Synchrotron light applied to the Earth Sciences

Bjorn von der Heyden

Stellenbosch University

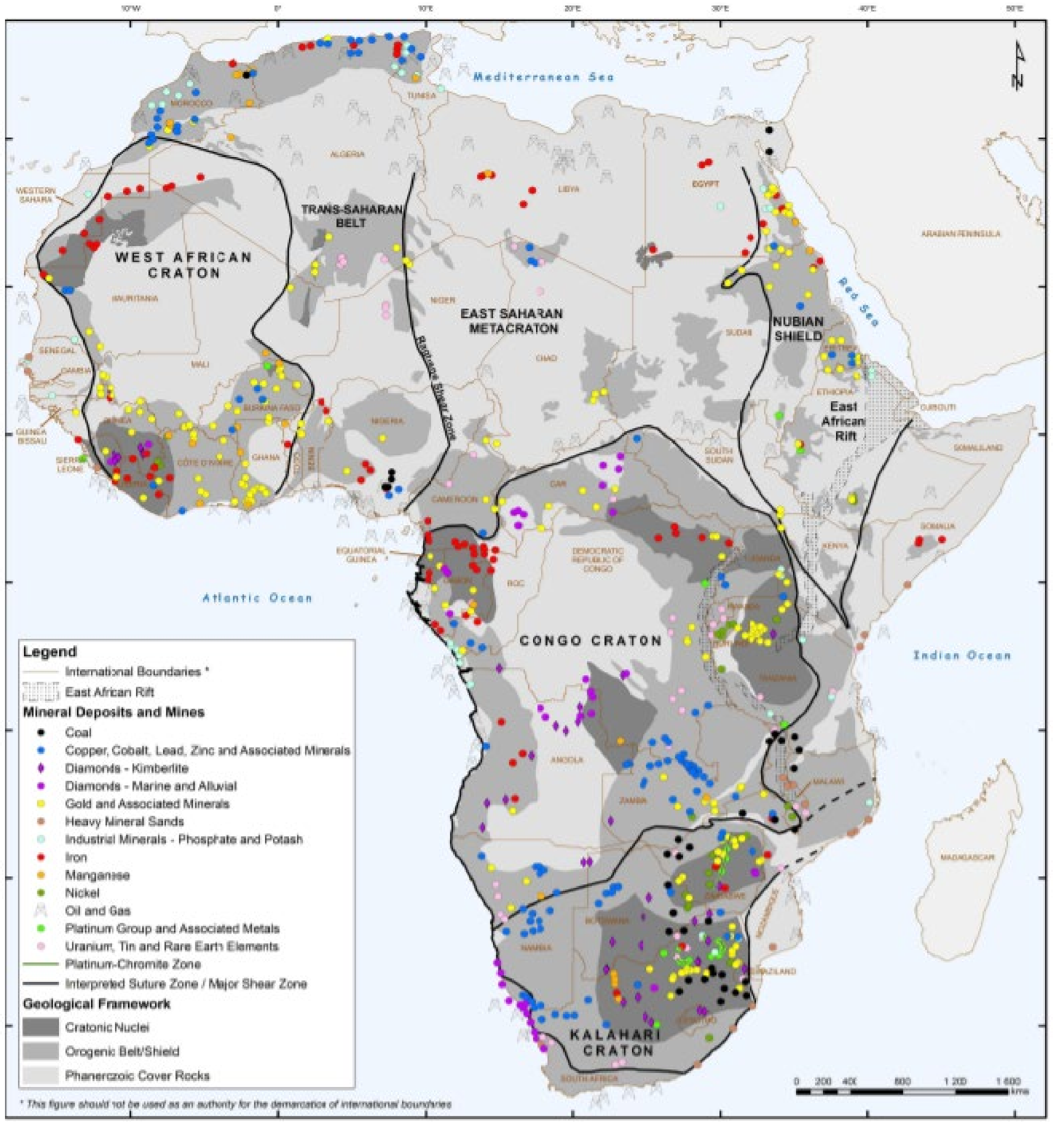
NRF National Research Foundation | RISA Research and Innovation Support and Advancement

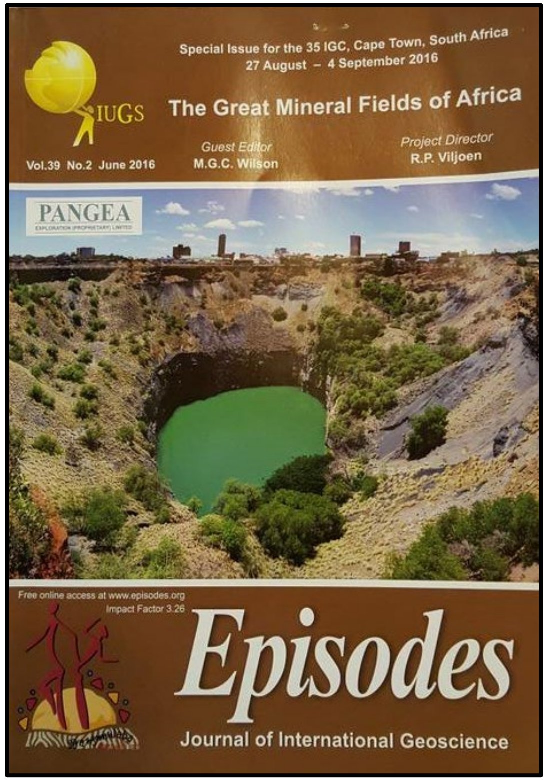
cimera DST-NRF Centre of Excellence for Integrated Mineral and Energy Resource Analysis

Background photo credit: www.esrf.eu

Ore deposits in Africa

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

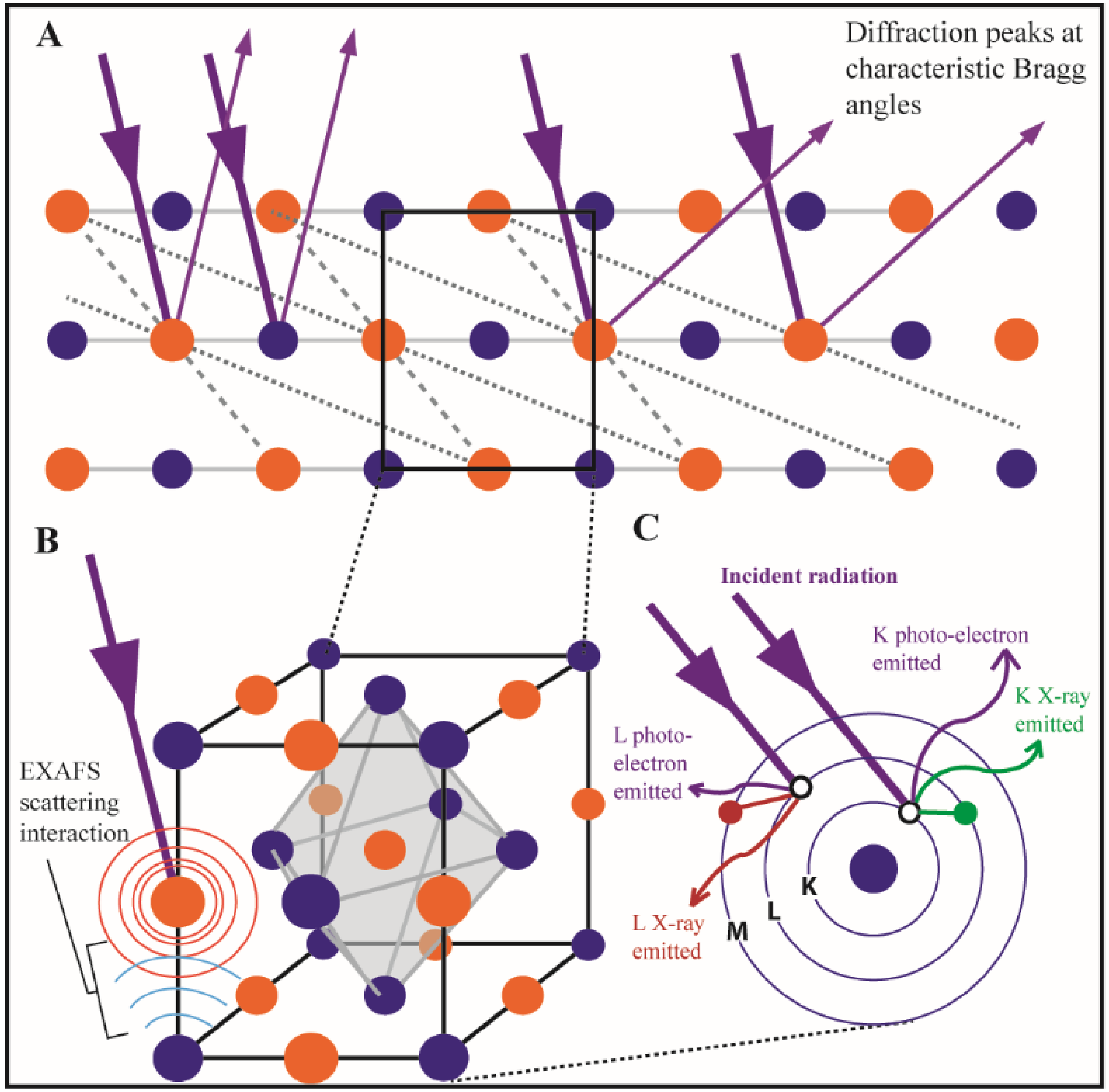




Frost-Killian et al., Episodes (2016)

Synchrotron light:

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

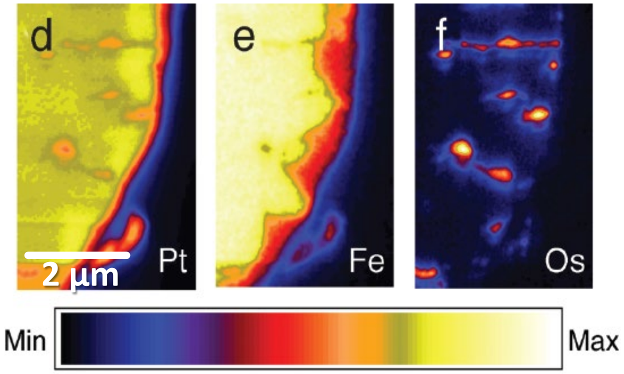


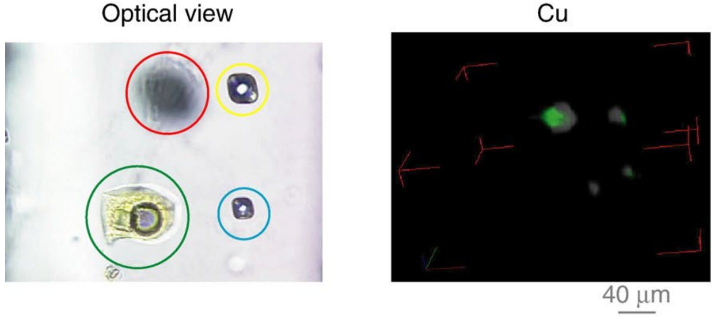
Von der Heyden, in prep.

Synchrotron techniques:

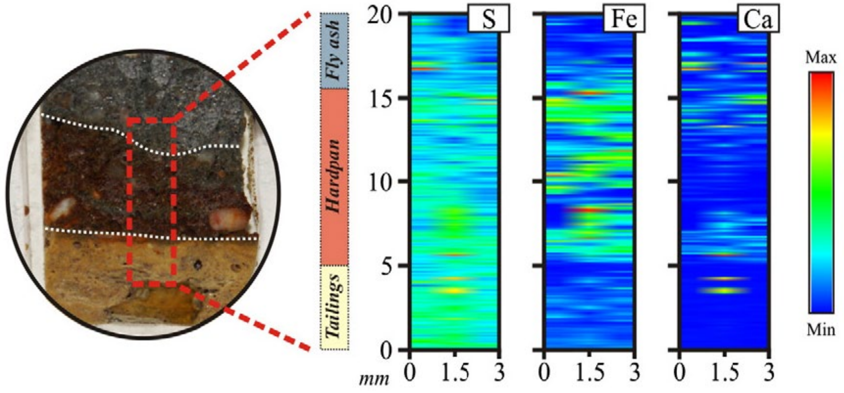
Based on three fundamental properties:

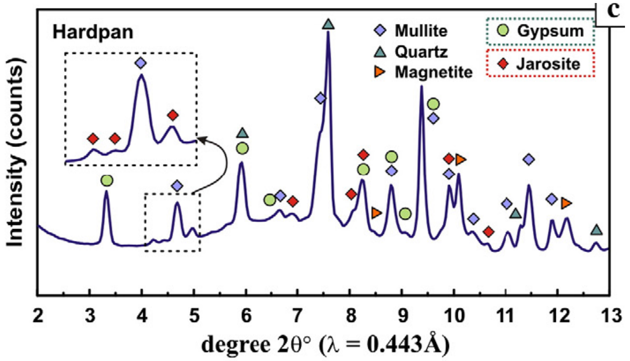
X-ray imaging:



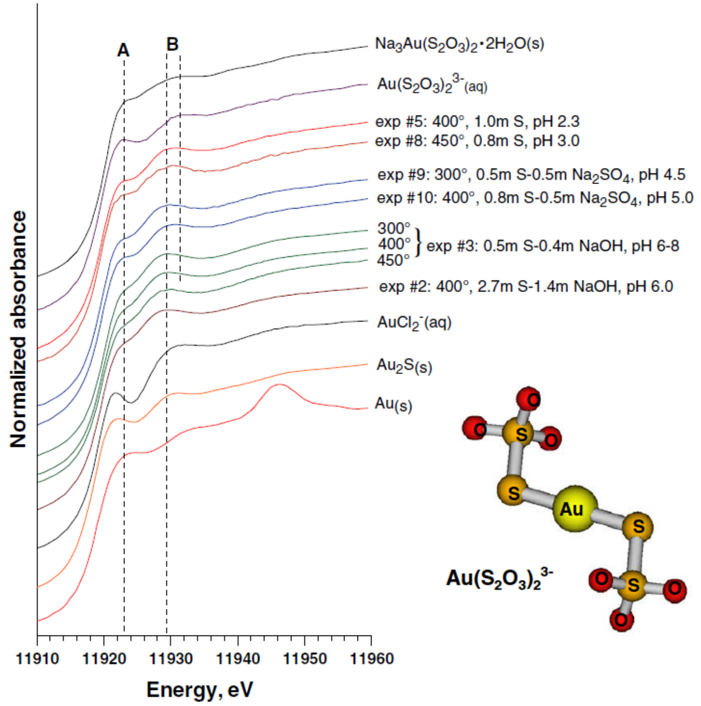


X-ray scattering:





X-ray spectroscopy:



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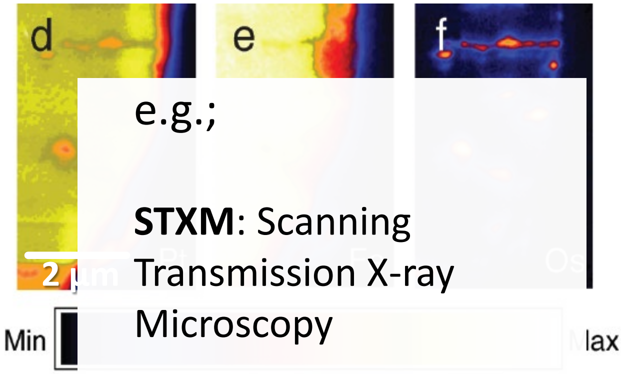


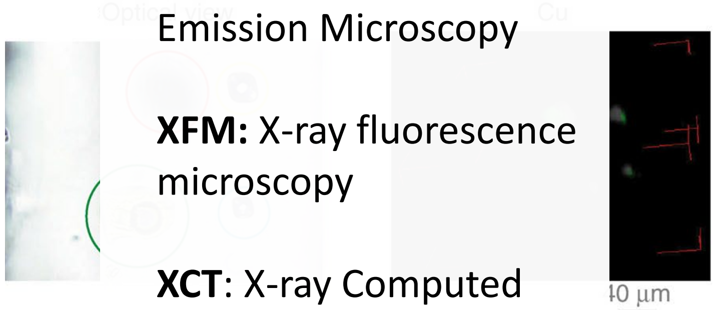
e.g.;

STXM: Scanning Transmission X-ray Microscopy

PEEM: Photoelectron Emission Microscopy

XFM: X-ray fluorescence microscopy

XCT: X-ray Computed Tomography



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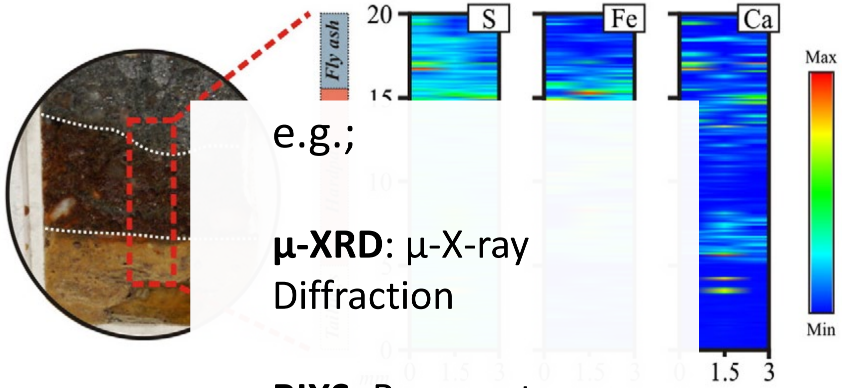
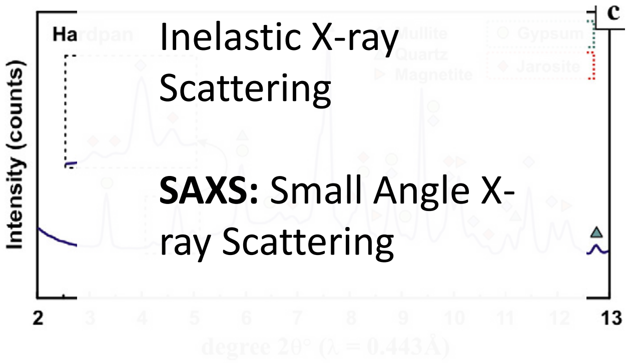


e.g.;

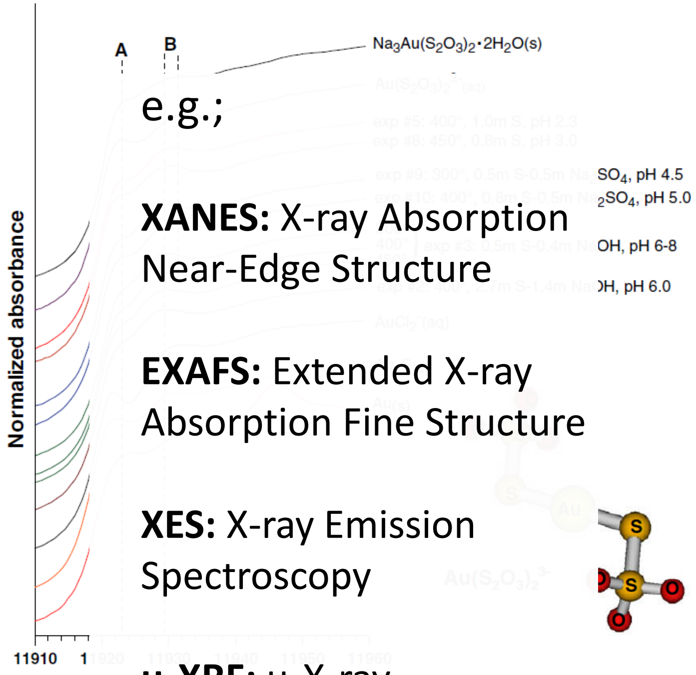
μ-XRD: μ-X-ray Diffraction

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

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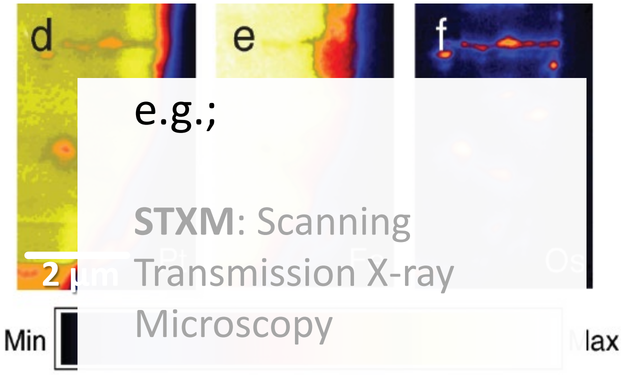

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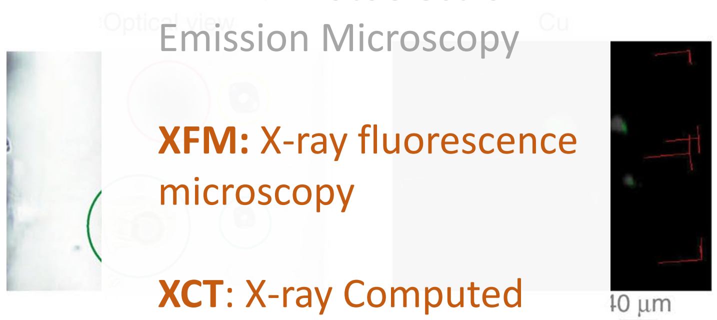
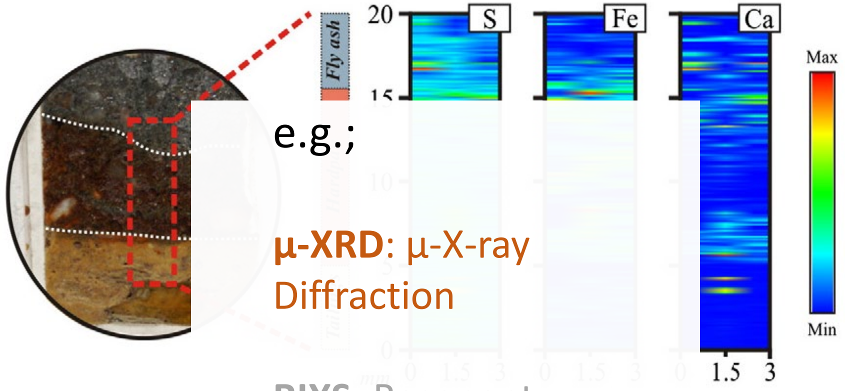


X-ray scattering:



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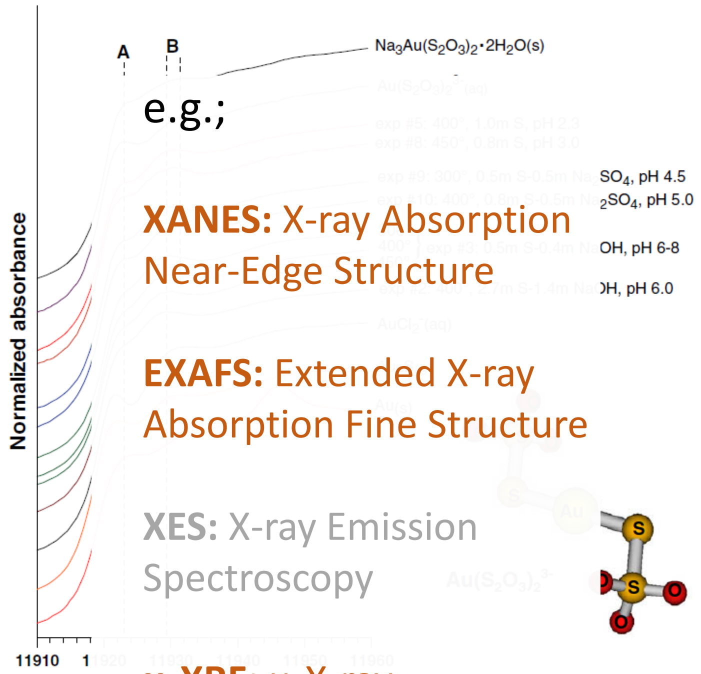

e.g.;

XANES: X-ray Absorption Near-Edge Structure

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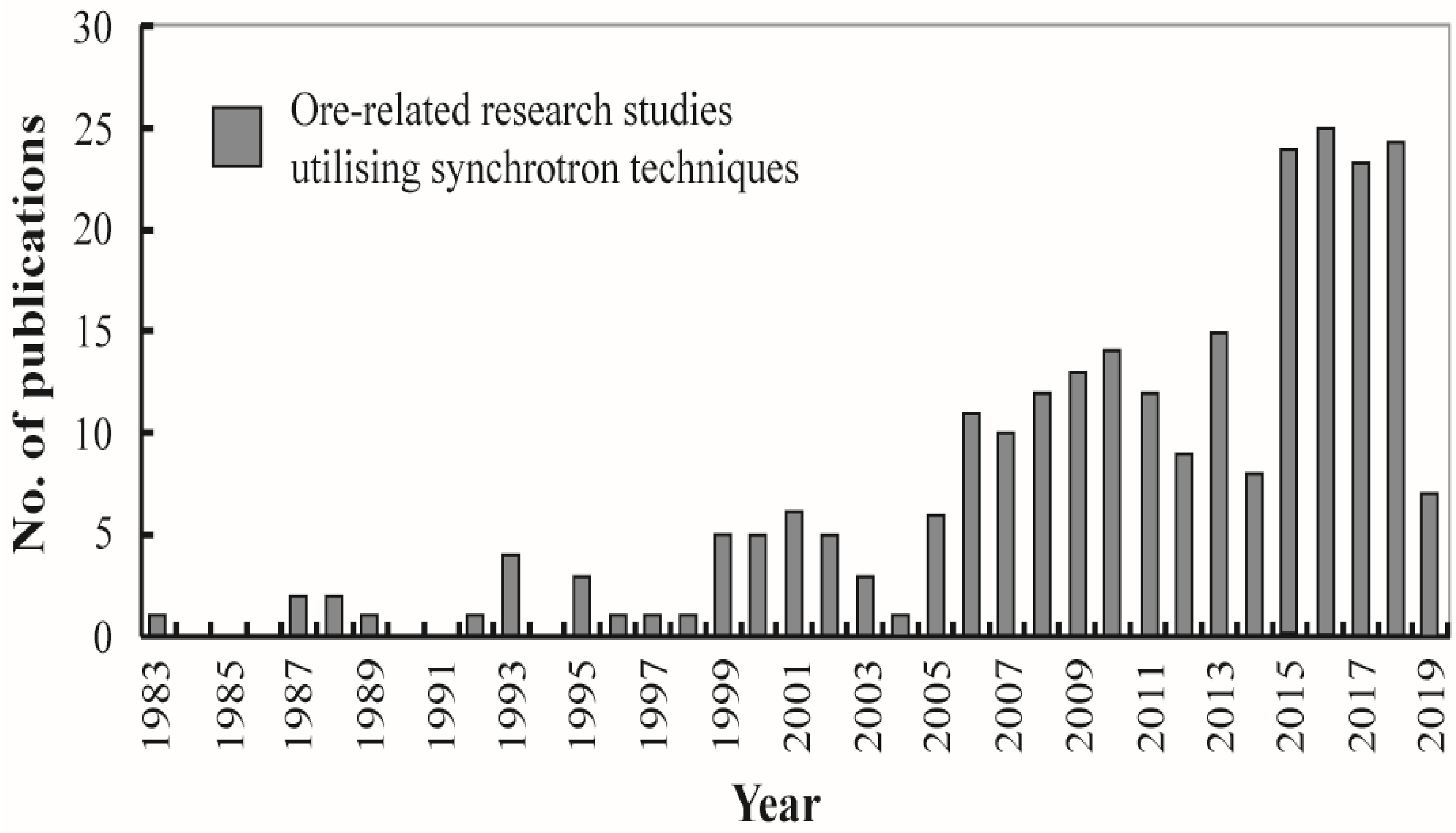
XES: X-ray Emission Spectroscopy

µ-XRF: µ-X-ray Fluorescence

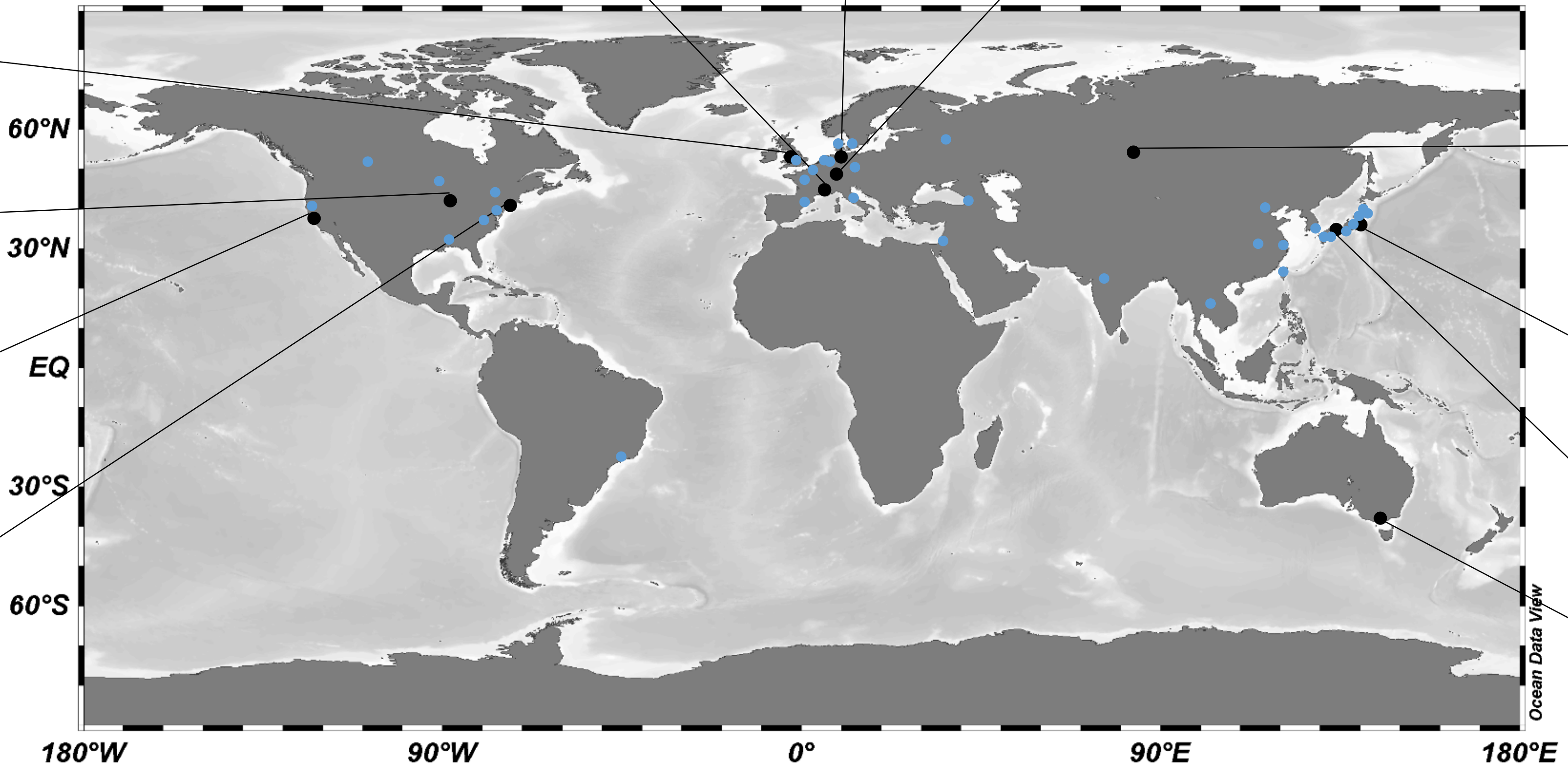
Synchrotrons and ore deposits

- Steady increase in the use of synchroton techniques in ore deposit research.
- Of 178 published studies evaluated:
  - 60 µXRF
  - 82 XANES/EXAFS
  - 19 µXRF and XANES/EXAFS
  - 17 other (µXCT, XRD etc.)
- Many of these studies have been produced by a small number or research groups with prior experience in synchrotron work, or with established links to synchrotron facilities.



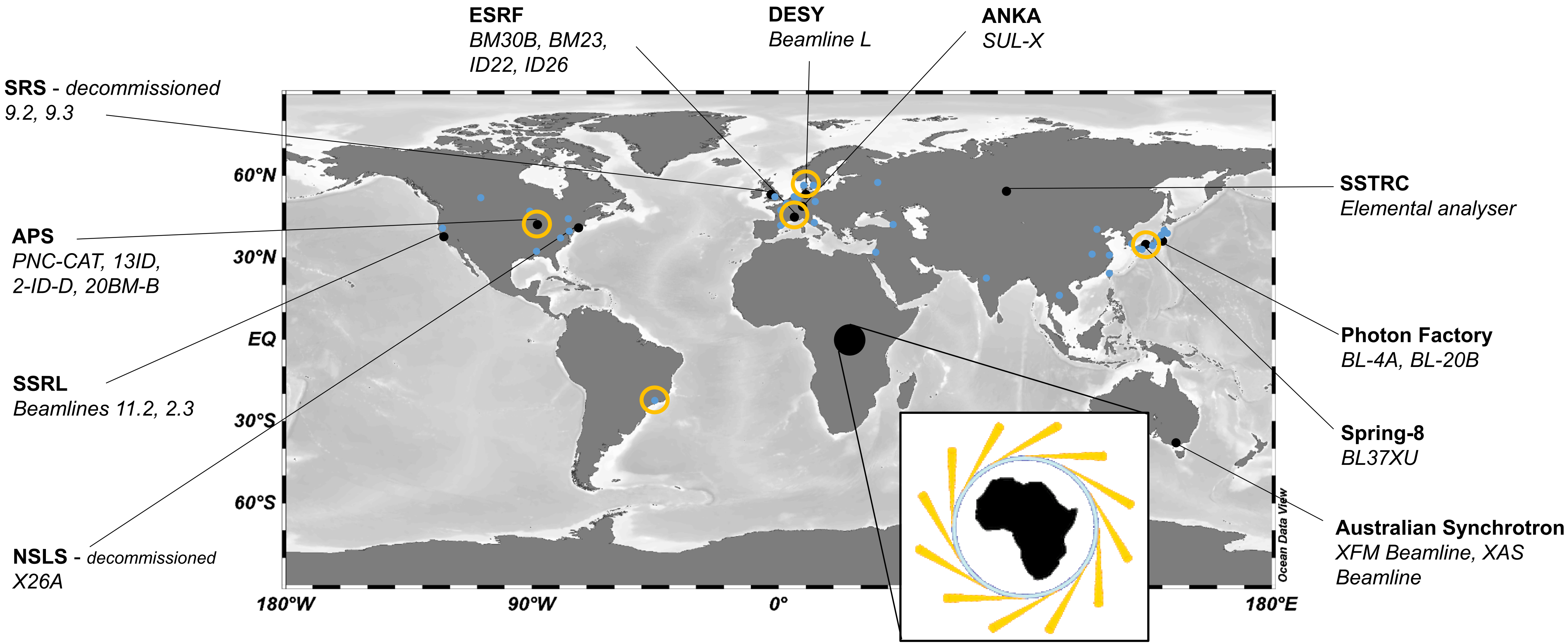
Global synchrotron facilities:

Synchrotron facilities and beamlines that are commonly used in ore deposit related research:



Global synchrotron facilities:

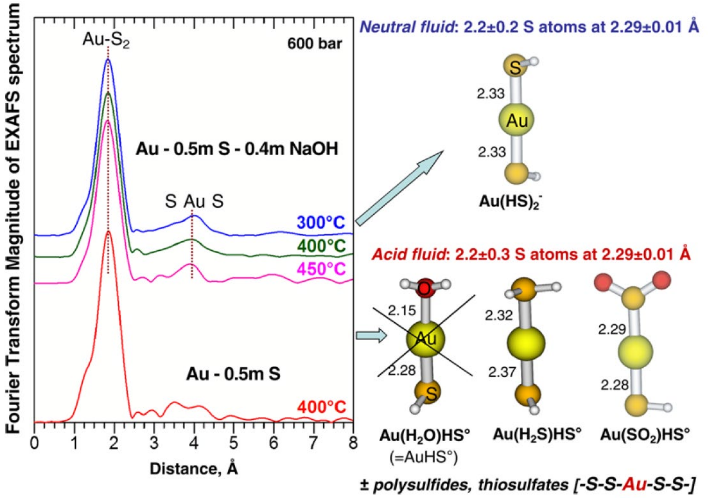
"Fourth generation light sources exceed the performance of previous sources by an order of magnitude or more in an important parameter such as brightness, coherence or pulse duration." – Winick, 1998



Synchrotrons and ore deposits

Case study 1: Gold

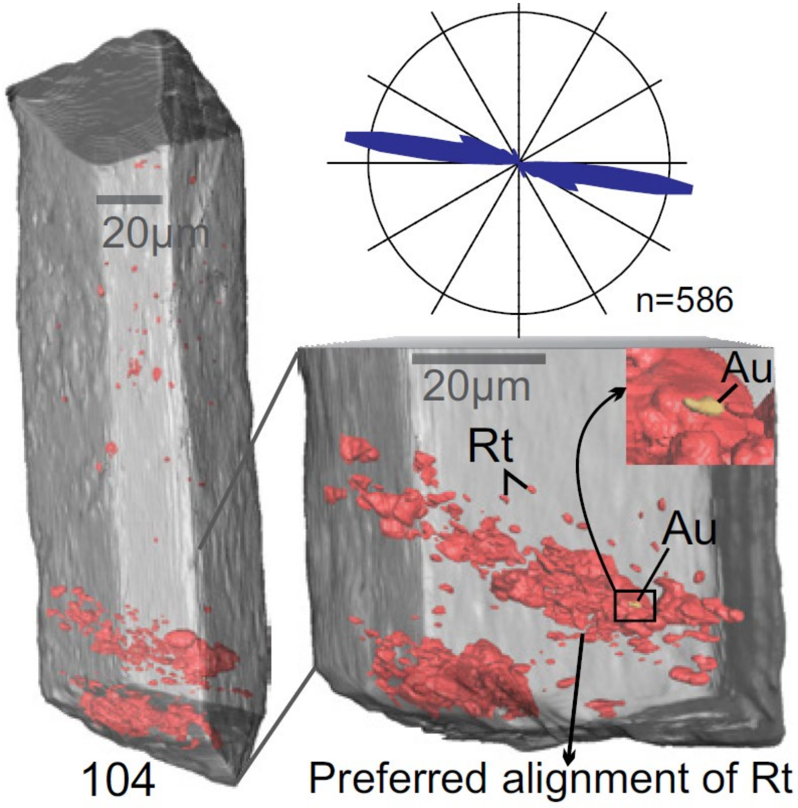
Au mobility in mineralising systems



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

- Experimental results for Au complex speciation up to 500°C and 600 bar pressure.
- Solubility and relative stability of Au hydrogen sulphide relative to halide and amine ligands.
- Fluid inclusion studies used to confirm experimental findings.

Mineral parageneses associated with Au

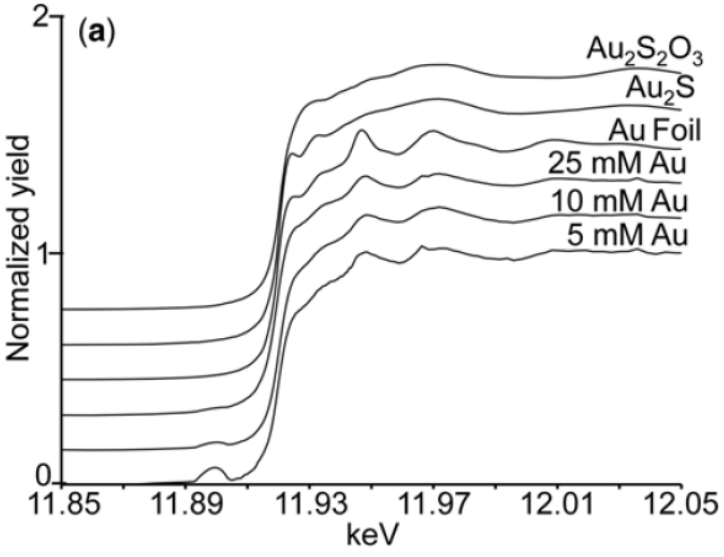


Sayab et al., Geology (2016)

- Au redox and local coordination especially in As-sulphides.

Low temperature biogeochemical cycle of Au

- Map changes to Au speciation in bio-reaction experiments.
- Au-sulphide associations with biogenic framboids (Hu et al. 2016).



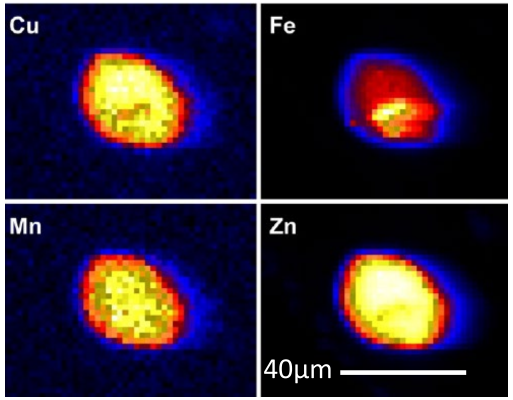
Shuster et al., Geol. Soc. London. Spec. Publ.. (2013)

Synchrotrons and ore deposits

Case study 2: Base metals

Metal complexation and fluid inclusion analyses

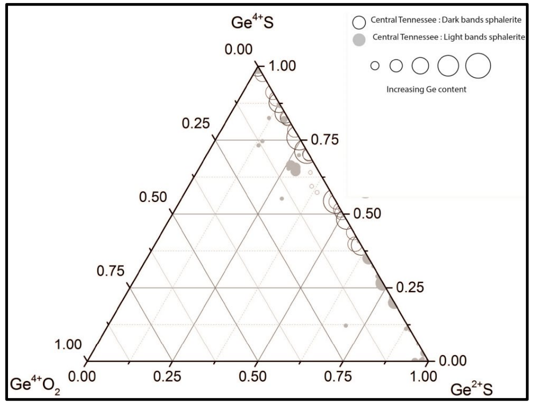
- Speciation and coordination of metal ligand complexes under variable pH, T, P and fluid composition conditions.
- Focussed largely on Cu and Zn complexes, less literature data for other base metals (e.g., Pb, Ni, etc.).
- Complementary work focussed on µXRF analysis of fluid inclusions from natural samples.



Berry et al., Chem. Geol. (2009)

Siting and speciation of contained trace metals

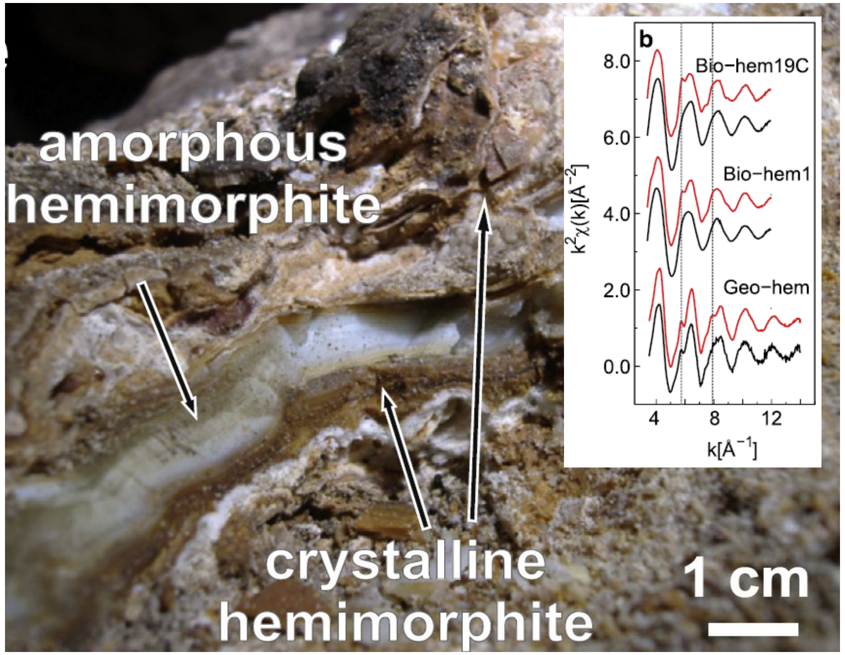
- Base metal sulphides concentrate various trace elements as inclusions and as ionic substituents.



- Studies focus specifically on local coordination of contained metals.
- Emphasis on 'sweetener' metals that add value to ore (e.g., Ag in galena; Ge in sphalerite)

Bonnet et al., Minerals (2016)

Non-sulphide base metal ores



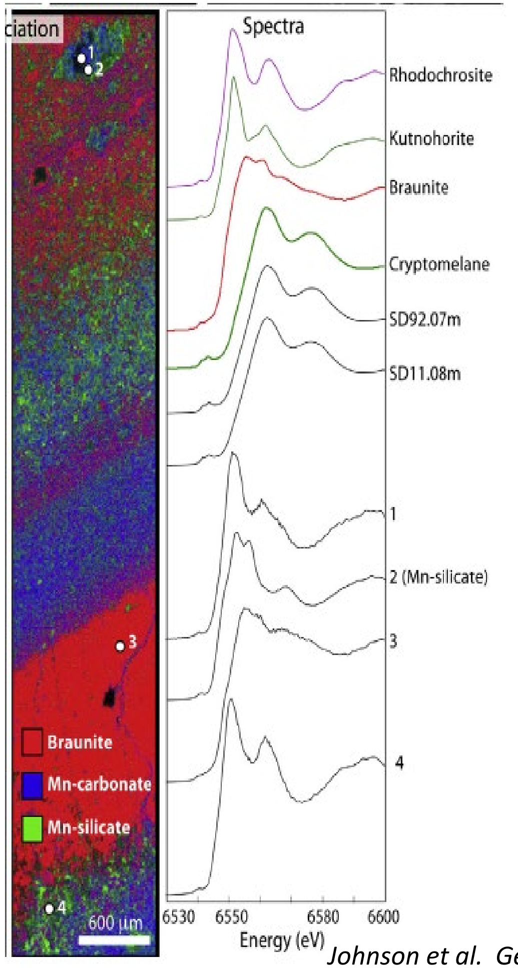
Mendez et al., Ore Geol. Rev. (2017)

- Important class of supergene Cu/Zn oxide deposits.
- µXRD and µXAS used to measure speciation in fine mineral precipitates.
- Application to geochemical mobility of trace elements in supergene zones.

Synchrotrons and ore deposits

Case study 3: Bulk commodities

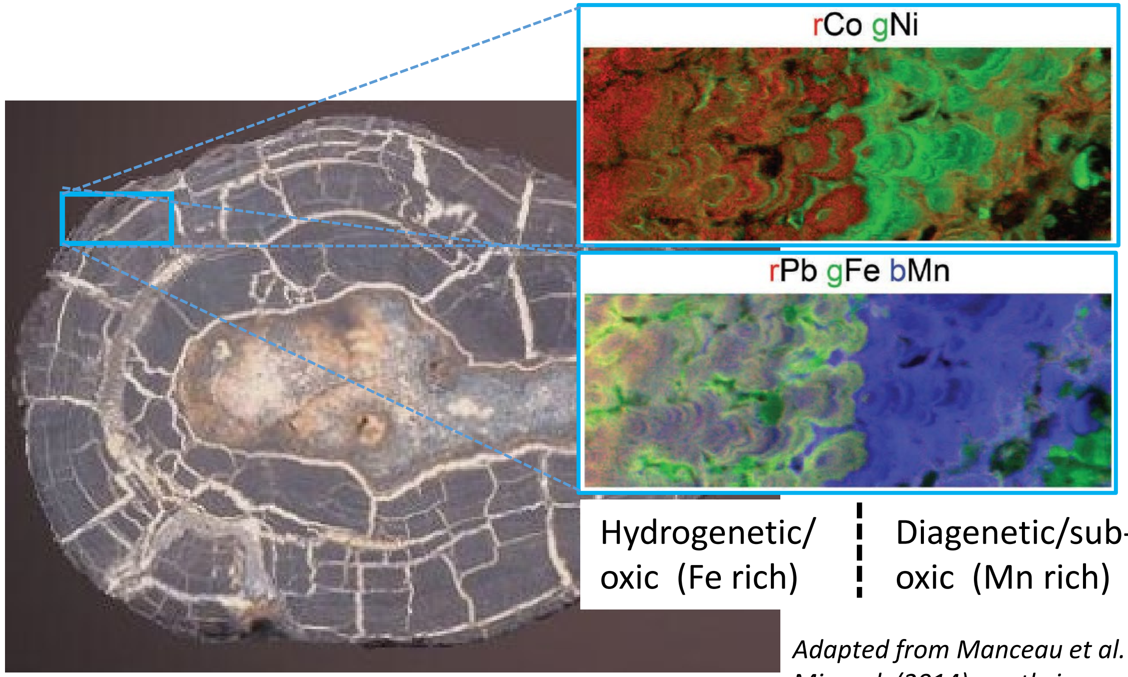
Stratiform Fe and Mn deposits and their relationship to the Great Oxidation Event



Johnson et al. Geochim. Cosmochim. Ac. (2016)

- 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.

Chemistry of Ferromanganese nodules



Adapted from Manceau et al. Am. Mineral. (2014); earthzine.org

- Modern chemical precipitates forming on the sea-floor.
- Unexploited resource of Mn ± Cu, Ni, Zn, Co, PGE.
- Manceau et al. 2014 provide excellent example of the power of combined µXRD, µXRD, µXANES and µEXAFS.
- PGE incorporated by ligand exchange reactions (Tanaka et al., 2017).

Synchrotrons and ore deposits

Work on the African continent

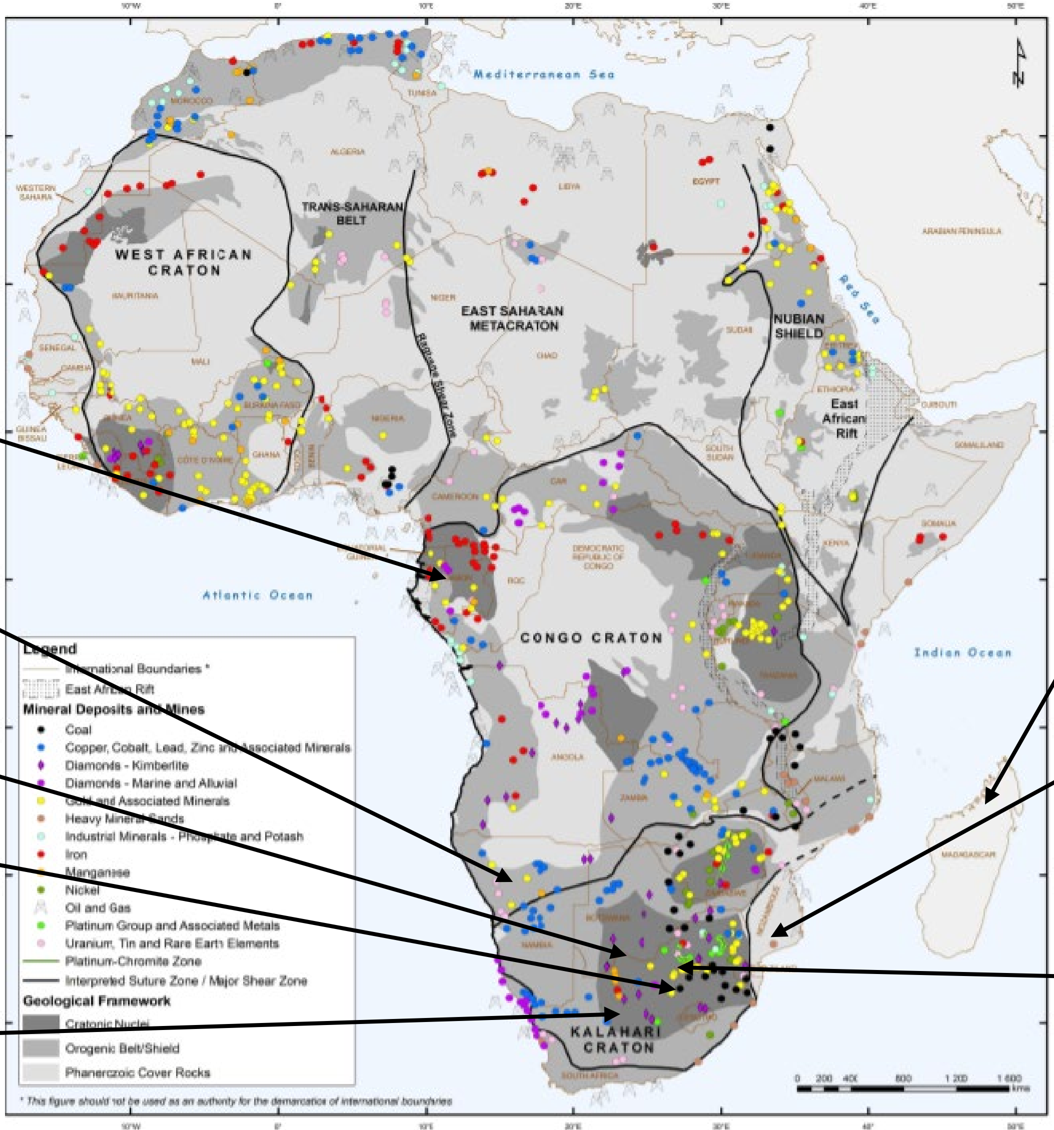
Pt associations, Monts de Cristal complex (Barnes et al. 2016)

PGE in molybdenite, Onganja mine (Takahashi et al. 2007)

Mn oxidation, KMF (Johnson et al. 2016)

Au fingerprinting, Black Reef (Gauert et al. 2007)

Diamond formation, Wesselton Mine (Hanger et al. 2015)



REE ion adsorption clays (Ram et al. 2019)

Beryl gemstone colouring (Figuieredo et al. 2008)

PGE and Cr mineralization, Bushveld Igneous Complex (Veksler et al. 2018; Darin et al. 2016)

Synchrotrons and ore deposits

Current applications and future directions

Prevalent current applications:

1. Coordination chemistry in fluids in geologically relevant P-T conditions
2. Fluid inclusion analyses
3. Distribution, crystallographic siting and redox speciation of trace elements within ore mineral parageneses
4. Characterisation of poorly crystalline and sub-micrometer scale mineral precipitates

Synchrotrons and ore deposits

Current applications and future directions

Perceived future directions:

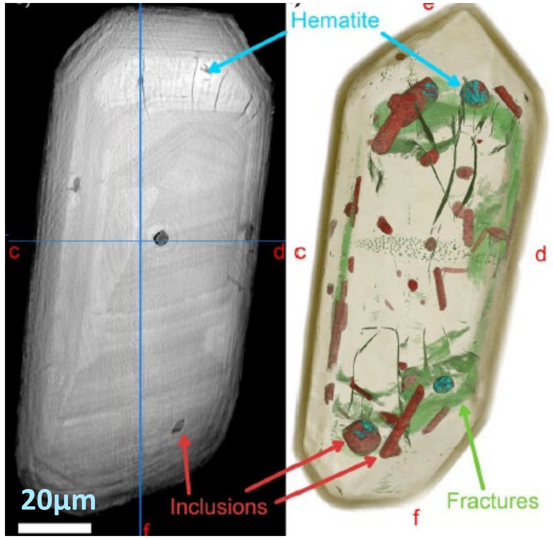
Fourth generation light sources will enable ore research at increasingly high spectral resolutions and elemental detection limits.

A. Ore research across higher-order dimensions

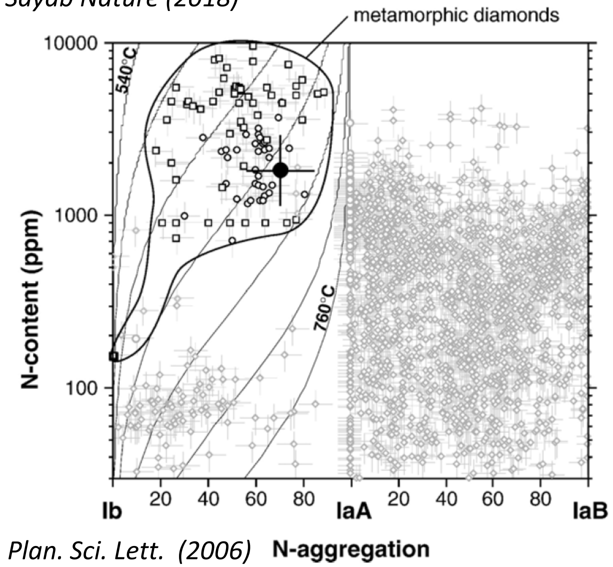
- Micro-computed tomography coupled with µXRD, µXRF and µXAS enable textural and chemical analyses across three dimensions.
- Time resolved measurements will enable kinetic measurements of ore fluid and mineral reactions.

B. Advances in lesser utilised synchrotron techniques

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



Suuronen and Sayab Nature (2018)



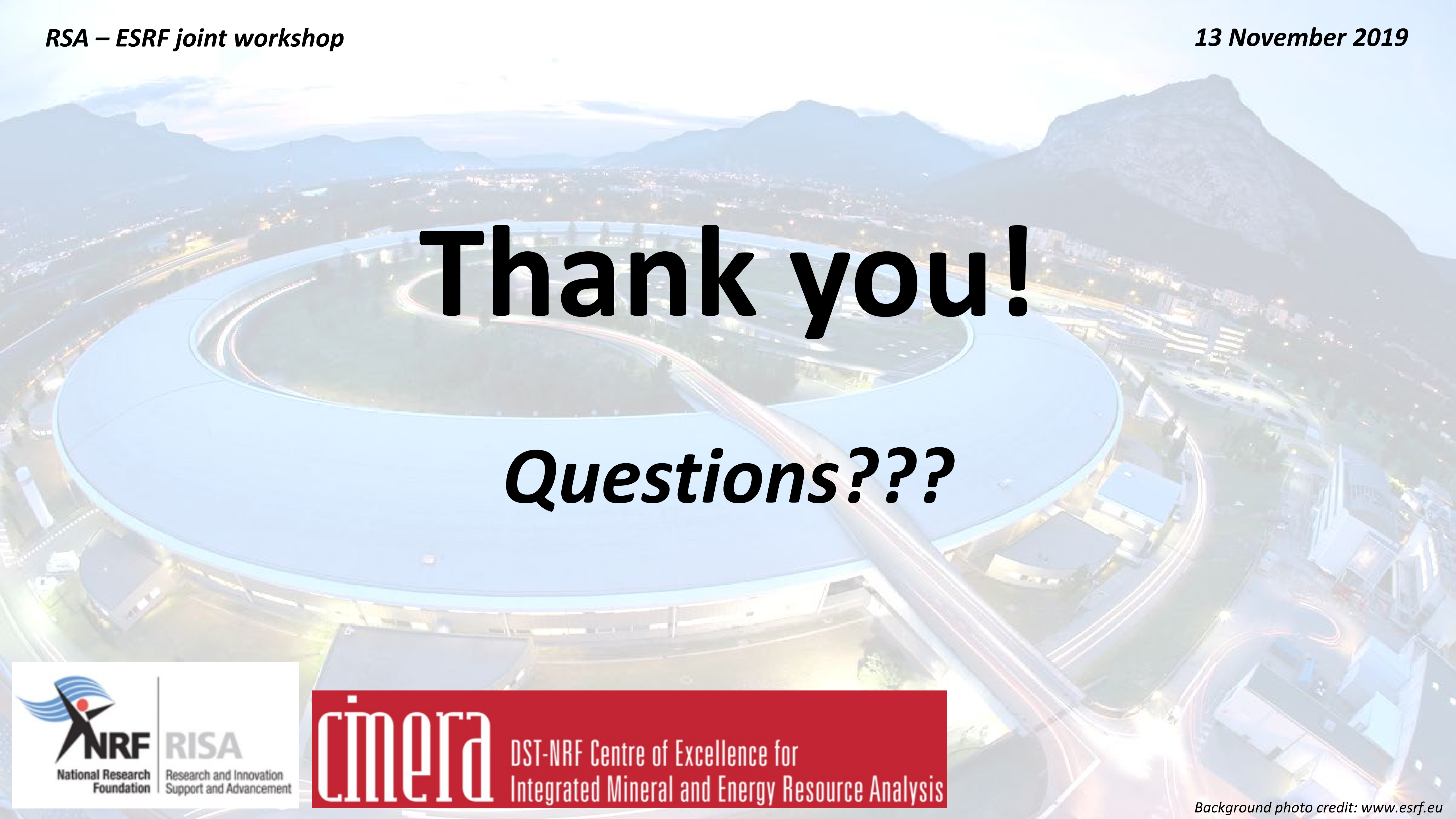
Dobrzhinetskaya et al. Earth Plan. Sci. Lett. (2006)

Conclusions and Implications for AFLS:

- Synchrotron techniques are highly applicable to ore geology science.
- An African Light Source will better place African scientists/countries to capitalise on their mineral endowments (whilst also ensuring sound environmental practice).

Design of an African Light Source should:

1. Be founded on thorough consultation and research of current trends and future research directions associated with the various sub-disciplines
2. Preferentially be equipped with beamline configurations/end stations that are currently over-subscribed.
3. Consider including ‘specialist’ facilities/affordances that would attract an international clientele, for example:
   - *High pressure and temperature autoclaves (BM-30B)*
   - *Multi-detector arrays (XFM beamline)*



Thank you!

Questions???

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