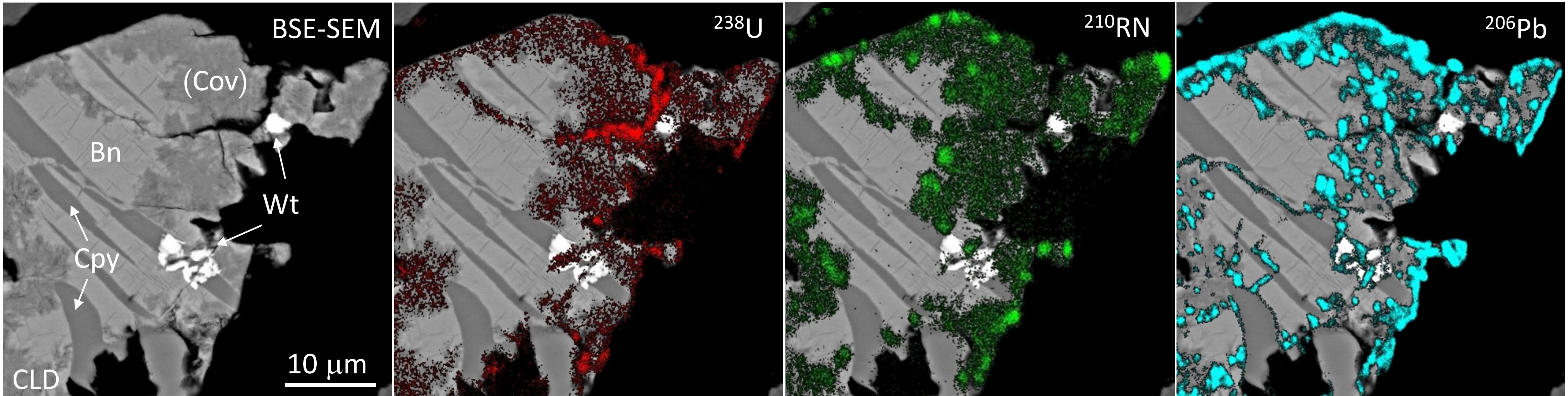
Mineralogical hosts of radionuclides in Olympic Dam copper concentrates

Kathy Ehrig (Superintendent Geometallurgy)

AusIMM Adelaide Branch Technical Lunch - 20 February 2020



Acknowledgements

Disclaimer: The views/opinions expressed are solely the presenter's.

BHP Olympic Dam

- +300 geoscientists, "metallurgists" and radiation physicists who have worked at Olympic Dam since discovery in 1975.

University of Tasmania

- Dima Kamenetsky
- Jocelyn McPhie
- Maya Kamenetsky
- PhDs Completed: Olga Apukhtina, Qiuyue Huang, Alex Cherry, Matthew Ferguson, Nathan Chapman
- CODES Laser Ablation Facilities

ANSTO (Australian Nuclear Science Technology Organisation)

University of Melbourne- Roland Maas

CSIRO Land and Water, Adelaide- Mark Raven

Geological Survey South Australia- Alan Mauger

Australian Government

Australian Research Council

SOUTH AUSTRALIA

Government of South Australia

Department for Energy and Mining

University of Adelaide

- Nigel Cook
- Cristiana Ciobanu
- PhDs Completed: Edeltraud Macmillan, Alkis Kontonikas-Charos, Sasha Krneta, Danielle Schmandt, William Keyser, Mark Rollog, Liam Courtney-Davies, Marija Dmitrijeva
- PhD Students:, Max Verdugo-Ihl
- Adelaide Microscopy

South Australian Mining and Petroleum Services Centre of Excellence (Department of State Development)

- Trace elements in iron oxides project (FOX project)
- Copper Uranium Hub project (joint ARC project IH130200033)

ARC Linkage LP130100438 (UTas) – Kamenetsky & McPhie

"The supergiant Olympic Dam uranium-copper-gold rare earth element ore deposit: towards a new genetic model"

ARC Linkage LP160101497 (Flinders University) – Allan Pring

"Reverse engineering Nature: metal extraction through mineral replacement"

Current State

Flotation concentrates contain ~1500-3000 ppm U_3O_8 and associated natural decay products in secular equilibrium.
After concentrate leach, U_3O_8 > 100 ppm with decay products, BUT are no longer in secular equilibrium.
OD copper sulfide concentrates (pre- and post-leach) are classified as radioactive.

Metallurgical Studies

Extensive metallurgical test work conducted to produce Cu-sulfide concentrates which can be processed off-site.
Bottom line: lowered the radionuclide activity levels, but not low enough.

WHY?

Radionuclide Mineralogy

Simple answer: Uranium minerals don't host all of the ^{238}U decay chain radionuclides (RNs).
In the OD deposit, RNs are partially to completely decoupled from U at the macro- to nano-scale.
Sulfuric acid leaching then further decouples U from its RNs…

We haven't solved the problem, but at least we now know why.

Today’s Presentation

Part 1:

Uranium and the uranium decay series

A few definitions - NORM, TENORM, parts per quadrillion (1 in 10^{15})

Part 2:

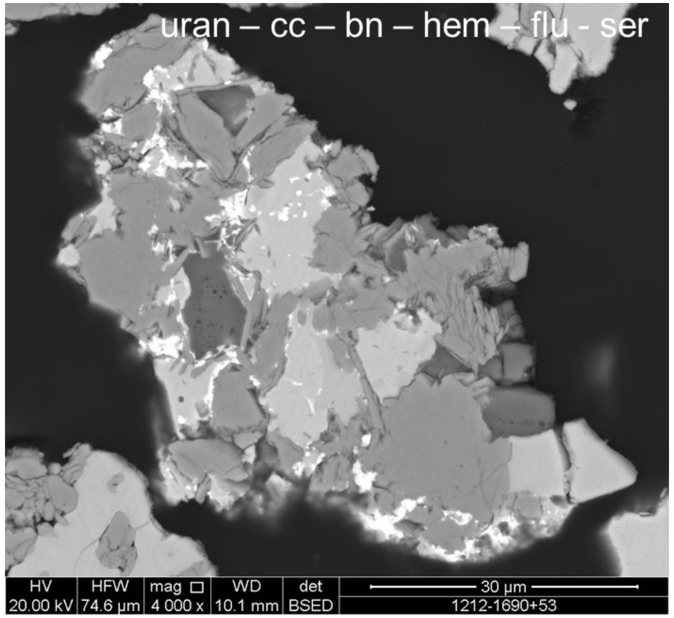
Uranium and its natural decay products – where they occur

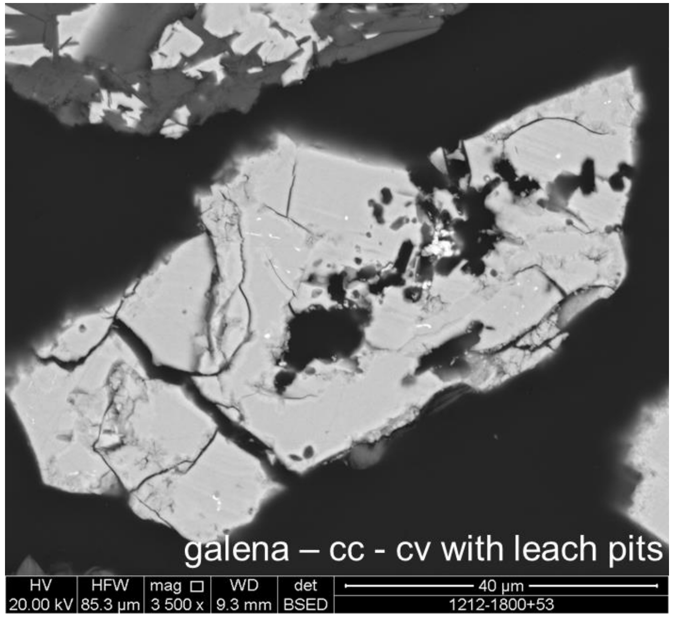
How does uranium get into our copper concentrates?

Concentrate leach – removes most of the U, but not much of the RNs

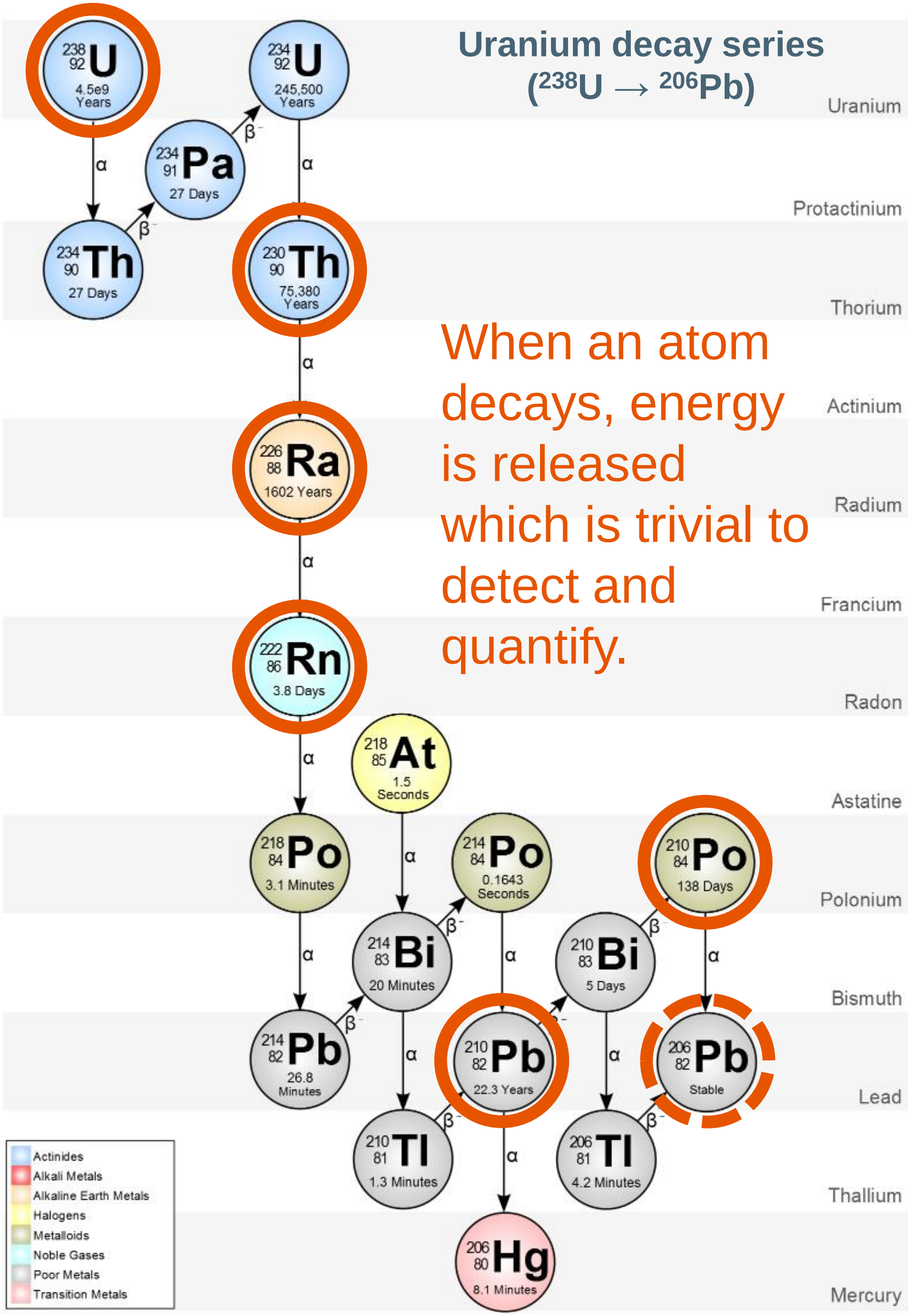
***“Metal has no value until it is in a saleable product”* (Munro, 2017)**

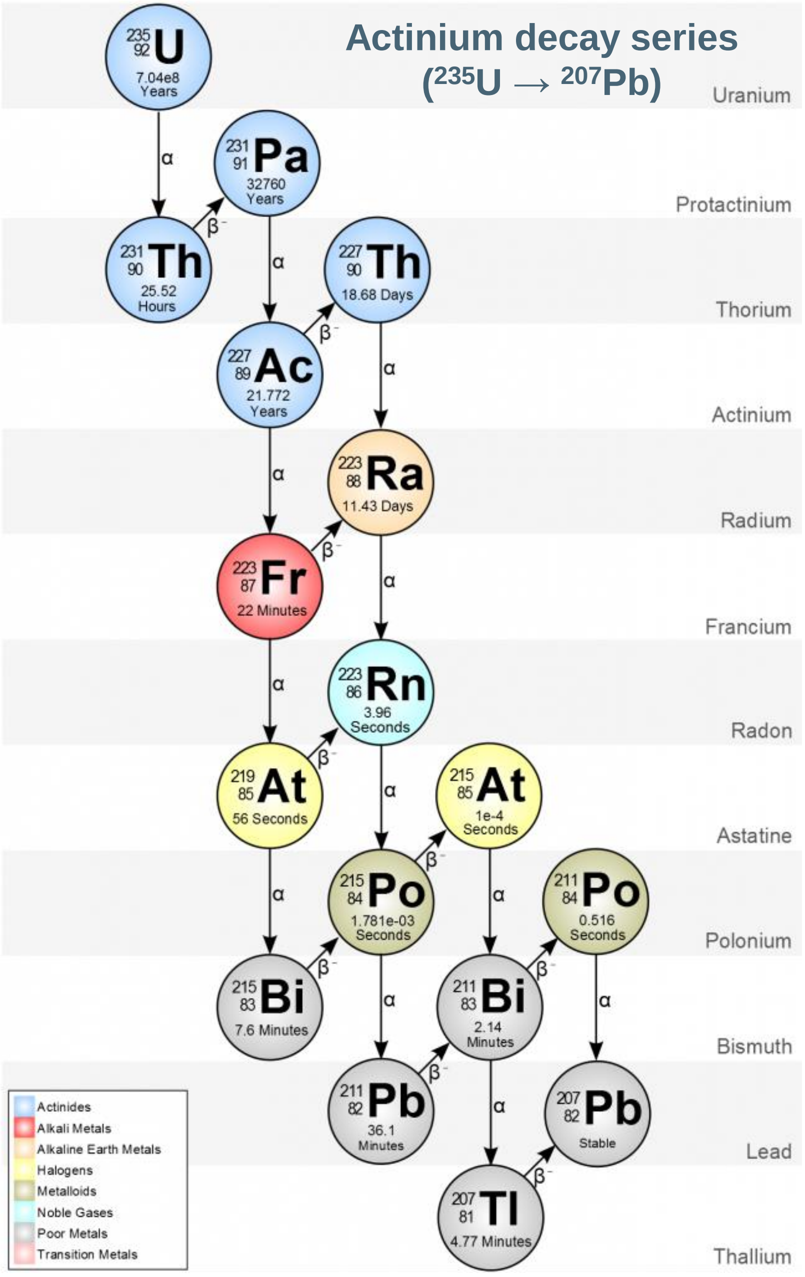
And finally, Why we don’t mine copper separate from uranium!

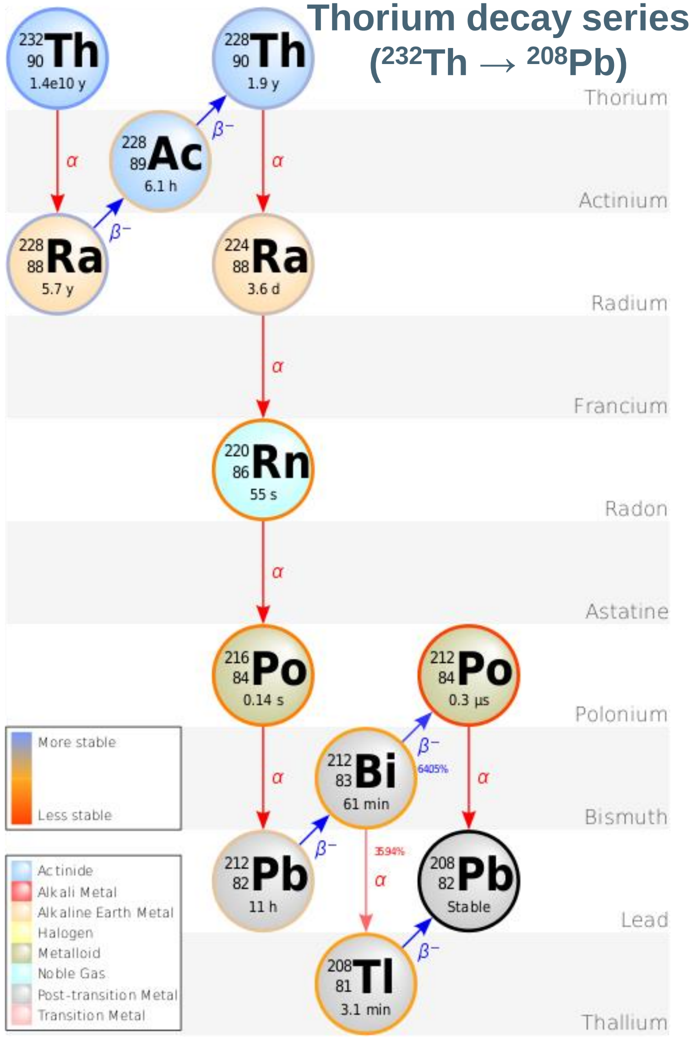




When an atom decays, energy is released which is trivial to detect and quantify.







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^{210}RN (^{210}Pb + ^{210}Po) concentrations? …not a lot…

^{210}Pb:
0.000000356 ppm
0.000356 ppb
0.356 ppt
(per 80.7ppm U)

^{210}Po:
0.00000000604 ppm
0.00000604 ppb
0.00604 ppt
(per 80.7ppm U)

NORM
TENORM

TABLE 1
Concentrations of Radionuclides in the Natural Uranium and Thorium Decay Chains for Uranium Ore containing 1 Bq/g of U-238[1] and Thorium Ore containing 1 Bq/g of Th-232 in Secular Equilibrium

U-238 Decay Chain	
Nuclide	Concentration (ppm)
U-238	8.07E+01
Th-234	1.17E-09
Pa-234m	3.95E-14
Pa-234	1.77E-14
U-234	4.46E-03
Th-230	1.34E-03
Ra-226	2.75E-05
Rn-222	1.76E-10
Po-218	9.60E-14
Pb-214	8.28E-13
Bi-214	6.15E-13
Po-214	8.43E-20
Pb-210	3.56E-07
Bi-210	2.19E-10
Po-210	6.04E-09

U-235 Decay Chain	
Nuclide	Concentration (ppm)
U-235	5.85E-01
Th-231	2.36E-12
Pa-231	2.63E-05
Ac-227	1.73E-08
Th-227	4.02E-11
Fr-223	4.47E-16
Ra-223	2.45E-11
Rn-219	9.63E-17
Po-215	4.25E-20
Pb-211	5.07E-14
Bi-211	2.99E-15
Po-211	3.67E-20
Tl-207	6.56E-15

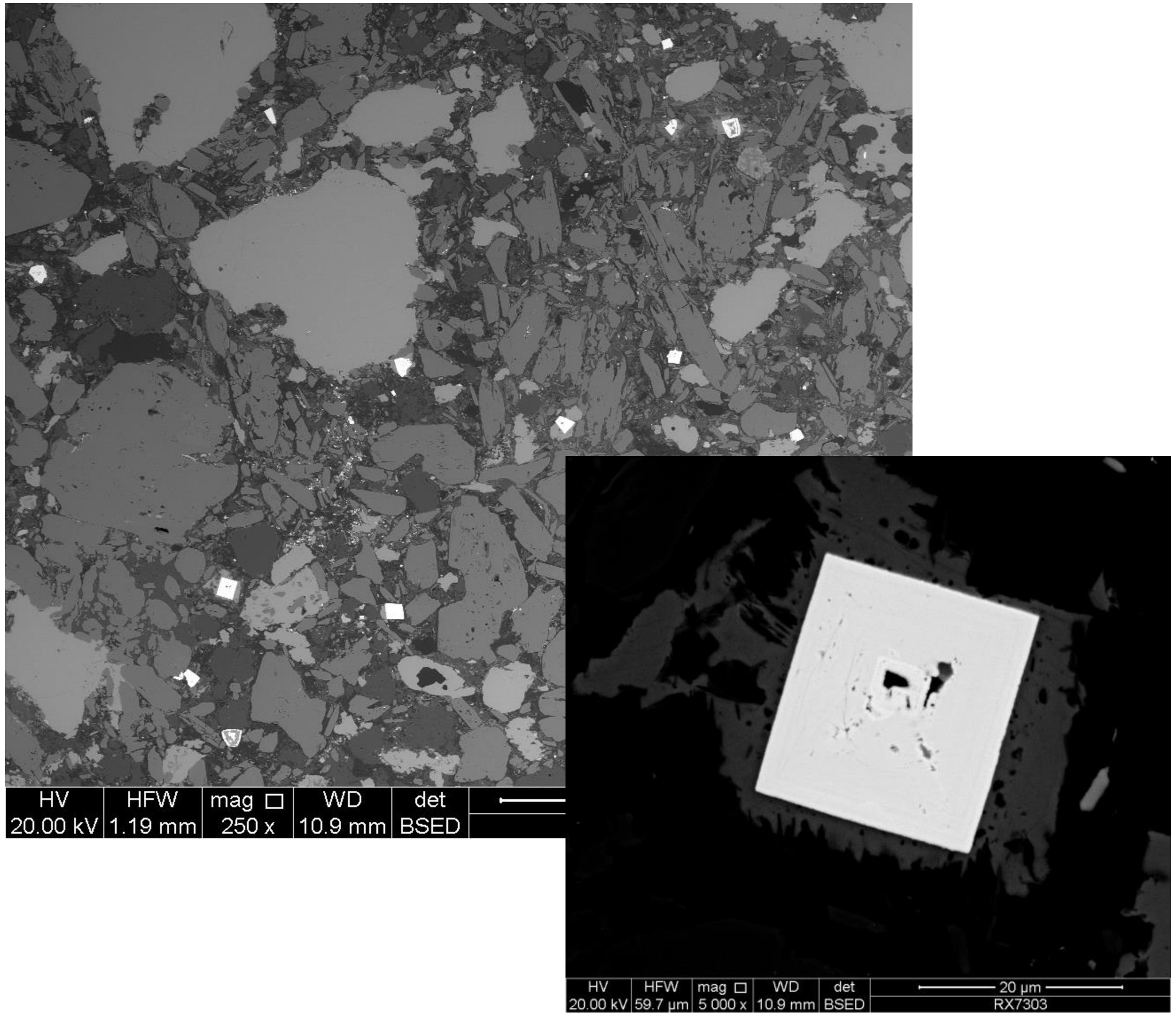
Th-232 Decay Chain	
Nuclide	Concentration (ppm)
Th-232	2.48E+02
Ra-228	9.96E-08
Ac-228	1.21E-11
Th-228	3.31E-08
Ra-224	1.70E-10
Rn-220	2.94E-14
Po-216	7.80E-17
Pb-212	1.95E-11
Bi-212	1.85E-12
Po-212	9.97E-23
Tl-208	3.31E-14

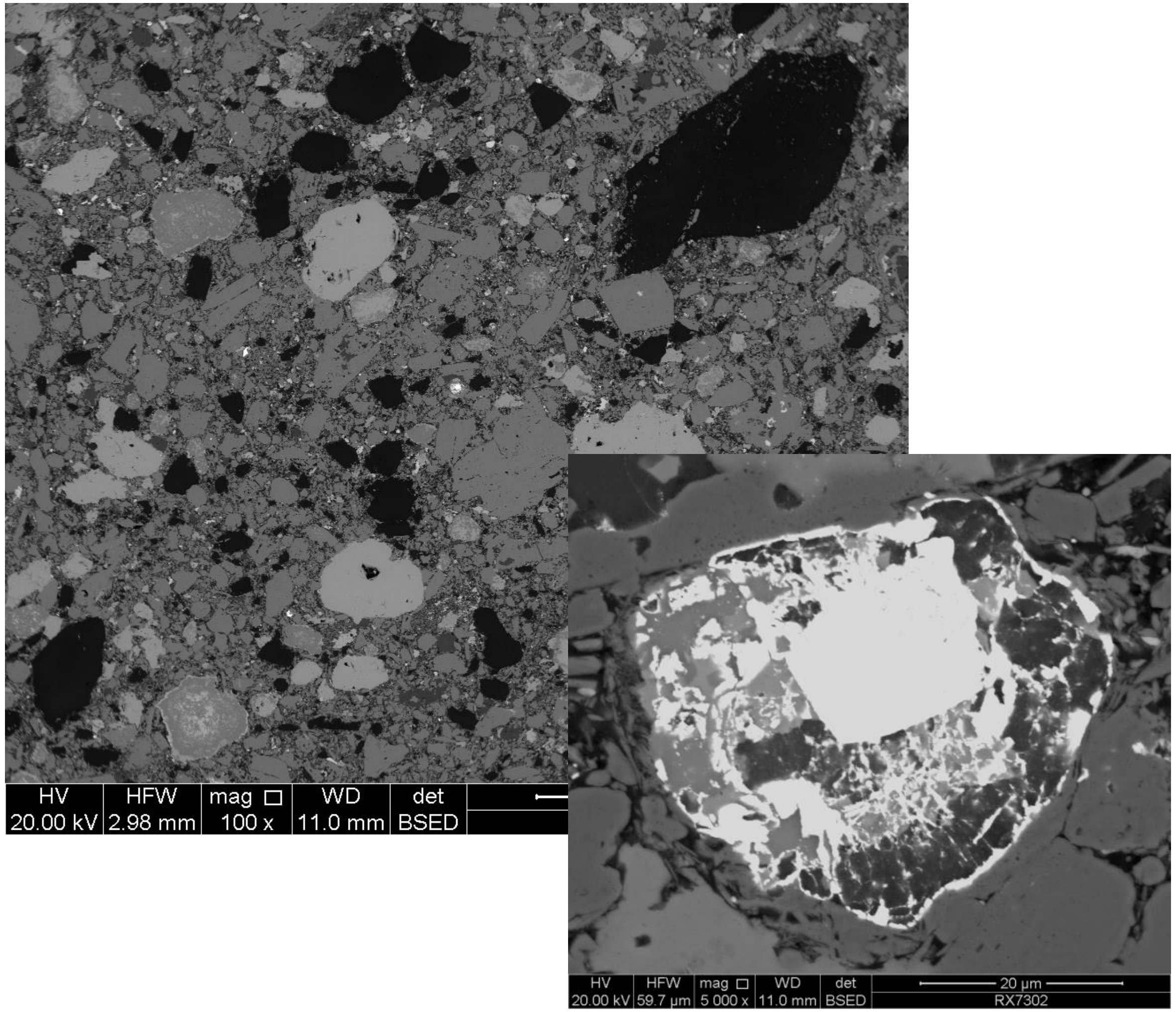
[1] An ore containing 1 Bq/g of U-238 contains 1.03 Bq/g of U-234 and 0.0046 Bq/g of U-235.

Very difficult to measure via chemical methods when concentrations < 1 ppb. Impossible to measure at the scale of an individual mineral, …until recently.

In situ Olympic Dam U-mineralogy provides the clues

It took a long time to fully comprehend and then understand the implications





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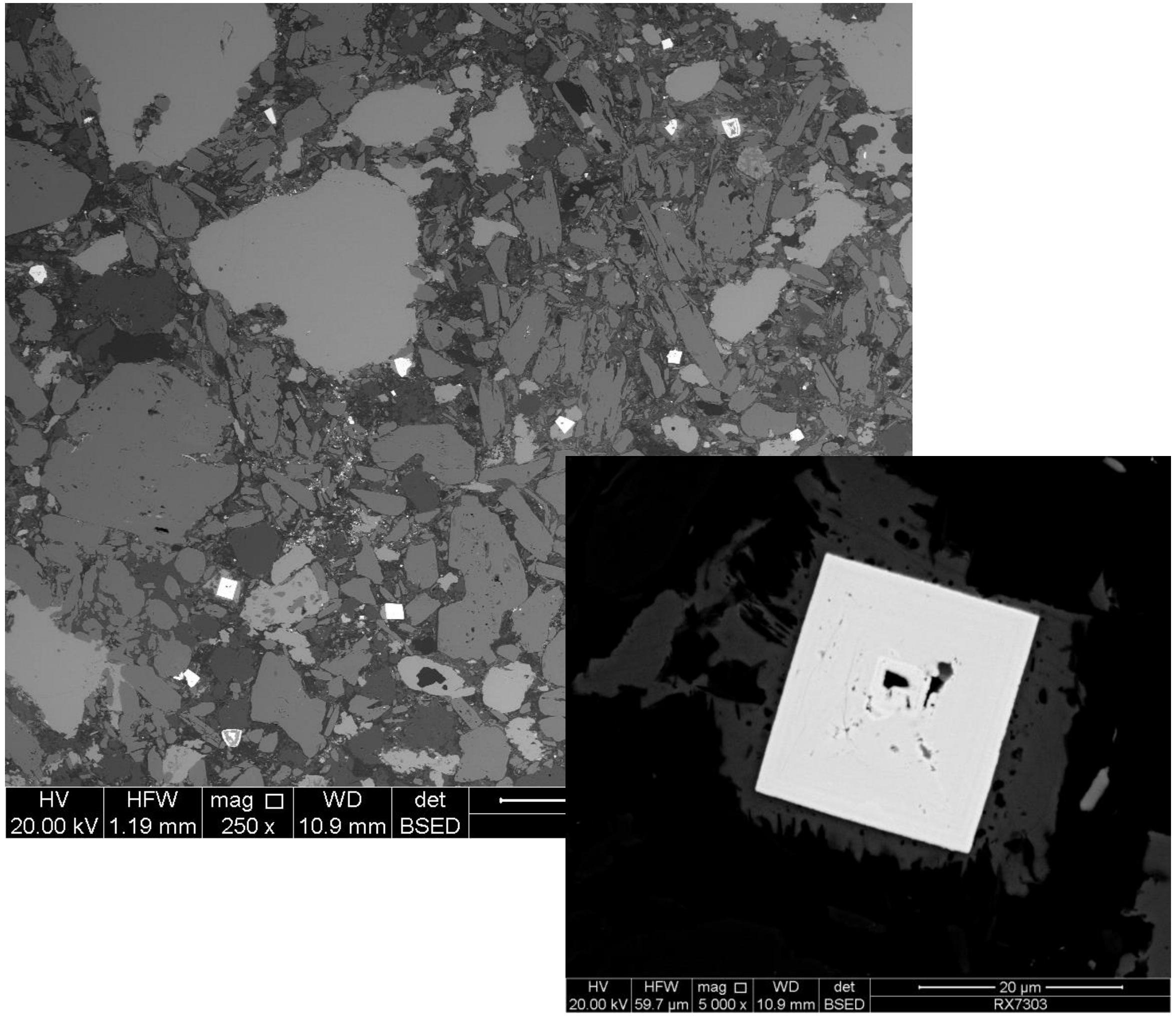

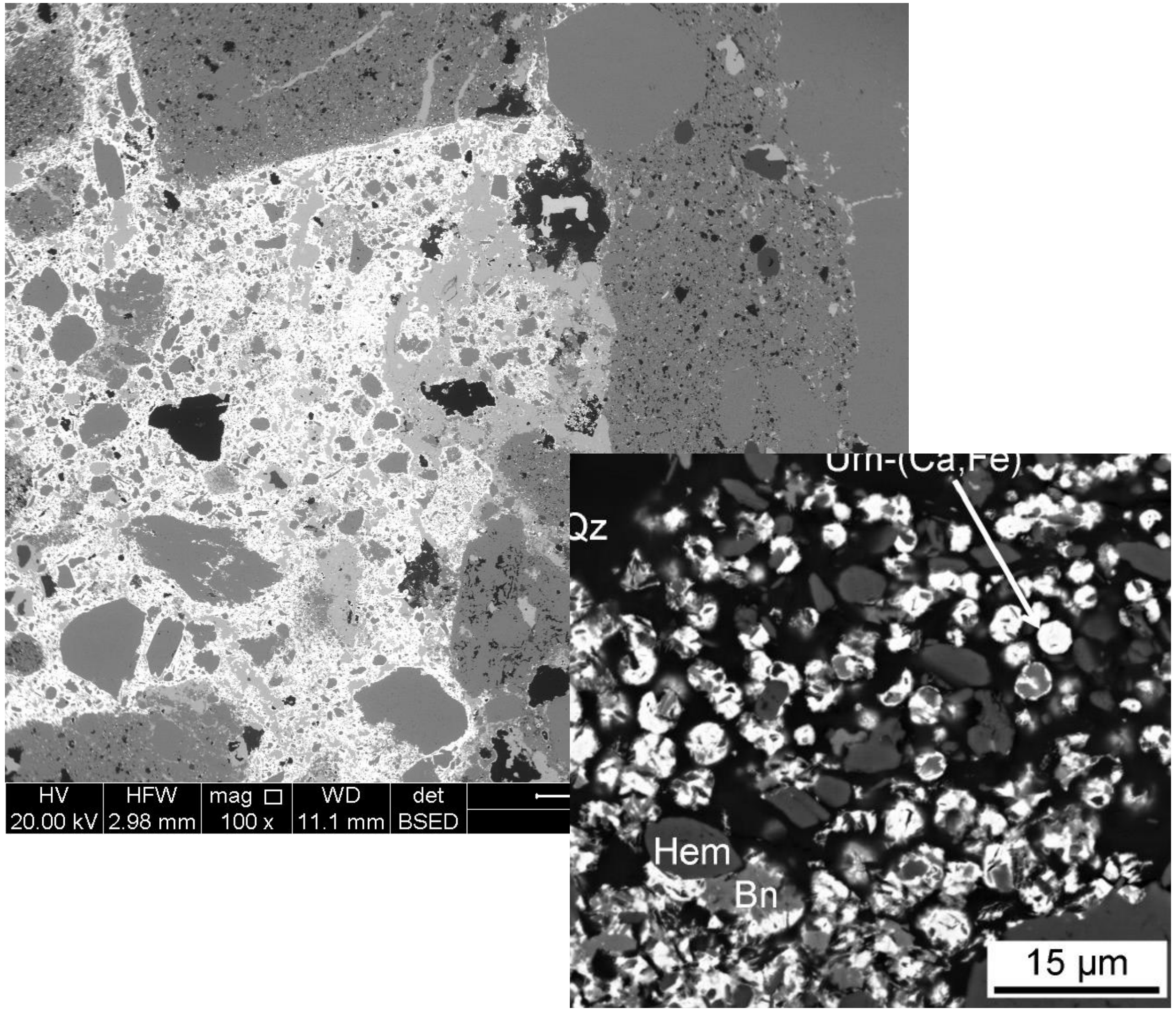

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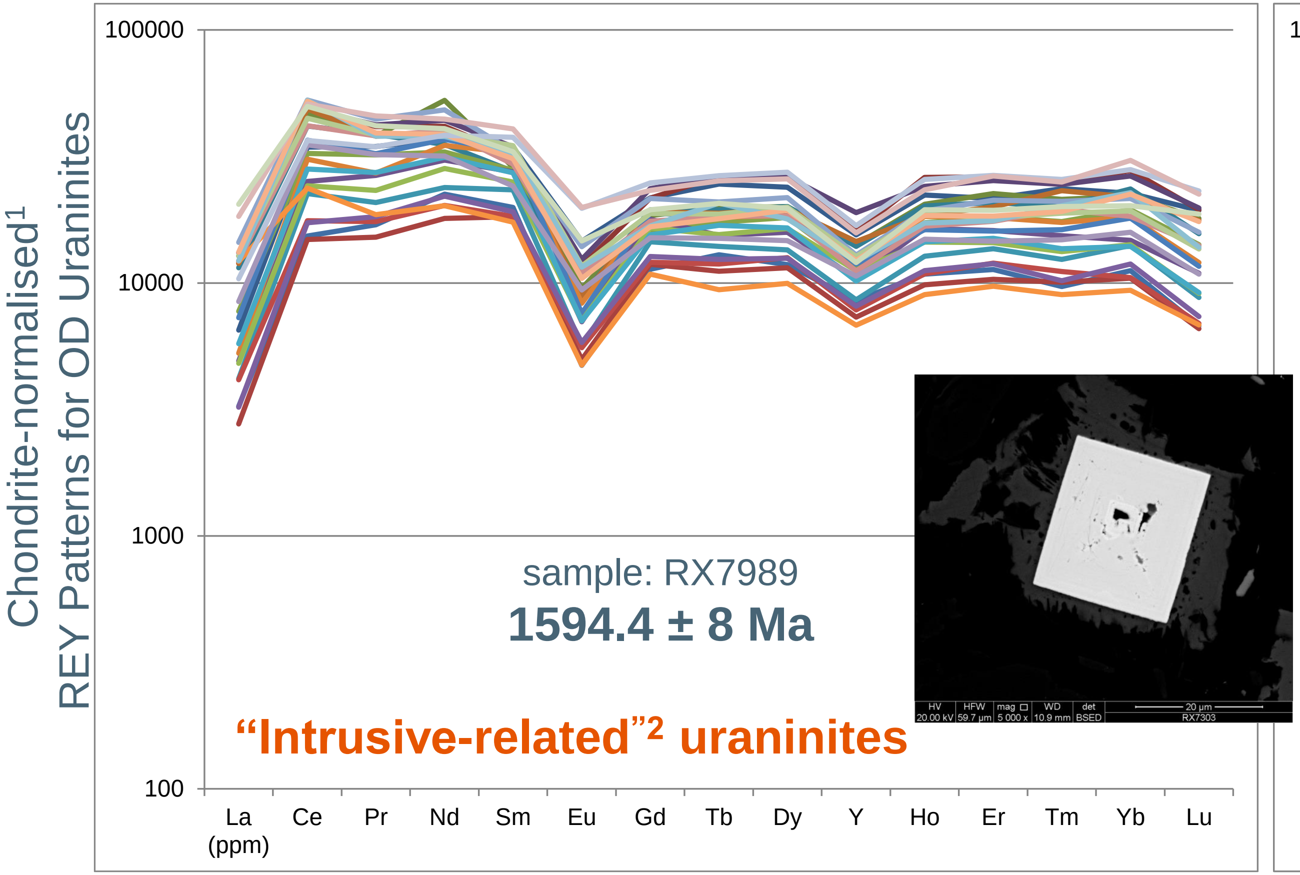
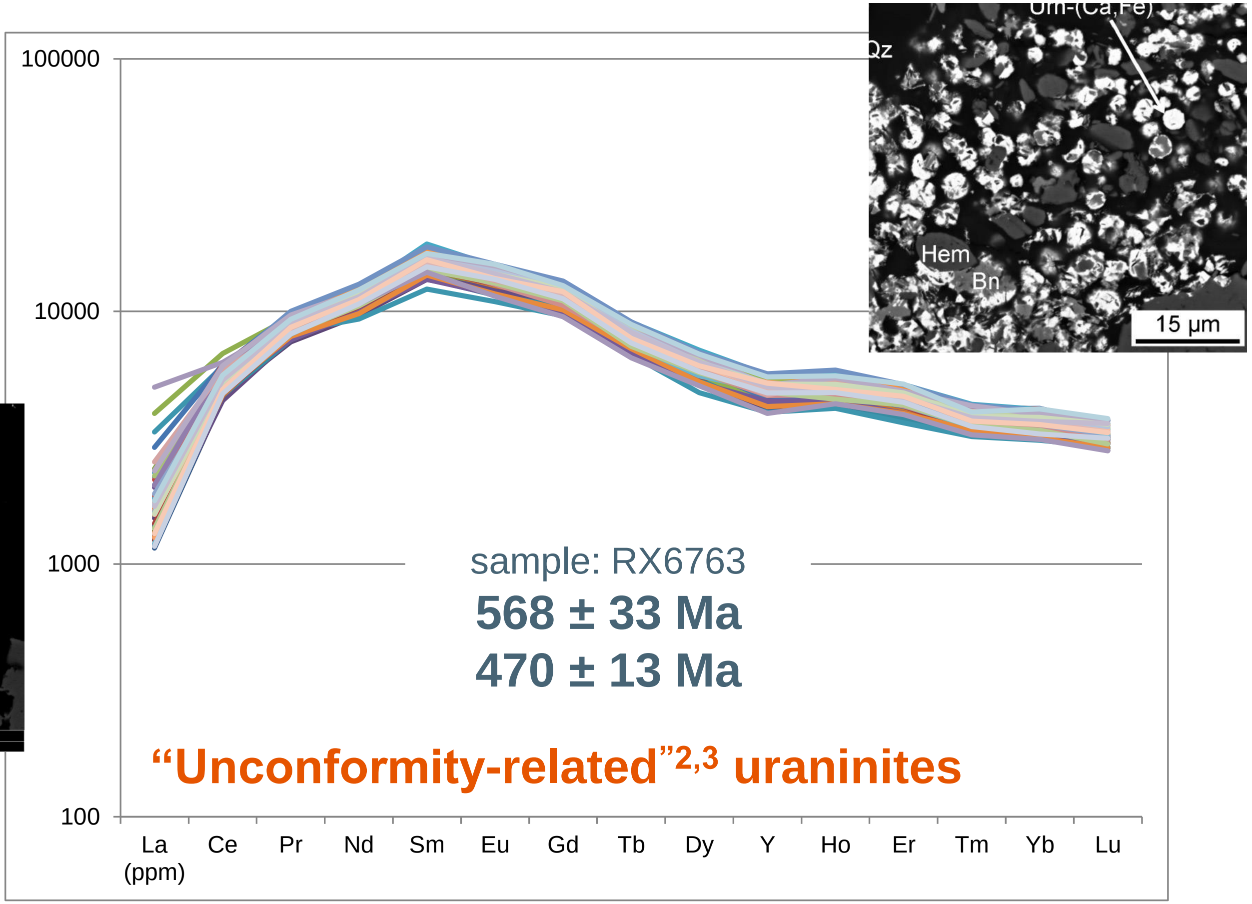
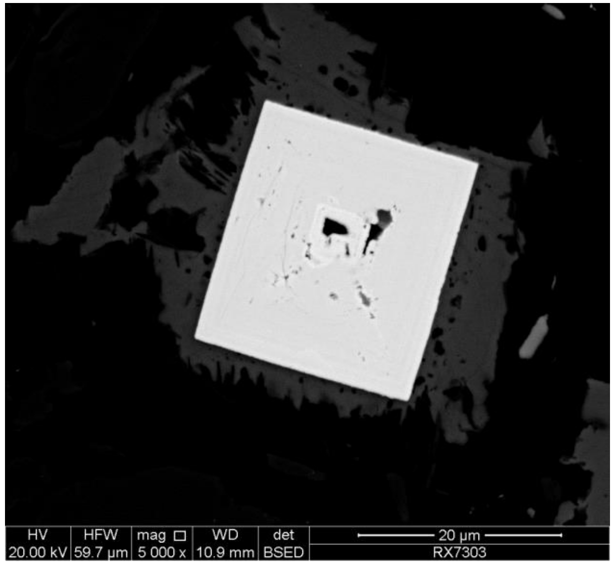


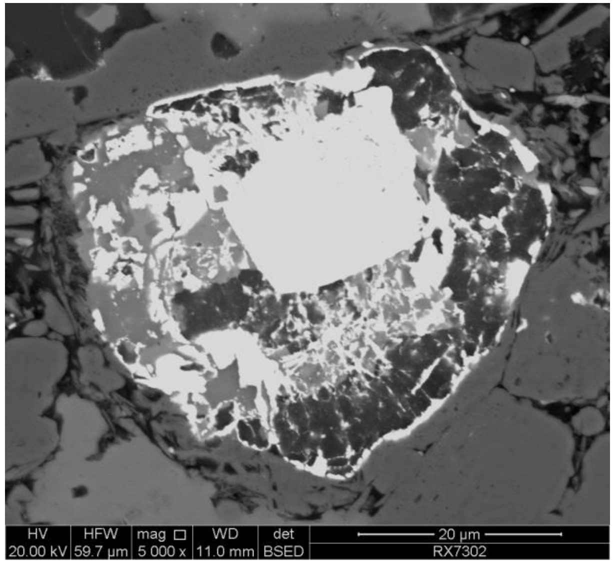


[1] chondrite values from McDonough and Sun (1995)

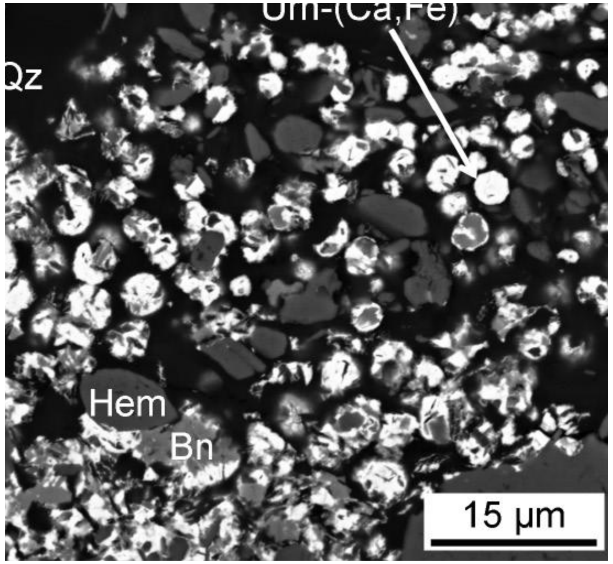
[2] Meradier et al. (2011), [3] Fremmel et al. (2014)

+1 billion yrs in the making

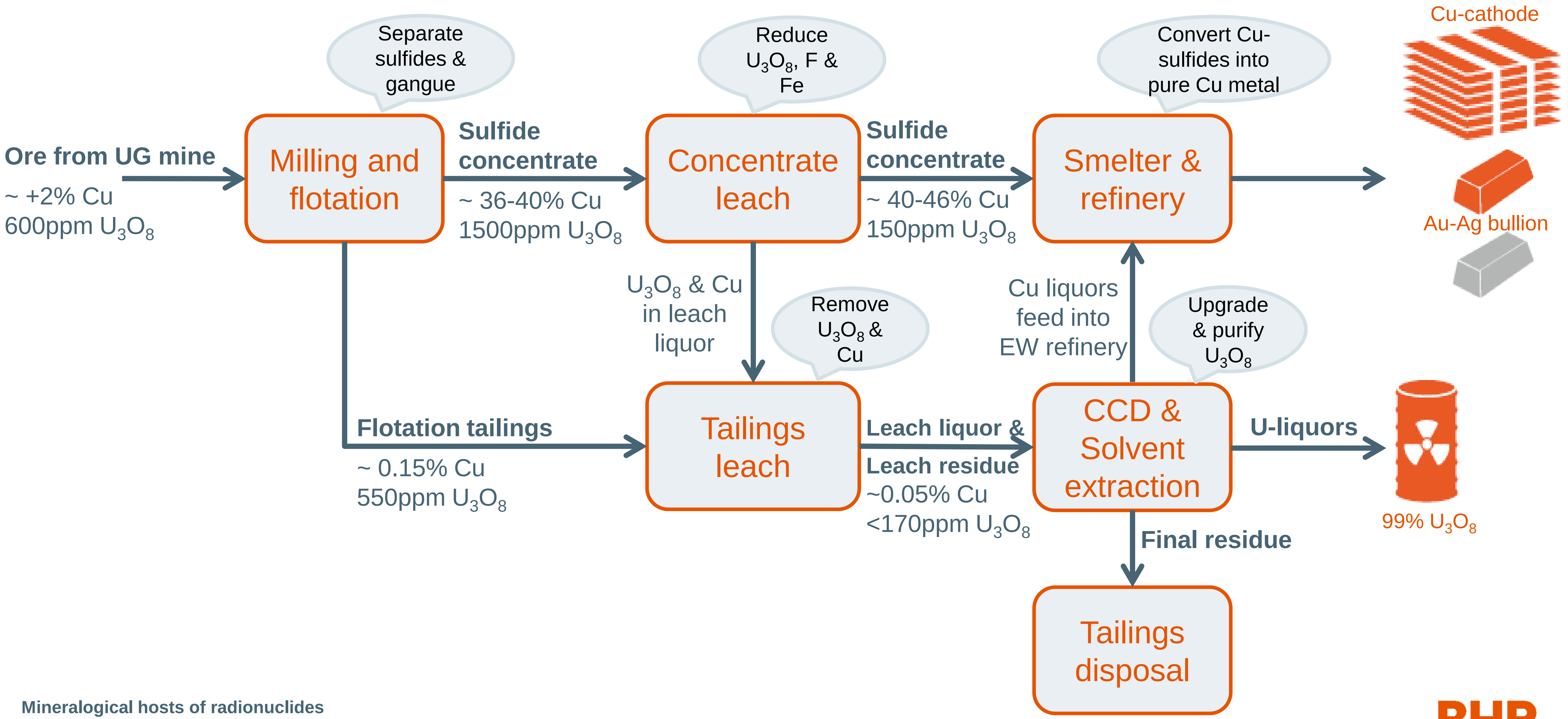




1. What is the fate of the RNs when U-minerals dissolve?
   – decouple from U at the mineral scale?
   – precipitate immediately?
   – migrate a short distance and then reprecipitate?
   – are some transported along with U^{+6}?
2. Do other minerals carry RNs which have become decoupled from U over 1.6 Ga?
3. Which minerals are the RNs likely to reprecipitate onto?
4. Relative solubility of RNs under acidic conditions?
5. What can be learned about the RNs during processing?



Very Simplified Olympic Dam process flow



OD radionuclide balance*

	Flotation feed (Bq/g)	Flotation tails (Bq/g)	Tails leach discharge (Bq/g)	CCD UF (Bq/g)	Unleached Cu-conc (Bq/g)	Leached Cu-conc (Bq/g)
U	600 ppm	533 ppm	160 ppm	105 ppm	2100 ppm	145 ppm
Th	<50 ppm	70 ppm	<50 ppm	<50 ppm	<50 ppm	<50 ppm
^{238}U	7.4	6.6	2.0	1.3	26	1.8
^{230}Th	7.5	7.5	4.4	4.5	30	2.5
^{226}Ra	7.0	6.8	6.2	5.8	24	27.5
^{210}Pb	6.6	7.2	5.7 ?	5.3	30	26 ?
^{210}Po	7.6	6.3	6.8	6.1	30	58
	secular equilibrium	secular equilibrium	non-secular equilibrium	non-secular equilibrium	secular equilibrium	non-secular equilibrium

What does the mineralogy show?
Beyond the limits of technology until ~ 5 years ago.

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Radionuclide balance in the processing of copper and uranium at Olympic Dam: ANSTO (2008), also reported in the 2009 EIS

WORLD FIRST (right here in Australia on OD samples): nanoSIMS used to map RN distribution at the mineral scale

nanoSIMS – University of Western Australia, Perth

- seven isotopes at one time
- to 40nm lateral resolution
- excellent mass resolution
- O^- or Cs^+ ion source
- to ppb detection limits

- only ~40 worldwide, 2 at UWA
- isobaric mass interferences
- not currently quantifiable (minerals)

ARC Research Hub for Australian Copper-Uranium

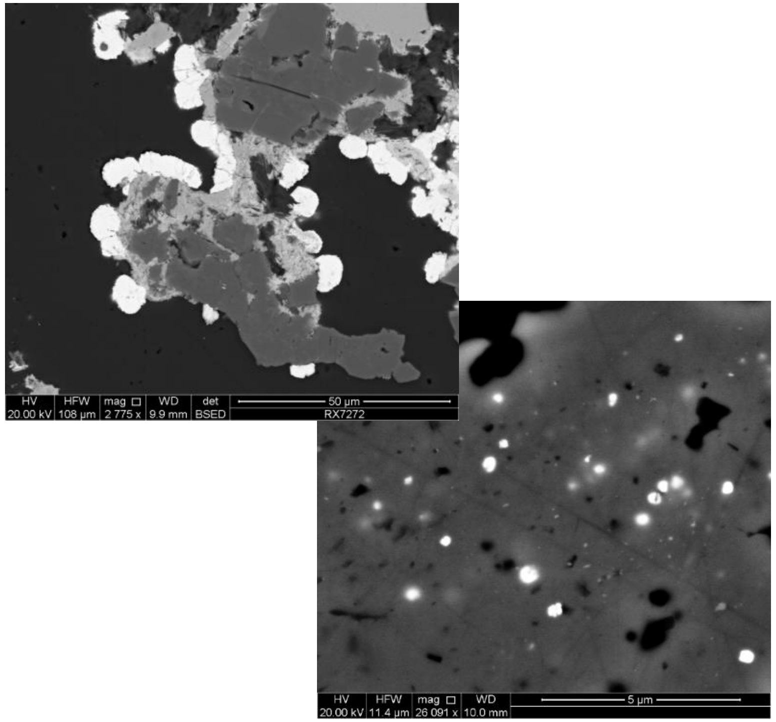
Mark Rollog was a PhD student (now completed) within the Hub. He identified the possibility of using nanoSIMS to map the distribution of radionuclides at the mineral scale. nanoSIMS was never used to map RNs prior to this project. He also produced the RN maps presented here. Once the method was established, other members of the Hub team started using nanoSIMS. **All of this work has been published.**

Mineral hosts of uranium and the radionuclides

NORM material (i.e. ores pre-sulfuric acid leach)

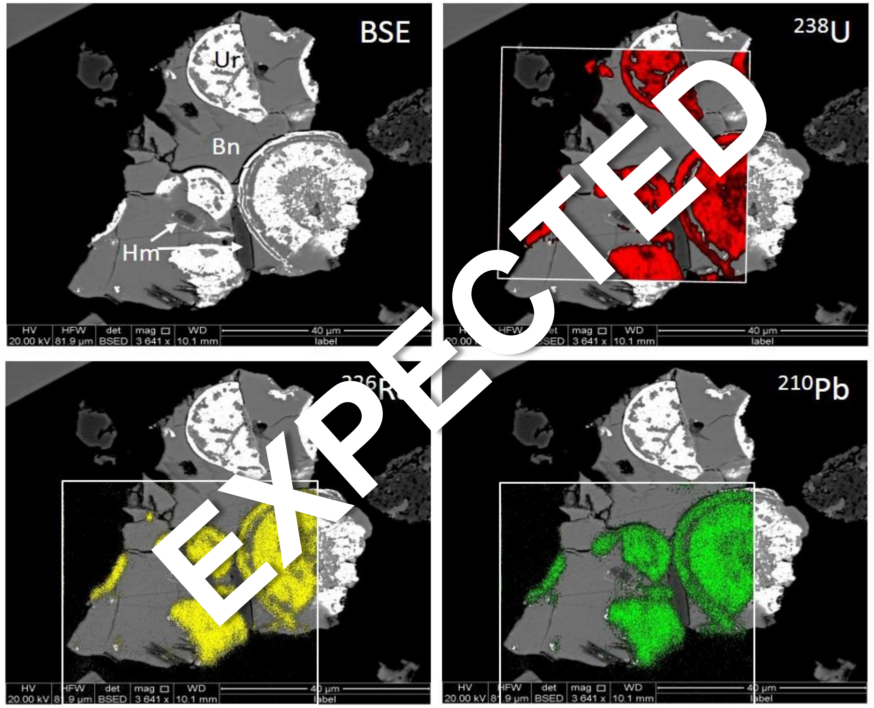
Mineral hosts of uranium

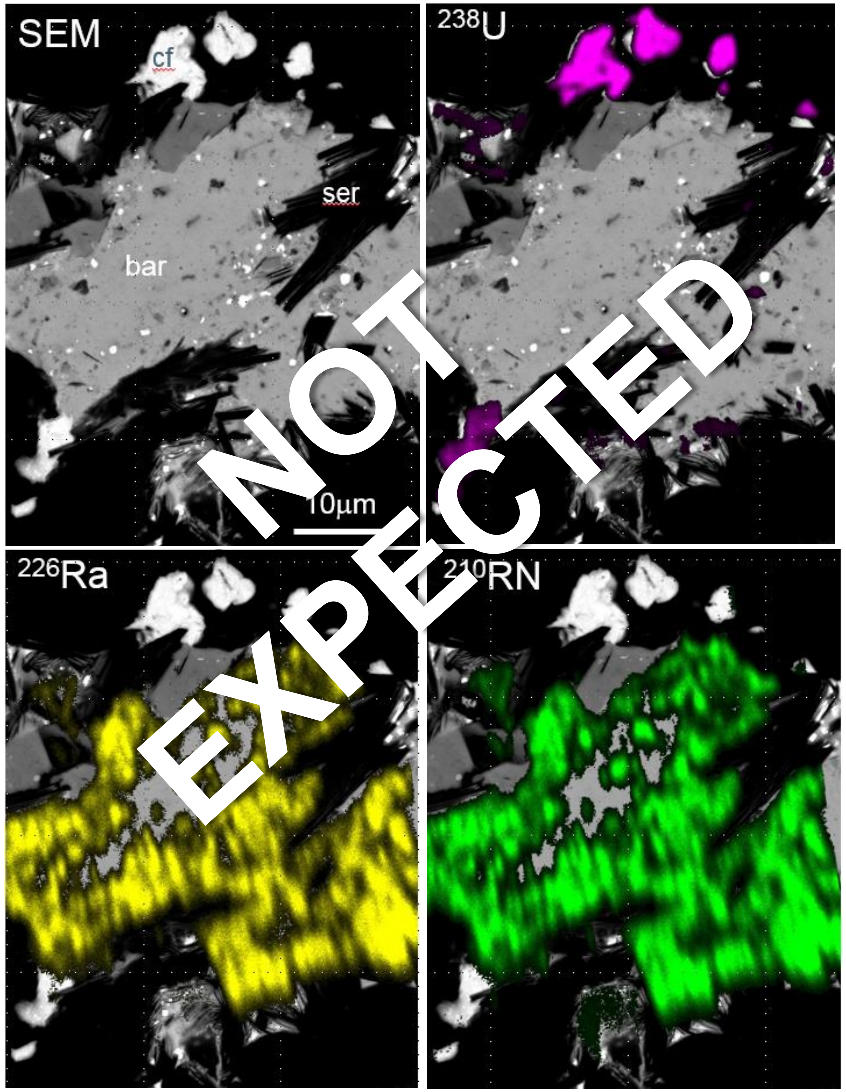
- **uraninite, coffinite, brannerite**
- **hematite**
- sulfide minerals
- REE minerals, sericite, chlorite



Mineral hosts of the radionuclides

- **uraninite, coffinite, brannerite**
- **hematite, barite,** REE minerals
- sulfide minerals (along grain boundaries)
- APS minerals, molybdenite, fluorite





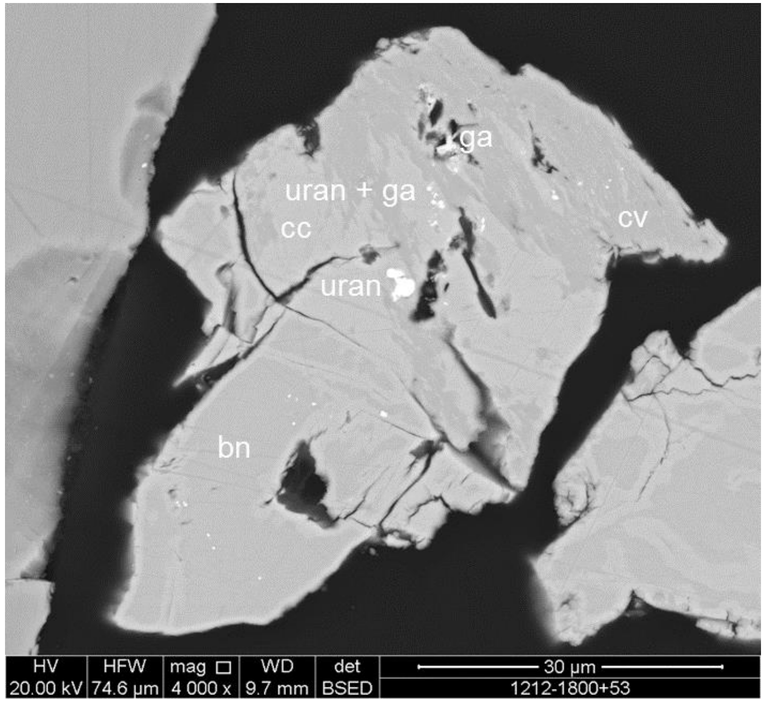
Technically not possible until ~ 5 years ago

Mineral hosts of uranium and the radionuclides

TENORM material (i.e. ores post-sulfuric acid leach)

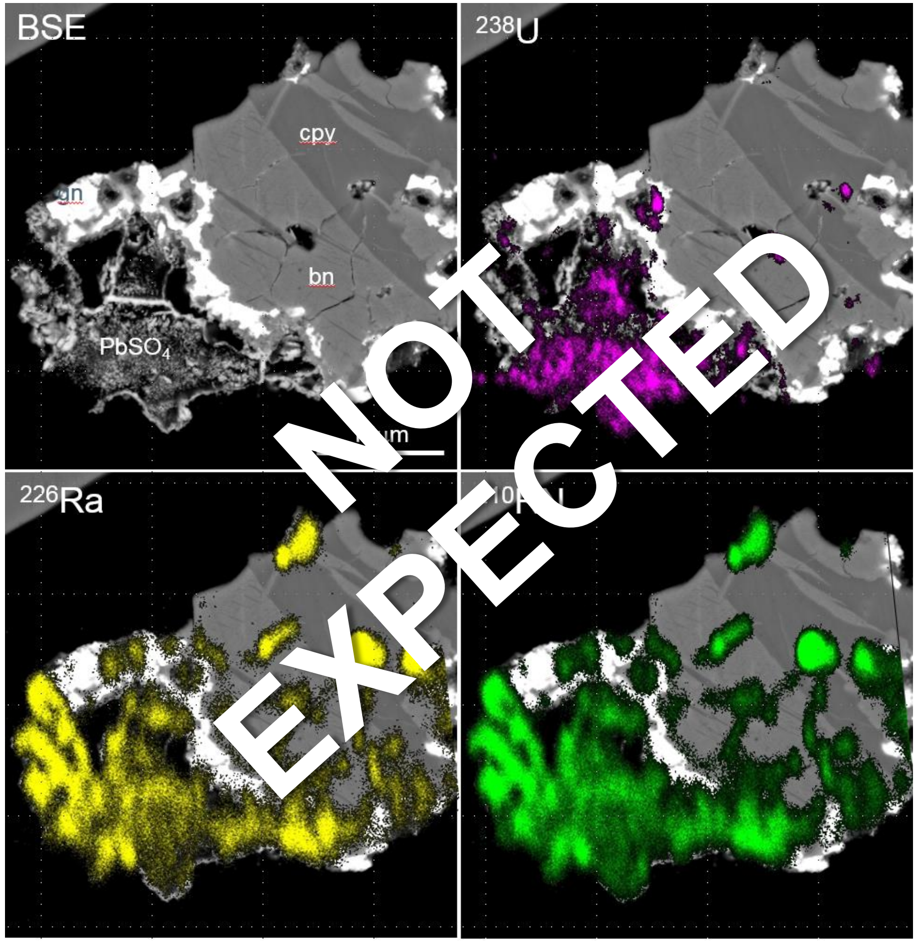
Mineral hosts of uranium

- **uraninite, coffinite, brannerite**
- **hematite**
- sulfide minerals
- REE minerals, sericite, chlorite



Mineral hosts of the radionuclides

- **uraninite, coffinite, brannerite**
- **hematite, barite**, REE minerals
- sulfide minerals
- **APS minerals, molybdenite, fluorite**
- **covellite, sulfates**
- **grain edges, pores, cracks, etc**



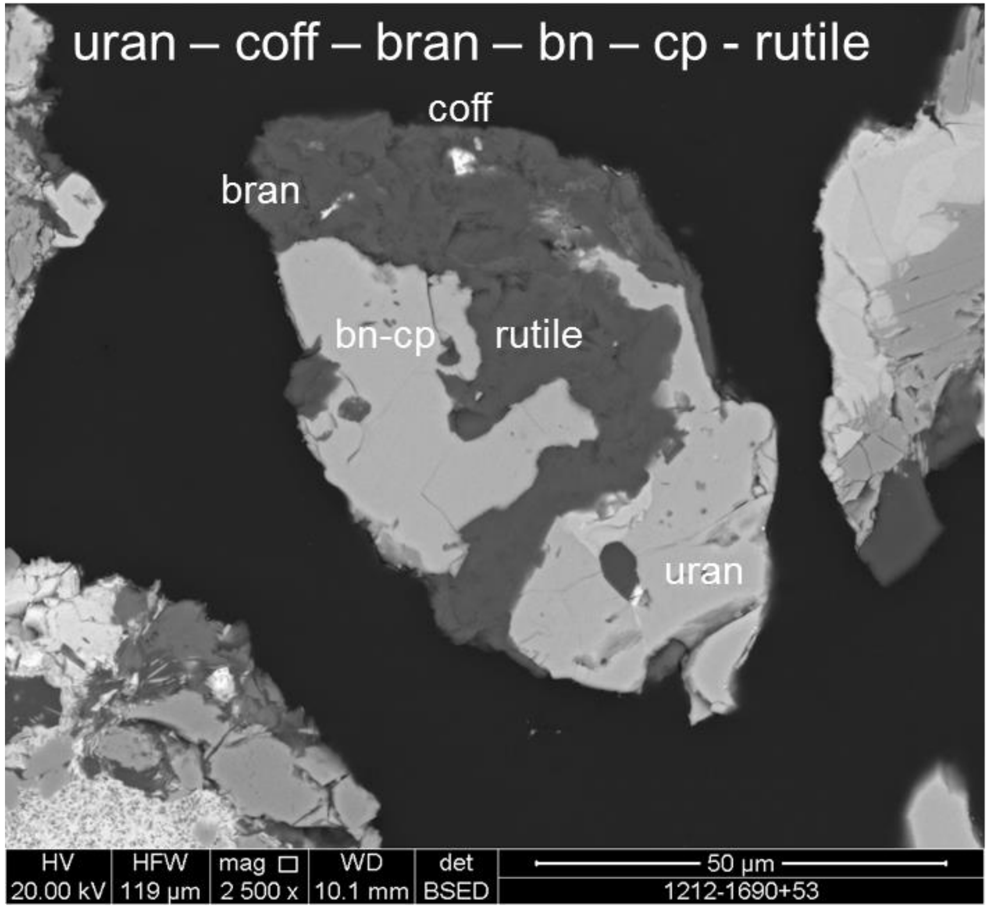
Technically not possible until ~ 5 years ago

How does U (and RNs) get into Cu concentrates at OD?

Copper sulfide flotation reagents are not selective for uranium minerals. However, uranium is recovered in copper concentrates.

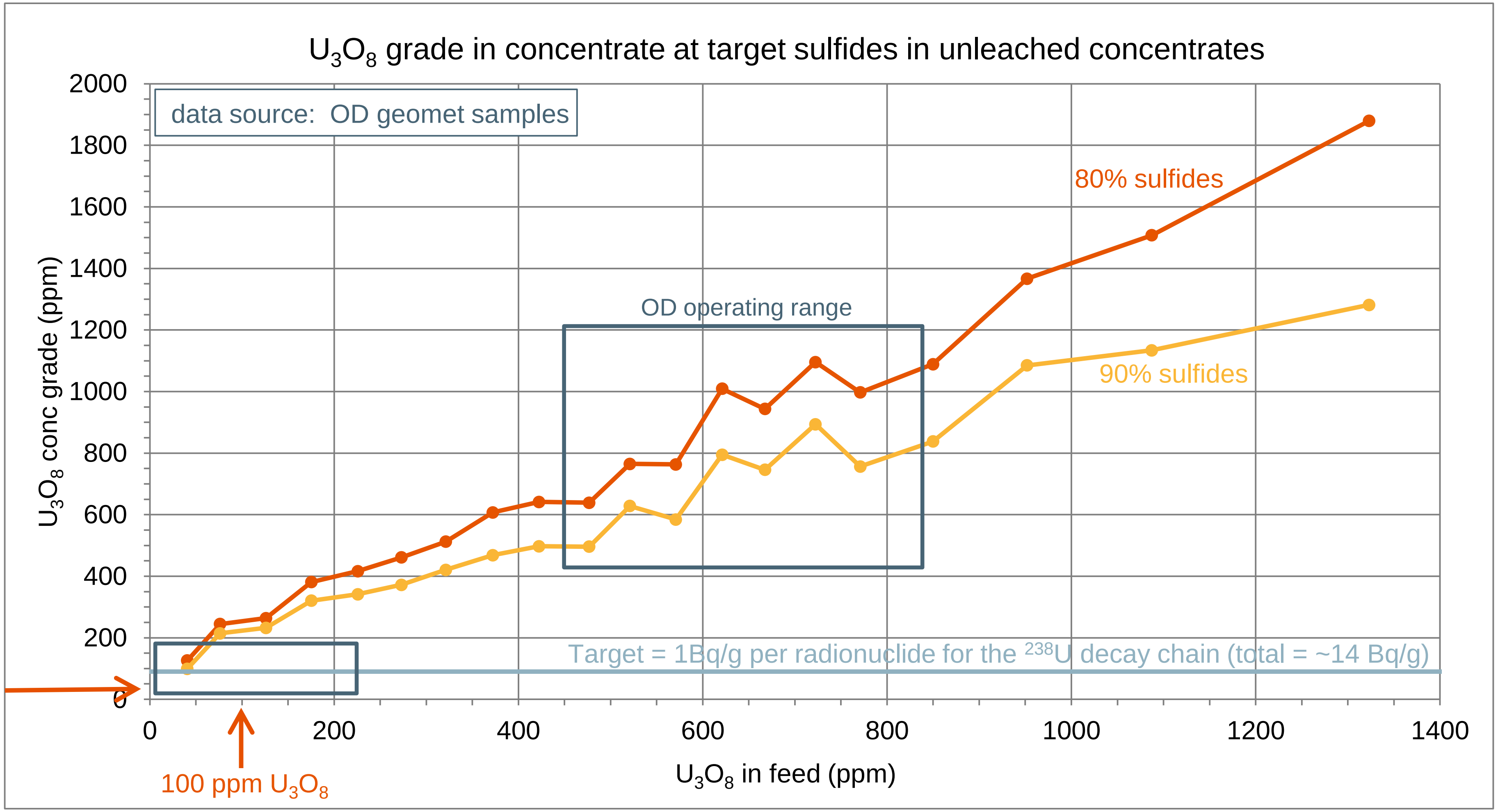
- sulfide-uranium mineral composites
- sulfide-gangue-uranium mineral composites
- entrained gangue-uranium mineral composites
- entrained fully liberated uranium minerals
- entrained hematite containing sub-μm sized or lattice substitution U

Uranium recovery (or upgrade) to flotation concentrates is a function of the U-grade in the feed. As the U-grade decreases, so does the U-recovery to concentrates.



Upgrade of uranium into copper concentrate

Max U3O8 content in mill feed to produce a ‘non-radioactive’ concentrate?

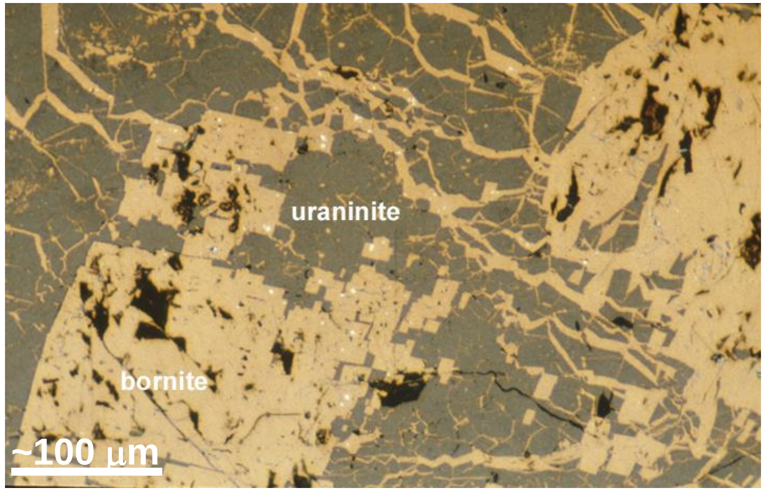


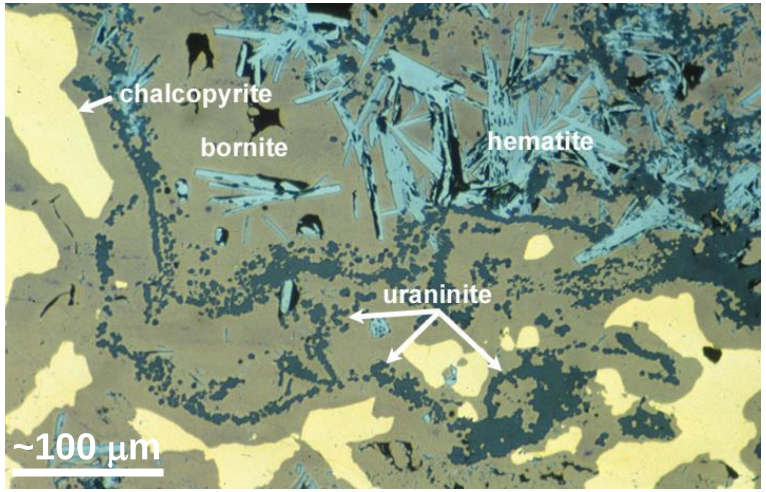
most other Cu-concentrates smelted = <10 ppm U_3O_8

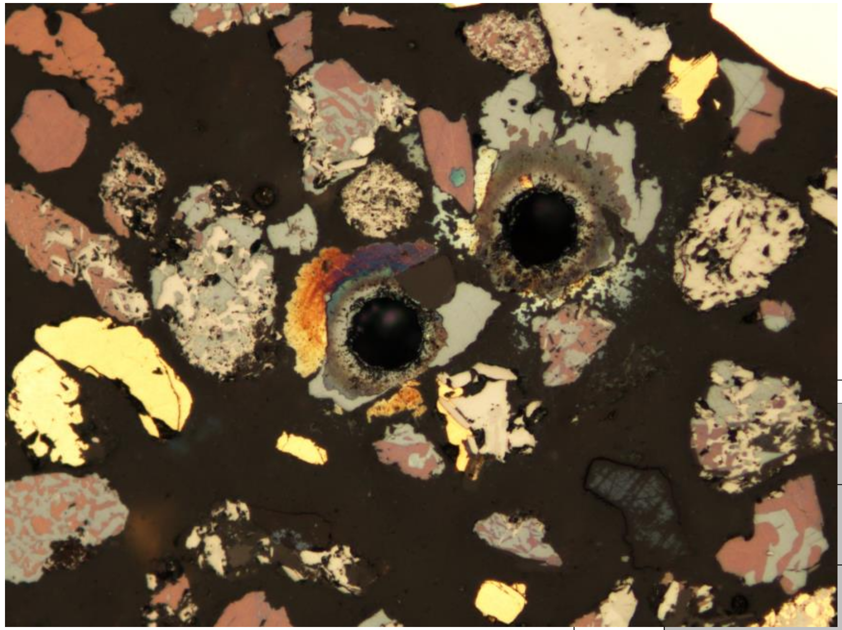
Vanessa Liebezeit produced this graph

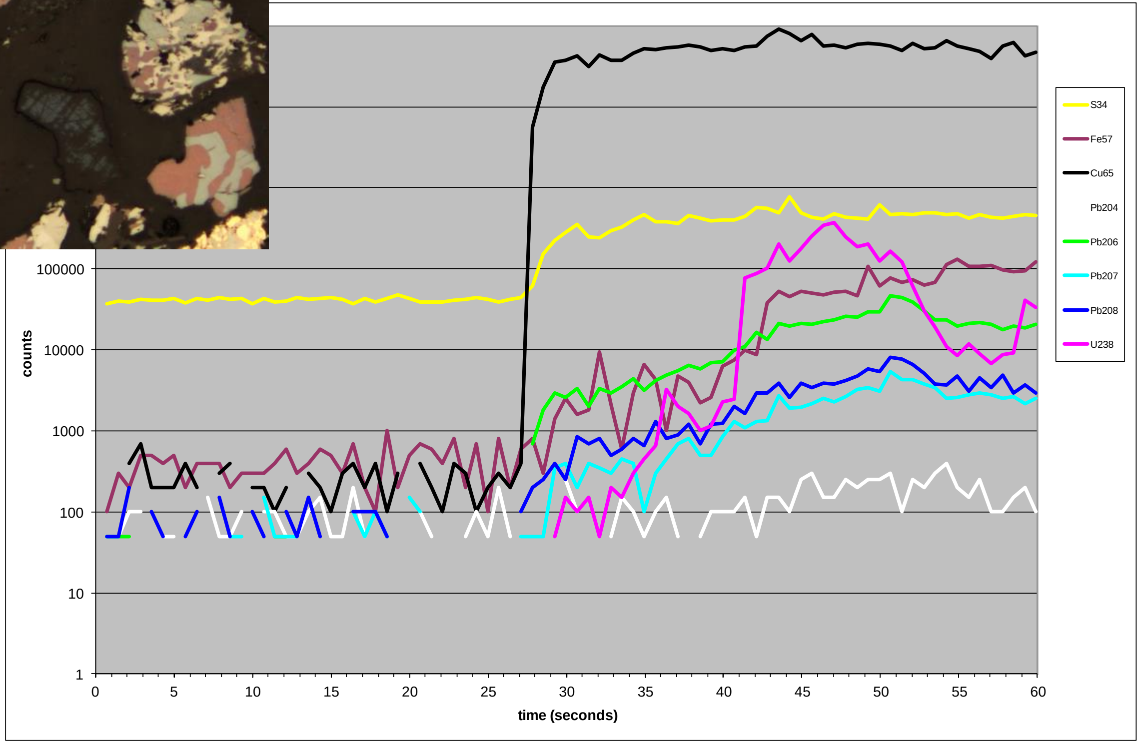
Why we don’t mine copper separate from uranium.

Micro- to nano-scale association of U with Cu minerals, and others…



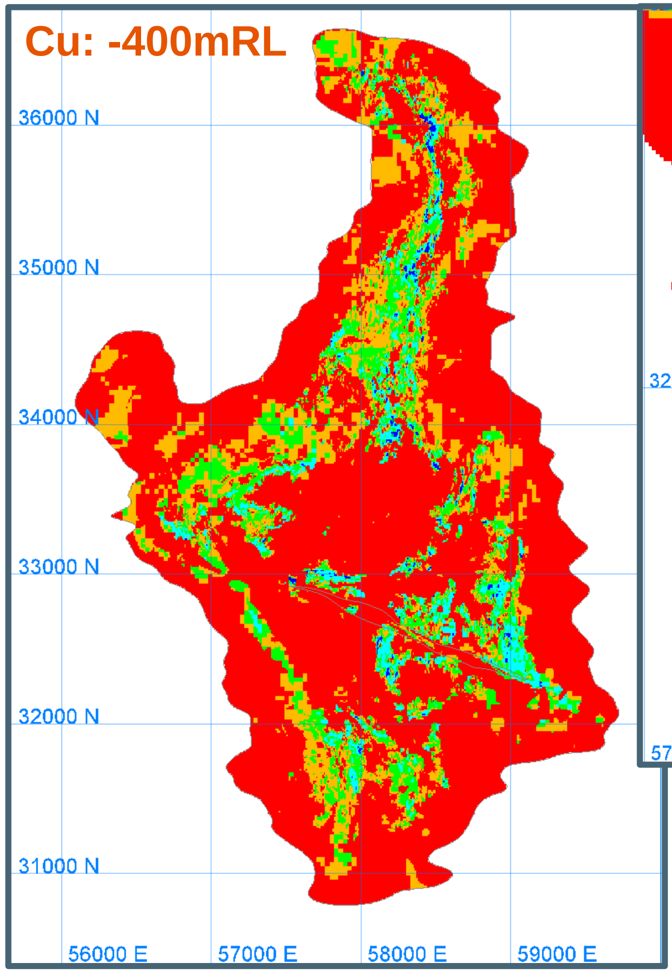


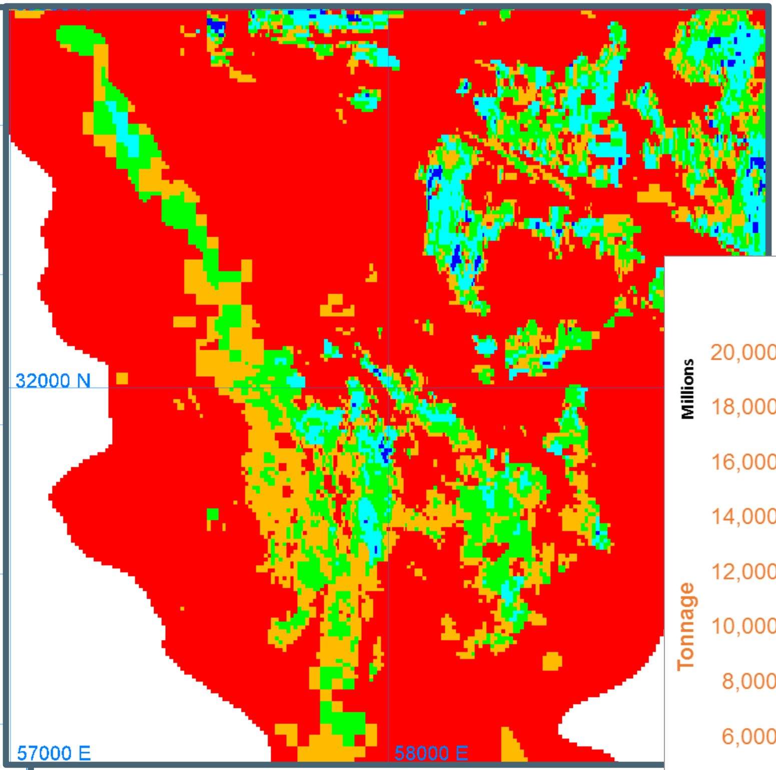




Why we don’t mine copper separate from uranium.

Deposit-scale association of U and Cu minerals





BLOCK : CU_LITE

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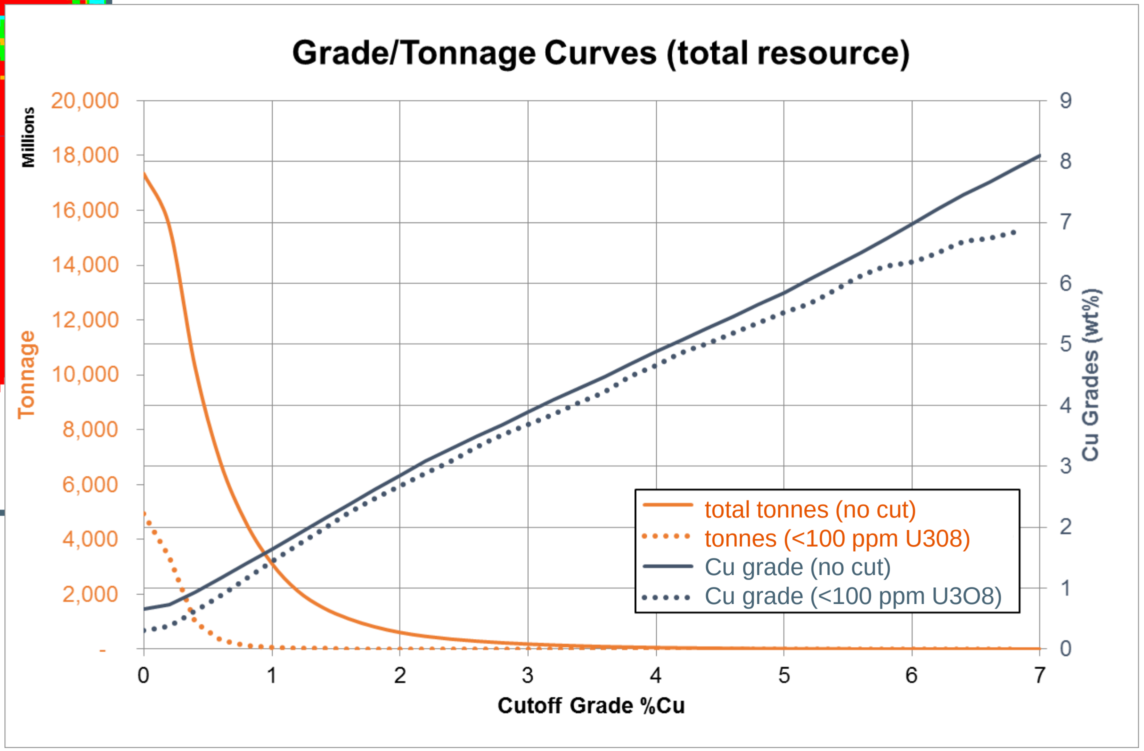
0.500 <=	(orange)	< 1.000
1.000 <=	(green)	< 2.000
2.000 <=	(cyan)	< 4.000
4.000 <=	(blue)	< 99.000



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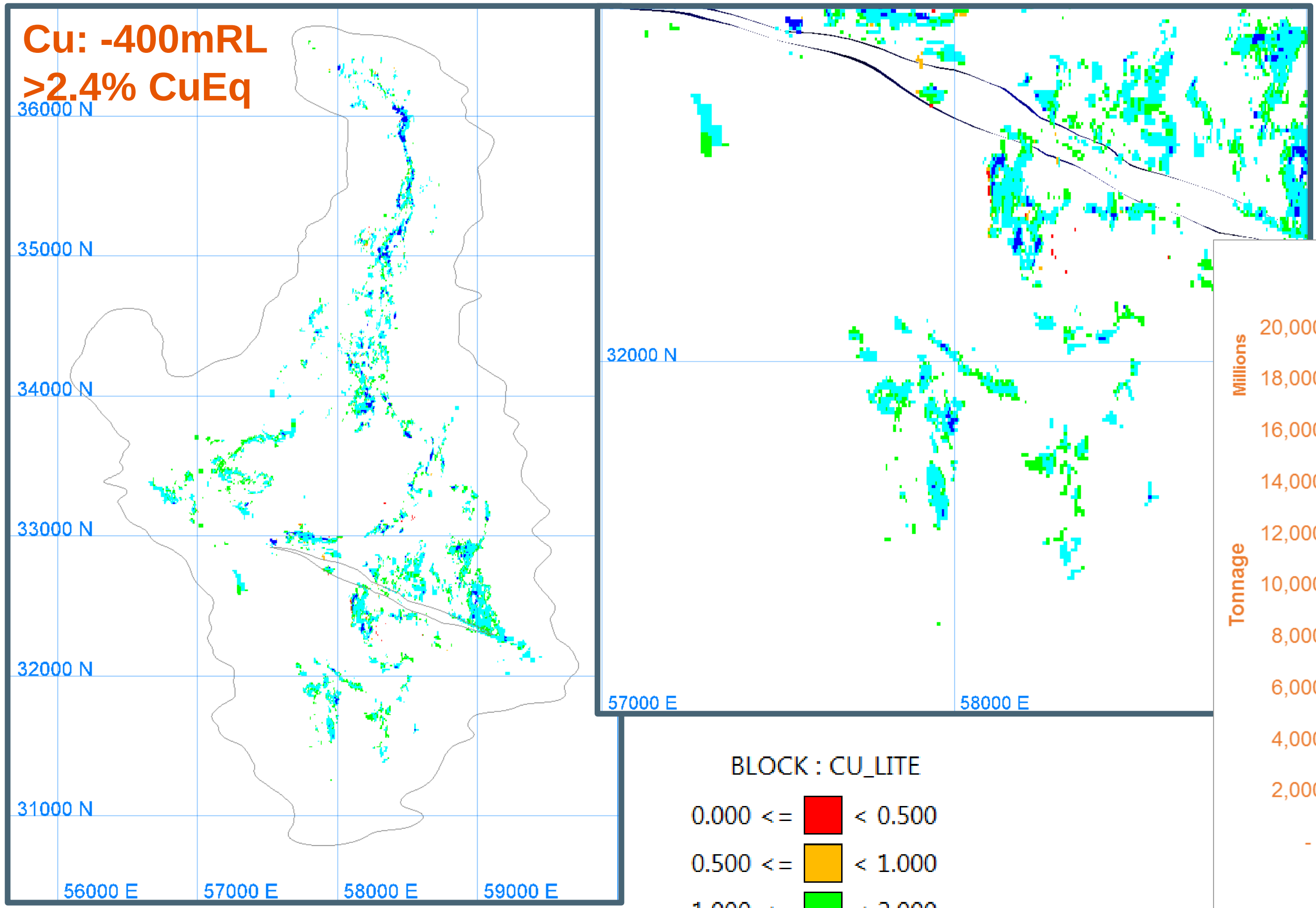

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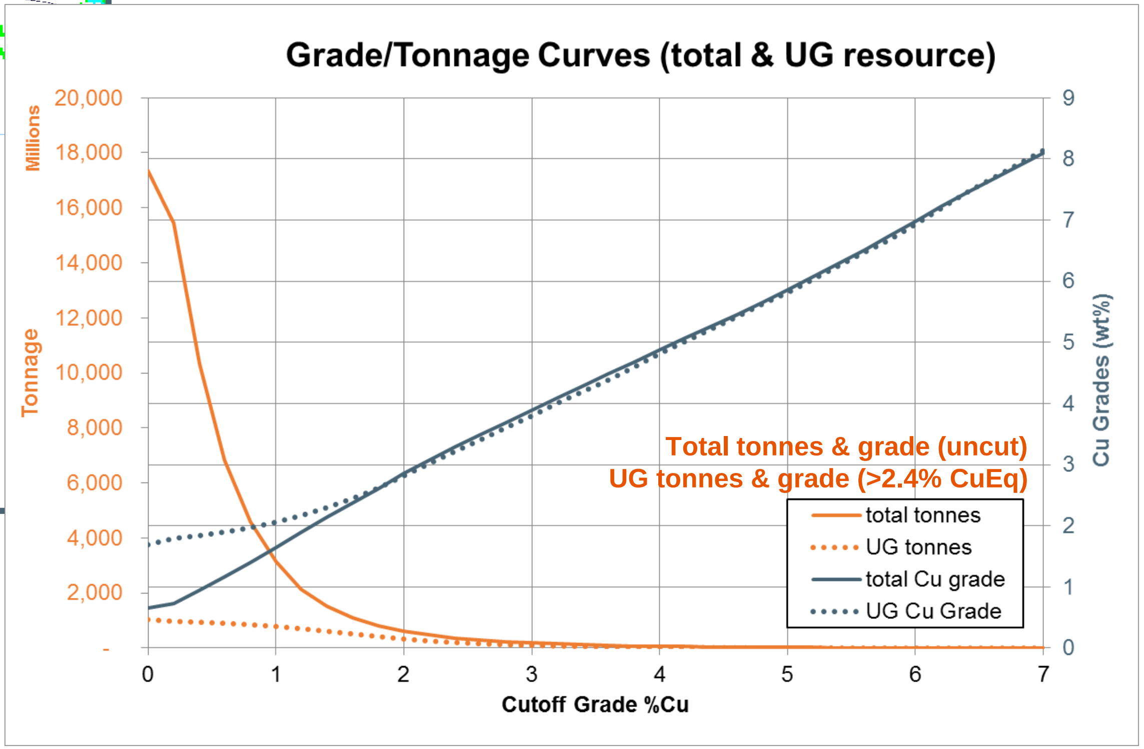

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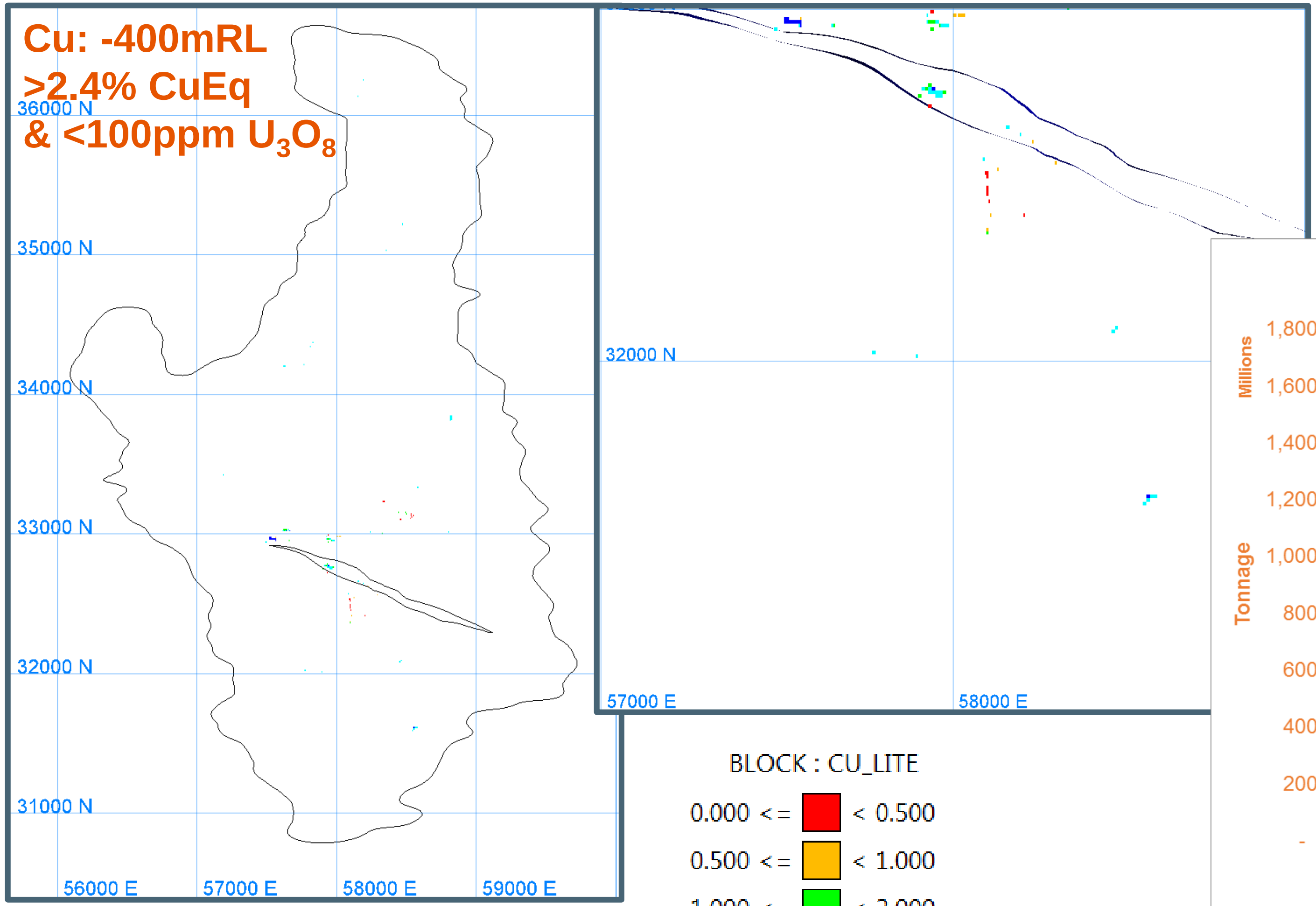

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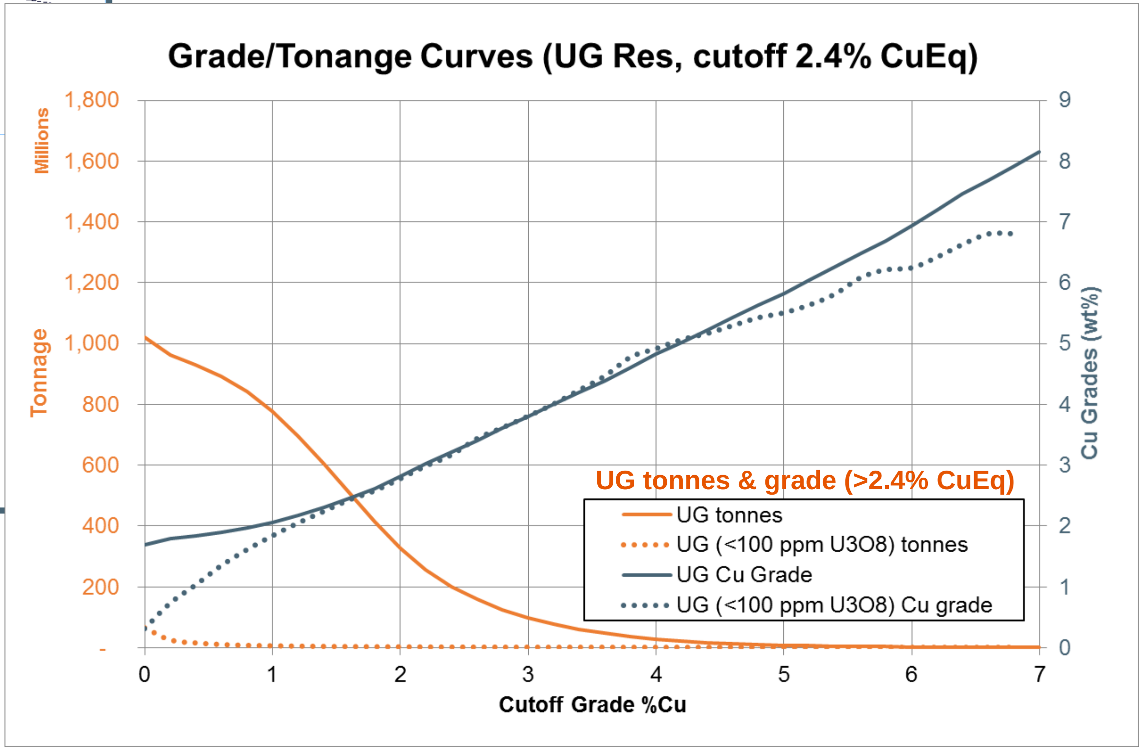

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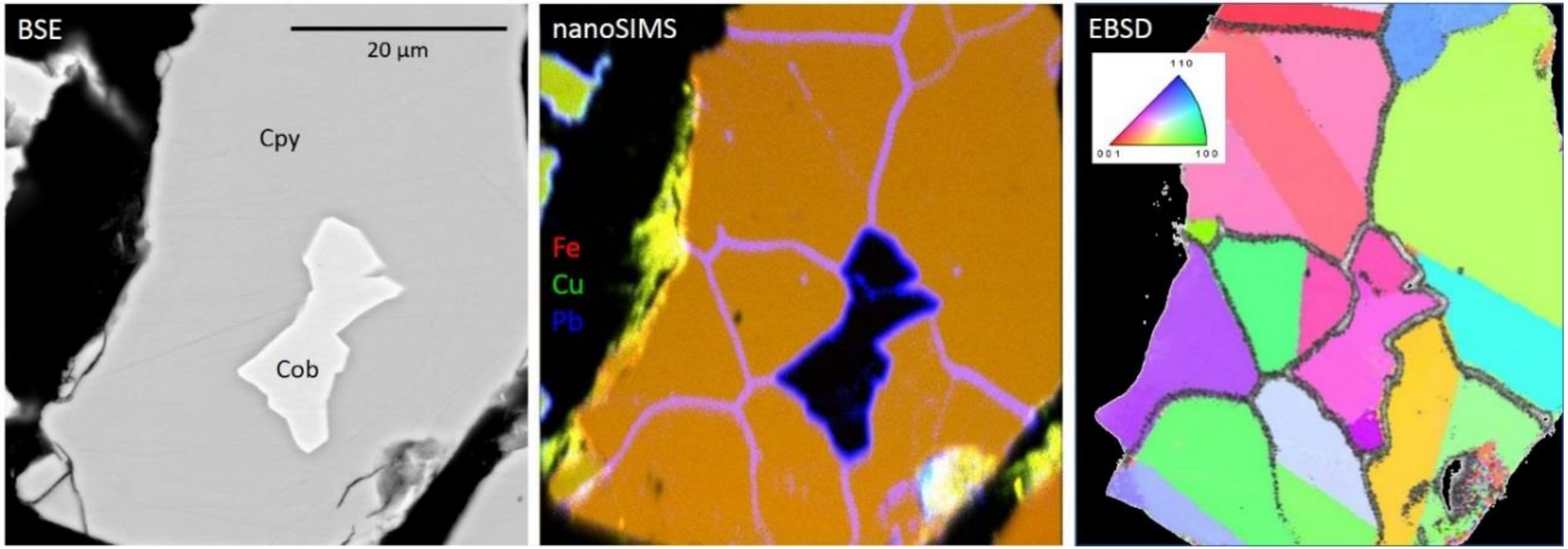
Conclusion: Understanding the Minerals does Matter

The chemistry of ^{238}U, ^{230}Th, ^{226}Ra, ^{222}Rn, ^{210}Pb, ^{210}Po is different, so the mineralogy will be different

Metallurgical Studies	**Extensive metallurgical test work conducted to produce marketable copper sulfide concentrates** **Bottom line: lowered the radionuclide activity levels, but not low enough** ***"Metal has no value until it is in a saleable product"* (Munro, 2017)**
Radionuclide Mineralogy	**Uranium minerals don't host all of the U238 decay chain radionuclides (RNs). TRANSFORMATIONAL** **In the OD deposit, RNs are partially to completely decoupled from U at the macro- to nano-scale.**



Mineralogical hosts of radionuclides

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