Radiation Effects on Materials in the Near-Field of a Nuclear Waste Repository

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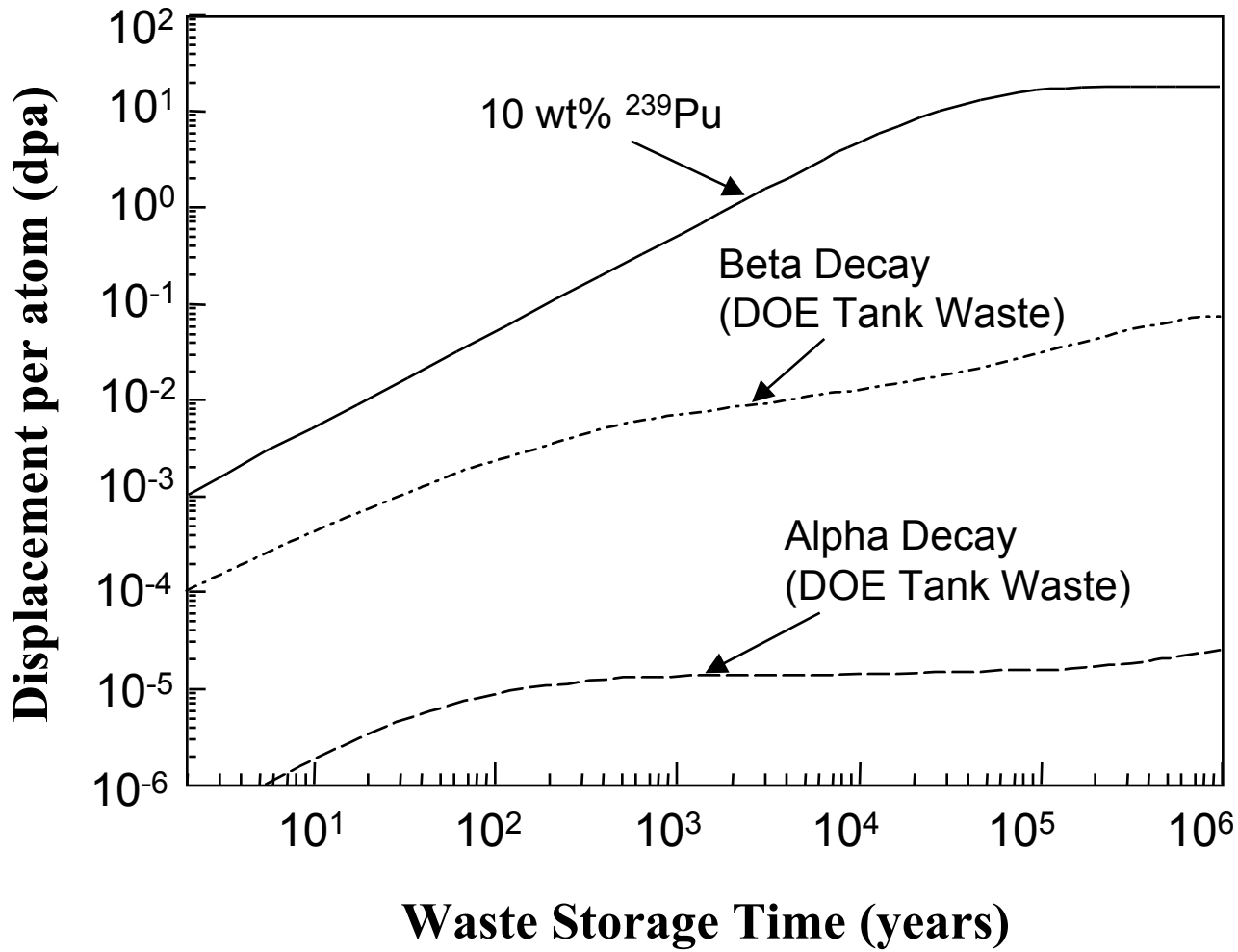
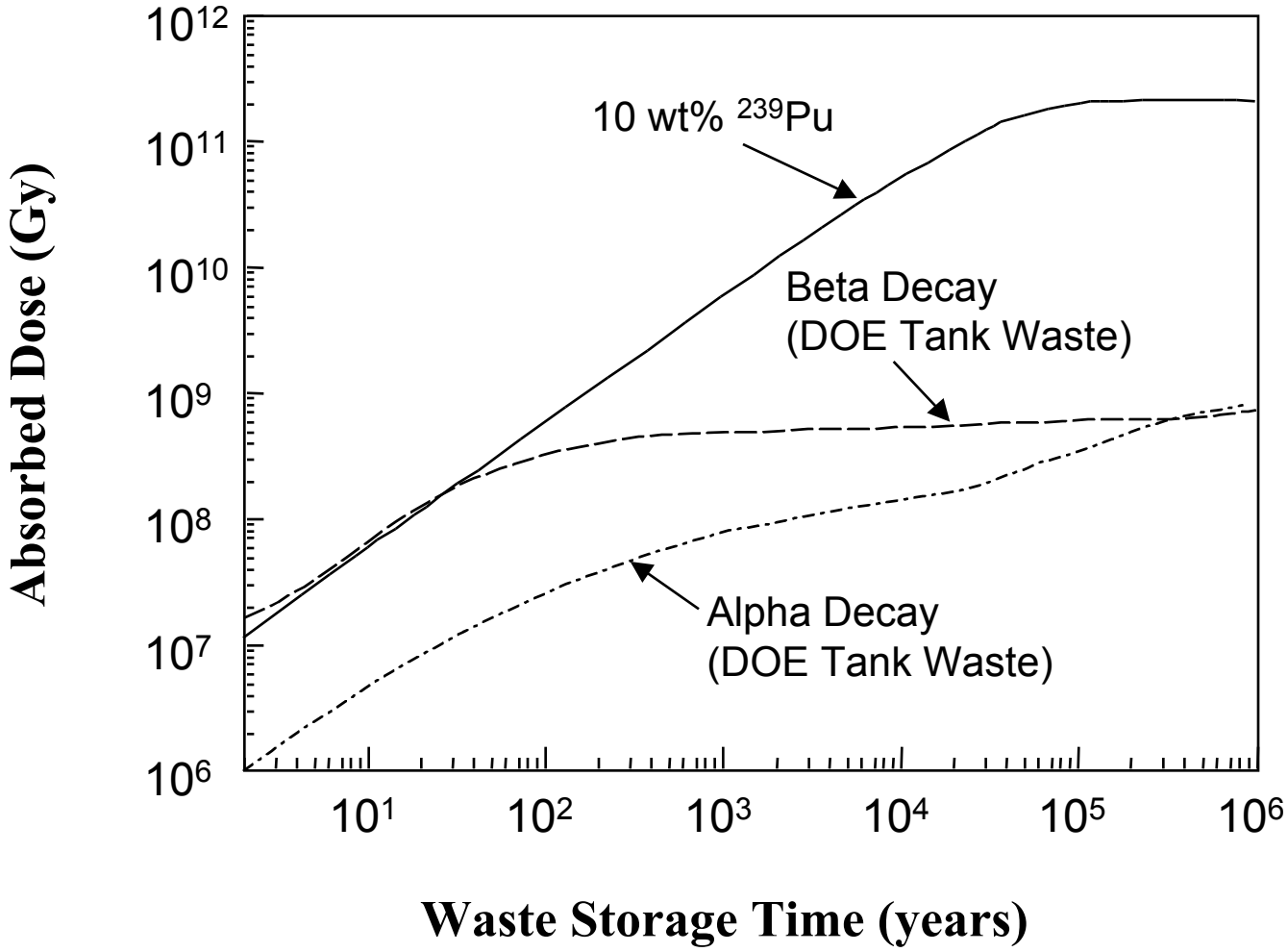
Introduction

Site restoration activities at DOE facilities and the permanent disposal of nuclear waste generated at DOE facilities involve working with and within various types and levels of radiation fields. Once the nuclear waste is incorporated into a final form, radioactive decay will decrease the radiation field over geologic time scales, but the alpha-decay dose for these solids will still reach values as high as 10^{18} alpha-decay events/gm in periods as short as 1,000 years. This dose is well within the range for which important chemical (e.g., increased leach rate) and physical (e.g., volume expansion) changes may occur in crystalline ceramics. Release and sorption of long-lived actinides (e.g., 237Np) can provide a radiation exposure to backfill materials, and changes in important properties (e.g., cation exchange capacity) may occur. The objective of this research program is to evaluate the long term radiation effects in the materials in the near-field of a nuclear waste repository with accelerated experiments in the laboratory using energetic particles (electrons, ions and neutrons). Experiments on the microstructural evolution during irradiation (particularly radiation-induced amorphization and bubble formation) in two important groups of materials, sheet silicates and zeolites, have been conducted and changes in chemical properties (e.g. cation exchange capacity and desorption rate for Cs and Sr) due to amorphization are being evaluated. The results of this study will have significant impact on the assessment of long term retention of radionuclides by sheet and porous materials in both near-field of a nuclear waste repository and high-level waste (HLW) tanks.

Displacement Damage Generated by β- and α-decay Events in Ceramics Containing DOE High-level Tank Waste and by α-decay Events in Ceramics Containing 10 wt.% ^{239}Pu



Cumulative Absorbed Dose in Ceramics Containing DOE High-level Tank Waste or Containing 10 wt.% ^{239}Pu



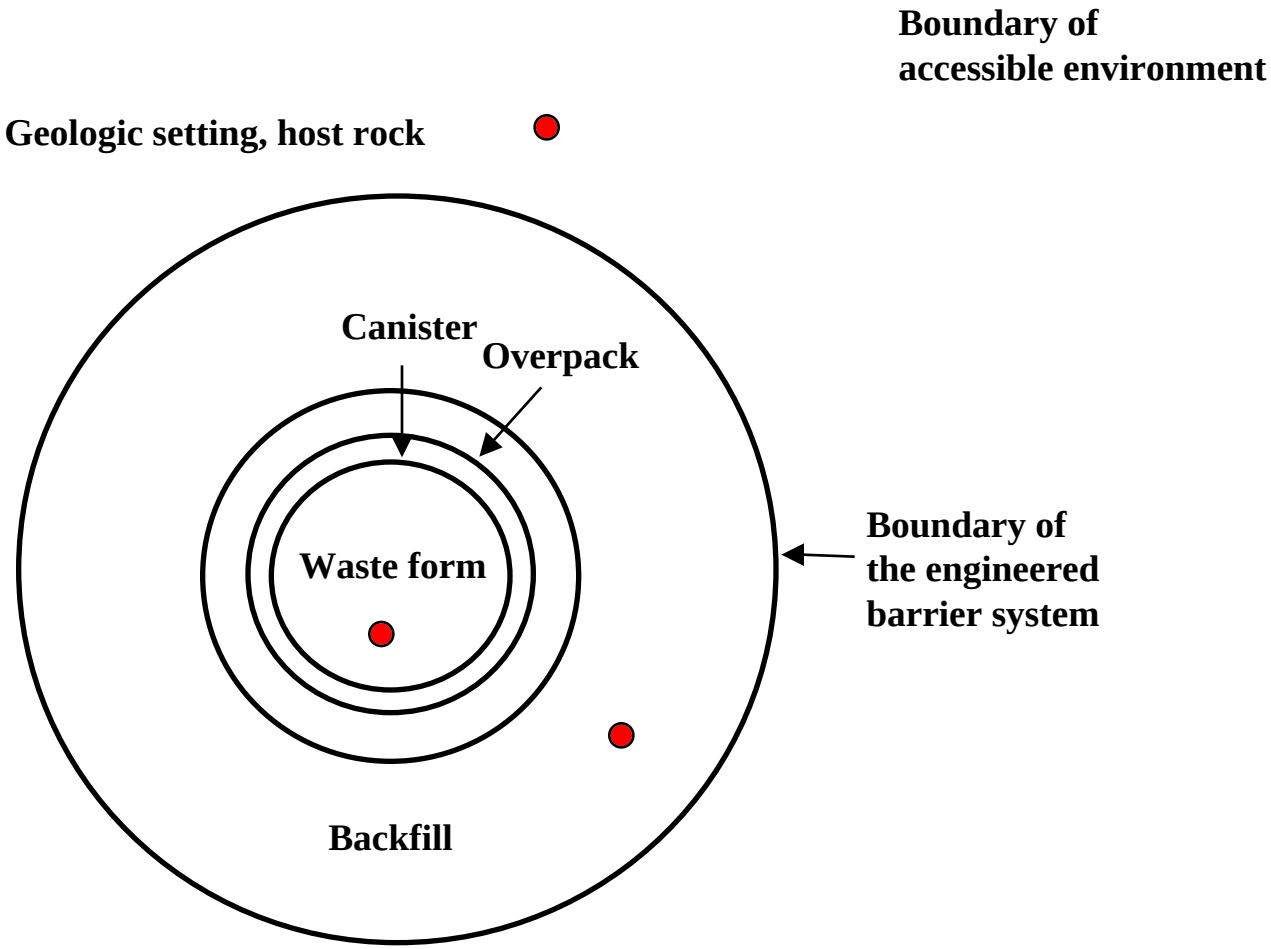
I

Radiation damage in sheet silicates and zeolites

INTRODUCTION

- Sheet silicates and zeolite group minerals may be present in various regions of the near-field of a repository system (as alteration products of borosilicate glass waste form or as waste form directly, back-fill material and in the cracks of host rocks).
- Sheet silicates and zeolites have high retention rate of radionuclides because their high sorption and/or ion-exchange capabilities.
- In the near-field, sheet silicates and zeolites will be exposed to high radiation dose due to the α- and β-decay events. Radiation effects on the structures of these materials may change the structures of these materials which results in changes in their ion-exchange, sorption and retention capability for the radionuclides.
- Radiation effects in sheet silicates and zeolites are investigated by electron and ion beam irradiations with *in situ* transmission electron microscopy in this study.

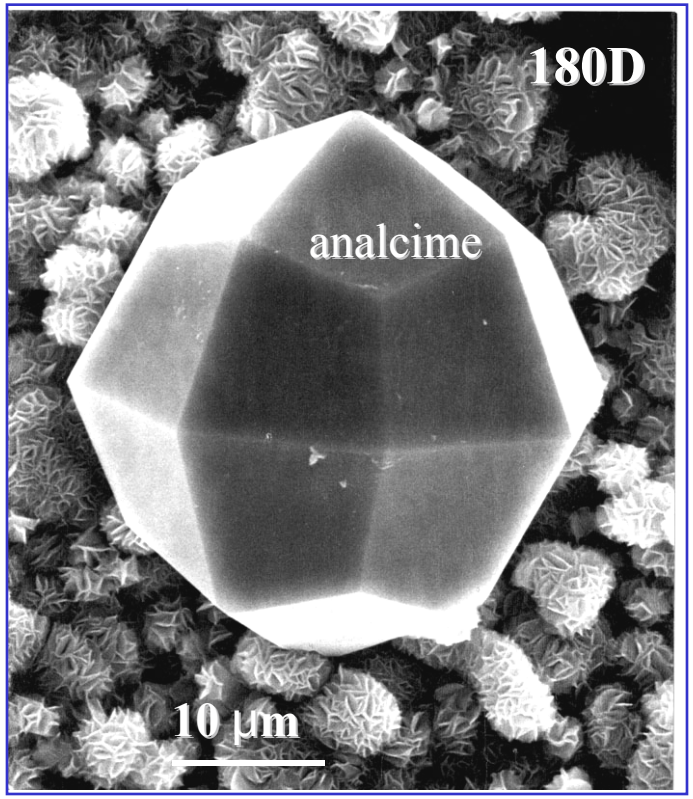
Locations where sheet silicates and zeolites may present in the near-field of a nuclear waste repository

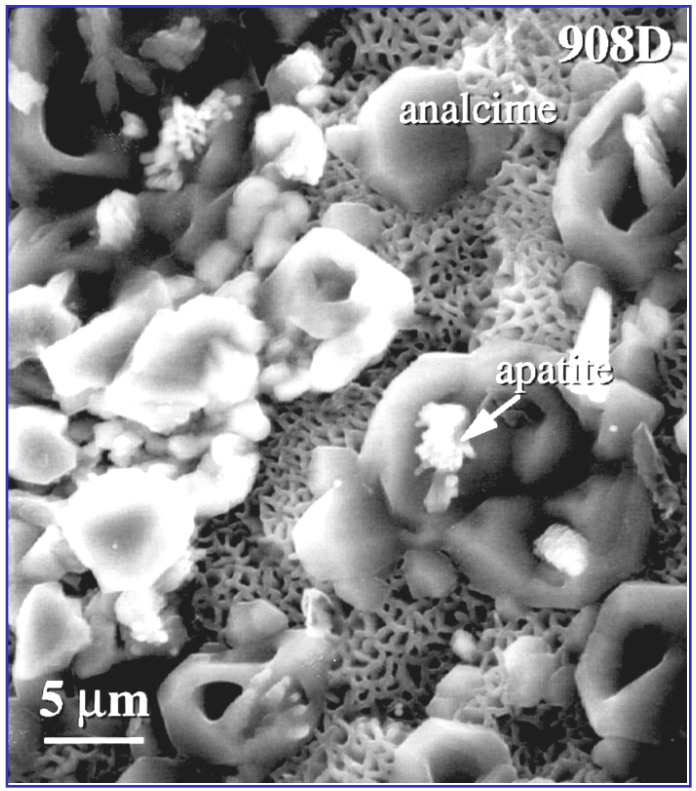


● Where sheet silicates and zeolites may present

Zeolite (analcime) Precipitates Formed on Top of a Smectite Layer on the Surface of a U.S. SRL131U Waste Glass

(after 180 or 908 days at 150 °C in saturated water vapor environment)





Experimental

Materials:

— four sheet silicate (mica) compositions:

muscovite [$KAl_2(AlSi_3O_{10})(OH,F)_2$],
phlogopite [$KMg_3(AlSi_3O10)(OH,F)_2$],
biotite [$K(Mg,Fe)_3(AlSi_3O_{10})(OH,F)_2$],
lepidolite [$K(Li,Al)_3(Al,Si)_4O_{10}(OH,F)_2$]

— four zeolite compositions:

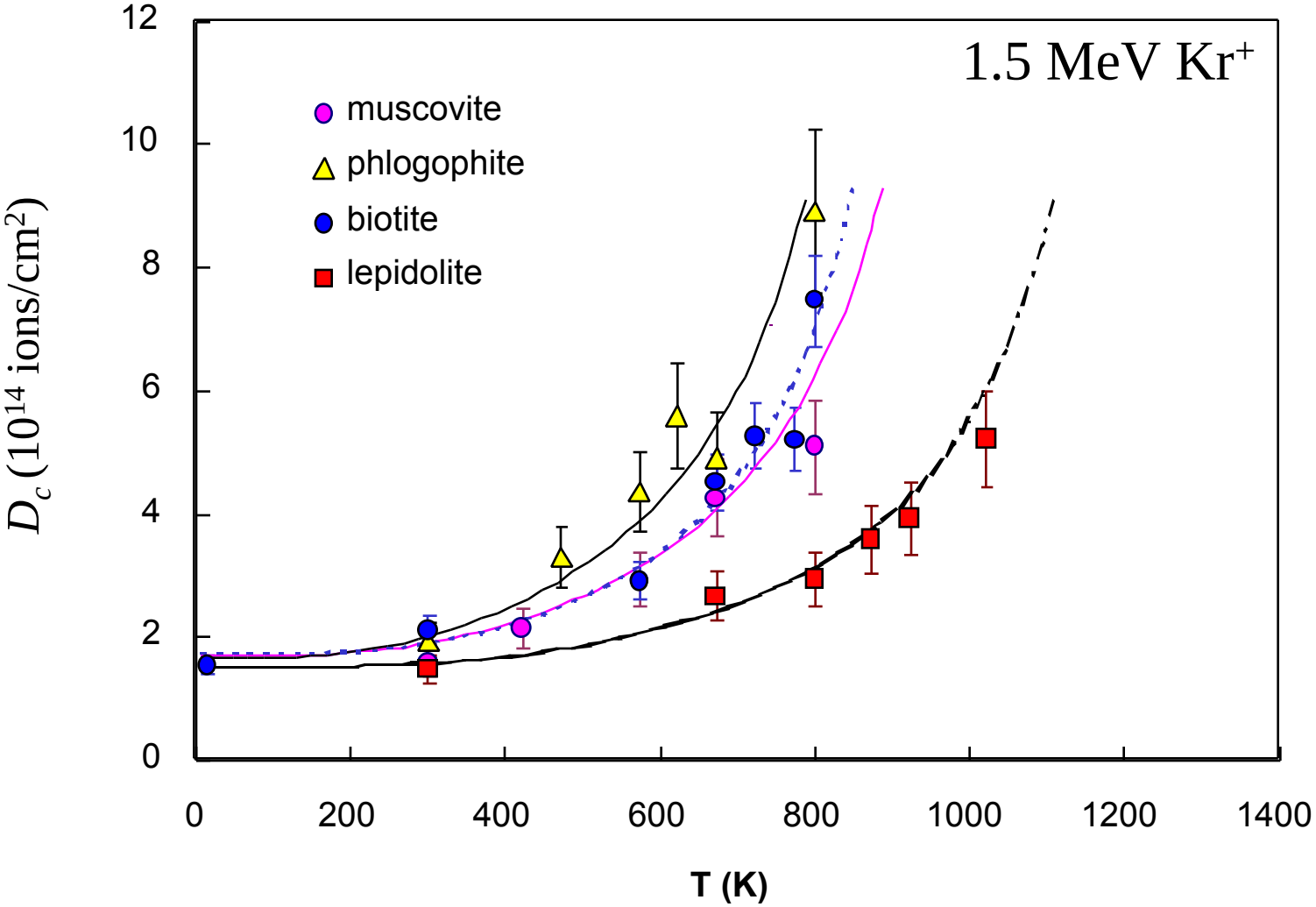
analcime ($NaAlSi_2O_6 \cdot H_2O$)
stilbite ($NaCa_2Al_5Si_{13}O_{36} \cdot 16H_2O$),
natrolite ($Na_2Al_2Si_3O_{10} \cdot 2H_2O$),
zeolite Y ($Na_7Al_7Si_{18}O_{50} \cdot xH_2O$)

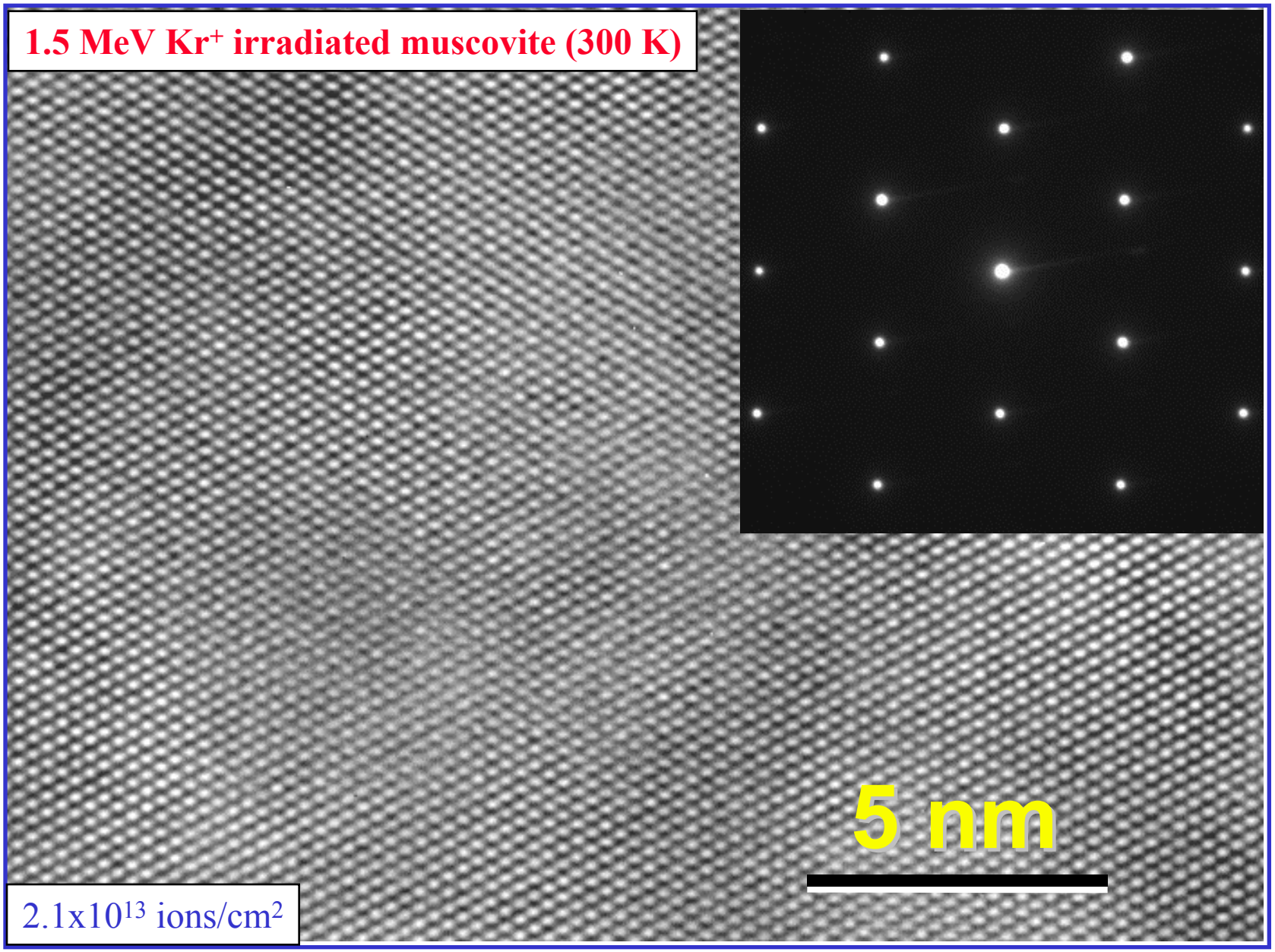
Irradiation:

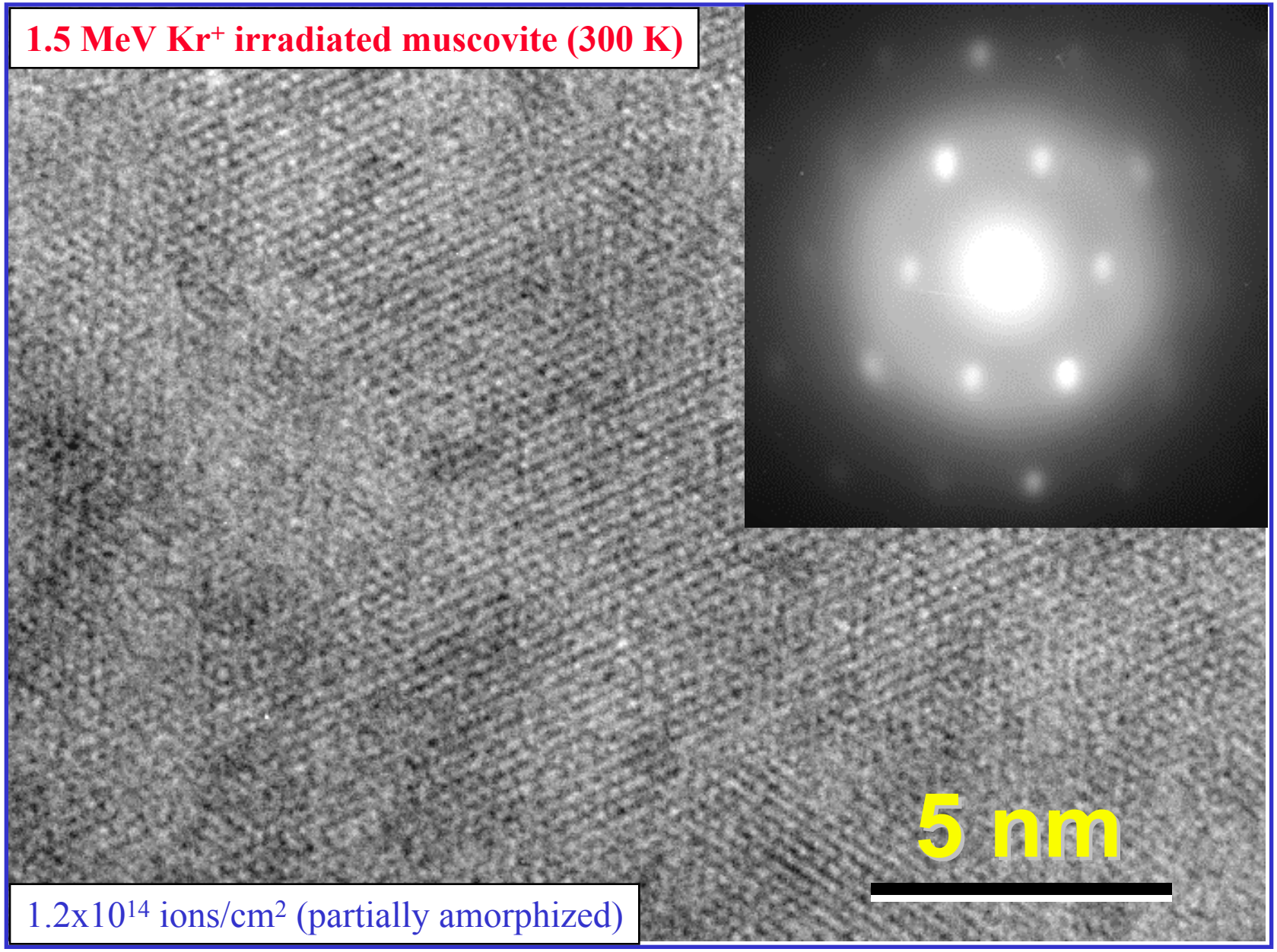
— 1.5 MeV Kr^+ ions at 20 - 1000 K with the HVEM-Tandem Facility at Argonne National Laboratory

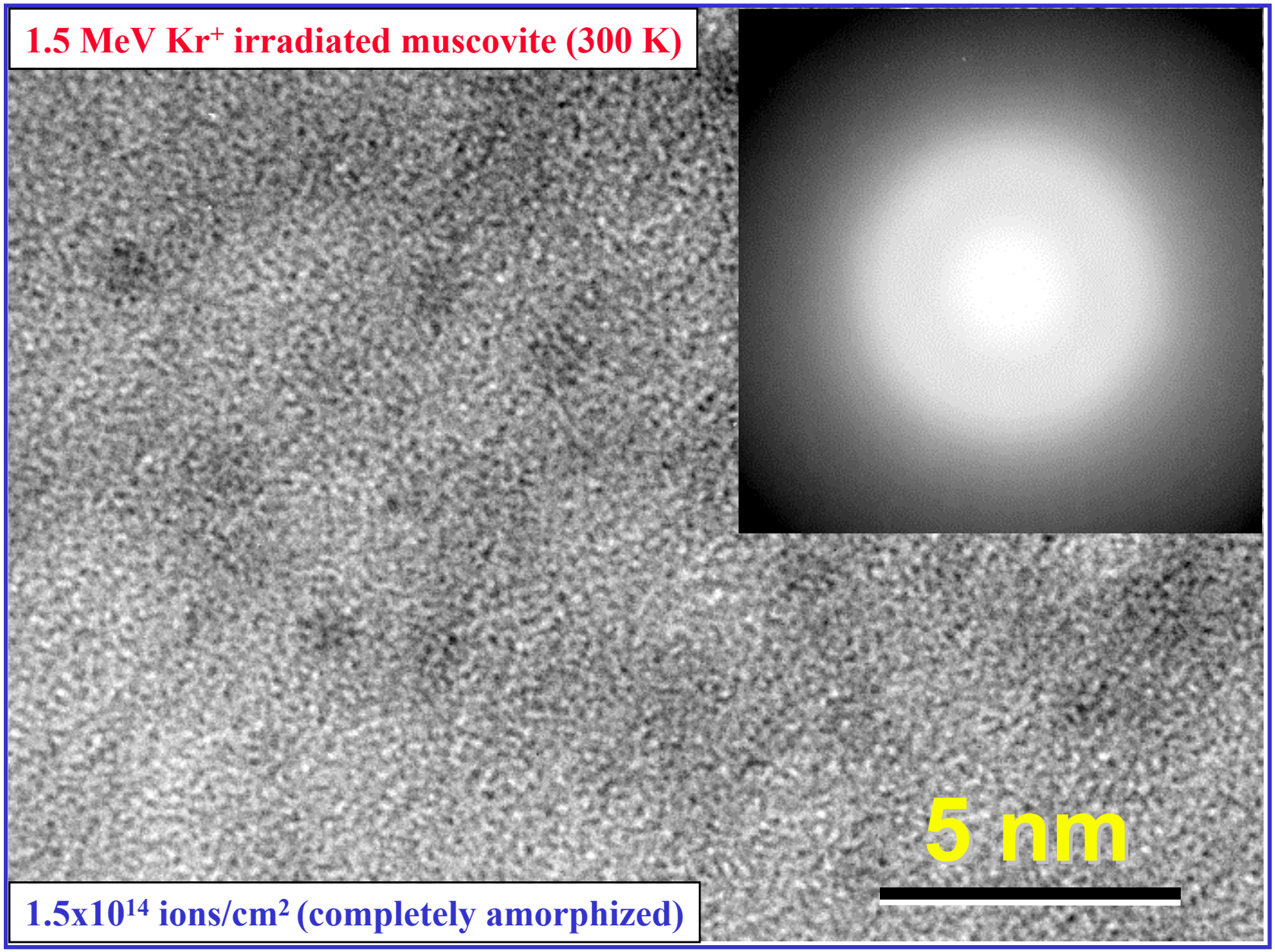
— 200 - 400 keV electrons at 300 - 800 K with transmission electron microscopes at the University of Michigan

Temperature dependence of amorphization dose of four sheet silicates (mica minerals)



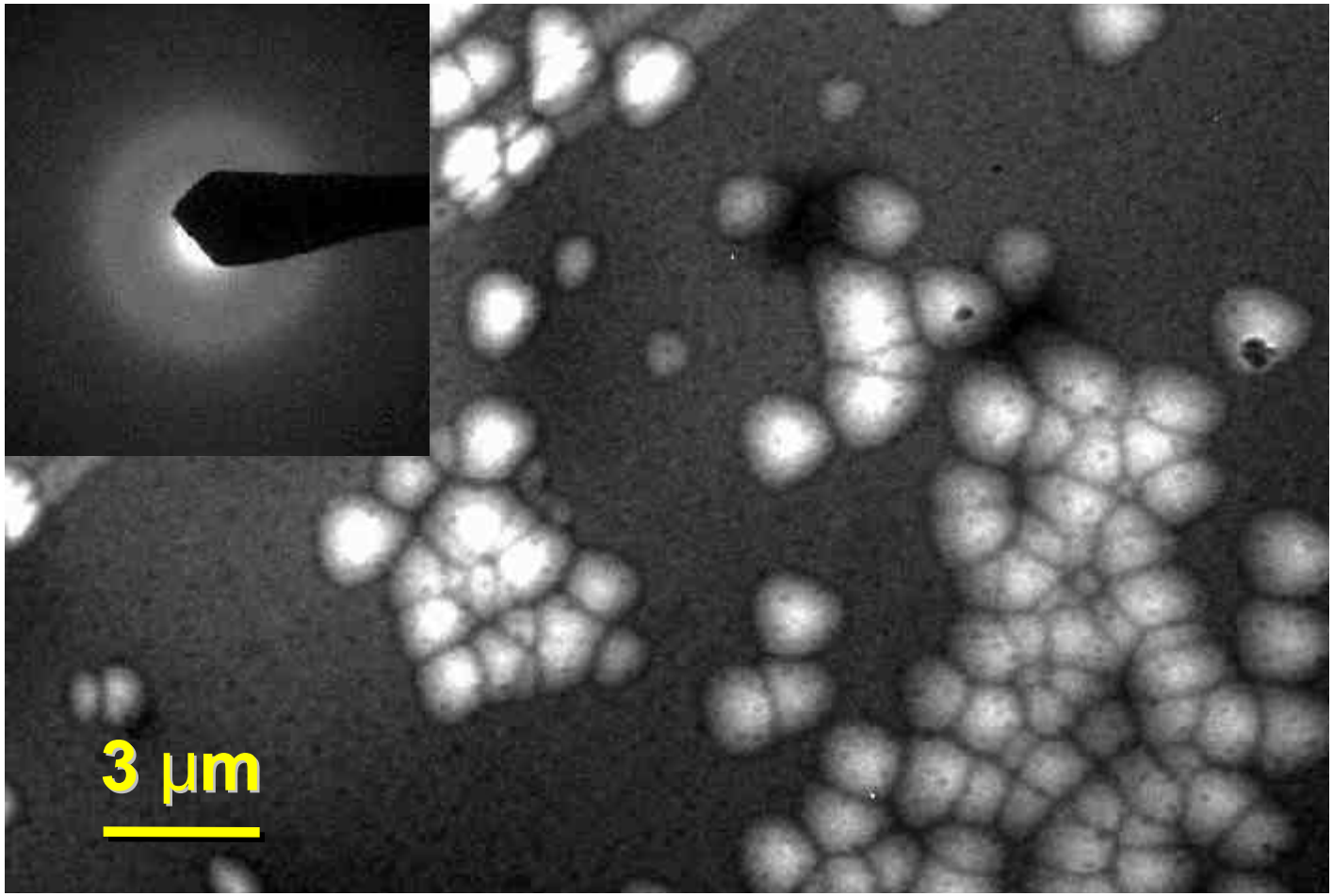

1.5 MeV Kr+ irradiated muscovite (300 K)
5 nm
2.1x10^13 ions/cm^2


1.5 MeV Kr+ irradiated muscovite (300 K)
5 nm
1.2x10^14 ions/cm^2 (partially amorphized)

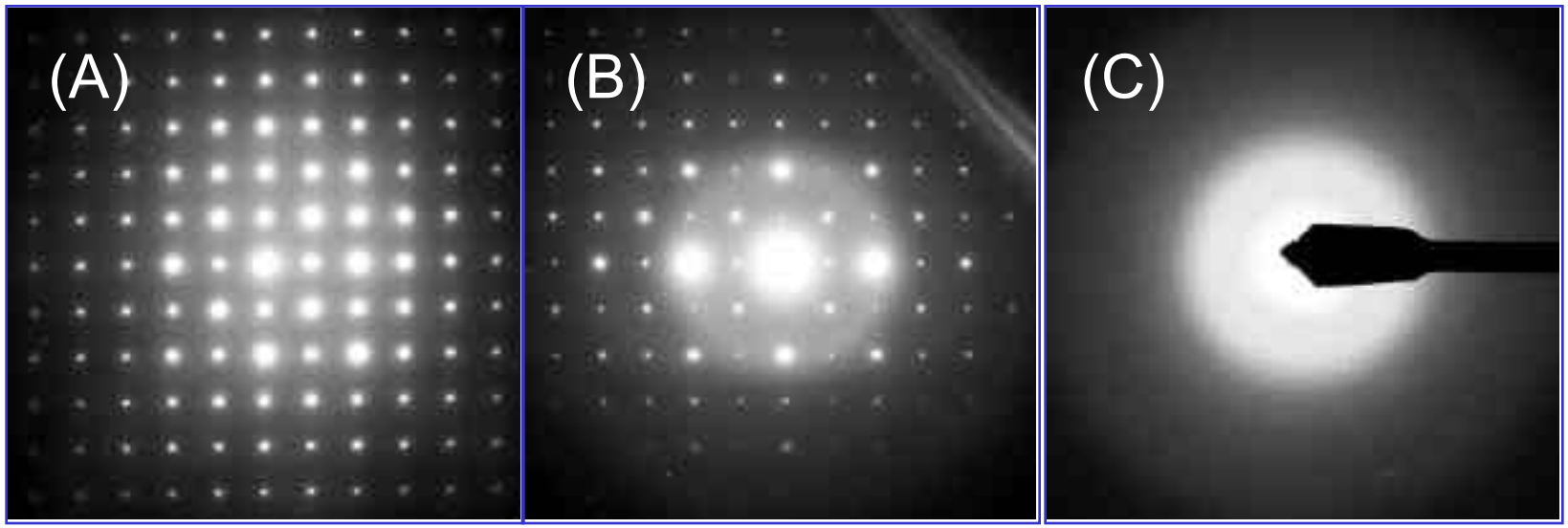

1.5 MeV Kr+ irradiated muscovite (300 K)
5 nm
1.5x10^14 ions/cm^2 (completely amorphized)

Bubble formation in 800 keV Kr^{2+} irradiated biotite

($1x10^{15}$ ions/cm^2 at RT with only 3 appm implanted Kr)



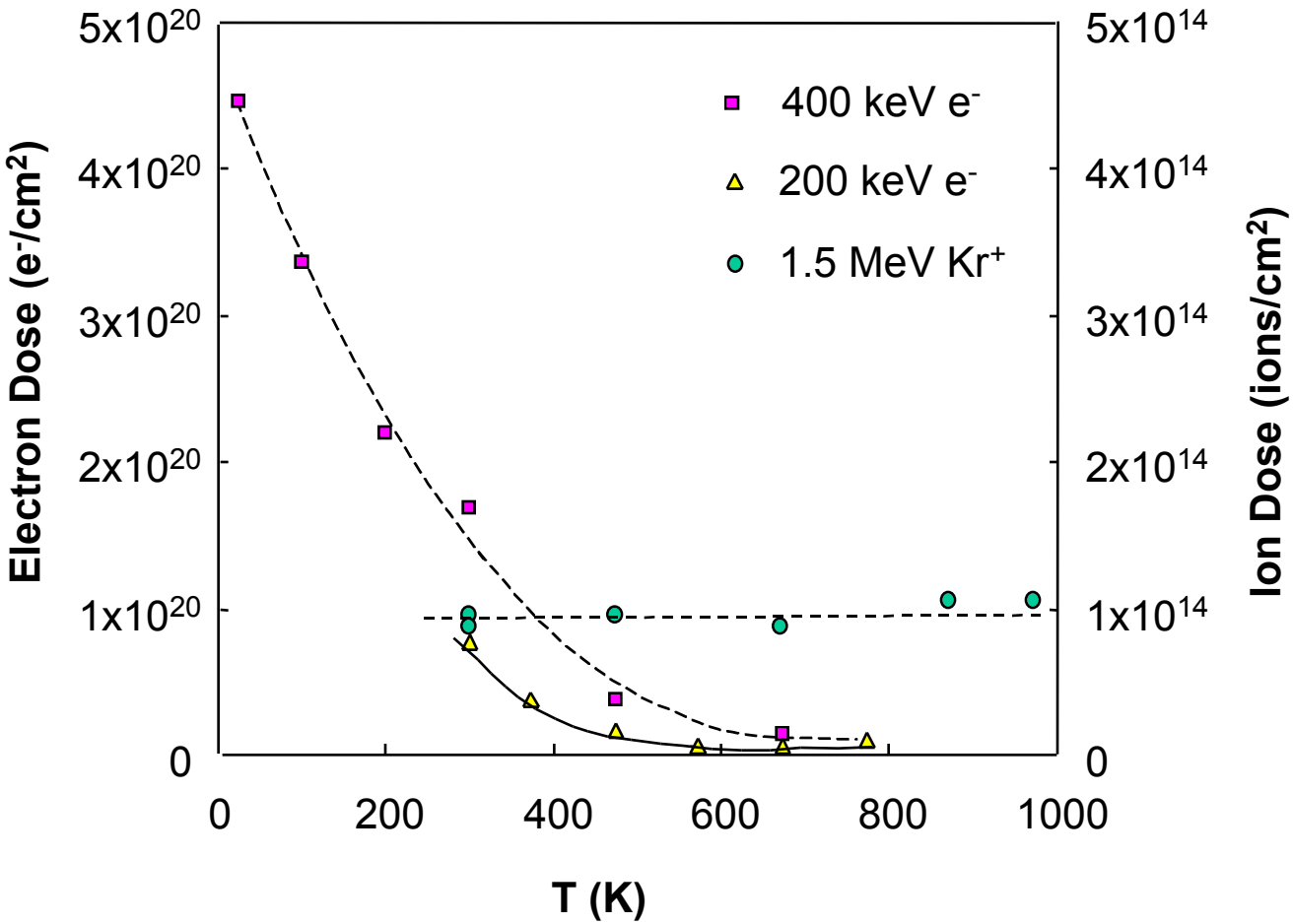
Selected Area Electron Diffraction Patterns of Analcime Showing the Process of Electron Beam-Induced Amorphization



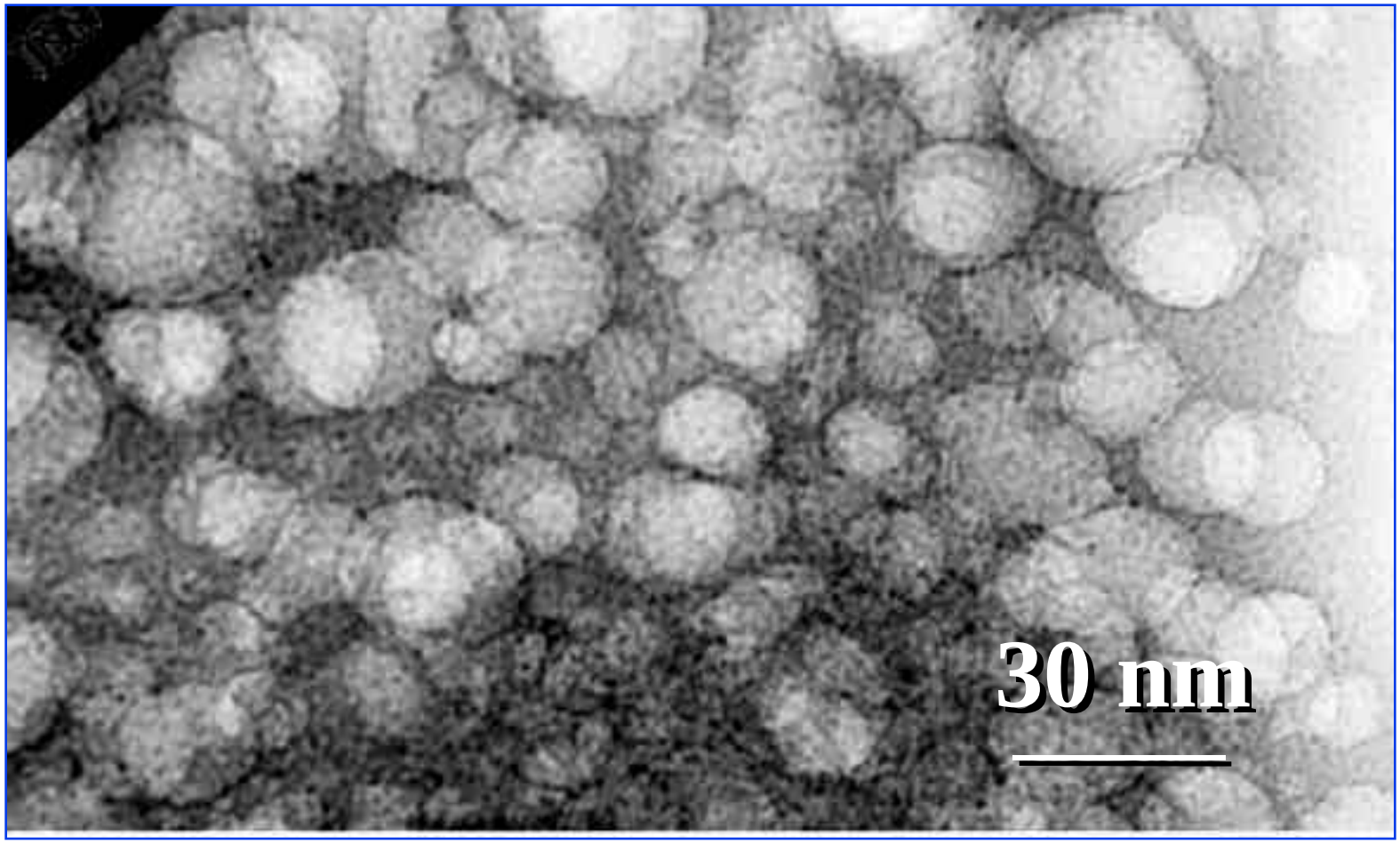
unirradiated | $3x10^{19}$ e^-/cm^2 | $8x10^{19}$ e^-/cm^2

(irradiation was conducted with 200 keV electrons at 300 K)

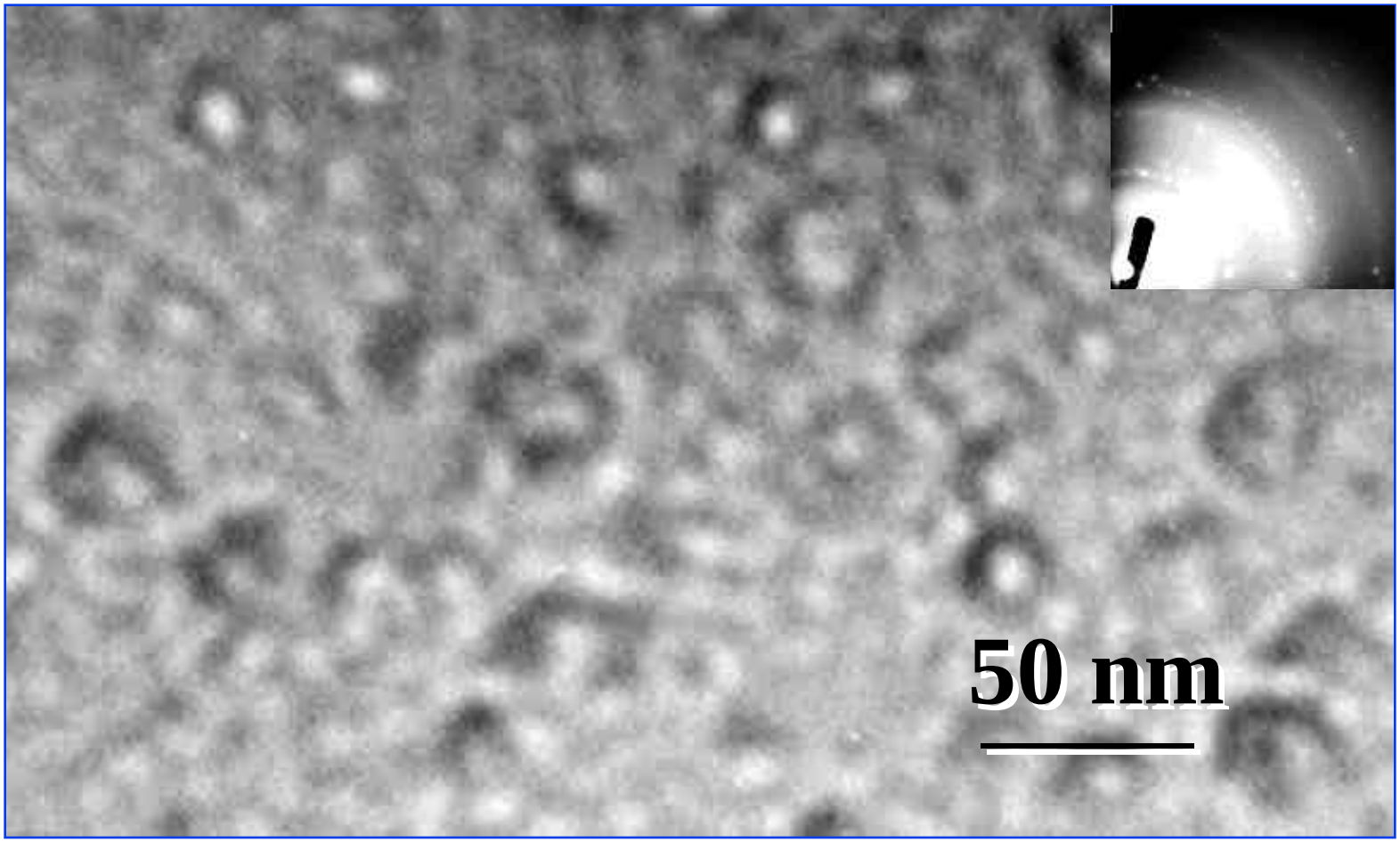
Temperatrue dependence of amorphization dose of analcime zeolite by electron and ion irradiations



Bright-field TEM image of 200 keV electron beam induced bubbles in analcime (image taken at 300 K)



Bright-field TEM image of electron beam induced bubbles in analcime (image taken at 200 K)



The electron diffraction pattern taken at 200 K (insert) matches of that of ice indicating that the bubbles are filled with the structural water.

Summary

- Both sheet silicates (mica) and zeolites are extremely susceptible to radiation-induced amorphization. Amorphization of these materials can be induced by both radiolysis and by collisional displacement mechanisms. At room temperature, complete amorphization were observed after ionizing doses of ~ $2x10^{10}$ Gy or displacement doses in the order of 0.1 dpa (equivalent to doses received in ~1,000 yrs. in a high loading waste form).
- Amorphization dose increases with increasing temperature in sheet silicates (mica) but decreases with increasing temperature in zeolites due to their thermoinstability.
- Accompanying amorphization, bubbles containing structure water and/or other volatile components of the materials may form under intense ionizing irradiation.
- Amorphization and bubble formation may change the sorption and/or ion exchange capacity of sheet silicates and zeolites as well as the release rate of radionuclides. Ion exchange experiments are being conducted to determine the radiation effects on these capacities.

II

Effects of thermally-induced amorphization on ion-exchange capacity and desorption rate for Cs and Sr in zeolite-Y

INTRODUCTION

- Electron and ion bean irradiation can cause the transformation from crystal to amorphous phase in zeolites.
- As a result, the ion-exchange, sorption and retention capacity of the radionuclides may be modified due to the change in material structure.
- In this study, Zeolite-Y was heat treated at elevated temperature (900ºC) to obtain the amorphous phase. The ion-exchange behaviors of the crystalline and amorphous zeolites were compared in order to predict the effect of radiation on the radionuclides adsorption capacity.
- Cesium and strontium exchanged zeolite-Y were amorphized by thermal treatment at elevated temperature. The leach rates of Cs^{+} and Sr^{2+} from crystalline and amorphized phases were compared in order to determine the effect of radiation on the radionuclides retention-capacity.

MATERIALS AND HEAT TREATMENT

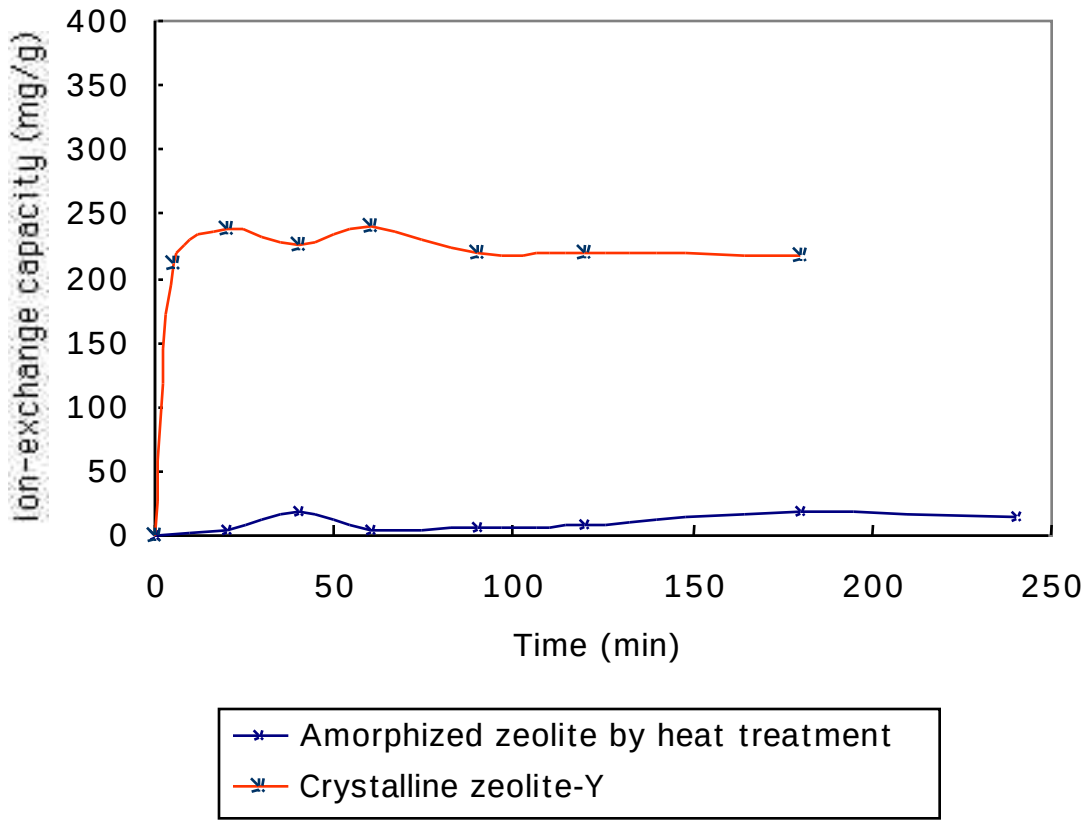
MATERIALS

- Zeolite-NaY (Si/Al=2.55)
  - Typical unit cell content: $Na_{56}[(AlO_2)_{56}(SiO_2)_{136}]_{.250}H_2O$
  - Na_2O content: 13%(wt)
  - Surface area: $900m^2/g$
- Cesium-exchanged zeolite-Y
- Strontium-exchanged zeolite-Y

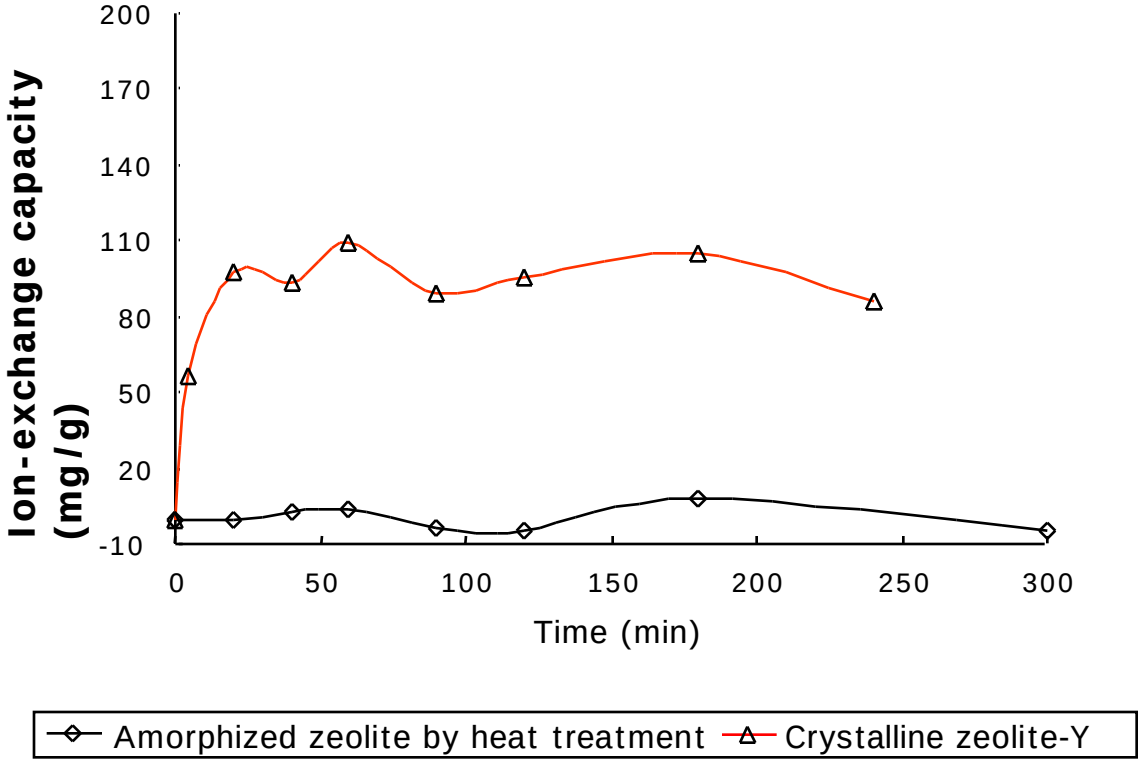
HEAT TREATMENT

- Zeolites were heated to 1000ºC and maitained at this temperature for 30 minutes, then cooled in air. Complete amorphization has been verified by x-ray diffraction.

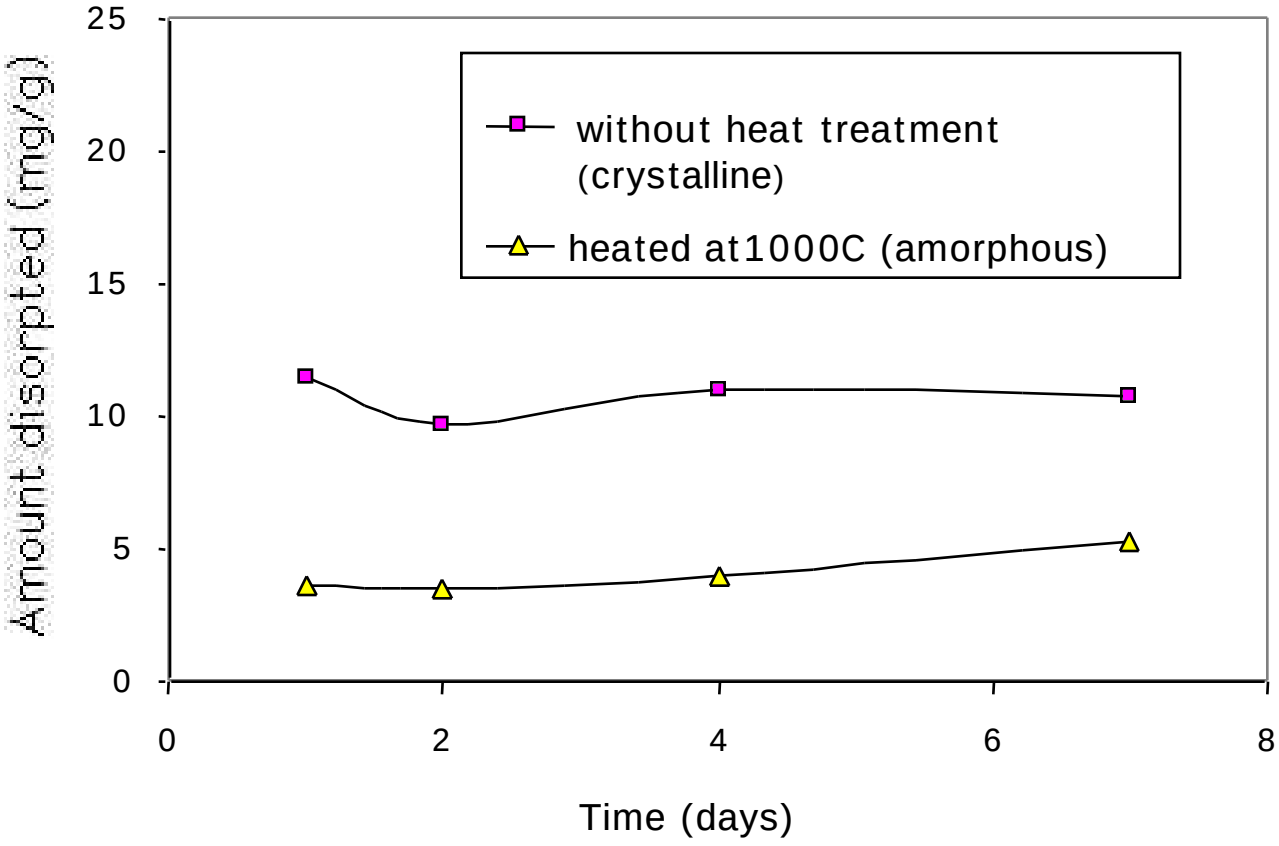
Variation of Ion Exchange Capacity of Cs^+ on Crystalline and Amorphous Zeolite-NaY with Time



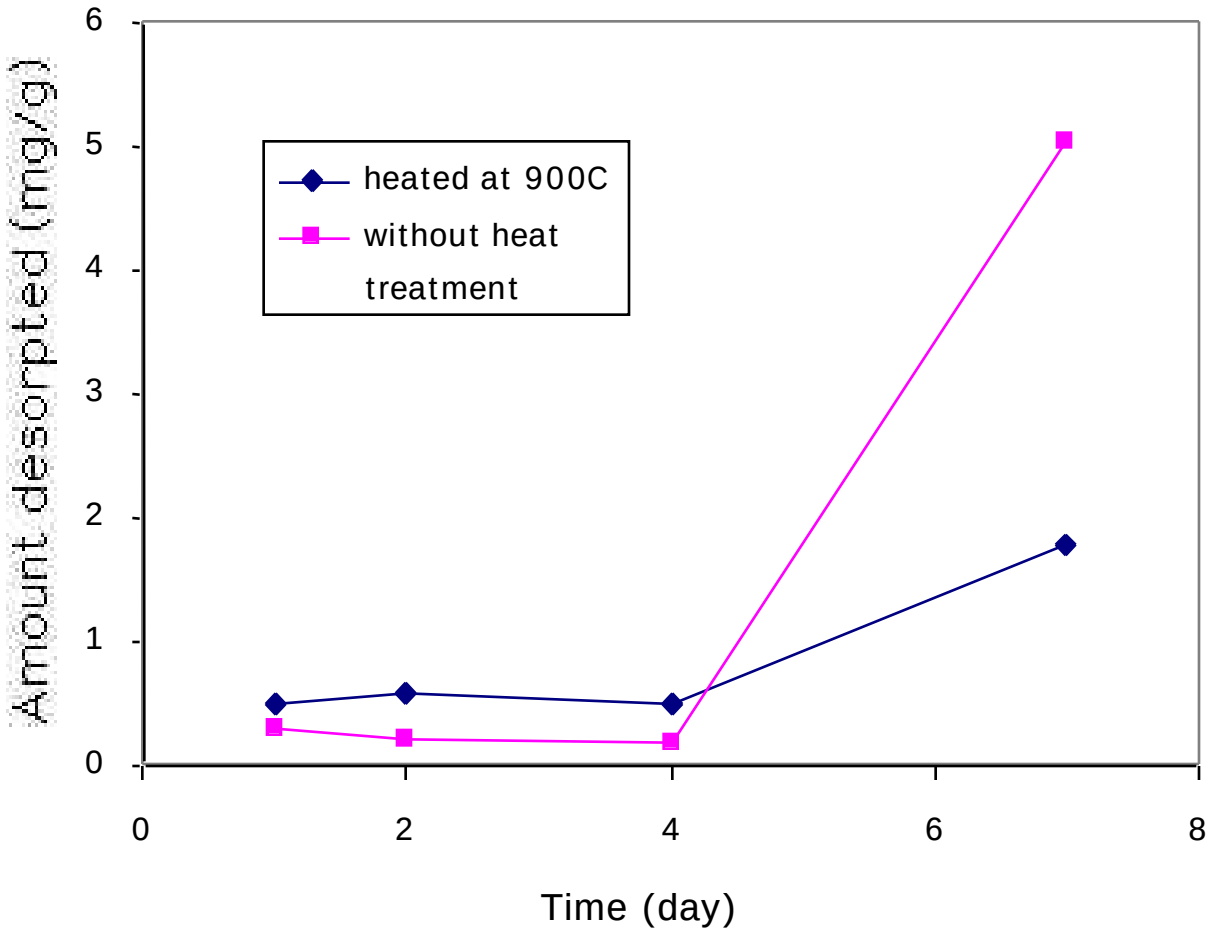
Variation of Ion Exchange Capacity of Sr^{2+} on Crystalline and Amorphous Zeolite-NaY with Time



Desorption of Cs^+ from Ion-exchanged Crystalline and Amorphous Zeolite-NaY



Desorption of Sr^{2+} from Ion-exchanged Crystalline and Amorphous Zeolite-NaY



SUMMARY

- Zeolite-Y, cesium and strontium-exchanged zeolite-Y as well as CST suffered structure damage under electron irradiation. The amorphization doses for the four types of materials at room temperature were close to each other due to their very similar framework structures.
- Zeolite-Y and its ion-exchanged products can be transformed to amorphous phase by thermal treatment. Cesium-exchanged zeolite had a higher thermal stability due to the formation of a second phase during ion exchange reaction.
- Cs-Na and Sr-Na exchange reactions on zeolite-Y under thoroughly stirred condition reached equilibrium within 10 minutes. The exchange capacity for Sr^{2+} is about 20% higher than for Cs^{+}.
- Zeolite lost its ion exchange capacity for both cesium and strontium ions due to the loss of framework charge when the structure collapsed to an amorphous solid.
- Desorption of adsorpted ions decreased when the materials were amorphized.