Natural Fission Reactors Other and Older than Oklo: Likelihood and Isotopic Data – a Scenario from Geo(photo)chemistry and Chemical Evolution

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Abstract

Geologically formed natural fission reactors (NFRs) might exist at sites other than S Gabon where they were identified in the 1970ies, but their formation requires presence of organic matter in kinds and amounts unlikely to have been available during any phase of chemical evolution except for optimum ^1H moderation conditions. Rather, if such NFRs with ages >> 2 bio. years should be found, they are related to surfacial **UO₂ photodeposition** next to biomats or sediments rich in biogenic organics like lipids, sugars and other esters, aldehydes. Ranges of isotopic data for rare medium-heavy elements ($Z \approx 50$) like Ru, Te and Xe strongly suggests such processes to be operative in the margins set by variation in $^{235}U/^{238}U$ outside Oklo. Intrinsic stability of such old NFRs in photochemical vs. thermal moderator modification is analyzed. Modern microbiota feeding on products of radiation chemistry like *Desulforudis audaxviator* might have evolved next to such NFR sites, like extremely radiation-tolerant bacteria, but there probably is no role in chemical evolution.

Introduction

The "Oklo phenomenon" refers to remains of (now inactive) stably self-sustained natural (geochemically arranged) nuclear fission reactors (NFRs) discovered in Southern Gabon in early 1972. The first to describe conditions for NFRs to form near surface of early Earth were G. Wetherill (in his 1953 PhD thesis) and P.K. Kuroda three years later, agreeing that it would take formation of high-grade uranium minerals near some chemical gradient, fractionation to remove neutron poisons and ample effective moderators to operate a reactor, the moderator being either water (maybe supercritical vapor like in some Oklo sites) or some organic or inorganic carbon compounds.

 Later-on bacteria were discovered which metabolize energy-rich compounds derived from radiation-chemical reactions alone or/and are highly resistant towards ionizing radiation (*Deinococcus radiodurans, Desulforudis audaxviator*). Probably such adaptations would not have evolved or preserved until today if there had not been valuable ecological niches for both (chemo-)auto- and heterotrophs in which metabolic energy and key compounds are afforded by radiation chemistry, and not just here or there but as a fairly common phenomenon. Beyond being a possible source of resources to bacteria, radiation-chemical processes hence might even have had a role in chemical evolution; corresponding work on amino-acid synthesis started already in the 1950ies (e.g., Palm & Calvin 1962). The prolific production of glycine, other amino acids, formamide, urea, hydantoin, and NCO^- from ionizing irradiation of aqueous cyanide (pH = 9) [Draganic et al. 1977[1], Shen-chu et al. 1981] and radiation-

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[1] Ogura et al. (1972) had already described formation of polymers and other nonvolatile compounds or precursors thereof (cyanates, aminonitriles) prior to acidic solvolysis yielding mainly HCHO, NH_4^+, glycine, oxalic acid from products of acidic HCN solution radiolysis but met little attention.

chemistry of moist CO + N_2 introducing N into organics by charged-particle beams (Kobayashi et al. 1989) were described only later.

In fact, it is very difficult to obtain HCN, HC_2CN, NO, amino acids etc. from EUV photolysis of moist CH_4/N_2-, CO/N_2- or hydrocarbon/alcohol+N_2 mixtures as both threshold wavelengths for N_2 photodissociation or CH formation from whatever hydrocarbon are very small [$\lambda \ll$ 170 nm], and both these photochemical transitions and secondary hydrocarbon- or water/N atom reactions are spin- or symmetry-forbidden. Yet the knowledge available in the 1970ies on radiation-chemical reactions and discoveries at Oklo prompted several authors to invoke similar NFRs to be crucial in chemical evolution as key processing sites producing appropriate energy, highly excited chemical intermediates and possibly catalysts. It is an open issue whether this assertion is viable given the present body of knowledge on radiation chemistry as well as uranyl-dependant photochemistry and Fe-containing phases of different ages on early Earth. Thus NFRs might be involved in biogenesis on Earth and possibly elsewhere: chemical transformations of C-, N- (including N_2) and P compounds induced by ionizing (particularly, charged particle) radiation copiously produce certain compounds which would be hardly available otherwise.

Due to decrease of ^{235}U (decaying some 6.3 times faster than ^{238}U) in uranium ore or mineral deposits, there are no recently operating NFRs; a fission reactor chain might be sustained on contemporary natural uranium only in conditions of ideal carbon (or deuterium, molten sodium which both are geochemically implausible) moderation now (Fermi 1942 [Stagg Field (Chicago) Reactor]. Matters were different in earlier times, meaning such NFRs were (much before Oklo [about 1.8 bio. Years old]) so abundant as to

a) sustain a specific biota based on its radiation chemistry and
b) leave behind traces in isotopic composition of rare elements certain isotopes of which (but not others[2]) ;

accordingly their role needs clarification even with evidence falling short of excavating such a structure as happened in S Gabon. Essentially disregarding the possibility of carbon moderation on a planet loaded with both carbonate minerals capable of forming $[UO_2(CO_3)_3]^{4-}$ ions and soil/sediment organics which would "shroud" photochemically active uranium-rich sites with hardly volatile organic photooxidation products , earlier authors missed conditions for NFR formation related to both uranyl(VI) cation photochemistry (e.g., Rao & Rao 1958 using lactic acid or the traces of diethyl ether soluble in water) and solution properties (which both are unique among inorganic photosensitizers [Greatorex et al. 1974, Fränzle 1992, Fränzle 1996]).

In addition there is a feedback loop as radioactive fission products can turn CO and other simple not fully reduced or oxidized compounds into organics given β⁻ electrons and γ radiation leak out into atmosphere or hydrosphere from the NFR surface, i.e., if it is not buried under thick sediment layers. Either process is bound to occur at some illuminated surface, be it on land or in shallow, clear waters. NFRs once formed there would be capable of enhanc-

[2] no information can be obtained from analyzing monisotopic elements produced from fission such as Rh

ing their moderation while there is a supply of soluble, somewhat lipophilic UO_2^{2+} which, however, requires some minimum ambient redox potential to maintain its state, mobility, photochemical activity and lipophilic and coordination-chemical accumulation features by erosion.

Materials and Methods: chemical data, analysis of isotopic distributions beyond chemical fractionation

Uranyl photochemistry, and density data of uraniferous minerals before and after thermal CO_2 loss are analyzed for moderator density evolution with time and energy input, also covering the issue of reactor stability:

- once formed and sustaining fission chain reactions, is it bound to become overcritical sooner or later or will it run in a stable manner?
- Considering radiation-chemical effects around the NFR, how will they possibly affect replenishment of uranium, removal of fission products and neutron poisons and possibly add more moderators from C sources in atmosphere or aqueous solutions?
- How stable are the involved components under different atmospheres? Is there some bias in isotopic fractionation which does differ in sign or relative size from those which are predictable from local chemical-kinetic fractionation?

Literature data and the author´s own experience on uranyl-sensitized organic and metal-complex photochemistries (symbolized by fig.1) are analyzed to answer the above questions. Experiments other than on U(VI) photochemistry were not yet done but are meant to be motivated by this report (see below).
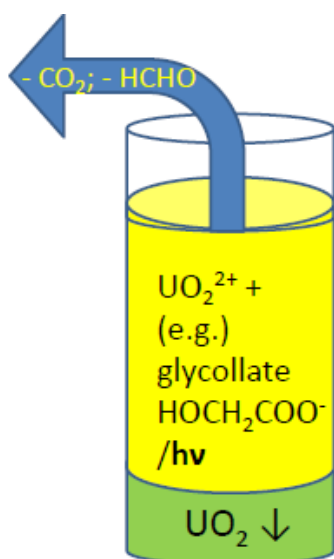

Fig. 1: UO_2 precipitation by photooxidation of organic acids releasing CO_2 and aldehydes. The yellow color of the liquid (aqueous-organic or purely organic) supernatant corresponds to that of uranyl dications.

The general setting: how to "make" a NFR

Beyond the general criteria outlined by Wetherill and Kuroda before, carbon moderation would modify (reduce) the threshold level of fissionable nuclides of NFR onset with respect to ^1H moderation, thus possibly extending the timeframe in which such structures could commence operation. Uranium getting accumulated by thermo- or photochemical reduction at some site requires prior mobilization of UO_2^{2+} and its extraction into unpolar phases, sediments which can be caused by contact with common ambient oxides like ferric oxides (fig.2b)
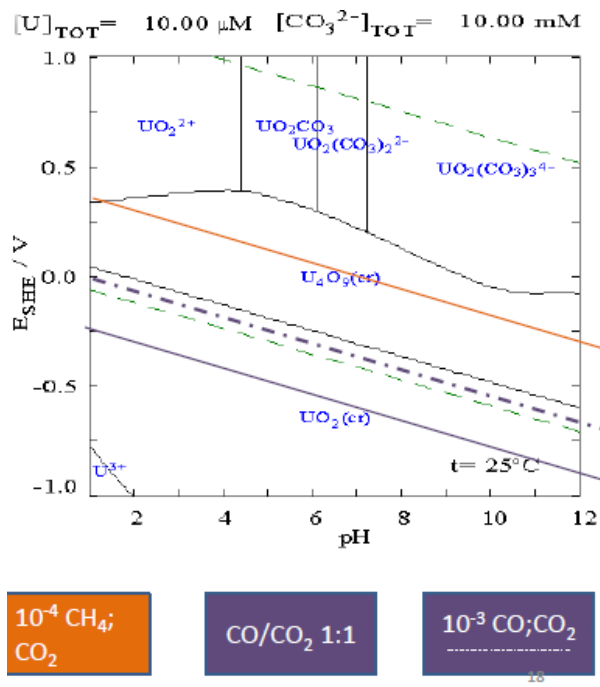

Fig. 2a: uranyl cations (complexed with carbonate if conditions are not distinctly acidic) are unstable towards reduction under every likely prebiotic (left: upper limit for methane content consistent with geochemical results, center: composition of Earth´s early atmosphere considered most likely now) and present Martian atmosphere ($CO_2/CO \approx 1000$; right) at any pH and next to organics like sugars while hematite layers and BIF-like assemblies can be produced by photochemical processes themselves (Braterman et al. 1983). Hence, U being driven into some shallow pond will (photo-)precipitate as UO_2 there, intercalating some organics thereafter acting as a moderator within the NFR.
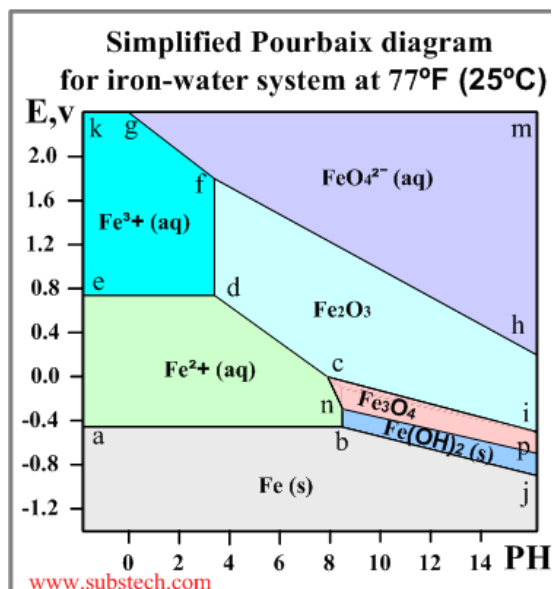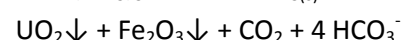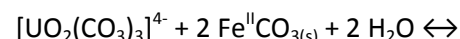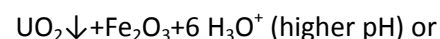

Fig.2b: Chance of realizing direct thermochemical rather than photochemical precipitation of UO_2 according to

$UO_2^{2+} + 2\ Fe^{2+} + 4\ H_2O \leftrightarrow$

$UO_2\downarrow + 2\ Fe(OH)^{2+} + 2\ H_3O^+$ or

$UO_2^{2+} + 2\ Fe^{2+} + 9\ H_2O \leftrightarrow$

$UO_2\downarrow + Fe_2O_3 + 6\ H_3O^+$ (higher pH) or

$[UO_2(CO_3)_3]^{4-} + 2\ Fe^{II}CO_{3(s)} + 2\ H_2O \leftrightarrow$

$UO_2\downarrow + Fe_2O_3\downarrow + CO_2 + 4\ HCO_3^-$
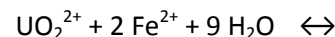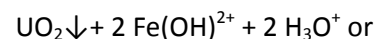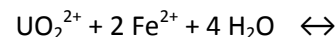
followed by decomposition of moist siderite (Fe(II) carbonate) to yield magnetite and organic compounds .

At the intersection of the violet pointed line with cd or ci the respective redox reactions become reversible. While interception of UO_2 can also be accomplished by photooxidation of something else, contact with ferric oxide phases would reproduce U(VI) mobility if pH < 5. Then, particles or complexes containing reduced uranium will be **oxidized** by contact with solid hematite, maghemite (or acidic [natro-]jarosite (Na, H, K)$Fe(SO_4)_2$*xH_2O) to yield soluble UO_2^{2+} which then will be extracted into unpolar oxyorganics, Fe^{2+} being a by-product. At pH > 8 (corresponding to present marine conditions or soda lakes) the U(IV/VI) line runs above the Fe_2O_3/Fe_3O_4 (magnetite) transition (line ci in the above diagram.

While aqueous uranyl(VI) is readily reduced on both pyrite and magnetite interfaces, a reduction on hematite (all three Fe materials are semiconductors) takes reducing the redox potential to - 0.1 V or less by an external bias (Renock et al. 2013). Accordingly if there is exposed or near-surface magnetite while presence of oxidants and liquid water elsewhere allows for uranyl elution (as possibly was on Mars) and subsequent deposition of UO_2 on magnetite. Conditions were different on prebiotic Earth, however. Thus magnetite cannot cause uranium mobilization by oxidation (see position of line np well at negative potentials), thus uranium could not be mobilized and enriched into high-grade ores/minerals before banded-iron formations containing Fe_2O_3 layers (BIFs) formed first (dated at some 3.1 – 3.2 bio. Years BP, corresponding to some 9 – 10% [235]U in the mixture). Older ferrous concretions, e.g. at Akilia and Isua sites (Western Greenland, both located next to Greenland´s capital city Nuuk and > 3.7 bio. years old, could not make use of solid U-containing particles. At 3.2 Gy, however, even ores or secondary sediments having just some 20% uranium content might sustain the reaction. Photooxidation of Fe^{2+} by triplet uranyl is rapid and efficient; however, unlike with alcohols or aldehydes which afford strongly reducing secondary radicals such as RCH-OH or R´-CO upon uranyl attack the reaction is likely to be reversible by backward electron transfer from $U^VO_2^+$ to Fe^{3+} or $Fe(OH)^{2+}$ (line de located above the U redox system) if pH is appropriate, less so in organic media.
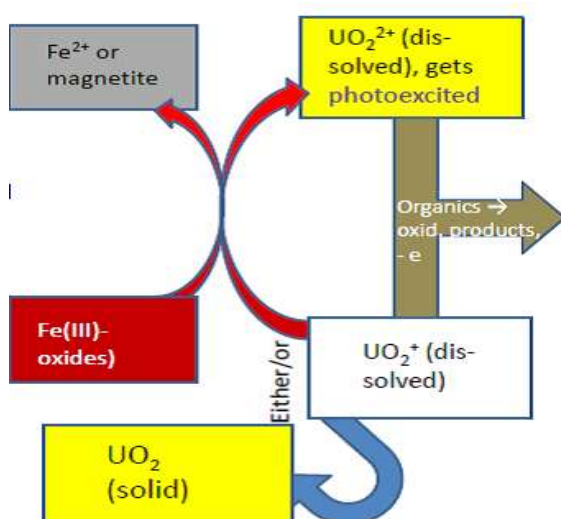
Building a fractionation cycle (fig. 2c)

Fig. 2c: mobilization of uranium in contact with ferric mineral phases, photoprecipitation of secondary UO_2.

and finally a sandwich assembly of UO_2 and water, carbonate, organic ^{12}C moderators (fig. 3) going to act as a NFR:
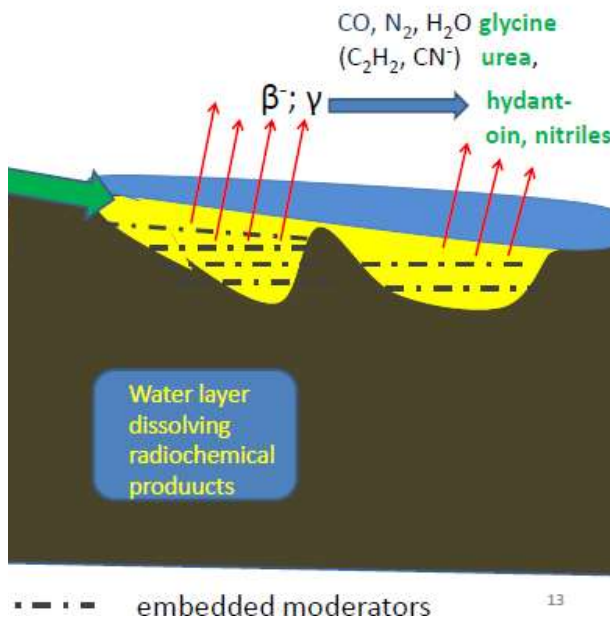

Fig. 3a: setting of a reactor to form and subsequent radiolysis of overlying matter producing additional organics which provide both a feedstock for radiation-insensitive organisms and a moderator for sustaining fission (amino acids are not volatile, and most of their simple and complex salts are hardly soluble in water. The same holds for alkaline-earth salts of long-chained carboxylic acids).
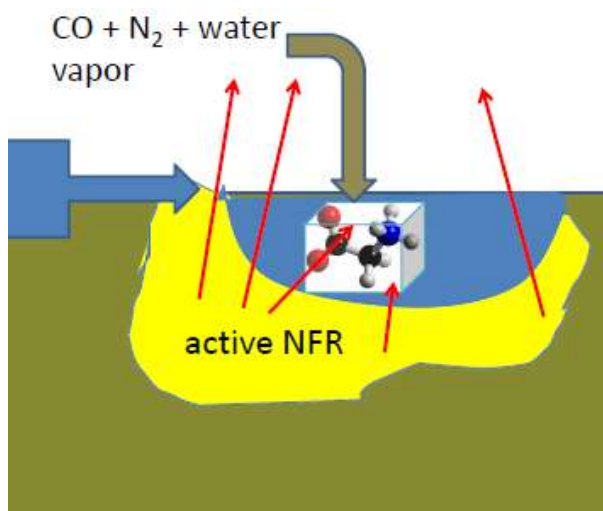
Fig. 3b: radiation-chemical production of organic potential moderators by β and γ radiation leaking from a close-to-surface NFR into a CO-containing atmosphere. The arrow from the left denotes inflow of water containing dissolved UO_2^{2+} or carbonatocomplexes thereof. In addition, aqueous volatiles or their precursors (water, HCN, CN^-) are turned into less volatile carbonaceous compounds retaining above and providing neutron moderation while penetrating the NFR structure, giving e.g. formamide, urea, glycine, and an oily organic polymer (see Shen-chu et al. 1981) at sizable radiation-chemical yields (i.e., G >> 0.1).

Fig. 3c: the complete matter cycle producing local heavy isotope enrichments. After erosion (this is a surface-confined phenomenon), traces would still be left in isotopic patterns varying with site.

Analysis of isotopic data for an Estimate of actual U Isotope Fission in pre-Oklo Times

The common two-hump distribution of fission product yields from ^{235}U means nuclides with masses around 95 and some 137 form at high yields (up to some 70 atoms/1,000 fissions induced by thermal 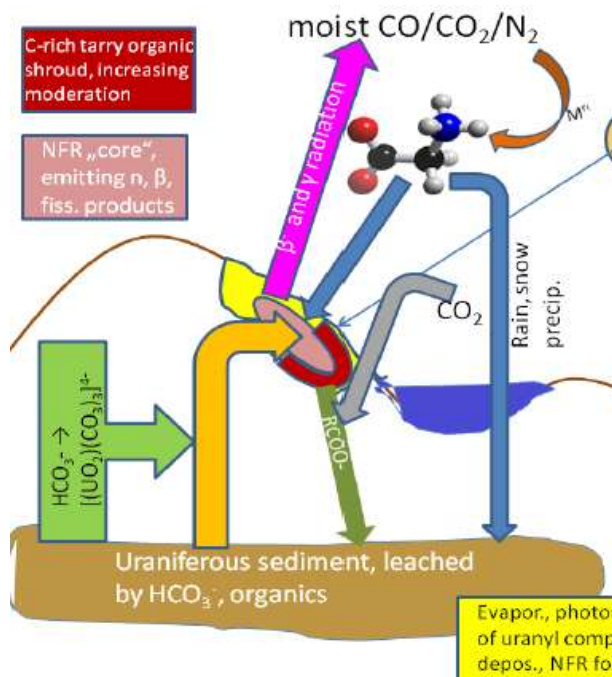neutrons [Seelmann-Eggebrecht et al. 1981]) unless "shielded" while those at A ≈ 115 – 120 or at the limits of fission product mass range (70 and > 160, respectively) are produced in amounts several orders of magnitude lower than at the maximum. The narrow range of $^{235}U/U^{tot}$ observed in Earthly (and meteoritic) samples gives a good account of possible fission losses in early times as

- Chemical separation is negligible
- Photochemical reduction rather produces a slightly reduced content of ^{235}U in the reduced U^{IV} precipitates [Buchachenko & Khudryakov 1991], and
- Meteorites and their likely parent bodies save Mars are way too small to have provided an environment for aqueous photochemistry of uranium with or without getting the product array critical any time afterwards.

This range is from lowest 0.7196% (excluding Oklo/Bangombe sites, of course), over the famous average 0.7202 % up to highest ^{235}U levels of 0.7207% in meteorites (Coplen et al. 2002). This implies that allowing for a generous $^{238}U \rightarrow ^{239}Pu/-\Delta^{235}U$ breeding factor of 0.5, the percentage of total uranium in any such site which once underwent fission is constrained to be of order 0.1% and 0.3% at most. This range of 0...0.3% ^{235}U (of a level of 4 – some 15% prior to Oklo times) loss then should be reflected in variations of contents/isotopic distributions of elements which contain fissiogenic stable isotopes besides of others which cannot

be produced by ^{235}U (n,f). pathway[3]. Meteorites use to represent matter which accumulated within this Solar System, implying that late-r-process fission would bring about fractionation only when very long-lived precursors got trapped. The sign and range of kinetic isotope effects are predictable except for involvement of excited states among which some might undergo selective disexcitation before the fractionating reaction takes place. As a result, unshielded fissiogenic isotopes (e.g. ^{104}Ru which is not produced in s-processes while more proton-rich isobar ^{104}Pd cannot be formed via a β$^-$ -decay chain) of rare elements with Z about 36 – 62 and even Z (odd-Z elements have two stable isotopes at most and thus hardly give a corresponding signal) will display a larger scatter in isotopic data if formation by fission superposes possible fractionation from chemical kinetic isotope effects: effects from the latter should be steadily variable with mass while some isotopes, like $^{96;98}$Ru in this case, cannot be produced by fission at all as they are shielded themselves by (prior formation of) stable ^{96}Zr and ^{98}Mo isobars. Long-lived unstable REE or main-group odd-Z element isotopes do not improve analysis as most of them, like ^{138}La (β$^-$) or $^{146;147}$Sm (α) are shielded while "classical" fission products are too short-lived, including ^{129}I, ^{94}Nb to be still detected. Data for indium (^{115}In) and palladium isotopic distribution ranges are not available but do exist for some sites only (Coplen et al. 2002).

Hence the width of variation of isotopic compositions within one element vs. mass is different once fission is involved, and it is going to remain so even if the products underwent complete chemical mixing, that is, complete erosion of the NFR structures, thereafter which is likely for most Archaean sites. There is a superposition of chemical fractionation when sinking down in precipitation and upper mantle chemistry (Ru) and of fission contributions. The lightest isotopes may be enriched vs. heavy/heaviest ones in reaction products such as secondary minerals to an extent depending on kind/complexity of reaction[4], that is, varying with local geochemical conditions whereas enrichments of heaviest ones like ^{104}Ru, ^{136}Xe, ^{130}Te (but not $^{114;116}$Cd) unbiased by later geochemistry (that is, escaping total secondary mixing) must be accounted for by formation after cosmogenesis of Solar System matter (it should be noted that Ru contents of meteorites are much higher [about 1 – 2 ppm] that in any common terrestrial sample except for very rare terrestrial minerals like RuAsS or Ru(Fe, Os, Co)S$_2$, indicating depletion into the mantle in early magma melts).

This means substantial variation here should be due to production of relatively heavy Ru, Te, Xe, while any possible effect would be obscured in abundant elements such as Ba, Ce completely. E.g., local chemical variations cause scatter in $^{122-125}$Te (none of which except for very little ^{125}Te can be produced by uranium fission) while there is virtually no variation in ^{126}Te abundances and $^{128;130}$Te can be shifted by fission. Given the local Te/Ba ratio is not too small and there is abundant U, presence of ^{130}Xe in the sample (which itself is not fissiogenic

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[3] Until in-situ fission had been pinpointed, nobody became intrigued by the presence of substantial light PGMs in Oklo samples although this combination was never observed in any other uranium lagerstätte, unlike with REEs which are frequently combined with uranium (notwithstanding peculiar isotopic compositions for the moment)

[4] Cp. ^{34}S/^{32}S ratios in ocean-water sulfate, FeS (troilite) in the isotopic standard (meteorite Canon Diablo), in biomass, subsequent to H_2O_2 oxidation of elemental sulfur and after S atom transfer reactions like in $S_2O_3^{2-}$ + CN$^-$ → SO_3^{2-} + SCN$^-$.

but is produced slowly by both ^{130}Ba (2ε)- and ^{130}Te (2β) decays) would indicate sample integrity ever after. To get this information the entirety of terrestrial samples (plus meteorites) must be considered which, in addition, is inhomogeneous in terms of chemical formation and alterations and thus possible (sign, extent of) chemical isotopic fractionations.

Here, partial precipitation of some compound (e.g. CdS or light PGM {Ru, Pd} arsenides) or redox fractionation among immiscible phases (Ru, Te[5]) would rather cause a signal which increases with mass differences (of course, taking into account the relative abundance of the respective isotopes which is fairly high in light Ru, Te isotopes), that is, two or more isotopes of comparable abundances across the mass range of stable (or observationally stable, only double-β-active nuclides like ^{96}Ru, $^{128;130}$Te) nuclides would display fractionations (and thus scatter of terrestrial isotopic abundances ΔA) roughly proportional to mass differences. The size of the general effect ΔA is

$\Delta A \ll \Delta M/M$,

that is, typically $\leq 3\%$ in chemical fractionation (precipitation, redox, generally speaking, kinetic isotope effects) except for deuterium, tritium. Among the elements in which possible chemical or diffusive (Kr, Xe) fractionation might take place as a background effect this criterion of similar isotopic abundances holds for $^{110;111;113}$Cd (some 12%) and to a lesser extent ^{116}Cd (7.5%), $^{128;130}$Te (each about 32%), $^{129;132}$Xe and $^{134;136}$Xe, $^{104;110}$Pd (some 11%), $^{105;106;108}$Pd (around 25% each), $^{99;100;101;104}$Ru (about 15%). Control of interpretation of the results is provided by the fact that a) fission yields of Pd and Cd isotopes are very low and b) ^{100}Ru, ^{110}Cd are shielded by stability of ^{100}Mo, ^{110}Pd, respectively.

Tab.1: Rare medium-Z elements with many stable isotopes, fission yields of heaviest and possible chemical enrichment of lighter nuclides. Data for In and Pd are missing; Mo, Ba, Ce are way too abundant to reveal significant effects

Element, Z	Mass of iso-tope	Total abundance times 10^4	Isotopic abundance scatter times 10^4	Relative isotopic abundance scatter [%]	fission yield from ^{235}U [atoms/ 10^4 fission events]	remarks
ruthenium (44)	96	554	14	2.5	0	
	98	187	3	1.6	0	
	99	1276	14	1.1	607.4	Local fractionation after fission contribution possible due to long half-life, chemical properties of ^{99}Tc
	100	1260	7	0.55	0	

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[5] Cp. the sulfur isotopic fractionation which occurs on partial oxidative dissolution of solid sulfur (S_8, mainly) to yield SO_4^{2-} by attack by aqueous H_2O_2 or chlorate in favor of $^{32;33}$S mobilization ($^{34;36}$S thus enrich in the solid sulfur which remains undissolved); however, there is no isotopic fractionation in gaseous COS or SO_2 photodissociations which both afford SO as primary product

Element	Mass					Comments
	101	1706	2	0.1	518.6	
	102	3155	14	0.45	433.6	
	104	1862	27	1.5	193	
cadmium (48)	106	125	6	4.8	0	Fission yields generally negligible, rather abundant element
	108	89	3	3.4	0	
	110	1240	18	1.45	0	
	111	1280	12	0.9	1.9	
	112	2413	21	0.9	1.3	
	113	1222	12	1.0	1.52	
	114	2873	42	1.5	1.32	
	116	740	18	2.4	1.6	
tellurium (52)	120	9	1	too rare for precise evaluation of scatter	0	
	122	255	12	4.7	0	
	123	90	3	3.3	0	
	124	474	14	3.0	0	
	125	707	7	1.0	2.92	
	126	1884	2	0.1	5.36	
	128	3155	14	0.45	35.2	
	130	3409	27	0.8	180.3	
xenon (54)	124	9.52	0.01	0.1	0	Geochemical isotopic fractionation is most unlikely as Xe is very hard to oxidize
	126	8.90	0.02	0.2	0	
	128	191	0.08	0.04	0	
	129	2640	82	3.1	75.7	unmixing by contribution from long-lived fissiogenic ^{129}I possible
	130	407	13	3.2	180.3	See above for exotic Ba, Te decays
	131	2123	30	1.4	289.2	
	132	2691	33	1.2	431.3	
	134	1044	21	2.0	787	highest fission yield of any fragment mass with ^{235}U target
	136	836	44	5.3	631.7	

Discussion: In which circumstances can moderator layers form around high-grade uranium ores?

Possibility of photochemical processing, stability of uranium ores under different atmospheres, fractionation from neutron poisons

Uranyl salts are known to readily accumulate in fairly unpolar organic solvents provided these contain O atoms as donor sites, including diethyl ether, higher (water-immiscible) ketones, alkyl acetates and other esters, or (the technical solvent used in PUREX process) tris-n-butyl phosphate. Anaerobic organisms are distinguished by very high C/N ratios (Sterner & Elser 2002, Fränzle 2010), that is, most of their metabolic products will be lipids, and thus esters rather than N-containing amino acids, proteins, porphyrines, or nucleic acids prevail in respective biomass samples. As a result, there are plenty of esters in biogenic sediments like degrading (dying) biomats[6]. UO_2^{2+} in overlying water (the present average level in ocean being 14 nM/l [Nozaki 1997]) will be extracted into and enriched in sediment much like unpolar organics (log $k_{OW} \geq 4$) are. In addition, aldehydes or alcohols, and thus sugars, undergo photooxidation by UO_2^{2+} affording UO_2 and oxidation products. UO_2 is insoluble and thus will produce a thin layer on the mainly organic matter (be it of biological or chemical-evolution[7] origins) which keeps on growing and intercalating organics (and thus moderators) as long as there is an influx of dissolved UO_2^{2+} (fig. 4).

With a water flow from which uranium is extracted by selective photoreduction, neutron poisons Mn, V, REEs (Gd, Dy[8]), Cd, and B are going to keep on being transported with the liquid (to the right), ensuring reactor operation (fig.4).

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[6] For bioaccumulation of hexavalent uranium in multicellular photosynthetic organisms (lichens, duckweed) which, however, did not yet exist in the times we discuss about see e,g, Haas et al. 1998, Mkandawire et al. 2006.

[7] In stark contrast to biomats chemical-evolution simulations afford but small amounts of compounds liable towards UO_2^{2+}-based photooxidation only, mainly formate, glycollate (fig. 1), lactate and simple aldehydes, whereas neither "tar" (which represents the majority of products) nor glycine, acetate, or urea undergo ready (or at all) UO_2^{2+}-based photooxidation. Hence under a realistic prebiotic atmosphere UO_2^{2+} photoreduction would take place at minute rates only, disregarding the question under which kind of atmosphere UO_2^{2+} or its complexes would be stable (fig. 2). If the potential photoreactants undergo metal ion coordination, like glycinate or oxalate or pseudohalides (e.g., CN^-, SCN^-) or halides ≠ F, selectivity for UO_2^{2+} photooxidation even becomes higher, protecting e.g. thiocyanato-, chloro- and CO ligands (Fränzle 1992).

[8] Selective photoreductive separation of REEs was demonstrated before, separating Eu from a REE mixture because it does undergo specific photoreduction by 2-propanol, then being precipitated as $Eu^{II}SO_4$ while all the other REEs remain dissolved. For U/Al- and U/REE photofractionations accomplished by sunlight and aq. ethanol, see Singh et al. 1959
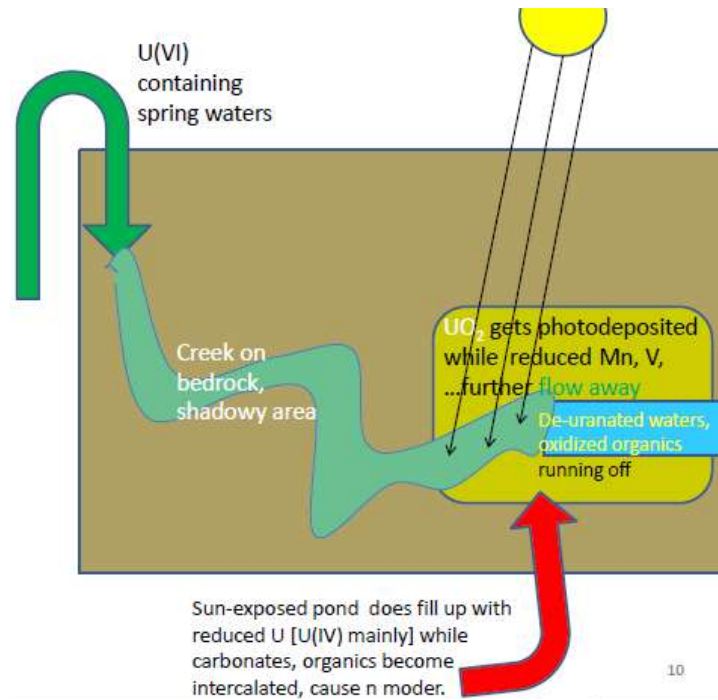
Fig. 4: Sketch of possible formation of NFRs. Note the pathway for removal of neutron poisons in this system.

Now for thermal rather than photochemical processing of uranium/carbon phases: in a carbonate-based NFR, onset of thermolysis of carbonatoligands bound to uranium(VI) will mean the system heats up until the $CaCO_3$ or similar matrix starts to decompose, also (at some 700 – 900°C, depending on external CO_2 partial pressure); then the NFR is destroyed for long at least without having generated large total amounts of energy before this meltdown. The isotopic data, however, suggest substantial processing of uranium (up to about 0.1% of entire [235]U then available) which implies the NFRs must have operated in a sustainable manner (like those at Oklo), that is, were moderated in a (either constantly or periodically, intermittent, like in Oklo) stable manner. Accordingly, carbon-based moderation relied upon photooxidation products of organics which underwent photooxidation chemistry along U(VI). The behavior of corresponding organics depending on functional groups is well-known, including the organics which are either produced by organisms or by processes implied to occur during chemical evolution (of course, there is some overlap between both groups of organics, especially concerning simple amino acids).

Results of chemical metamorphosis of U-bearing minerals by heating, photo- or radiochemistry

Certain uraniferous phases alter both U package density and (^{12}C) moderator concentration levels by thermal alteration; the latter might increase even if CO_2 gets lost from carbonatoligands. In photochemical transformations, there are similar effects (tab.2).

Tab.2: total and ^{12}C moderator densities in uranium-bearing phases, including both minerals and predominantly organic ones:

mineral	Density (g/cm^3)	Molar density (M/l)	C moderator density (M/l)	H moderator density (M/l)	remarks
liebigite Ca$_2$[(UO$_2$)(CO$_3$)$_3$]	2.41		13.6		
becquerelite	About 5.1		Low		
(UO$_2$)CO$_3$	5.7		17.3		Mineral names rutherfordine, didicherite; reacts with acids
UO$_3$ grains/colloids in vaterite	2.37+x		about 23		Produced by heating of liebigite
UO$_3$ grains/colloids in aragonite	2.73+x		26.2		"
UO$_3$ grains/colloids in calcite	2.93+x		28.2		"
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)			< 100	About 150 – 200	
UO$_2^{2+}$ in amino acids					
UO$_2$ in pure carbon (graphite)			Some 180		
UC	13.63		54.3		
U$_2$C$_3$	12.9		59.0		Stoichiometric compound

Hence NFR systems which thermally decompose carbonate while gaining density are inherently unstable with respect to moderation, bound to get overcritical once criticality is reached and the structure starts to heat up. U(VI)-based photochemistry, on the other hand, produces moderator accumulation in a controlled manner if the uranium lagerstätte is so close to the surface as to receive sunlight, and secondary heating/evaporation and radiation-chemical transformations, producing yet more moderator from a CO- or CH$_4$-containing atmosphere, will contribute to this effect. Thus, the range of possibly stable NFRs can be con-

strained, and their performance under different atmospheres can be analyzed in order to predict whether they might form on a still lifeless planet or other celestial body (that is, with little organic matter or CO available except in cryogenic bodies such as Titan).

Chances of NFR formation prior to biogenesis, possible roles in chemical evolution

The precipitation process along which moderator matter other than carbonatoligands do accumulate next to uranium obviously depends on light; the visible action spectrum (rather than UV) means it could occur under several dozen m of clear water also as the absorption maximum of UO_2^{2+} is close to the transparency maximum of water ($\lambda \approx 450$ nm). Subsequent radiation chemistry will perform better directly below the atmosphere, however, as HCO_3^- aqueous solution radiolysis just affords small steady-state levels of formate, oxalate, and HCHO but no more complicated or N-containing products even when using NH_4HCO_3 (Draganic et al. 1991), not even CO, $HCO\text{-}COO^-$ or NH_2OH, and allowing for CaC_2O_4 (whewellite) precipitation (*ibid*.). Hence both stabilization of NFR operation and possible contributions to chemical evolution or feeding a radiochemistry-related biota other than with *Desulforudis audaxviator*[9] require direct illumination, that is, photochemical UO_2 separation taking place at some surface.

For assessment of any possible role in chemical evolution we must both consider what NFR-derived radiation chemistry does to some plausible set of precursor compounds, ions and what will be the fate of organics next to illuminated UO_2^{2+} (at a maximum, e.g. some 10^4 glycine molecules obtained from the atmosphere by radiation leaking after a single fission event into a CO/N_2 atmosphere): in such a photochemical setting, sugars will rapidly degrade into CO_2 and formic acid (Greatorex et al. 1974), whereas (solid or liquid, not aqueous-solution) aldehydes will lose CO via RCO radical besides of RCOOH formation to (produce more CO-rich) metal carbonyl complexes forming there (Fränzle 1996) and most amino acids undergo oxidative α-H abstraction rather than decarboxylation (Greatorex et al. 1974). In addition, desamination of some amino acids by $^3UO_2^{2+}$-induced photochemical attack does occur in a manner reversing "advances" of chemical evolution, e.g. converting aspartic into malonic acid, formally removing a $=CH\text{-}NH_2$ unit ($C_4\text{-} \rightarrow C_3$ dicarboxylic acid) while simple carboxylates afford hydrocarbons and CO_2. Thus uranyl dication photoexcitation would rather be obstructive to chemical evolution whereas selected RCHYCOX educts like α-hydroxy esters (Y = OH, X = O-alkyl) might be used in both moderator-headspace layer formation and UO_2 precipitation (see below; conclusions). For a graphic summary, consider fig. 5 by the present author:

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[9] Enhanced sulfate levels do not change the pathways of radiation chemistry in this system, and ample H_2 is formed, so preconditions for a deep, dark, atmosphere-secluded *(D. audaxviator* is an anaerobic organism) biota "feeding" on radiation-chemical products are good

precursors
(energy source)

HCHO, higher RCHO, HCN, N so.

{HOCH$_2$CHO;
clays or Ba^{2+}}

sugars   amino acids

CO$_2$, HCOOH   CO, [M(CO)$_n$X$_y$]
                NH$_3$, RCOCOOH

uranyl-induced
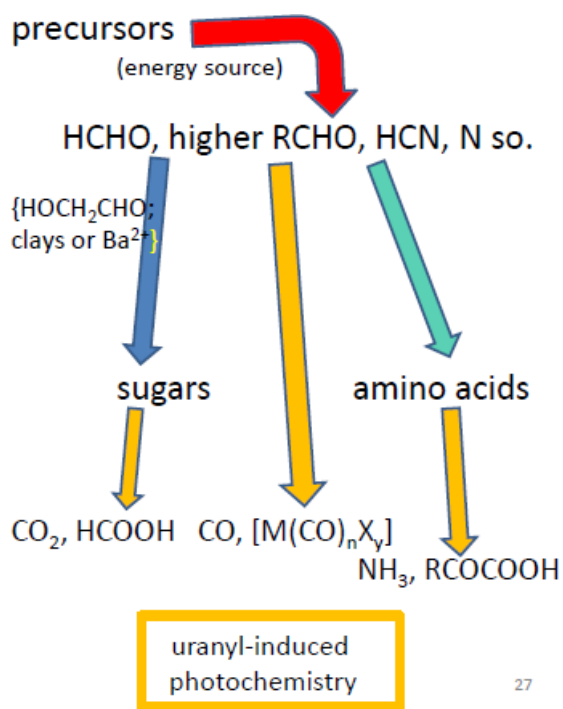photochemistry   27

Fig.5: generally speaking, uranyl photochemistry is obstructive towards chemical evolution. However, once U(VI) was reduced and the NFRs went into operation, this kind of photodecomposition ceased whereas radiation-chemical production of hardly volatile organics went on as long as there was substantial CO (e.g., CO/CO$_2$ > 0.1) in the atmosphere while in waters overrunning the NFR cyanide could be turned into nonvolatile potential moderators, too (cp. fig.3b and caption given there).

Conclusion: Should we build such devices for closer studies? Applications of similar structures in space research

The situation on Earth seems to be that NFRs could not have had their role in chemical evolution right because enrichment of U into high-grade ores could not occur until much after biogenesis. If such NFRs actually existed on Earth, they could form only with abundant lifeforms already around, and hence had no role whatsoever in chemical evolution, neither could form on other lifeless celestial bodies. For now, Western Australia probably is the best place on Earth to look for these structures or their geochemical or isotopic traces. There are the oldest sizable biogenic sediments (stromatoliths, up to some 3.5 bio. years old) as well as large uranium ore deposits some of which are likewise Archaean in age. Things might have been different on Mars given there still appears to be some production of (most likely oxygenated, suitable to reduce $^3UO_2^{2+}$) organics even today (evidence by the Pyrolytic Release Experiment [Viking 1 and 2 stationary Mars Lander Probes] in the 1970ies as well as data from Curiosity Rover nowadays) while near-surface soil redox conditions are far from equilibrium, yet there are both nitrate and perchlorate to maintained hexavalent uranium (Fe is partly reduced to divalent state, however, and heating of drilled soil and rock does release HCN, H$_2$S, chloromethanes and other reducing gases). Thus as long as liquid water was running under a sufficiently thick atmosphere (which contains CO even today) NFRs of this kind might have formed there even if there was no life there either then or now or earlier (that is, in Noachian times).

Especially considering previous body of experimental data on U isotopic fractionation occurring during partial reductive photoprecipitation (as UF$_4$) [Buchachenko & Khudyakov 1991], and the rule that building an actual device is the best way to show that a model does work indeed, we are posed to ask whether such a NFR could be built starting with uranyl salt solutions of some 10% ^{235}U content while photochemistry sensitized by $^3UO_2^{2+}$ both produces an

unpolar hardly volatile organic moderator overlayer from aqueous organic salts and precipitates uranium dioxide (cp. fig.1, replacing HOCH2COO- by long-chain hydroxicarboxylates or esters thereof). A simple small-scale device (being marginally subcritical before photochemical "completion") thus might be similar to the old (started test runs in 1964) Russian/Soviet Romashka design (fig. 6), except for considerably lower operation procedures and vapor-circulation systems of energy conversion (steam turbines or the like) in place of thermoelectric elements (also consider figs. 1, 3a, 3c, and 5 of this paper for design and photochemical constraints):
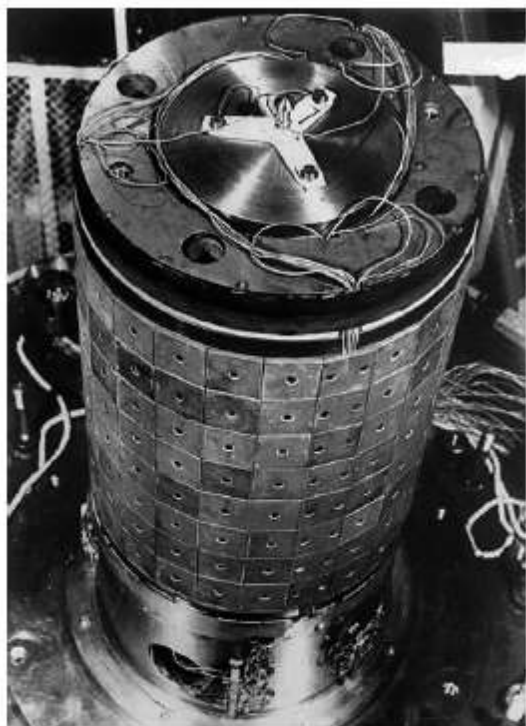

Fig.6. Romashka reactor and isolated fuel, moderator (= graphite) slabs. From Kukharkin et al. 2011; criticality is only achieved by the Be closure ("bucket") reflecting neutrons, like in the contemporary (mid-1960ies) US SNAP-10A setup.

might be dislocated in outer space, e.g. on a rover probe or in a remote site on Earth, bearing very little radioactivity after start, and activated/becoming critical ("switch on") only there by exposition to visible and UV light. The actual device would be a variety of Romashka coming with an overlying two-phase high-boiling solution system containing UO_2^{2+} in which a final, capping layer of UO_2 would be deposited by visible light impact much like depicted in fig.1 in the beginning of this text. Nonvolatile photooxidation organic products derived from some solvent would contribute to moderation over this surface layer, with a Be reflector grating then approached to the upper side. The aqueous supply phase from which UO_2^{2+} had

been extracted might finally be used in a steam engine or –turbine energy conversion system instead of thermoelectrics.

This modified version would probably meet more acceptance than a direct reproduction of the NFR outlined here as the latter would be bound to release radioactive dust and have lots of ionizing radiation getting into a toxic gaseous headspace volume.

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[10] The ion pairs ("Ionenpaare" in German) denote combinations of uranyl dication and complex anions containing ligands either labile or stabile towards photooxidation by UO_2^{2+} (mixed-ligand educts are used) suspended in non-ionizing organic solvents like aldehydes or DMF/glyoxylic acid which latter deliver CO to carbonylate these metal complexes (mostly such of osmium) upon illumination while UO_2 does precipitate

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