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Understanding Radiation Effects on Halite in Salt Repositories using Transmission Electron Microscopy

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Problem Statement

An important-unresolved issue for high-level-waste (HLW) disposal in a bedded salt repository is the stored energy generated in halide minerals by radiolysis (Weart, 2010).

Potential Problem: Stored Energy in halite

$$NaCl + \textit{photon} \rightarrow Na^0 + Cl^0$$

- Process occurs at surprisingly low absorbed energies ≈ 10eV

- Concern is of rapid re-combination of Na^0 and Cl^0

$$Na^0 + Cl^0 \rightarrow NaCl \qquad \Delta G_{rxn} = -411 \text{ kJ/mol}$$

- When saturated with radiolysis products, halite contains

$$10^1 - 10^3 \text{ J/g}$$

- Depth of penetration of radiation into halite ~ 1 foot

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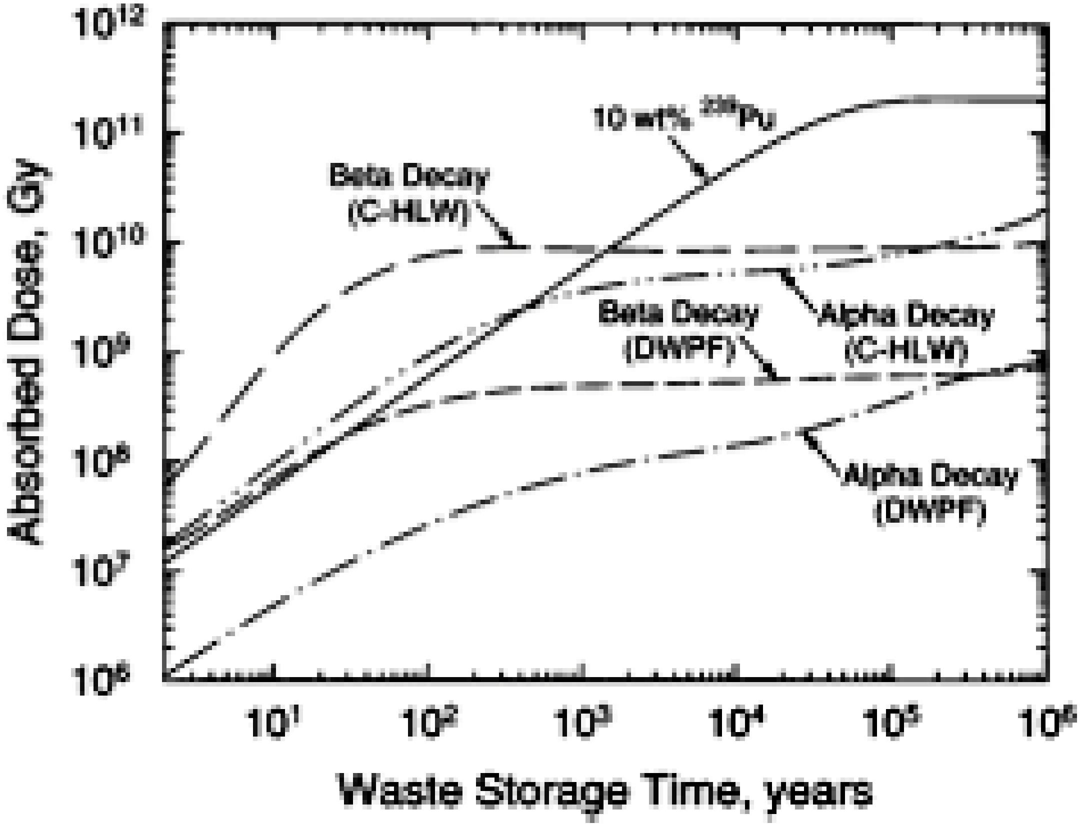
Stored Energy in Halite

- Explosive back reactions have been experimentally observed at T < 200°
  - Hartog et al. (1996)
- Fraction decomposed can be 1–10 mol % in peak damage regime
- Prij (1996) performed a PA-analysis of potential impacts of stored-energy release on waste containment in halite.

High-Level Waste Radiation Environment



High-level waste produces high-levels of ionizing radiation from α, β, γ, light ions

Salt surroundings will absorb 10^8-10^{10} Gy in 100 years **(mostly gamma, X-ray)**

1 Gy = 1 J/kg

Problem 1: NaCl is *the* solid *most* damaged by ionizing radiation
Problem 2: A significant fraction of this absorbed energy is retained as potential for chemical reaction

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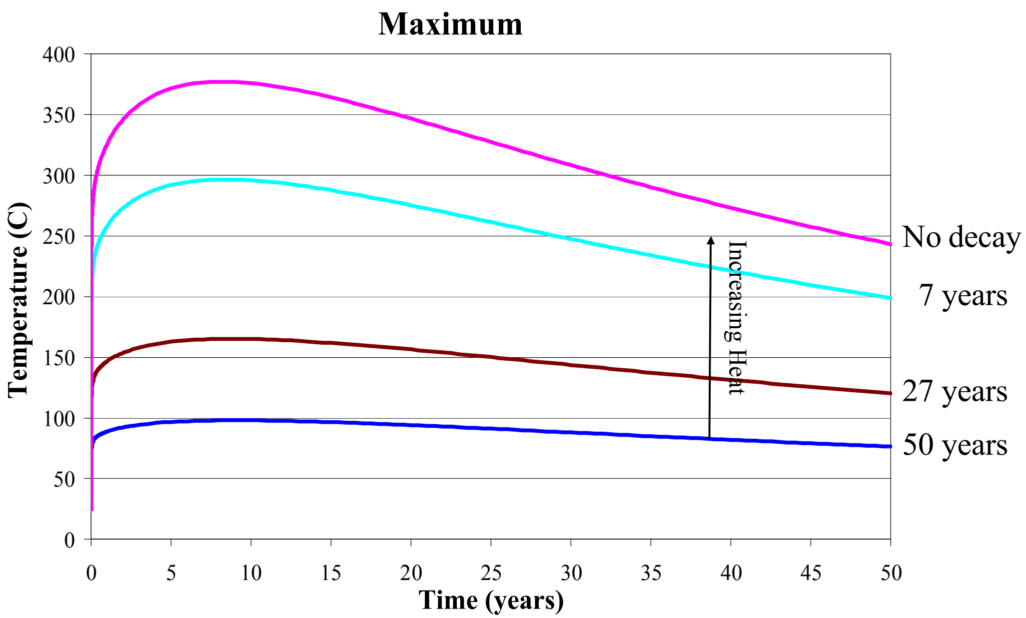
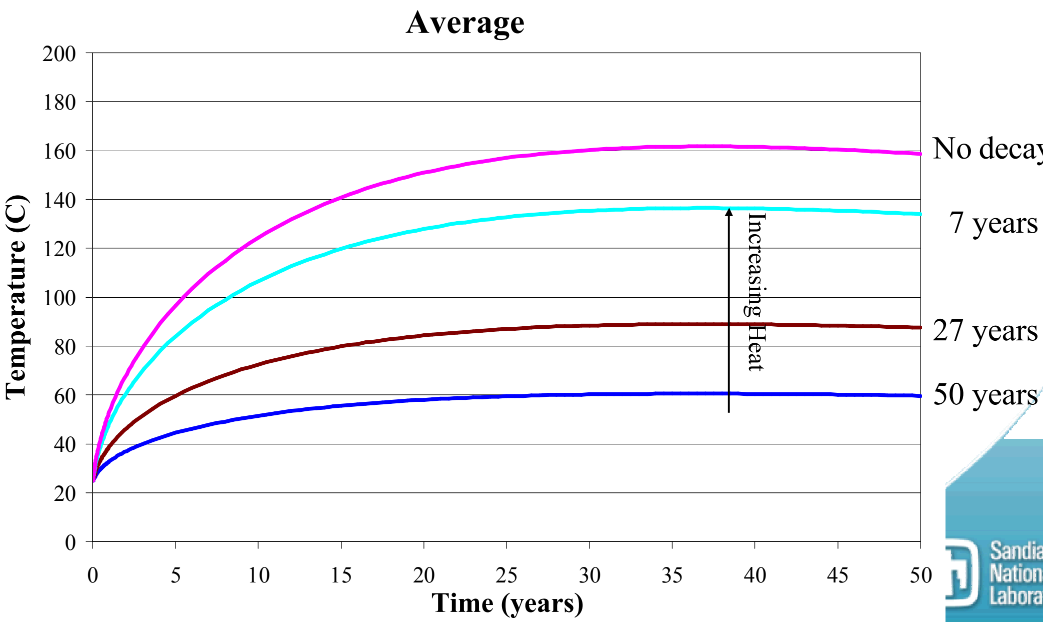
Temperature in Repository



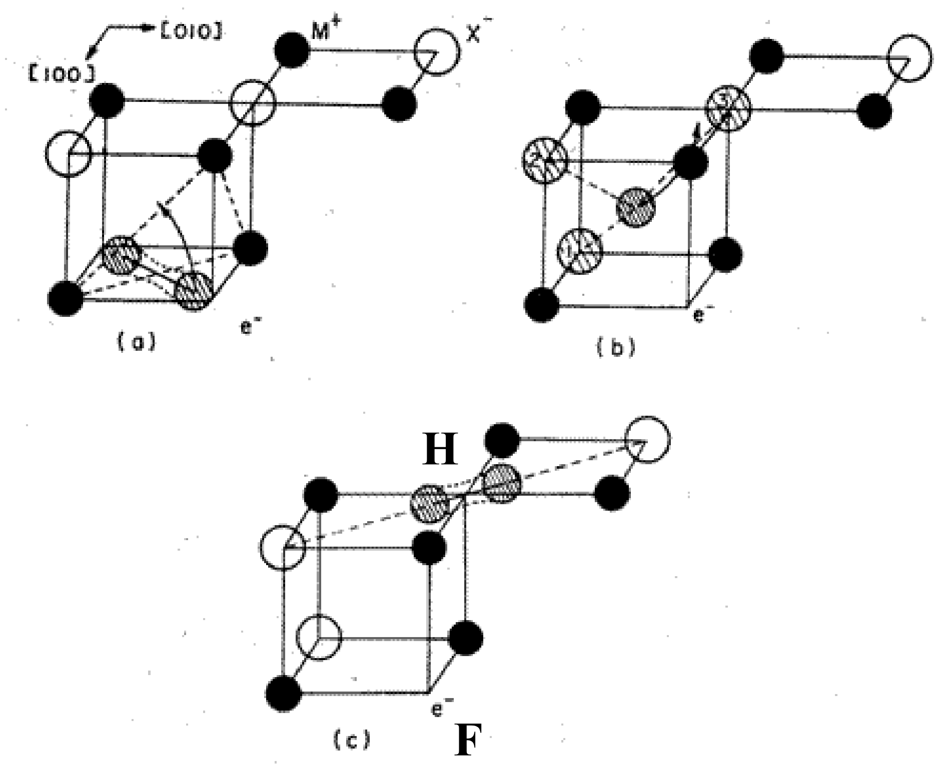
•Substantial period of time at T > 100 °C



D.J. CLAYTON and C.W. GABLE, "3-D Thermal Analyses of High Level Waste Emplaced in a Generic Salt Repository", SAND2009-0633P, Sandia National Laboratories, Albuquerque, NM (2009).

Radiolysis in halite

- The mechanism is radiolytic and begins with an exciton (e'-$h^\bullet$ pair) localized at two adjacent Cl^- ions
- Resulting $[Cl_2^-]^\bullet$ molecular defect is configurationally unstable and reverts to a Cl_2^- interstitial molecular ion occupying a Cl ion site (H center)
- Departing H center leaves behind a Cl vacancy (V_{Cl}) which traps the exciton electron (F center)
- F-H pair represents a Cl atom displacement requiring ~ 6 eV absorbed. Process is 50% efficient



~50% of energy absorbed from ionizing radiation ends up as atom displacements

Prior Work

- Extensive literature on radiolysis of halite
- Hobbs looked in detail at the nature and distribution of the radiolytic damage at the nanometer scale using transmission electron microscopy (TEM)
- TEM work was performed in 1960's –1970's

What has been accomplished using TEM

- Direct observation of Na colloids
  - Size (size is correlated with measured stored energy)

- Direct observation of dislocation loops
  - Final sink for radiolysis products
  - Enabled a model of halite radiolysis to be developed

Transmission Electron Microscopy of NaCl

Resolution in TEM is a statistical process.
1 nm resolution requires 10^4 electrons/nm^2

Problem: Electron beam deposits ionizing energy at the rate of 0.4 eV/nm

One image requires: 40 Grad = 400 MGy ≈ 200 eV/Cl ~ 20 dpa

Image recorded over t ~ 10 s: 2 dpa/s!

Contrast from accumulated damage from investigating electron beam *immediately* obscures all sub-micrometer features of the specimen.

Contrast is strain-field from dense dislocation network that is continually climbing at rates of 1 μm/s and so churns dynamically.

Every Cl atom displaced twice per second!

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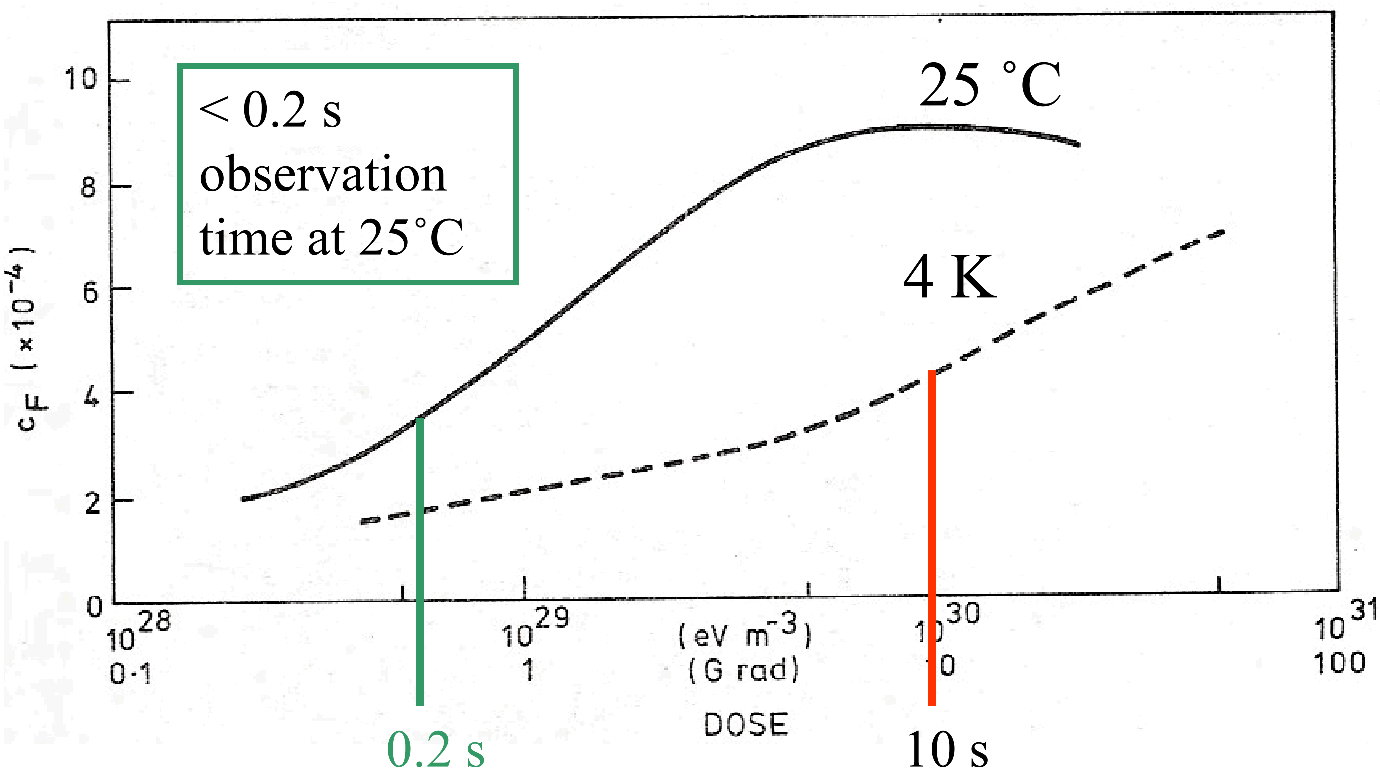
Damage accumulation at liquid-He temperatures (< 10 K): *the solution*

H center interstitial mobile *above 20 K*
Recombination kinetics athermal *below 10 K*



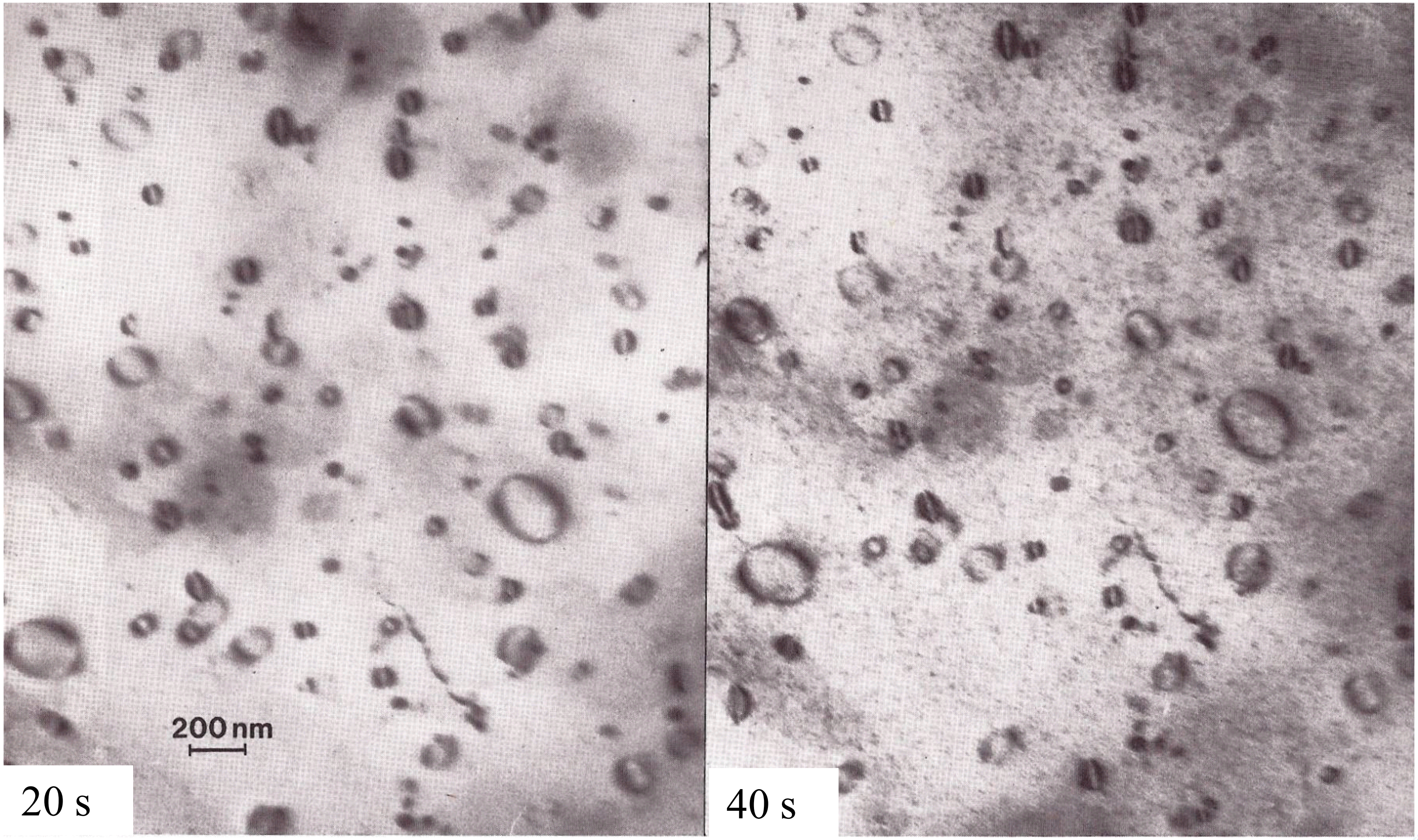
> 10 s observation time at 20,000× magnification at 15 K

Hobbs, L. W. (1975). Transmission Electron Microscopy of Extended Defects in Alkali Halide Crystals, in Surface and Defect Properties of Solids, Volume 4. London: The Chemical Society. Pg. 194.

Minimizing incidental radiation damage during TEM

(Interstitial dislocation loops from prior 4 MGy radiolysis at 25˚C)

J. Phys. Radium, 1973, V. 34 (C9), pp. 227

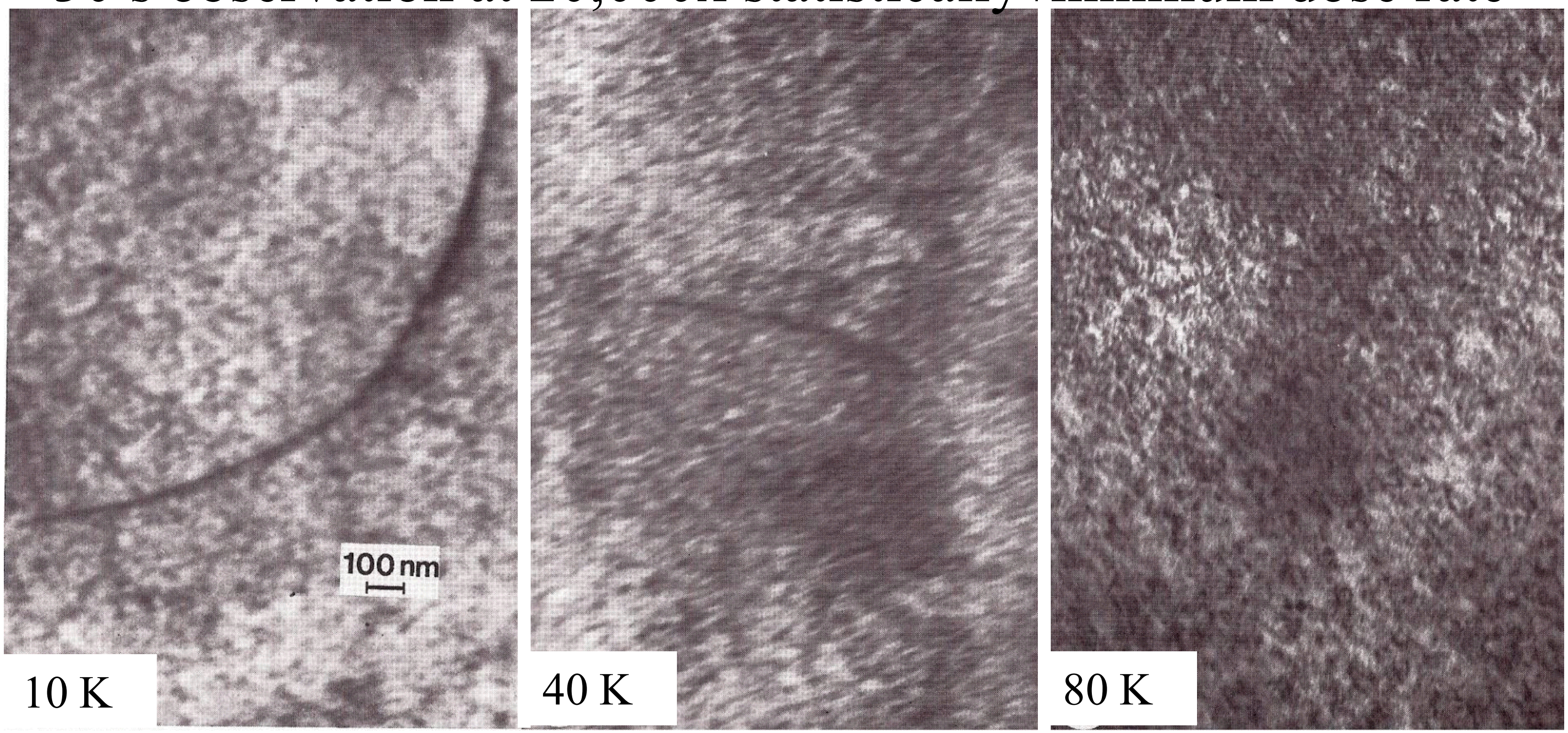


TEM at ~10 K, statistically minimum-dose conditions

About 30 s unimpeded observation possible

Choosing TEM specimen temperature

30 s observation at 20,000x statistically minimum dose rate



Radiolytically-displaced Cl interstitials (H centers) become mobile at ~20 K, migrate thermally to aggregate sinks, alter recombination kinetics

Normal TEM observations can proceed only at T < 20 K

Hobbs, L. W. (1975). Transmission Electron Microscopy of Extended Defects in Alkali Halide Crystals, in Surface and Defect Properties of Solids, Volume 4. London: The Chemical Society. Pp. 207.

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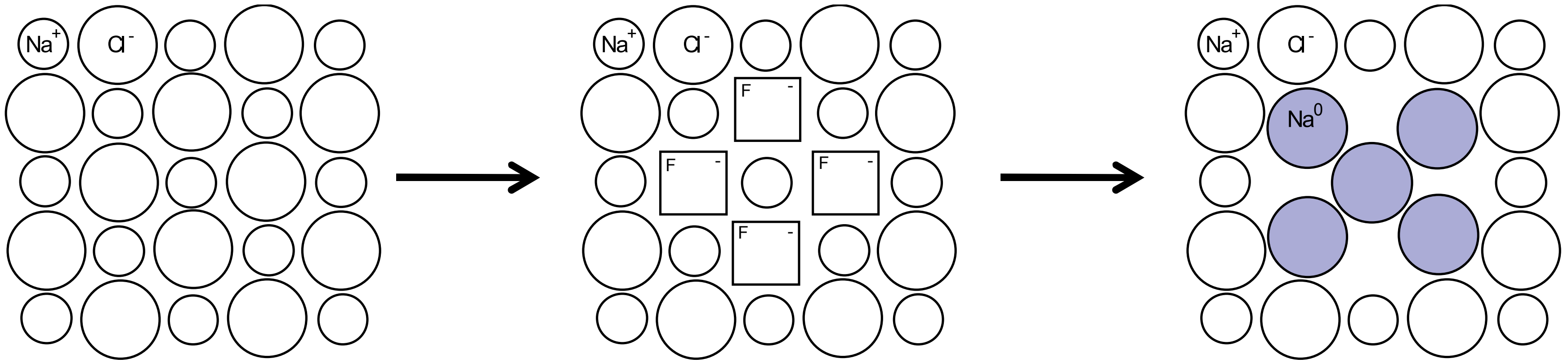
Fate of the Chlorine Vacancy:
Aggregation to Na colloids

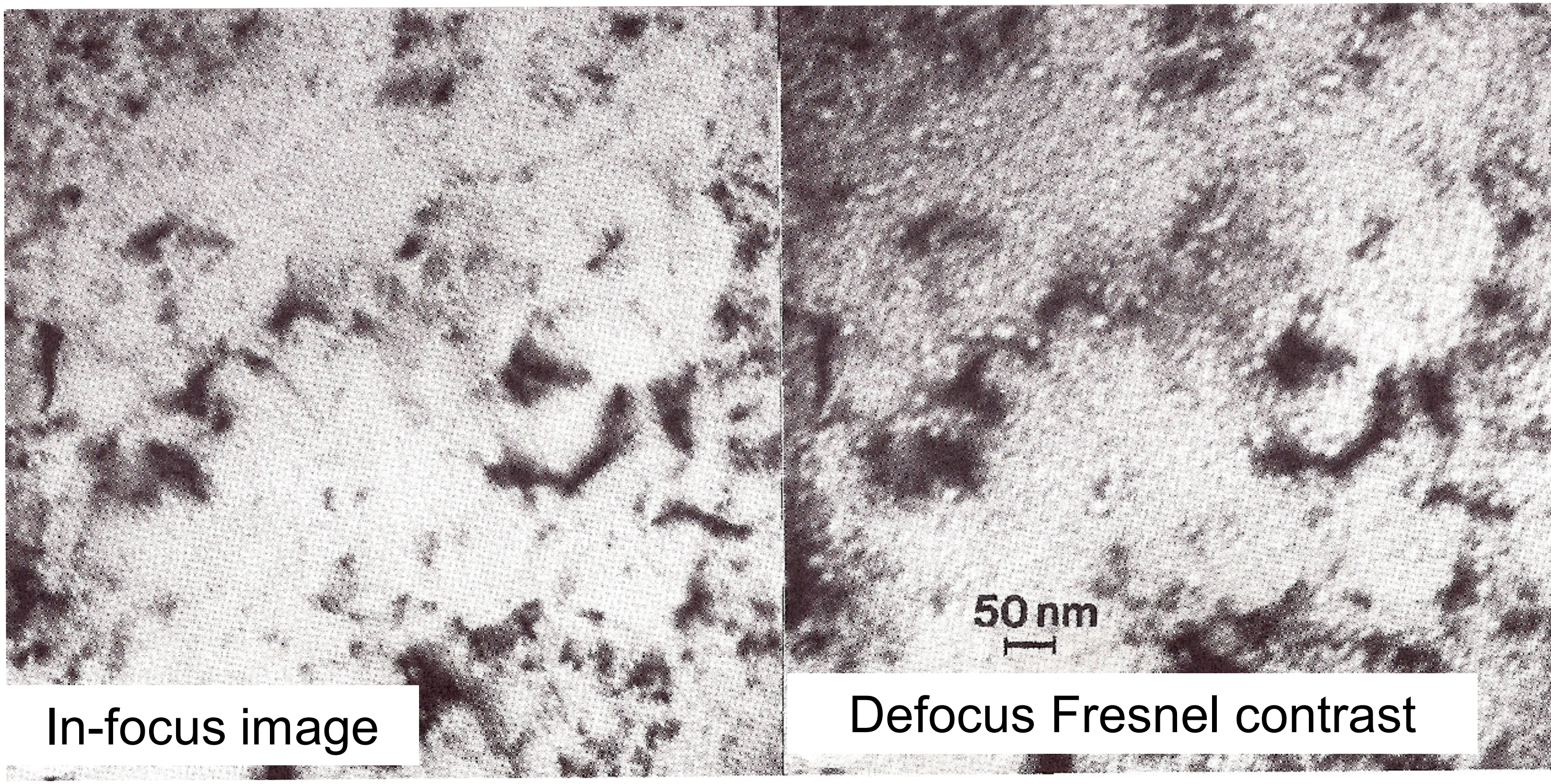


$$n\,V_{Cl} + n\,e^- + n\,Na^+ \rightarrow Na^0_n$$

Colloidal size Na metal particle

Fate of the Chlorine Vacancy: Aggregation to Na colloids

TEM, 10 K



400 MGy, 400 keV β irradiation, T = 150 ˚C

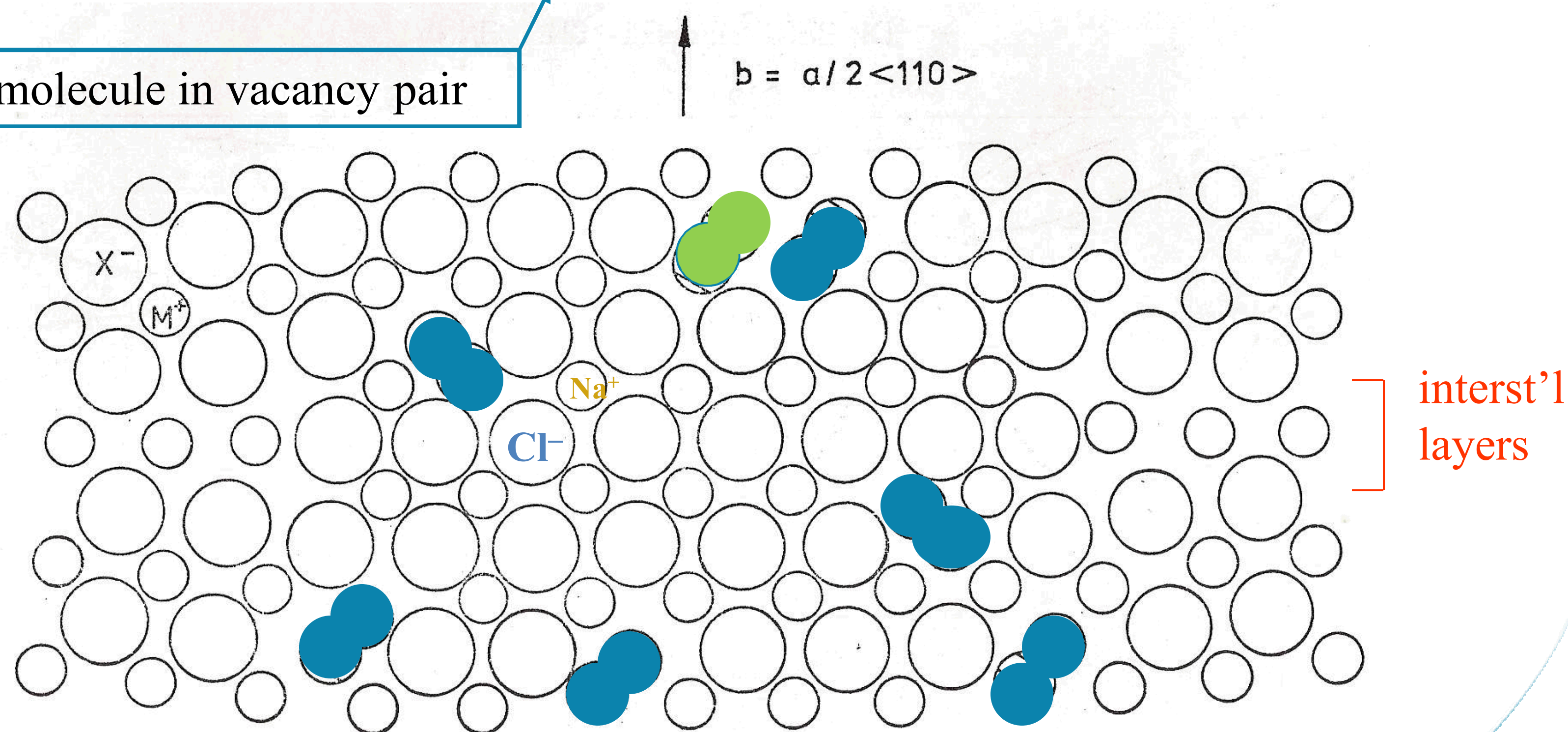
Hobbs, L. W. (1975). Transmission Electron Microscopy of Extended Defects in Alkali Halide Crystals, in Surface and Defect Properties of Solids, Volume 4. London: The Chemical Society. Pp. 225.

Fate of radiolytically displaced chlorine
Formation of stoichiometric dislocation loops

$$H + H = Cl_2^0 + 2\ Cl^-_{Cl}$$

$$Cl_2^0 + Na_{Na} + Cl_{Cl} = (Cl_2^0)_{Na,Cl} + Na_i^+ + Cl_i^-\ \text{(go into loop)}$$

Cl$_2$ molecule in vacancy pair

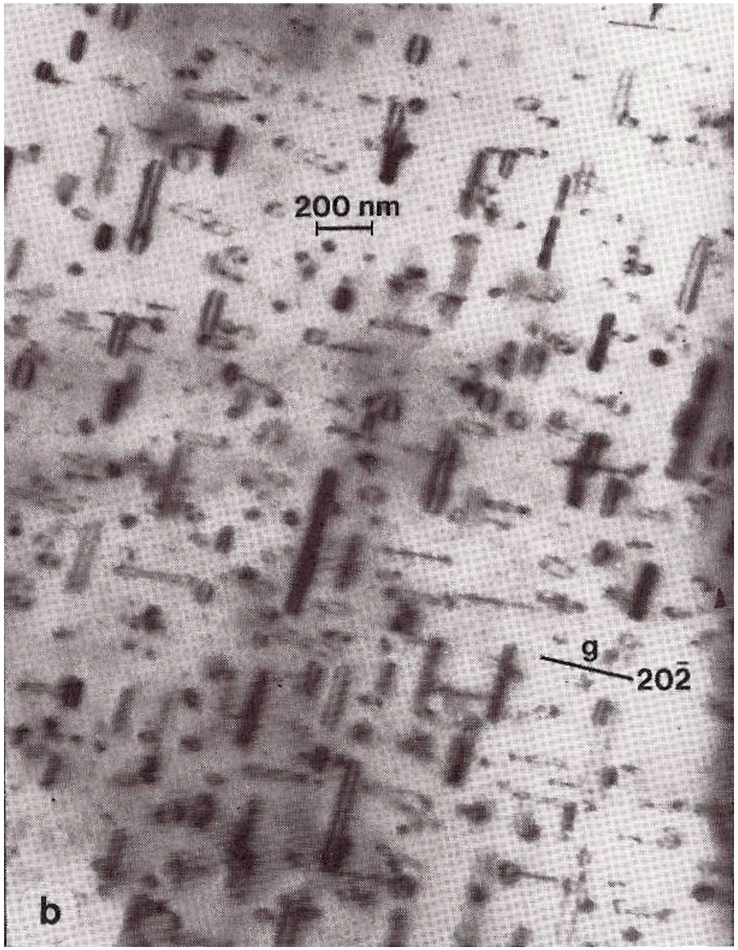


Na$^+$ ions are secondarily displaced in this process

Fate of the radiolytically displaced Cl:
Interstitial dislocation loop formation

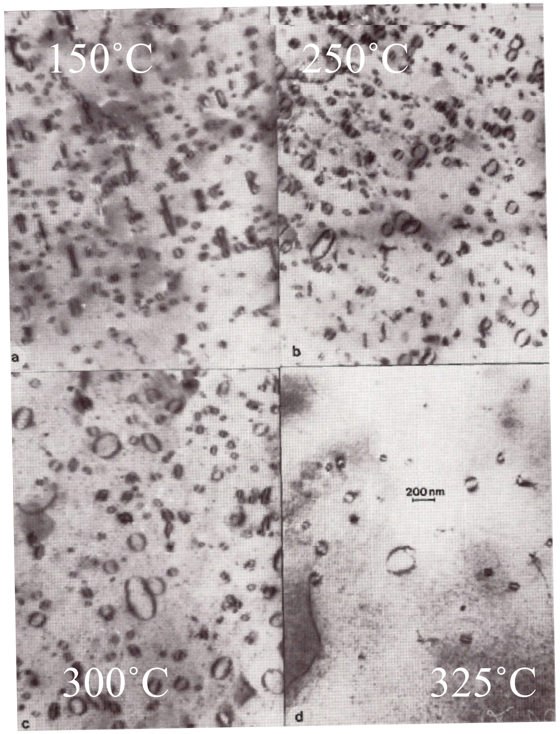
Hobbs, L. W. (1975). Transmission Electron Microscopy of Extended Defects in Alkali Halide Crystals, in Surface and Defect Properties of Solids, Volume 4. London: The Chemical Society. Pp. 214.

TEM, 10 K



0.4 MeV β irradiation to 4 MGy, 25˚C

Loops are perfect prismatic interstitial loops with b = 1/2 <110> elongated along <100>



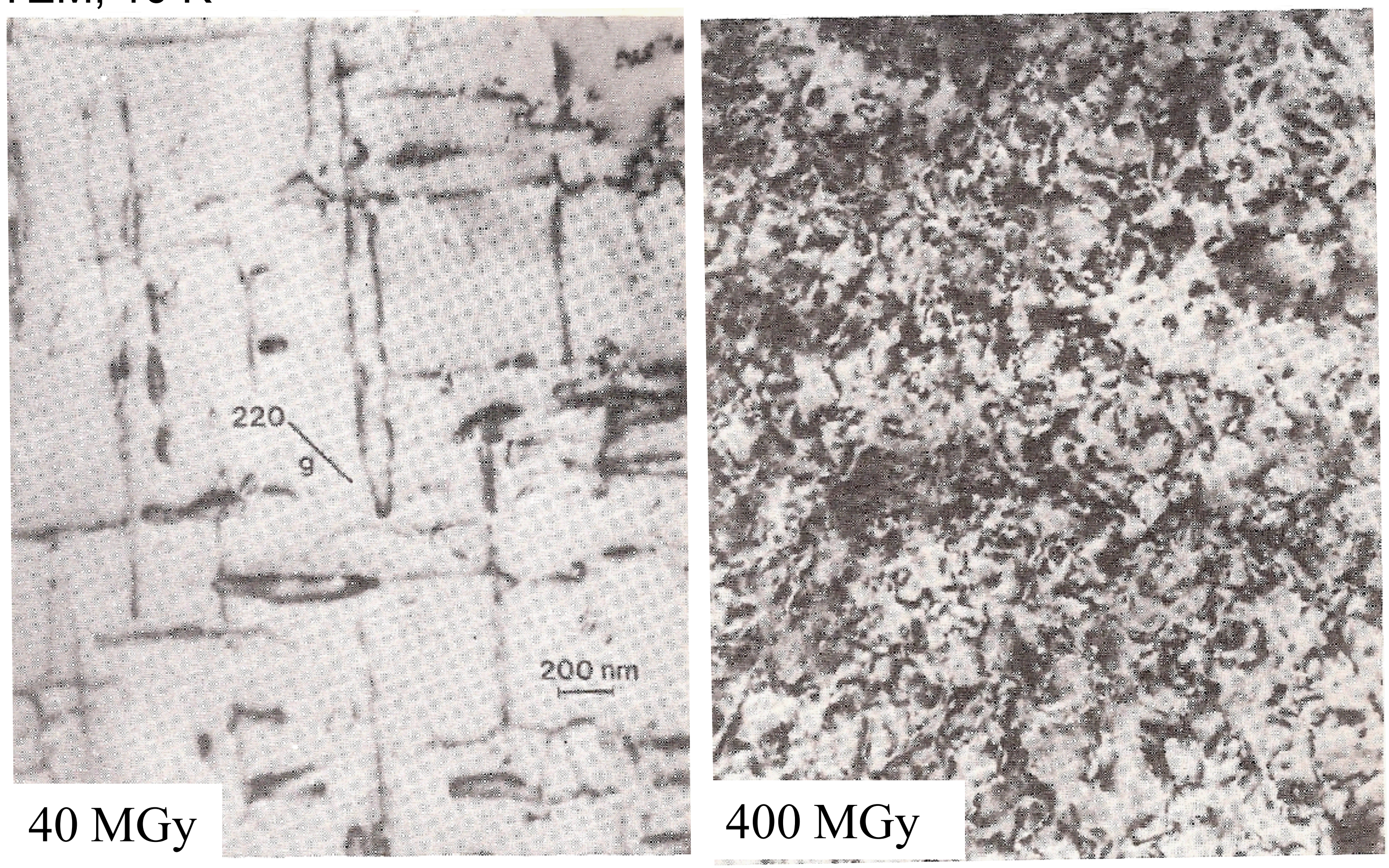
Annealed 12 h after 4 MGy irradiation at 25˚C

Loops coarsen on annealing (without further irradiation) and disappear by about 325 ˚C

Interstitial loop behavior at T of maximum defect accumulation

T = 150˚C, 400 keV β irradiation

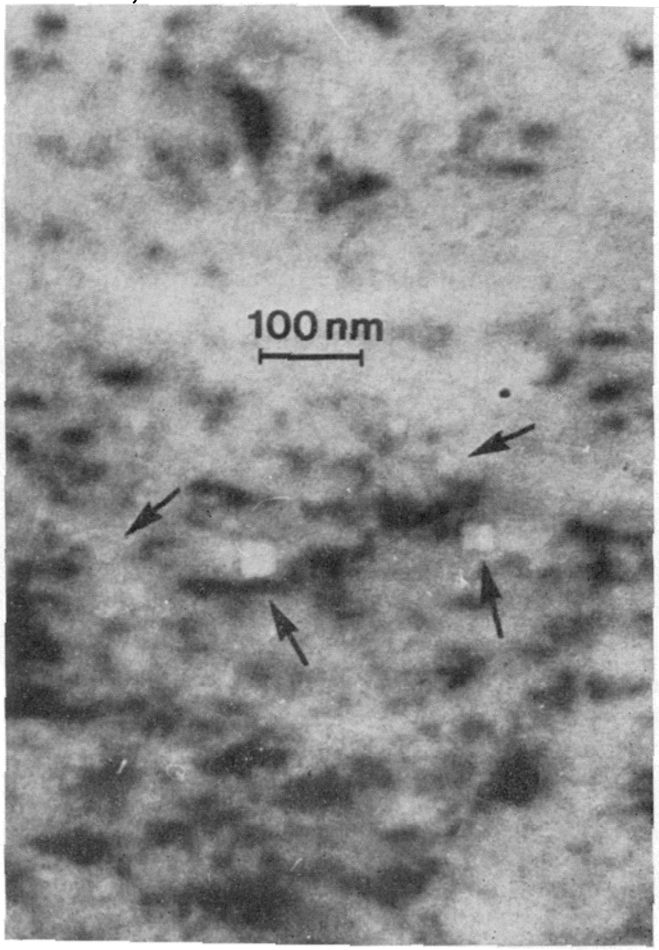
TEM, 10 K



Continued loop growth → Repeated loop intersections
→ Dense dislocation network

Fate of radiolytically displaced Cl: Voids

TEM, 10 K



T = 150˚C, 400 MGy

- Aggregation of vacancy pairs containing Cl_2^0 molecules =

  Void + Cl_2 at high density/pressure(GPa)

- Diffusion of Cl_2 molecules out of voids

Radiolysis leads to decomposition

$NaCl + photon = Na^0 + Cl_2$

Fraction decomposed can be 1-10% in peak damage regime

Influence of impurities

- Enhance Radiolysis
  - Presence of water
    - Brine is easily radiolyzed to hypochlorite
- Impede Radiolysis
  - Provide preferred sites for radiative decay of exciton
  - Hinder (immobilize) diffusion of H-centers

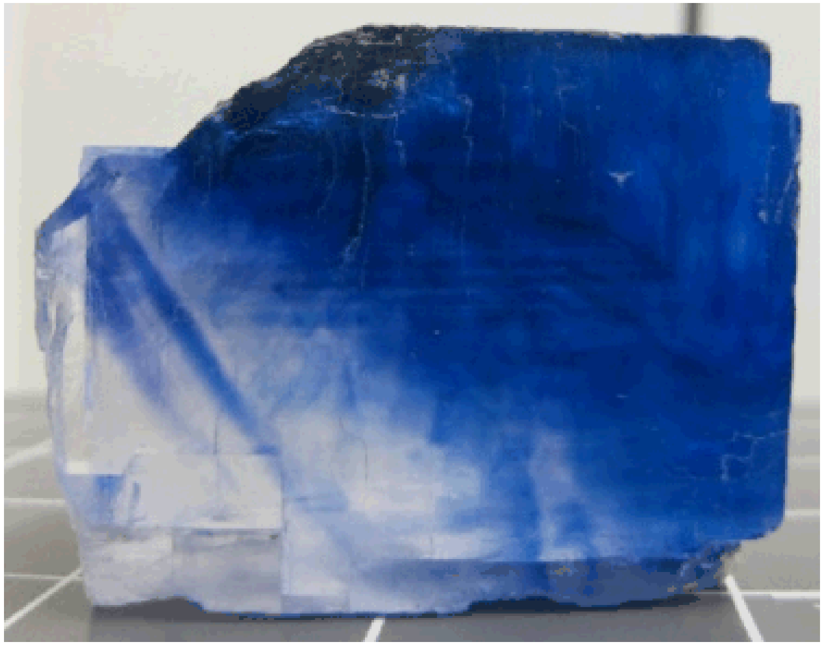
Influence of impurities

- ORNL (1974) performed radiolysis experiments on KS and NM samples
  - KS sample contained 40 % more stored energy than pure halite

- Weerkamp (1994)
  - K^{+}, Fe^{3+} ,F^{-} enhance colloid formation
  - Impurities affect size distribution of colloids
    - *Colloid size important for energy release*

Prior Work: Conclusions

- All previous TEM studies were performed on pure or doped single-crystal halite
- No one has looked at radiolysis products in geologic samples using TEM



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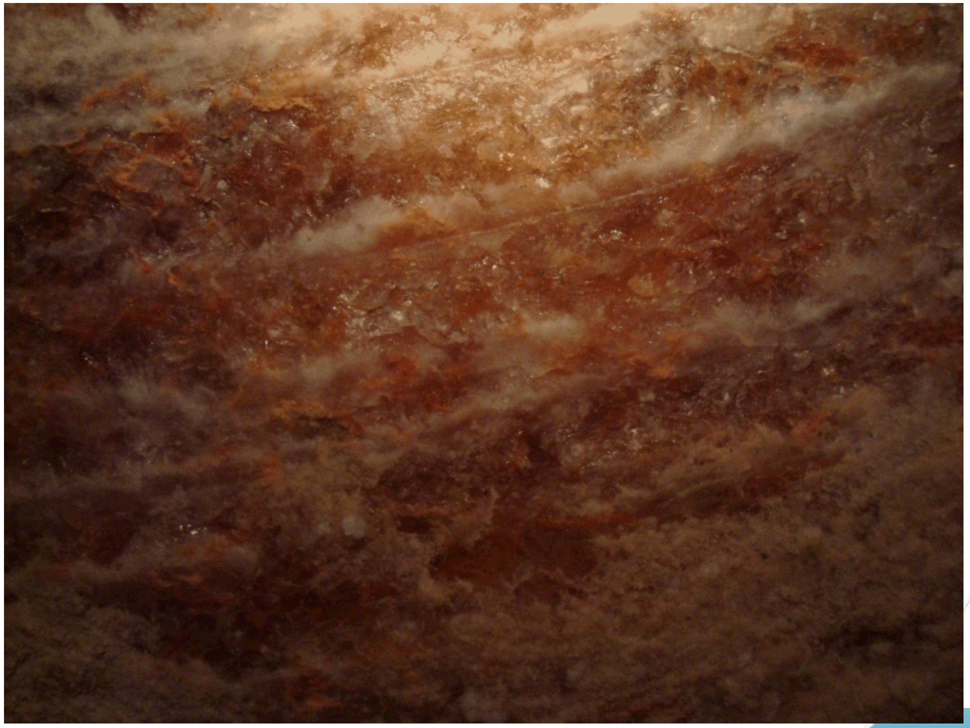
Geologic evaporites contain fluid inclusions, impurities, and polycrystalline sub-structure on all scales

polyhalite
infused halite



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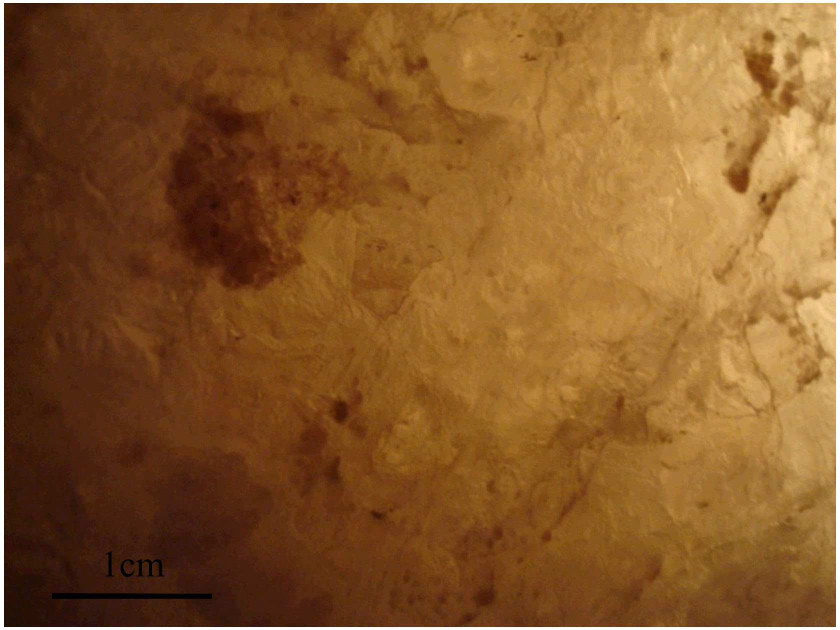
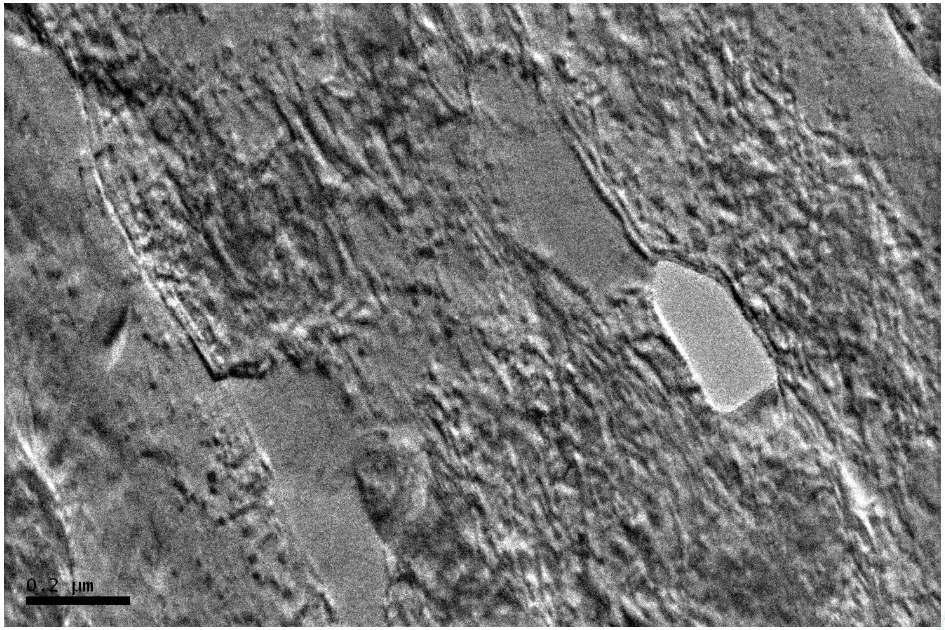
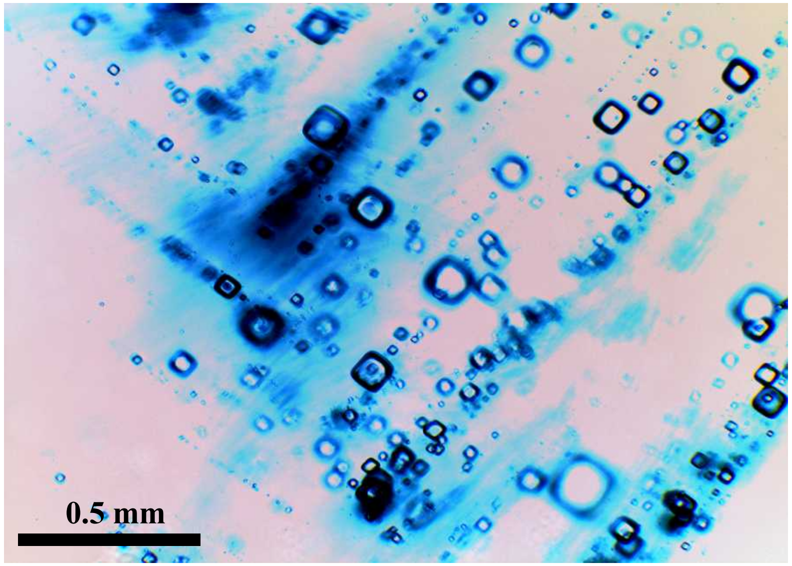
Polycrystalline on all scales

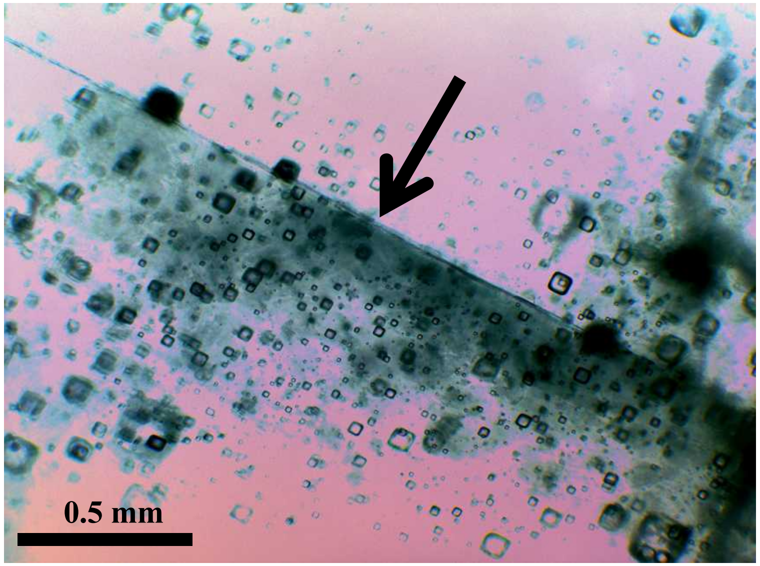




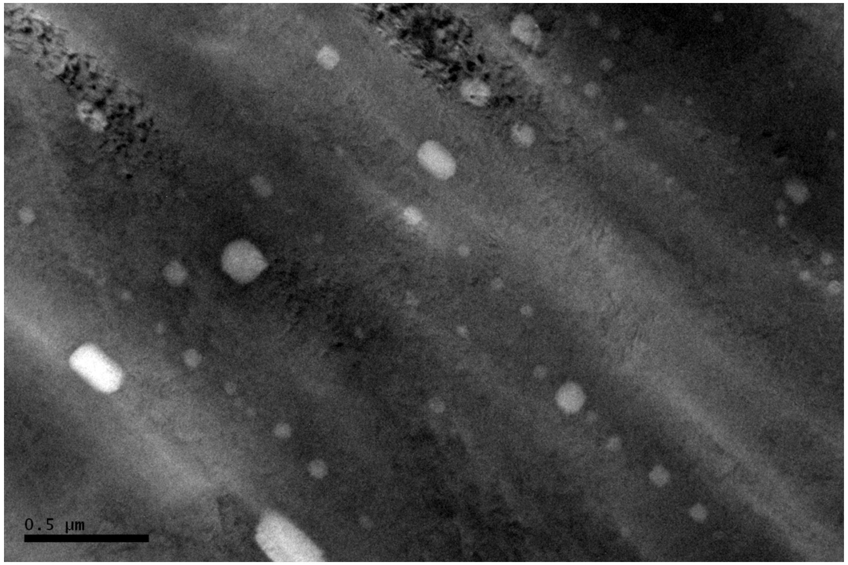
Fluid Inclusions, Fluid at Grain Boundaries at all scales



Primary inclusion in chevron bands



Inter-granular brine at grain boundaries



50 nm fluid inclusions

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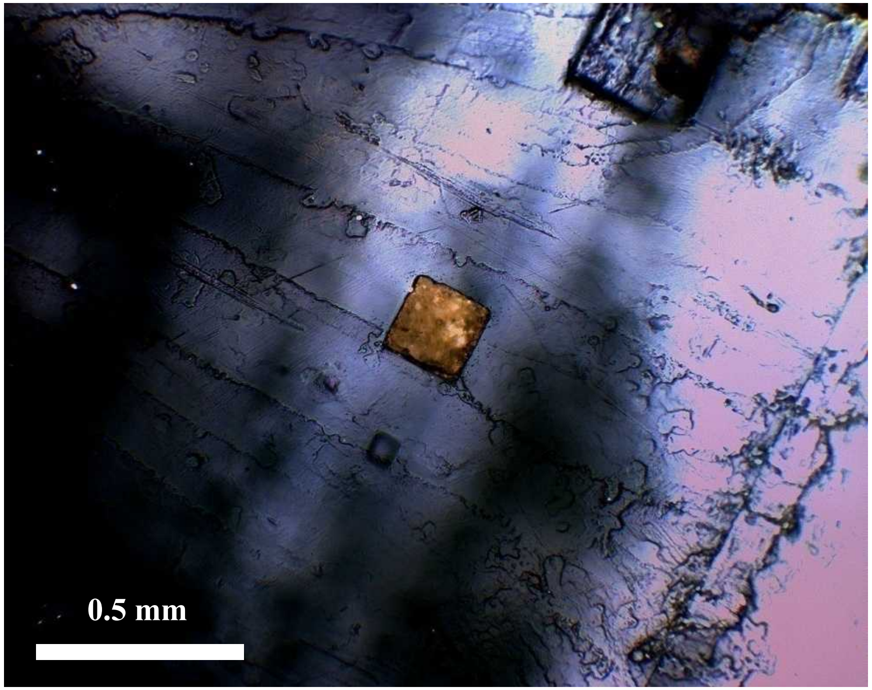
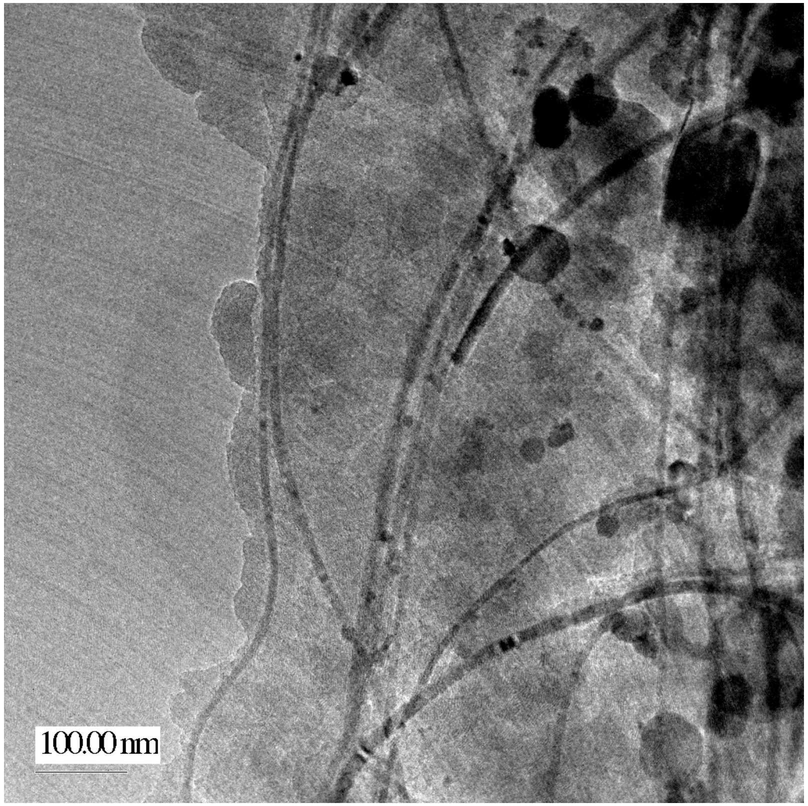
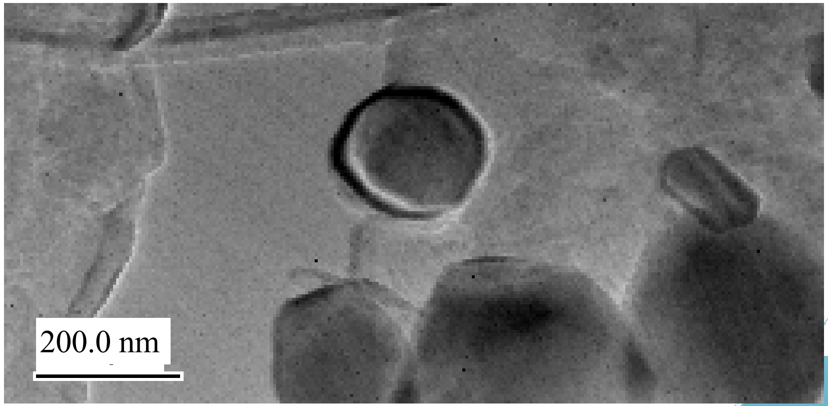
Impurity Particles on All Scales



Transmitted Light Microscopy, crossed polars





TEM 200kV, 25 °C

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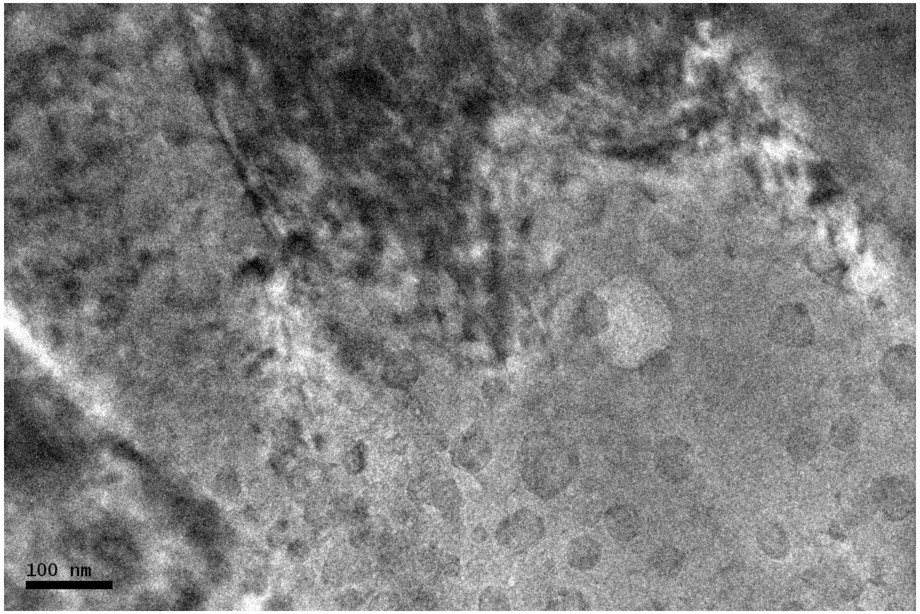
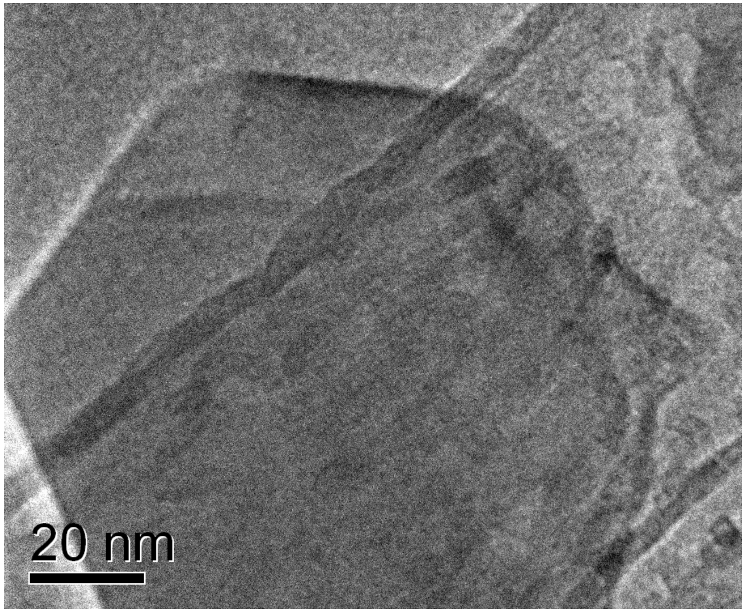
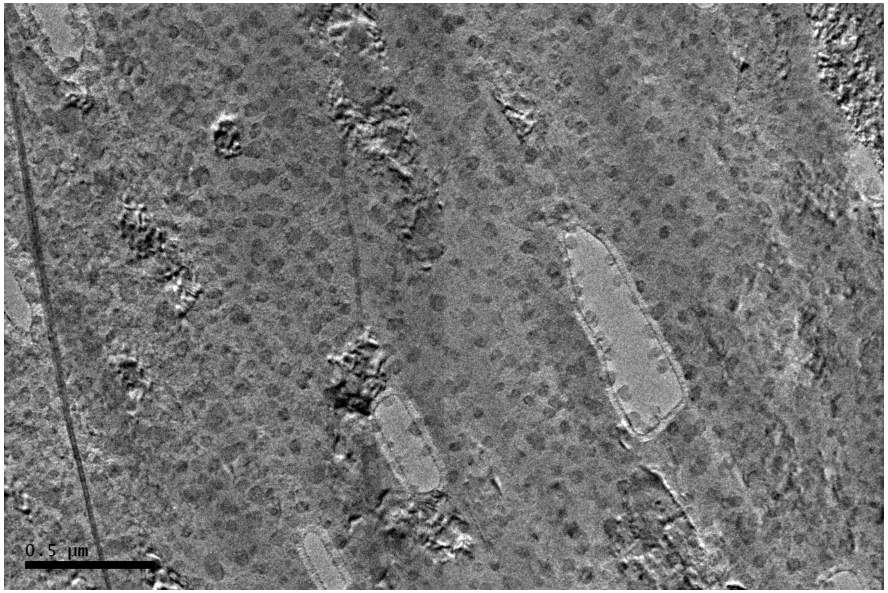
Defects may be quite different in geologic samples

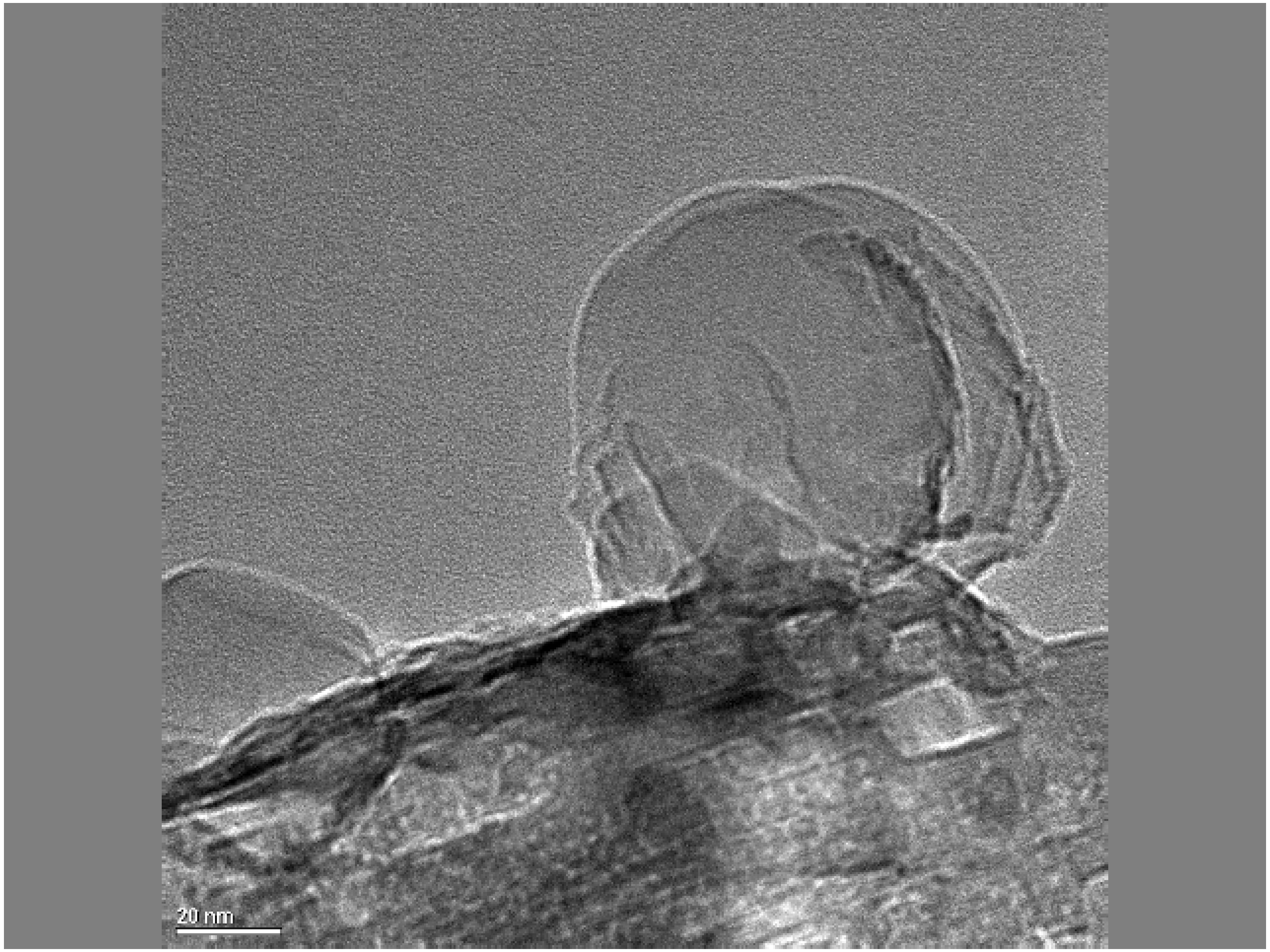






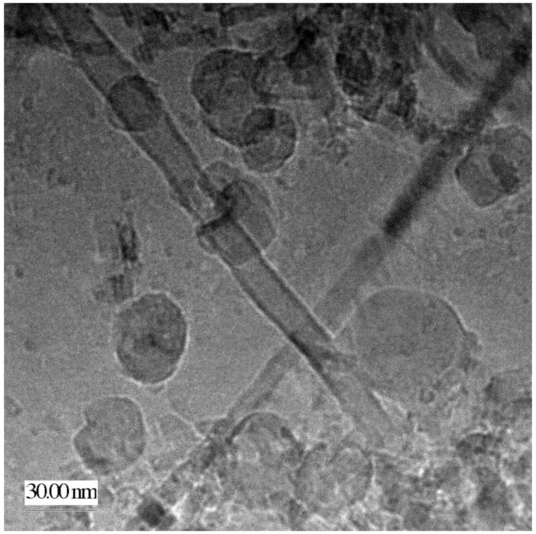
TEM 200kV, 25 °C

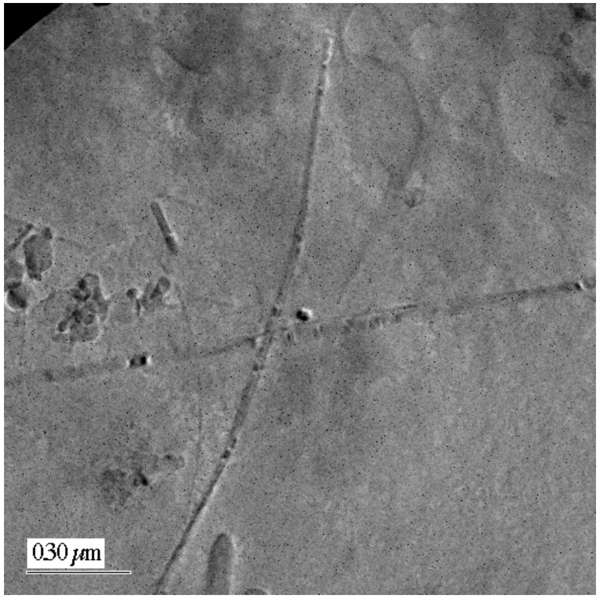
300kV produces large faceted nano-scale NaCl crystals

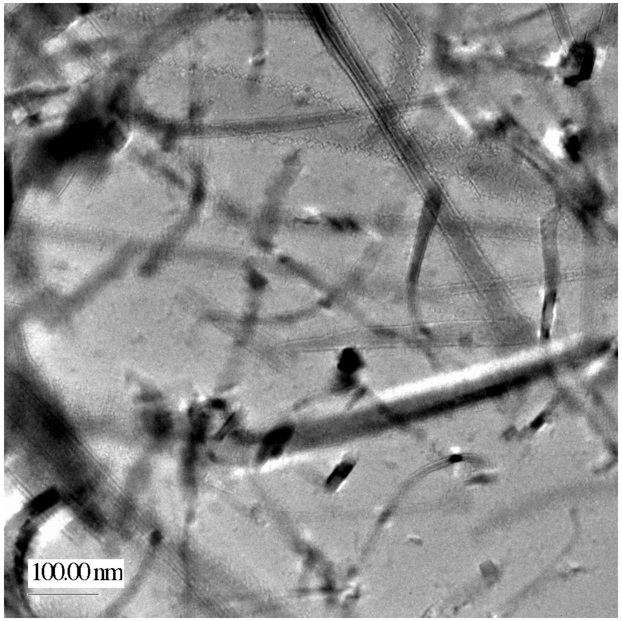


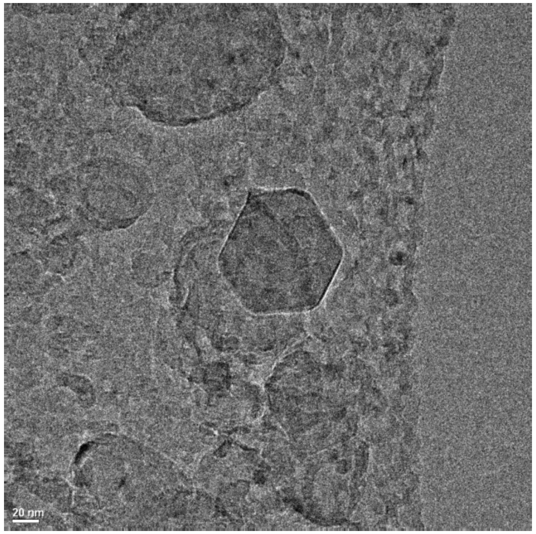
TEM 300kV, 25 °C

More strange TEM-generated halite particles









TEM 200kV, 25 °C

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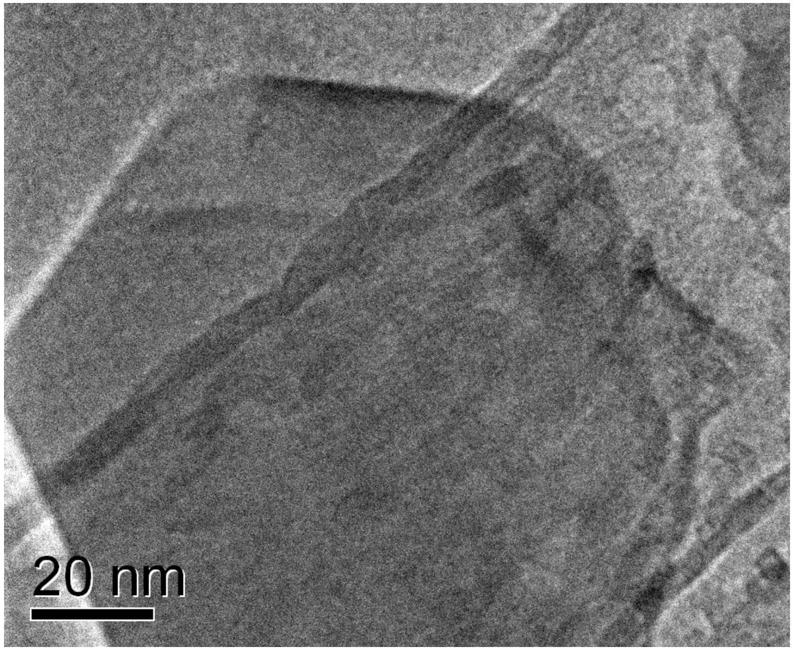
Atomistic Modeling

- Use MD simulations (Ahmed Ismail) to look at evolution of the observed TEM-generated nano-particles
- Build on earlier defect energetics modeling by Catlow, Diller & Hobbs (1980)



TEM 200kV, 25 °C