Isotopic Abundances Measurements a Key to Understanding the Oklo Phenomenon

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Dedicated to Prof. H. Hintenberger on the occasion of his **70th** *birthday*

The Oklo natural nuclear reactors have been studied mainly by isotopic and chemical analyses of uranium and fission products. Interpretation of these analyses allows parameters which characterize these reactions (flux, fluence,...), and also the age and duration of the nuclear reactions to be evaluated. The mechanisms and extent of fission-product migration can also be discussed. The behaviour of various elements formed in the Oklo uraninite and in oxyde fuels of pressurized water reactors is compared and found to be similar. Therefore, experience gained from the study of the Oklo phenomenon can provide valuable information on the long-term storage of radioactive wastes in geological media.

1. Introduction

In 1972, it was discovered that fission reactions spontaneously occurred some two billion years ago in the Oklo uranium ore in Gabon [1, 2, 3]. Since then, this phenomenon has been extensively studied, in order to understand how the nuclear reactions proceeded [4, 5, 6]. In the course of those studies it became evident that an explanation of the Oklo phenomenon would not only involve understanding a unique reactor, but also a wide geological and geochemical movement. Criticality has occurred in numerous places in the deposit, and several different reaction zones have been delimited. The state of preservation of these real "fossil nuclear reactors" appears to be exceptionally good, and one has to conclude that, despite some small remobilizations, uranium has preserved its original configuration, since the operation of the reactors to the present day. This is a basic observation that enables the detailed study of the migration of uranium, the main fission products and some other elements that were formed by the nuclear reactions.

2. Geological Environment of the Nuclear Reactors

The Oklo deposit is located in the south-east part of Gabon, in the intermediate Precambrian sedimentary basin of Franceville [7]. Uranium mineralization is exclusively located in a sandstone-conglomerate lens which shows a 40° mean slant, and which follows the rise of the crystalline basalt relative to the sedimentary cover.

At the time of the reactions, the uranium deposit was buried to a depth of many thousand meters under impervious sediments; later erosion processes have led to its rise close to the surface during recent geological times.

Many reaction zones have already been delimited. Figure 1 shows the first known group which contains four distinct zones; a second group now comprising three zones was discovered in March 1978, about 200 meters south of the first group. Another reaction zone has been located by drilling in the Okelobondo deposit about 1.5 kilometers south of the Oklo deposit.

A limited fraction of reaction zone 2 has been preserved by being anchored to the quarry wall (see Figure 1).

Each reaction zone consists of a compact accumulation of very rich uranium ore, virtually a single block and flattened in the direction of the stratum; the length ranges from 10 to 20 meters, the thickness is a few tens of centimeters. These uranium blocks are embedded in a clay gangue and are embanked in clays which are only present in the reaction zones, taking the place of the uranium ore sandstones-conglomerates sequences.

Figure 2 shows an outcrop of reaction zone 2 at level 367.5. It is possible to distinguish a uranium deposit zone with a concentration higher than 20% and in one single lens, then a transition zone where

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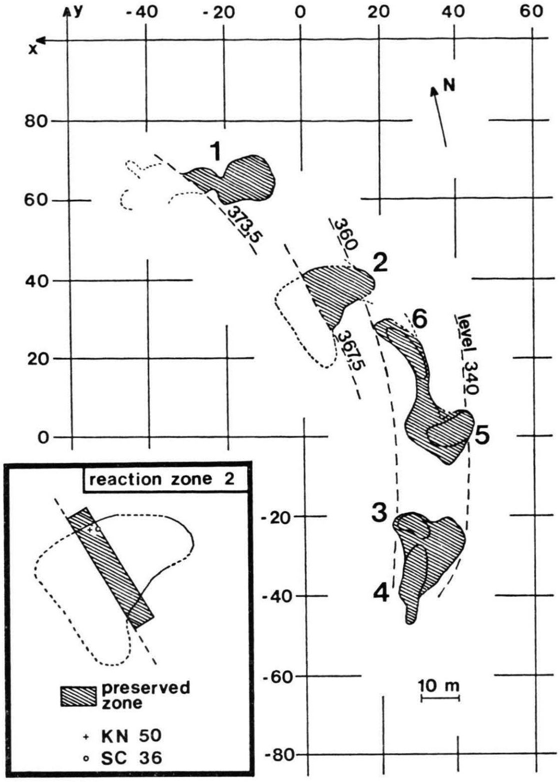

Fig. 1. Location of the first four reaction zones discovered and scheme of reaction zone 2 showing the KN 50 and SC 36 boreholes (from [8]).

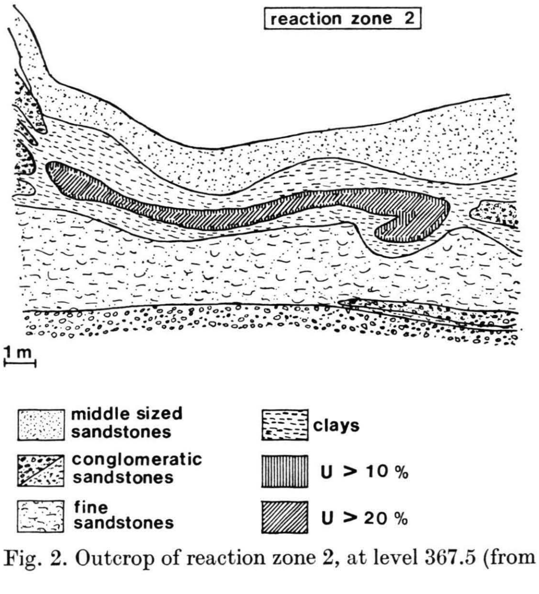

Fig. 2. Outcrop of reaction zone 2, at level 367.5 (from [9]).

the concentration rapidly decreases down to a few per cent over less than 10 centimeters and then down to the ordinary ore concentration, i.e. 0.5%. Finally, one finds the clays and sandstones areas surrounding the uranium ore.

In the Oklo deposit, uranium is present as pitchblende, except in the reaction zones where it is present as uraninite.

3. Neutronic and Nuclear Parameters Derived from Isotopic Measurements

The uranium fission products presently found in the reaction zones are the immediate products of the nuclear reactions, and their precise study enables one to evaluate the neutronic and nuclear parameters which characterize these reactions.

The methods for calculating the different parameters have already been published [10, 11, 12]. The results that we have obtained mainly relate to reaction zone 2, the samples analysed originate from the KN 50 and SC 36 cores (see Figure 1).

Chemical and analytical methods were specially adapted in our laboratory for the study of the Oklo phenomenon.

General conclusions derived from uranium and rare earths isotopic and chemical analyses are briefly reported below, more detailed information can be found in the three papers quoted above.

3.1. *Integrated Flux and Instantaneous Power*

In the center of reaction zone 2, the integrated neutron flux exceeds $1 \cdot 10^{21}$ n/cm^2, the instantaneous flux being close to 10^7 n/cm^2 s, if one adopts a continuous and constant reaction rate over the operation of the reactor. The reaction is estimated to have lasted for one million years (see below). It is clear that in spite of a high fluence, the neutron flux at Oklo was very low (the mean neutron flux in a man-made nuclear reactor ranges between 10^{12}–10^{14} n/cm^2 s).

In contrast, the total energy produced by the nuclear reactions was high, it is estimated to be more than 500 billion megajoules [8], but the average "power" was only about a few tens of kW assuming a constant reaction rate.

3.2. *Neutron Spectrum and Conversion Factor*

By comparing the measured isotopic abundances of fission products with the known variations of the capture cross-sections with neutron energy, it has been possible to conclude that the neutron spectrum was well thermalized, and the "spectral index" was smaller than 0.2. One can also compare the fluence that can be calculated from uranium isotopic depletion to that measured as having been received by the fission products. The latter is mainly derived from the study of the $^{143}Nd \rightarrow {}^{144}Nd$ transfer. As the depletion of ^{235}U is too small to account for the latter value, a large fraction of ^{235}U now present results of the α decay of ^{239}Pu, formed by neutron capture of ^{238}U. This enables the calculation of a "conversion coefficient" usually close to 0.5, which suggests that about half of the uranium destroyed by the nuclear reactions was regenerated via plutonium.

3.3. Fission of ^{238}U and ^{239}Pu

Isotopic compositions of elements such as rare earths, ruthenium and palladium depend on the nature of the fissile nucleus that produced them. They show a low fission proportion of ^{238}U and ^{239}Pu, both of which are only a small fraction of that of ^{235}U, which in general accounted for more than 90% of the fission.

3.4. Lifetime of the Reactors

The small fission proportion of ^{239}Pu implies that most of the plutonium formed decayed to uranium; thus, the duration of the nuclear reactions was long compared with the half-life of ^{239}Pu (24,000 years). More precise calculations lead to a duration of about 800,000 years for the reaction in zone 2. It is remarkable that from reactor to reactor the lifetime varies widely, some as low as 100,000 years have been found.

3.5. Age of the Reactions

Another important characteristic of the reactions that can be deduced from fission-product analyses is the date the nuclear reactions started. The amounts of fission products that were formed at Oklo are directly related to the neutron fluence and depend also on the initial uranium isotopic abundance. That abundance is a function of the different half-lives of the two main uranium isotopes, 235 and 238 [13].

The general mathematical expression was given in [11] and can, as a first approximation, be written as follows:

$$t = \frac{1}{\lambda_5} \ln \left[\frac{N_f}{U} \frac{A}{\tau} \right] \tag{1}$$

where

t is the age of the reactions;

N_f/U is the total number of fissions that occurred in the sample per atom of actual uranium;

τ is the fluence received by the sample;

λ_5 is the radioactive decay constant of ^{235}U;

A is a numerical factor which takes into account the irradiation conditions of the sample (spectrum index, conversion coefficient, proportion of fissions in ^{238}U and ^{239}Pu).

Table 1. Parameters derived from isotopic and chemical analyses of various Oklo samples.

Sample		Reaction Zone	%U (wt)	$\frac{^{235}U}{^{238}U}$ % (atom)	τ (10^{21} n/cm²)	N_f/U (%)				Age (10^9 years)				Duration of reaction (10^6 years)	Ref.
						Nd	Sm	Gd	Ru	Nd	Sm	Gd	Ru		
KN 50	323	2	7,0	0,482	1,12	2,79	2,78	2,73	2,89	2,02	2,01	1,99	2,05	0,90	
	3548	2	55,2	0,465	1,36	3,16	3,37	2,70	2,94	1,96	2,02	1,80	1,88	0,74	
2′P — 612		2	52,3	0,459	1,31	3,22	3,09	2,69	—	2,00	1,96	1,82	—	0,68	[16]
SC 9b — 882/1		2	63,2	0,511	1,09	2,50	2,44	2,30	—	1,91	1,88	1,82	—	1,04	[16]
SC 36	1402	2	2,73	0,665	0,69	1,89	1,37	1,14	0,59	1,99	1,67	(1,5)	(0,81)	—	
	1408/4	2	23,3	0,545	0,83	1,90	2,07	2,44	2,30	1,90	1,98	2,15	2,09	0,58	
	1410/3	2	57,8	0,527	1,09	2,57	2,46	1,98	2,49	1,90	1,86	1,64	1,87	0,95	
	1413/3	2	37,2	0,410	1,45	3,30	3,51	2,84	2,16	1,99	2,05	1,84	1,56	0,62	
	1418	2	57,9	0,574	0,96	2,35	2,28	1,97	2,06	1,88	1,85	1,70	1,74	0,77	
	1421/4	2	4,63	0,525	0,73	1,95	2,17	3,4	—	2,06	2,17	(2,6)	—	—	
	1423/5	2	9,37	0,547	1,01	2,80	2,84	3,1	—	2,04	2,05	2,13	—	—	
	1425/1	2	2,03	0,638	0,51	3,03	4,1	(10)	0,34	(2,8)	(3,1)	(4,0)	(0,57)	—	
SC 52	1472	3	32,0	0,664	0,25	0,60	0,57	0,31	—	1,87	1,82	(1,2)	—	—	[17]
SC 55	1852	3	47,0	0,694	0,14	0,34	0,31	0,25	—	1,83	1,74	(1,5)	—	—	[17]
KN 267	2194	5	55,7	0,621	0,50	1,45	1,28	0,81	—	1,95	1,8	(1,5)	—	≃0,1	

3.6. Migration of Fission Products

Conversely, knowing the age of the reactions and the relation between the age and the amounts of fission products formed, one can determine, after measuring the actual amounts present in the ore, if migration of some elements has occurred since the reactors operation, and what quantities did migrate.

4. Numerical Results

Table 1 shows data calculated from chemical and isotopic measurements on the number of fissions and the fluence of fifteen samples taken from different Oklo reaction zones. The calculated ages and reaction durations are given for each sample. Several fission products have been used, in the age calculations, the spread of results is shown.

Samples 1402 to 1425/1 were located on one borehole traversing reaction zone 2, the distance between two adjacent samples was about 10 centimeters; samples 3548, 612 and 882/1, all taken from reaction zone 2, were chosen as reference samples because of their high uraninite concentration and the high fluence they apparently received.

5. Discussion of the Results

The data reported in Table 1 specifically indicate some characteristic correlations. First of all, samples from reaction zone 2 (which show a high uranium concentration), are much depleted in ^{235}U, and the fluence they received is also very high. Second, the numbers of fissions per atom of total uranium are high, about 3%, and third, the three rare earths studied and ruthenium lead to about the same age value despite some small local remobilizations. For reaction zone 2 the value for the reaction age is a little less than 2 billion years, and the duration is about 800,000 years.

In the other reaction zones, despite some high local uranium concentrations, the rates of reaction were much lower, leading to less depleted uranium and lower values for the fluence, which rarely exceeded $5 \cdot 10^{20}$ n/cm^2.

The number of fissions were also much lower, generally under 1%. However, for other reaction zones, the age of the reaction is close to that calculated in reaction zone 2, at least for neodymium which is the rare-earth element with the highest fission yield. However, the duration of the reactions seems to have been much shorter than in reaction zone 2. In the case of samples taken from reaction zone 3, the calculated duration values of which (not reported in Table 1) are not precise because of the very low proportion of fissions in ^{239}Pu, the values seem to be several hundreds of thousand years. In the case of sample 2194 taken from the center of reaction zone 5, the proportion of fissions in ^{239}Pu is high, about 10%, and this leads to a reaction duration of only about 100,000 years. So, despite high uranium concentration, reaction zones south of reaction zone 2 underwent low reaction rates for times which were probably shorter. These observations can be explained by the geometry of these reaction zones, characterized by a much lower thickness of clay than in reaction zone 2 and also by interruptions and irregularities in the uranium concentrations [14].

Table 1 also clearly shows two other characteristics of the Oklo reactors: a general and remarkable constancy of the age and duration values in the center of the reaction zones, and small remobilizations both in the center and the immediately bordering samples (1402 and 1421/4 to 1425/1).

The remarkable reaction zones stability is well illustrated by Fig. 3 which shows the actual distribution of uranium and the three more important fission-product rare earths neodymium, samarium and gadolinium, along a borehole traversing reaction zone 2 (SC 36). All four element distributions are very similar.

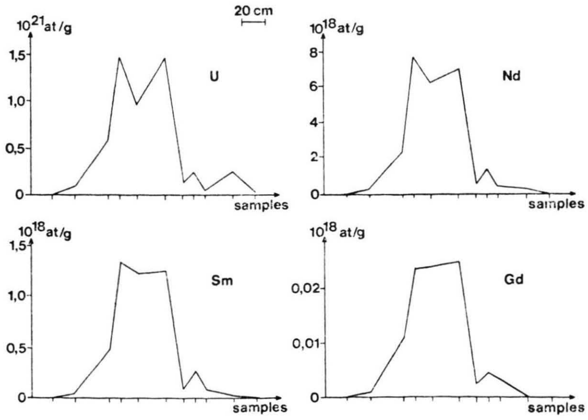

Fig. 3. SC 36 core — measured concentrations of uranium and fission rare earths.

However, small local remobilizations can also be observed both from the data in Table 1 (columns 6 to 9) and especially in Fig. 3, if one precisely compares the distributions of the three rare-earths on samples located in the center of the uranium deposit and on its borders.

By comparison with the reference samples, it is possible to estimate for each sample the difference between measured fission-product amounts and the calculated ones from the nuclear and neutron parameters provided by isotopic analyses. In the case of the SC 36 borehole, the differences are then compared to the averaged amount of fission products in the center of the reaction zone. This procedure enables evaluation of the extent of remobilization. The ratio between these calculated differences and the mean of the quantity measured in the core center are described by a Δ symbol. The variation of this Δ parameter along the SC 36 core is shown on Fig. 4 for the two fission products neodymium and ruthenium. When Δ is positive there is a fission-product excess with respect to the calculated amount, and vice-versa. Figure 4 also shows the present uranium distribution.

In the case of neodymium, Fig. 4 shows alternating deficits and excesses. Deficits are correlated to a maximum uranium concentration, whereas an excess is observed exactly in the center of the rich uranium ore but is correlated to a minimum in the uranium concentration. The samples farthest from the centre show a small fission neodymium excess. The migration of fission neodymium which was formed in reaction zone 2 leads to a levelling of the distribution in the reaction zone, tending to fill up the valleys and levelling the peaks of the curve, and to a slight spread in the bordering regions. But it must be noted that, in the case of neodymium, remobilizations affected only a very small fraction of that element. One can estimate that about 3% of the total amount of neodymium formed in the center was remobilized. For other fission rare earths, migration and spreading processes occurred in a very similar way, but with amplitudes which increase with the atomic number of the element, although not exceeding 15% to 20% in the case of gadolinium. In addition these migrations lead to considerable rare-earth fractionation, which also increases with increasing atomic number [15].

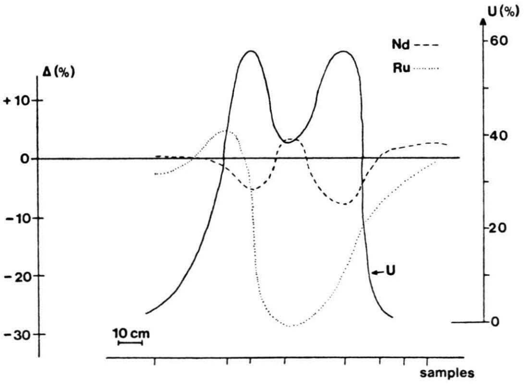

Fig. 4. SC 36 core — differences between the calculated and measured amounts of fission neodymium and ruthenium relative to the mean of the concentration at the core centre.

In the case of ruthenium, Fig. 4 shows that ruthenium migration at Oklo follows a completely different pattern from that of the rare earths, which is not surprising in view of its different chemistry. One observes a ruthenium deficit in the center of the uranium-rich ore, that is almost 30% of the total amount formed in the center. Remobilization at the borders, despite a small excess at the top of the core (left on Fig. 4), has not lead to a considerable movement of fission ruthenium out from the centre.

6. Retention of Fission Products

Figure 4 shows that the behaviour of fission products in the Oklo reactors varied from element to element. We have attempted a crude comparison of this particular behaviour in the Oklo uraninite with the behaviour in oxide fuels of pressurized water reactors. Many measurements have been carried out on such fuels, which operate at temperatures of a few hundred °C, the same range of temperatures that prevailed at Oklo [17].

The results of this comparison are shown on Table 2. The main fission products are distributed into five groups: a) gaseous compounds; b) volatile compounds; c) oxides which are soluble or d) insoluble in the fuel; e) metallic inclusions. In Table 2, the ionic radii are also given for each element.

The two last columns of Table 2 draw attention to the similarity in behaviour between fission products formed in an industrial fuel and those produced in the Oklo deposit. For example, the gaseous or volatile compounds accumulate in industrial fuels in the free volumes of the cladding, at Oklo they migrated outside the reaction zones. Elements forming oxides insoluble in the fuel also

Table 2. Behaviour of fission products in industrial reactors and in the Oklo natural reactors.

Chemical state	Eléments	Ionic radius (Å) [18]	Industrial reactors		Oklo natural reactors	
			Retention in the fuel	Localisation in the free volume of the cladding	Retention	Migration
Gaseous compounds	Kr	(4)		×		×
	Xe	(4)		×		×
Volatile compounds	I	(2,1)		×		×
	Te	0,60		×	×	
	Cs	1,8		×		×
Oxides insoluble in the matrix	Sr	1,21		×		×
	Ba	1,44		×		×
	Mo	0,73		×		×
Metallic inclusions	Tc	0,72		×	×	
	Ru	0,70		×	×	
	Rh	0,71	×		×	
	Pd	0,70	×		×	
Oxides soluble in the matrix	Y	0,98	×		×	
	Nb	0,72	×		×	
	Zr	0,92	×		×	
	rare-earths	1,02—1,13	×		×	
	Pb	1,02				
	Th	1,12				
	U	1,08				
	Pu	1,04				

tend to migrate to the surface of the fuel elements and at Oklo outside the reactor zones. Elements which form metallic inclusions or oxides soluble in the fuel remain located in the fuel material of industrial water reactors as well as in the reaction zones of the natural Oklo reactors.

In the case of gaseous fission products, the larger diameter of the two rare gases krypton and xenon in the crystalline lattice with respect to the uranium ionic radius in UO_2 explains why the rare gases formed tend to escape from the fuel. Fission gases must have escaped during irradiation, as shown by the lower fluence that is evident from their isotopic analyses [19]. Two main processes are involved, recoil or knock-out and diffusion, the latter prevailing at higher temperatures [20]. In industrial fuel material, fission gases diffuse to the free volume of the fuel element, usually as bubbles with a diameter of a few tens of Angström [21]. The proportion of gas released depends on the ratio of the sample surface to its volume, and Naudet [22] was able to show by neutron physics calculations that the porosity in the Oklo material was about 30%. The highly fractured environment of the Oklo reactors led to the progressive diffusion of the fission-gas bubbles and explains the fact that rare gases have almost completely escaped from the Oklo ore. Only one thousandth or even one ten thousandth of the total quantities of gases formed during the reactions remains in the deposit [19].

In irradiated fuels, the behaviour of iodine and tellurium has been studied in correlation with that of fission gases; the results show that the release characteristics of the halogens, tellurium and the rare gases are quite similar, and these fission products usually diffuse to the cooler end of the fuel [23]. In Oklo samples, isotopic analyses show that iodine behaviour was similar to that of xenon as is evident from measurements on ^{129}Xe and ^{130}Xe, which are daughter products of iodine. In contrast, tellurium appears to have been retained nearly quantitatively in the Oklo ore [24]. The small value of the ionic radius of Te^{4+} (see Table 2) may have contributed to the retention of tellurium in the matrix; under these conditions, it could be expected to have been retained in the Oklo deposit in the metallic form.

Some experiments have shown that caesium can sometimes be ejected from the fuel material in higher proportion than rare gases [25]. This is explained by migration to grain boundaries followed by a knock-out process and diffusion rare gases being retained in greater proportion by interlinkage of gas bubbles.

Also, because of its large ionic radius, caesium cannot be easily accomodated in the crystalline lattice. Because of these considerations, it was expected that caesium formed at Oklo would escape quantitatively; in fact the measured amounts only represent a few per cent of the original quantity [26, 27].

The fission products which usually do not exist as oxides in nuclear fuels include technetium, ruthenium, rhodium and palladium. In reactor fuels, they are formed as elements, frequently as metallic inclusions; these inclusions usually have a diameter of a few micrometers [28]. Some, which mainly contain palladium and rhodium may also contain elements from the fuel itself, such as uranium and plutonium [29]. All these elements should be metallic and chemically inactive if in the form of spherules. They are often located near the center of the fuel. The behaviour of these elements in the Oklo minerals is slightly different. Ruthenium appears to have been partially removed; deficits up to 30—40% have been reported in some samples [19]. Major migrations of technetium were also reported [19]; they lead to variable amounts of ^{99}Ru (formed by ^{99}Tc decay) and it is apparent from isotopic analyses that these two elements behave differently. This can be related to the existence of metallic inclusions containing uranium but no technetium [29]. Palladium formed in the Oklo minerals is always found with uranium [30] and its isotopic analyses also lead to the conclusion that the rhodium parent had a low mobility [12]. Generally, fission products which do not form oxides are found to have been well retained at Oklo, despite small remobilizations. The similarity of the ionic radii of these elements with that of uranium facilitates their retention in the uraninite lattice.

In fuel materials, molybdenum is sometimes found in inclusions, but is usually present as a hyperstoechiometric oxide. At Oklo, where the geological environment was water-saturated, it was also oxidized and may therefore be included in the group of elements which form oxides, not soluble in the UO_2 matrix, such as strontium and barium. In a reactor fuel, these elements mainly exist as separated oxidized species [31]. Moreover, strontium and barium formed at Oklo appear to migrate entirely outside the reactor zones, as isotopic and concentration data show that the measured quantities of these elements represent only a few per cent of the amount formed by fission [26]. They are also diluted by large amounts of natural elements. A similar situation prevails for alkali metals [27].

The other fission products that form oxides soluble in the initial UO_2 matrix include yttrium, niobium, zirconium and the rare earths. With the exception of niobium, these elements in oxides have ionic radii which are similar to that of uranium; therefore, retention is expected to be high and measurements in nuclear fuels have confirmed this expectation [28]. The same results are obtained in the Oklo reactors. Yttrium and niobium are well retained in the Oklo ore, where they have been found in uranium by ion probe analysis [30]. Zirconium analyses show no large migrations. Remobilizations have occurred but in general account for less than 30% of the total amount formed [19]. Moreover, it is well established that rare earths are located in uraninite and that remobilization only slightly affects the original distributions [10, 15].

One can conclude from the above comparisons that there is a general parallelism between the behaviour of elements in the reactor zones of the Oklo uranium deposit, and the observed behaviour in contemporary nuclear fuels.

7. Retention of Other Elements

Retention of ^{239}Pu that has decayed to ^{235}U is proved, e.g., by the coincidence of ^{235}U and ^{238}U ion probe images [30]. This can largely be explained by physico-chemical properties, similar to the uranium ones; for example, isomorphism between uranium and plutonium compounds is well known to exist, especially between UO_2 and PuO_2. The ionic radii of the species U^{4+} and Pu^{4+} are not very different (see Table 2).

The similarities between thorium and uranium also explain the retention of ^{232}Th formed at Oklo by radioactive decay of ^{236}U (with a half-life of $2.3 \cdot 10^6$ years). Again, as with Pu, the radii of the two ions (U^{4+} and Th^{4+}) are comparable (see Table 2). Moreover, thorium can only exist in the 4^+ state. As soon as it is formed, ^{232}Th is oxidized to ThO_2, which is isomorphous with UO_2. Since its formation, ^{232}Th has partly decayed into ^{208}Pb with a half-life of $1.4 \cdot 10^{10}$ years.

Lead, however, has different chemical properties and is largely deficient as shown by the Pb/U balance [32].

Retention of the other transuranium elements can be studied from the analyses of their descendants. The parent isotopes in this case consist mainly of ^{237}Np (which is formed by decay of ^{237}U, and which itself decays to ^{209}Bi with a half-life of $2.14 \cdot 10^6$ years), and also of isotopes of americium and curium.

8. Application to Nuclear Waste Storage

The long-time storage in geological media of radioactive wastes, originating from nuclear centers and reprocessing plants, is being widely studied. Experience gained from the study of the Oklo phenomenon can provide valuable information on these problems [19, 33]. Two recent publications by our group [34, 35] are related to this subject.

One main conclusion from studying the natural Oklo reactors is that actual uranium distributions are similar to those prevailing at the time of reactors' operation. One of the arguments supporting this conclusion is the sharpness of isotopic concentration gradients which are present today. Retention of fission products at Oklo was thus due to retention in the uranium oxide. A study of the results in Table 2 and comparaison with reactor fuels has allowed us to classify elements formed in the uranium oxide in two groups, according to the likelihood of forming compounds which are retained by the initial crystalline matrix or fuel:

1) Elements which fit the ionic lattice comprise those which form oxides soluble in the matrix (thorium, plutonium and other transuranium element oxides and the fission products yttrium, zirconium and rare earth oxides), as well as those found in metallic inclusions (which may or may not contain the fissile element). These elements remain in reactor fuels and have been retained in the Oklo uraninite for about two billion years. Irradiations and changing environmental conditions, notably tectonic accidents [39] have not perturbed them.

2) Elements forming oxides not soluble in the UO_2 matrix (including gaseous or volatile compounds) usually diffuse outside present-day nuclear fuels and were also almost totally lost from the Oklo reactors.

In the latter case, the clay areas surrounding the reactors did not constitute a good retention material for fission-product compounds which were not soluble in the UO_2 matrix. This material has also escaped from the clay. However, no comparison between these clay areas and the clay barriers which could be placed around deeply-stored nuclear wastes should be attempted. These latter barriers should retain wastes mainly by a cationic exchange process, and will only be efficient after a few decades of cooling of the fission products, when the external temperature will not exceed about 100—150 °C [36].

Thus, extrapolation of the results of the Oklo natural reactor studies to the storage of radioactive wastes in deep geological media is not straightforward. These studies show nevertheless that at one location retention of fission products and transuranium elements, in particularly resistant and well-preserved crystalline lattices has been achieved naturally, in a time-scale order of magnitude larger than what is required for practical purposes. For this reason some authors have advocated synthetic uraninite, or thorianite (because thorium cannot be oxidized), as a matrix for the long-term storage of radioactive products in geological sites. However, results of applied research often favor glasses, ceramics or even synthetic minerals. These should provide better retention for many more radionuclides, because volatilisation losses during incorporation of the fission products into the matrix are much greater for high melting point compounds [37, 38].

We conclude that for the storage of fission products, the Oklo studies show that there is hope that the problems should be soluble and that to some extent guidance can be derived from nature. They also show that actual solutions require detailed independent studies.

This work could not have been started if mass spectrometry had not achieved the current high degree of accuracy and precision in isotopic abundances measurements, and in resolution.

It is only just that this paper should be dedicated to Professor Hintenberger who devoted his lifework to the successful development of the art.

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