SAND2012-7427C

Exceptional service in the national interest

Sandia National Laboratories

Imaging and Quantification of Hydrogen Isotope Trapping

Richard Karnesky, Norm Bartelt

(Sandia National Laboratories)

Nick Teslich, Mukul Kumar

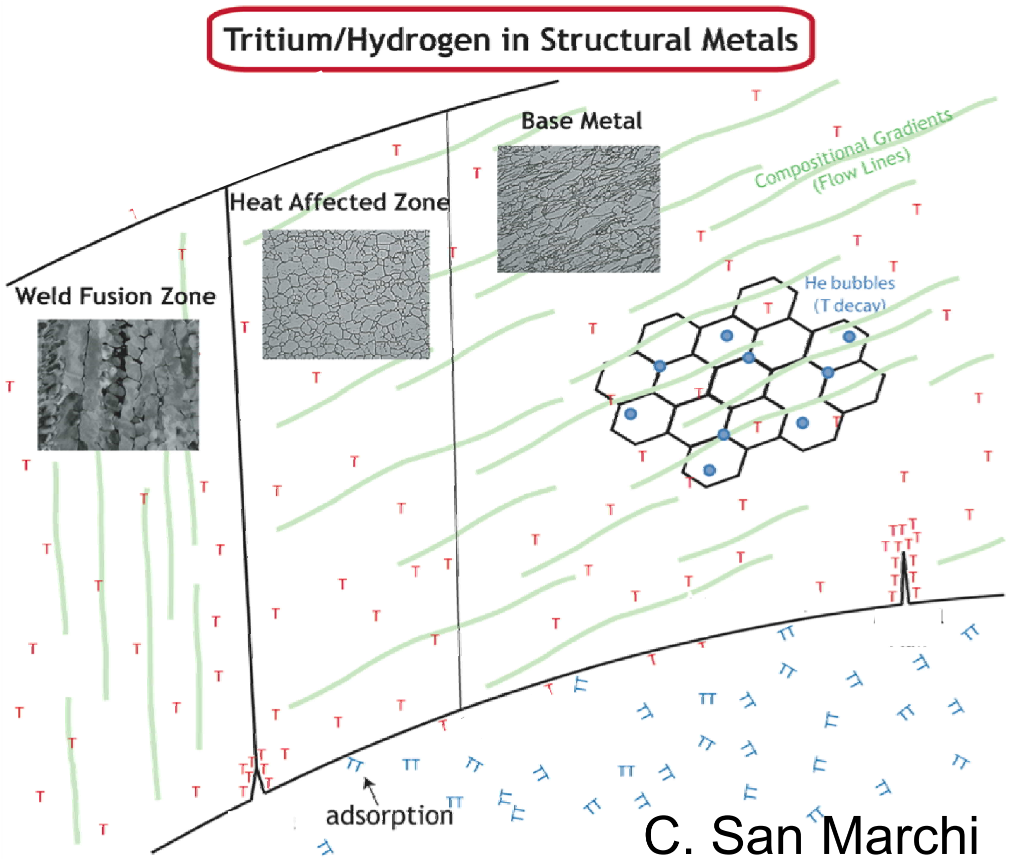
(Lawrence Livermore National Laboratories)

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

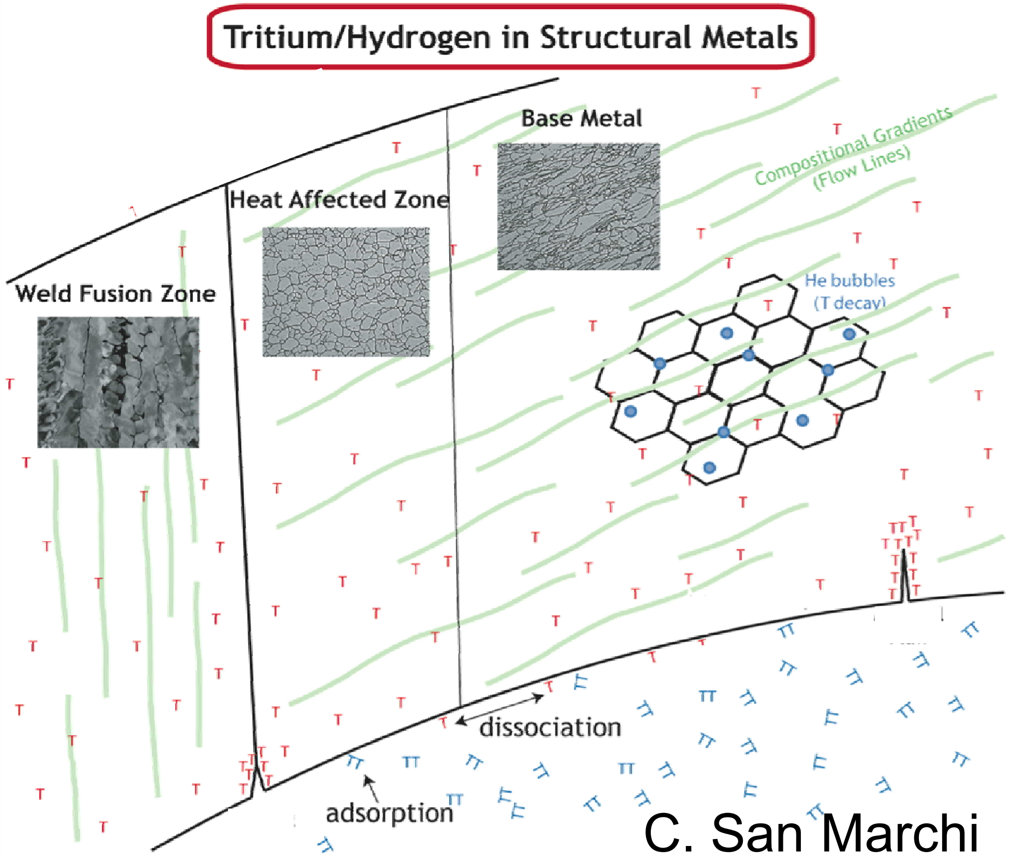
Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. SAND NO. 2012-7427 C

Hydrogen Isotopes in Metals



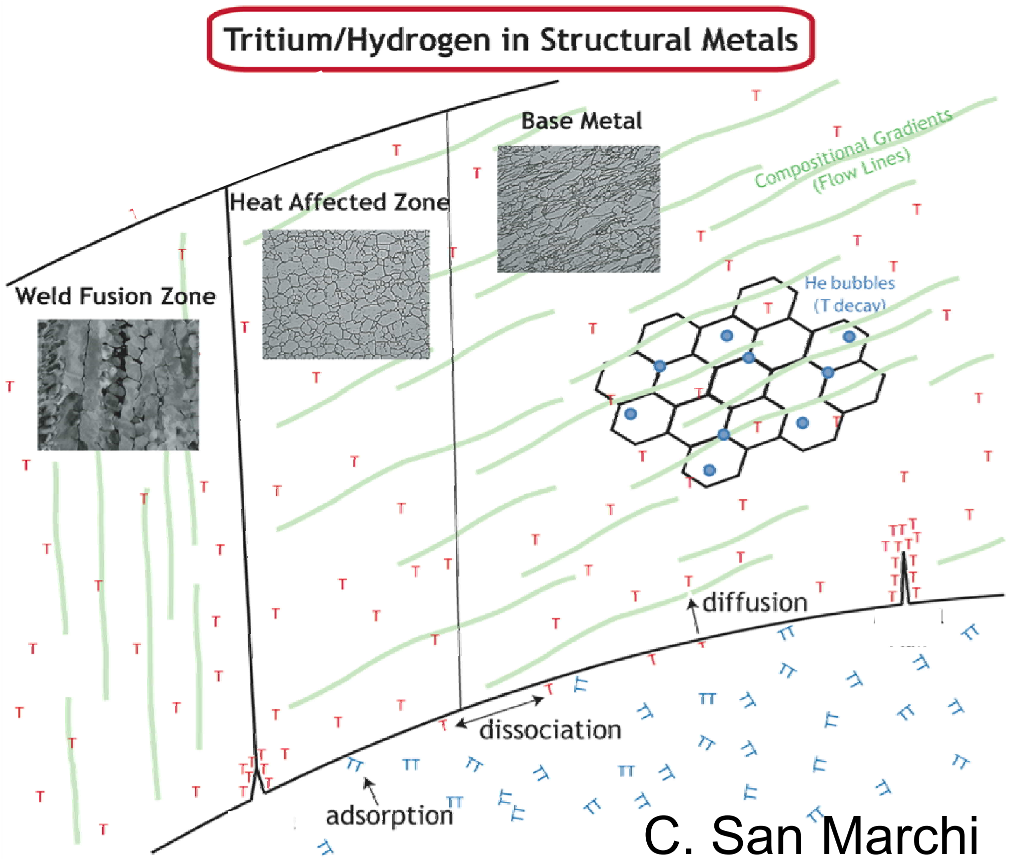
C. San Marchi

Hydrogen Isotopes in Metals

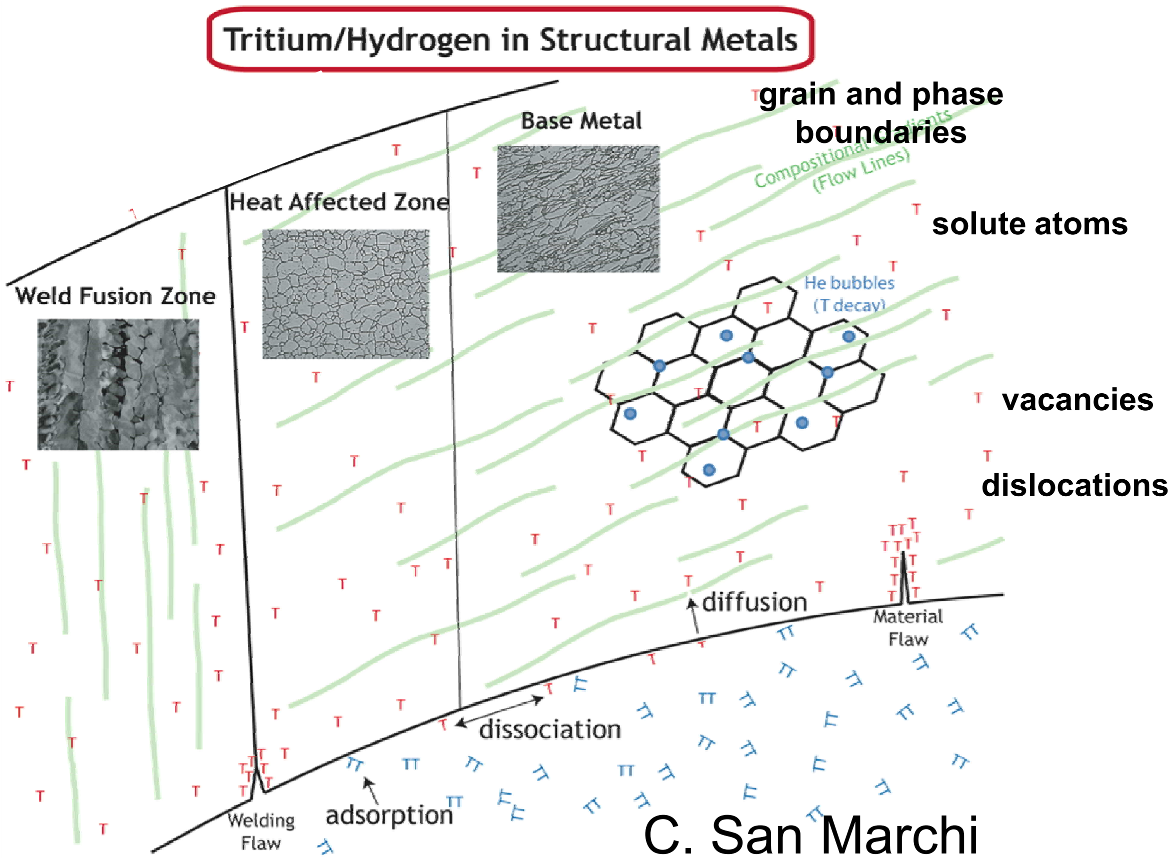


C. San Marchi

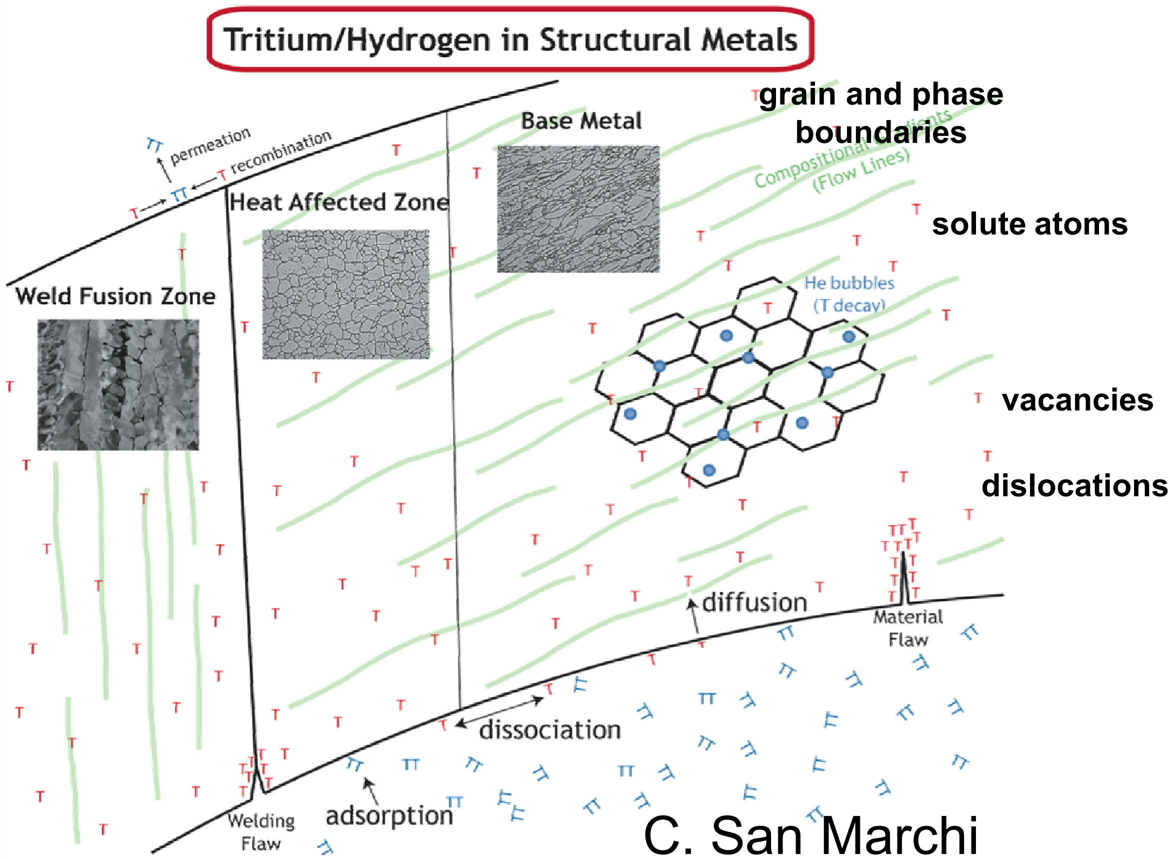
Hydrogen Isotopes in Metals



Hydrogen Isotopes in Metals



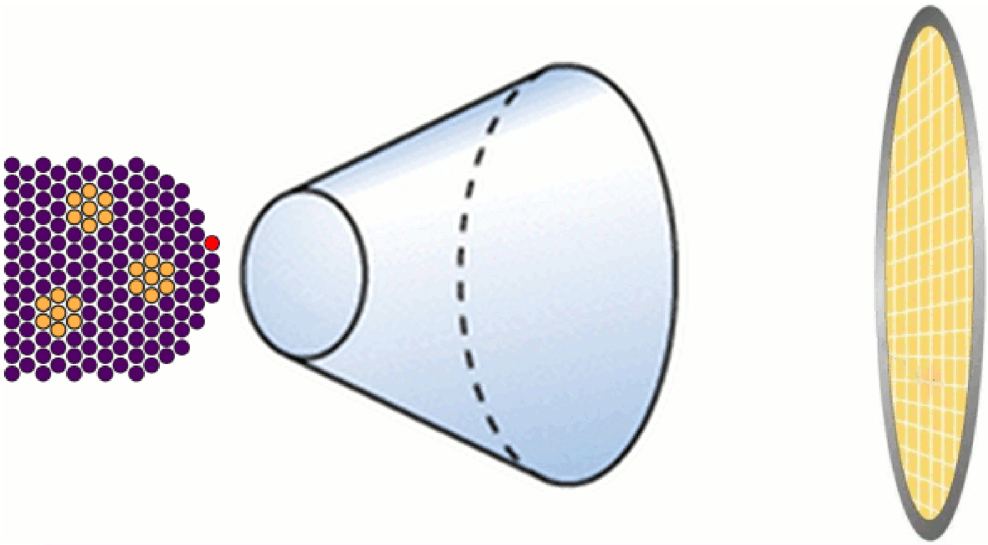
Hydrogen Isotopes in Metals



Local-Electrode Atom-Probe (LEAP) Tomography

Compositional and structural analysis at the atomic scale

- Pulse encodes z
- Area detector gives (x,y)
- TOF encodes mass/charge



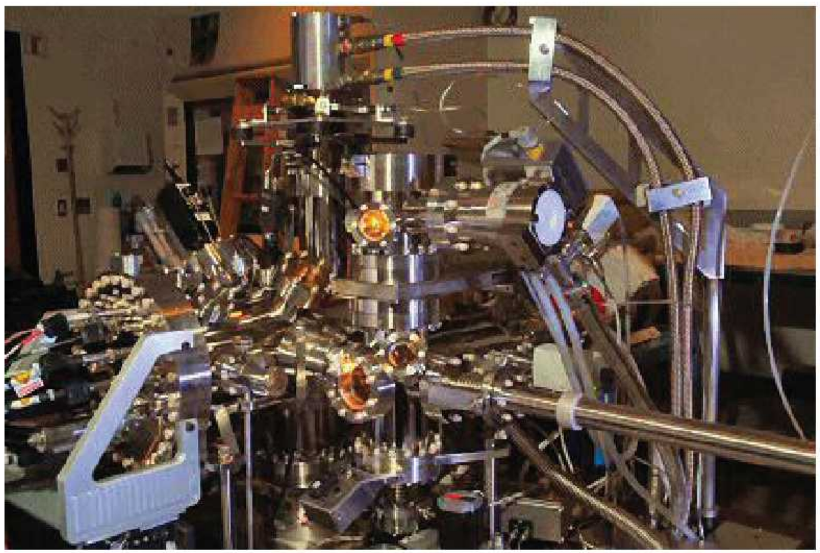


Photo courtesy of R.P. Koll

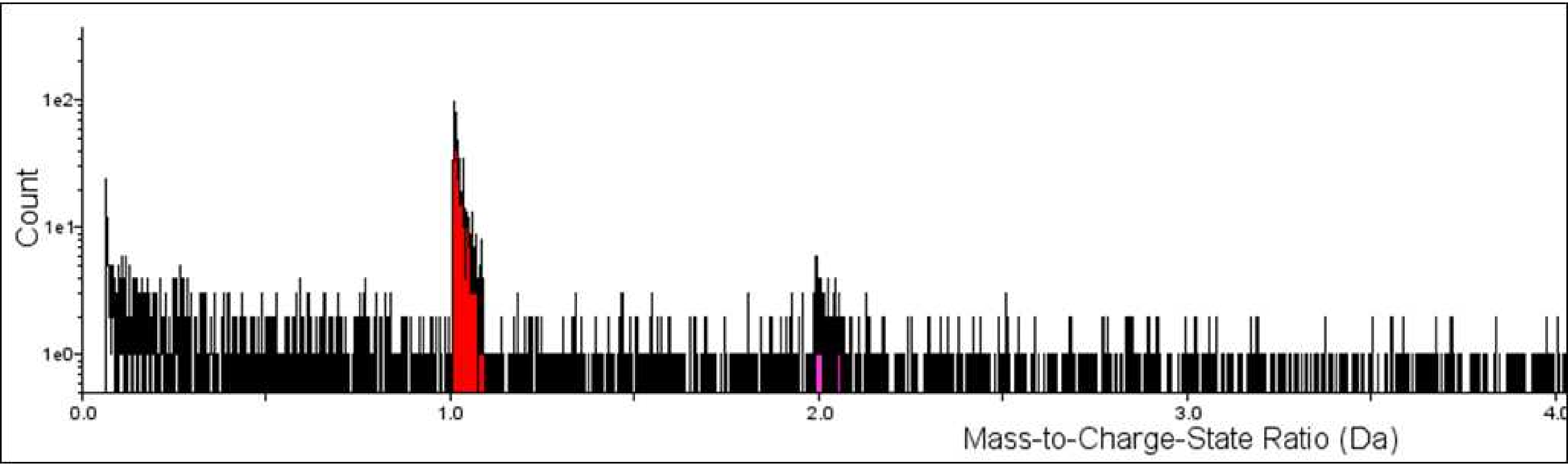
Instrument capability

- 10^6–10^7 nm^3 analysis volume
- 3×10^{-11}–10^{-10} torr UHV
- 20–100 K specimen temp.
- 200 kHz electrical pulsing

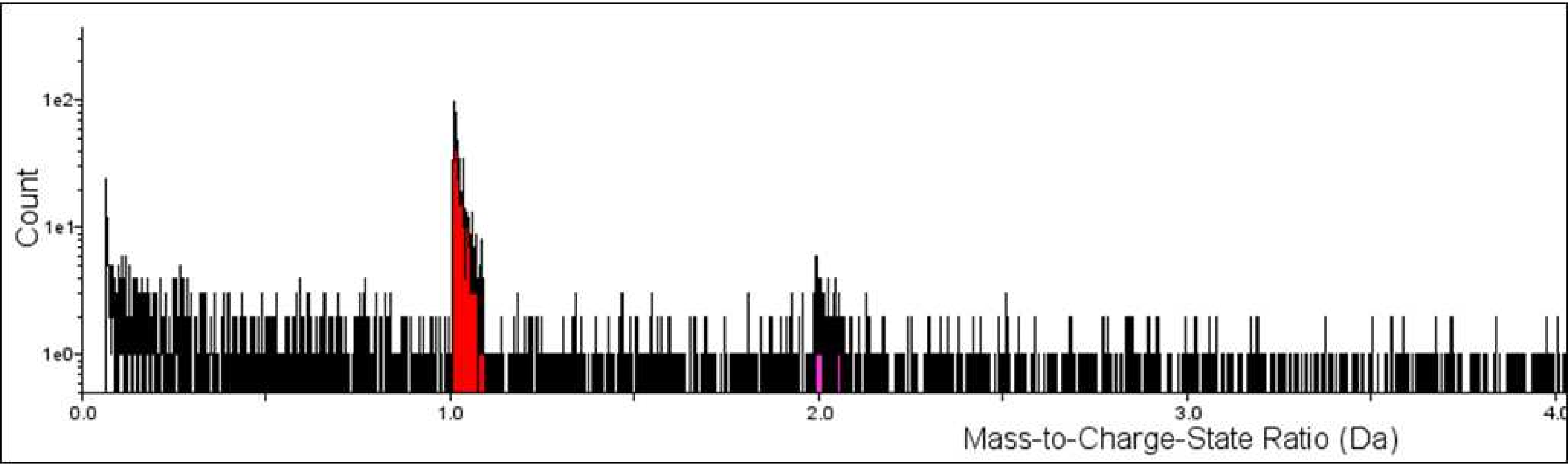
Specifications of Atom-Probe Tomography

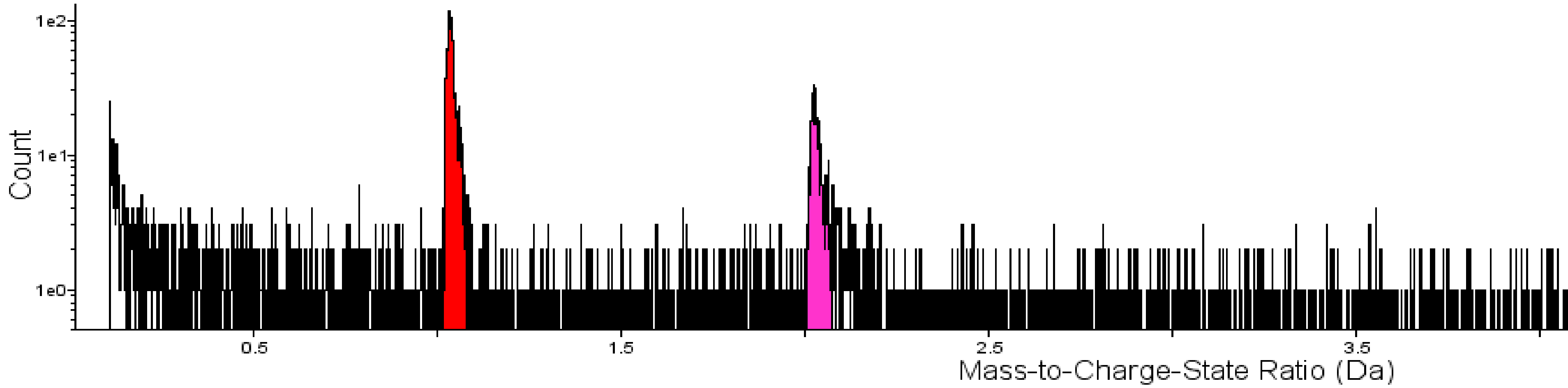
- 3-D
- Sub-nm resolution
- Equal sensitivity across periodic table
- 1 PPM detection
- 50-60% detection efficiency
- 200 kHz pulsing

Protium in Base Vacuum



Deuterium Signal can be Deconvolved





Material Systems Investigated

- UFG Al-Mg
- GB-engineered Ni
- 21-6-9 (Cr-Ni-Mn) SS with various amount of N

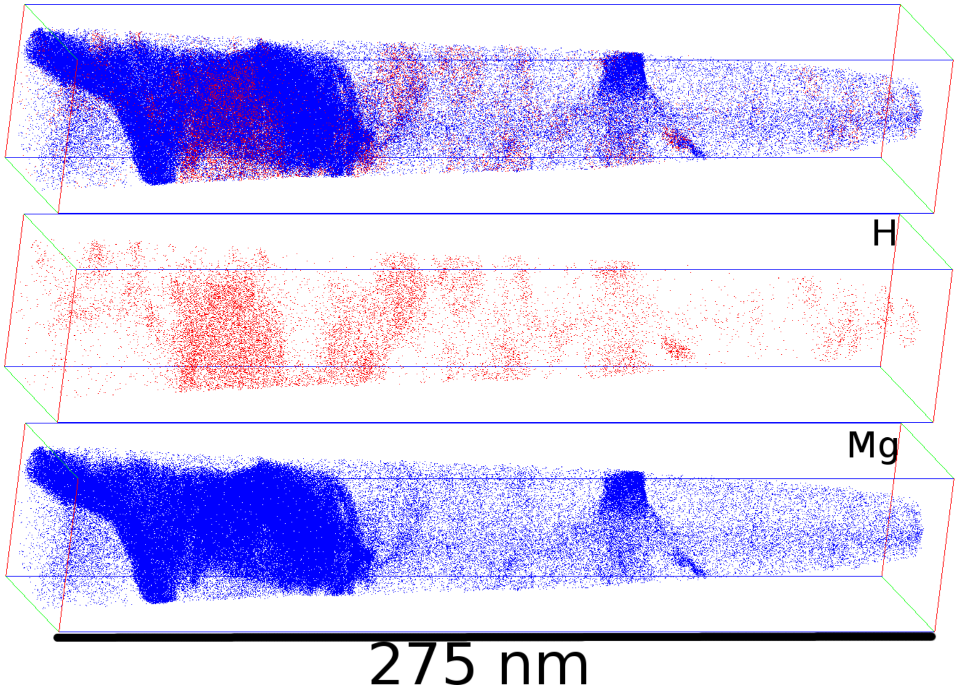
Observation of trapping sites

- **Observe trapped hydrogen isotopes by LEAP tomography**
  Establishes direct evidence of how microstructural features (solute atoms, precipitates, grain boundaries) trap hydrogen isotopes.

Approach:
- Cryomill Al-7.5Mg
- Consolidation
  - Hot Isostatic Pressing
  - Extrusion
- Precharge in 20 ksi, 300C
- Atom-probe tomography

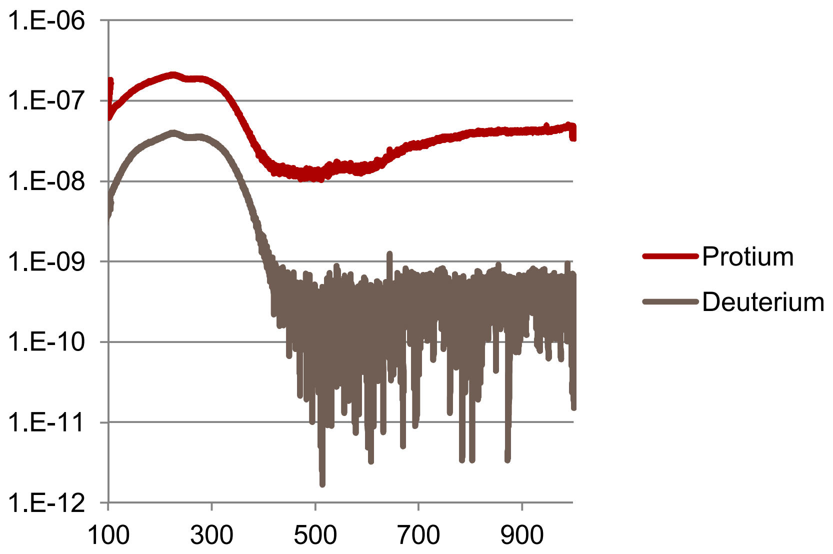
Results:
- Excess Mg segregate to GB
- H segregates to Mg-rich GB

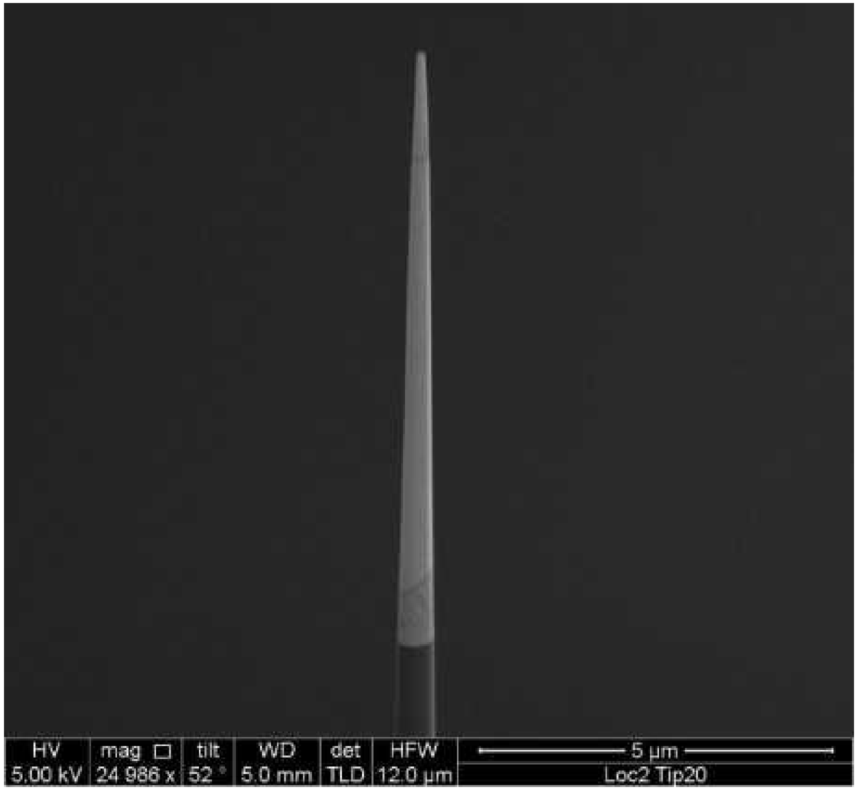
Protium in LEAP tomography



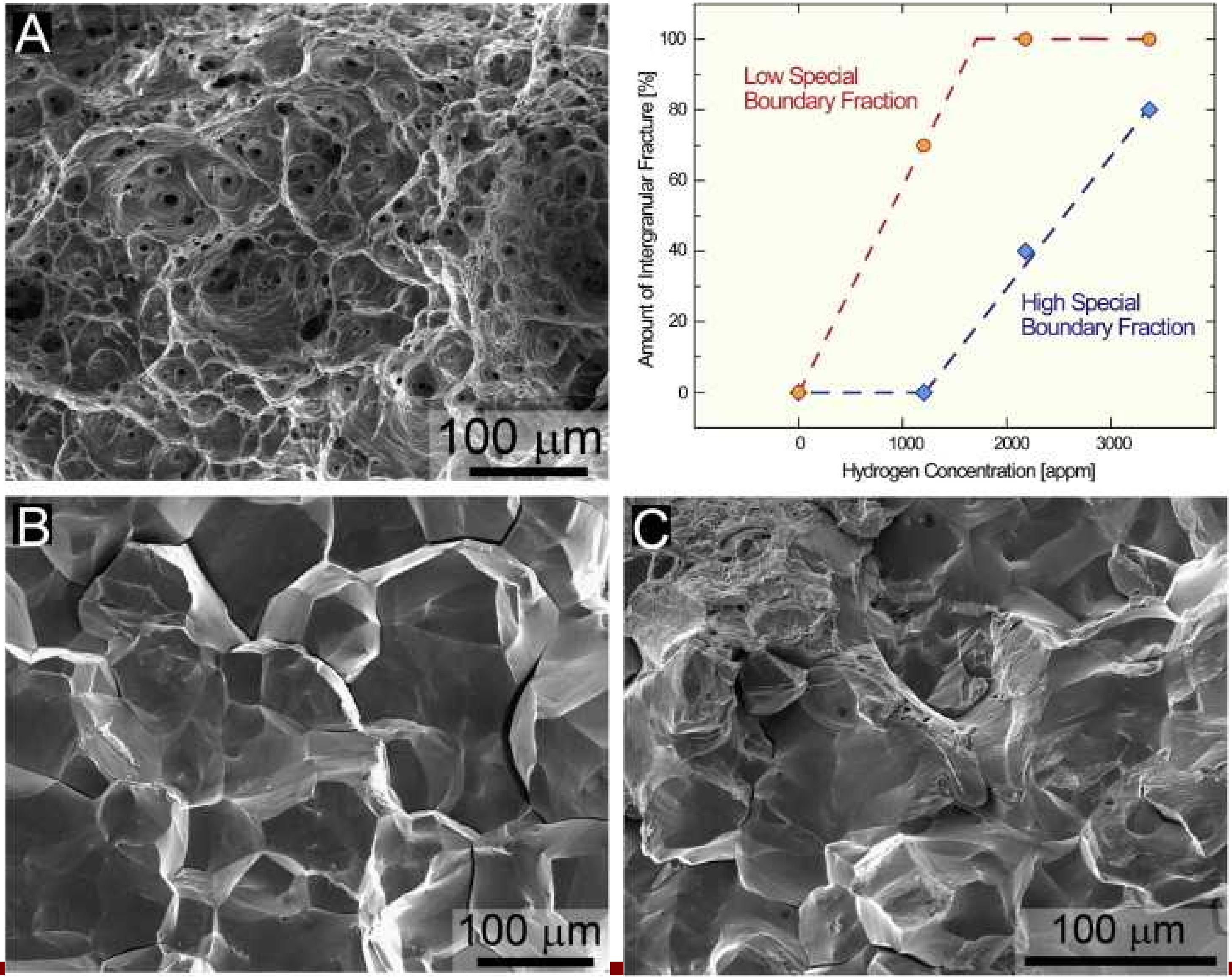
TDS of LEAP tips

- H replaces D during electropolishing
  - Ion-beam milled specimens; Charge pre-sharpened specimens



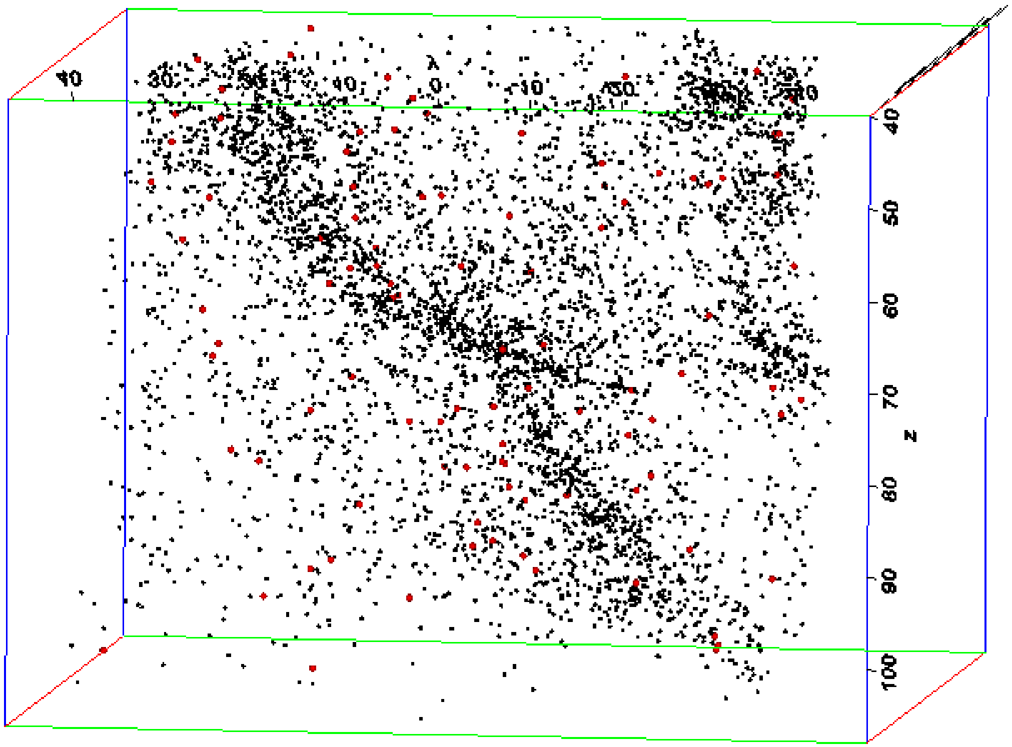


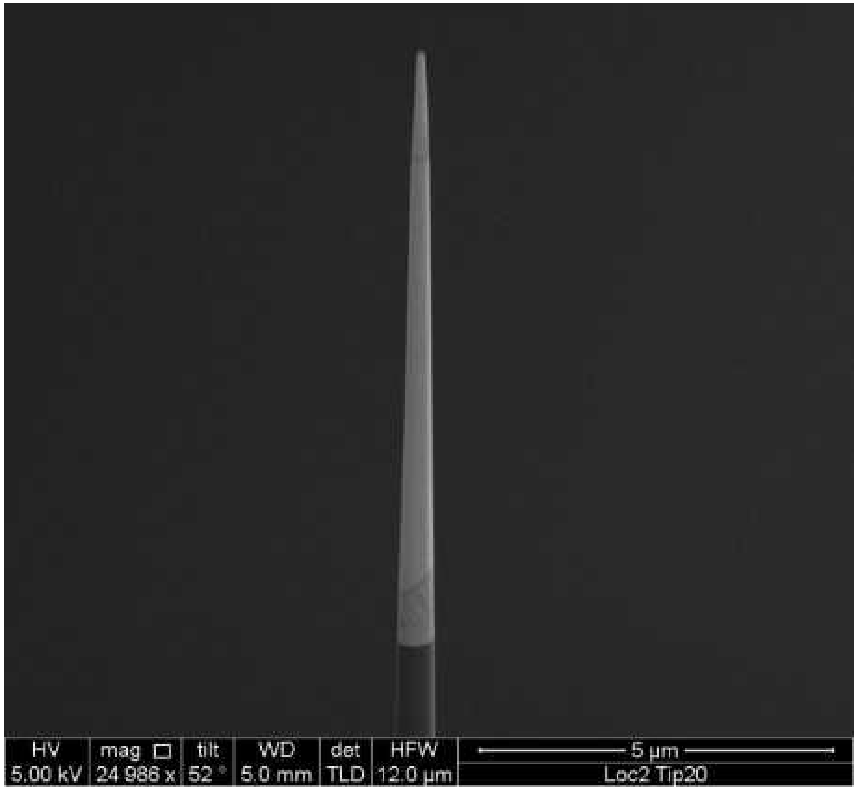
Intergranular Fracture Properties Depend on Microstructure and Environment



S. Bechtle, M. Kumar, B.P. Somerday, M.E. Launey, R.O. Ritchie (2009) *Acta Mater* **57**:4148-4157

S and D at "non-special" GB





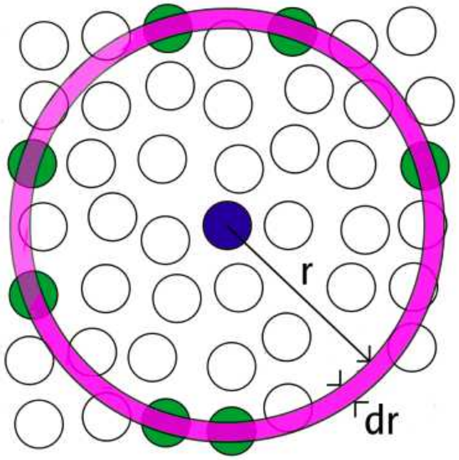
Deuterium Trapping to N in 21-6-9 Verified by RDF

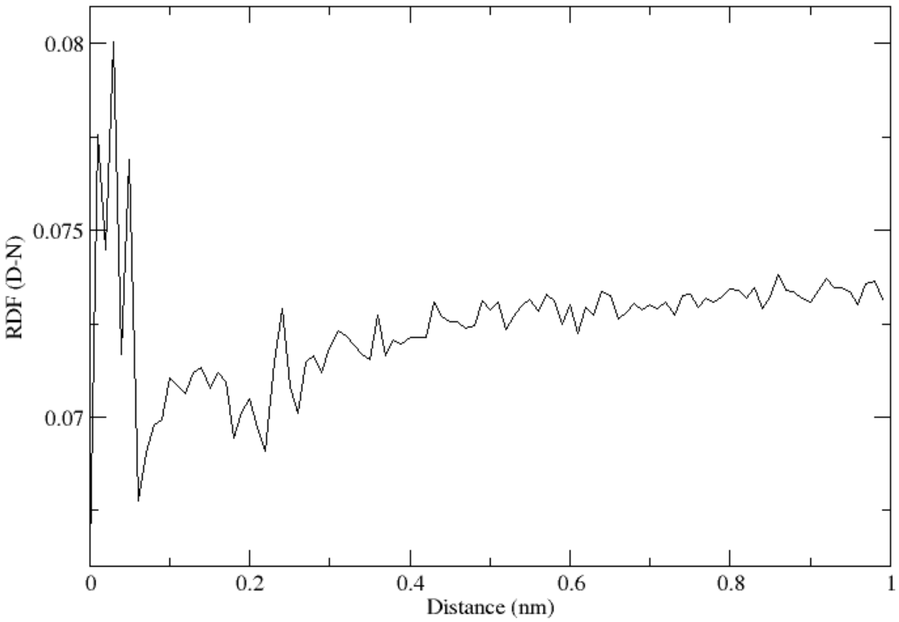
- **Measured deuterium near nitrogen using radial distribution functions**

  Confirm that nitrogen is an important trap

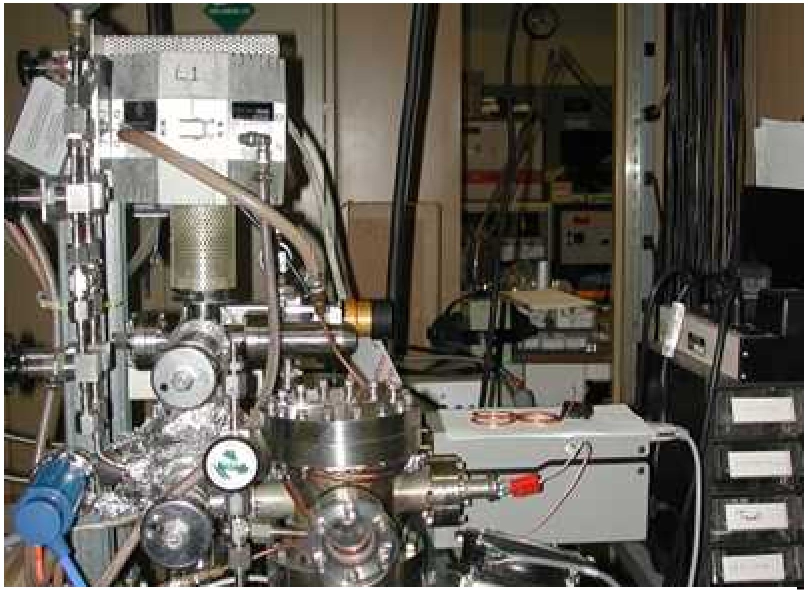
Results:

- No trapping is obvious visually.
- RDF shows there is a preference for D-N SRO

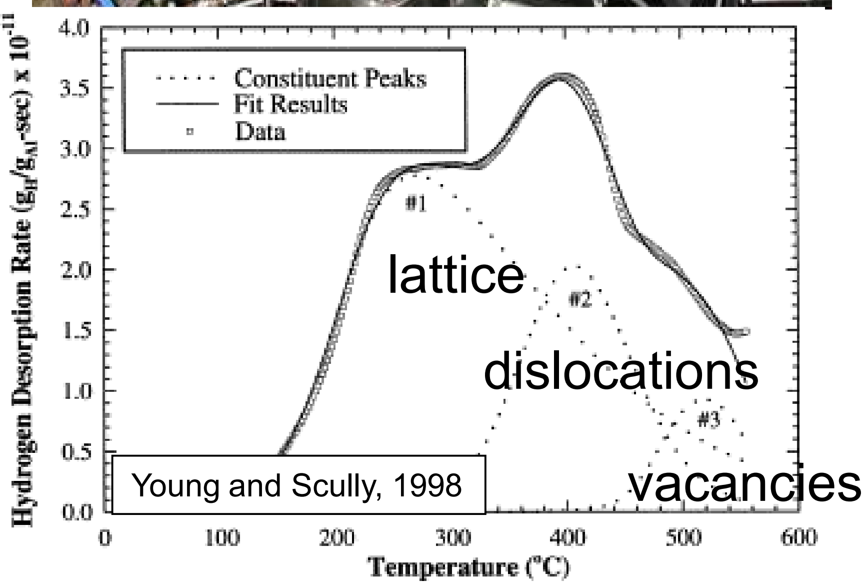


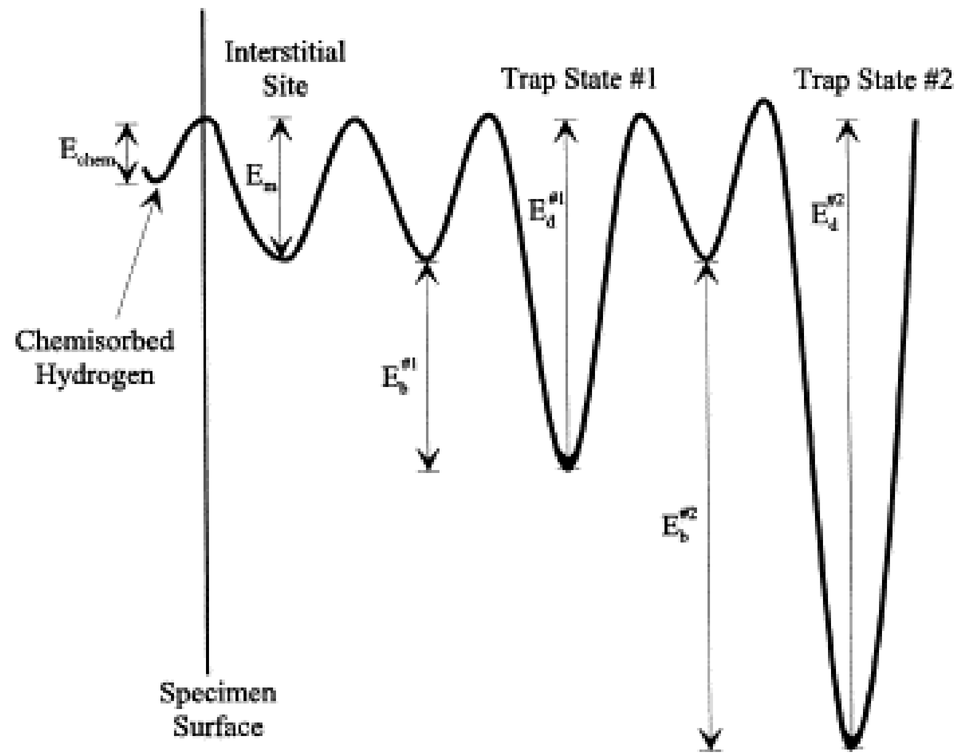


Bulk Analysis Using TDS



- Measures total dissolved and trapped hydrogen and deuterium using an RGA
- Peak fitting spectra reveals trapping energies and occupancies
  - IR furnace (>1000 ° C)
  - 10^{-9} torr base pressure





Measure hydrogen trapping energies

Sandia National Laboratories

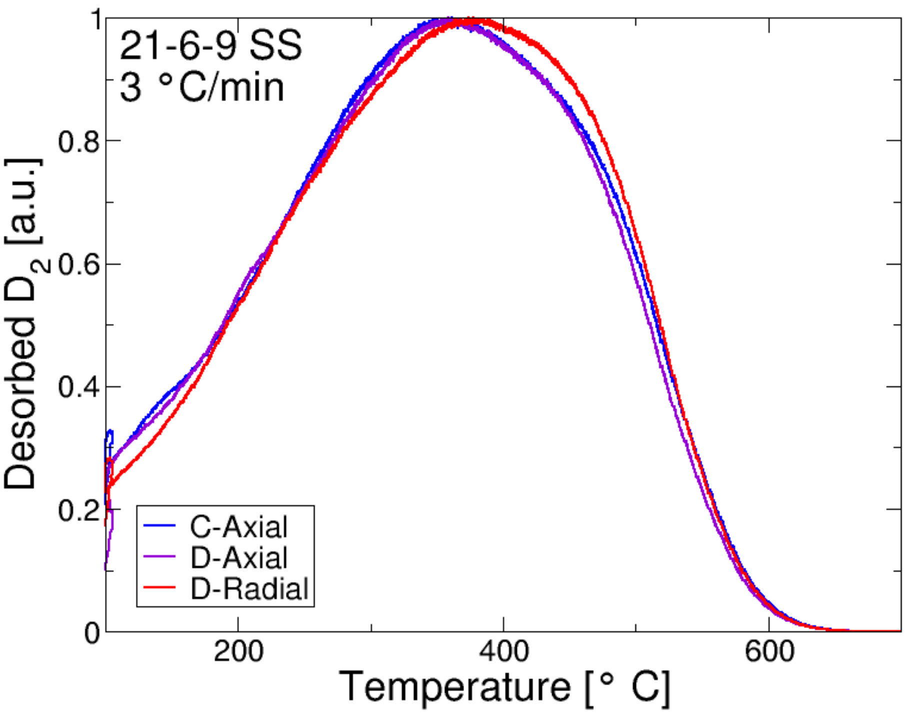
- **Measure trapping energies in stainless steel using TDS**

  Establishes energies to use in bulk transport models and can be compared to first principles approaches

Approach:
- Precharge in 20 ksi, deuterium at 300C
- Thermal desorption spectroscopy

Results:
- 21-6-9 with varying ferrite levels
  - Independent of ferrite orientation and content
- 21-6-9 with varying N
  - Height of 26 kJ/mol trapping peak varies with N
  - Similar E to dislocations and other solutes

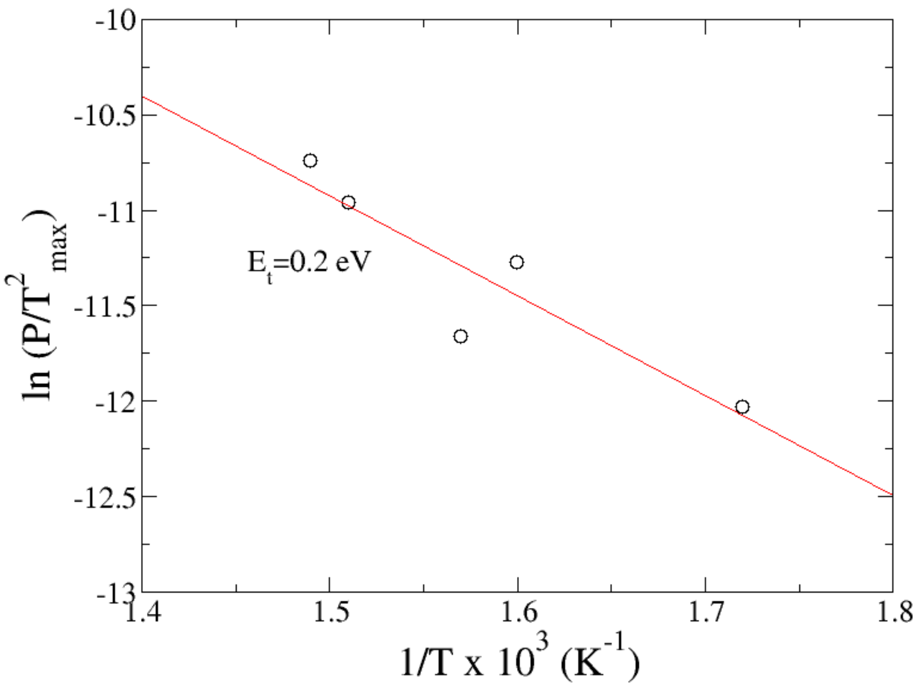
TDS of 21-6-9 with varying ferrite content



Trapping in 21-6-9 with N

- **Calculate hydrogen-solute binding energy in Fe** *and compare to experimental results*

- In agreement with VASP first principles model shows:
  - •N and D prefer octahedral sites
    - •RDF of LEAP data agrees
  - •Binding energy of 0.08 eV/atom (with no magnetism)
    - •Smaller than 0.2 eV measured
  - •With magnetism, there is actually repulsion
    - •Need to check with vacancies

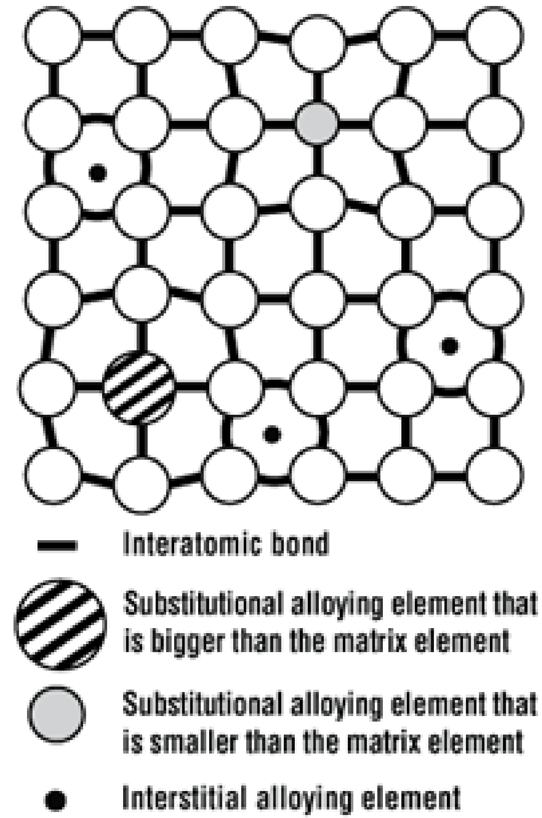


Model trap energies and densities

- **Calculate hydrogen-solute binding energy in Fe** *and compare to experimental results*

Approach:
- VASP first principles modeling

Status:
- Simulated lattices have been generated for solute studies.
- Solutes priority will be selected from LEAP results
- Elements of interest:
    - Cr, Ni, Mn, C, Cu, N, Co, V, W, Ti, Nb, Al, Mo, Si
    - Also vacancies
- More complicated features (dislocations, precipitates, grain boundaries in next FY)



Summary

- LEAP observations show:
  - GB segregation of Mg and H in UFG-Al-Mg
  - Segregation to "non-special" GB of S, D in CP Ni
  - SRO of N-D in 21-6-9 containing various N
- TDS observations show:
  - H replacement of D on electropolishing
  - 0.2 eV/atom trapping of D to N in 21-6-9

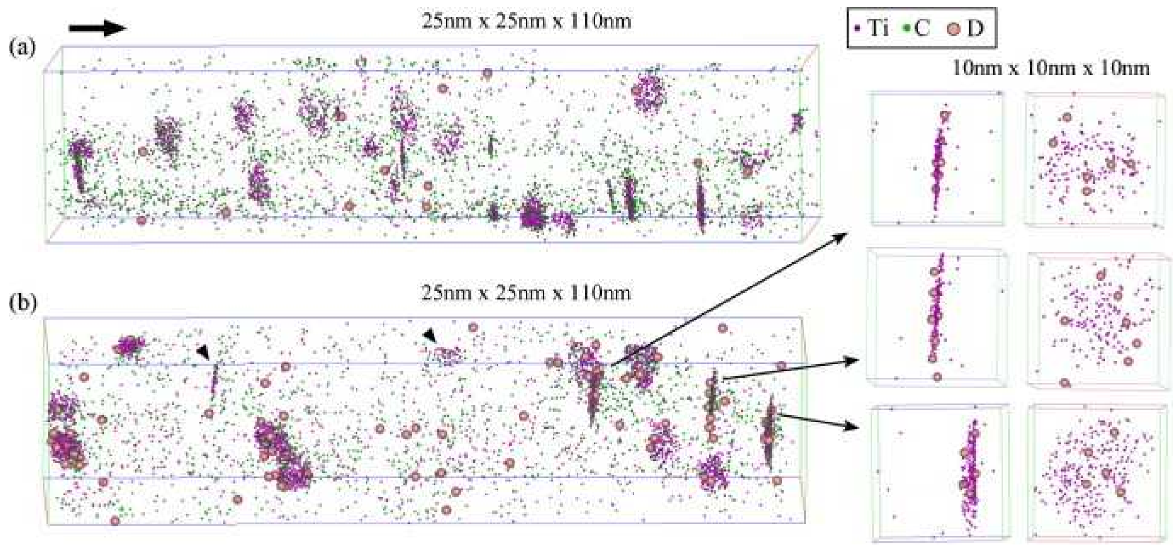
Acknowledgements

- SNL LDRD, GTS funding
- D Balch, C San Marchi, B Somerday (discussion)
- D Isheim

Summary

- LEAP observations show:
  - GB segregation of Mg and H in UFG-Al-Mg
  - Segregation to "non-special" GB of S, D in CP Ni
  - SRO of N-D in 21-6-9 containing various N
- TDS observations show:
  - H replacement of D on electropolishing
  - 0.2 eV/atom trapping of D to N in 21-6-9

LEAP of Trapped Deuterium



J. Takahashi, K. Kawakami, Y., Kobayashi, T. Tarui (2010) *Scripta Mater* ***63****:261-264*
J. Takahashi, K. Kawakami, Y., T. Tarui (2012) *Scripta Mater* ***67****:213-216*