

Computational Materials Modeling

Justin Haskins, Lauren Abbott, BJ Tucker

NASA Ames Research Center
Thermal Protection Materials Branch

NASA Langley/Ames EDL Seminar Series

Acknowledgments



Computational Material Group

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BJ Tucker, AMA / NASA Ames
Jaehyun Cho, AMA / NASA Ames

AERoBOND Project

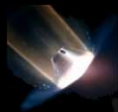
Frank Palmieri (PI), NASA Langley
Tyler Hudson (Co-PI), NASA Langley
Austin Smith, NASA Langley
Roberto Cano, NASA Langley
John Connell, NASA Langley
Jin Ho Kang, NIA / NASA Langley
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Bryson Clifford, Intern Program / NASA Langley
Isaac Barnett, Intern Program / NASA Langley

Asteroid Threat Assessment Project

Eric Stern (Task Lead), NASA Ames
Grant Palmer, AMA / NASA Ames
Pratibha Raghunandan, AMA / NASA Ames
Brody Bessire, NASA Ames
Francesco Panerai, UIUC

Solar Thermal Propulsion

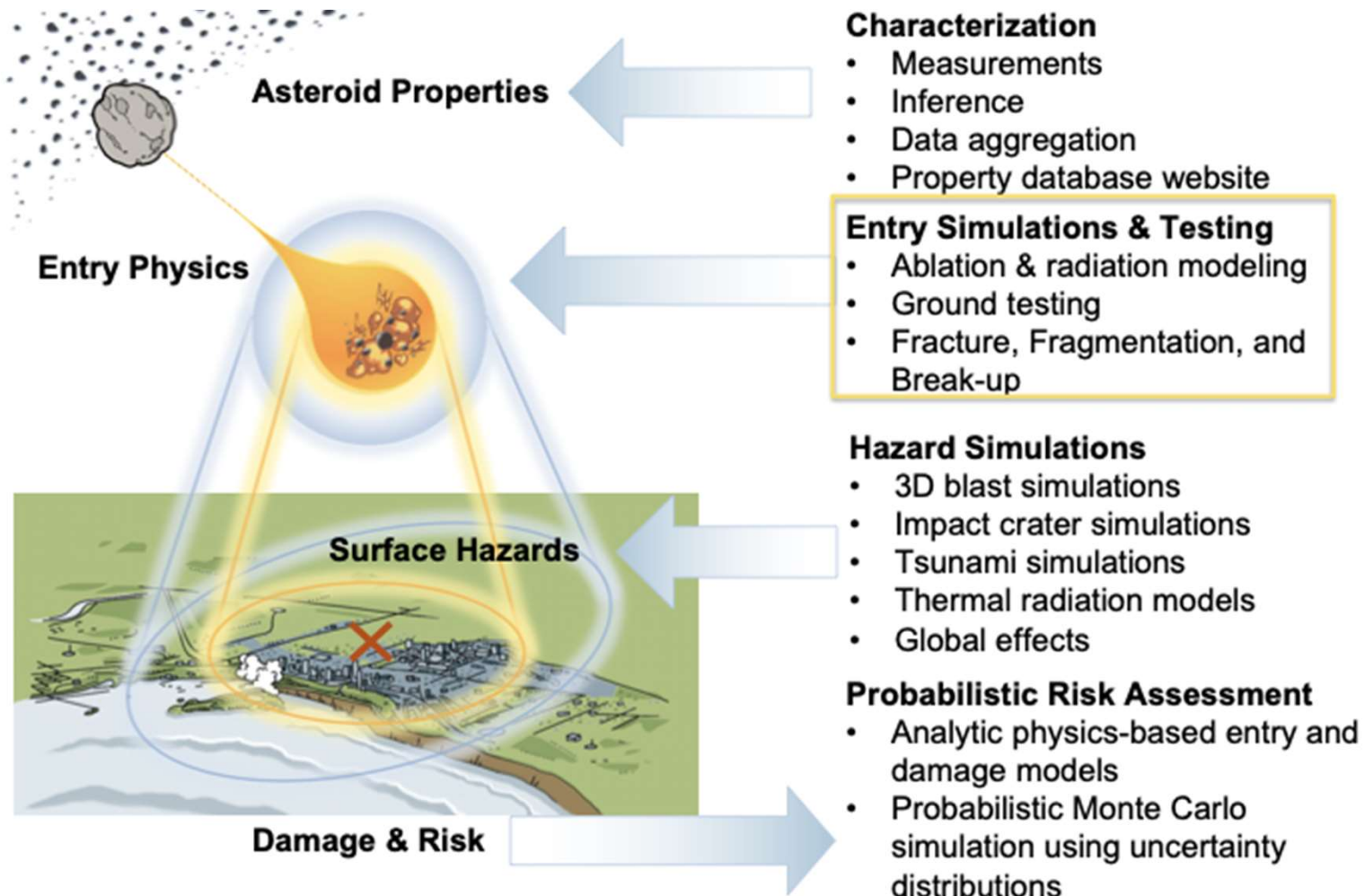
Dean Chiekh, Jet Propulsion Laboratory
Michael Preudhomme, Jet Propulsion Laboratory



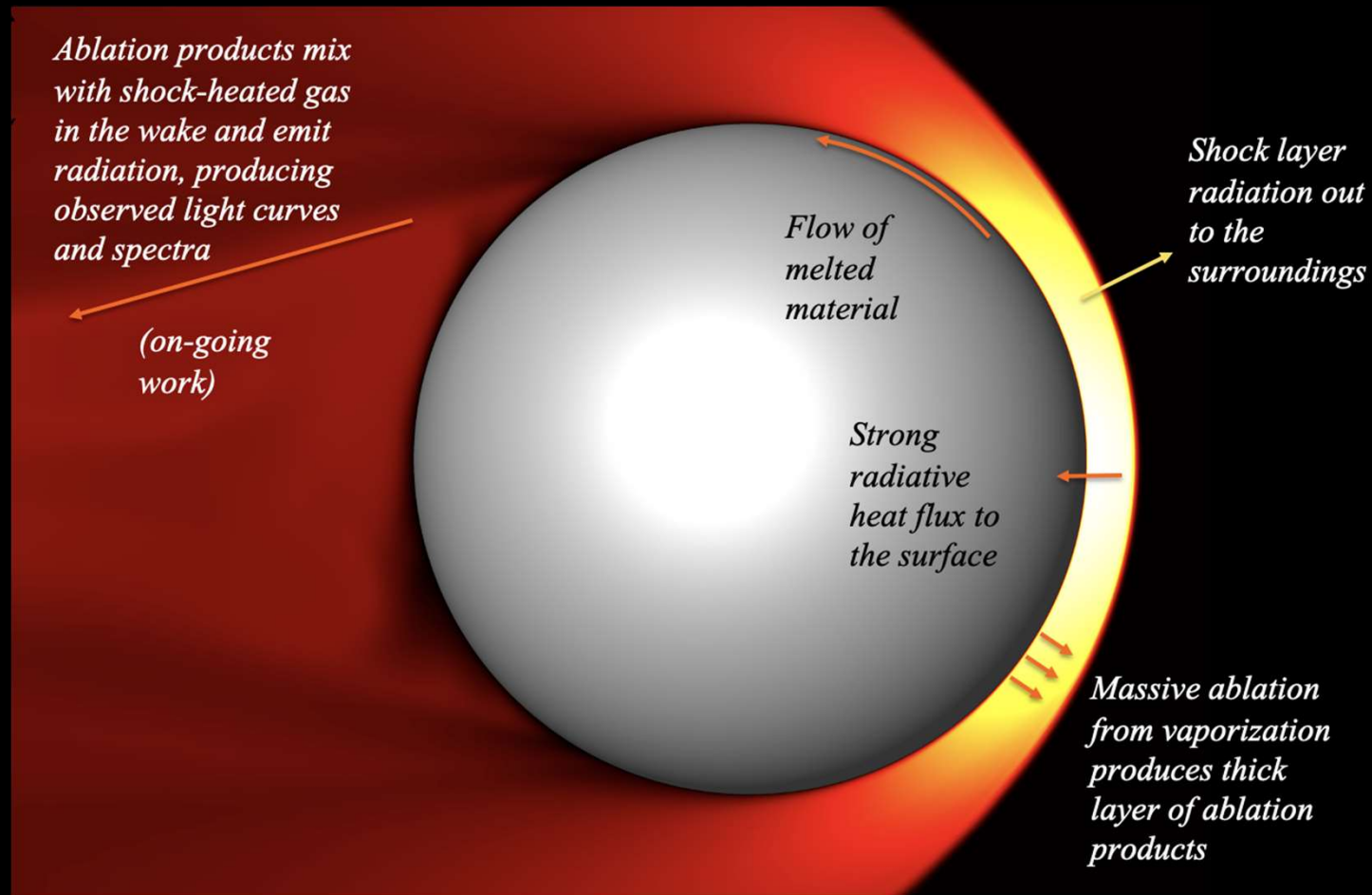
Part 1: Atoms and Asteroids

Justin Haskins

Asteroid Threat Assessment Project

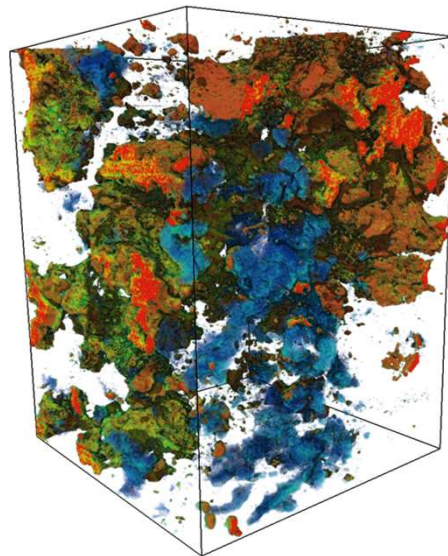
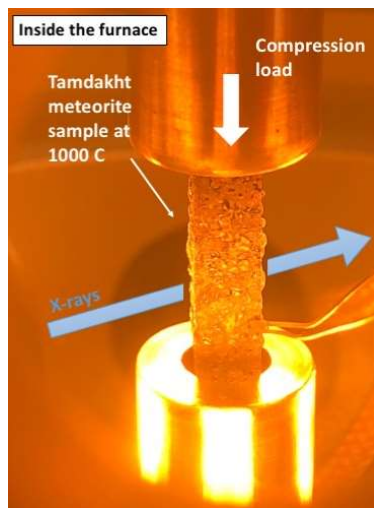


Effects associated with meteor/asteroids entry



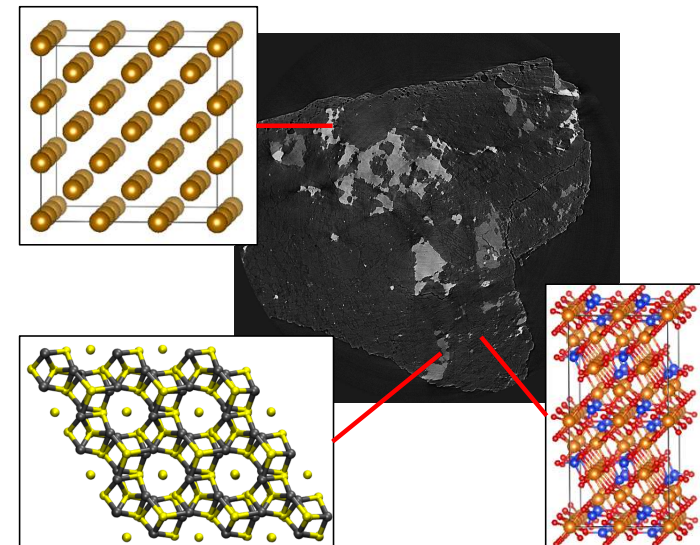
Meteorite Reactions During Heating

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



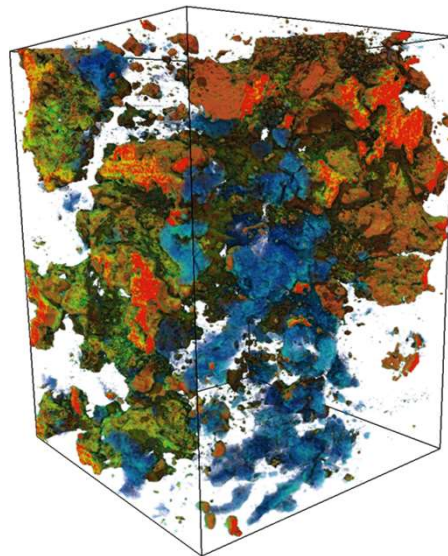
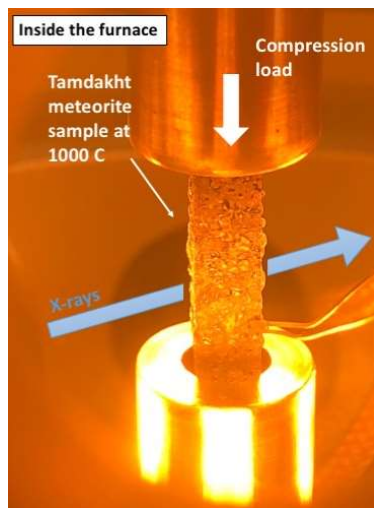
Meteorite Ablation

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



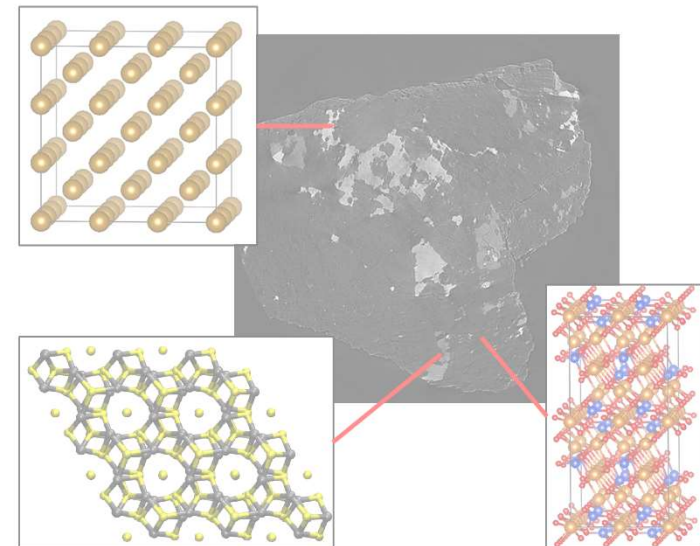
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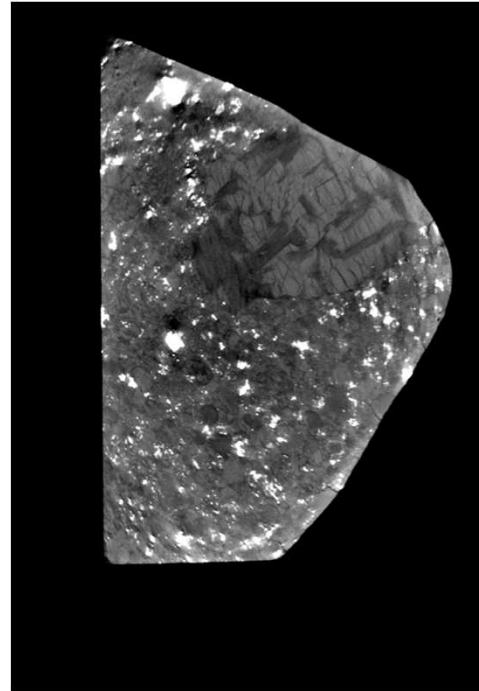
- Melt-Vaporization Ablation Model Development
- Ab Initio Molecular Dynamics Properties



Microtomography of Stony Meteorites (Chondrites)

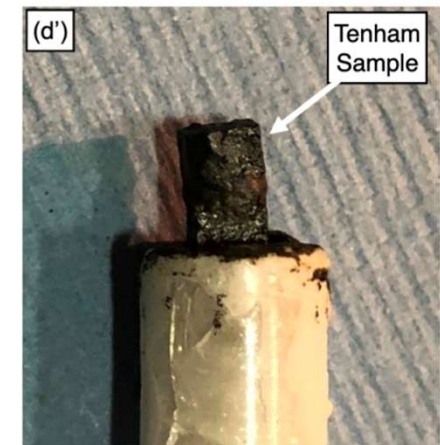
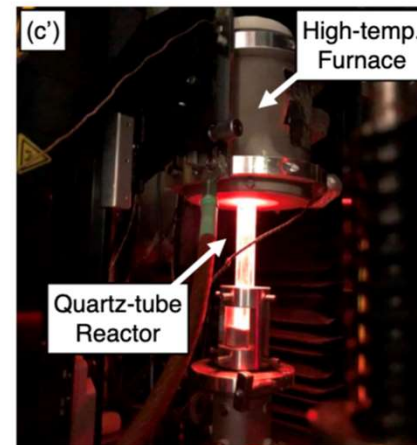
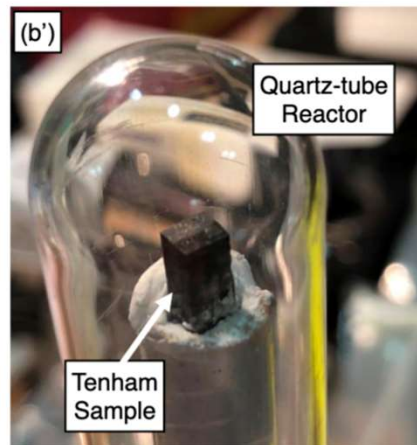
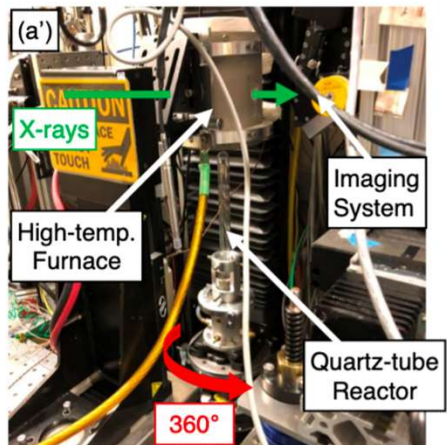
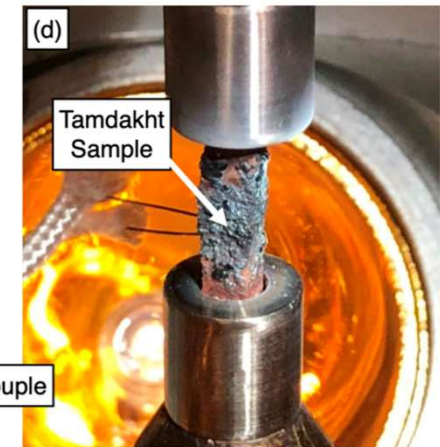
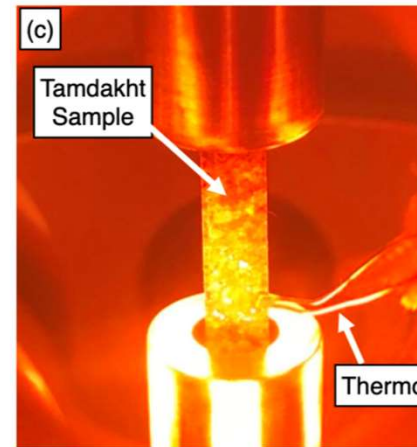
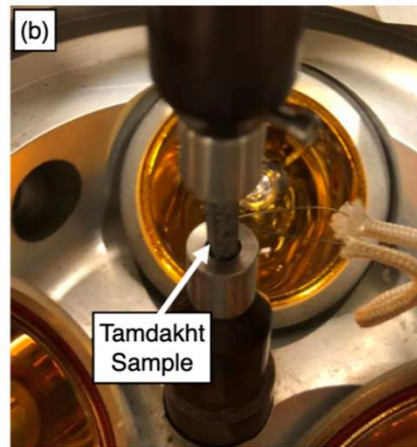
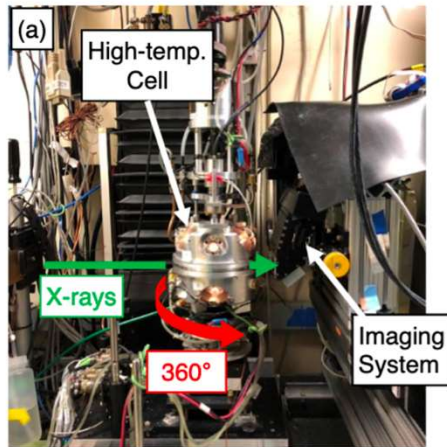


Power: 10 W
Magnification: 0.4x
Voxel size: 14.7 μm
Exposure time: 2 s
Projections: 3201



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

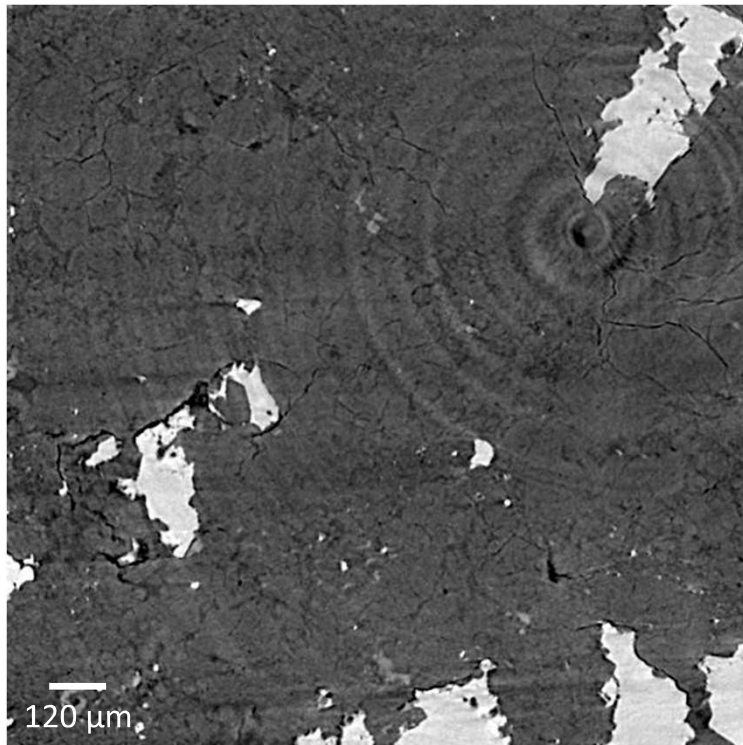
In Situ Microtomography of Stony Meteorites during Heating



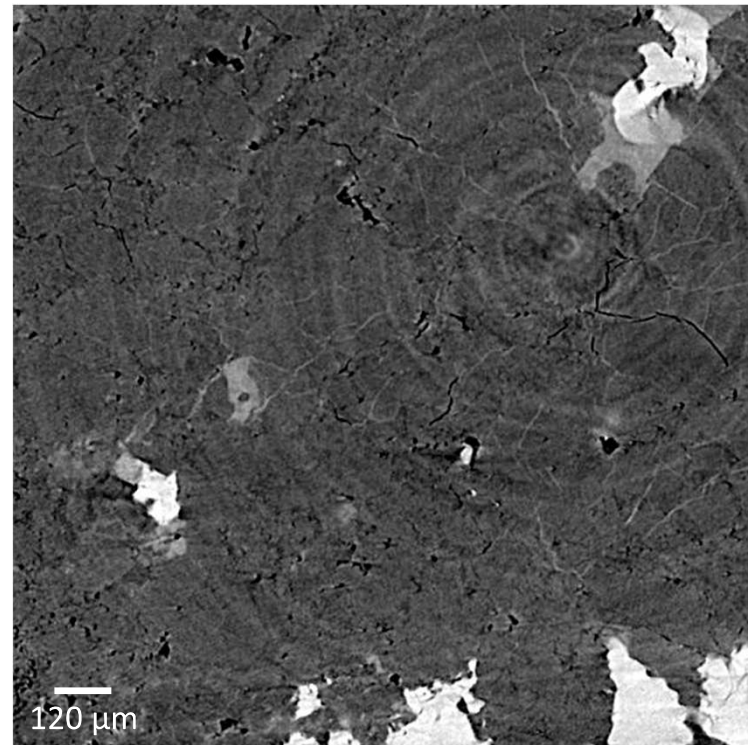
Changes in the Microstructure during Heating



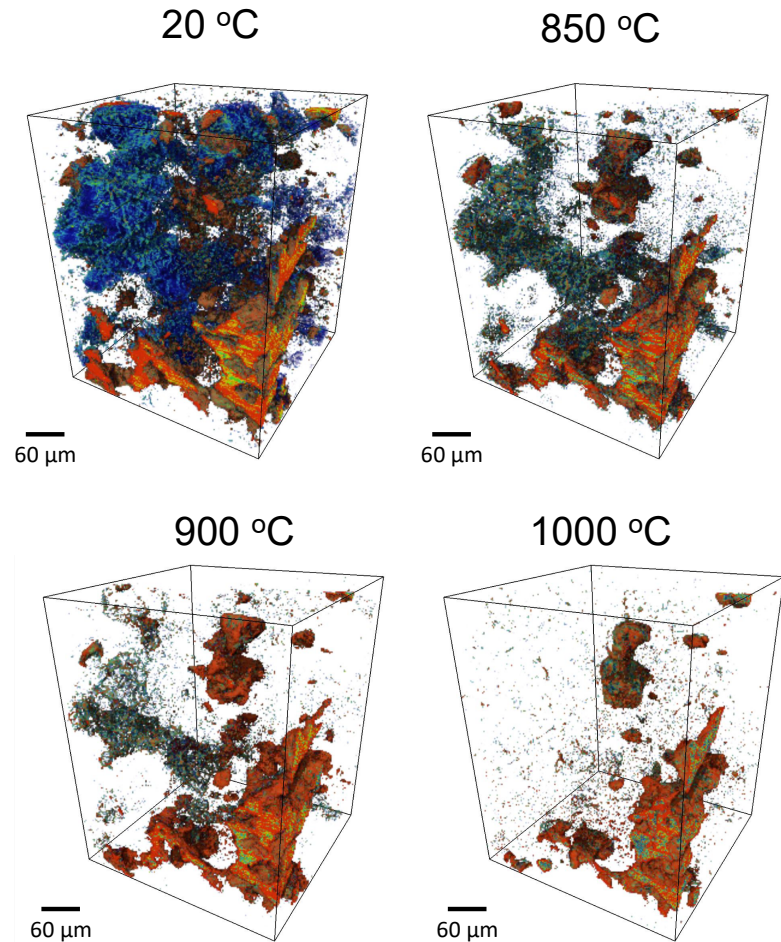
Room Temperature



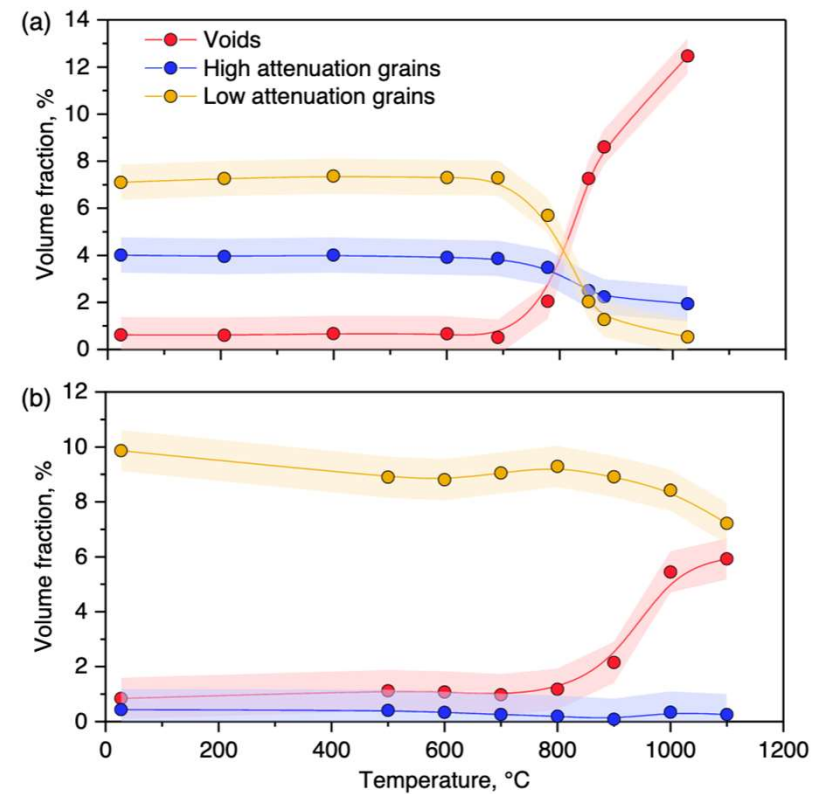
1200 K



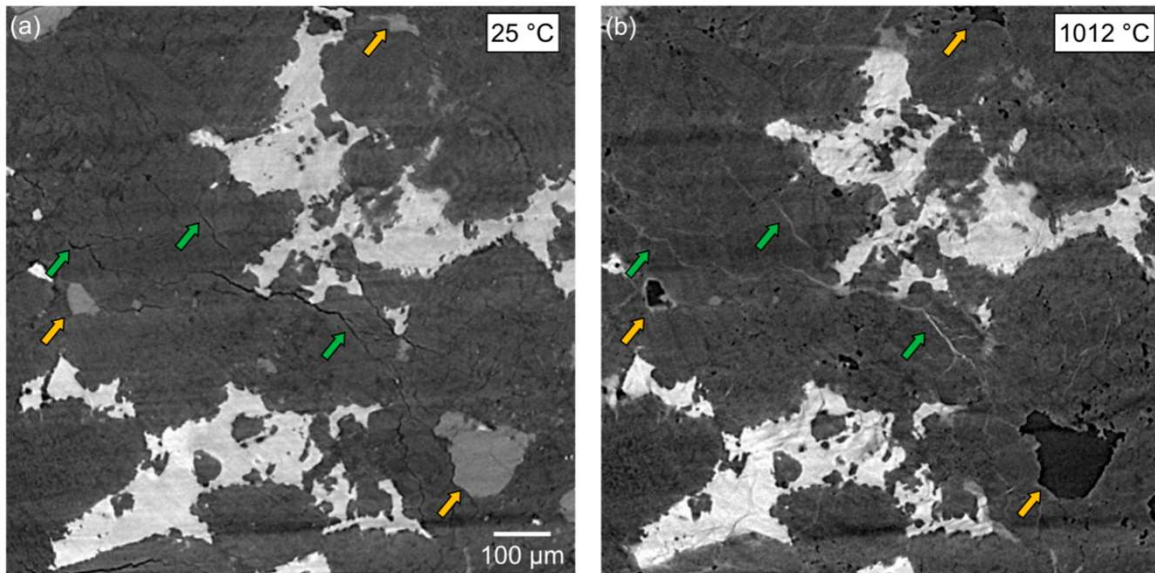
Volume resolved changes in porosity during heating



Void fraction seen to increase during heating



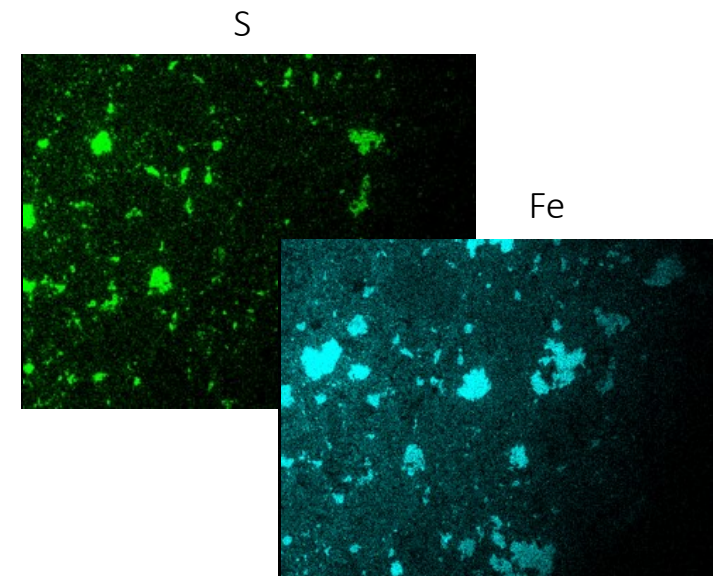
Identification of Lost Grain Material



Low attenuation grains melt/vaporize

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

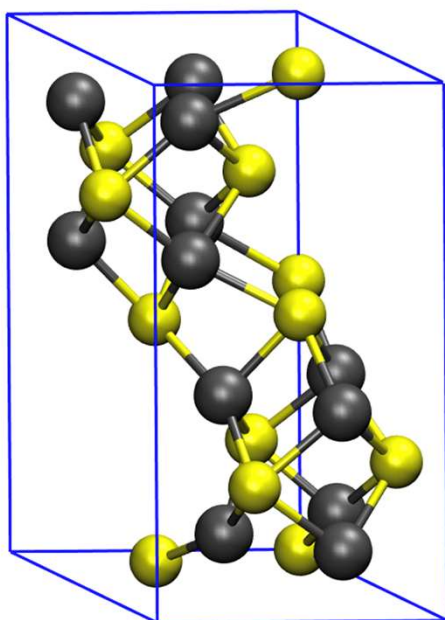
XPS image shows S and Fe in low attenuation grains



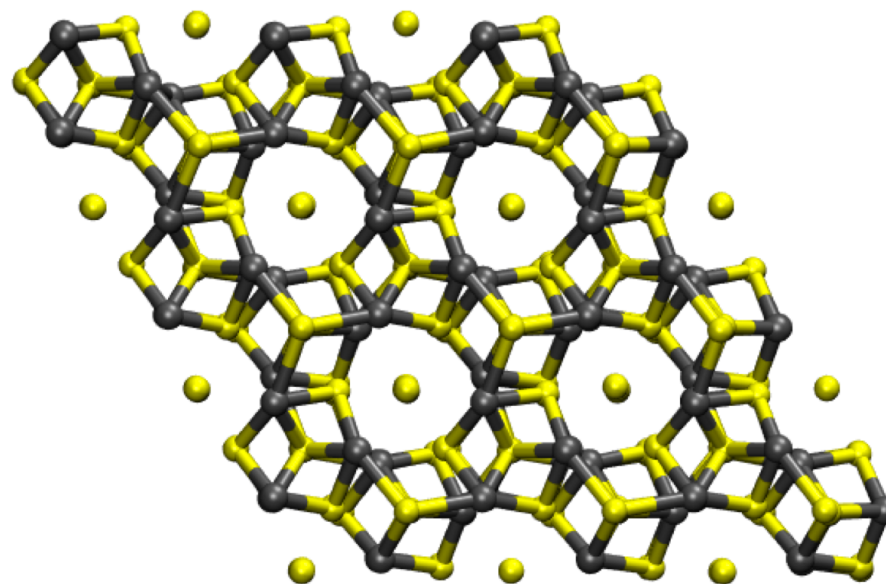
Iron sulfide (Troilite)



Unit cell of troilite for
computations

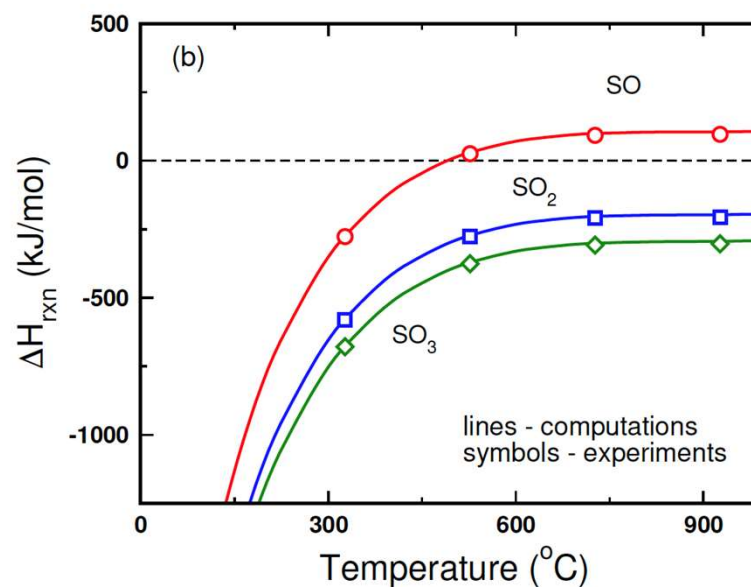
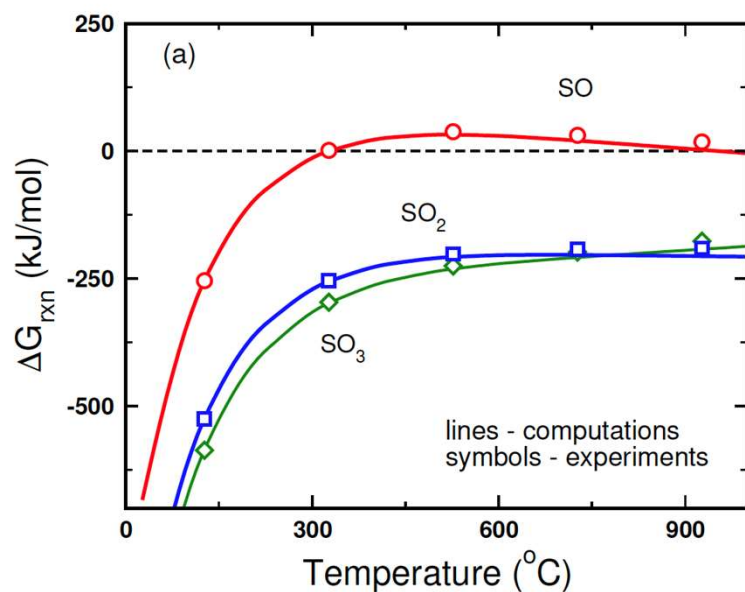
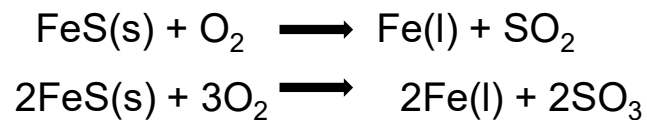


View of the [001] plane



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

Troilite reactions with oxygen

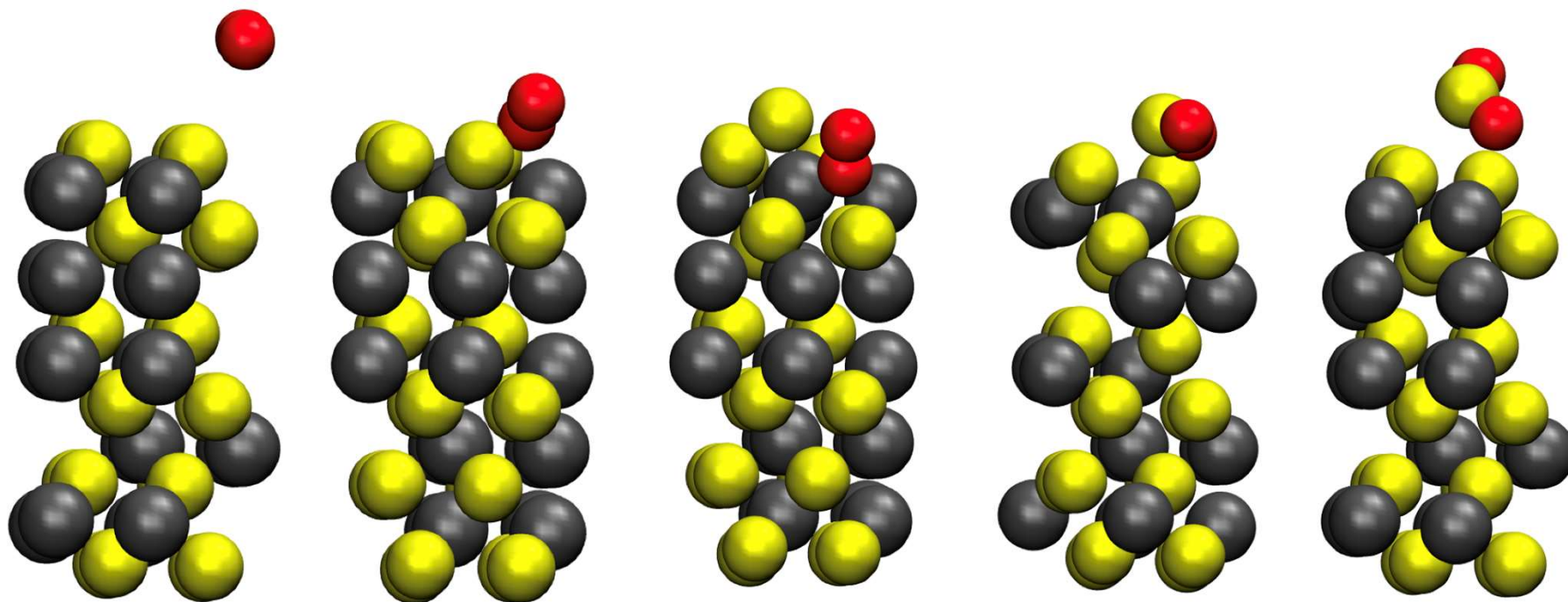


Formation of sulfide products very favorable at the high temperatures associated with CT experiments

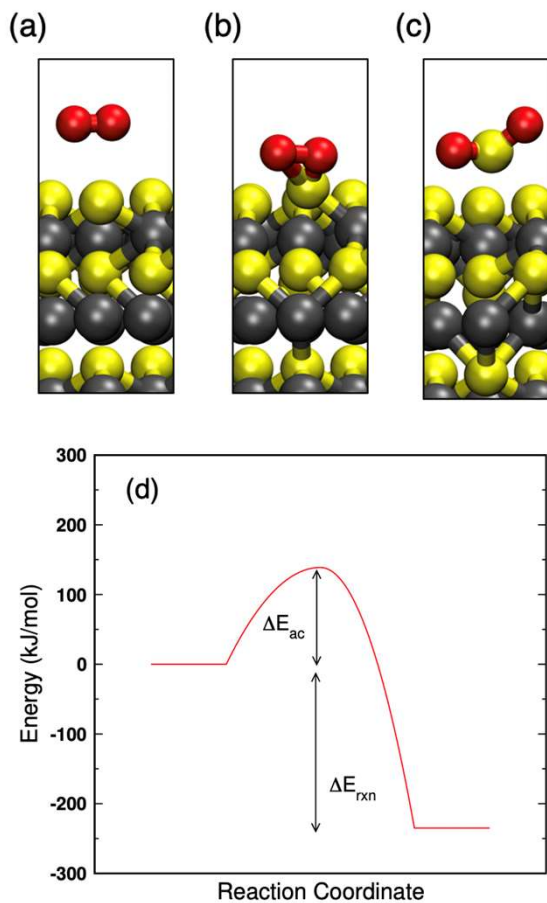
Kinetics of troilite oxidation



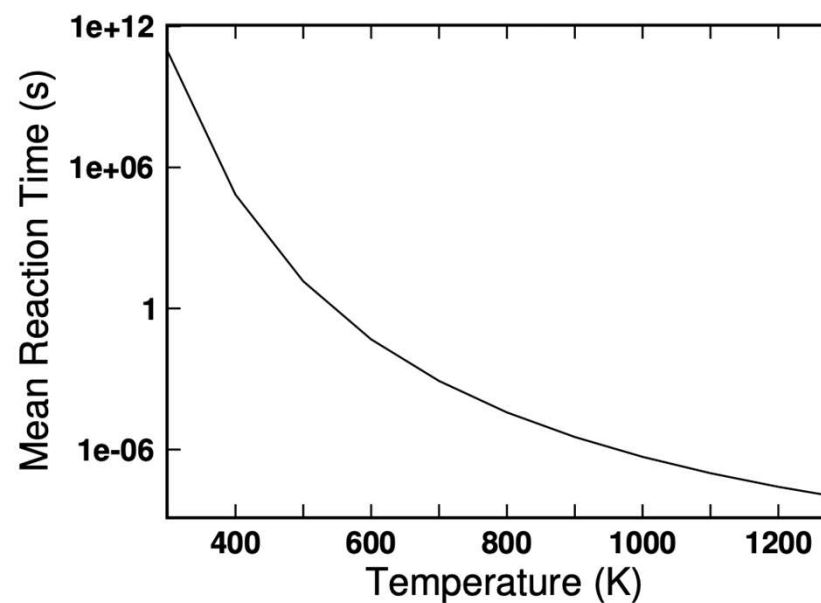
Reaction process of oxygen with the surface of troilite can be examined to understand kinetics



Kinetics of troilite oxidation



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



Summary



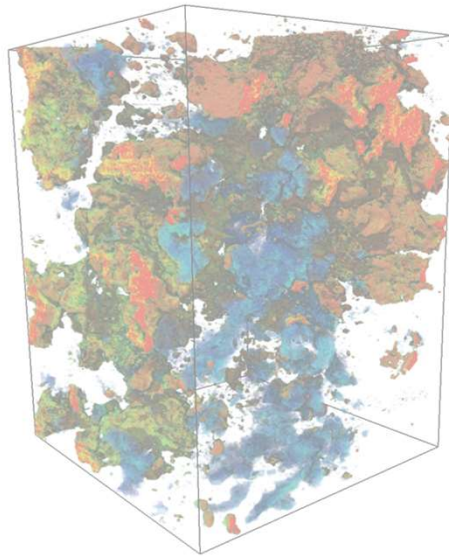
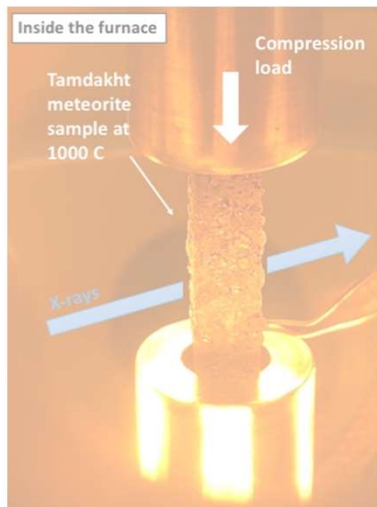
- CT/XPS experiments were interpreted to understand disappearance of meteoritic grains during heating
- Experiments indicate FeS is the material that vanishes
- Computations establish the oxidation mechanism and production of SOs and melting of iron

Outline



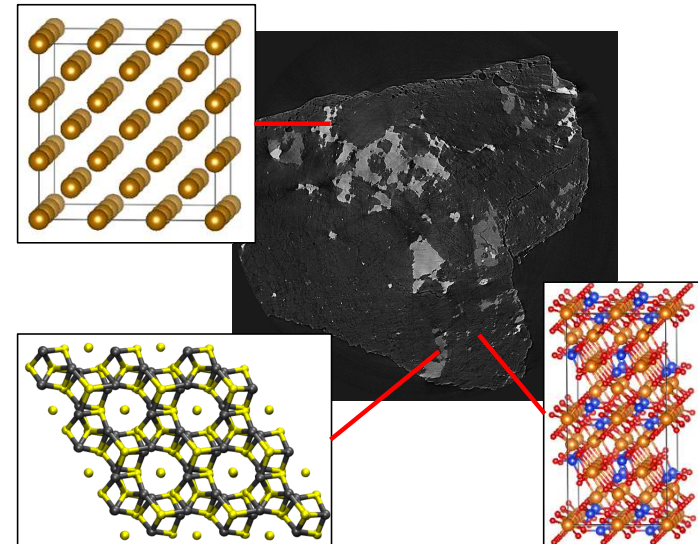
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Meteorite Ablation

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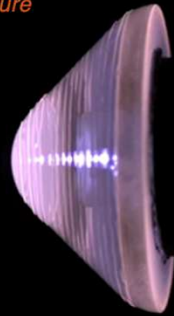


Arc jet ablation of meteorites and meteoritic simulants



Arc Jet Experiment

5 second exposure



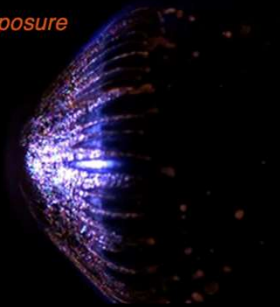
Pure Silica

5 second exposure



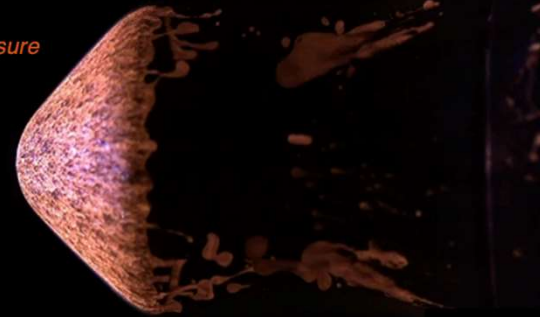
Terrestrial Basalt

3 second exposure



Campo del Cielo Iron Meteorite

2 second exposure

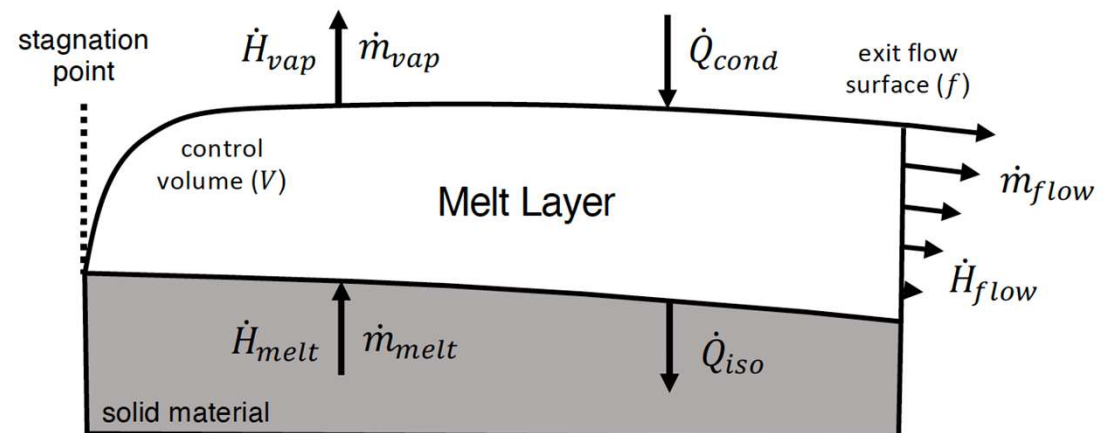


Tamdakht H5 Chondrite

Ablation model to describe melt and vaporization



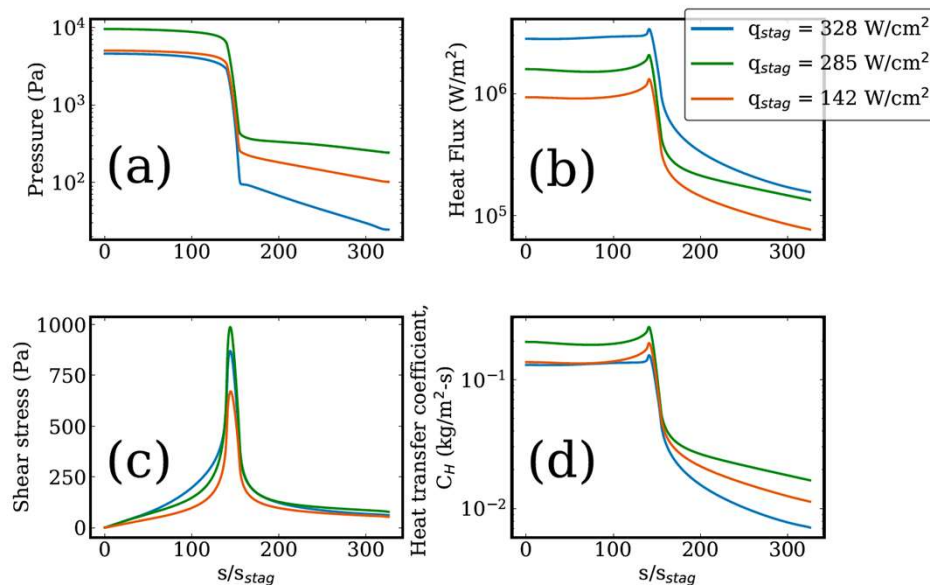
A melt ablation model describes the evolution and flow of a molten boundary layer at the surface of the material



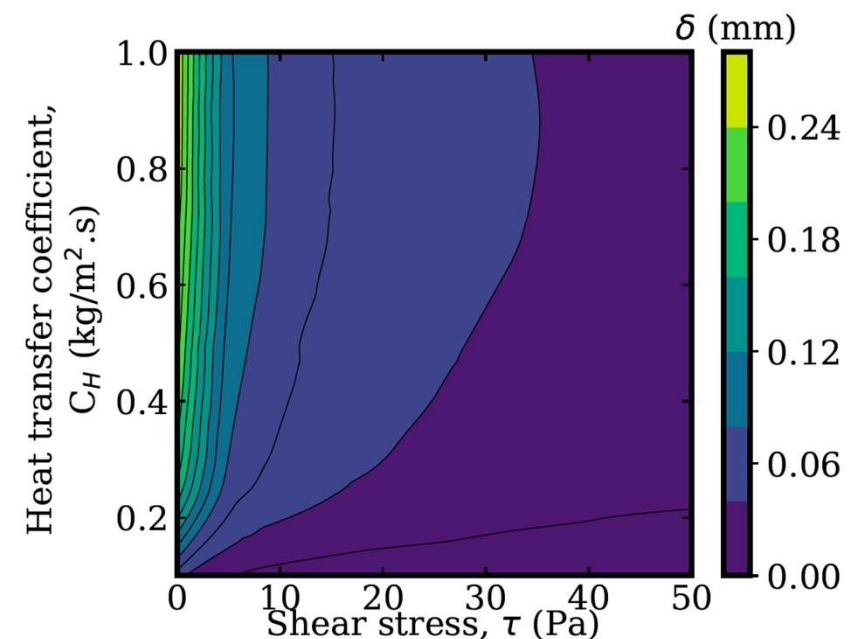
Ablation model boundary conditions and parametric study



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



Melt layer thickness examination for shear and heating conditions

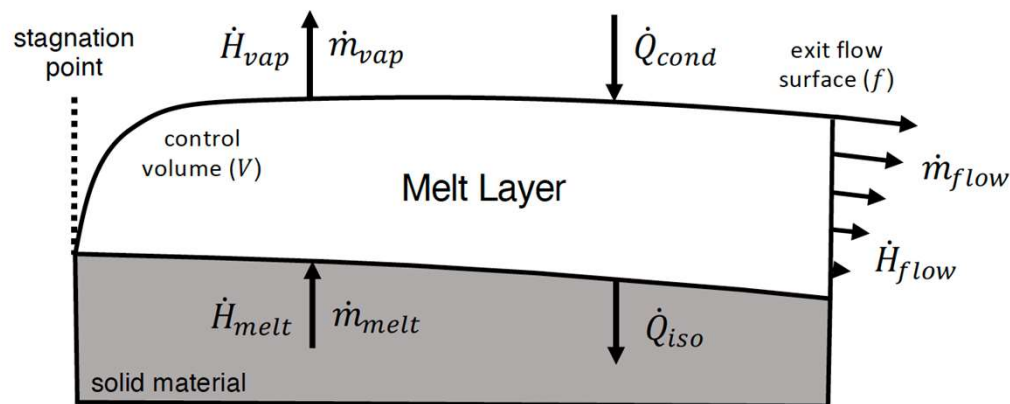


Model is well behaved and provides expected trends with shear and heating

Properties requires for accurate ablation modeling



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



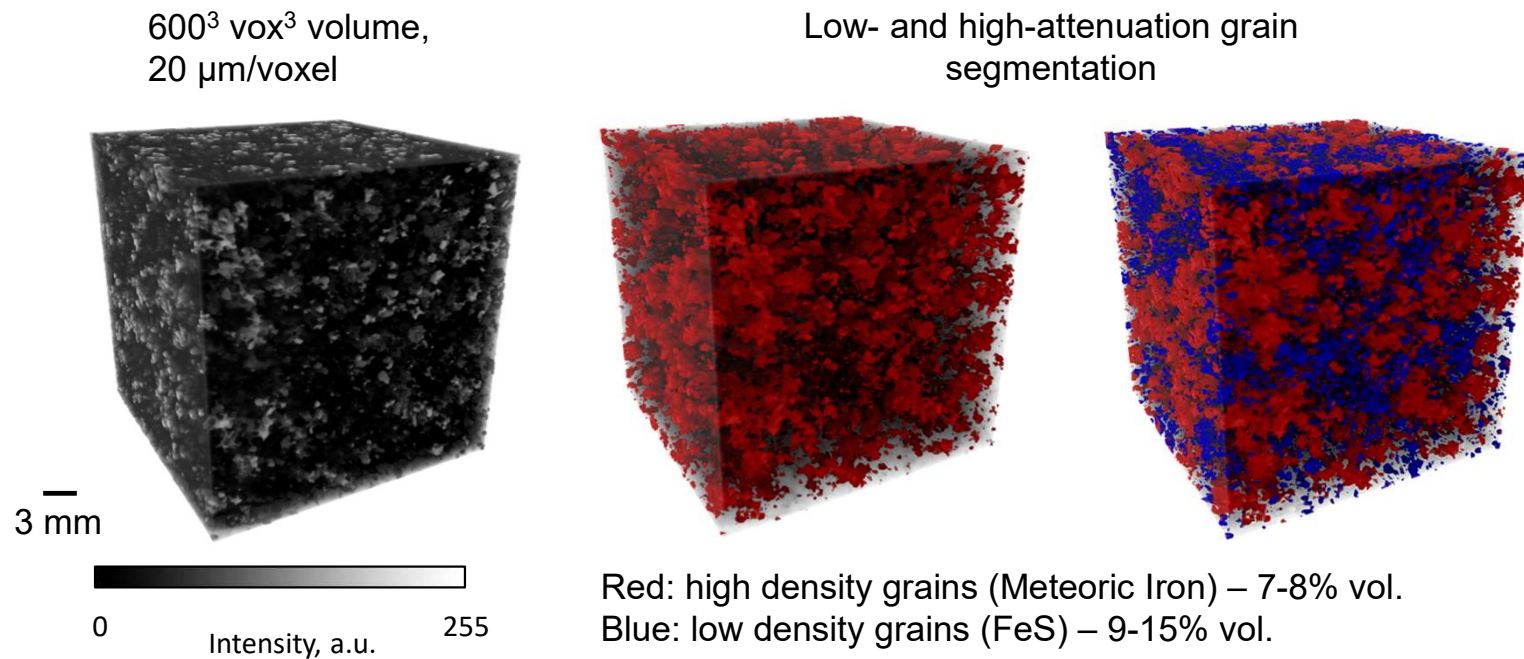
Solids:

- Heat capacity
- Thermal conductivity
- Optical properties

Liquids:

- Heat capacity
- Thermal conductivity
- Optical properties
- Viscosity

Material composition from grain segmentation

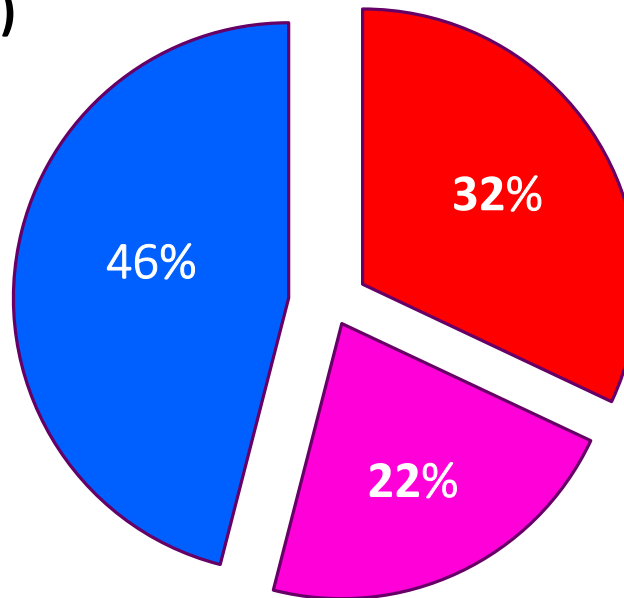
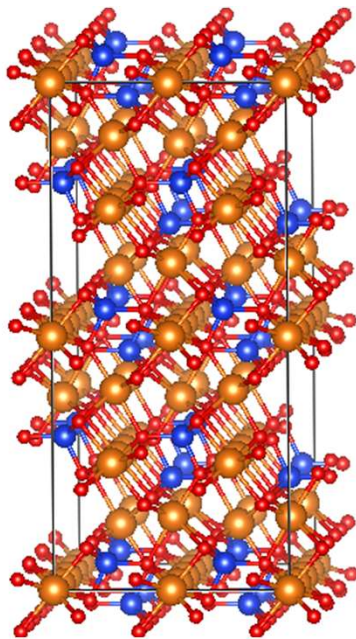


Composition of the meteorites can be determined from knowledge of segmented CT volumes

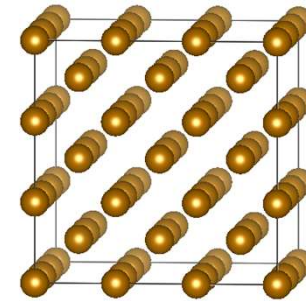
Model composition of stony meteorites



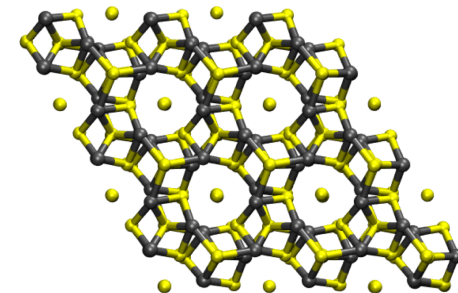
Olivine (MgFeSiO_4)



Iron (Fe)

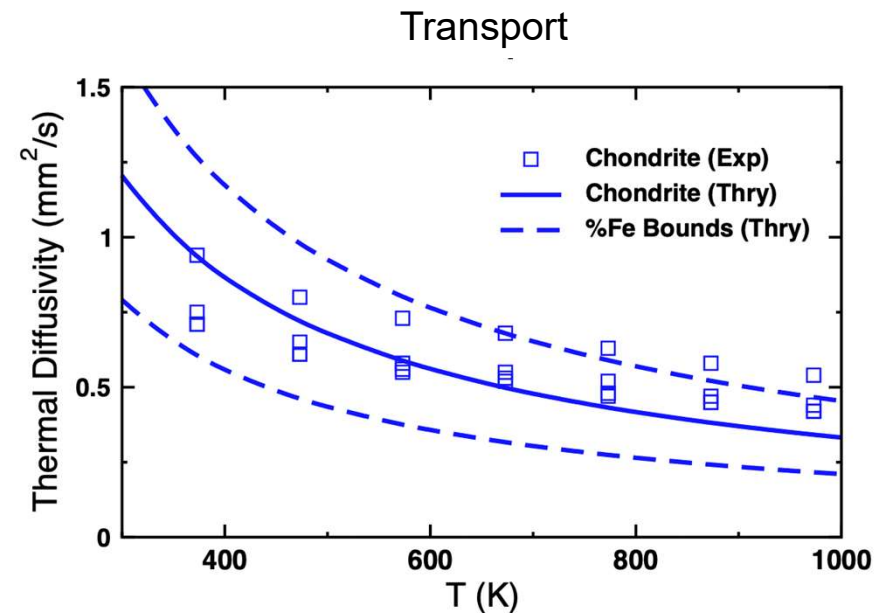
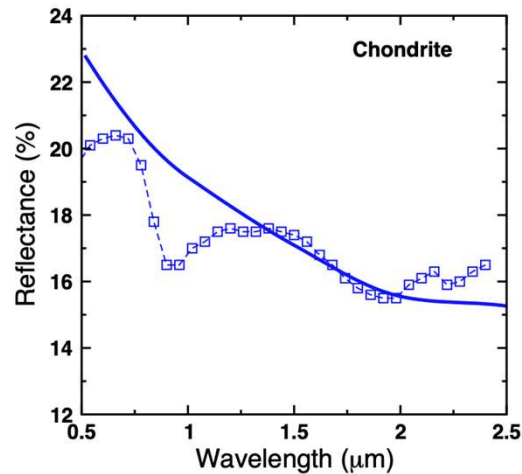
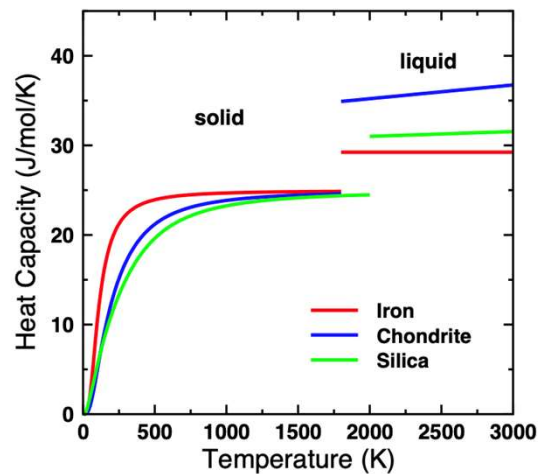


Troilite (FeS)



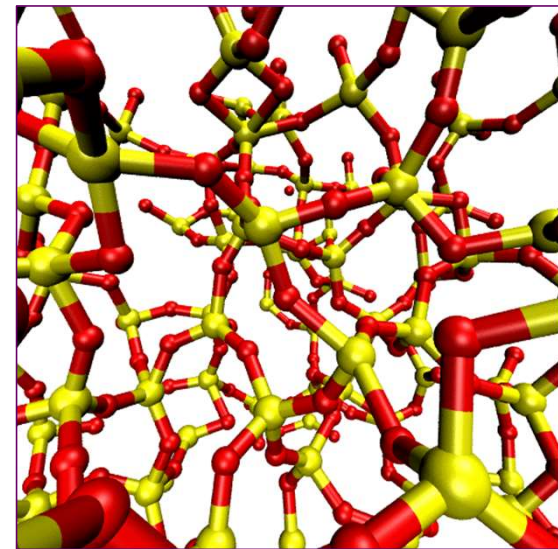
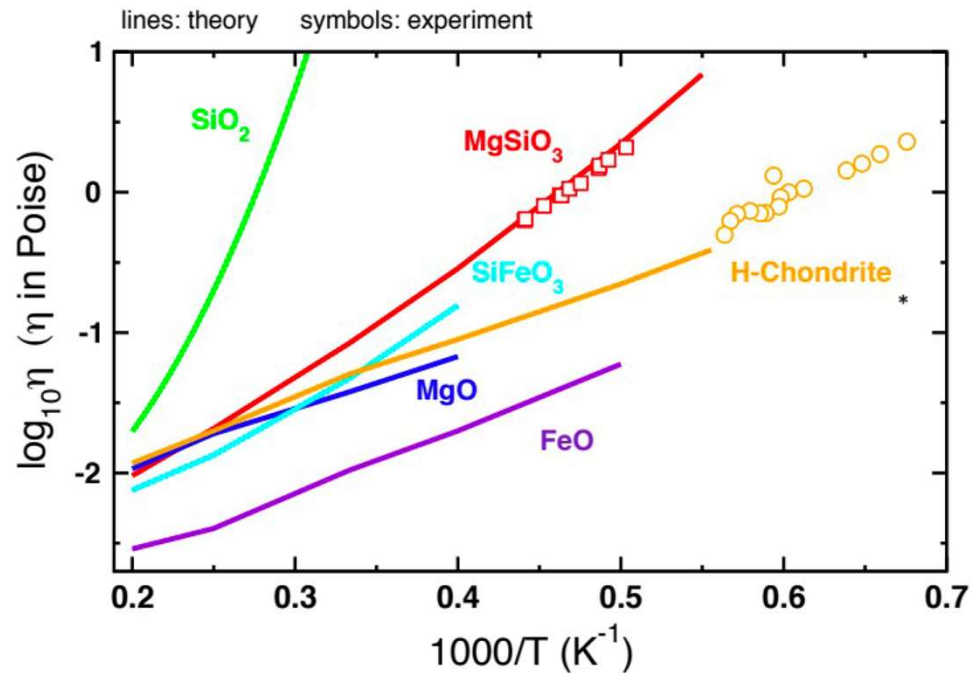
Convert the ratios into molar compositions of the predominant minerals for computation

Material response database development - solids



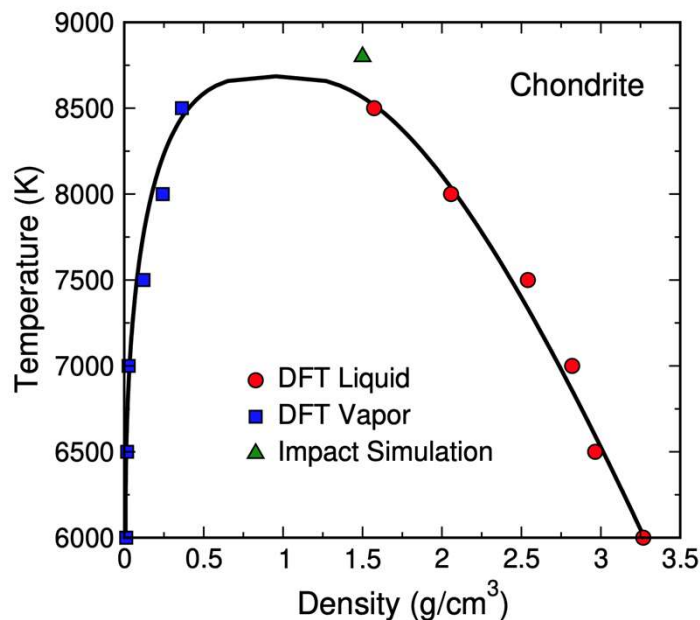
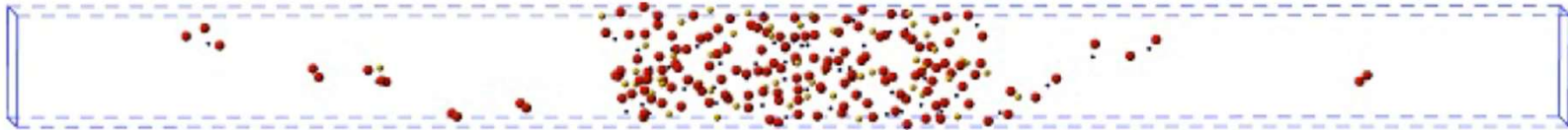
Ab initio molecular dynamics and lattice dynamic techniques used to update computational chondrite solid database with FeS content – presented previous generation at 10th Ablation workshop

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 $\sim 3300^\circ\text{C}$,
pressure is 1.1 atm

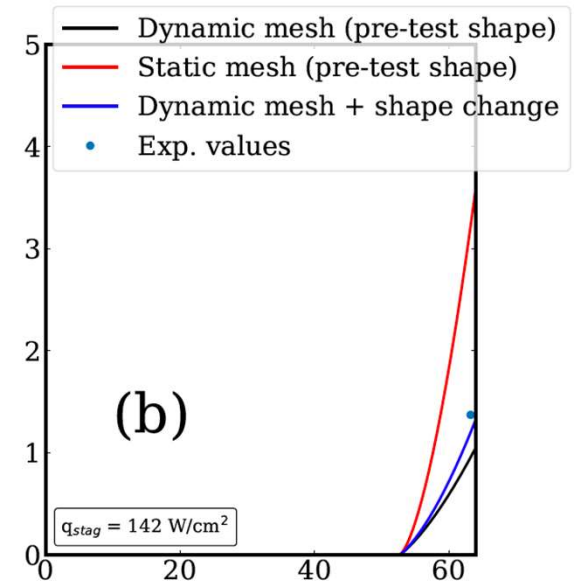
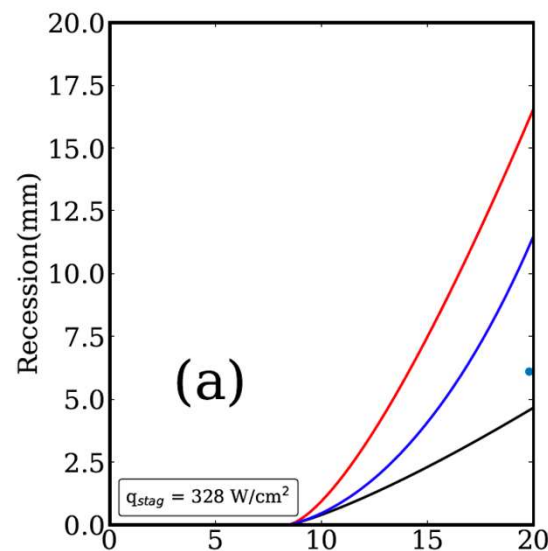
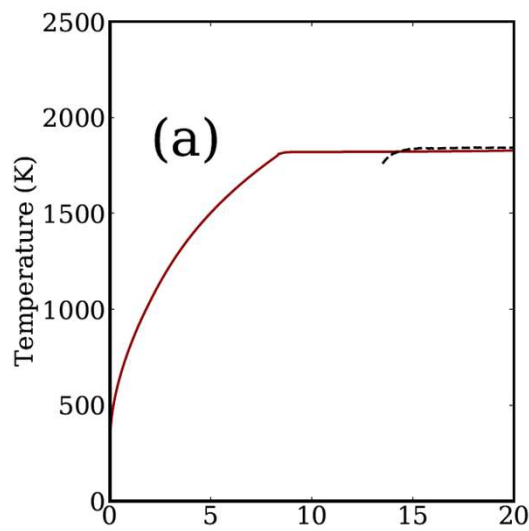
Expect to provide vapor pressure within
10 %

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

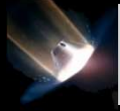
Application of the model to iron



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



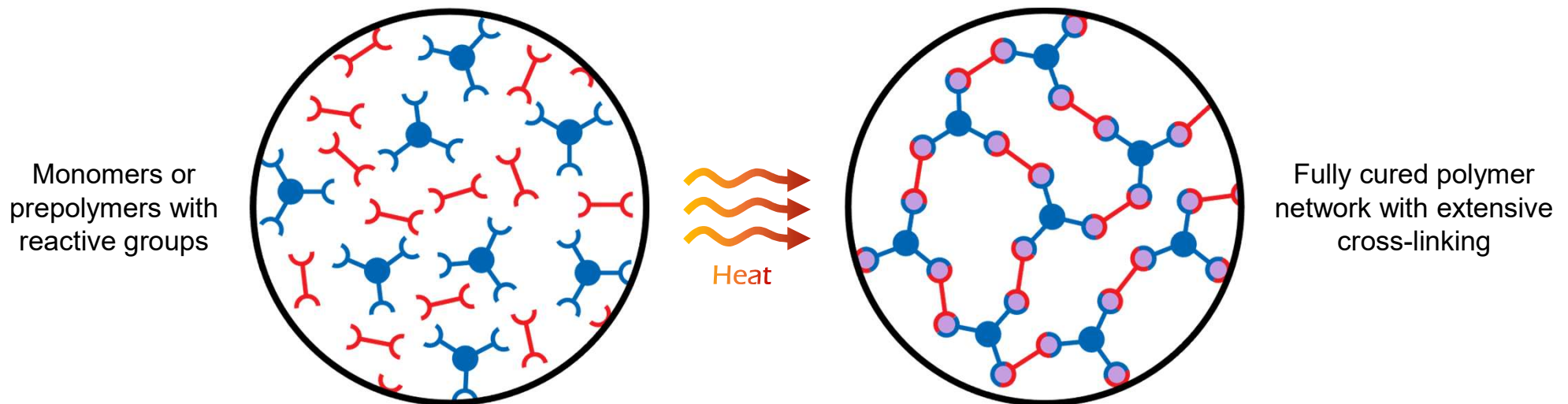
- Melt models for ablation require knowledge of properties that are not easily easily measured at high temperatures (viscosity)
- Properties can be computed from first principles molecular dynamics simulations to construct a material response database



Modeling Resins for Aerospace Composites: Spacecrafts to Aircrafts

Lauren Abbott

How can modeling resin materials and their curing help?

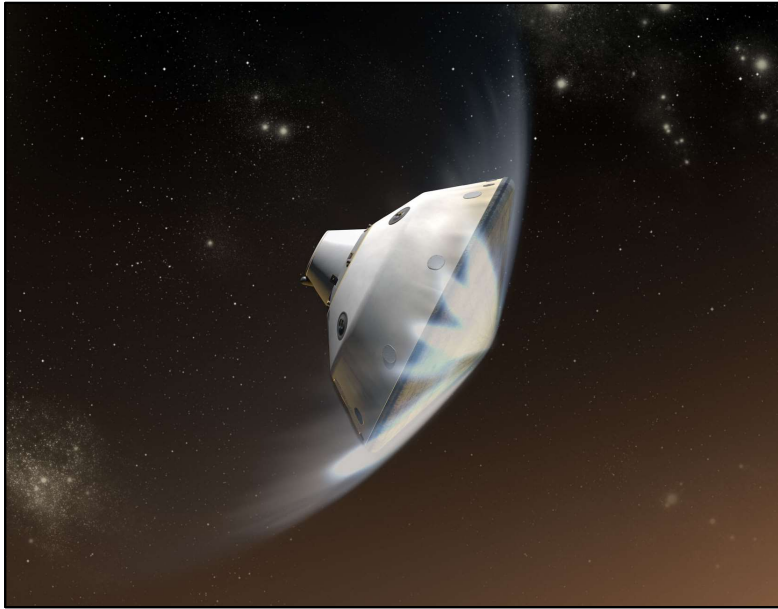


What is the molecular structure of the cured polymer network?
How does the structure affect the material properties and performance?
How do the structure and properties evolve during cure?

Resin modeling contributes to aerospace technology development



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



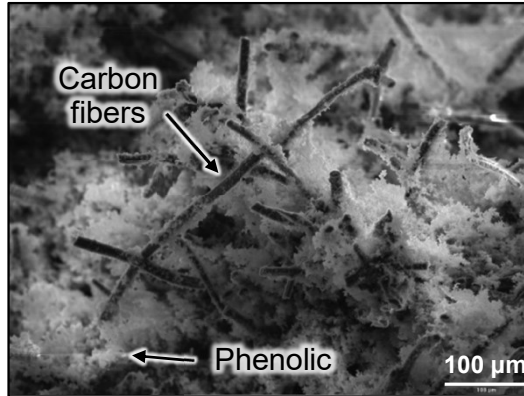
Latent cure epoxy resins underpin an adhesive-free composite joining technology to accelerate airframe manufacturing



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

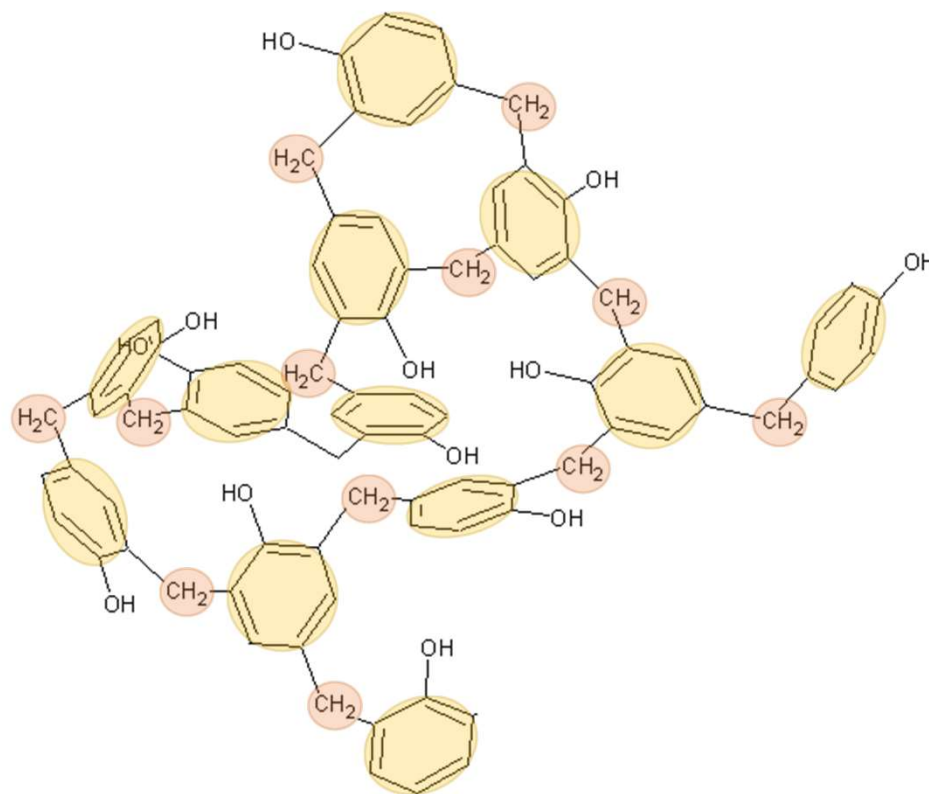
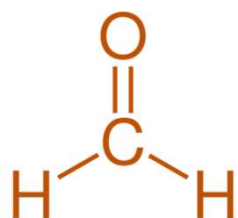


**Heatshield for Extreme Entry Environment Technology (HEEET)
3D Medium Density Carbon Phenolic (3MDCP)**
Mars Sample Return Earth Entry Vehicle

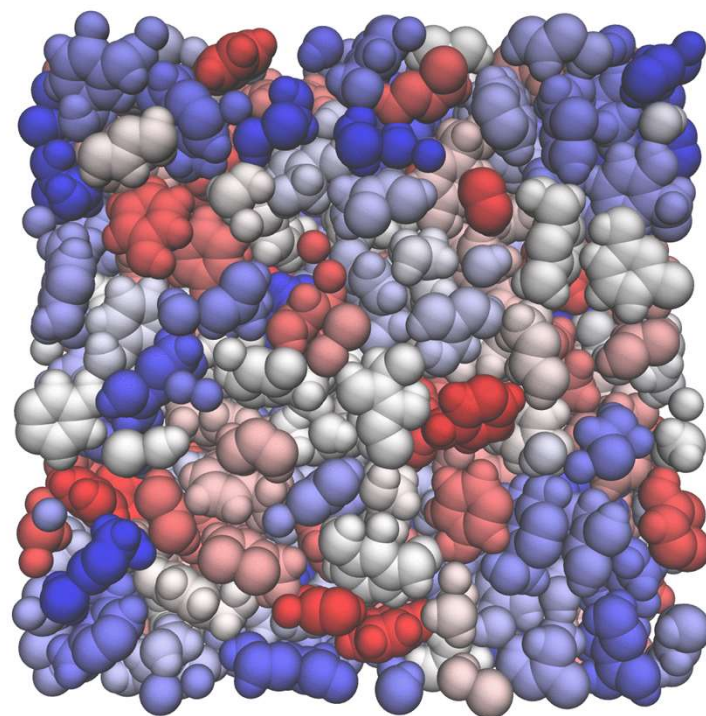
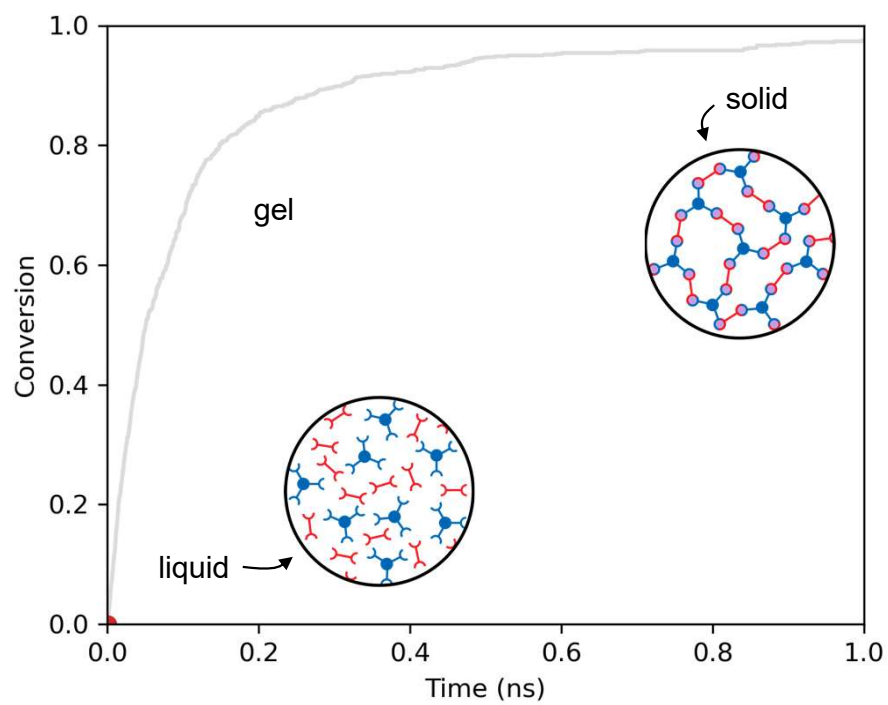
Phenolic structures are complex and highly process dependent



Formaldehyde (F) : Phenol (P)



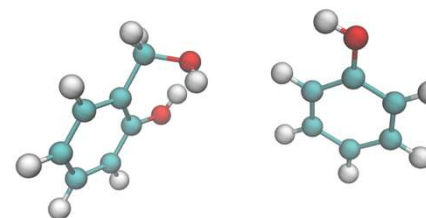
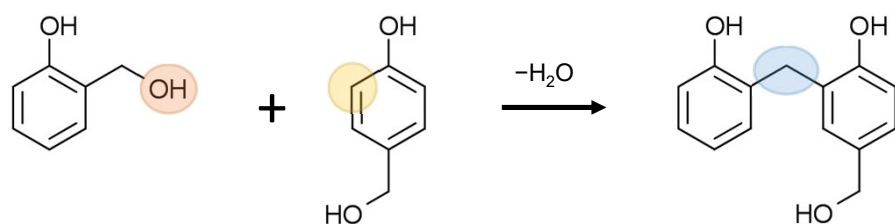
Phenolic cure is mimicked using molecular dynamics simulations



How do bridge chemistries affect the properties of phenolic?

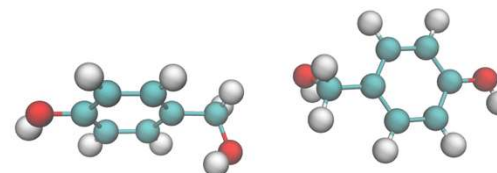
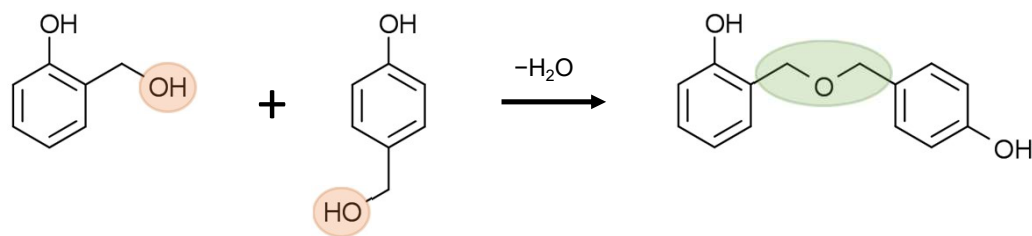


Methylene bridge:

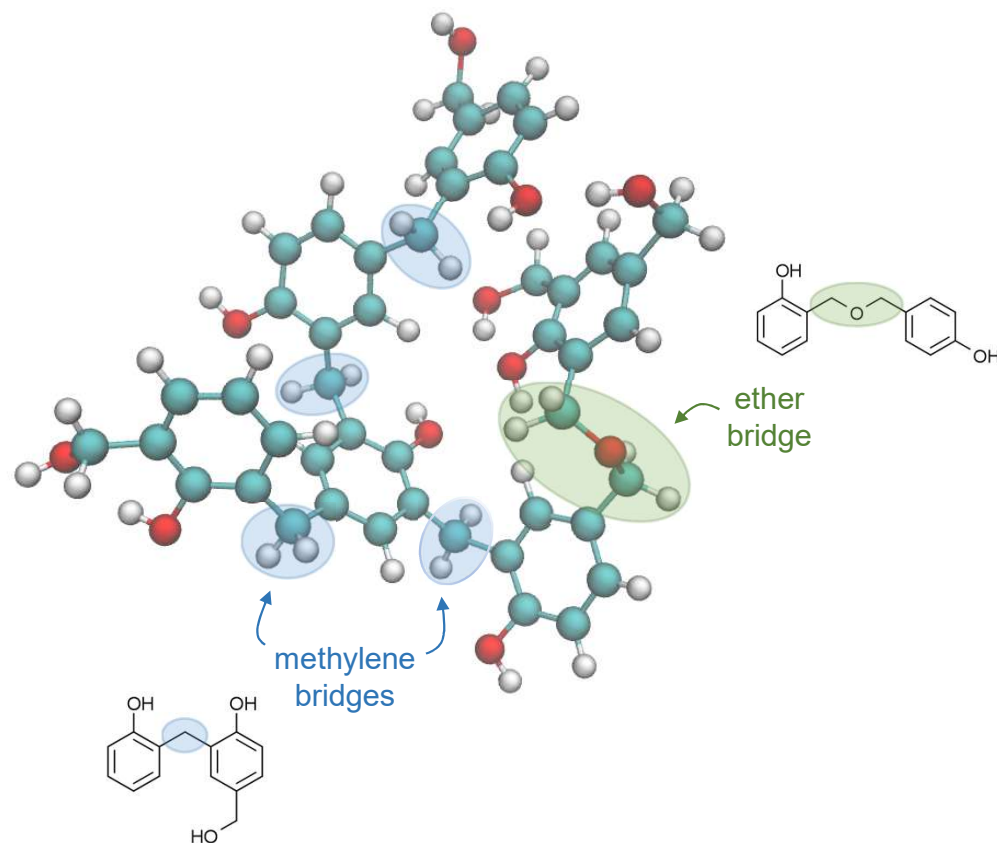
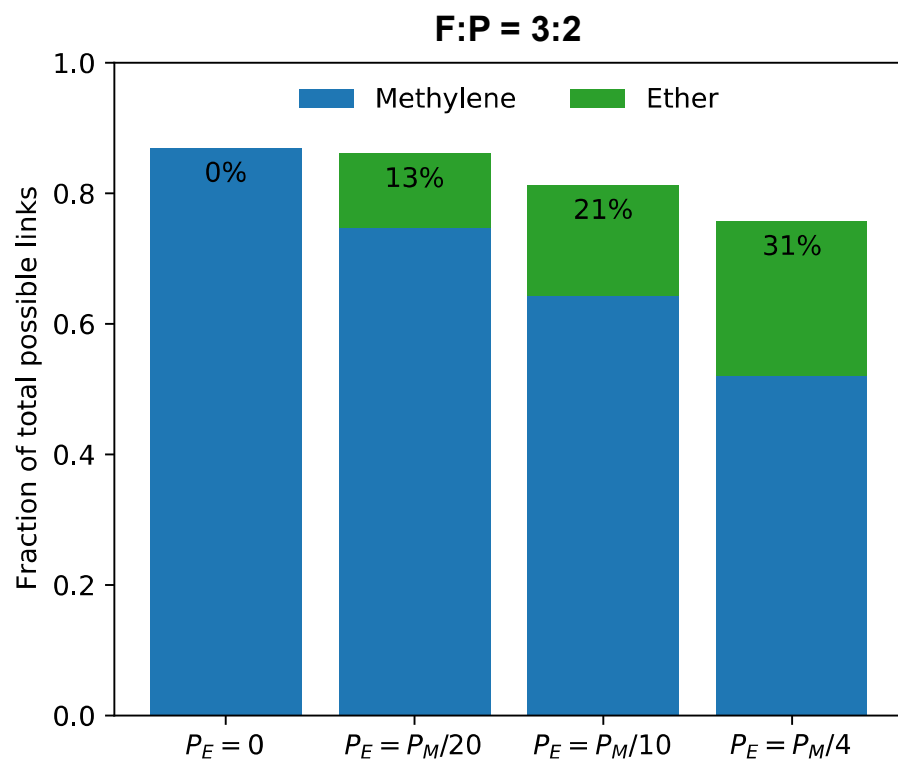


MD reaction
templates

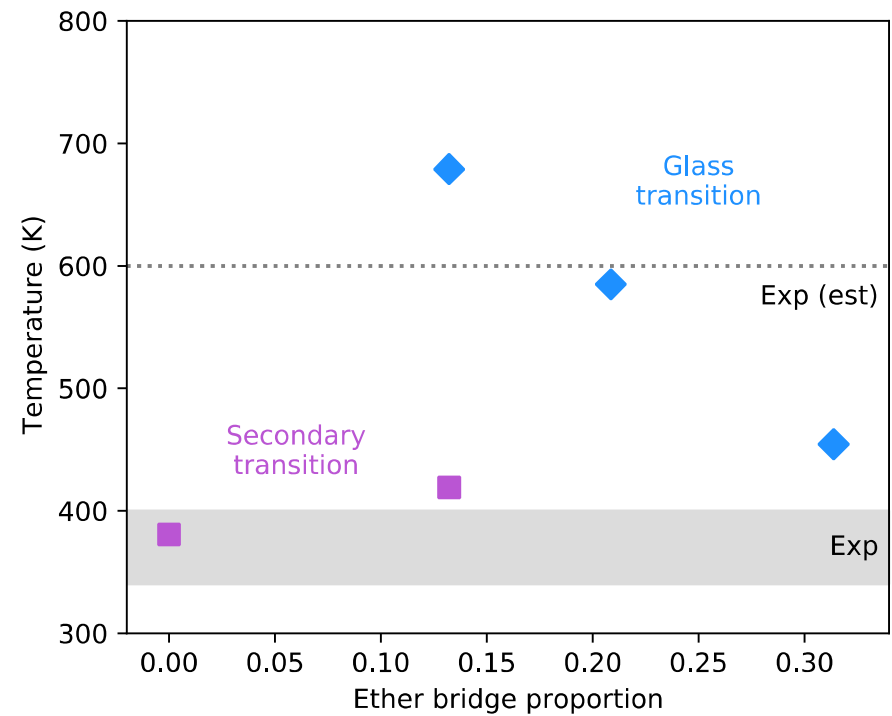
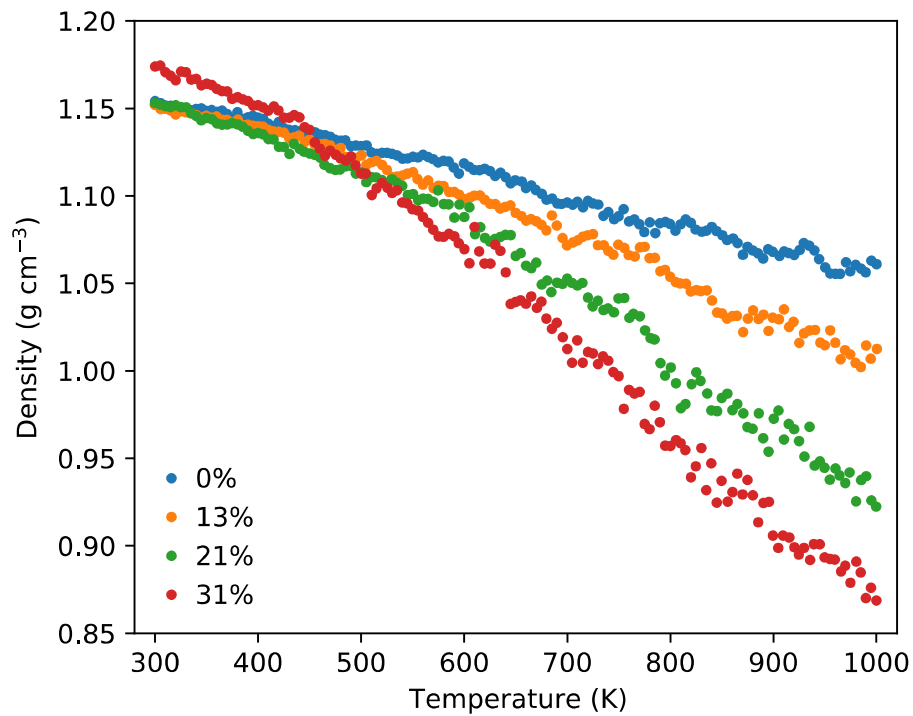
Dimethylene ether bridge:



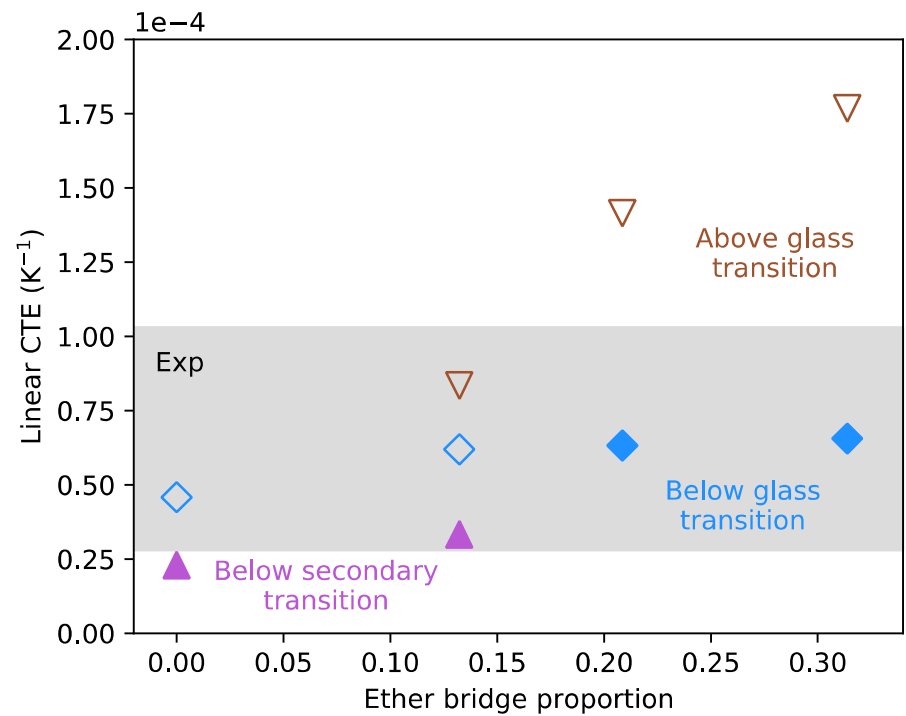
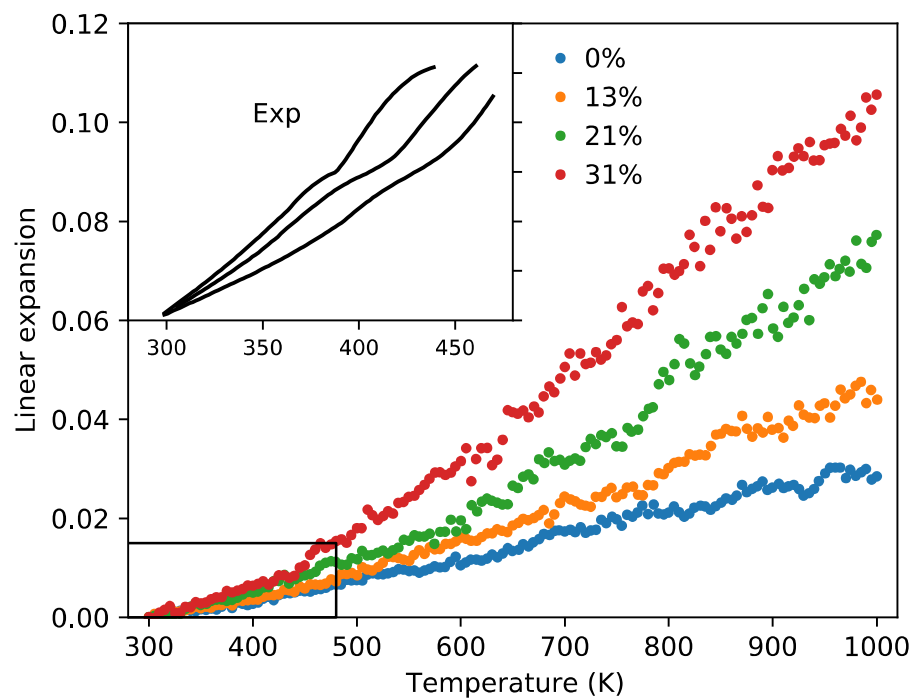
More ether bridges lead to less crosslinking and less rigidity



Thermal annealing reveals two characteristic thermal transitions



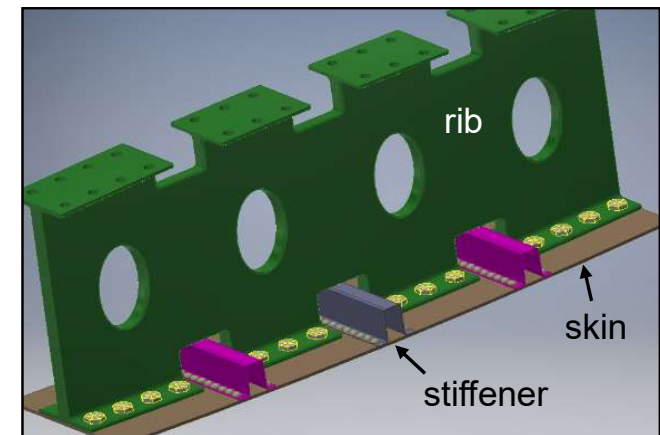
Thermal expansion is consistent with experimental data



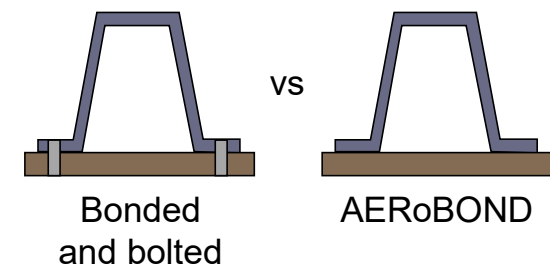
Summary and future directions for phenolic modeling



Installation of redundant fasteners is a bottleneck in production



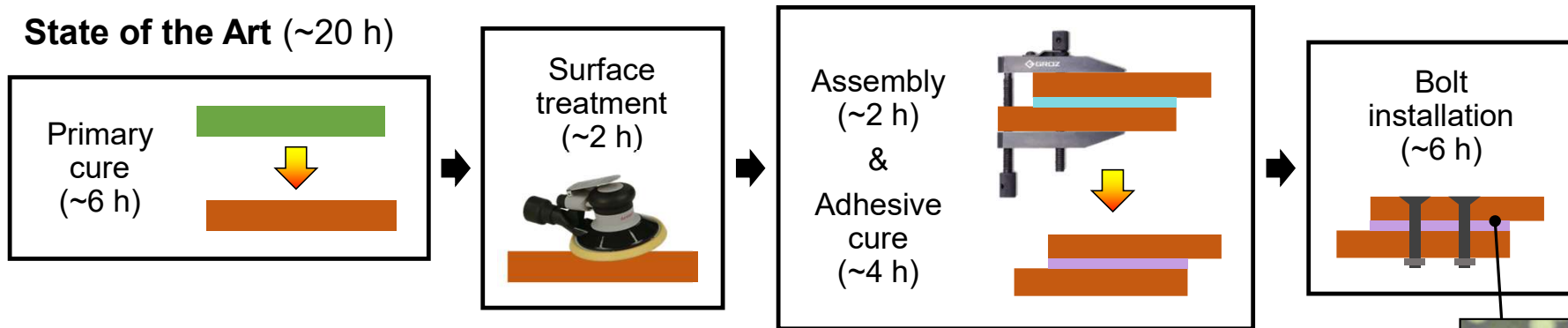
Assembly of composite parts in airframes requires installation of thousands of mechanical fasteners



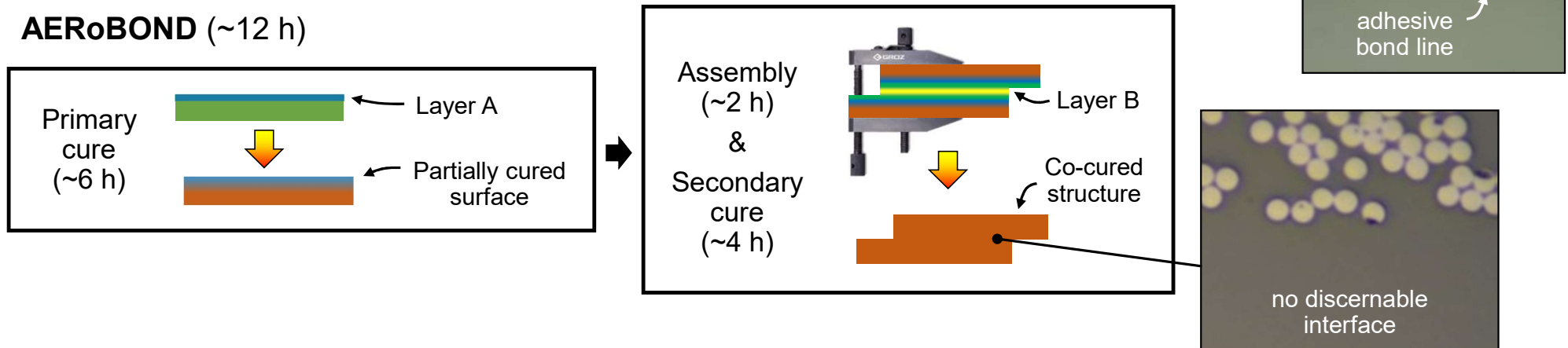
AERoBOND method is about 40% faster than state of art



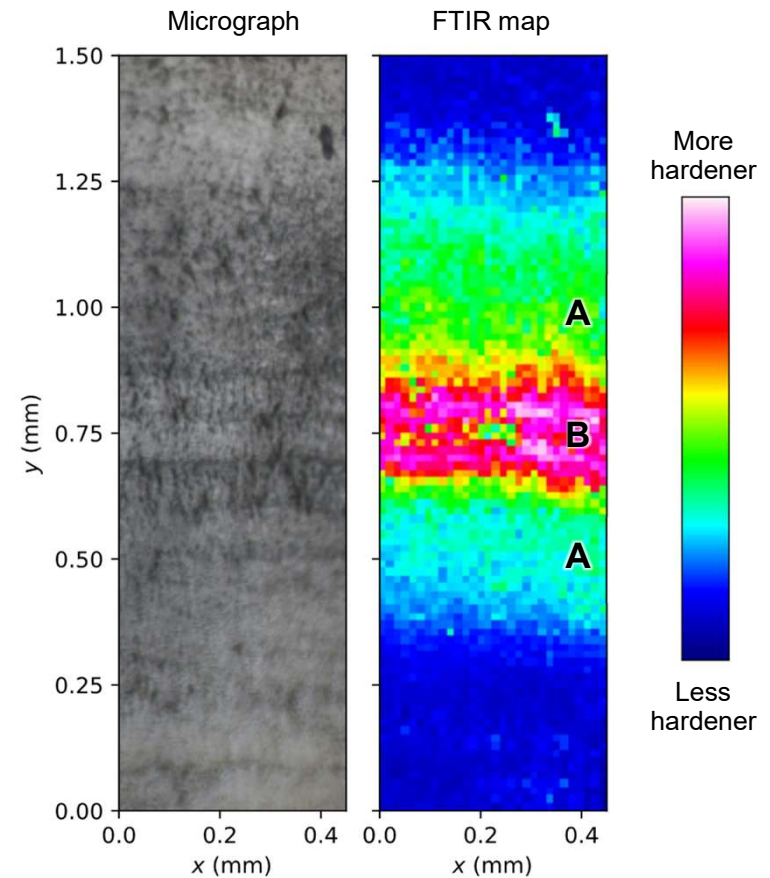
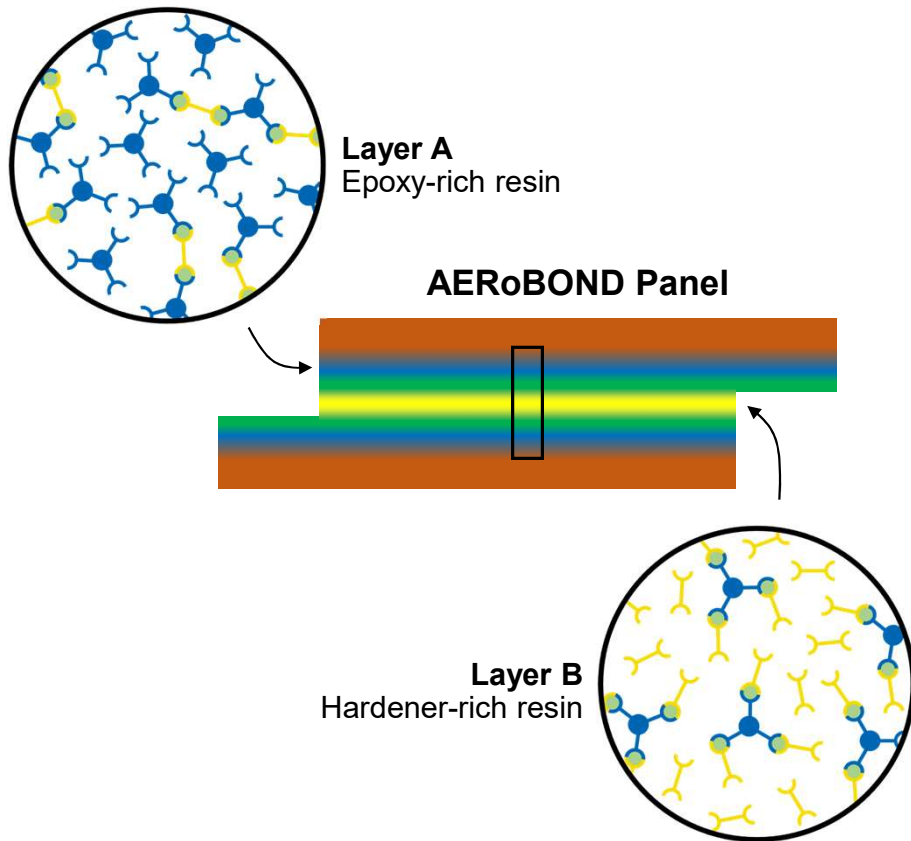
State of the Art (~20 h)



AERoBOND (~12 h)



AERoBOND process relies on reflow and mixing of resin layers



Process simulations can accelerate process optimization



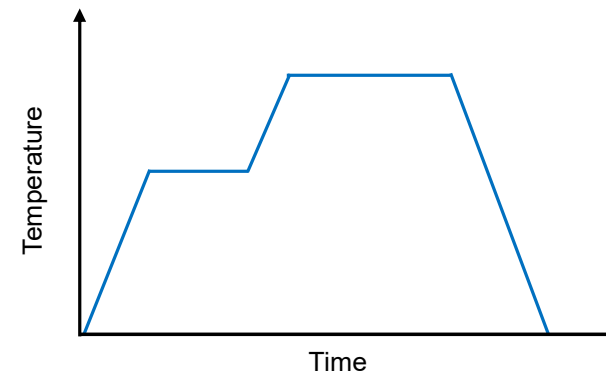
6 material / layup parameters:

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



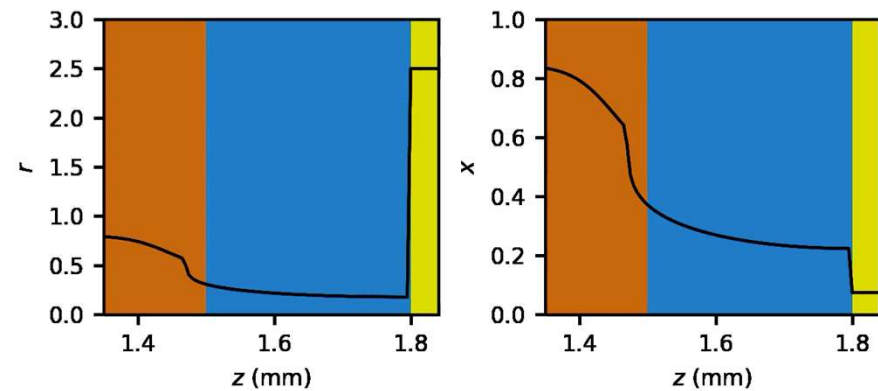
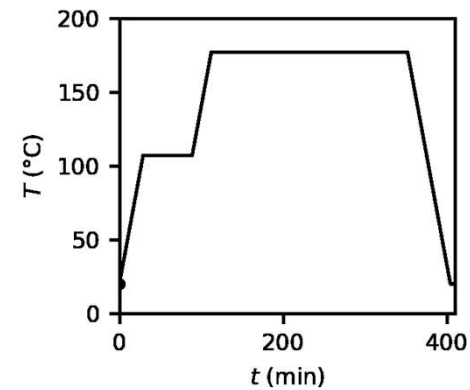
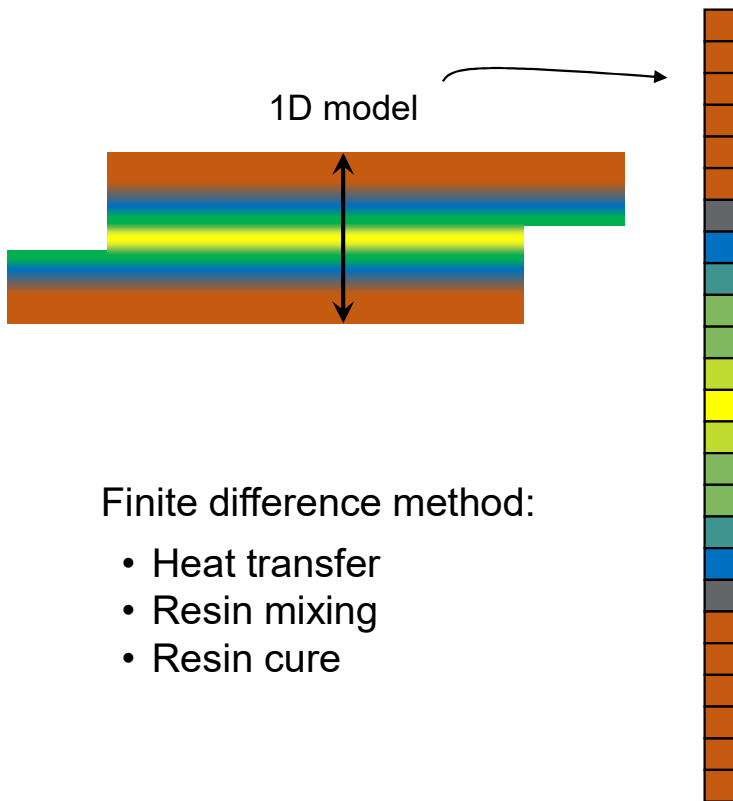
10 cure cycle parameters:

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

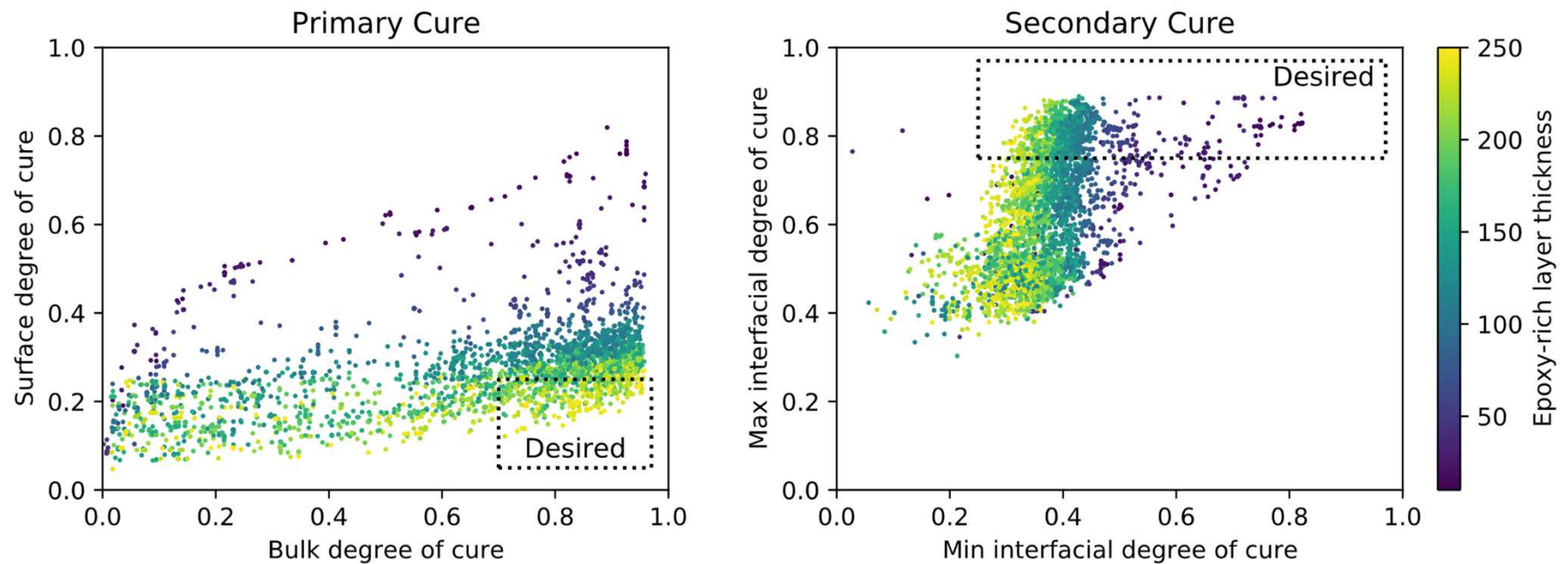


Process simulations can explore large parameter space more quickly
(~seconds/minutes per simulation vs ~days/weeks per experiment)

Simulations highlight competing effects of mixing and cure

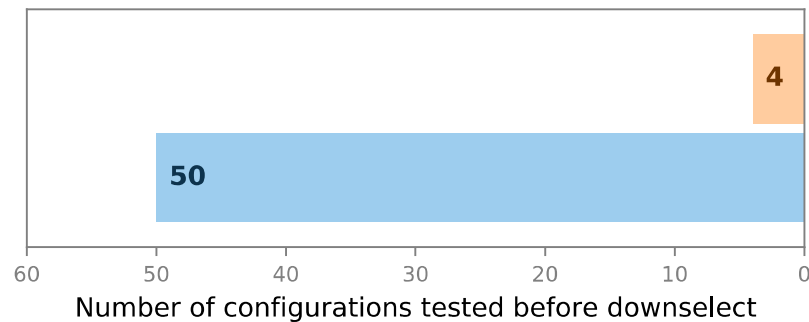


High-throughput screening identifies promising configurations

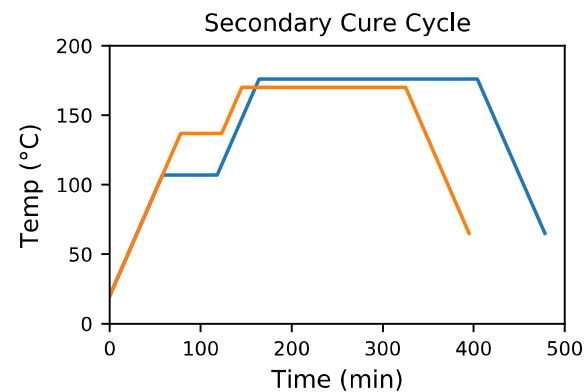
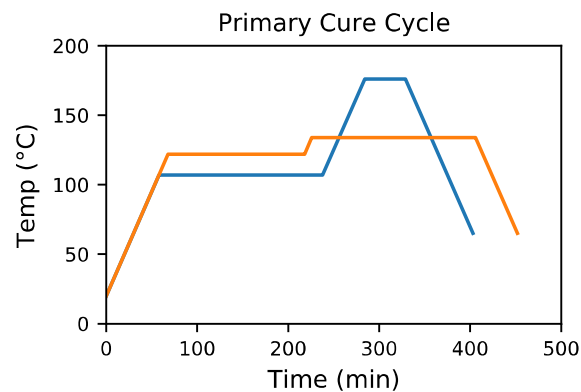
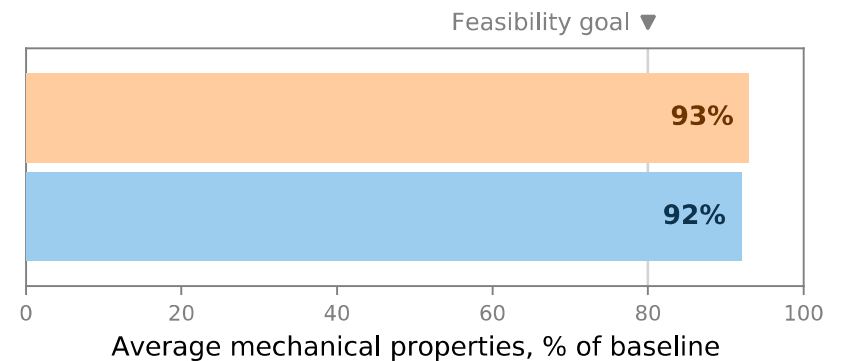


Simulated more than **5000** configurations and
proposed **4** for fabrication and testing

Model-based optimization can save time and money

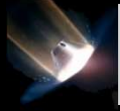


Model-based approach
Experimental approach



Summary for AERoBOND latent cure resin modeling





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

BJ Tucker

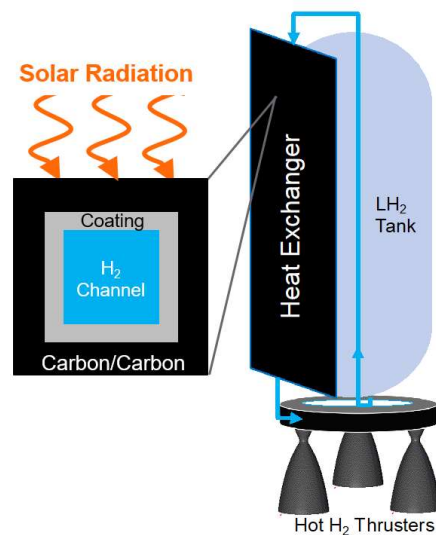
Emerging propulsion systems

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

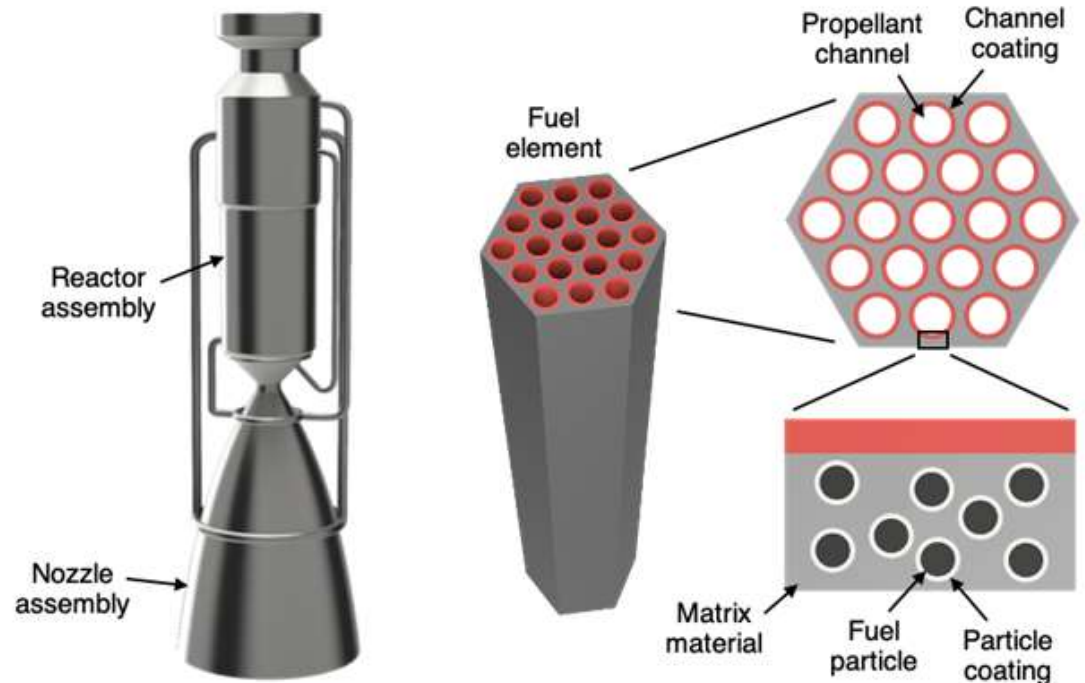
Solar thermal propulsion, nuclear thermal propulsion – high ISP

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)

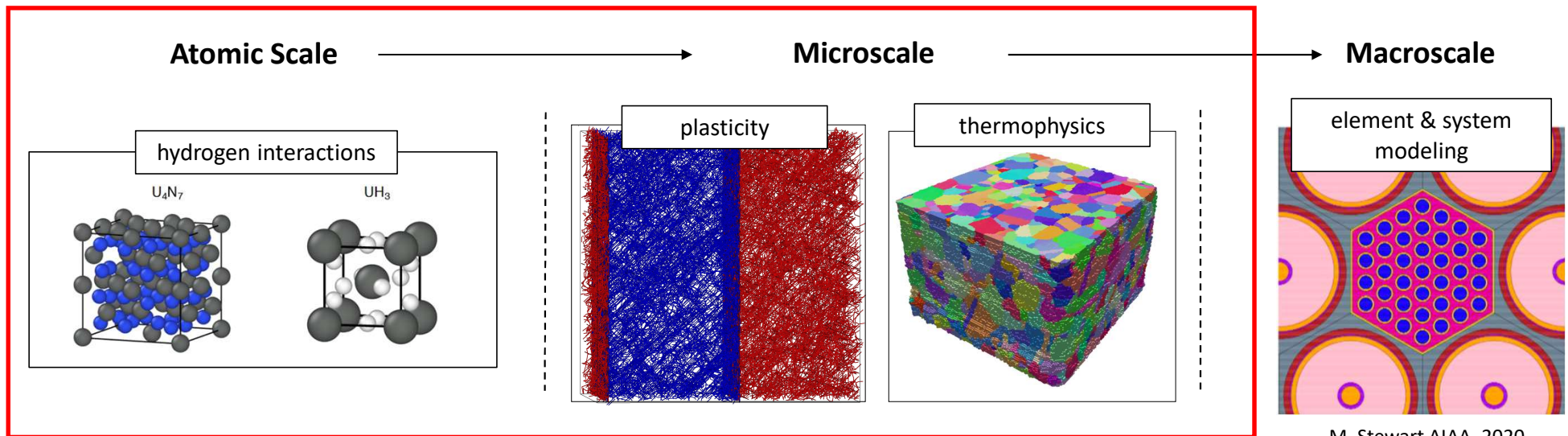
Atomic to microscale insight – discrete
dislocation dynamics (ParaDiS)

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



M. Stewart AIAA, 2020

Nuclear thermal propulsion materials



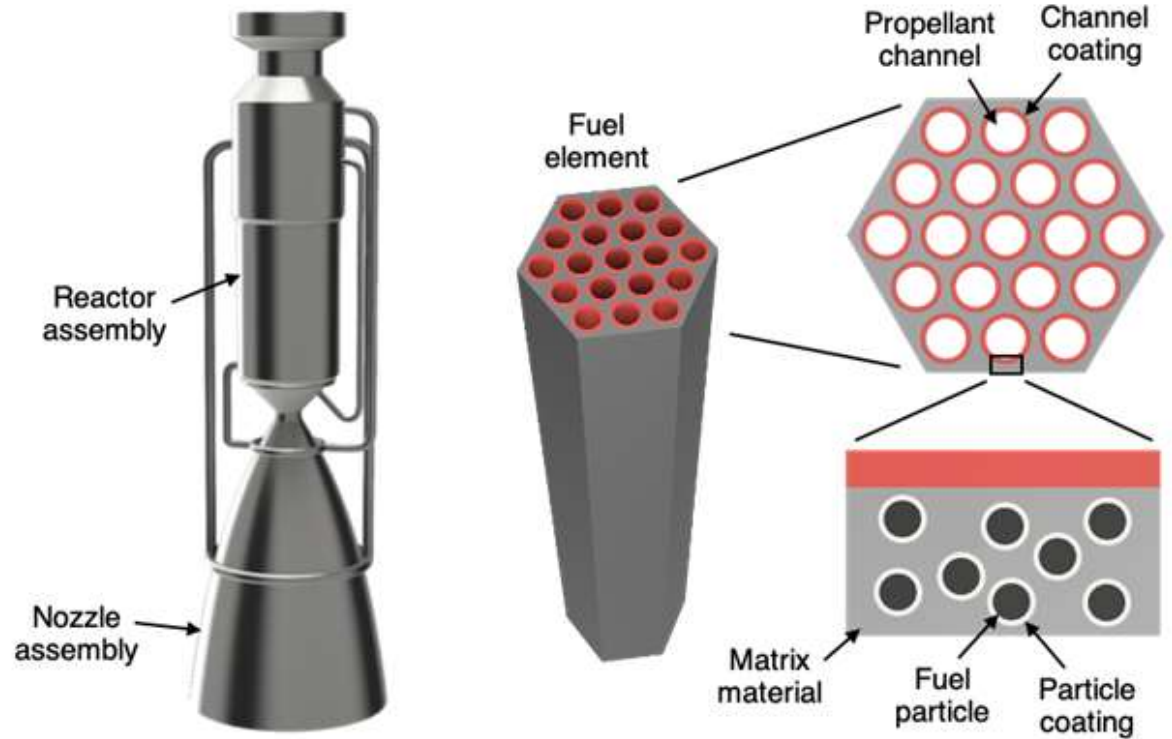
Three case studies:

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

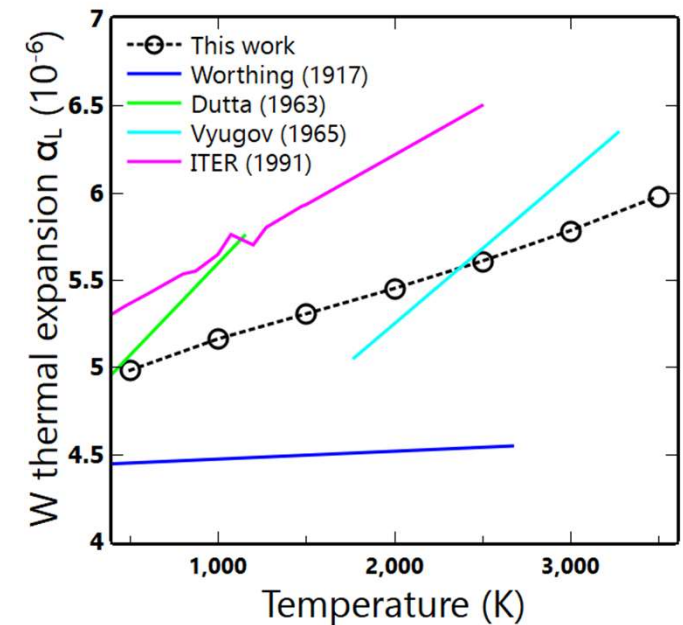
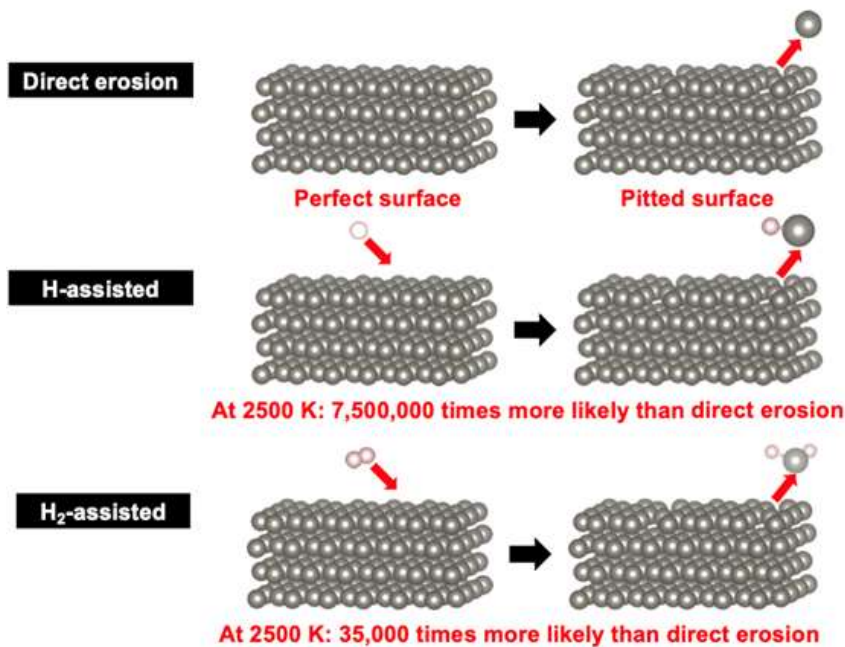
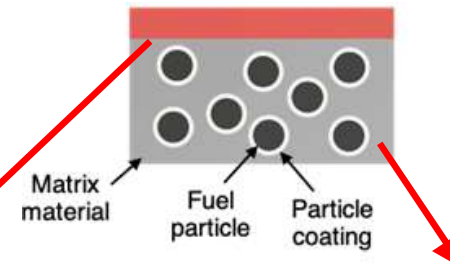


Matrix material properties

Idealized system for a first look – W for matrix

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

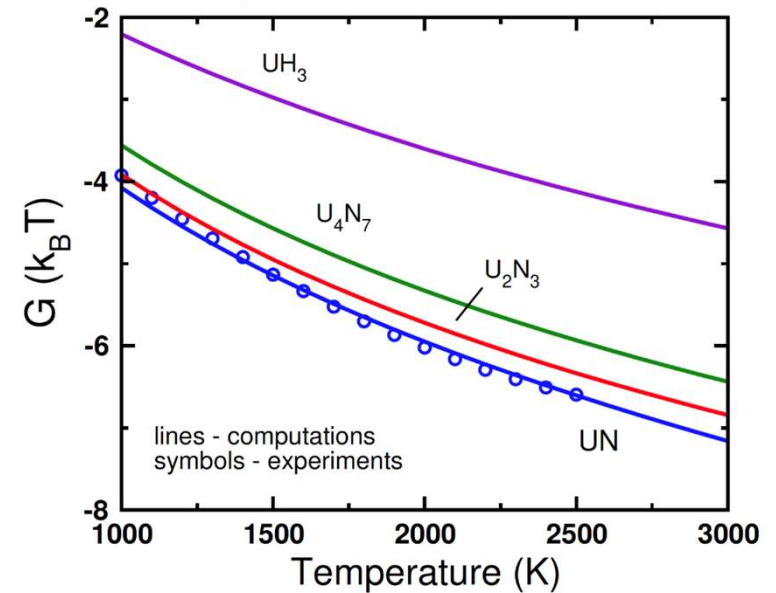
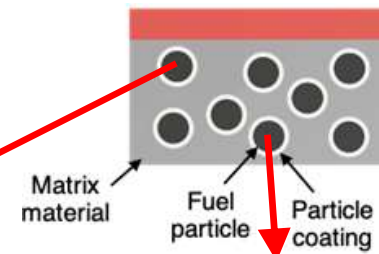
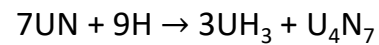
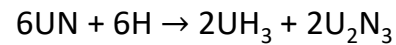
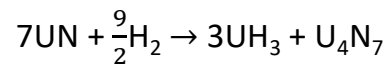
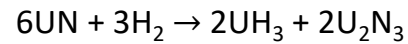
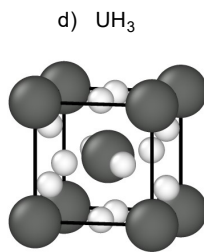
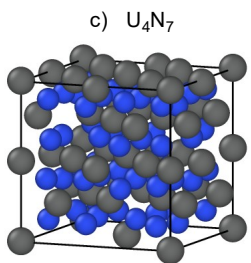
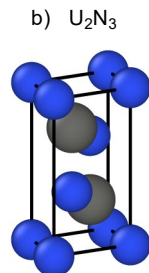
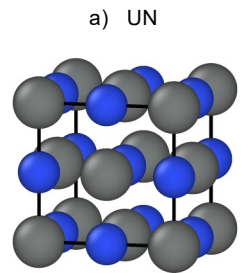
High temperature thermal expansion prediction



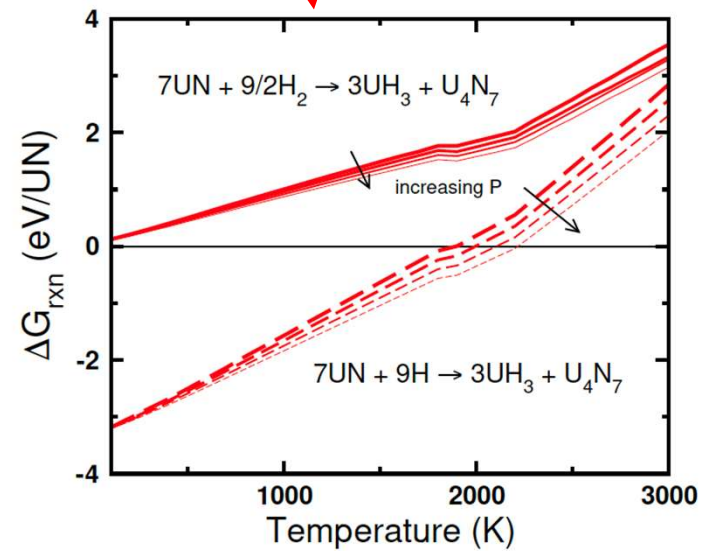
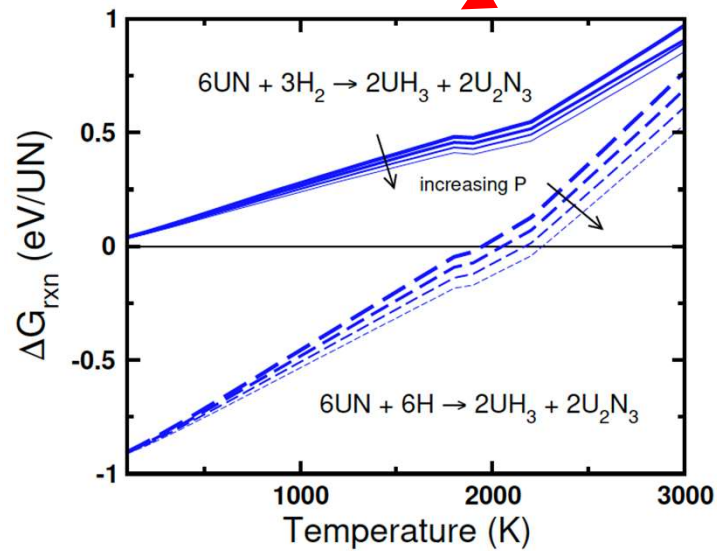
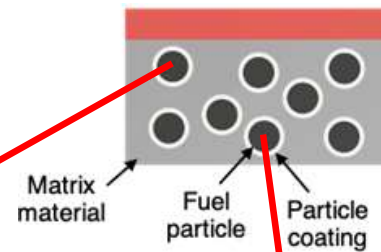
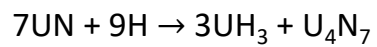
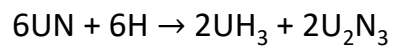
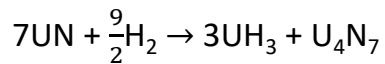
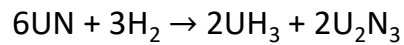
Fuel particle properties

Solid phases of U_xN_y that have been observed

Gibbs free energies calculated via harmonic approximation/phonons



Fuel particle properties

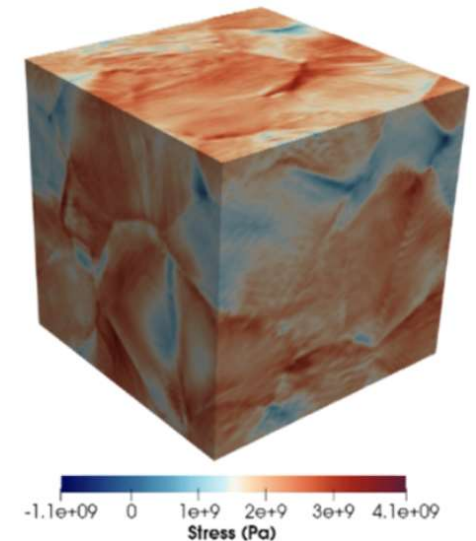
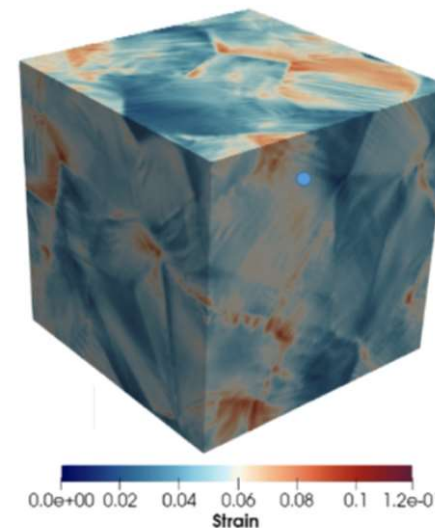
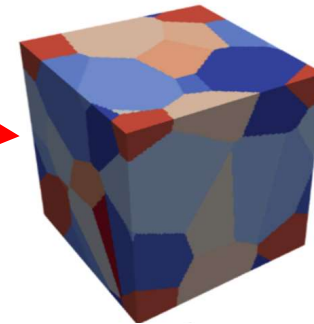
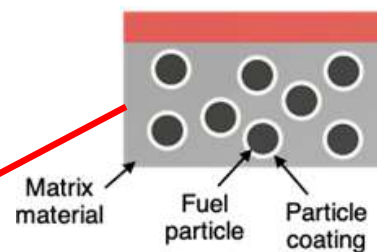
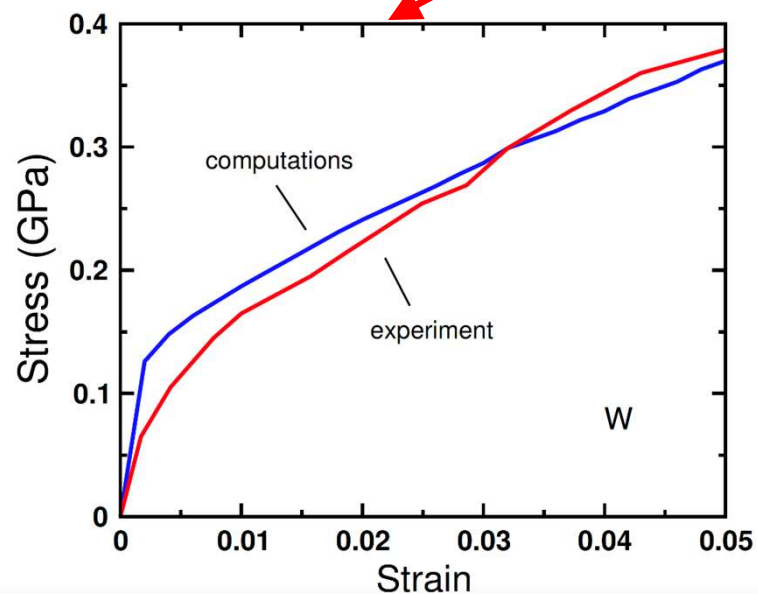


Matrix material failure

Stress-strain data is required at higher scales

Voronoi tessellation for microstructure, or experimental data if available

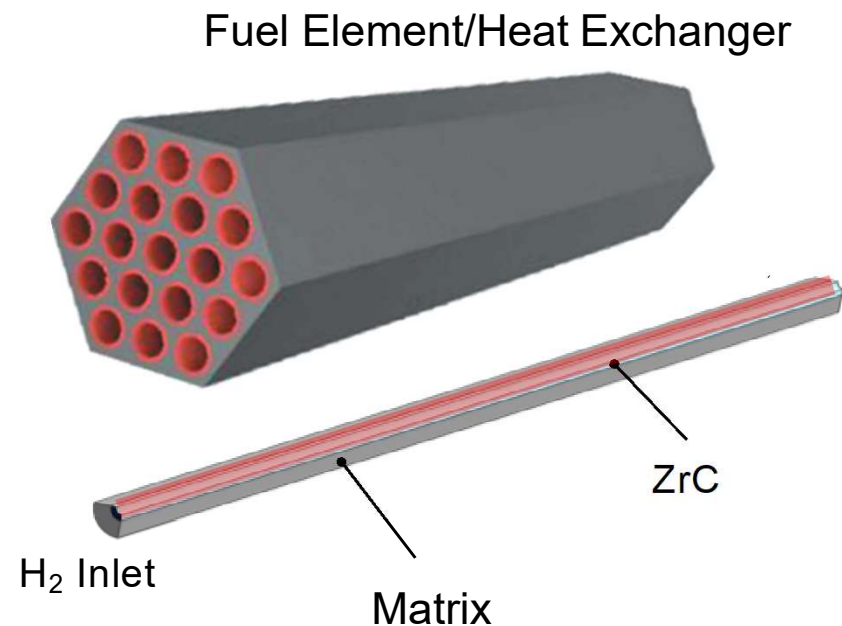
Crystal plasticity simulations yield favorable comparison with experiment



Channel coating materials



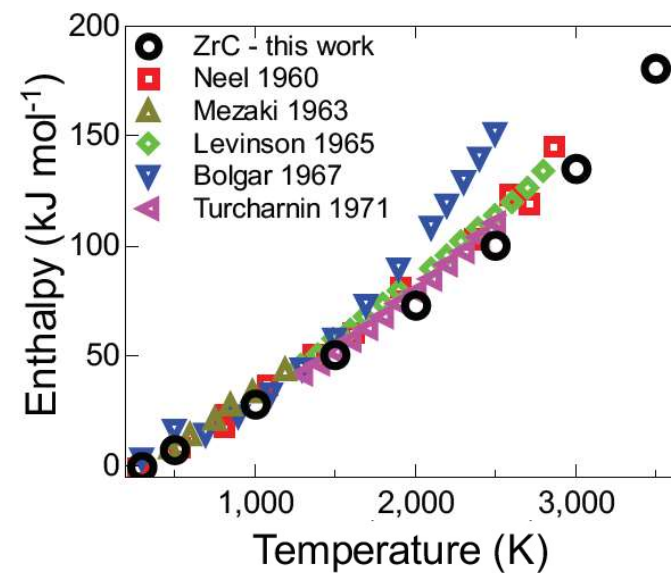
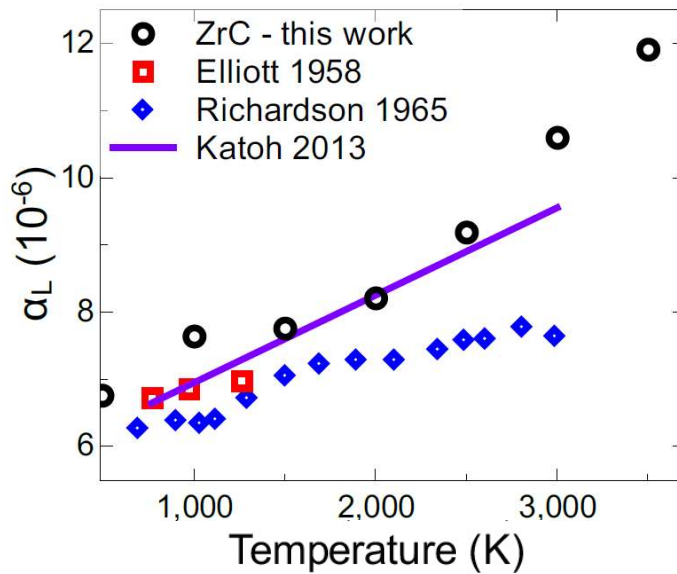
- Solar Thermal Propulsion – rapid transit to the interstellar medium (ISM)
- Nuclear Thermal Propulsion – rapid human transit to Mars
- Both have high propellant temperatures and ISP, and both require channel coatings to protect substrate
- Methods used here include electronic/computational chemistry, 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



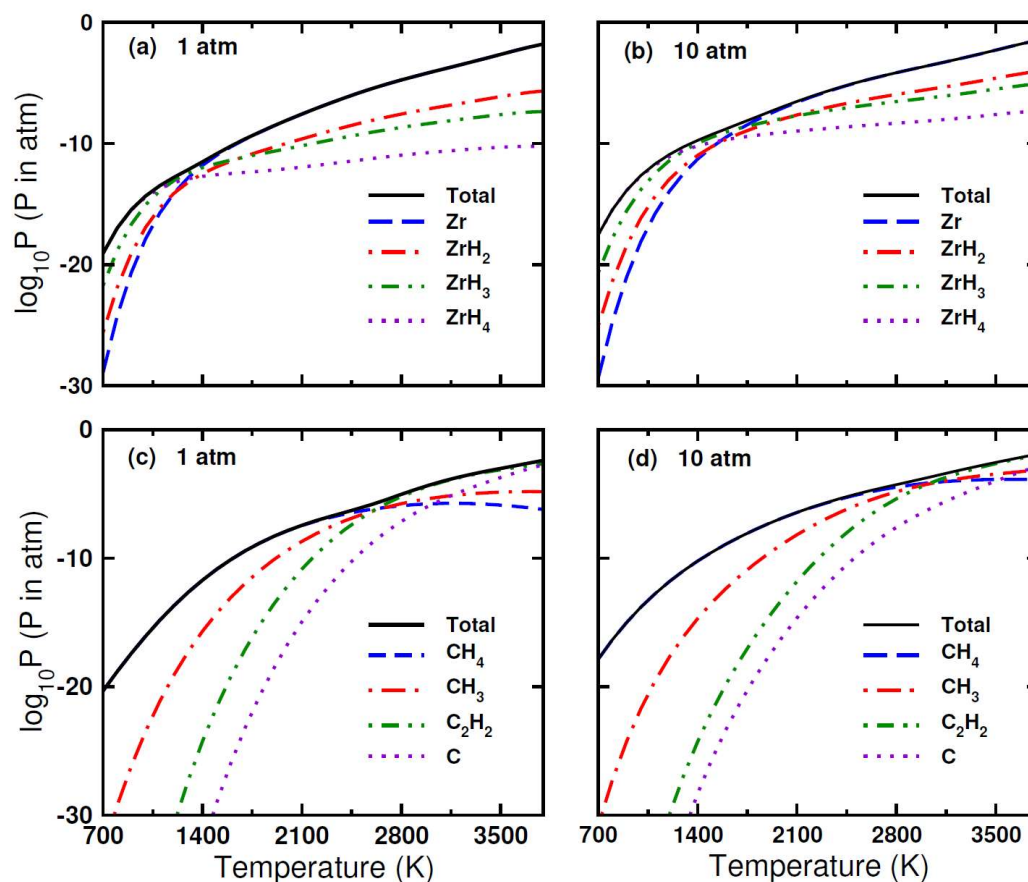
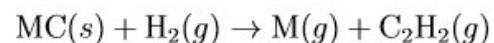
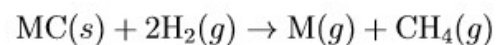
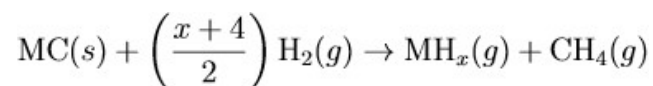
ZrC/H erosion product partial pressures



Pressures determined via thermodynamic properties predicted by DFT/phonon approximation

Hydrogen can react with either metal or carbon atoms

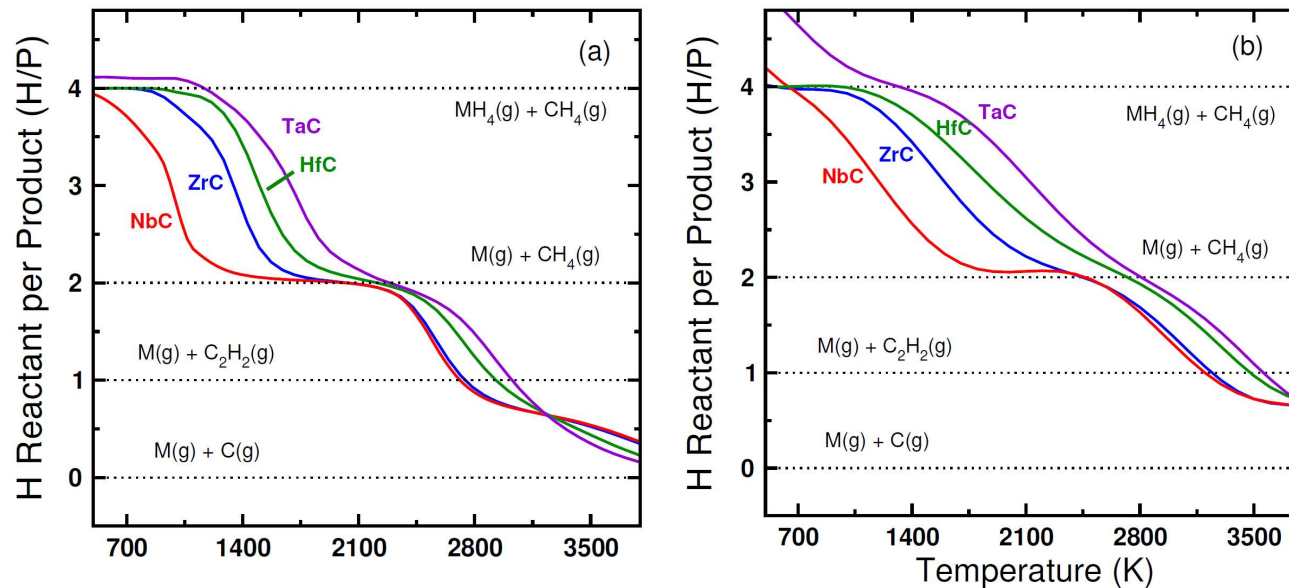
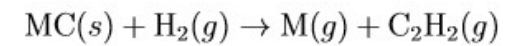
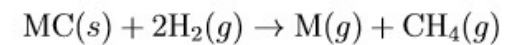
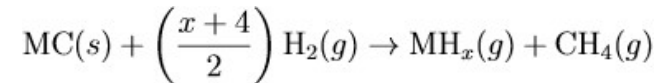
Below reactions considered for each metal M:



MC/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



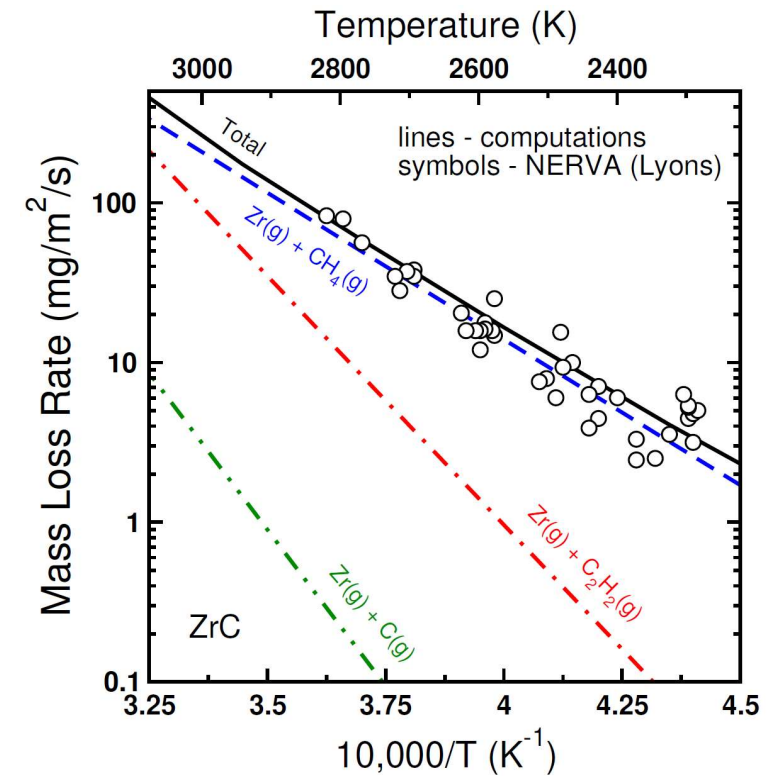
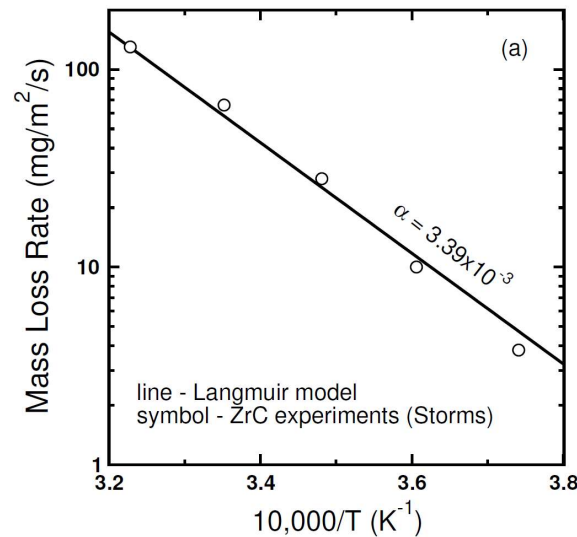
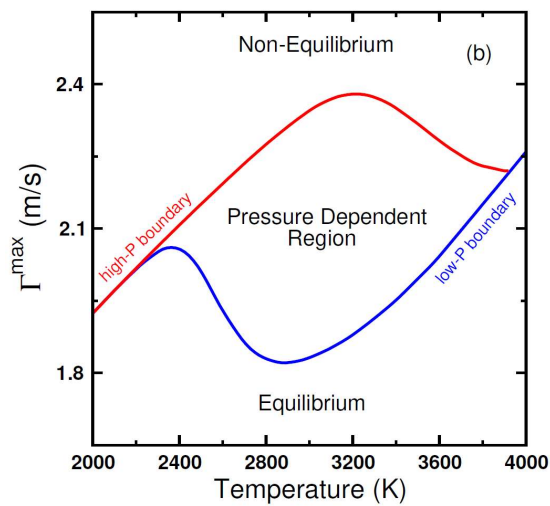
ZrC erosion – experimental comparison



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

Langmuir vaporization – Hertz-Knudsen expression for non-equilibrium

NERVA was in equilibrium regime



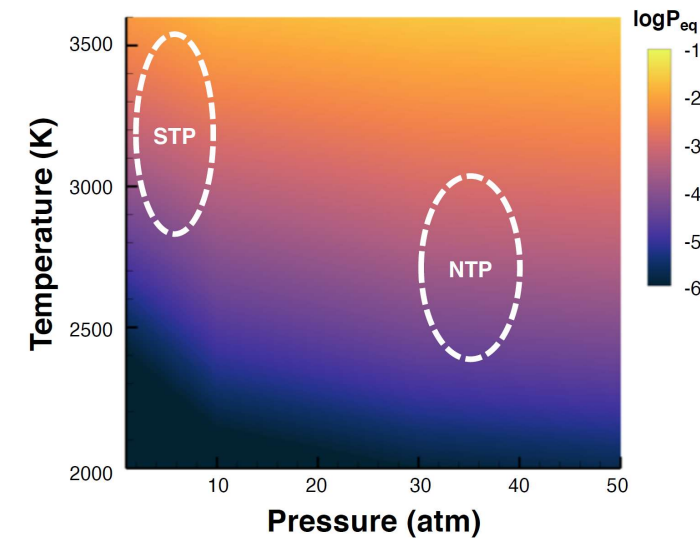
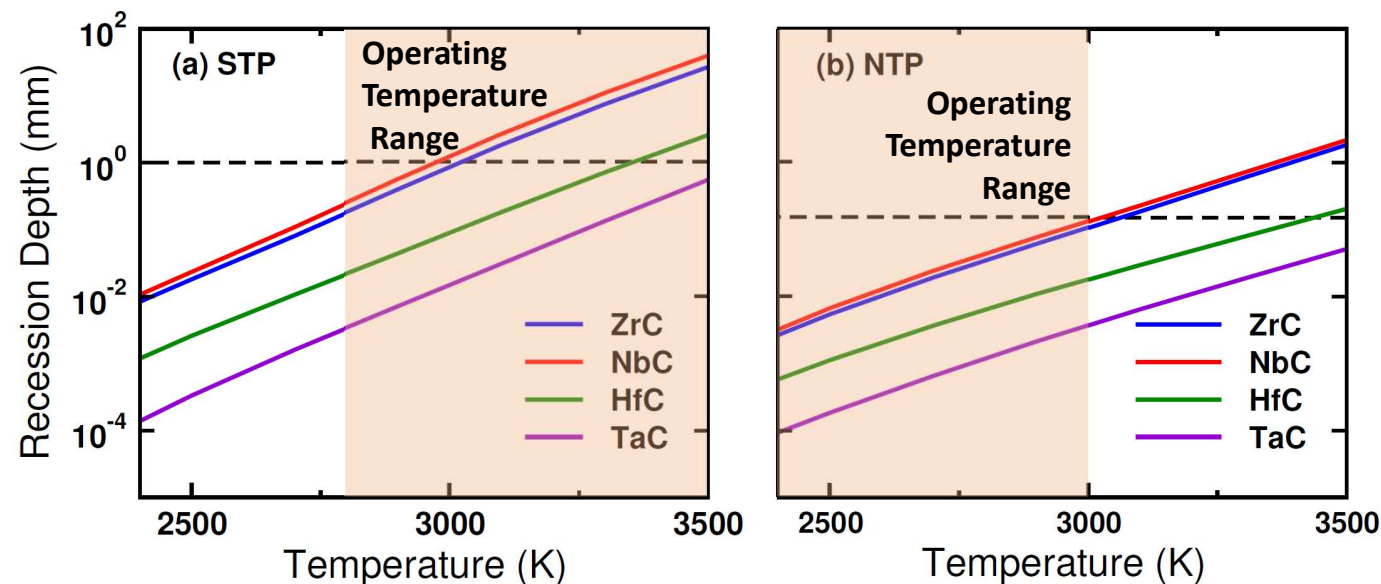
STP & NTP material recommendations



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



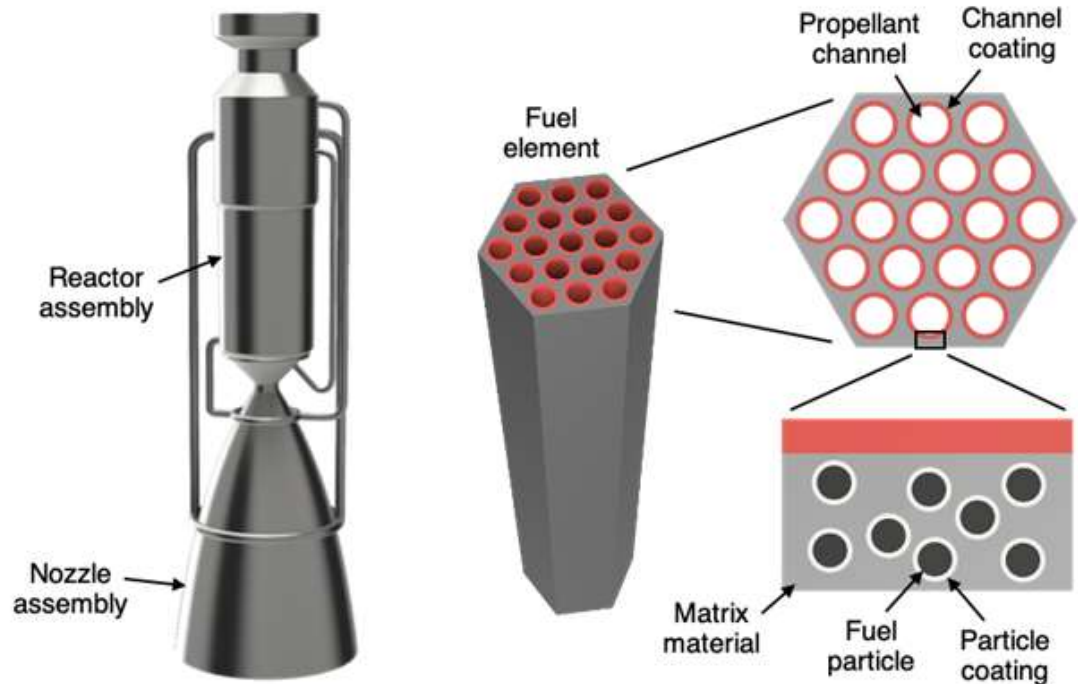
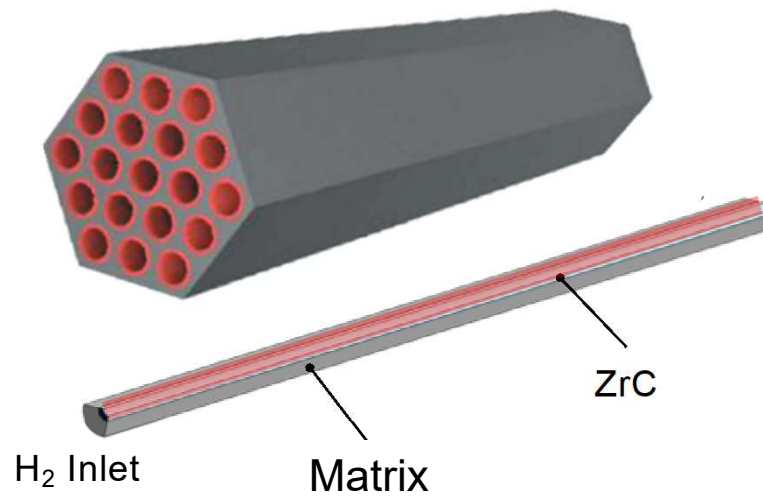
Summary



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



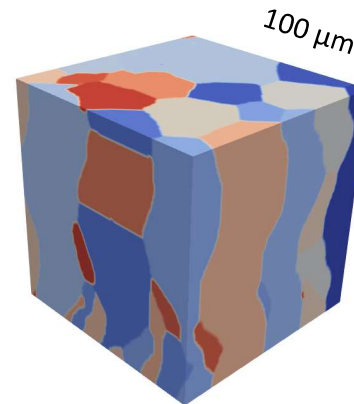
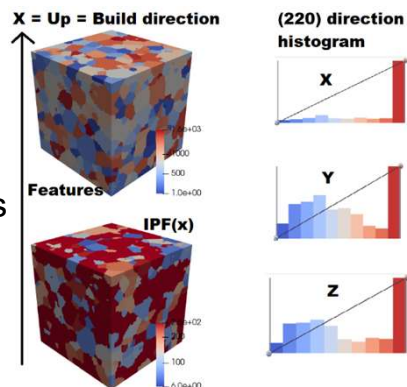
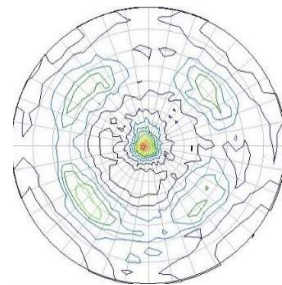
Additive manufacturing process modeling yields microstructure, or if possible, use experiments as input!

Experimentally informed microstructures

EBSD, pole figures as inputs

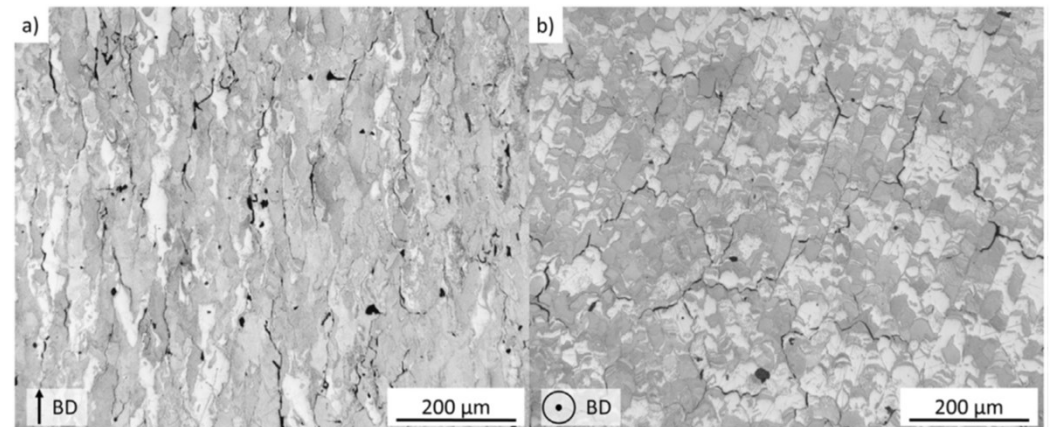
Matlab/MTEX
DREAM.3D

Microstructures have preferred orientations and grain size distributions

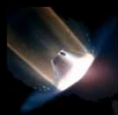


Synthetic microstructures informed by process modeling

SPPARKS
DREAM.3D



Braun, et al., JRFHM (2019)



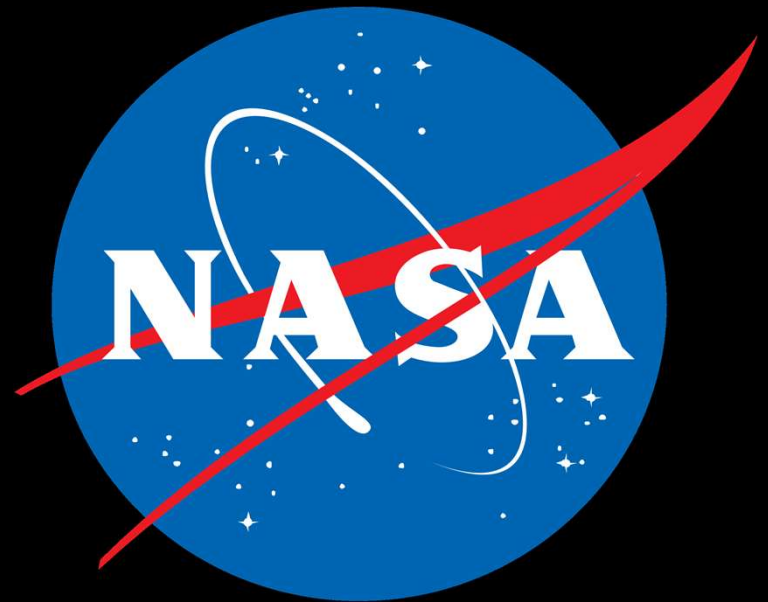
Questions/comments

Justin Haskins, Lauren Abbott, BJ Tucker

NASA Ames Research Center
Thermal Protection Materials Branch

NASA Langley/Ames EDL Seminar Series

National Aeronautics and Space
Administration



Ames Research Center
Entry Systems and Technology Division