



Natural fission reactors other and older than Oklo, likelihood and isotopic data – a scenario from geo(-photo)chemistry and chemical evolution





Principal conditions for non-anthropogenic reactor

(NFR) operation



George W Wetherill (1925 – 2006) and Paul K. Kuroda (1917 – 2001)

- Self-sustained neutron based chain reaction
- Sufficient concentration of fissile isotopes (for practical purposes, = ²³⁵U)
- moderator available
- No or few neutron poisons (less critical the older site is)
- Control by evaporation of part of moderator, while avoiding positive void coefficient regimes (neutron energy spectrum): graphite nonvolatile but most plausible organic compounds are

Time (mio. y BP)	²³⁸ U	²³⁵ U	²³⁴ U
-3850	Oldest sedi- ment rocks	about 18	
-2960	U gets mobile (hexavalent) in sediments, may enrich thereafter	7.5	
-1790	Oklo	2.9	
-4500	77.27535 %	22.72029 %	0.00436 %
-4000	83.68689 %	16.30839 %	0.00472 %
-3500	88.55684 %	11.43817 %	0.00500 %
-3000	92.10948 %	7.88532 %	0.00520 %
-2500	94.62553 %	5.36913 %	0.00534 %
-2000	96.37030 %	3.62426 %	0.00544 %
-1500	97.56263 %	2.43187 %	0.00550 %
-1000	98.36929 %	1.62516 %	0.00555 %
-500	98.91133 %	1.08309 %	0.00558 %

Oklo recalled – when, where, why, which geochemical difficulties

- U bound to francevillite in S Gabon before (i.e., V(V) – strongly oxidizing conditions)
- It takes a different manner of removing neutron poisons while enriching U (chem., not isotopically) – in which conditions?
- Kind of chromatography in sandstone pores?





Oklo 15 NFR site: accessible by tunnel, part of UNESCO World Heritage. U is yellow (U_3O_8) as U(V) is colorless

(below)

Curienite and francevillite (lead and Ba/Pb uranyl(VI) vanadate(V) hydrates from Mounana mine near Oklo



Photochemical enrichment of U(red) next to a surface

- Photoreduction/-precipitation of U reported already more than 200 years ago; many different e donors useful
- Uranyl salts can be extracted into O organic phases (ethers, ketones, esters, lipids) [cp. PUREX]
- UO₂²⁺ photoredox chemistry in ion pairs containing complexes (own work): aldehydes (sugars) transfer CO while U is precipitated
- Short lifetime of triplet state (<< 1 μs) provides selectivity
- Slight depletion of ²³⁵U in precip. reduced uranium
- UO_{2+x} precipitation → formation of highly enriched layers, occluding moderator materials
- which level of organics is required? (ion pairs, complexation counteract dilution)



Oster- and non-Oster photoreactions: the key to conditions for UO₂ deposition

Oster: photoexcited dye molecule (e.g. thiazine [methylene blue, flavines, quinones, UO_2^{2+}) oxidizes some organic donor (EDTA, sugar, alcohol); the reduced photosensitizer then is reoxidized and thus reactivated by another oxidant like Fe(III), Ce(IV), chromate, nitrate etc. . If secondary oxidant is missing, reduced photosensitizer will be precipitated or decompose after single photochemical charge transfer; otherwise there is photocatalytic oxidation of organics while e.g. uranyl reamins dissolved and active





Ion pairs, U-rich sediments, piles of fissionable matter

- Pronounced ion pairing/ association
- In photocarbonylation in uranylcomplex ion pairs, I, Br, ox (L^{reduc.}) can be replaced by CO, Hal', NCS⁻ (from added solvent, salt) while CI, CO, SCN/NCS, glyc (L^{inert}) are stable once introduced \rightarrow formation potential of Hal atoms, $CO_2^- \leq {}^{3}UO_2^{2+}$: self-limiting process
- $UO_2 \downarrow$ solid U accumulation in aqueous organic medium only
- Out there: same with sugars?
- Photochemical by-product solids, liquids rich in C \rightarrow efficient neutron production, moderation linked to ¹³C (α ,n)

Biochemical accumulation of uranium?

- Behavior of UO_2^{2+} in plant oils
- Lipid content of sediments
- U(VI) photoreduction in such solutions: esters do not react, carboxylates do but slowly
- U binds to cell walls, causes photodestruction of these and of DNA \rightarrow release of lipids in which UO_2^{2+} would accumulate
- C/N in early organisms >> 10 \rightarrow high lipid, sugar (= aldehyde) contents \rightarrow extractive concentration of hexaval. U, rapid photoreduction, remaining organics used/resorbed in regrowing biofilm
- Attachment of UO_2^{2+} to sugars, lipids, longchained ethers (Archaea), photokilling of prokaryote cells \rightarrow extent of lipid release depends on [C/N] and thus on biology/aerobic heterotrophy

Becquerelite and related (M,M'uran yl carbonate) minerals



Rock-dwelling lichens accumulate U (and survive it) but neither did exist then nor could reach relevant levels of U accum. directly

Secondary photoenrichment

 Organics from various sources, including destroyed biomass, accumulate in "pond"

Banded iron formation (age < 3.1 bio. years) [BIF]: intercalation of Fe(III)oxides/silicates and (shalelike) organics which provide neutron moderation. BIFs possibly were formed by photochemistry also



Radiochemical feedback: (hydrophilic) organic synthesis by β emitters produced in fission

- Requires CO (not CH₄ or CO₂) besides of N₂, moisture (H source)
- must take place next to surface as β, γ
 must partially penetrate into gas phase
- electron, proton or α beams are best way to introduce N₂ nitrogen into amino acids
- Organics deposit above NFR, leach U(VI) from below
- Some 10⁴ AA (mostly glycine) molecules from β electrons from fission products released by one ²³⁵U fission → (more than) sufficient as long as there is mobile U in the sediment and some CO in the atmosphere



The device used by Kobayashi et al. for making AA organics, etc. from moist CO/N_2 and its products (SR = synchrotron radiation)



Photodeposition and NFR formation

 UO_2^{2+} is distinguished by very high (ϕ > 0.5) yield, visible light ($\lambda \approx 450$ nm) photoreduction using quite different organics (and CN⁻ , Br⁻, SCN⁻...), much like photochemical REE separation (that of Eu from all the others) in non-Oster conditions



What happens in the system when a NFR starts?

- NFR emits ionizing radiation through overlying water layer, causing radiochemical alterations of solutes, atmosphere
- photo- and (when there is Fe(II)) radiochemical formation of oxalate leaches Fe, Zn, Al, etc from support while REEs (neutron poisons) are retained
- glycine made from moist CO/N₂
 deposited and photolyzed in water
- Polar organics most soluble in water
- Ca salt precipitation (oxalate, fatty acids) contributes to n moderation, heating makes symm. ketones



Products of aq. glycine radiolysis (\rightarrow pH increase [6.2 to 9]): NH₃, CH₃NH₂, ethanol amine (bases); HCO-COOH, ser, asp, OH-asp, H₂N-asp, hydantoins, others, get precipitated by Ca²⁺ \rightarrow leaching from sediment, removal of Cu

NFR formation, "ignition"

- Uranyl was associated with carbonate (still today: sites where ²³¹Pa, ²³⁰Th are present), organic ligands, emits α particles → NFR starts by
- ¹³C (α,n) ¹⁶O; primary neutron flux density: some
 0.05 n/s*cm³
- Abstraction/-removal of neutron poisons, binding moderators to the evolving NFR core

Next step: pond almost filled, NFR starts working, fission products emit radiation to pond and overhead atmosphere

- Organics required for
- U mineral leaching,
- photodeposition of UO₂,
- moderator accumulation
- are produced by radiochemistry when there is CO and > 10^{-3} of β^- ; γ released per fission event when some charged particles leak out to fluids following decays



The general scenario

- UO₂ is precipitated by a photochemical transition from UO₂²⁺, with C_{org} probably derived from some biofilm
- Carbonates and organics left behind provide a moderator, either interlayers or encircling the NFR core
- γ radiation penetrating into the atmosphere produces more organics (especially if Fe(II) is present); biofilm consortia below might feed on radiogenic organics



Pertinent Pourbaix diagrams

- Any role for U photochemistry requires U(VI) in adflowing waters
- UO_{<<3} deposition by thermal reduction at the surface (mantle kept at same oxidation state for some 4 bio. years now)?
- U(VI) [and Cr(VI)] in old sediments





Stabilities of different speciation forms/oxidation states of uranium with (lower left) and without (top right) carbonate

Uranyl(VI) is formally unstable here (combined with biogenic organics like sugars, alcohols but would not actually react in darkness¹⁵

Can mobile U and (solid) Fe, Mn oxides coexist?

Assumption: thermodynamic equilibrium



earlier times: **magnetite** near 3.8 Ga-Akilia greenstone, **hematite** in all other (younger) BIFs, no O₂ in "air" yet: what does **uranium** do?



the Oklo case: mobile U
separating from MnO₂
(Mounana lagerstätte) → pH
> 11 or "chromatography"

Plausibility of coexistence of U(VI) and

organic matter

- U(VI) exists in samples almost 3 bio. years old (Crowe [South Africa]) but not in older ones
- Interaction with organics
- Photochemical or shock-wave-related supply of organics sensitively depends on CO and CH₄ abundances if there is not yet autotrophic life around



Sudden change of Cr, Fe oxidation state ratios and U mobility 2.96 bio. years ago (Crowe et al. 2013)

Thermodynamic constraints: Fe, Cr, C, and U

- Potential lines controlling CO/CO₂- and CH₄/HCO₃⁻ coexistence vs. Uranium speciation
- Stability of carbonatouranates: thermal and thermodynamic
- Photodeposition can only start with U(VI), no lower oxidation states, but there might be metastability
- MnO₂ catalysis of oxidation (cp. Oklo/Mounana [Gabon, aerobic age]) → does mobilize uranium, with Mn being retained when there are oxidants



Change of moderator **volume density** upon photo-, thermochemical alterations

Chemical, photochemical changes alter C volume density and thus extent of moderation \rightarrow reactor may respond by stopping operation or (violently?) increase activity; Role of water, organic liquids as co-moderator



Attack by urea and NH_4 carbonates \rightarrow Cu and UO_2 dication leaching, then photodeposition



Uranyl carbonate (top), Ca carbonatouranates

Torbernite (Cu uranyl phosphate, hydrated

Carbon association, processing and neutron moderation

- C volume density (-changes)
- neutron reflection at submerged interfaces
- Moderators at one side only (in between and beneath, not to the top)

Can there stable critical assemblies be "made" in this way?

- Photodeposition yields a stable array, whereas thermal decomposition of carbonatouranates (starts at T > 110°C) does not (carbonatouranate decomposition makes
 - phases with higher C atom volume densities in spite of CO₂ losses). On the other hand photodecomposition is a steady process which vents C-based n moderators in a controlled

manner

Details: stability of NFR operation (void coeff. Etc.)

- Carbonatouranates decompose at 110 – 200°C and increase moderator density (¹²C) → intrinsically unstable
- Photodecomposition of U(VI)organics produces volatile by-products, limiting heating after NFR operation began
- → NFR stability particularly doubtful in CO₂-rich atmospheres (Venus, Mars)
- Mars: dry ice or CO₂ hexahydrate as a moderator, with little organics, carbonates around?
- → it takes both organics and U(VI) to get this kind of NFR started in a controlled manner → window of redox potential, comparison to old-time geochemistry, how much organic matter available [photosynthesis more prolific than prebiotic chemistry!)?

mineral	Density (g/cm³)	Molar density (M/I)	C moderator density (M/I)	H modera tor density (M/I)	remarks
Liebigite $Ca_2[(UO_2)(CO_3)_3]$	2.41	45	13.6		
becquerelite	About 5.1	17.3	Low		
(UO ₂)CO ₃	5.7		17.3		Mineral names rutherfordine, didicherite; reacts with acids
UO ₃ grains/col- loids in vaterite	2.37+x		about 23		Produced by heating of liebigite
UO ₃ grains/col- loids in aragonite	2.73+x		26.2		"
UO ₃ grains/col- loids in calcite	2.93+x		28.2		u
UO ₂ in hydrocarbons			60 – 70	>100	Possible residue of uranyl carboxylate photochemistry
water	1.00		0	111	
UO ₂ ²⁺ in carboxylic acids (salts of)	About 3	Depends on RCOOH chain length	< 100	About 150 – 200	
UO ₂ ²⁺ in amino acids	About 4.5		About 40		
UO ₂ in pure carbon (graphite)		<190	Some 180		
UC	13.63		54.3		
U_2C_3	12.9		59.0		Stoichiometric compound
UC ₂					Reacts violently with hot water

Photochemical and thermal processing of U/C associations

- Carbonatocomplexes
- Organic ligands
- Stability limits of U(VI) [reduction in darkness]
- Leaching from underneath sediment, photodeposition
- UO₂²⁺ photochemistry separates it from possible neutron poisons even at high local redox potentials



Would NFRs work here already (on prebiotic Earth [Mars etc.])? 24

How far back in time? Chemical evolution or biofilm, existence of U(VI)

- Oldest U(VI) lagerstätten, presence of organics (black shales) [age vs. biogenesis]
- Contemporary association of ²³¹Pa (←²³⁵U) and ²³⁰Th (←^{234;238}U) with carbonate enrichments → U does actually form carbonatocomplexes now
- Carbonatouranate(VI) minerals and their thermal stability, decay properties

When might this (have) happen(ed)?

- Prior to biogenesis: ²³⁵U > 15% → chances for fast, little-moderated fission
- Less than 3.6 gigayears ago: more organic matter, less CO, ²³⁵U < 12%
- < 3 gigayears ago: uranium oxidation under atmosphere, U becomes mobile (besides CO?)
- 2.8 gigayears: "time limit" previously estimated by Kuroda

(No) role of earlier NFRs in chemical evolution?

- Efficiency, chemical pattern uniqueness of electron-beam related chemical processing of paleoatmosphere
- Prebiological chemistry produces tars and little polymers in which, moreover UO₂²⁺ does not accumulate (photochemical yields of esters, higher ketones, or longchain fatty acids are very low)
- Uranyl photochemistry destroys key intermediates of chemical evolution rather than advancing complexity
- U(VI) and lots of CO next to each other?
- Early mantle, volcano chemistry, recent Mars
- Which traces of NFRs, fission products can survive erosion?



Living beings might not stand direct NFR radiation but rather use (= eat) the radiochemical products

- Desulforudis audaxviator (highly distributed in recent deep sedi-ment layers): an autotrophic clostridium reducing CO₂, N₂ by means of radiogenic H₂
- Deinococcus radiodurans (high Mn content)
- Products of radiochemistry might be digested, contain very little toxines such as cyanide
- U photoprecipitation controls both "export" of U from NFR sites and keeps uranium toxic effects manageable at least to bacteria, archaea (and there was nobody else then)



traces left behind?

- Age of oldest U lagerstätten: the Kuroda conjecture
- Erosion of thin surface films vs. Oklo conditions
- Isotopic pattern remnants in rare but possibly fissiogenic elements (r-process contrib. always present but an additional share not to be found in meteorites even if there were complete mixing on Earth afterwards)
- For comparison: banded iron formations (photooxidation?)
- Nowadays many chemolithoautotrophic Archaea can still use CO, and hydrogenases have CO (+ CN⁻) as a ligand



BIFs are still abundant although very old, but exist in bulk rather than as/on a surface

Isotopic evidence 1: possible fission products

- With ancient NFRs, there are sites with and without admixtures of fissiogenic nuclides regardless of meanwhile erosion
- Fission during r-process or closely thereafter → should be homogeneous throughout Solar System
- Pre-Oklo NFRs: detectable effects in rare elements (Ru, Pd, Xe) particularly
- Photochemical isotopic fractionation: some depletion of ²³⁵U in U(IV) deposits (UF₄)
- Fractionation from other (e.g. redox, precipitation, biochemical) processes



Absolute Cumulative Fission Yields

Oklo product distributions: evidence for incomplete moderation (fast n fission of ²³⁸U)

Isotopic evidence 2: Ru, Te, Xe, bandwidth of ²³⁵U abundance

106

108

110

111

112

113

114

116

96

98

99

100

101

102

104

120

122

123

124

125

126

128

130

Te

- Maximum difference ⁴⁸ ^{Cd} between meteorites and ancient Earthborne deposits, closing the gap by ²³⁹Pu breeding, α decay ⁴⁴ Ru
- Heaviest natural Xe isotopes (^{134;136}Xe), variations in Ru isotopic compositions
- Similar with Ba, Ce,Nd, Sm (Mo too abundant)
- Very small variations • 54 Xe 124 in heaviest isotopes 126 128 of elements at A \approx 129115 (= symm. Fission, 130 131 very low yields), e.g. 132 Cd (top right) 134 136



(Why) Oklo is pretty different (probably)

- Not linked to surface (evidence for supercritical water in moderation of Oklo IX [p about 30 MPa]), no pressure changes during operation (would have altered solubilities of clays, organics, REE salts and thus influenced moderation, relocated fission products) → T dependence of moderation in sc-water related to n absorption energy spectrum
- Sandstone did not dissolve next to active core (it would in supercritical-fluidic water!)
- Much younger, less ²³⁵U → "device" dimensions, n poison exclusion and moderation much more critical → S Gabon sites probably unique on Earth



Four NFR zones from Oklo in crosssection

Could it happen elsewhere in the Solar System?

- Venus: U detected (Venera missions), carbonate chemistry under massive atmosphere
- Mars: are there organics?
- Satellites with (fairly) thin ice above deep water oceans, basins → photoproducts on ice layer (H₂SO₄ hydrate on Europa) but no photoprecipitation of uranium
- No contribution to astrobiology as previous local biogenesis would be required Martian simulation



Fig. 1. TSM tests with hematite. The C and U data points are the Viking PR analyses at the Chryse and Utopia sites, respectively (Horowitz et al., 1977). The solid line is the regression line derived from laboratory data which was obtained in pre-Viking tests using heat sterilized soils or no soils.

formation of organics over hematite (left) and maghemite; uranium would be mobile in a chloride or carbonate brine while aq. pH is close to neutral, allowing for PEC deposition of U(IV)



Should we (humanity) build one of this kind?

- It is probably feasible but not necessarily wise as it requires direct exposition of dust-forming, lipophilic HEU salts to air, dryness and UV radiation, yet:
- Inspiration for very ٠ uncommon, compact reactor designs (maybe for space probes, only to be activated after leaving Earth orbit while containing way less intrinsic radiation amount than any RTG or non-²³⁵U-based microreactor)



---- embedded moderators



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