

Ge and Cu: *Technical Issues*



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SCHLOSS RINGBERG

Tagungsstätte der Max-Planck-Gesellschaft



High Altitude Overview



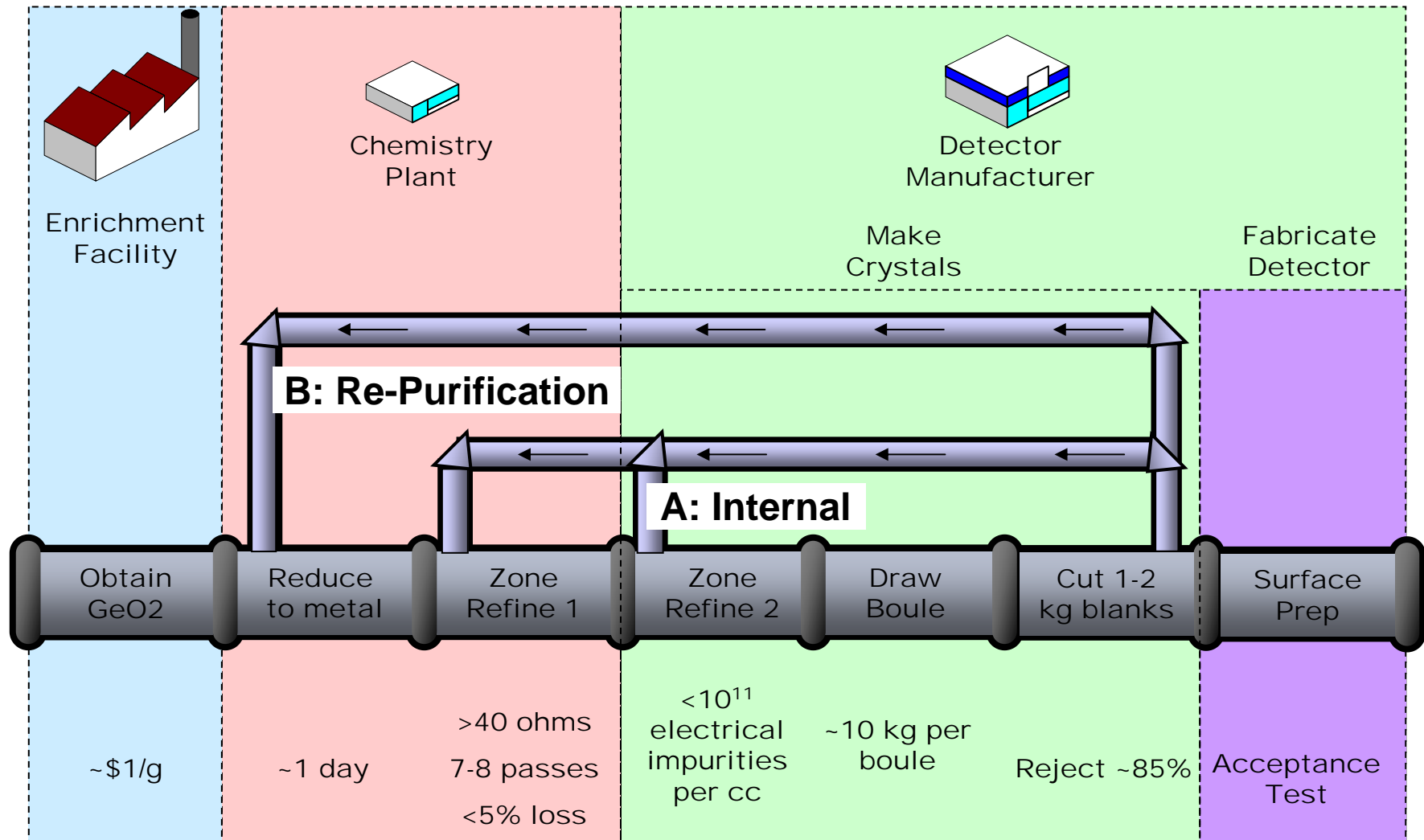
- Excerpts from DOE Review Dec 2006
 - Efficient Use of Ge
 - Review
 - Ultrapure Copper
 - Cu production improvements
 - Cu assay improvements
- Cu Update Feb 2007!
 - Assay is critical to success
 - Recent progress



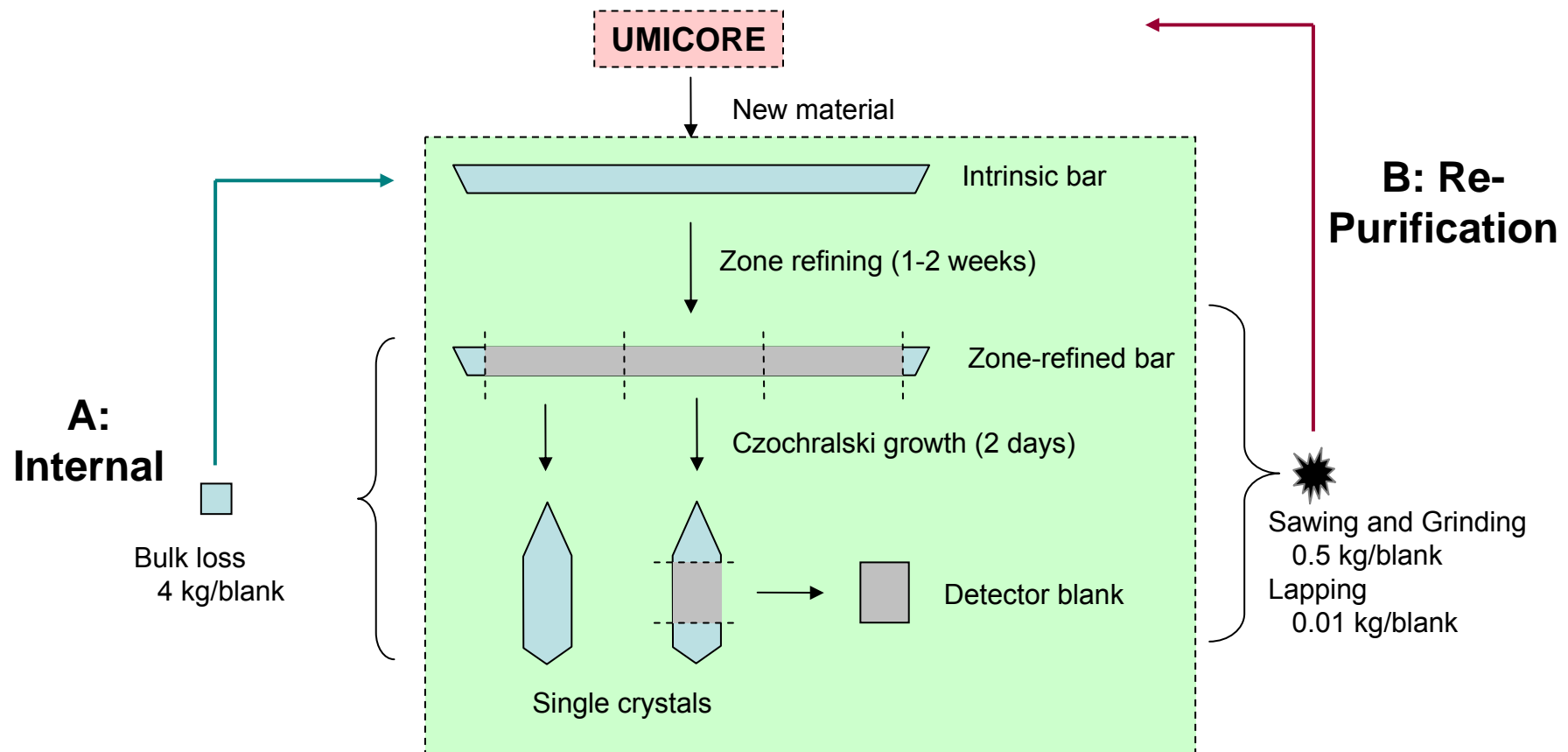
Germanium Processing Pipeline



Goal: Preventing wastes from becoming losses

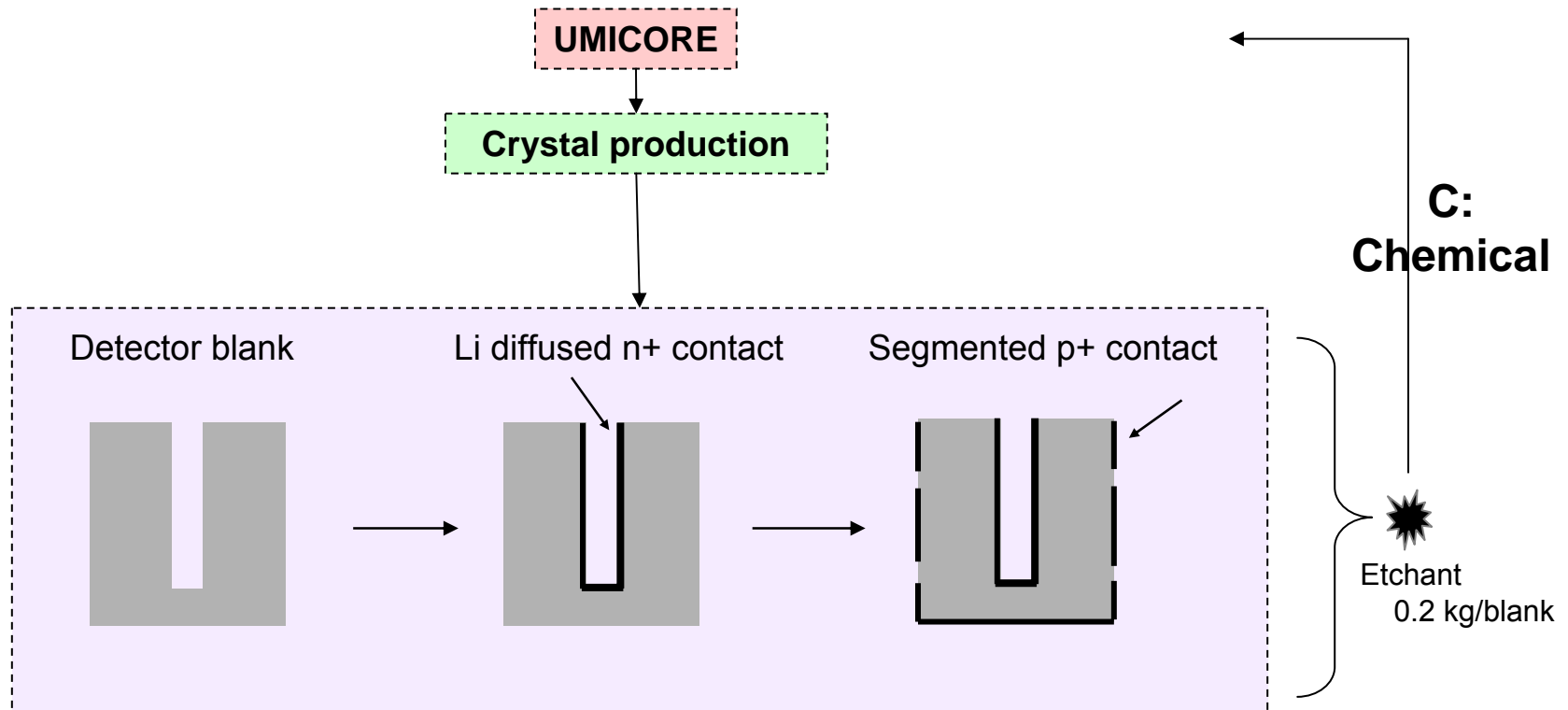


Crystal Production Losses



Waste values from discussions with manufacturers.

Detector Fabrication Losses



Waste values from discussions with manufacturers.

Detector Production Model



predicts location and accumulation of wastes

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y	Z	AA	AB	AC	AD	AE	AF	AG	AH
1				69.60	0.41																													
2				first																														
3	170	total		0.80						kg per	to QP	LOST		kg per	to QP	LOST		kg per	to QP	LOST		kg per	to QP	LOST	Orphan Ge	Accounting	DELTA	TOTAL	TOTAL kg		Det kg	purch	los det	
4				rest						boule	loss	per boule		boule	loss	per boule		boule	loss	per boule		boule	loss	per boule	5.62	170.00	0.00	36.78	127.6	106.7	150	115.5		
5	75	per year		0.96						0.60	0.20		0.60	0.20		0.60	0.20		0.60	0.20		0.60	0.20	23.2	23.2	0.00	0.00	0.288	126.50	175	137.5			
6			virgin	output	recycle	recycle	LOST at	recycle	input at	boles	zoner	other	remaining	boles	zoner	other	remaining	boles	zoner	other	remaining	boles	zoner	other	remaining	Ge for	Accounting	DELTA	TOTAL	TOTAL kg		Det kg	purch	los det
7			GeO2	polyxtl	input	output	Quapaw	at manuf	at xtal 1	1st pull	loss	loss	at manuf	2nd pull	loss	loss	at manuf	3rd pull	loss	loss	at manuf	4th pull	loss	loss	for recycle	Quapaw	puller	0.00	0.00	167.20	225	180.4		
8	neg contr	2009.250																								Ge	DELTA	TOTAL	TOTAL kg		Det kg	purch	los det	
9		2009.333																								Quapaw	0.00	0.00	187.00	250	202.4			
10	place orde	2009.417																								recycle	0.00	0.00	205.00	275				
11		2009.500																								Ge	0.00	0.00						
12		2009.583																								Quapaw	0.00	0.00						
13		2009.667																								recycle	0.00	0.00						
14	25	2009.750																								Ge	0.00	0.00						
15		2009.833	25.00	20.00	0.00	0.00	5.00		20.00	2	1.20	0.40	16.20	2	1.20	0.40	12.40	1	0.60	0.20	10.50	1	0.60	0.20	8.60	3.60	1.20	6.20	6.00	25.00	6.6			
16		2009.917						8.80	8.80	2	1.20	0.40	4.80	0	0.00	0.00	4.80	0	0.00	0.00	4.80	0	0.00	0.00	4.80	1.20	0.40	0.40	2.00	8.60	8.8			
17		2010.000						4.80	4.80	0	0.00	0.00	4.80	0	0.00	0.00	4.80	0	0.00	0.00	4.80	0	0.00	0.00	4.80	0.00	0.00	0.00	0.00	4.80	8.8	8.00		
18	25	2010.083						4.80	4.80	0	0.00	0.00	4.80	0	0.00	0.00	4.80	0	0.00	0.00	4.80	0	0.00	0.00	4.80	0.00	0.00	0.00	0.00	4.80	8.8			
19		2010.167	25.00	24.00	4.80	4.61	1.19	4.80	33.41	2	1.20	0.40	27.71	2	1.20	0.40	23.01	2	1.20	0.40	19.31	2	1.20	0.40	15.51	5.60	2.20	3.39	11.00	34.60	20.9			
20		2010.250						12.51	12.51																	Ge	0.60	0.60	3.00	12.51	24.2	14.00		
21		2010.333						6.81	6.81																	Quapaw	0.00	0.00	0.00	6.81	24.2			
22	25	2010.417						6.81	6.81																	recycle	0.00	0.00	0.00	6.81	24.2			
23		2010.500	25.00	24.00	8.40	8.06	1.34	6.81	38.87																	Ge	2.00	3.34	10.00	40.21	35.2	10.00		
24		2010.583						19.87	19.87																	Quapaw	1.40	1.40	7.00	19.87	42.9			
25		2010.667						6.57	6.57																	recycle	0.00	0.00	0.00	6.57	42.9			
26	25	2010.750						6.57	6.57																	Ge	0.00	0.00	0.00	6.57	42.9	7.00		
27		2010.833	25.00	24.00	10.20	9.79	1.41	6.57	40.36																	Quapaw	2.40	3.81	12.00	41.77	56.1			
28		2010.917						17.56	17.56																	recycle	1.20	1.20	6.00	17.56	62.7			
29		2011.000						6.16	6.16																	Ge	0.00	0.00	0.00	6.16	62.7	18.00		
30	25	2011.083						6.16	6.16																	Quapaw	0.00	0.00	0.00	6.16	62.7			
31		2011.167	25.00	24.00	10.80	10.37	1.43	6.16	40.53																	recycle	2.40	3.83	12.00	41.96	75.9			
32		2011.250						17.73	17.73																	Ge	1.40	1.40	7.00	17.73	63.6	19.00		
33		2011.333						4.43	4.43																	Quapaw	0.00	0.00	0.00	4.43	83.6			
34	25	2011.417						4.43	4.43																	recycle	0.00	0.00	0.00	4.43	83.6			
35		2011.500	25.00	24.00	11.40	10.94	1.46	4.43	39.38																	Ge	2.20	3.66	11.00	40.83	95.7	11.00		
36		2011.583						18.48	18.48																	Quapaw	1.40	1.40	7.00	18.48	103.4			
37		2011.667						5.18	5.18																	recycle	0.00	0.00	0.00	5.18	103.4			
38	20	2011.750						5.18	5.18																	Ge	0.00	0.00	0.00	5.18	103.4	7.00		
39		2011.833	20.00	19.20	10.80	10.37	1.23	5.18	34.74																	Quapaw	2.20	3.43	11.00	35.98	115.5			
40		2011.917						13.84	13.84																	recycle	1.00	1.00	5.00	13.84	121			
41		2012.000						4.34	4.34																	Ge	0.00	0.00	0.00	4.34	121	16.00		
42		2012.083						4.34	4.34																	Quapaw	0.00	0.00	0.00	4.34	121			
43		2012.167	0.00	0.00	9.60	9.22	0.38	4.34	13.56																	recycle	0.80	1.18	4.00	13.94	125.4			
44		2012.250						5.96	5.96																	Ge	0.00	0.00	0.00	5.96	125.4	4.00		
45		2012.333						5.96	5.96																	Quapaw	0.00	0.00	0.00	5.96	125.4			
46		2012.417						5.96	5.96																	recycle	0.00	0.00	0.00	5.96	125.4			
47		2012.500	0.00	0.00	2.40	2.30	0.10	5.96	8.26																	Ge	0.40	0.50	2.00	8.36	127.6	2.00		
48		2012.583						4.46	4.46																	Quapaw	0.00	0.00	0.00	4.46	127.6			
49		2012.667						4.46	4.46																	recycle	0.00	0.00	0.00	4.46	127.6			

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



Copper recap

- 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
- **We need new methods of Cu assay to assure that we will achieve required background goals for a ~1 ton experiment**



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 $\mu\text{Bq/kg}$ ^{208}Tl 0.4 $\mu\text{Bq/kg}$ ^{214}Bi	0.7-1.3 $\mu\text{Bq/kg}$	Current work also [Arp02]
NOSV Cu	Outer Cu Shield	0.26 $\mu\text{Bq/kg}$ ^{208}Tl 0.3 $\mu\text{Bq/kg}$ ^{214}Bi	<6 $\mu\text{Bq/kg}$	[Heu04]
Pb	Lead Shield	1 $\mu\text{Bq/kg}$ ^{208}Tl 5 $\mu\text{Bq/kg}$ ^{214}Bi	<7 $\mu\text{Bq/kg}$	[Heu04]
Plastic	Trays, Rings	10 $\mu\text{Bq/kg}$ ^{208}Tl 10 $\mu\text{Bq/kg}$ ^{214}Bi	1000 $\mu\text{Bq/kg}$	Current work also [Arp02]
Front End Electronics	LFEPS, Contacts, Capacitors	30 $\mu\text{Bq/kg}$ ^{208}Tl 200 $\mu\text{Bq/kg}$ ^{214}Bi	1000 $\mu\text{Bq/kg}$	Current work also [Arp02]
Cable	Cable	3 $\mu\text{Bq/kg}$ ^{208}Tl 10 $\mu\text{Bq/kg}$ ^{214}Bi	400 $\mu\text{Bq/kg}$	[Ams06]

Copper Assay Goals



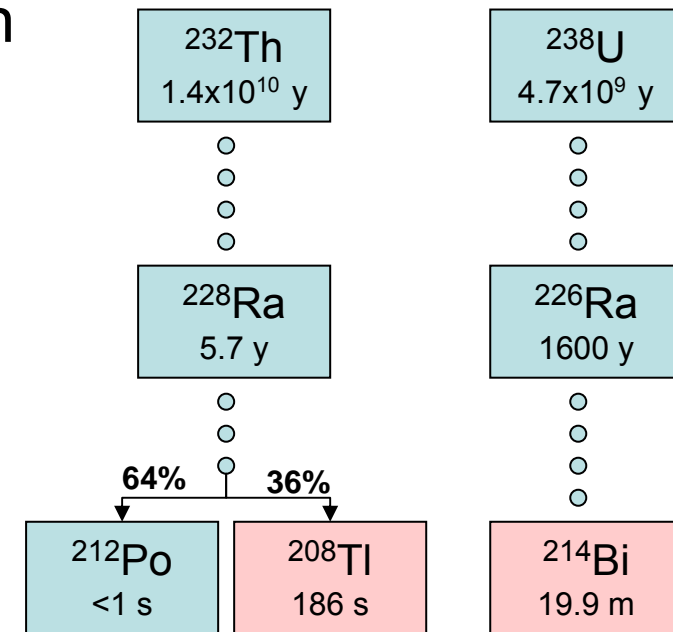
1. Show that our copper is not a show stopper for the experiment
 - Perhaps an expensive one-time effort
 - What we are working on today
2. Create a QA process for every part
 - Cost effective
 - Fast (not 90 days)
 - Low-waste solution preferred
 - Mass spec type solution fits

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



$$0.1 \mu\text{Bq/kg } ^{208}\text{Tl} = 0.27 \mu\text{Bq/kg } ^{232}\text{Th} = 70 \text{ fg/g Th}$$

Copper Starting Point



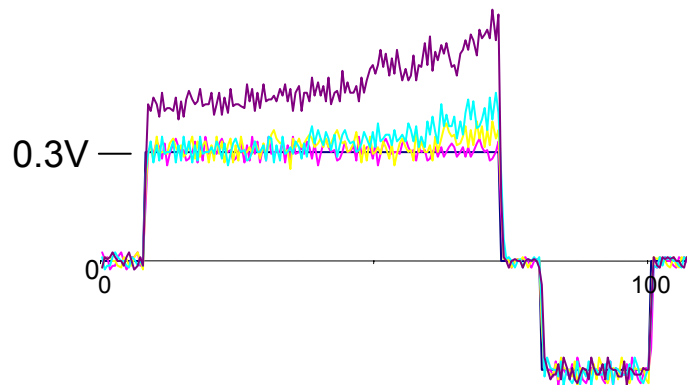
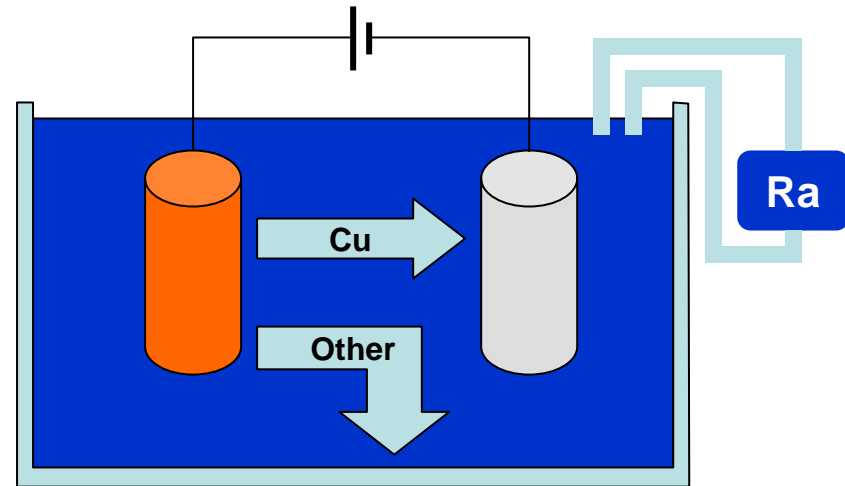
- Direct gamma assay
 - Require kg quantities and 60-90 day measurements underground
 - Table shows limits for U, Th chains in Cu of NOSV grade, similar to our starting stock
 - From 25 to 70 times U/Th goal
- Direct gamma measure of our Cu at about 10 $\mu\text{Bq/kg}$ Th
 - Just a limit, the actual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

^{228}Th (^{232}Th)	^{226}Ra (^{238}U)	Comment
$\mu\text{Bq/kg}$	$\mu\text{Bq/kg}$	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



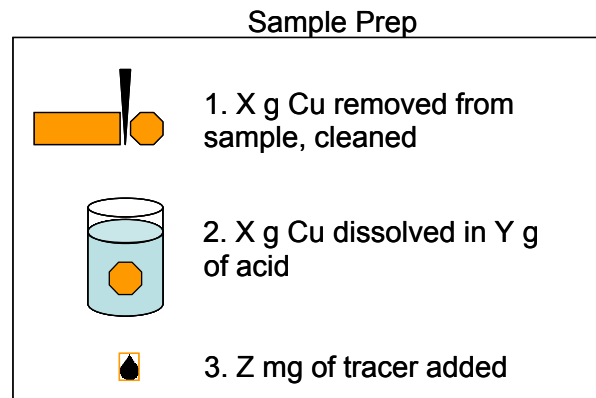
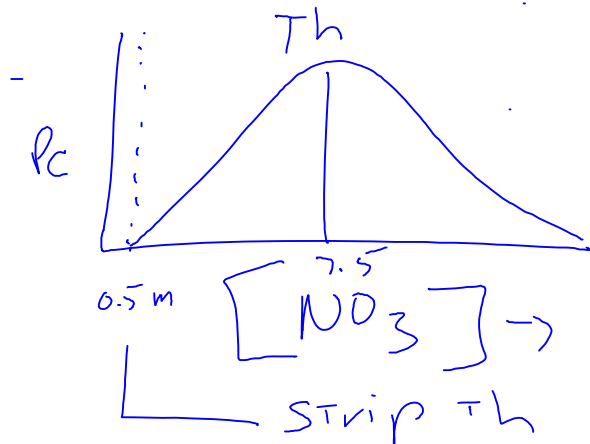
- **1995:** a limit of $<9 \mu\text{Bq/kg}$ for ^{232}Th set in IGEX electroformed copper.
 - This was a 90 day radiometric measurement of $\sim 10 \text{ kg}$ Cu at 4000 mwe
- **November 2004:** CuSO_4 bath used in electroforming could be purified extensively through recrystallization
- **April 2005:**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

Ion Exchange Assay Approach

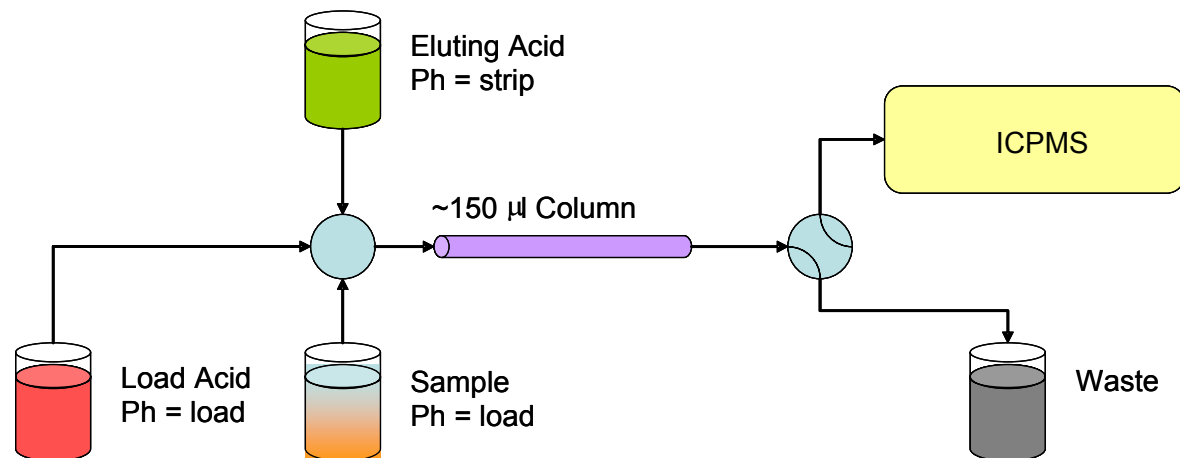


Approaches

- 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

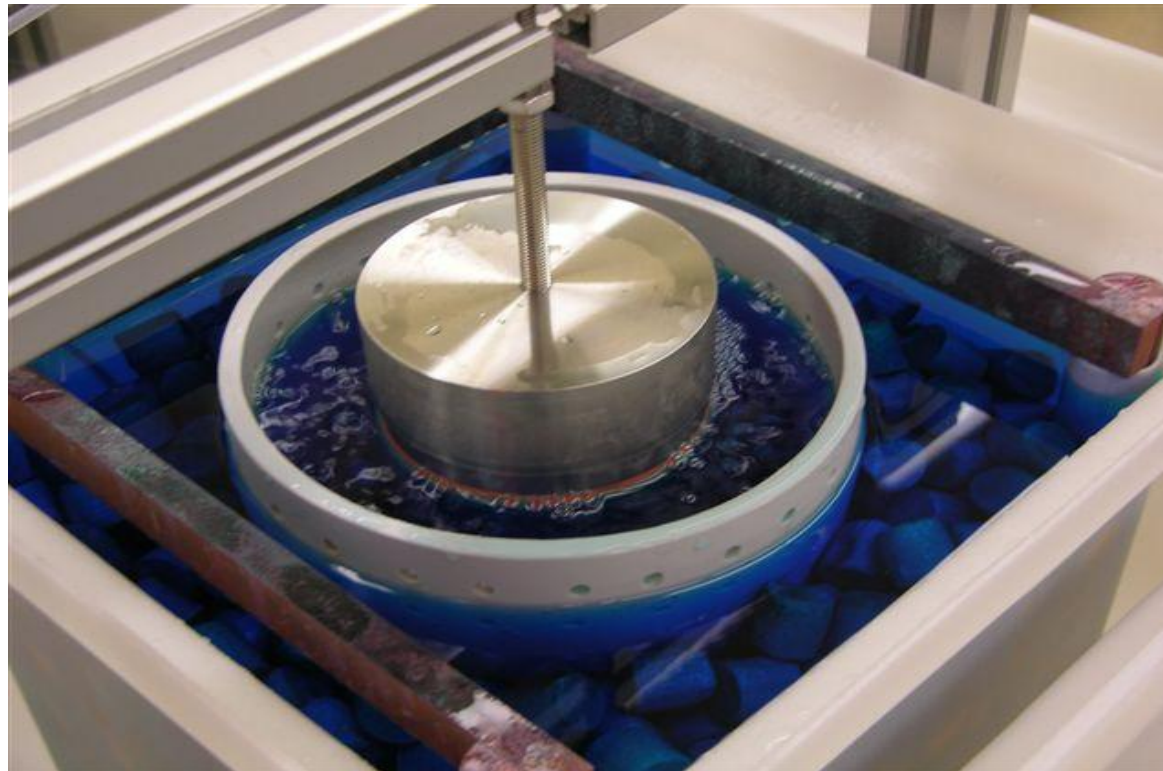


- New lab operating
 - Will be adding baths remaining FY07 and FY08, up to 8 total
 - Working toward cleanliness improvements
- Cu formation
 - Grain size is excellent, reducing machining
- Study: Th Rejection
 - Still waiting for ^{228}Th
- Assay methods being pursued
 - Laser Ablation MS
 - Ion exchange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

Copper Electroforming Operational



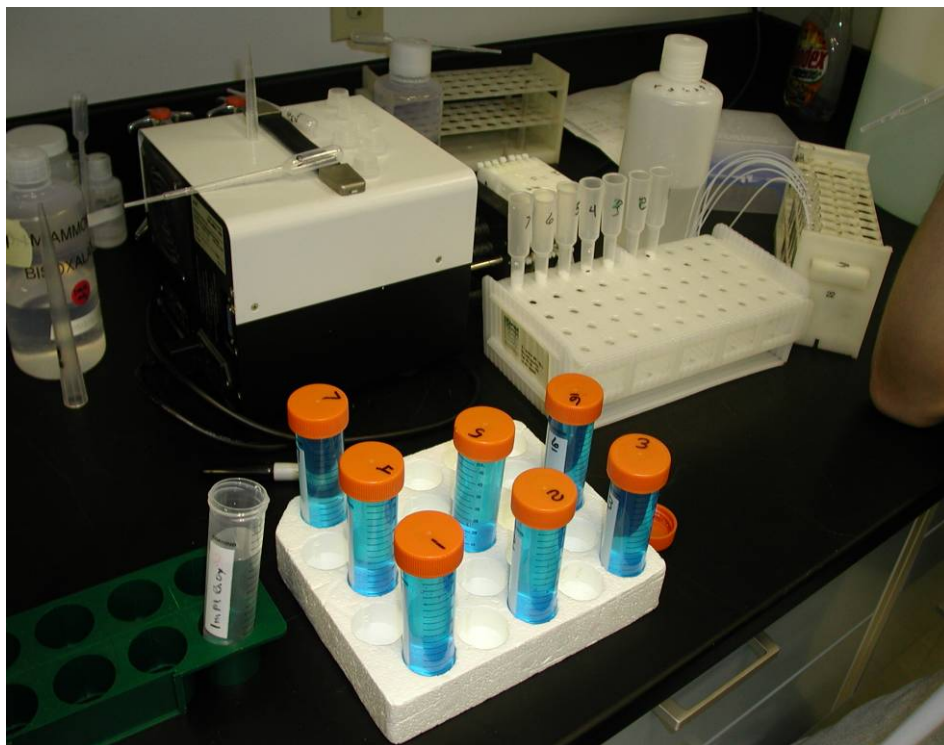
- Need to improve on lab cleanliness
- Plate for weeks without machining
- Build up slower than desired, 0.002-0.005"/day
- Still developing better recipes which may improve build up rate



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 μ m 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

$\mu\text{Bq } ^{232}\text{Th}/\text{kg}$ 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

$$(1.5 - 0.6)/3 = 0.3 \mu\text{Bq/kg } ^{208}\text{Tl with } \sim 50\% \text{ error}$$

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**

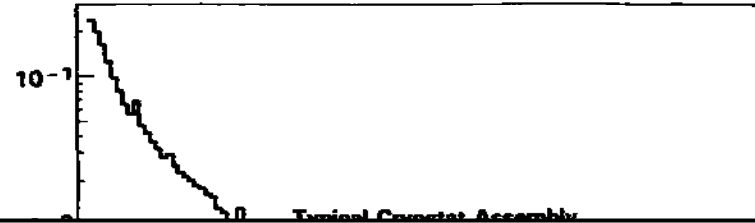
In Memoriam



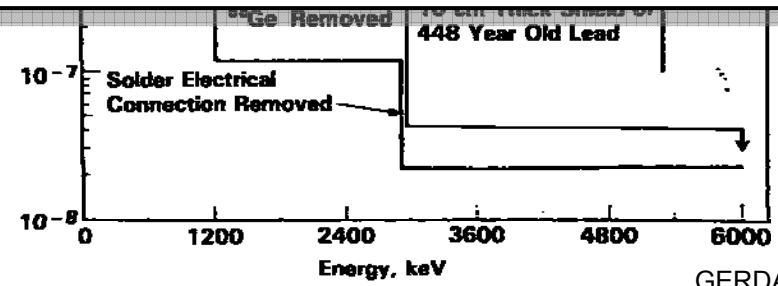
Ronald L. Brodzinski
1941-2006



Ge/Cu Technical Issues



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



Thank you! Questions?

