



# Radiation damage in X-ray spectroscopy

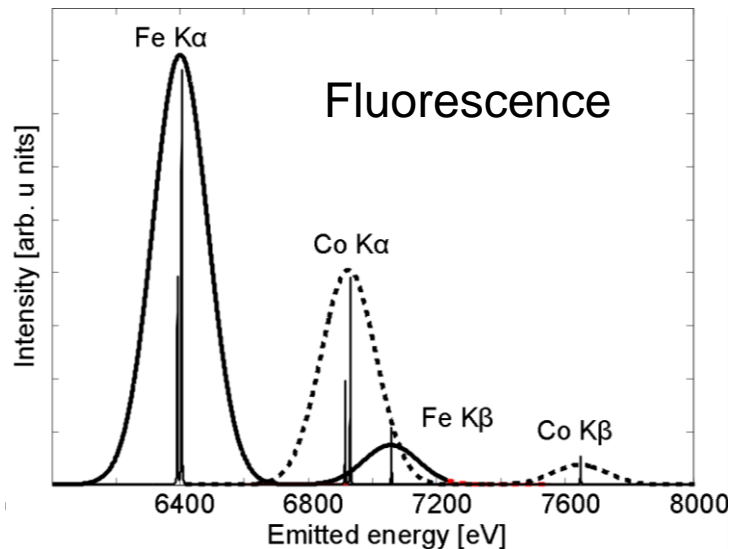
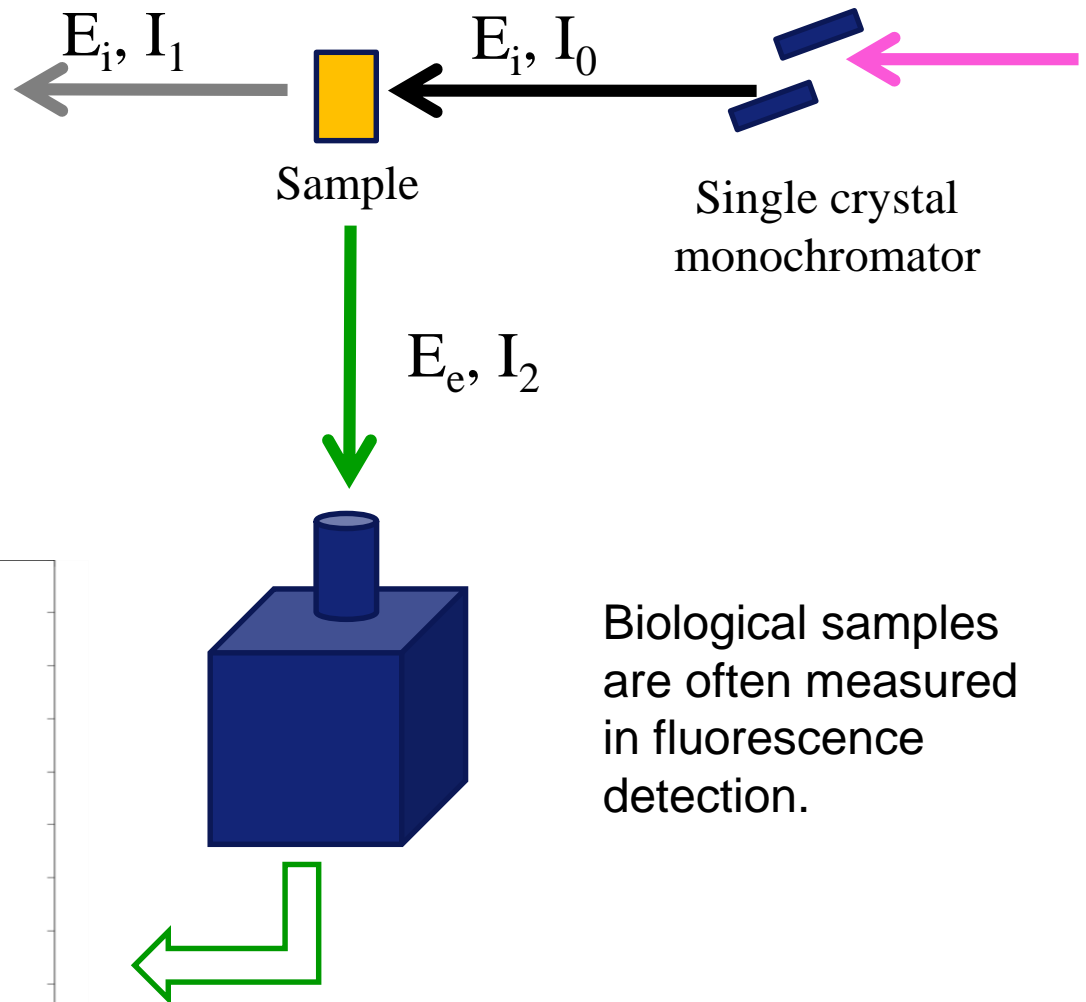
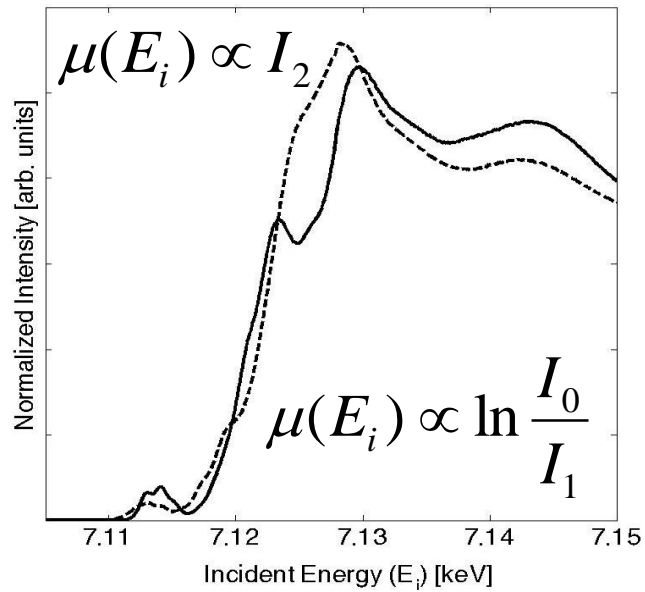
Pieter Glatzel



| The European Synchrotron

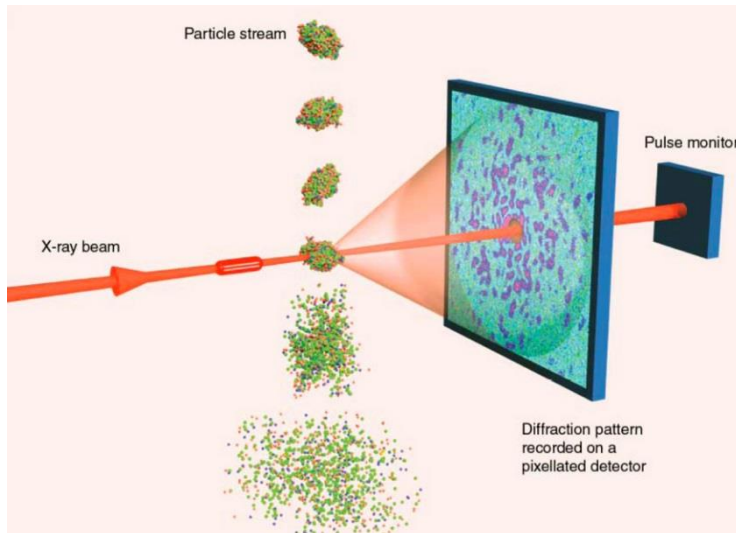


# Photon-in/photon out spectroscopy

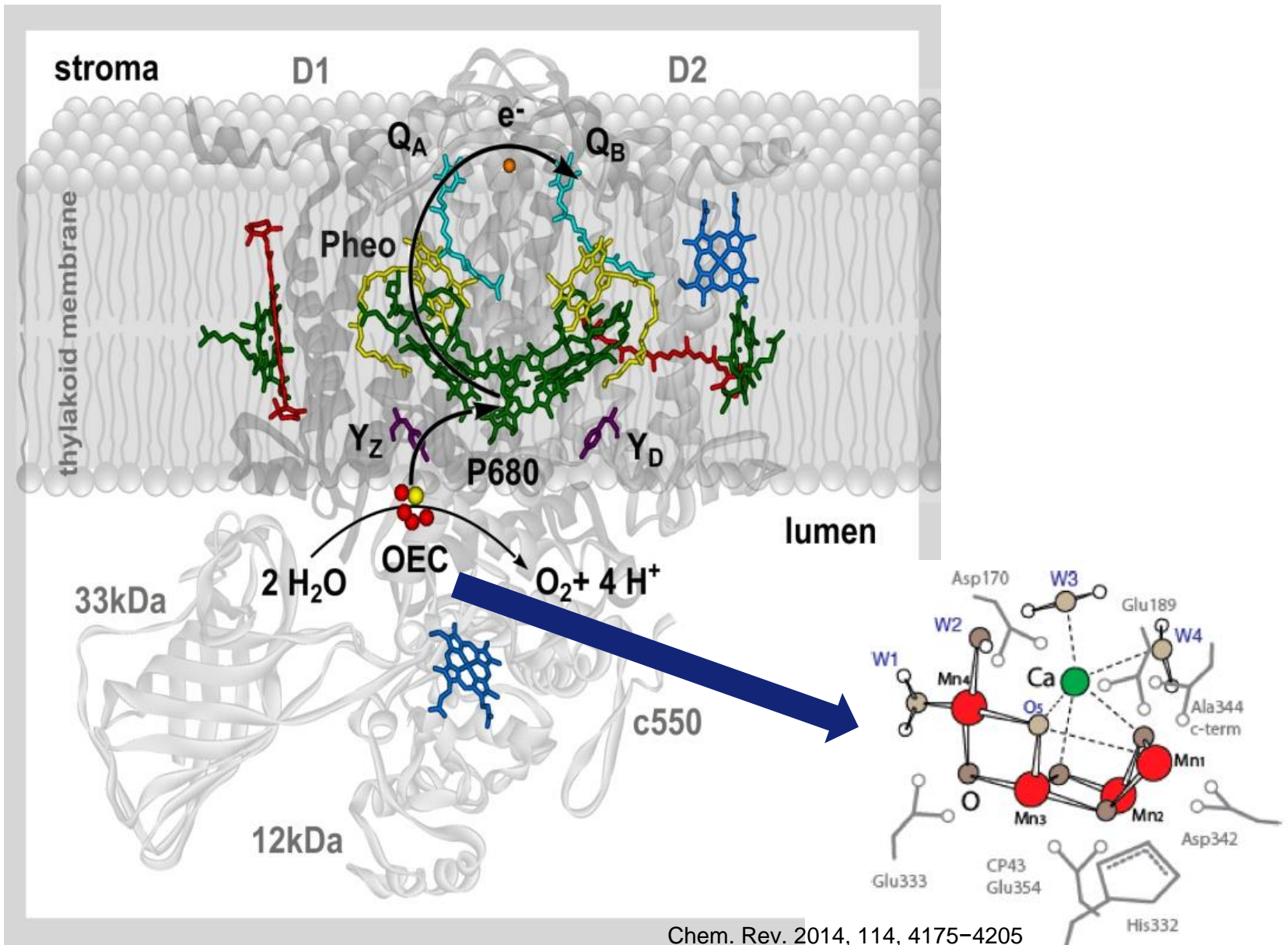


In case spectral changes are observed with increasing X-ray dose (radiation damage):

- 1) Increase detection efficiency
- 2) Use more sample
- 3) (Beat the radical diffusion time)

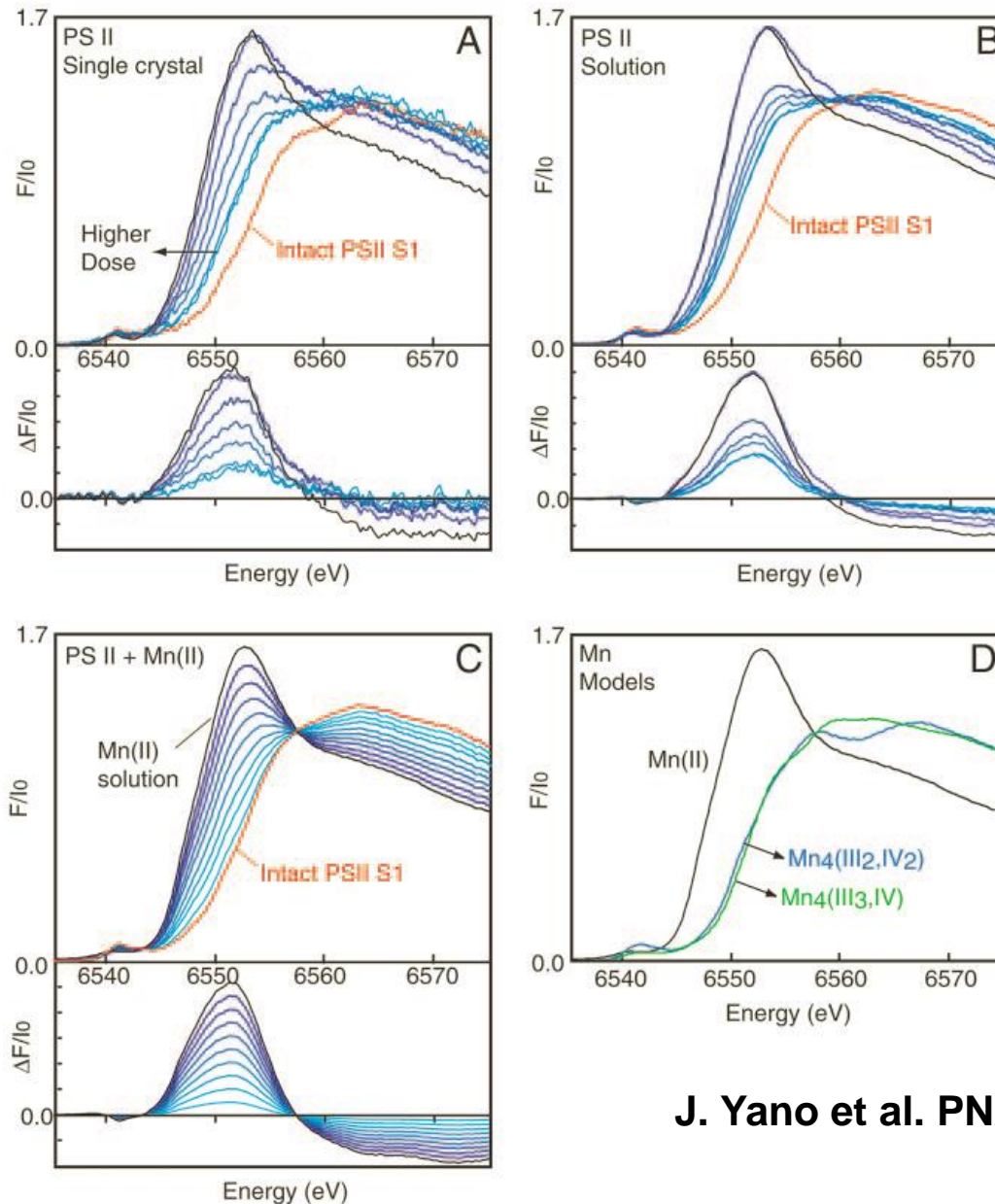


# Photosystem II



Chem. Rev. 2014, 114, 4175–4205

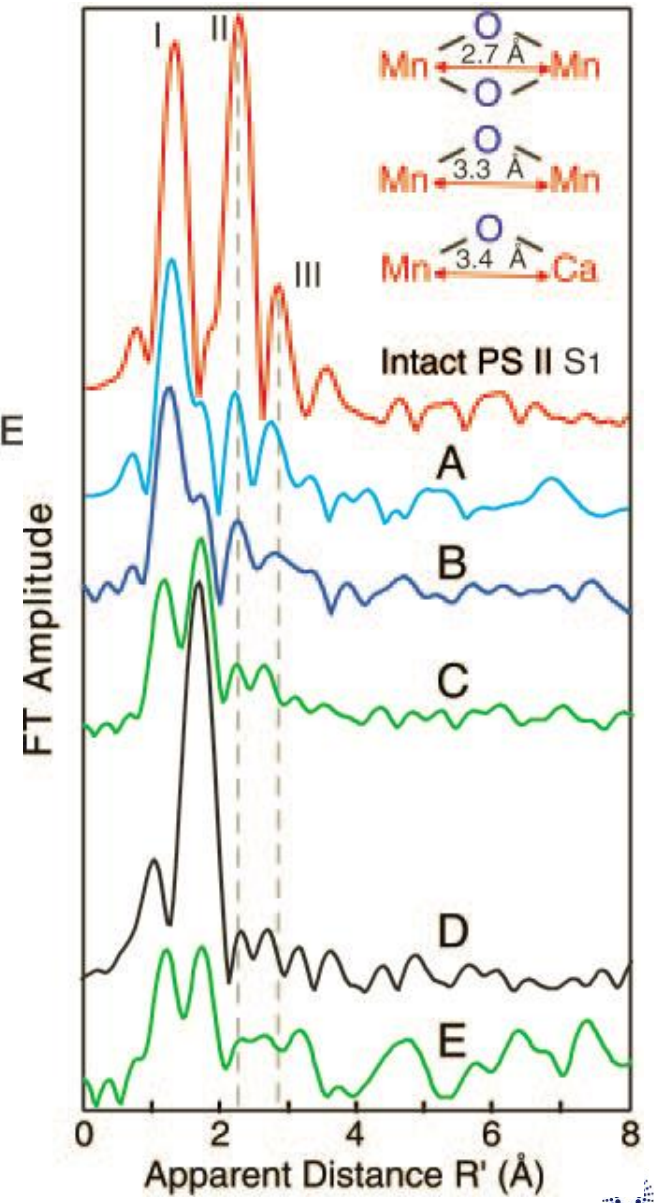
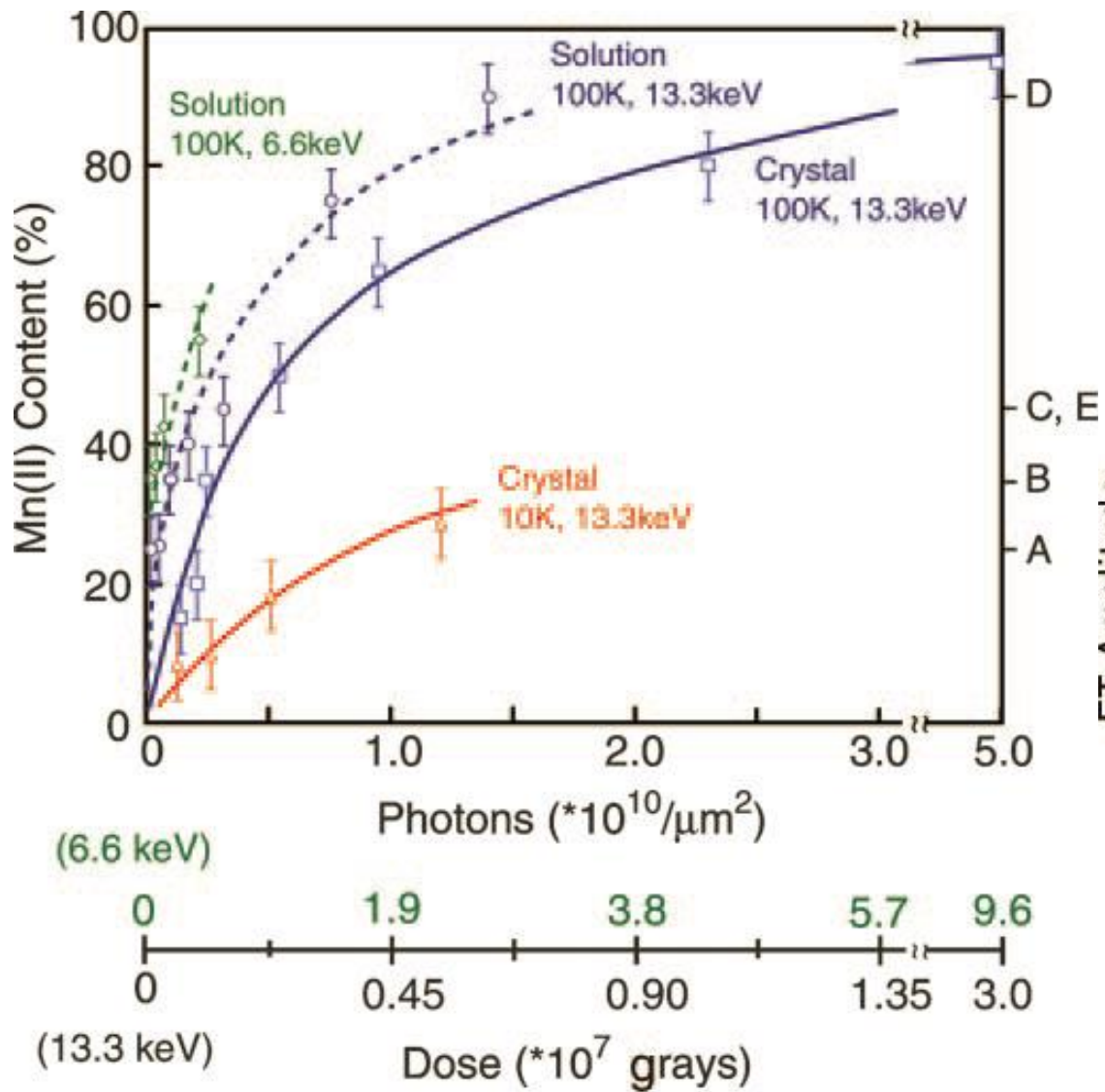
# X-ray damage as a function of dose and temperature



- Mn(III) and Mn(IV) are reduced to Mn(II) by X-rays
- Mn(II) resembles Mn in solution
- Spectroscopy sets an orders of magnitude lower dose limit than crystallography

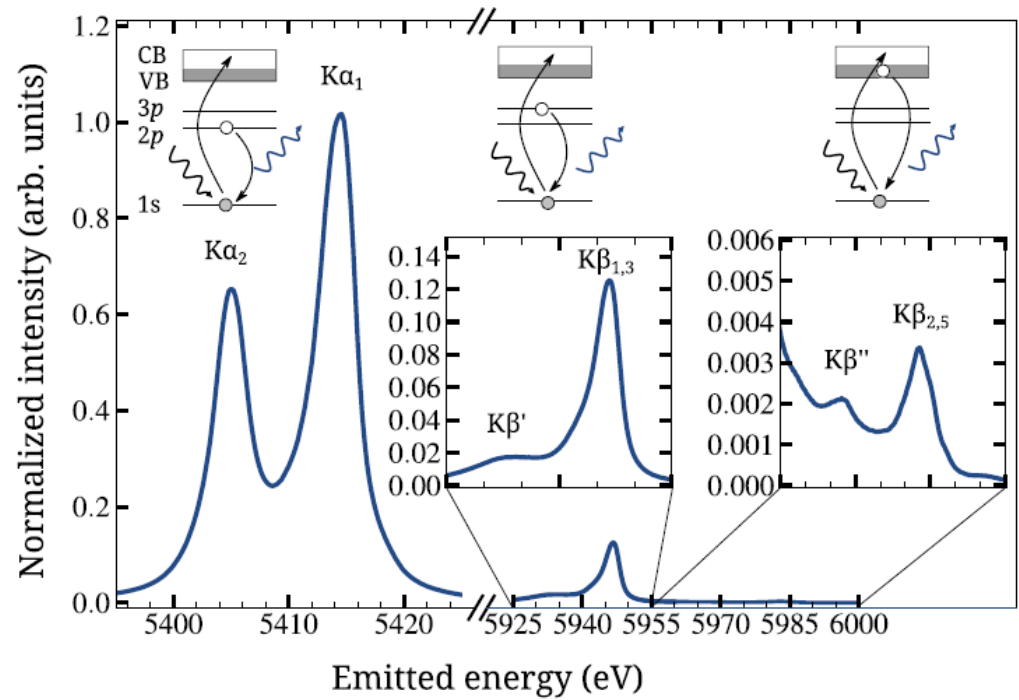
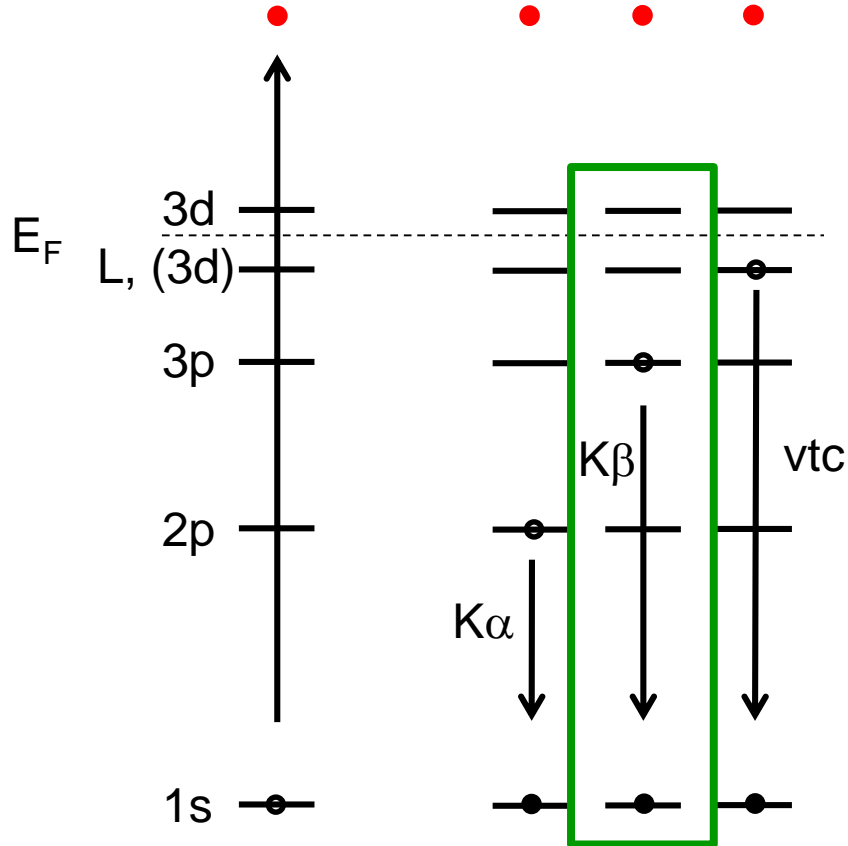
J. Yano et al. PNAS, 102, 12047 (2005)

# X-ray damage as a function of dose and temperature



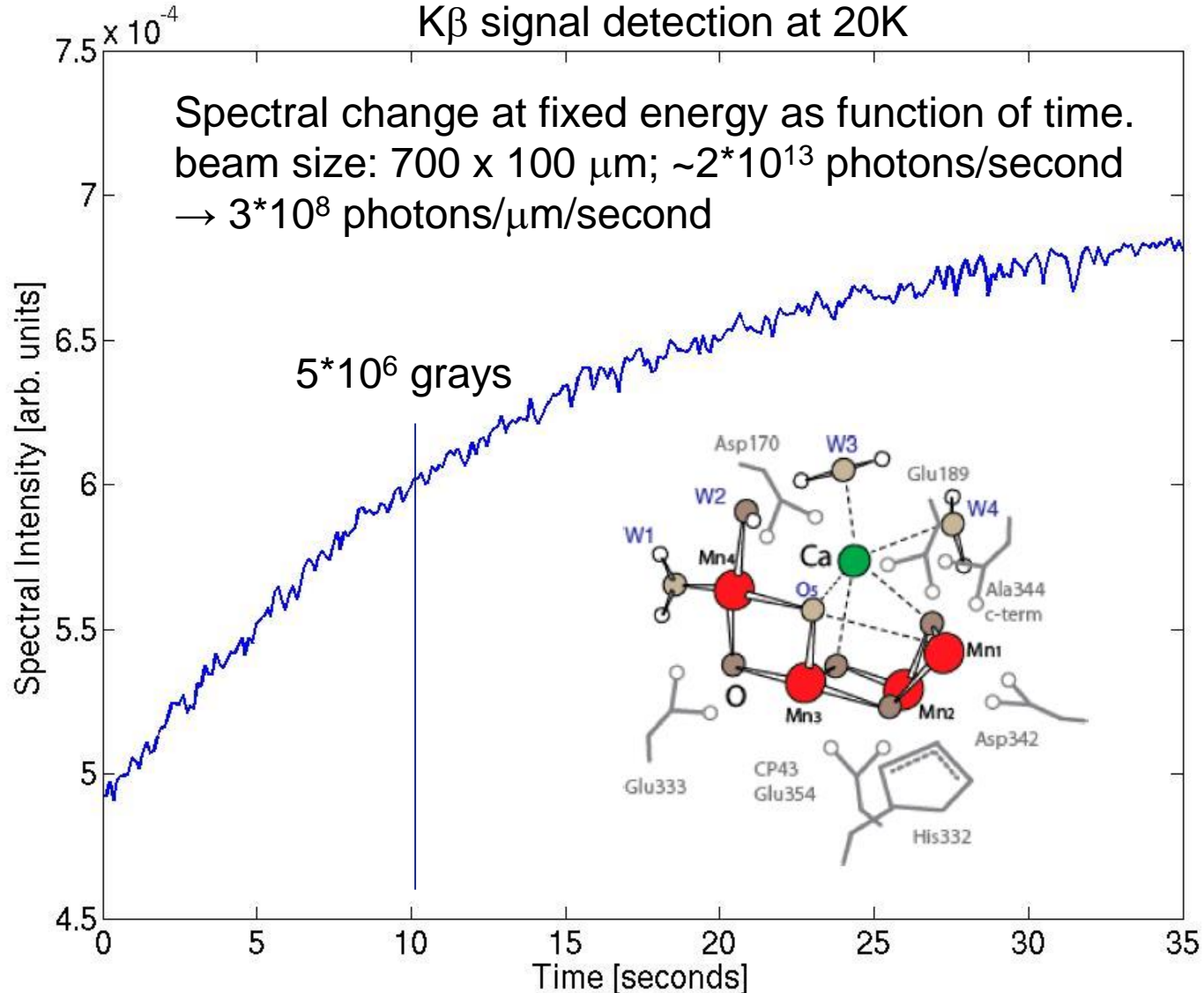
# Photon-in/photon-out spectroscopic techniques

Non-resonant



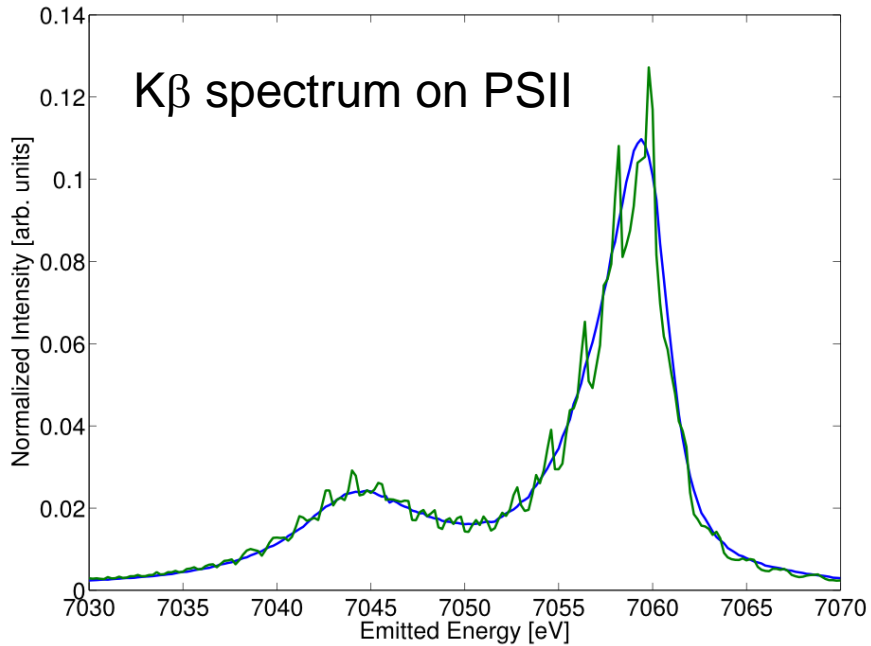
P. Glatzel and U. Bergmann, *Cord. Chem. Rev.* (2004)

M. Rovezzi and P. Glatzel *Semicond. Sci. Technol.* **29** 023002 (2014)



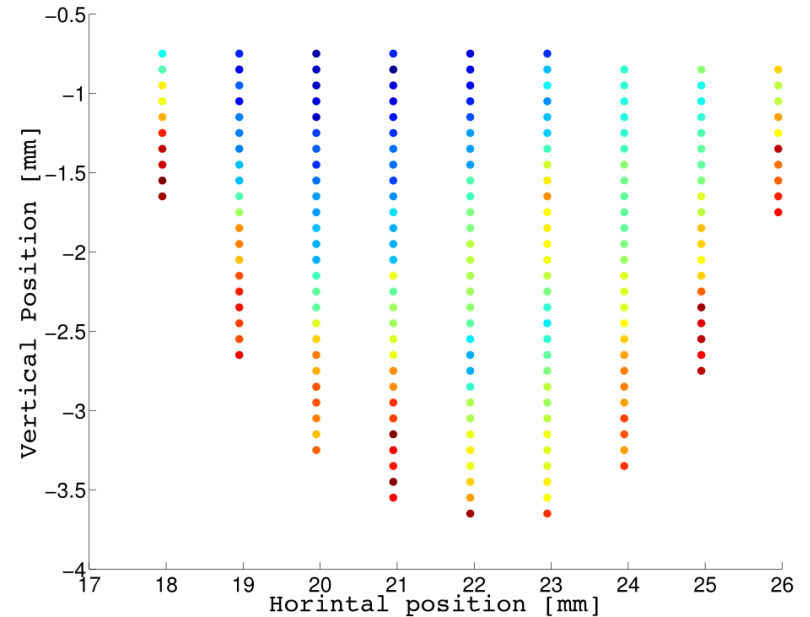


# Dealing with radiation sensitive samples



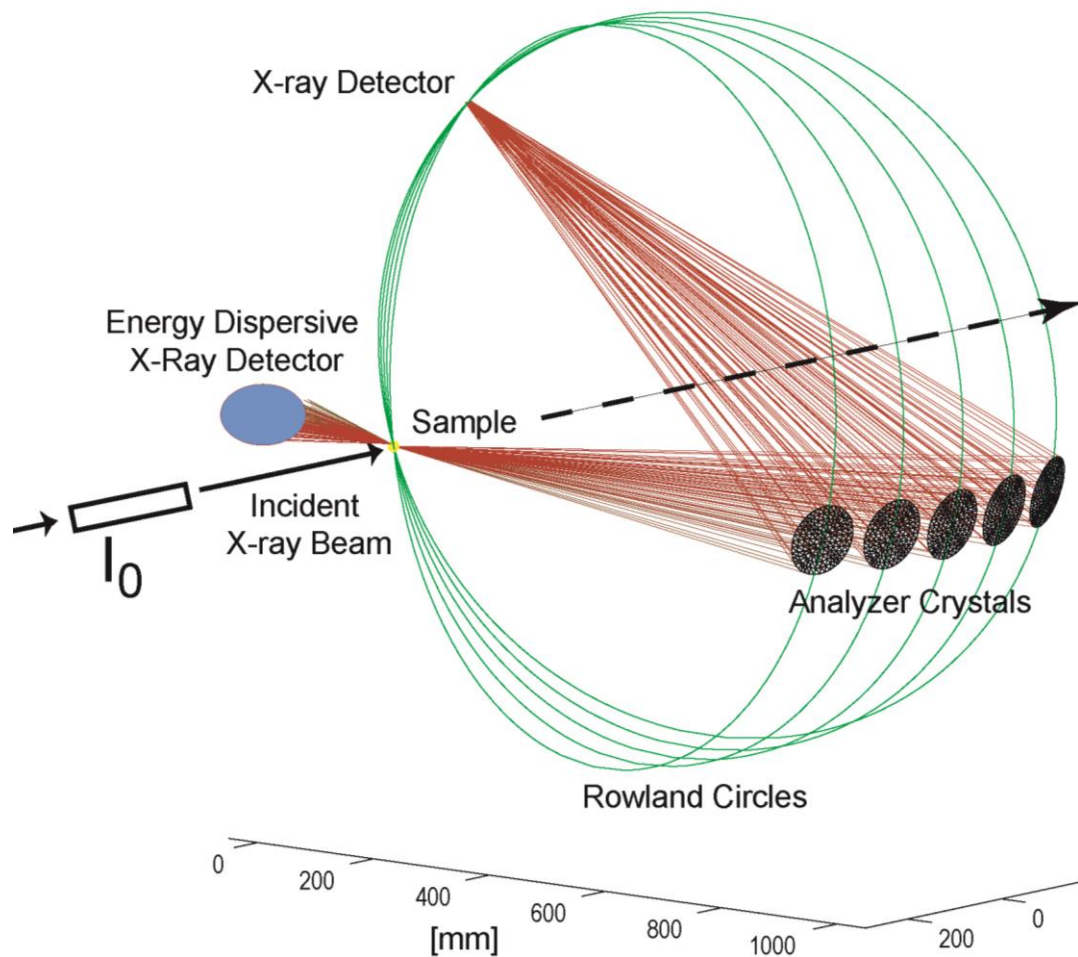
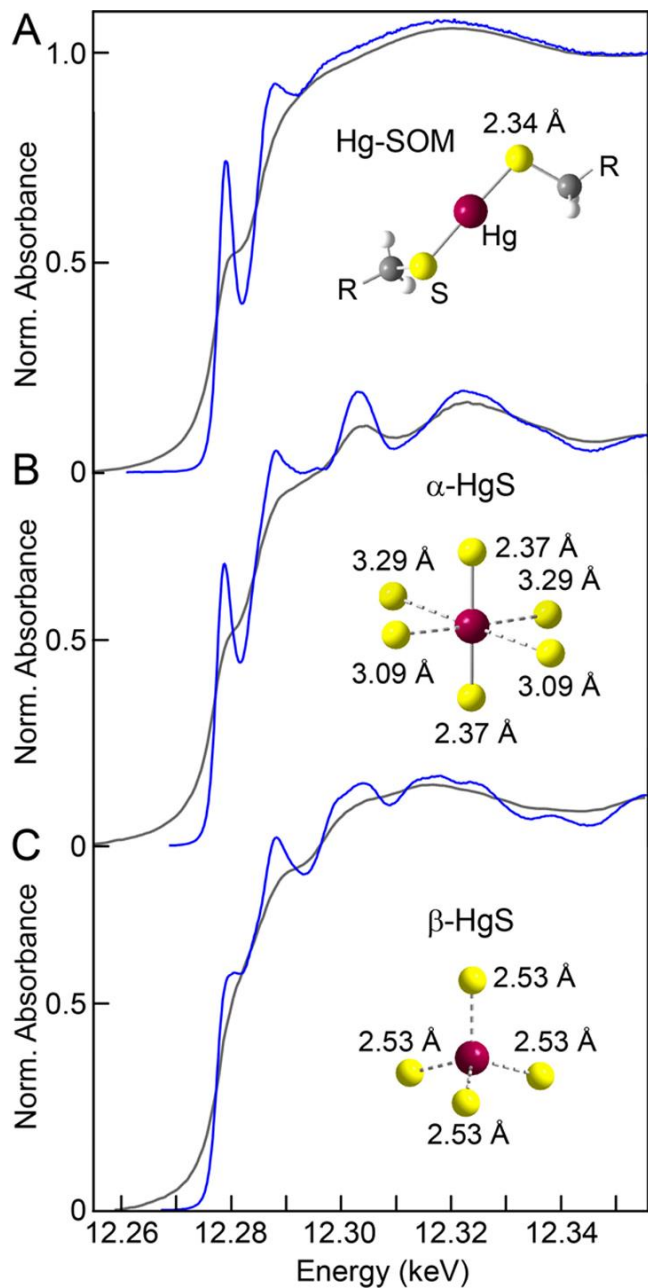
Take map of metal fluorescence response.

Each energy point measured in different position of beam on sample.



# Increasing the efficiency

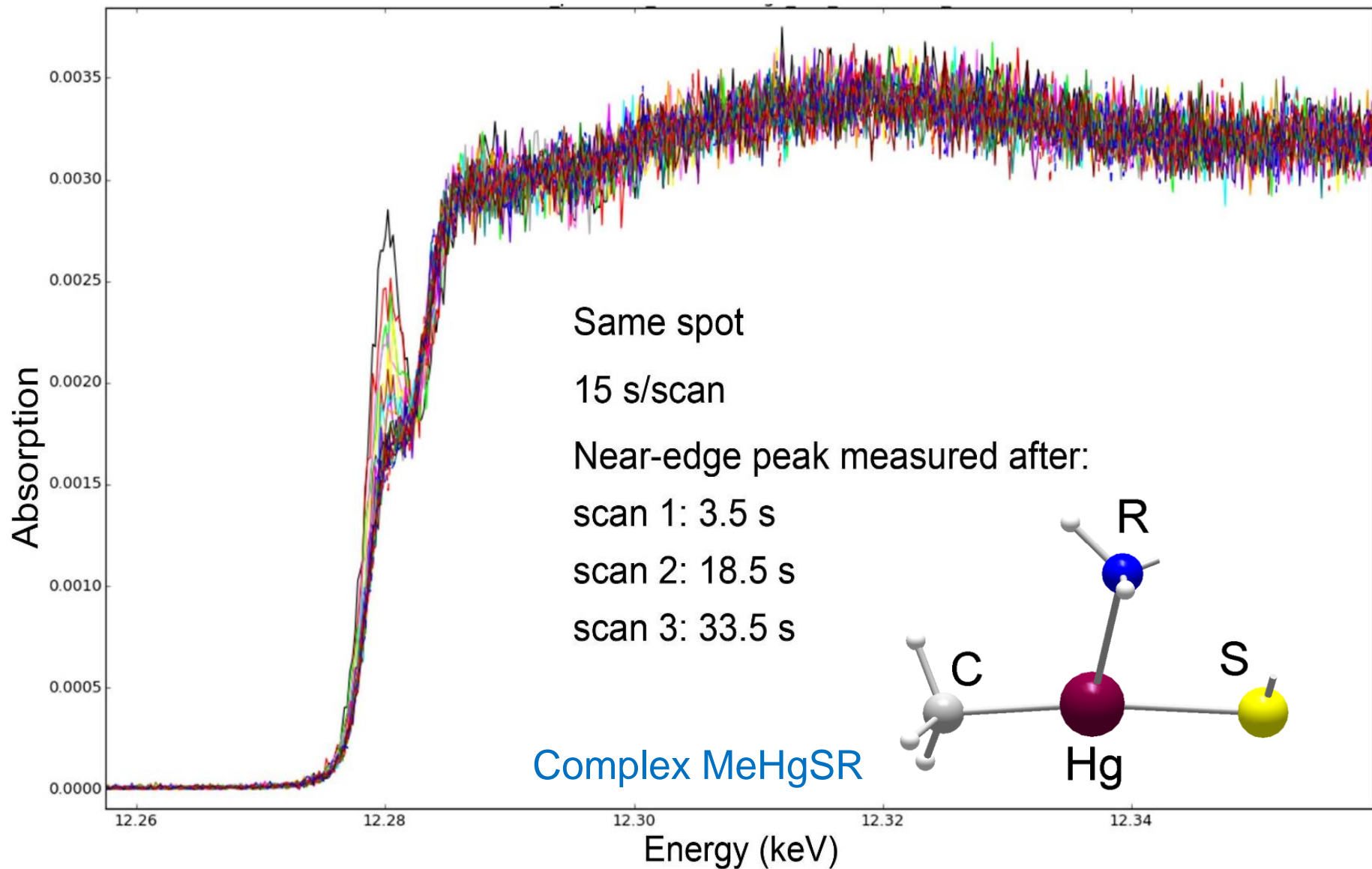
# HERFD-XANES in Hg



A. Manceau et al., *Env. Sci. & Techn* (2015)

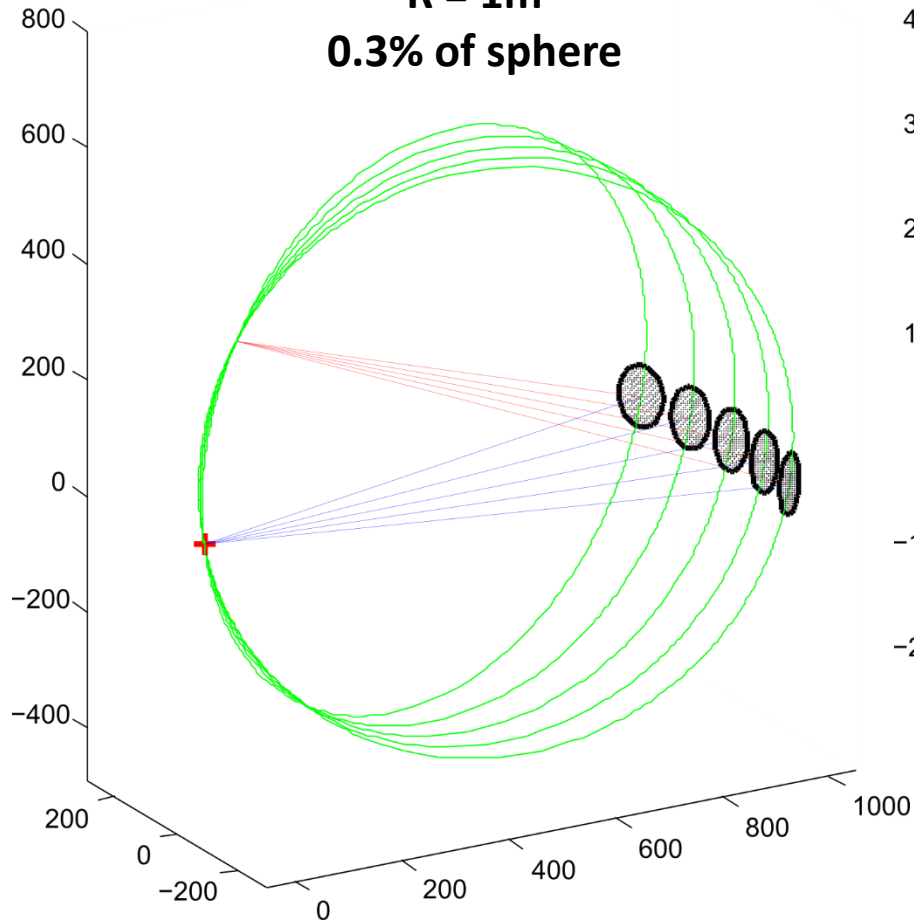
A. Manceau et al., *Inorg. Chem.* (2015)

# Radiation damage in Hg coordination complex

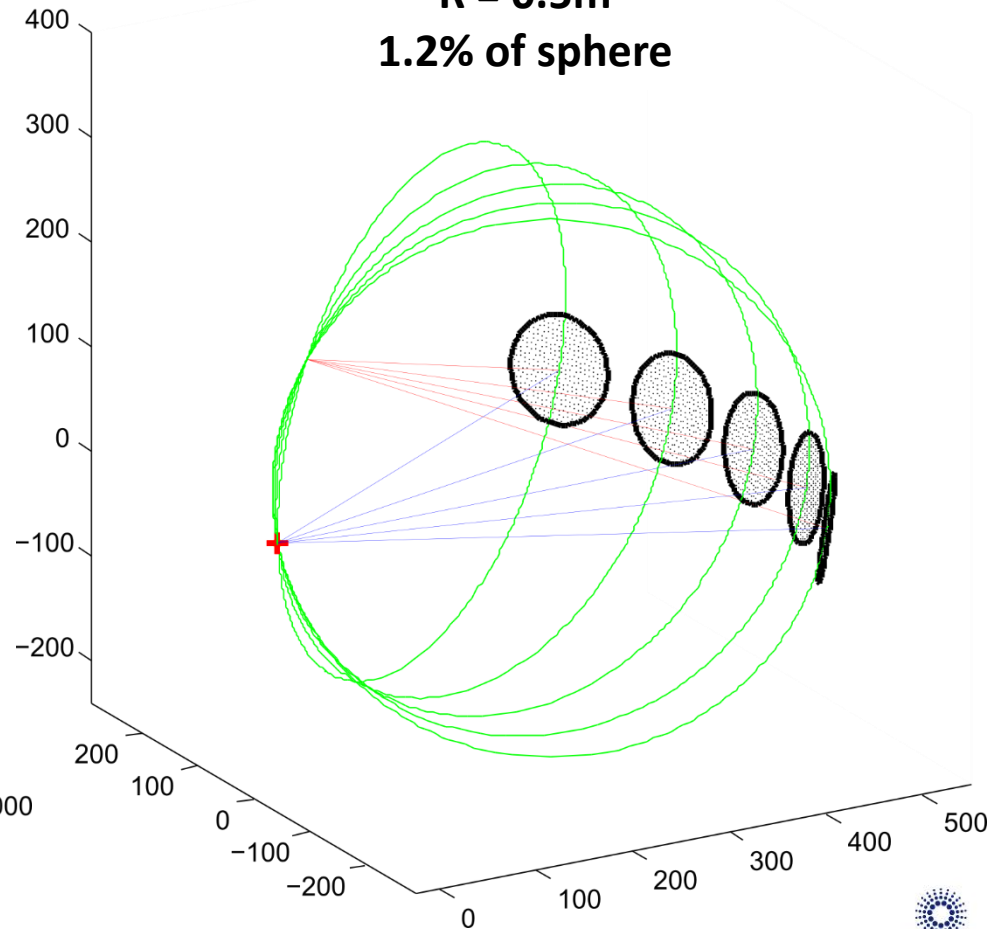


Increase solid angle by reducing the analyzer crystal bending radius.

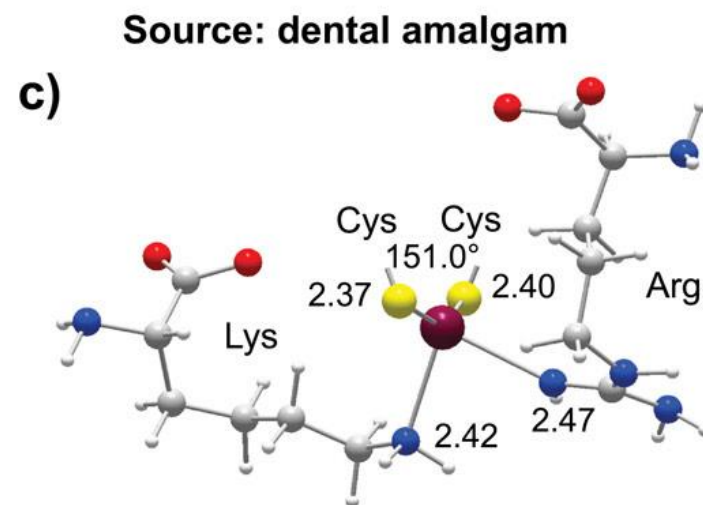
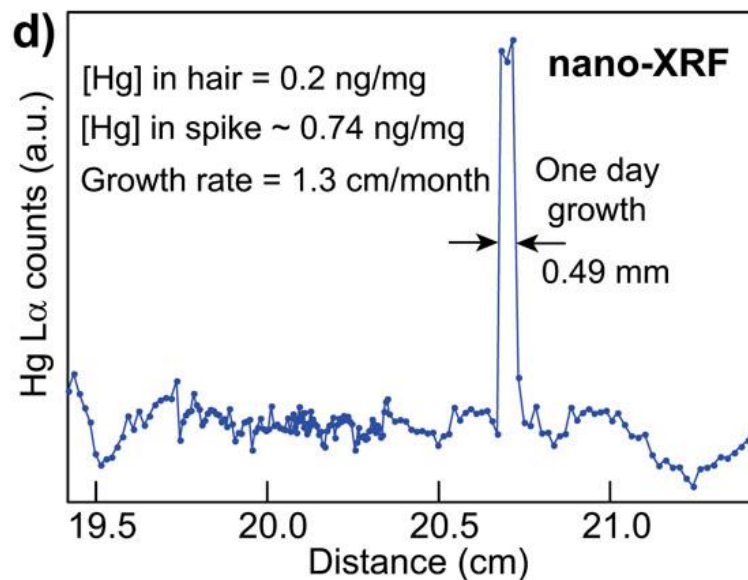
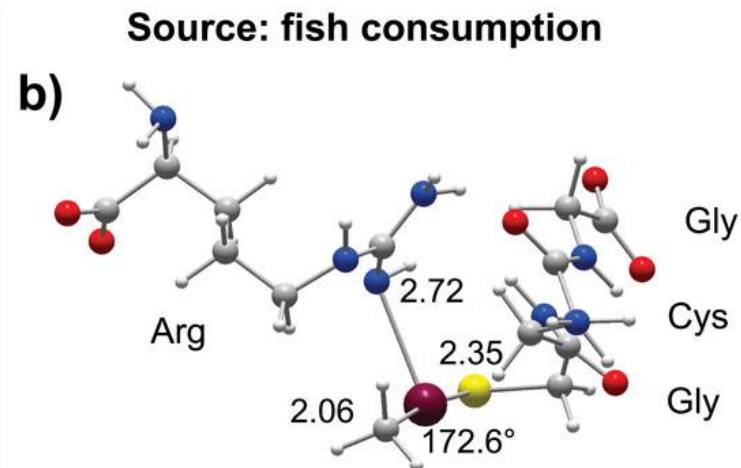
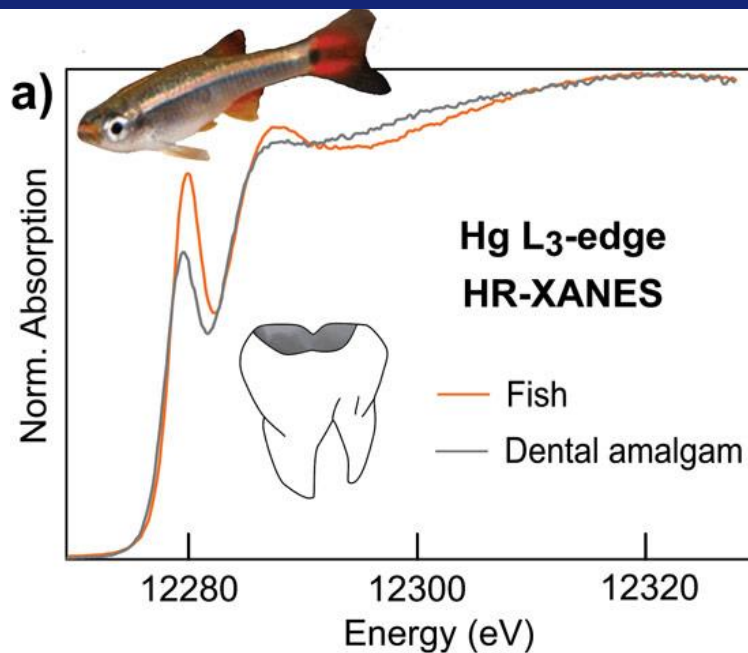
**R = 1m**  
**0.3% of sphere**



**R = 0.5m**  
**1.2% of sphere**

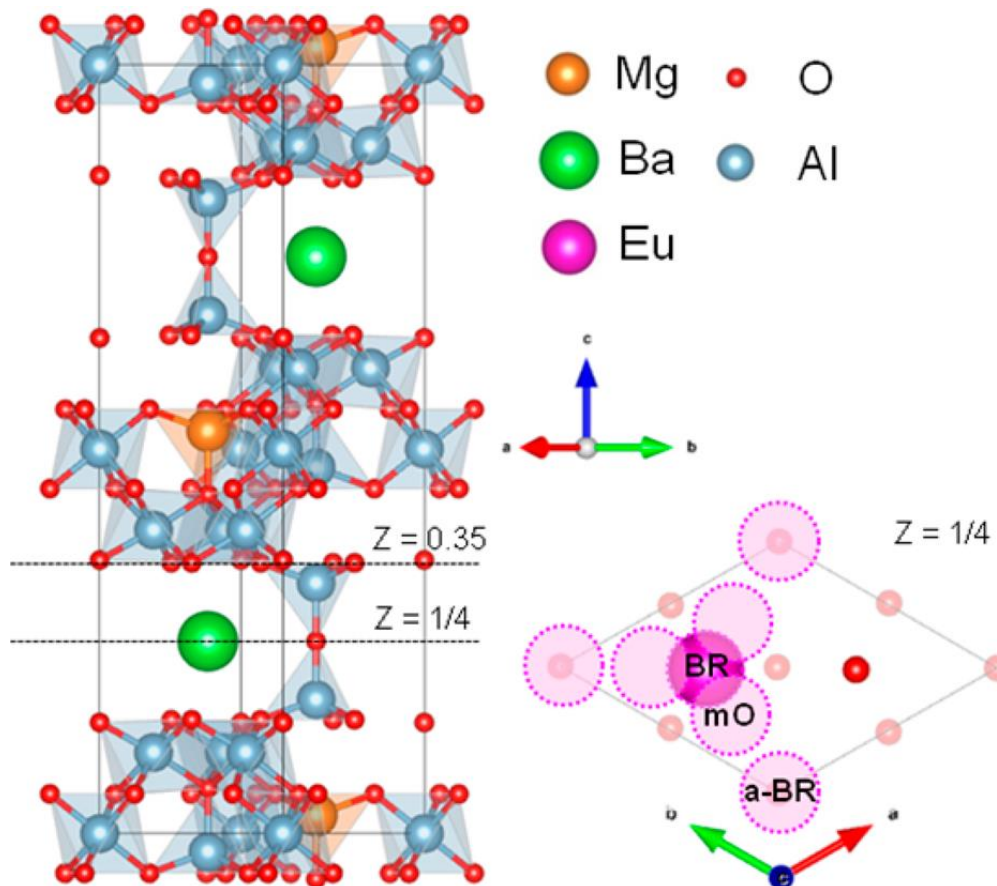


# HERFD-XANES in low concentration: Hg speciation in human hair



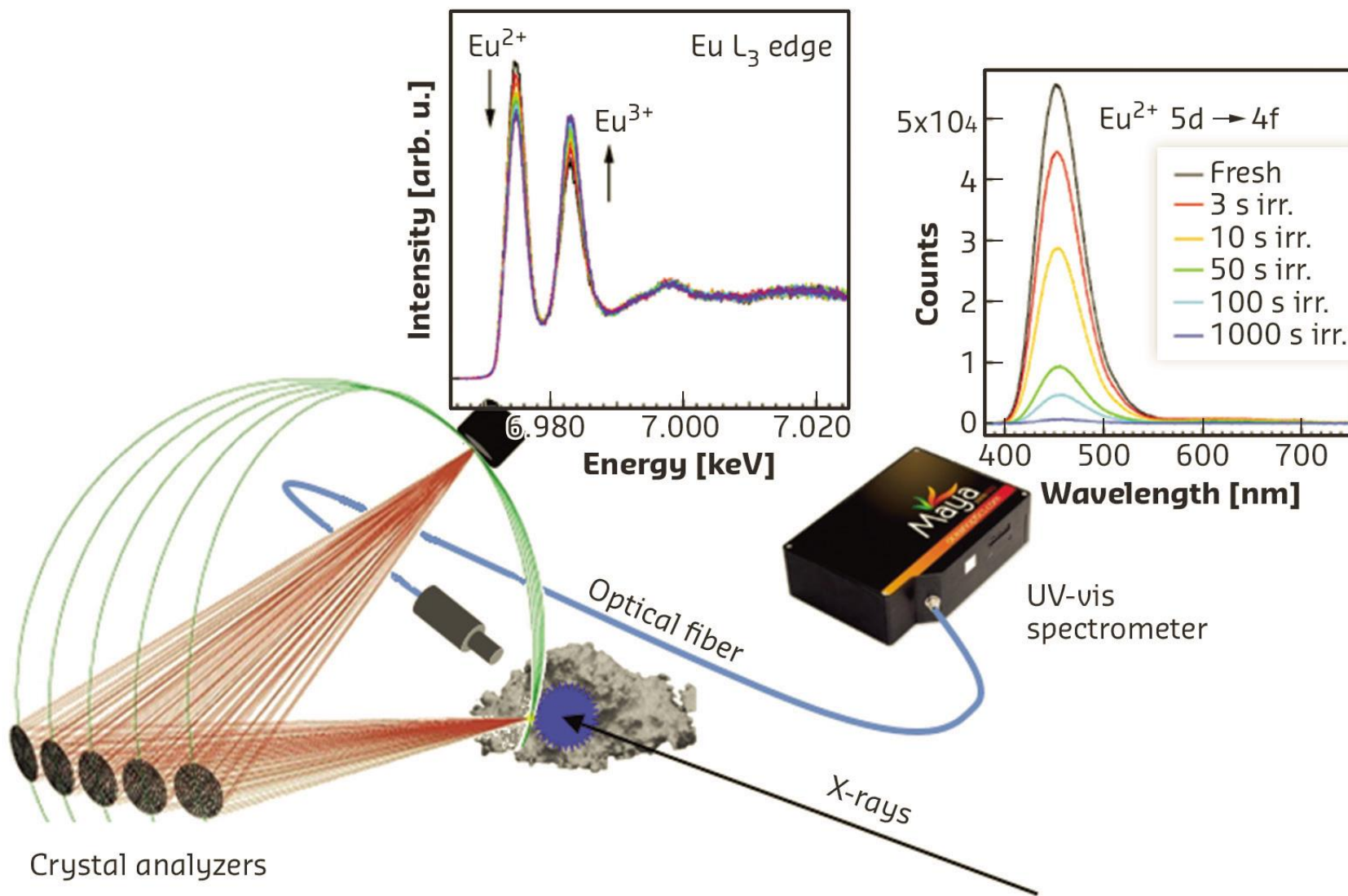
# Combining techniques

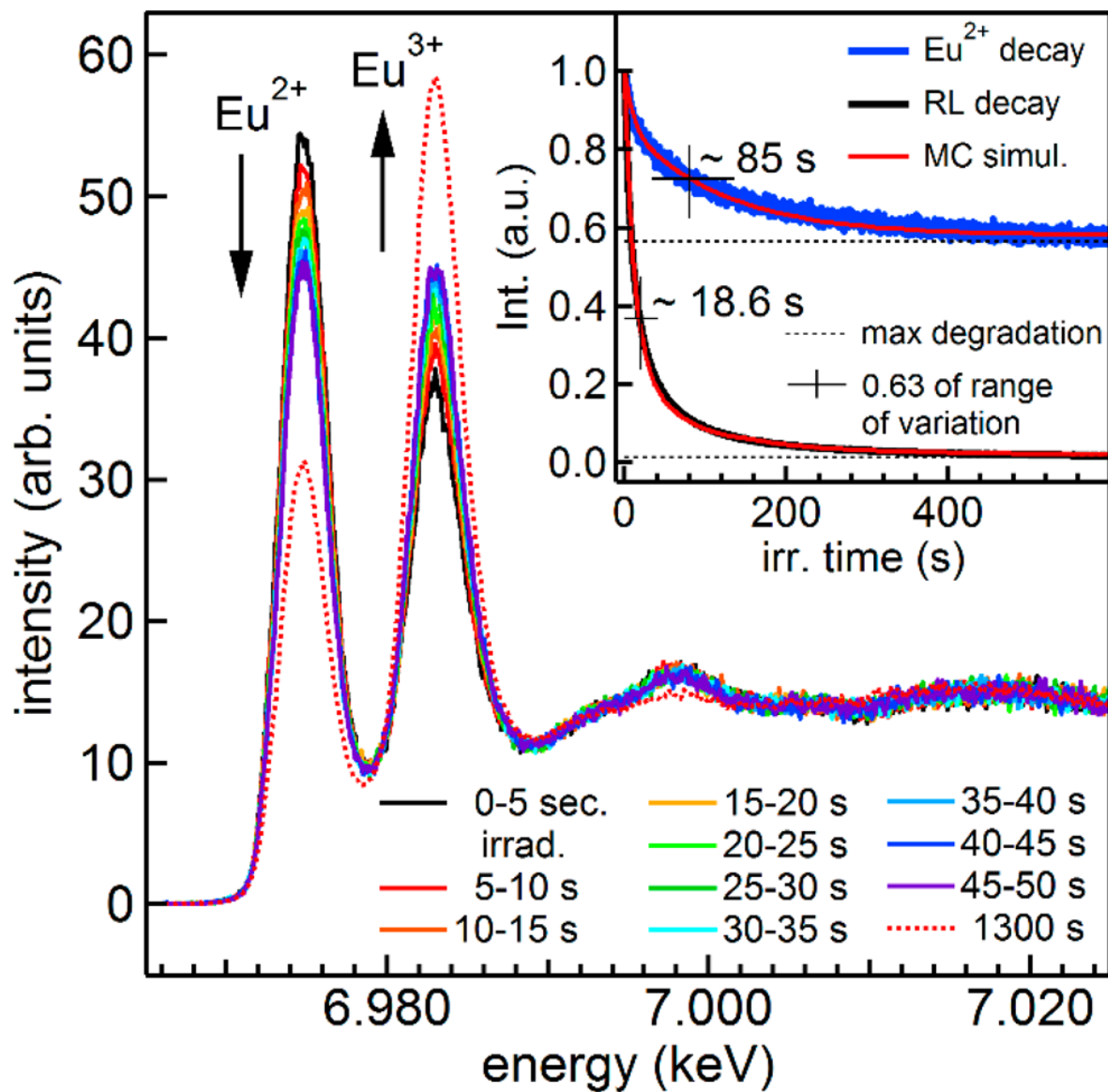
# Oxidation and Luminescence Quenching of Europium in Blue Phosphors





# Combine X-ray with UV-vis probe





The luminescence decay is faster and complete.  
 → “killer” centres suppress electron transfer

Thank you.