

# Speciation of Gd via Synchrotron X-ray Methods

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# Conflicts of Interest

No conflicts of interest reported.

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## What is Synchrotron Radiation?

- Very bright, focused, monochromatic, tunable, “high quality” X-rays
- Need a specialized electron/positron accelerator facility “Synchrotron Lightsource” which contains many specialized experimental stations or “beamlines”
- Run in US by DOE, leading facilities in US are NSLS-II (NY), APS (IL), ALS (CA), SSRL (CA)

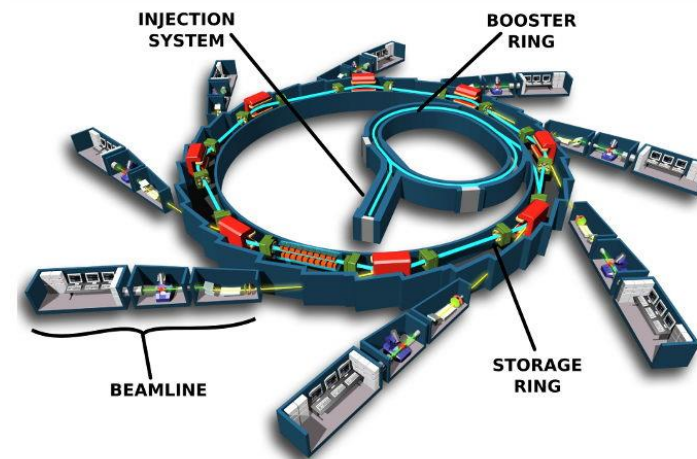


## Limitations of Synchrotron radiation:

- Access (free) is by application, peer-reviewed = long-lead times.
- Short “beamtimes” - typically 3 days (24 hour) 3x a year
- **Experiments limited to facilities at beamline**

## What can X-rays do for us?

- X-ray Fluorescence (XRF): detailed element composition, location
- **X-ray Absorption (XAS): local structure around Gd = speciation**
- Gd L-edges ( $2p \rightarrow$ ) at 7.24 keV more useful/sensitive than Gd K-edges ( $1s \rightarrow$ ) at 50.2 keV **but penetration in tissue or water only 1–2 mm**



## What sort of Samples?

- Not really *in vivo*: Fixed or frozen tissue sections, cell cultures
- Human or animal tissues: autopsy, biopsy.
- *Very* (very, very) small animals. Example: larval zebrafish
- Prepared materials: slurries, extracts, solutions



# Speciation of Gd : X-ray Fluorescence (XRF) Imaging

## Information?

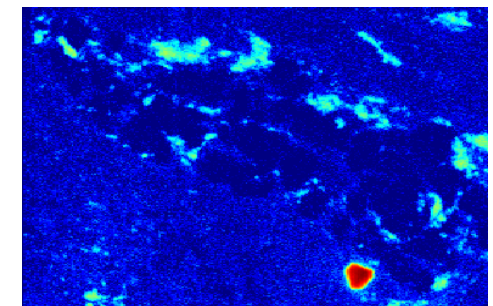
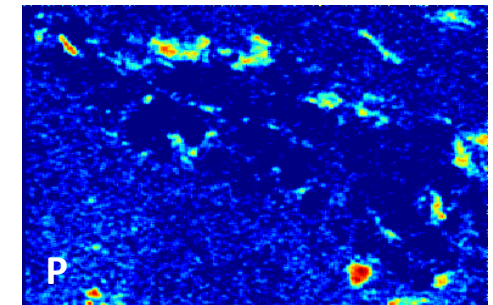
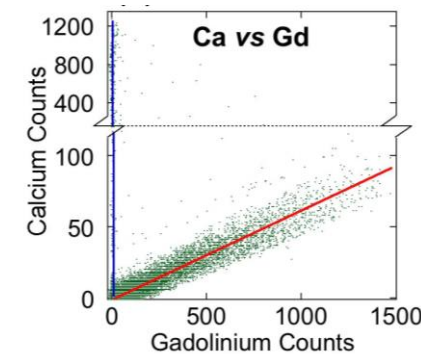
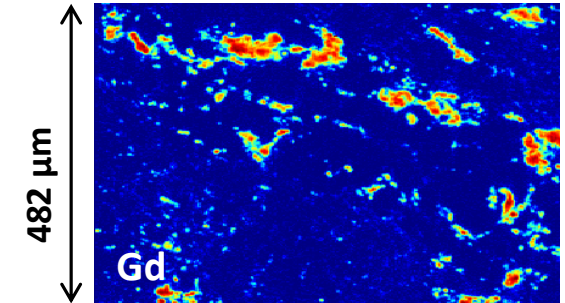
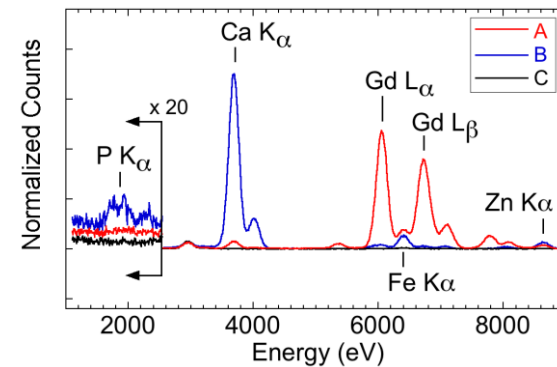
- Presence, amount and location of elements
- No inherent speciation

## Laboratory XRF

- Usually uses Gd K-edge (50 keV). Sensitivity <math>< 1\mu\text{g/g}</math>.
- Has been applied to Gd in bone *in vivo*.

## Synchrotron $\mu$ XRF Imaging for indirect speciation (like ICP)

- Rasters a micron size X-ray beam across sample while measuring XRF
- Element specific imaging: Gd, Ca, P, other elements
- Correlation plots identify any co-location of Gd with other elements.
- Gd Concentration minimum : <math>< 1\mu\text{g/g} \sim 1\text{ ppm}</math>
- Concentration minimum depends on exposure time, beamline brightness, X-ray beam size, detector
- Sample size: Typically 2 x 3 cm area. Can be much larger, depending on beamline  
No more than 2 mm thickness can be measured  
For precise element correlation should be <math>< 20\mu\text{m}</math> thick
- Sample type: Human or animal tissues (autopsy, biopsy, cultures)
- Frozen tissues should be straightforward but need specialized cryostat for  $\mu$ XRF  
- often talked about but not generally available



# Speciation of Gd : X-ray Spectroscopy : EXAFS

## Information?

- **Element sensitive chemical speciation**

## Near-edge region

- Gd ligand environment, oxidation state
- Not much use for Gd

## EXAFS region

- Element, number and distance of atoms close ( $< 5 \text{ \AA}$ ) to Gd
- Also fingerprint spectra
- Gd concentration minimum:  $\sim 100 \mu\text{m} = 15 \mu\text{g/g}$
- Fe and Co can interfere
- Need a really good beamline with focused X-ray beam, state of the art detector, cryogenic sample temperatures (sample cryostat)
- Sample size: limited by size of focused X-ray beam (10 x 1 mm to 100 x 100  $\mu\text{m}$ )
- Sample type: Human or animal tissues (autopsy, biopsy, cultures)  
Prepared materials: slurries, extracts, solutions
- For Gd deposition: need well designed samples and experiments
- **$\mu\text{XRF}$ -imaging plus EXAFS = regional speciation**
- **In principal EXAFS speciation maps possible - complement ICP and MALDI imaging**

