Radiation Effects in Nuclear Waste Materials

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Research Objectives

The objective of this research project is to develop a fundamental understanding of radiation effects in glasses and ceramics at the atomic, microscopic, and macroscopic levels, including the impact of such solid-phase radiation effects on dissolution kinetics.

This Research Addresses Several Needs of the Nuclear Materials & High-Level Waste Focus Areas

GOALS & IMPACTS

- Provide underpinning science and rationale for improved materials for immobilization of high-level tank wastes and stabilization of nuclear materials
- Develop scientifically-based predictive models of performance for nuclear waste forms and stabilized nuclear materials

Research Status / Accomplishments

Experimental Studies

- Detailed characterization of radiation-induced structural changes in Pu-containing glasses and zircons nearly complete
- Annealing study of Pu-containing zircons initiated
- Ion-irradiation studies of zircon and several titanate pyrochlores over a wide range of experimental conditions nearly completed
- Dissolution testing completed on several titanate pyrochlores
- Tentative performance models developed for apatite and zircon
- Performed ion/electron-beam studies of bubble formation in several glasses
- 7 glass compositions were γ-irradiated at 50, 100, 150, & 200°C to doses of 25, 75, and 150 MGy (highest dose equivalent to 25 years storage for defense HLW glasses)

Research Status / Accomplishments

Computer Simulations

- Oxygen vacancy migration pathways and energies calculated for fused silica and related structures (Ph.D dissertation research)
- Developed capability to study localized electronic excitations (self-trapped excitons) in silica and their effect on defect production and migration (Ph.D dissertation research)
- Developed and used computer simulation methods to determine threshold displacement processes/energies in zircon
- Initiated molecular dynamics study of collision cascades in zircon
- Calculated vacancy migration pathways and energies in zircon
- Calculated stable configurations for Pu substitution in zircon
- Developed and used kinetic Monte Carlo method to simulate amorphization process in zircon

Journal Publications

WJ Weber, RC Ewing, and A Meldrum, **The Kinetics of Alpha-Decay-Induced Amorphization in Zircon and Apatite Containing Weapons-Grade Plutonium or Other Actinides**, *J. Nucl. Materials*, **250** (1997) 147-155.

RE Williford, R Devanathan, and WJ Weber, **Computer Simulation of Displacement Threshold Energies for Several Ceramic Materials**, *Nucl. Instrum. and Methods*, **B 141** (1998) 98-103.

NJ Hess, WJ Weber, and SD Conradson, **X-ray Absorption Fine Structure of Aged, Pu-Doped Glass and Ceramic Waste Forms**, *J. Nucl. Materials*, **254** (1998) 175-184.

NJ Hess, WJ Weber, and SD Conradson, **U and Pu L_{III} XAFS of Pu-Doped Glass and Ceramic Waste Forms**, *J. Alloys and Compounds*, **271-273** (1998) 240-243.

KC Gorretta, ML Burdt, MM Cuber, LA Perry, D Singh, AS Wagh, JL Routbort, and WJ Weber, **Solid-Particle Erosion of Portland Cement and Concrete**, *Wear*, **224** (1999) 106-112.

RE Williford, WJ Weber, R Devanathan, and AN Cormack, **Native Vacancy Migrations in Zircon**, *J. Nucl. Materials* **273** (1999) 164-170.

RE Williford, BD Begg, WJ Weber, and NJ Hess, **Computer Simulation of Pu^{3+} and Pu^{4+} Substitutions in Zircon**, *J. Nucl. Materials*, **278** (2000) 207-211.

BD Begg, NJ Hess, WJ Weber, SD Conradson, MJ Schweiger, and RC Ewing, **XAS and XRD Study of Annealed ^{238}Pu- and ^{239}Pu-Substituted Zircons ($Zr_{0.92}Pu_{0.08}SiO_4$)**, *J. Nucl. Materials*, **278** (2000) 212-224.

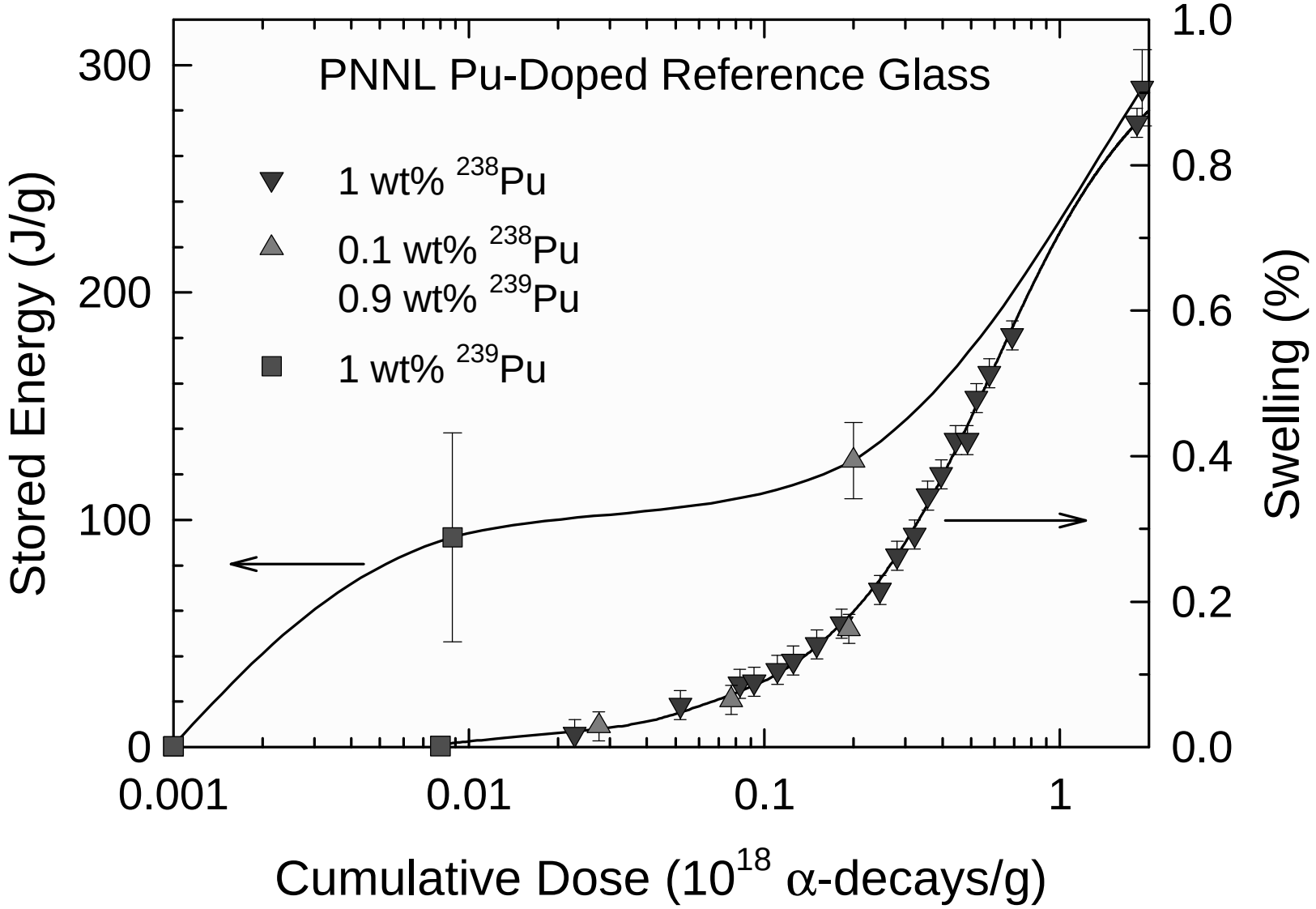
B Park, WJ Weber, and LR Corrales, **Molecular Dynamics Study of the Threshold Displacement Energy in MgO**, *Nucl. Instrum. and Methods*, **B166-167** (2000) 357-363.

J Song, H Jónsson and LR Corrales, **Self-Trapped Excitons in Quartz**, *Nucl. Instrum. and Methods*, **B166-167** (2000) 451-458.

BD Begg, NJ Hess, WJ Weber, R Devanathan, JP Icenhower, S Thevuthasan, and BP McGrail, **Heavy-Ion Irradiation Effects on Structures and Acid Dissolution of Pyrochlores**, *J. Nucl. Materials* (2000) submitted.

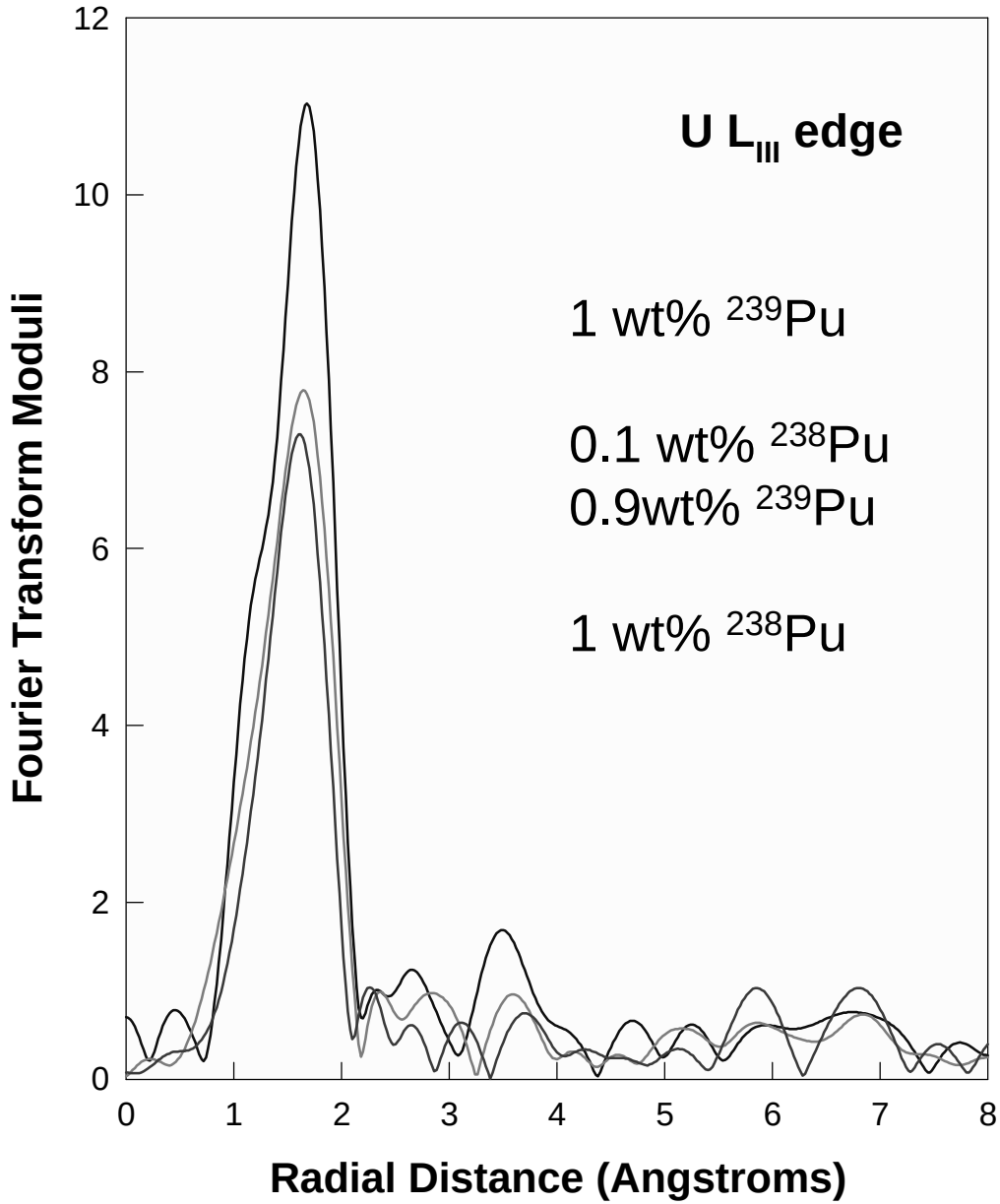
HL Heinisch and WJ Weber, **Kinetic Monte Carlo Simulations of Irradiation-Induced Amorphization of Zircon**, *J. Nuclear Mater.* (2000) submitted.

Stored Energy & Swelling in Pu-Doped Glass



Stored Energy (defect accumulation) increases more rapidly with cumulative dose than Swelling (network rearrangements).

EXAFS Results on Pu-Glasses



Results suggest that the concentration of U^{6+} is reduced with increasing dose, an interpretation that is consistent with the observed XANES profiles.

The lowest dose glass exhibits a Fourier transform peak at about 3.5 Å, which corresponds to a U--U scattering path at 3.62 Å, suggesting the presence of polymeric uranium species. The occurrence of polymeric uranium suggests that the uranium is not uniformly dispersed and uranium-rich domains or clusters are formed.

The absence of a U--U scattering path at higher doses suggests the absence of polymeric uranium and may reflect either a radiation effect or possible differences in synthesis conditions.

Reference: NJ Hess, WJ Weber, & SD Conradson, *Journal of Nuclear Materials* **254** (1998) 175-184.

Pu-Doped Glasses: XAS, XRD, EPR

- **No significant change in local cation coordination or cation-O bonds lengths with increasing dose.**
- **Decrease in concentration of U^{6+} with increasing dose.**
- **Decrease in Fe coordination with increasing dose.**
- **Contraction of Fe-Si, Mn-Si, and Pu-Si distances and broadening of silica O-O distances with increasing dose suggests changes in the Si-O-Si bond angle.**
- **EPR results (D. Griscom, NRL) suggest the breakup of Fe^{3+} clusters with increasing dose.**

To be done: Raman & Infrared Photoluminescence to probe for O_2; XAS to probe local B structure; Changes in Dissolution Kinetics.

Beta/Gamma Effects in Glasses

Seven glass compositions have and continue to be irradiated in PNNL ^{60}Co facility (1x10^4 Gy/hr) at 50, 100, 150, and 200°C

- Reference Waste Glasses: $10Na_2O$ - $10B_2O_3$ - $50SiO_2$ - 30(ZrO_2, TiO_2, Fe_2O_3, Al_2O_3,CaO, MgO, Cs_2O, Li_2O)
- Borosilicate Glasses: $15Na_2O$ - $20B_2O_3$ - $65SiO_2$ - (5FeO or Fe_2O_3)
- Fe-Phosphate Glasses: $15Na_2O$ - $30Fe_2O_3$ - $55P_2O_5$ - ($5CsO_2$)

Accumulated doses = 2.4x10^7, 7x10^7, and 1.5 x10^8 Gy (highest dose is equivalent to about 25 years storage for defense HLW glasses)

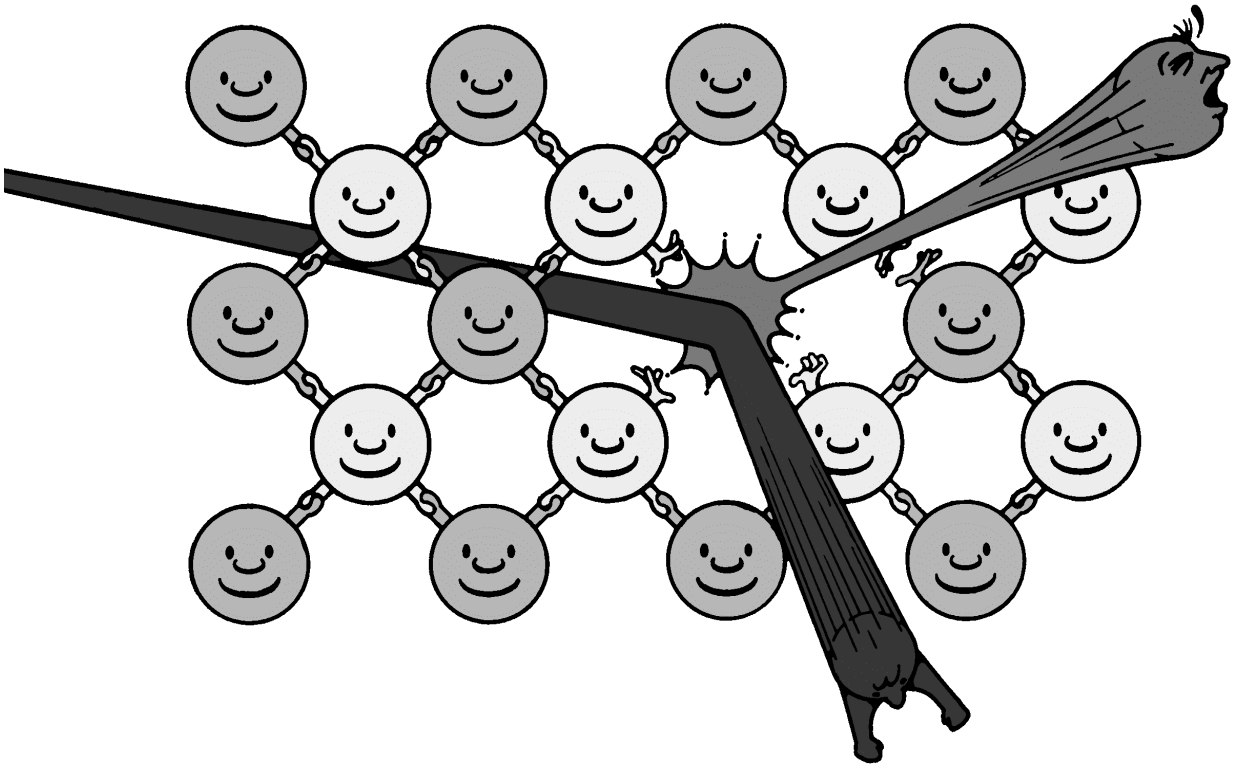
Characterization Methods

- UV-VIS, Raman, FTIR, and ESR

Observations

- No significant changes in volume
- Some electronic defects are observed in optical absorption spectra
- Peroxy radical defects formed at all temperatures (Fe-free glasses)
- Boron-oxygen hole centers produced in Na-borosilicate glasses

Threshold Displacement Energy



- Minimum Kinetic Energy to Displace an Atom from Its Normal Site
- Important Damage Parameter for Alpha Particles
- Important Damage Scaling Parameter for both Alpha-Recoils and Ion-Beam Simulation Experiments

For $ZrSiO_4$, Energy Minimization Methods Yield:

$E_d(Zr)=80$ eV, $E_d(Si)=20$ eV, and $E_d(O)=45$ eV

Threshold Displacement Processes in Zircon

Point defect notation

Replacement

Zr_{Zr}	Replacement of a Zr site by another Zr atom
Si_{Si}	Replacement of a Si site by another Si atom
O_O	Replacement of an O site by another O atom

Substitution

Zr_{Si}	Substitution of a Si site with a Zr atom
Si_{Zr}	Substitution of a Zr site with a Si atom

Interstitial

Zr_i	A Zr atom in an interstitial position
Si_i	A Si atom in an interstitial position
O_i	A O atom in an interstitial position

Vacancy

V_{Zr}	A vacancy in the Zr sublattice
V_{Si}	A vacancy in the Si sublattice
V_O	A vacancy in the O sublattice

Threshold Displacement Processes in Zircon

Results of Molecular Dynamics Simulations

Displacements: Zr sublattice

Direction	E_d (eV)	Point defect types							
		Zr_{Zr}	V_{Zr}	Zr_i	V_{Si}	Si_i	Zr_{Si}	Si_{Zr}	O_O
[110]	98 ± 2		1	1	1	1			
[111]	110 ± 3	1	1	1					
[001]	119 ± 6		1			1	2	1	
[210]	122 ± 3		1	1	1	1			
[101]	143 ± 3		1	1					
[100]	146 ± 3	1	1	1					
[011]	166 ± 3	3	1	1					3

Displacements: Si sublattice

Direction	E_d (eV)	Point defect types				
		V_{Si}	Si_i	V_O	O_i	O_O
$[\bar{1}0\bar{1}]$	48 ± 2	1	1	1	1	2
$[11\bar{1}]$	48 ± 2					3
[111]	52 ± 2					3
[011]	65 ± 5			1	1	1

Displacements: O sublattice

Direction	E_d (eV)	Point defect types		
		V_O	O_i	O_O
$[02\bar{1}]$	23 ± 2	1	1	
[111]	44 ± 2			3
[010]	34 ± 2	2	2	2
[201]	68 ± 2	1	1	
[001]	82 ± 4	1	1	3
[100]	93 ± 2	1	1	4
$[\bar{1}01]$	107 ± 6	1	1	3

Defect Migration Energies in Zircon

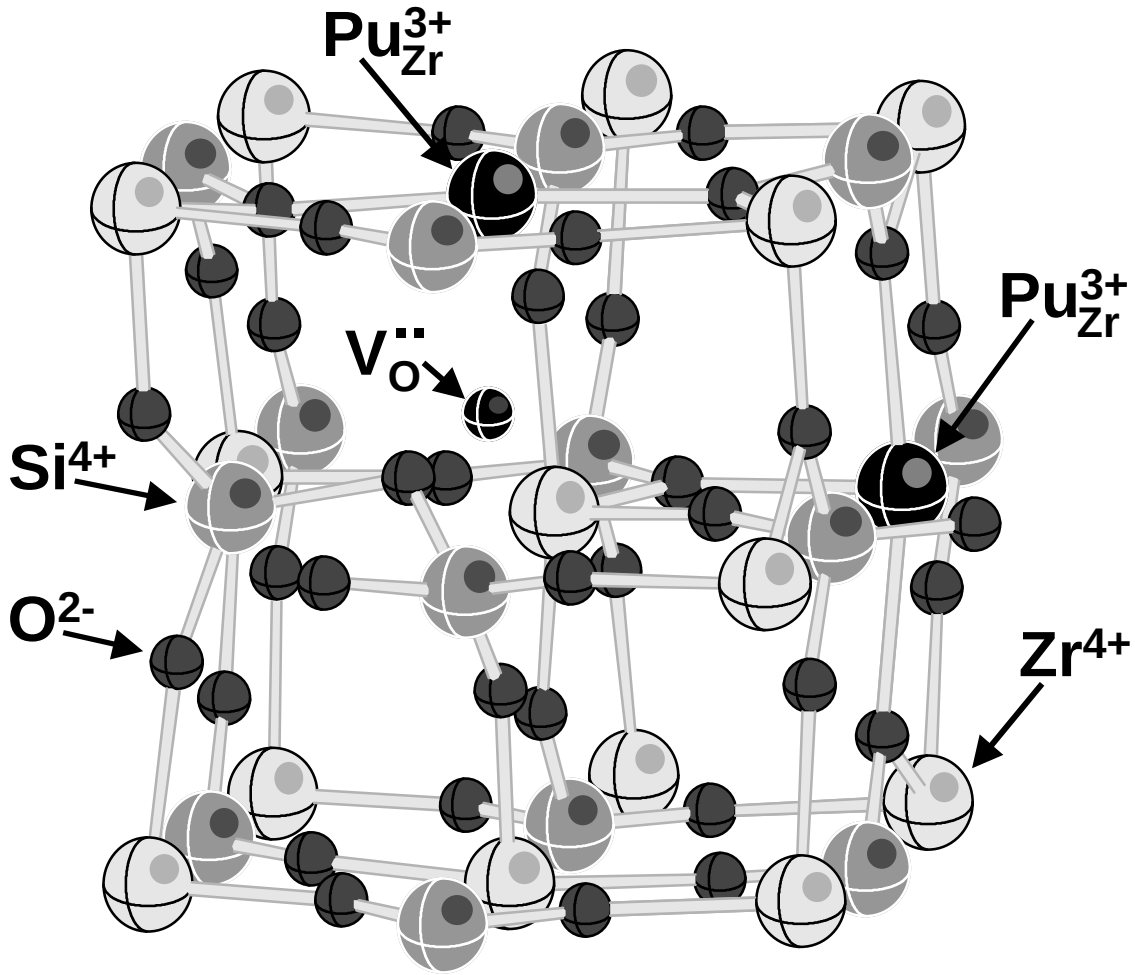
Vacancy Formation & Migration Energies
(calculated using energy minimization methods)

Type	Formation Energy	Migration Energy
O	**3.3 eV**	**1.2 eV**
Zr	**6.2 eV**	**1.2 eV**
Si	**--**	**--**

Reference: RE Williford, WJ Weber, R Devanathan, and AN Cormack, **Native Vacancy Migrations in Zircon**, *Journal of Nuclear Materials* **273** (1999) 164-170.

To be done: Determine Interstitial Migration Energies (these control many recovery processes under repository conditions). Calculate Defect Migration Energies in Pyrochlore Systems.

Lowest Energy Configurations for Pu in Zircon



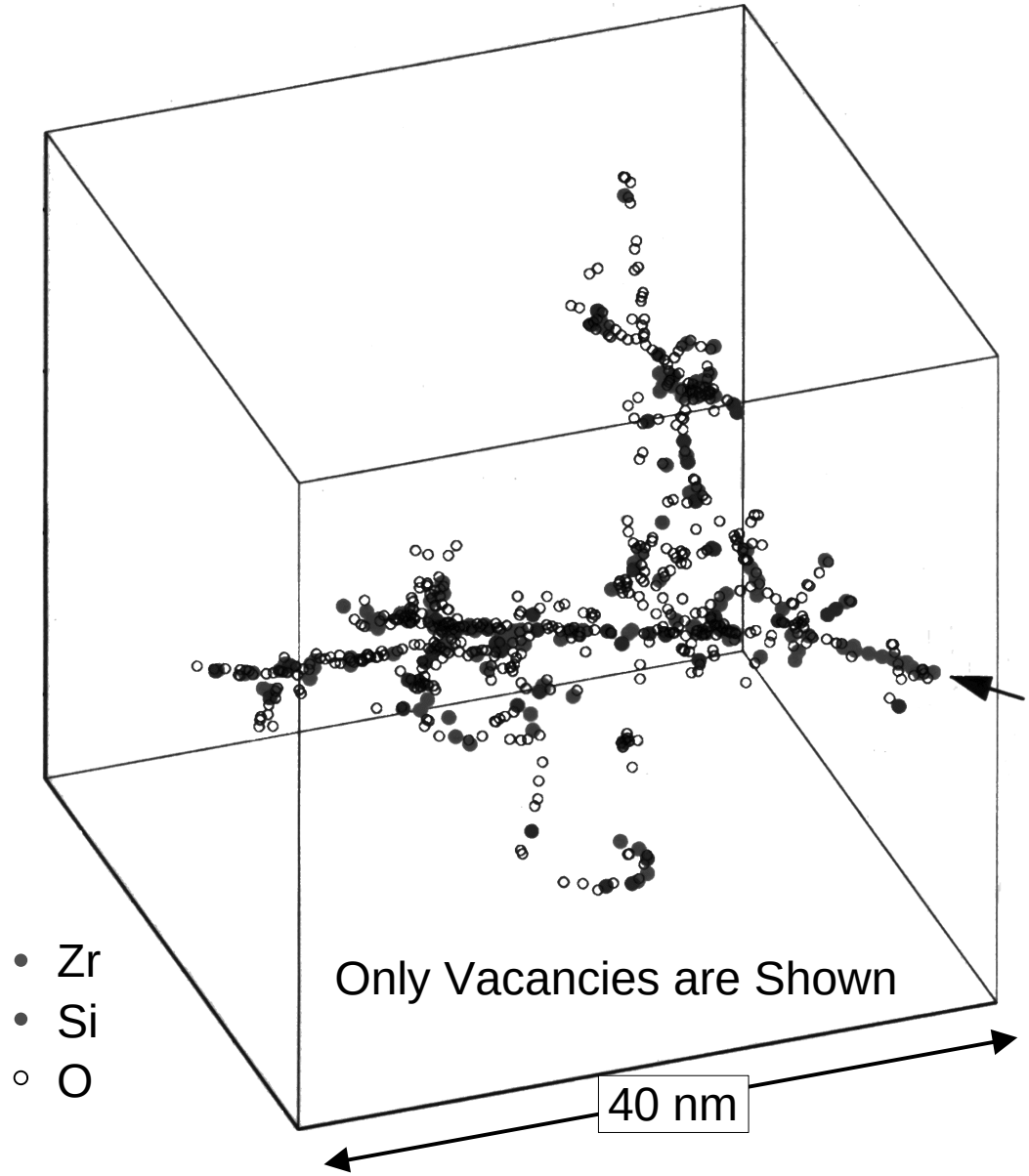
$Pu^{3+} \rightarrow 2Pu^{3+}_{Zr} + V_O$ defect cluster (1.0 eV/Pu)

$Pu^{4+} \rightarrow Pu^{4+}$ substituted on Zr^{4+} site (0.3 eV/Pu)

Reference: RE Williford, BD Begg, WJ Weber, and NJ Hess, **Computer Simulation of Pu^{3+} and Pu^{4+} Substituions in Zircon**, *Journal of Nuclear Materials* **278** (2000) 207-211.

Displacement Cascade in Zircon

94 keV ^{234}U-Recoil Cascade Calculated using Binary Collision Code MARLOWE



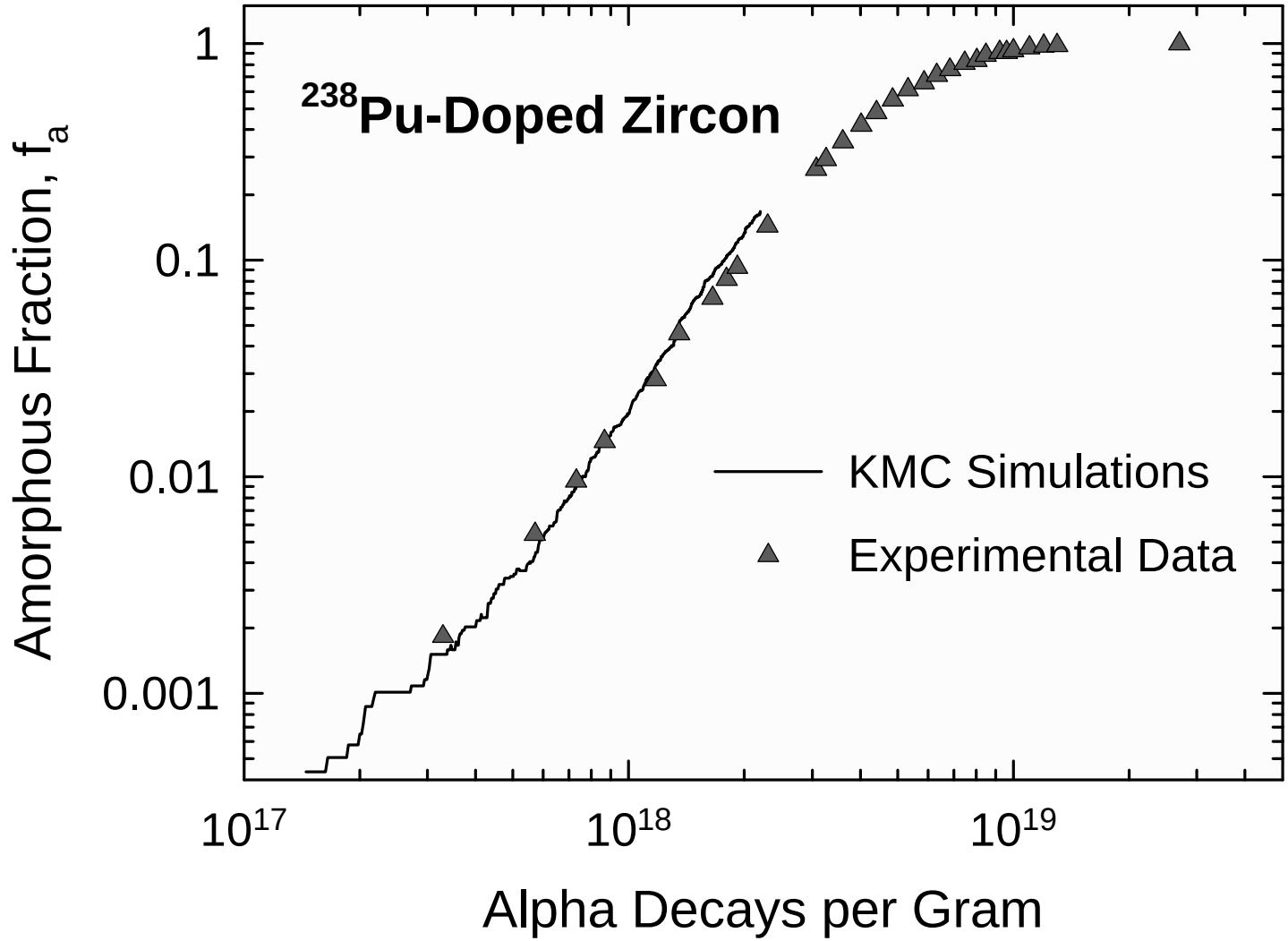
MARLOWE gives the most realistic description of defect production from alpha-recoil cascades available at this time.

Good first order approximation to cascade damage needed as input to kinetic Monte Carlo simulations.

Have generated hundreds of different high-energy cascades for good statistics

Zircon: Kinetic Monte Carlo Simulation

1000 ^{234}U cascades from MARLOWE randomly generated in simulation cell



Good Agreement between Experiment and Simulation.

Reference: HL Heinisch and WJ Weber, *Journal of Nuclear Materials* (2000) submitted.

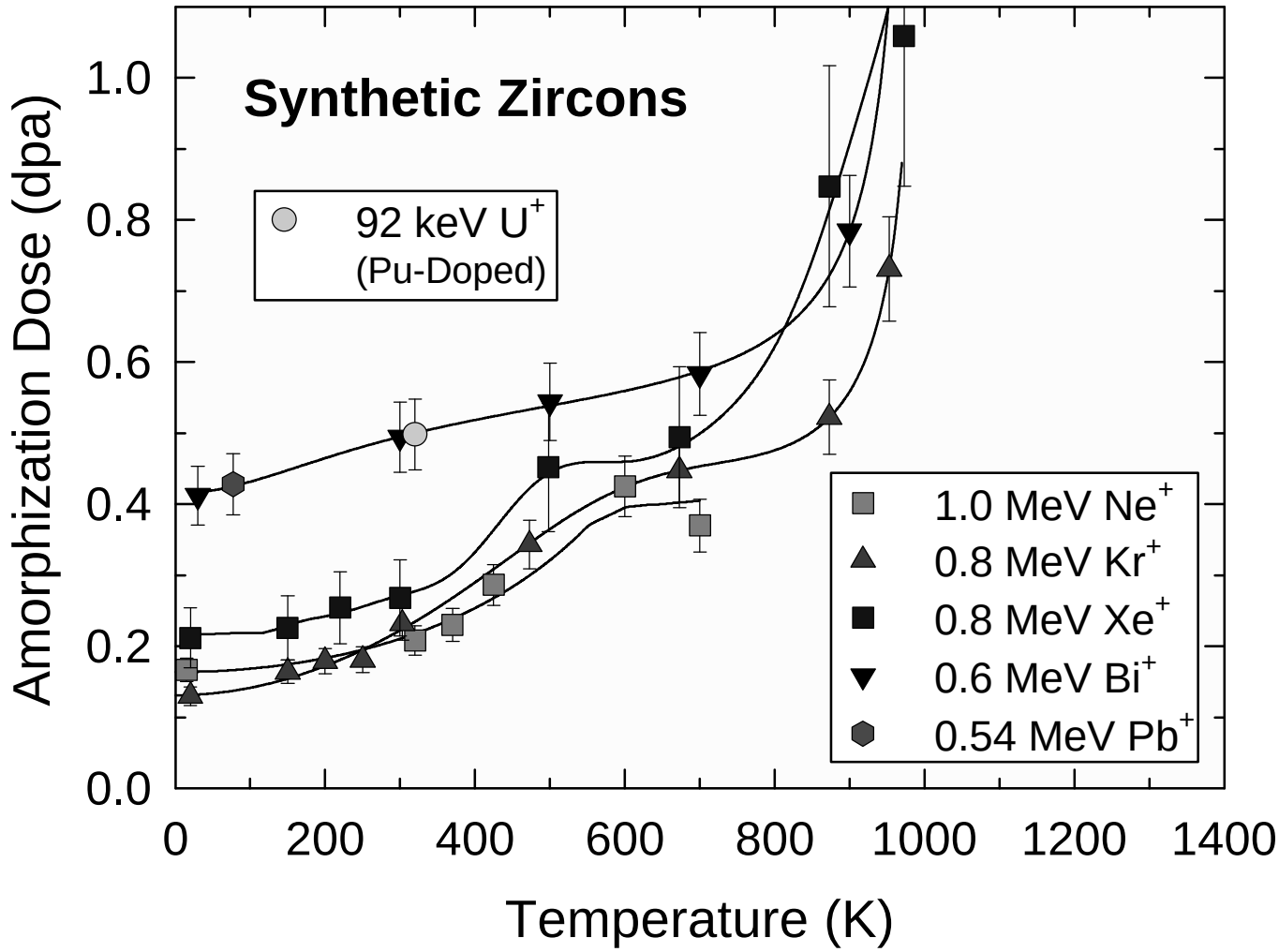
Pu-Containing Zircon: XAS & XRD Results

- Pu present as Pu^{3+} (preparation under Ar atmosphere).
- Pu^{3+} oxidized to Pu^{4+} below 1000°C.
- Amorphization state retains distorted zircon structure and stoichiometry, consisting of SiO_4 and ZrO_8 polyhedra rotated relative to each other.
- Direct recrystallization of crystalline zircon from amorphous state occurs at 1200°C if heated rapidly.
- Decomposition to oxides occurs if heated at 1000°C for 12 hours.

To be done: Annealing Study of Oxidation of Pu^{3+} to Pu^{4+} (determine relative oxygen vacancy mobility in crystalline and amorphous states) and Study of Changes in Dissolution Kinetics and Solubilities.

Amorphization Kinetics in Zircon

In Situ Study of Temperature and Ion-Mass Dependence

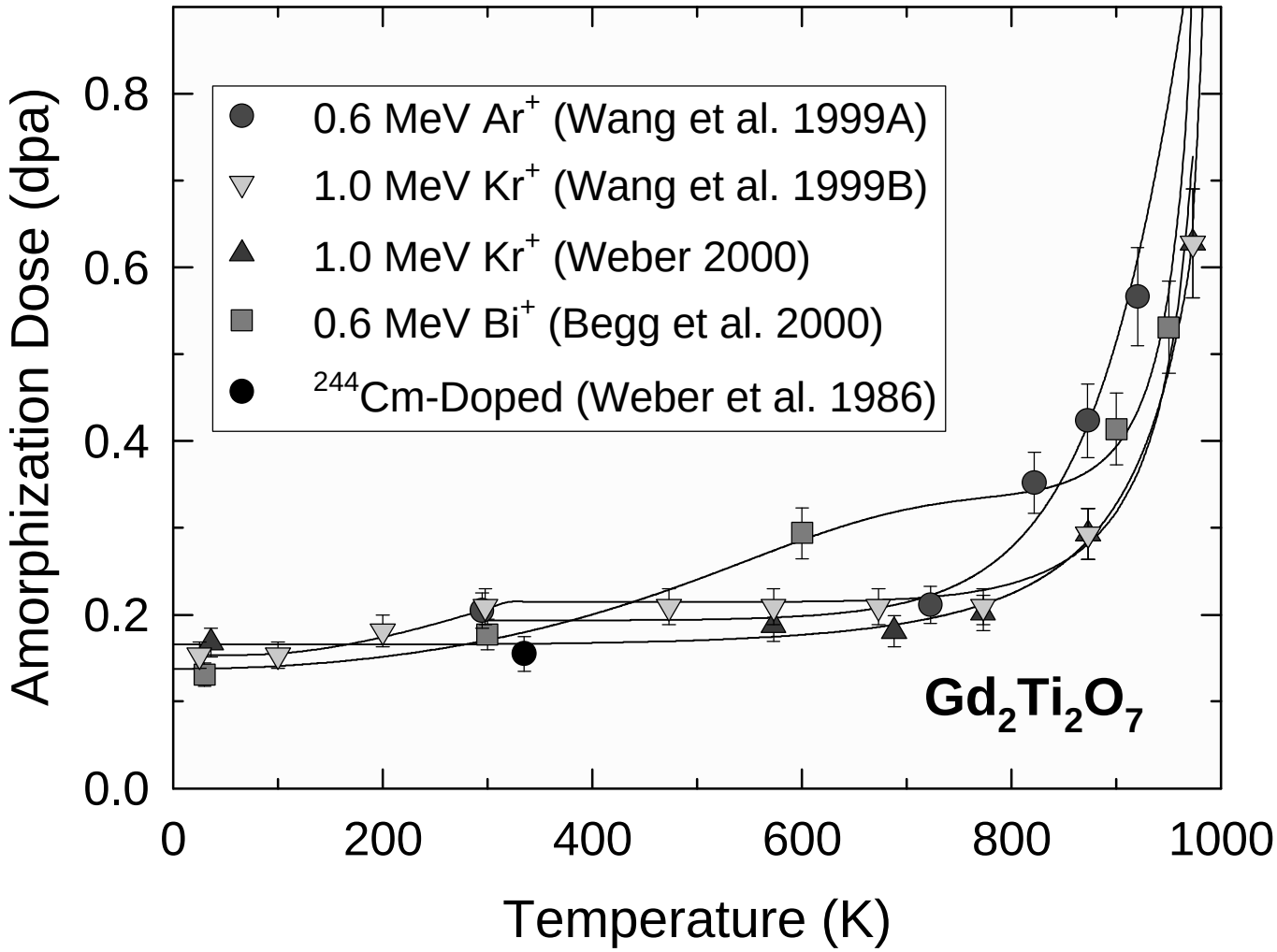


Good agreement between heavy-ion (Pb & Bi) simulations and ^{238}Pu results.

Heavy ions are less effective in amorphization of zircon. This may be due to decreased defect survival from in-cascade recovery processes.

Reference: WJ Weber et al., *MRS Symp. Proc.* **540** (1999) 367-372.

Amorphization Kinetics in Gadolinium Titanate

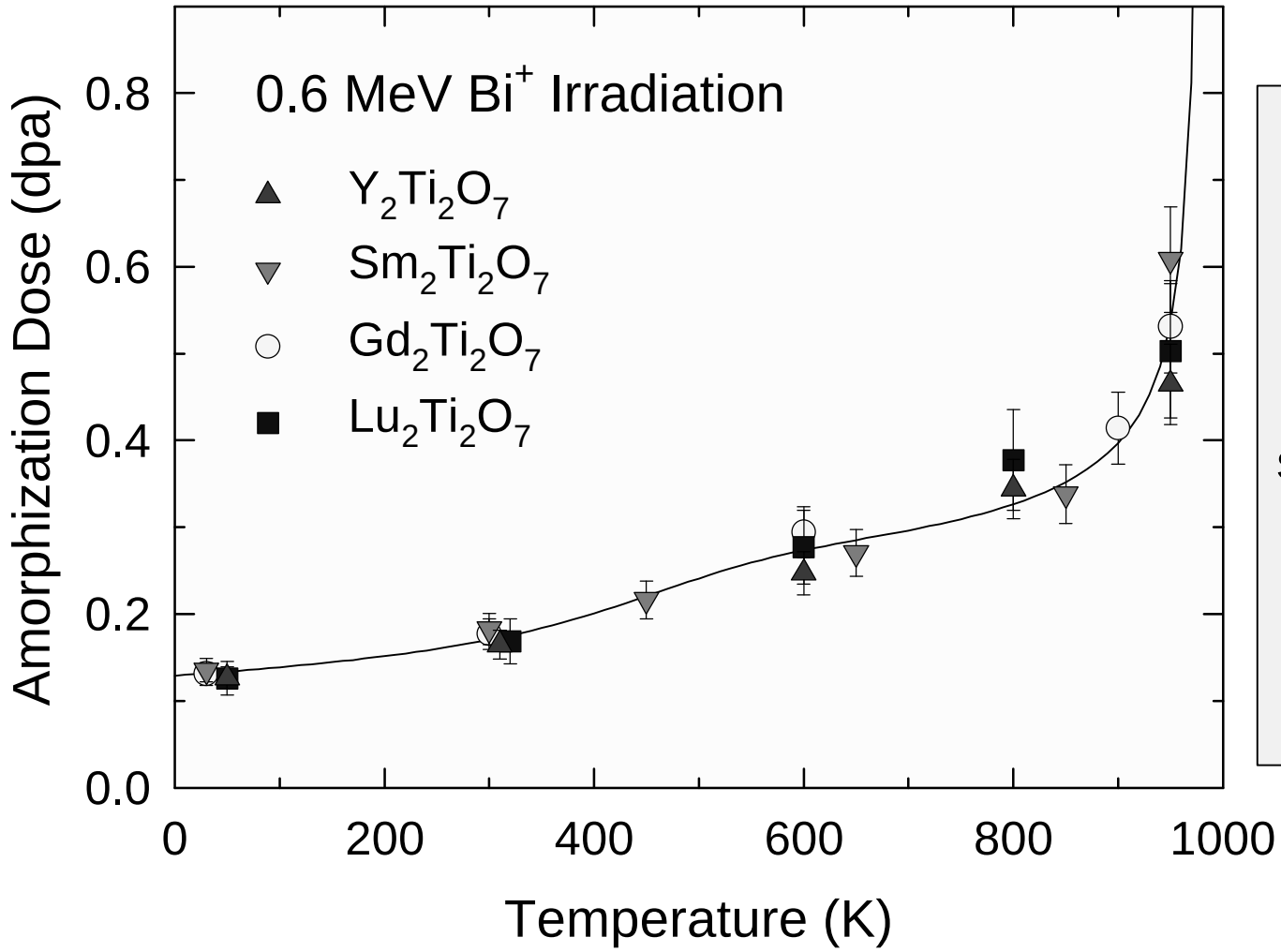


Results indicate good agreement between ion-beam simulations and ^{244}Cm doping experiments.

The critical temperature, T_c, appears independent of ion mass, which suggests T_c is determined by a thermal recovery process.

Amorphization in Pyrochlores

In Situ Study of Temperature and Composition Dependence



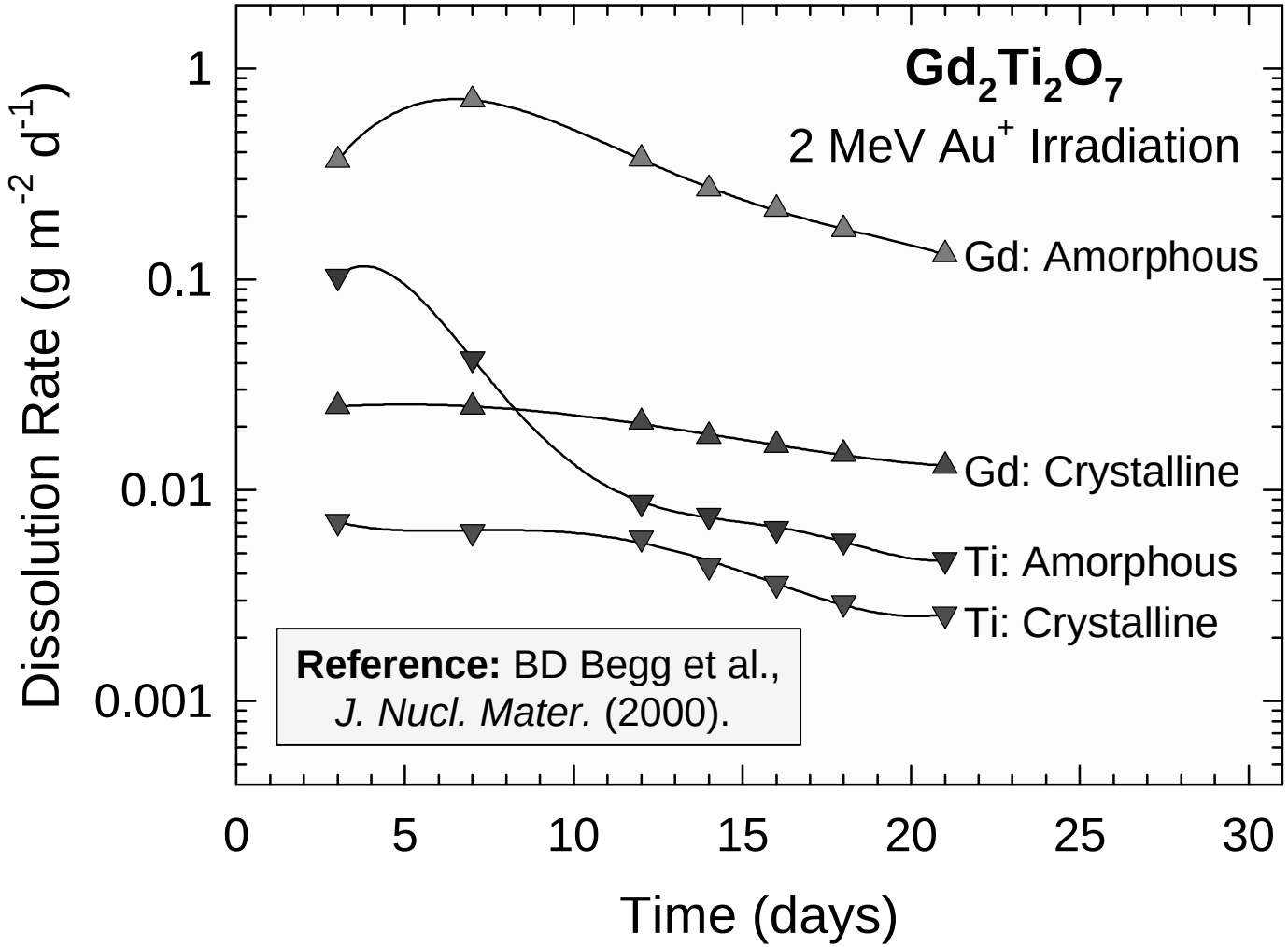
Results suggest that the temperature dependence of amorphization is similar for a range of rare-earth titanates with the pyrochlore structure.

Reference: BD Begg et al., *Amer. Ceram. Soc. Symp. Proc.* (2000) in press.

Dissolution Rates for Gadolinium Titanate

Radiation-Induced Amorphous State vs Unirradiated Crystalline State

Single-Pass Flow-Through Test Method: 90°, pH 2



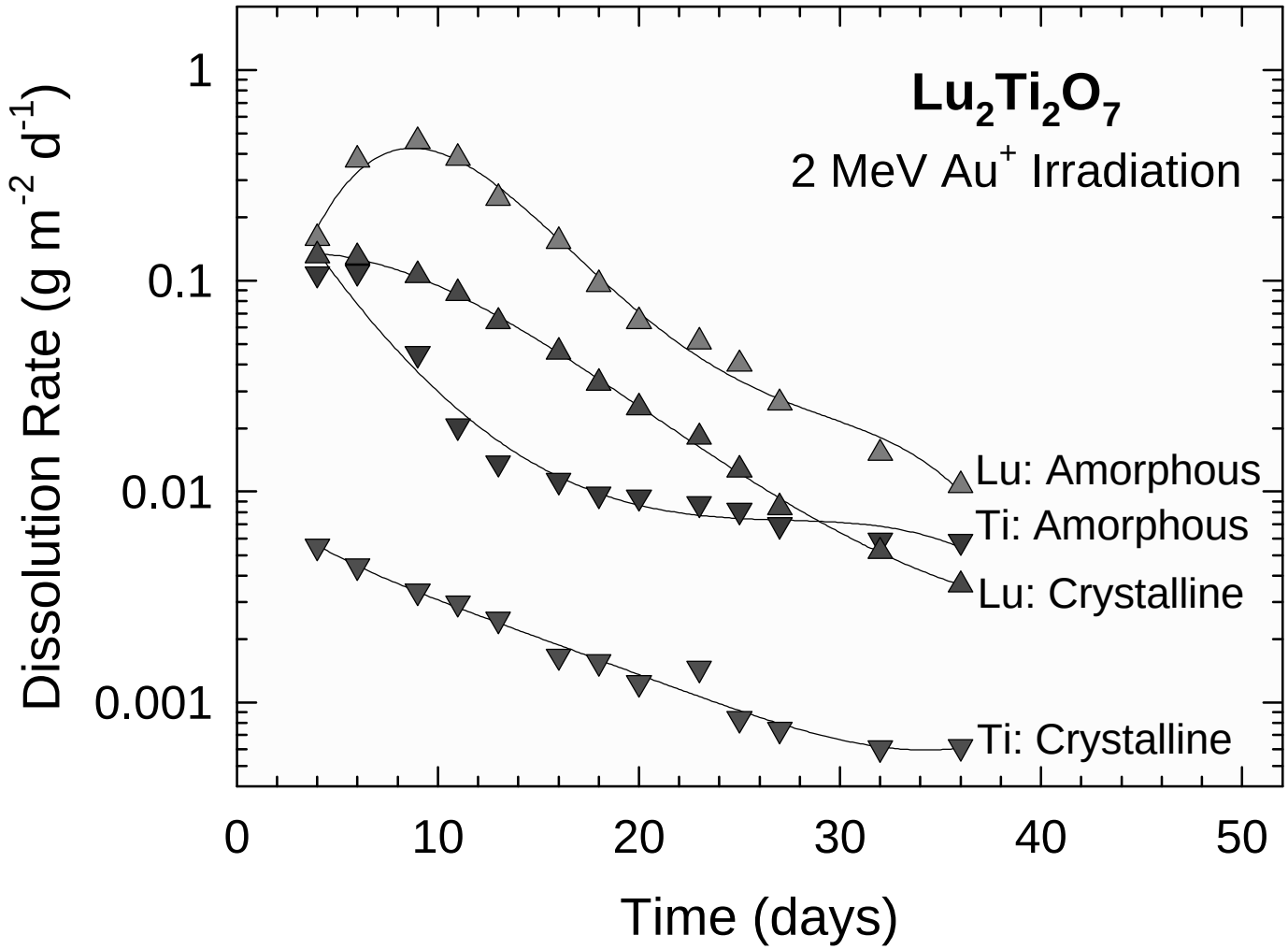
Results suggest incongruent dissolution and that radiation-induced amorphization increases the dissolution rates for Gd by ~10x and for Ti by ~2x.

These results are also consistent with the 20x and 50x increases in dissolution rates for Cm and Pu, respectively, in Cm/Pu-doped $Gd_2Ti_2O_7$ (Wald & Weber, 1984).

Dissolution Rates for Lutetium Titanate

Radiation-Induced Amorphous State vs Unirradiated Crystalline State

Single-Pass Flow-Through Test Method: 90°, pH 2



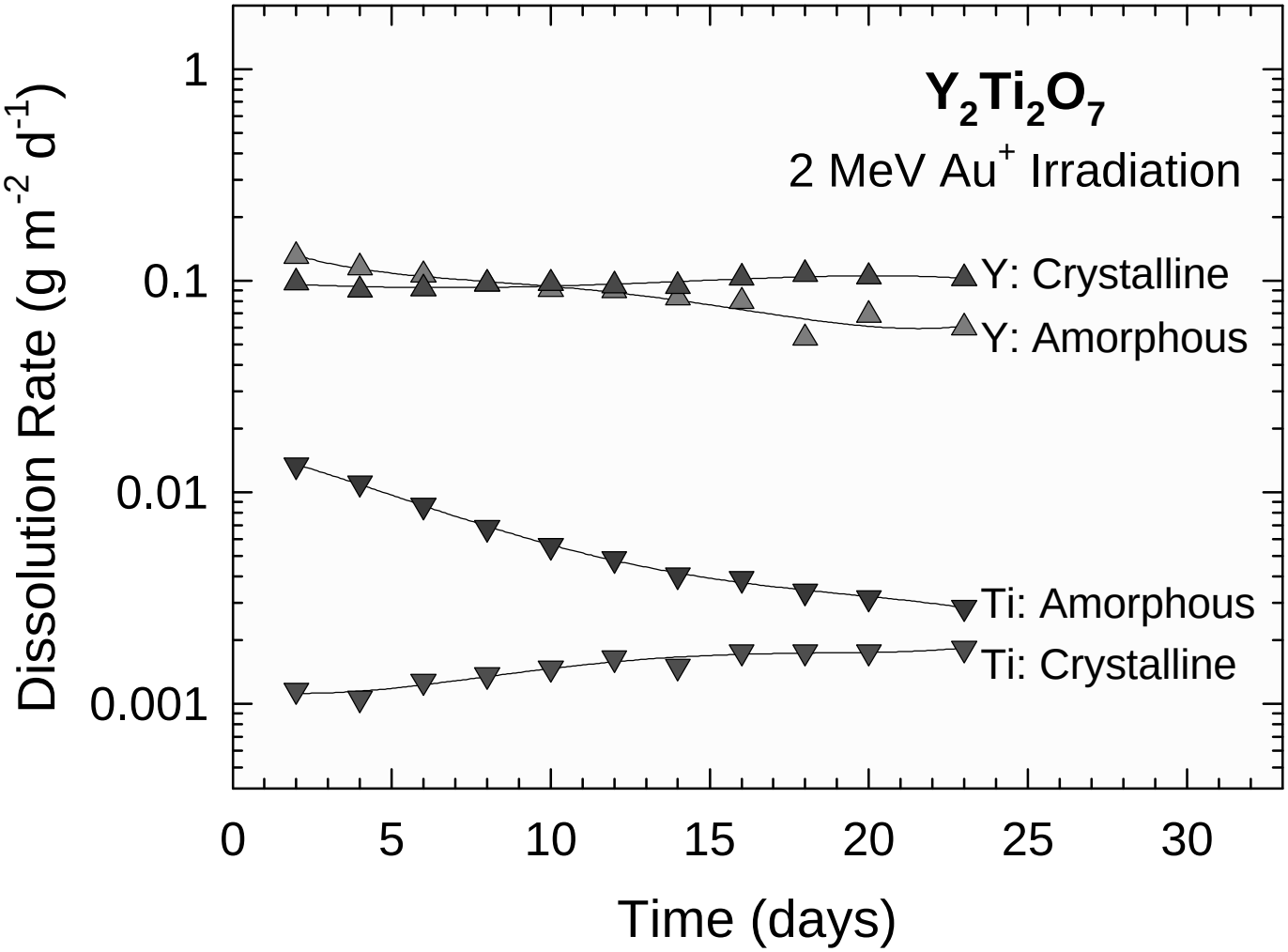
Results suggest radiation-induced amorphization increases the dissolution rates for Lu by ~3x and for Ti by ~10x. Results also support incongruent dissolution

Reference: BD Begg et al., *Journal of Nuclear Materials* (2000) submitted.

Dissolution Rates for Yttrium Titanate

Radiation-Induced Amorphous State vs Unirradiated Crystalline State

Single-Pass Flow-Through Test Method: 90°, pH 2



Results suggest radiation-induced amorphization decreases the dissolution rate for Y by ~1.5x and increases the dissolution rate for Ti by ~1.7x. Results also support incongruent dissolution

Reference: BD Begg et al., *Journal of Nuclear Materials* (2000) submitted.

Potential Benefits

New Scientific Understanding and Scientifically-Based Models on the Effects of Radiation on Structure and Chemical Durability will lead to the following benefits:

- Development of Improved Materials for the Immobilization of High-Level Tank Wastes and Stabilization of Nuclear Materials
- Development of Scientifically-Based Predictive Models of Performance for Nuclear Waste Forms and Stabilized Nuclear Materials
- Stronger Scientific Basis for Performance Assessments will assist with Regulatory Approval and Public Acceptance