

Title:

RADIONUCLIDE RELEASES FROM NATURAL ANALOGUES OF SPENT NUCLEAR FUEL

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Submitted to:

Migration '93 - Charleston, SC - December 12-16, 1993

MASTER

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RADIONUCLIDE RELEASES FROM NATURAL ANALOGUES OF SPENT NUCLEAR FUEL

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Abstract: Measures of ^{99}Tc , ^{129}I , ^{239}Pu and U concentrations in rock samples from uranium deposits at Cigar Lake and Koongarra have been used to study processes of radionuclide release from uranium minerals. Rates of release have been immeasurably slow at Cigar Lake. At Koongarra release rates appear to have been faster, producing small deficiencies of ^{99}Tc , and larger ones of ^{129}I . The inferred differences in radionuclide release rates are consistent with expected differences in uranium mineral degradation rates produced by the differing hydrogeochemical environments at the two sites.

Introduction – Objectives and Approach

Radioactive nuclides are produced in the earth by nuclear reactions. In some geologic settings abundances of these nuclides can be measured by modern analytical methods, and the results used to further our understanding of nuclear and non-nuclear processes in the geologic environment. Rocks containing abundant uranium have high concentrations of natural nuclear products. Uranium is the primary source of neutrons that induce many of the nuclear reactions, and it is the parent of many of the reaction products. Among these are ^{99}Tc and ^{129}I , fission products produced by spontaneous and neutron-induced uranium fission, and ^{239}Pu produced by neutron capture of ^{238}U .

Materials containing radionuclides produced exclusively *in-situ* by nuclear reactions will achieve a state of nuclear equilibrium in which these radionuclide abundances are functions of rates of production and decay. Such a condition will be referred to as secular equilibrium, to emphasize the analogy with the more familiar condition established by decay of naturally radioactive long-lived parent nuclides to shorter-lived radioactive progeny. Systematics of natural nuclear processes are understood and in principle can be used to predict radionuclide concentrations at secular equilibrium. We are measuring abundances of radioactive nuclear products in samples from uranium deposits and comparing them with abundances predicted at secular equilibrium to characterize the timing, rates, and chemical effect of processes affecting the release of radionuclides from uranium minerals in different geochemical and hydrologic environments.

If samples contain secular equilibrium abundances, one can draw the following conclusions regarding non-nuclear processes in the system: 1) No process has impacted the system from a time in the past equivalent to several daughter half-lives to the present; or 2) the process rate was significantly slower than the radionuclide production rate; or 3) the process did not selectively add or remove the daughter element relative to the parent.

If abundances of radioactive natural nuclear products are not at secular equilibrium: 1) The system has been disturbed within the time domain of the nuclear process; *and* 2) the process rate was faster than or comparable to the radionuclide production rate; *and* 3) the process selectively added or removed daughter relative to the parent. We characterize the state of secular equilibrium by calculating a disequilibrium factor (α) by normalizing the measured daughter/parent ratio to the daughter/parent ratio at secular equilibrium. Disequilibrium factors are exactly analogous to daughter/parent activity ratios used in characterizing disequilibrium between radionuclides in uranium and thorium decay chains: Unity indicates a condition of secular equilibrium. Values greater than or less than unity represent systems in which there have been, respectively, a relative enrichment or depletion of daughter relative to parent. As with uranium/thorium decay series, interpretations regarding non-nuclear processes from disequilibrium of nuclear products are often ambiguous. We seek to minimize ambiguity by working in well-characterized hydrogeological, mineralogical, and geochemical systems where knowledge of conditions constrains interpretations of chemical and temporal effects associated with release of radionuclides.

Natural analogues of repository processes

Aqueous transport from a repository to the accessible environment is a scenario common to performance assessments of geologic repositories for radioactive waste. In the Sandia Total Safety Performance Assessment (TSPA) (1), such a scenario is developed by considering "well-defined connected sequences of features, events, or processes. Features [boundary conditions] are the geologic or hydrologic properties of the site or system which are expected to be durable. Processes ['the physics'] are phenomena that have gradual continuous interactions with the system. Events [initial conditions or forcing terms] are occurrences that have a specific starting time (and usually a duration shorter than the time being simulated)." An aqueous transport scenario is simulated by mathematical descriptions of the operative "processes" given the "features" of the proposed repository site. Predictions of cumulative releases to the accessible environment, expressed as probability distributions, are measures of performance resulting from these coupled models.

The TSPA describes a model hierarchy in which probabilistic estimates are produced by models near the top of the hierarchical structure. These are supported by mechanistic process models that lie near the bottom of the hierarchical pyramid. Process models "are indispensable in achieving the detailed understanding needed for the NRC and the DOE to feel reasonably assured that the repository will behave as predicted....models higher in the pyramid must be firmly grounded on the lower models because they must successfully reproduce all the phenomena that are significant to the performance of the total repository system."(1). Source term models calculate radionuclide releases from the engineered barrier system and near field environment into the far field region (1, 2, 3). They are developed from conceptual processes that include radionuclide release to water by waste form degradation in near field environments. "Upon contact with water, radionuclide releases may be constrained by the solubility

of the UO_2 matrix, the solubility of the radionuclide-bearing precipitate, or the rate of physicochemical alteration of the UO_2 matrix. Which of these processes is, in fact, limiting will depend on factors such as the chemistry of the given nuclide, the abundance of the nuclide within the UO_2 matrix, the chemical composition of the contacting water, the temperature, and, in particular, the redox potential." (1).

In the TSPA, radionuclide releases are calculated using a range of solubilities determined from laboratory studies and model calculations. Matrix alteration rates are parameterized by a log-uniform distribution bounded by results of spent fuel leaching tests. Values were chosen to represent "features" of a potential repository at Yucca Mountain, Nevada.

Natural Analogue Field Sites

We are diagnosing processes of radionuclide release from uranium minerals in geologic environments by characterizing abundances of ^{99}Tc , ^{129}I , ^{239}Pu , and U in rock and water samples from the uranium enriched system. We are not attempting to study geologic settings that duplicate the "features" at a specific repository site. Rather we are attempting to determine if process characteristics inferred from our observations are consistent with those considered in performance assessment models under the conditions of the geologic setting that is being studied.

Our current work considers two sites representing a range of geologic, hydrologic, and geochemical conditions. Cigar Lake is a chemically reduced ore body 450 m below surface at the contact between Middle Proterozoic (1.5×10^9 yr) sandstone and Lower Proterozoic/Archean metamorphic basement in the Athabasca Basin of northern Saskatchewan, Canada. Thick lenses of high-grade uranium occur in a clay-rich mineralized zone. Uraninite (UO_{2+x}) is the principal uranium bearing mineral; Two types are distinguished by texture and abundances of lead, silicon and less abundant elements. Much smaller quantities of uranium are contained in the silicate mineral coffinite. Petrographic properties show evidence of uranium mineral alteration in Cigar Lake ore. Alteration is probably the consequence of hydrothermal events of $>10^7$ yrs ago (4). However, coffinite petrogenesis is complicated, and it is possible that minor quantities of that uranium silicate mineral may reflect low temperature uraninite alteration in the ore zone.

Koongarra is a near surface uranium deposit conformable within steeply dipping quartz-chlorite schists of the lower member of the Cahill Formation in Northern Australia. The deposit can be most generally characterized as two zones; highest grade ores occur in unweathered schist at depths between 30 and 100 m (5). Uranium mineralogy in the deep zone can be attributed to uranium loss from primary uraninite, with the resultant radiogenic lead enrichment, and to formation of secondary minerals, principally secondary uraninite, uranyl, and lead uranyl silicates (6). Secondary mineralization occurs in a near-surface zone of weathered schist. Uranium in this zone has been altered and dispersed by groundwater. Secondary uranium mineralogy is a complex and diverse assemblage dominated by uranyl phosphates. Uranium dispersed down the hydrologic gradient is primarily associated with iron

and manganese oxides (5).

Hydrogeochemistry of the two sites is also quite different. The Cigar Lake mineralized zone, overlain by a highly permeable sandstone aquifer, has a characteristic low permeability so that groundwater flow is largely deflected over and around it. Any flow through the mineralized zone will be fracture controlled. Water samples from the ore zone can be characterized as dilute, neutral to alkaline, and reducing, containing uranium concentrations on the order of 10 ppb (7). The aqueous chemistry appears to be controlled by interaction between sandstone formation water, and rocks in the hydrothermal alteration halo and the underlying ore body (8).

Hydrology of the Koongarra ore zone is complex. The weathered schist is a laterally variable aquitard between surficial sands that act as an unconfined aquifer in the wet season, and a partially confined fractured-rock aquifer in the deep, unweathered schist. Water levels show dramatic yearly, daily and semidiurnal fluctuations (9). Water chemistry at Koongarra is variable with systematic changes as a function of depth (10). Relative to that from Cigar Lake ore, Koongarra water is more acidic, and much more oxidizing. Bicarbonate concentrations are 5-10 times greater, and phosphate concentrations are orders of magnitude greater. Uranium concentrations are variable but typically 20 times greater in the Koongarra weathered zone and 5 times greater in the deep zone than in the Cigar Lake ore zone. "The origins of the present-day waters can best be attributed, from a purely chemical standpoint, to vertical recharge by rainwater that progressively evolves by reaction with the chlorite schist..." (10).

As high-level radioactive waste analogues, Cigar Lake and zones at Koongarra might be thought of as "snapshots" in time representing progressive oxidative alteration and dissolution of spent fuel in response to exposure to oxidizing meteoric groundwater. Uranium mineralogy in the ore bodies is similar to the "interpretative paragenetic sequence" observed in laboratory experiments characterizing uranium release rates from extended exposure of UO_2 to dripping oxygenated water (11). Our work could be considered as a similar experiment in which we are characterizing radionuclide releases from uranium bearing minerals over geologic times rather than laboratory times. There is the obvious disadvantage of having to infer natural experimental conditions.

Nuclear Reaction Product Abundances

Uranium, ^{99}Tc , ^{129}I , and ^{239}Pu abundances in samples from uranium deposits at Koongarra and Cigar Lake are presented in Tables 1, 2, and 3. Technetium abundances were measured by isotope dilution mass spectrometry (12). Quantities measured in samples and blanks are presented in Table 1 to show the effects of contamination introduced during analyses on final results. These data show that the smallest quantity of technetium measured in samples was four times higher than the detection limit. The latter is defined as three standard deviations in the distribution of quantities of technetium measured in blanks. Technetium concentrations, in Table 1, have been corrected for the average quantity of technetium measured in blanks. Uncertainties reported for measured $^{99}Tc/U$ are calculated from the

Table 1. Technetium in Uranium Ores

Sample ID	Measured Values			Calculated Value		
	Uranium Wt. %	⁹⁹ Tc pg	⁹⁹ Tc pg/g	⁹⁹ Tc/U Atomic x 10 ¹²	Secular ⁹⁹ Tc/U Atomic x 10 ¹²	Disequilibrium Factor (α_{Tc})
Cigar Lake						
CS-627	23.2%	0.60	0.16	1.7 ± 0.4	1.9 ± 0.1	0.9 ± 0.2
CS-604	45.3%	3.65	0.38	2.0 ± 0.4	2.2 ± 0.1	0.9 ± 0.2
CS-609	6.7%	3.56	0.38	13.5 ± 2.8	1.7 ± 0.1	8.0 ± 1.7
W83C	46.8%	1.22	0.40	2.1 ± 0.4	1.8 ± 0.2	1.2 ± 0.3
Koongarra						
G-4674	11.5%	0.72	0.07	1.5 ± 0.3	1.9 ± 0.1	0.8 ± 0.2
G-2698	19.1%	1.12	0.12	1.5 ± 0.3	1.9 ± 0.1	0.8 ± 0.2
Standard						
BL-5	7.09%	0.40	0.039	1.3		
BL-5	7.09%	0.68	0.060	2.0		
BL-5	7.09%	0.53	0.052	1.8		
Average BL-5				1.7 ± 0.4	2.2 ± 0.1	0.8 ± 0.2
Blanks						
Mauna Loa Basalt		0.15				
Mauna Loa Basalt		0.12				
Mauna Loa Basalt		0.05				
Mauna Loa Basalt		0.06				
Cigar Lake Sandstone		0.08				
Reagent		0.05				
Reagent		0.11				
Reagent		0.06				
Ave. Blank		0.08				
Std. Dev. Mean		0.01				
Std. Dev.		0.04				
Detection Limit		0.11				

percent standard deviation measured in triplicate analyses of Canadian reference ore BL-5.

Measures of ²³⁹Pu reported in Table 2 were also made by isotope dilution mass spectrometry (13). Sample results that do not include a measure of total ²³⁹Pu mass were reported previously (14). Newly reported results have been corrected for the blank values presented in Table 2. All ²³⁹Pu concentrations have been corrected for appropriate blanks. The two data sets may be judged by comparing abundances measured in aliquots of BL-5 analyzed in conjunction with each. Although derived in different ways, the magnitude of uncertainties in all results are comparable, and provide a consistent measure of data quality.

Table 2. Plutonium in Uranium Ores

Sample ID	Measured Values			Calculated Value		Disequilibrium Factor (α_{Pu})	
	Uranium Wt. %	^{239}Pu pg	^{239}Pu pg/g	$^{239}Pu/U$ Atomic $\times 10^{12}$	Secular $^{239}Pu/U$ Atomic $\times 10^{12}$	Value	Range
Cigar Lake							
CS-615	51.5%	20.0	4.1	7.9 ± 0.1	6.1 ± 0.8	1.3	0.65–2.6
CS-604	45.3%	16.6	5.1	11.3 ± 0.1	5.9 ± 0.8	1.9	0.95–3.8
CS-620B	44.7%	5.0	1.9	4.2 ± 0.6	6.6 ± 1.0	0.6	0.3–1.2
W83A	40.8%	-----	1.2	3.0 ± 0.2	3.2 ± 0.8	0.9	0.45–1.8
W83C	46.8%	-----	1.3	2.8 ± 0.2	3.2 ± 0.8	0.9	0.45–1.8
CS235L	54.6%	-----	1.0	1.9 ± 0.1	3.2 ± 0.8	0.6	0.3–1.2
Koongarra							
G-4674	11.5%	-----	0.2	1.4 ± 0.1	2.5 ± 0.7	0.6	0.3–1.2
G-2698	19.1%	-----	0.5	2.6 ± 0.1	3.2 ± 0.8	0.8	0.4–1.2
Standard							
BL-5	7.09%	-----	0.22	3.1 ± 0.4			
RL-5	7.09%	1.33	0.29	4.1 ± 0.5			
			0.26	3.6 ± 0.7	3.0 ± 0.5	1.2	0.6–2.4
Blanks							
Hi Purity Si Reagent		0.02					
		0.02					

Iodine-129 results reported in Table 3 were measured by isotope dilution accelerator mass spectrometry. All ^{129}I data were previously reported and discussed in volume 15 of the Alligator Rivers Analogue Project final report (15).

Table 3. Iodine 129 in Uranium Ores

Sample ID	Measured Values			Calculated Value		Disequilibrium Factor (α_I)	
	Uranium Wt. %	^{129}I pg/g	$^{129}I/U$ Atomic $\times 10^{12}$	Secular $^{129}I/U$ Atomic $\times 10^{12}$	Value	Range	
Cigar Lake							
W83A	40.8%	0.41	1.8 ± 0.2	2.8 ± 1.0	0.6	0.3–1.2	
W83C	46.8%	0.71	2.8 ± 0.3	2.8 ± 1.0	1.0	0.5–2.0	
CS235L	54.6%	0.3	2.1 ± 0.3	2.8 ± 1.0	0.8	0.4–1.8	
Koongarra							
G-4674	11.5%	0.2	1.0 ± 0.3	3.7 ± 0.9	0.3	0.15–0.8	
G-2698	19.1%	0.1	1.3 ± 0.4	3.9 ± 0.8	0.3	0.15–0.8	

Modelling Secular Equilibrium Ratios

Secular ratios in Tables 1, 2, and 3 are model values calculated using the Monte Carlo Neutron and Photon Transport code (MCNP) (16) to simulate nuclear production reactions in the geologic environments represented by the samples. Fabryka-Martin and Curtis (15) provide a comprehensive discussion of results produced by nuclear reaction model calculations. Reported uncertainties of secular equilibrium values reflect the sensitivity of calculated results to compositional variability in the geologic setting from which the samples were taken. However, they do not reflect inaccuracies associated with the model representation of the system. Calculations of secular $^{99}\text{Tc}/\text{U}$ are relatively insensitive to the choice of model because the largest portion of ^{99}Tc is produced by spontaneous ^{238}U fission, a process in which secular $^{99}\text{Tc}/\text{U}$ is independent of the environment. Consequently the $^{99}\text{Tc}/\text{U}$ disequilibrium factors (α_{Tc} in Table 1), have relatively small uncertainties and are good measures of the state of disequilibrium between ^{99}Tc and U. Spontaneous fission establishes a well defined lower limit for secular $^{99}\text{Tc}/\text{U}$; a measured ratio less than 1.57×10^{-12} is unambiguously in a state of disequilibrium.

Determination of secular equilibrium $^{239}\text{Pu}/\text{U}$ is more uncertain. Plutonium-239 is produced exclusively by neutron capture by ^{238}U at a rate that is dependent on the abundance and geometrical distribution of elements within about 50 cm of the sample of interest. Because it is difficult to assess the geometrical configuration of critical elements in a heterogenous setting, it is difficult to assess inaccuracies in secular $^{239}\text{Pu}/\text{U}$ values derived from models in which this configuration is a critical parameter.

Uncertainties in model predictions of secular $^{129}\text{I}/\text{U}$ fall between the extremes represented by $^{99}\text{Tc}/\text{U}$ and $^{239}\text{Pu}/\text{U}$. Again, spontaneous fission imposes an unambiguous lower limit of 6.7×10^{-13} on secular $^{129}\text{I}/\text{U}$ values. However in contrast to technetium, neutron-induced fission generally dominates total ^{129}I production in uranium ores. Thus, as with $^{239}\text{Pu}/\text{U}$, predictions of secular $^{129}\text{I}/\text{U}$ are sensitive to inaccuracies associated with model representations of neutron induced processes in heterogenous environments.

We are developing a model independent approach to predicting ^{129}I and ^{239}Pu production rates by using the ratio $^{36}\text{Cl}/\text{Cl}$ as an *in-situ* neutron monitor (15). In the meantime we are conservatively reflecting uncertainties introduced by inaccuracies in conceptual models, by arbitrarily assigning ranges to disequilibrium factors that include 0.5x to 2.0x the calculated $^{239}\text{Pu}/\text{U}$ and $^{129}\text{I}/\text{U}$ α values.

Interpretation of Radionuclide Equilibrium/Disequilibrium

A mathematical model may be constructed relating ^{99}Tc , ^{129}I , or ^{239}Pu disequilibrium factors to radionuclide release rates(17). If it is assumed that daughter/parent ratios reflect a state of dynamic equilibrium established by the nuclear processes *and* a continuous, non-nuclear first order process involving only daughter loss, then the relationship between the rate constant for the non-nuclear process (Δ), the radioactive decay constant for the daughter radionuclide (λ_{D}), and the disequilibrium factor (α) is defined by equation (1).

$$\Delta = \lambda_{\text{D}}(1 - \alpha) / \alpha \quad (1)$$

The assumption of a first order process exclusively involving daughter loss is likely to be a reasonable approximation if the quantity of released radionuclide is below the solubility limits of radionuclide bearing solid phases, if the radionuclide is not coprecipitated with secondary phases, and if it has no sorptive properties. Both ^{99}Tc and ^{129}I are likely to meet these criteria in many natural settings. However, plutonium has a high capacity for sorption in most geological settings(18), is likely to coprecipitate with uranium and thorium bearing minerals and thus may not conform with assumptions inherent in equation (1).

It is impossible to unambiguously determine whether radionuclide releases were continuous or episodic. However, disequilibrium factors in a suite of selected samples from a well characterized site may permit construction of convincing arguments regarding the nature of the release processes. For instance, because of their very different half-lives, ^{239}Pu , ^{99}Tc , and ^{129}I each probe a uniquely different process rate domain: on the order of 10^{-5} yr^{-1} , 10^{-6} yr^{-1} , and 10^{-8} yr^{-1} respectively. Consequently, if processes releasing these radionuclides were continuous and first order with respect to the daughter, only a few possible states exist: These states are summarized in Table 4.

Table 4. Allowed States in Continuous Process Model

Process rate (yr^{-1})	α_I	α_{Tc}	α_{Pu}
$\Delta < 5 \times 10^{-8}$	1	1	1
$5 \times 10^{-8} < \Delta < 10^{-7}$	<1	1	1
$5 \times 10^{-6} < \Delta < 10^{-5}$	0	< 1	1
$5 \times 10^{-5} < \Delta < 10^{-4}$	0	0	< 1
$10^{-4} < \Delta$	0	0	0

Any other combination of disequilibrium values indicates that processes other than those being modelled have been operative. Two simple possibilities: If $0 < \alpha_I = \alpha_{\text{Tc}} = \alpha_{\text{Pu}} < 1$, it is likely to represent uranium gain rather than daughter loss. Disequilibrium factors >1 indicate daughter gain or uranium loss: If $\alpha_I = \alpha_{\text{Tc}} = \alpha_{\text{Pu}} > 1$, it is likely to indicate the preferential loss of uranium.

The previously discussed imprecision in our ability to define disequilibrium factors constrains our ability to characterize the state of equilibrium of a system. We will consider a daughter/parent pair to be in secular equilibrium if the range of α includes unity.

Interpretation of Cigar Lake Results

Samples W83A, W83C, and CS235L were pulverized from a few cm lengths of roughly 3 cm diameter core provided by the exploration company. They represent undiscriminated samples of small volumes of the Cigar Lake ore. The other samples were taken from a 6 m length of core 220 collected specifically for the natural analogue study. Pulp samples were prepared from lengths ranging from 3 to 55 cm of the quartered core. Decisions regarding the length of core for sampling were based upon visual inspec-

tion of the lithology, mineralogy, and radioactivity. A large variety of other studies have been done on other sections of this core (19,20). These are samples representing ore volumes with visually discernable common properties.

Within the precision of our ability to characterize it, all but one of the samples from Cigar Lake appear to be in a state of secular equilibrium with respect to all of the daughter radionuclides. The single exception is CS-609 which appears to contain an enormous excess of ^{99}Tc . The data is consistent with the previously described first state of equilibrium in which $\Delta < 5 \times 10^{-8} \text{ yr}^{-1}$. Assuming that the excess of ^{99}Tc is not an unrecognized analytical problem, it would suggest that although the rates of release appear to be too slow to characterize by our methods, there has been a release of ^{99}Tc from its source, and a process of ^{99}Tc concentration operative in CS-609. The inference of imperceptibly slow release from minerals is consistent with processes that would be expected under conditions inferred in the ore zone.

In a context of slow release, the huge excess of ^{99}Tc in a single sample reflects processes that were concentrated ^{99}Tc in a small volume of rock. Laboratory studies have shown that large fractions of technetium can be removed from aqueous solutions by some minerals (21). Sulfides are particularly effective in this regard. We could speculate that ^{99}Tc enrichment was the result of mass transport by fracture flow and enrichment by scavenging on sulfide minerals. Conjecture regarding the nature of the process could be tested by characterizing the mineralogy and petrography of this sample.

Interpretation of Koongarra Results

Koongarra samples were taken from pulp created by the exploration company from 1-2 meter sections of rock core. Consequently they represent poorly characterized macroscale samples of the regions from which they were taken. Sample G-2698 is a 1 meter thick sampling of the transition zone between weathered and unweathered schist. In the shallow portions of the sampled region there is blue black pitchblende associated with strong hematitic alteration, and yellow secondary uranium minerals enclosing relict pitchblende almost wholly replacing schist. Deeper portions of the sampled region contain sklodowskite and kasolite, uranium minerals characteristic of the unweathered zone (22). Sample G-4674 is a pulp of about one meter of core from deep in the unweathered zone. It is a sample of primary pitchblende hosted in crushed and slightly brecciated quartz chlorite schist (22).

We cannot distinguish any ^{239}Pu disequilibrium in these samples. Our measure of disequilibrium factors for ^{99}Tc suggests barely perceptible deficiencies in ^{99}Tc . However, even the poorly resolved measures of ^{129}I disequilibrium indicate significant releases of this radionuclide at Koongarra. Significant releases of ^{129}I are also manifest in elevated concentrations of this radionuclide in water from Koongarra (15). All data from the two samples are consistent with a process of continuous release at rates at the high end of the ^{129}I rate domain, and the low end of the ^{99}Tc rate domain. The inferred release rate constant would then be on the order of $\Delta \approx 10^{-7} \text{ yr}^{-1}$.

Summary and Conclusions

We have presented the application of a technique to characterize the timing, rate, and chemical effects of natural processes affecting the release, transport, and retention of natural radionuclides in the geologic environment. The results show that such processes have been operative at some time between the present and 10^8 years ago in uranium deposits in extremely different geologic environments at Koongarra, Australia, and Cigar Lake, Canada. Model-dependent radionuclide release constants from the uraninite-bearing rocks at Cigar Lake are $< 5 \times 10^{-8} \text{ yr}^{-1}$. The existence of operative release processes at Cigar Lake have only been manifest in an apparent enrichment of ^{99}Tc in one sample from the ore zone. Given the observation of imperceptible rates of release, the ^{99}Tc enrichment manifests extremely effective ^{99}Tc enrichment processes in that environment.

We discern no ^{239}Pu deficiencies, small deficiencies of ^{99}Tc and larger deficiencies of ^{129}I in samples from the unweathered portion of the uranium deposit at Koongarra. The observations are consistent with model process rates on the order of 10^{-7} yr^{-1} . The faster release rates at Koongarra than at Cigar Lake are consistent with expectations of differences in anticipated uranium mineral degradation rates under the geologic conditions at the two sites. Low uraninite solubility in a reducing environment and small water flux through impermeable rock would inhibit the rate of uraninite degradation and thus the rate of radionuclide release in the Cigar Lake ore zone. At Koongarra higher mineral solubilities induced by higher oxidation potentials and higher aqueous concentrations of carbonate and phosphate and greater water fluxes would be expected to produce higher rates of uranium mineral degradation.

We conclude that our data are consistent with uranium mineral degradation being the radionuclide release rate controlling process. The model dependent release rates inferred in two very different hydrogeochemical settings are more than an order of magnitude slower than those used as a minimum limit for the spent fuel alteration rate in the TSPA (1).

Acknowledgments: This work was supported by the United States Department of Energy, Office of Civilian Radionactive Waste Management, Office of Strategic Planning and International Programs, and the United States Department of Energy, Office of Basic Energy Sciences, Office of Mathematics, Engineering, and Geosciences. The authors express their gratitude to Henry Shaw for his comments on parts of the manuscript, and Tom Isaacs, Bob Levich, Tom Ricketts, and George Kolstat for their personal efforts on behalf of this work. We are grateful to Elaine Roybal and Rhea Coleman for their able assistance in the manuscript preparation.

References

1. Barnard, R. W., M. L. Wilson, H.A. Dockery, J.H. Gauthier, Kaplan, P.G., Eaton, R.R., Bingham, F.W., Robey, T.H.. 1991, TSPA 1991: *An initial total-system performance assessment for Yucca Mountain*, Sandia Report, SAND91-2795-UC-814.
2. Kossik, Richard, Ian Miller, and Mark Cunnane. 1992, Integrated performance assessment model for waste package release and radionuclide release. In: *Proceedings of the Third International Conference on High Level Radioactive Waste Management*, Las Vegas, Nevada, April 12-16, 1992. 2, pp. 1786-1791.
3. Apted, M. J., W. J. O'Connell, K. H. Lee, A. T. Macintyre, T.-S Ueng, W. W. -L. Lee and T. H. Pigford. Preliminary Calculation of Release Rates of Tc⁹⁹, I¹²⁹, and Np²³⁷ from spent fuel in a potential repository in tuff, Earth Sciences Division, Lawrence Berkeley Laboratory, University of California, LBL-31069, UC-814. (1990)
4. Janeczek, J., and R. C. Ewing. Dissolution and alteration of uraninite under reducing conditions. *J. Nuc. Mat.*, 190, p. 157 (1992).
5. Snelling, A.A.. Uraninite and its alteration products, Koongarra uranium deposit. In: *Proceedings of International Uranium Symposium on the Pine Creek Geosyncline*. p. 487 (1980).
6. Isobe, H., T. Murakami, and R.C. Ewing. Alteration of uranium minerals in the Koongarra deposit, Australia: Unweathered zone. *J. Nuc. Mat.*, 190, p. 174 (1992).
7. Cramer, Jan, and John Smelle, *Final report of the AECL-SKB Cigar Lake analog study* AECL-10851, (1994).
8. Cramer, J.J., and H.W. Nesbitt, Hydrologic, isotopic, & major element constraints on genesis and evolution of waters from the Cigar Lake Area. In: Appendix A, AECL/SKB/USDOE Cigar Lake Project, Progress Report for the Period November 1991- March 1992. CLR-92-2, (1992).
9. Norris, Richard James. Preliminary hydraulic characterization of a fractured schist aquifer at the Koongarra uranium deposit, Northern Territory, Australia. In: *Alligator Rivers Analogue Project Progress Report, 1 March 1989-31 May 1989*. Ed. by P. Duerden, Australian Nuclear Science and Technology Organization (1990).
10. Sverjensky, Dimitri A.. Geochemical modelling of the Koongarra uranium deposit. In: *3rd Annual report of the Alligator Rivers Analogue Project, 1990-1991*. Ed. by P. Duerden. p. 25 (1992).
11. Wronekiewicz, David J., John K. Bates, Thomas J. Gerding, Ewald Veleckis, and Benjamin S. Tanl. Uranium release and secondary phase formation during unsaturated testing of UO₂ at 90°C. *J. Nuc. Mat.*, 190, p. 107 (1992).
12. Rokop, Donald J., Norman C. Schroeder, and Kurt Wolfsberg. Mass spectrometry of technetium at the subpicogram level. *Anal. Chem.* 62, p. 1271 (1990).

13. Attrep, Moses, Jr., F.R. Roensch, R. Aguilar, and J. Fabryka-Martin. Separation and purification of plutonium in uranium ores for mass spectrometric measurement. *Radiochim. Acta*, 57, p. 15 (1992).
14. Curtis, David, June Fabryka-Martin, Ruben Aguilar, Moses Attrep, Jr, and Fred Roensch. Plutonium in uranium deposits: Natural analogues of geologic repositories for plutonium-bearing nuclear wastes. In: *Proceedings of the Third International Conference on High Level Radioactive Waste Management*, Las Vegas, Nevada, April 12-16, 1992. 1, p. 338 (1992).
15. Fabryka-Martin, J.T., and David Curtis. Geochemistry of ^{239}Pu , ^{129}I , ^{99}Tc , and ^{36}Cl . In: *Final Report Alligator Rivers Analogue Project*, 15, Ed. by Australian Nuclear Science and Technology Organization. (1992).
16. MCNP—A general monte carlo code for neutron and photon transport, Version 3A. Ed. by J. PBriesmeister, Los Alamos National Laboratory Report LA-7396-M, Rev. 2 (manual). 583p. (1986).
17. Curtis, David B., June Fabryka-Martin, and Paul Dixon, Natural constraints on radionuclide release rates. In: *Proceedings of the 6th Natural Analogue Working Group*, Ed. by H. von Maravic, Commission of the European Communities (1993).
18. Meijer, A.. A strategy for the derivation and use of sorption coefficients in performance assessment calculations for the Yucca Mountain site. In: *Proceedings of Workshop on Radionuclide Adsorption*, Los Alamos, NM, September 11-12, 1990, LA-UR-91-3747. Los Alamos National Laboratory, Los Alamos, NM (1991)
19. Cramer, Jan, and John Smelle. *Annual Report of the AECL/SKB Cigar Lake Project Phase I: 1989-1990*. CLR-90-02 (1990).
20. Cramer, Jan, and John Smelle. *Second Annual Report of the AECL/SKB Cigar Lake Project, Year 2 1990-1991*. (1991).
21. Strickert, R., A.M. Friedman, and S. Fried, The sorption of technetium and iodine radloisotopes by various minerals. *Nuc. Tech.*, 49, p. 253 (1980).
22. Personal Communication - Notes copied from Noranda Mining Co. core log book with A.A. Snelling, 1984.