



Natural Nuclear Fission Reactors (NFRs) older than Oklo: Biogeochemistry, photochemical Constraints, Relationship to ancient Biotas, Design and Applications of similar Arrays

Stefan Fränzle

Germany



Where is Zittau?

- Nearby former uranium mining sites ([old times-] GDR, CŠSR, Poland)
- Geochemistry, geological age of these sites
- Reactors at/next to Oklo (Gabon)
- Possible even earlier sites (Kuroda)









Oklo uranium open pit now after U mining was terminated

Recall some facts on early-Earth NFRs

- Oklo (Gabon): 1.8 bio. years old, moderation of NFRs by very hot to supercritical water; some 20 NFRs were excavated and identified
- Older ones: just indirect evidence; probably Cmoderated by organics, photochemical "ignition"
- Evidence from scatter of certain element isotopic patterns (cp. ISINN-22 proceedings, p.379 ff.)
- There are specialized bacterial biota which make use of radiogenic compounds for "running" chemolithoautotrophy, now distributed worldwide within "low biosphere"

Oklo XV NFR site, now accessible via a tunnel



F_P Pelit

- U(VI) is sole photo-active species → redox potential!
- UO_2^{2+} is activated by visible light ($\lambda \approx 450$ nm)
- Spin transfer and decay of triplet states of organics like aldehydes, ketones, amines, alkenes or
- Electron or H atom transfer (e.g. methyl ketones
 R-CO-CH₃ → ketene CH₂=CO → R; U^VO₂⁺ (water)
- E of excited state ≈ 2.4 V vs. SCE, τ_{triplet} < 1 μs → high selectivity, redox and spin deexcitation do compete depending on ambient compounds/ions, product UO₂⁺ is fairly unstable
- Only electron transfer will cause precipitation of UO₂ or other insoluble oxides, U chemical enrichment
- → formation of reactor depends on both presence of appropriate organics (must most likely be afforded by biota) and redox potential levels
- Effect of ionizing (ir-)radiation on redox potentials of mineral couples → NFR stability after formation, onset of criticality controlled by environment also

Photochem. U deposition



Ion pairs: spin (multiplicity) does matter while many ligands are stable towards photooxidation

- Photoredox processes in uranyl ion pairs: Os(III) does readily react whereas Ir(III) complexes bearing the same ligands (ox²⁻, Br⁻, I⁻) are inert (d⁵ vs. d⁶; electron transfer spin-allowed or not):
- Decomposition of aldehyde (solvent) → (several) CO ligands transferred to Os, permitting synthesis of unstable polycarbonyls also
- should likewise apply to Fe(III) vs. Fe(II) [second criterion for external redox potential!]
 - photochemical H abstraction by $[UO_2(OH)]^+$ (**pH = 5 – 8**), then elimin. of water;



Region of disproportionation of UO_2^+ , oxide precipitation



Radiation chemistry: ϵ of an electrode does increase under β -, α -, p- or sometimes n irradiation

- Effect independent of pH
- Some reported work includes effects from nuclear reactions (e.g. for W- or WO₃ electrodes exposed to 260 MeV protons [260-MeV projectiles would overcome Z = 74 Coulomb barrier for every projectile up to about Ni]), other
- Results consistent in sign of effect $(\Delta \varepsilon \approx + 30...+ 400 \text{ mV})$
- Low-T activation by semiconducting catalyst phases doped with radionuclides, e.g. ammonoxidation by Bi/Mo(⁹⁹Mo) oxides or CO oxidation by Ce (¹⁴⁴Ce or ²³⁸Pu)O₂





Left: mixed/intermediate oxid. State chalcogenide (gener.ptype), right: highest oxidation level Partition between sediment/NFR and aqueous overlayer by complexation: a blueprint for...?

Once sediment was produced involving biota, it contains lots of lipids and other esters

→ pronounced affinity towards UO₂²⁺ while other ions, including fission products get readily leached into water phase above, there causing radiation-chemical transformations

Principles of radiation-chemical ligand, "food" production

Ionizing radiation does process CO₂ and N₂, then CN⁻, ligands produced mobilize electron source Fe²⁺ and catalysts like Mo salts, Pb²⁺ as complexes





Ionizing radiation emitted by NFR or radioactive minerals Located in water or upper sediment solid phase reservoir of metal ions (mineral assembly, clays...); leached by ligands

General features of radiationchemical autocatalysis

Autocatalysis means an active species is multiplied by the very chemical or nucoear process (n in reactors!), with materials taken from some reservoir Desamination prevails over N inclusion, whereas HCHO, formate, glyoxalate etc. are readily formed from CO_2 by radiation \rightarrow elements for which $x_{2d} < 0$ are best extracted from solids (REEs, alkaline earths \neq Be,Mg; Mn, Mo, **not** V, Fe, Cu or Zn)

CO₂ (Fe²⁺/ α) → HCHO, HCOOH, succ² NH₄⁺ + RCOOH (β , γ) → AAS , lipids

catalyze transformations of HCHO, $CH_2=N(OH)$, possibly N_2 , CO Then more ligands increase metal ion leaching unlessbeing eaten by some biota ligated Fe²⁺, P

Alteration of inorganic species by radiation, change of element extraction (patterns) after onset of NFR activity

Radiation-induced organic chemistry in water layer, air affords organics most of which act as ligands, extracting some metals including fission products to the water layer, causing secondary radiation chemistry

Feedback interaction between some primitive biota and a NFR enabled by it

Distance NFR \leftrightarrow biofilm protects the latter from overly radiation while chemical entities can diffuse



fission-derived decay chains vs. AC feedback in radiation-

chemical catalytic chemistry

- Mo through Pd produce hydrolytically stable complex anions; Kr, Xe, Zr, Nb do not
- Radiation chemistry of some intermediate does produce certain ligands, enhancement and autocatalysis occur if
- a) ligands mobilize stable isotopes of same element (not prolific/impossible for Tc, PGMs, Ag but effective for Mo, Ce) and
- b) some ligand-forming reaction is catalyzed by the very element (e.g. Mo)
- → production of nutrients then available to biota even rather far from radiation source (NFR)
- Fission product elements effective in this respect, their substrates and pertinent products

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Is there an $(\varepsilon + \Delta \varepsilon)$ interval at near neutral pH which permits all

-0.4

-0.6

components to co-exist?

- Fe(II) required (not trivalent Fe!), Pb(II) must be stable
- N as NH₄⁺ rather than oxidized, N₂
- ε close to or above CH₄/CO₂- or CH₄/HCO₃⁻ -limits
- Which is the (redox) state of Mo then?
- Potential and pH range
- Possible precursor minerals; do they exist in Archaean sediments?



11

ńН

- 0.25 V

13

States of Ba, Pb, Mo determine fate of HCHO, yields of

amino acids

- Carbonate, sulfate levels, available Ba, Pb and catalysis of formose reaction (contribution by clays?)
- Radiolysis of cyanide (→ glycine, urea, some polymers) vs. its oxidation
 states of Pb, Mo

(right)



pH

Pb²⁺, Ba²⁺ are fully stable but anion-sensitive (precip.) while Mo forms MoO_2^+ (prone to disproportionation) but not Mo^{3+} (the latter might reduce both N_2 and oximes)



NFR with partial shielding of surrounding SC minerals

- Uranyl(VI) in lipophilic sediment layer; reoxidation near irradiated oxides → constrains external potential though CO₂ (besides CO) can contribute to radiation syntheses of substrates, ligands, nutrients
- G values for glycine etc. formation
- radiation-chemical processing of cyanide vs. stability of glycinato-, succinato complexes of various metals



HCHO produced from CO₂ would also react with cyanide, eventually both producing glycolate and catalyzing HCN transformations radiation-chemical potential shift and –shielding spatially organize e flow pathways

- E does increase (few exceptions) when exposed to ionizing radiation regardless whether oxide film on metal is a p- or n-type semiconductor;
- hydrogen-activating metals (Pt, Ni, Ru) turn into hydrogen electrodes upon irradiation → electrons will flow from radiationshielded to –exposed regions in mixedvalence (one- or twophase) systems, with clay, sand getting conductive in radiation



White arrows: direction of redox/radiation-induced electron flows, eventually releasing Fe²⁺ to water

Energy yields, G values during NFR formation and

Educt(s)	product	Kind of ioniz- ing radiation	G value [mol- ec./100 ev]
CO2, Fe ²⁺	НСООН	α (40 MeV)	
	succinic acid		
CN ⁻ _{aq}	Glycine	β (⁶⁰ Co)	
	Urea		
CO + N ₂ , water vapor	glycine	electron beam (1 MeV)	
	alanine		
Reducing mixture (alkanes, NH ₄ +)	glycine		
Alkanes, CO ₂ , moisture	Fatty acids		
glycine	HCO-COOH, aspartic and diamino suc- cinic acids	α, ⁷ Li (about 1.5 MeV)	

operation

Conversion of "excess" neutrons into ionizing (and causing radiation chemistry) entities:

- Fission, plus
- β decay of fission products
- (n, p)- or (n, α) reactions of ⁶Li, ¹⁰B, ³⁵Cl If a radiation-chemistry product does extract metal ions efficiently from NFR "core", G must be > 10⁻⁴

Radiation-chemical feedback by selective extraction of certain fission products besides of U(IV, VI)

- $CN^{-} \rightarrow glycine$, urea, polymers
- Moist CO + $N_2 \rightarrow$ amino acids
- CO₂ α, Fe²⁺ → HCOOH, HCHO, acetic, glycolic, malonic, and succinic acids
- Glycinate does form stable complexes with many metal ions which do not make stable cyano- or oxalato complexes → extraction, upwelling → fission products contribute to radiation chemistry near water/air interface, besides of halide ions (⁸²⁻⁸⁵Br, ¹³¹I...)
- Which elements will behave like this (minutes to days after precursors were produced by fission)? -
- Mass range for ²³⁵U fission 82 106 and 128 152 but only some fulfil chemical, radiation- and half-life criteria

The entire system: NFRs obtaining U from surroundings, fission products retained in aqueous phase

- Water over sludge; radiation can penetrate partly into air if water overlayer is sufficiently thin
- Partition changes along decay series and during prolonged irradiation of compounds in aqueous layer, fatty sediments, and air
- No secondary thermal alteration of glycine (stability conditions) but radiolysis
- Reoxidized (e.g. by contact with irradiated Fe oxides) U returns to lipid/ester-containing sediment, increasing NFR efficiency and lifetime
- Radioactive decay series mean isobars will deliver radiation energy to different layers/phases and thus irradiate different comp.



NFRs would leave behind tell-tale isotopic pattern shifts in certain elements

- Isotope patterns from fission are highly dissimilar of common ones (Ru, Nd at Oklo!)
- Even-Z or odd-Z where to look for the effects?
- Even Z: largest scatter of terrestrial, meteorite isotopic abundances associated with fissiogenic isotopes, such as ^{99;101;102;104}Ru vs. the other (lightest stable and ¹⁰⁰Ru) ones

Isotopic shieldimg in m = 113 is reduced by population of isomeric nuclear states \rightarrow compos. (variations) of indium can be used for detection!



Isotopic scatter evidence; even-Z elements Ru, Xe,

Sb, Ag

- Odd-Z elements have two stable isotopes at best
- Mattauch's rules preclude isobaric shielding in odd-M fission product decay series, unlike fission yields then cause isotopic shifts vs. "common" or "standard" distributions provided $[m_1/m_2] \neq [y_{m1}/y_{m2}]$
- "suitable" elements: Rb, Ag, In, (Sb), Eu
- Data avail. for Ag, Sb

element	Masses of "stable" isotopes	Abund- ance ratio	Fission yield ratio	remarks
Rb	85; (87)	2.593	0.515	Correction for decay of ⁸⁷ Rb
Ag	107; 109	1.076	4.454 (total yields small)	
In	113; (115)	0.0449	1.434 (total yields very small)	36% isobaric shielding by ¹¹³ Cd, no loss by decay of ¹¹⁵ In
Sb	121; 123	1.342	0.816 (total yields very small)	
Eu	(151 [α]); 153	0.916	2.590	no loss by α decay of ¹⁵¹ Eu; ¹⁵¹ Sm, ¹⁵¹ Eu n capt-ure cross- sections

But NFRs could **not** contribute to chemical, prebiotic evolution!

- Uranyl accumulation takes lipid-enriched sediments, and reduced forms of U can only form in appropriate potentials or from U(IV), organic coillumination (photochemistry)
- More heavy xenon (i.e., ^{134;136}Xe, possibly fissiogenic) in sediments << 3.0 bio. years old, unlike 3.5 Ga North Pole (W Australia)

Stability region of U in pre-Oklo NFR conditions allows U to stay in ist place while local oxidant avalability is required to transport to NFR site



No role of NFRs in biogenesis – but might someone feed on the products?

- Productivity, G values of radiation-chemical and/or catalytic transformations
- Carboxylic acids are readily formed in radiation chemistry whereas G for amino acid production is very small while β, α, ⁷Li nuclei (from ¹⁰B + n) cause efficient desamination (directly, not via H₂O₂) → any organism which exploits this C^{red}; (indirectly, by leaching) M^{essent.} source must tap another N source, e.g. radiogenic nitrate or NO from lightnings
- M supply from leachable sediment, minerals is reduced by consuming ligands by some biota

 → causes P limitation also, works best if x_{2d} < 0 (essent. metals: Mn, Mo)
- Desulforudis audaxviator
- A role for radiation chemistry in early nitrogen assimilation, besides making and transforming HCN, amino acids?
- Nitrogenases don't like free oxygen while [C/N] becomes smaller in aerobic organisms
- *D. audaxviator* also can use $N_2!$



D. audaxviator depends on radiogenic H₂ for sulfate reduction, ATP synthesis while fixing C from CO₂, carbonate)

Ru as a key fission product and its biorelated chemistry

 R'

R^{__N}

- RCN \leftrightarrow RCH₂NH₂ \leftrightarrow RCO-NH₂, including aminonitriles, hydantoin formation, (CN)₂ into AAN
- Ru complexes attack esters, lactones by hydrogenation but not amides/peptides
- Ru is enriched in laurite (Ru; Os)S₂, erlichmanite (Os; Ru)S₂, ruarsite (Ru; Fe)AsS particles (laurite pretty much distributed over Earth crust)
- Cytostatic agent; Ru(III/II) nucleobase complexes are photoactive
- Fission yields of ^{99;101;102;104}Ru
- Ru may do an excellent (hydrogenation or oxidation catalysis) job to bacteria, archaea next to some laurite... part-icle/crystal (provided ester hydrogenolysis is avoided) – but will a few cm³ with distinguished chemical properties/Ru accessability do to support an "exotic" stem of bacteria?
- (per)halogenates may be replaced with MnO₂ for oxygen transfer
- Ru in chemical evolution (Rasmussen)?

Species of vertebrates, large insects which did survive although restricted to few m² total area for long periods of time

- Fishes, frogs, toads, chameleons
- "Tree lobster"
- → when some m²/m³ will do in sustaining entire species of animals of 3 – 10 cm size (20 – 200 individuals), bacteria can run on much less space/ volume (probably ≤ 1 cm³)!
- → look for Ru-dependent stems/enzymes around sites where there are laurite particles!!
- Role of Ru in prebiotic evolution?
- Secondary replacement of Ru in enzymes by Fe, Co, Ni, Mo (nitrogenase)?
- Steps of evolution (towards chemolithoautotrophy?) around early NFRs?

Tiny chameleon Brookesia micra living under a single tree at a creek on a small Madegassian island

the entire habitat of desert pupfish *Cyprinodon diabolis* – 5 by 1.8 m!

How to build a NFR-similar microreactor – and for

- Reactors can start on very much lower intrinsic radioactivity levels than RTGs (25 kg ²³⁵U ≈ 2 GBq, α-emitters releasing some 5 kW therm ≈ 6 PBq)
- Criticality is achieved only after secondary blue/violet/ NUV irradiation on spot of operation
- Ester/formamide derivative partition, with DMF inducing photoreduction of uranium

G values for $(NO_2 + N_2)$ formation from aq. nitrate solutions; G ≈ 0.02 (3 M NO_3^-) corresponds to some $10^5 \text{ NO}_2/\text{fiss.}$ event \rightarrow efficient oxidative leaching from U supply even with dilute nitrate feed solutions

what purpose(s)

Design, properties of photoactivated NFR-inspired microreactors

- Combines U extraction and –photodeposition
- Subcritical when deployed, "missing" U then located in remote parts of solution phase(s)
- Photochemical production of extraction agent
- Carbon moderation by high-boiling organic layer to "cap" region where U is and gets deposited
- Avoiding criticality accidents prior to photochemical activation (in-solvent-moderation!) by e.g. Dy-(phosphate) glass or Ta-tubings for storage, photochemistry washes solid products to deposition
- Steam turbine run with (small part of) organic moderator
- Power output in kW range
- Needs less shielding than a RTG!

Radiation chemistry on top of a reactor and controlled self-supply, photoactivation

- radiation-chemical products oxidize UO₂ and mobilize, lipophilize uranium via UO₂²⁺, then there is
- reprecipitation by photochemistry directly above reactor, providing controlled supply, "ignition" of reactor
- ²³³U (from thorium dioxide blanket) or fissile transuranium isotopes might be transported in a similar manner
- Access of light (sun or artificial) activates reactor to add fissile matter to compact volume including moderator slabs or –liquids (bright green, bottom right)

Conclusion: neutrons, Fe(II) and uranium and CO_2 make modest food for bacteria, sustaining some NFR system!

Thank you very much for your kind attention!