# Diffusion Studies in Mg-Al-Zn

**Bruce Warmack, Nagraj Kulkarni, Bala Radhakrishnan**

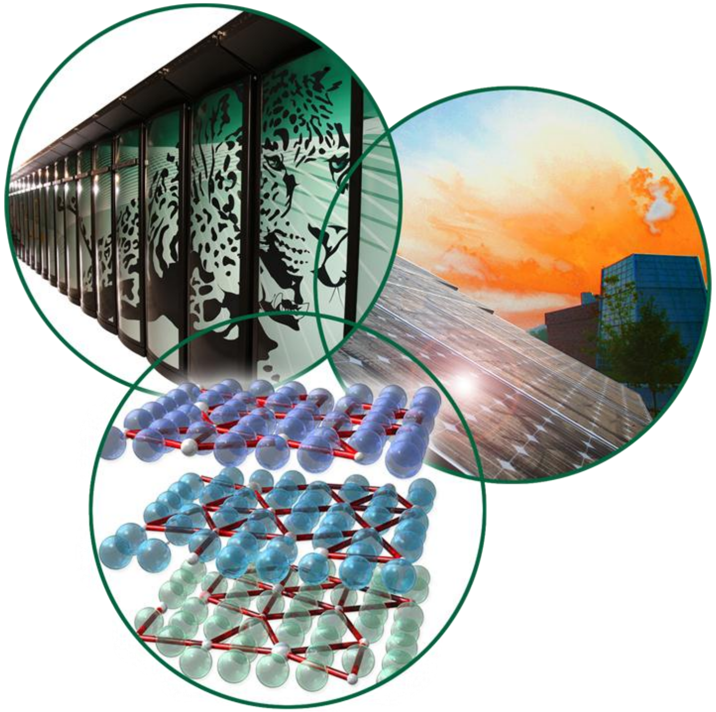
**Jerry Hunter, Jay Tuggle**

**Yongho Sohn, Cathy Kammerer, Kevin Coffey, Ed Dein**

**Graeme Murch, Irina Belova**

**John Mundy (retired)**

**Bruce Davis**



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# Acknowledgements

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Joe Carpenter: Former program manager, Automotive Lightweight Materials Program, DOE

Phil Sklad, Dave Warren: Automotive Lightweight Materials Program, ORNL

# Collaborations and Coordination

**Oak Ridge National Laboratory**
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

- Annealing
- Analysis
- Modeling

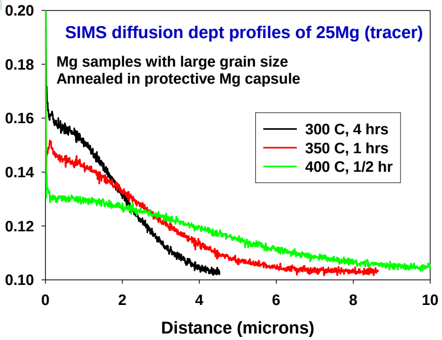
**THE UNIVERSITY OF NEWCASTLE AUSTRALIA**

**Theory**

$$\delta C = C_0 \frac{\delta\xi}{2\sqrt{\pi D t}} \exp\left(-\frac{\xi^2}{4Dt}\right)$$

**VirginiaTech**
*Invent the Future*

- SIMS
- XPS
- Characterization



**UNIVERSITY OF CENTRAL FLORIDA**

- Coating
- Interdiffusion
- Analysis

**Magnesium Elektron**
SERVICE & INNOVATION IN MAGNESIUM

- Material casting
- Extrusion

**ORNL**
project
coordination

**ICME-CI**

# Objective

- To develop a Mg tracer diffusion database for Mg, Zn, Al in magnesium-rich alloys for incorporation in the Integrated Computational Engineering (ICME) project

# Approach/Strategy

- Measure tracer diffusion coefficients of Mg and Zn in the Mg-Al-Zn-Mn system using secondary ion mass spectrometry (SIMS)
- Tracer diffusion data are preferred for database incorporation: robust, accurate, assumption-free, easier to utilize
- In case of a monoisotopic element such as Al, interdiffusion data will be combined with measured tracer diffusivities along with thermodynamics to extract tracer coefficients using diffusion theory (e.g., Darken/Manning theories)

# Onsager Diffusion Formalism

- **Intrinsic fluxes where driving forces are chemical potential gradients (Onsager):**

$$J_k = -\sum_i L^n_{ki}\,\mathrm{grad}(\mu_i) \qquad \sum_k J_k = \text{-}J_v$$

- **$L_{ki}$'s obtained from tracer diffusion data using Manning relations:**

$$L_{ii} = \frac{C_i D_i^*}{kT}\left(1 + \frac{2C_i D_i^*}{M_0 \sum_k C_k D_k^*}\right) \qquad L_{ij} = \frac{2C_i D_i^* 2C_j D_j^*}{kT M_0 \sum_k C_k D_k^*} \qquad i \neq j$$

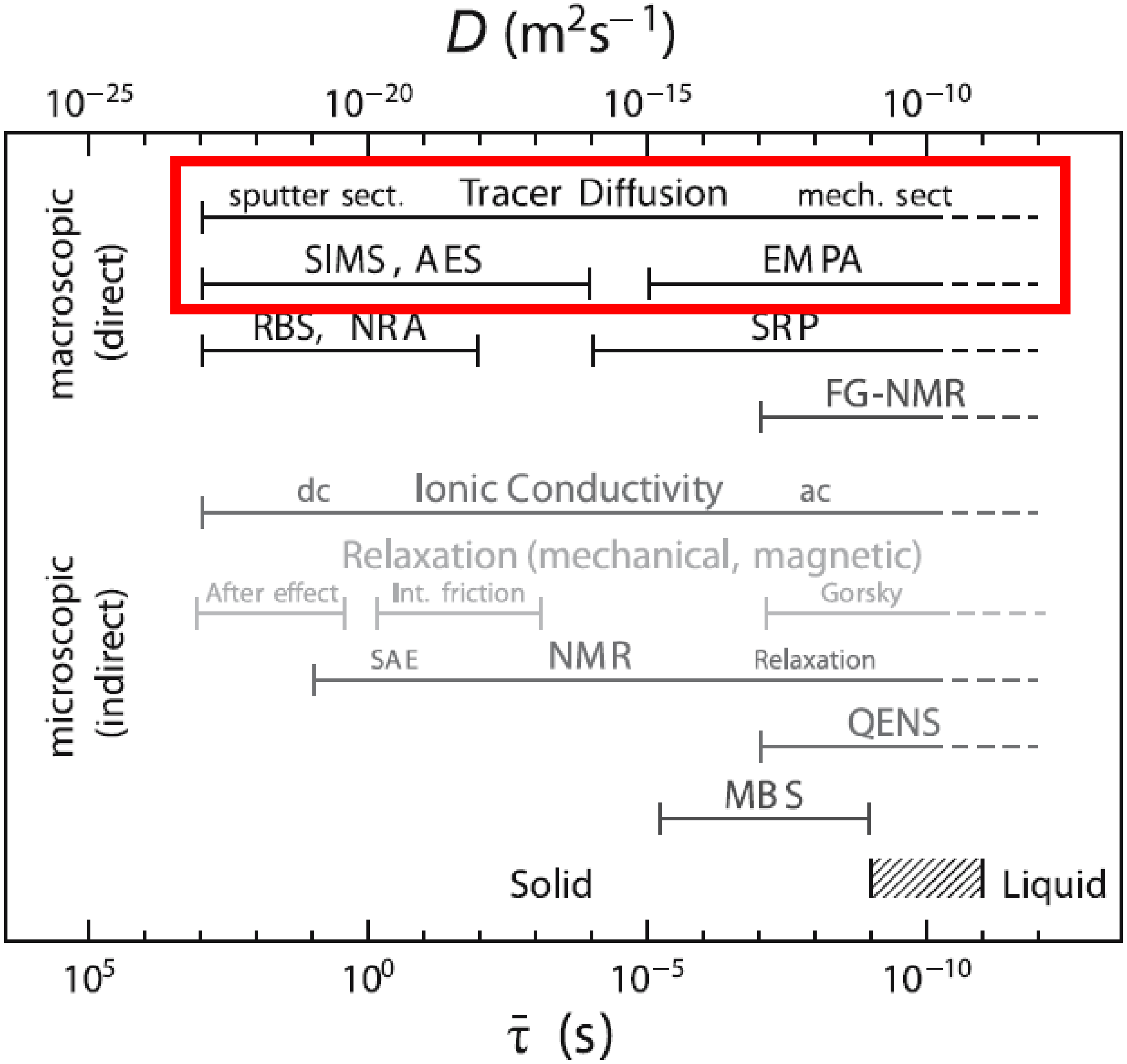
- **Chemical potentials from thermodynamic database**

➢ *Cross-terms are not ignored as in Darken (correlation effects influence cross-terms)*

➢ *Tracer diffusion data is independent of thermodynamic database*

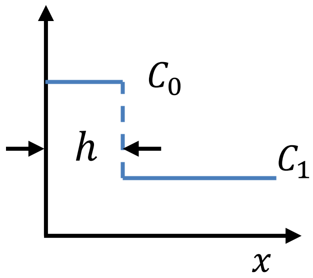
# Tracer Diffusion

## Data over large temperature range



Typical ranges of diffusivity (Mehrer, “Diffusion in Solids”)

# 1D Theory

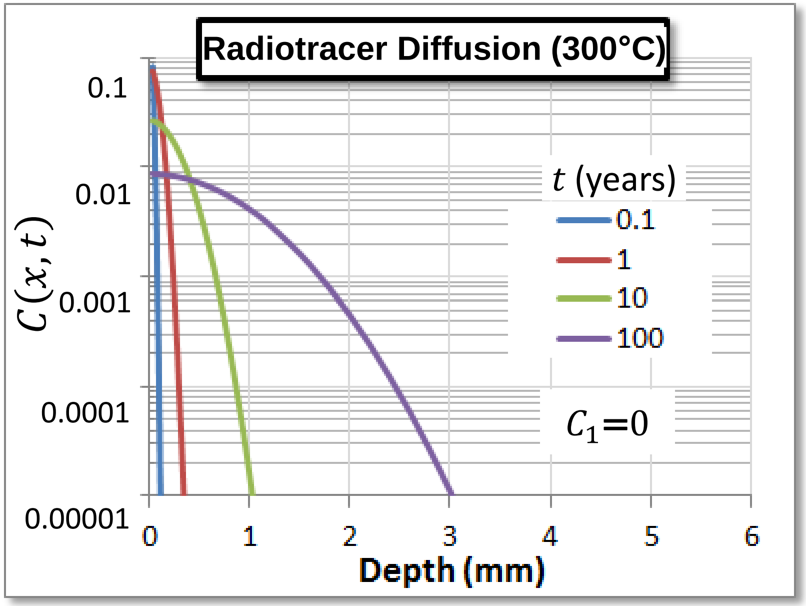


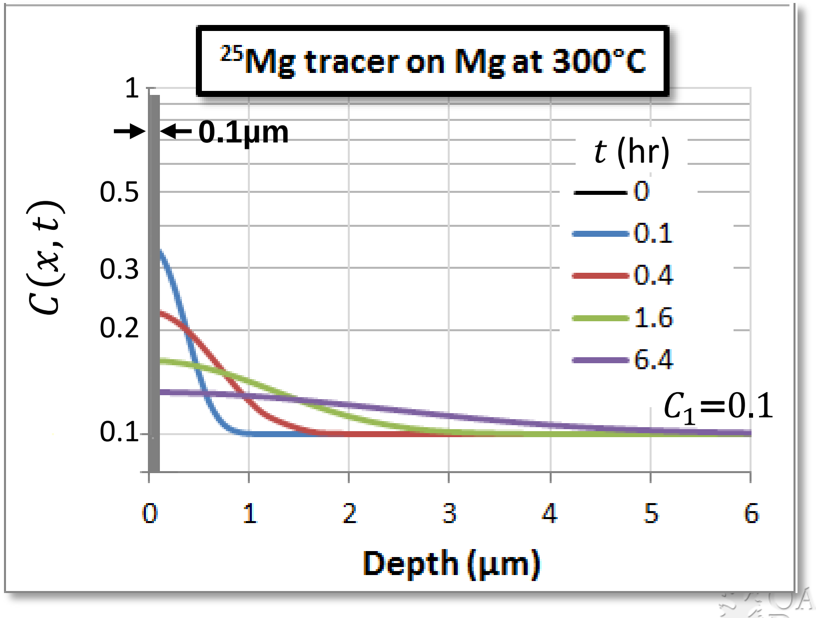
## Slab diffusing into material (constant $D$)

$$C(x,t) - C_1 = \frac{(C_0 - C_1)}{2}\left[\operatorname{erf}\left(\frac{x+h}{2\sqrt{Dt}}\right) - \operatorname{erf}\left(\frac{x-h}{2\sqrt{Dt}}\right)\right]$$

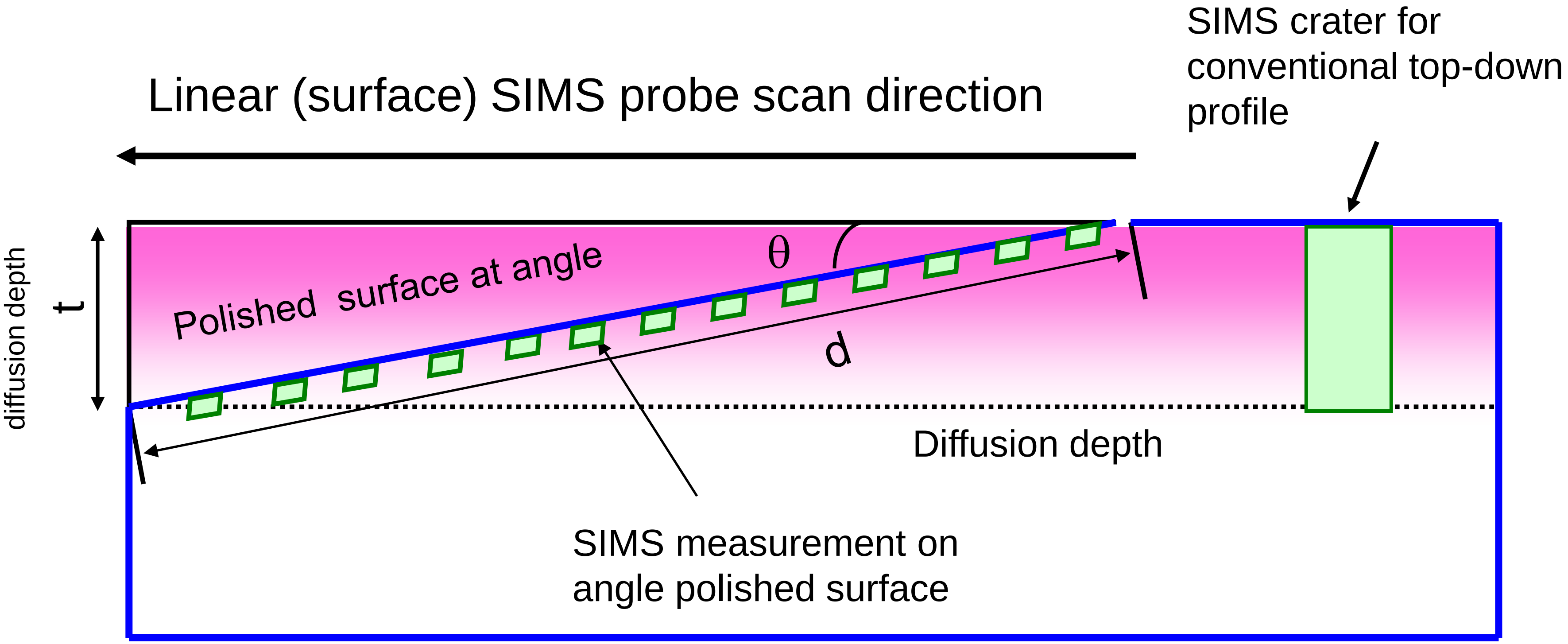
$$C(x,t) - C_1 \approx (C_0 - C_1)\frac{h}{\sqrt{\pi D t}}\exp\left(-\frac{x^2}{4Dt}\right) \qquad h<<2\sqrt{Dt}$$

| Mg Abundances | | | |
|---|---|---|---|
| Isotope | $^{24}$Mg | $^{25}$Mg | $^{26}$Mg |
| Natural | 0.7899 | 0.1001 | 0.1100 |
| Tracer | 0.0180 | 0.9787 | 0.0033 |


Radiotracer Diffusion (300°C)


$^{25}$Mg tracer on Mg at 300°C

# Angle polish SIMS for shallow or deep diffusion depths



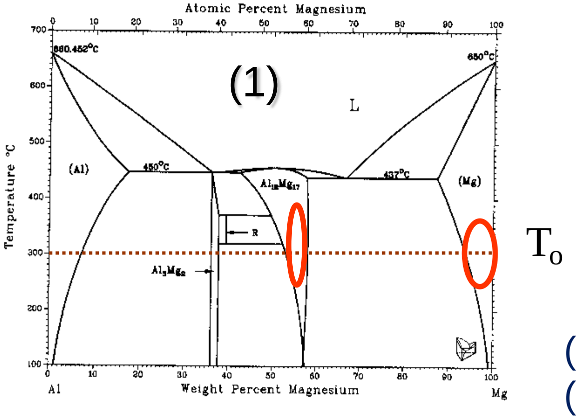
$d = t / \sin(\theta)$ : angle polish surface used for SIMS discrete/depth profile measurements

$t = 100\ \mu m$: tracer diffusion depth

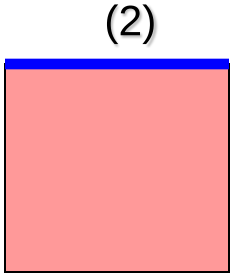
$\theta = 1$ deg; $d = 5730\ \mu m$; Magnification = 5730 /100 ~ 57

Hence, 5730/20 ~ 286 discrete SIMS measurements every 20 μm along d

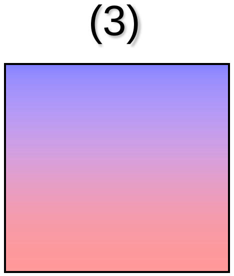
# Tracer Diffusion: SIMS-based thin-film stable-isotope technique



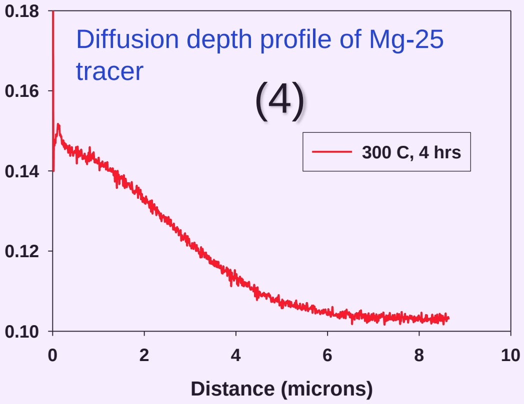
(1) Prepare single phase alloy sample (e.g., Mg-5%Al) at $T_o$



(2) Deposit thin film (100 nm) of stable isotope of an alloy element (e.g., $Mg^{26}$) on annealed sample



(3) Anneal at $T_o$ for desired times (mins to hrs) to cause isotope to diffuse inwards

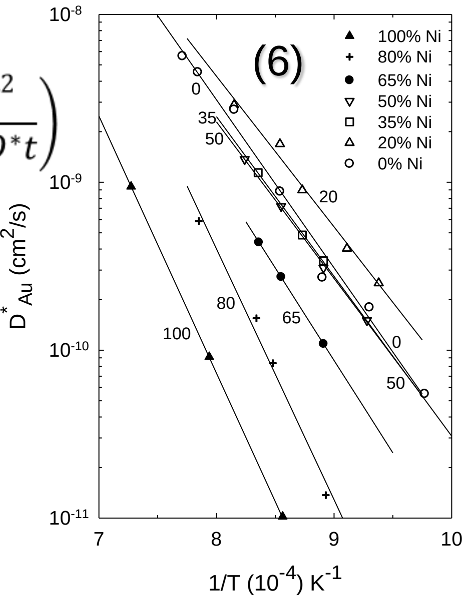


(4) Measure depth profile of isotope or isotope ratio with SIMS

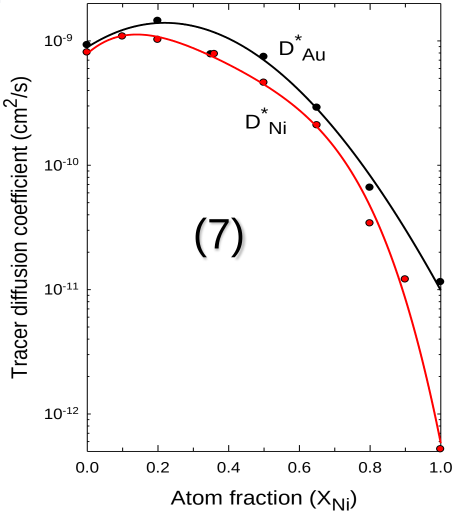
(5)

$$C^*(x,t) \approx \frac{h}{\sqrt{\pi D^* t}} \exp\left(-\frac{x^2}{4D^* t}\right)$$

(5) Fit depth profile data for isotope in (4) with above thin-film solution to extract tracer diffusivity $D^*$.



(6) Repeat for different temperatures and compositions to check for Arrhenius fits (e.g. Au in Au-Ni alloys, *Kurtz et al., Acta Met.'55*)



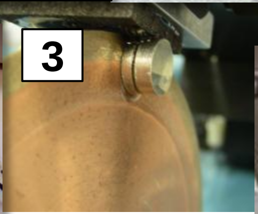
(7) Fit using suitable polynomials for functional form of isotopic diffusivity $D_k^*(X_1, X_2, \ldots, T)$ (e.g. Au-Ni tracer diffusion at 900°C, *Reynolds et al. Acta Met. '57* )

# Process Sequence

1. Single phase alloy extrusion
2. Homogenization and grain-growth anneal
3. Sectioning
4. Conditioning anneal
5. Polishing/Coating
6. Annealing
7. SIMS profiling
8. Analysis


1


2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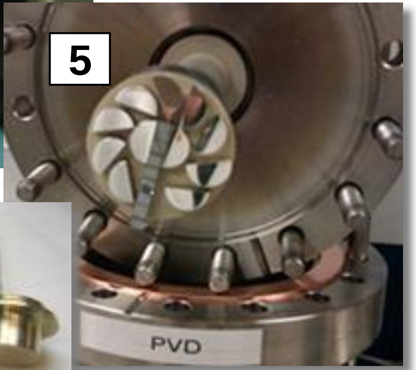
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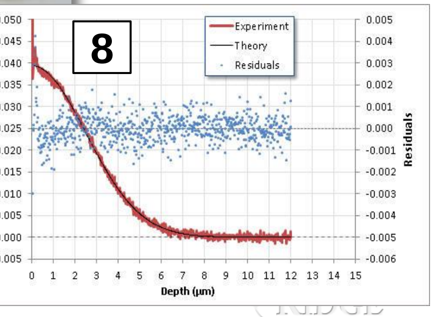
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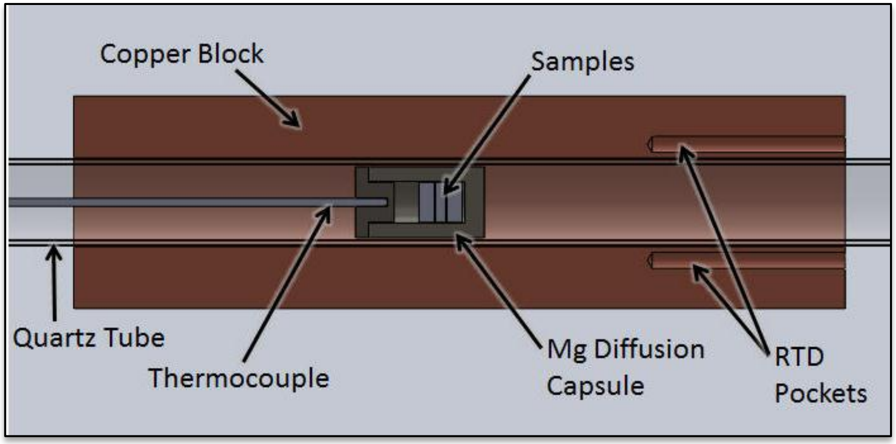
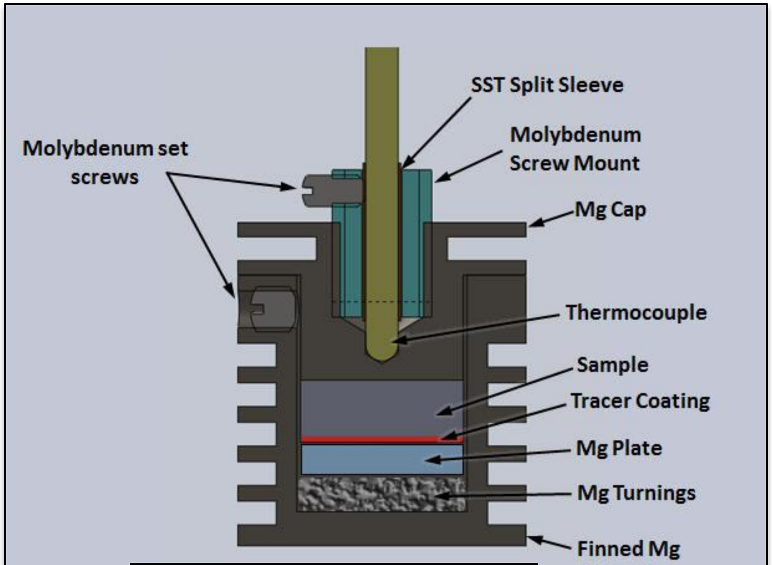
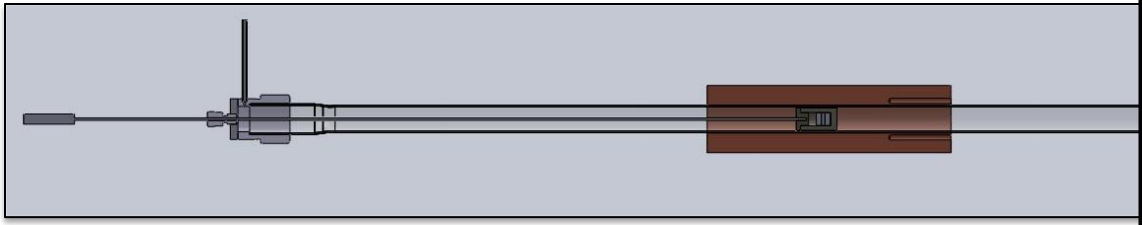
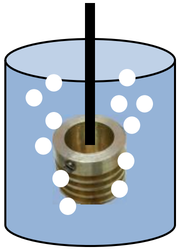
# Diffusion annealing technique









- ➢ Design allows rapid heating (Cu block, fin design) and cooling (liquid nitrogen)
- ➢ Mg capsule & turnings act as natural getter to prevent oxidation
- ➢ Thermocouple in capsule allows full correction and more accurate analysis especially for short anneal times (10 minutes)

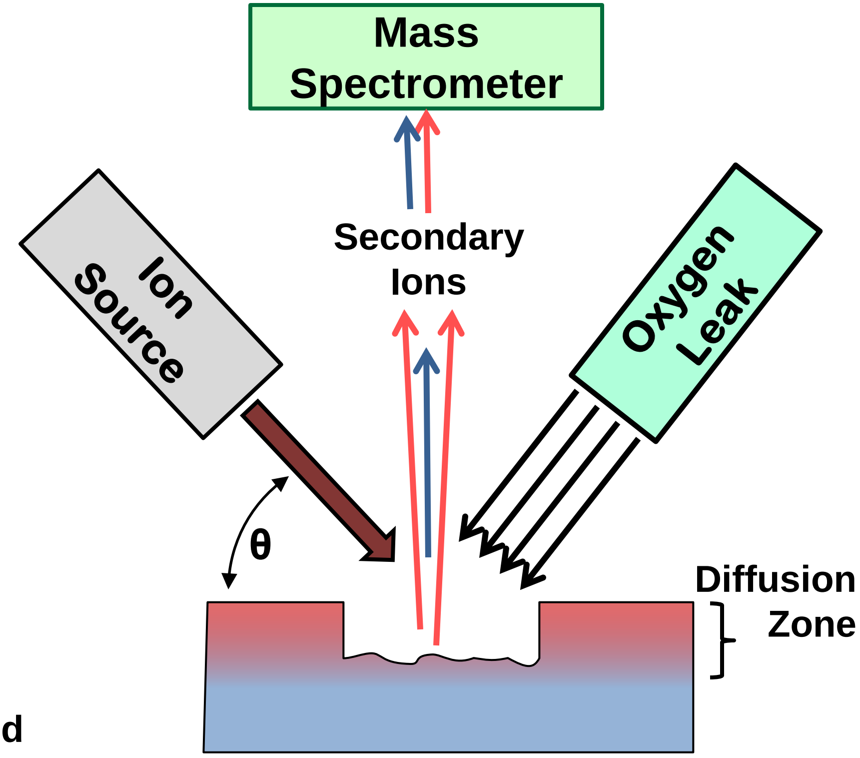
# Secondary Ion Mass Spectrometry

- Roughness increases with sputter depth for polycrystalline samples due to grain orientation
- Oxygen leak creates an amorphous oxide surface to reduce grain orientation effects
- Also, energy and angle are optimized to reduce roughness

| Energy, kV | O-leak | Angle | Roughness, nm |
|---|---|---|---|
| Unsputtered | | | 7.2 |
| 3 | yes | 37 | 10.7 |
| 2 | yes | 40.6 | 10.7 |
| 3 | yes | 40.6 | 12.2 |
| 3 | yes | 46 | 17.4 |
| 3 | no | 46 | 30.7 |
| 5 | no | 44 | 37.7 |

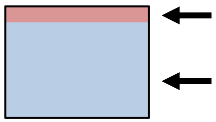
} Optimized

← Typical

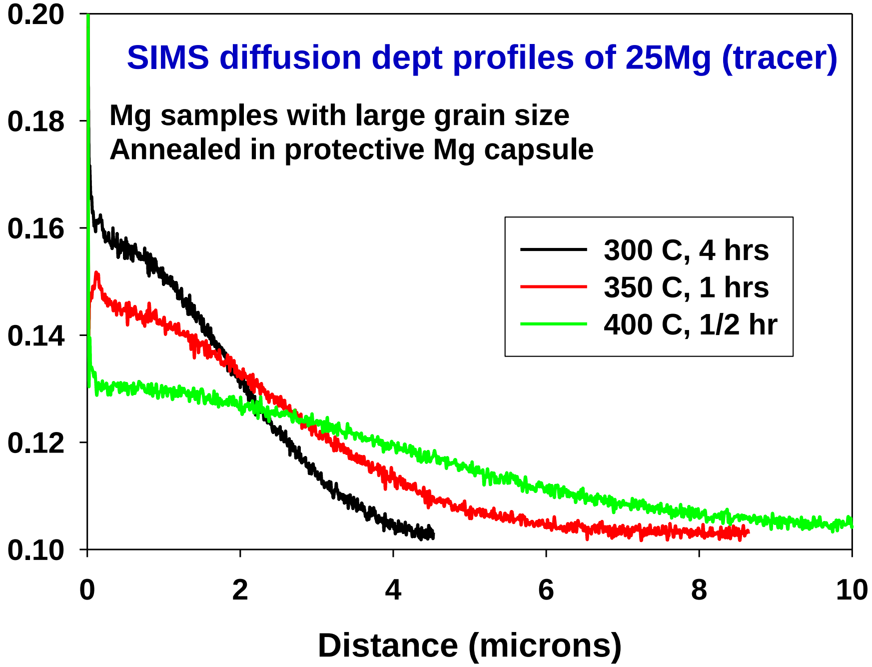


# Experimental Mg self-diffusion

**Initial**

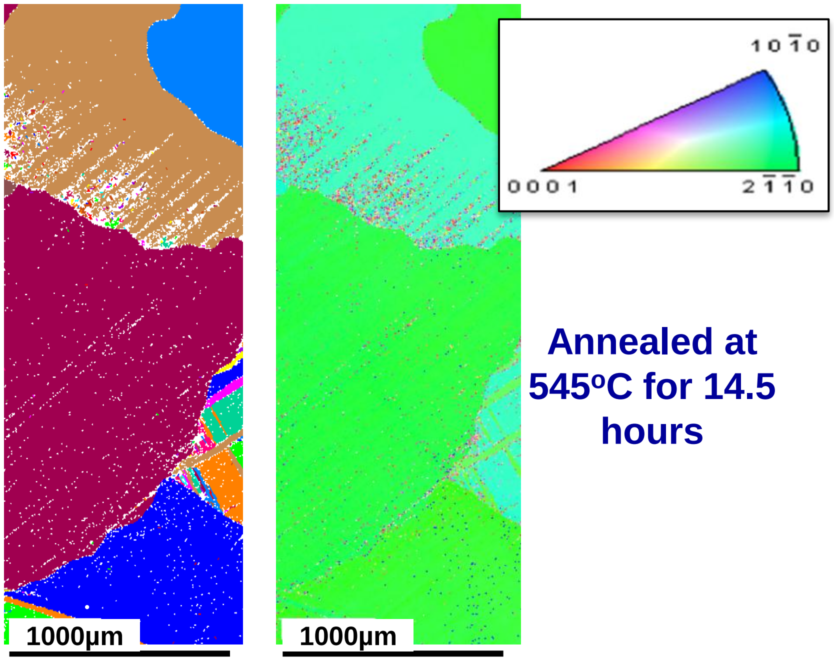


| | $^{24}$Mg | $^{25}$Mg | $^{26}$Mg |
|---|---|---|---|
| Tracer | 0.018 | 0.979 | 0.003 |
| Bulk | 0.790 | 0.100 | 0.110 |



SIMS concentration depth profiles of $^{25}$Mg

**Annealing produces large grains**



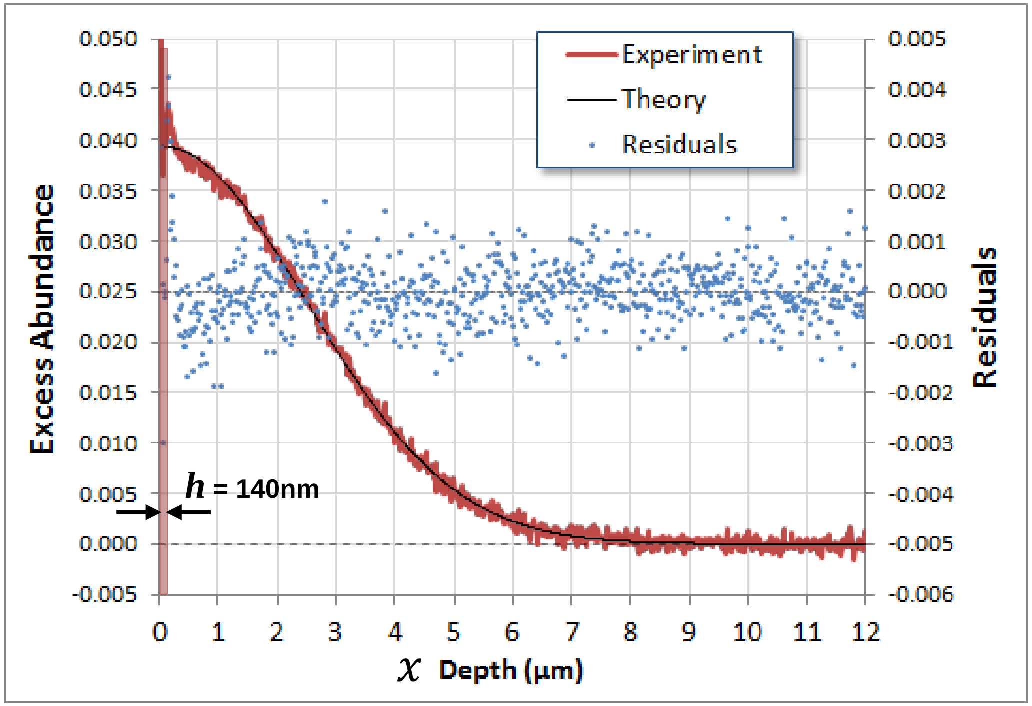
**Annealed at 545°C for 14.5 hours**

Electron Backscatter Diffraction (EBSD) map (inverse pole figure – top right) of grain orientations in a pure polycrystalline Mg rod after annealing treatment. *left*: Identical grain structure map with enhanced contrast.

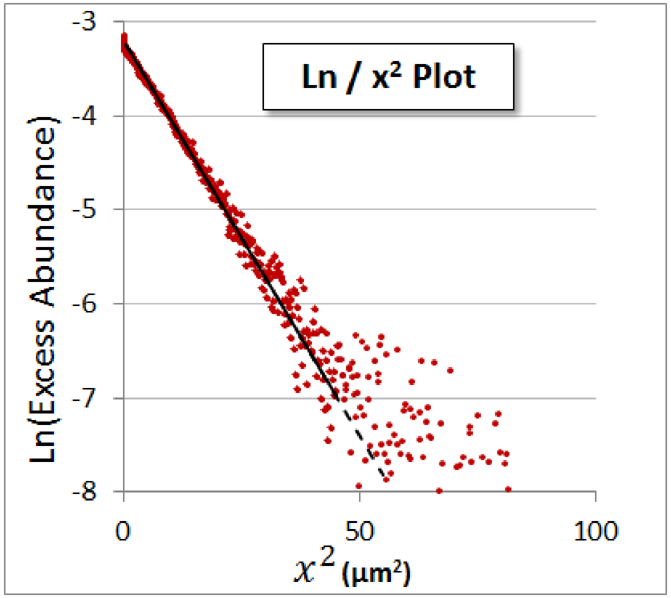
- ***Optimized SIMS profiles within single grains yield more accurate bulk diffusivities***

# Fitting of diffusion depth profiles

## Example: SIMS measured excess 25Mg tracer after 350°C ~1hr



**Log-linearized plot has fitting problems at low signal levels**



**Replace concentration with abundance:** $C(x,t) - C_1 = \frac{(C_0 - C_1)}{2}\left[\mathrm{erf}\left(\frac{x+h}{2\sqrt{Dt}}\right) - \mathrm{erf}\left(\frac{x-h}{2\sqrt{Dt}}\right)\right]$

**Nonlinear fit of $D$, $h$ and $A$ by minimizing the sum of the square of the residuals:**

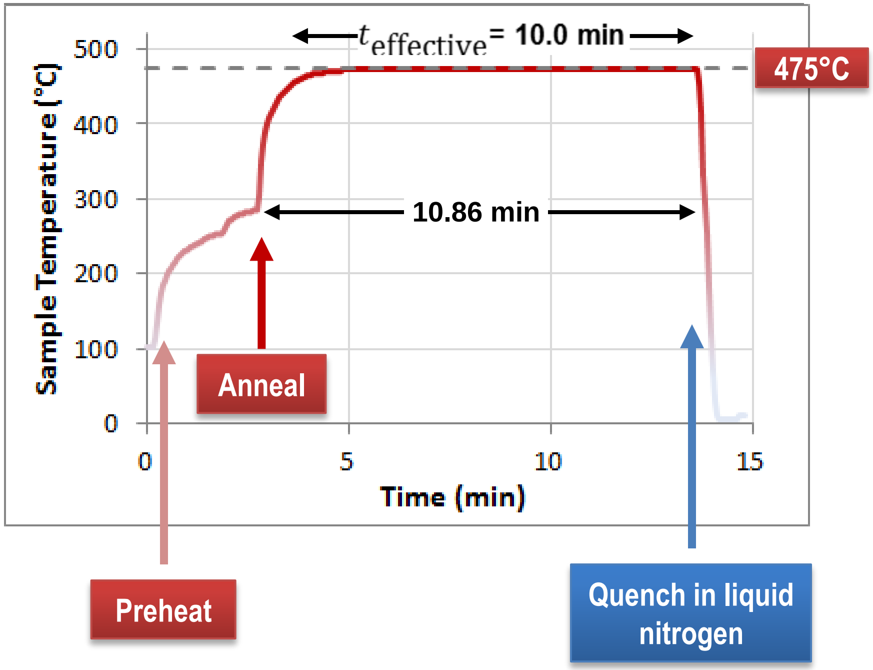
$$\sum_x \left\{ \underbrace{\left[\frac{I_{tracer}(x)}{\sum I_{all\ isotopes}(x)} - A\right]}_{\text{Experiment}} - \underbrace{\frac{(A_{tracer} - A_{natural})}{2}\left[\mathrm{erf}\left(\frac{x+h}{2\sqrt{Dt}}\right) - \mathrm{erf}\left(\frac{x-h}{2\sqrt{Dt}}\right)\right]}_{\text{Theory}} \right\}^2$$

**Excess Abundance:**

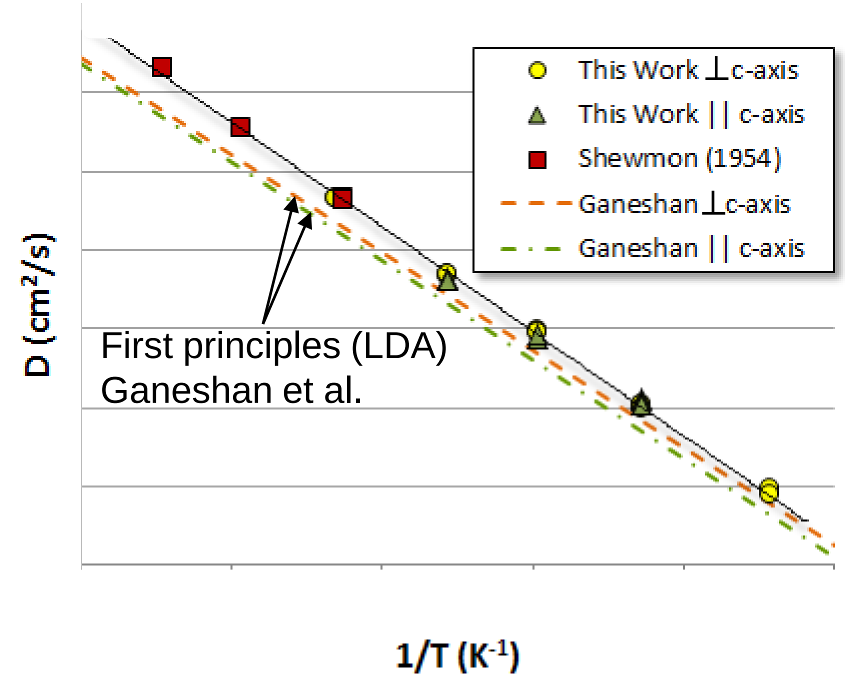
# Temperature profile correction

- Effective time at annealing temperature can be calculated using the actual profile and the activation energy (Rothman 1984) using numerical integration
- Capsule design allows rapid change and real-time temperature measurement for precise correction, even for times < 10 minutes
- Example shows 8.6% correction for Mg at 475°C for ~10 minutes

$$t_{\text{effective}} = \int \exp\left[-\frac{Q}{R}\left(\frac{1}{T(t)} - \frac{1}{T_{\text{anneal}}}\right)\right] dt$$



# Mg self-diffusion



**Spread in fitted diffusivities and comparison of orthogonally cut samples, annealed together at each temperature**

| T(°C) | s.d. (%) | Max-Min (%) | s.d. (%) | Max-Min (%) | $D_{\perp}$ - $D_{\|\|}$ (%) |
|---|---|---|---|---|---|
| | ⊥ C-axis | | \|\| C-axis | | |
| 475 | 0.8 | 1.1 | - | - | - |
| 400 | 3.2 | 6.4 | 1.6 | 3.1 | 13.3 |
| 350 | 2.4 | 4.9 | 7.7 | 14.6 | 14.2 |
| 300 | 5.5 | 10.3 | 9.3 | 20.8 | -11.2 |
| 250 | 14.5 | 20.5 | - | - | - |

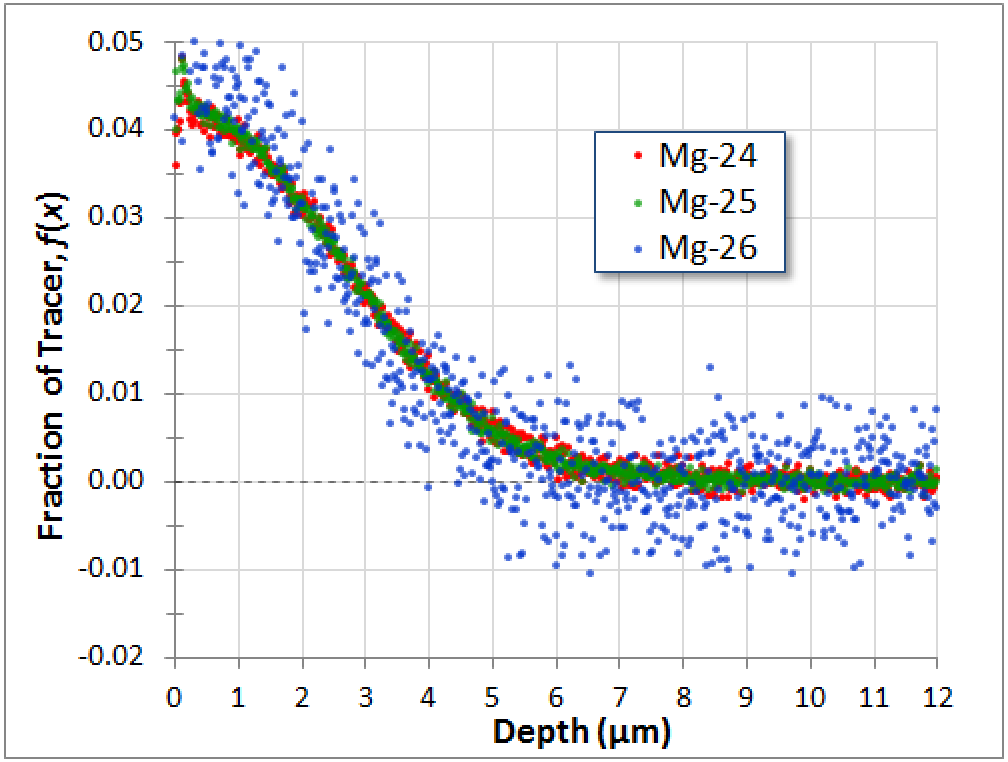
- ***Experimental results consistent with polycrystalline radiotracer measurements***
- ***Tracer diffusivities in directions parallel to rod axis (⊥C-axis) are typically higher compared to diffusivities normal to rod axis (|| C-axis)***

# Mg Isotope Comparison

$$f(x) = \frac{A_i(x) - B_i}{T_i - B_i}$$

$A_i(x)$ — measured abundance
$B_i$ — bulk abundance
$T_i$ — tracer abundance

- **Alternative fitting determines the tracer concentration using each isotope**
- **The SIMS instrumental bias for each isotope is fully corrected to obtain the abundances with depth, $A_i(x)$ for each isotope $i$**
- **Fit of $D$ & $h$ performed**
- **Small trend observed in $D$ with isotope mass — i.e., lower $D$ with increasing mass**

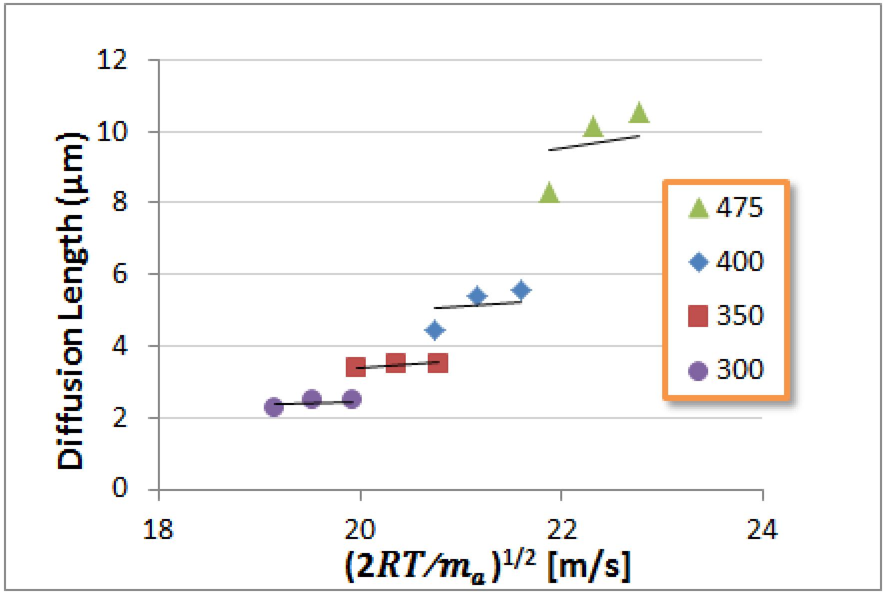


**Minimize $D$, $h$ for each isotope $i$:**

$$\sum_x \left\{ \frac{A_i(x) - B_i}{T_i - B_i} - \frac{1}{2}\left[\operatorname{erf}\left(\frac{x+h}{2\sqrt{Dt}}\right) - \operatorname{erf}\left(\frac{x-h}{2\sqrt{Dt}}\right)\right]\right\}^2$$

# Isotope Effect?

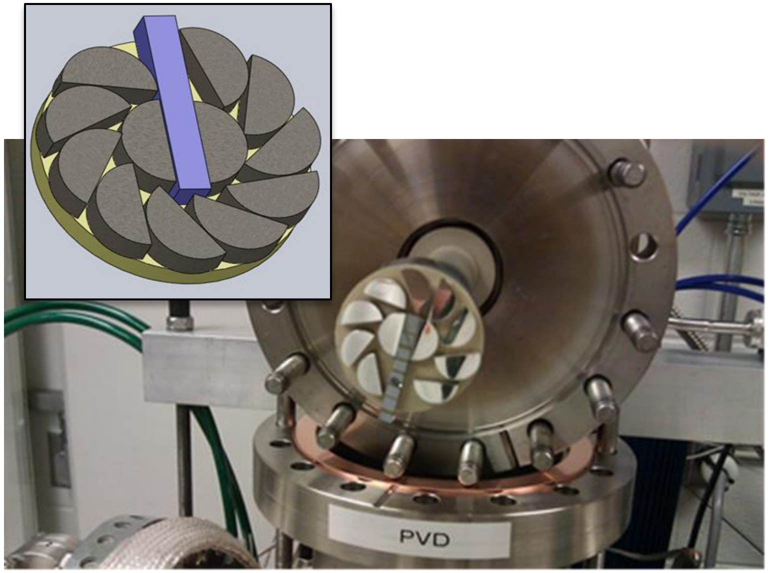
- Trend for slightly lower diffusivity with isotope mass



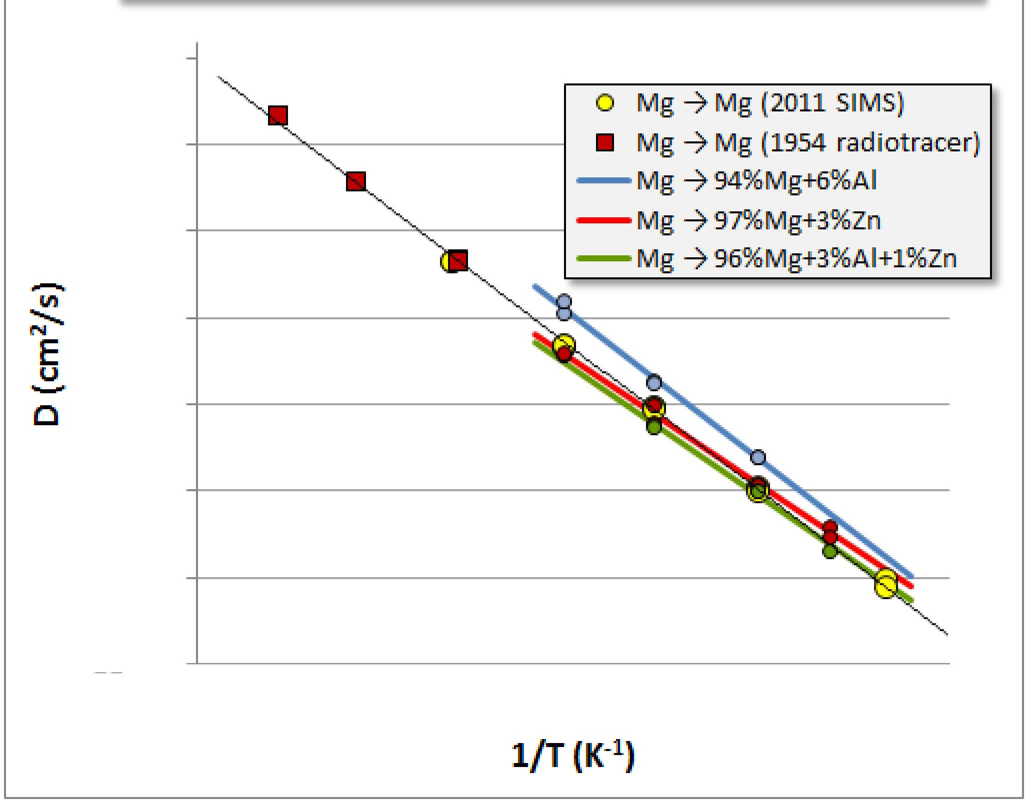
Diffusion length $\sqrt{4Dt}$ with thermal velocity $\sqrt{2Rt/m}$

# Mg tracer diffusion in polycrystalline Mg-Al-Zn alloys

**Setup for thin film sputter deposition on Mg alloy samples.**



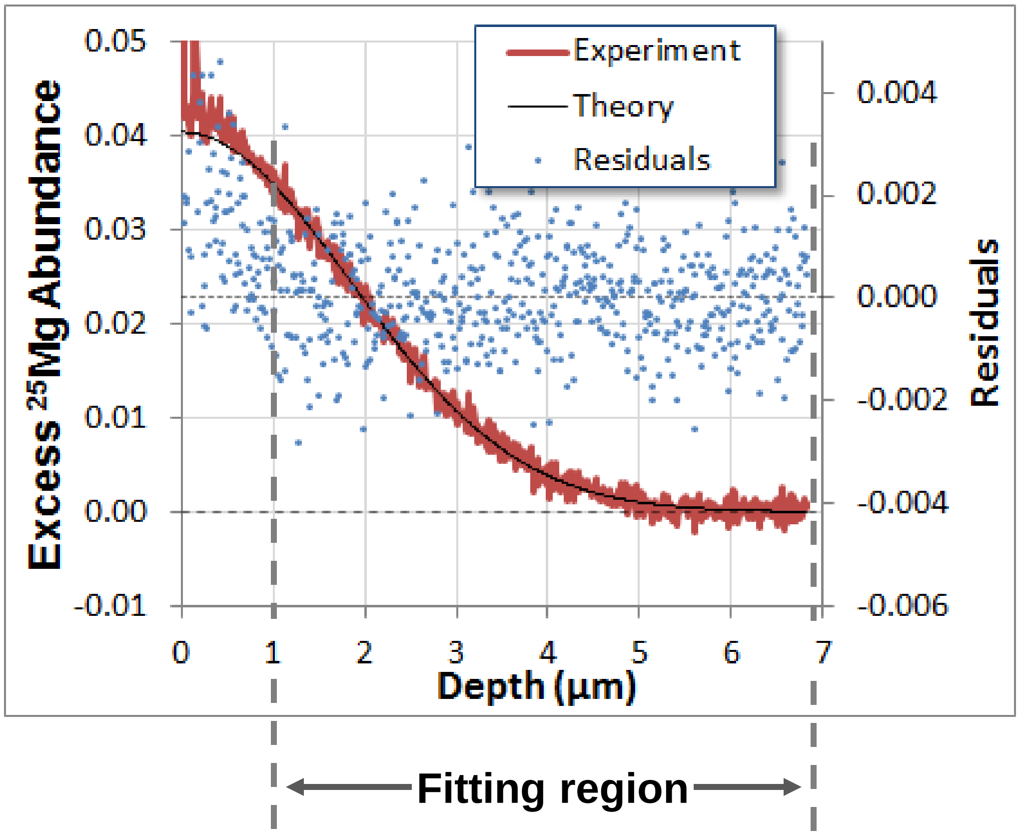
**Mg tracer diffusivities as a function of reciprocal temperature for pure Mg and three Mg alloys (Wt %)**



# Fitting example

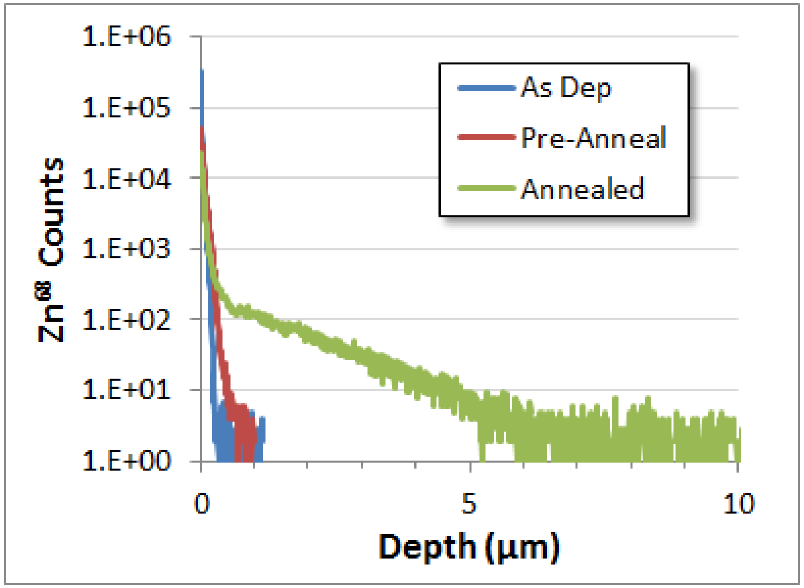
- **Fitting excludes the Mg-rich zone near the surface**

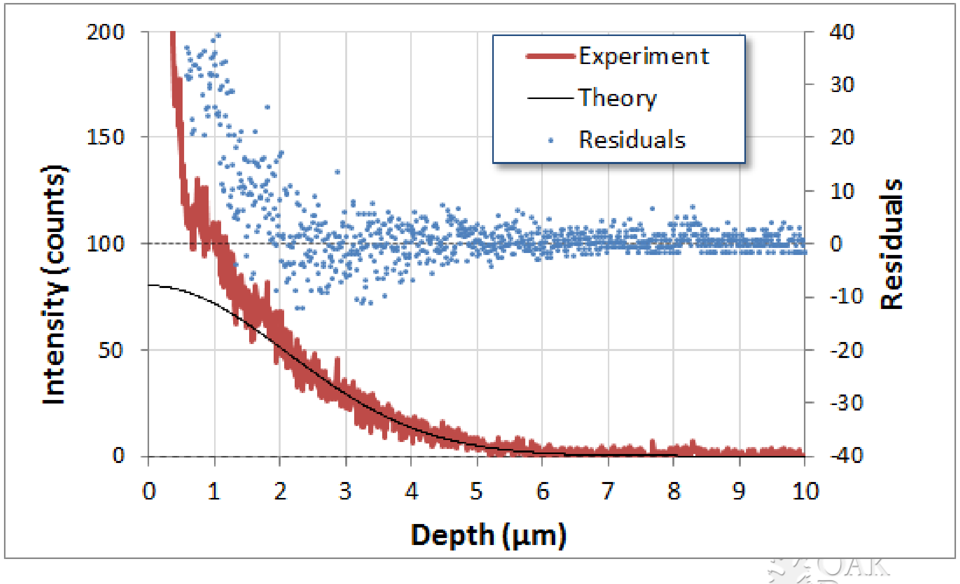
**Example: Self diffusion of Mg in MZ3 (Mg: 97wt%, Zn: 3wt%)**



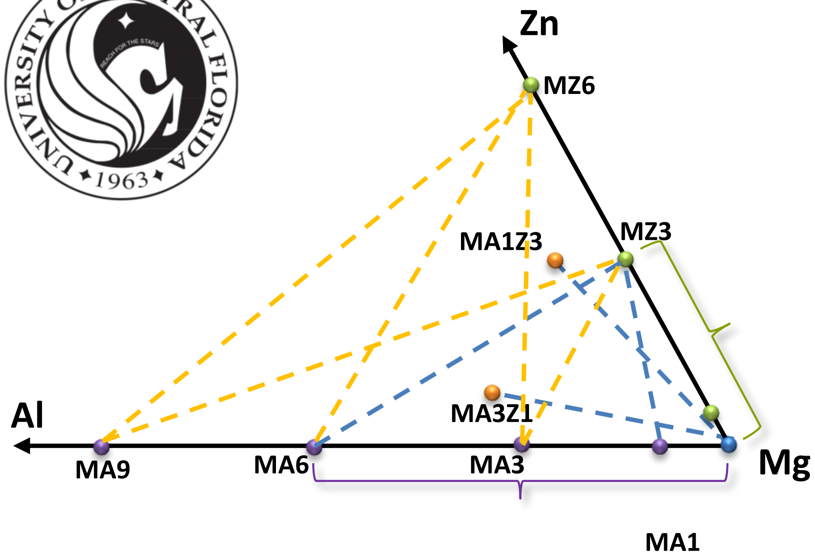
# Zn Diffusion

- **Pure zinc has a high vapor pressure and would evaporate even at 270°C (~450nm/min)**
- **Solution: Drive in Zn at 200°C (loss rate of ~5nm/min) to ~100nm, then anneal at diffusion temperature**
- **Zinc is only weakly soluble in Mg at low temperatures and forms a number of compounds $Mg_XZn_Y$**
- **Holdup region near surface but good fit in dilute region**

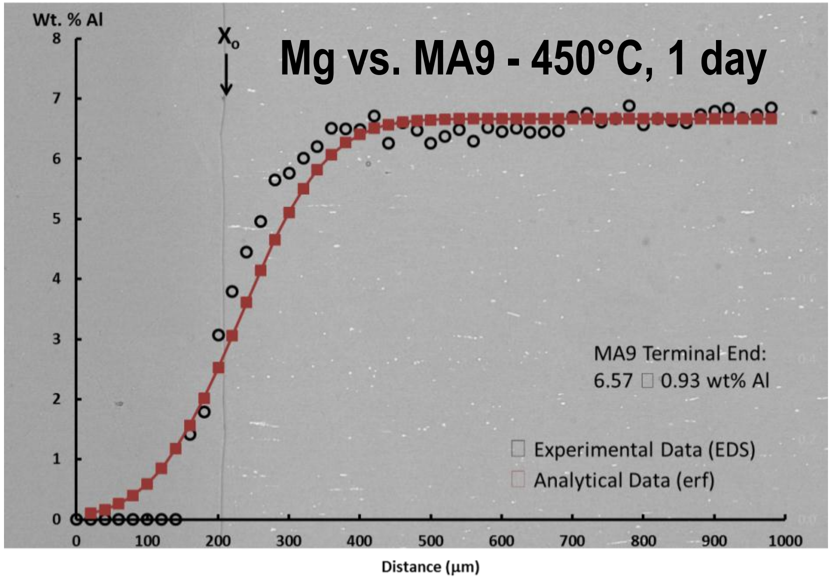




# Interdiffusion Studies in Mg-Al-Zn

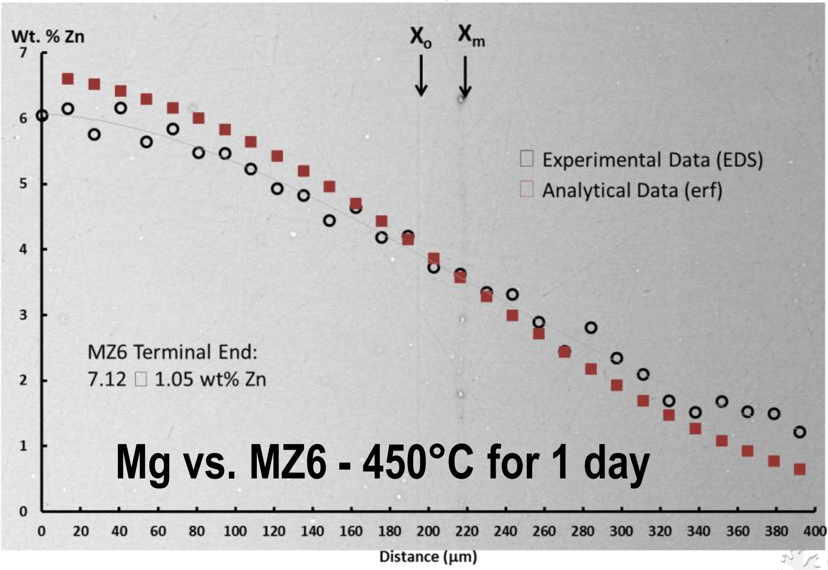


**Selected diffusion couples in hcp Mg-Al-Zn for interdiffusion studies**


Mg vs. MA9 - 450°C, 1 day

MA9 Terminal End:
6.57 □ 0.93 wt% Al

□ Experimental Data (EDS)
□ Analytical Data (erf)


Mg vs. MZ6 - 450°C for 1 day

MZ6 Terminal End:
7.12 □ 1.05 wt% Zn

□ Experimental Data (EDS)
□ Analytical Data (erf)

- ➢ ***Interdiffusion data combined with measured Mg tracer (this work) and thermodynamic data (Φ) is used to compute unknown Al tracer diffusivity using diffusion theory (Darken-Manning relations)***

$D_{inter}$ (Mg s.s.) = [ $X_{Mg} D^*_{Al} + X_{Al} D^*_{Mg}$ ] $\Phi * S$    Manning relation in binary Mg-Al

# ORNL Diffusion website

- http://www.ornl.gov/sci/diffusion (private)

Page 1 of 4

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**Isotopic Diffusion Databases for Magnesium Integrated Computational Materials Engineering (Mg-ICME)**

*Principal Investigator: Nagraj Kulkarni, Oak Ridge National Laboratory (865) 576-0592; e-mail: kulkarnins@ornl.gov*

*Industrial Partner: U.S. Automotive Materials Partnership Integrated Computational Materials Engineering (ICME) Team, Magnesium Electron North America*

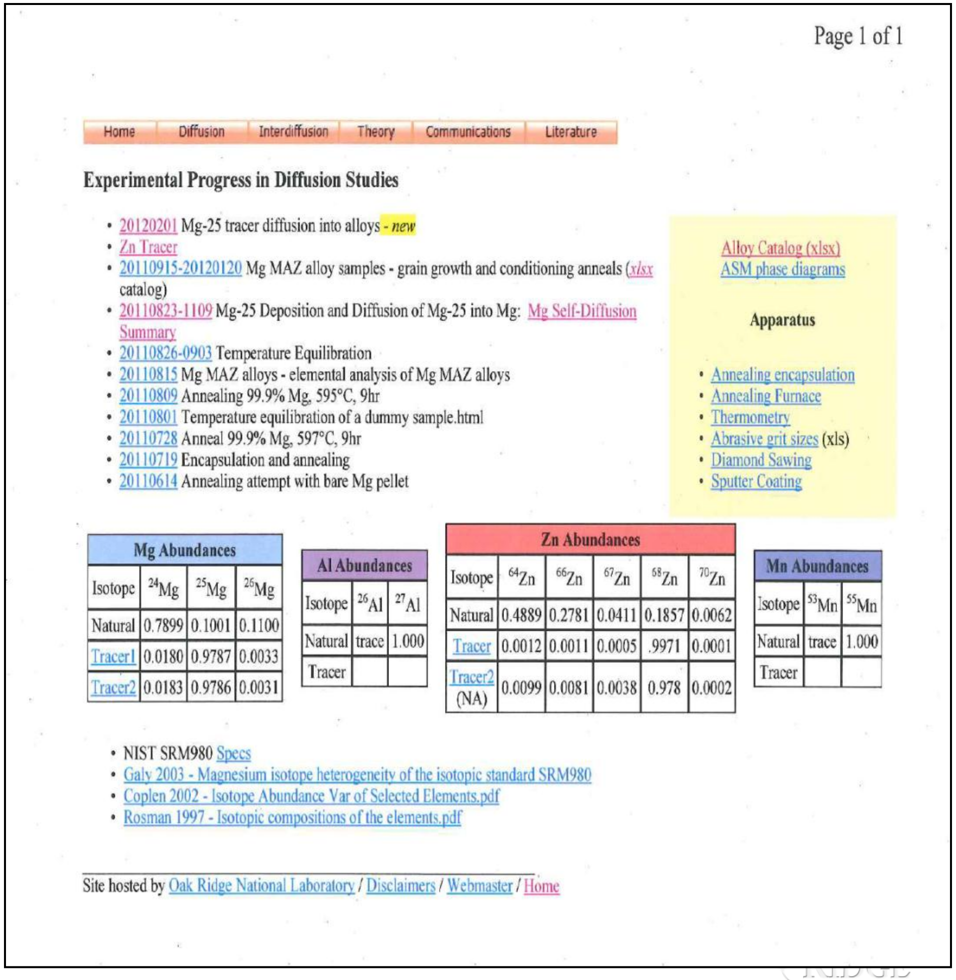
**Resources**

- Team Personnel
- UCF Facilities
- SIMS-XPS VaTech

*Collaborators:*

***Oak Ridge National Laboratory***
Bruce Warmack, (865) 574-6202; e-mail: warmackrj@ornl.gov
Balasubramaniam Radhakrishnan, (865) 241-3861; e-mail: radhakrishnb@ornl.gov
Peter Todd [retired]
***Argonne National Laboratory***
John Mundy [retired]
***Virginia Tech***
Jerry Hunter (540) 391-0366; e-mail: hunterje@vt.edu
Jay Tuggle, jaysmail@vt.edu
***University of Central Florida***
Yongho Sohn, (407) 882-1181, ysohn@mail.ucf.edu
Katrina Bermudez, kbermudez@knights.ucf.edu
Kevin Coffey, (407) 823-2175, krcoffey@mail.ucf.edu
Edward Dein, (407) 823-3584, Edward.Dein@ucf.edu
***University of Newcastle, Australia***
Graeme Murch, 61(2)49216191; e-mail: graeme.murch@newcastle.edu.au
Irina Belova, 61(2)49215717; e-mail: irina.belova@newcastle.edu.au

http://www.ornl.gov/sci/diffusion/index.html 2/29/2012



Page 1 of 1

**Experimental Progress in Diffusion Studies**

- 20120201 Mg-25 tracer diffusion into alloys *- new*
- Zn Tracer
- 20110915-20120120 Mg MAZ alloy samples - grain growth and conditioning anneals (*xlsx* catalog)
- 20110823-1109 Mg-25 Deposition and Diffusion of Mg-25 into Mg: Mg Self-Diffusion Summary
- 20110826-0903 Temperature Equilibration
- 20110815 Mg MAZ alloys - elemental analysis of Mg MAZ alloys
- 20110809 Annealing 99.9% Mg, 595°C, 9hr
- 20110801 Temperature equilibration of a dummy sample.html
- 20110728 Anneal 99.9% Mg, 597°C, 9hr
- 20110719 Encapsulation and annealing
- 20110614 Annealing attempt with bare Mg pellet

Alloy Catalog (xlsx)
ASM phase diagrams

**Apparatus**

- Annealing encapsulation
- Annealing Furnace
- Thermometry
- Abrasive grit sizes (xls)
- Diamond Sawing
- Sputter Coating

| Mg Abundances | | | |
|---|---|---|---|
| Isotope | $^{24}$Mg | $^{25}$Mg | $^{26}$Mg |
| Natural | 0.7899 | 0.1001 | 0.1100 |
| Tracer1 | 0.0180 | 0.9787 | 0.0033 |
| Tracer2 | 0.0183 | 0.9786 | 0.0031 |

| Al Abundances | | |
|---|---|---|
| Isotope | $^{26}$Al | $^{27}$Al |
| Natural | trace | 1.000 |
| Tracer | | |

| Zn Abundances | | | | | |
|---|---|---|---|---|---|
| Isotope | $^{64}$Zn | $^{66}$Zn | $^{67}$Zn | $^{68}$Zn | $^{70}$Zn |
| Natural | 0.4889 | 0.2781 | 0.0411 | 0.1857 | 0.0062 |
| Tracer | 0.0012 | 0.0011 | 0.0005 | .9971 | 0.0001 |
| Tracer2 (NA) | 0.0099 | 0.0081 | 0.0038 | 0.978 | 0.0002 |

| Mn Abundances | | |
|---|---|---|
| Isotope | $^{53}$Mn | $^{55}$Mn |
| Natural | trace | 1.000 |
| Tracer | | |

- NIST SRM980 Specs
- Galy 2003 - Magnesium isotope heterogeneity of the isotopic standard SRM980
- Coplen 2002 - Isotope Abundance Var of Selected Elements.pdf
- Rosman 1997 - Isotopic compositions of the elements.pdf

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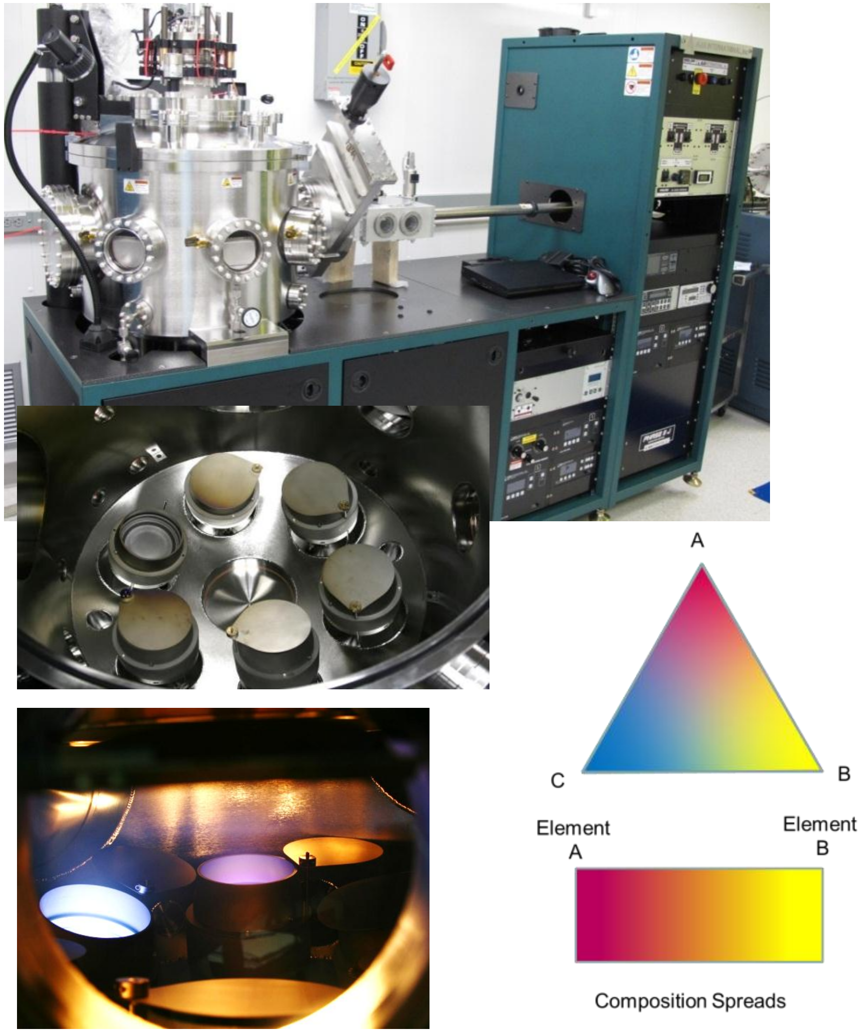
# Future Work

- **Continue Mg, Zn tracer diffusion experiments and analysis in Mg-Al-Zn-Mn alloys**
- **Interdiffusion measurements using incremental diffusion couples in Mg-Al-Zn-Mn alloys to extract Al, Mn tracer diffusivities**
- **Mg, Nd, Ce tracer diffusion studies in Mg-Al-Nd, Ce alloys (only preliminary data likely)**
- **Initiate experimental work on continuously selectable alloys (co-sputtered) and grain-boundary diffusion**
- **Ongoing theoretical grain-boundary studies**

# Alloy film magnetron co-sputtering for Mg-alloys & compounds

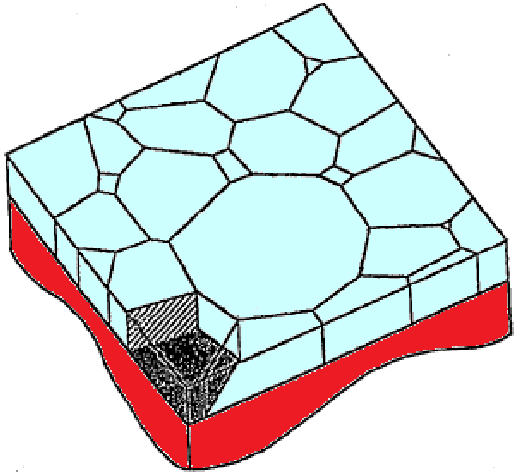


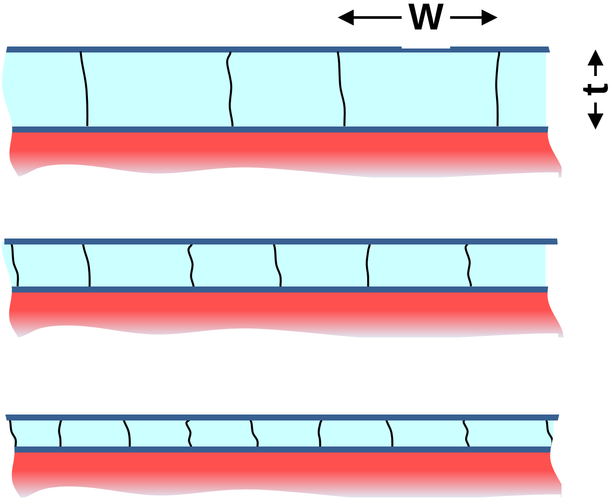
- Multiple source sputtering system to produce continuously variable alloys and films for grain-boundary studies
  - Uniform composition
  - Wedge variable composition
- Tracer-film deposition *in situ*
- Substrate heating
- UHV base pressure of $10^{-9}$ Torr
- Load lock sample exchange

**Magnetron Co-sputtering System**

# Grain boundary diffusion using thin films

- The proportion of diffusion due to bulk and boundary effects can be controlled through grain size
- Grain size is generally pinned by top and substrate boundaries to be ~2X the thickness of annealed thin films
- Co-deposition of Mg, Al and Zn produces variety of alloy films for diffusion studies





# Summary

- Relevance
  - A tracer diffusion database in Mg alloys is of fundamental importance to the ICME and other integrated materials design efforts (e.g., Materials Genome Initiative) in establishing design and modeling tools, optimizing manufacturing processes, and predicting performance requirements.
- Key accomplishments/progress
  - Established SIMS based tracer diffusion technique
  - Obtained Mg self-diffusivities in pure polycrystalline Mg samples using our SIMS-based thin-film stable-isotope technique, validating and extending historic radiotracer measurements to lower temperatures.
  - Obtained Mg & Zn tracer diffusivities in a number of alloys in the Mg-Al-Zn system.
  - Developed a superior annealing technique for Mg based on the Shewmon-Rhines approach.
  - Diffusion website facilitates communication between local and international collaborators, and served as a repository for data, experiments, analysis, theory and relevant literature.