

NATURAL NUCLEAR FISSION REACTORS (NFRs) OLDER THAN OKLO: BIOGEOCHEMISTRY, PHOTOCHEMICAL CONSTRAINTS, RELATIONSHIP TO ANCIENT AND PRESENT MICROBIOTAS, DESIGN AND APPLICATION OF SIMILAR POWER-SUPPLY ARRAYS

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Abstract

A previous contribution (this author, Proceedings ISINN-22, pp. 379 – 96) dealt with the possible superposition/crosswise influence **of formation of early NFRs from uranium** (which then was much more rich in fissionable ^{235}U) by leaching minerals, photochemical or redox deposition and (possibly) of **chemical evolution** predating origins of life. It was shown that for Earth's and similar conditions development of living organisms and biogenic organic-rich sediments must *occur before* NFR formation instead, even at the expense of an already reduced concentration of fissionable isotopes. UO_2^{2+} -related photochemistry is involved in both U oxide deposition and processing of organic moderators whereas any kind of thermal decomposition of carbonates would cause the NFR system to exceed criticality. However, as a rule UO_2^{2+} -related photochemistry does not alter the +VI redox state of uranium, both precluding separation of insoluble oxides and implying hexavalent uranium is fairly stable if in contact with the atmosphere and ambient minerals, unless for certain conditions and reaction partners.

The latter fact now is applied to constrain conditions and co-reagents of NFR formation. Much unlike Oklo (where moderation was accomplished by compressed hot to supercritical water vapor), this earlier NFR formation had to occur at an illuminated interface (Fränze 2015). One can consider contemporary bacteria making use of radiogenic compounds for chemolithoautotrophic self-support or/and displaying an exceptional degree of tolerance towards ionizing radiation as evidence of an early similar biota and its likely biogeochemical requirements. A meaningful **design of phototriggered fission microreactor** derived from such a NFR assembly is outlined and applications are suggested.

Introduction

Ever since fossil nuclear reactors were first presumed to possibly exist on Earth (Kuroda 1956) and then shown to have actually existed in Gabon (in 1972), but apparently not elsewhere (Apt et al. 1978) conditions of their formation and geochemical implications of their existence were discussed. This soon prompted assumptions (e.g. Draganic et al. 1983) inspired by organic and CN^- radiochemistry that these NFRs – or in fact much older ones, possibly operating in different conditions, using moderators other than water and so on – might have been involved in **chemical evolution**. This was assumed to have occurred either by radiochemical processing of otherwise rather inert chemical precursors (e.g., N_2 making NO_3^- in

water or HCN plus amines in an atmosphere containing CO and/or hydrocarbons). A possible pathway into “intriguing” compounds not considered before (see below) in spite of their role in technical organic synthesis would be on-early-Earth production of potent catalysts likely to increase yields of “interesting” products¹. Some of these catalysts are chemical elements or complexes thereof which were not present to appreciable amounts before rather than organic catalysts²; this implies in turn they had to be produced by neutron capture from rather abundant precursors or by nuclear fission (e.g. ^{99;101}Ru by n capture of Mo or, along heavier stable isotopes ^{102;104}Ru, by fission, with ⁹⁹Ru formation lagged behind by long lifetime of ⁹⁹Tc). Formation of powerful and versatile inorganic catalysts (during or preceding chemical evolution) by nuclear processes missed consideration before although multiple experiments in chemical evolution were done relying on such (however, non-fissiogenic) catalysts, e.g. Kobayashi & Ponnampuruma 1985, Saladino et al. 2012 (summed up in Markert et al. [2015]).

Except for α,n reactions using Be or ¹³C, this means there must be a more prolific neutron source than cosmic radiation or a natural nuclear reactor. Since mobility and accumulation of uranium are apparently linked to

- a) its being in the most-oxidized (i.e., hexavalent) state and
- b) to presence of oxygenated organics (esters, ketones, aldehydes, certain polymers) while the former is slightly oxidizing,

it is not yet obvious from which point of change of conditions on either Earth or Mars this might have happened, particularly whether any productive protobiological chemical evolution might have been possible in such conditions. From a chemist’s point of view, the assumptions by Draganic et al. (1983) and others require that

- 1) conditions of uranium accumulation, UO₂ precipitation, removal of possible neutron poisons and a setting for effective neutron moderation match each other and keep to the then limiting geochemical conditions and
- 2) postulated processes do agree with knowledge on pathways, yields of carbon-centered radiation chemistry (both productive, in terms of G values and destructive [radiolysis], including radiochemical equilibria) of species like amino acids, hydrocarbons + CO₂/carboxylic acids.

For example a postulated extraction (binding of uranium into some insoluble complex while leaving all the neutron poisons such as some REE isotopes, ¹¹³Cd behind³) or some precipitation process involving radiation-chemical products can be sustained only if radiochemical energy transfer by fission products (β decay will provide a sufficient number of ligands per radiation emission event, that is, $G \gg 10^{-3}$), allowing for radiation shielding by the outer layers of an NFR and its surroundings.

¹ E.g. ruthenium complexes (Ru isotopes contribute > 10% of ²³⁵U fission products) can mutually convert ethylene diamine derivatives and 2-aminonitriles, or the addition product of CH₂NH₂⁺ to acetate (-esters) into HCN trimer aminomalonodinitrile and *vice versa*, both mentioned compounds being starting points of further chemical evolution. Presence of transition metal catalysts will also “focus” reactions of known precursors (HCO-NH₂, [Saladino et al. 2012] aldoximes, hydantoine) in favor of “prebiotic” products such as amino acids.

² see e.g. Schwartz et al. (1984) for the role of aldehydes and α -substituted nitriles in HCN oligomerization

³ this can be done neither by reduction nor by H₂S (being radiolabile but not precipitating REEs but by **oxalate** (which is radiogenic, formed from aq. cyanide at very high doses or by CO₂ radiochemical reduction). Oxalatouranates and ion pairs with oxalatocomplexes of certain other elements are active, in addition.

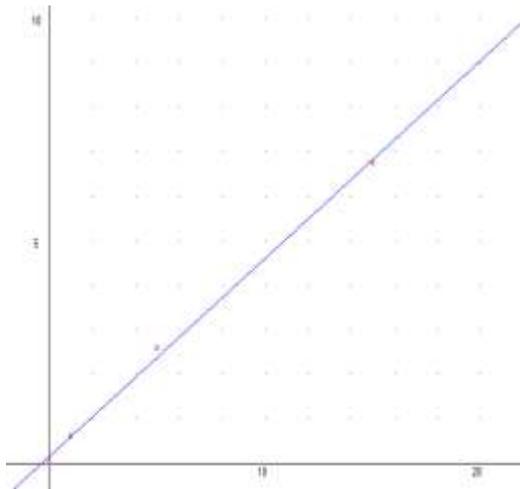
Previous work: U(VI)-induced photoredox chemistry, phase transfer, deposition to biomass

U(VI) dissolved in O-containing organic media (in particular, various aldehydes) to form ion pairs with complex salts of certain elements can simultaneously release CO and oxidize ligands like iodide, bromide or oxalate (but not chloride, glycinate, either linkage isomer of thiocyanate SCN^- or CO) in photochemical experiments to eventually produce multiply carbonylated (that is, containing M-bound CO) thiocyanatohalidometallates (and solid UO_2) (Fränzle 1992, 1996). More specifically, this author showed before (Fränzle 1992) that when solid oxalic acid $(\text{COOH})_2$ is suspended in a mixture of *mer*- $[\text{OsBr}_3(\text{CO})(\text{ox})]^{2-}$ and NaSCN codissolved in aliphatic aldehydes (propanal or butanal⁴) and exposed to glass-filtered sunlight along with **uranyl(VI) nitrate** (that is, $\lambda \geq 370$ nm), the dicarboxylic acid was consumed during irradiation. Besides of CO ligands released from aldehyde HCO groups, this affords a water-insoluble colorless solid without U(VI) undergoing reduction, thus requiring preelution of uranyl nitrate by diethyl ether on some silica column before separating the (TEA)-salts of (oligo)carbonylthiocyanatoosmates(II) like *mer*- $[\text{OsCO}_3\text{Br}(\text{NCS})(\text{SCN})]^-$ or *cis*- $[\text{Os}(\text{CO})_2(\text{NCS})_2\text{ClBr}]^{2-}$. However, uranium(VI) in ion pairs can also undergo photoreduction itself like in the formation of *fac*- $[\text{Os}(\text{CO})_3(\text{SCN})_2(\text{NCS})]^-$ and of several other SCN^- -containing di- and tricarbonylosmates(II) if **oxalate is absent** except for oxalato ligands in the educt complex⁵. Then, there will be no precipitates forming during irradiation, and U(IV) products (probably oxyhalides) can be removed along sodium salts NaSCN and NaNO_3 by chloroform extraction directly before chromatography. When replacing osmium in *mer*- $[\text{OsBr}_3(\text{CO})(\text{ox})]^{2-}$ by the respective iridium complex, however, spin conservation rules preclude an electron-transfer attack of $^3\text{UO}_2^{2+}$ on ligands of the complex; hence no reaction takes place.

Quite recent work showed that deposition of U on both chitin (an N-containing polysaccharide) and heat-devitalized moss (essentially, cellulose) has a substantial photochemical contribution increasing bound amounts of U steadily over 15 days at least, unlike all the other 17 elements (many transition and main group metals, Ce, coinage metals Cu and Ag, non-metals As, and Sb) investigated in this work on features of biomonitoring outflows from an abandoned uranium mine in Southern Poland (figs. 1 a-c). For these elements, adsorption to either moss or chitin is completed within a few hours then to keep constant or undergo some leaching (Fränzle, Gebauer, Kosior and others, to be published). Owing to the methods used for analyte retrieval it is not clear whether the observed continuous uranium(VI) photodeposition on chitin implies its reduction, however. Literature reports on cellulose acetate and cellobiose differ in this respect.

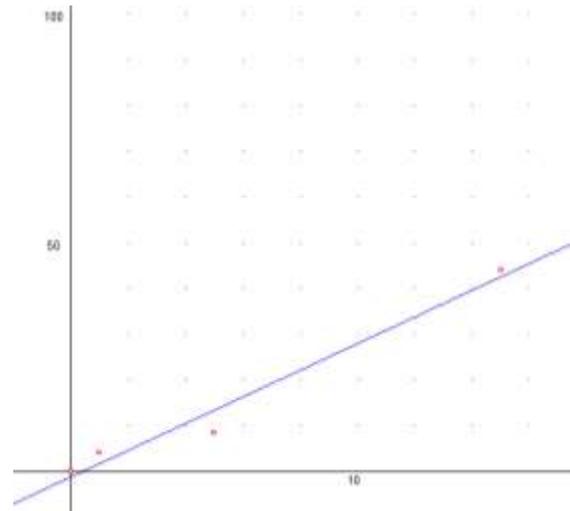
⁴ Oxidative attack onto bromo- or oxalato ligands (which both are replaced completely in these conditions) by triplet UO_2^{2+} ion pairs will introduce both CO and the linkage isomers of NCS^- but will end up in coordination polymers unless you add some halogenated hydrocarbon to the reagent mixture to provide additional halide ligands (Fränzle 1992)

⁵ although oxalate is an excellent precursor for metal ion photoreductions with CO_2^- radical anion as an intermediate, the same suppression of uranyl photoredox processes (also: Horvath & Stevenson 1992) is observed upon co-irradiation of UO_2^{2+} with oxalic acid or $\text{C}_2\text{O}_4^{2-}$ in either water or other solvents (e.g. Greatorex et al. 1974).



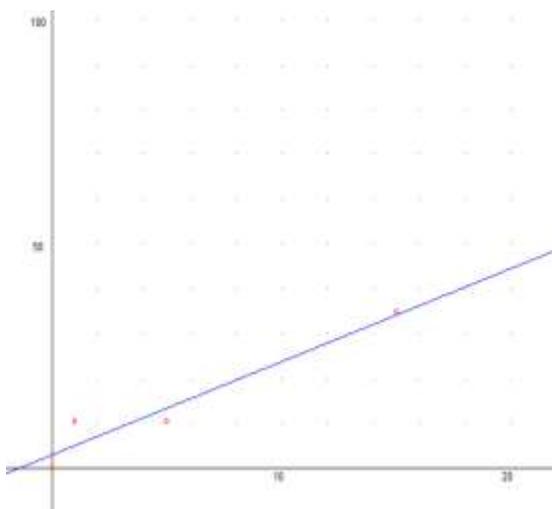
t (days)

Fig. 1a: Uranium content on chitin vs. time, 1st layer (slide/moss bag 2) [values in $\mu\text{g}/\text{cm}^2$].



t (days)

Fig. 1 b: Uranium content on chitin vs. time, sum of all layers (slide/moss bag 2) [values in $\mu\text{g}/\text{cm}^2$].



t (days)

Fig. 1c: Moss uranium content vs.time (moss bag 5) [values in $\mu\text{g}/\text{g}$].

Behavior of, ϵ shift in irradiated electrodes/metal oxide interfaces

When metal interfaces covered by oxides, aquoxides or sulfides of the corresponding metals⁶ are exposed to ionizing radiation (containing charged particles rather than X-rays or γ -radiation), the redox potential of the electrode will increase, making it more oxidizing (Byalobzeskiy 1971). This happens mainly by adsorption of OH radicals, then injecting h^+

⁶ This holds for every metal or alloy except of gold. The radiation chemical effect is largest for p-type surfaces like with Ni, Cu or Mn (some 300 – 400 mV) but occurs generally.

into valence band of surface chalcogenide or halide films, prevailing over that of H atoms (Feates 1960). Hence, if the surface layer does represent an intermediate (that is, neither the lowest nor the highest stable) oxidation state of the metal (which normally means it acts as a p-type conductor [e.g. Cu_xO , Fe_3O_4 , MnO_2 , $(\text{Fe,Ni})_y\text{S}$]), the irradiated part will become reduced (radiochemical disproportionation), obtaining electrons from shielded sites/region which latter thus become oxidized to the most, e.g. Fe approaching Fe_2O_3 by partial spatial irradiation of magnetite (with sulfides, the likely result will be formation of soluble M^{n+} and elemental sulfur). The result is given in fig. 2:

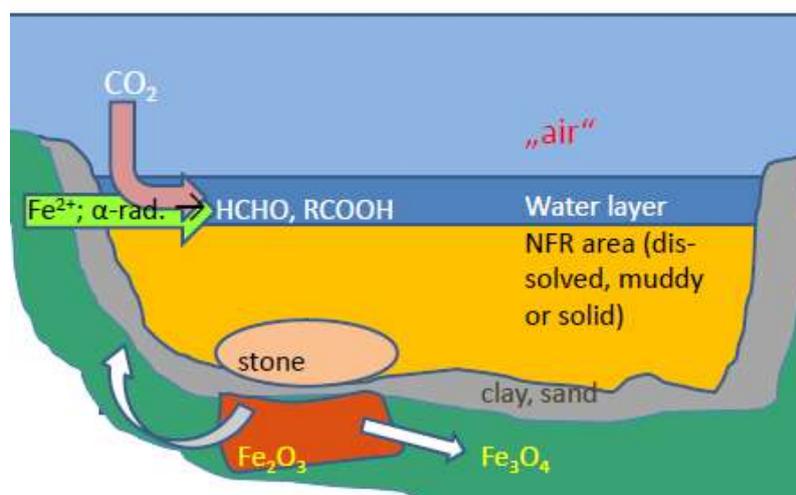


Fig.2: (mostly) biogenic organic matter, with some contributions from radiation chemistry one the NFR does operate, does attract and enrich uranium from a source. Whereas UO_2 would be stable besides of Fe(II) containing phases like magnetite, siderite, direct contact with hematite or other ferric oxides will oxidize, mobilize and "lipophilize" uranium. A stone on the ground can shield Fe-containing phases from ionizing radiation, producing an area where disproportionation of Fe takes place, with the white arrows depicting electron flow directions. Among the stones then U(VI) will ascend into the NFR layer, becoming back-reduced by photochemical processes and precipitating into the NFR core once it approached an illuminated surface. The organic matter in and around the NFR core is superior to (common) water in terms of neutron moderation. Also consider figs. 2 and 3.

A self-organized Reactor: Photochemical reduction of UO_2^{2+} concentrated owing to its lipophilic behavior, getting the Reactor critical

Given the pH is appropriate, Fe(III) thus enriched can oxidize tri- or- tetra- or pentavalent uranium (cp. fig. 3b for Pourbaix diagram of uranium [Takeno 2005]) into UO_2^{2+} , rendering it accessible both towards enrichment by oxygenic organics (e.g. biogenic sediments which use to be rich in lipids [fatty acid esters, long-chain ethers] produced by either bacteria or archaeans in the solid) and to photochemical precipitation. Accordingly, as long as there are stable mixed-valence Fe oxides (which means there are alkaline conditions as magnetite is stable only if $\text{pH} \geq 9$), radiation from an already operating NFR will dissolve uranium in lower oxidation states to have it precipitated by a combination of its lipophilic properties and photochemistry (both in hexavalent state) right there where the radiation is coming from while the

radiolyzed organics still contribute to neutron moderation. If phosphate is present⁷ photoredox yields and thus back-cycling of uranium will increase. In addition the combined radiation-chemical, photochemical and lipophilicity-related transport and (re-)deposition process of U will leave behind (and outside the going-to-be) NFR core neutron poisons present in common uranium minerals. In turn, certain fission products will be removed by hydroxycarboxylic acids from both the biota and radiochemical processing of sludge (cp. fig.4).

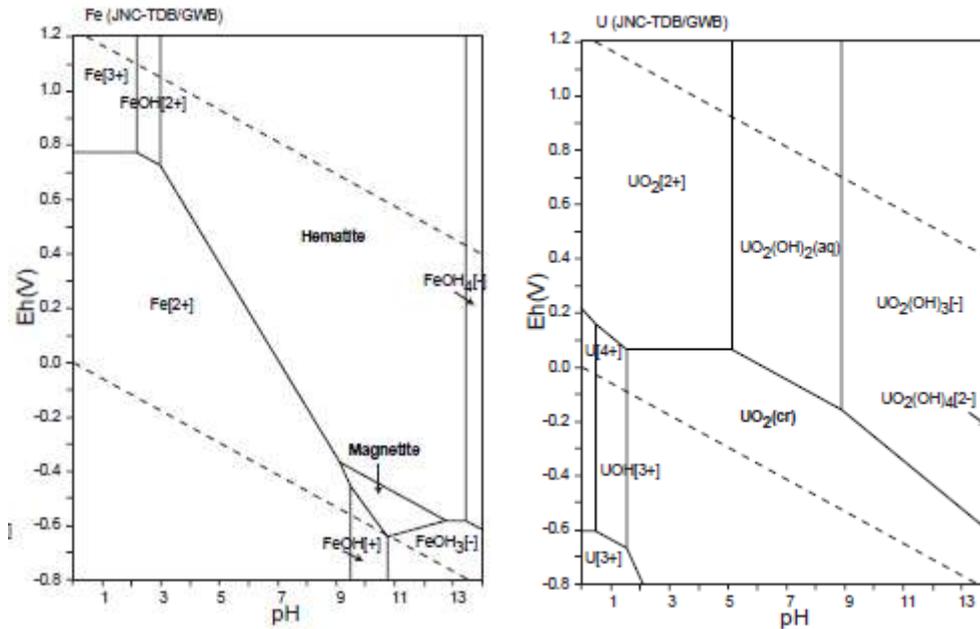


Fig. 3: ferric oxides (BIFs) would oxidize UO_2 once pH gets acidic ($\text{pH} \leq 6.5$). From Takeno (2005).

Moderation Regime, Control of Fuel Inflow

UO_2^{2+} is a rather peculiar metal (oxo-)cation insofar as it is rather lipophilic, can be readily extracted from aq. or aq. acidic media into esters, ethers, ketones (see the PUREX process involving tris-n-butyl phosphate for this purpose). Once organics are processed by radiation or Cu-catalyzed decarboxylation of R-COO^- , water solubility will decrease and the products will the more contribute to neutron moderation. Accordingly, the assumption NFRs were involved in chemical evolution and biogenesis amounts to defining a consistent scenario which affords such compounds (esters, ethers, ketones) at yields far in excess of any known “prebiotic” simulation while UO_2^{2+} would have to be mobilized subsequent to irradiation or oxidation of Fe-rich deposits far older than any known banded iron formation (for which $T \leq 3.1$ bio. y).

A depletion of fissionable isotopes (assuming ^{239}Pu breeding factor $\ll 1$) will thus be compensated by more efficient neutron moderation, meaning the reactor will keep steady operation. More UO_2^{2+} will be “attracted” by both (biogenic) esters (lipids). On pronounced heating, carbonates will decompose into CO_2 (Fränze 2015 for detailed data) while carboxylates

⁷ M(II)-uranyl or REE-uranyl mixed phosphates, e.g. torbernite ($M = \text{Ca}$) are rather common minerals. In presence of phosphate, the lifetime of excited $^3\text{UO}_2^{2+}$ (usually $1 - 3 \mu\text{s}$) does increase to $> 200 \mu\text{s}$, increasing yields of electron transfer with respect to fluorescence as a competing deexcitation pathway.

produce ketones (more volatile) and CO₂, in either case decreasing moderator efficiency while the latter thermolysis also reduces U accumulation in a sediment. Partition between some organic-rich sediment and overlying water⁸ also occurs with fission products, giving the following general features (fig. 4):

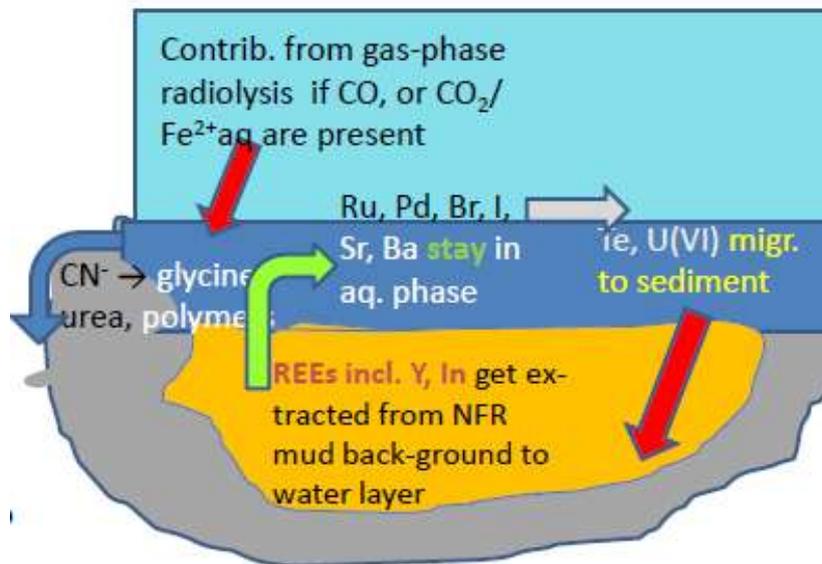


Fig.4: Processes to occur in and above the NFR during its operation. Since there is continuous inflow of fissile U and removal of fission products including neutron poisons while the moderators do not change chemical state or phase during operation, the "earlier" NFR is likely to operate continuously rather than in the intermittent fashion known from Oklo, oscillating between hot liquid (hydrothermal) and supercritical water.

Autocatalysis: catalytic chemical Feedback towards Reactor Operation and Processing of Organics

Autocatalysis here refers to any positive feedback mechanism, be it either chemical, biochemical or nuclear, by which operation of a NFR is supported by (some among) its very direct or indirect products. In every nuclear fission chain reaction, neutrons can be considered an autocatalyst as they both a) induce fission and b) [in excessive amounts] are produced by it. Likewise any kind of chemical process in which some fission product (most likely Ru or Pd) does induce formation of neutron moderators which more effective than water (i.e., some organics, here C_nH_y) or increase "inward" transport of uranium by complexation and/or extraction behaves as an autocatalyst with respect to enhancing nuclear fission rates, e.g.



Likewise, green plants produce N-free and nitrogenous compounds by way of photosynthesis which in turn depends on Mg complexes chlorophyll and rubisco, with nitrogen derived from soil liquid-derived nitrate by reduction effected by Mo and Fe and porphyrin (incl. chloro-

⁸ In contemporary aquatic sediments which are of biochemical organics mainly accordingly to log *k*_{ow}, that is, phase transfer enthalpies for cations between water and cyclohexanone or methyl isobutyl ketone (Marcus 1987) can be used to estimate accumulation in the solid phase.

phyll) biosynthesis from TCA intermediates and NH_4^+ being promoted by Zn, while the organic acids afforded by photosynthesis and consecutive reactions sequester all Mg, Zn, Fe from soil as an outer reservoir (Mo is absorbed by means of the sulfate carrier). Hence, when there are roots and Mg, Zn, Mo, Fe available photosynthesis is an autocatalytic (photoinduced catalytic) process. Thus a green plant is kind of a device operating on these four metals (plus other elements, of course) to process C and N resources into forms sequestering more Mg, Fe, Zn, Mo; right this is the essence of autocatalysis, with the effect amplified by growth and reproduction of the plant.

What might happen if light PGMs and other catalytically highly active elements are produced by fission in a NFR? Autocatalysis occurs once organic products obtained due to (in particular, but not exclusively) PGM-induced catalytic activity would improve neutron moderation and thus fission yields or else remove neutron poisons (by complexation and leaching) from the core. Much after biogenesis, effective moderators from an organic-rich soil might arise either from radiolysis or biological activity which draws upon some radiolysis products would give similar feedback provided G values are sufficiently high. Light PGMs (all Ru [most produced and also most efficient in these terms], Rh, and Pd) can reduce CO_2 (+ ammonium salts, nitrates) into organics when there is dihydrogen (either as such or produced from $\text{Fe}^{2+}_{\text{aq}}$ by radiation); among these organics carboxylic acids will dominate, like with α irradiation in the $\text{CO}_2/\text{Fe}^{2+}_{\text{aq}}$ system [Garrison et al. 1951]), then to mobilize uranium. As hydrogenation occurs in a catalytic manner here, using radiogenic aldehydes, amines (from hydrocarbons + N_2) or biogenic sugars as H sources, small amounts of Ru can finally transport sufficient U to sustain fission while parts of the catalytically produced organics will contribute to neutron moderation or/and photochemical (blue to NUV light) deposition of reduced U (and may "feed" nearby heterotrophic biota).

Amino acids, by the way, can be produced by ionizing radiation (X-rays, γ -, β -, p-, α - or heavier charged particles) in a direct fashion only in minute amounts (e.g., Dose & Etre 1958, Hasselstrom 1957; $G_{\text{glycine}} < 10^{-3}$) except for certain very well-defined conditions (CO-dominated moist phase [Kobayashi et al. 1989] or aq. cyanide/HCN buffer solution [Draganic et al. 1977]). Side chains of amino acids usually are not involved in metal ion complexation (Irving & Williams 1953; Sovago et al. 1993), hence complexes formed by the latter ligands are not more stable than those of glycinate, while the amount of the latter was decreased. Thus irradiation of an amino acid- or cyanide solution (in addition destroying most of NH_3 coproduced) would reduce mobilities of elements like Fe, Co, coinage metals but hardly influence dynamics of fission products other than light PGMs. Conversely $\text{CO}_{2\text{aq}}$ or CO_2/lipid radiochemistry in the reactor core affords (partly hydroxylated) carboxylic acids capable of removing REE fission products from the NFR "core" some of which, like ^{149}Sm , have very large n capture cross sections.

However, in more common conditions amino acids will be rapidly destroyed by radiation desamination (e.g. glycine in a ^{10}B solution exposed to neutrons to afford MeV-range ^7Li and α particles will be converted into glyoxylate and small amounts of aspartic and diaminosuccinic acids [Dale et al. 1949]). Matters would be different given there is ruthenium as a dehydrogenation catalyst (Murahashi et al. 2000) operating on **primary** amines radiochemically produced from N_2 and hydrocarbons; then, derivatives of sarcosine (N-alkyl glycines) will form besides of carboxylic acids both of which fully withstand some combined Ru/ H_2 catalytic attack.

(Biological) Catalysis by Fission Products, or: why to look for organisms/enzymes thereof depending on Ruthenium

On average, ruthenium is a very rare element on Earth (Emsley 2001) although there are mineral particles highly enriched in Ru (laurite, ferrolaurite $\text{Ru}_{1-x}\text{Fe}_x\text{S}_2$, ruarsite $\text{Ru}(\text{AsS})$, etc.). Every NFR must be distinguished by exceptionally high levels of Ru since the latter is a prominent fission product tending to stay at the spot. In „colloquial“ uranium mineral assemblies there are no distinctive enrichments of Ru or other PGMs whatsoever. Frankly, the % - level amounts of Ru present in Oklo lens uranium (rather than considering the strange isotopic compositions of both U and Ru, and other elements like Nd) alone thus should have caused considerations that something highly unusual had happened here.

Accordingly remnants of an adapted biota (which obviously then was entirely prokaryotic and monocellular given the range of ages of the phenomenon) might have retained requirement of Ru for some biochemical transformations best performed using ruthenium, while fissionogenic formation of much more abundant elements like Mo, Se, I... involved in biochemistry cannot be identified now against the high(-er) ubiquitous background of these elements, and a possible contribution from now extinct (decayed) Tc ($^{99,101}\text{Tc}$ forming Ru again) did vanish long ago. Candidate enzymes include both hydrogenases⁹ and oxidases converting glycine residues in peptides into oxamide bridges. Hence particular bacteria or archaeons might be spotted next to Ru-rich particles or in respective mines (many of which are located in Russia) as an evidence of former such situations even though the former NFRs were long dispersed by erosion, just leaving behind unbalanced isotopic distribution scatters (Fränzle 2015). As fairly stable populations of sizable vertebrates (certain kinds of fishes [e.g. *Cyprinodon diabolis*], frogs, and chameleons (like *Brookesia micra*]) and even much bigger arthropods (phasmid *Dryococelus australis*) can persist if the entire species is confined to a few m^2 (Glaw et al. 2012, Stohr 2009, Priddel 2003, Ritter 2006) in single water-holes or under single trees/scrubs (examples in tab.1), then sustainable populations of monocellular organisms might survive in $\ll 1 \text{ cm}^3$ net volume around such particles, that is, within the range of fast diffusion transport. Like recently essentiality of cerium was pinpointed in bacteria living near an Italian fumarole (Anonymus 2013), or the role of nickel in methanogenesis or reduced nitrogen cycling in plants was proven, corresponding bacteria or archaeons obtained from near such particles should be cultivated successfully only if there is an addition of Ru complexes to the culture medium (background levels being extremely low for PGMs other than Pd).

⁹ Contemporary hydrogenases operate on Fe and sometimes Ni, their structure (ligands like CO and cyanide besides of thiolate next to the two metal centers) suggesting a very ancient origin of these enzymes. In biology, the prim. amine/nitrile- or prim. amine/carboxamide (de-)hydrogenation equilibria are only established by Mo/Fe- or V/Fe combinations in nitrogenases which are poorer in performance concerning this reaction to a multitude of Ru complexes, including such which contain only ligands plausible in early biochemistry (e.g., no phosphanes)

Tab.1: examples of sizable animals which are confined to minute natural habitats (see text)

| Kind/taxon of an animal, max. body size | picture | habitat, size and location of minimal population known (year) | Picture, remarks |
|---|---|---|--|
| <i>Brookesia micra</i> (chameleon), 3 cm total |  | Under one tree near creek on Nosy Hara Island, Madagascar some 50 (in 2008) |  |
| <i>Dryococelus australis</i> ("tree lobster", arthropod), up to 16 cm |  | Under a shrub on cliff of Ball's Pyramid islet, Australia 24 (in 2001) |  |
| <i>Cyprinodon diabolis</i> (desert pupfish), 4.5 cm (male) |  | Devil's Hole Spring, New Mexico (USA) 41 adults (in 2006), total 70 – 100 |  water surface of pool ≈ 5 by 1.8 m |

Isotopic Traces of pre-Oklo Reactors: Evidence given by odd-Z Elements

Whereas the number of stable or very long-lived (e.g. ^{100}Mo , ^{130}Te) isotopes can be much larger in even-Z elements (up to 10 in Sn), and isotopic distribution scatters are large in otherwise sufficiently rare even-Z elements with Z between some 40 – 60 (Fränze 2015), Mattauch's rules of isobars produce likewise telling effects in odd-Z elements: except for D, ^6Li , ^{10}B , ^{14}N , ^{50}V , and $^{180\text{m}}\text{Ta}$, all stable odd-Z nuclides have odd M and thus even-numbered neutron numbers, and there is only a single "really stable"¹⁰ odd-M isobar in each case even though few isobars are very long-lived; hence there is hardly any isobaric shielding in β^- decay chains after production of some isobar by fission (e.g., fig.4) which f.e. precludes

¹⁰ Forming the minimum of potential curve of $^{2m+1}\text{E}^{2p+1}$ (where m and p are integer numbers), notwithstanding possible α or cluster emission decays, e.g. in ^{209}Bi and all heavier nuclides of this kind.

fissionogenic production of ^{96}Mo or ^{96}Ru owing to relative stability of ^{96}Zr . Accordingly large is the difference between “normally” observed isotopic distribution in odd-Z elements having (the maximum of) two stable or almost stable isotopes, and the results from fission. While for all these elements signals are large (tab. 2),

Tab.2: actual isotopic distributions and yield ratios from ^{235}U thermal neutron fission for odd-Z elements having > 1 (meta-)stable isotopes.

| element | masses of „stable“ isotopes | Abundance ratio in average terrestrial samples (light/heavy isotope) | 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 capture cross-sections |

| | | | | | | | |
|--|--|---------------------------------------|---|--|---|---------------------------------------|---------------------------------------|
| Sn112 0+ 0.97 | Sn113 115.09 d 1/2+ EC * | Sn114 0+ 0.65 | Sn115 1/2+ 0.34 | Sn116 0+ 14.53 | Sn117 1/2+ 7.68 * | Sn118 0+ 24.23 | Sn119 1/2+ 8.59 * |
| In111 2.8047 d 9/2+ EC * | In112 14.97 m 1+ EC,β * | In113 9/2+ 4.3 * | In114 71.9 s 1+ EC,β * | In115 4.41E+14 y 9/2+ β ^{met} * | In116 14.10 s 1+ EC,β * | In117 43.2 m 9/2+ β * | In118 5.0 s 1+ β * |
| Cd110 0+ 12.49 | Cd111 1/2+ 12.90 * | Cd112 0+ 24.13 | Cd113 5/2E+15 y 1/2+ β ^{met} * | Cd114 0+ 28.73 | Cd115 53.46 h 1/2+ β * | Cd116 0+ 7.49 | Cd117 2.49 h 1/2+ β * |
| Ag109 1/2- 48.161 * | Ag110 23.6 s 1+ EC,β * | Ag111 7.45 d 1/2- β * | Ag112 3.130 h 2(-) β * | Ag113 5.37 h 1/2- β * | Ag114 4.6 s 1+ β * | Ag115 20.0 m 1/2- β * | Ag116 2.68 m (2-) β * |
| Pd108 0+ 26.46 | Pd109 13.7012 h 5/2+ β * | Pd110 0+ 11.72 | Pd111 23.4 m 5/2+ β * | Pd112 21.03 h 0+ β * | Pd113 93 s (7/2)+ β * | Pd114 2.42 m 0+ β * | Pd115 25 s (5/2+) β * |
| Rh107 21.7 m 7/2+ β | Rh108 6.0 m (5+) β * | Rh109 80 s 7/2+ β | Rh110 3.2 s 1+ β * | Rh111 11 s (7/2+) β * | Rh112 2.1 s 1+ β * | Rh113 2.90 s β | Rh114 1.85 s 1+ β * |

Fig.5: there is reduced isotopic shielding of ^{113}In formation owing to intermediate populations of nuclear isomers (36% of $^{113\text{m}}\text{Cd}$) in m = 113 β decay series.

isotopic ratios and their scatter in terrestrial samples are not so well known as with certain even-Z elements as to identify such effects readily. In Sb, the fissiogenic isotopic shift (and thus scatter among samples) would be small, and additionally in the direction of smaller shares of the heavier isotope, like with chemical kinetic isotopic fractionation. In Ag, In, and Eu effects would be dramatic and contrary to possible results of chemical fractionation; among these only Eu would undergo redox speciation in ambient conditions (both reductive and photochemical [consuming quite diverse kinds of organics] formation of Eu^{2+} [Horvath & Stevenson 1992; Nozaki 1997]). Data on scatter of isotopes compositions of odd-Z elements are less available and precise than for certain even-Z elements. Data are available for Ag ($\pm 0.05\%$) [Desaulty et al. 2011, Chugaev et al. 2009], Sb (depletion of ^{123}Sb of some 0.3% in earth crust/upper mantle [the regions where remains of early fossil reactors would turn up after erosion and/or subduction] (Rouxel et al. 2000)). Nevertheless one can guess that in early NFRs located in the uppermost Earth crust some 0.1 – 0.2% of original ^{235}U underwent fission.

Conclusions

Some Role in Chemical Evolution? , or: why this kind of reactors would not operate unless there already is an extant Biota

Given realistic geochemical conditions on a Protobiotic Earth, the yields of water-immiscible uranium-attracting organics (thereafter to act as an efficient combined [H and ^{12}C -] neutron moderator additionally) would be very small, and in addition this effect is limited to hexavalent uranium (not even UO_2^+). The oldest geological sample where there is evidence for this highest oxidation state of U is < 3 bio. years old, well after the phase of chemical or protobiological evolution). However, banded-iron formations are a little older and capable of mobilizing uranium at appropriate pH.

Fossil Reactors were not suited for making Life in the Beginning but possibly then could sustain it Locally: the lesson from *Desulforudis audaxviator* and highly radiation-tolerant bacteria

Radiation chemistry can provide some nutrient accessible particularly to chemolithoautotrophs if the latter either withstand radiation or the product, such as H_2 , readily undergoes diffusion into “safe” sites. Accordingly some microbial biota (the only one existing then unless for large bacteria-made colonies such as stromatolithes) might feed on radiation-chemical products given these display sufficient radiostability to escape radiation sterilization or destruction of primary products. A realistic setting might produce N-formyl amino acids and peptides from amino acids when there are (fissiogenic) Ru as a catalyst and some source of H_2 while oxalate formed by radiolysis of HCO_3^- or glyoxylate oxidation will bring about precipitation of REEs, Sr and Ba leaching out of the core. Biological consumption of either product in turn will stabilize reactor performance over time, with lipids from some biofilm enhancing uranium enrichment at the NFR site particularly if exposed to radiation (radio-chemical carboxylation of hydrocarbons).

Design and possible Applications of similar Devices (microreactors)

Colloquial RTGs (Seebeck-effect devices converting heat emitted from radionuclides such as ^{242}Cm , ^{238}Pu , ^{210}Po , ^{227}Ac , ^{90}Sr ;Y or ^{147}Pm into direct current omitting moving parts) used in

deep-space missions are distinguished by extremely high initial radioactivity: useful thermal outputs of several kW (e.g. in 125-W_{el}-power supply device in “Curiosity” Mars rover), that is, an energy release rate of several 10²² eV/s which translates into typical activities of some five PBq with α-emitters and even several dozen PBq with β emitters. Compared to this, the initial activity of a somewhat subcritical mass of ²³⁵U (and even of ²³³U) is outright negligible. We thus can use the process of photochemical U^{red} deposition to amass a critical mass required to start a nuclear fission reactor only after bringing it to its position, e.g. operating in a spaceprobe. For this purpose, the oxidant properties of NO₂ can be used to transport additional U(VI) to an almost completed reactor where light or UV radiation will deposit it as UO₂ using some organic¹¹ compound as both a sacrificial oxidant and additional neutron moderator (N,N-dimethyl formamide is completely miscible with water, for the radiation chemistry of either neat, FeCl₃-containing or aq. DMF see Colebourne et al. 1963)

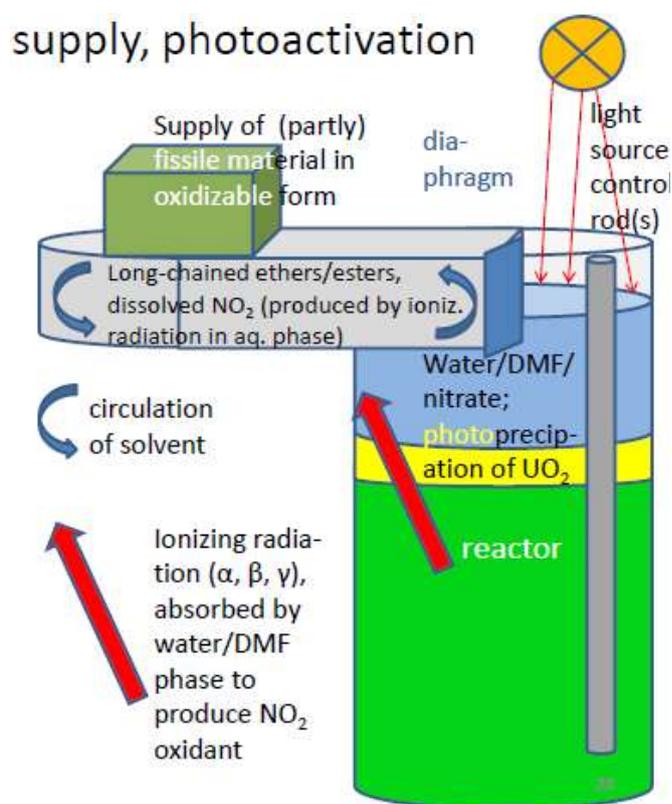


Fig. 6: irradiation of a nitrate solution affords NO₂ capable of oxidizing and dissolving UO₂. The uranyl salts forming do partition between water/DMF¹² and are precipitated on top of the protoreactor (design similar to Romashka [USSR 1964]) to reach criticality after some period of illumination. Dimethyl formamide acts both as a photoreductant (cp. Greatorex et al. 1974) and moderator component.

¹¹ Inorganic photoreductants like bromide or iodide could likewise be used but afford colored (impeding further photoreduction) and reversibly acting oxidant species, thus decreasing net quantum yields.

¹² Long-chained ethers do dissolve uranyl salts while they are as immiscible with formamides like with water. Extraction of metal complexes from DMF solution into such ethers by long-chain quaternary ammonium salts was demonstrated in the author's lab (2015, unpubl.).

After placing the reactor at the site where it is going to operate, light will be shined on top of the water/DMF layer covering the reactor core. Photoprecipitation of additional UO_2 will render the device critical then, with the control rods and the transport rate of U from some external reservoir (top left) jointly controlling output and –continuity of power. The internal structure would be fairly simply, with intermittent slabs of nuclear fuel and moderator like in the Romashka device. Since such organic solvents will not withstand temperatures $\gg 200^\circ\text{C}$ for long, power conversion cannot efficiently be done by the Seebeck effect but has to make use of moving parts.

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