The Abdus Salam International Centre for Theoretical Physics

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**2015-17**

**Joint ICTP/IAEA Workshop on Advanced Simulation and Modelling for Ion Beam Analysis**

***23 - 27 February 2009***

# Relieving Ambiguity by using Particle-Induced X-ray Emission self-consistently with Particle Scattering

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*U.K.*

# Relieving Ambiguity by using Particle-Induced X-ray Emission self-consistently with Particle Scattering

*Joint ICTP/IAEA Workshop on Advanced Simulation and Modelling for Ion Beam Analysis*

*23 - 27 February 2009, Miramare - Trieste, Italy*

Thursday February 26th 2009

**Chris Jeynes**

*University of Surrey Ion Beam Centre*

Guildford, England

# Contents

- PIXE process
- IBA: PIXE
- PIXE as a complementary IBA technique
- Examples of PIXE/RBS and PIXE/EBS
  - Corrosion
  - Paint layers
  - Carbon nanotube surface treatment
  - Photovoltaic materials
  - Inhomogeneous geological samples
- Discussion

# PIXE process I
## tickling the atom

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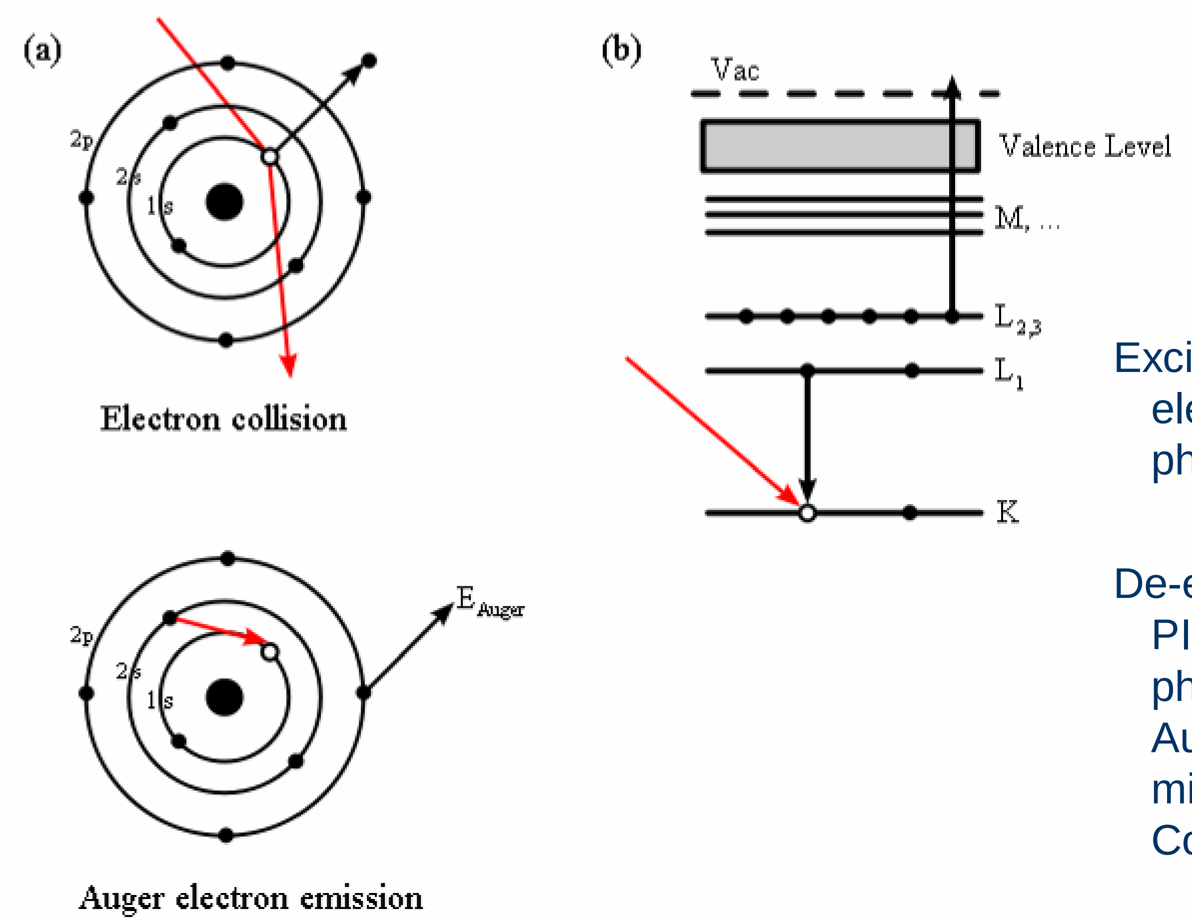


Excitation: ions (PIXE),
electrons (SEM-EDS, AES),
photons (XRF, XPS)

De-excitation: photons (XRF, PIXE, SEM-EDS),
photoelectrons (XPS),
Auger electrons (AES),
mixed possibilities through the Coster-Kronig process

Taken from the Wikipedia article on Auger Electron Spectroscopy 18Feb09
Auger_Process.svg from Wikipedia Commons.

# PIXE process II

## exciting the atom with protons

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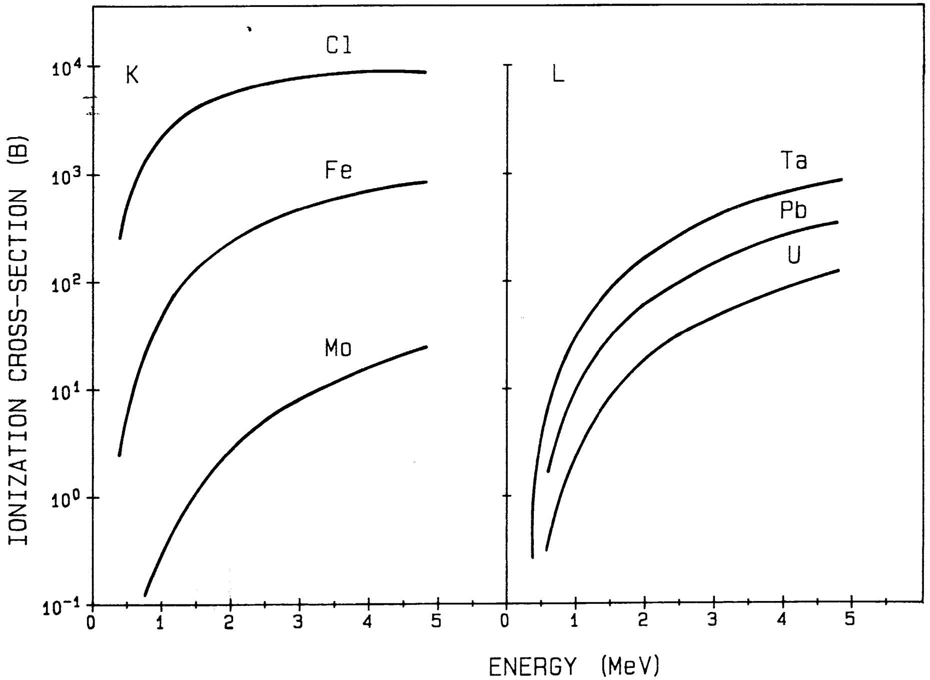


Figure 2.1 The K- and L-shell ionization cross-sections as functions of proton energy *E* and target atom. The values are the theoretical ECPSSR predictions [6]

**S.A.E.Johansson & J.J.Campbell PIXE: a novel technique for elemental analysis, Chichester: Wiley, 1988**

**ECPSSR predictions from D.D.Cohen & M.Harrigan *At. Data & Nucl. Data Tables* 33, 1985, 255**

**ECPSSR is energy-loss Coulomb-repulsion perturbed-stationary-state relativistic theory (W.Brandt & G.Lapicki *Phys. Rev.* A23, 1981, 1717)**

## Position in 1988 (!)

- ECPSSR theory has been used to get ionisation cross-sections for both H and He
- Semi-classical approximation treats Coulomb repulsion "rather exactly" (H.Paul) and improves on ECPSSR for high Z (or low proton energy)
- He can be treated as ~ H with ¼ of the energy with 4*ionisation probability ($Z^2$)

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# PIXE process III

## what X-rays might you get?

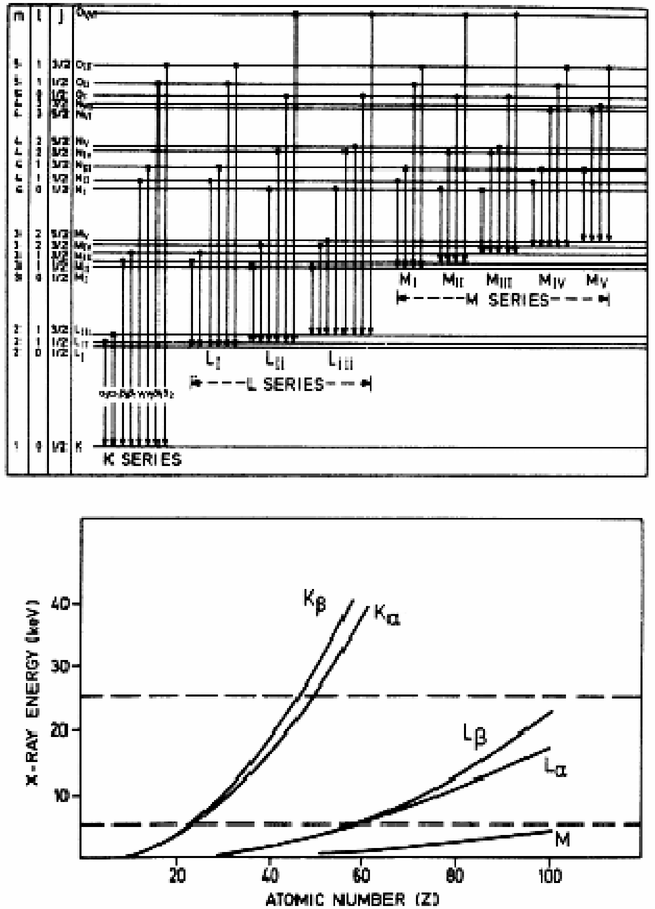



Figure 1.2 Atomic level diagram showing the main K and L X-ray transitions [4]. Reproduced by permission of the author

From V.Valcović *Trace Element Analysis*, London: Taylor & Francis 1987; reproduced in S.A.E.Johansson & J.J.Campbell *PIXE: a novel technique for elemental analysis*, Chichester: Wiley, 1988

Atomic de-excitation starts by electron falling radiatively (or non-radiatively) into the vacancy

Photons produced in the radiative process are characteristic of the element

Photon energies for the three main line groups are well known

# PIXE process IV

## getting the X-rays

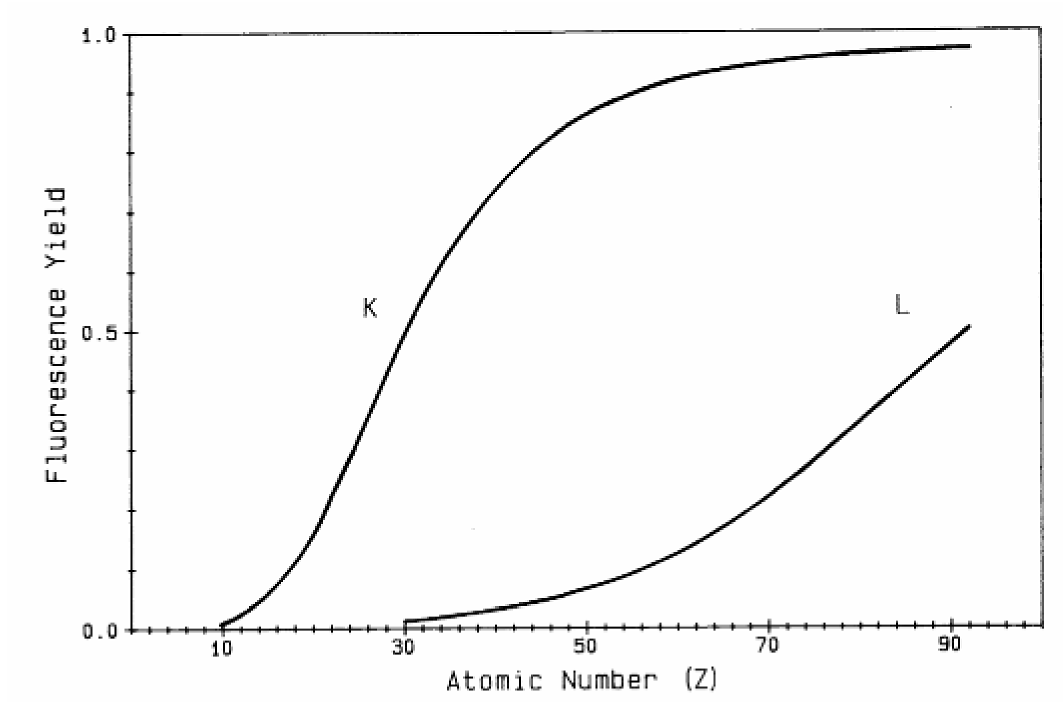



Figure 1.1 The K- and L-shell fluorescence yields as functions of atomic number $Z$

S.A.E.Johansson & J.J.Campbell PIXE: a novel technique for elemental analysis, Chichester: Wiley, 1988

Semi-empirical fit to data, which agrees with Dirac-Hartree-Slater bound atomic electron wavefunctions (M.H.Chen, B.Crasemann H.Mark *Phys.Rev.* A21, 1980, 436)

Figure shows the radiative de-excitation probabilities for K and L shell vacancies

The non-radiative de-excitation process (the inverse probability) is via the Auger electron. Mixed processes are also possible

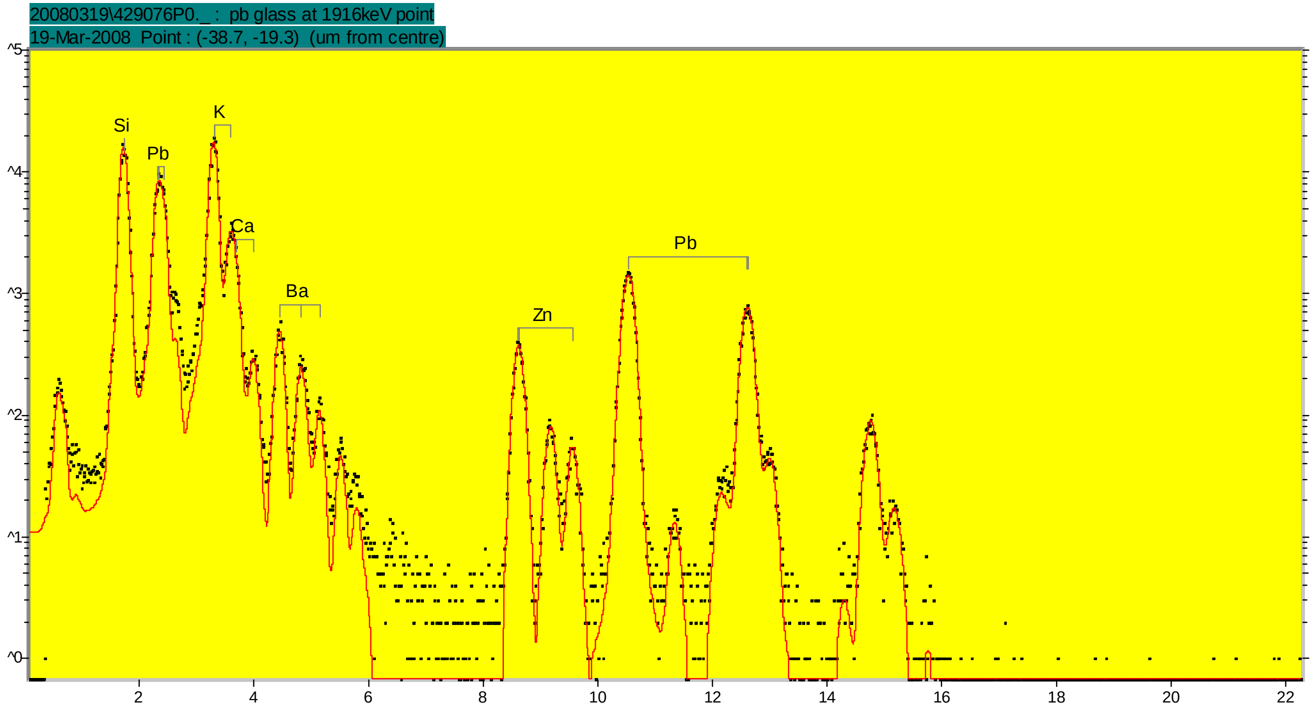
Coster-Kronig effect is when a vacancy executes a non-radiative transfer to a higher sub-shell (special case of Auger effect) – important for the L lines. Complicated, and not well known

K-shell fluorescence yield is known rather precisely from both theory and experiment:

| | |
|---|---|
| Z=10—20: | 3—5% |
| Z=20—30: | 1—3% |
| Z=30—40: | 0.1—1% |
| Z>40: | 0.3—0.5% |

# PIXE as an IBA technique

## what are the spectra like?




- 1.9 MeV protons, Si(Li) detector at $135^0$ with 130μm Be filter
- BCR126a lead glass standard:
- Si, K, Ca, Ba, Zn, Pb = 27, 8.3, 0.74, 0.82, 0.93, 22.3 (wt%)
- Note ordinate in log scale

# PIXE as an IBA technique

## how to use it?

## how to interpret the spectra?

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- High cross-section gives high absolute sensitivity (~fg with μbeam)
  - trace element sensitivity means EDX not WDX is appropriate
  - rapid mapping with μbeam
- Background: secondary electron Bremsstrahlung
  - low signal:noise gives very low detection limits (μg/g)
  - ‘no’ Brehmsstrahlung from the primary beam
- Absorption
  - highly wavelength and matrix dependent
- Raw information is characteristic line intensities
  - no direct depth information
- Indirect depth information
  - from “differential PIXE”: varying energy changes excitation volume
  - from “differential PIXE”: varying geometry changes absorption

# PIXE as complementary in IBA

*In layered structures, need depth profile to correctly calculate PIXE absorption*

***PIXE strength***

- High sensitivity
- Excellent specificity

***BS strength***

- Traceable accuracy
- Excellent depth resolution

***BS weakness***

- Low sensitivity
- Poor mass resolution

***PIXE weakness***

- Poor traceability
- Poor depth resolution

*NB: PIXE information depth is usually significantly larger than for BS*

# Self-consistent PIXE/RBS/EBS

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- DataFurnace: fitting code based on the simulated annealing algorithm or a local minimisation algorithm; molecules, roughness, multiple spectra, non-Rutherford backscattering
- Use DataFurnace (Jeynes++, *JPhysD* 2003; **36**: R97-R126)
- Use LibCPIXE (Pascual-Izarra++, *NIMB* 2006; **249**: 820-822)
- LibCPIXE uses DATTPIXE (Reis++, *NIMB* 1996; **109/110**: 134-138)
- Add PIXE module to NDF (Pascual-Izarra++, *NIMB* 2006; **249**: 780-783)
- Get X-ray line areas from GUPIX using OMDAQ
  (Campbell++, see Blaauw++ *NIMB* 2002; **189**: 113-122; Grime, *NIMB* 1995; **109**: 170-174)
- Check NDF against GUPIX, and critically compare PIXE with SEM-EDX
  (Bailey, Jeynes, Grime++, 'accepted' in *X-ray Spectrometry*)

***PIXE / BS is VERY NEW!***

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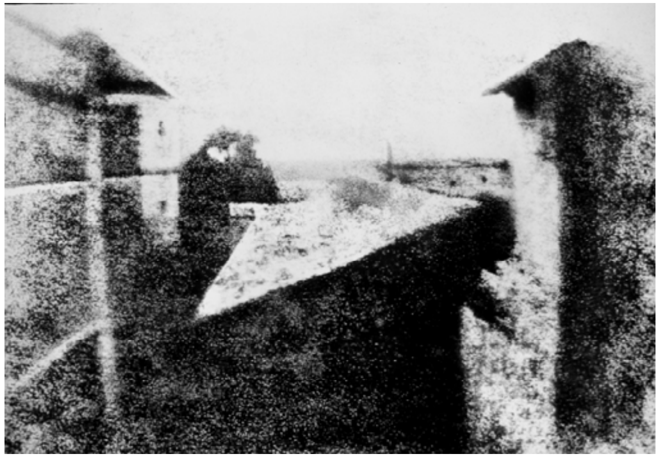
# Towards truly simultaneous PIXE and RBS analysis of layered objects in cultural heritage

Ion Beam Centre

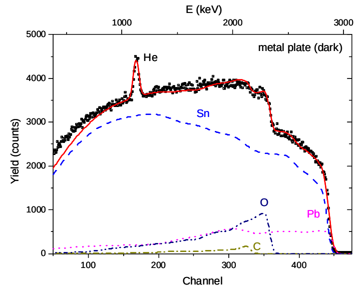
**C. Pascual-Izarra (Madrid), N. P. Barradas, M. A. Reis (Lisbon),**
**C. Jeynes (Surrey), M. Menu, B. Lavdrine, J. J. Ezrati, S. Röhrs (Louvre)**

**Nucl. Instrum. Methods B261, 426-429 (2007)**

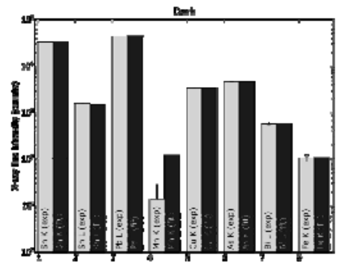


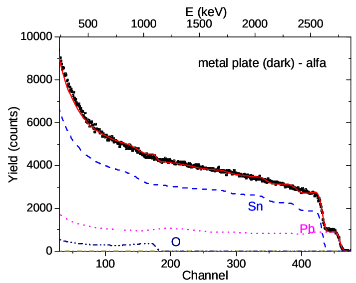
**Niepce's first Heliography:**
**Paysage à Saint-Loup de Varennes (1827)**

## Corrosion products demonstrated by PIXE/RBS/EBS to be tin oxide in a tin/lead matrix

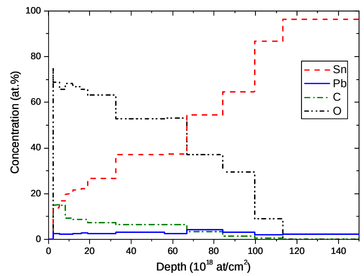



Fitted RBS spectrum for 3 MeV $H^+$ beam on the dark spot (corroded area). Calculated partial spectra for each element are also shown




Fitted RBS spectrum for 3 MeV $^4He^+$ beam on the dark spot (corroded area). Calculated partial spectra for each element are also shown




Concentration profiles for the dark spot (corroded area), as obtained from a simultaneous fit to 3 MeV proton PIXE and RBS, and 3 MeV alpha RBS.

# Characterization of paint layers by simultaneous self-consistent fitting of RBS/PIXE spectra using simulated annealing

University of Surrey
Ion Beam Centre

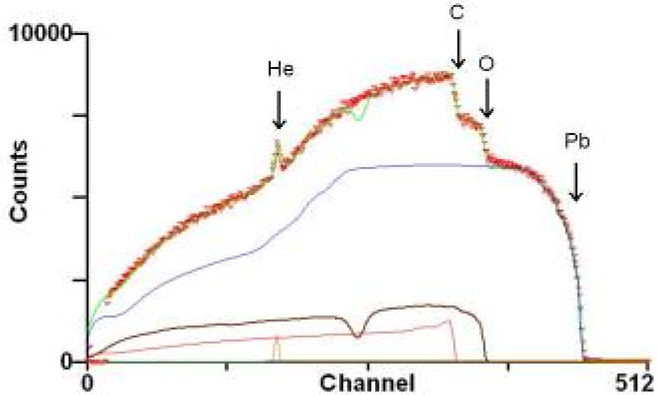
L. Beck (Louvre), C. Jeynes (Surrey), N.P.Barradas (Lisbon)

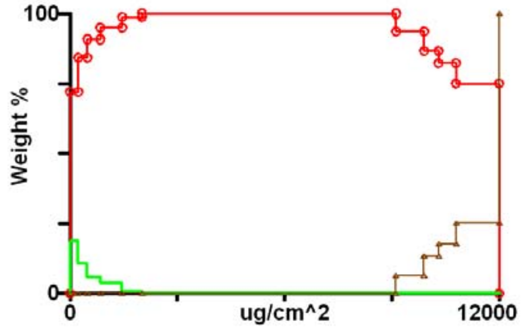
Nucl. Instrum. Methods B266, 1871-1874 (2008)

*"La Bohémienne"* , Frans Hals 1630

*AGLAE : Accélérateur Grand Louvre d'Analyse Élémentaire*

**Ochre (haematite) pigment located and quantified by PIXE/RBS/EBS**

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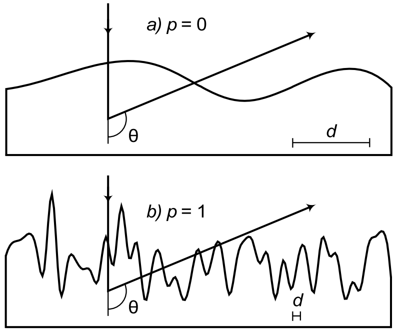
# Roughness

**Molodtsov, Gurbich & Jeynes, J.Appl.Phys. D: Appl. Phys., 41 (2008) 205303 (7pp)**

Ion Beam Centre

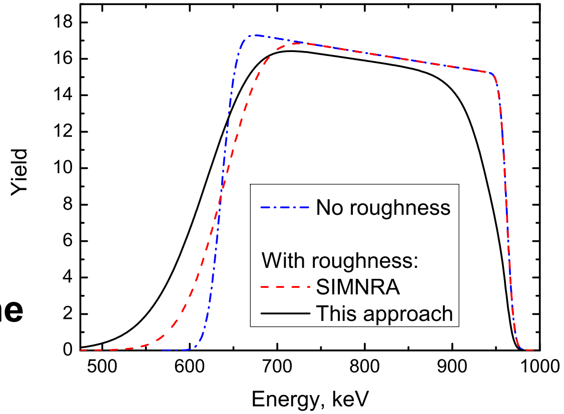


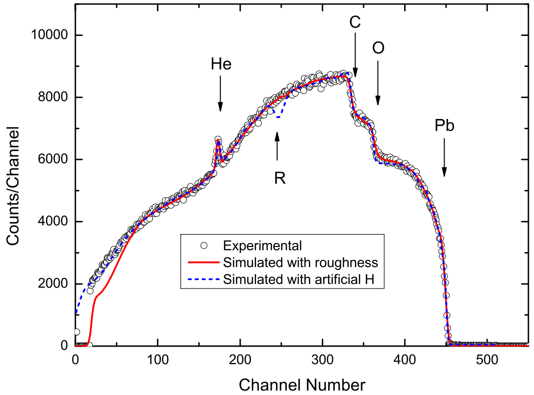

- *Beam re-entering through surface asperities gives extra surface energy loss due to extra pathlength x*
- *Generate a general rough surface giving a pathlength density function f(x)*
- *Characterise roughness with TWO PARAMETERS: "sharpness" σ and "scale" p*
- *Parameterise f(x) explicity using extensive Monte Carlo calculations*

$$f(x) = (1-n)\delta(x) + n\frac{b^{a+1}}{\Gamma(a+1)}x^a \exp(-bx)$$

**SIMNRA (and NDF) can simulate only some of the roughness effect**

**New algorithm calculates the high energy effect and the lower max yield**




**New algorithm correctly calculates the smearing of the EBS resonances "R".**

**The effect on the depth profiles is LARGE**

- ***Most real samples are ROUGH!***
- ***This algorithm can extract scale and sharpness of real rough samples from BS spectra without MonteCarlo***
- ***Valid for RBS, EBS, ERD, PIXE, NRA***
- ***Correct depth profiles!***

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# RBS/EBS/PIXE measurement of single-walled carbon nanotube modification by nitric acid purification treatment

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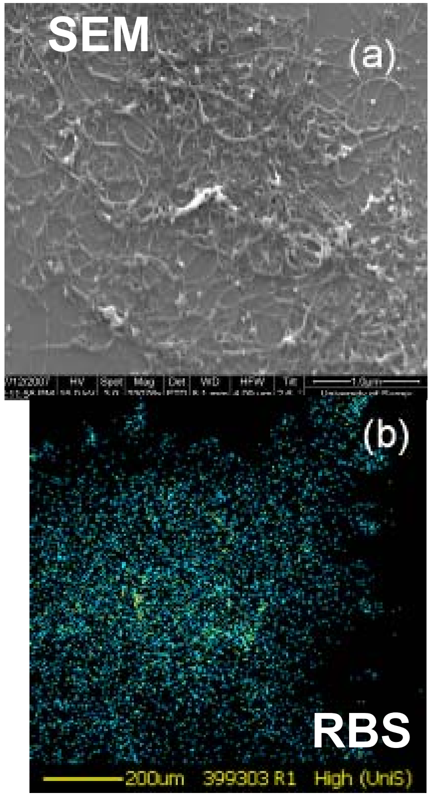
**J.C.G. Jeynes, C. Jeynes, K.J. Kirkby, M. Rümmeli, S.R.P. Silva**

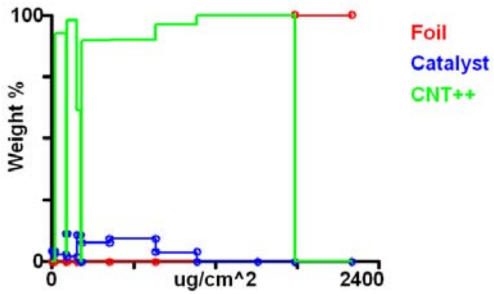
**Nucl. Instrum. Methods B266, 1569-1573 (2008)**



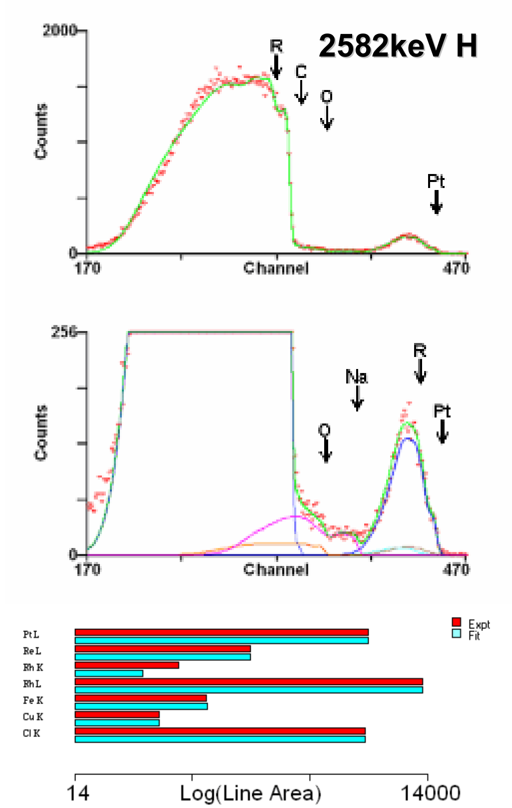

*SWCNT on mylar*

**O and N quantified by PIXE/RBS/EBS in the presence of mixed heavy metal catalyst content of CNT with heavy roughness**

**Catalyst contains Pt, Rh, Re, Fe, Cu, Cl, Na. Roughness effects marked "R"**




*Fitted depth profile*




*RBS/EBS & PIXE data & fits*

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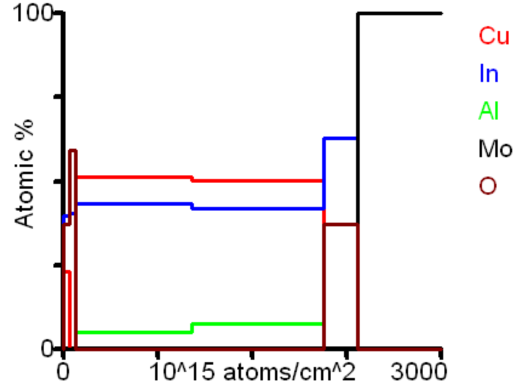
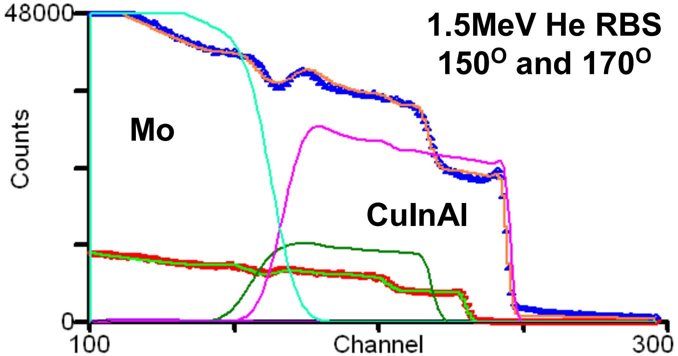
# Characterisation of thin film chalcogenide PV materials using MeV ion beam analysis

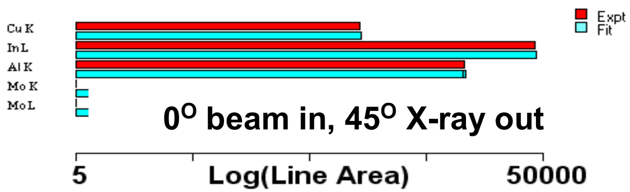
**Chris Jeynes, G.Zoppi, I.Forbes, M.J.Bailey, N.Peng**

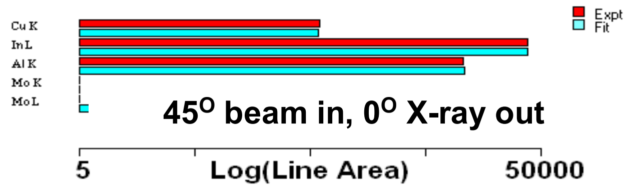
**SuperGen conference, Shanghai, April 2009**

University of Surrey
Ion Beam Centre




- CIAS semiconductor on Mo electrode
- Precursor material (not selenided yet)
- Al invisible in backscattering
- Strong layering: PIXE uninterpretable without profile independently available
- Differential PIXE to profile Al
- Essential to fit roughness to reproduce RBS spectra
- Good fit essential for reliable profile

# PIXE/EBS of Darwin glass

Bailey, Howard, Jeynes: *Characterisation of Inhomogeneous Inclusions in Darwin Glass using IBA*, NIMB (in press)

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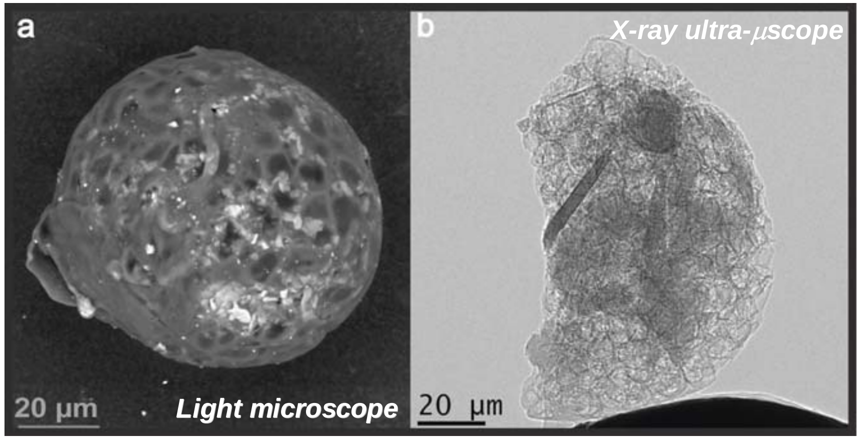
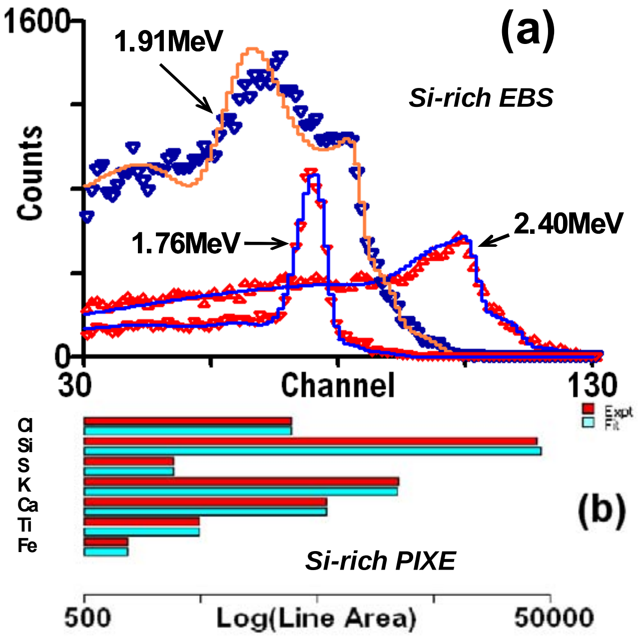
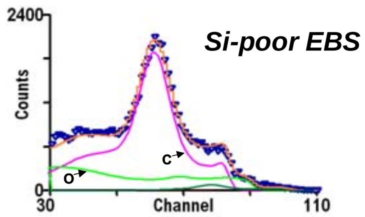


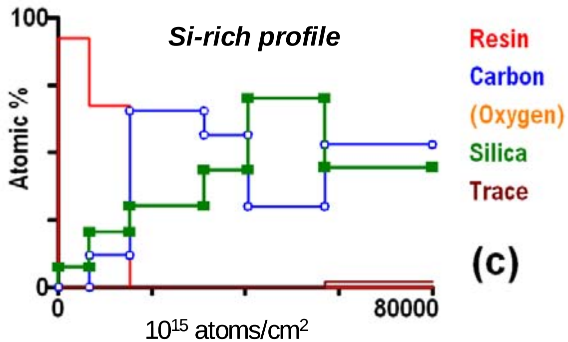

Impact glass from 800,000 year old meteor strike crater at Mt.Darwin, Tasmania

Inclusions are Carbon and Silicon (silica) rich: confirmed by PIXE/EBS

Inclusions highly heterogeneous: silica observed by EBS/PIXE




Silica (quartz by XRD) not observable without PIXE. Unequivocal profiling down to ~15µm with EBS

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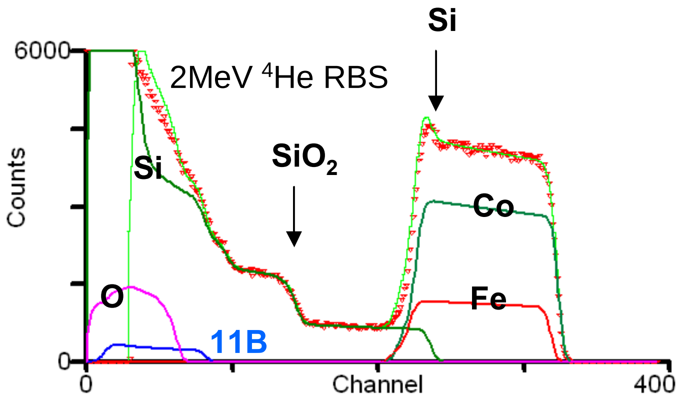
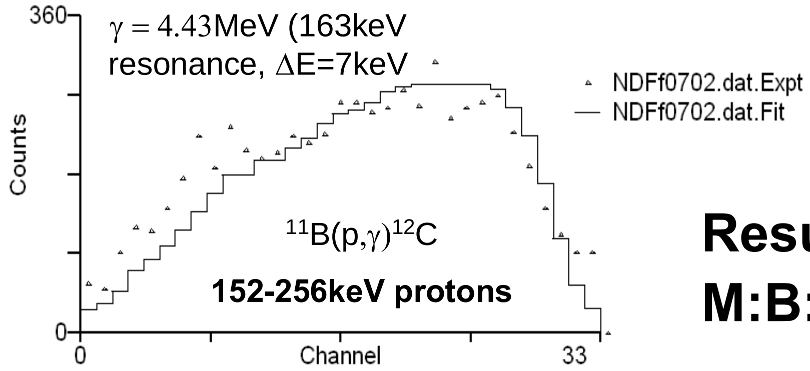
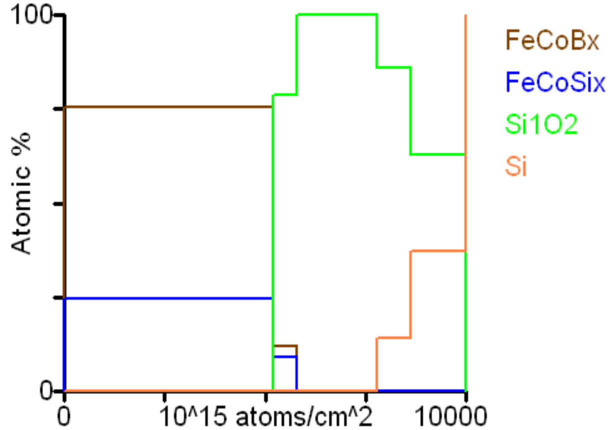
# NRP (PIGE) of metal boro-silicide sample




- **Sample structure from RBS (boron content poorly determined)**
- **Co/Fe=3.8 from 2.2MeV PIXE**
- ***Direct PIGE signal for B with a proton beam scanned 0.1-0.3 MeV***




**Result is:**
**M:B:Si = 26:58:16**




***DataFurnace integrates RBS/PIXE/PIGE for self-consistent analysis***

# Discussion

- BS probes relatively shallow: PIXE probes deeper (no energy loss on exit path, PIGE probes deeper still (no absorption on exit)
- PIXE + BS gives sensitivity to all elements (except F, Na)
- PIXE + BS is now interpretable even for complex samples
- Roughness can be partially modelled, correct algorithm available. When correct algorithm is implemented ***any*** sample will be solvable
- PIXE is useful to relieve ambiguity in broad beam RBS/EBS
- RBS/EBS is useful to relieve ambiguity in μbeam PIXE
- Evaluated cross-sections available on SigmaCalc for EBS/PIXE
- *NB: low backscattering count rates in μbeam does* ***not*** *preclude good analysis*