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Plutonium and Technetium

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Nature's Uncommon Elements: Plutonium and Technetium

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Abstract

Natural ^{99}Tc and ^{239}Pu were measured in ores from the Cigar Lake uranium deposit, in which U concentrations ranged from 0.3 to 55 wt %. Atomic ratios ranged from 1.4×10^{-12} to 51×10^{-12} for $^{99}\text{Tc}/\text{U}$ and 2.4×10^{-12} to 44×10^{-12} for $^{239}\text{Pu}/\text{U}$. Measured concentrations are compared to those expected if the ores had behaved as closed systems with respect to U and its products. Under conditions of secular equilibrium in closed systems, ^{99}Tc and ^{239}Pu concentrations are solely a function of the neutron flux, U content, and decay rates. The neutron production rate and physical and chemical parameters that control the *in-situ* neutron flux were measured in several samples. Neutron transport modeling of the sample environs using the MCNP code indicated that about half of the samples showed apparent excesses of ^{99}Tc and ^{239}Pu beyond the amounts predicted for secular equilibrium. The excess quantities strongly suggest the redistribution of these element within the deposit. The failure to observe complementary deficiencies within the deposit suggests that the redistribution processes enriched the elements, removing small proportions of the elements from large uraniferous masses of rock, and concentrating them in smaller, less uraniferous, masses. The consistency of $^{239}\text{Pu}/\text{U}$ and $^{99}\text{Tc}/\text{U}$ ratios in bulk rock suggests that the redistribution processes observed at Cigar Lake are localized and in no case result in large-scale losses or gains of these nuclear products from the deposit as a whole.

Introduction

On earth, most natural elements are primordial, formed by stellar processes and agglomerated into terrestrial matter. In a few instances, primordial elements are composed entirely of radioactive isotopes. If all the constituent isotopes for a particular element have radioactive lifetimes that are short relative to the time that has passed since stellar synthesis, then none of the primordial component of that particular element will still be present in the earth. Such exclusively radioactive elements proved elusive to the early chemists who sought to isolate and characterize them. As the nuclear sciences developed, many of these elements were artificially produced before they were found in nature. Predictions based on limited understanding of their nuclear properties suggested that they would exist in the earth only as products of localized nuclear reactions. An overview of the origin of elements may be found in Kuroda (1982).

Element 94, plutonium, is one example of an element whose primordial component decayed away comparatively soon after its initial formation. It was discovered in nature soon after the man-made element was separated and characterized. Seaborg and Perlman described their findings in a secret report to the "Uranium Committee" in April 1943 although the results were not publicly available for another five years (Seaborg and Perlman, 1948). In 1951 Peppard *et al.* isolated plutonium from uranium ore process wastes and showed it to be monoisotopic ^{239}Pu . On the basis of this observation, they speculated about the formation of natural plutonium by ^{238}U neutron capture, and about the production of neutrons in the earth. A more comprehensive effort by Levine and Seaborg (1951) in the same year measured $^{239}\text{Pu}/\text{U}$ ratios in several uranium ores derived from a variety of geochemical environments. Data from these samples provided the basis for more detailed discussions of the origin of this rare actinide. Significant differences in plutonium production rates that were inferred from the $^{239}\text{Pu}/\text{U}$ ratios were attributed to the effects of the different elemental compositions of the ores on the *in-situ* neutron fluences.

The search for element 43, technetium, can be traced back to the early 19th century although early reports of its existence proved erroneous (Kenna, 1962). In 1925, Noddack et al. identified an unknown radioactive isotope at mass 43 in several uranium ores, based on X-ray spectra; but the evidence was discounted by the scientific community at the time as being unconvincing because the results could not be reproduced (van Assche, 1988; Kenna, 1962). It was not until 1937 that element 43 was identified as the product of a nuclear reaction when molybdenum irradiated with deuterons for several months in the Berkeley cyclotron produced a strong but unknown radioactivity. The element was separated and characterized by Perrier and Segre (1937) who proposed the name "technetium," derived from the Greek word for "artificial". More than two decades passed before the presence of natural technetium in terrestrial matter was reported. In 1961 and again in 1963, Kenna and Kuroda reported the measurement of ^{99}Tc extracted from more than a kilogram of pitchblende. Based upon the $^{99}\text{Tc}/\text{U}$ ratio in the ore, they concluded that technetium was predominantly a product of ^{238}U spontaneous fission. The possibility that small proportions could also have been produced by neutron-induced fission of ^{235}U was discussed.

Because of their unique modes of production by nuclear reactions involving uranium, natural technetium and plutonium have distinctive geochemical properties. Both are monoisotopic radioactive elements with well-defined natural lifetimes. The mean life of ^{99}Tc is 3.1×10^5 years, and of ^{239}Pu is 3.5×10^4 years. In natural systems that have been undisturbed for comparable periods of time, the distributions of plutonium and technetium in the rock or ore should parallel those of the parent uranium.

Maximum concentrations of natural plutonium and technetium are a function of their production rates. Even in the natural environment that is most conducive to high production rates, concentrations are extraordinarily low, on the order of 10^{-12} grams per gram of uranium. If these elements are released from their host phase, their

extraordinarily low concentrations will be a dominant factor in determining their subsequent geochemical behavior.

Previous studies of these two elements generally characterized the nuclear production processes responsible for their existence in the geologic environment (Seaborg and Perlman, 1948, Levine and Seaborg, 1951, Peppard *et al*, 1951, Kenna and Kuroda, 1964). These works typically involved heroic efforts to measure very small concentrations in very large sample masses. We have taken advantage of the extremely sensitive method of thermal ionization mass spectrometry to measure technetium and plutonium concentrations in sample masses that are smaller by as much as three orders of magnitude than those used in the early research efforts. The work reported in this paper extends our understanding of the geochemistry of plutonium and technetium by developing detailed descriptions of their associations in well-characterized geologic samples, and by using modern neutron-transport modeling tools to better interpret the meaning of the results.

Geologic Settings

Analyses were conducted on samples from three uranium ore deposits selected for their contrasting geochemical environments. The Cigar Lake deposit is an unweathered, unaltered primary ore in a reducing environment which is expected to closely approximate a system that is closed with respect to uranium and its products. The Koongarra deposit is a shallow system, both altered and weathered, subject to active ground water flow. Finally, a sample from the Beaverlodge deposit is included because it is a commercially-available uranium ore standard that allows demonstration of the precision of the analytical results. All samples are in secular equilibrium with respect to ^{230}Th , ^{234}U , and ^{238}U , indicating that the uranium minerals in these samples have not undergone incongruent dissolution. The following section provides descriptions of the geologic settings and samples analyzed from each of these deposits.

Cigar Lake

The Cigar Lake uranium deposit is located in northern Saskatchewan, central Canada, and has been studied by Atomic Energy of Canada Ltd. (AECL) as a natural analogue since 1982 (Cramer et al., 1986). It is of hydrothermal origin (Fouques et al., 1986; Bruneton, 1987, 1993) and was formed about 1.3 Ga ago (Cumming and Krstic, 1992). Uraniferous mineralization is comprised primarily of uraninite and pitchblende with subordinate coffinite at an average grade of 15 to 20% U. The deposit is localized 430 m below the current surface in an altered sandstone at, and immediately above, the unconformable contact with underlying metamorphic Precambrian basement. The highly-permeable sandstone that overlies the deposit is the main regional aquifer.

Uranium mineralization forms an irregular lens 2 km long, 20 to 100 m wide and 1 to 20 m thick. Cigar Lake mineralization is in a clay-rich matrix dominated by illite and chlorite (Percival et al., 1993) with minor carbonates (siderite and calcite) and accessory phases (e.g. zircon, rutile, and phosphates). Present fluids in the ore zone are chemically reducing, so little dissolution of uraninite has occurred. The clay-rich matrix and surrounding halo are covered by a quartz-cemented cap, all of which have relatively low permeabilities compared with the overlying sandstone and effectively seal the ore zone from bulk groundwater flow through the deposit (Cornett et al., 1996).

In addition to uranium-bearing minerals, the ore contains elevated concentrations of sulphides, arsenides and sulph-arsenides incorporating a broad suite of elements (e.g. nickel, cobalt, molybdenum, radiogenic lead, zinc, manganese and iron). Three stages of mineralization can be identified (Bruneton, 1987), of which the first two are considered to be of a hydrothermal nature. The last stage of mineralization is characterized by a low-temperature assemblage, and is much younger, estimated to have occurred between 320 and 293 Ma ago (Cumming and Krstic, 1992; Philippe et al., 1993).

Results reported in this study were obtained from core samples taken from depths indicated in Table 1. Cigar Lake samples from borehole 220 represent a 6-meter profile of

uranium ore from the middle of the western portion of the main high-grade orebody. The 48-mm diameter drillcore was subdivided into 31 sample intervals based on lithologic criteria (i.e., mineralogy, heterogeneity, color) and on total β,γ activity (measured on contact at 5-cm intervals). Each sample was cut lengthwise in half, and one half was cut again lengthwise: half of each core sample was preserved for future reference, one quarter was used for instrumental analyses (e.g., XRD, SEM, XPS, microprobe) and one quarter was powdered and homogenized for chemical analyses including those reported here. The mineralization in this borehole is typical of the Cigar Lake deposit, averaging 12 wt % uranium. The matrix is dominated by clay minerals. Sulfides appear to correlate with uranium minerals. Details of the lithology and geochemistry of this core are described in Cramer and Smellie (1994) and Cramer et al. (1997). Samples 235L, W83A, and W83C are similarly typical of high-grade uraniferous samples taken from other regions of the deposit.

Samples 228 and 230 were taken from bleached sandstone host rock above the uranium deposit. They are grey clay-rich sandstone without uranium mineralization. Samples 405 and 406 are also "barren" clay-rich sandstone, representative of the rock that hosts the deposit. They were taken from a location that is up-gradient of the deposit in the current hydrogeological regime, at a distance believed to be about 200 m laterally from the uranium deposits.

Koongarra

The Koongarra uranium deposit in the Northern Australian Territory has been studied by the Australian Nuclear Science and Technology Organization since 1981. Detailed descriptions of the deposit may be found in the various volumes of the Final Report of the Alligator Rivers Analogue Project (Duerden, 1992). The Koongarra deposit offers a vivid contrast to the one at Cigar Lake. Located in a weathered quartz-muscovite schist at depths less than 100 m from the present surface, many of the geochemical and mineralogic properties of the deposit are the result of recent weathering. The highest uranium concentrations occur in weathered primary ore. Large fractions of the uranium

reside in secondary phosphate minerals. Down the hydrologic gradient, uraniferous rock is the product of mobilization and dispersion of uranium from the weathered primary zone. In the dispersion fan, uranium is largely associated with secondary oxides of iron and manganese.

Groundwater movement in the Koongarra deposit is complex and difficult to generalize because significant flow occurs preferentially in the fractures of the host rock rather than its pores, and because the shallow water table aquifer is subject to large seasonal shifts in the direction and magnitude of the local hydrologic gradient. Water chemistry in the weathered zone is undersaturated with respect to uraninite and other uranium minerals in the deposit, consistent with the idea that present groundwaters may still be dissolving and dispersing the uranium. Where water intersects the primary deposit, its dissolved uranium content increases dramatically. Down gradient, uranium concentrations in the water decrease due to dilution and mixing by local recharge with seasonal rainwater, and by adsorption of uranium onto the minerals of the substrate through which the waters flow.

The two samples from Koongarra (Table 1) were taken from coarse fragments of drillpulp created by the exploration company from sections of rock core. They represent poorly-characterized macroscale samples of the regions from which they were taken. Sample G2698 is from a meter of core from the transition zone between weathered and unweathered schist. In the shallow portion of this sample, blue-black pitchblende is associated with strong hematitic alteration, and yellow secondary uranium minerals enclose relict pitchblende almost wholly replacing schist. Deeper portions of the core contain sklodowskite and kasolite, uranium minerals characteristic of the unweathered zone. Sample G4674 is pulp of a meter of core from deep in the unweathered zone. In this sample, primary pitchblende is hosted in crushed and slightly brecciated quartz chlorite schist (Noranda Mining Co., pers. commun., 1984).

Beaverlodge

Sample BL-5 from the Beaverlodge deposit is a commercially available uranium ore standard from the Canada Centre for Mineral and Energy Technology (CANMET). The standard was prepared by CANMET as a large batch of finely ground, homogenized material in order to provide laboratories with a suitable standard for analytical results (Ingles et al., 1977). BL-5 has a certified uranium content of $7.09 \pm 0.03\%$ (CANMET, no date). Replicate analyses of BL-5 show it to be homogenous with respect to plutonium and technetium concentrations (Dixon et al., 1997). The geologic setting from which the sample was taken is not known.

Experimental Results

Radionuclide Analyses

Detailed descriptions of the analytical methods and a discussion of their capabilities and limitations are found in Dixon *et al.* (1997). Results from quality-control samples define a detection limit of 11×10^{-15} g (11 fg) for ^{99}Tc , and 0.44×10^{-12} g (0.44 pg) for ^{239}Pu . To define the procedural precision, Canadian Reference Material BL-5 was analyzed routinely with samples. Eight replicate analyses of BL-5 measured 58.8 ± 1.2 fg $^{99}\text{Tc/g}$, giving a $^{99}\text{Tc/U}$ atom ratio of $2.00 (\pm 0.04) \times 10^{-12}$. Seven replicate analyses of BL-5 for ^{239}Pu measured 1.02 ± 0.01 pg/g of this nuclear product, for a $^{239}\text{Pu/U}$ atom ratio of $14.3 (\pm 0.2) \times 10^{-12}$.

Measured concentrations of ^{99}Tc and ^{239}Pu in the Cigar Lake and Koongarra samples are presented in Tables 2 and 3. Results have been corrected for measured blanks, and the stated uncertainties reflect these corrections. The tables report both the sample number as well as an aliquot number, which is a unique physical portion of the sample. Tc and Pu results with identical aliquot numbers refer to measurements on the same physical sample. For instance, technetium and plutonium were measured on the same portion of 615 (aliquot 86), and plutonium was measured in four different portions of 620B (aliquots 48, 56, 107 and 201).

Neutron Production Rates

To determine the effects of natural physiochemical processes on the fate of technetium and plutonium, it is necessary to understand the local effects of nuclear processes. Such understanding provides the means to characterize the degree to which measured concentrations manifest retention of the elements at the site of production and to what degree they represent deficiencies or excesses resulting from processes of release, transport and retention. To make such a distinction requires comparison of measured daughter/parent ratios with those that result from the equivalency of rates of nuclear

production and destruction (nuclear equilibrium). At nuclear equilibrium, the magnitude of this ratio is proportional to the nuclide production rates.

Plutonium-239 is produced exclusively by ^{238}U neutron-capture. Nearly all technetium-99 in nature is produced as a fission product of the spontaneous fission of ^{238}U . In some environments, such as uranium ore bodies, small but significant proportions of ^{99}Tc are also produced by neutron-induced fission of ^{235}U and possibly, to a much lesser extent, of ^{238}U . Neutron-capture by ^{98}Mo is an additional reaction that may be significant in some environments. Consequently, production rates of both plutonium and technetium depend upon the neutron flux and its associated energy spectrum to which the sample has been subjected.

A key parameter controlling the magnitude of the neutron flux in the subsurface is the primary neutron production rate. Neutrons are produced passively in geologic media by spontaneous fission of ^{238}U , a process that proceeds at a rate dependent only on the concentration of uranium. It can thus be readily calculated if the uranium concentration is known. A significant proportion of neutrons also arise by emission from light elements when these elements capture α -particles emitted by natural radionuclides in the uranium and thorium α -decay series. Although energy-dependent cross-sections for such reactions are well known and α -emission rates are easily calculated knowing the half-lives and concentrations of α -emitting nuclides, the rate of neutron emission from this process in rock is not a straightforward calculation (Ensslin, 1991). The effective range of an α -particle is only a few microns, and thus the rate of production by (α, n) reactions is dependent upon the micro-distribution of α -emitting radionuclides relative to elements with significant (α, n) cross sections. These properties are not easily characterized. Fortunately, in samples with high uranium concentrations such as the ones used in this work, total neutron production rates can be measured directly by a passive, non-destructive technique (Stewart, 1991; Fabryka-Martin and Cramer, in prep.). The measured neutrons are called "primary" neutrons to distinguish them from secondary

neutrons that are emitted during induced fission of uranium isotopes in the deposit. The measured rates are presented in Table 1.

Production-rate modeling

Primary neutrons interact with nuclei in the media that capture the neutrons or attenuate their energy. The details of these complex interactions define the spatial distribution of the *in-situ* neutron flux and energy spectrum and thus the rate of production of neutron-induced isotopes. Neutron histories are difficult to predict because of the large number of different interactions that are possible in natural materials. It is even more problematic when the elemental composition changes frequently along the path of a neutron.

One technique used to calculate the fate and consequences of interactions of neutrons with complex matter is the Monte Carlo method, which uses statistical techniques to predict the proportion of a large number of neutrons that will behave in some manner of interest. The Monte Carlo method allows detailed three-dimensional models to be constructed mathematically to simulate a physical situation (Rinard, 1991). We used the Monte Carlo Neutron and Photon (MCNP) transport code (Briesmeister, 1986) to simulate technetium and plutonium production rates in an 8-m long section of hole 220 from Cigar Lake, as well as in other samples from Cigar Lake, Koongarra and Beaverlodge. The user specifies the geometry of the problem, the elemental composition and density of the media, neutron transport and cross-section data libraries to be used, characteristics of the neutron sources, and the type of answers desired (e.g. nuclear reaction rates). In a very heterogeneous media such as an ore body, creating such a model is problematic. The mean free path of a neutron is a function of the composition of the media. In geologic media the mean free path is variable, being typically on the order of 0.5 meter for most rocks but less than 10 cm in uranium ore (this study; a similar conclusion was reached by neutron modeling of the Oklo deposit as reported in Oversby, 1996, p. 14). Consequently, the flux to which a gram-size ore sample is exposed is determined by the quantity and distribution of elements in perhaps 100 dm³ of rock surrounding the

sample. Such distributions can only be approximated, and the results of the models are only as accurate as the approximations. Agreement between measured and calculated production rates is most likely when the data are representative of larger volumes of the geologic environment. Detailed discussions of this approach to modeling nuclear reaction product concentrations are found in Fabryka-Martin and Curtis (1992) and Fabryka-Martin *et al.* (1994).

For the modeling effort, we measured the elemental compositions and neutron production rates of Cigar Lake samples CS235L, W83A, W83C, and 9 of the 31 distinct stratigraphic intervals identified in the hole 220 core, and in samples from Koongarra and Beaverlodge. These parameters were estimated for the remaining sample intervals from hole 220. Each stratigraphic interval in the hole 220 profile was modeled as being of infinite extent in the horizontal direction with a finite vertical dimension defined by the thickness of the interval. The modeled reactions included induced fission of uranium isotopes, ^{99}Tc production from neutron capture by ^{98}Mo , ^{239}Pu production from neutron-capture by ^{238}U , and ^{36}Cl production from neutron capture by ^{35}Cl . The latter nuclide was included as a measure of the validity of the modeling results and as an *in-situ* monitor of ^{235}U fission rates (Cornett et al., in prep.). These calculations also provided the basis for estimated production rates in Cigar Lake samples CS235L, W83A, and W83C. Calculated results for the Koongarra samples were similarly derived from a model simulation of a layered heterogeneous media in that ore body. Beaverlodge sample BL-5 was modeled assuming that it came from an infinitely homogenous media with the same composition as that measured for the sample. This simplification is likely to be a good approximation for the Beaverlodge sample. However, this approach will overpredict reaction rates for small uraniferous samples embedded in rock matrices with much lower uranium contents.

To bound production rates for the Hole 220 samples, concentrations of key elements with a dominant influence on the neutron flux and energy distribution were varied over reasonable ranges in the modeling scenarios. These included elements with

large neutron-scattering cross-sections relative to their capture cross-sections (H, Fe) and elements with large capture cross-sections (B, Sm, Gd, As). A lower limit for H was established by assuming 1% porosity throughout the profile, in combination with 1400 ppm H present as structural water in the mineral phases. An upper limit for H was established by assuming 15% porosity in rubbly intervals and 5% porosity elsewhere, 1400 ppm H as structural water in uranium minerals and 13,000 ppm H as structural water in silicate minerals. Lower and upper limits for Fe, As, B, Sm and Gd were established by assuming 70% and 130% of their nominal values for each interval. For the remaining Cigar Lake ore samples (CS235L, W83A and W83C), because no information was available about the geochemical environs of these samples, the range of ^{99}Tc and ^{239}Pu production rates was determined from the minimum and maximum values calculated by the MCNP code for any Hole 220 interval containing at least 15% U. For the Koongarra samples, the minimum and maximum production rates were estimated as described in Fabryka-Martin and Curtis (1992), in which the 1-m lengths of drillcore represented by G2698 and G4674 were subdivided into 10-cm segments in the model. Upper and lower limits for production rates were then established by varying the H, Sm, and Gd concentrations used in the model.

Altogether, 14 modeling cases were run for the Hole 220 samples, with upper and lower bounds on production rates shown in Figure 1. The best match between model predictions and measured values for $^{36}\text{Cl}/\text{Cl}$ ratios for these samples was for cases in which the neutron flux was poorly thermalized, with 5% porosity in the rubbly intervals and 2% porosity elsewhere (Cornett et al., in prep.). Because the modeling exercise confirmed that the $^{36}\text{Cl}/\text{Cl}$ ratio is a near-ideal monitor of the ^{235}U fission rate, this same case is assumed to provide the best prediction of ^{99}Tc production rates from fission of uranium isotopes. For this particular modeling case, the predicted $^{99}\text{Tc}/\text{U}$ ratios from uranium fission range from 1.6×10^{-12} to 3.0×10^{-12} in the 31 modeled intervals, indicating as much as half of the ^{99}Tc in some samples may derive from induced fission. Nine of the hole 220 samples have $^{99}\text{Tc}/\text{U}$ ratios above the upper bound of this range (Figure 1, Table

3). Consideration of ^{99}Tc production from neutron capture by ^{98}Mo increases the upper bound for the $^{99}\text{Tc}/\text{U}$ ratio to 7×10^{-12} for this modeling case, using measured Mo concentrations in the model when available (300 to 15,400 ppm) and otherwise assuming 500 ppm Mo. Hence, this mechanism may be significant relative to fission production where low-U intervals containing percent levels of Mo abut high-U intervals. Nonetheless, this mechanism does not appear to be able to account for all of the high $^{99}\text{Tc}/\text{U}$ results, insofar as it is overwhelmed by the fission component if U concentrations exceed 15% and Mo concentrations are less than 1%.

Predicted $^{239}\text{Pu}/\text{U}$ ratios for the Hole 220 profile range over two orders of magnitude, from 0.2×10^{-12} to 25×10^{-12} (Figure 1, Table 2). The maximum values are predicted for narrow (3-10 cm thick) intervals of low-grade ore where these are immediately adjacent to massive intervals of high-grade ore. Such enhancement of ^{239}Pu production at these locations may result from a shift in the neutron energy spectra to slightly lower energies, where reaction cross-sections are higher, or from an increased neutron flux due to reflection of neutrons by the higher-H content of the low-U interval.

Discussion

The origin of natural plutonium and technetium

In the discussion that follows, a condition of nuclear equilibrium between a radioactive parent and daughter is assumed to exist in a sample if the following conditions are met:

The measured daughter/parent ratio is within the range of calculated values (i.e., the measured ratio, or the average ratio for multiple analyses, is within two standard deviations of the calculated range).

Results of replicate analyses are in close agreement with one another, indicating homogeneity of the sample on the scale of the aliquot size (i.e., all replicate analyses are within two standard deviations of the average ratio).

Samples meeting these conditions for ^{239}Pu and ^{99}Tc are marked as such in Table 2 and 3. Plutonium production rates extend over an order of magnitude, as reflected in the range of $^{239}\text{Pu}/\text{U}$ ratios in equilibrated samples. This variability is attributed to the sensitivity of plutonium production processes to shifts in neutronics produced by small-scale compositional changes in the ore body. The lowest plutonium production rate was 0.3 atoms/min/g U in sample 610, and the highest rate was greater by nearly an order of magnitude, 2.9 atoms/min/g U in sample 614. These two samples contain similar uranium concentrations (4%) and were separated by less than a meter in the ore body (Table 1). In this case, differences in ^{239}Pu production rates in these two samples are clearly unrelated to the concentration of uranium *in the samples themselves*. However, sample 614 lies adjacent to a sample containing 51% U, while sample 610 is bounded by samples with similar or lower U contents than its own. Hence, the U contents of adjacent intervals can exert a controlling influence on the production rate of neutron-induced reactions. A similar enhancement of production rates is observed in sample 602, which also has a high $^{239}\text{Pu}/\text{U}$ ratio and which lies adjacent to rock containing 50 times more uranium.

These observations suggest that plutonium production processes are accelerated by "edge effects", perhaps from neutron moderation at the interface between low-uranium and high-uranium intervals. The existence of such effects emphasizes the uncertainty associated with modeling neutron-induced processes on this scale in a highly heterogeneous environment. The inability to accurately describe localized compositional variations increases the uncertainty of model predictions.

Uranium-normalized technetium abundances in samples at nuclear equilibrium are less variable than those of plutonium. Eight of the nine such samples in Table 3 define a tight population of ^{99}Tc production rates with an average of 0.033 atoms/min/g and a relative standard deviation of only 15%. This consistency is due to the predominance of spontaneous fission in the production of this element and the fact that fission yields for mass 99 are essentially identical for spontaneous and neutron-induced fission of uranium;

hence the spontaneous fission component is sufficiently large to buffer the total inventory of this element. Spontaneous fission of one gram of uranium produces 0.025 atoms ^{99}Tc per min or about a picomole in 10^8 years. At nuclear equilibrium, the $^{99}\text{Tc}/\text{U}$ ratio produced by spontaneous fission is 1.57×10^{-12} . Ignoring the possibility of technetium production by molybdenum neutron capture, excesses over this value are the result of neutron-induced fission of ^{235}U . On the average, 25% of the ^{99}Tc in these eight samples was produced by this process.

Sample 614 meets the criteria for equilibrium but also contains $^{99}\text{Tc}/\text{U}$ that is far higher than those for the other eight equilibrated samples. The technetium production rate in this sample was more than twice that of the second highest measured rate, and three times higher than the average rate for the other eight equilibrated samples. About 70% of the ^{99}Tc in sample 614 was produced by neutron-induced fission of ^{235}U . This same sample had the highest plutonium production rate, and hence the technetium result supports the hypothesis presented earlier that neutron-induced reactions may be enhanced when samples lie adjacent to ones with much higher levels of uranium.

Uncertainties in model predictions that arise from our inability to define local element distributions with sufficient accuracy may be minimized by analyzing larger samples. If chemical and isotopic analyses are done on volumes of rock that are on the same scale as the length of several neutron mean free paths (decimeters), then the dependence on localized compositional variations is reduced. Simpler geometric models can be used to describe the neutron-induced rates, and the requisite compositional parameters can be measured directly in the sample. Such an approach obscures spatial details of the nuclear processes, but reduces uncertainties associated with understanding measured concentrations of the nuclear products. We have simulated the properties in a large volume of Cigar Lake ore by calculating composite values of the results from the full set of sample results for this ore body. For instance, the bulk value for the abundance of plutonium relative to uranium in the ore body is the sum of plutonium concentrations (Pu/g), in each interval i , times the mass sample from each interval (g) shown in Table 1,

relative to the sum of uranium concentrations $(U/g)_i$ in each of intervals, times the mass of the interval: $[(Pu/U)_{Bulk} = \sum_i ((Pu/g)_i \times g)_i / \sum_i ((U/g)_i \times g)_i]$. The result is the same as though the samples had been combined, powdered and homogenized, and aliquots of this mix then analyzed for the constituents. These composite values are labeled as "Bulk ore" in Tables 2, 3 and 4.

Table 4 presents bulk abundances of nuclear products in Cigar Lake ore along with those reported for large samples from other deposits (Levine and Seaborg, 1951, Dixon et al., 1997). Although not specifically stated, we assume that the samples analyzed by Levine and Seaborg represent samples of ore batches from uranium processing plants (the common approach for this type of work at that time), and are thus representative of large ore masses. In Table 4, these ores are designated by the names of their primary uranium-bearing minerals as a means of characterizing and distinguishing the deposits. The range of $^{239}Pu/U$ ratios varies by only a factor of two in six of the nine deposits. The extreme values of $^{99}Tc/U$ in four large samples from three deposits only differ by 25%. These seem like remarkably small differences for samples from such diverse geologic settings, especially when compared to the range of variations observed over a distance of less than 6 meters in the Cigar Lake core. The consistency shows that chemical and physical differences between these deposits had relatively small effects on the rate of neutron-induced production for the bulk ore.

The smaller values of $^{239}Pu/U$ in the North Carolina monazite and the fergusonite and carnotite from Colorado demonstrate the effects of certain elements on the neutron induced production rates. These ores were chosen by Levine and Seaborg to verify that natural plutonium was produced by neutron-capture processes by demonstrating that samples with high abundances of neutron-absorbing elements have reduced $^{239}Pu/U$ ratios. Lower relative concentrations of plutonium were anticipated because of the reduction in the plutonium production rate resulting from the attenuated neutron flux. The unexpected result from Levine and Seaborg was the similarity between the $^{239}Pu/U$ ratios in Brazilian

monazite and pitchblende ores. Monazite is a rare-earth phosphate mineral and thus should significantly suppress the neutron flux. Levine and Seaborg speculated that the unexpectedly high plutonium production rate might be the result of enhanced production of primary neutrons in the unusual chemical melange found in monazite ores. A more comprehensive study of the relationships between the abundances of critical elements and radionuclide production rates in samples of large masses of uranium ore would better characterize the chemical parameters influencing such processes.

Redistribution of plutonium and technetium

Seven of the twenty samples from the Cigar Lake deposit do not meet the criteria for nuclear equilibrium with respect to plutonium (Table 2). These samples contain plutonium in excess of the maximum abundances calculated by the model simulations. However, in all but one of these samples, the excesses are elevated above the maximum modeled value by less than a factor of two, and the measured $^{239}\text{Pu}/\text{U}$ ratios are still less than the maximum values measured in samples that do meet the criteria for nuclear equilibrium. Given the sensitivity of the plutonium production rates to local compositional variables, as well as the difficulty of describing these variables in the model, the failure of these six samples to fall within the calculated values may not necessarily be indicative of nuclear disequilibrium at these locations.

However, the interpretation of nuclear disequilibrium with regard to ^{239}Pu in sample 611 seems to be unambiguous. One aliquot of this sample (611) contains twice and the other five times as much ^{239}Pu as the maximum calculated for its uranium concentration (Table 2). The $^{239}\text{Pu}/\text{U}$ ratio in the latter aliquot is at least twice as high as that of any other measured sample from the ore body. In this case, the evidence for nuclear disequilibrium seems quite convincing. This sample contains the lowest uranium concentration of all of the analyzed ore samples (0.33% Table 1). Thus, the plutonium enrichment in this particular sample may be particularly apparent because of the small quantities of indigenous plutonium produced by the small quantities of parent uranium: The plutonium background is ten to a hundred times less than in the other samples. For

instance, if the concentration of plutonium that produced the high and variable $^{239}\text{Pu}/\text{U}$ ratios in sample 611 were added to sample 612 (3.4% U), it would double the $^{239}\text{Pu}/\text{U}$ ratio in that sample but would still not shift it outside of the range used to define equilibrium conditions. The same concentration added to sample 620B (44% U) would not even distinguish itself from the suite of replicate analyses.

The excess ^{239}Pu in sample 611 supports the hypothesis that relatively small proportions of plutonium produced within the deposit are being released and redeposited within the deposit. The mass of the mobile component is such a small proportion of the total mass of plutonium in the deposit that its presence or absence is often not readily distinguishable in uraniferous samples from within the deposit. In contrast, the mobility of small quantities of plutonium is unambiguously apparent in samples outside the deposit. Plutonium is below detection in the samples collected up-gradient of the deposit (405 and 406). However, excess plutonium was readily detectable in samples 228 and 230, host rock taken above the deposit. As in sample 611, concentrations of indigenous plutonium in host rocks are small relative to those in the deposit, such that small quantities of excess plutonium are readily distinguishable as anomalously high $^{239}\text{Pu}/\text{U}$ ratios.

If our criteria for nuclear equilibrium accurately distinguishes samples in a state of nuclear equilibrium from those that are not, then significant proportions of plutonium are being redistributed in and around the ore body. For example, assuming the maximum calculated $^{239}\text{Pu}/\text{U}$ ratio for sample 615 (7.2×10^{-12}) represents the quantity of indigenous plutonium in this particular interval, then 38% of the plutonium measured in that sample is excess, representing a concentration of 2.2 pg $^{239}\text{Pu}/\text{g}$ rock. This quantity is comparable to the bulk ore concentration of this element (2.0 pg/g, Table 2). One of the aliquots of host rock sample 228 also unambiguously contains 1 pg/g of excess ^{239}Pu (Table 2).

Redistribution of technetium at Cigar Lake is even more readily apparent. Samples such as 602, 613, and 611 contain large excesses of technetium, much more than

the model predicts could have been generated *in-situ* without invoking significant input from neutron capture by molybdenum. Conditions that would support significant production from molybdenum do not appear to be present in the Cigar Lake samples. In addition, replicate analyses of other samples such as 609, 620B, and 625 produced significantly different results. Such large variability suggests a heterogeneous distribution of technetium that is incompatible with *in-situ* production. Finally, as was the case with plutonium, significant quantities of technetium are contained in the barren samples 228 and 230 that were collected outside the ore body.

There thus appears to be clear evidence that more plutonium and technetium is present in some Cigar Lake samples than could have been produced *in-situ* and that processes are releasing these elements from their primary hosts and are transporting them to other parts of the deposit where they are retained. If so, then we should expect that such processes would also lead to deficiencies in some of the Cigar Lake samples. The insensitivity of the criteria for identifying samples where plutonium is in a state of disequilibrium might preclude our ability to identify relatively small deficiencies of this element. However, spontaneous fission establishes an unambiguous lower limit of 1.57×10^{-12} for an equilibrium $^{99}\text{Tc}/\text{U}$ ratio. Only one value lower than this threshold was observed among the 43 sample analyses reported in Tables 3 and 4 (1.4×10^{-12} , sample 620B, Table 3). This supports the concept that the processes must only release extremely small fractions of plutonium and technetium from large masses of rock, and then enrich them by selective retention in smaller masses, similar to processes that are known to concentrate more common elements to form ore bodies. We believe that such enrichment processes operate locally. The consistency among $^{239}\text{Pu}/\text{U}$ and $^{99}\text{Tc}/\text{U}$ ratios measured in bulk rock from several deposits (Table 4) suggests that processes of redistribution of the nuclear products are not large in scale because they show no evidence of large-scale enrichment or depletion of these elements in any of the geologic settings. The only deviations from the consistency of these results can be explained by compositionally-induced suppression of nuclear production rates.

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Table 1. Characteristics of analyzed samples

Deposit	Borehole	Sample ID	Average depth below surface (m)	Sample mass (g)	Uranium content (%)	Measured neutron production rate (n/min/g U)
Cigar Lake	139	405	375.8	NA	0.00027 ± 0.00005	Not measured
		406	413.2	NA	0.00027 ± 0.00005	Not measured
Cigar Lake	99	228	300.65	101.65	0.046 ± 0.001	Not measured
		230	402.50*	102.56	0.018 ± 0.001	Not measured
Cigar Lake	220	602	432.78	50	1.05 ± 0.07	Not Measured
		603	432.98	44	55 ± 3	Not Measured
		604	433.1	101	47 ± 5	1.91 ± 0.06
		605	433.3	101	14.3 ± 0.7	2.17 ± 0.08
		606	433.50	50	1.83 ± 0.07	Not Measured
		607	433.65	35	31 ± 2	Not Measured
		609	433.8	101	6.7 ± 0.2	2.53 ± 0.09
		610	434.26	100	4.1 ± 0.2	2.57 ± 0.1
		611	434.54	34	0.33 ± 0.02	Not Measured
		612	434.73	50	3.4 ± 0.3	Not Measured
		613	434.98	50	10.4 ± 0.3	Not Measured
		614	435.10	17	3.8 ± 0.3	Not Measured
		615	435.28	101	51 ± 3	1.81 ± 0.05
		619	435.99	100	5.4 ± 0.2	2.22 ± 0.08
		Cigar Lake	145	W83C	445.2	109
W83A	445.2			100	39 ± 2	1.48 ± 0.05
Bulk ore (calculated)				1743	31	1.84
620B	436.36			101	44 ± 1	2.09 ± 0.07
Cigar Lake	113	CS235L	419.4	90	54 ± 3	1.75 ± 0.06
			625	437.58	101	2.6 ± 0.1
Cigar Lake	113	CS235L	438.05	101	23.8 ± 0.8	2.14 ± 0.05
			627	438.05	101	23.8 ± 0.8
Koongarra	DDH 58	G2698	31	19.1	19 ± 2	2.59 ± 0.07
Koongarra	DDH 87	G4674	70	12.4	12 ± 1	1.71 ± 0.05
Beaverlodge	Not known	BL-5	Not known	500	7.09 ± 0.03	1.76 ± 0.06

Data sources: Uranium analyses for Cigar Lake ore samples from Cramer et al. (in review). Measured neutron production rates from Fabryka-Martin and Cramer (in prep.).

*"Bulk ore" is the sum of the concentration of all samples of the Cigar Lake ore body each weighted by the mass of sample from the interval

Table 2. Plutonium abundances in Cigar Lake samples

Bore-hole	Sample ID	Aliquot ID	Aliquot mass g	Measured ^{239}Pu pg/g	Measured $^{239}\text{Pu}/\text{U} \times 10^{-12}$ (± 1 st dev)	Modeled $^{239}\text{Pu}/\text{U} \times 10^{-12}$	
						Min	Max
139	405	154	9.78	ND	ND	Not calc.	Not calc.
	406	155	10.69	0.002 ± 0.002	900 ± 900		
99	228	102	9.59	1.07 ± 0.02	2340 ± 50	0.03	Not calc.
		198	10.20	ND	ND		
	230	46	8.92	0.079 ± 0.018	450 ± 120	0.07	Not calc.
		54	10.01	0.017 ± 0.008	100 ± 90		
		83	10.05	0.022 ± 0.018	100 ± 200		
		138	10.27	0.017 ± 0.008	95 ± 90		
220	602	166	10.60	0.16 ± 0.03	15 ± 3 *	6.6	15.5
		197	9.47	0.17 ± 0.02	16 ± 2 *		
	603	167	1.91	4.07 ± 0.09	7.4 ± 0.2	3.9	5.8
	604	57	3.07	5.11 ± 0.10	10.8 ± 0.2	4.5	6.0
		148	3.48	4.19 ± 0.05	8.8 ± 0.1		
	605	47	6.01	0.84 ± 0.03	5.8 ± 0.2 *	5.0	8.4
		55	7.06	0.87 ± 0.03	6.0 ± 0.2 *		
	606	168	9.43	0.15 ± 0.02	8.4 ± 1.0 *	6.5	19.2
	607	169	3.65	1.07 ± 0.04	3.4 ± 0.1 *	2.1	4.1
	609	58	10.10	0.25 ± 0.01	3.7 ± 0.2 *	2.6	6.0
		105	9.04	0.23 ± 0.02	3.4 ± 0.3 *		
		200	9.50	0.28 ± 0.02	4.2 ± 0.3 *		
	610	85	10.01	0.10 ± 0.02	2.4 ± 0.4 *	1.9	3.9
	611	170	10.06	0.15 ± 0.02	44 ± 5	1.0	8.1
		194	10.02	0.06 ± 0.02	17 ± 7		
	612	171	9.55	0.13 ± 0.02	4.0 ± 0.5 *	2.7	5.8
	613	172	8.63	0.68 ± 0.02	6.6 ± 0.2 *	3.3	6.5
	614	173	10.94	0.84 ± 0.02	22.0 ± 0.5 *	13.2	21.1
		196	6.19	0.77 ± 0.03	20.3 ± 0.9 *		
	615	86	3.26	5.59 ± 0.07	11.0 ± 0.2	5.0	7.2
		108	2.92	6.20 ± 0.06	12.2 ± 0.1		
	619	87	10.05	0.52 ± 0.02	9.7 ± 0.3 *	5.2	11.2
	620B	48	2.74	4.72 ± 0.22	10.8 ± 0.5	5.5	7.9
		56	3.10	4.92 ± 0.08	11.3 ± 0.2		
		107	3.53	5.02 ± 0.10	11.5 ± 0.2		
		201	3.26	4.95 ± 0.08	11.4 ± 0.2		
	625	104	9.70	0.18 ± 0.02	6.7 ± 0.6	1.9	3.7
		199	10.47	0.17 ± 0.01	6.4 ± 0.6		
	627	103	5.34	1.29 ± 0.04	5.4 ± 0.2	3.5	5.7
		202	4.36	1.46 ± 0.04	6.2 ± 0.2		
145	W83C	151	2.41	4.60 ± 0.12	9.8 ± 0.3 *	2.0	10.4
	W83A	152	3.50	4.06 ± 0.05	10.3 ± 0.1 *	2.0	10.4
113	CS235L	153	1.81	3.41 ± 0.25	6.3 ± 0.5 *	2.0	10.4
Bulk ore (calculated)			1743	2.0	6.4		

* Indicates that the $^{239}\text{Pu}/\text{U}$ ratio measured for this sample meets the criteria for nuclear equilibrium (see text).

"Bulk ore" is the sum of the concentration of all samples of the Cigar Lake ore body each *weighted by the mass of sample from the interval* (see text).

Table 3. Technetium abundances in Cigar Lake samples

Deposit	Bore-hole	Sample ID	Aliquot ID	Aliquot mass G	Measured ⁹⁹ Tc pg/g	Measured ⁹⁹ Tc/U x 10 ⁻¹²	Modeled ⁹⁹ Tc/U x 10 ⁻¹²	
							Min	Max
Cigar Lake	99	228	111	10.83	0.0149 ± 0.0006	79 ± 5	1.6	1.6
			188	10.20	0.0138 ± 0.0021	73 ± 12		
		230	54	10.01	0.0564 ± 0.0022	800 ± 100	1.6	1.6
			83	10.05	0.0027 ± 0.0007	40 ± 10		
			112	10.13	0.0035 ± 0.0021	50 ± 30		
	220	602	158	10.60	0.222 ± 0.003	51 ± 3	1.9	2.3
			187	9.47	0.140 ± 0.002	32 ± 2		
		603	159	1.91	0.38 ± 0.04	1.67 ± 0.19 *	1.9	2.7
		604	n.a.	9.61	0.39 ± 0.01	1.97 ± 0.23 *	2.0	2.8
			57	3.07	0.37 ± 0.01	1.87 ± 0.22 *		
			139	3.48	0.39 ± 0.01	2.00 ± 0.23 *		
		605	55	7.06	0.185 ± 0.004	3.10 ± 0.17	1.8	2.2
		606	160	9.43	0.0375 ± 0.0005	4.92 ± 0.20	2.1	3.5
		607	161	3.65	0.278 ± 0.001	2.12 ± 0.10 *	1.7	2.1
		609	n.a.	9.46	0.386 ± 0.006	13.8 ± 0.4	1.7	2.0
			58	10.10	0.094 ± 0.002	3.36 ± 0.11		
			114	9.04	0.087 ± 0.011	3.10 ± 0.40		
			190	9.50	0.182 ± 0.008	6.51 ± 0.33		
		610	85	10.01	0.0884 ± 0.0008	5.18 ± 0.22	1.6	1.7
			115	9.02	0.0864 ± 0.0010	5.07 ± 0.21		
		611	162	10.06	0.081 ± 0.001	59 ± 4	2.3	9.7
			184	10.02	0.073 ± 0.008	53 ± 7		
		612	163	9.55	0.124 ± 0.001	8.82 ± 0.76	1.8	2.0
		613	164	8.63	1.424 ± 0.003	33 ± 2	2.0	2.8
		614	186	6.19	0.093 ± 0.004	5.89 ± 0.50 *	4.4	6.7
			165	10.94	0.109 ± 0.001	6.90 ± 0.53 *		
		615	86	3.26	0.319 ± 0.004	1.51 ± 0.09	2.0	3.0
			117	2.92	0.417 ± 0.010	1.98 ± 0.13		
		619	87	10.05	0.0585 ± 0.0007	2.63 ± 0.10 *	2.1	3.0
		620B	56	3.10	0.258 ± 0.003	1.42 ± 0.05	2.1	3.0
			116	3.53	0.643 ± 0.024	3.55 ± 0.17		
			191	3.26	0.310 ± 0.019	1.71 ± 0.11		
		625	113	9.70	0.260 ± 0.012	24 ± 2	1.6	1.7
			189	10.47	0.0635 ± 0.0007	5.85 ± 0.28		
		627	n.a.	3.70	0.185 ± 0.022	1.87 ± 0.24 *	1.8	2.2
			192	6.36	0.207 ± 0.001	2.09 ± 0.07 *		
			140	5.34	0.176 ± 0.004	1.78 ± 0.07 *		
	145	W83C	n.a.	3.03	0.431 ± 0.006	2.21 ± 0.05 *	1.7	3.0
		W83A	41	3.05	0.372 ± 0.003	2.27 ± 0.11 *	1.7	3.0
	113	CS235L	40	3.05	0.369 ± 0.003	1.64 ± 0.08 *	1.7	3.0
		Bulk ore (calculated)		1743	0.26	2.00		

n.a. Aliquot numbers were not assigned for this initial set of analyses.

Indicates that the ⁹⁹Tc/U ratio measured for this sample meets the criteria for nuclear equilibrium (see text)

"Bulk ore" is the sum of the concentration of all samples of the Cigar Lake ore body each *weighted by the mass of sample from the interval* (see text).

Table 4. Properties of bulk samples from uranium deposits

Deposit	Sample ID	Uranium (% wt)	$^{239}\text{Pu}/\text{U}$ ($\times 10^{12}$)	$^{235}\text{Te}/\text{U}$ ($\times 10^{12}$)
Cigar Lake	Bulk	31	6.4	2.0
Beaverlodge	BL-5	7.09 ± 0.03	14.3 ± 0.2	1.99 ± 0.03
Koongarra	G2698	19.1 ± 2	—	1.59 ± 0.07
	G4674	11.5 ± 1	—	1.60 ± 0.09
Canadian pitchblende*		13.5	7.1	
Belgium Congo pitchblende*		38	12	
Colorado pitchblende*		50	7.7	
Brazilian monazite*		0.24	8.3	
N. Carolina monazite*		1.64	3.6	
Colorado fergusonite*		0.25	<4	
Colorado carnotite*		10	<0.4	

* Data from Levine and Seaborg (1951).

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