Applications of Synchrotron-based Techniques in Agri-Environmental Sciences

Dalton Abdala, PhD.
Brazilian Synchrotron Light Laboratory

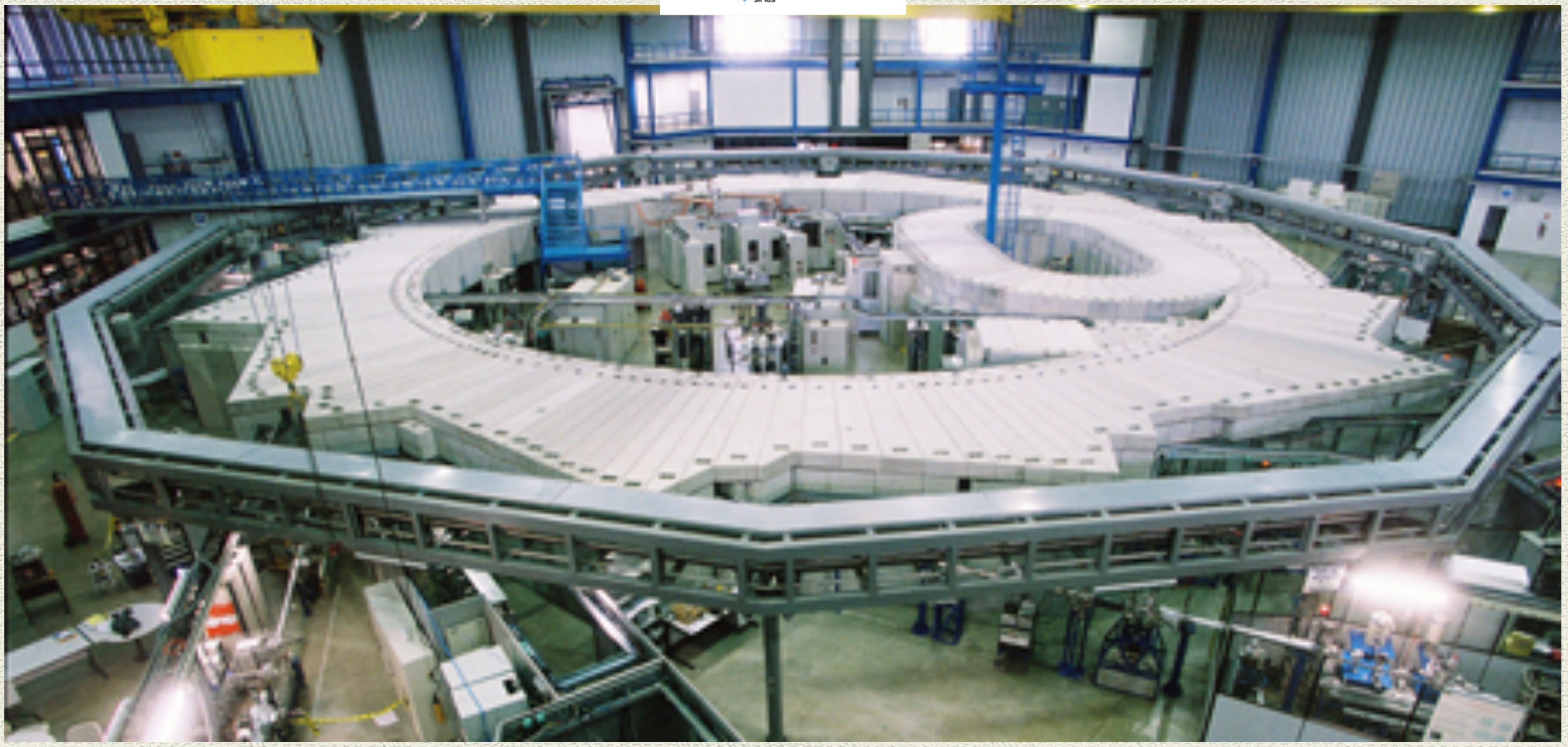
What is synchrotron radiation anyway?

Advanced Photon Source

MAX IV LABORATORY

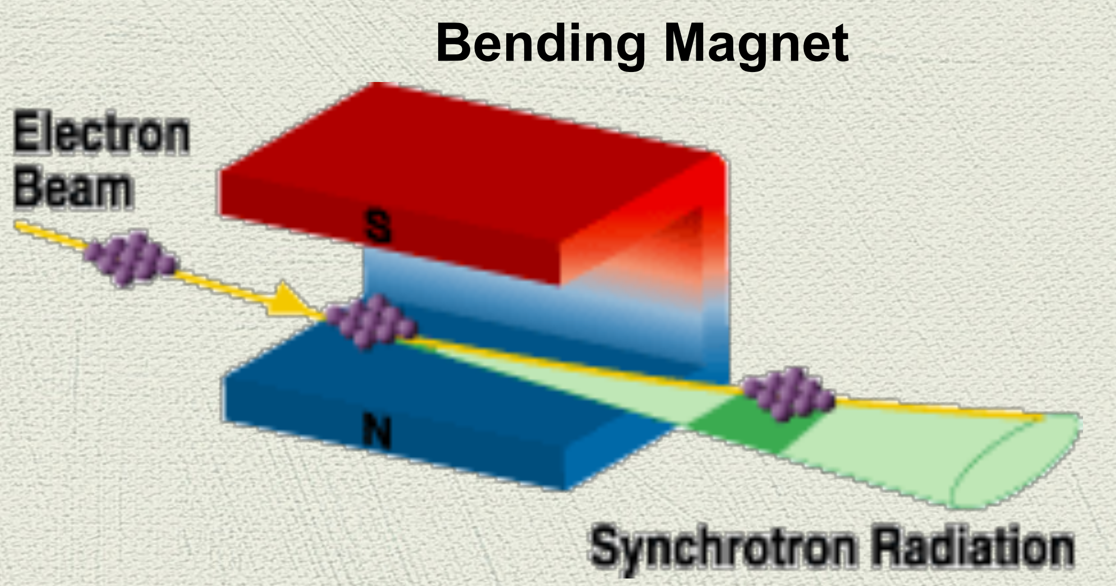
SPring-8

LNLS Brazilian Synchrotron Light Laboratory
sirius



What is synchrotron radiation anyway?

the radiation which occurs when charged particles are accelerated in a curved path or orbit



Characteristics and properties

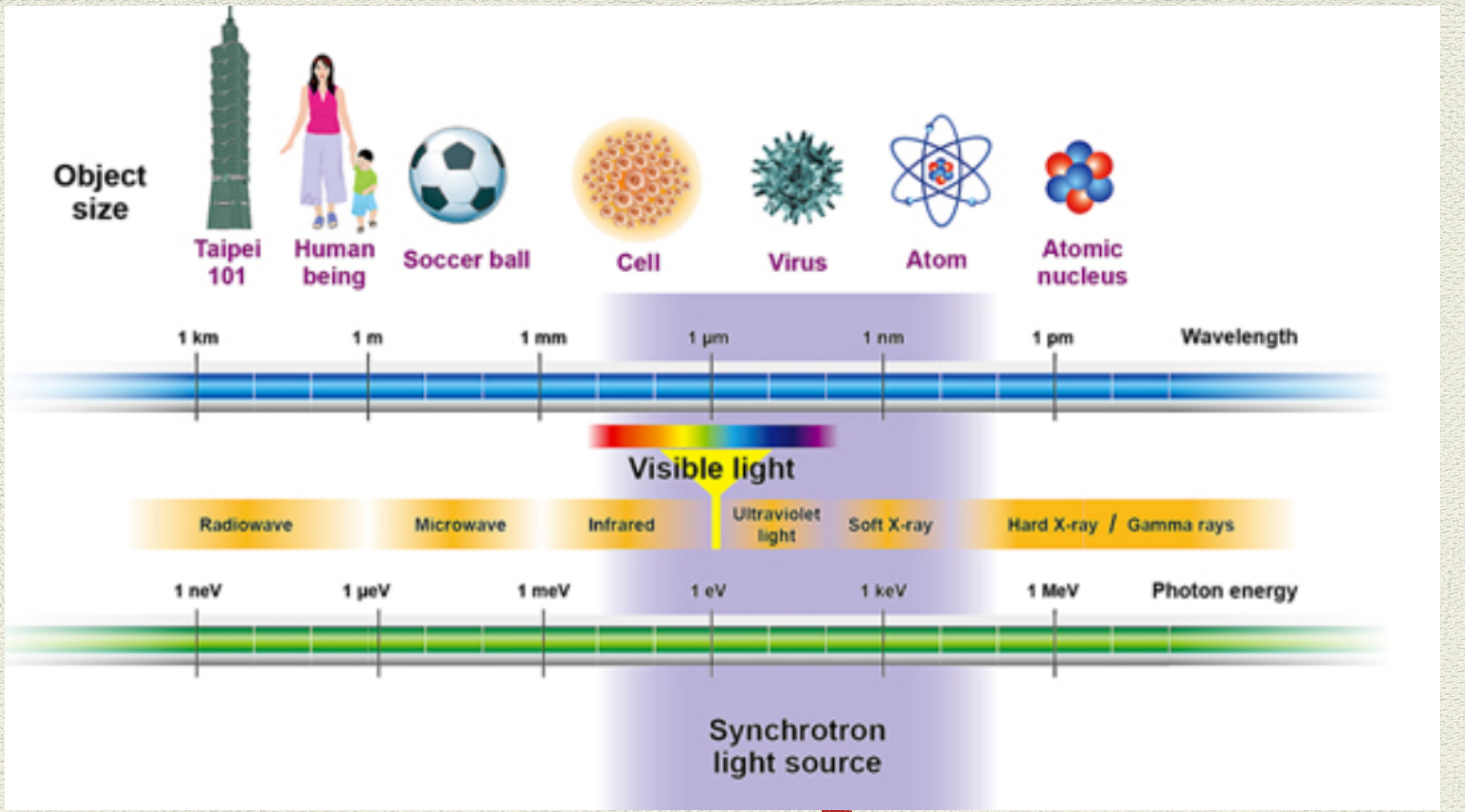
Broad spectrum: a desired wavelength can be selected to perform a given experiment

High flux: high intensity photon beam allowing rapid experiments

High brilliance: highly collimated photon beam generated by a small divergence and small size source

High stability: submicron source stability

a powerful tool to understand the properties of matter at small scales

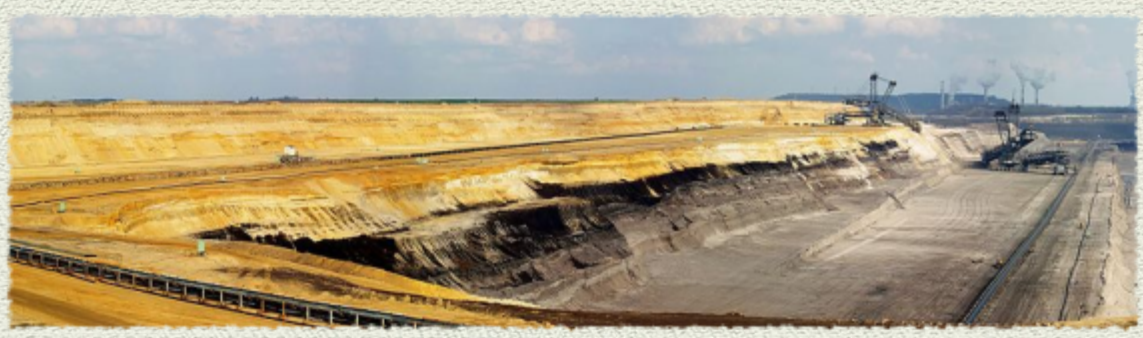


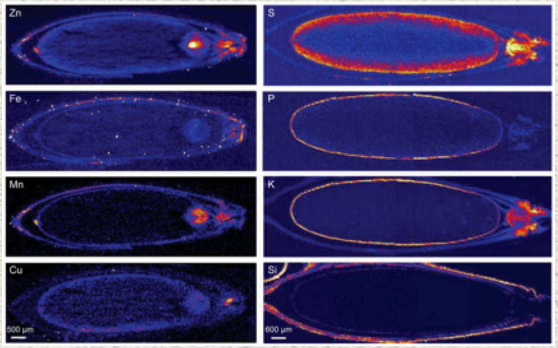
at a synchrotron facility, electrons travel at relativistic speeds

wavelengths are comparable to interatomic distances

a high intensity and collimated light is produced - *synchrotron light*

Agri-environmental research at the LNLS





mining areas

Above and below ground water contamination

Rehabilitation of mined areas

agriculture

Waste management

Contamination of surface and ground waters

nutrients and the environment

Mineral reserves running low

Need for more efficient fertilizers

Nutrient losses in the environment

food quality

Biofortification of staple crops

Improving nutrient bioavailability in staple foods

On the importance of soils

- **life-supporting system**
  - can be simply described by "***1*** **+ 2 =** ***3***"

Weathering and soil formation processes

rocks
minerals

1 Parent material

+

physical
chemical
biological

2 Weathering agents

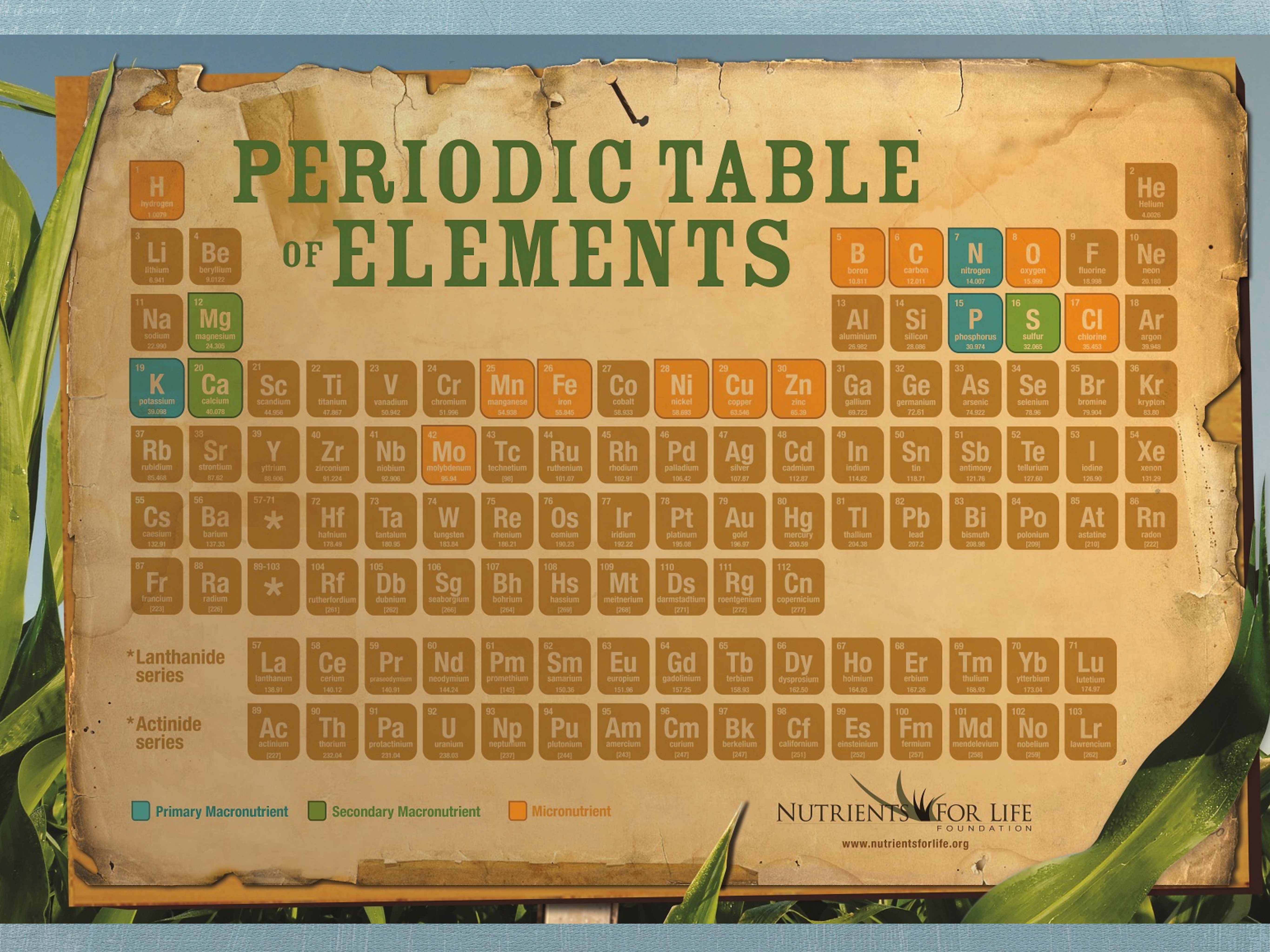
=

3 SOILS

PRODUCT of
weathering agents
acting on the **parent material**

On the importance of soils

- **life-supporting system**
    - ***we wished it could*** be simply described by "***1 + 2 = 3***"
    - **high complexity and heterogeneity**


PERIODIC TABLE OF ELEMENTS
1 H hydrogen 1.0079
2 He Helium 4.0026
3 Li lithium 6.941
4 Be beryllium 9.0122
5 B boron 10.811
6 C carbon 12.011
7 N nitrogen 14.007
8 O oxygen 15.999
9 F fluorine 18.998
10 Ne neon 20.180
11 Na sodium 22.990
12 Mg magnesium 24.305
13 Al aluminium 26.982
14 Si silicon 28.086
15 P phosphorus 30.974
16 S sulfur 32.065
17 Cl chlorine 35.453
18 Ar argon 39.948
19 K potassium 39.098
20 Ca calcium 40.078
21 Sc scandium 44.956
22 Ti titanium 47.867
23 V vanadium 50.942
24 Cr chromium 51.996
25 Mn manganese 54.938
26 Fe iron 55.845
27 Co cobalt 58.933
28 Ni nickel 58.693
29 Cu copper 63.546
30 Zn zinc 65.39
31 Ga gallium 69.723
32 Ge germanium 72.61
33 As arsenic 74.922
34 Se selenium 78.96
35 Br bromine 79.904
36 Kr krypton 83.80
37 Rb rubidium 85.468
38 Sr strontium 87.62
39 Y yttrium 88.906
40 Zr zirconium 91.224
41 Nb niobium 92.906
42 Mo molybdenum 95.94
43 Tc technetium [98]
44 Ru ruthenium 101.07
45 Rh rhodium 102.91
46 Pd palladium 106.42
47 Ag silver 107.87
48 Cd cadmium 112.87
49 In indium 114.82
50 Sn tin 118.71
51 Sb antimony 121.76
52 Te tellurium 127.60
53 I iodine 126.90
54 Xe xenon 131.29
55 Cs caesium 132.91
56 Ba barium 137.33
57-71 *
72 Hf hafnium 178.49
73 Ta tantalum 180.95
74 W tungsten 183.84
75 Re rhenium 186.21
76 Os osmium 190.23
77 Ir iridium 192.22
78 Pt platinum 195.08
79 Au gold 196.97
80 Hg mercury 200.59
81 Tl thallium 204.38
82 Pb lead 207.2
83 Bi bismuth 208.98
84 Po polonium [209]
85 At astatine [210]
86 Rn radon [222]
87 Fr francium [223]
88 Ra radium [226]
89-103 *
104 Rf rutherfordium [261]
105 Db dubnium [262]
106 Sg seaborgium [266]
107 Bh bohrium [264]
108 Hs hassium [269]
109 Mt meitnerium [268]
110 Ds darmstadtium [271]
111 Rg roentgenium [272]
112 Cn copernicium [277]
*Lanthanide series
57 La lanthanum 138.91
58 Ce cerium 140.12
59 Pr praseodymium 140.91
60 Nd neodymium 144.24
61 Pm promethium [145]
62 Sm samarium 150.36
63 Eu europium 151.96
64 Gd gadolinium 157.25
65 Tb terbium 158.93
66 Dy dysprosium 162.50
67 Ho holmium 164.93
68 Er erbium 167.26
69 Tm thulium 168.93
70 Yb ytterbium 173.04
71 Lu lutetium 174.97
*Actinide series
89 Ac actinium [227]
90 Th thorium 232.04
91 Pa protactinium 231.04
92 U uranium 238.03
93 Np neptunium [237]
94 Pu plutonium [244]
95 Am amercium [243]
96 Cm curium [247]
97 Bk berkelium [247]
98 Cf californium [251]
99 Es einsteinium [252]
100 Fm fermium [257]
101 Md mendelevium [258]
102 No nobelium [259]
103 Lr lawrencium [262]
Primary Macronutrient
Secondary Macronutrient
Micronutrient
NUTRIENTS FOR LIFE FOUNDATION
www.nutrientsforlife.org

On the importance of soils

- **life-supporting system**
  - ***we wished it could*** be simply described by "***1 + 2 = 3***"
  - high complexity and heterogeneous
  - **complexity *vs* scales**

Soil Is An Amazing Substance.

A complex mix of minerals, air, and water, soil also teems with countless micro-organisms, and the decaying remains of once-living things. Soil is made of life and soil makes life.

To the farmer, soil is where crops grow.

To the engineer, soil is a foundation upon which to build.

To the ecologist, soil supports communities of living things.

To the archaeologist, soil holds clues to past cultures.

To the city dweller, soil nurtures grass and gardens.

To the soil scientist, soil is all of these things.

Soil has been called "the skin of the earth" because it is the thin outermost layer of the Earth's crust.

Like our own skin, we can't live without soil.

Source: Soil Science Society of America

DIG DEEPER

MYSTERIES IN THE SOIL

National Association of Conservation Districts
nacdnet.org

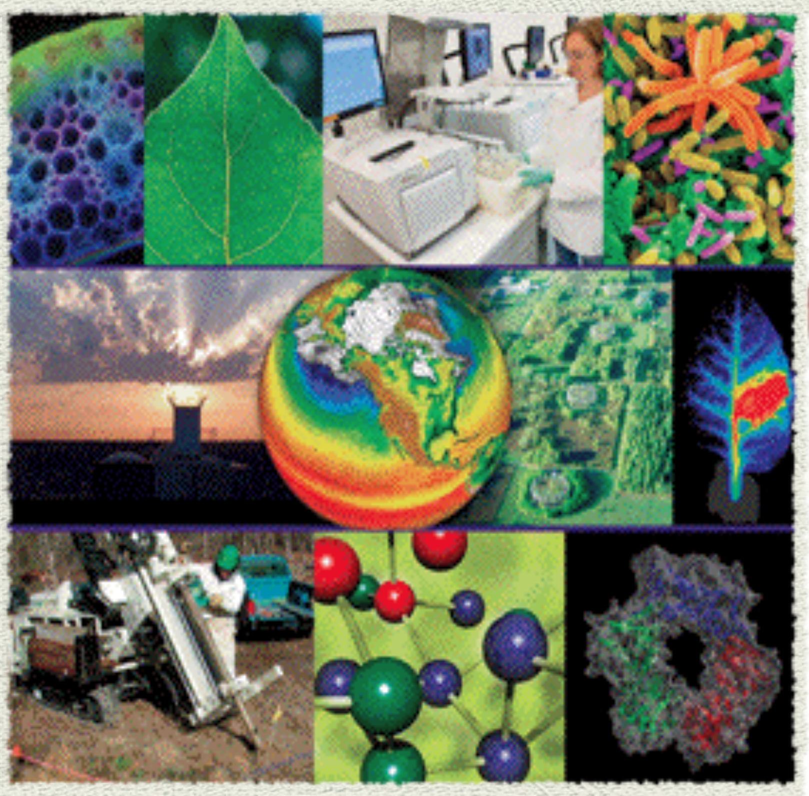
Soil Science Society of America
soils.org

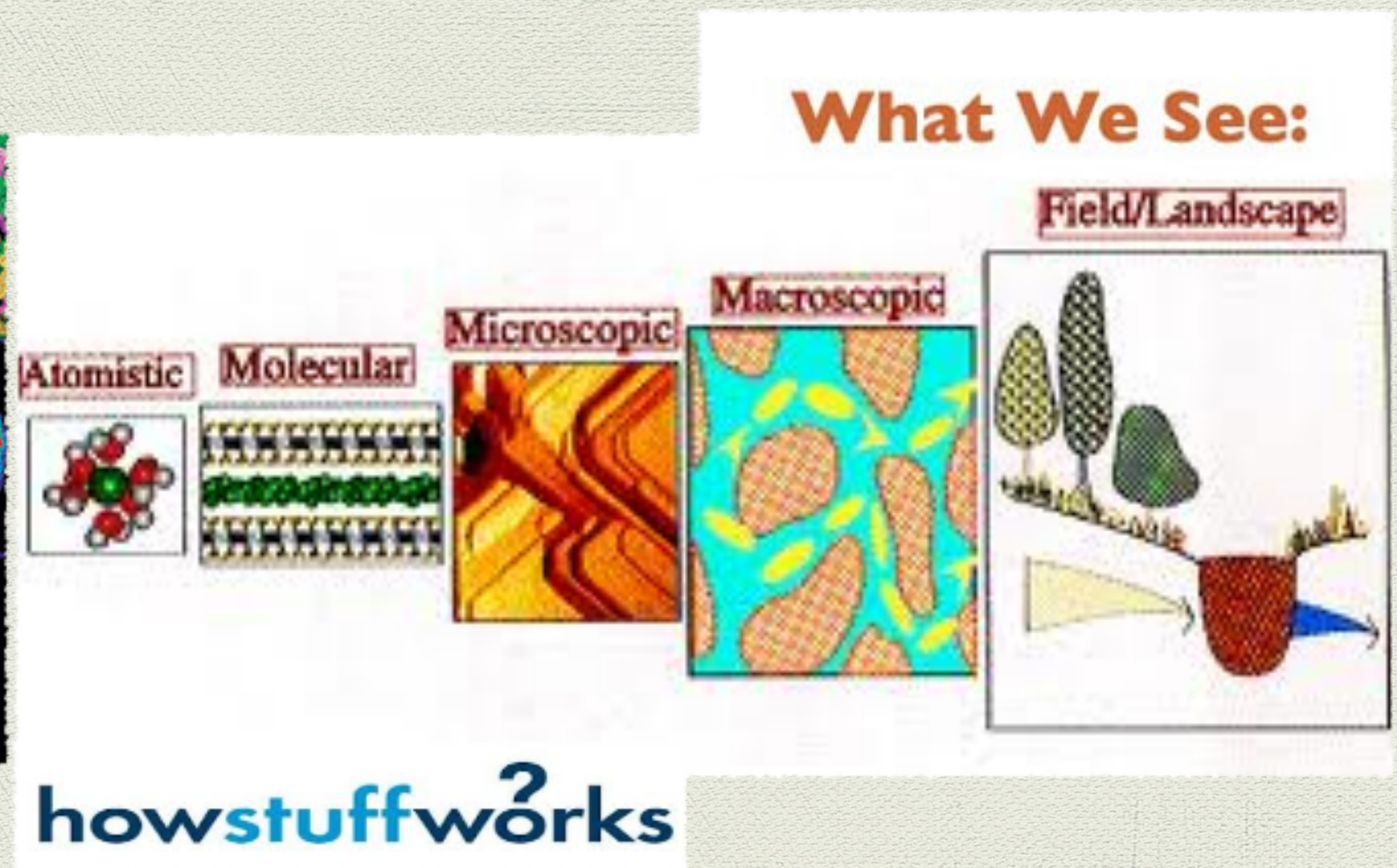
Soil image Ned M Seidler/National Geographic Creative | Education activities link to nacdnet.org/education/resources/digdeeper

On the importance of soils

- **life-supporting system**
  - *we wished it could* be simply described by "*1 + 2 = 3*"
  - high complexity and heterogeneous
  - complexity *vs* scales
  - **requires a set of analytical techniques**

Scales of Earth Sciences





Unveiling the properties of matter

Source: http://www.regional.org.au/au/asssi/supersoil2004/keynote/sparks.htm

“one giant leap for soil sciences”

In Situ X-ray Absorption Study of Surface Complexes: Selenium Oxyanions on α-FeOOH

KIM F. HAYES, A. LAWRENCE ROE, GORDON E. BROWN, JR., KEITH O. HODGSON, JAMES O. LECKIE, GEORGE A. PARKS

A novel application of x-ray absorption spectroscopy has provided structural information for ions sorbed at oxide-water interfaces. As an example, in situ extended x-ray absorption fine structure (EXAFS) measurements of adsorbed selenate and selenite ions at an α-FeOOH(goethite)–water interface have been performed; these measurements show that selenate forms a weakly bonded, outer-sphere complex and that selenite forms a strongly bonded, inner-sphere complex. The selenite ion is bonded directly to the goethite surface in a bidentate fashion with two iron atoms 3.38 angstroms from the selenium atom. Adsorbed selenate has no iron atom in the second coordination shell of selenium, which indicates retention of its hydration sphere upon sorption. This method provides direct structural information for adsorbed species at solid-liquid interfaces.

Hayes et al., **1987** - Science

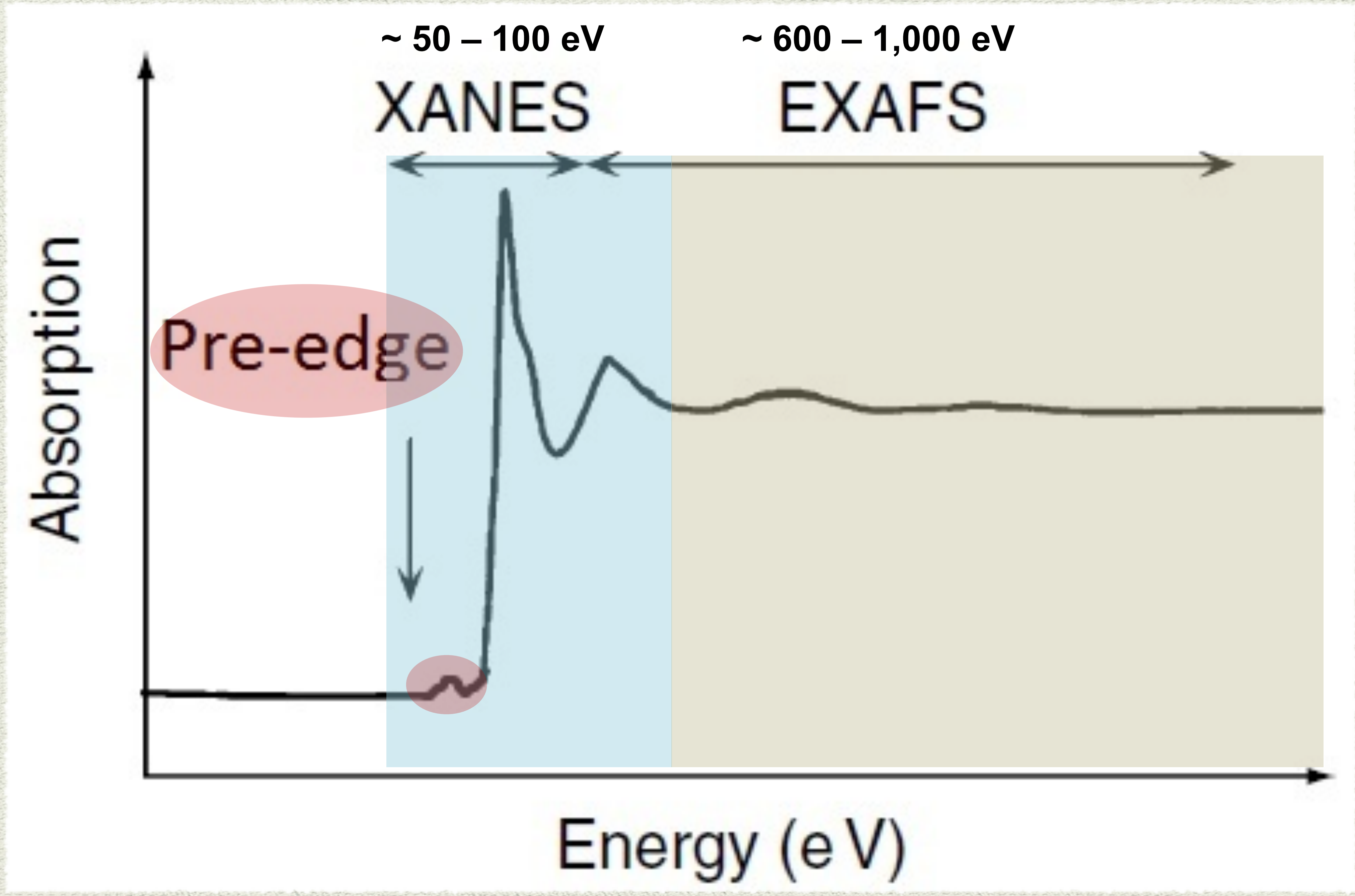
Synchrotron radiation and scientific achievements attained in soil sciences

- HAYES et al., 1987. **Selenium bonding configurations** at the goethite/water interface
- SCHEIDEGGER et al., 1997. Elucidation of **Layered Doubled Hydroxide structure**
- TAPPERO et al., 2006. Elucidating the mechanisms for **metal accumulation** in hyper-accumulating plants
- GINDER-VOGEL et al., 2009. Using **Quick-XAFS for spectroscopic and kinetic determination** of Cr oxidation at the mineral/water interface
- CHEN et al., 2014. Studying **Soil carbon complexation** via C1s XANES and Synchrotron Transmission X-ray Microscopy
- ABDALA et al., 2015. Examining **phosphate surface complexation** at the goethite/water interface

Synchrotron-based techniques of major interest in agri-environmental sciences

- X-ray absorption spectroscopy
- X-ray fluorescence spectroscopy
- X-ray diffraction
- X-ray μ-computed tomography

XAS can be operationally divided into XANES and EXAFS



XANES spectroscopy in soils

Mostly used as a "**fingerprint**" technique

Electronic transitions

Diagnostic features

Electronic transitions give rise to the diagnostic features seen in the XANES spectrum

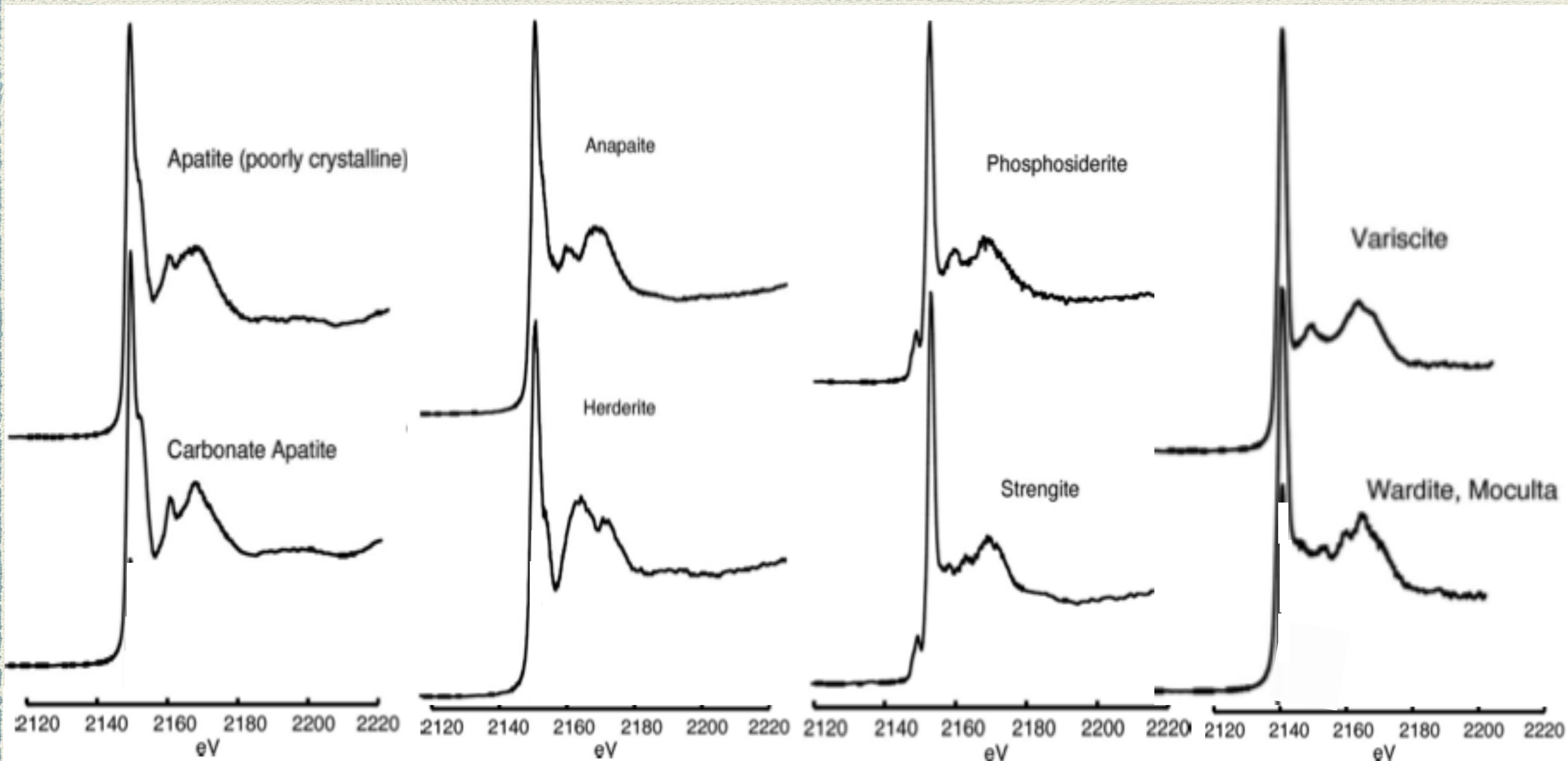
Linear Combination analysis - matching between standards and samples

Visual inspection of spectral features, principal component analysis (PCA), etc…

Fingerprint of chemical compounds

Calcium Phosphates

apatite group | (non-apatite group) | Iron phosphates | Aluminum phosphates



All you need is a match!

match.com®

alternatively…

Demeter is a comprehensive system for **processing** and **analyzing** X-ray Absorption Spectroscopy data

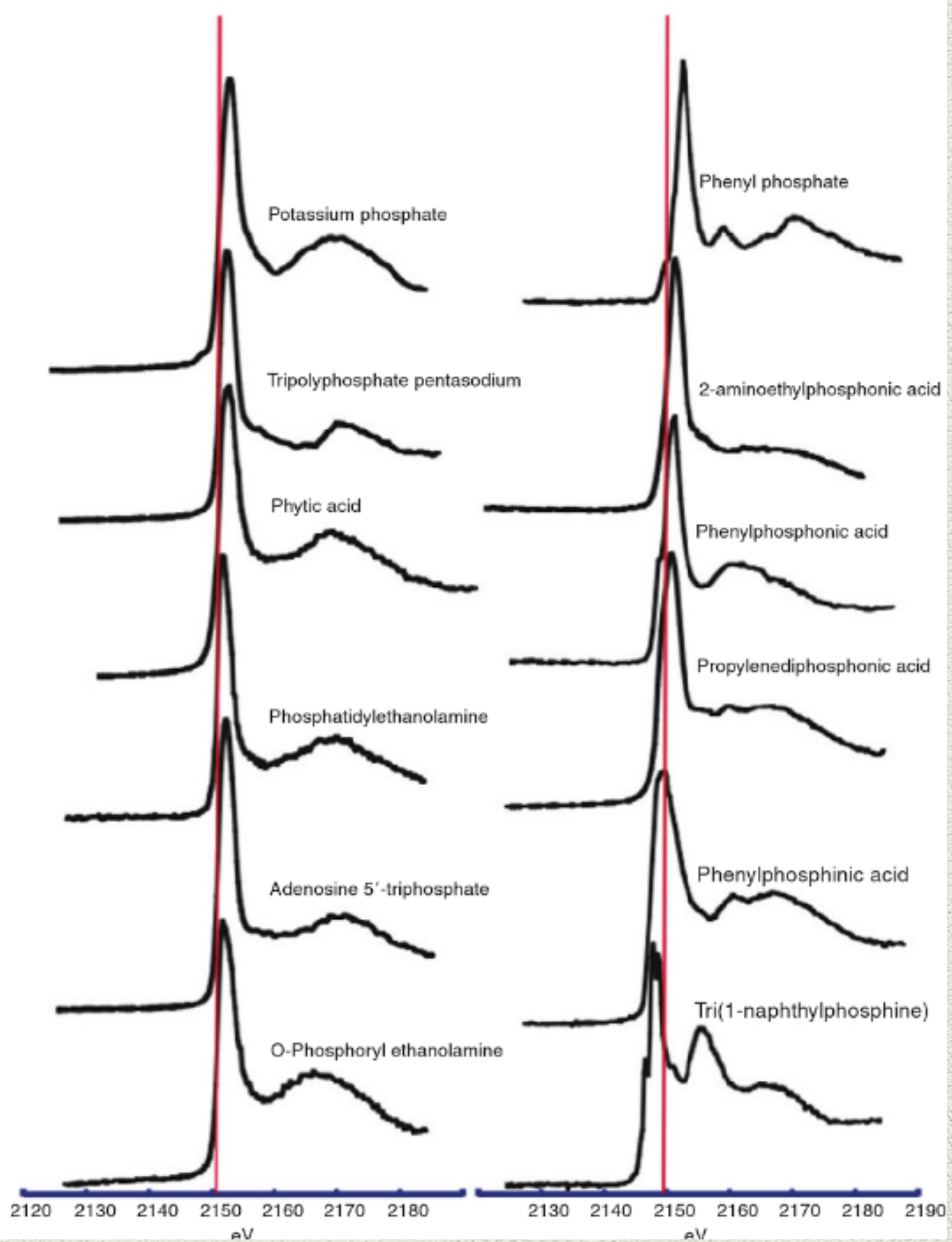
by ***Dr. Bruce Ravel***

SIXPACK is a single analysis package that can guide the user through data **averaging** and **calibration**, **background removal**, and many aspects of **fitting**.

by ***Dr. Samuel Webb***

…and many others

Build your own library of reference spectra!



Normalized phosphorus K-edge XANES spectra of potassium phosphate and various organic P species

(reprinted from Brandes et al., 2007 with permission from Elsevier)

Users are advised to build their own library of reference spectra

Remember: it is very likely that you won't get your job done without a good library of reference spectra

How do I compile a good library of reference spectra?

First off…

you got to think through your experiment!!!

knowing the composition of the materials contained in your sample helps (I mean, a lot!!!)

which intermediates do you expect to find along the reaction?

in other words, give an educated guess!

Journal of
Synchrotron
Radiation
ISSN 0909-0495

Phosphorus $L_{2,3}$-edge XANES: overview of reference compounds

Jens Kruse,[a]* Peter Leinweber,[a] Kai-Uwe Eckhardt,[a] Frauke Godlinski,[b] Yongfeng Hu[c] and Lucia Zuin[c]

Received 25 November 2008
Accepted 5 January 2009

Journal of
Synchrotron
Radiation
ISSN 0909-0495

Phosphorus *K*-edge XANES spectroscopy of mineral standards

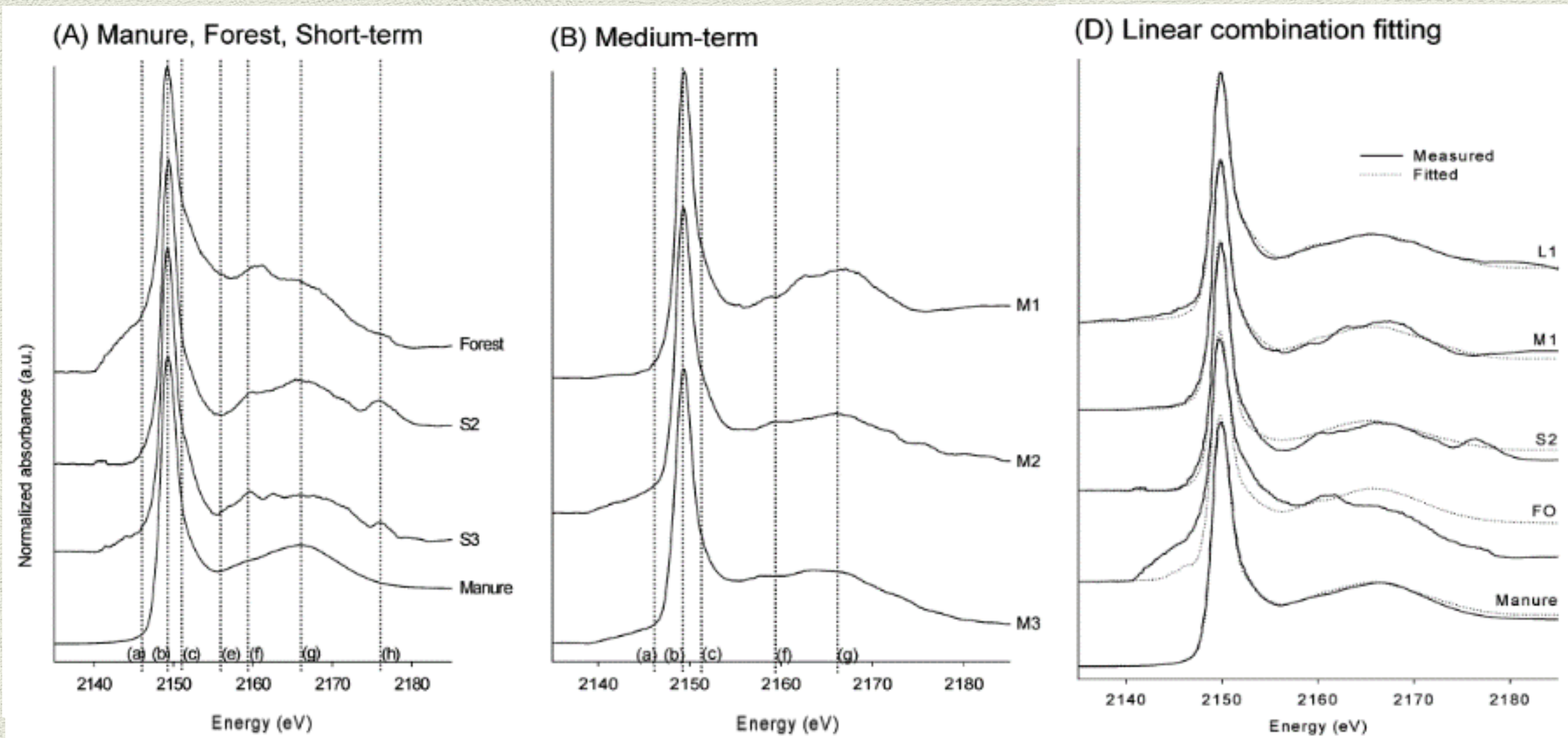
Ellery D. Ingall,[a]* Jay A. Brandes,[b] Julia M. Diaz,[a] Martin D. de Jonge,[c] David Paterson,[c] Ian McNulty,[d] W. Crawford Elliott[e] and Paul Northrup[f]

Received 30 July 2010
Accepted 4 November 2010

Nitrogen K-edge XANES - An overview of reference compounds used to identify 'unknown' organic nitrogen in environmental samples

Article *in* Journal of Synchrotron Radiation 14(Pt 6):500-11 · November 2007
DOI: 10.1107/S0909049507042513 · Source: PubMed

Assessing land use and management effects with XANES



Source: Sato et al., 2005 – Environmental Science & Technology

EXAFS spectroscopy

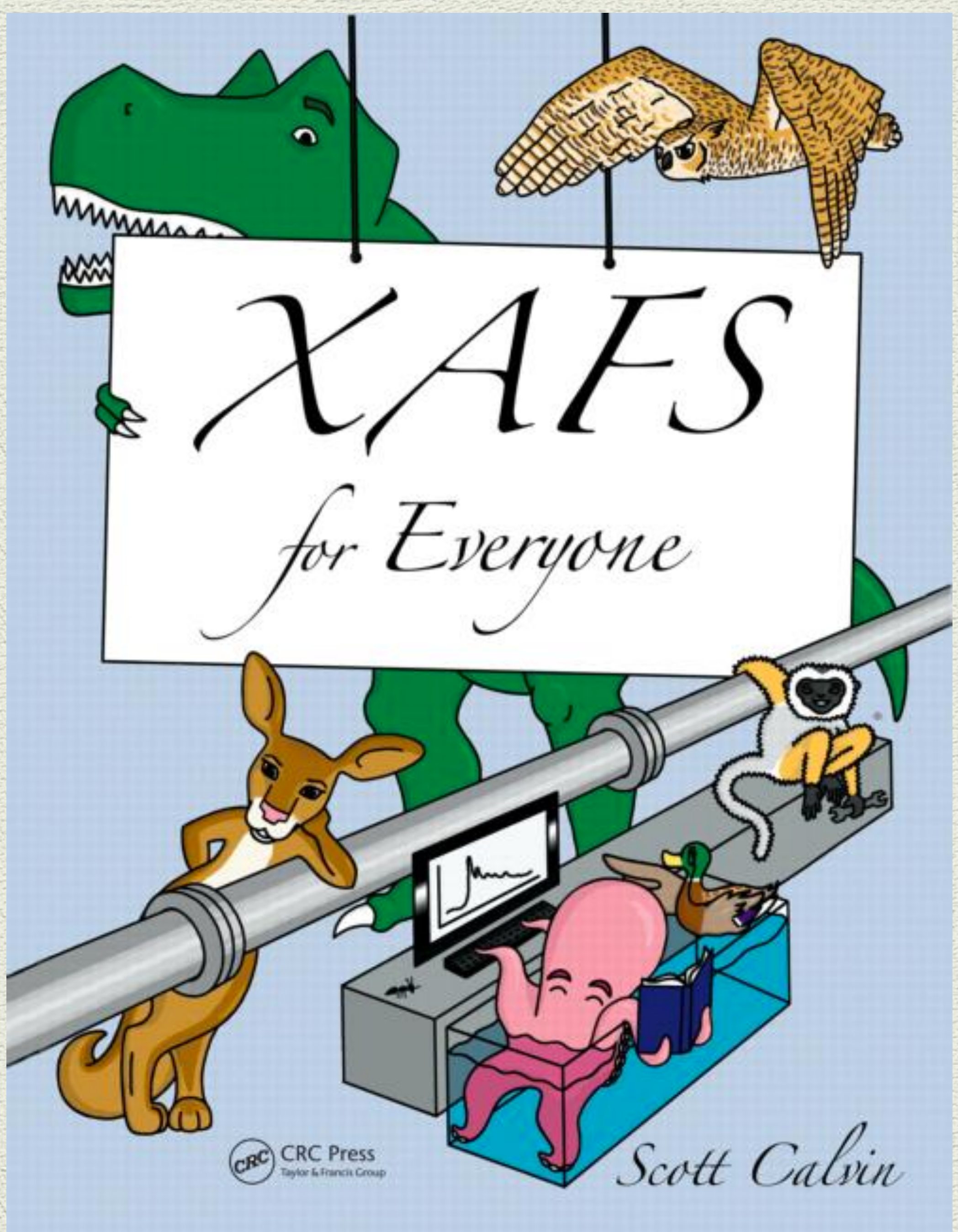
At higher energies, wavelengths get shorter, comparable to interatomic distances

$E >>> E_0$

single scattering >>> multiple scattering

Interferences between the outgoing photoelectron and surrounding atoms give rise to the oscillations seen in EXAFS

structural information can be derived from this events!



EXAFS spectroscopy for soil analysis

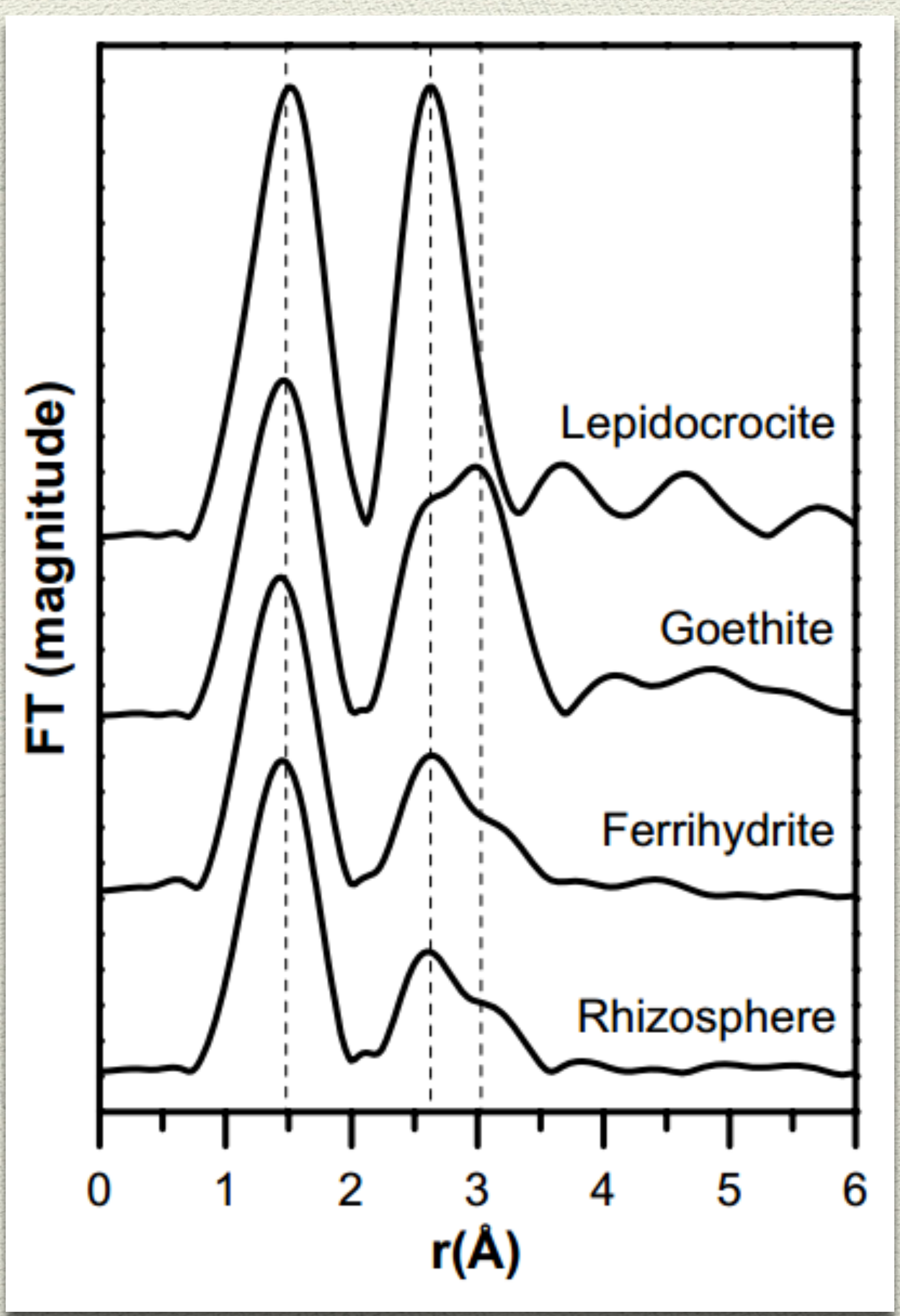
Interatomic distances

Identity of neighboring atoms

Number of neighboring atoms

Shell-by-shell fitting

Using Fe K-edge EXAFS to differentiate among Fe-(hydr)oxide minerals



Fourier-transformed Fe K-edge EXAFS spectra of reference minerals and rhizosphere soil.

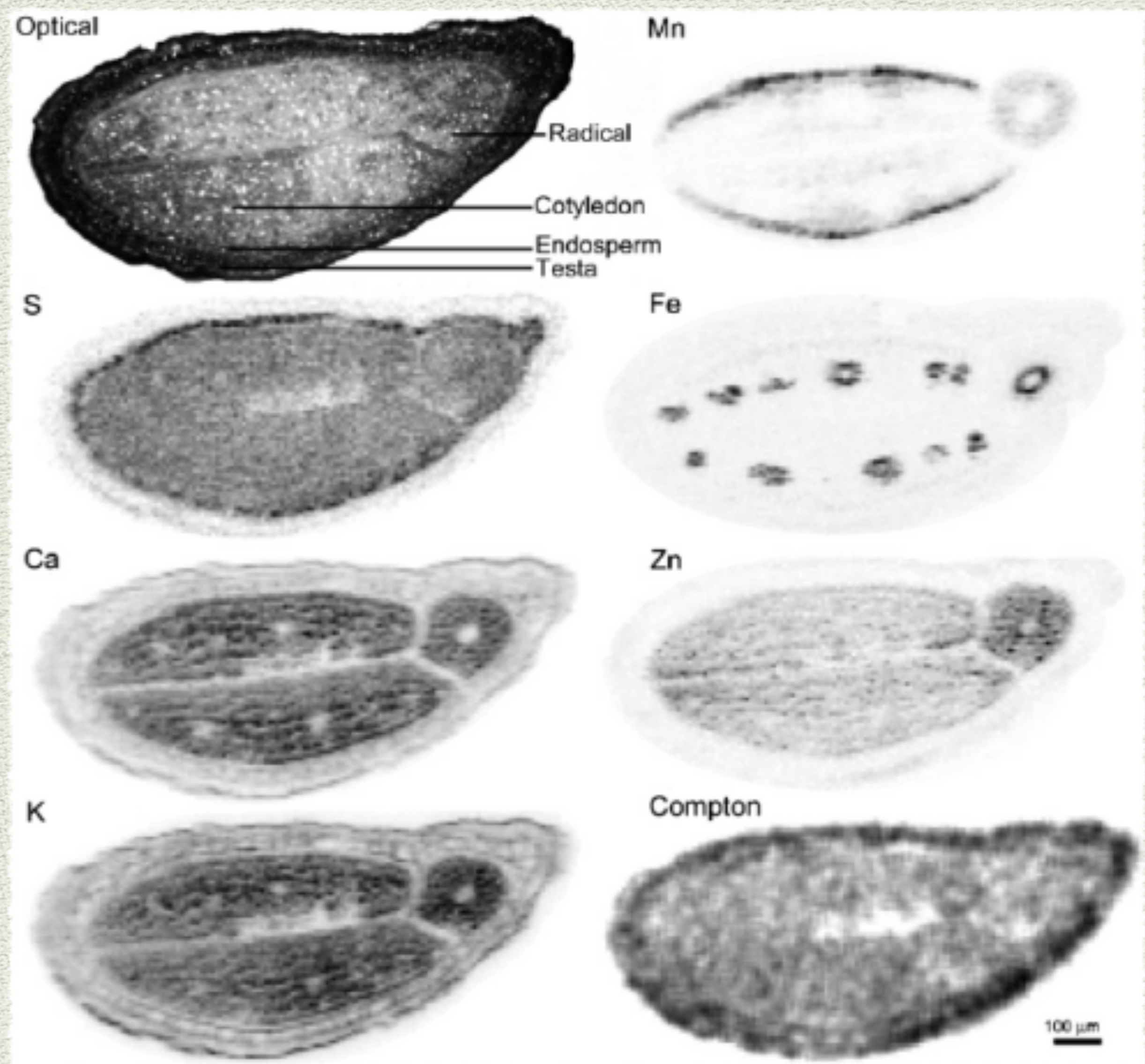
The dashed vertical lines at 1.5, 2.65 and 3.05 A indicate the approximate positions of peaks arising from the backscattering contributions of first shell O, second shell edge-sharing Fe and second shell corner-sharing Fe, respectively.

Based on some characteristics of a well known standard, such as peak position and shape, one can determine what mineral species are found within a given sample

Source: Voegelin et al. (2007) – Geochimica et Cosmochimica Acta

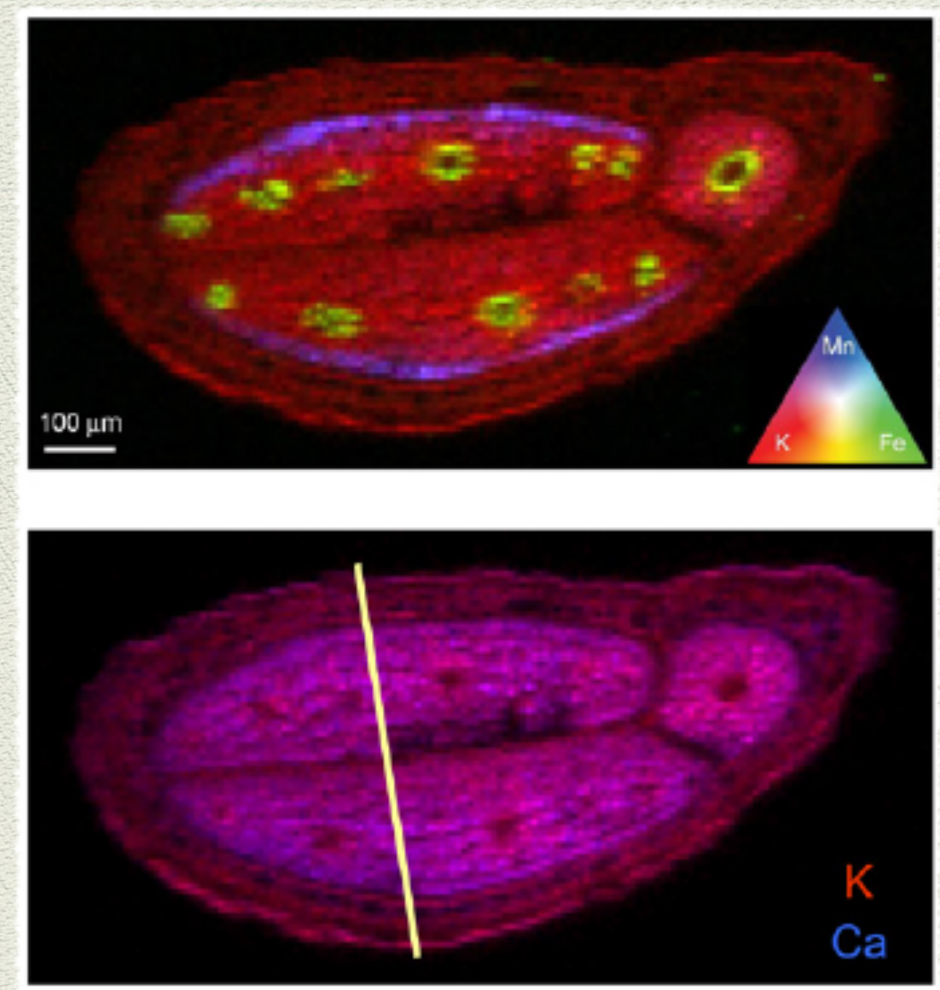
Spectromicroscopy

coupling XAS with XRF techniques



Grayscale synchrotron-based X-ray microfluorescence (µSXRF) images in negative contrast showing the distribution of S, Ca, K, Mn, Fe, and Zn in a Noccaea seed (20 µm thick tissue cryosection) along with an optical camera image and the image of the Compton scatter

Elemental maps showing the elemental distribution within a plant tissue



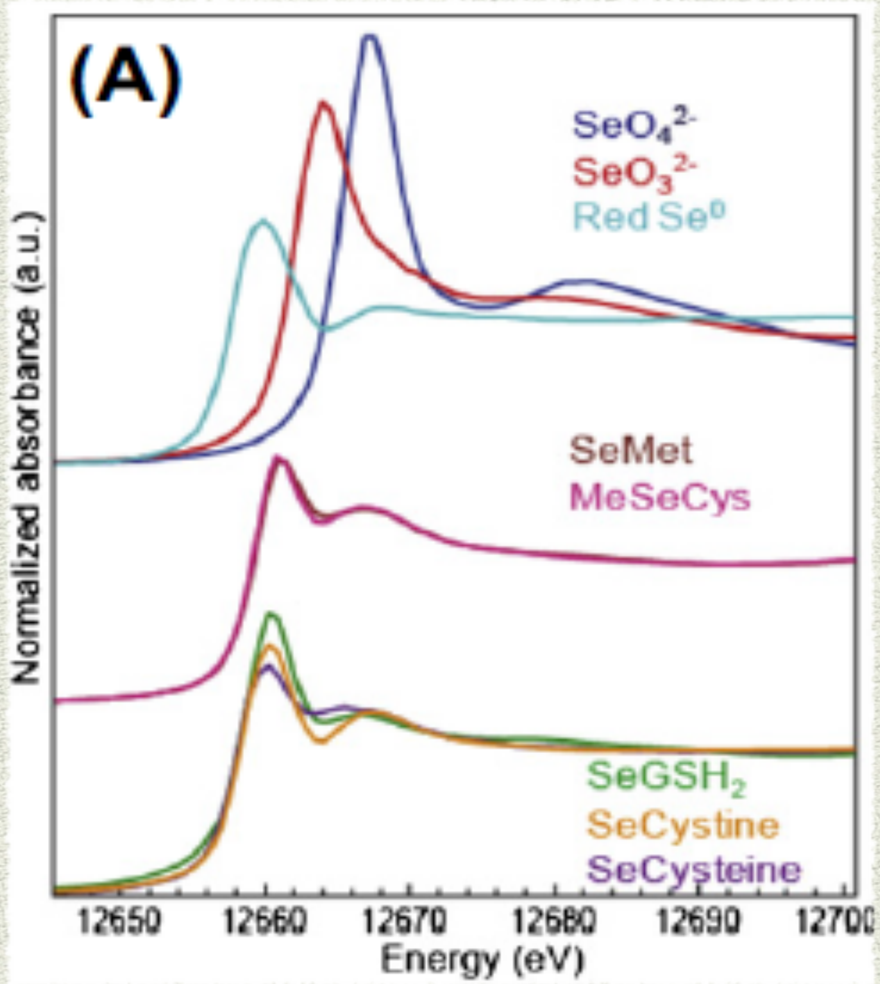
Tricolor image of K, Fe, and Mn with color triangle and bicolor image of K and Ca in the Noccaea seed.

Source: Sarret et al., 2013 – Advances in Agronomy

Spectromicroscopy

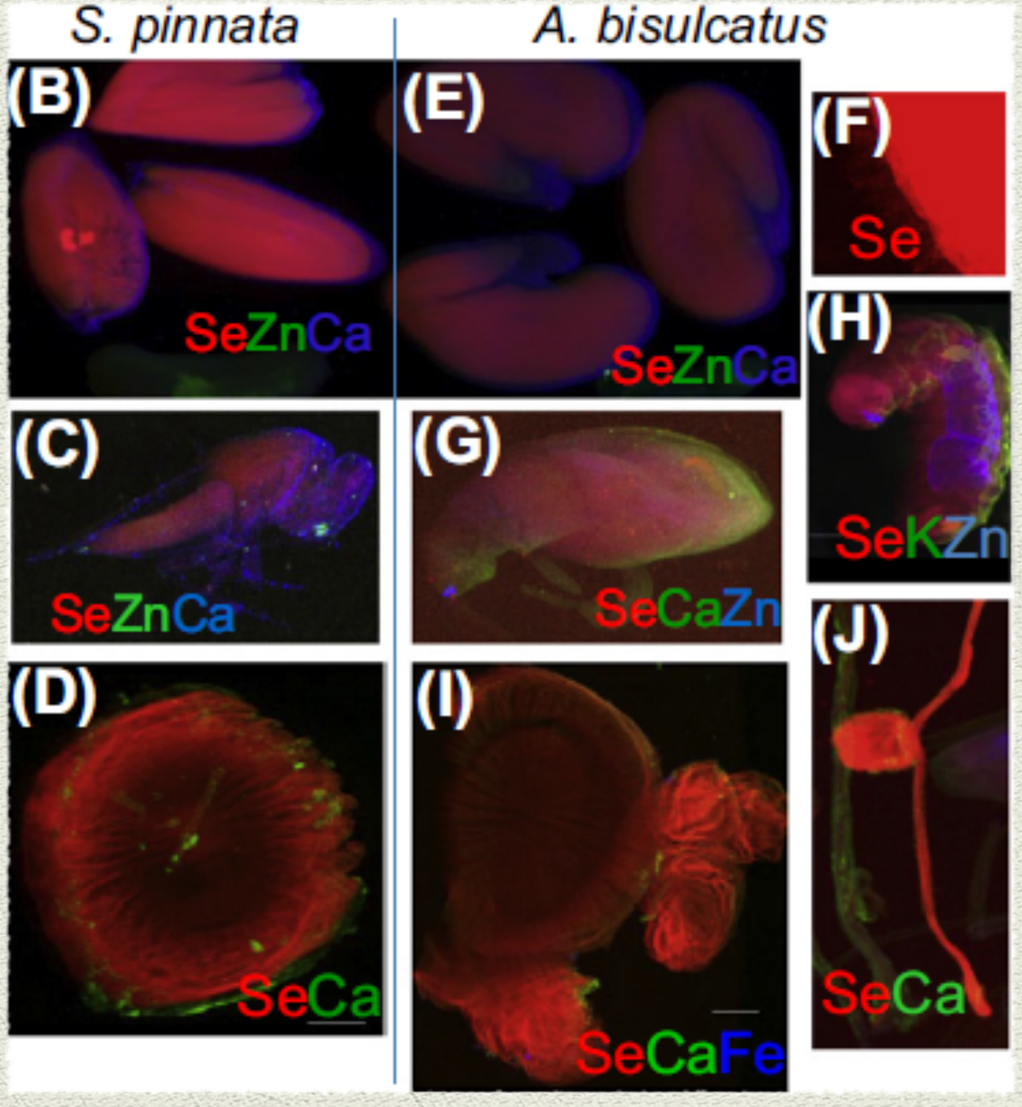
coupling XAS with XRF techniques

A: Se K-edge XANES spectra from different selenocompounds.



SeMet: Selenomethionine;
MeSeCys: methyl-selenocysteine;
SeGSH2: Selenodiglutathione

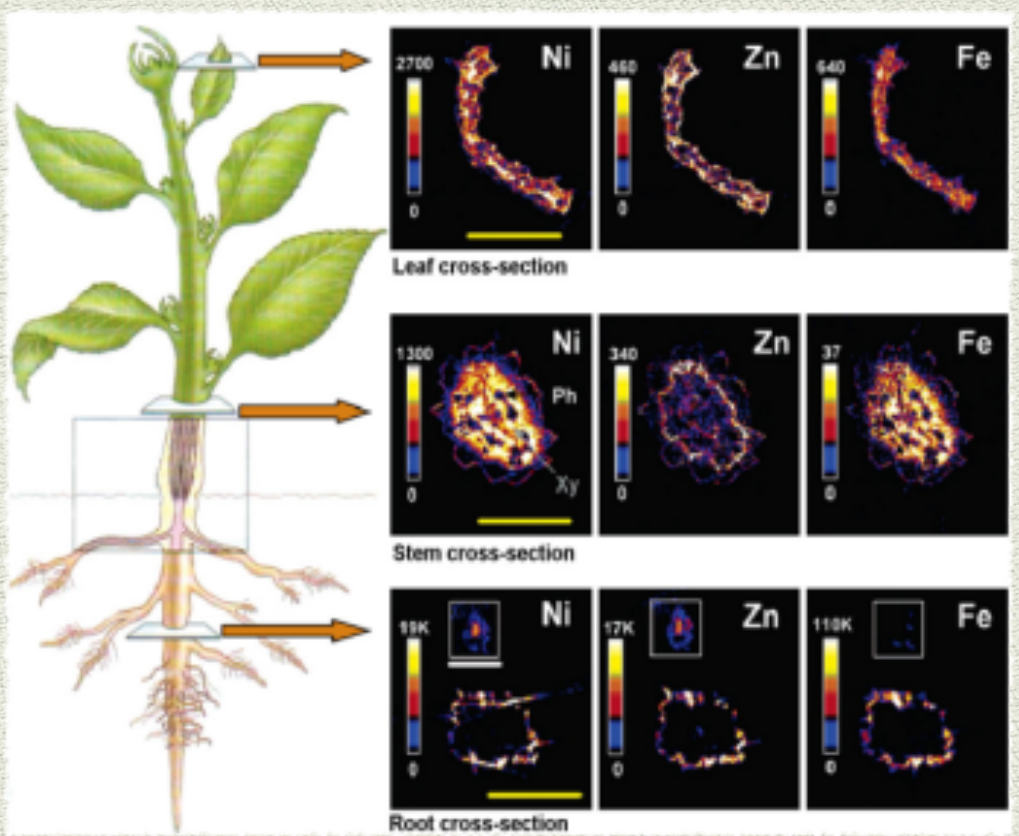
B–J: μ-X-ray fluorescence maps of Se (in red) and other elements in two hyperaccumulator plant species and their Se-resistant ecological partners.



Source: Sarret et al., 2013 – Advances in Agronomy

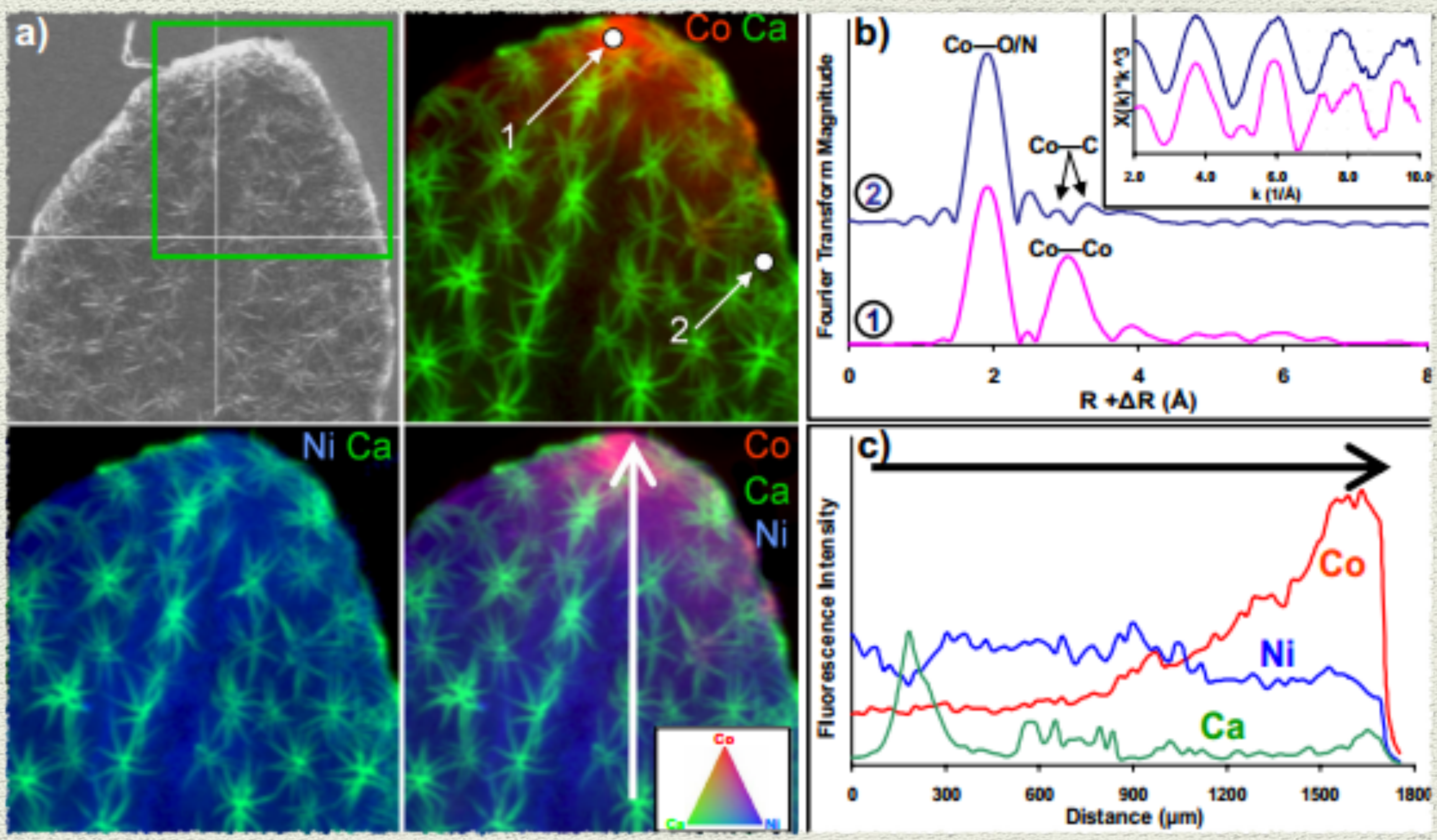
Phytorremediation: using plants for soil decontamination

Metal localization and elemental associations in accumulator plants is crucial to understanding the mechanisms of hyperaccumulation and tolerance



Source: Lombi et al., 2011 – E&EB

μ-SXRF: localization and determination of the local atomic environment of Co in hyperaccumulating *Alissum murale*



Hyperaccumulating *Alissum murale* accumulates up to 3% of Co

Source: Tappero et al., 2007 – New Phytologist

The **Carnaúba beamline at Sirius**

- **the "basic tool-kit" of soil and environmental scientists**
  - ***X-ray Absorption Spectroscopy***
  - ***X-ray Fluorescence Spectroscopy***
  - ***X-ray Diffraction***
  - beam size at sample position: 80 nm
  - energy range: 1.5 up to 14 keV
  - access to the K-edges of Al, Si, P, S, K, Ca and some transition metals up to Se

Molecular Environmental Sciences at the LNLS

Thecno-Scientific Meeting on Synchrotron Applications to Geosciences

SAGe 2015

http://daltonabdala.wix.com/dalton-abdala

Thank you

dalton.abdala@lnls.br