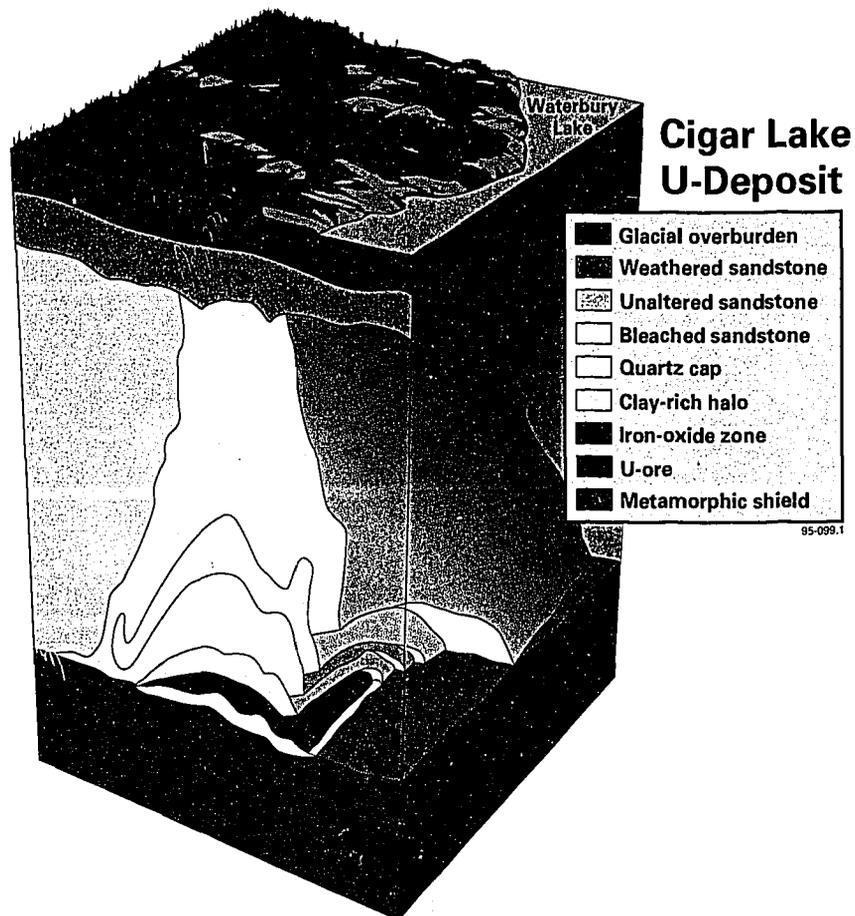


AECL-11204, COG-94-524

The Cigar Lake Uranium Deposit: Analog Information for Canada's Nuclear Fuel Waste Disposal Concept

Information tirée du gisement d'uranium de Cigar Lake, Analogie naturel du stockage permanent envisagé pour les déchets de combustible nucléaire du Canada

J.J Cramer



May 1995 mai



THE CIGAR LAKE URANIUM DEPOSIT:
ANALOG INFORMATION FOR CANADA'S
NUCLEAR FUEL WASTE DISPOSAL CONCEPT

by

J.J. Cramer

AECL
Whiteshell Laboratories
Pinawa, Manitoba, Canada R0E 1L0
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ABSTRACT

The Cigar Lake uranium deposit, located in northern Saskatchewan, has many features that parallel those being considered within the Canadian concept for disposal of nuclear fuel waste. The study of these natural structures and processes provides valuable insight toward the eventual design and site selection of a nuclear fuel waste repository. The main feature of this analog is the absence of any indication on the surface of the rich uranium ore 450 m below. This shows that the combination of natural barriers has been effective in isolating the uranium ore from the surface environment. More specifically, the deposit provides analog information relevant to the stability of UO_2 fuel waste, the performance of clay-based barriers, radionuclide migration, colloid formation, radiolysis, fission-product geochemistry and general aspects of water-rock interaction. The main geochemical studies on this deposit focus on the evolution of groundwater compositions in the deposit and on their redox chemistry with respect to the uranium, iron and sulphide systems.

This report reviews and summarizes the analog information and data from the Cigar Lake analog studies for the processes and scenarios expected to occur in the disposal system for used nuclear fuel proposed in Canada.

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INFORMATION TIRÉE DU GISEMENT D'URANIUM DE CIGAR LAKE, ANALOGUE NATUREL DU STOCKAGE PERMANENT ENVISAGÉ POUR LES DÉCHETS DE COMBUSTIBLE NUCLÉAIRE DU CANADA

par

J.J. Cramer

RÉSUMÉ

Le gisement d'uranium de Cigar Lake, situé dans le nord de la Saskatchewan, présente de nombreuses caractéristiques que l'on peut mettre en parallèle avec celles prises en compte dans le concept canadien de stockage permanent des déchets de combustible nucléaire. L'étude de ces structures et processus naturels donne de précieux renseignements pour la conception finale et la sélection du site d'un dépôt de déchets de combustible nucléaire. La principale caractéristique de cet analogue est l'absence de toute indication à la surface du riche minerai d'uranium situé 450 m plus bas. Cela atteste que la combinaison de barrières naturelles a été efficace pour isoler le minerai d'uranium de l'environnement superficiel. De façon plus précise, ce gisement offre à titre d'analogue des renseignements très pertinents quant à la stabilité des déchets de combustible d' UO_2 , au comportement des barrières à base d'argile, à la migration des radionucléides, à la formation des colloïdes, à la radiolyse, à la géochimie des produits de fission et aux aspects généraux de l'interaction de l'eau et de la roche. Les principales études géochimiques menées sur ce gisement se concentrent sur l'évolution de la composition de l'eau souterraine dans le gisement et sur la chimie redox de celle-ci en ce qui a trait aux systèmes d'uranium, de fer et de sulfures.

Le présent rapport examine et donne un résumé des données et des renseignements tirés de l'analogue naturel que constitue le gisement de Cigar Lake et qui sont applicables aux processus et scénarios qui pourraient avoir lieu dans le système de stockage du combustible nucléaire irradié proposé au Canada.

EACL
Laboratoires de Whiteshell
Pinawa (Manitoba) Canada R0E 1L0
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CONTENTS

	<u>Page</u>
1. INTRODUCTION	1
2. THE CIGAR LAKE URANIUM DEPOSIT	3
3. ANALOG FEATURES OF THE DEPOSIT	6
4. RESULTS OF ANALOG STUDIES	8
4.1 GEOLOGICAL SETTING AND HISTORY	8
4.2 UO ₂ STABILITY	12
4.3 CLAY SEALING	15
4.4 RADIOLYSIS	17
4.5 GROUNDWATER CHEMISTRY AND WATER-ROCK INTERACTION	19
4.6 EFFECTS OF COLLOIDS, ORGANICS AND MICROBES	23
4.7 MASS-TRANSPORT OF RADIONUCLIDES	25
5. CONCLUSIONS	26
ACKNOWLEDGEMENTS	27
REFERENCES	28

1. INTRODUCTION

Atomic Energy of Canada Limited (AECL), with support from Ontario Hydro under auspices of the Candu Owners Group, has developed a concept for the safe disposal of nuclear fuel waste in Canada (AECL 1994). The disposal concept is to place used CANDU* fuel in long-lasting containers and emplace the containers, surrounded by engineered barriers, in a vault excavated at a depth of between 500 and 1,000 m in plutonic rock of the Canadian Shield. Humans and the environment would be protected from contaminants in the waste by several barriers: the waste itself, the container, various sealing materials, and the host rock. This disposal concept permits a great deal of flexibility in its implementation, which means that a wide range of circumstances could be accommodated. Guidelines issued by the Atomic Energy Control Board (AECB 1987) for the safety of nuclear fuel waste disposal require quantitative predictions for up to 10^4 a and qualitative predictions (or reasoned arguments) for performance thereafter.

AECL has prepared an Environmental Impact Statement (EIS) on the concept for disposal of Canada's nuclear fuel waste (AECL 1994). The EIS provides information requested by the federal Environmental Assessment Panel (EAP) which is appointed to conduct a review of the proposed concept and to examine a broad range of issues related to nuclear fuel waste management. For this review, neither a site nor a site-specific design could be assessed, because no disposal site selection has been undertaken. Instead, two assessment case studies of hypothetical systems were performed: the preclosure and postclosure assessment case studies. After the EAP has reviewed the information from AECL and other parties, and has considered the findings of the Scientific Review Group (which the EAP established to provide a scientific evaluation of the concept), it will hold public hearings. Once the EAP has completed the review process, it will make recommendations to assist the governments of Canada and Ontario in reaching decisions on the acceptability and possible implementation of the disposal concept.

The development of the disposal concept and assessing its safety are based on thorough knowledge and understanding of the materials and processes involved. This knowledge and understanding provide both the qualitative (conceptual models) and quantitative (databases) input to the assessment of the disposal concept. Information derived from extensive laboratory and field research is used. However, this research is carried out, by necessity, over relatively short periods of time, i.e., in the order of tens of years. Therefore, additional information and data are required to provide confidence in the safety of the disposal concept and in the predictions from assessment models when extrapolating to time periods of thousands-to-millions of years.

Studies of natural analogs provide important information for evaluating and improving our knowledge and understanding of the disposal concept. Better conceptual models and databases, in turn, result in better assessment models, enhancing the level of confidence in the safety predictions from these models. In addition, analogs are valuable tools to help illustrate the disposal concept and its many aspects to the public and non-experts.

* CANada Deuterium Uranium, registered trademark of AECL.

The Cigar Lake uranium deposit (Figure 1), located in northern Saskatchewan, Canada, has been studied to obtain analog information on a number of processes and parameters relevant to nuclear fuel waste disposal. AECL has carried out analog studies on the Cigar Lake deposit since 1984. From 1989 to 1992, AECL was joined by the Swedish Nuclear Fuel and Waste Management Company (SKB) in a three-year collaborative study. The Los Alamos National Laboratory (LANL) joined the analog studies program in 1991 with funding for five years from the United States Department of Energy (USDOE). The technical data from these studies have been interpreted and documented in a recent publication (Cramer and Smellie 1994).

This report reviews and summarizes the analog information and data from the Cigar Lake analog studies for the processes and scenarios expected to occur in the disposal system for used nuclear fuel proposed in Canada (AECL 1994; Cramer 1994).

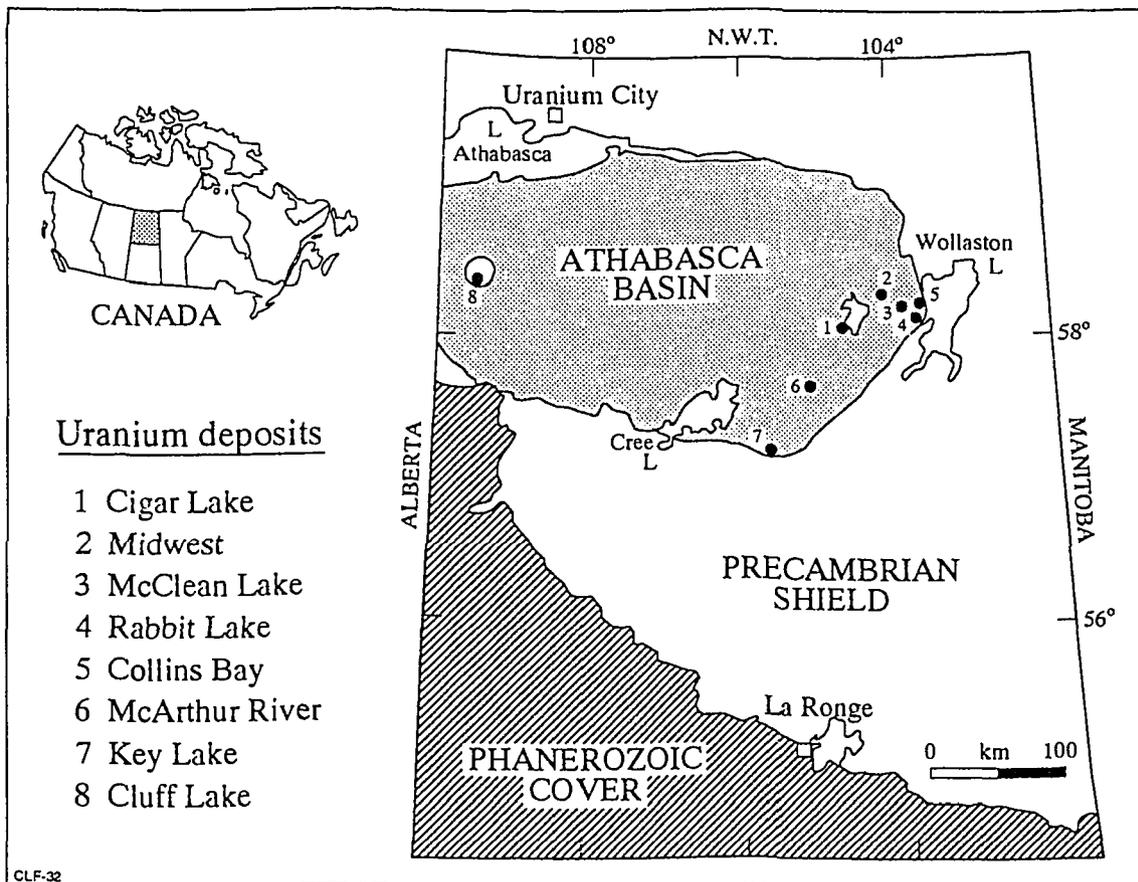


FIGURE 1: Location map showing uranium deposits of the Athabasca Basin in northern Saskatchewan, Canada.

2. THE CIGAR LAKE URANIUM DEPOSIT

The Cigar Lake uranium deposit is located in northern Saskatchewan at the southwestern tip of Waterbury Lake (Figure 1). The deposit is of hydrothermal origin and Proterozoic age, and is one of many unconformity-type, sandstone-hosted uranium deposits that characterize the Athabasca Basin uranium province (Fouques et al. 1986; Bruneton 1987, 1993). These deposits are all relatively high-grade, with some containing average ore grades of several percent uranium. The Cigar Lake deposit is notable because it is located well below the surface at a depth of about 430 m, and the deposit has no direct surface signatures to indicate its presence.

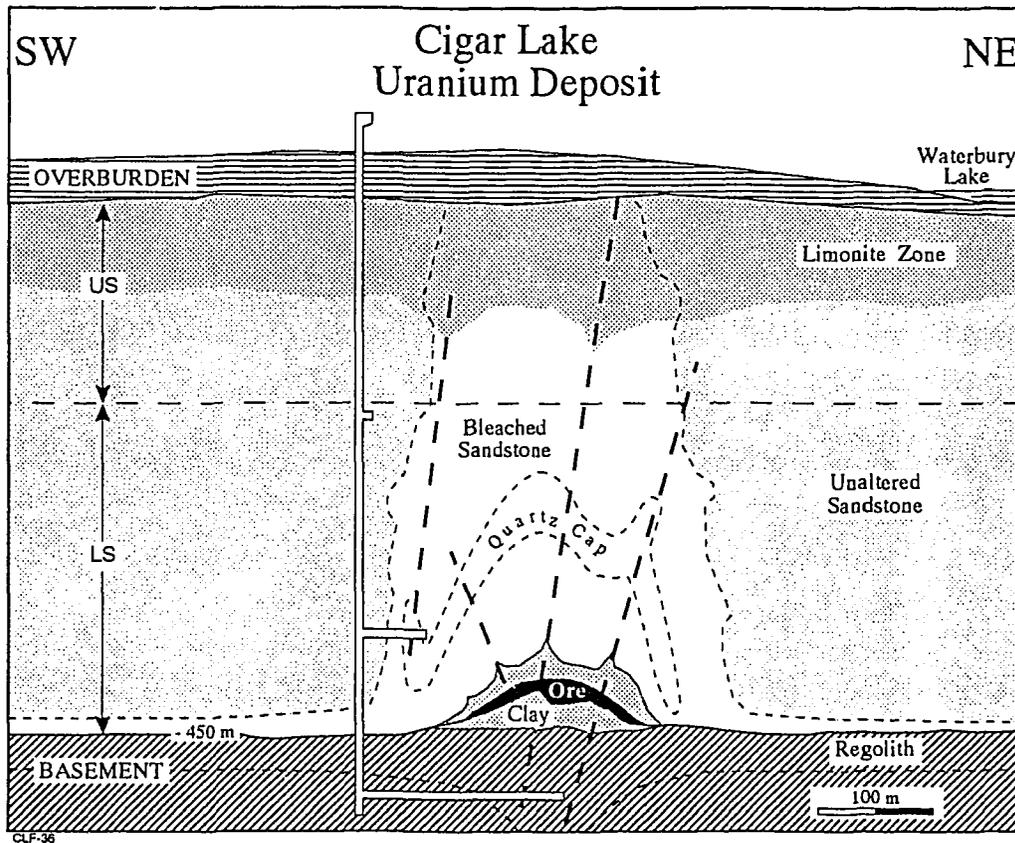


FIGURE 2: Schematic cross section through the Cigar Lake deposit showing the uranium mineralization and its host rocks, including the lithologic characteristics related to hydrothermal alteration and weathering. (US= Upper Sandstone; LS= Lower Sandstone).

The mineralization, consisting primarily of uraninite and pitchblende, with subordinate coffinite, formed about 1.3 Ga ago (Cumming and Krstic 1992) at an estimated depth of more than 2.5 km below surface in hydrothermally altered sandstone. The mineralization is located (Figure 2) at the contact of the host sandstone of the Athabasca Group and the

metamorphic Precambrian basement (metapelites and calc-silicate gneisses). It is currently situated at a depth of ~430 m below ground surface, following millions of years of erosion. The uranium mineralization occurs in a clay matrix and is shaped like an irregular lens that measures approximately 2,000 m long, 20 to 100 m wide and 1 to 20 m thick. The average grade of the total mineralization is around 8 wt.% U, with local concentrations reaching values as high as 55 wt.% U. The geological reserve has been calculated to be 1.5×10^5 Mg U. The Cigar Lake deposit has many features in common with other unconformity-type deposits in the region, which all tend to form long linear deposits that overlie graphitic metapelites subcropping at the unconformity (Hoeve and Quirt 1984; Sibbald et al. 1990). (An unconformity represents an old erosion surface that separates younger strata from the older eroded rocks.)

The ore zone consists of the uranium mineralization in a very clay-rich matrix which is dominated by illite and chlorite with minor carbonates (siderite and calcite) and accessory phases (e.g. zircon, rutile, phosphates etc.). In addition to uranium, the ore contains elevated concentrations of sulphides, arsenides and sulph-arsenides incorporating a broad suite of elements (e.g. Ni, Co, Mo, Pb (radiogenic), Zn, Mn and Fe). Three stages of mineralization can be recognised (Bruneton 1987), of which at least the first two are considered to be of a hydrothermal nature: I) euhedral uraninite and pitchblende associated with primary As-S minerals of Ni, Co and Fe, II) pitchblende associated with secondary As-S minerals, in addition to Cu, Mo, Pb, Zn and Fe sulphides, and III) pitchblende and coffinite associated with ferrihydrites. The first stage produced the bulk of the Cigar Lake mineralization, whereas the last stage occurred on a local and uneconomic scale, dispersing ore above (perched mineralization along fractures) and also below (minor basement mineralization) the primary ore body. The first two stages have been dated at 1362 Ma and 1287 Ma respectively (Cumming and Krstic 1992). The last stage of mineralization is characterized by a low-temperature assemblage, and is much younger, dated at 293 Ma ago (Cumming and Krstic 1992).

The hydrothermal event associated with the formation of the Cigar Lake uranium mineralization was responsible for the characteristic alteration of the host sandstones (Figure 2). Reducing hydrothermal fluids (150 to 200 °C), after having been in contact with the graphite-containing metapelites in the basement, were discharged into the sediment basin along a major lineament in the unconformity contact. Uranium mineralization occurred where these reducing solutions interacted with the more oxidising diagenetic uranium-bearing solutions of the red-bed-type sandstones. The resulting alteration of the sandstones includes the following main characteristic features: a) reduction of Fe(III) from hematite to Fe(II) in marcasite/pyrite, forming a nearly symmetrical plume of "bleached" sandstone above and parallel to the lineament, b) dissolution and mobilization of matrix quartz from the sandstone causing a progressive enrichment of refractory clay and accessory minerals toward the high-temperature side, and reprecipitation of the dissolved silica toward the cooler side of the hydrothermal system, and c) intense fracturing caused by volume readjustments in response to the quartz redistribution mentioned under b). Thus, upon descending, and approaching laterally, through the host sandstone, alteration of the

sandstone is characterized by increasing clay-mineral contents reaching 80 to 100% locally in and around the mineralized zone. However, a quartz-cemented zone (or "quartz cap") marks the location of the silica reprecipitation in the altered sandstone before the zone reaches a clay-mineral content of about 30 %. Below this quartz cap (Figure 3), the altered sandstone is highly permeable, densely fractured and locally friable until the clay-mineral content reaches about 60% in the so-called clay-rich halo (or "clay zone"). This clay zone is 5 to 30 m thick, contains elevated uranium contents and surrounds the high-grade uranium mineralization. The hydrothermal alteration also affected the basement rocks underneath the mineralization, extending the clay-rich zone past the unconformity into the basement regolith. This alteration and the paleo-weathering (producing the ~50-m-thick regolith) of the basement resulted in local obliteration of the original metamorphic textures and mineral assemblages. The effects of hydrothermal alteration extend about 300 m upwards into the sandstone and about 100 m downwards into the basement below the unconformity.

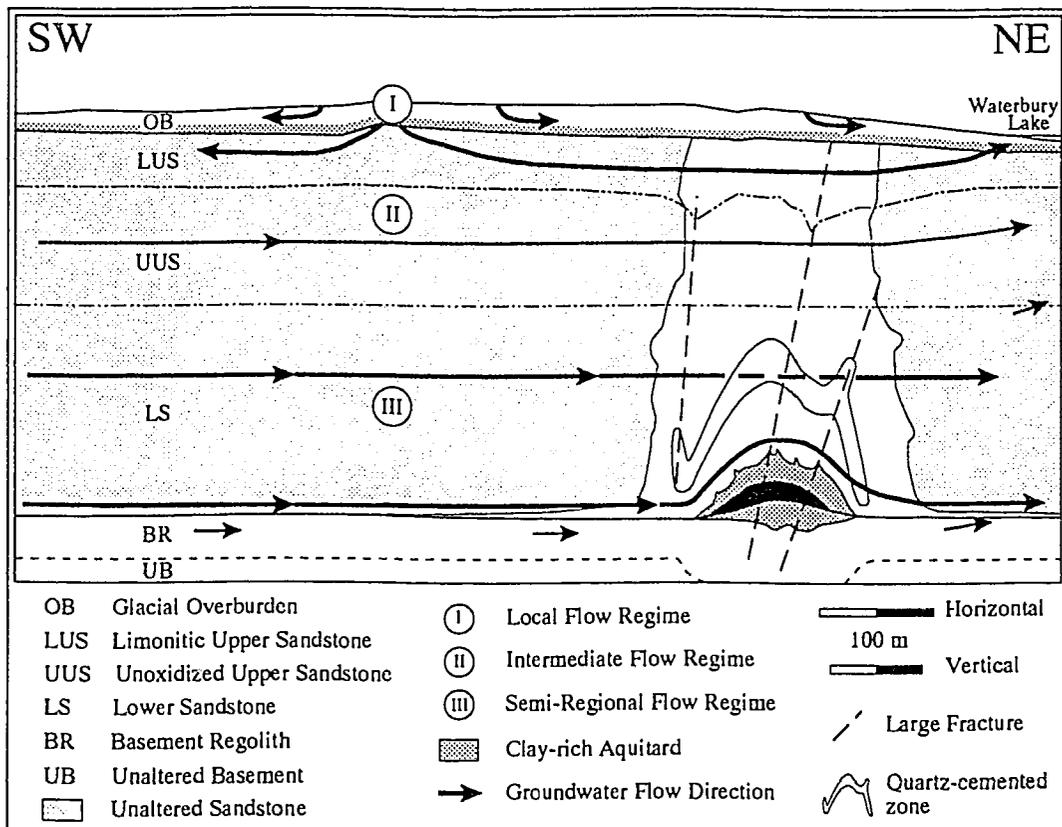


FIGURE 3: Cross section parallel to the direction of regional groundwater flow showing the conceptual hydrogeological model for the Cigar Lake site. Flow lines are illustrated on the diagram, and although hypothetical, they are constrained by the available hydrologic and geologic data.

The ~100-m-thick limonite zone at the top of the sandstone formation (Figure 2) is a late alteration (glacial and post-glacial) superimposed on both unaltered and bleached sandstones. It represents a zone in which downward infiltration of oxidizing, surface-derived waters causes precipitation of ferrihydrites (including limonite), giving the rocks an orange colour.

Three groundwater flow regimes have been identified in the local stratigraphy at Cigar Lake (Figure 3; Winberg and Stevenson, 1994). The uppermost Local Regime is unconfined and includes waters of the glacial overburden. The Intermediate Regime lies in the upper sandstone unit between the Local Regime above and the Semi-Regional Regime in the lower sandstone unit below. The Semi-Regional Regime is confined below by the altered top ("regolith") of the basement and the clay-rich halo surrounding the uranium ore in the deposit. The primary groundwater flow direction in the Semi-Regional Regime is from southwest to northeast, intersecting the deposit through the highly permeable altered sandstone overlying the clay and ore zones (Figure 3).

The clay-rich matrix and halo surrounding the uranium mineralization play an important role in the long-term preservation of the main ore zone in this deposit. The clay-rich rocks and zones have relatively low permeabilities compared with the overlying altered and unaltered sandstone, which acts as the main aquifer, and effectively seal the ore zone from bulk groundwater flow through this zone. In addition, the clay-rich rocks and the hydrothermally altered sandstones are enriched in iron-sulphides (pyrite/marcasite), providing efficient redox buffering in this natural system.

3. ANALOG FEATURES OF THE DEPOSIT

The Cigar Lake ore has been well-preserved at the base of a natural aquifer without specially designed man-made barriers, and, yet, no direct evidence of its existence has been observed at the present-day land surface. Because the current topography and overburden were formed during the last glaciation and deglaciation which ended about 10^4 a ago, any potentially significant migration of radionuclides from the ore apparently has not reached the surface environment during at least 10^4 a. This time frame is similar to that of the regulatory guidelines for quantitative predictions in the safety assessment of the Canadian concept for disposal of nuclear fuel waste (AECB 1987). Thus, the spatial arrangement of the UO_2 ore surrounded by natural barriers, including a clay zone and several hundreds of metres of host rock in a tectonically stable formation, is similar in many respects to the disposal concept proposed in Canada.

In addition to this general analogy, many analogous processes and materials can be found in the Cigar Lake deposit and studied in more detail. These include processes that occur both in the present-day system and those that occurred during the ~1-Ga history of the deposit since its formation. For example, current processes that have been studied include water-rock interaction, evolution of groundwater compositions, redox geochemistry, stability and

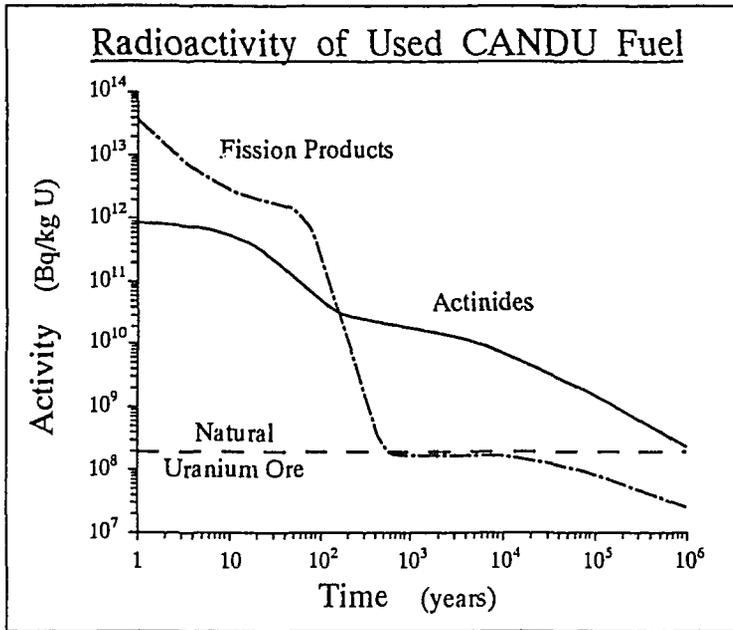


FIGURE 4: The change in radioactivity of used CANDU fuel versus time shows the relatively rapid decay in the activity of the fission products and the slower decay of the actinides.

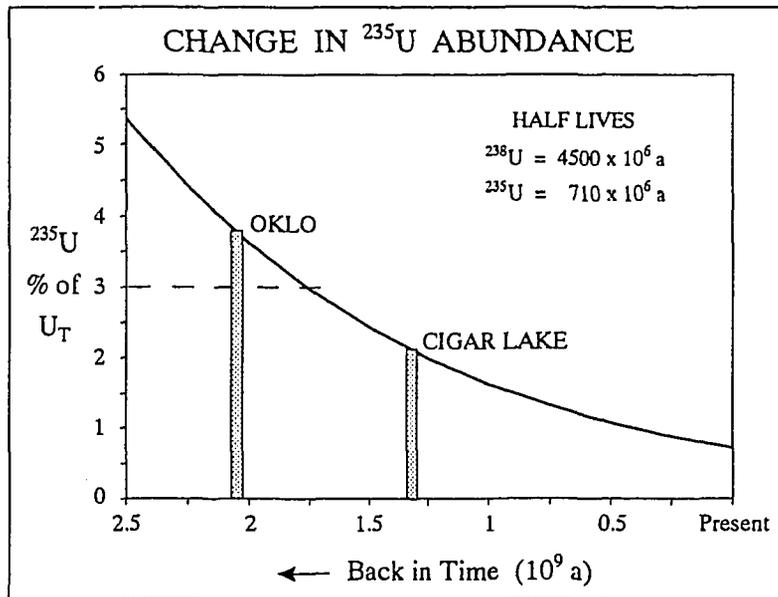


FIGURE 5: The change in the abundance of ^{235}U relative to that of ^{238}U (due to different half lives) versus geological time. The ^{235}U content of $> 3\%$ at ~ 2 Ga ago in the Oklo deposit caused nuclear fission reactions in the natural high-grade uranium ore. However, the ^{235}U content of the Cigar Lake deposit at 1.3 Ga ago was too low for sustained nuclear fission to occur.

dissolution of uranium and clay minerals, sealing by clay, formation and properties of colloids, activity and role of microbes, and the production and mobility of nuclear reaction products. On the other hand, the effects of paleo-processes that can be evaluated from the geological record include those of erosion, uplift and glaciation, paleo-hydrology, water-rock interaction, redox buffering, mineral stability and radionuclide mass transport.

The Cigar Lake deposit also has an important illustrative role in demonstrating the long-term safety of the Canadian disposal concept. The activity of used CANDU fuel, contributed by fission and activation products from the nuclear reaction processes, decays relatively quickly during the first 1000 years (to less 0.001 % of its initial value) following removal from the reactor (Figure 4). Also shown in this figure is the activity of natural uranium (in secular equilibrium) and its associated daughter products, and the activity of used fuel waste will eventually approach that of natural uranium. Although the age of the Cigar Lake deposit precluded the occurrence of sustained fission reactions (Figure 5), natural spontaneous-fission and neutron-capture reactions produce very small amounts of nuclear reaction products in this deposit (Fabryka-Martin et al. 1994; Curtis et al. 1994). Thus, both the total ore reserve (1.5×10^5 Mg U) of the Cigar Lake deposit and the presence of nuclear reaction products (e.g., ^{36}Cl , ^{99}Tc , ^{129}I and ^{239}Pu) in the ore provide analogies with the inventory and composition of used CANDU fuel in the disposal concept.

The following sections of this report review the results of the detailed studies on a number of analog processes and materials that can be observed in the present-day Cigar Lake system. This review includes the relevance of the results and conclusions with respect to aspects of the safety assessment of the disposal concept, i.e., relating specifically to the reference disposal system used in the case study of the assessment for AECL's Environmental Impact Statement (AECL 1994; Goodwin et al. 1994).

4. RESULTS OF ANALOG STUDIES

4.1 GEOLOGICAL SETTING AND HISTORY

The Cigar Lake uranium deposit and other such deposits in the Athabasca Basin represent local geological and geochemical anomalies in the host rock sandstones of this Basin. The deposits are subsystems, primarily, in the Manitou Falls Formation, where the structural, lithological and geochemical parameters contribute to the stability and preservation of the uranium ores. The red-bed-type sandstones of this Formation are hydraulically conductive ($\sim 10^{-6}$ to 10^{-7} m/s; Winberg and Stevenson 1994) in which both the mineralogy (i.e., hematite) and the redox potential of the groundwaters (i.e., ~ 250 to 300 mV; Cramer and Nesbitt 1994b) indicate relatively oxidizing conditions. On the other hand, the Cigar Lake deposit itself represents a system with a reducing environment in which the clay-rich matrix of the uranium ore provides both hydraulic isolation and redox buffering to the U(IV) oxides and silicates.

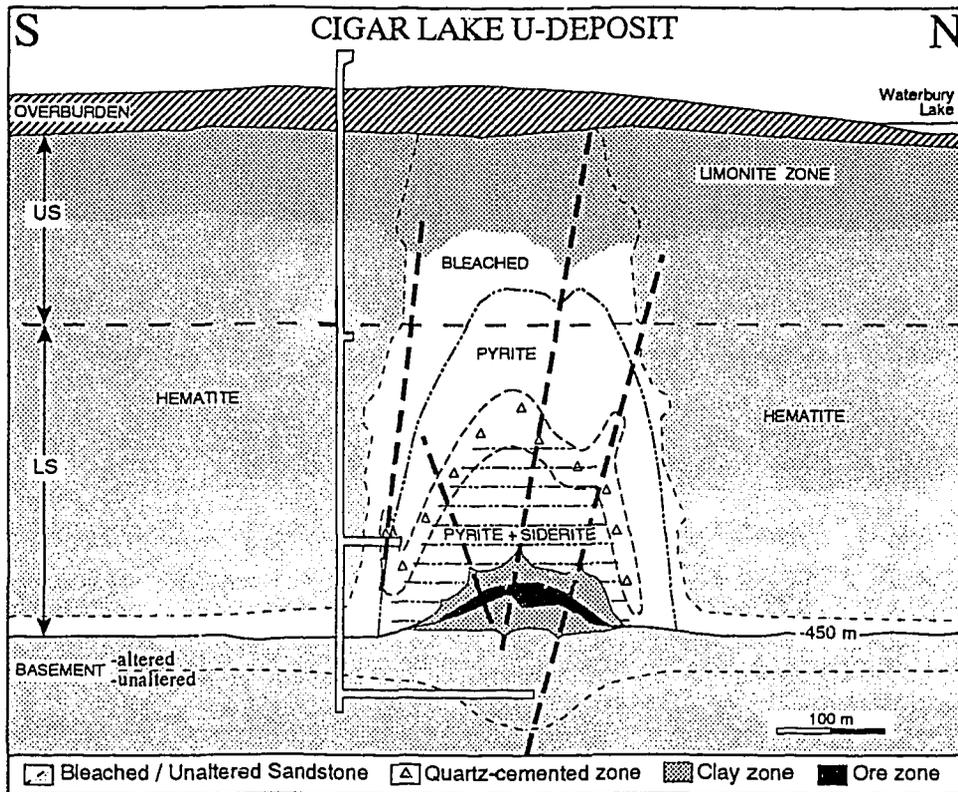


FIGURE 6: Schematic cross section through the Cigar Lake deposit showing the uranium mineralization and its host rocks, including the lithologic characteristics related to hydrothermal alteration and weathering. (US= Upper Sandstone; LS= Lower Sandstone; horizontal lines= altered sandstone (AS) incl. pyrite + siderite).

The current depth (~430 m below surface) of the Cigar Lake deposit has preserved an important part of the original hydrothermal system in which the uranium ore was formed more than 1 Ga ago. The section in Figure 6 shows the extent of the oxidizing redox front descending along permeable fractures and overprinting both the unaltered sandstones and the bleached and hydrothermally altered rocks of the Cigar Lake system. This weathering front is the result of oxygen-rich surface waters infiltrating the bedrock, and oxidizing any ferrous iron to ferric phases (limonite). However, the hydrothermally altered rocks below this weathering front have been preserved and contain various ferrous-iron minerals that help to maintain reducing conditions in these rocks. Also preserved in these rocks is a uranium distribution pattern (Figure 7) that is of primary, hydrothermal, origin. Extensive work by the uranium exploration company (COGEMA) was carried out to study the distribution patterns of major and trace elements in the sandstones overlying the deposit. This information and that reported by Clark (1987) was used to obtain a 3-dimensional picture of the distribution of uranium, thorium and lead in the overlying sandstones. The resulting

distribution patterns in the top of the sandstone bedrock, occurring >350 m vertically above the mineralization, show a good correlation between the abundance of these elements and the outline of the uranium mineralization. Such patterns indicate that at least the distribution of uranium is predominantly of primary origin, because these patterns vertically transect the horizontal lithological and hydrological stratigraphies, and their abundances of thorium and lead correlate with a radiogenic origin from decay of the corresponding uranium.

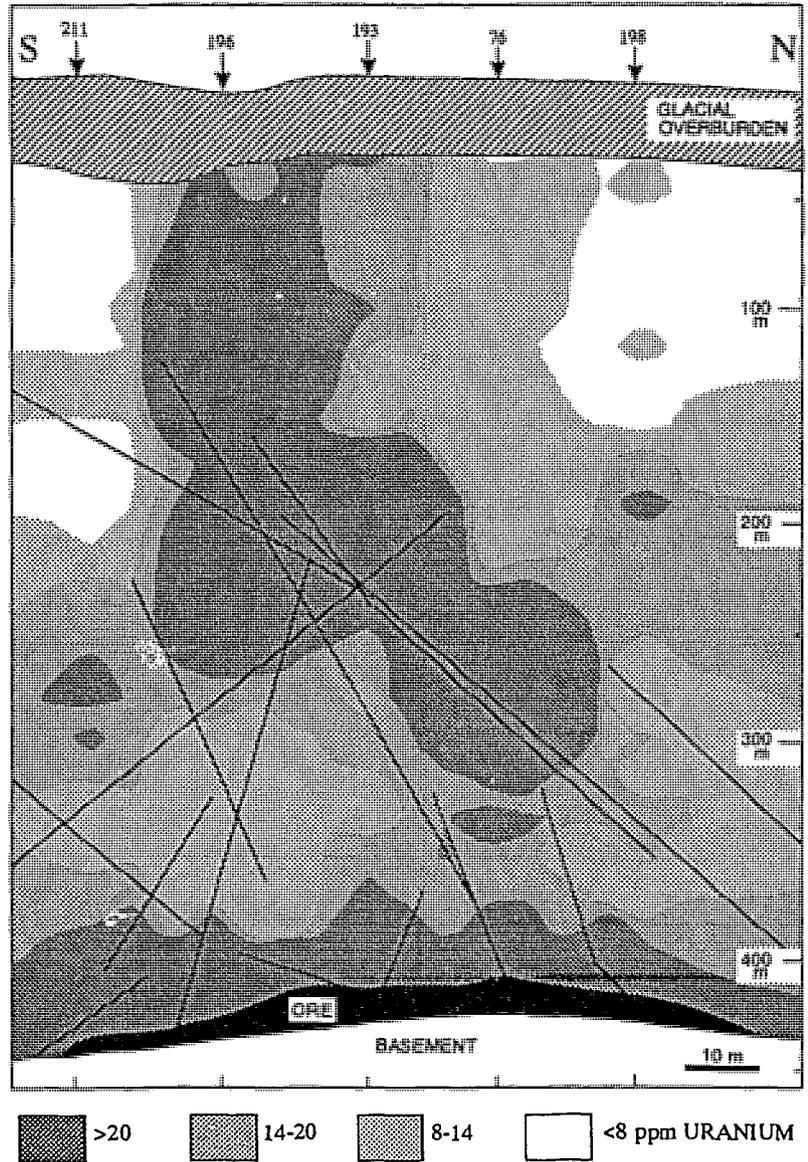


FIGURE 7: Section 10775E along five boreholes through the main ore body showing the distribution of uranium in the sandstone host rock above the mineralization and the distribution of major fractures as interpreted from core logging (COGEMA 1986).

Remobilization of the primary uranium minerals in the Cigar Lake deposit occurred either along selected fractures in the sandstone above the ore zone (so called perched mineralization) or along the unconformity in the basement rocks just underneath the ore zone. The low-temperature perched mineralizations are only found locally along steeply dipping fractures up to about 350 m above the ore, and they only contain low-grade dispersed pitchblende (<5,000 ppm U). The locations of these remobilizations indicate fracture-controlled flow paths for the uranium-containing solutions and suggest, because of the sub-vertical fracture orientations, a disturbance in the otherwise predominantly horizontal hydraulic flow field. The perched mineralizations at Cigar Lake have been dated at about 293 Ma (Cumming and Krstic 1992), coinciding with a period of tectonic activity involving rapid uplift of the sandstone basin (see Figure 8). It is not known whether the uranium in the perched mineralizations is derived from remobilization of uranium from weathered sandstone higher up in the stratigraphy, or from the primary ore several hundred metres lower in the stratigraphy.

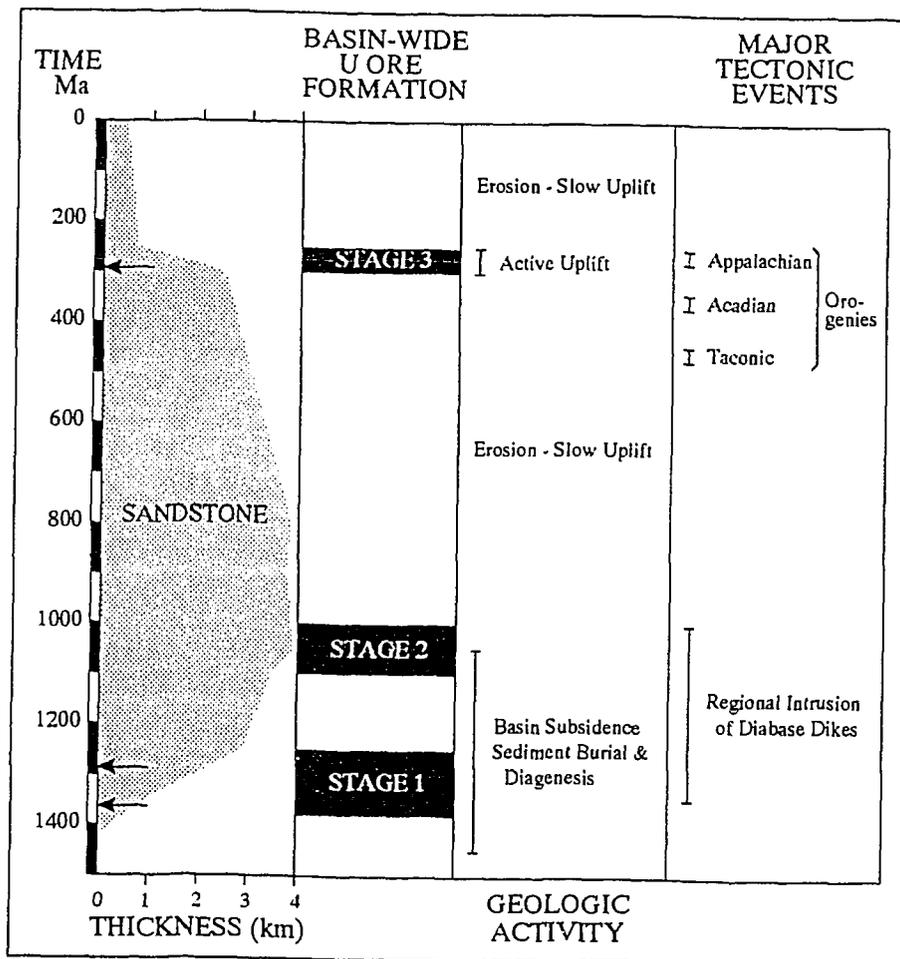


FIGURE 8: Schematic diagram illustrating the geological evolution of the Cigar Lake deposit, showing ages of uranium mineralization (arrows), stages of ore formation in the Athabasca Basin, and major tectonic events.

One possible scenario for the remobilization of uranium about 300 Ma ago involves the opening of fracture flow paths by the major tectonic activity associated with the Appalachian Orogeny (Figure 8). The timing of this remobilization corresponds to a basin-wide event of increased meteoric water flow along reactivated faults and fractures resulting in both major kaolinization and uranium mobilization between about 350 and 250 Ma ago (Hoeve and Quirt 1984; Kotzer and Kyser 1990, 1991). The Appalachian Orogeny represents major tectonic stresses in the North American plate, causing rapid uplift and temporary stress-relaxation along existing faults and fractures in the Athabasca Basin area (Hoeve and Quirt 1984). The increase in recharge of oxidizing meteoric waters along such fractures is a likely cause of uranium remobilization downward from an intersected uranium-enriched host rock or from ore-grade mineralization. Examples of such remobilizations may be found in the deep Cigar Lake deposit and in the shallow Key Lake deposit (Kettlewell 1994). Whereas both these deposits formed similarly, including an illite-rich clay matrix to the ore, geochemical modelling (Kettlewell 1994) of the Key Lake deposit indicates that this deposit has been strongly affected by recharging meteoric waters including large-scale kaolinization of illite and dissolution of the primary uranium ore.

The large uranium mineralization at Cigar Lake has been preserved for more than 1 Ga without any evidence of major uranium remobilization into the surrounding host rocks. Both major and minor geological disturbances have occurred during the deposit's history, including >900 Ma of gradual uplift (of >2.5 km) caused by erosion and glaciation, and at least one period of major hydraulic disturbance caused by tectonic activity. The uranium ore at Cigar Lake remains currently protected by its clay-rich matrix and redox-buffering host rocks, at a depth of at least 300 m below the surface-derived weathering front.

4.2 UO₂ STABILITY

The used CANDU fuel consists of a crystalline uranium-oxide (UO₂) matrix together with small quantities (<2 wt.%) of fission and activation products from the nuclear reaction process. Some of the radioactive isotopes, or radionuclides, are in solid solution in the UO₂. Others, such as ¹⁴C, ¹²⁹I and ¹³⁵Cs, may be present as interstitials or in microscopic inclusions with the UO₂ grains, or may be released from the grains in small quantities during reactor irradiation. The fuel-sheath gap comprises the space between the Zircaloy fuel sheath and the UO₂ pellets together with any cracks or fissures that develop in the UO₂ pellets during irradiation in the reactor. The inventory present in this gap is released rapidly upon contact with water, while the inventory at grain boundaries appears to be released more slowly as the UO₂ matrix dissolves. However, because of limited data on the rate of release of fission products at grain boundaries, it has been conservatively assumed, in modelling the dissolution of used fuel (Johnson et al. 1994), that this grain boundary inventory is also immediately released upon exposure of the fuel to groundwater.

In the Vault Model for the EIS case study (Johnson et al. 1994), the release model for those radionuclides in solid solution in the UO_2 is based on congruent dissolution of the UO_2 matrix through limited oxidation of UO_2 to U_4O_9 - U_3O_7 . This model assumes that (1) UO_2 is the stable, solid phase for uranium, based on thermodynamic data; and (2) all nuclides in the UO_2 matrix are released at the same rate. Thus, the information being sought from natural analogs is

- whether UO_2 is stable and under what conditions (including radiolysis),
- what is the solubility of UO_2 and what the controlling parameters are,
- whether the release of radionuclides contained in the UO_2 matrix occurs congruently upon dissolution of the UO_2 , and
- what is the retention capability of UO_2 for natural radionuclides and nuclear reaction products.

In addition to testing the validity of the UO_2 -dissolution model, natural water-rock interaction in the Cigar Lake deposit can be used to test computer codes for speciation of dissolved uranium and other radionuclide species. The comparison of predictions from a speciation code with the actual observed phases in the water provides feedback on the quality of the codes. Although natural uraninite has the structure of UO_2 , its composition is not pure UO_2 , containing small amounts of both non-radioactive (e.g., Pb, Ca, Si, etc.) and radioactive (e.g., ^{99}Tc , ^{129}I , ^{239}Pu , etc.) elements. However, the analogy of natural UO_2 with UO_2 -based fuel waste is justified based on the fact that CANDU nuclear fuel waste also includes small quantities of other elements (see above).

Characterization studies of the uranium minerals from the Cigar Lake ore zone (Sunder et al. 1988, 1992) show that some of the uraninite (natural UO_2) has been exposed to interaction with fluids and/or groundwaters. The exposed uraninite crystals have a micro-crystalline surface-oxidation layer for which $\text{U}^{\text{VI}}/\text{U}^{\text{IV}}$ values have been determined by XPS to be in the range of 0.20 to 0.57. The associated dissolved-U concentrations, measured in groundwaters from the ore zone, show corresponding low values of $< \sim 10^{-7}$ mol/L U. This information indicates reducing conditions for the natural water-rock interaction, and corresponds to the low redox potentials measured in present-day groundwaters ($\text{Eh} < \sim 0.2$ V; Section 4.5). Thus, the dissolution, and therefore the stability, of UO_2 appears to be controlled by a thin surface layer of higher oxides with $\text{U}^{\text{VI}}/\text{U}^{\text{IV}}$ of up to 0.57. These field observations are supported by a) experimental work and theoretical considerations (e.g., Shoesmith and Sunder 1991; Garisto and Garisto 1986) showing that the oxidative dissolution rate of UO_2 does not become significant until it is oxidized beyond the $\text{UO}_{2.33}$ (U_3O_7 , theoretical $\text{U}^{\text{VI}}/\text{U}^{\text{IV}}$ ratio of 0.5) stage, and b) the predictive calculations (using measured groundwater compositions and the code PHREEQE (Bruno and Casas 1994)) of the uranium phases at equilibrium, which mostly give U_3O_7 with some overlap to U_4O_9 .

The uranium ore at Cigar Lake occurs in a large clay-rich deposit: the high-grade ore is located inside a clay-rich matrix in the centre and is surrounded by a clay-rich halo containing low-grade to very minor uranium mineralization. The boundary between the high- and low-grade uranium mineralizations is fairly sharp and well defined. Water access to the uranium ore inside the clay deposit is very limited and probably controlled by distinct fractures through the clay, accounting for the long residence time for water in the ore zone of $\sim 10^5$ a (see Section 4.3). Geological, geochronological and petrological information shows that the oxidation layers observed on exposed uraninite surfaces resulted from only a few discrete, major disturbances, of which the youngest can be dated at 293 Ma (Cumming and Krstic 1992). Thus, the composition of the uranium minerals observed in the ore zone today reflects the result of water-rock interaction over a period of millions of years. The chemical composition of the uraninites is further characterized by a) $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ activity ratios ranging between 0.98 and 1.00, and 1.05 and 1.11 respectively (Cramer and Nesbitt 1994b), b) high contents of radiogenic Pb (Janeczek and Ewing 1994; Cumming and Krstic 1992), and c) relatively high contents of fission and activation products from naturally occurring nuclear reactions (Curtis et al. 1994). These characteristics suggest that the isotopes show good retention in, rather than selective release from, the natural- UO_2 , which may be explained by congruent matrix dissolution over a 10^6 -a-period.

The redox conditions of current water-rock interaction in the mineralized zones at Cigar Lake are controlled mainly by the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple and are buffered by Fe-sulphides (pyrite/marcasite) and siderite (Cramer and Nesbitt 1994b). The corresponding measured redox potentials (Eh) of $< \sim 0.2$ V thus favour the solubility-controlled dissolution of UO_2 , which is in agreement with calculated redox potentials of > 0.2 V (also using pyrite and siderite) required for oxidative dissolution of UO_2 . This is further supported by recent experimental work (Sunder et al. 1992) indicating that oxidative dissolution of UO_2 does not become important until the redox potential reaches values above +0.14 V.

The following conclusions on UO_2 stability can be drawn from the Cigar Lake analog study:

- Natural uraninite under low-temperature reducing conditions shows long-term stability at least on a time scale of 10^8 a. This supports the assessment predictions of long-term stability of UO_2 -based fuel waste under similar conditions, based on thermodynamic data, solubility control and limited water access (Johnson et al. 1994).
- Dissolution of natural UO_2 at Eh values of < 0.2 V appears to be controlled by surface alteration similar to that observed in experimental systems.
- Natural uraninite under low-temperature conditions shows good retention of nuclear reaction products, such as thorium and plutonium, occurring either in solid solution or as separate phases within the UO_2 matrix.

4.3 CLAY SEALING

The uranium ore has been deposited in the clay-rich part of the highly-altered sandstone. The thickness of this clay zone above the high-grade ore varies between 1 and 30 m and contains 30 to 80% clay minerals (illite and kaolinite). The ore itself occurs in a clay-rich matrix consisting of illite and chlorite with only minor quantities of sudoite (a Mg-chlorite) and trace abundances of kaolinite (Percival et al. 1993; Bruneton 1987). The thinner clay zone below the ore contains about 30% clay minerals (illite and chlorite).

In the deposit the dominant clay mineral, illite, probably formed during high-temperature diagenesis of the basin sediments through alteration of kaolinite and possibly of a mixed-layer illite/smectite precursor (Percival et al. 1993). The original kaolinite and illite/smectite represent weathering products from the older Shield rocks, and formed part of the sediments laid down in the Athabasca Basin. The illites from the deposit have been dated, using the K-Ar method, at between 1148 and 1255 Ma. These ages are younger than the U-Pb age of 1320 Ma for the primary uranium ore, and probably indicate closing ages (the time that the crystal structure became closed to further loss of Ar gas) for illite during the thermal decay of the hydrothermal system. Within the deposit, hydrothermal activity, in the range of 150 to 200°C, has increased the crystallinity of illite locally to reflect low-grade metamorphic conditions. Minor quantities of kaolinite, chlorite (sudoite) and a chlorite/illite mixed-layer phase also occur in the clay-rich halo surrounding the ore zone. No distinction can be made between illites of possible diagenetic and hydrothermal origin, based on D and ¹⁸O data. The illites have D and ¹⁸O values similar to illites from other uranium deposits in the Athabasca Basin. However, these latter illites, all from deposits located close to the present-day surface, have high H₂O contents, indicating degradation or retrograde alteration of the original illite. Illites in the deep, clay-rich, Cigar Lake deposit have low H₂O contents, which is consistent with the lack of evidence for retrograde alteration of illite to kaolinite. These observations indicate that advective mass transport, requiring a significant flux of meteoric waters through the clay-rich deposit, has not occurred. This is an important observation in the context of using a clay-based buffer as a sealing material in the Canadian disposal concept. Bentonite, the preferred clay mineral for the buffer in the concept, has superior swelling and sorption properties compared to illite, whereas illite can form as a hydrothermal alteration product after bentonite.

The low permeability of the clay zone in the Cigar Lake deposit is an important factor in the effective isolation of the ore zone from the large and highly conductive aquifer in the altered sandstone. The ore zone is water-saturated and any connection of the water in the ore zone with that of the overlying aquifer in the altered sandstone would be restricted to fractures through the clay zone. The bulk permeability values for the clay zone range from 10⁻⁶ to 10⁻⁹ m/s, whereas the values for the unfractured matrix clay range from 10⁻⁸ to 10⁻⁹ m/s, similar to that of the ore zone. The compositions of groundwater in the ore zone also indicate effective isolation from the sandstone aquifer under natural undisturbed conditions and during short-term disturbances caused by groundwater pumping. This conclusion is based on isotopic data, representing a timescale of ~10⁴ a, and on pH, Eh, dissolved oxygen, uranium and radium measurements during a large-scale, 9-day pump test.

Measurements of the ^{36}Cl concentration in the groundwaters from the ore zone show relatively high values (up to $8,300 \times 10^{-15} \text{ }^{36}\text{Cl}/\text{Cl}$, Cornett and Cramer 1994), which can be attributed to the production of ^{36}Cl by neutron capture on ^{35}Cl in the ore zone waters. Leaching of ^{36}Cl directly from the ore will be minimal, because the bulk of the hydraulically conducting horizons in the ore zone are not directly in contact with the highest grades of the uranium mineralization, which are surrounded by a clay matrix. In addition, leaching experiments demonstrate that only very small amounts of chloride can be leached from the ore resulting in a $< 4\%$ contribution from leaching of high-grade ore to the $^{36}\text{Cl}/\text{Cl}$ value of the groundwater. Thus, because of the long half life for ^{36}Cl , the build-up of the high ^{36}Cl -abundance indicates a relatively long residence time for groundwater in the ore zone in the range of 10^5 a, which is directly related to the effective sealing capacity of the clay-rich host rock to the ore.

The study of colloids (Vilks et al. 1993) and dissolved organics (Pettersson et al. 1994) in the groundwaters from the deposit also corroborates the other evidence for a low flux of water through the mineralized zone. Uranium-series isotopic data for particles suspended in groundwaters collected from the mineralized zone show calculated ages for the particles of up to 8×10^3 a. Furthermore, the composition of the particles in this zone is distinct from that in the host sandstone outside the clay-rich deposit. This indicates that the transport of particles from the ore through the clay-rich zones has been negligible, and the mobilization of clay particles from the clay-rich zones into the sandstone has not been important. The groundwaters in the mineralized zone of the deposit contain up to ~ 11 mg/L total organic carbon, and measurements of ^{14}C contents in the extracted dissolved-humic fraction give calculated ages for the humics of $> 1.5 \times 10^4$ a.

Additional qualitative evidence for this sealing capacity also comes from observations made during the underground drilling program carried out by the Cigar Lake Mining Corporation. When boreholes were drilled up into the ore zone, from a drift in the basement underneath the deposit, very little ore-zone water was recovered from each hole (< 50 L) and no observable recharge occurred into the hole from the large aquifer in the overlying sandstone, unless the drilling accidentally penetrated through the clay zone into the aquifer.

The present-day measurements of the permeability of the clay-rich matrix and halo likely represent an upper limit for this parameter during the deposit's geological history. The reduction in lithostatic pressure, caused by the erosion of more than 2.5 km of overlying sandstone (Figure 8) during the deposit's > 1 Ga history, likely has resulted in an increase of the original permeability of the clay-rich rock over the past ~ 1 Ga. This suggests that the sealing capacity of the clay-rich matrix may have been even greater in the past, i.e., that groundwater penetration from the sandstone aquifer was less, and that residence times of groundwater in the mineralized zone was longer. However, an equally important effect is the gradual exposure of critical mineral phases in the clay-rich matrix by the gradual lithostatic decompression. The study of the groundwater geochemistry and evolution has shown that the iron and sulphur redox couples strongly control the redox conditions of water-rock interaction in the deposit (Section 4.5). The ferrous sulphides pyrite and marcasite are found throughout the deposit in both the clay-rich rocks and the hydrothermal

alteration halo in the overlying host sandstones. These sulphides occur in the clay-rich rocks both as larger crystals and aggregates in the ore zone, and as finely disseminated minerals throughout the clay matrix surrounding the ore. The gradual exposure of these sulphides over time has ensured that the redox buffering capacity of the clay-rich rocks has been maintained for million of years. Continued erosion and uplift would likely increase the permeability even further, cause fractures to open up, and eventually bring the deposit to within the range of the oxidizing weathering front. Here increased interaction with recharging meteoric waters would cause widespread kaolinitization of the illite and exhaust the redox buffering capacity of the system over time. This latter scenario has been successfully modelled for the shallow Key Lake deposit (Kettlewell 1994), where the primary uranium ore has been dissolved from the clay-rich host rock above the unconformity and redeposited in the basement rocks below the unconformity.

The following conclusions summarize the role of clay in the long-term preservation of the Cigar Lake deposit:

- The illite-rich clay matrix, with an average current permeability of between 10^{-8} and 10^{-9} m/s, plays an important role in limiting the flux of groundwater through the mineralized zone of the deposit.
- Illite is stable for millions of years in contact with low-potassium groundwater, with a pH in the range of 6 to 8, in the radiation field of the high-grade uranium ore (Cramer and Nesbitt, 1994b).
- The clay-rich matrix can provide a suitable medium for control of redox processes by both retardation of groundwater flow and gradual exposure of critical redox-buffering phases.
- The illite-rich clay matrix is an effective barrier to colloid and radionuclide migration from the mineralized zone to the aquifer in the host sandstone.
- Illite, which may form by alteration of bentonite and in comparison has inferior swelling and sorption properties, has been effective as a natural barrier in the long-term preservation of the large Cigar Lake deposit.

4.4 RADIOLYSIS

The transition from low uranium content to high-grade ore in the clay-rich rock is relatively sharp (both upper and lower contacts of the ore zone) and corresponds with the disappearance of kaolinite and a marked increase in chlorite content. The upper clay-ore contact is red-green in colour and may be 1 to 3 m thick, with the greater thickness localized

along fractures. This upper contact obtains its reddish colouration from Fe(III) phases including both hematite and amorphous to poorly-crystallized ferrihydrites. Very locally, siderite may form up to 50 % of the rock.

The red clay zone along the upper contact of the high-grade uranium mineralization represents a redox anomaly in the deposit. Whereas the deposit and its host rocks contain a ferrous-iron, sulphide and uranium-IV mineral assemblage that is indicative of reducing conditions (see Figure 6), the ferric phases in the red clay zone indicate local oxidizing conditions. Initially a radiolysis model was proposed (Cramer 1986) to explain the red colouration (from precipitation of ferrihydrites) through scavenging of radiolysis-produced oxidants by dissolved Fe^{2+} in the ore-zone waters.

Calculations for different radiolysis scenarios in the deposit were subsequently carried out (Christensen 1994) to test several models for the formation of the red clay contact. Although the calculations confirm that products from α -radiolysis of water can oxidize dissolved Fe^{2+} to Fe^{3+} , it is uncertain whether the ferrihydrites (and hematite) in the red clay contact can be accounted for by this process. In fact, the initial model scenario, based on α -radiolysis and requiring direct contact of water with the uranium minerals, had to be revised to also consider γ -radiolysis when it was observed that most of the uranium ore is encapsulated inside the clay matrix of the ore zone. The alternate scenario thus includes groundwaters being subjected primarily to γ -radiation inside the more permeable, and more common, water-bearing horizons or fractures.

The modelling results show that any radiolysis occurring in the Cigar Lake ore zone does not have a strong effect on the redox potential. In fact, calculations using radiolysis models with a threshold redox potential (Eh) of 0.12 V for UO_2 dissolution show that the Cigar Lake ore should have been totally oxidized within 18 to 170 Ma (Bruno and Casas 1994). As this is not the case, and as indicated by recent experimental work, the 0.12 V threshold potential appears to be unreasonably low, and oxidative dissolution of UO_2 does not become important until the redox potential (Eh) reaches values above 0.14 V (Shoesmith and Sunder 1992).

The conclusion of the radiolysis modelling is that the effects of α - and/or γ -radiolysis are insufficient to cause significant oxidation of the UO_2 , even when integrated over the lifetime of the deposit. A simple extrapolation of the currently observed maximum width of the red clay zone over the 1-Ga-lifetime of the deposit shows that radiolysis would only account for a 30- μm -wide oxidized zone in 10^4 a. This extrapolation assumes that the radiolysis effects would have been constant during the 1 Ga period - an unlikely scenario given, for example, the different isotopic composition of the uranium ore when it was first formed (e.g., see Figure 5). However, the extent of radiolysis taking place in the current steady-state system of the ore zone is still an open question, and what causes the red oxidized clay contact is as yet unresolved. The established importance of dissolved Fe^{2+} as a fast oxidant-scavenger, combined with the measured high concentrations of dissolved H_2 in groundwaters from the ore zone (Section 4.5), suggest that, if radiolysis takes place locally and only on a minor

scale, the natural system of clay and ferrous minerals can buffer the redox potential to maintain reducing conditions to well within the stability field of UO_2 .

4.5 GROUNDWATER CHEMISTRY AND WATER-ROCK INTERACTION

The geochemistry and evolution of groundwaters at Cigar Lake are described in detail by Cramer and Nesbitt (1994a and b). In general, the groundwaters in and around the uranium deposit are characterized by neutral to near-neutral pH ($\sim 6-8$), by low contents of total dissolved solids ($\sim 60-240$ mg/L) and carbonate (< 100 mg/L HCO_3^-), by decreasing redox potentials toward the ore zone (Eh from about $+0.25$ to -0.25 V), and by overall low U content (usually $\ll 30$ $\mu\text{g/L}$ or $10^{-6.5}$ mol/L). Within the ore-zone groundwaters, marked increases in the contents of certain isotopes (e.g., ^3H and ^{36}Cl) are observed as a result of nuclear reactions occurring in situ.

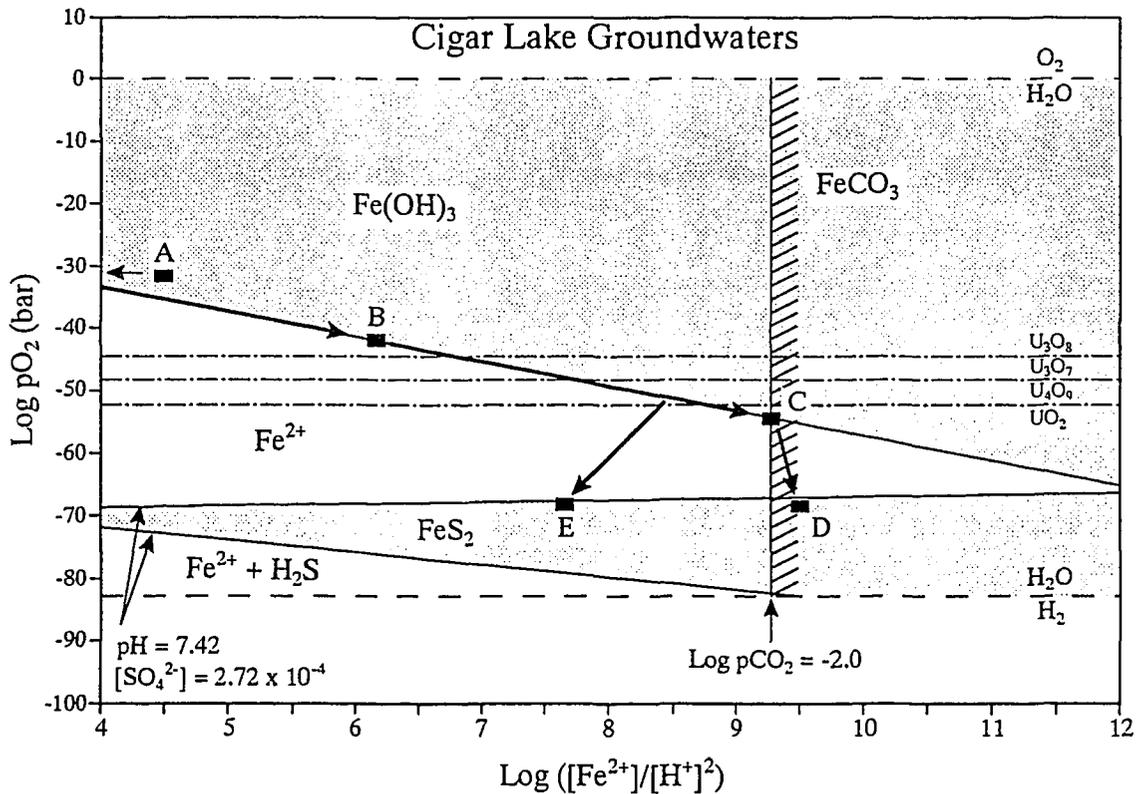


FIGURE 9: Redox diagram for water-rock interaction in the Cigar Lake deposit. Groundwater compositions evolve from A (overburden) to B (unaltered sandstone and limonite zone), to C (altered sandstone), to D/E (clay and ore zones). Semi-dashed lines represent stability boundaries for various solid uranium oxides. See text for further explanation.

The hydrogeochemical model for the evolution of groundwater compositions at Cigar Lake is illustrated on the redox diagram in Figure 9. This evolution is characterized by the interaction of the waters primarily with the clay and iron minerals in the rocks. Surface precipitation (rain and snow) reacts with illite and kaolinite, dissolving iron from various minerals in the overburden and producing a recharge water to the Upper Sandstone unit (Figure 3) that is already equilibrated with the main clay minerals and is rich in iron (point A in Figure 9). Reaction of this oxidizing recharge water with the Upper Sandstone produces precipitation of ferrihydrites down to a depth of about 100 m, overprinting both the unaltered and bleached sandstone ("limonite" zone; B in Figure 9). Upon approaching the clay and ore zones of the deposit, subsequent reaction of the waters with Fe sulphides and siderite in the bleached sandstone reduces the oxidation potential of these waters (decreasing pO_2 : B→C→D/E in Figure 9) to well within the UO_2 stability field. The redox-buffering capacity of the Fe sulphides in the ore and its host rocks plays an important role in maintaining reducing conditions, and thus preserves the stability of the uranium mineralization.

Recharge of meteoric waters from surface to the aquifer in the Lower Sandstone (Figure 3) occurs mainly along fractures, and these waters are descending well into the Upper Sandstone before they lose their oxidation potential as indicated by the limonite alteration in the matrix and along fractures in the Upper Sandstone. The uranium-series data for samples collected from the limonite zone (Figure 6) show that oxidative bulk dissolution of uranium occurs in these rocks (i.e., $^{234}U/^{238}U = 0.87-0.88$ and $^{230}Th/^{234}U = 1.10-1.29$). In addition, the occurrence of kaolinite along fractures in the Upper Sandstone and in the upper ~70 m of the Lower Sandstone indicates significant groundwater flux causing retrograde alteration of illite to kaolinite. Some of these steeply dipping fractures contain minor perched mineralizations of uranium (see Section 2). Smellie et al. (1994) report on one such occurrence (depth 270 m; ~5,000 ppm U) where the uranium-series activity ratios indicate some remobilization of uranium (i.e., $^{234}U/^{238}U = 0.92$ and $^{230}Th/^{234}U = 1.24$). In contrast, the uranium-series isotopes in samples from deeper within the deposit have close to equilibrium activity ratios for $^{234}U/^{238}U$ and $^{230}Th/^{234}U$. These observations suggest that some minor recharge from the intermediate to the semi-regional regime in the Lower Sandstone may occur along fractures in the upper part of the Lower Sandstone, at least in the highly fractured zone above the Cigar Lake deposit.

Kaolinization is also observed in the highly conductive Altered Sandstone (between the clay/mineralized zones and the quartz-cemented zone, Figure 2) where it is associated with fractures. However, the uranium contents and the uranium-series activity ratios measured in groundwaters, in ore samples and in hostrock samples indicate that bulk dissolution of uranium is not now occurring in the Altered Sandstone and other locations deep in the deposit. The low concentrations of dissolved uranium in the waters combined with the equilibrium ratios of both $^{234}U/^{238}U$ ($0.95-1.00 \pm 0.05$) and $^{230}Th/^{234}U$ ($0.95-1.05 \pm 0.05$) in the ore and rock samples indicate reducing conditions for both current and recent water-rock interaction. These reducing conditions of the waters in the Lower and Altered Sandstones result from interaction with the ferrous mineral phases (mostly pyrite and/or

marcasite) within the hydrothermal alteration halo of the deposit (Cramer and Nesbitt 1994b).

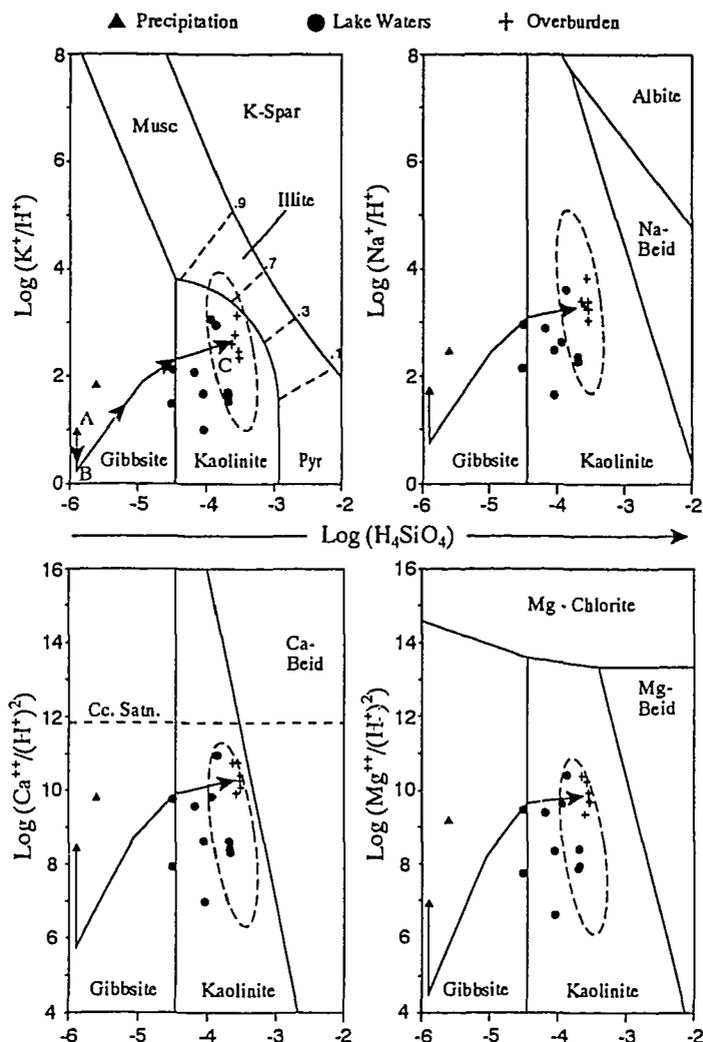


FIGURE 10: Activity-activity diagrams for the Na-, K-, Ca- and Mg-Al-Si-O-H systems. The trend emanating from precipitation (A) traces the evolutionary path to overburden water compositions (C). Reactions driving the solution composition from point B to point C is dissolution of kaolinite and illite primarily, but possibly feldspars and quartz. The elongated field (dashed curve) includes all bedrock groundwaters.

Thus, the redox potential of groundwater is lowered to reducing conditions upon entering the hydrothermal alteration halo of the deposit, so that these waters are already equilibrated with sulphide and uranium-IV phases before they contact or penetrate the clay-rich rocks hosting the uranium ore. The several hundred metres of overlying sandstone act as a natural

buffer zone, shielding the deposit from oxidizing meteoric waters recharging directly down into the reduced system. The Key Lake deposit is a good example of a situation where such a buffer zone has been removed by erosion and where the effects can be seen of direct recharge of meteoric waters on the stability of the uranium mineralization. Pervasive kaolinitization of illite and limonitization of all fractures, and complete dissolution of the primary uranium minerals have occurred in the sandstone-hosted location of the original deposit (De Carle 1986; Ruhrmann 1986). However, modelling indicates that such conversions may take millions of years and requires high groundwater fluxes to achieve the observed degree of alteration (Kettlewell 1994).

The evolution of groundwater compositions at Cigar Lake shows a strong control on the major-ion content by the clay minerals of the rocks. In fact, the composition of waters in the overburden sediments, which contain the same mineralogy as the sandstone bedrock, is most strongly affected by cation exchange reactions with the clays as well as the illite-to-kaolinite alteration (Cramer and Nesbitt 1994b). Thus, the groundwaters have already been conditioned and equilibrated with the reactive clay mineralogy in the sandstone bedrock prior to being recharged from the overburden (Figure 10). The timeframe for conditioning the composition of precipitation (rain and snow) to that of the overburden waters recharging into the bedrock is in the order of only a few years. Similar conditioning of water compositions is predicted for groundwater contacting and passing through the clay buffer in a disposal vault (Johnson et al. 1994). However, the Na-bentonite clay proposed for the buffer has about a ten-fold higher cation exchange capacity compared to illite, and is therefore more sensitive to the composition of the groundwaters contacting the buffer. Given the relatively low $K^+/(Ca^{2+} + Mg^{2+} + Na^+)$ ratio in deep groundwaters in the Canadian Shield (Gascoyne 1988) and the expected low permeability and groundwater flux in and around a disposal vault, the alteration of bentonite will be extremely slow. The composition of groundwater passing through the buffer will, however, be affected by cation exchange reaction on the bentonite clay without much prior conditioning in the clay-poor host rock surrounding the disposal vault.

The conclusions on the observed water-rock interaction in the Cigar Lake deposit are:

- The iron and sulphur redox couples are the primary controls on the redox geochemistry during water-rock interaction.
- The major-ion composition of groundwater is strongly controlled by interaction with clay minerals.
- Water-rock interaction in several hundred metres of host rock containing redox sensitive minerals provides a good natural buffer zone for a deposit containing high-grade uranium-IV ore.

4.6 THE EFFECTS OF COLLOIDS, ORGANICS AND MICROBES

Although theoretical considerations indicate that radionuclide mobility may be affected by the presence of particles (through sorption), dissolved organic compounds (through complexation) and microbial activity (through redox buffering), there is a very limited database on these processes in deep natural systems. The Cigar Lake deposit provided an opportunity to study these aspects in a deep natural system containing a relatively concentrated source of uranium and other radionuclides.

The colloid studies at Cigar Lake (Vilks 1994; Vilks et al. 1988, 1993) were focussed on determining the concentration, size and composition of particles throughout the deposit, and on determining the trace-element and radionuclide sorption on the particles. Aspects of particle migration were addressed by determining particle-size distributions, looking for evidence of particle dispersion away from the ore zone, studying particle behaviour in a flow field, and assessing mechanisms of particle generation. The results of these studies include the following observations:

- In the case of reversible radionuclide sorption onto the particles, the average particle contents in the dilute Cigar Lake groundwaters are too low to have a significant impact on radionuclide migration.
- In the case of irreversible sorption, some radionuclides (e.g., U, Th, Ra) can remain fixed on particles for thousands of years (up to 8,000 a) and may thus contribute to radionuclide migration.
- A large portion of natural particles in Cigar Lake groundwaters are generated by erosion of fragments from minerals and alteration products from the host rock. Thus, particle concentrations are highest in friable rock and lowest in well-consolidated rock.
- The composition of groundwater particles in the ore zone is distinct from that in the host sandstone, indicating that the transport of particles from the ore through the clay zone has been negligible, and the mobilization of clay particles from the clay into the sandstone has not been important.

The studies at Cigar Lake lead to an overall conclusion that the role of colloids is not important in radionuclide migration, at least on a time scale of 10^4 a based on the 8,000-a-old particles found in the ore zone waters.

The characterization of organic compounds in the Cigar Lake groundwaters (Pettersson et al. 1994; Vilks and Bachinski 1994) included the determination of total organic carbon (TOC) in all waters, of volatile and solvent extractable organics and of humic compounds, and detailed characterization of fulvic acids (including ^{14}C ages). The results of these studies include the following observations:

- The TOC content in all surface and groundwaters is ≤ 2 mg/L, except in ore zone waters (up to ~ 11 mg/L). Volatile and solvent-extractable organics account for $\ll 10$ % of the TOC (most of which are probably contaminants), and only 15 to 25 % of TOC are humic substances except in the altered sandstone (< 10 %) and in the ore zone (< 2 %).
- The humic fraction in all groundwaters consists largely of low-molecular-weight fulvic acid, with the oldest ^{14}C ages measured for humics from the ore zone (ranging up to 15,000 a).
- The abundance and complexing capacity of fulvic acids in all groundwaters is insufficient to have a significant influence on the speciation of either U^{4+} or U^{6+} .

From the studies at Cigar Lake, the overall conclusion on the role of organics is that the humics in the groundwaters are unlikely to play any significant role in either speciation or mobilization of uranium or any other actinide with a valency of ≥ 4 .

Microbial studies on both water and rock samples from the Cigar Lake deposit (Stroes-Gascoyne et al. 1994; Francis et al. 1994) were focussed on the identification and quantification of micro-organisms, and on evaluating the effect of microbial activity on the redox and uranium chemistry. The results of these studies include the following observations:

- Despite low nutrient contents in the groundwaters, micro-organisms are present in all groundwaters and seem capable of surviving in radiation fields.
- Anaerobic bacteria are, on average, about 10 times more abundant than aerobic bacteria, in agreement with the prevailing reducing chemical environment in the deposit.
- Sulphate-reducing, iron-related and denitrifying bacteria are common in both groundwaters and rocks from the most reducing parts of the deposit, and their mediation in redox reactions may contribute to the redox-buffering capacity of the system.

From the studies at Cigar Lake, the overall conclusion on the role of micro-organisms is that bacteria can survive in natural radiation fields and their activity may contribute toward maintaining a reducing chemical environment, thereby reducing the potential for dissolution and mobilization of redox-sensitive radionuclides.

4.7 MASS-TRANSPORT OF RADIONUCLIDES

One of the objectives for the detailed litho- and hydrogeochemical studies on the Cigar Lake deposit was to identify the occurrence and location of radionuclide migration from the mineralized zones. However, no evidence was found from studies of the ore-clay-altered sandstone sequence of significant radionuclide migration taking place, either currently or during the recent ~ 1-Ma history of the deposit. In contrast, active radionuclide migration may occur at shallower depths as the result of lateral groundwater flow through the limonitic and bleached sandstones (see Figures 2 and 3). To test this hypothesis, uranium-series isotopes were analysed in rock samples from potential transport paths (i.e., fractures and obviously permeable horizons) in the ore, clay and altered sandstone units. The uranium-series data indicate that some mobilization of uranium, and possibly radium, has taken place, but only on a small, localized scale (i.e., both preferential removal and deposition of isotopes occur side by side). This is supported by the isotopic composition of the reducing groundwaters (from the permeable zones) in these rock units, where high $^{234}\text{U}/^{238}\text{U}$ values likely result from α -recoil rather than from dissolution processes. Furthermore, the amounts of dissolved uranium and other radionuclides in groundwaters from either side of the clay zone can be compared to give concentration gradients across the clay zone that have either positive, zero or negative slopes. Thus, the general conclusion with regard to radionuclide migration at Cigar Lake is that any modelling of mass transport in the deposit must be considered as being only hypothetical, i.e. none is actually observed.

A series of iterative, generic models were developed to evaluate various mass-transport scenarios in the Cigar Lake deposit (Liu et al. 1994). These generic models were based on the assumption that any potential radionuclide migration takes place from the ore zone through the clay zone to the aquifer in the altered sandstone (i.e., a positive concentration gradient across the clay zone). The models that were developed consider a range of scenarios for the source term and transport processes, including solubility-controlled and oxidative dissolution of UO_2 , diffusion and advection, and coupling of mass-transport and geochemical processes. The results from this generic modelling include the following general conclusions:

- The extent of a uranium plume breaking through the clay/altered sandstone interface would not exceed 0.5 m into the altered sandstone.
- The one-dimensional modelling results are in good agreement with most measured parameters.
- At the dissolved- O_2 levels measured in the ore-zone waters, the modelling predicts that oxidation of the clay/ore contact over a distance of 1 m is reasonable.
- The low-permeability clay zone surrounding the mineralization is the most important parameter in limiting radionuclide mass transport.

5. CONCLUSIONS

The analog studies on the Cigar Lake uranium deposit have provided valuable information and insight on a number of safety-assessment aspects related to the Canadian concept for disposal of nuclear fuel waste. The important general conclusions can be summarized as follows:

- UO₂ dissolution and stability:
 - UO₂ is stable under reducing conditions over geological time;
 - little dissolution of UO₂ occurred during 100 Ma; and
 - congruent dissolution of UO₂ is controlled by surface alteration.

- Clay sealing:
 - clay (in this case illite) can provide effective, long-term sealing;
 - illite is stable under suitable conditions over geological time; and
 - clay is an efficient barrier to radionuclide and colloid migration.

- Radiolysis:
 - a radiolytic-oxidation model for UO₂ dissolution appears overly conservative for assessment of AECL's disposal concept; and
 - dissolved Fe²⁺ is an important scavenger of radiolytic oxidants.

- Groundwater chemistry:
 - interactions with clay minerals control the bulk composition of groundwater;
 - redox geochemistry is strongly controlled and buffered by the iron and sulphur redox couples; and
 - the evolution of groundwater compositions can be predicted by existing geochemical codes.

- Colloids:
 - colloid and particle contents in groundwater are generally lowest in competent rock and highest in friable rock;
 - only a small fraction of radionuclides in water is attached to colloids;
 - colloids can be effectively sealed in by clay-rich rocks; and
 - colloids were not important in radionuclide migration at Cigar Lake, at least on the time scale of the last 10⁴ a.

- Organics and Microbes:
 - low humic contents in dilute water are unlikely to play a significant role in either speciation or mobilization of radionuclides;
 - microbes can survive in radiation fields, and they can mediate in redox control and buffering; and
 - organics and microbes are unlikely to adversely affect radionuclide migration in the near field.

- Radionuclide migration:
 - natural hydrologic barriers and appropriate geochemical conditions in a relatively open, natural system are effective in limiting radionuclide migration over any significant distance; and
 - clay sealing is an important barrier to radionuclide migration.

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