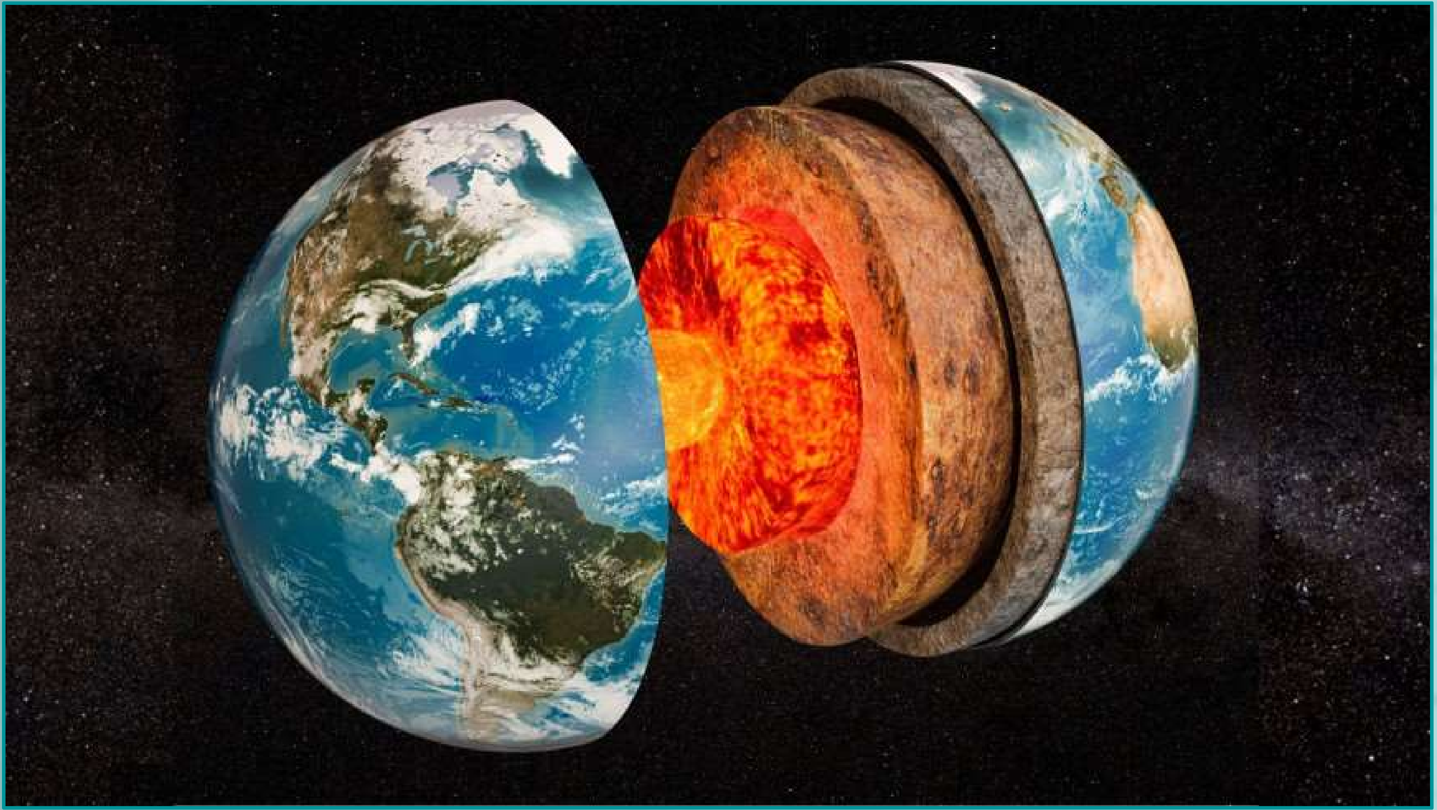
School on
Synchrotron Light Sources
and their Applications

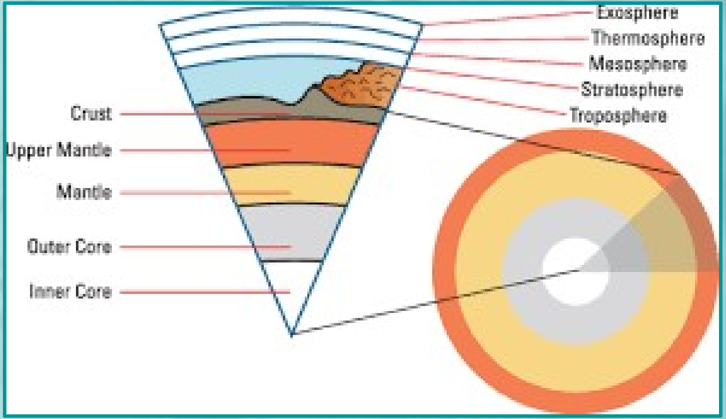
ICTP

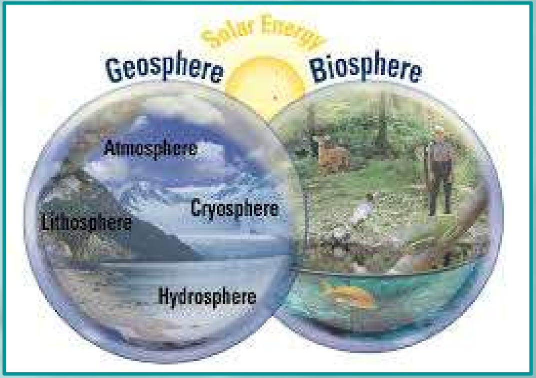
Synchrotron light and the Earth Sciences

Bjorn von der Heyden
Stellenbosch University
31 January 2023

What are the Earth Sciences?



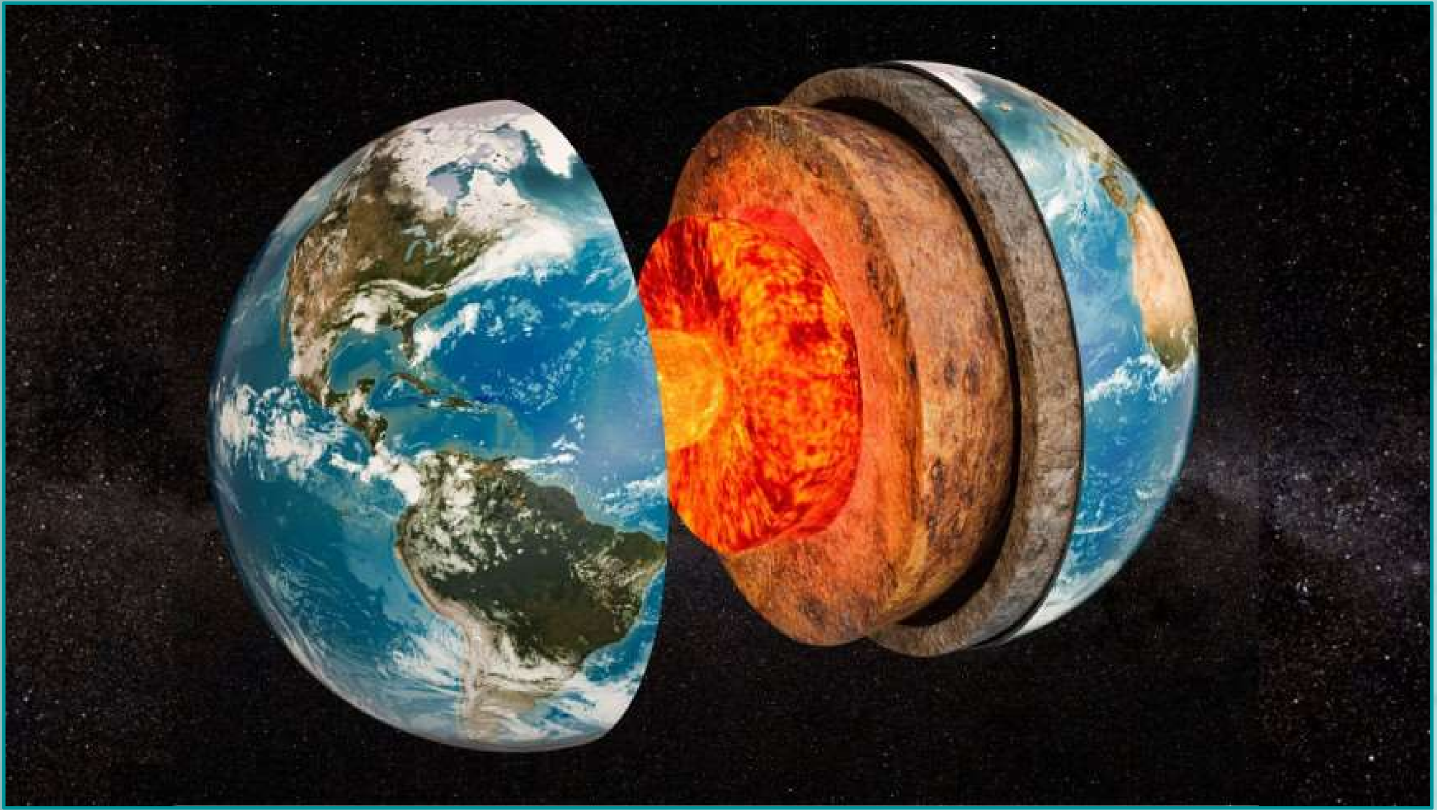




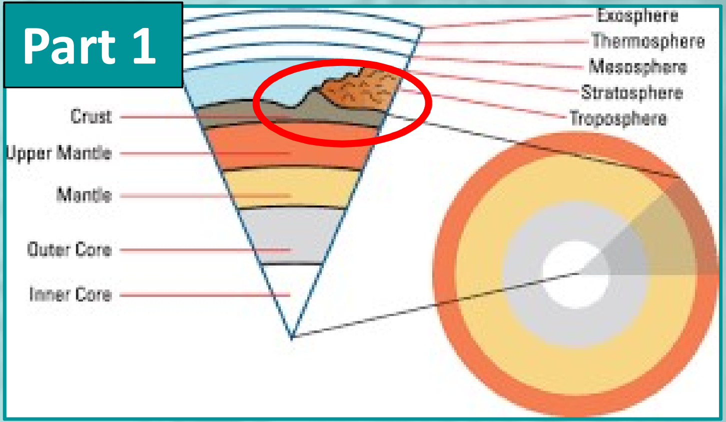
Sphere: *realm (world) of something or physical dimensions / area of something, or both of these (Quora.com).*

Image credits: interestingengineering.com; dummies.com; geographyrealm.com

What are the Earth Sciences?



Part 1

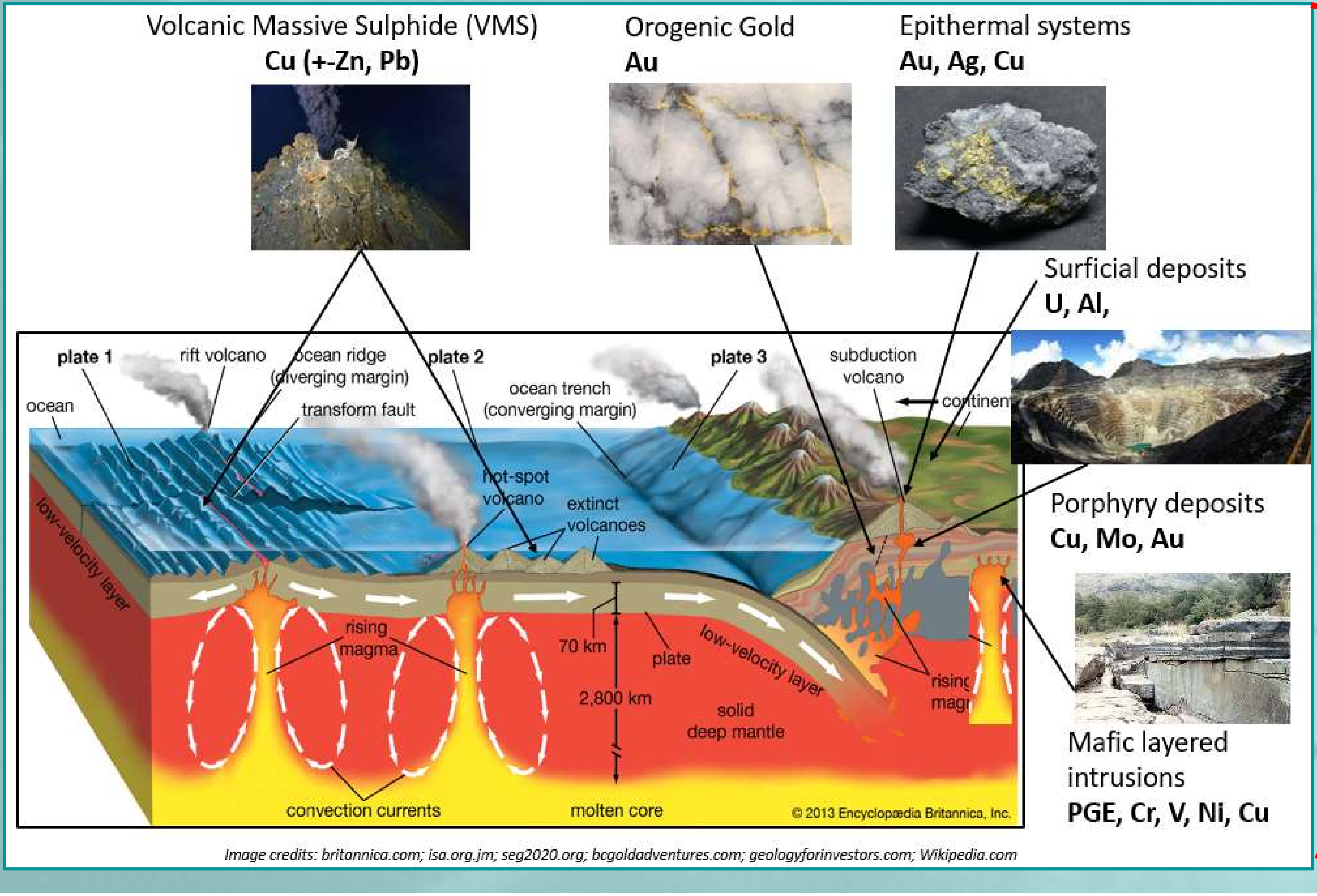


Part 2

Sphere: *realm (world) of something or physical dimensions / area of something, or both of these (Quora.com).*

Image credits: interestingengineering.com; dummies.com; geographyrealm.com

What are the Earth Sciences?



Volcanic Massive Sulphide (VMS)
Cu (+-Zn, Pb)

Orogenic Gold
Au

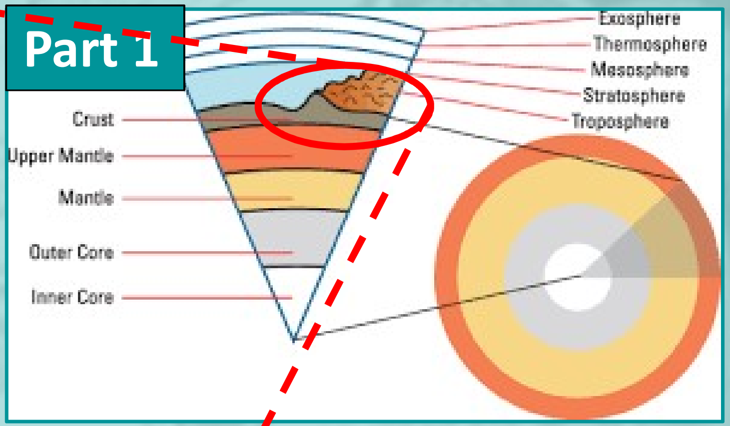
Epithermal systems
Au, Ag, Cu

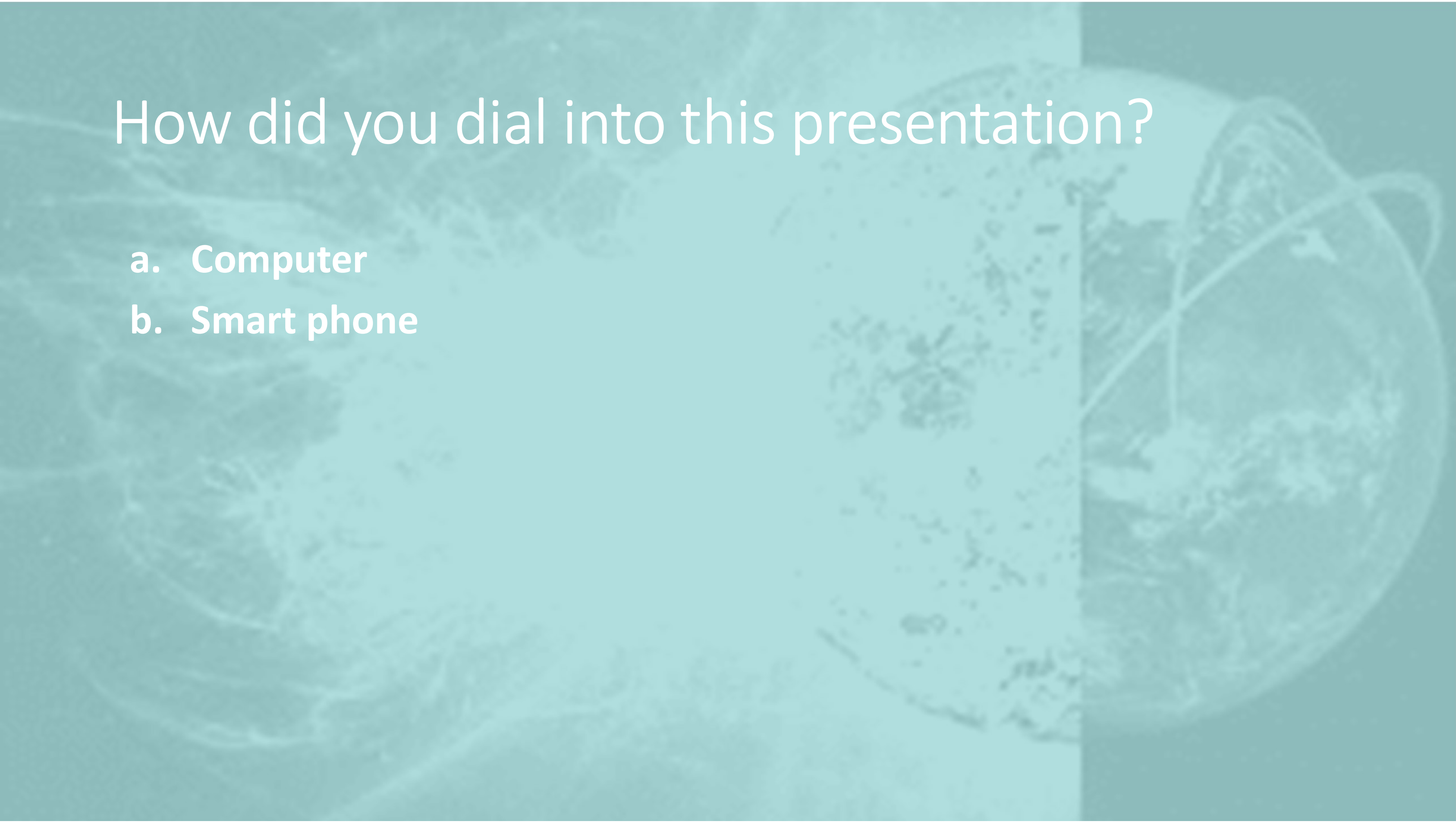
Surficial deposits
U, Al,

Porphyry deposits
Cu, Mo, Au

Mafic layered intrusions
PGE, Cr, V, Ni, Cu

Image credits: britannica.com; isa.org.jm; seg2020.org; bcgoldadventures.com; geologyforinvestors.com; Wikipedia.com





How did you dial into this presentation?

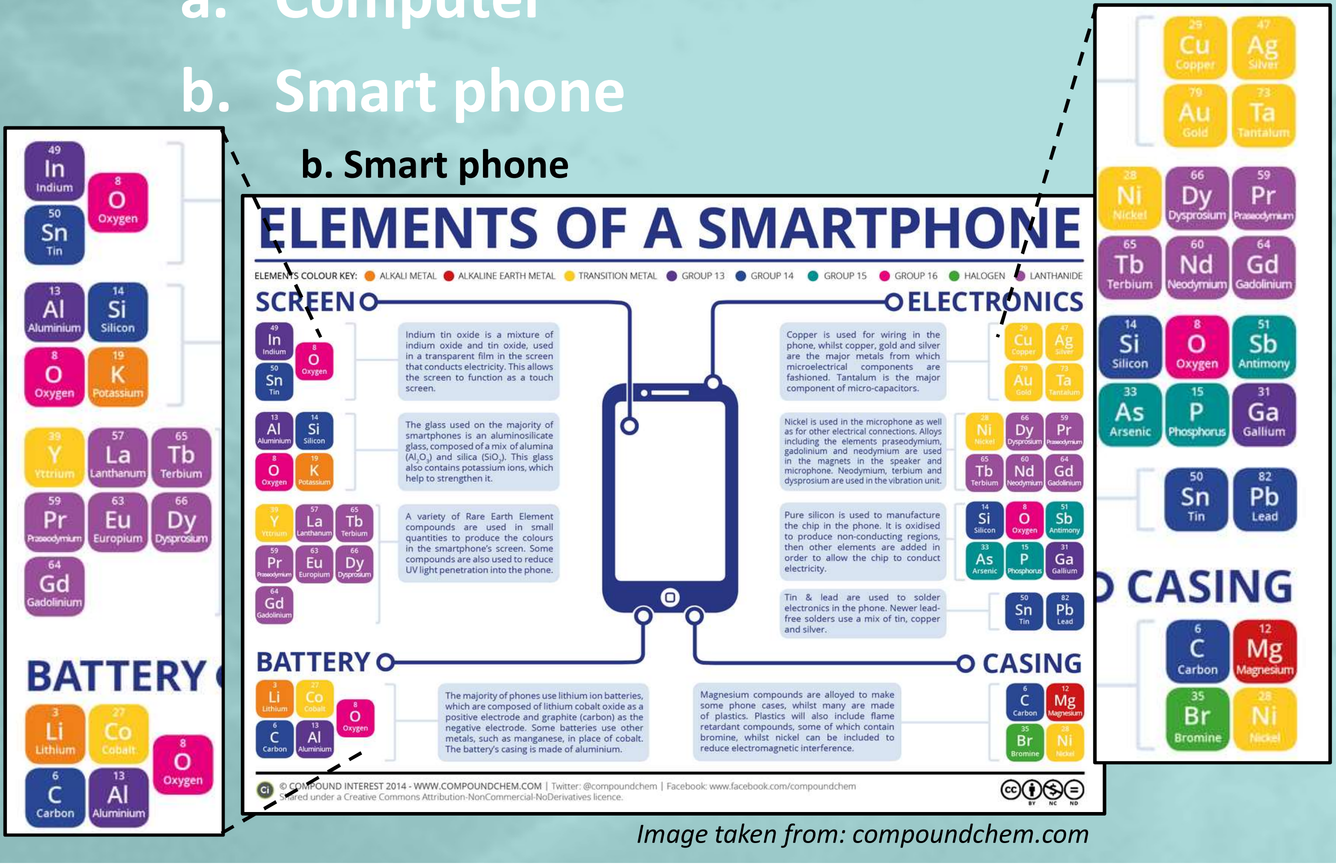
a. **Computer**
b. **Smart phone**

How did you dial into this presentation?

a. **Computer**

b. **Smart phone**

b. Smart phone



Indium tin oxide is a mixture of indium oxide and tin oxide, used in a transparent film in the screen that conducts electricity. This allows the screen to function as a touch screen.

The glass used on the majority of smartphones is an aluminosilicate glass, composed of a mix of alumina (Al_2O_3) and silica (SiO_2). This glass also contains potassium ions, which help to strengthen it.

A variety of Rare Earth Element compounds are used in small quantities to produce the colours in the smartphone's screen. Some compounds are also used to reduce UV light penetration into the phone.

Copper is used for wiring in the phone, whilst copper, gold and silver are the major metals from which microelectrical components are fashioned. Tantalum is the major component of micro-capacitors.

Nickel is used in the microphone as well as for other electrical connections. Alloys including the elements praseodymium, gadolinium and neodymium are used in the magnets in the speaker and microphone. Neodymium, terbium and dysprosium are used in the vibration unit.

Pure silicon is used to manufacture the chip in the phone. It is oxidised to produce non-conducting regions, then other elements are added in order to allow the chip to conduct electricity.

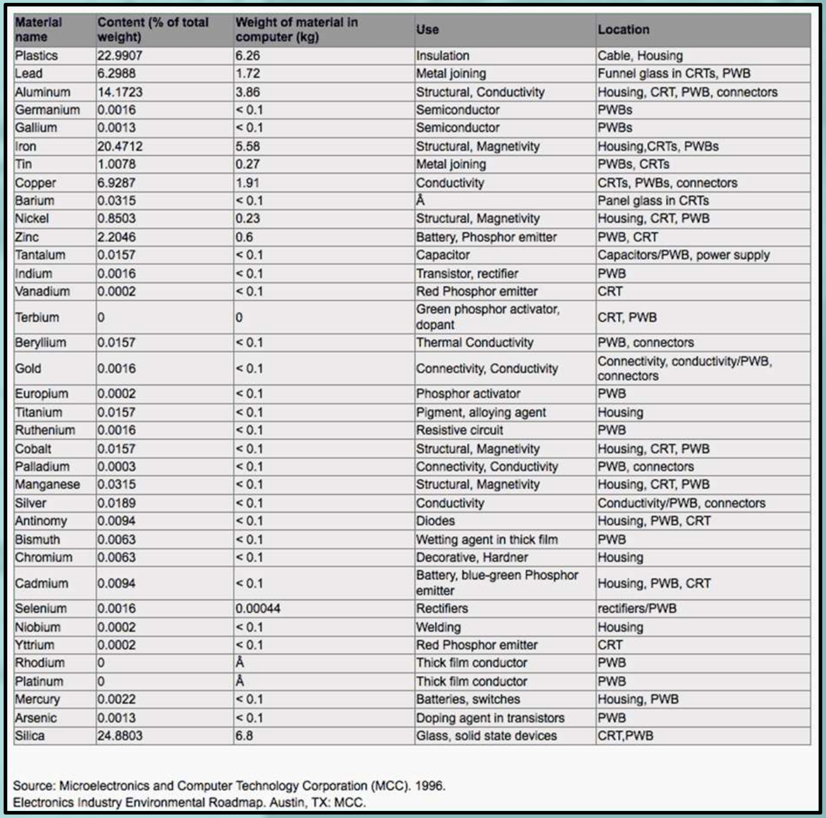
Tin & lead are used to solder electronics in the phone. Newer lead-free solders use a mix of tin, copper and silver.

The majority of phones use lithium ion batteries, which are composed of lithium cobalt oxide as a positive electrode and graphite (carbon) as the negative electrode. Some batteries use other metals, such as manganese, in place of cobalt. The battery's casing is made of aluminium.

Magnesium compounds are alloyed to make some phone cases, whilst many are made of plastics. Plastics will also include flame retardant compounds, some of which contain bromine, whilst nickel can be included to reduce electromagnetic interference.

Image taken from: compoundchem.com

a. Computer



Material name	Content (% of total weight)	Weight of material in computer (kg)	Use	Location
Plastics	22.9907	6.26	Insulation	Cable, Housing
Lead	6.2988	1.72	Metal joining	Funnel glass in CRTs, PWB
Aluminum	14.1723	3.86	Structural, Conductivity	Housing, CRT, PWB, connectors
Germanium	0.0016	< 0.1	Semiconductor	PWBs
Gallium	0.0013	< 0.1	Semiconductor	PWBs
Iron	20.4712	5.58	Structural, Magnetivity	Housing,CRTs, PWBs
Tin	1.0078	0.27	Metal joining	PWBs, CRTs
Copper	6.9287	1.91	Conductivity	CRTs, PWBs, connectors
Barium	0.0315	< 0.1	Å	Panel glass in CRTs
Nickel	0.8503	0.23	Structural, Magnetivity	Housing, CRT, PWB
Zinc	2.2046	0.6	Battery, Phosphor emitter	PWB, CRT
Tantalum	0.0157	< 0.1	Capacitor	Capacitors/PWB, power supply
Indium	0.0016	< 0.1	Transistor, rectifier	PWB
Vanadium	0.0002	< 0.1	Red Phosphor emitter	CRT
Terbium	0	0	Green phosphor activator, dopant	CRT, PWB
Beryllium	0.0157	< 0.1	Thermal Conductivity	PWB, connectors
Gold	0.0016	< 0.1	Connectivity, Conductivity	Connectivity, conductivity/PWB, connectors
Europium	0.0002	< 0.1	Phosphor activator	PWB
Titanium	0.0157	< 0.1	Pigment, alloying agent	Housing
Ruthenium	0.0016	< 0.1	Resistive circuit	PWB
Cobalt	0.0157	< 0.1	Structural, Magnetivity	Housing, CRT, PWB
Palladium	0.0003	< 0.1	Connectivity, Conductivity	PWB, connectors
Manganese	0.0315	< 0.1	Structural, Magnetivity	Housing, CRT, PWB
Silver	0.0189	< 0.1	Conductivity	Conductivity/PWB, connectors
Antinomy	0.0094	< 0.1	Diodes	Housing, PWB, CRT
Bismuth	0.0063	< 0.1	Wetting agent in thick film	PWB
Chromium	0.0063	< 0.1	Decorative, Hardner	Housing
Cadmium	0.0094	< 0.1	Battery, blue-green Phosphor emitter	Housing, PWB, CRT
Selenium	0.0016	0.00044	Rectifiers	rectifiers/PWB
Niobium	0.0002	< 0.1	Welding	Housing
Yttrium	0.0002	< 0.1	Red Phosphor emitter	CRT
Rhodium	0	Å	Thick film conductor	PWB
Platinum	0	Å	Thick film conductor	PWB
Mercury	0.0022	< 0.1	Batteries, switches	Housing, PWB
Arsenic	0.0013	< 0.1	Doping agent in transistors	PWB
Silica	24.8803	6.8	Glass, solid state devices	CRT,PWB

Source: Microelectronics and Computer Technology Corporation (MCC). 1996. Electronics Industry Environmental Roadmap. Austin, TX: MCC.

Image taken from: specialtymetals.com

Importance of earth sciences to society

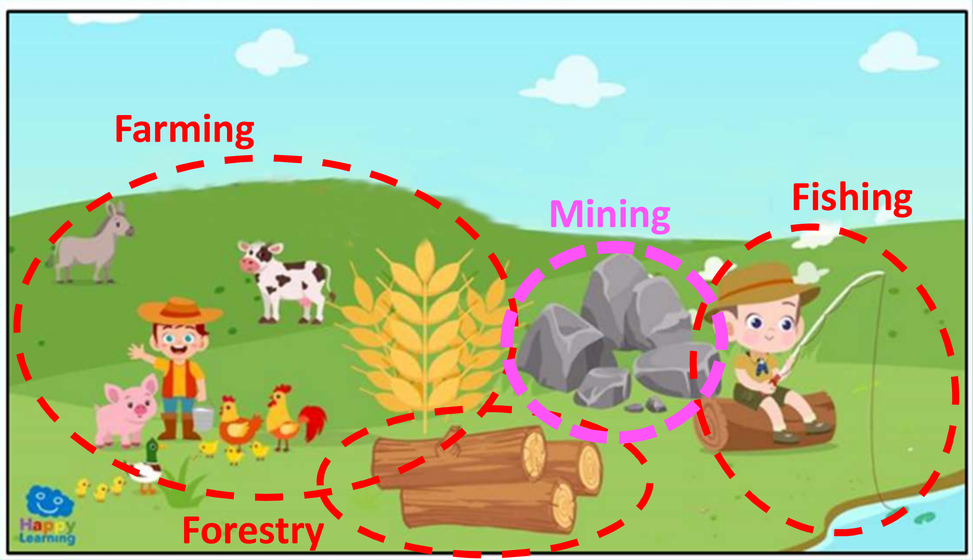


Image taken from: happylearning.tv

- The African economy is still highly reliant on the ‘primary sector’ as a major income generator which sustains millions of livelihoods.
- Direct linkages between earth sciences and mining, less direct linkages with forestry, fishing and agriculture.
- However, these latter sectors certainly require a healthy natural environment.


Journal of African Earth Sciences 172 (2020) 104012

Contents lists available at ScienceDirect

Journal of African Earth Sciences

journal homepage: www.elsevier.com/locate/jafrearsci

Synchrotron X-ray radiation and the African earth sciences: A critical review

Bjorn P. von der Heyden[a,*], Julien Benoit[b], Vincent Fernandez[c,d], Alakendra N. Roychoudhury[a]

[a] Department of Earth Sciences, Stellenbosch University, Private Bag X1, Matieland, 7602, South Africa
[b] Evolutionary Studies Institute (ESI) and School of Geosciences, University of the Witwatersrand, PO Wits, 2050, Johannesburg, South Africa
[c] European Synchrotron Radiation Facility, Beamline ID19, 71 rue des Martyrs, 38000, Grenoble, France
[d] Imaging and Analysis Centre, Natural History Museum, Cromwell Road SW7 5BD London, UK

ARTICLE INFO

Keywords:
Synchrotron
X-rays
Geology
Geochemistry
Palaeontology

ABSTRACT

Synchrotron-based X-ray analytical techniques are gaining in prominence as a crucial yet highly specialized tool for advancing knowledge within the broad field of the Earth Sciences. In terms of global scientific competitiveness, African scientists are somewhat disadvantaged by not having access to their own synchrotron on the African continent. However, there currently exists a strong drive towards obtaining a synchrotron X-ray facility on the African continent and the purpose of this critical and timeous review is thus to highlight the importance of such equipment for the local earth science community (e.g., geologists, geochemists and palaeontologists). Our review shows that various high-level synchrotron X-ray spectroscopies have been successfully applied to African earth samples and that the outputs of these studies have measurable societal benefit in terms of improved understanding of fundamental earth processes (including the molecular level controls on earth climate cycles), improved characterization of important and economic ore commodities (including drill core samples), and improved understanding of the fate and mobility of deleterious elements in the surface environment (e.g. soils and waterways). Similarly, the high phase contrast and rapid acquisition capabilities of synchrotron X-ray computed tomography (sXCT) have added important insights into a wealth of samples derived from Africa's fossil inventory (>350 specimens). Not only these studies advance our understanding of all ancient life forms, shedding light on our origins, they contributed to the training of the next generation of palaeontologists and the dissemination of science in Africa. It is foreseen that this review will stimulate further use of synchrotron technologies by the local earth science community whilst concomitantly developing a strong scientific case for considering and incorporating the needs of the earth sciences when the time comes to develop an African synchrotron facility (i.e., the African Lightsource).

1. Introduction

Synchrotron ‘light’ comprises electromagnetic waves ranging from the infra-red range (−1 meV–1.6 eV) to the short-wavelength ‘hard’ X-ray energy range (i.e., >5 keV). Although light of these wavelengths is commonly produced by bench-scale equipment, synchrotron facilities produce much ‘brighter’ light by utilizing electromagnets to accelerate particles around large circular trajectories (e.g., the European Synchrotron Radiation Facility (ESRF) has a circumference of 844 m and produces X-rays that are 100 billion times brighter than those produced by hospital X-ray equipment (www.esrf.eu)). Although synchrotron light sources have been operational since 1968 (Winick, 1997), rampant technological and computational advancements have firmly established the era of third- and fourth generation light sources (Beaurepaire et al., 2013; Ice et al., 2011). These so-called Advanced Light Sources (AdLS) are characterised by ultra-high brilliance light (i.e., greater than 10^{22} photons/sec/0.1%BW/mm^2/mrad^2 (Ice et al., 2011)), which renders them particularly useful for conducting high-calibre science using a variety of synchrotron analytical methodologies (Table 1). For example, ultra-high brilliance synchrotron light is now capable of mapping chemical distributions at <10 nm resolution; measuring elemental concentration in the sub-ppm range (e.g. (Stromberg et al., 2019));

---

[*] Corresponding author.
E-mail address: bvon@sun.ac.za (B.P. von der Heyden).

https://doi.org/10.1016/j.jafrearsci.2020.104012
Received 8 April 2020; Received in revised form 4 September 2020; Accepted 15 September 2020

Importance of mineral commodities to society

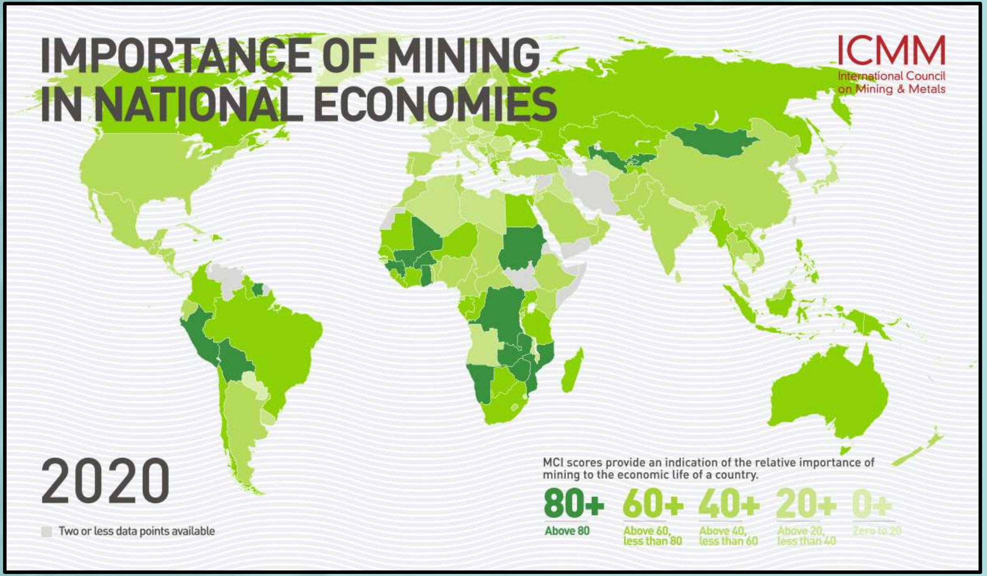


Image taken from: www.icmm.com (5th Mining Contribution Index (2020))

- The African economy is still highly reliant on the 'primary sector' as a major income generator which sustains millions of livelihoods.
- Direct linkages between earth sciences and mining, less direct linkages with forestry, fishing and agriculture.
- However, these latter sectors certainly require a healthy natural environment.
- Focus on the mining sector and its effect on the environment.

Ore Geology Reviews 117 (2020) 103328

Contents lists available at ScienceDirect

Ore Geology Reviews

journal homepage: www.elsevier.com/locate/oregeorev

Review

Shedding light on ore deposits: A review of synchrotron X-ray radiation use in ore geology research

Bjorn P. von der Heyden

Department of Earth Sciences, Stellenbosch University, Stellenbosch 7600, South Africa

ARTICLE INFO

Keywords:
Synchrotron
X-rays
XANES
EXAFS
XAS
XRF
Mineralisation

ABSTRACT

Geology researchers commonly confront critical research questions that require microscopic and sub-microscopic level observations (e.g., distribution of chemical elements of economic interest, nature of mineralising fluid) in order to explain the macroscale phenomena related to the characterisation of and controls on ore mineralisation. The emergence and technological evolution of fourth generation synchrotron radiation light sources render these facilities as important, but still largely under-utilised tools for advancing the frontiers of ore related research. To this end, the present contribution seeks to critically review and highlight the power and affordances of synchrotron X-ray techniques specifically to the fields of fundamental- and applied ore geology. The review introduces a range of commonly applied synchrotron X-ray techniques, before comprehensively highlighting past applications of synchrotron X-rays to a range of commodities and ore deposits types. A synthesis of this information highlights the historical importance of synchrotron X-ray techniques towards (1) understanding ore textures and chemical relationships at high (μm) spatial resolutions; (2) understanding coordination chemistry of metals in aqueous fluids at geologically relevant P-T conditions; (3) in situ evaluation of the chemistry and speciation of fluid inclusions; (4) evaluating the coordination environment of deleterious and economic trace metal substitutions in major mineral structures; and (5) understanding the biogeochemical behaviour and transformations of metals in the low temperature (supergene) mineralising environment. These applications as well as recommendations for future work are described in the hope that a greater diversity of ore geology researchers will incorporate synchrotron X-ray tools into their existing suite of analytical and experimental techniques.

1. Introduction

Although storage ring synchrotron light sources have been operational since 1968 (Winick, 1997), the use of this technology for ore deposit research has only really started to gain prominence over the last 10–15 years (Fig. 1). Early work in 1980's included a synchrotron X-ray Flourescence (sXRF) investigation into Au concentrations in pyrite from a Carlin-type Au ore sample (Chen et al., 1987), and structural investigations of the chemical coordination of ore metals (e.g., Cu, Ag (Charnock et al., 1989, 1988); Ge (Bernstein and Waychunas, 1987)) in ore minerals. Since then, synchrotron science has evolved significantly through extensive technological, theoretical, and computational advancements. The current review is thus timeous as we now straddle the advent of the era of ultrahigh brilliance fourth generation synchrotron light sources (Ice et al., 2011; Beaurepaire et al., 2013). The enhanced brilliance of these lights sources will markedly improve on the affordances that synchrotron X-rays offer to scientists interested in the molecular-level to mineral-scale properties of ore deposits and the reactions resulting in their formation. For example, the spatial resolution of fourth generation light sources is expected to allow chemical mapping at spatial step sizes less than 10 nm; the spectral resolution in the hard X-ray range is now on the order of 0.05 eV (Merkulova et al., 2019), and the detection limits for the various X-ray analytical techniques will enable improved measurements at concentrations of less than 1 ppm (Stromberg et al., 2019).

Previous reviews of the application of synchrotron light to the geological sciences include works by Basset and Brown (1990), Henderson et al. (1995), Henderson and Baker (2002), Jones (2000), Quartieri (2016). In addition, several critical reviews focus on key thematic areas such as the utilisation of synchrotron microtomography in structural geology (Fussels et al., 2014), and the low temperature biogeochemistry minerals and their associated metals (Kemner et al., 2005; Templeton and Knowles, 2009). An important contribution by Brugger et al. (2010) represents the most recent review of synchrotron (and neutron) studies focussed on the broad theme of ore geology (Brugger et al., 2010), and (Stromberg et al., 2019) provides a detailed

E-mail address: bvon@sun.ac.za.

https://doi.org/10.1016/j.oregeorev.2020.103328
Received 8 March 2019; Received in revised form 5 September 2019; Accepted 10 January 2020
Available online 13 January 2020
0169-1368/ © 2020 Elsevier B.V. All rights reserved.

Journal of African Earth Sciences 172 (20

Contents lists available at Scien

Journal of African Ear

journal homepage: www.elsevier.c

Synchrotron X-ray radiation and the African ea
critical review

Bjorn P. von der Heyden [a,*], Julien Benoit [b], Vincent Fern
Alakendra N. Roychoudhury [a]

[a] Department of Earth Sciences, Stellenbosch University, Private Bag X1, Matieland, 7602, South A
[b] Evolutionary Studies Institute (ESI) and School of Geosciences, University of the Witwatersrand,
[c] European Synchrotron Radiation Facility, Beamline ID19, 71 rue des Martyrs, 38000, Grenoble,
[d] Imaging and Analysis Centre, Natural History Museum, Cromwell Road SW7 5BD London, UK

ARTICLE INFO

Keywords:
Synchrotron
X-rays
Geology
Geochemistry
Palaeontology

ABSTRACT

Synchrotron-based X-ray ar
for advancing knowledge
tiveness, African scientists
African continent. Howev
on the African continent
such equipment for the
review shows that vario
earth samples and that
derstanding of fundam
improved characteriz
improved understand
and waterways). Sin
computed tomograp
fossil inventory (>3
shedding light on o
dissemination of s
technologies by th
considering and t
chrotron facility (i.e.,

1. Introduction

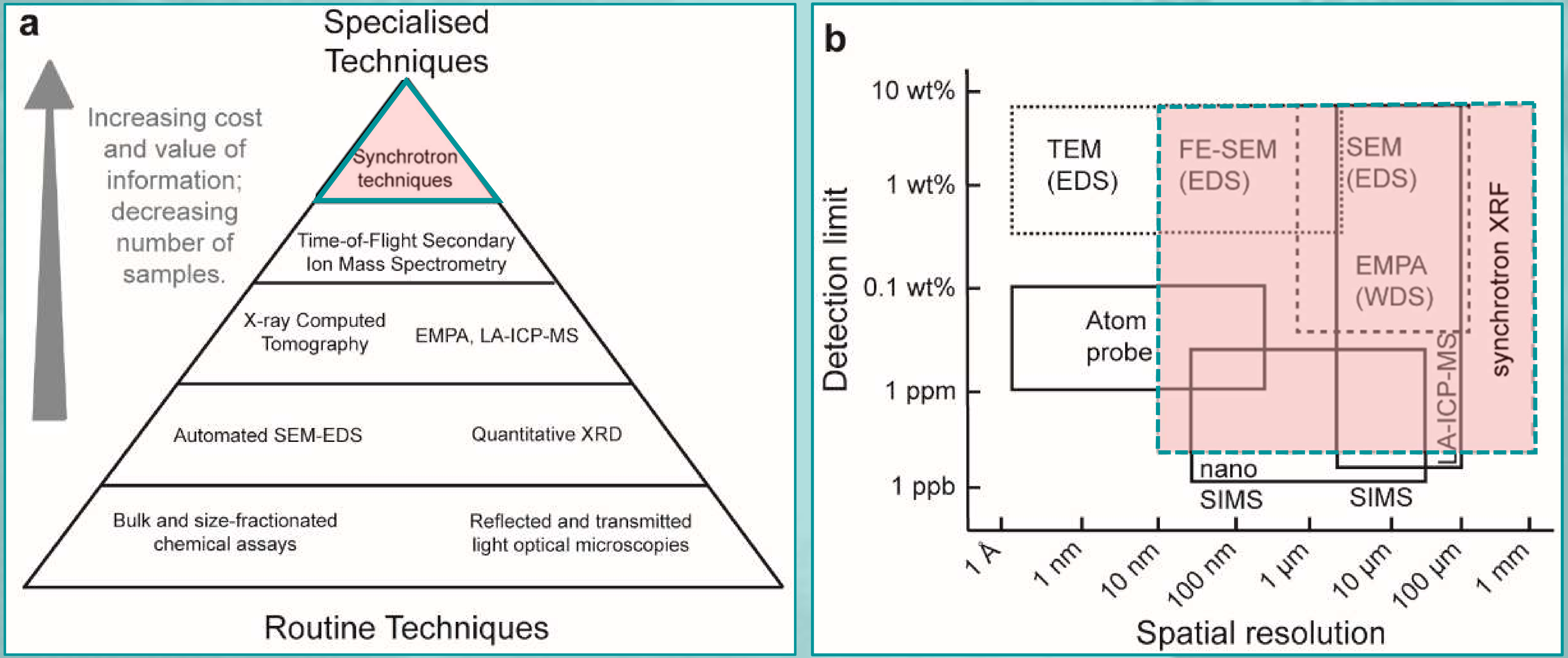
Synchrotron 'light' comprises electromagnetic waves ranging from the infra-red range (~1 meV–1.6 eV) to the short-wavelength 'hard' X-ray energy range (i.e., >5 keV). Although light of these wavelengths is commonly produced by bench-scale equipment, synchrotron facilities produce much 'brighter' light by utilizing electromagnets to accelerate particles around large circular trajectories (e.g., the European Synchrotron Radiation Facility (ESRF) has a circumference of 844 m and produces X-rays that are 100 billion times brighter than those produced by hospital X-ray equipment (www.esrf.eu)). Although synchrotron light sources have been operational since 1968 (
technological and computational advancements have firmly estab
the era of third- and fourth generation light sources (Beaurepaire et al., 2013; Ice et al., 2011). These so-called Advanced Light Sources (AdLS) are characterised by ultra-high brilliance light (i.e., greater than 10^{22} photons/sec/0.1%BW/mm^2/mrad^2 (Ice et al., 2011)), which renders them particularly useful for conducting high-calibre science using a variety of synchrotron analytical methodologies (Table 1). For example, ultra-high brilliance synchrotron light is now capable of mapping chemical distributions at <10 nm resolution; measuring elemental concentration in the sub-ppm range (e.g. (Stromberg et al., 2019));

---

* Corresponding author.
E-mail address: bvon@sun.ac.za (B.P. von der Heyden).

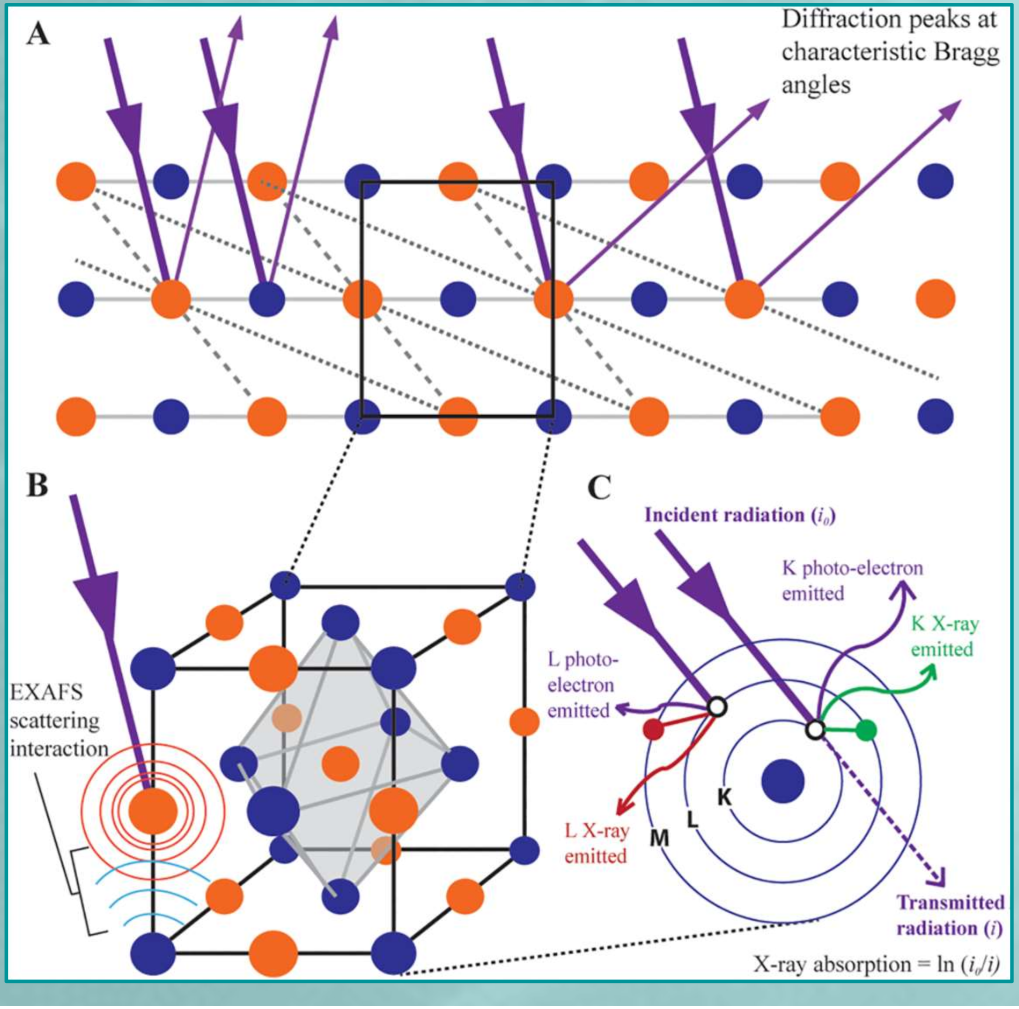
https://doi.org/10.1016/j.jafrearsci.2020.104012
Received 8 April 2020; Received in revised form 4 September 2020; Accepted 15 September 2020
Available online 21 September 2020
1464-343X/© 2020 Elsevier Ltd. All rights reserved.

Synchrotron light and ore deposits



Figures from von der Heyden et al. (2020), originally adapted respectively from Becker et al (2016), and Reich et al. (2017) and Stromberg et al. (2019).

Synchrotron light and ore deposits



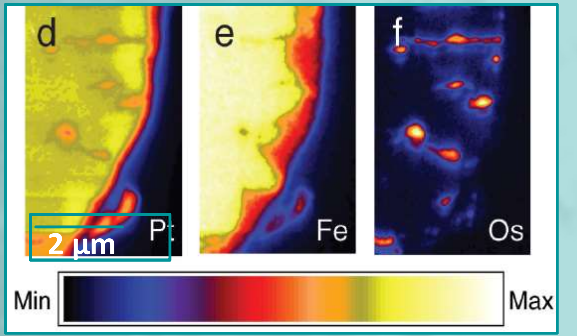
Von der Heyden, 2020

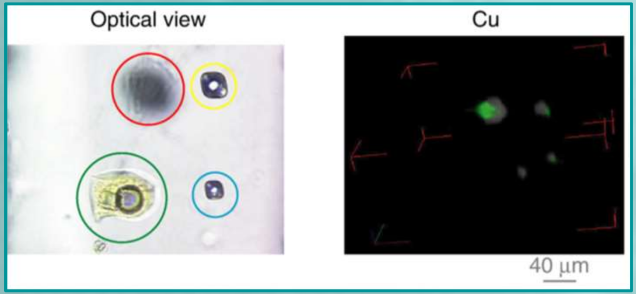
- Energy tuneability
- Excellent spatial resolutions
- Sub-ppm concentration detection limits.
- Chemical insights into the molecular-level bonding environments.

Synchrotron light and ore deposits

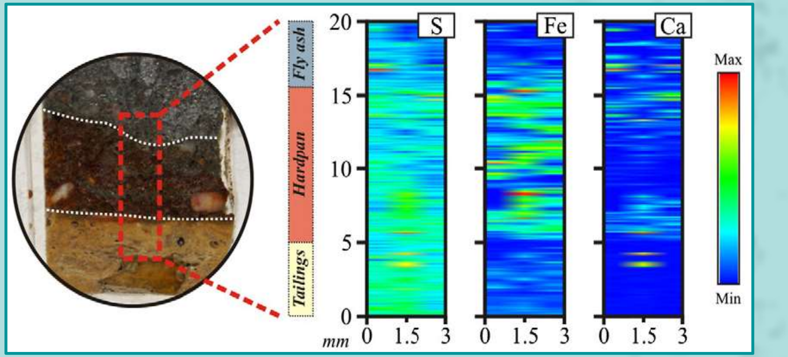
Based on three fundamental properties:

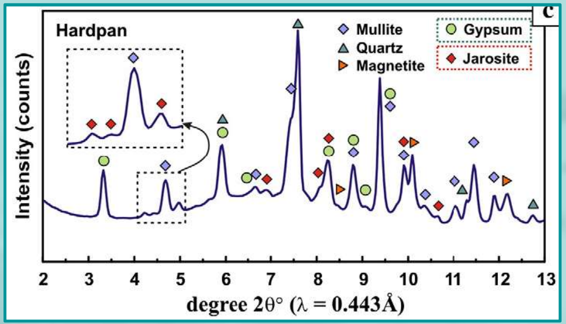
X-ray imaging:



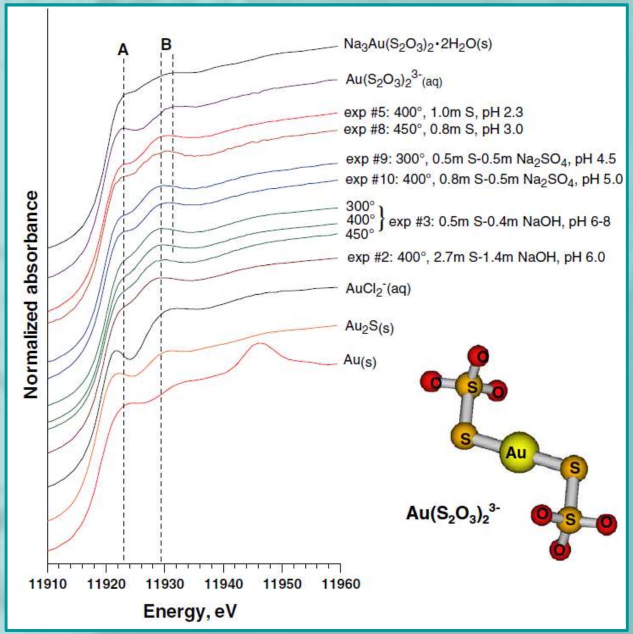


X-ray scattering:





X-ray spectroscopy:

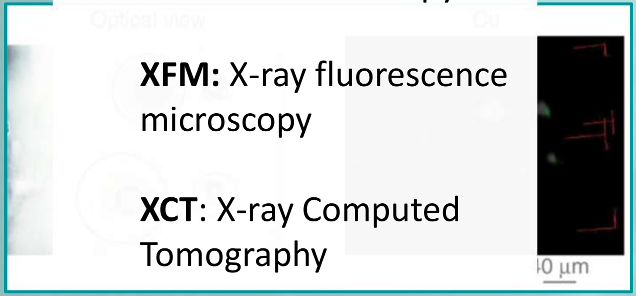


Images from various published literature sources. Subject to copyright.

Synchrotron light and ore deposits

Based on three fundamental properties:

X-ray imaging:



e.g.;

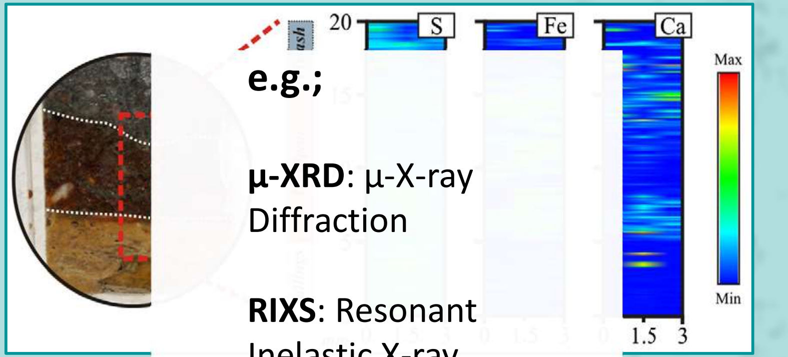
STXM: Scanning Transmission X-ray Microscopy

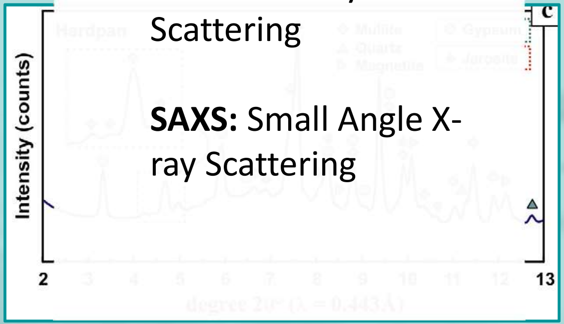
PEEM: Photoelectron Emission Microscopy

XFM: X-ray fluorescence microscopy

XCT: X-ray Computed Tomography

X-ray scattering:





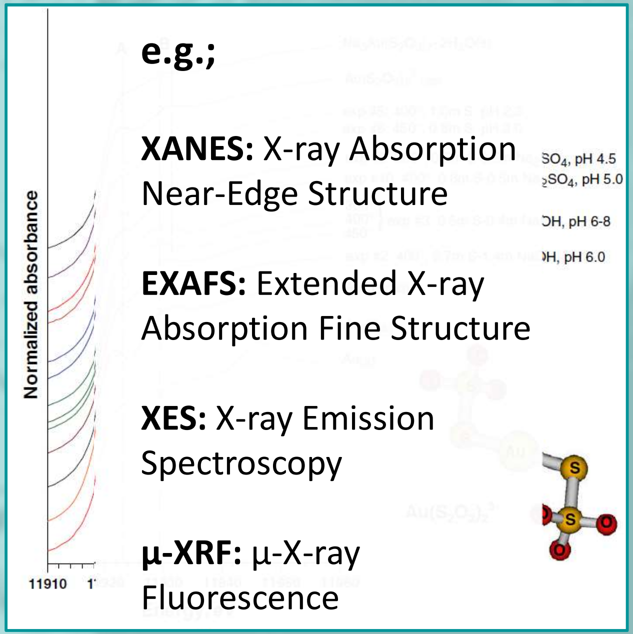
e.g.;

µ-XRD: µ-X-ray Diffraction

RIXS: Resonant Inelastic X-ray Scattering

SAXS: Small Angle X-ray Scattering

X-ray spectroscopy:



e.g.;

XANES: X-ray Absorption Near-Edge Structure

EXAFS: Extended X-ray Absorption Fine Structure

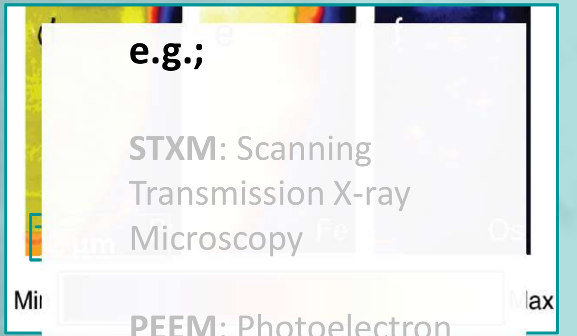
XES: X-ray Emission Spectroscopy

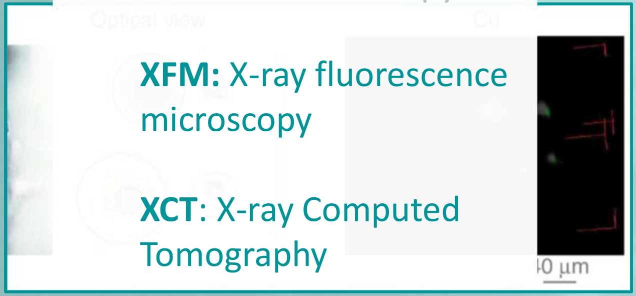
µ-XRF: µ-X-ray Fluorescence

Synchrotron light and ore deposits

Based on three fundamental properties:

X-ray imaging:





e.g.;

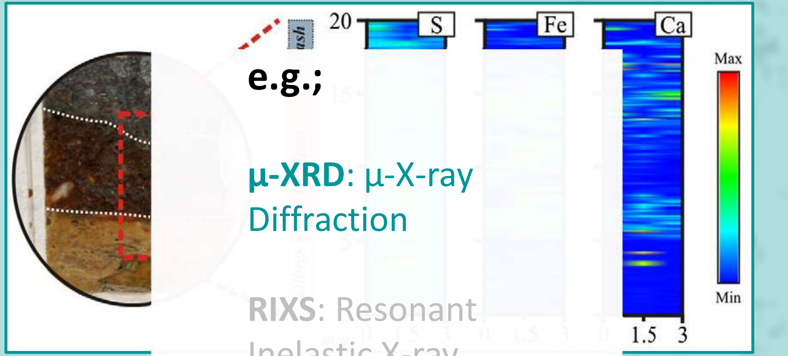
STXM: Scanning Transmission X-ray Microscopy

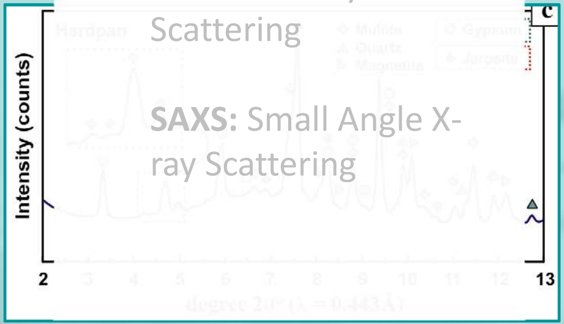
PEEM: Photoelectron Emission Microscopy

XFM: X-ray fluorescence microscopy

XCT: X-ray Computed Tomography

X-ray scattering:





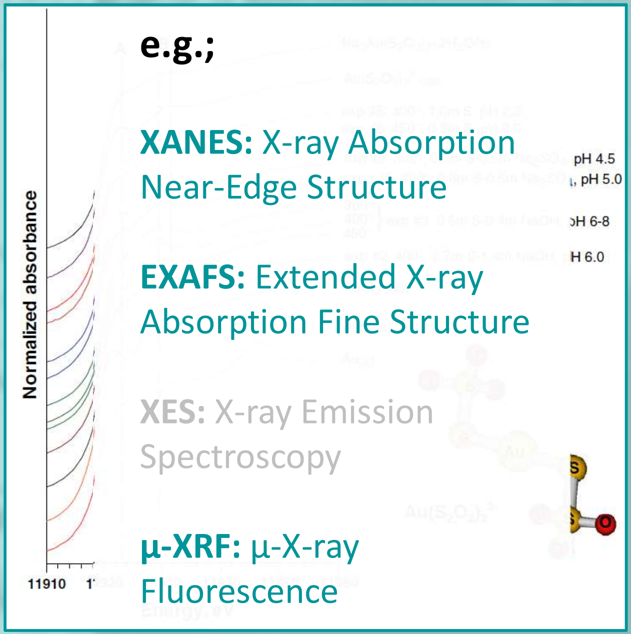
e.g.;

µ-XRD: µ-X-ray Diffraction

RIXS: Resonant Inelastic X-ray Scattering

SAXS: Small Angle X-ray Scattering

X-ray spectroscopy:



e.g.;

XANES: X-ray Absorption Near-Edge Structure

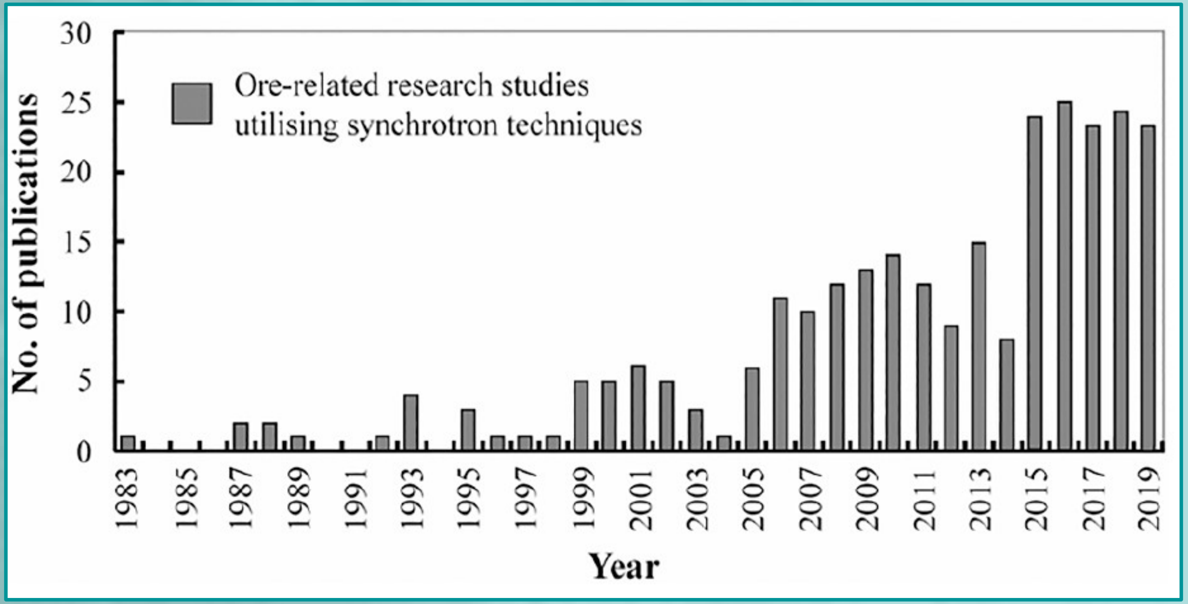
EXAFS: Extended X-ray Absorption Fine Structure

XES: X-ray Emission Spectroscopy

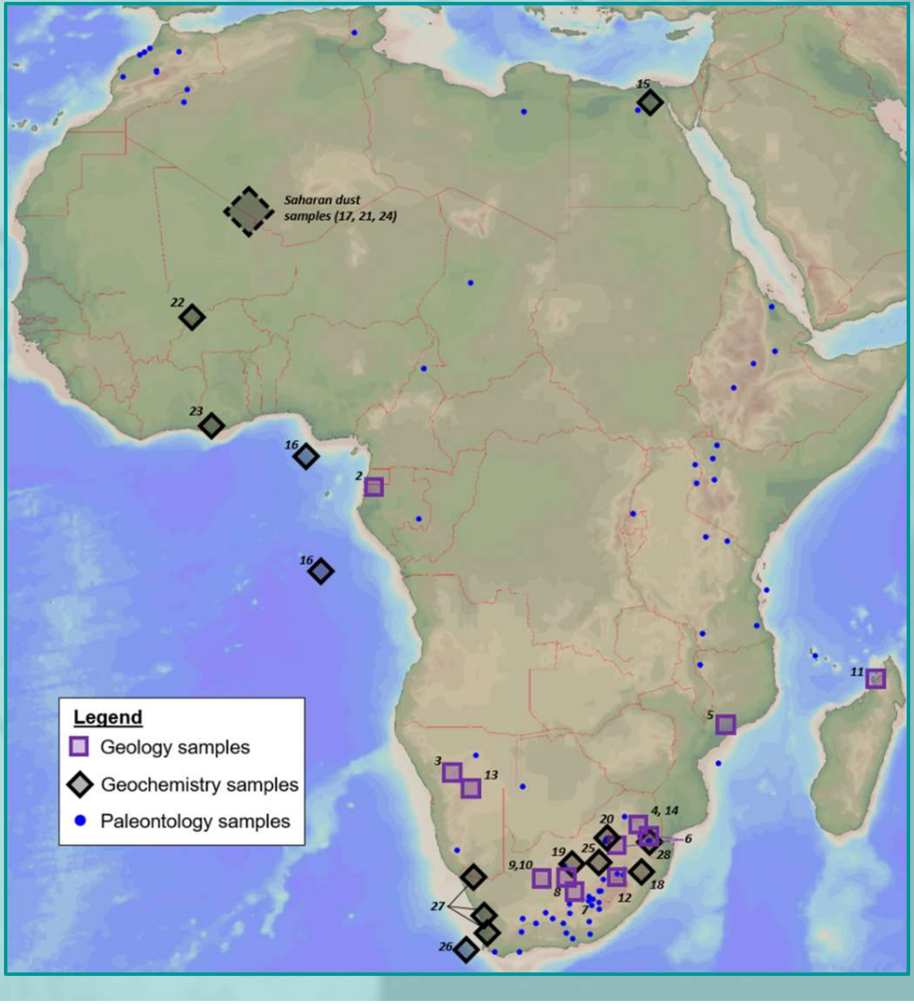
µ-XRF: µ-X-ray Fluorescence

Images from various published literature sources. Subject to copyright.

Synchrotron light and ore deposits

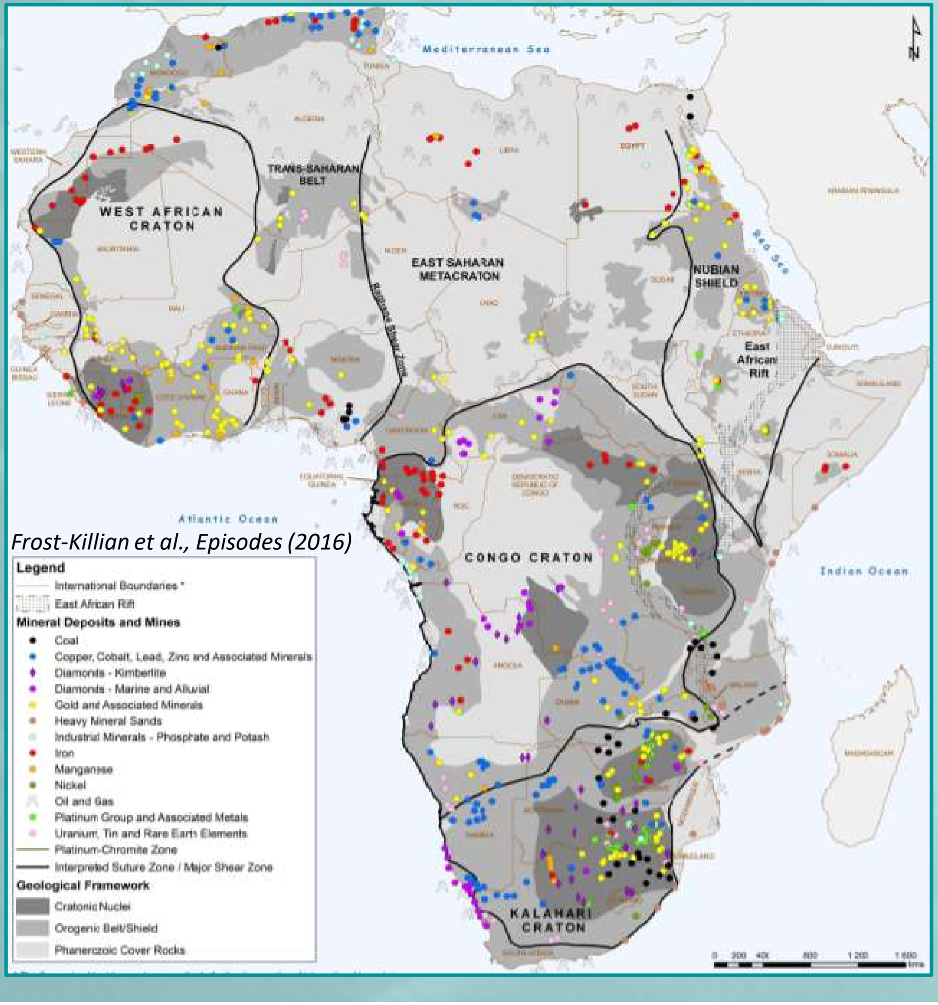


Von der Heyden, 2020

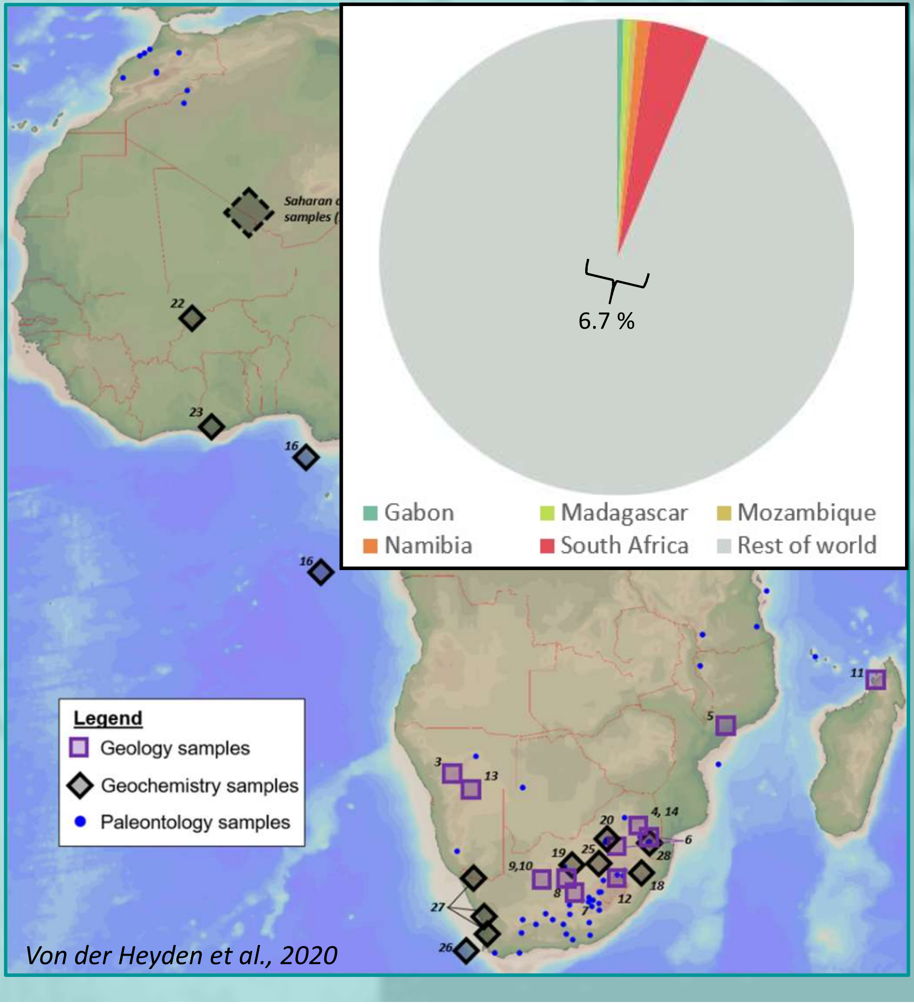


Von der Heyden et al., 2020

Synchrotron light and ore deposits

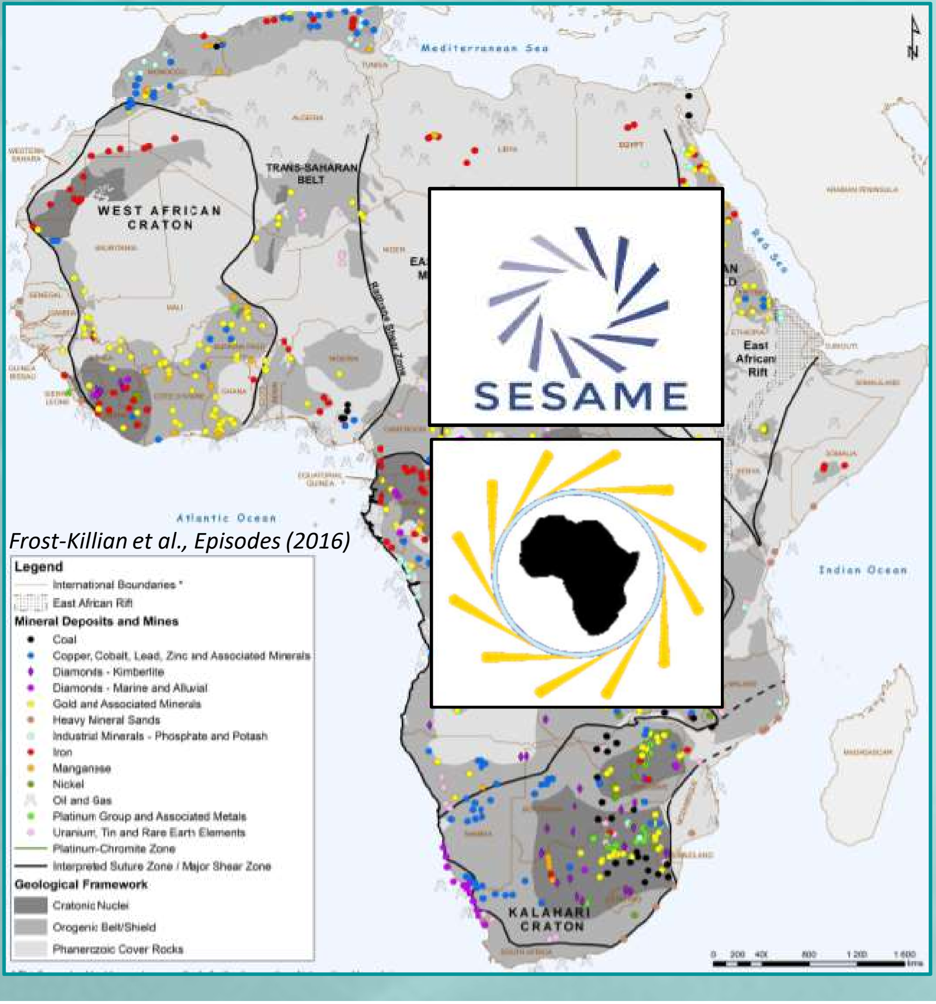


Frost-Killian et al., Episodes (2016)



Von der Heyden et al., 2020

Synchrotron light and ore deposits

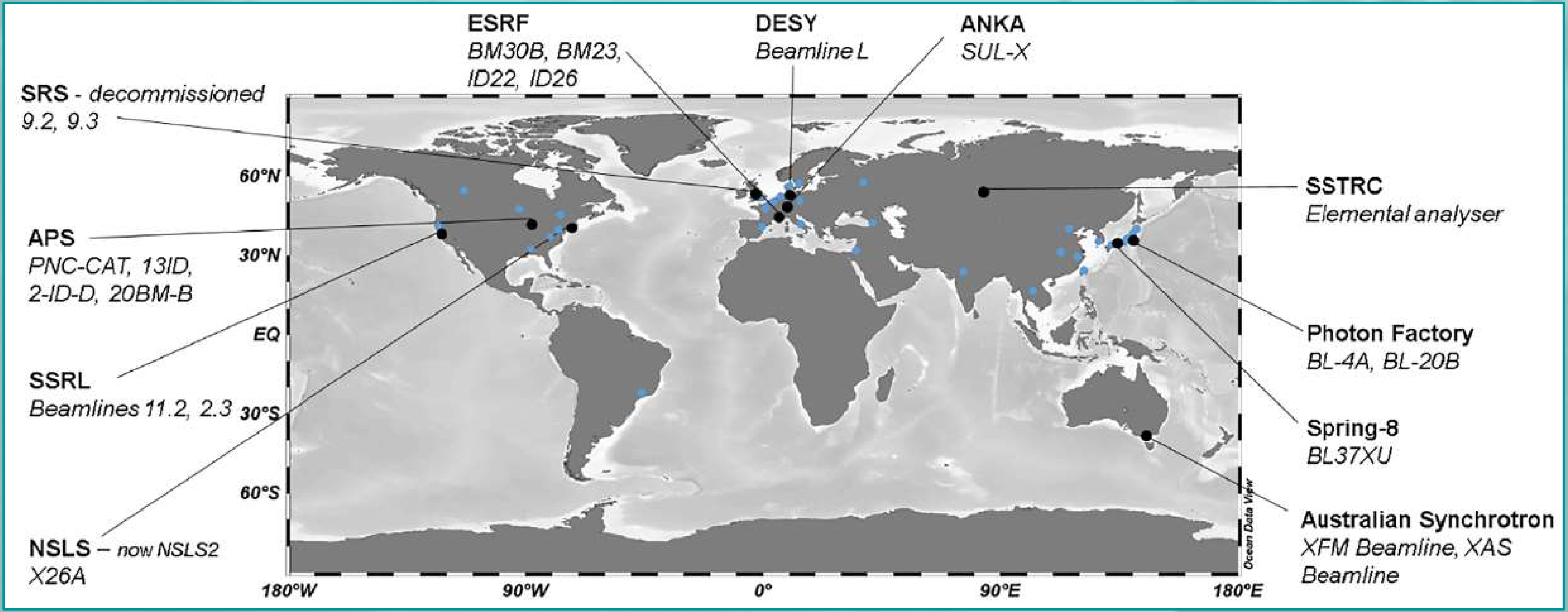


Frost-Killian et al., Episodes (2016)

- African samples under-represented despite significant mineral endowments.
- African earth science researchers under-represented in the global research arena.
- African light source or collaborations with partners to mitigate these under representations.

Synchrotron light and ore deposits

Synchrotrons and beamlines most frequently used in ore geology research:

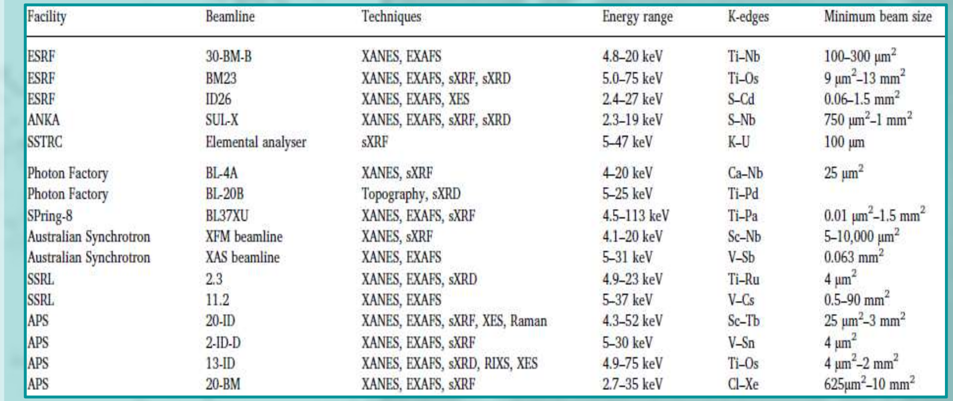


Von der Heyden, 2020

Synchrotron light and ore deposits

Synchrotrons and beamlines most frequently used in ore geology research:

- Factors to consider in selecting a beamline:
    - sXRF (mapping) versus XANES/EXAFS (spectroscopy).

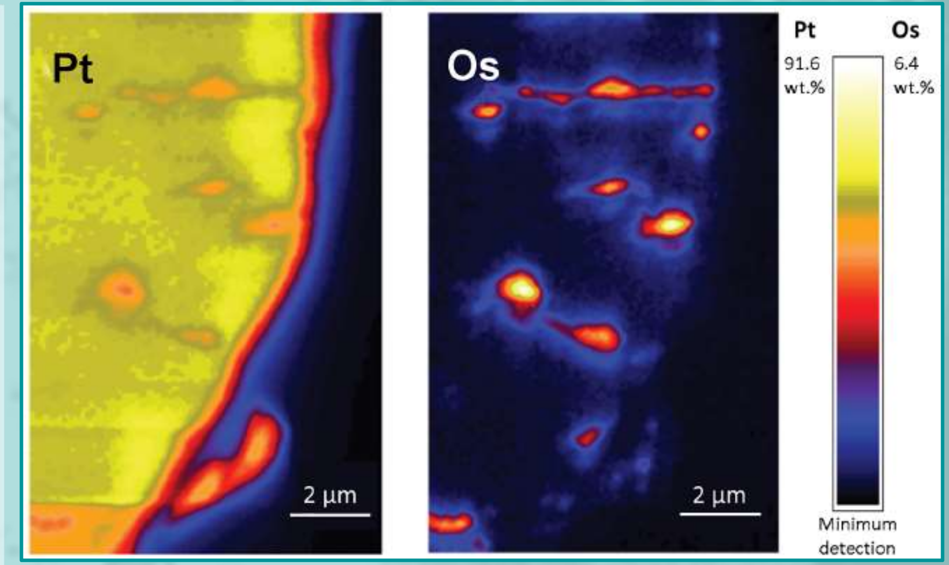


Facility	Beamline	Techniques	Energy range	K-edges	Minimum beam size
ESRF	30-BM-B	XANES, EXAFS	4.8–20 keV	Ti–Nb	100–300 μm^2
ESRF	BM23	XANES, EXAFS, sXRF, sXRD	5.0–75 keV	Ti–Os	9 μm^2–13 mm^2
ESRF	ID26	XANES, EXAFS, XES	2.4–27 keV	S–Cd	0.06–1.5 mm^2
ANKA	SUL-X	XANES, EXAFS, sXRF, sXRD	2.3–19 keV	S–Nb	750 μm^2–1 mm^2
SSTRC	Elemental analyser	sXRF	5–47 keV	K–U	100 µm
Photon Factory	BL-4A	XANES, sXRF	4–20 keV	Ca–Nb	25 μm^2
Photon Factory	BL-20B	Topography, sXRD	5–25 keV	Ti–Pd	
SPring-8	BL37XU	XANES, EXAFS, sXRF	4.5–113 keV	Ti–Pa	0.01 μm^2–1.5 mm^2
Australian Synchrotron	XFM beamline	XANES, sXRF	4.1–20 keV	Sc–Nb	5–10,000 μm^2
Australian Synchrotron	XAS beamline	XANES, EXAFS	5–31 keV	V–Sb	0.063 mm^2
SSRL	2.3	XANES, EXAFS, sXRD	4.9–23 keV	Ti–Ru	4 μm^2
SSRL	11.2	XANES, EXAFS	5–37 keV	V–Cs	0.5–90 mm^2
APS	20-ID	XANES, EXAFS, sXRF, XES, Raman	4.3–52 keV	Sc–Tb	25 μm^2–3 mm^2
APS	2-ID-D	XANES, EXAFS, sXRF	5–30 keV	V–Sn	4 μm^2
APS	13-ID	XANES, EXAFS, sXRD, RIXS, XES	4.9–75 keV	Ti–Os	4 μm^2–2 mm^2
APS	20-BM	XANES, EXAFS, sXRF	2.7–35 keV	Cl–Xe	625μm^2–10 mm^2

Synchrotron light and ore deposits

Synchrotrons and beamlines most frequently used in ore geology research:

- Factors to consider in selecting a beamline:
  - sXRF (mapping) versus XANES/EXAFS (spectroscopy).
  - Energy range required.
  - High spatial resolution for sXRF mapping.

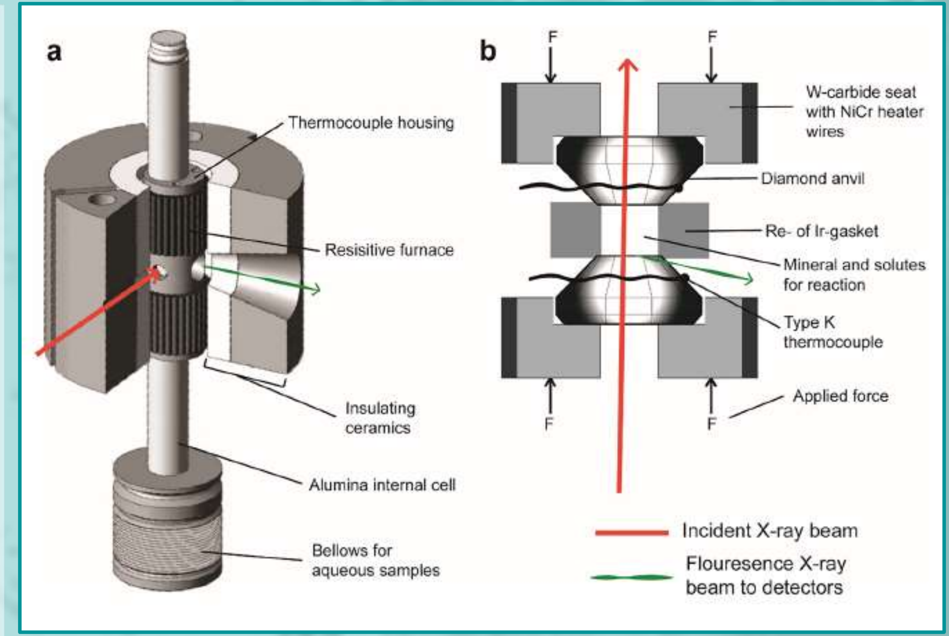


Campbell et al. 2015

Synchrotron light and ore deposits

Synchrotrons and beamlines most frequently used in ore geology research:

- Factors to consider in selecting a beamline:
    - sXRF (mapping) versus XANES/EXAFS (spectroscopy).
    - Energy range required.
    - High spatial resolution for sXRF mapping.
    - Specialized end station equipment:
        - High pressure – high temperature cells

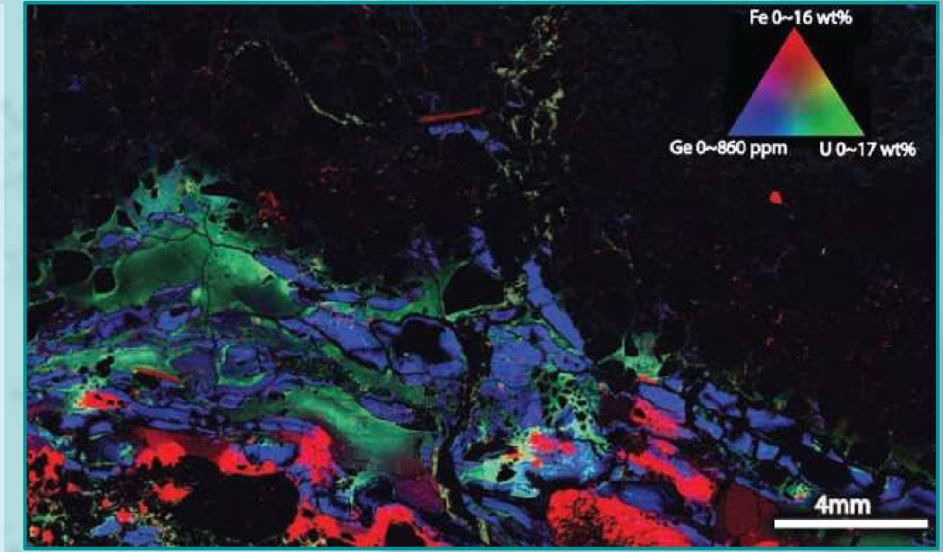


After Testemale et al. 2005; Schmidt and Rickers, 2003

Synchrotron light and ore deposits

Synchrotrons and beamlines most frequently used in ore geology research:

- Factors to consider in selecting a beamline:
  - sXRF (mapping) versus XANES/EXAFS (spectroscopy).
  - Energy range required.
  - High spatial resolution for sXRF mapping.
  - Specialized end station equipment:
    - High pressure – high temperature cells
    - Multi-detector arrays for expedited mapping at µm resolution over large areas.



Distribution of U and Ge in the Pannikan U deposit (Australia). The full slide (34×17 mm; Li et al., 2016) was mapped for chemical information at 5 µm pixel resolution using sXRF at the XFM beamline (Australian Synchrotron) for a total duration of 315 min.

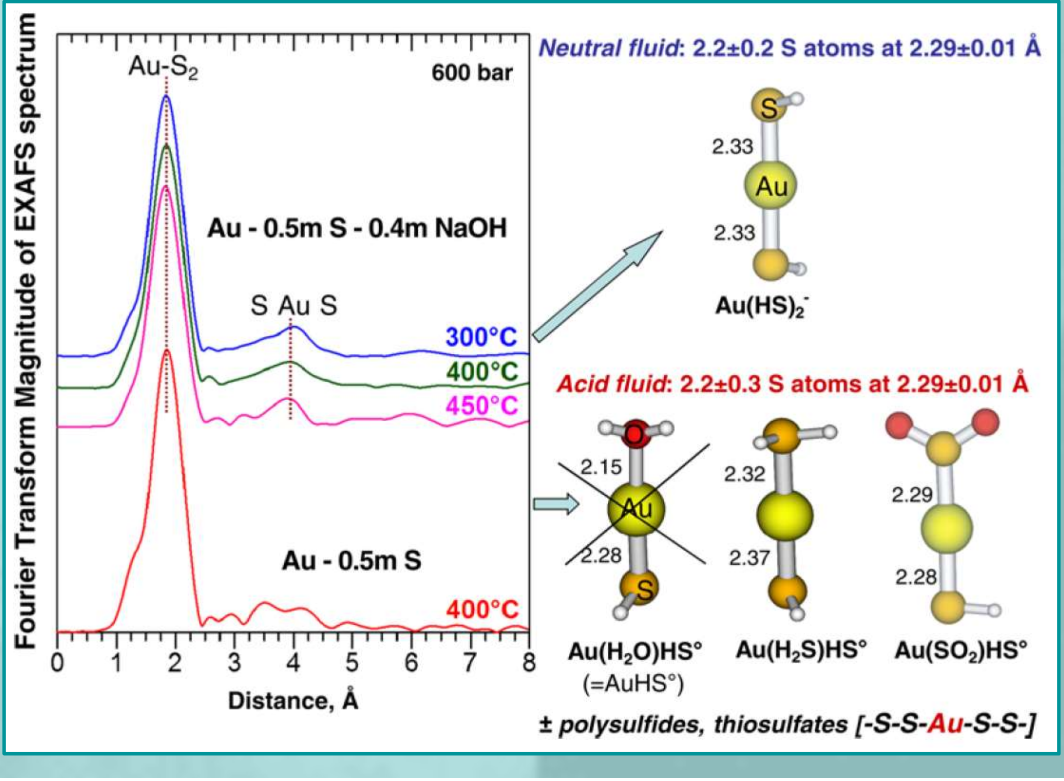
Synchrotron light and ore deposits

Major sub-themes of ore geology research studied using synchrotron light:

1. Application to fundamental ore geology research

   1.1. Metal solubility and complexation in model hydrothermal fluids

- Understanding mobility and ultimate precipitation of ore minerals from ore fluids is reliant on full characterization of the metal-ligand speciation data.
- Conducted in high T-high P cells e.g., 500°C and 600 bar pressure.
- Typically XAFS: redox state, coordination number, ligand identity, bond distances, solubility.
- Scope remains for lessor studied moieties and for studies in melt systems.



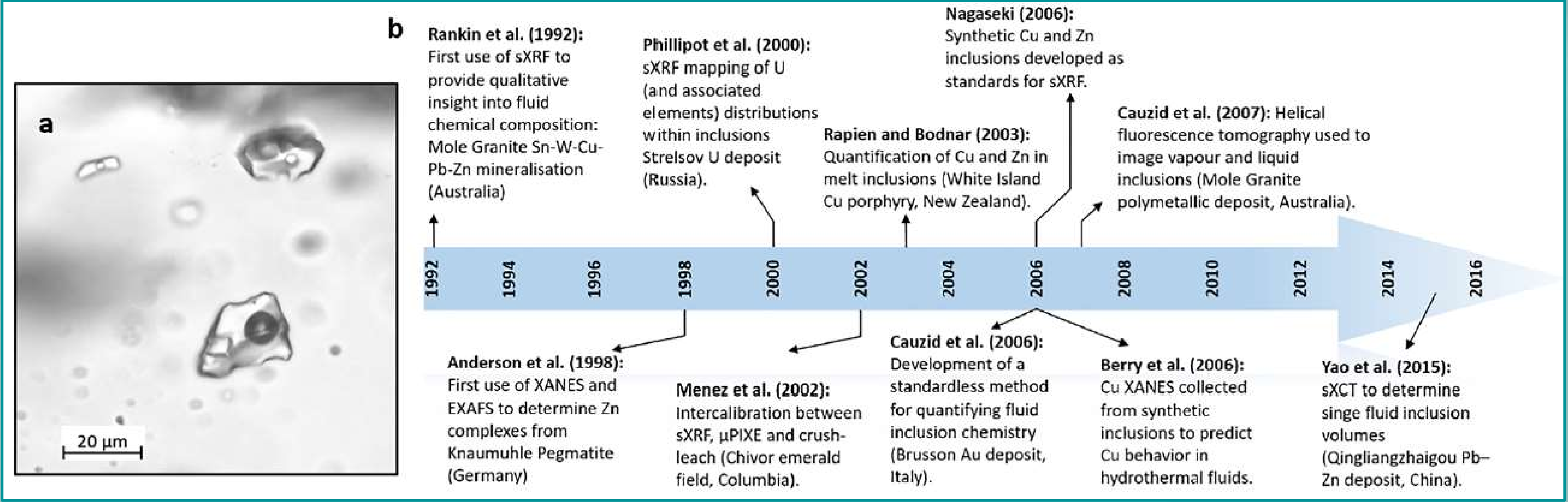
Pokrovski et al., Geol. Soc. London. Spec. Publ.. (2014)

Synchrotron light and ore deposits

Major sub-themes of ore geology research studied using synchrotron light:

1. Application to fundamental ore geology research

1.2. Empirical investigations of ore fluids using information from fluid inclusions



Rankin et al. (1992): First use of sXRF to provide qualitative insight into fluid chemical composition: Mole Granite Sn-W-Cu-Pb-Zn mineralisation (Australia)

Phillipot et al. (2000): sXRF mapping of U (and associated elements) distributions within inclusions Strelsov U deposit (Russia).

Nagaseki (2006): Synthetic Cu and Zn inclusions developed as standards for sXRF.

Rapien and Bodnar (2003): Quantification of Cu and Zn in melt inclusions (White Island Cu porphyry, New Zealand).

Cauzid et al. (2007): Helical fluorescence tomography used to image vapour and liquid inclusions (Mole Granite polymetallic deposit, Australia).

Anderson et al. (1998): First use of XANES and EXAFS to determine Zn complexes from Knaumuhle Pegmatite (Germany)

Menez et al. (2002): Intercalibration between sXRF, µPIXE and crush-leach (Chivor emerald field, Columbia).

Cauzid et al. (2006): Development of a standardless method for quantifying fluid inclusion chemistry (Brusson Au deposit, Italy).

Berry et al. (2006): Cu XANES collected from synthetic inclusions to predict Cu behavior in hydrothermal fluids.

Yao et al. (2015): sXCT to determine singe fluid inclusion volumes (Qingliangzhaigou Pb–Zn deposit, China).

Von der Heyden, 2020

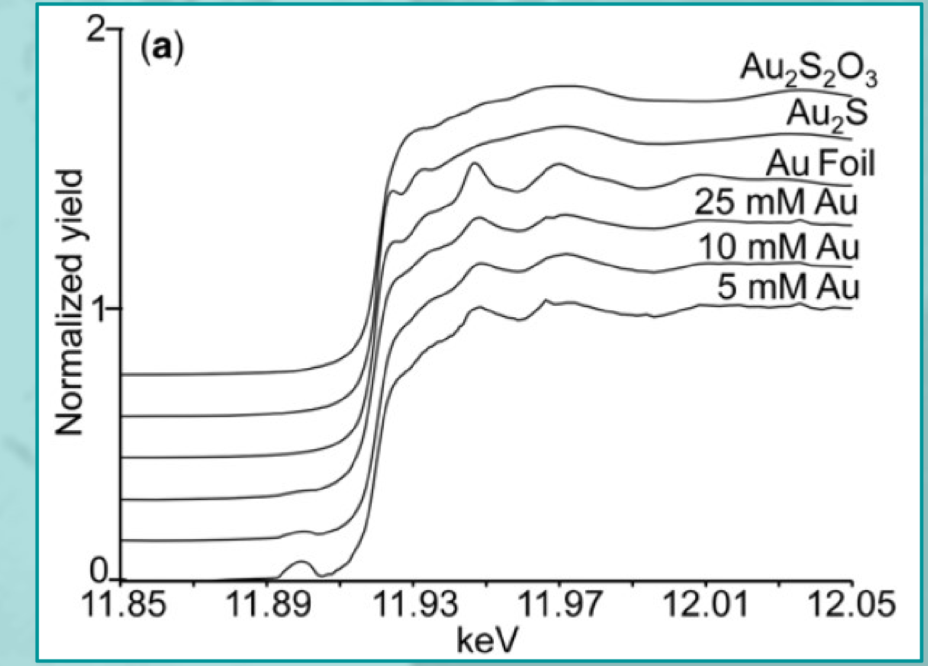
Synchrotron light and ore deposits

Major sub-themes of ore geology research studied using synchrotron light:

1. Application to fundamental ore geology research

   1.3. Low-temperature biogeochemical transformations experienced by ore commodities

- Low temperature systems typically comprise small particles that are commonly poorly crystalline.
- XAFS techniques used to understand the speciation of these phases.
- Common applications include:
  - biogenic precipitates,
  - surficial ore deposits arising from weathering reactions
  - mineral bi-products and surface complexes (particularly deleterious ones) resulting from mining activity.



Shuster et al., Geol. Soc. London. Spec. Publ.. (2013)

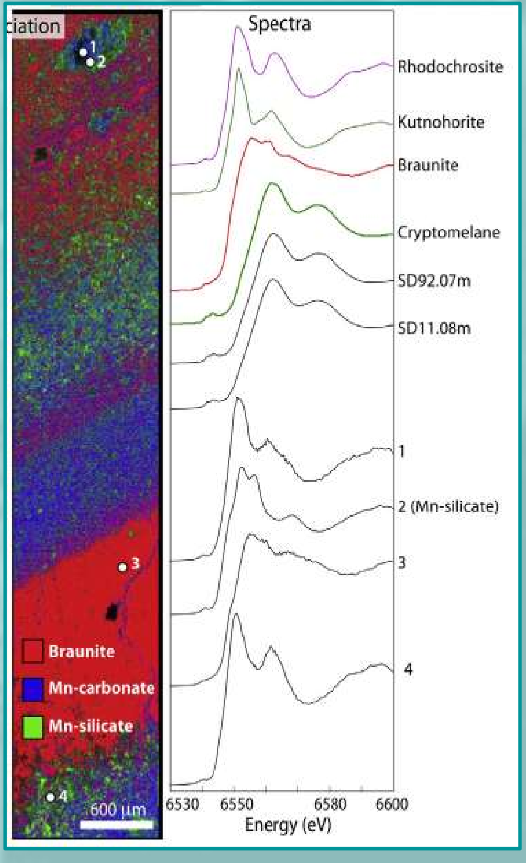
Synchrotron light and ore deposits

Major sub-themes of ore geology research studied using synchrotron light:

1. Application to fundamental ore geology research

   1.4. Ore deposit formation linked to Earth's metallogenic evolution

- Synchrotron techniques well suited to evaluate valence speciation at high spatial resolution.
- Tracking Mn valence state in the rock record has been used to infer Mn oxidation prior to the Great Oxidation Event (~2.4 Ga).
- Reaction cells used to track early diagenetic changes to Fe and Mn mineralogy to provide insights into BIF/bedded Mn deposit formation.



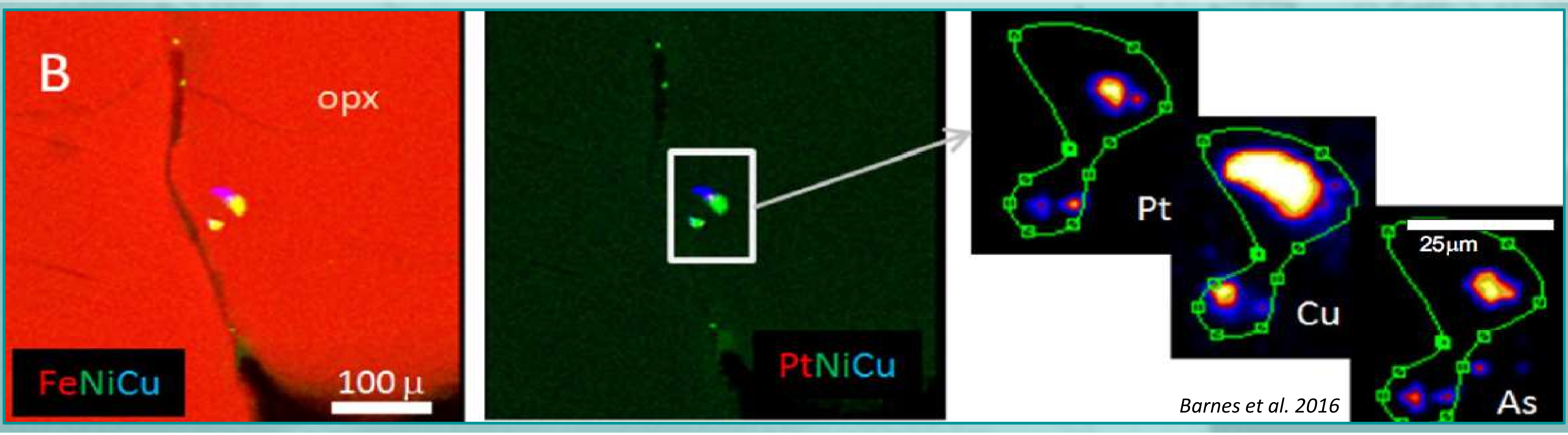
Johnson et al. (2016)

Synchrotron light and ore deposits

Major sub-themes of ore geology research studied using synchrotron light:

2. Application of synchrotron light to applied ore geology research

- sXRF used extensively to show fine-scale spatial and elemental relationships between ore minerals and gangue.
- XAFS used to show coordination of metals hosted as refractory phases within other minerals: straddles the fundamental-applied nexus.

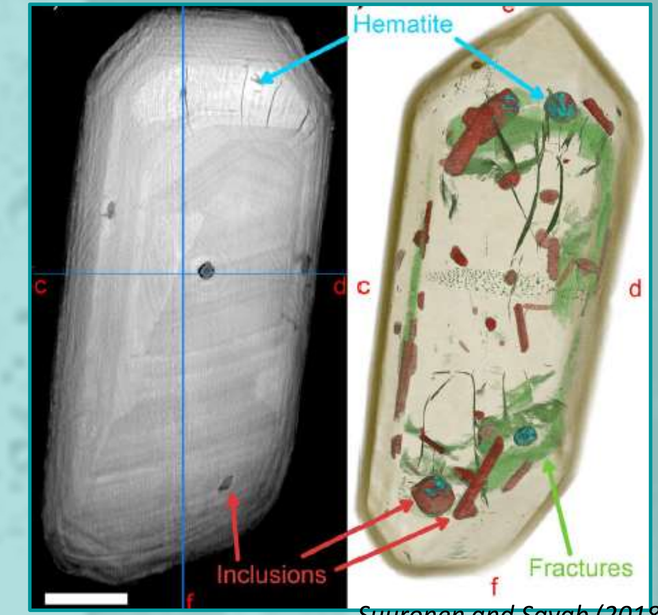


Barnes et al. 2016

Synchrotron light and ore deposits

Perceived future directions:

Fourth generation light sources will enable ore research at increasingly high spectral resolutions and elemental detection limits.



Suuronen and Sayab (2018

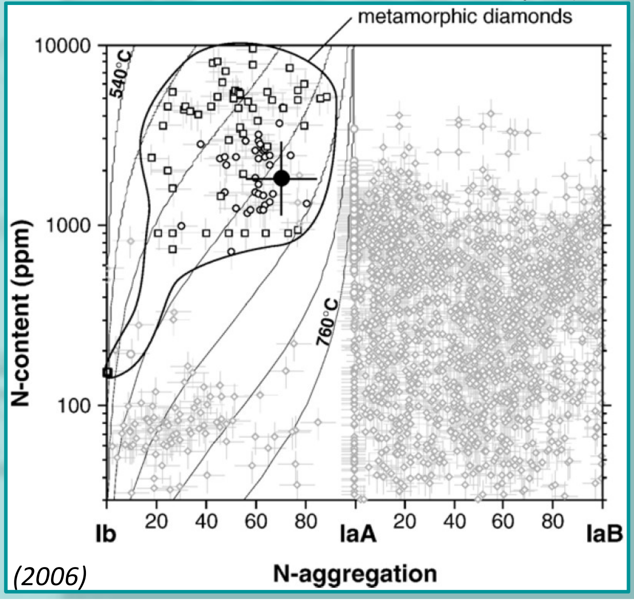
A. Ore research across higher-order dimensions

- Micro-computed tomography coupled with µXRD, µXRF and µXAS enable textural and chemical analyses across three dimensions.
- Time resolved measurements will enable kinetic measurements of ore fluid and mineral reactions.

B. Advances in lesser utilised synchrotron techniques

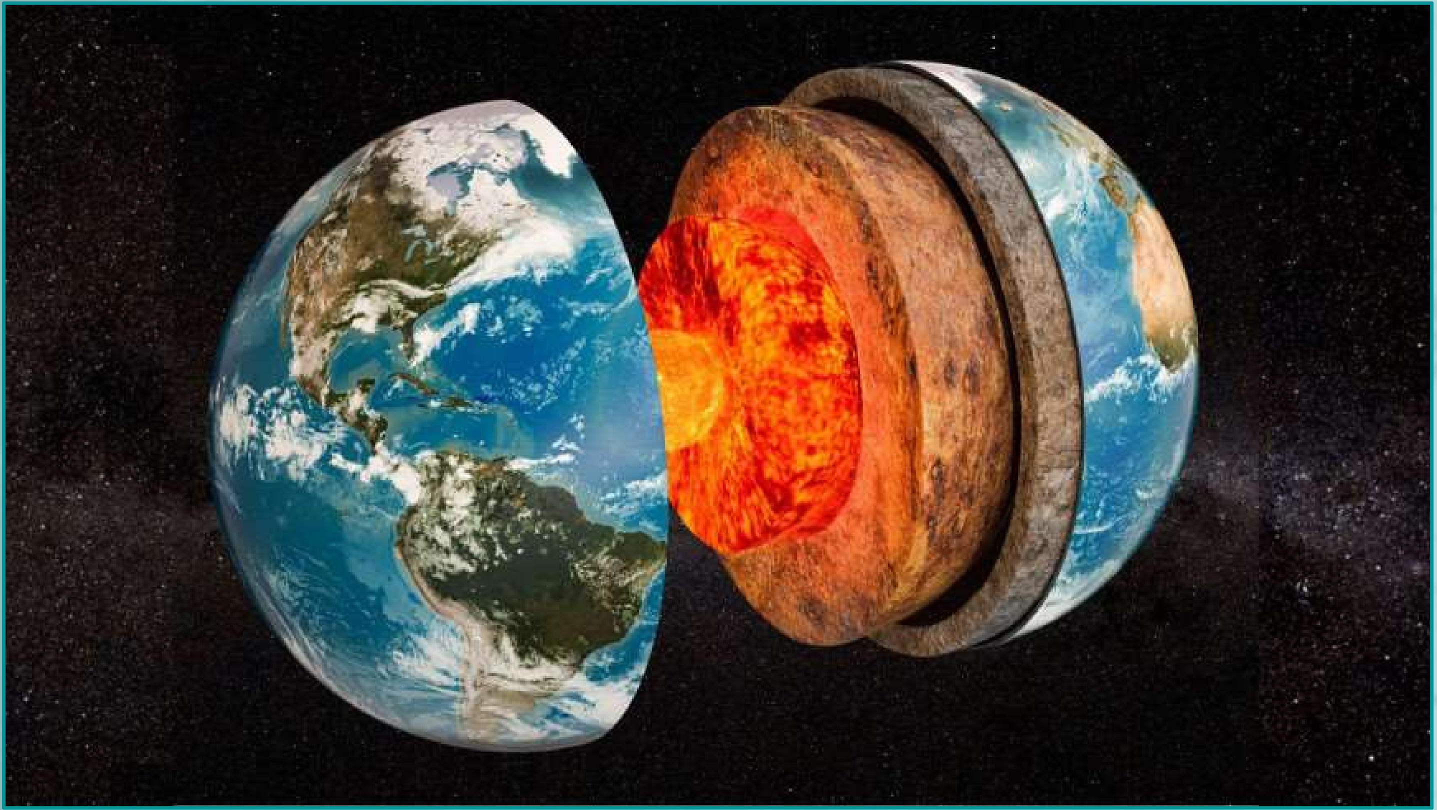
- Scope for application of µRaman, µIR, µXPS and SAXS techniques.
- Correlative approaches

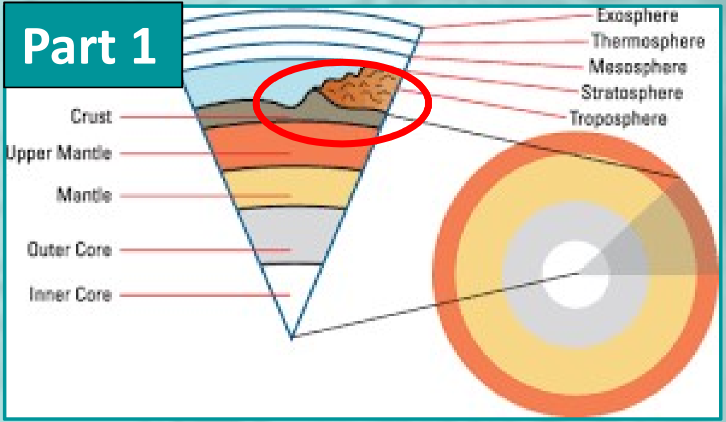
C. Incorporation of synchrotron study techniques at the front end of geological investigation

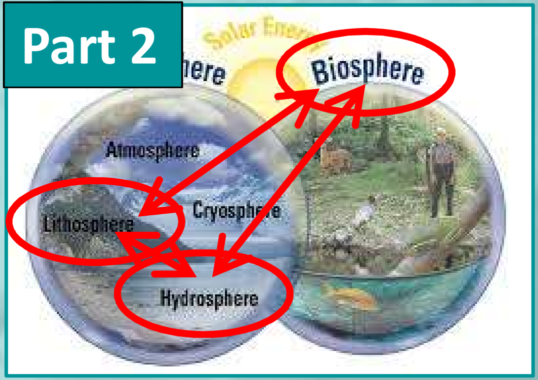


Dobrzhinetskaya et al. (2006)

What are the Earth Sciences?







Sphere: *realm (world) of something or physical dimensions / area of something, or both of these (Quora.com).*

Image credits: interestingengineering.com; dummies.com; geographyrealm.com

The environmental sciences

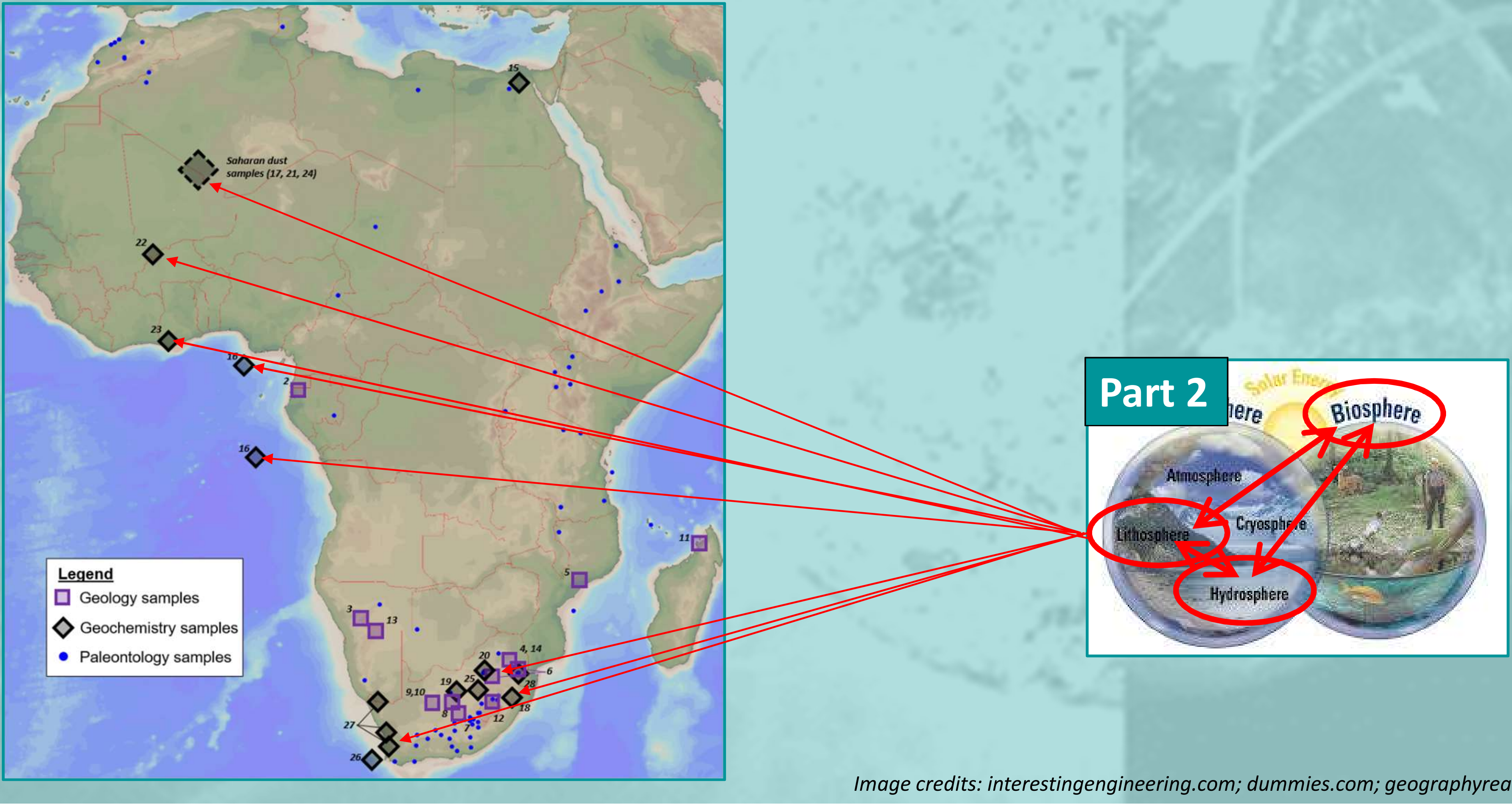


Image credits: interestingengineering.com; dummies.com; geographyrealm.com

The environmental sciences

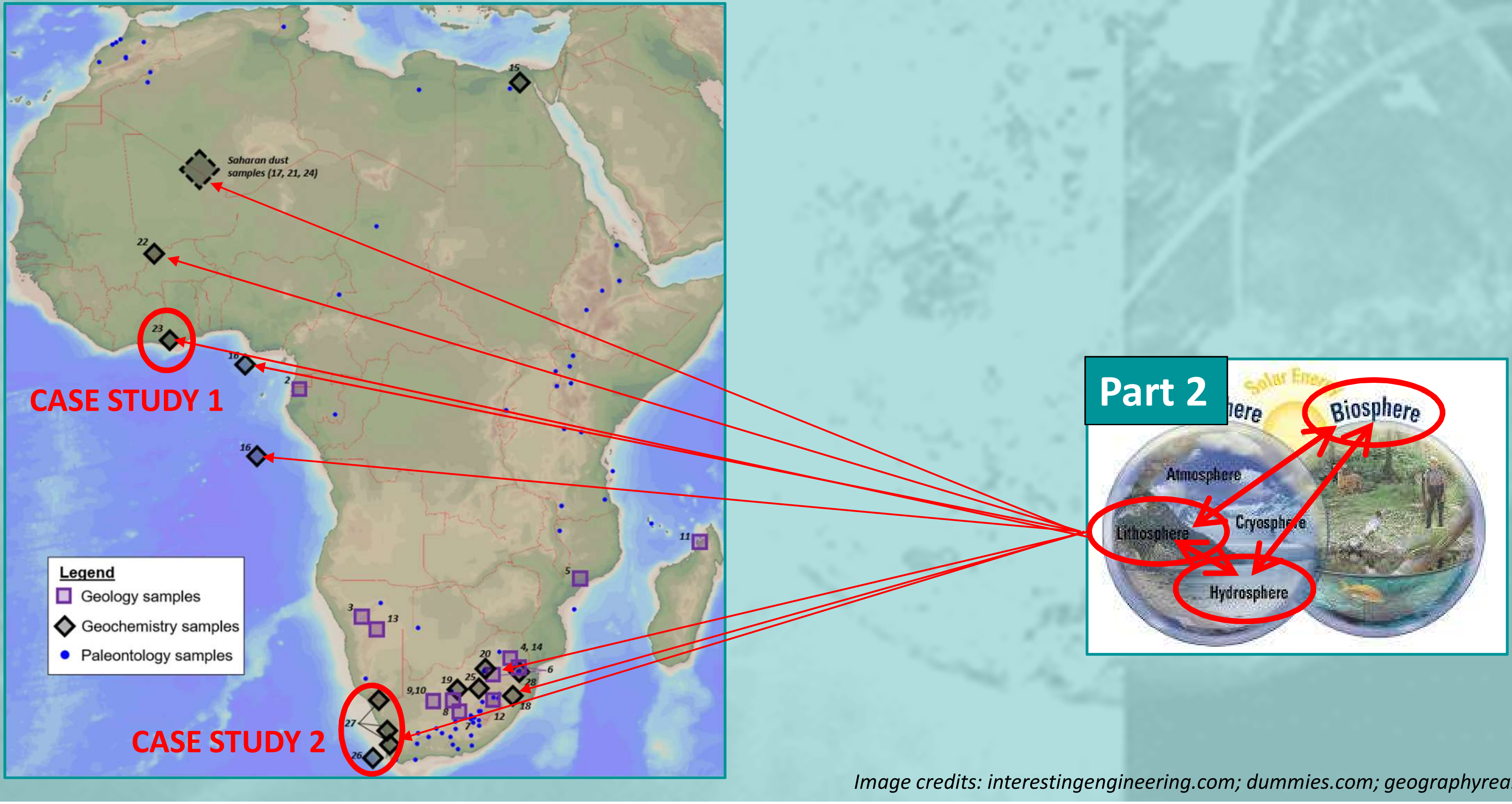
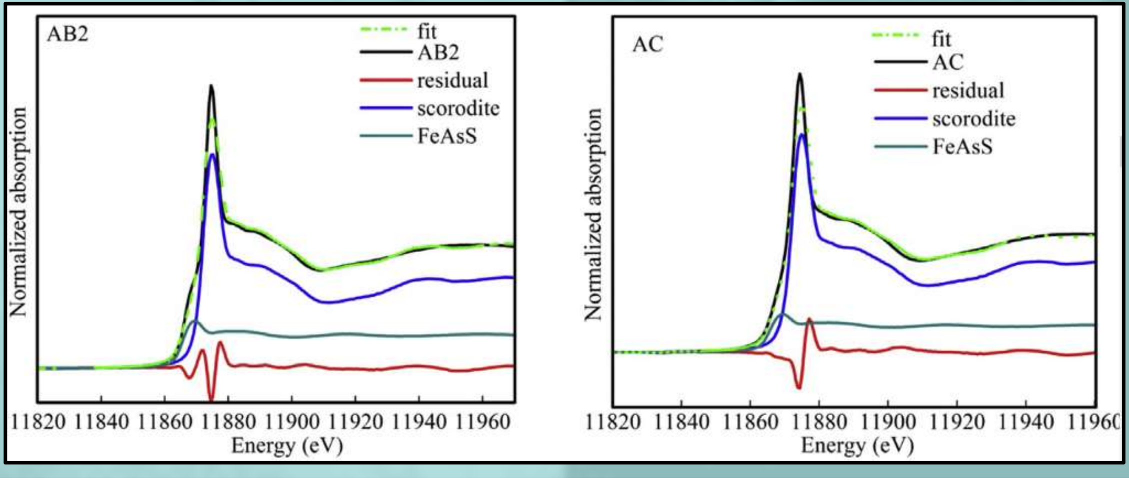


Image credits: interestingengineering.com; dummies.com; geographyrealm.com

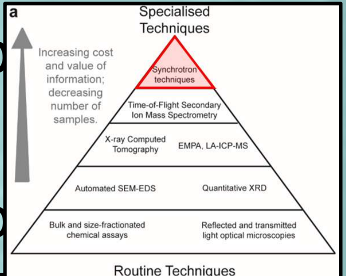
Case study 1: Arsenic speciation in tailing materials from gold mines in Ghana *(Mensah et al., 2020)*

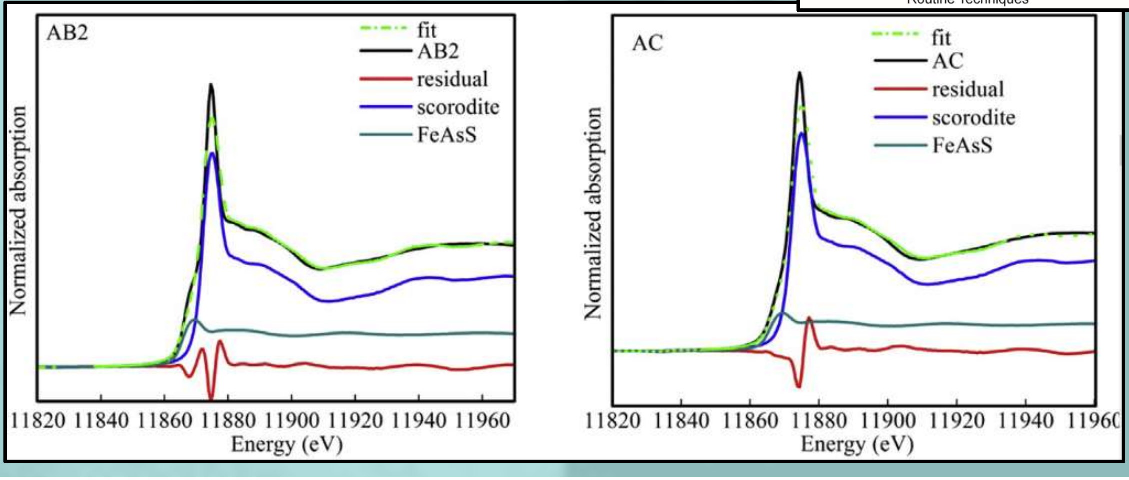
- TLS 07A beamline, National Synchrotron Radiation Research
- Centre (NSRRC), Taiwan.
- Au and As are strongly associated. Au mining can be a notable point source of As release into the environment.
- As toxicity is strongly controlled by its speciation, As(III) more toxic than As(V).
- Scorodite and arsenopyrite are the two major forms of As in the spoils, typically associated with fine fractions.



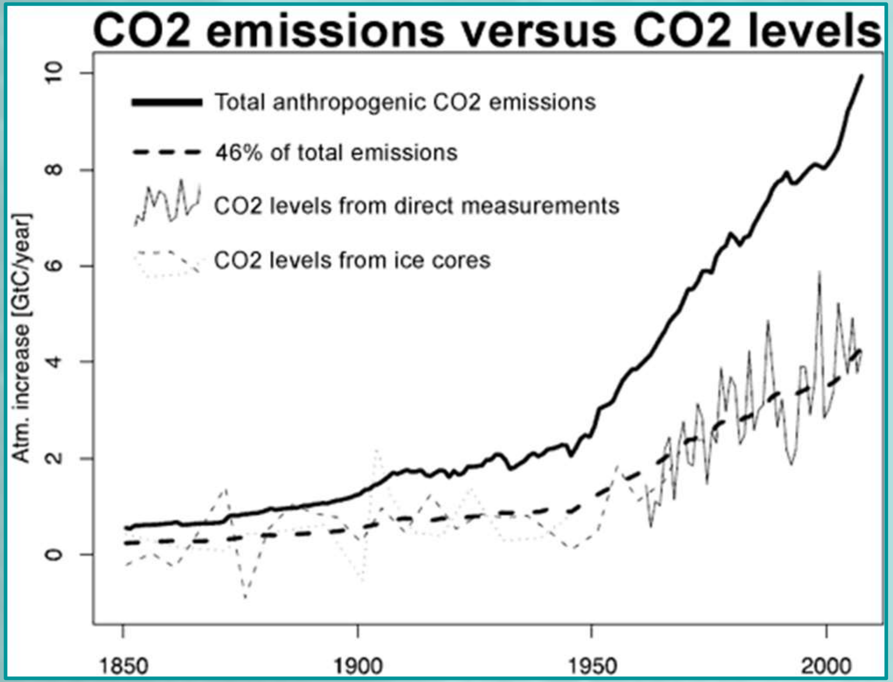
Case study 1: Arsenic speciation in tailing materials from gold mines in Ghana *(Mensah et al., 2020)*

- TLS 07A beamline, National Synchrotron Radiation Research
- Centre (NSRRC), Taiwan.
- Au and As are strongly associated. Au mining can be a notable p source of As release into the environment.
- As toxicity is strongly controlled by its speciation, As(III) more to than As(V).
- Scorodite and arsenopyrite are the two major forms of As in the spoils, typically associated with fine fractions.





Case study 2: Fe L-edge investigations of marine Fe speciation



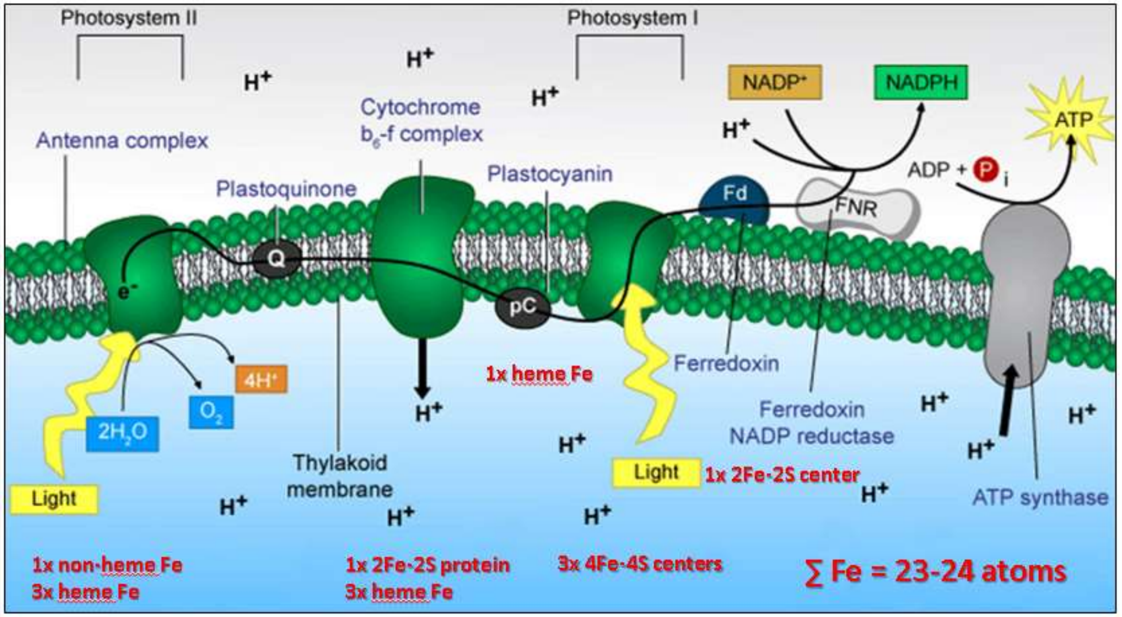
Unprecedented rise in atmospheric CO_2 levels, due to anthropogenic activities.

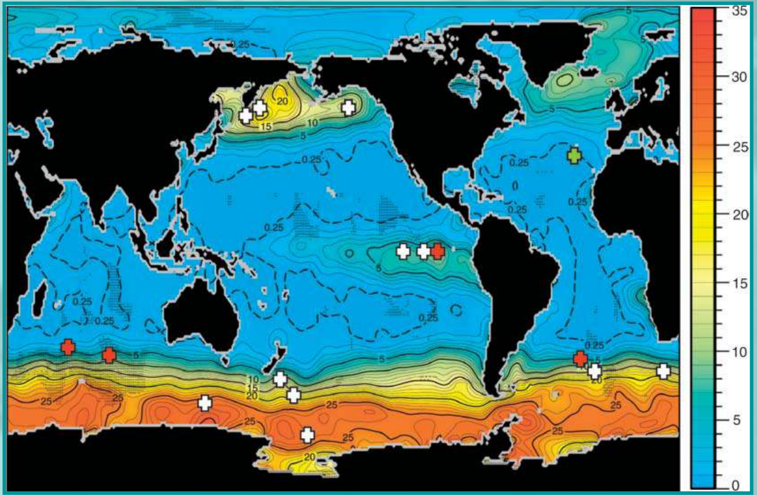
After Knorr, 2009

Sinks for atmospheric CO_2 include:

1) Terrestrial plants and soils
2) **Marine phytoplankton (the ocean's "biological pump")**
3) Seawater inorganic chemistry (the ocean's "physical/solubility pump")

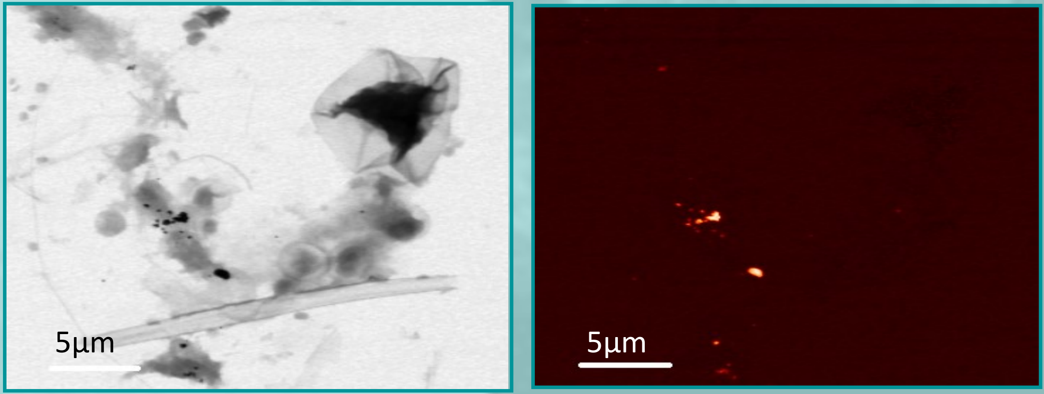
Case study 2: Fe L-edge investigations of marine Fe speciation





After Boyd et al., 2007

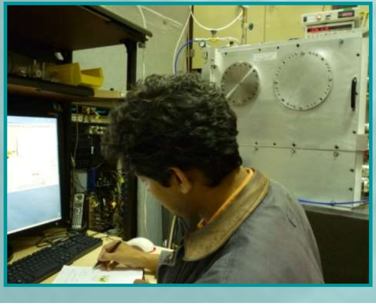
Refs: Dept. Biol. Penn State (2004); Michel and Pistorius (2004)

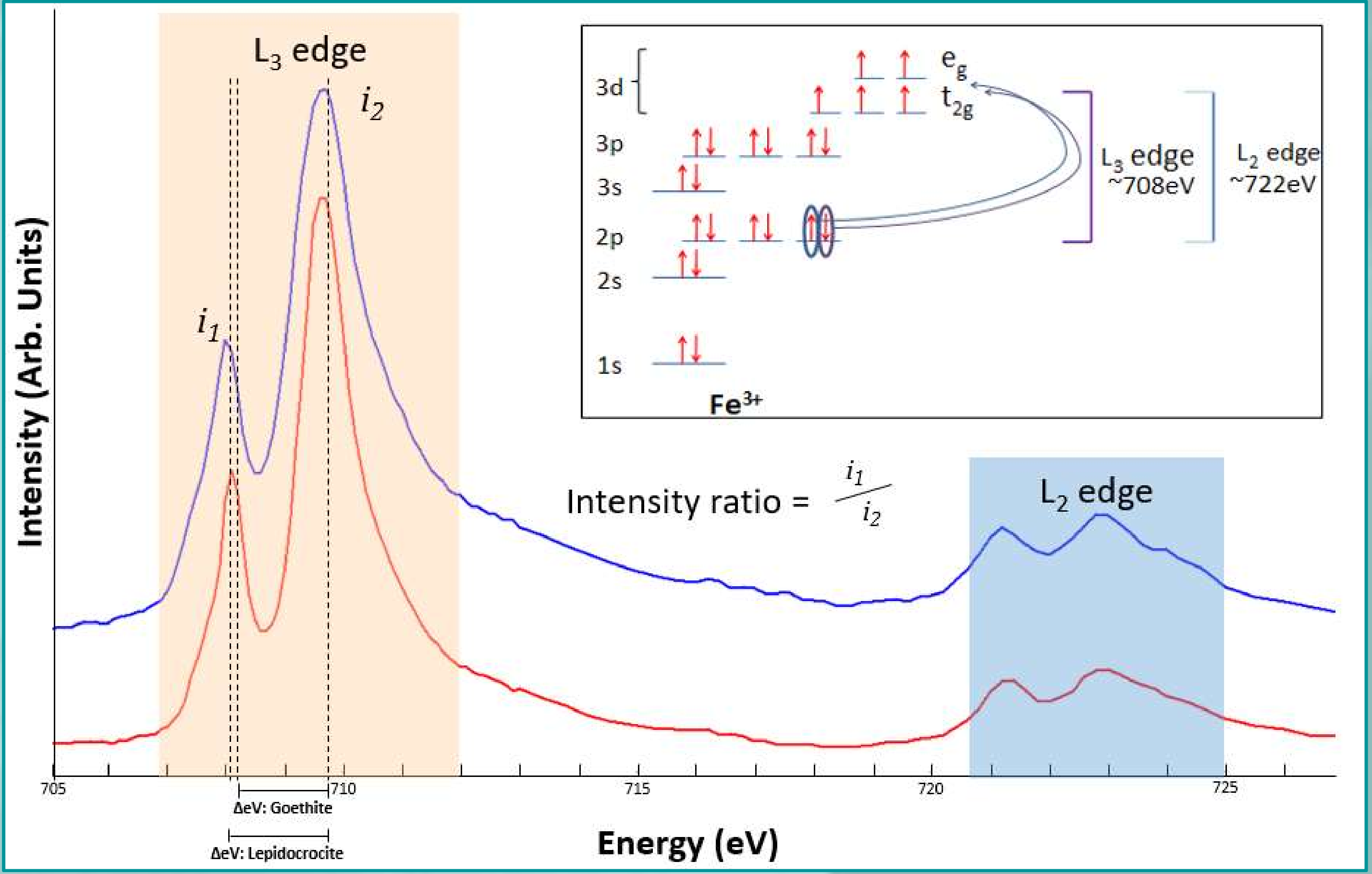


Von der Heyden et al. 2012

- Fe is an important trace element needed for the growth of photosynthetic organisms
- Constituent of the electron transport chain in the thylakoid membrane of cyanobacteria
- However, in large tracts of the world's oceans; low Fe concentrations limit primary productivity

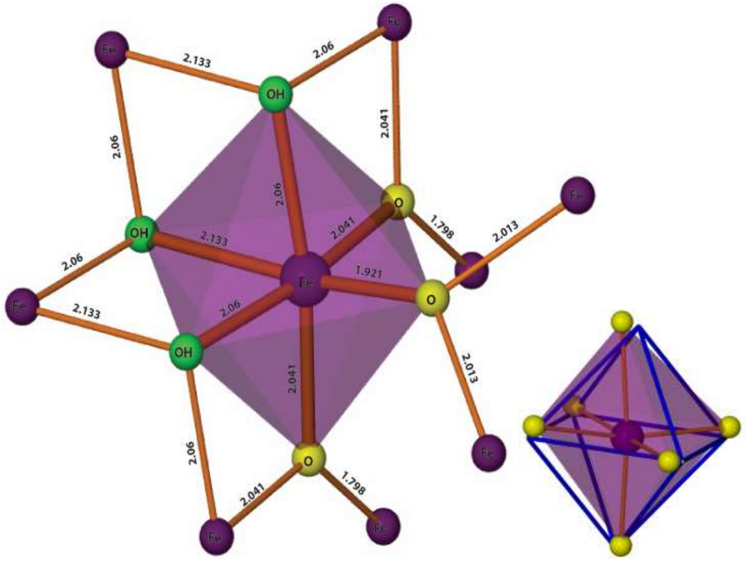
Case study 2: Fe L-edge investigations of marine Fe speciation





Case study 2: Fe L-edge investigations of marine Fe speciation

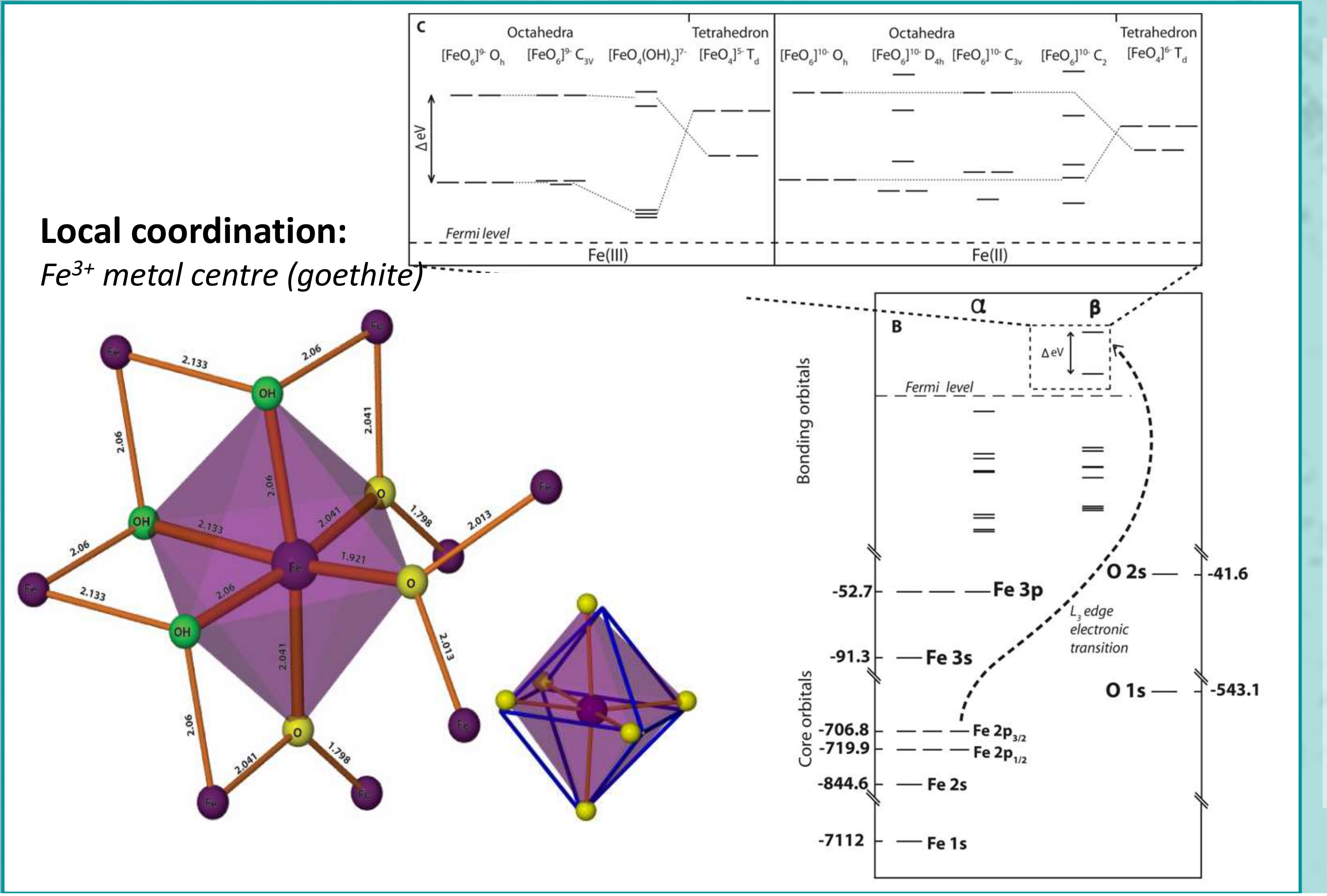
Local coordination:
Fe^{3+} metal centre (goethite)



- Fe $L_{2,3}$-edge probes local coordination
- ΔeV reflects energies of valence orbitals
- Intensity ratio reflects the chemical character of the valence orbitals

- Spectral parameters affected by:
  - Valence state
  - Coordination number
  - Coordinating ligands
  - Distortion effects
- ➢ *All of which are reflected in a mineral's* ***chemistry*** *and* ***mineralogy****!*

Case study 2: Fe L-edge investigations of marine Fe speciation



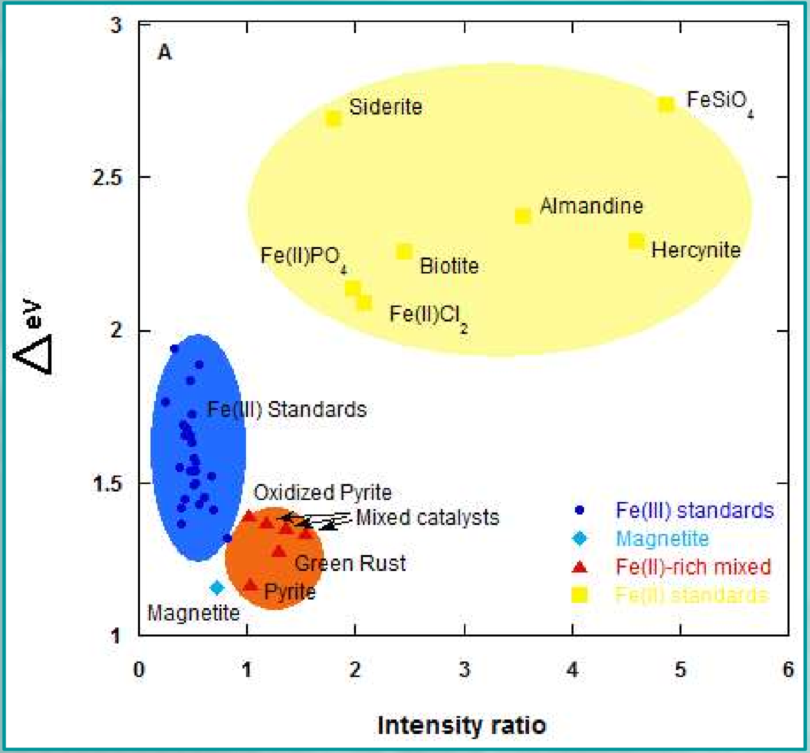
Local coordination:

Fe^{3+} metal centre (goethite)

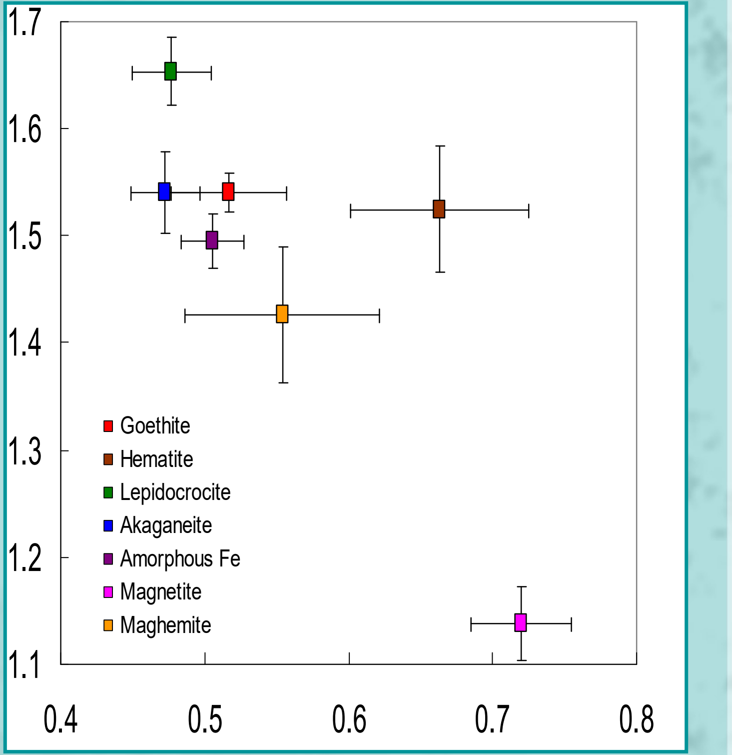
- Fe $L_{2,3}$-edge probes local coordination
- ΔeV reflects energies of valence orbitals
- Intensity ratio reflects the chemical character of the valence orbitals

- Spectral parameters affected by:
    - Valence state
    - Coordination number
    - Coordinating ligands
    - Distortion effects
- ➢ *All of which are reflected in a mineral's **chemistry** and **mineralogy**!*

Case study 2: Fe L-edge investigations of marine Fe speciation



Literature standard Fe phases



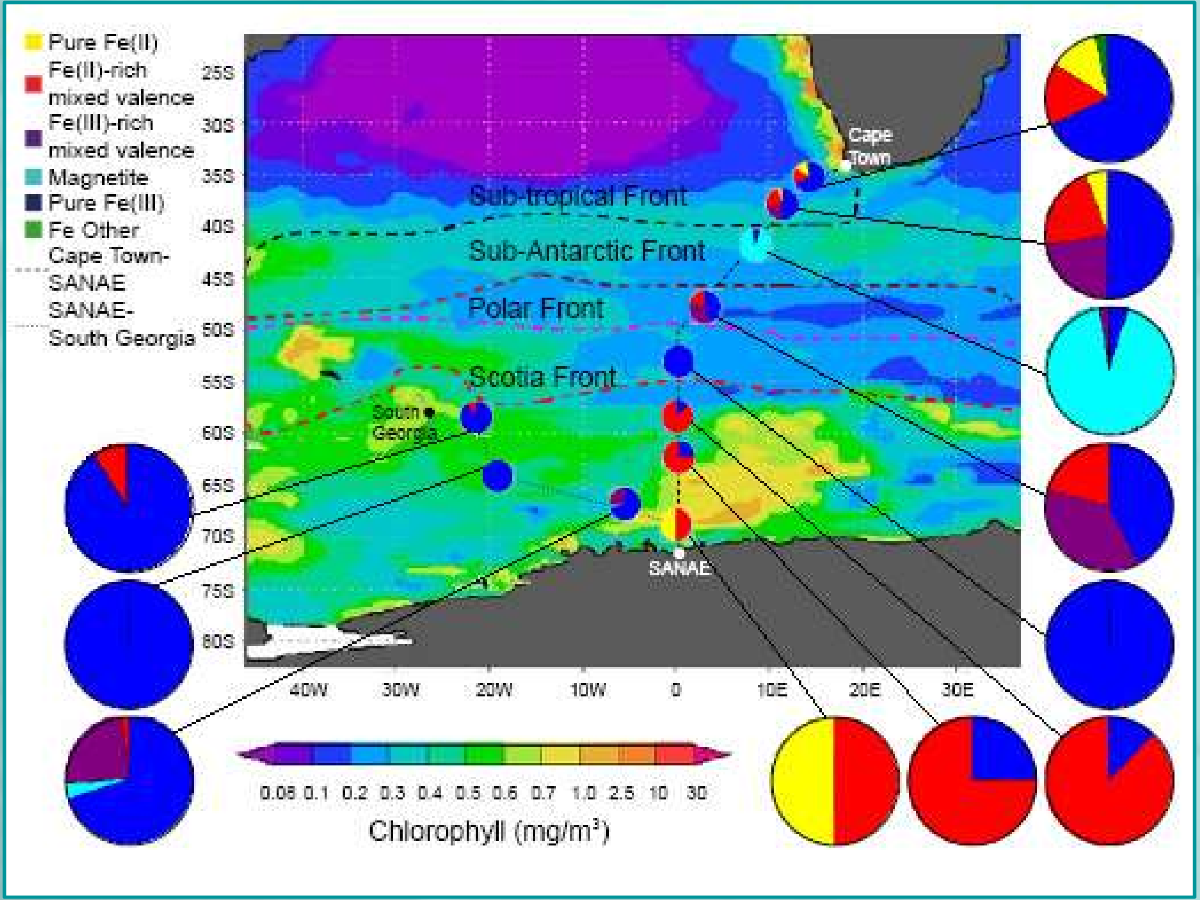
Standard Fe oxide and oxyhydroxide phases

- Fe $L_{2,3}$-edge probes local coordination
- ΔeV reflects energies of valence orbitals
- Intensity ratio reflects the chemical character of the valence orbitals

- Spectral parameters affected by:
  - Valence state
  - Coordination number
  - Coordinating ligands
  - Distortion effects

➢ *All of which are reflected in a mineral's **chemistry** and **mineralogy**!*

Case study 2: Fe L-edge investigations of marine Fe speciation

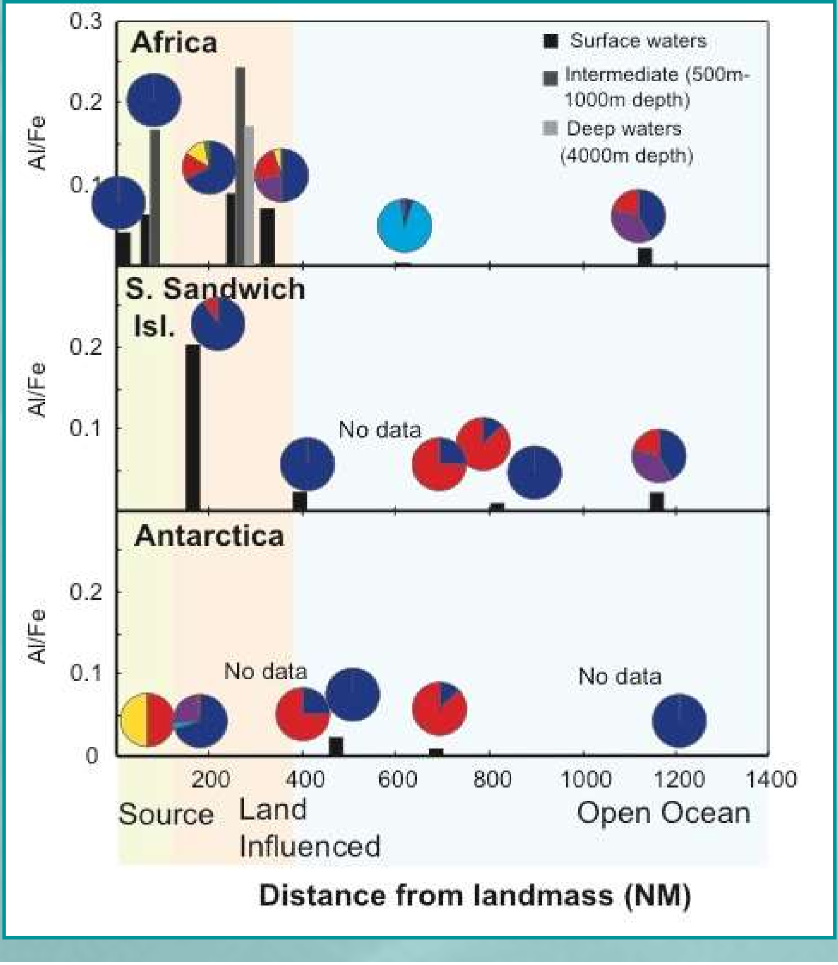


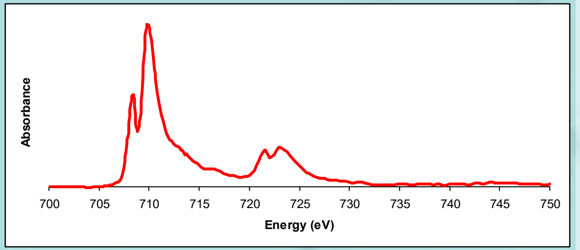
After von der Heyden et al., 2012

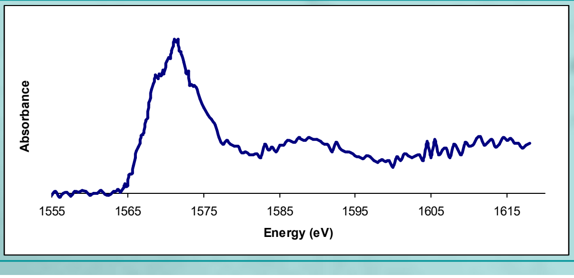
Distribution of Fe mineralogy in the Southern Ocean reflecting:

- High degree of heterogeneity
- Magnetite in the Sub-Antarctic Frontal Zone
- Increased prevalence of Fe(II) in the high latitudes
  - Biological control
  - Slower oxidation kinetics
  - Fe(II) sources
- Coinciding with greater chlorophyll

Case study 2: Fe L-edge investigations of marine Fe speciation





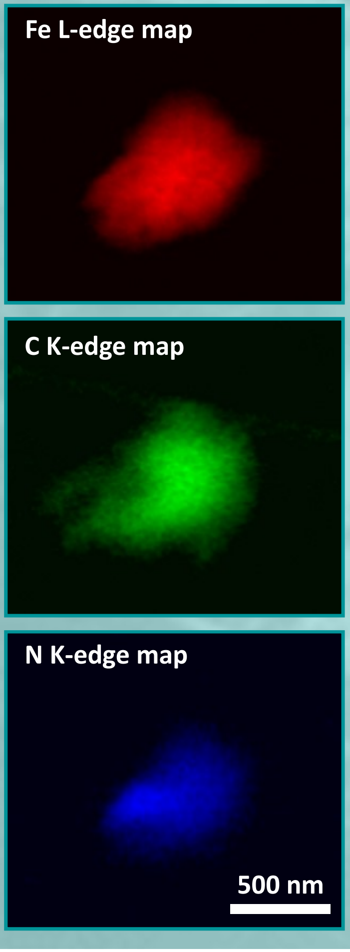


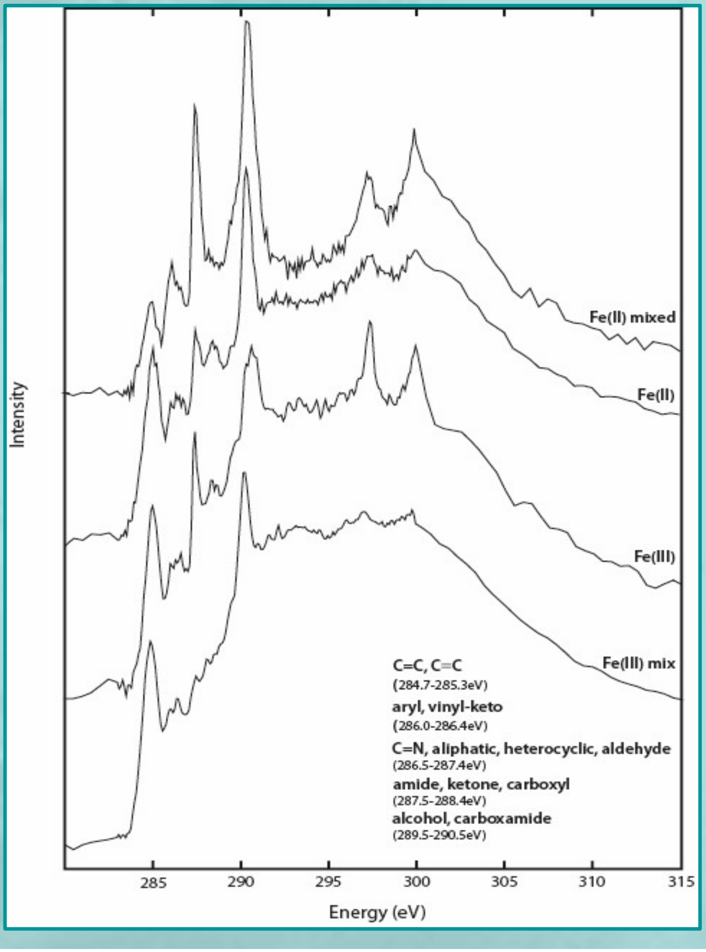
Distribution of Al/Fe ratios evaluated in particles collected in the Southern Ocean:

- Al/Fe ratios increase with distance from source, then decrease in Open Ocean
- Higher values at depth (0.17) relative to surface (0.08)
- Role as a chemical tracer
- Effects on solubility

After von der Heyden et al., 2012, 2018

Case study 2: Fe L-edge investigations of marine Fe speciation





After von der Heyden et al., 2014

Evaluation of particles from Southern Ocean, Pacific Ocean, two lacustrine environments:

- Fe(II) stable in a range of oxic aquatic environments
- Strongly *associated* with organic carbon
- Preferentially associated with alcohol and carboxamine functional groups

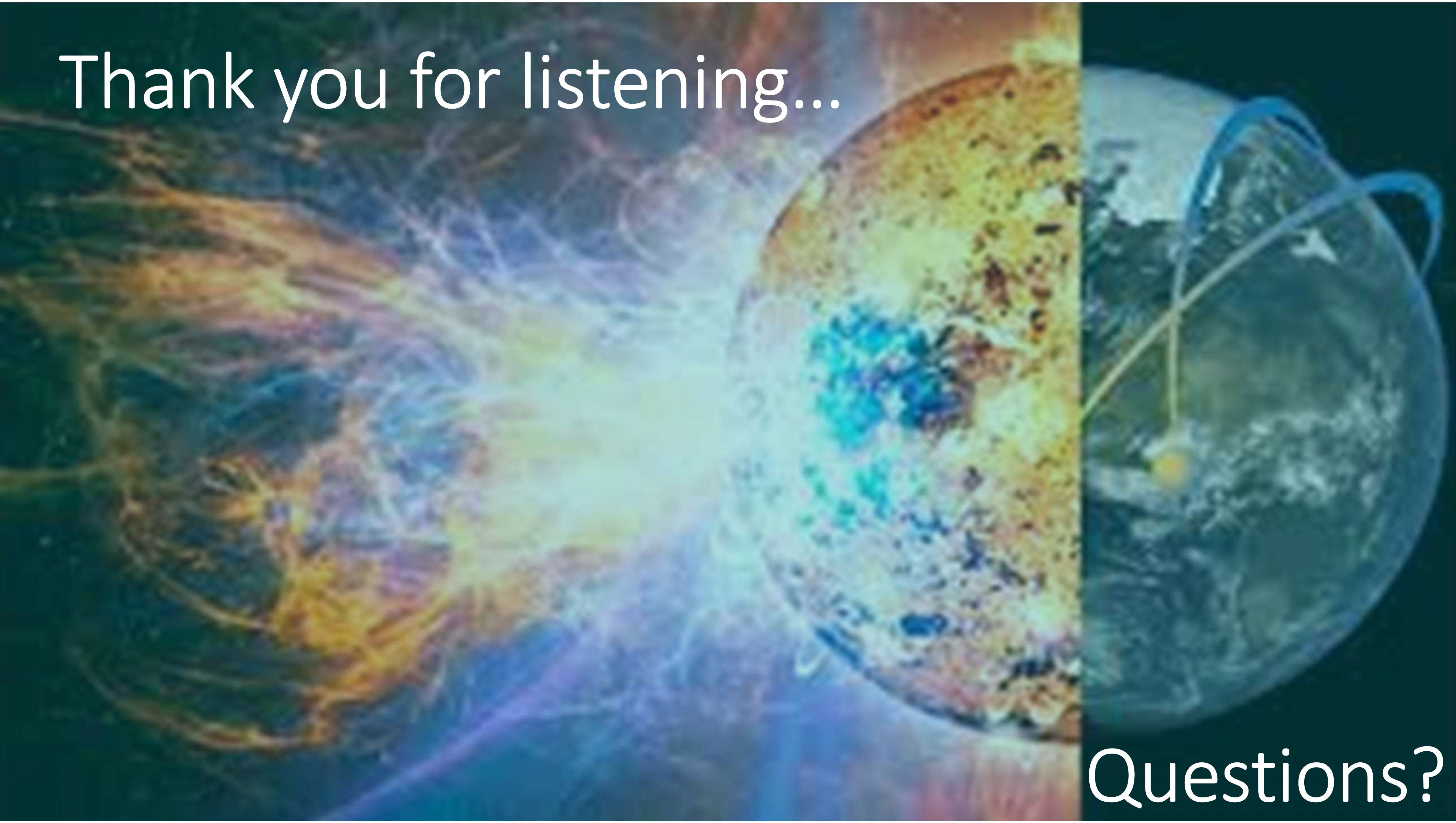
Concluding remarks

“Global science continues to evolve towards a paradigm in which molecular-, sub-micrometer- and micrometer-scale observations are used to add important insights into macro- or even global-scale processes, synchrotron-based X-ray methodologies will continue to rise in prominence as a tool to conduct cutting-edge scientific research.”

- sXRF techniques are superior to contemporary techniques for mapping and quantifying elemental distributions of earth samples
- Synchrotron spectroscopies such as XANES and EXAFS provide unique and detailed molecular-level chemical information of e.g., element redox state in ore minerals and environmental contaminant moieties (generally not obtainable by conventional analytical methodologies)

- Techniques have already been successfully applied to Earth Science samples, however, number of studies is still on the low end of the spectrum.
- Challenge remains to attract a larger synchrotron user base from the Earth Sciences, several disciplines and communities (notably the African scientific community) are presently under represented.

Thank you for listening…



Questions?