SESAME - AFRICA ONLINE WORKSHOP

Synchrotron light applied to the African Earth Sciences

Bjorn von der Heyden

Stellenbosch University

DST-NRF Centre of Excellence for Integrated Mineral and Energy Resource Analysis

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Synchrotron light applied to the African Earth Sciences

Journal of African Earth Sciences

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

Bjorn P. von der Heyden, Julien Benoit, Vincent Fernandez, Alakendra N. Roychoudhury

ARTICLE INFO

ABSTRACT

1. Introduction

Bjorn von der Heyden

Stellenbosch University

NRF National Research Foundation

RISA Research and Innovation Support and Advancement

cimera DST-NRF Centre of Excellence for Integrated Mineral and Energy Resource Analysis

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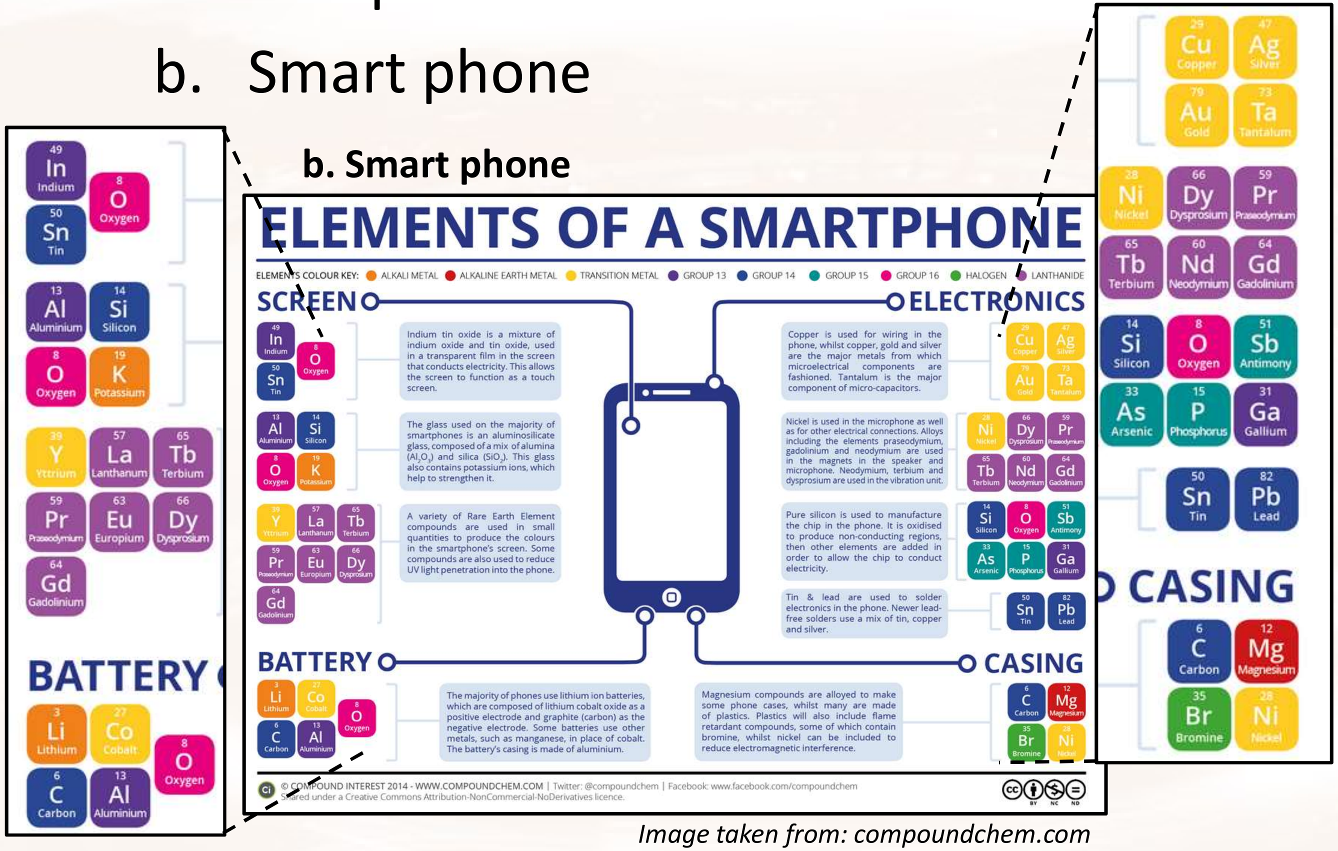


Image taken from: compoundchem.com

a. Computer

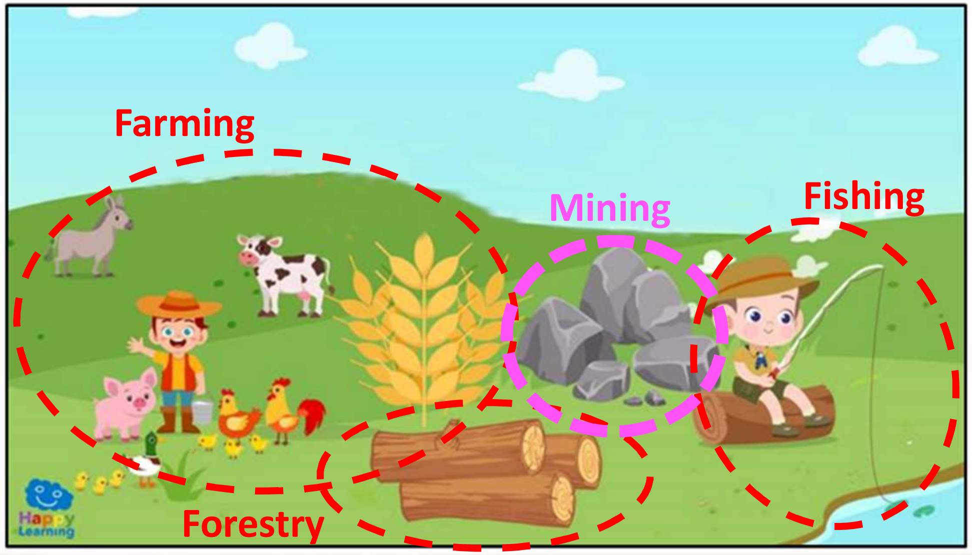
Material name	Content (% of total weight)	Weight of material in computer (kg)	Use	Location
Plastics	22.9907	6.26	Insulation	Cable, Housing
Lead	6.2988	1.72	Metal joining	Funnel glass in CRTs, PWB
Aluminum	14.1723	3.86	Structural, Conductivity	Housing, CRT, PWB, connectors
Germanium	0.0016	< 0.1	Semiconductor	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

Earth Sciences and the African economy

- 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 natural environment



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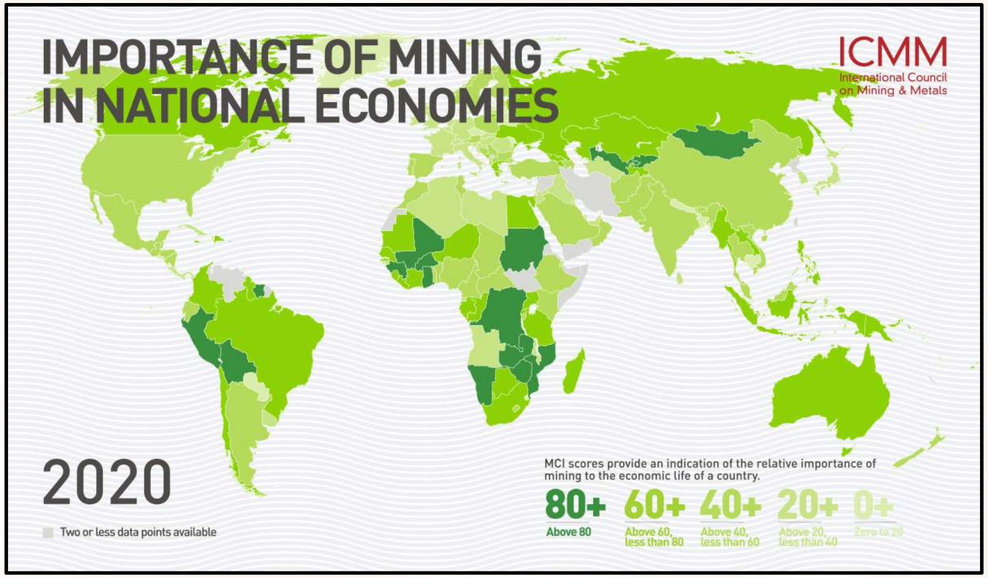


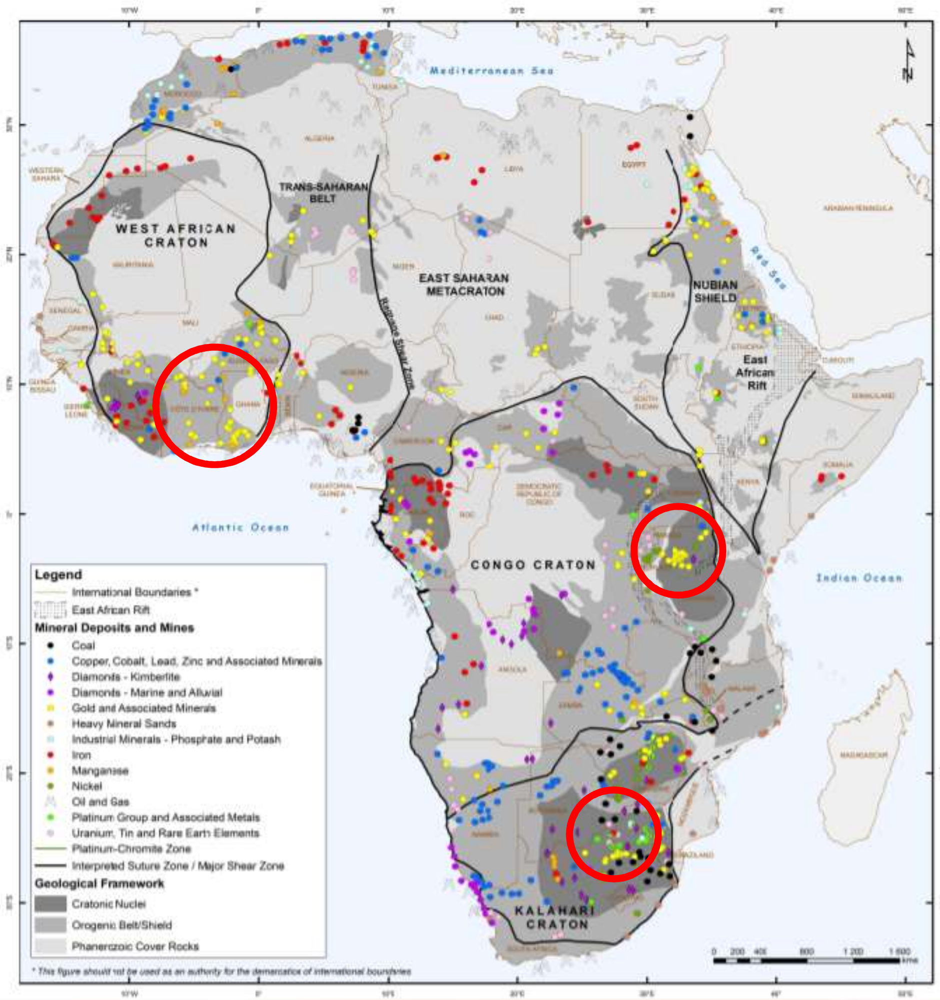
Image taken from: www.icmm.com (5th Mining Contribution Index (2020))

Africa’s mineral endowments

- Africa is blessed with a rich mineral endowment.

- Examples of great mineral fields include:
    - Lake Victoria, West African, and Witwatersrand gold fields
    - Central African Copper Belt
    - Karoo-aged coal fields
    - Kalahari Manganese Fields
    - Moroccan sedimentary phosphate
    - Southern African diamond fields
    - West African Bauxite
    - Bushveld igneous complex

- Associated environmental degradation influenced by speciation, mobility and chemical fate of deleterious elements released during mining.



GOLD

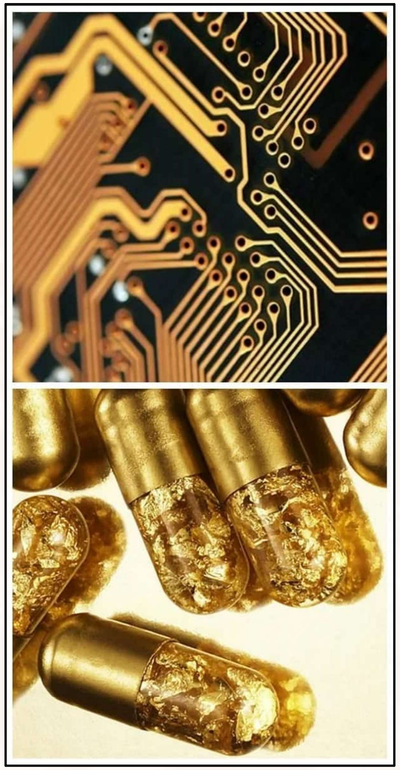


Image from: legit.ng

Frost-Killian et al., Episodes (2016)

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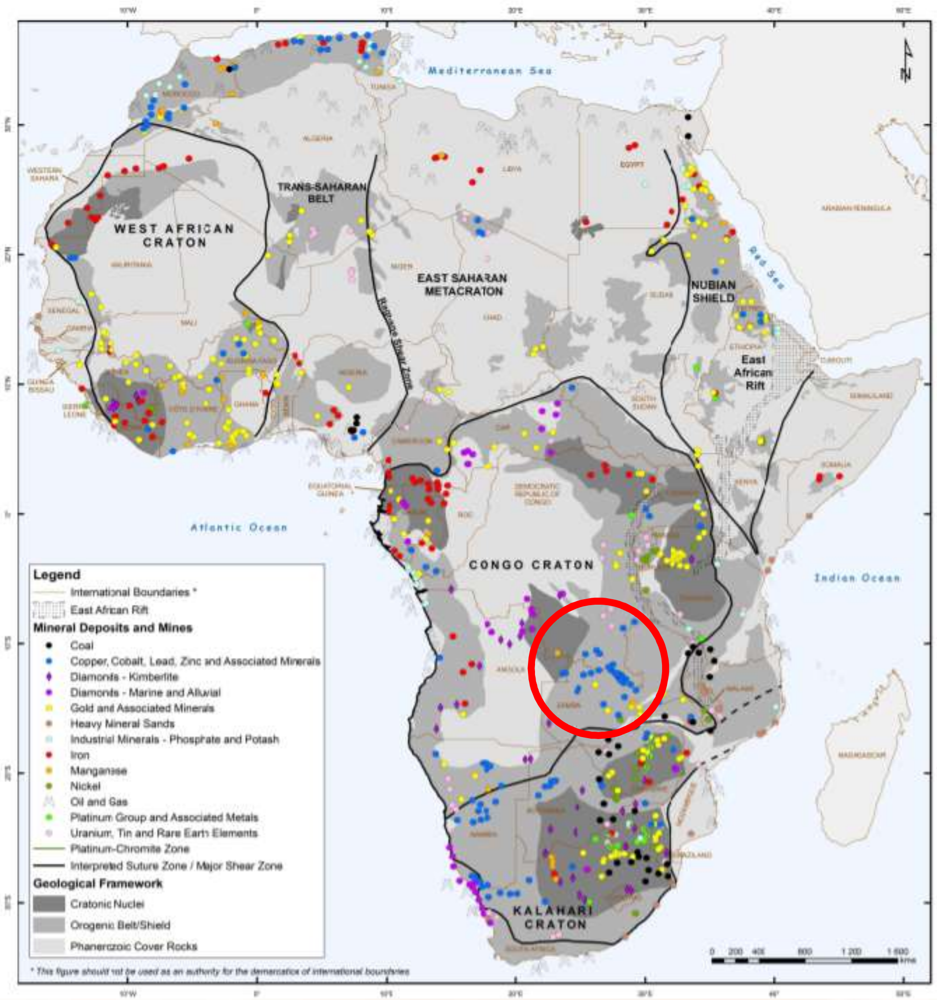

Frost-Killian et al., Episodes (2016)

COPPER

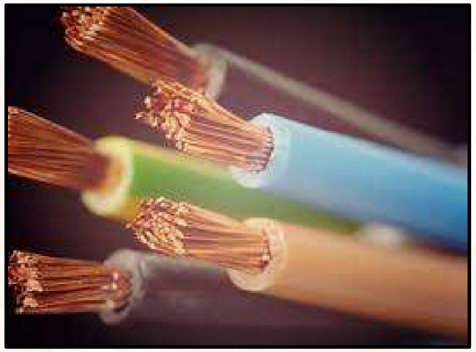

Image from: globaltrading.com

COBALT

Image from: investingnews.com

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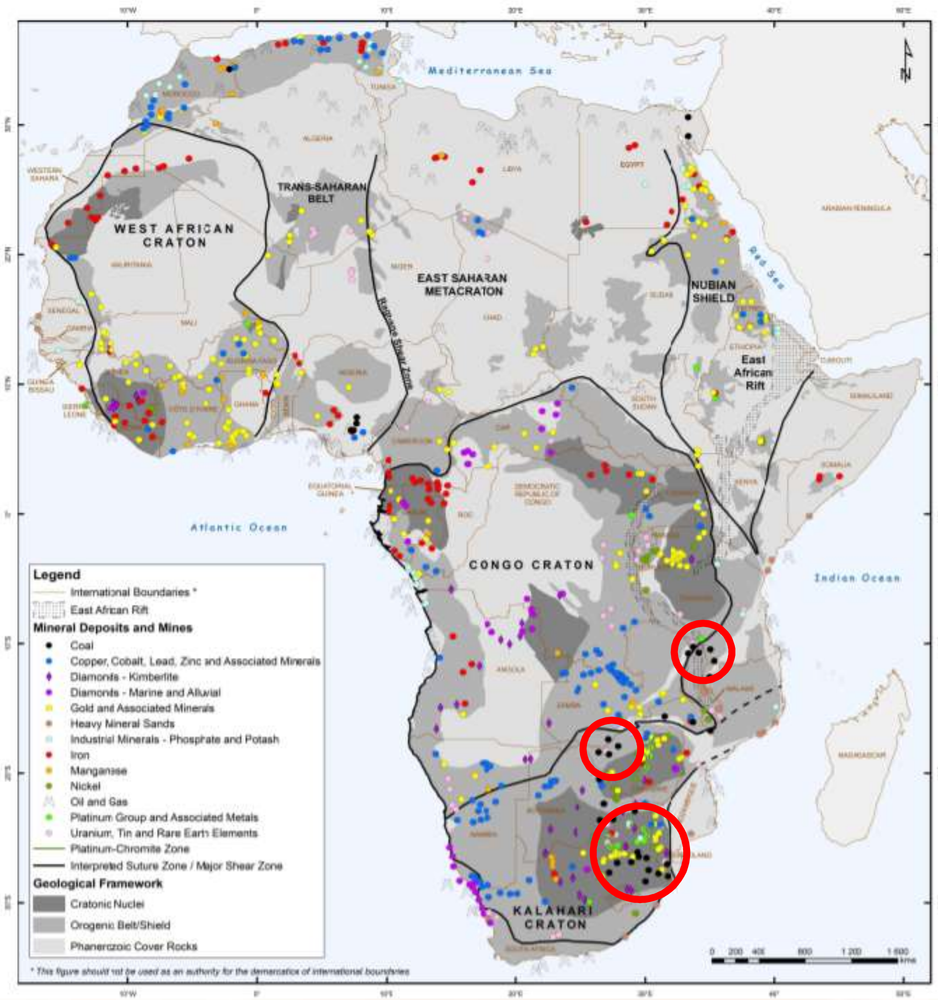

Frost-Killian et al., Episodes (2016)

COAL

Image from: usgs.gov

Image from: sustainable-carbon.org

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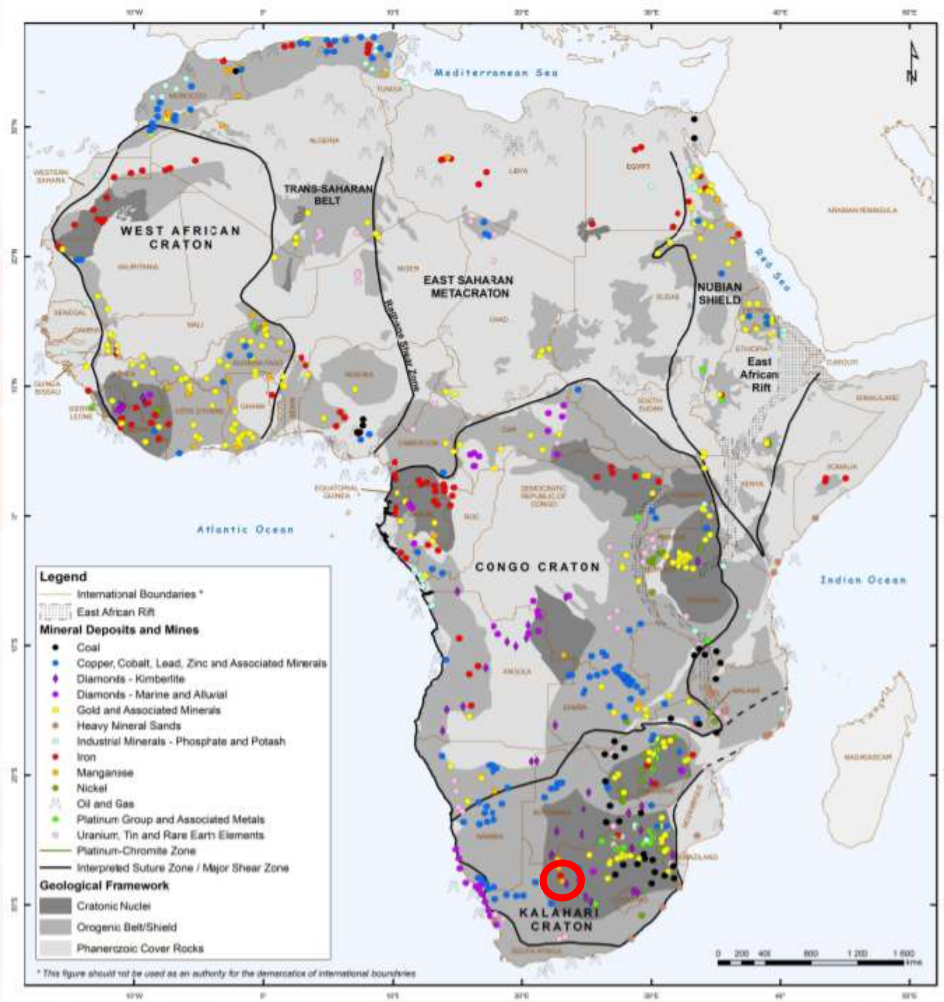

Frost-Killian et al., *Episodes (2016)*

MANGANESE

Image from: relianttechnologyinstitute.com

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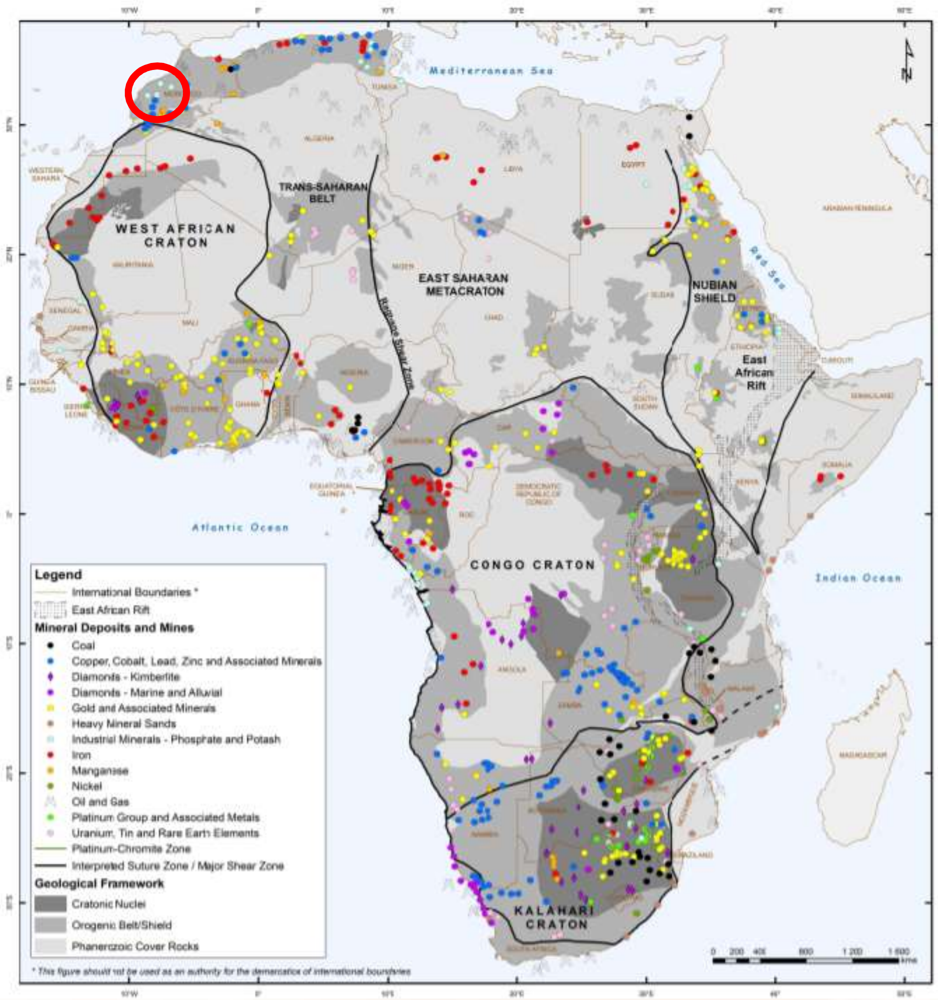

Frost-Killian et al., Episodes (2016)

Phosphate

Image from: Alibaba.com

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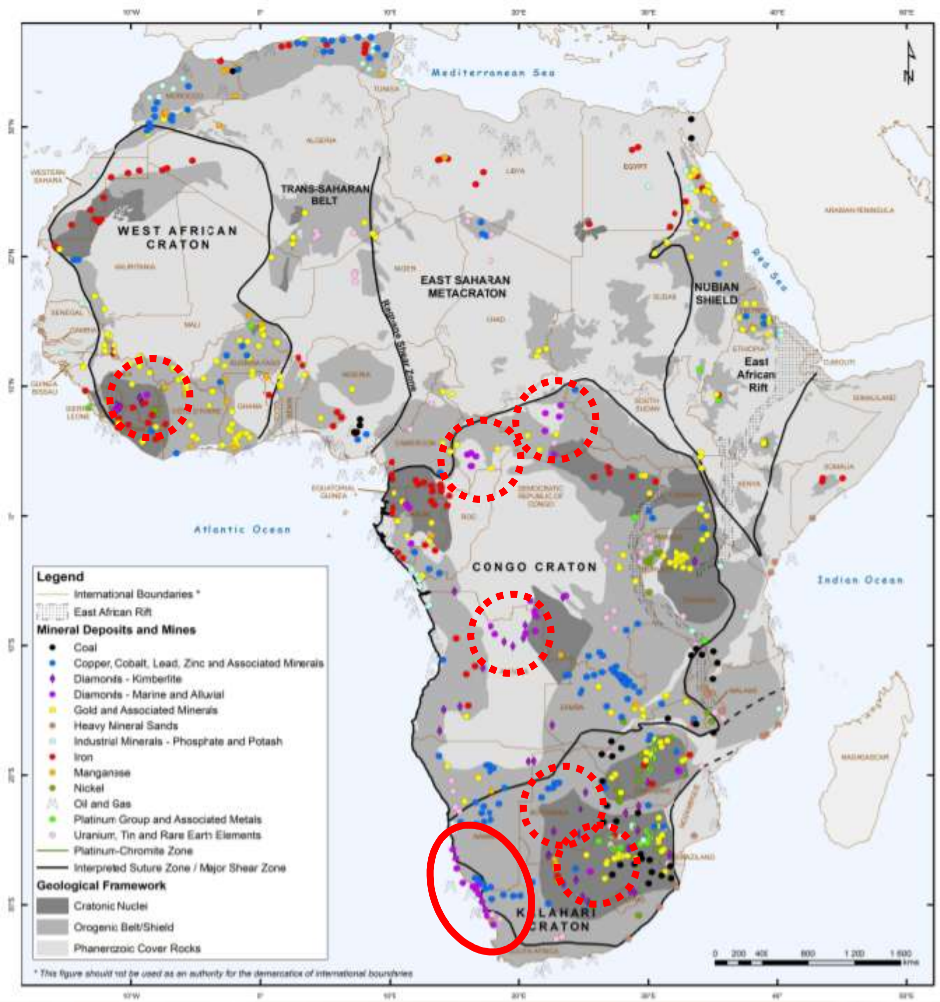

Frost-Killian et al., *Episodes* (2016)

Diamonds

Image from: advancedsciencenews.com

Image from: strategiesonline.net

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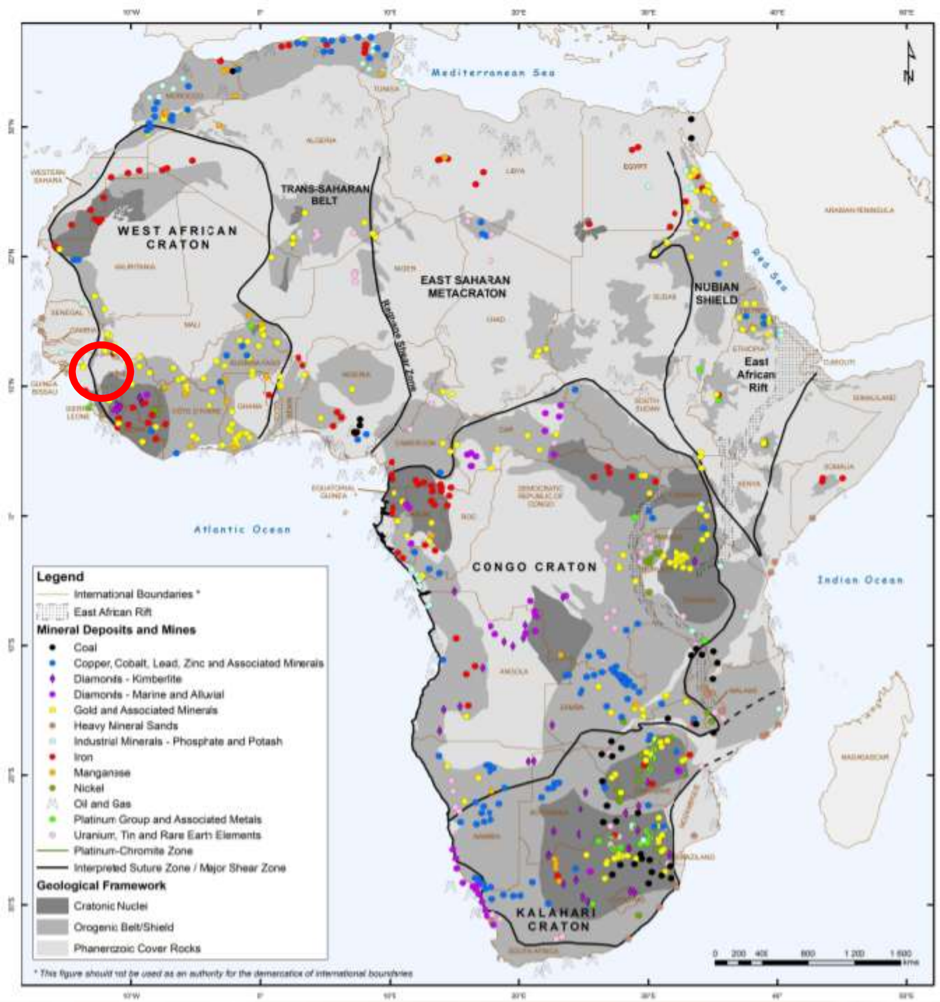

Frost-Killian et al., *Episodes* (2016)

Aluminum

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Image from: boraluminyum.com

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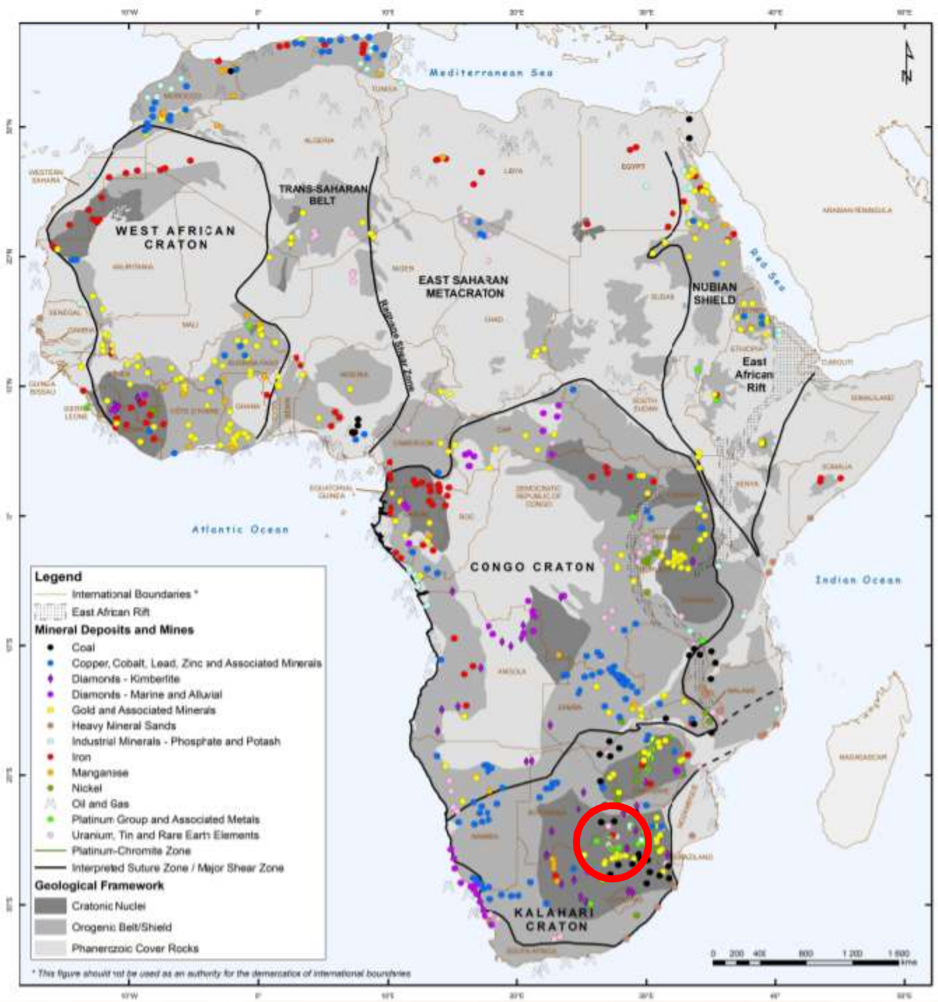

Frost-Killian et al., Episodes (2016)

Platinum

Palladium

Chromium

Vanadium

Andalusite

Image from: platinum-info.weebly.com

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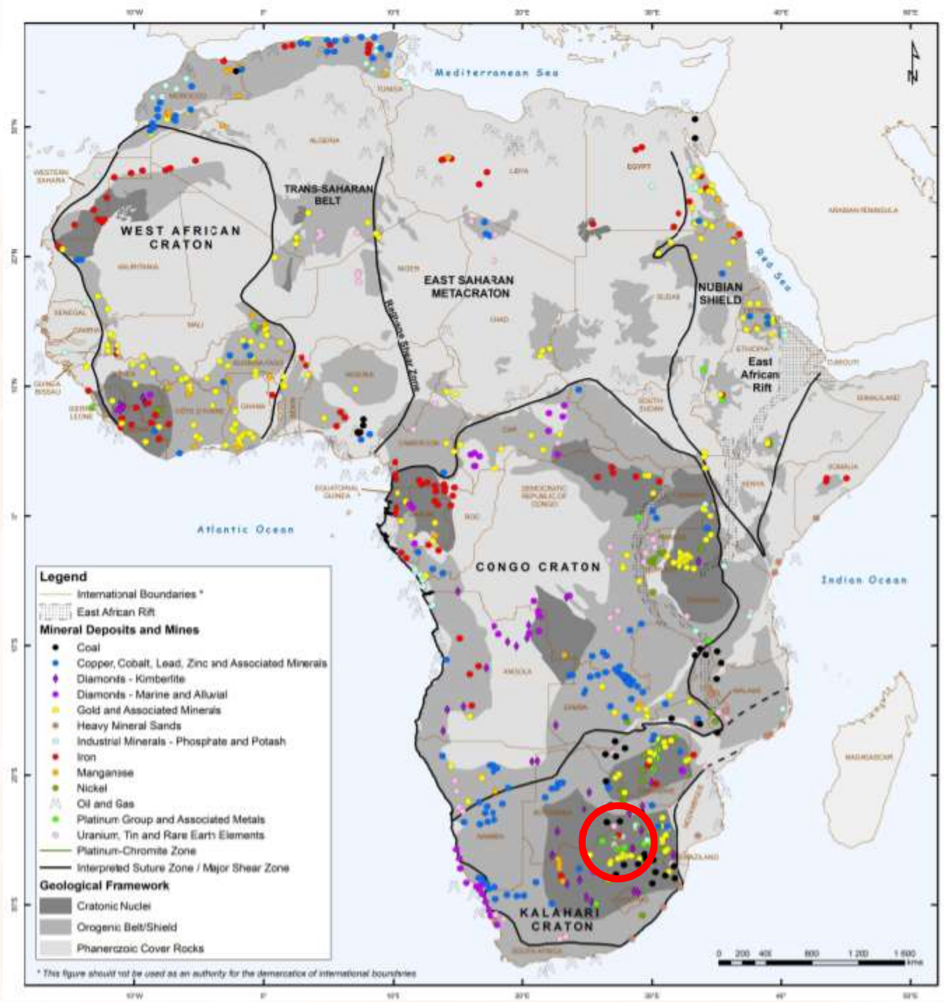

Frost-Killian et al., Episodes (2016)

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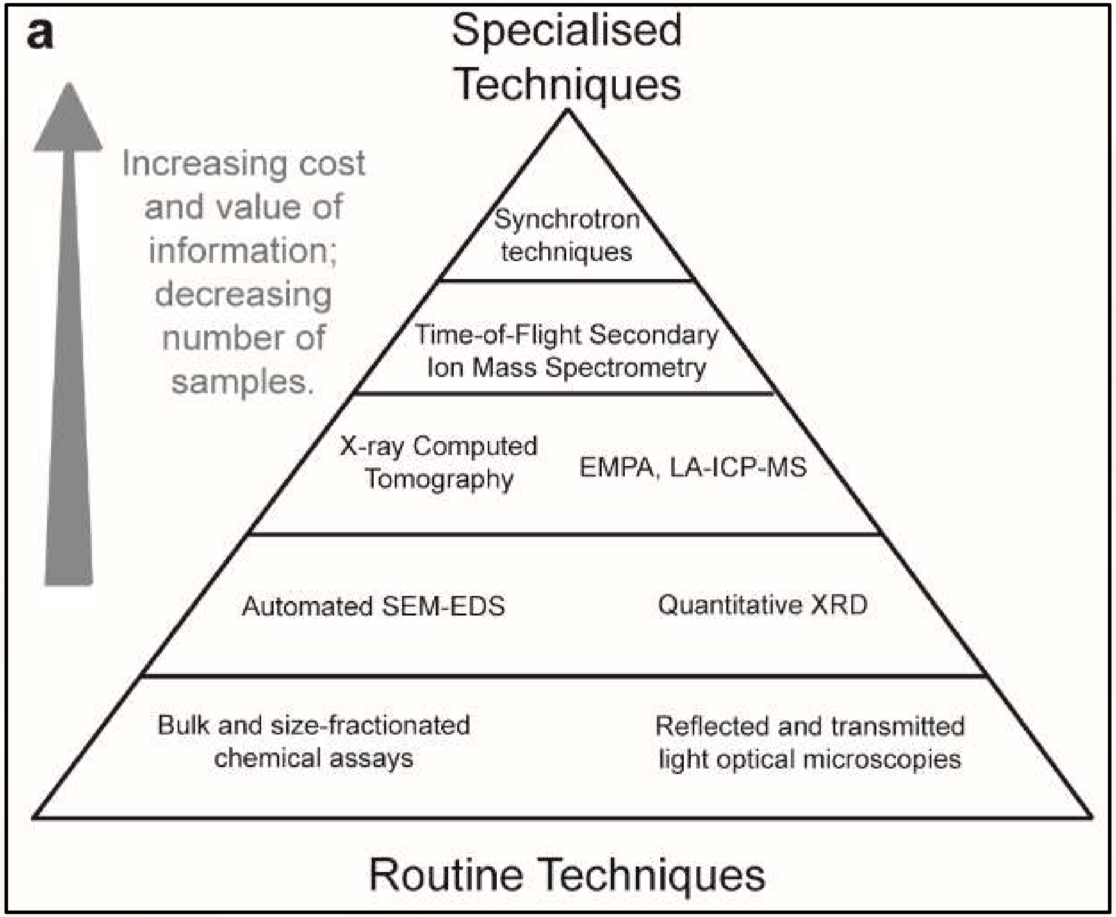
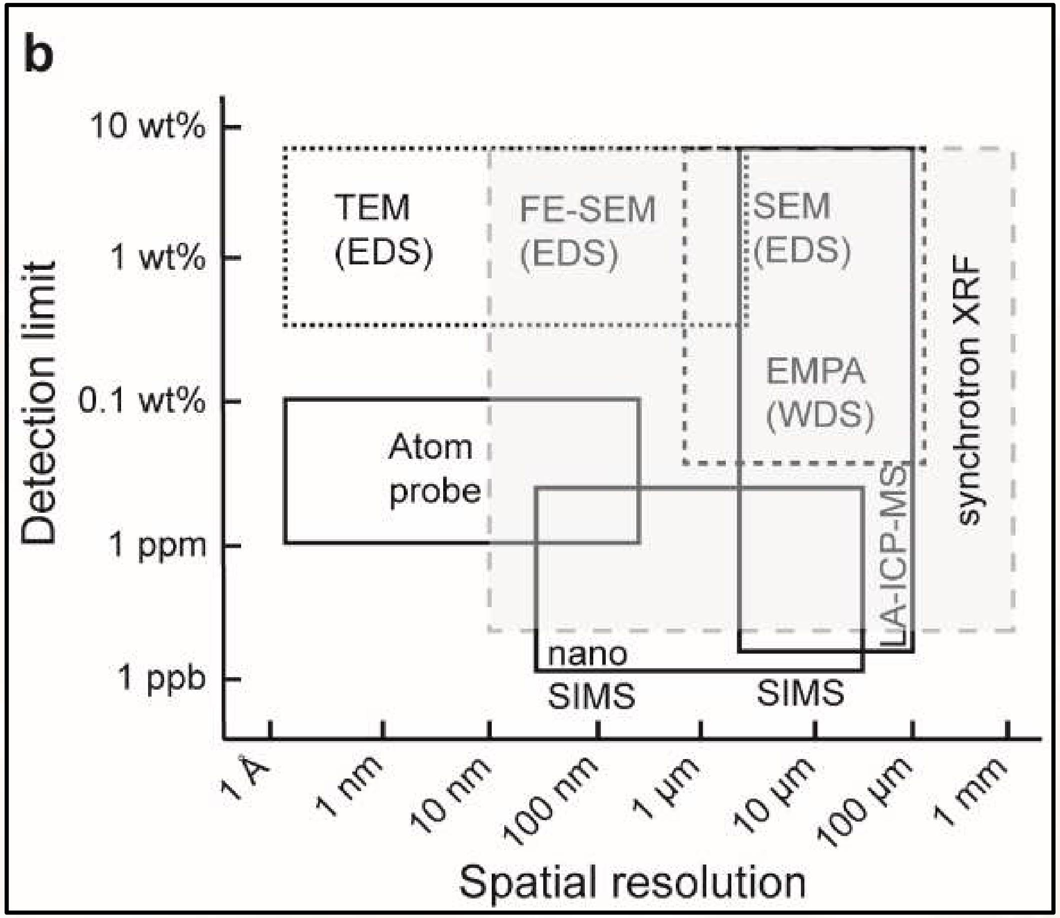
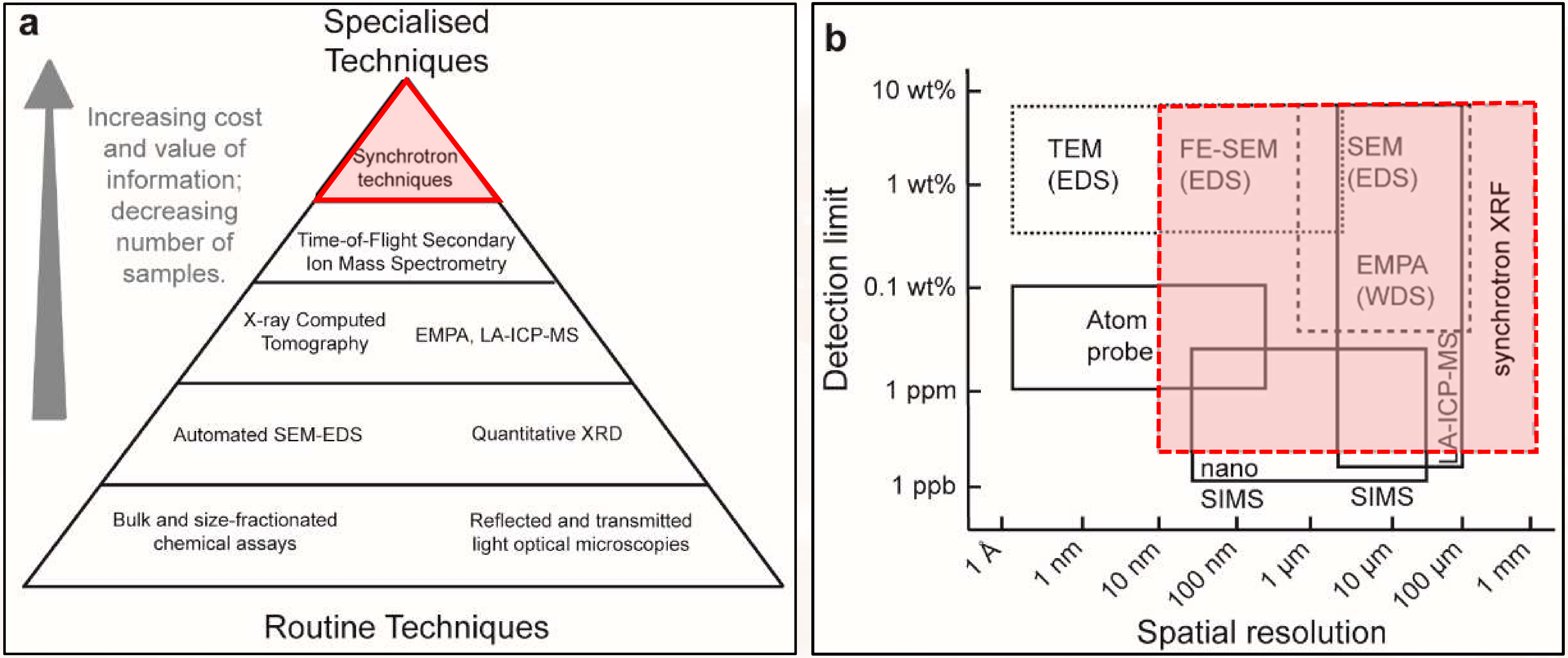
How can we study these mineral endowments?





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).

How can we study these mineral endowments?



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).

But what about impacts on the environment?

- Inasmuch as legislature serves to protect the natural environment, it does not guarantee that spills, leakages from tailings facilities and other forms of emissions will not take place.
- Strong need to understand the fate and degradation products associated with addition of deleterious moieties into the natural environment.

Niger delta oil spills

Image from: dw.com

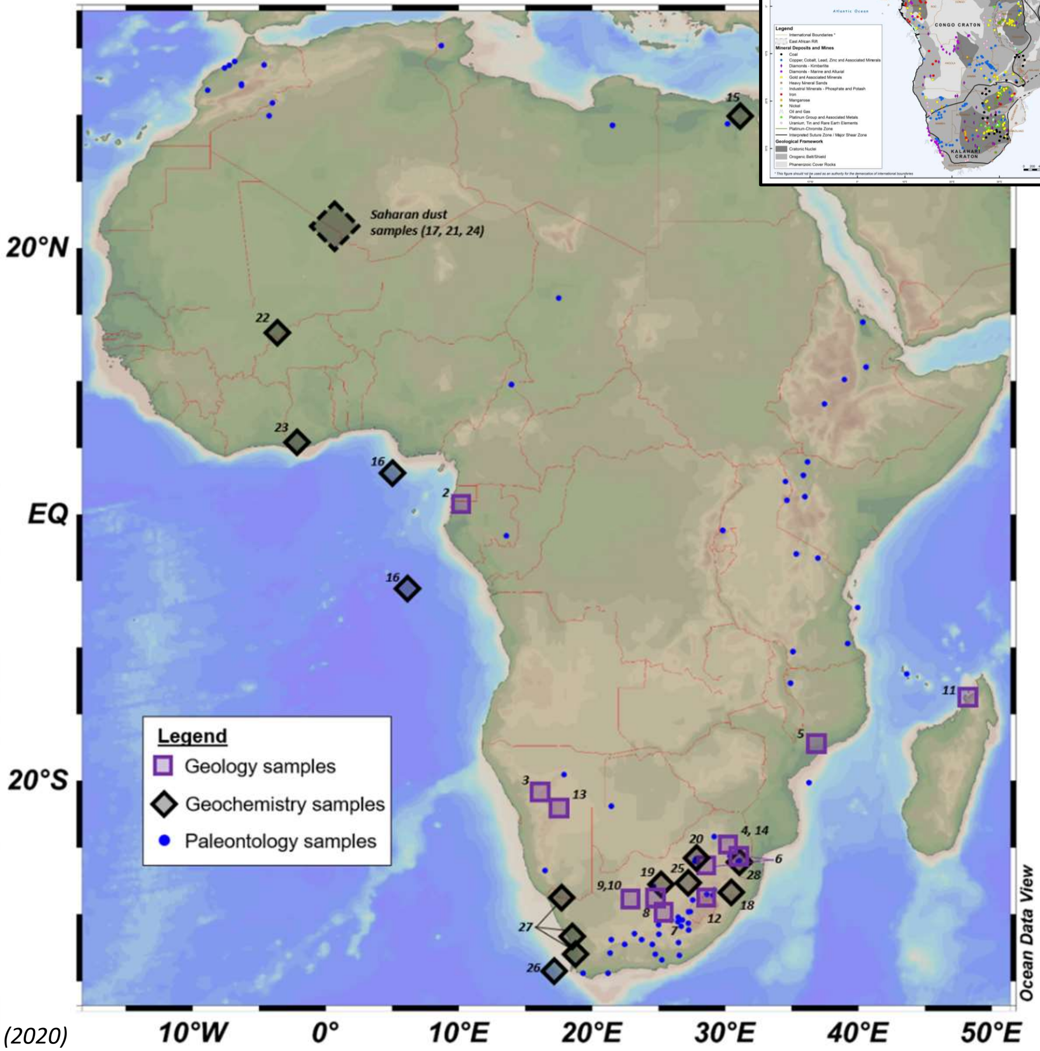
Merriespruit tailings dam disaster (1994)

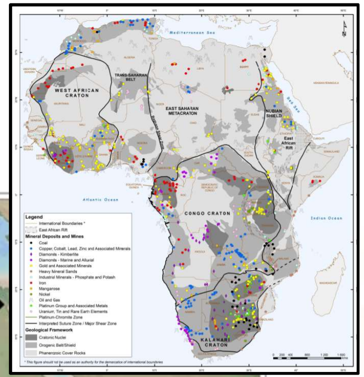
Image from: floodlist.com

Past use of synchrotron in the African earth sciences

#	Study	Sample location	Technique	Beamline (Facility)	Key findings
Geological Sciences:					
1.	Acres et al. (2010)	Gauteng, South Africa	sXPS	14ID (AS)	Effect of bornite on oxidation and leaching of chalcopyrite
2.	Barnes et al. (2016)	Monts de Cristal igneous complex (Gabon)	sXRF mapping	XFM beamline (AS)	High Pt concentrations associated with As- and Cu–Ni sulphides and forms during Pt saturation during magmatic crystallization.
3.	Buhn et al. (1999)	Kalkfeld carbonatite complex (Namibia)	sXRF	Beamline L (HASYLAB)	Chemistry of REE-carbonate burbankite crystals hosted in carbonatite fluid inclusions.
4.	Darin et al. (2016)	UG1 chromitite (South Africa)	sXRF	Elemental Analysis station (SSTRC)	Scanning of 20 trace elements' distribution in a layered sequence, with special emphasis on PGE.
5.	Figueiredo et al. (2008)	Licungo pegmatite (Mozambique)	Fe K-edge XANES	ID21 (ESRF)	Fe in octahedral Al sites possibly gives rise to blue colouration in beryls.
6.	Gauert et al. (2015)	Witwatersrand and Barberton gold (South Africa)	sXRF	BAMLine (BESSY-II)	Inter-calibration for trace element fingerprinting in gold (sXRF, EMPA, LA-ICP-MS).
7.	Guilhaumou et al. (2005)	Jagersfontein kimberlite (South Africa)	sFTIR	MIRAGE beamline (LURE)	Chemical evaluation of μm-scale melt inclusions from kimberlite garnets reveals a complex ascent history for 'ultra-deep' kimberlite material.
8.	Hanger et al. (2015)	Wesselton kimberlite (South Africa)	Fe K-edge XANES	XFM beamline (AS)	$Fe^{3+}/\sum Fe$ ratios used to evaluate oxidation conditions during kimberlite metasomatism.
9.	Johnson et al. (2013)	Kalahari Mn Fields	Mn K-edge XAS	Beamlines 4–1 and 10–2 (SSRL)	Mn redox chemistry indicates Mn oxidation in the absence of O_2 (i.e., prior to the great oxygenation event).
10.	Johnson et al. (2016)	Kalahari Mn Fields (South Africa)	Mn K-edge XAS	Beamlines 2–3 and 10–2 (SSRL)	Mn redox chemistry shows a change in the primary mineralogy between ancient- and more modern sedimentary Mn deposits.
11.	Ram et al. (2019)	Ampasibitika intrusion (Madagascar)	sXRF; Ce L-edge XAS	XFM beamline (AS)	Diverse Ce chemical speciation in ion adsorption clays (associated with Zr, with clay minerals as Ce^{3+}, and with Fe/Mn oxides as Ce^{4+}). Implications for LREE cycling in surficial deposits.
12.	Song et al. (2001)	Lesotho Highlands (Lesotho)	sXCT	X27C (NSLS)	Quantitative characterization of vesicle morphology provides insight into magmatic processes (e.g., volatile content, lava flow, etc.).
13.	Sommer et al. (2014)	Robert Victor kimberlite (South Africa)	sFTIR	(ANKA)	Detection of C:O:H volatiles in defect sites in garnets suggest microdiamond growth in eclogites.
14.	Takahashi et al. (2007)	Onganja mine (Namibia)	Re and Os L-edge XAS	BL12-C (PF); BL37XU (SPring-8)	Determination of Re and radiogenic Os local coordination environments in molybdenite mineral structure. Difference in relative diffusion rates has implications for Re–Os geochronology.
15.	Vekaler et al. (2018)	UG2 chromitite (South Africa)	sXRF	Elemental Analysis station (SSTRC)	Variable trace element distributions in chromitite seams interpreted to reflect permeability and element diffusivity in crystallising mafic melts.
Environmental Geochemistry Sciences:					
16.	Abozied et al. (2015)	Giza (Egypt)	SXRF	FLUO beamline, (KIT)	Elemental analysis of urban aerosols
17.	Bourry et al. (2007)	Congo-Angola basin	SXRD	ID31 (ESRF)	Small concentrations of H_2S and CO_2 affect the type 1 CH_4 clathrate cubic lattice structure.
18.	Doherty (2012)	West Africa	SXRD, sXRF	X26 (NSLS)	Elemental map, mineralogy
19.	Eascott (2010)	KwaZulu Natal (South Africa)	SXRD, sXRF	X26A (NSLS)	Paint samples on artifacts
20.	Eroglu et al. (2018)	Neoarchean Campbellrand-Malmani carbonate platform (South Africa)	XANES	ID24 (ESRF)	Fe speciation in carbonate rich shelf sediments
21.	Herries et al. (2014)	Haasgat (South Africa)	SXRF	(AS)	Elemental maps of Karst samples
22.	Longo (2016)	Sahara Desert	XANES	2ID-D (APS)	Fe oxidation state and structural arrangement of atoms
23.	Mazel et al. (2007)	Mali	SFTIR, sXRF	ID21 (ESRF)	Vibration bands, Elemental maps
24.	Mensah et al. (2020)	Gold mine in western region of Ghana	XANES	TLS 07A (NSRRC)	As K-edge for As speciation in soil samples
25.	Petrosselli et al. (2019)	Sahara Desert	XANES, EXAFS	BM08 (ESRF)	Fe K-edge, Fe coordination structure
26.	Solomon et al., (2005), 2009	Free State Province (South Africa)	XANES	X19A (NSLS)	S K-edge for S speciation in arable soils
27.	von der Heyden et al., 2012	Cape Basin (South Africa) and Southern Ocean	STXM, Fe L-edge XAS	11.0.2 (LBNL)	Determination of valence and local coordination environment of Fe in suspended marine particulates and nanoparticles; provides insights into biogeochemical cycling of this important bio-active trace nutrient.
28.	von der Heyden et al., 2018	Orange, Olifants and Berg Rivers (South Africa)	STXM, Fe L-edge XAS	11.0.2 (LBNL)	Concentration and local coordination environment of Al within Fe-rich suspended particulates; with implications for Fe particle solubility.
29.	Westall et al. (2011)	Barberton Greenstone Belt, (South Africa)	XANES, STXM	ID21 (ESRF) X1A (NSLS)	S K-edge, C K-edge and elemental mapping of S

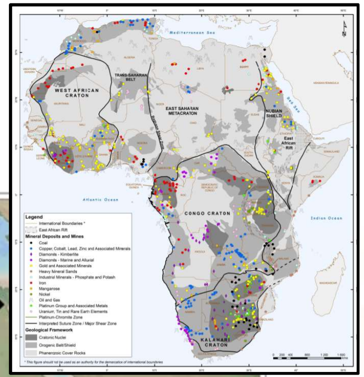
von der Heyden et al., Journal of African Earth Sciences (2020)

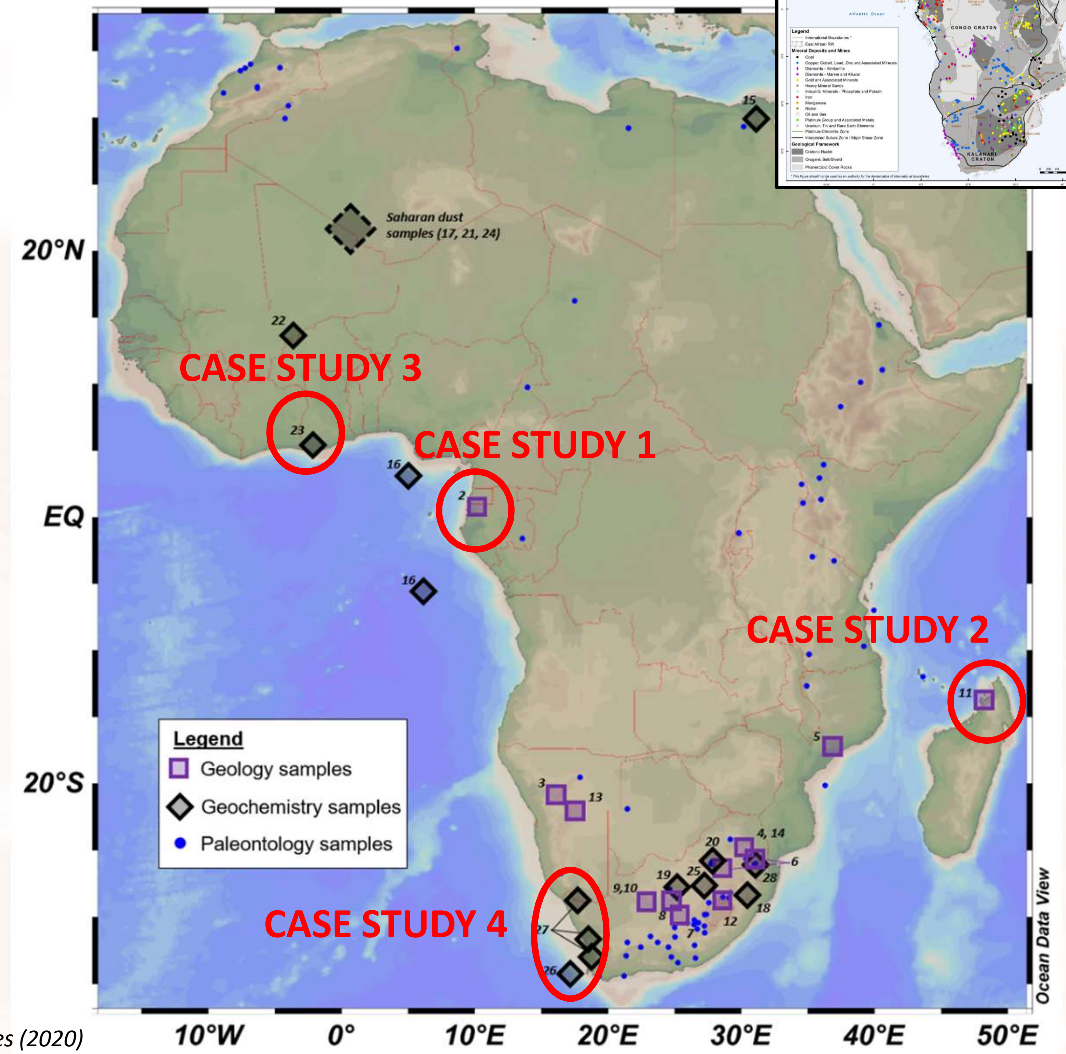




Past use of synchrotron in the African earth sciences

- **Case study 1:** Mineral resources geology
  - Platinum associations in a Cu-Ni magmatic sulphide system (Barnes et al. 2016)
- **Case study 2:** Mineral resources geology
  - LREE cycling in surficial deposits (Ram et al. 2019)
- **Case study 3:** Environmental geochemistry
  - As speciation in soils (Mensah et al. 2020)
- **Case study 4:** Environmental geochemistry
  - Fe speciation in aquatic systems (von der Heyden et al. 2012, 2014, 2018)

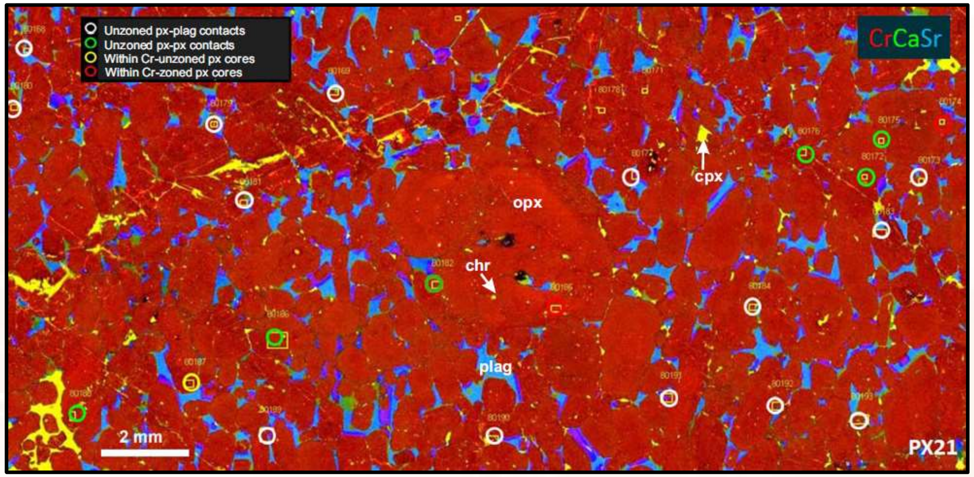


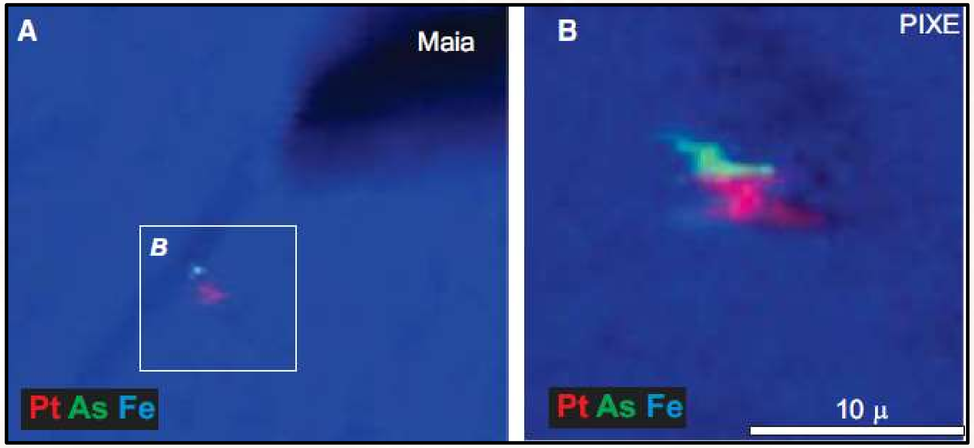


von der Heyden et al., Journal of African Earth Sciences (2020)

Case study 1: Platinum in the Monts de Cristal Complex, Gabon (Barnes et al., 2016)

- XFM beamline at the Australian Synchrotron (equipped with Maia detector array).
- *“Pt minerals less than 5 µm in diameter can be detected in samples containing 10 s of ppb Pt, with scanning times of a few hours per standard sized thin section.”*
- Synchrotron used to locate grains of interest for both further synchrotron study and interrogation using µPIXE.
- Studies concludes that Pt alloys (and arsenides) can crystallize directly from magmatic systems when saturation occurs at the Pt solubility limit.





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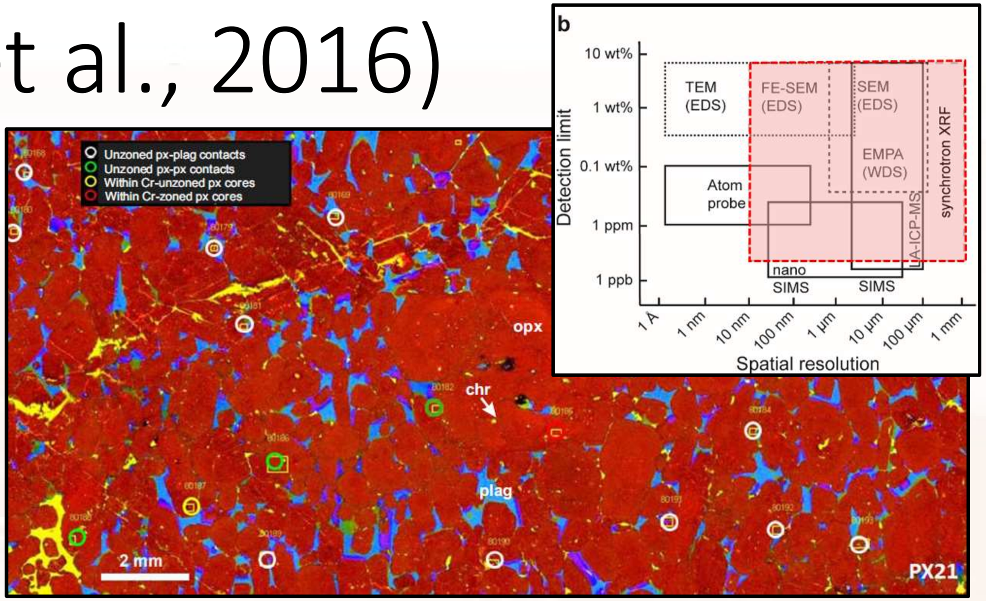
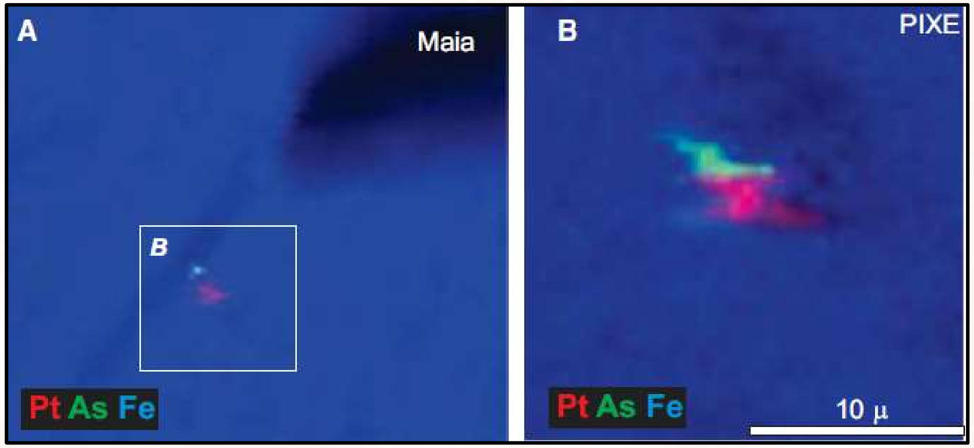
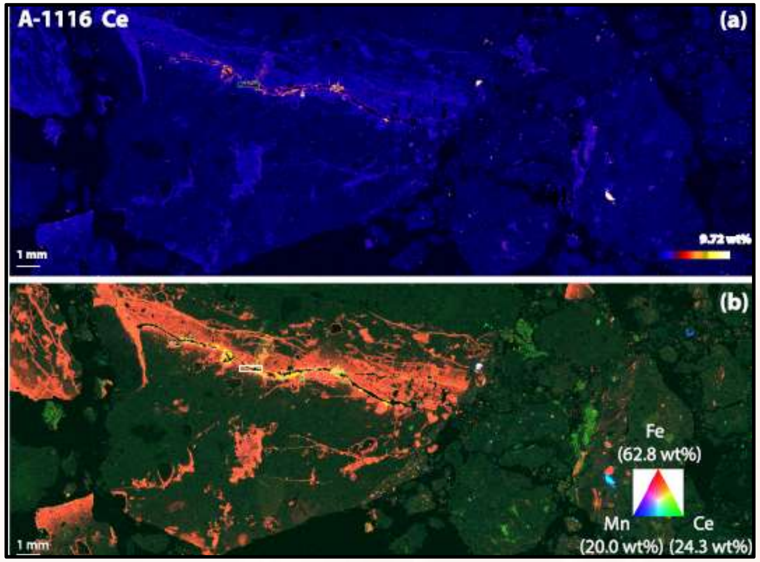
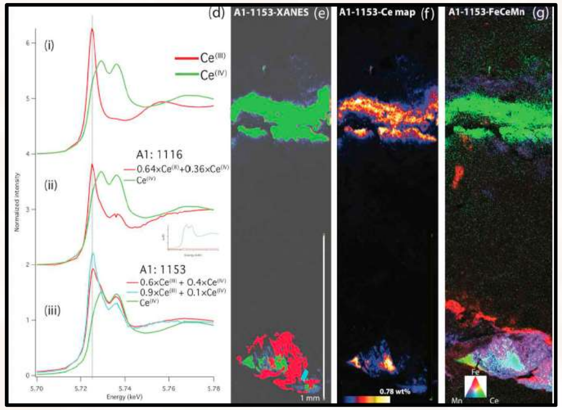




Case study 2: REE characterization in ion-adsorption clays in Madagascar (Ram et al., 2019)

- XFM beamline at the Australian Synchrotron (equipped with Maia detector array).
- REE distributions within a heterogeneous clay mineralogy using sXRF. Show some associations with Zr and Fe-Mn oxides.
- Additional insights related to Ce speciation obtained from XANES analysis.
- Identification of Ce(IV) has implications for beneficiation strategies, with a net result of increasing the HREE grade of the deposit.





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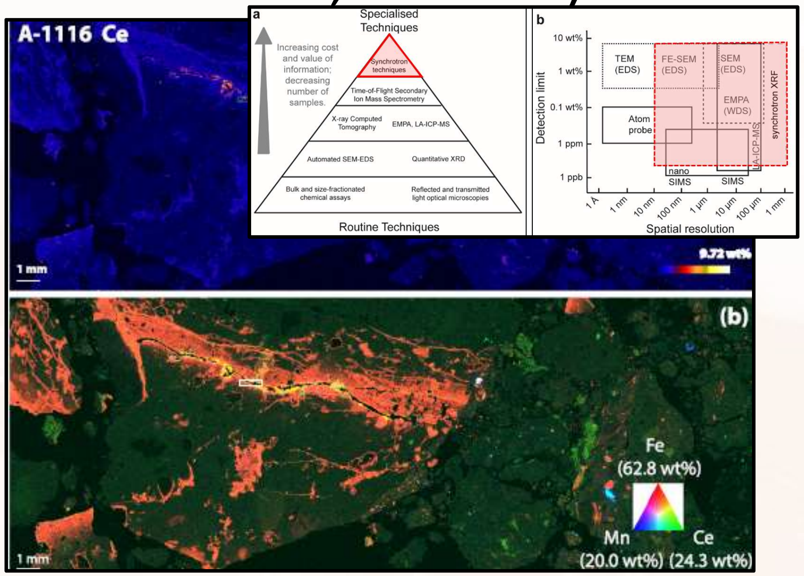
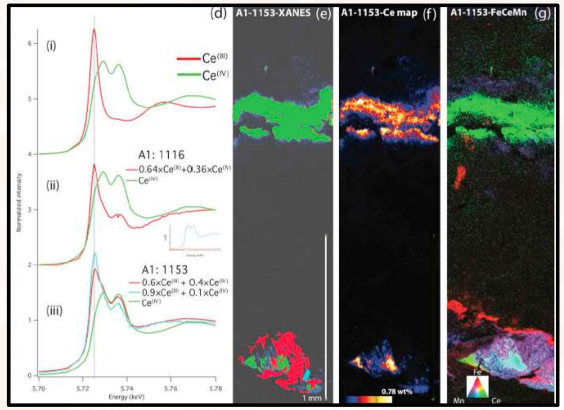
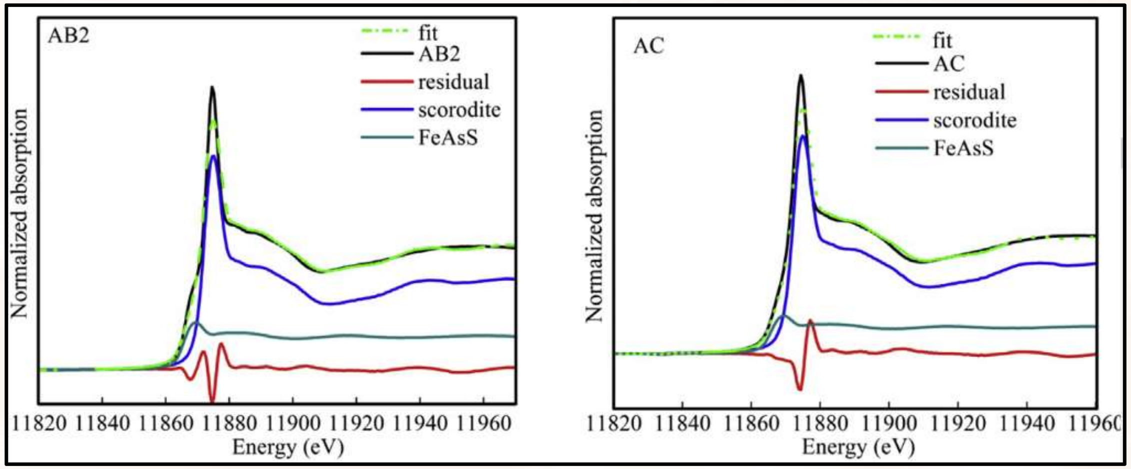




Case study 3: Arsenic speciation in tailing materials from gold mines in Ghana (Mensah et al., 2020)

- 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.



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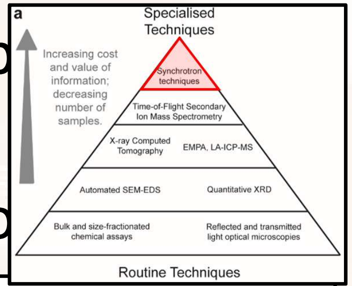
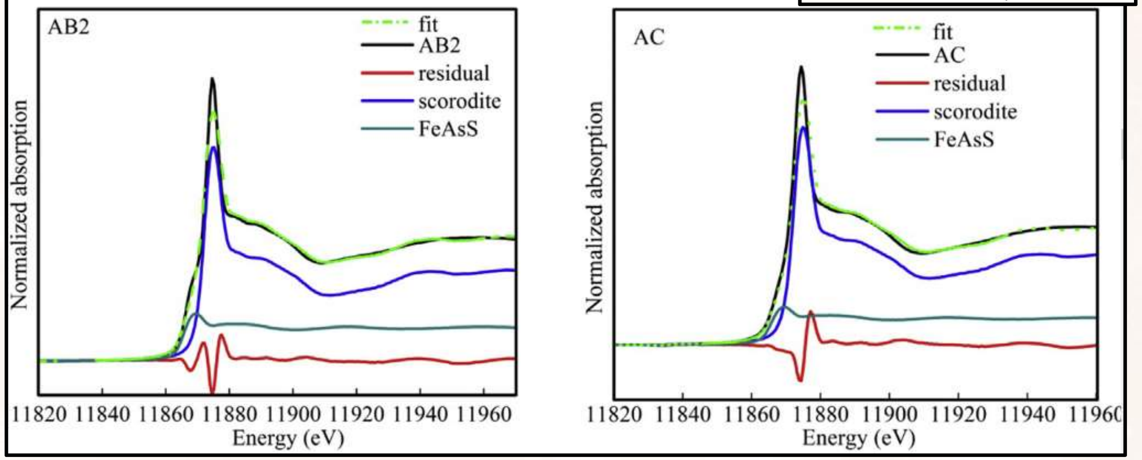
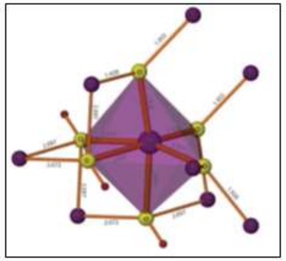


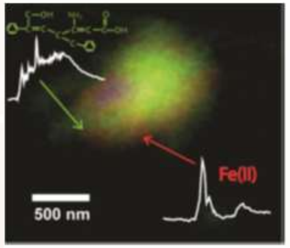


Case study 4: Fe speciation in aquatic particles, South Africa (von der Heyden et al.)

- Beamline 11.0.2 at the Advanced Light Source, USA.
- Soft X-ray spectroscopy allows evaluation of natural colloids and nanoparticles at ambient conditions.
- Series of studies showed differences in Fe speciation, associations between Fe(II) and organic matter, and variable levels of Al substitution.



Von der Heyden et al., Am. Min. (2017)



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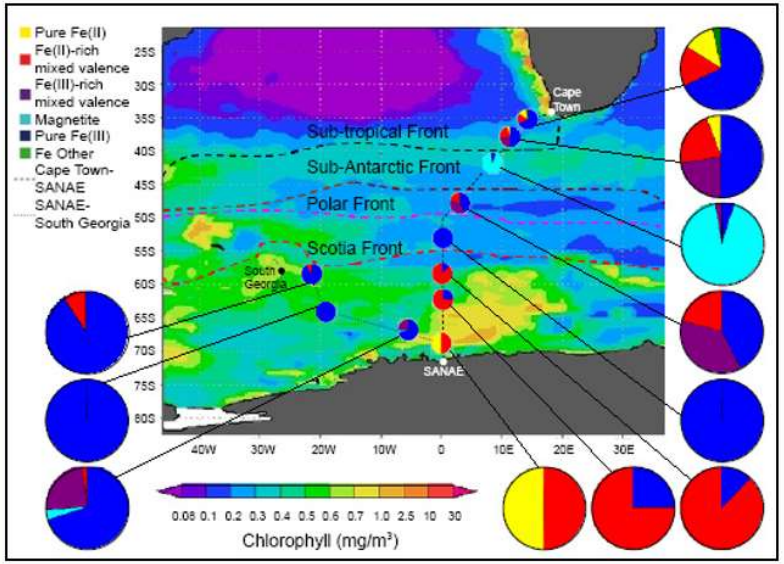

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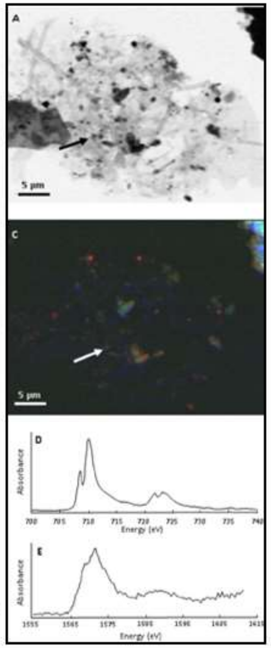

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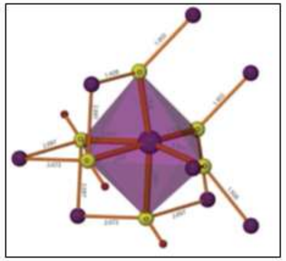

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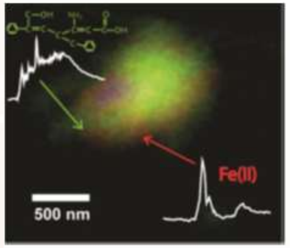

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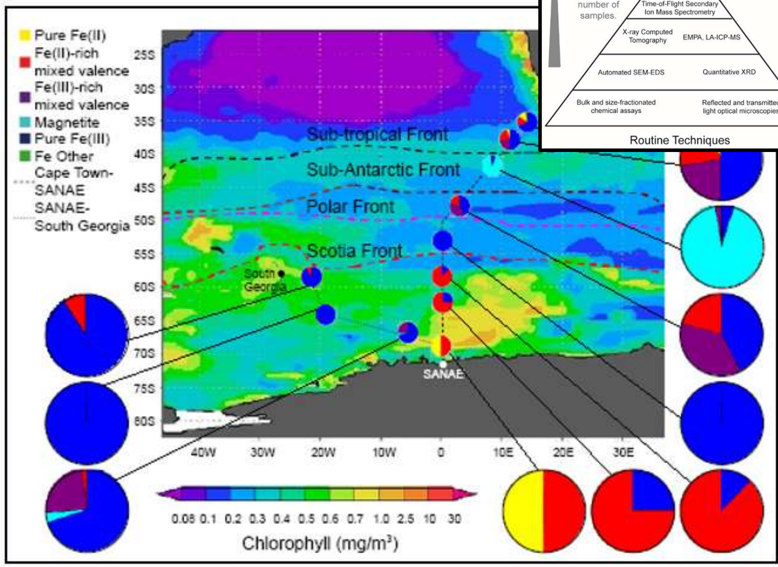

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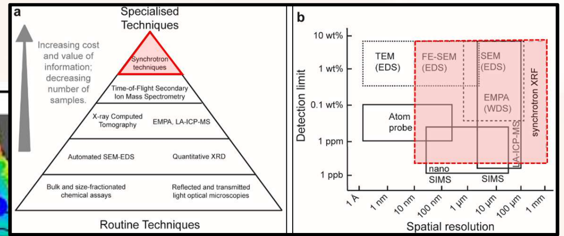

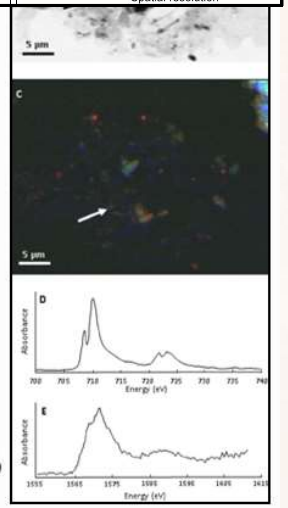

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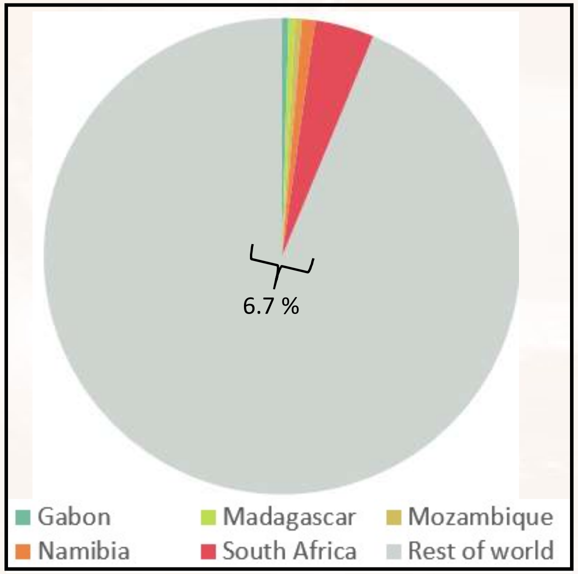
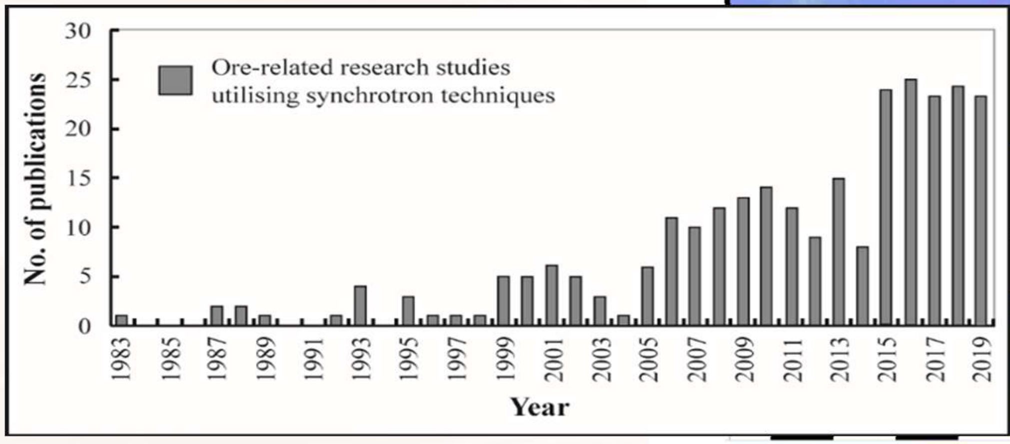
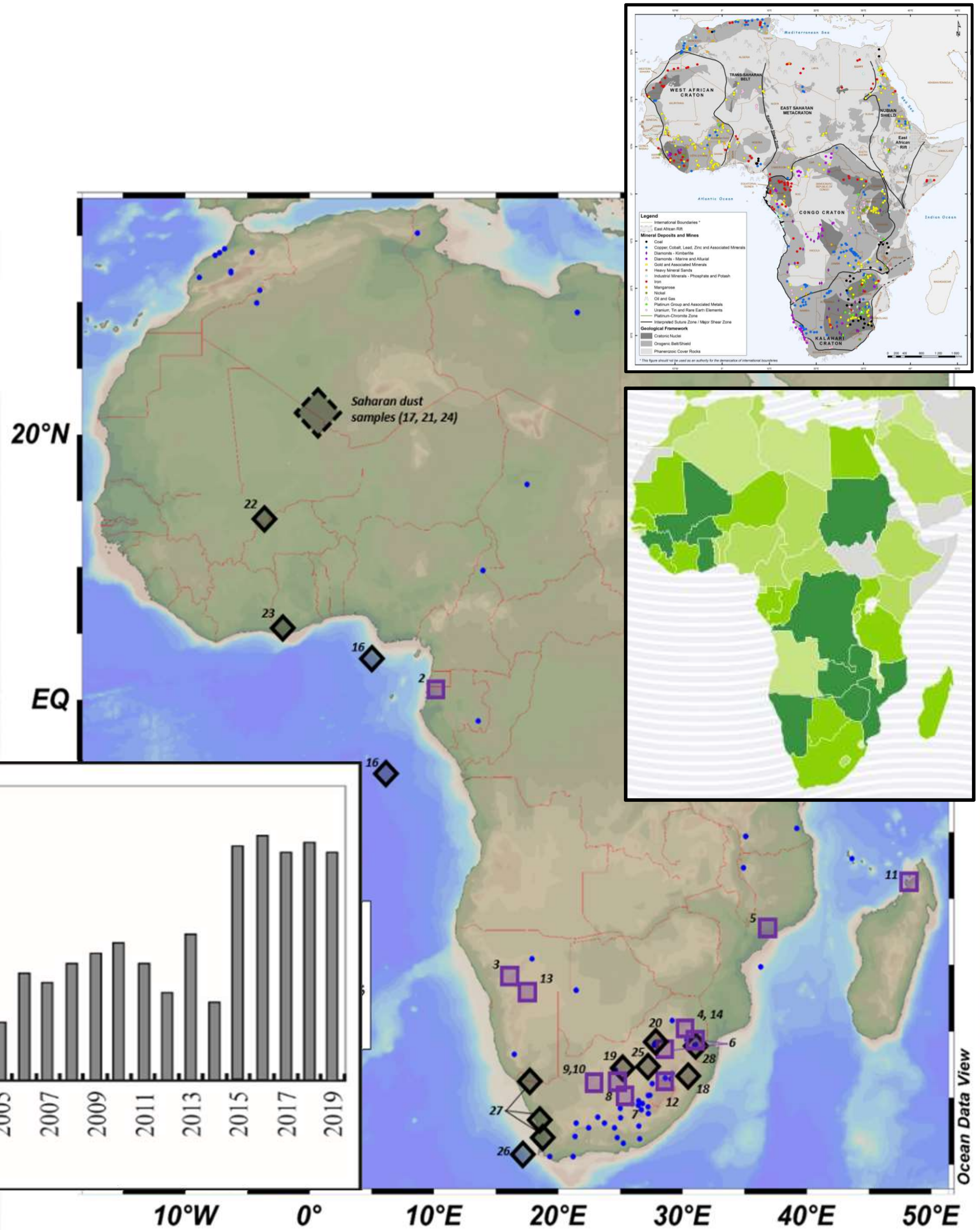
Conclusions

- African samples under-represented despite significant endowments.
- African earth science researchers under-represented in the global research arena.





von der Heyden 2020



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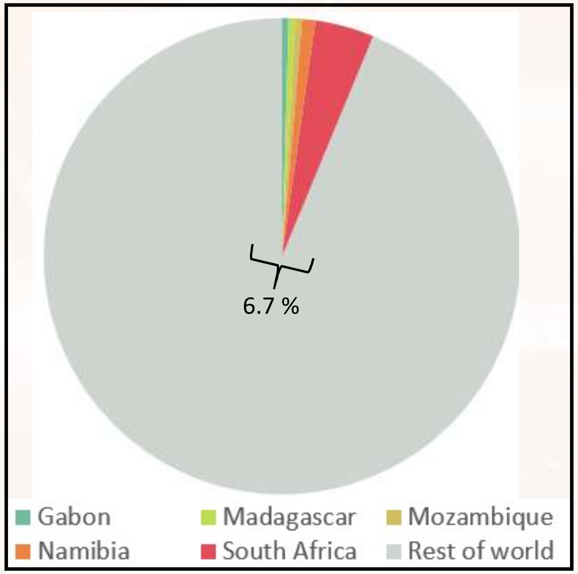
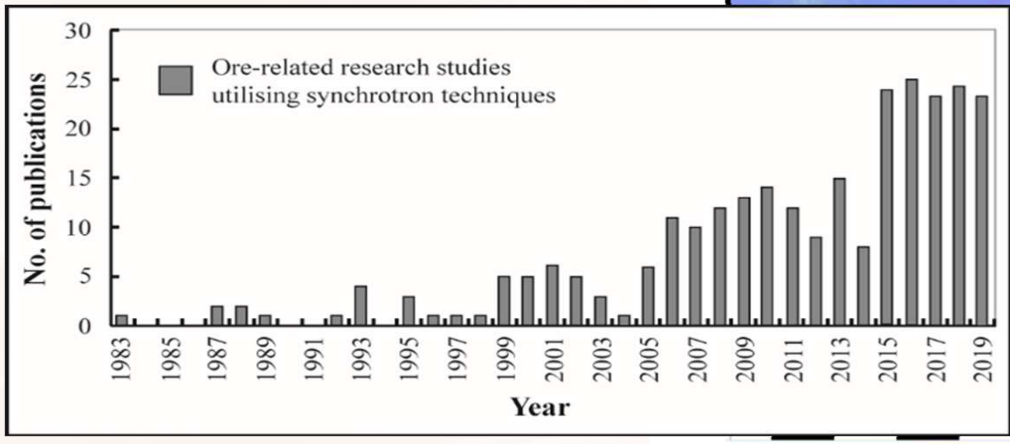
- African light source or collaborations with partners to mitigate these under representations.





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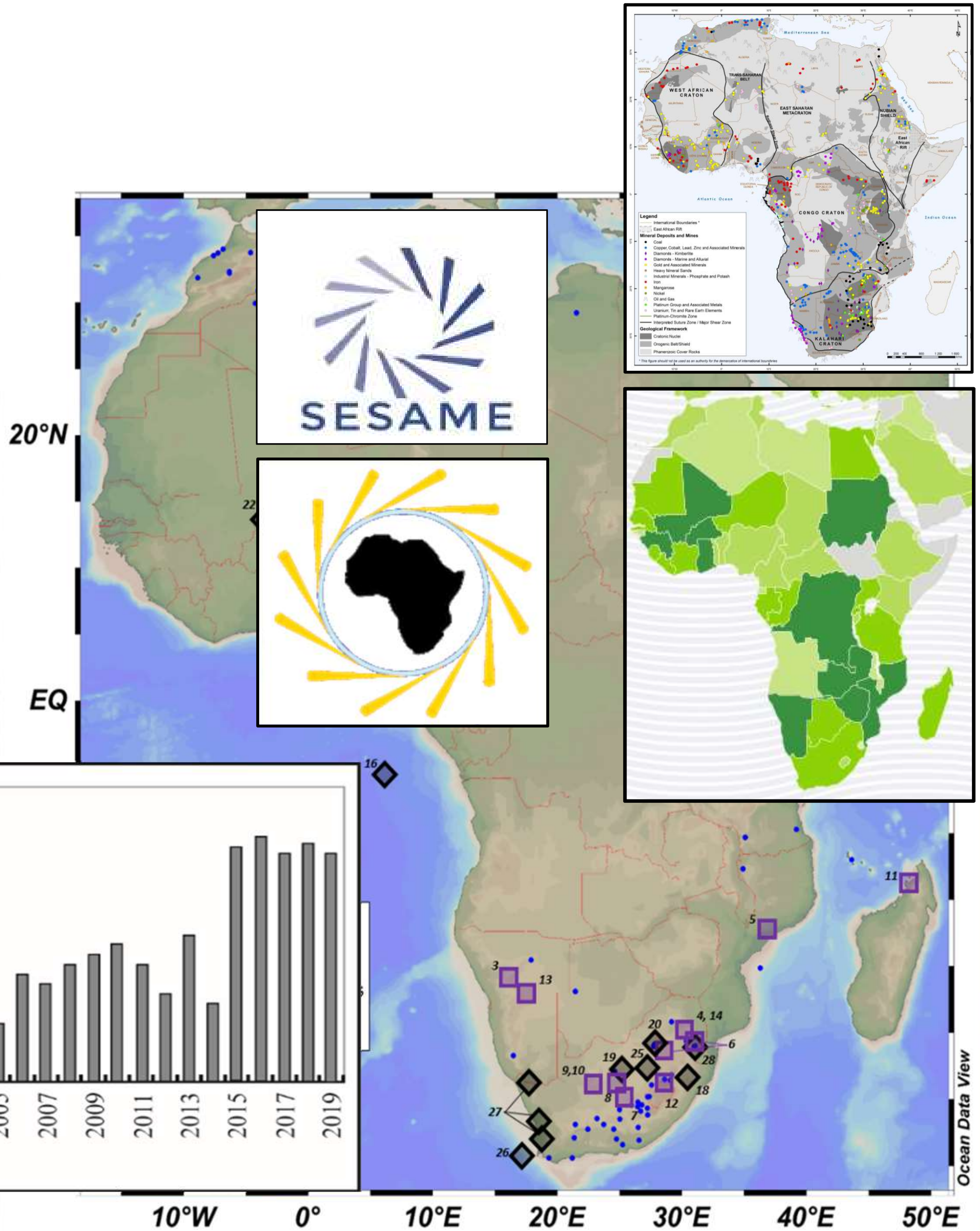

SESAME

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SESAME - AFRICA ONLINE WORKSHOP

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- You as the audience.
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NRF | RISA
National Research Foundation | Research and Innovation Support and Advancement

cimera DST-NRF Centre of Excellence for Integrated Mineral and Energy Resource Analysis

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Questions??

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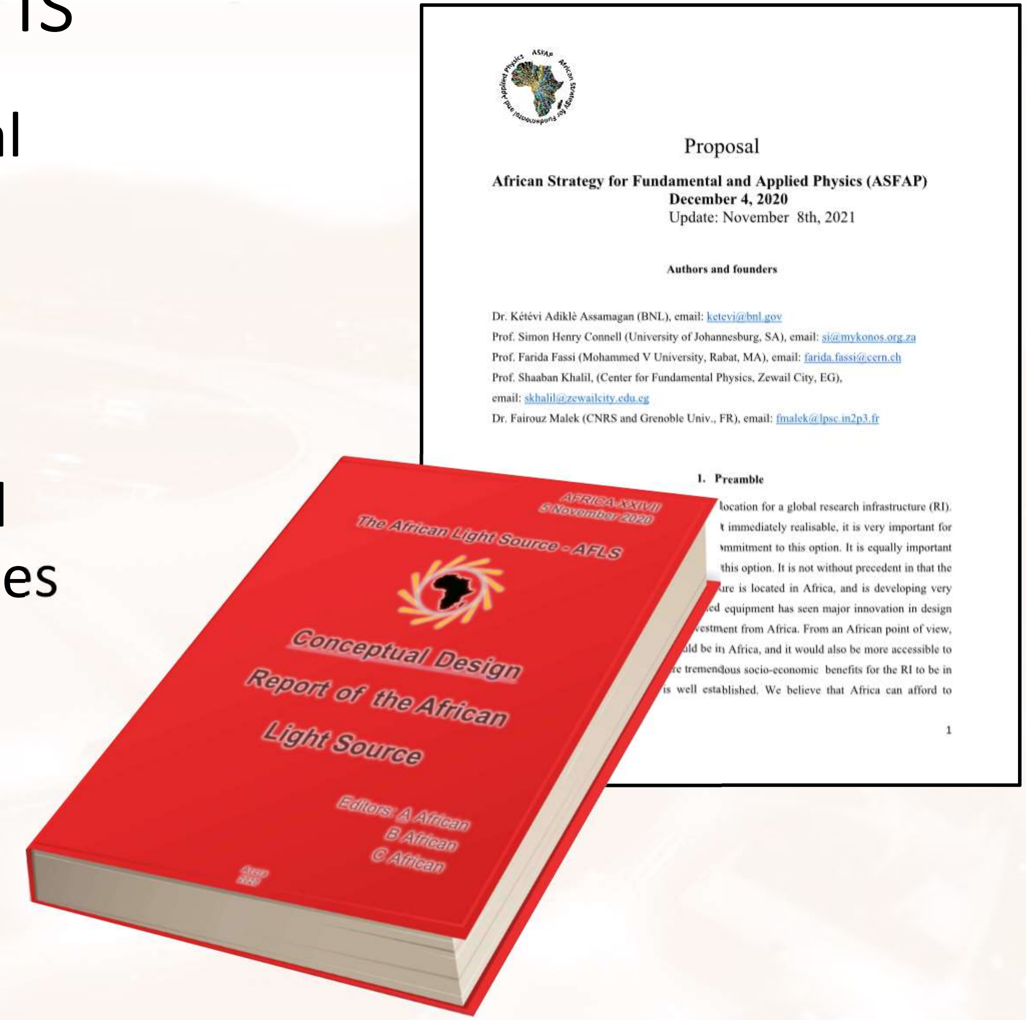
Ongoing interventions towards advancing earth sciences interactions

- African Light Source (AfLS) conceptual design report
  - Letters of interest can be emailed to bvon@sun.ac.za

- African Strategy for Fundamental and Applied Physics (ASFAP): Earth Sciences working group
  - Letters of interest can be emailed to ASFAP-EarthScience@cern.ch



What are the Earth Sciences?

- Broad umbrella term: necessarily an inter-disciplinary and 'systems science' field of study.
- 'Multi-spheric' – comprising lithosphere, hydrosphere, biosphere, cryosphere, troposphere, stratosphere, and all the way out to the exosphere.
- Selected sub-disciplines include:
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Image taken from: https://science.nasa.gov/earth-science

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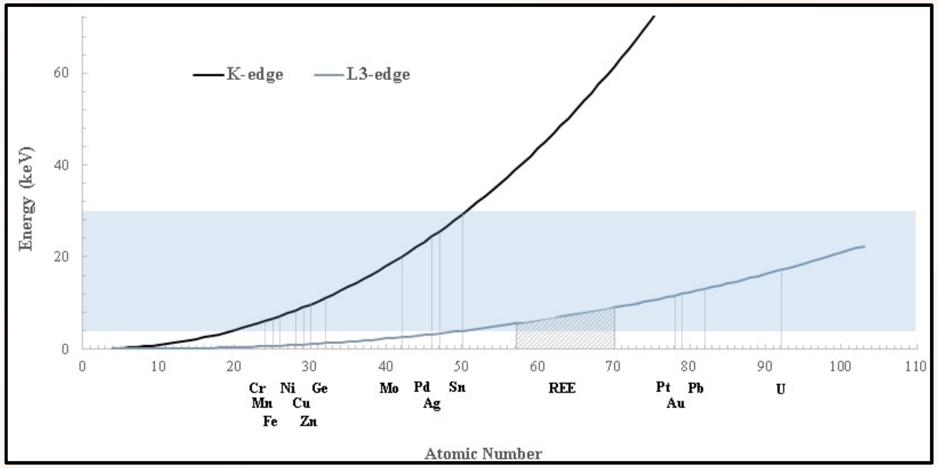
Questions??

Overview of the synchrotron needs of the African Earth Sciences community

- Geological sciences
  - Hard X-ray beamline
  - Should access an energy of at least 40 keV to evaluate important metal K-edges.
  - Tuneable spot size.
  - Possibly a specialized end-station configuration.



- Multi-detector array
- An array of 384 silicon-based detector elements which enables fast (0.2 ms per pixel) elemental mapping at spatial resolutions as small as 2 µm over relatively large sample areas (e.g., 7 cm^2).
- Preferably accessing X-ray energies up to 40 keV with spot size as small as 2 µm.

Case study 1: Platinum in the Monts de Cristal Complex, Gabon (Barnes et al., 2016)

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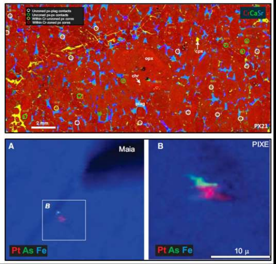

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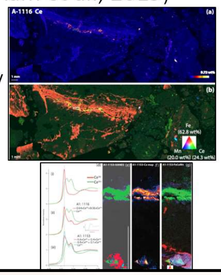
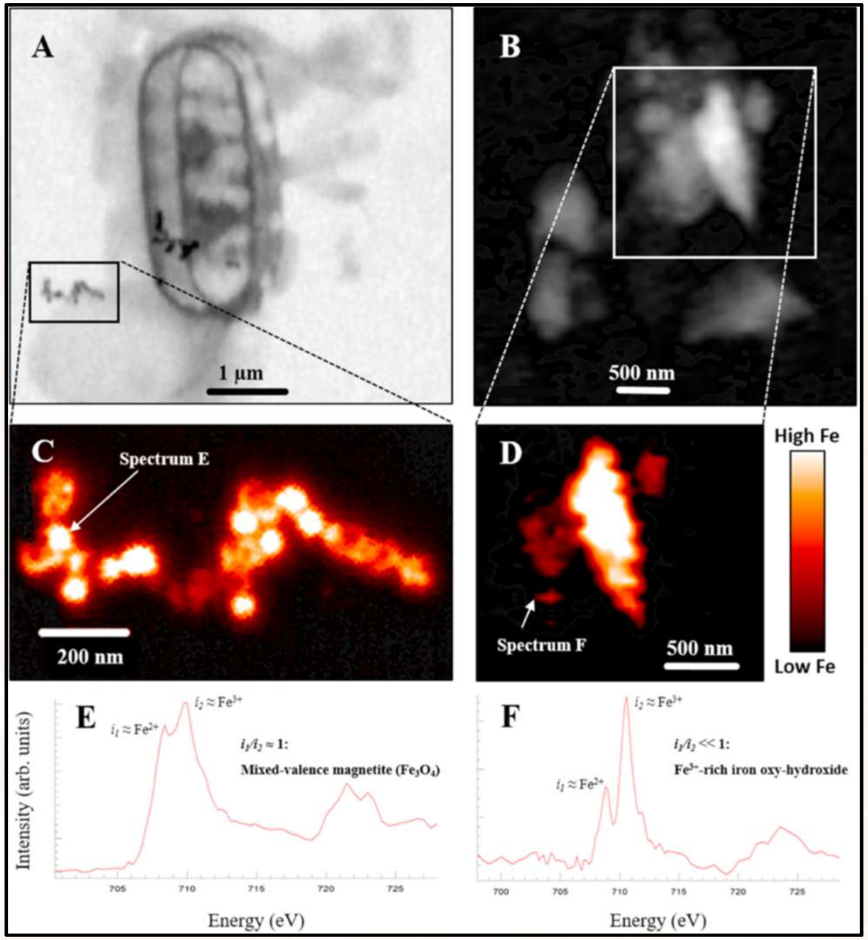


Overview of the synchrotron needs of the African Earth Sciences community

- Environmental geochemistry beamline
  - Soft X-ray spectroscopy
  - Environmental samples are commonly composed of low molecular weight elements, contain biological fractions or are analysed as thin films that are prone to beam damage when exposed to high energy beams.
  - Soft X-ray beamline (50 eV–2000 eV) and should have both spectroscopic and microscopic capabilities (e.g., STXM).
  - Spectral resolution of at least 0.2 eV, and spatial resolution of 10 nm or better.
  - Operate under atmospheric and high vacuum conditions.
  - Time resolved measurements



von der Heyden et al., 2019, 2020