Nuclear microprobe facility at iThemba LABS in multidisciplinary applications – key elements of a success story

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Background:

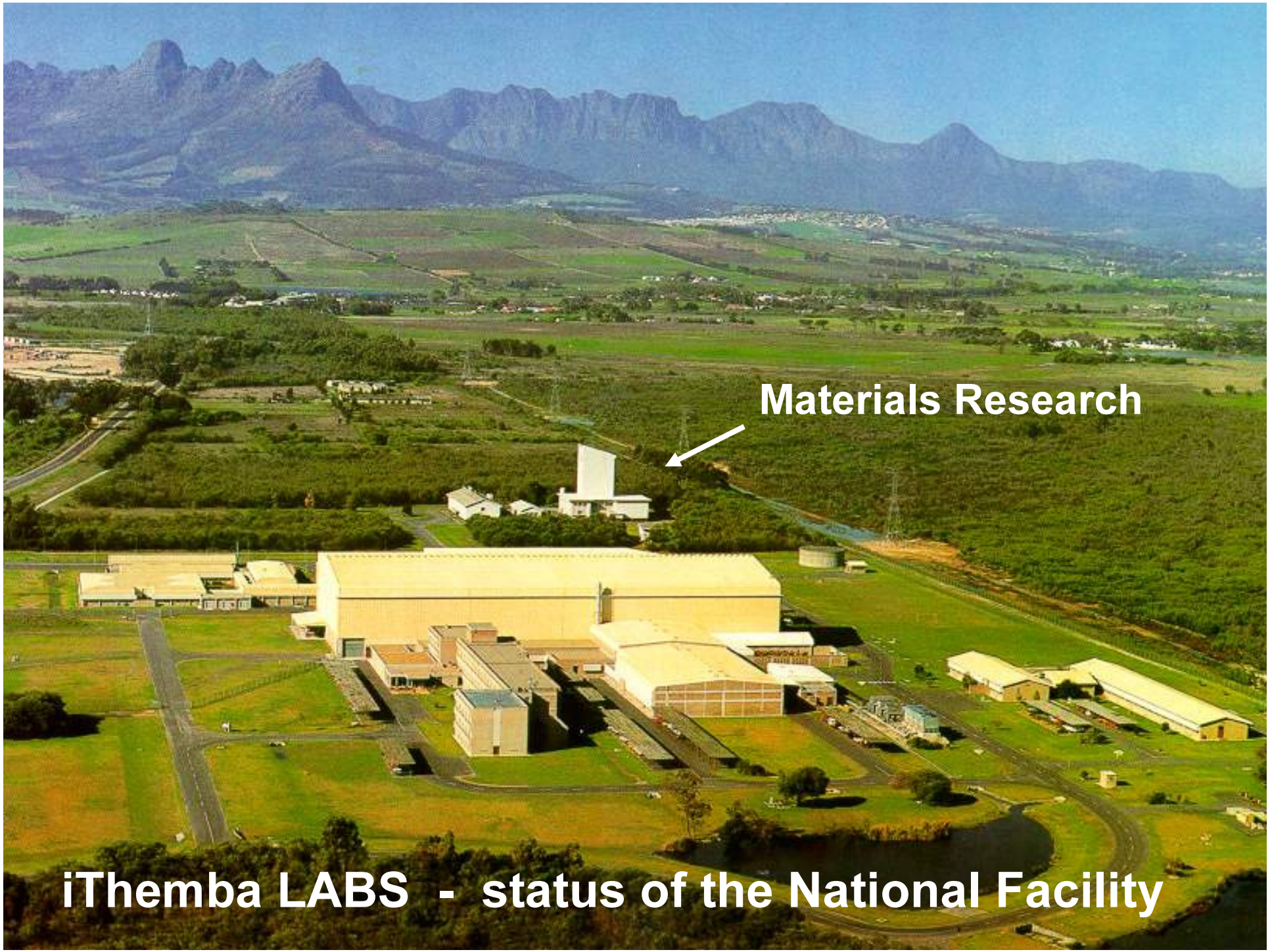
(from IAEA technical meeting, Cape Town, 7-10 November 2005)

"Accelerator-based physics has grown from its roots in nuclear physics research into a mature broad ranging science and technology serving social and economic development

Innovations in accelerator technologies, techniques, and nuclear instrumentation are continuing to enable successful solutions to many challenging problems,

both in the traditional application areas of engineering and physical sciences and increasingly, in the areas of environmental and life sciences."

This is well reflected in usage of our van de Graaff accelerator at Materials Research Department of iThemba LABS



iThemba LABS - status of the National Facility

Basic requirements to reach disciplines other than physics and to make accelerator-based techniques competitive:

Reliable accelerator operation

-Operators (maintenance + standby availability)

-Long-term stability, small terminal voltage ripple

Proper equipment

-Permanent setup (electronic modules, measurement geometry)

-Data acquisition suitable for the needs (flexible but easy to use)

-Best available software for data processing

Dedicated, experienced scientist(s) (analysts)

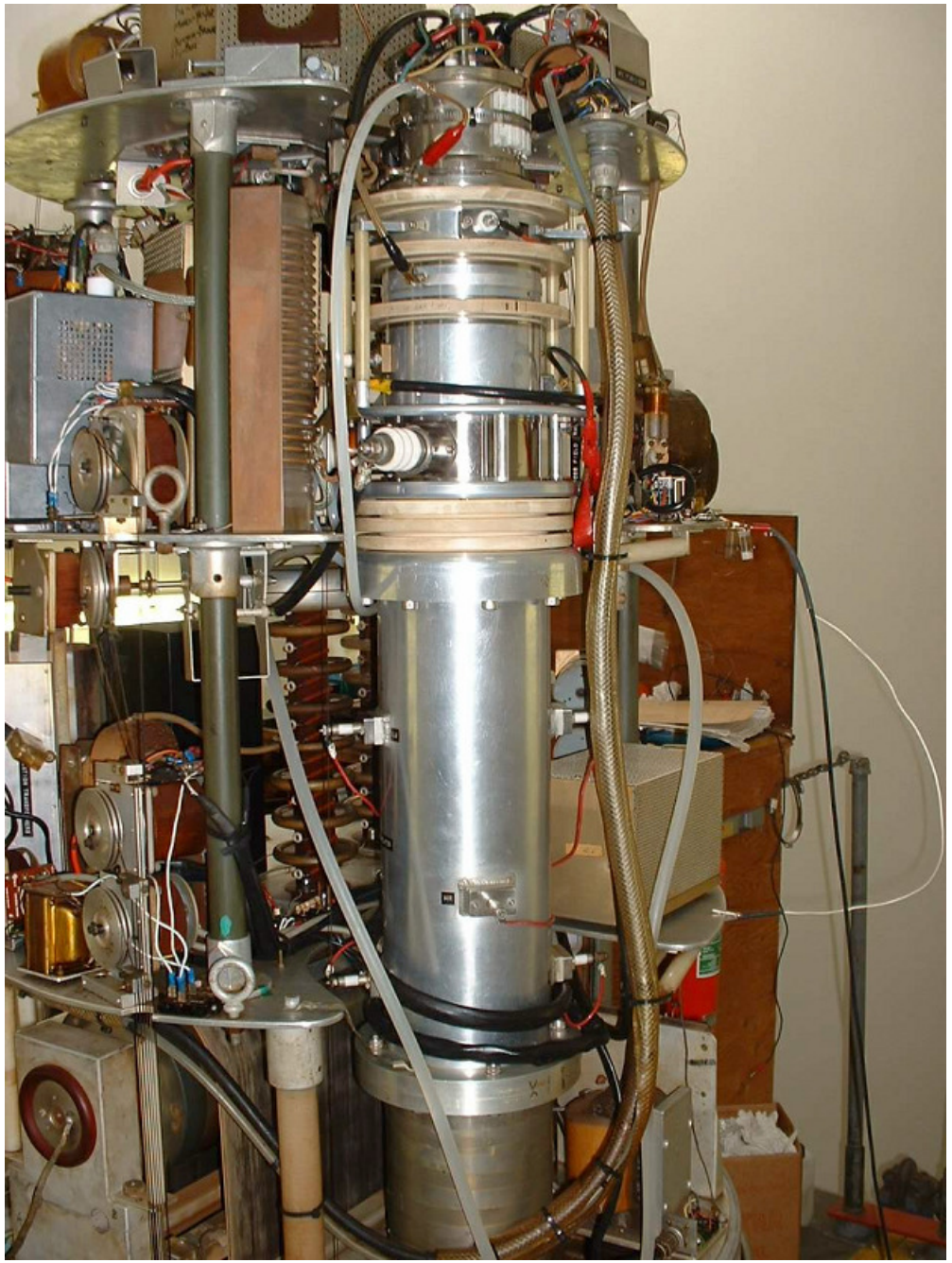
Auxiliary equipment available on-site

Cryo-preparation laboratory and expertise in specimen preparation

6 MV CN Van de Graaff Accelerator

- Manufactured by High Voltage Engineering – USA.
- Installed in 1963
- Vertical machine, Voltage range: 0.6 to 6 MV
- Tank 18 ton. Pressure: 16 Bar, Gas: N_2=80% and CO_2=20%
- Gas compressor, dryer and storage tank.
- Opening cycle 27 hours
- Current: DC 20 uA max. 1.5 nS, Pulsed @ 2 MHz 5 uA
- Drive motor 10 kW 60 Hz 1700 RPM, Belt speed 60 km/h
- Terminal generator 115 V 400 Hz 2 kW max
- Column/accelerating tube: 2 tubes with 132 insulated rings in total, with a resistor chain of 10^{11} ohm

The high-voltage terminal of the accelerator with the dome removed



Development of the Van de Graaff accelerator and beam lines

Courtesy: L. Conradie, Accelerator Department, iThemba LABS

Replacement of the 30 year old resistor chain

Replace the top section of the acceleration tube

Installation of 8 new steerer magnets

Installation of 8 new Faraday cups along the beam lines

Installation of improved energy stabilization slit system

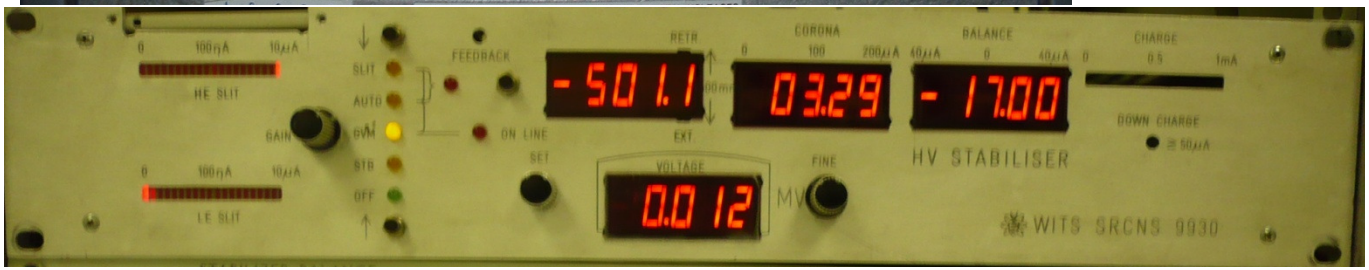
Increase the apertures of the existing quadrupole magnets

Installation of a complete vacuum control system

Installation of a computer controlled safety interlocking system for the protection of staff and equipment

Computer control system for all the power supplies and slits of the beam lines

Van de Graaff terminal-voltage stabilizing unit

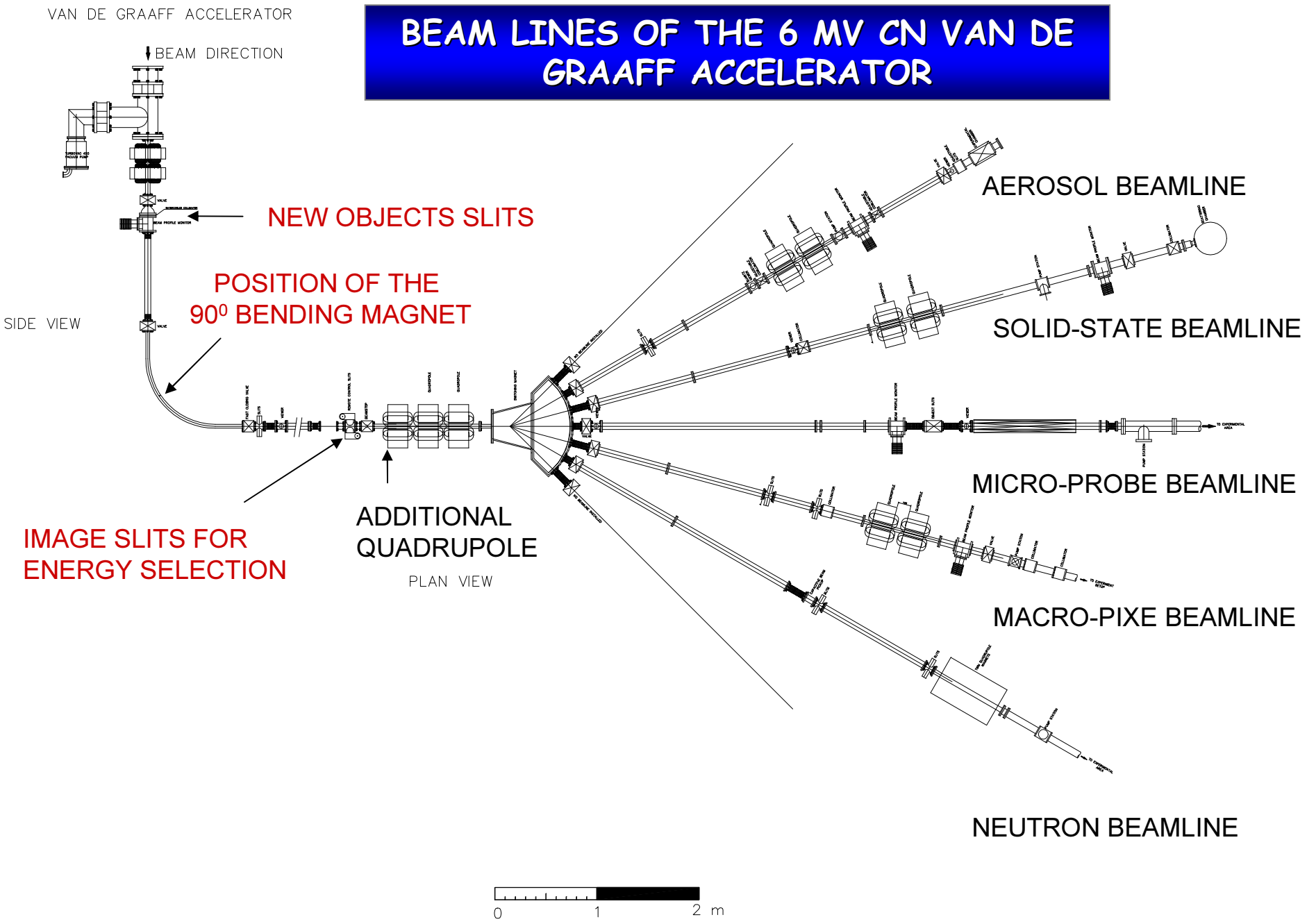


The newest Terminal Potential Stabilizer - NEC TPS 6.0

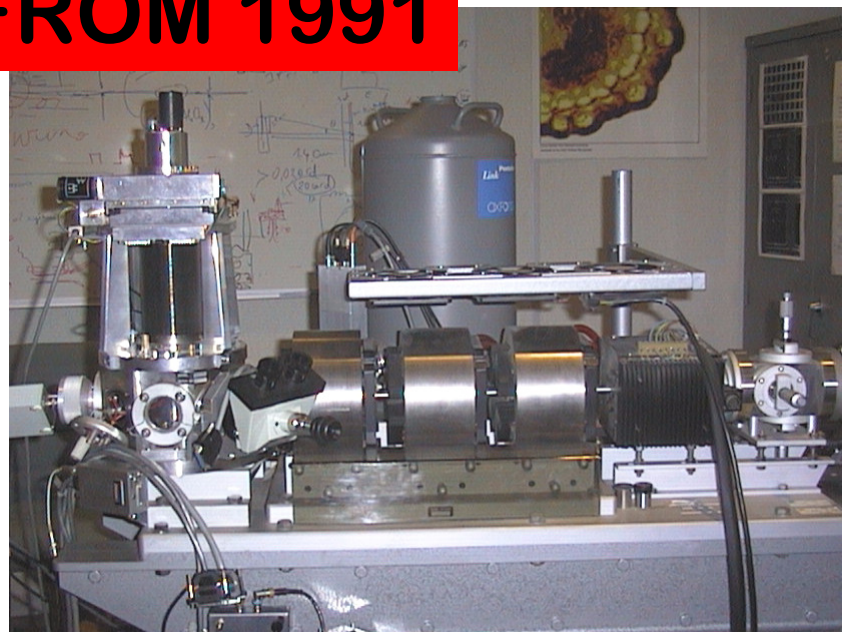
Beam ripple now ~ 900 V at 3 MV

Was ~ 1400 V

BEAM LINES OF THE 6 MV CN VAN DE GRAAFF ACCELERATOR



FROM 1991



Features:

•OM150 Triplet and scanning system
(Oxford Microbeams) Best beam spot at 100 pA
X – 1.6 μm ; Y – 0.6 μm
Typical sizes used here X – 3 μm ; Y – 3 μm
•Chamber modified on-site with stepper motors for automated specimen movement;

• permanently mounted set of standards:
44 pure metals, 53 minerals, fused glasses

•On-demand beam deflection system
(loop time ca. 900 ns)

Inside the NMP chamber:

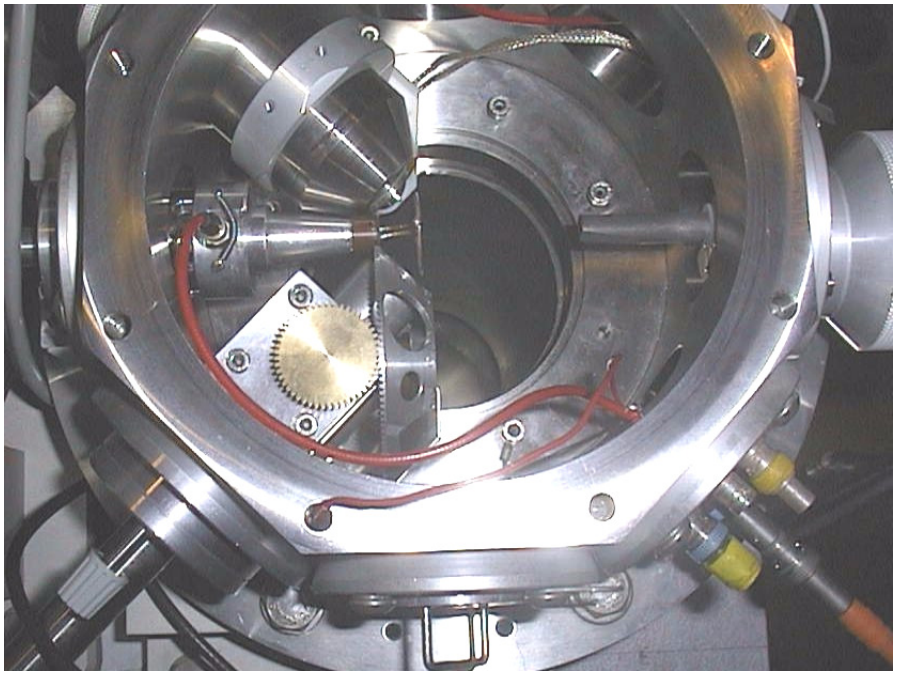
•Si(Li) detector 80 mm^2 and wheel with filters or HPGe detector 100 mm^2

•Annular Si surface –barrier detector for backscattering analysis (BS, RBS)

•Microscope (specimen viewed at 45^0)

•Faraday cup and PIN diode for on/off axis STIM

•Channeltron for Secondary Electron imaging



Beam size:

300 nm for 100 pA proton beam current
(best laboratories)
100 pA is considered as low current limit for analytical work
– PIXE, (R)BS, NRA, PIGE

100-200 nm for low current techniques (STIM, techniques based on single ion hits)

Our present performance:

2.6 μm x 3 μm for 100 pA protons (3 MeV)

1.2 μm x 2.3 μm for 100 pA alpha particles (2 MeV) short
2.6 μm x 2.2 μm for 100 pA long run (overnight)

Techniques utilizing focused beam:

Combination PIXE-RBS used most often;
results in complementary information

PIXE – very easy identification of elements Na – U down to ppm level,
but limited depth information

(R)BS - very good depth information;
identification of the layer thickness,
limited to major and minor elements;
identification of light elements (C, O, N);
best material: high Z layer on low Z substrate

ERDA - Hydrogen analyses in materials at lateral resolution down
to 30-50 micrometers

NRA - selective analysis of light elements and their isotopes
(e.g. B, Li, F), depth profiling;

PIGE - sensitive for F (down to tens of ppm); also B, Li

Data acquisition:
XSYS software on VAX station 4000/VLC acquiring data over ETHERNET LAN from VME/CAMAC front end

Processing of PIXE spectra and elemental mapping:

DEC 2300 Alpha Server running VMS and GEOPIXE-I software

True elemental images obtained ON-LINE using DYNAMIC ANALYSIS

OLD
List-mode files possible
but **SELDOM USED**
GEOPIXE-I software
on Alpha Server

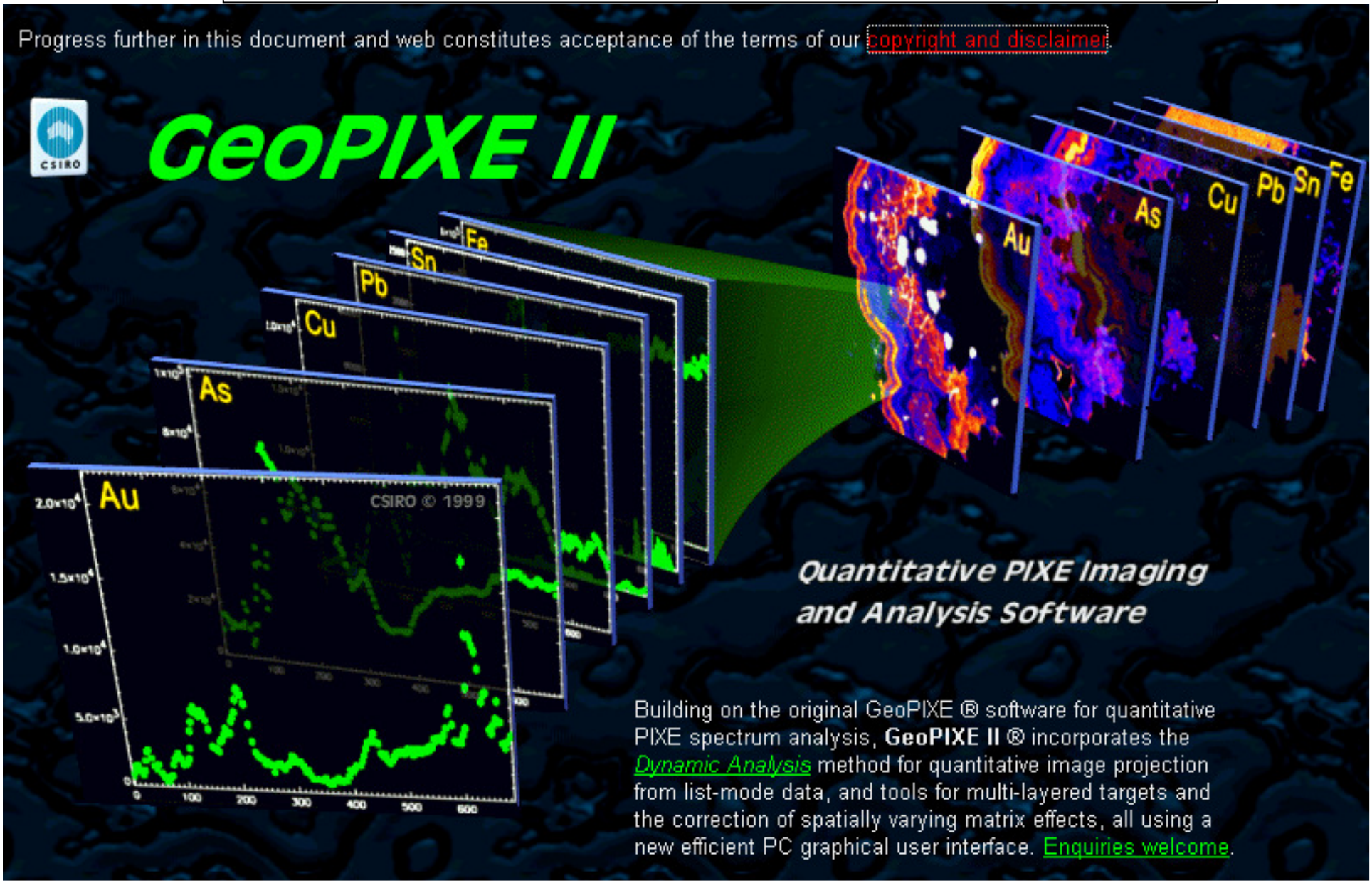
Quantitative maps from scanned areas

PRESENT

List-mode files **ALWAYS USED**
GEOPIXE-II software
on PC and laptop if needed
Quantitative maps with all new features
+ PIXE, BS, PIGE
extracted from selected areas

Processing of list-mode data

http://www.syd.dem.csiro.au/research/hydrothermal/chris/



Some features:

Data sorting from all detectors (not only PIXE but PIXE+BS+PIGE+…)

Spectrum fit generates Dynamic Analysis transform matrix

Projection of EVT data onto quantitative elemental images

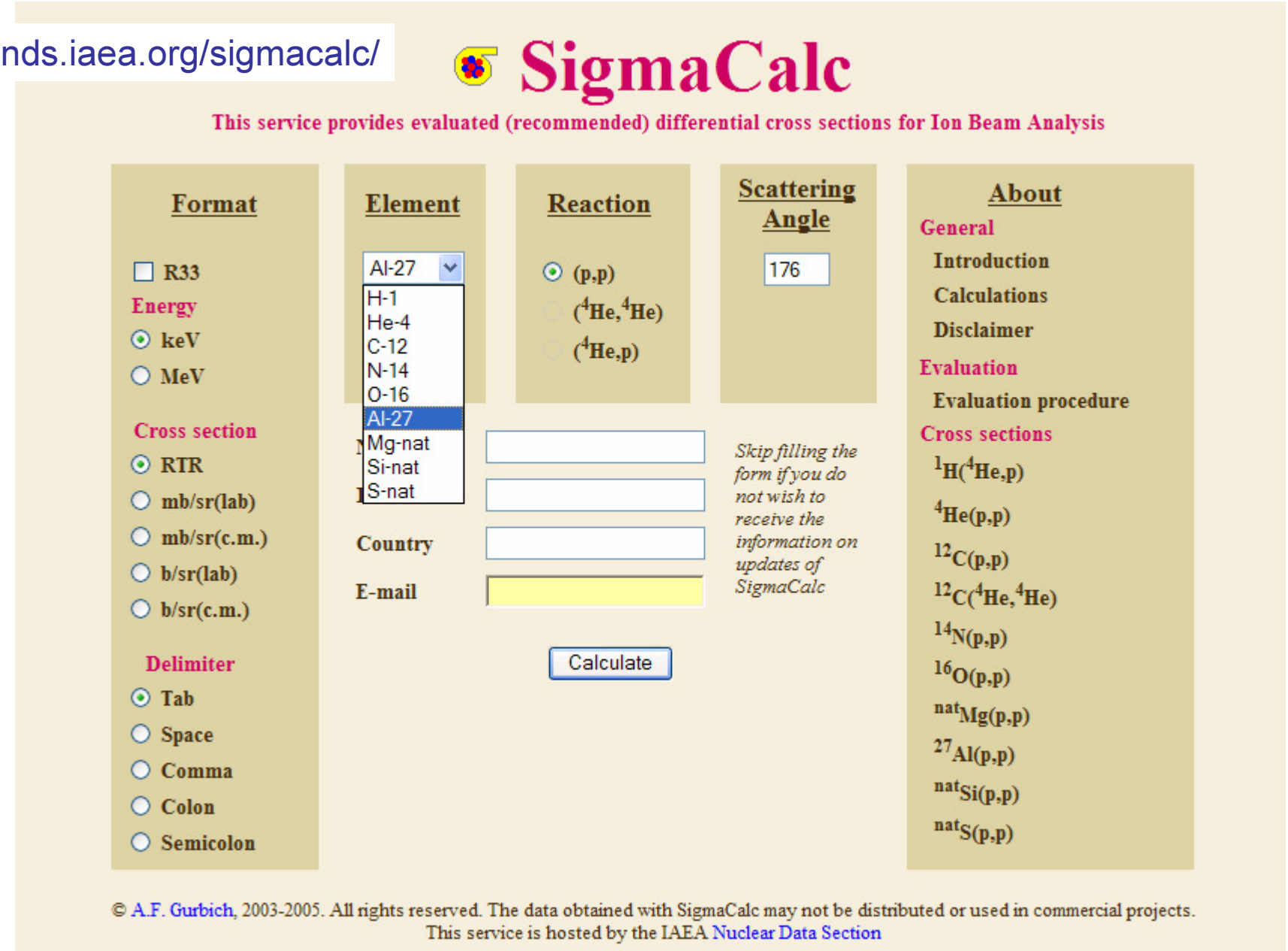
- **resolves element overlaps**
- **rejects artefacts from overlapping elements, detector response effects (escape peaks, tails)**
- **subtracts background**
- **groups of lines (K, L) used for construction of images**

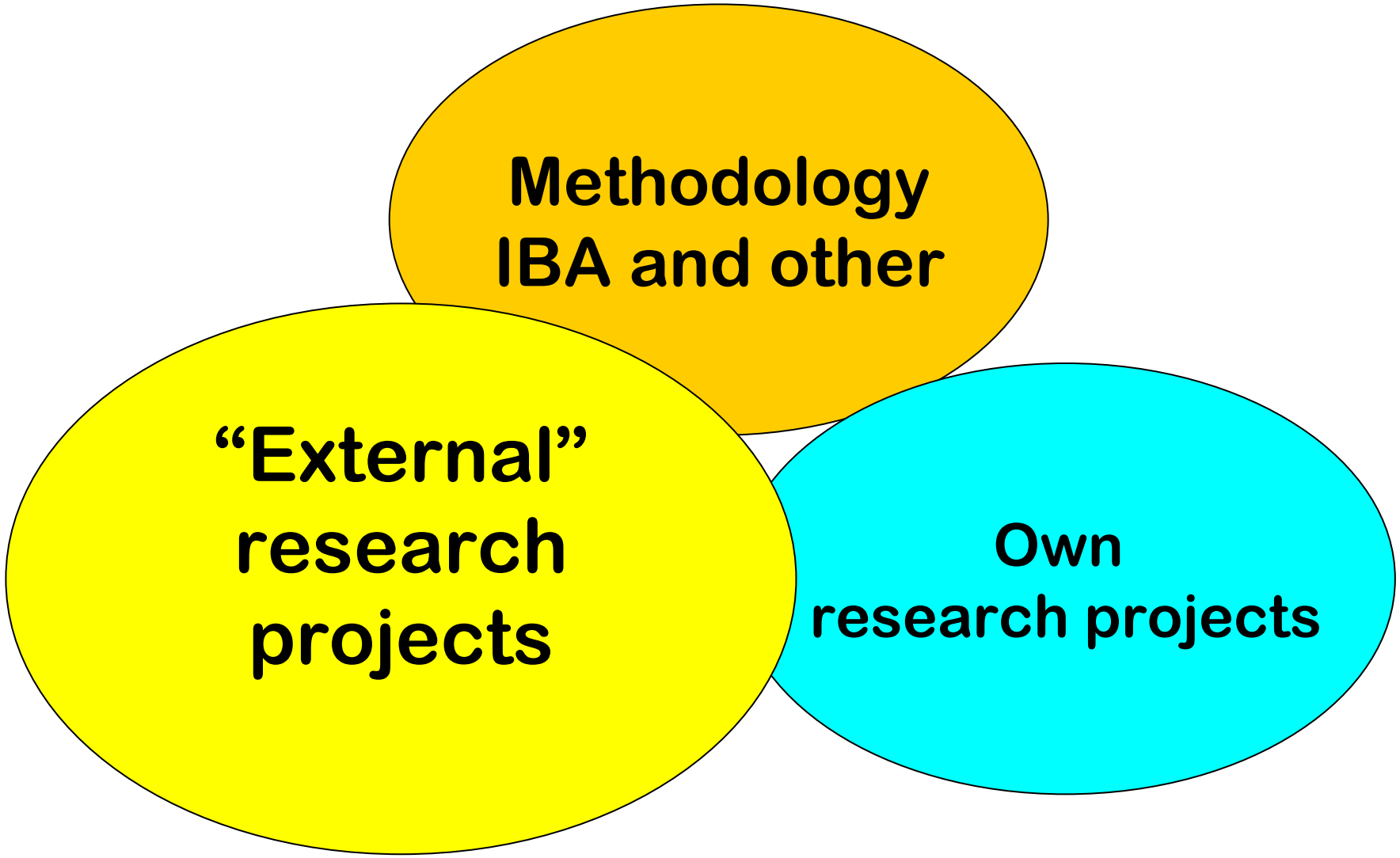
- **treatment of pileups:**
  - **using spectrum**
  - **using images (the only software with this option?)**

Extraction of concentration data from selected “regions”

(R)BS fitting: RUMP with cross-sections from SigmaCalc
We rely on this development!

//www-nds.iaea.org/sigmacalc/




Methodology
IBA and other
“External”
research
projects
Own
research projects

Accurate and precise elemental microanalysis is required

Analytical techniques
with NO spatial resolution

AES
AAS
AFS
ICP-AES
ICP-MS
XRF
TXRF
PIXE

A microanalytical technique

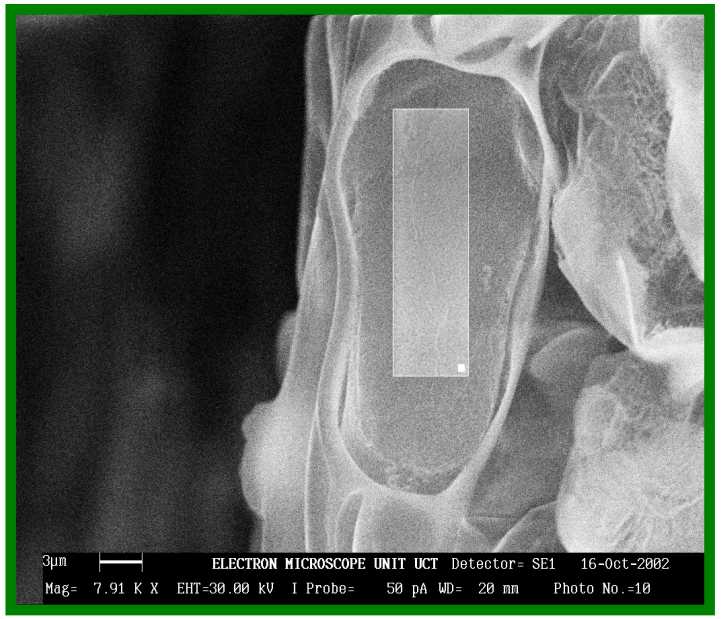
Micro-PIXE

Typically
Mass needed 1 mg or more

Electron microscopy
Morhological studies with excellent
spatial resolution

but

Sensitivities of EDS, WDS
not sufficient for studies
of elemental balances
of minor and trace elements



Main Microanalytical Techniques for Imaging – Quantification – Speciation of Chemical Elements in Cells

ELEMENTAL MICROANALYSIS	Analytical depth	Limit of detection	Spatial Resolution	Selectivity	Results	Biolgogical samples
Electron Microscope	0.1 to 1 µm 0.05 to 0.1 µm	EDS 100 to 1000 µg/g EELS, 100 to 1000 µg/g	0.1 to 1 µm 0.001 µm	Multielement Multielement, chemical species	Semi-Quantitative Semi-Quantitative	Dehydrated Hydrated, frozen Dehydrated (thin sections)
Nuclear Microprobe	**10 to 100 µm**	**1 to 10 µg/g**	**1 µm**	**Multielement**	**Quantitative (PIXE + RBS)**	Dehydrated **Hydrated, frozen**
Synchrotron Radiation Microprobe	> 100 µm	0.1 µg/g	0.1 to 1 µm	Multielement, chemical species	Semi-Quantitative	Dehydrated Hydrated, frozen
Secondary Ion Mass Spectrometry (SIMS)	0.1 µm	< 0.1 µg/g	0.05 µm	Multielement (isotopes)	Quantitative (Dynamic mode)	Dehydrated (thin sections)
Fluorescence Microscopy	Cell depth	0.01 µg/g	1 µm	Fluorophores (Na, Mg, Cl, K, Ca, Zn)	Quantitative	Living cells

Courtesy: R. Ortega (slide modified)

Facility available free of charge:

This big advantage can be lost if no true interest in collaboration exists on both sides

How to make interdisciplinary research productive:

- Try to identify needs

Research seminars at users' work place
Pilot experiments
Earlier results and publications

-Project proposals and initial discussions

-Collaborators from other disciplines present and active during measurements; co-supervision of students

-Very strong emphasis on data evaluation and reporting
(do not leave your collaborators with the results, be involved in the discussions, conference presentations, publications)

Applications

(1) Characterisation of materials

thin films, surface coatings etc.

materials crucial for SA research and industry

e.g. related to catalytic converters,

water purification,

Solar cells, superconducting microelectronics

Characterisation of nanomaterials at “micro-scale”

(2) Geology and Ore Processing

Elemental mapping capabilities remain an advantage

Micro-PIXE and LA-ICP-MS

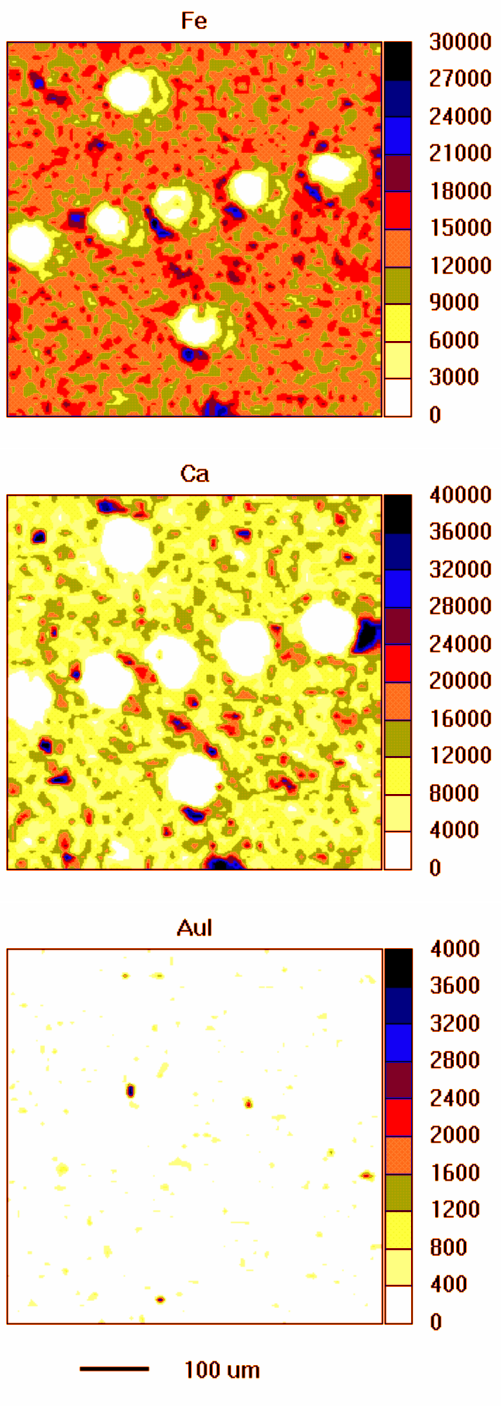
G. Stevens, W. Przybylowicz, L. Martin

X-ray Spectrometry 2004, 33: 216-221.

Studies of gold transport in granitoid and silica-undersaturated magmas

Initial analyses of the samples using LA-ICP-MS indicated that gold was dissolved within all of the glasses analysed. However, due to the destructive cratering of the technique (figure), the gold content is either diluted (by silicate and oxide presence) or concentrated (where gold crystals are incorporated).

The true required Au content is that within the melt alone.



One example when true elemental mapping is crucial

Electrochemical accumulation of visible gold on pyrite and arsenopyrite surfaces

P. Möller and G. Kersten, Mineral. Deposita 29, 404-413 (1994)

In galvanic cell arrangements gold is electrochemically deposited on semiconducting sulphide minerals (pyrite, arsenopyrite, chalcopyrite) from aerated as well as H_2S-saturated, gold-bearing 1M KCl solutions.

Observed cell potential differences (0.4 - 0.6 V) are comparable with known "self-potentials" of natural sulphide ore bodies.

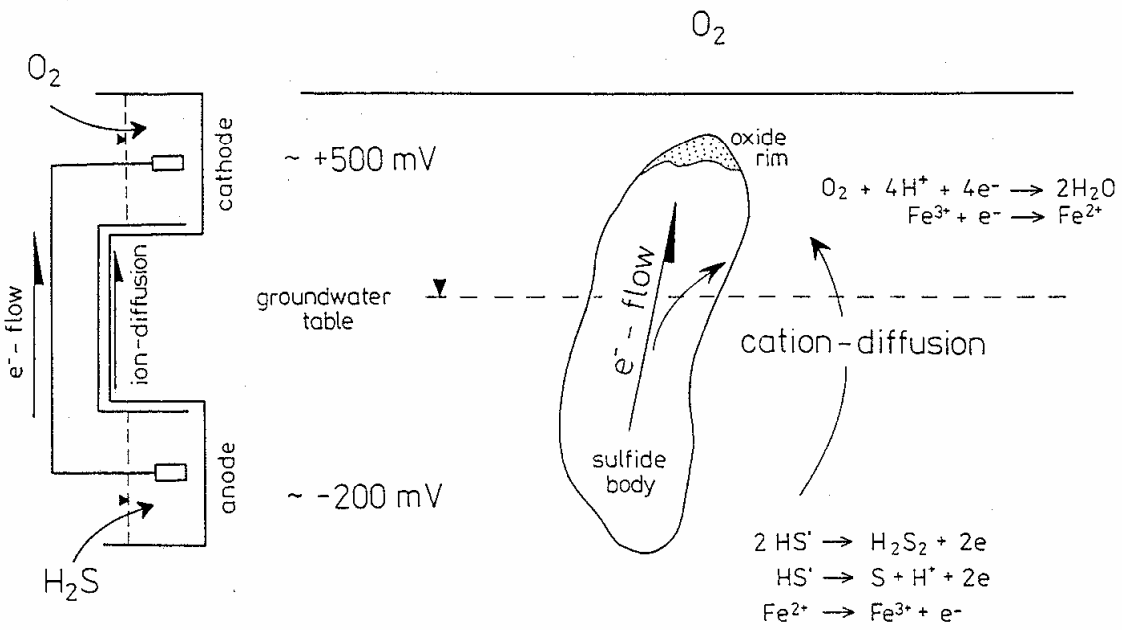


Fig. 9. Comparison of electrochemical reactions at a sulfide ore body and an experimental setup of a galvanic cell. Indicated chemical reactions might only be the most important ones in controlling the potential differences of about 700 mV

Gold preferentially accumulates on the cathode, i.e. under oxidizing conditions.

Galvanic cells simulate conditions occurring at surfaces of chemically inhomogeneous single crystals (zonated).

Sulphide minerals show either **n- or p- type conductivity**. **Visible gold** is accumulated on individual domains of sulphide surfaces that act as **cathodes, i.e. p-type conductors** in n-p junctions.

Arsenic is the most important element in establishing **p-type conductivity** of pyrite and arsenopyrite.

This explains why **As** is such a powerful pathfinder in gold exploration.

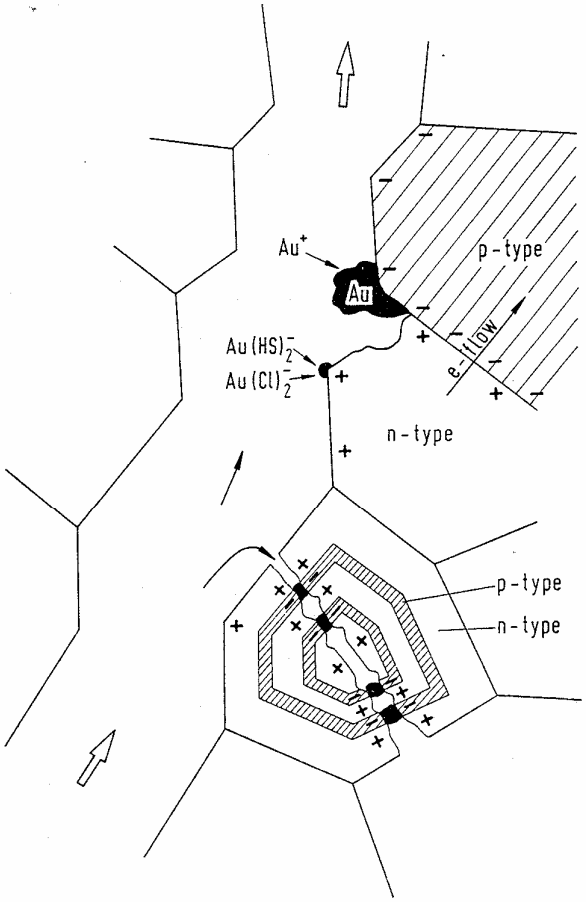
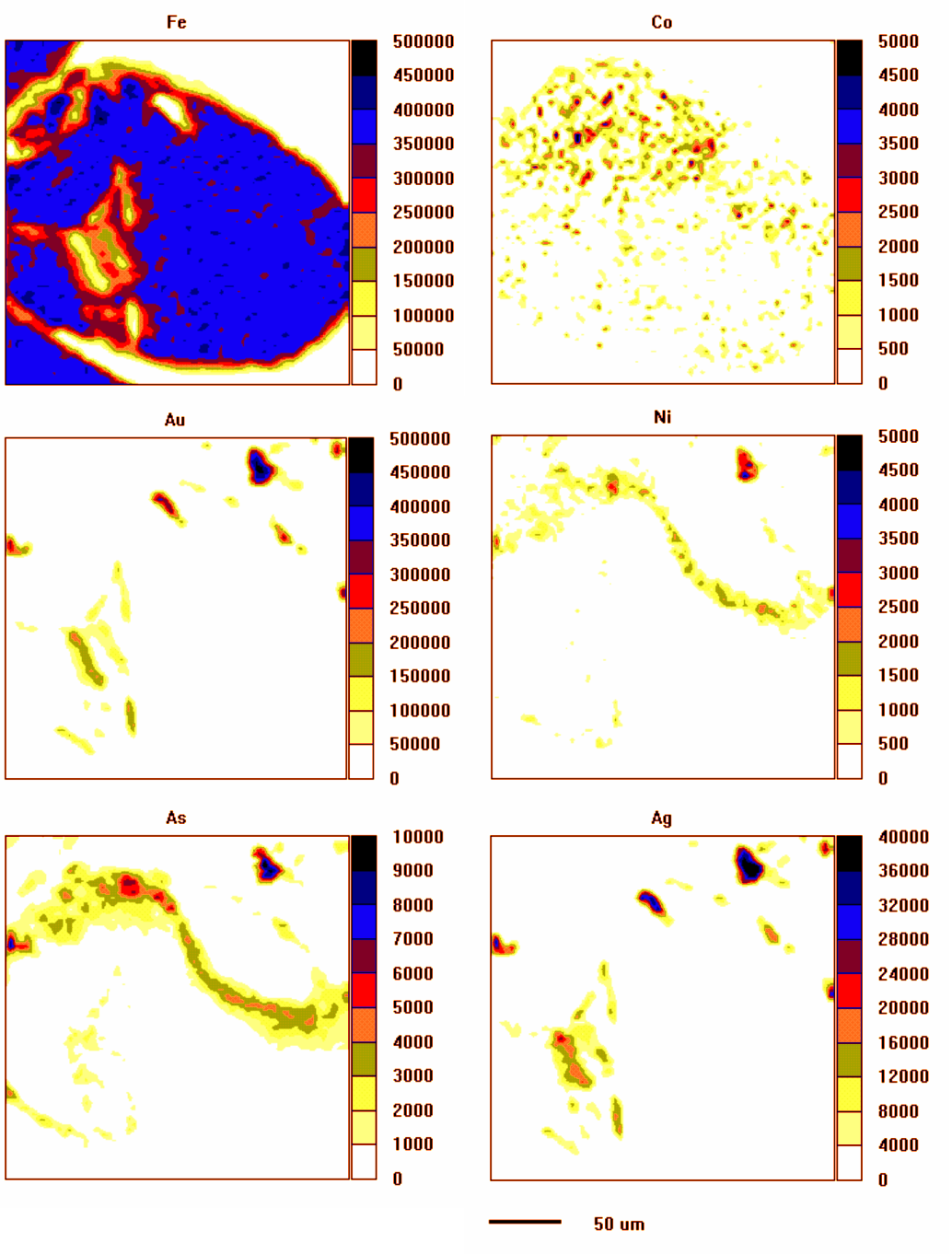


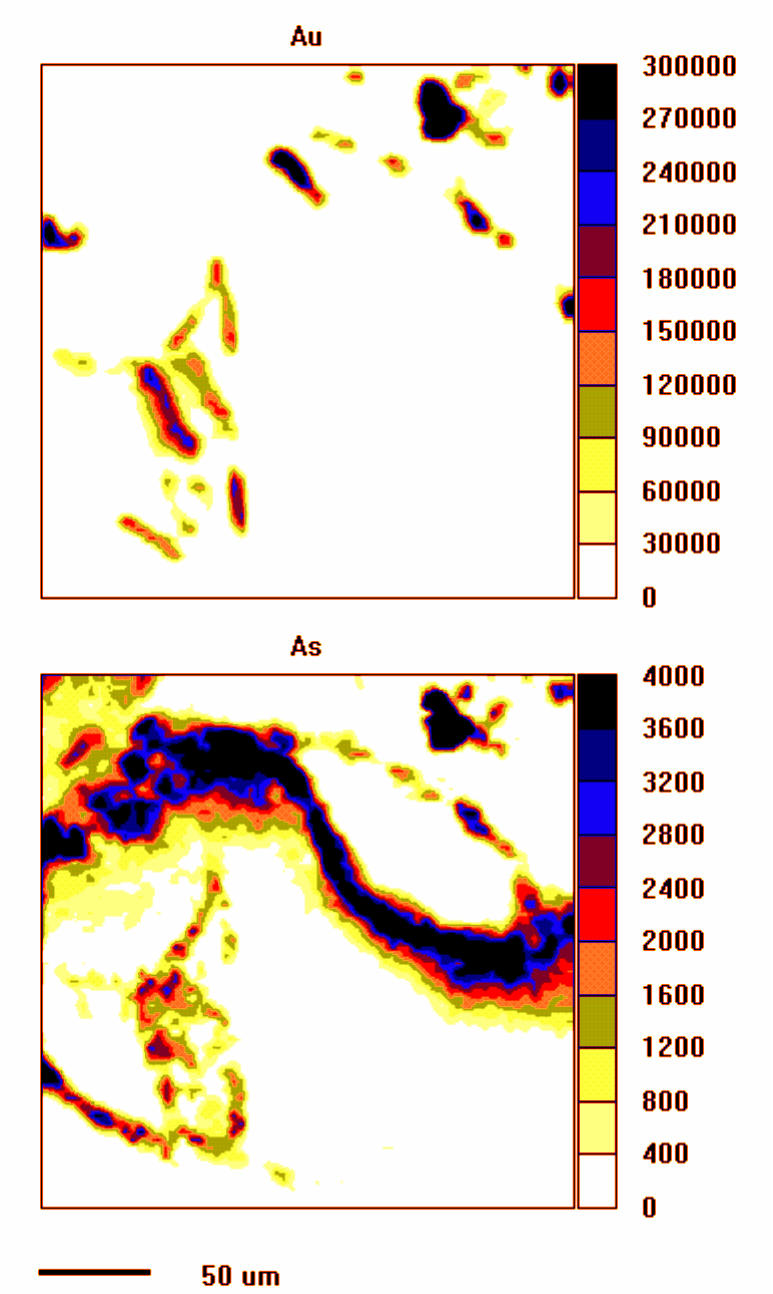
Fig. 10. Electrochemical reactions of a gold-bearing fluid moving along a pore made up of n-type and p-type sulfides as well as fractured n- and p-type zoned crystals.



True elemental maps.

Pyrite grain from the Steyn facies of the Basal Reef, Unisel Gold Mine in the Welkom Goldfield.

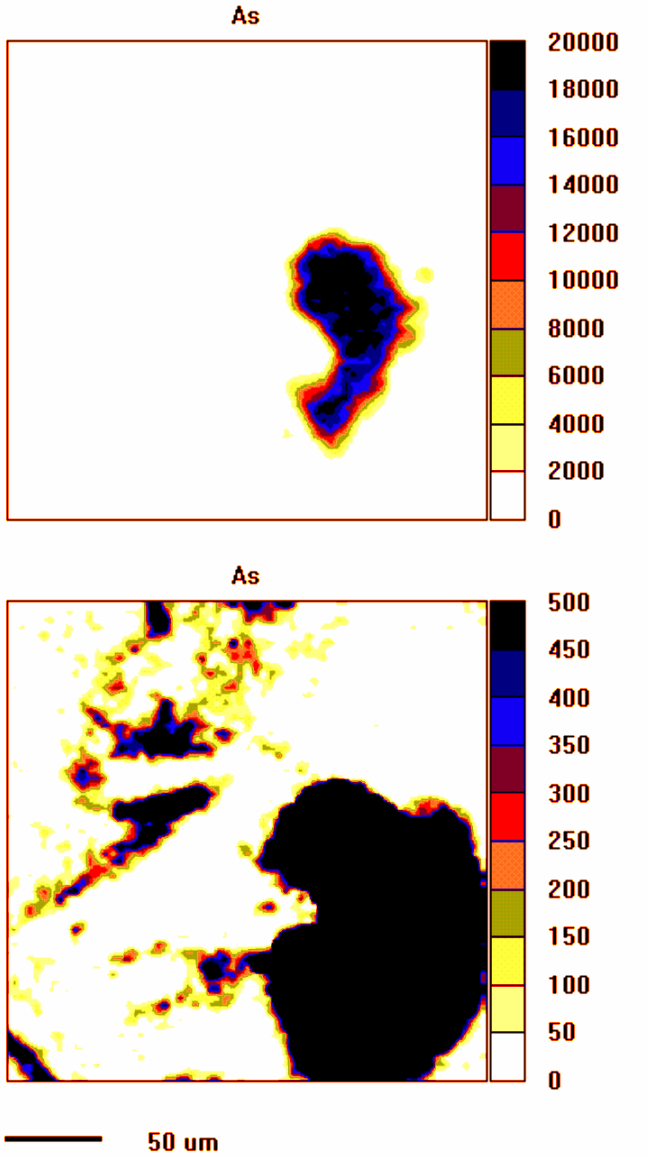
3 MeV protons, absorber 160 μm Al and 75 μm Kevlar window



True elemental maps.

Au - As relation.

Reduced scale of concentration.



True elemental maps of As zonation in two round, compact pyrite grains from Witwatersrand reef.

Additional details can be distinguished after reduction of the concentration scale from 20000 ppm to 500 ppm.

W.J. Przybylowicz et al. Nucl. Instr. and Meth. B104 (1995) 450-455.

(3) Biology and environment; medicine

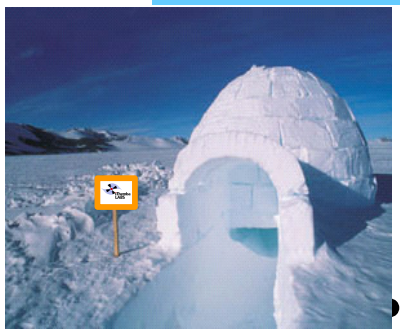
unique combination of techniques
related to specimen preparation and microanalysis
at ONE research centre

Active long-term research program and established collaborations

Where a nuclear microprobe can be applied?

- Elemental transport and accumulation
- Micro-nutrient uptake and their function in metabolism
- Studies on the function of trace elements
- Elemental deficiency and toxicity
- Environmental pollution

Equipment available in the iThemba cryo-laboratory



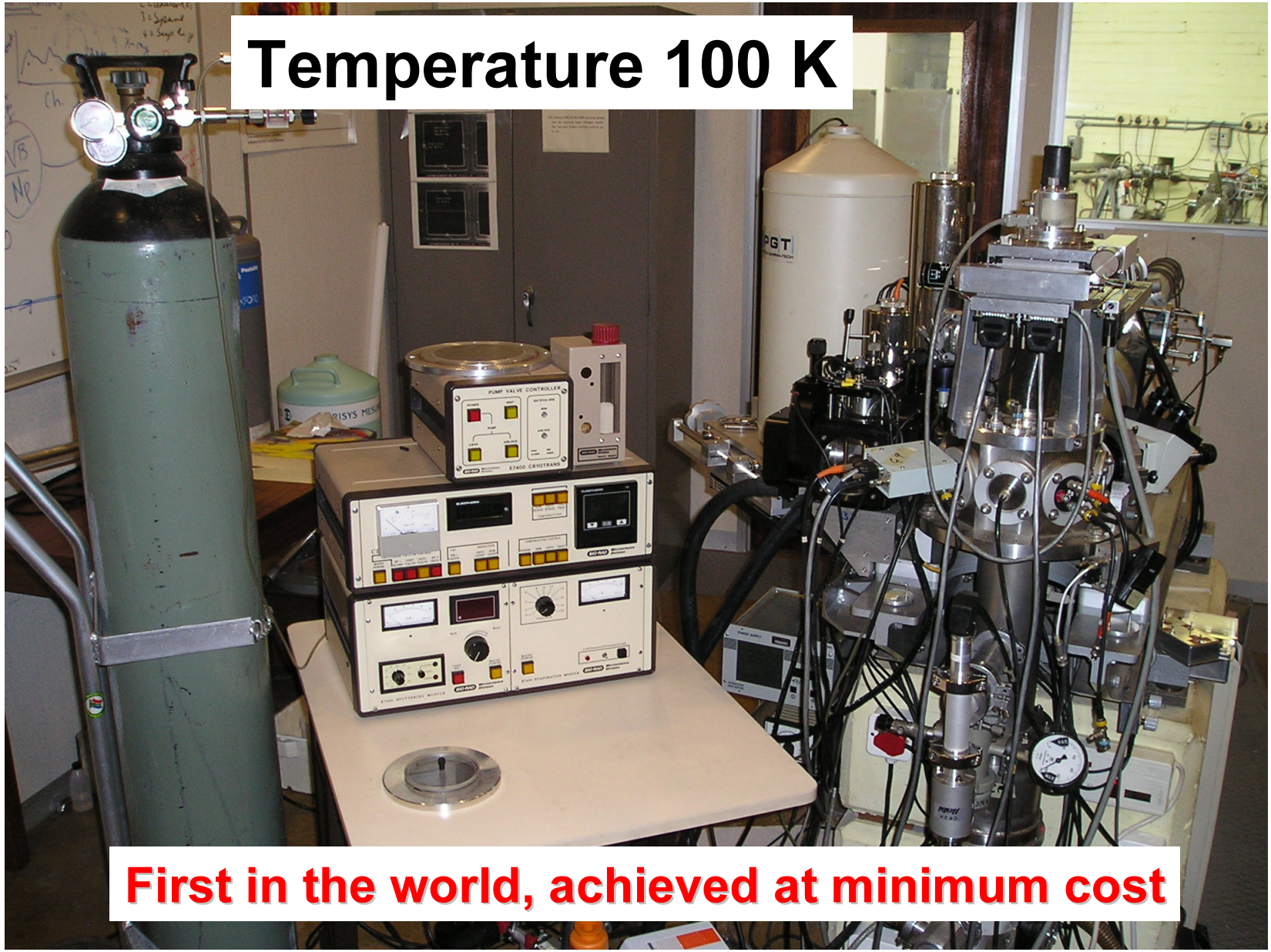
Cryo-fixation

- **HPF – High Pressure Freezer**
- Leica EM CPC-Cryoworkstation

Further cryo-preparation

- Leica EM CFD Cryosorption Freeze Dryer
- Leica EM AFS Automatic Freeze Substitution
- Cryo-ultramicrotome
- Dewars for long term storage

Present – with cryotransfer (frozen hydrated specimens)

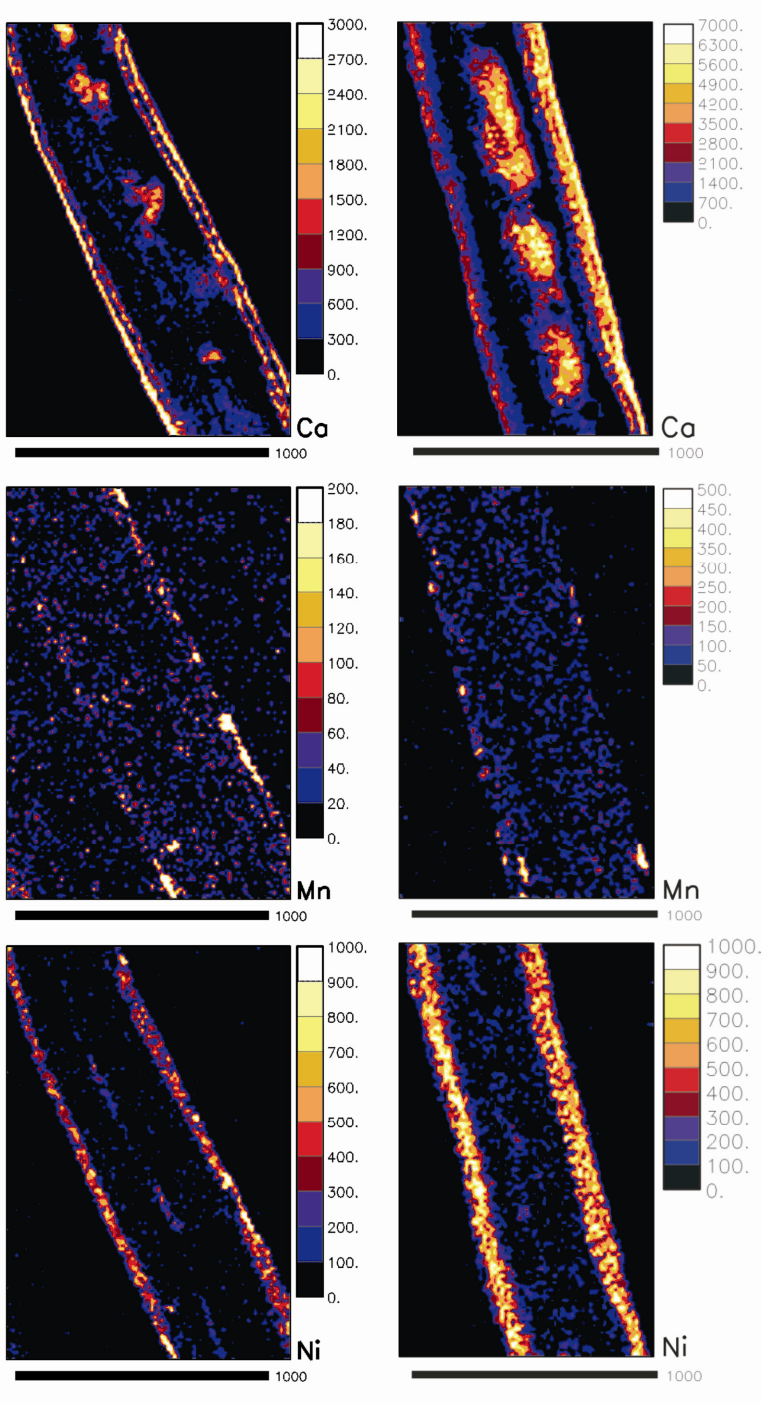


Comparison of distribution in frozen-hydrated and freeze-dried leaf cross-section

FH

FD

Senecio anomalochrous

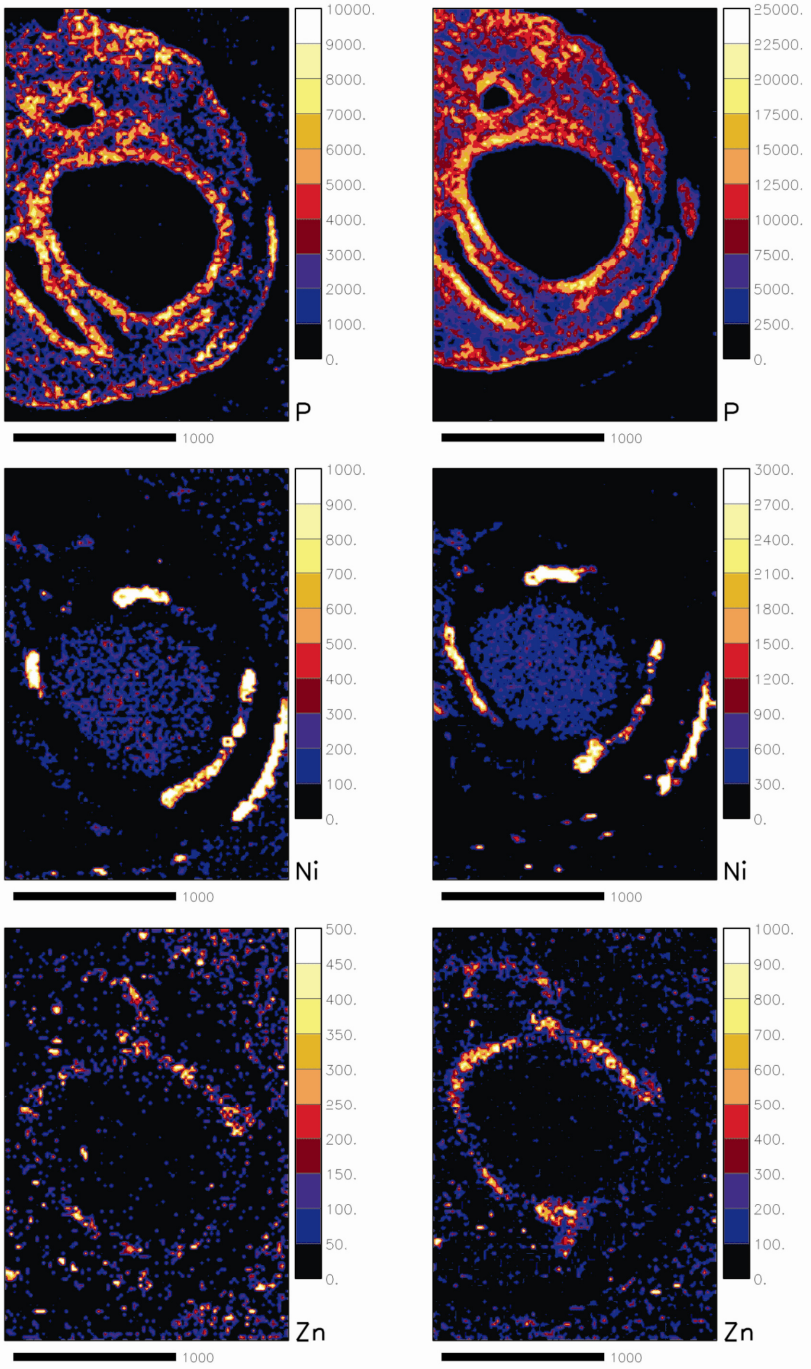


Tylko G. , Mesjasz-Przybyłowicz J., Przybyłowicz W.J.
Microsc. Res. Techn. (2007) 70: 55-68.

Chrysolina pardalina larvae

Comparison of distribution in frozen-hydrated and freeze-dried abdominal tissue

FH

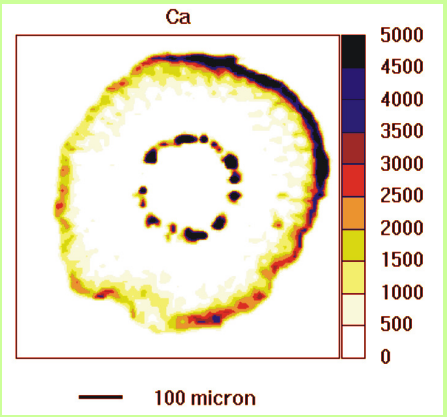


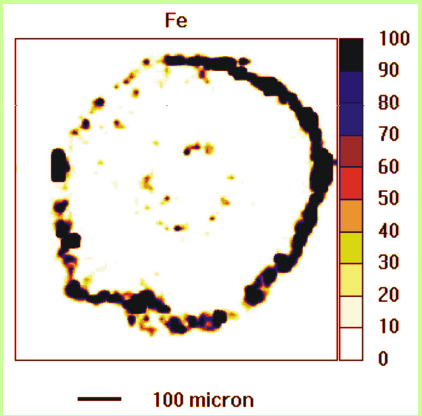
FD

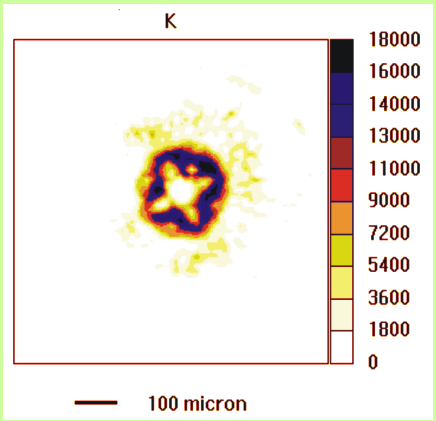
Tylko G. , Mesjasz-Przybyłowicz J., Przybyłowicz W.J.
Microsc. Res. Techn. (2007) 70: 55-68.

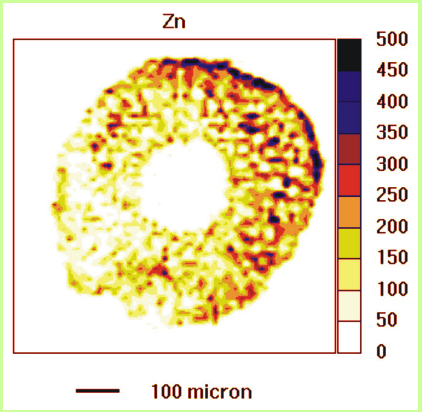
Studies of the mechanism of Zn uptake in

Phaseolus vulgaris







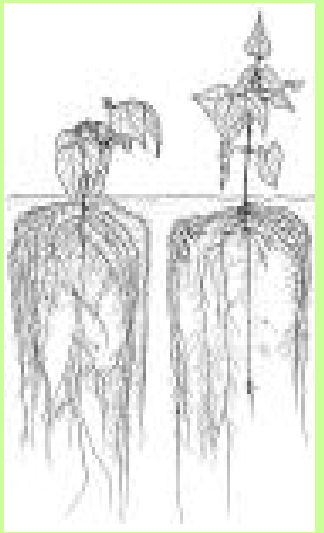


- Zinc is one of the essential micronutrients and an important component of a number of enzymes.

- The results clearly indicate **higher concentrations of zinc in the cortex**

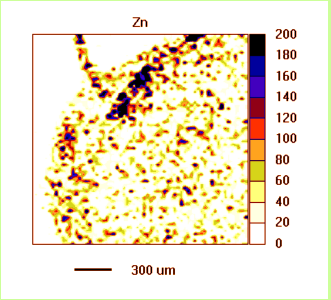
- **Zinc** is not transported to the xylem due to a **passive absorption mechanism**.

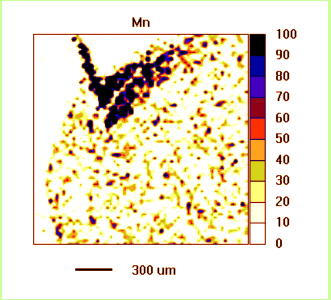
- In contrast, **potassium** was mainly located inside the endodermis which may be an evidence for an **active transport across the endodermis** into the conducting tissue of the xylem

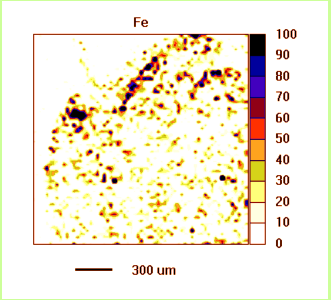


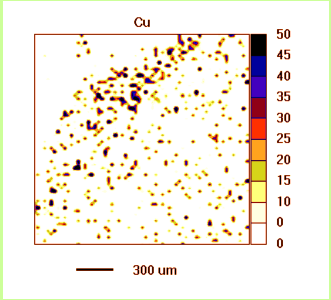
J. A. van As, J.H. Jooste, J. Mesjasz-Przybylowicz, W.J. Przybylowicz. Proc. 34th Conf. Electron Microsc. Soc. South Afr. 25 (1995) 34.

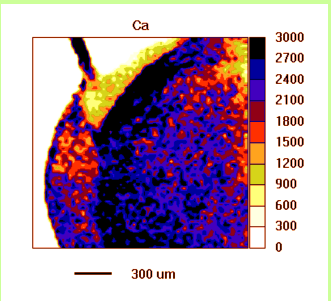
Studies of elemental distribution in seeds of *Biscutella laevigata* from zinc wastes in Olkusz, Poland

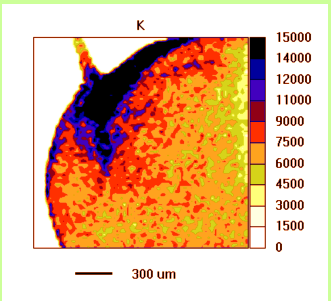


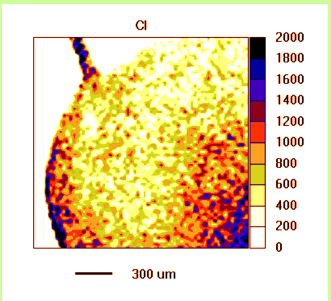


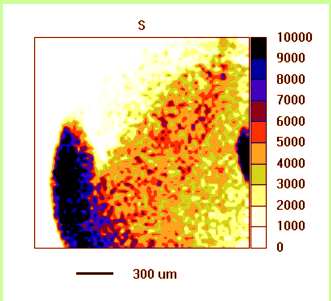








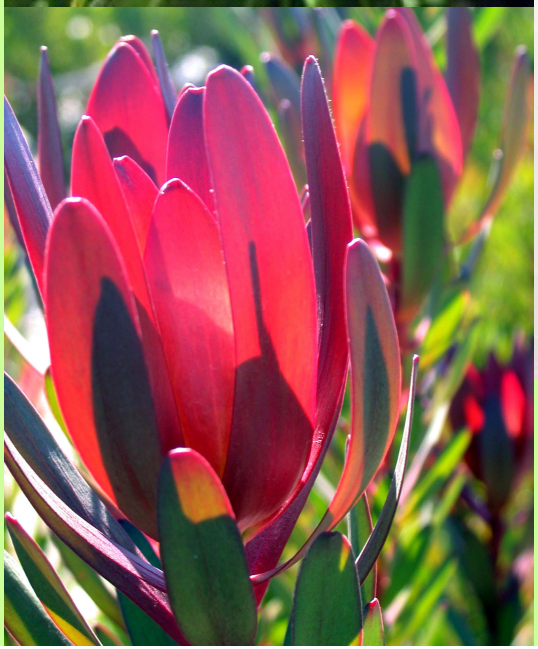


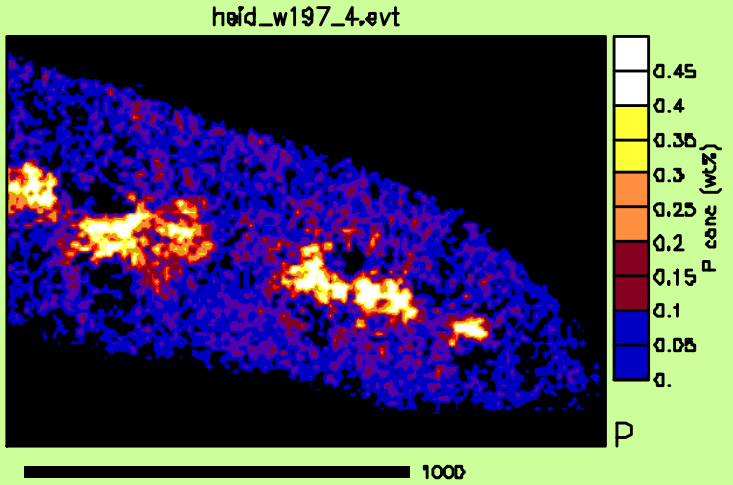


The endosperm works as a barrier actively controlling elemental uptake and preventing access of toxic amounts to embrionic parts. That could explain mechanism of adaptation to hostile environment.

J. Mesjasz-Przybylowicz, K. Grodzinska, W.J. Przybylowicz, B. Godzik, G. Szarek-Lukaszewska. Nucl. Instr. and Meth. B181 (2001) 634.

PROTEA FARMING
Phosphorus toxicity – a problem for Protea farming on previously agricultural land

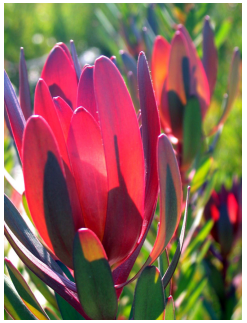




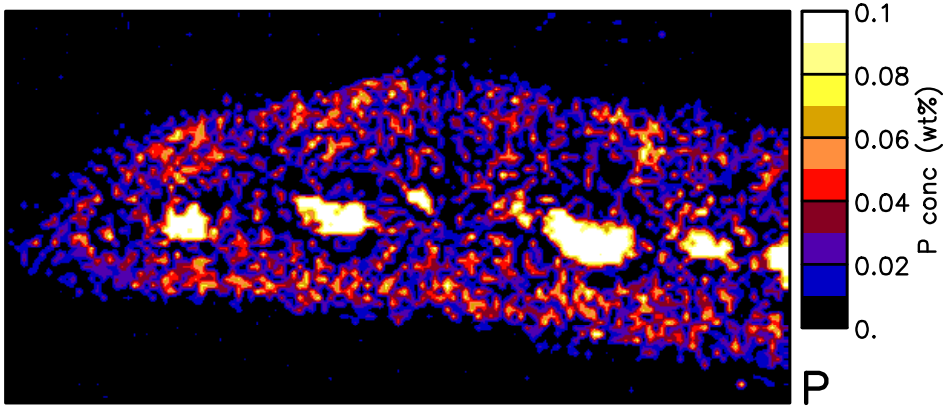
H.-J. Hawkins, H. Hettasch, L. Louw, C. O'Brian, J. Mesjasz-Przybylowicz, W. Przybylowicz, M.D. Cramer. Scientia Horticulturae, 117 (2008), 357-365.

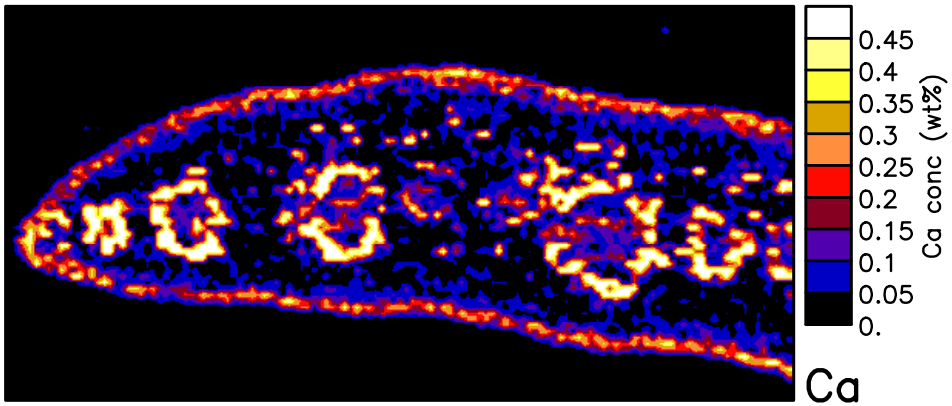
PROTEA FARMING

Phosphorus toxicity – a problem on previously agricultural land



Leucadendron
'Safari Sunset'





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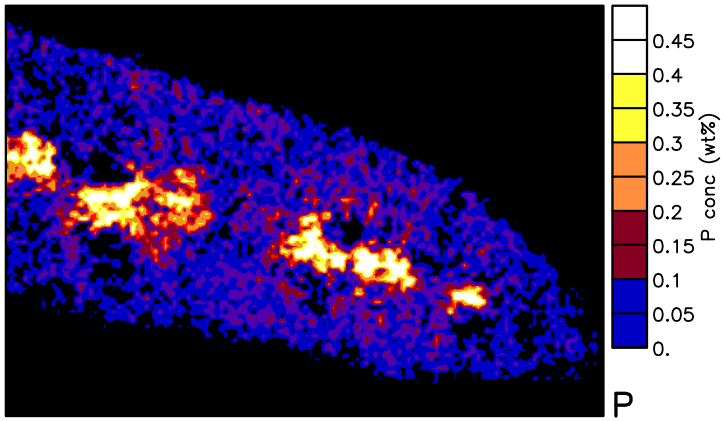

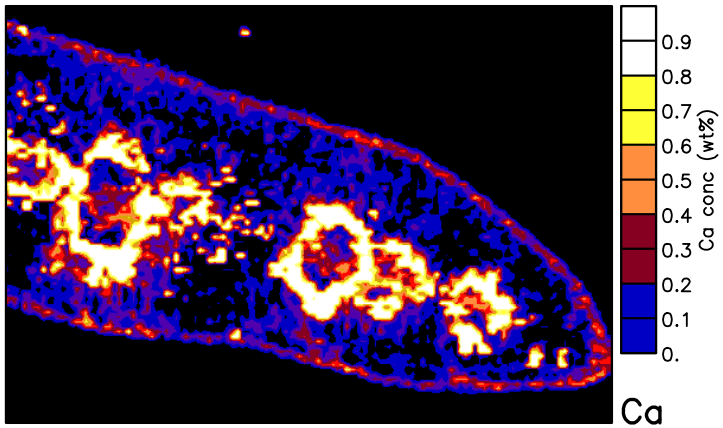

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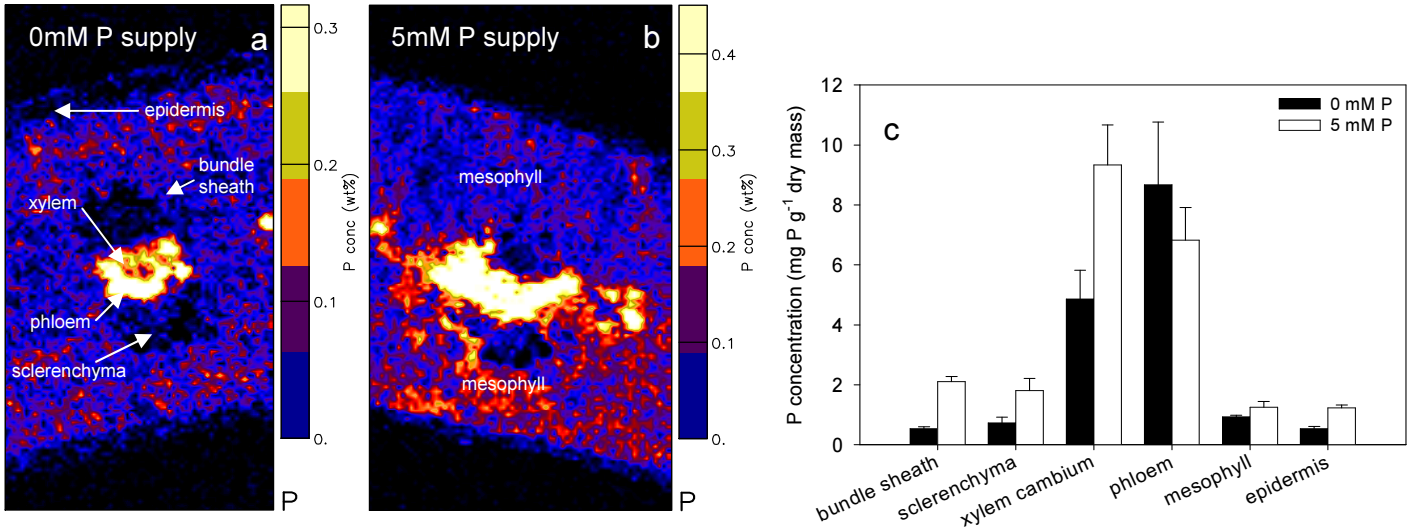
Phosphorus toxicity in Proteaceae plants: an association with non-exchangeable binding forms of calcium, iron and manganese in leaf tissues

H.-J. Hawkins[1], H. Hettasch[2], J. Mesjasz-Przybylowicz, W.J. Przybylowicz, M. D. Cramer[1]
[1]Department of Botany, University of Cape Town, [2]Arnelia Farms, Hopefield



Location of phosphorus in cross-sections of *Leucadendron* 'Safari Sunset' leaves supplied with no phosphorus (a), high phosphorus (b); and phosphorus concentrations in various leaf tissue types (c).

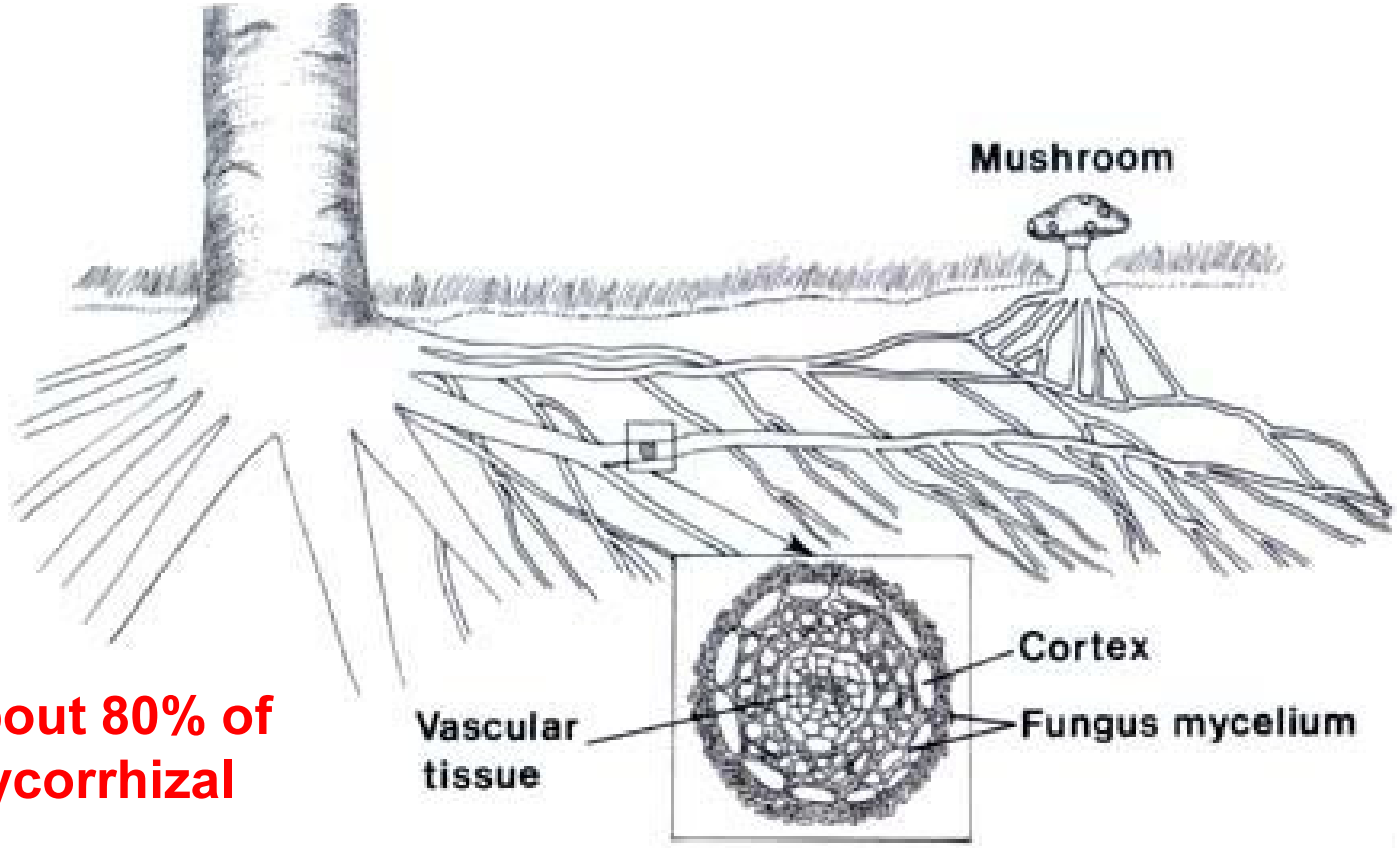
MYCORRHIZA

From Greek:

Myco – “fungus” and rhiza – “root”

symbiosis between plant roots and fungi;

modifies the interaction between plants and soil



The roots of about 80% of plants are mycorrhizal

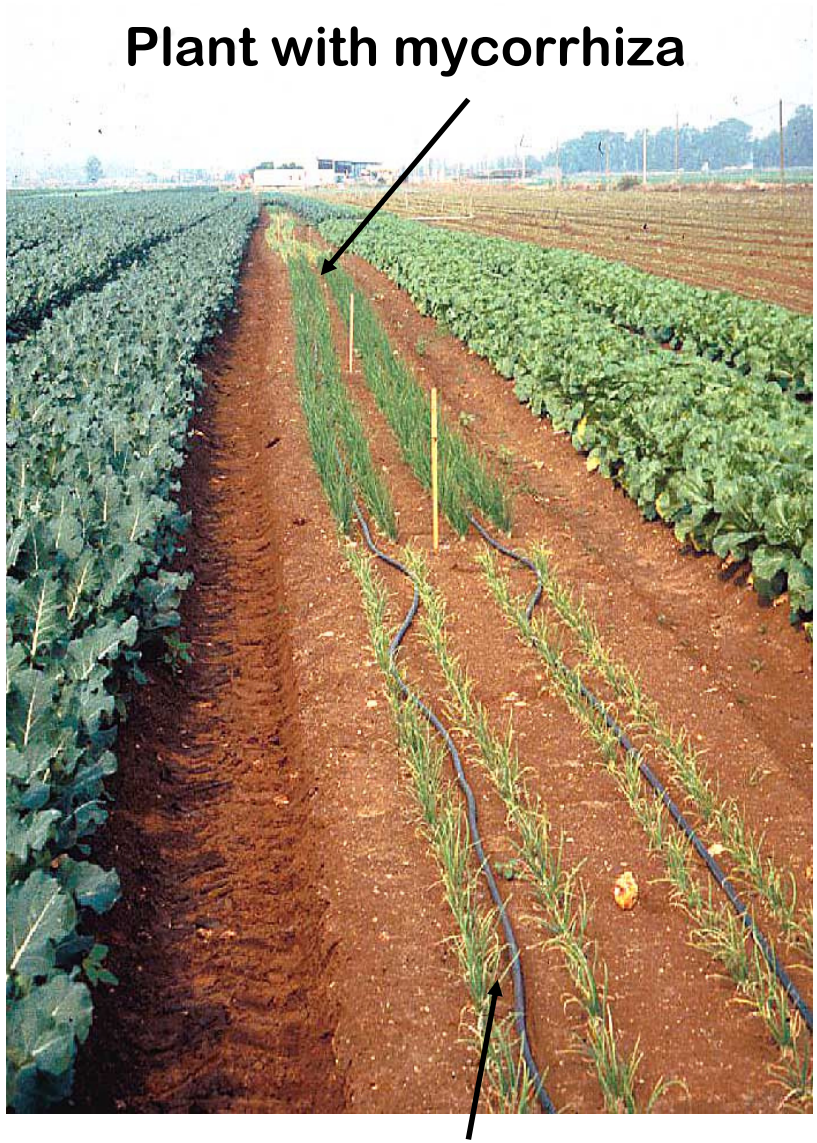
Specific ways in which mycorrhiza assists plants:

- ❑ Improves Storage of Carbohydrates
- ❑ Improves Mineral Nutrition
- ❑ Improves Water Transport
- ❑ Can interconnect different host plants
- ❑ Assists in heavy metal tolerance

Knowledge of elemental concentrations and distribution is essential in studying these processes

Mycorrhiza is important in agriculture, forestry, studies of environmental pollution

Mycorrhiza is popular



Maize – always with mycorrhiza

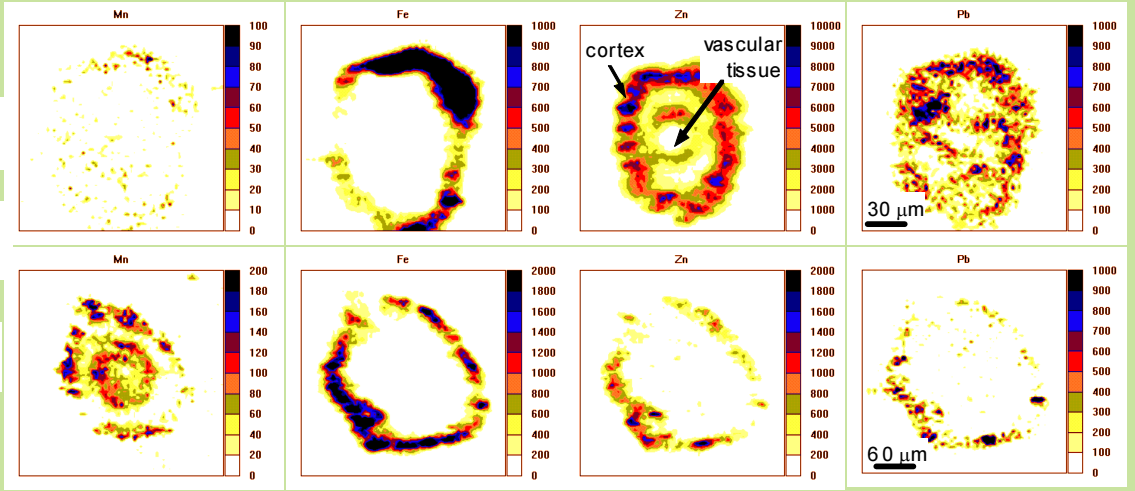
Mycorrhizal and nonmycorrhizal *Plantago lanceolata* L.

six weeks, greenhouse conditions, rhizo-boxes with industrial waste

mycorrhizal

Quantitative maps of roots

Non-mycorrhizal



different filtering mechanisms of Zn/Pb and Fe/Mn, both enable plants to cope with metals present in the environment.

W.J. Przybylowicz, J. Mesjasz-Przybylowicz, P. Migula, M. Nakonieczny, M. Augustyniak, M. Tarnawska, K. Turnau, P. Ryszka, E. Orlowska, S. Zubek, E. Glowacka. X-ray Spectrometry 2005, 34, 285.

Hyperaccumulation in plants

Certain species accumulate metals to concentrations several orders of magnitude higher than those found in other species on the same site

(above toxicity level for most plants)

Elements reported to be hyperaccumuated:

Al, As, Cd, Co, Cu, Mn, Ni, Pb, Se, Zn

Shoots show metal enrichment in comparison with roots (usually the opposite)

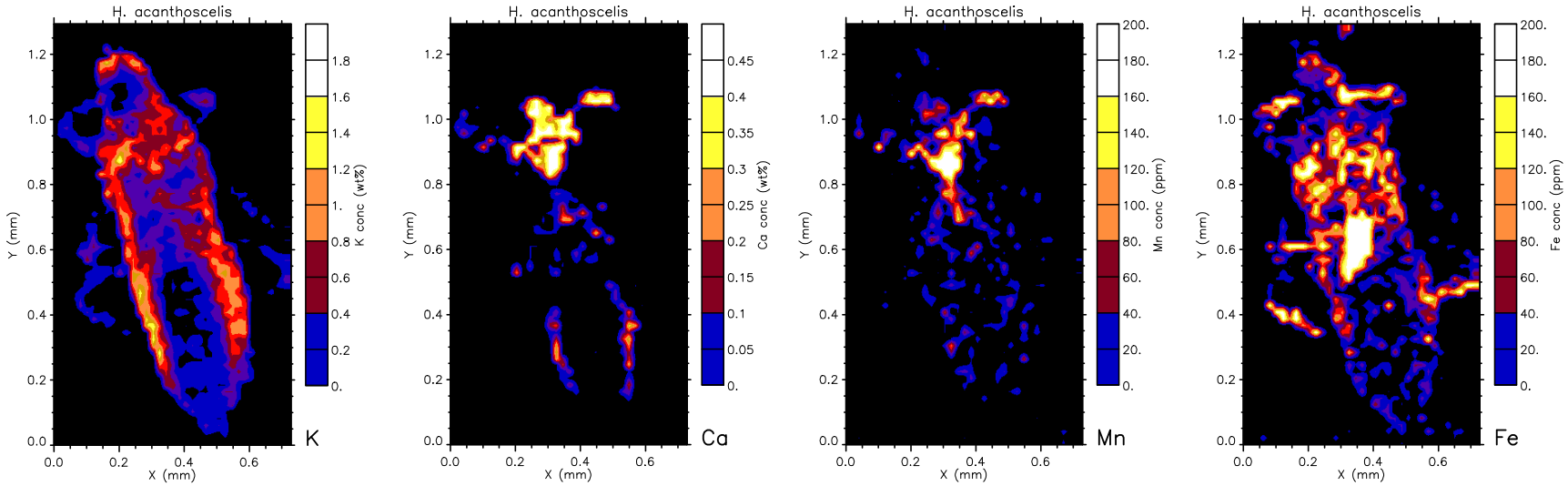
Plant-insect herbivore interaction

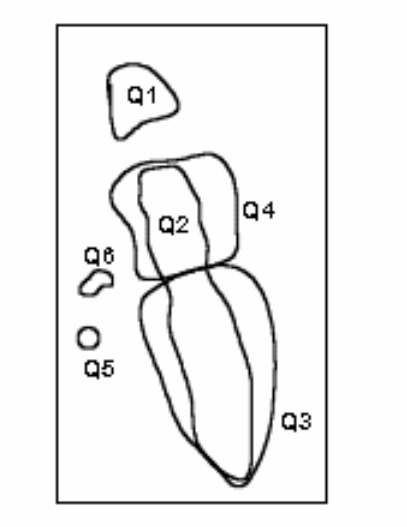
Chrysolina pardalina

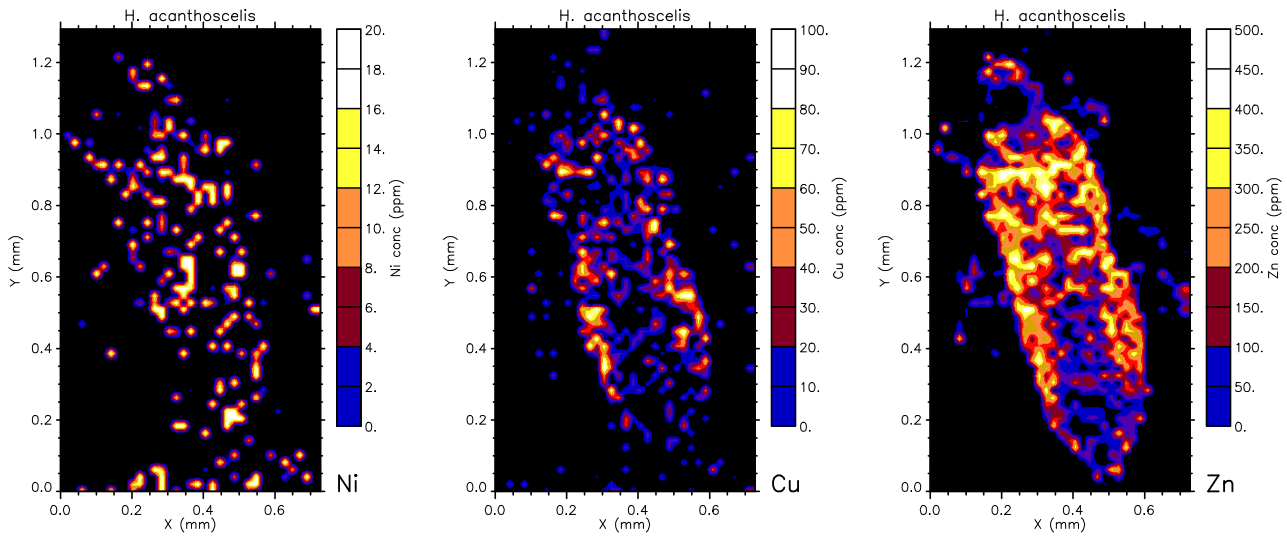
It has been proved that this beetle is able to complete its full life cycle for several generations feeding exclusively on *Berkheya coddii* leaves

Haplothrips acanthoscelis (Thysanoptera)

Quantitative maps of the whole body and concentrations from marked areas

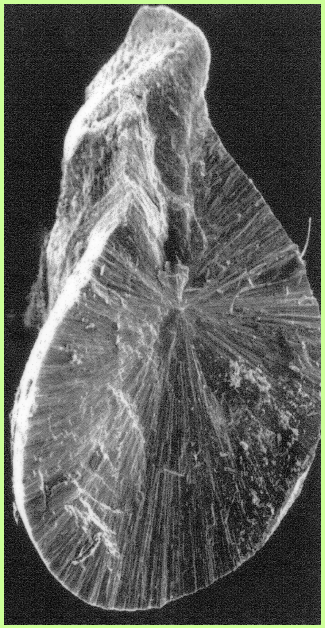


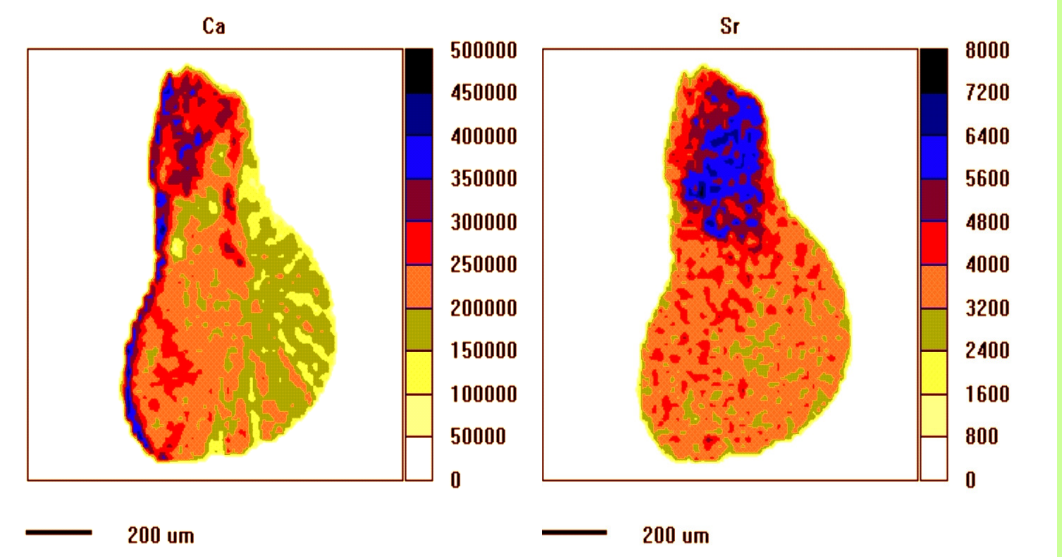




Elemental mapping in statoliths of Cephalopods

Statoliths are a part of the balance and movement receptor system





Sr is concentrated in regions adjacent to the macula where the clearest increments are found; this supports the hypothesis linking Sr with the regulation of statolith deposition and the definition of daily increments.

Statolith of squid *Loligo vulgaris reynaudii*

M.D. Durholtz, M.R. Lipinski, W.J. Przybylowicz and J. Mesjasz-Przybylowicz. The Biological Bulletin 193 (1997) 125.

Collaborations related to biology, environment and geology

83 articles in refereed journals
65 refereed conference proceedings
258 conference presentations

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All collaborators and contributors

Thank you!