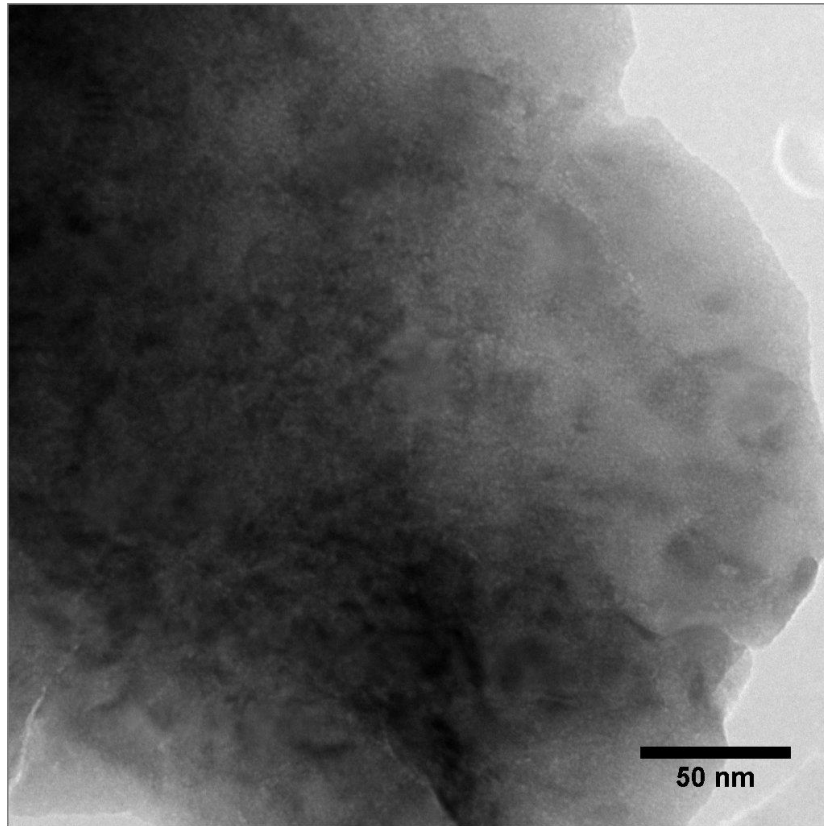


# Helium Behavior in Pyrochlore Type Nuclear Waste Form Materials

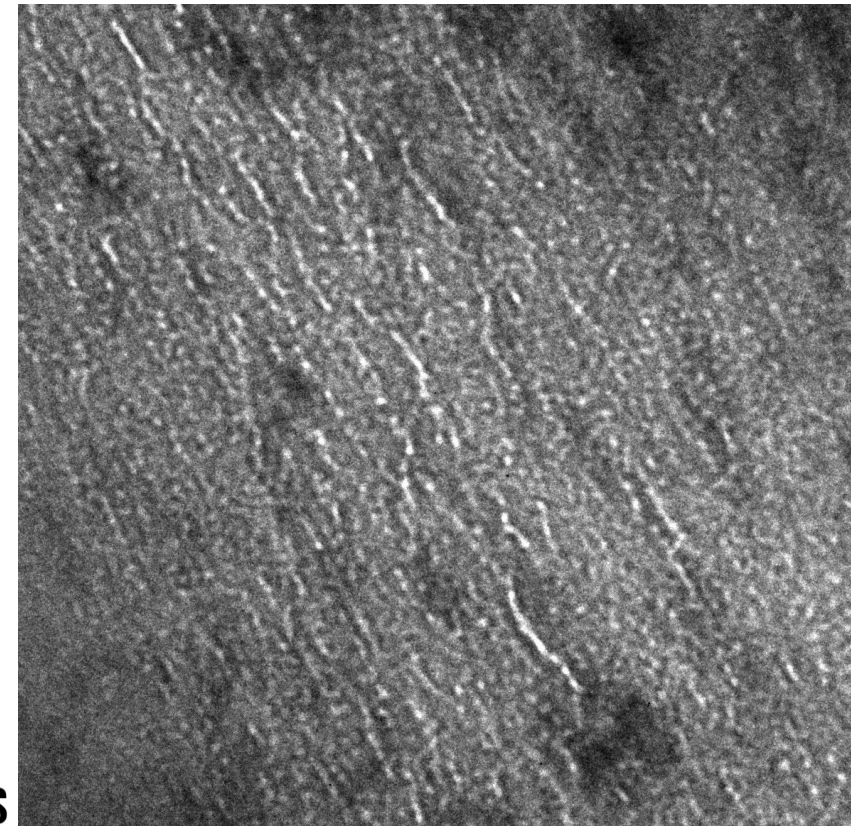
SAND2017-5651C

Caitlin A. Taylor<sup>1,2</sup>, Maulik K. Patel<sup>2</sup>, Jeffery A. Aguiar<sup>3</sup>, Xunxiang Hu<sup>4</sup>, Yanwen Zhang<sup>4,2</sup>, Miguel L. Crespillo<sup>2</sup>, Juan Wen<sup>5</sup>, Haizhou Xue<sup>2</sup>, Yongqiang Wang<sup>5</sup>, William J. Weber<sup>2,4</sup>, Khalid Hattar<sup>1</sup>



1. Sandia National Laboratories
2. University of Tennessee, Knoxville
3. Idaho National Laboratory
4. Oak Ridge National Laboratory
5. Los Alamos National Laboratory

May 22<sup>nd</sup>, 2017



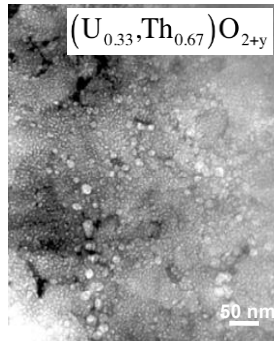
This work was supported by the US Department of Energy, Office of Basic Energy Sciences and the Nuclear Energy University Program. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.



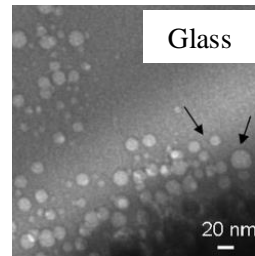
# Background on Crystalline Nuclear Waste Forms

In crystalline waste forms, radionuclides are incorporated into lattice site positions

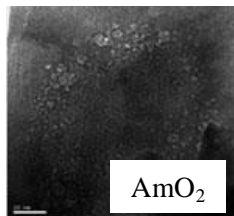
- **Complex** crystal structures
- Increases **chemical durability** (i.e. lower leach rates)
- Allows for easier **prediction of corrosion and alteration** mechanisms
- Mineral analogues provide long-term points of comparison



T. Wiss *et al.*, JNM (2014)

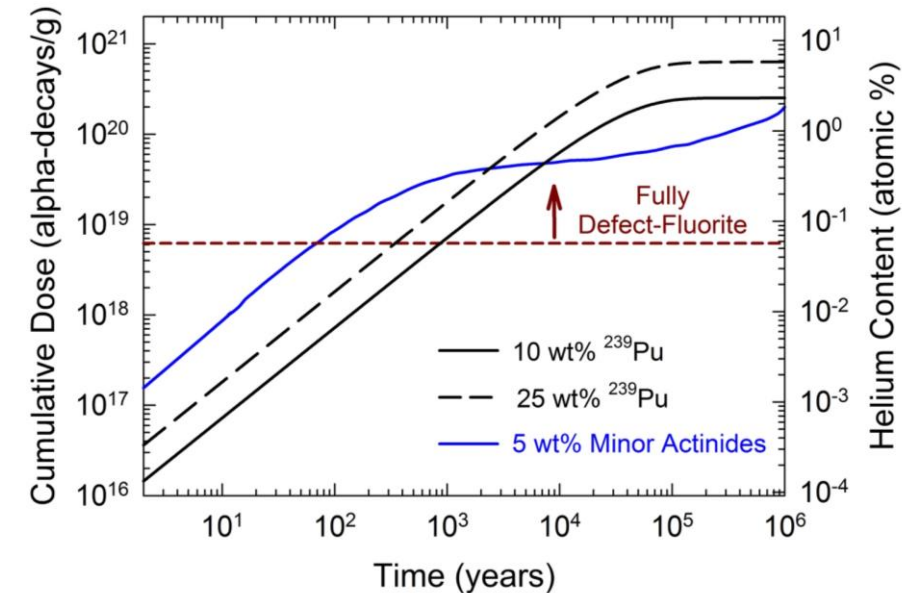


G. Gutierrez *et al.*, JNM (2014)



T. Wiss *et al.*, JNM (2015)

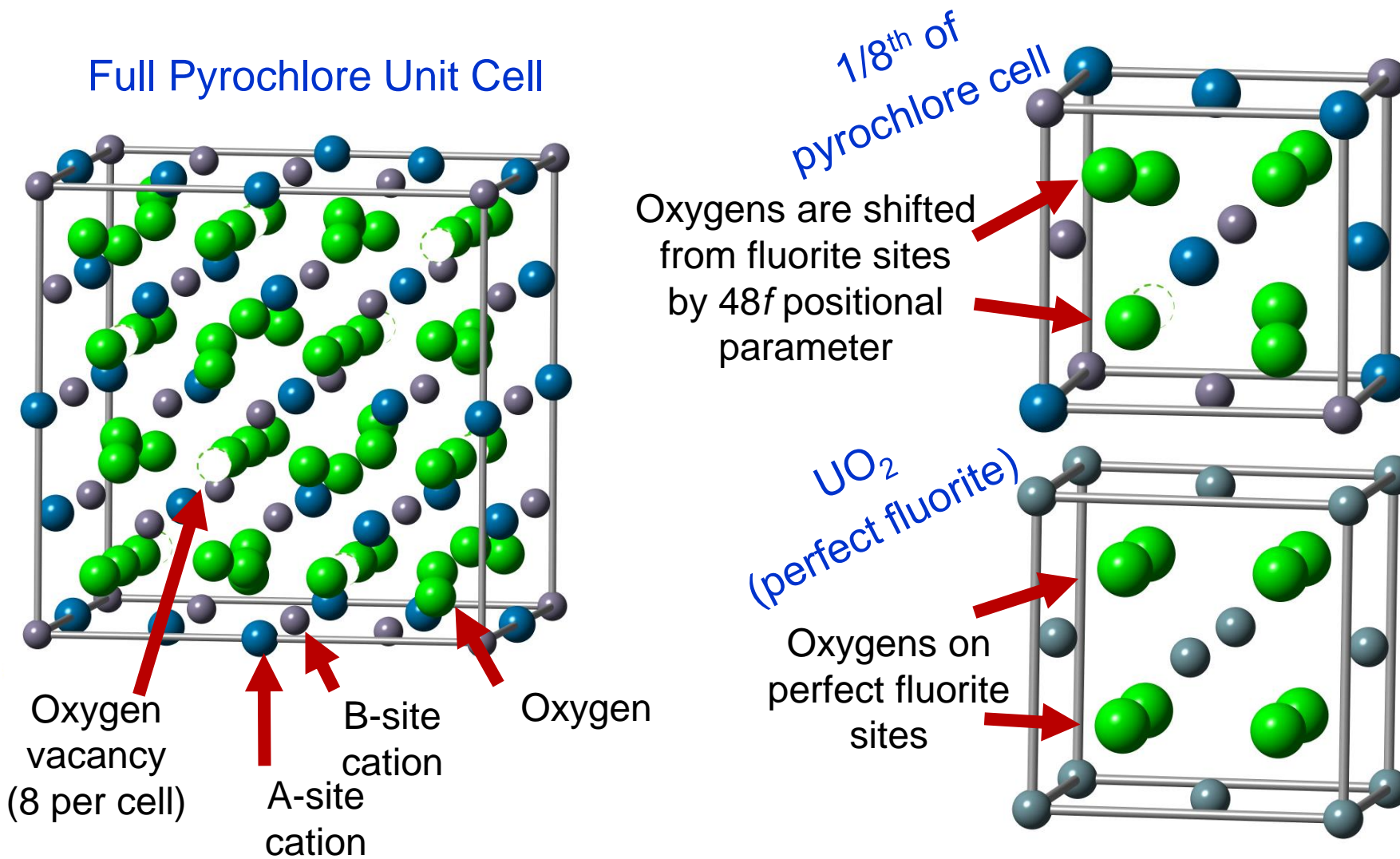
## Evolution of $\alpha$ -decay dose in $Gd_2Zr_2O_7$ over geological time



Alpha-decay produces both damage and He buildup in the lattice

- High He concentrations expected over geologic time will **strain** the crystalline lattice
- Helium buildup can result in nano-sized **bubble formation** at high concentrations (several at.%) in ceramics, which leads to cracking at high concentrations

# Pyrochlore, $A_2B_2O_7$ , is Similar to Fluorite in Structure

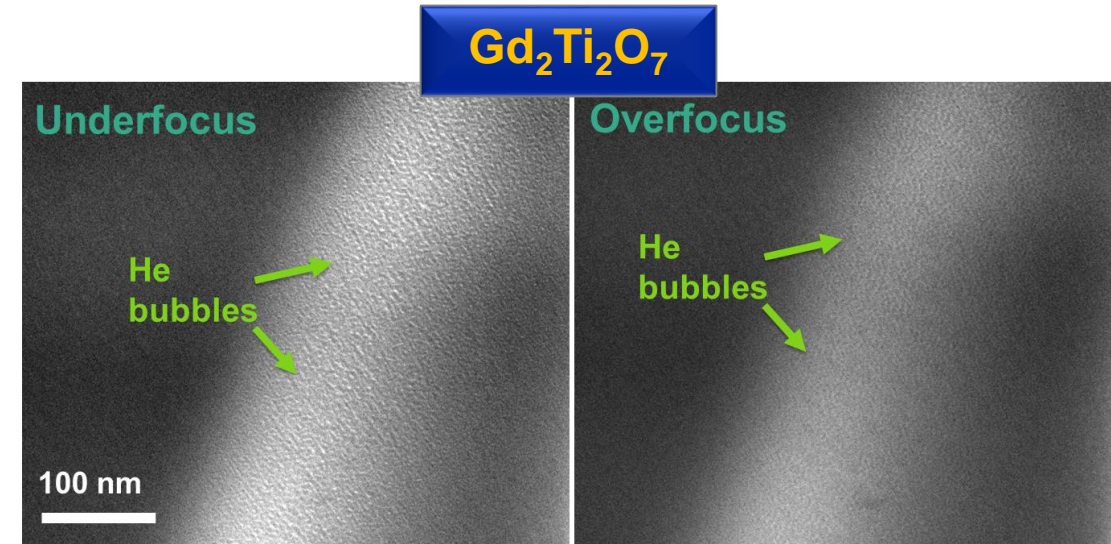
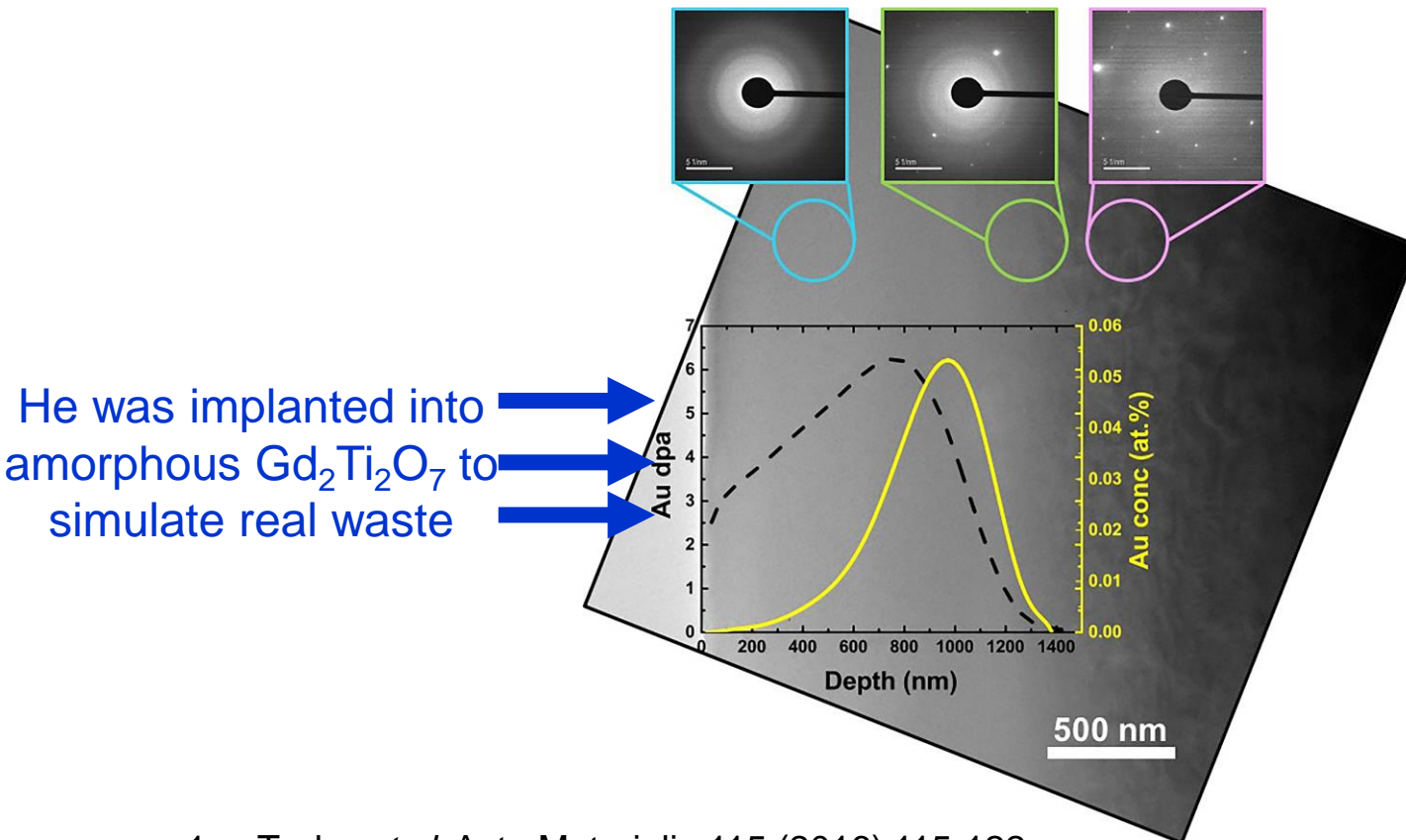


## Under Irradiation

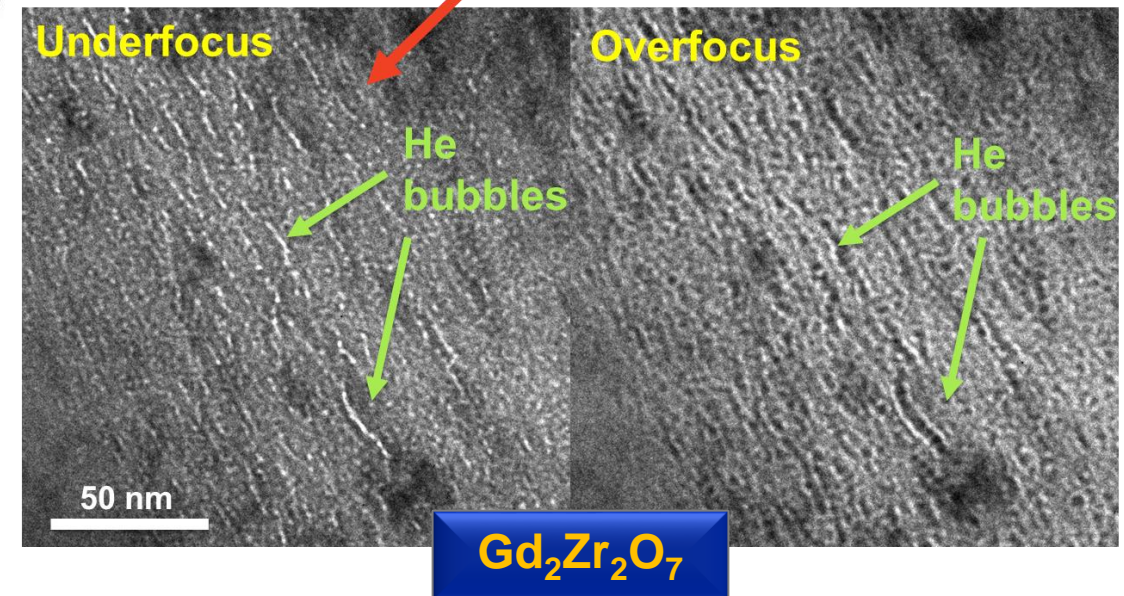
- $Gd_2Ti_2O_7$  undergoes a pyrochlore to **amorphous** transformation
- $Gd_2Zr_2O_7$  undergoes a pyrochlore to **defect-fluorite** transformation
  - Cations and oxygen vacancies completely disordered

# He Bubble Formation in Pyrochlore Pre-Damaged with 7 MeV Au<sup>3+</sup>

- Bulk samples were pre-damaged with 7 MeV Au<sup>3+</sup> to induce phase transformations, then implanted with He
- Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> formed bubbles at ~6 at.%, Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> formed bubbles at ~4.6 at.%



Individual bubbles formed "chains" 10-30 nm in length

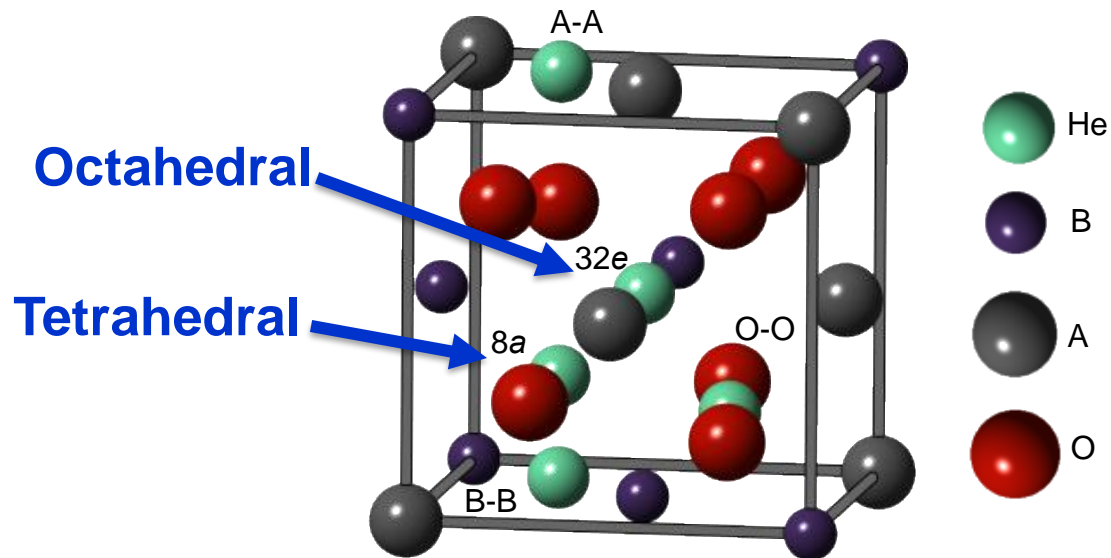


1. Taylor *et al.* Acta Materialia 115 (2016) 115-122
2. Taylor *et al.* Journal of Nuclear Materials 479 (2016) 542-547

# Preferred site for interstitial He can be predicted using Voronoi volume calculations

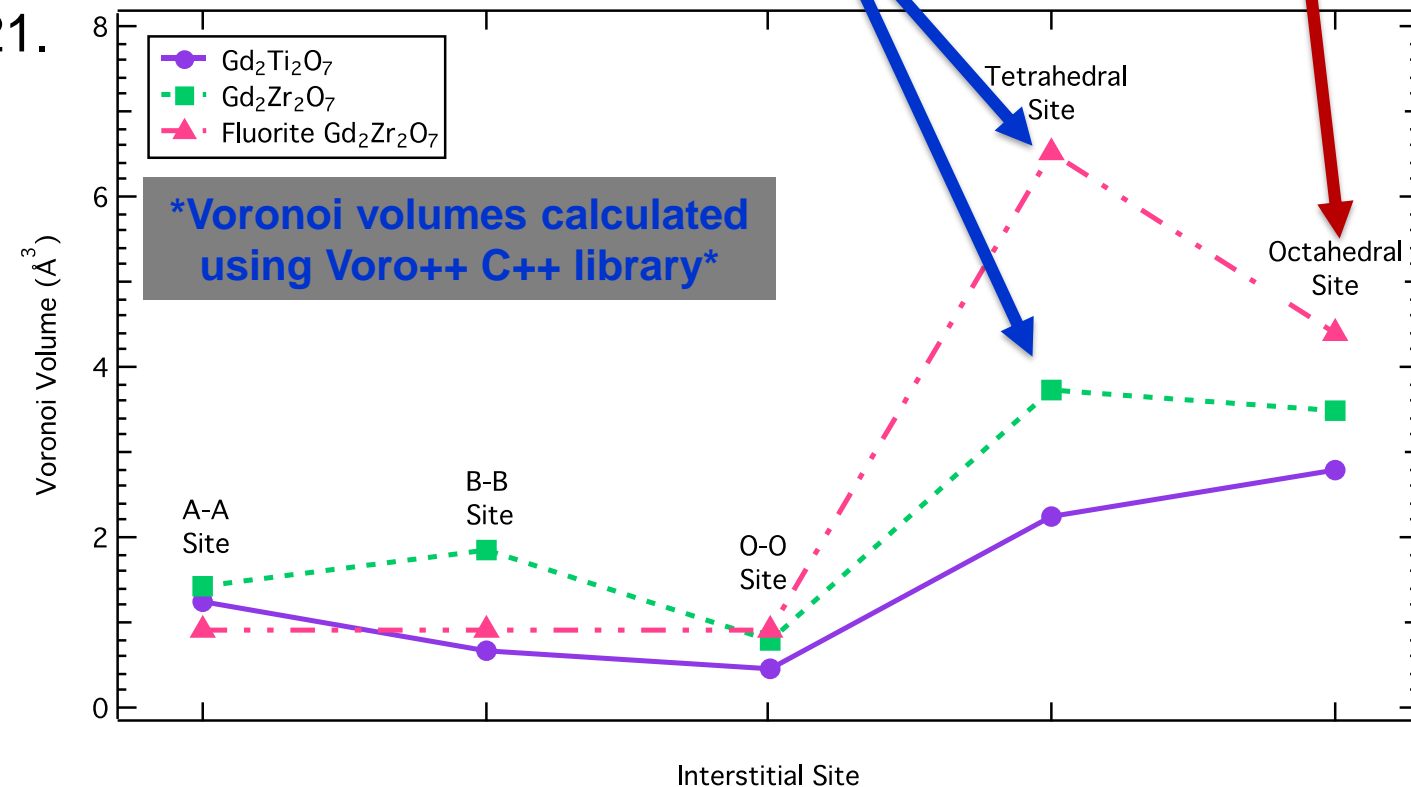
- In a perfect lattice, He will reside in interstitial sites.
- He was shown to prefer the octahedral interstitial site in  $\text{Y}_2\text{Ti}_2\text{O}_7$ , prefers individual sites as opposed to clustering → **did not consider vacancy binding**
  - Danielson *et al.* JNM **452** (2014) 189-196.
  - Yang *et al.* JAP **115** (2014) 143508.
- Interstitial He diffuses between octahedral sites with  $E_m \sim 0.5$  eV in  $\text{Y}_2\text{Ti}_2\text{O}_7$ 
  - Danielson *et al.* JNM **477** (2016) 215-221.

**He prefers larger interstitial sites**



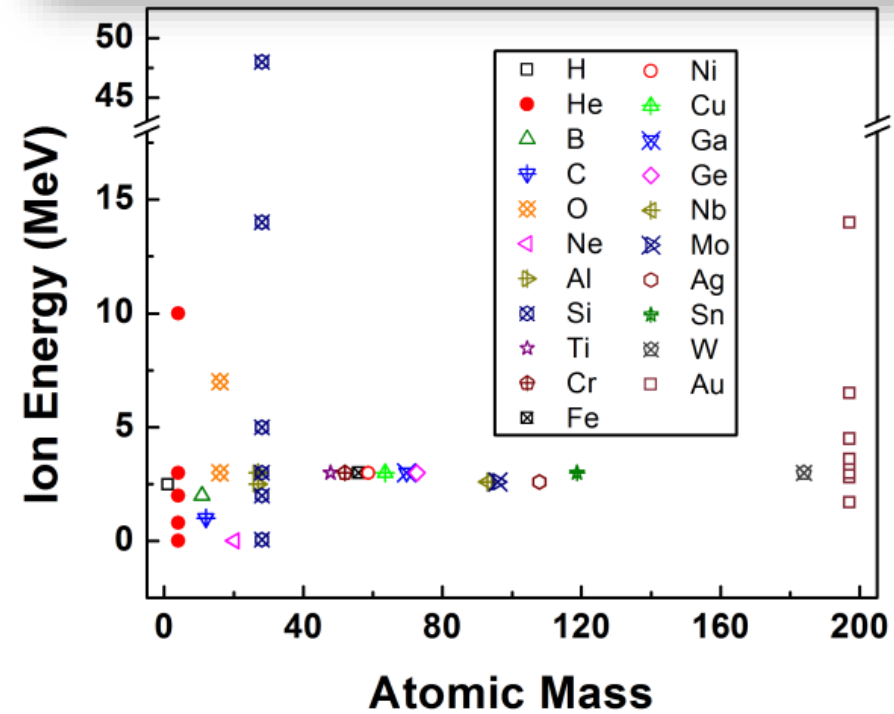
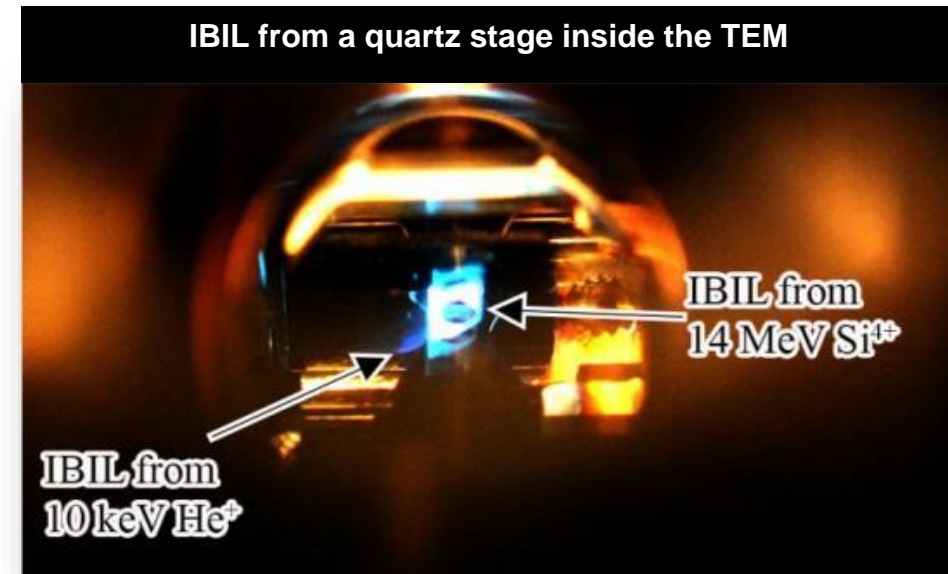
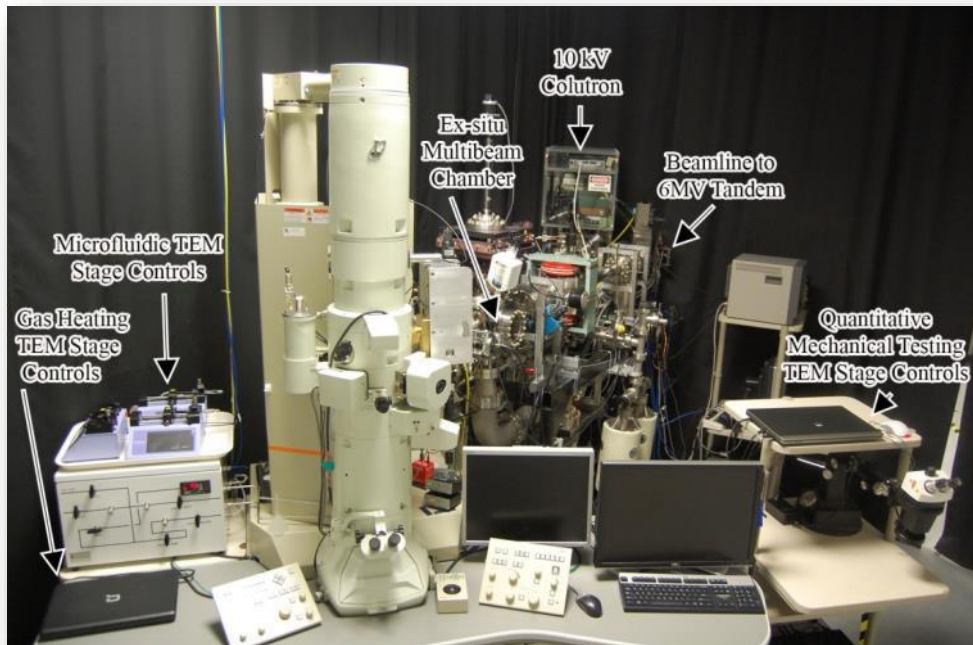
**Tetrahedral site appears most favorable in pyrochlore and fluorite  $\text{Gd}_2\text{Zr}_2\text{O}_7$**

**Octahedral site most favorable in  $\text{Gd}_2\text{Ti}_2\text{O}_7$**



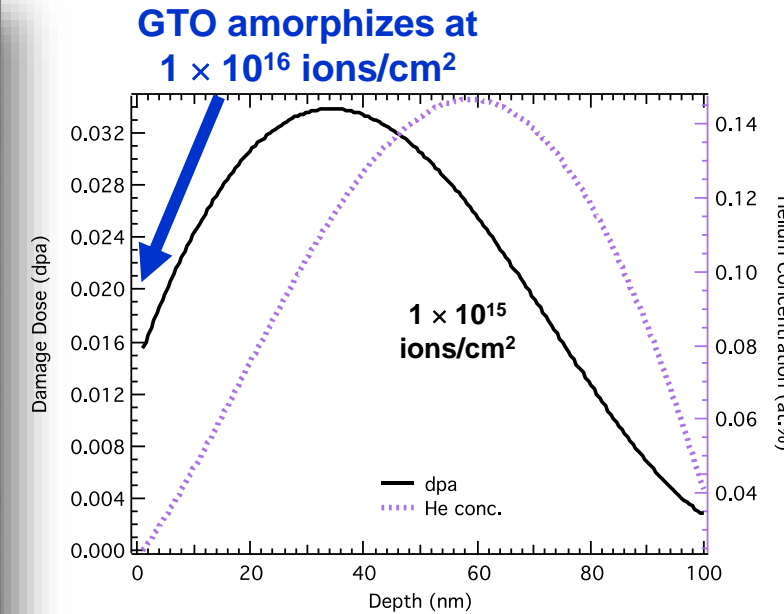
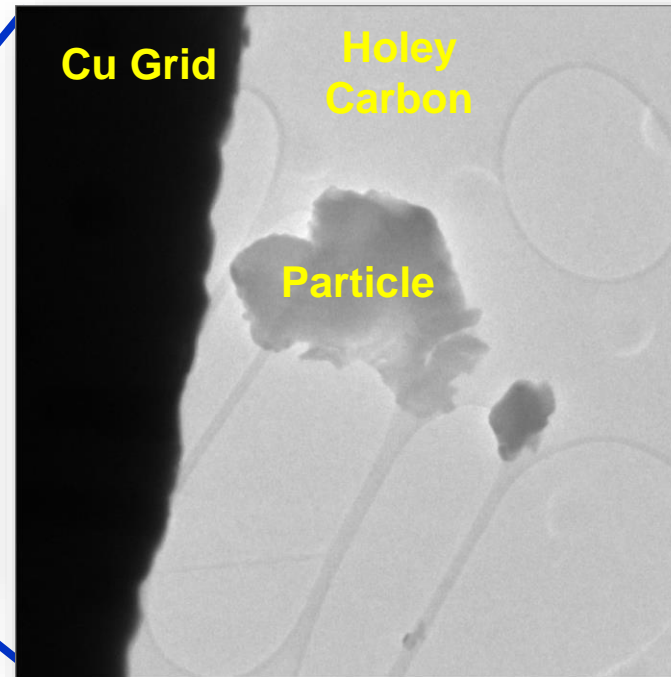
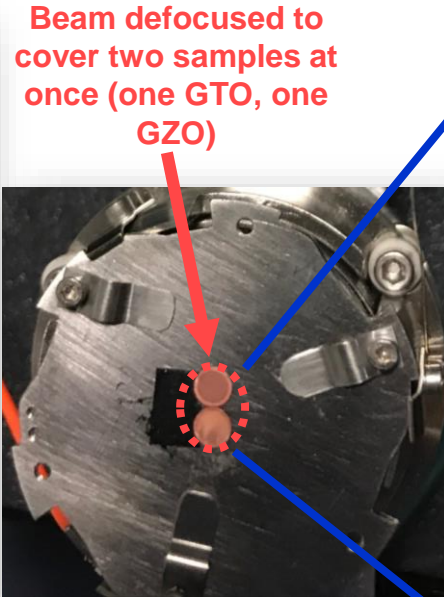
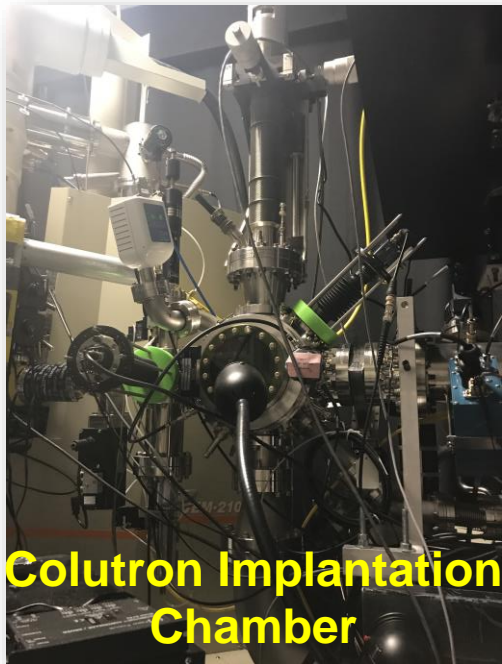
# Sandia's Concurrent *In situ* Ion Irradiation TEM Facility

10 kV Colutron - 200 kV TEM - 6 MV Tandem



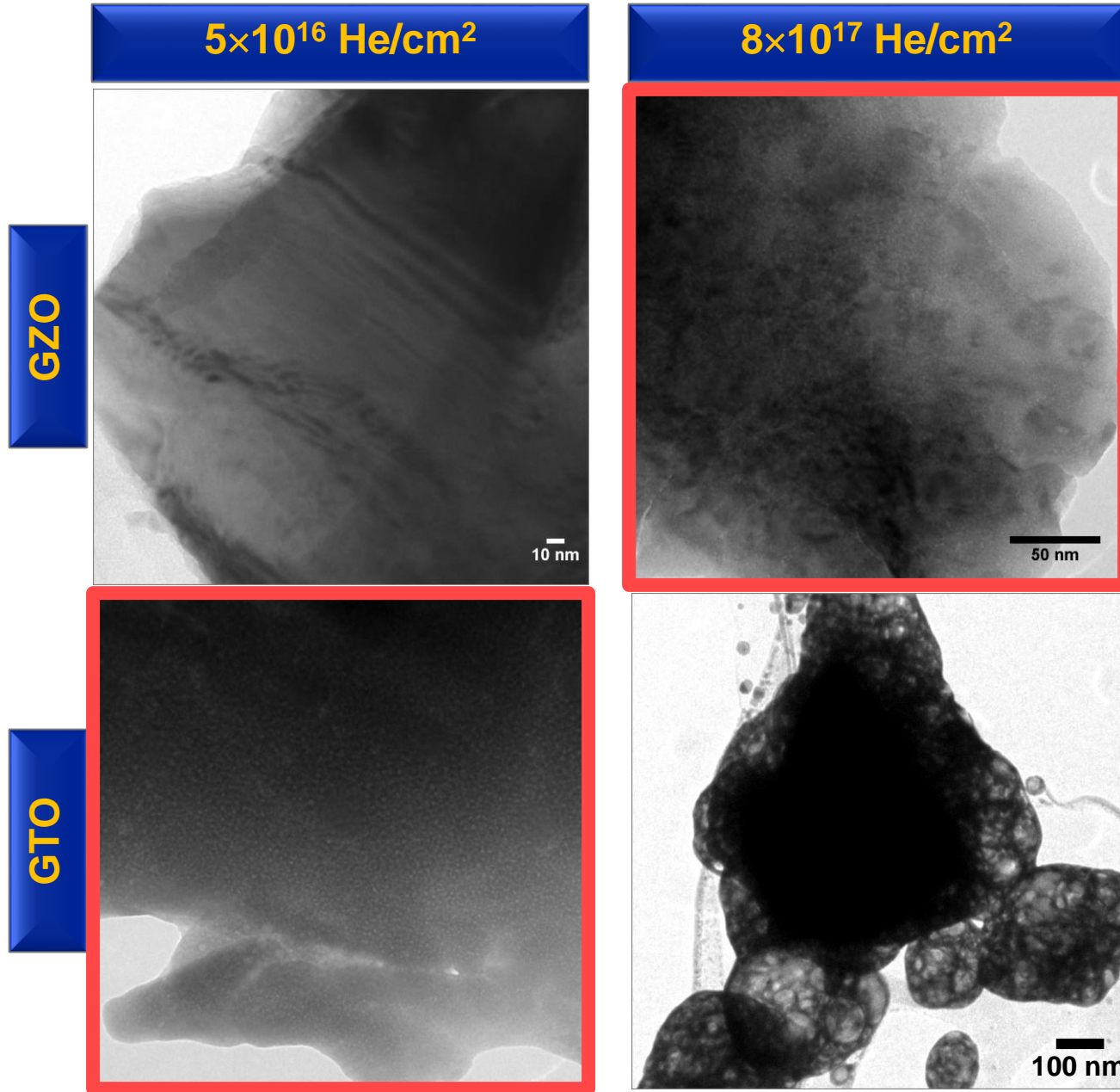
# Effect of Particle Size on Bubble Growth

- GTO and GZO TEM samples were prepared by drop-casting powders onto holey-C TEM Grids
- Samples were implanted ex-situ at 300 K using the Colutron



**Goal is to compare ex-situ implants/in-situ annealing with in-situ implants at RT and HT**

# He Bubbles Formed at Higher Dose in GZO than in GTO



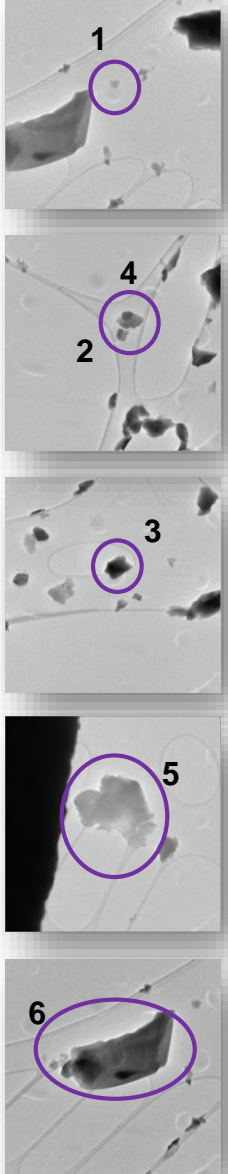
- No bubbles observed in GZO sample implanted with  $5 \times 10^{16}$  He/cm<sup>2</sup>
- High density of small bubbles observed in GTO sample implanted with  $5 \times 10^{16}$  He/cm<sup>2</sup>
- High density of small bubbles observed in GZO sample implanted with  $8 \times 10^{17}$  He/cm<sup>2</sup>
- Large cavities observed in GTO sample implanted with  $8 \times 10^{17}$  He/cm<sup>2</sup>
  - Dissolve under e-beam

**Samples with high density of small bubbles were annealed in-situ:**

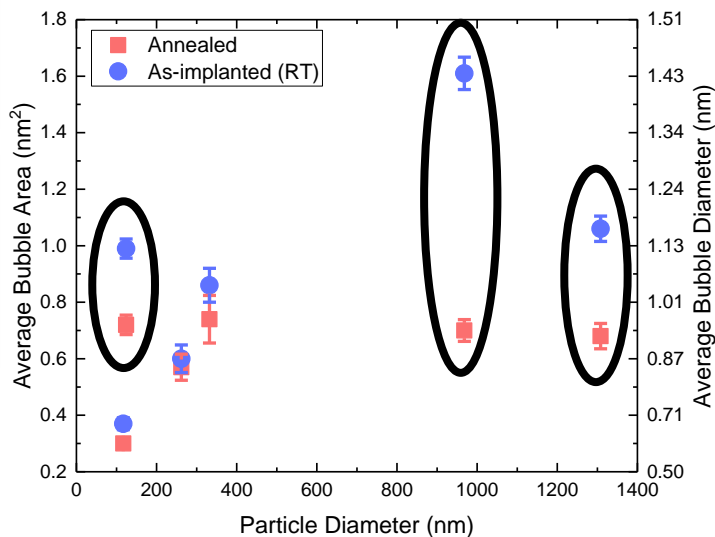
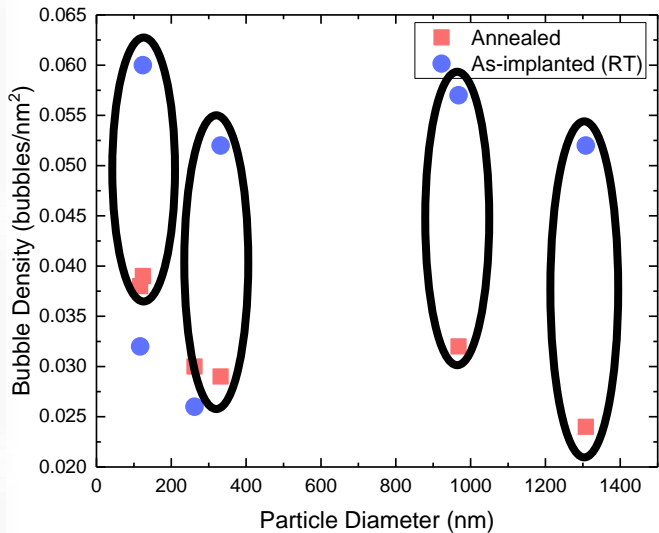
- **Annealed in steps of 100°C, stopping at each step for 20 min, up to 700°C**

# Effect of Particle Size on Bubble Growth and Density Changes

Particles  
12,000x



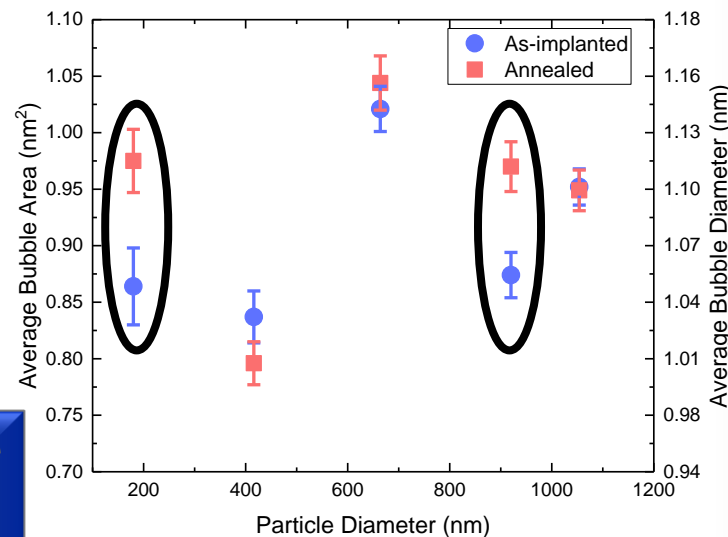
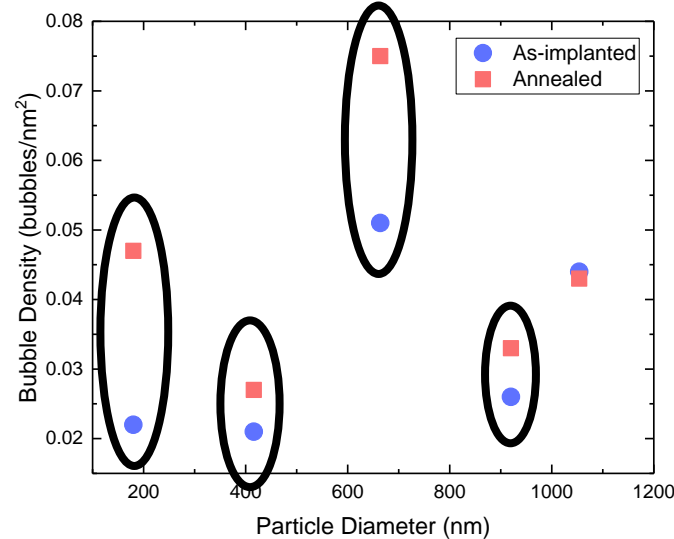
GTO after  $5 \times 10^{16}$  He/cm<sup>2</sup>



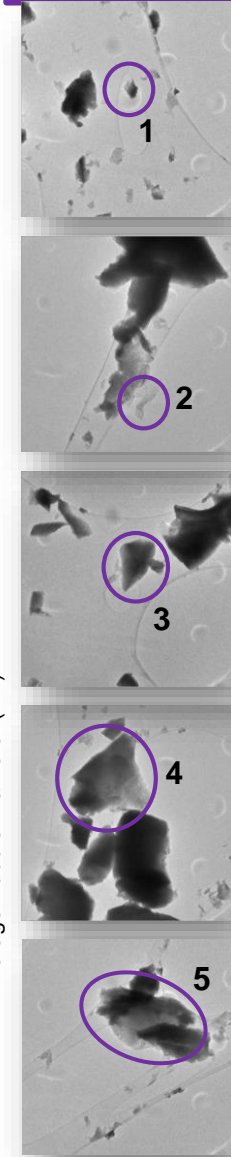
- ❖ Bubble density *decreased* after annealing in 4/6 GTO particles and *increased* after annealing in 4/5 GZO particles. **No strong dependence on particle size.**
- ❖ Bubble area *decreased* in 3/6 GTO particles after annealing (others unchanged), and *increased* in 2/5 particles in GZO (others unchanged). **Larger particles had larger decrease in bubble area in GTO, no apparent particle size effect in GZO.**

**Observed trends may be due to thickness, not diameter**

GZO after  $8 \times 10^{17}$  He/cm<sup>2</sup>

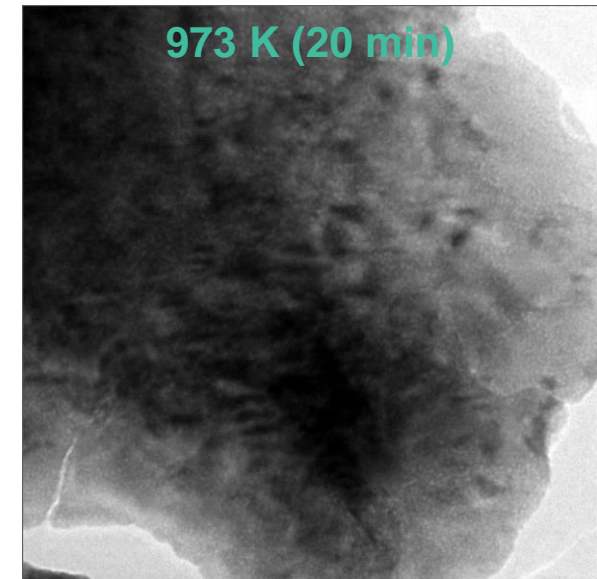
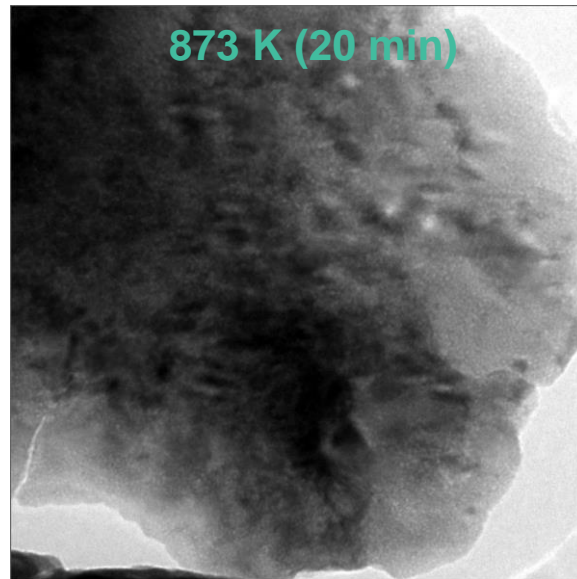
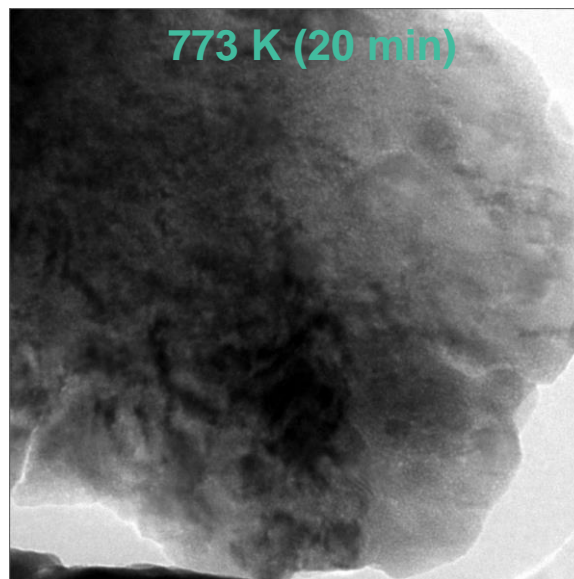
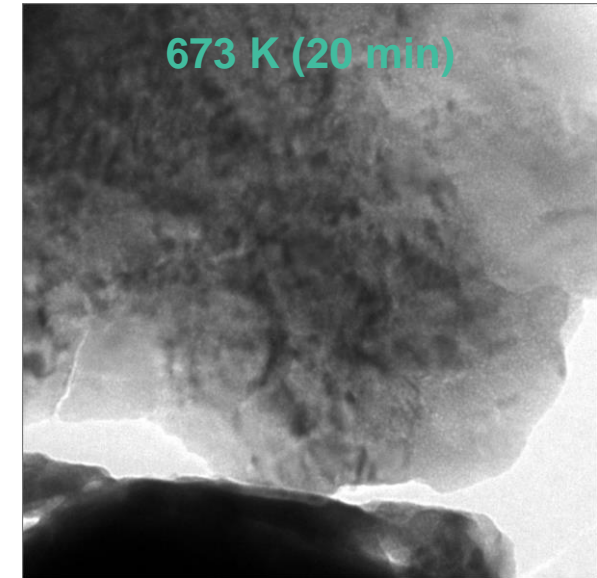
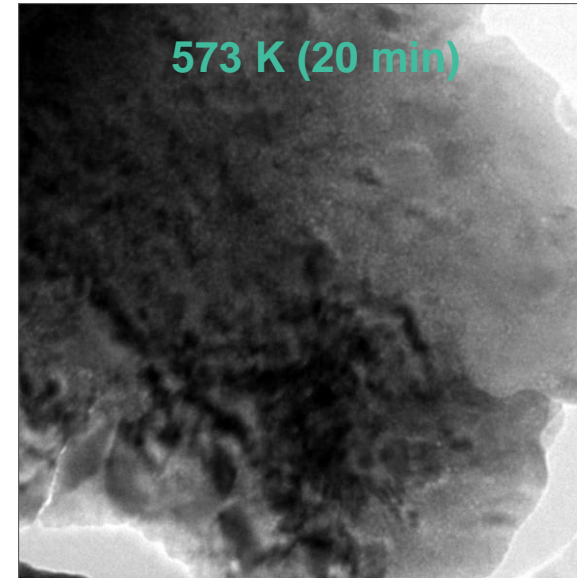
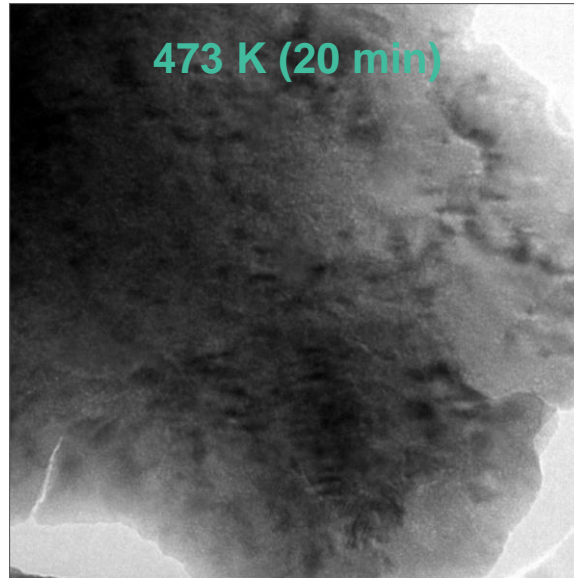
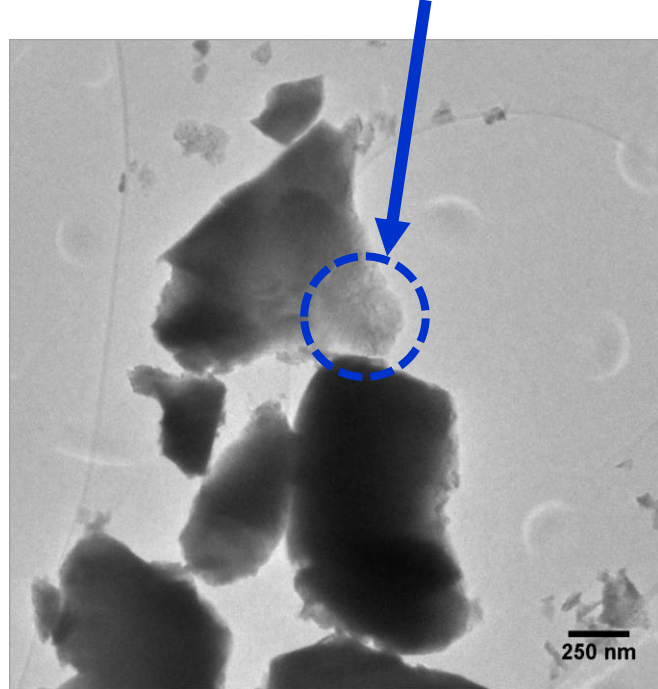


Particles  
12,000x



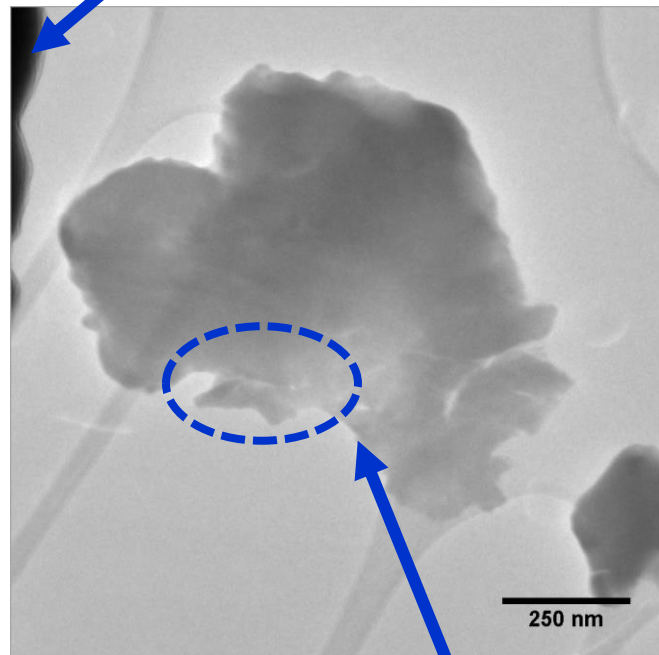
# In-situ annealing experiments revealed kinetics of He evolution with high density of bubbles present in material- $\text{Gd}_2\text{Zr}_2\text{O}_7$

Imaged region in grid window (not over C film)



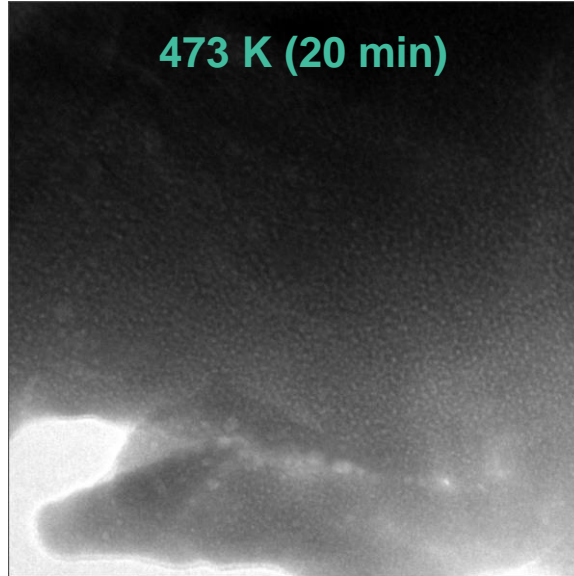
# In-situ annealing experiments revealed kinetics of He evolution with high density of bubbles present in material- $\text{Gd}_2\text{Ti}_2\text{O}_7$

Chose particle close to Cu grid for best thermal flow

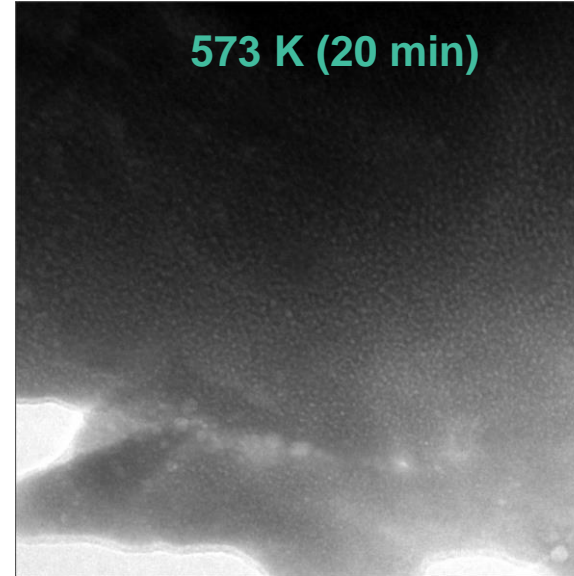


Imaged region in grid window (not over C film)

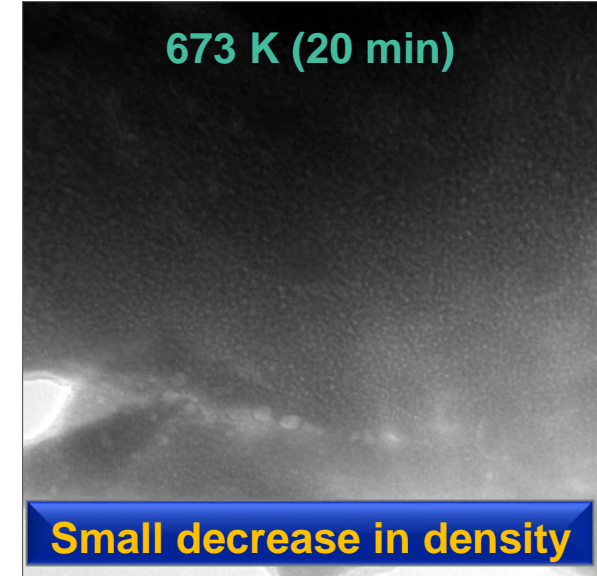
473 K (20 min)



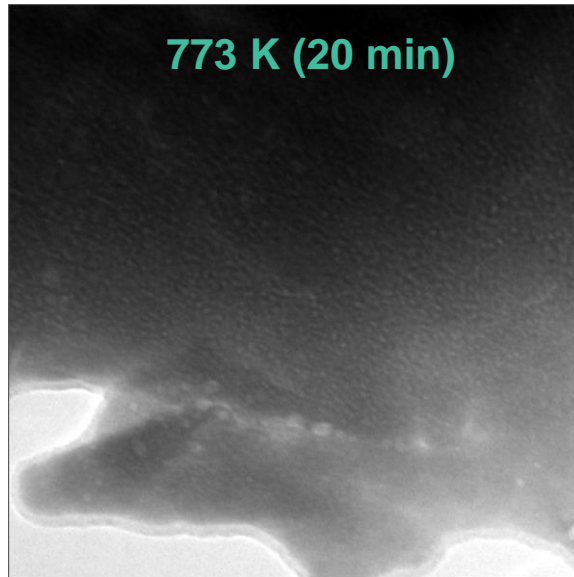
573 K (20 min)



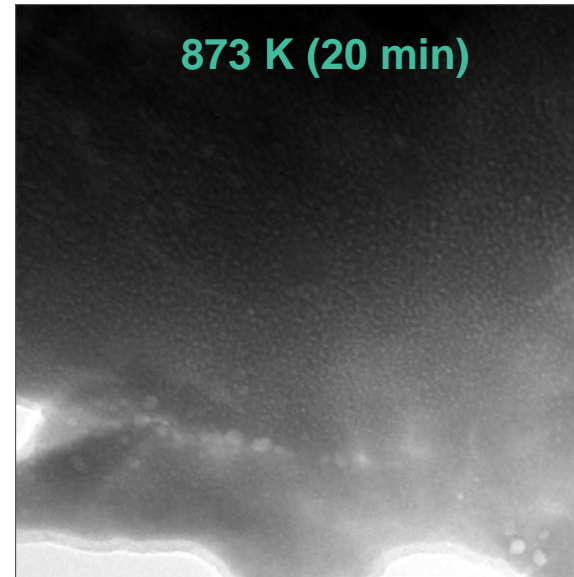
673 K (20 min)



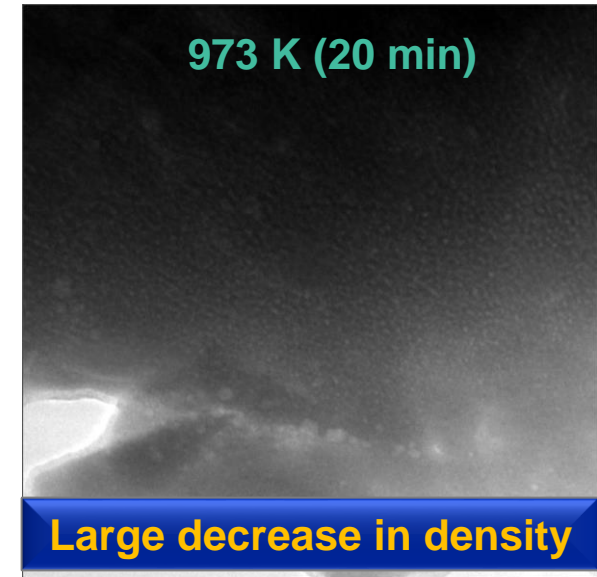
773 K (20 min)



873 K (20 min)

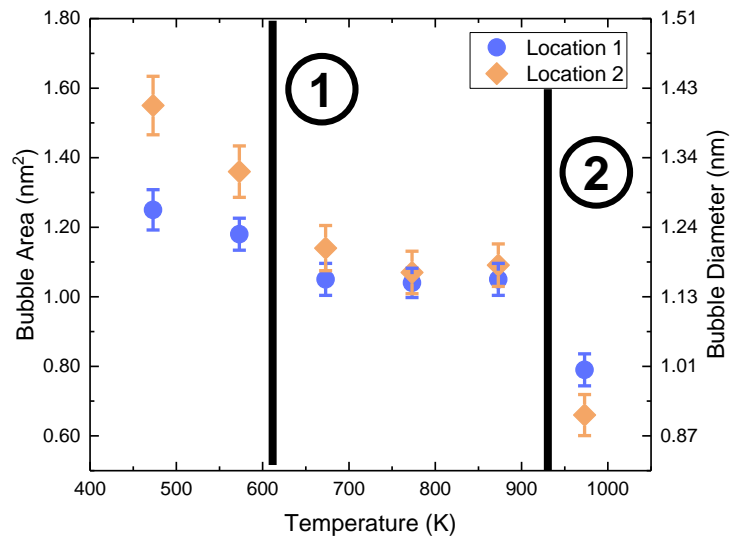
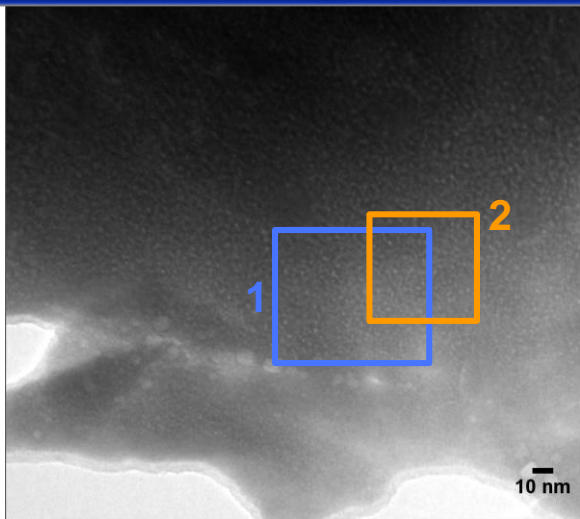


973 K (20 min)

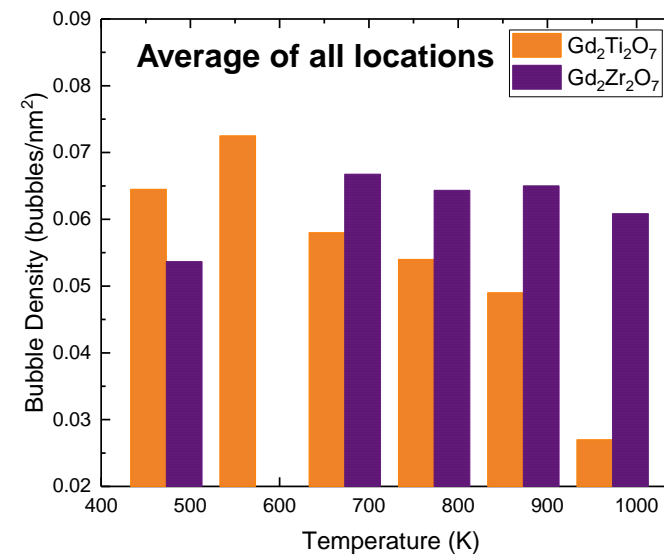


# Quantifying bubble size and density changes during annealing

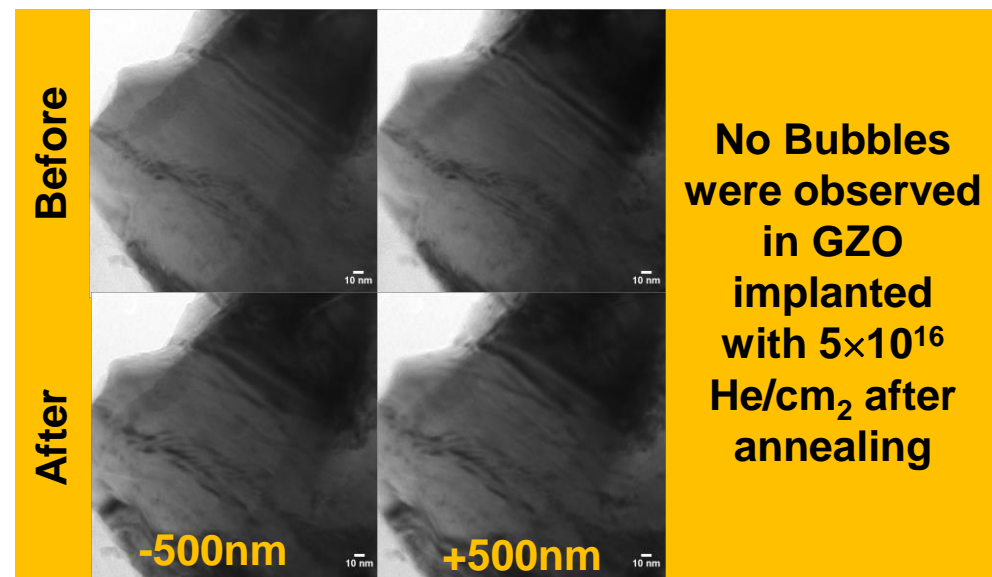
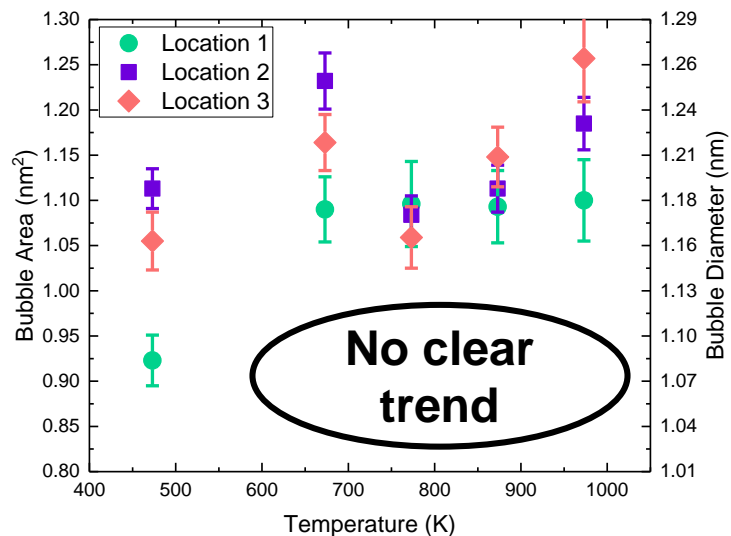
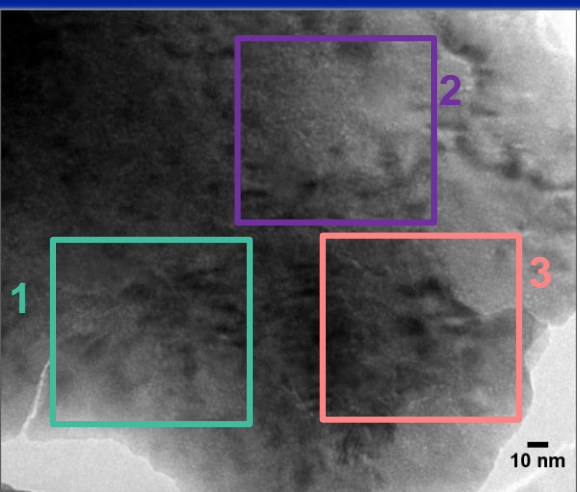
GTO after  $5 \times 10^{16}$  He/cm<sub>2</sub>



Bubble Density



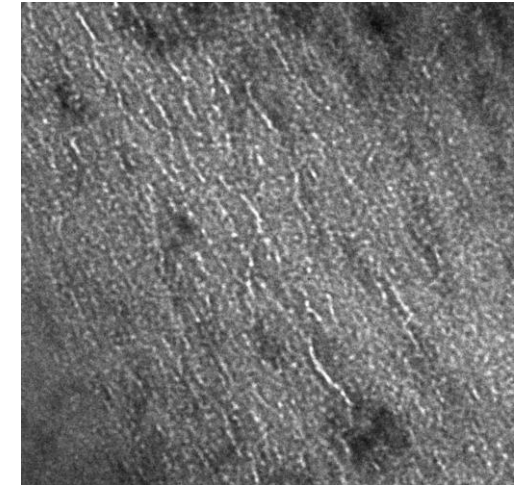
GZO after  $8 \times 10^{17}$  He/cm<sub>2</sub>





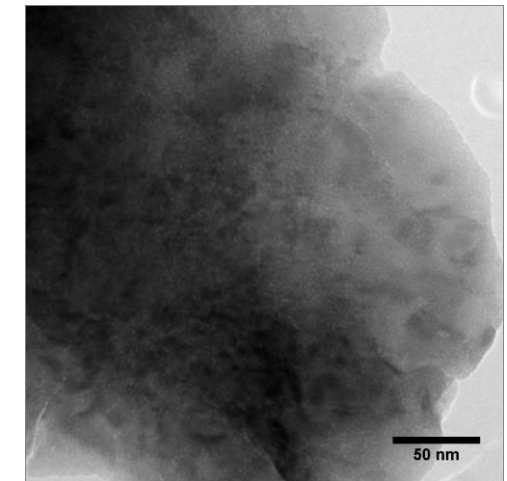
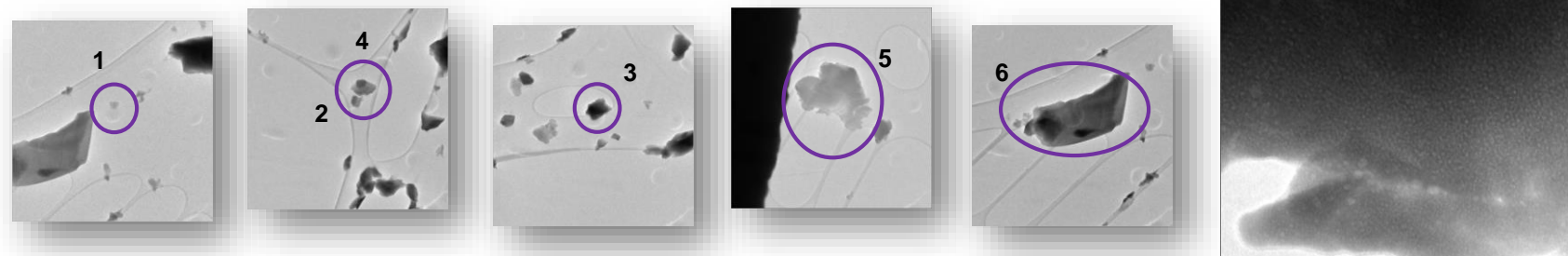
## ➤ Summary

- He implants into TEM samples resulted in a high density of bubbles at  $5 \times 10^{16}$  ions/cm<sup>2</sup> in GTO and at  $8 \times 10^{17}$  ions/cm<sup>2</sup> in GZO
  - In GTO, bubbles were about the same density and size as in bulk at 7 at.%
    - Amorphizes quickly, then seems to more easily trap He
  - In GZO, bubbles formed at a much higher fluence than in pre-damaged bulk
    - Becomes defect-fluorite, but then seems to need buildup of defects before trapping He
- Annealing of GZO implanted with  $5 \times 10^{16}$  ions/cm<sup>2</sup> resulted in no bubbles
  - Suggests that He was either very strongly trapped, or that most He diffused out of the sample during the implant



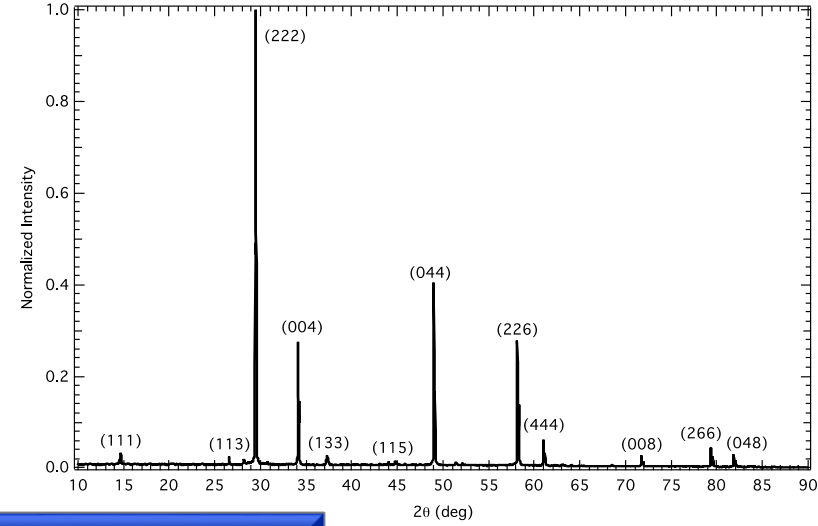
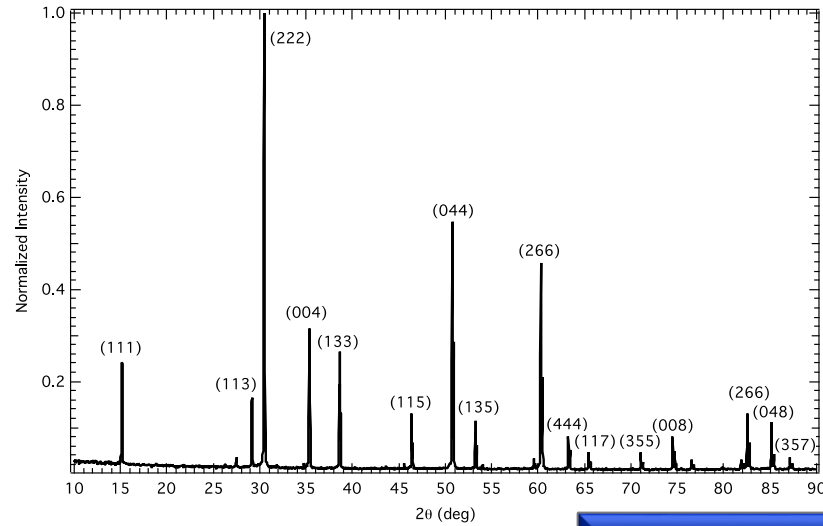
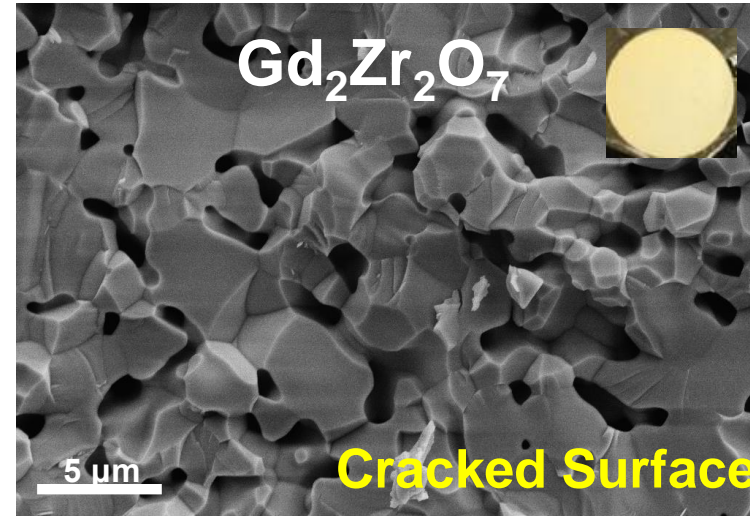
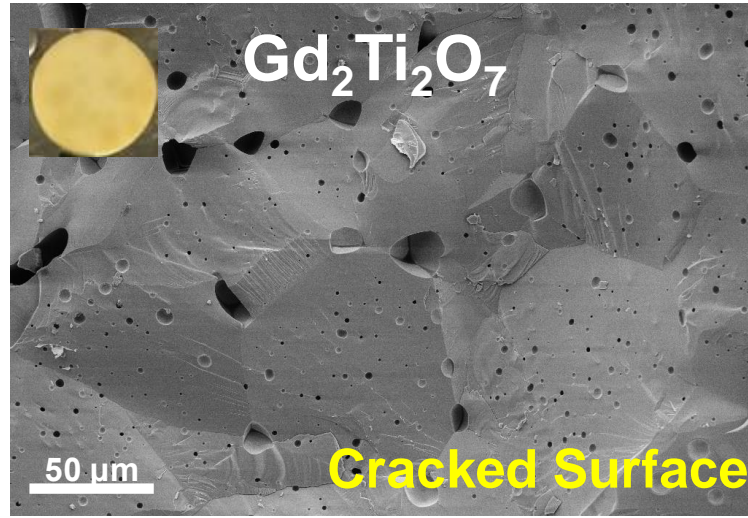
## ➤ Future Work

- Repeat annealing studies with additional fluences
- In-situ HT He implantations
- In-situ dual beam ion irradiation (Au + He)



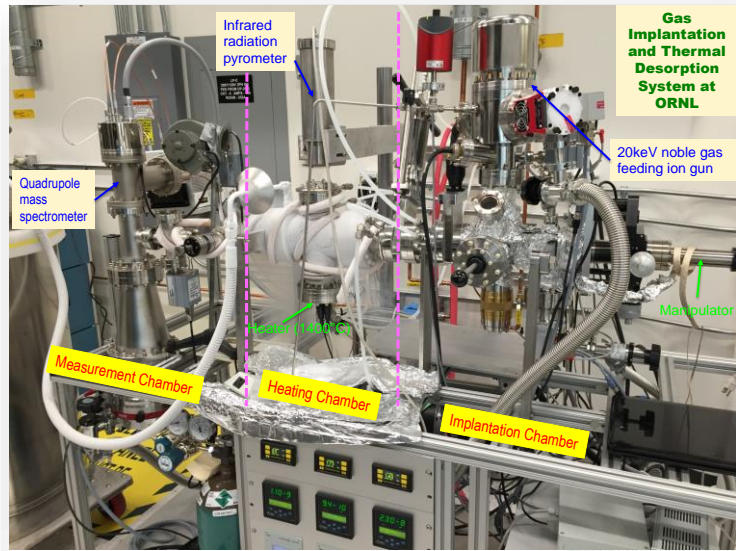


# Pyrochlore Samples Were Prepared by Conventional Solid State Synthesis in Air



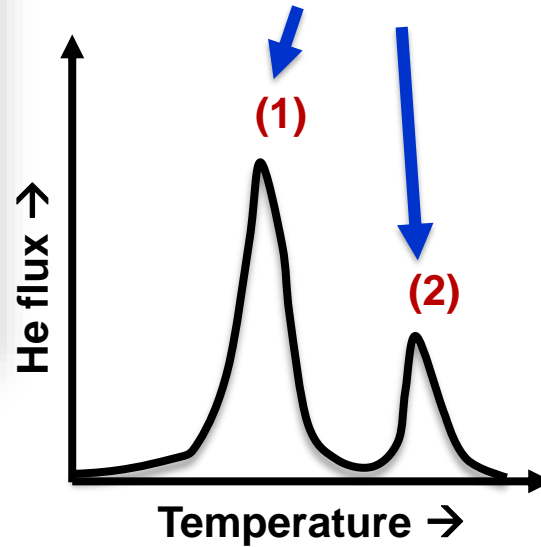
**Perfect Single Phase**

# Thermal desorption spectroscopy was used to study He trapping in $Gd_2Ti_2O_7$ and $Gd_2Zr_2O_7$



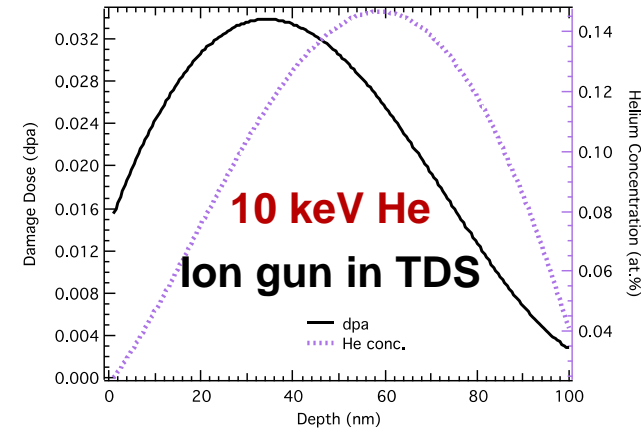
THDS measurements were performed by **Xunxiang Hu** at Oak Ridge National Laboratory

Each peak corresponds to He dissociation from a different trapping site



Defect trapping sites can be determined by comparing THDS data with  $E_D$  calculated by DFT

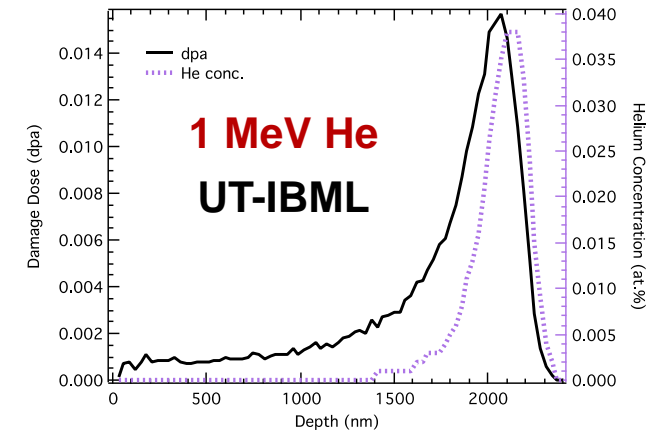
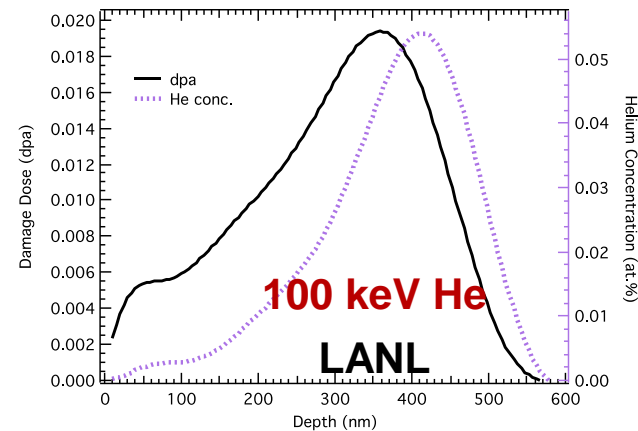
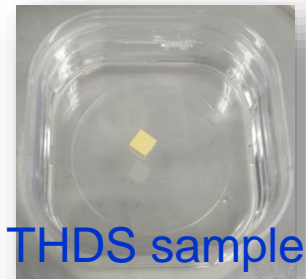
## SRIM Calculations



$1 \times 10^{15}$  ions/cm<sup>2</sup>  
for all energies

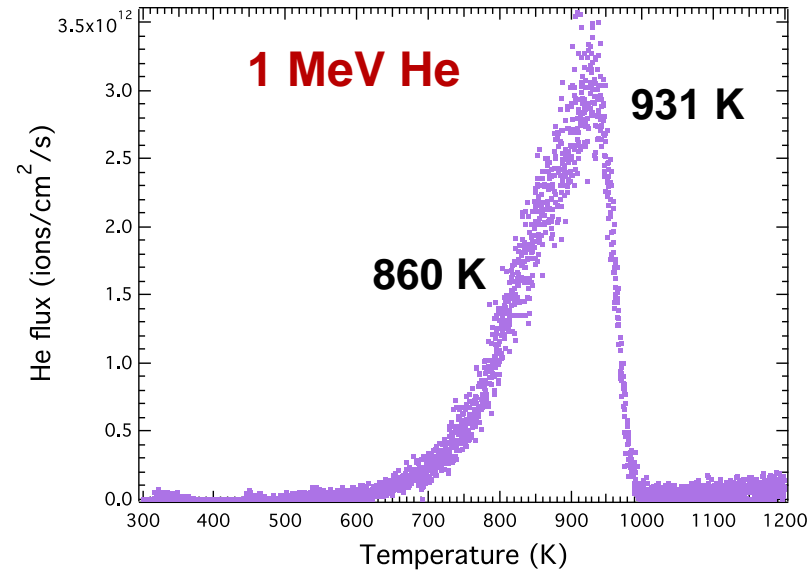
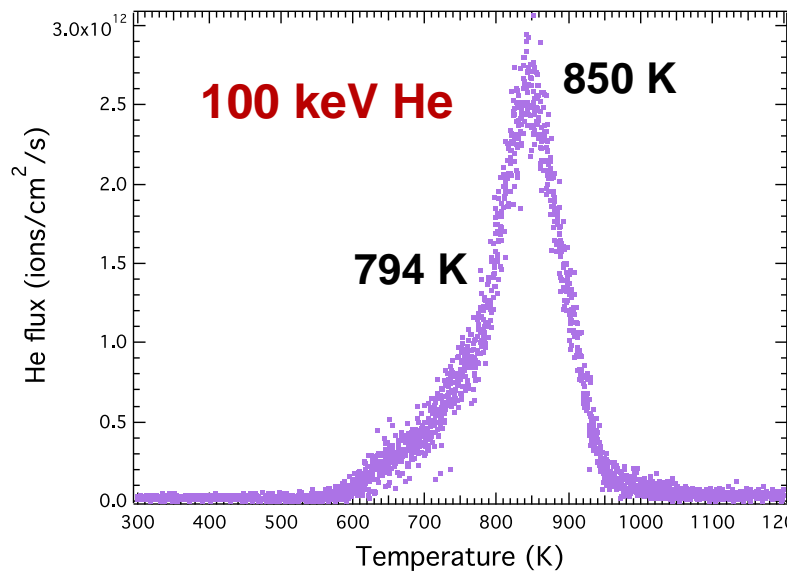
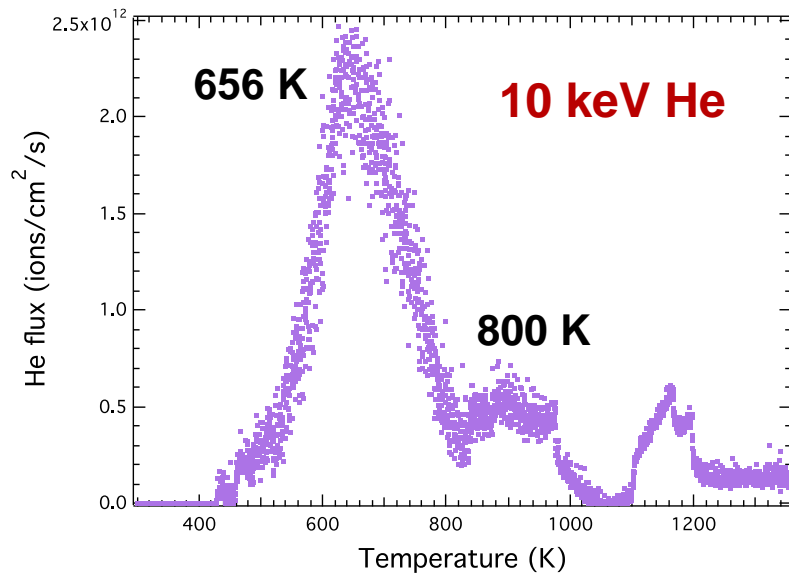
$$\ln(R/T_m^2) = -E_D/k_B T_m + \ln(\nu k_B/E_D)$$

$$E_D = E_m + E_B$$

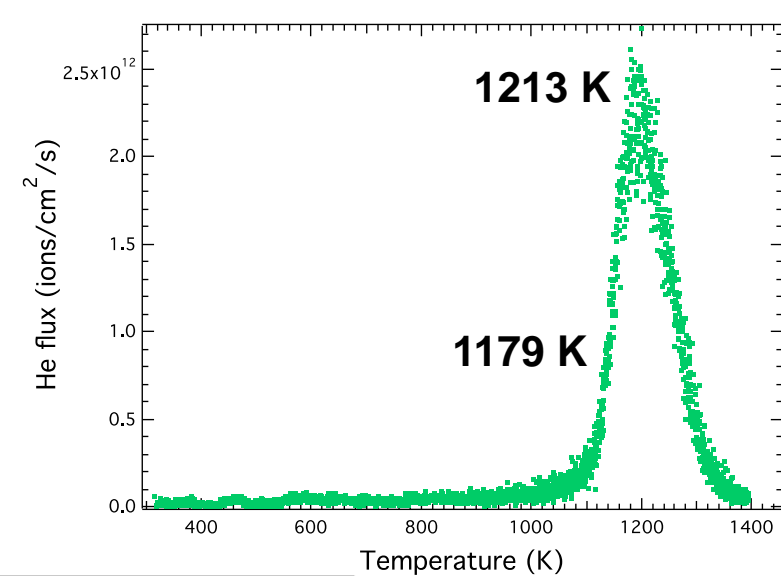
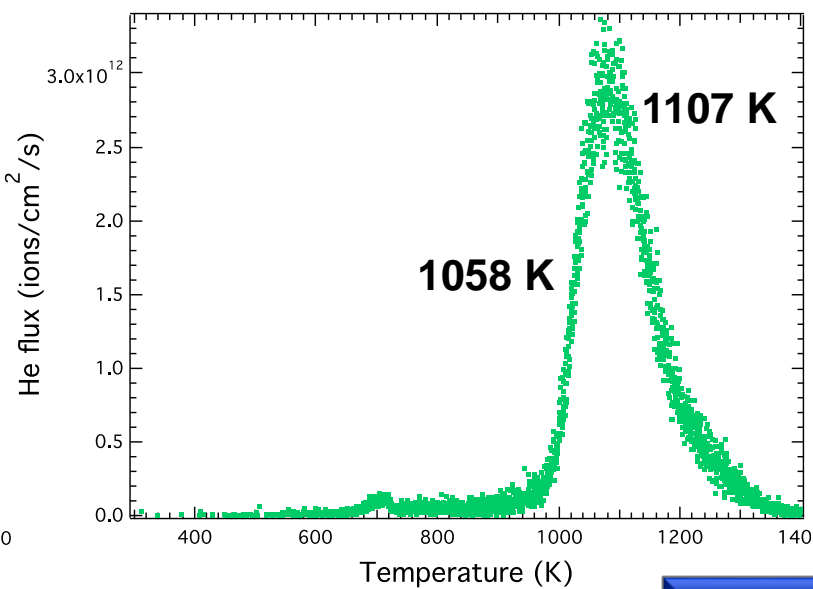
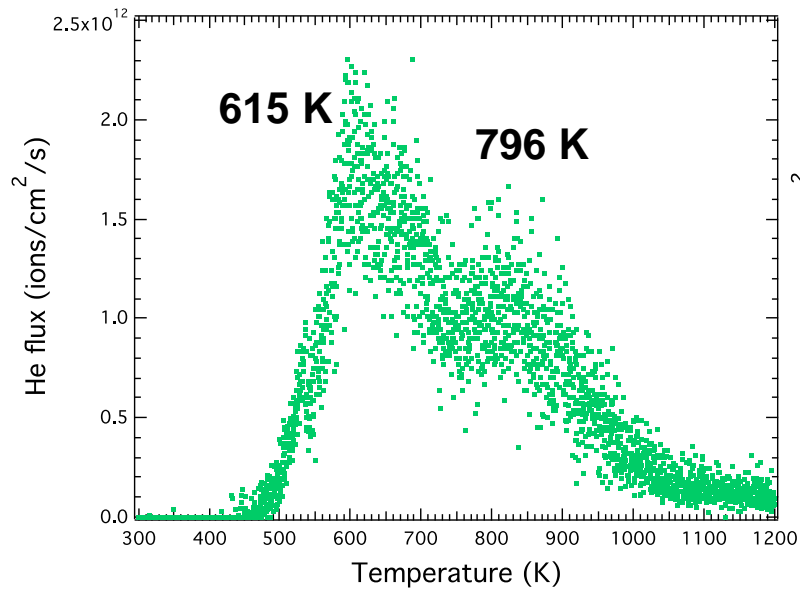


# Desorption Spectra Differed for Each Implantation Energy

**Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>**



**Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>**



**$E_B$  in GTO >  $E_B$  in GZO**