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Preliminary R&D of Beryllium Carbide as a Future MSR Moderator

Anne Campbell, Ercan Cakmak, Adam Willoughby, Yuri Osetskiy (ORNL)
Stephen Raiman, Diego Muzquiz (University of Michigan), David Holcomb (INL)

Argonne NATIONAL LABORATORY
INL Idaho National Laboratory
Los Alamos NATIONAL LABORATORY
OAK RIDGE National Laboratory
Pacific Northwest NATIONAL LABORATORY
Sandia National Laboratories
U.S. DEPARTMENT of ENERGY Office of Nuclear Energy

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Grand Question

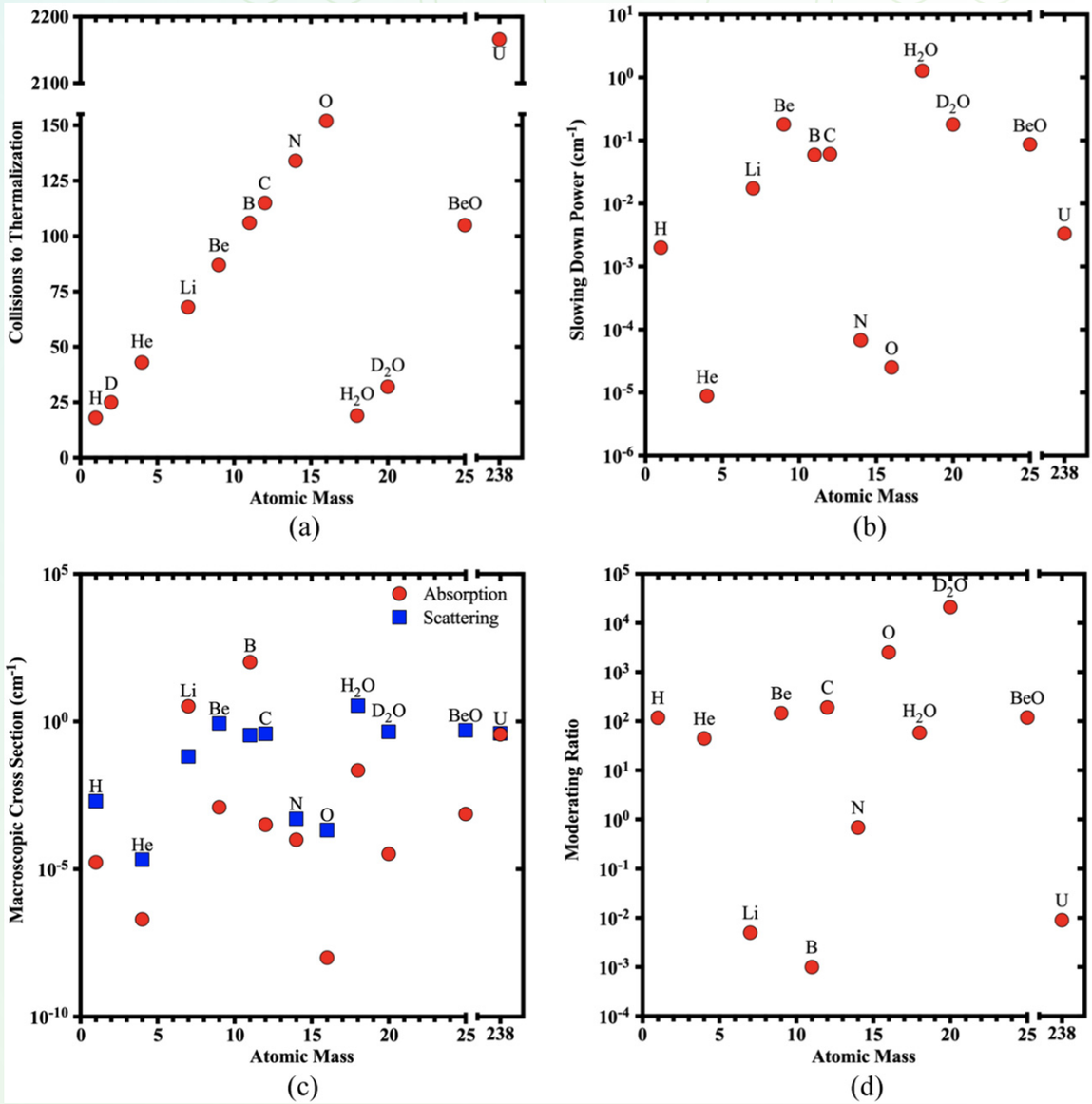
Can beryllium carbide be used in future reactors as a replacement moderator for graphite?

Long-term (10+ years) to answer this question, but can perform preliminary screening

Why Beryllium Carbide?

- High moderating efficiency and low absorption cross section
- Be slowing down power ~2.5x > than carbon
- Chemically compatible with coolant salts
- Antifluorite crystal structure – the same crystalline configuration (with anions and cations reversed) as exceptionally radiation damage resistant fluorite type crystals (e.g., UO_2)
  - The anti-fluorite crystal (Li_2O) has also been shown to have high radiation damage tolerance [1,2]

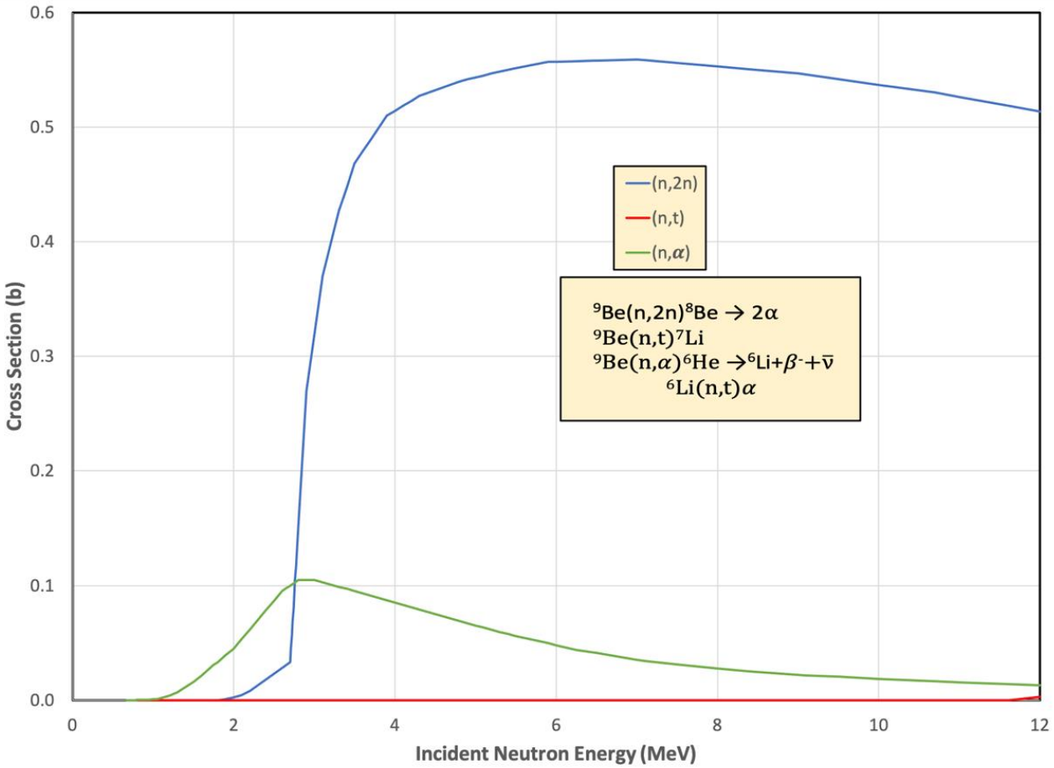
Campbell & Burchell Timothy D. (2020). Radiation Effects in Graphite. Comprehensive Nuclear Materials 2nd edition, vol. 3, pp. 398–436



[1] Moriyama et al., *Journal of Nuclear Materials*, **258-263**, (1998) 587-594.
[2] Noda, et al., *Journal of Nuclear Materials*, **123**, (1984) 908-912

Technical Challenges with Beryllium Carbide

- Long history of graphite as neutron moderators (CP-1, X-10 ~80 years) research and knowledge – only limited low dose studies in Be_2C [1-3]
- Be_2C is brittle, vulnerable to thermal stress cracking
  - Can we mitigate brittle nature via fiber reinforcement?
- Be_2C is toxic, moisture sensitive, chemically reacts with U
  - Would need a protective layer (NbC)
- Be_2C is a methanide (when exposed to H it decomposes into methane)
  - Can this be utilized for tritium management strategy?
  - Methane is easily trapped and doesn't diffuse through metal alloys
- Be does have gas generating reactions with neutrons (He and ^3H)
  - May be beneficial for fusion systems for ^3H production



Be gas generating reactions (data from ENDF/B-VIII.0)

[1] Maya et al., GA-A-17842; (1985)
[2] Marion & Muenzer, SAND--78-0227C, CONF-780622, (1978)
[3] Feldman & Silverman, NAA-SR-114, (1951)

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What are the first steps?

- Need solid Be_2C samples – concern is production and processing is export controlled technology
- Understand high temperature stability of Be_2C
- Preliminary understanding of irradiation effects in Be_2C
- Degradation behavior when exposed to hydrogen
- Understand thermal properties

High Temperature Stability Testing

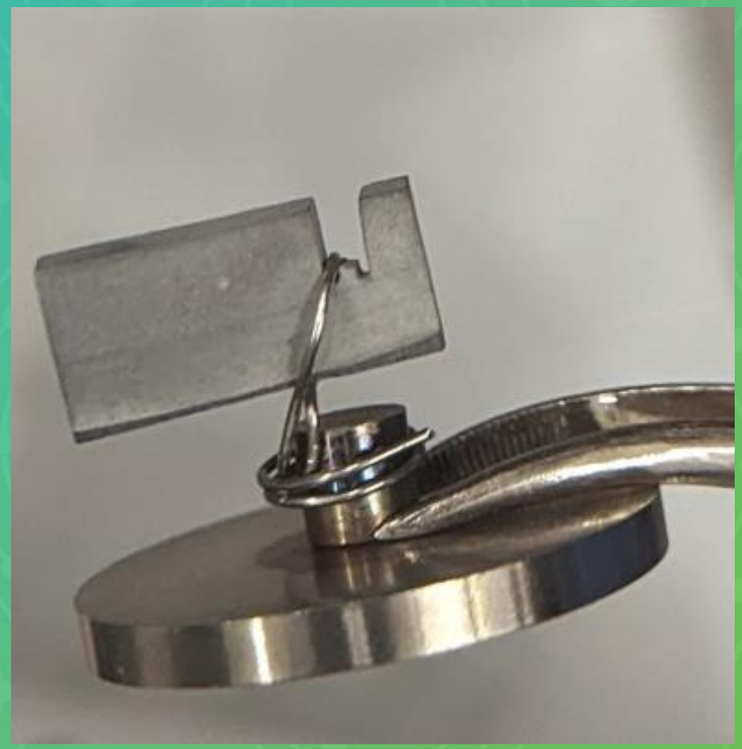
D. Sulejmanovic

A. Willoughby

E. Cakmak

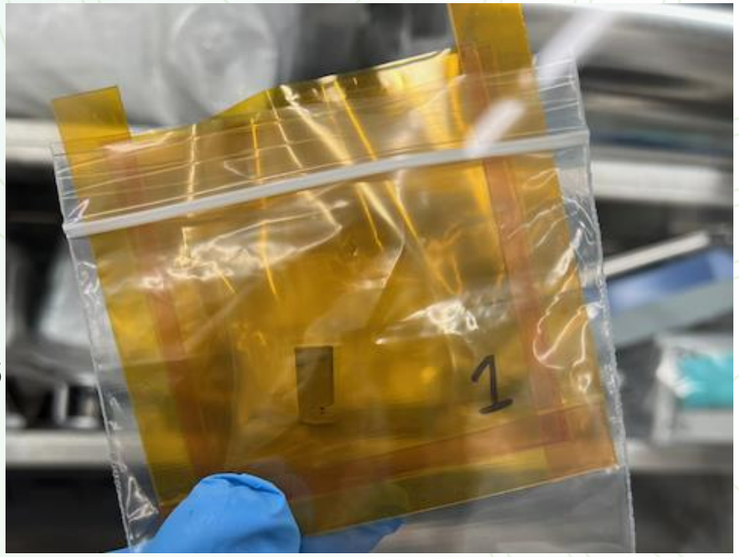
B. Henry

S. Fiscor



Phase Composition Measurement

- Make Kapton packets, load Be_2C into packet and seal shut with 2 pieces of Kapton tape
- Panalytical X'pert diffractometer (CuKα)
  - θ-2θ setup 20 – 100° 2θ, with a scan rate of 0.0167 deg/s (~30 minute scan time), 1/4° fixed slits, 1/2° anti-scatter slit, 0.04 soller slits coupled with a 10 mm mask, and zero-background plate was positioned below the specimens to remove any peaks from the metal specimen stage
  - Phase identification used a search match with the Jade software and the ICDD database



Static Capsule Testing

- Mass specimens
- Specimens loaded into 316L stainless steel double-containment capsules
- Fill with desired environment (Ar gas)
- Electron beam welded shut
- Put into box furnace at desired temperature for pre-determined time

Before exposure

After exposure

Inner and outer capsules (courtesy J. Keiser)

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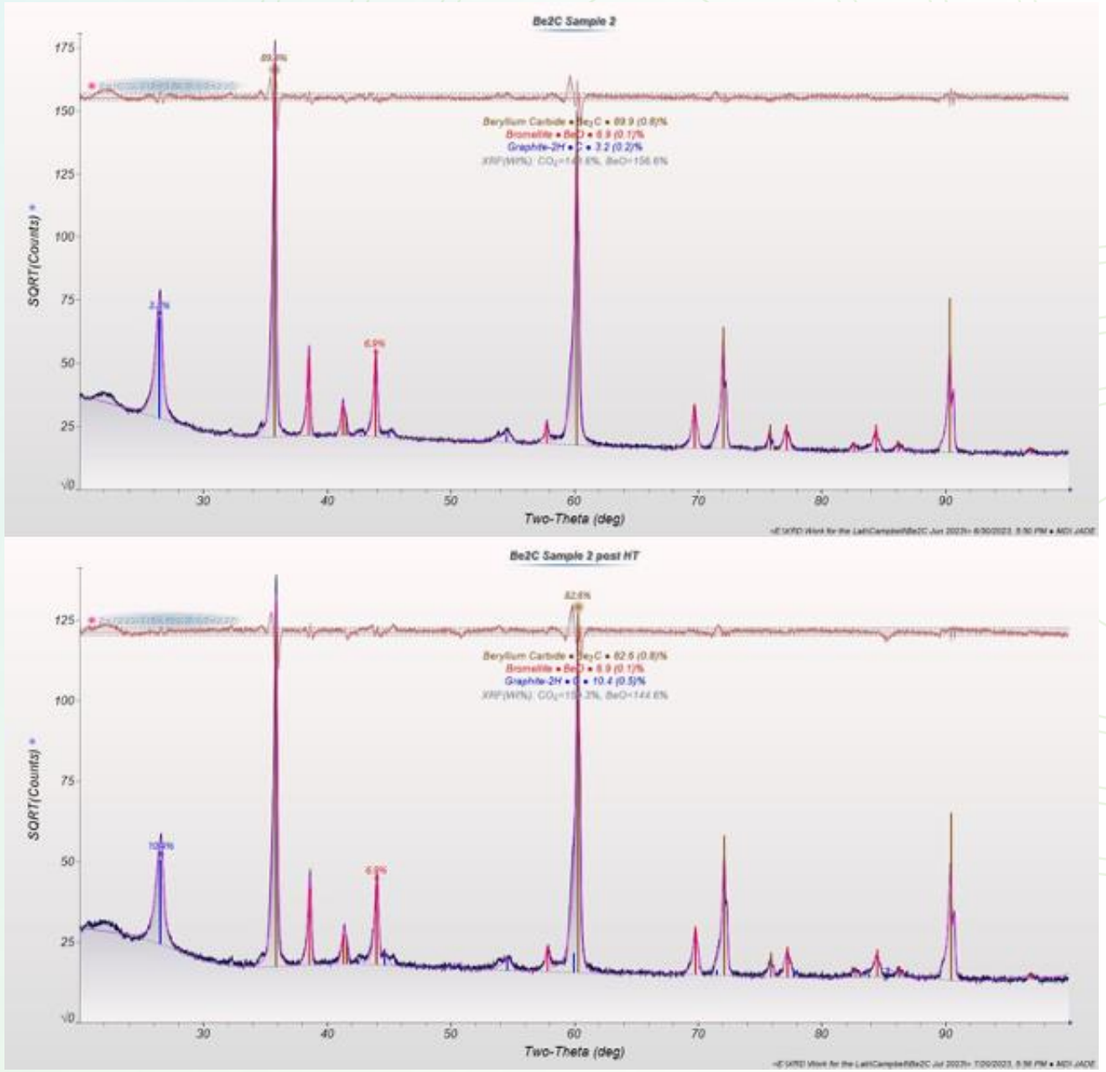
Post-Exposure Analysis

- Open capsules
- Remeasure specimen mass (mass loss)
- Package in new Kapton packets
- XRD (determine phase composition)



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Summary of Changes 650°C Exposures

Specimen #	Exposure Time	Pre-exposure mass (g)	Post-exposure mass (g)	Mass loss (%)	Be_2C Phase % before / after	BeO Phase % before / after	Graphite Phase % before / after
1	1 day	0.5596	0.5559	0.66	90.2 / 87.2	7.0 / 7.3	2.1 / 5.5
2	1 week	0.6283	0.6234	0.78	89.9 / 82.6	6.9 / 6.9	3.2 / 10.4
3	2 weeks	0.5960	0.5939	0.35	89.6 / 84.4	7.1 / 7.6	3.3 / 8.0

Before exposure

After exposure

Specimens have dull grey finish before exposure.
After exposure, all specimens have dark surface (graphite buildup as Be converts to BeO and sloughs off?)

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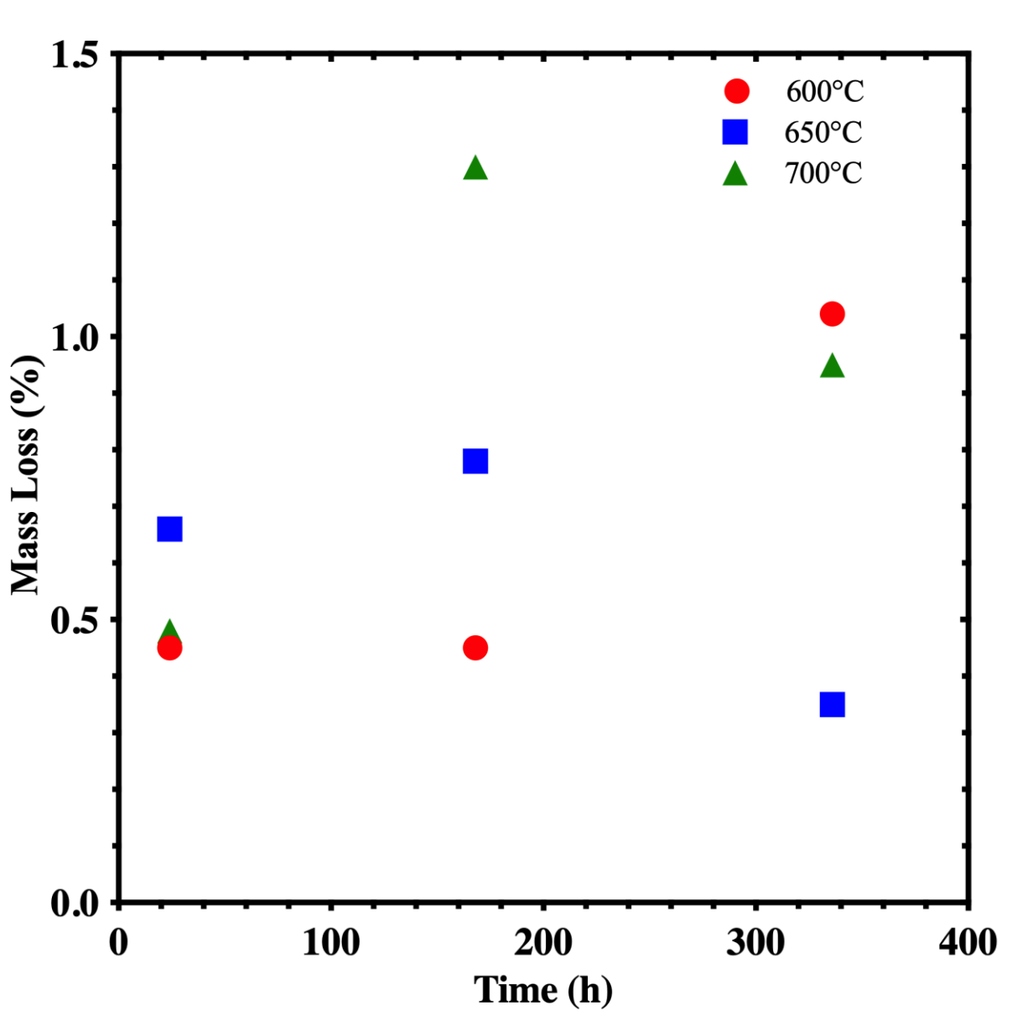
Additional Temperature Exposures

Specimen #	Exposure Time	Pre-exposure mass (g)	Post-exposure mass (g)	Mass loss (%)
A1	1 day	0.5587	0.5562	0.45%
A2	1 week	0.4687	0.4666	0.45%
A3	2 weeks	0.3667	0.3629	1.04%
1	1 day	0.5596	0.5559	0.66
2	1 week	0.6283	0.6234	0.78
3	2 weeks	0.5960	0.5939	0.35
A4	1 day	0.3939	0.3920	0.48%
A5	1 week	0.5135	0.5068	1.30%
A7	2 weeks	0.5288	0.5238	0.95%



In-situ Chemical Compatibility Testing

- Be_2C degrades to methane in the presence of hydrogen
  - Can this be used for ^3H mitigation?
- Plan to test small coupons in Nezsch skimmer under different Ar and Ar+H conditions
  - Equipment having issues with communications between Netzsch TGA and 3rd party mass spectrometer

Specimen	Mass (g)	Exposure Temperature (°C)	Exposure Gas Composition
S1	0.0076	650	Ar
S2	0.0094	600	Ar + 1% H
S3	0.0409	600	Ar + 4% H

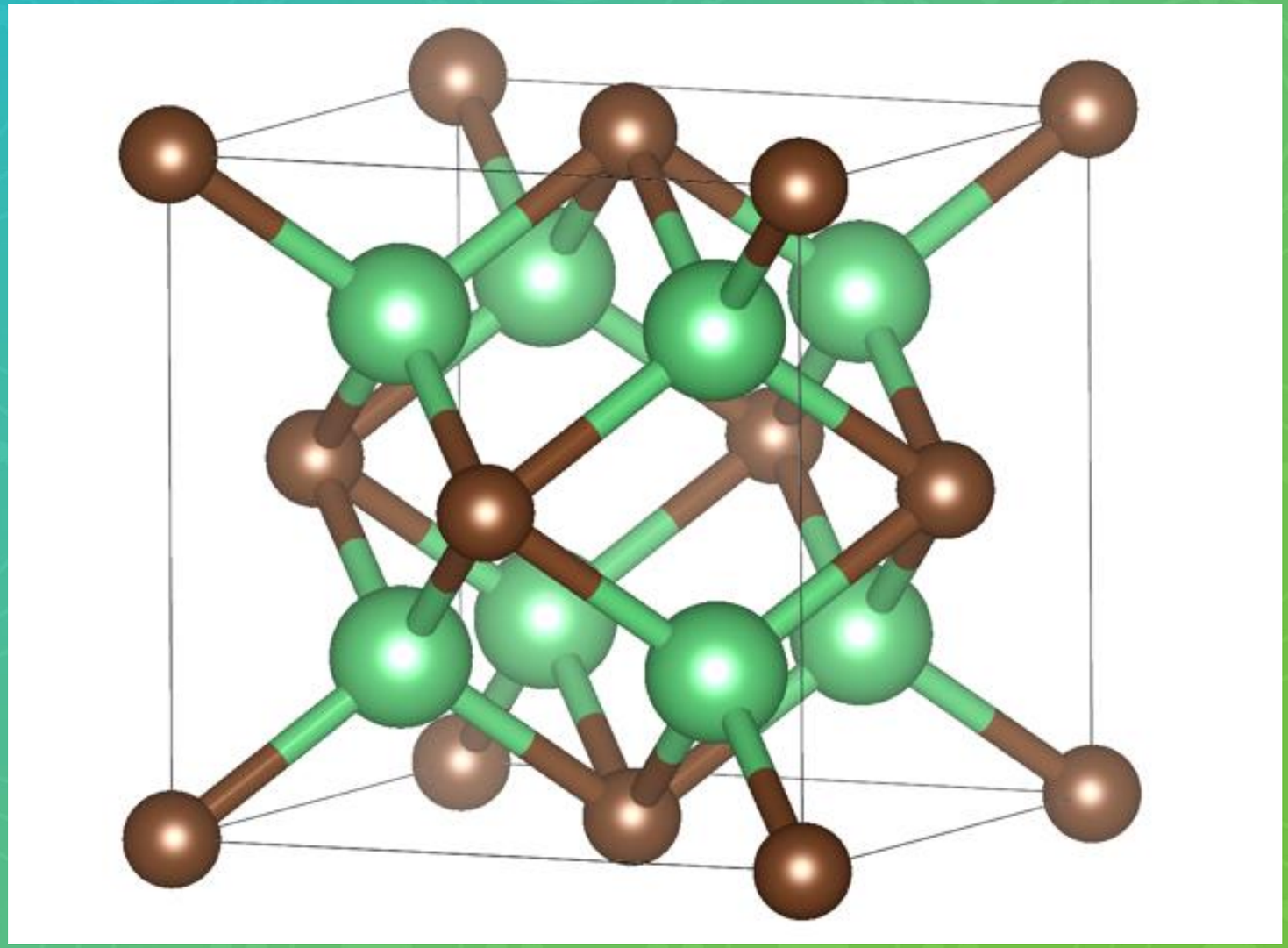
Modeling Beryllium Carbide

Yuri Osetskiy

Eva Zarkadula

Mao-Hua Du

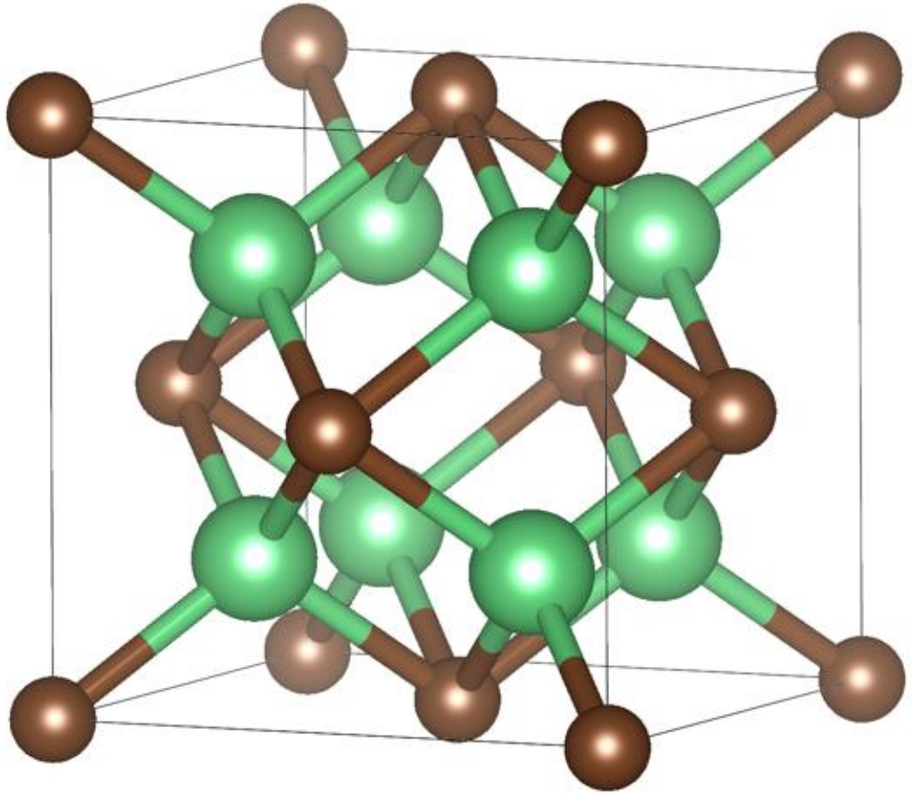
German Samolyuk



Paper submitted to journal and under review

First principles modeling in Be_2C

- DFT modeling in VASP
- Supercells of three sizes were used to investigate different effects: 3x3x3 (324 sites), 4x4x4 (768 sites) and 5x5x5 (1500 sites).
- Advanced computing facilities: National Energy Research Scientific Computing Center (NERSC) at LBNL and Compute and Data Environment for Science (CADES) at ORNL.



Atomic structure of anti-fluorite Be_2C structure: Be – green, C – brown

Band structure

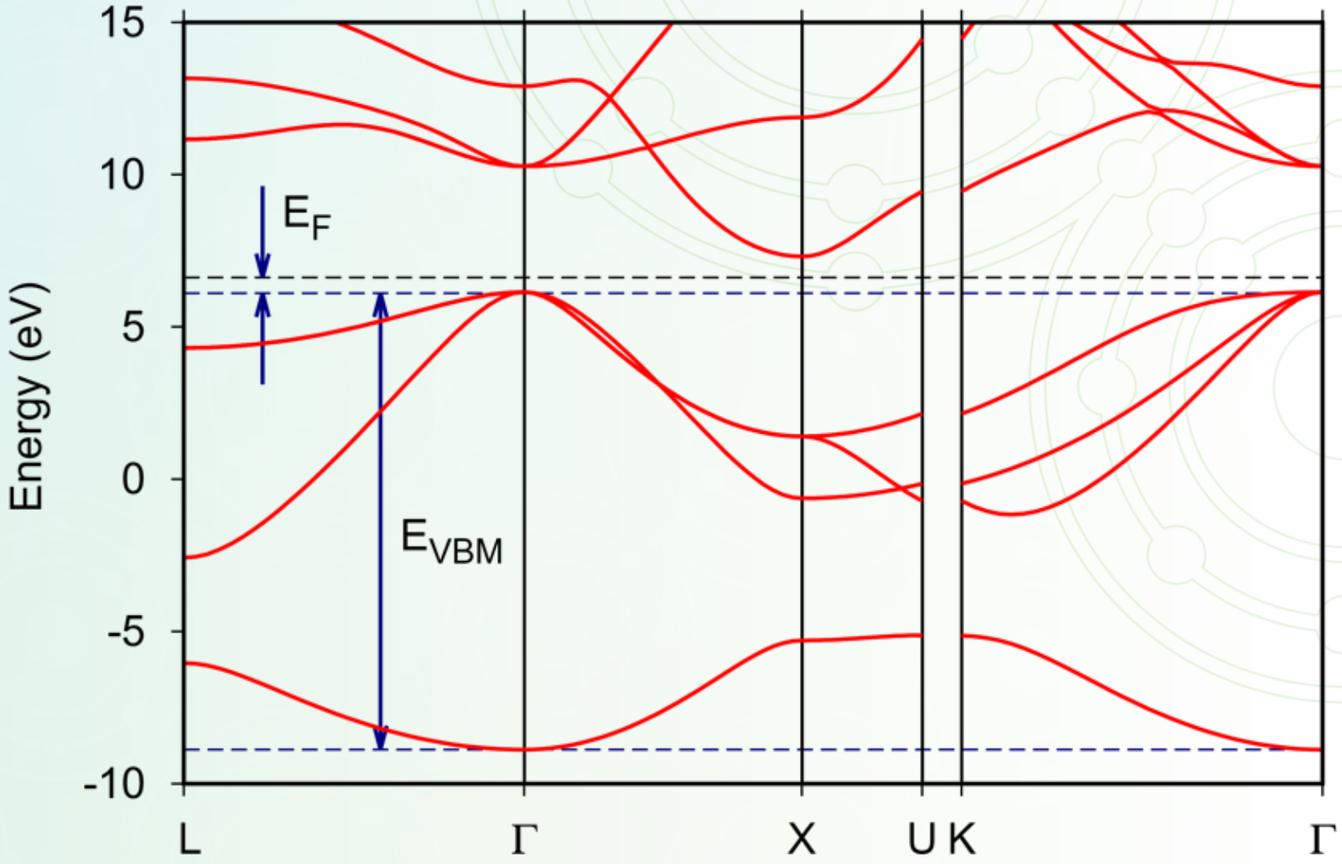
- Be_2C is weak semiconductor with relatively narrow band gap:

  E_g = 1.212 eV

- Estimated Fermi energy:

  E_{Fermi} = 6.271 eV

- Density of states in the perfect Be_2C crystal. EF is Fermi energy estimated from the valence band maximum – EVBM.



Density of states and point defects

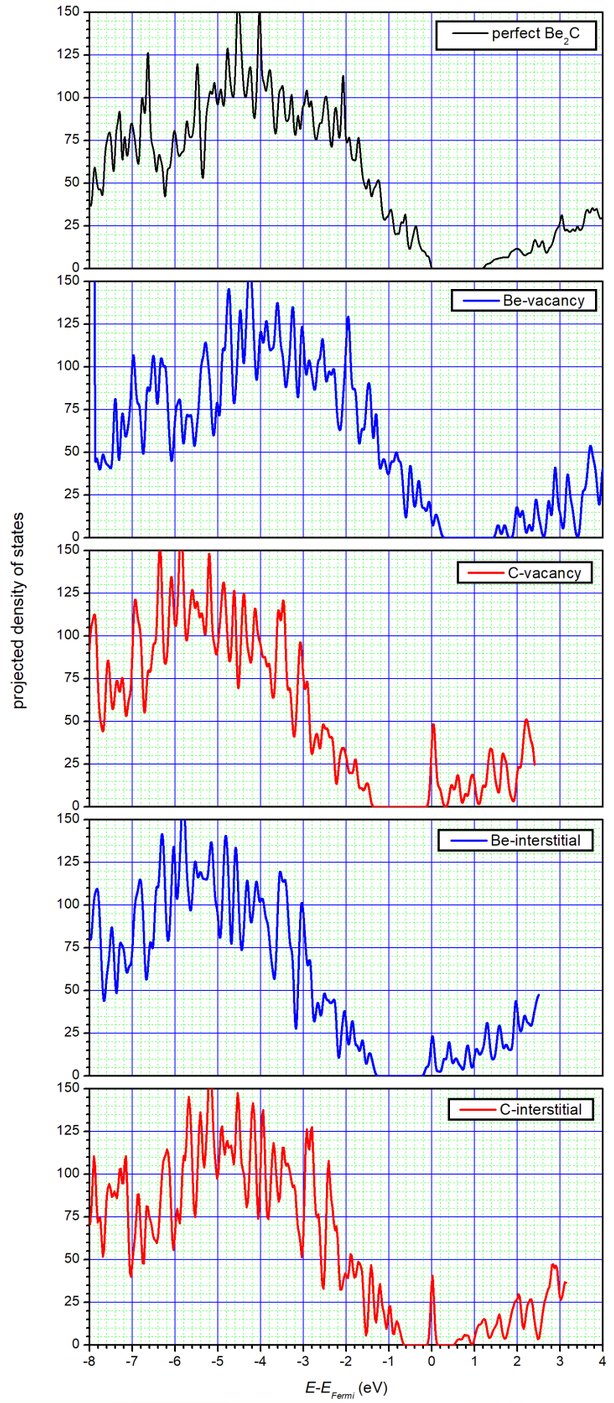
- Be_2C is weak semiconductor with relatively narrow band gap:

  E_g = 1.212 eV

- Estimated Fermi energy:

  E_{Fermi} = 6.271 eV

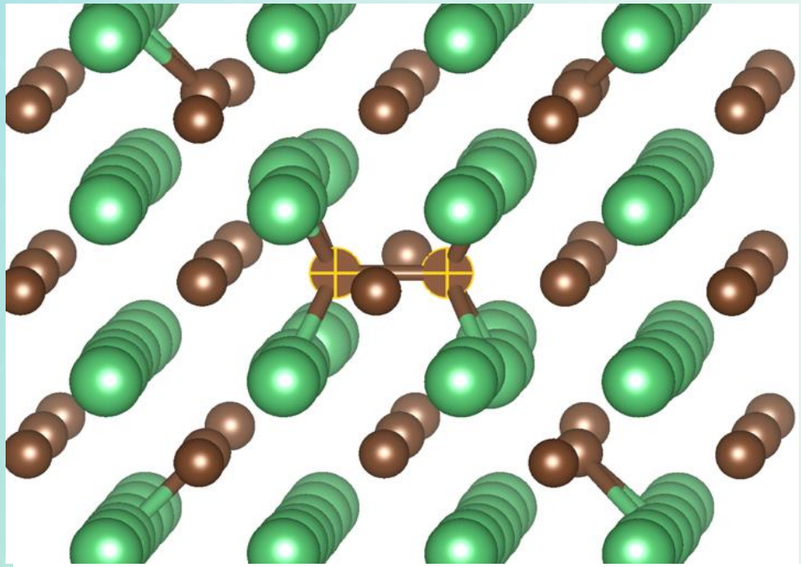
- Defects change electronic structure by shifting energy and introducing new electronic states.
- Projected density of states in Be_2C crystals top to bottom: perfect, and containing neutral Be-vacancy, C-vacancy, Be-interstitial and C-interstitial



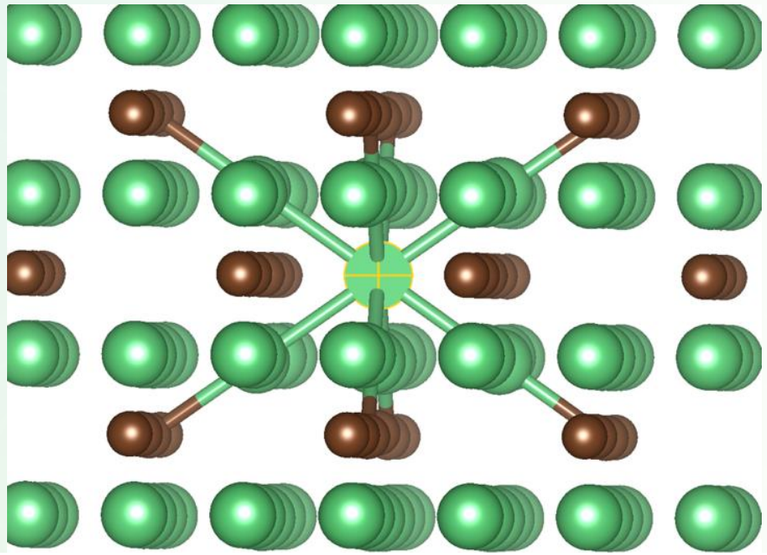
Point defects properties interstitial structures

- Anti-fluorite Be_2C structure assumes many possible configurations of interstitial atoms
- For estimating the ground state configuration, we applied DFT molecular dynamics modeling – annealing over 4 ps at 1200K followed by relaxation to 0K

Ground state configurations:



Symmetric split C-C dumbbell along [100] direction;



Octahedral Be-interstitial between the Be (001) planes.

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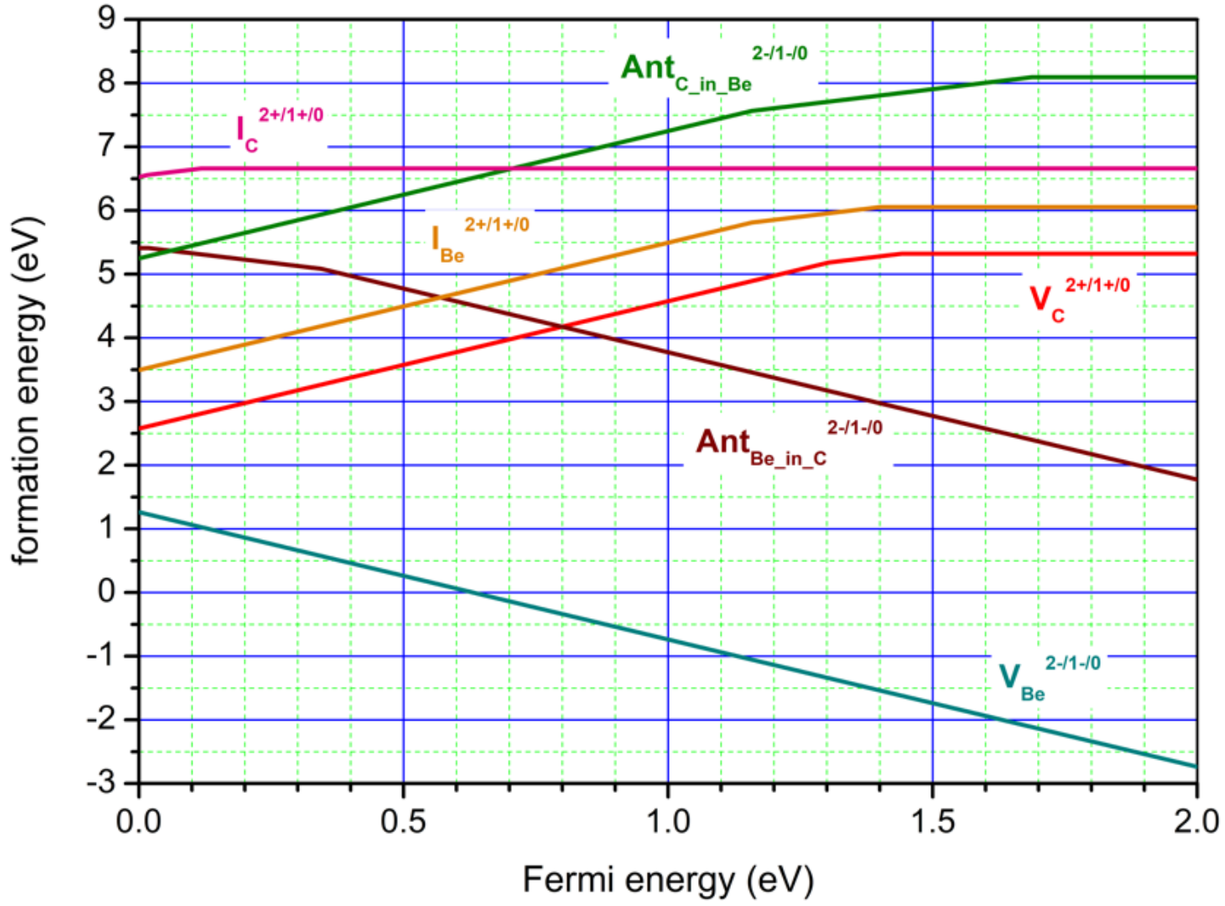
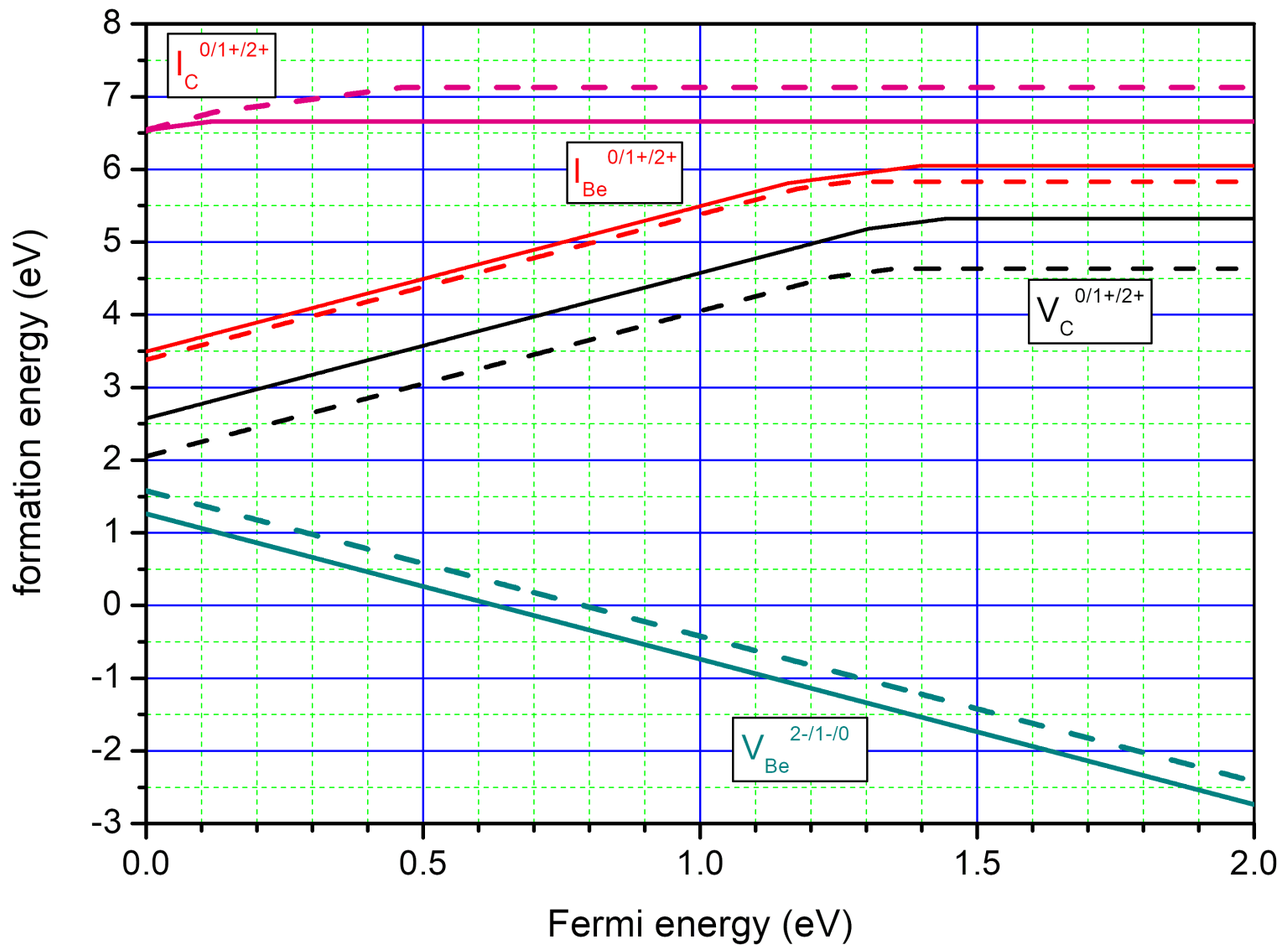
Point defects properties – energy formation

- Formation energy of point defects strongly depends on their charge state;
- Defects presented in the plot :
  - I_c – C-interstitial atom
  - I_{Be} – Be-interstitial atom
  - V_C – vacancy in C-site
  - V_{Be} – vacancy in B-site
  - $Ant_{Be\_in\_C}$ – Be atom in C site
  - $Ant_{C\_in\_Be}$ – C atom in Be site



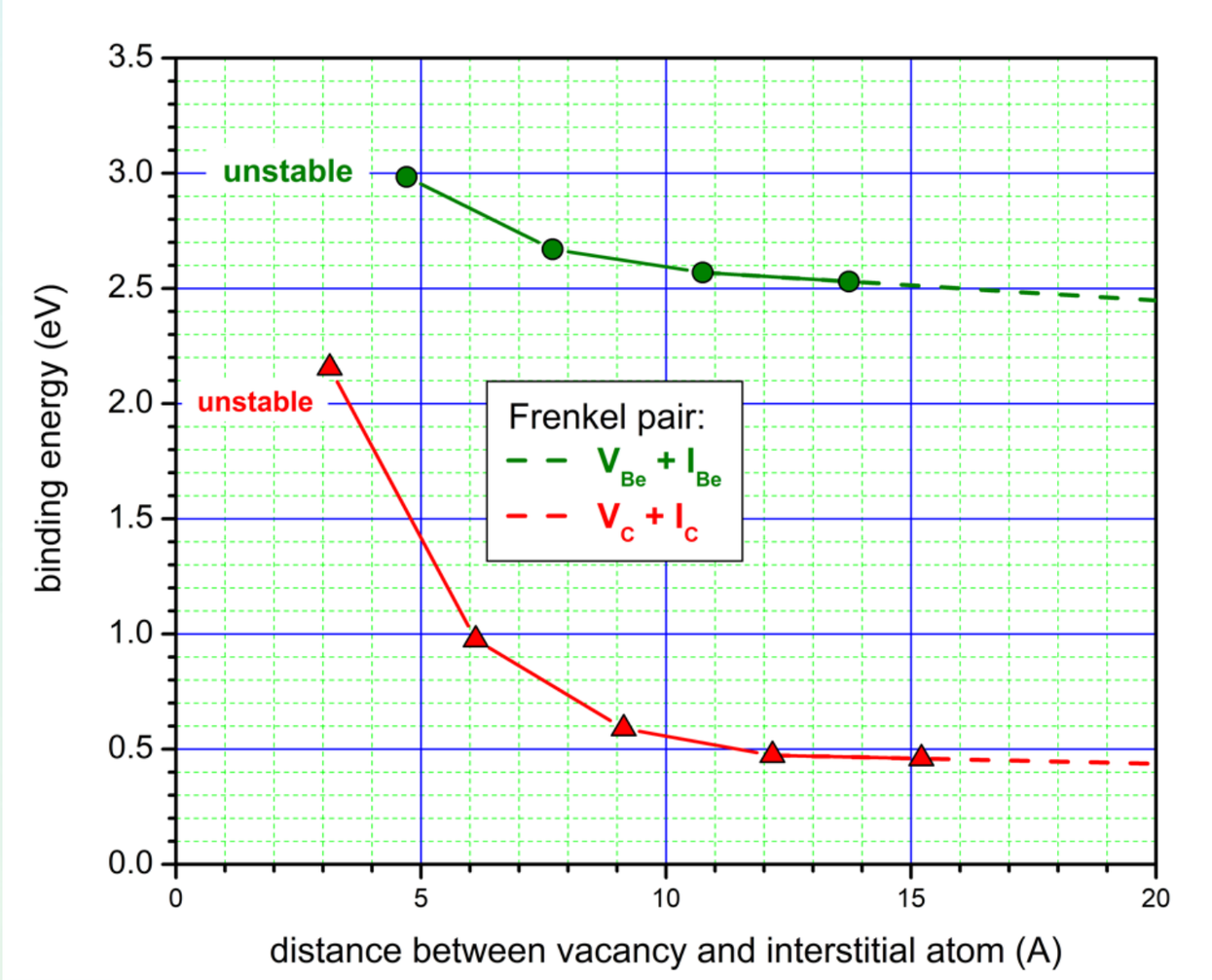
Point defects properties – model size effect

Vacancy and interstitial atom formation energies in the smallest, i.e. 3x3x3, (solid lines) and largest, i.e. 5x5x5, (dashed lines) supercells.



Point defects properties – Frenkel pairs

- Be and C FP modelled in the large supercell 5x5x5 (1500 sites)
- Vacancy and interstitial atoms were separated by different distance along close to <111> direction.
  - Pair in the first coordination spheres were unstable.
- Binding energy was calculated relatively the neutral point defects:
  - Reasonable for C-FP when energy drops to ~0.5 eV (instead of 0 eV)
  - Unlikely for Be-FP where energy saturates at ~2.5 eV



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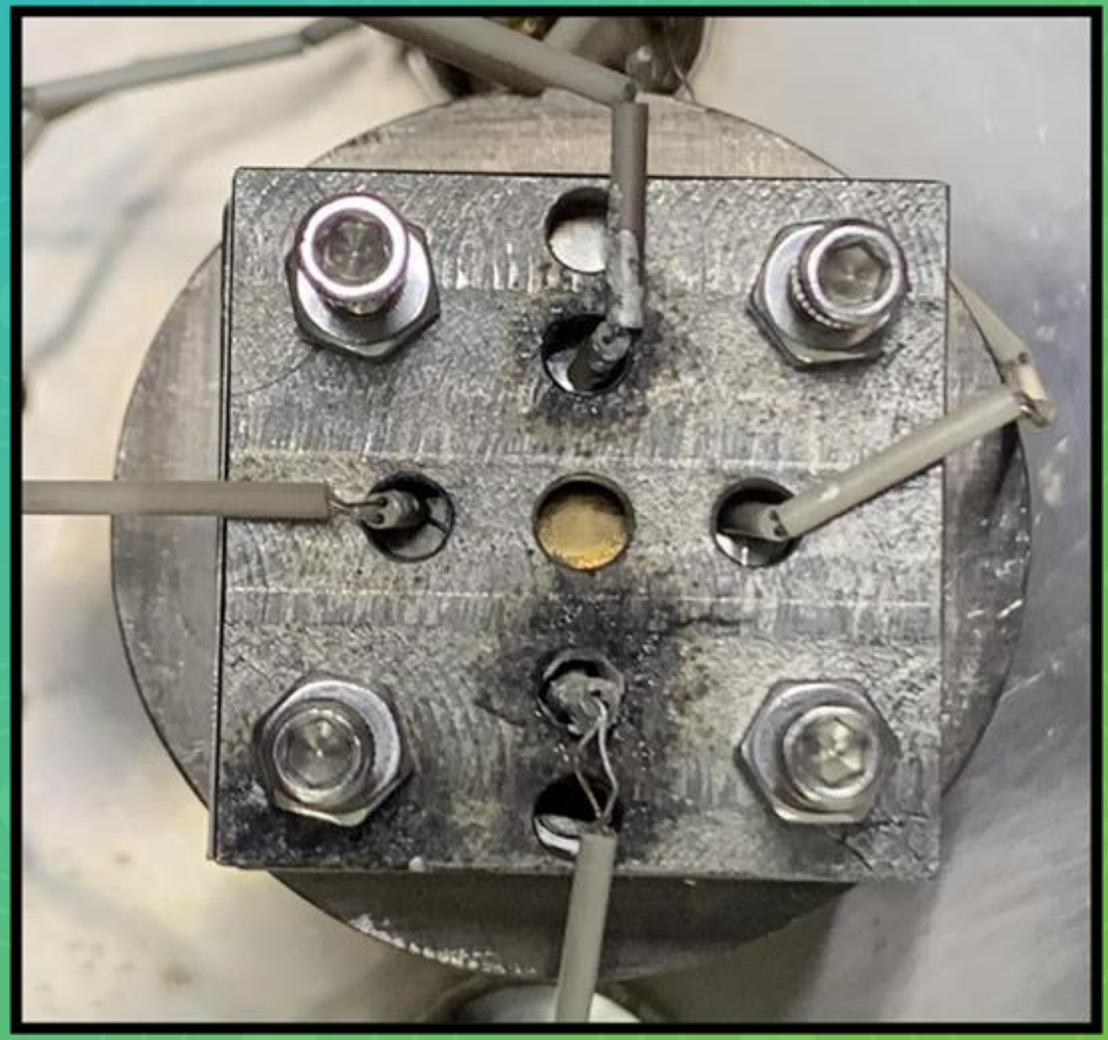
Ion Irradiation of Be_2C

Diego Múzquiz

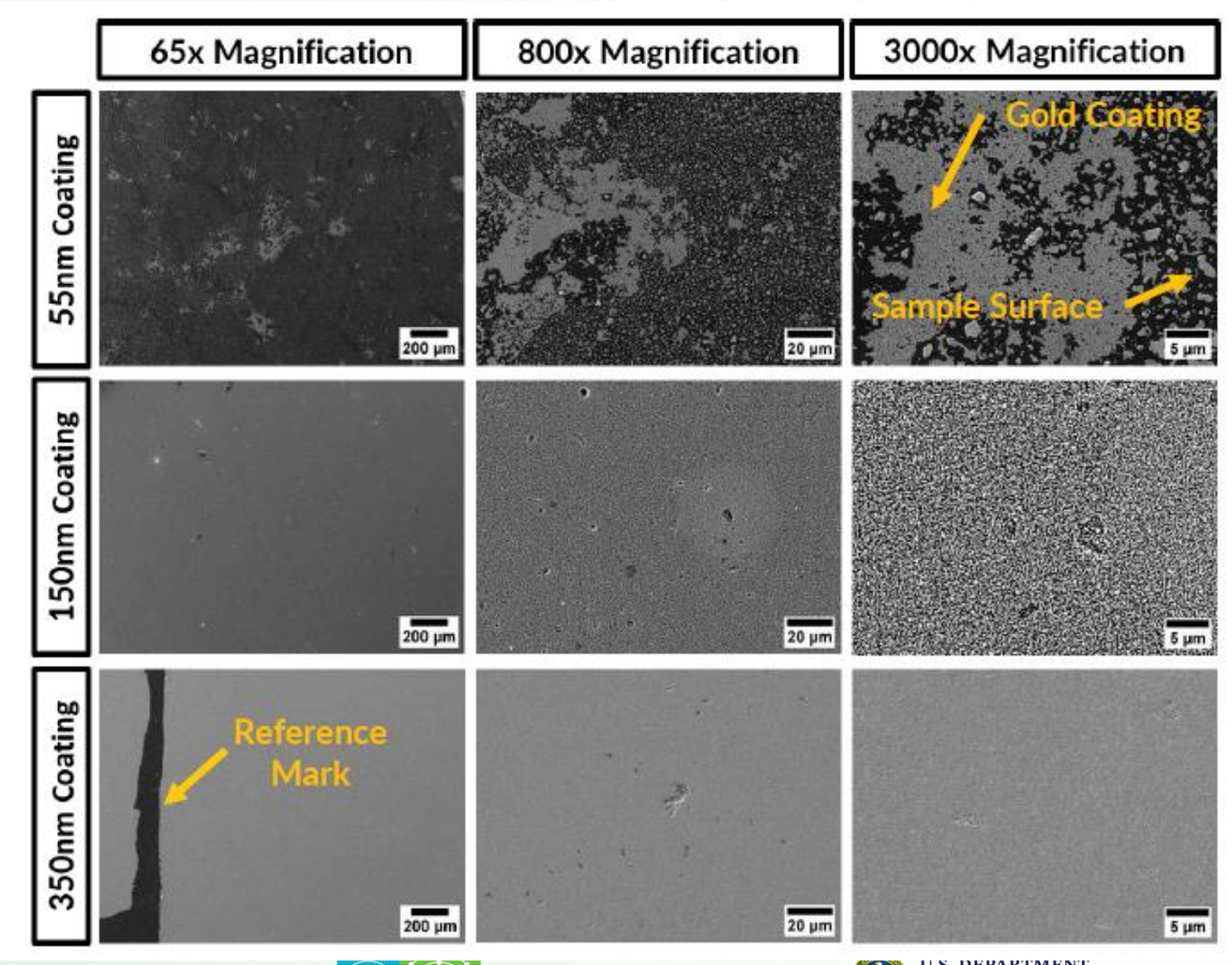
Stephen Raiman

Paper submitted to journal and under review

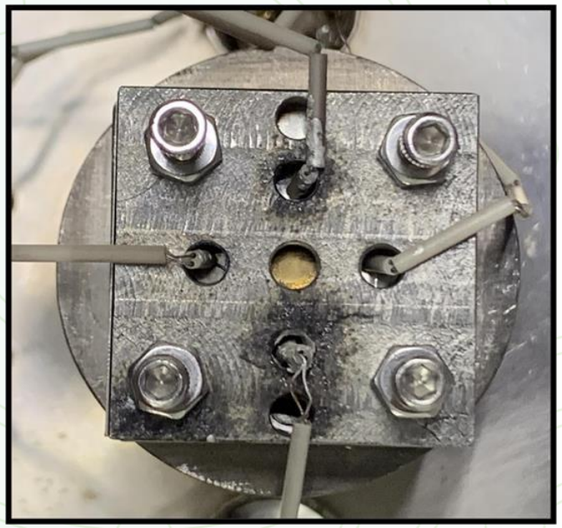


Primary Containment for Irradiations

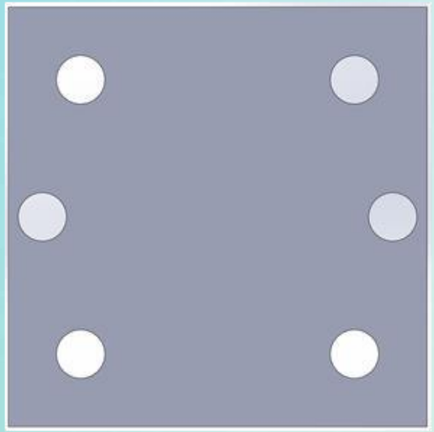
- Irradiation parameters minimize sputter yield to an acceptable limit
- Gold Layer further reduces sample sputtering
- 3 different coating were tested on SiC to support simulated results



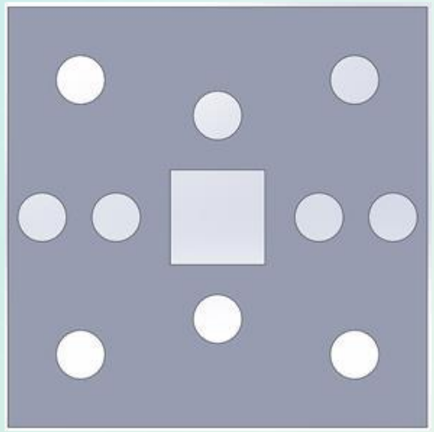
Secondary Containment Failsafe



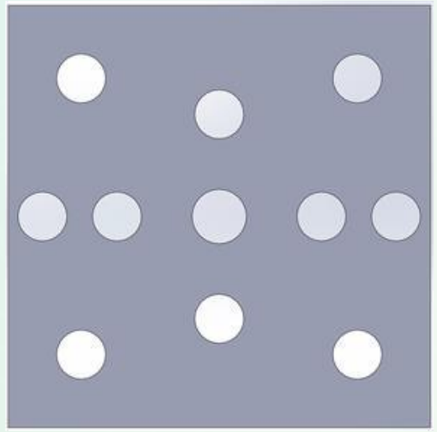
- Sample inside custom **molybdenum box** attaches to stage
- Molybdenum has **high heat transfer** while not melting at experimental temperatures



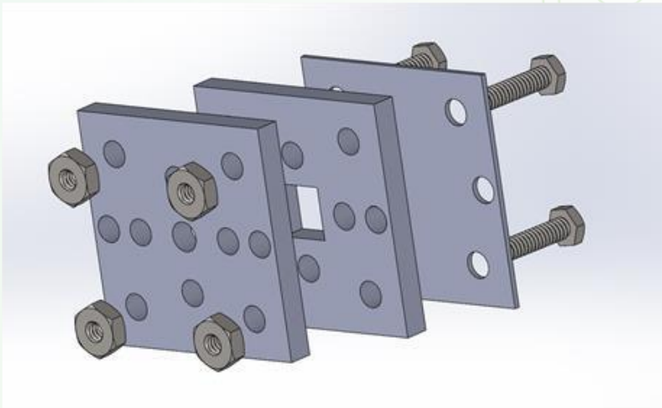
Thermal plate



Holding plate



Sputter plate



Assembly

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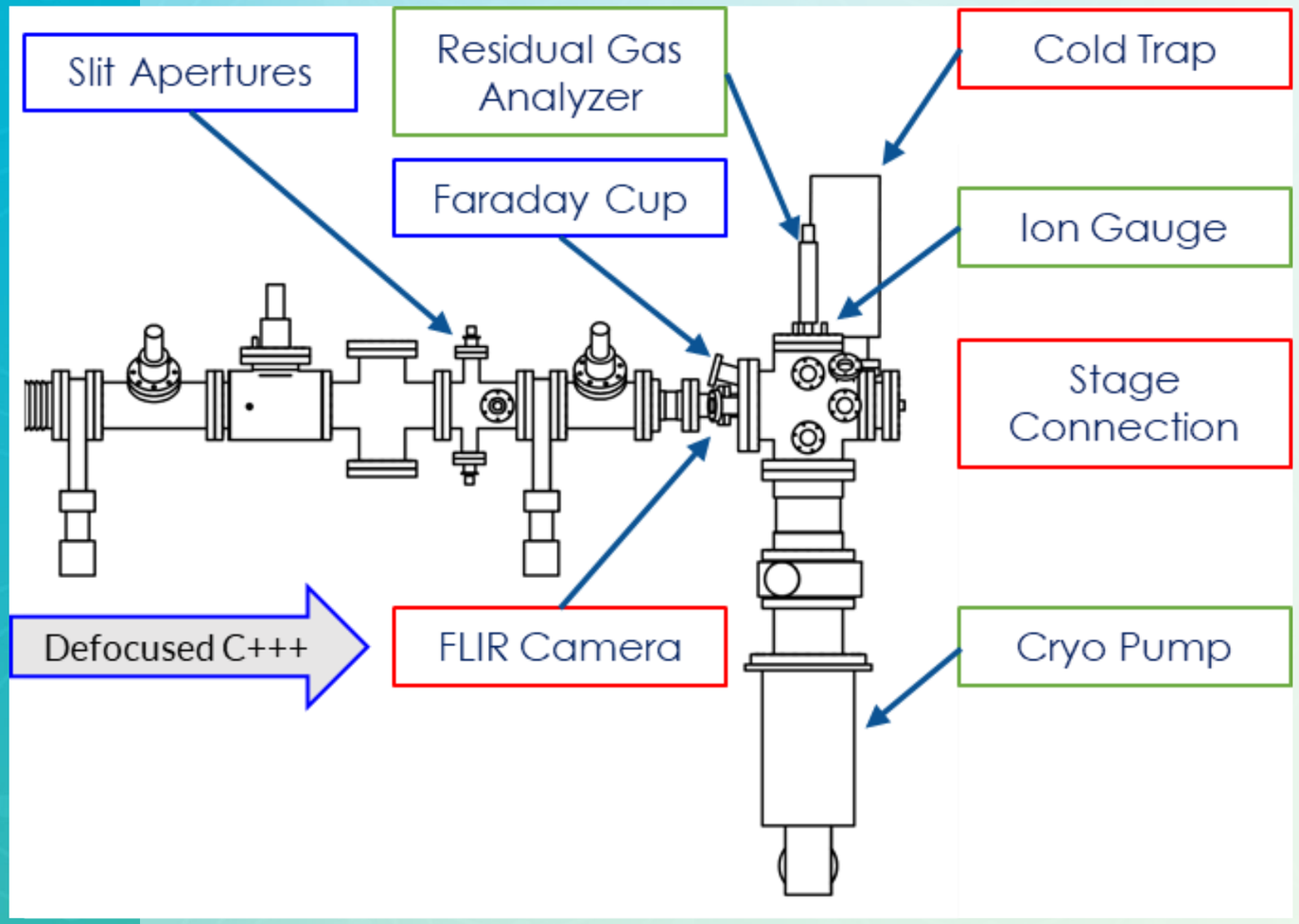
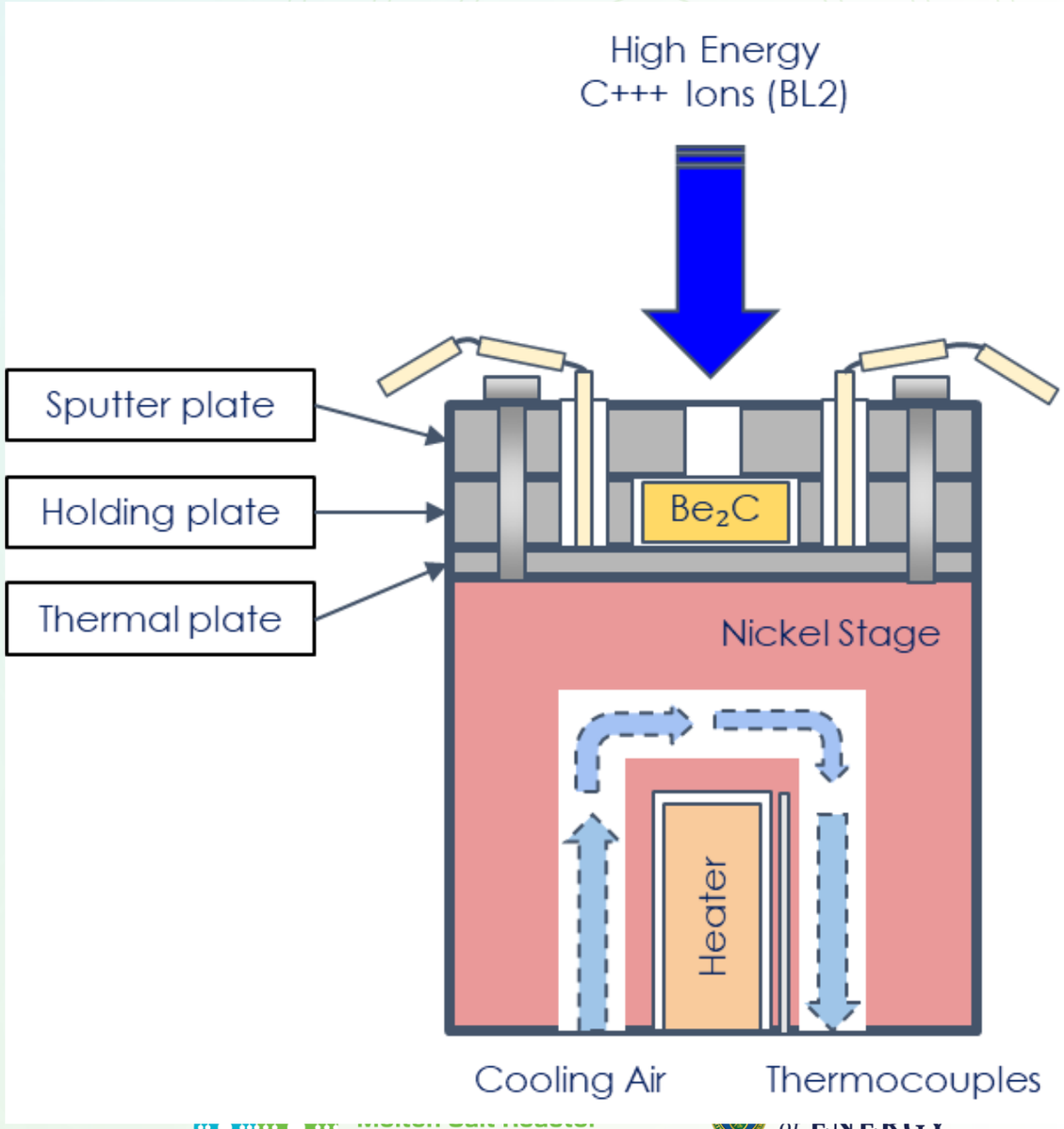
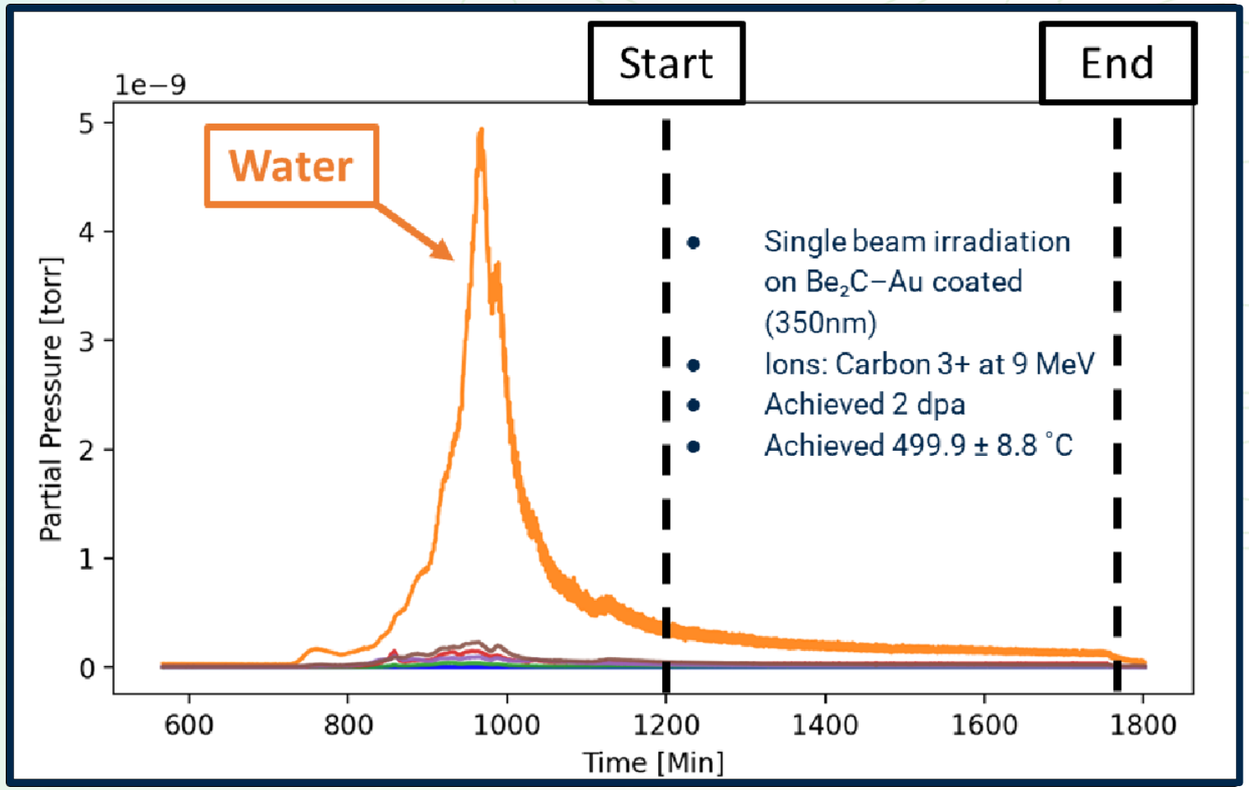
Irradiation Experimental Setup





Containment Monitoring and Swab Testing Post Irradiation

- The RGA monitors the inside of the chamber
- Post irradiation, cleaning with a HEPA rated vacuum
- Swab tests are done post cleaning to ensure no beryllium remains



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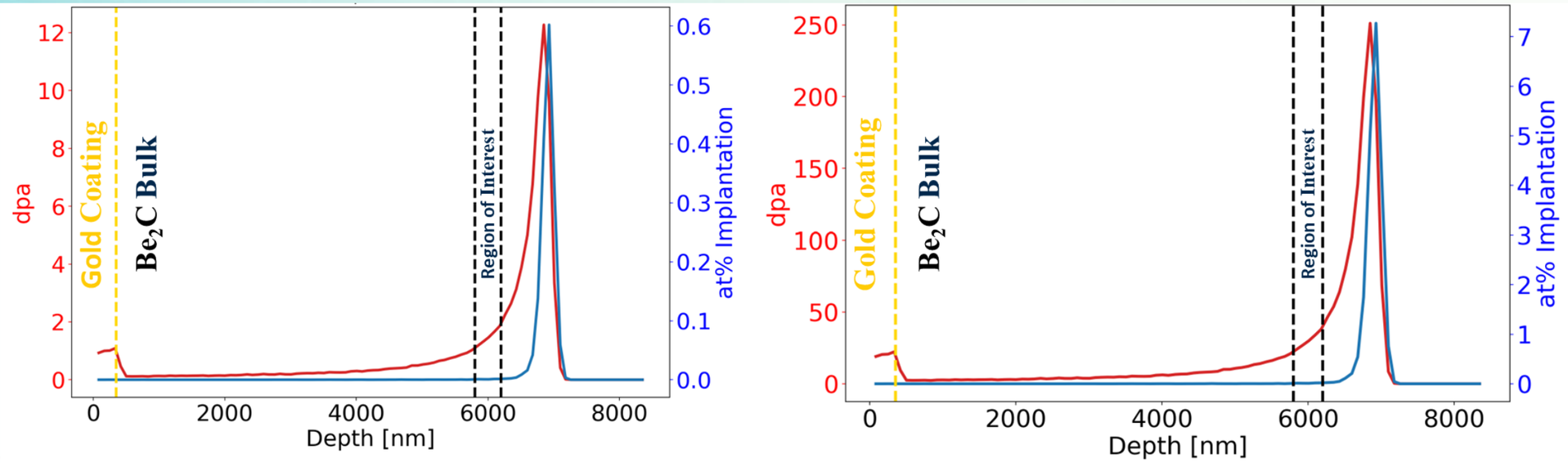
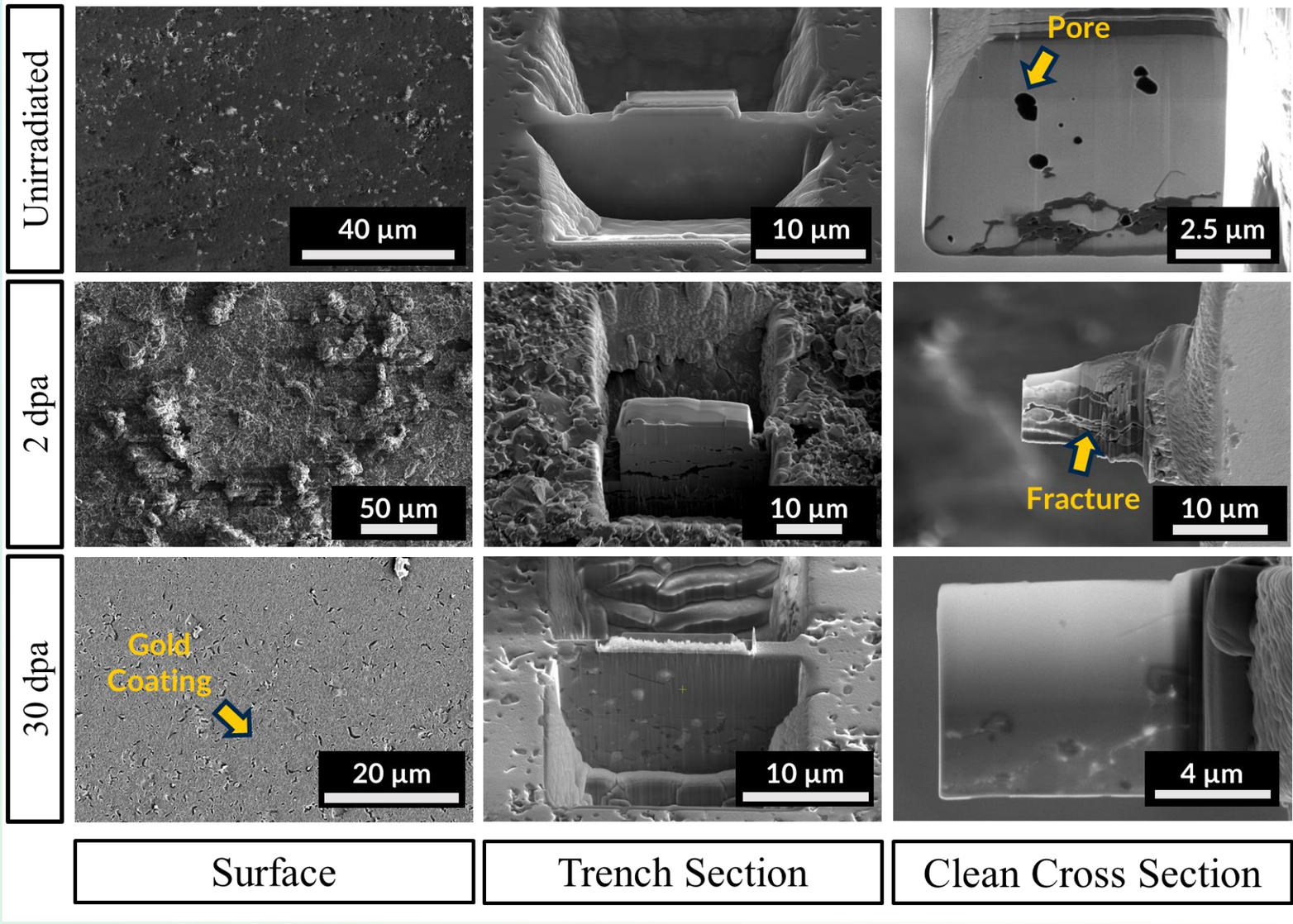
Ion Irradiation Conditions

Parameters	Experiment 1	Experiment 2
Dose	2	30
Damage Rate [dpa/s]	1.21×10^{-4}	1.51×10^{-4}
Temperature [C]	499.9 ± 8.8	504 ± 7.9
Current [μA]	0.211	0.472
Energy [MeV]	9.00	9.00
Time [h]	10.55	55.11
Beam Area [cm^2]	0.09	0.126
Incident Ion	C^{3+}	C^{3+}



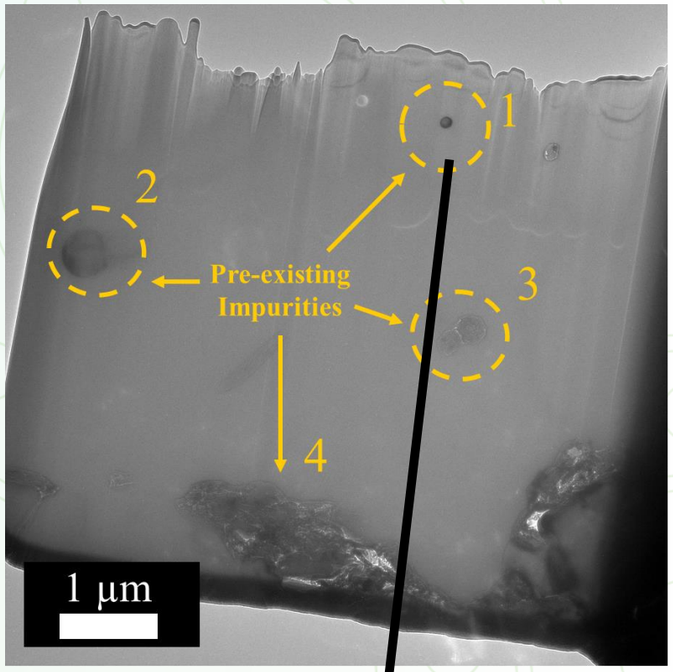
Scanning Electron Microscopy

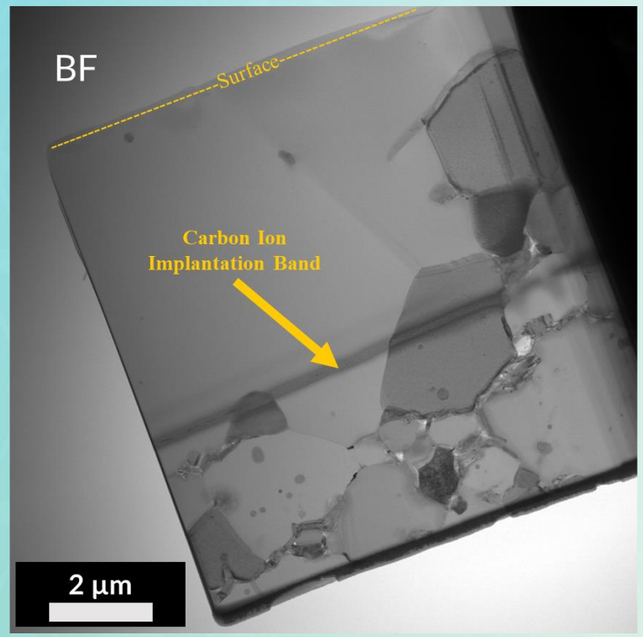
- Inclusions and non-uniform microstructure expected from XRD results
- 2 dpa specimens not stored in Ar glove box for 5 months prior to SEM – some environmental effects
- Same issues not observed in 30 dpa

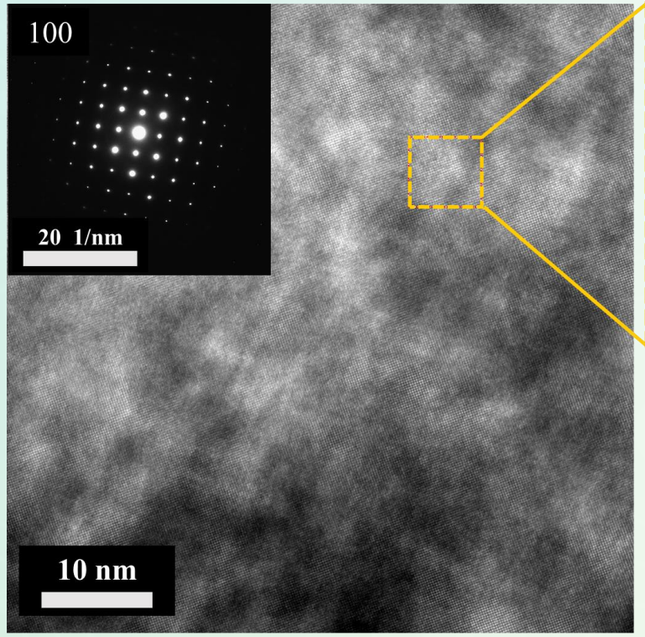


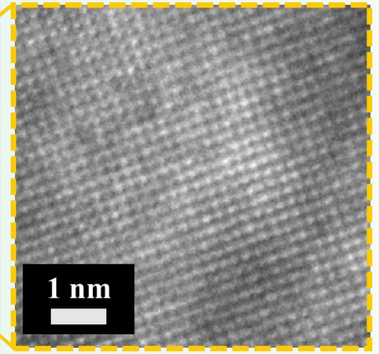
Transmission Electron Microscopy

- Small (<100 nm) inclusions in unirradiated Be_2C
  - STEM EELS shows inclusions are BeO
- Features in 30 dpa specimen easy to see
  - No observed loss of crystallinity at 30 dpa

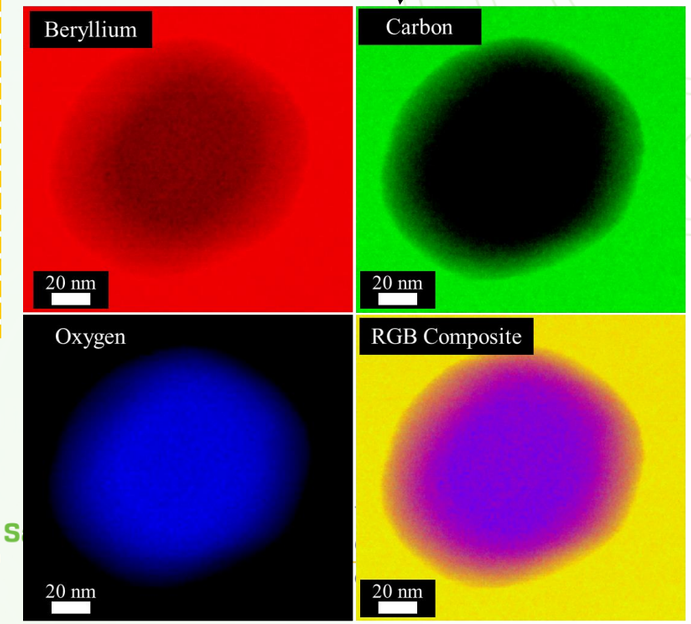








30 dpa
530°C



Upcoming Work

A. Willoughby

E. Cakmak

K. Johnson

B. Henry

E. Paxton

S. Fiscor

Suggested future modeling activity

Understanding mechanisms of radiation damage and microstructure evolution assumes the following modeling activity:

- Predicting diffusion:
  - ✓ vacancy – vacancy jump barriers and kinetic Monte Carlo modeling vacancy diffusion;
  - ✓ interstitial atoms – because of the complexity of diffusion mechanisms, direct molecular dynamics modeling should be applied;
- Defect-defect interactions:
  - ✓ dilatation properties of vacancy and interstitial defects needed for long-range interaction in strain fields;
  - ✓ extended defects nucleation and growth mechanisms and energy and structure properties;
  - ✓ charge effects in defect-defect interactions;
- Development of kinetic Monte Carlo model for the overall dynamics of microstructure evolution.

Additional Ion Irradiation Studies

- Expand dose and temperature range
- Use ion implantation to study H and He diffusion characteristics
- In-Situ dual-beam irradiation (C^+ with simultaneous H implant)
- Static and flowing FLiBe exposures

Beyond FY25?

- From these preliminary results evaluate if a neutron irradiation campaign is viable.
- Work with Materion to develop advanced processing methods to tailor material properties
- Any future work will require setup of capabilities for handling and testing solid Be_2C both pre- and post-irradiation
  - Glove boxes, testing equipment (mass/dimensions, elastic properties, strength, CTE, thermal diffusivity, etc.)

Questions?

Anne Campbell

campbellaa@ornl.gov