# Foretaste of Sample Radiation Damage at the SRX Beamline

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Workshop 4: Radiation Effects at X-ray Doses From MegaGrays to PetaGrays and Above – The Impact for Science at NSLS-II

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# What is Radiation Damage? Chemical Description

Change in elements oxidation states, rupture and creation of chemical bonds

Radiolysis of liquid water

$$H_2O \longrightarrow OH^{\bullet},\ e_{hyd}^{-},\ H^{+},\ H^{\bullet},\ H_2O_2,\ ,O_2^{\bullet -}$$

$$e_{hyd}^{-} + Zn^{2+} \rightarrow Zn^{+}$$

$$OH^{\bullet} + HCR_3 \rightarrow {}^{\bullet}CR_3 + H_2O \quad \text{or} \quad OH^{\bullet} + R_2C{=}CR_2 \rightarrow {}^{\bullet}CR_2(OH)\text{-}CR_2$$

Decomposition of solid glycine at 77 K

$$NH_2CH_2COOH \longrightarrow NH_3,\ CHOCOOH,\ CH_3COOH,\ CH_3NH_2,\ CO_2,\ H_2$$

Within a certain (often broad) range:

Amount of net chemical change = *G* x Radiation dose (*D* = absorbed energy/unit mass; 1 Gray = 1 Gy = 1 J/kg)

Rate of chemical change = *G* x Radiation dose rate (*DR* = *D*/unit time; 1 Gy/s)

and the proportionality coefficients (radiation yields, aka *G*-values), which are the measure of damage, are often accurately known

# What is Radiation Damage? Operational Description

Change in observables

| Sample | Observable | Damage criterion | Dose (MGy) |
|---|---|---|---|
| Protein, DNA or RNA cryo-cooled crystal | X-ray diffraction | 50% loss of diffraction | **20** (Henderson limit) |
| Photosystem II cryo-cooled crystal<br>Photosystem II RT crystal | X-ray spectroscopy | 50% change in $Mn_4Ca$ cluster | **~2**<br>**~0.04** |
| Superoxide reductase cryo-cooled crystal | X-ray diffraction | 25% change in Fe(III) site | **~0.3** |
| Yeast cells at RT | X-ray microscopy | 50% change cell survival | **~0.04** |
| Fe coordination cryo-cooled compounds | X-ray spectroscopy | 50% change in spectrum | **20 - 4000** |

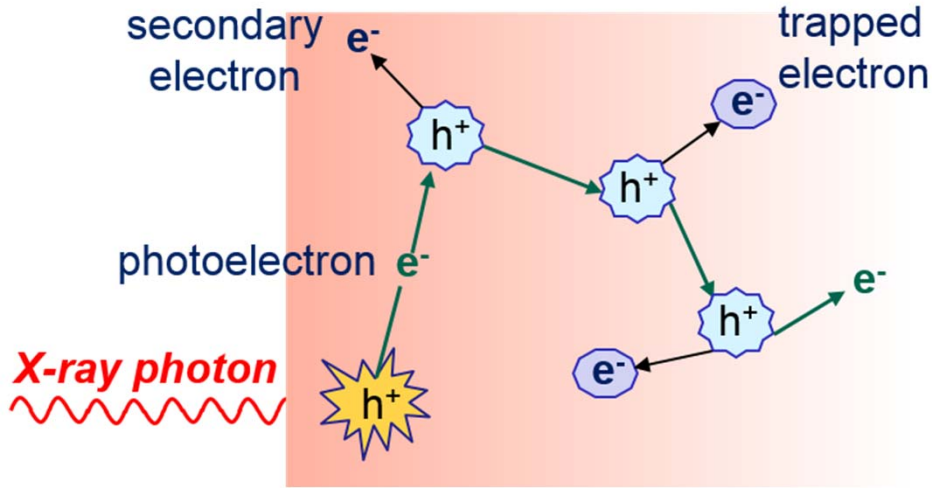
As with chemical change, change in observables $\propto$ Radiation dose

Fujisaki et. al., *J. Microsc.* (1996) **182**, 79; Adam et. al., *Structure* (2004) **12**, 1729; Yano et. al., *PNAS* (2005) **102**, 12047; George et. al., *Inorg. Chim. Acta* (2008) **361**, 1157; Davis et. al., *J. Phys. Chem. Lett.* (2012) **3**, 1858

# Origin and Timing of Radiation Damage

- At 10 keV, 80+% of X-ray photons are absorbed through photo-electric effect; the rest undergo inelastic (Compton) and elastic (Rayleigh) scattering.

- Each photoelectron carries ~10 keV and can produce hundreds of secondary electron-hole pairs




*Coincides with observables*

X-ray absorption and scatter. Photoelectrons, secondary electrons and holes are produced

*Very fast (ps < t < ns), but not very sample-specific*

*Significant damage to some observables*

Electron trapping and bond cleavage. Radicals are produced.

*Much slower, but very sample-specific and temperature-dependent. Cryo-cooling helps!*

*Extensive damage to observables*

Diffusion-controlled radicals reactions and electron tunneling. Stable final products are produced.

# Why Should We Be Concerned about Sample Radiation Damage at SRX Beamline?

Beamline purpose: submicron resolution X-ray spectroscopy, imaging, tomography, element mapping, diffraction

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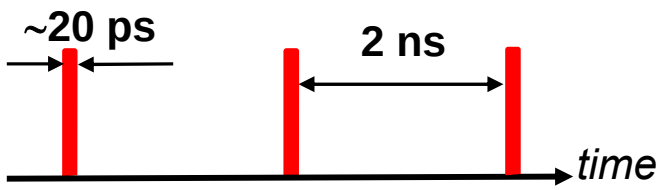
Very tightly focused X-ray beam

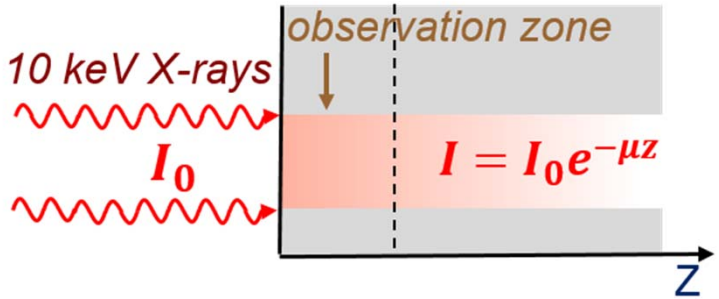



Energy range 4.7–25 keV

Frequency 500 MHz; duty factor ~1%

| Spot size | X-ray flux | X-ray flux density | Rel. FD |
|---|---|---|---|
| SRX beamline at NSLS II (quasi-CW at 500 MHz) | | | |
| $0.06 \times 0.06\ \mu m^2$ | $6 \times 10^{11}$ phot/s | $1.7 \times 10^{22}$ phot/(s cm$^2$) | **1** |
| 23ID-B beamline at APS (quasi-CW) | | | |
| $0.8 \times 0.88\ \mu m^2$ | $1.3 \times 10^{9}$ phot/s | $1.8 \times 10^{17}$ phot/(s cm$^2$) | **~$10^{-5}$** |
| Coherent X-ray Imaging Instrument at LCLS (< 50 fs pulses at 120 Hz) | | | |
| $1.5 \times 1.5\ \mu m^2$ | $5 \times 10^{13}$ phot/s | $2 \times 10^{21}$ phot/(s cm$^2$) | **~0.1** |
| | $4 \times 10^{11}$ phot/pulse | ~$3 \times 10^{29}$ phot/(s cm$^2$) | **~$2\times10^{7}$** |

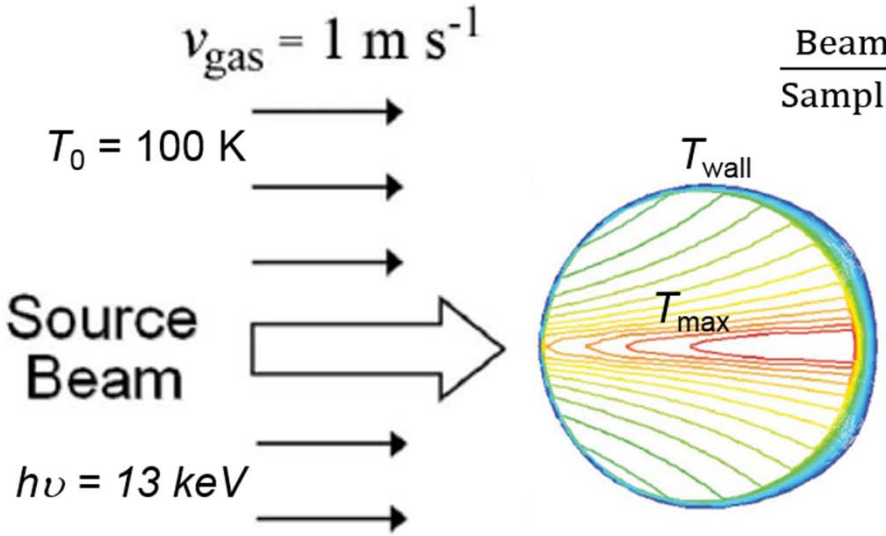
# Estimates of Dose Rates at SRX Beamline




For a protein crystal: $\mu/\rho$ = 10 g/cm$^2$, $\rho$ = 1.36 g/cm$^3$

| Spot μm$^2$ | Flux $10^{13}$/s | Dose rate Giga Gy/s | Photoionizations / aminoacid s | Time to Henderson limit, ms |
|---|---|---|---|---|
| SRX beamline at NSLS II | | | | |
| 0.8 | 1.3 | **26** | **3** | **0.8** |
| 0.64 | 0.9 | **22** | **2.6** | **0.9** |
| 0.0084 | 0.1 | **190** | **22** | **0.1** |
| 0.0036 | 0.06 | **270** | **31** | **0.08** |
| 23ID-B beamline at APS | | | | |
| 0.7 | $1.3\times10^{-4}$ | **0.0028** | **0.0003** | **7000** |

# Will Sample Heating Be a Problem?




$$\frac{\text{Beam } \emptyset}{\text{Sample } \emptyset} = \frac{1\ mm}{2\ mm}$$

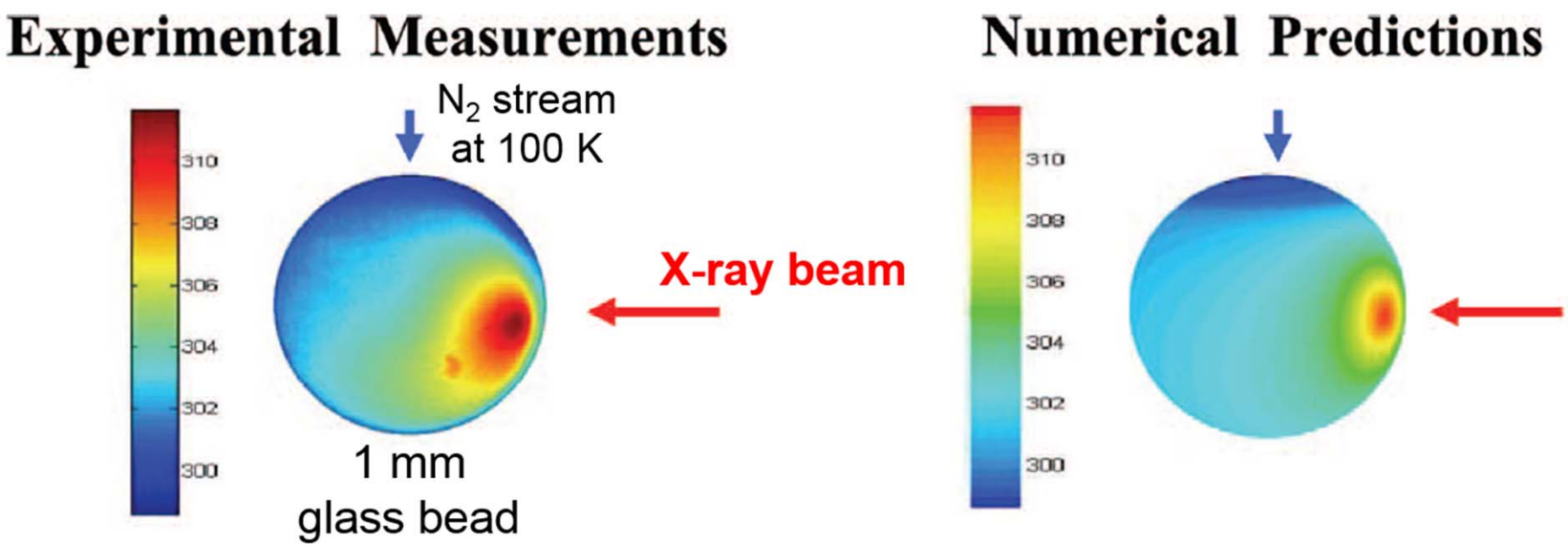
Steady-state model

Parameters:
Linear absorption coefficient
$\mu$ = 5 cm$^{-1}$
Thermal conductivity
0.6 W/(m K)
Convective heat-transfer coefficient
346 W/(m$^2$ K)

| Incident power, W/cm$^2$ | X-ray flux phot/(s cm$^2$) | $T_{wall} - T_0$ K | $T_{max} - T_{wall}$ K |
|---|---|---|---|
| Using data from Mhaisekar et. al., *J. Synchrotron Rad.* (2005) **12**, 318 | | | |
| 84 | $4\times10^{16}$ | 14 | 1.1 |
| 840 | $4\times10^{17}$ | 142 | 11 |
| At SRX beamline | | | |
| $3\times10^{6}$ | $1.4\times10^{21}$ | **$5\times10^{5}$ ?!** | **$4\times10^{4}$ ?!** |
| $3\times10^{7}$ | $1.4\times10^{22}$ | **$5\times10^{6}$ ?!** | **$4\times10^{5}$ ?!** |

$\Delta$T values scale essentially linear with X-ray flux and beam size in this model

# How Good Is the Theoretical Model?




Kazmierczak et. al., *J. Heat Transfer* (2007) **129**, 936

Good agreement between theory and experiment suggests that heating may be extensive for some samples at the SRX beamline , which will promote radiation damage. Helium cooling may be required to reduce these effects.

# Techniques for Combating Radiation Damage

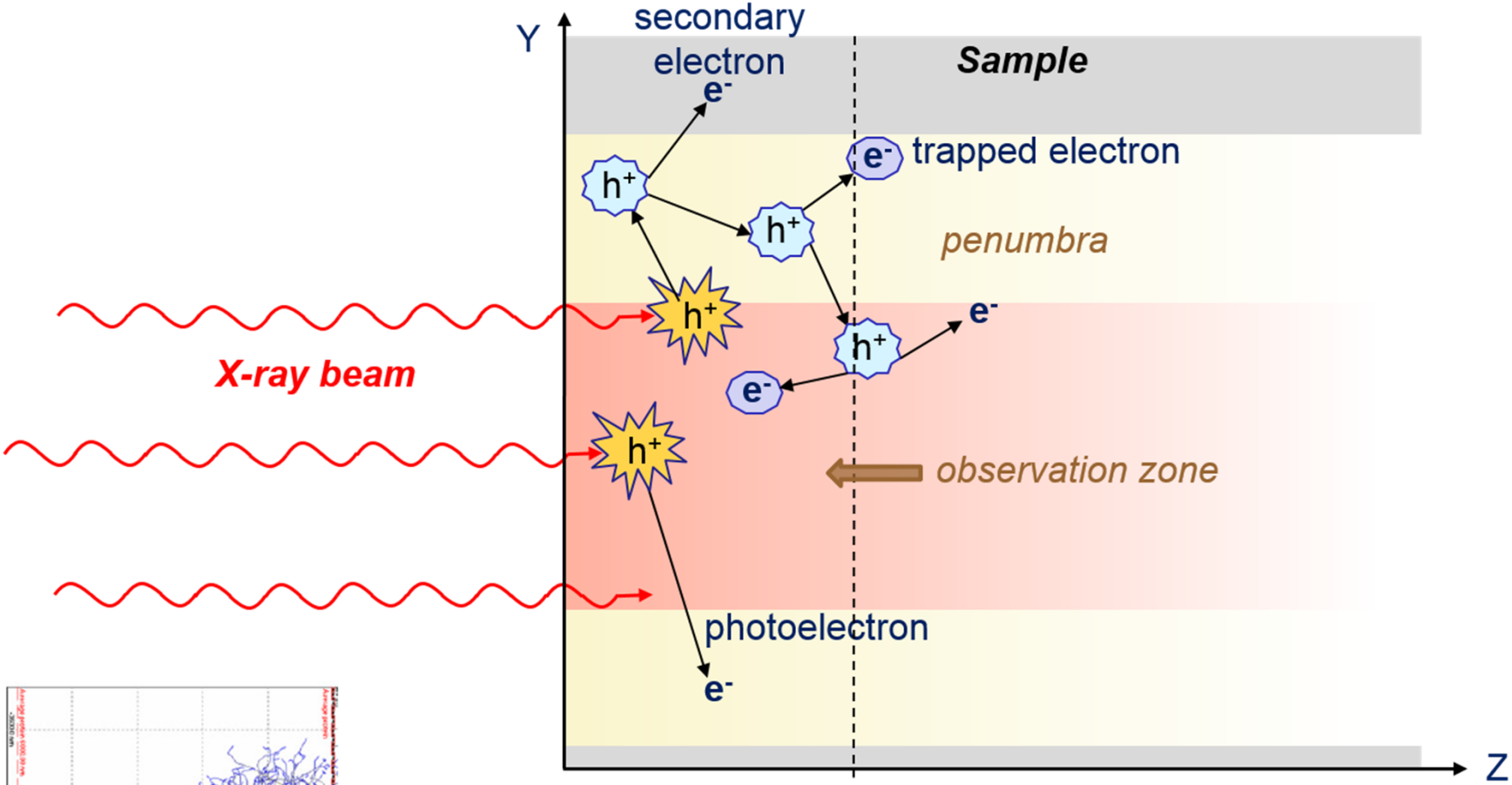
- Cryo-cooling to prevent diffusion-controlled radicals reactions

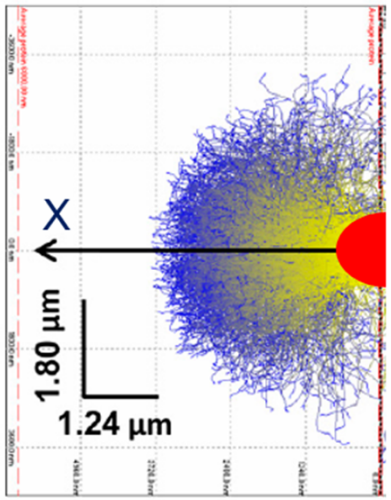
- Adding radical scavengers; e.g., co-crystallization of proteins with ascorbate

- Outrunning damage:
  - decreasing beam exposure by employing beam shutters, bunched x-ray pulses, or shortening data collection time
  - using “diffraction before destruction” approach; available only with free-electron lasers (e.g., recent experiments with < 50 fs X-ray pulses at LCLS: Kern et. al., *PNAS* (2012) **109**, 9721)

- Using tightly-focused X-ray beams:
  - sample translation to expose a fresh observation area
  - export damage outside observation zone

# Spatial Distribution of Radiation Dose

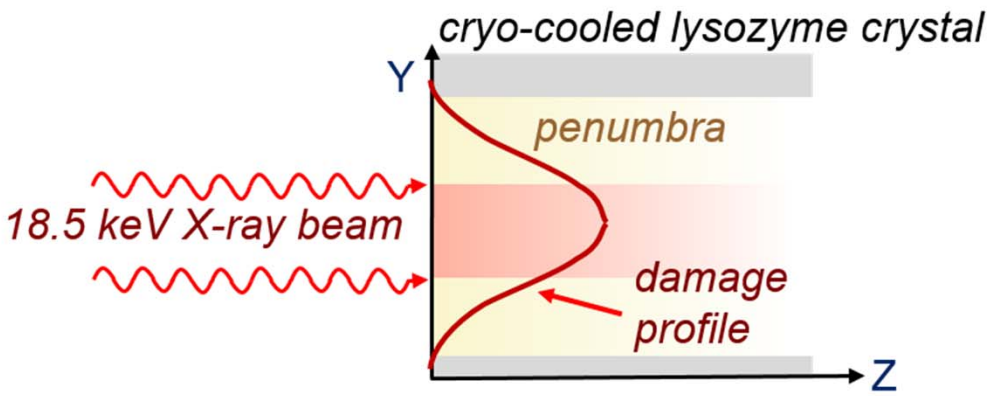


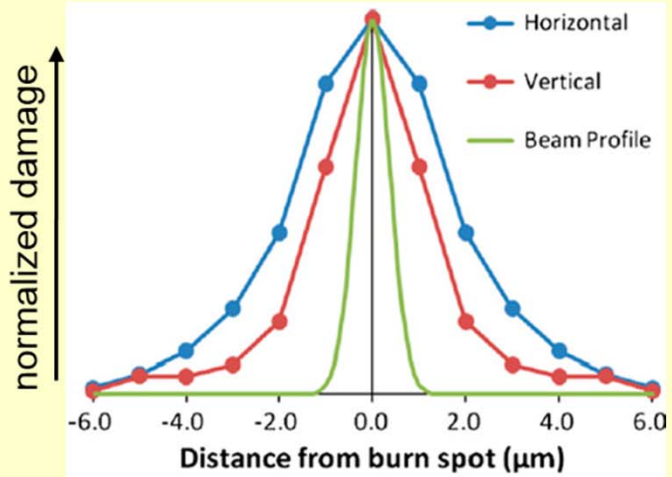




Monte Carlo simulation of photoelectron trajectories for 1 µm diameter horizontally-polarized 14.4 keV X-ray beam. Photoelectron range ~ 3.5 µm

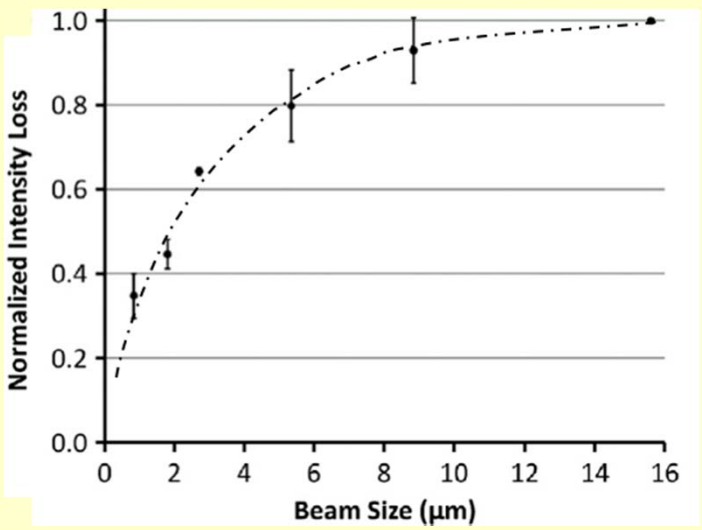
Sanishvili et. al., *PNAS* (2011) **108**, 6127

# Export of Radiation Damage from Observation Zone




Spread of radiation damage for 18.5 keV, 0.84 μm beam




Decrease in damage rate with decrease of beam diameter from 15.6 to 0.84 μm

- Significant fraction of radiation energy is deposited in ~5 μm penumbra, outside illuminated volume
- This fraction may reach over 90% for sub-100 nm beams

Sanishvili et. al., *PNAS* (2011) **108**, 6127

# Conclusions

- The SRX beamline will expose samples to extremely high (well over 100 Giga-Gy/s) radiation dose rates. Sample damage will be very rapid and extensive. Sufficiently fast detection and/or X-ray beam modulation will be required for outrunning the damage.

- Radiation heating may be extensive for some samples at the SRX beamline, which will further promote radiation damage. Helium cooling may be required to mitigate these effects.

- Significant stopping range of photoelectrons will export a substantial fraction of radiation damage outside observation zone. This effect will decrease radiation damage in the observation zone, but may compromise spatial resolution in imaging, tomography, or element mapping.