Reconstruction of cumulative fission yield curve and geochemical behaviors of fissiogenic nuclides in the Oklo natural reactors

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Isotopic ratios and elemental abundances of rare earth elements (REE), Rb, Sr, Zr, Mo, Ru, Pd, Ag, Te, Ba and U in four samples from two Oklo Reactor Zones 7, 8, 9 and 10 were determined by thermal ionization mass spectrometry. These elements have unusual but reasonable isotopic anomalies due to the effect of fission and/or neutron capture reactions. In order to discuss the retentivity of fissiogenic nuclides, the fission product yield curves covering the wide mass range from 90 to 160 were reconstructed on the basis of our results. We have estimated the behavior of fissiogenic nuclides by means of the differences between the measured curves and empirical ones.

From comparison of these two sets of curves, measured and empirical, the behaviors of fissiogenic nuclides were deduced. Our results are in agreement with previous Oklo work at the following points:

(I) Ru, Pd, Te and most of a series of REE (except for La and/or Ce) have been well retained in the samples,

(II) Rb, Sr and Ba have been lost to a great extent, and their isotopic ratios are nearly the same as those of terrestrial standard values, and

(III) Zr, Mo and Ag have been partially removed from the reactors. The behaviors of Zr and Mo seem to have been highly affected by the chemical and geological environments in and around the reactors.

The present work reveals that, among REE, La and Ce might have been partially removed in contrast to the good retention of other REE. Also, there is a possible remobilization of ^{90}Sr during operation of the Oklo reactors.

INTRODUCTION

Burial in suitable rock strata is the current concept for radioactive waste disposal. In this connection, the detailed understanding of the behaviors of radioactive nuclides in the geological media is required. Geochemical studies on the Oklo natural reactors are well known as natural analogues of radioactive waste repository, and are expected to provide us with useful information on the mobilities of various fissiogenic nuclides. Many of fissiogenic nuclides produced in these reactors have been preserved for about 2.0 Ga. Except for the Oklo reactors,

it is impossible to trace the geochemical behavior of radioactive nuclides for a long time interval.

From the view point of stability of elements between solid and liquid phases, the mobilities of various elements have been predicted by use of Eh-pH diagrams (Brookins, 1978, 1984). In general, most of these data are in agreement with the observations at the Oklo site. Many studies on the isotopic compositions of various elements in Oklo samples have been performed, and the behaviors of fissiogenic nuclides have been discussed (*The Oklo Phenomenon*, 1975; Roth, 1977; *The Natural Fission Reactors*, 1978; De Laeter *et al.*, 1980; Holliger and Devillers, 1981;

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Loss *et al.*, 1984; Curtis *et al.*, 1989). These works as a whole cover nearly all aspects of isotopic abundances, but in general have been rather fragmentary individually, although they had focal points of their own in order to understand the features of the Oklo reactors.

We have evaluated the mobilities of fissionogenic nuclides on the basis of cumulative fission product yield curves, and have recognized that the deviation of measured curves from empirical ones can be one of the useful indicators of the mobilities of fissionogenic nuclides. In our attempt to reconstruct the fission product yield curves, attention was paid to rare earth elements (REE), Rb, Sr, Zr, Mo, Ru, Pd, Ag, Cd, Sn, Te, Ba and so on. Here we report the isotopic ratios and abundances of REE, Rb, Sr, Zr, Mo, Ru, Pd, Ag, Te and Ba in samples from Oklo ores by the use of thermal ionization mass spectrometry.

SAMPLES

Since the discovery of the first Oklo reactor in 1972, sixteen reactors have been found. Geological study on the Oklo uranium ore deposit has been reported by Gauthier-Lafaye and Weber (1989).

In our present study, four samples were analyzed. The official nomenclatures of these four samples are unknown. One is "sample A" of our previous REE study (Hidaka *et al.*, 1988). This sample comes from reactor Zone 7, 8, 9 and it is uraninite. The other three samples from Zone 10 were collected from a borehole. Zone 10 has been located underground, and is now being investigated in detail (Holliger, 1991). A schematic cross section of Zone 10 is shown in Fig. 1. SF-29 is a blackshale, and contains uraninite. SF-42 is composed of two parts, slate (SF-42SL) and sandstone (SF-42SS), and is located around the boundary between sandstone and the center of reactor (Bunno *et al.*, 1985). Descriptions of samples are compiled in Table 1. Three samples from Zone 10 are not high-grade U ores, but it is easily recognized that ^{235}U is depleted and the fission products are contained to some extent in each sample. The neutron fluence evaluated from Gd isotopes is also listed in Table 1.

CHEMICAL PROCEDURES

Rock samples were digested by hot HF, HClO₄ and HNO₃, and were finally dissolved in

Fig. 1. Geologic cross section of reactor zone 10 (Holliger, 1991). Each name of stratigraphic sections has been defined by Gauthier-Lafaye and Weber (1989).

Table 1. Description of samples

	A	SF-29	SF-42SL	SF-42SS
Zone	7, 8, 9	10	10	10
Rock Type	uraninite	blackshale	slate	sandstone
U conc. (wt.%)	51.1	5.86	0.256	0.0427
$^{238}\text{U}/^{235}\text{U}^a$	146.8 ± 0.3	158.7 ± 0.7	151.7 ± 1.6	151.7 ± 2.1
neutron fluence ^b ($\times 10^{20}$ n/cm ²)	1.9	0.28	0.17	0.085

^a) Errors are 2σ mean. Terrestrial standard value of $^{238}\text{U}/^{235}\text{U}$ is 137.5 ± 0.2

^b) The values are calculated from Gd isotope ratios (Hidaka and Masuda, 1988).

diluted HCl. Fractions for each element of REE were separated by cation exchange resin columns with α -hydroxyisobutyric acid (α -HIBA) (Hidaka *et al.*, 1988). Separation procedures and mass spectrometric techniques of other elements were conventional: Rb and Sr (Faure and Powell, 1972), Zr (Shima, 1978), Mo (Tromp *et al.*, 1981, Kawashima, 1990), Ru (Terada *et al.*, 1975), Pd, Ag and Te (Loss *et al.*, 1983), Ba (Eugster *et al.*, 1969), U (Chen and Wasserburg, 1981). In mass spectrometry of Ru, Pd, Ag and Te, a V-shaped Re single filament with silica gel and phosphoric acid was employed. Since there are some contaminant peaks attributed to silica gel and phosphoric acid, careful preheating of a filament at about 1000°C was necessary prior to beginning of the measurements.

At first, isotopic measurements were performed by thermal ionization mass spectrometer (JEOL-JMS-05RB) equipped with an electron multiplier. In the isotopic measurements, the absence of isobaric interferences was always confirmed by monitoring non isobaric mass range. And in prebaking of filaments, much attention was paid to reduce the natural Mo contamination from the Re filament. In the measurement of Pd, some contamination at mass number 110 could not be completely removed. The origin of this contamination was not definitely identified. Thus, the abundance of ^{110}Pd could not be precisely determined.

After the determination of isotopic compositions, elemental abundances were measured by

isotope dilution method. Moreover, the determinations of monoisotopic abundances of REE (Pr, Tb, Ho and Tm) were carried out by ICP-MS (VG PlasmaQuad type I) (Hirata *et al.*, 1988).

RESULTS AND DISCUSSION

Cumulative fission product yield curves for ^{235}U , ^{238}U and ^{239}Pu

Isotopic compositions and concentrations of various elements (REE, Rb, Sr, Zr, Mo, Ru, Pd, Ag, Te and Ba) in four samples are presented in Tables 2 and 3. On the basis of these data, the proportions of fissiogenic nuclides to total abundances of nuclides could be approximately evaluated. Details of this evaluation were reported previously (Hidaka *et al.*, 1988). These evaluated values are compiled in Table 4.

In this paper, "relative fission yield" refers to the relative number of atoms of fissiogenic nuclide. In practice, abundance (ppm) of each of fissiogenic nuclides is divided by its mass and the obtained value is designated as ppm/mass. Therefore, plotting ppm/mass values against mass number corresponds to relative fission product yield curve (Hidaka *et al.*, 1988). The comparison of these curves and the reference curves makes it possible to estimate the retentivity of fissiogenic nuclide in Oklo samples (Hagemann and Roth, 1978). As to SF-42SS, the amounts of fissiogenic nuclides are much less than those in other three samples (see Table 4). It is actually impossible to construct a fission product yield curve for SF-42SS because of small amount of fission products in the sample, and it is difficult to discuss the behavior of nuclides in SF-42SS by use of fission product yield curves. Therefore the discussions will be restricted to the remaining three samples, A, SF-29 and SF-42SL.

It is empirically well known that fission product yield curves for uranium 235, 238 and plutonium 239 have binary maximal peaks around regions of 90–100 and 130–140 in mass number. The patterns of fission product yields are slightly different among these three nuclides. In the Oklo natural reactors, uranium 235, 238 and plutonium 239 have fissioned. Using conven-

Table 2. Isotopic compositions (atom %)

(a) REE

		Standard	A*	SF-29	SF-42SL	SF42-SS
La	138	0.0888 (2)	0.0618	0.0253 (2)	0.0552 (5)	0.0809 (2)
	139	99.911 (209)	99.938	99.975 (505)	99.945 (873)	99.919 (305)
Ce	136	0.192 (4)	0.114	0.0826 (11)	0.169 (5)	0.172 (1)
	138	0.241 (3)	0.159	0.111 (1)	0.222 (5)	0.231 (1)
	140	88.30 (10)	73.64	69.39 (11)	84.39 (24)	86.26 (2)
	142	11.26 (10)	26.08	30.42 (9)	15.22 (4)	13.34 (2)
Nd	142	27.19 (6)	4.97 (2)	8.05 (3)	20.47 (3)	23.85 (4)
	143	12.18 (3)	24.44 (3)	22.58 (7)	15.56 (2)	14.00 (2)
	144	23.80 (4)	27.18 (6)	26.88 (7)	24.75 (5)	24.41 (4)
	145	8.29 (2)	16.81 (3)	15.59 (5)	10.70 (2)	9.64 (2)
	146	17.17 (3)	15.13 (1)	15.39 (5)	16.49 (2)	16.79 (3)
	148	5.74 (1)	7.74 (1)	7.55 (2)	6.51 (2)	6.06 (1)
	150	5.62 (1)	3.73	3.97 (1)	5.52 (2)	5.26 (1)
	152	26.65 (3)	12.96 (1)	17.74 (2)	24.15 (14)	25.66 (5)
Sm	144	3.12 (1)	0.343 (9)	1.202 (2)	2.57 (2)	2.95 (1)
	147	15.11 (2)	52.76 (1)	40.62 (6)	22.20 (14)	17.90 (3)
	148	11.30 (2)	2.54	5.39 (1)	9.68 (4)	10.73 (2)
	149	13.86 (2)	1.04	1.54	5.90 (5)	9.53 (2)
Eu	150	7.39 (1)	25.88 (2)	23.34 (3)	16.36 (10)	12.07 (2)
	152	22.57 (3)	4.48 (1)	10.17 (1)	19.13 (12)	21.17 (4)
	154	47.88 (6)	38.50	37.41 (5)	42.66 (12)	
	153	52.12 (7)	61.50	62.59 (8)	57.34 (16)	
Gd	152	0.201 (2)	13.73 (3)	4.83 (1)	1.201 (2)	0.517 (1)
	154	2.17 (2)	4.38 (1)	3.09 (1)	2.450 (4)	2.274 (2)
	155	14.78 (3)	0.844 (1)	4.49 (1)	8.54 (2)	12.49 (2)
	156	20.46 (6)	32.69 (4)	29.95 (5)	26.77 (7)	22.80 (5)
	157	15.67 (6)	0.146	0.745 (2)	4.37 (1)	9.18 (2)
	158	24.79 (9)	31.92 (4)	36.81 (6)	35.26 (9)	31.06 (6)
	160	21.92 (6)	16.29 (2)	20.08 (3)	21.39 (4)	21.68 (4)
	156	0.060 (1)	0.0706 (15)	—	—	—
Dy	158	0.968 (6)	0.117 (2)	—	—	0.123 (3)
	160	2.41 (1)	3.03	2.74 (2)	2.30 (2)	2.410 (3)
	161	19.05 (4)	18.60 (1)	19.01 (4)	19.30 (5)	19.06 (4)
	162	25.66 (4)	27.93 (1)	26.60 (6)	26.82 (8)	25.67 (5)
	163	24.71 (4)	30.01 (1)	26.04 (6)	24.91 (8)	25.27 (5)
	164	28.00 (11)	20.23 (2)	25.62 (5)	26.66 (9)	27.47 (5)
	162	0.1450 (3)	0.139	—	—	0.151 (3)
	164	1.602 (2)	1.58	—	1.58 (2)	1.58 (3)
Er	166	33.37 (2)	34.91 (1)	—	33.52 (9)	33.61 (7)
	167	22.87 (4)	13.94 (1)	—	21.57 (6)	21.51 (4)
	168	26.99 (4)	35.18	—	18.28 (10)	28.26 (5)
	170	15.00 (3)	14.38 (1)	—	15.04 (6)	14.88 (3)
	168	0.1364 (4)	0.0425 (28)	0.105 (1)	—	—
	170	3.072 (3)	4.62 (1)	3.261 (4)	—	3.06 (1)
	171	14.29 (2)	13.88	14.30 (1)	—	14.30 (5)
	172	21.79 (2)	22.01 (1)	21.93 (1)	—	21.99 (5)
Yb	173	16.14 (3)	15.55 (2)	16.06 (1)	—	16.04 (3)
	174	31.78 (2)	31.38 (2)	31.70 (2)	—	31.91 (8)
	176	12.79 (2)	12.51 (2)	12.65 (1)	—	12.70 (7)
	175	97.44 (9)	99.40	98.12 (10)	97.60 (9)	—
	176	2.56	0.600	1.88	2.40	—
	176	2.56	0.600	1.88	2.40	—

(b) Others

		standard	A	SF-29	SF-42SL	SF-42SS
Rb	85	72.17 (19)	72.05 (27)			
	87	27.83 (8)	27.95 (11)			
Sr	84	0.558 (3)	0.560 (4)			
	86	9.863 (2)	9.876 (14)			
	87	7.005 (1)	7.115 (9)			
	88	82.57 (2)	82.45 (12)			
Zr	90	50.95 (6)	36.68 (17)	50.16 (14)	50.55 (19)	50.73 (18)
	91	11.25 (2)	14.65 (7)	12.28 (8)	12.06 (5)	11.76 (3)
	92	17.28 (2)	18.62 (7)	17.16 (9)	17.14 (9)	17.18 (3)
	94	17.63 (3)	19.65 (13)	17.29 (10)	17.41 (9)	17.47 (6)
	96	2.90 (1)	10.40 (9)	3.09 (1)	2.83 (2)	2.85 (1)
Mo	92	14.63 (2)		7.01 (6)	14.32 (15)	
	94	9.21 (1)		4.72 (4)	9.18 (10)	
	95	15.93 (2)		20.99 (10)	15.85 (18)	
	96	16.67 (2)		8.56 (8)	16.82 (24)	
	97	9.54 (1)		17.01 (9)	9.90 (12)	
	98	24.23 (5)		24.03 (14)	24.22 (40)	
	100	9.79 (2)		17.68 (7)	9.70 (12)	
Ru	96	5.53 (1)	—	—		
	98	1.86 (1)	—	—		
	99	12.73 (4)	29.74 (7)	30.80 (9)		
	100	12.62 (3)	—	—		
	101	17.03 (4)	33.06 (8)	30.87 (9)		
	102	31.49 (7)	24.92 (6)	26.61 (7)		
	104	18.73 (5)	12.59 (2)	11.72 (5)		
Pd	102	1.027 (3)	—	—	—	
	104	11.24 (3)	5.64 (2)	—	4.22 (7)	
	105	22.57 (8)	59.13 (30)	60.68 (53)	66.37 (82)	
	106	27.24 (8)	26.53 (13)	24.88 (22)	21.32 (52)	
	108	26.22 (9)	6.27 (3)	9.69 (6)	5.17 (11)	
	110	11.70 (6)	2.44 (1)	<4.8	<3.0	
Ag	107	51.93 (7)		60.95 (19)	52.49 (11)	51.58 (21)
	109	48.07 (6)		39.05 (12)	47.51 (10)	48.42 (21)
Te	120	0.0968 (4)		—	—	—
	122	2.620 (21)		—	—	—
	123	0.915 (7)		—	—	—
	124	4.692 (37)		—	—	5.80 (5)
	125	7.094 (32)		1.37 (3)	3.34 (5)	13.20 (42)
	126	18.78 (8)		2.84 (3)	4.97 (8)	14.56 (54)
	128	31.80 (8)		16.84 (11)	39.04 (7)	29.71 (52)
	130	34.00 (9)		78.95 (52)	52.65 (9)	36.74 (65)
Ba	130	0.1056 (2)	0.1038 (3)	0.1059 (3)	0.1063 (2)	0.1047 (4)
	132	0.1007 (2)	0.0968 (6)	0.1019 (4)	0.1028 (2)	0.1004 (4)
	134	2.430 (2)	2.438 (3)	2.444 (4)	2.443 (3)	2.448 (9)
	135	6.616 (4)	6.640 (9)	6.635 (12)	6.706 (9)	6.627 (18)
	136	7.872 (6)	7.949 (12)	7.873 (27)	7.916 (9)	7.892 (22)
	137	11.209 (8)	11.289 (10)	11.148 (21)	11.283 (11)	11.258 (12)
	138	71.67 (4)	71.48 (6)	71.69 (9)	71.44 (10)	71.57 (7)

Numbers in parentheses are 2σ errors of the last figures indicated. The errors less than half unit of the last are omitted.

*REE data of sample A are from Hidaka and Masuda (1988).

Table 3. concentrations of elements(ppm)

	A	SF-29	SF-42SL	SF-42SS
Rb	9.56±0.07			
Sr	(2.11±0.01)×10			
Zr	(1.26±0.01)×10 ³	(9.20±0.10)×10 ²	(7.36±0.07)×10 ²	(9.27±0.11)×10
Mo		(1.22±0.03)×10 ²		
Ru	(3.50±0.04)×10 ²	(5.40±0.09)×10		
Pd	(5.33±0.06)×10	3.02±0.09	(6.00±0.29)×10 ⁻²	
Ag		3.87±0.04	1.66±0.02	
Te		5.66±0.19	(7.76±0.21)×10 ⁻¹	
Ba	(6.66±0.04)×10 ²	(2.24±0.02)×10 ²	(2.37±0.02)×10 ²	(2.86±0.02)×10
La	(1.00±0.01)×10 ²	(2.80±0.02)×10	3.84±0.03	(2.80±0.02)×10
Ce	(3.41±0.03)×10 ²	(1.07±0.01)×10 ²	(1.26±0.01)×10	(4.74±0.04)×10
Pr	(8.68±0.04)×10	(2.03±0.02)×10	1.05±0.01	3.59±0.04
Nd	(3.55±0.03)×10 ²	(9.88±0.10)×10	4.56±0.02	(1.27±0.01)×10
Sm	(7.36±0.07)×10	(1.89±0.02)×10	(9.71±0.08)×10 ⁻¹	1.32±0.01
Eu	(1.16±0.01)×10	4.16±0.04	(2.58±0.03)×10 ⁻¹	(1.24±0.01)×10 ⁻¹
Gd	(1.59±0.01)×10	8.60±0.08	1.05±0.01	(8.78±0.09)×10 ⁻¹
Td	1.74±0.01	(9.95±0.08)×10 ⁻¹	(1.39±0.01)×10 ⁻¹	(9.16±0.09)×10 ⁻²
Dy	5.02±0.04	4.45±0.05	(8.31±0.08)×10 ⁻¹	(4.34±0.04)×10 ⁻¹
Ho	1.96±0.01	(8.40±0.08)×10 ⁻¹	(3.07±0.03)×10 ⁻¹	(6.63±0.06)×10 ⁻¹
Er	3.77±0.03	2.16±0.02	(9.12±0.09)×10 ⁻¹	(2.18±0.02)×10 ⁻¹
Tm	(4.34±0.04)×10 ⁻¹	(2.03±0.02)×10 ⁻¹	(1.30±0.02)×10 ⁻¹	(2.03±0.02)×10 ⁻²
Yb	2.91±0.03	1.35±0.01	(7.70±0.08)×10 ⁻¹	(1.83±0.02)×10 ⁻¹
Lu	(5.27±0.05)×10 ⁻¹	(2.22±0.02)×10 ⁻¹	(1.74±0.02)×10 ⁻¹	(3.82±0.05)×10 ⁻²

Table 4. Proportions of fissiogenic abundance to the total (fissiogenic plus natural) for each element (%)

	A	SF-29	SF-42SL	SF-42SS
Rb	0.3			
Sr	0			
Zr	40	2.0	0	0
Mo		53	0	
Ru	100	100		
Pd	100	100	100	
Ag		29	1.8	0
Te		91	12	
Ba	0	0	0	0
La	32	72	38	9.0
Ce	40	52	11	5.0
Nd	82	70	25	12
Sm	89	62	18	5.4
Eu				
Gd	14	4.8	1.2	0.78

tional method by Te, Pd, Nd, Sm and/or Gd isotope ratios (Ruffenach *et al.*, 1976), the proportions of fission for ²³⁵U, ²³⁸U and ²³⁹Pu to total fission can be calculated. However, the results obtained here show a wide variation of the proportions in question and it is difficult to evaluate definitely their numerical values. (References about empirical yields for ²³⁵U(thermal), ²³⁸U(fast) and ²³⁹Pu(thermal) are after Crouch (1977).) When considerations are restricted to isotopic compositions of Pd and Te

in samples A, SF-29 and SF-42SL, it is concluded that the fission products depend greatly on the fission of ²³⁵U. In the following, we will deal with the fission in our samples in terms of the contribution from pure ²³⁵U.

We have examined the geochemical behavior of fissiogenic nuclides from the comparison of fission patterns between empirical curves and measured ones. In addition, most of the nuclides corresponding to 140–150 mass range, i.e. light REE, have large neutron capture cross sections and are subject to interaction with neutrons. The isotopic compositions of these elements offer much important information concerning neutron fluence. On the other hand, the nuclides corresponding to another maximal yield peak (90–100 in mass region involving Zr, Mo and Ru) are not sensitive to neutrons, because they own very small neutron capture cross sections. It is considered that the isotopic anomalies of these nuclides are caused largely by fission, and not affected by neutron capture reactions. Moreover, the fission yields of nuclides in the valley between two fission peaks, are sensitive to neutron energy (e.g., Crouch, 1977), and will give a clue to the average neutron energy. Especially these three mass regions, (two max-

Fig. 2. Measured fission product yield curves of samples (a) A, (b) SF-29, and (c) SF-42SL. The broken lines in the figures are theoretical curves obtained for pure ^{235}U fission (See text).

imal yield regions, i.e., 90–100 and 130–140, and minimal yield region, 100–130, in mass number) are important in the construction of the fission yield curves. Figures 2-a, 2-b and 2-c show fission product yield curves for samples A, SF-29 and SF-42SL, respectively. In these diagrams, open circles connected with solid lines represent measured values. For the sake of reference, the empirical curves (broken lines) are adjusted to the measured curve with respect to the points for Pd, Te and Gd isotopes. The reasons of choice of Pd, Te and Gd for curve fitting are as follows: (i) It has been previously reported that the retention of Te is excellent, and that of Pd is also considerably good (Curtis *et al.*, 1989). (ii) In our previous paper (Hidaka and Masuda, 1988), Gd isotopes were found to be reliable for the estimation of nuclear parameters because of their good retentivity. (iii) Actually, as an independent

result in our observations in overlapping the obtained plot with the empirical curve, the empirical curve is in fairly good agreement with the measured one at the positions of Pd, Te and Gd.

The clear difference between measured and empirical curves appear at the valley, because the empirical lines in Figs. 2-a, 2-b and 2-c are fission-products yield curves for pure ^{235}U . Besides, it must be born in mind that the fission product yield curves are more or less variable depending on the neutron energy for the same parent nuclides. But those two curves are in fair agreement in other regions. Anyway, the current data are admittedly too limited to further quantitative considerations about the pre-fissioned nuclides, particularly with respect to the minimal valley.

We can apply the degree of deviation of "actually measured" from empirical fission yield curves to estimate the retentivities of fissiogenic nuclides.

Behavior of REE

Isotopic compositions and abundances of REE in some Oklo samples had been already reported (Loubet and Allegre, 1977; Holliger and Devillers, 1981; Hidaka *et al.*, 1988). Because some of REE nuclides are greatly affected by neutron capture reactions and that the retentivities of REE are generally good, isotopic data of REE have served as relative indicators of nuclear parameters (neutron fluence, temperature etc.). Previous estimations of these parameters have been made successfully by use of combination of Nd and Sm isotopic data (Holliger and Devillers, 1981; Loubet and Allegre, 1977; Hidaka and Masuda, 1988).

Isotopic anomalies of REE can be theoretically interpreted. As shown in Table 2, isotopic compositions of light REE are very anomalous, whereas those of heavy REE are less anomalous. Production of light REE by fission are much higher than those of heavy REE, and considerable amounts of fission fragments have been accumulated in samples. In addition, some REE nuclides (for example ^{149}Sm , ^{155}Gd and ^{157}Gd etc.) have so large neutron capture cross

sections that such nuclides are subject to neutron capture, and their isotopic abundances are much less than those of terrestrial standard values. Naturally, the frequency of neutron capture reactions mainly depends on neutron fluence in the reactors. To be sure, the extent of isotopic fractionation of such nuclides derived from neutron capture, as ^{150}Sm , ^{156}Gd and ^{158}Gd correlates with the amount of neutron fluence (see Table 1 and isotopic data in Table 2). Thus far, it has been estimated that these isotopic anomalies can be recognized at present owing to the good retention of fissiogenic REE in the reactors. However, scrutiny of details of retentivity of each REE in the reactor has not been carried out yet.

The data regarding Eh-pH diagrams (Brookins, 1978) suggest that a series of REE are difficult to move and have been well retained in the reactors. In this paper, we shall discuss the mobilities of lanthanides from the view point of cumulative fission product yields obtained by quantitative measurement of nuclides concerned.

As seen in Fig. 2, it is easy to recognize that Nd, Sm and Gd in A, SF-29 and SF-42SL fall on the same curve, but that only La and/or Ce is evidently off the curve. Further, deviations of La and Ce in A, and La in SF-29 are negative, while those of La and Ce in SF-42SL are positive.

Three interpretations are conceivable about positive deviation of La from the curve for SF-42; (i) the effect of neutron capture by ^{138}Ba , (ii) local enrichment of fissiogenic La and Ce, and (iii) the error derived from limitation of the method of estimation. Detailed explanation of each possibility is as follows.

(i) In the reactor, ^{138}Ba captures neutron and turns to ^{139}La by β^- decay in the following way:

The neutron capture cross section of ^{138}Ba is not so large (0.4 barn for thermal neutron). But the effect of neutron capture of Ba cannot be neglected because of the large difference in abundance between ^{138}Ba and ^{139}La . The observed abundance of ^{138}Ba (170 ppm) is higher than that

of fissiogenic ^{139}La (0.34 ppm). Simply judging from the evaluated neutron fluence (1.7×10^{19} n/cm²) and each amount of ^{138}Ba and ^{139}La , only 0.4% of ^{139}La is estimated to have been produced by the neutron capture of ^{138}Ba . As shown in the isotopic composition of Ba (Table 2), however, considerable amount of Ba, including fissiogenic Ba, might have been removed from this sample. There is a possibility that much more Ba existed during criticality, and a certain amount of La was produced by neutron capture. Unfortunately one cannot quantitatively estimate the amount of Ba during the reactor operation, because the isotopic composition of sample is nearly the same as that of terrestrial standard.

(ii) Strictly judging from the pattern of measured yield curve, the yield of not only La but also Ce is slightly higher than the expected yield based on the measured curve for Nd, Sm and Gd. In other words, there is a possibility of enrichment of fissiogenic La and Ce in this sample. Fissiogenic La and/or Ce may be enriched as a counterpart of leakage from the central zone of the Oklo reactors.

(iii) In the case of SF-42SL, the amounts of fissiogenic REE were substantially lower than those of SF-29. The curve of SF-42SL composed of Nd, Sm and Gd is smooth at the first glance, but it is argued here that the percentages of fissiogenic fractions are generally low for this sample. So, each value in the yield curve of SF-42SL has some errors and the numerical values calculated for La and Ce can be subject to relative overestimation, and fall off above the curve.

On the other hand, the fission yield curves of samples A and SF-29 have negative anomalies of La and/or Ce. Contents of fissiogenic La and Ce

in two samples are relatively high, and the effect of nuclear production on ^{139}La derived from ^{138}Ba discussed above must be negligibly low. These deviations indicate the partial leakage of fissiogenic ^{139}La , ^{140}Ce and ^{142}Ce out of the reactors. Complex causes are likely to be responsible for the partial leakage processes of these fissiogenic nuclides; selective dissolution, adsorption and coprecipitation affected by inclusions such as organic matter (Nagy *et al.*, 1991) and by pH and redox conditions (Brookins, 1984) in or around reactor. But in the case of REE, their chemical behaviors are coherent with each other. Here our attention should be paid to the chain reactions producing La and Ce. Primary product decays by successive beta decay processes to its stable isobar. In the case of fissiogenic ^{139}La , ^{140}Ce and ^{142}Ce , they temporarily become radioactive precursors other than REE in their fission chains, such as Xe, Cs and Ba. That is, it is likely that the precursors of fissiogenic La and/or Ce nuclides have behaved differently from those of other REE nuclides. Strictly speaking, fissiogenic ^{143}Nd , ^{144}Nd , ^{145}Nd and ^{146}Nd also temporarily become precursory nuclides other than REE in their fission chains. However, the total half-lives of precursors at elemental stages of Xe, Cs and Ba leading to those Nd nuclides are much shorter than those of the corresponding precursors for ^{139}La , ^{140}Ce and ^{142}Ce (Lederer and Shirley, 1978). In addition, other fissiogenic REE nuclides experience only REE precursors in the fission chains. This study shows again that negative deviation of fissiogenic La and/or Ce appears in some Oklo samples with abundant fission products. It should be noted here that the deviation of La is markedly larger than that of

Table 5. Deviations of isotopic composition of barium from standard values

(deviations in permil)

	130/134	132/134	135/134	136/134	137/134	138/134
A	-20±4	-42±6	+0.3±2.1	+6.5±2.3	+3.8±1.9	-5.9±1.8
SF-29	-2.9±3.9	+6.1±4.8	-2.9±2.6	-5.6±3.9	-11±3	-5.4±2.3
SF-42SL	+1.3±3.1	+15±3	+8.2±2.1	+0.2±2.0	+1.2±1.9	-8.5±2.1
SF-42SS	-16±6	-10±6	-5.8±4.6	-4.8±4.7	-3.1±4.0	-8.7±3.9

Errors are 2σ mean.

Ce, in conformity with the reasoning coming from the considerations of precursors.

In parallel with the interpretation of negative anomaly of La and Ce in A and SF-29, it is highly probable that the positive anomalies for La and Ce in SF-42SL are due to local enrichment of fissionogenic La and Ce.

Rubidium Strontium and Barium

Rb, Sr and Ba had been theoretically produced in great quantities in the reactor. However, their retention is not so good and most of them have disappeared. The isotopic compositions of these three elements in the samples are almost the same as those in terrestrial standards, indicating the complete loss of fissionogenic Rb, Sr and Ba.

One of our purposes of Ba isotope measurement was to trace ^{135}Cs ($T_{1/2}=2.95 \times 10^6$ y) and ^{137}Cs ($T_{1/2}=30$ y) from the isotopic deviation of ^{135}Ba and ^{137}Ba . Table 5 shows the deviations of the isotopic composition for Ba from the Ba standard. Isotope ratios are normalized against ^{134}Ba , because ^{134}Ba is non-fissionogenic. SF-42SL shows a relatively large deviation $+8.2 \pm 2.1\%$ for ^{135}Ba , and a slight deviation $+1.2 \pm 1.9\%$ for ^{137}Ba . Sample A also has positive deviations for ^{135}Ba and ^{137}Ba . These observations would suggest the addition of fissionogenic Cs to the samples, but there are also other possibilities to cause a slight isotopic deviation, such as the neutron capture reaction of Ba and Cs, and a trace amount of fissionogenic Ba remaining in the samples. In particular, the deviations of ^{130}Ba and ^{132}Ba with primarily low isotopic abundance may be enhanced by these factors. On the other hand, SF-29 and SF-42SS have negative deviations for ^{135}Ba and ^{137}Ba . ^{134}Ba is non-fissionogenic, but is produced by neutron capture of ^{133}Cs . Therefore, in these two cases the effect of addition of ^{134}Cs produced by neutron capture of ^{133}Cs might be higher than those of ^{135}Cs and ^{137}Cs . Overall, one cannot readily evaluate the behavior of fissionogenic Cs from our isotopic study of Ba, and further precise and systematic investigations are required.

Palladium, Silver and Tellurium

As it is evident from the fact that the best fit between the empirical and the observed yield curves was achieved at the points for Pd and Te, their fissionogenic nuclides have been retained considerably in SF-29 and SF-42SL samples. The relative retentivity of Pd to Te is quantitatively evaluated to be 0.85–0.90 for these two samples, compared with the empirical values for fission of ^{235}U . (That of Gd is also high, 0.94–1.1.)

Primordial Pd and Te must be rare in samples, and most of them reflect typically fissionogenic isotopic composition. The presence of ^{104}Pd in samples A and SF-42SL reveals its production by the neutron capture of ^{103}Rh . Especially, for fissionogenic Pd and Te, the fission yields of their constituent isotopes change substantially with change in mass number. These fission yields vary depending on parent nuclides (^{235}U , ^{238}U and ^{239}Pu) as described above. Relative cumulative fission yields of Pd and Te for thermal and/or epithermal neutrons have been precisely measured (Shima *et al.*, 1978, and De Laeter *et al.*, 1982). These empirical yields for Pd and Te are to a considerable extent subject to the energy of induced neutrons. In our study, the evaluation of fission contribution for ^{235}U , ^{238}U and ^{239}Pu from isotopic data of Pd and Te was of limited success. But it may be possible to determine this contribution, if more dependable and precise data are available about the dependency of fission yields on neutron energy.

It is difficult to estimate the proportions of primarily fissionogenic Ag isotopes to total Ag,

Table 6. Isotopic abundance and fission product yield of zirconium

Mass number	composition (atom %)		yield		
	calcd.	obsd.	calcd.	obsd.	obsd./calcd.
90	19.20	14.32	1.48	0.799	0.540
91	19.40	19.82	1.50	1.09	0.727
92	19.67	20.91	1.52	1.14	0.750
94	21.14	23.05	1.63	1.23	0.755
96	20.58	21.89	1.59	1.15	0.723

calcd. = calculated value

obsd. = observed value of sample A

owing to the effects of neutron capture reactions. Ag has only two isotopes, and both of two nuclides have enough neutron capture cross sections to react. However it is difficult to consider that significant amount of fissiogenic Ag has disappeared because of only neutron capture reactions. Among REE, some fissiogenic nuclides with larger cross sections than those of Ag isotopes have remained unaffected. In Figs. 2-b and 2-c, the currently observed values for Ag nuclides are plotted without any corrections taking into account the effect of neutron capture reactions. Judging from the total amount of Ag, it can be roughly estimated that more than half of fissiogenic Ag has disappeared.

Zirconium

It is empirically known that Zr nuclides are produced in large quantities by fission. In particular, one could expect some irregularity of ^{90}Zr among Zr nuclides, because ^{90}Zr becomes radioactive precursor ^{90}Sr with a half-life of 28.8 y. Other Zr nuclides than ^{90}Zr do not experience such a long life precursor as ^{90}Sr . But the isotope compositions of Zr in samples SF-29, SF-42SL and SF-42SS are almost the same as that of the terrestrial standard. We speculate that the intense redistribution between the fissiogenic and natural Zr brought about the results observed here. Because of such considerable terrestrial contamination, the estimation of fissiogenic fraction turns out to be difficult. In view of the nearly normal isotopic composition and rather high abundance of Zr in these samples, primarily fissiogenic Zr is considered to have been removed.

However, as shown in Fig. 2-a, fissiogenic Zr have been preserved in uraninite with high uranium content, such as sample A. Zr fission product yields of sample A are presented in Table 6. The "calculated values" in this Table are from Crouch (1977). The fissiogenic nuclides of Zr, except for ^{90}Zr , turn out to have been retained at 71–75%. However, only ^{90}Zr was significantly lowered relative to other Zr nuclides. According to our calculation, 17–20% of the fissiogenic ^{90}Zr is more depleted than the

Table 7. Fission product yield (ppm/mass) of ruthenium

mass number	sample A			SF-29		
	calcd.	obsd.	obsd./calcd.	calcd.	obsd.	obsd./calcd.
99	1.55	1.05	0.677	0.204	0.168	0.82
101	1.29	1.15	0.891	0.170	0.165	0.97
102	1.00	0.855	0.855	0.139	0.141	1.01
104	0.463	0.424	0.916	0.0608	0.0609	1.00

calcd. = calculated value

obsd. = observed value

other four fissiogenic nuclides. This implies that ^{90}Sr might have been lost to some extent during criticality of the Oklo reactors.

Molybdenum

Fission product yields of ^{95}Mo , ^{97}Mo , ^{98}Mo and ^{100}Mo are high. Isotopic anomalies in SF-29 are reasonable and endorse the considerably good preservation of the fissiogenic Mo nuclides. On the other hand, isotopic composition of SF-42SL is nearly the same as that of terrestrial standard value, suggesting that the retentivity of fissiogenic Mo is variable depending on the environmental conditions.

Ruthenium

The contents of Ru in the Oklo samples are high in contrast to those in common crustal rocks because of accumulation of high yield fission fragments. Further, isotopic compositions of Ru in samples A and SF-29 are found to be fissiogenic; non-fissiogenic nuclides ^{96}Ru , ^{98}Ru and ^{100}Ru could not be detected. As can be seen from Figs. 2-a and 2-b, fissiogenic Ru have been well retained in the reactor.

There is a possibility that behavior of Tc could be estimated from isotopic fractionation of ^{99}Ru (Curtis, 1986). ^{99}Ru has behaved differently from other fissiogenic Ru nuclides, because ^{99}Ru temporarily becomes ^{99}Tc with a long half-life ($T_{1/2} = 2.1 \times 10^5$ y) in its fission chain. Table 7 shows the comparison of fission product yields between calculated and measured values in samples A and SF-29. Fissiogenic Ru has been well preserved in both two samples, A and SF-

29, but the relative abundance values of ^{99}Ru are lower than those of other three Ru nuclides. The depletion of ^{99}Ru suggests the partial leakage of ^{99}Tc out of the Oklo reactors.

CONCLUSIONS

Construction of cumulative fission product yield curves over a wide range based on nuclide abundances leads us to the following information on retention of fissiogenic nuclides. One can conclude that Ru, Pd, Te and most of REE (Nd, Sm, Gd) have been well retained on the macroscopic scale. These nuclides seem fairly stable even under the geological conditions where Rb, Sr, Zr, Mo and/or Ba have been redistributed. In particular, the retention degrees of fissiogenic Zr and Mo greatly depend upon the chemical and geochemical conditions around the reactor. The nuclides whose precursors behave differently from such end products as ^{90}Zr , ^{99}Ru , ^{139}La , ^{140}Ce and ^{142}Ce may reflect the behaviors of their precursors to a considerable extent. The degree of deviation connected with the different behaviors of precursory nuclides is mainly affected by life-time of their precursors.

Reactor 10 was located underground and was not studied as well yet as reactors 1–9. For this reason, it can be expected that new results may be obtained from the analysis of reactor 10 samples. Our data obtained from fission product yield curves are in general agreement with previous work, but this is the only work carried out on many elements of underground zone samples. The detailed mining works at Oklo reactor zones including ones in the open pit and underground are being carried out. If we can find out a region with a significant enrichment of fissiogenic Ba in Oklo ores, light will be shed on the more detailed behavior of ^{137}Cs in geological media over a long time span.

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