Nuclear Prehistory

Jake Hecla

Learning Objectives

Agenda

1. Introduction
2. Natural nuclear reactors
3. First encounters with radiation-induced illness
4. Pre-nuclear industrial uses of U

W1L2 Objectives

1. Describe natural nuclear reactors in the Franceville basin, their origin, geology, and possible involvement of early life
2. Describe Radon-induced disease and early efforts to investigate its cause
3. Describe industrial uses of U in glass, ceramics and consumer products, as well as possible early uses of such

Sources used (images, text, quotes)

- Gauthier-Lafaye, François. "Time constraint for the occurrence of uranium deposits and natural nuclear fission reactors in the Paleoproterozoic Franceville Basin (Gabon)." *Geological Society of America Memoirs* 198 (2006): 157-167.
- Mathieu, R., Zetterström, L., Cuney, M., Gauthier-Lafaye, F., and Hidaka, H., 2001, Alteration of monazite and zircon and lead migration as geochemical tracers of fl uid paleocirculations around the Oklo-Okélobondo and Bangombé natural nuclear reaction zones (Franceville basin, Gabon): Chemical Geology, v. 171, p. 147–171
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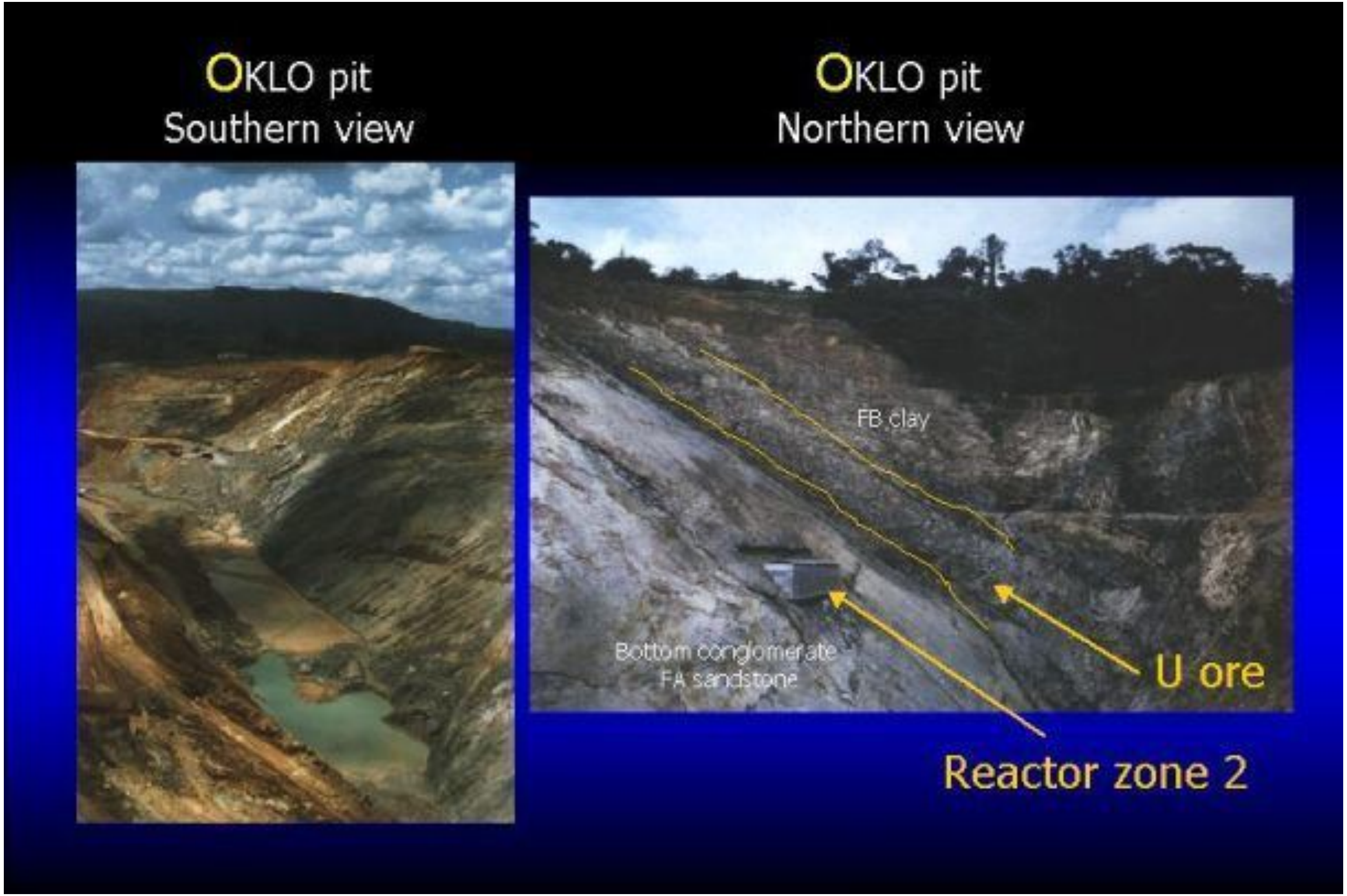
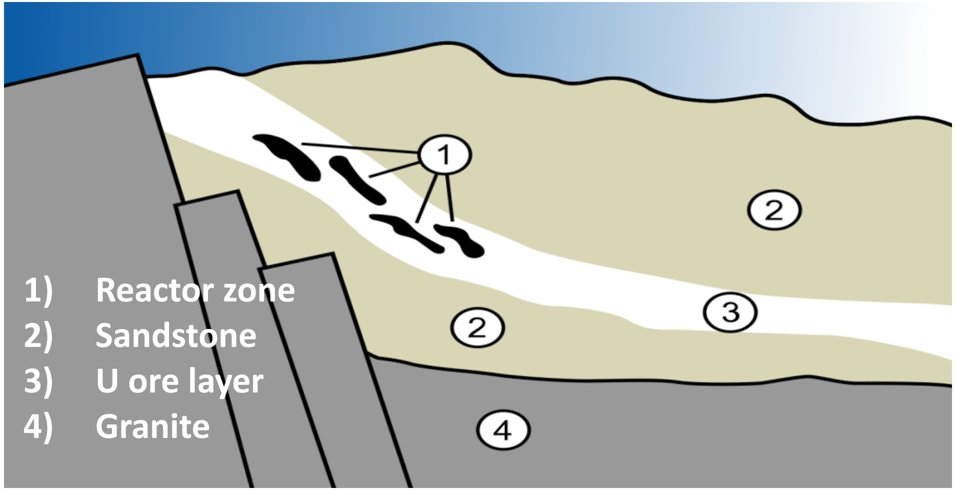
Part I: The First Few Billion Years

Oklo deposits as they existed in ~2000



- Natural uranium:
  - 99.28% U-238
  - .72% U-235

- Uranium from Franceville:
  - As low as .29% U-235
  - MS confirmed it had been "burned" ~2Ga ago
  - ~30 reactor sites spread across 30km, all contemporaneous (Oklo, Oklebondo and Bangombe mines)



Reactor zones[a]	Size (length × width) (m × m)	Thickness of the core (cm)	Maximum UO_2 (%)	Maximum $^{235}U/^{238}U$ depletion (%)
RZ1	40 × 18	20–30	40	0.409
RZ2	12 × 18	20–50 locally 100	50–60	0.292
RZ7-8-9	Total length 30	A few	25–30	0.543 RZ9 0.579 RZ7
RZ10	27 × 30 × 15	a few to 100	65	0.479
RZ13	10 × 6	20–30	87	0.380
Bangombe	1.5 km²	5–15	54	0.590

a

The region that show the anomaly in isotopes of uranium. They are considered as the reaction center of the ancient nuclear reactors.

Image from IAEA "Oklo: Natural Analogue- phase 1"

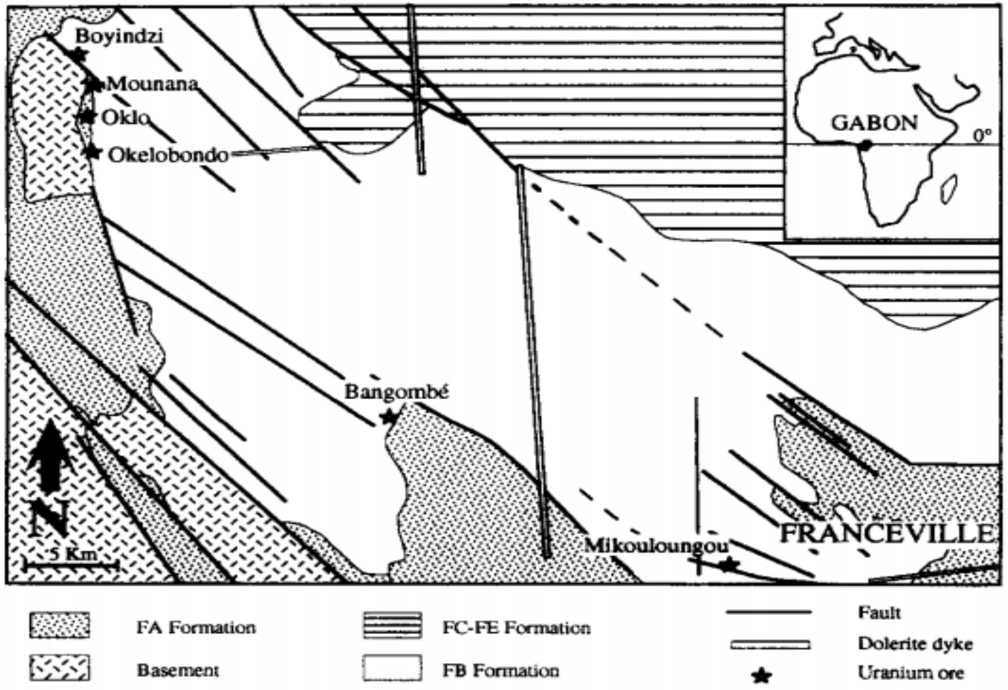
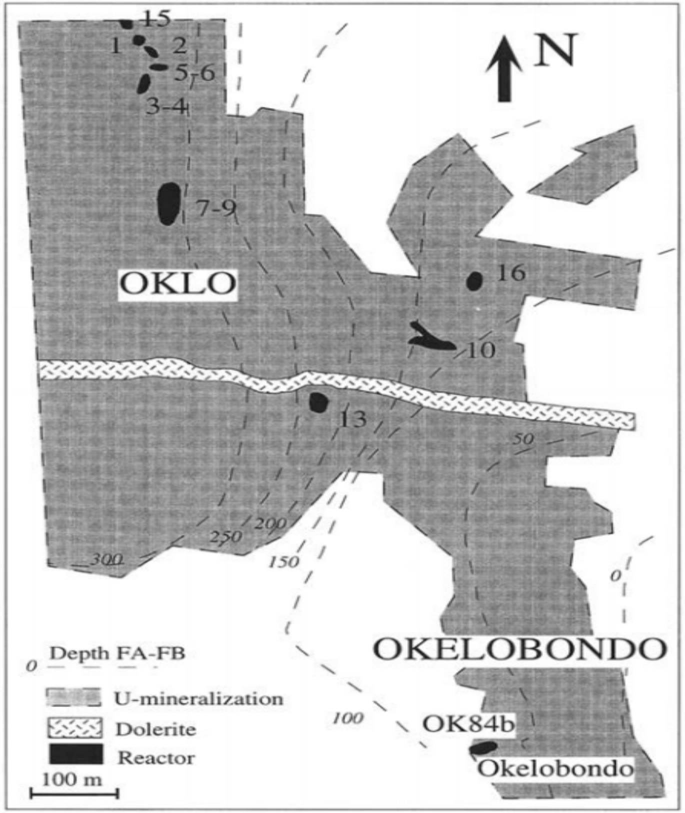


FIG. 1. Geological map of the Franceville basin.



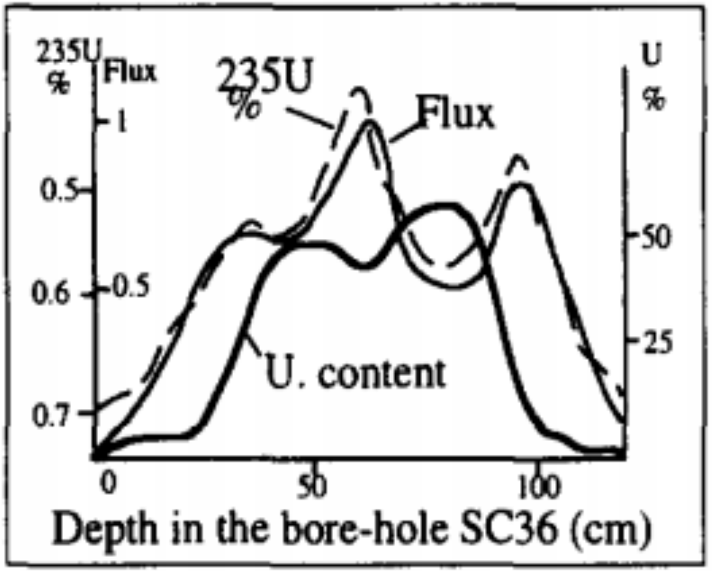
Reactor operations

- Operational lifespan 24k-1Ma
- Reactors created ample Pu-239 (5-10 tons over lifetime), burned a similar quantity of U-235
- Typical cycle:
  - Water floods voids, causing criticality
  - Water is heated as the reaction proceeds, eventually boiling (~100kWth)
  - Negative void coefficient and/or neutron poisoning shuts reactor down
  - Heat creates additional U reduction by OM, increasing reactivity
  - Fission product poisons keep reactor off until cycle repeats
- Periodicity of ~1-3 hours
  - On-period of ~30min
  - Suggests neutron poisons probably main mechanism for cycling

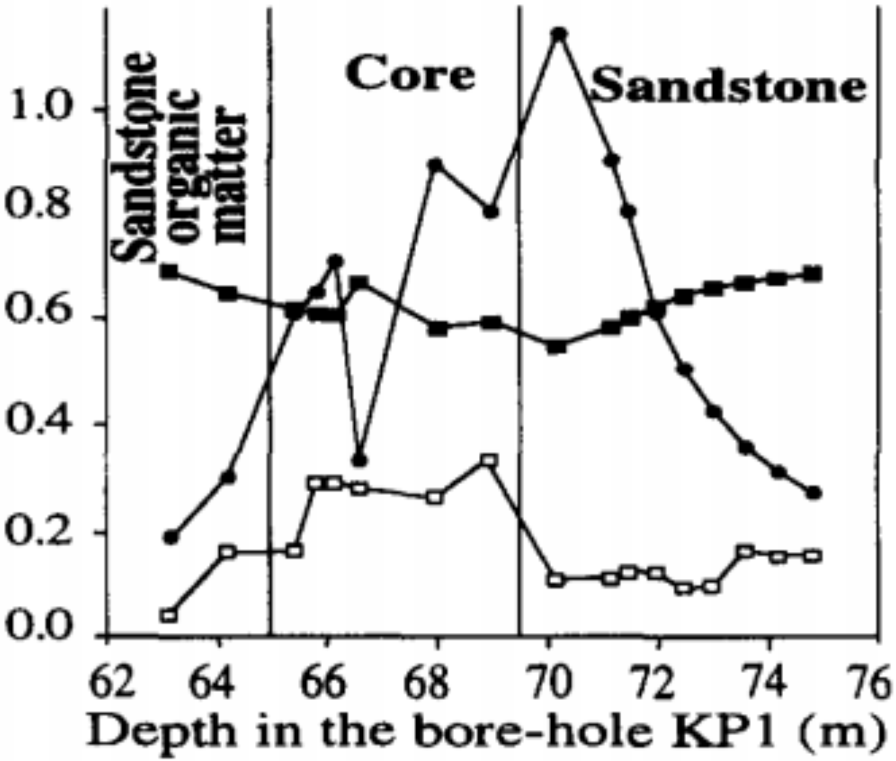
Organics in FB and water in FA created neutron reflectors

Reactor 2

(from Naudet and Renson, 1975, modified)



Reactor7



□ U % x 100
■ 235U / 238U %
● Fluence (n/kb)

Oklo likely resembled a geothermal geyser or pool

The conditions that created the Franceville reactor complex were not fundamentally unique, however, the conditions that *preserved* them were.

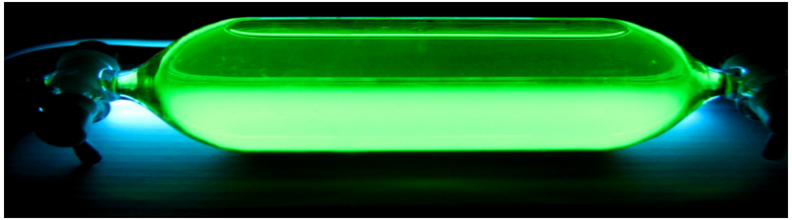
Other reactors *almost certainly* existed on earth and beyond.

Part II: The role of life

- The Franceville reactor complexes were made possible by the existence of bacteria which created oxidizing conditions
- Additionally, bacteria may have contributed to U and Pu reduction in the reactor zones
- Reactors may have provided a rich source of complex molecules

U deposits formed in the Franceville Basin 2.14-2.05Ga

1. Oxidation



U(VI) in solution; 100-170C, 800-1200 bar. Concentrations of a few ppm

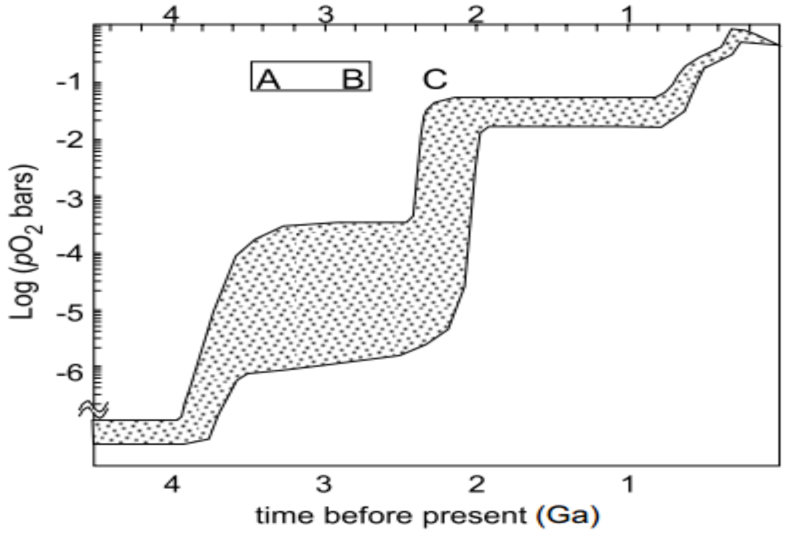
2.Reduction

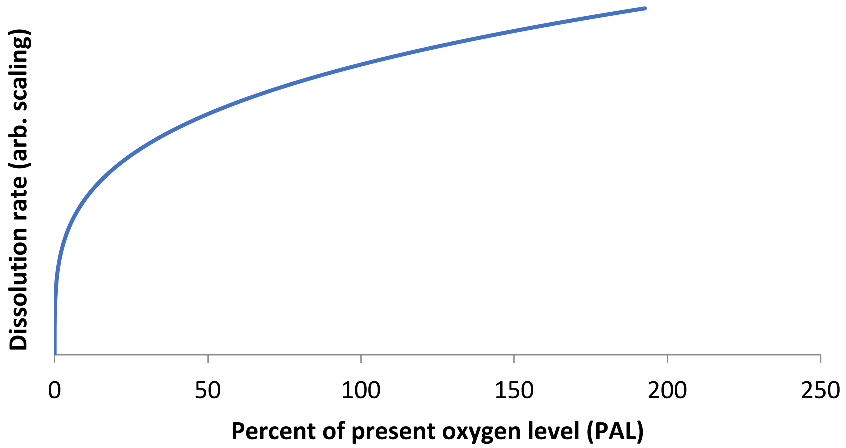
Detrital grains containing .1-.5% U(IV) by mass (common in anoxic sediments)

Deposition in “FA sandstone” layer. U(IV) content 40-60% by mass

Mathieu, R., Zetterström, L., Cuney, M., Gauthier-Lafaye, F., and Hidaka, H., 2001, Alteration of monazite and zircon and lead migration as geochemical tracers of fl uid paleocirculations around the Oklo-Okélobondo and Bangombé natural nuclear reaction zones (Franceville basin, Gabon): Chemical Geology, v. 171, p. 147–171

1: Oxidation from detrital grains difficult with known oxygen levels



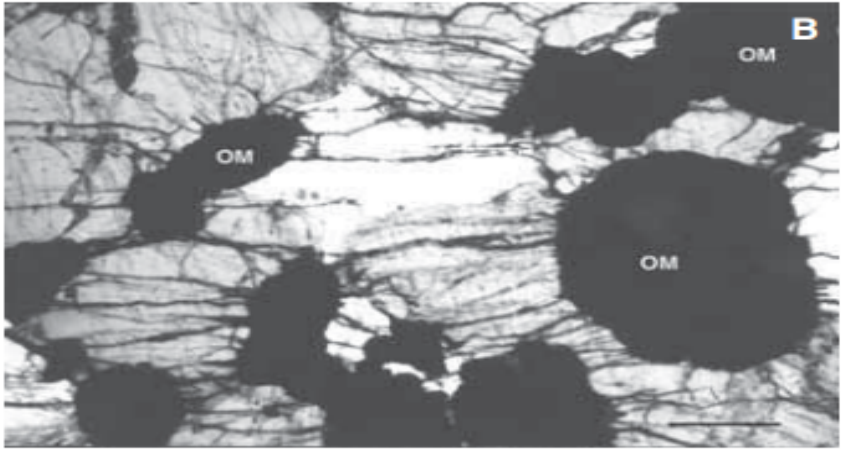


- **The total O2 required transport the Oklo uranium deposit is 10x larger than the amount estimated to have existed in the reservoir**
    - Surface water oxygen increase caused by photosynthetic bacteria “oases”?
    - Abnormally large circulation and gas exchange with the surface?

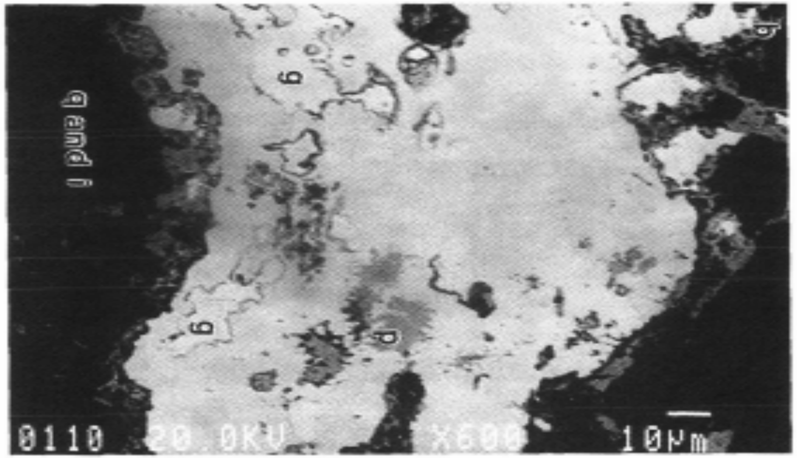
Lyons, Timothy W., Christopher T. Reinhard, and Noah J. Planavsky. "The rise of oxygen in Earth/'s early ocean and atmosphere." *Nature* 506.7488 (2014): 307-315.

2: Unclear reduction mechanism of U(VI →IV) in some sediments

1. U-bitumen deposit



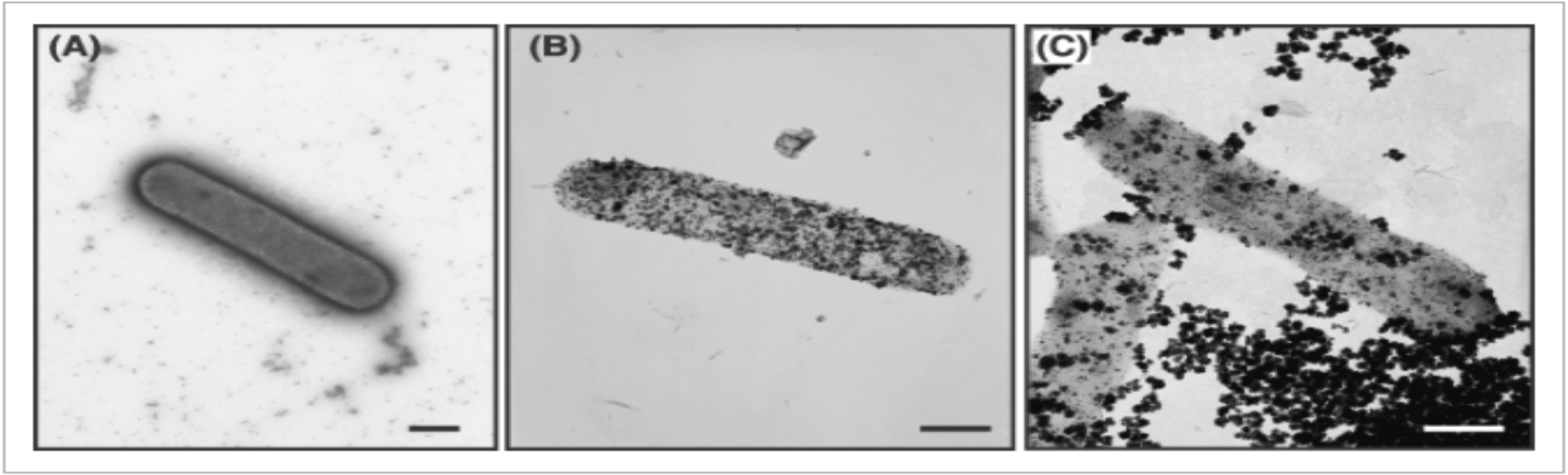
2. U-hematite-galena deposit



Reaction of U(VI) with organic matter creates U(IV) rapidly above 200C. This explains the left sample, which contains U(IV) in bitumen. The sample at right, however, is primarily galena, hematite and uraninite (>10% U by mass). This ***could*** be explained by abiotic redox, but conditions don’t appear favorable in the deposit samples known.

Gauthier-Lafaye, François. "Time constraint for the occurrence of uranium deposits and natural nuclear fission reactors in the Paleoproterozoic Franceville Basin (Gabon)." *Geological Society of America Memoirs* 198 (2006): 157-167.

Uranium reducing bacteria?



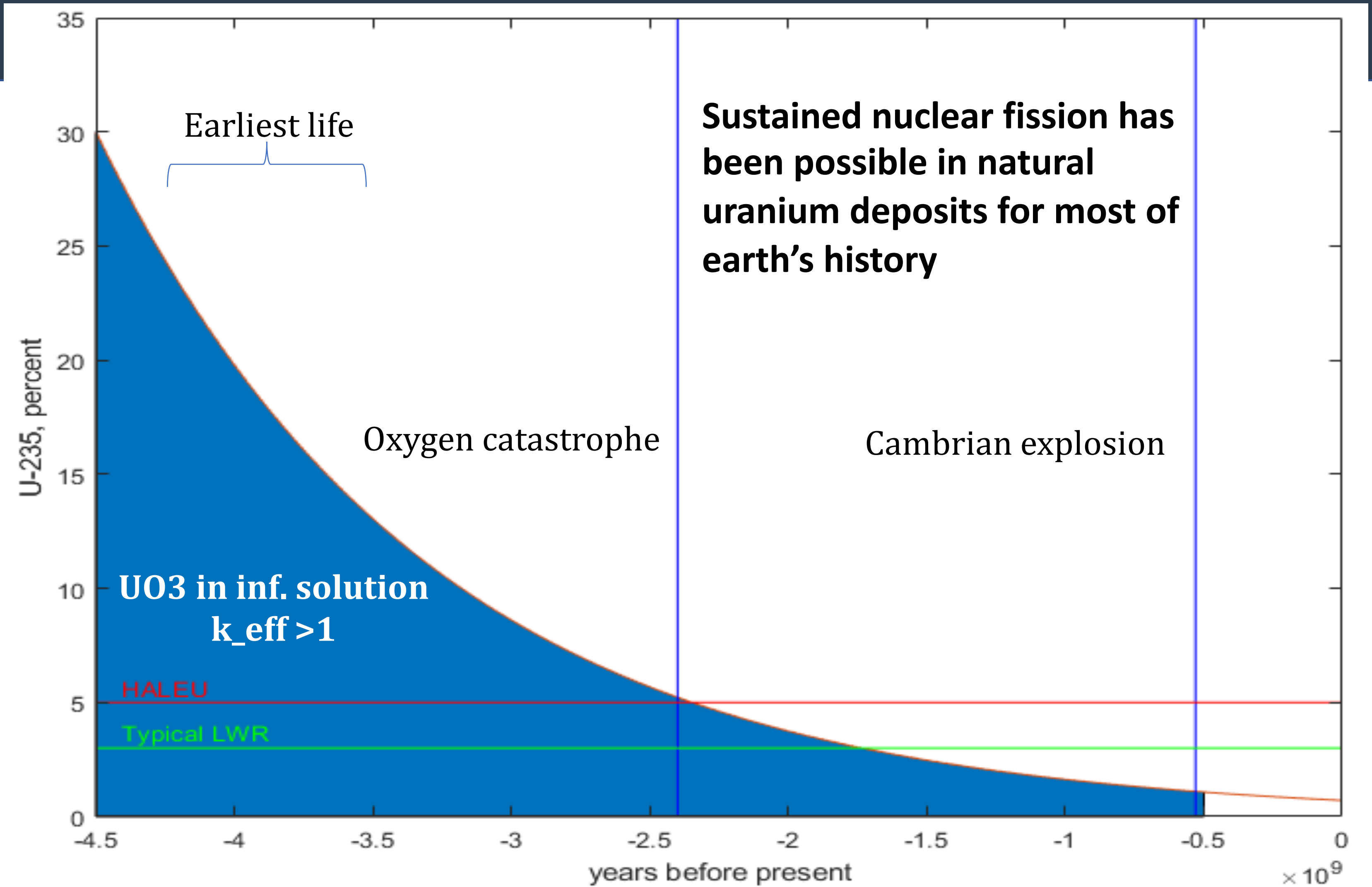
Pyrobaculum Islandicum precipitates U(VI) as U(IV) in the presence of hydrogen as an electron donor at 100-120C. From left to right: t=0, 60, 140 minutes. Note that this bacteria also reduces Fe(III) to fine-grained hematite, which is also found in abundance at Oklo. **I am not proposing this bacteria as a mechanism, but stating that these metabolisms exist and that some version may have been involved, though evidence for such has not yet been found.**

Image from: Kashefi, K., B. M. Moskowitz, and D. R. Lovley. "Characterization of extracellular minerals produced during dissimilatory Fe (III) and U (VI) reduction at 100 C by Pyrobaculum islandicum." *Geobiology* 6.2 (2008): 147-154.

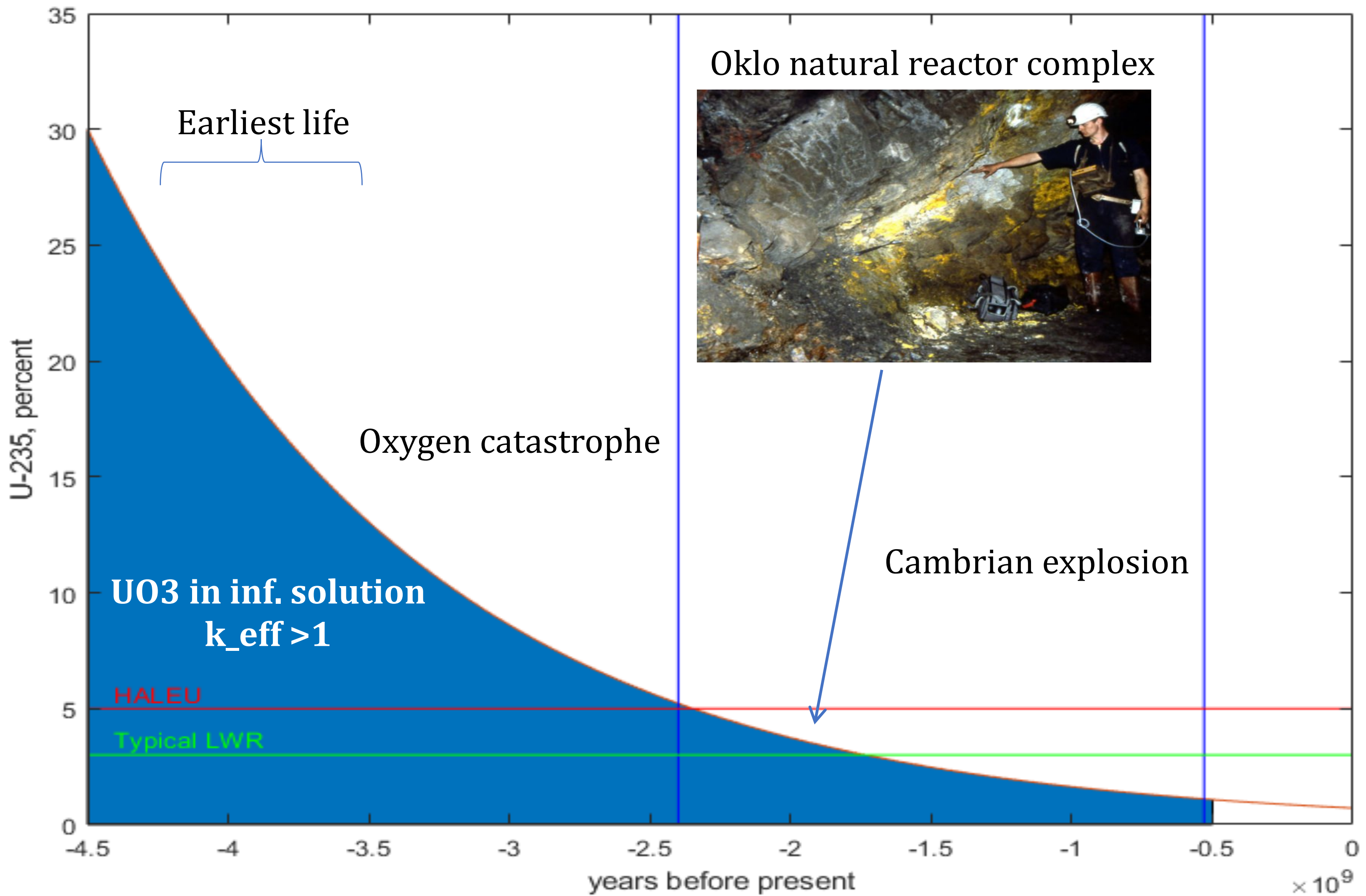
U(VI) reducing bacteria exist and can thrive in Oklo-like conditions

Bacterium	Reference(s)	Bacterium	Reference(s)
Anaeromyxobacter dehalogenans strain 2CP-C	78	*Desulfovibrio sulfodismutans* DSM 3696	51
Cellulomonas flaigena ATCC 482[a]	82	*Desulfovibrio vulgaris* Hildenborough ATCC 29579	51
Cellulomonas sp. WS01	82	*Geobacter metallireducens* GS-15	50
Cellulomonas sp. WS18	82	*Geobacter sulfurreducens*	38
Cellulomonas sp. ES5	82	*Pseudomonas putida*	4
Clostridium sp.	22	*Pseudomonas* sp.	4
Clostridium sphenoides ATCC 19403	21	*Pseudomonas* sp. CRB5	57
Deinococcus radiodurans R1	24	*Pyrobaculum islandicum*	39
Desulfomicrobium norvegicum (formerly *Desulfovibrio baculatus*) DSM 1741	51	*Salmonella subterranea* sp. nov. strain FRC1	87
Desulfotomaculum reducens	92	*Shewanella alga* BrY	14, 93
Desulfosporosinus orientis DSM 765	91	*Shewanella oneidensis* MR-1 (formerly *Alteromonas putrefaciens*, then *Shewanella putrefaciens* MR-1)	50
Desulfosporosinus spp. P3	91	*Shewanella putrefaciens* strain 200	11
Desulfovibrio baarsii DSM 2075	51	*Veillonella alcalescens* (formerly *Micrococcus lactilyticus*)	99
Desulfovibrio desulfuricans ATCC 29577	49	*Thermoanaerobacter* sp.	77
Desulfovibrio desulfuricans strain G20 (to be renamed *Desulfovibrio alaskensis*)	68	*Thermus scotoductus*	43
Desulfovibrio sp. UFZ B 490	72, 73	*Thermoterrabacterium ferrireducens*	42

Wall, Judy D., and Lee R. Krumholz. "Uranium reduction." *Annu. Rev. Microbiol.* 60 (2006): 149-166.

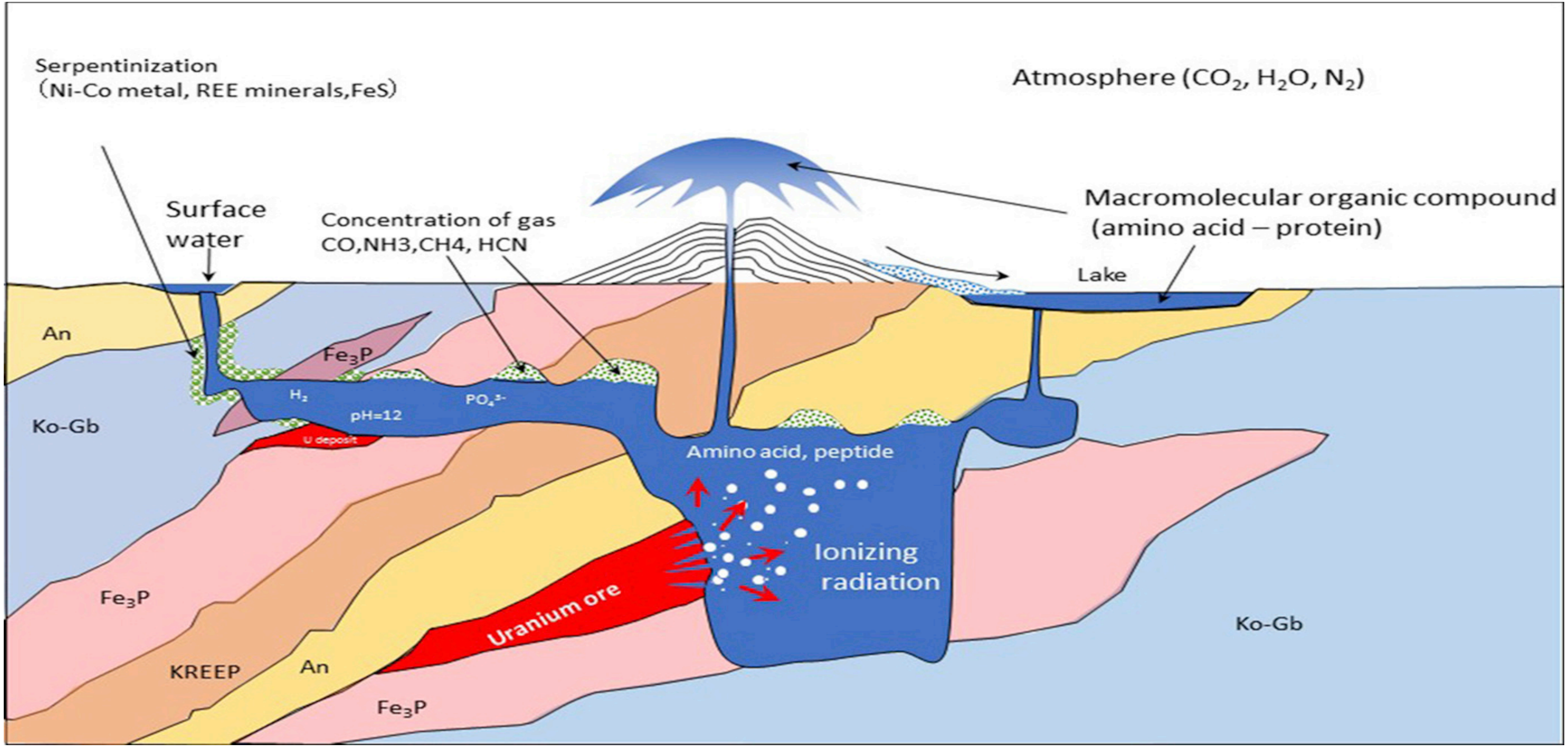


Earliest life
Sustained nuclear fission has been possible in natural uranium deposits for most of earth's history
Oxygen catastrophe
Cambrian explosion
UO3 in inf. solution
k_eff >1
HALEU
Typical LWR
U-235, percent
years before present
× 10^9



Oklo natural reactor complex
Earliest life
Oxygen catastrophe
Cambrian explosion
UO3 in inf. solution
k_eff >1
HALEU
Typical LWR
U-235, percent
years before present
× 10^9
35
30
25
20
15
10
5
0
-4.5
-4
-3.5
-3
-2.5
-2
-1.5
-1
-0.5
0

Nuclear geysers: A source of organic macromolecules?



Toshikazu Ebisuzaki, Shigenori Maruyama, Nuclear geyser model of the origin of life: Driving force to promote the synthesis of building blocks of life, Geoscience Frontiers,Volume 8, Issue 2, 2017, Pages 275-298.

In summary: the first billion years of nuclear energy

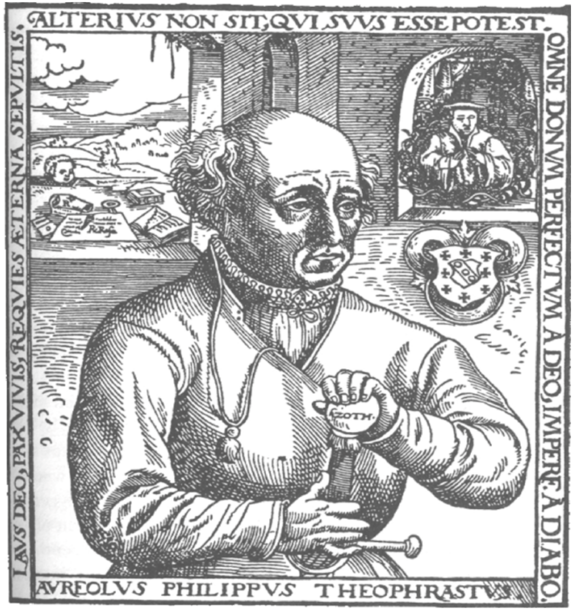
- Life has coexisted with nuclear energy for billions of years
- The first reactors likely formed as a result of oxygen produced by photosynthetic bacteria
- Further, it is likely bacteria figured out how to exploit fission long before we did (reducing U, likely Pu)
- Early life may have benefitted from organic macromolecules generated by these sources of heat and ionizing radiation

Part III: Humans encounter radiation

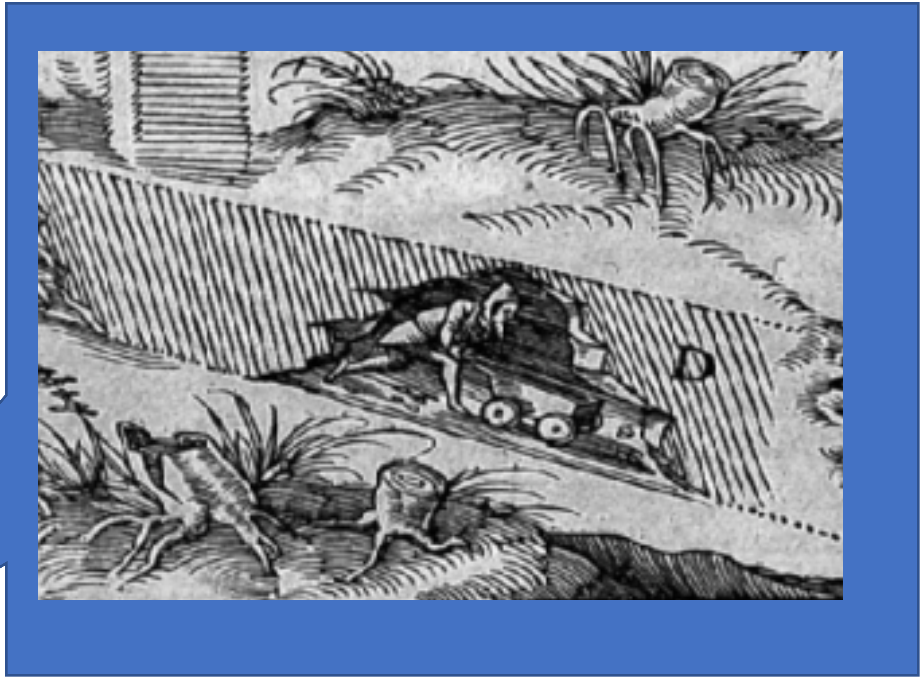
- Humans suffered from radiation related illnesses as early as 1470
- Human unknowingly worked with radioactive materials (U) and used them in glass potentially as early as the 1st century AD
- Pottery, glassware and a variety of consumer products used U from the 1830s-1950s

Schneeburg Lung Disease

- Agricola *De Re Metallica (1494-1555)* identified “Mala Metallorum,” which was first described in local accounts around 1470
  - Described as shortness of breath, culminating in cachexia and death in short order.
  - Present even in young men (miners mostly died before 40)
- Paracelsus (1493-1541) wrote *Uber die Bergsucht und andere Bergkrankheiten* (About the ‘Bergsucht’ and other Miner’s Diseases)
  - 75% of miners in the region died of some form of lung disease; Paracelsus ascribed it to As dust



Agricola


B
A
C
D

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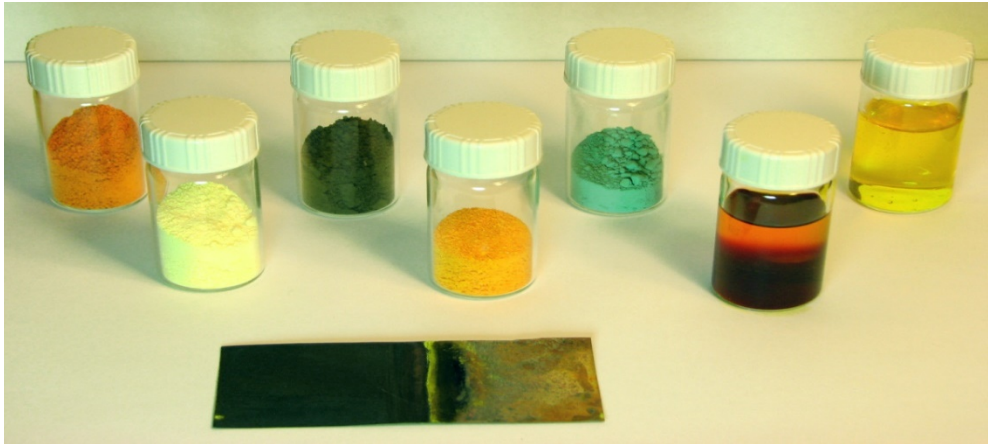
1789: Uranium discovered

- Discovered in “pitchblende” in 1789 from Joachimsthal (ores up to 40% U by weight)

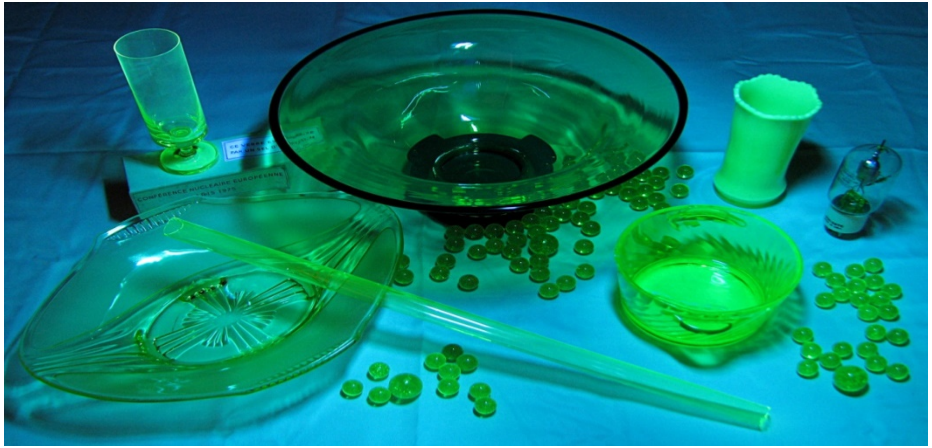
Botyroidal pitchblende
(mostly uraninite)



Various U compounds synthesizable at home
(pc: Carl Willis)

Industrial uses proliferated

- Pottery glazes (blaze orange, yellow, green, grey, black)
- Glass additive (yellow, green allowing glow under UV at dawn/dusk)



However, Klaproth was not the first to use U in glass

A mosaic found in a niche in Pausilypon used unusual glass

GLASS MOSAIC AT THE BACK OF A NICHE IN THE IMPERIAL VILLA.

A. Twisted glass rod from border. Full size.

From Archaeologia LXIII.

Gravimetric analysis yielded fascinating results

- Though written off as a mistake until the late 1990s, later radiometric analysis in 2011 of the sole remaining sample established the glass as containing several % U

- Celtic origin proposed (2011)

IMPERIAL ROMAN VILLA NEAR NAPLES

Composition of the green-tinted glass.

Silica	62·11 %
Iron oxide	2·70 %
Alumina	1·76 %
Lime	8·90 %
Magnesia	2·90 %
Uranium oxide	1·25 %
Potassium oxide	20·38 %
	100·00 %

Backup Slides

- Questions?
- Discussion items?