Computational Materials Modeling

Justin Haskins, Lauren Abbott, BJ Tucker

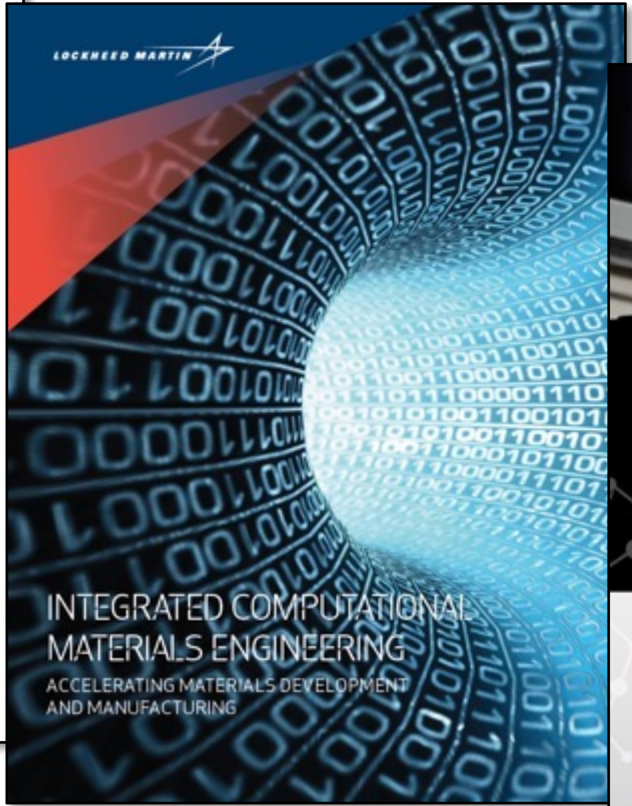
NASA Ames Research Center
Thermal Protection Materials Branch

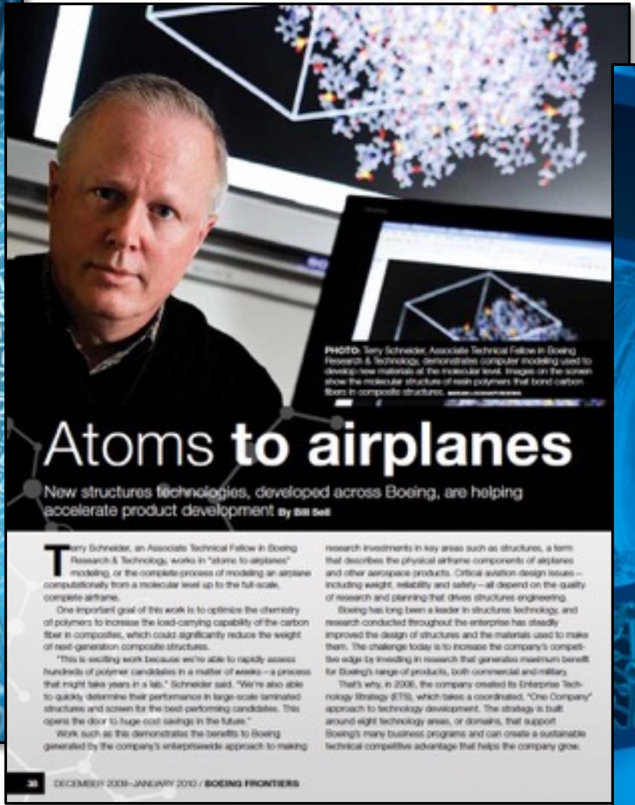
NASA Langley/Ames EDL Seminar Series

Integrated materials modeling accelerates development

Integrating computational materials tools "will enable cost effective, rapid, and revolutionary design of fit-for-purpose materials"

VISION 2040 (2018)

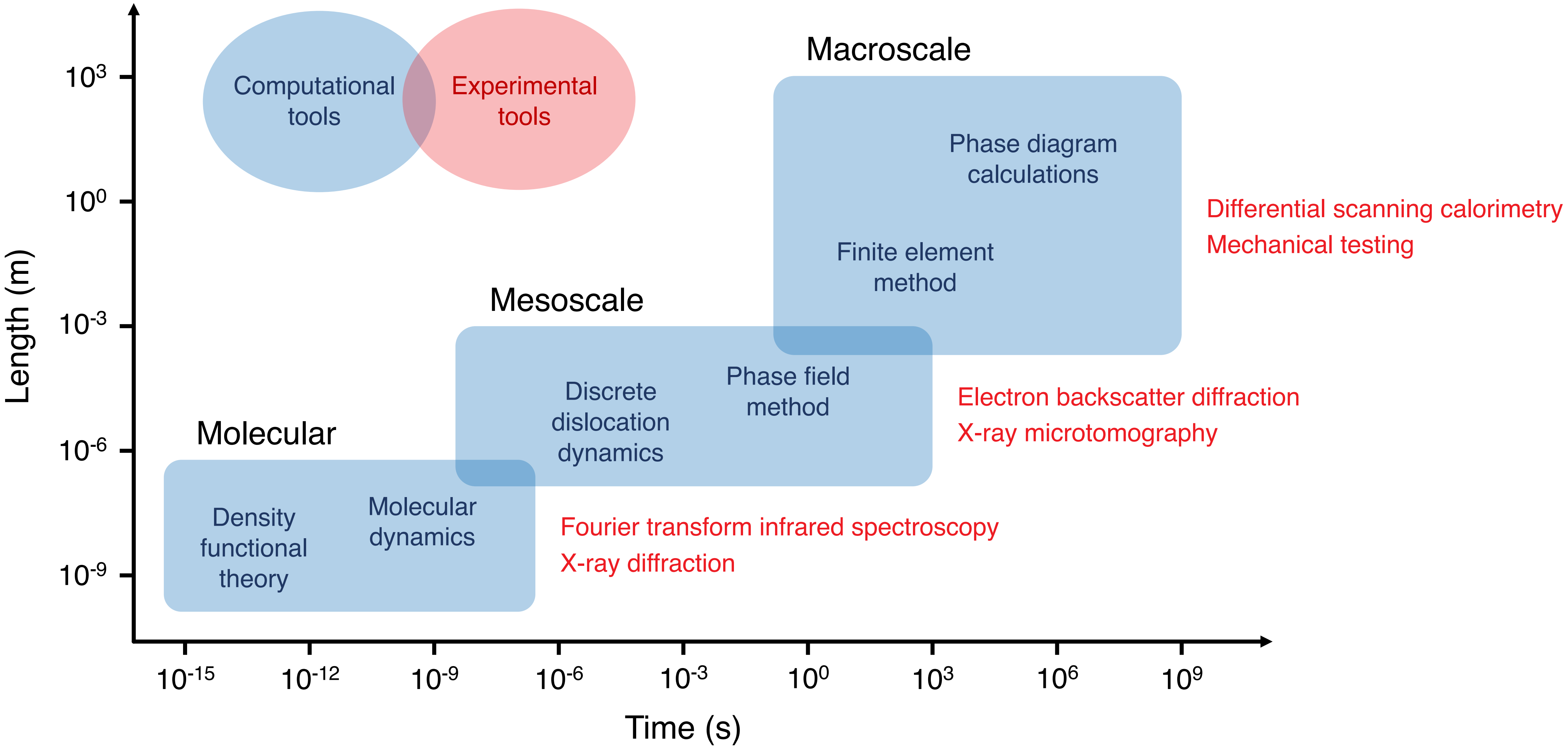




U.S. MGI (2011)

Integrating computational tools will help "to discover, develop, manufacture, and deploy advanced materials at least twice as fast"

Multi-scale problems require multi-scale tools



Acknowledgments

Computational Material Group
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AERoBOND Project
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Asteroid Threat Assessment Project
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Pratibha Raghunandan, AMA / NASA Ames
Brody Bessire, NASA Ames
Francesco Panerai, UIUC

Solar Thermal Propulsion
Dean Chiekh, Jet Propulsion Laboratory
Michael Preudhomme, Jet Propulsion Laboratory

Entry Systems Modeling – TPS Certification
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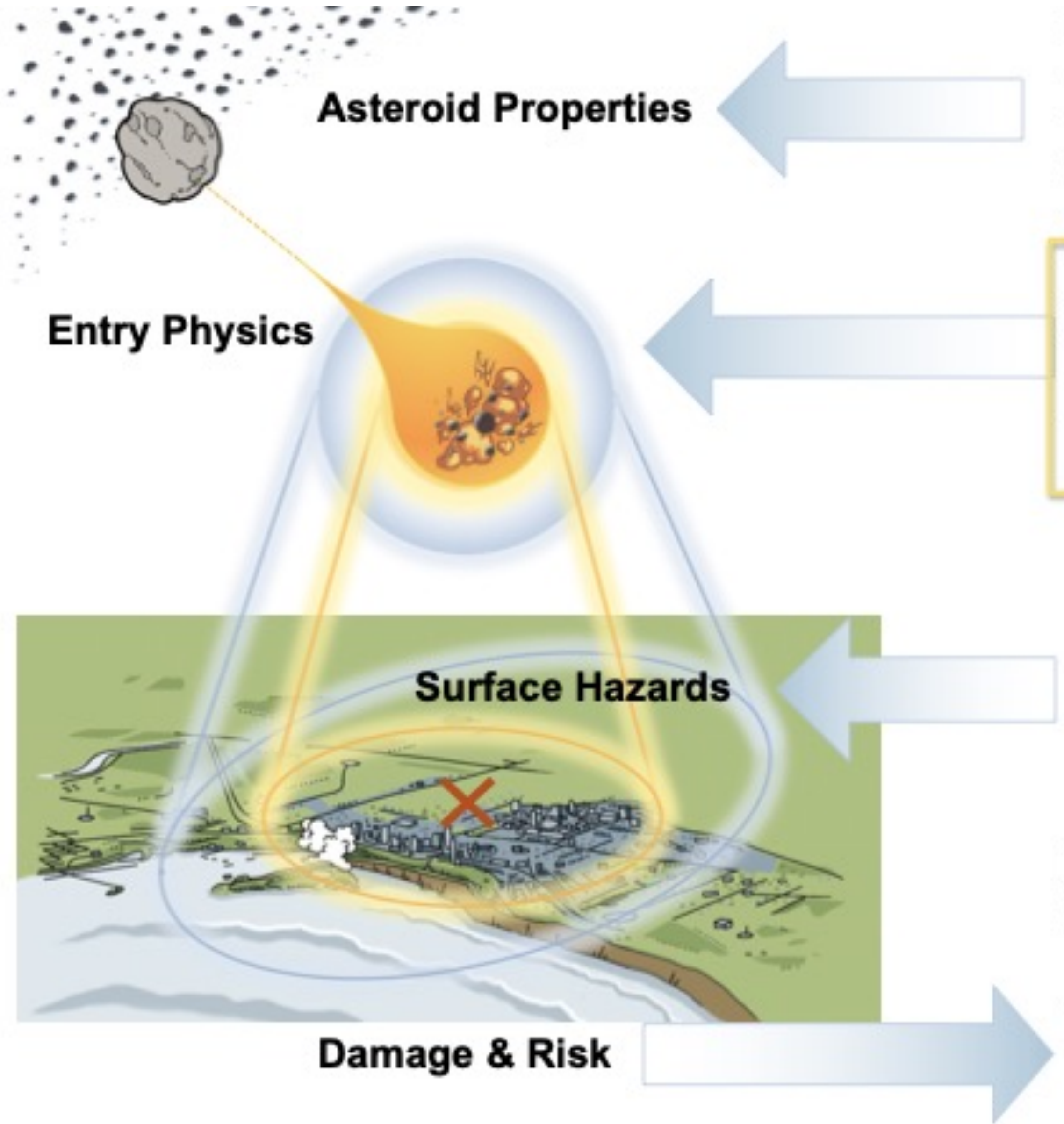
Sander Visser, AMA / NASA Ames
Kevin Wheeler, NASA Ames
Vasyl Hafiychuk, KRB / NASA Ames
Michael von Pohle, USRA / NASA Ames
Trenton Ricks, NASA Glenn
Brett Bednarcyk, NASA Glenn
Evan Pineda, NASA Glenn
Subodh Mital, University of Toledo / NASA Glenn

Part 1: Atoms to Asteroids

Justin Haskins

Supported by Asteroid Threat Assessment Project

Asteroid Threat Assessment Project



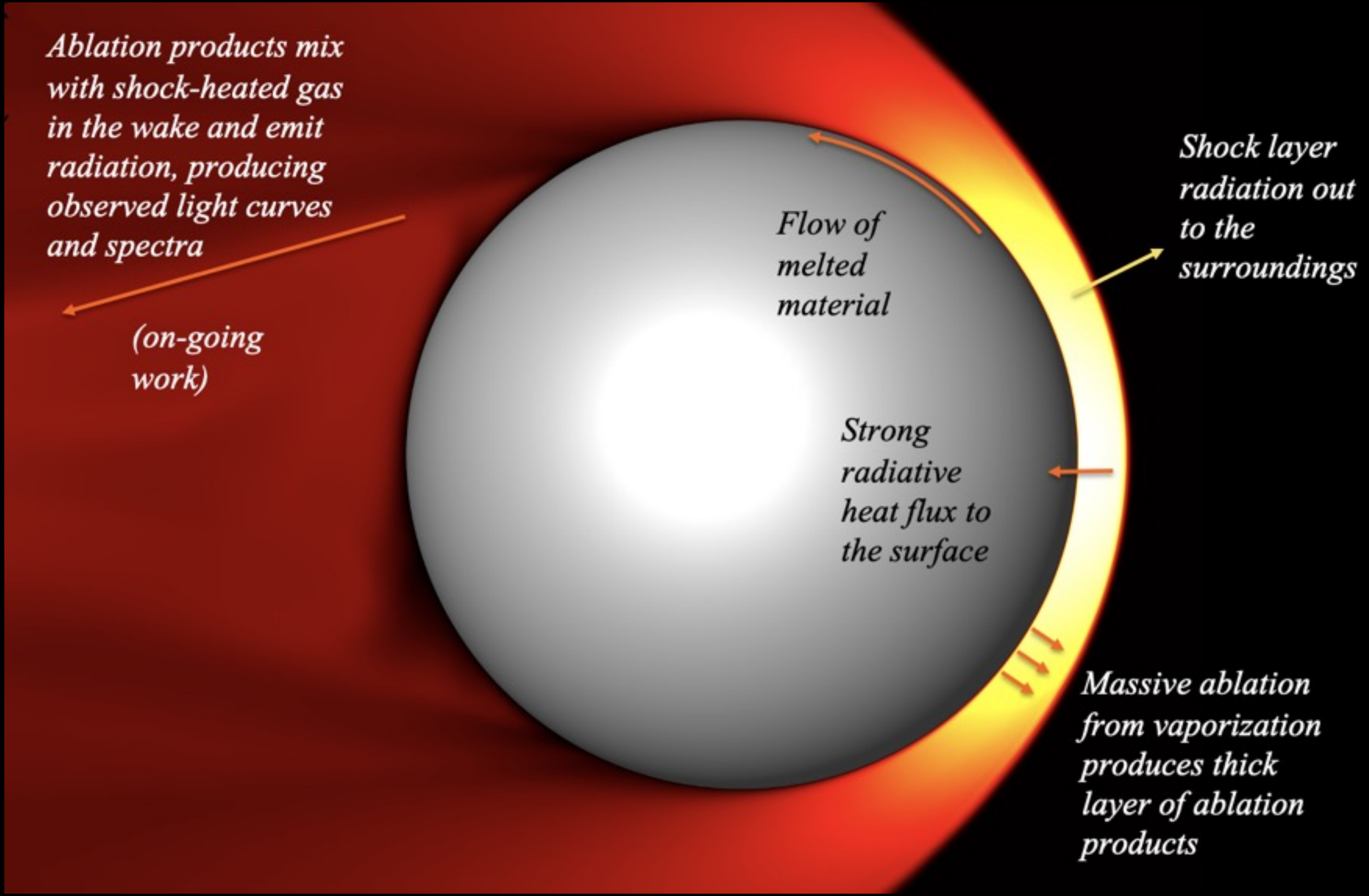
Characterization
- Measurements
- Inference
- Data aggregation
- Property database website

Entry Simulations & Testing
- Ablation & radiation modeling
- Ground testing
- Fracture, Fragmentation, and Break-up

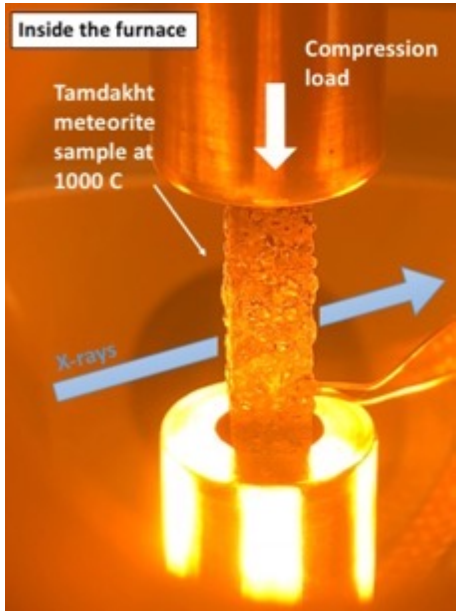
Hazard Simulations
- 3D blast simulations
- Impact crater simulations
- Tsunami simulations
- Thermal radiation models
- Global effects

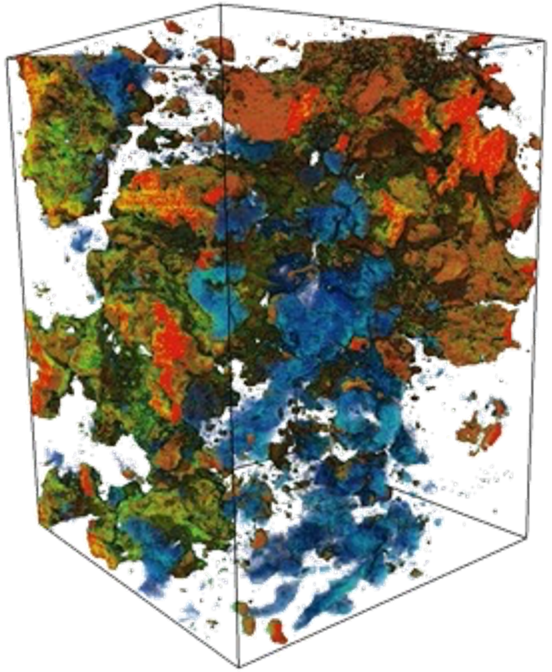
Probabilistic Risk Assessment
- Analytic physics-based entry and damage models
- Probabilistic Monte Carlo simulation using uncertainty distributions

Effects associated with meteor/asteroids entry

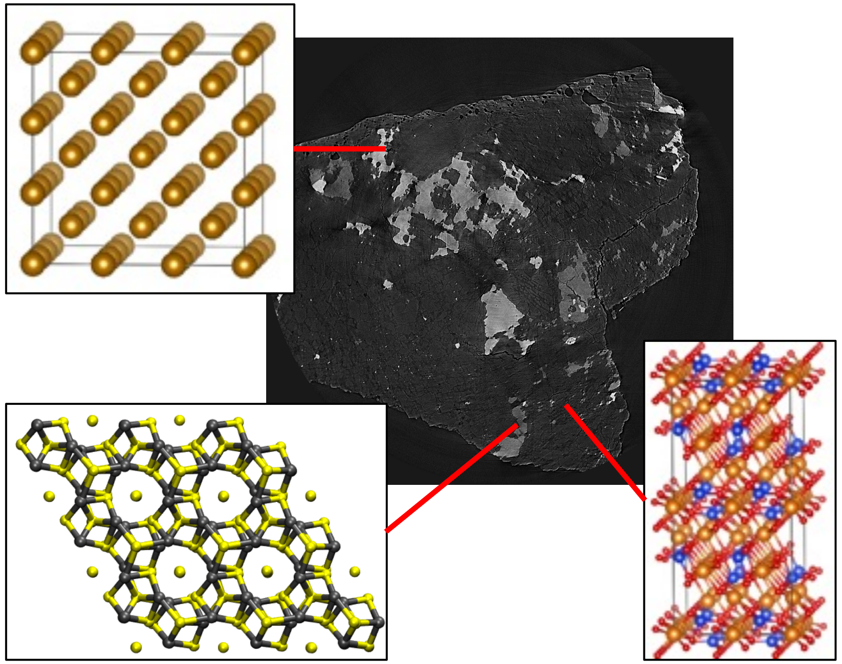


Meteorite Reactions During Heating
- In Situ X-ray Tomography of Heating Behavior
- Computational Chemistry Interpretation of Results





Meteorite Ablation
- Melt-Vaporization Ablation Model Development
- Ab Initio Molecular Dynamics Properties



Outline

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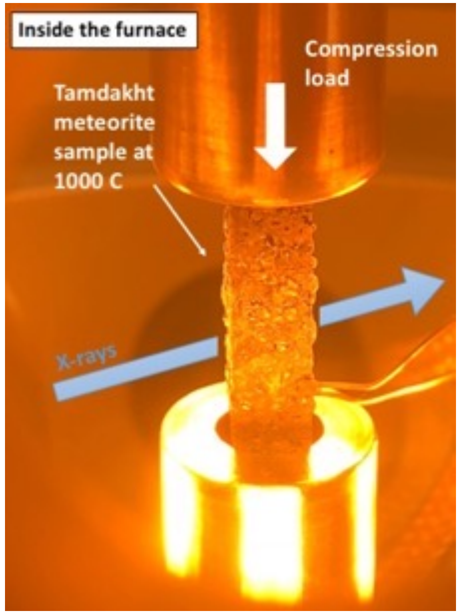

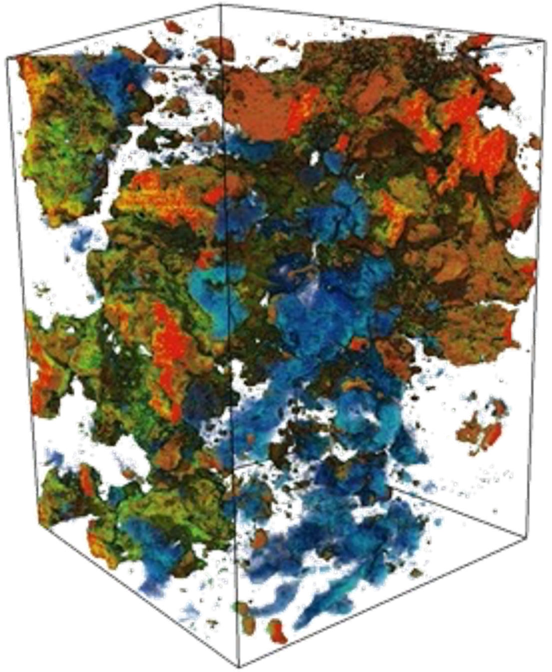

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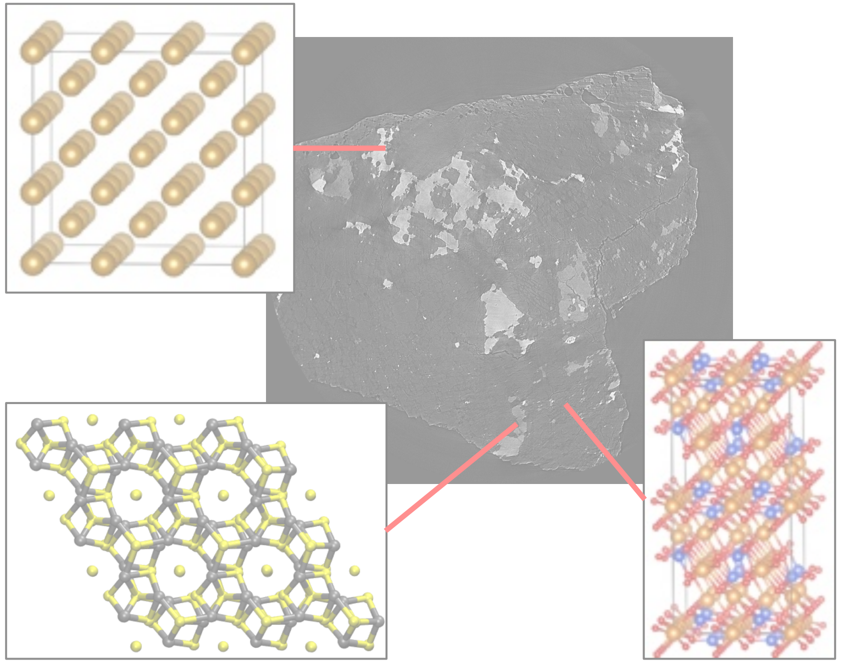
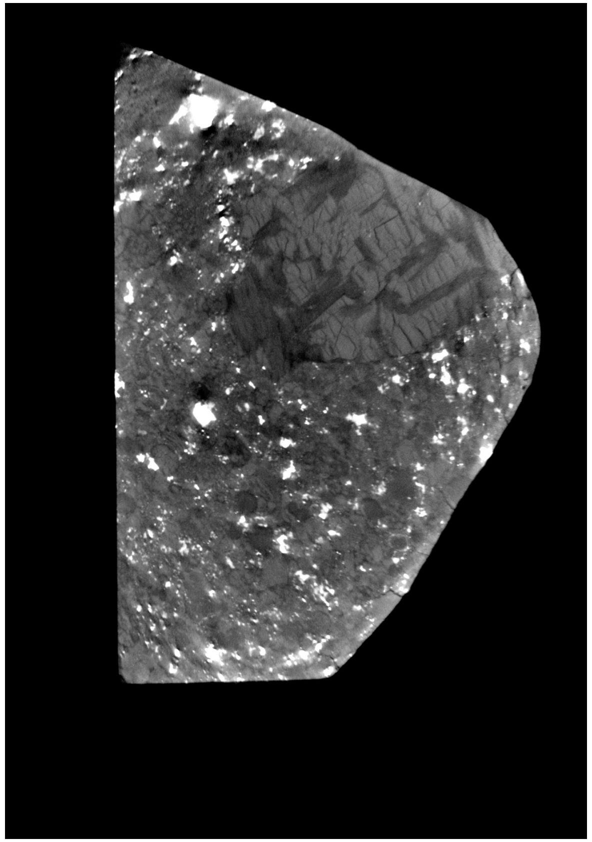


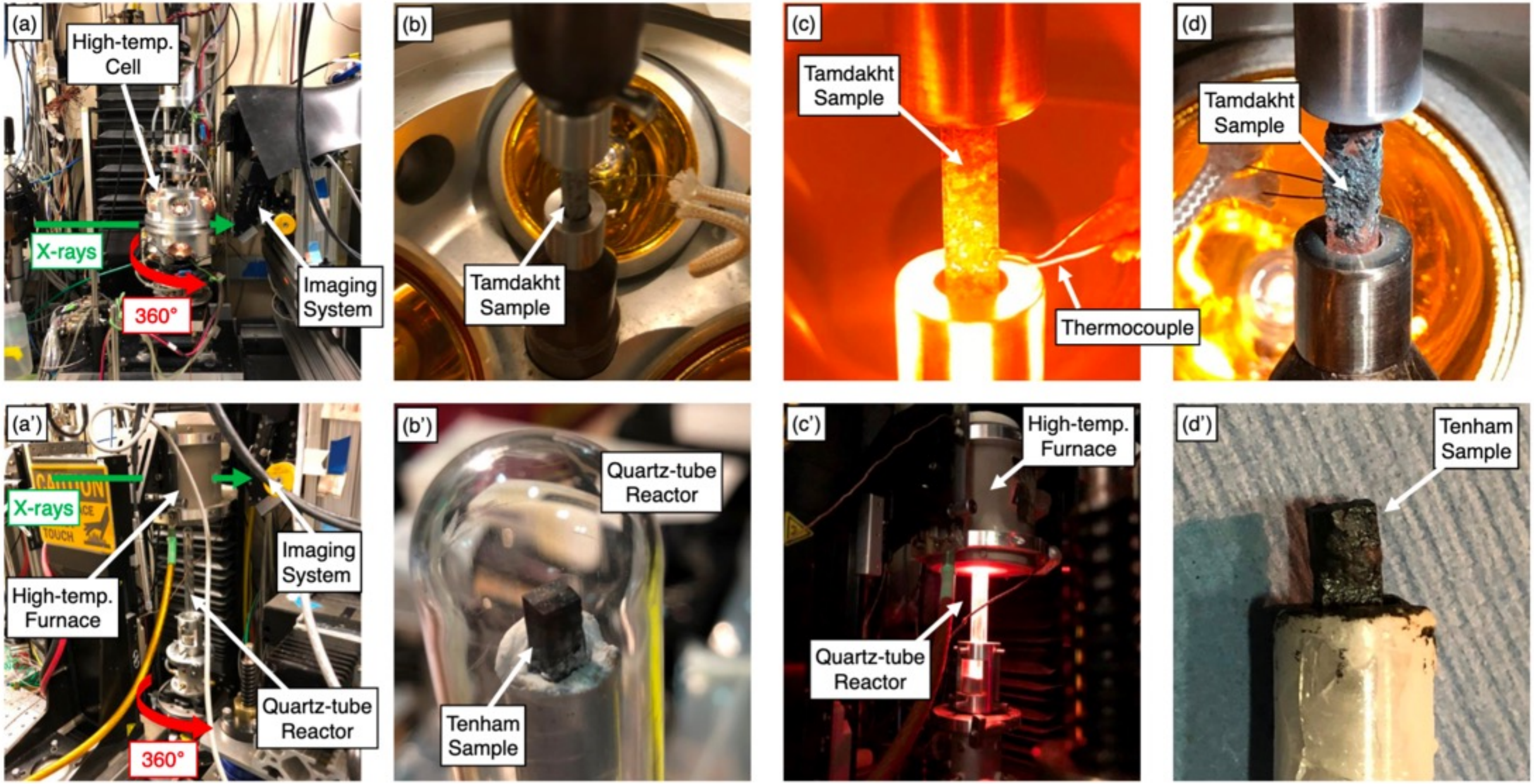
Microtomography of Stony Meteorites (Chondrites)

Power: 10 W
Magnification: 0.4x
Voxel size: 14.7 µm
Exposure time: 2 s
Projections: 3201



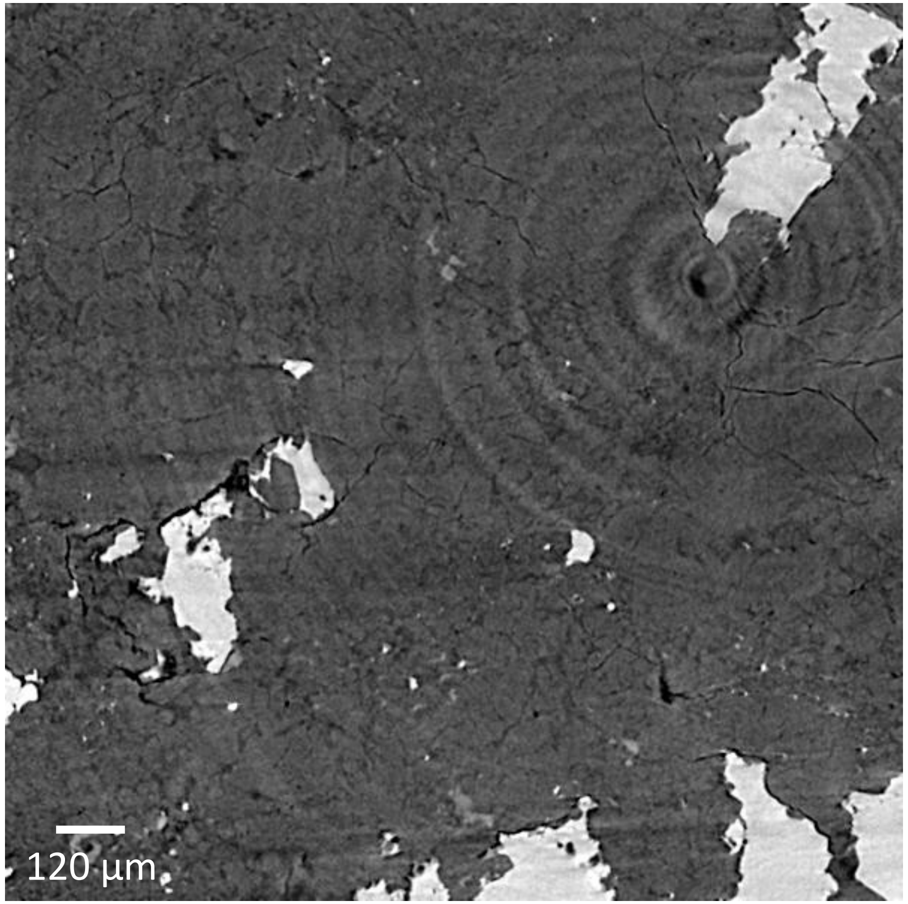
Focus on most common meteorites, chondrites, which are stony with a heterogeneous grain structure – microtomography identify grain densities and population as a first step to a compositionally accurate database

In Situ Microtomography of Stony Meteorites during Heating

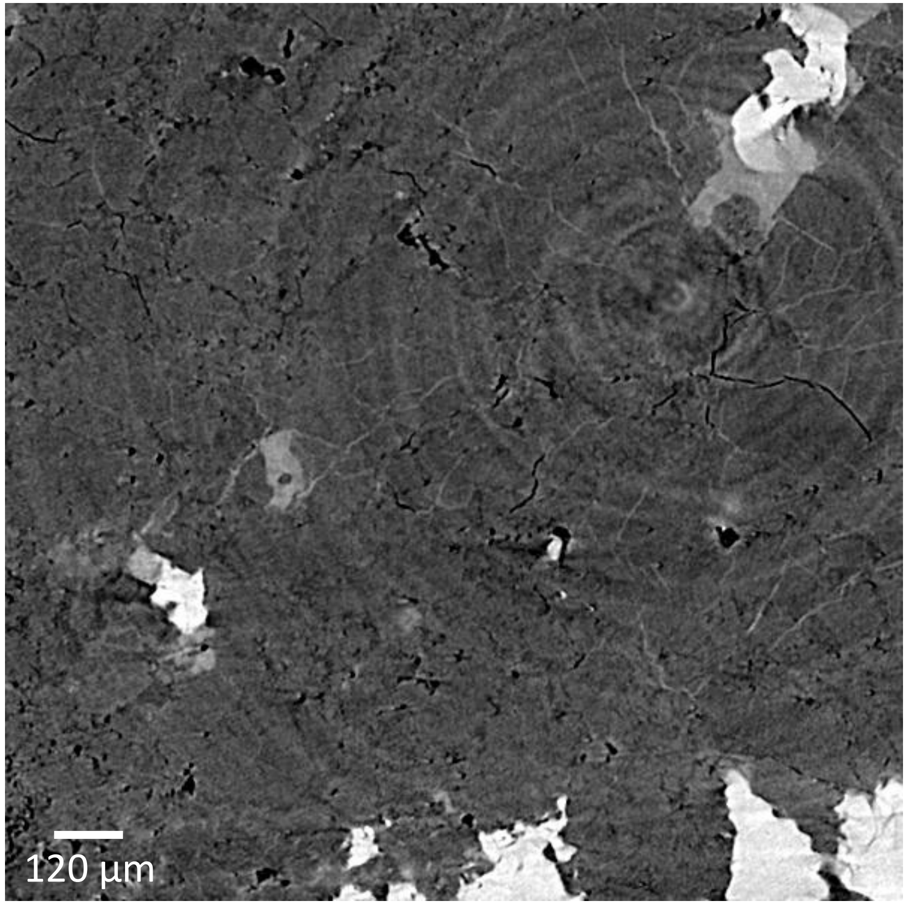


Changes in the Microstructure during Heating

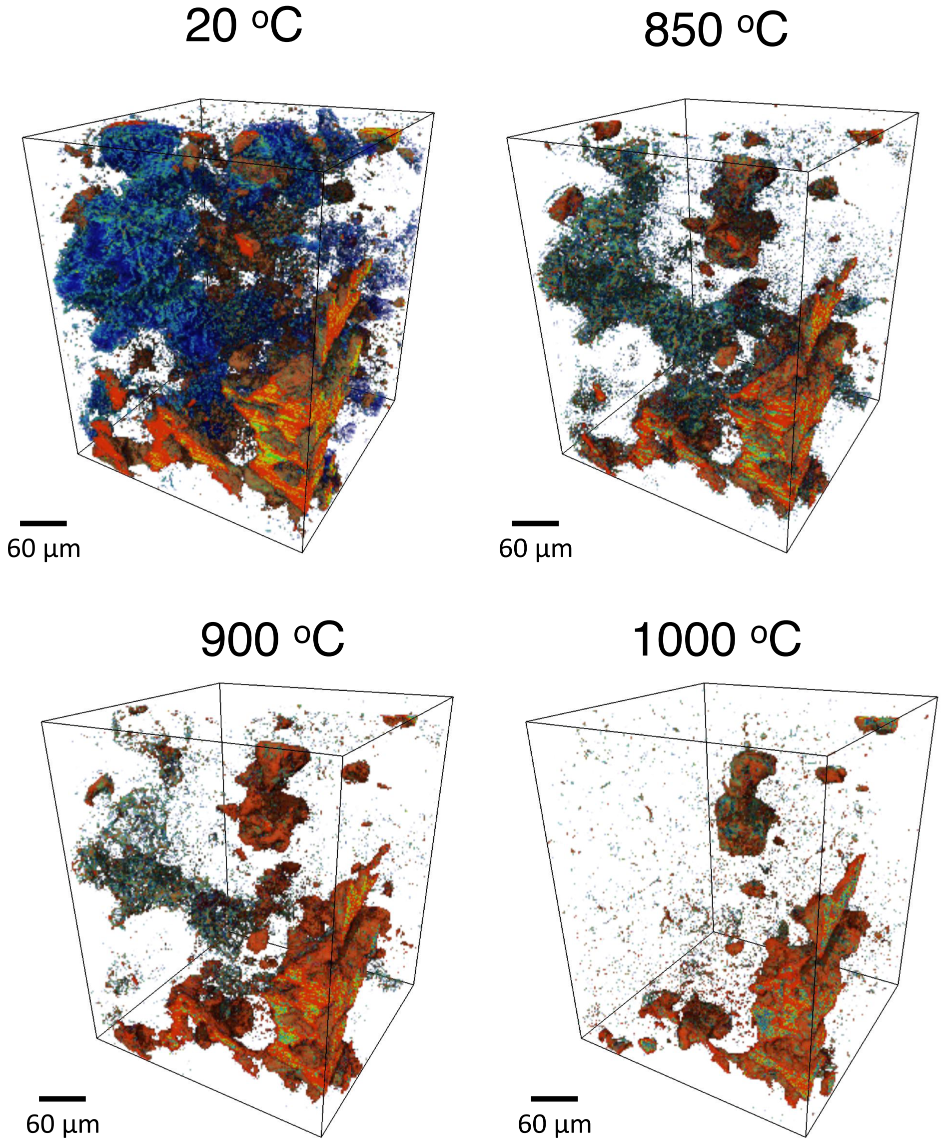
Room Temperature



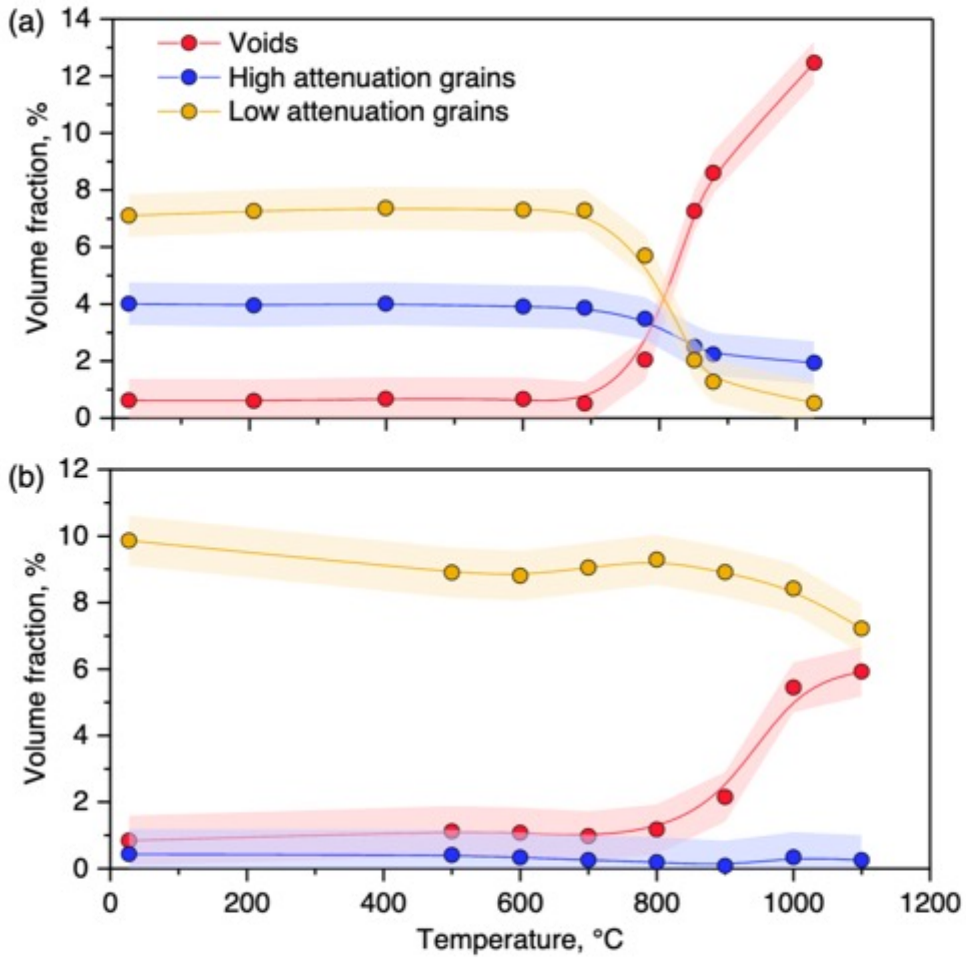
1200 K



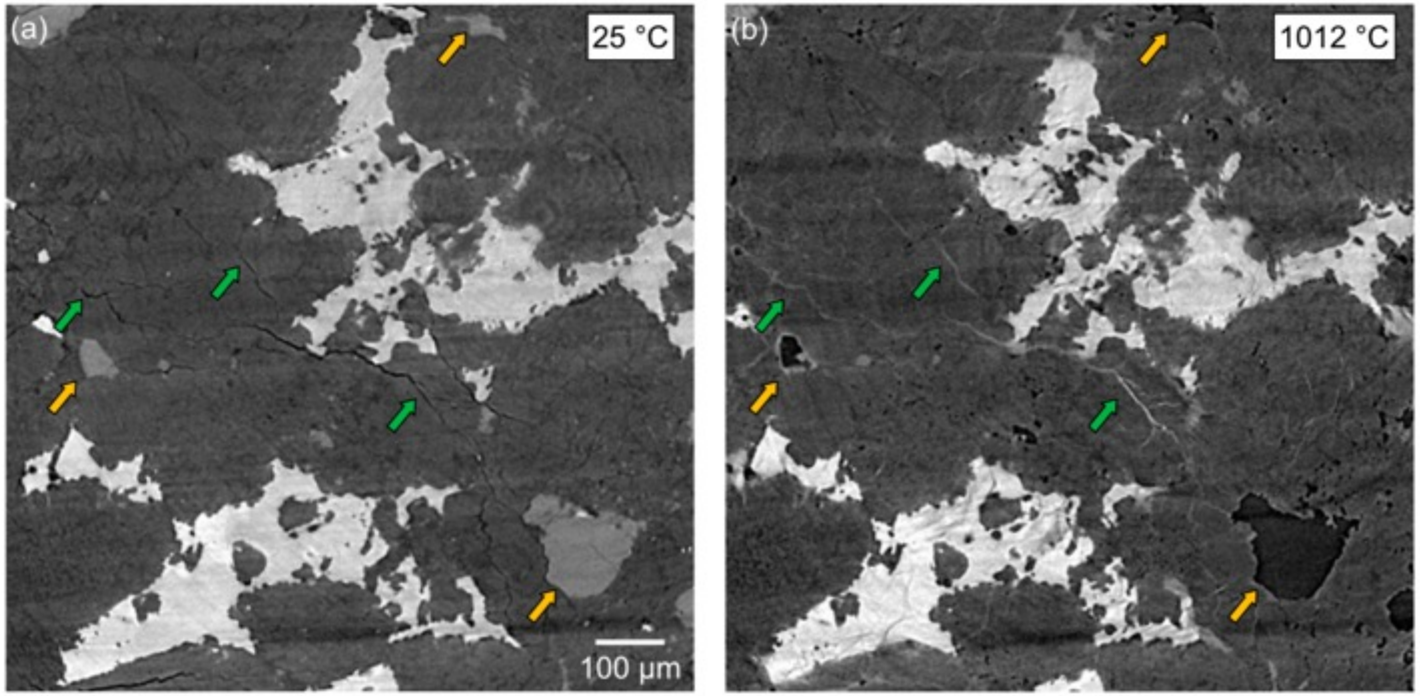
Volume resolved changes in porosity during heating



Void fraction seen to increase during heating

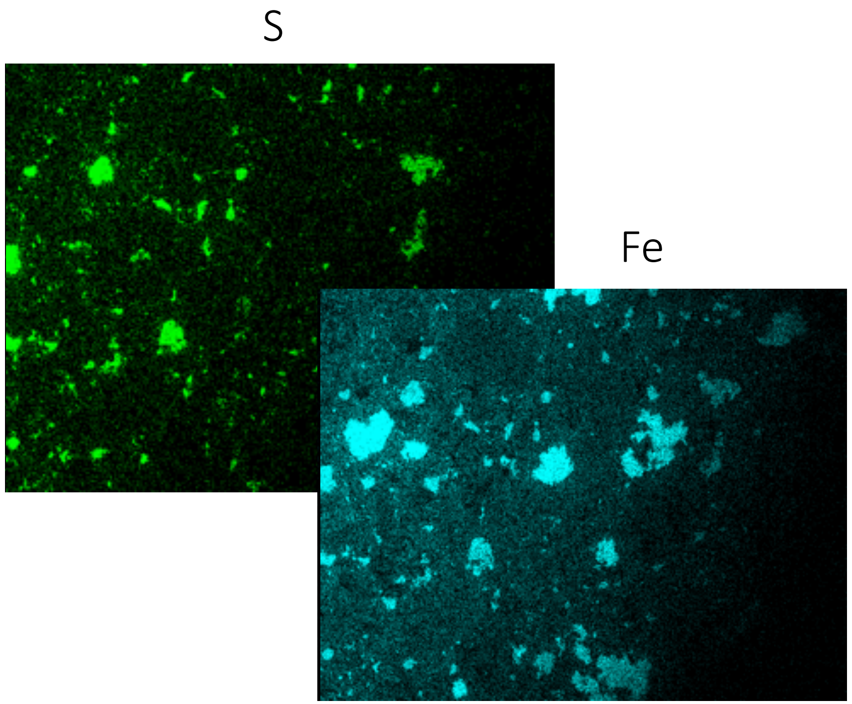


Identification of Lost Grain Material



Low attenuation grains melt/vaporize

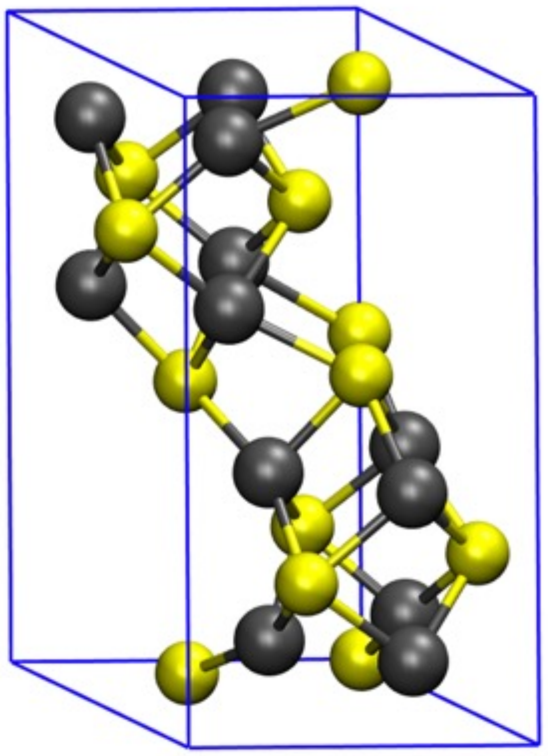
XPS image shows S and Fe in low attenuation grains



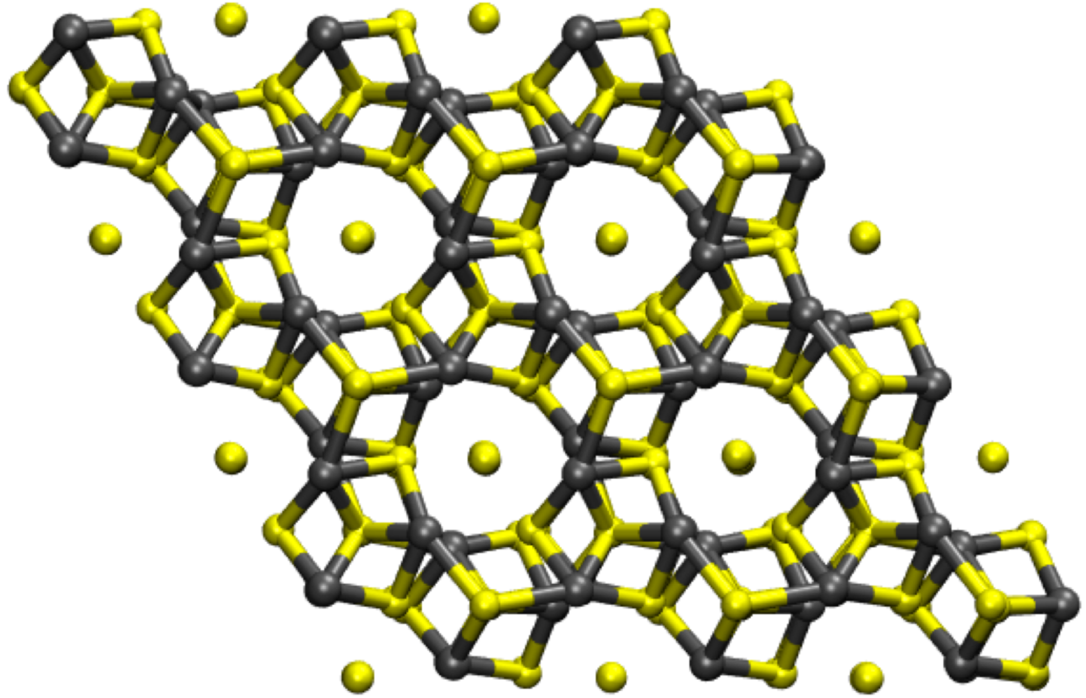
Cross referencing with meteoritic compositions indicate troilite (FeS) vaporizes or melts during heating

Iron sulfide (Troilite)

Unit cell of troilite for computations



View of the [001] plane

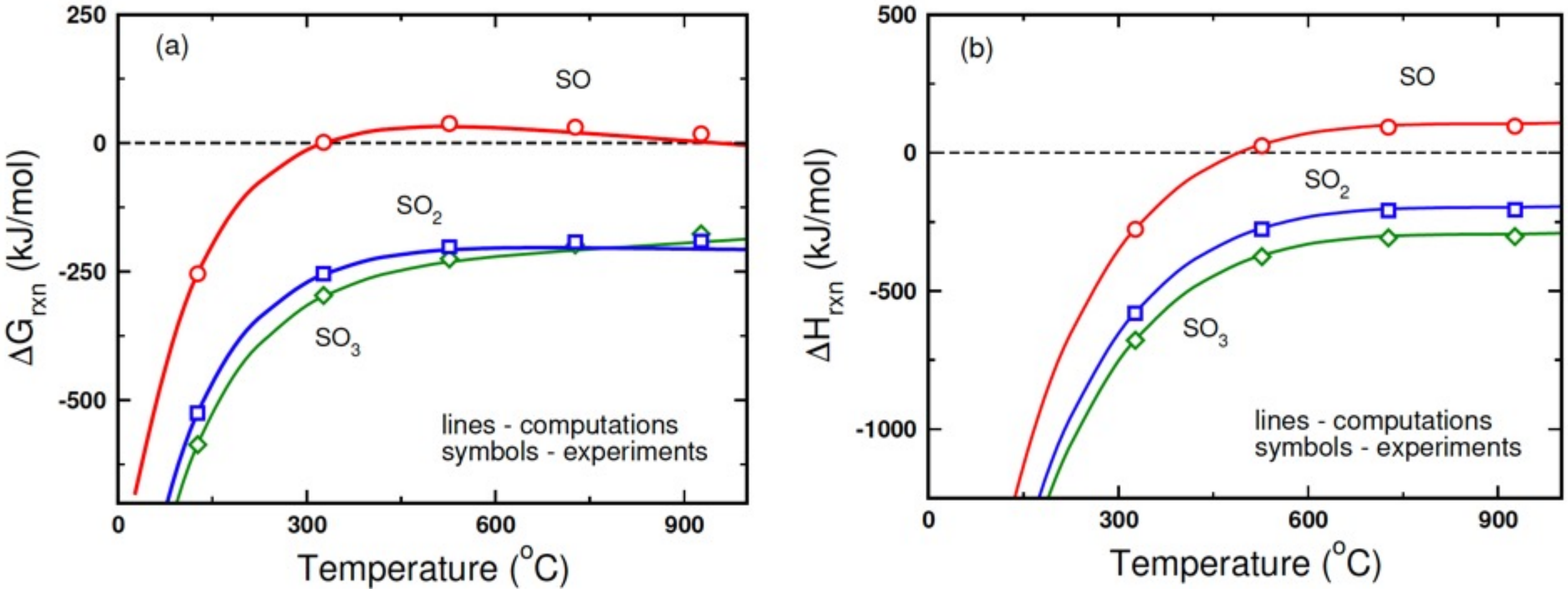


Structures of troilite are well-known and form the basis of characterizing stability in oxygen

Troilite reactions with oxygen

$$FeS(s) + O_2 \longrightarrow Fe(l) + SO_2$$

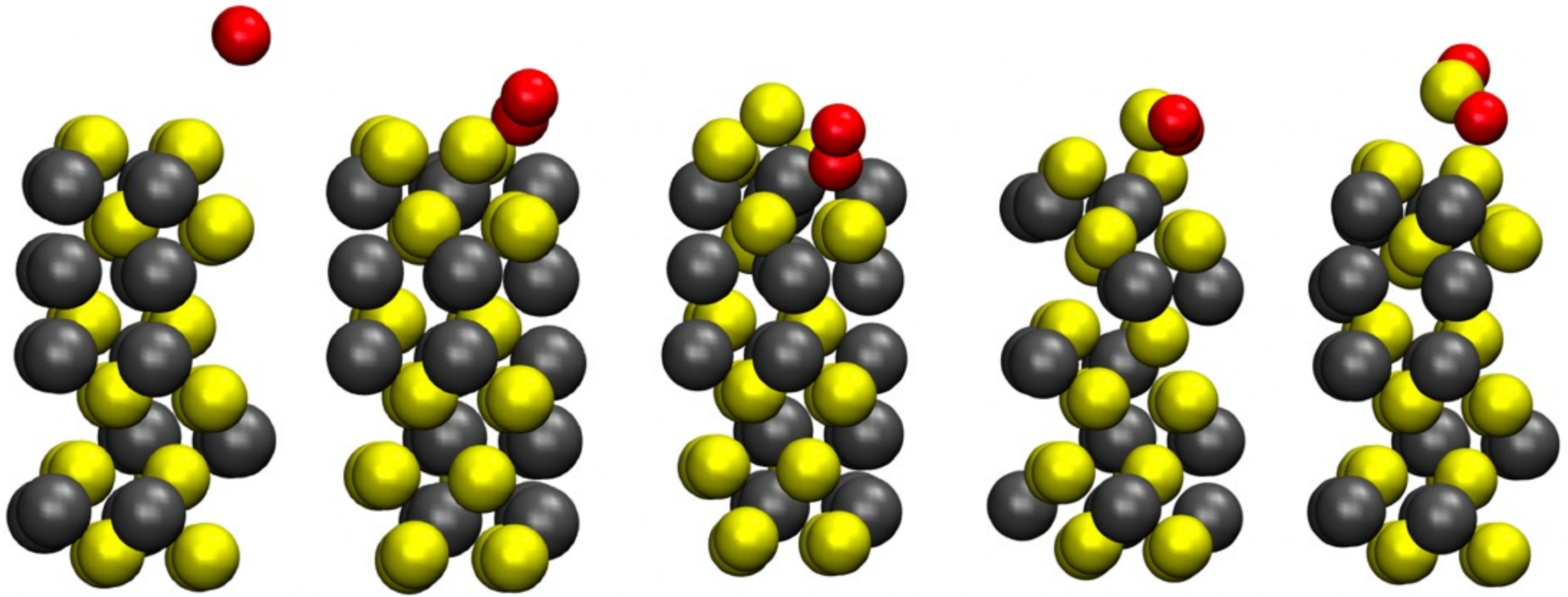
$$2FeS(s) + 3O_2 \longrightarrow 2Fe(l) + 2SO_3$$



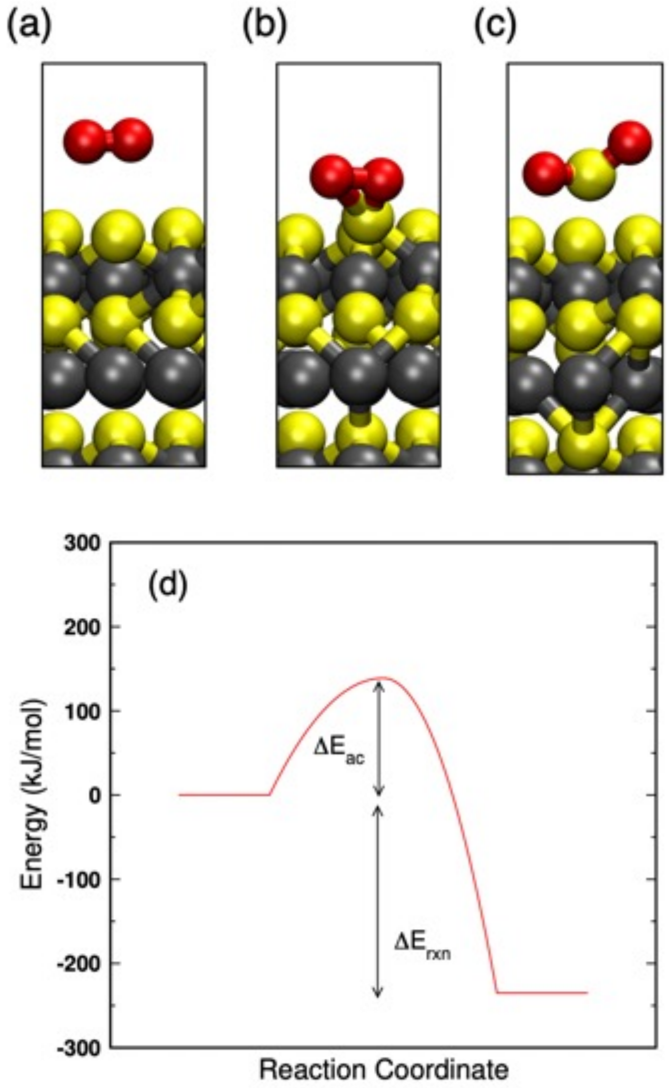
Formation of sulfide products very favorable at the high temperatures associated with CT experiments

Kinetics of troilite oxidation

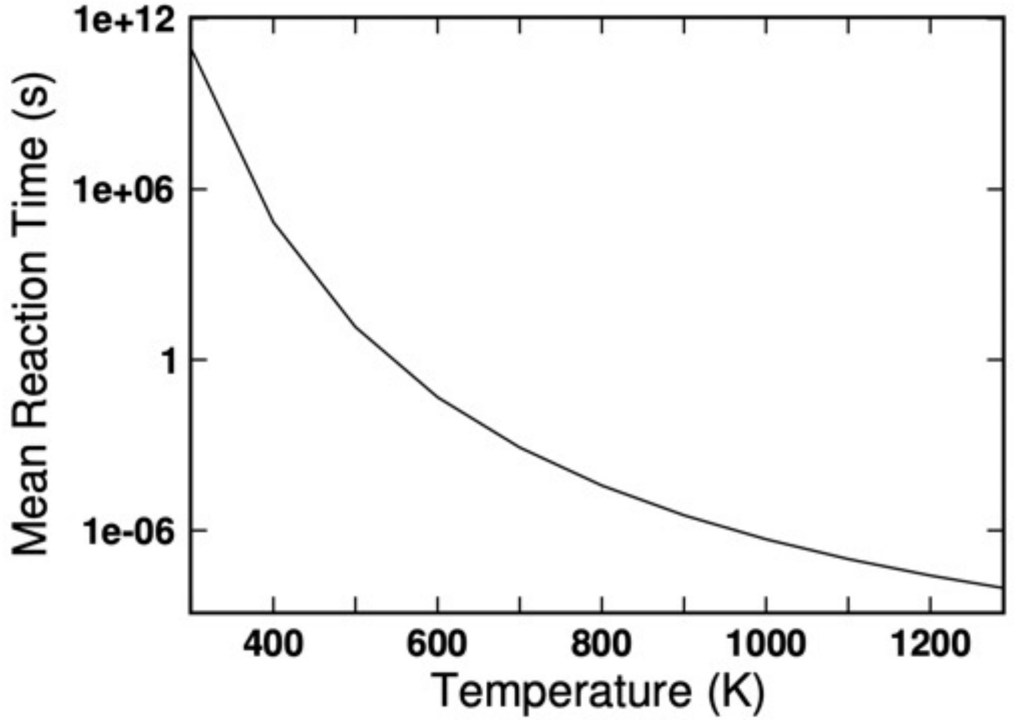
Reaction process of oxygen with the surface of troilite can be examined to understand kinetics



Kinetics of troilite oxidation



Barriers to the reaction can be computed and the reaction rate estimate from transition state theory (Eyring approximation)



Summary

- CT/XPS experiments were interpreted to understand disappearance of meteoritic grains during heating

- Experiments indicate FeS is the material that vanishes

- Computations establish the oxidation mechanism and production of SOs and melting of iron

Outline

Meteorite Reactions During Heating

- In Situ X-ray Tomography of Heating Behavior
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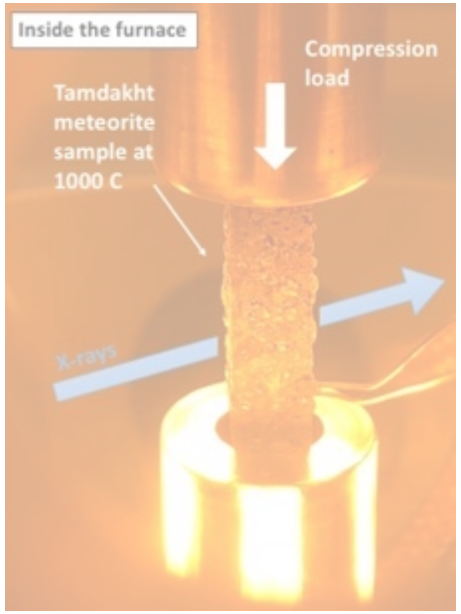
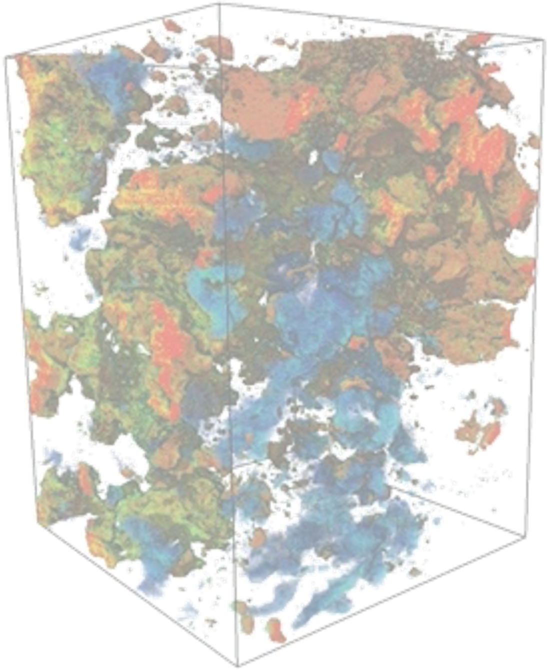
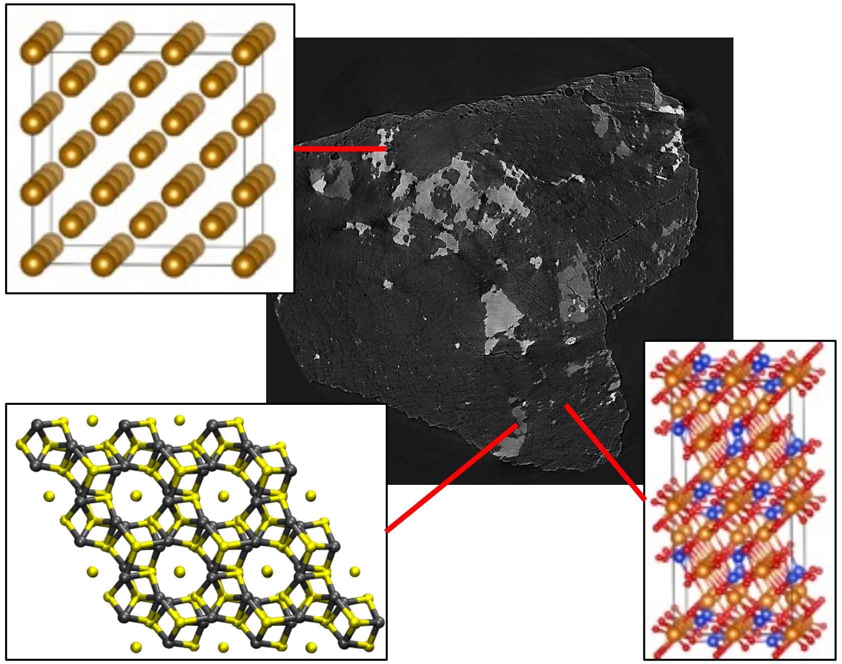




Meteorite Ablation

- Melt-Vaporization Ablation Model Development
- Ab Initio Molecular Dynamics Properties



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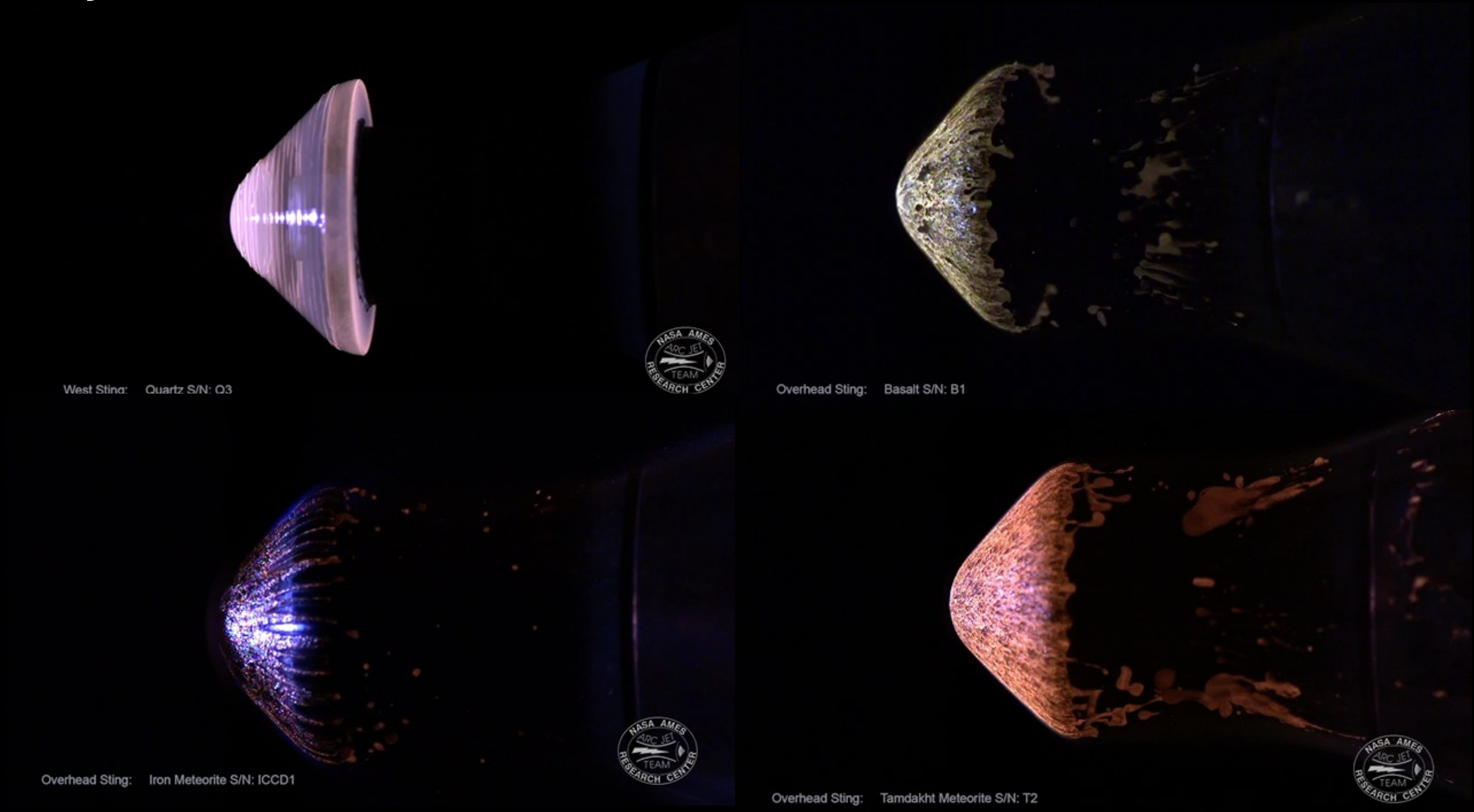
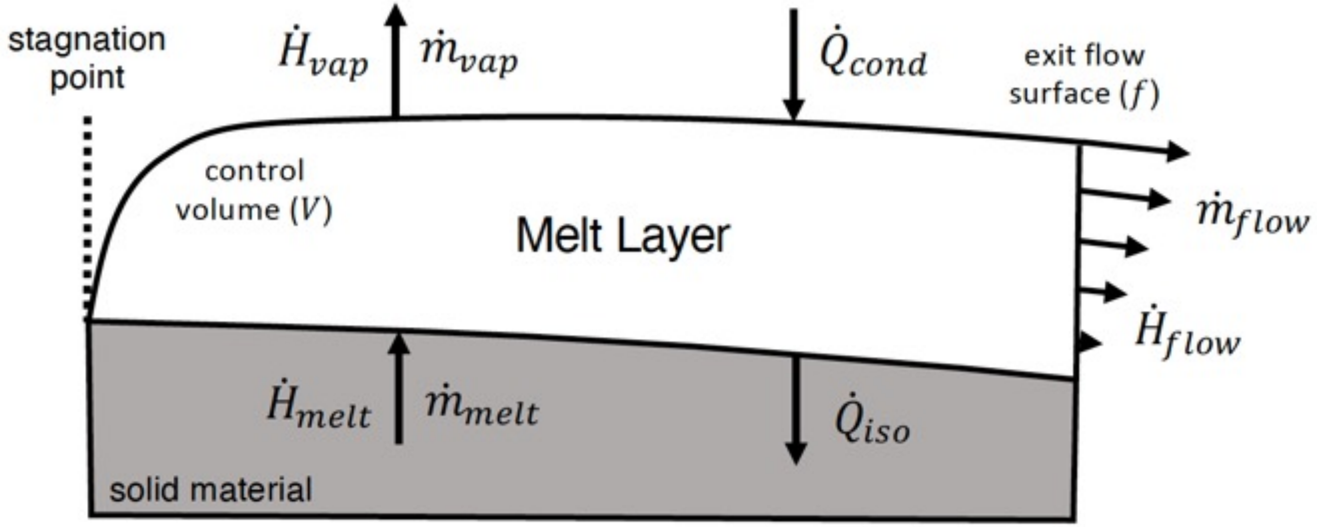
Arc jet ablation of meteorites and meteoritic simulants



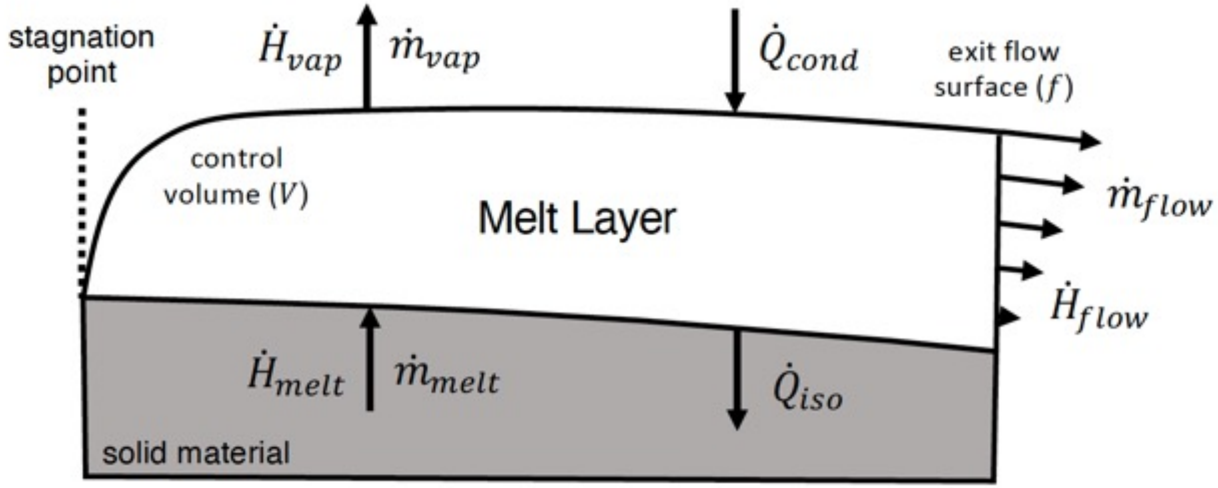
Ablation model to describe melt and vaporization

A melt ablation model describes the evolution and flow of a molten boundary layer at the surface of the material



Properties requires for accurate ablation modeling

Melt ablation modeling requires various properties that are difficult to obtain from experiments

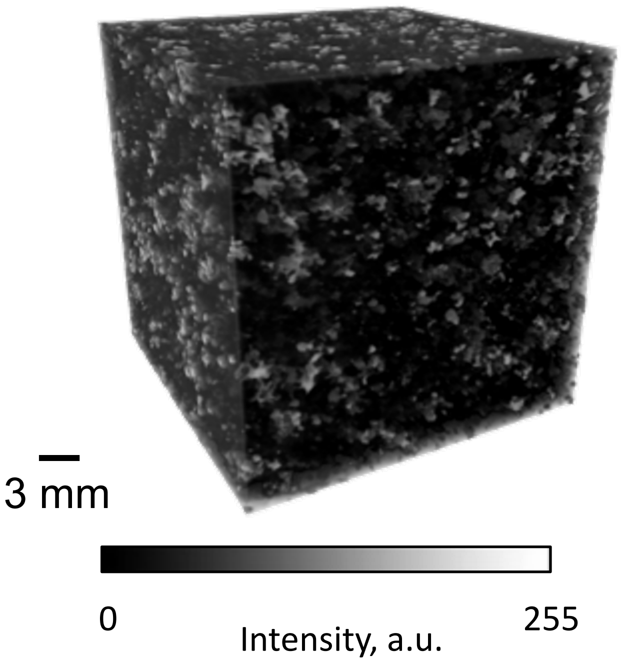


Solids:
- Heat capacity
- Thermal conductivity
- Optical properties

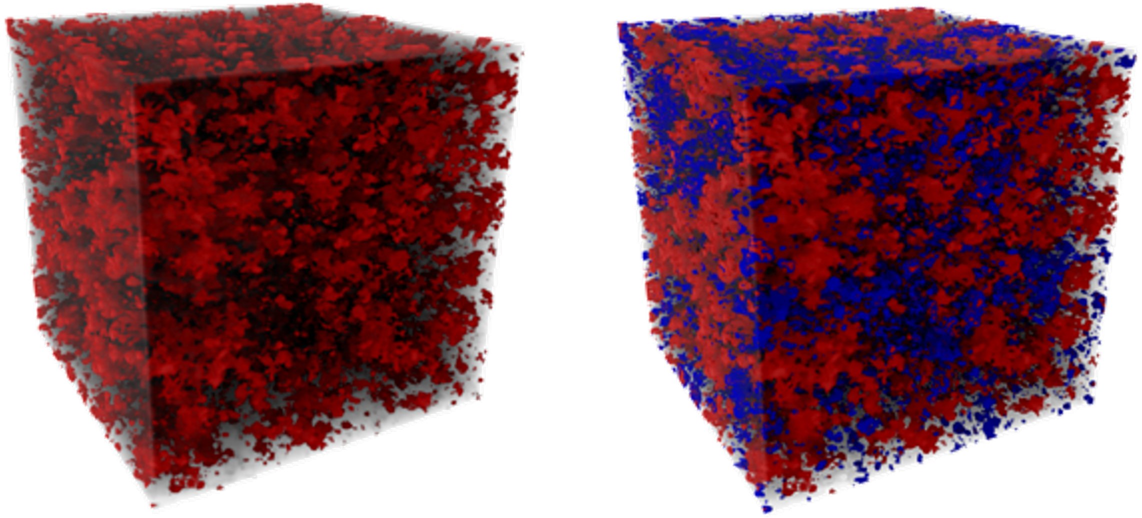
Liquids:
- Heat capacity
- Thermal conductivity
- Optical properties
- Viscosity

Material composition from grain segmentation

600^3 vox^3 volume,
20 μm/voxel



Low- and high-attenuation grain segmentation

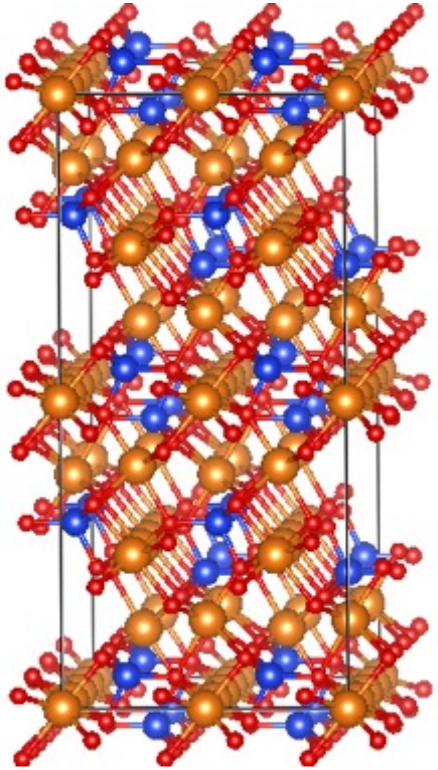


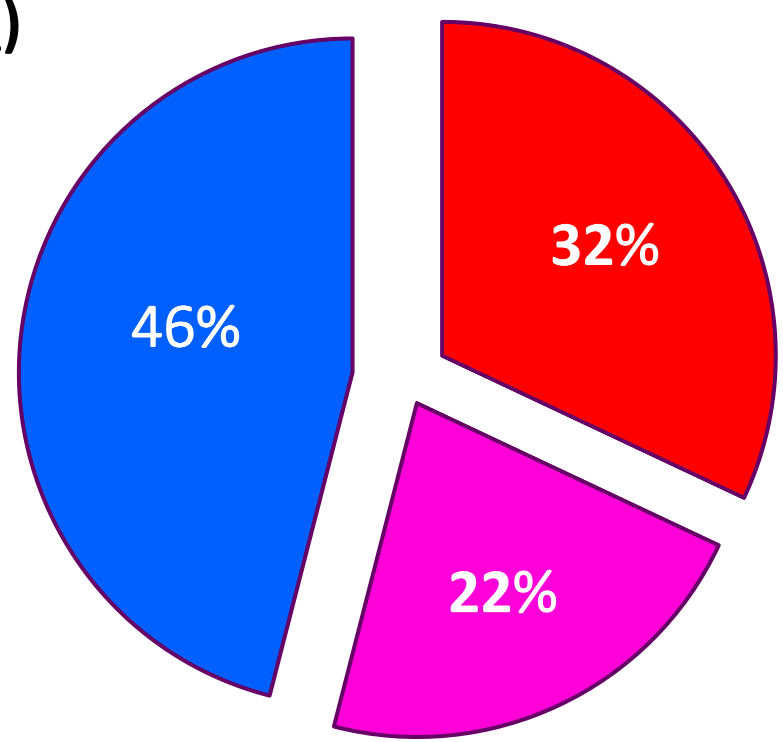
Red: high density grains (Meteoric Iron) – 7-8% vol.
Blue: low density grains (FeS) – 9-15% vol.

Composition of the meteorites can be determined from knowledge of segmented CT volumes

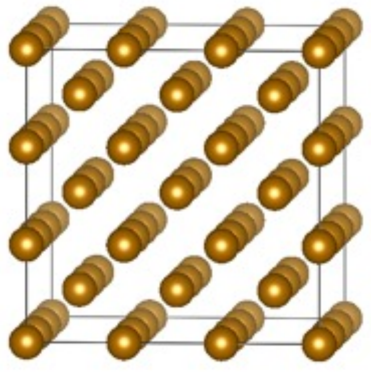
Model composition of stony meteorites

Olivine ($MgFeSiO_4$)

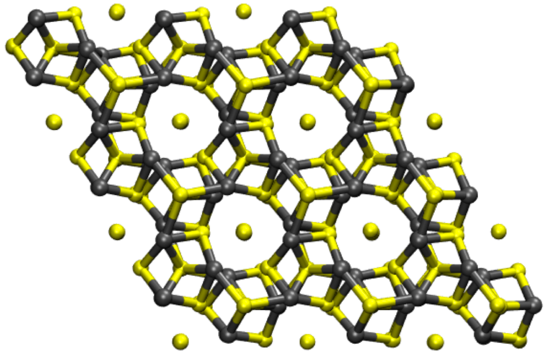




Iron (Fe)

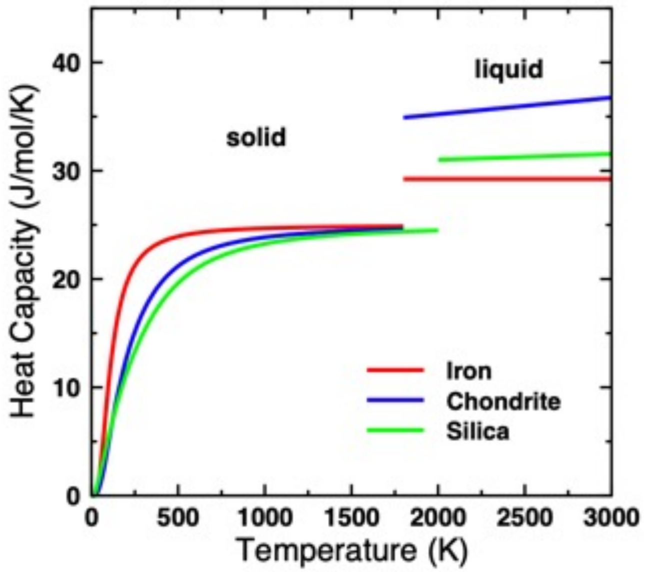


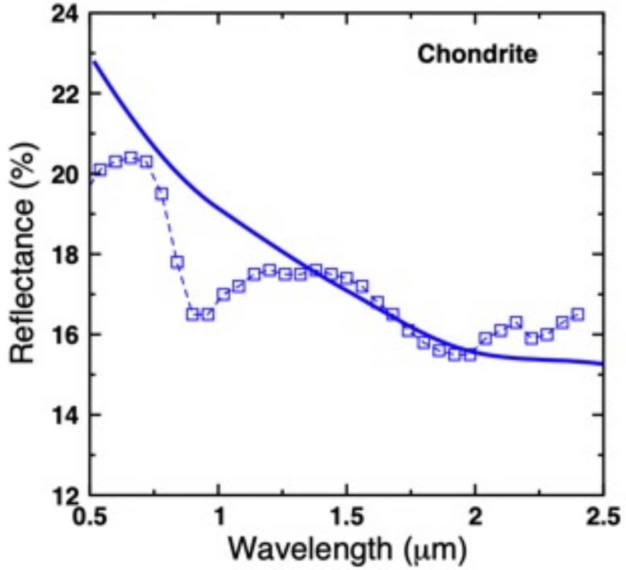
Troilite (FeS)



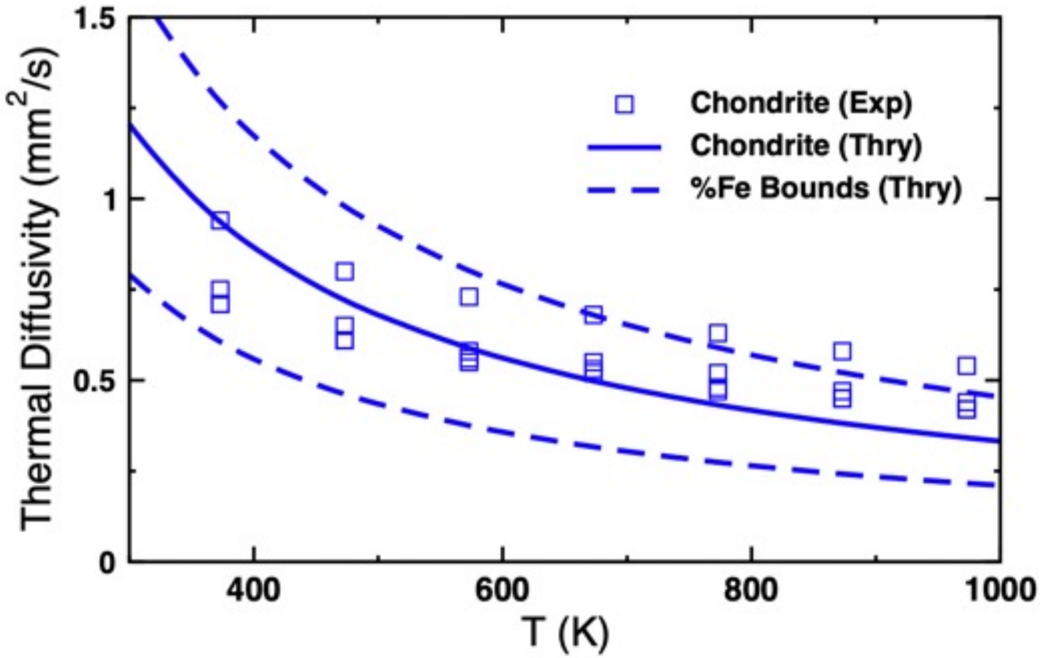
Convert the ratios into molar compositions of the predominant minerals for computation

Material response database development - solids



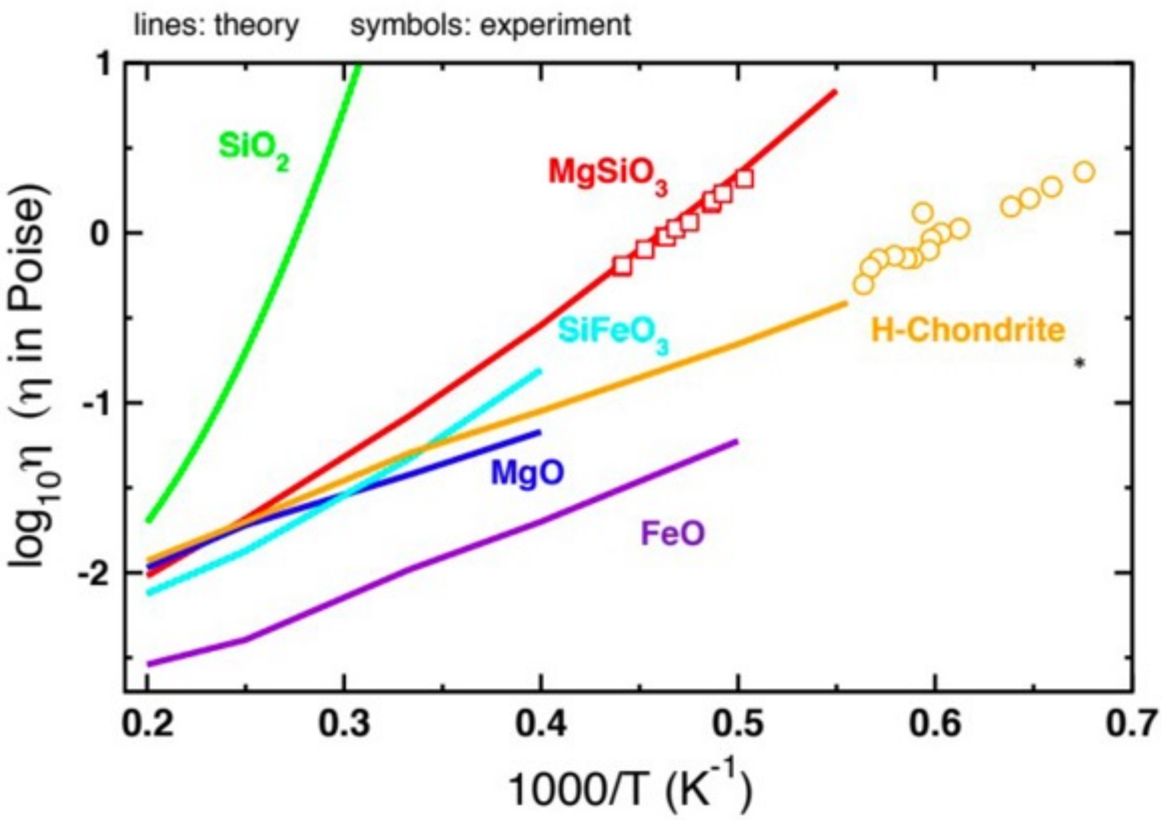


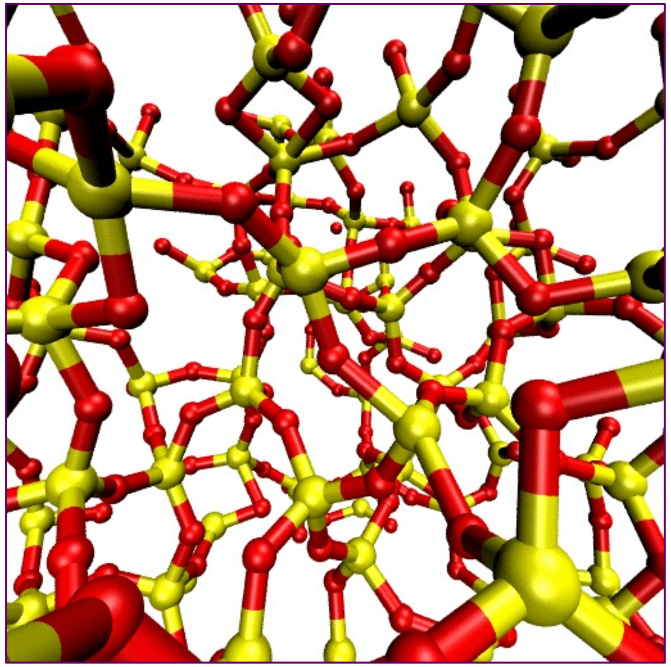
Transport



Ab initio molecular dynamics and lattice dynamic techniques used to update computational chondrite solid database with FeS content – presented previous generation at 10^{th} Ablation workshop

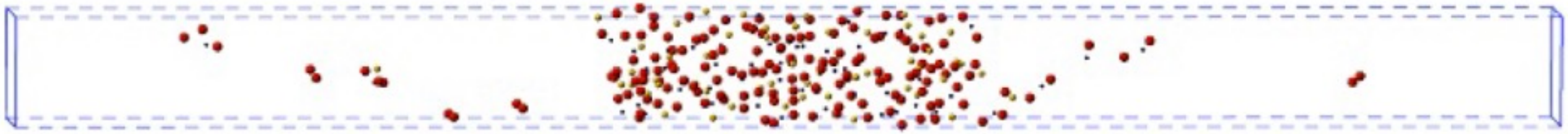
Material response database development – molten material

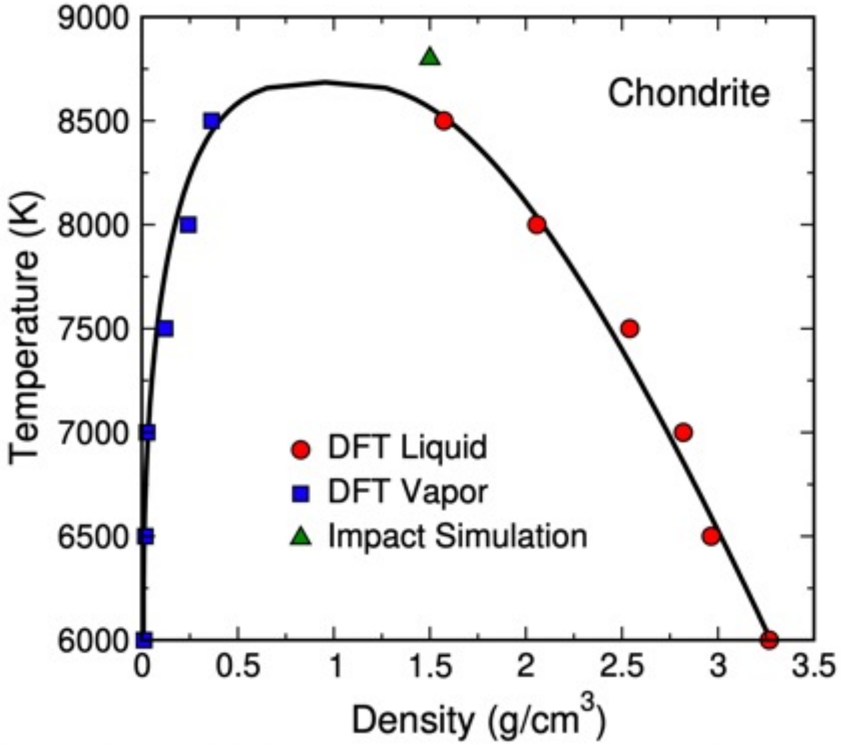




Ab initio molecular dynamics can be used to characterize melt viscosity

Material response database development – melt vaporization





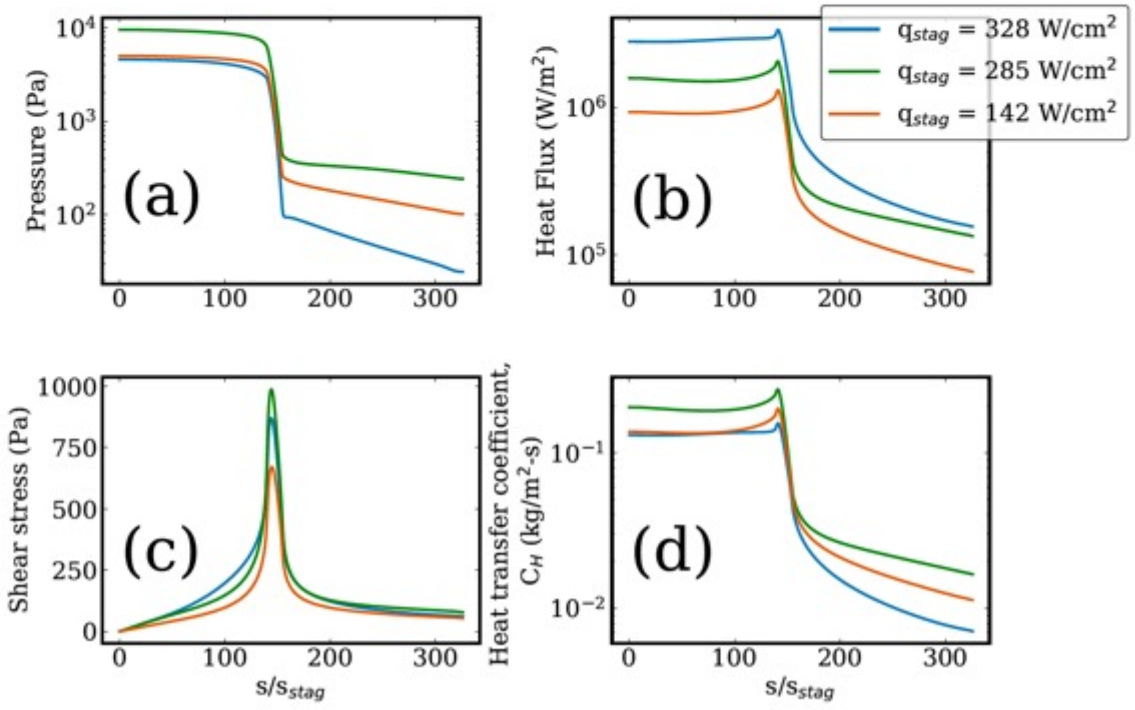
Extrapolate to the boiling point ~3300 ^{o}C, pressure is 1.1 atm

Expect to provide vapor pressure within 10 %

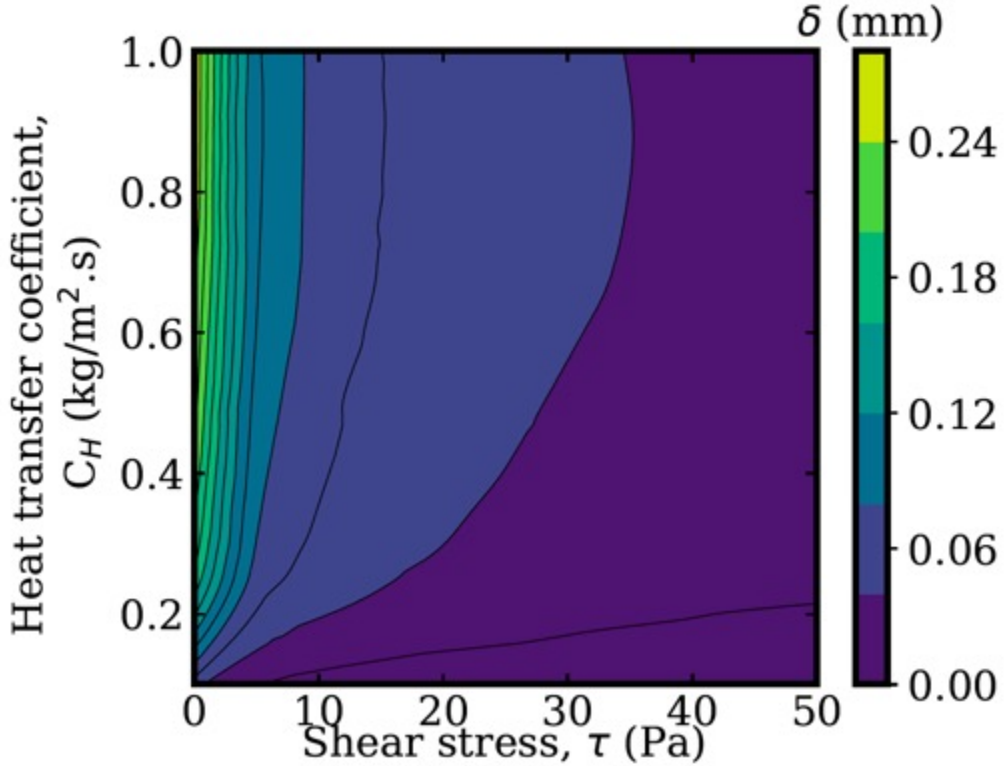
Liquid-vapor coexistence curves can be generated by examining the gas composition and density

Ablation model boundary conditions and parametric study

CFD provides boundary conditions (heating and shear) needed for the melt model



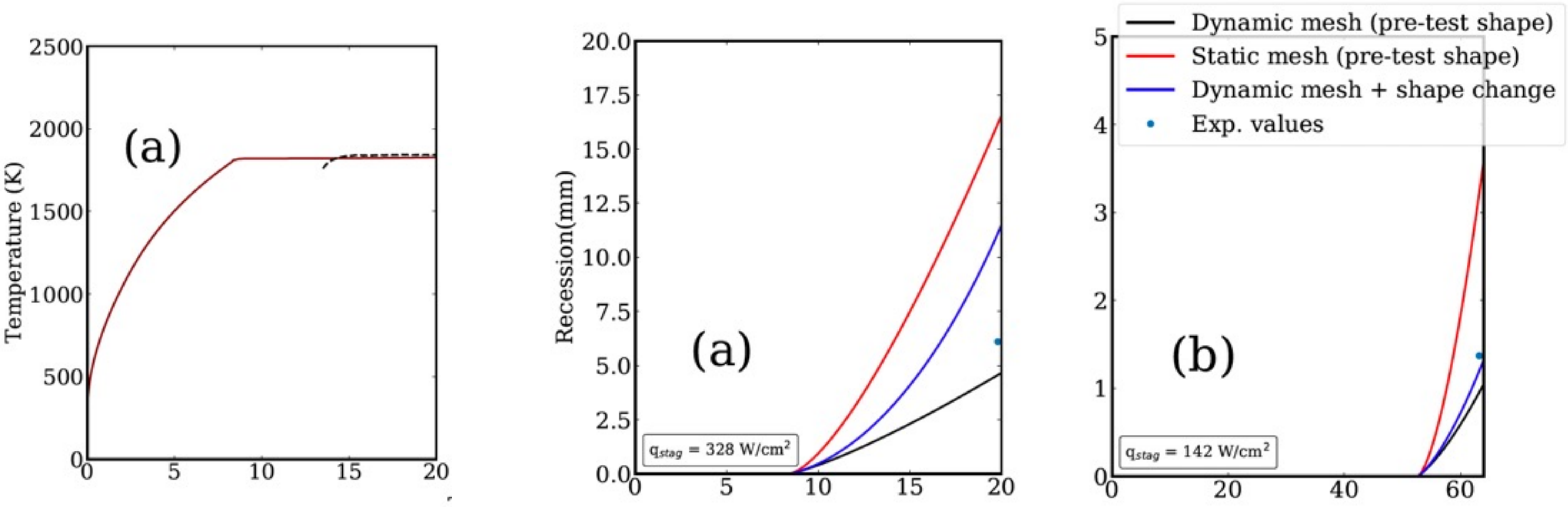
Melt layer thickness examination for shear and heating conditions



Work and images prepared by Pratibha Raghunandan (ATAP)

Application of the model to iron

Surface temperatures and recession rates well described for melt ablation HyMETS tests



Work and images prepared by Pratibha Raghunandan (ATAP)

Summary

- Melt models for ablation require knowledge of properties that are not easily easily measured at high temperatures (viscosity)

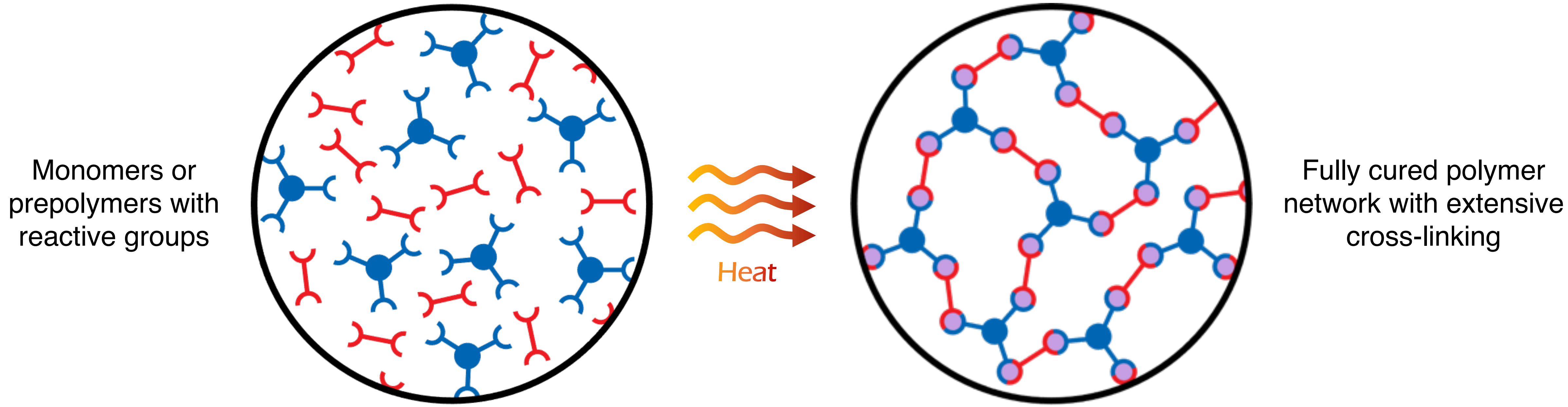
- Properties can be computed from first principles molecular dynamics simulations to construct a material response database

Part 2: Modeling Resins for Aerospace Composites: Spacecrafts to Aircrafts

Lauren Abbott

Supported by Entry Systems Modeling Project and AERoBOND Project

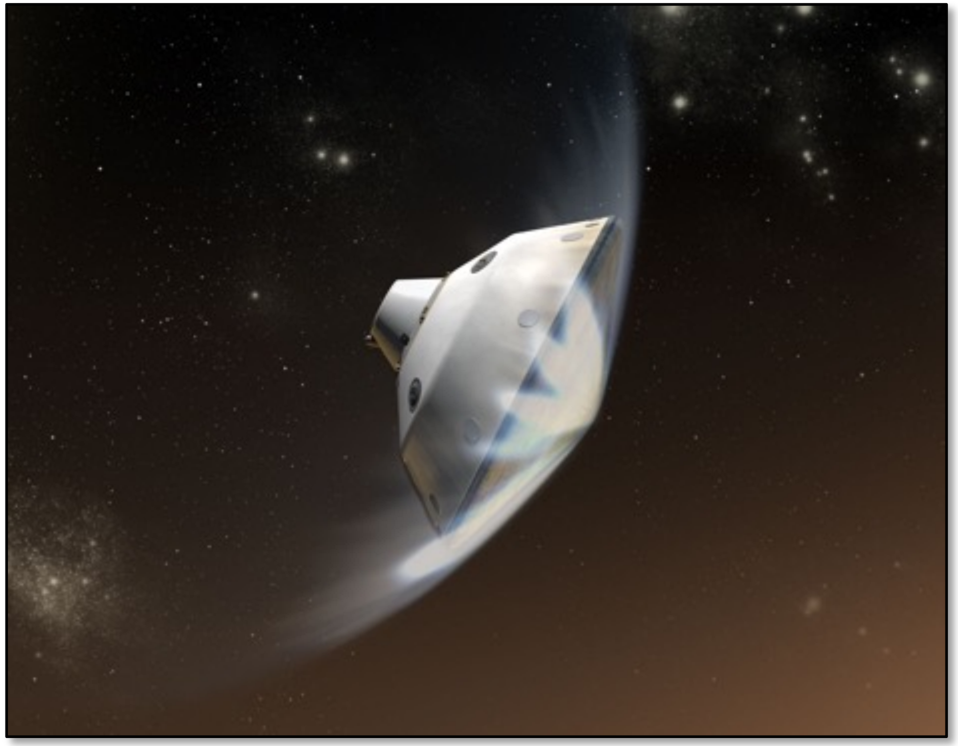
How can modeling resin materials and their curing help?



What is the molecular structure of the cured polymer network?
How does the structure affect the material properties and performance?
How do the structure and properties evolve during cure?

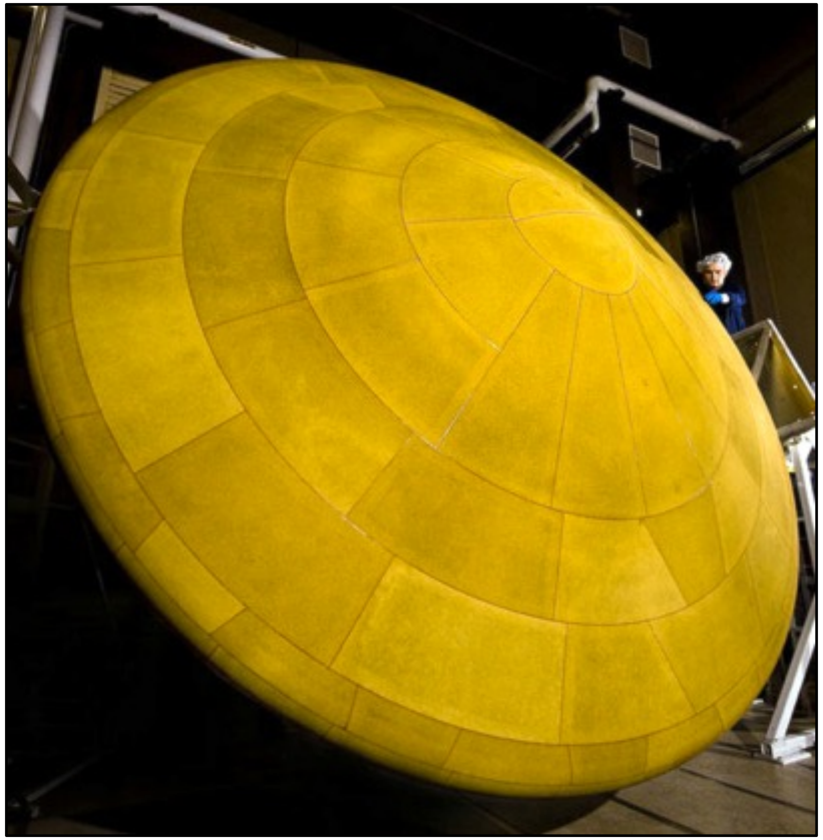
Resin modeling contributes to aerospace technology development

Phenolic resins are important constituents of ablative heat shield materials in entry vehicles

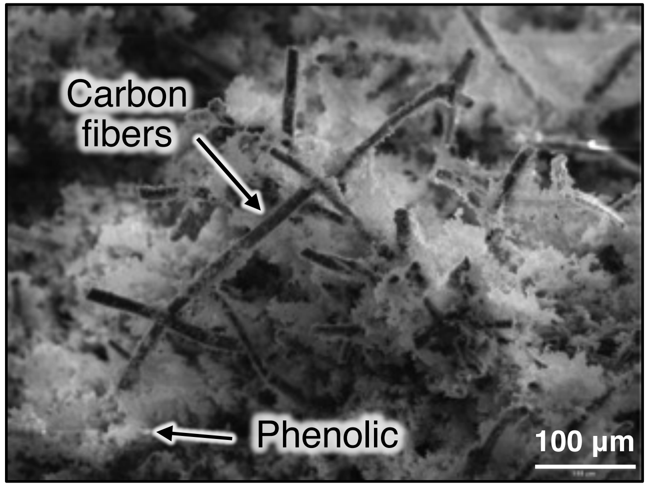


Latent cure epoxy resins underpin an adhesive-free composite joining technology to accelerate airframe manufacturing

Mars mission heat shields leverage phenolic-based materials



Phenolic-Impregnated Carbon Ablator (PICA)
Mars Science Laboratory, Mars 2020

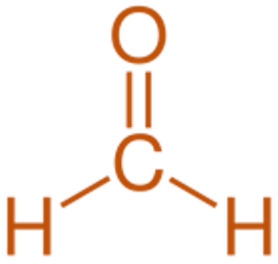


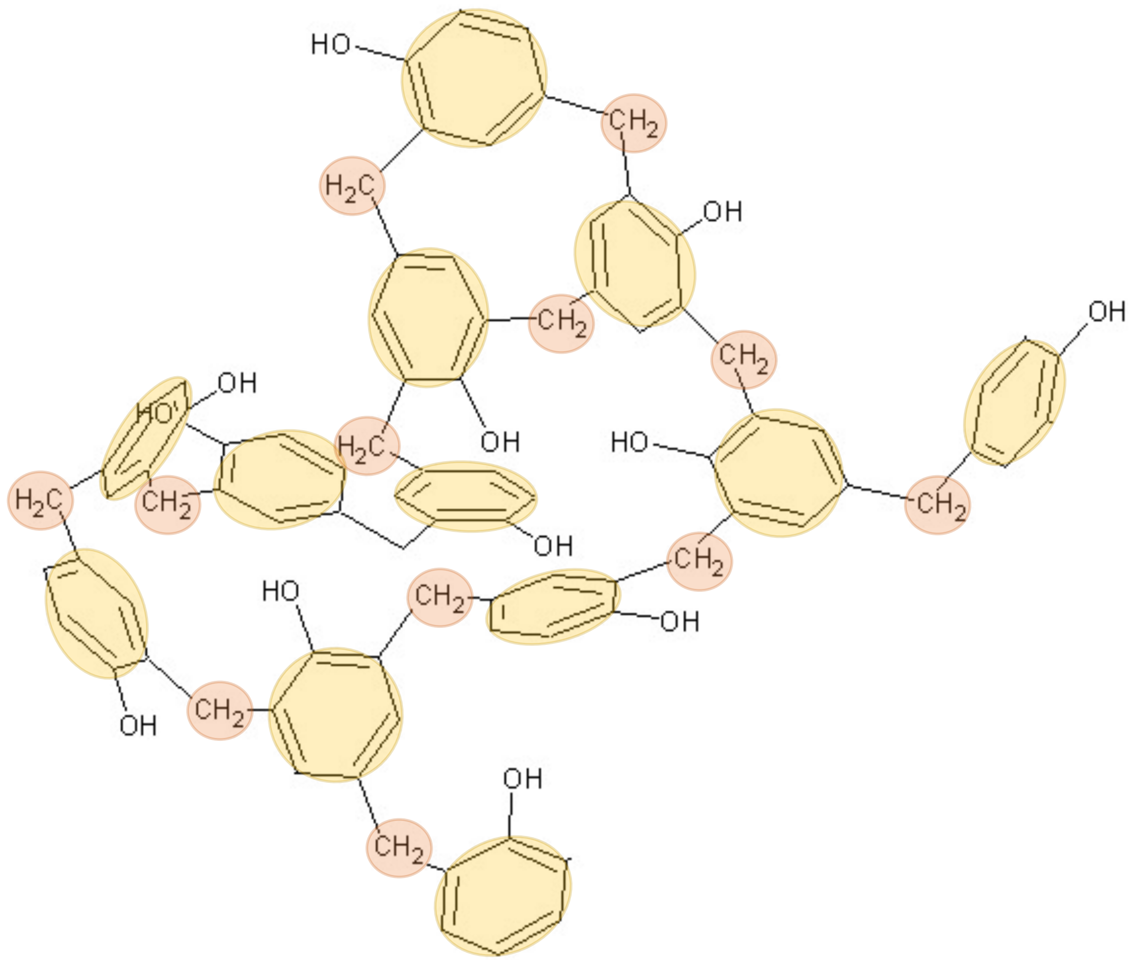
P Agrawal, Journal of Spacecraft and Rockets, 2013

Heatshield for Extreme Entry Environment Technology (HEEET)
3D Medium Density Carbon Phenolic (3MDCP)
Mars Sample Return Earth Entry Vehicle

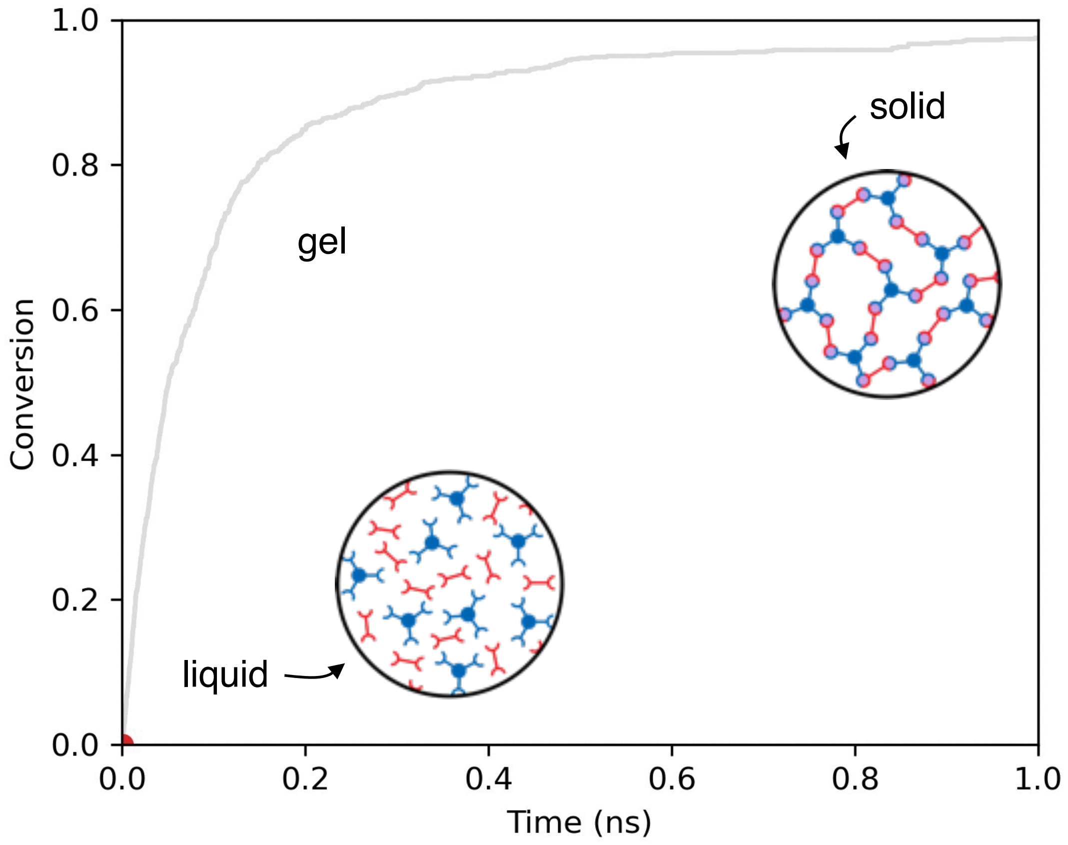
Phenolic structures are complex and highly process dependent

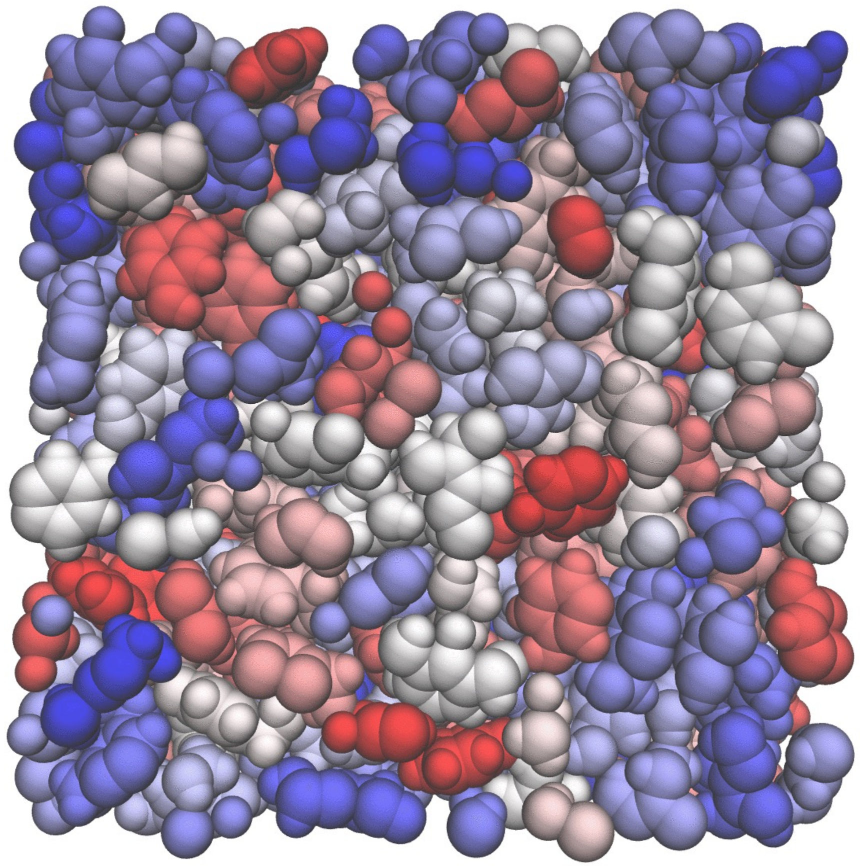
Formaldehyde (F) : Phenol (P)





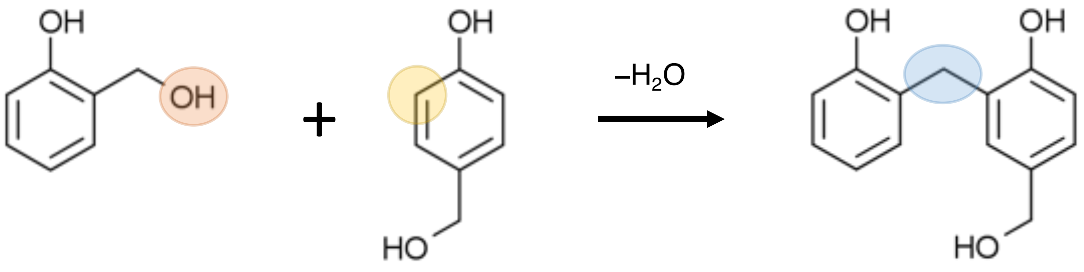
Phenolic cure is mimicked using molecular dynamics simulations

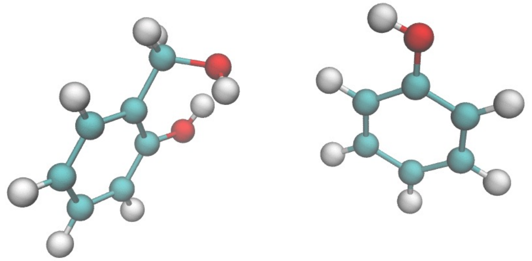




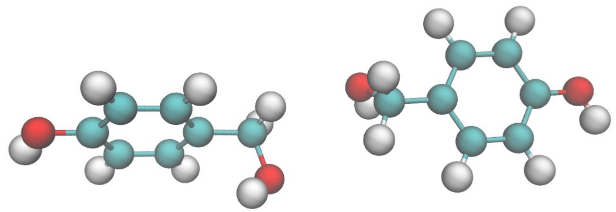
How do bridge chemistries affect the properties of phenolic?

Methylene bridge:

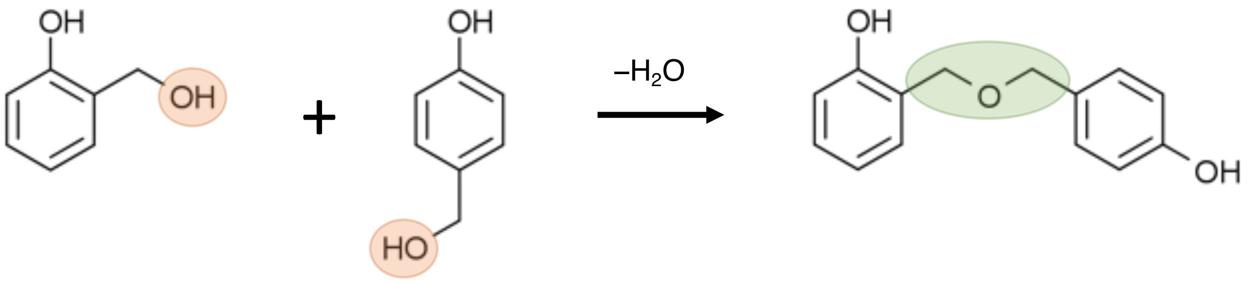




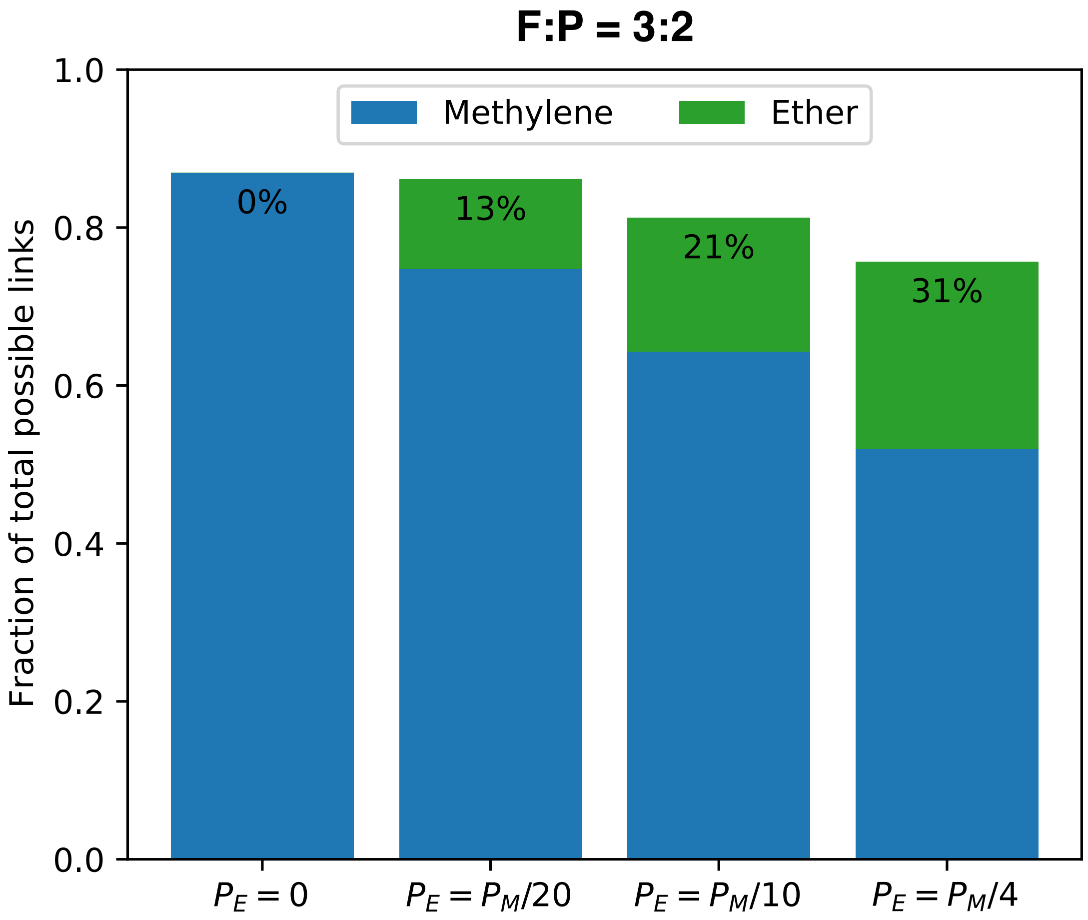
MD reaction templates

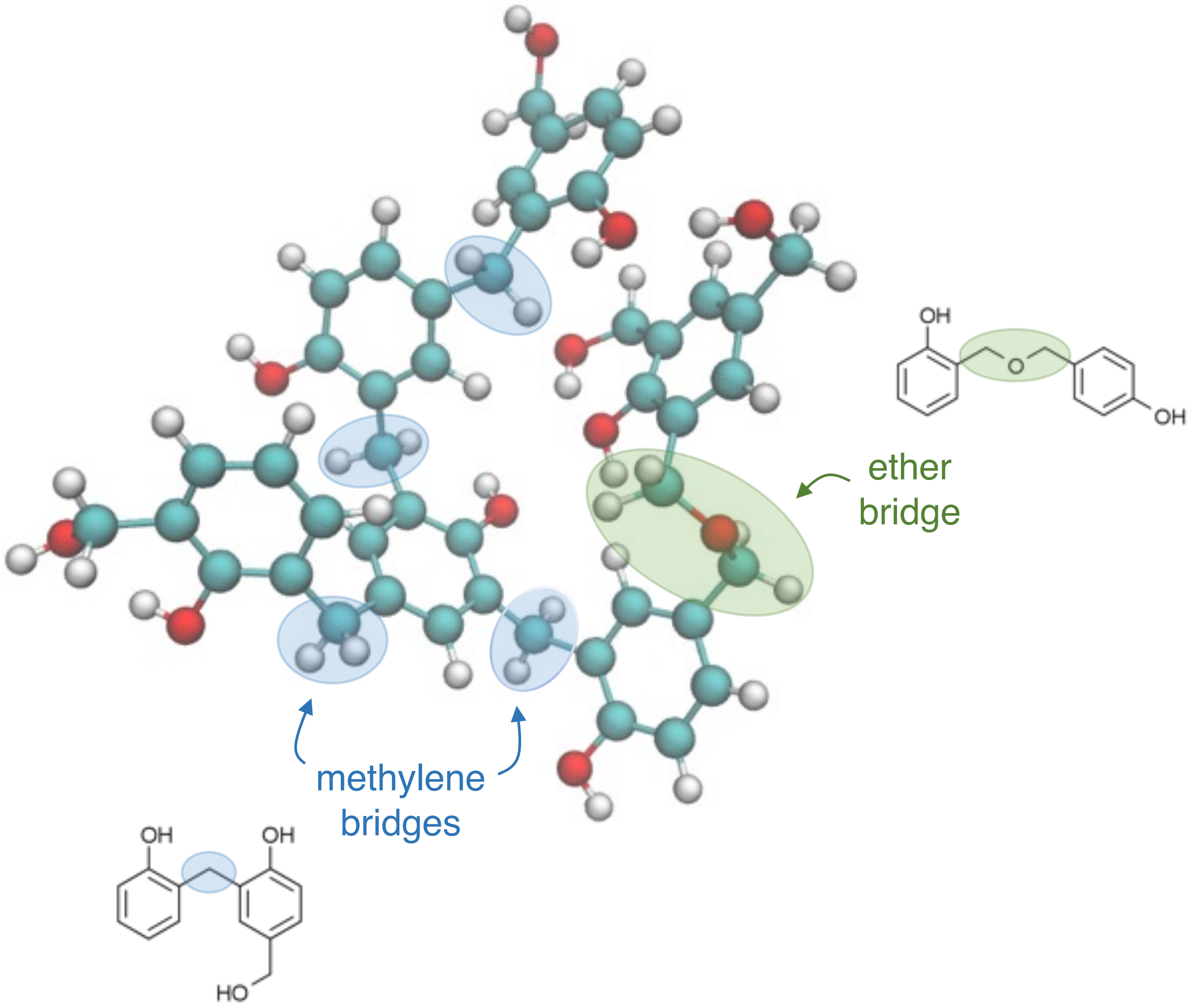


Dimethylene ether bridge:

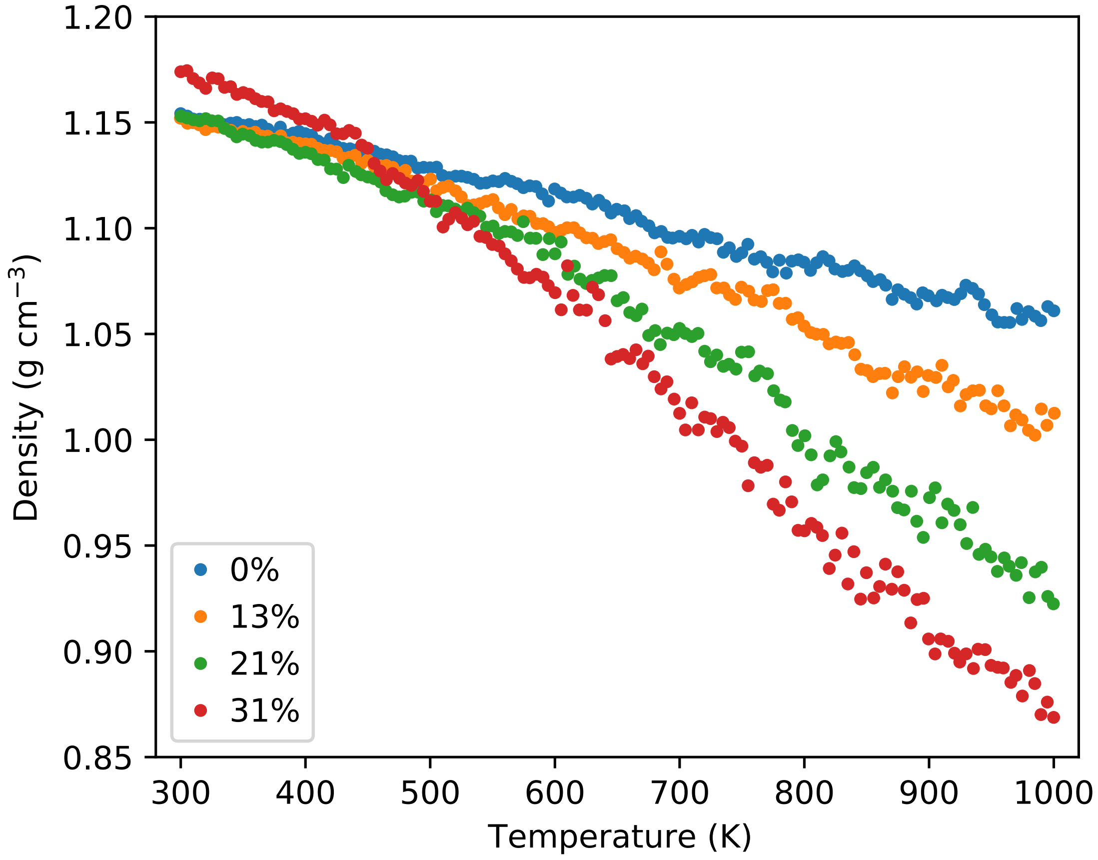


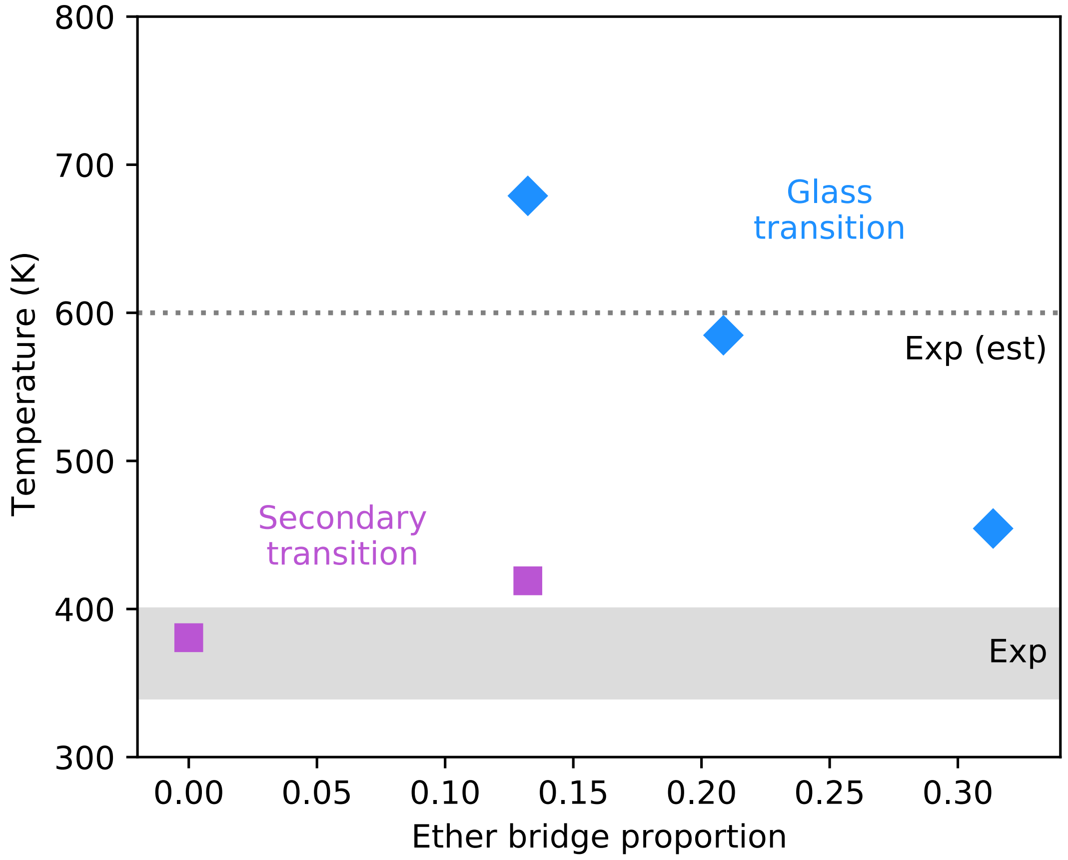
More ether bridges lead to less crosslinking and less rigidity



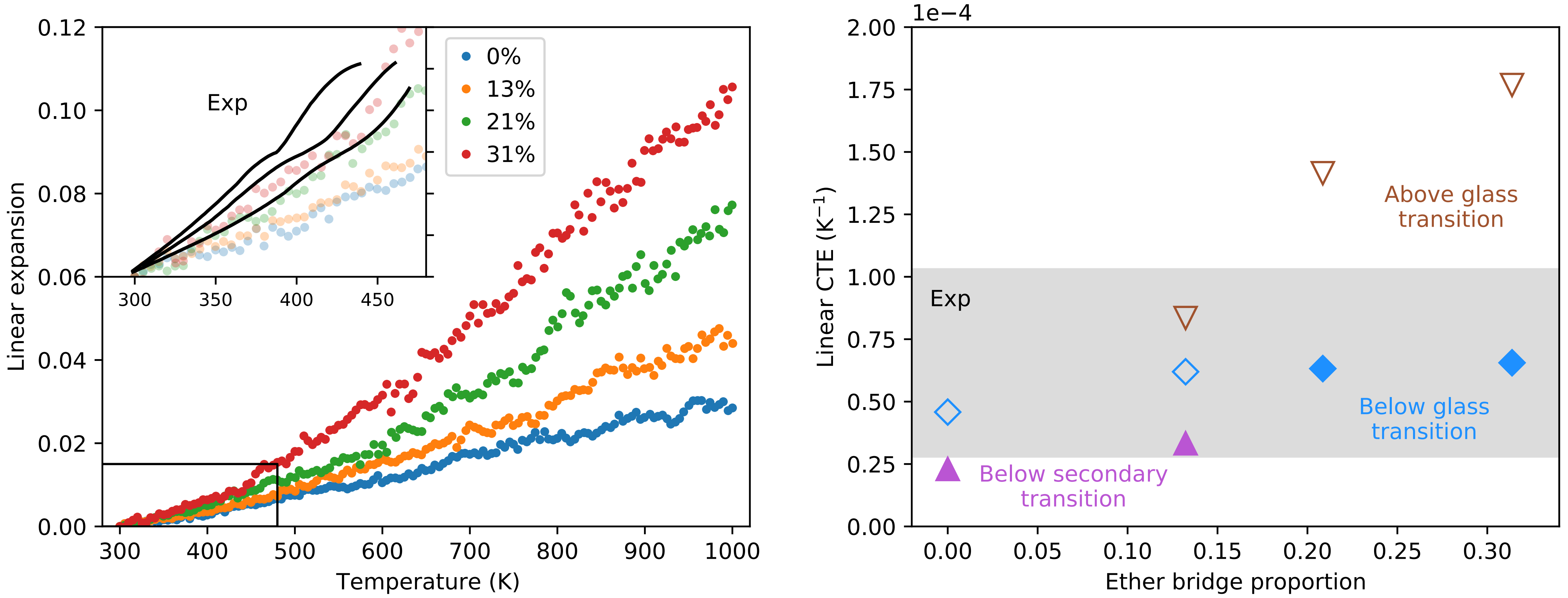


Thermal annealing reveals two characteristic thermal transitions





Thermal expansion is consistent with experimental data



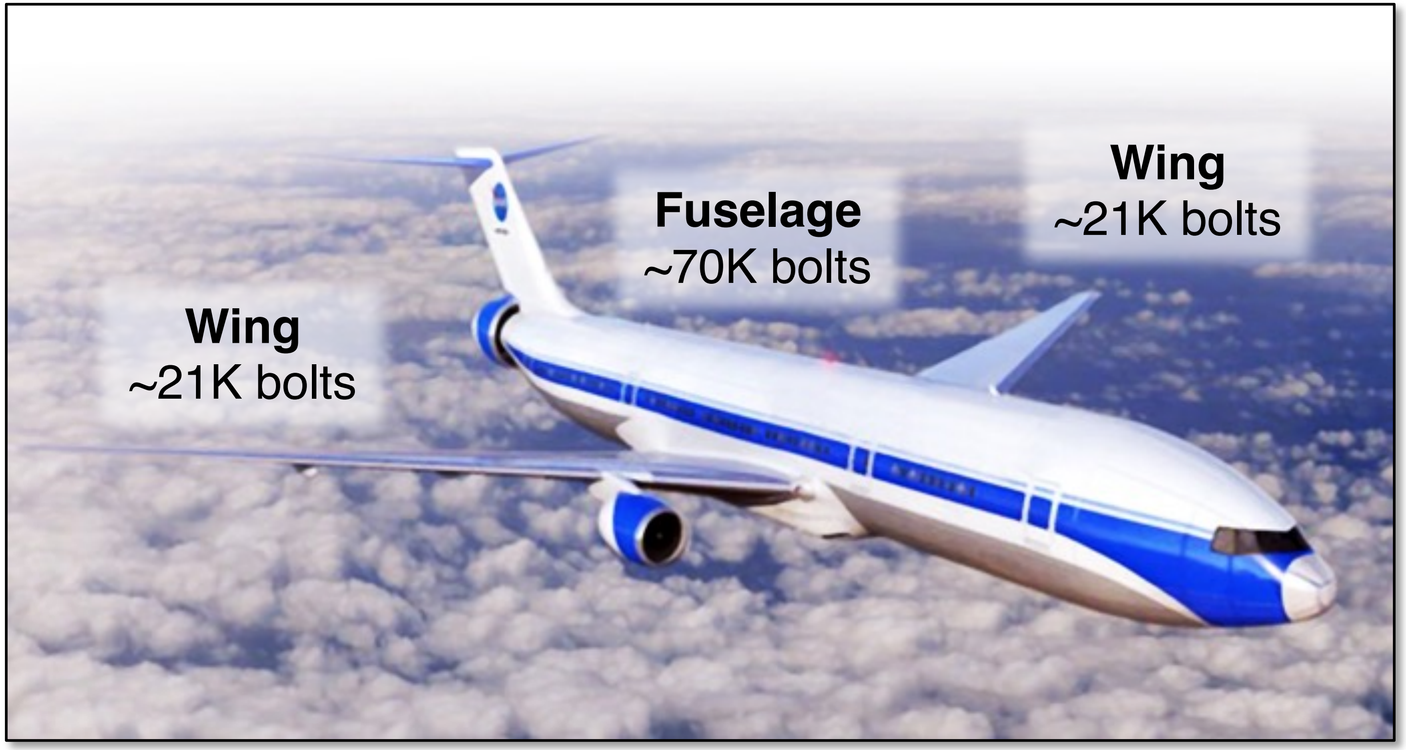
Summary and future directions for phenolic modeling

- Molecular dynamics cure simulations can capture complex phenolic structures
- Phenolic properties are sensitive to degree of cure and bridge chemistries
- Experimental characterization is critical to informing models

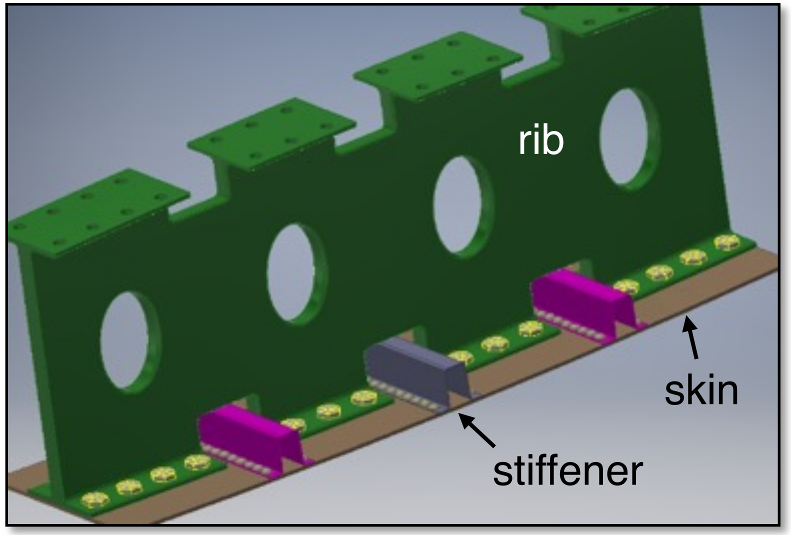
Future directions:

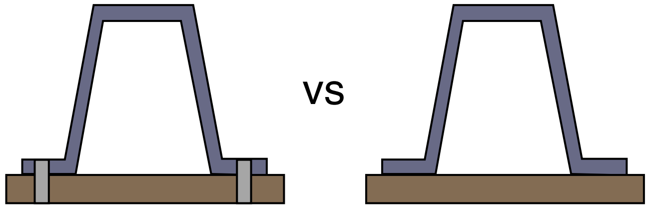
- Extend model construction to low-density phenolic materials
- Calculate material properties to inform modeling efforts
- Investigate phenolic ablation and char formation

Installation of redundant fasteners is a bottleneck in production

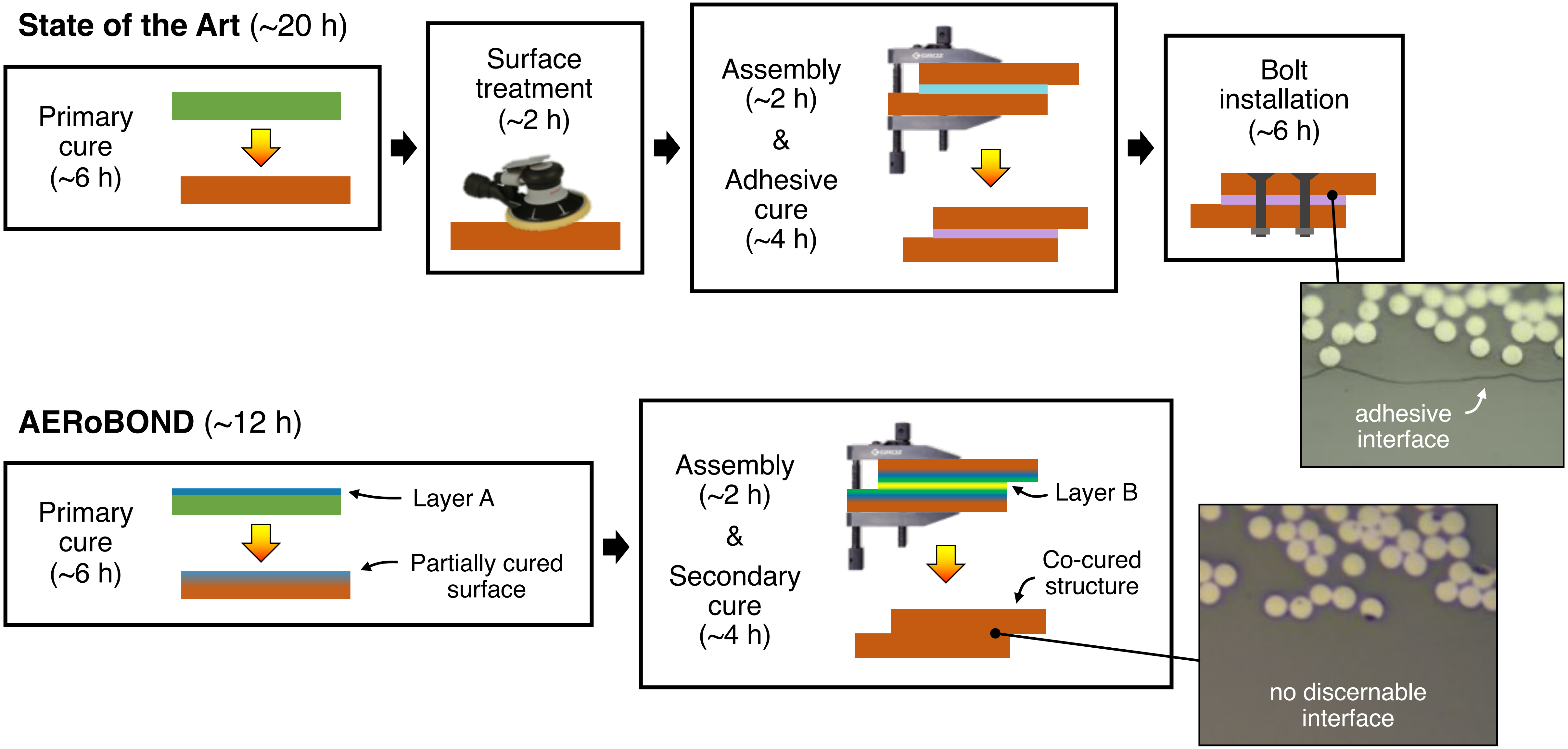


Assembly of composite parts in airframes requires installation of thousands of mechanical fasteners

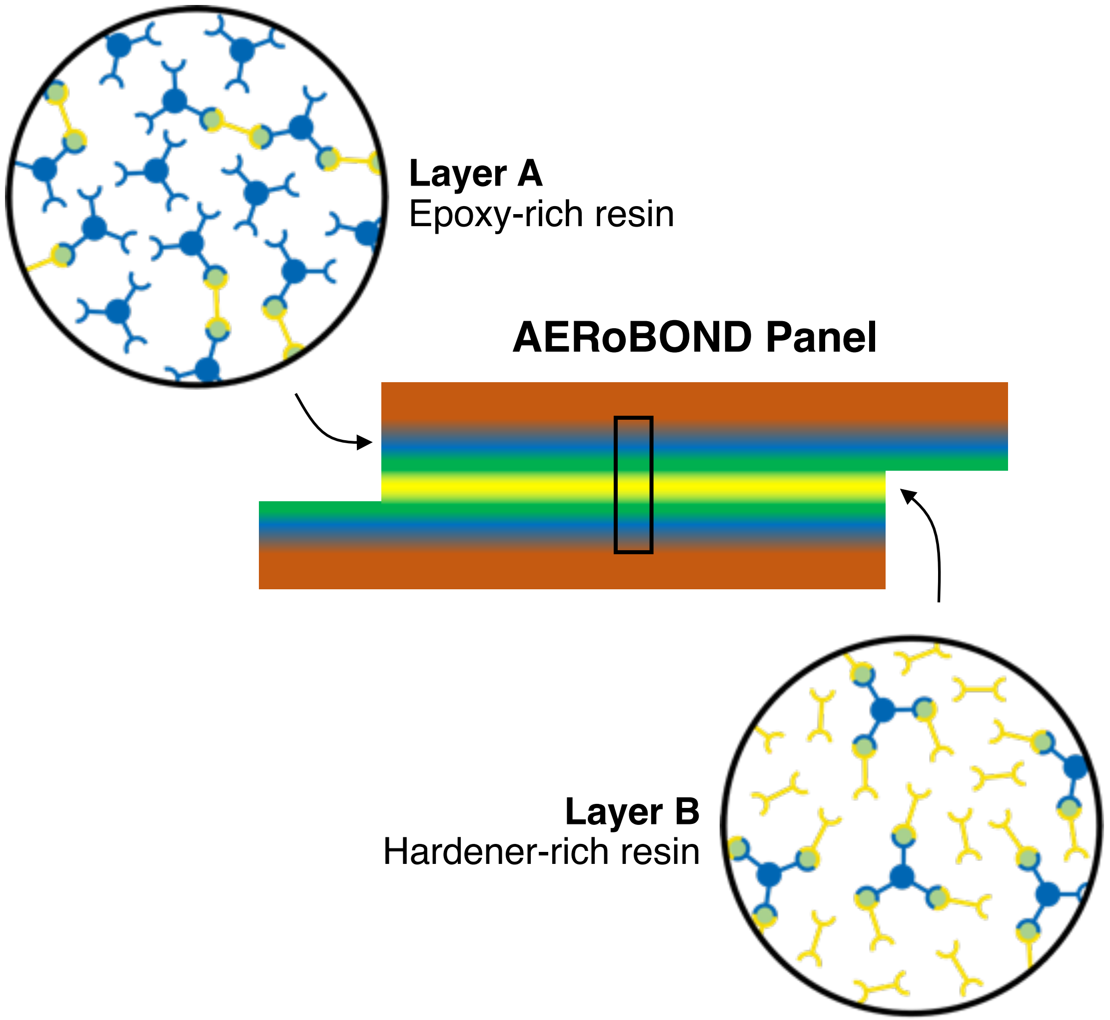


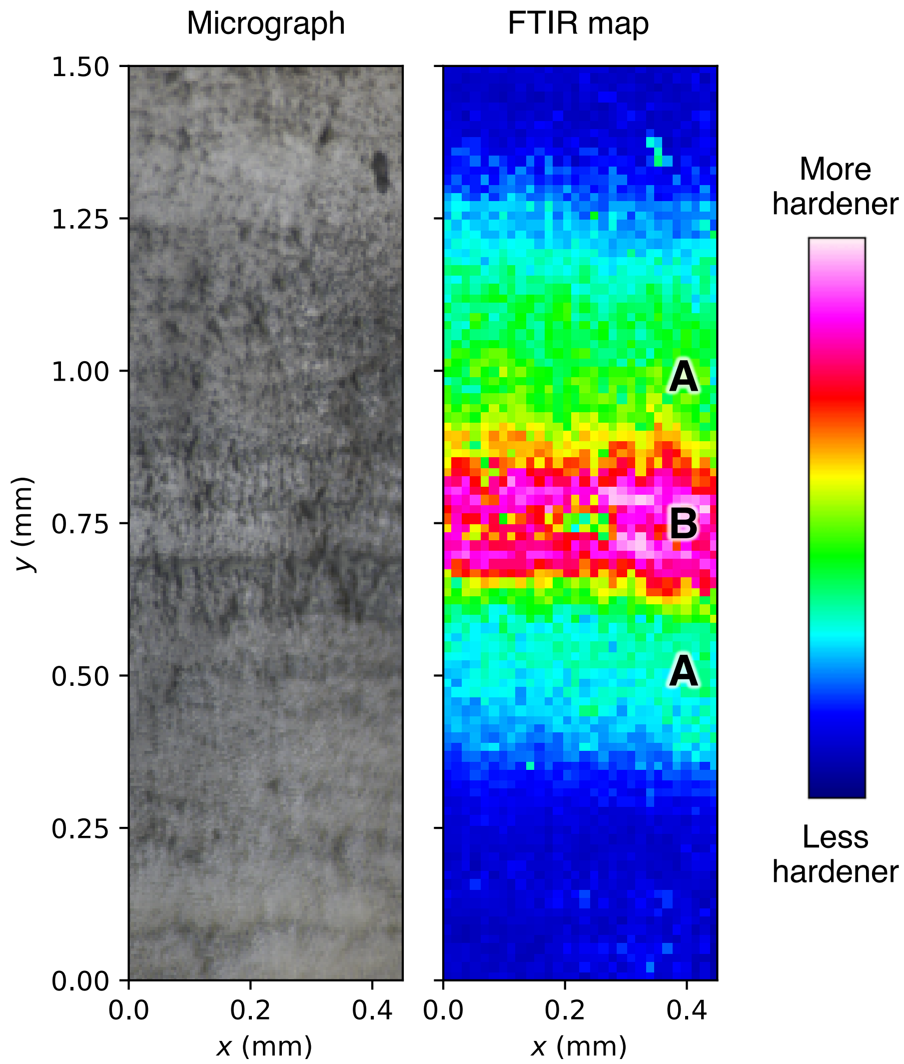


AERoBOND method is about 40% faster than state of art



AERoBOND process relies on reflow and mixing of resin layers





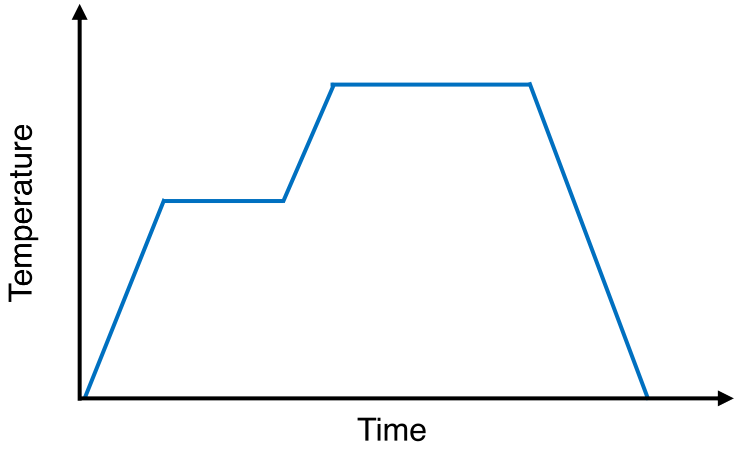
Process simulations can accelerate process optimization

6 material / layup parameters:

- Resin A & B compositions
- Resin A & B initial degrees of cure
- Layer A & B thicknesses

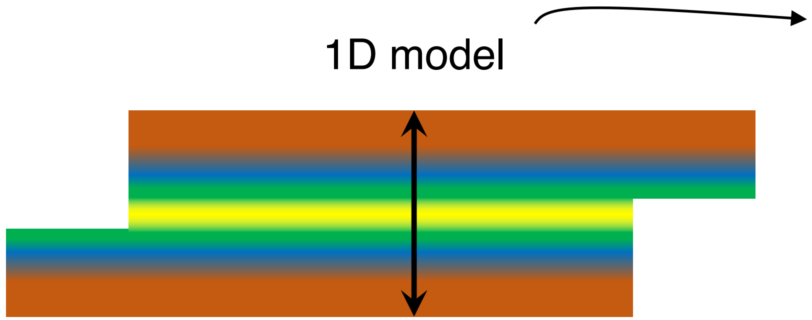
10 cure cycle parameters:

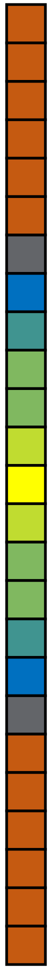
- Primary & secondary cure hold temperatures
- Primary & secondary cure hold times
- Primary & secondary cure heating rates



Process simulations can explore large parameter space more quickly
(~seconds/minutes per simulation vs ~days/weeks per experiment)

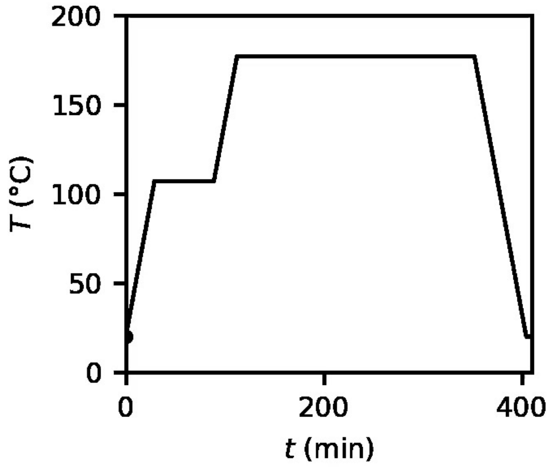
Simulations highlight competing effects of mixing and cure

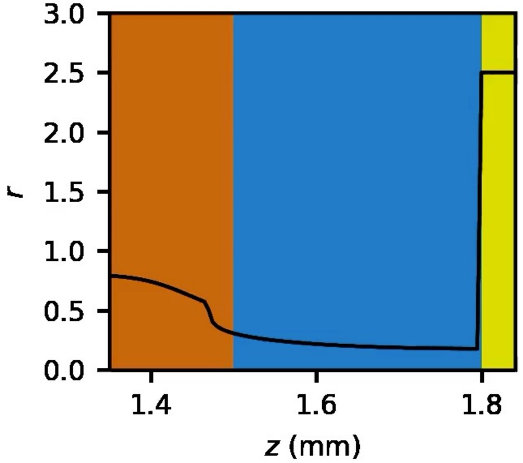


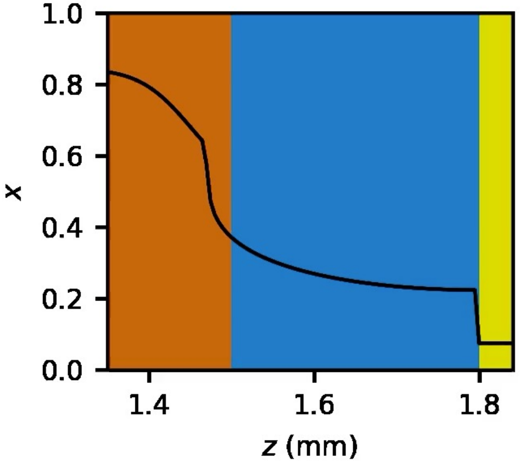


Finite difference method:

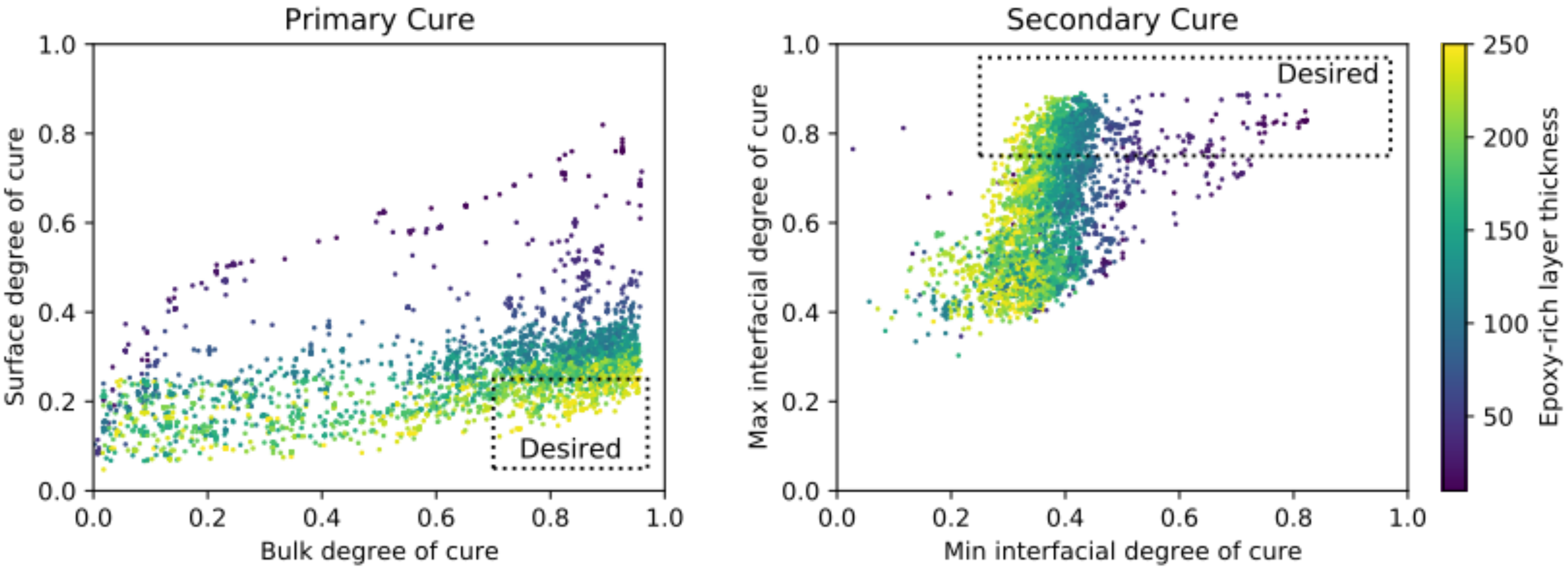
- Heat transfer
- Resin mixing
- Resin cure





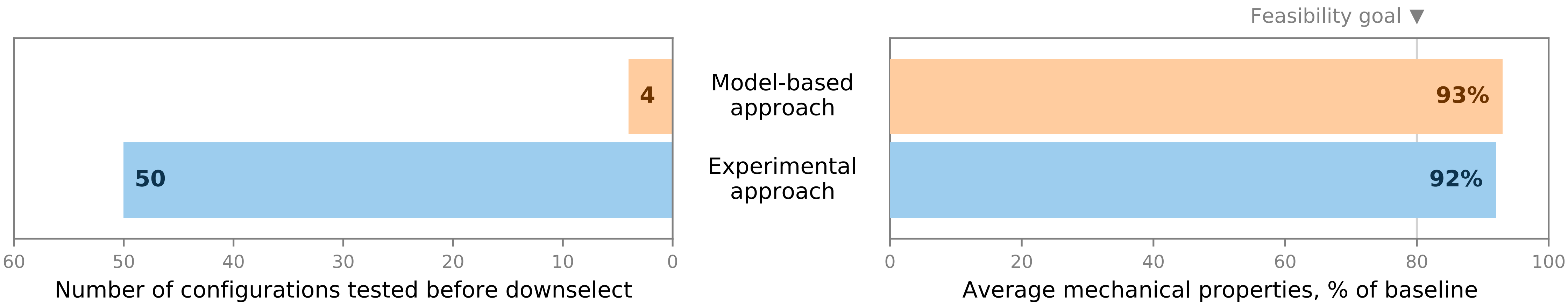


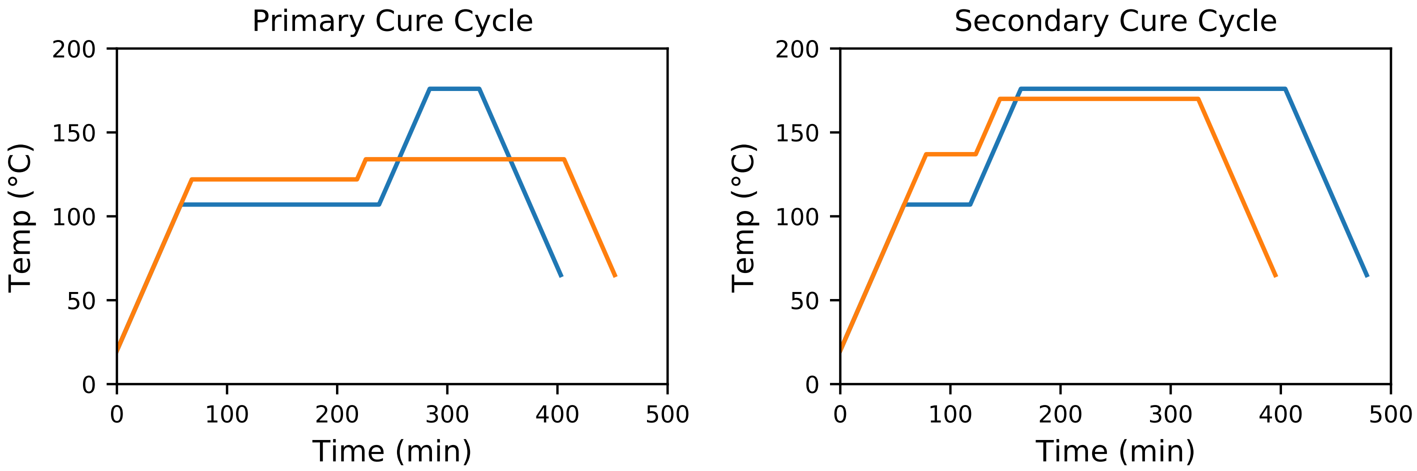
High-throughput screening identifies promising configurations



Simulated more than **5000** configurations and proposed **4** for fabrication and testing

Model-based optimization can save time and money





Summary for AERoBOND latent cure resin modeling

- AERoBOND is a promising adhesive-free composite joining technology
- Process models can enable rapid exploration of a large parameter space
- Model-based process optimization requires less experimental testing

Part 3: Enabling Nuclear and Solar Thermal Propulsion with the Computational Laboratory: Faster and Cheaper Materials Characterization

BJ Tucker

Supported by CIF and STMD seedling funding

Work done in collaboration with:
Dean Chiekh, Jet Propulsion Laboratory
Michael Preudhomme, Jet Propulsion Laboratory

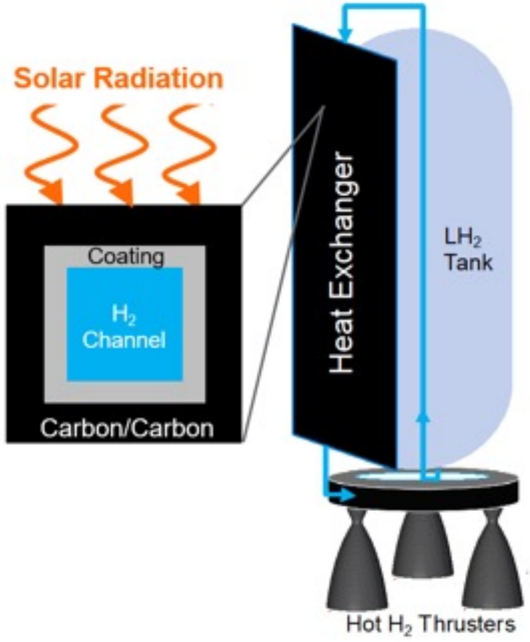
Emerging propulsion systems

More efficient means of propulsion required for long-distance mission profiles

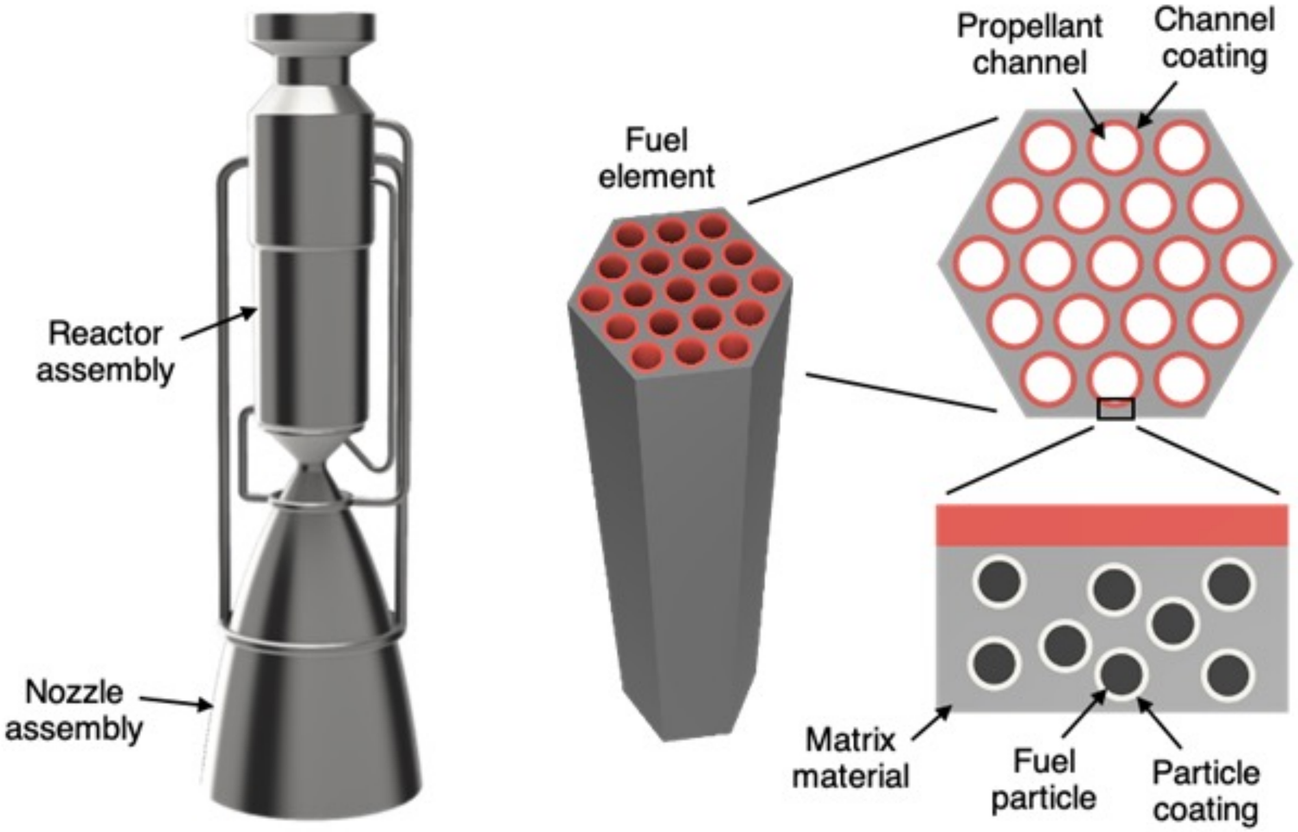
Solar thermal propulsion, nuclear thermal propulsion – high ISP

Fuel element materials – matrix, fuel particles, channel coatings

Solar Thermal Propulsion (STP)



Nuclear Thermal Propulsion (NTP)



The computational toolbox

Computational/quantum chemistry (Gaussian, NWChem)

DFT (VASP)

Molecular dynamics (LAMMPS)

Atomic to microscale insight – discrete dislocation dynamics (ParaDiS)

Microscale tools – additive manufacturing, grain structure and processing (SPPARKS, DREAM.3D, DAMASK)

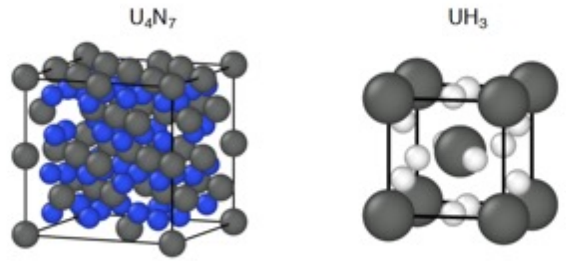
Can "test" materials at conditions not achievable experimentally at a reasonable cost

Experimental verification along the way is key

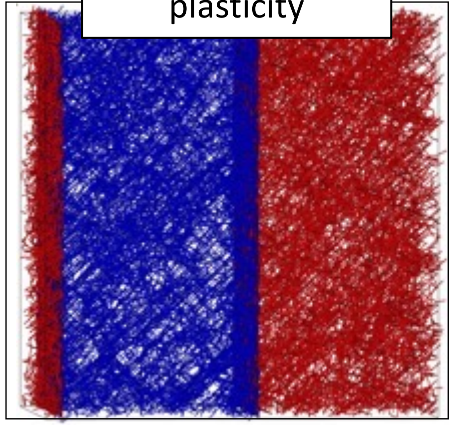
This presentation

Atomic Scale → **Microscale** → **Macroscale**

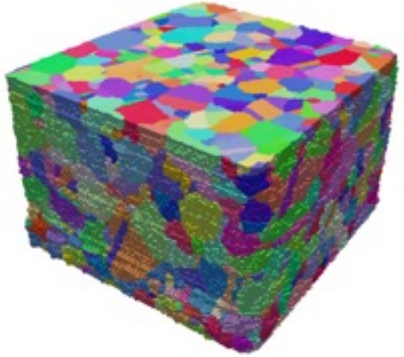
hydrogen interactions



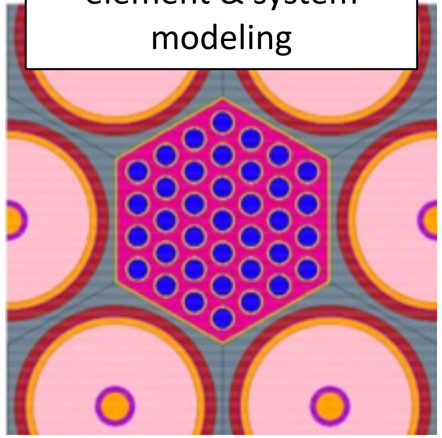
plasticity



thermophysics



element & system modeling



M. Stewart AIAA, 2020

Nuclear thermal propulsion materials

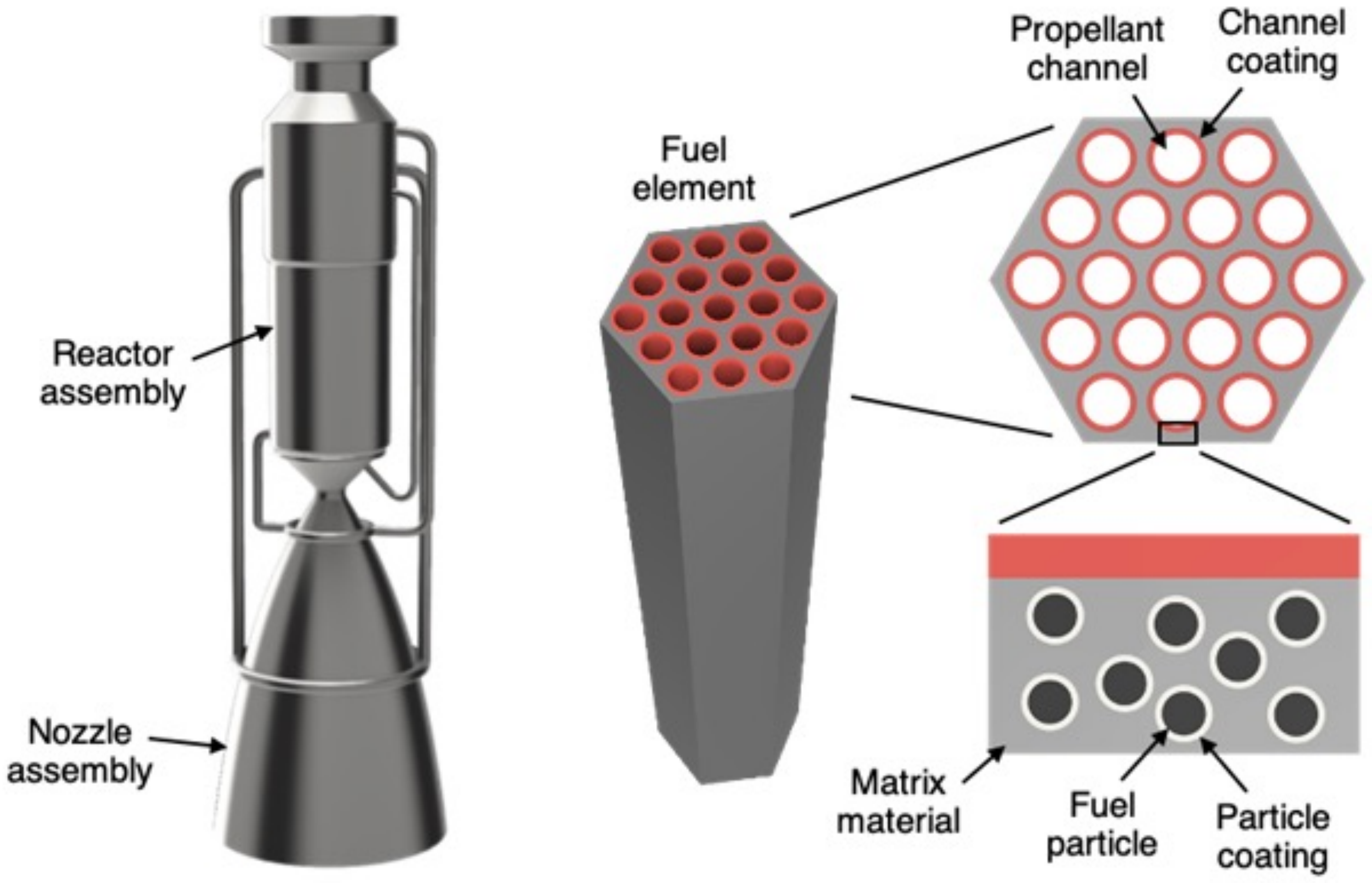
Three case studies:

1. Substrate and Coating Stability and Erosion in Hydrogen
2. Fuel Chemical Stability in the Presence of Hydrogen
3. Fuel Thermal-Mechanical Stability

Idealized system for a first look – W for matrix, UN thermochemistry

Methods:

- Density functional theory
- Molecular dynamics
- Crystal plasticity

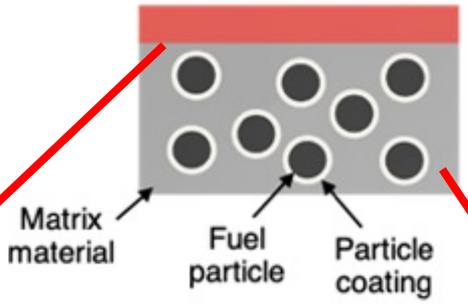


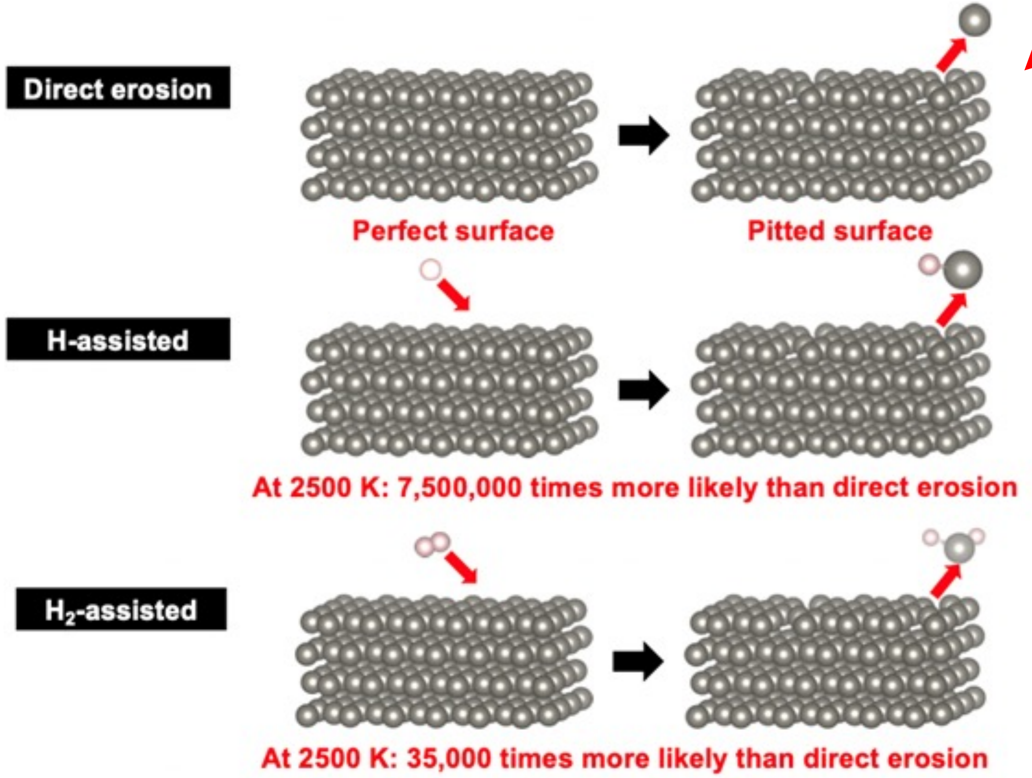
Matrix material properties

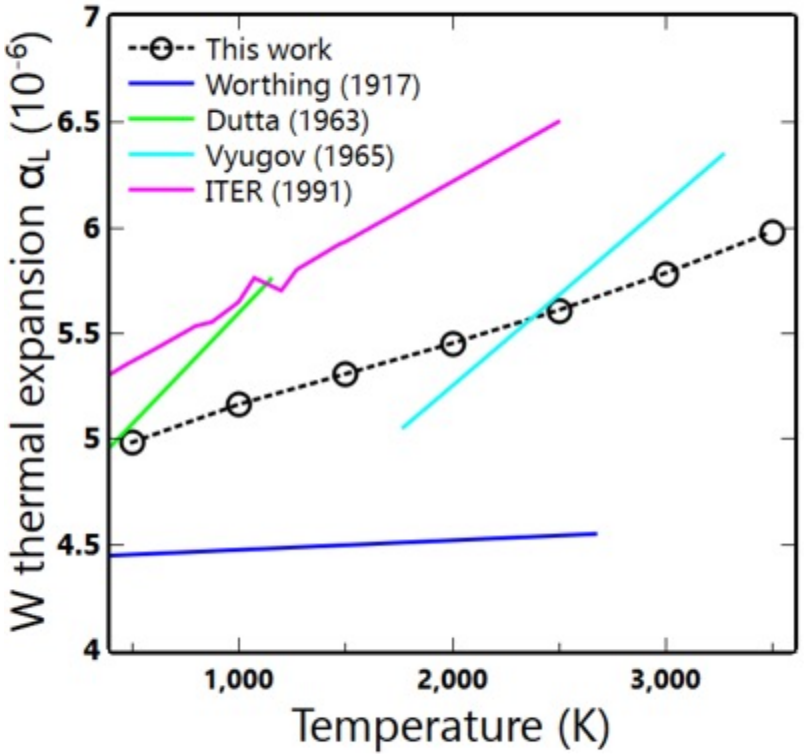
Idealized system for a first look – W for matrix

What if hydrogen breaks through coating, or there is none?
Look at vacuum mass loss

High temperature thermal expansion prediction



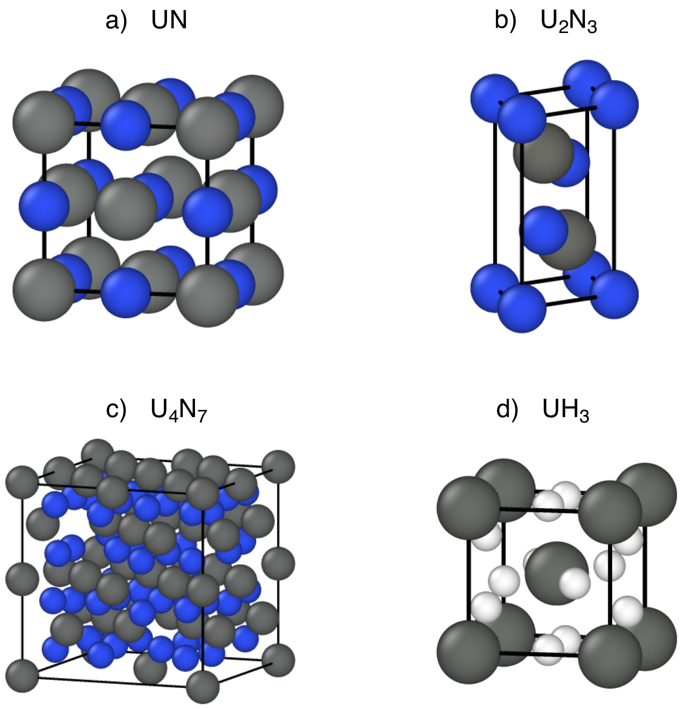




Fuel particle properties

Solid phases of U_xN_y that have been observed

Gibbs free energies calculated via harmonic approximation/phonons

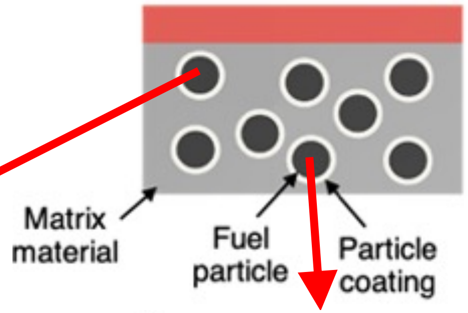


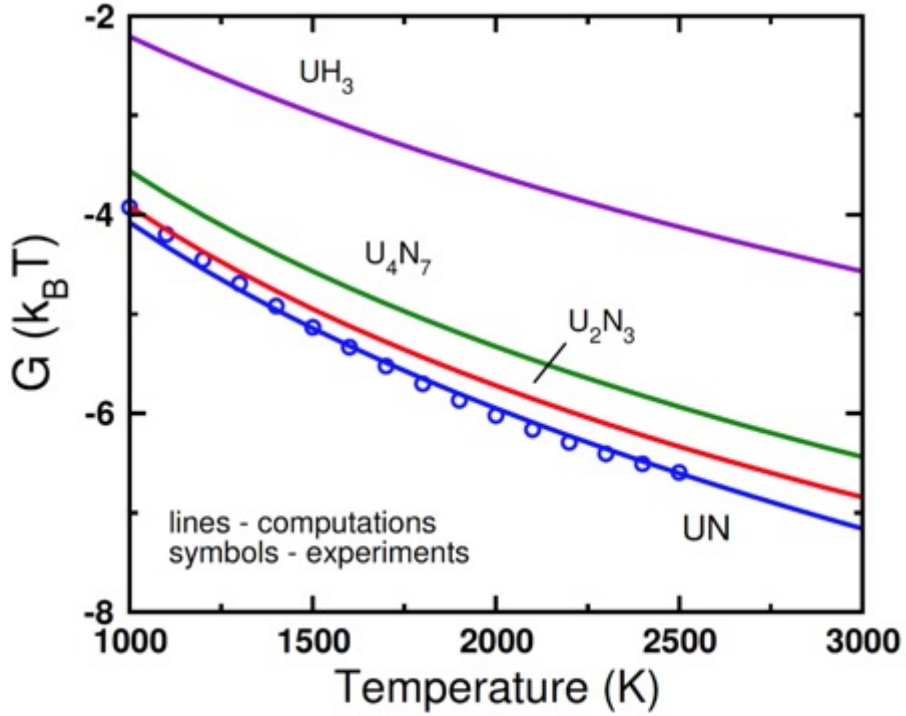
$$6UN + 3H_2 \rightarrow 2UH_3 + 2U_2N_3$$

$$7UN + \frac{9}{2}H_2 \rightarrow 3UH_3 + U_4N_7$$

$$6UN + 6H \rightarrow 2UH_3 + 2U_2N_3$$

$$7UN + 9H \rightarrow 3UH_3 + U_4N_7$$





$$6UN + 3H_2 \rightarrow 2UH_3 + 2U_2N_3$$

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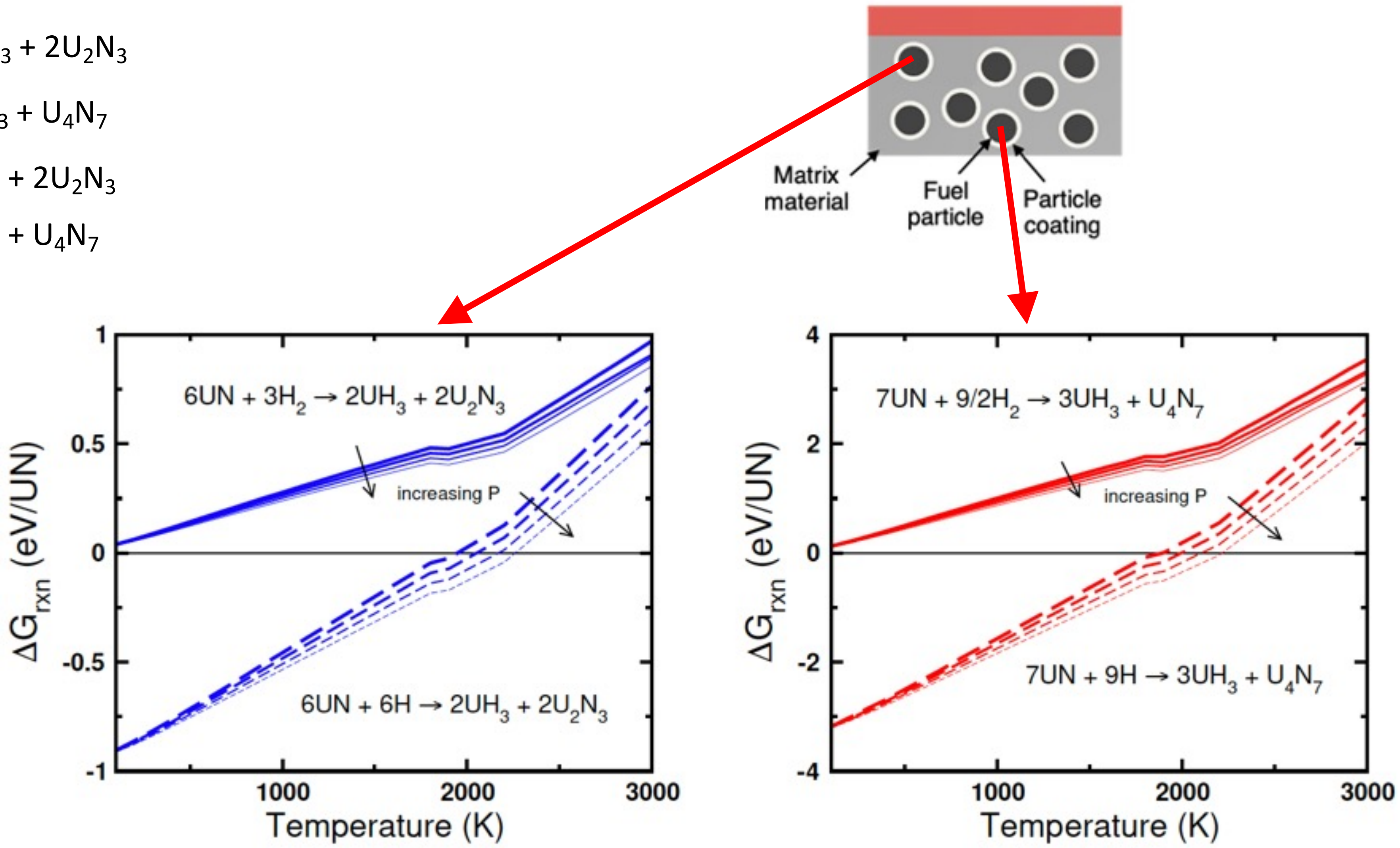
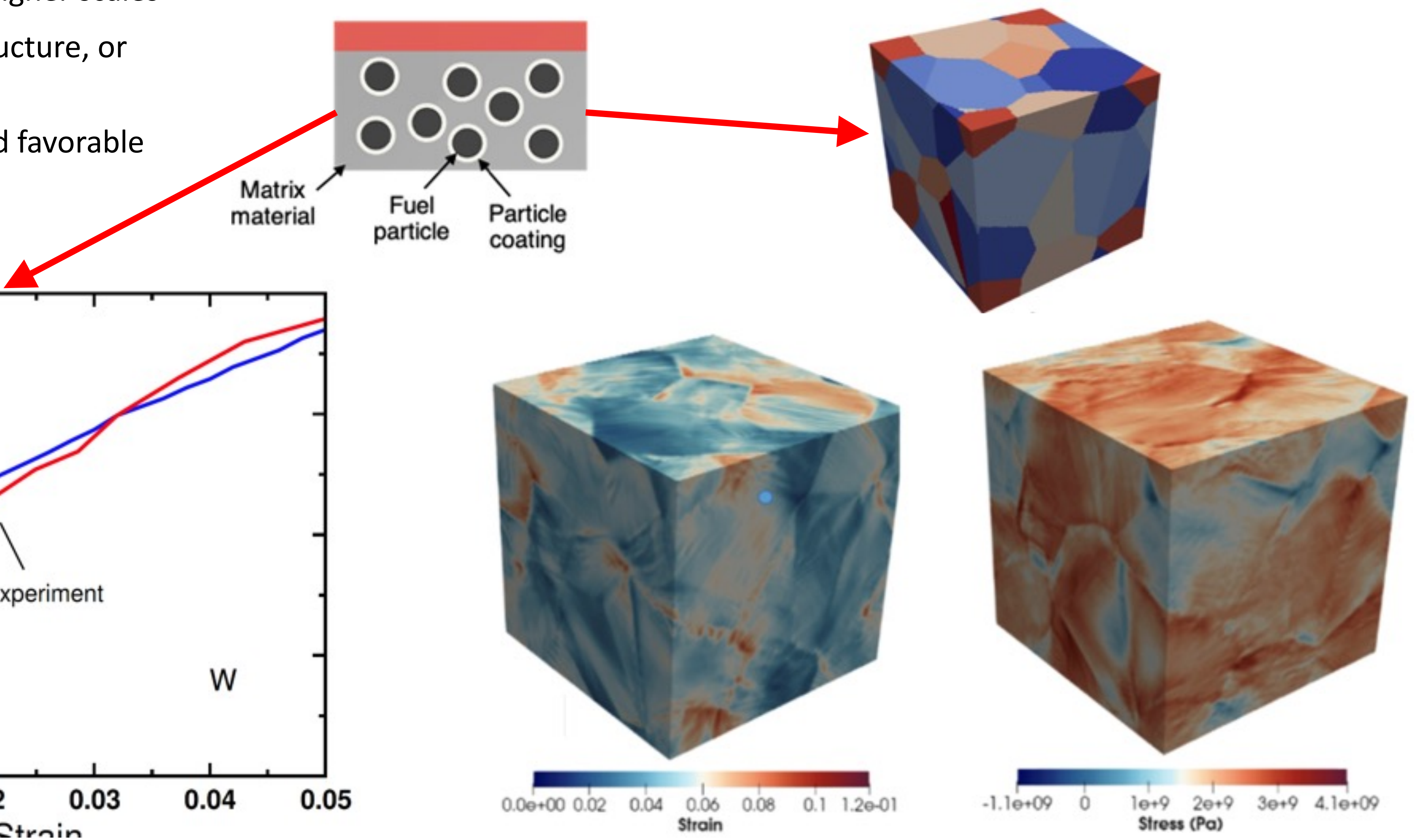


Matrix material failure

Stress-strain data is required at higher scales

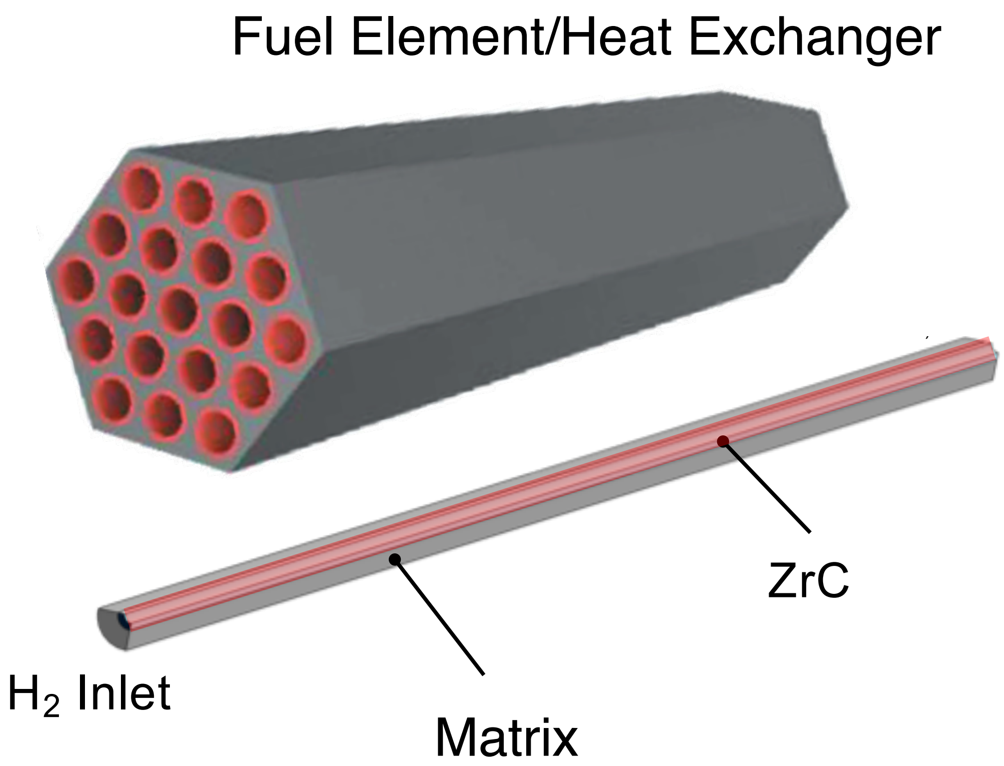
Voronoi tessellation for microstructure, or experimental data if available

Crystal plasticity simulations yield favorable comparison with experiment



Channel coating materials

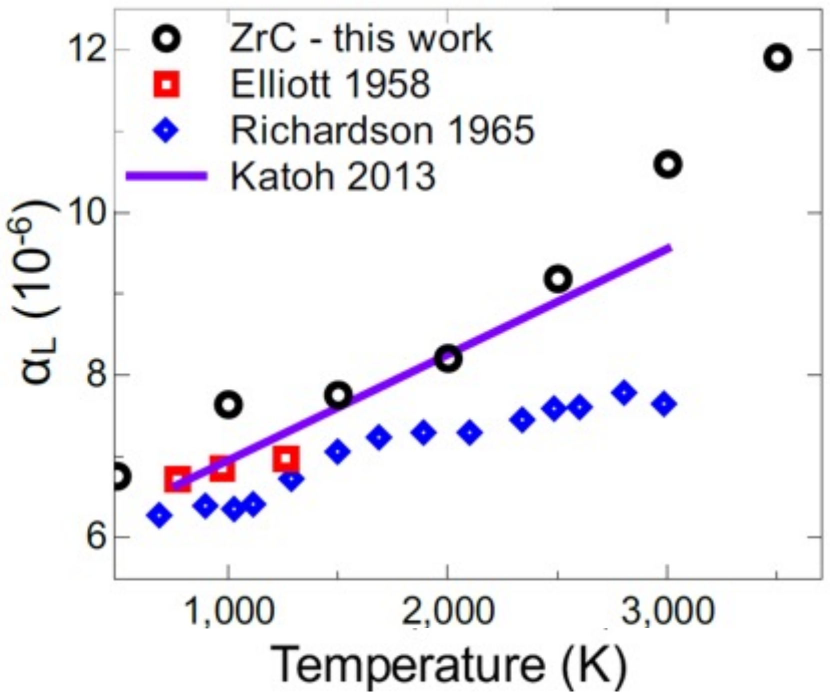
- Solar Thermal Propulsion – rapid transit to the interstellar medium (ISM)
- Nuclear Thermal Propulsion – rapid human transit to Mars
- Both have high propellant temperatures and ISP, and both require channel coatings to protect substrate
- Methods used here include electronic/computational chemistry, density functional theory (static and dynamic), Mutation++ thermo solver
- Experiments can verify models, but data is sparse for these materials

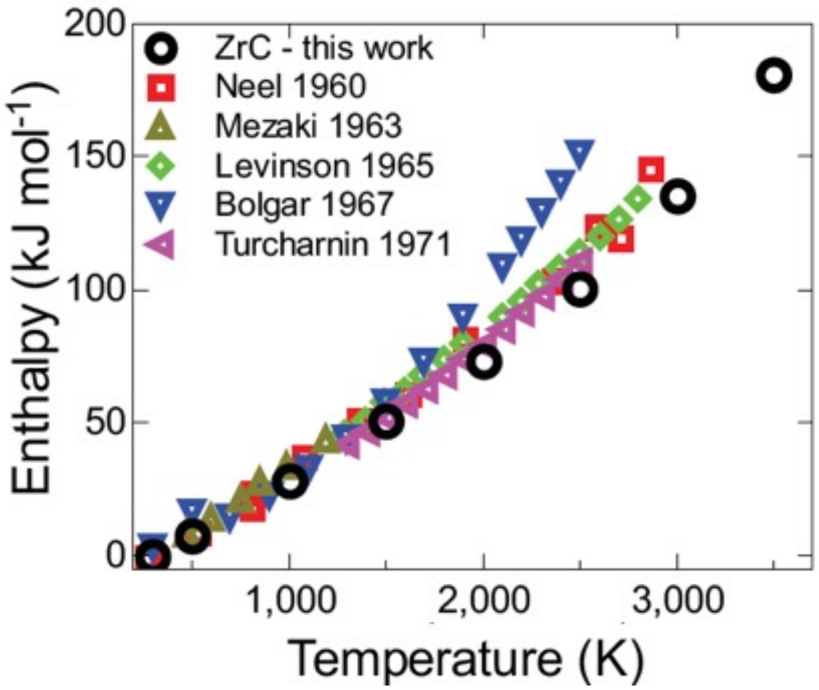


High temperature expansion and enthalpy

CTE calcs generally agree better with more recent experiments utilizing XRD measurements

Predicted enthalpies agree very well with experiment





ZrC/H erosion product partial pressures

Pressures determined via thermodynamic properties predicted by DFT/phonon approximation

Hydrogen can react with either metal or carbon atoms

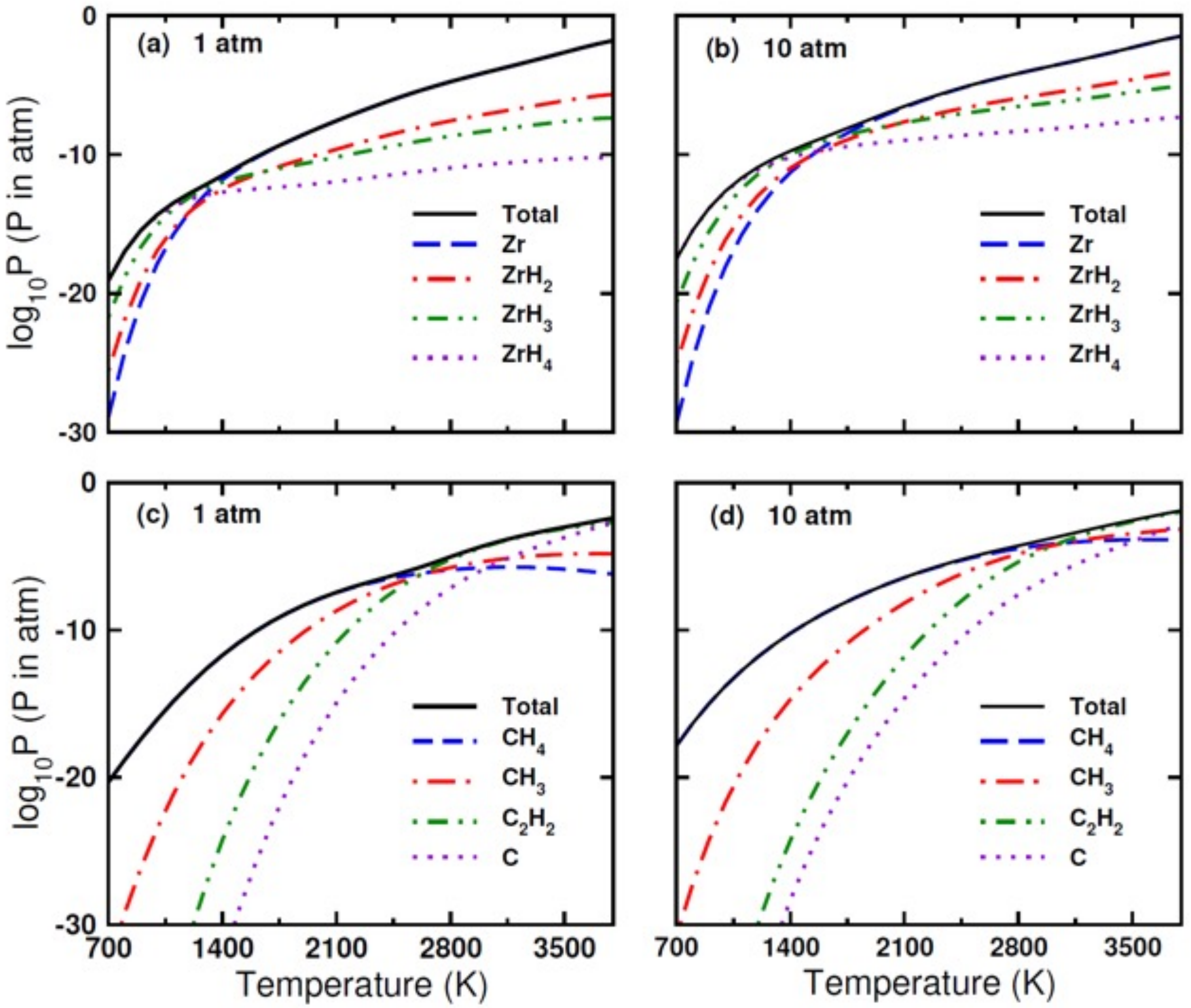
Below reactions considered for each metal M:

$$MC(s) + \left(\frac{x+4}{2}\right) H_2(g) \rightarrow MH_x(g) + CH_4(g$$

$$MC(s) + 2H_2(g) \rightarrow M(g) + CH_4(g)$$

$$MC(s) + H_2(g) \rightarrow M(g) + C_2H_2(g)$$

$$MC(s) \rightarrow M(g) + C(g)$$



MC/H product characterization

Trend of less hydrogenated species at higher temperature holds for all four materials of interest

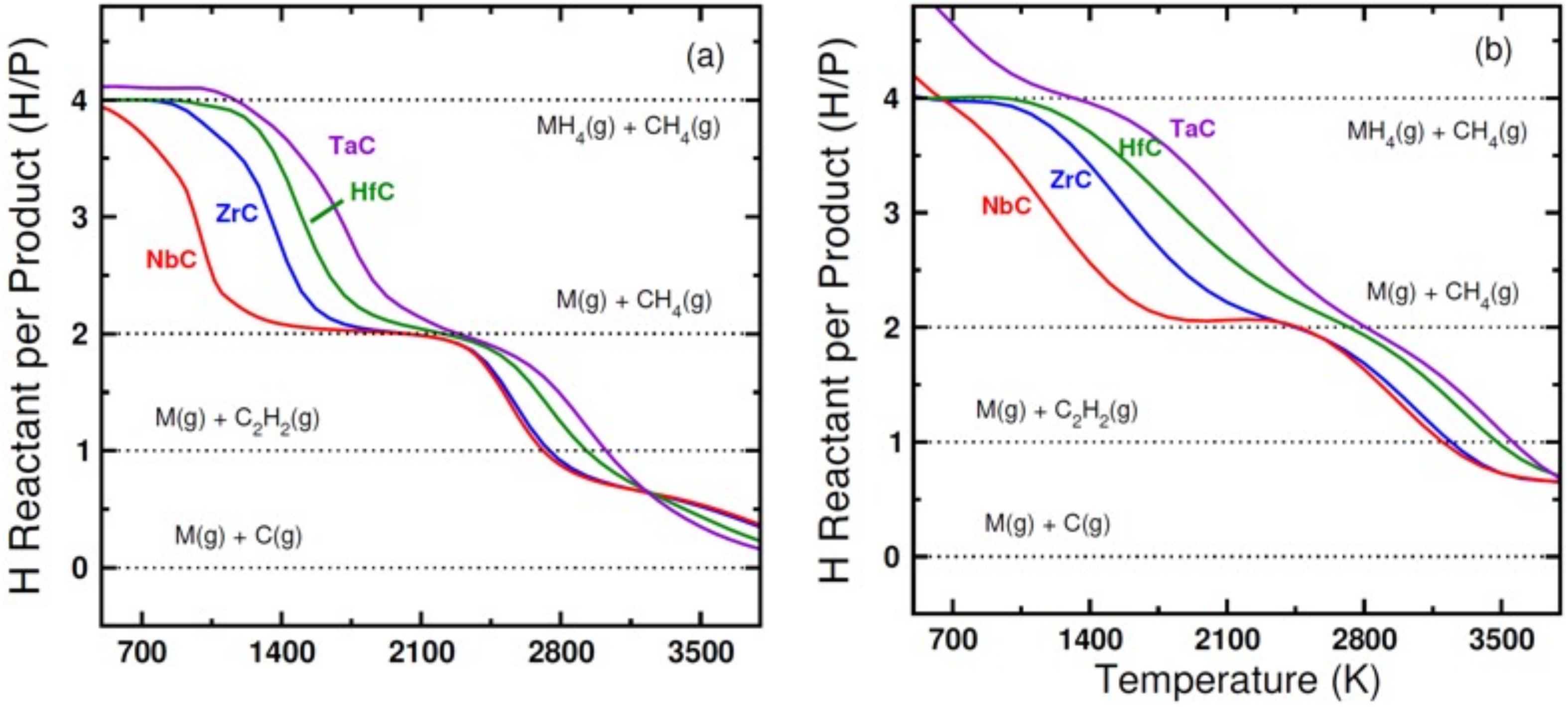
As hydrogen pressure increases, less direct erosion occurs

$$MC(s) + \left(\frac{x+4}{2}\right) H_2(g) \rightarrow MH_x(g) + CH_4(g$$

$$MC(s) + 2H_2(g) \rightarrow M(g) + CH_4(g)$$

$$MC(s) + H_2(g) \rightarrow M(g) + C_2H_2(g)$$

$$MC(s) \rightarrow M(g) + C(g)$$

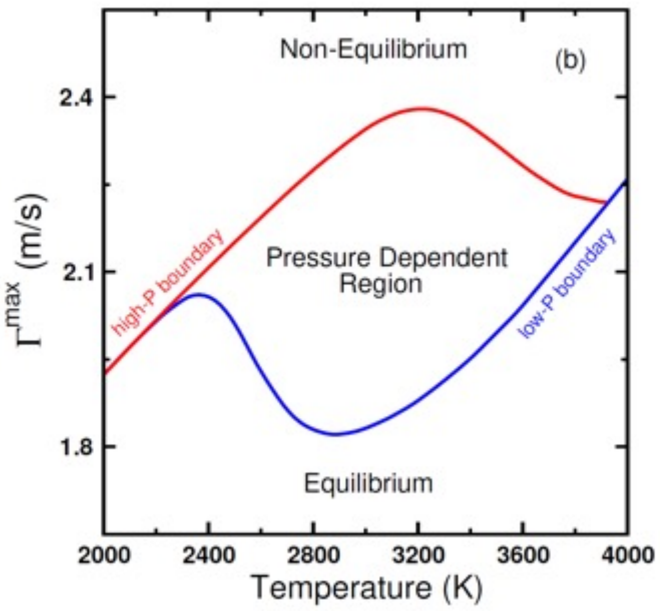


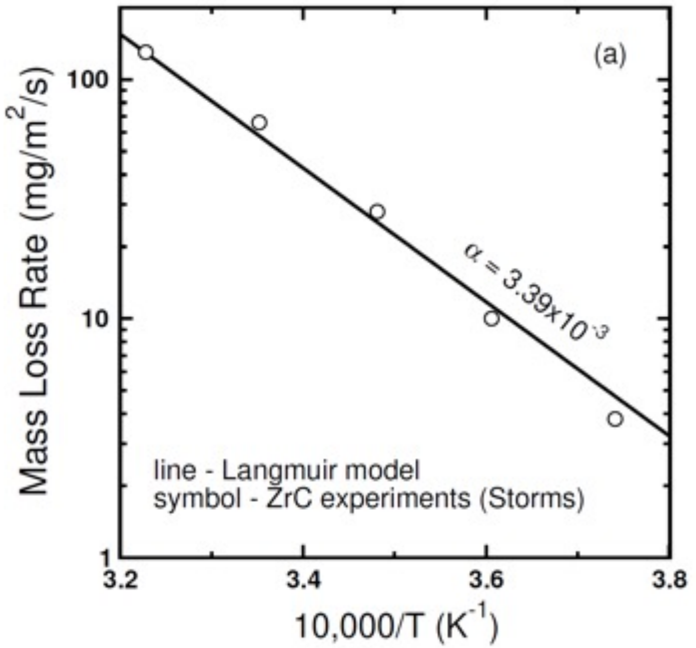
ZrC erosion – experimental comparison

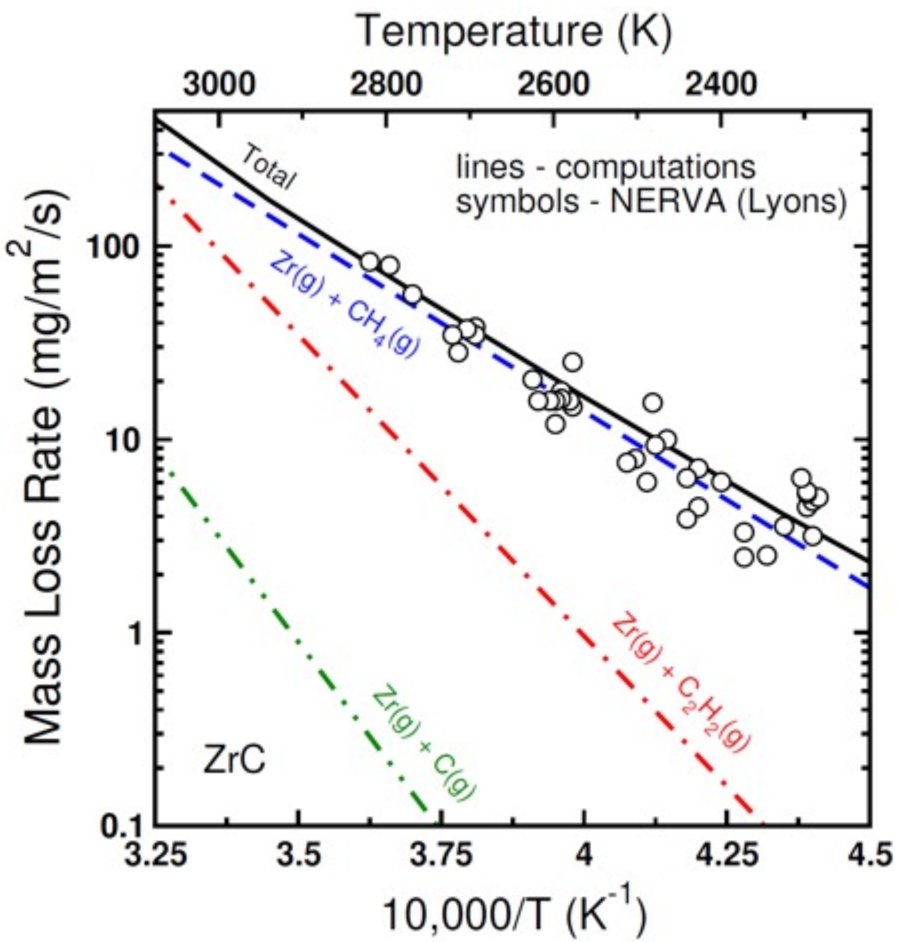
When is erosion due to equilibrium vs non-equilibrium effects?

Langmuir vaporization – Hertz-Knudsen expression for non-equilibrium

NERVA was in equilibrium regime





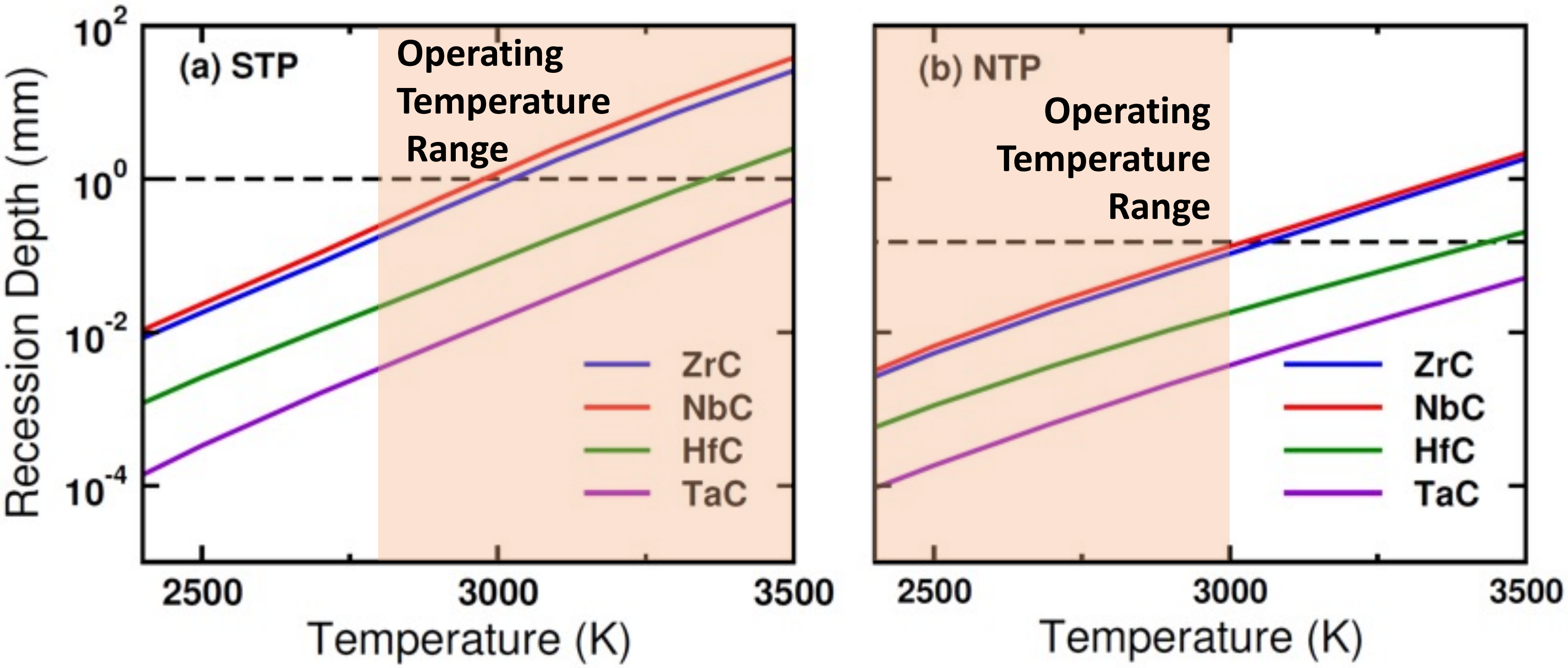


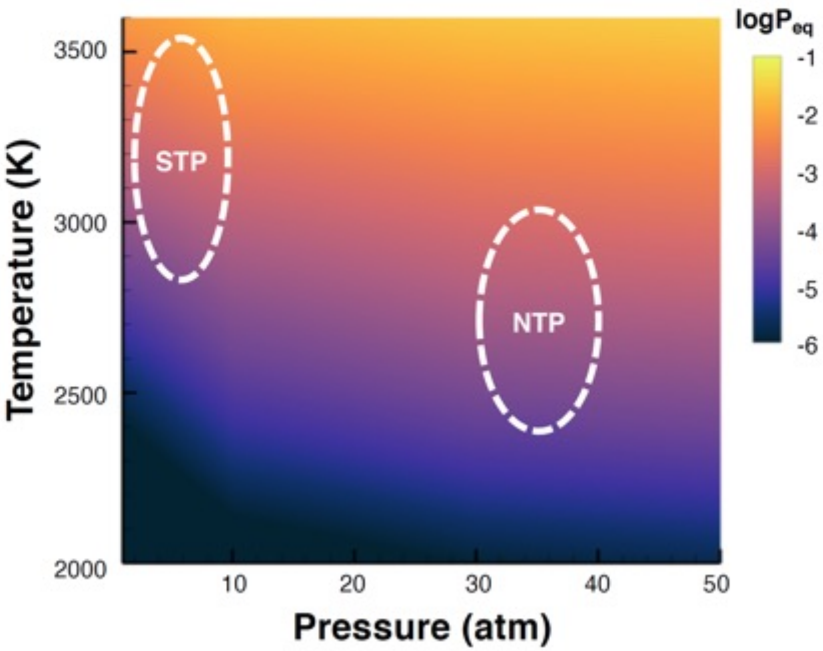
STP & NTP material recommendations

Temperature has a stronger influence on erosion than propellant pressure

STP environment more aggressive, only TaC yields acceptable erosion, although HfC works for lower temperature range

For NTP, all of the carbide materials meet the recession criterion



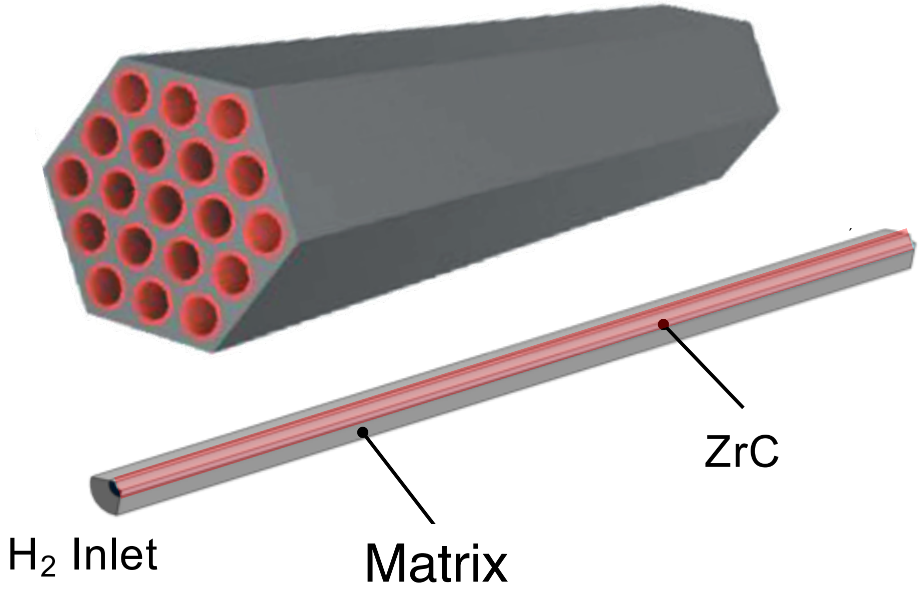


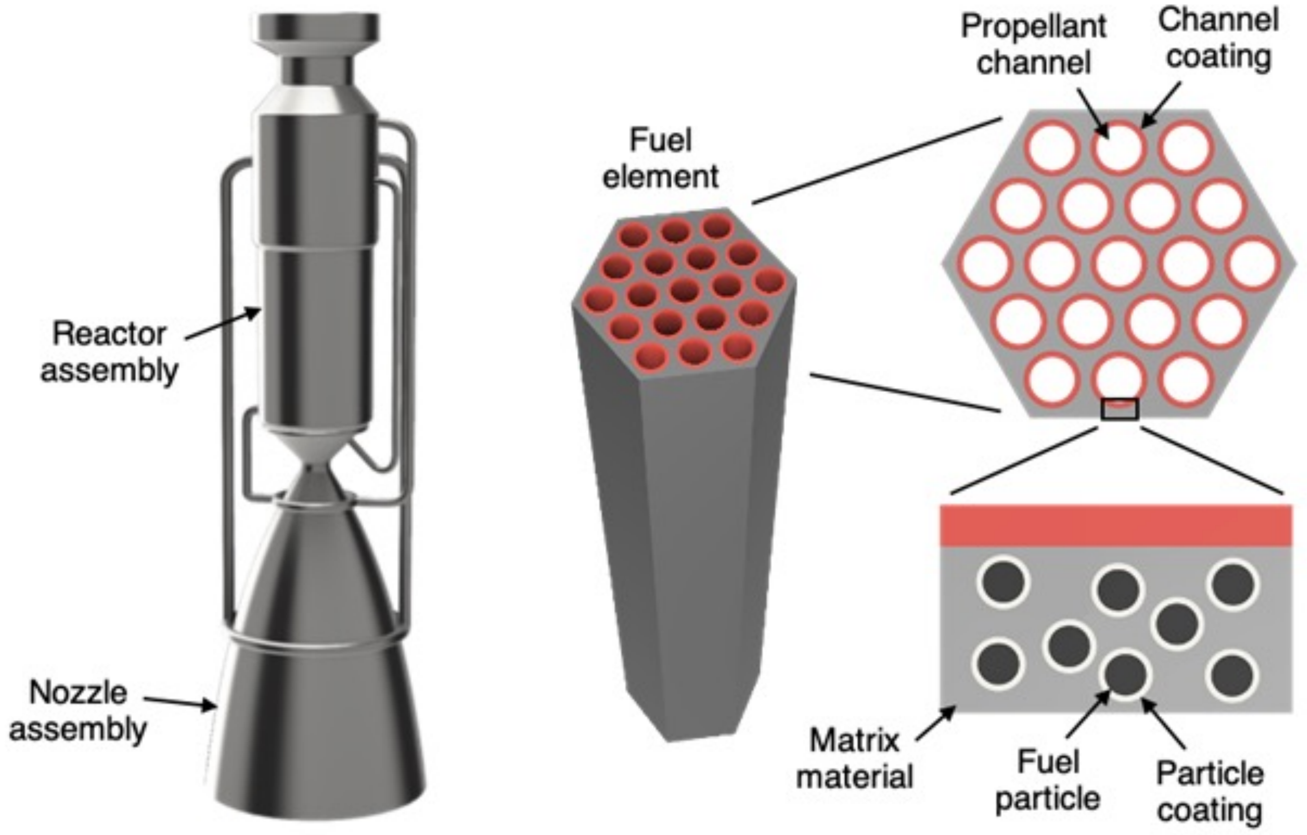
Summary

Computational techniques based on physics can be used to extrapolate to conditions beyond the laboratory

These techniques must be calibrated

Experimental verification is always important! Don't simulate in a vacuum

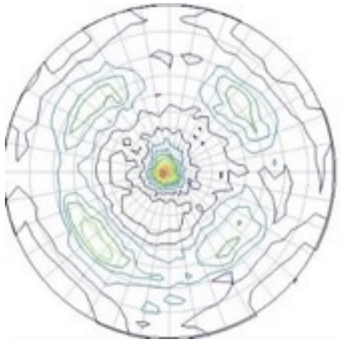




Related efforts & future directions

Additive manufacturing process modeling yields microstructure, or if possible, use experiments as input!

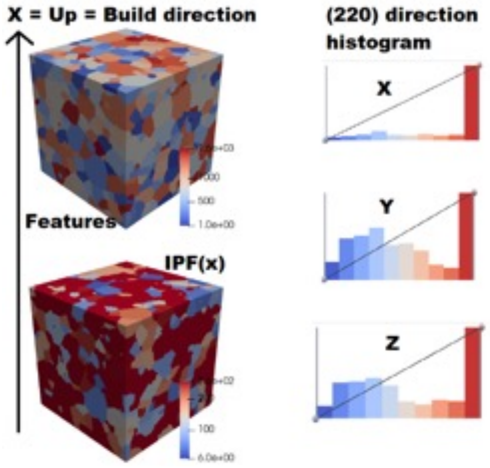
Experimentally informed microstructures

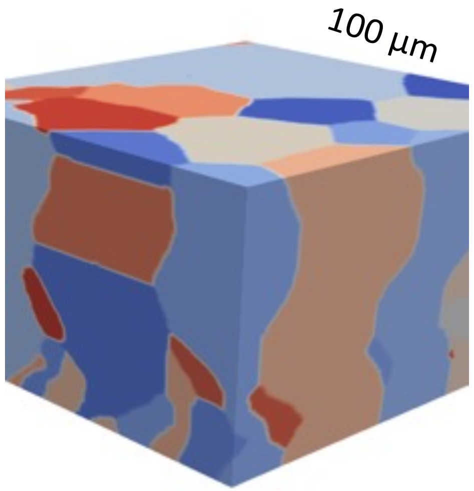


EBSD, pole figures as inputs

Matlab/MTEX
DREAM.3D

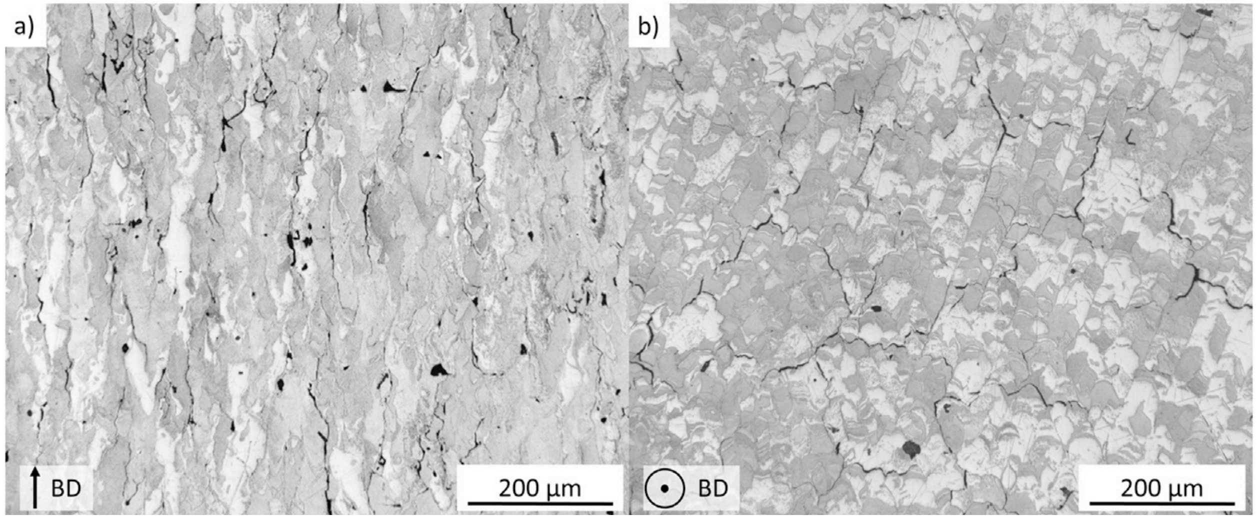
Microstructures have preferred orientations and grain size distributions





Synthetic microstructures informed by process modeling

SPPARKS
DREAM.3D



Braun, et al., IJRFHM (2019)

Questions/comments

Justin Haskins, Lauren Abbott, BJ Tucker

NASA Ames Research Center
Thermal Protection Materials Branch

National Aeronautics and Space Administration

Ames Research Center
Entry Systems and Technology Division