Some theories (& history) of sputtered ion formation

Peter Williams

Arizona State University

"when primary Canalstrahlen strike against a plate of metal, secondary rays are produced. These . . . are for the most part uncharged, but a small fraction carry a positive charge"

J.J. Thomson, Phil. Mag. 20 (1910) 752.

A New Process of Negative Ion Formation

By F. L. Arnot, Ph.D., Lecturer in Natural Philosophy, and J. C. Milligan, M.A., B.Sc., The University, St. Andrews

(*Communicated by H. S. Allen, F.R.S.—Received 27 March, 1936*)

$$Hg^{+} \rightarrow W \rightarrow Hg^{-}$$

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The formation of negative ions by positive-ion impact on surfaces

By R. H. Sloane, D.Sc. and R. Press, M.Sc.
Queen's University, Belfast

(*Communicated by E. V. Appleton, F.R.S.—Received* 12 *July* 1938)

Formation of hydrocarbon cluster ions in poor vacuum

JOURNAL OF APPLIED PHYSICS VOLUME 31, NUMBER 4 APRIL, 1960

On the Yield and Energy Distribution of Secondary Positive Ions from Metal Surfaces*

HENRY E. STANTON
Argonne National Laboratory, Lemont, Illinois

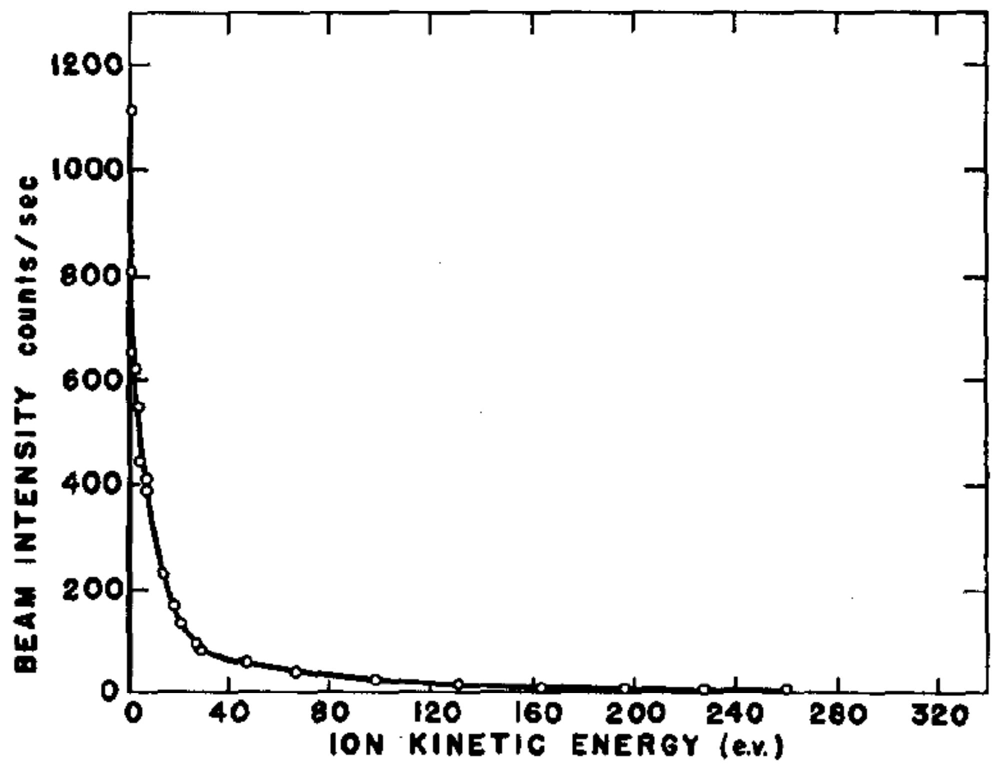

FIG. 8. The distribution of kinetic energy of Be^+ ions driven from the target under bombardment by neon ions of 1000-ev energy.

-- not a simple Boltzmann thermal distribution

Arifov Institute (Tashkent, Uzbekhistan)

Morov & Ayukhanov, Radio Engineering & Electron Physics **8** 280 (1963)

-- observed that ion yields from ionic substances, e.g. NaCl could be very high, e.g. ~ 30% for Cl^- from NaCl

Title: SUR LEMISSION ELECTRONIQUE SECONDAIRE DES METAUX BOMBARDES PAR DES IONS POSITIFS

Author(s): SLODZIAN G

Source: COMPTES RENDUS HEBDOMADAIRES DES SEANCES DE L ACADEMIE DES SCIENCES 246 (26): 3631-3634 **1958**

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First ion microscope; observed ion yield enhancement by oxygen

Arifov Institute (Tashkent, Uzbekhistan)

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-- observed that ion yields from ionic substances, e.g. NaCl could be very high, e.g. ~ 30% for Cl^- from NaCl

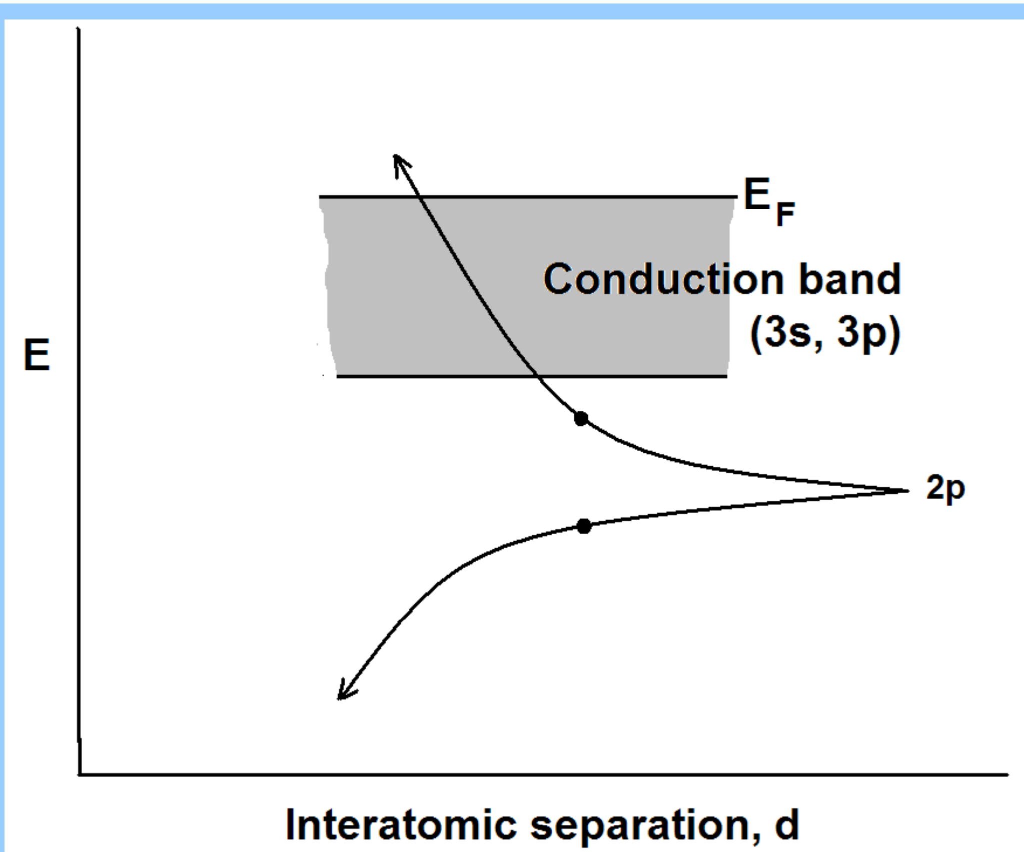
"Intrinsic" ion emission from "clean" metal surfaces

Issues:

-- how are ions created in (at) the surface?

-- how do ions escape from the surface un-neutralized?

Joyes (1968-70): Auger de-excitation model



Collisional electron promotion model of Joyes for Mg, Al, Si (P. Joyes, 1968-70):

a) An electron in an antibonding state derived from the 2p orbital can be promoted to an energy above the Fermi level, and detach, leaving an excited atom with a 2p hole

b) IF the 2p hole lifetime is long enough (~10 fs for Mg, Al, Si) the atom can move > 5 A from the surface before Auger de-excitation ejects 1 or 2 e's, giving 1+ or 2+ ions that cannot then be neutralized by electron tunneling

Evidence for electron-promotion model:

-- observation of multiply-charged ions of Mg, Al, Si at relatively low energies

-- observation of ion-induced Auger electrons

-- works even for 4^{th}-period elements (initially thought to have too short core-hole lifetimes)

PHYSICAL REVIEW B VOLUME 46, NUMBER 23 15 DECEMBER 1992-I

Doubly charged sputtered ions of fourth-row elements

Stephen N. Schauer
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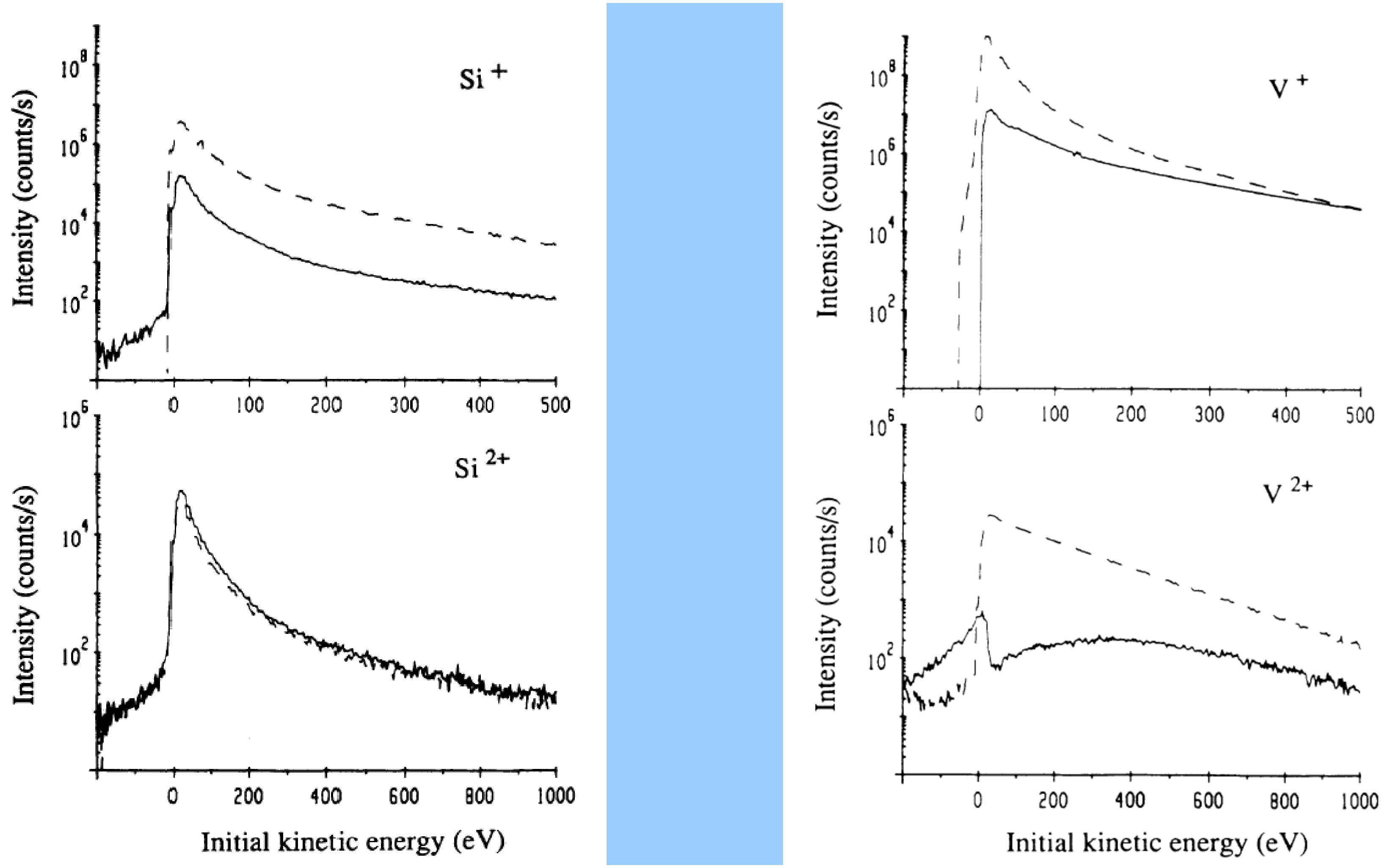
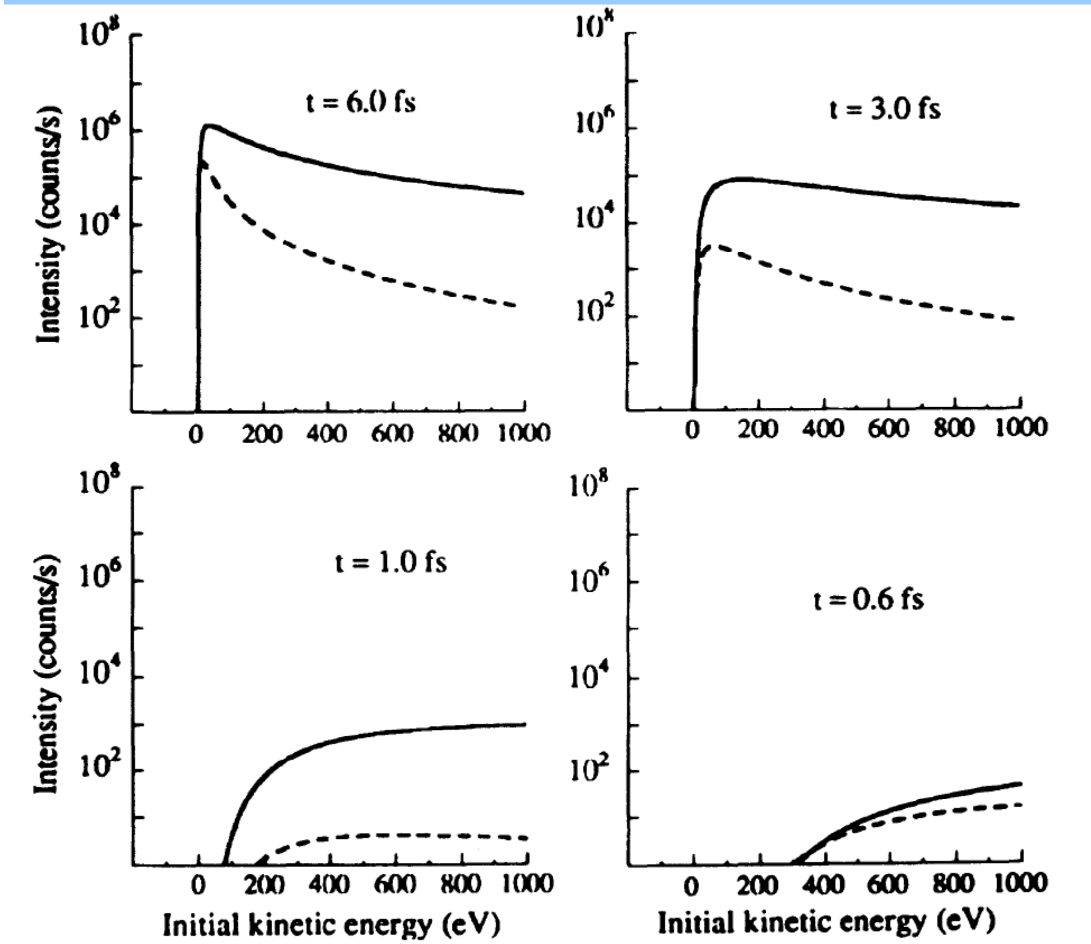
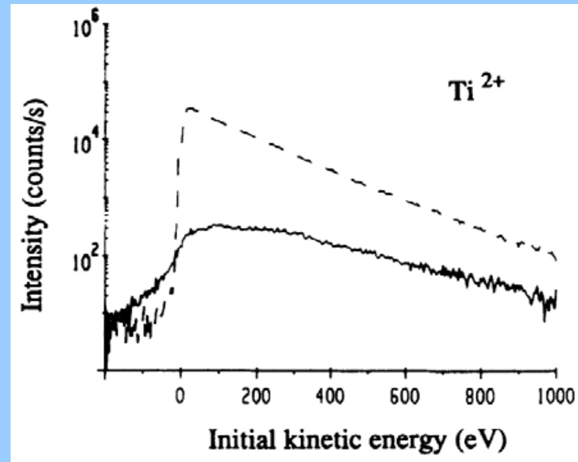
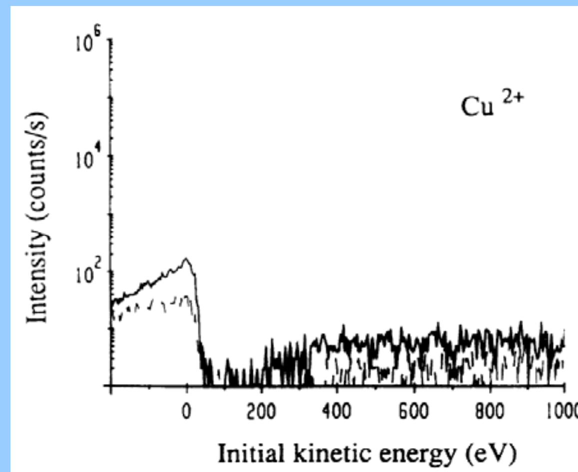
Peter Williams
Department of Chemistry, Arizona State University, Tempe, Arizona 85287-1604



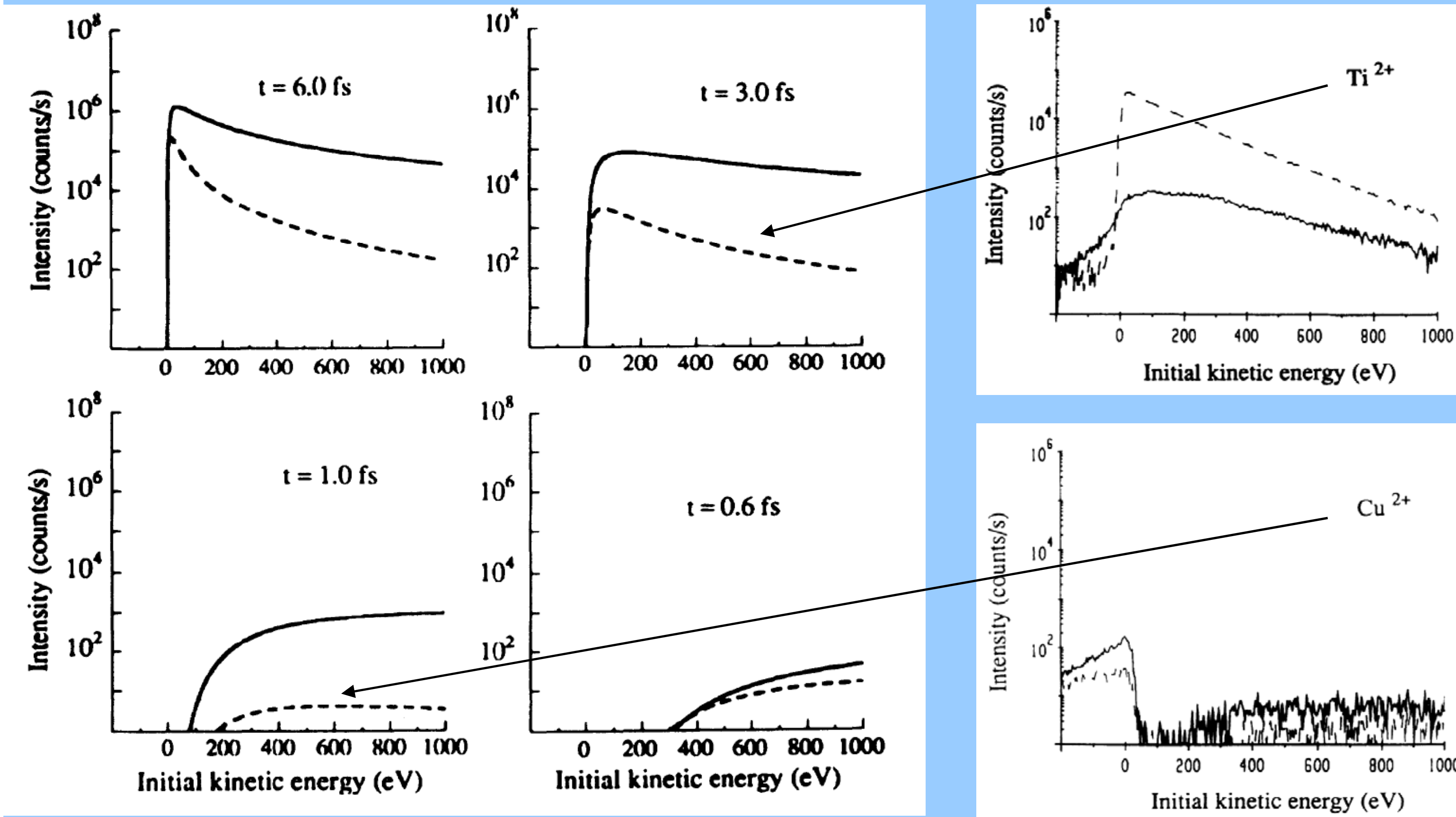






Predicted energy distributions for different vacancy lifetimes

(Solid lines: total E; dotted lines: after transmission through MS)



Predicted energy distributions for different vacancy lifetimes

“Intrinsic” ion emission from “clean” metal surfaces

Issues:

-- how are ions created?

-- how do ions escape from the surface un-neutralized?

Perturbation model: Blaise & Slodzian 1970, Nourtier 1976, Blandin,Nourtier & Hone 1976, Norskov & Lundqvist 1979… atoms are excited (ionized) by the perturbation associated with rapid detachment from the surface; then survive neutralization (by electron transfer from the surface) to escape as ions

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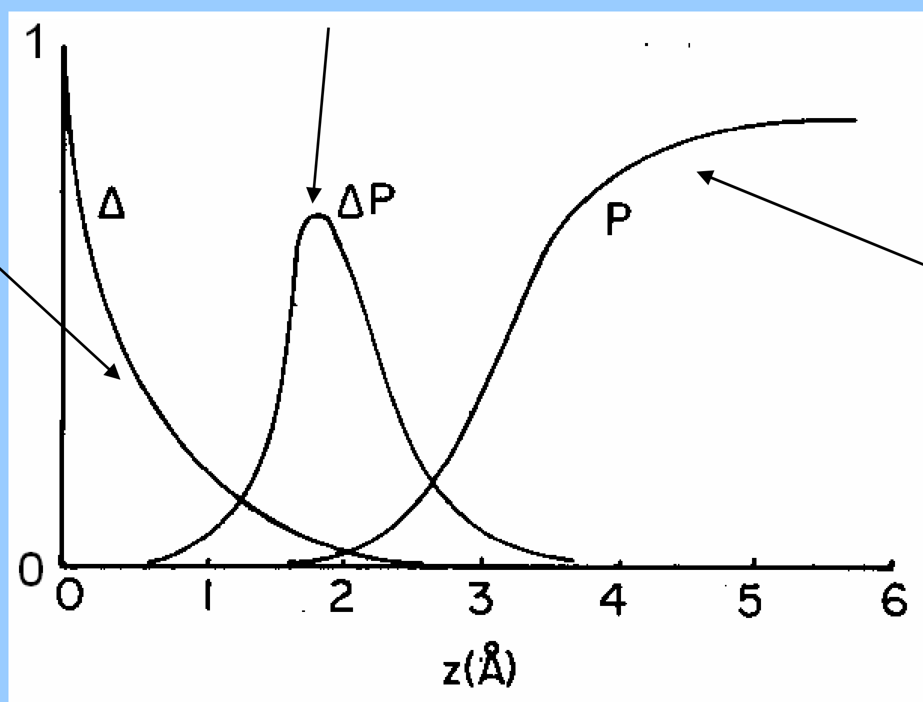
Excitation probability *Ionization probability (x 10^n)*



Escape probability

Issues with the perturbation model:

a) How to accurately characterize the "surface" during the sputtering event?
-- see MD simulations

b) Is there really an "average" sputtering event?

c) Is there really a "kinetic" emission process on "clean" surfaces?

-- i.e. Ion yields (~ 10^{-4} – 10^{-6}) are comparable to the level of oxygen contamination in the bulk or from the vacuum

-- is all ionization associated with oxygen?

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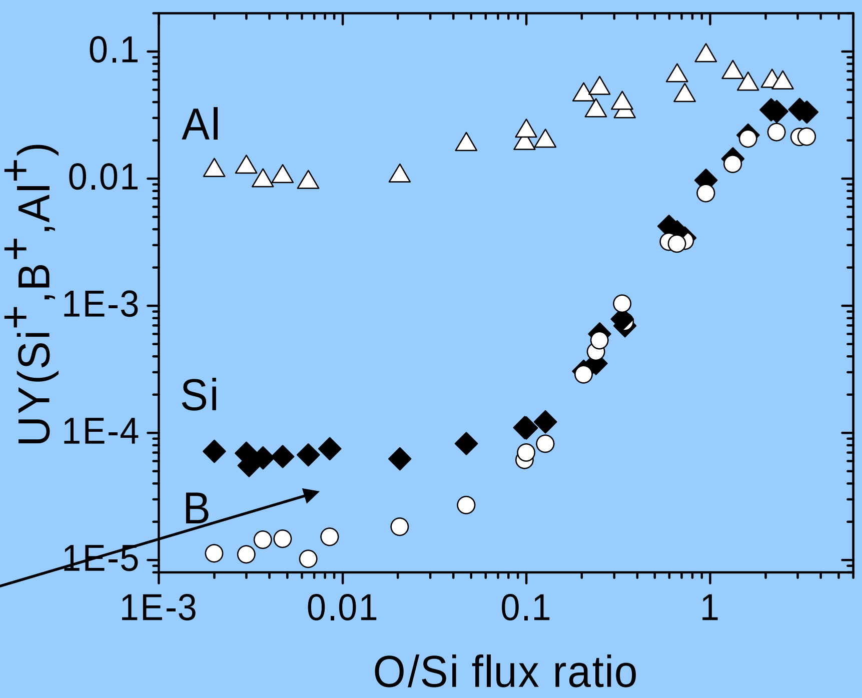
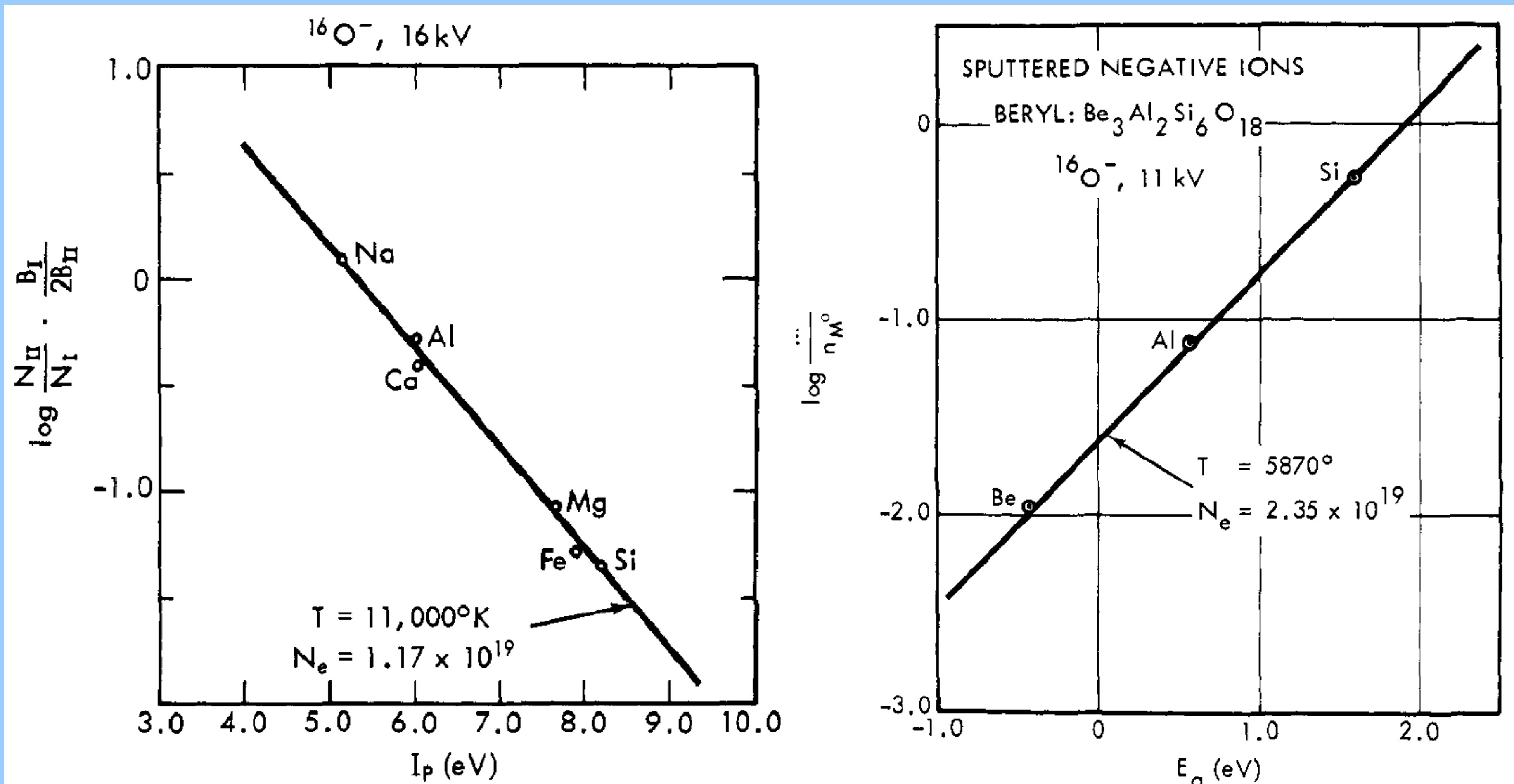


NO – kinetic emission does occur

C.A. Andersen & J.R. Hinthorne 1973: “CARISMA”



Saha-Eggert:

(“plasma eqn.)

$$K_{n^+} = \frac{n_{M^-}\, n_{e^-}}{n_{M^0}} = \left(\frac{2\pi}{h^2}\,\frac{m_{M^+} m_{e^-}}{m_{M^0}}\,kT\right)^{3/2} \frac{B_{M^+} B_{e^-}}{B_{M^0}}\, e^{-E/kT}$$

C.A. Andersen & J.R. Hinthorne 1973: "CARISMA"

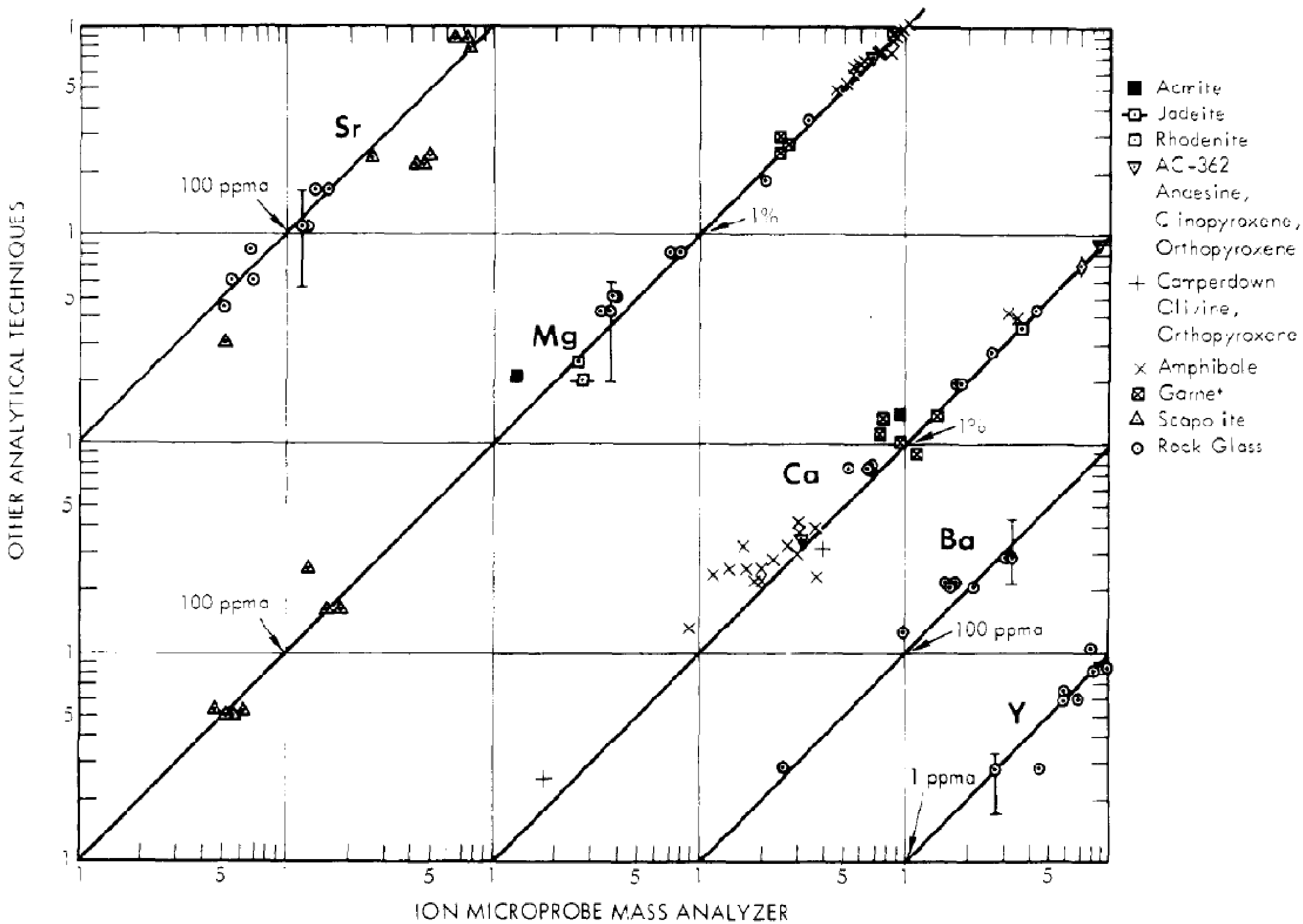


Figure 6. Comparison of the analyses of the ion microprobe mass analyzer with those of other analytical techniques for the alkaline earth elements plus yttrium in silicate matrices

“CARISMA” was infuriating because it was

(a) proprietary – hard to check. Used extensive compilations of partition functions and a proprietary computer program

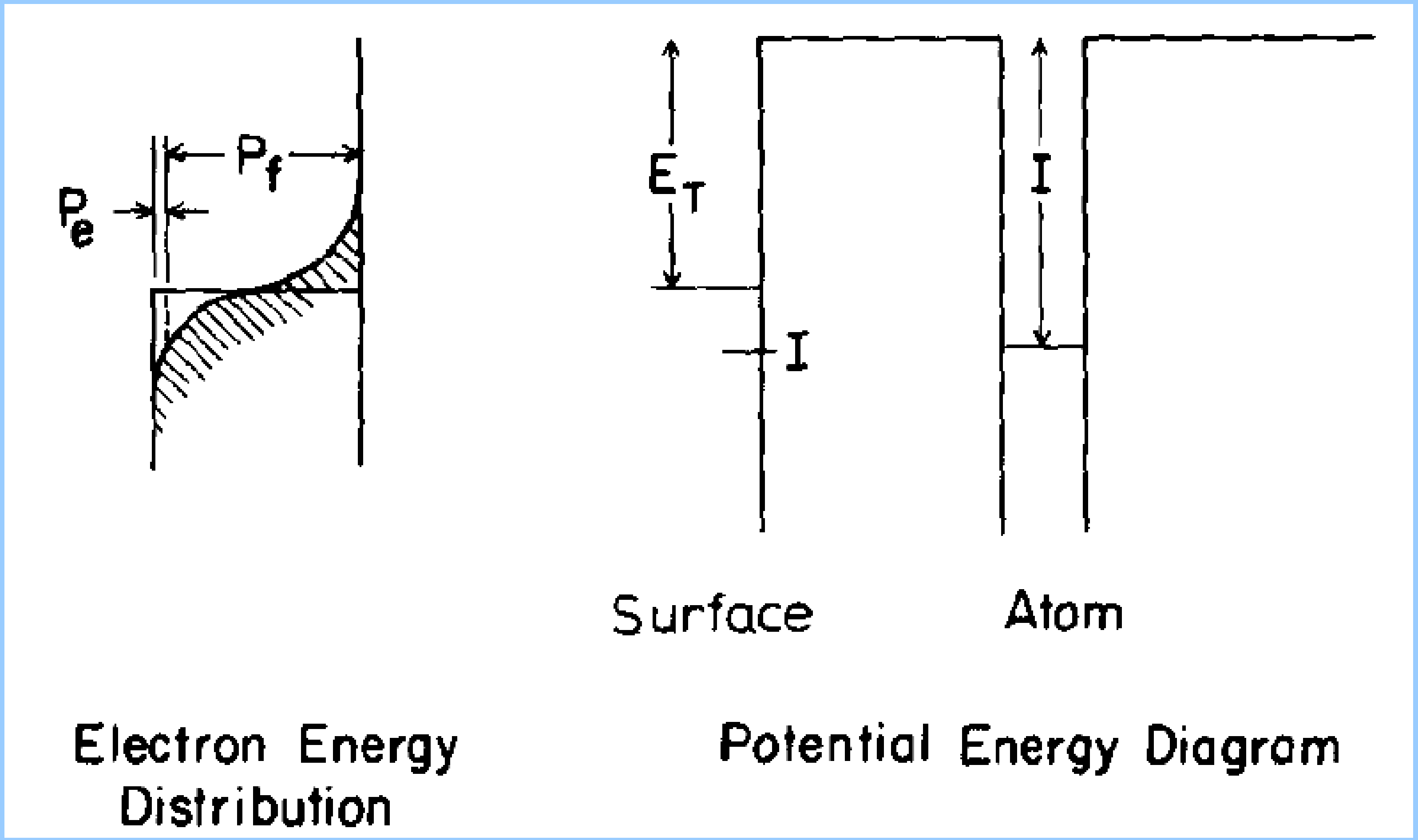
(b) physically unreal – i.e. there is NO physical evidence for a plasma in thermodynamic equilibrium at the sputtering site

(c) it worked

1974: Drew Evans asked Dave Simons to look into this: Dave produced a much simpler approach that worked equally well

-- showed that a Saha-Langmuir equation fit the data equally well if ϕ and T are allowed to be fitting parameters

$$\frac{n^+}{n_0} = \frac{A^+}{A_0} \exp \frac{-(I - \phi)}{k\text{"}T\text{"}}$$



"Surface excitation" model (PW 1979): assume collisionally excited electrons equilibrate to a Fermi-Dirac distribution on a time scale faster than the ion departs

-- then a Saha-Langmuir equation for ionization follows

Slodzian: metal positive ion yields enhanced by oxygen

-- "bond-breaking model" -- rupture of ionic M-O bonds yields M^+, O^-

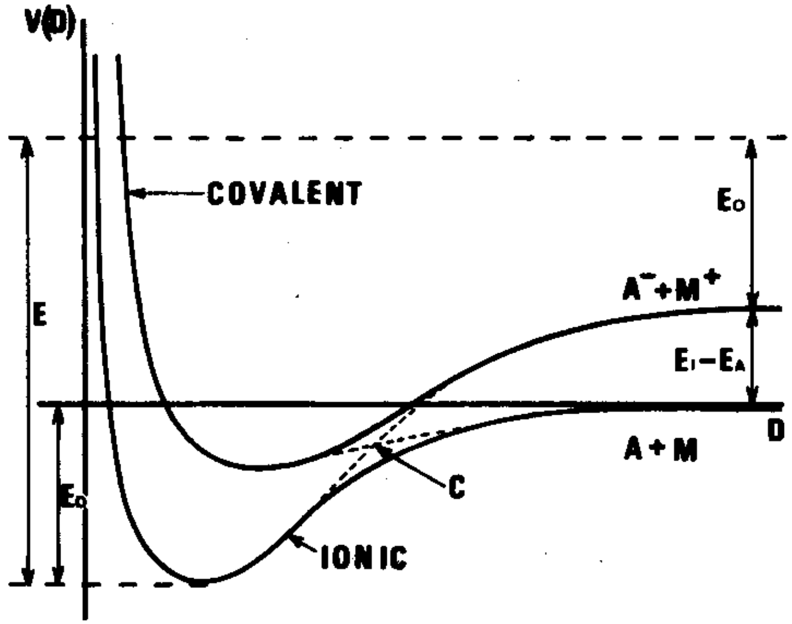
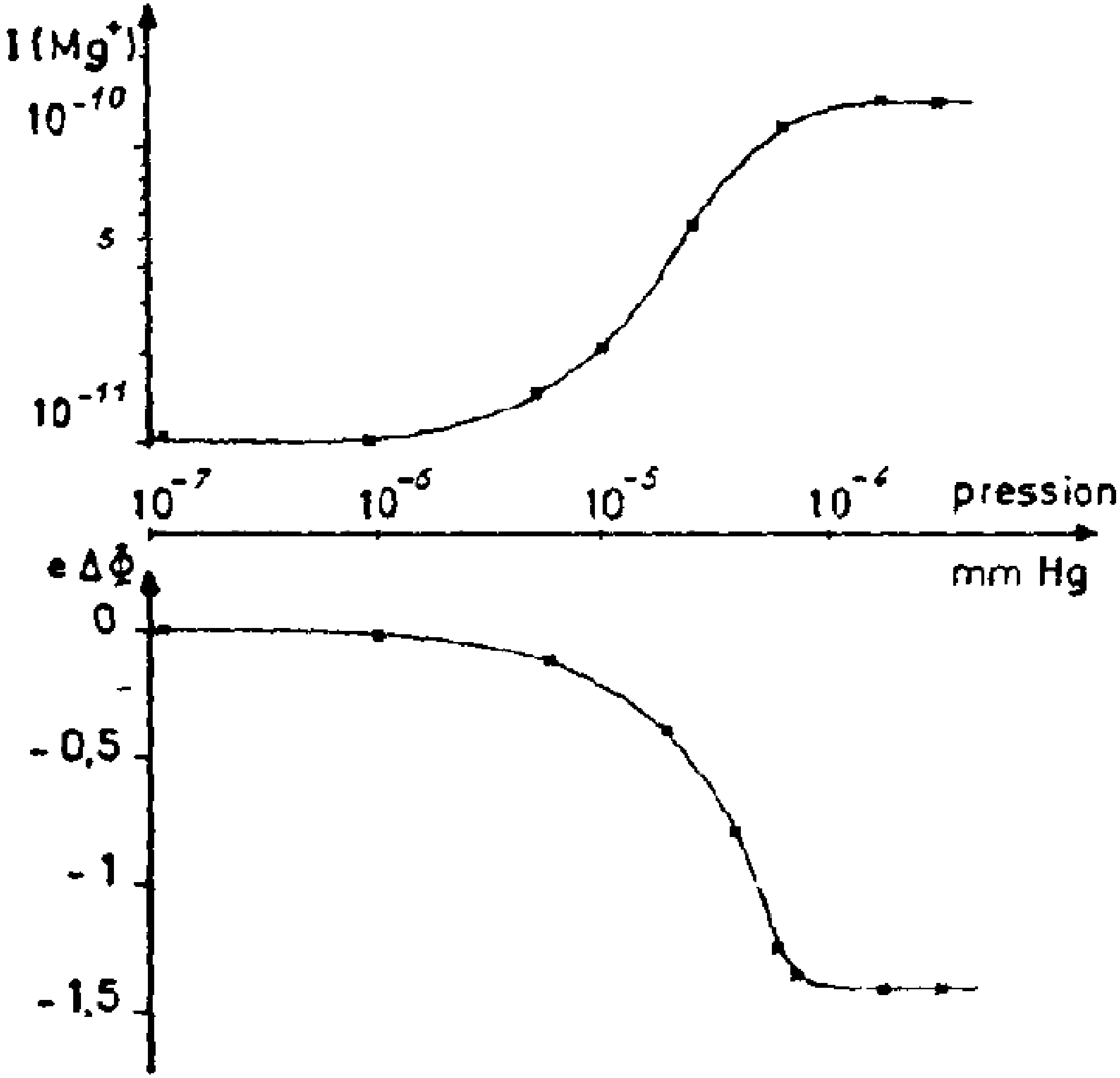


Fig. 12. Anticrossing diagram used in LZS model: E_I ionization energy of M, E_A electron affinity of the complex anion A, E_D dissolation energy, D distance between the two "nuclei" A and M, E energy received by M in the last collision, E_0 kinetic energy of M^+ [46].

From Slodzian, Physica Scripta 1982



"work function" is not a good parameter to explain positive ion effects of oxygen

G. Blaise and G. Slodzian. Surface Sci. 40 (1973) 708.

EFFETS COMPARÉS DE L'OXYGÈNE SUR L'ÉMISSION IONIQUE ET LE POTENTIEL DE SURFACE DES MÉTAUX

Primary oxygen ion implantation effects on depth profiles by secondary ion emission mass spectrometry

R. K. Lewis

Cameca Instruments, Incorporated, Elmsford, New York 10523

J. M. Morabito

Bell Telephone Laboratories, Allentown, Pennsylvania 18100

J. C. C. Tsai

Bell Telephone Laboratories, Reading, Pennsylvania 19600
(Received 23 May 1973)

Appl. Phys. Lett., Vol. 23, No. 5, 1 September 1973

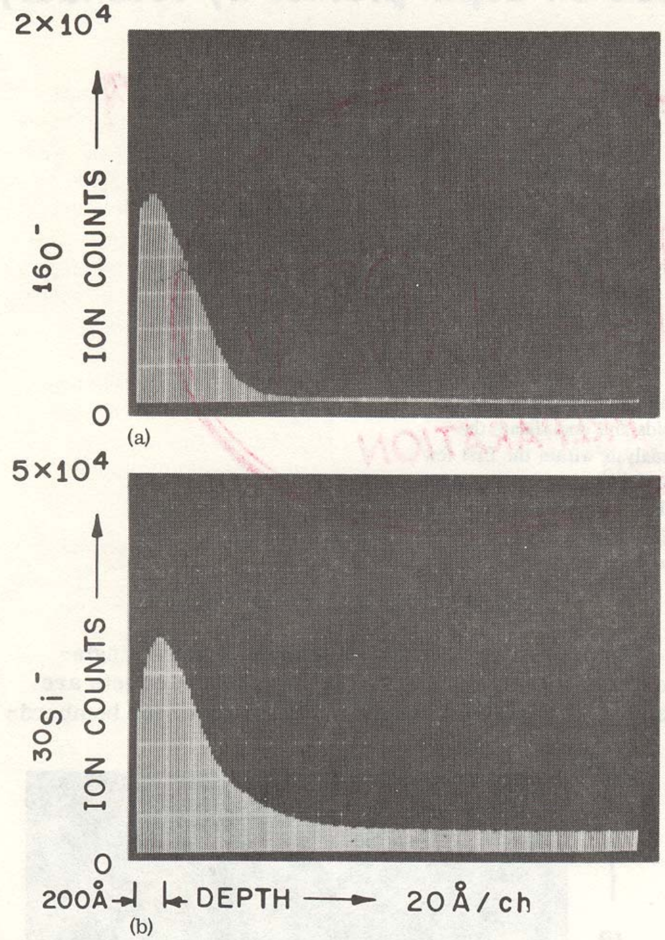
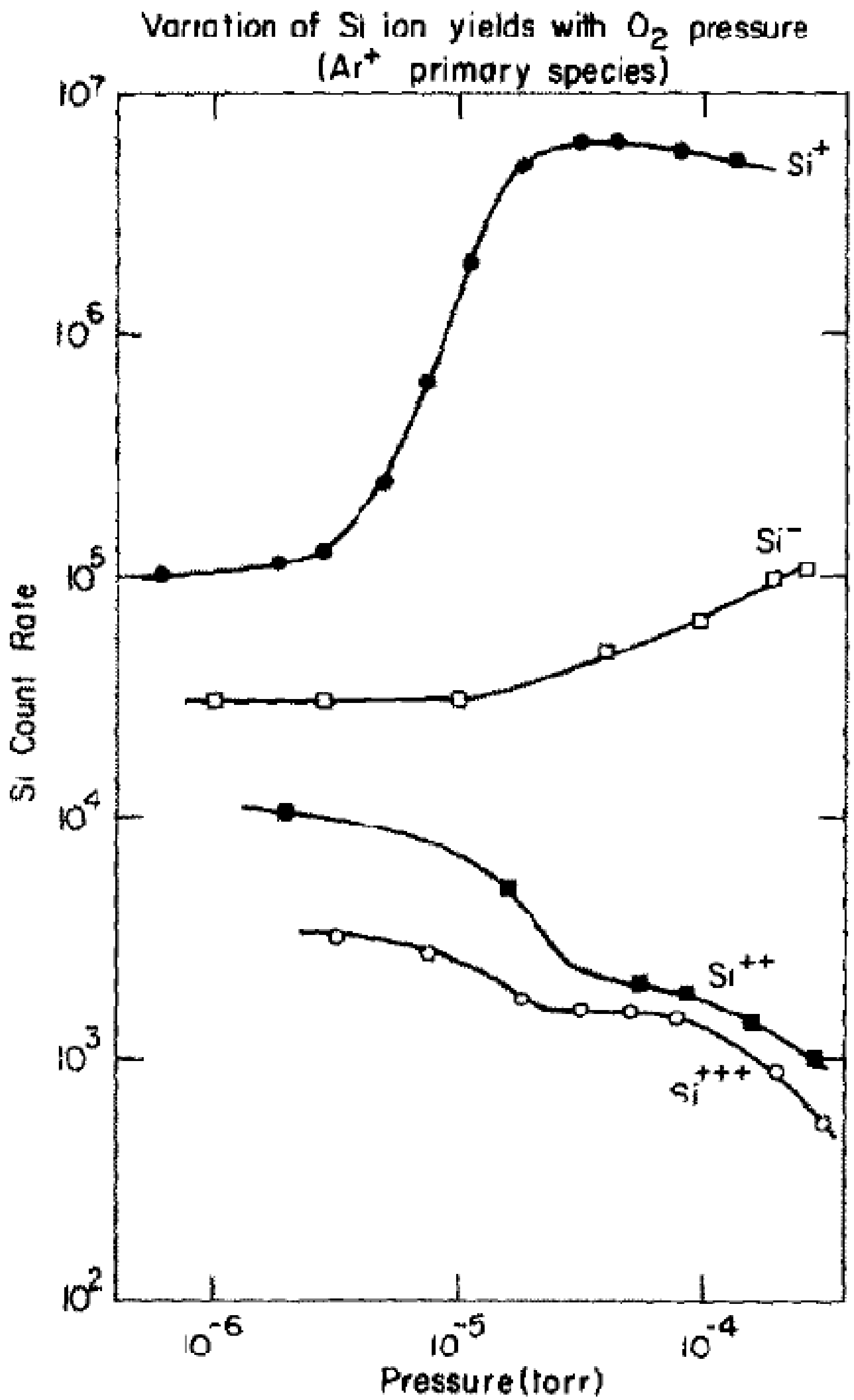


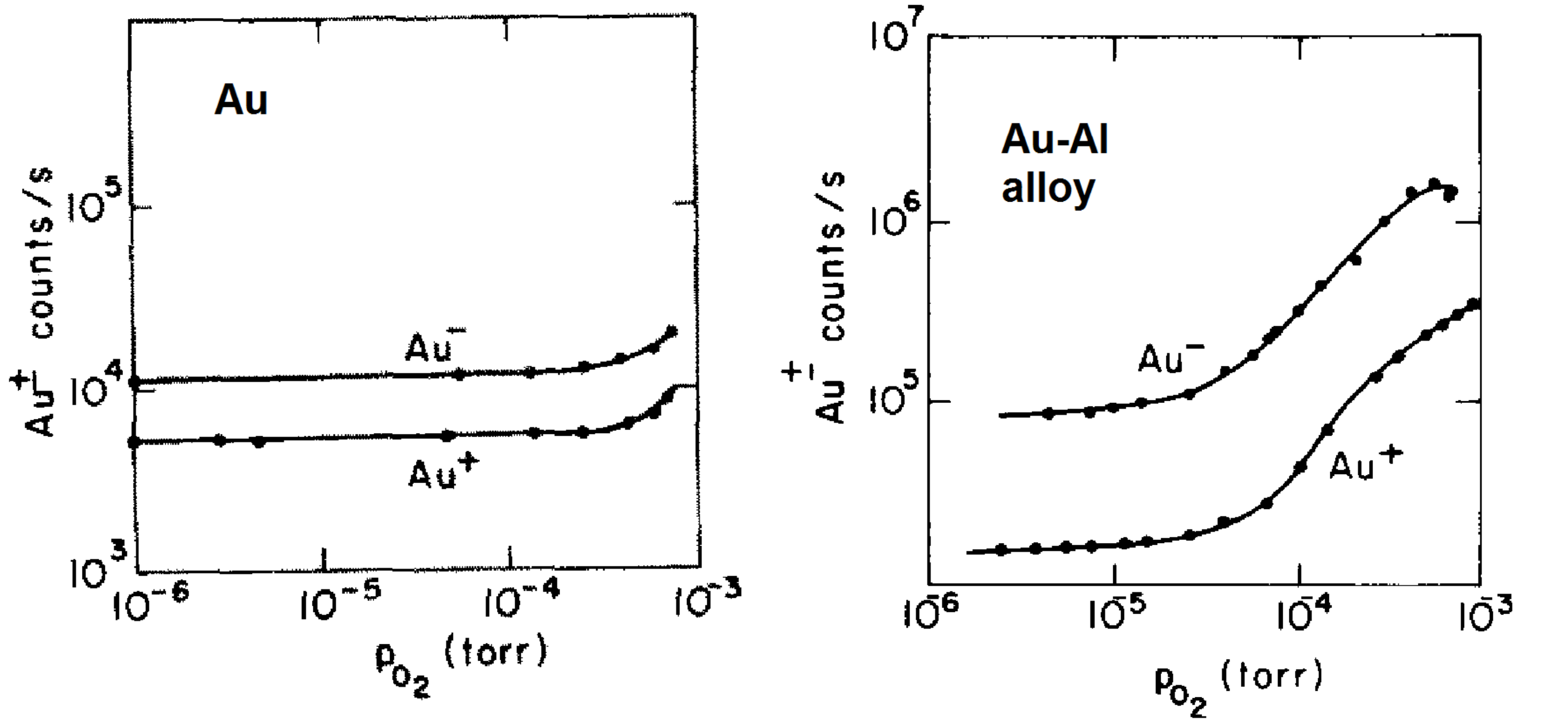
FIG. 2. Comparison of (a) oxygen and (b) silicon signals in a previously measured crater in sample A. Primary ion, Ar^+ at 14.5 keV. Sputtering rate, 100 Å/sec.



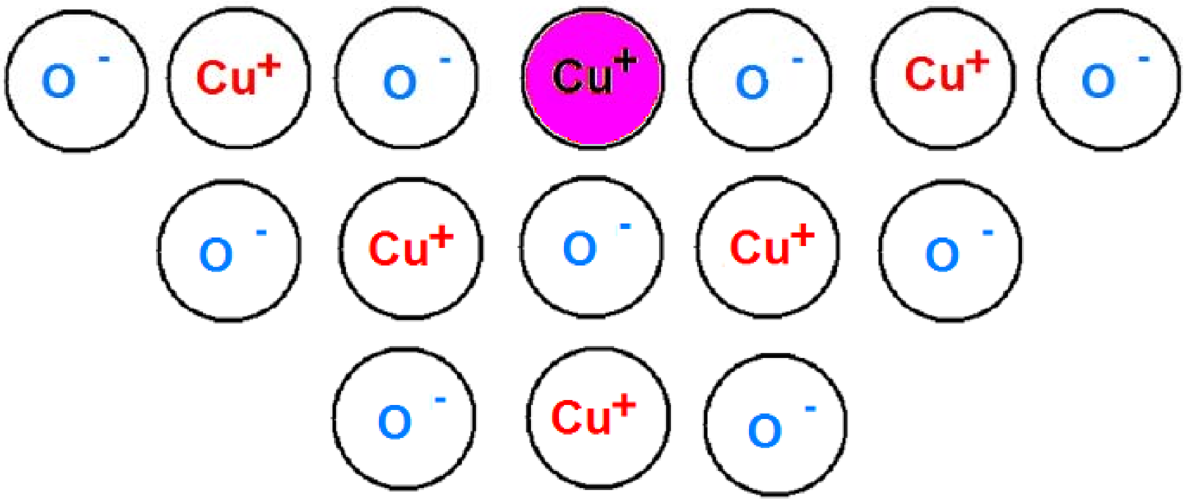
ANOMALOUS ENHANCEMENT OF NEGATIVE SPUTTERED ION EMISSION BY OXYGEN

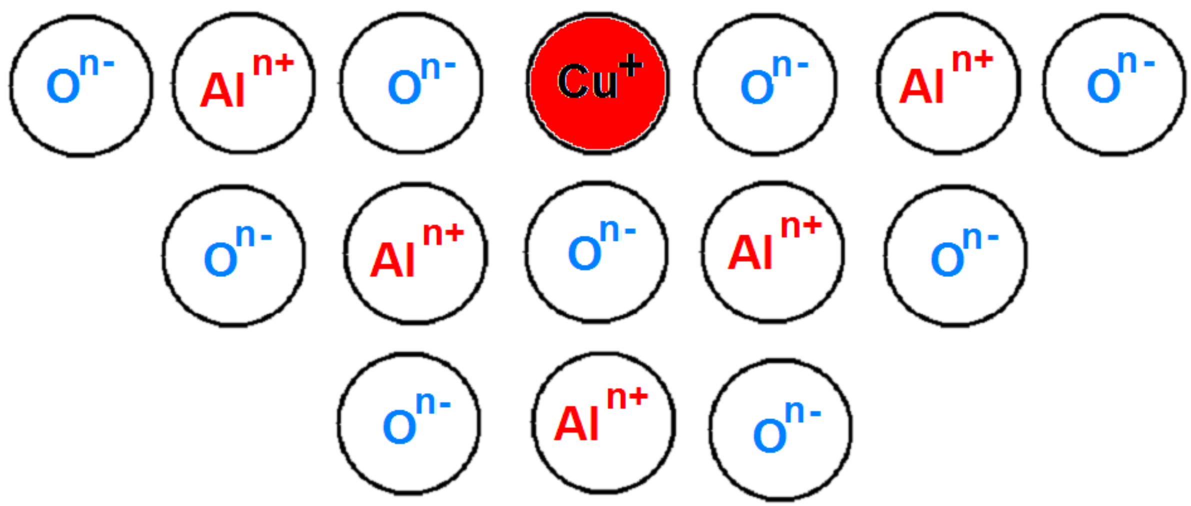
Peter WILLIAMS and Charles A. EVANS, Jr. *

Surface Science 78 (1978) 324–338

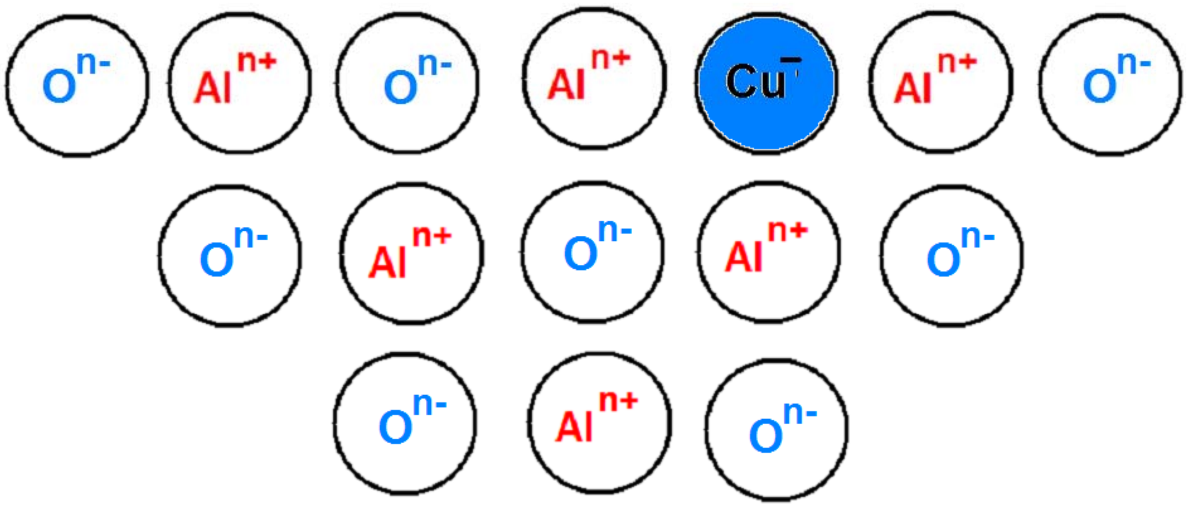


O$_2$-induced enhancement of Au$^-$, Au$^+$ yields in pure Au and Au-Al alloy


O -
Cu+
O -
Cu+
O -
Cu+
O -
O -
Cu+
O -
Cu+
O -
O -
Cu+
O -



O n-
Al n+
O n-
Cu+
O n-
Al n+
O n-
O n-
Al n+
O n-
Al n+
O n-
O n-
Al n+
O n-



O n-
Al n+
O n-
Al n+
Cu −
Al n+
O n-
O n-
Al n+
O n-
Al n+
O n-
O n-
Al n+
O n-

Summary:

-- Sputtered ion formation is COMPLICATED

- -- how do we define/describe a surface?
- -- how do we treat complex many-body collisions in the sputtering site?
- -- do thermal models have ANY validity?
    - -- maybe an electron "temperature" is a valid concept
- -- need clean experiments