

Low background crystal growth and purification at CUP

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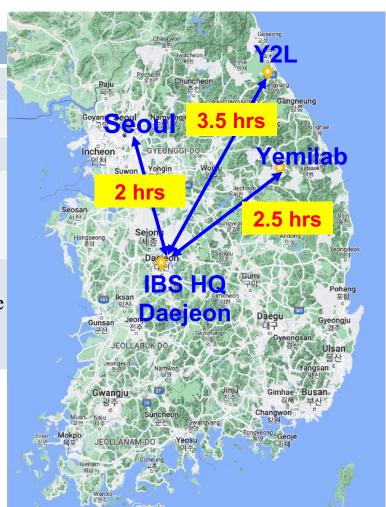


- ☐ Rare-process search experiments
- ☐ Radioassay (ICP-MS, HPGe, alpha)
- ☐ Purification of raw materials for crystal growing
- ☐ Ultra-pure crystal growth at CUP
- ☐ Low background scintillating crystals grown

Rare-process search experiments at CUP

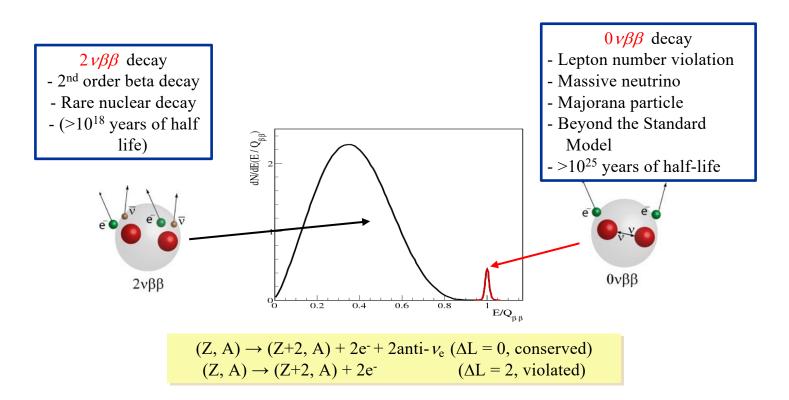


	Y2L	Yemilab
Location	Yangyang	Jeongseon
Depth (m)	700	1000
Area (m ²)	350	~3000
Rock Radioactivity (ppm)	U: 3.9(14) Th: 10.5(65) K: 40000	U: 0.8(3) Th: 3.3(4) K: 11800
Experiments	KIMS (WIMP) AMoRE-I (0 νββ) COSINE-100 (WIMP)	AMoRE-II COSINE-100 upgrade COSINE-200 +



AMoRE: 0v\beta\beta\beta\beta\text{decay search}

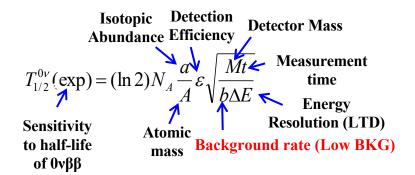
The goal of **AMoRE** is to search for neutrinoless double beta $(0\nu\beta\beta)$ decay of ¹⁰⁰Mo using Mo-based scintillating crystals and low-temperature detectors (LTD).



AMoRE: Sensitivity



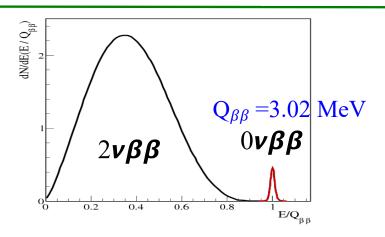
Sizable background case:

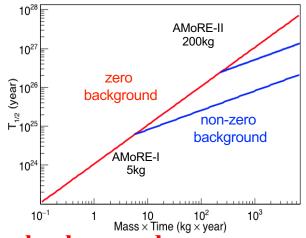


"Zero" background case:

When b is $\sim O(1)$,

$$T_{1/2}^{0\nu}(\exp) = (\ln 2)N_A \frac{a}{4} \varepsilon Mt$$





AMoRE is aiming for zero background.

AMoRE Parameters

0.8

o.4

15 10

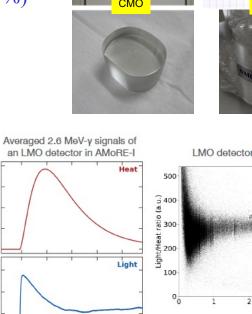
Time /ms

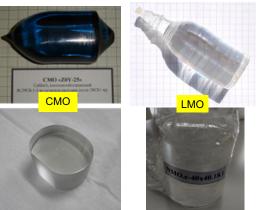


Crystals: ⁴⁰Ca¹⁰⁰MoO₄(CMO) or XMO

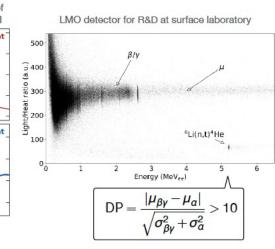
(X: Li, Na, or Pb studied)

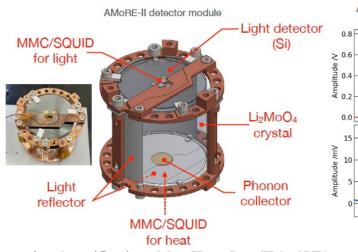
- 100 Mo enriched: > 95%
- 48 Ca depleted: < 0.001% (N.A. of 48 Ca: 0.187%)
- Low-temperature (LT) detector: @10 30 mK
- Energy resolution: ~5 keV @ 3 MeV (goal)
- Excellent PID for α vs. e/γ









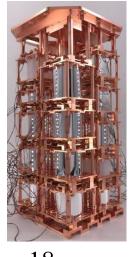


AMoRE phases summary



	Pilot	Phase I	Phase II
Mass (Crystal)	1.9 kg (CMO)	6 kg (CMO + LMO)	~160 kg (CMO + LMO)
BKG [keV·kg· year]-1	< 0.5	< 0.03	< 10-4
T _{1/2} Sensitivity [years] 90%CL	$< 3.2 \times 10^{23}$	< 3.3×10 ²⁴	6×10 ²⁶
<m<sub>ββ > Sensitivity [meV]</m<sub>	600 - 1000	190 - 340	20 - 35
Location	Y2L	(700 m depth)	Yemi Lab (1000m depth)
Run period	2015 - 8	2020 - 2023	2024 -







6 ea

18 ea

360 ea

AMoRE CMO crystals (FOMOS)













- 3 years (2015-17) for procurement of SE1-9 (9 CMOs)
- LY, resolution, transmittance, RT background measurements done.
- SB28, SB29, S35, SS68 (4 CMOs) already procured before.
- In total, 13 CMOs (4.8 kg).

Critical radioactivity



- \square Go through all known nuclei decaying β with $Q_{\beta\beta} > 3.02 \text{MeV}$ in NNDC database.
- ☐ Cosmogenic excitation is negligible after 1 year underground.
- □ Only Th and U natural radio-activities are critical for Q > 3.02 MeV. \rightarrow Great advantage to run high Q-value nuclei!

Element	Decay	$T_{1/2}$	Q (MeV)	Mother	Chain	Comment
²⁶ Al	EC	$7.4 \times 10^5 \text{y}$	4.004	N/A		Long lifetime
⁵⁶ Co	EC	0.21y	4.567	N/A		Short lifetime
^{88}Y	EC	0.29y	3.623	⁸⁸ Zr (0.23 y)		Short lifetime
¹⁰⁶ Rh	B-	30s	4.004	106 Ru(1.02y)		
¹²⁶ Sb	B-	12.5d	3.670	126 Sn(2.3x10 5 y)		Long lifetime
¹⁴⁶ Eu	EC	4.61d	3.878	¹⁴⁶ Gd (0.13 y)		Short lifetime
²⁰⁸ Tl	B-	3.05m	4.999	²²⁸ Th (1.91 y)	²³² Th	Main
²⁰⁹ Tl	B-	2.16m	3.970	²³³ U(159200y)	^{233}U	2.1% branching
²¹⁰ Tl	B-	1.3m	5.482	²²⁶ Ra(1600y)	^{238}U	0.02% branching
²¹⁴ Bi	B-	19.9m	3.269	²²⁶ Ra(1600y)	^{238}U	Main

AMoRE CMO: RT measurement at 4π setup



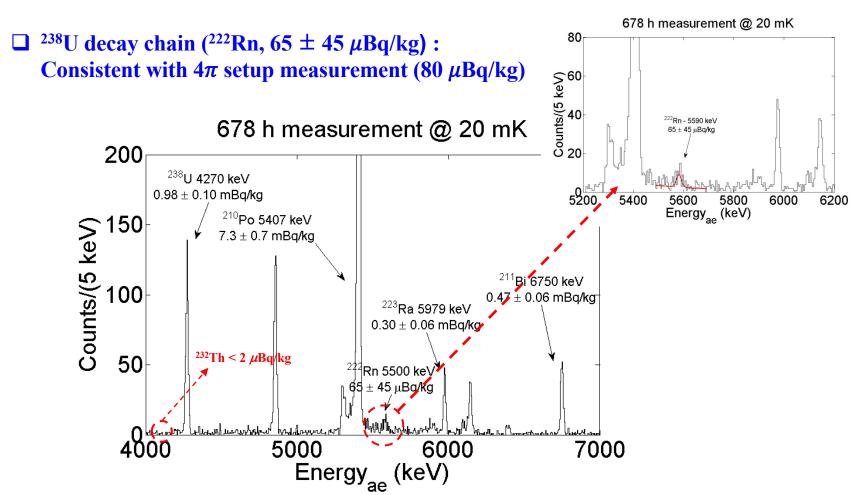
[µB/kg]	²²⁷ Ac (²¹⁵ Po) (²³⁵ U family)	²²⁶ Ra (²¹⁴ Po) (²³⁸ U family)	²²⁸ Th (²¹⁶ Po) (²³² Th family)	Alpha	Relative Light Yield
Qualification*	< 500	<100	<50	<1000	
SE1	60 ± 8	40 ± 6	50 ± 6		0.43
SE2	90 ± 10	20 ± 3	< 100		0.58
SE3	30 ± 6	6 ± 3	30 ± 6	28000	0.75
SE4	30 ± 6	10 ± 3	10 ± 3	3200	0.60
SE5	40 ± 6	10 ± 3	10 ± 3		0.70
SE6	35 ± 6	100 ± 10	70 ± 10		0.62
SE7	80 ± 10	30 ± 5	65 ± 10		0.60
SE8	40 ± 6	20 ± 5	40 ± 6		0.55
SE9	0 ± 6	<11	50 ± 6		0.66

^{*}Expect to have 10⁻³ counts/keV/kg/y at AMoRE-I

J.Y. Lee et al., IEEE TNS vol. 65 No. 8 (2018) 2041

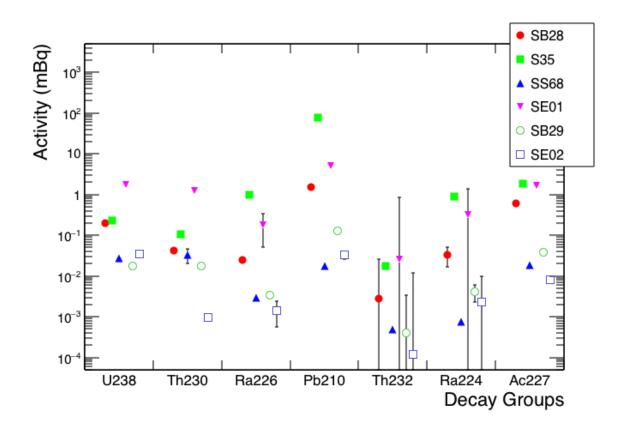
Internal alpha background of SB28 (AMoRE-Pilot)





AMoRE-Pilot: Internal Activities from α rates





- Most of the ²¹⁰Pb are bulk contribution.
- Internal backgrounds between crystals differ more than an order, even two orders.

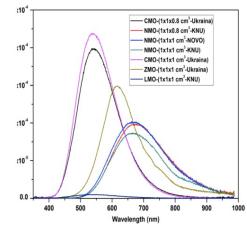
Decision on crystals for AMoRE-II

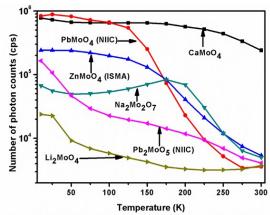


- □ CMO (CaMoO₄) is a very good crystal with the largest light output, but CMO has a disadvantage in that we need ⁴⁸Ca depleted isotopes, expensive.
- □ CUPID-Mo group decided to use LMO (Li₂MoO₄).
- We worked on LMO, PMO (PbMoO₄), & NMO (Na₂Mo₂O₇) crystals, and LMO was chosen due to its easiness of growth and machining and low background.

Crystals	$\lambda_{ m em}$	Decay time [µs]	E_(LED) [%]	E_(⁹⁰ Sr) [%]
CaMoO ₄	540	237	100	100
ZnMoO ₄ (ISMA)	620	_	22	32
PbMoO ₄ (NIIC)	545	20	13	105
Pb ₂ MoO ₅ (NIIC)	600	5	3	22
Li ₂ MoO ₄	540	23	1	5
$Cs_2Mo_2O_7$	701	363[31]	12	1
$Na_2Mo_2O_7$	663	756 ^[36]	55	9

 λ_{em} , peak emission wavelength; E_(LED), energy deposited by a 280 nm UV LED source; E_(90 Sr), energy deposited by a 90 Sr beta source.



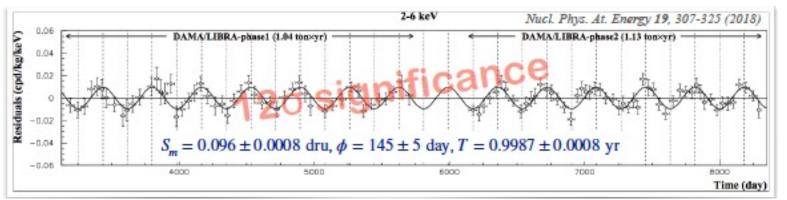


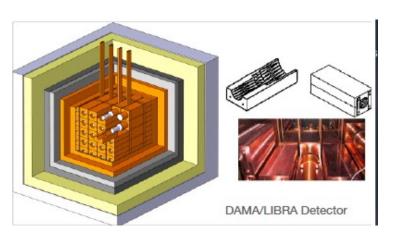
H.J. Kim et al., Crystal Research & Technology, Nov. 2019

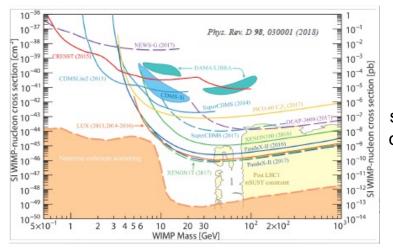
WIMP DM search: COSINE-100



To test the DAMA/LIBRA's annual modulation signal with the same NaI(TI) detectors.



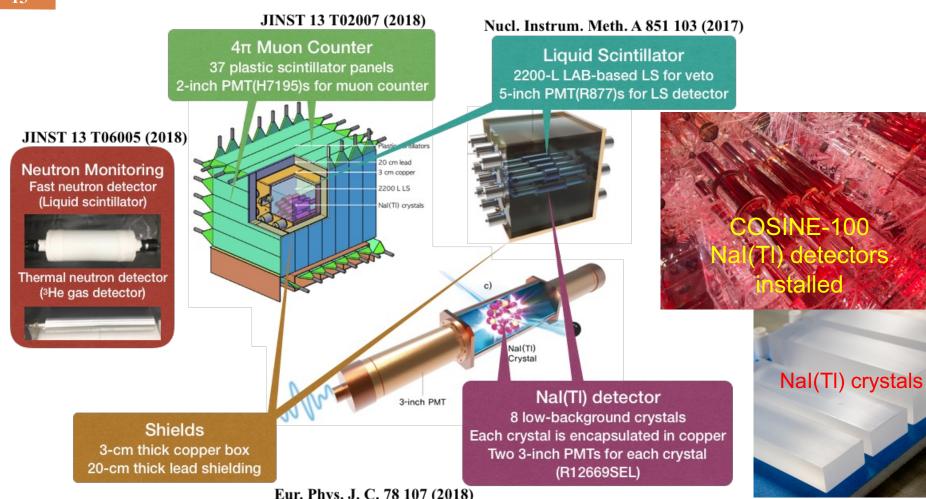




No other experiments succeeded in observing the DM signal.

COSINE-100 instrument





COSINE-100 NaI(Tl) crystal detector



- □ 8 ultra low-background NaI(Tl) crystals with a mass of 106 kg in total □ U/Th/K levels are less than DAMA, but total alphas (210Pb) are higher
- than DAMA.

 ☐ Higher light yield (15 p.e/keV) than DAMA
- ☐ Can make the threshold lower easily
- ☐ Total background level is 2-3 times that of DAMA.

Crystal	Mass (kg)	Powder	Alpha rate (mBq/kg)	⁴⁰ K (ppb)	²³⁸ U (ppt)	²³² Th (ppt)	Light yield (p.e./keV)
Crystal 1	8.3	AS-B	3.20 ± 0.08	43.4 ± 13.7	< 0.02	1.31 ± 0.35	14.88 ± 1.49
Crystal 2	9.2	AS-C	2.06 ± 0.06	82.7 ± 12.7	< 0.12	< 0.63	14.61 ± 1.45
Crystal 3	9.2	AS-WS II	0.76 ± 0.02	41.1 ± 6.8	< 0.04	0.44 ± 0.19	15.50 ± 1.64
Crystal 4	18.0	AS-WS II	0.74 ± 0.02	39.5 ± 8.3		< 0.3	14.86 ± 1.50
Crystal 5	18.0	AS-C	2.06 ± 0.05	86.8 ± 10.8		2.35 ± 0.31	7.33 ± 0.70
Crystal 6	12.5	AS-WSIII	1.52 ± 0.04	12.2 ± 4.5	< 0.018	0.56 ± 0.19	14.56 ± 1.45
Crystal 7	12.5	AS-WSIII	1.54 ± 0.04	18.8 ± 5.3		< 0.6	13.97 ± 1.41
Crystal 8	18.3	AS-C	2.05 ± 0.05	56.15 ± 8.1		< 1.4	3.50 ± 0.33
DAMA			< 0.5	< 20	0.7 - 10	0.5 – 7.5	5.5 – 7.5



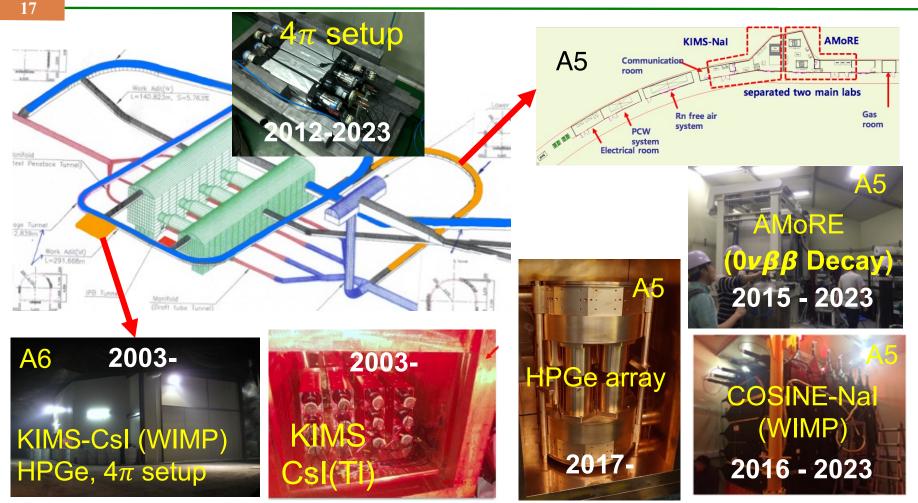




Eur. Phys. J. C. 78 107 (2018)

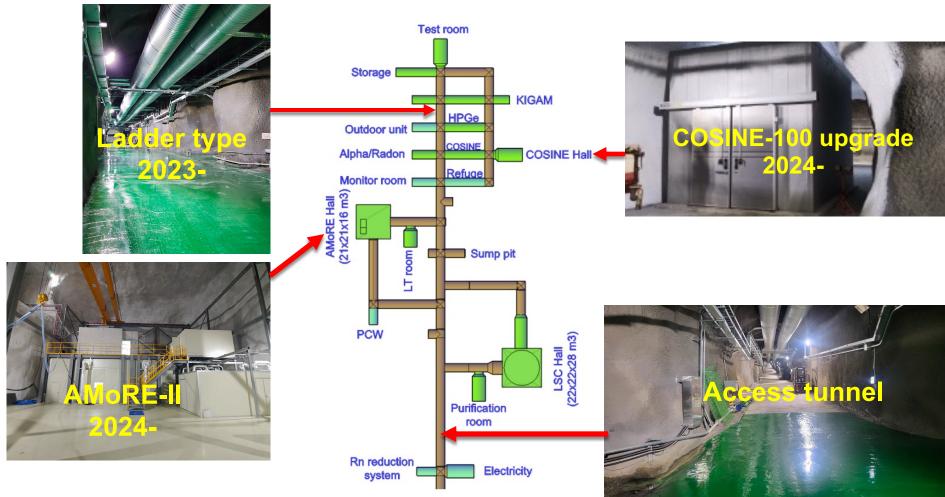
Experiments at the Y2L





Yemilab: Underground experiments



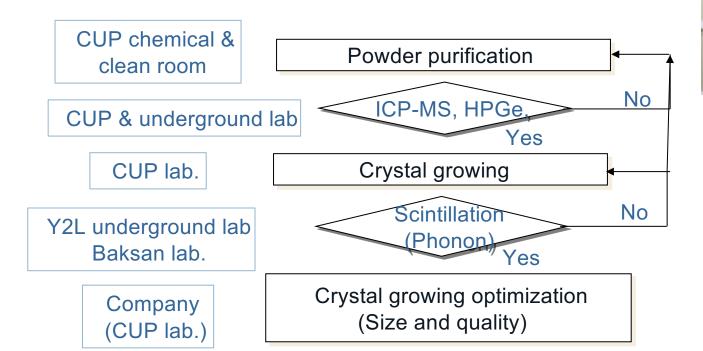


Ultra-low background crystal production



Ultra-low background powder R&D is difficult and needs quick feedback

(Purification and measurement of 10 μ Bq/kg ²³⁸U, ²³²Th & total radioactivity of alpha < 1 mBq)

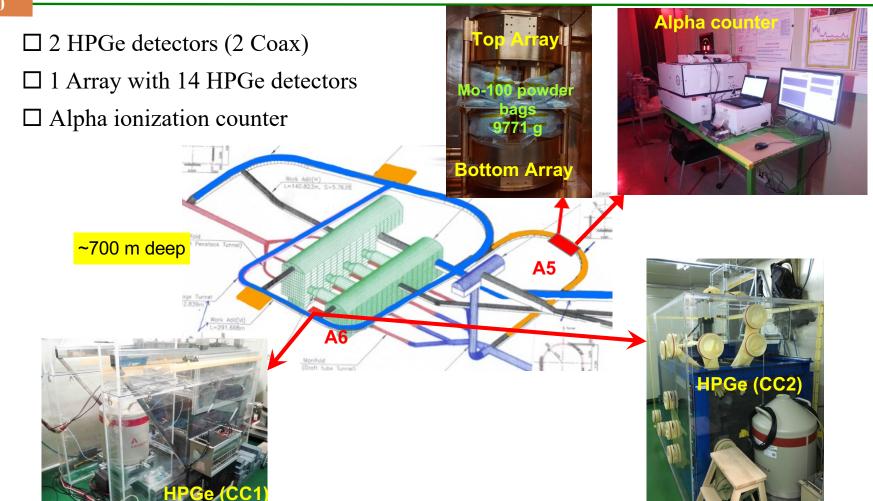


Re-crystalization









Radioassay at IBS HQ, Daejeon: ICP-MS



- ☐ Agilent 7900, the highest sensitivity single MS system in 2015 when purchased.
- ☐ Under operation since Oct. 2015. (Moved to IBS HQ in spring 2018)
- \square In a cleanroom nominally designed as class 1000, > 150 air changes/hour.
- ☐ A Millipore DI system, in-house acid distillation with a 3 linear meters of chemical hood space.
- ☐ Dissolve sample in liquid form, uptake in argon (Ar) gas stream, ionize gas, extract into mass spectrometer, measure trace contaminants.
- ☐ Confirmation of purification methods by measuring isotopic or chemical tracers.
- ☐ Confidence in systematics at ultra-trace levels is not easily achievable through outsourced measurements.



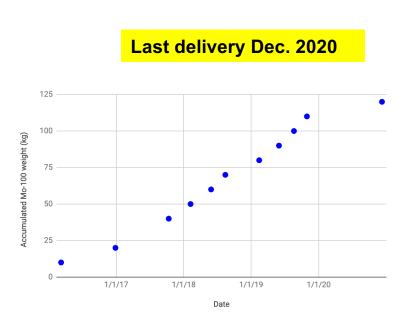


¹⁰⁰MoO3 powder (ECP) for AMoRE-II



Total 120 kg of ¹⁰⁰Mo

		D. II.
Date(weight)	Lot	Delivery@ Y2L
`	#1(3172)	2/0/46
2015 (10 kg)	#2(3328)	3/9/16
2016 (10 kg)	3434	12/28/16
2016 (10 kg)	3497	10/12/17
2016 (10 kg)	3535	10/12/17
2017 (10 kg)	3589	2/7/18
2017 (10 kg)	3649	5/29/18
2017 (10 kg)	3675	8/14/18
2017 (10 kg)	3741	2/13/19
2018 (10 kg)	3803	5/31/19
2018 (10 kg)	3824	8/20/19
2018 (10 kg)	3848	10/29/19
2018 (10 kg)	3922	12/8/20





HPGe Array meas. (9/13 - 11/28/2017)

- 226 Ra chain (238 U):1.6 \pm 0.3 mBq/kg
- 228Th chain (232Th): 244 \pm 50 μ Bq/kg (first measurement)
- 88 Y: 33 \pm 8 μ Bq/kg (cosmogenic)

Purification & Crystal: Motivation & Manpower



Motivation

- Lack of commercial producers for ultra-pure crystals needs in AMoRE-II and COSINE-200.
- The company who produced CaMoO₄ for AMoRE-pilot & I does not want to provide information which is critical in improving the background levels at the grown crystals.
- The company who produced ultra-pure NaI(Tl) crystals for DAMA/LIBRA does not know how to grow the ultra-pure pure NaI(Tl) crystals any more.
- The company who produced pure NaI(Tl) for COSINE-100 could not provide ultra-pure crystals for COSINE-200.

Manpower

- Purification working group (Led by Dr. Olga Gileva)
 - 4 peoples: 1 Chemist (PhD), 2 Material Scientists (MS), 1 Chemist (BS)



- 4 peoples: 4 Scientists (MS)
- Collaborators
 - Prof. Vitaly Milyutin, IPCE RAS, Russia (Purification)
 - Dr. Yan Vasiliev / Dr. Vladimir Shlegel, NIIC, Russia (AMoRE crystals)
 - Mr. Alan Iltis (NaI crystal, Former Saint Gobain employee)
 - Prof. HongJoo Kim at Kyungpook National University, Daegu, Korea (Crystal R&D)
 - Prof. HyangKyu Park at Korea University, Sejong, Korea (Purification)











Purification facility for AMoRE



- □ Main goal: Low BKG raw materials for crystals growing.
- Deep purification of Li₂CO₃ MoO₃ powders ($< 50 \mu Bq/kg$ for U, Th chains) for AMoRE-II (The goal achieved).



Purified powder after sublimation





	Purified 100 MoO ₃ powder (examples)													
	Amount	Al	K	Cr	Mn	Fe	Ni	Cu	W	Sr	Ва	Pb	Th	U
S/N	(kg)	(ppb)	(ppb)	(ppb)	ppt	ppt								
1	1.1	585	409	<200	<30	39	<20	<200	33	< 0.15	3.9	0.3	<10	<7
31	1.2	<30	153	<200	<30	136	<20	<200	711	< 0.15	<3.0	< 0.5	<10	<7
32	1.3	<30	150	<200	<30	26	<20	<200	648	< 0.15	<3.0	< 0.5	<10	<7

Purification facility for COSINE(-200)



- ☐ Extremely pure crystal development
 - Background level less than that of DAMA/LIBRA (1 dru)
 - In-house development for the entire processes
 - Purification of NaI powder achieved the goal.



Crystal grade NaI [99.99(5) %]

Material	Initial [ppb]	Purified [ppb]
³⁹ K	45.1	6.0
²⁰⁸ Pb	3.3	0.8
²³² Th	< 0.1	< 0.1
²³⁸ U	< 0.1	< 0.1

J. Rad. Nucl. Chem. 317 1329 (2018)

MoO₃

99.5%

MoO₃

1st Sub.

MoO₃

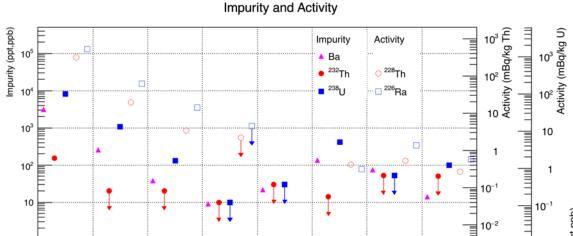
2nd Sub.

MoO₃ 2nd

Sub+Wet Pur. by NIIC

AMoRE-II: Purification of XMO crystals



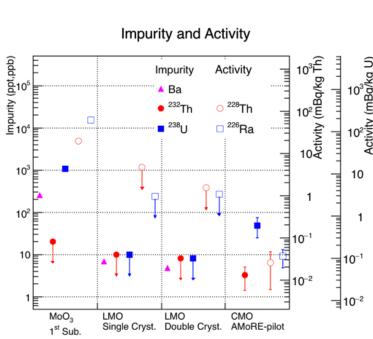


MoO₃ Purified

Li₂CO₃

Na₂CO₃

☐ Ba is a good indicator for Ra since they are in the same family.



Molybdate crystals growth at CUP

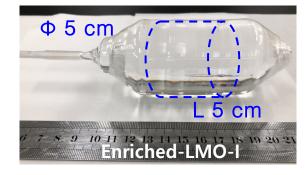


- □ Successful in growing molybdate crystals. Growing time ~ 1 week.
- ☐ The purities of the grown crystals are measured by ICP-MS and confirmed.
- ☐ Enriched LMO crystals have been growing at NIIC and CUP for AMoRE-II.



CMO & LMO crystals by CUP





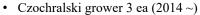
Purified CMO (Ir, Annealed)

^{48depl}Ca¹⁰⁰MoO₄ (AMoRE-Pilot/I): Excellent but ^{48depl}Ca & Ca deep purification necessary.

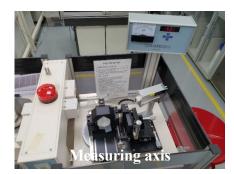
Crystal production at CUP (AMoRE)



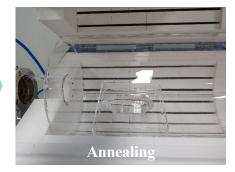




- Fused alumina refractory (less impurities)
- Platinum crucible (99.95 %) 1600 °C
- High purity (99.999 %) Air



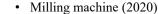
- Crystal orientation unit (2019)
- · X-ray goniometer



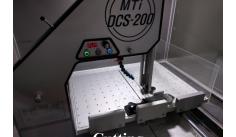
- Annealing furnace (2019)
- Quartz tube
- High purity (99.999 %) Air
- Temperature: 500 °C

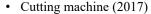


Coring



- · Diamond core drill bit
- Mineral oil (for hygroscopic crystal)





- Diamond band saw
- Mineral oil (for hygroscopic crystal)



- Polishing machine in a glove box (2019)
- SiC + oleic acid and colloidal silica
- · Polytex pad



Purities of CUP grown LMO crystals



Element		Al	K	Ba	Sr	Pb	Th	U				
No.	sample	(ppb)	(ppb)	(ppb)	(ppt)	(ppt)	(ppt)	(ppt)				
Single crystallized natural LMO (w/o purification)												
CMD 113	L1701-1	48.1	347.3	5.445	<15	< 300	<15	<16				
CMD 113	L1701-2	21.7	449.2	5.401	75	< 300	<15	<16				
	Si	ngle crys	tallized natu	ral LMO (M	OO3 sublime	ed)						
CMD163.1	CZ02-L1706-T	<11	38	7.579	< 50	<100	<8	<8				
CMD163.2	CZ02-L1706-B	<11	83	9.617	< 50	<100	<8	<8				
	Do	uble crys	tallized natu	ıral LMO (M	IoO ₃ sublim	ed)						
CMD191.1	CZ02-L1801-T	<11	<30	4.744	< 50	<100	<8	<8				
CMD191.2	CZ02-L1801-B	<11	<30	5.814	< 50	<100	<8	<8				
		En	riched LMO	(w/o purific	cation)							
CMD00236.2	CZ02-L1803E-T	1437	<40	6.82	<31	<225	<6	<6				
CMD00236.3	CZ02-L1803E-B	1484	<40	7.07	<31	<225	<6	<6				
CMD00236.1	CZ02-L1803E-RM	3824	249	28.58	4110	12290	71	472				

Ultra-pure LMO crystals grown at CUP



LMO sample name	K	Ва	Sr	Zr	lr	Pb	Th	U
	(ppb)	(ppb)	(ppt)	(ppt)	(ppt)	(ppt)	(ppt)	(ppt)
CZ01-L2110ED-4-T	<50	<3	<50	<150	<70	<150	<6	<6
CZ01-L2110ED-4-B	<50	<3	<50	<150	<70	<150	<6	<6
CZ01-L2111ED-4-T	<50	<3	<50	<150	<70	<150	<6	<6
CZ01-L2111ED-4-B	<50	<3	<50	<150	<70	<150	<6	<6
CZ01-L2112ED-4-T	<50	<3	<50	<150	<70	<150	<6	<6
CZ01-L2112ED-4-B	<50	<3	<50	<150	<70	<150	<6	<6
CZ01-L2113ED-4-T	<50	<3	<50	<150	<70	<150	<6	<6
CZ01-L2113ED-4-B	<50	<3	<50	<150	<70	<150	<6	<6

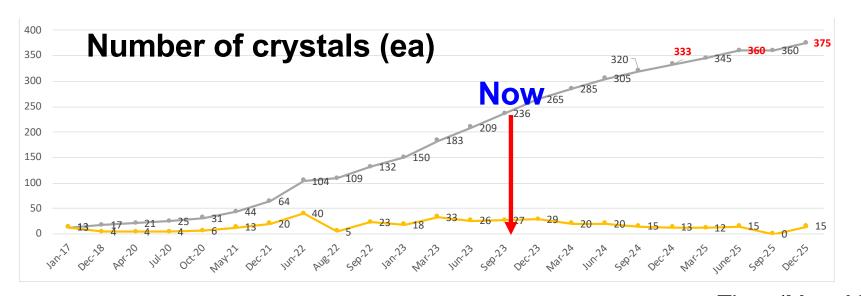
- □ CUP-grown LMO crystals with CUP-purified raw materials (¹¹⁰MoO₃ and Li₂CO₃ powders) give detection limit values in ICP-MS measurements.
- We have a great progress toward AMoRE-II crystals. Waiting for confirmation of the background levels at the low temperature (~10 mK) with cryogenic detectors.

AMoRE-II crystal production schedule



Total at CUP:

- □ 15 CMO, 108 (5 cm) & 77 (6 cm) LMO
- \square 200 ea, ~ 75.4 kg
 - Production both at NIIC and CUP



Time (Mon.-Yr)

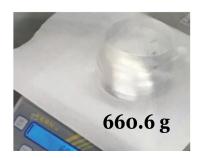
- ☐ By the end of 2024: 143 kg, 333 ea
- ☐ By mid 2025: 157 kg, 360 ea (Max.)

NaI(Tl) crystal growth for COSINE(-200)

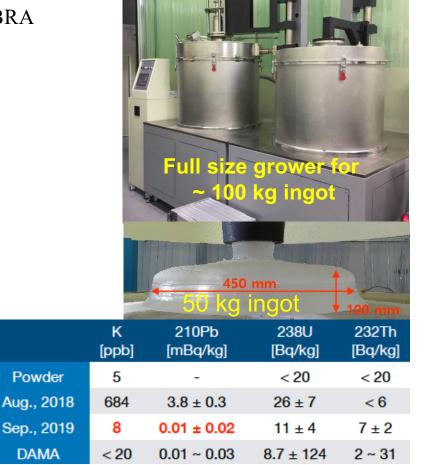


- ☐ Extremely pure crystal development
 - Background level less than that of DAMA/LIBRA
 (1 dru)
 - In-house development for the entire processes
 - Full-size NaI(Tl) crystal grower
- ☐ The current COSINE-100 shield is designed to accommodate sixteen 12.5 kg crystals (200 kg).









Summary



CUP has two major rare process experiments running in the Y2L & Yemilab (AMoRE DBD & COSINE DM). CUP has been running an ultra-low background radioassay facility in the Y2L and IBS HQ to screen raw materials for the detector components (i.e., crystals) since 2014. Background levels of AMoRE-Pilot CMO crystals measured both in RT and LT are consistent with each other. Background levels of nine FOMOS CMO crystals measured in RT confirmed that they meet the requirement of 10⁻³ ckky in AMoRE-I. AMoRE-II with 200 kg of crystals requires an even lower background level of 10⁻⁴ ckky. Purification and growth of molybdate crystals at the CUP started in 2016, are in the massproduction stage for AMoRE-II (LMO). COSINE-100 has 106 kg of NaI(Tl) crystals with similar or lower background levels in ⁴⁰K/U/Th than those of the DAMA except ²¹⁰Pb. It has 2-3 more background than that of the DAMA in low energy. □ COSINE's next phase is going to use ultra-pure NaI(Tl) crystals with ~200 kg mass to confirm/dispute the DAMA's annual modulation in a model-independent way. Purification and crystal growth of NaI(Tl) started at the CUP in 2017 and are in good progress.