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Mobilization and mechanisms of retardation in the Oklo natural reactor zone 2 (Gabon)—inferences from U, REE, Zr, Mo and Se isotopes

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Abstract

Mineralogical and isotopic studies were carried out on the natural nuclear reaction zone 2 from the Oklo deposit to evaluate the mobility of several nuclear reaction products in response to the alteration of the reaction zone and to identify the mechanisms which could retard the transport of released radionuclides. To address these issues, in situ isotopic analyses by SHRIMP and a selective extraction procedure were performed to constrain the structural location of nuclear reaction products (exchangeable and non exchangeable) and their association with mineral phases. The distribution patterns of U, REE, Zr and Mo isotopes reveal that substantial amounts were released from the core and migrated through the hydrothermal alteration halo over metric distances, owing to uraninite dissolution and advective transport by hydrothermal solutions during and soon after criticality. The results emphasize the mobility of Zr at Oklo, this element being often considered as “immobile” during water–rock interactions. The main output is the demonstration of the net effects of sorption and coprecipitation processes. Chlorite and to a lesser extent illite were found to have adsorbed significant amounts of U, REE, Zr (and probably Th) and less sorbing elements such as Mo. Coprecipitation of secondary UO₂ and P-rich coffinite within the alteration halo is also an important means of retardation. The concentration of radionuclides released from the reactor were probably high and they display solubility limited transport behaviour. No retention effect was found for Se in the immediate vicinity of the reactor and this element may have moved farther from its source of production. These results have interesting implications for the evaluation of long-term containment of radionuclides. They provide a simple illustration of the performance of a clay barrier in the uptake of radionuclides by sorption onto clays and reincorporation in secondary U-minerals. This study also demonstrates the robustness of these retention processes over extremely long periods of time.

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1. Introduction

Deep underground geological burial is one possible method for the disposal of commercially generated radioactive wastes. Existing information supports the belief that appropriate geological media in conjunction

with engineered barriers will be required to isolate wastes from the biosphere. Radionuclides potentially released from the waste form will interact with repository materials and host rock surfaces, retarding the movement of solutes relative to that of water passing through the system. Retardation processes that may affect radionuclide transport in groundwaters include adsorption, ion-exchange, matrix diffusion, precipitation and mineralization, and they are therefore beneficial for repository safety (McKinley and Hadermann,

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1984). Sorption is expected to be the dominant process at low concentrations of radioactive solutes and it is considered irreversible if the kinetics of desorption is sufficiently slow compared to the time of interest (Miller et al., 2000). Precipitation of mineral phases may occur if saturation is reached in the groundwater. Both irreversible sorption and precipitation are important to long-term predictions of repository safety because these mechanisms can immobilise radionuclides very efficiently. However, they are difficult to demonstrate and most performance assessment models make the assumption that retardation processes are reversible. Studies of element transport and retardation in natural systems such as U orebodies may provide convincing evidence for such mechanisms. Of particular interest are the naturally occurring nuclear reactors found in the Oklo and Bangombé U deposits. About 2 billion years ago, U-rich zones underwent nuclear fission chain reactions (Bodu et al., 1972; Neuilly et al., 1972) sustained over periods of several hundred ka (Hagemann et al., 1975; Ruffenach, 1979). The exceptionally good state of preservation of these reactors makes them suitable natural analogues of repository conditions although no global comparison with a repository site is legitimate. The fission products and other nuclides subjected to neutron capture and radioactive decay can be used as isotopic tracers to evaluate their mobility in the reactors and in the surrounding geological formations. In this paper, new data are presented on the mineralogy of the Oklo reactor 2 and the geochemical distributions of U, REE, Zr, Mo and Se isotopes in and around the reactor. The first studies of this reactor zone concluded uraninite showed excellent stability under reducing conditions allowing the retention of radionuclides compatible with the structure of uraninite such as Pu, Am, Th and REE. However, later studies have shown geochemical alteration of uraninite during regional heating and emplacement of dolerite dykes 1000–600 Ma ago as well as corrosion during recent supergene weathering (Janeczek and Ewing, 1995; Jensen and Ewing, 2000). The role of the alteration halo as a barrier limiting the transfers of radioelements was almost unexplored and little was known about 1) the spatial extension of syncritical migrations around the reactor and 2) the identification of processes which could retard released elements such as the sorption onto clays and the coprecipitation by secondary mineral phases. Subsequent mineralogical studies have suggested the retardation of fission products by precipitation of secondary mineral phases (e.g. Jensen and Ewing, 2001) but this interpretation was not supported by isotopic data. To address these issues, in situ isotopic analyses by sensitive high resolution ion micro-probe (SHRIMP) and a selective extraction procedure coupled with element and isotopic analyses were performed to constrain the structural location of several reactor products (namely exchangeable and non

exchangeable sites) and to provide insights on the mechanisms of mobilization and retardation.

2. Geological setting and sampling

The U deposit of Oklo is located at the SW border of the Franceville basin which is located in the south-eastern part of Gabon. The Francevillian is a sedimentary, clastic and volcano-sedimentary series of lower proterozoic age (Weber, 1968; Gauthier-Lafaye and Weber, 1989; Bros et al., 1992) which lies unconformably on an Archean crystalline basement. The basal FA sandstones contain the mineralization which occurred during the burial diagenesis of the basin, in oil traps formed during a phase of formation of the basin. The mineralization has been dated to 2050 ± 30 Ma by the U-Pb method (Gancarz, 1978). Nuclear reactions started in specific areas when the critical mass of U had been reached (Naudet, 1991). The reactor operation has been dated to 1950 ± 40 Ma by Ruffenach (1979) using the abundance of U, Th and fissionogenic lanthanides. The reaction zones (RZ) denoted 1–9 and “crochon” are located in the Oklo open pit (Fig. 1). Four reactors named 10, 13, 16 and Okélobondo RZ were excavated in underground galleries, in the southern part of Oklo and at Okélobondo, the southern extension of the Oklo deposit. The RZ 1–6 located in the northern part of the Oklo open pit are characterized by strong U accumulations where 800 tons of U have been affected by criticality and 6 tons of ^{235}U fissioned to produce 540×10^{15} J of released energy (Naudet, 1991). The integral neutron flux exceeded locally 1.5×10^{25} n/cm² and the reactions lasted $1-8 \times 10^2$ ka (Hagemann et al., 1975). In reactor 2, thick layers of massive uraninite have been described and the reactor is surrounded by a hydrothermal alteration halo which replaced the original C1 conglomerate layer (Gauthier-Lafaye et al., 1989). These features are related to intense circulation of groundwaters initiated by the heat released during the nuclear phenomenon. Heating and leaching by hydrothermal solutions caused quartz dissolution, as the result of increasing solubility of silica with temperature, and replacement by mainly chlorite and illite. Nearly 80% of the silica migrated out of the reactor 2 due to the hydrothermal alteration (Tchibena-Makosso, 1982). Similar numbers were calculated for Okélobondo RZ by Jensen and Ewing (2001) using a geometric model. Today reactor 2 consists of a 12 m long and 18 m deep lense. The thickness of the reactor core ranges from 20–50 cm and reaches 1 m in some places (Gauthier-Lafaye et al., 1996). The reactor core corresponds to a very high-grade U ore in which fission reactions took place. This facies contains 20–60 wt.% U. The reactor is surrounded by a hydrothermal alteration halo formed during the fission reactions and containing 0.1–3 wt.% U. Several samples have been

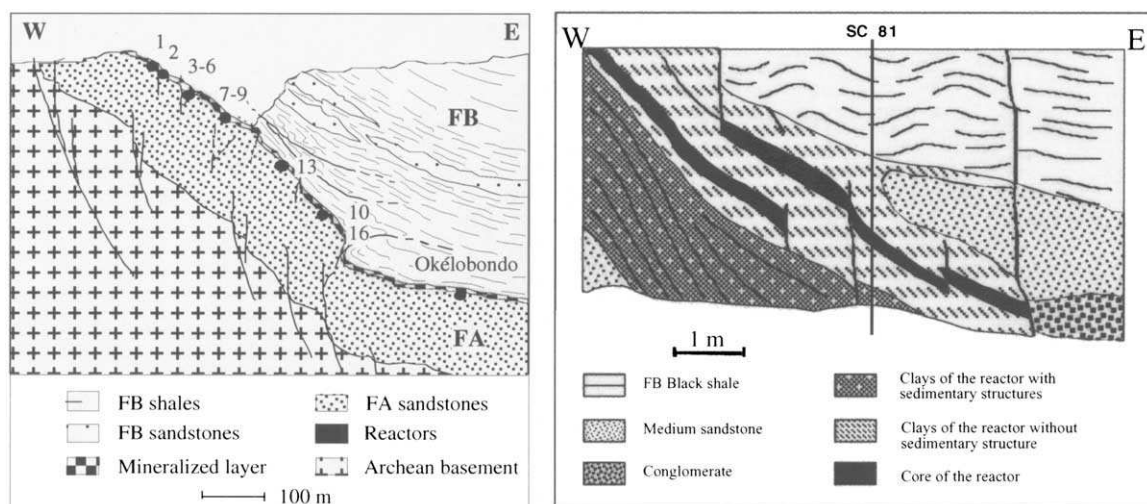


Fig. 1. left: cross-section through the Oklo and Okélobondo deposits and location of the different reaction zones; right: cross-section through the Oklo reaction zone 2 (after Gauthier-Lafaye et al., 1996).

collected from drill-core SC81 which cross-cut reactor 2 (Fig. 1). They correspond to a high-grade core sample (7.15 m), mineralized sandstone below the reactor (7.40 m) and hydrothermal alteration halo overlying the reactor (6.10 m).

3. Analytical techniques

3.1. Electron microprobe

The mineral parageneses were defined through optical observation of thin sections in transmitted and reflected light. Further mineral identification and element distribution through area mapping, line and WDS/spot analysis were determined using an electron microprobe analyzer (JEOL JXA-8600) equipped with a back scattered electron imaging system. The mineral phases were analyzed by in situ chemical analysis with a beam size of 1 μm . The operating conditions were current intensity of 50 nA (U minerals) and 5 nA (clays), voltage of 15 kV, counting time of 20–30 s. The standards used for the calibration of the microprobe were synthetic glass for Si–Al–Ca–Ti–Ce–La, adularia for Na and K, MgCO_3 for Mg, apatite for P, pyrite for Fe and S, uraninite for U and Pb, ThSiO_4 for Th, ZrSiO_4 for Zr, metallic V for V.

3.2. In situ SHRIMP analysis

The Sensitive high resolution ion micro-probe recently installed at the University of Hiroshima (SHRIMP II) was used for in situ isotope analysis. The small size of the beam (5–20 μm) allows the measurement of isotopic compositions in individual mineral

phases and the study of isotope redistribution at the μm -scale level. SHRIMP is a powerful tool for micro-isotopic analysis often used to measure the U–Th–Pb ages of zircons (e.g. Compston et al., 1986; Hidaka et al., 2003) as well as REE, U and Pb isotopic ratios for geochemical applications (e.g. Nagano et al., 2000; Hidaka, 1998). SHRIMP is optimized for high sensitivity when operating at high mass resolution, which is achieved by the combination of wide slits and a large secondary mass analyzer. The samples were polished to provide a flat surface for sputtering of secondary ions. After the surface was finished by 0.25 μm diamond paste, they were coated by thin Au plate to prevent charging the sample surface by a primary beam. After one night under vacuum, the sample was introduced into the ion source chamber. A few nA of O_2^+ primary beam focused onto a 5–20 μm -diameter spot was used for sputtering the polished section. The pit position was manipulated under a microscope with CCD camera. Although predominant secondary ions were oxide species (e.g. $\text{NdO}^+/\text{Nd}^+ = 1.5$ in uraninite), non-oxide species were detected for the analysis because of less isobaric interferences on the mass spectra. The mass resolution is set to 5500 at 1% peak height by adjustment to 80 mm width of source slit and 100 mm width of collector slit. In the case of Nd, Sm and Eu analyses, a mass resolution of 8000 was applied by setting a 70 mm width source slit and 45 mm width collector slit because unidentified isobaric interferences were observed. A 0.1–0.5% a.m.u. instrumental mass fractionation occurs during REE isotopic analysis. No correction of mass fractionation was done because isotopic deviations at Oklo are much larger than instrumental mass fractionation. Neodymium, Sm, Eu and U were analyzed at the same time and an average of 50 runs were taken for each sample.

3.3. Sequential extraction and isotopic analyses by ICP-MS

A sequential extraction procedure was applied following a procedure derived from Yanase et al. (1991). About 4 g of powdered material was shaken at room temperature for 4 h with 40 ml of 1M Na acetate adjusted to pH 5.0 with acetic acid. The extraction with Na acetate solution removes adsorbed/exchangeable trace metals. At the end of the extraction, the suspended solution was separated by a combination of centrifugation and filtration using a 0.1 μm Millipore filter. The residue of the filter was shaken with 40 ml of Tamm's solution (10.9 g/l oxalic acid + 16.1 g/L ammonium oxalate) in the dark at room temperature for 4 h. Tamm's reagent is used to dissolve amorphous minerals of Al, Fe and Si, and ferrihydrite (Chao and Zhou, 1983). The residue from fraction 2 was stirred with 40 ml of CDB solution (1 g sodium dithionite + 60 ml of 0.3 M trisodium citrate + 0.2 M sodium hydrogen carbonate) at 85 °C for 30 min and the extraction was repeated several times. Crystalline Fe minerals such as hematite and goethite are dissolved by the CDB solution whereas clays and quartz are not affected (Lowson et al., 1986). At the end, in order to dissolve the remaining resistant minerals, the residual fraction was dissolved by a HF–HNO₃–HCl mixture in a teflon beaker over 3 days at 100 °C. Then, the sample was evaporated to dryness and redissolved in 1M HNO₃ for chemical and isotopic analysis.

The concentrations of U, Se, REE, Mo, Zr and the ²³⁵U/²³⁸U, ¹⁴⁷Sm/¹⁴⁹Sm, ⁹⁰Zr/⁹¹Zr, ⁹⁵Mo/⁹⁸Mo isotopic ratios of leachates and residual fractions were measured by ICP-mass spectrometry and ICP-AES. To avoid isobaric interferences with Mo, Ru and (Ti)₂ isotopes, Zr was purified separately on another aliquot following a procedure derived from Hidaka et al. (1994) using an anion exchange resin packed column then a cation exchange resin. The isotopic composition of other elements was determined on bulk solution without isobaric overlap. Instrumental mass fractionation was corrected using natural standard solutions and a linear law.

4. Petrographic and isotopic evidence of reactor product remobilization

4.1. Mineral parageneses

In the reactor core, massive uraninite consists of dense, cubic, cubo-octahedral and octahedral crystals and large irregular grains embedded in an illitic matrix. Uraninite exhibits various stages of alteration and dissolution such as embayed and fractal grain boundaries, remnants of partially dissolved material (Fig. 2). The inner part of uraninite grains is often partially or

entirely dissolved and replaced by illite, chlorite, coffinite and galena, forming an “atoll-shape” texture mentioned by Janeczek (1999). Chemical alteration and replacement by coffinite, $\text{USiO}_4 \cdot n(\text{H}_2\text{O})$ is observed in back-scattered electron images as low contrast areas and along cracks, fractures and grain margins, corroborating previous observations (Geffroy, 1975; Janeczek and Ewing, 1992, 1995; Bros et al., 1995; Jensen et al., 1997; Jensen and Ewing, 2000). This process of alteration by Si-bearing fluids is particularly effective along hydraulically conductive fractures and grain boundaries. Coffinite from the core of the reactor has low amounts of P (0.4 wt.% P_2O_5) and undetectable amounts of Ce and Zr in the EMPA analysis, whereas coffinite from the alteration halo is enriched in these elements (Table 1). The low total in the coffinite analysis (82.3–94.1%) indicates the presence of water as molecular H_2O or OH^- compound. Secondary uraninite contains fairly high amounts of impurities such as Fe (1.5–2.0% FeO), Ce (0.3–0.7% Ce_2O_3) and Pb (1.7–4.7% PbO) of radiogenic origin, likely substituting U in the UO_2 lattice. The low PbO contents and low totals (84.4–91.7 wt.%) in contrast to previous data on uraninite (Janeczek and Ewing, 1995; Jensen and Ewing, 2000) suggest that uraninite in the alteration halo might have been oxidized. In several veinlets (Fig. 3g), illite is associated with minute grains of coffinite enriched in P (3.2–3.8% P_2O_5), Ce (0.47–0.67% Ce_2O_3) and Zr (0.4–1.05% ZrO_2). Other impurities include Ca (0.8–1.2% CaO), Fe (1.0–8.3% Fe) and Ti (up to 6.2% TiO_2). Titanium cannot enter the structure of coffinite and therefore the high Ti content is probably due to small inclusions of TiO_2 . The enrichment in P and Ce might indicate a solid solution between coffinite and ningyoite, $(\text{U}, \text{Ca}, \text{Ce})(\text{PO}_4)_2 \cdot 1\text{--}2\text{H}_2\text{O}$. The coupled substitution, $\text{U}^{4+} + \text{Si}^{4+} = \text{P}^{5+} + \text{REE}^{3+} + \text{Zr}^{4+}$ may explain the occurrence of P-, REE- and Zr-rich coffinite in the clay halo of RZ 2 (Janeczek, 1999). This substitution is limited due to structural differences between these two phases. Coffinite is a tetragonal orthosilicate isostructural with zircon, ZrSiO_4 , hafnon, HfSiO_4 , thorite, ThSiO_4 , and synthetic PuSiO_4 and NpSiO_4 (e.g. Finch and Murakami, 1999) in which Zr, Hf and actinides occupy triangular-dodecahedral sites coordinated by isolated Si tetrahedra (Burns, 1999), whereas, ningyoite is an hexagonal phosphate (Hikichi et al., 1989). The relatively high concentration of Zr also suggests a range of solid-solution between coffinite and zircon. Such U–Zr rich silicates have been already described at RZ10 and Okélobondo (Jensen and Ewing, 2000, 2001). Rounded grains of Ti-oxides, likely anatase, are abundant in the clay halo of RZ 2. These grains are often rimmed by coffinite enriched in P and Ce (Fig. 3h) suggesting an early stage of U sorption onto Ti-oxide, followed by mineralization by Si- and P-bearing solutions. These mineralogical observations are generally

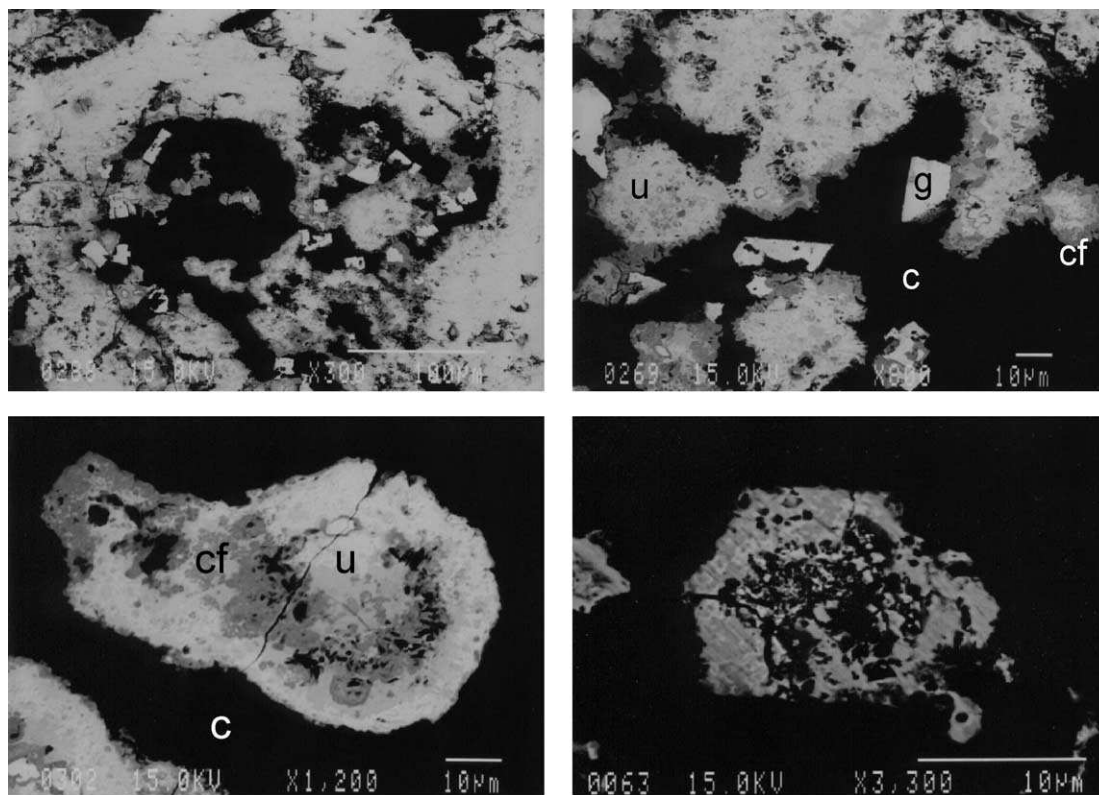


Fig. 2. Back scattered electron images showing various stages of alteration and dissolution of uraninite in the core of reactor 2 (sample SC81/7.15 m). The lower contrast is related to increasing amounts of Si and coffinitization of uraninite (grey) and replacement by clays (black); u = uraninite; cf = coffinite; c = undifferentiated clays; g = galena.

similar to those reported for the deeply situated Okélobondo RZ.

Electron microprobe analysis of chlorite indicates a Fe–Mg content of 7.9–14.4% MgO and 8.6–17.2% FeO, respectively (Table 2). Several chlorite grains display an Al-rich character (up to 31% Al_2O_3). Such Al chlorites are generally associated with hydrothermal alteration and often occur in polymetallic deposits (e.g. Alysheva et al., 1977). Their presence suggests formation in contact with the high temperature fluids associated with the nuclear reactions. However, chlorite in RZ2 is not as rich in Al as those observed in RZ10 and Okélobondo (Jensen and Ewing, 2001). K-illite is a minor, discrete phase which occurs as impregnations or filling small veinlets (Fig. 3), therefore post-dating chlorite. The low K_2O content ranging from 1.3 to 2.7% might be related to the presence of water in interfoliar sites. In contrast to illite, chlorite has played a significant role in fixing U. This is indicated by relatively high concentrations of UO_2 ranging from 0.26 to 0.61% in chlorite whereas illite particles contains lower amounts, 0.11–0.23% UO_2 . The affinity of U for chlorite has already been noticed (Bros et al., 1993; Eberly et al., 1995). However, associated with illite, agglomerates

of fibrous uraninite are observed and developed between sheets of illite. These agglomerates are also associated with pyrite displaying a “worm-like” habit (Fig. 3e). This paragenesis suggests contemporaneous formation of these minerals, the reducing potential of the mineralizing fluids and the availability of Fe^{2+} and S in groundwater during the stage of illitization.

4.2. Isotope micro-distribution by *in situ* SHRIMP analysis

4.2.1. Uranium isotopes

A sample from the alteration halo (SC81/6.10 m) was investigated for the isotopic signature in secondary uraninite, P-rich coffinite and chlorite. The location of analyzed spots is shown in Fig. 3c and the isotopic results are reported in Table 3. Due to the small beam size (5–20 μm), the SHRIMP data sometimes may not necessarily represent single grain analysis, but rather mineral mixtures because of the small size of possible mineral inclusions. The $^{235}\text{U}/^{238}\text{U}$ isotopic ratio is significantly depleted, ranging from 0.00639 to 0.00681 instead of 0.007252 for natural U. This reveals that ^{235}U -depleted U migrated from the reactor core and

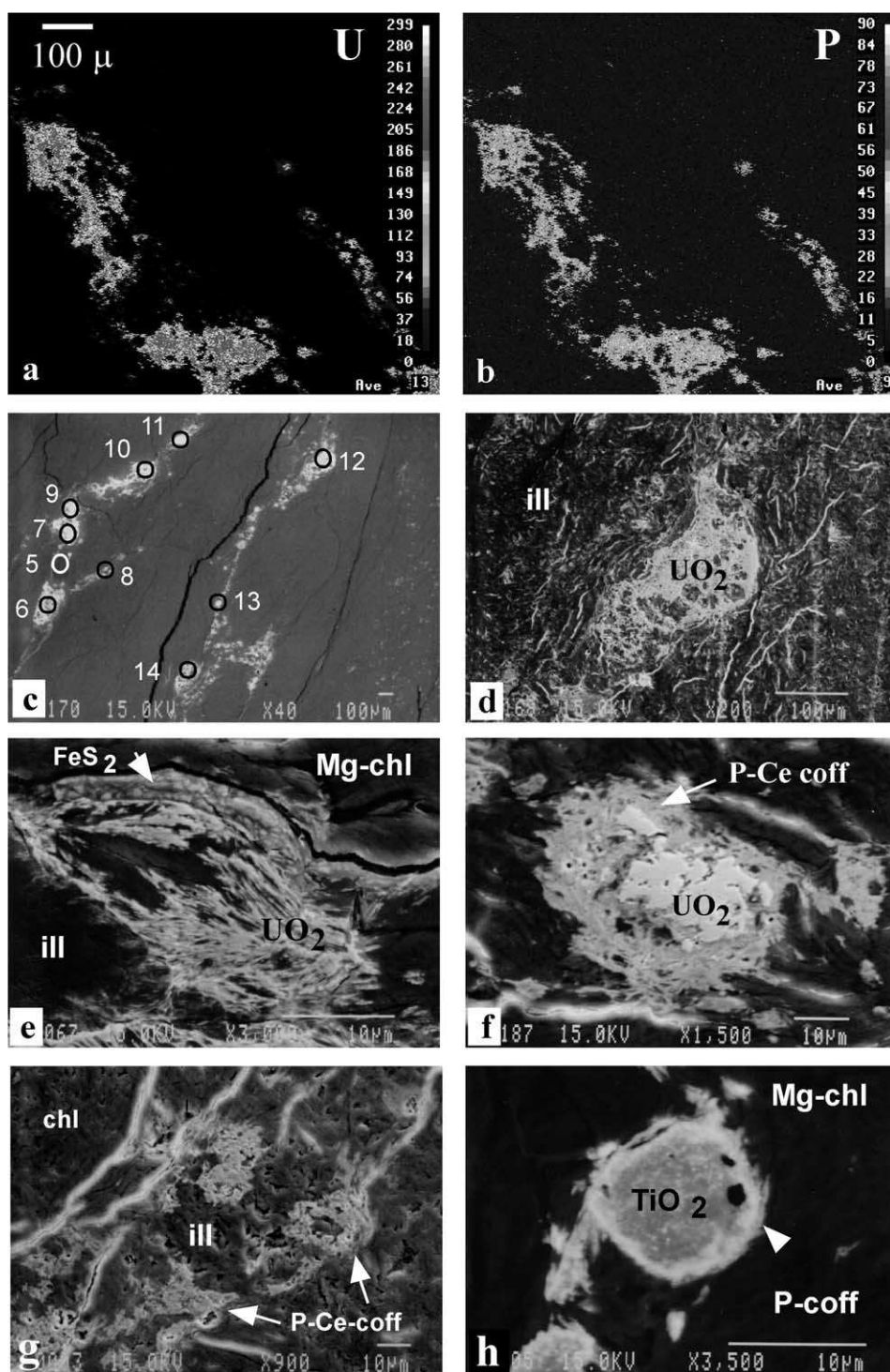


Fig. 3. Electron microprobe images and element mapping in the clay halo of reactor 2 (sample SC81/6.10 m). (a–b): distribution of U and P; (c): location of uraninite, coffinite and chlorite spots analyzed by SHRIMP (see isotopic data in Table 3); (d–g): different habitus of uraninite and P–Ce-rich coffinite in the illite and chlorite matrix; (h): rounded crystal of Ti-oxide, likely anatase, rimmed by P-rich coffinite; coff = coffinite; ill = illite; chl = chlorite.

Table 1

Electron microprobe analysis (expressed in % oxides) of secondary uraninite (U) and coffinite (Cf) from the clay halo of RZ2)

Oxide	U5	U6	U7	U9	U10	U11	U13	U14	Cfc	Cf2	Cf3	Cf16	Cf19	Cf20	Cf21	Cf22
SiO ₂	0.71	0.79	1.04	0.69	0.52	0.99	0.68	0.73	15.08	14.26	11.79	12.33	13.95	14.28	14.23	13.98
UO ₂	78.41	78.83	81.81	82.91	83.93	81.63	81.46	81.66	65.03	58.76	59.48	62.54	57.28	55.23	55.84	56.54
ThO ₂	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.13	0.33	0.41	0.33	0.16	0.31	0.40
TiO ₂	0.12	0.04	0.06	0.05	0.08	0.10	0.05	0.08	0.12	0.16	0.68	4.29	6.19	4.82	3.05	0.59
ZrO ₂	<DL	<DL	<DL	0.05	<DL	0.05	0.10	<DL	<DL	0.60	1.05	0.75	0.38	0.41	0.42	0.98
Al ₂ O ₃	0.28	0.24	0.59	0.23	0.09	0.33	0.12	0.15	0.83	1.27	1.27	0.90	3.56	3.75	2.93	3.56
MgO	<DL	0.01	0.04	<DL	0.02	<DL	0.02	<DL	<DL	0.04	0.17	0.13	0.25	0.32	0.27	0.27
Ce ₂ O ₃	0.70	0.57	0.53	0.47	0.55	0.37	0.50	0.48	<DL	0.65	0.60	0.66	0.47	0.54	0.67	0.58
FeO	1.98	1.86	1.92	1.81	1.50	1.87	1.60	1.45	0.53	1.02	4.85	2.40	5.62	4.95	5.77	8.30
PbO	4.51	4.60	4.04	3.85	4.22	4.74	1.69	2.31	3.03	0.55	0.99	1.24	1.10	1.22	1.07	1.22
CaO	0.09	<DL	0.06	0.11	0.17	0.16	0.18	0.08	0.06	1.18	1.10	0.93	0.81	0.79	0.77	0.84
V ₂ O ₃	ND	ND	0.23	0.17	0.24	0.21	0.22	0.18	ND	ND	ND	0.43	0.64	0.60	0.36	0.09
P ₂ O ₅	0.37	0.27	0.32	0.36	0.39	0.28	0.41	0.31	0.41	3.66	3.93	3.83	3.36	3.22	3.24	3.35
SO ₃	ND	ND	<DL	<DL	<DL	<DL	<DL	<DL	<DL	ND	ND	0.13	0.17	0.21	0.45	0.64
Total	87.17	87.21	90.67	90.71	91.71	90.75	87.02	84.42	85.09	82.29	86.24	90.99	94.13	90.49	89.39	91.34

Cfc: coffinite from the core of RZ2; <DL : below detection limit; ND : not determined

Table 2

Electron microprobe analysis (expressed in% oxide) of illite (I) and chlorite (ch) from the clay halo of reaction zone 2

Oxide	I-3	I-4	I-8	I-10	I-11	I-12	I-18	ch-1	ch-2	ch-5	ch-6	ch-9	ch-13	ch-14	ch-17	ch-19
SiO ₂	47.75	44.73	49.17	47.95	46.91	49.37	43.35	30.80	30.53	34.48	30.53	38.88	35.51	30.23	31.70	30.12
UO ₂	0.18	0.23	0.18	0.15	0.12	0.11	0.14	0.49	0.43	0.67	0.49	0.26	0.39	0.43	0.61	0.47
ThO ₂	0.08	0.18	0.07	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.11	0.03	0.09	<DL	0.05	0.09
TiO ₂	<DL	<DL	0.02	0.04	0.03	0.03	<DL	<DL	0.06	0.10	0.13	0.02	0.07	0.03	0.04	0.12
ZrO ₂	0.24	<DL	0.26	0.06	0.19	0.03	<DL	<DL	2.20	<DL	<DL	0.35	<DL	<DL	<DL	<DL
Al ₂ O ₃	27.51	29.75	33.12	34.22	33.50	32.50	29.49	19.02	21.48	23.90	20.37	31.08	26.51	22.61	22.88	23.23
MgO	2.26	2.46	1.01	0.80	0.79	1.19	2.05	14.43	13.11	11.66	9.09	8.36	14.05	12.08	7.91	11.86
Ce ₂ O ₃	0.21	0.28	0.05	<DL	<DL	0.08	0.15	<DL	<DL	0.16	<DL	0.03	<DL	<DL	0.24	0.05
FeO	4.99	6.59	2.11	1.65	1.06	1.38	7.33	14.77	13.56	17.24	13.66	8.58	12.16	12.79	13.90	14.81
PbO	0.05	<DL	<DL	<DL	<DL	0.01	0.01	<DL	<DL	0.12	0.09	0.11	0.23	<DL	0.09	0.12
CaO	0.11	0.09	0.10	0.12	0.14	0.10	0.20	0.63	0.37	0.35	0.06	0.10	0.27	0.16	0.75	0.50
V ₂ O ₃	0.15	0.04	0.01	0.05	0.01	0.01	0.06	0.08	0.11	0.03	0.06	0.01	0.04	0.03	0.05	0.06
P ₂ O ₅	<DL	<DL	0.04	<DL	0.24	<DL	<DL	0.03	0.05	<DL	0.08	0.06	<DL	0.04	0.11	<DL
SO ₃	0.05	0.01	0.09	0.01	0.02	0.03	0.02	0.04	0.01	0.01	0.10	<DL	0.06	0.04	0.06	0.10
Na ₂ O	0.25	0.15	0.17	0.07	0.08	0.10	0.14	0.08	0.10	0.13	0.08	0.08	0.08	0.05	0.13	0.06
K ₂ O	2.71	1.44	1.27	1.28	2.18	1.76	1.69	<DL	<DL	<DL	0.19	0.14	0.50	0.37	0.54	<DL
Total	86.5	85.9	87.7	86.4	85.3	86.7	85.4	80.4	82.0	88.9	75.1	88.1	89.9	78.9	79.1	81.6

Table 3

U, Nd, Sm and Eu isotopic ratios (error at σ level) of uraninite (U), coffinite (Cf) and chlorite (Ch) determined by in situ SHRIMP analysis

Sample	$^{235}\text{U}/^{238}\text{U}$	$^{143}\text{Nd}/^{145}\text{Nd}$	$^{146}\text{Nd}/^{145}\text{Nd}$	$^{149}\text{Sm}/^{147}\text{Sm}$	$^{151}\text{Eu}/^{153}\text{Eu}$
U1	0.00642 (3)	1.459 (8)	1.411 (9)	0.340 (3)	0.872 (10)
U2	0.00639 (5)	1.489 (11)	1.439 (13)	0.348 (3)	0.908 (32)
U3	0.00639 (3)	—	—	—	—
U4	0.00673 (4)	1.553 (14)	1.428 (17)	0.349 (11)	0.895 (6)
Ch5	0.00656 (9)	2.091 (52)	1.368 (28)	0.323 (9)	0.063 (2)
U6	0.00671 (3)	1.219 (105)	1.856 (142)	0.306 (11)	0.794 (61)
U7	0.00676 (5)	1.470 (11)	1.421 (9)	0.349 (4)	0.882 (9)
Cf 8a	0.00657 (3)	1.483 (14)	1.447 (11)	0.345 (3)	0.901 (10)
Cf 8b	0.00657 (7)	—	—	—	—
U9	0.00679 (3)	—	—	—	—
U10	0.00670 (4)	1.570 (14)	1.448 (24)	0.338 (8)	0.893 (18)
U11	0.00681 (3)	—	—	—	—
U12	0.00676 (5)	1.556 (9)	1.402 (12)	0.336 (4)	0.938 (14)
U13	0.00674 (5)	—	—	—	—
U14	0.00681 (5)	1.502 (22)	1.438 (31)	0.332 (7)	0.893 (10)
Natural	0.007252	1.467	0.886	0.92	0.915

The location of analyzed spots is shown in Fig. 3.

precipitated in the form of uraninite and coffinite after metric scale transport. The $^{235}\text{U}/^{238}\text{U}$ ratio has been measured in a large chlorite grain ($100 \times 200 \mu\text{m}$) denoted Ch5 in Table 3. The depleted $^{235}\text{U}/^{238}\text{U}$ ratio of the chlorite grain is similar to that of P–Ce rich coffinite (Coff 8a, 8b) suggesting the contemporaneity of these two mineral phases. However, it is possible that the isotopic anomaly is related to the presence of fine-sized U inclusions in the chlorite matrix (Evins, 2002). Secondary UO_2 aggregates (U6, U7, U9, U10, U11, U12, U13, U14) display higher values ranging from 0.00670 to 0.00681, suggesting the existence of different fluid generations responsible for the precipitation of uraninite and coffinite.

4.2.2. Rare earth elements

High amounts of rare-earth elements (REE) were produced by fission in the reactors. These elements are sensitive indicators of nuclear reactions: light REE (namely La, Ce, Pr and Nd) have high fission yields and several isotopes (i.e. Sm-149, Gd-155) have large neutron-capture cross-sections. As a result, fissionogenic and non-fissionogenic REE display markedly different isotopic compositions (e.g. Hidaka and Gauthier-Lafaye, 2000). REE are also suitable chemical analogues of long-lived radionuclides such as Pu, Am and Cm (Chapman and Smellie, 1986). Examination of fission-product yield curves for several reactor zones indicated a high retention of REE in the core of the reactor zones (Hidaka and Holliger, 1998). This is partly due to the relatively small differences in ionic radii of U^{4+} and REE^{3+} that make REE compatible with the uraninite structure. However, mobilization of REE in and around reactors have been observed (Curtis et al., 1989; Hemond et al.,

1992; Menet et al., 1992; Bros et al., 1993, 1995, 1996; Gauthier-Lafaye et al., 1996; Hidaka and Gauthier-Lafaye, 2000; Jensen and Ewing, 2001). In the present study, all the spots analyzed show significant anomalies of the Nd, Sm and Eu isotopic composition. The $^{146}\text{Nd}/^{145}\text{Nd}$ ratio varies from 1.368 to 1.856 instead of 0.886 for natural Nd. The increase in the $^{146}\text{Nd}/^{145}\text{Nd}$ ratio is related to the higher fission yield of ^{146}Nd relative to ^{145}Nd . The calculated proportions of reactor-derived Nd and natural Nd are 18.1–59.3 and 43.6–81.9%, respectively (Fig. 4). ^{149}Sm is distinctly characterized by a high neutron capture cross-section

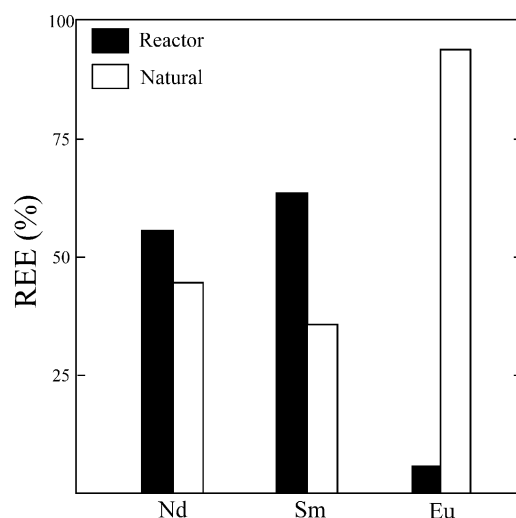


Fig. 4. Proportions of natural (non-fissionogenic) and reactor-derived REE in secondary U minerals from the clay halo of RZ 2 calculated from in situ SHRIMP analyses.

(40 000 barns) and is consumed in spent reactor fuel. The $^{149}\text{Sm}/^{147}\text{Sm}$ ratio is therefore a valuable tracer to identify potential transport and immobilization of reactor-derived Sm. The $^{149}\text{Sm}/^{147}\text{Sm}$ ratio ranges from 0.306 to 0.349 instead of 0.92 for natural Sm and the calculated proportions of reactor-Sm and natural Sm are 62.3–67% and 33–37.7%, respectively. The $^{151}\text{Eu}/^{153}\text{Eu}$ ratio ranges from 0.794 to 0.908 instead of 0.915 for natural Eu. The calculated proportions are 0.9–15.8% (reactor) and 84–99% (natural). As for U, the existence of isotopic anomalies of REE implies that they have been

mobilized from the reactor then incorporated into secondary uraninite and coffinite when these phases crystallized. Hydrothermally formed chlorite has also fixed reactor-derived REE as indicated by isotopic anomalies. Although the presence of very small U-mineral inclusions cannot be ruled out, sorption onto chlorite is the likely mechanism of fixation as indicated by the results of selective extraction discussed in the next section.

4.3. Sequential extraction

4.3.1. Uranium

The core of reactor 2 (SC81/7.15 m) has a high U concentration (57.6%) and a significantly depleted $^{235}\text{U}/^{238}\text{U}$ ratio of 0.00592 (Table 4) indicating that the sample has been strongly affected by nuclear reactions. The different components extracted during the sequential leaching procedure (namely Na acetate, NH_4 oxalate, citrate-dithionate and insoluble fraction) have the same $^{235}\text{U}/^{238}\text{U}$ ratio within analytical error and no isotopic heterogeneity was found. This result provides information on the migration behaviour of Pu. ^{239}Pu ($T_{1/2}$: 24400 a) is produced by neutron capture on ^{238}U and regenerates ^{235}U by α decay. First investigations on reactors 1–6 lead to the conclusion that Pu has not migrated outside reactor core uraninite (Naudet, 1991). Later investigations on deep reactors 10 and 16 revealed the occurrence of Pu mobilization followed by the incorporation of this radioelement in hydrothermally formed Al-chlorite and fluoroapatite (Bros et al., 1993, 1996). Preferential mobilization of Pu outside uraninite

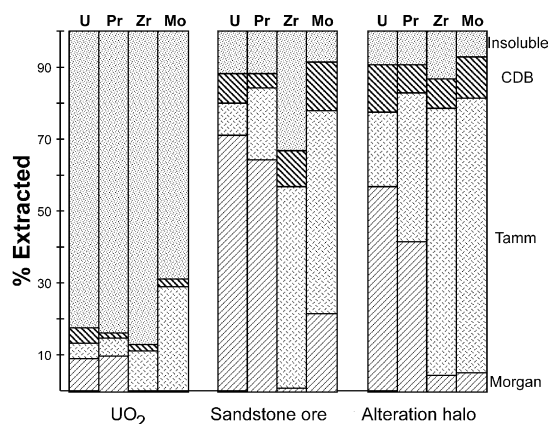


Fig. 5. Distribution of U, Pr, Zr and Mo in the different leachates and insoluble fraction of reactor core uraninite (SC81/7.15), U-sandstone (SC81/7.40 m) and alteration halo (SC81/6.10 m) from reaction zone 2.

Table 4

$^{235}\text{U}/^{238}\text{U}$ isotopic ratio (error at σ level), U and Se concentrations of untreated samples (U), Morgan (MOR), Tamm (TAM), CDB and insoluble residue (R)

Sample	Petrography	U ($\mu\text{g/g}$) (% extracted)	$^{235}\text{U}/^{238}\text{U}$	Se ($\mu\text{g/g}$)
5.15/U	Shale	260	0.00705 (9)	0.9
6.10/U	Alteration halo	6900	0.00665 (6)	1.5
6.10/MOR		4030 (58.5%)	0.00667 (7)	0.3
6.10/TAM		1400 (20.3%)	0.00664 (8)	0.3
6.10/CDB		850 (12.3%)	0.00663 (8)	0.5
6.10/R		613 (8.9%)	0.00655 (7)	0.2
7.15/U	Uraninite (reactor core)	57.6%	n.d.	27.1
7.15/MOR		54280 (9.4%)	0.00591 (4)	1.9
7.15/TAM		23770 (4.1%)	0.00591 (5)	1.4
7.15/CDB		19925 (3.5%)	0.00590 (6)	3.3
7.15/R		47.8% (83%)	0.00592 (5)	23.2
7.40/U	Sandstone ore	3.6%	n.d.	5.7
7.40/MOR		26010 (72.5%)	0.00603 (5)	1.2
7.40/TAM		2975 (8.3%)	0.00602 (5)	1.2
7.40/CDB		1952 (5.4%)	0.00601 (6)	2.5
7.40/R		4935 (13.8%)	0.00602 (5)	1.3

Table 5

Nd concentration, $^{149}\text{Sm}/^{147}\text{Sm}$, $^{146}\text{Nd}/^{145}\text{Nd}$ and $^{143}\text{Nd}/^{145}\text{Nd}$ isotopic ratios (error at σ level) and decomposition of fissiogenic and natural Nd

Sample	$^{149}\text{Sm}/^{147}\text{Sm}$	^{141}Pr	Nd $\mu\text{g/g}$	$^{143}\text{Nd}/^{145}\text{Nd}$	$^{146}\text{Nd}/^{145}\text{Nd}$	Nd _{reacto} $\mu\text{g/g}_r$	Nd _{natural} $\mu\text{g/g}$
Shale							
5.15/U	0.805 (1)	ND	15.4	1.440 (3)	1.856 (4)	2.8	12.6
Alteration halo							
6.10/U	4.9	30.3					
6.10/MOR	0.346 (1)	1.9	11.2	1.430 (3)	1.455 (2)	5.4	5.8
6.10/TAM	0.347 (1)	1.8	11.4	1.434 (6)	1.455 (4)	5.5	5.9
6.10/CDB	0.353 (2)	0.4	2.5	1.433 (5)	1.468 (7)	1.2	1.3
6.10/R	0.356 (2)	0.3	1.9	1.420 (3)	1.433 (3)	0.9	1.0
Reactor core							
7.15/U	255	1902					
7.15/MOR	0.013 (1)	24	194.2	1.405 (2)	0.873 (2)	178.2	16
7.15/TAM	0.013 (1)	12	92.7	1.405 (3)	0.871 (2)	85.2	7.5
7.15/CDB	0.013 (1)	4.9	49.4	1.405 (4)	0.870 (2)	45.4	4.0
7.15/R	0.012 (1)	206	1550	1.392 (2)	0.863 (1)	1434	116
Sandstone ore							
7.40/U	29.2	228					
7.40/MOR	0.064 (1)	18.3	133	1.418 (3)	1.121 (1)	97.3	35.7
7.40/TAM	0.070 (1)	5.5	42.8	1.419 (3)	1.147 (3)	30.5	12.3
7.40/CDB	0.071 (1)	1.1	10.0	1.453 (13)	1.165 (7)	7.0	3.0
7.40/R	0.061 (1)	3.2	19.7	1.408 (4)	1.122 (3)	14.4	5.3

Table 6

$^{90}\text{Zr}/^{91}\text{Zr}$ and $^{95}\text{Mo}/^{98}\text{Mo}$ isotopic ratios and amounts of reactor and natural components

Sample	Zr	$^{90}\text{Zr}/^{91}\text{Zr}$ ($\mu\text{g/g}$)	Zr _{reactor} ($\mu\text{g/g}$)	Zr _{natural} ($\mu\text{g/g}$)	Mo ($\mu\text{g/g}$)	$^{95}\text{Mo}/^{98}\text{Mo}$ ($\mu\text{g/g}$)	Mo _{reactor} ($\mu\text{g/g}$)	Mo _{natural}
Shale								
5.15/U	27.3	4.414 (15)	0.7	26.6	1.2	0.653 (5)	0.1	1.1
Alteration halo								
6.10/U	48.3	1.9						
6.10/MOR	2.1	4.104 (17)	0.23	1.87	0.1	0.691 (8)	0.02	0.08
6.10/TAM	34.3	4.181 (5)	3.07	31.23	1.3	0.678 (1)	0.17	1.13
6.10/CDB	3.8	4.127 (69)	0.40	3.40	0.2	0.659 (19)	0.02	0.18
6.10/R	6.2	4.223 (9)	0.48	5.72	0.1	0.690 (7)	0.02	0.08
Reactor core								
7.15/U	2270	195						
7.15/MOR	12.7	1.934 (11)	9.06	3.64	0.3	0.942 (12)	0.19	0.11
7.15/TAM	244	1.925 (2)	174.6	69.4	60	0.918 (3)	35.8	24.2
7.15/CDB	41.5	2.186 (23)	26.69	14.81	5.2	0.894 (4)	2.9	2.3
7.15/R	1990	1.881 (5)	1448.3	541.7	141	0.957 (4)	95.1	45.9
U-sandstone								
7.40/U	430	12.5						
7.40/MOR	4.2	4.053 (26)	0.53	3.67	2.5	0.671 (3)	0.3	2.2
7.40/TAM	245	4.109 (4)	26.85	218.15	6.5	0.672 (2)	0.8	5.7
7.40/CDB	39.3	4.078 (25)	4.65	34.65	1.6	0.649 (5)	0.1	1.5
7.40/R	136	4.087 (13)	15.7	120.3	0.9	0.678 (7)	0.1	0.8

untreated (U), Morgan (MOR), Tamm (TAM), CDB and insoluble residue (R).

soon after fission reactions and hence an increase in the Pu/U ratio would be witnessed by greater a $^{235}\text{U}/^{238}\text{U}$ ratio for exchangeable U represented by Na acetate and NH_4 oxalate, eventually leading to enrichment in ^{235}U ($^{235}\text{U}/^{238}\text{U} > 0.00725$). Since the different reagents and the insoluble fraction have the same depleted $^{235}\text{U}/^{238}\text{U}$ ratio, fractionation of the Pu/U ratio soon after nuclear reactions is unlikely. As shown on Fig. 5, only small amounts of U were removed by Morgan (9.4%), Tamm

(4.1%) and CDB (3.5%) and the major part of U remains in the residual fraction (83%). In sandstones located below the reactor core, the U concentration is much lower (3.6%) and the $^{235}\text{U}/^{238}\text{U}$ ratio is depleted (0.006). Here too, there is no heterogeneity of the U isotopic composition between the different components separated by selective extraction and therefore a Pu/U fractionation is unlikely. In clays overlying the reactor, the $^{235}\text{U}/^{238}\text{U}$ ratio is significantly depleted; at 6.10 m

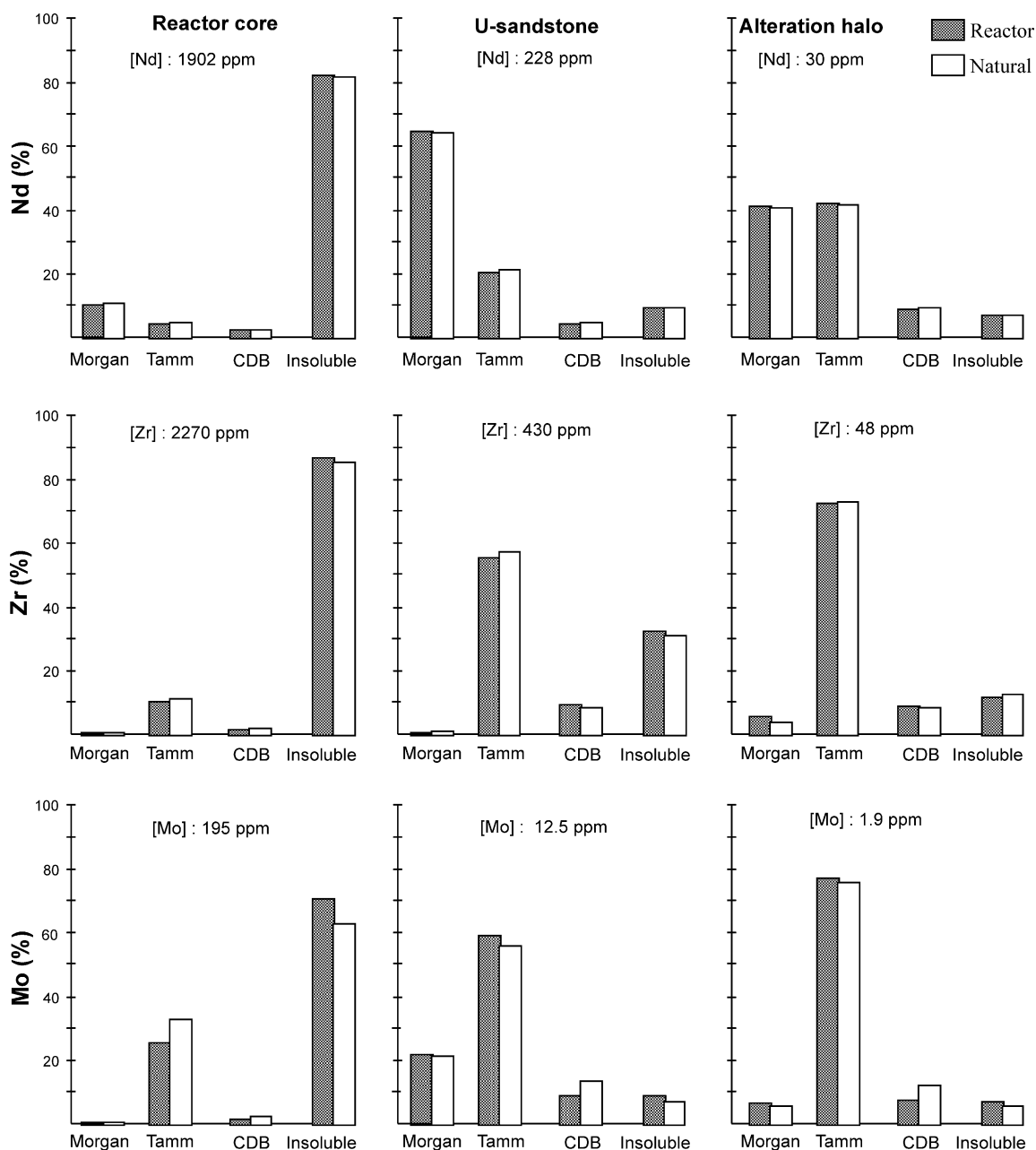


Fig. 6. Distribution of reactor- and natural Nd, Zr and Mo in leachates and insoluble fractions (reactor core SC81/7.15 m; U-sandstone: SC81/7.40 m; alteration halo: SC81/6.10 m).

(1 m above the core), the U concentration is fairly high (6900 ppm) and the $^{235}\text{U}/^{238}\text{U}$ ratio is significantly depleted (0.0066). The insoluble fraction (9% of total U) most likely corresponds to U in coprecipitated secondary uraninite and P-Ce coffinite filling veinlets within the clay matrix (see Section 4.1). The exchangeable fraction accounts for more than 3/4 of total U and most likely corresponds to U adsorbed onto clays. The small anomaly observed at 5.15 m ($^{235}\text{U}/^{238}\text{U}=0.0070$) indicates the minimum distance of U migration (nearly 2 m) from the reactor to the top of the clay sequence.

4.3.2. Rare earth elements

In the reactor core, the $^{149}\text{Sm}/^{147}\text{Sm}$ ratio is extremely low (0.013) compared to the ratio of non-fissiogenic Sm (1.055). This is the result of high neutron capture by ^{149}Sm (Table 5). High Nd concentration (1900 ppm) and anomalous $^{143}\text{Nd}/^{145}\text{Nd}$ and $^{146}\text{Nd}/^{145}\text{Nd}$ isotopic ratios are related to the production of fissiogenic Nd isotopes with different fission yields. Most of the fissiogenic Nd is associated with the insoluble fraction (82.3%) and remains in non exchangeable sites in reactor core uraninite (Fig. 6). Low amounts of Nd were removed by Morgan (10.2%), Tamm (4.9%) and CDB (2.6%) reagents. Similarly, monoisotopic ^{141}Pr is mainly associated with insoluble uraninite, 83.4% (Fig. 5) and, as for other REEs, the high amount of Pr (255 ppm) corresponds to a mixture of fissiogenic and detrital compounds. The alteration halo and the overlying shale also display significant anomalies of the $^{149}\text{Sm}/^{147}\text{Sm}$ and $^{146}\text{Nd}/^{145}\text{Nd}$ ratios, 0.346–0.805 and 1.433–1.856, respectively. As for U, the inferred minimum distance of REE transport is nearly 2 m. At this distance, the amount of reactor-derived Nd is rather low, 2.8 ppm together with substantial amounts of natural Nd. In sample SC81/6.10, anomalous $^{149}\text{Sm}/^{147}\text{Sm}$ ratios of exchangeable components (Na acetate and NH_4 oxalate) suggest that reactor-derived Sm has been adsorbed onto chlorite. With regard to Nd, this exchangeable fraction is dominant since Morgan and Tamm's reagents represent 41.5 and 42.3% of total Nd, respectively (Fig. 6). The insoluble fraction accounts for 6.9% of Nd and may correspond to a fraction incorporated in non exchangeable sites of secondary U-minerals. Praseodymium has a low concentration (4.9 ppm) and the respective proportions of non exchangeable and exchangeable Pr are similar to those of Nd, underlining the similar behaviour of these two REEs.

4.3.3. Zirconium

Among isotopes with mass numbers 88–104, Zr has several isotopes characterized by high fission yields ranging from 5.8 to 6.3%. This element is compatible with the structure of uraninite and the first studies of the Oklo phenomenon lead to the conclusion that Zr has been quantitatively well retained in the reactors

(Naudet, 1991). However, migrations of Zr relative to Nd have been observed (Maeck et al., 1975) and ascribed to the formation of zirconate ($\text{Ba,Sr})\text{ZrO}_3$ which occurs in commercial reactors as a form separated from UO_2 (Bradbury et al., 1965). The behaviour of radioactive Sr can be inferred from the distribution of ^{90}Zr since the later isotope is the stable daughter of short-lived ^{90}Sr (29.1 a). In the core of reactor 10, a large discrepancy was observed between expected (estimated from fission yields) and measured values of the $^{90}\text{Zr}/^{91}\text{Zr}$ ratio (Hidaka et al., 1994); the enrichment in ^{90}Zr resulted from enrichment of its precursor, ^{90}Sr , and a chemical fractionation between Sr and Zr that occurred before ^{90}Sr completely decayed. The Zr concentration and $^{90}\text{Zr}/^{91}\text{Zr}$ ratio are shown in Table 6, together with calculated amounts of fissiogenic and non fissiogenic Zr in the measured material. The $^{90}\text{Zr}/^{91}\text{Zr}$ ratio ranges between natural (4.5) and fissiogenic (0.99) values. A value as low as 1.88 in the residual fraction of sample SC81/7.15 m and the high Zr content (2270 ppm) underline the high production of Zr isotopes during the fission process. Low amounts were extracted during the sequential treatment and only Tamm removed significant amounts of Zr (10.6%), emphasizing the higher binding capacity of NH_4 oxalate, relative to Na acetate (Figs. 5 and 6). Most of Zr (87%) is associated with the residual fraction, reflecting the high retentivity of this element by uraninite. Significant deviations of the $^{90}\text{Zr}/^{91}\text{Zr}$ ratio are observed in U-rich sandstones and alteration halo samples, revealing that Zr has been mobilized from the core and redeposited in the vicinity. Two meters above the reactor, the abundance of fissiogenic Zr is low (0.7 ppm) and diluted by greater amounts of natural Zr (27 ppm) of detrital and diagenetic origin. In the alteration halo (SC81/6.10 m), Zr is mainly extracted by the Tamm's reagent (73.3%) and lower amounts were removed by Morgan's solution (5.7%). This indicates that most of the Zr is exchangeable and was adsorbed onto clays. Lower quantities (11.5%) are associated with the insoluble fraction and assumed to be associated with secondary uraninite and coffinite. This is further supported by relatively high Zr contents measured in situ by electron microprobe (see Section 4.1). Zirconium (and other elements such as Ti) is widely regarded as an "immobile" element during hydrothermal alteration (Finlow-Bates and Stumpfl, 1981). However, Zr can be highly mobile in F-rich hydrothermal systems related to alkalic, F-rich magmatic suites (Rubin et al., 1993). The presence of F in fluids associated with nuclear reactions is a possible explanation for the removal and transport of Zr around Oklo reactor, however there is no evidence indicating the presence of significant amounts of F in fluids related to nuclear reactions. Other examples of hydrothermal Zr mobility are associated to prograde mylonitisation in shear zones and marked by the presence of patchy

zircon and zircon overgrowths (Wayne and Sinha, 1988). Such fluids are generally $\text{H}_2\text{O}-\text{CO}_2$ mixtures with no significant concentrations of F (Kerrick and Fyfe, 1981). It is possible that high concentrations of CO_2 and organic acids have played an important role in the remobilization and transport of Zr at Oklo. It is noteworthy that no positive isotopic anomaly ($^{90}\text{Zr}/^{91}\text{Zr} > 4.5$) which would have witnessed a fractionation of the $^{90}\text{Sr}/\text{Zr}$ ratio was found in and around the reactor. Hydrothermal solutions should have had a high Zr/Sr ratio during reactor operation or more likely groundwater circulation and removal of Zr may have continued after complete decay of ^{90}Sr , i.e. more than 300 a after the neutron flux ceased, therefore leading to the accumulation of ^{90}Zr .

4.3.4. Molybdenum

After decay of fission products with atomic masses 95 and 98, the cumulative fission yields of ^{95}Mo and ^{98}Mo are 6.5 and 5.8% respectively, considering a pure fission of ^{235}U . Therefore, compared to the natural value (0.659), the $^{95}\text{Mo}/^{98}\text{Mo}$ ratio tends to increase in samples containing reactor-derived Mo. A $^{95}\text{Mo}/^{98}\text{Mo}$ ratio as high as 0.957 in the insoluble fraction of the reactor core and high Mo concentration (195 ppm) emphasize the high production rate of Mo isotopes during the nuclear reactions (Table 6). Lower isotopic ratios in Morgan and Tamm reagents are related to higher amounts of natural Mo in exchangeable sites. Most of the fissiogenic Mo was extracted by the Tamm's reagent (26.7%), underlining the higher binding capacity of NH_4 oxalate and the occurrence of an exchangeable fissiogenic compound outside the crystal structure of uraninite (Figs. 5 and 6). The fraction of Mo associated to the insoluble residue (71%) is significantly lower than those of U, REE, Zr and also suggests the release of Mo from the uraninite matrix. Around the reactor, the samples display significant isotopic anomalies indicating that Mo has been mobilized from the reactor core and redeposited. In the uppermost shale sample SC81/5.15 m, the concentration of fissiogenic Mo is low (0.1 ppm) and accompanied by greater amounts of natural Mo (1.1 ppm). In the alteration halo sample SC81/6.10 m, the major part of the Mo was extracted by Tamm reagent (76%) and lower amounts were removed by Morgan (5.9%), indicating that nearly 80% of Mo is in exchangeable positions. In reactor zone 9, 80–90% of fissiogenic Mo migrated from the reactor core and was retained within the first meters, possibly incorporated in sulfide minerals (e.g. Brookins, 1988; Curtis et al., 1989). Molybdenite (MoS_2), presumably containing fissiogenic Mo was observed in illite adjacent to uraninite from reactor 10 (Janeczek and Ewing, 1995). In the present study, molybdenite was not observed either in the core or in sandstones and clays enclosing the reactor. Pyrite and galena were observed as minor, discrete phases (few

grains disseminated in the clay matrix), however electron microprobe analyses do not indicate the presence of significant amounts of Mo within these phases. Therefore, as inferred from the results of selective extraction, it is likely that exchangeable Mo has been sorbed onto clays.

4.3.5. Selenium

Selenium has several fissiogenic isotopes with mass numbers 72–82 including ^{79}Se that has a fairly long half-life (65,000 a) and has already disappeared at Oklo because of the old age of the deposit. Selenium can substitute for S in seleniferous pyrite and other Se-bearing sulfides (Brookins, 1988). Galena from U-bearing sandstone containing Se as a minor element (400 ppm) has been mentioned (Holliger and Gauthier-Lafaye, 1996). In the present study, Se was not detected as an individual Se phase or in other sulfides such as pyrite or galena. The Se concentration measured along the SC81 profile and in leachable and insoluble fractions is reported in Table 4. One measurement of a FB black-shale gave an Se concentration of 1.8 ppm that represents the background concentration of sediments from the Franceville basin. In the reactor core, the Se content (27.1 ppm) is in fairly good agreement with the amount expected to be produced by fission. This is further suggested by the results of sequential extraction which show that 80% of Se is fixed in the crystalline phases. This has to be compared with data obtained for Te, which indicated a good retention of this element at Oklo, despite its apparent incompatibility with the structure of uraninite (Ruffenach, 1979). As for Te, the retention of Se may have been facilitated by incorporation into sulfides associated with Pt group element sulfides and sulfarsenides observed in RZ10 (Holliger and Gauthier-Lafaye, 1996), Okélobondo (Jensen and Ewing, 2001) and Bangombé (Janeczek and Ewing, 1996). However, in RZ2 these minerals have never been observed and the retention of Se may be due to encapsulation in uraninite itself. In the alteration halo and shale overlying the reactor, the Se content is low (0.9–1.5 ppm) and similar to the concentration of normal sediments located far from the reactor. Therefore, little or no reactor-derived Se released during criticality seem to have been immobilized by the clay halo.

5. Mechanisms of transport and retardation

The nuclear phenomenon at Oklo caused circulation of hot fluids and an intense alteration of the surrounding host rock sandstones. Convective fluid circulations were local since the heat produced during the nuclear reactions based on modeling would dissipate within 20 m of the reactor zone (Gérard et al., 1998). The hydrothermal fluids in the reactor zone also caused dissolution

and alteration of uraninite during reactor operation. Groundwaters reached high temperatures (300–500 °C) and they were moderately saline (3–10 wt.% eq. NaCl) as indicated by numerous studies on fluid inclusions and stable isotopes (Openshaw et al., 1978; Dubessy et al., 1988; Gauthier-Lafaye and Weber, 1989; Gauthier-Lafaye et al., 1989; Savary and Pagel, 1997; Mathieu and Cuney, 1998; Michaud, 1998). Dissolution and alteration of uraninite probably continued during cooling of the reactor that resulted in lower temperatures (100–300 °C) ranging between the temperature of burial diagenesis and that of fission reactions. The high salinity (> 23 wt.% eq. NaCl) of late fluids could have enhanced the dissolution of uraninite, even under the reducing conditions prevailing at Oklo (Janeczek and Ewing, 1992). The alteration of the reactor core in RZ2 and radionuclide transfers may have continued a long time after the neutron flux ceased (> 100 ka) when ^{90}Sr and ^{239}Pu had already disappeared; this is suggested by the absence of a positive anomaly of the $^{90}\text{Zr}/^{91}\text{Zr}$ and $^{235}\text{U}/^{238}\text{U}$ ratios. Curtis and Gancarz (1983) estimated that 10% of the U would have been dissolved and mobilized from reactor zones during criticality, whereas 90% remained in the reactor despite the action of fluids. Other estimations indicate that as much as 63% of the U would have been released during or soon after fission reactions (Janeczek and Ewing, 1992). Chemical alteration and massive Pb loss would have occurred 1000–500 Ma ago (Jensen and Ewing, 2000; Evins, 2002) leading to the loss of 10 wt.% UO_2 from uraninite in RZ10. Similar to higher losses were reported in other reactor zones but it is unclear whether these late regional alteration events influence the present data of sequential extraction. Subsequently, supergene weathering of RZ2 has occurred leading to local oxidation of uraninite in the clay halo and to the formation of uranyl minerals (Jensen and Ewing, 2000). It is therefore possible that supergene weathering has an impact on the distribution of nuclear reaction products described in this study. The hydrothermal alteration of the reaction zone and the fate of products released from reactor uraninite during and soon after criticality are schematically represented in Fig. 7. Elements which are compatible with the structure of UO_2 , such as light REE, Zr and Th were released by bulk dissolution of uraninite. Congruent (non selective) dissolution is supported by similar distributions of exchangeable and non exchangeable fractions of U, Pr and Zr (Fig. 5). In this respect, the exchangeable fraction of Zr in reactor core sample SC81/7.15 m, 12% of total fissionogenic Zr, is believed to approach the dissolution rate of uraninite in RZ2. The distribution of Mo on the other hand reflects the cumulative effects of uraninite dissolution and diffusion loss because of the partial incompatibility of this element with UO_2 . It has been estimated that only 10% of fissionogenic Mo remained in the core of reactor 2 (Naudet,

1991). Other elements which were not or partially retained in the structure of uraninite are alkaline elements (Rb, Cs), alkaline earths (Ba, Sr), halogens (I), Cd, Pb, Sn, Ag and noble gases (Xe, Kr) as summarized by Gauthier-Lafaye et al. (1996). The present results revealing the migration of several nuclear reaction products around reactor 2 contradict to some extent the conclusions drawn by Ruffenach (1979) and Naudet (1991). They studied in great detail the drill-core SC36 that cross-cut reactor 2 and calculated the main parameters of the nuclear reactions taking into account the isotopic composition and the content of U, Th and least mobile fission products (REE, Ru). These parameters are the fluence, the restitution factor of ^{239}Pu (abundance of ^{235}U produced by α decay of ^{239}Pu over the amount of fissioned ^{235}U), the number of fissions for ^{235}U , ^{238}U and ^{239}Pu , the duration and the age of fission reactions. The calculated age is 1950 ± 40 Ma. The validity of these parameters prerequisites depends on the geochemical stability of U relative to Th and fissionogenic REE. The good agreement observed between the abundance of U and Th, the $^{235}\text{U}/^{238}\text{U}$ ratio and the amount of fissionogenic Sm and Nd suggests that there was no preferential migration of U during the fission reactions and during the presence of ^{236}U ($T_{1/2}$: 23.4 Ma) produced by neutron capture by ^{235}U . In fact, the drill-core SC36 represents a very specific case of good stability of uraninite and the conclusions of these studies on the long-term preservation of uraninite allowing the retention of actinides and fission products were probably over-estimated. The present results emphasize that reactor 2 behaved far from a perfectly closed system with respect to U, fissionogenic REE and Zr, even though radionuclide mobilization should have been quantitatively and spatially limited. This corroborates the conclusions of other studies indicating remobilization around the reactors 7–9, 10, 13, 16 and Okélobondo

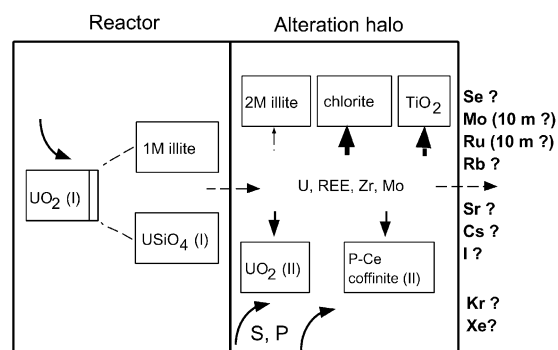


Fig. 7. Schematic two box model showing fluid circulations, mineral transformations and mobilization/redeposition of reactor products during the alteration of the reactor zone; dashed arrows represent element transfers during alteration; non-dashed arrows represent sorption onto illite, chlorite and Ti-oxide and precipitation by secondary UO_2 and coffinite.

(e.g. Loss et al., 1989; Curtis et al., 1989; Hemond et al., 1992; Menet et al., 1992; Bros et al., 1993; Hidaka et al., 1994; Holliger and Gauthier-Lafaye, 1996; Janeczek and Ewing, 1995; Bros et al., 1996; Gauthier-Lafaye et al., 1996; Jensen and Ewing, 2001). Around reactor 2, radionuclide transport was advective and enhanced by the important quantities of hot hydrothermal solutions circulating through the reactor zone. After transport of metric-scale distance, U, REE, Zr (and probably also strongly adsorbed Th) released from the core were taken up by adsorption onto hydrothermal sheet silicates (mainly chlorite and to a lesser extent illite) and detrital Ti-oxide grains. The sheet silicates crystallized during the nuclear reactions at temperatures ranging between 200 and 225 °C under a thermal gradient of 100 °C/m as indicated by O isotope data from illite from RZ 2 (Gauthier-Lafaye et al., 1989). The formation of phyllosilicates, secondary U-oxide and P-rich coffinite occurred under chemically reducing conditions as indicated by their close association with Fe-sulfides. However in some places, the radiolysis of groundwater induced by the high radioactivity of the ore may have created locally oxidizing conditions (Curtis and Gancarz, 1983; Dubessy et al., 1988; Savary and Pagel, 1997) enhancing the dissolution of uraninite. A substantial fraction of U, REE and Zr was coprecipitated by U-oxide and P-rich coffinite forming in the clay halo. This occurred while the concentrations of U, Si and P in groundwaters were high enough to exceed the saturation level of these phases. Part of the Mo released from the reactor was adsorbed onto clays but it is unclear whether or not this element was incorporated in the structure of secondary U-minerals. A large fraction of Mo should have been transported farther from the reactor and reprecipitated in sulfides. This hypothesis was invoked for fissionogenic Mo and Ru isotopes in a case study of RZ9 from the southern part of the Oklo open-pit (Curtis et al., 1989; Loss et al., 1989). Molybdenum-rich pyrites and molybdenite were found in fractures around reaction zones 10, 13 and 16 (Raimbault and Peycelon, 1995; Janeczek and Ewing, 1995; Raimbault et al., 1996). In contrast, no evidence of Se immobilization was found in this study, neither by surface sorption onto clays nor by coprecipitation by U-phases. This underlines the high mobility of this element which was removed from reaction zones. However, the possibility that Se may have been immobilized by selenides or substituting for S in sulfides such as galena, pyrite or chalcopyrite, which are abundant in reactor zones, cannot be ruled out. For example, Se-rich galena were identified in deep RZ10 (Holliger and Gauthier-Lafaye, 1996). Long-lived fissionogenic isotopes of Rb, Sr, Ba and Cs were almost completely removed from the core of reactor 2 because of their large ionic radius and their incompatibility with the structure of UO_2 (e.g. Brookins et al., 1975; Ruffenach, 1979). Similarly, in RZ10, only

5% of these elements remained in the core of the reactor (Hidaka et al., 1994). Despite large removal from the reactor core, Rb and Sr have a natural isotopic composition in the alteration halo of RZ10 (Bros, 1993; Bros et al., 1993). This suggests that, after release from the reactor core, these two elements were exchanged and released during late (post-criticality) groundwater circulations. Fissionogenic noble gases (Xe, Kr) and volatile I have high fission yields and were produced in great amounts during the nuclear phenomenon. Their large ionic radii make them incompatible with the structure of uraninite and consequently massive loss from the reactor zones occurred (Hagemann and Roth, 1978; Shukolyukov et al., 1977). Gas migration may explain specific microstructures of uraninite such as crenellated edges, channels and cracks (Gauthier-Lafaye et al., 1996). No evidence of retention effect was found for noble gases in the near-field alteration halo of RZ2 and this emphasizes their extremely high mobility and their migration far away from their source of production.

6. Conclusions

Mineralogical and isotopic studies were carried out on the nuclear reactor zone 2 from the north of the Oklo deposit. The distribution patterns of U, REE, Zr and Mo isotopes around reactor 2 reveal that substantial amounts were removed from the core and migrated through the hydrothermal alteration halo over metric distances. The results emphasize the mobility of Zr, often considered as an “immobile” element during water-rock interactions, under the hydrothermal conditions prevailing at Oklo. The main output is the demonstration of the net effects of sorption and coprecipitation processes. The sheet silicates, mainly chlorite and to a lesser extent illite were found to have adsorbed significant amounts of U, REE, Zr (and probably Th) and less sorbing elements such as Mo. Coprecipitation of secondary U minerals such as UO_2 and P-rich coffinite formed within the alteration halo is also an important means of retardation. No evidence of sorption onto clays or coprecipitation by U-, selenide or sulfide minerals was found for Se which is characterized by a higher mobility and should have migrated farther from the reactor. The analogy with the conditions of a radioactive waste disposal is mainly that Oklo is the only place in the world where actinides and fission products have remained in a natural environment for extremely long periods of time (2000 Ma). This has to be compared to natural analogue studies on the migration of radionuclides released from atomic bomb tests (e.g. Nevada) or accidents (Chernobyl) for which the time factors do not exceed 60 a. However, the temperature conditions of reactor alteration and uraninite dissolution during criticality at Oklo should have been higher

than temperatures expected in a repository system (80–150 °). Also, the hydrothermal alteration halo cannot be considered as a complete analogue to either argillaceous host rocks or bentonite-type clay buffer/backfill material. The alteration halo of reactor 2 formed during the hydrothermal alteration of sandstones at temperatures (200–250 °C) higher than temperatures expected in the repository. The mode of transport at Oklo was dominated by advection controlled by groundwater movements whereas it is expected to be mainly diffusive in man-made repositories. The concentration of radionuclides released from the reactor core were probably high and they display solubility limited transport behaviour. This contrasts with conditions expected in repositories in which radionuclides would be released in such diluted concentrations that they would remain below solubility limits. Despite these differences, this study has interesting implications for the evaluation of long-term containment. It provides a simple and comprehensive illustration of the effectiveness of a sheet silicate barrier in the uptake of radionuclides by sorption onto phyllosilicates and reincorporation in secondary U minerals such as uraninite and coffinite. It also demonstrates the robustness of these retention processes over extremely long periods of time despite circulation of groundwaters during the late diagenesis of the basin, the thermal effects of regional events (1000–600 Ma), the opening of the Atlantic Ocean and the effects of recent supergene weathering.

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