

# Sulphides and their dirty secrets

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So just how  
dirty can  
sulphides  
get?



Sulphide-rich mine dumps, Røros, Norway

Alas this talk is general-rated and is also not about sulphides  
being dirty with respect to the environment



...even if the environmental behaviour of sulphides is dependent upon their sub-microscale chemistry and structures

My focus is on the hidden chemistry within some of the most common sulphides.

They are **dirty** because hidden away in them are all kinds of trace elements, mineral inclusions and microstructural features.

These secrets are now being revealed - and explained - thanks to the range of microanalytical instrumentation available today

This talk will look at **sphalerite** ( $\text{ZnS}$ ) and **pyrite** ( $\text{FeS}_2$ ), with some comment on **molybdenite** and **bornite** towards the end.

So what about these trace elements in the common sulphides?

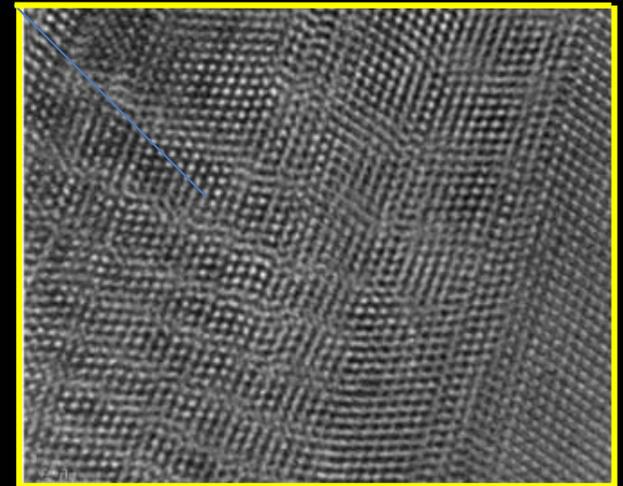
Each sulphide mineral has a crystal structure that can adapt so as to allow elements to be incorporated - either as visible inclusions, nanoparticles, in solid solution or along structural defects. Minerals may also undergo phase transformation to incorporate or release minor and trace elements.

Keys for understanding element incorporation can be found by looking at ore textures and nanoscale structures.

Element distributions and reconcentrations also have to be addressed in the context of ore deformation and/or overprinting

Need to understand the contrasting ductile/refractory deformation mechanisms of the different sulphides (e.g. pyrite vs. chalcopyrite)

How can other minerals (e.g. sphalerite) modify their structures to accommodate a wider chemical range?



Stacking faults in sphalerite

Sphalerite is the chief ore of zinc in all sulphide-rich base metal sulphide deposits.

The simple formula,  $ZnS$ , belies the fact the mineral can be a garbage bin for a wide range of trace elements.



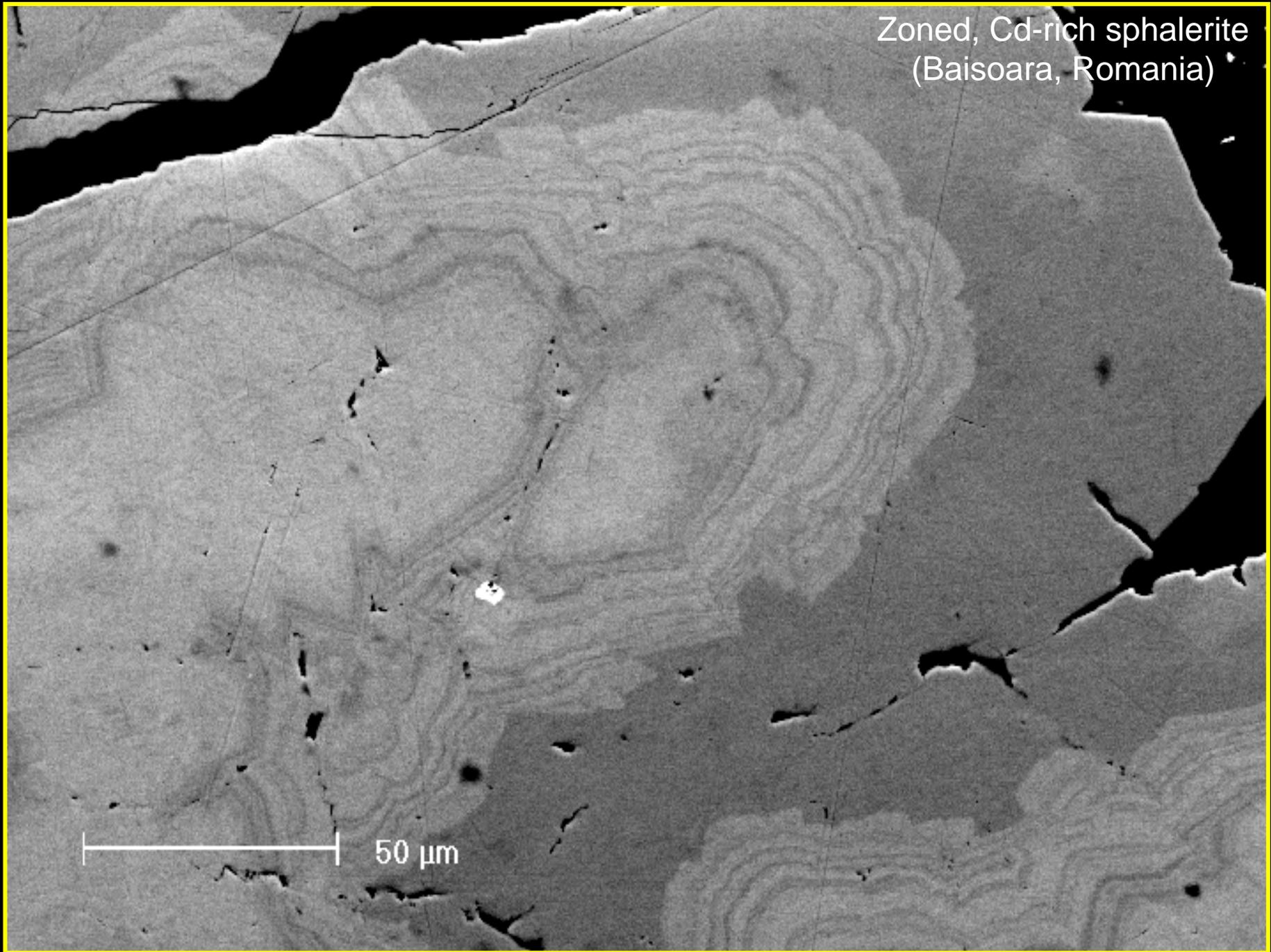
Sphalerite is the main carrier of by-product **Ga**, **Ge** and **In** - more rarely of other valuable elements (e.g. **Ag**). But never **Au**!

Harmful elements may also be concentrated in sphalerite: **Mn**, **Hg**, **As**, **Tl**, **Cd** (at higher concentrations, this is exploited economically as a by-product).

The range of trace elements is reflected by the colors shown by natural specimens. Dark black color normally indicates high **Fe**; other elements (e.g., **Mn**, **Co**), even at much lower concentrations, play a role in determining color.

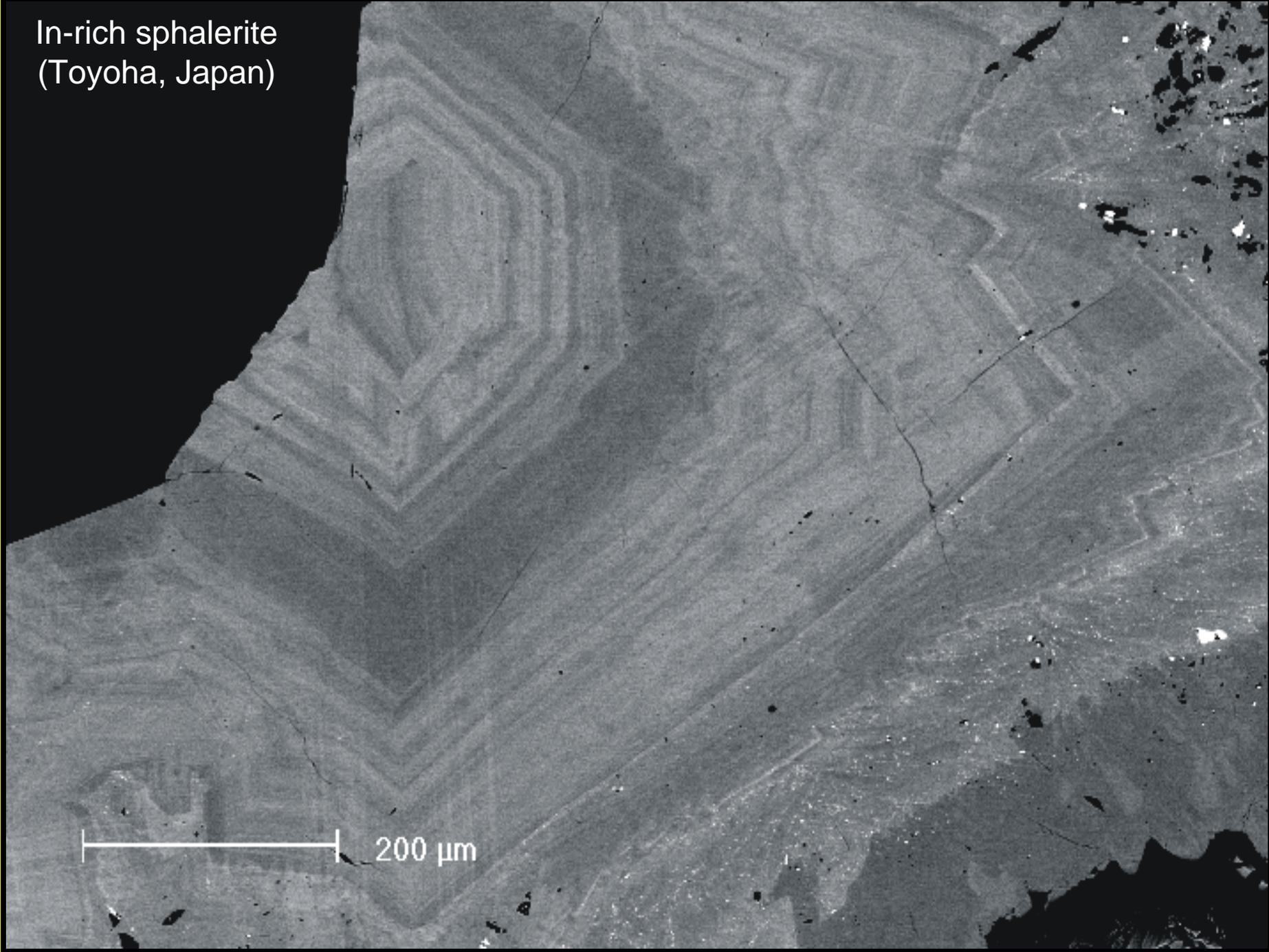


Zoned, Cd-rich sphalerite  
(Baisoara, Romania)



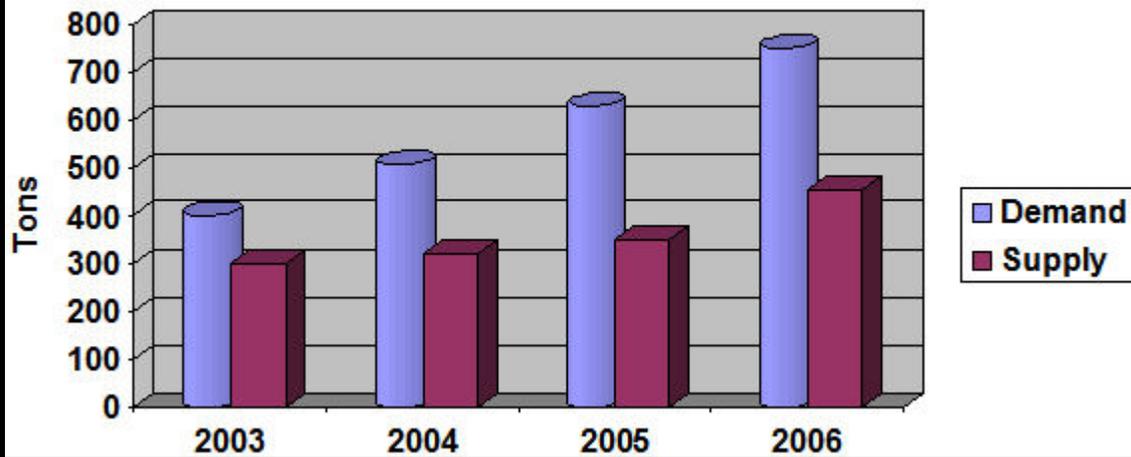
50  $\mu\text{m}$

In-rich sphalerite  
(Toyoha, Japan)



200  $\mu\text{m}$

Indium Supply vs. Demand



Indium is indispensable for liquid crystal displays, HD televisions, semiconductor materials, batteries, low-temperature solders.

....prices of indium surged 20% over the past week to 10 month highs on fears of shortages.....  
Spot prices of indium on the European market rose to US\$ 520 per kg last week. The metal has gained 65% since the middle of July.

The majority of world indium production is consumed in Japan and Korea.

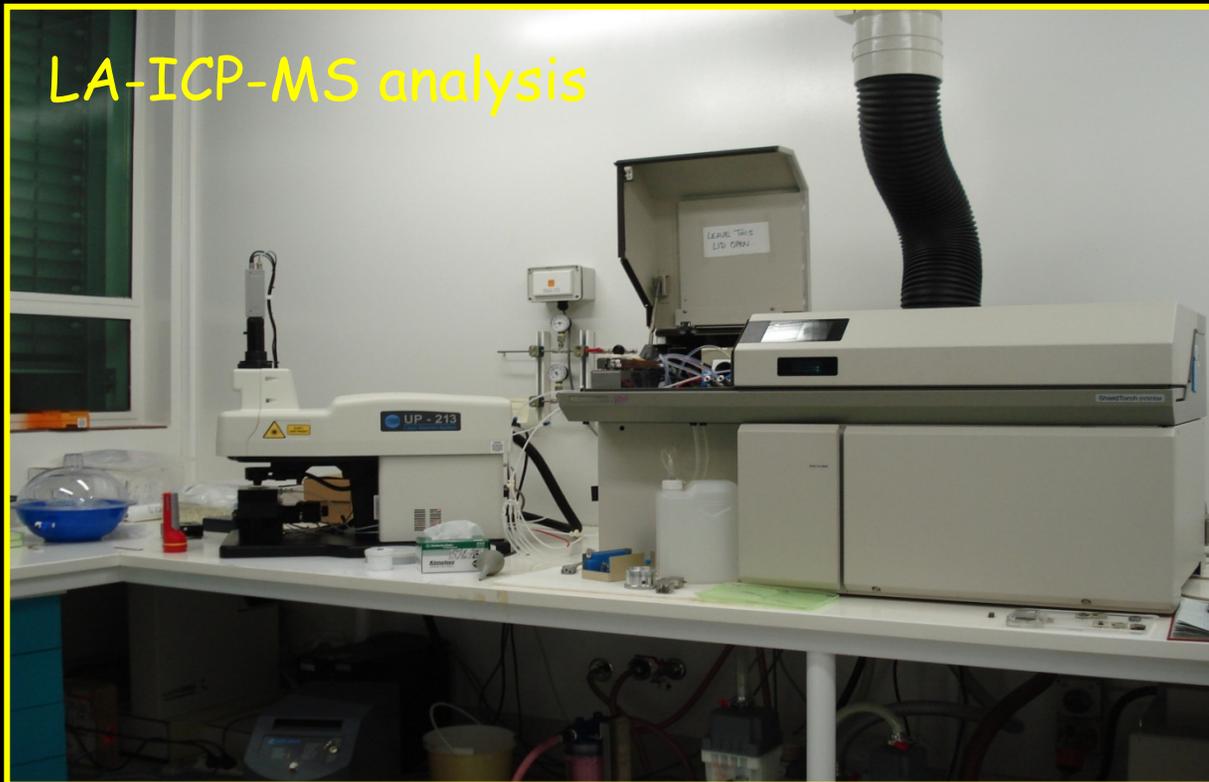
Reuters 11.09.2009



So what do we really know about the distribution of **indium**, **germanium** and other elements in sphalerite?

Can observed assemblages and element abundances be interpreted in terms of published phase data?

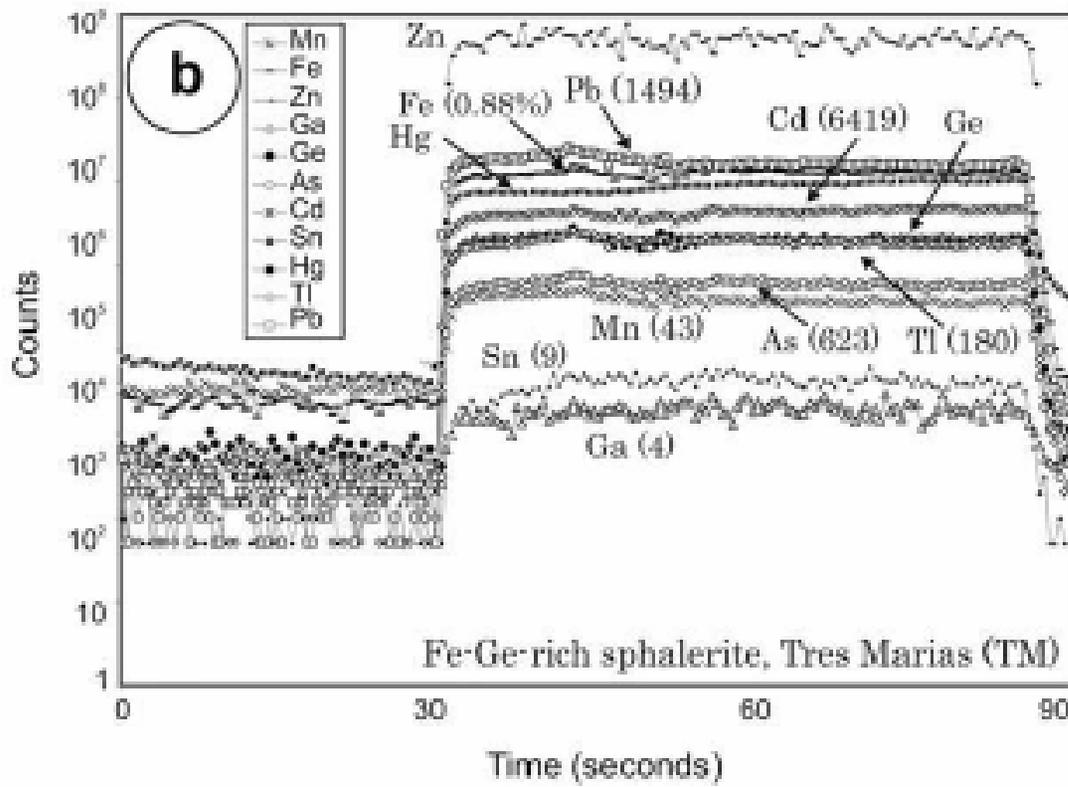
Basis for ongoing research targeting sphalerite mineral chemistry



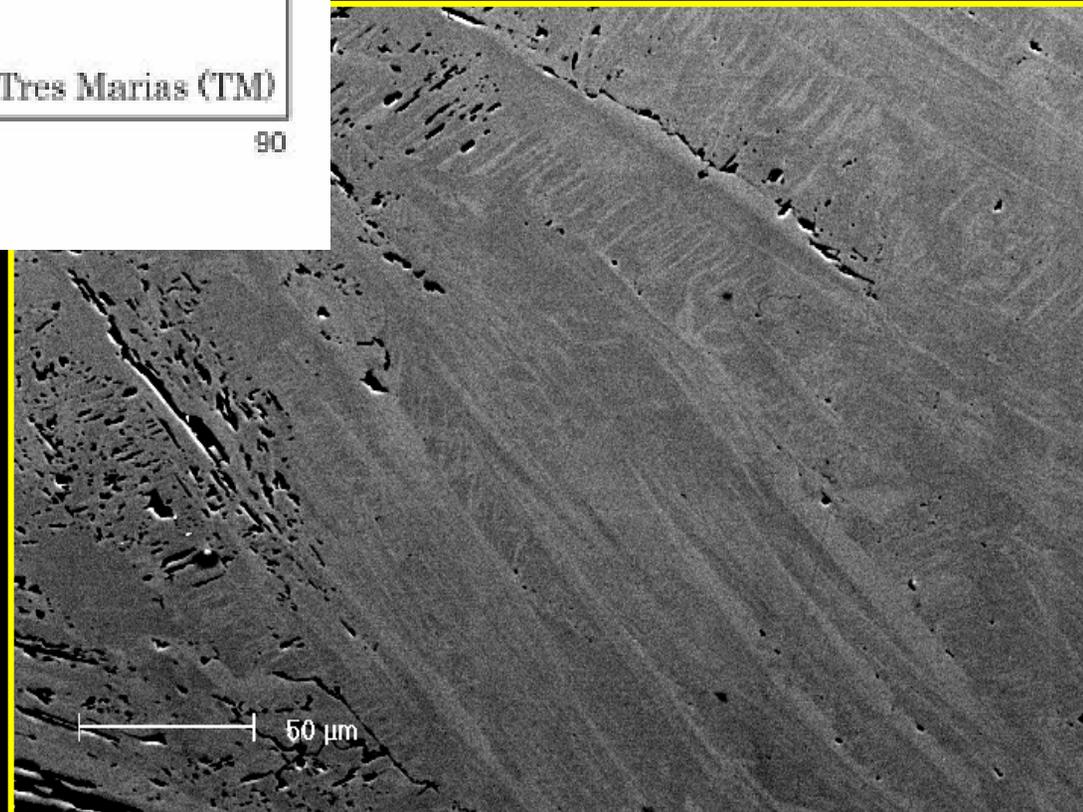
Spot analysis (40-80  $\mu\text{m}$  in diameter)

# Quantitative in-situ multi-element analysis of sphalerite from different deposits

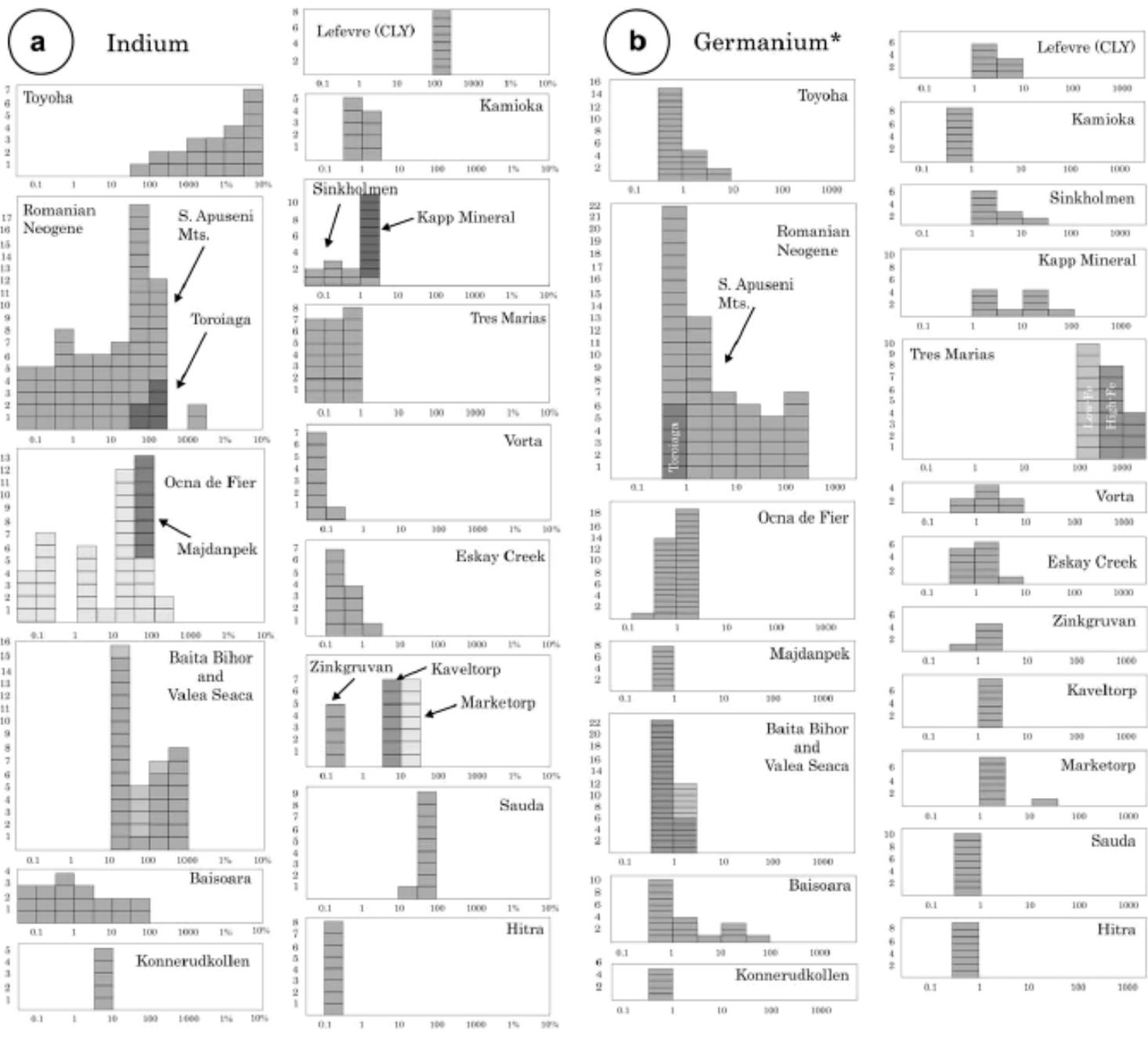
Ge-rich sphalerite  
Tres Marias Mexico



Cook et al. (2009b)



# Database of element distributions in sphalerite from different ore types



Controls on trace element distributions in sphalerite include:

- Type of deposit
- Crystallization temperature
- Metal source
- Cooling history
- Proportion of sphalerite in the ore

Local metal source, crystallization temperature and cooling history may contribute to the partitioning of trace elements (In, Ga, Ge etc.) between sphalerite and discrete minerals of these elements.

Sphalerite geochemistry can be a petrogenetic indicator of fluid sources

# Bedrock of Finland

1 : 5 000 000

## Caledonian tectonic units

- 1 Schists, gneisses or intrusions of variable origin

## Paleozoic

- 2 Alkali rock pipe (livaara) and carbonatite (Sokli)
- 3 Sandstone and shale, Cambrian

## Neoproterozoic

- 4 Sandstone and shale, Vendian

## Mesoproterozoic

- 5 Dolerite dykes, northern Finland
- 6 Dolerite sills, Jotnian
- 7 Sandstone and shale, Jotnian
- 8 Rapakivi granite
- 9 Gabbro-anorthosite
- 10 Dolerite dyke swarms, Subjettian

## Paleoproterozoic

- 11 Quartzite and conglomerate, molasse of Lapland
- 12 Postorogenic granitoids c. 1.8 Ga
- 13 Late orogenic granites 1.85 - 1.8 Ga
- 14 Granite and granodiorite 1.88 - 1.86 Ga
- 15 Pyroxene granite and monzonite 1.885 - 1.87 Ga
- 16 Granodiorite 1.89 Ga
- 17 Gabbro-diorite 1.89 - 1.87 Ga
- 18 Tonalite 1.92 - 1.91 Ga
- 19 Mica schist and migmatite
- 20 Mica schist
- 21 Metavolcanic rocks 1.92 - 1.88 Ga
- 22 Serpentinite and other rocks of ophiolite c. 1.96 Ga
- 23 Garnet gneiss and diorite; Lapland granulite belt
- 24 Anorthosite
- 25 Foliated gabbro and granodiorite 1.95 - 1.93 Ga
- 26 Gneissic granite and hornblende gneiss
- 27 Quartzite and conglomerate
- 28 Metavolcanic rock and mica schist, the Kittilä allochthon
- 29 Calc-silicate rock, black schist, basic volcanic intercalates
- 30 Quartzite with intercalates c. 2.3 - 2.0 Ga
- 31 Layered intrusions 2.44 Ga
- 32 Mafic, intermediate and felsic metavolcanic rocks 2.5 - 2.0 Ga

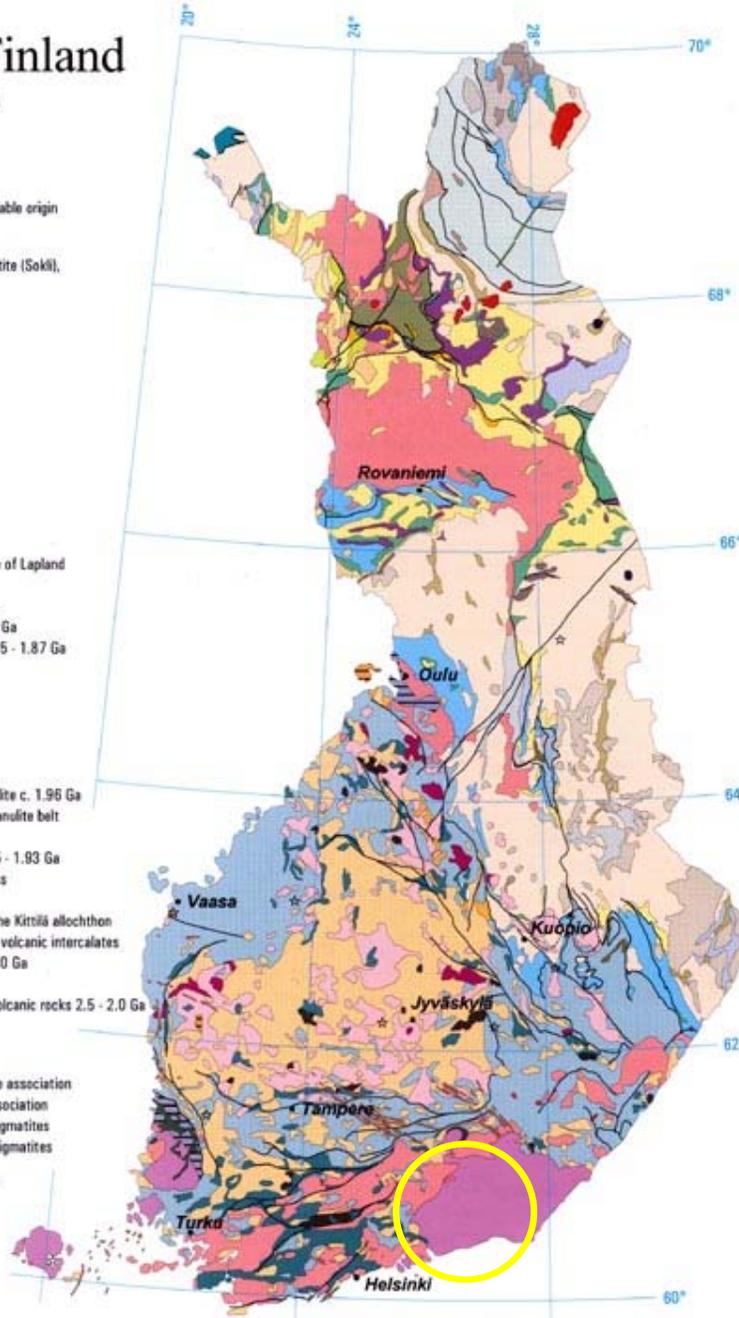
## Archean

- 33 Latest Archean granitoids
- 34 Metavolcanic rocks of the greenstone association
- 35 Metasediments of the greenstone association
- 36 Biotite ± hornblende gneisses and migmatites
- 37 Tonalite-trondhjemite gneisses and migmatites

Faults and major shear or thrust zone

Kimberlite province

☆ Impact site



## Case study: 1.64 Ga Wiborg batholith (Southeast Finland)



Rapakivi granite massif  
generally considered  
barren of ore deposits

# Getmossmalmen (In-bearing massive magnetite-sphalerite lens)



Jungfrubergen (Zn-Cu-Pb-Ag-In-bearing greisen veins)

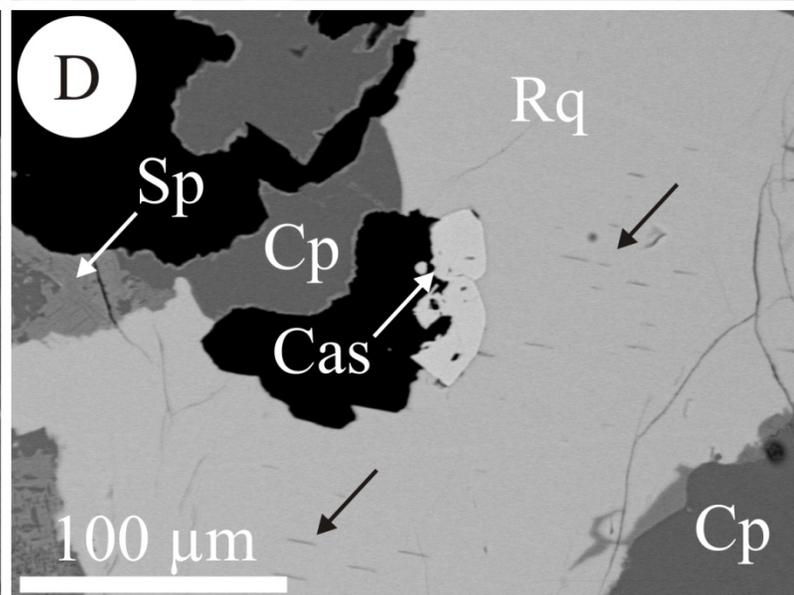
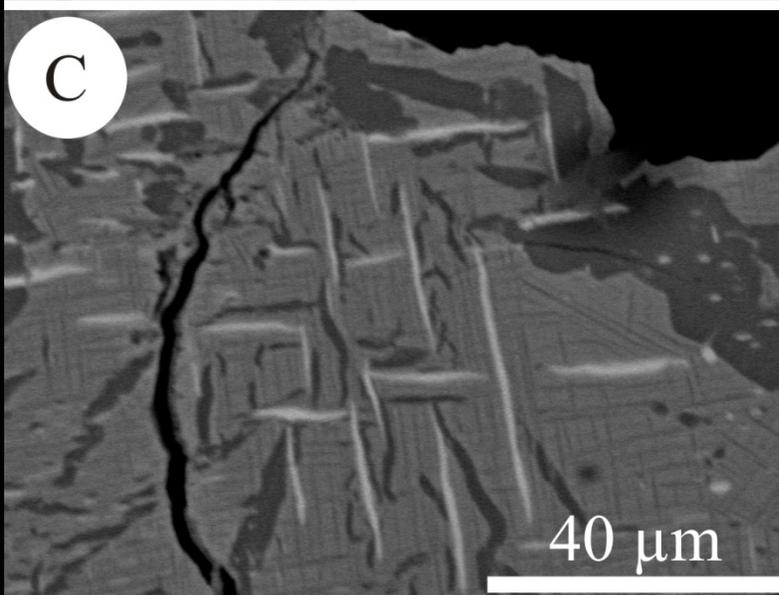
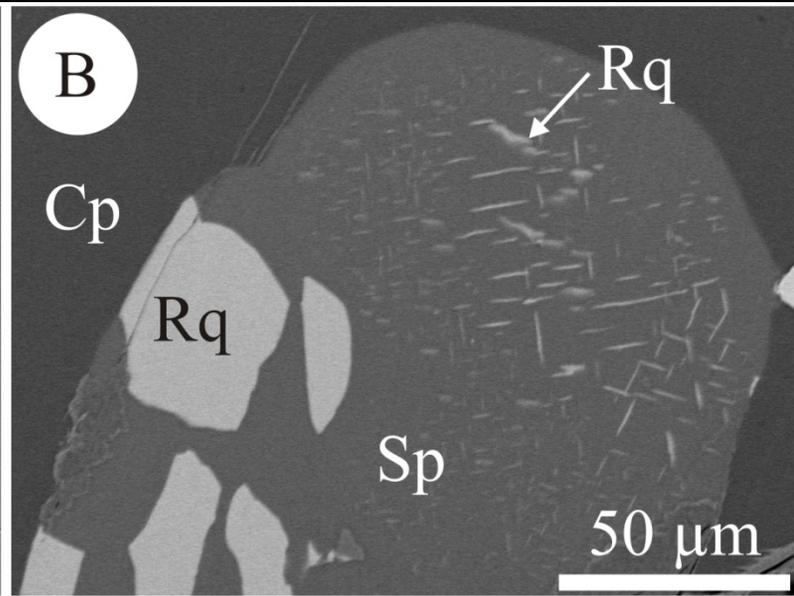
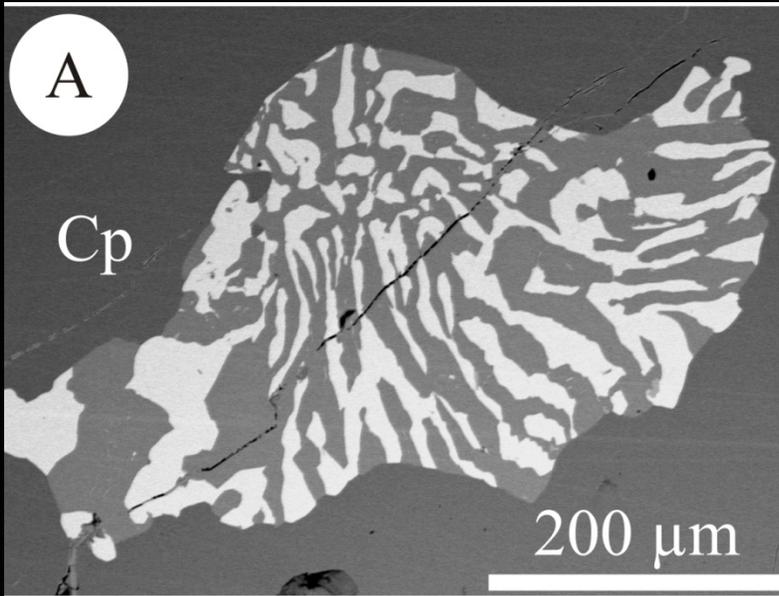
# Vein occurrences at Korsvik



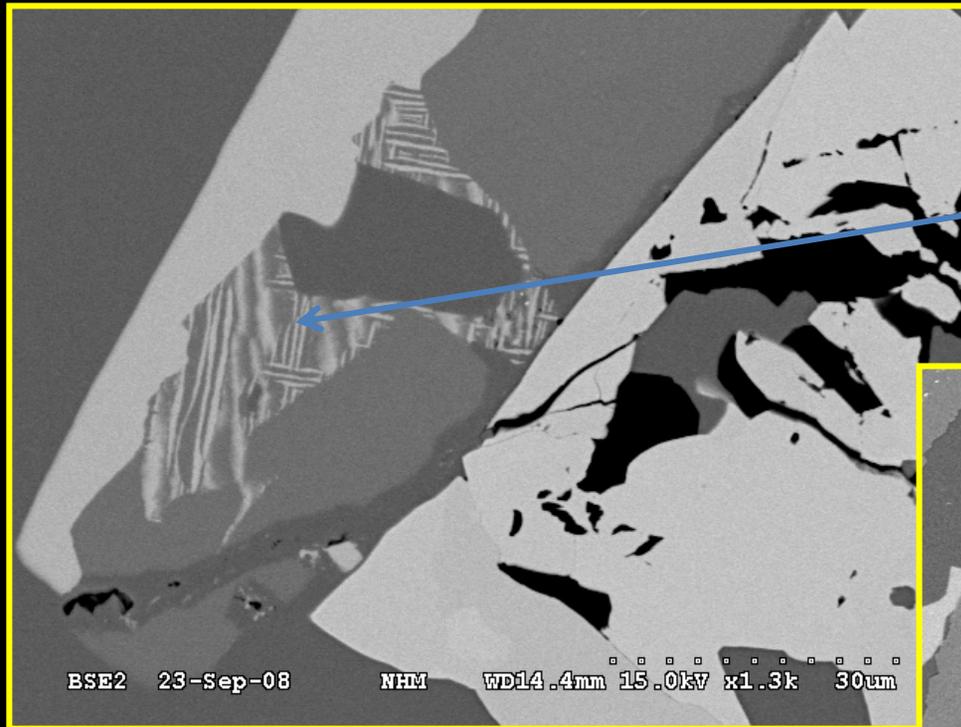
# Vein occurrences at Korsvik and Högberget



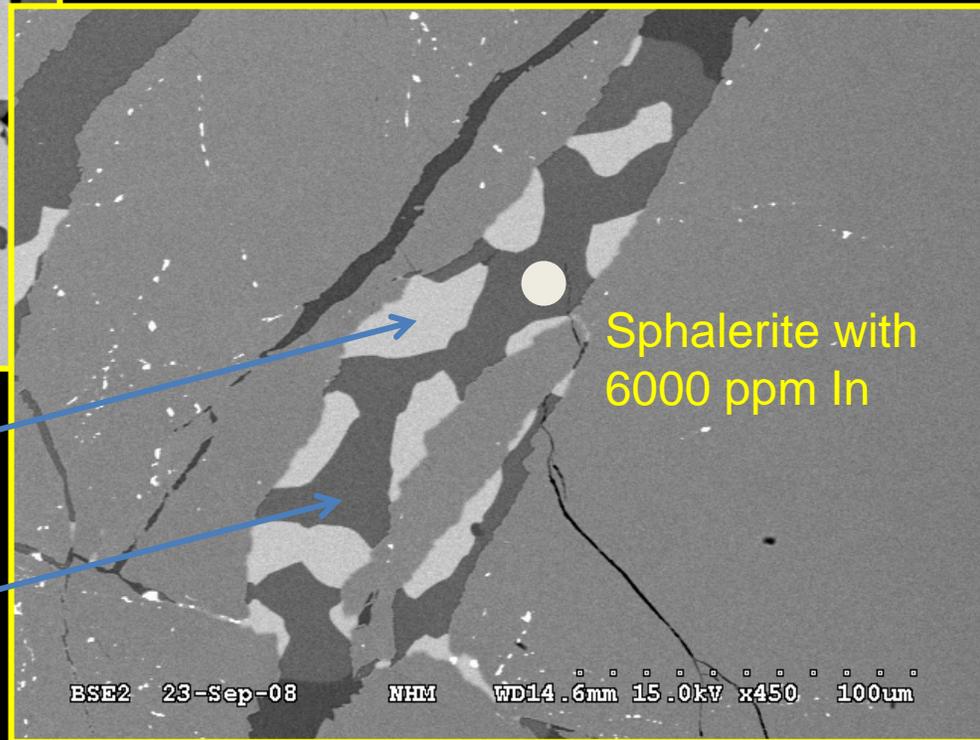
# Partitioning of indium between sphalerite and roquesite ( $\text{CuInS}_2$ )



# Project aims to establish the ranges of indium solid solution in natural sphalerite and the controls on partitioning between sphalerite and roquesite



Sphalerite with crystallographically-oriented exsolutions of roquesite ( $\text{CuInS}_2$ )



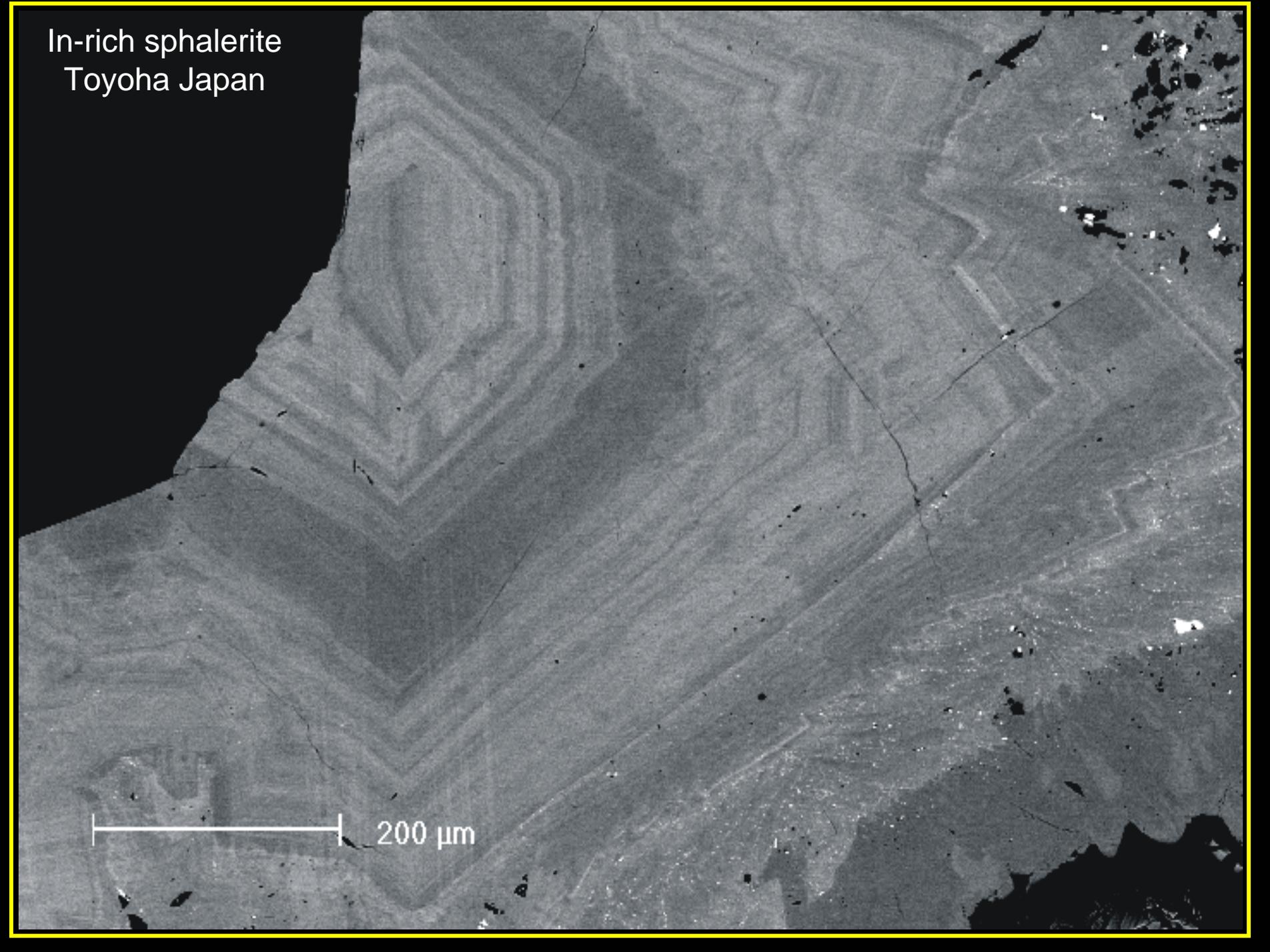
Sphalerite with 6000 ppm In

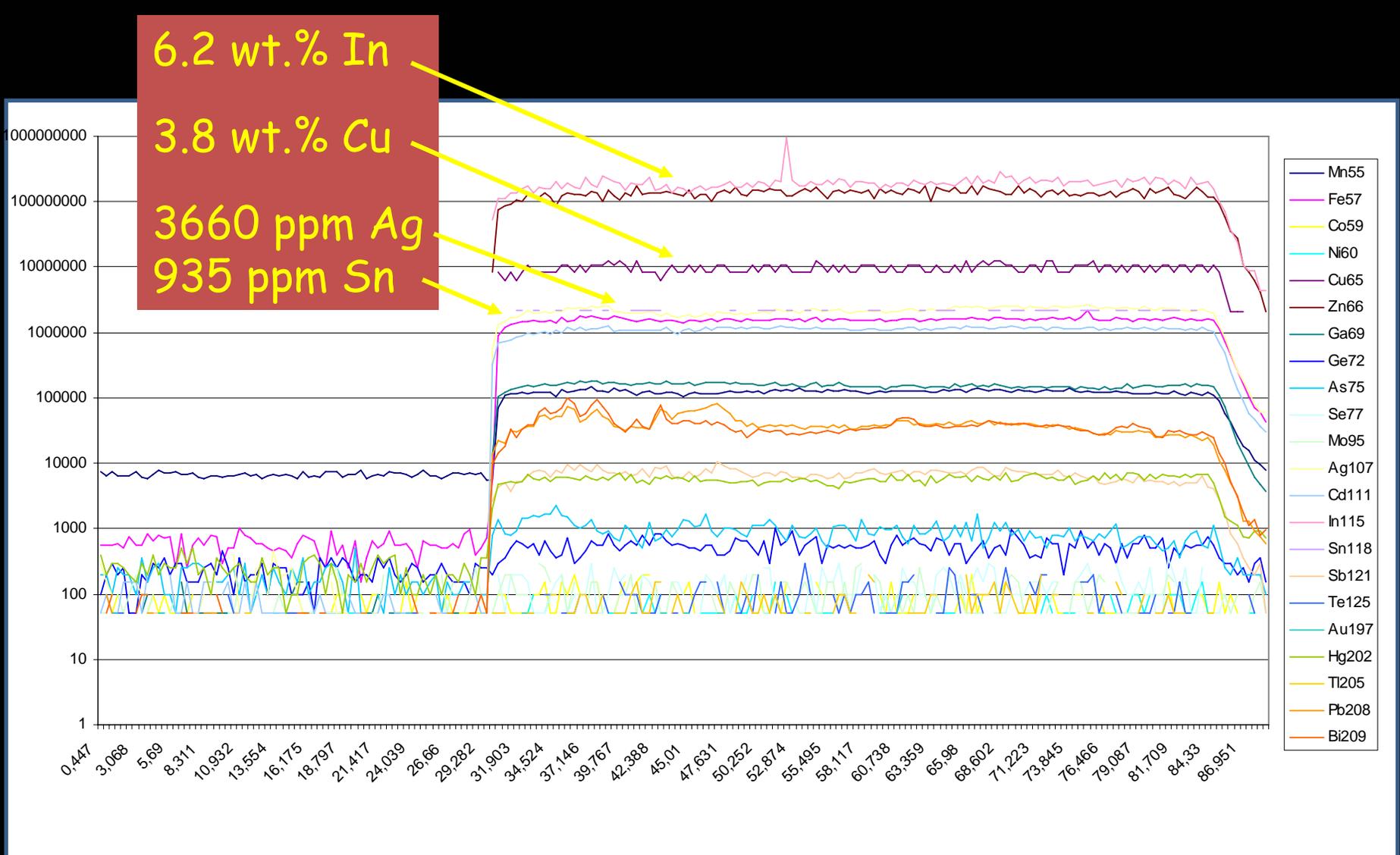
Roquesite

Sphalerite

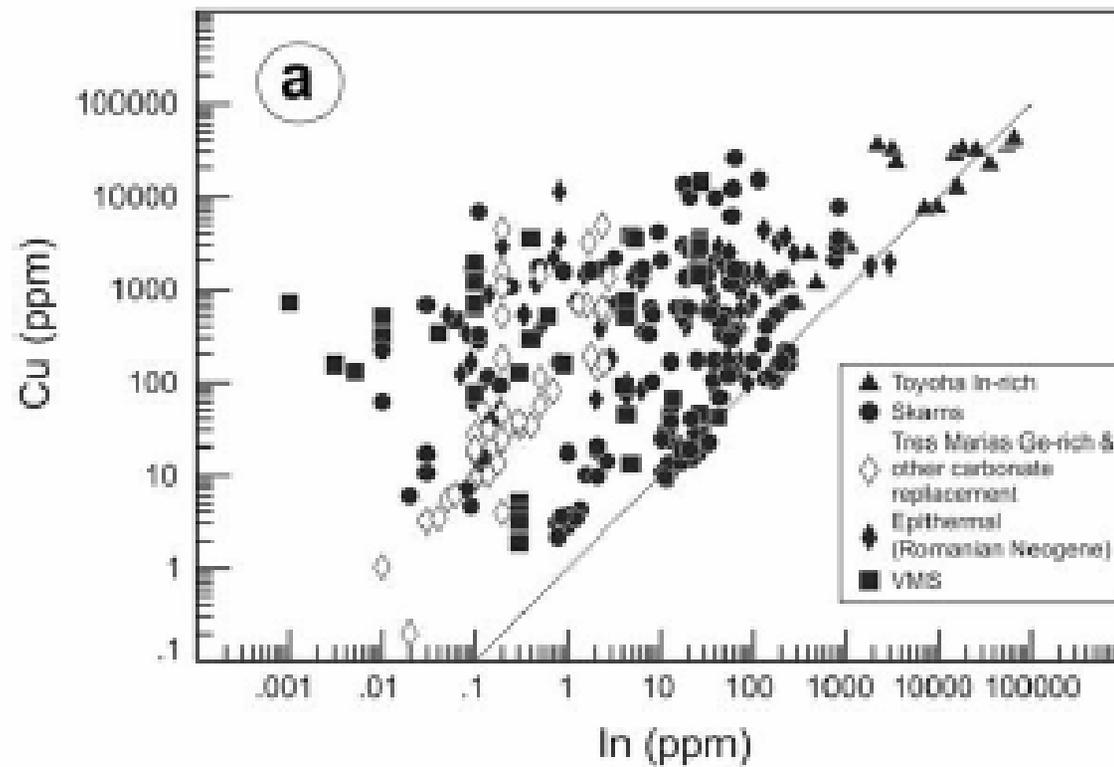
In-rich sphalerite  
Toyoha Japan

200  $\mu\text{m}$

A black and white micrograph showing the intricate, interlocking crystalline structure of In-rich sphalerite. The crystals exhibit a complex, layered, and somewhat dendritic morphology, with various shades of gray representing different crystal orientations and grain boundaries. A scale bar at the bottom left indicates a length of 200 micrometers. The overall appearance is that of a highly textured, polycrystalline material.

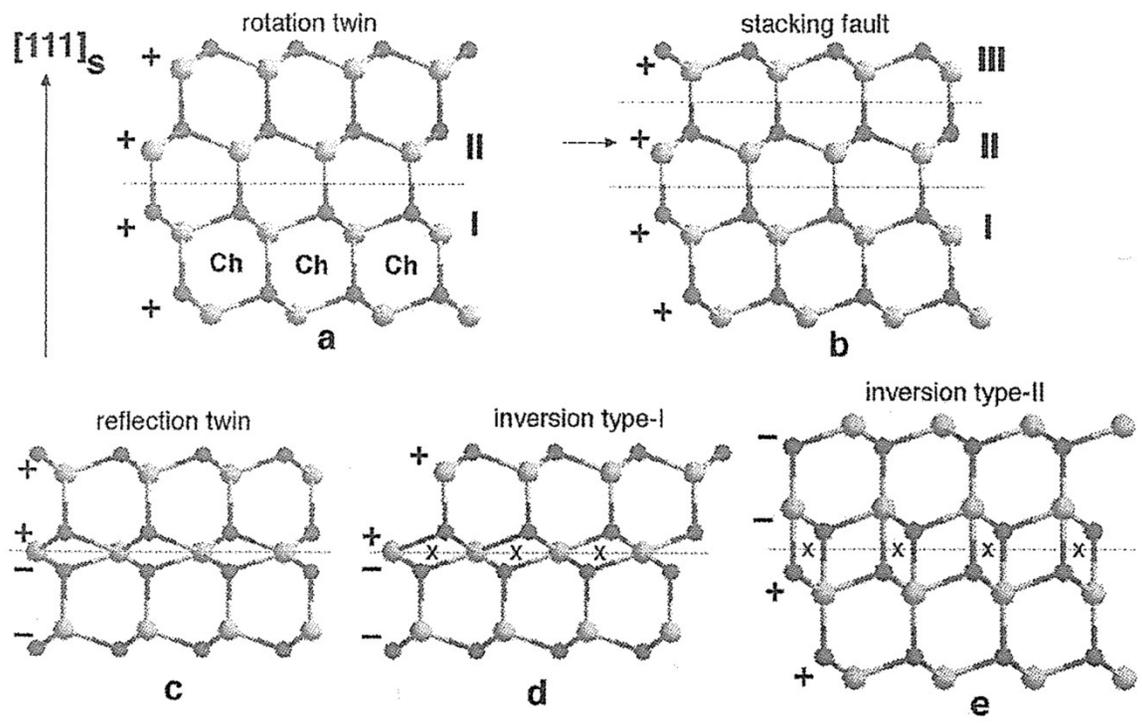


**Representative ablation spectrum  
In-rich sphalerite, Toyoha, Japan**



What controls the zoned distribution of trace elements in these crystals?

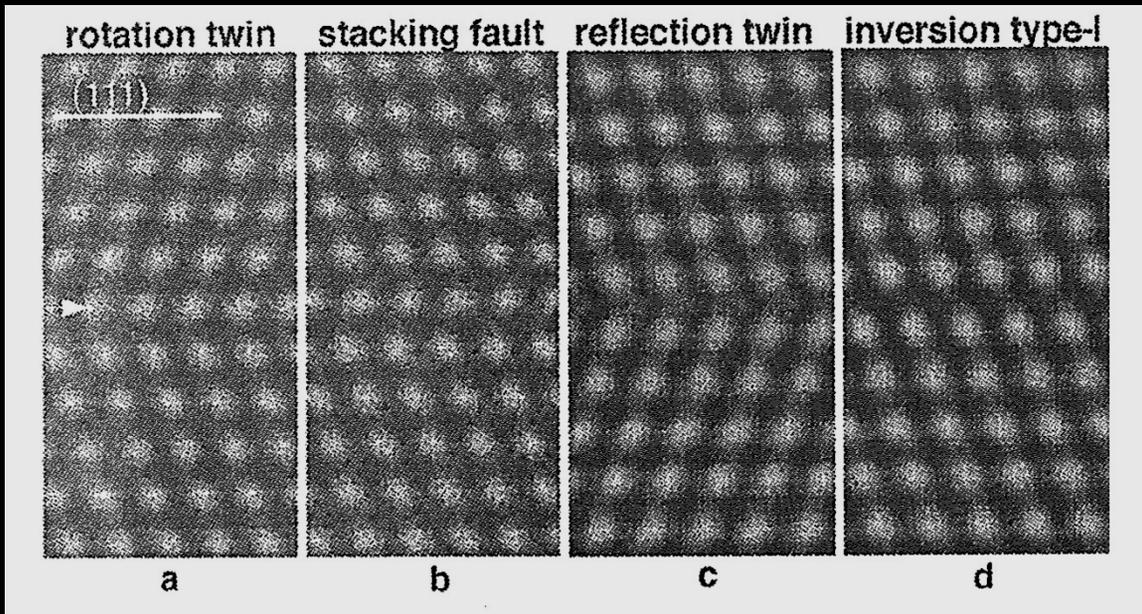
What are the relationship between element distributions and crystal structures?

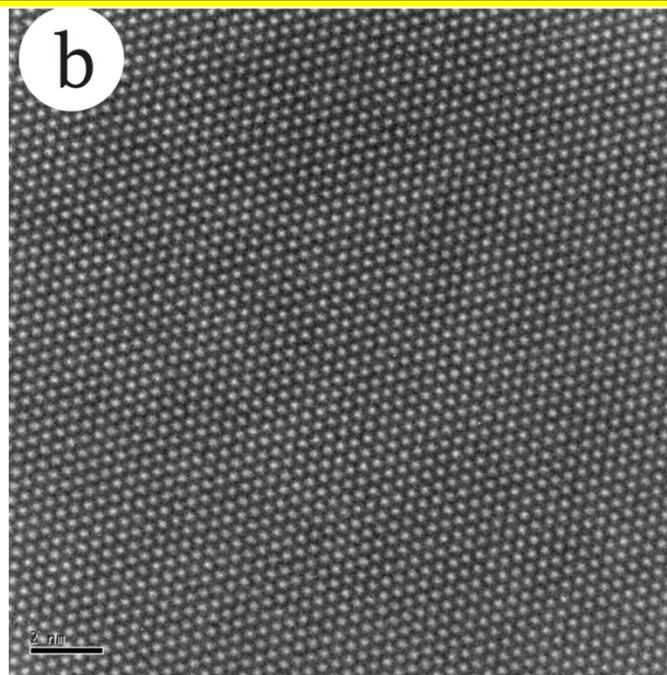
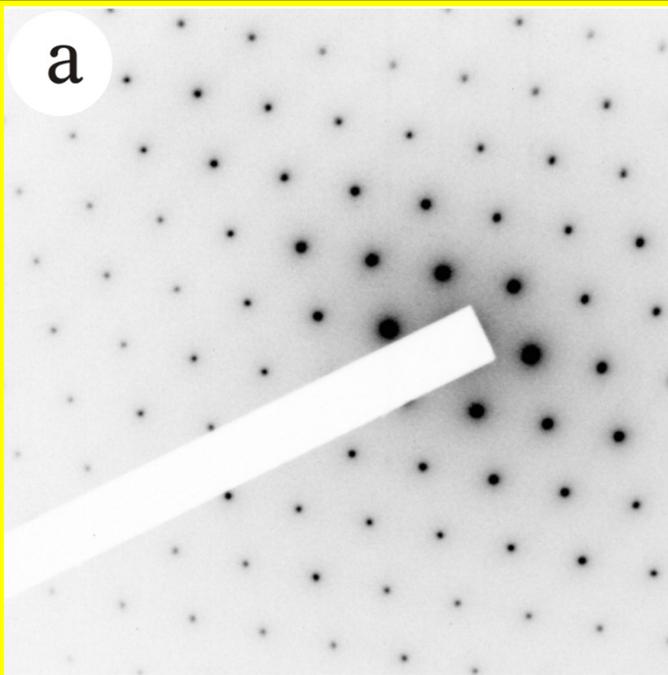


The cubic diamond type sphalerite structure allows various types of twinning and stacking faults

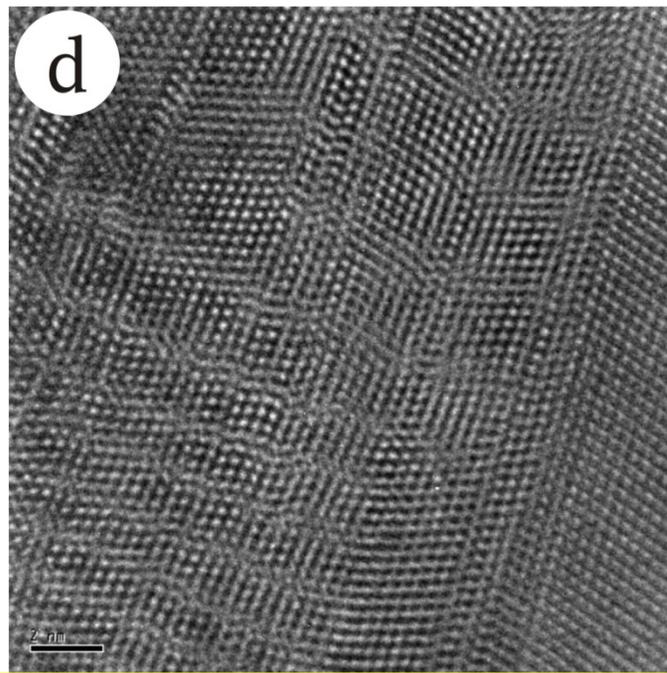
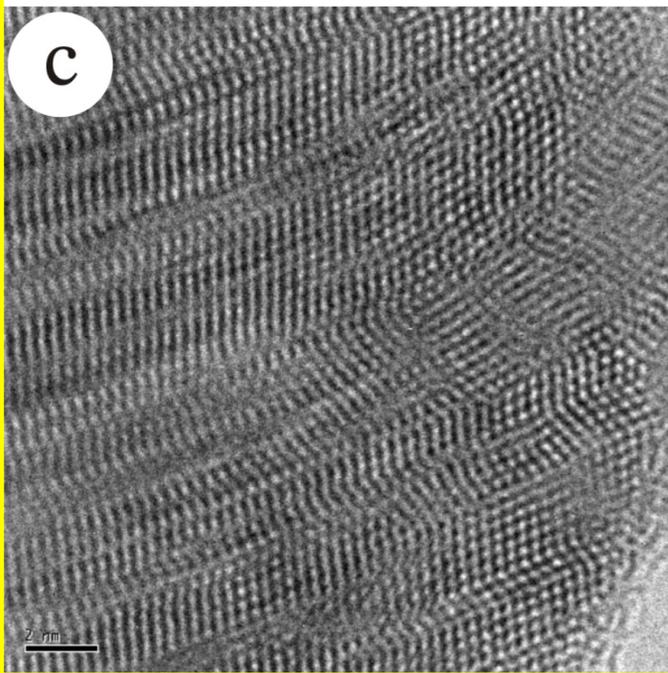
Sphalerite structures (Posfai, 1997)

Simulation (Posfai, 1997)





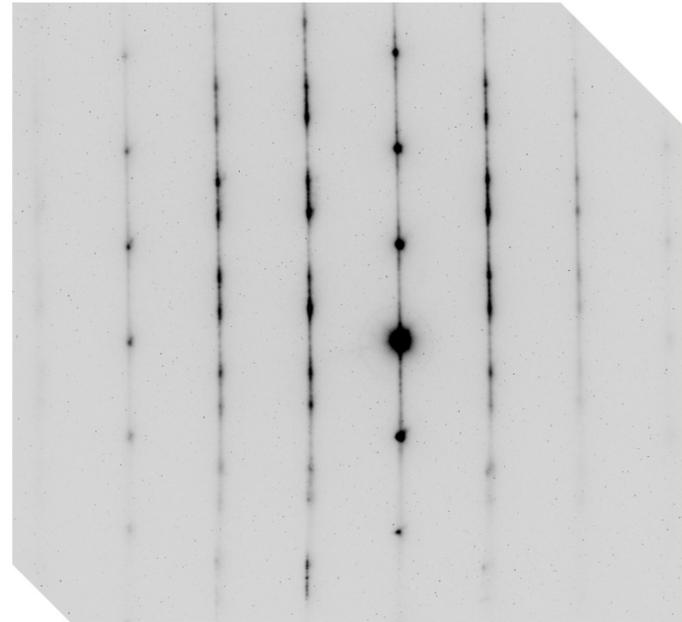
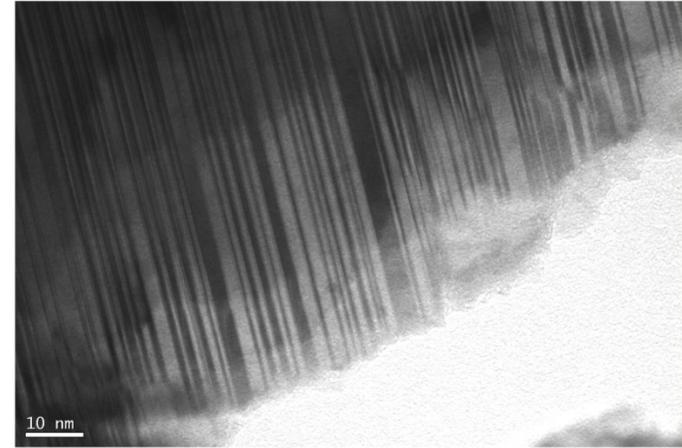
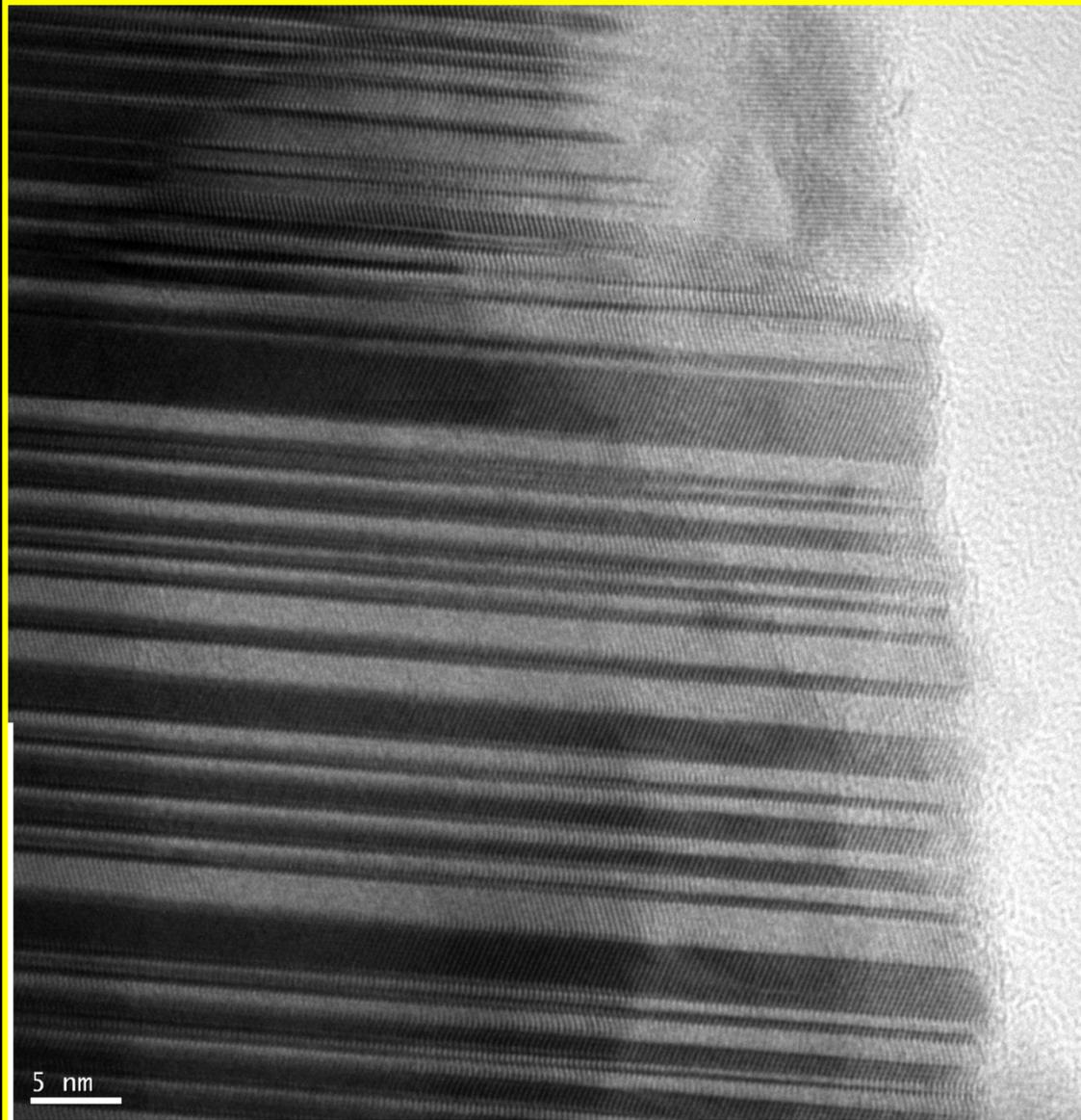
'normal'  
sphalerite



Zoned, In-  
rich  
sphalerite



We obtain the same type of irregular, cyclic zonation from the In-rich sphalerite from Toyoha

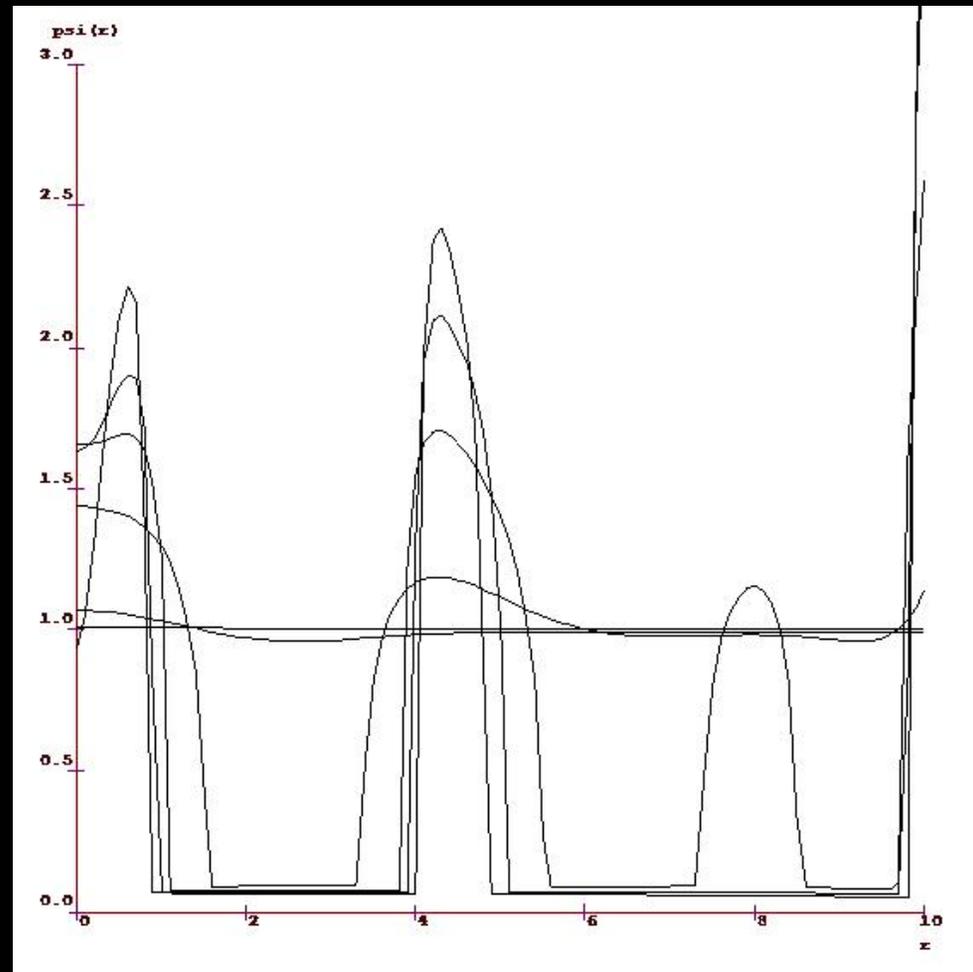


Commonly assumed that zonation due to fluctuation in fluid chemistry

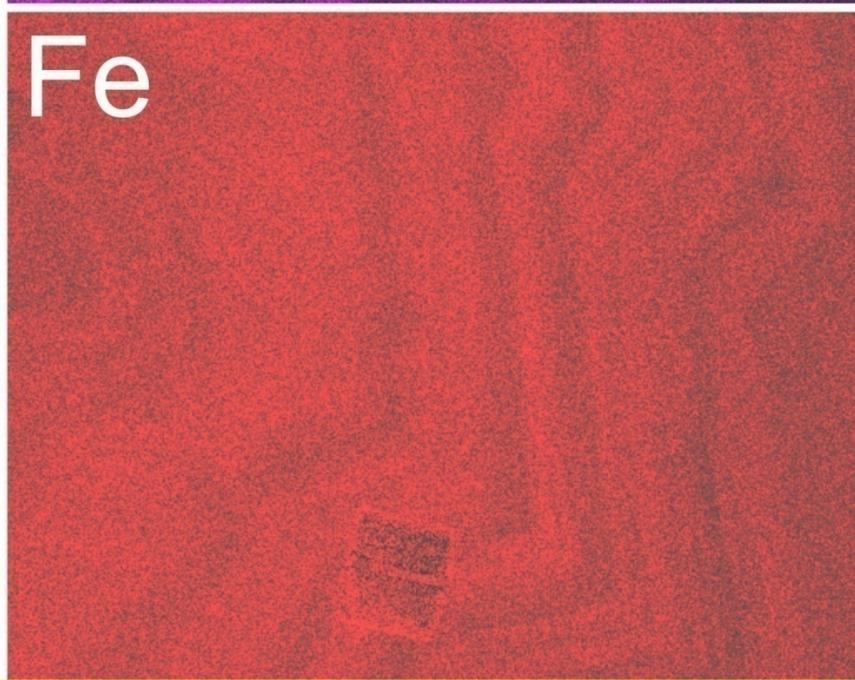
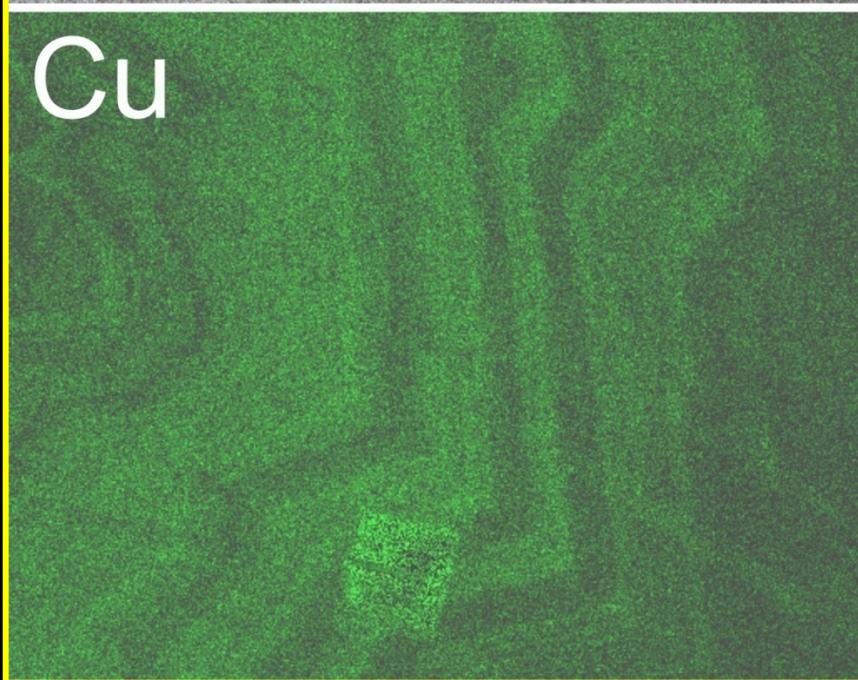
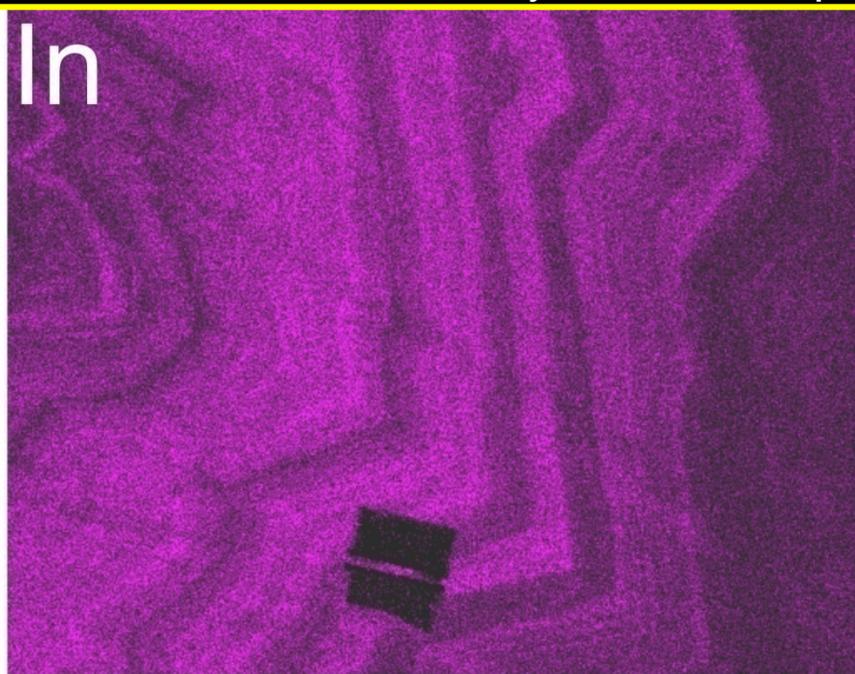
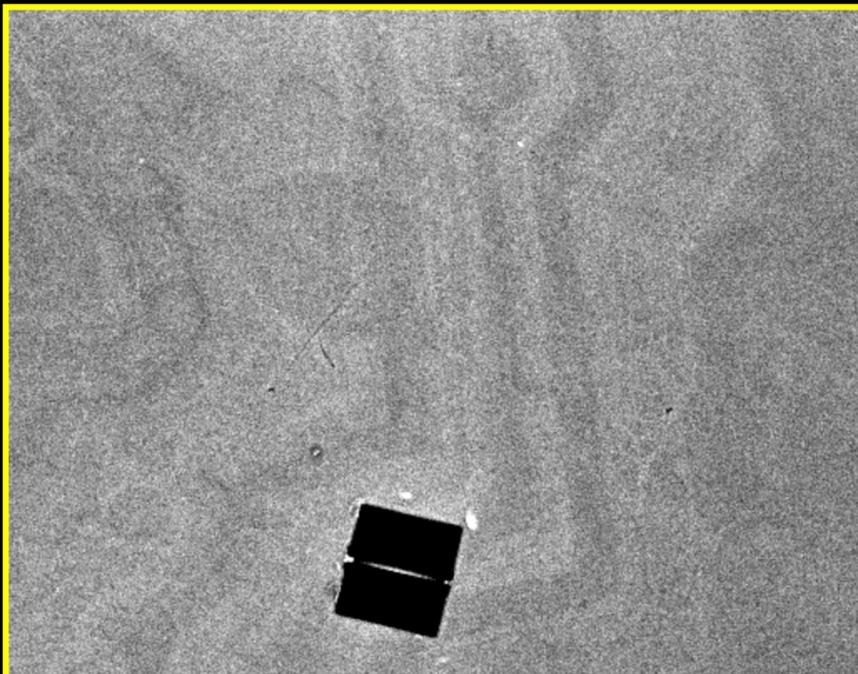
But what if this is due to self-patterning?

..in which case the system is closed and patterning results from far-from-equilibrium thermodynamics

We have simulated one of the models (competitive particle growth) (Ortoleva, 1995)



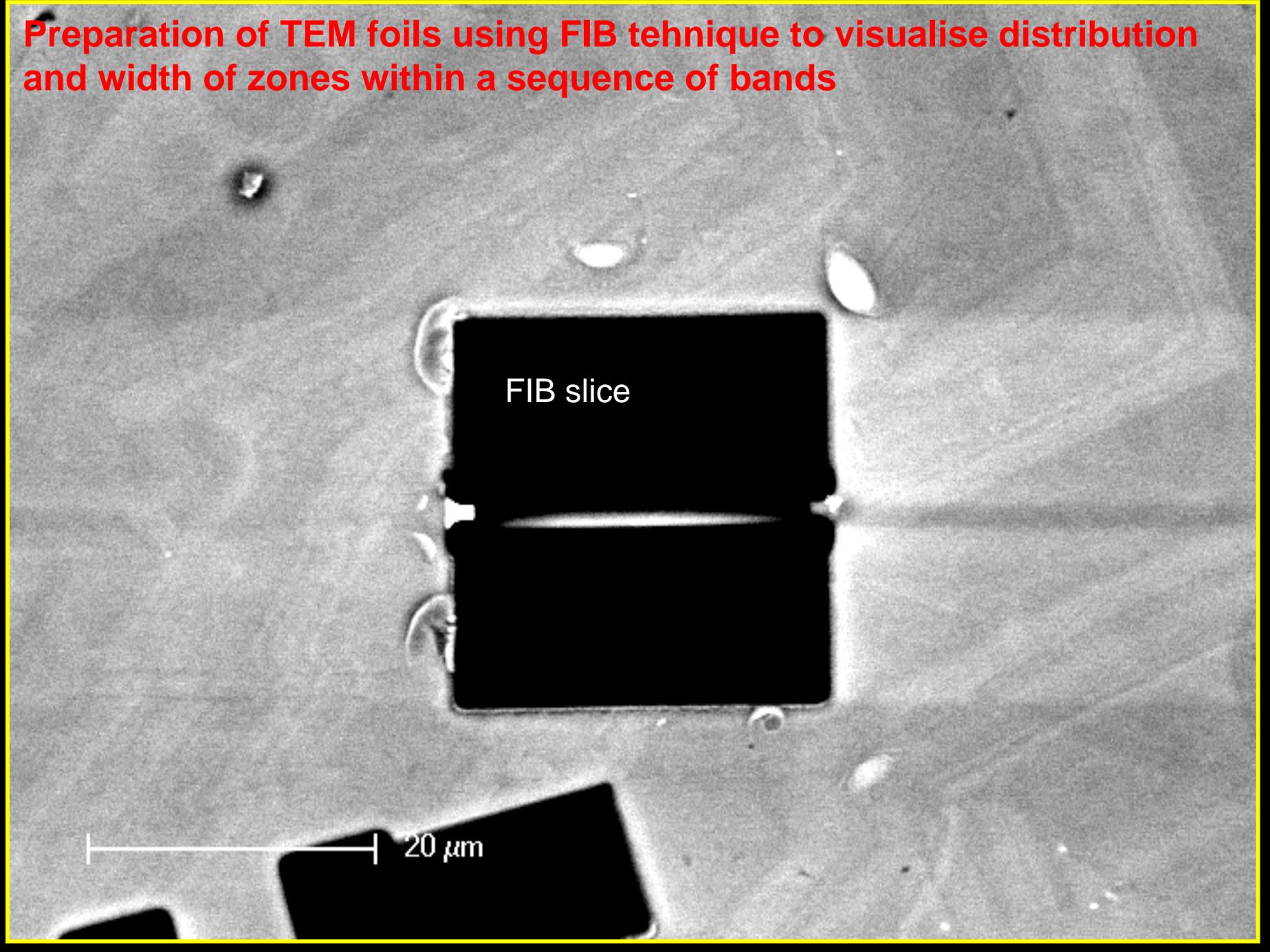
..but need more detail of the zonation sequence across the bands we see at the nanoscale



Preparation of TEM foils using FIB technique to visualise distribution and width of zones within a sequence of bands

FIB slice

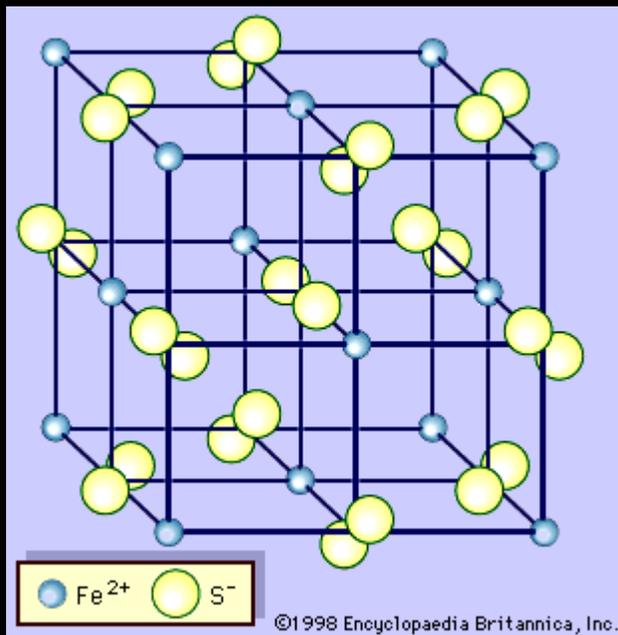
20  $\mu\text{m}$



# Pyrite ( $\text{FeS}_2$ )

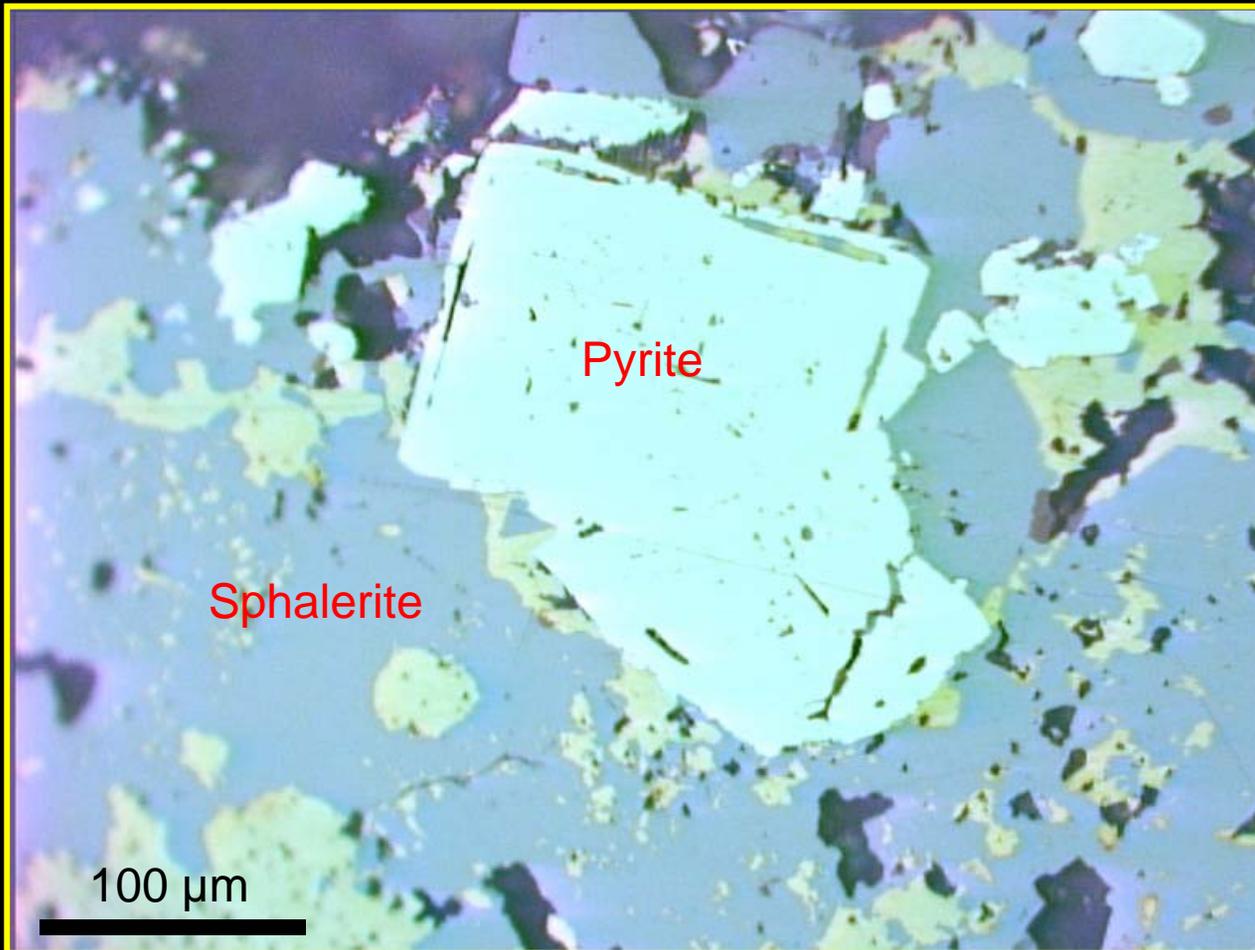
The most abundant sulphide on Earth.

Pyrite is a key mineral of economic interest in a range of gold ores

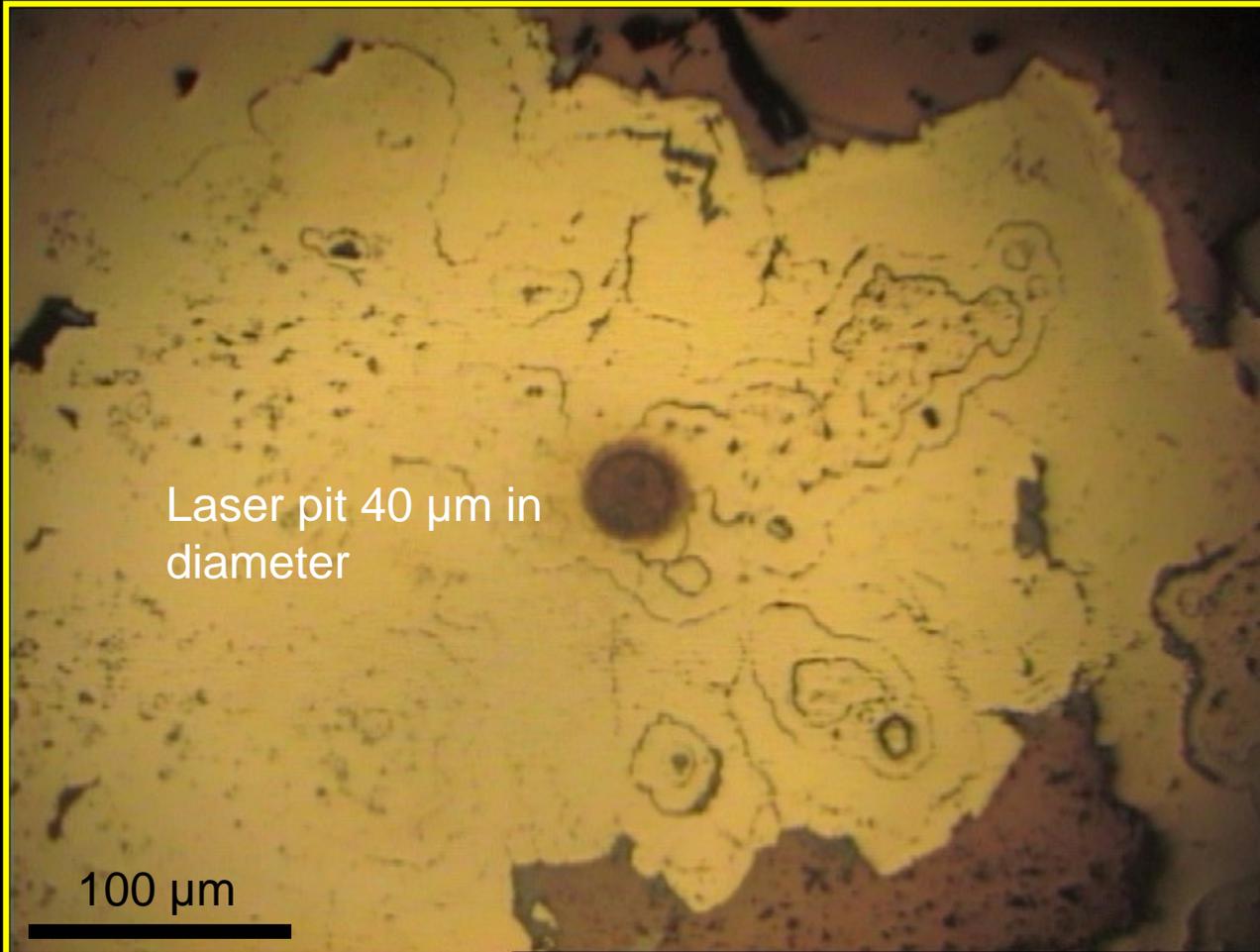


## 'Invisible' gold:

Gold in solid solution ( $\text{Au}_{\text{ss}}$ ) and of colloidal size (nanoparticles) found in sulfide ores with refractory behavior to cyanidation.



LA-ICP-MS is a relatively inexpensive method to obtain quantitative trace element data for Au and other elements in pyrite



Au-bearing colloform pyrite, Chelopech HS epithermal deposit, Bulgaria

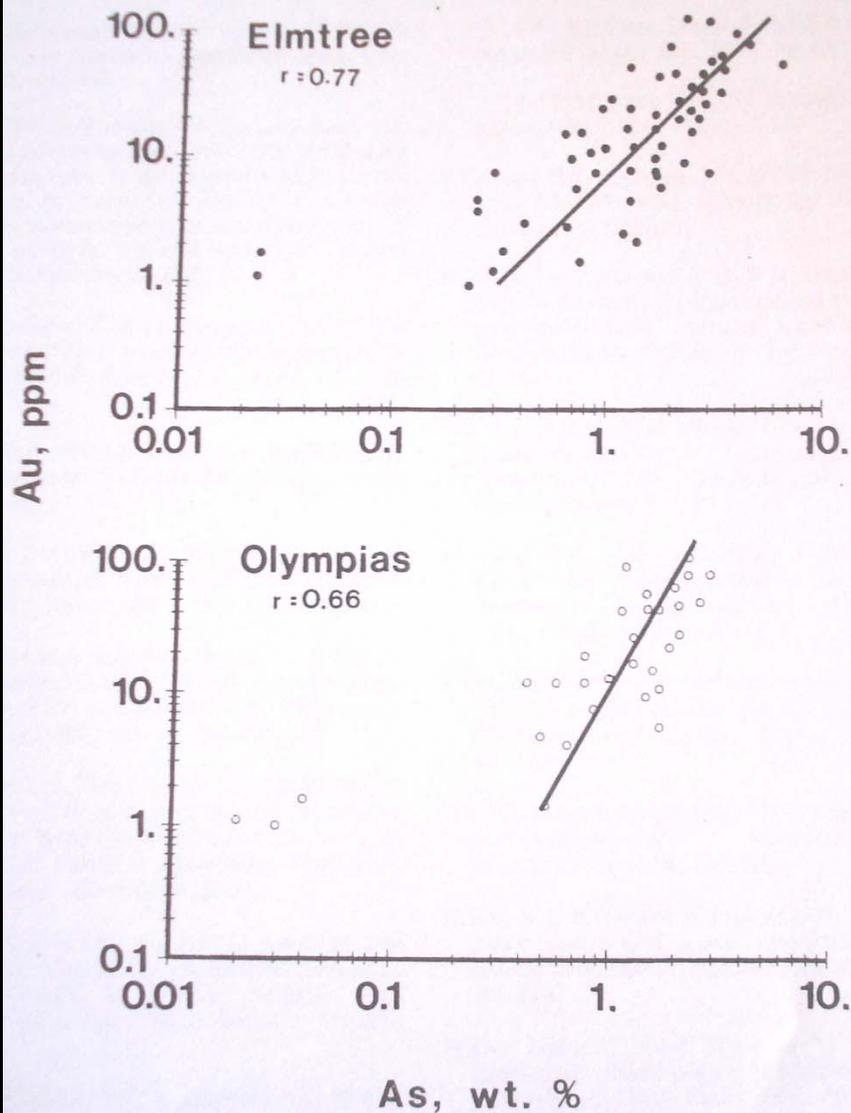


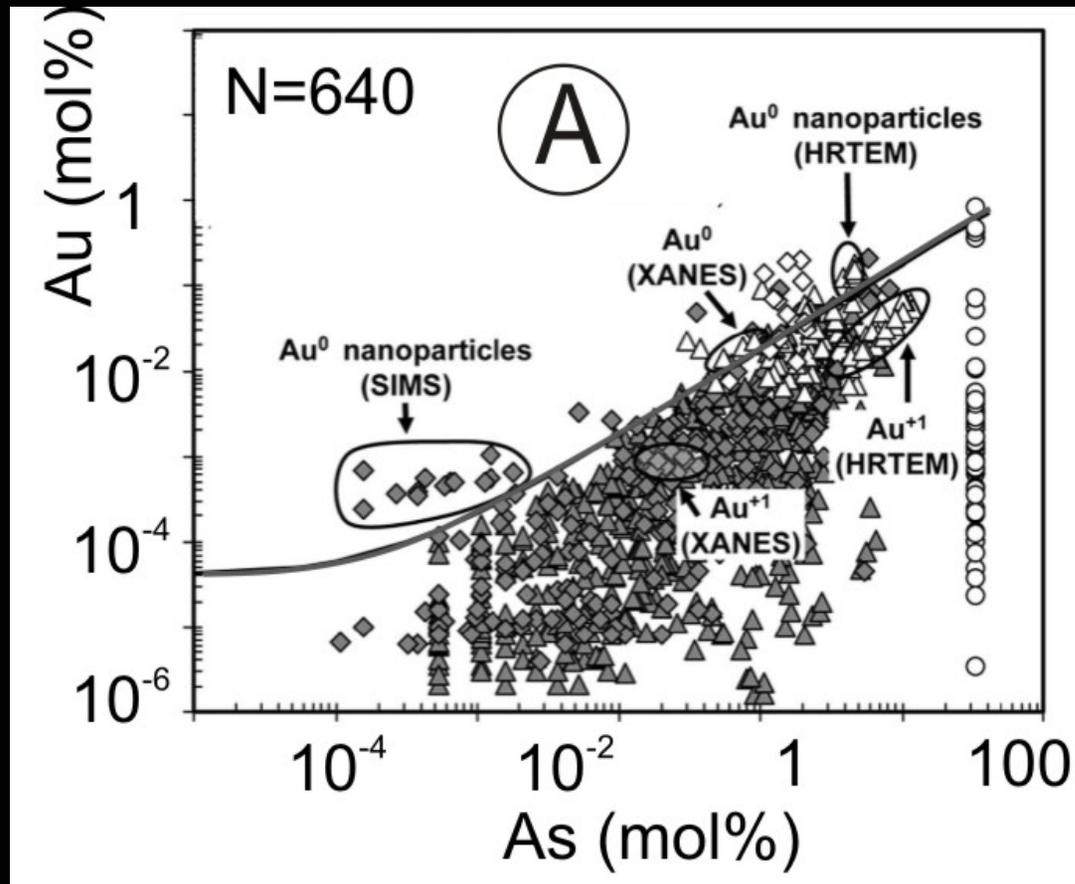
FIG. 9. Plot of As content against concentration of "invisible gold" in pyrite and arsenian pyrite from the Elmtree and Olympias deposits, indicating the correlation between gold and arsenic in each case.

Pioneering studies showed that gold is tied to the As content of pyrite

... dozens of papers have since addressed the issue

creating a paradigm of gold trapped in pyrite?

Indeed, arsenic is generally accepted as the key to Au incorporation in pyrite



Bias towards Carlin-style deposits

Reich et al. (2005)

Gold present in solid solution and as gold nanoparticles

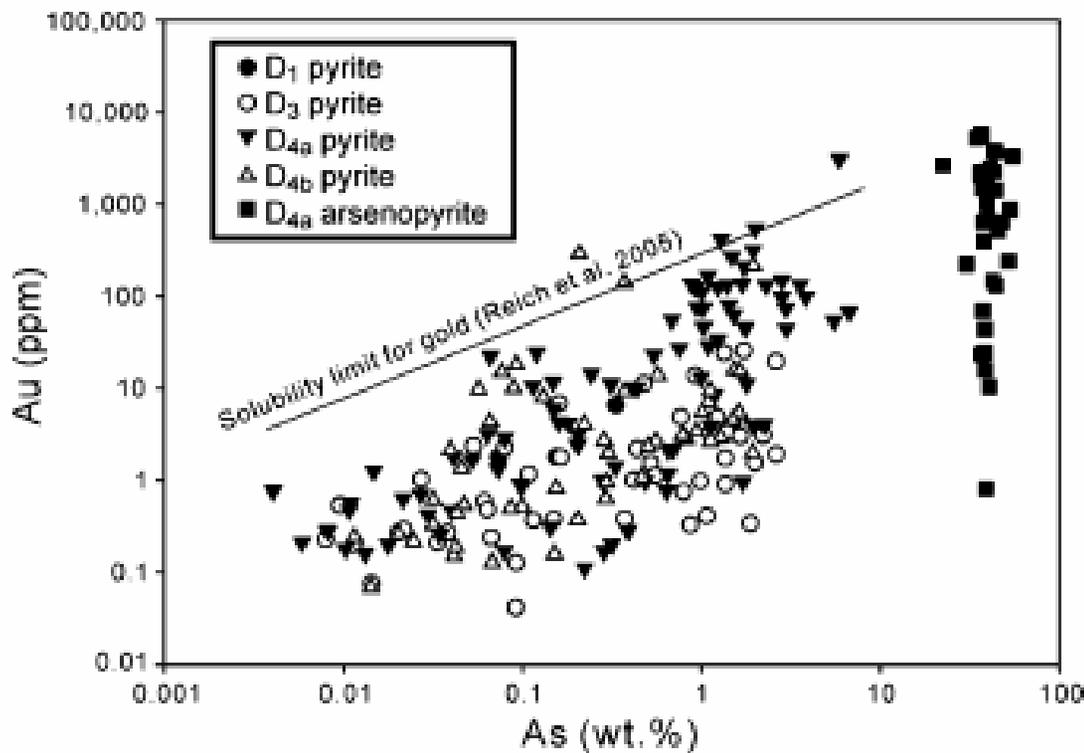
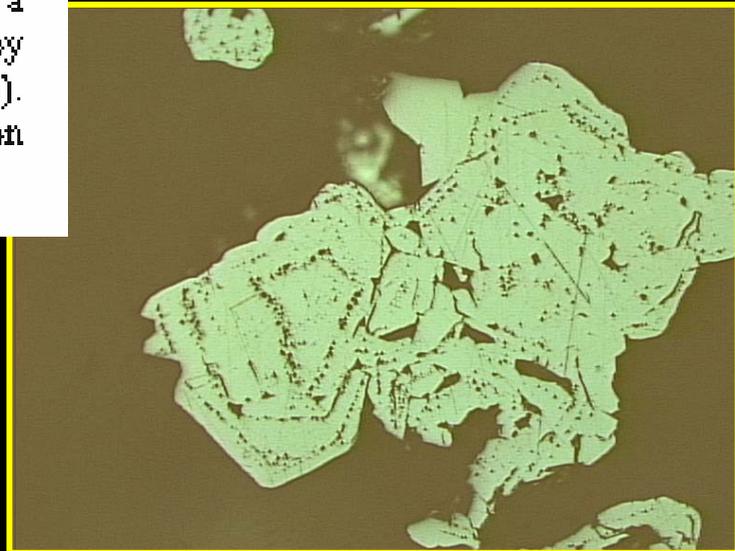


Fig. 6 Plot of Au vs. As concentrations for arsenian pyrite (as a function of ore stage) in the Sunrise Dam gold deposit analyzed by LA-ICP-MS. Solubility limit for gold is based on Reich et al. (2005). The five analyses plotting above the solubility limit were obtained on pyrite grains from the WSZ (D<sub>4a</sub>) and Mako (D<sub>4b</sub>) orebodies

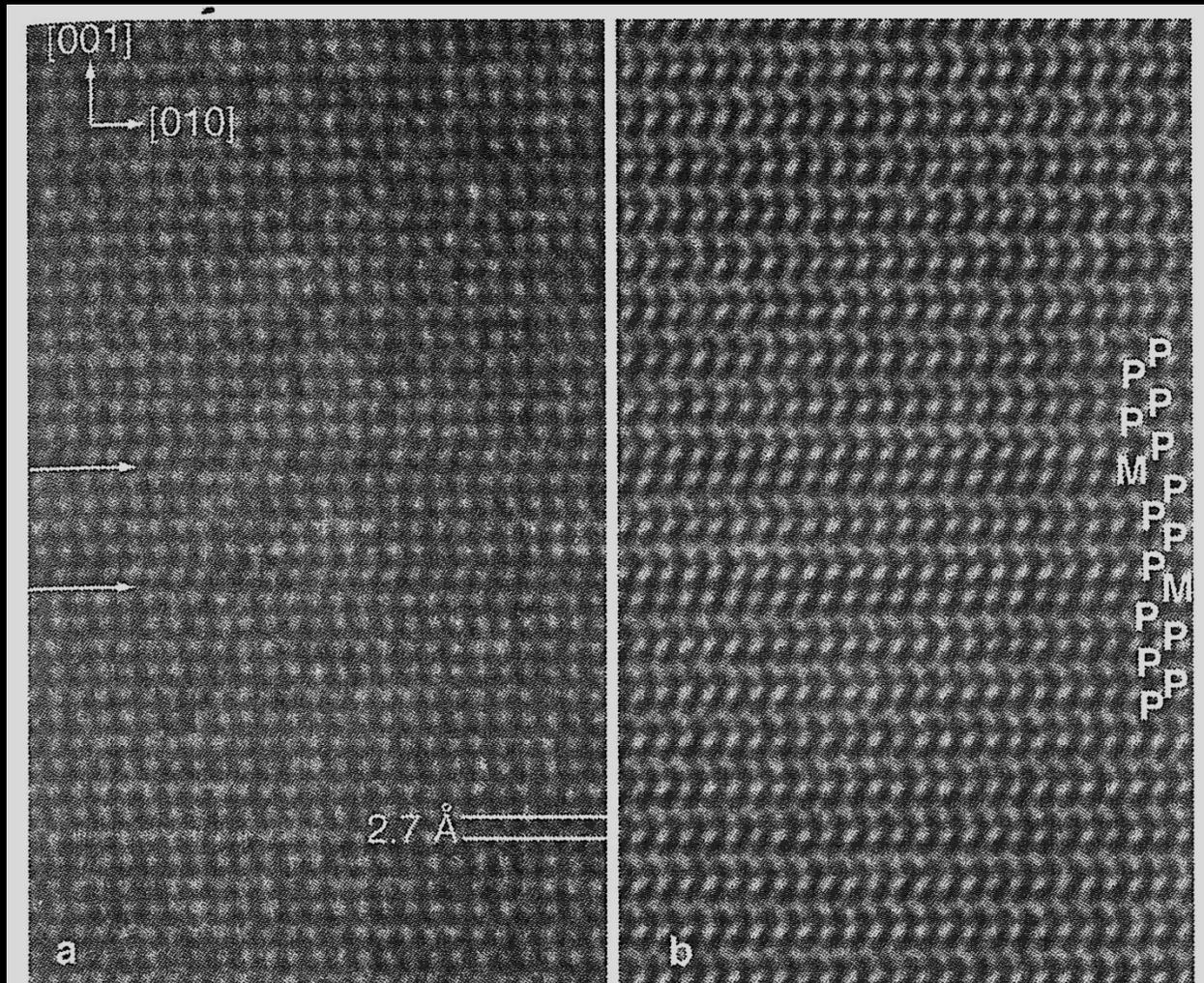
The model in which As enrichment is necessary for invisible gold is pyrite true in most cases

Sung et al. (2009)

Reinforced by observable zonation in pyrite with respect to arsenic



...and by observation of marcasite-like lamellae within arsenian pyrite



*Fig. 17.* HRTEM images of two individual marcasite lamellae in pyrite (Recsk), marked by white arrows in (a) and by M in (b). (a) and (b) were obtained at different objective-lens defocus values.

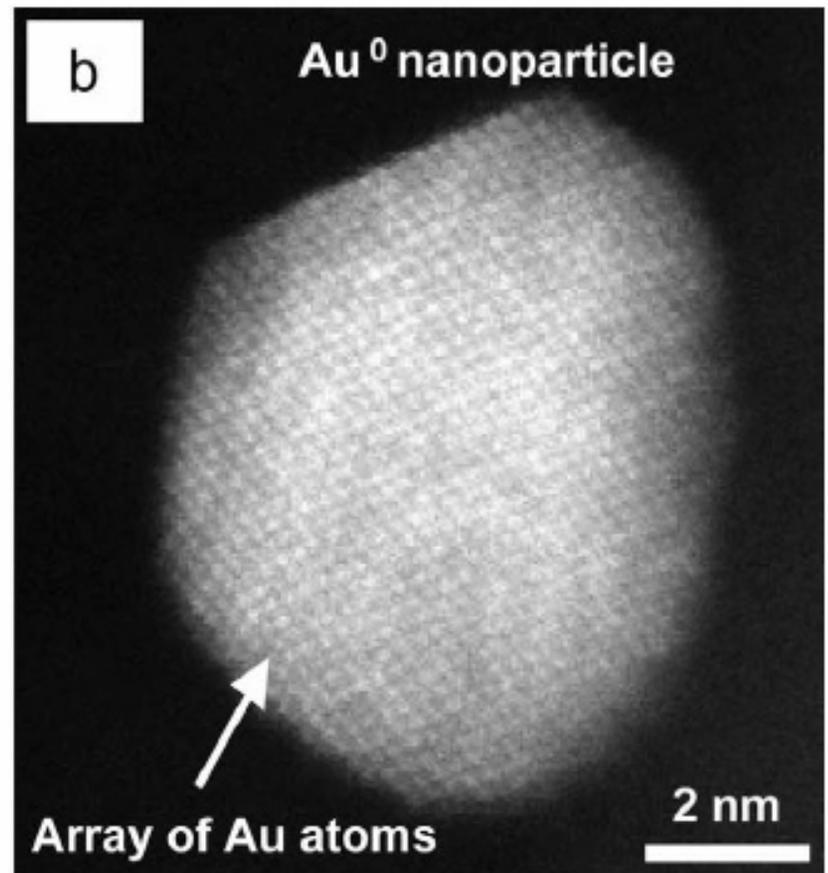
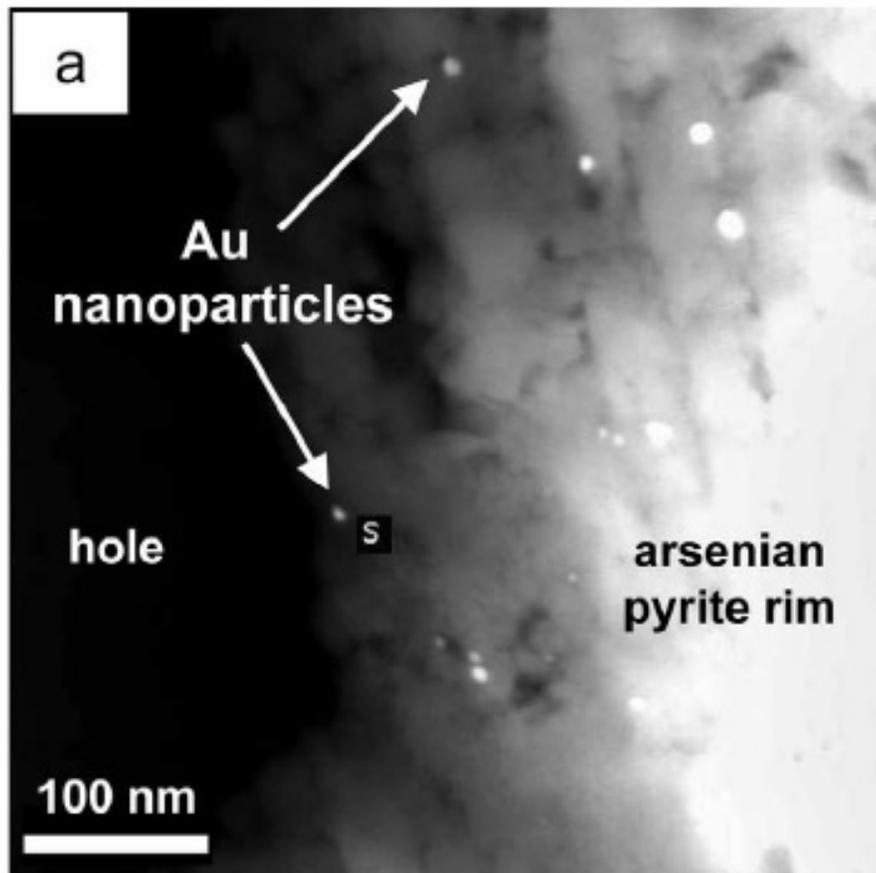


Fig. 7. High-angle annular dark field (HAADF) images of arsenian pyrite rims from sample SJ-323C-1326 (Screamer). (a) Bright, high average atomic mass ( $Z$ ) contrast Au particles are disseminated throughout a lower- $Z$  arsenian pyrite matrix. (b) High-magnification ( $4 \times 10^6$  times) image of an individual Au nanoparticle (labeled "S") shows the rounded shape and well defined boundaries of the particle, as well as the array of Au atoms.

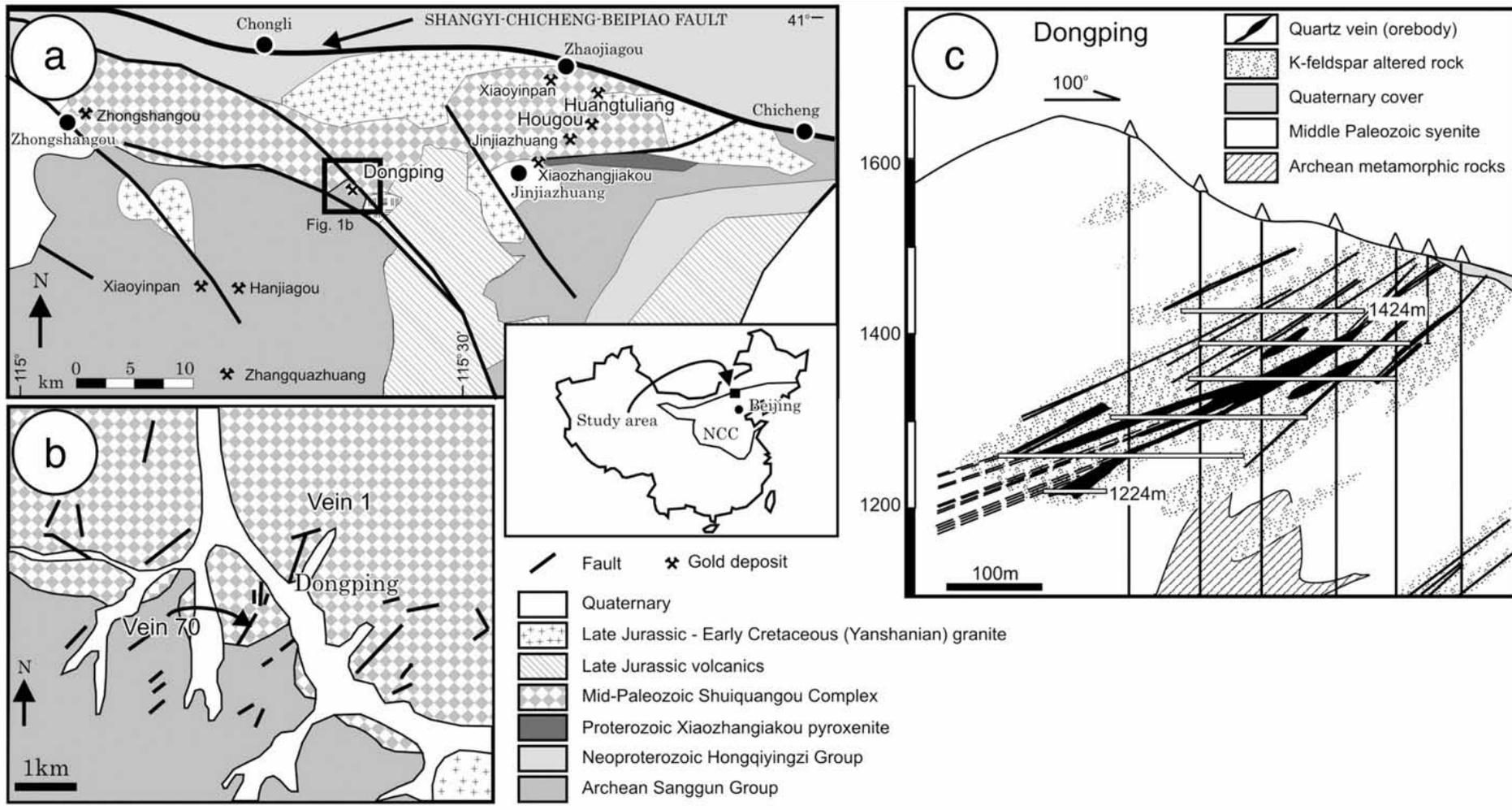
Reich et al. (2005)

Direct observation of gold nanoparticles a significant step forward

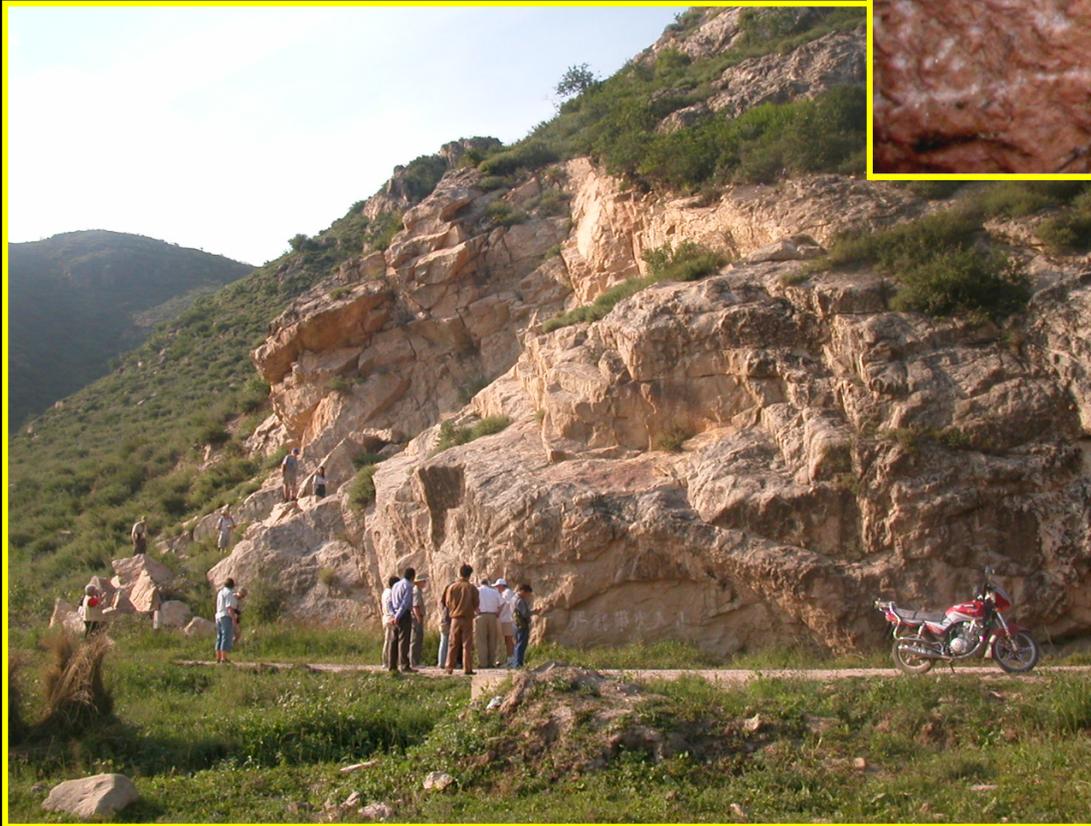
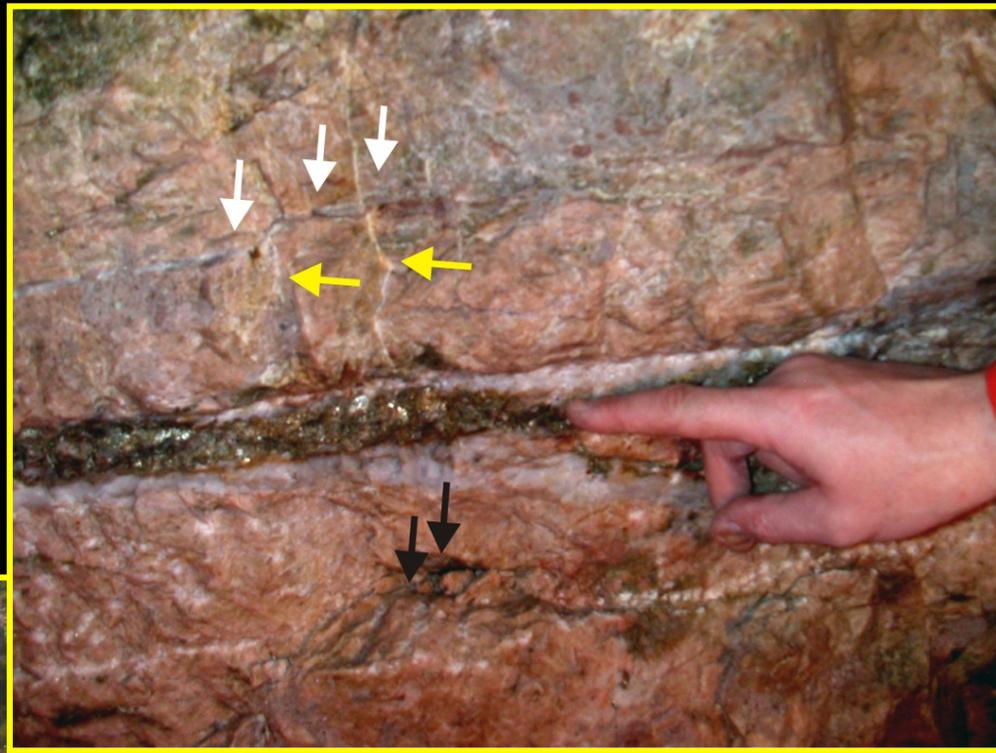
But is arsenic enrichment in pyrite that carries Au the symptom rather than the cause?



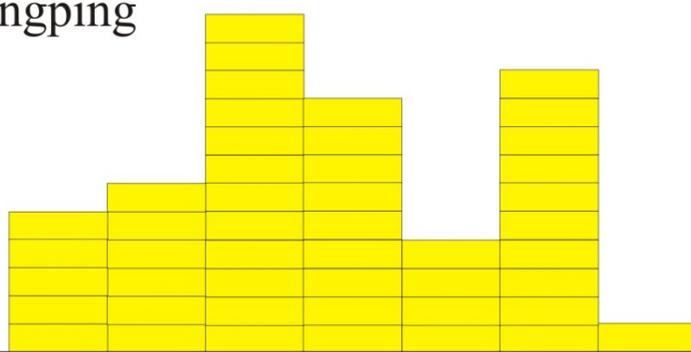
# Au deposits from North China Craton, Hebei, China



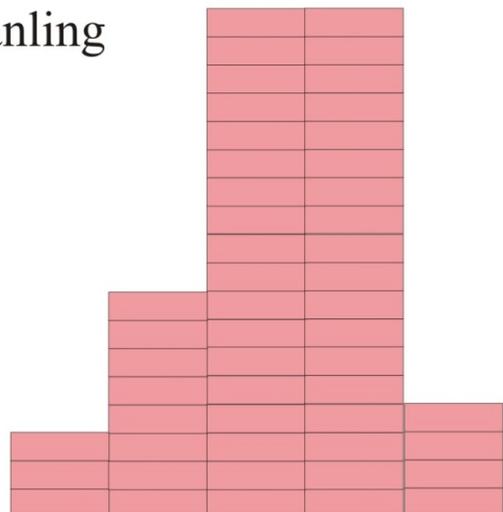
Au deposits from North  
China Craton, Hebei:  
Variscan alkaline  
intrusions, Alpine  
orogenic overprint



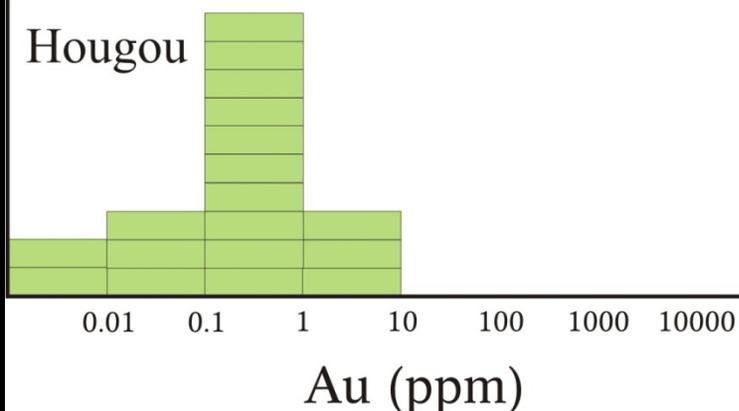
Dongping



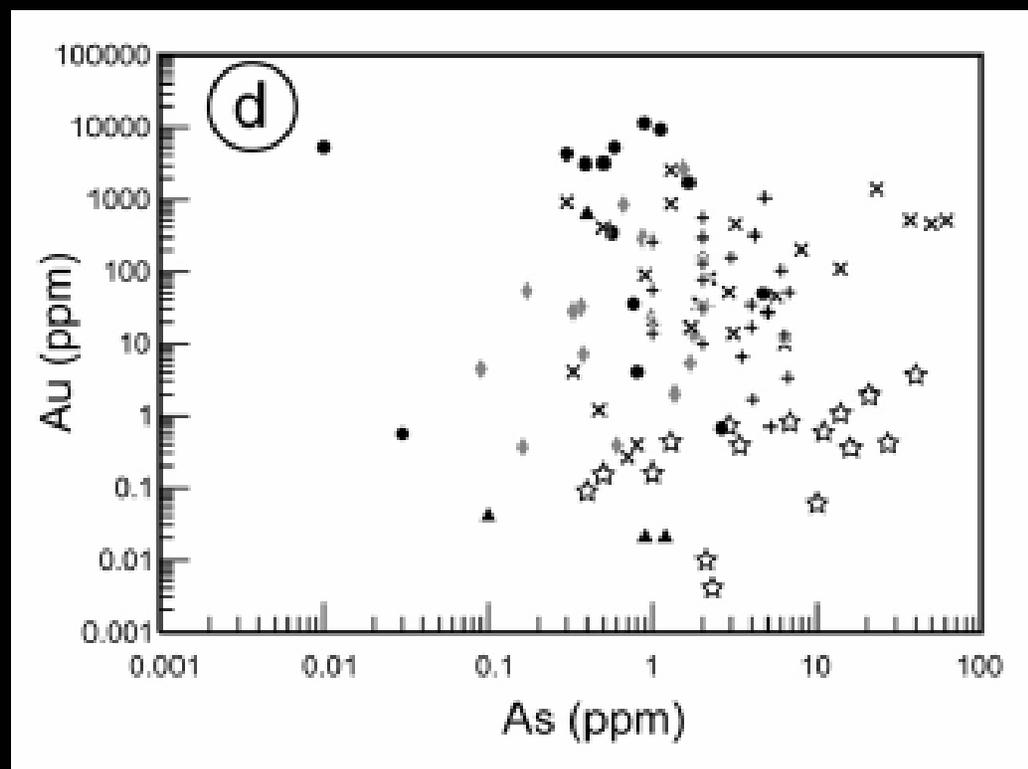
Huantuanling



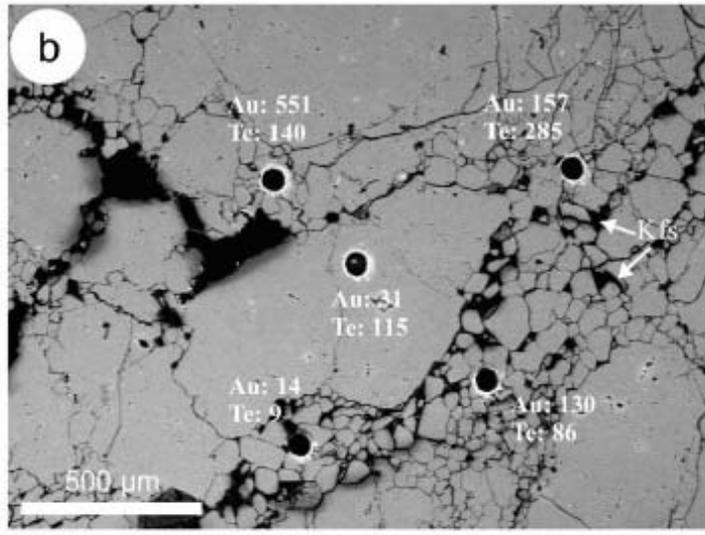
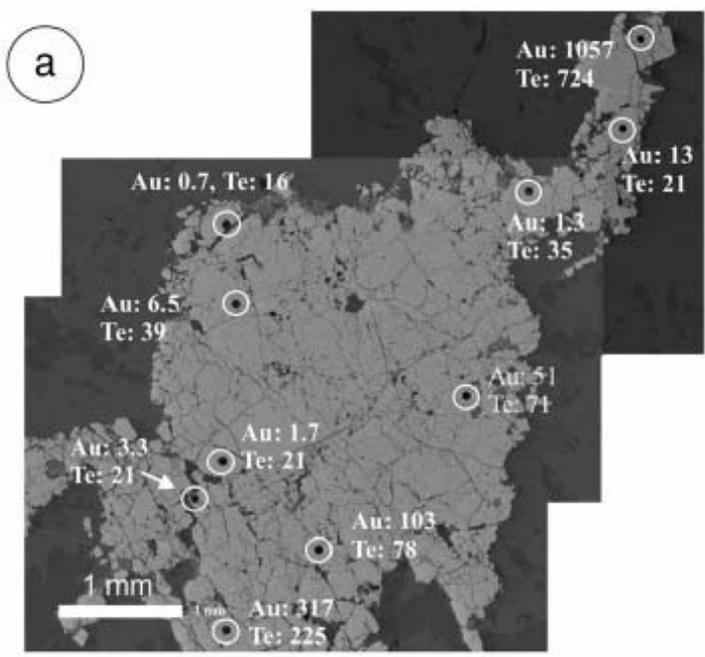
Hougou



Pyrite carries hundreds or thousands of ppm gold, but without significant arsenic



Cook et al. (2009a)



# Strong textural control on gold concentrations in pyrite

## Correlation between Au and Te, Bi and even Pb

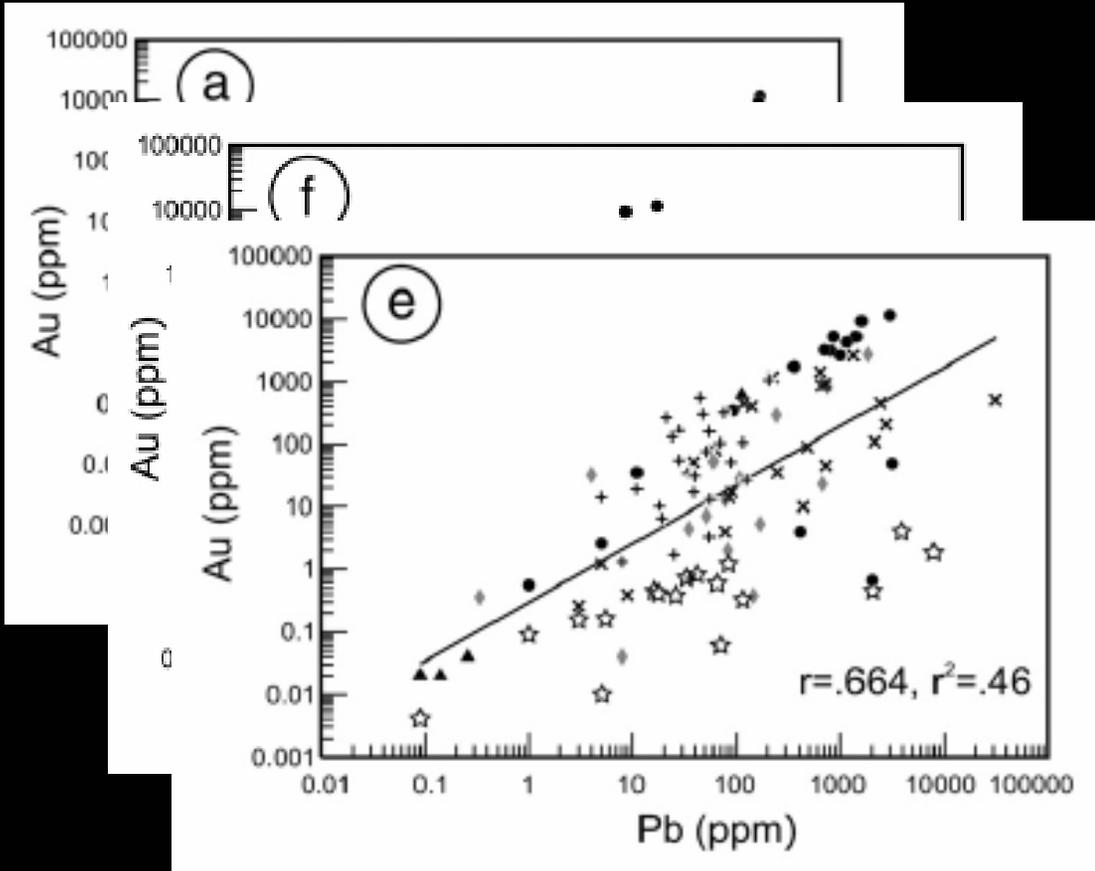
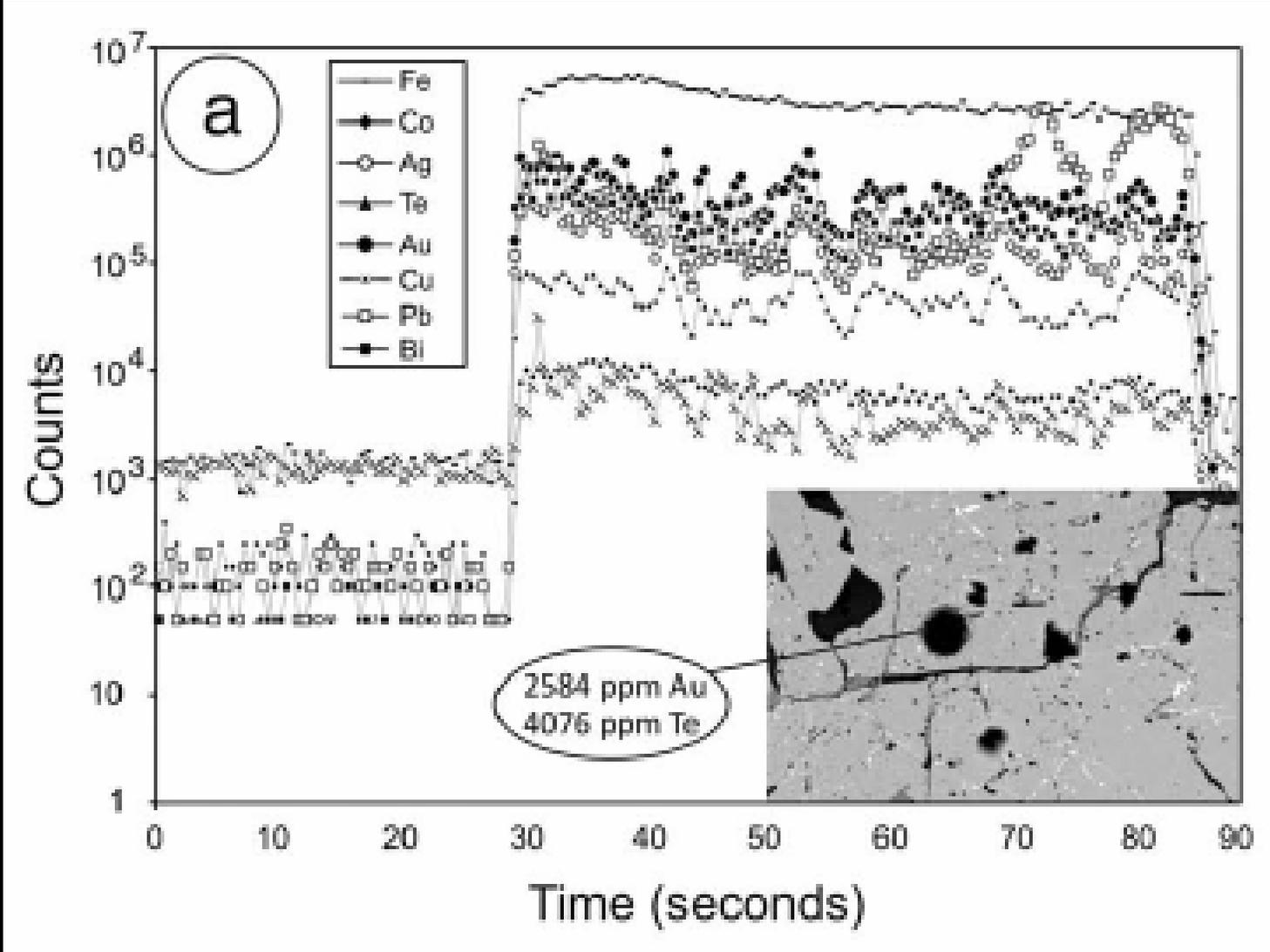


Fig. 5. Back-scattered electron images showing aspects of ore petrography, Huangtuliang deposit, showing laser-ablation craters with measured concentrations of Au and Te in each. (a) Shows an aggregate of brittle-deformed pyrite grains, (b) and area consisting of coarse (relictic?) pyrite surrounded by recrystallized pyrite fragments ('foam'-textured pyrite).

# Gold concentrated in pyrite both in solid solution and as nanoparticles



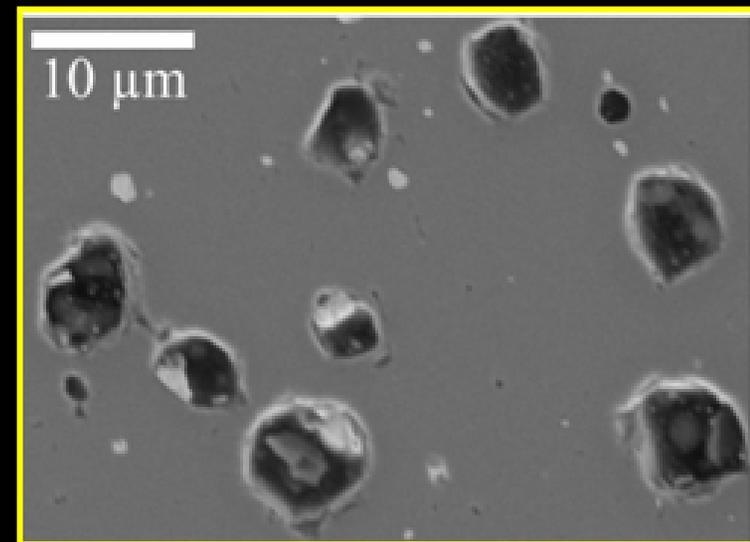
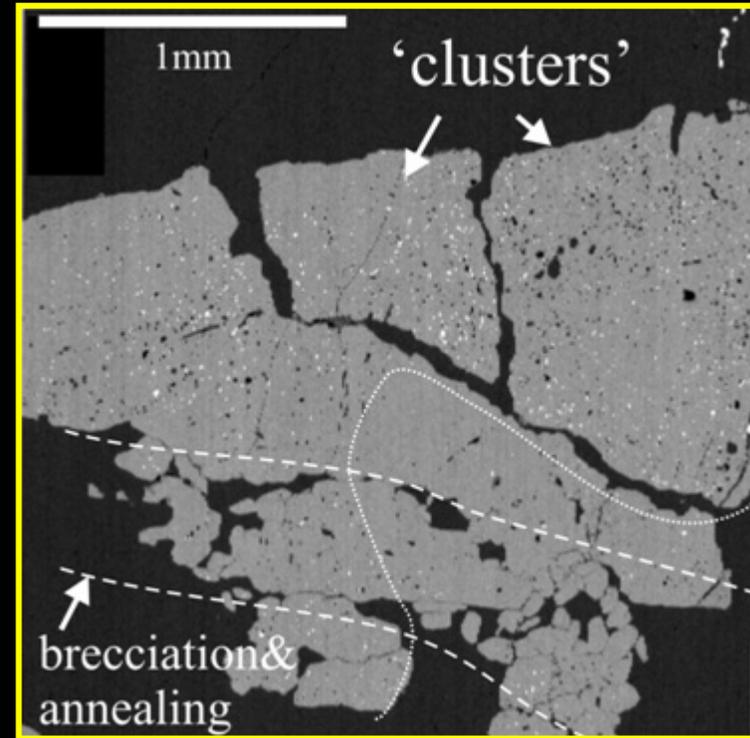
Cook et al. (2009a)

Model: low melting point chalcophile elements (LMCE) assist local-scale trace element remobilisation during overprinting.

Clusters: areas of high-porosity hosting inclusions of gold and gold-telluride inclusions, as well as fluid inclusions.

These represent sites of interaction via coupled dissolution replacement reaction (CDRR) between early pyrite and later fluids.

Despite an irregular distribution of telluride inclusions in pyrite, and their composite, variable character, there are excellent correlations between Au and Te, Ag and Pb, Bi. *As is not an issue!*



Further work will address the paradigm of invisible gold in pyrite

Au-enrichment via local scale remobilisation when LMCE (Te and Bi) are present. Fluid-mineral interaction via CDRR

Correlation between microfabrics, trace elements & isotope signatures in pyrite: EBSD, LA-ICPMS, PIXE, X-ray fluorescence, nanoSIMS

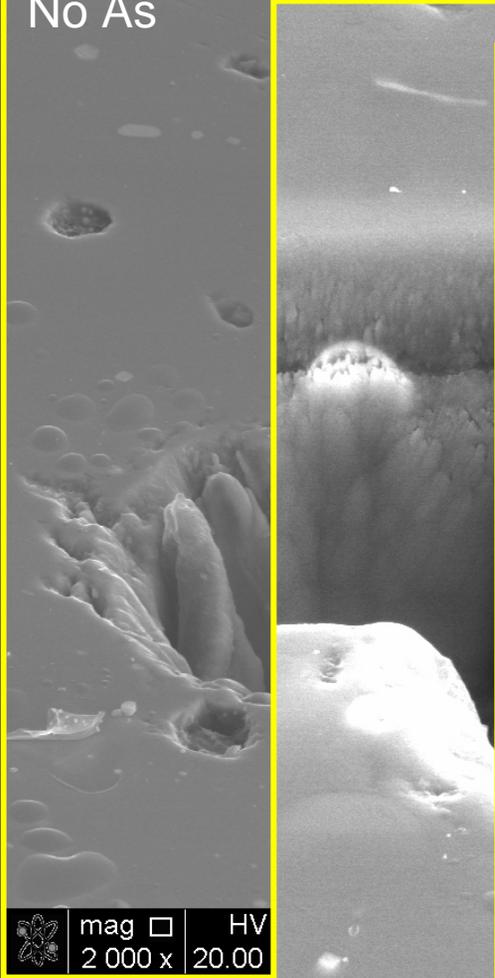
Nanoparticles - occurrence and behaviour under thermal induced gradients: FIB-TEM, High Angle Annular Dark Field-Scanning Transmission Electron Microscopy (HAADF-STEM)

Diffusion and precipitation of Au and LMCE: dry and hydrothermal experiments

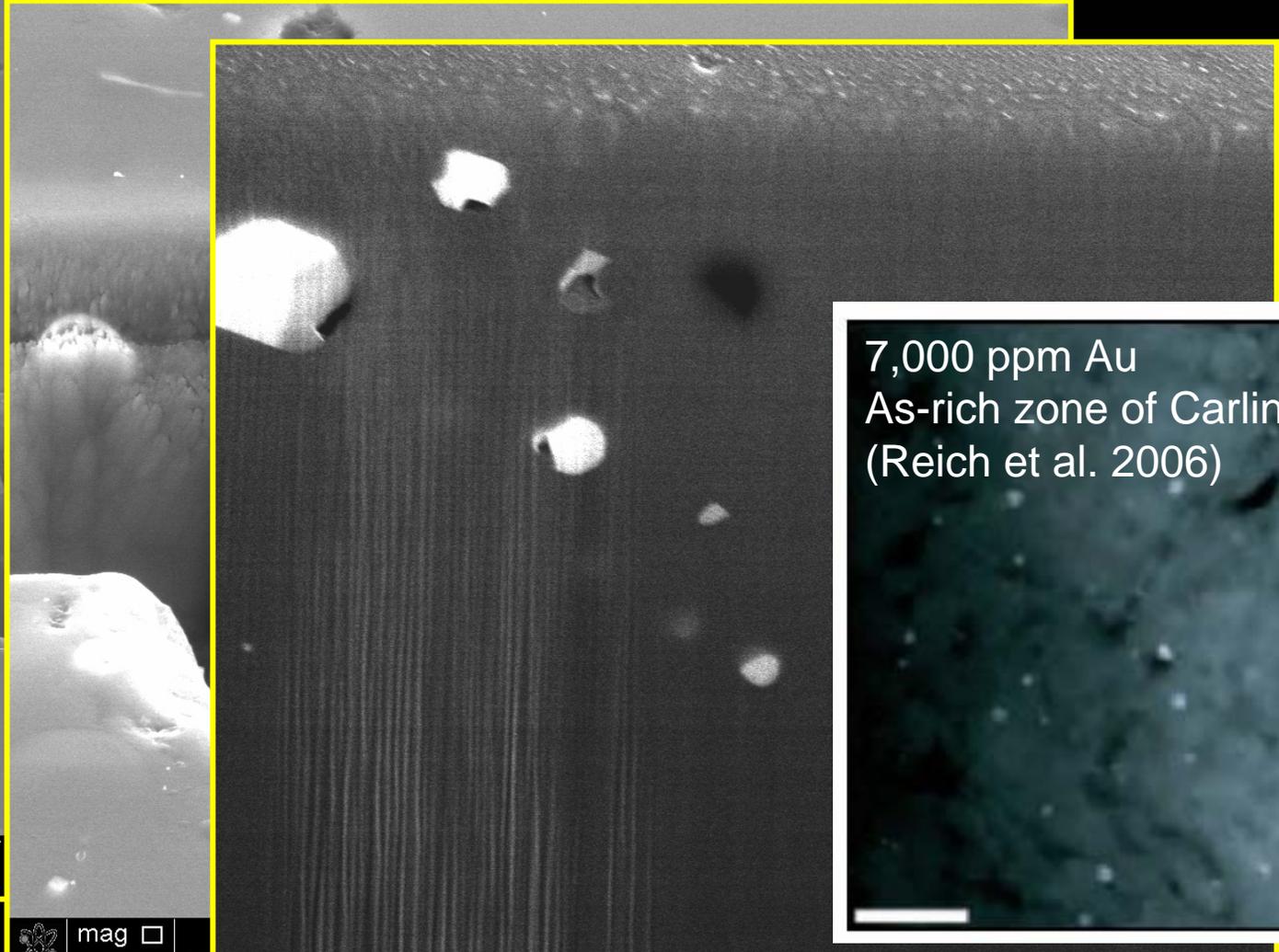
Petrogenetic models for orogenic and intrusion-related Au deposits (application to mineral exploration, processing and mitigation of environmental hazards)

# First attempts to investigate the distribution of the inclusions in 3 dimensions (Focussed ion beam)

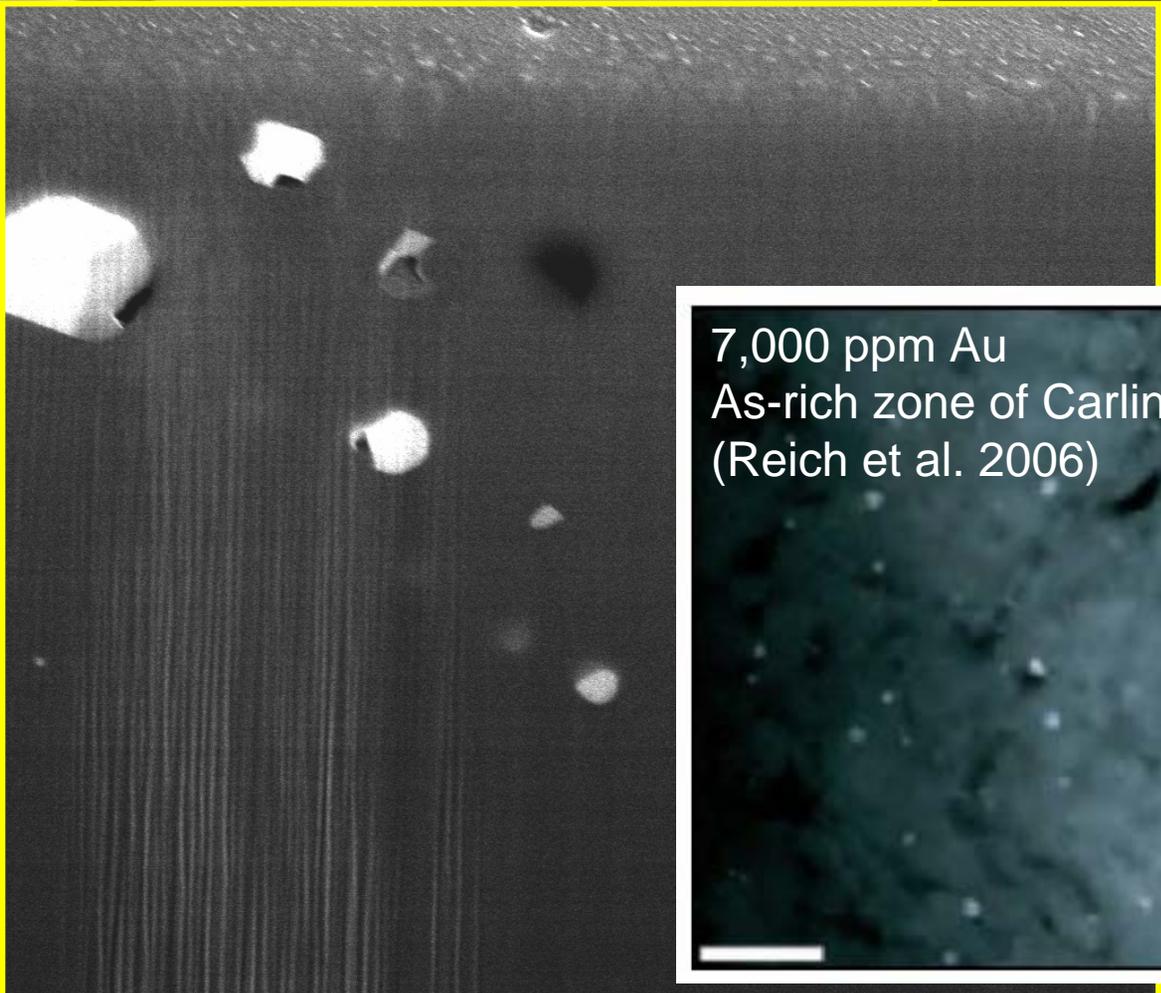
10,000 ppm Au  
No As



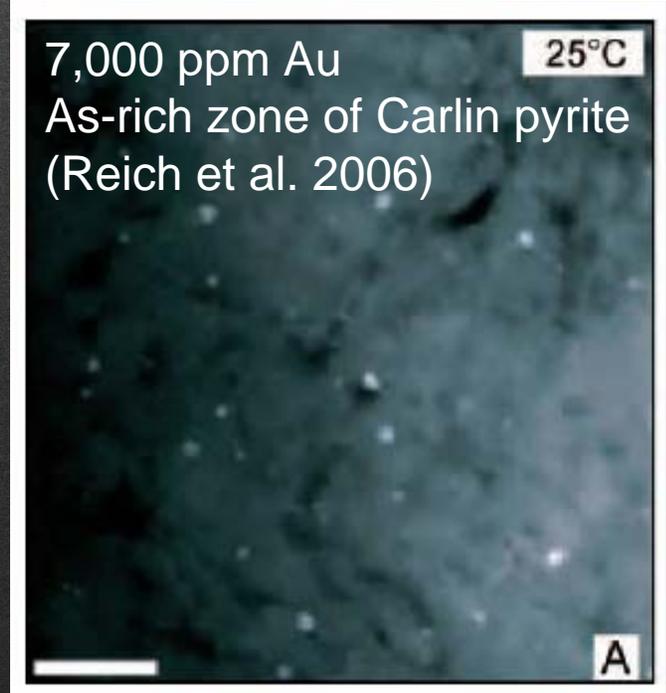
mag  HV  
2 000 x 20.00



mag   
4 000 x 30



mag  HV curr mode WD HFW  
16 463 x 20.00 kV 0.69 nA SE 4.4 mm 15.5 μm



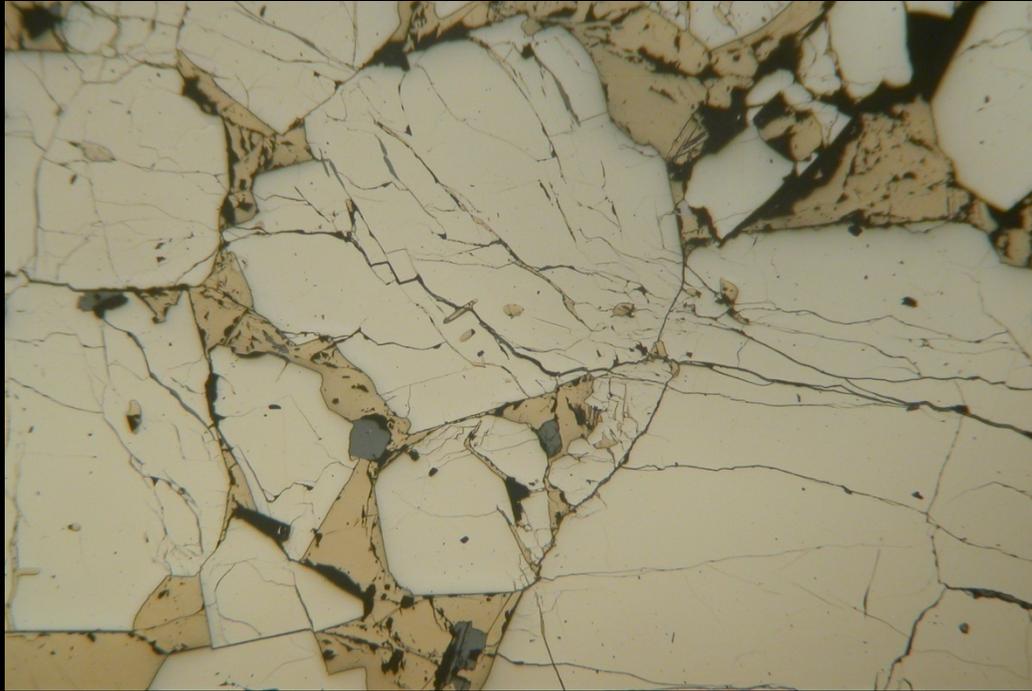
7,000 ppm Au  
As-rich zone of Carlin pyrite  
(Reich et al. 2006)

25°C

A

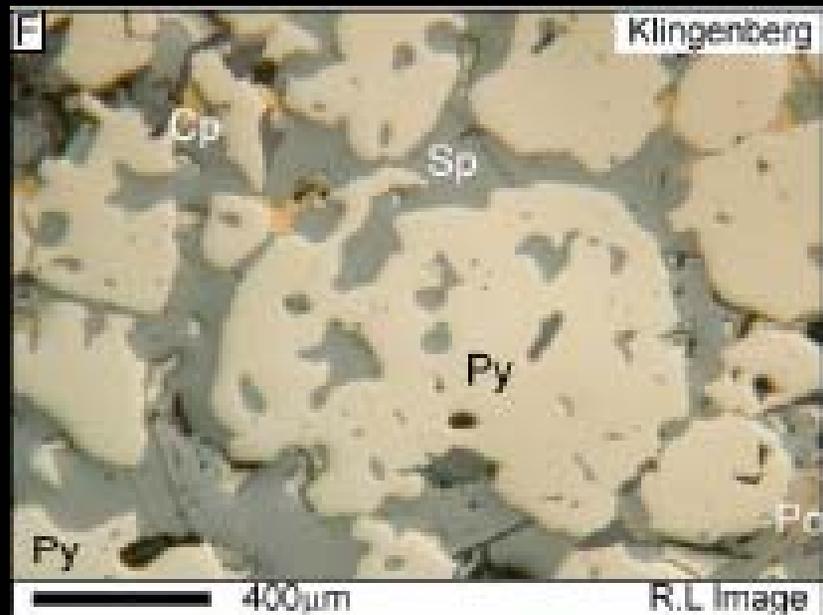
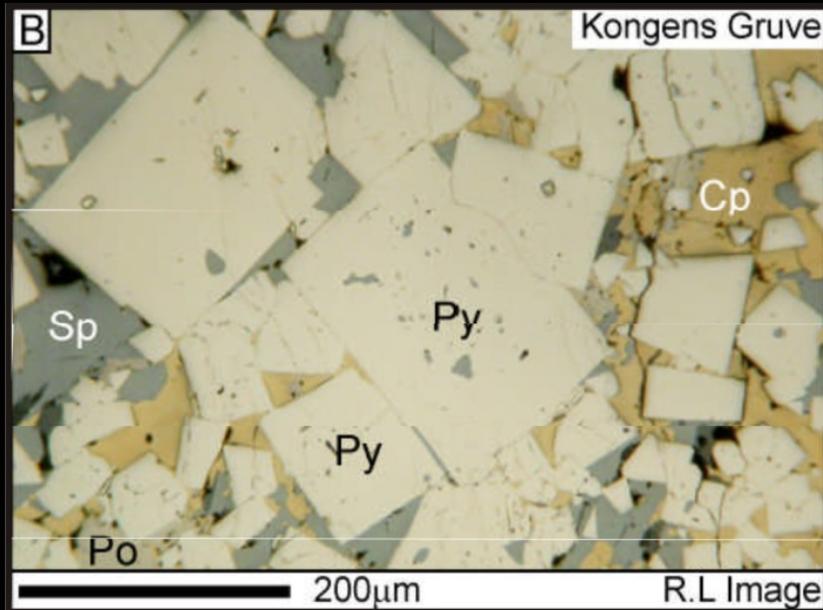
5 μm  
Helios D433

Textures in any sulphide (including pyrite and sphalerite ) are important



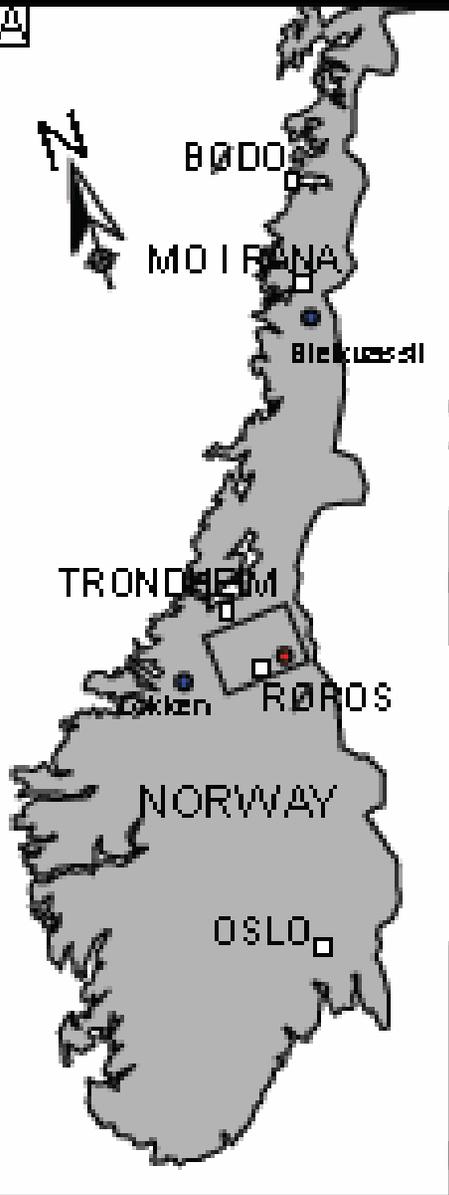
Sulphide chemistry can be placed in the context of a given deposit and its genesis by looking at ore textures.

Focus on inclusions and their spatial distributions and orientations relative to stress/strain. Grain deformation can be assessed by electron back-scattered diffraction (EBSD).



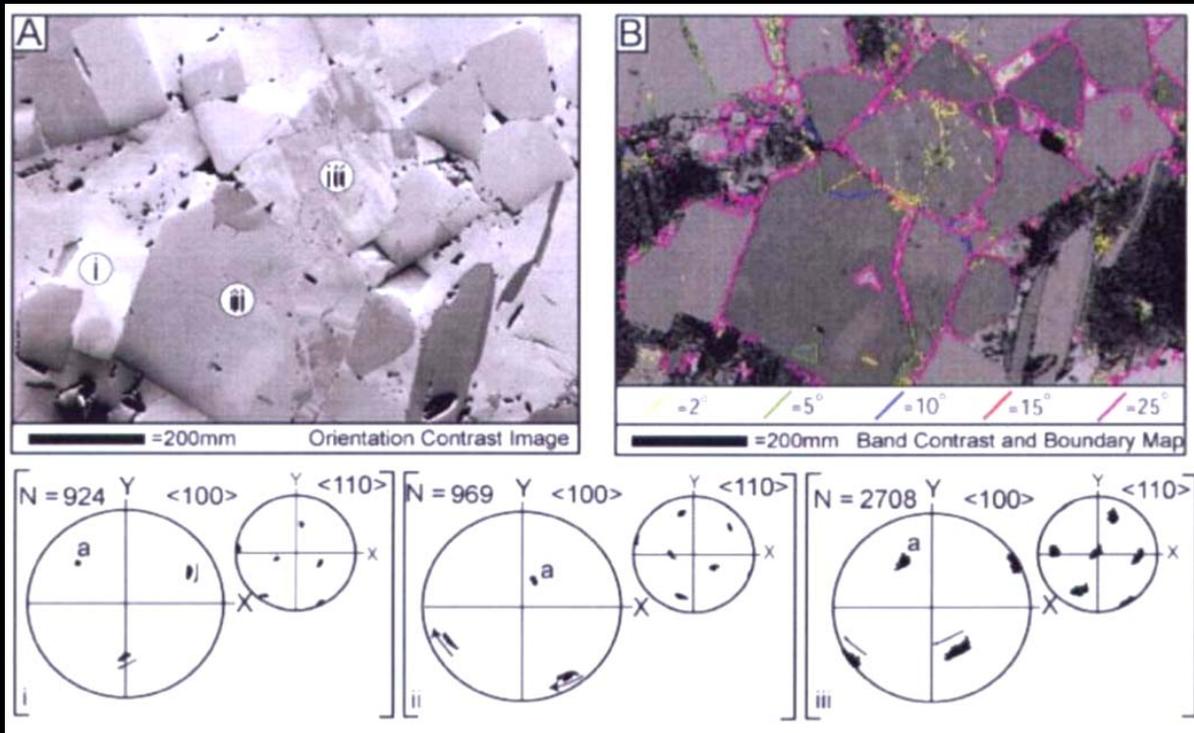
**Electron Back-Scattered Diffraction (EBSD) offers potential to track deformational events in refractory sulphides**

**Combined with element mapping at the micro- and sub-microscale, this can help develop models of grain-scale remobilisation**

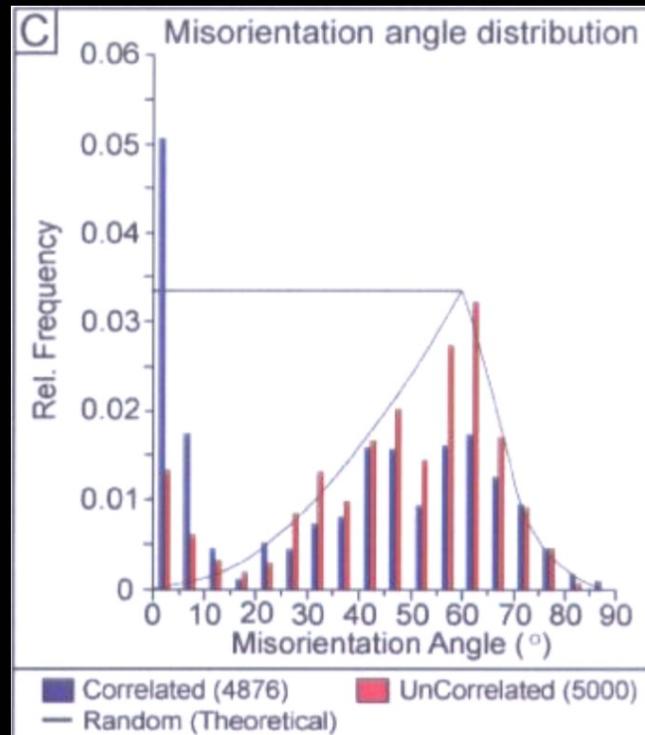


The Røros orefield (Norwegian Caledonides) contains a suite of massive pyritic ore deposits, which preserve different grain-sizes, compositions and textures.

Reflected light observations indicate that foam textures overprinted by brittle fracturing are dominant - suggesting annealing of the ores at peak metamorphic conditions followed by brittle deformation during cooling.



Combined orientation contrast imaging and electron backscatter diffraction (EBSD) analysis indicate that pyrite in all deposits within the district are dominated by plastic deformation, regardless of grain-size or inferred metamorphic grade.



## Applications to bornite ( $\text{Cu}_5\text{FeS}_4$ )?

Bornite (chalcocite, digenite) are major Cu minerald in different deposit types (IOCG - e.g. in SA)

Bornite may host Au, Ag and other elements

Controls an trace element contents poorly understood



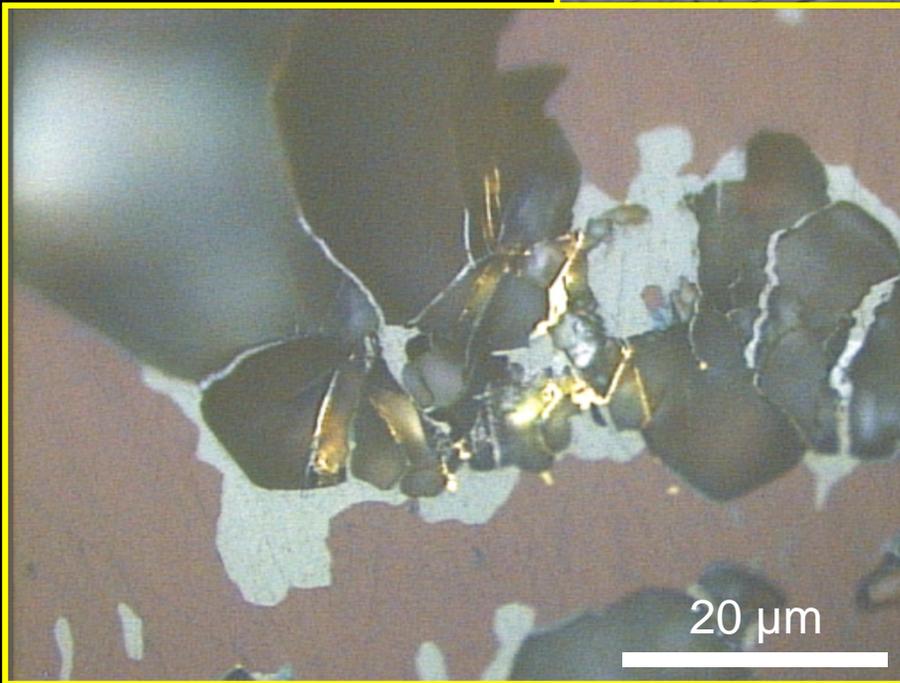
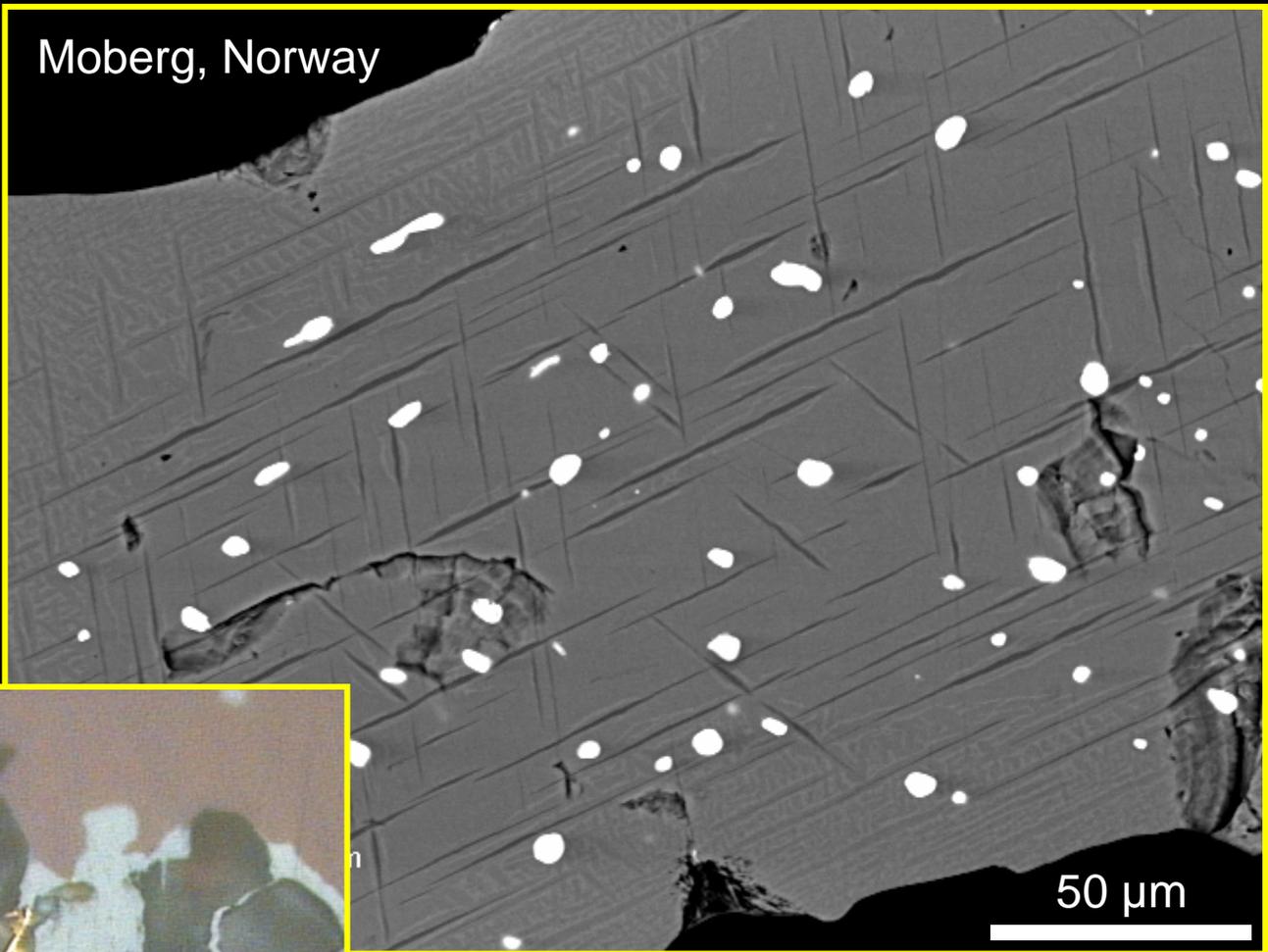
Implications for exploration and ore processing

Prominent Hill, SA

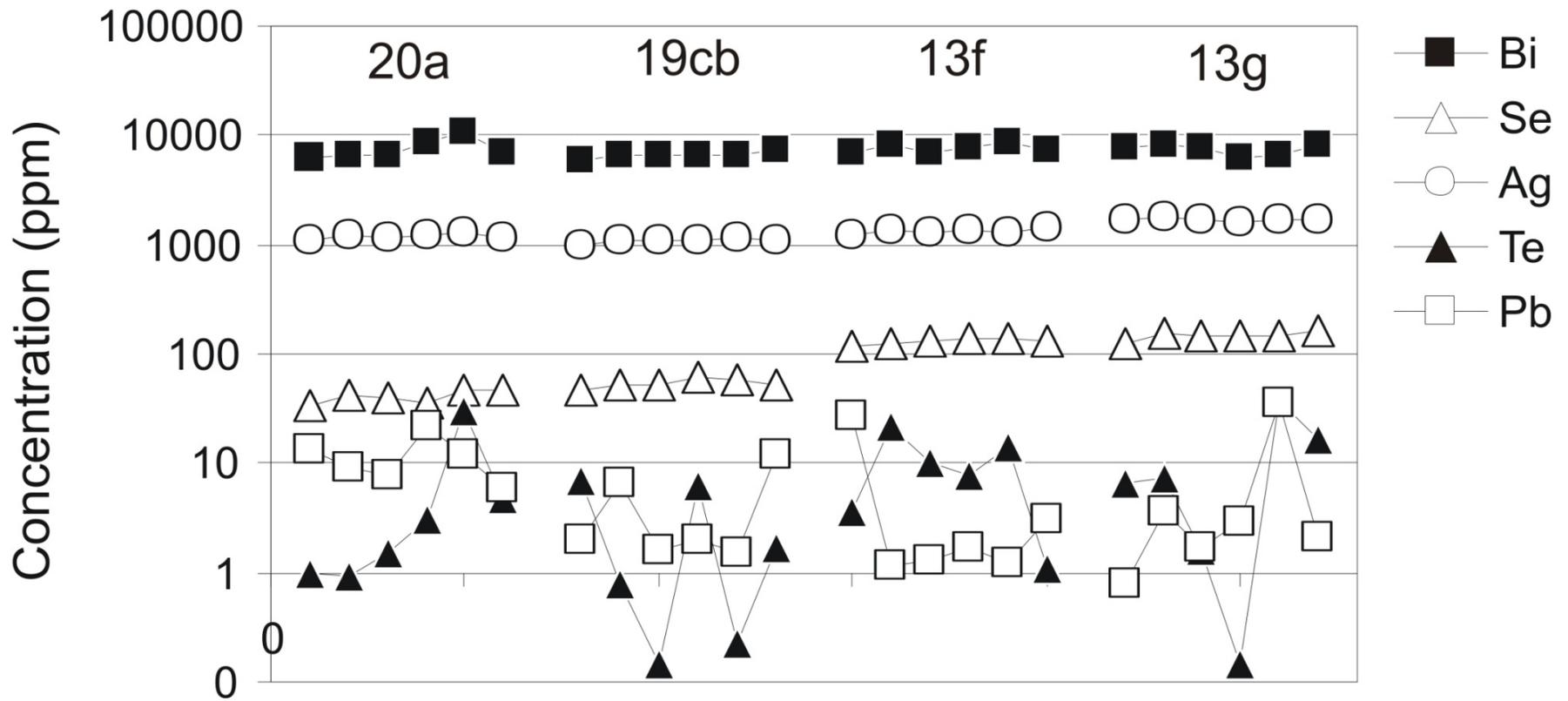
# Complex phase relationships in Cu-Fe-S system.

## Sequence of mineral exsolution in bornite

Moberg, Norway



Exsolution of Au and Ag - why? when? how?



First LA-ICP-MS data for bornite in 4 samples of skarn Cu ore

**Bornite** and other Cu-Fe sulphides in IOCG in SA to be tested for their potential to include precious metals

Why do most examples not retain Au (Ag) ? - controls on, and conditions of exsolution?

Bornite occurs in several superstructures

Can trace element contents be correlated with superstructure type in any way?

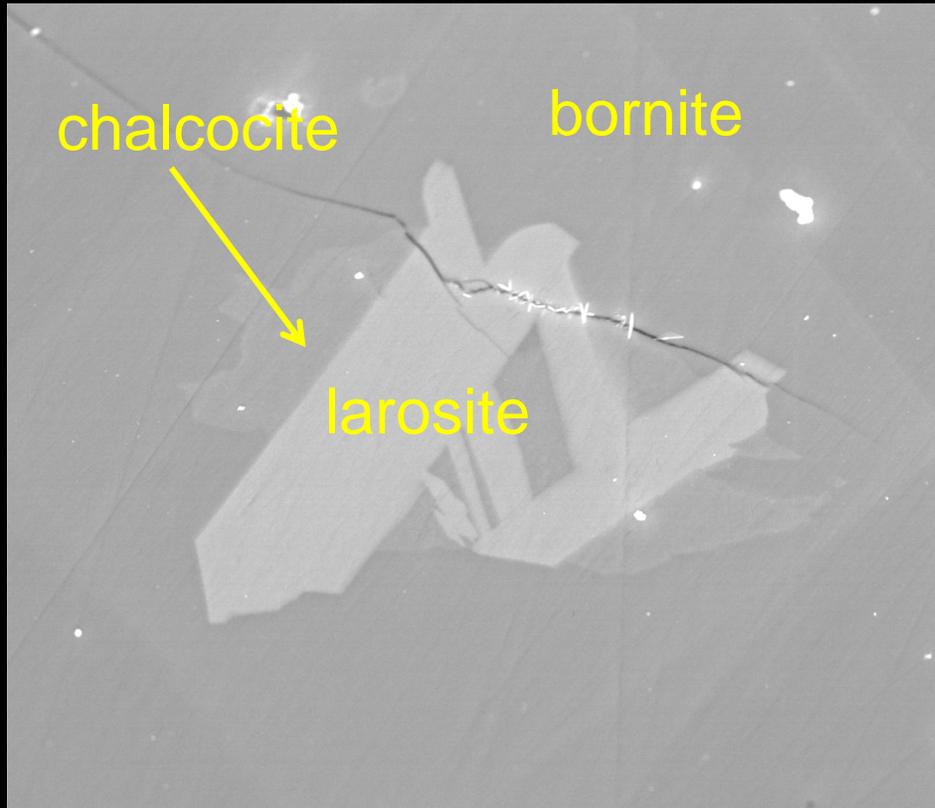
Again, what can be learnt about relationships between trace element contents and remobilisation?

If bornite can efficiently scavenge Au(Ag) from fluids, can superimposed events lead to reconcentration in, e.g. high-grade shearzones and breccia?

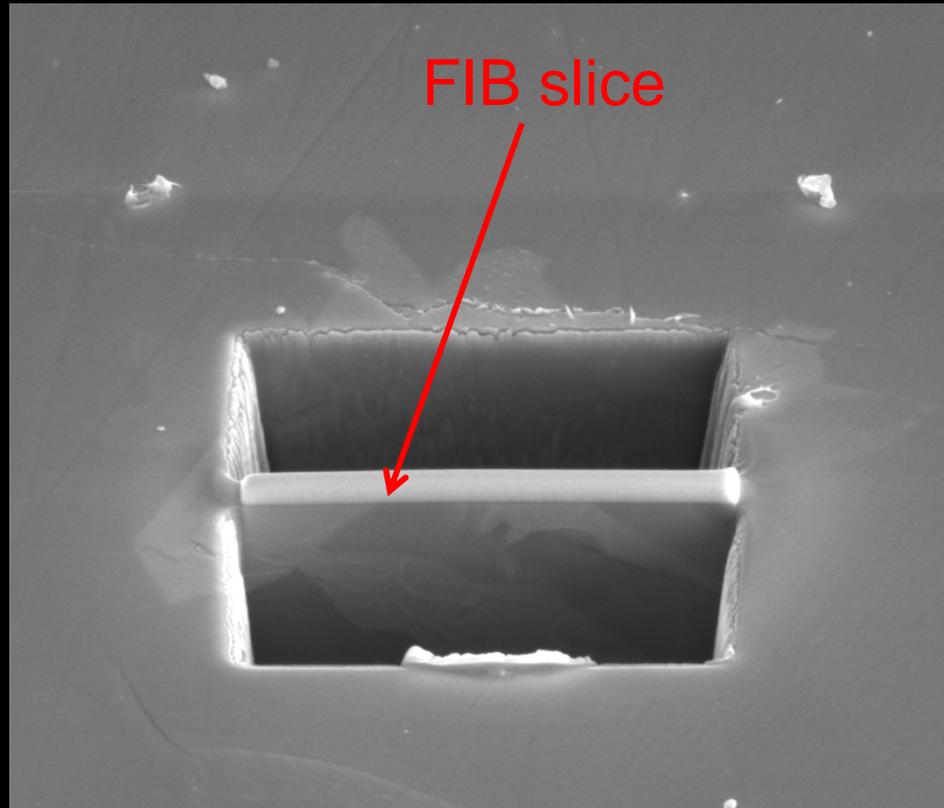
# Study of mineral exsolved within bornite

FIB used to cut a slice

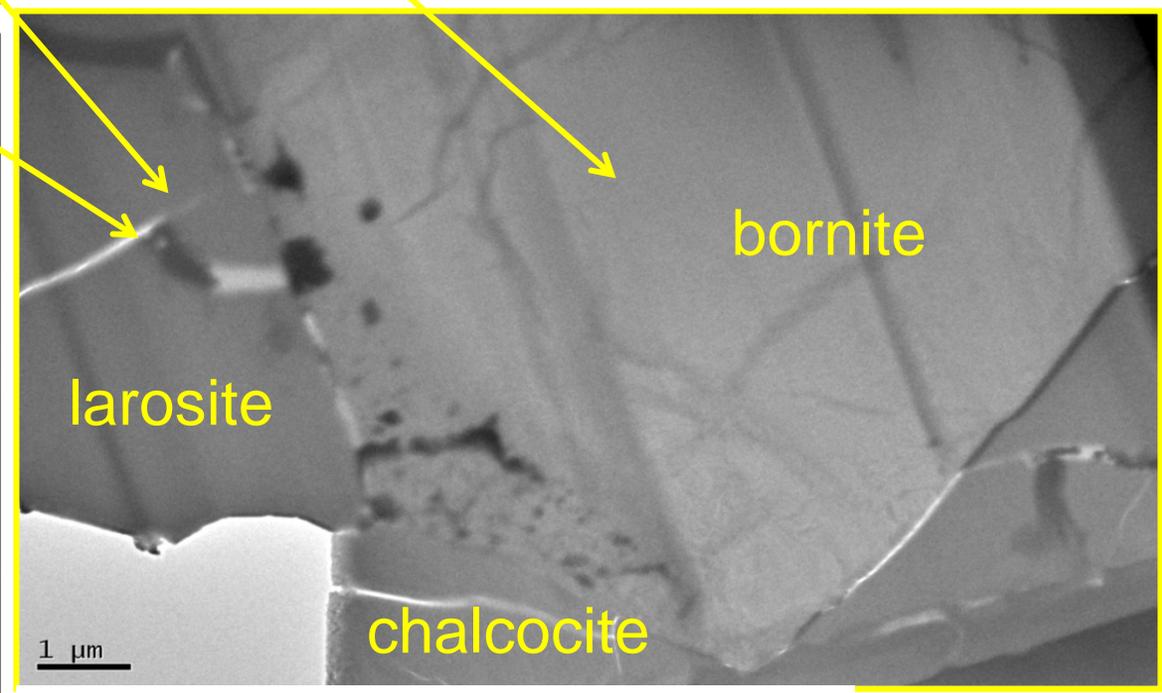
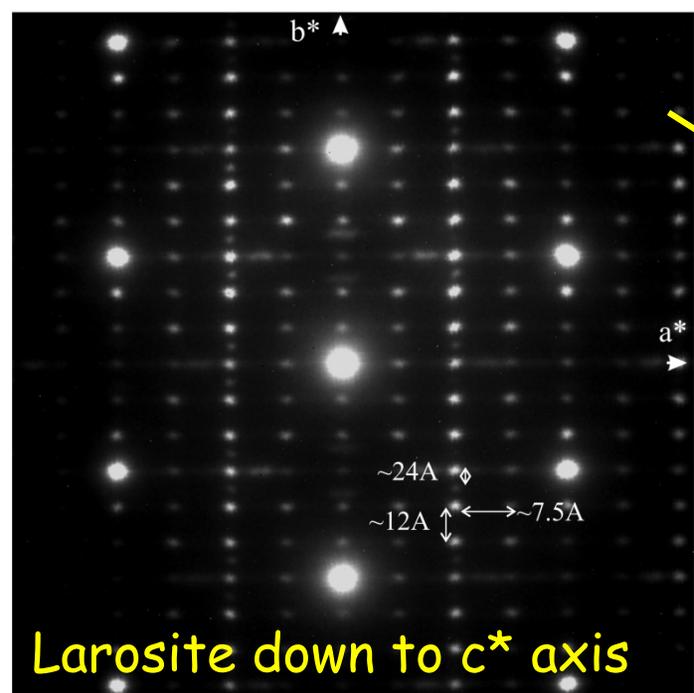
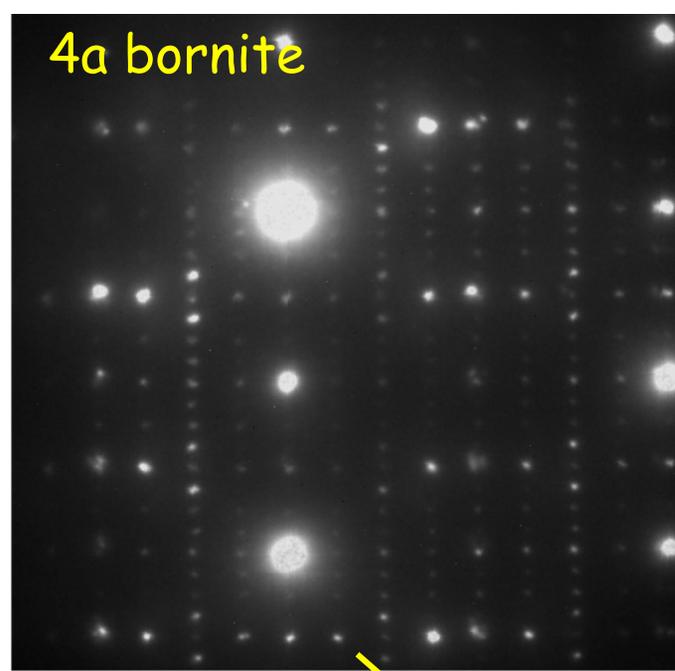
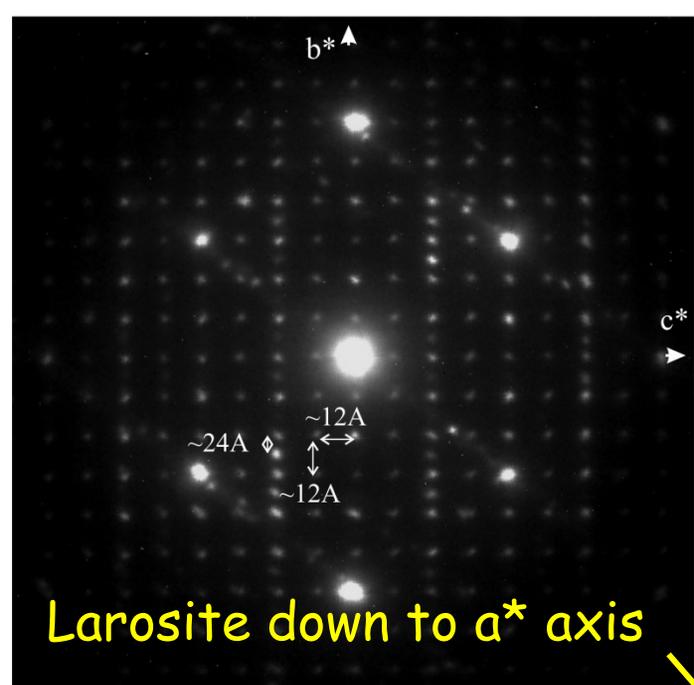
Larosite  $(\text{Cu,Ag})_{21}\text{PbBiS}_{13}$



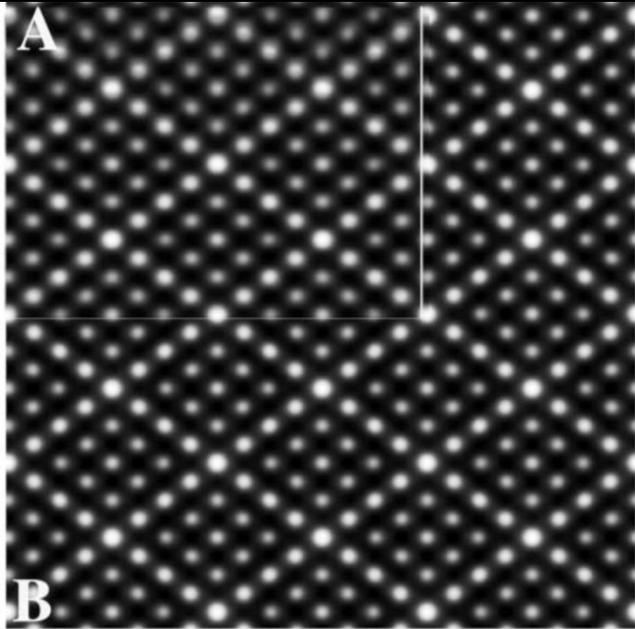
mag	HV	curr	mode	WD	HFW	20 μm	
4 004 x	20.00 kV	0.17 nA	SE	4.4 mm	63.9 μm	Helios D433	



mag	HV	curr	mode	WD	HFW	10 μm	
4 979 x	20.00 kV	1.4 nA	SE	5.0 mm	51.4 μm	Helios D433	

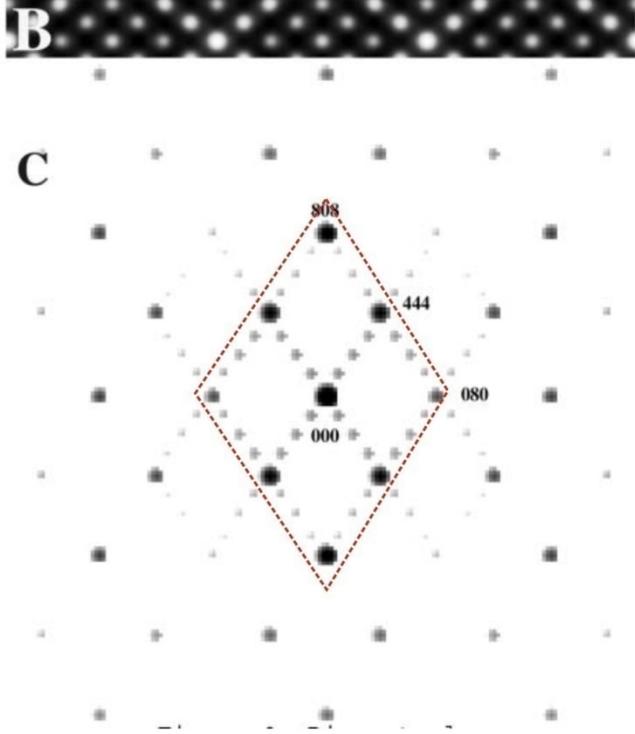


Low-resolution TEM image on FIB foil

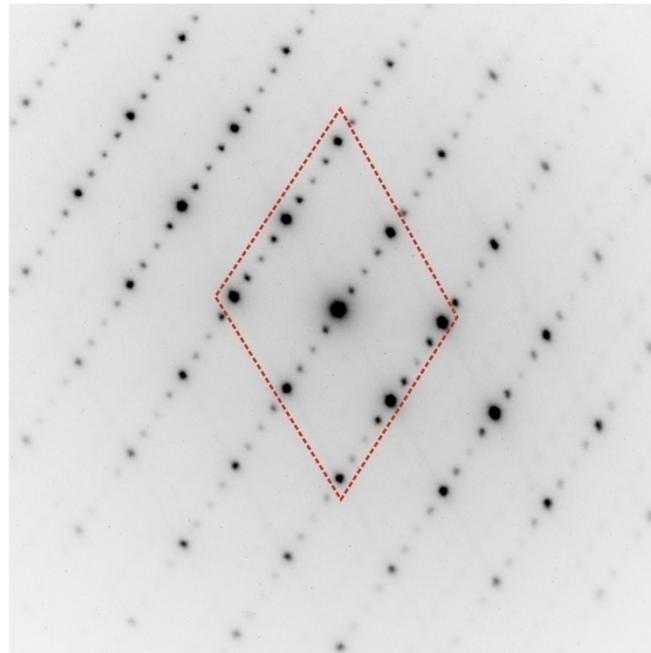


4a bornite down to 10-1 zone

Both larosite and 4a bornite are rare in nature.  
The connection between the superstructure of bornite and the exsolved mineral is probably not coincidental.



Case study:



Simulation from Ding (2005)

## Applications to molybdenite ( $\text{MoS}_2$ )?

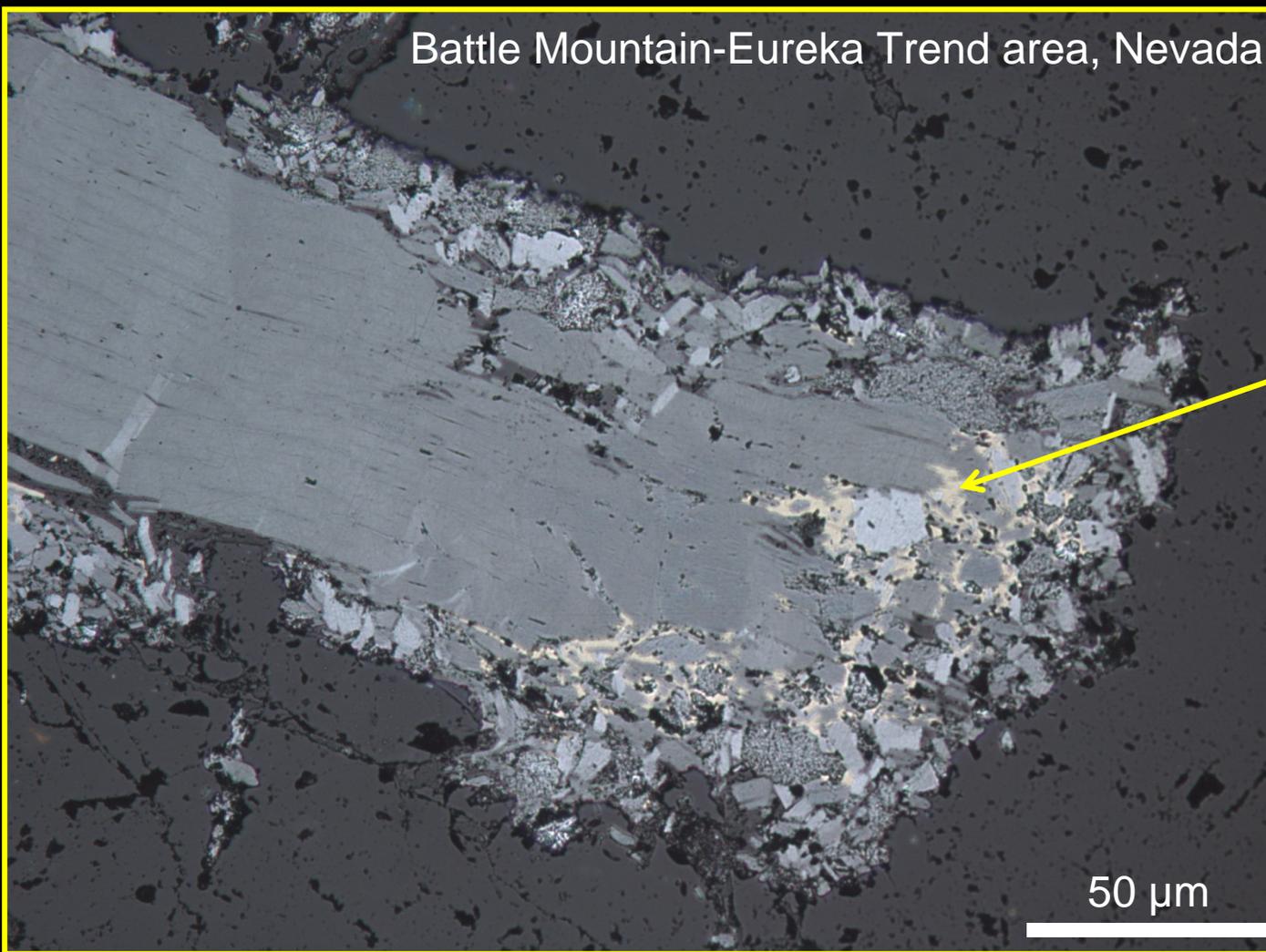
Abundant accessory mineral and principal ore mineral in Mo (porphyry)

Magmatic association, possible new resources present around IOCG systems



Two polytypes (2H and 3R)

Battle Mountain-Eureka Trend area, Nevada



3R molybdenite characteristically 'dirty' - structure offers ready traps for small particles, inclusions  
3R typically enriched in a range of trace elements (U, Bi, Te, Au, W, Re)

## Rhenium:

77<sup>th</sup> least abundant element on Earth

Crustal abundance: 0.04 ppb

Price: US\$11,303 per kg (mid-2008), now US\$ 5,600

Annual world production ~ 45 tonnes

Rhenium used in nickel based alloys used in turbine blades for gas turbine engines (aircraft).

What are the controls on occurrence of the two molybdenite polytypes?

What is the significance of co-existing molybdenite polytypes?

Behaviour of the trace components during remobilisation and reconcentration in veins and breccias



THANK YOU