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MIGRATION PATHS FOR OKLO REACTOR PRODUCTS AND APPLICATIONS TO THE PROBLEM OF GEOLOGICAL STORAGE OF NUCLEAR WASTES*

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ABSTRACT

Escape of the products from the Oklo reactor proceeds, first, by escape from the uraninite (UO_2) grains and, second, by transport out of the gangue. Escape from the grain by fission recoil accounts for prompt deposition in the gangue of 5-10% of the products. Escape by volume diffusion is very slow. The rate of loss by diffusion was highest during the operating period of the reactor and may have been of the order of 10^{-6} fraction/a for the most volatile elements. The least volatile elements have been retained in the grains. Their diffusion rates are less than 5×10^{-10}/a.

If similar loss rates can be achieved in synthetic uraninite (or thorianite), the overall rate of transport of most reactor products would be sufficiently limited by diffusion to insure that essentially all of the radioactive species would decay in situ. The principal geochemical requirements for a suitable storage site are those that insure the survival of the UO_2 matrix, particularly that the pH and Eh are similar to the values at Oklo.

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Previous work [1,2,3] has demonstrated wide variations in the rates of transport of Oklo products out of the reactor zones. Quantitative or semi-quantitative estimates of these rates can be made for those elements which were retained in significant amounts but the estimates become qualitative for the very mobile elements. On a relative scale the losses are lowest in a group of elements including Zr, Nb, Ru, Pd, Ag, Te, the rare earths, Bi, Th, U, and Pu, and are high in a group including Sr, Mo, Ba, Kr, Xe, Rb, and Cs. Retention of the various reactor products varied from $\geq$ 90% down to $\sim$ 0.01%.

In order to evaluate the possible application of studies concerning the relative mobility of Oklo products to current and long-range planning for the management of reactor wastes, we begin with an examination of the processes which governed the escape of reactor products from the uraninite grains in which they were formed into the immediately surrounding gangue. We then examine their transport from the gangue to regions outside the reactor zones.

ESCAPE FROM URANINITE GRAINS

a) Escape by Recoil

The recoil range, R, of fission products in mg/cm^2 of UO_2 can be expressed as $R = 16.40 \cdot 0.0825\ M$ where M is the mass of the fission fragment [4]. If the density of the grain is 10 and the grain radius is 50 μm [5], the loss by recoil of mass 90 fragments is 15% and of mass 137 fragments is 7.6%. In the highest grade ore at Oklo at least one-third of the fragments terminated in other grains. Thus the loss of fission products to the gangue by prompt recoil is of the order of 10% for the light masses and 5% for the heavy masses.

b) Escape by Dissolution and Recrystallization of Grains

Information presented at this meeting on uranium solubilities in the Oklo reactor zones [6] leads us to conclude that individual uraninite grains preserved their characteristic ^{235}U-depleted isotopic ratios to distances of the order of 1 μm or less from the edge of the grain. From the correspondence between uranium concentration, ^{235}U depletion, and fission product concentrations in many regions of the reactor, it is also evident that the initial uranium abundances and geometry of the reactor have, in general, been well-preserved.

We interpret these observations to mean that a large part of the ore body has retained its initial structure and that the grains have not been altered by dissolution and recrystallization. Consequently, except for the fission recoil fraction, release of fission products must have been controlled by the rates of diffusion from the uraninite grains for each of the product elements rather than by dissolution or recrystallization of the grains. The compositional stability of the uraninite contrasts with the surrounding clay gangue which appears to have been completely altered since the nuclear chain reaction.

c) Escape by Diffusion

Uraninite grains crystallize in the fluorite structure. The crystals are very stable and resist metamictization even at very high radiation

levels. Boyko [7] found only a broadening of diffraction peak maxima at exposures of UO_2 up to 3.4×10^{18} fissions/cm^3. The broadening was due principally to lattice strain. Thus, for example, Wait [8] found the lattice expansion of single crystal UO_2 saturated at a value of 0.004 Å at 1.9×10^{16} fissions/cm^3 exposure and then undergoes no further change at 50 times this exposure. The effect disappeared completely on annealing at 200°C. At very high exposures, of the order of 10^{21} fissions/cm^3, structural changes and apparent onset of vitrification occurs. The fission density at Oklo was of the order of 10^{20} fission/cm^3.

Measurements of the rate of diffusion of fission products in high temperature reactor fuel elements indicate that the process is highly complex and is probably dominated by the vapor pressures of the elements at temperatures of the order of 2000°C. But at the low temperatures and moderate burnups in the Oklo reactor, volume diffusion probably prevailed. Rates of migration by volume diffusion in the stable fluorite lattice vary greatly with the element involved but are, in general, very slow. On the basis of ionic size only, elements which do not fit the lattice very well, including Nb, Mo, Tc, Ru, Rh, Ag, In, Sn, Sb, Te, Ba, and Pb, should migrate out of the uraninite in geological times. Elements which fit poorly into the lattice, such as Kr, Xe, Rb, and Cs, should diffuse much more rapidly. Elements which approximately match the lattice size and may be significantly retained are Zr, Pd, and Sr. Elements with ionic radii most compatible with the lattice size include the rare earths, the actinides (in +3 and +4 states), Bi, and the divalent cations of Ca and Cd.

Some ion probe observations of the distribution of elements between uraninite and the immediately surrounding gangue exist for Si, K, Ca, Ti, Fe, Sr, Zr, Ru, Pd, Ce, Nd, Pb, and Th [3]. In the rich irradiated ore the uraninite grains contain essentially all of the Ca, rare earths, Pd, Pb, and Th. Sr and Ru are in the gangue. Zr is disseminated between uraninite and clay.

The degree of retention is not known for all of the reactor product elements. However, based on the existing measurements, we have used an approximate solution for diffusion to estimate values or limits on D/a^2 for the diffusion of several of the product elements from the uraninite grains. The approximation used is:

$$\frac{C_f}{C_i} \sim e^{-(\pi^2 D/a^2)t}$$

where C_i is the initial concentration, C_f the final concentration, and a is the grain radius.

Among the elements which appear to have been retained quantitatively in the uraninite are Pd, the lighter rare earths, and Th. We also include Pu, Am, and Cm in this group because they form solid solutions in the uraninite, fit the ionic lattice, and should behave like Th. D/a^2 for these elements is $\leq 5 \times 10^{-12}/a$. For this group of elements diffusion from uraninite is so slow that it is clear that their losses from the reactor zone were entirely controlled by the diffusion rate and not by their subsequent geochemical behavior. This observation is important because it means that the transport rate of such elements is determined by the initial matrix. The necessary

geochemical conditions are only those which insure the survival of the uraninite.

Other elements which appear to have been retained nearly quantitatively in the ore include Nb, Zr, Ru, Ag, and Te. Because they do not fit the crystalline lattice well and are observed, in some cases, to have diffused out of the uraninite, it can be assumed that they underwent secondary precipitation to a highly insoluble mineral form after diffusion and were retained in the gangue. We assume that values of D/a^2 for such elements can be as high as 1×10^{-10}/a leading to losses of the order of 90% from the uraninite into the gangue.

The extent to which Sr and Ba were retained in the reactor appears to vary within the range 0.1%-10%. Mo was retained to the extent of $\sim$ 10%. The corresponding values of D/a^2 in uraninite fall in the range 1-3.5 x 10^{-10}/a.

Elements which have been poorly retained in the reactor, from 1% down to 0.01%, include Kr, Rb, and Xe. The group may also include Cs, Cd, and I. The estimate for D/a^2 for losses $\geq$ 99% is $\geq 2.3 \times 10^{-10}$/a. An upper limit on D/a^2 for retention of 0.01% of a reactor product is 5×10^{-10}/a. For reasons discussed below, major losses of the more volatile fission products could have occurred during a high temperature ($\sim$ 400°C) operating period of the reactor and the subsequent diffusion rates at lower temperatures may have been lower.

The isotope ^{90}Sr has a 29 a half-life. Maeck [9] compared the isotopic abundance of ^{90}Zr to other fission product Zr isotopes and concluded that $\sim$ 5% of mass 90 may have been lost, presumably due to the higher geochemical mobility of ^{90}Sr before it decayed to ^{90}Y and then ^{90}Zr. However, this loss, if it is real, could be due to the recoil of mass 90 fragments into the gangue followed by their transport out of the reactor in times comparable to the ^{90}Sr half-life. Diffusion of ^{90}Sr from uraninite grains in times comparable to 29 a was probably much too low to be measurable.

Deficits of ^{99}Ru of 20-30% have been reported in some samples within the reactor zones [9,10]. There is also an excess of ^{99}Ru in some peripheral samples [11]. These effects are attributed to the diffusion and subsequent removal from the gangue of ^{99}Tc in times comparable to its half-life (2.13×10^5 a). A value of D/a^2 of $\sim 10^{-7}$/a for Tc would account for the highest observed losses. This value is considerably higher than any of the previously calculated numbers but can not be compared directly with them. The ^{99}Tc could only have diffused during the operating period of the reactor when the temperature may have been of the order of 400°C [12]. If the 25°C value of D/a^2 for Tc is assumed to be 2×10^{-10}, the activation energy for diffusion between 25°C and 400°C would have to be 6 kilocalories/mole to account for the value 10^{-7} at the higher temperature. This low energy of activation is characteristic of the diffusion process at temperatures below the so-called Tamman temperature, i.e., the point at which it is assumed that temperature-caused defects in the crystal become greater than the population of initial defects. It would be useful to check these assumptions by irradiating some of the Oklo ore and measuring the Tc diffusion rate as a function of temperature. It may be possible to use the ^{99}Ru deficit to estimate reactor temperatures.

Lead appears to be a relatively mobile element. Approximately 75% of

the lead, made chiefly by alpha decay of ^{238}U, has diffused out of uraninite. A fraction of this amount, $\sim$ 10%, has been retained as galena (PbS) in the gangue.

The problem of lead diffusion from minerals has been considered in Pb-U geochronological applications. Using the notation of Tilton [13] we may write

$$\frac{\bar{C}}{N} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{\lambda(e^{\lambda t - n^2\pi^2 Dt/a^2} - 1)}{n^2(\lambda t - n^2\pi^2 D/a^2)}$$

where $\bar{C}$ is the average concentration of lead in a spherical grain, N is the present concentration of uranium, λ is the uranium decay constant, and a is the effective grain radius. Solutions for this equation have been tabulated by Nicolaysen [14] for various values of $\lambda a^2/D$. We have used the equation to estimate a value of D/a^2 for Pb in Oklo, if the loss is due to continuous diffusion from spherical grains, of 3.5×10^{-11}/a. This rate is characteristic of lower grade portions of the Oklo deposit as well as the very rich reactor zones.

Discordancy in the ages of a number of natural minerals appears to be due to the diffusion of ten to fifty percent of the radiogenic lead. The corresponding diffusion rate is somewhat lower than at Oklo. For example, some discrepancies in Finnish and U.S. zircons which give $^{206}Pb/^{238}U$ ages of $\sim$ 1800 m.a. in contrast with $^{207}Pb/^{206}Pb$ ages of $\sim$ 2600 m.a. [14] can be explained by assuming continuous diffusion of lead with a rate corresponding to a value of D/a^2 of $\sim 10^{-11}$/a.

ESCAPE FROM THE REACTOR ZONE

Brookins discusses the geochemical stability and relative mobility of a number of fission products after they have wholly or largely diffused out of the uraninite grains [15]. As mentioned earlier in this paper, on the basis of ionic size the elements which diffused out of the uraninite include Kr, Xe, Rb, Cs, Nb, Mo, Tc, Ru, Rh, Ag, In, Sb, Te, Ba, and Pb. Some of these elements then formed insoluble compounds. According to Brookins, elements which might form stable sulfides in the gangue include Mo, Tc, Ru, Ag, Cd, In, Sb, and Pb. Elements which might have been retained as oxides include Nb, Tc, Ru, In, and Sn. Zr is most stable as the silicate but might have been retained as an oxide. Rh and Te would probably be retained as the metal.

Quantitative data for Zr, Nb, and Ru indicate that they were wholly retained. A small fraction of ^{99}Tc and a major fraction of the Mo and Pb were lost. Qualitative data indicate that Cd may have been lost. Rh, Ag, and Te were significantly retained. On the whole, these observations suggest that the elements which were least mobile after leaving the uraninite formed insoluble oxides, silicates, or metals. The elements which precipitated as sulfides were relatively more mobile.

Due to the fact that large quantities of lead were formed from the decay of uranium, more detailed estimates of lead transport rates can be made for Oklo. The ore contains macroscopic crystals of galena formed from almost pure radiogenic lead. Based on the data presented by Branche [16], only 5% of the lead which diffused from the uraninite has been retained as galena although pyritic sulfur is present ($\sim$ 1% pyritic S by weight). If

we assume that an approximate equilibrium has been approached between the amount of lead which leaves the uraninite and the amount which leaves the reactor zone, we can estimate the rate for transport out of the reactor zone from the equation:

$$N_{Pb(\text{in U})}\ \lambda_{\text{diffusion}} = N_{Pb(\text{in gangue})}\ \lambda_{\text{transport out}}.$$

The ratio of lead in the uraninite to lead in the gangue is ~ 10. Based on the previous estimate of D/a^2 for lead, we take $\lambda_{\text{diffusion}}$ equal to 3.5×10^{-10}/a. Therefore, $\lambda_{\text{transport out}}$ is $\sim 3.5 \times 10^{-9}$/a.

Although iron pyrites present in the Oklo gangue are presumably considerably less mobile than galena, based on observations of the relative mobility of these sulfides in other Precambrian deposits, the iron shows no evidence of exposure to neutrons and appears to have been largely replaced which tends to support the suggestion that the insoluble sulfides in the Oklo ore have been mobilized.

CONCLUSIONS AND REMARKS ABOUT APPLICATIONS TO REACTOR WASTE MANAGEMENT

The Oklo data demonstrate that, in general, the uraninite grains were remarkably stable. This conclusion is based not only on the absence of replacement effects on the uranium isotopic ratios at the edges of uraninite grains but also on the agreement between uranium concentrations, isotopic depletions, and retained rare earth concentrations. Indeed, small uranium and fission product migration effects are observed, particulary at the borders of reactor zones, which give rise to dispersion "haloes." But if uranium loss rates had averaged more than 10^{-10}/a over the reactors, much larger anomalies should have occurred. Similar loss rate limits should apply to Pu, Am, and Cm which form solid solutions in the uraninite lattice and which should diffuse out of the lattice at even slower rates than the limit on the dissolution rate of the uraninite.

Reactor products which diffused out of the uraninite matrix and subsequently formed insoluble oxides, silicates, or metals were largely retained in the reactor zones. Several elements which were more stable as insoluble sulfides were only partially retained. The remaining elements were largely lost in the form of soluble ions or complexes.

The overall loss rates estimated here are probably never appreciably higher than 10^{-6}/a for the most volatile elements during the operating period of the reactor. If a highly stable matrix such as synthetic uraninite were used for the storage of reactor wastes in appropriate geological and geochemical environments and if the storage temperature could be held below 400°C, the highest loss rates from the matrix to the immediately surrounding environment should remain less than 10^{-6}/a. The least volatile elements, such as Pu, should be released at rates considerably less than 10^{-10}/a. The released radioactive elements would be further retained and reduced before entering the biosphere by additional interactions with the surrounding medium.

This picture is clearly oversimplified. It contains several assumptions. The most important assumptions are 1) that synthetic uraninite will behave like the natural Oklo uranium mineral; 2) that the early intense radiation

field will not lead to loss of the desirable crystalline properties of uraninite; 3) that temperatures of the stored material will not rise to values so high that they lead to a different pattern than at Oklo; and 4) that the geochemical conditions which were responsible for the stability of the Oklo uraninite can be sufficiently specified, satisfactorily reproduced, and assumed to persist for a long period. A detailed discussion of each of these problems falls outside the planned scope of this paper. However, we believe that these uncertainties will probably be favorably resolved and that synthetic uraninite (or synthetic thorianite) will eventually prove useful for the long-term storage of reactor products in geological sites.

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