Modelling radiation damage in crystalline and amorphous waste forms

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My research interests:

- Theory (dynamics and thermodynamics) of liquids, liquid-glass transition and supercritical state
- Link to field theory and fundamental physical constants
- Modelling radiation damage effects (nuclear and fusion applications)

Today's talk

Molecular dynamics of radiation damage in waste forms

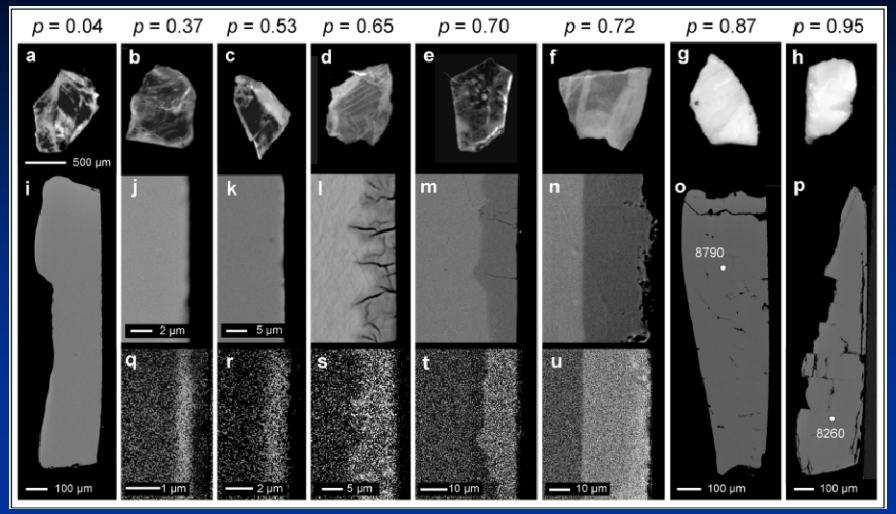
Effect of radiation-induced amorphization on diffusion

What are long-term (millions of years) effects of irradiation on the performance of waste forms?

Case study: zircon $ZrSiO_4$ minerals are ~1 billion years old, completely amorphous yet intact

Absorbs large ions like Pu on Zr site

Can we learn from Nature?


p = 0.04
p = 0.37
p = 0.53
p = 0.65
p = 0.70
p = 0.72
p = 0.87
p = 0.95
a
b
c
d
e
f
g
h
500 µm
i
j
k
l
m
n
o
p
8790
8260
2 µm
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2 µm
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10 µm
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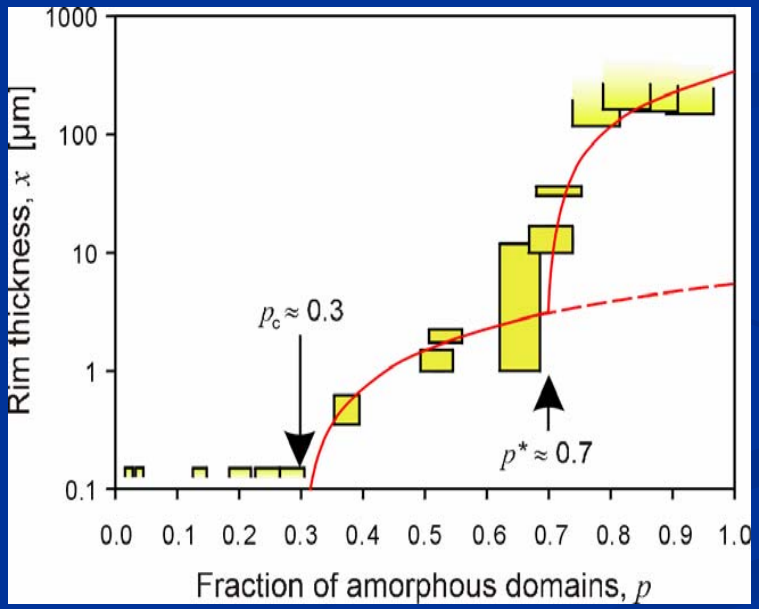
100 µm
100 µm


Rim thickness, x [µm]
1000
100
10
1
0.1
$p_c \approx 0.3$
$p^* \approx 0.7$
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Fraction of amorphous domains, p

What are the effects of radiation damage?

Processes are too fast and collision cascades are too small for experiments -> MD simulations

Challenge of large energy and large size:

Recoil energies: 100-500 keV

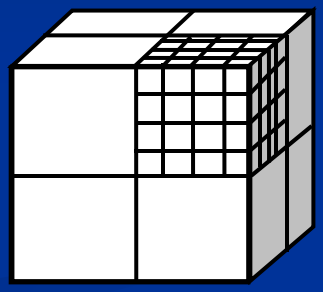
Require very large MD boxes

Not achievable previously

Molecular dynamics simulation of radiation damage: challenge of large energy and large size

Details:

1. Empirical potentials; short-range ZBL potential at short distances



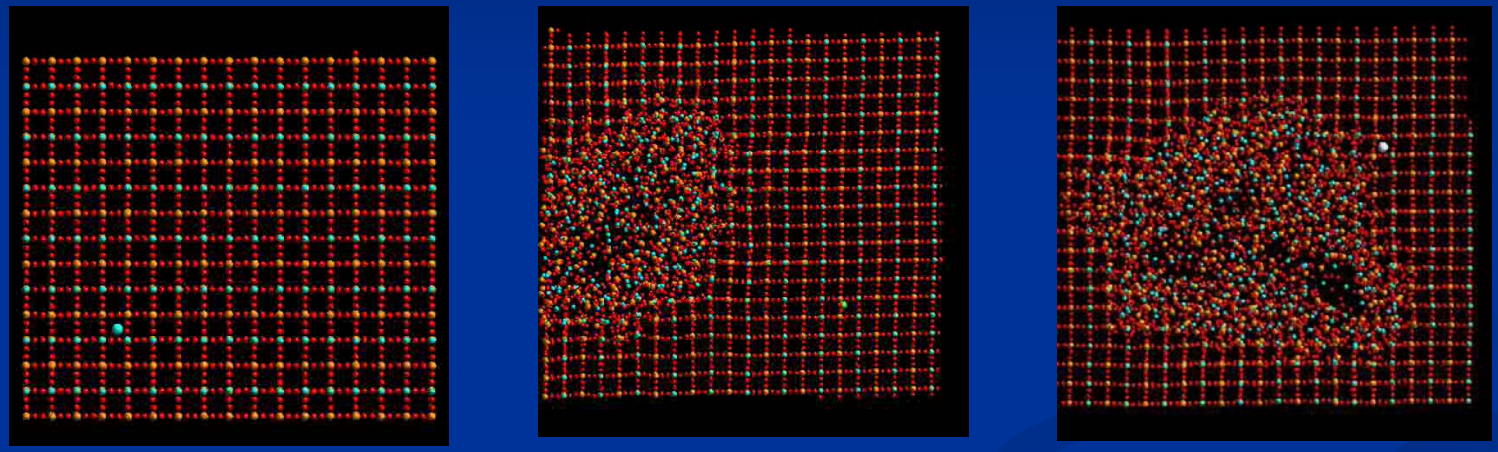
2. **Perfectly scalable** MD code based on domain decomposition strategy (DL_POLY MD package)

3. Parallel computers (Cambridge HPC, HPCx, HECToR, Archer)

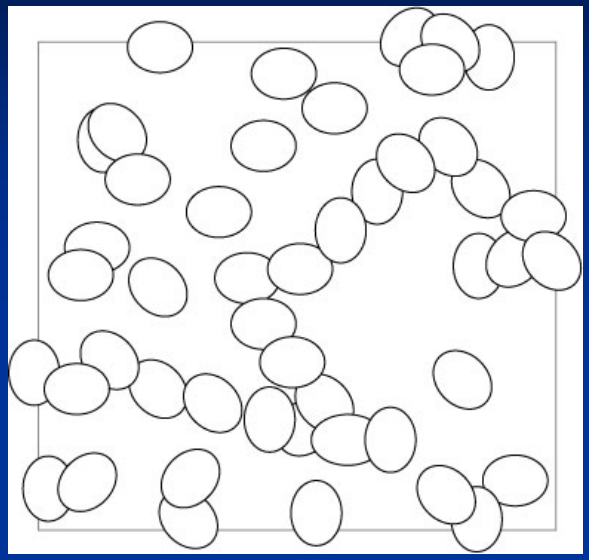
4. Adapted MD code to handle out-of-equilibrium conditions (variable time step, boundary scaling). Supported by 3 EPSRC grants.

High-energy U recoils in $ZrSiO_4$

50 keV U recoil and their overlap



Density variations appeared inside cascades and during their overlap
Seen in diffuse X-ray scattering

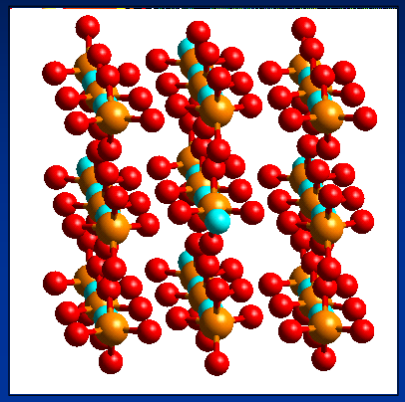


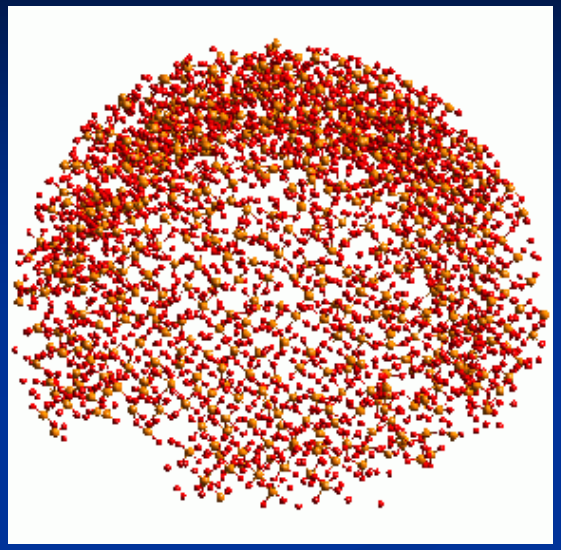
The value of percolation threshold in the continuum percolation is p_c=0.3 (approx.)

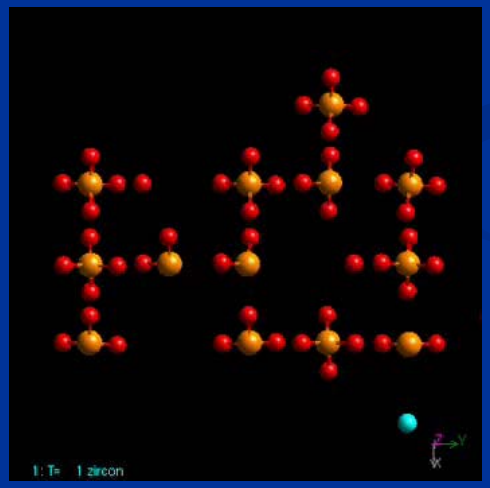
(non-trivial because it is continuous percolation)

This gives channels of increased diffusion and explains percolation-type increases of transport

Amorphizability







A material is amorphizable if it is able to form a covalent network

Resistant vs amorphizable materials

Some materials are easily amorphized (silicates and titanates)

Others are extremely resistant to amorphization (e.g., ZrO_2, $Gd_2Zr_2O_7$)

What is the nature of the process of resistance to amorphization by radiation damage?

The same question is relevant in other areas:

GaN and ZnO are considerably more resistant than GaAs, GaSb, Si etc

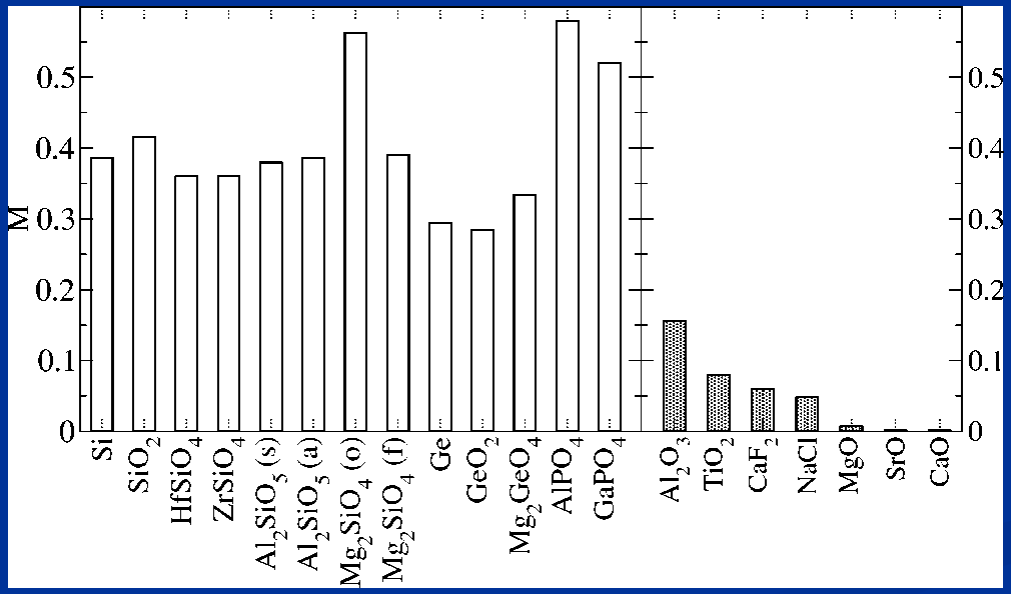
Understanding resistance to amorphization to radiation damage

Resistance is governed by **activation barriers for damage recovery and the nature of the bond**

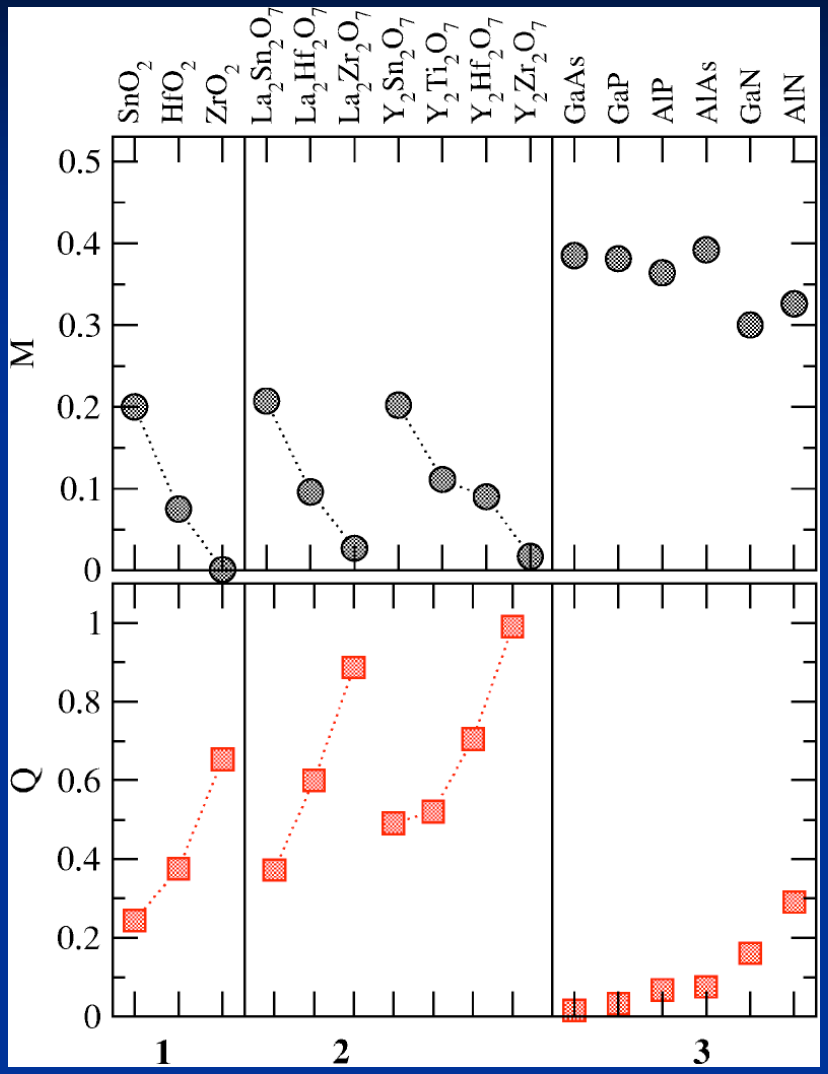
(but may or may not correlate with ratio of ionic "radii", topology, coordinations, defect disorder energetics etc)

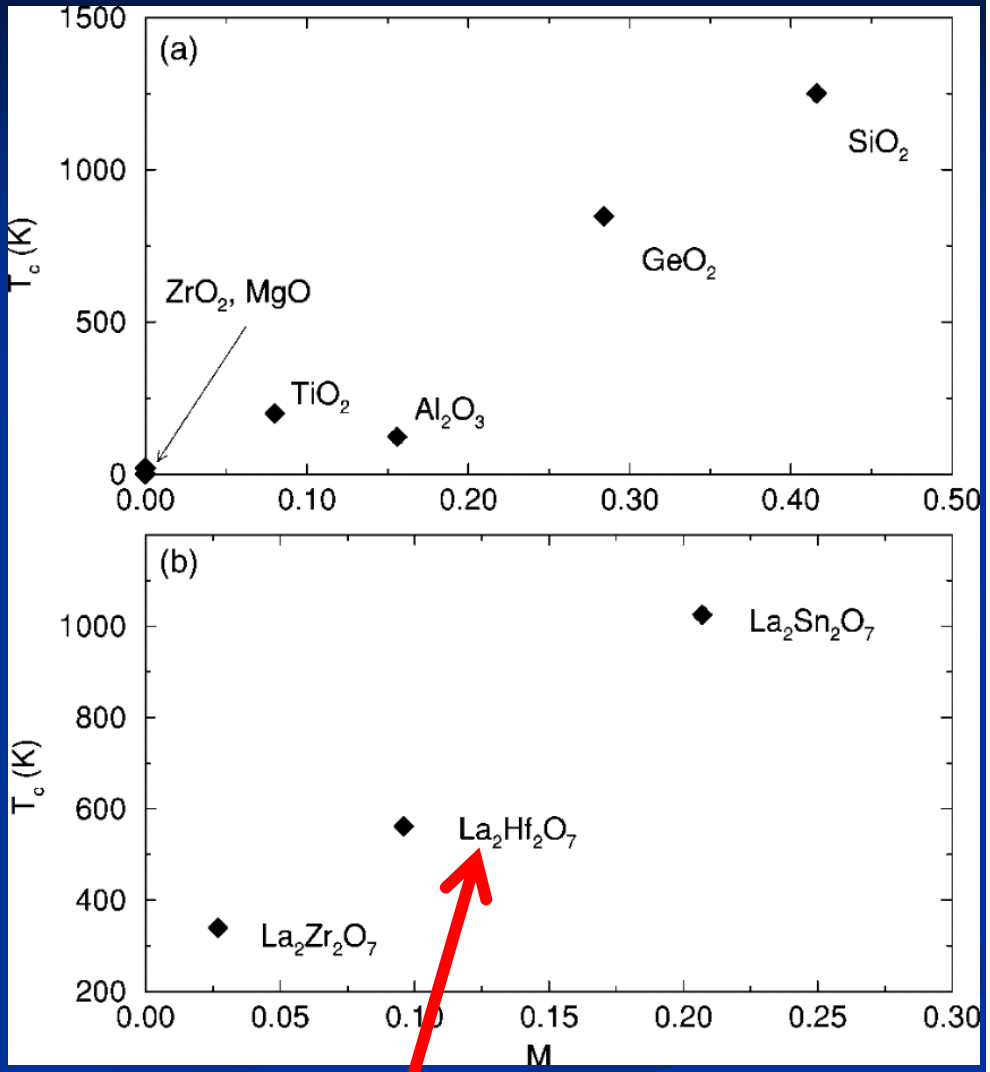
Understanding resistance to amorphization

- Many criteria do not generally work (review in JPCM 2004)
- Out of ~10 criteria, Naguib&Kelly (1975) empirically noticed that for binaries, resistance increases with ionicity (Pauling ionicity scale). Many other followed.
- Need: generality and applicability to all systems =>physical explanation
- Way to quantify: need hard numbers. Neither Pauling nor Phillips scales work generally!



Understanding resistance to amorphization

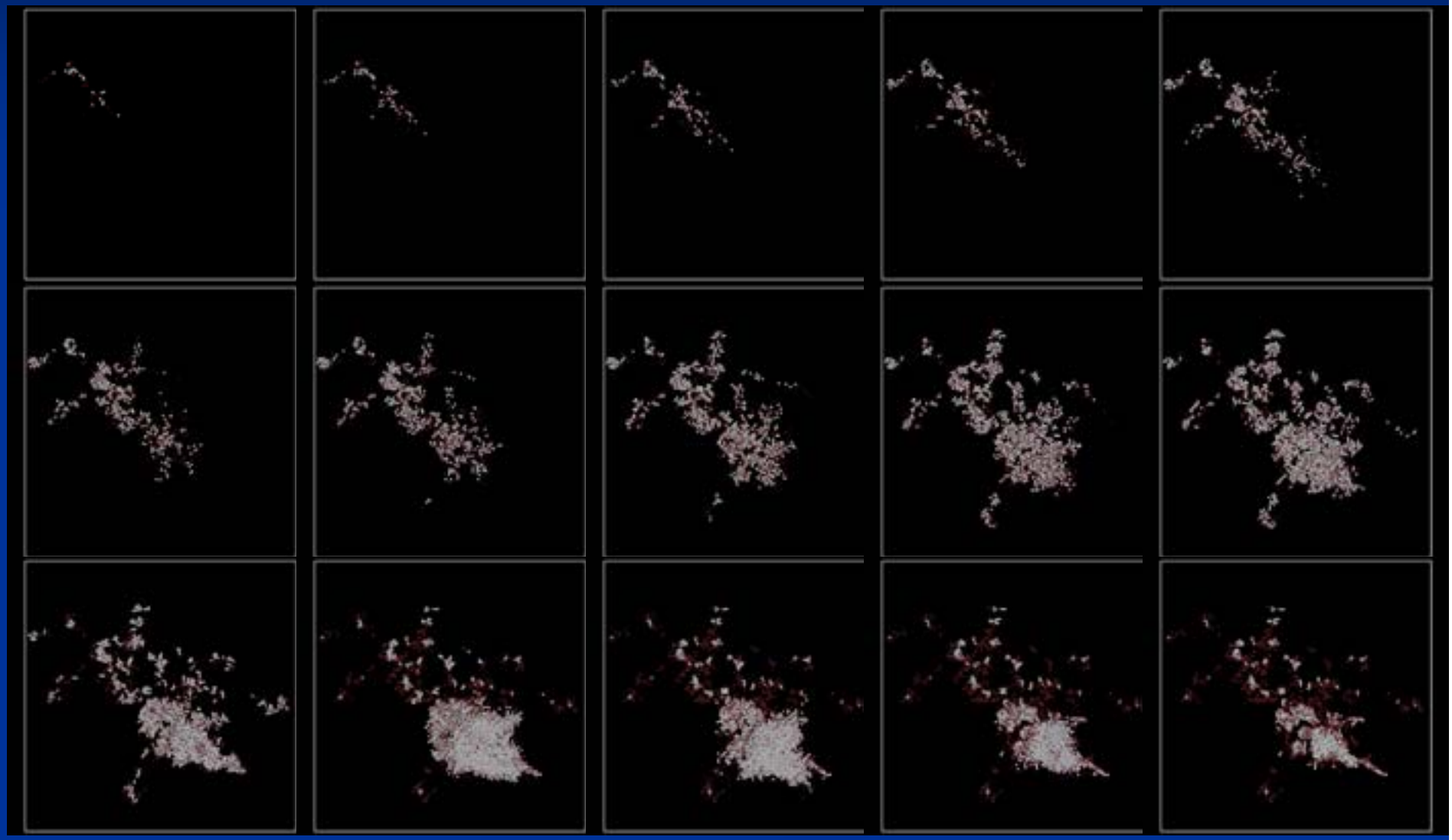




Prediction, verified experimentally

Molecular dynamics: look at the process in detail

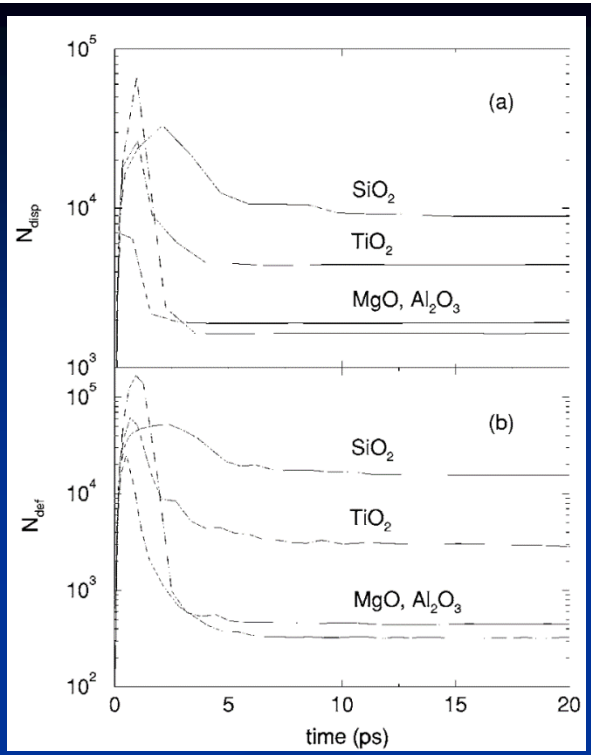
Rutile TiO_2



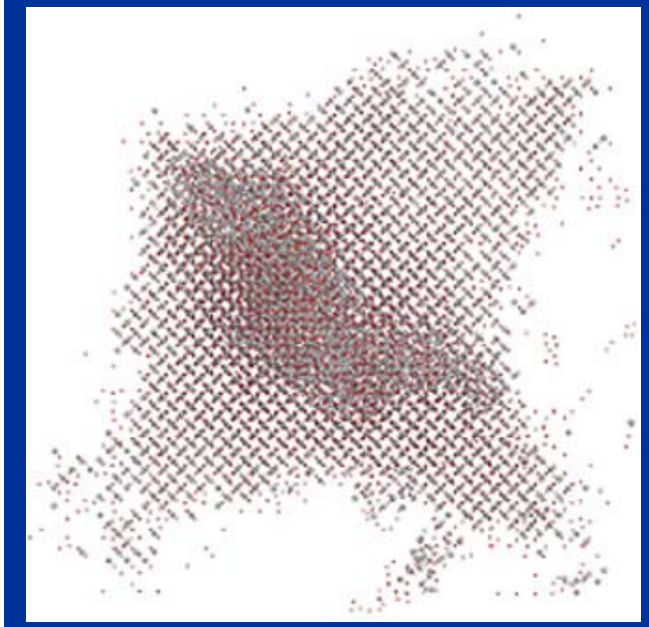
Two types of damage relaxation:

1. Elastic reversible relaxation of crystalline lattice around the swollen cascade – large peak in N_{def}

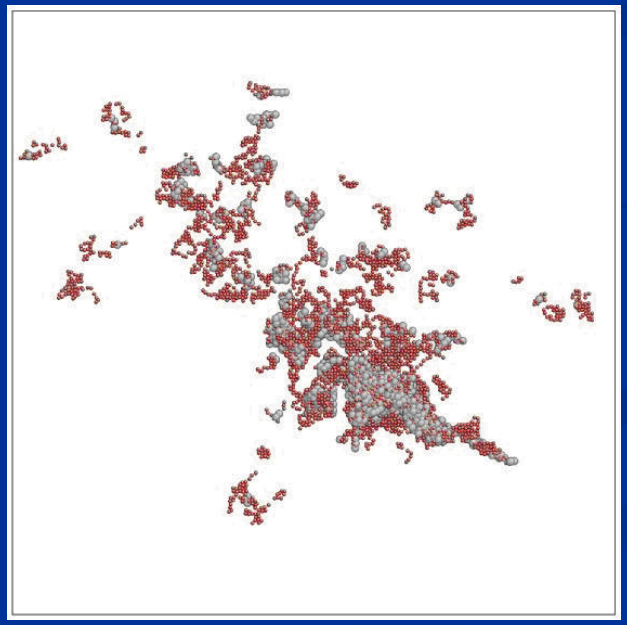
2. Irreversible topological damage



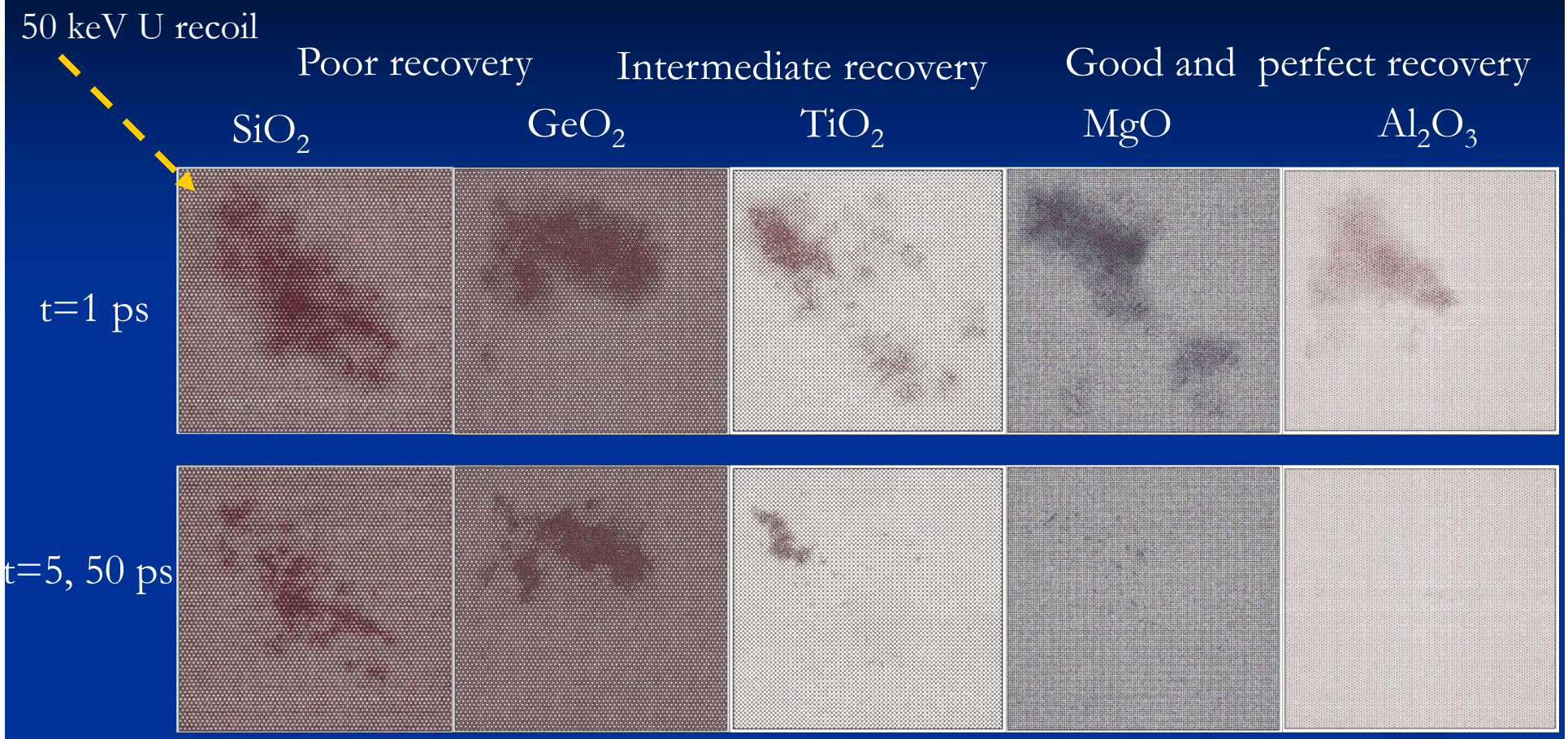
1-2 ps



50-100 ps



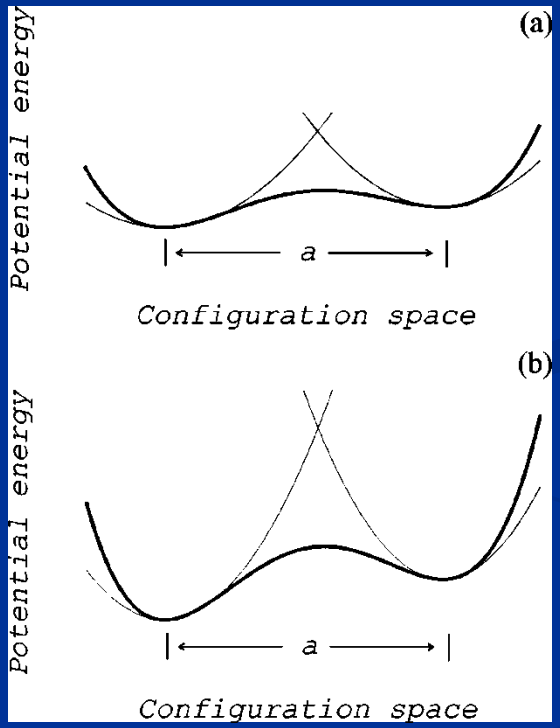
Resistance to amorphization



MD simulations **reproduce** experimental behaviour of resistance to amorphization.

Damage increases with the **stiffness** of O-O interaction

Why do empirical potentials reproduce activation barriers that govern damage recovery?



Resistance to amorphization

- Classical MD simulations **reproduce** experimental behaviour of resistance to amorphization

- MD simulations can be used to **predict highly resistant materials** where resistance to amorphization operates on the time scale of picoseconds. Successfully predicted resistance of series of pyrochlores.

- Slower recovery processes are possible. Even then, predictions work if the barriers are sufficiently high (cascade size in MD simulations on ps time scale=in billion-year-old samples from NMR experiments)

Radiation damage in iron

Simulate radiation damage in fusion reactors: ~1 MeV Fe recoil atoms from 14 MeV neutrons

Also relevant for nuclear fuels: fission products (many MeVs)

These energies were not studied before, yet are important to simulate

DL_POLY development work

(supported by the EPSRC grant)

Radiation damage-specific developments:

- Identification of radiation damage and defects
- Electronic energy loss mechanism (friction term and two-temperature models)
- Tuning potentials to very non-equilibrium conditions

DL_POLY development work

(supported by the current EPSRC grant)

General developments related to very large system sizes:

- Calculation of properties on the fly (one configuration of 250 mln atoms is about 100 Gb, 10,000-frame history file is Petabyte in size)

- Change the paradigm of how to run&analyze MD results – **MD of the future**

- Relevant for many interested in phenomena operating on microscale: shock, fracture, initiation of micro-cracks, micro-structural changes, interfacial effects, macromolecules, biological systems and so on

0.2 - 0.5 MeV Fe recoils in iron

These energies have not been simulated before

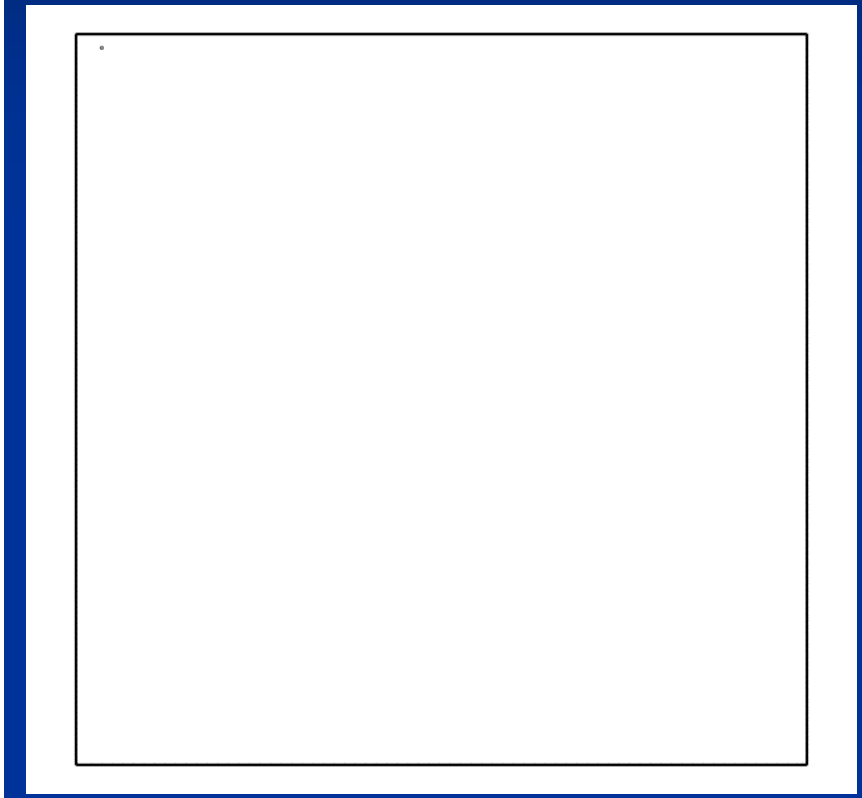
- Many-body (embedded atom) potential optimized against several defect energies in alpha-iron
- 100-500 million atoms, system size ~100-200 nm
- 24,000-60,000 parallel HeCTOR processors
- Great PhD student!

1. What does the collision cascade actually look like? First visualization of high-energy cascades

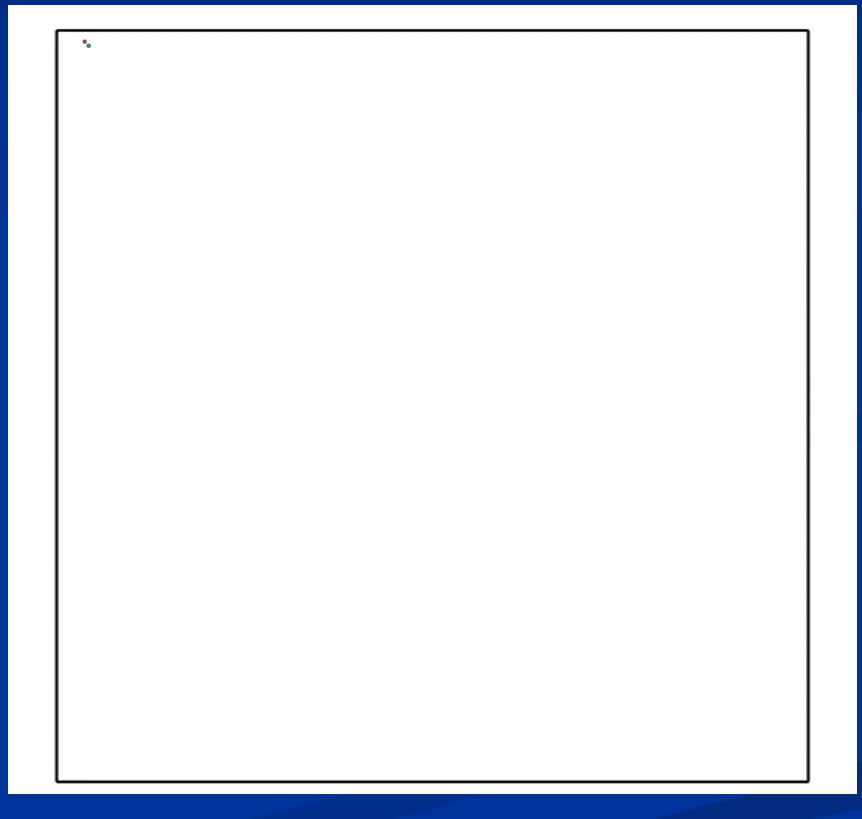
2. Novel insights into the cascade structure: continuous damage morphology vs sub-cascade branching

0.5 MeV recoils in Fe

Displaced atoms

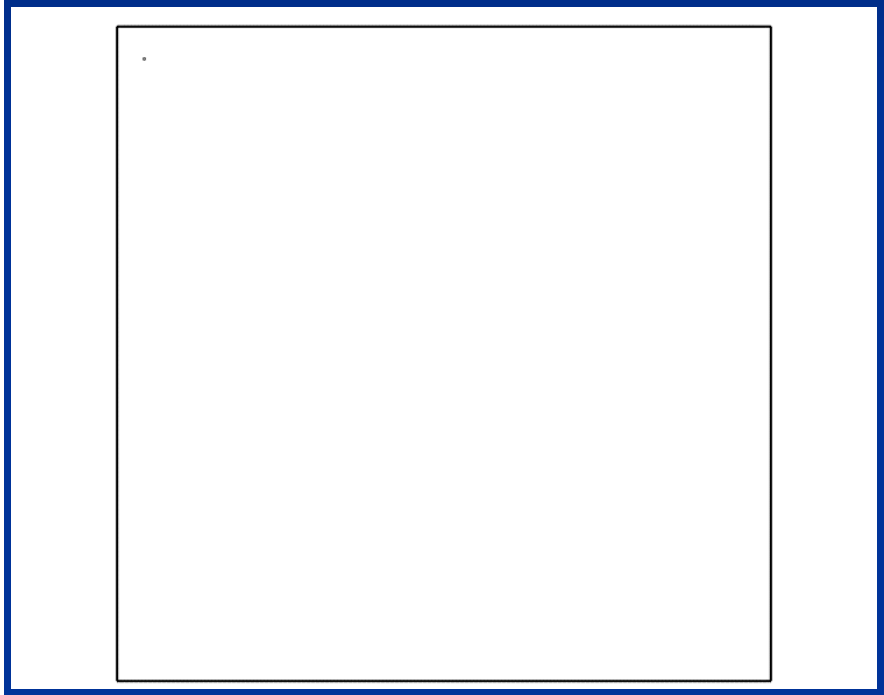


Defect atoms

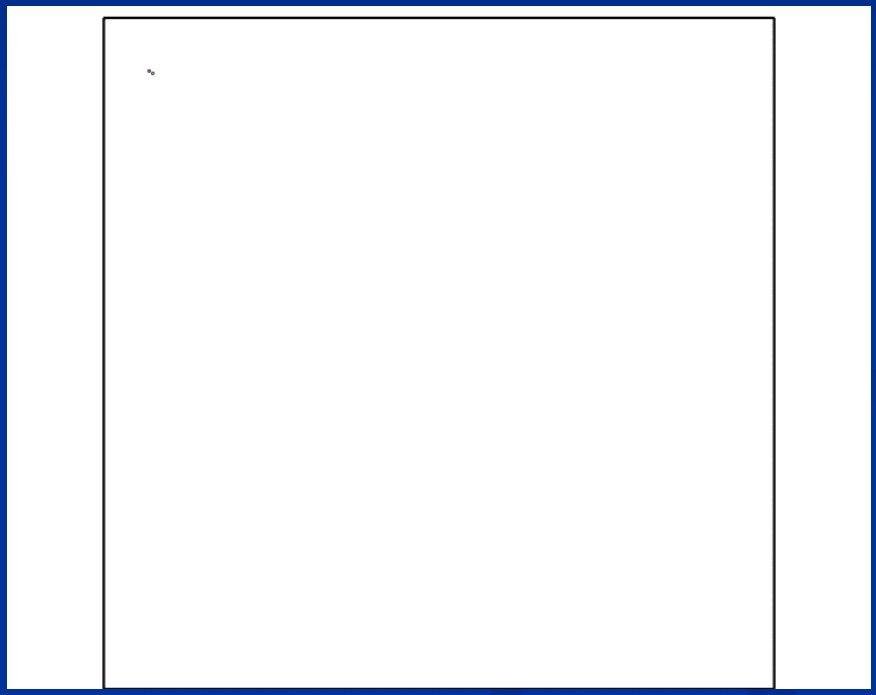


0.5 MeV recoils in Fe

Displaced atoms



Defect atoms

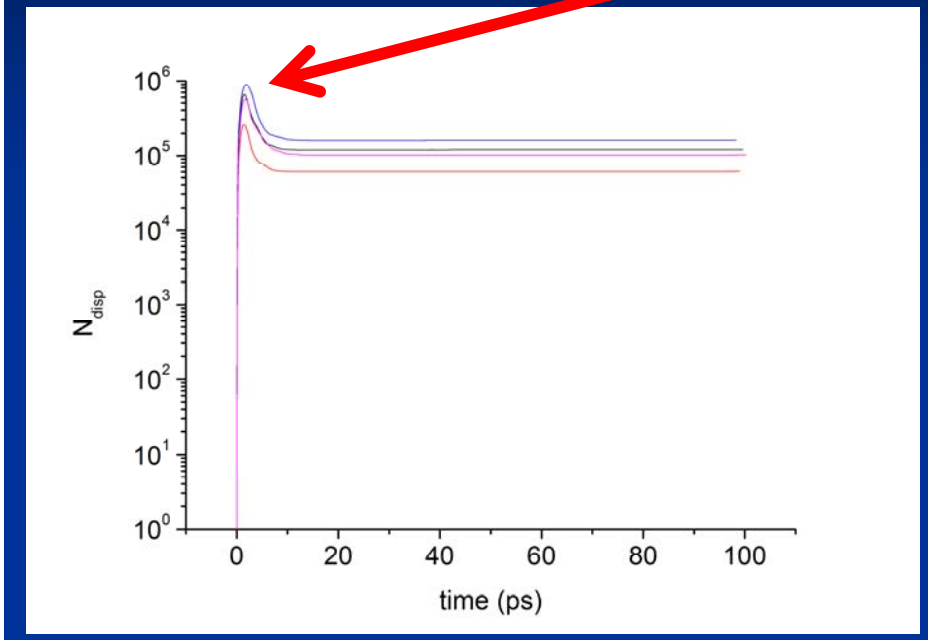


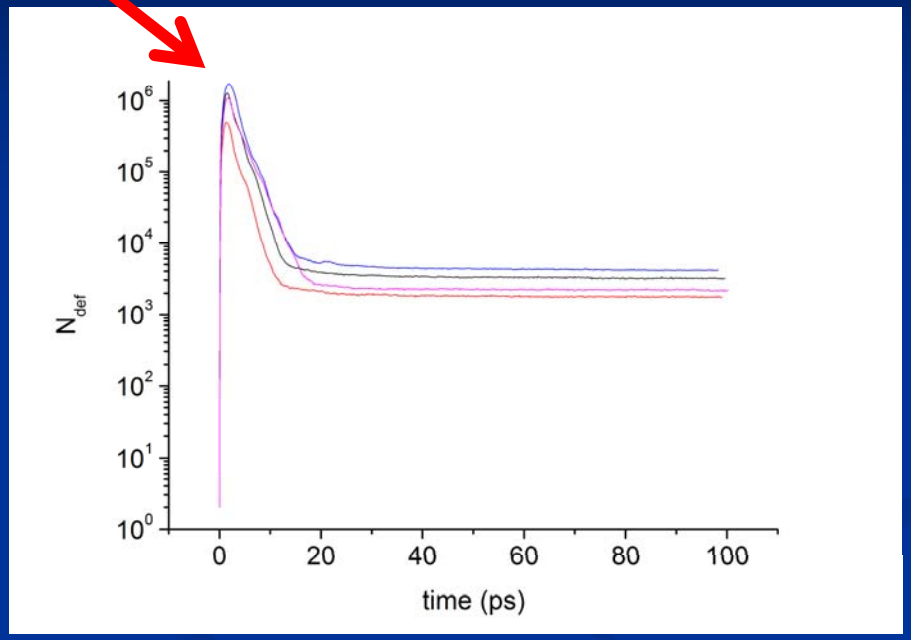
500 keV Fe recoils in iron

anharmonicity

displaced atoms

defect atoms

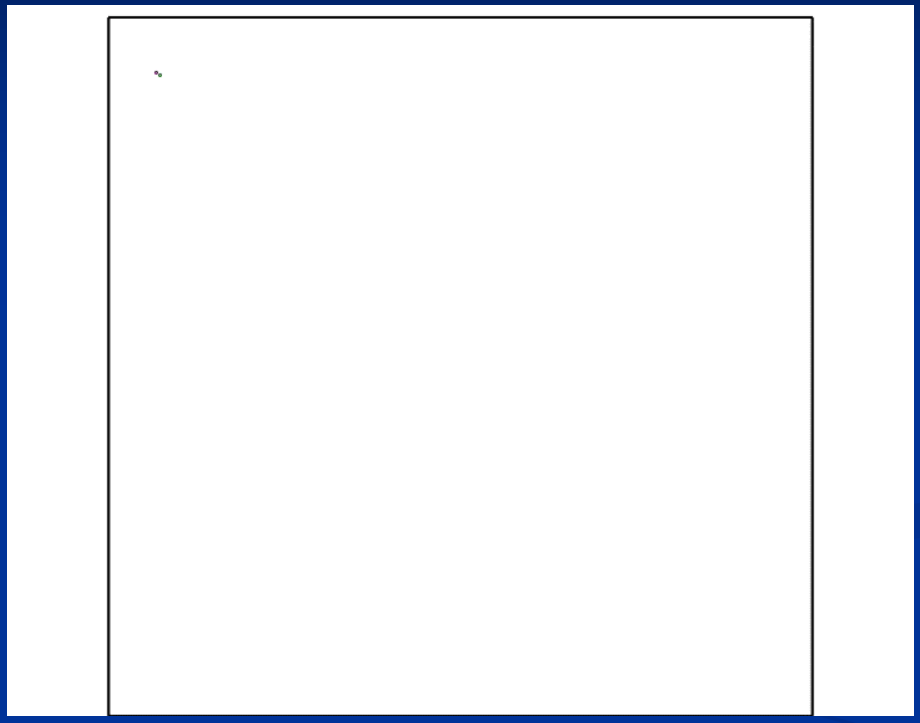




Look at defects locally:

Novel large (~100 atoms) clusters of interstitials and vacancies. Quantify and discuss their stability.

Shock waves



Can the damage due to shock waves be permanent?

Modelling radiation damage in disordered waste forms

Current waste form of choice in the UK: zirconolite $CaTiZr_2O_7$

Will become amorphous after ~1000 years

The damage will be in the amorphous phase during
100,000-1,000=99,000 years

Need to understand radiation damage in glasses

Questions:

1. What is the nature of radiation damage in amorphous systems?
(glass structure is hard to ascertain experimentally – A. Wright)

2. How does the amorphous structure evolve during progressive introduction of radiation damage?
   - Can an amorphous structure produced by liquid quench (glass) can be made 'more amorphous' by radiation damage (in a sense of reducing the degree of order in the short- and medium range)?
   - Does the damaged structure **converge** to a distinct amorphous state with new short- and medium range order and what is the nature of this new amorphous state?

3. Are radiation-induced and liquid-quench amorphicity different?

Two ways to produce an amorphous structure:

(a) Multiple overlap of 70 keV collision cascades
(b) Melting and quenching the crystal

Defining "defects" in a disordered system:

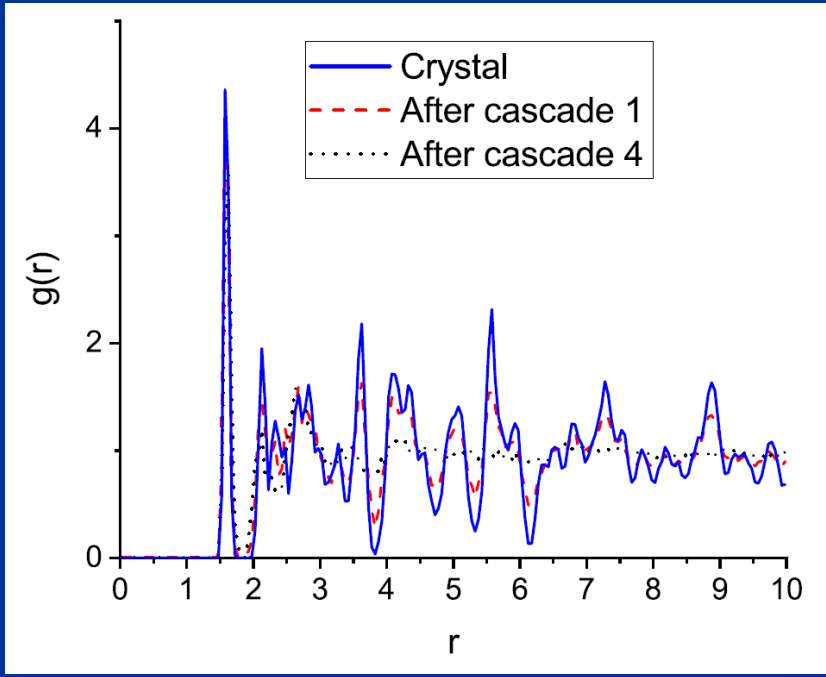
(a) a change to the specific atoms it is coordinated to, and
(b) it is displaced by more than a cutoff distance from its initial position (based on RDF)

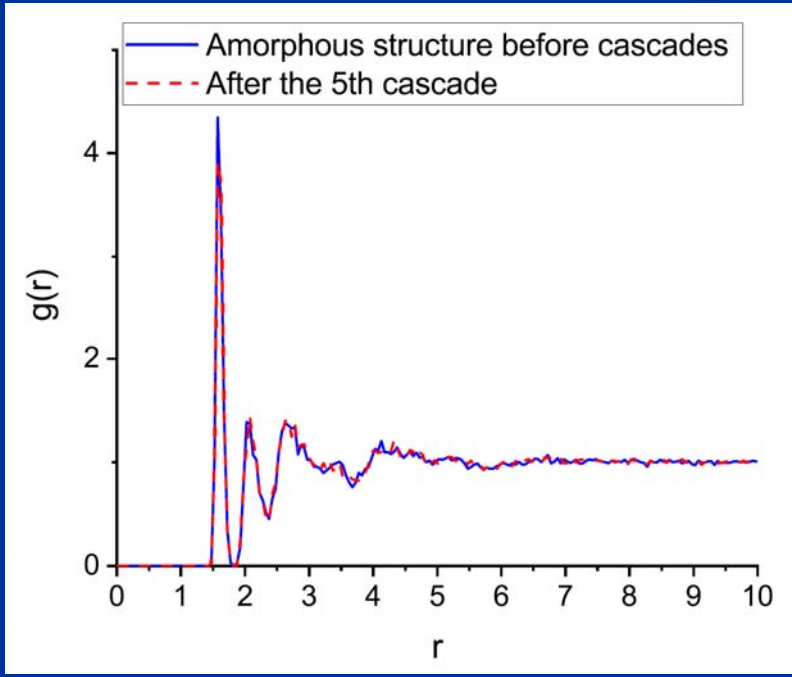
(Eg a Si atom that remains bonded to the same O atoms that form its tetrahedral cage is not considered a displaced atom, regardless of any translation, as it does not lead to a change in the glass network)

We studied both zircon $ZrSiO_4$ and zirconolite $CaZrTi_2O_7$ (Diver et al, JPCM 2020, Diver et al, J Nucl Mater 2021)

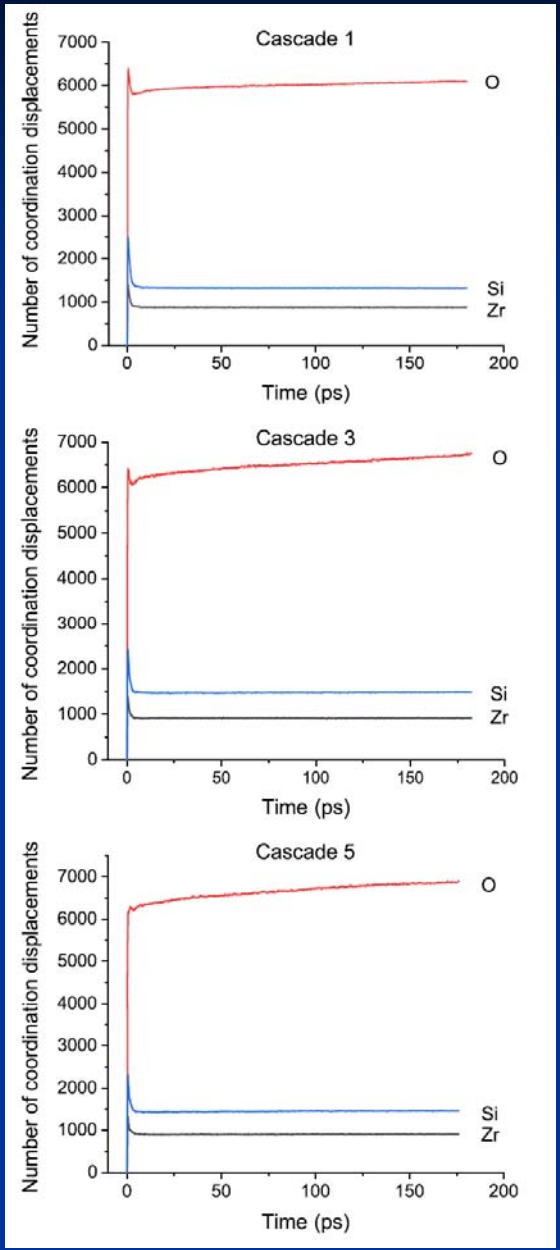
Results are very similar, shown below are results for zircon

Pair distribution function

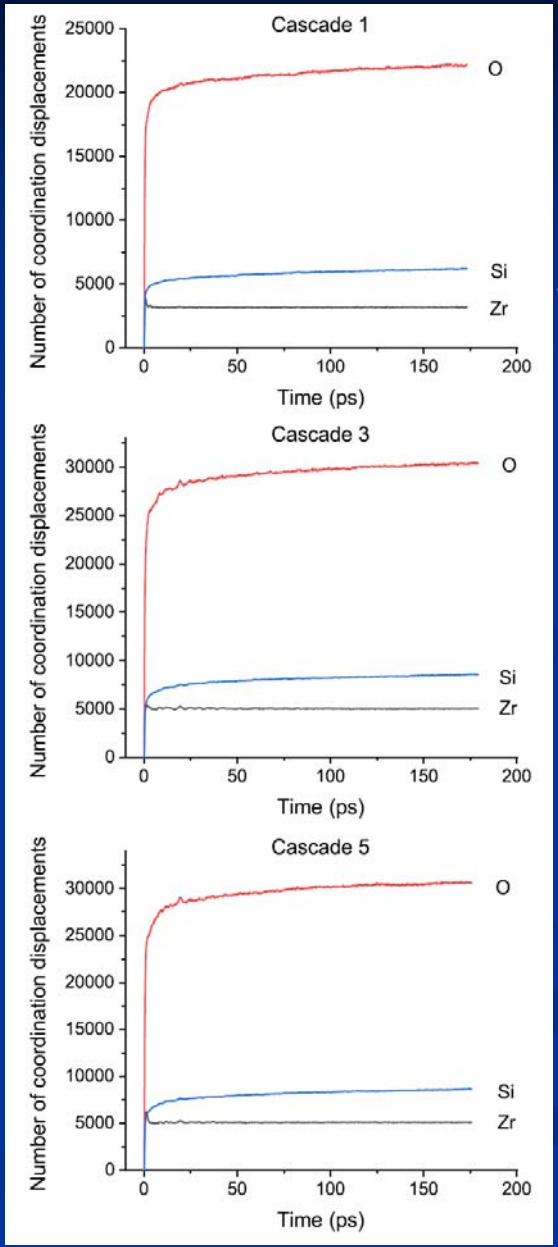




Crystalline zircon



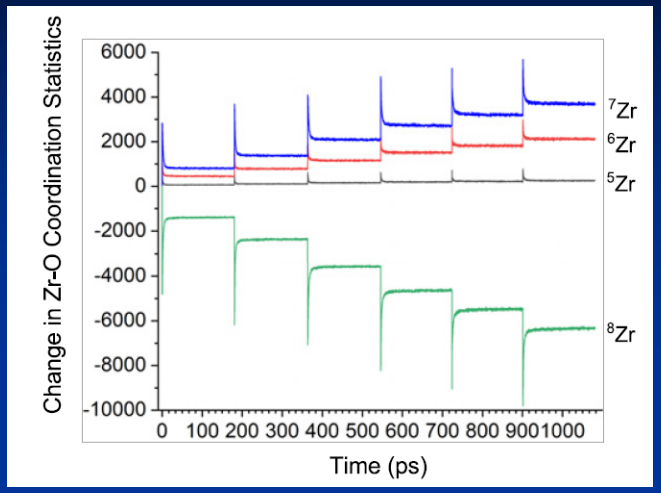
Amorphous zircon



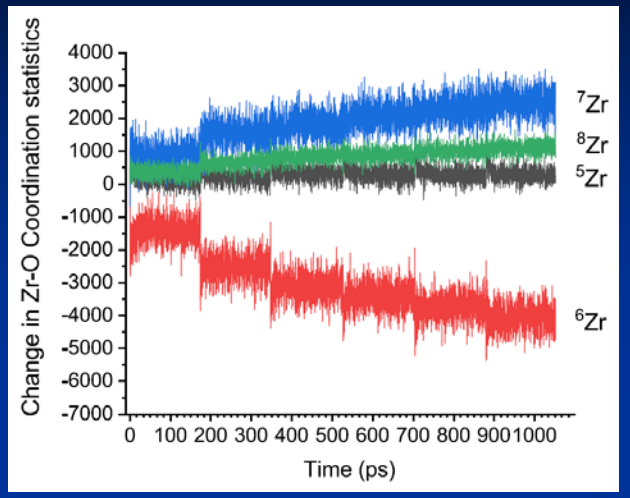
- softer overall

- response is more "slack"

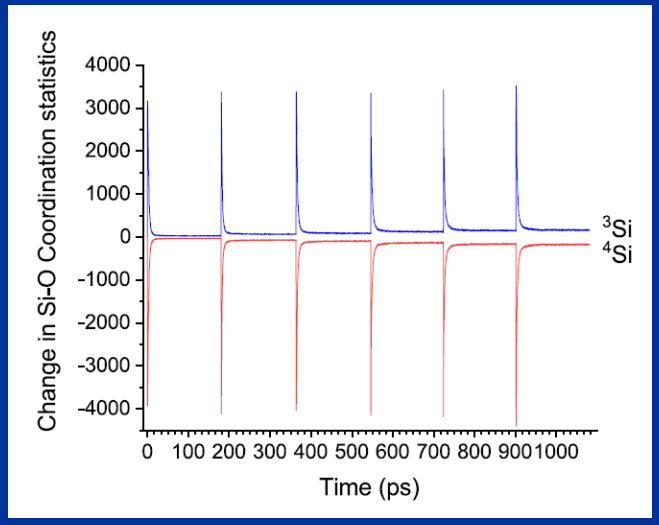
Crystalline zircon

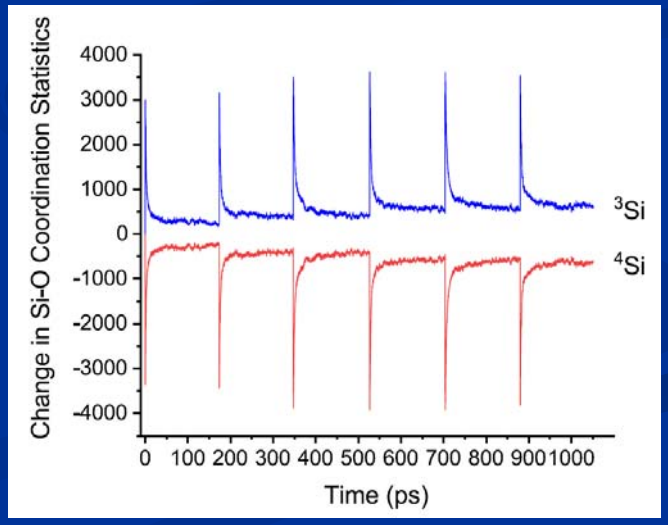


Amorphous zircon



Zr structure keeps evolving

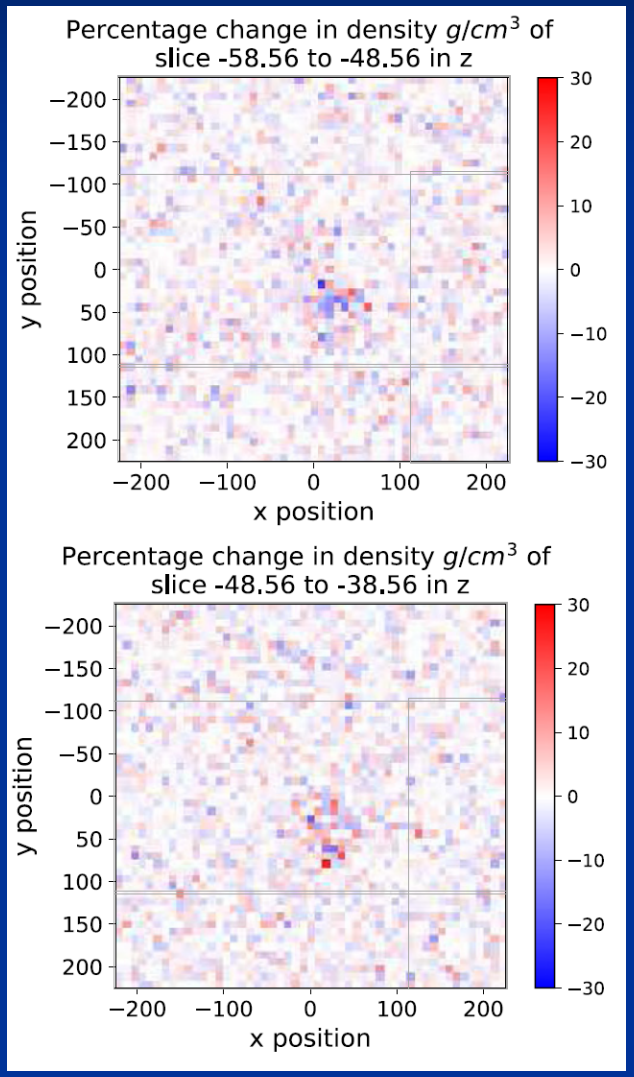




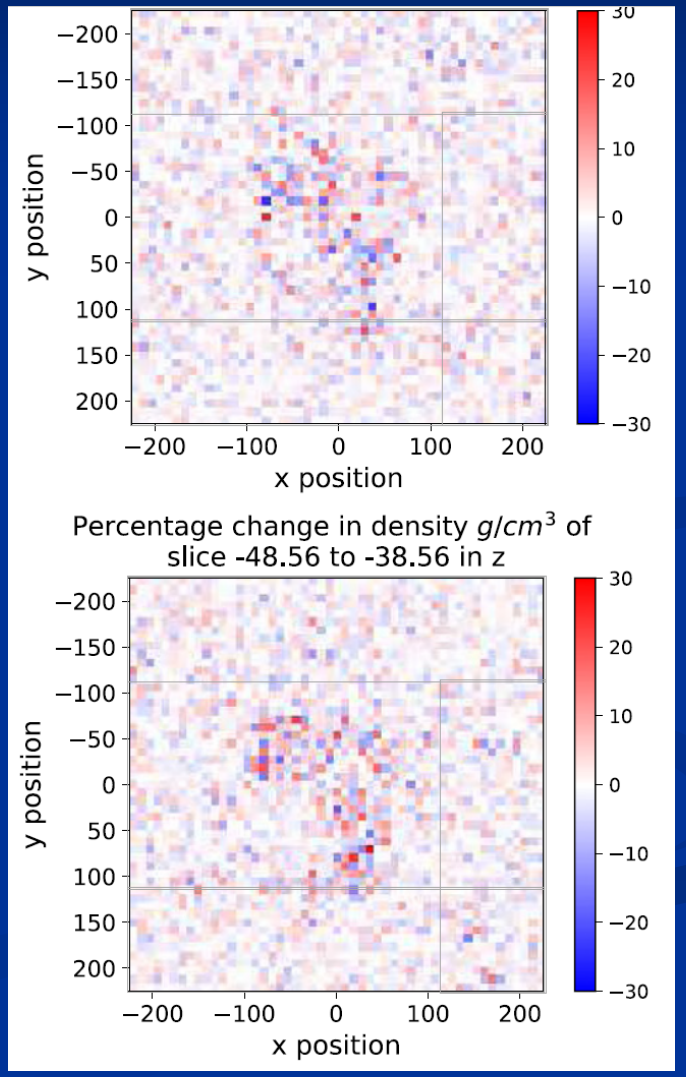
So does Si structure but less so

Density changes in amorphous zircon

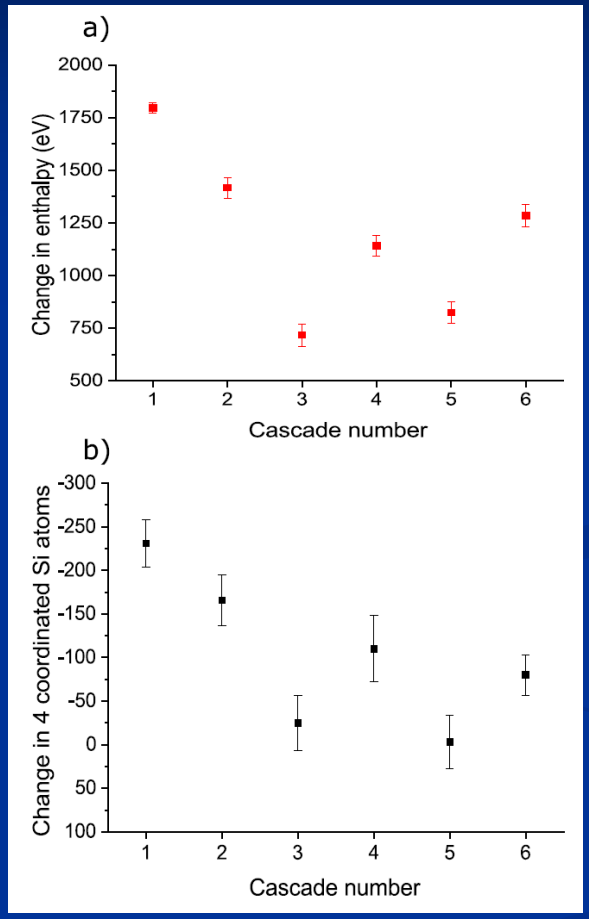
1 cascade



5 overlapping cascades



Correlation of structural and energetic changes



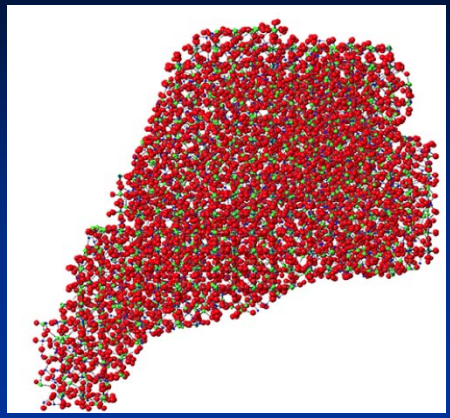
Still have not reached a converged structure of the radiation-damaged amorphous waste form:

amorphous structure keeps evolving

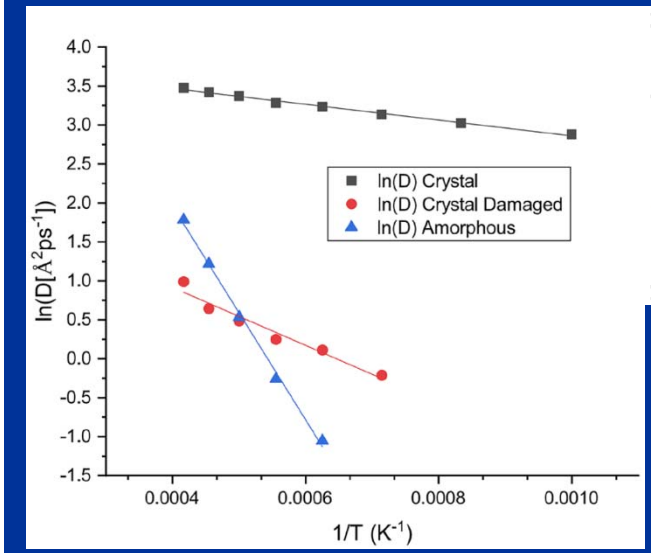
Local density inhomogeneities (also different from glasses)

He diffusion in radiation-damaged zircon

6 overlapping 70 keV cascades in ~10 mln atom system



100,000 He atoms introduced and $<x^2>$ is calculated at different T



Structure	Activation energy (kJ/mol)	Activation energy (eV)
Crystalline	8.44 ± 0.26	0.0874 ± 0.0024
Amorphous	114 ± 3.22	1.182 ± 0.033
Damaged	30.87 ± 3.93	0.320 ± 0.041

Disorder blocks fast diffusion pathways->slower diffusion (even with 16% swelling of the amorphous structure)

He tends to accumulate in damaged regions

Full story in Diver et al, J Mater Res 2021

Thank you