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Science and Technology Supporting the Tritium Sustainment Program

DJ Senor

40th Tritium Focus Group Meeting, Albuquerque, NM

23 October 2018

U.S. DEPARTMENT OF ENERGY BATTELLE

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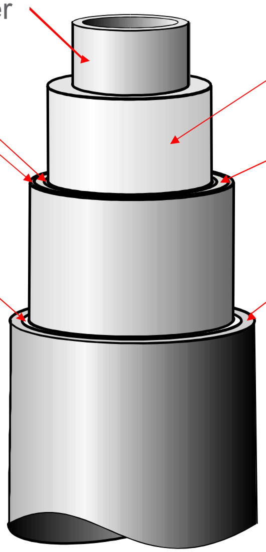
PNNL-SA-138954

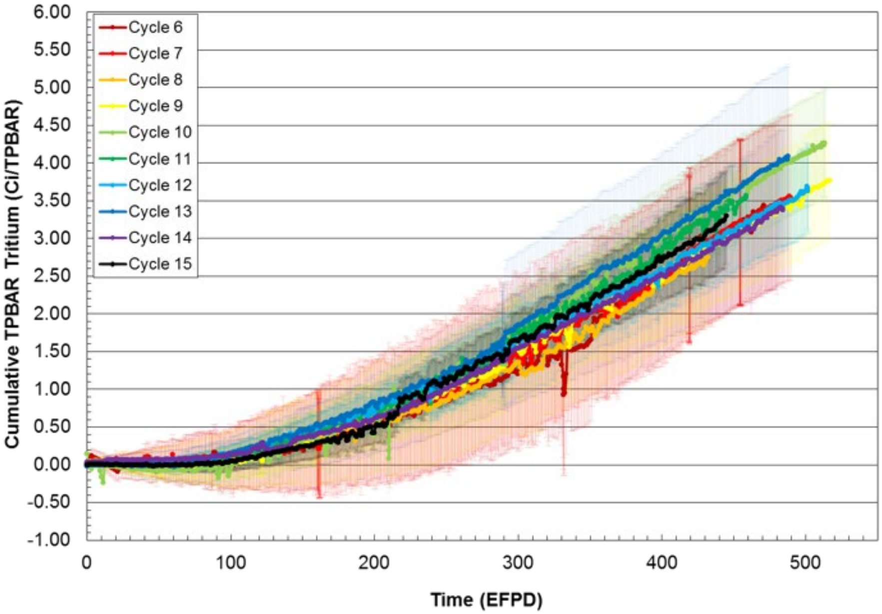
U.S. Tritium Production

- Tritium-Producing Burnable Absorber Rods (TPBARs) are irradiated in the Watts Bar Nuclear power plant
- There are numerous mechanistic questions associated with TPBAR component performance that can only be addressed by implementing a diverse basic science and technology research program
- One example is the mechanisms behind microstructural evolution in the LiAlO2 pellets that impacts multiple performance features
  - Structural integrity
  - Dimensional stability
  - Tritium retention/release



Origins of the Tritium S&T Program

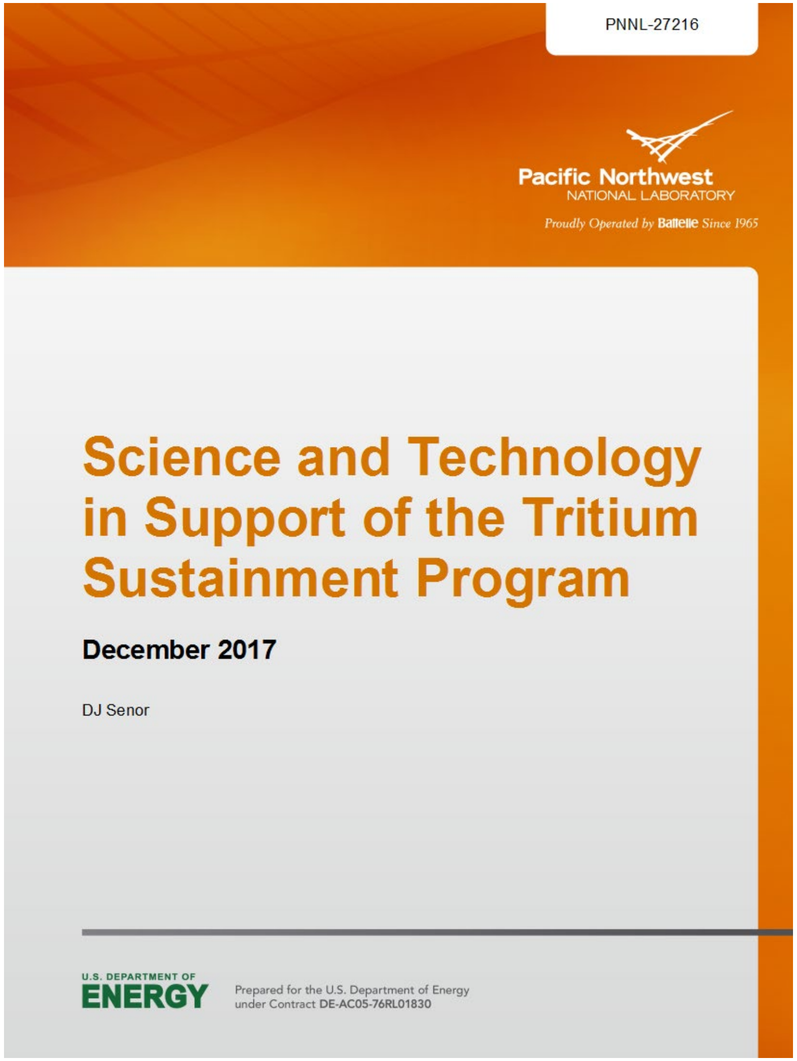
- Tritium permeation was higher than expected in first production cycle
  - Resulted in limitations on TPBAR quantities
  - Mark 9.2 design change was intended to address postulated permeation mechanisms, but had no effect
  - Cycle 6 and Cycle 9 PIE campaigns highlighted other unexpected performance attributes
- The S&T program was started in 2007 to address permeation but later expanded as new information became available



Cycle	Cycle Start Date	TPBAR Design	Number of TPBARs	Average Tritium Production (g/TPBAR)	Cycle Length (EFPD)
6	Fall 2003	Production	240	0.974	475.9
7	Spring 2005	Production	240	0.972	489.5
8	Fall 2006	Production	240	0.911	426.4
9	Spring 2008	Mark 9.2	368	0.949	515.0
10	Fall 2009	Mark 9.2	240	1.000	508.5
11	Spring 2011	Mark 9.2	544	0.893	460.0
12	Fall 2012	Mark 9.2	544	0.996	498.5
13	Spring 2014	Mark 9.2	704	0.980	485.2
14	Fall 2015	Mark 9.2	704	0.867	482.9
15	Spring 2017	Mark 9.2	1104	0.916*	472.7*
16	Fall 2018	Mark 9.2	1588		
				*Projected	

Science and Technology Plan

- Science and Technology Needs and Priorities
  - Defined in Science and Technology Plan
  - Recommendations collected from all Tritium Sustainment Program stakeholders via a series of workshops coordinated by Science, Design and Testing PRT
    - ✓ NNSA
    - ✓ Utility (TVA)
    - ✓ TPBAR Fabricator (WesDyne)
    - ✓ Tritium Extraction Facility
    - ✓ Laboratories (PNNL, SNL, SRNL, INL, NETL)
  - S&T Plan contents
    - ✓ TPBAR irradiation history at the Watts Bar Nuclear power plant and the drivers for improved understanding of TPBAR performance
    - ✓ Evolution of the S&T program since its beginning in 2006
    - ✓ Summary of results to date
    - ✓ Programmatic and technical objectives for S&T
    - ✓ Knowledge gaps
    - ✓ TPBAR performance modeling roadmap
    - ✓ Specific recommendations


PNNL-27216

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Science and Technology in Support of the Tritium Sustainment Program

December 2017

DJ Senor

U.S. DEPARTMENT OF ENERGY

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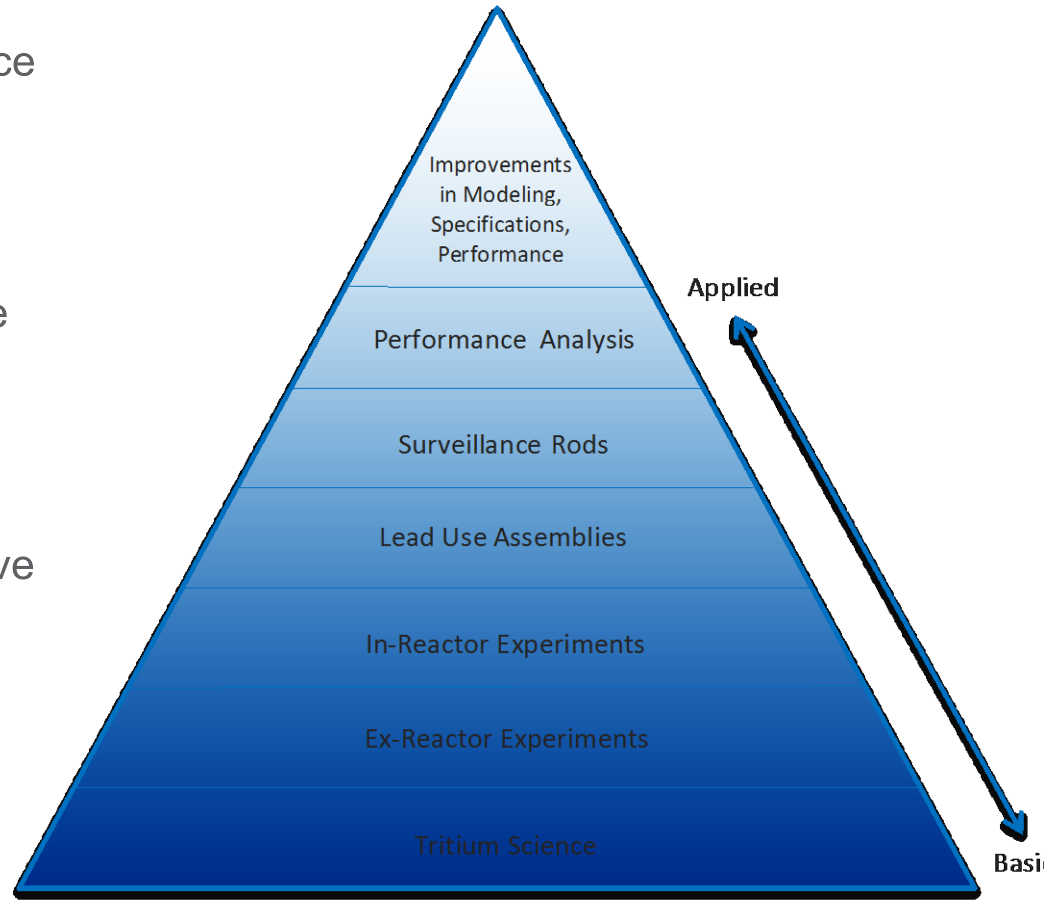
S&T Program Objectives

- The principal objective is risk reduction by improving comprehensive understanding of TPBAR performance during irradiation and extraction
- The principal desired outcome is improvement of predictive models thereby reducing uncertainty on performance
- Achieving the objectives will enable
  - Explaining and predicting TPBAR performance, reducing risk to TVA and TEF operations and NNSA production schedules
  - Reliable predictions if TVA changes reactor operating conditions or cycle durations
  - Optimization of tritium extraction and minimization of TEF plant degradation
  - Ensuring specifications for TPBAR components control all relevant properties and characteristics that influence performance
  - Evaluation and response to changes in component suppliers and fabrication processes
  - Making incremental design changes to improve TPBAR performance with high confidence

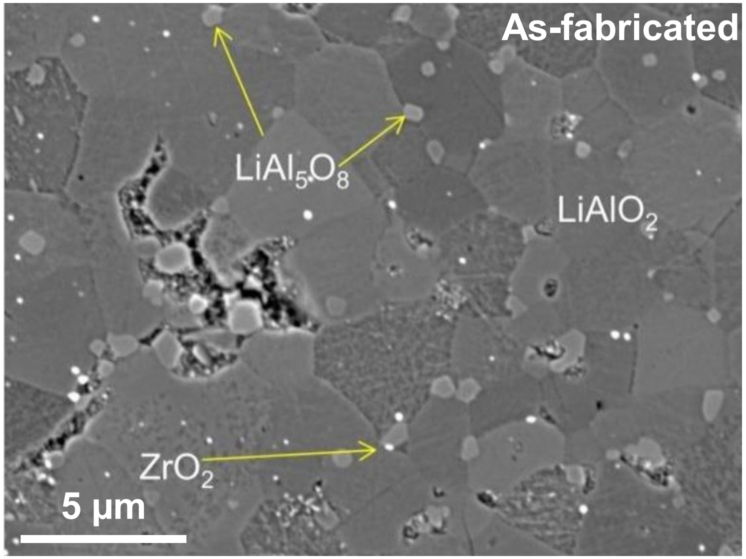
S&T Program Structure

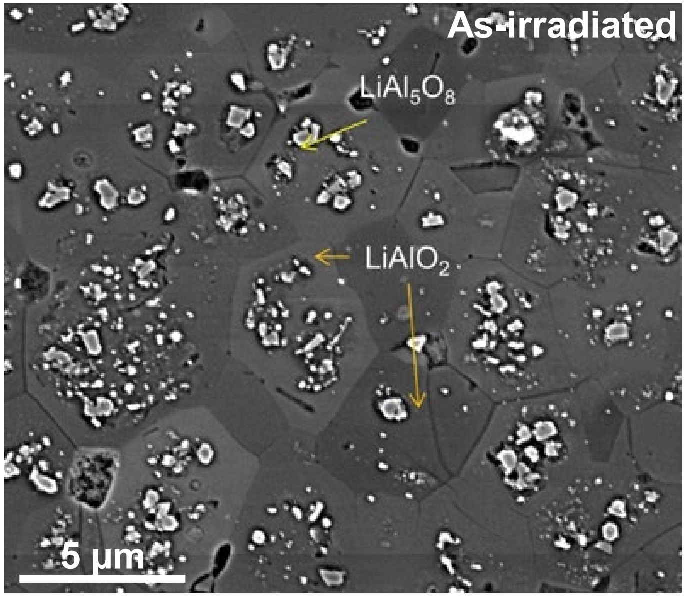
- Activities range from basic science to highly applied and include a variety of complementary efforts
- The ability to develop insight into TPBAR component performance would not be possible without the full range of science and technology activities performed over the past several years
- A comprehensive and integrated S&T program is necessary to drive improvements in performance modeling, design specifications and ultimately, TPBAR performance
- A bibliography of publications produced by the S&T program is available



Microstructural Evolution of $LiAlO_2$ Pellets

- Before irradiation
  - Small quantity of $LiAl_5O_8$ precipitates on grain boundaries
  - Porosity exclusively on grain boundaries
- After irradiation
  - Larger quantity of $LiAl_5O_8$ precipitates located within the grains
  - As-fabricated porosity still on grain boundaries, but additional porosity located within the grains
  - Intragranular porosity is associated with the $LiAl_5O_8$ precipitates
  - Some grain boundary separation evident
  - Dense $LiAlO_2$ adjacent to grain boundaries

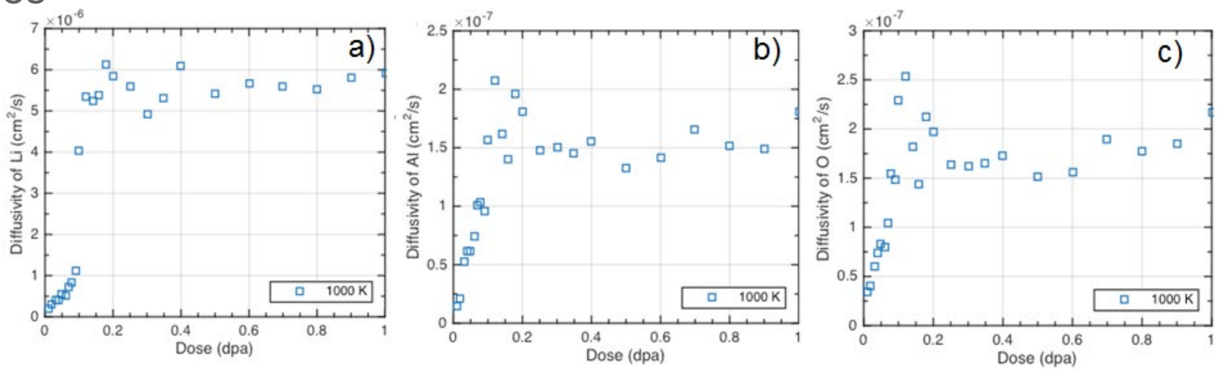




Buck et al. 2018. *PNNL-SA-138156*

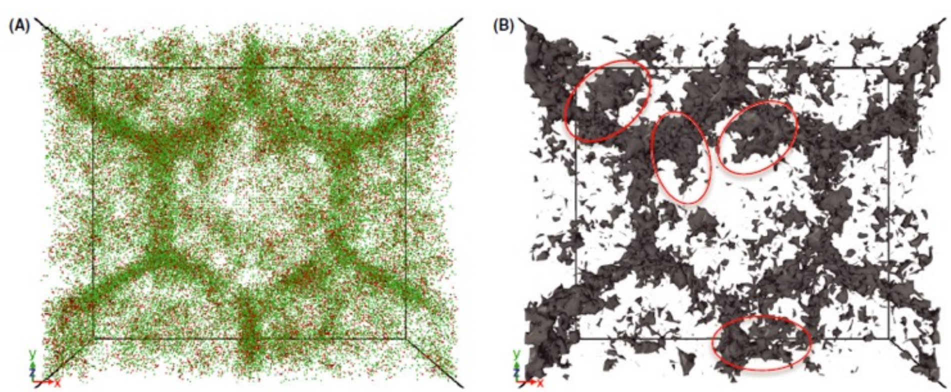
Atomistic-Scale Modeling

- Molecular dynamics simulations indicate that Li mobility in a radiation-damaged $LiAlO_2$ lattice is much higher than Al or O, and that Li would be lost from free surfaces

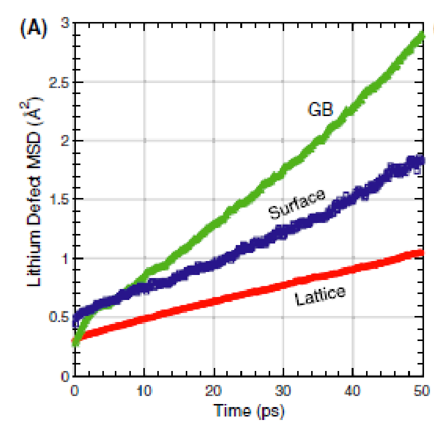


Setyawan and Devanathan. 2016. *PNNL-25938*

- The simulations also suggest that disorder from radiation damage tends to nucleate near free surfaces and grain boundaries and that Li diffusion is fastest along grain boundaries



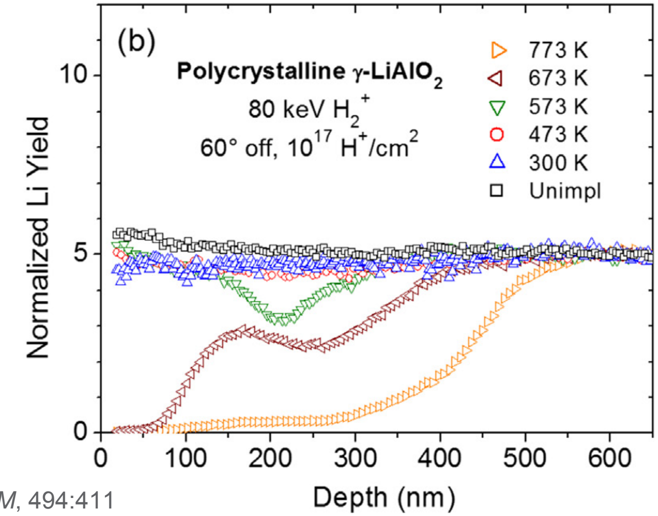
Setyawan et al. 2018. *J. Am. Ceram. Soc.*, DOI: 10.1111/jace.16051



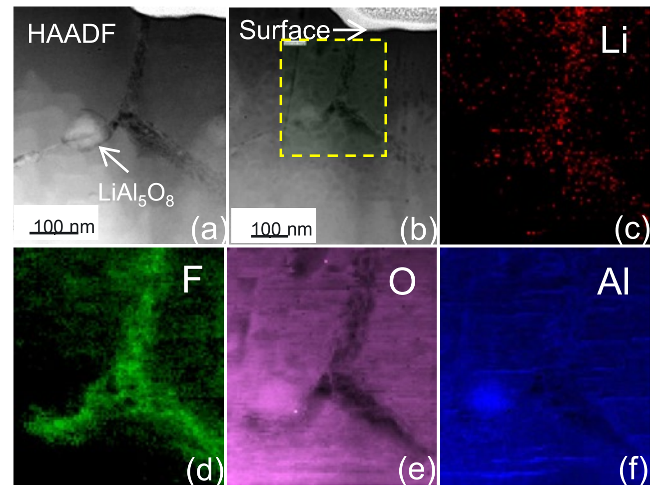
Nandipati et al. 2018. *PNNL-28096*

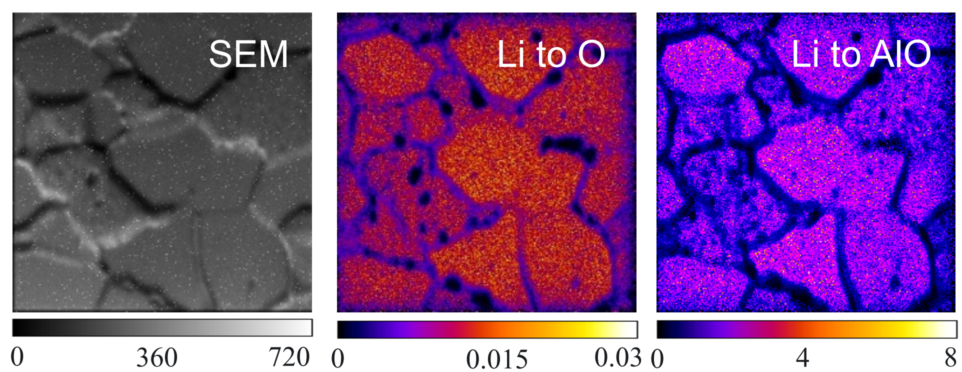
Ion Irradiations

- Ion irradiation followed by ToF-SIMS confirmed the MD simulation of Li loss from the surface of polycrystalline γ-$LiAlO_2$ at irradiation temperatures of 300°C or higher
- Ion irradiation followed by STEM-EELS confirmed the MD simulation of Li movement along grain boundaries, but only because of trapping by an unintentional contaminant
- Ion irradiation followed by nano-SIMS shows Li-depleted grain boundaries confirming rapid Li diffusion and loss



Jiang et al. 2017. *JNM*, 494:411





Jiang et al. 2018. *JNM*, 511:1

Microscopy of TPBAR Pellets

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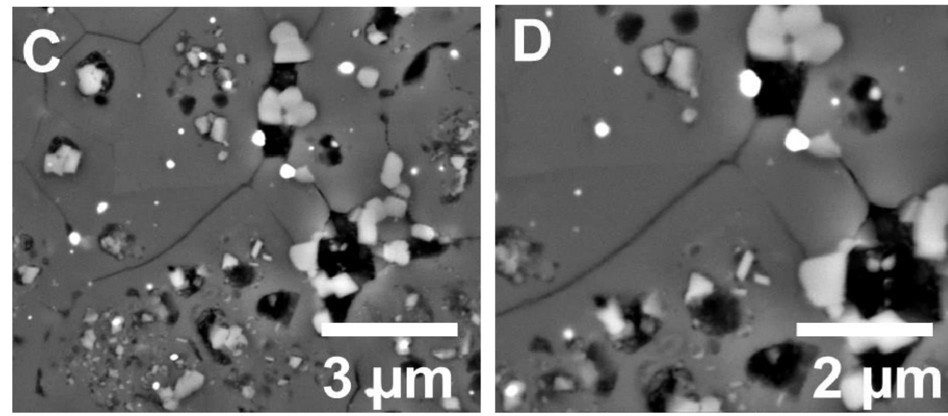
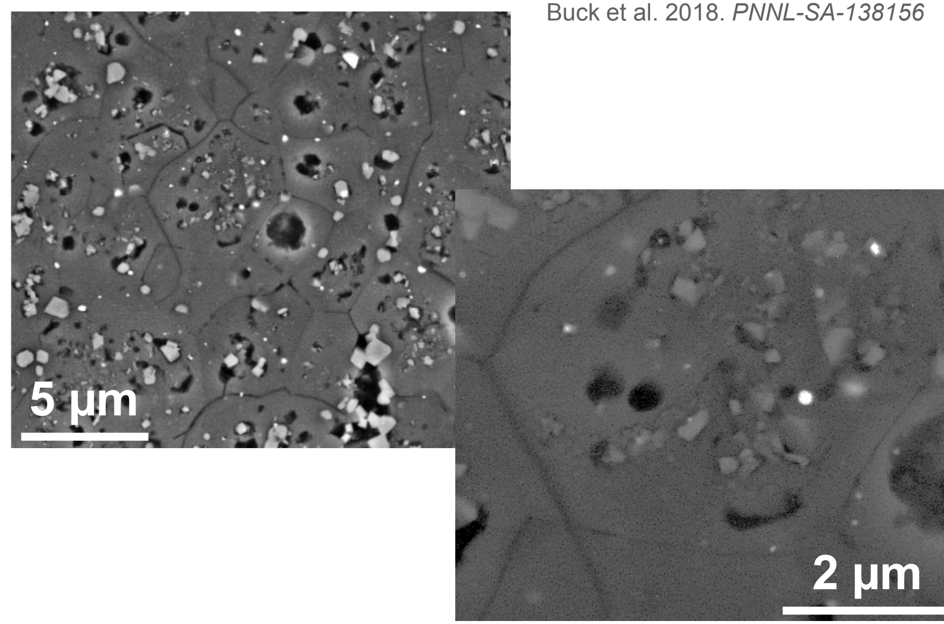
- Scanning electron microscopy clearly shows numerous open grain boundaries
  - Perhaps caused by localized decrease in density resulting from disorder nucleating at grain boundaries?
- Preliminary EBSD results suggest some amorphization near free surfaces
  - Also consistent with MD simulations

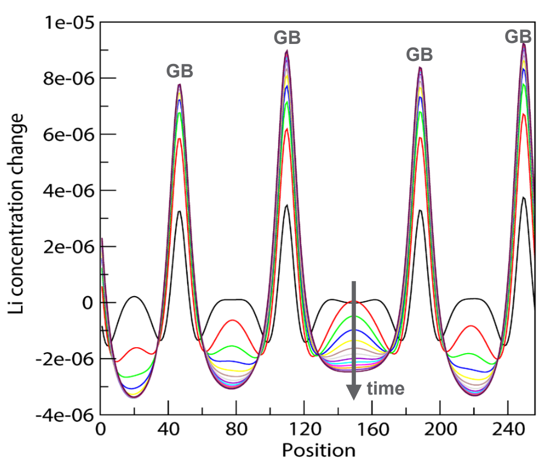


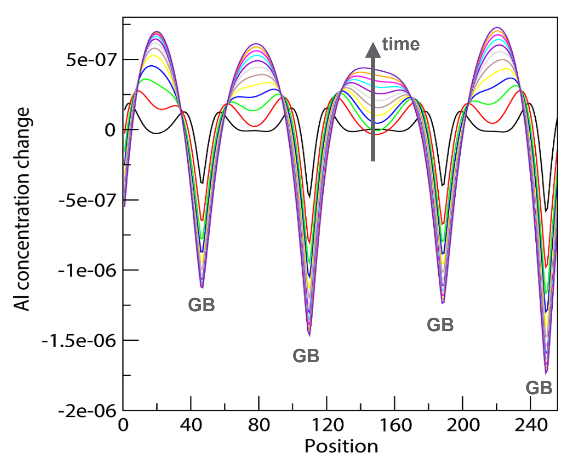
Buck et al. 2018. *PNNL-SA-138156*

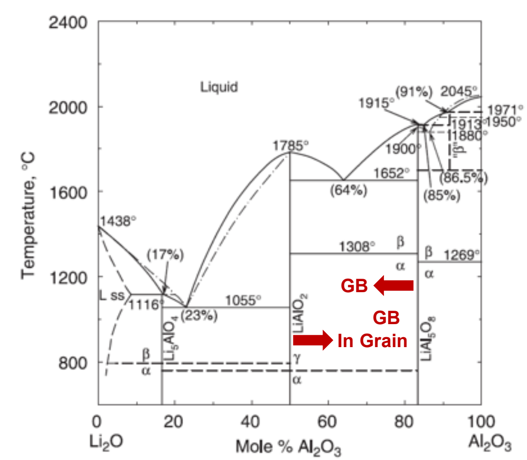


Phase Field Modeling

- Using the MD results for production of defects, phase field models were developed to simulate meso-scale microstructural evolution
  - The results are necessarily parametric in nature because of uncertainty in defect properties such as migration and binding energies, thermodynamic properties, etc.
  - DFT studies are under way to address these knowledge gaps
- The phase field model results indicate Li depletion in the middle of grains and Li migration toward grain boundaries with increasing irradiation dose
  - Consistent with with microscopy
  - Explains formation of $LiAl_5O_8$ in the middle of grains and elimination of $LiAl_5O_8$ on grain boundaries







Hu et al. 2018. *PNNL-SA-138165*

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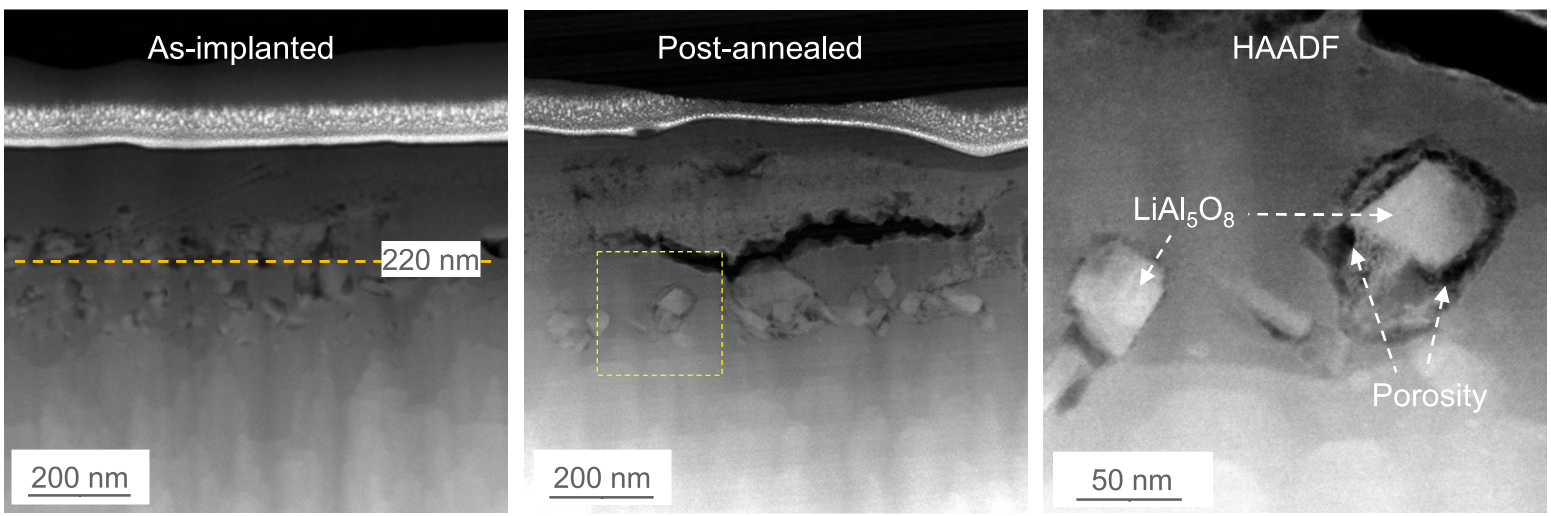
Ion Irradiations

- Porosity in the middle of grains is likely due to density change between $LiAlO_2$ (2.62 g/cm^3) and $LiAl_5O_8$ (3.61 g/cm^3)
  - Porosity always associated with $LiAl_5O_8$ precipitates
  - Porosity is not likely the result of void clustering because MD simulations indicate increasing defect formation energy with decreasing defect spacing
- Similar $LiAl_5O_8$ precipitates have been observed near Li-depleted surfaces in ion irradiated and annealed $LiAlO_2$
  - These precipitates have associated porosity similar to that observed in neutron irradiated $LiAlO_2$



2×10^{17} He^{+}+H^{+}/cm^2

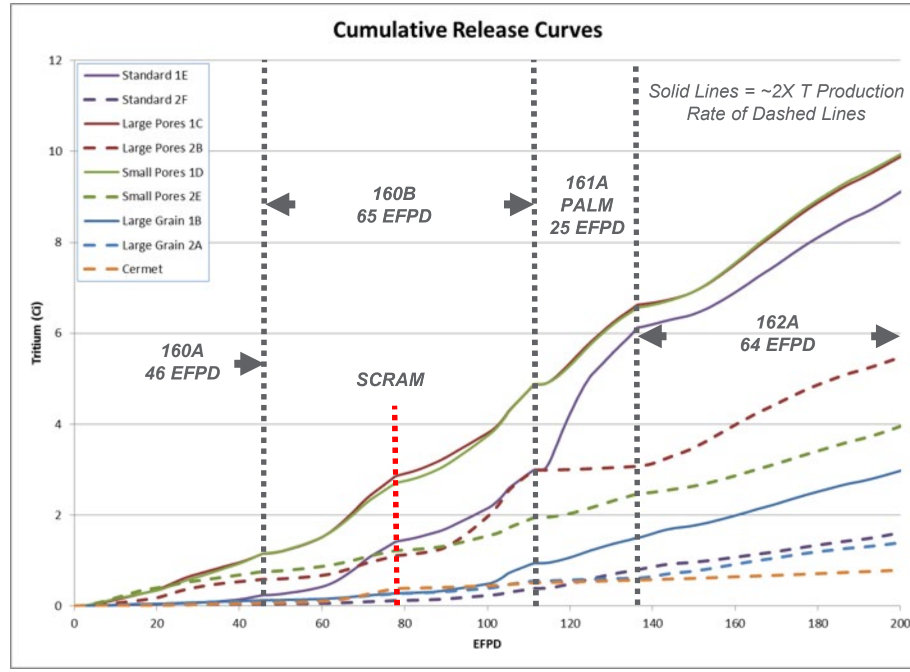
2×10^{17} He^{+}+H^{+}/cm^2
Anneal at 873 K, 30 min

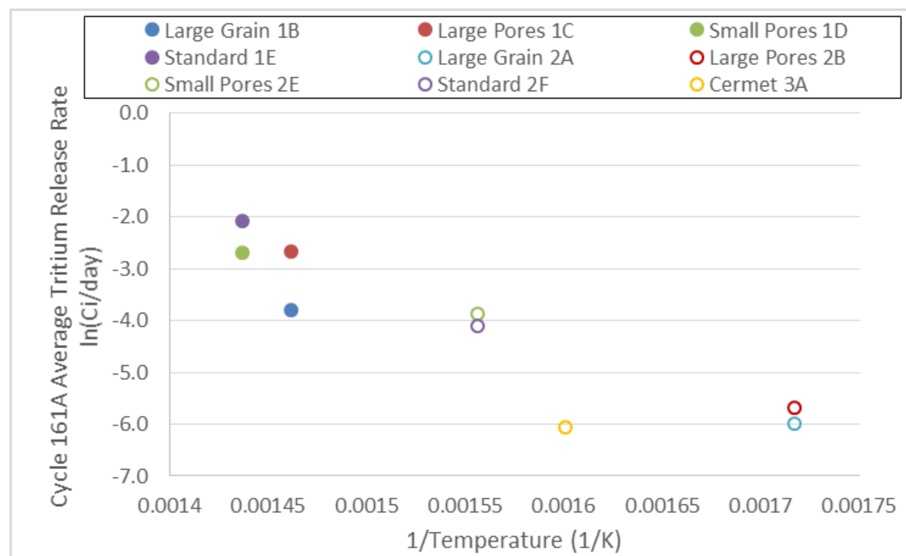
2×10^{17} He^{+}+H^{+}/cm^2
Anneal at 873 K, 30 min

Jiang et al. 2018. *JNM*, 511:1

Neutron Irradiation Experiment

- TMIST-3 is a pellet irradiation experiment at the Advanced Test Reactor with active temperature control and online tritium release measurement
  - Tritium release rate from pellets is a function of production rate, pellet microstructure and temperature
- The activation energy deduced from the PALM cycle Arrhenius plot suggests that intragranular diffusion is the rate-limiting step in tritium release
  - 102 kJ/mol consistent with tritium diffusion in $LiAlO_2$ (80-130 kJ/mol)
  - Perhaps explains lower release rate of large-grain versus fine-grain pellets





Luscher et al. 2018. *PNNL-SA-134677*

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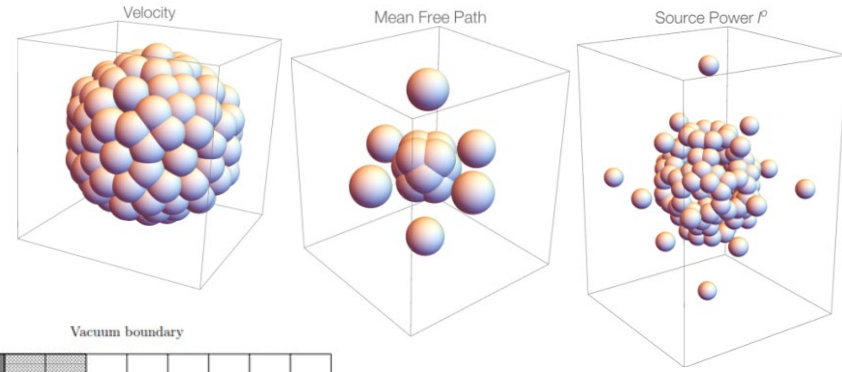
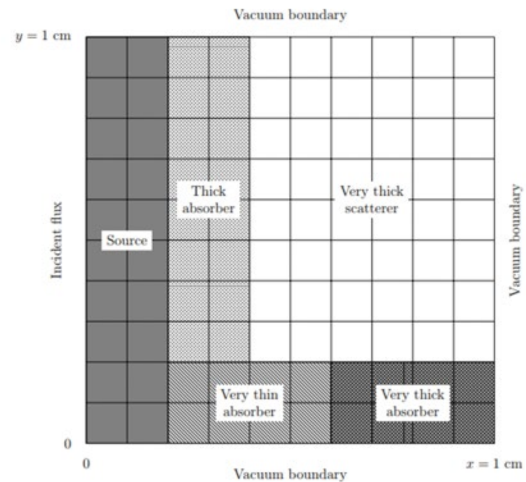
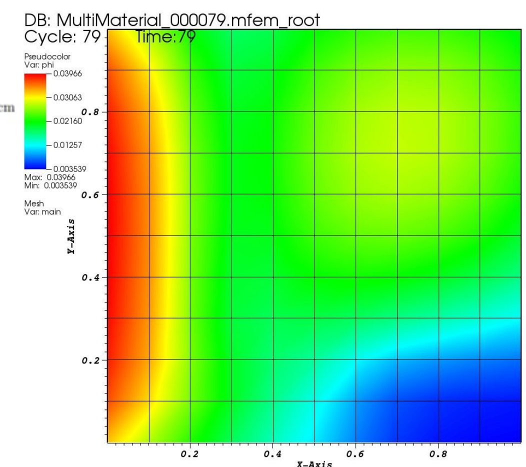
Thermal Conductivity Modeling



- The formation of porosity and $LiAl_5O_8$ precipitates in the middle of grains likely degrades pellet thermal conductivity
  - Could result in higher pellet temperatures as a function of ^{6}Li burnup
  - TMIST-3 data show that tritium release is strongly dependent on temperature
  - Therefore, increasing pellet temperature with burnup could increase pellet tritium release rates with burnup
- A thermal conductivity model is being developed using neutron transport methods to simulate phonon interactions in a radiation damaged lattice





Burkes et al. 2018. *PNNL-SA-134739*
(Images courtesy N. Whitman, T. Palmer and A. Greaney)

Putting It All Together

- The unique combination of models and experiments are combining to provide significant insight into the mechanisms responsible for pellet performance
  - Microstructural evolution
    - ✓ Enhanced Li mobility in a radiation damaged lattice leads to Li depletion in the middle of grains
    - ✓ $LiAl_5O_8$ precipitates form in the middle of grains as a result of Li depletion
    - ✓ Porosity forms in association with the $LiAl_5O_8$ precipitates due to the density change from $LiAlO_2$
  - Tritium release/retention
    - ✓ In-situ tritium release data show a dependence on grain size, porosity and temperature
    - ✓ Preliminary data for activation energy of pellet tritium release is consistent with grain boundary diffusion
    - ✓ The formation of precipitates and porosity likely degrades thermal conductivity and raises pellet temperature, which could increase tritium release with burnup
- If we understand the mechanisms behind pellet performance, it may be possible to engineer the pellet microstructure to tailor performance
  - Increase burnup limit
  - Increase tritium production
  - Decrease tritium release

Additional S&T Highlights to Date

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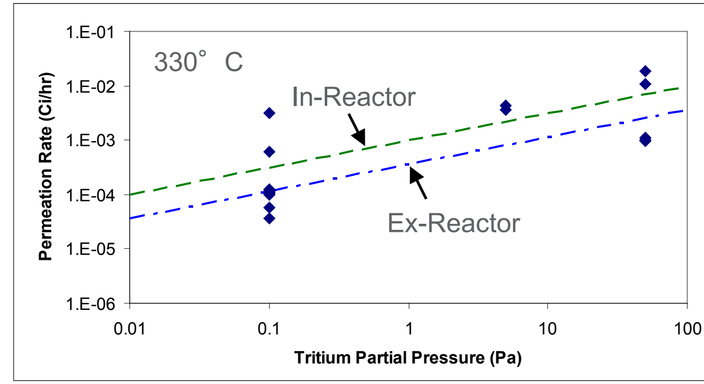
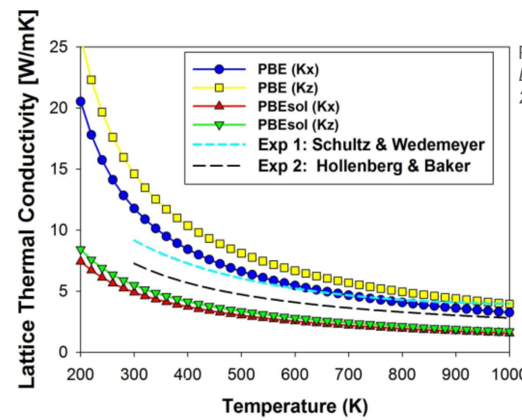
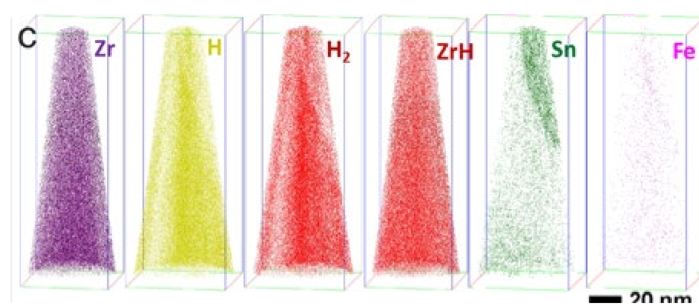
- Performance Analysis
  - Confirmed that secondary source rods contribute tritium to WBN coolant while fuel rods do not
- Lead use and surveillance PIE
  - Demonstrated viability of thin wall and large grain pellets
- In-reactor and ex-reactor experiments
  - Observed differences in component performance between separate effects and integral environments
  - Quantified irradiation enhancement of tritium permeation through 316SS
  - Confirmed in-reactor tritium permeation through 316SS is diffusion rate-limited
  - Observed differences in hydrogen isotope partial pressures over Zr versus Ni-plated Zircaloy-4
- Tritium Science
  - Developed new techniques to assess TPBAR component performance in PIE (APT, AFM, SANS, EELS, electrochemical etching)
  - Calculated and measured fundamental material properties (diffusion coefficients, thermal conductivity)
  - Improved understanding of hydride phase formation mechanisms
  - Developed insight into mechansims possibly responsible for irradiation enhancement of tritium permeation in stainless steel

Luscher et al., *JNM*, 437:373-379, 2013.





Paudel et al., *DOE/NETL-PUB-21464*, 2017.



Devaraj et al., *PNNL-27132*, 2017.