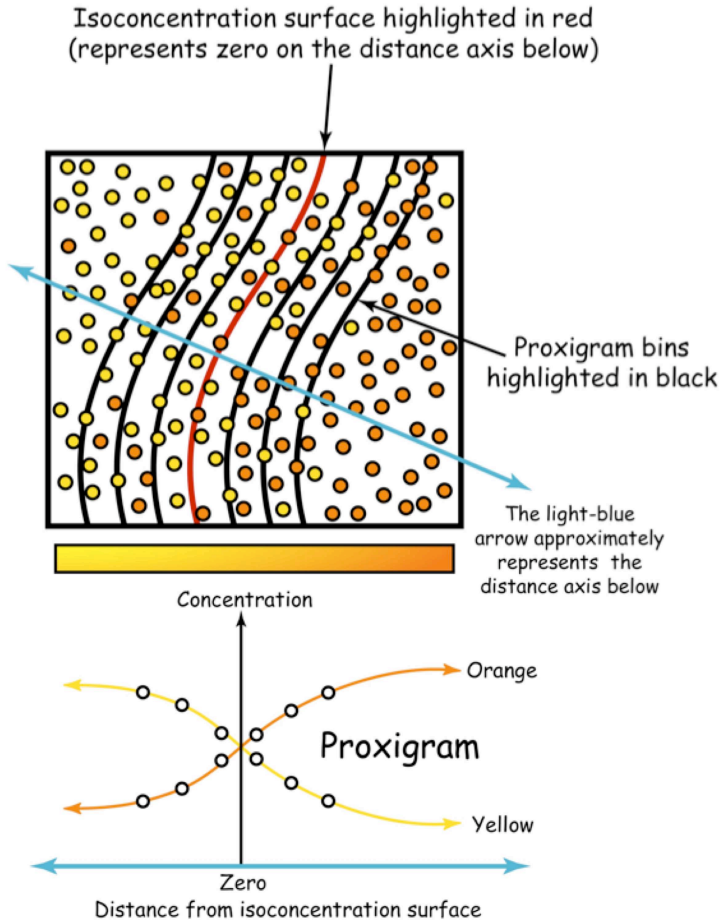
Nb and O atoms with 30 at. % Nb isosurface



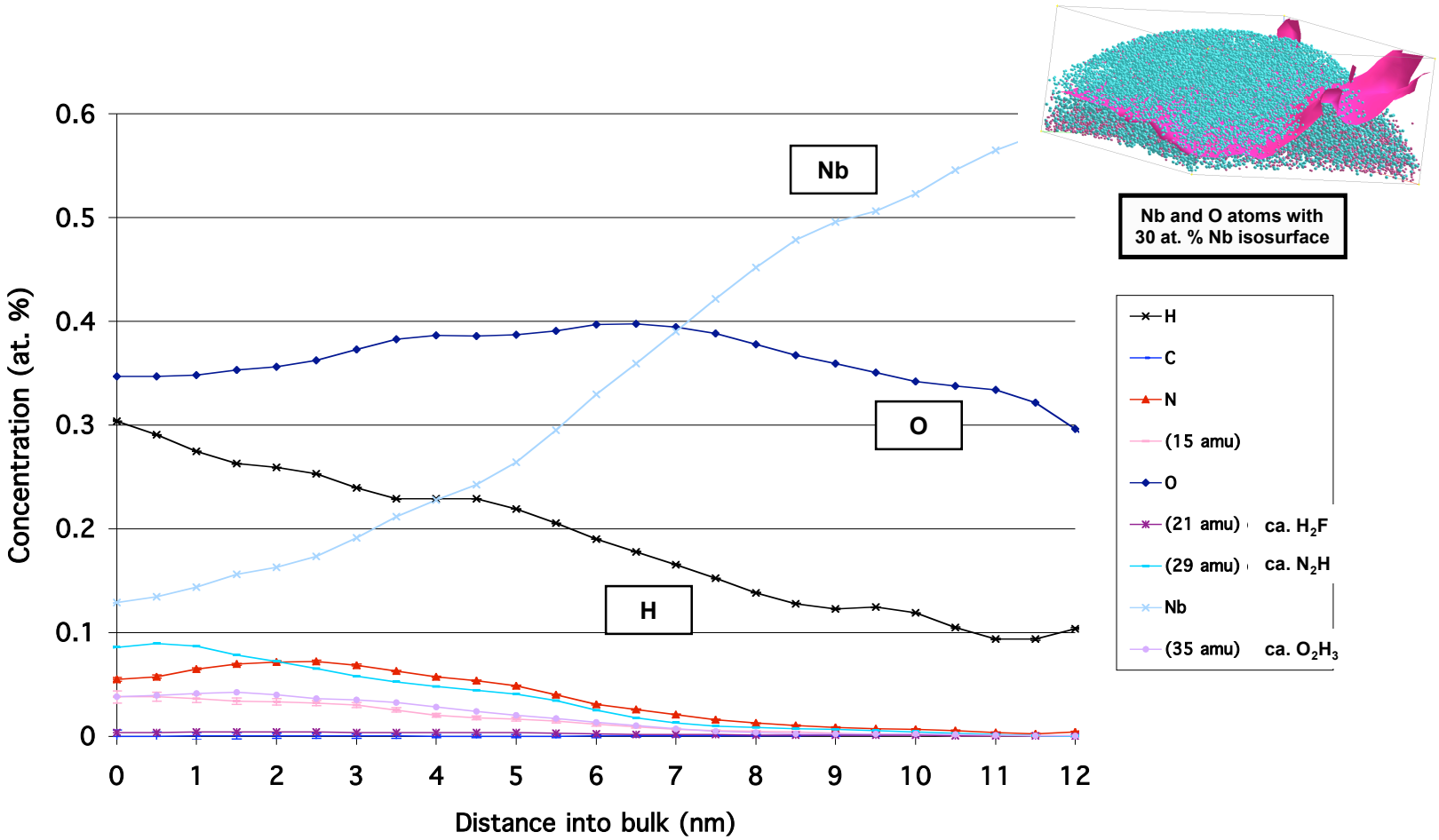
O atoms with 30 at. % Nb isosurface

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

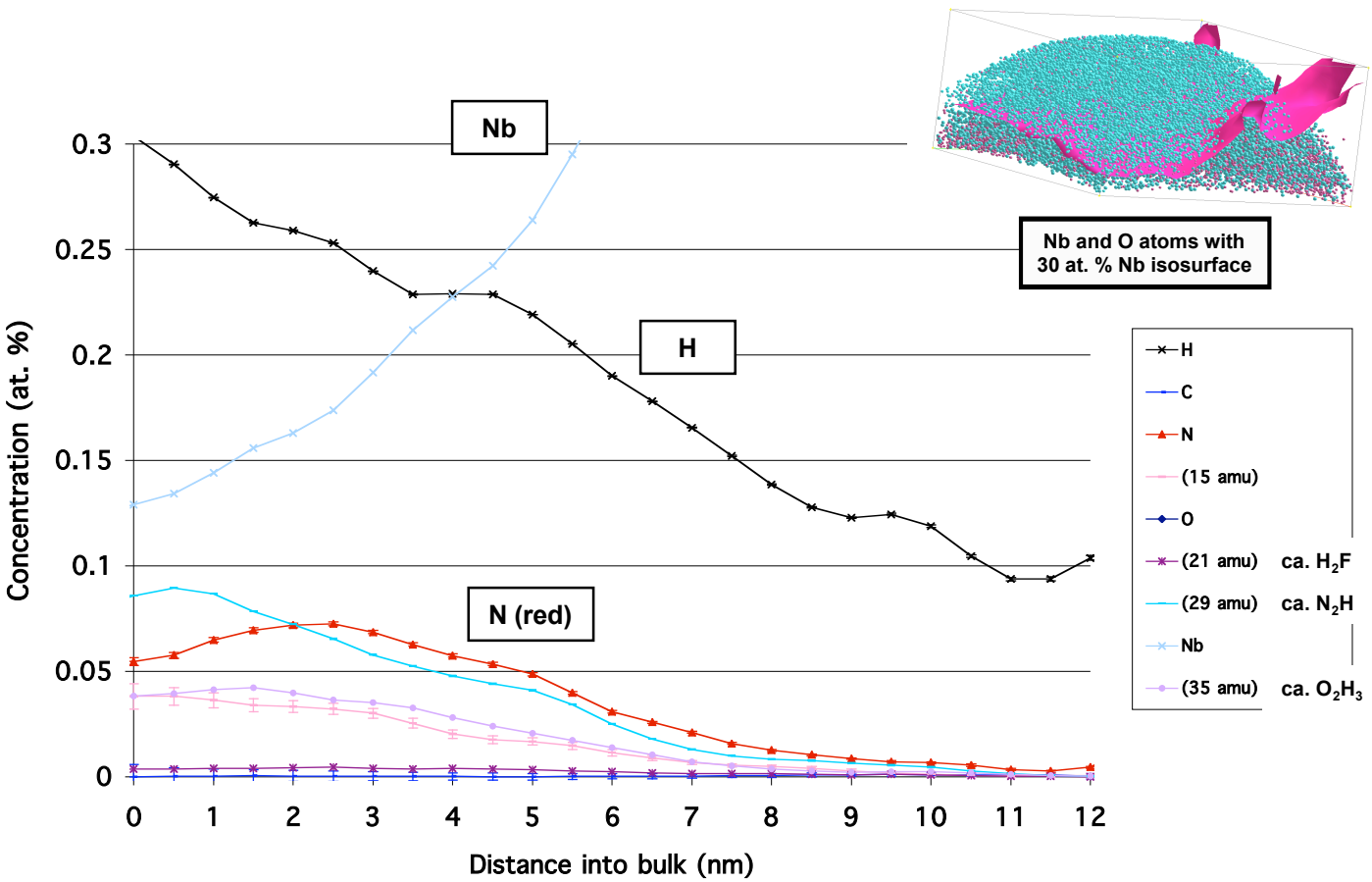




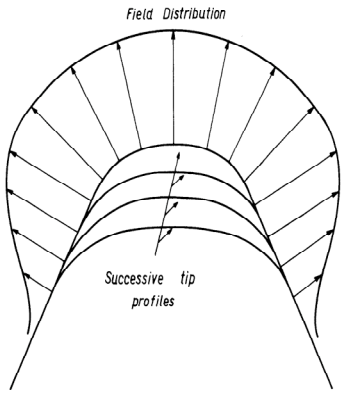
30% Nb proxigram - we see the transition from oxygen to niobium



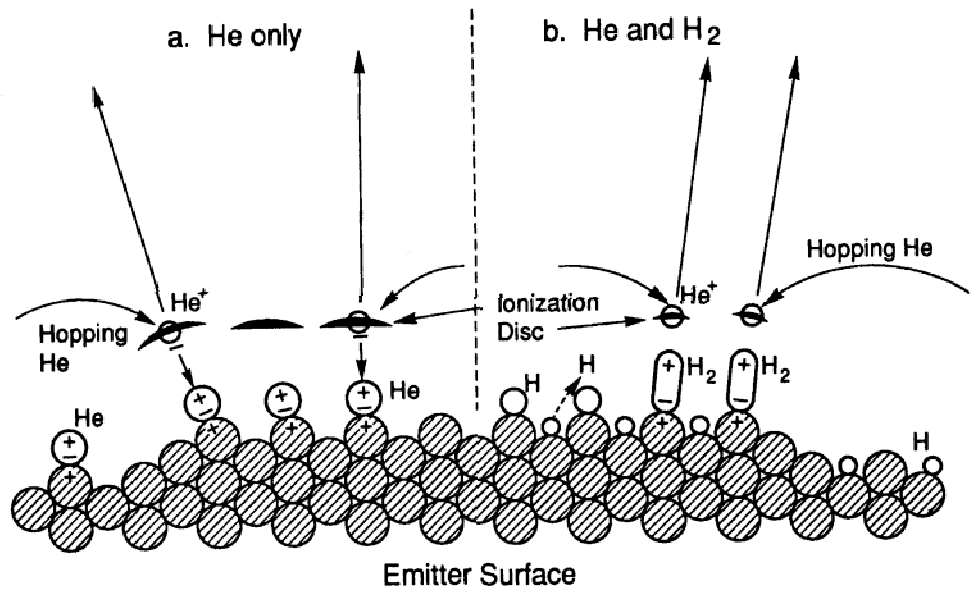
Hydrogen, residual gas atoms, and other "UFO" peaks make up nearly 50% of the ions collected



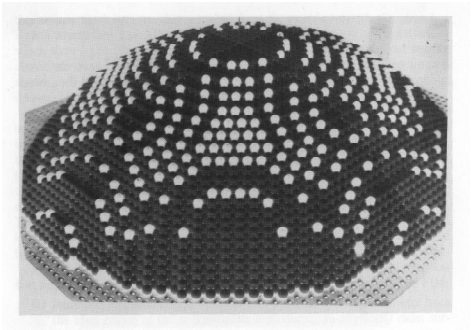
Hydrogen and residual gas atoms can come from "outside the specimen"



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



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

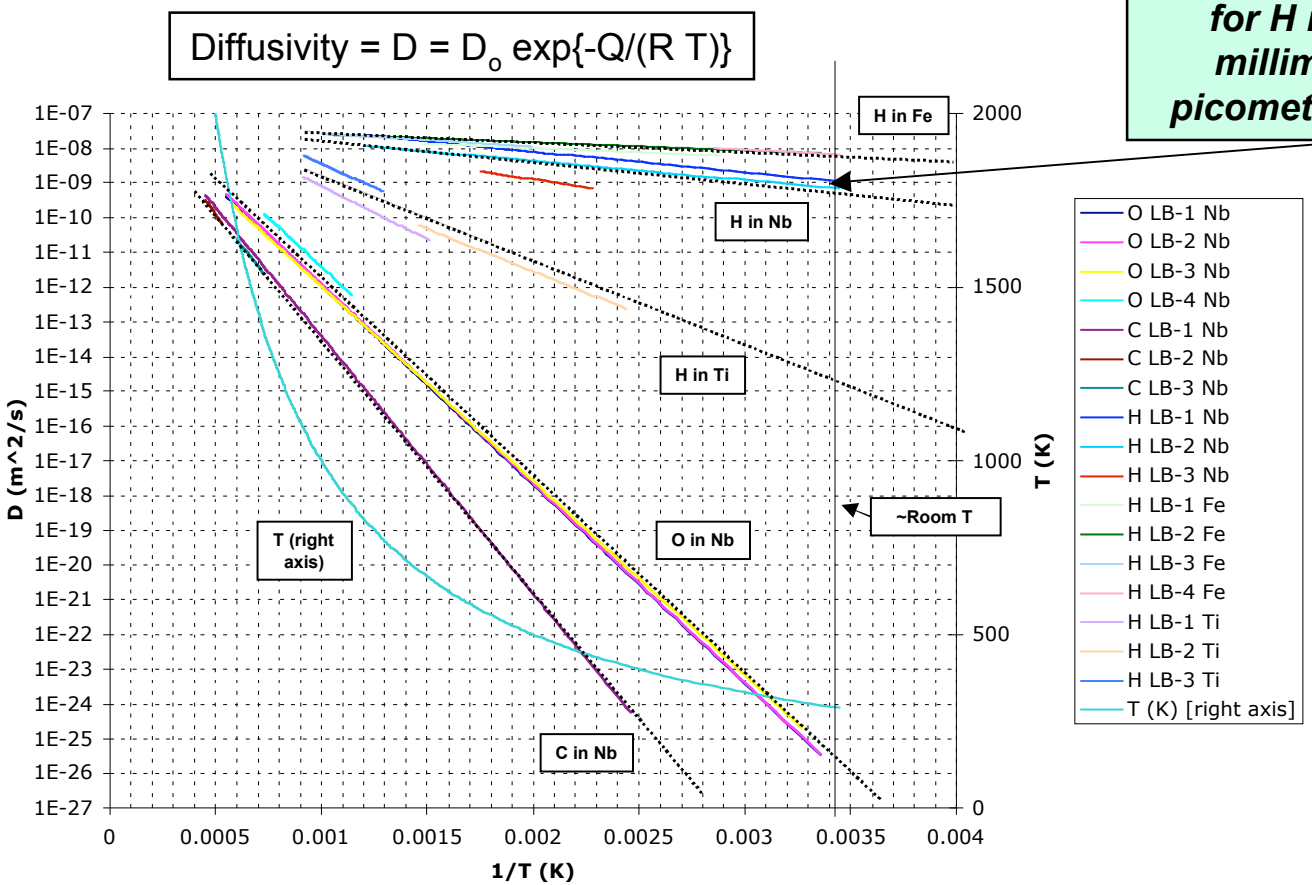


Ball model of an atom-probe tip surface (schematic)

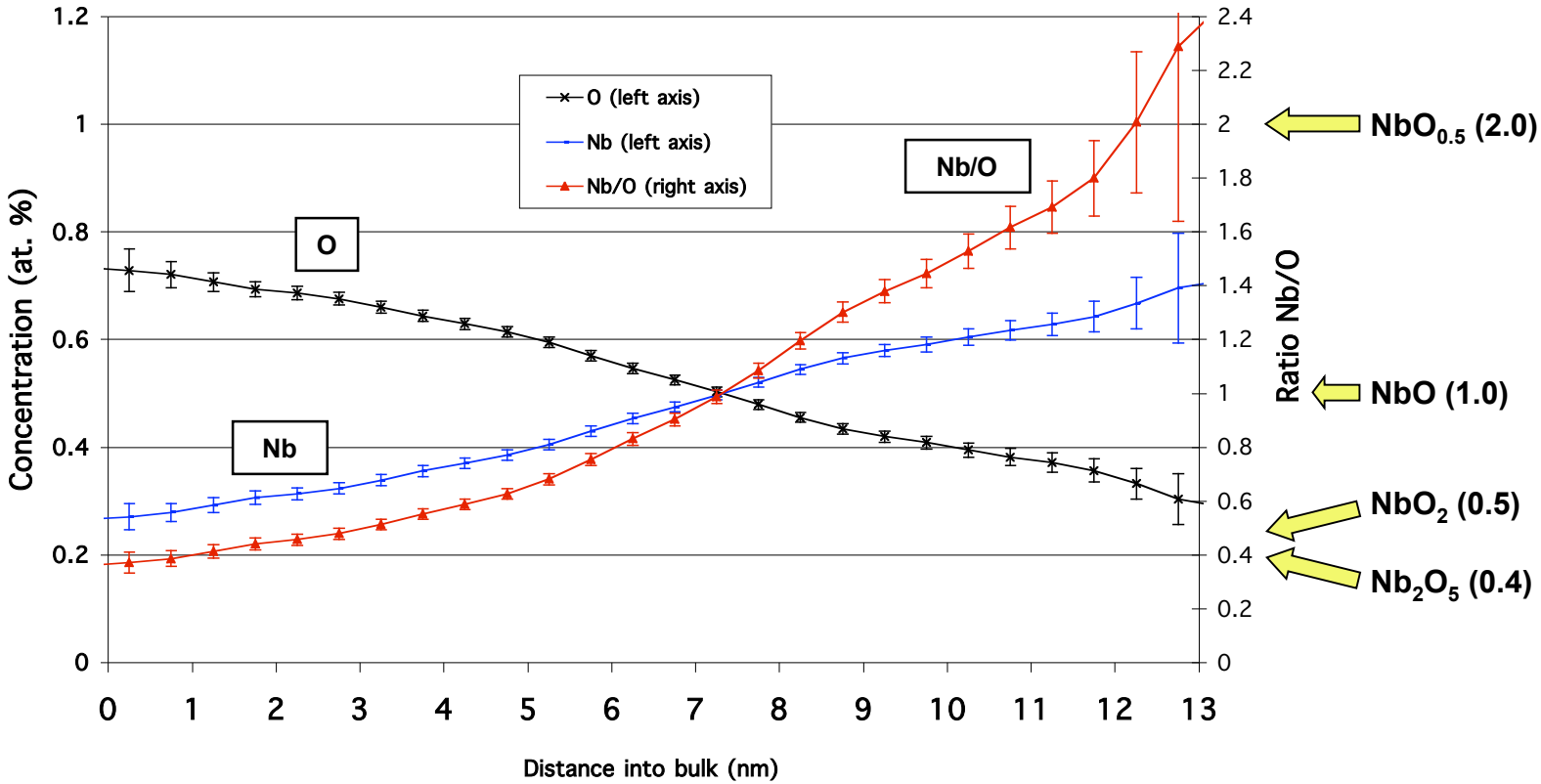
From Miller et al., (1996)

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

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

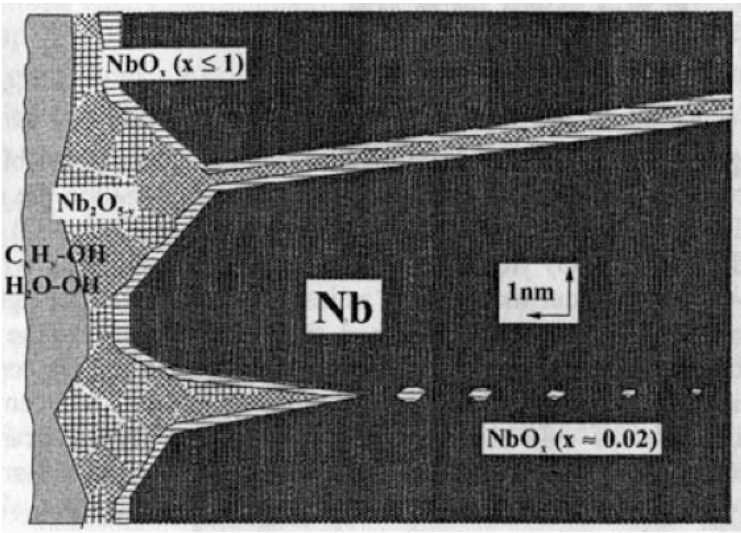


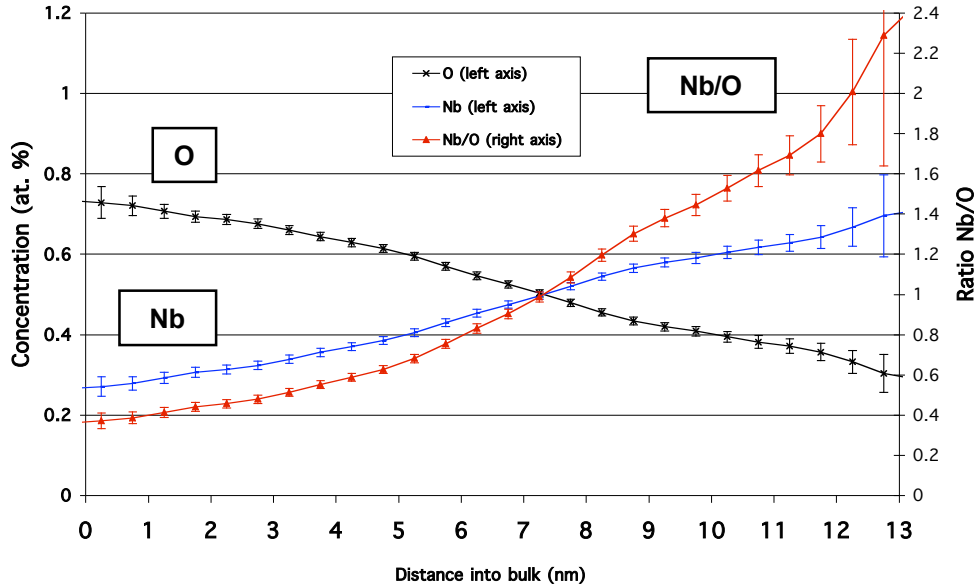
Removal of the hydrogen and residual gas atoms from the concentration gives a better picture of the transition through the oxide layer



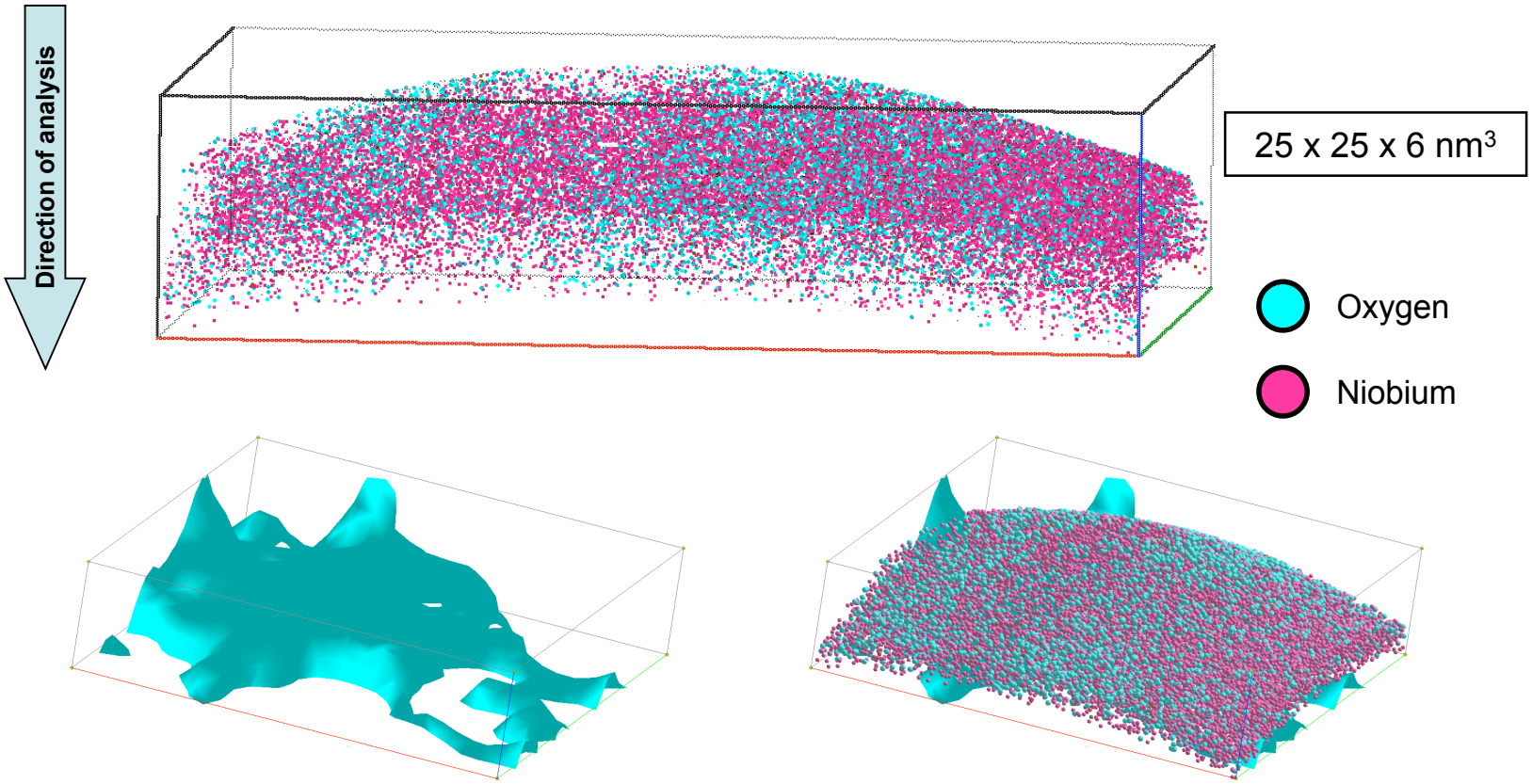
We see a clear and smooth transition from Nb_2O_5 to $NbO_{0.5}$ (= Nb_2O)

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

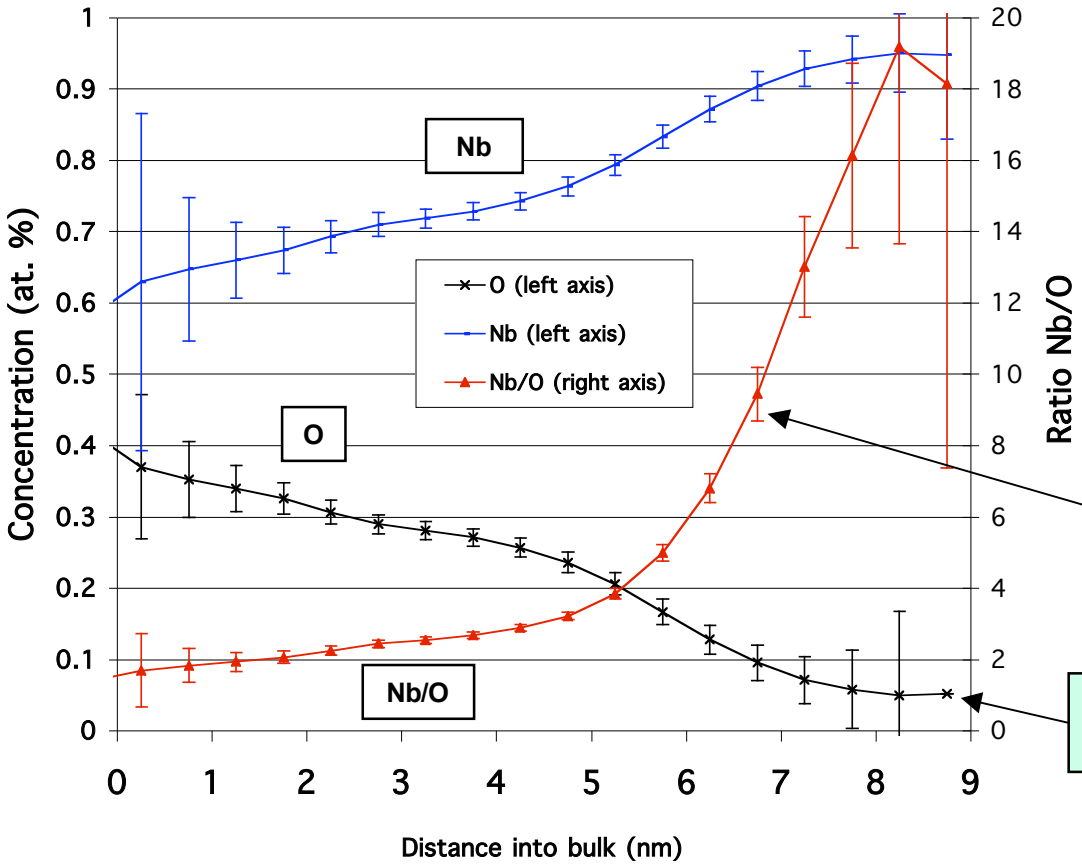


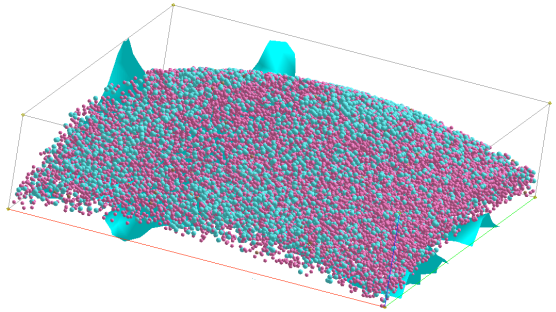


Second Nb analysis - more Nb-rich



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

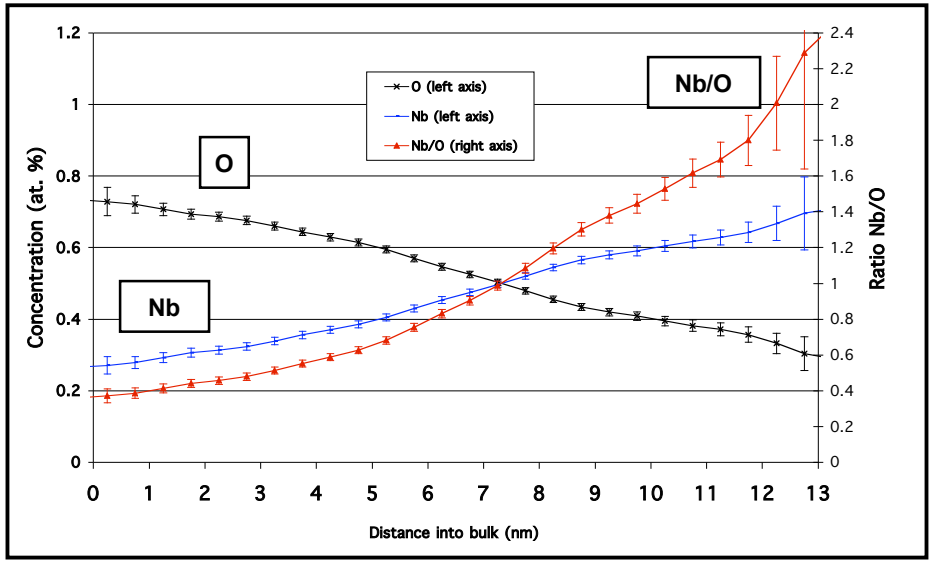




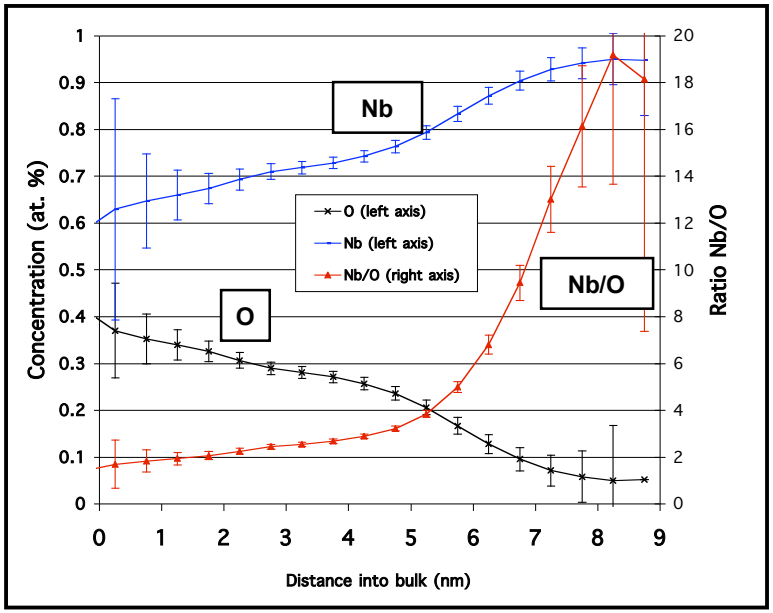
The transition from oxide to metal may be marked by a rapid increase in the ratio of Nb and O concentrations

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

Second analysis … a "continuation" of the first analysis

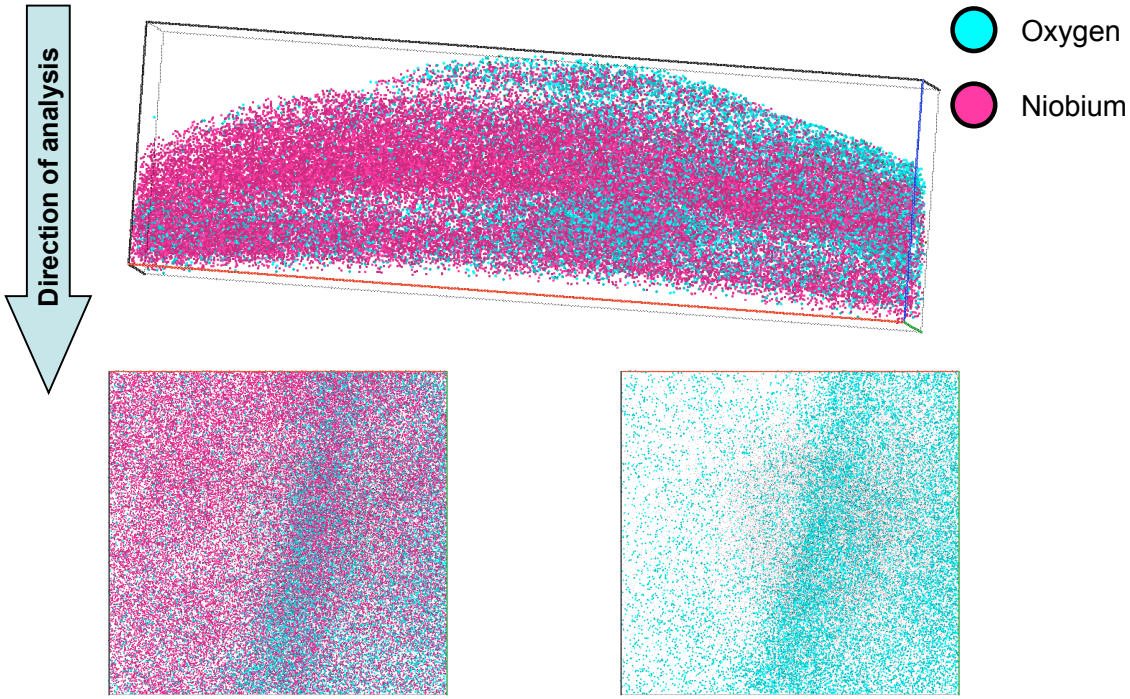


First analysis (Nb_2O_5 to Nb_2O)

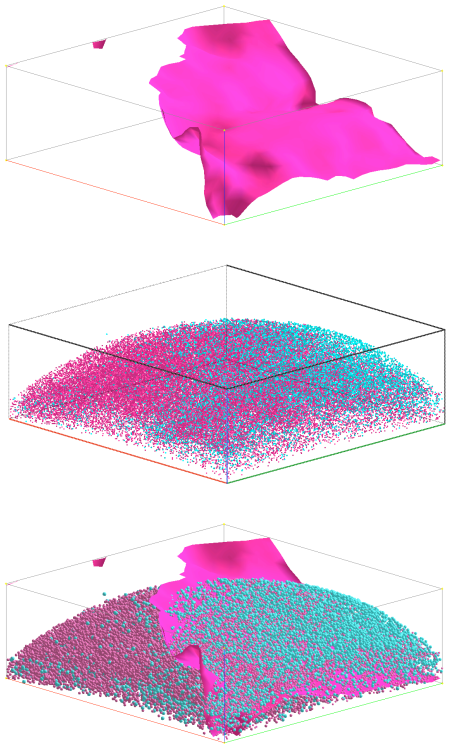


Second analysis (Nb_2O to Nb metal [?])

Third Nb analysis - an oxide metal interface

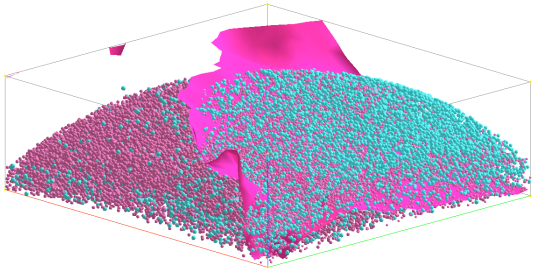


27 x 26 x 9 nm^3
~95 k atoms



55 at. % Nb isosurface

55% Nb isosurface and proxigram



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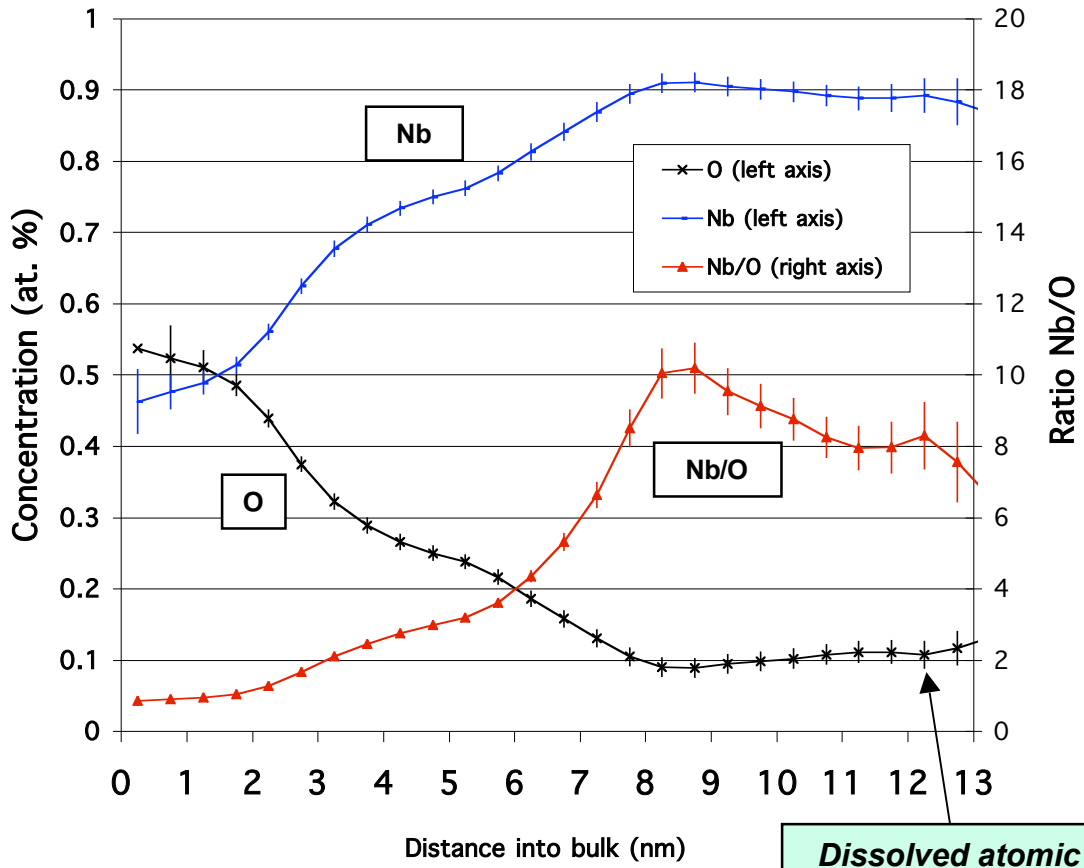
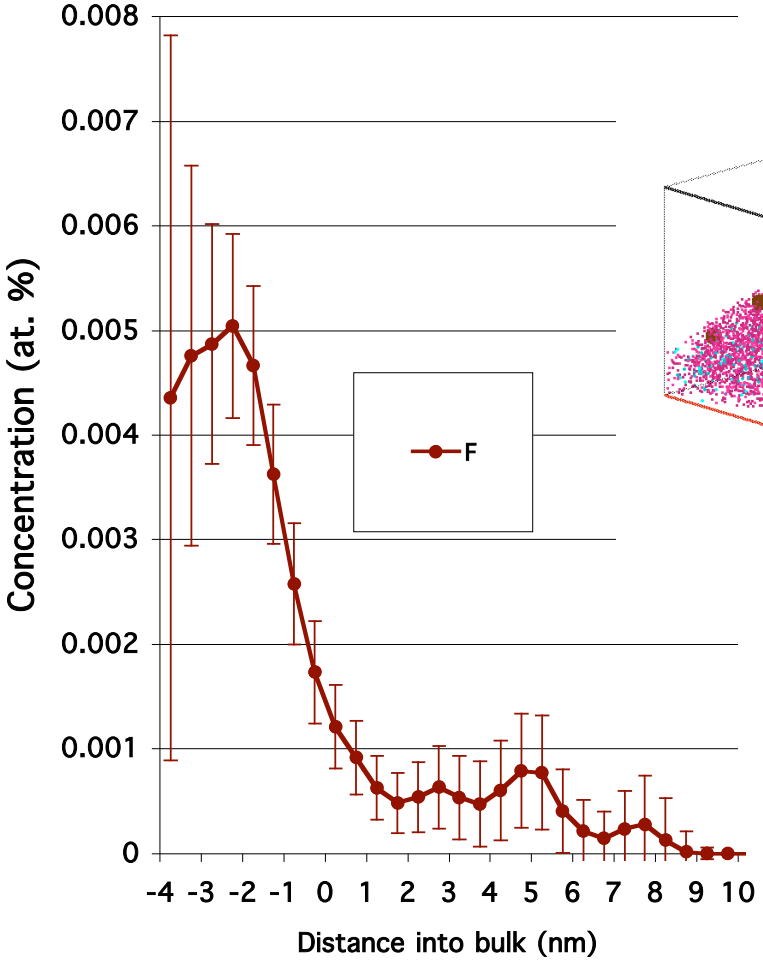
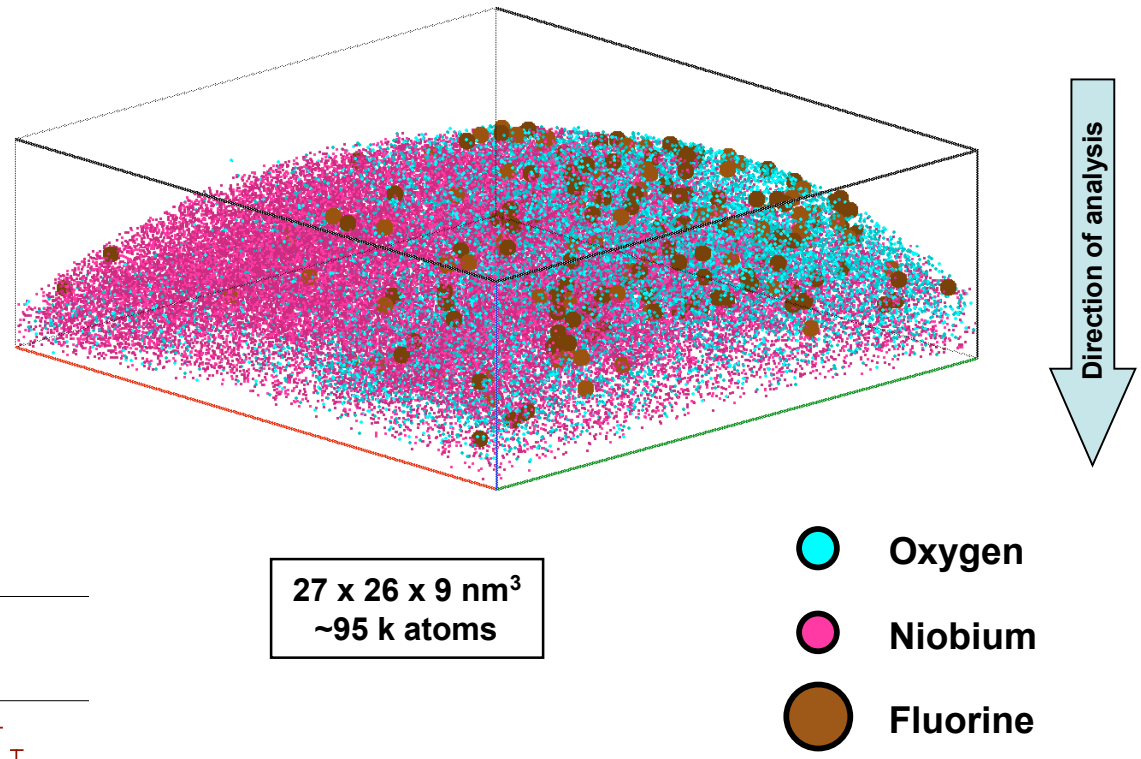


Dissolved atomic oxygen in Nb metal (~10 at. %)

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



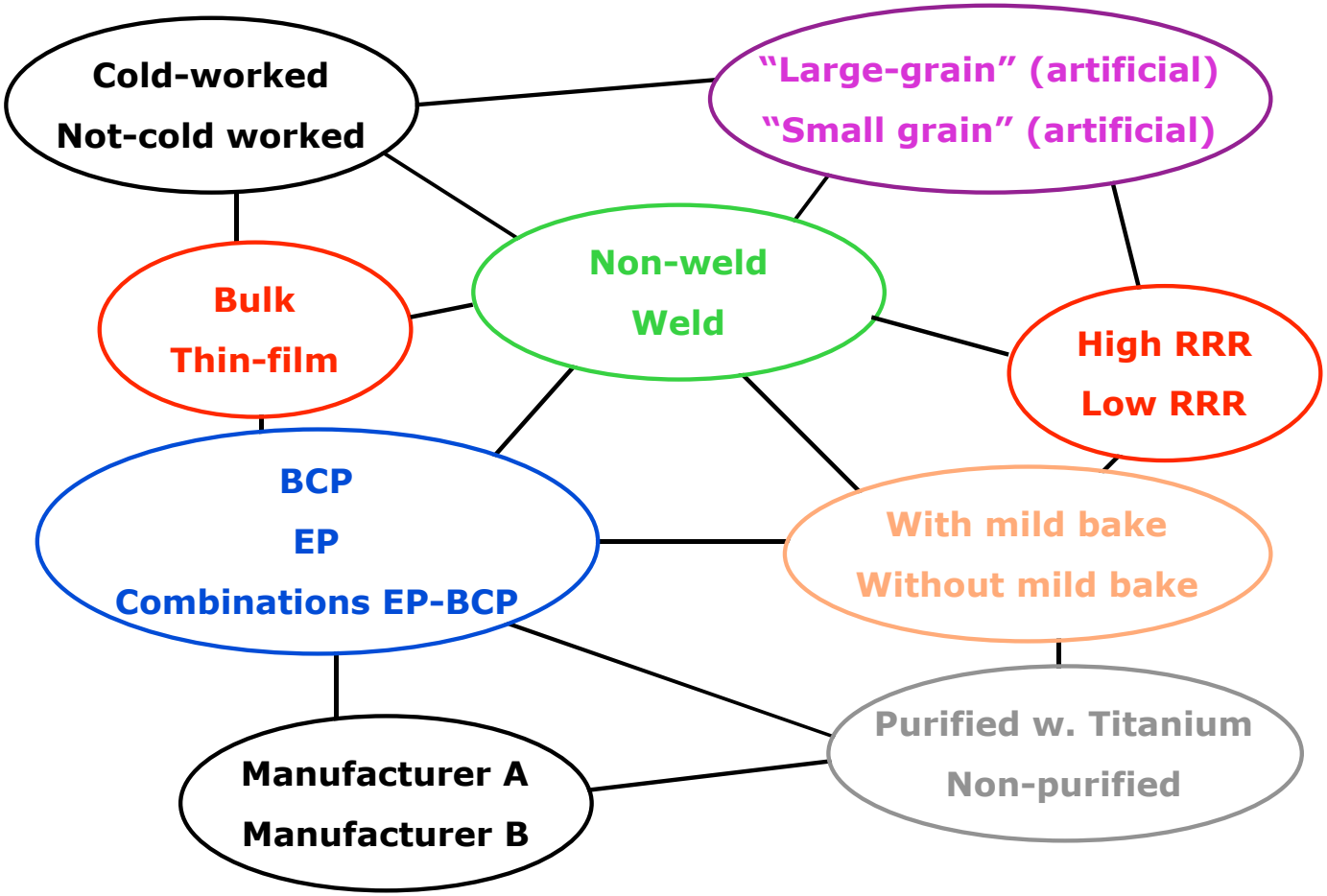


Conclusions and next steps

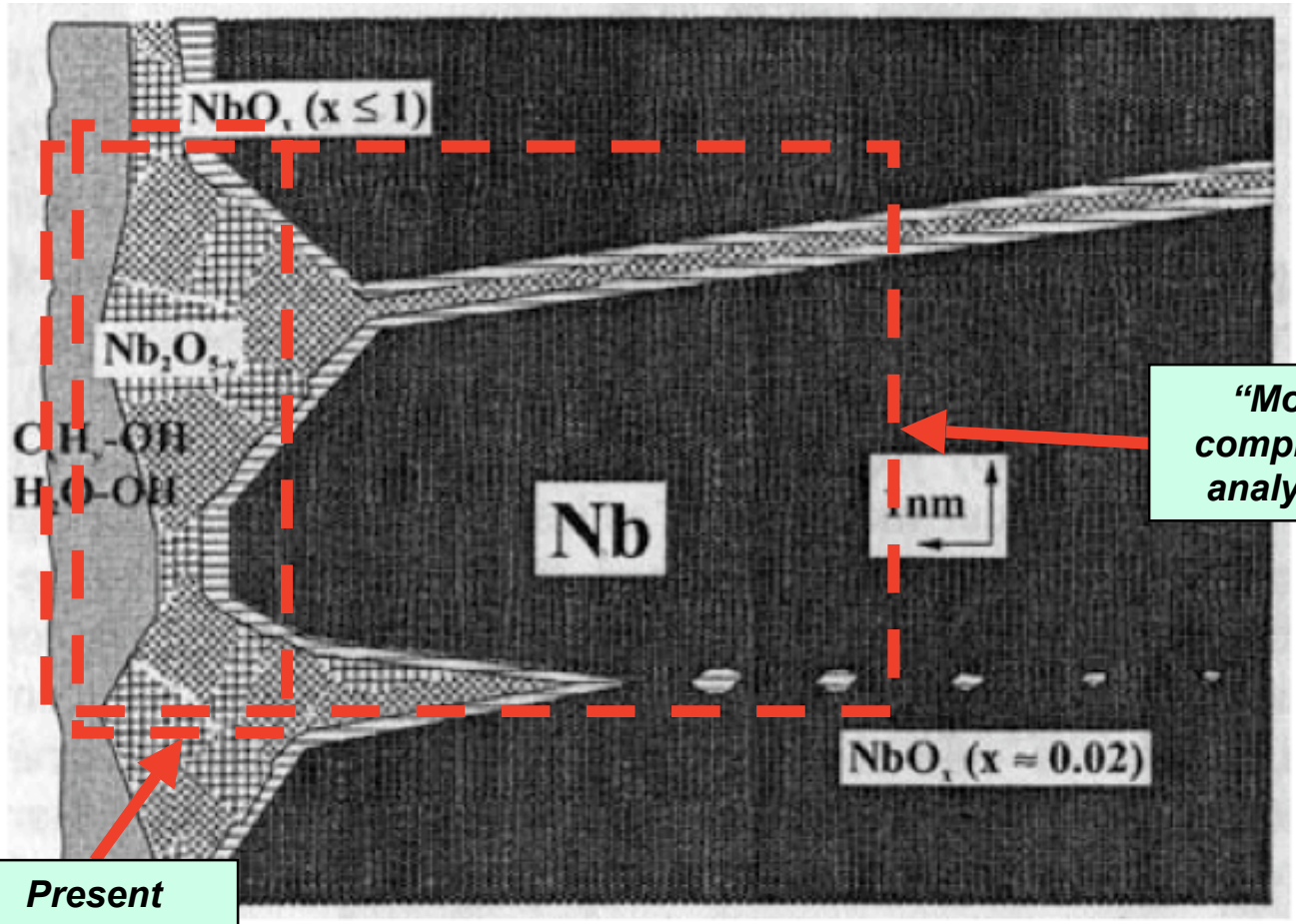
- Nanochemical, atomic scale analyses of the oxide surface and of the near-surface bulk niobium are being performed
  - "Smooth" transition from surface Nb_2O_5 to Nb_2O (and into the bulk Nb)
  - Ability to detect small number of contaminant atoms in the oxide surface and in the near-surface bulk niobium
  - Levels of oxygen in the near-surface bulk niobium (metal) of 5-10 at. %

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

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



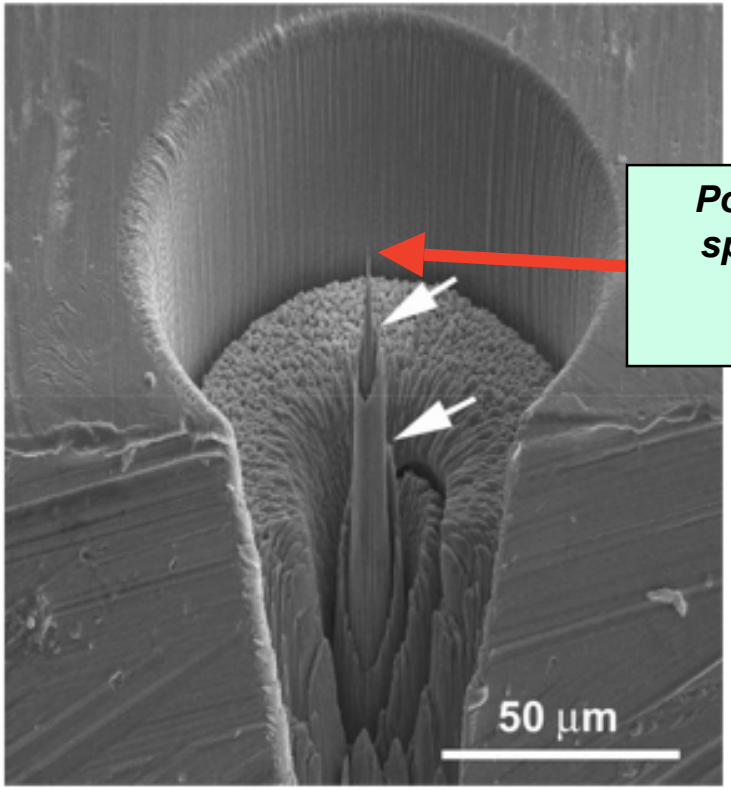
A “more complete” run would capture much more of the atomic chemistry of the oxide surface and of the near-surface bulk niobium



“More complete” analyses

Present analyses

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.