NEWLY DISCOVERED, ORGANIC MATTER-RICH NATURAL FISSION REACTORS AT OKLO AND BANGOMBÉ: ARE THEY USEFUL ANALOGS FOR LONG-TERM ANTHROPOGENIC NUCLEAR WASTE CONTAINMENT?

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ABSTRACT

Sixteen known natural fission reactors at Oklo and one at Bangombé (south of Oklo) consist of small, highly uranium-rich pockets in uranium ore bodies which are located in sandstones and shales in the Paleoproterozoic Francevillian Basin, Republic of Gabon, equatorial west Africa. Nuclear criticality occurred 1968±50 Ma ago and was sustained for 0.1 to 1 Ma. Water acted as a moderator in the natural reactors. The absence of neutron poisons and the fact that ^{235}U was five times more abundant ~2000 Ma ago than it is today facilitated attainment of nuclear criticality in the uranium-rich pockets. These fortuitous geological conditions permitted the evolution of six natural reactors which generally contain only traces of organic matter, and eleven additional natural reactors which are rich in organic substances, mainly solid graphitic bitumens. In the organic-rich natural reactors liquid bitumen was generated during criticality by hot water from abundant solid organic matter chemically resembling coal. This organic solid is called kerogen, which is finely dispersed in shales and sandstones. This hydrothermal process is referred to as hydrous pyrolysis in the petroleum industry. It is generally accepted by petroleum scientists that petroleum was generated by hydrous pyrolysis from kerogen; bitumen is a viscous petroleum. During criticality U(VI) in aqueous solutions was reduced by the evolving liquid bitumen to U(IV), resulting in the precipitation of uraninite. This was accompanied by the co- precipitation and trapping of fissiogenic isotopes in uraninite. These uraninite grains became enclosed in bitumen, which soon became a solid consisting of polycyclic aromatic hydrocarbons and intimately admixed fine grained, cryptocrystalline graphite. This solid bitumen prevented uranium and fission product losses and migration from its enclosed and immobilized uraninite grains in the organic-rich natural reactors. A severe geological event, the intrusion of a dolerite dike swarm (molten rock intruding into newly opened fractures in the rock strata) near the natural reactors, occurred ~1200 Ma after criticality. The graphitic bitumen matrix was not sufficiently disrupted by this event to lose all its immobilized uranium and fission product content, although a quantity of radionuclides were released at this time from the natural reactors. The organic-poor reactors lost virtually all of several of their fission products, possibly even before this geological episode. Solid, graphitic bitumen at Oklo has attributes, such as its ability to restrain uranium and fission product migration, as well as its inducible plasticity and non-flammability, which merit careful study when considering the Oklo organic-rich natural fission reactors as time-tested analogs for anthropogenic nuclear waste containment. It is to be noted though that comparison of prospective nuclear waste storage strategies with natural analogs constitutes a complex problem which requires careful, in-depth assessment before considering any practical utility.

INTRODUCTION

The first natural fission reactors were discovered in 1972 at Oklo in the Republic of Gabon in equatorial West Africa. These natural nuclear reactors contained only traces of organic matter. They were studied in detail and described in two reports in 1975 and 1978 (1,2) published by the International Atomic Energy Agency. Following the discovery of the six organic matter-poor natural reactors, ten organic-rich natural fission reactors have been found at Oklo and one at Bangombé south of Oklo. Detailed studies of the organic-rich reactors commenced only a few years ago and these natural reactors are still not well known. Yet their significance regarding long-term radionuclide containment already arose interest among a number of organic and isotope geochemists, nuclear physicists, hydrologists and nuclear engineers. This interest is demonstrated by ongoing cooperative international research programs.

The reason why the newly discovered organic-rich natural reactors at Oklo and Bangombé did not yet receive the same attention with respect to nuclear waste containment as the six organic-poor natural reactors may be attributed to misunderstanding. It has been assumed by a number of investigators that evidence obtained from the early studies has already shown that uranium and fission products exhibited little or minimal migration from the organic-poor reactors. Even though the mechanism(s) responsible for such radionuclide containment has not been satisfactorily elucidated, the need to focus investigations on the chemically more complex organic-rich natural reactors was not compelling when the assumption of fission product containment by the organic-poor reactors appeared to be correct. However, to a large extent this assumption is not correct (3,4), but this was generally overlooked because of the relative inaccessibility of pertinent reports. The reason for the misunderstanding is that significant attention has not been given in these early studies to the retention of uranium and fissiogenic isotopes in the organic-poor reactor zones. Because the focus of the early studies was to determine nuclear parameters in order to elucidate how and why U-rich pockets in the uranium ores reached nuclear criticality, samples which showed little or no mobility of uranium and fission products were mainly selected. For example, samples from a bore hole in the organic-poor natural reactor

2 have been extensively studied. Samples from this bore hole showed minimal migration of uranium and fission products. However, several other bore holes have been drilled in this reactor (5), and samples from these, although less extensively studied, showed evidence for radionuclide loss. On the other hand, it is now apparent that migration of uranium and fission products from the organic-rich natural reactors was significantly restrained by the agency of organic matter (6,7). Therefore, it appears that sufficient attention should be focused on the organic-rich natural reactors, rather than on the organic-poor ones when assessing time-tested analogs for long-term nuclear waste containment. This report considers organic-rich reactors 7 to 9.

The organic-rich Oklo natural fission reactors contain abundant organic matter in heterogenous distribution. For example, part of an organic-rich natural reactor contains 65.9 percent organic carbon. (Other parts of this and other organic-rich reactors may contain less or no $C_{org.}$.) In the portions where organic matter is not abundant the major constituent is usually the clay mineral illite. Conversely, restricted parts of the organic-poor natural reactors may also contain small amounts of organic matter (8,9); it is possible that samples showing minimal radionuclide migration in natural reactor 2 also contain local concentrations of organic substances.

In the organic-rich natural fission reactors in Gabon, solid bitumen physically restrains uranium and fissiogenic isotope migration. Also, bitumen caused virtually no migration of uranium at the Elliot Lake uranium ore deposits in Ontario, Canada (10), which, of course, did not reach criticality. Radionuclide immobilization in nature suggests that using solid and graphitic bitumen in radioactive waste burial sites merits careful study.

THE ORGANIC-RICH NATURAL FISSION REACTORS IN GABON

Geological Setting and the Natural Reactors

All known natural fission reactors in Gabon are located in sedimentary rocks of the Paleoproterozoic Francevillian Series. This Series of rock strata is 1000 to 4000 m thick, consists of abundant clastic (sandstones and shales) sedimentary rocks, which often contain dispersed organic matter (11) and which show no discernible signs of more than minimal metamorphism. The natural reactors occur in epigenetic uranium ore deposits in the 7 to 10 m thick C1 layer of the basal FA Formation. The C1 layer consists of ancient beach sands and tidal deposits; the FA Formation is characterized by fluvial deposition of sediments followed by marine transgression (16,18). The Francevillian Series sediments were deposited ~2100 Ma ago (12), and the natural reactors reached criticality 1968±50 Ma ago (13). After deposition, the Francevillian rock strata were subjected to subsidence and uplift. The rocks were extensively fractured; the uranium ores and the natural reactors are located in highly fractured zones. The fractures may have served as conduits for uranium-bearing aqueous solutions. A remarkable temporary rise in the O_2 content of the Earth's early atmosphere has been proposed (14,15) during the time span when the Francevillian sediments were deposited and the uranium ore bodies evolved. Therefore, oxidizing aqueous solutions could have entered and migrated through the Francevillian rocks at this time, carrying dissolved uranyl ions, particularly through the fractures which facilitated fluid flow to the sites of organic-rich rocks. Organic matter at these locations reduced U(VI) to U(IV), causing the precipitation of UO_2 and forming the uranium ore bodies (16).

At certain highly fractured sites considerable amounts of uranium were precipitated and concentrated from the percolating aqueous solutions. Uranium-rich pockets were formed at these locations within the ore bodies of lower U contents than the U-rich pockets. These U-rich pockets subsequently became the natural fission reactors. In addition to high uranium abundances, criticality was also facilitated by the lack of neutron poisons in these U-rich pockets and by the fact that ^{235}U was approximately five times more abundant ~2000 Ma ago that it is today. Water in the U-rich pockets acted as a moderator. Criticality lasted between 0.1 to 1.0 Ma and the temperature in the reactors was between 160° and 360°C (17,18).

The Francevillian rock strata experienced a major tectonic-igneous event ~1200 Ma after the natural nuclear reactors reached criticality. This was caused by the intrusion of an extensive swarm of dolerite dikes (19). One of these dikes is located only tens to hundreds of meters from the natural reactors. This event caused the first major loss of radionuclides from the organic-rich natural reactors, but it is noteworthy that even this severe geological episode, and subsequent tectonic events, did not seriously interfere with the retention of a significant portion of ^{235}U and fission products encased and protected by organic matter of inducible plasticity in the organic-rich natural reactors.

Nature, Evolution and Effects of Organic Matter in the Organic-Rich Natural Reactors

Most of the sandstones and shales in the Francevillian Basin contain solidified decomposition products of ancient microorganisms (cyanobacteria). This substance is called kerogen. It usually occurs finely dispersed and in low abundances in sedimentary rocks of various ages; when all kerogen is accounted for in sedimentary rocks, it is the most abundant organic substance on Earth (20). Chemically kerogen is somewhat similar to coal, it virtually does not migrate during geological time and it is insoluble in common solvents. When sedimentary rocks rich in kerogen are subjected to hot aqueous solutions *in situ* they yield organic liquids remarkably similar to petroleum (21,22). This reaction is called hydrous pyrolysis. At the time of this writing, it is generally accepted in petroleum science that petroleum was generated from kerogen by hydrous pyrolysis. Bitumen is a viscous petroleum.

Organic matter in the natural fission reactors is mainly a solid bitumen. It was generated during criticality as a liquid by hydrous pyrolysis from kerogen (and also likely from solid precursor bitumens). Water and elevated temperatures in the natural reactors made hydrous pyrolysis possible, although there are ample indications that petroleum was also generated in the Francevillian Basin at locations other than in the natural reactors, wherever local hydrothermal environments permitted hydrous pyrolysis to occur. The liquid bitumen in the natural reactors soon polymerized into a solid containing cryptocrystalline graphite, through the action of heat and radiation. The now solid bitumen in the natural reactors and in their vicinity consists of an intimate mixture of polycyclic aromatic hydrocarbons and fine grain size cryptocrystalline graphite, determined by pyrolysis-gas chromatography-mass spectrometry and microfocused laser Raman spectroscopy

(6,7). A model of the graphitic bitumen in and at the vicinity of the organic-rich natural reactors at Oklo is shown in Fig. 1. There is organic petrographic evidence that there were at least three episodes of bitumen generation occurring prior to, during and following criticality (7,23).

During nuclear criticality the aqueous environment in the natural fission reactors appears to have been oxidizing (6). At this time pitchblende, uraninite and several fission products went into solution. However, when U and other dissolved species encountered sufficient quantities of liquid bitumen, as it was increasingly generated by hydrous pyrolysis, U(VI) was reduced to U(IV) as uraninite and many of the fissiogenic isotopes co-precipitated with and became trapped in the uraninite microcrystals. These small grains of UO_2 became admixed with and then enclosed in the growing yield of liquid bitumen. While bitumen was still a liquid, and particularly prior to it while U and fission products were in the aqueous phase, radionuclide loss from the organic-rich reactors appears to have taken place. However, such U and fission product migration soon ceased, when heat and radiation effects polymerized the liquid bitumen into an immobile solid, thereby also immobilizing its enclosed uraninite crystals and the fission products contained in UO_2 (6,7). The evolution and then the proliferation of graphitic moieties within the polycyclic aromatic hydrocarbon matrix resulted in increasingly firm encasement of uraninite in this solid bitumen, to the point that when faults opened up and were filled with molten rock in the vicinity of the natural reactors, the graphitic bitumen matrix was not sufficiently disrupted by these events to lose all of its ^{235}U and fission product content. It may be useful to consider the behavior of the graphitic bitumen under severe geological environments when considering the organic-rich natural reactors as potential analogs for certain aspects of nuclear waste containment. However, further investigations are needed to properly evaluate if the Oklo organic-rich natural reactors are fully appropriate analogs to anthropogenic nuclear waste containment.

CONTAINMENT OF URANIUM AND FISSION PRODUCTS BY GRAPHITIC BITUMEN

Laser microprobe isotope mass spectrometry (7) and pyrolysis-high resolution organic mass spectrometry (6) provided qualitative evidence that uranium and fissiogenic isotopes are not present in the molecular moieties of bitumen but are held only in uraninite crystals in the natural reactors. The first quantitative evidence was obtained for the retention of fissiogenic isotopes in uraninite protected by graphitic bitumen by determining and comparing the U-Pb and the lanthanide fission products/U ages of nuclear criticality (7,13). In the process of obtaining the fission product age, the neutron fluence was calculated (7,17,24): 0.503×10^{21} n/cm^2. It was also found that 1.3% of U atoms fissioned. The fission product and the U-Pb ages of nuclear criticality were the same within experimental error; i.e. the lanthanide fission product age was ~1960 Ma and U-Pb age was ~1970 Ma (7,13). Therefore, lanthanides were not lost from uraninite when this mineral was enclosed in bitumen, otherwise the fission product ages and the U-Pb ages would have been different (3,4,7). In the absence of protective bitumen as much as 30% fissiogenic Nd was lost, relative to U, in reactor core samples (6). Restricted, local migration of lanthanides was also observed from uraninite not protected by organic matter (6) in the organic matter-poor, natural reactor 2. Second, quantitative data showed

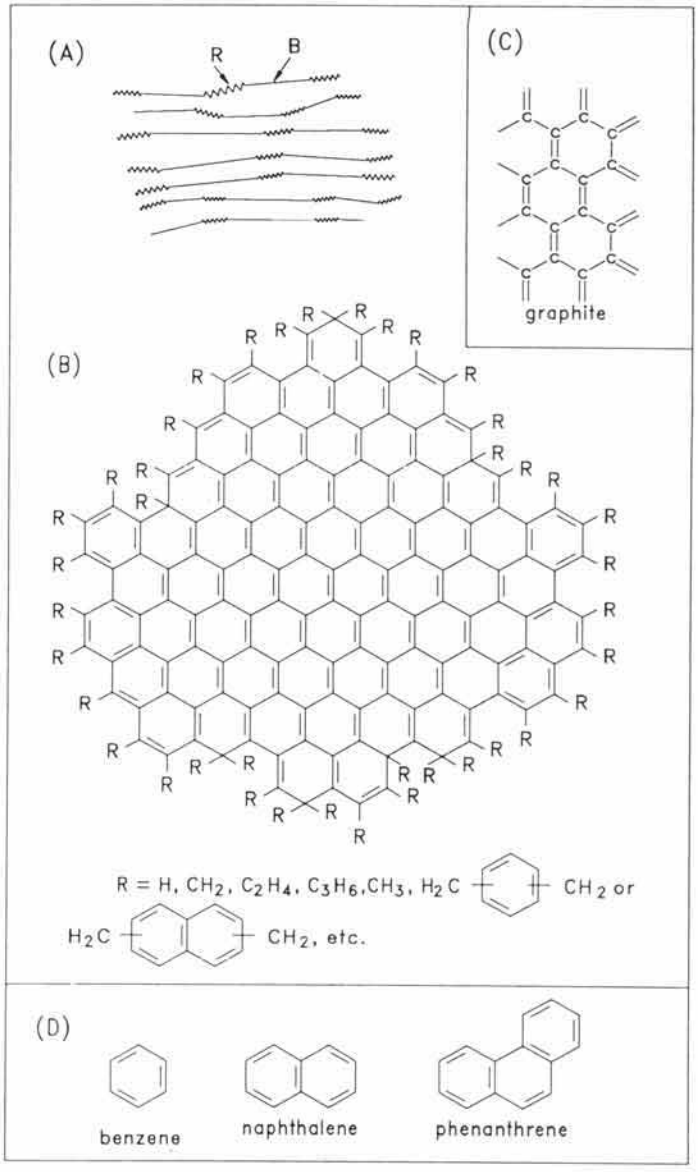

Fig. 1. A model of the solid, graphitic bitumen at the Oklo natural fission reactors indicated by recent but continuing analyses. (A) Cross-sectional view of the macromolecular bitumen structure showing sheets of graphite moieties and polycyclic aromatic hydrocarbons (shown by arrow B), connected by aliphatic and aromatic bridges (shown by arrow R). (B) View of the macromolecular structure rotated 90° with respect to (A). The substitutions R may include higher molecular weight polycyclic aromatic hydrocarbons. The diameter of the aromatic sheet is larger in nature than as illustrated. (C) The structure of graphite according to Pauling ("Nature of the Chemical Bond," Cornell University Press, 1948). The carbon atoms in the hexagonal structure are marked, unlike C atoms in similar position in (B) and (D). (D) Benzene and two polycyclic aromatic hydrocarbons.

that substantially less Sr, Cs, Rb, Ba (7,25,26), Ag and Te (6) were lost in samples which were protected by organic matter than in those containing only clay minerals. Partial migration of these fissiogenic isotopes and substantial loss of fissiogenic Mo and Sn in the organic-rich reactors (6) may be attributed

to two major causes. One was, as noted above, migration in the aqueous phase before sufficient amounts of bitumen were generated during criticality to arrest radionuclide mobility. The second cause is based on the observation (6) that clay minerals, in those portions of the natural reactors which do not contain organic matter, seem to be less effective than bitumen at preventing the migration of uranium and fissiogenic isotopes. These two causes of uranium and fission product losses could be prevented by appropriate measures in anthropogenic nuclear waste burial sites. The studies which yielded the Oklo radionuclide containment data, although still in progress, suggest that solid, graphitic bitumen is an effective medium to contain uraninite and fission products in the dispersed, solid phase in the natural fission reactors.

IS SOLID, GRAPHITIC BITUMEN A SUITABLE AGENT TO ENHANCE ANTHROPOGENIC RADIOACTIVE WASTE CONTAINMENT AT BURIAL SITES?

Solid bitumen has certain properties which suggest that it may be one appropriate agent for anthropogenic nuclear waste containment.

a. Solid, graphitic bitumen immobilized fine grain size uraninite, containing fission products, at Oklo, and thereby prevented radionuclide migration. Furthermore, even during severe seismic disturbances, the solid bitumen retained some of its containment efficiency in nature. However, based on the Oklo analog, to make solid bitumen an effective barrier to radionuclide migration, anthropogenic waste should be enclosed and dispersed in it as small grain size solids, e.g. glass or Synrock particles. At this time it is not known how large such glass or Synrock particles in bitumen may be. Alternatively, perhaps glass, Synrock, etc. containing containers may be immersed in sufficiently sized volumes of graphitic bitumen.

b. Graphitic bitumen is hydrophobic and it effectively shielded uraninite in nature for close to 2000 Ma from exposure to migrating aqueous solutions. As known, depending on its chemical composition, temperature, pH and Eh, migrating aqueous solutions can adversely affect radioactive waste storage in the inorganic phase, when not shielded by suitable hydrophobic barriers.

c. If properly prepared, solid, graphitic bitumen may have inducible plasticity. Such plasticity helps seal cracks and fissures at burial sites and/or in radioactive waste containers.

d. If properly prepared, solid, graphitic bitumen is not a flammable substance. Appropriate environmental control at waste burial sites should further assure nonflammability.

e. Radiation damage over geological time in Oklo made the macromolecular structure of graphitic bitumen less tightly bonded than at locations distant from the natural reactors (and away from intense radiation effects). However, in the natural reactors the graphitic bitumen still remained sufficiently solid and hydrophobic to prevent loss of ^{235}U and fission products (6,7).

f. Bitumen (also called asphaltenes, asphalt, resins, etc.) is a relatively inexpensive residue of petroleum refinery operations.

Using solid, graphitic bitumen in radioactive waste containment merits careful study. Basic and applied concepts of petroleum-chemistry and -geochemistry need to be considered for the appropriate assessment of the use of bitumen in radioactive waste containment.

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