Ge and Cu: *Technical Issues*

Harry Miley

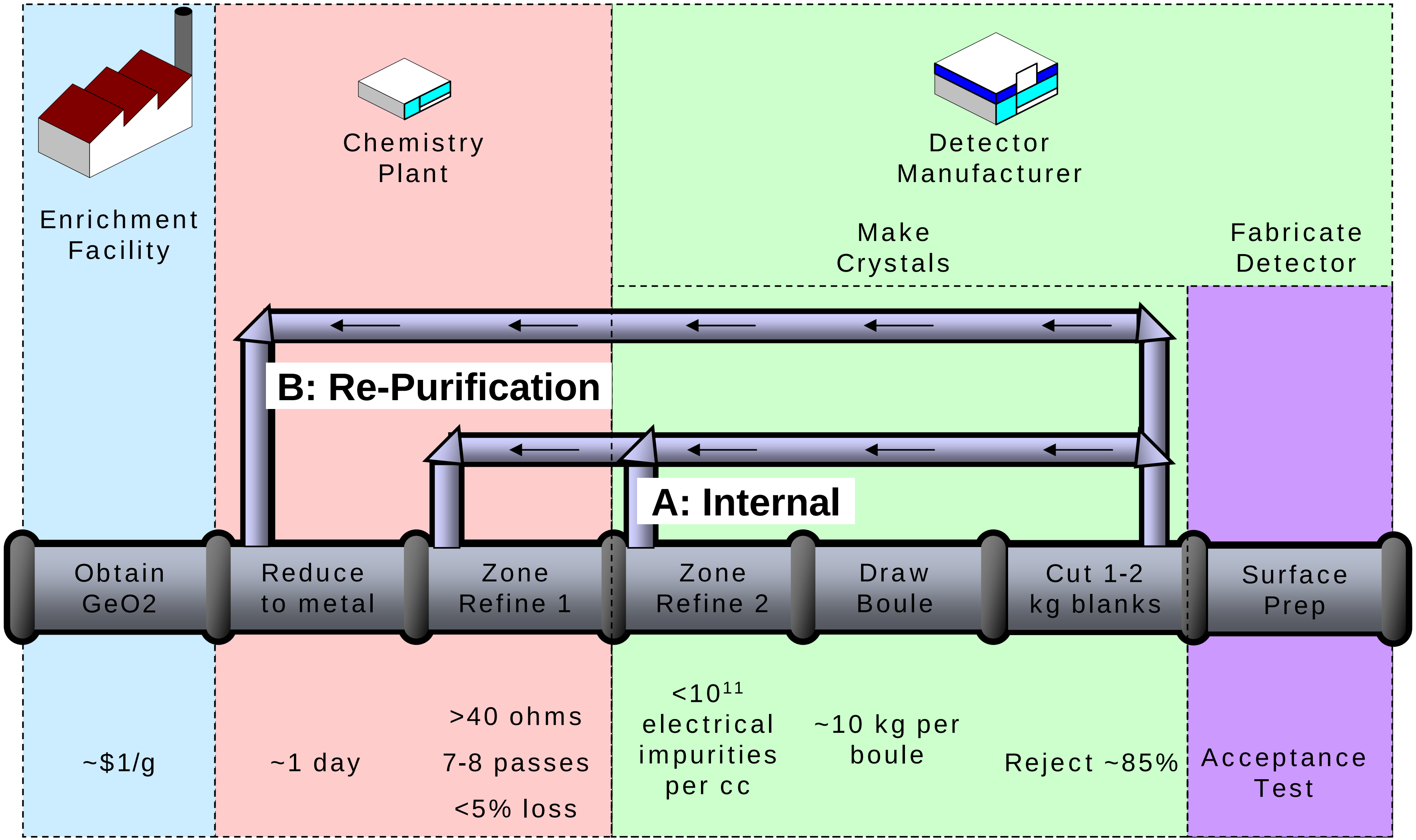
Pacific Northwest National Laboratory

High Altitude Overview

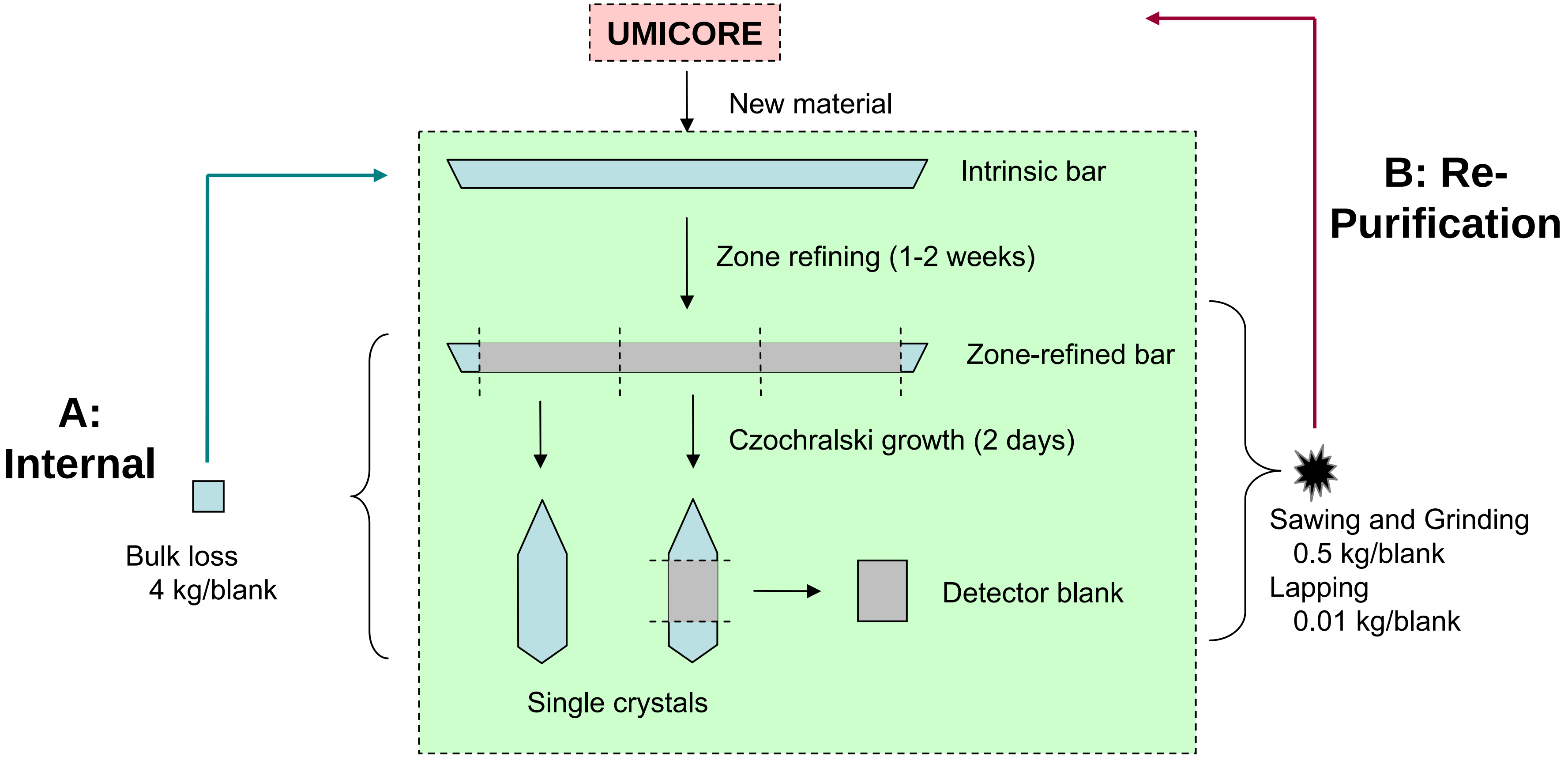
- Excerpts from DOE Review Dec 2006
  - Efficient Use of Ge
    - Review
  - Ultrapure Copper
    - Cu production improvements
    - Cu assay improvements
- Cu Update Feb 2007!
  - Assay is critical to success
  - Recent progress

Germanium Processing Pipeline

Goal: Preventing wastes from becoming losses

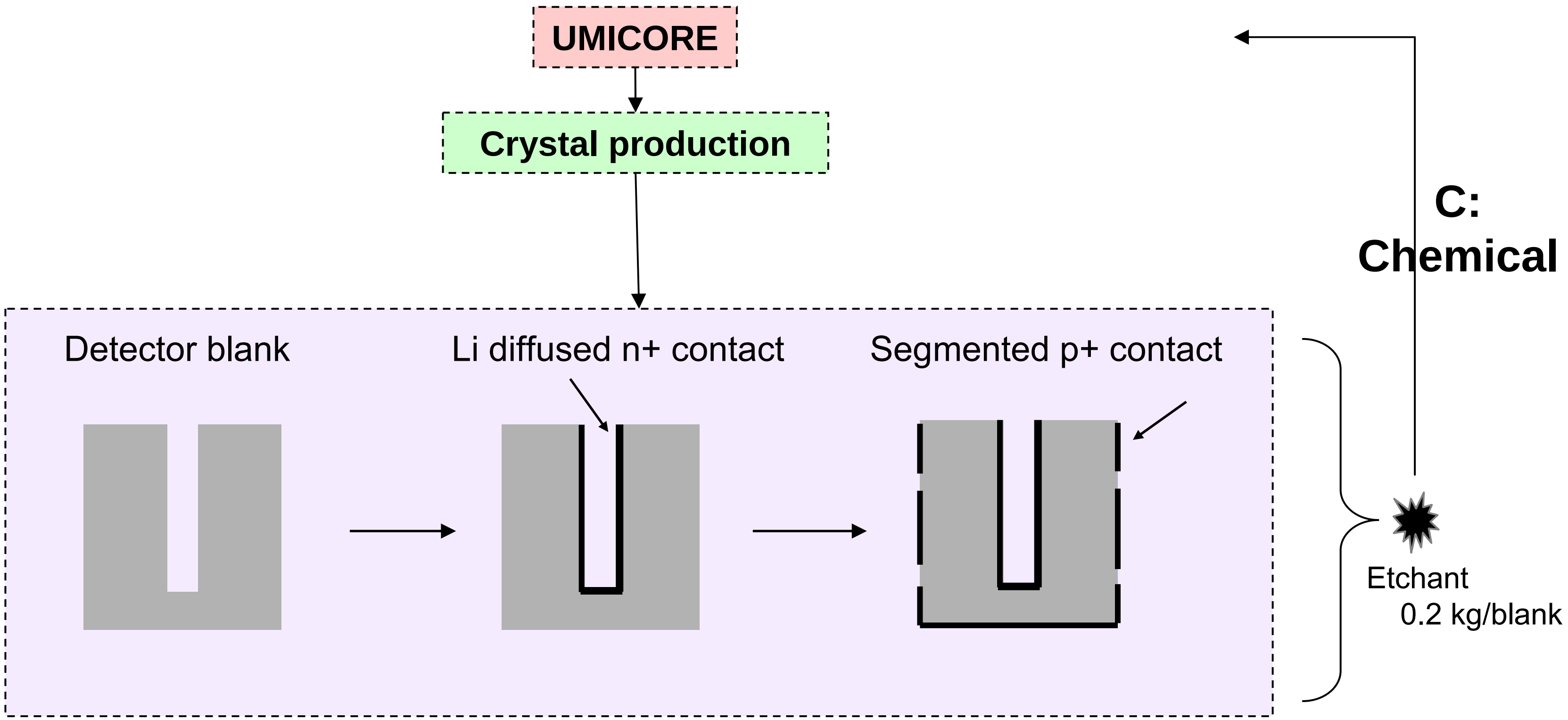


Crystal Production Losses



Waste values from discussions with manufacturers.

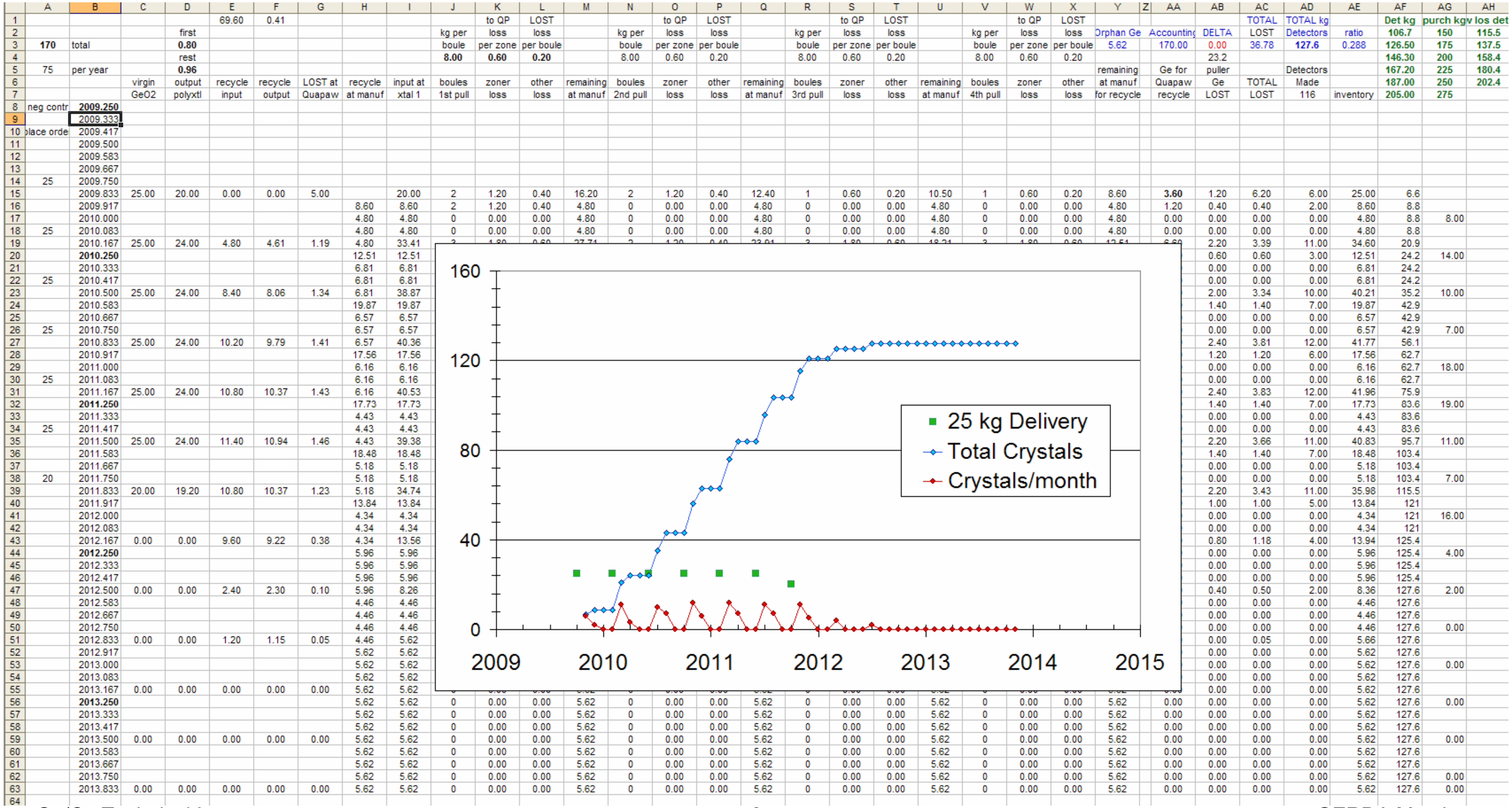
Detector Fabrication Losses



Waste values from discussions with manufacturers.

Detector Production Model

predicts location and accumulation of wastes



Model Features

- Inputs
  - 95% efficiency of chemical purification
  - 1-2 1.1 kg crystals in each boule (rest to recycle A)
  - ~1/3 of material returns to chemical purification (B)
  - Manufacturer’s production rates, waste fraction into each type, etc

- Recycling of A and B waste streams is already done by manufacturer, and improvements will have little impact on total Ge needed.
- Chemical or “C-type” waste streams are not currently (at <$1/g raw Ge) considered economic to recycle.
  - At ~$50/g, recovery of this stream will result in a significant Ge savings

Cu Introduction

<u>Copper recap</u>

- Majorana needs ultra-pure Cu for several purposes
  - Pure inner shielding material
  - Cryostat and support pieces
- We electroform Cu to purify it
  - Based on the low half-cell potential for Cu
  - Many shapes and sizes possible
- ***<u>We need new methods of Cu assay to assure that we will achieve required background goals for a ~1 ton experiment</u>***

Low-background detector and electroformed cryostat during assembly

Reminder: Materials Goals

Material	Uses	Contaminant	Equivalent Achieved Assay	Reference
Germanium	Detectors	1 atom/kg/day ^{68}Ge 3.5 atom/kg/day ^{60}Co		[Avi92]
E-formed Cu	Support Rods, Cryostat, Inner Cu Shield	0.1 μBq/kg ^{208}Tl 0.4 μBq/kg ^{214}Bi	0.7-1.3 μBq/kg	Current work also [Arp02]
NOSV Cu	Outer Cu Shield	0.26 μBq/kg ^{208}Tl 0.3 μBq/kg ^{214}Bi	<6 μBq/kg	[Heu04]
Pb	Lead Shield	1 μBq/kg ^{208}Tl 5 μBq/kg ^{214}Bi	<7 μBq/kg	[Heu04]
Plastic	Trays, Rings	10 μBq/kg ^{208}Tl 10 μBq/kg ^{214}Bi	1000 μBq/kg	Current work also [Arp02]
Front End Electronics	LFEPS, Contacts, Capacitors	30 μBq/kg ^{208}Tl 200 μBq/kg ^{214}Bi	1000 μBq/kg	Current work also [Arp02]
Cable	Cable	3 μBq/kg ^{208}Tl 10 μBq/kg ^{214}Bi	400 μBq/kg	[Ams06]

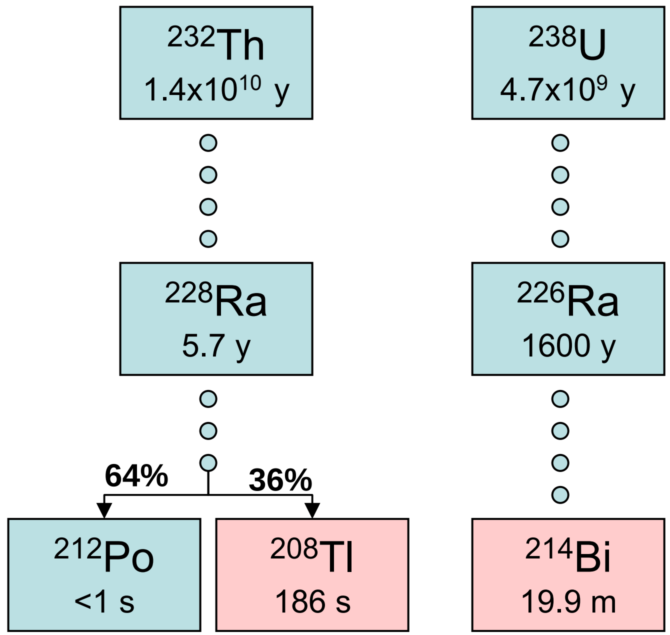
Copper Assay Goals

1. Show that our copper is not a show stopper for the experiment
   – Perhaps an expensive one-time effort
   – What we are working on today
2. Create a QA process for every part
   – Cost effective
   – Fast (not 90 days)
   – Low-waste solution preferred
      – Mass spec type solution fits

Problem Isotopes and Precursors in Cu

To achieve Majorana background goals

- Establishing low U and Th is a necessary but not sufficient condition
  - Gamma assay is giving way to ICPMS
- Must have low Ra also
  - Tracer studies planned
- ICP/MS hardware has sensitivity
  - About 10 fg/g (or 10^{-14} g/g) Th
- ICP/MS has some drawbacks
  - Cannot inject 1g Cu into the machine
  - Sample prep introduces Th from EVERYWHERE, limits sensitivity



0.1 μBq/kg ^{208}Tl = 0.27 μBq/kg ^{232}Th = 70 fg/g Th

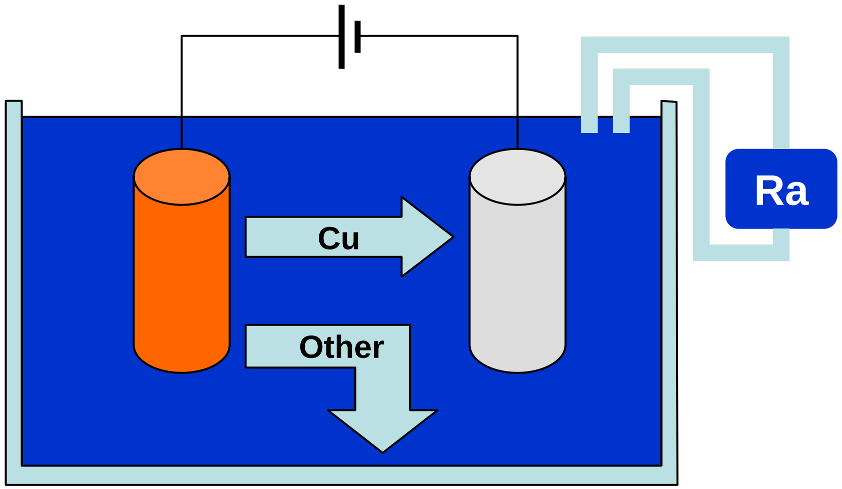
Copper Starting Point

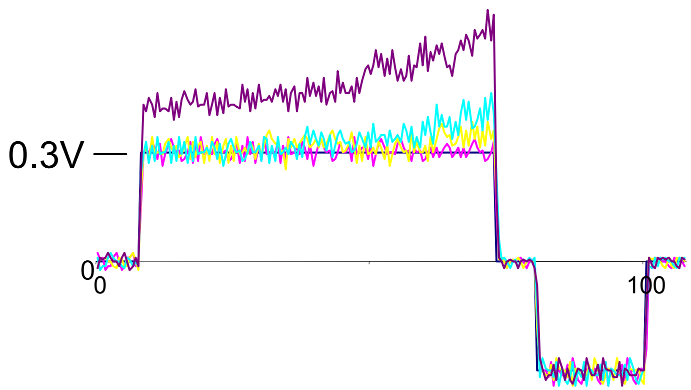
- Direct gamma assay
  - Require kg quantities and 60-90 day measurements underground
  - Table shows limits for U, Th chains in Cu of NOSV grade, similar to our starting stock
  - From 25 to 70 times U/Th goal
- Direct gamma measure of our Cu at about 10 μBq/kg Th
  - Just a limit, the actual value may conform to our purity goals

^{228}Th (^{232}Th)	^{226}Ra (^{238}U)	Comment
μBq/kg	μBq/kg	**Commercially obtained electrolytic Cu**
< 28	< 25	Motta et al, Nuclear Physics B (Proc. Suppl.) 118 (2003) 45 1
< 12		Rugel, et al, Nuclear Physics B (Proc. Suppl.) 143 (2005) 564
< 19	< 16	Heusser et al, Proc. of Intern. Conf. Isotop. Environm. Studies Aquatic Forum 2004, 25 - 29 October 2004, Monte-Carlo, Monaco
≤ 0.3	≤ 0.4	**Goal of this Effort**
		In-house ultra-pure electroformed Cu
< 9	< 26	Brodzinski, et al, JRNC 193 No.1 (1995) 61-70

Electroplating Copper to Purify

- Electrolytic process that dissolves starting material, purifies Cu
  - Low potential for Cu
  - Strongly rejects Th, U





Study of purity, density, strength, grain size and more vs. plating current, bath mixing, temperature and more

- Many methods for enhancing process
  - I, V, T, chemistry
- Start with commercial electrolytic copper drawn from the center of a melt
  - NOSV-equivalent

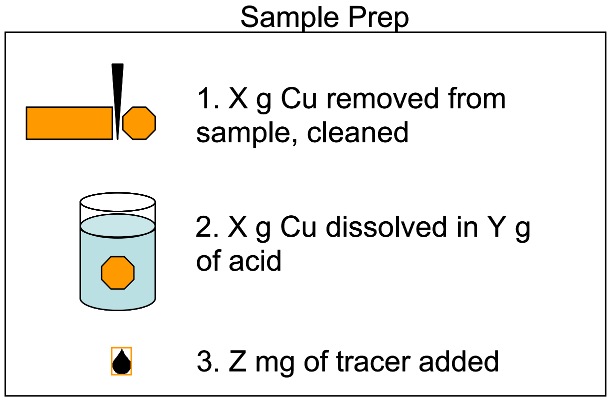
Copper assay progress timeline: Dec 06

- 1995: a limit of <9 µBq/kg for ^{232}Th set in IGEX electroformed copper.
  - This was a 90 day radiometric measurement of ~10 kg Cu at 4000 mwe
- November 2004: $CuSO_4$ bath used in electroforming could be purified extensively through recrystallization
- April 2005: a limit of <8 µBq/kg for ^{232}Th was set on MEGA copper.
  - This was a 1 minute measurement of <1 g Cu with ion-exchange + ICPMS
- April 2005: Electroforming shown to suppress ^{229}Th by >8000x
- May 2005: Assay sensitivities of 2-4 µBq/kg ^{232}Th achieved via ICPMS
  - Reagents handled precisely as Cu eluent would be
- April 2006: Starting stock identified with <12 µBq/kg for ^{232}Th
- April 2006: Samples prepared using electrochemical methods show levels of ^{232}Th that were essentially background, indicating <2 µBq/kg in Cu

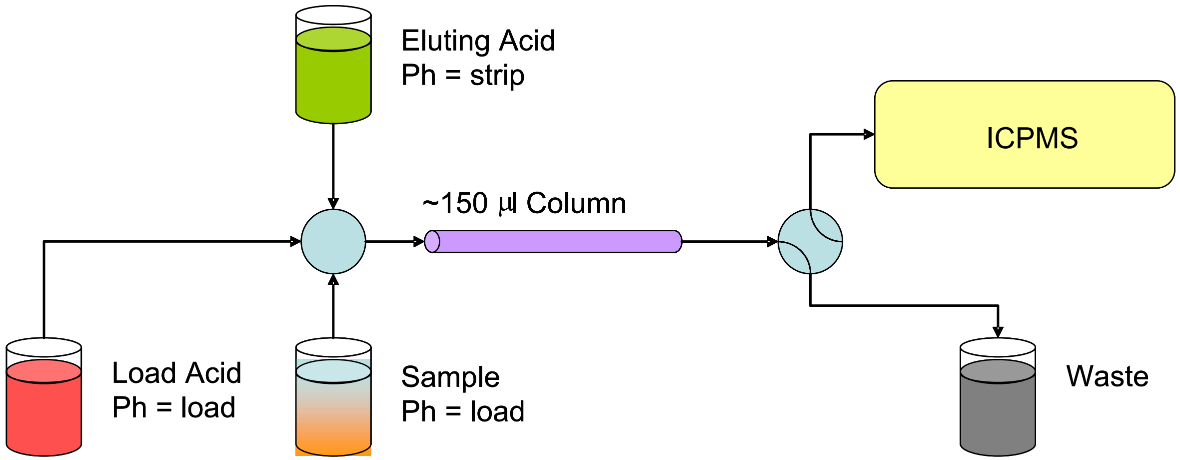
Ion Exchange Assay Approach

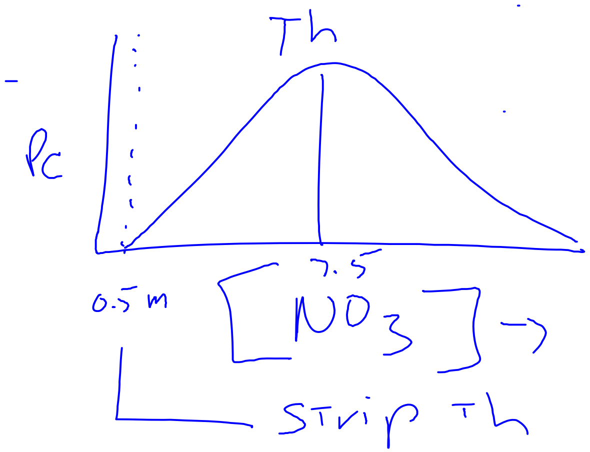
Approaches

- Ion exchange
  - Th held on column
  - Cu held on column
- Alternative
  - Cu removed from solute by precipitation, electrochemistry, etc



4. Wash w/loading acid, eluent to waste
5. Clean w/eluting acid, to waste
6. Condition w/loading acid, to waste
7. Load sample, eluent to waste
8. Elute w/eluting acid, eluent to ICPMS





Status of the Electroformation of Ultra High Purity Cu and Material Assay via ICP/MS

February 9 2007

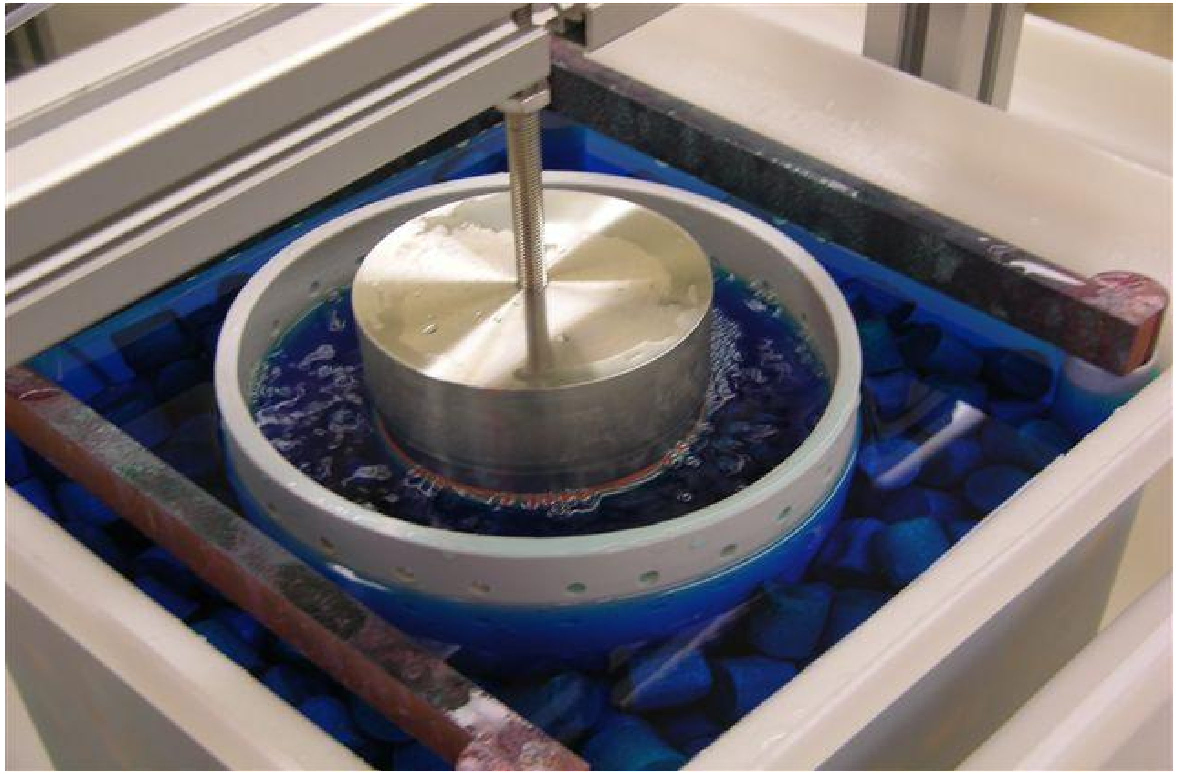
Eric Hoppe, Craig Aalseth, Tom Farmer, Jim Fast, Martin Liezers, Harry Miley, Jim Reeves

Copper Production Highlights 07

- New lab operating
  - Will be adding baths remaining FY07 and FY08, up to 8 total
  - Working toward cleanliness improvements
- Cu formation
  - Grain size is excellent, reducing machining
- Study: Th Rejection
  - Still waiting for ^{228}Th
- Assay methods being pursued
  - Laser Ablation MS
  - Ion exchange
  - Classic precipitation
  - Alternative sample concentration using electrochemistry. To be developed during and following ^{228}Th studies

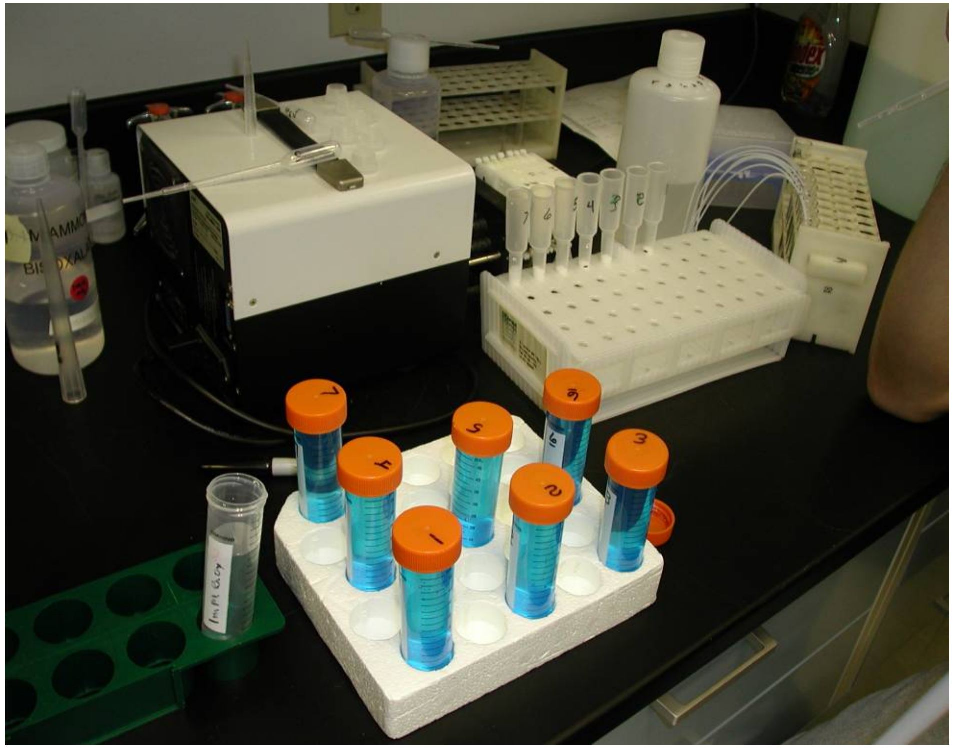
Copper Electroforming Operational

- Need to improve on lab cleanliness
- Plate for weeks without machining
- Build up slower than desired, 0.002-0.005”/day
- Still developing better recipes which may improve build up rate



Assay using ion exchange sample prep

New sample prep campaign started in November 06



- Analysis of 7 aliquots from a single copper sample dissolved in nitric acid
- 10 ml columns loaded with 0.8 ml of TRU resin using Millipore LC 10 µm filter to retain resin
- Work performed manually on bench top with open columns

^{229}Th % Recovery from Ion Exchange Prep

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Ave	Std Dev
Column 1	12	40	35	18	38	43	54	34	14.6
Column 2	33	28	25	21	21	38	55	32	12.1
Column 3	35	27	34	23	21	32	55	32	11.3
Column 4	44	32	32	22	23	36	56	35	11.9
Column 5	36	34	42	28	29	43	38	36	5.9
Column 6	21	18	21	19	20	29	40	24	7.9
Column 7	34	20	25	16	23	27	53	28	12.3
Ave	31	28	31	21	25	35	50	**32**	10.8
Std Dev	10.7	7.7	7.3	3.9	6.5	6.4	7.7	4.2	3.0
% Std Dev	34.7	27.2	23.8	18.6	25.8	18.1	15.3	13.2	27.2

μBq ^{232}Th/kg in Blanks from Ion Exchange

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	**Ave 4-7**	Std Dev 4-7
Column 1	67.2	10.4	2	0.7	0.7	1.7	1.1	1.0	0.46
Column 2	22.3	8.2	1.3	0.7	0.1	0.6	0.6	0.5	0.27
Column 3	26.6	7.8	1.7	0.5	0.6	0.6	0.5	0.6	0.05
Column 4	32.1	6.9	1.2	0.4	0.4	0.7	0.5	0.5	0.15
Column 5	36.0	7.8	1.5	0.5	0.3	0.6	0.7	0.5	0.17
Column 6	21.3	7.6	1.6	0.3	0.5	0.3	0.6	0.4	0.13
Column 7	34.5	6.2	2.1	0.8	0.4	0.5	0.6	0.6	0.17
Ave	**34.3**	**7.8**	**1.6**	**0.6**	**0.4**	**0.7**	**0.7**	**0.6**	0.20
Std Dev	15.6	1.3	0.3	0.2	0.2	0.4	0.2	0.2	0.13
% Std Dev	45.5	16.7	20.6	32.5	46.1	62.9	30.0	34.9	65.5

Results from a real Cu sample

	% 229Th Rec in Cu Sample	% 229Th Rec from Blanks	µBq 232Th per kg Cu Sample	µBq 232Th per kg in Blanks
Column 1	20		1.7	
Column 2	22		1.6	
Column 3	20		1.4	
Column 4	28		1.5	
Column 5	28		1.8	
Column 6	17		1.0	
Column 7	19		1.3	
Ave	22	32	**1.5**	**0.6**
Std Dev	4.4	4.2	0.25	0.21
% Std Dev	19.8	13.2	16.8	34.9

(1.5 - 0.6)/3 = 0.3 μBq/kg ^{208}Tl with ~50% error

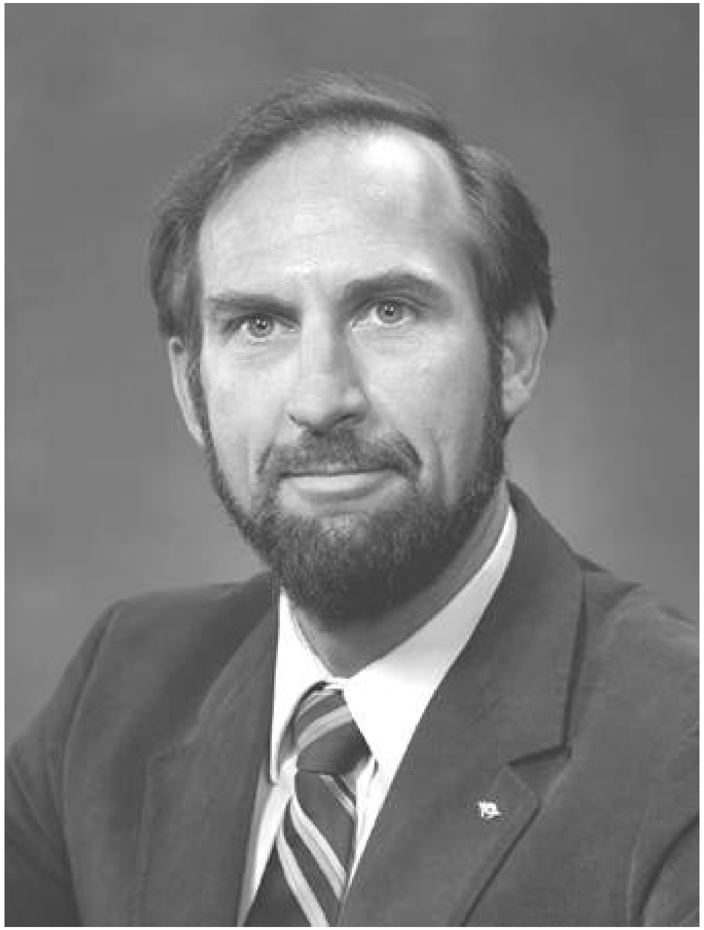
Copper sample is the starting material for plating
Center cut OF-OK Copper Outo Kumpu, Finland

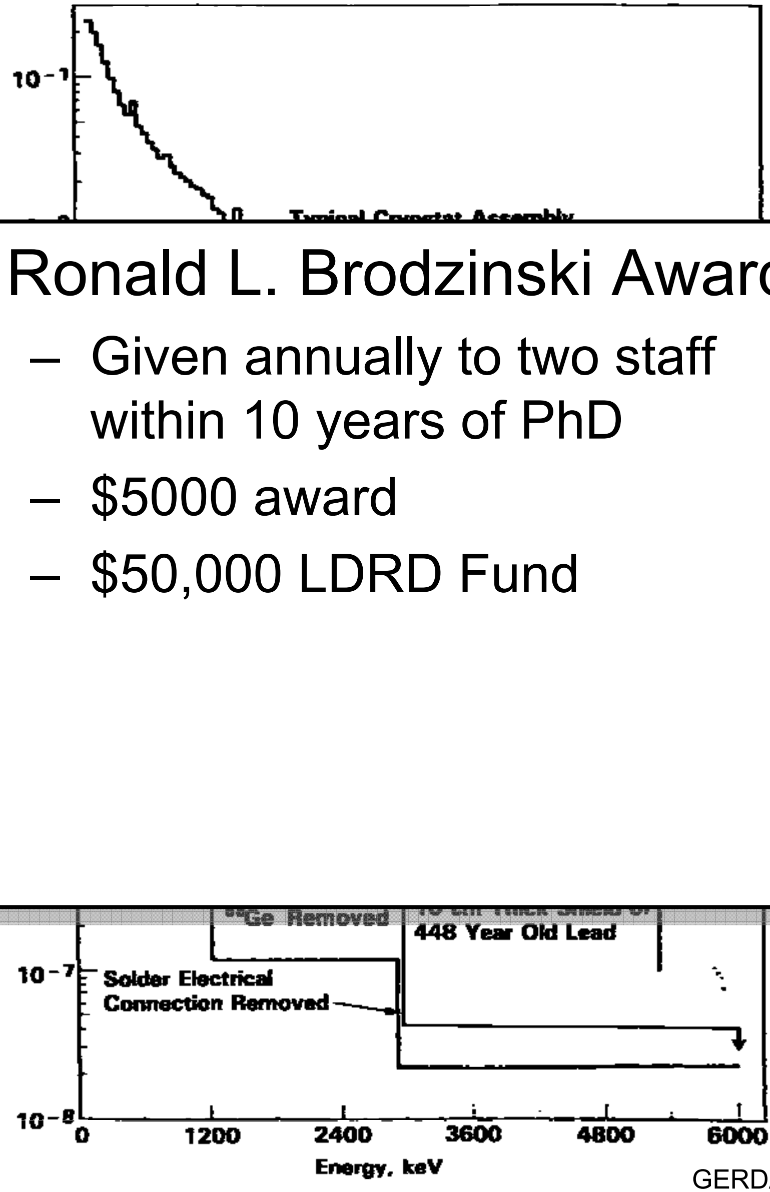
Summary and Directions

- Laser Ablation MS
  - Fast, easy assay, plus obtains surface vs. bulk (plastic, Cu, etc)
  - Looks promising but requires matched matrix for quantitation
  - Electroforming Cu from baths spiked with ^{232}Th now, requires bulk assay later
- Ion exchange sample preparation
  - Factor ~8 improvement since last fall!
  - Preliminary: Blank at 2x, starting stock 3x ultimate goal!
  - Need to lower blank values further
  - Building automated and sealed system now
- Classic precipitation
  - Looks promising but ^{229}Th recoveries are low
  - Time consuming
  - Latest sample set ready and are going to ICP/MS analysis now
- Electrochemical Methods
  - Stalled until ^{228}Th tracer obtained to determine rejection rates
  - Should begin next month
- Conclusion
  - We are very close to our goal for Cu purity for Majorana (after 3 yrs!)
  - Current campaign may prove GERDA Cu is quite pure enough wrt Th

In Memoriam

Ronald L. Brodzinski
1941-2006





- Ronald L. Brodzinski Award
  - Given annually to two staff within 10 years of PhD
  - $5000 award
  - $50,000 LDRD Fund

Thank you! Questions?