XAS investigation of 'invisible' gold impurities in synthetic sulfide minerals

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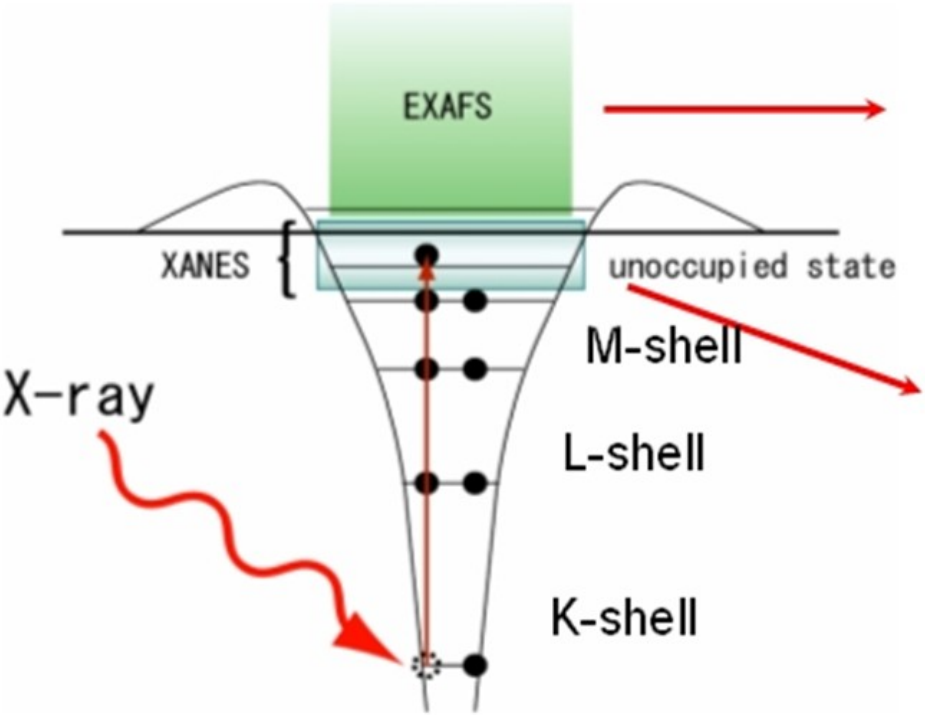
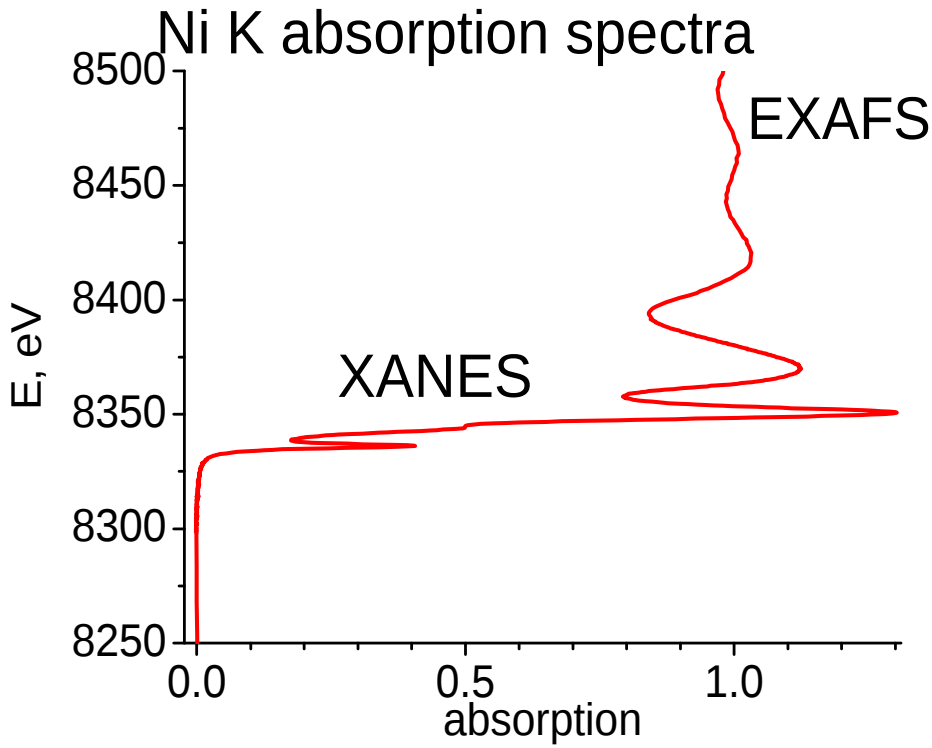
X-ray absorption spectroscopy (EXAFS и XANES)

- EXAFS – oscillations in energy region 50-1000 eV above edge X-ray absorption edge, which originate from photoelectron scattering on surrounding atoms.
- XANES – near edge structure of X-ray absorption spectra, corresponds to transitions from core state to empty states near Fermi level.

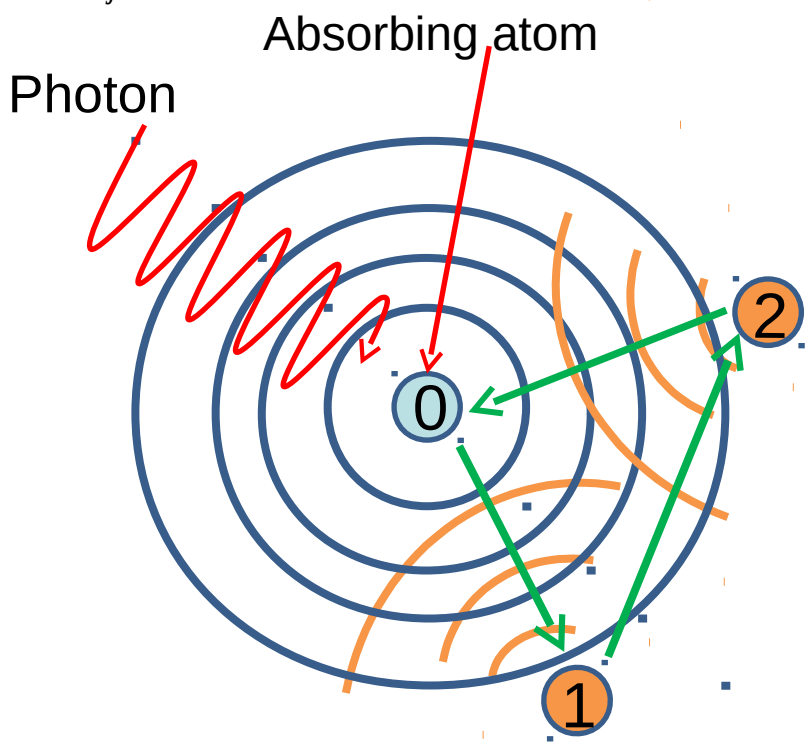




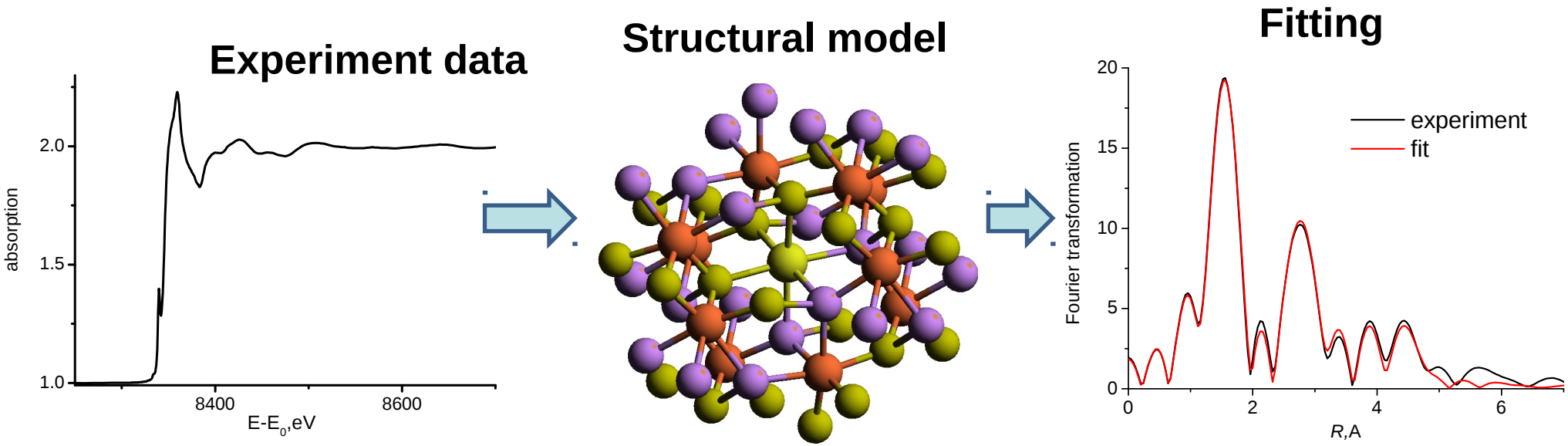
EXAFS spectra in a plane wave approximation

In a plane wave and single scattering approximations oscillation part of EXAFS spectar can be calculated be formula:

$$\chi(k) = -\frac{1}{k}\sum_j \frac{N_j S_0^2 |f_j(k,\pi)|}{R_j^2} \sin(2kR_j + \phi_j(k)) \exp(-2\sigma_j^2 k^2 - 2R_j \lambda(k))$$



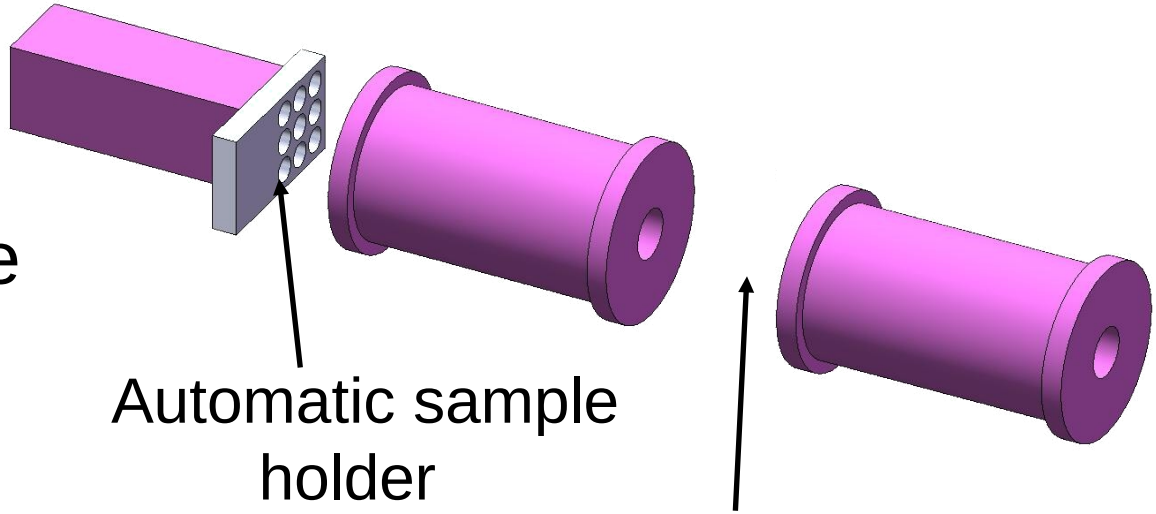
Quantitative analysis of EXAFS



Quantitative analysis of EXAFS spectra consist in choosing a proper structural model and fitting calculated spectra to experimental data. As a result one obtain geometrical parameters, coordination numbers and mean square displacement of atoms from equilibrium positions.

XAFS experiment in transition and fluorescence modes

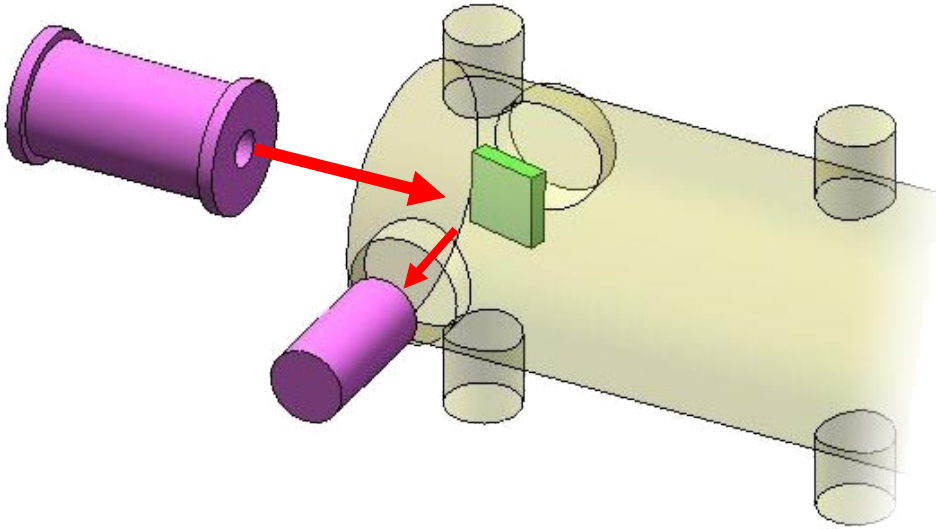
Transition mode



Automatic sample holder

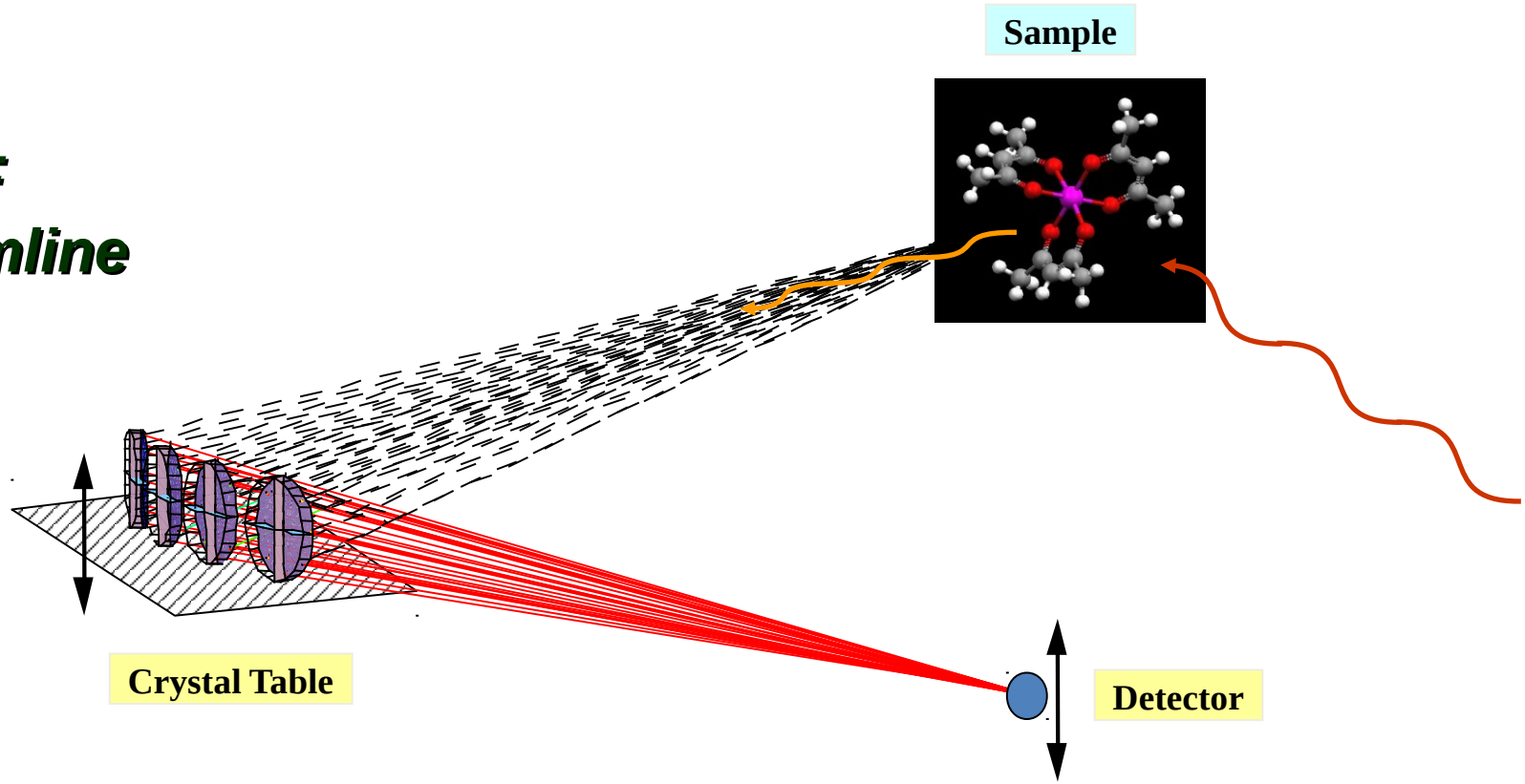
Place for reference sample

Fluorescence mode



High Energy Resolution Fluorescence Detection (HERFD)

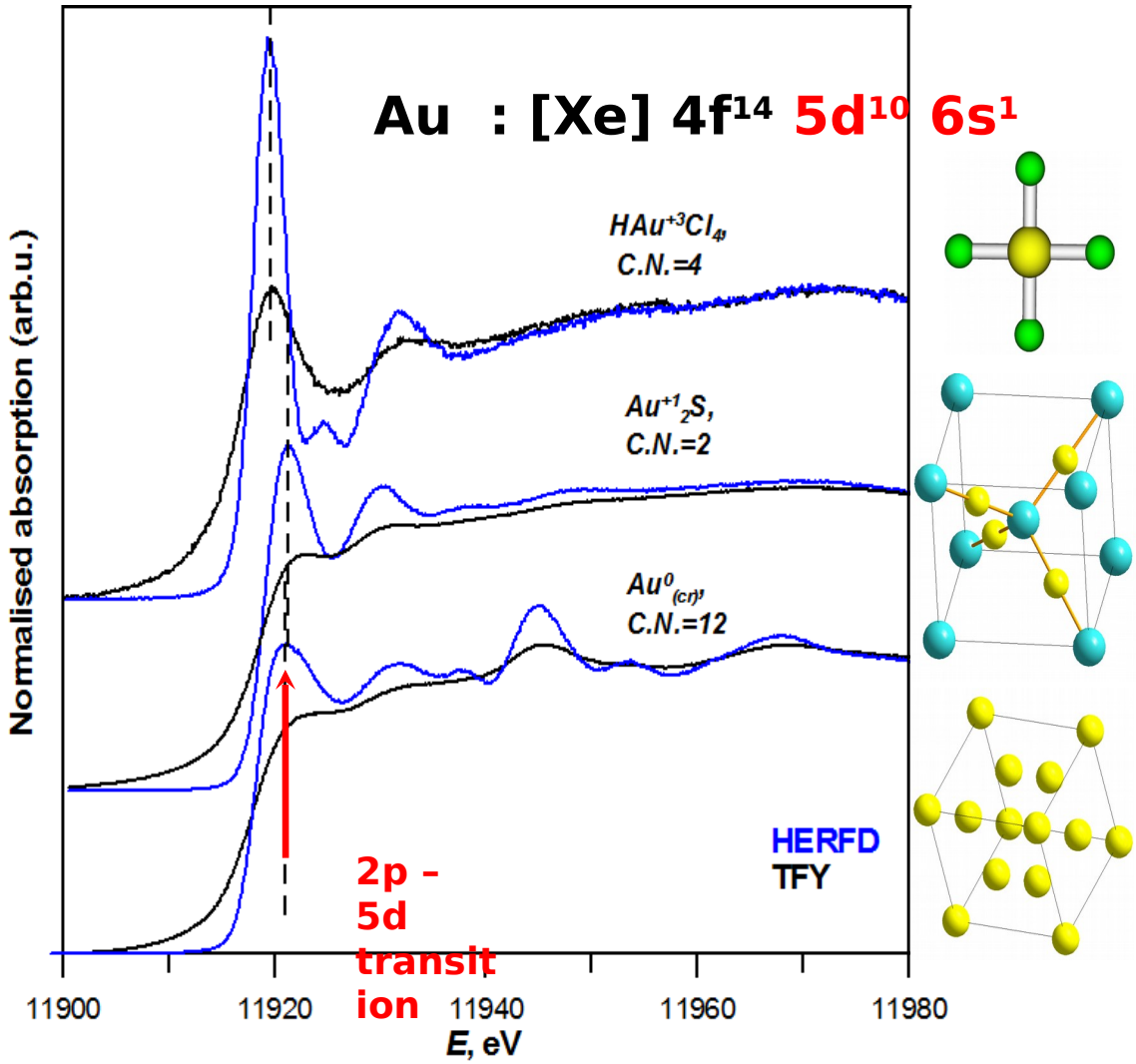
ESRF
ID26 beamline



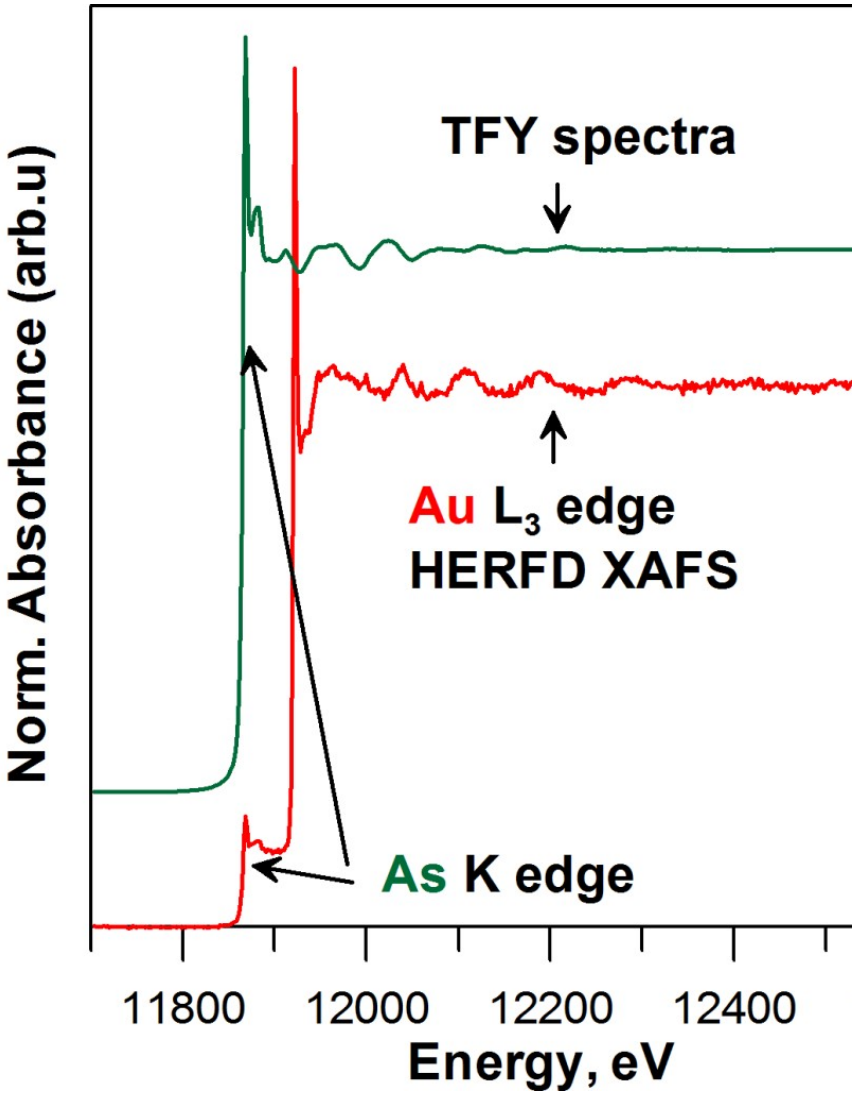
Improve energy resolution by a factor > 200 !

Au L_3 edge HERFD XANES vs. TFY XANES spectra

Au^{+3} vs. Au^{+1} vs. Au^{0}

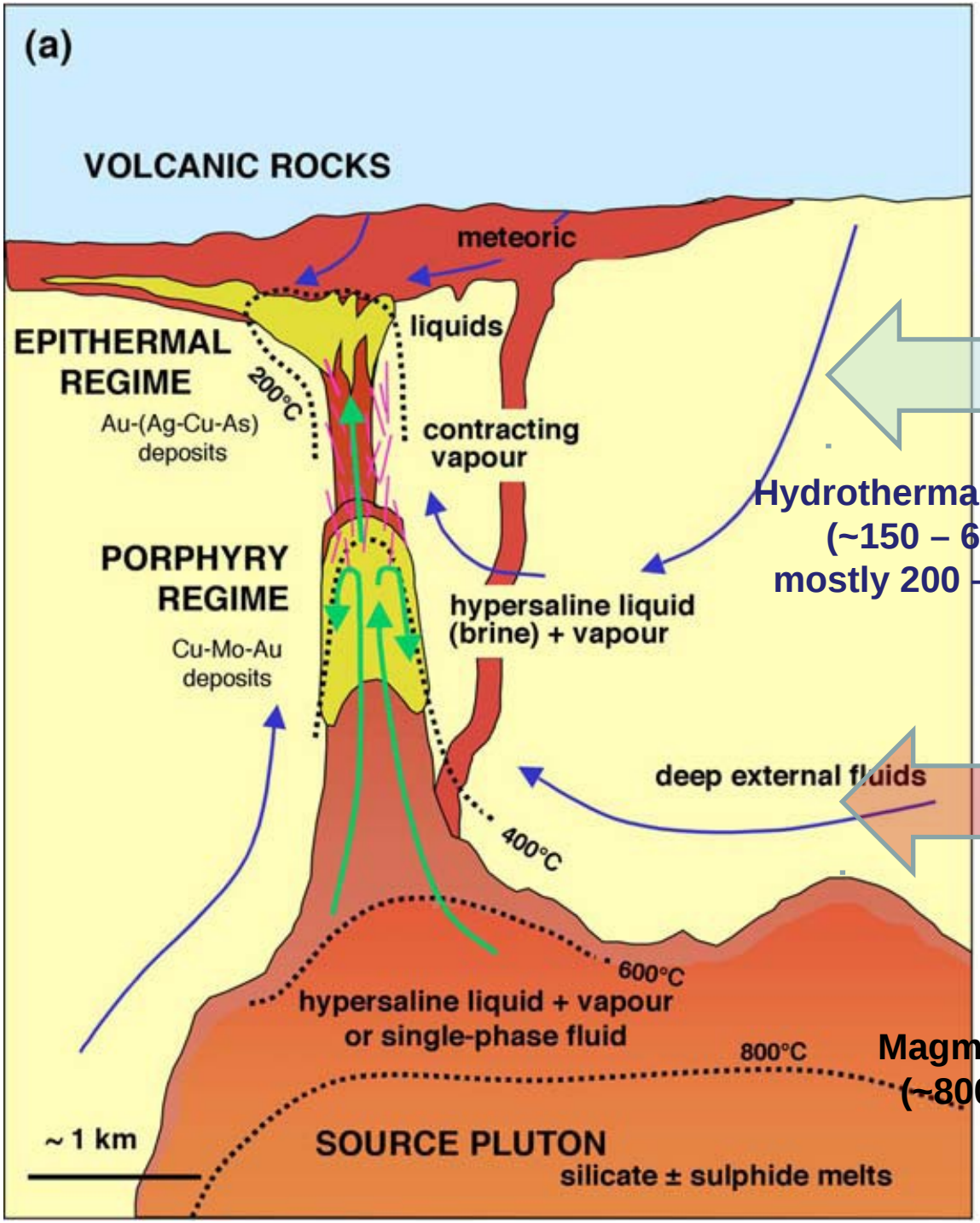


Au L_3 edge HERFD XAFS spectra of Löllingite $FeAs_2$ + 50 ppm Au

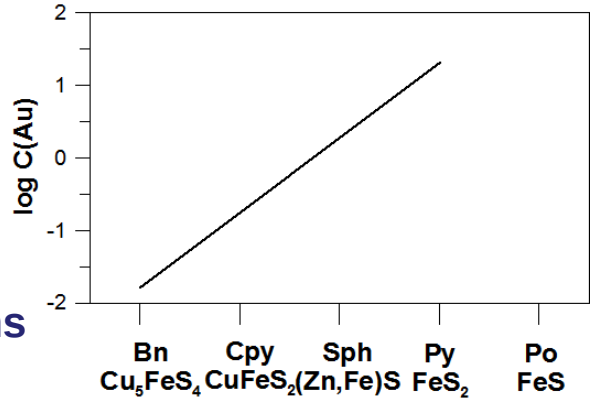


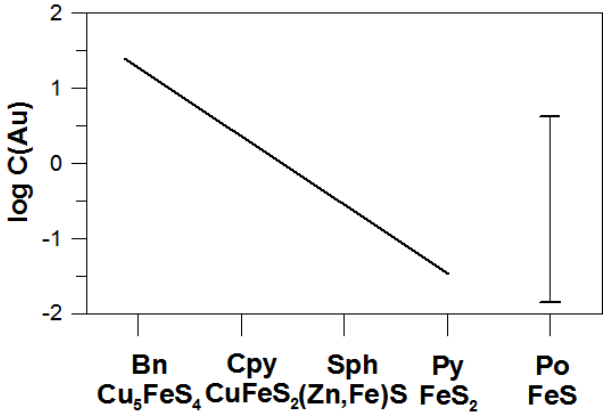
Schematic cross section of magmatic hydrothermal system

(adapted from Heinrich, Mineralium Deposita (2005) 39: 864–889)



Hydrothermal systems (~150 – 600 °C, mostly 200 – 350 °C)





Magmatic deposits (~800 to 1500 °C)

Synthesis methods

Hydrothermal method
(autoclaves, t = 450°C, P=1 kbar):
Pyrite FeS_2
Covellite CuS

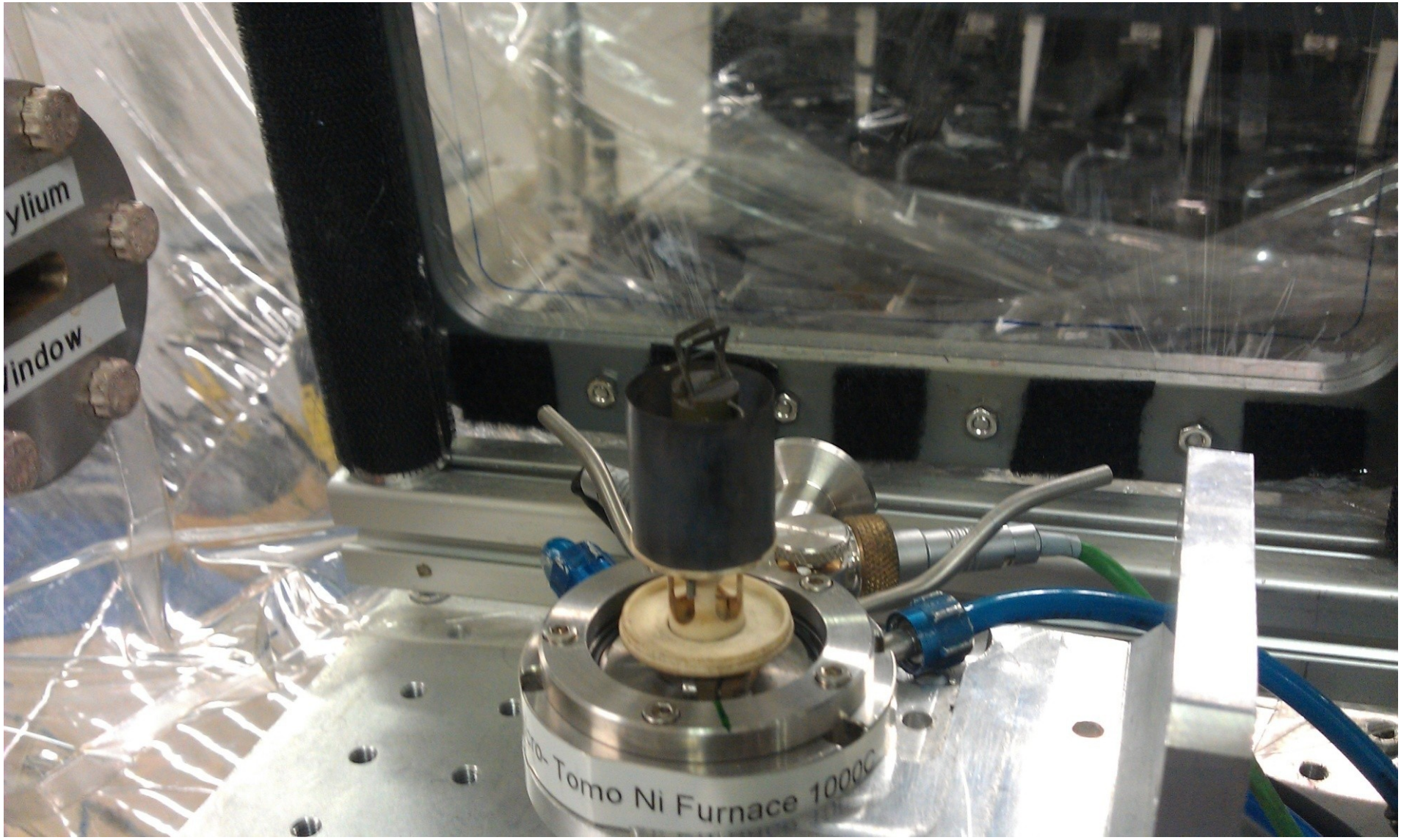
Salt flux method
(silica glass tubes,
t = 350 – 700 °C):

$AlCl_3$/KCl/NaCl,
CsCl/NaCl/KCl,

Arsenopyrite FeAsS
Löllingite $FeAs_2$
Covellite CuS

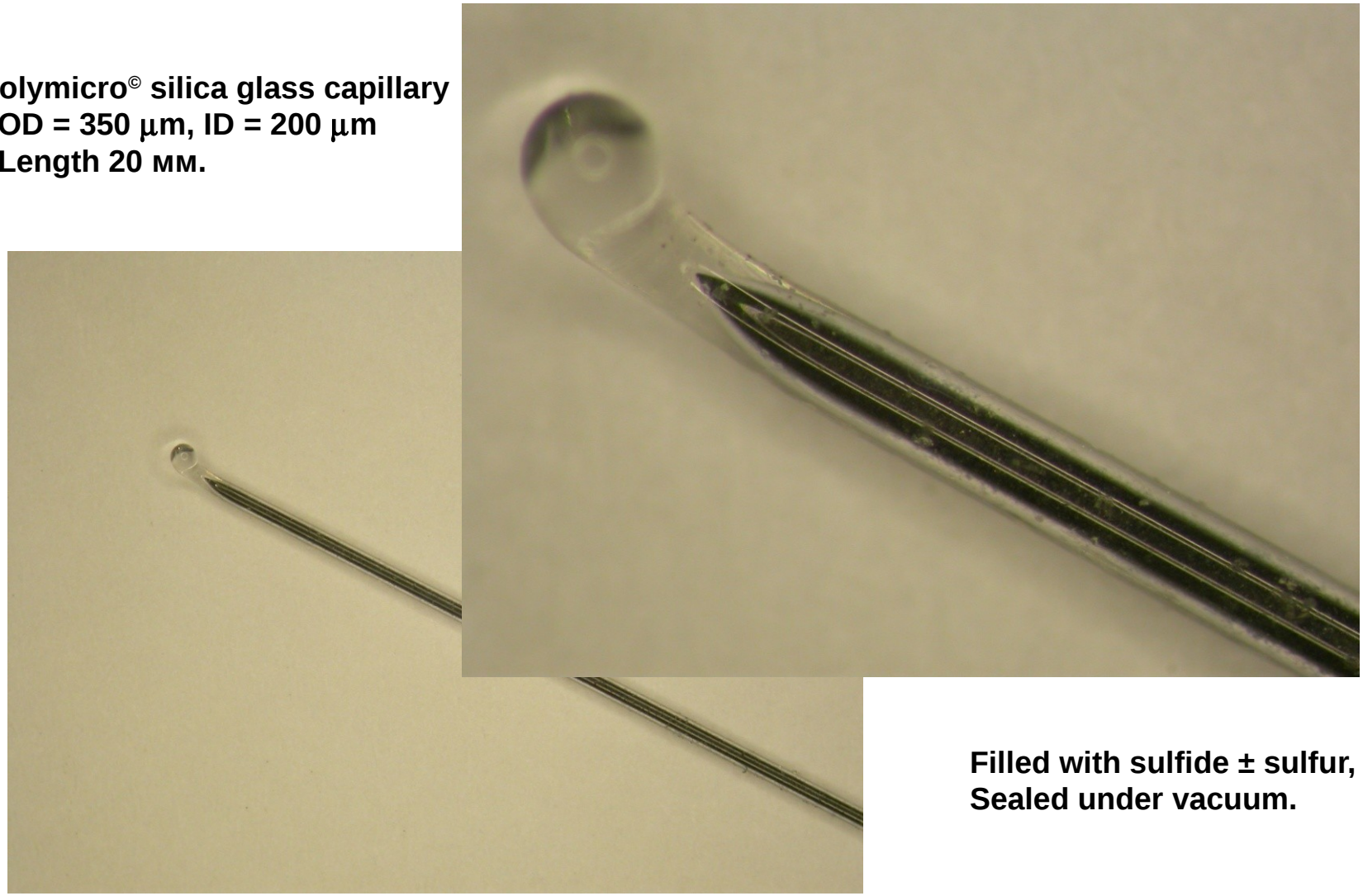
Salt flux =
transport medium

Furnace with capillaries



Heating experiment: *capillary*

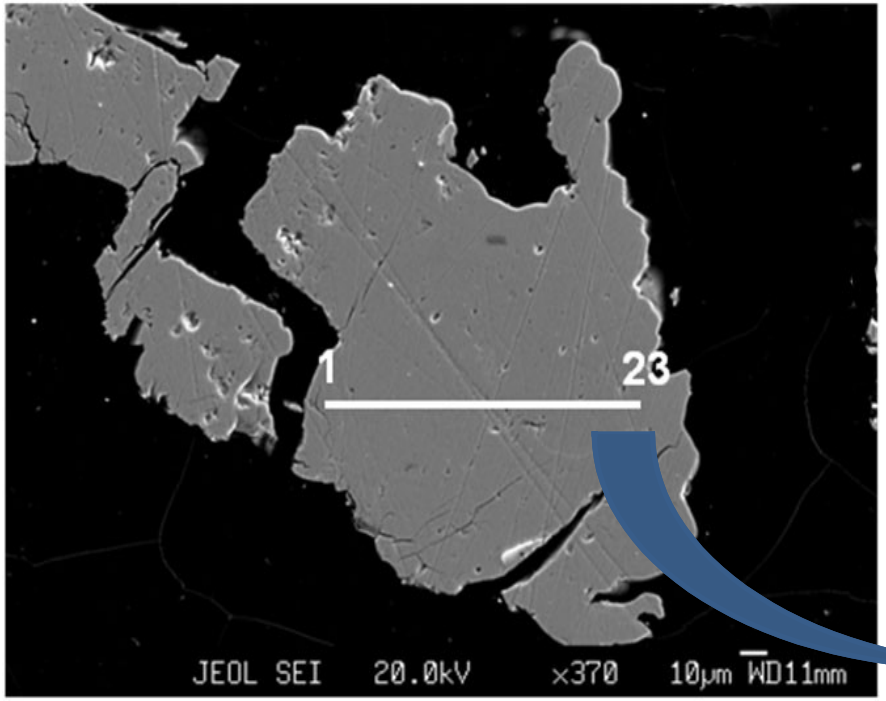
Polymicro© silica glass capillary
- OD = 350 μm, ID = 200 μm
- Length 20 мм.

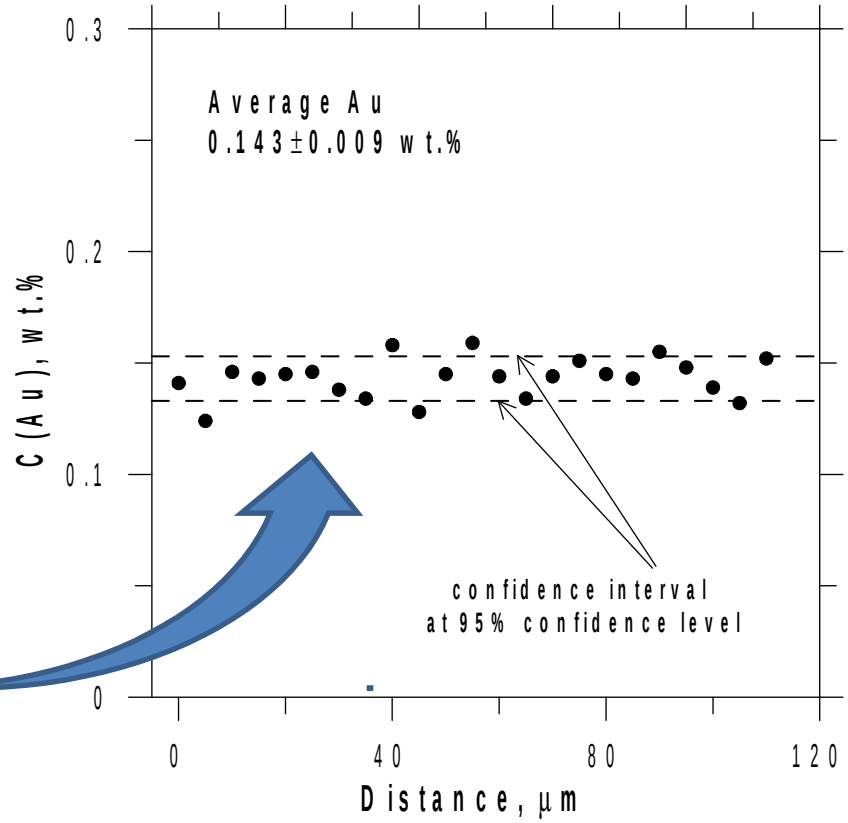


Filled with sulfide ± sulfur,
Sealed under vacuum.

- Chou I-M., Song Y. and Burruss R. C. A new method for synthesizing fluid inclusions in fused silica capillaries containing organic and inorganic material. Geochimica et Cosmochimica Acta, 2008, 72, 5217-5231.
- EMU notes in Mineralogy, V. 12, Eds. J. Dubessy, M.-C. Caumon and F. Rull, 2012.

Au in COVELLITE CuS

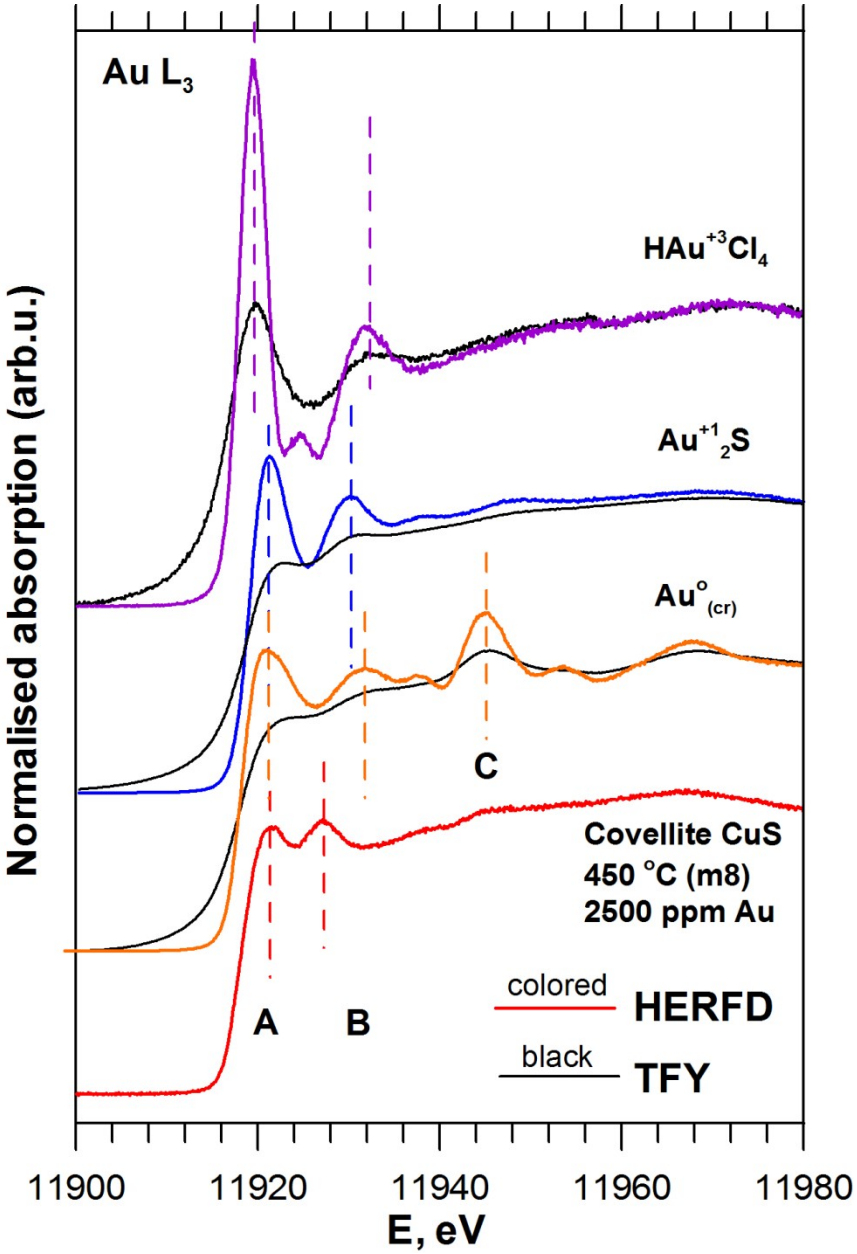


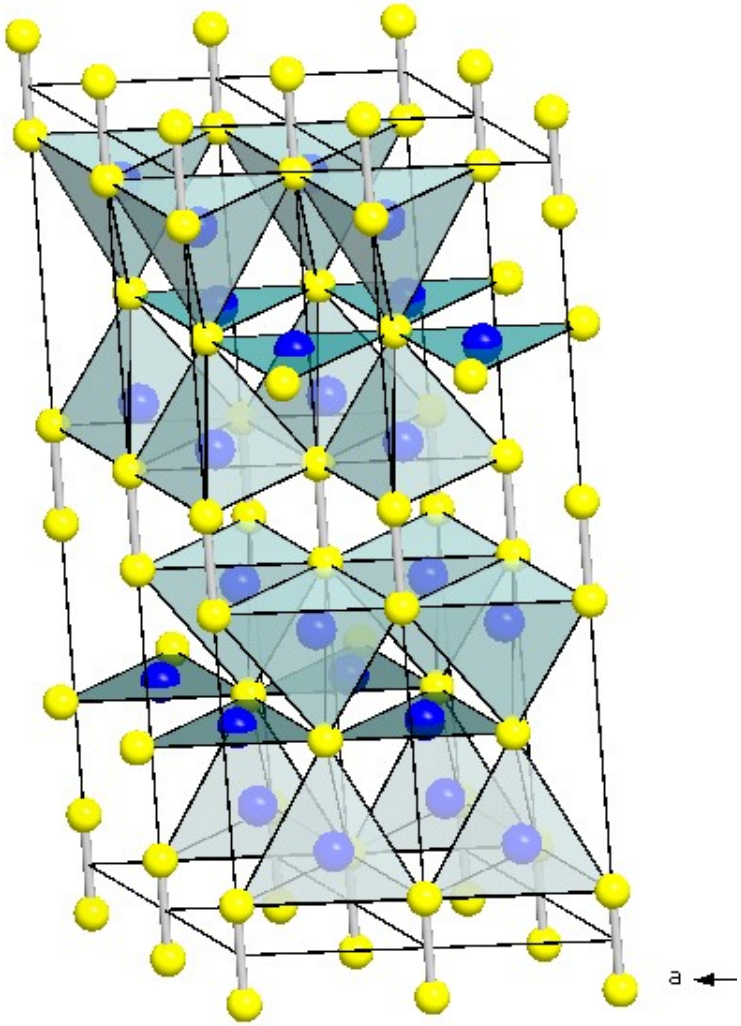


Concentration profile of Au in covellite determined with EPMA,

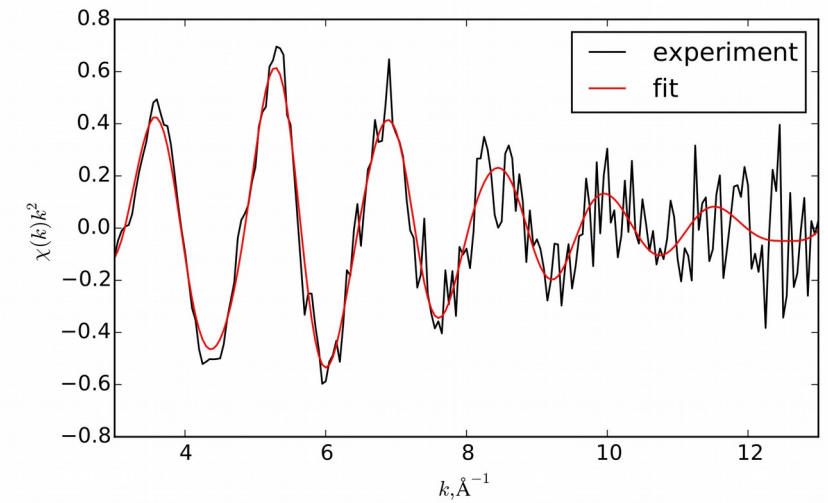
No crystalline Au!

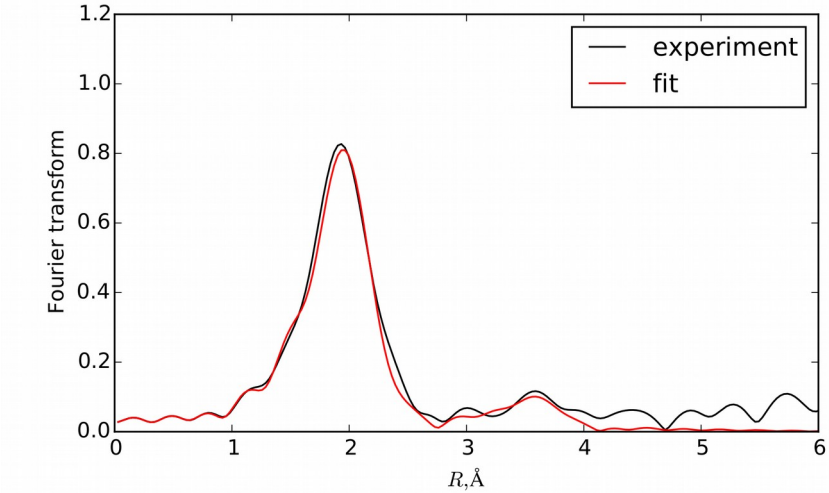
HERFD XAS experimental data





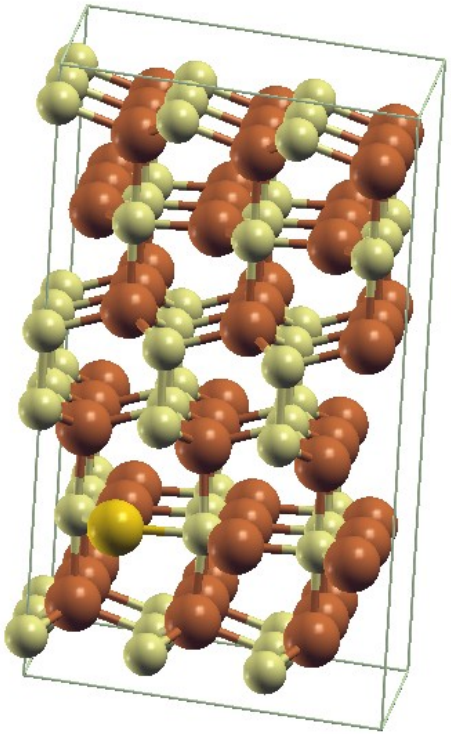
EXAFS analysis

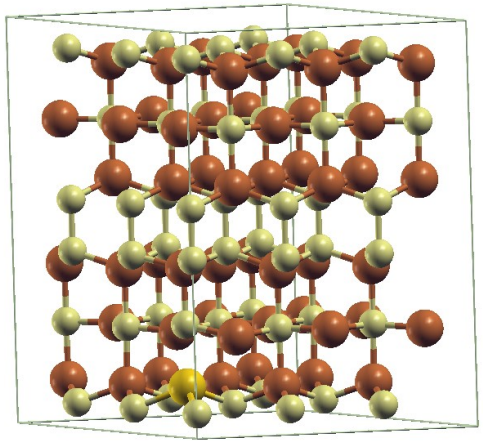




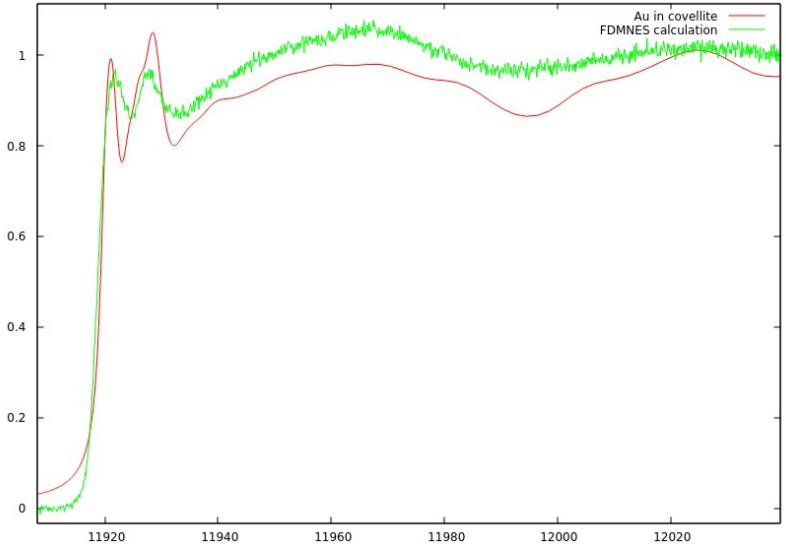
	EXAFS	QE
R,Å	2.38	2.34
N	3	3
R,Å	3.24	3.22
N	6	6
R,Å	3.92	3.84
N	6	6

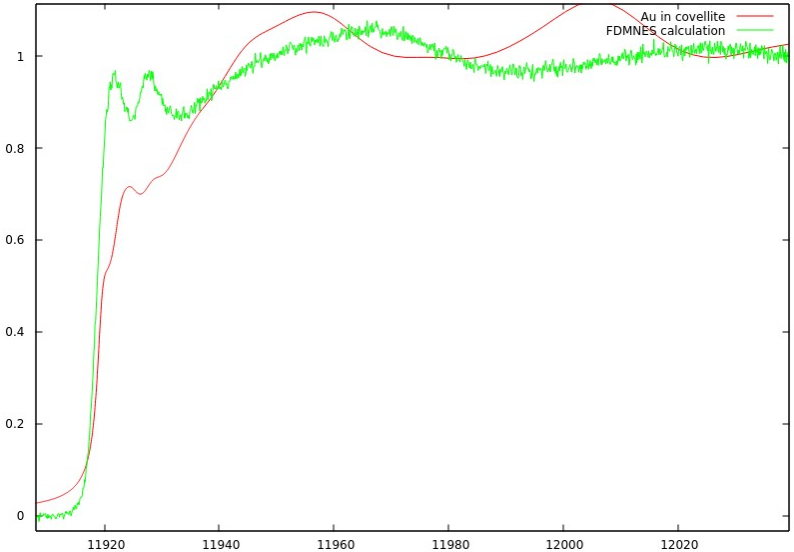
Models optimized be QE DFT code



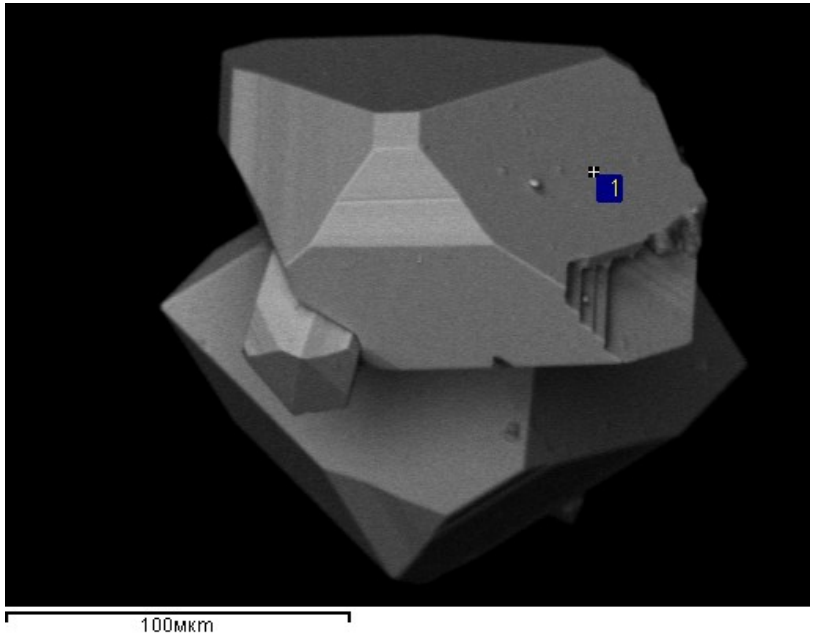


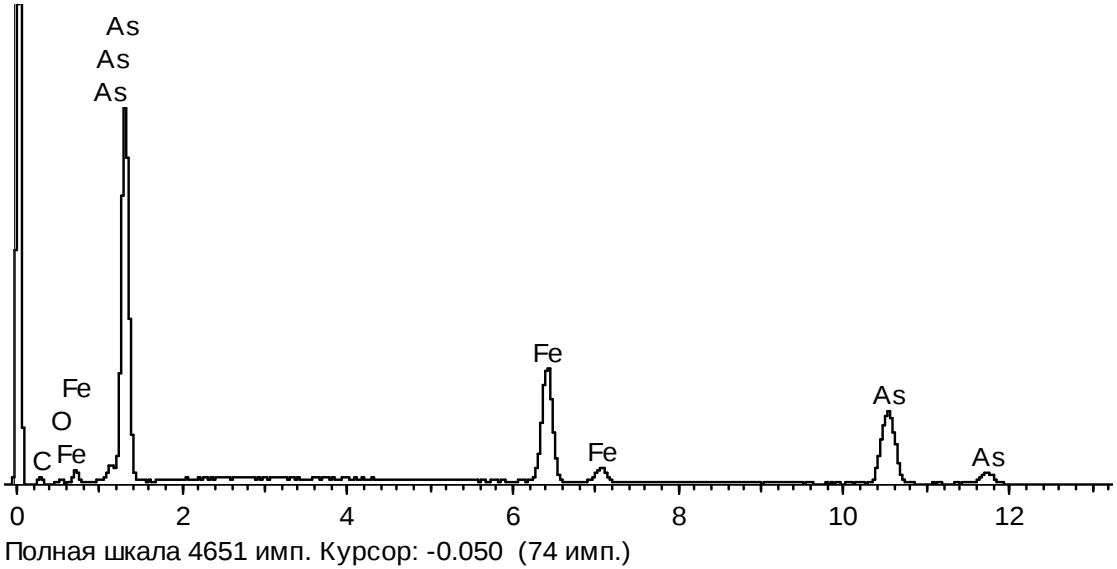
FDMNES calculation





Au in Lollingite $FeAs_2$



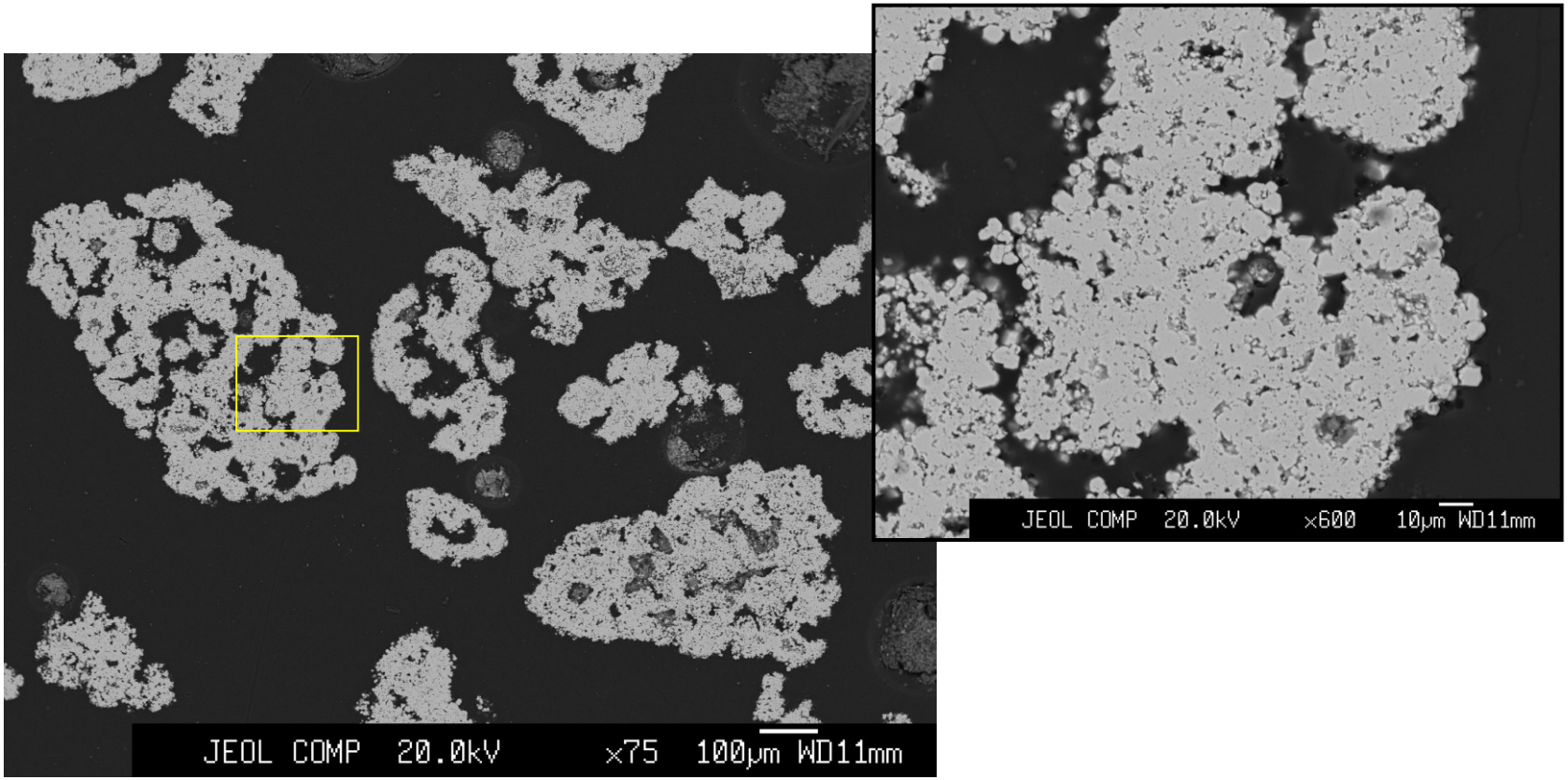


Crystalline structure ;

•Concentration of ‘invisible’ Au is 50 ppm;

• No crystalline Au!

Au in PYRITE FeS_2



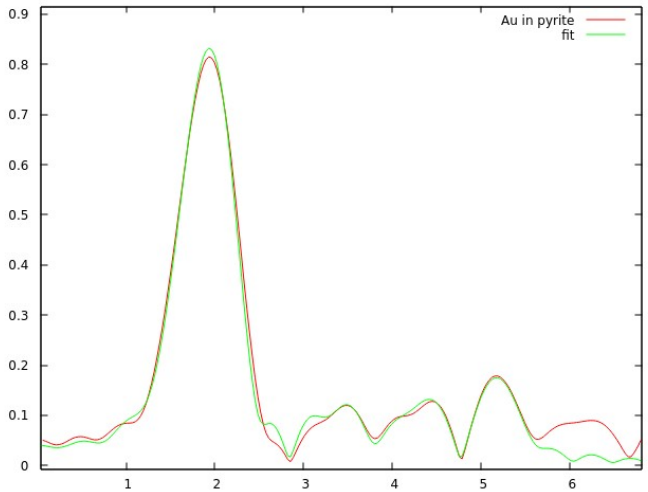
Fine-grained aggregates ;

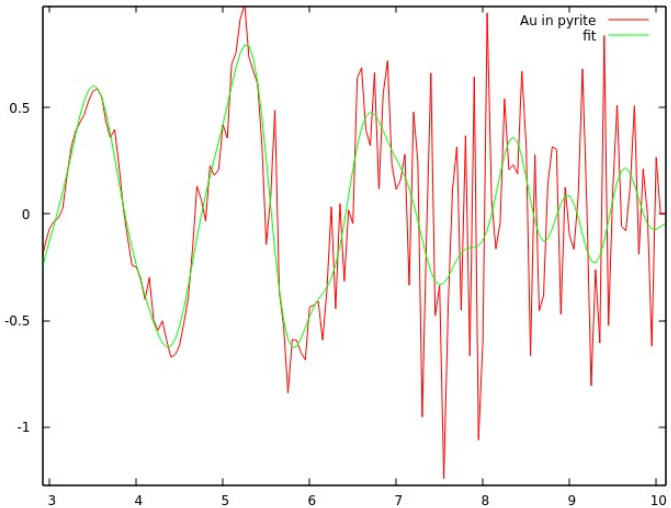
•Concentration of ‘invisible’ Au is 40 ppm;

• No crystalline Au!

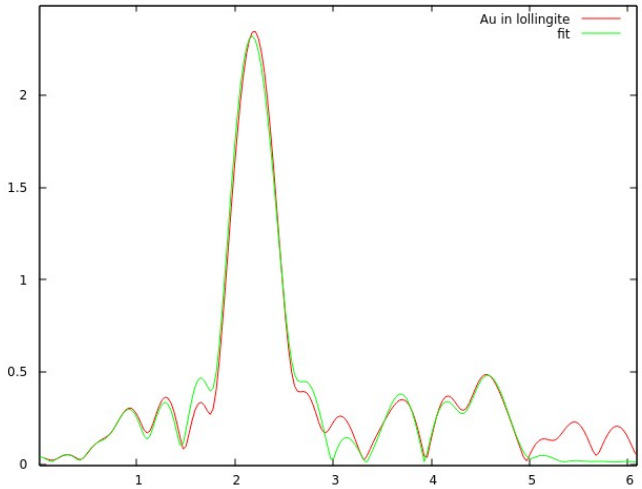
EXAFS analysis points that Au atoms are placed in positions of Fe atoms: isomorphic substitution

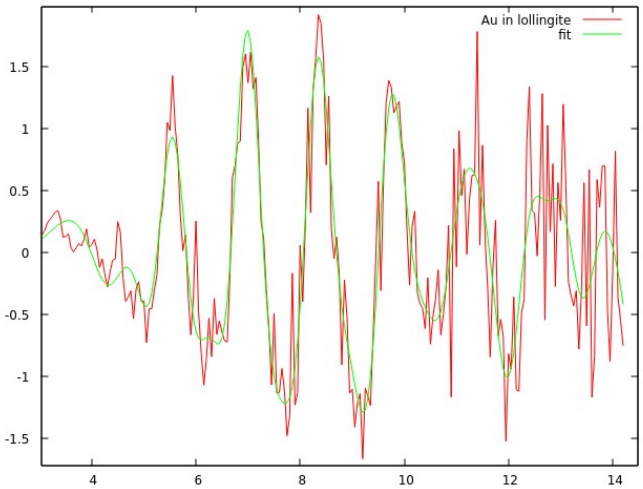
Pyrite



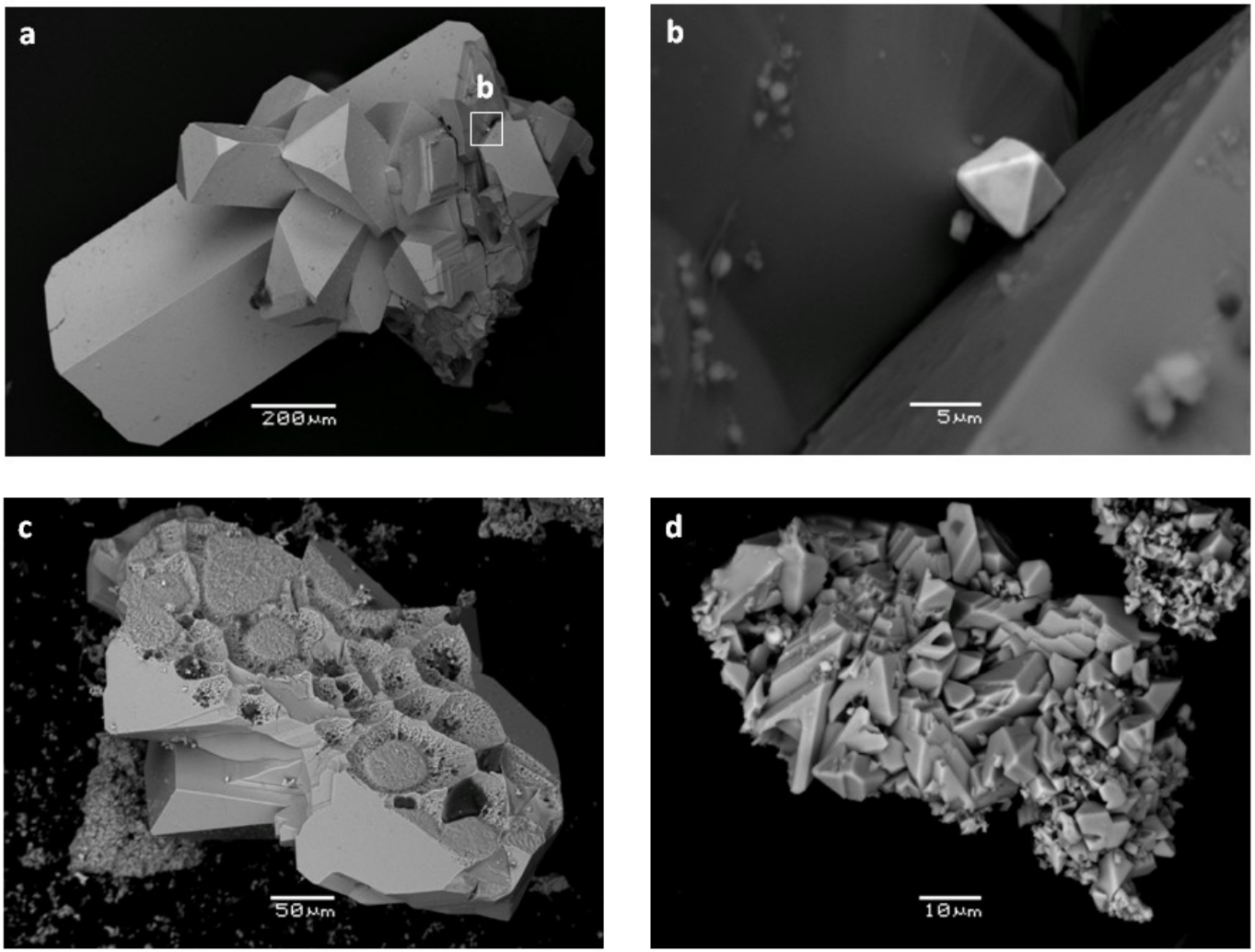


Lollingite





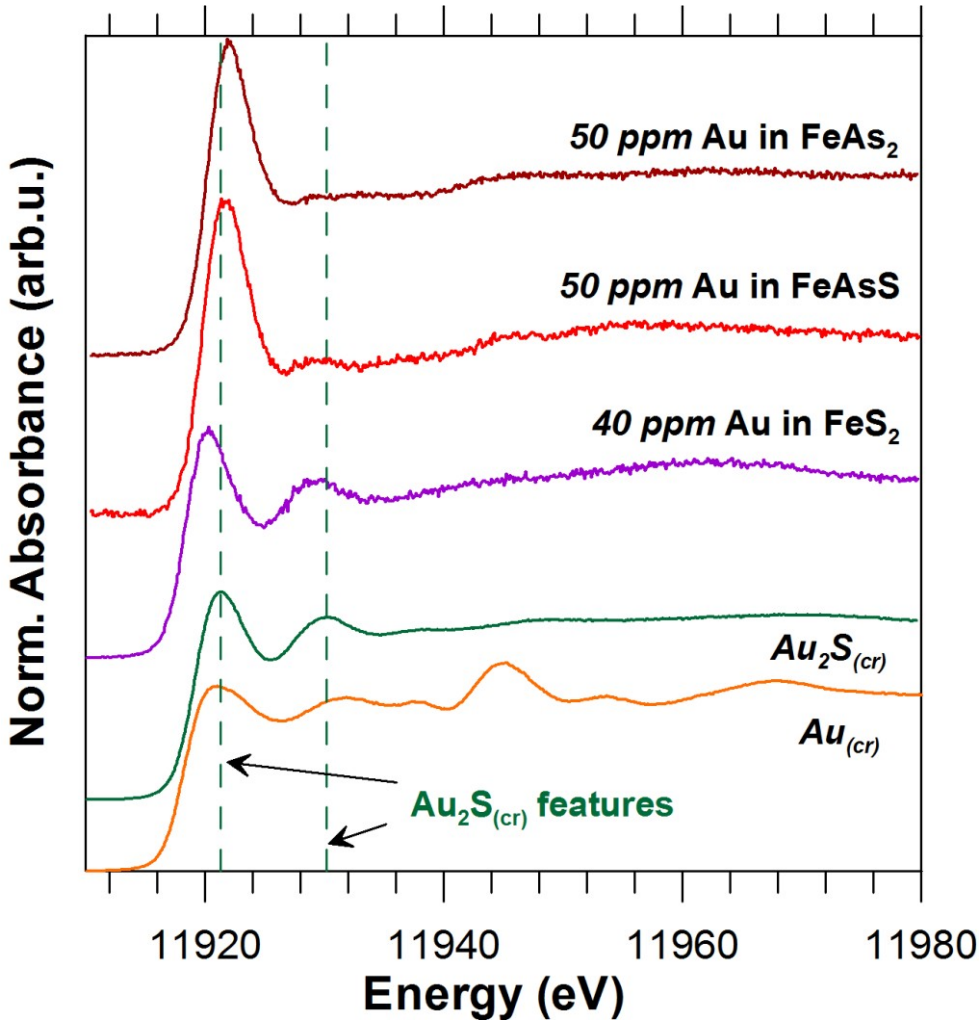
Au in ARSENOPYRITE FeAsS

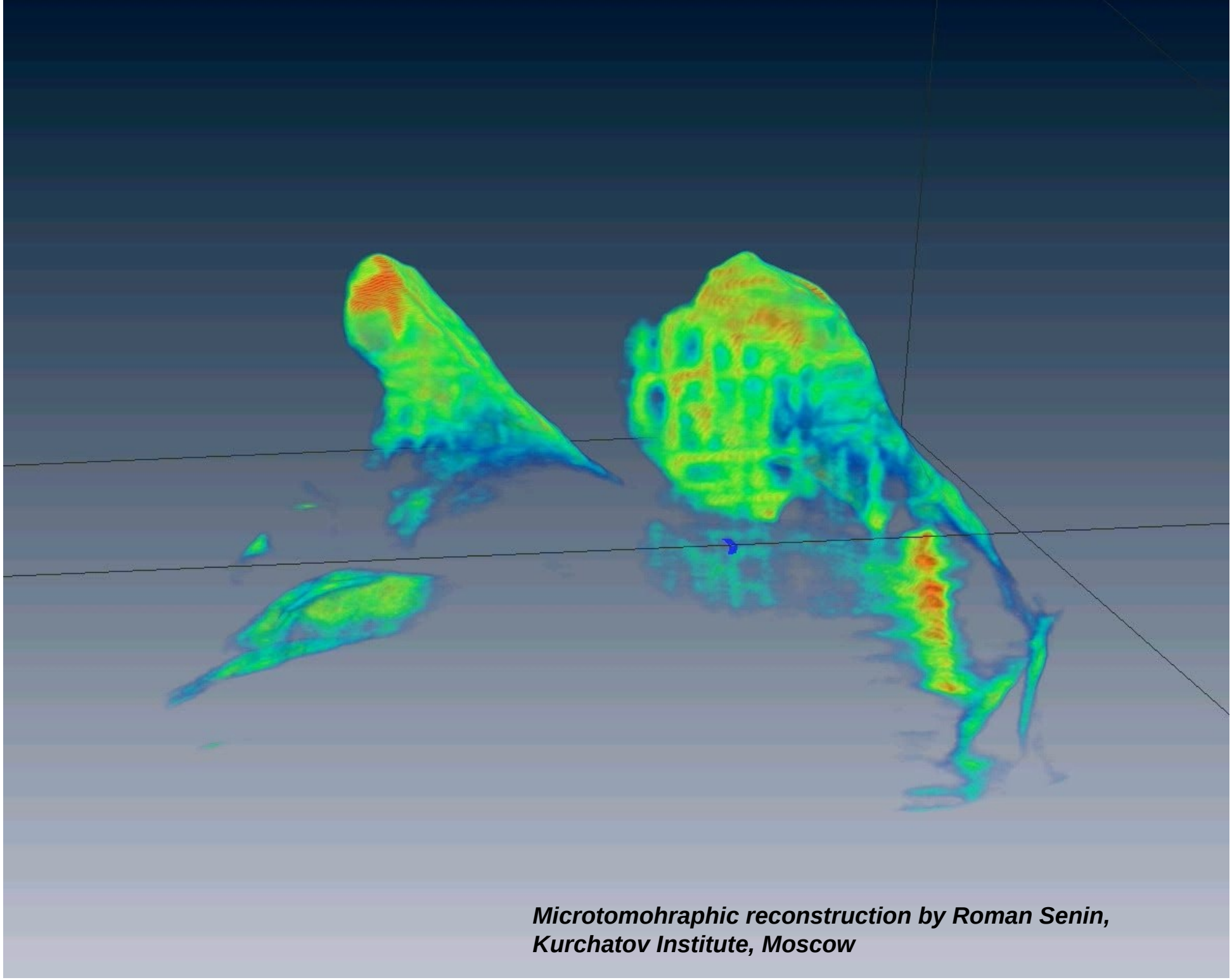


Crystalline structure;

•Concentration of ‘invisible’ Au is 50 ppm;

Au L_3 edge HERFD XANES spectra of Pyrite FeS_2 – Arsenopyrite FeAsS - Löllingite $FeAs_2$





Microtomohraphic reconstruction by Roman Senin, Kurchatov Institute, Moscow

Thank you for attention!