

# Phénomènes Impliquant les Matériaux Isolants en Microscopie Électronique

***Pr. Raynald Gauvin, Ph.D.***

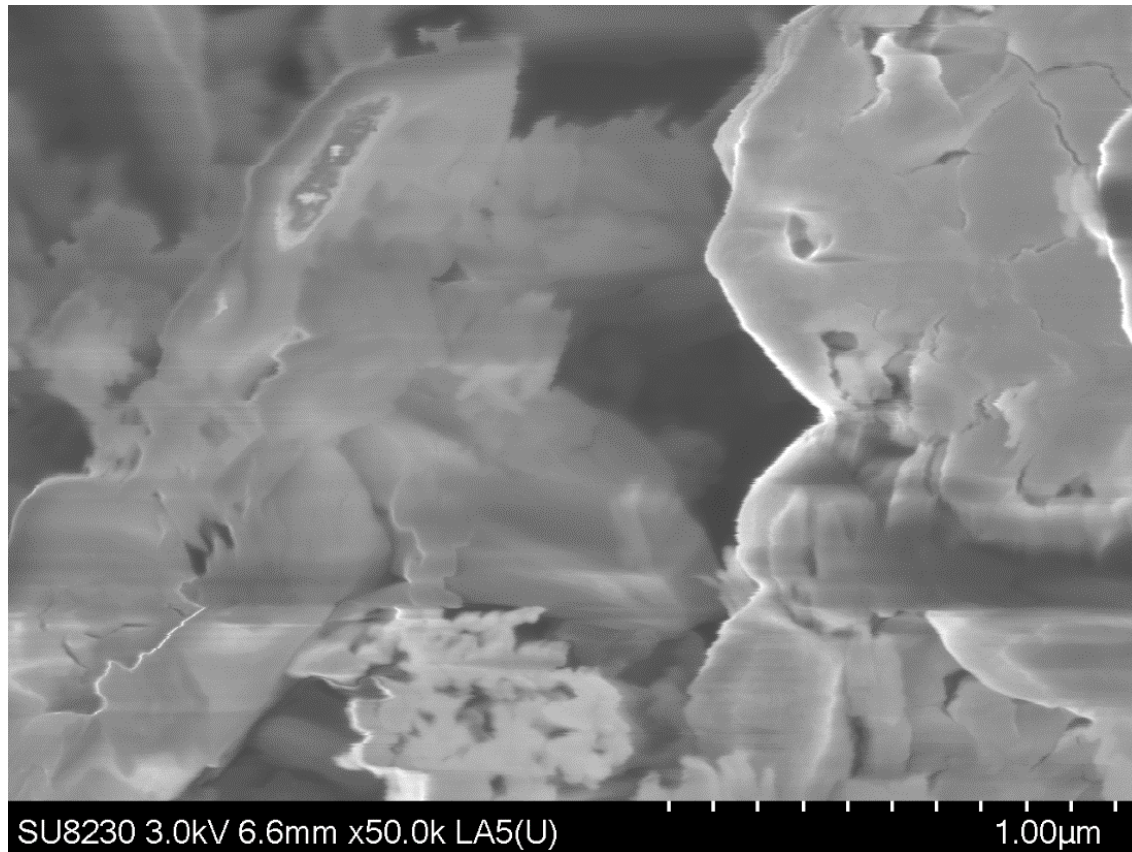
Nicolas Brodusch, M.Sc. A.



**McGill**

Montréal, Québec, Canada.

# Minéral de Terres Rares



# Charge et Champs Électrique

$$\frac{\partial E_x}{\partial x} + \frac{\partial E_y}{\partial y} + \frac{\partial E_z}{\partial z} = \frac{\rho}{\varepsilon}$$

$\rho =$  Densité de Charge  
(Nombre d'electrons par unité de volume)

$\varepsilon =$  Constante Dietectrique

$$\vec{F} = e\vec{E}$$

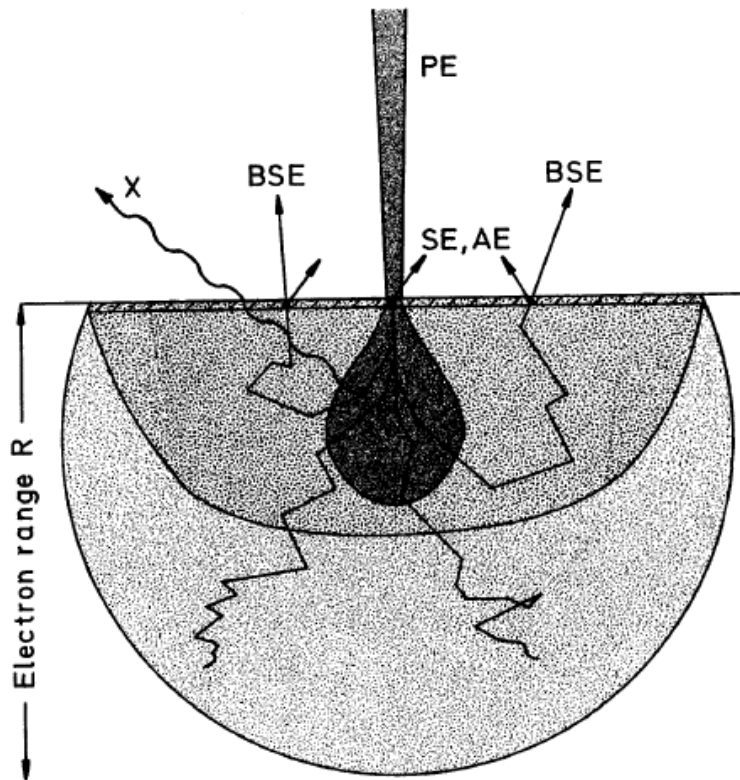
# Phénomènes de Charge

- Les métaux sont conducteurs, les charges ne s'accumulent pas, donc  $\rho = 0$  et  $F = 0$ . Pas de Charge.
- Les céramiques et les polymères sont des isolants, les charges s'accumulent, donc  $\rho \neq 0$  et  $F \neq 0$ . Chargement. Fortes distorsions des images. Affecte également EDS et EBSD.
- Solution Classique, utiliser un revêtement de C, Au-Pd, Cr ou autre métal.
- Le dommage par ionisation mène aux phénomènes de charge, importance pour matériaux technologiques à base de Li par exemple.



# Signaux générés dans le microscope électronique à balayage (MEB)

## Échantillon Massif



- PE = Électrons Incidents
- SE = Électrons secondaires ;  
contraste topographique.
- BSE = Électrons rétrodiffusés ;  
contraste chimique.
- X = Rayons X caractéristiques ;  
informations chimiques à  
l'intérieur du volume  
d'interaction. Microanalyse  
quantitative aux rayons X.
- AE = Électrons Auger.

# Balance de Charge

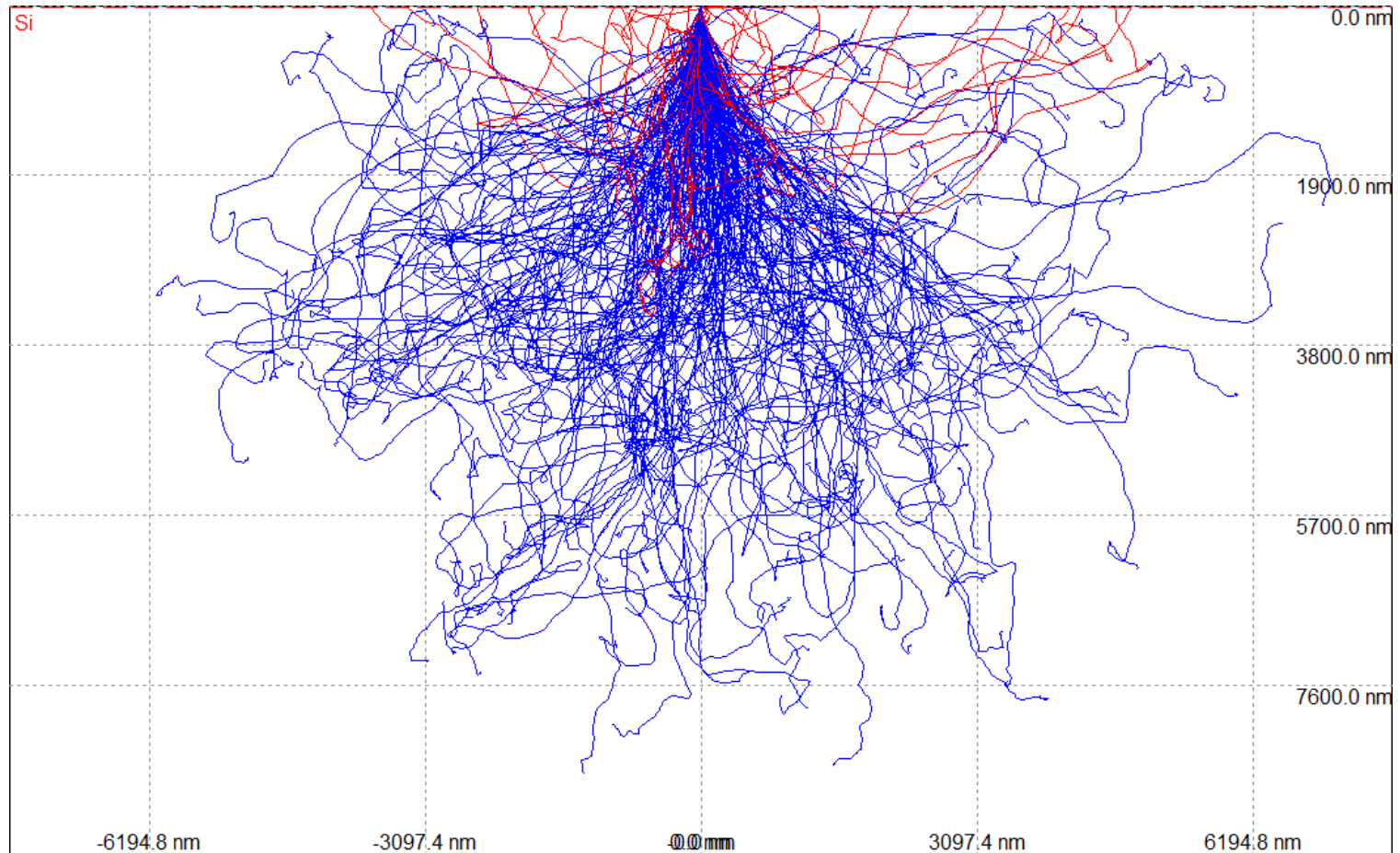
$$Q_{Net} = Q_{PE} - Q_{SE} - Q_{BSE} - Q_{AE}$$

$$Q_{Net} = \frac{it}{e} (1 - \delta - \eta - Q_{Io}(1 - \omega)\varepsilon_{out})$$

$$Q_{Io}(1 - \omega)\varepsilon_{out} \ll \delta + \eta$$

$$Q_{Net} \cong \frac{it}{e} (1 - \delta - \eta)$$

# CASINO



[CASINO: A new Monte Carlo code in C language for electron beam interaction .1. Description of the program](#)

By: Hovington, P; Drouin, D; Gauvin, R

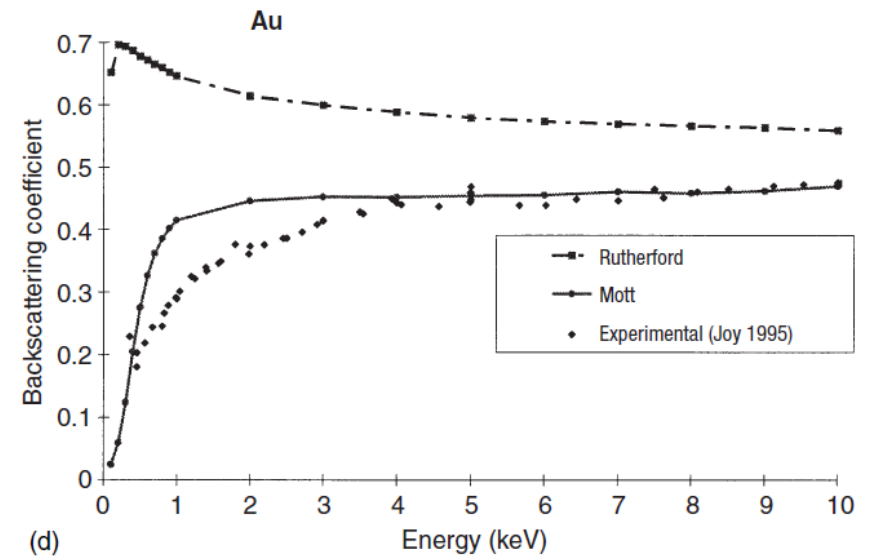
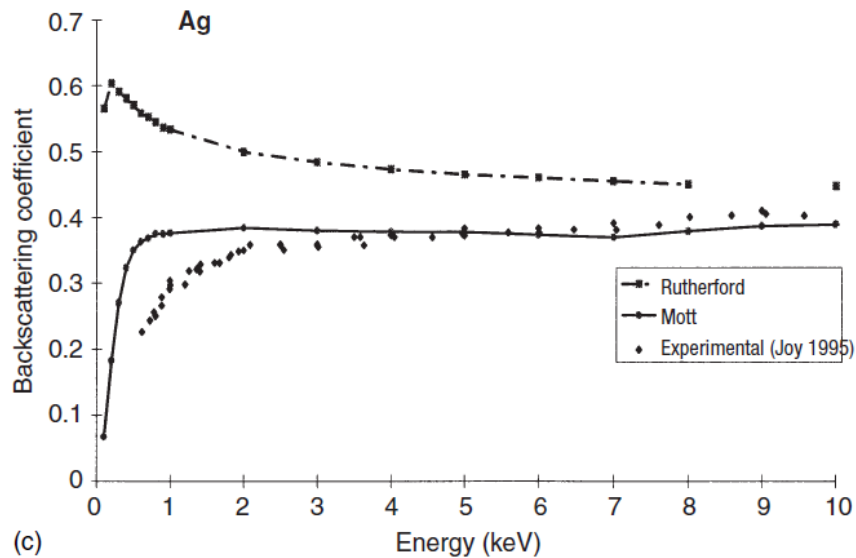
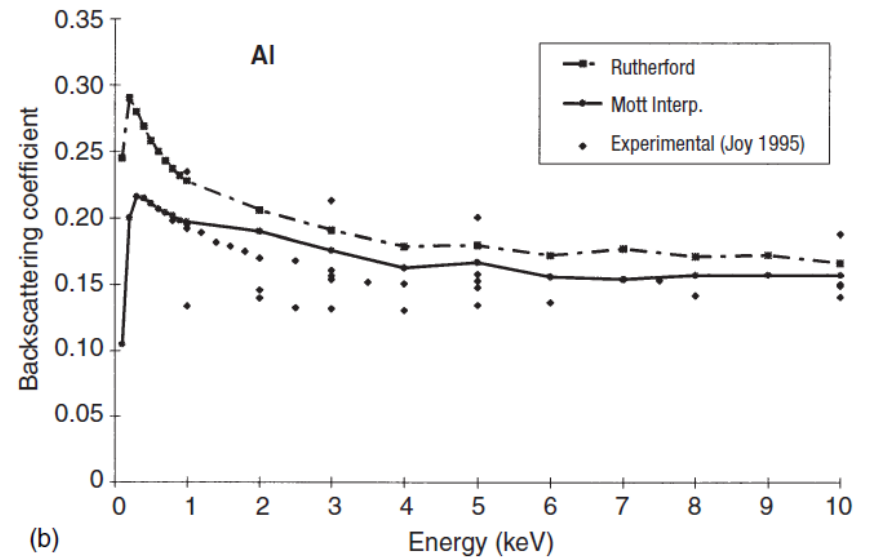
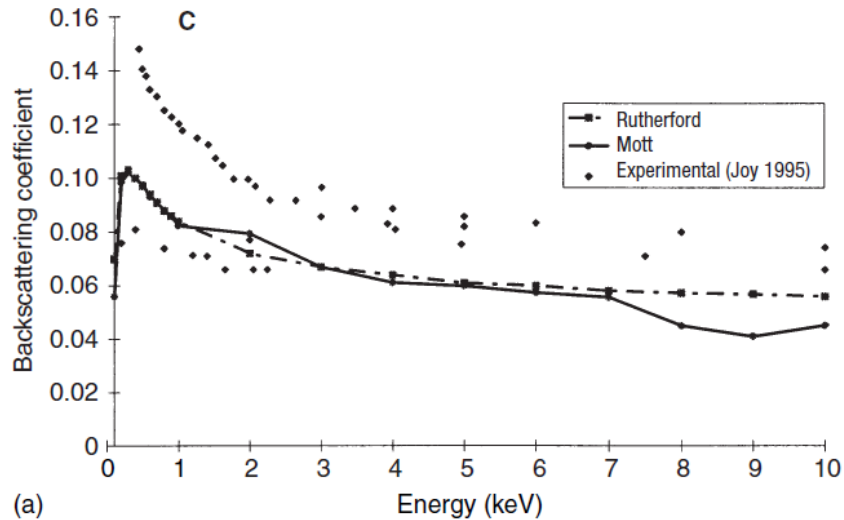
SCANNING Volume: 19 Issue: 1 Pages: 1-14 Published: JAN 1997 **868 Citations Google Scholar (22/11/24)**

[CASINO V2.42 - A fast and easy-to-use modeling tool for scanning electron microscopy and microanalysis users](#)

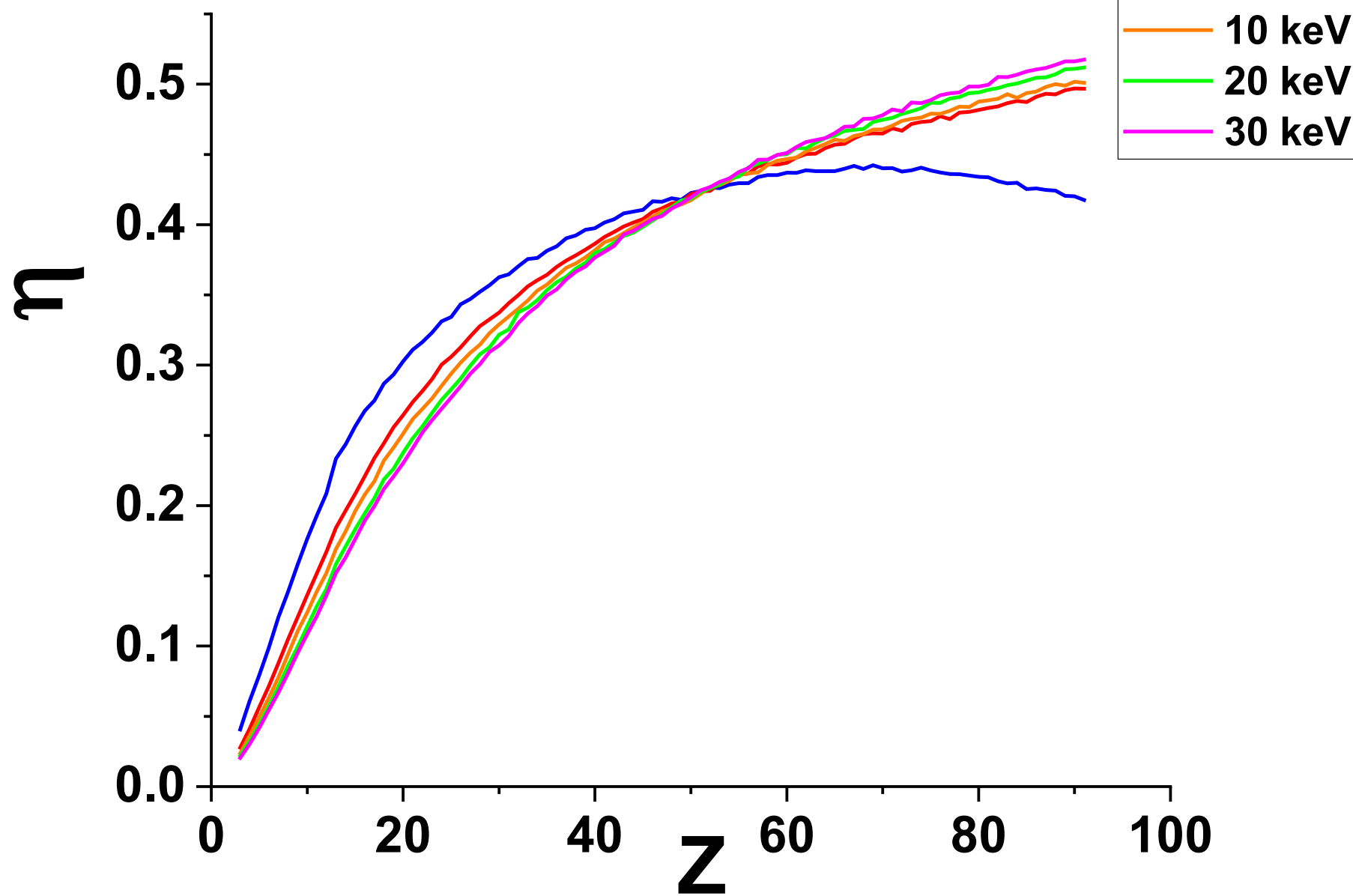
By: Drouin, D.; Couture, A. R.; Joly, D. and Gauvin, R.

SCANNING Volume: 29 Issue: 3 Pages: 92-101 Published: MAY-JUN 2007 **1827 Citations Google Scholar (22/11/24)**

# CASINO 1997

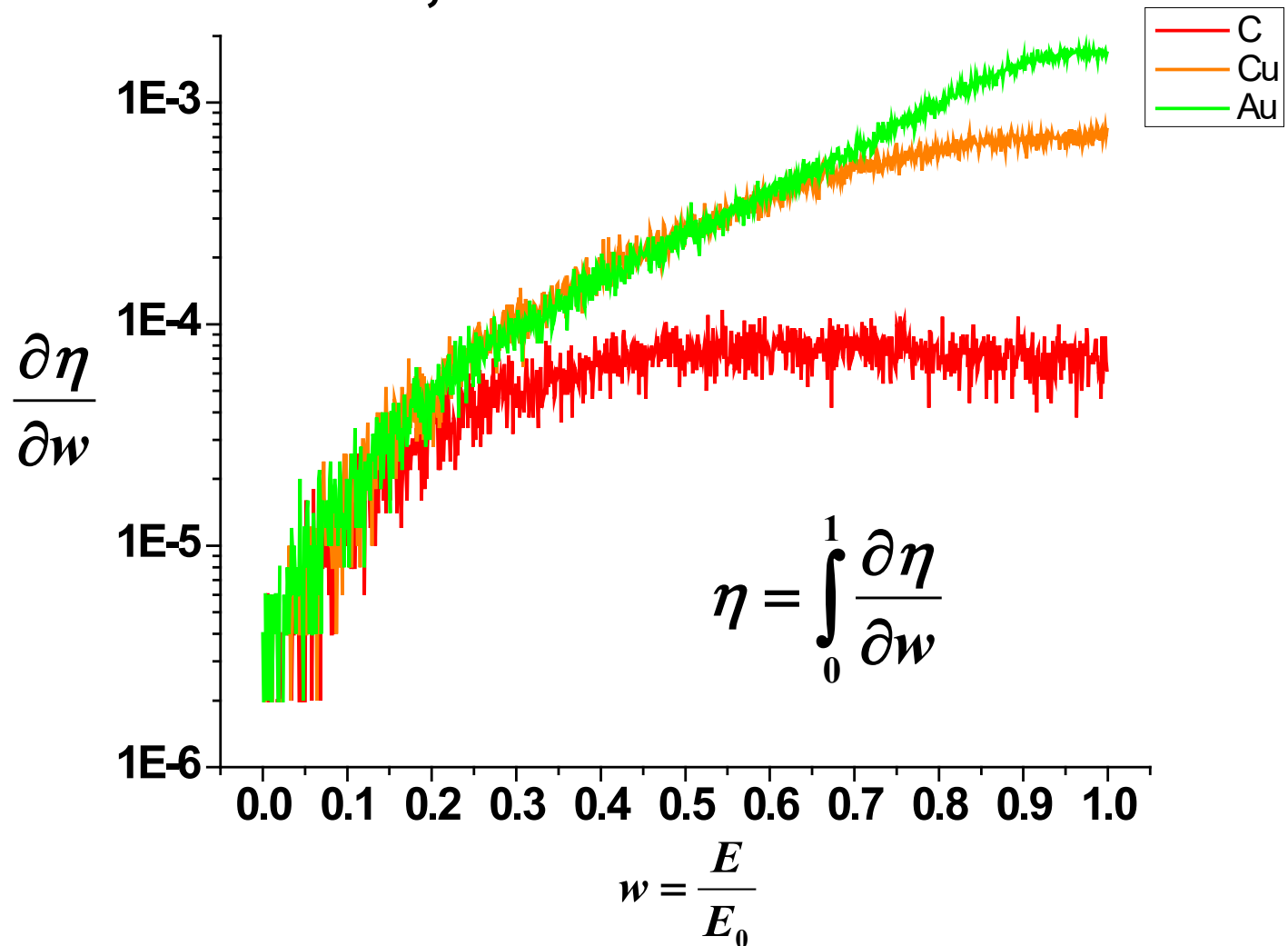


200 000 electron trajectories



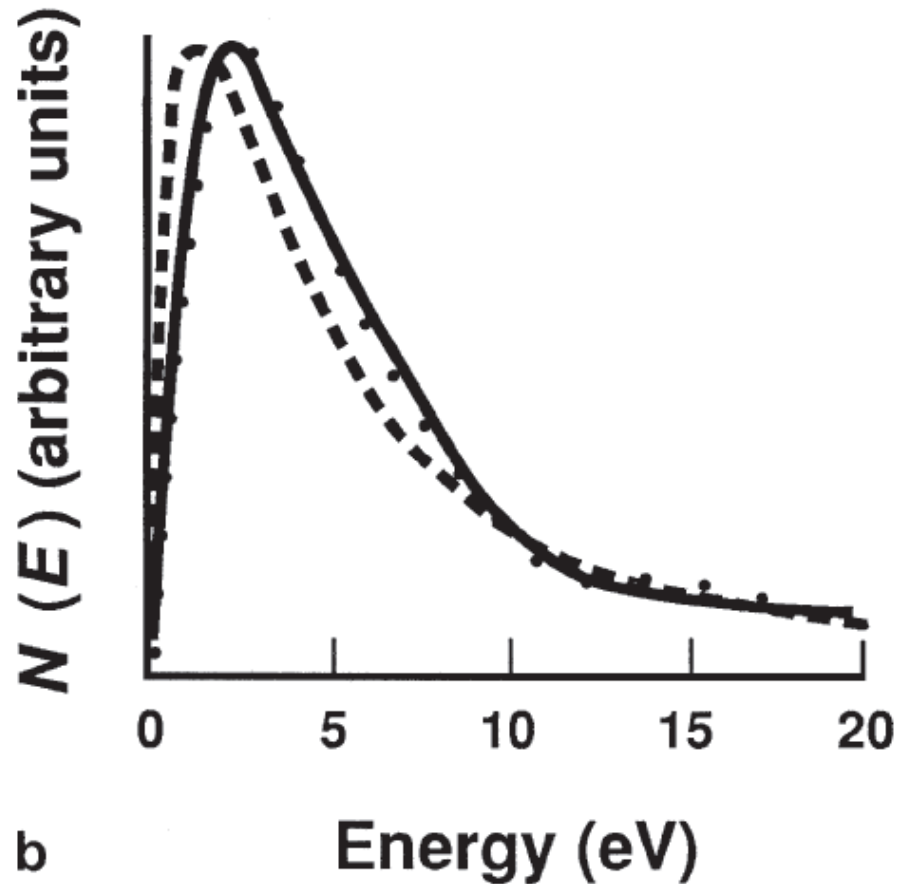
# Distribution de l'énergie des BSE

20 keV, 500 000 e



$z$	$E_{BSE}/E_0$
6 (C)	0.5
79 (Au)	0.8

# Distribution Énergétique des Électrons Secondaires



Typiquement, entre 3 et 15 eV, faible énergie

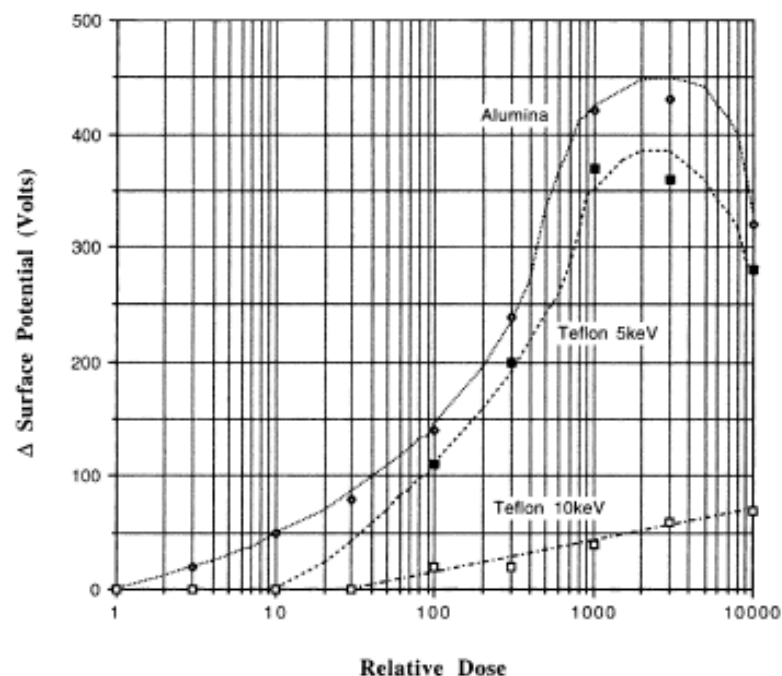


## Dynamic Charging in the Low Voltage SEM

David C. Joy<sup>1,2\*</sup> and Carolyn S. Joy<sup>1</sup>

<sup>1</sup>F239 Walters Life Sciences Bldg., University of Tennessee, Knoxville, TN 37996-0810;

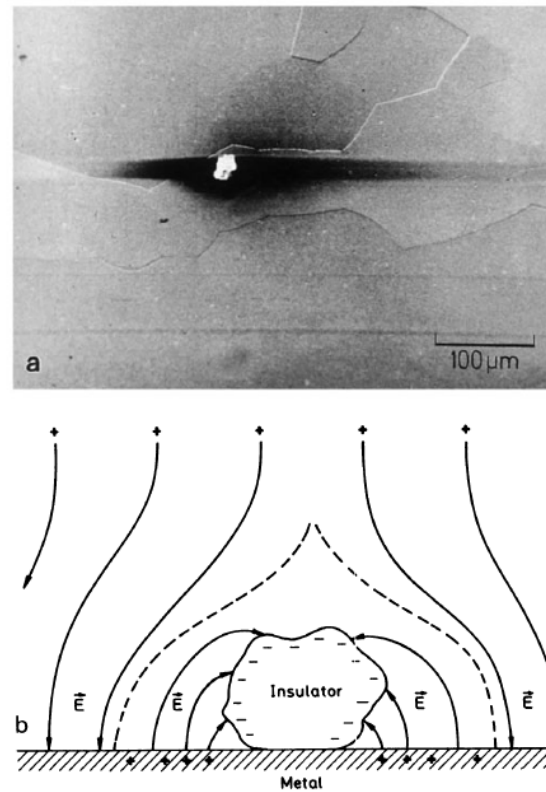
<sup>2</sup>Oak Ridge National Laboratories



**FIGURE 3.** The variation in surface potential as a function of relative beam dose for alumina observed at 5 keV, and for Teflon observed at 5 and 10 keV.

Potentiel de surface  
: 100 -1000 eV

# Particule sur Al – Reimer 1998



**Fig. 3.35.** (a) SE micrograph of a dust particle (bright), which is charged negatively, on an aluminium substrate causing (b) an electric field, which connects induced positive charges on the metal substrate to the negative charges on the particle, resulting in dark voltage contrast beside the particle within the range indicated by the dashed line

# Choix des Électrons: Matériaux

## Isolants : BSE

- Les électrons secondaires ont toujours une énergie entre 3 et 15 eV, très sensibles aux potentiels de surfaces induits par les électrons piégés, 100 -1000 eV typiquement.
- Pour le C a 20 keV, l'énergie moyenne des BSE est de 10 000 eV, (Au, 16000 eV) beaucoup moins sensible aux effets de charges.
- Moyenne de plusieurs images rapides en BSE (Muli-Frames).

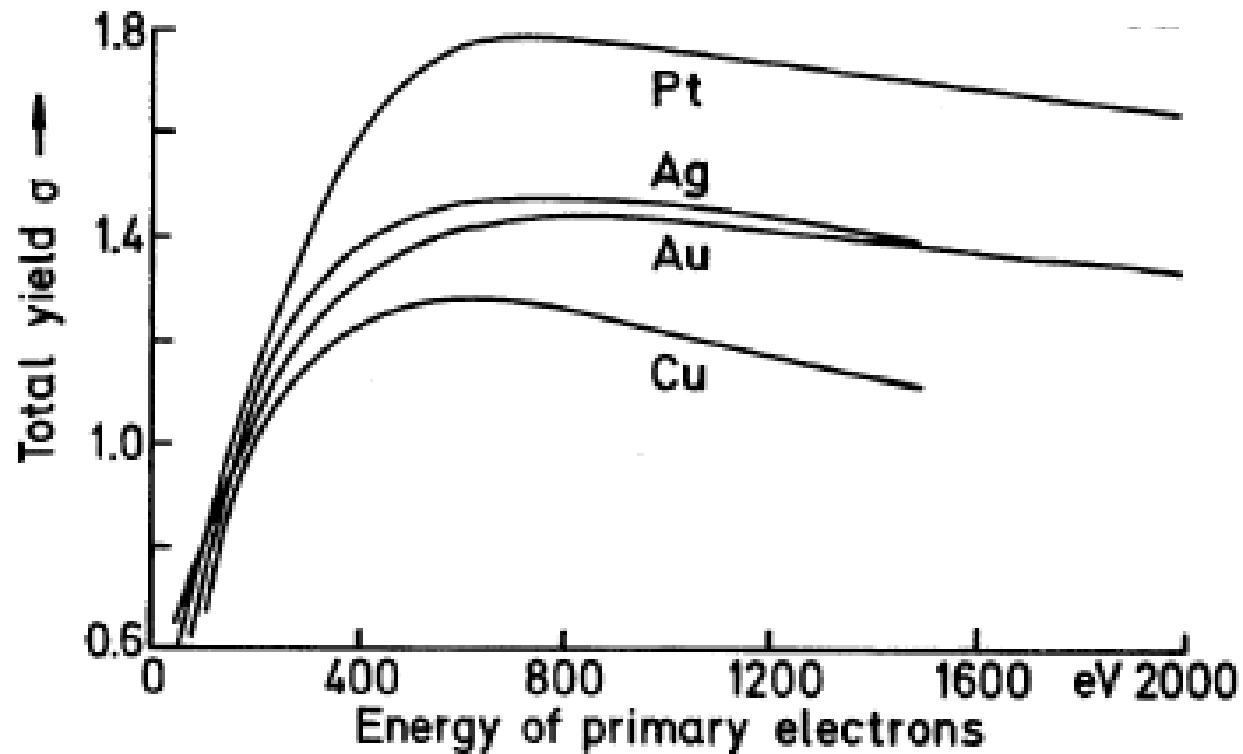
# Les Revêtements (Coatings)

- Machines pour déposer des revêtements de 1 à 20 nm (et plus si nécessaire).
- C, Au-Pd, Au, Cr et autres métaux disponibles.
- Excellent pour faible grossissement et échantillons avec beaucoup de topographie.
- Haute Résolution, on image le revêtement.
- Dans mon laboratoire, solution de dernier recours mais souvent utilisés

Pour paraphraser Jacques Cazaux, ce n'est pas parce que on a une belle image d'un matériau isolant qu'il n'y a pas de phénomènes de charges à l'intérieur!!!

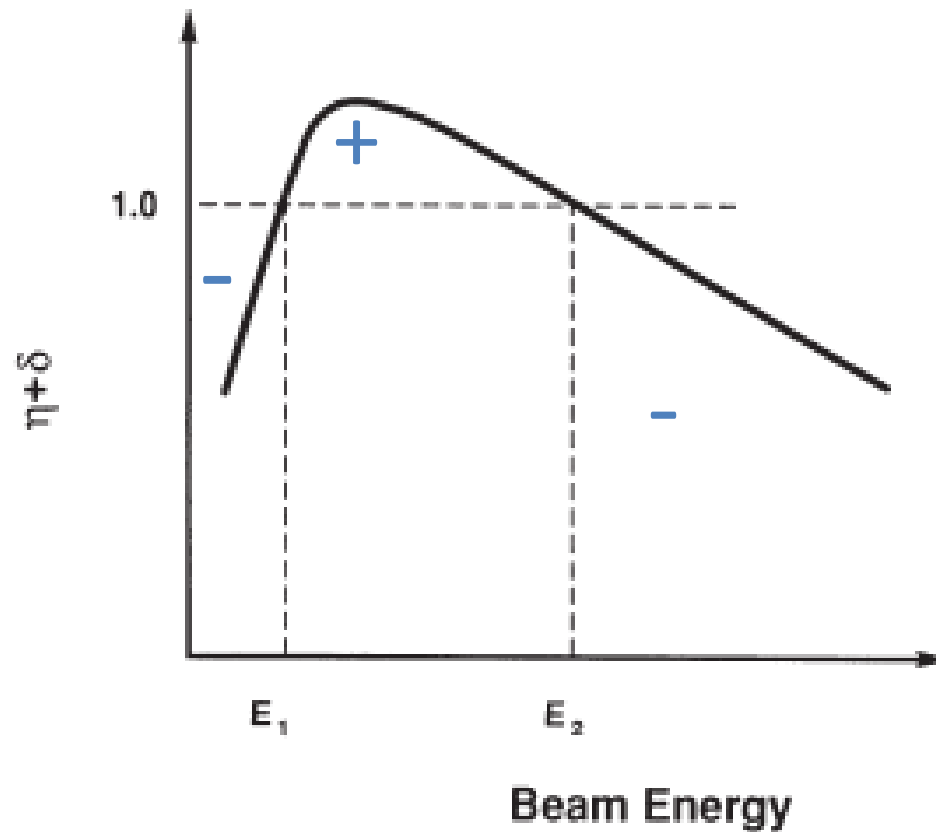
(Les revêtements neutralisent les charges à la surface).

$\delta$  vs  $E_0$



Reimer (1998)

# Energie $E_2$



À  $E_2$ ,  $Q_{\text{Net}} = 0$ . Pas de phénomènes de charges

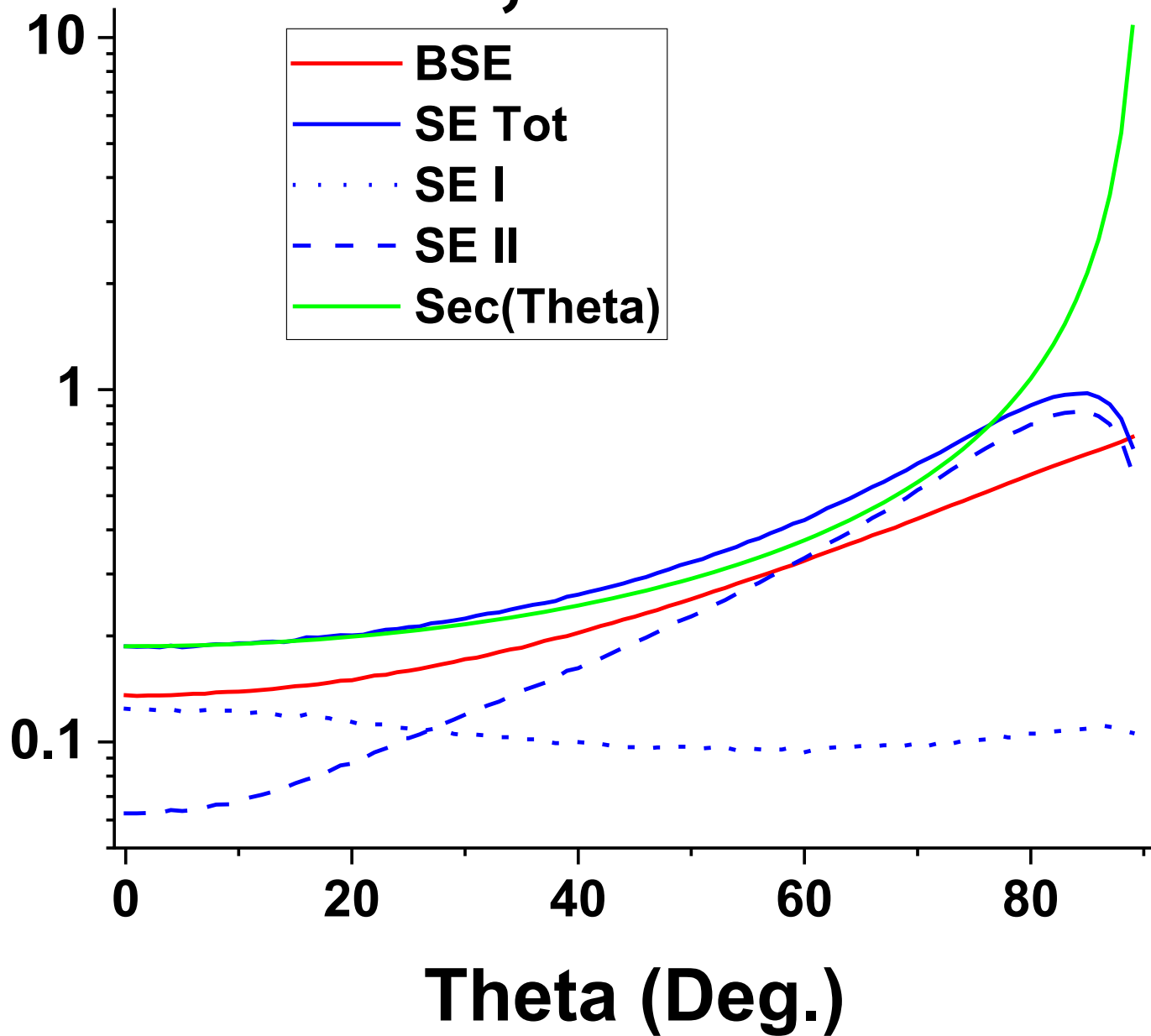


# E<sub>2</sub> Energy

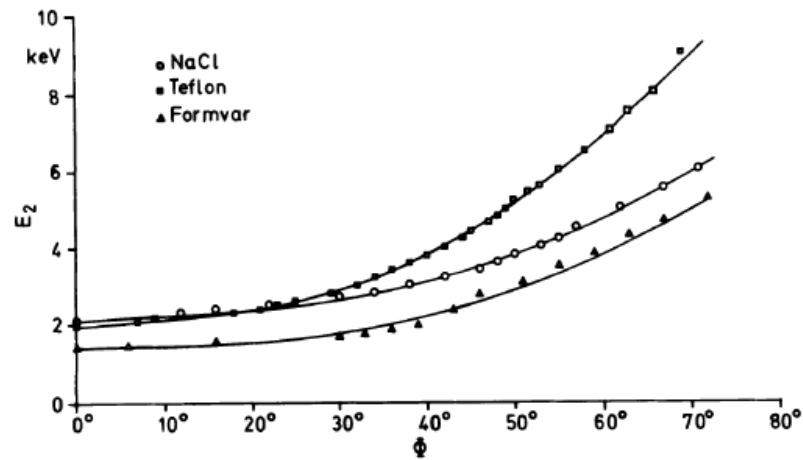
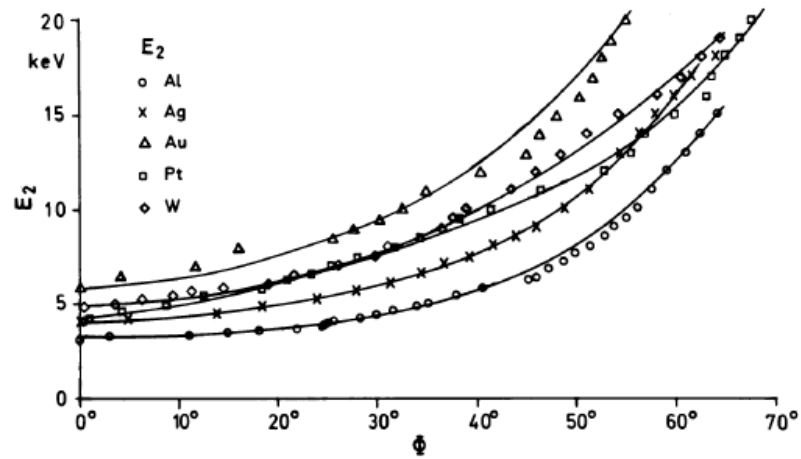
**Table 3.7.** Upper Crossover Energy for Various Materials (Normal Beam Incidence)

Material	$E_2$ (keV)	Reference
Kapton	0.4	Joy (1988)
Electron resist	0.55–0.70	Joy (1987)
Nylon	1.18	Joy (1988)
5% PB7/Nylon	1.40	Krause <i>et al.</i> (1982, 1987)
Acetal	1.65	Vaz (1986)
PVC	1.65	Vaz (1986)
Teflon	1.82	Vaz and Krause, (1986)
Glass passivation	2.0	Joy (1987)
GaAs	2.6	Joy (1987)
Quartz	3.0	Joy (1987)
Alumina	4.2	Joy (1988)

# Si, 5 keV



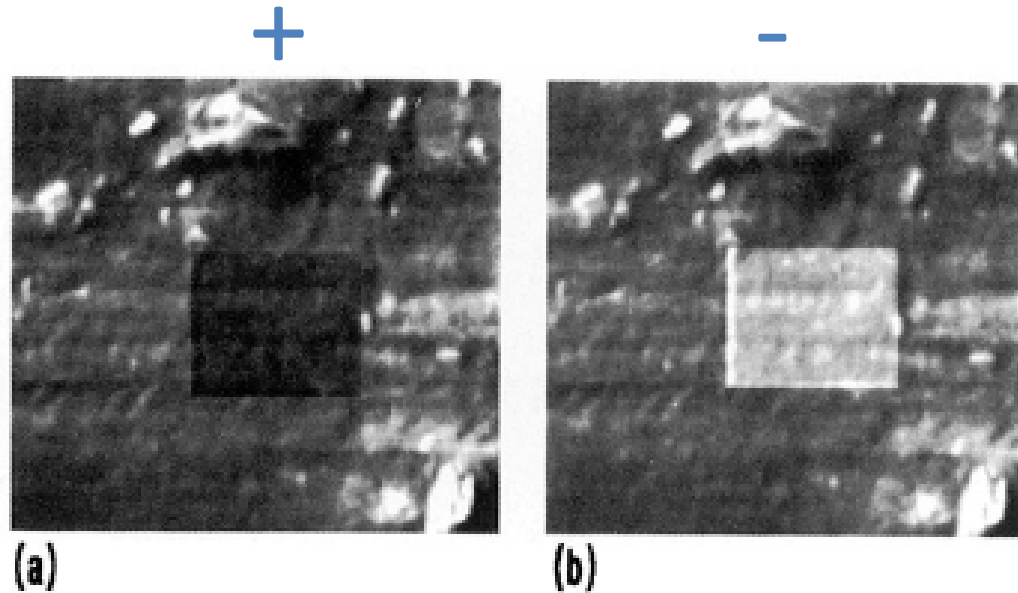
# $E_2$ vs $\theta$



Reimer (1988)

# Détermination de $E_2$

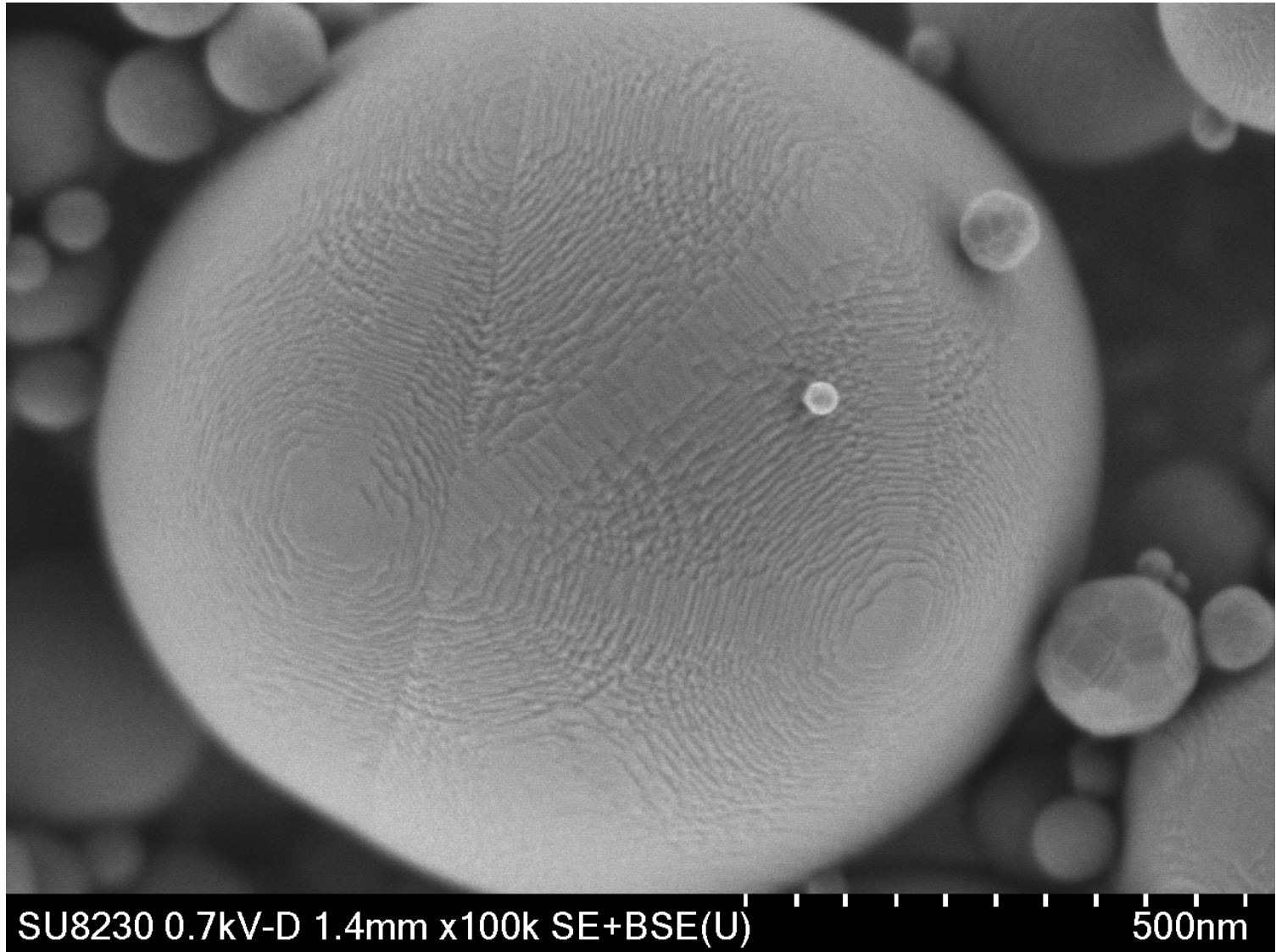
## Méthode de Joy & Joy (1995)



**Figure 2.** The scan square test (a) a dark square showing positive charging and (b) a bright square showing negative charging.

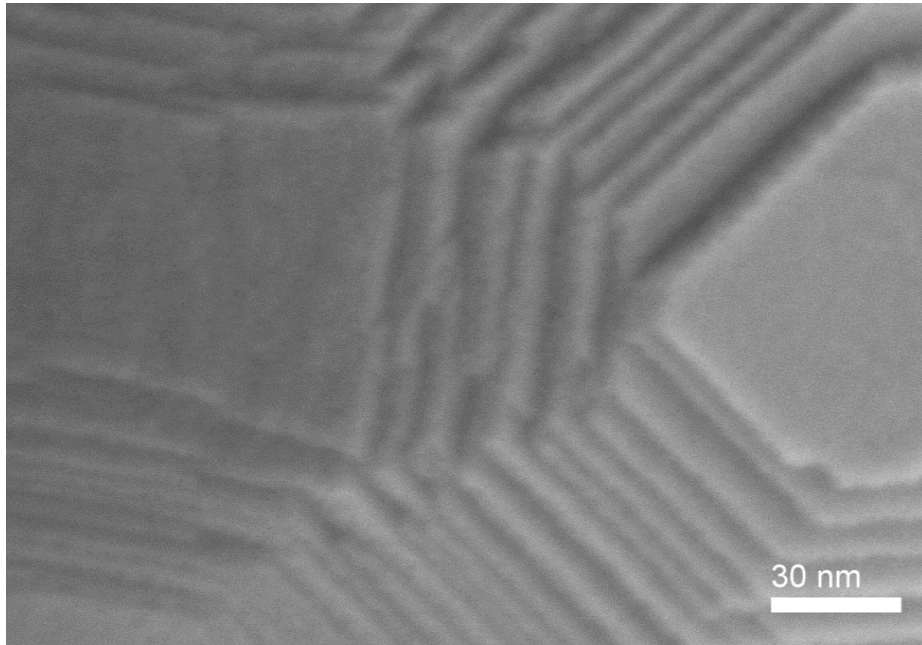
La Contamination par le  
Carbone est un  
Problème

# Alumine, 0.7 keV

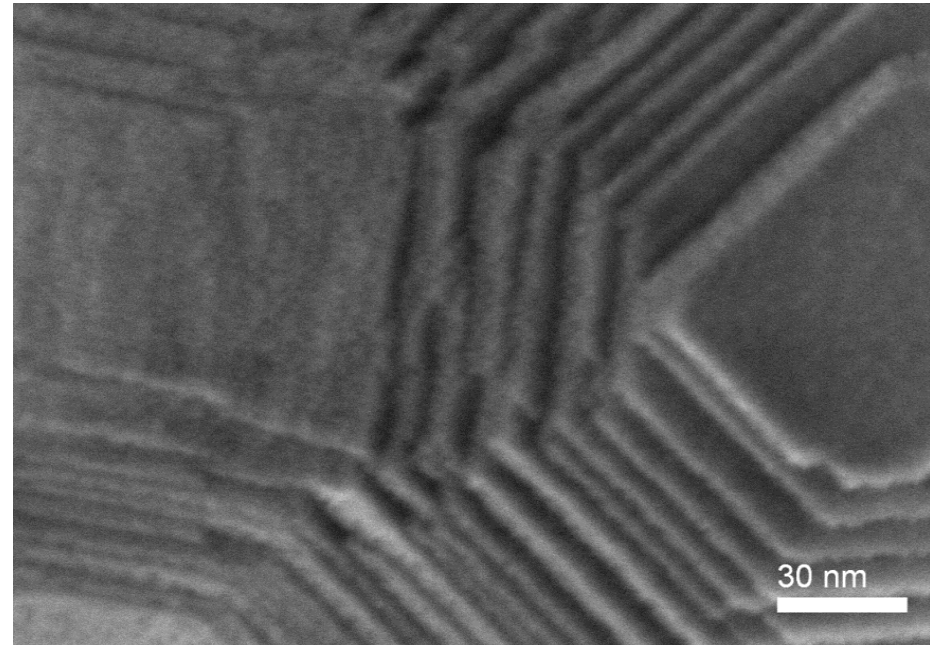


# Alumine, 0.7 keV

Upper

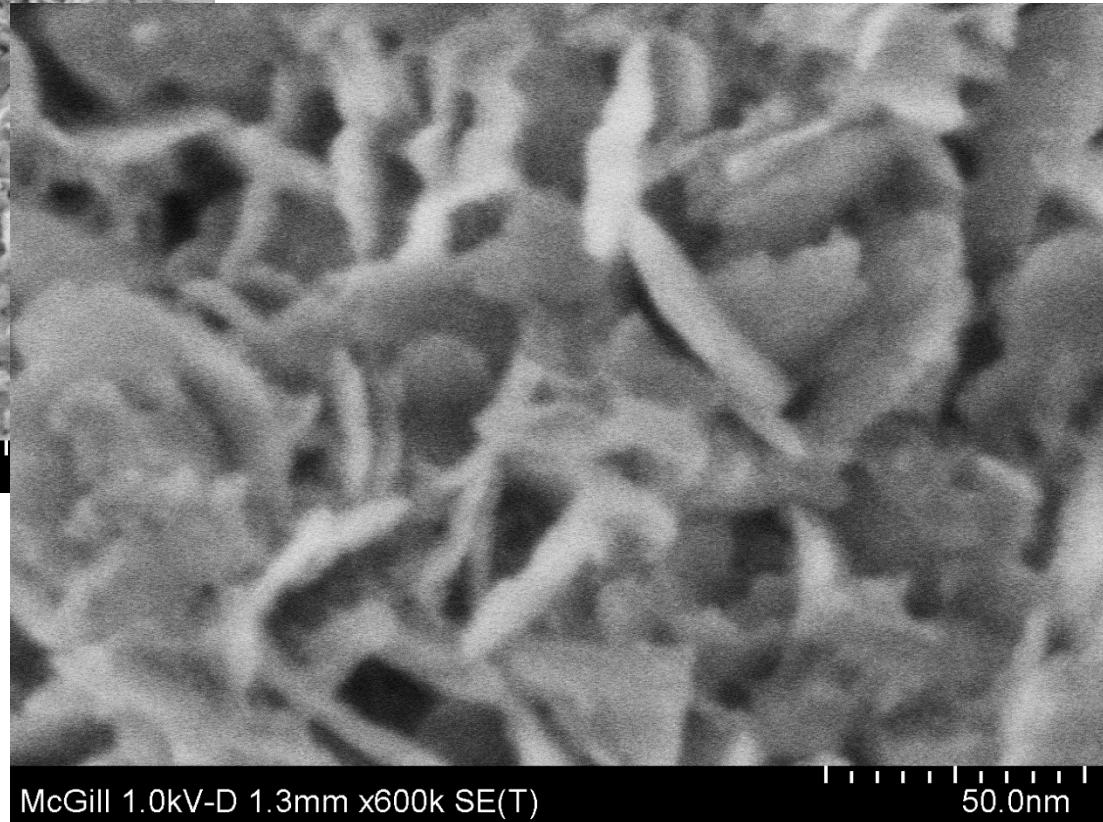
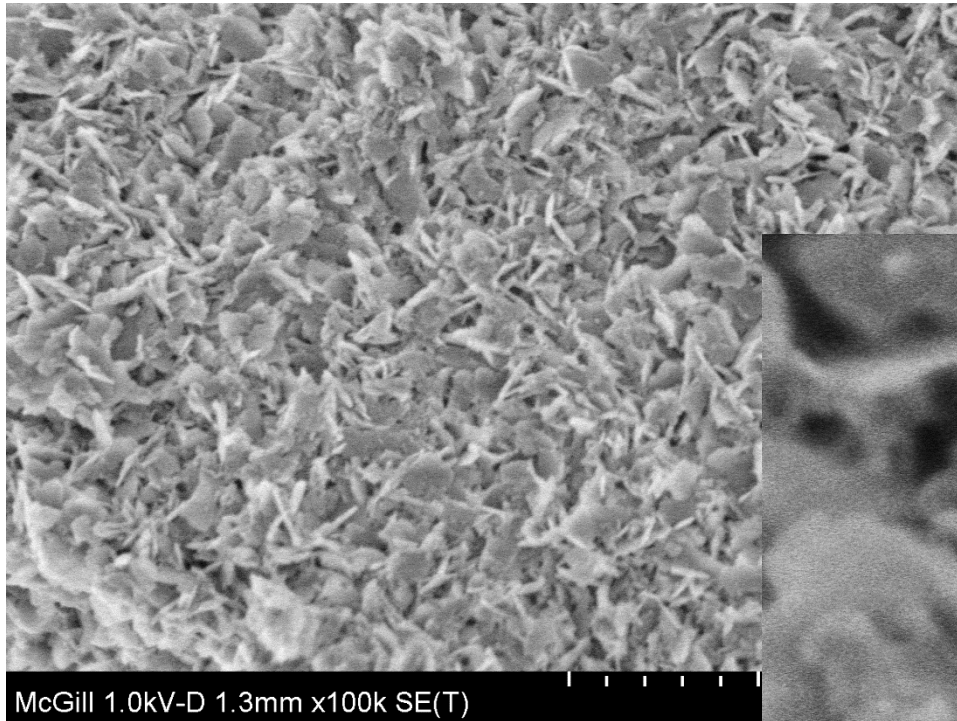


TOP





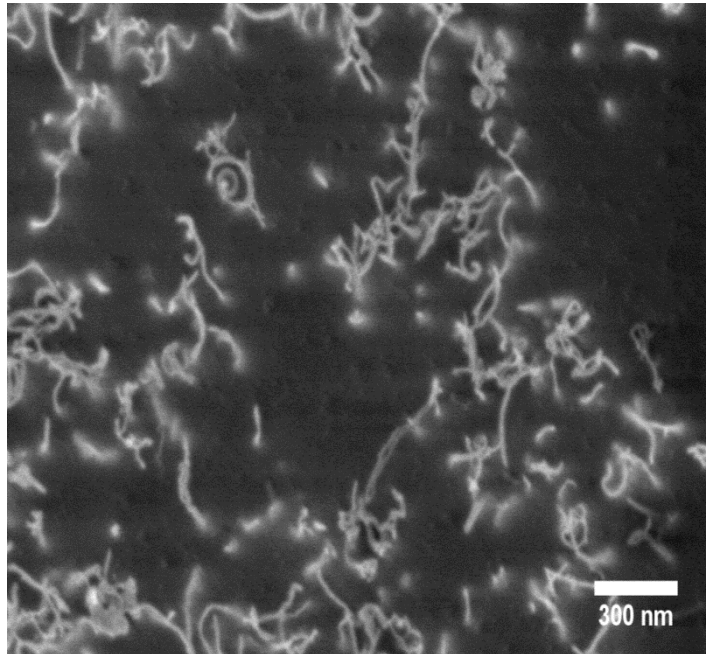
# Hydrous lithium titanate ( $\text{Li}_{1.81}\text{H}_{0.19}\text{Ti}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ ) à $E_0=1$ keV (mode décélération)



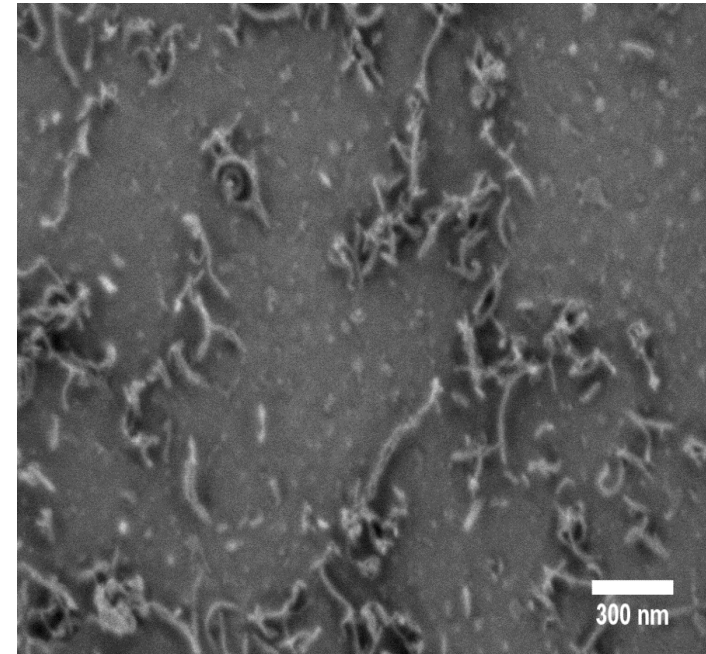


# Nano-composite d'époxy renforcé de nanotubes de carbone

Top



Upper



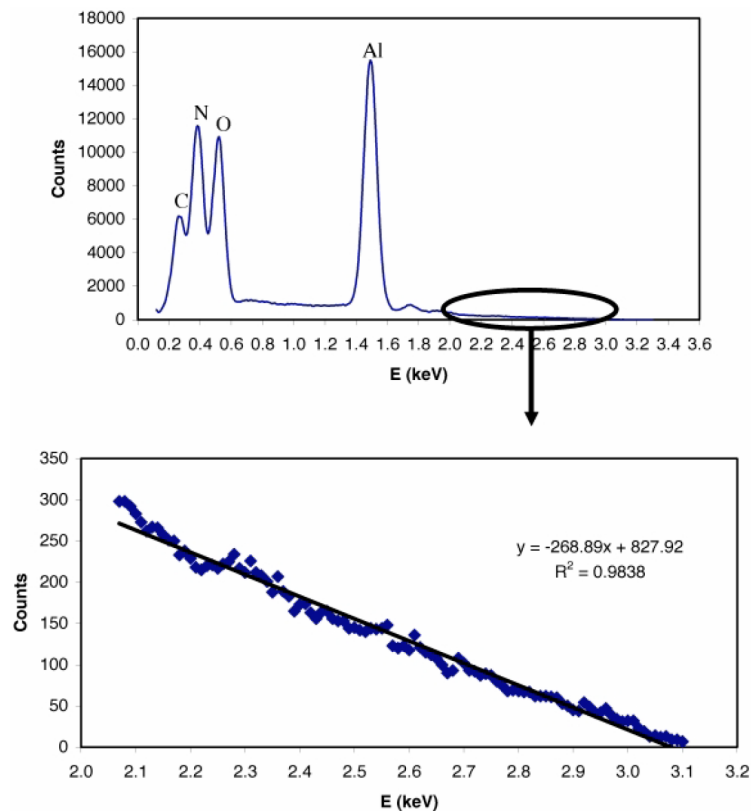
200 V

## Determination of $E_2$ for Nitride Ceramics Using FE-SEM and the Duane–Hunt Limit Procedure

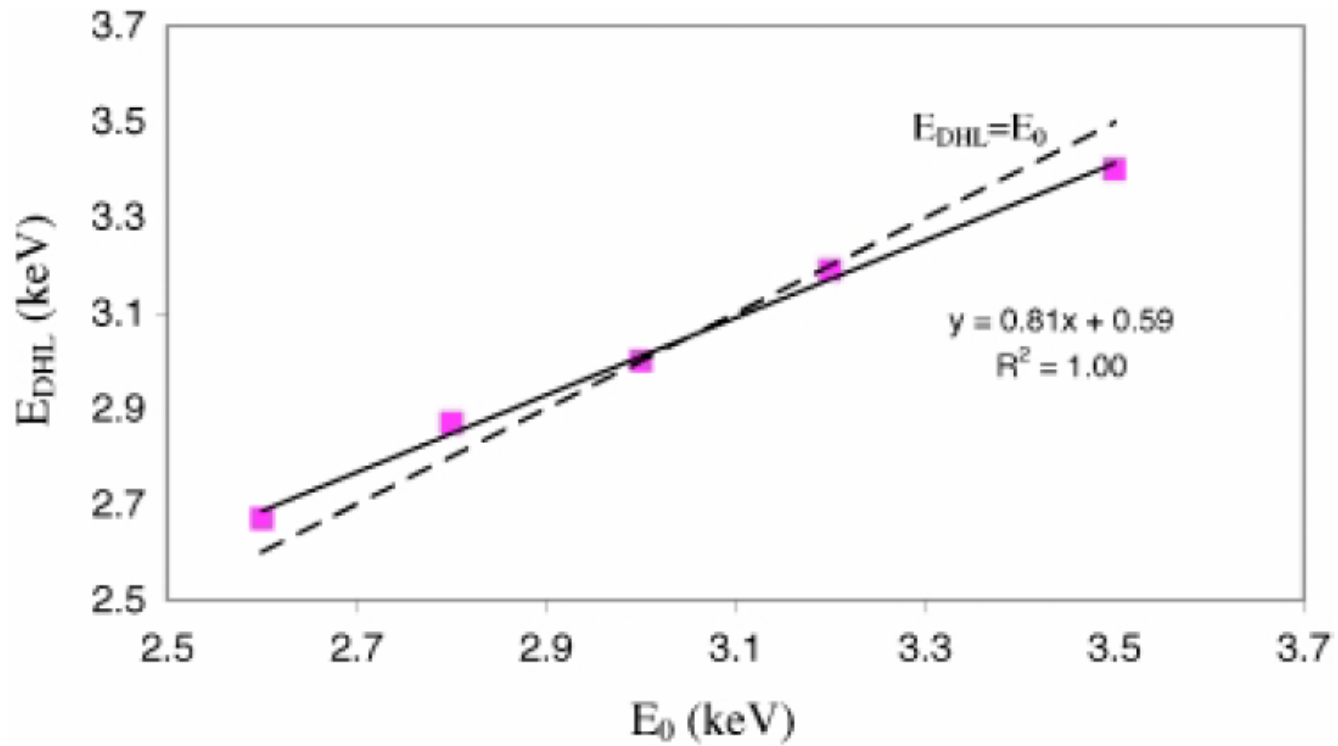
M. Brochu,<sup>1</sup> H. Demers,<sup>1</sup> R. Gauvin,<sup>1</sup> M.D. Pugh,<sup>2</sup> and R.A.L. Drew<sup>1,\*</sup>

<sup>1</sup>Metals and Materials Engineering Department, McGill University, 3610 University Street,  
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<sup>2</sup>Mechanical Engineering Department, Concordia University, 1455 Blvd. De Maisonneuve West,  
Montreal, Quebec H3G 1M8, Canada



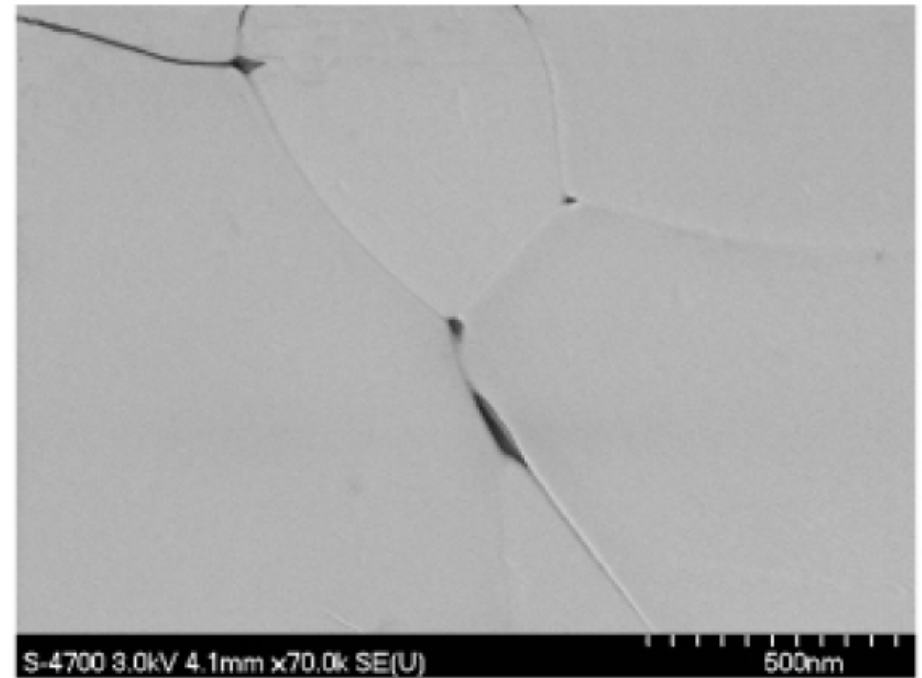
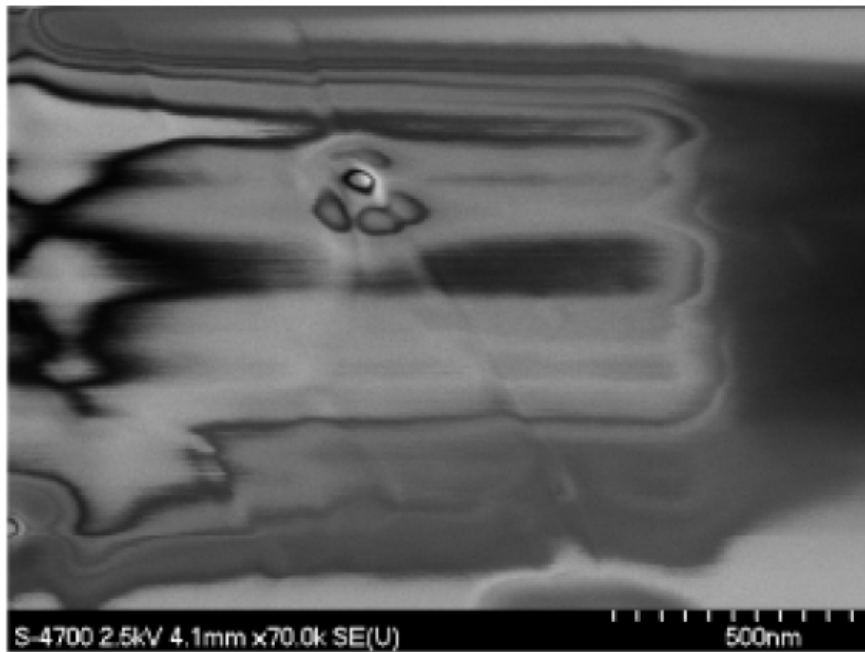
**Figure 4.** Example of linear fit of the last portion of the bremsstrahlung for an AlN sample ( $E_0 = 3.1$  keV, 500 time).



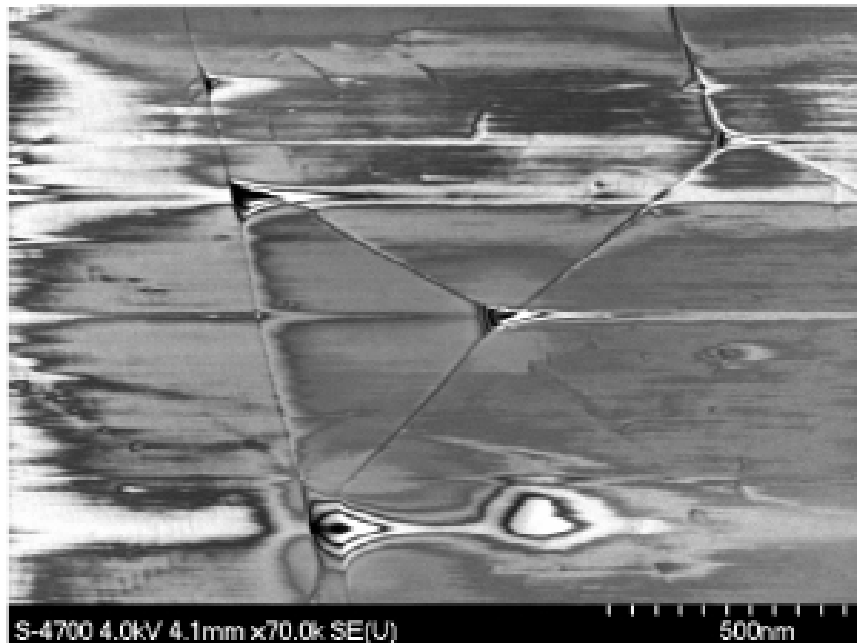
**Figure 9.**  $E_{\text{DHL}}$  measurement versus  $E_0$  for  $\text{Si}_3\text{N}_4$  ceramic.



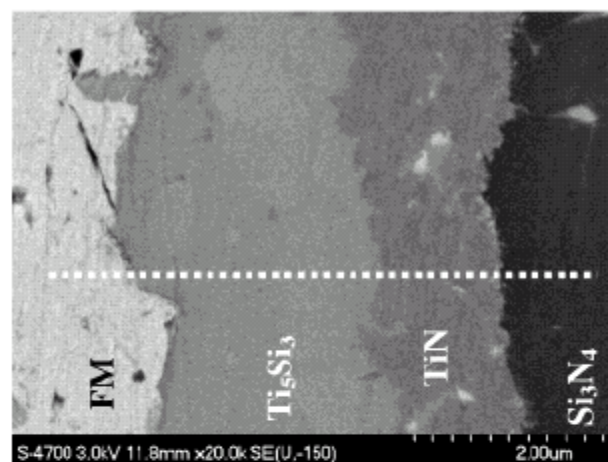
← 2.5 keV



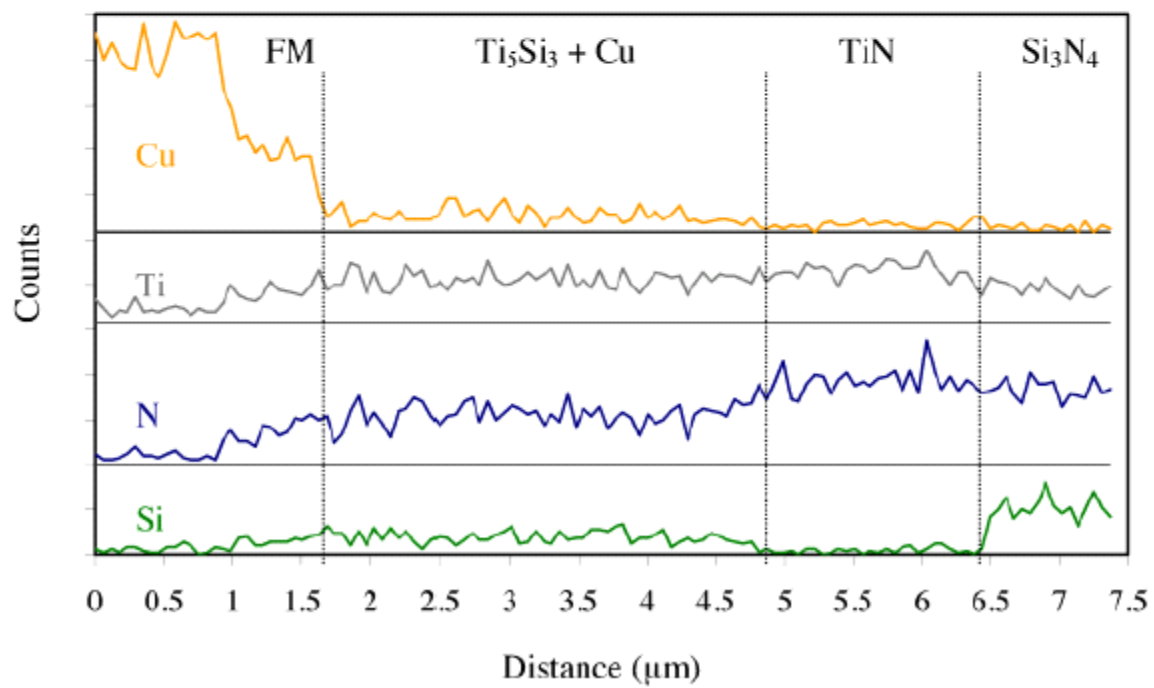
← 4 keV



↑  
3 keV



(a)



# EDS Matériaux Isolants – Utiliser $E_{DHL}$

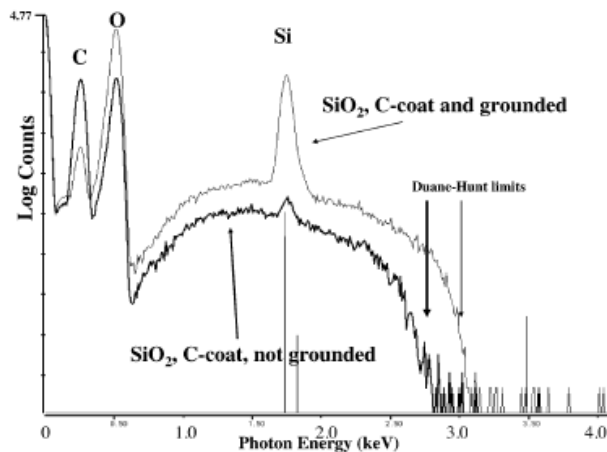
Microsc. Microanal. 10, 739–744, 2004  
DOI: 10.1017/S143192760404070X

Microscopy AND  
Microanalysis  
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Assessing Charging Effects on Spectral Quality for X-ray  
Microanalysis in Low Voltage and Variable Pressure/  
Environmental Scanning Electron Microscopy

Dale E. Newbury\*

National Institute of Standards and Technology, Gaithersburg, MD 20899-8371, USA



**Figure 3.** Energy dispersive (Si-EDS) spectra of a nonconductive specimen,  $\text{SiO}_2$ , with a thin carbon coating. In one case the C coating is connected to ground, whereas in the other the ground path is interrupted. Incident beam energy,  $E_0 = 3 \text{ keV}$ ; logarithmic intensity axis. The Duane–Hunt limit is nominal for the grounded specimen, but reduced in value due to charging when the ground path is interrupted.

$E_{DHL}$  est utilisé dans les modèles de corrections.

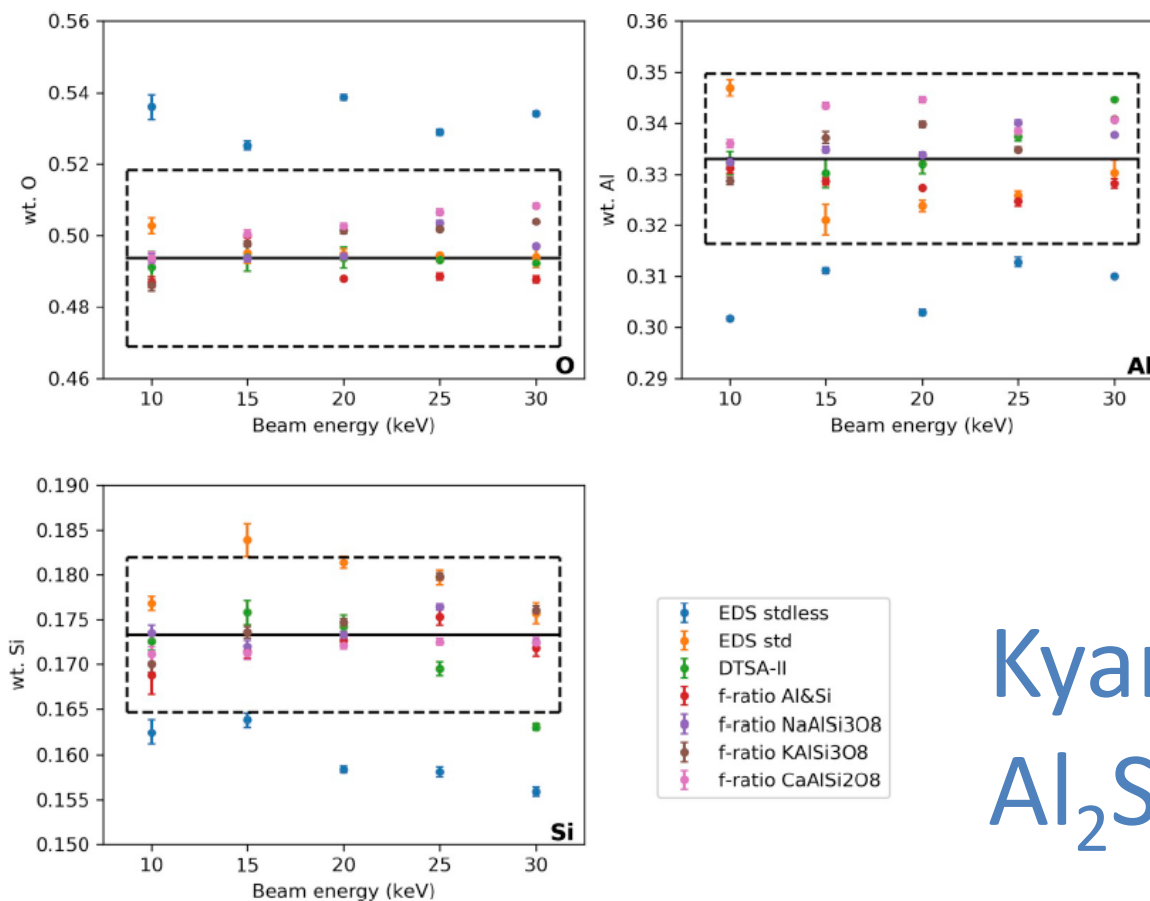
Reimer (1998) le propose aussi.



# The $f$ -ratio quantification method applied to standard minerals with a cold field emission SEM/EDS

Chaoyi Teng\*, Yu Yuan, Raynald Gauvin

*Department of Mining and Materials Engineering, McGill University, Montreal, Quebec, H3A 0C5, Canada*



Kyanite  
 $\text{Al}_2\text{SiO}_5$

Fig. 3. Quantification results of the kyanite specimen with the beam-energy-dependent calibration factors.

Analyse avec des standards  
de composition similaire  
donnent les meilleurs  
résultats.

Compensation des effets de  
charge.



# Ionic Liquid-Based Observation Technique for Nonconductive Materials in the Scanning Electron Microscope: Application to the Characterization of a Rare Earth Ore

NICOLAS BRODUSCH,\* KRISTIAN WATERS, HENDRIX DEMERS, AND RAYNALD GAUVIN

*Mining and Materials Engineering Department, McGill University, Montréal, Québec, H3A 0C5, Canada*

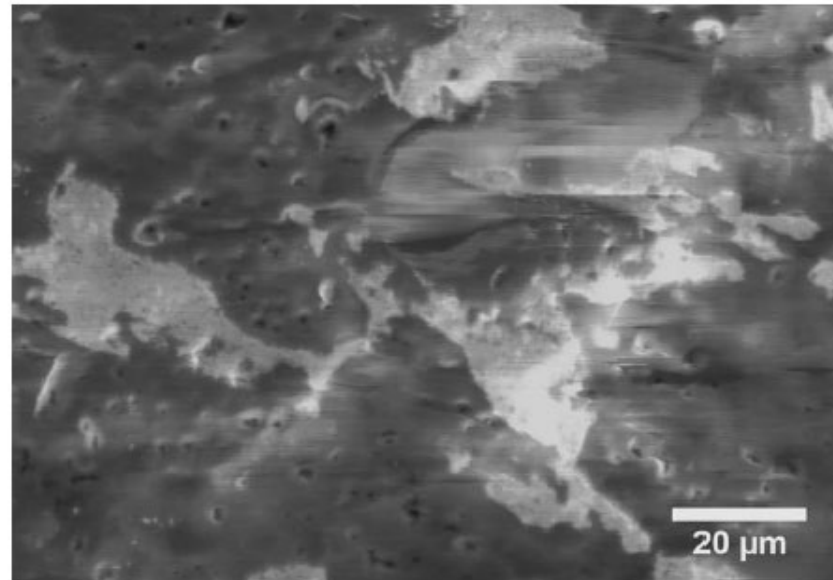


Fig. 1. BSE micrograph of the untreated Nechalacho ore cross-section with an accelerating voltage ( $E_0$ ) of 20 kV. The charging appears as bright streaks on the image that distort the surface details.

Le liquide ionique (IL) utilisé est le 1-butyl-3-methylimidazolium tetrafluoroborate (BMI-BF<sub>4</sub>).  
10 minutes de trempe.

# Fergusonite et Quartz

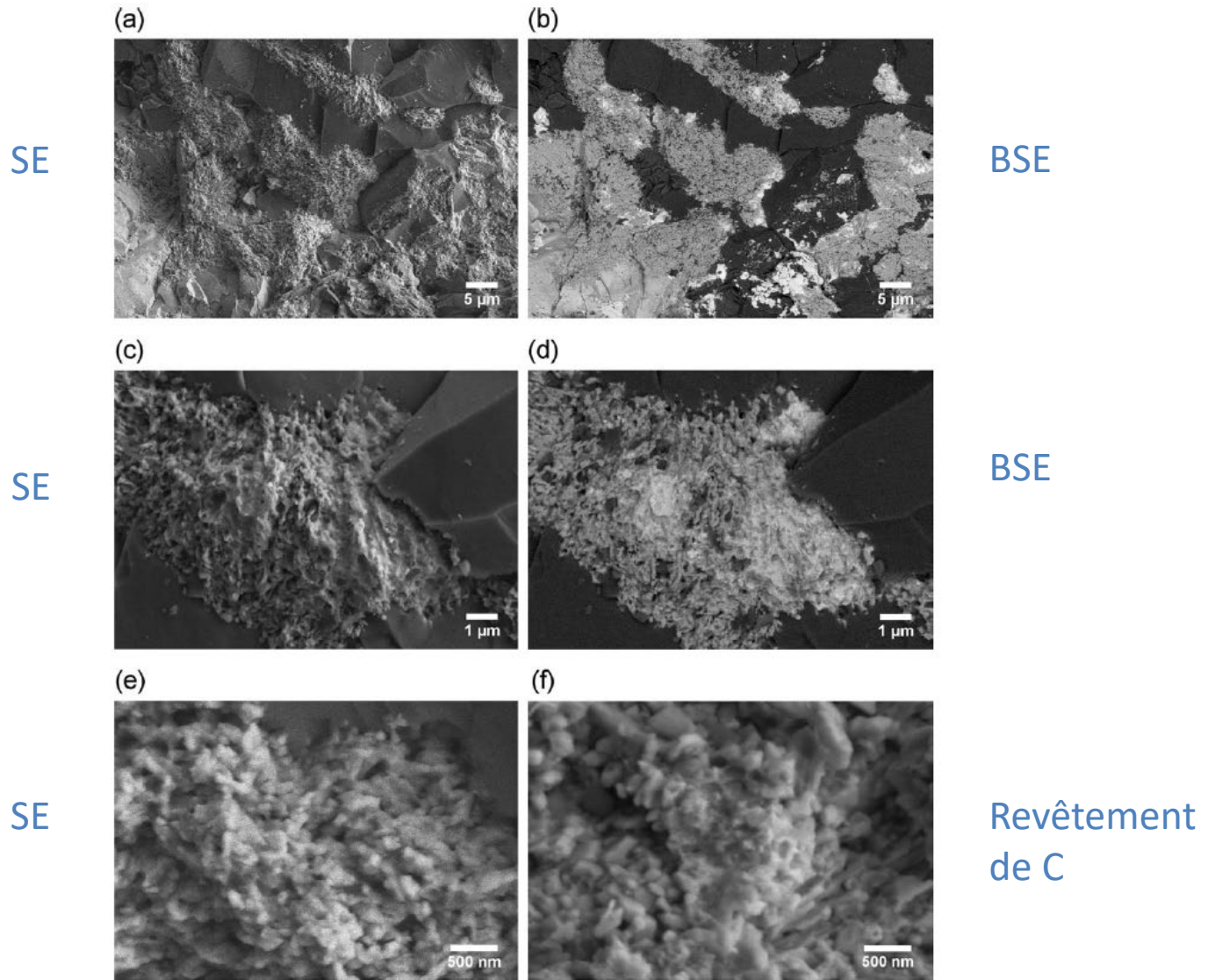


Fig. 2. SE (a, c, and e) and BSE (b and d) micrographs of the fractured specimen after IL-treatment at  $E_0 = 5$  kV at low (a and b), medium (c and d) and high magnification (e). f: SE micrograph of the

carbon coated fractured specimen. Charging was not observed and permitted to reveal the close relationship between zircon (dark gray) and fergusonite-Y (light gray) particles encased in quartz (dark).

# EDS

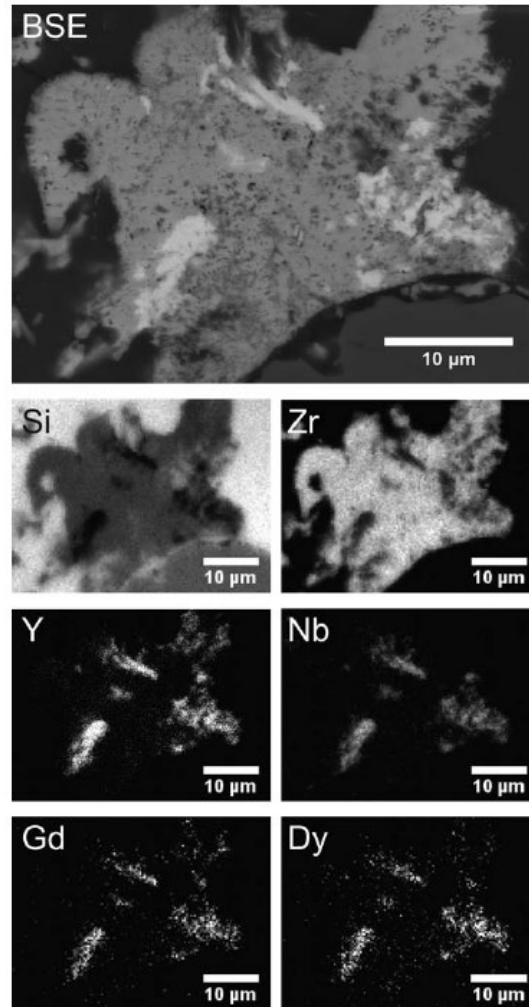


Fig. 4. BSE and x-ray maps based on raw counts of the same area as in Figure 3 at  $E_0 = 20$  kV. The x-ray lines were Si ( $K\alpha$ ), Y ( $L\alpha$ ), Zr ( $L\alpha$ ), Nb ( $L\beta_1$ ), Gd ( $L\alpha$ ), and Dy ( $L\beta_1$ ). The image drift was  $<10\%$  and the acquisition time was 30 min. The presence of Gd and Dy in the fergusonite-Y structure is obvious.

# EBSD

Revêtement C

IL

Revêtement C

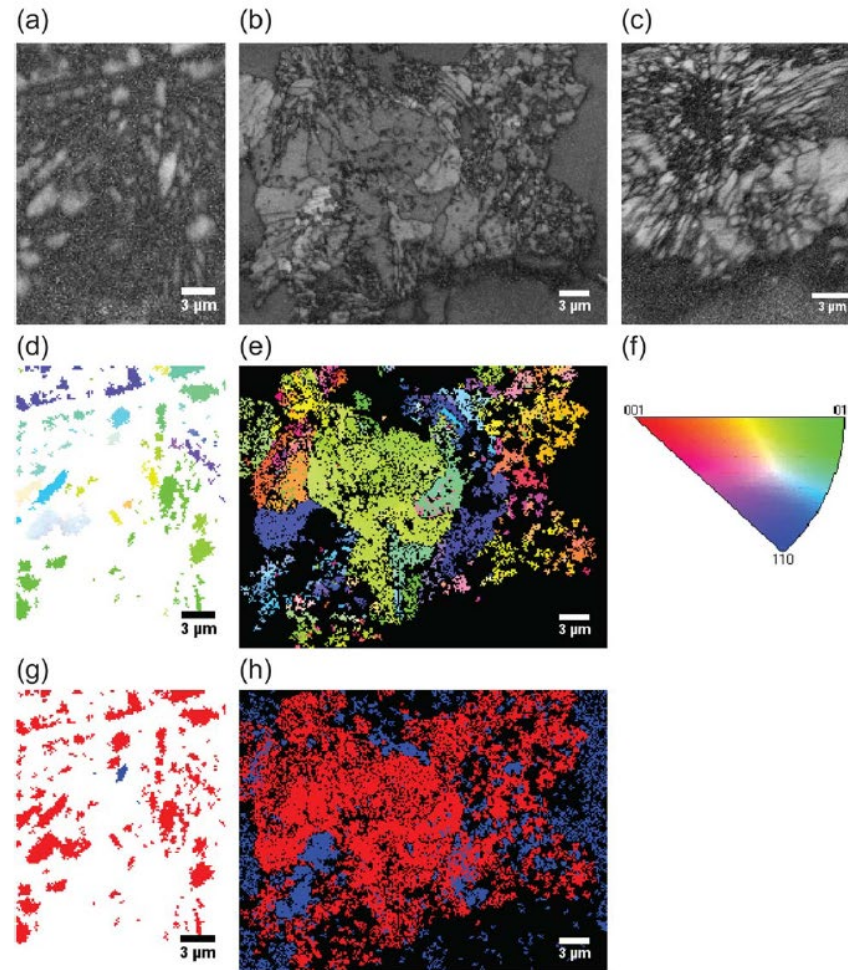
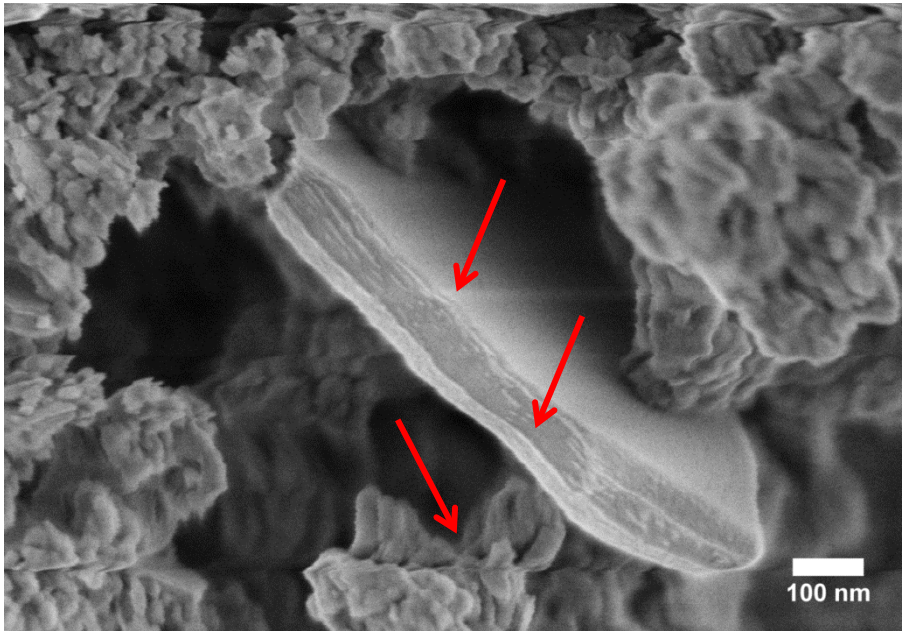


Fig. 6. EBSD maps of a Nechalacho ore area containing zircon and fergusonite-Y in the carbon coated (a, c, d, and g) and the IL-treated (b, e, and h) cross-sections at  $E_0 = 30$  and 20 kV, respectively. a–c: Band contrast maps, (d and e) IPF, (g and h) phase maps, and (f) IPF maps legend. The band contrast, IPF, and phase maps in the carbon

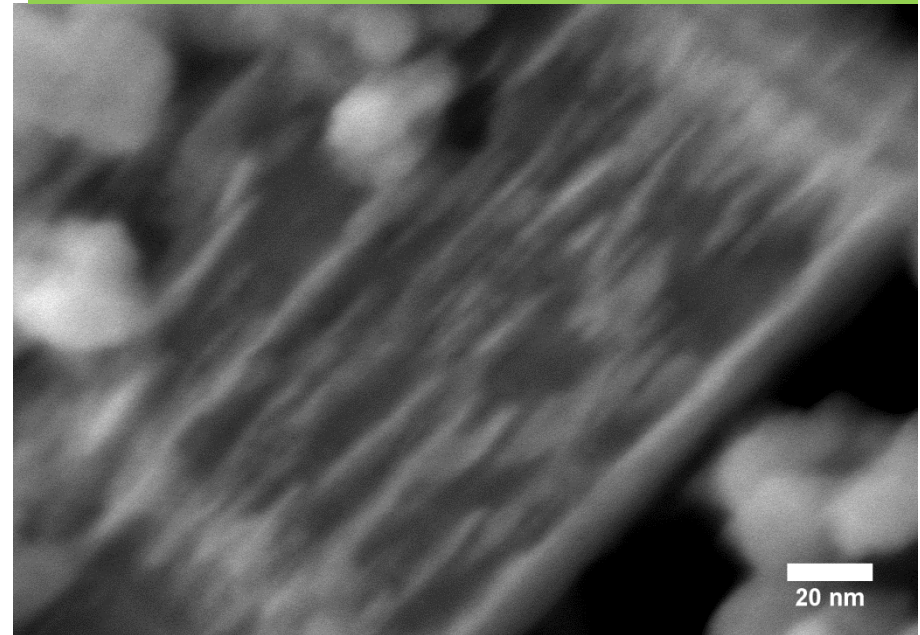
coated specimen demonstrate the lack of spatial resolution due to the use of high voltage and image drifting whereas the IL-treated specimen exhibits high spatial resolution and no drifting. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



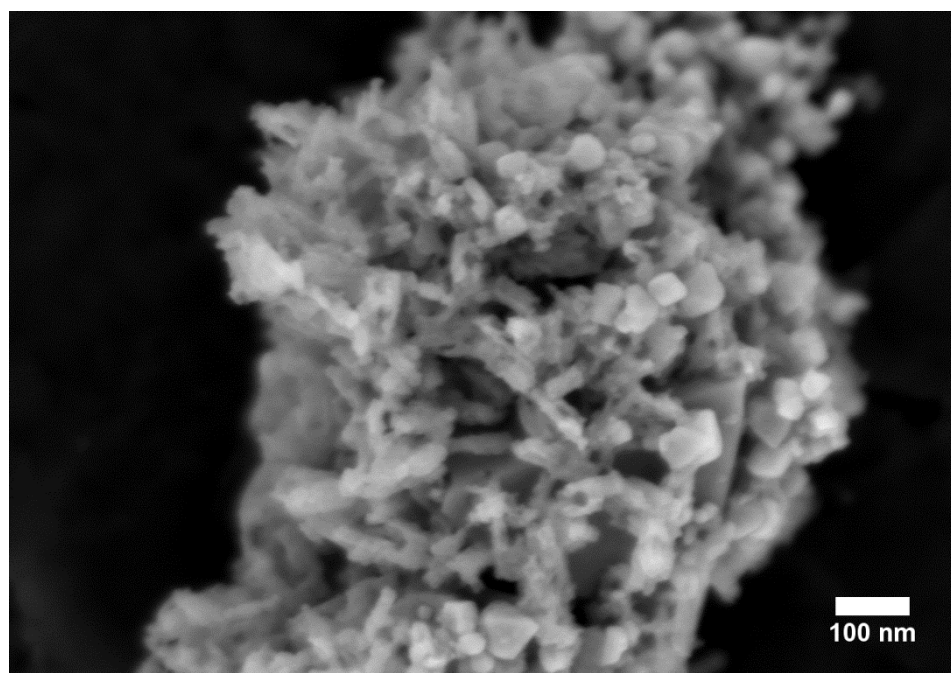


Pas de préparation, pas de revêtement

Avec IL ( $\text{BMI-BF}_4$ ), pas de revêtements

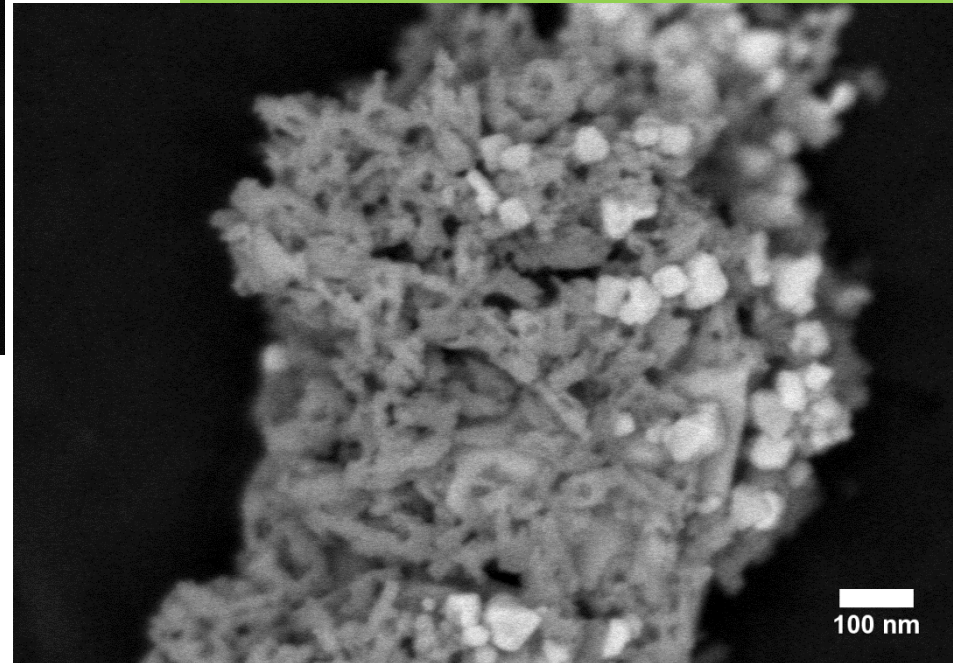


# $\text{Li}_2\text{FeSiO}_4$ avec filtration en énergie ( $E_0 = 2.2 \text{ kV}$ ) et IL



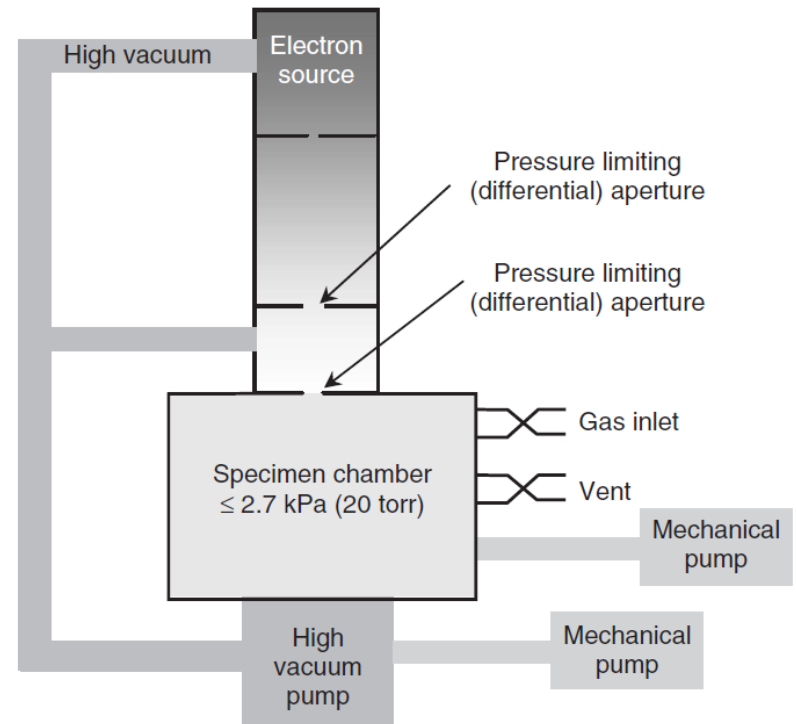
Upper detector (filter bias = 8-9 V)

Top detector avec filtration (80%)



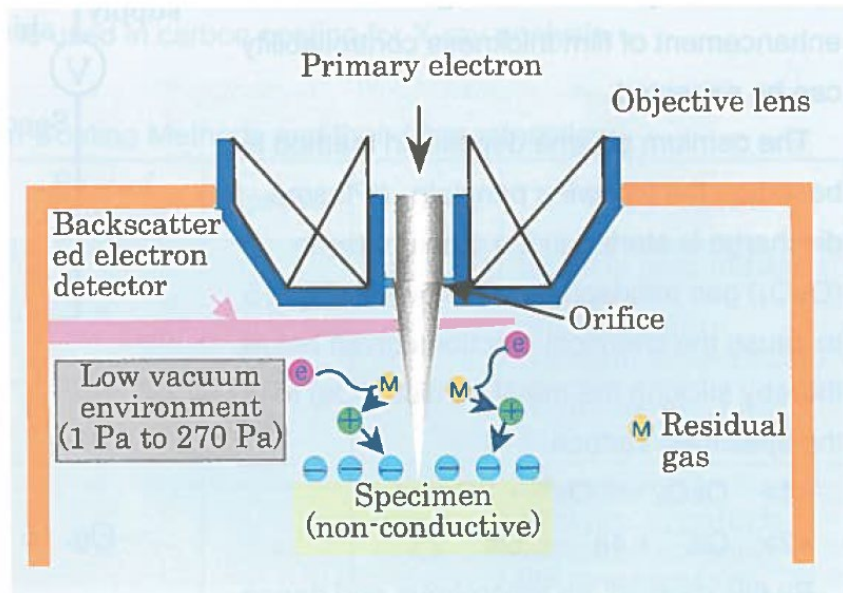
# ESEM et VP-SEM

- Environmental SEM (ESEM)
  - Maximum de Pression
  - 2700 Pa (20 Torr)
- Variable Pressure SEM (VPSEM)
  - Plus basse pression
  - 266 Pa (2 Torr)
- MEB sous vide:  $10^{-3}$  Pa ou moins, SU-9000  $10^{-7}$  Pa





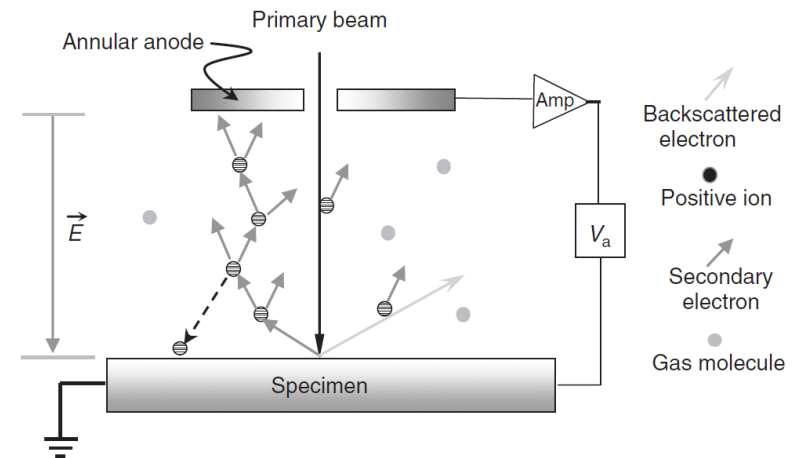
# Neutralisation de Charge



- Production d'ions;  
Ionisation du gaz par les SE
  - Ions Positifs:  $O_2 \rightarrow O_2^+ + e^-$
  - Ions Négatifs:  $H_2O \rightarrow H^+ + OH^-$
- Ions positifs neutralisent les surfaces négatives.
- Ions négatifs neutralisent les surfaces positives.

# Imagerie au ESEM et VPSEM

- Détection directe des BSE
- Détection directe des SE?
- Ions et SE avec un Voltage de biais
  - Gaseous SE detector (GSED)
  - Ultra variable-pressure detector (UVD)
- Courant Induit
- (specimen current)
  - Environmental secondary electron detector (ESED)



# Silicon Nitride

P = 0 Torr



P = 2.8 Torr, H<sub>2</sub>O

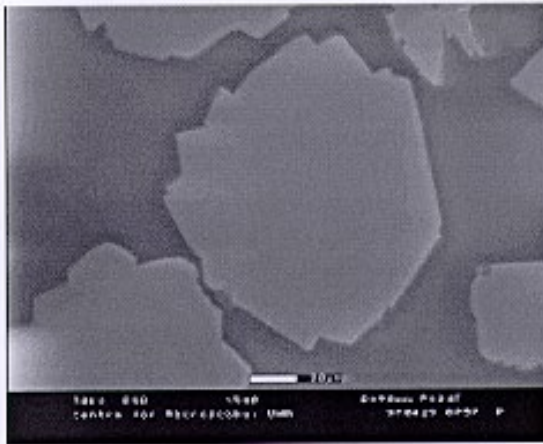


De an Introduction to ESEM , Philips Electron Optics

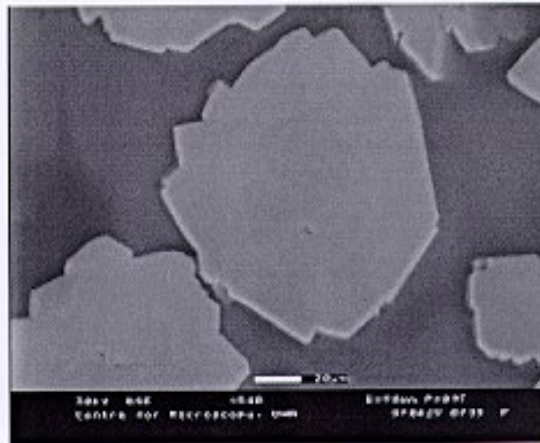


# Charge Contrast Imaging (CCI)

SE



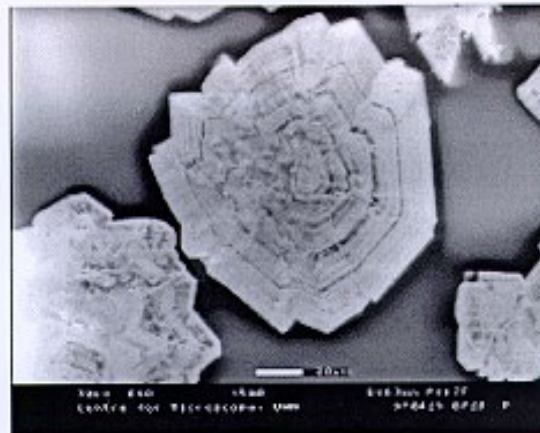
BSE



La variation de charge à la surface crée un contraste. Les zones cultivées sont observées par CL et CCI.



## Cathodoluminescence (CL)

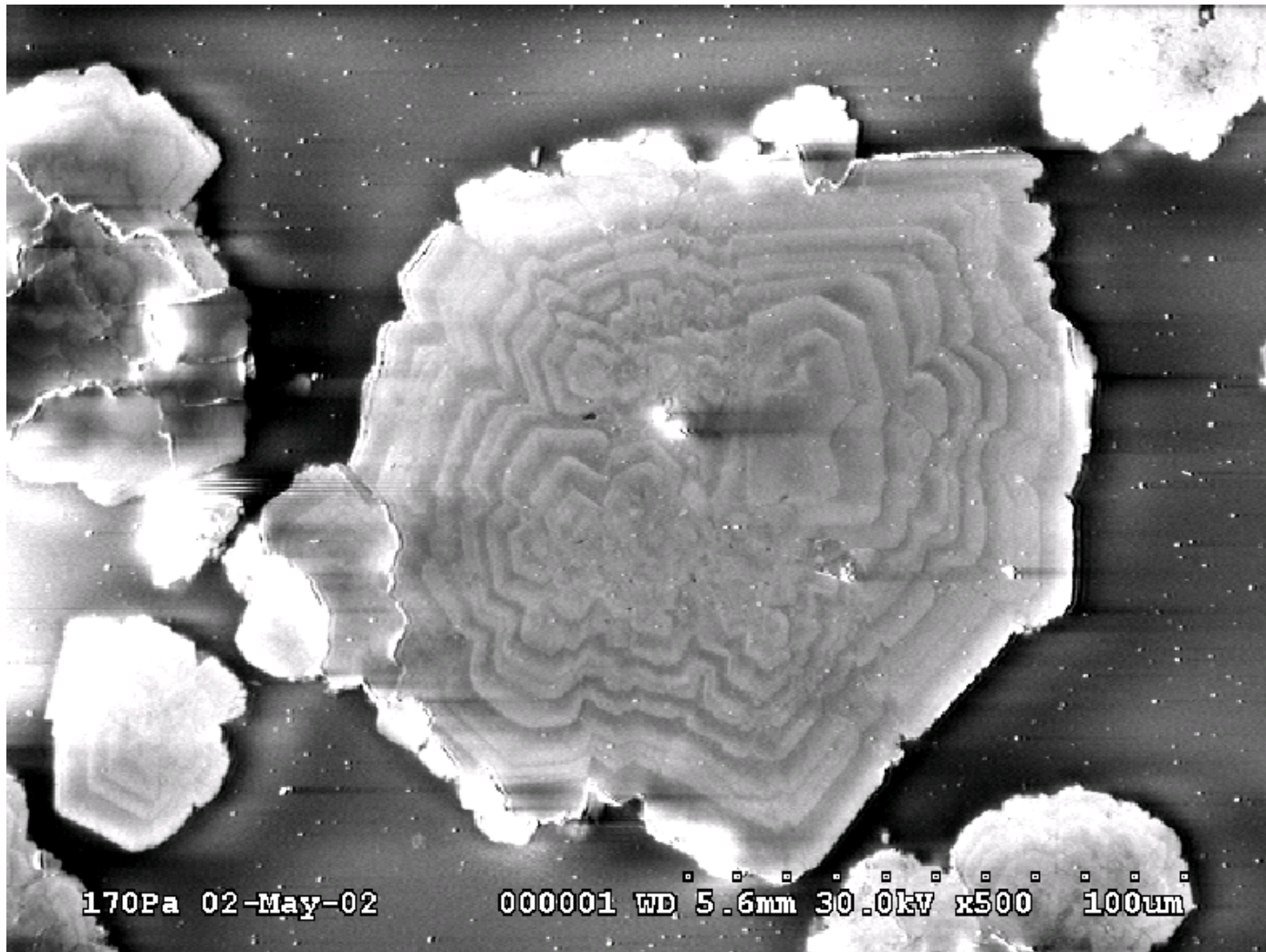


## Charge Contrast Imaging

## Fameuses images de Brendan J. Griffin de la Gibbsite à 30 keV dans un ESEM

# Gibbsite, 30 keV, ESED

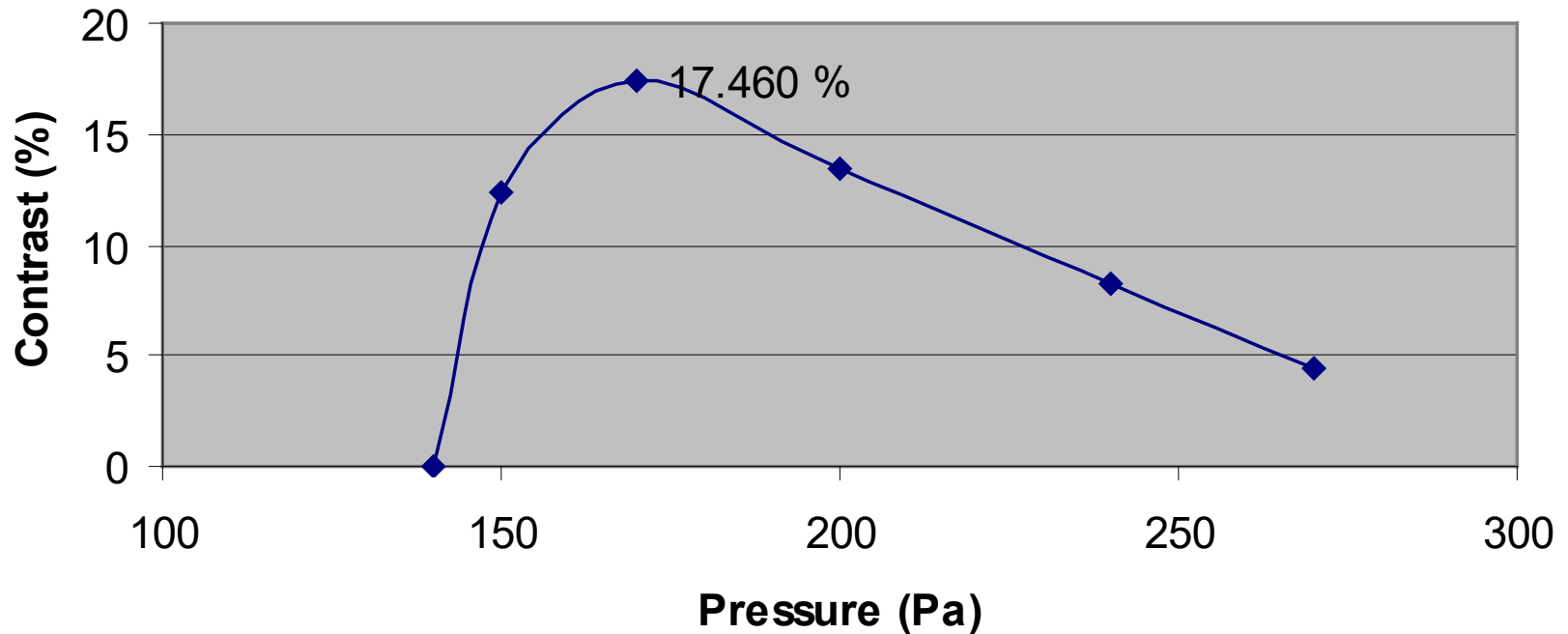
Robertson, Gauvin & Finch (2002)



# Gibbsite, 30 keV, ESED

## Contrast-Pressure Plot 1

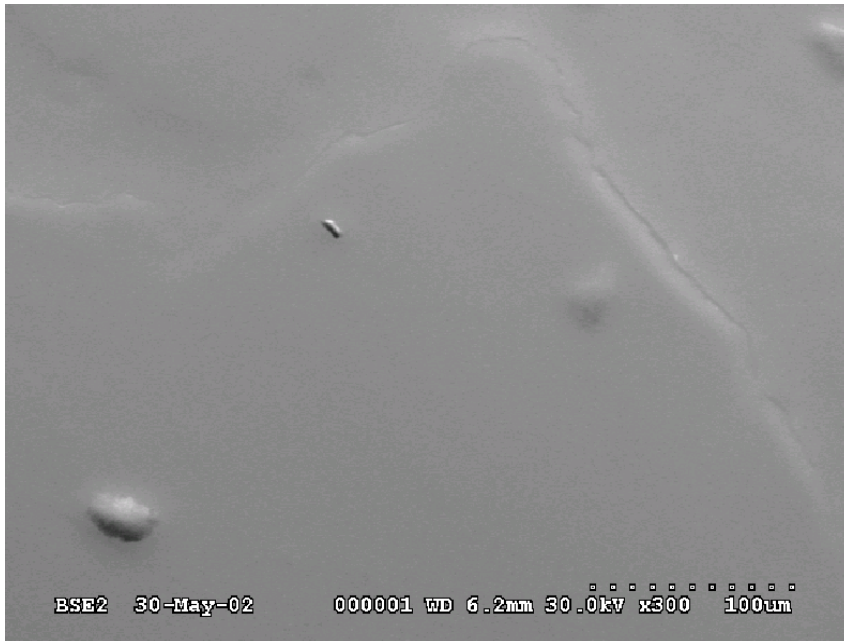
(30 keV, 300 V, 15 mm, 55 SS)



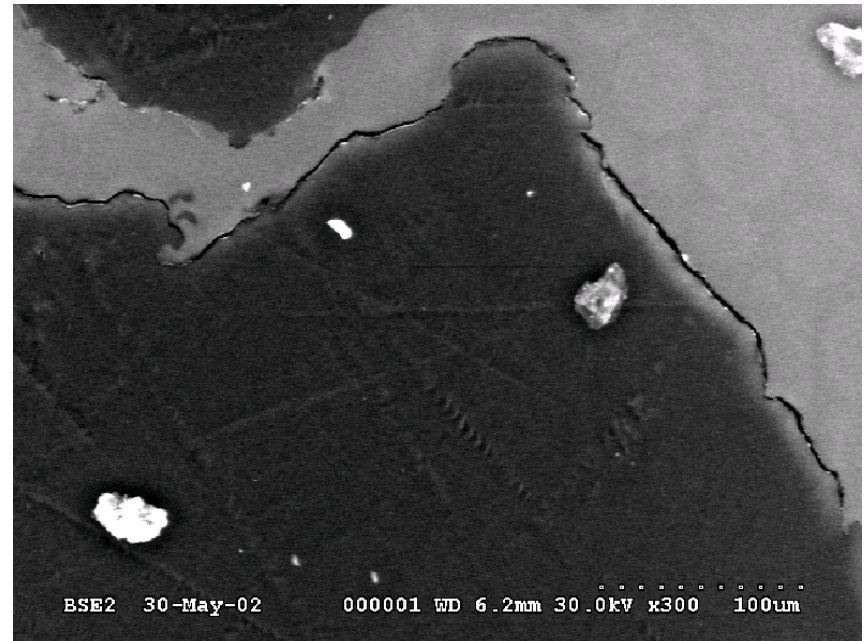


# Low-Density Polyethylene (LDPE)

BSE topography

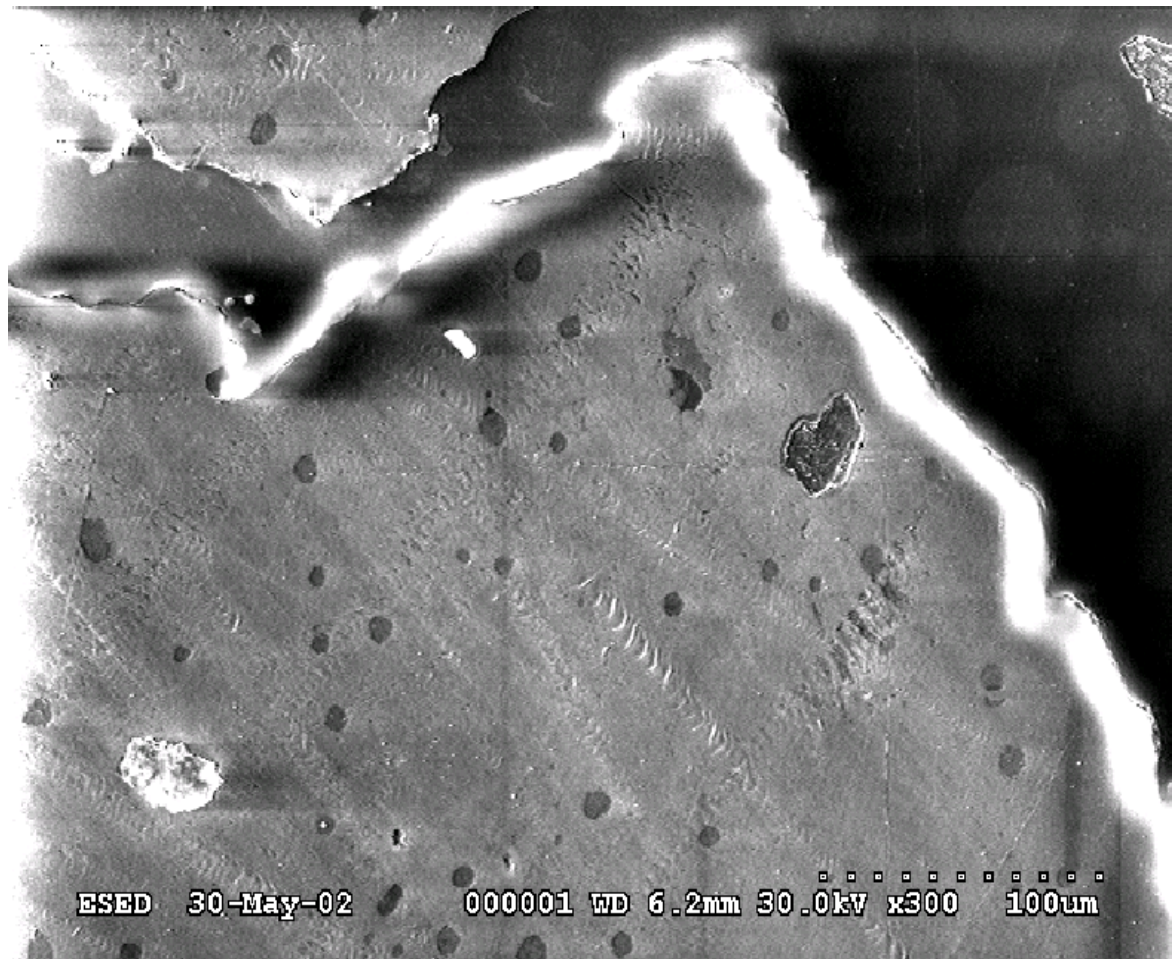


BSE composition



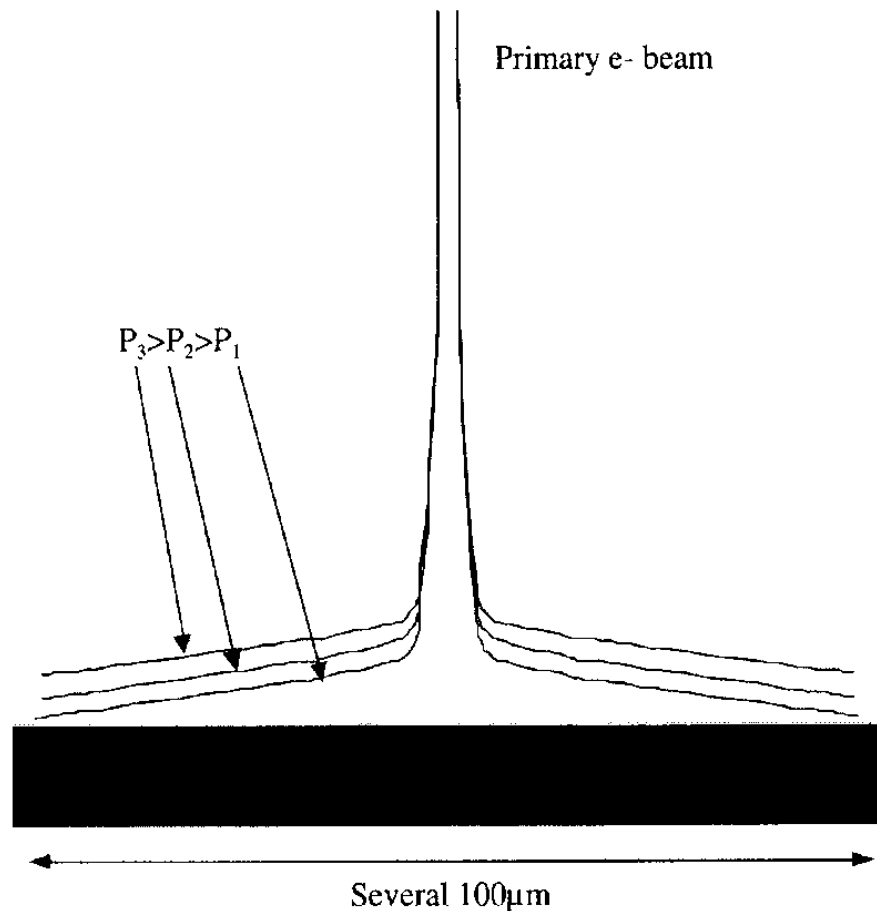
# LDPE, ESED

Gauvin, LeBerre, Robertson & Finch (2002)





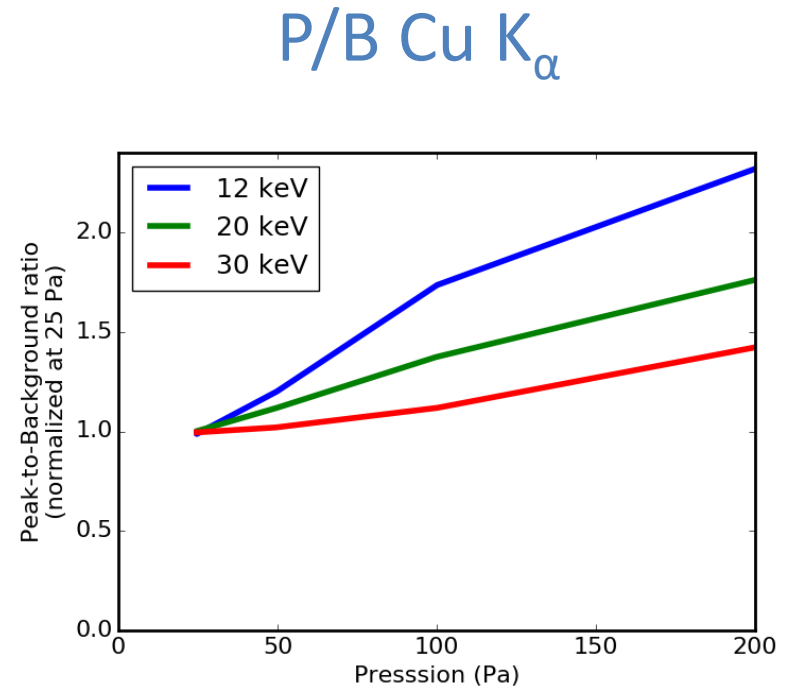
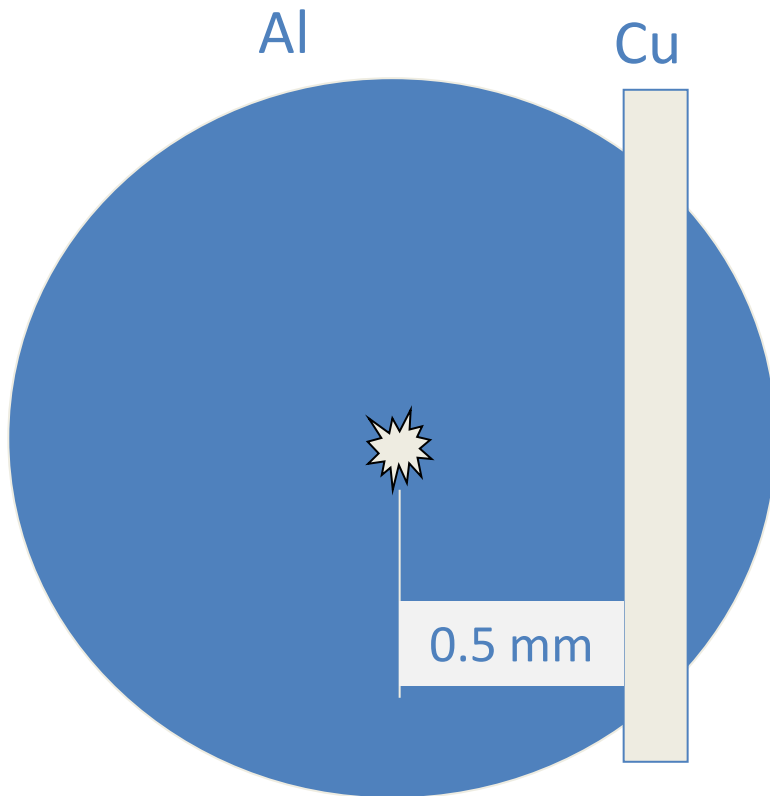
# X-Ray Microanalyse RX au VP-SEM et ESEM



**Il faut corriger pour le Skirt**

# Bande de Cu sur Al

## SN-3500, Air



# Méthode Basé sur la fraction des électrons non diffusés : $f_p$

$$f_p = \exp \left[ \frac{-0.035 P D \tilde{Z}}{T E_0} \right]$$

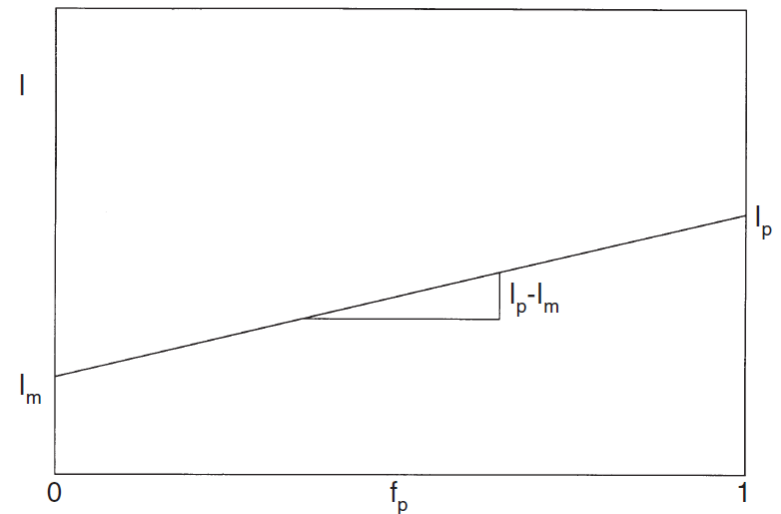
- P: Pression (Pa)
- D: Distance de travail (mm)
- T: Temperature (K)
- $E_0$ : Énergie des Électrons Incidents (keV)
- $\tilde{Z}$ : Numéro atomique moyen du gaz

R. Gauvin (1999), Scanning, Vol. 21, pp. 388-393.

# Principe de la Methode

$$I = f_p I_p + (1 - f_p) I_m$$

- $I$  est l'intensité mesurée à la pression  $P$
- $I_p$  intensité générée par le faisceau
- $I_m$  intensité générée par le skirt
- $f_p$  fraction du faisceau non diffusé



$$I = (I_p - I_m) f_p + I_m$$

R. Gauvin (1999), Scanning, Vol. 21, pp. 388-393.

# Méthode avec 2 Points

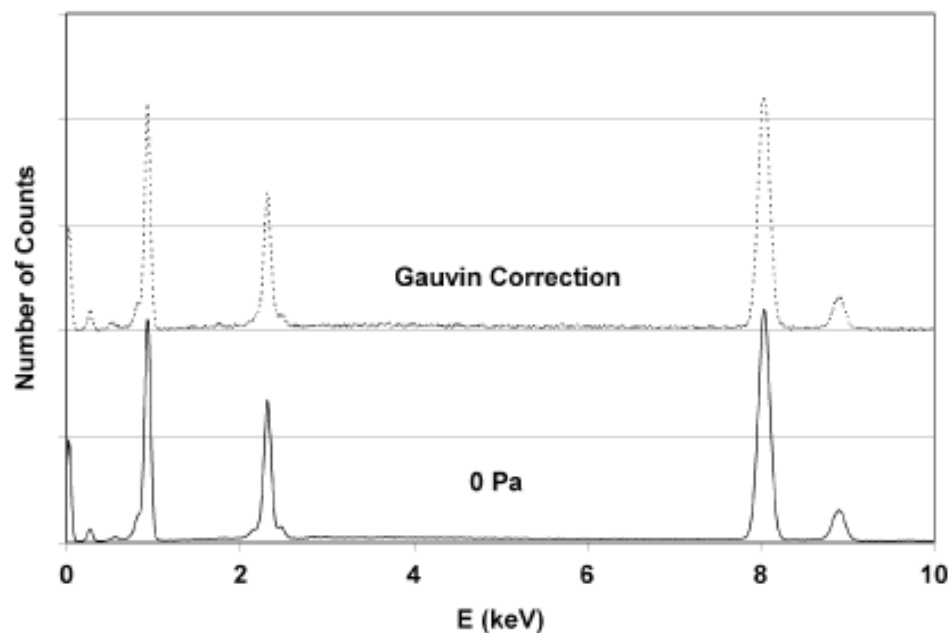
$$I_P = \frac{I_1(1 - f_P^2) - I_2(1 - f_P^1)}{f_P^1 - f_P^2}$$

R. Gauvin (1999), Scanning, Vol. 21, pp. 388-393.

## Skirting: A Limitation for the Performance of X-ray Microanalysis in the Variable Pressure or Environmental Scanning Electron Microscope

J. F. LE BERRE, G. P. DEMOPOULOS, R. GAUVIN

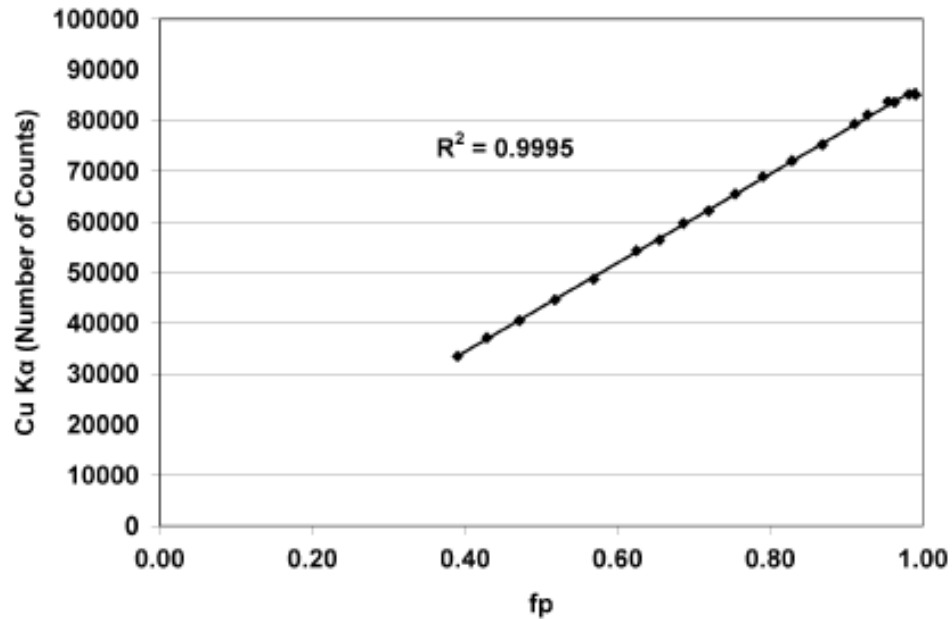
Department of Mining, Metals and Materials Engineering, McGill University, M. H. Wong Building, 3610 University Street, Montreal, QC, H3A 2B2, Canada



Method	Error (%)
2 points	5.7
Extrapolation	1.6

Fig 10. Gauvin Two Points method at 30 keV with  $P_1 = 200$  Pa and  $P_2 = 100$  Pa.

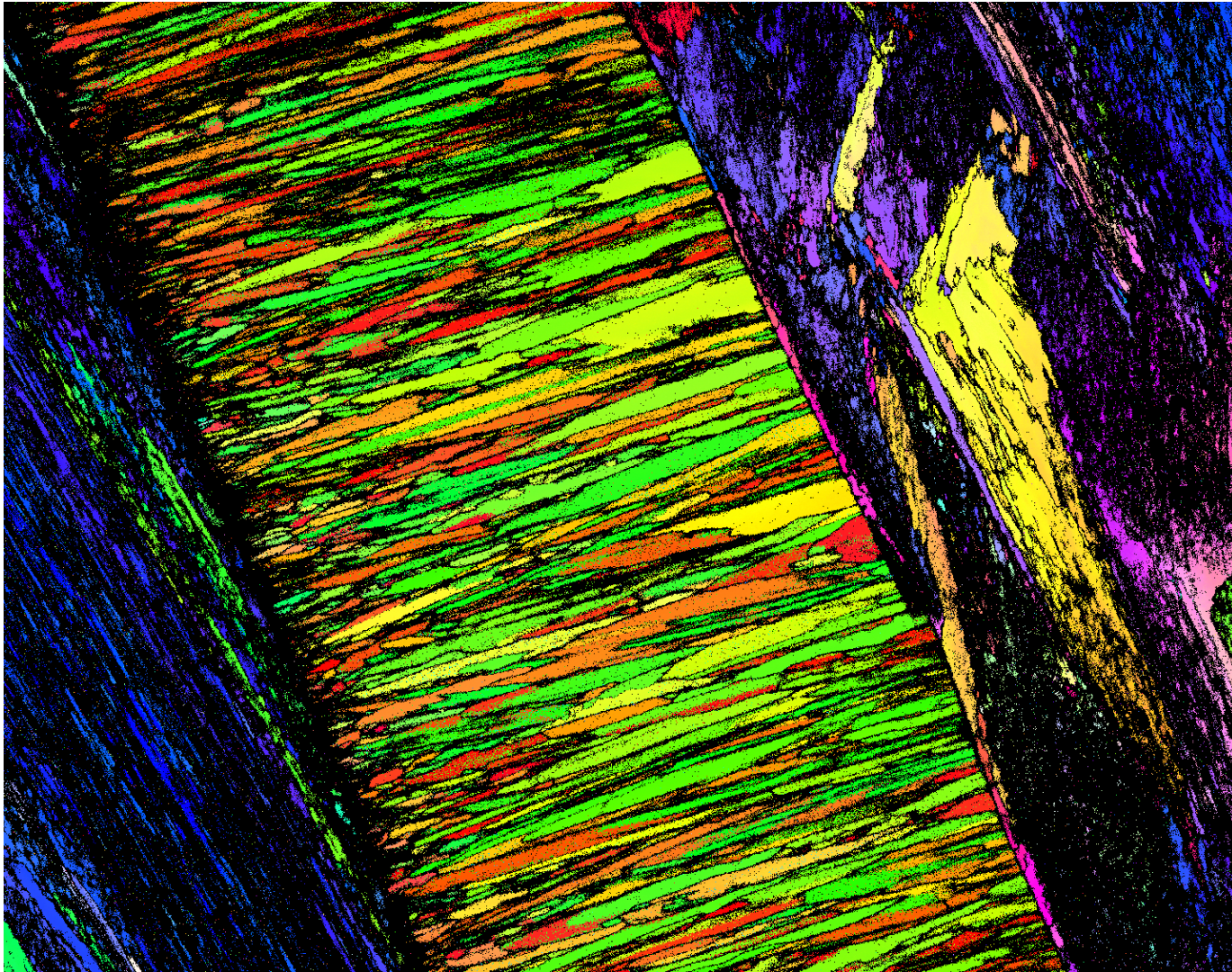
# Méthode d'extrapolation de Gauvin, P jusqu'à 10 Torrs



Method	Error (%)
2 points	2.31
Extrapolation	2.29

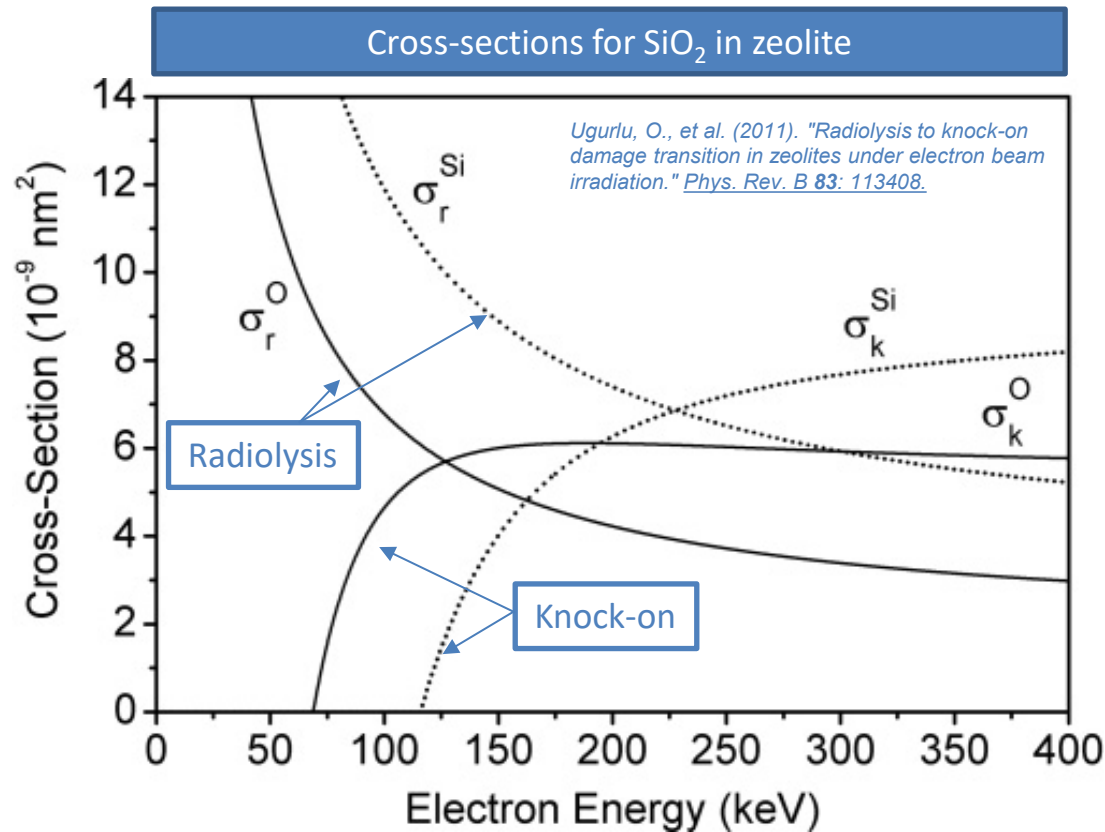
Fig 11. Gauvin Extrapolation method for Cu K $\alpha$  at 30 keV with  $P_{\max} = 1330$  Pa.

Coquille St-Jacques,  $\text{CaCO}_3$ , VP-SEM  
Aragonite (Orthorhombique) dans Calcite  
(Hexagonal)

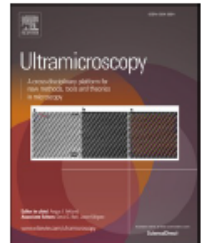




# Endommagement Radiolysis (Ionization) vs Knock-on Damage



- ➡ Radiolysis augmente significativement pour  $E_0 < 100 \text{ kV}$
- ➡ Limitation pour matériaux sensibles



## Prediction of primary knock-on damage during electron microscopy characterization of lithium-containing materials

Ali Jaber<sup>\*</sup>, Nicolas Brodusch, Jun Song, Raynald Gauvin<sup>\*</sup>

*Department of Materials Engineering, McGill University, Montreal, Quebec, Canada*

$$P_{KOD} = \frac{1 - e^{-t/\lambda}}{1 + \left(\frac{\theta_{min}}{\theta_0}\right)^2}$$

## Radiation damage in the TEM and SEM

R.F. Egerton\*, P. Li, M. Malac

*Department of Physics, University of Alberta, Faculty of Science, 412 Avadh Bhatia Phy, Edmonton T6G 2J1, Canada*

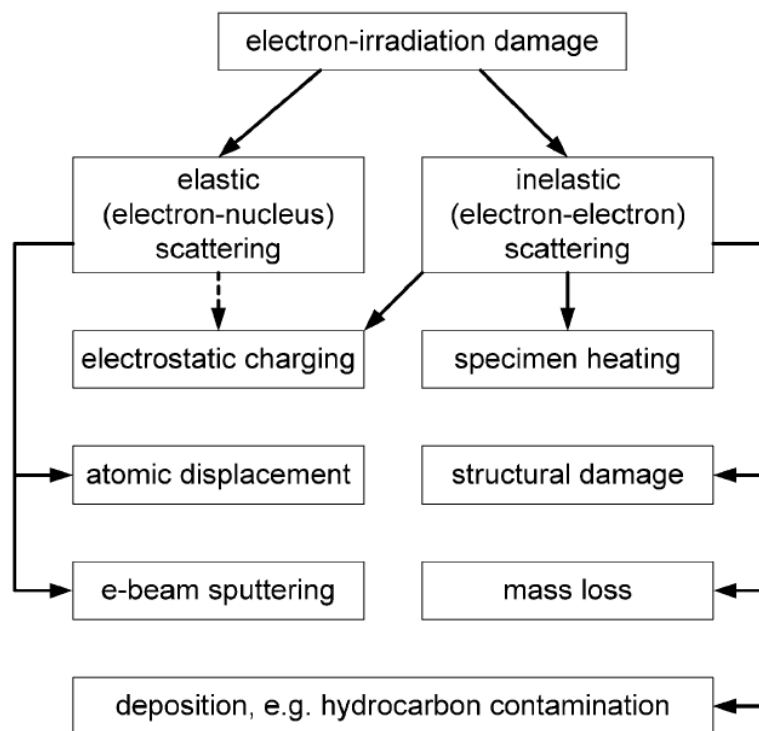
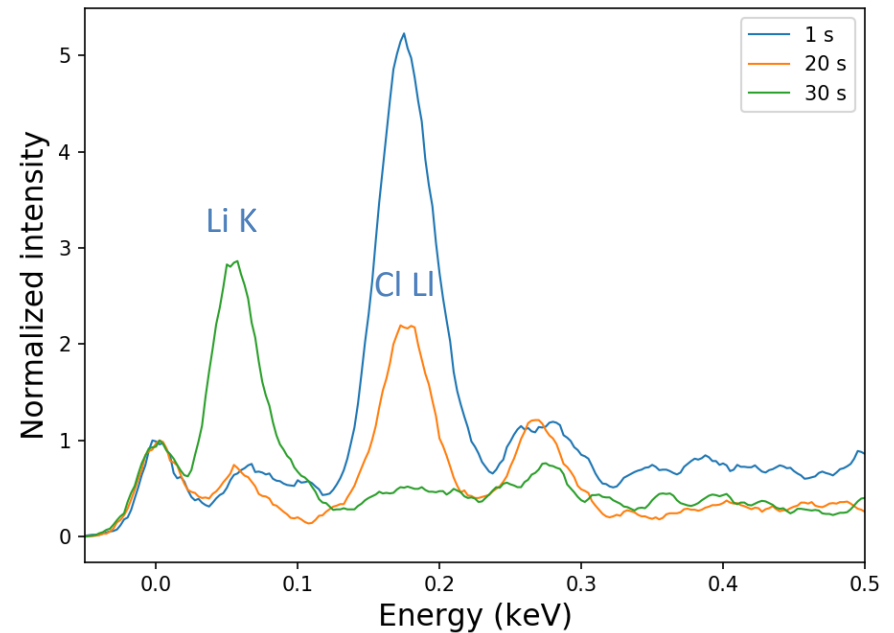
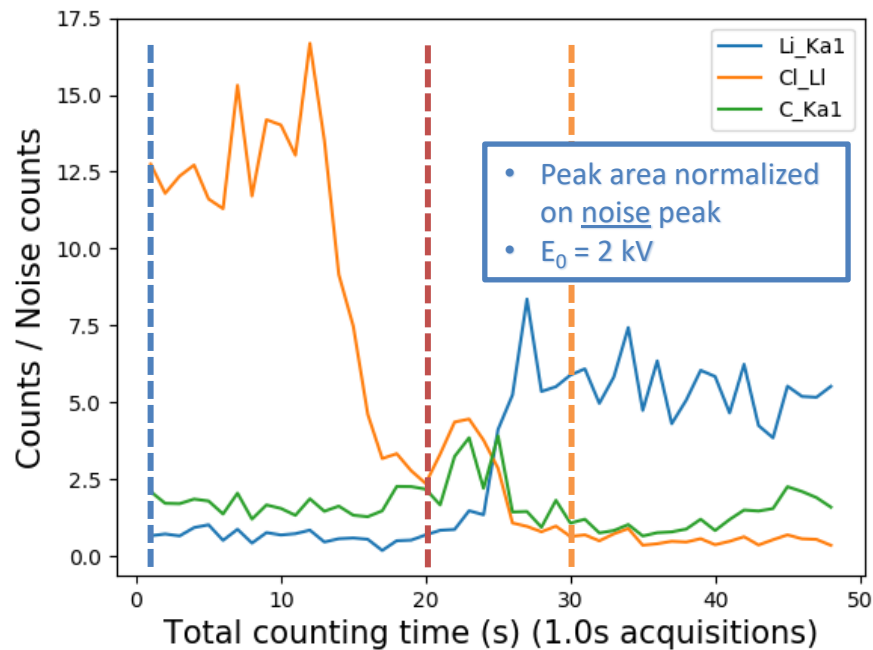
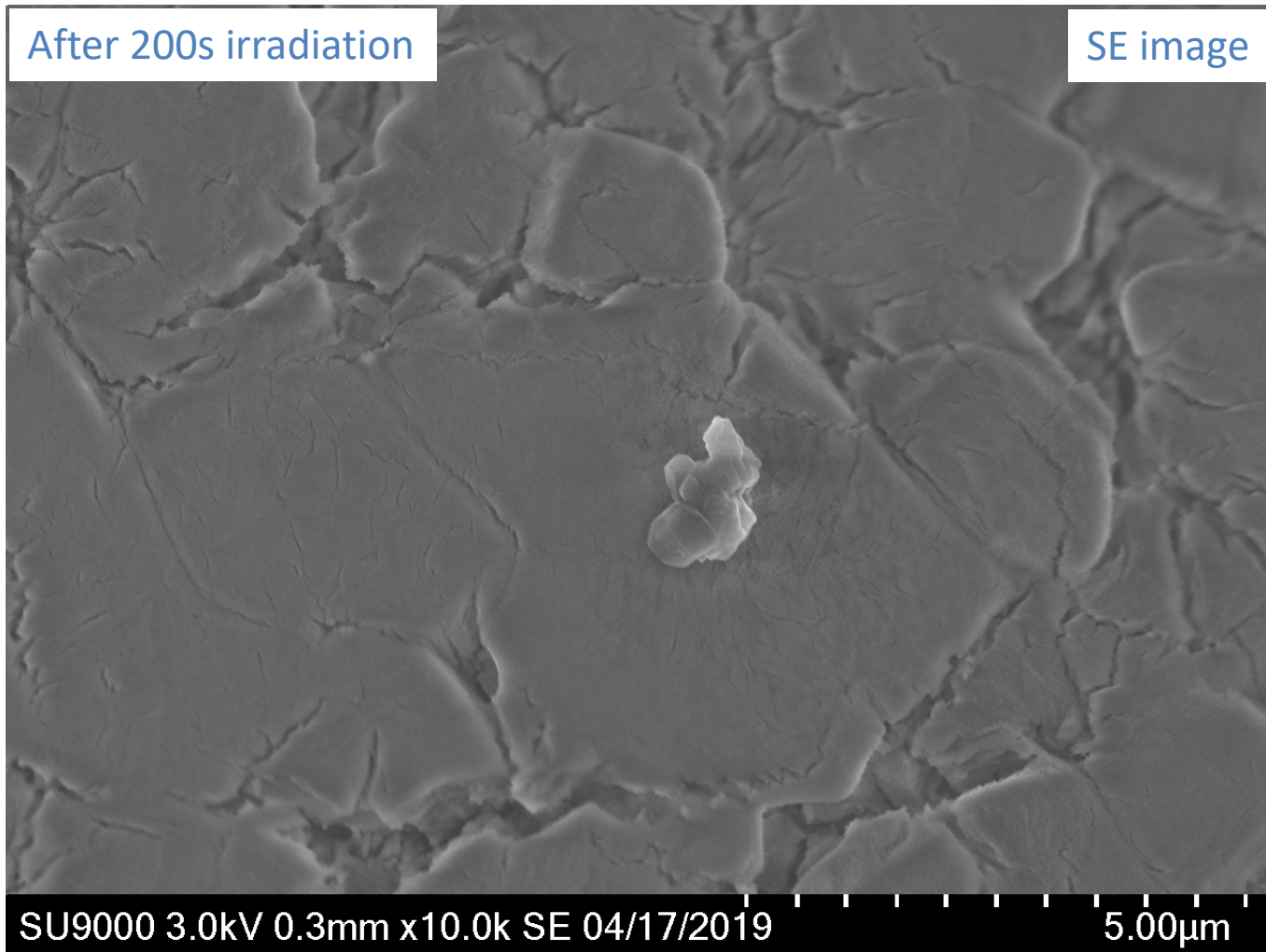


Fig. 1. Classification of radiation damage according to the type of electron scattering and according to the effects produced in a specimen.

# Lithium Chloride: Intensities vs irradiation time

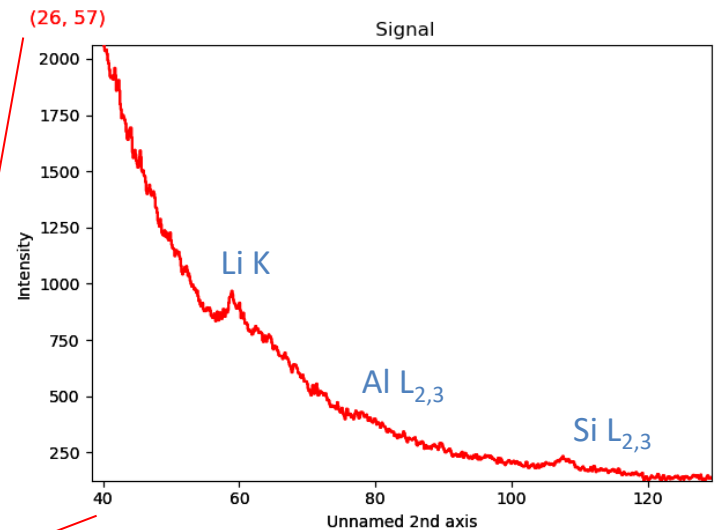
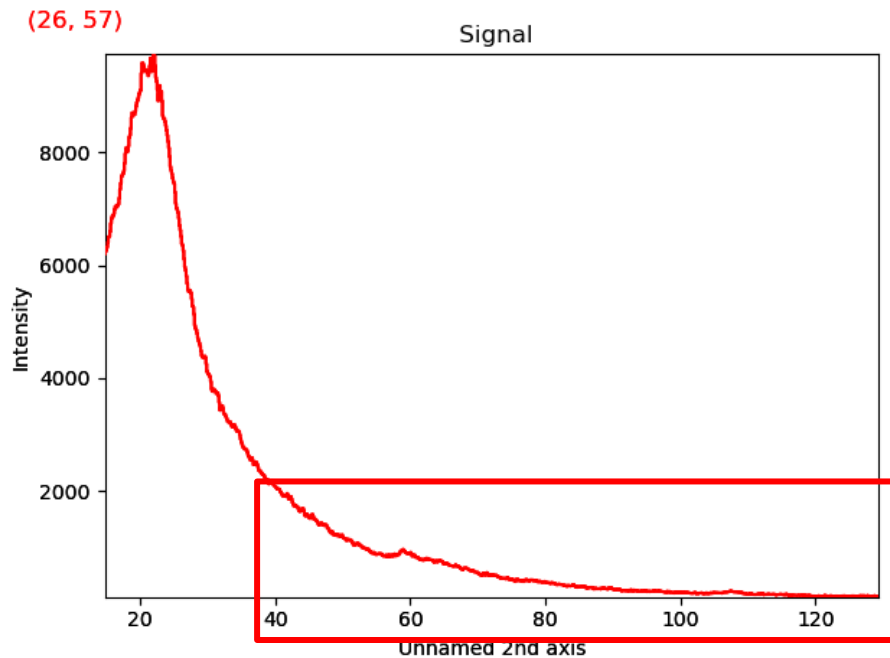


# Beam damage on lithium chloride



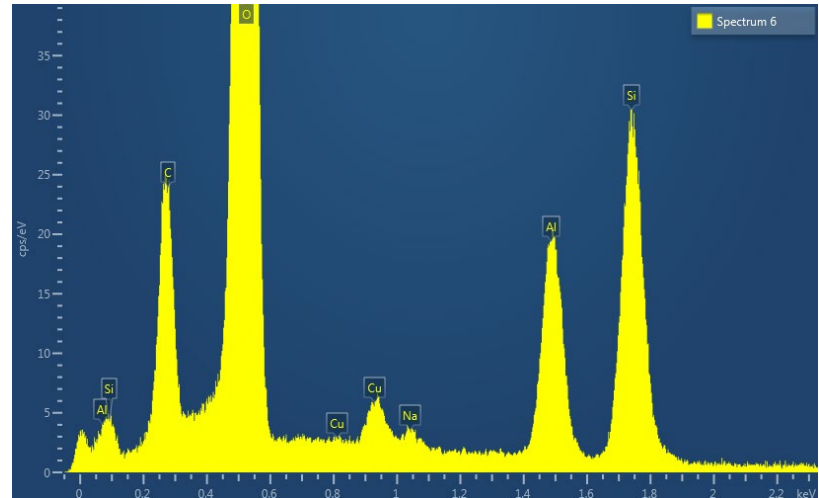
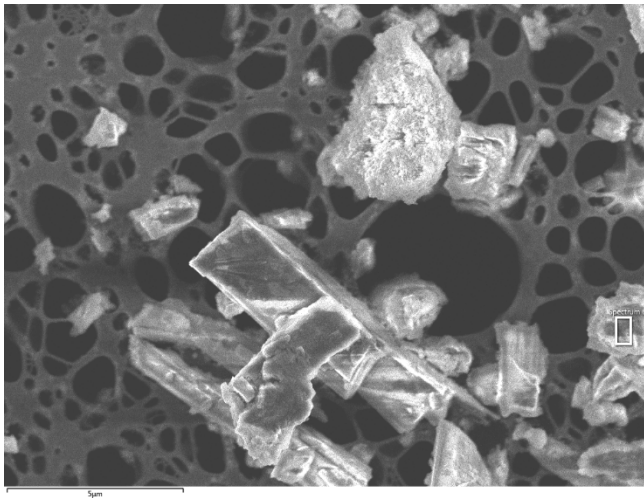
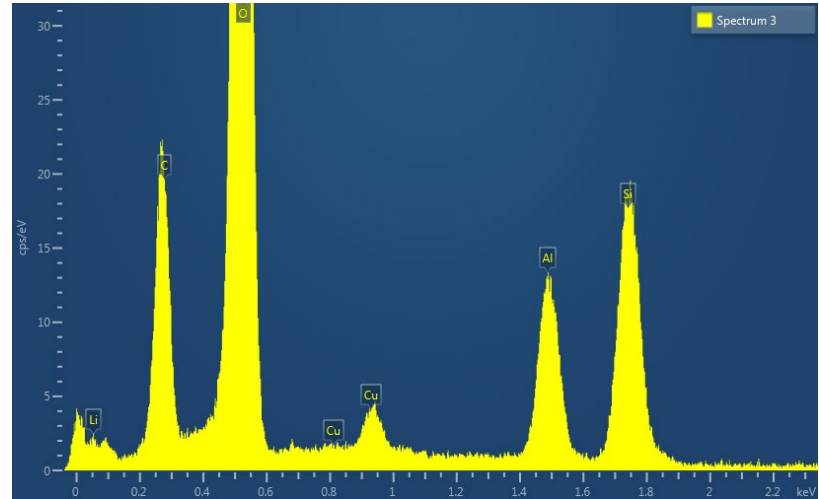
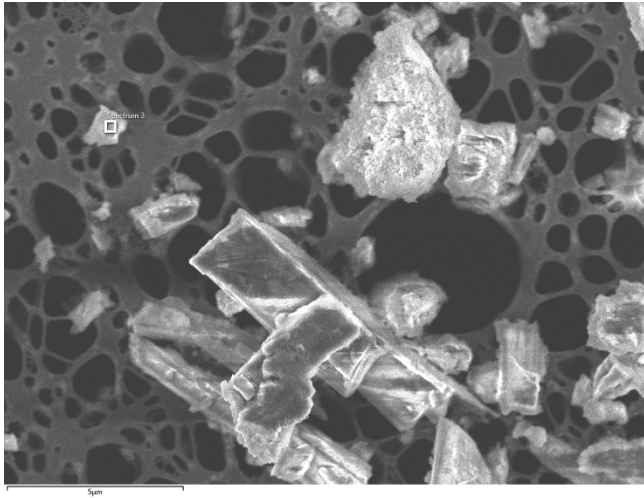
# Spodumene EELS - 30keV

## Cryo-holder, 77 K



494 e/nm<sup>2</sup>s

# Spodumene – $\text{LiAlSi}_2\text{O}_6$





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Journal of Electron Spectroscopy and Related Phenomena 105 (1999) 155–185

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**JOURNAL OF  
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[www.elsevier.nl/locate/elspec](http://www.elsevier.nl/locate/elspec)

## Mechanisms of charging in electron spectroscopy<sup>☆</sup>

Jacques Cazaux

*LASSI/DTI EP 120 CNRS, BP 1039, 51687 Reims, Cedex 2 France*

Received 4 February 1999; received in revised form 8 July 1999; accepted 8 July 1999

$$Q_{Net} = \frac{it}{e} (1 - \delta - \eta - Q_{Io}(1 - \omega)\varepsilon_{out})$$
$$Q_{Io}(1 - \omega)\varepsilon_{out} \ll \delta + \eta$$

*Mais  $Q_{Io}(1 - \omega)\varepsilon_{In}$  peut être élevé !!!*



Les électrons  
Auger induisent  
de la charge au  
MEB et au XPS !!!

# Le Synchrotron Grenoble





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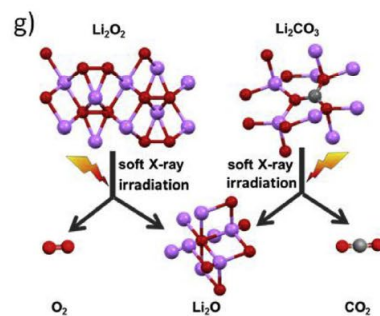
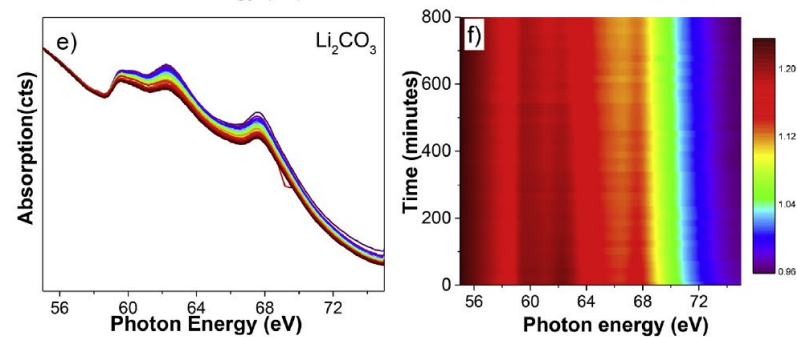
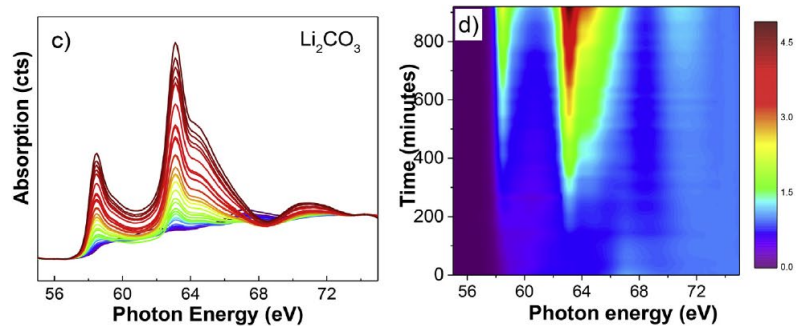
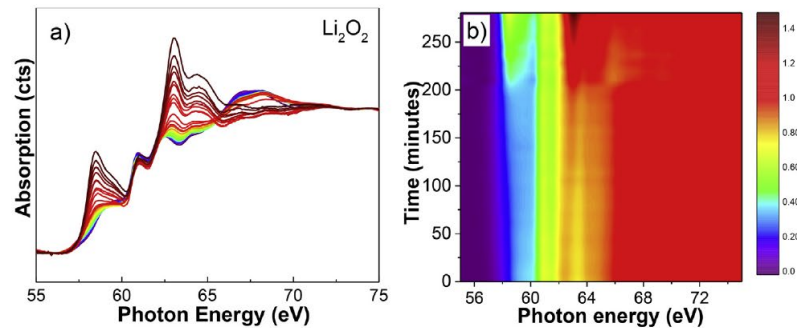


# Li K-edge X-ray absorption near edge structure spectra for a library of lithium compounds applied in lithium batteries



Dongniu Wang<sup>\*</sup>, Lucia Zuin

*Canadian Light Source Inc., 44 Innovation Boulevard, Saskatoon, Saskatchewan S7N 2V3, Canada*



$I_0 \frac{\mu}{\rho} (1 - \omega) \varepsilon_{In}$  est élevé

au Synchrotron

$$I_0 \rightarrow \infty$$

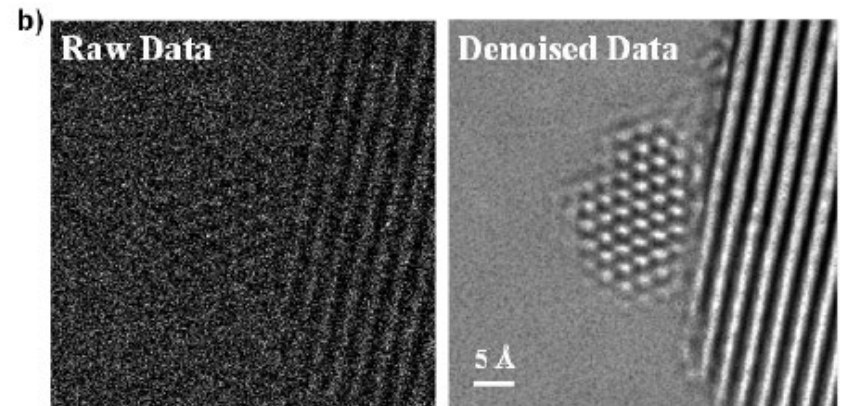
Pour le Li

$$\frac{\mu}{\rho} \rightarrow \infty \text{ et } (1 - \omega) \cong 1$$

# Microscopie à Faible dose avec Détection Directe des électrons et Machine Learning

## Atomic Resolution Observations of Nanoparticle Surface Dynamics and Instabilities Enabled by Artificial Intelligence

Peter A. Crozier<sup>1\*</sup>, Matan Leibovich<sup>2</sup>, Piyush Haluai<sup>1</sup>, Mai Tan<sup>1</sup>, Andrew M. Thomas<sup>3</sup>, Joshua Vincent<sup>1</sup>, Sreyas Mohan<sup>4</sup>, Adria Marcos Morales<sup>4</sup>, Shreyas A. Kulkarni<sup>4</sup>, David S. Matteson<sup>5</sup>, Yifan Wang<sup>1</sup>, and Carlos Fernandez-Granda<sup>2,4\*</sup>



**Figure 1: a) *Unsupervised Deep Denoising*:** The proposed



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