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CLAY MINERALOGY, GEOCHEMISTRY, AND PARTITIONING
OF URANIUM WITHIN THE ALTERATION HALO OF THE
CIGAR LAKE URANIUM DEPOSIT,
SASKATCHEWAN, CANADA

by

JEAN BARBARA McCANN PERCIVAL, B.Sc., B.Ed., M.Sc.

A thesis submitted to the Faculty of Graduate
Studies and Research in partial fulfillment of
the requirements for the degree of
Doctor of Philosophy

Ottawa-Carleton Geoscience Centre
Department of Earth Sciences
&
Geotechnical Science Laboratories,
Department of Geography

Carleton University
Ottawa, Ontario

November 30, 1989

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The undersigned hereby recommend to
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acceptance of the thesis

Clay Mineralogy, Geochemistry and Partitioning
of Uranium Within the Alteration Halo of the
Cigar Lake Uranium Deposit,
Saskatchewan, Canada

submitted by

Jean Barbara McCann Percival

in partial fulfillment of the requirements
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Frontispiece: Aerial view of Cigar Lake, looking south.

ABSTRACT

The high-grade, unconformity-type, Cigar Lake uranium deposit, occurs close to the unconformity between Athabasca Group sandstones and crystalline basement rocks of the Churchill Province. An alteration halo grades outwards from the deposit through zones characterized by: (1) Fe-chlorite + illite $\pm$ carbonate $\pm$ uraninite $\pm$ gersdorffite; (2) sudoite + illite $\pm$ hematite $\pm$ sulphides; (3) illite + hematite; and (4) illite $\pm$ kaolinite $\pm$ hematite. Detrital kaolinite was almost completely transformed to illite. Illite polytypes grade from 3T-2M₁ mixtures near the ore, to 2M₁, to 2M₁-1M mixtures in overlying sandstone. In the alteration zone, Kübler indices of illite crystallinity indicate high-grade diagenetic to anchimetamorphic, with local epizonal, conditions.

Although the alteration to illite extends upwards and outwards hundreds of metres, U and trace elements are concentrated only within 50 m of the ore. These elements have been passively concentrated by removal of silica. Mass balance calculations indicate a possible volume change of 94%.

Stable isotopic measurements for illite-rich samples indicate little disturbance to the alteration halo since primary mineralization, ca. 1300 Ma ago. Average δD (-82 o/oo) and $\delta^{18}O$ (+10 o/oo) values for illite-rich clay are

comparable to similar samples from other Athabasca U deposits, indicating fluids of regional extent. Illite K-Ar dates range from 1255 ± 28 to 1148 ± 28 Ma, suggesting either recrystallization, or re-setting by hydrothermal fluids, possibly related to the emplacement of the Mackenzie dyke swarm ca. 1267 Ma ago. A more recent event is recorded in a sudoite + illite mixture from the basement, at 815 ± 30 Ma, that corresponds with a regional event recorded elsewhere in the basin. An Fe-chlorite-bearing ore sample shows evidence for interaction with present-day meteoric waters.

Carbonate, uraninite, amorphous Fe-oxides, crystalline Fe-oxides, and residual silicate phases were analyzed for U using selective sequential extraction. About one-third of the extractable U occurs as uraninite, and 4 - 60% is associated with the clay minerals. The restricted distributions of U and other elements, which mimic radionuclides of concern in nuclear fuel waste disposal, indicate that the illite-rich materials have provided an effective sorptive barrier for about 1300 Ma.

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CHAPTER ONE

INTRODUCTION

1.1 IMPORTANCE OF RADIONUCLIDE MOBILITY STUDIES

1.1.1 Introduction

Trace element mobility and the interaction of fluids with rock, water and soil at surface temperatures are important to mineral exploration and the study of element migration from waste disposal sites. There is special concern about the potential release of long-lived radionuclides (e.g., ^{226}Ra , ^{237}Np , ^{239}Pu and ^{241}Am) into the biosphere from high-level nuclear fuel waste repositories. Although laboratory experiments of short duration are commonly used to address these problems, it is difficult to extrapolate these results to the time spans necessary for safe isolation of radioactive contaminants.

Field studies of natural analogues to nuclear waste repositories complement laboratory research by providing a link between laboratory results and long-term prediction for isolation of long-lived radionuclides. By studying the alteration history of a rock body from its time of crystallization to current interactions with the hydrosphere, inferences can be made about the mobility and redistribution of certain elements (Kaminen, 1986). Alteration products, such as clay minerals, are sensitive indicators of low-temperature geologic processes (Hoeve and Quirt, 1984) and

can provide useful information about the history and timing of rock alteration.

1.1.2 Mechanisms for Retardation of Radionuclides

The mobility of radionuclides in the geosphere depends on two main factors: (1) the solubility of their compounds in groundwater and other fluids; and (2) sorption by minerals along fluid flow paths. Sorption includes simple adherence to charged mineral surfaces and incorporation into mineral structures (Krauskopf, 1986a). These processes are controlled by temperature, pressure, extent and nature of the solid surface, pH, Eh and ionic strength of the interacting solutions, as well as the presence of competing ions and ligands that form stable complexes.

Clay minerals, composed of variably arranged octahedral (trioctahedral or dioctahedral) and tetrahedral structural units, stacked in the direction of the c-axis, have both high surface area and high adsorption capacity (e.g., smectite and illite). Thus radionuclide mobility may be inhibited by cation adsorption to broken-bond edges or exchange with other cations on clay mineral surfaces (Hall, 1987).

1.1.2 Field Studies

In Canada, the Canadian Nuclear Fuel Waste Management Program, under the auspices of Atomic Energy of Canada

Limited, has evaluated the potential for burial of high-level nuclear fuel waste in plutonic rocks of the Precambrian Shield. In particular, granitic plutons in Ontario (Eye-Dashwa Lakes pluton, Atikokan) and Manitoba (Lac du Bonnet batholith, Lac du Bonnet) as well as gabbroic rocks in Ontario (East Bull Lake gabbro-anorthosite pluton, near Massey) have been sites for detailed geological, geochemical, geophysical and hydrogeological investigations (see Kaminen, 1986; Kaminen et al., 1986; McCrank et al., 1989; Scott and Gibb, 1989). Similar sites are under investigation in Sweden and the U.S.A. (Krauskopf, 1986a). In addition, salt domes, thick salt beds, rhyolite tuffaceous units and basalt flows are under consideration in the U.S.A. Shales and argillites are being studied in Belgium and Italy and salt domes in the Federal Republic of Germany (Krauskopf, 1986a).

Unconformity-type uranium deposits in northern Saskatchewan are under study in Canada as natural analogues of the high-level nuclear waste disposal concept. These ore bodies occur in or near the unconformity between Proterozoic sedimentary rocks of the Athabasca Group and the metamorphic basement of the Churchill Province. Extensive alteration of the host rocks has formed a clay-rich envelope, which has limited U mobility (Cramer 1986a). The factors controlling the stability of the U-ore minerals for over 1 Ga in these

open, water-saturated deposits are of special interest. These factors include the thermal history of the ore body, composition of ore, host rocks and groundwaters, distribution and history of trace elements, and spatial and age relationships (Cramer, 1986a; Cramer et al., 1987). The Cigar Lake deposit was chosen for detailed study because it has simple geometry, occurs above the unconformity entirely within the Athabasca Group, and is sufficiently deep so that it has not been affected by recent weathering and erosion.

1.2 OBJECTIVES AND APPROACH TO THE STUDY

A suite of samples was selected from the alteration halo around the Cigar Lake deposit to study the influence of mineralogy, specifically the clay minerals, on U mobility.

The overall objectives were to:

- (1) determine the distribution, composition and genesis of the clay minerals;
- (2) define the distribution of trace elements within the alteration halo;
- (3) analyze the stable isotopic (H and O) composition of the clay minerals to assess the involvement of groundwater in the alteration process;
- (4) constrain timing of alteration using geochronology;
- (5) determine the bonding site(s) for U;
- (6) infer the pattern and process of U mobility; and

- (7) discuss the results in the context of a natural analogue to a high-level nuclear fuel waste repository.

Samples were selected in August, 1985, from the core racks at the Cogema drilling camp at Waterbury Lake, Saskatchewan. The samples were processed for petrographic, mineralogical and geochemical studies at Carleton University.

1.3 ORIGINAL CONTRIBUTIONS

The thesis has contributed to the understanding of the Cigar Lake deposit and to radionuclide/trace element associations and mobility in the following ways:

- (1) determination of the distribution of clay minerals in the Cigar Lake alteration halo using semi-quantitative X-ray diffraction techniques;
- (2) estimation of the degree of illite crystallinity in the halo;
- (3) identification of the illite polytypes and their distribution;
- (4) determination of the structure and composition of the dominant chlorite species;
- (5) analysis of major, trace and rare earth elements indicating consistent enrichment factors for Cigar Lake samples with respect to regional background values;
- (6) estimation of volume/mass changes during hydrothermal alteration and subsequent silica dissolution, using

mass balance calculations;

- (7) discovery of on-going low-temperature alteration based on stable isotopic and K-Ar age determinations;
- (8) determination of the forms and associations of U in the alteration halo;
- (9) deduction of limited U mobility in the alteration halo since ore formation;
- (10) application of the results within the natural analogue context.

CHAPTER TWO

GEOLOGICAL SETTING OF THE CIGAR LAKE DEPOSIT

2.1 INTRODUCTION

The Cigar Lake uranium deposit occurs in the Athabasca basin of northern Saskatchewan (Figure 2.1), near the unconformity between Early Proterozoic metapelites of the Wollaston Group and flat-lying Middle Proterozoic sandstones of the Manitou Falls Formation of the Athabasca Group. Unlike most unconformity-type deposits in the basin (e.g., Key Lake, Midwest, Collins Bay), the Cigar Lake deposit is hosted by the sandstones above the unconformity. The deposit is continuous, of simple geometry, and contains massive mineralization with intense host-rock alteration (Bruneton, 1987).

Cogema Canada Limiteé discovered the deposit in 1981 when a drill hole, to test basement geophysical conductors, encountered mineralization. The deposit is now undergoing development and will be brought into production in the early 1990s by the Cigar Lake Mining Corporation, a consortium of joint ventures including Cameco (50.75%; merger between Saskatchewan Mining and Development Corporation and Eldorado Resources Limited), Cogema Canada Limiteé (32.625%), Idemitsu Exploration Canada Limited (12.875%) and Corona Grande

Figure 2.1: Regional geology of northern Saskatchewan (after Macdonald and Broughton, 1980).

Exploration Corporation (3.75%; subsidiary of Cogema) (Bruneton, 1987).

2.1 REGIONAL GEOLOGY

2.2.1 Crystalline Basement

The crystalline basement of northern Saskatchewan is composed of Archean and Aphebian sedimentary, volcanic and plutonic rocks of the western Churchill Structural Province. It forms part of the Trans-Hudson Orogen (Hoffman, 1981). The rocks were variably affected by thermotectonic events during the Hudsonian orogeny (ca. 2000 - 1700 Ma) (Lewry et al., 1985).

The basement rocks in northern Saskatchewan can be subdivided into three tectonic zones (Lewry et al., 1985). From southeast to northwest they are (Figure 2.1): (1) Rottenstone-La Ronge Magmatic Belt; (2) Cree Lake (Mobile) Zone; and (3) Northwestern Cratonic or Amer Lake Zone. The Northwestern Cratonic and Cree Lake Zones, comprising the ensialic portion of the Trans-Hudson Orogen, contain the Athabasca basin and are separated from the ensimatic part of the orogen by the Needle Falls Shear Zone. These tectonic zones have been further subdivided into lithostructural domains based on lithological, structural and metamorphic characteristics (Lewry and Sibbald, 1977, 1979; Lewry et al., 1985).

The Rottenstone-La Ronge Magmatic Belt (formerly called the Eastern Complex (Tremblay, 1982)) has been identified by Lewry et al. (1981) as a major Hudsonian, Cordilleran-type arc massif, composed of Hudsonian migmatites in the Rottenstone Domain and thick, folded metasedimentary and meta-volcanic rocks in the La Ronge Domain (Tremblay, 1982).

The Cree Lake (Mobile) Zone consists of Aphebian meta-sedimentary rocks, unconformably overlying Archean granite gneisses. The miogeoclinal Aphebian rocks of a basal graphite-bearing pelite interlayered with quartzite, are overlain by arkoses and calc-silicate rocks and are capped by quartzite, amphibolite and more calc-silicate rocks. Both the Aphebian and Archean rocks have undergone intense Hudsonian deformation and metamorphism (Tremblay, 1982; Sibbald, 1985).

The Western Cratonic Zone (now called Amer Lake Zone) is bounded on the east by the Virgin River-Black Lake Shear Zone and includes the area north of Lake Athabasca as well as the Clearwater, Firebag and Western Granulite Domains of Lewry and Sibbald (1977). The Western Cratonic Zone may represent a former stable cratonic foreland of Archean crust overlain by Aphebian supracrustals. It has been affected by Late Kenoran high grade metamorphism, Hudsonian deformation and Aphebian anatexis (Tremblay, 1982; Lewry et al., 1985).

2.2.2 Sub-Athabasca Group Regolith

Chemical weathering of the Aphebian and Archean crystalline basement produced a regionally-developed, laterite-like regolith, which is partly preserved under the Athabasca Group sediments. Four laterally correlatable zones, based on colour, were reported by Macdonald (1980, 1985) and comprise an upper bleached zone, a hematite zone, a white zone and a green/red zone. The lower three zones, chemically and mineralogically similar to modern lateritic profiles (Macdonald, 1985), exhibit mineralogical zonation. Kaolinite occurs in the hematite and white zones, whereas illite + chlorite occur in the green/red zone. The presence of the upper bleached zone is inconsistent with an oxidizing, weathering environment. Macdonald (1985) suggested that the bleached zone, which is proximal to the unconformity, was produced by reducing diagenetic fluids from the Athabasca Group sediments.

2.2.3 Athabasca Group

Wrench faults in the basement initiated three north-east-southwest trending sub-basins following late Hudsonian orogenic activity (see Figure 2.1). Transgressive sediments quickly filled the sub-basins, eventually coalescing to form the larger Athabasca basin (Ramaekers, 1981, 1983; Sibbald, 1985). Four marine transgressive sequences and one regres-

sive fluvial wedge comprise the Athabasca Group (Figure 2.2). The Athabasca Group sedimentary succession covers an area in excess of 100 000 km², and reaches a thickness of 1400 m (Sibbald, 1985).

The early, marine sandstones of the Fair Point Formation were deposited in the Jackfish sub-basin (not shown on Figure 2.1; west of Carswell Structure), with fluvial and marine sandstones, pebbly sandstones and conglomerates of the Manitou Falls Formation (unit A) deposited in the Mirror sub-basin. Coarse alluvial fans of the Manitou Falls Formation (unit B) developed in the Cree sub-basin, and graded westward into distal, braided-stream deposits (units C and D). Units B, C and D form an eastward-thickening wedge (up to 1000 m) of fluvial (regressive cycle) sandstones (Ramaekers, 1979, 1980, 1983; Sibbald, 1985).

A second marine transgression into the Mirror sub-basin deposited the pebbly sandstones of the Lazenby Lake Formation (in the southwest), and the sands, silts and muds of the Wolverine Point Formation. The Wolverine Point Formation is overlain by pebbly sandstones of the Locker Lake, Otherside and Tuma Lakes Formations. The Athabasca Group is capped by shallow marine sandstones, siltstones and mudstones of the Douglas Formation and oolitic and stromatalitic dolomites of the Carswell Formation. These latter two

formations are exposed in the Carswell structure (Sibbald, 1985).

The Athabasca sandstones have undergone a complex history of diagenesis, intensive oxidation, and post-depositional leaching which generated their red-bed characteristics (Hoeve et al., 1980). The Athabasca sandstones are now composed of orthoquartzites with an illite- and kaolinite-rich matrix, and significant, but variable, amounts of hematite (Ramaekers, 1983).

2.2.4 Quaternary Geology

The Athabasca basin and surrounding crystalline terrain are covered with glacial drift. The area in the eastern part of the basin was deglaciated about 8300 years ago (Schreiner, 1983). The presence of the glacial landforms and drift with subsequent post-glacial modification have produced a rolling landscape, with muskeg and lakes filling depressions between hills and ridges.

2.2.5 Geochronology

The Athabasca Group was deposited during Helikian time. Whole rock Rb-Sr dating of the tuffaceous unit of the Wolverine Point Formation yields ages of 1450 ± 30 Ma (Bell, 1981) and 1430 ± 30 Ma (Armstrong and Ramaekers, 1985). Authigenic illites have been dated by K-Ar method and yield

"diagenetic" ages between 1350 and 1050 Ma (Clauer et al., 1985; Wilson et al., 1987). Primary mineralization and incipient hydrothermal alteration commenced 100 to 150 Ma after deposition, based on U-Pb dates of pitchblende which range from 1350 to 1200 Ma (Wendt et al., 1978; Cumming and Rimsaite, 1979; Hoeve et al., 1981; Baadsgaard et al., 1984; Trocki et al., 1984; Bell, 1985; and Ruzicka and LeCheminant, 1986). Rocks of the Athabasca Group were later cut by a series of northwest-trending diabase dykes that have been dated, by U-Pb on baddeleyite fractions, at 1270 ± 4 Ma (LeCheminant and Heaman, in press) and, by Rb-Sr mineral isochrons that yield ages of 1310 ± 70 , 1160 ± 40 Ma and 1100 ± 100 (Armstrong and Ramaekers, 1985).

2.3 URANIUM MINERALIZATION

Uranium deposits in the Athabasca basin are found mainly near the eastern margin (Figure 2.3). Other deposits are found in the Carswell Structure, and along the northern margins of the basin. Characteristics of the uranium deposits include (Sibbald, 1985; Table V, p. 145): (1) spatial association with the sub-Athabasca unconformity; (2) proximity to graphite-bearing rocks in the basement; (3) structural controls including thrust faults, basement relief and solution collapse in both the basement and the Athabasca Group; (4) high grade mineralization (e.g., up to 14% U in Cigar Lake);

Figure 2.3: Location of uranium deposits in the Athabasca basin (1 = Rabbit Lake; 2 = Collins Bay; 3 = Eagle Point; 4 = Dawn Lake; 5 = McClean Lake; 6 = Midwest Lake; 7 = Cigar Lake; 8 = Key Lake; and 9 = Cluff Lake).

(5) occurrence of pitchblende and coffinite as primary uranium minerals; (6) complex mineralogy and geochemistry; (7) presence of glassy hydrocarbons in ore; (8) extensive alteration haloes; and (9) age of initial mineralization around 1300 Ma.

Hoeve and Quirt (1985a) correlated two stages of hydrothermal activity with basin evolution and prograde diagenesis. The early phase (1350 - 1250 Ma) is represented by formation of pitchblende, Ni-Co arsenides and sulpharsenides. This phase was accompanied by high-grade diagenesis (150 - 200 °C) which produced clay alteration zones which rise hundreds of metres into overlying sandstones. Concomitant dissolution of quartz in the sandstones led to collapse of the overlying sandstones and to clay enrichment. Uranium ore bodies formed in a redox environment which also produced an inner reduced, hematite-free zone and an outer oxidized, specular hematite-bearing zone (Hoeve and Quirt, 1984, 1985b).

The second phase (1100 - 1050 Ma) is characterized by the presence of dull, massive pitchblende, base metal sulphides, siderite, ferrous iron chlorite and veining of tourmaline and euhedral quartz. Extensive bleaching is superimposed on the first-phase alteration (Hoeve and Quirt, 1985b).

A diagenetic-hydrothermal model has been proposed for genesis of the unconformity-type uranium deposits (Hoeve and Sibbald, 1976, 1978; Hoeve et al., 1980; Hoeve and Quirt, 1984, 1985b, 1987). Saline, oxidized, U-bearing diagenetic solutions penetrated the unconformity via fault zones, and reacted with graphite-bearing basement rocks. A new reduced fluid, containing hydrocarbons and carbon dioxide, emerged at the unconformity; mineralization occurred when the two fluids met. Temperatures of the solutions were between 150 and 200 °C, based on fluid inclusion studies (Pagel, 1975, 1977) and stable isotopic data (Wallis et al., 1983). The salinities are reported to be in the order of 250 to 350 g/L TDS (Cramer, 1985).

2.4 DETAILED GEOLOGY

2.4.1 Cigar Lake Uranium Deposit

The Cigar Lake uranium deposit is located southwest of Waterbury Lake (see Figure 2.2). The deposit is about 1800 m long, trends in an east-west direction and ranges from 20 to 105 m in width (Figure 2.4). The ore body has been subdivided into two parts. Estimated reserves for the "East Zone" are 110 000 t of U with an average grade of 12.3% and for the "West Zone", 40 000 t at 4% grade (Bruneton, 1985, 1987; Fouques et al., 1986). The deposit occurs at the unconformity between the Athabasca Group sandstone and the

Figure 2.4: Plan view of the Cigar Lake uranium deposit showing boreholes sampled (after Fouques et al., 1986; Brunet, 1987).

Aphebian basement, about 410 to 450 m below the surface (Figure 2.5).

The deposit is underlain by biotite-cordierite graphitic metapelites and calc-magnesium pyroxene-amphibole gneisses of the Wollaston Group. The graphitic metapelites have been subdivided into fine-grained metapelites and augen-textured metapelites. The ore body occurs predominantly above the augen metapelites, which formed a basement topographical ridge (Bruneton, 1985, 1987; Fouques et al., 1986).

Evidence for upper amphibolite grade of metamorphism is reported by Bruneton (1987) and includes the absence of primary muscovite, the presence of sillimanite-cordierite-garnet association and anatectic quartzofeldspathic pegmatoids. Sericitization of cordierite and feldspar, and chloritization of cordierite, biotite, amphibole and garnet are indicative of retrograde metamorphism in the basement.

Bruneton (1987) reported that the paleoweathering profile in the Waterbury Lake area is consistent with that described by Macdonald (1980, 1985) elsewhere in the basin. Three colour zones have been recognized in drill core: an orange to yellow zone, a red oxidized zone and a green zone. The orange to yellow zone is thin (< 2 m) and consists of quartz grains in a kaolinite matrix. The red and green zones are similar to the hematite and green zones described

Figure 2.5: Schematic cross-section of alteration halo surrounding the Cigar Lake ore deposit. The ore deposit, at 450 m below the surface, occurs above the unconformity between crystalline basement and the Manitou Falls Formation of the Athabasca Group. The alteration halo has been subdivided into a series of distinct zones above the ore: quartz-cemented cap, altered sandstone, clay-rich halo and hematite-rich zone. Crystalline basement below the ore is characterized by argillic alteration (after Cramer, 1986b; Fouques et al., 1986).

above. The regolith is well-developed in the calc-magnesium gneisses and fine-grained metapelites (up to 60 m), and poorly developed in the coarse-grained graphitic metapelites (Bruneton, 1987).

Poorly-sorted and gritty sandstones of the Manitou Falls Formation (units B, C and D) directly overlie the ore deposit. Quartz, biotite and accessory minerals, such as zircon, tourmaline and titanomagnetite, comprise the detrital fraction, with about a 5 to 20% illite and kaolinite matrix (Bruneton, 1985; Fouques et al., 1986). The sandstones, pink to purple in colour, have well-developed Liesegang bands and rings. The upper 100 m was affected by a late, limonitic alteration, and the 30 m above the unconformity was affected by chloritization (Bruneton, 1987).

Bruneton (1987) recognized three stages of mineralization. The first hydrothermal stage formed radiating pitchblende and euhedral uraninite with later Ni-Co arsenides, sulpharsenides and Ni-Co-Fe sulphides, which brecciated the pitchblende. Ruzicka and LeCheminant (1986) reported a 1300 Ma U-Pb concordia age for pitchblende samples.

The second stage of mineralization is characterized by two pitchblende-bearing phases. The first is associated with secondary Ni-Co arsenides, sulpharsenides, sulphides and Fe-Cu sulphides, with the second phase associated with Fe-Cu sulphides only. Bruneton (1987) reported that these

phases occur in different structures than the first-stage mineralization. The third stage is characterized by the replacement of pitchblende by Fe-oxides and -hydroxides, formed between 450 and 200 Ma ago.

Perched mineralization, located in the sandstone, up to 300 m above the ore body, consists of pitchblende and coffinite with microdisseminated pyrite and marcasite. According to Bruneton (1987) the perched mineralization is probably the result of U remobilization along steeply-dipping faults and fractures.

Basement mineralization occurs as two types: (1) pitchblende vein-type ore and (2) breccia-type ore (Bruneton, 1987). Thin mineralized veins or zones that occur near the unconformity probably resulted from migration of U along faults and fractures.

2.4.2 Alteration Halo

The ore body is surrounded by an intense hydrothermal alteration halo which can be subdivided into distinct zones, schematically shown in Figure 2.5. The pink to purple sandstone of the Manitou Falls Formation grades through a slightly altered grey sandstone characterized by dissolution textures, lower quartz content and slightly higher clay content, into the quartz-cemented cap of the alteration halo proper (see blow-up on Figure 2.5). The quartz-cemented cap

contains fractures lined with drusy or euhedral quartz crystals. A second zone of altered grey sandstone occurs between the quartz-cemented cap and the clay-rich zone.

Quartz dissolution textures are more pronounced in the altered sandstone and clay contents range from 10 to 30%, increasing towards the ore. The clays in the clay-rich halo have been subdivided into: (1) white, pale yellow, pale green or pale grey "soft" clay containing illite; (2) pale green to pale or dark grey "intermediate" clay containing Fe-Mg illite and chlorite; and (3) dark green to dark brown "indurated" (hard and competent) clay containing Fe-Mg illite and chlorite, "ferrikaolinite" and siderite (Fouques et al., 1986; Bruneton, 1987). The clay-rich zone grades into a secondary hematite-rich clay zone above the ore.

In the basement below the ore zone, argillic alteration, extending down to about 5 m, is accompanied by the concomitant disappearance of original rock textures. The main clay minerals are illite and Al-Mg chlorite (sудоite; Percival and Kodama, 1989).

CHAPTER THREE

SAMPLE CLASSIFICATION AND DESCRIPTION

3.1 SAMPLE SELECTION

Core samples were selected from 10 boreholes transecting the eastern alteration halo and ore zone of the Cigar Lake deposit, along five north-south grid lines (7 + 50E to beyond 9 + 50E), and from one drill hole (139) from a distal location (see Figure 2.4). The suite includes 52 unaltered and 93 variably altered sandstone samples from the Manitou Falls Formation of the Athabasca Group, and 7 altered basement samples. Cores from boreholes WDG1-119 and -139 were sampled approximately every 30 m, from the overburden/bed-rock contact to below the unconformity.

Distribution of the lithologies of the sampled boreholes are briefly described and illustrated in Appendix A (Figures A.1 to A.4). Table A.1 provides information about sample characteristics (number system, depth, colour and lithology). Details about sample preparation are also given in Appendix A.

3.2 TEXTURE AND CLASSIFICATION

3.2.1 Sample Texture

As an aid to sample classification, the particle-size distribution was determined for all altered sandstone and

basement samples. The procedure for particle size analysis, sedimentation with pipette sampling, is described in Appendix A. Results of the analysis are shown in Figure 3.1 and Table A.2 (Appendix A). On a ternary diagram, with apices corresponding to clay-, silt- and sand-sized distribution, the particle-size data plot in a field extending from near the sand apex toward the clay - silt join. Progressively more altered samples show a decrease in sand-sized particles. The sand content ranges from 20 to 97% with about 67% of the samples containing > 50% sand-sized particles.

The particle size distribution of the Fe-rich samples after deferration, using the dithionite-citrate-bicarbonate (DCB) method of Jackson (1975), indicates an increase in the amount of clay-size and silt-size material with respect to untreated samples (Figure 3.2). Increases of up to 25% in the composite and basement specimens are registered for both silt and clay. These results indicate that Fe-oxides have acted as cementing agents. With more aggressive treatment, the particle-size distribution of all samples (Figure 3.1) probably would shift toward the silt - clay side of the ternary diagram.

The principal constituents of the altered sandstone samples are quartz and clay minerals, and of the basement samples, clay minerals. Several criteria indicate recrystallization: coarse clay minerals; clay mineral aggregates;

Figure 3.1: Particle-size distribution for all altered samples. Note continuum of particle-size distribution with respect to lithological classification of altered sandstone specimens.

Figure 3.2: Particle size distribution of Fe-rich samples before and after extraction by DCB. Note shift away from sand apex toward clay - silt join after treatment.

and cemented quartz silt- to sand-sized aggregates. It is possible that dispersion, using Calgon, was insufficient to break down the coarse aggregates. Examination of a few specimens by scanning electron microscopy revealed clean separations of the $< 2 \mu\text{m}$ and $2 - 5 \mu\text{m}$ fractions. Sand-sized material from a few samples was examined petrographically and only discrete quartz grains were identified. The particle-size distribution may not be a true representation of the actual particle sizes, because of variably coherent aggregates. However, the analysis does provide a basis for subdividing the altered samples.

3.2.2 Sample Classification

Samples have been classified into 5 types based on appearance, competence (intact vs. friable) and particle size-distribution. The five types are: (1) sandstone; (2) clayey sandstone; (3) sandy claystone; (4) composite; and (5) basement. The lithological terms do not have any genetic significance.

In hand specimen, the white to grey, pink or purple sandstones can be massive or graded, and they are generally poorly sorted. They contain subrounded to rounded quartz grains in a clay-rich matrix. Two examples are shown in Figure 3.3a and b. Hematite is present as disseminated particles in the clay-rich matrix (Figure 3.3b) and as oxid-

Figure 3.3a: Sandstone containing 90 - 95% subrounded quartz grains set in an illite/sericite matrix. Sample 49-15 is faintly laminated with some development of stylolites (scale in cm).

Figure 3.3b: Graded sandstone containing about 85 - 90% subrounded quartz with illite/sericite matrix, disseminated hematite and siderite cement. Note good development of cross-laminations on right side of sample 60-13 (scale in cm).

ation spots, Liesegang bands and rings (Figure 3.4). Figure 3.4 shows a typical example of the red-bed sandstones of the Manitou Falls Formation.

The clayey sandstone samples are similar in composition to the sandstone specimens but tend to be more friable. They generally are white to buff in colour and contain from 5 to 30% silt and clay (Figure 3.5a).

Red, white or green sandy claystone samples are massive and consist dominantly of clay- and silt-sized particles, with some gritty layers. They are commonly indurated and compact, but may be friable. Based on the particle-size distribution (Table A.2, Appendix A) the sandy claystone samples contain up to 35% clay-sized material ($< 2 \mu\text{m}$) and up to 50% silt ($2 - 50 \mu\text{m}$). A typical example is shown in Figure 3.5b. Bruneton (1987) subdivided this sample type into soft, intermediate and indurated clays.

Composite samples, as the name implies, have characteristics of both clayey sandstone and sandy claystone samples, intercalated on a cm scale. The particle-size distribution of the composites appears to be intermediate, between the clayey sandstone and sandy claystone samples (Figure 3.1). Basement samples, taken from immediately below the unconformity, are bleached, massive and clay-rich.

Figure 3.4: Liesegang bands and rings in unaltered sandstone of the Manitou Falls Formation. The rings cross cut the original bedding and are a result of rehematization of irregularly bleached red-bed sandstones.

Figure 3.5a: Example of a bleached, friable clayey sandstone containing about 30% silt- and clay-size material. Sample 53-11.

Figure 3.5b: Example of a massive, sandy claystone containing about 70% silt- and clay-size material. Sample 118-02 is bleached and consists almost entirely of illite/sericite with minor gritty layers of quartz.

3.3 PETROGRAPHY

3.3.1 Sandstone:

Sandstones lying above the ore deposit are massive to graded, fine- to coarse-grained, very poorly-sorted to moderately well-sorted quartzose sandstone and quartz-pebble conglomerate. Quartz grains are either grain-, or matrix-supported. Matrix content ranges from 5 to 40% of the rock and generally increases with depth. Quartz is the dominant detrital mineral; mica can form up to 10% of the rock. Porosity is variable, but generally less than 20%. Sandstones taken from the barren hole, WDG1-139, are indistinguishable in composition and texture from samples taken above the ore zone.

Subrounded to rounded, monocrystalline and polycrystalline quartz grains vary in size from coarse silt to pebble. Grain contacts are commonly straight, concavo-convex or rarely sutured. Floating grains and point contacts are observed in sandstones with high matrix contents. Quartz overgrowths on monocrystalline grains are abundant, especially in the closely-packed sandstones that contain little matrix; the overgrowths are commonly delineated by clay/opaque dust rims.

Other detrital minerals include muscovite, biotite, zircon and opaques. Detrital mica commonly appears to be bent around quartz grains. Heavy mineral layers consist of

zircon and opaques (leucoxene and traces of pyrite). Zircons are subhedral to euhedral and may be rimmed by REE-bearing xenotime or monazite (Figure 3.6a, b). The energy dispersive X-ray analysis shows that the rims contain Dy, Gd, Y and Co. The zircon grains are generally zoned and show little evidence of chemical degradation. The energy dispersive X-ray analysis of leucoxene suggests that leucoxene probably formed from ilmenite (Figure 3.7). According to Hoeve and Quirt (1984), some leucoxene grains contain goethite-rutile cores.

The interstitial material is fine-grained, recrystallized illite/sericite that may be matrix or cement. Early diagenetic stages are represented by clays that form skins or cutans around detrital grains. Clay fibres are oriented parallel to grain boundaries. A later stage of diagenesis is probably marked by clay fibres oriented perpendicular to detrital grain surfaces. The clay fibres also occur in randomly-oriented clusters, packets (stacked, parallel orientation) or individual fibres; some show radiating or fan-shaped patterns. In a few samples, illite/sericite exhibits a vermiform texture suggesting replacement of detrital kaolinite. Most matrix clay contains small inclusions of rutile(?) and opaques (hematite?). Detrital quartz grains and overgrowths become increasingly replaced by the interstitial clay with depth.

Figure 3.6a: SEM micrograph of detrital, zoned zircon (Z) surrounded by illite (I) matrix and sub-rounded quartz (Q) grains. Grain in centre of zircon is pyrite (P). Small white grains are ilmenite (T). Magnification 276X, bar scale = 36.2 μm , sandstone sample 60-01, backscatter image (BSI).

Figure 3.6b: SEM micrograph showing close-up of zircon grain in (a). Rm (rim) is probably xenotime or monazite. Magnification 1030X, bar scale = 9.71 μm , BSI.

Figure 3.7: SEM micrograph of sandstone sample 60-01 showing quartz (Q) and variably altered leucosene (L) grains after ilmenite(?) set in an illite (I) matrix. Magnification 103X, bar scale = 97.1 μm , BSI.

Some clay-rich layers that occur are slightly contorted. They resemble stylolites and probably are the result of compaction and dewatering, during diagenesis.

Carbonate (probably siderite) and hematite cements are present in a few samples, normally lower down in the stratigraphic column. When in contact with quartz grains or quartz overgrowths, the grain outlines appear to be corroded by the carbonate cement. The carbonate cement is partly replaced by the illite/sericite matrix and hematite cement (Figure 3.8).

At least three generations of Fe-oxides are recognized: (1) fine-grained dust, outlining authigenic overgrowths; (2) specular hematite, disseminated throughout the clay matrix; and (3) hematite cement, replacing carbonate cement. Hoeve and Quirt (1984) reported that the Athabasca Group rocks have been variably affected by chemical reduction of iron, manifested as bleached zones. Within these zones, rehematization produced the bright-red liesegang rings, made up of fine-grained hematite. Renewed bleaching occurred along fractures and joints. This, followed by more recent re-oxidation, formed liesegang rings of limonite (yellow-brown to orange), which are visible in some cores.

Figure 3.8: Photomicrograph of sample 44A-19 showing carbonate (C) and hematite (H) cement in quartz (Q) framework sandstone. The hematite appears to replace the carbonate and quartz. The illite/sericite (I) matrix may be contemporaneous with the carbonate cement (XPL, field of view = 0.63 mm).

3.3.2 Altered Sandstones

Bleaching, loss of cohesion and increase in clay content, within the sandstone unit above the deposit suggest intense hydrothermal alteration and diagenesis. Fracture- and permeability-controlled bleaching resulted in extensive Fe reduction. Loss of cohesion and enrichment in residual clay resulted from quartz dissolution; cohesion generally decreases towards the ore until the sandstone is completely replaced by clay (Hoeve and Quirt, 1984).

Sandy claystones, and to a lesser extent clayey sandstones, show microtextural evidence of alteration. Quartz grains are completely altered, and with few exceptions, pseudomorphed by clay. The clay pseudomorphs are dark in plane light and clearly outlined by the illite/sericite matrix resulting in a patchy appearance (e.g., see Figures 3.12a and 3.14a as examples). Relict quartz cores are present in some samples. The degree of preservation of the sedimentary characteristics of these rocks is variable.

Coarse-grained detrital micas have lamellae that tend to be bent or warped (Figures 3.9 and 3.10a, b). Detrital mica forms < 15% of the rock and appears to be relatively fresh. The energy dispersive X-ray analysis of the large mica grain in Figure 3.9 shows slightly higher K, Fe and Mg than the matrix surrounding the grain. Microprobe analyses of some detrital mica grains (Table A.4 of Appendix A) sug-

Figure 3.9: SEM micrograph of a detrital mica (M) grain showing warping of lamellae. Large white grain is zircon (Z). Randomly oriented fibres of illite (I) surround the detrital grains. Magnification = 268X, bar scale = 37.3 μm , sample 60-08, BSI.

Figure 3.10a: SEM micrograph showing another view of sample 60-08. Illite (I) fibres in recrystallized matrix are oriented parallel to the detrital mica (M) grain. Further away from the mica the fibres become randomly oriented. Large white grain is zircon (Z) and large black areas are holes. Magnification 333X, bar scale = 30.0 μm , BSI.

Figure 3.10b: Close-up view of Figure 3.10a. Illite (I) fibres are tangential to mica (M) grain and are randomly oriented about 10 μm away. Randomly oriented fibres contain minor amounts of Fe; tangentially oriented fibres do not. Magnification 1000X, bar scale = 10 μm , BSI.

gest that the micas are either muscovite or hydromuscovite.

Trace amounts of zircon, rutile, hematite, tourmaline and staurolite occur in heavy mineral layers. Higher modal amounts are noted in the altered rocks. Tourmaline grains are up to 1 mm in size; hematite occurs as discrete disseminated grains.

The matrix of illite/sericite, and chlorite is extensively recrystallized in the sandy claystone samples. In contrast to the clay pseudomorphs, the matrix clay forms grains up to 30 μm in size and individual fibres can be easily recognized, running parallel, tangential or perpendicular to original (quartz) grain boundaries. In large, interstitial spaces between clay pseudomorphs, the orientation of the fibres is generally random. In some samples, the matrix clay occurs within randomly-oriented clusters. Scanning electron micrographs clearly show orientation of the matrix clay fibres. For example, in Figures 3.10a and b, the matrix clay is oriented tangentially to a detrital mica grain. The orientation changes to a more random pattern less than 10 μm away from the mica grain (Figure 3.10a). The randomly-oriented fibres contain minor amounts of Fe as determined by energy dispersive X-ray analysis; Fe was not detected in any of the detrital micas. Composition of the matrix clay was indeterminate, using microprobe analyses, as poor totals resulted from the porous nature of the

material (e.g., see Figure 3.10b).

Euhedral REE-bearing phosphate minerals (goyazite or florencite of the crandallite group of minerals) are dispersed among the clay fibres but are only visible with the SEM (Figure 3.11). These minerals have been observed in all units of the Athabasca Group by Wilson (1985), who suggested that they are authigenic or early diagenetic in origin. Dravite has been reported (Hoeve and Quirt, 1984; Bruneton, 1985, 1987) to be common in such material, but none was observed in the suite examined in this study.

Stylolitized clay layers in the sandstones appear to be preserved in the altered samples, and are associated with heavy mineral layers.

Hematite-bearing samples that underwent bleaching have a mottled red, olive-green and buff appearance. In the olive-green areas, tiny euhedral sulphide minerals (pyrite?) are dispersed throughout the matrix. In the reddish-coloured zones, hematite is common, as well as, minor to trace amounts of leucoxene and pyrite.

Siderite (Table A.5, Appendix A) occurs as clusters, individual euhedral rhombs (Figures 3.12a, b), and cement (Figure 3.13); it may have formed during the bleaching and formation of sulphides. The presence of siderite indicates moderate- to strongly-reducing conditions (Scholle, 1979). Because siderite rhombs and siderite cement do not occur in

Figure 3.11: SEM micrograph of goyazite (G) crystallites associated with illite (I) fibres. Magnification = 1340X, bar scale = 7.46 μm , sample 60-03, BSI.

Figure 3.12a: Photomicrograph of sample 118-06 showing individual and clusters of siderite (S) rhombs embedded in illite (I) matrix (XPL, field of view = 1.3 mm).

Figure 3.12b: Close-up view of Figure 3.12a showing relation of randomly-oriented illite (I) fibres and late-stage siderite (S) rhombs (sample 118-06, XPL, field of view = 0.3 mm).

Figure 3.13: Photomicrograph of siderite (S) cement replaced by hematite (H) cement (sample 103-05, XPL, field of view = 0.6 mm) (c.f., Figure 3.8).

the same samples, the relationship between them is difficult to ascertain. Siderite rhombs seem to have replaced specular hematite and interstitial clay (Figure 3.12b). The siderite cement in sample 103-05 is pervasive and appears to penetrate along cleavage planes of some detrital micas. The cement is partly replaced by a later hematite cement (Figure 3.13), similar to that observed in the sandstone samples. The presence of hematite suggests a change in the environment to oxidizing conditions.

3.3.3 Altered Basement

Hydrothermal alteration below the unconformity has masked any previous alteration and any original textures (Bruneton, 1987). Based on relict textures and extrapolation from unaltered basement, the deposit is underlain by biotite-cordierite-graphitic metapelites. The metapelites are divided into augen gneisses, which occur directly below the deposit, and fine-grained metapelites which occur on either side of the augen gneisses. Calc-magnesium gneisses, that occur south of the deposit, are intercalated with fine-grained metapelites (Bruneton, 1985, 1987).

Primary textures are absent in all of the samples collected (Figure 3.14a). The samples consist entirely of illite/sericite with or without chlorite. Mica grains are preserved, and lenses of rutile along cleavage planes sug-

Figure 3.14a: Photomicrograph showing patchiness typical of highly altered samples. The fine-grained clay pseudomorphs (Cp) have been replaced by the recrystallized clay (C) (basement sample 139-18, plane light, field of view = 2.6 mm).

Figure 3.14b: SEM micrograph of illite (I) with sudoite (S). Sudoite appears to penetrate along frayed edges of the illite grain. Rutile (R) occurs along cleavage planes of illite; goyazite (G) is associated with sudoite (long bar = 100 μ m; BSI).

gest a biotite precursor (Figure 3.14b; cf., Mellinger, 1985). Illite and chlorite (variety sudoite; Percival and Kodama, 1989) make up the remainder of the rocks, with sudoite replacing illite/sericite (Figure 3.14b).

Basement samples from borehole WDG1-139 resemble those from the other boreholes and suggest continuity of the alteration zone along the unconformity. Samples from close to the unconformity contain dispersed, irregularly-shaped hematite grains whereas deeper samples are bleached and contain fine-grained, disseminated pyrite.

3.4 PARAGENESIS

The diagenetic and hydrothermal alteration history of the Athabasca basin are complex and reflect basin-wide events. A sequence of events was established by Hoeve and Quirt (1984) based on detailed studies of host-rock alteration at the Midwest Lake, Key Lake, Collins Bay B and McClean Lake deposits, in conjunction with regional aspects of clay mineral distribution and diagenetic patterns. Following is a brief summary of the mineralization and alteration stages according to Hoeve and Quirt (1984):

(1) Euhedral uraninite and lustrous, radiating pitchblende were deposited, ca. 1350 - 1250 Ma ago (first stage of mineralization);

(2) Formation of Ni-Co sulphides and sulpharsenides, and Ni-Co-Fe sulphides;

(3) Alteration to illite and chlorite, accompanied by quartz dissolution and residual clay enrichment, collapse of sandstone, formation of secondary hematite halo, graphite dissolution and formation of hydrocarbons;

(4) Development of second-stage mineralization, ca. 1100 - 1050 Ma ago, characterized by dull pitchblende, associated with secondary Ni-Co arsenides, sulpharsenides and sulphides, and Fe-Cu-rich sulphides;

(5) Extensive bleaching of host rock, accompanied by formation of euhedral quartz and tourmaline, development of the olive-green alteration, and continued dissolution of graphite and formation of hydrocarbons;

(6) Formation of sooty pitchblende and extensive kaolinitization, ca. 300 - 250 Ma ago (third mineralization stage).

Hoeve and Quirt (1984) suggested that the first two stages of mineralization and alteration are related to prograde burial and diagenesis whereas the third stage is probably related to uplift and retrograde diagenesis.

Textural observations on the Cigar Lake samples are the basis of a paragenetic sequence (Figure 3.15) which complements the regional framework. Following deposition, the sediments of the Manitou Falls Formation, consisting essentially of detrital grains in a kaolinite-rich matrix, were

Figure 3.15: Proposed paragenetic sequence for the alteration halo at Cigar Lake.

compacted and dewatered. Evidence for compaction includes bending of detrital mica plates around quartz grains. At this time, fine-grained hematite, precipitated from solution, formed thin diffuse rims along quartz grain boundaries. Quartz overgrowths bind the detrital framework grains. Carbonate cement, partly replacing quartz grains and their overgrowths (e.g., Figure 3.8), may be contemporaneous with the formation of clay coatings around quartz or their overgrowths. Specular hematite, formed by dehydration and recrystallization of colloidal limonite (Hoeve and Quirt, 1984), was then deposited in the interstitial matrix during early diagenesis, forming liesegang bands and rings (e.g., Figure 3.4). Extensive dissolution of quartz and development of the 200-m scale clay-rich halo followed. This process probably preceded clay recrystallization, as clay pseudomorphs appear to be replaced by the interstitial clay (cf., see Figure 3.14a).

As diagenesis proceeded, recrystallization of interstitial matrix to illite/sericite took place. The authigenic clays initially grew perpendicular to quartz grain surfaces and then filled interstitial spaces with randomly-oriented fibres, commonly replacing quartz and carbonate cement. Hoeve and Quirt (1984) reported that sudoite was formed at the same time as matrix recrystallization and development of the alteration halo (i.e., during first stage of mineraliza-

tion) but Bruneton (1987) inferred that it is associated with the second stage of mineralization. Evidence from this study suggests that sudoite replaced illite/sericite, and therefore was formed after the first stage of mineralization.

Following recrystallization of the clay matrix/cement, secondary porosity formed through partial carbonate dissolution. The initial quartz, matrix and carbonate cement were then partly replaced by hematite (Figure 3.13), possibly produced during a second hematitization event described by Hoeve and Quirt (1984). This hematite forms an envelope around the ore and is thought to mark the extent of an oxidizing front related to the initial formation of the high-grade ore, ca. 1350 - 1250 Ma ago (Hoeve and Quirt, 1984, 1987).

Extensive zones of bleaching, associated with the second stage of mineralization cross-cut the secondary hematite zone (Hoeve and Quirt, 1984). Hematite-rich rocks are altered to an olive-green Fe-chlorite-bearing material. The bleaching is apparently contemporaneous with the formation of siderite and sulphides.

Late-stage remobilization of Fe from hematite is recorded in the bleaching and rehematization in the lower Manitou Falls Formation, possibly a result of late oxida-

tion-reduction cycles. Liesegang bands and rings of yellow-brown limonite represent the most recent oxidation phase (Hoeve and Quirt, 1984).

3.5 AUTORADIOGRAPHY

Autoradiography of some representative samples was used to map the α -radioactivity associated with weakly radioactive mineral grains. In sandstones, the α -activity appears to be associated with heavy mineral layers, in particular with rutile, magnetite, pyrite and hematite. Some U was found in rutile by microprobe analyses.

In altered sandstone the level of α -activity is very high, especially in samples containing pervasive hematite or sulphides. In one sample, 44-21, microprobe analyses along a short traverse (Figures 3.16 and 3.17; 100 μm) was used to identify the U-bearing minerals. Uranium varies from very low in pyrite and rutile (even below detection levels) but is high in the clay-rich matrix surrounding the pyrite and rutile grains. Microprobe analyses (Figure 3.16) of the clay matrix (Table A.5, Appendix A) confirm that the clays contain from about 3 to 16% UO_2 . It is difficult, however, to determine from the photomicrograph in Figure 3.16, if these are U-bearing clays or if microdisseminated pitchblende occurs within the interstitial clay. Ruzicka and

Figure 3.16: Photomicrograph of sample 44-21. Alpha-activity appears to be associated with the clay-rich (I) areas between the pyrite (P) and rutile (R) grains. Location of spot analyses (Table A.5) also shown (reflected light, field of view = 0.3 mm).

Figure 3.17: Relative uranium intensity obtained along a traverse through pyrite, clay, rutile and clay in sample 44-21 (see Figure 3.16).

LeCheminant (1986) reported pitchblende (second stage) replacing kaolin matrix and enclosing rutile needles in sandstone of the Cigar Lake deposit.

CHAPTER FOUR

CLAY MINERALOGY

4.1 INTRODUCTION

Clay minerals are sensitive indicators and recorders of the low temperature geological environment (Keller, 1970; Hoeve and Quirt, 1984). They generally occur at or near the earth's surface in weathering, sedimentary or diagenetic/hydrothermal environments. They can be formed by precipitation from solution, by crystallization of amorphous colloidal material (neoformation) or transformation of non-clay and clay precursor minerals (Hall, 1987). Both neoformed and transformed clays can be authigenic or diagenetic.

Clay minerals, particularly illite, record temperature change through modification to their composition, structure and crystallinity. From the nature and extent of these alterations it is possible to estimate depth of burial and to assess conditions of diagenesis in the sedimentary environment (Burst, 1959; Velde and Hower, 1963; Kübler, 1968; Dunoyer de Segonzac, 1970; Hower et al., 1976; Kisch, 1983). Although clay mineral studies have been primarily used to characterize diagenetic and low-grade metamorphic environments, they also have widespread application in petroleum exploration and reservoir recovery (Weaver, 1960; Longstaffe, 1981). Clay minerals have been used to delineate alteration haloes associated with lead-zinc deposits of

the Mississippi Valley District (Heyl et al., 1964), porphyry copper in the Highland Valley, British Columbia (Jambor and Delabio, 1978), the Kuroko deposits, Japan (Iijima, 1974) and unconformity-type uranium deposits in the Athabasca basin, Saskatchewan (Hoeve et al., 1981; Hoeve and Quirt, 1984) and Jabiluka, Australia (Binns et al., 1980; Nutt, 1989).

4.2 CLAY MINERAL TRANSFORMATIONS

The most important changes during diagenesis are the progressive replacement of kaolinite and smectite by illite and chlorite. Kaolinite breaks down at lower temperatures than smectite (Kisch, 1983, 1987; Srodon and Eberl, 1984). The replacement of kaolinite is favoured by high porosity, high permeability and the presence of K, Fe and Mg (Kisch, 1983). Under Fe- and Mg-poor conditions, however, kaolinite can be replaced by a dioctahedral chlorite (sудоite or tosudite). Hunziker (1986) suggested that kaolinite becomes unstable under anchimetamorphic conditions (200-300 °C), converting to pyrophyllite according to the reaction (Frey, 1970):

In a K-rich environment, the replacement of smectite occurs through progressive illitization, with concomitant decrease in the percentage of expandable layers, as K is supplied by decomposition of detrital mica or feldspar, or from smectite itself. In an Fe- and Mg-rich environment, trioctahedral chlorite forms by way of a smectite-corrensite-chlorite transition (Frey, 1970). In an Fe- and K-poor environment, Frey (1970) reported that a dioctahedral chlorite could form under anchizonal conditions at the expense of an illite-smectite (I/S) mixed-layer mineral such that:

where I/S would become unstable by the middle of the anchizone (~ 250 °C). If Fe and Mg are present, I/S would break down at a lower temperature and paragonite/phengite mixed-layer minerals would appear at the diagenetic/anchizone boundary (~ 200 °C; Hunziker, 1986). Small amounts of smectite layers can persist, however, until the anchizone/epizone boundary (~ 300 °C) (Srodon and Eberl, 1984).

Illite can also form when detrital biotite and muscovite break down with increasing temperature (Kisch, 1983; Srodon and Eberl, 1984). Kisch (1983) reported that detrital biotite from clastic sedimentary rocks can alter to

chlorite-hydromuscovite "packets" during late diagenesis.

Structural polytypes and crystallinity are especially affected by increase in temperature, depth of burial and diagenesis. For example, as temperature increases illite polytypes change from $1\bar{M}_4$ to $1\bar{M}$ to $2\bar{M}$ ($2\bar{M}_1$ or $2\bar{M}_2$) and crystallinity increases. Kaolinite may be replaced by the $2\bar{M}_1$ polytype, dickite. Chlorite composition may change from initially Fe-rich to more Mg-rich with increasing diagenesis. Polytype conversion of chlorite from $I\bar{b}$ ($\beta = 90^\circ$) to $II\bar{b}$ ($\beta = 97^\circ$) may also be evident (Kisch, 1983; Curtis et al., 1985).

4.3 ILLITE CRYSTALLINITY

Illite crystallinity is controlled primarily by temperature (Kisch, 1983) and thus it has become a useful parameter in delineating temperature zonation in burial-diagenetic, and low-grade metamorphic areas. Crystallinity is determined from the shape of the (001) illite X-ray diffraction peak. Weaver (1960, 1961) was the first to quantify crystallinity by measurement of the ratio of peak height at 1.0 nm to the intensity at 1.05 nm. Kübler (1964, 1968) refined the method of Weaver and measured the width of the (001) peak at half height at specific instrumental settings. Kübler's index overcame the inability of Weaver's index- to measure the very crystalline, narrow peaks.

According to Blenkinsop (1988) percentage errors of both indices increase with crystallinity but Kübler's index is preferable.

Kübler (1968) documented an increase in the crystallinity of illite with depth of burial and thereby identified the anchizone, a zone between high-grade diagenesis and low-grade metamorphism (epizone). Kübler (1968) defined a value of 4.0 mm ($0.4^\circ 2\theta$) as the high-grade diagenetic/anchizone boundary and a value of 2.5 mm ($0.25^\circ 2\theta$) as the anchizone/epizone boundary. Kübler's two boundaries correspond to Weaver's (1961) incipient and weak metamorphic boundaries respectively. The Kübler index decreases with increasing crystallinity. Variations of these ranges are common in the literature (e.g., Dunoyer de Segonzac, 1970; Kisch, 1983; Blenkinsop, 1988), but in this study Kübler's original boundary values of K_i are adopted.

Esquevin (1969) suggested that the ratio of $Al/(Fe + Mg)$ in illite, reflected in the $I(002)/I(001)$ X-ray diffraction peak intensity ratio (I_r), was also a sensitive monitor of changes in temperature and therefore a useful diagenetic indicator. In an extensive study of illites in sedimentary basins in Europe and north Africa, Dunoyer de Segonzac (1970) distinguished five environments of recrystallization using Esquevin diagrams (K_i vs. I_r plot; Figure 4.1): (I) incipient diagenesis; (II) low-grade diagenesis;

Figure 4.1: Esquevin diagram showing the relationship between Kübler Index of illite crystallinity (in mm) and I(002)/I(001) X-ray diffraction intensity ratio. I(002)/I(001) is related to Al/(Fe + Mg) composition in that I(002)/I(001) > 0.26 indicate Al-rich illites. Five environments of crystallization have been identified by Dunoyer de Segonzac (1970). These are: (I) incipient diagenesis; (II) low-grade diagenesis; (III) high-grade diagenesis; (IV) anchizone; and (V) epizone or low-grade metamorphic zone.

(III) high-grade diagenesis; (IV) anchizone; and (V) epizone or low-grade metamorphism. The peculiar trend of the anchizone field is a consequence of aluminous illites ($I(002)/I(001) > 0.26$) becoming crystalline more rapidly than Mg-illites ($I(002)/I(001) < 0.26$) and the peak widths of Mg-illites being less affected by increase in temperature.

4.4 PREVIOUS STUDIES OF CLAYS IN THE ATHABASCA BASIN

Detailed studies of clay minerals at the Saskatchewan Research Council have been used to constrain the history of sedimentation, diagenesis and U mineralization in the Athabasca basin. Hoeve and Quirt (1984) reported that about thirty thousand samples had been quantitatively analyzed for clay minerals.

Clay mineral characteristics define the diagenetic state of the Athabasca Group. High-grade diagenetic conditions are indicated by: (1) the presence of dickite in fracture fillings; (2) mixture of $2M_1/1M$ illite polytypes; (3) absence of I/S mixed-layer minerals in most units (exception is 10 - 15% expandable layers in upper Wolverine Point Formation); and (4) Kübler index values of illite crystallinity between 4 and 5 for lower portions of the sedimentary basin, and values as high as 15 for stratigraphically higher sediments (Hoeve and Quirt, 1984).

The environment of deposition for the Athabasca Group sediments was reinterpreted by Hoeve and Quirt (1984) using clay mineral distribution and diagenetic patterns. They suggested that only two marine incursions had occurred. The presence of detrital kaolinite in the Manitou Falls, Lazenby Lake, Fairpoint, lower Wolverine Point and Otherside Formations is indicative of a terrestrial environment. Diaspore also occurs in the Lazenby Lake and Locker Lake Formations, and may reflect periods of non-deposition and intense weathering (i.e., paleoweathering profile) or transportation from a nearby weathering profile (Hoeve and Quirt, 1984).

Chlorite found in the upper Wolverine Point Formation suggests an influx of marine clays (first of two marine incursions), but kaolinite also occurs in clay/silt layers and intraclasts suggesting a terrestrial origin. The second marine incursion includes the illite-chlorite-bearing shales and sandstones of the Douglas Formation and stromatolitic dolomites of the Carswell Formation. Hoeve and Quirt (1984) proposed that the Athabasca Group was deposited in an intracontinental basin with limited contact with the open sea. Ramaekers (1980, 1981) had proposed an unstable continental margin setting with several transgressive-regressive cycles.

Illite, chlorite and kaolinite are associated with the Athabasca U deposits in varying proportions. Illite occurs above and below the unconformity and is characterized by a

3T polytype structure near the ore zones. Sudoite (Al-rich dioctahedral chlorite) generally occurs below the unconformity but may occur in highly altered basal sandstones above the unconformity. Trioctahedral or Fe/Mg-rich chlorites occur in the lower part of the paleoweathering profile or associated with the ore (Hoeve and Quirt, 1984).

Illite forms a plume-shaped halo around the Midwest, Collins Bay and McClean Lakes deposits (Ayers et al., 1983; Hoeve and Quirt, 1984; Wallis et al., 1983, 1985), decreasing in abundance with distance from the ore. At Key Lake, both illite and kaolinite haloes occur. The illite is probably associated with the first phase of mineralization, whereas kaolinite was formed during late-stage remobilization (ca. 300 - 250 Ma ago; Hoeve and Quirt, 1984).

Bruneton (1987) reported that illite is the dominant clay mineral in the clay alteration zone above the Cigar Lake ore deposit.

Knowledge of the distribution and characteristics of the clay minerals associated with sedimentary rocks and ore deposits provides valuable information on diagenetic history and environments of formation. Identification of minerals may also provide additional criteria that can be used in exploration.

4.5 SEMI-QUANTITATIVE ANALYSIS

4.5.1 Theory

The practice of semi-quantitative mineralogical analysis by X-ray diffraction (XRD) is based on the relationship (Brindley, 1961):

$$\frac{I_i}{I_j} = K \frac{X_i}{X_j} \quad (3)$$

where K represents a constant which includes the nature, density and mass absorption coefficients of components i and j as well as the geometry of the XRD equipment. A linear relationship between intensity ratio (I_i/I_j) and the ratio of weight fractions (X_i/X_j) is assumed in equation (3). If K is evaluated experimentally for two mineral components using synthetic mixtures, the weight fractions of unknowns of similar mineralogical composition can be estimated from measurements of the intensity ratios of selected peaks (Kodama et al., 1977; Hoeve et al., 1981; Hoeve and Quirt, 1984).

4.5.2 Method

Suspensions of clay (< 2 μm) and fine silt (2 - 5 μm) fractions were pipetted onto glass slides and air-dried overnight to produce oriented mounts. Clay mineralogical analyses of these fractions were conducted at the Sask-

atchewan Research Council in Saskatoon, Saskatchewan, using two Phillips-Norelco diffractometers with Cu K α radiation and Ni filters, at 30 mA (25 mA for machine 2) and 30 kV (40 kV for machine 2) with scanning speeds of 1° 2 θ /minute.

The clay mineral proportions were estimated to $\pm$ 10% using multi-component mixtures as external standards (Mellinger, 1985). X-ray diffraction peak areas were compared to reference materials collected from the Athabasca basin. The reference collection includes kaolinite, illite, di-trioctahedral chlorite (sudoite), trioctahedral Fe- and Mg-rich chlorites, dickite, berthierine and an illite/smectite (I/S) mixed-layer mineral containing about 10% expandable layers (Hoeve and Quirt, 1984). The height above background and the width at half-height were measured for the following basal reflections: (001) and (002) for illite (I); (001) and (002) for kaolinite (K); and (001), (002), (003) and (004) for chlorite (C). The (100) peak of quartz and (104) peak of hematite were also measured. Overlaps occur between K(001)-C(002), K(002)-C(004) and C(003)-I(002) peaks. The first overlap, K(001)-C(002) is corrected indirectly (Mellinger, 1985) and the other two can be resolved by extrapolation of the peaks to the baseline on the XRD chart.

From the X-ray measurements, normalized peak areas, normalized clay proportions ($I + K + C = 100\%$), Kübler

Indices, and intensity ratios of I(002) and I(001) were calculated. In addition, mineral proportions were also calculated, where possible, for quartz, hematite or other minerals (i.e., goethite, siderite).

Selected samples were glycolated or glycerol-treated to determine the presence of expandable layers. Where kaolinite/chlorite mixtures were suspected, the samples were heat-treated to 350 and 550 °C. If the 0.7 nm peak remained after heat treatment, it provided evidence for the presence of kaolinite.

The Kübler Index (Ki) of illite crystallinity was determined as the width, in mm, at half height of the (001) illite peak. The Saskatchewan Research Council's diffractometers have been calibrated against a series of illite standards provided by Prof. Kübler's laboratory in Neuchâtel, Switzerland (Hoeve and Quirt, 1984).

Ten samples were selected to determine the illite structure. Illite polytypes were measured by X-ray diffraction of these samples using Gandolfi (114.6 mm diameter, Cu K α radiation; Carleton University) and Guinier - de Wolff cameras (53.6 mm diameter, Co K α radiation; Land Resources Research Centre) using the XRD criteria of Bailey (1984).

4.6 RESULTS AND DISCUSSION

4.6.1 Mineralogy

Semi-quantitative clay mineral results, for the $< 2 \mu\text{m}$ fraction are given in Table B.1 of Appendix B and are statistically summarized in Table 4.1. The results show that illite is the dominant clay mineral in the Cigar Lake samples, with subordinate kaolinite and chlorite. This contrasts with unaltered sandstones of the Manitou Falls Formation which commonly contain equal amounts of kaolinite and illite (Hoeve et al., 1981). The clay-size fractions of the sandstone samples are dominated by quartz in the upper parts of the boreholes, and illite content increases with depth. The clayey sandstone, sandy claystone, composite and basement samples are almost all dominated by illite, with kaolinite and chlorite contents that range from 0 to 36% and 0 to 86% respectively. Chlorite abundance increases with depth, particularly within and below the ore zone. Hematite occurs in trace quantities in most samples, although it can constitute up to 17% by volume in a few samples. Minor amounts of goyazite, gypsum, siderite or goethite were detected in some samples.

The main chlorite mineral is a dioctahedral, Al-rich variety, sudoite (Percival and Kodama, 1989). This mineral is identified by its intense (006) XRD reflection (based on a 2-layer structure) at 0.474 nm with respect to the (004)

Figure 4.3: XRD pattern of 44-01 showing shift of the illite (001) peak from 1.002 to 0.998 nm after glycerol treatment. Sample was also heat treated to 550 °C.

2

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS
STANDARD REFERENCE MATERIAL 1010a
(ANSI and ISO TEST CHART No 2)

Table 4.1: Summary statistics of mineral data for Cigar Lake samples, clay-size ($< 2 \mu\text{m}$) fraction. Number in parenthesis indicates total number of samples; n = number of samples containing detectable amounts ($> 0.0\%$) of mineral component; $\bar{x}$ = mean value; and s = standard deviation.

	SANDSTONE (51)	CLAYEY SANDSTONE (30)	SANDY CLAYSTONE (52)	COMPOSITE (11)	BASEMENT (7)
ILLITE					
n	50	30	52	11	7
$\bar{x}$ (%)	55.6	89.4	93.4	84.2	68.1
s (%)	26.5	14.6	6.8	26.9	20.1
range (%)	0-95	47-100	77-100	84-100	60-99
KAOLINITE					
n	10	11	18	1	1
$\bar{x}$ (%)	1.2	2.7	2.5	1.5	0.1
s (%)	3.1	7.0	4.0	4.8	0.4
range (%)	0-15	0-37	0-12	0-16	0-1
SUDOITE					
n	4	10	13	3	6
$\bar{x}$ (%)	1.3	3.1	3.3	6.3	31.0
s (%)	6.5	7.7	6.3	11.6	20.5
range (%)	0-40	0-36	0-23	0-38	0-40
QUARTZ					
n	51	2	-	-	-
$\bar{x}$ (%)	40.6	0.1	-	-	-
s (%)	25.8	0.4	-	-	-
range (%)	4-100	0-2	-	-	-
HEMATITE					
n	30	9	9	-	2
$\bar{x}$ (%)	0.9	0.8	0.1	-	0.8
s (%)	2.8	3.1	0.2	-	1.9
range (%)	0-15	0-17	0-1	-	0-5
KUBLER INDEX					
n	51	30	52	11	7
$\bar{x}$	4.3	4.4	4.0	4.2	4.6
s	1.0	1.1	0.7	1.0	0.8
range	2.6-6.7	2.0-5.7	2.2-5.7	2.6-4.7	3.2-5.1
I(002) I(001)					
n	51	30	52	11	7
$\bar{x}$	0.44	0.57	0.61	0.66	0.55
s	0.08	0.12	0.10	0.19	0.22
range	0.23-0.72	0.27-0.81	0.38-0.82	0.45-0.78	0.49-0.74

Table 4.1: Summary statistics of mineral data for Cigar Lake samples, clay-size ($< 2 \mu\text{m}$) fraction. Number in parenthesis indicates total number of samples; n = number of samples containing detectable amounts ($> 0.0\%$) of mineral component; $\bar{x}$ = mean value; and s = standard deviation.

	SANDSTONE (51)	CLAYEY SANDSTONE (30)	SANDY CLAYSTONE (52)	COMPOSITE (11)	BASEMENT (7)
ILLITE					
n	50	30	52	11	7
$\bar{x}$ (%)	55.6	89.4	93.4	84.2	68.1
s (%)	26.5	14.6	6.8	26.9	20.1
range (%)	0-95	47-100	77-100	84-100	60-99
KAOLINITE					
n	10	11	18	1	1
$\bar{x}$ (%)	1.2	2.7	2.5	1.5	0.1
s (%)	3.1	7.0	4.0	4.8	0.4
range (%)	0-15	0-37	0-12	0-16	0-1
SUDOITE					
n	4	10	13	3	6
$\bar{x}$ (%)	1.3	3.1	3.3	6.3	31.0
s (%)	6.5	7.7	6.3	11.6	20.5
range (%)	0-40	0-36	0-23	0-38	0-40
QUARTZ					
n	51	2	-	-	-
$\bar{x}$ (%)	40.6	0.1	-	-	-
s (%)	25.8	0.4	-	-	-
range (%)	4-100	0-2	-	-	-
HEMATITE					
n	30	9	9	-	2
$\bar{x}$ (%)	0.9	0.8	0.1	-	0.8
s (%)	2.8	3.1	0.2	-	1.9
range (%)	0-15	0-17	0-1	-	0-5
KUBLER INDEX					
n	51	30	52	11	7
$\bar{x}$	4.3	4.4	4.0	4.2	4.6
s	1.0	1.1	0.7	1.0	0.8
range	2.6-6.7	2.0-5.7	2.2-5.7	2.6-4.7	3.2-5.1
I(002) I(001)					
n	51	30	52	11	7
$\bar{x}$	0.44	0.57	0.61	0.66	0.55
s	0.08	0.12	0.10	0.19	0.22
range	0.23-0.72	0.27-0.81	0.38-0.82	0.45-0.78	0.49-0.74

reflection at 0.71 nm. In contrast, trioctahedral chlorites (Fe/Mg variety) have more intense (002) and (001) reflections (based on a 1-layer structure) relative to the (003) peak. The sudoite is associated with the intense alteration zone surrounding the ore, whereas the Fe-chlorite is associated directly with the ore.

Many samples contain trace amounts of a mixed-layer clay mineral. Two samples analyzed at the Land Resource Research Centre (Agriculture Canada) shows a 1.17 nm peak (Figure 4.2) that can be attributed to an illite-chlorite (I/C) interstratified, mixed-layer mineral containing < 30% chlorite layers (MacEwan et al., 1961 after Hendricks and Teller, 1942; Ahn et al., 1988). In addition, an expandable layer component associated with illite was detected in a few samples by the shift of the (001) peak from 1.002 to 0.998 nm after glycerol treatment (Figure 4.3). This illite-smectite (I/S) interstratified component forms < 5% of the total illite content (H. Kodama, personal communication, 1988).

The 2 - 5 μm fractions of the clayey sandstone and sandy claystone samples are dominated by illite (Table 4.2; Table B.2 of Appendix B). Kaolinite, chlorite and hematite are present in trace to minor amounts (i.e., up to 10%). Only a few samples contain traces of the I/C mixed-layer mineral.

Figure 4.2: XRD pattern of sample 44-01 containing illite (I) and regularly interstratified illite-chlorite (I/C) mixed-layer mineral identified by the 1.17 nm peak. Sample was analyzed after air-drying, glycerol-treatment and heating to 550 °C.

Figure 4.3: XRD pattern of 44-01 showing shift of the illite (001) peak from 1.002 to 0.998 nm after glycerol treatment. Sample was also heat treated to 550 °C.

Table 4.2: Summary statistics of mineral data for Cigar Lake samples, silt-size (2-5 μ m) fraction. Number in parenthesis indicates total number of samples; n = number of samples containing detectable amounts (> 0.0%) of mineral component; $\bar{x}$ = mean value; and s = standard deviation.

	CLAYEY SANDSTONE (7)	SANDY CLAYSTONE (36)	COMPOSITE (3)
<hr/>			
ILLITE			
n	7	36	3
$\bar{x}$ (%)	84.3	97.2	97.3
s (%)	15.8	4.2	3.8
range (%)	59-100	85-100	93-100
KAOLINITE			
n	4	16	1
$\bar{x}$ (%)	6.0	1.1	0.3
s (%)	9.5	2.1	0.6
range (%)	0-26	0-10	0-1
SUDOITE			
n	-	6	1
$\bar{x}$ (%)	-	1.1	2.3
s (%)	-	2.7	4.0
range (%)	-	0-10	0-7
QUARTZ			
n	1	2	-
$\bar{x}$ (%)	0.01	0.3	-
s (%)	0.04	1.6	-
range (%)	0-0.1	0-10	-
HEMATITE			
n	3	12	-
$\bar{x}$ (%)	2.2	0.4	-
s (%)	7.0	0.8	-
range (%)	0-15	0-4	-
KUBLER INDEX			
n	7	36	3
$\bar{x}$	3.7	3.2	3.4
s	1.0	1.1	0.9
range	2.6-5.1	1.3-5.5	0.45-0.59
I(002)/I(001)			
n	7	34	3
$\bar{x}$	0.52	0.53	0.52
s	0.10	0.07	0.07
range	0.39-0.67	0.4-0.7	0.45-0.59

Near the ore zone, the clay matrix of the Manitou Falls Formation sandstone becomes illite-rich, a change that is attributed to local hydrothermal alteration. Alteration is also indicated by the loss of cohesion of the sandstone and the enrichment in clay relative to quartz. Hoeve and Quirt (1984) suggested that the illite formed by replacement of detrital kaolinite.

4.6.2 Mineral Composition

The chemistry of clay-size and silt-size illite from the alteration halo, in the Athabasca Group (above) and in the basement (below), of the Cigar Lake deposit are compared to several reference samples in Table 4.3. Illites from the Athabasca portion of the halo have high K_2O and Al_2O_3 and low SiO_2 relative to the reference illites, and approach the composition of hydromuscovite. Halter et al. (1987) found similar illites at Cluff Lake. Illite from the basement samples is relatively enriched in Al_2O_3 and has an SiO_2 content intermediate between the Eldorado and Fithian illite reference samples.

Structural formulae for the Athabasca and basement samples (Table 4.4) were calculated using the data in Table 4.3. To account for the presence of microscopic amounts of goyazite, apatite(?) and pyrite, detected by low quantities of P and S in the XRF analyses, appropriate amounts of Al,

Table 4.3: Comparison of chemical composition for illite samples from the Cigar Lake deposit to illite samples reported in the literature. Athabasca illite from borehole-44A; Basement illite from borehole-53.

ELEMENT	ATHABASCA ¹ ILLITE ($< 2 \mu\text{m}$)	ATHABASCA ¹ ILLITE ($< 2 \mu\text{m}$)	BASMENT ² ILLITE (FINE)	BASMENT ² ILLITE (COARSE)	ELDORADO ³ ILLITE ($0.7-2 \mu\text{m}$)	FITHIAN ⁴ ILLITE	HYDRO- ⁴ MUSCOVITE
SiO ₂	45.42	46.26	51.34	51.41	48.95	56.91	46.54
TiO ₂	0.36	0.20	0.23	0.35	tr	0.81	0.17
Al ₂ O ₃	35.28	35.70	32.51	32.46	25.89	18.50	36.37
Fe ₂ O ₃	1.40	0.90			5.02	4.99	0.72
FeO			0.73	0.72	2.40	0.26	0.36
MnO	0.00	0.00	0.01	0.01	0.08	-	0.00
MgO	2.14	0.72	2.47	2.24	2.25	2.07	0.50
CaO	0.28	0.18	0.05	0.07	0.45	1.59	0.22
Na ₂ O	0.42	0.64	0.03	0.03	0.15	0.43	0.46
K ₂ O	8.98	10.54	8.21	7.69	6.70	5.10	8.06
S	0.08	0.10	-	-	0.24	-	-
CO	-	-	-	-	0.95	-	-
P ₂ O ₅	2.50	0.40	-	-	-	-	0.06
TOTAL	96.86	95.64	95.06	95.50	93.08	90.66	93.40

¹Analyzed by XRF.

²Analyzed by microprobe.

³Kodama and Dean (1980).

⁴Deer, Howie and Zussman (1966).

Table 4.4: Calculated formulae for illite from Athabasca (borehole 44A) and altered basement (borehole 53) samples, compared to Fithian illite and hydro-muscovite.

	ATHABASCA		BASEMENT		FITHIAN ¹	HYDRO- ¹
	< 2 μm	2-5 μm	< 2 μm	2-5 μm	ILLITE	MUSCOVITE
Si	6.37	6.20	6.50	6.67	7.50	6.00
Al(vi)	<u>1.63</u>	<u>1.80</u>	<u>1.50</u>	<u>1.33</u>	<u>0.50</u>	<u>2.00</u>
	8.00	8.00	8.00	8.00	8.00	8.00
Al(iv)	3.45	3.71	3.36	3.63	2.38	3.53
Ti	0.03	0.02	0.25	0.03	0.08	-
Fe	0.15	0.09	0.08	0.08	0.53	0.11
Mn	0.00	0.00	0.00	0.00	-	-
Mg	<u>0.45</u>	<u>0.15</u>	<u>0.46</u>	<u>0.44</u>	<u>0.41</u>	<u>0.10</u>
	4.08	3.97	4.15	4.18	3.40	3.74
K	1.60	1.80	1.32	1.28	0.86	1.33
Na	0.12	0.16	0.01	0.01	0.11	0.11
Ca	<u>0.04</u>	<u>0.02</u>	<u>0.01</u>	<u>0.01</u>	<u>0.22</u>	<u>0.02</u>
	1.76	1.98	1.34	1.30	1.19	1.46

¹ Deer, Howie and Zussman (1966).

Ca and Fe were subtracted from the illite data. The Athabasca samples range in composition from $(\text{Na}_{.12}\text{Ca}_{.04}\text{K}_{1.60})(\text{Fe}_{.15}\text{Mg}_{.45}\text{Ti}_{.03}\text{Al}_{3.45})(\text{Si}_{6.37}\text{Al}_{1.63})\text{O}_{20}(\text{OH},\text{F})_4$ for the $< 2 \mu\text{m}$ fraction to $(\text{Na}_{.16}\text{Ca}_{.02}\text{K}_{1.80})(\text{Fe}_{.09}\text{Mg}_{.15}\text{Ti}_{.02}\text{Al}_{3.71})(\text{Si}_{6.20}\text{Al}_{1.80})\text{O}_{20}(\text{OH},\text{F})_4$ for the $2 - 5 \mu\text{m}$ fraction. The clay-size material is more illite-like than its silt-size equivalent. In comparison, the basement samples have the composition $(\text{Na}_{.01}\text{Ca}_{.01}\text{K}_{1.32})(\text{Fe}_{.08}\text{Mg}_{.46}\text{Ti}_{.25}\text{Al}_{3.36})(\text{Si}_{6.50}\text{Al}_{1.50})\text{O}_{20}(\text{OH},\text{F})_4$ for the fine, and $(\text{Na}_{.01}\text{Ca}_{.01}\text{K}_{1.28})(\text{Fe}_{.08}\text{Mg}_{.44}\text{Ti}_{.03}\text{Al}_{3.63})(\text{Si}_{6.67}\text{Al}_{1.33})\text{O}_{20}(\text{OH},\text{F})_4$ for the coarser-grained material. Comparison of these formulae to reference compositions of muscovite and illite (Table 4.4) indicates that the basement samples approach an illite composition and the Athabasca samples approach muscovite composition. The compositional differences between the Athabasca and basement samples probably reflect different precursors. Rutile lenses, occurring along cleavage planes in coarse illite grains from the basement samples, suggest a biotite precursor (Percival and Kodama, 1989). Illite occurs at the expense of kaolinite, as noted above, in the Athabasca samples.

High H_2O contents (6 - 8%), determined by loss on ignition, are found in some of the Cigar Lake samples. Wilson et al. (1987) found similarly high H_2O values in illite from other deposits in the Athabasca basin and con-

cluded that this indicated retrograde alteration or degradation. Illites from the alteration halo and ore zone of the Cluff Lake deposit also have high H_2O (about 7%) contents (Halter et al., 1987).

Microprobe analyses of sudoite from basement sample, 53-15, indicates the composition $(Al_{2.86}Mg_{1.92}Fe_{.13})(Si_{3.30}Al_{.70})O_{20}(OH,F)_8$. No data are available for the trioctahedral chlorite, although Hoeve and Quirt (1984) reported that dark, olive-green chamosite (Fe-chlorite) occurs in the ore zone at the Collins Bay B deposit. The trioctahedral chlorite identified at Cigar Lake is probably of the same variety. Hoeve and Quirt (1984) indicated that chloritization (sudoite) was contemporaneous with sericitization during the first phase of mineralization and that formation of chamosite is correlated with the bleaching event associated with the second phase of mineralization.

4.6.3 Polytypism

Illite changes from the $1M_d$ to the $2M$ polytype with increasing temperature (Kisch, 1983). The $1M_d$ disordered type is typical of low-temperature authigenic illite whereas the $2M$ polytype characterizes metamorphic and diagenetic illite formed at higher temperatures. Kisch (1983) suggested that the $1M$ mica polytype may be an intermediate form in the formation of $2M$ mica at the expense of kaolinite.

Hoeve and Quirt (1984) reported that illite from the rocks of the Wolverine Point Formation, Athabasca Group, usually consists of $1M_d/1M$ mixtures with other formations having $1M$ and $2M$ mixtures.

Illites from sandy claystone samples contain mixtures of $2M_1$ and $3T$ polytypes whereas in the less-altered clayey sandstones and sandstones, illites are a mixture of $1M$ and $2M_1$ polytypes. Illites associated with sudoite in the regolith are of the $2M_1$ polytype.

Illites from alteration haloes and ore zones of the Collins Bay, Midwest, Key and McClean Lakes deposits also have mixtures of $2M$ and $3T$ polytypes (Wilson et al., 1987). The presence of the $2M_1$ and $3T$ polytypes, nearer to the ore at Cigar Lake, suggests high formation temperatures, and indicates that illite is diagenetic rather than authigenic.

Although sudoite can form under high-grade diagenetic conditions, it is more commonly inferred to be of hydrothermal origin, based on its association with ore minerals (Bailey and Tyler, 1960; Hayashi and Oinuma, 1964) and its high-temperature structural, IIb polytype (Bailey and Brown, 1962; Fransolet and Bourguignon, 1978). The sudoite at Cigar Lake is of the IIb polytype, based on XRD criteria reported in Bailey (1988) and Lin and Bailey (1985). No data are presently available about the structural type that occurs on a regional scale in barren areas.

4.6.4 Illite Crystallinity

The Kübler index data from the $< 2 \mu\text{m}$ Cigar Lake illites lie in the high-grade diagenesis zone and the anchizone (Figures 4.4b, c and e). Ir values for clay-size illites from the sandstone samples (Fig. 4.4b) cluster around the phengite/muscovite boundary ($\text{Ir} = 0.4$) whereas the basement samples occur only in the muscovite field. The clay-rich samples (Figures 4.4c and e) show average Ir values greater and Ki values similar to the sandstone samples. The illites distal to the ore (e.g., borehole 139) have similar Ki values to illites proximal to the ore. The ore sample (60-16), however, appears to be anomalous in that it has a high Ki value (6.3; poor crystallinity) and very low Ir. As this sample is dominated by an Fe-rich chlorite, it is probable that the composition of the illite is also Fe-rich, thus accounting for its poorly crystalline nature.

Ir values for illites from the fine silt-size fraction (Figures 4.4d and f) cluster between 0.4 and 0.7 and, based on Ki values, are equally distributed among the high-grade diagenetic, anchizone and epizone fields. Coarse particles of illite are less affected by degradation and hydration (Dunoyer de Segonzac, 1970), and this is reflected in their higher crystallinity values.

The clay mineral data suggest regional diagenesis has been upgraded locally to anchizonal conditions. As the clay

Figure 4.4: (a) Esquevin diagrams for: (b) sandstone and basement clay-size separates; (c) clayey sandstone and composite clay-size separates; (d) clayey sandstone and composite silt-size fraction; (e) sandy claystone clay-size separates; and (f) sandy claystone silt-size fraction.

mineral content increases from sandstone to sandy claystone rock types, crystallinity and intensity ratios increase. The mean K_i value for sandstone, clayey sandstone and sandy claystone is 4.3 ± 1.0 ($n = 50$), 4.4 ± 1.1 ($n = 27$) and 4.0 ± 0.7 ($n = 48$) respectively. The mean I_r values are 0.44 ± 0.08 , 0.57 ± 0.12 and 0.61 ± 0.10 respectively. Anchizonal conditions are also indicated by the presence of $2M_1$ and $3T$ illite polytypes, the paucity of kaolinite in the upper reaches of the boreholes sampled, and the lack of kaolinite and I/S mixed-layer minerals in the alteration halo proximal to the ore. The illite crystallinity in the halo indicates that the temperature of alteration approximates or is greater than 200°C , that reflects the temperature at the diagenetic/anchizone boundary (Frey, 1970; Kisch, 1983; Hunziker, 1986), and is in agreement with Pagel's (1975) temperature estimate for the basin. The data for Cigar Lake agrees with other studies from the basin.

In a broader framework, illites from clay/silt seams of the Manitou Falls Formation plot in the high-grade diagenetic and anchizone fields (Hoeve and Quirt, 1984). Halter et al. (1987) reported that illite from the Cluff Lake deposit also formed under high-grade diagenetic to anchimetamorphic conditions, and that illites within and distal to the Cluff Lake ore zone have similar K_i values. Wilson et al. (1987) noted that illites associated with the ore zones

of other Athabasca deposits (Collins Bay, Midwest, Key and McClean Lakes) were indistinguishable from illites in the unaltered Athabasca sandstones, based on their Ki and Ir values.

Dunoyer de Segonzac (1970) argued that mixed-layer clay minerals are generally absent from the anchizone. The presence of I/C mixed-layer minerals at Cigar Lake, however, shows that, in this case, such minerals can be stable under anchizone conditions. There are two possible explanations. First, the I/C mineral could be produced by prograde diagenesis (Lee and Peacor, 1985), or second, they represent recent degradation of illite by 'opening' or expansion of the illite layers in a manner similar to the illite-vermiculite-smectite weathering sequence observed in soils (Srodon and Eberl, 1984). D. Quirt (personal communication, 1988) has also recently detected mixed-layer clay minerals in other U occurrences within the Athabasca basin.

4.6.5 Bulk Mineralogy

Qualitative XRD analyses of many of the bulk powdered samples were made in order to compare the mineral content of the clay-size fraction to the whole sample. Results are tabulated in Table B.3 of Appendix B. The sandstone samples are dominated in the bulk fraction by quartz with minor to trace amounts of illite, kaolinite and hematite. For the

of other Athabasca deposits (Collins Bay, Midwest, Key and McClean Lakes) were indistinguishable from illites in the unaltered Athabasca sandstones, based on their Ki and Ir values.

Dunoyer de Segonzac (1970) argued that mixed-layer clay minerals are generally absent from the anchizone. The presence of I/C mixed-layer minerals at Cigar Lake, however, shows that, in this case, such minerals can be stable under anchizone conditions. There are two possible explanations. First, the I/C mineral could be produced by prograde diagenesis (Lee and Peacor, 1985), or second, they represent recent degradation of illite by 'opening' or expansion of the illite layers in a manner similar to the illite-vermiculite-smectite weathering sequence observed in soils (Srodon and Eberl, 1984). D. Quirt (personal communication, 1988) has also recently detected mixed-layer clay minerals in other U occurrences within the Athabasca basin.

4.6.5 Bulk Mineralogy

Qualitative XRD analyses of many of the bulk powdered samples were made in order to compare the mineral content of the clay-size fraction to the whole sample. Results are tabulated in Table B.3 of Appendix B. The sandstone samples are dominated in the bulk fraction by quartz with minor to trace amounts of illite, kaolinite and hematite. For the

altered sandstone samples, many have comparable mineralogy between the bulk and clay-size fractions. Illite is the dominant clay mineral for most samples whereas kaolinite, chlorite, hematite and accessory minerals tend to occur in minor to trace amounts. In a few samples, however, hematite, siderite, or calcite are abundant. Accessory minerals such as pyrite, rutile and zircon were detectable in some samples. The ore-bearing sample, 60-16, contains a minor amount of uraninite and a trace amount of gersdorffite. Many of these accessory minerals were not detectable in the clay-size fraction.

In barren areas of the Manitou Falls Formation, kaolinite and illite occur in sub-equal amounts in the clay-size fraction, with kaolinite content higher in the fine silt-size fraction (D. Quirt, personal communication, 1988). XRD analysis of a sample collected north of the Waterbury Lake area (labelled AB-06 in Table B.3, Appendix B), near the Collins Bay area, indicated that it contains quartz with minor kaolinite and hematite for both the bulk and clay-size fractions. Illite was not detectable in this unaltered sample. In contrast, all Cigar Lake samples contain abundant illite. Sericitization and chloritization of kaolinite is very apparent from the regional XRD data.

4.6.6 Clay Mineral - Depth Relationships

Variations in clay mineralogy, Ki and Ir with depth, for three representative boreholes, are shown in Figure 4.5. Illite is the dominant clay mineral in all three boreholes. Kaolinite occurs generally, but not exclusively, in the clay-size fraction of the sandstone samples and is abundant in the unmineralized borehole (139). Chlorite content increases with depth towards the basement. The Ki ranges from 3.0 to 5.7 and tends to covary with the chlorite content for borehole WDG1-53. Intensity ratio values vary antithetically to Ki in the upper parts of the columns, are sub-parallel to Ki in the middle zone and are random elsewhere.

4.7 SUMMARY

The dominant clay mineral at Cigar Lake is illite. Kaolinite, sudoite (Al-chlorite), Fe-chlorite and an illite/chlorite (I/C) mixed-layer mineral are subordinate. Kübler indices of illite crystallinity for $< 2 \mu\text{m}$ separates indicate high-grade diagenetic to anchimetamorphic conditions. Most samples that contain traces of the I/C mixed-layer mineral recrystallized under high-grade diagenetic conditions. Indices of a few silt-size ($2 - 5 \mu\text{m}$) samples show that illites formed under epizonal conditions. The silt-size samples are devoid of the I/C mineral.

Figure 4.5: The relationship of clay composition, Kuber index and intensity ratio with depth for samples from boreholes WDG1-139, -60, and -53. Summation of I (illite) + K (kaolinite) + C (chlorite) = 100%.

All samples, but one, have $I(002)/I(001)$ intensity ratios greater than 0.26, and many are greater than 0.4, the value that marks the phengite-muscovite boundary. The one exception, sample 60-16, is dominated by Fe-chlorite. Its $I(002)/I(001)$ ratio is < 0.26 , suggesting an Fe- or Mg-rich illite, and hence the Kübler index is of little use in delineating the true extent of recrystallization.

Crystallinity indices and intensity ratios for illite from the unmineralized borehole (139) are indistinguishable from those measured from illites in the alteration halo, above and below the ore zone. Temperature estimates for the high-grade diagenetic-anchizone are about 200 °C and for the anchizone-epizone about 300 °C (Hunziker, 1986). The regional temperature estimated for the Athabasca basin is about 200 °C, based on fluid inclusion thermometry (Pagel, 1975). The Kübler indices for the dominant, $2M_1$ polytype illite from the Cigar Lake deposit confirm these estimates. Some samples from the alteration halo show evidence of higher temperatures in the form of $3T$ illite polytypes.

CHAPTER FIVE

GEOCHEMISTRY

5.1 GEOCHEMICAL SIGNATURES OF THE ATHABASCA DEPOSITS

Ore deposits in the Athabasca basin are polymetallic in nature. Uranium is generally associated with Ni, Co, Mo, Cu, Pb, Zn, Mn, Fe, V, Ag, Au, Pt-group metals, As, S, Se, Te, Bi, B and others (Hoeve and Quirt, 1987). Bruneton (1987) reported at Cigar Lake that As, Cu, Pb, Ni, Co, Zn and Mo were directly associated with U.

A variety of techniques have been used in exploration for the Athabasca U deposits. Uraniferous boulder trains led to discovery of the Rabbit Lake, Collins Bay, Key Lake, Midwest Lake and Cluff Lake deposits (Sopuck et al., 1983). The Cigar Lake, Dawn Lake and McClean Lake deposits were detected by drilling geophysical conductors in the basement. Radioactive surveys provided only limited information at the McClean Lake (Wallis et al., 1985) and Cluff Lake (Tona et al., 1985) deposits. Jagodits et al. (1986) indicated that rocks belonging to the Athabasca Group tend to act as a barrier to radioactive gaseous emanations such as radon. In an exploration feasibility study, Clark (1987) analyzed total and leachable U and other trace elements from the upper 10 m of sandstone above the Cigar Lake and Dawn Lake deposits and detected near-surface lithogeochemical haloes.

Hydrothermal alteration, a metasomatic process, involves changes in the composition of rocks and minerals (Meyer and Hemley, 1967). These changes, which include gains or losses of elements with or without changes in mass or volume, can be evaluated using lithogeochemistry. For example, in the Athabasca deposits, major element composition provides information on the extent and distribution of alteration products (e.g., clay minerals). High concentrations of K_2O , Al_2O_3 , and MgO reflect variable illite, kaolinite and chlorite contents. Mellinger et al. (1987) suggested that trace and ore-element signatures reflect the mineralization processes. They related Sr, precipitated in phosphates, to a diagenetic-hydrothermal environment associated with mineralization. U/Ni ratios have been used to deduce the redox potential in the deposit at the time of deposition or alteration (Golightly et al., 1983). At the McClean Lake deposit the U/Ni ratio generally decreases with depth toward the ore, indicating an increase in pH and decrease in Eh (Wallis et al., 1983).

Host-rock alteration associated with the ore deposits form plume-, or bell-shaped haloes that extend hundreds of metres into the rocks that lie above the unconformity (Hoeve and Quirt, 1987). The haloes are characterized by illite, kaolinite and chlorite, whose relative abundance can be determined using K_2O/Al_2O_3 and MgO/Al_2O_3 ratios. Illite-

dominated haloes have K_2O/Al_2O_3 ratios > 0.18 and MgO/Al_2O_3 ratios < 0.15 ; kaolinite-dominated haloes have K_2O/Al_2O_3 and MgO/Al_2O_3 ratios < 0.04 ; and chlorite-rich haloes have MgO/Al_2O_3 ratios > 0.125 and K_2O/Al_2O_3 ratios < 0.04 (Sopuck et al., 1983). The background K_2O/Al_2O_3 ratio ranges from 0.10 to 0.16 (Ibrahim and Woo, 1985). The trace elements U, Ni, As and Co are above background in the haloes above the ore deposits, but dispersion is restricted to tens of metres (Sopuck et al., 1983), thus limiting their utility as pathfinder elements.

5.2 ANALYTICAL PROCEDURES

5.2.1 X-Ray Fluorescence

Major (SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , MgO , CaO , Na_2O , K_2O , MnO , P_2O_5 and S) and trace (Ba, Cr, Nb, Ni, Sr, Rb, V, Y, Zn and Zr) elements were determined by X-ray fluorescence (XRF) analysis. Total iron is expressed as Fe_2O_3 . Loss on ignition (LOI) was determined on separate aliquots of the same sample and included the determination of H_2O , CO_2 and other volatiles. Details of the analytical procedure are given in Appendix C. Data are reported in weight percent oxides for the major elements and ppm for the trace elements. Information concerning precision and accuracy of data is presented in Appendix C and Tables C.1 and C.2.

5.2.2 Neutron Activation

Rare earth elements (REE) and other trace elements (As, Co, Cr, Cs, Hf, Sb, Sc, Ta, Th, U and W) were determined by instrumental neutron activation analysis (INAA). Analytical procedure is outlined in Appendix D. Trace element results are reported in ppm. Details on precision and accuracy are given in Appendix D and Tables D.2 and D.3.

Interferences from U can produce problems in the analysis of some of the REEs. For example, the isotopes ^{140}La , ^{141}Ce , ^{143}Ce and ^{147}Nd are produced as fission products of ^{235}U in the reactor, and would not be distinguishable from naturally occurring REEs. Similarly, activation of ^{238}U produces ^{239}Np , which causes spectral interferences for ^{153}Sm and ^{172}Lu . Landsberger and Simsons (1987) showed that there could be up to 81% error in the determination of Sm after a 7-day decay time. They indicated that it is not necessarily the high levels of U [Th and Gd] but the ratio of U/Sm [Th/Sm and Gd/Sm] that dictates the error. Corrections can be applied for Lu and Sm because the peak ratios for γ - and X-ray peaks of ^{239}Np tend to be constant (Kennedy and Fowler, 1983).

Ho analysis is also highly sensitive to the U content. An experimentally-determined correction factor (J.L. Bastien, *École Polytechnique*, personal communication, 1986) was applied to the Ho results, but the data plotted well above

the extrapolated chondrite-normalized curve of the REE, and therefore have not been used. The Tm data obtained from INAA also appeared high when plotted on the chondrite-normalized diagrams; calibration problems are possible.

Uranium was also determined by neutron activation analysis (NAA) using the delayed neutron counting (DNC) procedure (Boulanger et al., 1975) at Atomic Energy Radiochemical Company (now called Nordion International). Data are reported in ppm.

5.2.3 Stable Isotopic Analysis

Oxygen was extracted from clay concentrates using BrF_5 ; oxygen was converted to CO_2 using the method of Clayton and Mayeda, (1963); hydrogen was liberated using the method of Kyser and O'Neil (1984). Stable isotopic ratios were measured using Finnigan-MAT 251 and VG (Model 260B) mass spectrometers for ^{18}O and D respectively, at the University of Saskatchewan (Saskatoon). Data are reported relative to the V (Vienna)-SMOW standard. Reproducibility for the clay separates is ± 0.2 o/oo (2σ) for $\delta^{18}\text{O}$ and ± 0.3 o/oo (2σ) for δD (Wilson and Kyser, 1986). Duplicate analyses of Cigar Lake samples fall within these limits.

5.2.4 K-Ar Geochronology

K-Ar dates, obtained from $< 2 \mu\text{m}$ separates of illite-rich samples, were determined at the U.S. Geological Survey laboratory in Denver, Colorado. Analytical procedures are given in Dalrymple and Lanphere (1969). Potassium was determined by isotope dilution.

5.3. RESULTS AND DISCUSSION

5.3.1 Major Element Geochemistry

Major oxide results for bulk samples are given in Table C.3 (Appendix C). Average concentrations of some of the major oxides for each sample type are summarized in Table 5.1. The average sandstone composition from Cigar Lake is very similar to the regional average for the unaltered A and B units of the Manitou Falls Formation. However, the K_2O content of the Cigar Lake sandstones is 7x that of the unaltered average, suggesting illite rather than kaolinite as the major clay mineral.

The major oxide concentrations of TiO_2 , Al_2O_3 , Fe_2O_3 , MgO , CaO and K_2O increases with increasing alteration from sandstone to sandy claystone, whereas the SiO_2 content decreases. The altered basement samples contain the lowest concentrations of SiO_2 and the highest of MgO . The $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratios are > 0.27 for 90% of the samples analyzed. In contrast to the regional background values of 0.10 to 0.16

Table 5.1: Mean concentrations for some major oxides (weight %) and trace elements (ppm) for principal categories of samples and for Fe-rich ($>4\%$ Fe_2O_3) and Fe-poor ($<4\%$ Fe_2O_3) groups. Total iron determined as Fe_2O_3 . Numbers in parenthesis indicates number of samples. Mean concentrations for regional, unaltered Manitou Falls Formation (MFF) shown for comparison.

SAMPLE TYPE	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O	Ni	Rb	Sr	U	V	Zn	Zr
Sandstone (51)	94.07	0.12	2.5	0.76	0.11	0.04	0.63	10	10	105	13	13	13	210
Clayey Sandstone (28)	71.48	0.83	14.2	3.81	0.86	0.09	3.92	48	42	545	235	155	50	1170
Composite (11)	60.46	1.41	19.9	4.23	0.89	0.11	5.12	33	49	620	89*	160	26	1930
Sandy Claystone (54)	44.34	1.43	28.9	7.06	1.36	0.27	8.09	81	84	800	205	485	68	2400
Basement (7)	41.59	1.44	32.4	3.19	6.26	0.19	5.62	230	80	330	95	365	66	430
<u>Fe-Rich</u>														
Clayey Sandstone (4)	41.52	0.80	18.5	20.3	2.70	0.27	4.80	210	65	240	730	270	67	1820
Composite (1)	40.22	1.20	29.1	13.1	0.80	0.10	8.12	34	70	930	103	185	10	2400
Sandy Claystone (16)	33.79	1.18	26.0	18.8	1.61	0.62	7.32	64	88	570	215	620	58	2075
Basement (2)	40.13	1.55	31.9	5.64	6.01	0.15	5.60	150	69	250	129	620	31	360
<u>Fe-Poor</u>														
Clayey Sandstone (24)	76.48	0.84	13.5	1.06	0.56	0.06	3.78	23	38	585	180	140	42	1315
Composite (10)	62.49	1.43	19.0	3.35	0.90	0.11	4.82	30	46	585	87	160	28	1875
Sandy Claystone (38)	48.78	1.54	30.1	2.10	1.25	0.12	8.42	82	82	905	200	430	67	2545
Basement (5)	42.17	1.40	32.6	2.21	6.35	0.21	5.63	260	84	360	81	260	80	460
<u>Regional Average</u>														
MFF Units A + B	94.83	0.11	2.7	1.25	0.03	0.01	0.09	10	2	160	1	9	14	180
MFF Units C + D	95.59	0.09	1.92	1.38	0.03	0.03	0.13	14	3	170	2	11	5	200

* Mean value excluding sample 60-16 containing 13.7% U.
Data taken from Quirt (1985).

reported by Ibrahim and Woo (1985), the high ratios reflect the abundance of illite in the Cigar Lake samples.

Samples were subdivided into Fe-rich and Fe-poor groups on the basis of their red colour. The mean total Fe content determined for each group indicated that 4% Fe_2O_3 could be used to separate both groups. For the clayey sandstones, the Fe-rich samples have higher Al_2O_3 , MgO, CaO and K_2O contents than the Fe-poor group, whereas, for the sandy claystones, the Fe-rich group has lower concentrations of TiO_2 , Al_2O_3 and K_2O than the Fe-poor group. The major oxide trends of decreasing SiO_2 and increasing Al_2O_3 , MgO and K_2O with increasing alteration are exhibited by the Fe-poor group. The concentration differences between the clayey sandstone and sandy claystone samples of the Fe-rich group are less than that observed for overall and Fe-poor samples.

Major oxides, plotted against depth and lithology, for borehole WDG1-60 are shown in Figure 5.1. On these plots, the sandstones [specimens 60-01 (405 m) and 60-13 (417 m)] are readily distinguished by their SiO_2 , Al_2O_3 and K_2O contents. The clayey sandstone samples (60-10, 413.5 m; 60-11, 414 m) contain lower SiO_2 (< 40%), and higher Al_2O_3 (23 - 27%) and K_2O (3 - 8%) than the sandstone samples. Relative to the clayey sandstones, the sandy claystones (60-02, 408 m; to 60-09, 413.3 m; 60-12, 415 m; 60-14, 419 m; and 60-15,

WDG1-60

Figure 5.1: Major elements (wt. %) plotted against depth for borehole WDG1-60. Lithology taken from 1:500 scale drill core logs.

421 m) have slightly higher SiO_2 contents ($> 45\%$) and generally higher Al_2O_3 (17 - 34%) and K_2O (3 - 10%).

The major oxide chemistry of the samples is reflected in the bulk mineralogy. Samples rich in K_2O and Al_2O_3 tend to be dominated by illite, those rich in MgO , by sudoite. In the lower portion of the hematite zone depicted in Figure 5.1, siderite, coexisting with hematite, is reflected by the increased CaO content as well as total Fe contents.

Mean concentrations for sandy claystones (bleached, illite-rich samples) by particle size are listed in Table 5.2. Individual sample results are presented in Table C.4 (Appendix C). The major oxide concentrations are similar for each fraction and reflect the dominant presence of illite. The Fe_2O_3 content of the clay-size fraction is elevated due to the presence of one Fe-rich sample (~ 32 wt. % Fe_2O_3). If this sample is omitted from the calculation, the average is 2.22%.

5.3.2 Trace Element Geochemistry

Results of trace element analyses for bulk samples by XRF are presented in Table C.5 (Appendix C) and by INAA in Table D.4 (Appendix D). Average concentrations of some trace elements are summarized in Table 5.1.

The concentration of all trace elements increases with increasing alteration, and show similar trends to those

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Table 5.2: Mean concentration of major oxides (wt %) and trace elements (ppm) for sandy claystone particle-size separates. XRF analyses performed on ignited samples. Number of samples averaged in parenthesis.

	< 2 μm (20)	2-5 μm (6)	5-20 μm (5)
Major Oxides			
SiO ₂	45.04	47.68	47.21
TiO ₂	0.19	0.20	0.76
Al ₂ O ₃	34.17	35.81	35.27
Fe ₂ O ₃	3.70	1.46	1.76
MnO	-	-	-
MgO	1.76	1.25	1.19
CaO	0.30	0.18	0.40
Na ₂ O	-	-	-
K ₂ O	9.46	10.47	10.26
P ₂ O ₅	1.48	0.27	0.32
S	0.1	0.1	0.1
Trace Elements			
Ba	272	173	147
Cr	-	16	34
Nb	-	-	14
Ni	83	39	151
Rb	101	95	98
Sr	2585	685	305
V	684	399	198
Y	112	56	177
Zn	107	74	74
Zr	1430	427	791
TOTAL	96.74	97.62	97.47
LOI	5.89	5.35	5.34

- not detectable in most samples

shown by the major oxides, with the exception of SiO_2 . The basement samples are generally enriched in trace elements relative to sandstones; however, Sr and Zr are lower and Ni is higher relative to the overlying sandy claystones. Fe-rich clayey sandstones have higher Ni, Rb, U, V, Zn and Zr contents than the Fe-poor group; Fe-rich sandy claystones have less Sr and Zr than the Fe-poor group.

The trace elements are plotted against depth and lithology for borehole WDG1-60 in Figures 5.2 and 5.3. Concentrations are low for the sandstones (60-01 and 60-13), and variable for clayey sandstones (60-10 and 60-11) and sandy claystones (60-02 to 60-09, 60-12, 60-14 and 60-15). Similar variations with depth are exhibited by Ni and U. Samples 60-10, 60-15 and 60-16 reflect the polymetallic nature of the Cigar Lake deposit; Ni, Rb, U, V, Zn (Figure 5.2), As, Co and Sb (sample 60-15 only; Figure 5.3) are concentrated relative to the other samples.

Average U concentrations for the sandy claystone and clayey sandstone types are similar (205 ppm vs. 235 ppm, respectively) and higher than the mean concentration for basement (95 ppm) and sandstone (13 ppm) samples. The concentrations of U in the sandstones, however, are much higher than the regional average of 1 ppm. Figures 5.4 to 5.6 show U, Al_2O_3 and Fe_2O_3 plotted against depth and lithology for 3 bore-holes, WDG1-49 (Figure 5.4), -53 (Figure

WDG1-60

Figure 5.2: Trace elements (in ppm) plotted against depth for borehole WDG1-60. Lithology taken from 1:500 scale drill core logs.

Figure 5.3: Trace elements (in ppm) plotted against depth for borehole WDG1-60. Lithology taken from 1:500 scale drill core logs.

Figure 5.4: Relationship between U, Al₂O₃ and Fe₂O₃ with depth for borehole WDG1-49. Lithology taken from 1:500 scale drill core logs. Elevation of 50 m above mean sea level indicated by arrows to the left of the stratigraphic column.

Figure 5.5: Relationship between U, Al_2O_3 and Fe_2O_3 with depth for borehole WDG1-137. Lithology taken from 1:500 scale drill core logs. Elevation of 50 m above mean sea level indicated by arrows to the left of the stratigraphic column.

Figure 5.6: Relationship between U, Al₂O₃ and Fe₂O₃ with depth for borehole WDG1-53. Lithology taken from 1:500 scale drill core logs. Elevation of 50 m above mean sea level indicated by arrows to the left of the stratigraphic column.

5.5), and -137 (Figure 5.6), which occur along an E-W transect of the ore zone (see Figure 2.4). Uranium appears to covary with Al_2O_3 in all three boreholes and both elements increase with depth in WDG1-49 (Figure 5.4). Because Al_2O_3 probably reflects the clay content, U content may be related to the degree of alteration. From Table 5.1, the Fe-rich samples tend to be higher in U than the Fe-poor group but a depth-related correlation between U and Fe_2O_3 is not apparent in Figures 5.4 to 5.6.

Trace element analyses for particle size separates are given in Table C.6 (Appendix C; XRF) and Table D.5 (Appendix D; INAA). Concentrations of trace elements in the clay are higher than the silt-size fraction (Table 5.2). This may be attributed to the adsorption capacity of the clay-size particles. The high concentration of Sr in the clay-size fraction is probably due to the presence of goyazite (see Figure 3.11).

5.3.3 Rare Earth Element Geochemistry

Rare earth element (REE) data for bulk samples are listed in Table D.6 (Appendix D). REE data (normalized to the Leedey chondrite values of Taylor and Gorton, 1977) are plotted in Figure 5.7 (note: Gd is estimated by extrapolation between Sm and Tb). The data from the bleached and pale red sandy claystone and clayey sandstone (shaded band)

Figure 5.7: Chondrite-normalized plot of REE for a variety of bulk samples. Shaded region marks the complete range of REE contents of the clayey sandstone, sandy claystone and basement samples. The sandstone data are from samples 60-01 (upper curve) and 60-13 (lower curve). Data for sample 60-15 shown separately because of its unusual trend; data for 60-16 taken from Smith et al. (in press).

samples indicate light REE (La to Eu) enrichment with values up to 800x chondrites, La/Yb ratios from 6.5 to 31.2 and negative Eu anomalies. Although the patterns are similar to average North American Shale, the REE abundances are 5 to 7x richer. Sandstone specimens (60-01 and 60-13) show similar trends but are less enriched in the light REE. Sample 60-15, a dark grey sandy claystone, does not show a negative Eu anomaly. It contains abundant calcite and Fe-Mg chlorite, and contains 100 ppm of As. It is located proximal to the ore.

The ore sample, 60-16, was analyzed for REE after a pre-concentration separation of interfering elements (i.e., alkali and alkaline earth elements, Fe, Sc, Th and U; see Smith et al., in press). The chondrite-normalized trend for this sample is quite different to those observed from other samples. Sample 60-16 is enriched in the heavy REE rather than the light, although it does exhibit a negative Eu anomaly. The presence of the negative Eu anomaly in the ore sample, as well as the alteration halo samples, suggests that reducing conditions during ore formation may have extended upwards, into the surrounding alteration halo. Sample 60-15, although similar in texture and mineralogy to the ore sample, contains only ~130 ppm U but does not show a negative Eu anomaly. It is possible that the presence of

alkaline earth elements (i.e., Ca) may have affected the measurement of the REEs.

REE data for clay-size separates are listed in Table D.7 (Appendix D). All samples but one are from borehole WDG1-60. These were chosen in an attempt to examine compositional variation with depth of a suite of bleached, illite-bearing samples of similar textural appearance. In most of the samples, U is concentrated in the clay-size fraction relative to the coarser components. The coarse silt-size fraction (5 - 20 μm) generally has a slightly higher U content than the fine silt-size fraction. A similar pattern is seen for other trace elements analyzed by INAA (see Table D.5), including Co, Hf, Sb, Sc, Ta and W.

REE data (normalized to the Leedey chondrite values of Taylor and Gorton, 1977) for the various size fractions are plotted in Figure 5.8, and show an enrichment in the LREE. Typically, the < 2 μm fractions contain LREE values of 700 to 1700x chondrites and have La/Yb ratios between 27.2 and 57.2. The fine silt-size samples are also enriched in LREE (225 to 800x chondrites), with La/Yb ratios of 22.8 to 54.0. The coarse silt-size samples have LREE value of only 145 to 340x chondrites and La/Yb ratios of 4.1 to 8.3. All samples have negative Eu anomalies. Particle-size separates have similar REE patterns to the bulk samples. The enrichment of REE in the silt-sized and especially the clay-sized frac-

Figure 5.8: Chondrite-normalized plot of REE for sized-separates of sample 60-05. Particle size fractions include $< 2 \mu\text{m}$ (-2), $2-5 \mu\text{m}$ (-5) and $5-20 \mu\text{m}$ (-20).

tions probably result from the higher adsorption capacity of the clay minerals due to their small particle size and hence, their large surface area.

5.3.4 Major and Trace Element Correlations

Correlation coefficients (r) for some of the major oxides and trace elements (Table 5.3) show that SiO_2 is negatively correlated with all other elements. For example, as alteration and hence Al_2O_3 content increases for Fe-poor samples, the SiO_2 content decreases (Figure 5.9). For the highly altered samples with $\text{SiO}_2 < 45\%$ and $\text{Fe}_2\text{O}_3 > 4\%$ (Fe-rich group), a positive correlation is shown between Al_2O_3 and SiO_2 (Figure 5.10). The samples in Figure 5.10 show a negative correlation between Fe_2O_3 and Al_2O_3 (Figure 5.11). The decrease in SiO_2 with increase in Al_2O_3 is related to the concomitant dissolution of quartz and enrichment in clay in the Fe-poor samples. The opposite trend exhibited by the Fe-rich group probably reflects the increase in hematite relative to the illite content.

Trace element data for all samples show moderate to high positive correlations between Ni and MgO ($r = 0.67$), Rb with K_2O ($r = 0.79$) and CaO ($r = 0.66$), Sr with TiO_2 ($r = 0.79$), Zr ($r = 0.79$) and K_2O ($r = 0.65$), and Zr with TiO_2 ($r = 0.91$), Sr ($r = 0.79$) and K_2O ($r = 0.71$). Uranium does not statistically correlate with any of the other elements, but

Table 5.3: Pearson correlation coefficients (r) for all samples.

SAMPLE NUMBER	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	K ₂ O	Na	Rb	Sr	U	V	Zn	Zr
SiO ₂	1.00													
TiO ₂	-0.65	1.00												
Al ₂ O ₃	-0.88	0.68	1.00											
Fe ₂ O ₃	-0.58	0.09	0.17	1.00										
MgO	-0.53	0.27	0.46	0.17	1.00									
CaO	-0.35	0.14	0.19	0.33	0.24	1.00								
K ₂ O	-0.84	0.63	0.97	0.16	0.24	0.21	1.00							
Na	-0.48	0.31	0.46	0.15	0.67	0.12	0.33	1.00						
Rb	-0.61	0.44	0.67	0.08	0.25	0.66	0.72	0.21	1.00					
Sr	-0.55	0.79	0.62	0.05	0.02	0.04	0.65	0.10	0.37	1.00				
U	-0.16	0.35	0.04	0.03	0.02	0.08	-0.04	0.10	0.25	0.21	1.00			
V	-0.54	0.38	0.46	0.37	0.19	0.07	0.45	0.13	0.18	0.30	0.18	1.00		
Zn	-0.51	0.47	0.48	0.23	0.19	0.28	0.49	0.28	0.49	0.23	0.34	0.52	1.00	
Zr	-0.65	0.91	0.67	0.19	0.03	0.08	0.71	0.19	0.38	0.79	0.38	0.36	0.46	1.00

Figure 5.9: Plot of SiO_2 vs. Al_2O_3 for Fe-poor ($< 4\% \text{Fe}_2\text{O}_3$) bulk samples. The samples include sandstone (lower right), clayey sandstone (central area), sandy claystone (upper left) and some composites.

Figure 5.10: Plot of SiO_2 vs. Al_2O_3 for Fe-rich bulk samples. Samples include sandy claystone, composite and basement.

Figure 5.11: Plot of total iron as Fe_2O_3 against Al_2O_3 for suite of Fe-rich samples shown in Figure 5.8. Samples 60-15 and 60-16 are the two points that lie off the curve.

it does show similar depth-related trends with Ni, Rb and Zn contents (Figure 5.2). Within the ore zone, Bruneton (1987) reported that U is associated with As, Co, Cu, Mo, Ni, Pb and Zn.

For those samples analyzed by INAA, Zr is positively correlated with Hf (Figure 5.12), La (Figure 5.13) and Ce (not shown; similar pattern to La). Some of these associations can be explained in terms of the geochemical affinity between elements such as Rb - K and Ni - Mg. Other elemental associations reflect the relative mobility or immobility of the elements. For example, the positive correlation between Zr and TiO_2 , Hf and La may be due to their occurrence in detrital, resistant minerals which restrict their mobility.

Multivariate analysis of geochemical data is a common approach to isolating factors which determine the inter-relationships among variables (e.g., major oxides and trace elements). The data set presented in Appendix C (Tables C.3 and C.5) was evaluated using principal component analysis, a descriptive factor analysis method in which the factors are expressed in the pattern of variances and co-variances between variables (Davis, 1986). Details about factor analysis are presented in Appendix C.

About 83% of the variance was accounted for by five factors. The first factor, accounting for about 45% of the

Figure 5.12: Plot of Zr vs. Hf for suite of bulk samples.

Figure 5.13: Plot of La vs. Zr for suite of bulk samples.

variance, heavily weights the contributions of Zr, Sr, Nb, Ti, K and Al and a negative weighting of Si. This factor can be interpreted in terms of detrital mineralogy, illite and possibly goyazite (Sr-Al phosphate). The second factor, accounting for 13% of the variance, is heavily weighted in Mg and Ni and is likely related to the chlorite content. Factors 3, 4 and 5 appear to be related to apatite (Ca and P), Fe-oxides (Fe) and uraninite (U), respectively. The factor plot (varimax rotation; see Appendix C for explanation) is shown in Figure 5.14. Silicon, negatively weighted on factor 1, plots in an opposite trend to all the other elements. Al and K (illite) plot close together, with Rb contained along the same trend (or vector). The similarity between Ni and Mg may result from Ni substitution for Mg^{2+} in the chlorite structure (Mellinger et al., 1987) or an overlap of a Ni-rich zone with the chlorite zone near the unconformity. The Ni - Mg trend is distinct from the Al - K trend and may reflect two different types of alteration (i.e., chloritization and sericitization). Uranium appears to plot close to Ca and Fe, near the origin, possibly due to the co-existence of siderite/calcite and Fe-bearing chlorite within the ore zone and immediately overlying hematite zone. The proximity of the elements to the origin suggests that the variance of these variables is not accountable by these two factors.

Figure 5.14: Multivariate analysis factor loadings for varimax rotation, principal component analysis.

Using correspondence analysis Mellinger (1984) and Mellinger et al. (1987) determined that 70 - 75% of the variance of the data from a number of Athabasca deposits (Dawn Lake, Midwest Lake, Key Lake, Collins Bay and Maurice Bay) could be accounted for by two factors. The first factor was related to the ratio of detrital quartz to clay minerals and the second to the quantity of hematite. The variation of some trace elements can be explained in terms of their affinity for clay minerals. For example, Rb was associated with illite (K), Ni with chlorite (Mg) and Li with illite and chlorite (Mellinger, 1984). Mn was found to be associated with siderite, Th and Zr with detrital minerals, and Sr with phosphate; B, associated with dravite, was thought to indicate a diagenetic-hydrothermal environment (Mellinger et al., 1987). Uranium, however, showed only an indirect association with the other elements and no direct relationship to the alteration processes (i.e., sericitization and chloritization; Mellinger, 1984). Similar results for the Dawn Lake and Cigar Lake deposits were reported by Clark (1987).

The results of the factor analysis indicate that the variation in the major and trace element data is controlled by a few mineral phases. Mellinger et al. (1987) suggested that the trace elements were concentrated as a result of alteration rather than redox conditions that existed during

U mineralization. The factor data for Cigar Lake supports this idea. Uranium does not appear to correlate with sericitization (Al - K), chloritization (Mg - Ni) or quartz dissolution processes that have occurred.

5.3.5 Chemical Trends and Alteration

Diagenesis or hydrothermal alteration can produce compositional changes which can be revealed by comparing the chemistry of altered and unaltered materials. Altered sandstones and sandy claystones from the Cigar Lake alteration halo are compared to the unaltered Manitou Falls Formation (units A + B) in Figure 5.15. Mean concentrations for the Cigar Lake samples have been normalized to an average composition for unaltered sandstones (see Table 5.1), which plots as 1 on Figure 5.15. The tops of the bars represent the average concentration of the sandstones and sandy claystones.

The Cigar Lake sandstones suggests little change in Si, Al and Zn and moderate depletion in Fe, Ni and Sr relative to the unaltered equivalents. Slight enrichment in Ti, V and Zr and stronger enrichment in Mg, Ca, K, Rb and U are also evident. The enrichment in Mg, Ca, K, Rb and U in the Cigar Lake sandstones cannot be explained simply as a result of high-grade diagenesis, because the regional sandstones have been subjected to similar conditions. It is possible

Figure 5.15: Mean concentrations for altered sandstones and sandy claystones normalized to the mean concentration for unaltered, Manitou Falls Formation, units A + B. The tops of the horizontal and vertical shading represent the mean concentration of the element for the respective rock type.

that enrichment is related to addition by hydrothermal-diagenetic fluids that circulated during mineralization, and that these elements may have originated from the Athabasca Group rocks themselves.

The average sandy claystone is depleted in Si and enriched in all other elements relative to the unaltered and altered sandstones. There is a consistent enrichment factor of 10.3 (average) for Ti, Al, Fe, Mg, Ca, K, Ni, Rb, Sr, U, Zn and Zr between the sandy claystones and the Cigar Lake sandstones, except for V which is 37x more enriched.

Concentrations of major oxides, traces and REEs in two samples that lie close to one another (60-01 at 405 m and 60-02 at 408 m) are plotted in Figure 5.16. The enrichment factors range from 1.6 to 11.5 with an average of 6.5. Many elements (e.g., Al_2O_3 , K_2O , Rb, Sr, Zr, Y, Th, U and the REEs) exhibit an enrichment factor of about 8.7. Si is depleted by a factor of 0.5. Cramer (1986a) observed a similar pattern of consistent enrichment for geochemically dissimilar elements for Dawn Lake, which he attributed to removal of a barren phase (i.e., quartz) during ore formation.

The gains and losses of elements can be quantitatively assessed using "isocon diagrams" developed by Grant (1986) as a simple graphical solution to Gresens' (1967) mass balance equations for metasomatic alteration. Grant (1986) rearranged Gresens' equation to produce a diagram with linear

ELEMENTAL COMPONENTS

Figure 5.16: Concentrations for major oxides (wt. %), traces (ppm) and rare earth elements (ppm) for two samples in borehole WDG1-60. The top of each bar (vertical and horizontal shadings) represents the concentration of the element for each sample.

relationship between elemental concentrations of altered relative to unaltered rocks. This element ratio produces a line through the origin, termed an isocon. The slope of the isocon defines the mass change during alteration (Grant, 1986). From the densities of the altered and original rock, volume changes can also be assessed.

Isocon diagrams are shown in Figures 5.17 and 5.18. The concentrations of the major oxides and trace elements have been scaled down (or up) to fit concentration units of 0 - 30 wt. % and 0 - 300 ppm on the graphs. From Grant's (1986) discussion, elements that lie above and below the best-fit isocon provide estimates of the gains and losses, respectively, that have occurred. For example, if constant mass is assumed ($\text{slope} = (M^0/M^A) = 1$), there is a gain in the elements that lie to the left of the isocon and loss to those that lie to the right. Volume changes can be estimated using $(M^A/M^0) \times (\rho^A/\rho^0)$.

In Figure 5.17, the composition of altered, Cigar Lake sandstones (average of 51) is compared to the average, unaltered regional Manitou Falls Formation (units A + B). The elements Si, Fe and Ti lie on a straight line that is coincident with an isocon of constant mass ($\text{slope} = 1$). If constant mass is assumed, losses in Al, Ni, Sr and Zn, and gains in Zr, V, K, Mg, Ca and U are indicated. However, if constant Al is assumed, as Al is considered to be an immo-

Figure 5.17: An isocon diagram for average Manitou Falls Formation (MFF), units A + B (C^0) and average Cigar Lake sandstones (C^A). Concentrations are scaled up or down so that oxides are plotted from 0 - 30 wt. % and traces from 0 - 300 ppm. Isocons are shown to represent constant mass and constant Al.

Figure 5.18: An isocon diagram for samples 60-01 (C^0) and 60-02 (C^A). Concentrations are scaled up or down so that oxides are plotted from 0 - 30 wt. % and traces from 0 - 300 ppm. A best-fit isocon is indicated as well as constant mass and constant Al isocons. If constant Al is assumed, losses in the components S, Zn, Ni, Fe, Ba, Nb and Si is greatest and less for V, Ti and Zr.

bile element, the isocon passing through Al would have a slope of 0.93 which is equivalent to a mass gain $M^A/M^0 = 1.07$. If the assumption that Al is constant is correct, and that there are no density differences, then a volume increase of 7% is implied. This would correspond to a gain in Si of 7%, possibly reflected by an increase in quartz content of sandstones above the alteration halo (e.g., quartz-cemented cap). Gains in Zr, V, K, Mg, Ca and U are still indicated as well as in Fe.

Elemental concentrations for samples 60-01 (405 m) and 60-02 (408 m) are compared in Figure 5.18, using 60-01 as the unaltered material. A best-fit isocon can be drawn through most elements on the far left-side of the diagram. The slope of 7 ($M^0/M^A = 7 \equiv M^A/M^0 = 0.14$; mass decrease of -0.86) corresponds to a mass change of 86%. Silica lies to the right of the constant-mass isocon suggesting a loss of Si. The best-fit isocon is very close to a constant-Al isocon (slope of 10). If constant Al is assumed, then mass and/or volume changes are inferred. The specific gravities of samples 60-01 and 60-02 are 2.37 and 1.44 respectively, which would represent a 94% change in volume ($M^A/M^0 = 0.1$; $V^A/V^0 = 0.1$ ($1.44/2.37$) = 0.06). Because many elements (i.e., K, Rb, Sr, U, Y) lie close to the constant-Al isocon, it is probable that during mineralization these elements were concentrated along with Al in the alteration halo as Si

was dissolved and removed. Those elements that lie between the best-fit and constant-mass isocon (i.e., S, Zn, Ni, Fe, Ba and Nb) may have been preferentially mobilized during the later bleaching and sulphide mineralization event.

Quartz solubility depends on temperature, and is independent of pH between 2 and 9 (Siever, 1962). The solubility increases by a factor of about 2 for a 50 °C rise in temperature (Siever, 1962; Hoeve and Quirt, 1984). Dissolution and removal of quartz could provide the necessary space to accommodate an ore deposit (Cramer, 1986a). Hoeve and Quirt (1984) proposed that hot fluids emanating from the basement, undersaturated with respect to silica, caused quartz dissolution in the overlying sandstones; the sandstone was probably the source of the metals. Red-beds are considered sources of economically important metals (Zielinski et al., 1983) such as U, V, Se, As, Mo, Pb and Cu (Levinson, 1974).

The consistent enrichment of major (excluding Si) and trace elements, including U, in the clay-rich alteration halo suggests that the metals were concentrated in the alteration zone by removal of quartz. Remobilization appears to be limited to a few trace elements, including Ba, Fe, Ni, Nb, S and Zn, and is probably due to the second stage of mineralization (i.e., bleaching and sulphide formation). Although the source of the elements is debatable (sandstone

vs. basement), it appears that they were present from the time of initial mineralization and hydrothermal alteration.

5.3.6 Stable Isotope Geochemistry

Oxygen and hydrogen isotopic compositions can be used to evaluate the source and evolution of aqueous fluids associated with ore zones. The oxygen isotopic compositions of minerals reflect isotopic equilibrium between mineral phases and hydrothermal fluids, while the D/H ratio is a sensitive indicator of the source of H₂O (Sheppard, 1986).

The δD , $\delta^{18}O$, clay mineralogy and total U contents for clay-size separates are presented in Table 5.4. A reference suite of samples includes sandstone and basement specimens from the barren borehole, WDG1-139. Clay mineral content (reported as percent illite, chlorite and kaolinite) and U concentration of bulk samples are given for comparison.

Samples that contain 99 - 100% illite have δD values (see Table 5.4 and Figure 5.19) between -64 and -108 o/oo (average = -82) and $\delta^{18}O$ values between +9.0 and +10.7 o/oo (average = +10). Illite from a reference sandstone sample (139-12) is enriched in D (-74 o/oo) relative to the illite from the other sandstone sample (53-12; -97 o/oo). The two samples that contain minor (< 5%) kaolinite (sandy claystone samples 44-18 and 60-04) have δD values within the range of the illite-rich samples and are slightly lower than the

Table 5.4: Stable isotope (D and ^{18}O) data for a suite of < 2 μm separates. Sample type (Sst = sandstone; Cl. Sst = clayey sandstone; Clst = sandy claystone; Base = altered basement), clay mineralogy (I = illite, C = chlorite; K = kaolinite; I + C + K = 100%) and U concentration of bulk samples shown for comparison. K-Ar age given in last column (see Table 5.5).

SAMPLE NUMBER	SAMPLE TYPE	CLAY MINERALOGY			U (ppm)	δD (o/oo)	$\delta^{18}\text{O}$ (o/oo)	AGE (Ma)
		I	C	K				
44-01	Cl. Sst	100	0	0	42	-67	10.2	
44-04	Clst	100	0	0	66	-77	10.5	
44-06	Clst	100	0	0	104	-95	10.3	1210
44-08	Cl. Sst	100	0	0	245	-86	10.7	
44-11	Clst	99	0	1	233	-81	10.4	
44-18	Clst	88	0	12	116	-88	10.7	
49-12	Clst	100	0	0	318	-80	9.0	
49-13	Clst	100	0	0	110	-66	10.7	
53-02	Sst	100	0	0	3	-97	9.7	
53-15	Base	53	47	0	52	-50	9.1	815
60-03	Clst	100	0	0	71	-78	10.7	1255
60-04	Clst	95	0	5	189	-89	9.3	
60-16*	Cl. Sst	11	89	0	13.7%	-142	5.5	-
113-02	Clst	100	0	0	245	-81	10.0	
113-04	Clst	100	0	0	100	-73	9.9	
118-03	Clst	99	0	1	177	-97	10.1	
118-06	Clst	100	0	0	146	-108	10.3	
137-01	Cl. Sst	100	0	0	185	-64	9.7	1148
139-12	Sst	100	0	0	1.5	-74	9.4	
139-18	Base	68	32	0	8	-58	9.6	

*Sample taken from top of ore zone; contains Fe-chlorite, other samples contain sudoite (Al-chlorite).

Figure 5.19: Stable isotopic composition of clay-sized fractions of whole rock samples from the Cigar Lake deposit. δD and $\delta^{18}\text{O}$ measured relative to the V-SMOW standard.

average illite-rich samples (-88 and -89 respectively vs. -82 o/oo). Basement samples that contain sudoite and illite (53-15 and 139-18) generally have similar $\delta^{18}\text{O}$ values but higher δD values (-50 o/oo and -58 o/oo, respectively) than the illite-rich samples. Sample 60-16, an Fe-chlorite-illite sample, is significantly different from any of the other samples, and has an average δD value of -142 o/oo and $\delta^{18}\text{O}$ of +5.5 o/oo. There is no correlation of δD or $\delta^{18}\text{O}$ with depth or bulk U content.

The Fe-chlorite-illite sample (60-16) associated with the ore zone is depleted in D (isotopically lighter) relative to the illite-rich samples. This may reflect the behaviour of Fe-rich minerals which do not concentrate D relative to Mg- and Al-rich minerals (Suzuoki and Epstein, 1976). In contrast, the basement sudoite-illite samples have δD values higher than the average illite-rich sample (-50 and -58 vs. -82 o/oo). Because the Al, Mg and Fe contents of illite and sudoite are similar (see Table 4.3), mineral chemistry cannot explain the variation in δD values. Whitney and Northrop (1987) predicted that chlorite in mixed clay assemblages could lower the bulk δD relative to pure illite. However, their samples from the San Juan Basin, New Mexico, showed the opposite trend, and they proposed that low-temperature smectites were replaced by higher temperature illite-chlorite assemblages, resulting in higher δD

(or less negative) values. A similar reaction could explain sudoite-illite vs. illite data from the Cigar Lake samples. It is possible that the sudoite-illite assemblage, which is stable under high-grade diagenetic to low-grade metamorphic conditions (Fransolet and Schreyer, 1984), has replaced a pre-existing lower δD assemblage (I/S or kaolinite ?).

Figure 5.20 compares data from Cigar Lake and other sites in the Athabasca Basin (see Figure 2.3). Wilson et al. (1987), on the basis of stable isotopic composition, defined two types of illite in clay concentrates from various uranium deposits in the Athabasca Basin. These included "normal" illite with δD values near -70 o/oo and $\delta^{18}O$ values of +12 o/oo and "shifted" illites with δD values as low as -169 o/oo and $\delta^{18}O$ values as high as +15 o/oo. Illites and chlorites associated with U mineralization at Cluff Lake (Halter et al., 1987) are strongly depleted in D (-90 to -170 o/oo), whereas illites from the barren zones are similar to the "normal" illites of Wilson et al. (1987) (Figure 5.20). The data from the Cigar Lake samples are very similar to the data reported by Wilson et al. (1987) and Halter et al. (1987). The Cigar Lake ore sample is slightly more enriched in D than the Cluff Lake ore samples and "shifted" illites, but is more depleted in ^{18}O .

Wilson et al. (1987) maintain that "normal" illites equilibrated with a mid-latitude basinal brine with a δD of

Figure 5.20: Comparison of stable isotopic data from Cigar Lake with samples from other deposits in the Athabasca basin. Data for Key Lake, Collins Bay, Midwest and McClean Lakes from Wilson et al. (1987) and Cluff Lake from Halter et al. (1987). The meteoric water line (MWL) and the calculated illite- and montmorillonite-meteoric water lines at 25 °C are shown. Illite fractionation factors used were those of Eslinger and Savin (1973) and Yeh (1980); montmorillonite fractionation factors were those of Savin and Epstein (1970).

-60 o/oo and a $\delta^{18}\text{O}$ of +5 o/oo. Bray et al. (1988) also estimated δD and $\delta^{18}\text{O}$ values for the original Athabasca pore water fluids to be about -45 o/oo and +6 o/oo respectively. It is apparent that the fluid(s) which reacted with the clay minerals is regionally significant because the isotopic signature of illites from both barren and mineralized areas are similar.

The "shifted" illites of Wilson et al. (1987) contain high K_2O and H_2O contents, and K-Ar dates obtained from these samples are significantly lower (e.g., 414 ± 11 Ma) than dates obtained from the "normal" illites (e.g., 1131 ± 24 Ma). Wilson et al. suggested that the "shifted" illites have undergone retrograde alteration by meteoric waters, similar to present-day surface waters, and represent an early stage in the formation of I/S mixed-layer minerals. Because the D-depleted illite samples described by Wilson et al. (1987) are enclosed in an envelope of undepleted illite, Bray et al. (1988) argued that fluids similar to present-day surface waters could not have passed through rocks of the Athabasca Group and exchanged with illite in some layers and not in others. They suggested rather that the depletion may have resulted from reaction with isotopically light hydrogen from $\text{CH}_4 + \text{H}_2\text{S} + \text{H}_2$ -bearing fluids derived from graphitic metapelites, common in the basement.

Interaction with late meteoric-hydrothermal solutions may cause retrograde H isotopic exchange in hydrous minerals, and could account for low D/H ratios (Sheppard, 1977). Interaction with meteoric waters similar to present-day water, cannot be ruled out as a possible explanation for the D- and ^{18}O -depleted values of the Cigar Lake ore sample. Lack of correlation between δD and $\delta^{18}\text{O}$ with depth and U content suggests that fluid-rock interaction does not involve the mineralizing solutions, but may reflect the inherent permeability and porosity of the individual samples.

5.3.7 K-Ar Dates

K-Ar dates from illites are presented in Table 5.5 along with K and ^{40}Ar contents. The three illite-rich samples (44-06, 60-03 and 137-01) have K-Ar ages in the range 1255 ± 28 to 1148 ± 28 Ma. The Basement sudoite-illite sample, 53-15, yields an age of 815 ± 30 Ma. The chlorite-illite-bearing ore sample (60-16) does not contain any radiogenic ^{40}Ar , and thus has an apparent age of zero.

The Cigar Lake samples, with the exception of the basement sample (53-15), indicate a trend of decreasing K-Ar age with increasing U content based on a somewhat limited data base. The $\delta^{18}\text{O}$ value (see Table 5.4) decreases from +10.7 to +5.5 with decreasing K-Ar age while δD decreases from -50

Table 5.5: K-Ar age determination for illite-bearing (44-06, 60-03, 137-01), illite-sudoite-bearing (53-15) and Fe-chlorite-illite-bearing (60-16) samples. K content determined by isotope dilution. ⁴⁰Ar measured in duplicate.

SAMPLE NO.	DEPTH (m)	¹ K (wt%)	⁴⁰ Ar -10 (10 mol/g)	⁴⁰ Ar (%)	AGE ² (Ma ± 2σ)
137-01	401.15-401.36	7.906	221.8 218.5	96.4 95.3	1155 ± 28 1142 ± 28
44-06	402.22-402.32	7.752	232.3 231.1	99.2 98.9	1212 ± 28 1208 ± 28
60-03	409.00-409.13	7.782	245.3 244.0	95.0 94.6	1257 ± 29 1253 ± 28
60-16	422.57-422.70	1.375	no ⁴⁰ Ar found	-	-
53-15	444.00-444.15	4.671	83.67 82.23	74.9 74.5	817 ± 25 813 ± 30

¹K determination by K. Futa and S. Mahan (U.S.G.S.)

²Ar determination and age calculation by H. Mehnert (U.S.G.S.)

to -142 with increasing uranium content (52 ppm to 13.7%) for four of the five dated samples (exception sample 137-01). Resetting of the K-Ar system by circulating meteoric-hydrothermal fluids has been correlated with depletion in δD (O'Neil, 1979). Sample 60-16 is depleted in δD relative to the illite-rich samples, and also shows the lowest K-Ar date.

Dates similar to those listed in Table 5.5 have been reported from other parts of the Athabasca basin. Bell (1985) reported $^{40}\text{Ar}/^{39}\text{Ar}$ dates that range from 1615 to 500 Ma for alteration products from Cluff Lake. K-Ar dates for both illites and chlorites from Collins Bay, Midwest, Key and McClean Lakes deposits range from 1493 to 110 Ma (Wilson et al., 1987) while dates in the range 1322 to 130 Ma were obtained from Cluff Lake illites (Halter et al., 1987). In the latter two studies, the younger ages (< 800 Ma) were associated either with illites that display the isotopic shift towards lighter D values ("shifted" illites) or with mineralized samples.

Halter et al. (1987) and Bray et al. (1987) noted an inverse correlation between uranium concentrations and K-Ar ages. Bray et al. (1987) suggested that a 639 ± 3 Ma $^{40}\text{Ar}/^{39}\text{Ar}$ date obtained from one sample reflected argon loss caused by α -radiation damage because the illite was taken from a sample that lay about 2 mm from a pitchblende nodule.

Alternatively, they suggested that heat production due to radioactive decay locally enhanced the temperature and fluid flow. Bell (1985), however, suggested that the wide range of K-Ar dates observed at Cluff Lake could reflect different degrees of Ar loss through a single event or alteration, or possibly reflect a re-setting through diagenetic or episodic mineralization, associated with orogenic activity.

Deposition of the Athabasca Group sediments has been estimated to be about 1450 ± 50 Ma (Bell, 1981; Armstrong and Ramaekers, 1985), and diagenetic ages to be within the range 1300 - 1000 Ma, contemporaneous with mineralization (Hoeve and Quirt, 1987). The main mineralizing event occurred between 1350 - 1250 Ma, coeval with the onset of tectonic reactivation and diabase activity in the basin (Bell, 1981; Hoeve and Quirt, 1984, 1987). A second stage of mineralization, from 1100 - 1050 Ma, represents renewed basin-wide activity of the hydrothermal system, possibly in response to on-going basic magmatism (ca., 1350 - 1000 Ma; Hoeve and Quirt, 1984). A cluster of U-Pb dates between 900 and 700 Ma from various deposits suggests sporadic activity at this time (Hoeve and Quirt, 1984). A further event, indicated by U-Pb dates of 300 - 200 Ma, involved remobilization of uranium accompanied by sulphide formation, kaolinitization and retrograde alteration. This stage was probably caused by epeirogenic uplift in the basin (Hoeve and

Quirt, 1984). Further remobilization(?) is reflected by the young dates reported for Cluff Lake (365 Ma; Bell, 1985; 130 Ma; Halter et al., 1987), Key Lake (110 Ma; Wilson et al., 1987; 89 Ma; Gatzweiler et al., 1979), Fond-du-Lac (80 Ma; Homeniuk et al., 1982) and the Beaverlodge area, north of the basin (100 - 0 Ma; Koepfel, 1963).

The relationship between uranium mineralization and diabase dyke activity has been discussed widely. Although a genetic link between mineralization and MacKenzie diabase dyke activity has been suggested (Bell, 1981; Hoeve and Quirt, 1984), Bray et al. (1987) concluded on the basis of 1160-1080 Ma Rb-Sr dates by Armstrong and Ramaekers (1985) that the dykes were too young to be coeval with the main mineralizing event. Armstrong and Ramaekers (1985), however, also reported a 1310 Ma Rb-Sr date for the Diabase Peninsula dyke at Cree Lake, and the MacKenzie swarm has been dated at 1267 ± 2 Ma, based on U-Pb in baddeleyite (LeCheminant and Heaman, in press). The dykes are thus similar in age to fluid migration in the Thelon and Athabasca basins (LeCheminant, personal communication, 1989). A K-Ar date of 1266 ± 31 Ma for illite cement from the Thelon basal conglomerate (Miller, 1988) suggests that fluid migration may well be related to the intrusion of the MacKenzie dykes.

The K-Ar dates for the Cigar Lake suite, with the exception of the "zero"-age sample, are similar to the age of uranium mineralization from elsewhere in the basin. Primary mineralization at Cigar Lake has been dated by U-Pb on pitchblende at 1300 Ma by Ruzicka and LeCheminant (1986), whereas dates for the three illite-rich samples (1255 - 1148 Ma) may represent K-Ar resetting due to recrystallization by late, circulating hydrothermal fluids. The 815 ± 30 Ma age from the basement sample may be related to mineralizing events between 900 and 700 Ma, may indicate Ar loss from non-retentive chlorite, or may result from partial Ar loss during interaction with meteoric waters.

The "zero"-aged sample is interesting and probably reflects Ar loss during recent alteration caused by circulating meteoric waters. Recent events have been documented for the basin. Episodic lead loss between 0 and 100 Ma for the Beaverlodge area, has been attributed to epeirogenic reactivation of faults with attendant resetting of pitchblende dates (Koeppel, 1968). It is possible that recent disturbances, as reported by Wilson et al. (1987) and Halter et al. (1987), occurred throughout the Athabasca basin.

5.4 SUMMARY

Increase in alteration with depth towards the ore is reflected by decreasing SiO_2 content and increasing major

oxides and trace elements. The K_2O/Al_2O_3 ratios are > 0.27 for 90% of the samples selected, whereas regional background values range from 0.1 to 0.16. Multivariate analysis indicates that about 58% of the variance in the major and trace element data can be explained using two factors. Factors 1 and 2 are heavily weighted with respect to detrital and clay minerals. There does not appear to be any correlation between U and the clay minerals. Samples from the alteration halo show enrichment in LREE, but the ore specimen (60-16) is enriched in HREE. Most samples display a negative Eu anomaly, indicative of similar redox conditions for the migrating fluids.

Enrichment of major and trace elements in sandy claystone samples relative to the altered and regionally unaltered sandstones is fairly consistent. This data suggests that the concentration of elements other than SiO_2 , including U, resulted from the concentration of clay minerals in the original sandstone matrix as quartz was dissolved and removed. This idea is supported by mass balance calculations suggesting a volume change of about 94%.

Average δD and $\delta^{18}O$ values for illite-rich (99 - 100%) clay-size separates from both mineralized and unmineralized areas are -82 o/oo and +10 o/oo respectively. Illite with minor kaolinite is slightly depleted in D relative to the illite-rich samples, whereas sudoite- and illite-bearing

samples are enriched in D. The ore sample, 60-16, is significantly depleted in D and ^{18}O relative to the illite-rich samples. These data are within the range reported from other unconformity-type deposits in the Athabasca basin. The relative enrichment of the sudoite-illite samples and depletion of the ore sample in D may simply reflect minerals rich in Mg and Al. Low-temperature retrogressive H isotopic exchange with meteoric water, similar to present-day water, could have produced the low D/H ratio observed in the ore sample.

K-Ar dates for 3 illite-rich, clay-size separates range from 1255 ± 28 to 1148 ± 28 Ma, dates that may reflect either recrystallization or resetting of the K-Ar system by hydrothermal fluids circulating after U mineralization. The timing of this alteration may be related to the emplacement of the MacKenzie dyke swarm ca. 1267 Ma ago. The 815 ± 30 Ma K-Ar date, on the other hand, probably corresponds to the 900-700 Ma period of mineralization documented from other deposits. The apparent "zero" age for the ore sample is probably due to ^{40}Ar loss during recent interaction with meteoric water, or continuous diffusion from non-retentive minerals.

CHAPTER SIX

SEQUENTIAL PARTIAL EXTRACTION OF URANIUM

6.1 INTRODUCTION

6.1.1 Properties of Uranium

Uranium, the heaviest naturally-occurring element, has three isotopes: two of which (^{238}U and ^{235}U) account for 99.99% of the element's abundance; ^{234}U , a radiogenic daughter of ^{238}U , accounts for the remainder. Uranium occurs in oxidation states U^{4+} , U^{5+} and U^{6+} , but only U^{4+} and U^{6+} have importance in geochemistry. Uranium has a moderately large ionic radius (0.09 nm), large coordination number (6 or 8) and has a strong tendency to bond with oxygen.

U^{4+} is an essential constituent of a few minerals (e.g., uraninite, coffinite and brannerite). It can substitute for Th^{4+} , Zr^{4+} and some rare earth elements, such as Ce^{4+} , and has limited solubility in most low temperature solutions (Nash et al., 1981). Uraninite is stable under low Eh and mildly acidic to alkaline conditions. Coffinite is stable under these same conditions but at higher silica activities.

Under oxidizing conditions, U^{6+} is stable and usually occurs as the uranyl ion, UO_2^{2+} (Boyle, 1982). The uranyl ion dominates up to pH 5. As pH increases UO_2^{2+} reacts with carbonate to form three different carbonate complexes: UO_2CO_3 , $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ (Figure 6.1). Under

Figure 6.1: Eh-pH relation for uraninite and aqueous solution with CO₂, demonstrating the necessity for reducing conditions for precipitation of uraninite at most pHs (Langmuir, 1978, Figure 11, p. 46).

reducing conditions, UO_2^{2+} is either reduced to U^{4+} and precipitated as the oxide UO_2 (uraninite) or precipitated in the hexavalent state as complex hydrated oxides, hydroxides, silicates, phosphates, arsenates, vanadates, molybdates, selenites, tellurites and carbonates, depending on ligand availability (Boyle, 1982). It is important to note that Eh appears to be the dominant control on uranium mineralization; sorption of U^{6+} , however, by organic matter or clays may precede its reduction to U^{4+} and serve as a catalytic or preconcentration mechanism (Maynard, 1983). The general cycle of U^{4+} and U^{6+} and their interconversions in nature is shown in Figure 6.2.

6.1.2 Mobility of Uranium

In temperate surface environments, U is mobile (Ames et al., 1983a). The factors influencing U concentration dissolved in natural surface and ground waters include (Langmuir, 1978): (1) U content of source rocks, sediments or soils and its leachability; (2) proximity of water to the U source; (3) degree of hydraulic isolation of the water from dilution by fresher water; (4) climatic effects, seasonal variability and influence of evapotranspiration; (5) the pH and Eh of the water; (6) concentration of complexing agents (complex hydrated oxides listed above) which form U-complexes or insoluble U minerals; and (7) presence of highly

Figure 6.2: Cycle of U^{4+} and U^{6+} interconversions in nature (after Boyle, 1982).

sorptive materials such as organic matter, Fe-, Mn- and Ti-oxyhydroxides and clays. Leachability of U from source rock is dependent upon mineral association; U in uraninite (soluble mineral) is easily removed, whereas that in resistant minerals such as zircon is not readily available (Durrance, 1986).

The role of adsorption in controlling U mobility is only qualitatively known (Hsi and Langmuir, 1985). Studies of adsorption of U by clays (Goldsztaub and Wey, 1955; Rancon, 1973; Borovec, 1981; Tsunashima et al., 1981; Ames et al., 1983a, b; Fiala and Ciml, 1985; and Berthelin et al., 1987), Fe-oxyhydroxides (Starik et al., 1958; Ames et al., 1983c; Hsi and Langmuir, 1985; Van der Weijden et al., 1985b; Berthelin et al., 1987), organic matter (Van der Weijden and Van Leeuwen, 1985) and amorphous silica, Ti- and Zr-oxyhydroxides (Maya, 1982) have shown that amorphous Ti- and Fe³⁺-oxyhydroxides generally have the greatest adsorption capacity (Langmuir, 1978; Hsi and Langmuir, 1985). Boyle (1982) noted that the chemistry of U in nature is further complicated by organic complexes formed with UO_2^{2+} , especially humic materials. These complexes can be formed by chelation, ion exchange or chemisorption (Nash et al., 1981).

Borovec (1981) reported that fine fractions of kaolinite, illite and montmorillonite were effective in adsorbing

uranyl and hydroxy complexes from uranylacetate solutions, with the maximum adsorption potential proportional to the cation exchange capacity (CEC) and specific surface area of the minerals. Tsunashima et al. (1981) found that complete saturation of montmorillonite by U was possible with dilute uranyl nitrate or uranylacetate solutions. Uranyl ions were adsorbed more strongly than Na^+ and K^+ but less than Mg^{2+} , Ca^{2+} and Ba^{2+} . Fiala and Ciml (1985) determined that adsorption of U^{6+} from uranylacetate solutions by smectite, illite, kaolinite and chlorite increased with increasing temperature and decreasing pH. They noted that the weakest adsorption was by montmorillonite, the mineral with the highest CEC. In a study comparing the adsorption capacities of finely ground muscovite ($\text{CEC} = 0.95 \pm 0.06 \text{ meq/100 g}$), biotite ($15.3 \pm 1.1 \text{ meq/100 g}$) and phlogopite ($1.17 \pm 0.15 \text{ meq/100 g}$), Ames et al. (1983b) determined that muscovite, behaving as an anion-exchange mineral, was more effective in adsorbing uranyl-carbonate than were biotite or phlogopite between pH 6.5 and 9.2.

In a study of U adsorption on Fe-oxyhydroxides, Hsi and Langmuir (1985) reported that, between pH 5 and 6, dissolved uranyl species were strongly adsorbed onto amorphous Fe^{3+} -oxyhydroxides and goethite and less so onto synthetic and natural specular hematite. Complexing of UO_2^{2+} by carbonate radicals inhibited uranyl adsorption, especially in alkaline

solutions. Their study supported the earlier findings of Starik et al. (1958) who had noted that the maximum sorption of U by Fe-oxyhydroxides occurred at about pH 5 and that U was desorbed in the presence of a carbonate solution. In another study, Ames et al. (1983c) determined that sorption of U by Fe-oxides occurred at low U concentrations (~ 93 ppb) independent of alkaline earth metal concentrations.

Concentration of U through sorption, such as that shown by Fe-oxyhydroxides from surface and ground waters, is an important ore-forming process (Ames et al., 1983a; Hsi and Langmuir, 1985). Desorption of U, however, can occur through aging and crystallization of goethite and hematite, and/or by increasing the alkalinity of water (Hsi and Langmuir, 1985).

6.1.3 Partitioning of Uranium

Ore-forming metals and pathfinder elements released during weathering of primary minerals are transported by hydromorphic dispersion or mechanical transport into the secondary environment (Chao and Theobald, 1976; Chao, 1984). Scavenging of heavy metals occurs by one or more mechanisms. Included among these are: (1) co-precipitation; (2) adsorption; (3) surface complex formation; (4) ion exchange; and (5) penetration of crystal lattices (Chao and Theobald, 1976). Fe- and Mn-oxides in soils and stream sediments act

as sinks for these metals (Jenne, 1968); organic matter, clay minerals and other hydrous oxides may also be suitable substrates (Tessier et al., 1985).

Partitioning of the trace elements among the substrates and mechanisms of retention can be estimated using sequential selective extraction procedures in which a series of single, partial extractions, attack samples with increasing severity. A sequential selective extraction procedure was developed to determine partitioning of U in some Cigar Lake samples. Of particular interest is the partitioning of U in: (1) exchangeable sites; (2) carbonates; (3) sulphides; (4) amorphous Fe-oxides; (5) crystalline Fe-oxides; (6) clay minerals; and (7) accessory minerals.

6.2 PARTIAL AND SEQUENTIAL EXTRACTION METHODS

6.2.1 Introduction

Many partial extraction techniques have been used to differentiate among the various mineral phases in soils and sediments (Mehra and Jackson, 1960; McKeague and Day, 1966; Biermans and Baert, 1977; Jackson, 1979; Chao and Zhou, 1983; Borggaard, 1988), to enhance anomalies relative to background during exploration programmes (Olade and Fletcher, 1974; Sondag, 1981; Tessier et al., 1982; Chao, 1984) and in recent sediment studies (Robbins et al., 1984; Förstner, 1985; Fitzgerald et al., 1987). These methods may

be non-selective or selective (Table 6.1). Non-selective extractants consist of inorganic and organic acids that dissolve metals from geologic materials (Chao, 1984). The non-selective reagents as well as strong acid decomposition or fusion, are commonly used to extract the total amount of metals, with the extractable metals labelled as "cold-extractable" or "hot-extractable". Selective extractants attack specific inorganic or organic materials and the metals released are "extractant-dependent" (Chao, 1984). The identification of the materials that act as sinks for trace metals and possibly the mechanisms of incorporation (as listed above) can be evaluated using partial extraction methods (Tessier et al., 1982).

6.2.2 Sequential Extraction Schemes

Table 6.2 lists some of the sequential extraction procedures that have been used in various geochemical studies. The first seven schemes have been reviewed by Chao (1984). With time, the procedures have become more complex, with each scheme designed for specific applications and materials. The simple procedure used by Rose and Suhr (1971), in combination with regressive analysis of trace-metal concentrations, enabled reduction in the background variations for stream sediments. The more complex scheme of Miller et al. (1986) was an attempt to separate adsorbed from occluded

Table 6.1: Non-selective and selective single partial extractions commonly used in soil and geochemical studies (after Chao, 1984).

NON-SELECTIVE

Inorganic acids	HCl, HNO ₃ , aqua regia
Organic acids and salts	HOAc-NH ₄ OH, EDTA, NH ₂ OH.HCl± citrate

SELECTIVE

Water-soluble	distilled water
Exchangeable metals	NH ₄ -acetate, NH ₄ -citrate, CaCl ₂ , MgCl ₂ , BaCl ₂ etc.
Carbonates	HOAc, NaOAc-HOAc, EDTA
Organic matter	H ₂ O ₂ , NaOCl, Na ₄ P ₂ O ₇ or K ₄ P ₂ O ₇
Sulphides	H ₂ O ₂ -ascorbic acid, aqua regia, HNO ₃ -tartaric acid, Br in CCl ₄ , KClO ₃ -HCl
Mn-oxides	NH ₄ OAc + hydroquinone, NH ₂ OH.HCl-HNO ₃
Amorphous Fe-oxides	Tamm's reagent ((NH ₄) ₂ C ₂ O ₄ -H ₂ C ₂ O ₄ in darkness), NH ₂ OH.HCl-HCl, EDTA, Tiron
Crystalline Fe-oxides	Tamm's reagent (UV light), NH ₂ OH.HCl-HOAc, HCl, Na dithionite-Na citrate-Na bicarbonate (DCB), NH ₂ NH ₂ .HCl-HCl
Residual minerals or total digestion	Hot concentrated acids HF ± H ₂ SO ₄ , HNO ₃ , HCl, HClO ₄

Table 6.2: Examples of sequential selective extraction procedures used in exploration geochemistry and soil studies. The first seven procedures are reviewed in Chao (1984).

Rose and Suhr (1971)

- (1) Soluble, exchangeable and carbonates: NaOAc, pH 5.0
- (2) Organic matter, Mn-oxides and sulphides: H_2O_2
- (3) Fe-oxides: DCB
- (4) Residue: atomic emission spectroscopy of various sized fractions

Chao and Theobald (1976)

- (1) Mn-oxides and "reactive" Fe-oxides: 0.1 M $NH_2OH.HCl$ - 0.01 M HNO_3
- (2) Amorphous Fe-oxides: 0.25 M $NH_2OH.HCl$ - 0.25 M HCl
- (3) Crystalline Fe-oxides: Na dithionite - Na citrate (DC)
- (4) Sulphides and resistant Fe minerals: $KClO_3$ - HCl and HNO_3
- (5) Residual silicates: HF and HNO_3

Gatehouse et al. (1977)

- (1) Water-soluble: distilled H_2O
- (2) Exchangeable and some carbonates: 1 M NH_4OAc - $HOAc$, pH 4.5
- (3) Mn-oxides: 0.1 M $NH_2OH.HCl$ - 1 M NH_4OAc , pH 4.5
- (4) Organic matter and sulphides: H_2O_2 and 1 M NH_4OAc
- (5) Hydrous Fe-oxides: $NH_2NH_2.HCl$ and HCl , pH 4.5
- (6) Residue silt and clay: HF

Hoffman and Fletcher (1979)

- (1) Organic matter: $NaOCl$, pH 9.5
- (2) Mn-oxides: 0.1 M $NH_2OH.HCl$, pH 2.5
- (3) Amorphous Fe-oxides: 0.175 M $(NH_4)_2C_2O_4$ - 0.100 M $H_2C_2O_4$, pH 3.5
- (4) Crystalline Fe-oxides: DCB, pH 7
- (5) Residue: $HClO_4$ and HNO_3

Filipek and Theobald (1981)

- (1) Exchangeable and carbonates: 1 M $HOAc$
- (2) Mn-oxides: 0.1 M $NH_2OH.HCl$ - 0.01 M HNO_3
- (3) Organic matter and sulphides: H_2O_2 and NH_4OAc in 6% HNO_3
- (4) Hydrous Fe-oxides: 0.25 M $NH_2OH.HCl$ - 25% $HOAc$
- (5) Residue: HF , HNO_3 and HCl

Table 6.2: Continued

Sondag (1981)

- (1) Water-soluble, exchangeable and some carbonates: 1 M NH_4OAc , pH 4.5
- (2) Mn-oxides: 0.1 M $\text{NH}_2\text{OH} \cdot \text{HCl}$, pH 4.5
- (3) Organic matter: 35% H_2O_2
- (4) Amorphous Fe-oxides: 0.175 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ - 0.100 M $\text{H}_2\text{C}_2\text{O}_4$, pH 3.3
- (5) Clay and silt residue: HF and HCl

Bogle and Nichol (1981)

- (1) Organic matter, exchangeable and sulphides: NaOCl
- (2) Mn-oxides: 0.1 M $\text{NH}_2\text{OH} \cdot \text{HCl}$
- (3) Hydrous Fe-oxides: 0.25 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ - 0.25 M HCl
- (4) Crystalline Fe-oxides: 0.1 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ - 25% HOAc
- (5) Residue: HNO_3

Tomiyama and Kitano (1982)

- (1) Water-soluble: distilled H_2O
- (2) Exchangeable and carbonates: 1 M CH_3COOH
- (3) Fe- and Mn-hydroxides: 1 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ - 25% HOAc
- (4) Unstable clay minerals: 1.2 M HCl
- (5) Residual silicates: HClO_4 and HF

Cardoso Fonseca and Martin (1986)

- (1) Exchangeable and some carbonates: NH_4OAc , pH 4.5
- (2) Mn-oxides: $\text{NH}_2\text{OH} \cdot \text{HCl}$, pH 2.0
- (3) Amorphous Fe-oxides: NH_4 - oxalate (dark)
- (4) Organic matter and sulphides: H_2O_2
- (5) Crystalline Fe-oxides: NH_4 - oxalate (UV light)
- (6) Residue: HCl, HNO_3 and HF

Miller et al. (1986)

- (1) Water soluble: distilled H_2O
- (2) Exchangeable: 0.05 M $\text{Pb}(\text{NO}_3)_2$ + 0.1 M $\text{Ca}(\text{NO}_3)_2$
- (3) Acid soluble: 0.44 M HOAc + 0.1 M $\text{Ca}(\text{NO}_3)_2$
- (4) Mn-oxide: 0.1 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ - 0.1 M HNO_3
- (5) Organic matter: pyrophosphate
- (6) Amorphous Fe-oxide: 0.175 M NH_4 - oxalate (dark)
- (7) Crystalline Fe-oxide: NH_4 - oxalate (UV light)
- (8) Residual: aqua regia and HF

metals, in particular Cu, in agricultural, polluted and waste-amended soils.

6.2.3 Application to Uranium

Only a few examples of sequential extraction procedures applied to U exploration have been reported, and three of these are shown in Table 6.3. Lehto (1981), using the first procedure outlined in Table 6.3, found that organic matter retained significant amounts of U in lake, stream and bog sediments from northern Saskatchewan, but Fe-hydroxides and detrital minerals were also important U hosts for lake and stream sediments respectively. Çagatay (1983) investigated the partitioning of U in sediments from the abyssal plain and continental slope of the Black Sea as part of a study to evaluate various fluorometric methods in analyzing U. Airey et al. (1983) and Airey (1986) determined that U and Th were associated with Fe-oxides and Ra with clay/quartz in weathered ore of the Alligator Rivers Uranium Province, Northern Territory, Australia. Landa (1982) assessed geochemical associations of U, ^{230}Th and ^{226}Ra in U-ore blend and tailings using the second procedure outlined in Table 6.3. Most of the extractable U was associated with a readily acid-soluble fraction for both the ore and tailings. Bolle et al. (1988) (third procedure in Table 6.3) examined 300 soil and stream sediment samples and determined that Tamm's

Table 6.3: Examples of sequential selective extraction schemes that have been used to assess the geochemical associations of uranium.

Lehto (1981)

- (1) Organic matter: NaOCl, pH 9.5
- (2) Carbonates and some clay minerals: H_2O - HCl
- (3) Amorphous Mn-oxides: 0.1 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ - HCl
- (4) Amorphous Fe-oxides: 0.175 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ - 0.100 M $\text{H}_2\text{C}_2\text{O}_4$
- (5) Crystalline Fe-oxides: $\text{NH}_2\text{NH}_2 \cdot \text{HCl}$ - HCl, pH 4.5
- (6) Residual: HF, HNO_3 , and HClO_4

Landa (1982)

- (1) Water-soluble: distilled H_2O
- (2) Exchangeables: 0.1 M NaCl
- (3) Carbonates and readily acid-soluble: 1 M HOAc
- (4) Fe- and Mn- hydrous oxides: 1 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ - 25% (v/v) HOAc
- (5) Alkaline earth sulphates and organic matter: 1.3% (w/v) NaOH, 2.6% DTPA and 1.2% triethanolamine

Bolle et al. (1988)

- (1) Water-soluble, exchangeables, and some carbonates: 1 M NH_4OAc , pH 4.5
- (2) Mn-oxides: 0.1 M $\text{NH}_2\text{OH} \cdot \text{HCl}$, pH 4.5
- (3) Amorphous Fe-oxides: 0.175 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ - 0.1 M $\text{H}_2\text{C}_2\text{O}_4$, pH 3.3
- (4) Organic matter and some sulphides: 35% H_2O_2
- (5) Crystalline Fe-oxides: 0.175 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ - 0.1 M $\text{H}_2\text{C}_2\text{O}_4$
- (6) Residual silt and clay: HCl, HNO_3 , and HF

reagent, under ultraviolet conditions, was effective in delineating U anomalies. Zielinski et al. (1983) assessed mobility and distribution of heavy metals, including U, during the formation of first-cycle red-beds. They suggested that Eh and pH changes could lead to release of trace elements previously adsorbed by the red-beds during diagenesis.

6.3 ANALYTICAL PROCEDURES

6.3.1 Sequential Extraction Procedure

The sequential partial extraction procedure established for this study is outlined in Figure 6.3. The reagents used were tested individually on a small group of samples in order to determine their selectivity and effectiveness in extracting U. XRD analyses were made of samples before and after extraction to evaluate the extent, if any, of dissolution of the clay minerals, with additional monitoring by atomic spectrophotometric analysis of some major cations (K, Al, Mg, Fe) and NAA-DNC analysis of U in the extractant solutions. These results are discussed separately in Appendix E. The rationale for, and effect of, each step in the sequential extraction procedure are discussed below. All reagents used were analytical grade. The criteria used for selection included: (1) the procedure should be selective; and (2) the procedure should be independent of small

SEQUENTIAL EXTRACTION PROCEDURE

Figure 6.3: Final sequence of reagents used to partition U in some Cigar Lake samples.

changes in concentration, extraction time and temperature (Borggaard, 1988).

Step 1: Carbonates

1 M NaOAc, pH 5.0 (Tessier et al., 1979; 1982).

This solution should attack all carbonates (except siderite), and should remove carbonate-associated, easily acid-soluble and exchangeable forms of U. This partial extraction method replaced the $MgCl_2$ partial extraction method for exchangeable metals, because no U was detectable in the initial experiments using $MgCl_2$ (see Appendix E).

Twenty mL of 1 M NaOAc, adjusted to pH 5.0 with acetic acid (HOAc), were added to 0.5 g oven-dried (105 °C overnight) samples in 50 mL polycarbonate centrifuge tubes. Samples were shaken on an oscillating shaker at room temperature for 5 hours, then centrifuged at 4500 rpm (radius = 16.8 cm) for 20 minutes. The supernatant liquids were then decanted and collected. This procedure was repeated. The samples were then washed with 10 mL of doubly demineralized water (DDW), shaken for 30 minutes, centrifuged and the washings added to the supernatant solutions.

Step 2: Uraninite

30% H_2O_2 plus 2.5% Na_2CO_3 (Olade and Goodfellow, 1979).

Solutions of Na_2CO_3 or $(\text{NH}_4)_2\text{CO}_3$ with H_2O_2 are used to extract uranium ores (Fletcher, 1981). Following the method of Olade and Goodfellow (1979), this partial extraction was added to the initial sequential extraction procedure to remove uraninite and/or organic-bound U. Sulphide-bound U may also be leached, because some sulphides are attacked by this solution.

The residue from (1) was digested with 1 mL of 30% H_2O_2 and allowed to stand for 1 hour at room temperature. One mL of DDW was then added, and samples shaken on a Vortex Mixer (American Scientific Products) for 1 minute. Eight mL of 2.5% Na_2CO_3 were then added, samples were again shaken using the Vortex Mixer and set in an ultrasonic bath for 1 hour (output = 120 W, 80 kcs). After sonication, the samples were heated for 30 minutes in a water bath at 90 °C to 'boil off' excess H_2O_2 . The samples were then centrifuged, the supernatant decanted and collected, and the procedure repeated. Finally, samples were washed with DDW following the method outlined in (1) and the washings decanted into the bottles.

Step 3: Amorphous Fe-Oxides

0.25 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ in 0.25 M HCl (Chao and Zhou, 1983).

Three extraction techniques were evaluated for selectivity of amorphous Fe-oxides. These were: acid ammonium oxalate (AAO), hydroxylamine hydrochloride (HAH) and Tiron (catecholdisulphonic acid di-sodium salt). These extractants were initially tested on the following four samples: (1) a bulk sample with high Fe content (~ 55 wt. % Fe_2O_3); (2) an Fe-rich fine silt-size fraction ($2 - 5 \mu\text{m}$); (3) a bulk sample containing a moderate Fe content (~ 10 wt. % Fe_2O_3); and (4) a clay-size sample ($< 2 \mu\text{m}$) with a moderate Fe content. The samples were leached once and a duplicate set was leached 10 times to test selectivity of the reagent and assess particle size effects. XRD analyses of the residues and atomic absorption analyses of the supernatant solutions for Fe, Al, K and Mg were determined to aid in the evaluation and selection of an amorphous-selective method. The HAH extraction (Chao and Zhou, 1983) was found to be the most suitable. Details of these experiments are presented in Appendix E.

The residue from (2) was extracted with 20 mL of 0.25 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ in 0.25 M HCl for 30 minutes in a 50°C oven. Samples were then centrifuged and the supernatant solutions collected. This procedure was repeated, followed by washing with DDW as outlined in steps 1 and 2.

Step 4: Crystalline Fe-Oxides

0.68 M Na Citrate plus Na Dithionite (Sheldrick, 1984).

Dithionite-citrate (DC) attacks both hematite and goethite and would extract amorphous Fe-oxides if they had not been previously removed. The residue from step 3 was extracted with 25 mL of 0.68 M Na citrate to which about 0.4 g Na dithionite was added. The samples were shaken overnight and then centrifuged, and supernatants collected. The procedure was repeated once for most samples and up to five times for the Fe-rich samples. The procedure was stopped when a colour change from red to white was observed. Each sample was then washed with DDW, centrifuged and the wash-ings added to the supernatant solutions.

Step 5: Residual Silicates

HClO₄ plus HNO₃ plus HF followed by 4 M HNO₃.

The samples were finally digested in a HF-HNO₃-HClO₄ acid mixture to extract uranium associated with residual silicates and any other remaining accessory minerals. A separate sample was digested in similar fashion to determine total digestible U. The mixture was evaporated to dryness and then leached with about 4 M HNO₃. Many samples were digested twice to produce a clear supernatant solution.

6.3.2 Analysis of Uranium

The most commonly used techniques for U determinations include instrumental neutron activation-delayed neutron counting (DNC), X-ray fluorescence, conventional and laser-induced fluorometric analysis and α -particle counting. Ward and Bondar (1979) recommended the DNC technique because of its precision and sensitivity for low concentrations of total U, and conventional fluorometric analysis for partial and/or selective extractions. The DNC technique has been successfully used in sequential extraction studies by Landa (1982), Zielinski et al. (1983) and Çagatay (1983). Fluorometric analysis has been used in sequential selective extraction (Bolle et al., 1988) and selective leaching (Olade and Goodfellow, 1979; Van der Weijden et al., 1985a; Clark, 1987) studies. Alpha-particle counting has been used to determine U after sorption (Ames et al., 1983a, b), selective leaching (Torma et al., 1985) and sequential extraction (Airey et al., 1983) studies.

Uranium, in extractant solutions, was analyzed by delayed neutron counting (DNC) at Atomic Energy Radiochemical Company (now called Nordion International) following the method of Boulanger et al. (1975). This technique was selected over others (see Appendix E) because it was relatively inexpensive, reproducible, and not prone to matrix interference. In this method, it is assumed that the ratio

tration was at the detection limit (e.g., < 3 ppm), the detection limit was used as a maximum for that fraction in the summation. Because the total U contents are variable, intersample comparison was made on the basis of the percentage or proportion of U extracted by the individual steps. These results are summarized in Table 6.5. Average values have been calculated for the two groups of samples (bulk and clay-size).

Step 1:

The amount of U extractable by step 1 is variable, ranging from 4 to 37% of the total U. The results are plotted in order of increasing total U content in Figure 6.4. No apparent correlation is observed, based on the variability shown for both bulk and clay-size samples in Figures 6.4a and b, respectively. This lack of relationship also holds between extractable U (step 1) and total Fe_2O_3 or Al_2O_3 contents (not shown).

Uranium extractable by step 1 derives from exchangeable, easily-acid soluble and carbonate-bound forms (except siderite). From the results of preliminary experiments and data from other methods of investigation, it is possible to assess the relative contributions from each extractable form. Initial experiments showed that the amount of U

3

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS
STANDARD REFERENCE MATERIAL 1010a
(ANSI and ISO TEST CHART No. 2)

of U isotopes is consistent with their natural abundance (i.e., the U-decay series is in equilibrium).

Because of low U concentrations in the extractant solutions, the supernatant solutions were concentrated. Solutions were passively evaporated to dryness using a heat lamp. Residues were then dissolved in about 5 to 10 mL of 4 M HNO_3 and the U analyzed by DNC. Difficulties arose in concentrating the dithionite-citrate solutions due to excessive amounts of dissolved solids.

6.4 RESULTS AND DISCUSSION

6.4.1 Sequential Partial Extractions

Thirty bulk, powdered and clay-size samples were leached using the sequential extraction procedure described above (see Figure 6.3). A subsample of each specimen was digested in concentrated acids (step 5 only); sample 60-16 was analysed in duplicate and the DH-1 standard was included as a check on the reliability of the procedure and U analysis.

Results for the sequential partial extraction procedure are listed in Table 6.4 for the 17 bulk and 13 clay-size samples. If data were unavailable for one step of the procedure, the total digestible U (see Table 6.6; column 2) minus the summation of the available fractions, was used as an estimate of the missing data. In cases where the concen-

Table 6.4: Concentration of U (in ppm, determined by Delayed Neutron Counting), extracted from powdered bulk samples and clay-size separates using steps 1 to 5 of the sequential extraction procedure.

Sample No.	1	2	3	4	5
Bulk Samples					
44-08	16	20	7	48	95
44-10	644	848	18	127	104
44-11	22	87	5	41	72
44-17	112	254	27	168	153
44-21	437	762	86	359	180
49-12	19	69	3	31	168
53-15	5	8	5	12	45
57-02	11	9	5	23	46
60-02	6	22	<3	13	52
60-03	3	17	<3	12	43
60-07	57	113	14	33	97
60-09	5	20	3	14	37
60-15	16	54	18	8	50
60-16	49940	40430	16390	3400	24840
60-16	30190	37930	17790	3480	26190
103-05	13	26	6	33	7
113-02	16	79	5	45	101
119-30	29	28	<4	13	56
<2 μm Fraction					
44-08	92	245	8	121	236
44-11	37	215	11	218	129
49-12	145	344	14	155	552
53-15	16	37	<5	12	51
57-02	24	42	9	49	57
60-02	9	60	<3	9	67
60-03	10	127	5	33	-
60-07	28	77	8	38	83
60-09	6	90	5	51	117
60-15	7	53	<3	21	31
60-16	9850	28780	1400	810	1490
103-05	15	21	23	90	17
119-30	22	66	4	13	32

- 1 NaOAc + HOAc - extractable/carbonate-bound, exchangeable and easily acid soluble.
- 2 H_2O_2 + Na_2CO_3 - extractable/uraninite and organic bound.
- 3 $NH_2OH:HCl$ - extractable/amorphous Fe-oxide bound.
- 4 Dithionite - Citrate - extractable/crystalline Fe-oxide bound.
- 5 $HF + HClO_4 + HNO_3$ - extractable/residual silicates.
- not determined
- < at detection limit

tration was at the detection limit (e.g., < 3 ppm), the detection limit was used as a maximum for that fraction in the summation. Because the total U contents are variable, intersample comparison was made on the basis of the percentage or proportion of U extracted by the individual steps. These results are summarized in Table 6.5. Average values have been calculated for the two groups of samples (bulk and clay-size).

Step 1:

The amount of U extractable by step 1 is variable, ranging from 4 to 37% of the total U. The results are plotted in order of increasing total U content in Figure 6.4. No apparent correlation is observed, based on the variability shown for both bulk and clay-size samples in Figures 6.4a and b, respectively. This lack of relationship also holds between extractable U (step 1) and total Fe_2O_3 or Al_2O_3 contents (not shown).

Uranium extractable by step 1 derives from exchangeable, easily-acid soluble and carbonate-bound forms (except siderite). From the results of preliminary experiments and data from other methods of investigation, it is possible to assess the relative contributions from each extractable form. Initial experiments showed that the amount of U

Table 6.5: Percentage of U extractable by steps 1 to 5 of the procedure. Averages determined for each group (bulk and clay-size samples).

Sample No.	1	2	3	4	5
Bulk Samples					
44-08	8	11	4	26	51
44-10	37	49	1	7	6
44-11	10	38	2	18	32
44-17	16	36	4	23	21
44-21	24	42	5	19	10
49-12	6	24	1	11	58
53-15	7	10	7	16	60
57-02	12	10	5	24	49
60-02	6	23	<3	14	54
60-03	4	22	<4	15	55
60-07	18	36	4	11	31
60-09	6	25	4	18	47
60-15	11	37	12	6	34
60-16*	31.5	31.5	13.5	3	0.5
103-05	15	31	7	39	8
113-02	7	32	2	18	41
119-30	22	22	<3	10	43
Ave. (n=17)	13	28	4	17	37
<2 μm Fraction					
44-08	13	35	1	17	34
44-11	6	35	2	36	21
49-12	12	28	1	13	45
53-15	13	31	<4	10	42
57-02	13	23	5	27	32
60-02	6	41	<2	6	45
60-03	3	35	1	9	52
60-07	12	33	3	16	36
60-09	2	33	2	19	44
60-15	6	46	<3	18	27
60-16	23	68	3	2	4
103-05	9	13	14	54	10
119-30	16	48	3	10	23
Ave. (n=13)	10	36	3	18	32

* average of two analyses.
 < at detection limit.

Figure 6.4: NaOAc + HOAc-extractable U (step 1) as a percentage of the total U for (a) bulk samples and (b) clay-size separates. The samples are arranged according to increasing total U contents. Sample numbers are shown on top of each bar, total U content (ppm) inside.

associated with exchangeable sites was commonly non-detectable (Appendix E).

A detailed study of ore samples from Cigar Lake using X-ray photoelectron spectroscopy (XPS) and XRD, failed to detect inorganic C in the XPS spectra. This indicates that U does not occur in carbonate/bicarbonate-containing minerals (Sunder et al., 1988). They determined, however, that U occurred as uraninite (UO_2), coffinite (USiO_4) and as an oxidized form, $\alpha\text{-U}_3\text{O}_7$, associated with UO_2 . Although abundant to trace amounts of calcite occur in some samples, it is unlikely, based on their findings, that this extractable U is solely associated with carbonates. This leaves only the possibility of an association with an easily-acid soluble fraction. As two samples (60-15 and 60-16) contain an Fe-rich chlorite, the acidic nature ($\text{pH} = 5$) of this extraction may have been sufficient to attack, but not destroy, this mineral. Evidence from field relations at Key Lake shows a high correlation between chlorite and U (Wilson and Kyser, 1986); hence, breakdown of the Fe-chlorite may have contributed, in part, to the total extractable U from step 1. The U associated with this fraction is probably the most mobile form of U that occurs in these samples.

Step 2:

The total U extractable by step 2 ranged from 10 to 49% and 13 to 68% for bulk and clay-size samples respectively. Extractable U is plotted against increasing total U content in Figure 6.5. A larger proportion of the total U content of each individual sample was extractable by step 2, than step 1, although there is still no apparent correlation between extractable U and total U. Also no obvious trends exist between extractable U and total Fe_2O_3 or Al_2O_3 (not shown).

Uraninite, organic-bound U and possibly sulphide-bound U should be extracted by step 2. As there was no visible reaction on addition of H_2O_2 , it is unlikely that an organic-bound form of U is present. Uraninite is assumed to be the main digestible fraction by this treatment. Of the 4 samples containing high concentrations of U (samples 44-10, 44-17, 44-21 and 60-16), uraninite was only detected by XRD in bulk sample 60-16. However, these results suggest that at least some dispersed uraninite is present in all the samples.

Step 3:

With a few exceptions, the lowest proportions of U, ranging from the detection limit to about 14% were extracted during step 3. Samples arranged in order of increasing

Figure 6.5: $\text{H}_2\text{O}_2 + \text{Na}_2\text{CO}_3$ -extractable U (step 2) as a percentage of the total U for (a) bulk samples and (b) clay-size separates. The samples are arranged according to increasing total U contents. Sample numbers are shown on top of each bar, total U content (ppm) inside.

total U content (Figure 6.6) show no apparent relationship. The highest proportion of U extracted was from the bulk samples 60-15 and 60-16, both Fe-chlorite bearing samples, and from the clay-size sample, 103-05, a hematite-rich sample. If the data from sample 103-05 are ignored in Figure 6.6b (clay-size fraction), then the proportion of extractable U becomes relatively constant and low. Comparison between extractable U and total Fe_2O_3 contents is shown in Figure 6.7. No trend is observed for bulk or clay-size samples.

Step 4:

The proportion of U extracted by step 4 is highly variable, ranging from 3 to 39% U for the bulk samples and 2 to 54% U for the clay-size separates. The relationship between extractable U and increasing total U content is shown in Figure 6.8. No relationship is apparent. Comparison between extractable U and total Fe_2O_3 also shows no relationship (Figure 6.9).

Step 4 of the procedure should extract U associated with crystalline Fe-oxides. Although U is reported to be intimately associated with Fe-oxides in other studies (e.g., Airey et al., 1983; Zielinski et al., 1983; Hsi and Langmuir, 1985) step 4 only accounts for about one-third of the U in these samples (excluding the clay-size sample, 103-

Figure 6.6: $\text{NH}_2\text{OH} \cdot \text{HCl}$ -extractable U (step 3) as a percentage of the total U for (a) bulk samples and (b) clay-size separates. The samples are arranged according to increasing total U contents. Sample numbers are shown on top of each bar, total U content (ppm) inside.

Figure 6.7: $\text{NH}_2\text{OH} \cdot \text{HCl}$ -extractable U (step 3) as a percentage of the total U for (a) bulk samples and (b) clay-size separates. The samples are arranged according to increasing total Fe_2O_3 contents. Sample numbers listed on top of each bar, total Fe as Fe_2O_3 (wt. %), listed inside.

STEP 4

Figure 6.8: Dithionite-Citrate (DC)-extractable U (step 4) as a percentage of the total U for (a) bulk samples and (b) clay-size separates. The samples are arranged according to increasing total U contents. Sample numbers are shown on top of each bar, total U content (ppm) inside.

Figure 6.9: Dithionite-Citrate (DC)-extractable U (step 4) as a percentage of the total U for (a) bulk samples and (b) clay-size separates. The samples are arranged according to increasing total Fe_2O_3 contents. Sample numbers listed above each bar, total Fe as Fe_2O_3 (wt. %), listed inside.

05). Observations from autoradiographs (not shown) indicate that in some samples U is associated with specular hematite, but U appears to be more commonly associated with rutile, leucoxene and clays (see chapter 3).

Overall, a much smaller proportion of extractable U is associated with the amorphous Fe-oxide fraction (step 3, Table 6.5) than this fraction. Only with the Fe-chlorite-bearing samples, 60-16 (bulk and clay-size separate) and 60-15 (bulk), did the $\text{NH}_2\text{OH}.\text{HCl}$ extraction remove more U than the DC extraction. This may be related to further attack of Fe-chlorite due to the acidic nature of the $\text{NH}_2\text{OH}.\text{HCl}$ reagent.

Step 5:

Uranium extracted during step 5 is associated mainly with the residual silicates. These include the clay minerals illite, sudoite and kaolinite as well as quartz, zircon and tourmaline. In addition, any remaining accessory minerals such as apatite, ilmenite (leucoxene) and rutile may be included. The amount extracted by this step ranges from 4 to 60% of the total U, with a larger proportion, on average, extracted from the illite-rich samples. No distinct trends are evident when the results are plotted against increasing total U content (Figure 6.10).

Figure 6.10: HF + HClO₄ + HNO₃-extractable U (step 5) as a percentage of the total U for (a) bulk samples and (b) clay-size separates. The samples are arranged according to increasing total U contents. Sample numbers are shown on top of each bar, total U content (ppm) inside.

6.4.2 Relationship to Depth

The relationship between extractable U and depth is shown in Figures 6.11 and 6.12 for samples from boreholes WDG1-44A and -60. The bulk samples (Figure 6.11) exhibit some interesting trends. Two opposing trends became apparent for WDG1-44A samples if data from sample 44-10 are ignored. Step 1-extractable U appears to increase with increasing depth whereas step 5-extractable U decreases. The U associated with steps 3 and 4 (the Fe-oxides) is relatively constant. Uranium extracted by step 2 is low for sample 44-08 and relatively constant for samples 44-11 to 44-21. The WDG1-44A samples contain illite with or without minor kaolinite; samples 44-17 and 44-21 also contain hematite.

Sample 44-10 is of special interest. Its total U content is high (~ 1900 ppm) compared to samples 44-08 (245 ppm) and 44-11 (233 ppm). The proportion of U extractable by steps 1 and 2 is significant, ~ 35 and 49% respectively. The remaining fractions account for only 14% of the total extractable U. The high proportion of readily-extractable (step 1) and uraninite-bound (step 2) U indicates that the U may have been remobilized and precipitated at this site. This sample probably reflects "perched mineralization" similar to that described by Bruneton (1985, 1987) at Cigar Lake. Radiometric dating would be necessary to confirm this.

Figure 6.11: Relationship between extractable U and depth for bulk samples from boreholes (a) WDG1-44A and (b) WDG1-60. Sample numbers listed on top of each bar, depth listed below.

Figure 6.12: Relationship between extractable U and depth for clay-size samples from boreholes (a) WDG1-44A and (b) WDG1-60. Sample numbers listed on top of each bar, depth listed below.

A similar, but less obvious trend is exhibited by the bulk samples from WDG1-60 (Figure 6.11). The upper three samples (60-02, 60-03 and 60-07) contain illite with or without kaolinite. The deeper samples contain illite with sudoite (60-09) or Fe-chlorite (60-15 and 60-16). In general, the proportion of U extractable by step 5 decreases with increasing depth. Uranium extracted by steps 1 and 3 increase with depth only for the illite + chlorite-bearing samples (i.e., 60-09 to 60-16). Variable to constant proportions of U are associated with the other extractable fractions (steps 2 and 4).

Similar trends are exhibited by the clay-size illite + chlorite-bearing samples (60-09 to 60-16, Figure 6.12). The proportion of U extractable by step 2 increases with depth whereas the proportion of U extractable by step 4 decreases.

6.4.3 Precision and Accuracy of Data

Total U contents, determined by three methods are compared in Table 6.6. Total extractable U is the summation of the five extraction steps (column 1) whereas total digestible U is that extracted by the concentrated acids alone (column 2). The total U content, reported in column 3, was determined on dry, powdered samples. Total digestible U not only provides a check on the sequential extraction procedure

Table 6.6: Comparison of total U (in ppm, measured by delayed neutron counting) determined in three ways: sequential extraction procedure (1), total digestion (2), and dry powders (3). Fe_2O_3 (wt.%) content given in column 4.

Sample No.	1	2	3	4
Bulk Sample				
44-08	186	280	245	0.53
44-10	1741	2020	1920	2.26
44-11	227	256	233	0.67
44-17	714	751	713	13.43
44-21	1824	2191	2160	9.25
49-12	290	362	318	1.16
53-15	75	61	52	1.07
57-02	94	107	105	9.68
60-02	96	133	106	0.56
60-03	78	74	71	0.61
60-07	314	301	322	2.27
60-09	79	108	88	3.05
60-15	146	175	131	8.52
60-16	135000	137350	137000	5.83
60-16	115580	137000	137000	5.83
103-05	83	76	61	55.00
113-02	246	276	245	0.69
119-30	130	165	141	7.52
<2 μm Fraction				
44-08	702	-	638	0.72
44-11	610	531	574	1.24
49-12	1210	1253	1215	1.42
53-15	121	-	135	1.40
57-02	181	210	207	34.86
60-02	148	154	145	0.70
60-03	-	361	349	0.86
60-07	234	266	233	2.14
60-09	269	275	278	4.38
60-15	115	109	~130	-
60-16	42330	40870	33100	6.24
103-05	166	441	~130	-
119-30	137	106	147	7.52
Standard				
DH-1*		1772	1790	
DH-1		1721		
DH-1		1755		
<p>1 Summation of extractable U measured by the sequential extraction procedure.</p> <p>2 Total acid digestible U; $\text{HF} + \text{HClO}_4 + \text{HNO}_3$ digestion of a separate sample.</p> <p>3 Total U determined from dry powdered samples.</p> <p>4 Fe_2O_3 (in percent) measured by XRF analysis.</p> <p>* CANMET U standard with reported value of 1770 ppm (Ingles et al., 1977).</p> <p>- not determined ~ determined on ignited (from LOI) residues</p>				

but also provides an additional method in order to evaluate the DNC analysis for U in solutions.

Replicate analyses of the standard DH-1 indicate that total digestible U content is similar to the reported value of 1770 ppm (Ingles et al., 1977). These results fall within analytical uncertainty limits.

Duplicate samples of 60-16 leached using the sequential extraction procedure differ by $\pm 15\%$, largely as a result of step 1 of the procedure. The average total extractable U is 8.5% less than the total U content given in column 3.

Total extractable U for bulk and clay-size samples, excluding sample 60-16, plotted against total U in Figure 6.13 has a correlation coefficient of 0.98. There is very good agreement among most samples except for two of the samples which have the highest U concentrations.

A similar plot for digestible U against total U is shown in Figure 6.14. Sample 60-16 has been omitted. The correlation coefficient is 0.98, excluding the point from clay-size sample 103-05. Total digestible U for the clay-size sample 103-05 is about 3 times greater than the total U content.

These results indicate that the application of the sequential extraction procedure was successful. Uncertainty limits are at best $\pm 15\%$, with a few exceptions.

Figure 6.13: Comparison between total uranium determined on dry, powdered samples and total extractable uranium by the sequential extraction procedure. The line drawn represents total U = total extractable U.

Figure 6.14: Comparison between total uranium determined on dry, powdered samples and total digestible uranium by concentrated acids. The line drawn represents total U = total digestible U.

6.4.4 Mobilization of Uranium at Cigar Lake

Although disturbances such as diabasic magmatism, post-Grenvillian rifting, uplift and erosion (Hoeve and Quirt, 1984) have occurred in the Athabasca basin and in the Cigar Lake area since primary mineralization, the concentration of U in the overlying sandstone has remained low, indicating limited migration of U. Partitioning of U among the five extractable phases also indicates that very little hydromorphic dispersion of U has occurred. Most of the U appears to be associated with uraninite (step 2), residual silicates (step 5) and crystalline Fe-oxides (step 4). This association suggests that any U, dispersed by hydrothermal alteration, may have been incorporated into neoformed clay minerals and oxyhydroxides.

The low amount of U associated with the amorphous Fe-oxides at Cigar Lake is probably due to the negligible amounts of amorphous Fe-oxides that are present. Sorption studies have shown that U is preferentially adsorbed by amorphous oxyhydroxides relative to hematite, with crystallization of the amorphous forms eventually resulting in the desorption of previously adsorbed metals (Hsi and Langmuir, 1985). In addition, trace metals can be liberated if pH and Eh conditions are lowered and secondary Fe-oxides dissolve (e.g., bleaching) (Zielinski et al., 1983). Because the Cigar Lake samples have undergone extensive bleaching, it is

possible that any U associated with Fe-oxides was desorbed and incorporated into minerals, such as clays, rutile or sulphides.

The results presented in this study suggest that U was dispersed by primary ore-forming, rather than secondary alteration, processes. Evidence includes: (1) low concentrations (generally < 10 ppm) of U in the sandstones overlying and distal to the ore zone (e.g., WDG1-139), except in areas of perched mineralization along fractures; (2) low concentrations of the easily-mobilized forms of U associated with carbonate-exchangeable-acid-soluble fractions; (3) the occurrence of U associated with dispersed uraninite; (4) the abundance of extractable U associated with residual silicates, primarily the clay minerals illite, sudoite and any remaining Fe-chlorite; and (5) the decrease with depth of the proportion of extractable U associated with residual silicates.

Other studies have also shown that there is little evidence for present-day movement of U around the Cigar Lake deposit. Dissolution of primary U ore minerals has been limited, due to the reducing conditions that occur in the deposit (Cramer, 1988). Buffers, such as graphite in the basement, sulphate- and methane-reducing bacteria, dissolved Fe^{2+} in the basement and ore body, sulphides and UO_2 , all help to sustain the reducing conditions (Vilks et al.,

1988). Sunder et al. (1988) reported Eh values of 0.0 to +0.2 v for pumped groundwaters, measured at surface, and low concentrations of dissolved U ($10^{-7.5}$ to 10^{-9} mol/dm³). Under reducing conditions the solubility of UO₂ is very low ($10^{-9.6}$ mol/dm³; Parks and Pohl, 1985 as cited in Sunder et al., 1988), but, limited, low-Eh transport of U can occur as colloidal uraninite (Giblin et al., 1981). Concentrations of total colloids in groundwaters at Cigar Lake range from 0.6 to 261 mg/L vs. regional levels of 1 to 3 mg/L (Vilks et al., 1988). Colloid samples are dominated by clay minerals and amorphous Fe-Si hydroxides, however, in some groundwater samples, Vilks et al. (1988) reported higher concentrations of colloidal U than dissolved U. Vilks et al. (1988) predicted that, under oxidizing conditions, radiocolloids will coprecipitate with the Fe-Si hydroxides and probably will be sorbed onto other mineral surfaces, thereby limiting their mobility.

6.5 SUMMARY

A sequential partial extraction procedure was used to determine the partitioning of U in (1) carbonates, easily-acid soluble and exchangeable sites; (2) uraninite; (3) amorphous Fe-oxides; (4) crystalline Fe-oxides; and (5) residual silicates, and to identify if the distribution of U resulted from primary ore-formation or secondary alteration.

Partitioning of U is related to mineralogy with no apparent relationship to total U and Fe_2O_3 contents. The proportion of U extracted by step 1 is variable, and appears to increase with depth. On average, about one-third of the total U was extractable by step 2 of the procedure, probably as uraninite. The lowest amount of the total U was extracted by step 3, amorphous Fe-oxide-bound, and low to moderate amounts by step 4, crystalline Fe-oxide-bound. The proportion of extractable U was highest in step 5, residual silicates, indicating an intimate association between U and the clay minerals. Accessory minerals, such as zircon, rutile and ilmenite, may also have contributed to this fraction. The results suggest that most of the dispersion of U in the alteration halo occurred during primary ore-formation and hydrothermal alteration, except for perched mineralization (dated at 300 Ma; Bruneton, 1987) caused by later, low-temperature secondary redistribution.

CHAPTER SEVEN

APPLICATION TO NATURAL ANALOGUES

7.1 INTRODUCTION

Migration of radionuclides in the terrestrial environment is under intense study as a result of concerns for the safe disposal of radioactive wastes (Ivanovitch and Hardy, 1986). Radioactive wastes are by-products of the nuclear industry. They range from low-level wastes, in liquid, gas and solid (e.g., filters, ion-exchange resins) forms from laboratories and hospitals, to the high-level wastes of un-reprocessed and reprocessed irradiated spent fuel (Bird and Fyfe, 1982; Durrance, 1986). The main concerns in handling these wastes are their intense radiation; the high temperatures that result from their radioactive decay (Krauskopf, 1986a); and their hazardous and carcinogenic nature over time spans of up to 250 000 years (Dyne, 1975a, b).

Burial in rock formations below the water table is the favoured method of containment in all countries that generate nuclear power (Krauskopf, 1986a). Laboratory studies of radionuclide migration are generally restricted to short time periods (e.g., days, months or a few years). The long half-lives of the transuranic elements and their fission products in the spent fuel require the laboratory data to be extrapolated to much longer time periods, on the order of 10^5 to 10^6 years. It is also possible that the results of

experiments conducted under laboratory conditions may not be directly applicable to the natural environment (Shea and Foland, 1986). Brookins (1984) and others have suggested that valuable information can be gained from the study of "natural analogues". Although analogues of a complete containment system do not exist, certain natural environments, such as ore deposits, can provide analogues to the physico-chemical and chemical conditions of a waste disposal repository (Chapman and Smellie, 1986).

7.2 WASTE DISPOSAL CONCEPT

The preferred method of disposal of high-level radioactive waste is burial at considerable depth in geologic formations (IAEA, 1981; Bird and Fyfe, 1982; Krauskopf, 1986a). This waste disposal concept makes use of a combination of engineered and natural barriers intended to isolate the waste from the biosphere until the radionuclides decay to harmless levels (Airey and Ivanovitch, 1986; Krauskopf, 1986a). The critical nuclides include ^{90}Sr , ^{99}Tc , ^{129}I , ^{137}Cs , ^{226}Ra , ^{237}Np , ^{239}Pu , and ^{241}Am (Airey and Ivanovitch, 1986; Chapman and Smellie, 1986).

A multiple barrier approach involves placement of used fuel in corrosion resistant containers in a vault several hundreds of metres below the surface (Figure 7.1). The containers would be surrounded by a clay-rich buffer/backfill

Figure 7.1: Schematic illustration of the multiple barrier approach to high-level nuclear fuel waste disposal (after Bird and Fyfe, 1982, Figure 1, p.2).

material and separated from the biosphere by the low-permeability rock mass. In the event that the containers are breached and the engineered containment system fails, radionuclides could potentially migrate upward into the biosphere via groundwater flowing through fractures and pore networks.

7.3 GEOLOGICAL/GEOCHEMICAL ANALOGUES

A variety of materials, trace elements and geological systems can be used to model waste disposal. For example, archaeological Fe and Cu artifacts and Cu deposits can be used as analogues for corrosion-resistant containers (Fe-, Cu- and Ti-based materials). Understanding the behaviour of smectite in the natural environment (e.g., sedimentary basins, hydrothermal deposits) may be useful in predicting the behaviour of bentonite as a candidate for backfill/buffer material. Uranium in pitchblende and uraninite ore will have similar chemical characteristics to the UO_2 pellets of the spent fuel (Krauskopf, 1988), and some naturally-occurring trace elements such as U, Th and REE are possible analogues for the long-lived radionuclides in the high-level wastes (Table 7.1) (Barretto and Fujimori, 1986; Chapman and Smellie, 1986; Lei et al., 1986). Analogue studies, although site specific, can at least provide

Table 7.1: Possible chemical analogues for the long-lived radionuclides present in high-level nuclear fuel waste. Elements in boldface are considered most suitable for chemical analogues (after Chapman and Smellie, 1986).

Element	Oxidation State in Nature ¹	Ionic Radius ² (Å)	Possible Chemical Analogue
Tc	red.IV ox.VII	0.64	Re(IV)? Re(VIII)?
Pa	red.V ox.V	0.78	Th, U(IV) ³
U	red.IV ox.VI	0.76 0.73	U(IV), (Th,Zr,Hf) U(VI)
Np	red.IV ox.V	0.87 0.75	U(IV), (Th,Zr,Hf) U(VI)
Pu	red.III IV ox.IV V	1.00 0.86 0.86 0.74	Lanthanides ⁴ U(IV), (Th,Zr,Hf) U(IV), (Th,Zr,Hf) U(IV) ⁵
Th	red.IV ox.IV	0.94	Th
Am	red.IV ox.III	0.98	Lanthanides
Cm	red.III ox.III	0.98	Lanthanides

¹ Reducing: Eh derived from Fe(II)/Fe(III); Oxidizing: Eh derived from O₂.

² For 6th coordination state, various values are cited in literature.

³ The chemistry of Pa(V) is more similar to the 4+ valency actinides than to the chemistry of the 5+ valency actinides (U, Np, Pu).

⁴ Lanthanides: best analogue is Nd; acceptable analogues are Ce, Pr, Sm, Eu, Gd, Tb, Dy and Ho; less acceptable are La (too large), Er, Tm, Yb, Lu (too small) and Y.

⁵ No suitable analogues for 5+ valency actinides. The best appears to be U(IV) in the presence of carbonate at a pH > 6 -7.

qualitative estimates for long-term prediction of radionuclide behaviour in repository settings.

The Oklo natural reactors, in the Republic of Gabon, are unique as natural analogues. These reactors went critical 1800 Ma ago and fission was sustained for about 0.5 Ma (Brookins, 1984). The ^{235}U content (3.2%, similar to U enrichment necessary for nuclear reactors), the U/H₂O ratio and the lack of neutron poisons (e.g., V, Se, Mo and Fe) created a favourable environment for fission to occur (Brookins, 1984; Durrance, 1986). The remains of 13 nuclear reactors have been discovered in rock lenses, each of about 10^3 m^3 (Curtis, 1986).

Based on fluid inclusion studies, temperatures in the natural reactors reached about 400 °C or more and in the host rock about 200 - 250 °C (Openshaw et al., 1978; Brookins, 1984). Many fission products were retained or only locally redistributed despite the high temperature and radiation fields (NRC, 1983; Brookins, 1984). Clay minerals in the outer zones did not undergo radiation damage (Dran et al., 1978). Fissiogenic elements retained within host pitchblende or locally redistributed included Ag, Bi, In, Nb, Np, Pb, Pd, Pu, REE, Rh, Ru, Sb, Sn, Th, Y and Zr. The more mobile elements included Cd, Cs, I, Mo, Rb, Sr, Tc, U and Xe (Bryant et al., 1976; NRC, 1983; Brookins, 1984; Curtis, 1986). Retention or loss of the fission products by

uraninite and pitchblende provided a measure of their mobility at the Oklo site (NRC, 1983) which can, to some degree, be used to predict mobility of radionuclides in a repository.

Some striking similarities occur between the Oklo and Athabasca deposits, in terms of their geological setting and clay mineral zonation. The Oklo deposits occur in middle Precambrian unmetamorphosed volcanic and sedimentary rocks that lie unconformably on metamorphosed basement. The mineralized zones occur at the top of a thick fluviatile sandstone and conglomerate unit containing argillaceous and carbonate cements (Curtis et al., 1981). Gauthier-Lafaye et al. (1980) documented changes that occurred in clay minerals from "normal" sandstones toward the reactors. Illite polytypes changed from $1M_2$ in the sandstone to $2M$ in the transition zone (1 - 2 m away from the ore) to $1M$ in the clay-rich zone adjacent to the ore. Chlorite changed from Fe-rich in the sandstone to Mg-rich in the clay-rich zone; quartz dissolved and sedimentary structures disappeared towards the ore. Hematite and leucoxene are also abundant near the ore (Gauthier-Lafaye et al., 1980).

Another analogue of special interest is the Th and REE deposit at Morro do Ferro, Brazil. Geochemically the REEs are believed to behave in a similar way to the trivalent actinides Am and Cm, whereas Th behaves like Pu and possibly

Np (see Table 7.1) (Krauskopf, 1986b; Lei et al., 1986). At Morro do Ferro, Th, REEs and refractory minerals accumulated through in situ concentration following hydrothermal alteration and intense weathering. Silica, alkaline elements and U were leached away (Barretto and Fujimori, 1986). Eisenbud et al. (1984) and Barretto and Fujimori (1986) have suggested that Th, and possibly the REEs, occur as amorphous complexes sorbed onto clay mineral and Al- and Fe-oxyhydroxide surfaces, in addition to forming primary (Th-REE-silicates, cheralite, monazite, microlite, zircon and allanite) and secondary (cerianite, thorianite, thorbastnaesite) minerals. The relative immobility and long residence time of these elements in this deposit, indicates that long-term storage or retention of the long-lived radionuclides Am, Cm and Pu (and possibly Np) in a repository is feasible.

Migration of elements due to igneous activity has been used in other analogue studies. Detailed isotopic and petrographic studies of the Eldora-Bryan stock have shown that elemental migration has been restricted to about 3 - 4 m from the contact (Brookins, 1984, 1986). A similar study of the Alamosa River monzonite intrusion into tuffaceous and andesitic rocks showed limited migration of elements (e.g., Cs, Th and Co) away from the contact zone (Brookins et al., 1983; Brookins, 1984, 1986; Airey and Ivanovitch, 1986). Kamineni (1986) has shown that remobilization of U and REEs

during hydrothermal alteration of the Eye-Dashwa Lakes granite pluton has been restricted due to adsorption on clay and other fracture-filling minerals. Thorium showed little evidence for mobility. Similar behaviours of these elements were also observed in the Lac du Bonnet batholith (Kaminen et al., 1986).

The extent and timing of migration of naturally-occurring radionuclides can be assessed through U-series disequilibrium studies (Gascoyne, 1982; Schwarz et al., 1982). For example, Shirvington (1980, 1983) investigated U migration in clays above the Austatom uranium prospect in Australia and determined that oxidation and subsequent mobilization of U had been counteracted by the readsorption of U in the clay layers overlying the surrounding country rock. The $^{230}\text{Th}/^{234}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ activity ratios indicated negligible migration over the past $1 - 2 \times 10^5$ years (Shirvington, 1983).

In many of these studies, element migration has been very limited in spite of favourable conditions (e.g., high temperatures, intense radiation, oxidation and deep weathering). This suggests that many geological systems behave, over long periods of time, as closed systems.

7.4 CIGAR LAKE ANALOGY

7.4.1 Introduction

The Cigar Lake deposit is under investigation as a natural analogue under the Canadian Nuclear Fuel Waste Management Program. Similarities between this unconformity-type uranium deposit and the proposed disposal concept are illustrated in Figure 7.2 (Cramer, 1986a). Similarities include:

- (1) The cross-section of the disposal vault is similar to that of the uranium deposit. For example, the waste (ore) is stored in a clay-rich buffer zone (clay-rich halo) and then separated from the biosphere by 1 km of plutonic rock (about 450 m of sandstone).
- (2) The temperature in the vault and near-field environment are predicted to be in the order of 150 °C for a period of a few thousand years. During ore formation at Cigar Lake, the temperature was about 200 °C, which may have persisted for several million years.
- (3) The salinities reported for groundwaters of the Precambrian Shield are generally lower than 10 g/L total dissolved solids (TDS) above 650 m and locally as high as 325 g/L within fault or shear zones below 650 m (Frape et al., 1984). The salinities determined by fluid inclusion studies for the ore-forming and late diagenetic solutions at Cigar Lake are about 250 - 350 g/L TDS.

Figure 7.2: Comparison of common features of the unconformity-type uranium deposits (left) to the high-level nuclear waste disposal concept (right) (after Cramer, 1986a, Figure 2, p. 271).

(4) Fractionation of U and Pb occurred after initial mineralization through groundwater interaction. The youngest event took place at ~ 200 Ma ago (Pagel, 1983). Fractionation would be similar to waste-water interactions and subsequent dispersion of radionuclides.

Differences between the proposed waste disposal system and the ore deposit are also evident. They include (Cramer, 1986a):

(1) There is a lack of engineered containment barriers in the ore deposit. In the vault the waste would be emplaced in a durable, resistant container. In the ore deposit, the ore is in direct contact with the host rocks.

(2) The close association of U deposits with fault structures. The vault would be excavated in a zone free of major fractures and faults to ensure minimum migration of groundwater.

(3) The Athabasca Group sedimentary rocks have 10 - 100 times the porosity of plutonic rock ($< 1\%$ for granite). Thus, the ore deposit occurs in an open, more permeable system relative to a vault in plutonic rock.

(4) The ore deposits may have been buried more deeply than 1 km in the past. Pagel (1975) estimated an original thickness of 4 - 5 km based on fluid inclusion thermometry.

7.4.2 Water-Rock Interactions and Element Migration

Near the Cigar Lake deposit, high-grade diagenetic assemblages were subsequently altered by hydrothermal fluids. This alteration resulted in significant silica dissolution, residual clay enrichment, formation of 3T illite polytypes, formation of sudoite and the concentration of trace elements, including U. Distinct mineralogical zoning occurs around the deposit. Fe-chlorite (chamosite) and illite are associated with the ore. The ore is surrounded by a massive clay zone consisting of a sudoite - illite zone which grades outward into a hematite - illite zone and then into an illite-rich zone. This massive clay zone is surrounded by altered sandstone containing illite $\pm$ kaolinite in the matrix. The surrounding sandstones of the Manitou Falls Formation, in which illite predominates over kaolinite, suggests that the alteration extends upwards to the bedrock/overburden contact (up to 400 - 450 m) and outwards to at least 300 m (i.e., to borehole WDG1-139, see Figure 2.4). In contrast, U concentrations (and other trace elements) decrease dramatically within 50 m of the ore body, from as high as 60% to $\leq$ 10 - 15 ppm (see Table C.5; Figures 5.2, 5.4 to 5.6).

Stable isotopic measurements and K-Ar age determinations of the clay-rich samples from the alteration halo indicate little disturbance to this zone since the time of

mineralization, ca. 1300 Ma ago. The illite-bearing samples have average δD and $\delta^{18}O$ values comparable to similar samples from other Athabasca deposits. This suggests that similar fluid(s) interacted to form the other deposits over most of the region. The K-Ar ages, that range from 1148 to 1255 Ma, correspond to the first two phases of mineralization (1350 - 1250 Ma and 1100 - 1050 Ma; Hoeve and Quirt, 1984) in the Athabasca basin. The ages of these samples and their isotopic signatures reflect closed system behaviour within the alteration halo above the ore since mineralization. The exceptions to this are the faults and fractures that intersect the ore and contain perched mineralization; these have yielded dates between 230 and 300 Ma (Hoeve and Quirt, 1984, 1987; Cramer et al., 1987).

The stable isotopic signatures of the sudoite-illite samples differ from the illite-rich samples in their slightly higher D contents. This may simply reflect a dilution effect by sudoite, because Mg- and Al-bearing minerals tend to concentrate D relative to Fe-bearing minerals. Alternatively, the higher D contents may simply reflect a different fluid that interacted with the basement. The 815 Ma K-Ar age from sample 53-15 may date this event. The date corresponds to a possible, poorly-defined, third phase of mineralization dated at 900-700 Ma in the other Athabasca deposits (Hoeve and Quirt, 1984). If this mineralizing

event occurred at Cigar Lake and was caused by another pulse of fluid, it is possible that sudoite formed during this time at the expense of illite. Hoeve and Quirt (1984) suggested that chloritization accompanied illitization during the first phase of mineralization. However, textural evidence presented in chapter 3 (Figure 3.14b) suggests that sudoite formed after illite.

The isotopic composition of sample 60-16 is depleted in D relative to the illite-rich samples; the rock has an apparent K-Ar age of zero. These data suggest low-temperature alteration of this sample via interaction with present-day meteoric water. Bray et al. (1988) suggested that radiation damage to clays can account for the low δD values and low K-Ar ages of U-bearing samples. However, XRD analyses of 60-16 indicate that the clay minerals are crystalline and hence radiation damage is unlikely.

Isotopic compositions of groundwater samples from the deposit are shown in Figure 7.3. The sample lying on the meteoric water line (MWL), from borehole WDG1-139, is representative of the regional meteoric water. Cramer et al. (1987) suggested that depletion of D in the ore zone groundwater relative to the regional meteoric water indicates slow mixing, as the ore groundwaters have lower fractionation signatures, possibly of glacial meteoric waters. Calculated δD and $\delta^{18}O$ values for fluid in equilibrium with the clay-

Figure 7.3: Comparison of δD and $\delta^{18}O$ values for groundwater samples with the calculated fluid δD and $\delta^{18}O$ values for samples from this study. Sample on meteoric water line (MWL) is for groundwater from borehole WDG1-139. Groundwater data from Cramer et al. (1987). Isotope fractionation factors used for δD (illite and chlorite; 200 °C) taken from Marumo et al. (1980) and $\delta^{18}O$ (illite and chlorite) taken from Eslinger and Savin (1973) and Wenner and Taylor (1971) respectively.

rich samples of this study are also plotted in Figure 7.3 for comparison. Assuming that the illite-rich samples reacted with ore-forming fluids and have not been disturbed since that time, the isotopic compositions of sudoite-illite and ore-bearing samples suggest interaction with different fluids. It is interesting to note that the δD value for fluid in equilibrium with sample 60-16 corresponds to that of the regional groundwater from WDG1-139, suggesting interaction with present-day groundwaters.

Results from the sequential extraction experiments show that up to 60% of the total U is associated with the residual silicates and that the proportion associated with this fraction increases away from the ore zone. Residual silicates are dominated by clay minerals but also contain trace amounts of ilmenite, rutile and zircon. It is probable that isomorphic substitution of U in the clay mineral lattices has occurred (cf., Shirvington, 1983). From Grant's (1986) isocon diagrams (Figures 5.17 and 5.18), it is apparent that trace elements, as well as U, have been passively concentrated by removal of silica, assuming that Al has remained constant. Some trace elements (e.g., Ba, Fe, Ni, Nb, S and Zn) show minor remobilization, possibly during the second phase of mineralization. These results generally indicate very limited migration of U and other trace elements.

Cramer (1988) reported that the amount of dissolved U in groundwaters from the ore and clay-rich zones is very low but higher in the Fe-oxide-rich interface between the ore and clay-rich zones. The low concentration of dissolved U was attributed to reducing conditions in these two zones. Dissolved Fe^{2+} apparently reacts rapidly with any oxygen produced in the ore zone by radiolysis, thus preventing significant oxidation of the ore; dissolved U is probably then coprecipitated with Fe-colloids (Cramer, 1988). The lack of significant amounts of U in the groundwaters implies limited mobility, supporting the findings of this thesis.

7.4.3 Alteration Halo as Buffer/Backfill Material

If a nuclear-waste-filled container in a vault is breached, the first barrier encountered by the radionuclides would be the buffer/backfill material. This material serves to: (1) provide a low permeability barrier so that diffusion rather than advection is the main mechanism of transport; (2) adsorb radionuclides which may escape from the waste container; (3) provide mechanical support to the container and absorb stresses induced by possible rock movements; and (4) dissipate the heat generated by the waste to the surrounding rock (Klingsberg and Duguid, 1980; Oscarson and Cheung, 1983; Brookins, 1984; Roxburgh, 1987). Candidate materials under investigation are listed in Table 7.2.

Table 7.2: Candidate buffer/backfill materials
(after Nowak, 1980a).

CLAYS

Sodium Bentonite
Calcium Bentonite
Illite
Treated Sodium Bentonite

SAND

Quartz (10 - 230 mesh)

ZEOLITES

Clinoptilolite
13X
Zelon-900

METAL POWDERS OR FIBRES

Iron
Aluminum
Lead Oxide

MINERALS/ROCKS

Pyrite
Ferrosand (glaucinite)
Basalt
Tuff
Serpentine
Anhydrite

CHARCOAL

DESICCANTS

MgO and CaO

Compacted bentonite, a montmorillonite-rich clay, is being most seriously considered as the buffer/backfill material in waste disposal repositories (Pusch, 1979; Chapman et al., 1987; Oscarson and Dixon, 1989) because of its high CEC, low permeability and ability to swell on addition of water or other fluids. Bentonite, however, has a low bearing capacity and thermal conductivity (Brookins, 1984; Roxburgh, 1987). Thus addition of quartz sand, which has a higher bearing capacity and thermal conductivity, would help conduct heat away more rapidly. About 0.3 m of suitable material (e.g., bentonite clay and/or zeolites) could retard the release of ^{90}Sr and ^{137}Cs for $10^3 - 10^4$ years and Pu and Am for $10^4 - 10^5$ years (Nowak, 1980b). Clay minerals readily adsorb Cs and Rb, whereas zeolites retain Sr (Roxburgh, 1987). It is clear that a mixture of materials may be required in some disposal systems to ensure retardation of radionuclides until they have decayed to insignificant levels.

Although bentonite clay has many desirable properties for a repository, some problems may occur under certain conditions. Montmorillonite, stable under weathering conditions, may alter under moderate temperature and pressure (Dunoyer de Segonzac, 1970), resulting in layer collapse to 1.0 nm (mica-like structure). Under some conditions (temperature, pressure, presence of aqueous cations),

aggradation of montmorillonite to chlorite and/or illite or degradation to kaolinite is possible. It is well known that in older sedimentary basins or in thick sedimentary piles, montmorillonite is generally absent. Oscarson and Dixon (1989) have recently demonstrated that, in the presence of steam (possibly generated in a repository), the specific volume of loose bentonite was significantly reduced. The specific volume is a measure of the swelling capacity of bentonite.

The geological environment at Cigar Lake can be considered as an open, water-saturated system containing a 1 Ga old U deposit with no surface expression (Cramer et al., 1987). The results of this study indicate that U dispersion around the ore deposit is limited to the clay-rich portion of the alteration halo and probably resulted from primary ore-forming processes rather than secondary low-temperature alteration. Although some of the U has the potential for remobilization, the sorption capacity of the clay minerals and the redox buffering capacity of the alteration halo and deposit produce an effective barrier to migration. The stability of illite under hydrothermal conditions, combined with its moderate CEC, make it a suitable alternative or possibly preferable to bentonite clay as a backfill/buffer material.

CHAPTER EIGHT

SUMMARY AND CONCLUSIONS

The unconformity-type uranium deposits of northern Saskatchewan occur at or near the unconformity between younger, Precambrian sedimentary rocks of the Athabasca Group and older metamorphic basement of the Churchill Province. The Athabasca Group sediments were deposited in a tectonically active, intra-cratonic basin about 1450 Ma ago (Hoeve and Quirt, 1984), and underwent subsequent intense diagenesis and alteration. Hoeve and Quirt (1984, 1985a) recognized two main stages of mineralization which are inferred to be correlated with the introduction of diabase dykes. The first stage (ca. 1350 - 1250 Ma) is characterized by the formation of high grade U ore and Ni-Co arsenides and sulpharsenides, illitization and chloritization, quartz dissolution, graphite destruction, hydrocarbon formation and secondary hematization. The second stage of hydrothermal alteration (ca 1100 - 1050 Ma) is marked by the development of dull, massive pitchblende, base metal sulphides, siderite and Fe-chlorite, and extensive bleaching. These are superimposed on the products of the first-stage mineralization (Hoeve and Quirt, 1984, 1985b).

Uranium mobilization and subsequent precipitation in reducing traps have been attributed to diagenetic processes (Ramaekers, 1983) and can be explained in a diagenetic-

hydrothermal metallogenic model. According to the model, saline, oxidized, metal-bearing Athabasca pore waters penetrated the unconformity along fault and fracture zones and were reduced by reaction with the graphite-bearing basement rocks. When this reduced fluid emerged above the unconformity, it reacted with the metal-bearing Athabasca pore-waters to precipitate U and other metals, specifically in areas where a stationary redox front was maintained. The redox front is marked by a zone of secondary hematization (Hoeve and Sibbald, 1976; Hoeve and Quirt, 1984, 1987). Intense fracturing, quartz dissolution and the presence of concentric clay-bearing zones are evidence of the hydrothermal alteration that accompanied mineralization. The clay-rich zone can extend hundreds of metres outwards from the ore.

The influence of clay mineralogy on U migration was addressed by a clay mineralogical and geochemical study of the alteration halo around the Cigar Lake deposit. The alteration halo is characterized in sequence from the ore outwards, by an olive-green to grey Fe-chlorite zone associated with the ore, a bleached sudoite- and illite-bearing zone, and an illite-rich zone. Within the outer illite-rich zone, a hematite facies marks the stationary redox front described by Hoeve and Quirt (1984). Kaolinite occurs

sparingly in the overlying sandstone unit, in quantities much lower than the regional background values.

Kübler indices of illite crystallinity correspond to a temperature of about 200 °C and indicate high-grade diagenetic to anchimetamorphic conditions in the alteration halo. The presence of 2M₁ illite polytypes in many samples re-inforces the temperature estimate. A few samples have crystallinity values that approach the epizonal boundary of low-grade metamorphism (ca. 300 °C), suggesting that higher temperatures may have been reached locally. This is supported by the occurrence of 3T illite polytypes in association with 2M₁ polytypes in the illite-rich zone. Within the clayey sandstone and sandstone samples, the 1M and 2M₁ illite polytypes reflect a decrease in temperature away from the ore zone.

Illite in the Athabasca Group samples approaches the composition of hydromuscovite whereas illite from the basement is close to an ideal illite in composition. Illite probably formed at the expense of kaolinite in the Athabasca Group rocks. Evidence includes the paucity of kaolinite within and above the alteration halo, the presence of a 1M illite polytype (a form possibly intermediate in kaolinite to illite conversion) and the regional lack of illite/smectite minerals in the unaltered sandstones. In the base-

ment portion of the halo, rutile lenses along illite cleavage planes suggest a biotite precursor.

Evidence of subsequent degradation or retrograde alteration in some illite samples, possibly as a result of low-temperature rock-water interactions, is suggested by the presence of high H₂O content (6 - 8%) and minor amounts (~ 5 - 10%) of illite/smectite mixed-layer minerals.

Textural evidence from photomicrographs shows that sudoite, a dioctahedral Al-chlorite, may have formed at the expense of illite. The sudoite found at Cigar Lake is the high-temperature, IIb polytype, with the average composition $(\text{Al}, \text{Mg}, \text{Fe})_{4.91}(\text{Si}_{3.30}\text{Al}_{0.70})\text{O}_{20}(\text{OH}, \text{F})_8$.

An illite/chlorite mixed-layer mineral was observed in many of the < 2 μm samples. This mineral has not been reported elsewhere in the basin and may represent either a prograde diagenetic product or recent alteration of illite.

Increase in alteration towards the ore body in the halo is reflected by decrease in SiO₂ and concomitant increase in other major oxides and trace elements. Consistent enrichment of major and trace elements in clay-rich materials, relative to the altered and regionally unaltered sandstones, is observed. The enrichment of all elements except SiO₂ resulted from the dissolution and removal of quartz, and residual concentration of clays. Remobilization of the elements due to secondary processes has been restricted to

the alteration halo. Mass balance considerations indicate a volume change of 94%.

Average δD and $\delta^{18}O$ values for illite-rich (99 - 100%) clay-size samples are -82 o/oo and +10 o/oo respectively. Illite-bearing samples containing minor kaolinite are slightly depleted in D relative to these illite-rich samples whereas sudoite- and illite-bearing samples are enriched in D. A significant depletion in D and ^{18}O is shown by the Fe-chlorite-bearing ore sample relative to the illite-rich samples. Because Mg- and Al-bearing minerals tend to concentrate D relative to Fe-bearing minerals, the enrichment of the sudoite- and illite-bearing samples and depletion of the ore sample may simply reflect their mineral composition. However, the low D/H ratios of the ore sample may reflect low-temperature alteration by meteoric water having a similar composition to present-day water. The calculated isotopic composition of the fluid in equilibrium with this sample shows a good correspondence with the regional groundwater composition for D, estimated from borehole WDG1-139. The depletion in ^{18}O reflects exchange between O in the silicate structure and O in the water reservoir.

K-Ar dates for 3 illite-rich, clay-size separates range from 1255 ± 28 to 1148 ± 28 Ma, dates that may reflect either recrystallization or resetting of the K-Ar system by hydrothermal fluids circulating after primary ore formation.

The timing of this alteration may be related to the emplacement of the MacKenzie dyke swarm ca. 1267 Ma ago. The 815 ± 30 Ma K-Ar date of the altered basement sample probably corresponds to a 900 - 700 Ma period of mineralization dated in other deposits. The ore sample contains no radiogenic ^{40}Ar , and may reflect Ar loss during recent interaction with meteoric water or continuous diffusion from non-retentive chlorite.

Results from the sequential extraction procedure showed that about one-third of the U occurs as an $\text{H}_2\text{O}_2\text{-Na}_2\text{CO}_3\text{-}$ extractable or uraninite phase. The remaining U appears to be associated with residual silicates, in particular the clay minerals. The dispersion of U in the alteration halo probably resulted from primary ore formation and hydrothermal alteration rather than from secondary alteration processes. Low concentrations (< 10 ppm) of U in the overlying or distal sandstones and lack of surface expression of the deposit support this conclusion.

The Cigar Lake uranium deposit can be compared to the proposed geological repository for high-level nuclear fuel waste disposal in Canada. The limited dispersion of U away from the ore deposit is the result of physicochemical conditions that exist within the ore and enveloping alteration halo. An effective barrier was produced through redox buffering and sorption capacity of the clay minerals within the

alteration halo over a time span of 1300 Ma, despite repeated episodes of tectonic activity. The alteration halo thus provides an appropriate analogue to the buffer/backfill materials proposed for a geological repository.

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APPENDIX A

BOREHOLE AND SAMPLE CHARACTERISTICS

A.1 BOREHOLE LITHOLOGY

A typical cross-section of drill core through the clay-rich zone is shown in Figure A.1. Samples from borehole WDG1-60 from 409 to 426 m depth, show gradation from bleached clay, through hematized (red) clay, grey clay and mineralized black clay. The bleached zone, rich in illite, contains numerous, residual heavy mineral layers. The hematitic clay contains finely dispersed, specular hematite in an illite matrix and represents an oxidized zone above the ore. The grey clay contains illite and chlorite (sудоite or Fe-Mg chlorite), with some sulphides (e.g., pyrite) and sulpharsenides (e.g., gersdorffite) and represents a reduced zone surrounding the ore.

Lithology of the sampled boreholes, taken from 1:500 scale drill logs (unpublished data from Cogema Canada Limiteé), is shown in Figures A.2 to A.4. A brief description of each borehole follows.

WDG1-139 is located south and distal to the deposit, along the extension of line 4 + 50E (Figure A.2). Units B, C and D of the Manitou Falls Formation are indicated for reference. The lithology is characterized by interbedded sandstone and grit/conglomerate units throughout the entire intersection. Below the unconformity, fine-grained metapelites grade into augen gneisses.

Figure A.1: Cross section of drill core through alteration zone in borehole WDG1-60. The core grades from a bleached, illite-rich facies, through a red, oxidized, hematite-rich facies, through variegated greys to a black, reduced ore zone containing massive pitchblende.

Figure A.2: Drill core lithology for holes WDG1-139 and WDG1-119, taken from 1:500 drill core logs. For reference, WDG1-139 is subdivided into units B, C, and D of the Manitou Falls Formation. Sample location and type, and U concentration are indicated on the right and left sides of the stratigraphic column.

WDG1-119 (Figure A.2) located along line 8 + 00E, penetrates a section through fine-grained sandstone, massive clay, ore, fine-grained metapelite and augen gneiss. Several samples, selected from a sandstone unit between 410 and 423 m, shows variable alteration.

WDG1-49 (line 7 + 50E; Figure A.3) is located in the western part of the "east zone" of the deposit with samples selected from the interbedded sandstone and clay units. Two faults cut a thick clay unit above the unconformity. Although the halo does not intersect massive ore, pitchblende is disseminated throughout the lower clay and sandstone units, and the highest U concentrations occur within the hematized zone. The sedimentary rocks of the Manitou Falls Formation are underlain by altered or argillized basement which grade downward into metapelite and augen gneiss.

WDG1-103 (line 8 + 50E; Figure A.3) is characterized by a thin lens of ore surrounded by U-rich clays. Altered basement grades downward into metapelite.

WDG1-137 (line 9 + 00E; Figure A.3) intersects alternating massive clay and grit/conglomerate layers of the Manitou Falls Formation. Disseminated pitchblende occurs, in concentrations above 1250 ppm U, between 423 and 431 m. The basement consists of highly altered, clay-rich metapelites.

Figure A.3: Drill core lithology for holes WDG1-49, -103, -137 and -53 located along a W - E transect (see Figure 2.4). Sample location and type, and U concentration are indicated on the right and left sides of the stratigraphic columns. Lithology data taken from 1:500 drill core logs. Hematite-rich facies and faults are delineated by arrows.

WDG1-53 (line 9 + 50E; Figure A.3), located in the eastern part of the deposit, contains interbedded units of sandstone and grit/conglomerate. A thin, massive ore zone is surrounded by clay-rich, coarse-grained sandstone. Strongly altered metapelite below the unconformity grade downward into a fine-grained metapelite.

WDG1-44A (between lines 7 + 00E and 7 + 50E; Figure A.4) transects a thick, massive clay and ore zones. The upper clay unit is strongly hematized at the top; midway it becomes chloritic (dark green facies on diagram). The upper clay unit is overlain by interbedded grit/conglomerate and sandstone layers. Uranium is enriched in the clay unit both above and below the ore. The lower clay unit in the basement grades into metapelite.

WDG1-118A (line 8 + 00E; Figure A.4) cuts a thin massive ore zone surrounded by clay containing disseminated pitchblende. The clay-rich zone is overlain by a variably hematitic, altered sandstone. Pegmatite cuts the metapelite.

WDG1-60 (line 8 + 50E; Figure A.4) intersects a thick clay-rich zone that is interbedded with thin units of altered sandstone. Samples taken near and within the upper part of the ore zone are grey and contain sulphides and sulpharsenides. The basement consists of metapelite below the unconformity.

WDG1-113 (line 9 + 00E; Figure A.4) contains a thick mineralized zone surrounded by clay-rich units in the Manitou Falls Formation and basement. The sandstone units show evidence of strong local alteration to clay.

WDG1-57 (line 9 + 50E; Figure A.4) contains interbedded sandstone and grit/conglomerate units that overlie a hematitic, massive clay unit. The ore is brecciated and calcareous, and contains thucolites (hydrocarbon buttons containing U) associated with grey clay. The altered basement grades into augen gneiss.

WDG1-120 (line 10 + 50E; Figure A.4) contains a basal conglomerate overlain by interbedded clay and coarse sandstone containing a thin hematitic zone. The clay unit that overlies the basal conglomerate contains disseminated pitchblende.

Table A.1: Sample inventory showing sample number, depth interval, lithology (Sst = sandstone; Cl.Sst = clayey sandstone; Clst = sandy claystone; Comp = composite; Base = altered basement), and colour (W = white, including buff-coloured and very light grey; LG = light grey; G = grey; PR = pale red; DR = deep red to purple; PR-B = pale reddish-brown; PGr = pale green; PY = pale yellow) of drill core samples.

SAMPLE NO.	DEPTH INTERVAL (m)	LITHOLOGY	COLOUR
Borehole 44A			
44-01	394.30 - 394.45	Cl.Sst	W
44-02	396.85 - 396.95	Cl.Sst	W
44-03	398.85 - 399.00	Cl.Sst	W
44-04	400.10 - 400.28	Clst	W
44-05	401.83 - 401.91	Cl.Sst	W
44-06	402.22 - 402.32	Clst	W
44-07	403.10 - 403.20	Cl.Sst	W
44-08	404.40 - 404.50	Cl.Sst	W
44-09	406.72 - 406.88	Cl.Sst	W
44-10	407.70 - 407.77	Clst	W
44-11	408.40 - 408.50	Clst	W
44-12	409.41 - 409.50	Sst	W
44-13	409.86 - 409.93	Clst	W
44-14	410.20 - 410.27	Clst	W
44-15	410.90 - 411.00	Cl.Sst	W
44-16	411.12 - 411.20	Cl.Sst	W
44-17	411.33 - 411.40	Clst	W
44-18	411.51 - 411.57	Clst	LG
44-19	411.95 - 412.10	Sst	PR/LG
44-20	412.90 - 413.00	Clst	PR
44-21	413.07 - 413.20	Clst	PR
Borehole 49			
49-01	393.85 - 394.00	Sst	LG
49-02	397.85 - 397.90	Cl.Sst	W
49-03	398.80 - 398.90	Cl.Sst	W
49-04	400.40 - 400.50	Cl.Sst	W
49-05	404.10 - 404.21	Sst	W
49-06	410.85 - 410.90	Comp	W
49-07	411.70 - 411.80	Sst	W
49-08	413.30 - 413.45	Comp	W
49-09	414.80 - 414.90	Comp	W
49-10	415.30 - 415.50	Sst	W
49-11	416.85 - 417.00	Cl.Sst	W

Table A.1: Continued

SAMPLE NO.	DEPTH INTERVAL (m)	LITHOLOGY	COLOUR
49-12	418.85 - 418.95	Clst	W
49-13	419.10 - 419.50	Clst	W
49-14	419.80 - 419.90	Clst	W
49-15	420.30 - 420.48	Sst	W
Borehole 53			
53-01	402.70 - 402.86	Cl.Sst	W
53-02	410.40 - 410.50	Sst	W
53-03	410.73 - 410.85	Cl.Sst	W
53-04	415.30 - 415.45	Cl.Sst	W
53-05	418.61 - 418.75	Sst	W
53-06	420.65 - 420.74	Cl.Sst	W
53-07	423.00 - 423.10	Sst	W
53-08	423.80 - 423.95	Cl.Sst	W
53-09	426.30 - 426.45	Cl.Sst	W
53-10	426.45 - 426.64	Sst	LG
53-11	428.17 - 428.34	Clst	PR
53-12	429.50 - 429.64	Clst	PR
53-13	438.05 - 438.18	Base	PR
53-14	440.60 - 440.70	Base	W
53-15	444.00 - 444.15	Base	W
Borehole 57			
57-01	411.00 - 411.33	Clst	W
57-02	417.30 - 417.50	Clst	PR-B
57-03	419.30 - 419.46	Clst	PR
Borehole 60			
60-01	404.63 - 404.70	Sst	W
60-02	407.67 - 407.85	Clst	W
60-03	409.00 - 409.13	Clst	W
60-04	409.80 - 409.90	Clst	W
60-05	411.20 - 411.50	Clst	W
60-06	412.00 - 412.10	Clst	W
60-07	412.10 - 412.20	Clst	W
60-08	412.60 - 413.00	Clst	W
60-09	413.30 - 414.42	Clst	LG
60-10	413.58 - 413.73	Cl.Sst	PR-B
60-11	414.28 - 414.41	Cl.Sst	PR-B
60-12	415.44 - 415.57	Clst	PR
60-13	417.56 - 417.64	Sst	DR
60-14	419.53 - 419.68	Clst	PR
60-15	421.28 - 421.38	Clst	G
60-16	422.57 - 422.70	Comp	G

Table A.1: Continued

SAMPLE NO.	DEPTH INTERVAL (m)	LITHOLOGY	COLOUR
Borehole 103			
103-01	410.17 - 410.40	Clst	W
103-02	411.63 - 411.82	Clst	W
103-03	419.15 - 419.41	Clst	PR
103-04	420.35 - 420.58	Clst	DR
103-05	422.32 - 422.58	Comp	PR
Borehole 113			
113-01	399.04 - 399.11	Sst	W
113-02	406.93 - 407.04	Clst	PY
113-03	407.65 - 407.90	Clst	PY
113-04	408.92 - 409.06	Clst	W
113-05	412.20 - 412.35	Clst	LG
Borehole 118A			
118-01	408.03 - 408.19	Comp	W
118-02	413.30 - 413.57	Clst	W
118-03	418.20 - 418.28	Clst	LG
118-04	418.80 - 419.00	Clst	PR
118-05	419.54 - 419.69	Clst	PR
118-06	420.80 - 420.98	Clst	PGr
Borehole 119			
119-01	38.92 - 39.05	Sst	W
119-02	61.99 - 62.09	Sst	W
119-03	92.37 - 92.45	Sst	PR
119-04	119.11 - 119.23	Sst	PR/PGr
119-05	154.37 - 154.50	Sst	PR
119-06	179.40 - 179.54	Sst	W
119-07	210.63 - 210.75	Sst	W
119-08	246.28 - 246.43	Sst	W
119-09	273.37 - 273.42	Sst	PY
119-10	301.28 - 301.37	Sst	PY
119-11	333.91 - 334.00	Sst	W
119-12	361.37 - 361.47	Sst	W
119-13	377.40 - 377.51	Sst	W
119-14	383.25 - 383.35	Sst	W
119-15	384.00 - 384.09	Sst	W
119-16	392.21 - 392.27	Sst	W
119-17	393.76 - 393.88	Sst	W
119-18	402.87 - 402.95	Sst	W
119-19	405.17 - 405.28	Sst	W
119-20	408.32 - 408.45	Sst	W

Table A.1: Continued

SAMPLE NO.	DEPTH INTERVAL (m)	LITHOLOGY	COLOUR
119-21	412.16 - 412.30	Comp	W
119-22	414.14 - 414.23	Cl.Sst	W
119-23	415.20 - 415.29	Comp	W
119-24	416.92 - 417.02	Sst	W
119-25	418.13 - 418.24	Comp	W
119-26	419.58 - 419.77	Clst	W
119-27	419.88 - 419.99	Clst	W
119-28	422.42 - 422.50	Clst	W
119-29	422.87 - 422.97	Clst	W
119-30	423.29 - 423.41	Clst	PR
119-31	425.00 - 425.10	Clst	PR
119-32	425.46 - 425.86	Clst	PR
119-33	435.73 - 435.86	Base	LG
Borehole 126			
126-01	426.69 - 426.92	Comp	W
126-02	436.49 - 436.73	Clst	W
126-03	436.94 - 437.24	Clst	W
Borehole 137			
137-01	401.15 - 401.36	Cl.Sst	W
137-02	405.18 - 405.29	Sst	W
137-03	407.94 - 408.09	Cl.Sst	W
137-04	410.44 - 410.55	Cl.Sst	PR
137-05	415.15 - 415.62	Sst	W
137-06	417.43 - 417.53	Cl.Sst	W
137-07	421.06 - 421.20	Clst	LG
137-08	421.94 - 422.15	Clst	LG
137-09	422.22 - 422.61	Clst	PR
137-10	424.36 - 424.58	Comp	PR
137-11	425.08 - 425.18	Comp	W
137-12	436.42 - 436.53	Base	PR
Borehole 139			
139-01	37.73 - 37.81	Sst	W
139-02	77.45 - 77.57	Sst	W
139-03	76.98 - 77.08	Sst	PR
139-04	113.38 - 113.48	Sst	PR/W
139-05	163.30 - 163.48	Sst	DR/PR
139-06	203.35 - 203.43	Sst	W
139-07	256.86 - 256.97	Sst	PR
137-08	293.48 - 293.54	Sst	PR
137-09	342.05 - 342.15	Sst	DR

Table A.1: Continued

SAMPLE NO.	DEPTH INTERVAL (m)	LITHOLOGY	COLOUR
139-10	375.94 - 376.00	Sst	PR
139-11	413.35 - 413.44	Sst	PY/PR
139-12	424.22 - 424.32	Sst	W
139-13	431.11 - 431.17	Sst	W
139-14	433.26 - 433.31	Sst	W
139-15	442.77 - 442.86	Sst	W
139-16	445.07 - 445.19	Sst	W
139-17	446.71 - 446.83	Base	PY
139-18	447.87 - 448.00	Base	PY

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A.2 SAMPLE PREPARATION

A.2.1 Particle Size Analysis and Fractionation

Altered sandstone and basement specimens were lightly hand-crushed in a ceramic mortar and pestle. The material was dispersed in 1 L cylinders by adding sodium hexameta-phosphate (Calgon). Particle size distribution was determined by sedimentation using pipette sampling (Day, 1965). In addition, Fe was extracted from the Fe-rich samples using the dithionite-citrate-bicarbonate (DCB) procedure outlined by Jackson (1979). Samples were then analyzed for particle-size distribution as described above.

Clay ($< 2 \mu\text{m}$), fine silt ($2 - 5 \mu\text{m}$) and medium silt ($5 - 20 \mu\text{m}$) were fractionated by sedimentation and centrifugation (Jackson, 1979; Berry, 1987). Altered specimens were hand-crushed and dispersed in demineralized water using a sonic dismembrator (Model 12100, Quigley Rochester Inc.) for about 10 to 15 minutes. The sedimenting material was sampled by siphoning at the appropriate times (dependent upon temperature; Day, 1965) to extract the $< 20 \mu\text{m}$ and subsequently the $< 5 \mu\text{m}$ fractions. Centrifugation (centrifuge model K, equipped with a No. 240 head, International Equipment Co.) of the $< 5 \mu\text{m}$ fraction, at 1000 rpm for 2.5 minutes, separated the $< 2 \mu\text{m}$ fraction. The residue was then placed in a beaker and oven-dried at temperatures about 70°C . The clay fraction of the mill-crushed (sandstone)

samples was obtained by ultrasonic dispersion and centrifugation.

A.2.2 Petrography

Sandstone samples were cut and surfaces partially impregnated with a mixture of Araldite resin, Epoxide thinner and a blue-green dye made from Oracet yellow and Orasol blue powders. Oven-dried (105 °C for 30 minutes) stubs were placed in a vacuum desiccator and thin coats of the mixture repeatedly applied. Samples were cured in a 105 °C oven for a few hours. The stubs were cut for thin and polished thin sections.

Selected altered samples were impregnated with plastic solution, consisting of a mixture of acetone (2 L, technical grade), a polyester resin (2 L, Canus C-32), a catalyst (1 mL, Lupersol DDM) and an accelerator (0.2 mL, 1% cobalt naphthanate in styrene) (Sheldrick, 1984). Oriented stubs were cut for thin and polished thin sections in two directions.

A.2.3 Scanning Electron Microscopy

For detailed mineralogical and morphological analysis selected polished thin sections were examined using scanning electron microscopy. Samples were coated with 0.8 nm of Au and examined under an ISI DS 130 SEM equipped with a Tracor Northern EDX detector for qualitative energy dispersive

X-ray analysis. Operating conditions of 25 and 15 kV accelerating voltages were used with a 50 μ a emission current. Samples were set at a 25 mm working distance and a 15° tilt (K.J. George, personal communication, 1987). The bright/dark contrast of the photomicrographs is the result of back-scatter electron imaging (BSI); the higher the atomic number, the brighter the image.

A.2.4 Electron Microprobe

Specimens were analyzed on a Cambridge Microscan 5 electron probe using an energy dispersive system (EDS). Operating conditions were 20 kV accelerating potential and an absorbed current of 9 na; counting times between 100 and 150 seconds live time were used. The EDS spectrum was reduced using the program EDDI developed at the Geological Survey of Canada.

A.2.5 Autoradiography

Autoradiographs were made by superimposing X-ray film (Kodak DEF392) on thin and polished thin sections for about 1 month in a dark room. Images on the developed film were easily matched to thin section outlines.

A.2.6 Geochemistry

The surfaces of sandstone cores were removed using a Dremel constant speed carbide-tipped drill (Model 280); surfaces of the clay-rich specimens were removed using a stainless steel knife. The samples were then hand-crushed in a stainless steel mortar and pestle to about 10 mesh size. The fragments were then placed in a Bleuler rotary mill equipped with a stainless steel bowl and pulverized to 200 - 300 mesh size. The powdered samples were split to yield 5 - 10 g aliquots, and these were used for subsequent chemical analyses.

Table A.2: Particle size distribution for Cigar Lake samples, excluding sandstone.

SAMPLE NO.	> 50 μ m	20-50 μ m	5-20 μ m	2-5 μ m	< 2 μ m
44-01	74.7	4.5	6.5	1.3	13.0
44-02	88.5	2.3	3.8	1.6	3.8
44-03	97.0	1.0	0.4	1.0	0.6
44-04	59.2	8.4	12.0	6.6	13.8
44-05	90.7	1.2	3.7	1.4	3.0
44-06	60.4	7.6	11.0	6.5	14.5
44-07	98.8	0.2	0.7	0.3	0.0
44-08	88.6	3.3	5.2	1.0	1.9
44-09	96.3	0.8	1.2	0.9	0.7
44-10	53.6	8.1	16.7	7.9	13.7
44-11	53.7	3.3	14.8	11.5	16.7
44-13	53.6	3.9	13.5	11.5	17.5
44-14	59.8	9.0	10.8	9.7	10.7
44-15	72.1	9.1	8.1	3.5	7.2
44-16	71.7	6.2	8.6	5.9	7.6
44-17	59.8	5.7	11.2	9.8	13.5
44-18	39.2	6.3	17.5	16.7	20.3
44-20	40.2	11.0	18.6	14.7	15.5
44-21	39.3	14.4	17.4	13.8	15.1
49-02	97.2	0.4	0.8	1.0	0.6
49-03	97.1	1.1	0.3	0.9	0.5
49-04	98.6	0.6	0.4	0.3	0.1
49-06	57.0	4.4	9.7	8.6	20.3
49-08	68.6	3.3	7.6	5.6	14.9
49-09	63.1	6.3	9.0	6.4	15.2
49-11	66.7	5.5	9.2	5.2	13.4
49-12	58.1	6.1	11.6	6.6	17.6
49-13	39.8	3.5	16.8	17.2	22.7
49-14	40.8	9.2	18.4	11.8	19.8
53-01	91.5	0.1	1.7	2.4	4.3
53-03	91.5	1.6	1.5	2.7	2.7
53-04	97.7	0.0	1.0	0.8	0.8
53-06	88.9	1.4	3.0	2.6	4.1
53-08	73.9	2.9	6.4	6.2	10.6
53-09	75.5	1.2	6.8	6.3	10.2
53-11	67.1	3.4	8.7	8.9	11.9
53-12	51.9	7.1	11.6	14.2	15.2
53-13	84.2	4.0	4.6	2.3	4.9
53-14	81.4	6.1	3.4	2.4	6.7
53-15	82.0	6.8	5.0	1.2	5.0
57-01	61.9	3.6	9.3	8.5	16.7
57-02	31.9	6.8	16.4	15.7	29.2
57-03	34.1	5.6	19.1	16.8	24.4

Table A.2 Continued

SAMPLE NO.	> 50 μ m	20-50 μ m	5-20 μ m	2-5 μ m	< 2 μ m
60-02	47.7	9.8	11.1	10.7	20.7
60-03	62.3	6.7	9.1	7.4	14.5
60-04	44.7	5.5	13.6	15.3	20.9
60-05	56.5	5.8	11.7	9.9	16.1
60-06	45.7	6.7	15.2	11.8	20.6
60-07	32.3	4.6	16.3	16.9	29.9
60-08	66.3	6.7	8.9	6.1	12.0
60-09	48.5	9.1	14.8	11.0	16.6
60-10	85.2	4.4	4.5	2.5	3.4
60-11	83.3	4.1	5.2	2.5	4.9
60-12	67.6	7.8	10.4	5.4	8.8
60-14	64.4	7.8	10.9	5.5	11.4
60-15	50.1	15.2	12.8	5.9	16.0
60-16	88.9	4.3	2.6	0.9	3.3
103-01	36.1	4.7	15.4	15.5	28.3
103-02	20.0	6.8	21.6	18.0	33.6
103-03	71.9	5.7	8.3	5.8	8.3
103-04	73.1	3.9	14.0	4.6	4.4
103-05	84.8	4.2	5.4	3.7	1.9
113-02	44.2	6.6	16.0	10.9	22.3
113-04	47.2	3.4	12.6	14.8	22.0
113-05	51.0	3.9	16.2	12.5	16.4
118-01	61.7	1.2	7.1	9.7	20.3
118-02	29.5	3.2	16.7	22.0	28.6
118-03	31.3	3.9	17.9	17.0	29.9
118-04	48.7	4.8	15.6	11.9	19.0
118-05	70.1	4.5	8.9	5.3	11.2
118-06	50.3	4.5	15.5	11.6	18.1
119-21	66.6	5.0	8.5	8.0	11.9
119-22	89.7	2.9	2.3	2.0	3.1
119-23	60.1	7.6	11.1	7.9	13.3
119-25	65.6	2.5	10.5	6.8	14.6
119-26	65.5	4.6	10.3	6.1	13.5
119-27	71.3	3.9	9.4	4.6	10.8
119-28	62.0	5.1	10.1	8.2	14.6
119-29	26.8	3.6	18.0	18.8	32.8
119-30	45.2	4.7	11.9	12.9	25.3
119-31	63.1	6.6	8.9	7.3	14.1
119-32	63.0	12.7	8.7	7.1	15.1
119-33	91.2	2.7	2.5	0.6	3.0
126-01	25.4	37.3	23.9	2.9	10.5
126-02	30.6	43.3	8.8	6.9	10.4
126-03	28.0	49.2	7.8	5.9	9.1
137-01	71.6	2.3	9.1	5.1	11.9
137-03	63.7	1.9	11.2	7.0	16.2
137-04	52.7	3.5	15.3	7.8	20.7

Table A.2: Continued

SAMPLE NO.	> 50 μ m	20-50 μ m	5-20 μ m	2-5 μ m	< 2 μ m
137-06	58.3	3.6	13.4	8.9	15.8
137-07	62.2	4.9	11.5	7.3	14.1
137-08	56.6	3.0	12.7	9.0	18.7
137-09	63.0	4.3	10.7	7.4	14.6
137-10	72.4	2.5	7.3	6.7	11.1
137-11	78.7	4.1	5.8	2.5	8.9
137-12	42.5	3.2	14.3	16.8	23.2
139-17	85.4	2.8	4.6	1.6	5.6
139-18	81.1	3.5	5.5	2.0	7.9

Table A.3: Particle size distribution for Fe-rich samples, following Fe-oxide removal by the DCB method of Jackson (1975).

SAMPLE NO.	> 50 μ m	20-50 μ m	5-20 μ m	2-5 μ m	< 2 μ m
44-20	35.3	7.6	15.5	16.3	25.3
44-21	40.9	7.9	14.5	13.9	22.8
53-11	59.8	5.1	11.7	3.6	19.8
53-12	42.1	11.1	11.2	12.7	22.9
53-13	31.2	10.3	12.4	11.4	34.7
57-02	19.3	6.7	16.8	20.2	37.0
57-03	21.4	6.8	20.1	17.7	34.0
60-10	46.1	9.2	15.9	10.1	18.7
60-11	76.1	5.0	8.2	3.8	6.9
60-12	46.4	4.9	14.4	9.3	25.0
60-14	46.4	9.7	13.3	7.3	23.3
103-03	53.8	10.3	11.8	9.0	15.1
103-04	60.6	5.8	6.6	6.9	20.1
103-05	49.0	22.3	9.8	5.3	13.6
118-04	33.8	10.0	23.0	10.2	23.0
118-05	43.4	8.9	12.1	8.3	27.3
119-30	9.0	1.5	18.9	24.5	46.1
119-31	33.7	7.2	13.6	13.5	32.0
119-32	42.1	9.3	10.9	11.2	26.5

Table A.4: Microprobe analyses (wt %) and chemical formulae based on 22 (O and OH) anions for coarse-grained micas in altered sandstone samples.

	44-14 (n=2)	44-21 (n=1)	57-03 (n=5)	60-03 (n=1)
SiO ₂	46.73	42.42	49.74	48.53
Al ₂ O ₃	33.47	28.80	35.29	34.73
TiO ₂	0.05	0.03	0.05	0.07
FeO	2.30	11.07	0.39	0.56
MgO	0.52	1.26	0.89	0.30
CaO	0.21	0.22	0.20	0.13
Na ₂ O	0.18	0.50	0.08	0.14
K ₂ O	<u>9.29</u>	<u>7.78</u>	<u>10.09</u>	<u>10.08</u>
Total	92.74	92.08	96.73	94.54
Si	6.36	6.12	6.43	6.42
Al (iv)	<u>1.64</u>	<u>1.88</u>	<u>1.57</u>	<u>1.58</u>
	8.00	8.00	8.00	8.00
Al (vi)	3.72	3.01	3.80	3.84
Ti	0.01	0.00	0.01	0.01
Fe	0.26	1.33	0.04	0.06
Mg	<u>0.11</u>	<u>0.27</u>	<u>0.17</u>	<u>0.06</u>
	4.10	4.61	4.02	3.97
K	1.62	1.67	1.66	1.70
Na	0.05	0.12	0.00	0.04
Ca	<u>0.03</u>	<u>0.03</u>	<u>0.03</u>	<u>0.02</u>
	1.70	1.82	1.69	1.76

Table A.5: Microprobe analyses (wt %) for siderite, rutile and U-bearing minerals of sample 44-21.

SIDERITE (n=2)

FeO	61.07
MgO	0.53
MnO	0.19
<u>CaO</u>	<u>0.91</u>
Total	62.70

RUTILE (n=5)

TiO ₂	97.14
<u>FeO</u>	<u>0.08</u>
Total	97.22

U-BEARING MINERALS

	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
SiO ₂	23.50	6.84	34.88	14.28
TiO ₂	8.23	68.05	0.20	40.58
Al ₂ O ₃	14.09	3.92	22.73	8.21
FeO	1.24	0.77	1.53	1.46
MgO	0.00	0.00	0.00	0.00
MnO	0.00	0.00	0.03	0.00
K ₂ O	4.84	1.39	7.67	2.36
P ₂ O ₅	0.59	0.18	0.00	0.74
UO ₂	12.33	6.71	2.87	16.34
ZrO ₂	<u>2.71</u>	<u>1.00</u>	<u>0.90</u>	<u>3.66</u>
Total	67.53	88.86	70.81	87.63

APPENDIX B

CLAY MINERALOGY

Table B.1: Mineralogy, illite intensity ratio $[I(002)/I(001)]$ and Kubler Index of the $< 2 \mu\text{m}$ fraction of the Cigar Lake samples. Sum of the mineral components is 100% (I = illite; C = Al-Chlorite; K = Kaolinite; Q = quartz; H = hematite, ML = mixed layer mineral; Goy = goyazite; Gyp = gypsum; Goe = goethite; Sid = siderite). Sample type is indicated in column 1 (Set = sandstone; Cl. Set = clayey sandstone; Clst = claystone; Comp = composite; and Base = basement).

SAMPLE NUMBER /TYPE	I	C	K	MINERALOGY Q	H	OTHER	$\frac{I(002)}{I(001)}$	KUBLER INDEX
44-01/Cl.Set	100						0.65	4.4
44-02/Cl.Set	97		3		tr		0.49	4.2
44-03/Cl.Sst	100					ML(tr)	0.73	5.1
44-04/Clst	100					ML(tr)	0.52	5.5
44-05/Cl.Sst	100			tr		ML(tr)	0.65	5.5
44-06/Clst	100						0.62	3.2
44-07/Cl.Set	100				tr	ML(tr)	0.53	2.6
44-08/Cl.Set	100						0.44	5.5
44-09/Cl.Sst	99		1				0.51	3.2
44-10/Clst	99		1				0.45	4.7
44-11/Clst	99		1				0.60	4.4
44-12/Sst	73		3		tr		0.41	4.4
44-13/Clst	96		4	24			0.61	4.2
44-14/Clst	99		1				0.63	3.2
44-15/Cl.Sst	95		4.5		0.5		0.50	4.2
44-16/Cl.Sst	94		6		tr	ML(tr)	0.42	4.7
44-17/Clst	95		5				0.52	4.7
44-18/Clst	88		12			ML(tr)	0.58	3.2
44-19/Sst	58		tr	27	15		0.42	5.1
44-20/Clst	90		9.5		0.5		0.57	3.2
44-21/Clst	91		9		tr	ML(tr)	0.50	4.4

Table B.1: Continued

SAMPLE NUMBER /TYPE	I	C	K	MINERALOGY Q	H	OTHER	$\frac{I(002)}{I(001)}$	KUBLER INDEX
49-01/Sat	81			18.5	0.5	ML(tr); Goy(tr)	0.54	5.7
49-02/Cl.Sat	97		3				0.57	4.4
49-03/Cl.Sat	94		5		1	ML(tr); Goy(tr)	0.48	5.7
49-04/Clst	100					ML(tr)	0.51	3.2
49-05/Sat	95		tr	5		ML(tr)	0.45	4.7
49-06/Comp	100					ML(tr)	0.75	3.1
49-07/Sat	85			15	tr	Goy(tr)	0.59	3.8
49-08/Comp	100					ML(tr)	0.74	5.1
49-09/Comp	100					ML(tr)	0.67	4.7
49-10/Sat	82			17.5	0.5	ML(tr); Goy(tr)	0.41	4.7
49-11/Cl.Sat	96	4				ML(tr)	0.66	4.2
49-12/Clst	100					ML(tr)	0.57	4.4
49-13/Clst	100					ML(tr); Gyp(tr)	0.57	4.2
49-14/Clst	95		5				0.53	5.1
49-15/Cl.Sat	87		13			ML(tr)	0.57	3.2
53-01/Cl.Sat	97		3			ML(tr)	0.72	2.6
53-02/Sat	91			9		ML(tr)	0.39	4.2
53-03/Cl.Sat	79	21					0.68	2.0
53-04/Cl.Sat	92	6		2			0.54	5.1
53-05/Sat	93	3		4			0.49	4.4
53-06/Cl.Sat	98	2					0.53	4.8
53-07/Sat	86			14	tr	ML(tr)	0.51	3.8
53-08/Cl.Sat	94	6					0.55	3.2
53-09/Cl.Sat	91	9					0.66	3.7
53-10/Sat	89	6*		5			0.49	5.1
53-11/Cl.Sat	99.5	tr			0.5	ML(tr)	0.58	5.7
53-12/Cl.Sat	66	34			0.5		0.76	5.5
53-13/Base	66	29			5		0.50	5.1
53-14/Base	60	40					0.49	4.4
53-15/Base	64	36					0.74	5.1

Table B.1: Continued

SAMPLE NUMBER /TYPE	I	C	MINERALOGY			H	OTHER	$\frac{I(002)}{I(001)}$		KUBLER INDEX
			K	Q				I (002)	I (001)	
57-01/Clst	98		2				ML(tr)	0.66		3.4
57-02/Clst	81	18				1	ML(tr)	0.66		3.8
57-03/Clst	100					tr		0.50		4.2
60-01/Sst	90			10			ML(tr)	0.45		4.7
60-02/Clst	100						ML(tr)	0.73		3.2
60-03/Clst	100						ML(tr)	0.52		4.7
60-04/Clst	95		5					0.51		4.4
60-05/Clst	93		7					0.53		4.4
60-06/Clst	88		12					0.51		3.2
60-07/Clst	95		5					0.58		3.8
60-08/Clst	89		11				ML(tr)	0.68		3.8
60-09/Clst	85	15					ML(tr)	0.64		4.4
60-10/Cl.Sst	88	1	tr			3	Gyp(7); Goe(1); ML(tr)	0.38		5.1
60-11/Cl.Sst	70	30*						0.51		5.2
60-12/Clst	77	23*						0.63		5.1
60-13/Sst	50		6	24		10	Sld(10)	0.41		3.8
60-14/Cl.Sst	54	46*						0.61		5.2
60-15/Cl.Sst	64	36						0.27		5.1
60-16/Comp	11	89*						0.12		6.3
103-01/Clst	78	22					ML(tr)	0.61		3.0
103-02/Clst	91	9					ML(tr)	0.74		3.8
103-03/Clst	77	23					ML(tr)	0.49		3.2
103-04/Clst	88	11.5				0.5		0.63		4.7
103-05/Cl.Sst	46.5		36.5			17		0.61		3.2
113-01/Sst	78			21.5		0.5		0.40		4.7
113-02/Clst	100							0.73		4.7
113-03/Clst	100						ML(tr)	0.63		4.4
113-04/Clst	100						ML(tr)	0.55		3.8
113-05/Clst	87	13						0.61		4.4

Table B.1: Continued

SAMPLE NUMBER /TYPE	I	C	K	MINERALOGY Q	H	OTHER	$\frac{I(002)}{I(001)}$	KUBLER INDEX
118-01/Comp	100					ML(tr)	0.74	4.2
118-02/Clst	100					ML(tr)	0.64	3.0
118-03/Clst	98		2			ML(tr)	0.62	3.8
118-04/Clst	92		8		tr		0.58	5.7
118-05/Clst	94		6			ML(tr)	0.58	4.7
118-06/Clst	100					ML(tr)	0.48	5.1
119-01/Sst	23			77			0.41	3.6
119-02/Sst	15			75	10		0.29	3.8
119-03/Sst				100			-	-
119-04/Sst	30		15	55			0.30	5.1
119-05-Sst	51			48.5	0.5	Goy,(tr); Fe(tr)	0.54	4.4
119-06/Sst	33			67			0.36	3.2
119-07/Sst	17			83			0.48	3.2
119-08/Sst	40			60	tr		0.40	3.2
119-09/Sst	40			60			0.45	3.8
119-10/Sst	41		7	52	tr		0.51	3.8
119-11/Sst	66			34	tr	ML(tr)	0.45	5.7
119-12/Sst	44.5			55	0.5		0.47	2.2
119-13/Sst	55			44.5	0.5		0.44	5.7
119-14/Sst	45			54	1		0.51	5.7
119-15/Sst	54			46	tr	ML(tr)	0.40	4.2
119-16/Sst	56.5			43	0.5	ML(tr)	0.54	4.4
119-17/Sst	45			54	1		0.58	3.4
119-18/Sst	93			7	0.5	ML(tr)	0.48	4.4
119-19/Sst	77			22.5			0.41	2.6
119-20/Sst	95			5	tr		0.55	4.4
119-21/Comp	100					ML(tr)	0.53	2.6
119-22/Cl-Sst	91	9					0.72	4.4
119-23/Comp	93	7				ML(tr)	0.70	3.2
119-24/Sst	64			36	tr	ML(tr)	0.39	4.4
119-25/Comp	90	10				ML(tr)	0.81	3.4
119-26/Clst	93	7					0.82	3.2
119-27/Clst	99.5				0.5		0.38	4.4
119-28/Clst	100					ML(tr)	0.77	3.8
119-29/Clst	84					Gyp(16); ML(tr)	0.78	4.4
119-30/Clst	96	4					0.79	4.4

Table B.1: Continued

SAMPLE NUMBER /TYPE	I	C	MINERALOGY			H	OTHER	I (002) I (001)		KUBLER INDEX
			K	Q						
119-31/Clst	85		15				ML(tr)	0.64		5.3
119-32/Clst	94		6			tr		0.48		4.4
119-33/Base	33	67						0.38		4.4
126-01/Comp	86	14						0.72		3.8
126-02/Clst	90	10						0.47		3.8
126-03/Clst	88	12						0.69		2.6
137-01/Clst	100							0.65		3.4
137-02/Sst	60.5					0.5		0.46		2.6
137-03/Cl.Sst	100						ML(tr)	0.56		4.2
137-04/Cl.Sst	100						ML(tr)	0.49		5.7
137-05/Sst	82					tr		0.46		5.7
137-06/Cl.Sst	93		7					0.61		3.4
137-07/Clst	90	10						0.72		4.4
137-08/Clst	89	11					ML(tr)	0.79		3.0
137-09/Clst	96		4			tr	ML(tr); Goy(tr)	0.57		5.5
137-10/Comp	84		16				ML(tr)	0.78		4.4
137-11/Comp	62	38						0.74		5.1
137-12/Base	98.5		1			0.5	ML(tr)	0.59		3.2
139-01/Sst	16			84				0.23		3.8
139-03/Sst	25			75				0.30		6.3
139-04/Sst	39			61				0.47		3.8
139-05/Sst	17		2	81		tr		0.36		5.5
139-06/Sst	17			83				0.32		3.2
139-07/Sst	35			65				0.36		3.2
139-08/Sst	7		5.5	87		0.5	Goy(tr)	0.38		3.4
139-09/Sst	26		9.5	62		2.5		0.54		3.9
139-10/Sst	34		7	59				0.42		4.4
139-11/Sst	42		7	50.5		0.5	ML(tr)	0.37		6.7
139-12/Sst	93		7					0.46		4.2
139-13/Sst	76.5			23		0.5		0.51		3.2
139-14/Sst	85			14.5		0.5	ML(tr)	0.39		5.7
139-15/Sst	54	23		23		tr		0.47		4.4
139-16/Sst	37	40		23				0.59		5.1
139-17/Base	78	22						0.77		4.7
139-18/Base	77	23						0.65		5.5

* samples contain Fe-chlorite rather than Al-chlorite.

Table B.2: Mineralogy, illite intensity ratio $I(002)/I(001)$ and Kubler Index of the 2-5 μ m fraction of the Cigar Lake samples. Sum of the mineral components is 100% (I = illite; C = Al-chlorite; K = kaolinite; Q = quartz; H = hematite; Goy = goyazite; Ps = feldspar; ML = mixed layer mineral). Sample type is indicated in column 1 (Cl. Sst = clayey sandstone; Clst = claystone; and comp = composite).

SAMPLE NUMBER /TYPE	I	C	K	MINERALOGY Q	H	OTHER	I (002) I (001)	KUBLER INDEX
44-01/Cl.Sst	98		2	tr		Goy(tr); Ps(tr)	0.52	2.6
44-04/Clst	100						0.53	3.8
44-06/Clst	100						0.57	2.2
44-10/Clst	99		1				0.49	3.4
44-11/Clst	100						0.54	3.2
44-13/Clst	99		1				0.56	3.4
44-14/Clst	100		tr		tr		0.48	4.4
44-15/Clst	96		4		tr		0.43	4.7
44-16/Cl.Sst	100						0.55	2.6
44-17/Clst	99		1				0.51	3.0
44-18/Clst	90		10				0.51	3.8
44-20/Clst	94		5.5		0.5		0.53	3.8
44-21/Clst	100			tr			0.63	4.4
49-06/Comp	100						0.53	3.2
49-08/Comp	93	7					0.59	4.4
49-09/Comp	99		1				0.45	2.6
49-11/Cl.Sst	90		10			ML(tr)	0.60	4.2
49-12/Clst	99		1			Goy(tr); ML(tr)	0.47	4.7
49-13/Clst	100						0.59	1.3
49-14/Clst	100						0.47	2.1
57-02/Clst	90	9					0.44	3.8
60-02/Clst	100						0.59	2.0
60-03/Clst	100						0.48	2.0
60-04/Clst	100						0.55	1.7
60-05/Clst	99		1				0.63	3.8
60-06/Clst	95		5				0.47	4.4
60-07/Clst	99.5				0.5		0.47	4.4

Table B.2: Continued

SAMPLE NUMBER /TYPE	MINERALOGY			H	OTHER	I (002) I (001)		KUBLER INDEX
	I	C	K	Q		I	I	
60-08/Clst	100		tr			0.52		2.2
60-09/Clst	97	3			tr	0.59		2.0
60-11/Cl.Sst	77	23*				0.46		3.4
60-12/Clst	96	3			0.5	0.55		2.6
60-14/Cl.Sst	70	30*	0.5			0.39		5.1
103-01/Clst	100							
103-02/Clst	99.5				0.5	0.57		2.0
103-03/Clst	100					0.54		3.7
103-04/Clst	92		4		ML(tr)	0.48		4.4
103-05/Cl.Sst	59		26		15	0.48		3.8
						0.67		3.4
118-05/Clst	99		1			0.56		2.6
119-26/Clst	100							
119-27/Clst	97					0.57		2.0
119-28/Clst	100		0.5		2.5	0.40		4.4
119-30/Clst	89	6	4			0.51		3.6p
119-31/Clst	99		tr		1	0.51		4.4
119-32/Clst	97		2		1	0.70		2.0
						0.41		4.2
126-02/Clst	92	7.5						
126-03/Clst	85	5		9.5	0.5	0.63		2.2
					0.5	0.40		5.5

* Samples contain Fe-chlorite rather than Al-chlorite

Table B.3: Qualitative mineralogy of bulk powdered samples as determined by XRD analysis (Q = quartz, I = illite, C = Al-chlorite, C* = Fe-chlorite, K = kaolinite, H = hematite, S = siderite, Ca = calcite, Ge = gersdorffite, Go = goethite, Gz = goyazite, ML = mixed-layer, Py = pyrite, Ru = rutile, Ur = uraninite, and Zr = zircon). Sample type (Sst = sandstone, Cl.Sst = clayey sandstone, Clst = sandy claystone, Comp = composite, and Base = basement) listed for reference.

SAMPLE NO./TYPE	ABUNDANT	MINOR	TRACE
Borehole 44A			
44-10/Clst	Q, I		C, H, Py, Ru, ML
44-11/Clst	I, Q	H	Ca, K
44-12/Sst	Q	I	
44-13/Clst	I	K, H	
44-14/Clst	I	S, H	Q, K, Go
44-15/Cl.Sst	I	K	H, Q, ML
44-17/Clst	I	S, H	K
44-18/Clst	I	K, S	Q, H
44-19/Sst	Q	H	I
44-20/Clst	I	S, H, K	
44-21/Clst	I	S, H, K	
Borehole 49			
49-01/Sst	Q	I	
49-05/Sst	Q	I	
49-07/Sst	Q	I	
49-10/Sst	Q, I		
49-12/Clst	I		Q, C, Ru
49-13/Clst	I		Q, C, Ru, H, ML
49-14/Clst	I	K, H	Q
49-15/Cl.Sst	I, K	Q	H
Borehole 53			
53-02/Sst	Q	I	
53-05/Sst	I, Q		
53-06/Cl.Sst	Q, I		H
53-07/Sst	Q	I	
53-10/Sst	I	Q	K
53-11/Cl.Sst	I	S, H, K	
53-12/Cl.Sst	H, I	K, S	
53-13/Base	I, C	H	
53-14/Base	I, C		

Table B.3: Continued

SAMPLE NO./TYPE	ABUNDANT	MINOR	TRACE
Borehole 57			
57-02/Clst	I	H	K
57-03/Clst	I		H, K
Borehole 60			
60-01/Sst	Q, I		
60-02/Clst	I	C	H, ML
60-03/Clst	I		C, H, ML
60-04/Clst	I		K, H, ML
60-05/Clst	I		K, H, ML
60-06/Clst	I	K	H, ML
60-07/Clst	I	K	H
60-08/Clst	I	K	H, ML
60-09/Clst	I	C	H
60-10/Cl.Sst	I	K	H, S
60-11/Cl.Sst	I	C*	S
60-12/Clst	I	C*	S, H
60-13/Sst	Q	I	C, ML, H, S
60-14/Cl.Sst	I, S	C*, H	
60-15/Cl.Sst	Ca	I, C	Ge
60-16/Comp	C*	I, Ca, Ur	ML, Ge
Borehole 103			
103-02/Clst	I	Q, H	
103-03/Clst	I	S, K, H	Ru
103-04/Clst	I, S, H		
103-05/Cl.Sst	H, S	I, K	
Borehole 113			
113-01/Sst	I, Q		
113-02/Clst	I	H	ML, C, Ru
113-03/Clst	I	H	Q, Gz
113-04/Clst	I	H	Ru
113-05/Clst	I	C	H

Table B.3: Continued

SAMPLE NO./TYPE	ABUNDANT	MINOR	TRACE
Borehole 118			
118-02/Clst	I	H	Q, ML, K
118-03/Clst	I	H, Q	K, Gz
118-05/Clst	I	H, S	K, Ru
118-05/Clst	I	H	K
118-06/Clst	I		H
Borehole 119			
119-01/Sst	Q		
119-02/Sst	Q		K
119-03/Sst	Q		
119-05/Sst	Q		I
119-06/Sst	Q		I
119-07/Sst	Q		I
119-08/Sst	Q	I	
119-09/Sst	Q	I	
119-10/Sst	Q		I
119-11/Sst	Q	I	
119-13/Sst	Q		I
119-14/Sst	Q		I
119-15/Sst	Q	I	
119-16/Sst	Q	I	
119-17/Sst	Q		I
119-18/Sst	Q, I		
119-19/Sst	Q	I	
119-20/Sst	Q, I		
119-24/Sst	Q	I	
119-26/Clst	I	H	Q, Ru, K
119-27/Clst	I	C	H, Ru
119-28/Clst	I		H, C, ML
119-29/Clst	I	H	Q, C, Ru
119-30/Clst	I	K, H	
119-31/Clst	I	H	K
119-32/Clst	I		H, K, ML
119-33/Base	C, I		H
Borehole 126			
126-01/Comp	I, C	H	
126-02/Clst	I	C	H
126-03/Clst	I	C	H

Table B.3: Continued

SAMPLE NO./TYPE	ABUNDANT	MINOR	TRACE
Borehole 137			
137-02/Sst	Q	I	
137-05/Sst	Q, I		
137-07/Clst	I	C, H	ML
137-08/Clst	I, C		H, ML
137-09/Clst	I	H, S, K	
137-10/Comp	I	H, Q	K
137-11/Comp	I	H, S, K	ML
137-12/Base	I, C	H	
Borehole 139			
139-01/Sst	Q		I
139-04/Sst	Q	I	
139-05/Sst	Q		I, K
139-01/Sst	Q		
139-07/Sst	Q		I
139-08/Sst	Q	K	
139-09/Sst	Q		K, H
139-10/Sst	Q	K	I
139-11/Sst	Q	K	I
139-12/Sst	Q	I	
139-13/Sst	Q	I	
139-14/Sst	I	Q	Zr
139-15/Sst	Q	I	
139-16/Sst	Q		I, C
139-17/Base	I, C		
AB-06 (bulk)	Q		K, H
AB-06 (<2 μ m)	Q	K	

APPENDIX C

GEOCHEMISTRY - XRF

C.1 ANALYTICAL PROCEDURE - XRF

Exactly 1.300 g of sample (0.650 g of Fe-rich samples plus 0.650 SiO₂) were mixed with 0.433 g of Li₂CO₃ and 3.900 g Li₂B₄O₇ in a platinum crucible and fused into a glass disc using a Claisse Fluxer. The samples were analyzed, along with standards, using a semi-automated Philips PW1410 X-ray spectrometer (Department of Geology, University of Ottawa). Precision is given in Table C.1, based on duplicate analyses. Analyses of standards are compared to accepted values in Table C.2.

Table C.1: Mean ($\bar{x}$), standard deviation (s) and range of values for 7 replicate XRF analyses of an SiO_2 -reference material, Department of Geology, University of Ottawa. Major elements reported in wt % oxide, trace elements in ppm; total iron determined as Fe_2O_3 . XRF analyses of quartz crushed in (1) stainless steel and (2) tungsten carbide bowls, Bleuler Mill shown for reference.

	SiO_2 - REFERENCE			QUARTZ	
	$\bar{x}$	s	RANGE	1	2
Major Oxides					
SiO_2	98.55	0.28	98.30-99.10	99.67	99.2
TiO_2	0.03	0.01	0.00-0.03	0.00	0.00
Al_2O_3	0.38	0.16	0.02-0.45	0.06	0.05
Fe_2O_3	0.05	0.02	0.02-0.06	0.37	0.03
MnO	0.00			0.00	0.00
MgO	0.11	0.003	0.06-0.16	0.03	0.04
CaO	0.02	0.004	0.01-0.02	0.01	0.01
Na_2O	0.00			0.42	0.18
K_2O	0.06	0.025	0.06-0.07	0.00	0.005
P_2O_5	0.02	0.01	0.01-0.04	0.00	0.01
S	0.01	0.005	0.00-0.01	0.00	0.00
Trace Elements					
Ba	59	28	0-83	32	26
Cr	23	3	19-26	335	18
Nb	1	1	0-2	0	3
Ni	6	2	0-29	7	0
Rb	0			0	0
Sr	30	13	0-38	0	0
V	5	8	0-20	0	0
Y	9	4	0-11	0	3
Zn	18	11	5-34	18	20
Zr	58	26	0-69	0	0
TOTAL	99.25	0.45	98.38-99.90	100.62	99.54

Table C.2: Comparison of chemical analyses of standard rock samples as reported in Abbey (1983) with XRF analyses at the Department of Geology, University of Ottawa. The first row reports the accepted values for major elements (weight percent oxide). Mean ($\bar{x}$), sample population (n), standard deviation (s), minimum and maximum refer to the University of Ottawa XRF data. Total iron determined as Fe_2O_3 . Rock standards include: BHVO-1(basalt), DR-N (diorite), GS-N (granite), MRG-1 (Mont Royal gabbro) and RGM-1 (rhyolite).

STANDARD NUMBER	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	S	TOTAL
BHVO-1	49.90	2.69	13.85	12.23	0.17	7.31	11.33	2.29	0.54	0.28	0.01	100.18
$\bar{x}$ (n=2)	50.28	2.79	13.89	12.33	0.17	7.43	11.55	2.33	0.53	0.17	0.00	101.68
s	0.01	0.01	0.00	0.06	0.00	0.08	0.03	0.08	0.01	0.01	0.00	
min	50.27	2.78	13.89	12.28	0.17	7.37	11.53	2.27	0.52	0.16	0.00	
max	50.29	2.79	13.89	12.37	0.17	7.48	11.57	2.38	0.53	0.17	0.00	
DR-N	52.98	1.09	17.56	9.72	0.22	4.41	7.07	3.00	1.70	0.25	?	100.02
$\bar{x}$ (n=8)	53.03	1.06	17.48	9.69	0.22	4.40	6.95	2.94	1.70	0.19	0.03	97.88
s	0.19	0.01	0.08	0.05	0.00	0.09	0.02	0.17	0.01	0.04	0.005	
min	52.76	1.05	17.37	9.64	0.22	4.33	6.92	2.70	1.69	0.14	0.02	
max	53.24	1.07	17.59	9.80	0.22	4.59	6.98	3.18	1.71	0.26	0.03	
GS-N	65.98	0.68	14.71	3.76	0.06	2.31	2.51	3.78	4.64	0.28	0.01?	100.11
$\bar{x}$ (n=2)	66.18	0.66	14.64	3.74	0.06	2.15	2.43	3.76	4.64	0.32	0.01	98.88
s	0.35	0.00	0.09	0.02	0.00	0.09	0.01	0.04	0.01	0.02	0.00	
min	65.93	0.66	14.57	3.72	0.06	2.08	2.42	3.73	4.64	0.30	0.01	
max	66.42	0.66	14.70	3.75	0.06	2.22	2.43	3.78	4.65	0.33	0.01	
MRG-1	39.32	3.69	8.50	17.82	0.17	13.49	14.77	0.71	0.18	0.06	0.06	100.14
$\bar{x}$ (n=2)	39.17	3.82	8.57	17.74	0.17	13.88	14.86	0.72	0.18	0.00	0.03	99.39
s	0.11	0.00	0.03	0.12	0.00	0.18	0.00	0.06	0.00	0.00	0.00	
min	39.09	3.82	8.55	17.65	0.17	13.75	14.86	0.68	0.18	0.00	0.03	
max	39.25	3.82	8.59	17.82	0.17	14.00	14.86	0.76	0.18	0.00	0.03	
RGM-1	73.47	0.27	13.80	1.89	0.04	0.28	1.15	4.12	4.35	0.05?	0.01?	100.02
$\bar{x}$ (n=2)	73.12	0.26	13.73	1.84	0.04	0.31	1.17	4.13	4.31	0.03	0.00	99.09
s	0.01	0.00	0.06	0.01	0.00	0.06	0.00	0.14	0.01	0.03	0.00	
min	73.11	0.26	13.68	1.83	0.04	0.26	1.17	4.03	4.30	0.01	0.00	
max	73.12	0.26	13.77	1.84	0.04	0.35	1.17	4.23	4.32	0.05	0.00	

Table C.3: Major elements (weight percent oxide) as measured by XRF analysis. Loss on ignition (LOI) determined by ignition at 950 °C for two hours on a 1.0 g subsample. Dash (-) indicates element is undetectable. Samples 60-15, 60-16 and 103-05 analyzed by direct current plasma-atomic emission spectroscopy (DCP).

SAMPLE NUMBER	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	S	TOTAL	LOI
44-01	84.97	0.64	8.72	0.47	-	0.45	0.04	-	2.38	0.03	0.02	98.021	0.71
44-02	95.07	0.09	2.65	0.26	-	0.21	0.02	-	0.72	0.01	0.02	99.131	0.50
44-03	86.17	0.27	8.62	0.22	-	0.45	0.03	-	2.40	0.03	0.01	98.349	1.51
44-04	74.47	0.52	15.65	0.51	-	0.57	0.04	-	4.47	0.09	0.04	96.634	2.71
44-05	74.11	0.87	14.86	0.54	-	0.46	0.08	-	4.10	0.58	0.06	96.420	2.64
44-06	58.76	1.74	25.34	0.51	-	0.78	0.08	-	7.22	0.10	0.02	95.229	4.18
44-07	95.01	0.10	3.09	0.25	-	0.13	0.02	-	0.86	0.09	0.02	99.717	0.56
44-08	54.91	2.12	27.02	0.53	-	0.89	0.08	-	7.87	0.25	0.03	94.298	5.17
44-09	91.55	0.20	4.31	0.43	-	0.21	0.02	-	1.24	0.06	0.04	98.166	0.82
44-10	69.56	1.06	16.02	2.26	-	0.44	0.06	-	4.55	0.03	0.19	94.656	4.01
44-11	53.71	0.73	29.50	0.67	-	0.76	0.07	-	8.50	0.24	0.01	94.543	4.51
44-12	94.74	0.06	2.53	0.38	-	0.13	0.02	-	0.71	0.01	0.02	98.672	0.42
44-13	45.65	2.03	33.18	1.50	-	0.89	0.10	-	9.50	0.15	0.23	94.094	5.50
44-14	45.34	0.95	33.48	3.27	0.03	1.00	0.15	-	9.55	0.16	0.01	94.365	6.41
44-15	45.00	1.68	33.24	2.14	0.01	0.93	0.12	-	9.42	0.21	0.11	93.464	5.99
44-16	37.64	3.32	27.80	10.75	0.06	1.07	0.22	-	7.79	0.01	0.03	89.569	9.35
44-17	37.10	1.60	27.21	13.43	0.08	1.24	0.28	-	7.76	0.13	0.09	89.680	10.51
44-18	36.27	2.49	26.32	12.74	0.06	1.06	0.22	-	7.53	0.10	0.46	88.330	9.92
44-19	86.34	0.06	2.18	8.92	0.02	0.28	0.06	-	0.52	0.06	0.02	98.520	1.08
44-20	26.32	0.94	21.48	30.60	0.06	1.12	0.26	-	6.10	0.16	0.14	87.686	10.23
44-21	39.81	1.02	30.28	9.25	0.06	1.14	0.30	-	8.47	0.22	0.02	90.980	8.08
49-01	94.55	0.10	2.79	0.54	-	0.21	0.01	-	0.77	0.04	0.03	99.120	0.99
49-02	91.09	0.20	4.63	0.34	-	0.32	0.02	-	1.29	0.06	0.02	98.077	0.97
49-03	87.99	0.15	6.24	0.44	-	0.30	0.03	-	1.71	0.07	0.06	97.478	1.34
49-04	93.44	0.09	3.65	0.27	-	0.24	0.02	-	1.01	0.03	0.01	98.836	0.66
49-05	94.04	0.07	2.91	0.22	-	0.20	0.02	-	0.77	0.06	0.03	98.377	0.58
49-06	52.20	1.35	29.35	0.84	-	1.20	0.08	-	8.40	0.34	0.08	94.378	5.35
49-07	94.22	0.37	3.02	0.40	-	0.23	0.02	-	0.83	0.01	0.01	99.233	0.57
49-08	62.99	1.36	22.46	0.71	-	0.86	0.07	-	6.25	0.09	0.02	95.244	3.82
49-09	84.69	0.54	9.62	0.42	-	0.45	0.04	-	2.69	0.15	0.02	98.864	1.70
49-10	94.94	0.39	2.44	0.30	-	0.16	0.02	-	0.67	0.06	0.01	99.141	0.52
49-11	59.89	3.03	22.40	1.06	-	0.77	0.09	-	6.32	0.31	0.17	94.776	3.98
49-12	42.74	5.82	30.99	1.16	-	1.07	0.21	-	8.49	0.74	0.04	92.823	5.97
49-13	46.46	1.66	33.58	1.04	-	1.05	0.09	-	9.55	0.14	0.03	94.262	5.49
49-14	45.36	1.48	33.02	2.40	-	1.09	0.11	-	9.22	0.15	0.08	93.488	6.11
49-15	59.11	1.02	24.50	1.41	-	0.75	0.10	0.05	6.80	0.58	0.06	94.996	5.78

Table C-3 Continued

SAMPLE NUMBER	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	S	TOTAL	LOI
53-01	90.94	0.14	5.10	0.27	-	0.40	0.02	-	1.29	0.03	0.02	98.318	1.08
53-02	94.19	0.08	2.78	0.20	-	0.38	0.01	-	0.75	0.03	0.01	98.291	0.46
53-03	93.02	0.11	4.08	0.24	-	0.30	0.02	-	1.09	0.02	0.02	98.975	0.78
53-04	78.66	0.90	11.99	0.43	-	0.89	0.05	-	3.08	0.15	0.06	96.555	2.58
53-05	89.26	0.24	6.55	0.25	-	0.33	0.02	-	1.81	0.03	0.01	98.631	1.59
53-06	80.67	0.52	12.33	0.18	-	0.47	0.03	-	3.47	0.05	-	97.920	2.72
53-07	93.61	0.23	3.58	0.29	-	0.22	0.02	-	0.99	-	0.02	99.102	1.07
53-08	59.33	0.79	25.76	0.63	-	0.95	0.05	-	7.37	0.02	0.02	95.295	5.24
53-09	79.37	0.32	13.17	0.46	-	0.63	0.04	-	3.61	0.03	0.01	97.827	2.44
53-10	94.72	0.10	4.02	0.34	-	0.28	0.02	-	1.08	-	0.01	100.656	1.04
53-11	21.80	0.72	16.58	38.26	0.22	1.00	0.34	0.06	4.74	0.06	0.04	84.090	16.73
53-12	24.22	0.58	19.68	35.60	0.12	1.38	0.30	-	5.38	0.12	0.04	87.658	11.58
53-13	36.94	1.40	31.08	9.96	0.02	6.50	0.18	-	4.76	0.04	-	91.016	9.55
53-14	41.80	1.73	33.56	1.39	-	6.46	0.12	0.05	5.46	0.12	0.01	90.879	9.14
53-15	43.40	1.36	32.97	1.07	0.01	5.32	0.49	0.01	6.66	0.54	0.01	92.075	9.02
57-01	69.31	0.19	6.63	0.30	-	0.33	0.04	-	1.89	0.07	0.01	98.846	2.03
57-02	37.78	1.34	30.20	9.68	-	1.84	0.14	0.14	8.08	0.08	0.02	89.782	9.01
57-03	46.58	0.64	33.13	1.24	-	1.99	0.11	-	9.11	0.09	0.01	93.211	5.38
60-01	93.77	0.31	3.27	0.31	-	0.25	0.02	-	0.90	-	0.01	98.951	0.61
60-02	46.56	1.58	33.97	0.56	-	1.15	0.10	-	9.69	0.21	0.02	94.351	5.12
60-03	46.01	1.33	34.09	0.61	-	1.13	0.10	-	9.60	0.37	0.04	93.853	5.27
60-04	46.87	0.53	34.52	0.59	-	1.03	0.09	-	9.86	0.24	0.01	94.072	5.09
60-05	46.82	1.38	33.19	1.35	-	1.09	0.13	-	9.69	0.14	0.05	94.314	5.19
60-06	46.47	1.41	32.74	1.81	-	1.10	0.16	-	9.67	0.17	0.04	93.982	5.32
60-07	46.01	0.74	32.60	2.27	-	1.08	0.29	-	9.56	0.27	0.14	93.227	4.89
60-08	46.79	1.38	33.34	1.43	-	1.29	0.12	-	9.55	0.06	0.01	94.442	5.04
60-09	45.23	1.87	32.04	3.05	-	1.97	0.14	-	8.77	0.03	0.03	93.741	5.71
60-10	39.94	1.62	27.76	11.32	0.04	1.48	0.24	-	7.62	-	0.12	90.544	6.65
60-11	35.67	0.80	23.50	14.49	0.07	7.37	0.36	0.02	5.48	-	0.09	88.119	11.17
60-12	37.56	1.94	26.24	17.06	0.04	2.20	0.30	-	7.04	-	0.04	92.709	7.62
60-13	83.26	0.06	3.08	7.34	0.02	0.68	0.14	-	0.76	0.02	0.04	95.955	3.01
60-14	22.00	0.72	17.02	28.44	0.24	4.62	2.76	-	4.04	1.88	0.18	82.114	16.02
60-15	27.80	0.78	18.70	8.52	0.01	5.03	0.22	0.04	3.29	0.31	-	64.700	11.20
60-16	25.90	4.67	19.30	5.83	0.02	1.61	0.51	0.06	0.99	0.43	-	59.020	14.70

Table C.3: Continued

SAMPLE NUMBER	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	S	TOTAL	LOI
103-01	69.92	0.63	19.19	0.62	-	0.58	0.06	0.02	5.39	0.14	0.02	96.779	3.01
103-02	49.66	0.64	31.90	1.03	-	1.28	0.08	-	8.74	0.19	0.22	94.051	5.59
103-03	35.76	2.18	26.96	15.04	0.06	1.64	0.30	-	7.44	0.18	0.10	89.898	10.02
103-04	20.70	0.24	15.92	40.86	0.14	1.46	0.32	0.02	4.38	-	0.02	84.162	15.53
103-05	12.80	0.27	9.10	55.00	0.14	1.35	0.42	0.01	2.14	0.23	-	80.450	14.00
113-01	95.89	0.09	2.26	0.32	-	-	0.01	-	0.62	0.02	-	99.301	0.31
113-02	45.74	2.06	33.06	0.69	-	0.80	0.11	-	9.51	0.25	0.03	93.108	5.37
113-03	44.91	2.20	33.08	0.79	-	0.82	0.13	-	9.50	0.32	0.11	92.805	5.43
113-04	46.91	1.25	34.15	0.49	-	0.85	0.09	-	9.95	0.20	0.01	94.401	7.91
113-05	45.43	1.14	32.96	2.58	-	1.40	0.11	-	9.14	0.09	0.07	93.720	5.84
118-01	76.31	0.86	13.81	0.36	-	0.48	0.06	-	3.86	0.11	0.11	96.306	2.33
118-02	45.99	1.25	33.61	1.04	-	1.14	0.09	-	9.59	0.21	0.04	93.512	5.61
118-03	52.54	1.15	29.33	1.14	-	1.03	0.09	-	8.26	0.21	0.12	94.382	4.95
118-04	33.78	1.30	30.00	8.58	0.08	1.88	3.98	5.56	10.84	0.66	0.02	97.159	6.49
118-05	39.23	1.20	30.15	11.35	-	0.95	0.12	-	8.65	0.17	0.17	92.352	5.42
118-06	45.11	1.41	32.64	3.47	0.01	1.47	0.12	-	8.95	0.19	0.02	93.979	5.97
119-01	98.03	0.05	0.67	0.26	0.00	0.00	0.04	0.00	0.17	0.01	0.03	99.333	0.11
119-02	96.94	0.05	1.52	0.29	0.00	0.00	0.04	0.01	0.10	0.02	0.03	99.087	0.54
119-03	98.16	0.03	0.17	0.36	0.01	0.00	0.04	0.00	0.03	0.04	0.04	98.944	0.05
119-04	95.83	0.08	1.70	0.41	0.00	0.00	0.04	0.00	0.35	0.04	0.02	98.572	0.62
119-05	93.69	0.20	3.19	0.33	0.00	0.00	0.05	0.00	0.89	0.06	0.03	98.557	0.63
119-06	95.79	0.08	1.10	0.30	0.00	0.00	0.04	0.00	0.29	0.05	0.04	97.743	0.20
119-07	97.63	0.06	0.58	0.30	0.00	0.00	0.04	0.00	0.15	0.03	0.05	98.910	0.10
119-08	97.02	0.05	1.30	0.30	0.00	0.00	0.04	0.09	0.34	0.07	0.03	99.330	0.26
119-09	94.77	0.11	1.94	0.40	0.01	0.00	0.04	0.02	0.59	0.03	0.03	98.008	0.56
119-10	95.68	0.15	1.27	0.38	0.00	0.00	0.05	0.00	0.38	0.05	0.05	98.131	0.22
119-11	95.10	0.07	2.30	0.34	0.00	0.00	0.04	0.00	0.67	0.04	0.03	98.687	0.79
119-12	94.46	0.12	2.40	0.46	0.01	0.00	0.04	0.02	0.71	0.04	0.03	98.378	0.36
119-13	92.81	0.17	2.80	0.70	0.01	0.00	0.04	0.00	0.73	0.04	0.07	97.488	1.52
119-14	89.91	0.16	2.26	0.77	0.01	0.00	0.04	0.03	0.64	0.04	0.03	93.993	1.07
119-15	90.37	0.02	2.03	0.34	0.00	0.00	0.04	0.00	0.54	0.04	0.02	93.478	0.80
119-16	91.17	0.14	2.65	0.44	0.00	0.00	0.05	0.00	0.75	0.02	0.04	95.364	0.45
119-17	94.90	0.04	2.54	0.37	0.00	0.00	0.04	0.00	0.70	0.03	0.02	98.710	0.51

Table C.3: Continued

SAMPLE NUMBER	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	S	TOTAL	LOI
119-18	94.91	0.05	2.63	0.24	-	0.22	0.02	-	0.71	0.02	0.01	98.856	0.46
119-19	92.93	0.19	3.66	0.32	-	0.22	0.02	-	1.01	0.01	0.01	98.493	0.71
119-20	94.53	0.08	2.47	0.33	-	0.19	0.02	-	0.69	0.03	0.01	98.427	0.75
119-21	93.82	0.21	3.54	0.25	-	0.23	0.02	0.25	0.95	0.04	0.01	99.428	0.95
119-22	86.42	0.39	7.91	0.40	-	0.49	0.03	-	2.11	0.06	0.03	98.009	1.63
119-23	86.95	2.08	6.22	0.42	-	0.33	0.04	-	1.70	0.05	0.03	98.366	5.33
119-24	94.53	0.08	2.47	0.33	-	0.19	0.02	-	0.69	0.03	0.01	98.427	0.77
119-25	56.26	0.85	28.15	0.68	-	0.68	0.07	0.25	7.86	0.21	0.02	95.638	4.77
119-26	47.29	0.70	34.28	0.51	-	1.07	0.08	0.12	9.88	0.20	0.04	94.450	5.80
119-27	43.69	3.67	31.29	1.44	-	2.80	0.14	-	7.87	0.25	0.21	92.114	6.84
119-28	43.37	4.20	31.86	1.06	-	1.09	0.13	-	8.89	0.23	0.04	92.430	5.64
119-29	44.26	2.91	32.06	1.02	-	1.62	0.14	-	8.85	0.25	0.20	92.470	5.86
119-30	36.86	2.42	27.58	18.40	-	0.92	0.16	-	7.62	0.10	0.02	94.748	5.08
119-31	37.02	0.96	28.86	18.20	-	1.12	0.24	-	7.98	0.20	0.02	94.922	5.06
119-32	37.58	1.12	28.80	16.00	0.02	0.91	0.19	0.07	8.15	0.11	0.07	93.440	5.50
119-33	39.13	2.16	30.47	3.44	0.01	9.01	0.18	0.05	3.46	0.21	0.09	88.561	10.93
126-01	50.41	1.48	30.25	0.95	-	2.17	0.09	-	7.81	0.06	0.07	93.882	4.03
126-02	45.77	1.71	33.84	0.75	-	2.22	0.09	-	8.87	-	0.01	93.838	6.43
126-03	46.16	1.11	34.00	0.69	-	1.90	0.09	-	9.18	0.01	0.03	93.580	5.72
137-01	46.40	1.94	32.84	0.80	0.01	1.13	0.10	-	9.49	0.20	0.03	93.578	6.85
137-02	96.13	0.03	2.15	0.32	-	0.11	0.02	0.04	0.61	0.03	0.01	99.502	0.99
137-03	83.60	0.59	10.12	0.36	-	0.39	0.04	-	2.81	0.07	0.02	98.207	8.67
137-04	77.68	0.51	13.77	0.56	-	0.58	0.05	-	3.96	0.09	0.01	97.425	3.10
137-05	93.99	0.10	3.61	0.37	-	0.23	0.02	-	0.64	-	0.01	99.067	0.96
137-06	81.04	0.68	9.10	2.54	-	0.48	0.06	0.02	2.42	0.10	0.04	96.682	9.16
137-07	47.20	0.37	34.60	1.27	-	0.96	0.08	-	9.85	0.17	0.11	94.867	6.10
137-08	46.50	0.80	34.50	1.12	-	1.31	0.08	-	9.44	0.06	0.02	94.176	6.11
137-09	43.68	1.59	32.90	2.90	0.01	1.55	0.14	-	9.14	0.14	0.07	92.671	6.19
137-10	40.22	1.20	29.08	13.06	-	0.80	0.10	-	8.12	0.18	0.04	93.196	5.00
137-11	35.34	0.86	27.00	23.02	0.02	0.98	0.14	-	7.64	0.18	0.04	95.532	5.00
137-12	43.32	1.70	32.72	1.31	-	5.52	0.12	0.03	6.44	0.05	0.02	91.605	5.11

Table C.3: Continued

SAMPLE NUMBER	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	S	TOTAL	LOI
139-01	96.83	0.05	0.89	0.39	0.01	0.00	0.05	0.00	0.23	0.03	0.02	98.595	0.50
13 -03	96.32	0.05	0.66	0.36	0.01	0.02	0.04	0.00	0.18	0.04	0.04	97.776	0.32
139-04	96.84	0.05	1.03	0.33	0.00	0.00	0.04	0.00	0.27	0.03	0.03	98.708	0.16
139-05	95.51	0.09	1.03	0.38	0.01	0.00	0.04	0.00	0.24	0.04	0.03	97.438	0.20
139-06	96.99	0.03	0.66	0.30	0.00	0.00	0.04	0.01	0.17	0.04	0.02	98.328	0.43
139-07	97.37	0.15	1.07	0.38	0.00	0.00	0.04	0.06	0.30	0.02	0.04	99.552	0.30
139-08	94.94	0.31	1.57	1.02	0.00	0.00	0.05	0.00	0.18	0.12	0.05	98.457	0.51
139-09	92.88	0.11	2.06	3.44	0.01	0.00	0.04	0.05	0.29	0.08	0.03	99.097	0.86
139-10	94.23	0.12	2.38	0.50	0.00	0.00	0.04	0.00	0.47	0.04	0.02	97.932	0.54
139-11	94.85	0.04	2.15	0.58	0.01	0.01	0.04	0.00	0.46	0.03	0.04	98.295	0.61
139-12	90.02	0.09	5.40	0.59	0.00	0.08	0.05	0.00	1.60	0.04	0.02	98.002	0.88
139-13	92.99	0.12	3.65	0.51	0.00	0.19	0.05	0.00	1.05	0.04	0.03	98.735	0.58
139-14	86.53	0.13	8.19	0.58	0.00	0.12	0.05	0.15	2.29	0.07	0.05	98.304	1.33
139-15	94.11	0.06	2.95	0.39	0.00	0.26	0.05	0.00	0.62	0.03	0.02	98.566	1.05
139-16	94.47	0.26	2.55	0.35	-	0.61	0.02	-	0.37	0.04	0.01	98.787	0.93
139-17	43.48	1.08	33.19	2.10	0.01	6.02	0.11	0.04	5.85	0.05	0.01	92.184	10.11
139-18	43.04	0.68	32.84	3.04	0.02	4.96	0.14	-	6.70	0.10	0.02	91.704	7.93
AB-06	95.81	0.10	0.82	0.98	0.01	0.00	0.04	0.00	0.07	0.04	0.04	98.011	0.70

Table C-4: Major element concentrations (weight percent oxide) for particle size separates, measured by XRF on 1 g subsamples after loss on ignition (LOI). Dash (-) indicates undetectable amounts; asterisk (*) indicates average of two samples. Totals for samples 60-16 and 118-03 are low, possibly as a result of weighing errors.

SAMPLE NUMBER	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	S	TOTAL	LOI
< 2 μ m													
44-01	45.42	0.36	35.28	1.40	-	2.14	0.28	0.42	8.98	2.50	0.08	97.46	7.24
44-04	47.06	0.10	35.94	0.60	-	1.64	0.24	0.12	9.96	0.88	0.12	97.23	6.12
44-06	45.76	0.18	34.62	0.76	-	1.42	0.26	0.16	9.94	2.68	0.10	96.55	5.74
44-08	45.34	0.14	32.38	0.72	-	1.62	0.36	1.18	9.52	5.68	0.10	97.72	6.48
44-11	47.60	0.08	35.30	1.24	-	1.02	0.22	0.12	10.40	0.46	0.10	97.00	5.31
44-18	44.62	0.38	33.80	3.14	0.02	1.64	0.38	-	9.56	1.14	0.12	95.76	6.60
49-12	43.52	0.68	34.04	1.42	-	1.94	0.62	-	9.02	2.32	0.16	94.94	8.47
49-13	46.70	0.18	35.46	1.02	-	1.94	0.24	0.14	9.78	1.50	0.10	97.57	6.45
53-02	57.68	0.18	27.30	0.80	-	1.02	0.18	1.10	7.42	2.34	0.10	98.30	4.73
53-14	44.76	0.20	36.28	2.26	0.02	8.18	0.30	0.60	5.60	2.62	0.10	101.12	9.67
53-15	43.52	0.18	35.36	1.40	0.02	7.00	0.28	1.28	6.36	3.06	0.14	98.80	8.98
57-02	32.92	0.42	25.26	31.86	-	2.28	0.26	0.74	6.14	0.44	0.12	100.76	5.37
60-02	45.74	0.08	36.22	0.70	-	1.94	0.24	0.06	9.70	0.64	0.10	95.80	5.87
60-03	46.62	0.18	35.68	0.86	-	1.64	0.30	0.06	9.82	1.48	0.12	97.39	6.11
60-04	47.50	0.20	36.20	1.32	-	1.14	0.32	-	10.00	1.42	0.12	98.91	7.39
60-05	46.74	0.06	34.42	2.08	-	1.62	0.24	-	10.10	0.60	0.08	96.32	5.95
60-06*	47.42	0.08	33.75	3.70	-	1.53	0.30	0.43	9.94	0.46	0.11	98.02	5.53
60-07	48.84	0.24	34.46	2.14	-	1.70	0.26	0.14	10.22	0.34	0.12	98.73	5.36
60-08*	47.20	0.06	34.39	2.80	-	2.09	0.27	0.13	9.64	0.45	0.12	97.92	5.86
60-09	46.36	0.08	33.44	4.38	-	3.10	0.30	0.14	8.58	0.48	0.10	97.37	6.72
60-16	28.40	3.16	27.32	6.24	-	2.48	1.14	1.40	1.50	5.64	0.50	78.68	12.34
113-02	47.46	0.12	35.58	0.70	-	1.62	0.24	-	10.20	0.66	0.08	97.26	5.68
113-04	46.80	0.12	36.16	0.84	-	1.28	0.26	0.14	10.18	0.70	0.08	96.99	5.69

Table C.4 Continued

SAMPLE NUMBER	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	S	TOTAL	LOI
< 2 μ m													
118-03	34.80	0.18	31.78	1.84	-	1.50	0.40	0.50	8.56	4.52	0.14	84.77	6.51
118-06	43.04	0.24	32.92	5.06	-	1.98	0.40	0.40	8.62	3.42	0.14	96.96	6.48
119-30	44.16	0.10	33.94	7.52	-	2.20	0.28	0.14	8.88	0.36	0.10	97.97	6.52
137-01	46.32	0.10	34.62	1.10	-	3.82	0.24	0.52	8.58	2.44	0.12	98.17	6.90
139-12	57.64	0.16	28.70	1.66	0.02	1.08	0.16	0.72	8.30	0.44	0.10	99.13	4.49
139-18	48.68	0.08	35.32	1.68	0.02	5.20	0.18	0.38	7.94	0.06	0.10	99.77	7.37
2 - 5 μ m													
44-11	46.26	0.20	35.70	0.90	-	0.72	0.18	0.64	10.54	0.40	0.10	95.98	5.22
60-05*	48.30	0.15	36.14	1.12	-	1.04	0.16	0.25	10.60	0.40	0.10	98.33	5.34
60-06	47.78	0.08	35.68	2.08	-	1.06	0.22	0.30	10.52	0.18	0.10	98.13	5.42
60-07	48.08	0.10	35.96	1.22	-	1.10	0.16	0.30	10.56	0.16	0.10	97.86	5.00
60-08	47.88	0.22	35.90	1.20	-	1.24	0.16	0.32	10.56	0.30	0.10	98.06	5.34
60-09	47.78	0.46	35.50	2.22	-	1.80	0.18	0.42	10.04	0.18	0.12	98.91	5.80
5 - 20 μ m													
60-05	48.32	0.62	35.92	1.26	-	1.06	0.16	0.10	10.50	0.22	0.08	98.45	5.19
60-06	46.94	0.22	34.80	2.44	-	1.10	1.00	0.12	10.24	0.82	0.14	98.01	5.40
60-07	47.32	0.44	35.34	1.50	-	1.00	0.46	0.26	10.42	0.32	0.12	97.35	5.28
60-08	47.40	0.84	35.66	1.18	-	1.20	0.18	0.20	10.38	0.12	0.10	97.46	5.13
60-09	46.06	1.66	34.60	2.40	-	1.68	0.18	0.18	9.78	0.10	0.14	97.03	5.70

Table C.5: Trace elements (ppm) as measured by XRF analysis. U concentration determined by NAA-DNC. Dash (-) indicates element is undetectable; samples 60-15 and 103-05 were not analyzed. Data for 60-16 obtained from XRF analysis.

SAMPLE NUMBER	Ba	Cr	Nb	Ni	Rb	Sr	U	V	Y	Zn	Zr
44-01	102	100	14	26	19	367	42	62	79	124	1421
44-02	55	176	2	-	-	115	8	7	14	42	179
44-03	76	83	7	17	22	235	27	156	35	64	370
44-04	76	72	9	21	41	471	66	176	75	62	898
44-05	72	15	-	111	33	1671	88	162	1919	20	1917
44-06	128	46	30	18	70	1022	104	354	196	40	3169
44-07	40	174	-	9	1	190	40	8	397	15	249
44-08	180	59	59	15	104	1160	245	598	55	103	2067
44-09	63	156	5	2	14	195	44	87	11	37	257
44-10	48	90	45	11	84	533	1920	232	30	149	2454
44-11	110	54	22	13	76	887	233	469	30	52	919
44-12	48	251	2	15	4	84	6	-	8	10	105
44-13	86	39	54	62	83	999	275	1512	61	98	3108
44-14	135	9	22	16	83	667	149	667	37	73	1519
44-15	101	9	46	19	81	1159	366	230	45	56	2866
44-16	117	-	97	4	96	850	1980	166	50	141	5085
44-17	119	24	53	10	76	883	713	1244	35	152	2667
44-18	137	-	59	36	59	1122	116	1504	63	163	4491
44-19	86	230	-	16	-	74	4	40	16	14	122
44-20	136	28	22	-	42	880	74	2290	46	-	1612
44-21	229	4	38	14	120	690	2160	891	34	11	2065
49-01	58	145	3	24	7	87	32	-	17	20	205
49-02	69	154	-	2	9	146	37	36	17	15	346
49-03	83	137	8	5	17	241	55	25	24	25	800
49-04	78	159	-	-	11	88	28	2	20	17	265
49-05	71	121	-	4	8	88	6	-	10	15	79
49-06	167	-	18	42	86	1158	97	214	151	32	2253
49-07	45	273	3	6	4	107	15	-	16	-	504
49-08	107	102	21	18	59	622	106	61	72	20	2140
49-09	46	194	4	7	26	360	48	111	95	15	921
49-10	67	203	10	12	1	303	43	12	10	8	459
49-11	117	99	86	67	65	1300	347	282	110	31	3383
49-12	238	-	161	41	84	3594	318	310	108	51	7470
49-13	120	8	44	23	91	1085	110	536	55	20	2800
49-14	118	-	42	42	88	1009	152	493	57	39	2474
49-15	134	3	28	15	82	2807	327	197	37	49	1562

Table C.5: Continued

SAMPLE NUMBER	Ba	Cr	Nb	Ni	Rb	Sr	U	V	Y	Zn	Zr
53-01	74	147	3	25	8	117	29	41	34	-	359
53-02	50	162	-	5	4	51	3	-	10	2	67
53-03	60	160	4	32	8	50	14	11	15	16	206
53-04	106	79	17	59	33	486	52	450	70	55	1102
53-05	49	156	3	23	15	145	15	62	27	15	497
53-06	135	49	7	17	33	229	41	130	65	22	701
53-07	81	210	2	20	5	57	17	6	21	20	533
53-08	77	36	16	38	71	412	148	151	48	57	1875
53-09	91	73	8	12	29	207	88	220	17	35	636
53-10	82	179	2	6	7	53	27	36	7	16	252
53-11	116	84	22	-	32	400	55	586	32	-	1444
53-12	62	68	6	56	34	434	36	512	28	-	1178
53-13	194	206	24	152	44	192	53	146	40	12	348
53-14	33	142	30	131	62	408	114	156	66	39	359
53-15	24	184	19	105	85	414	52	506	76	28	269
57-01	47	68	2	12	15	171	11	10	41	8	252
57-02	184	46	-	142	62	554	105	316	824	16	2680
57-03	85	-	8	188	88	370	72	327	123	14	1025
60-01	66	222	5	12	4	108	11	29	22	20	382
60-02	145	-	22	39	93	845	106	144	207	32	2537
60-03	111	-	20	49	81	1330	71	144	244	36	2480
60-04	103	-	3	28	92	840	189	229	167	47	1046
60-05	106	27	22	50	87	661	29	231	199	88	2309
60-06	90	-	33	86	94	510	192	232	192	75	1738
60-07	89	5	14	87	97	321	322	116	121	64	1121
60-08	93	15	21	46	92	436	166	188	198	73	2600
60-09	83	9	39	132	76	411	88	304	190	49	3210
60-10	206	62	46	320	106	102	2040	198	170	146	3084
60-11	78	26	19	296	49	288	120	494	53	19	1571
60-12	226	50	32	100	56	214	138	1388	194	210	3082
60-13	174	130	-	60	2	40	25	34	18	30	118
60-14	218	40	8	202	34	98	140	218	72	30	1218
60-15	-	-	-	-	-	-	131	-	-	-	-
60-16	226	-	688	1032	1900	94	137000	2410	184	1740	1904

Table C.5: Continued

SAMPLE NUMBER	Ba	Cr	Nb	Ni	Rb	Sr	U	V	Y	Zn	Zr
103-01	62	84	15	12	51	486	43	106	35	5	870
103-02	99	-	12	116	83	672	166	302	60	37	1003
103-03	182	34	24	62	60	702	94	1396	334	282	3128
103-04	194	52	-	68	38	160	51	40	22	26	422
103-05	-	-	-	-	-	-	61	-	-	-	-
113-01	60	297	6	4	4	88	3	21	29	50	100
113-02	94	2	44	49	96	1294	245	461	249	109	4046
113-03	125	-	35	49	97	1564	281	241	312	56	4552
113-04	71	2	16	31	98	844	100	317	251	45	2081
113-05	89	-	18	89	82	641	232	2210	137	113	2098
118-01	111	99	10	24	38	680	132	53	102	24	2213
118-02	66	-	15	57	89	889	78	700	192	48	2098
118-03	79	16	14	532	74	893	177	252	183	16	1884
118-04	2288	-	40	24	524	470	84	86	64	186	1110
118-05	233	40	22	26	72	954	54	358	147	21	1746
118-06	82	33	27	120	76	1012	146	431	152	81	2389
119-01	104	230	-	-	-	90	8	13	5	12	111
119-02	131	193	-	4	-	87	44	43	4	9	138
119-03	94	305	-	-	-	109	10	-	4	11	41
119-04	63	214	2	-	-	97	109	17	3	8	220
119-05	116	193	4	1	-	204	30	-	8	7	261
119-06	26	234	-	-	6	56	6	1	0	10	68
119-07	67	259	-	-	-	46	13	-	6	12	159
119-08	78	236	-	4	-	169	7	6	9	6	96
119-09	70	263	2	1	4	101	8	-	5	16	190
119-10	133	308	-	-	-	88	14	5	143	-	170
119-11	93	266	2	5	1	157	5	15	5	4	108
119-12	101	358	1	4	4	92	6	-	13	17	164
119-13	105	225	3	14	3	69	25	9	29	2	451
119-14	121	285	3	22	2	83	38	7	17	2	263
119-15	88	261	-	-	3	36	6	4	7	11	56
119-16	108	291	2	20	3	95	11	1	10	11	223
119-17	106	237	-	8	-	60	5	-	7	24	51
119-18	53	174	-	-	4	57	12	-	14	29	127

Table C.5: Continued

SAMPLE NUMBER	Ba	Cr	Nb	Ni	Rb	Sr	U	V	Y	Zn	Zr
119-19	34	216	3	2	8	105	28	2	24	21	462
119-20	37	150	7	8	9	128	45	15	25	37	376
119-21	39	171	4	-	4	91	23	7	17	19	406
119-22	95	139	6	13	21	317	30	76	48	-	540
119-23	90	205	34	17	10	510	92	123	153	41	2893
119-24	26	262	-	3	-	53	7	5	14	28	111
119-25	139	45	23	22	74	631	159	108	97	45	1240
119-26	114	5	10	26	102	581	66	180	133	38	945
119-27	162	-	53	259	103	1230	93	489	325	61	2906
119-28	114	-	70	46	86	1624	234	268	294	46	6936
119-29	122	28	48	201	92	2017	167	230	251	55	5787
119-30	68	96	42	-	56	1114	149	156	222	44	4882
119-31	206	50	10	28	50	596	53	40	196	12	2036
119-32	253	53	2	18	58	489	71	564	297	31	2428
119-33	36	189	32	391	59	615	216	559	56	59	544
126-01	78	67	30	82	67	600	71	294	121	46	3169
126-02	24	27	33	286	80	403	47	93	53	179	3108
126-03	61	-	25	289	80	350	27	117	71	124	1904
137-01	134	-	24	31	96	994	185	131	322	43	3243
137-02	40	236	-	-	2	56	3	7	8	13	44
137-03	82	62	9	11	26	345	25	144	66	30	739
137-04	54	189	7	22	41	341	41	115	53	37	819
137-05	71	255	-	12	4	92	7	15	10	32	171
137-06	116	18	12	24	22	376	61	32	42	-	1380
137-07	116	-	4	14	97	749	52	164	32	42	742
137-08	105	16	20	28	83	439	51	185	24	37	1607
137-09	237	73	45	93	74	975	136	776	46	48	3136
137-10	202	44	32	34	70	934	103	186	40	4	2408
137-11	164	40	22	54	54	620	52	474	34	12	1642
137-12	10	232	28	150	94	304	205	1096	49	50	370

Table C.5: Continued

SAMPLE NUMBER	Ba	Cr	NB	Ni	Rb	Sr	U	V	Y	Zn	Zr
139-01	99	344	1	3	-	283	1	-	4	3	92
139-03	108	323	-	-	-	85	1	6	4	10	100
139-04	95	297	-	4	-	76	1	-	5	7	126
139-05	41	280	2	5	-	62	1	-	4	10	151
139-06	60	240	-	-	-	51	1	-	1	8	64
139-07	111	302	2	-	-	110	1	-	9	23	391
139-08	115	308	4	8	-	516	3	9	12	18	586
139-09	105	319	1	5	1	221	1	13	15	1	230
139-10	109	423	-	1	-	65	2	14	11	4	261
139-11	98	423	-	11	-	30	2	10	4	-	991
139-12	100	306	-	1	9	52	2	49	5	-	171
139-13	110	333	2	6	6	86	5	21	9	10	195
139-14	109	336	-	10	19	106	7	66	11	5	289
139-15	92	266	-	1	5	41	2	38	7	12	107
139-16	53	265	4	20	-	99	6	13	13	20	336
139-17	100	86	29	410	80	170	15	67	63	122	711
139-18	260	72	30	264	136	214	8	28	68	150	422
AB-06	41	324	-	-	-	83	2	5	3	7	292

Table C.6: Trace element concentrations (ppm) for particle size separates, measured by XRF after loss on ignition (LOI) determination. Dash (-) indicates undetectable amounts; asterisk (*) indicates average of two samples.

SAMPLE NUMBER	Ba	Cr	Nb	Ni	Rb	Sr	V	Y	Zn	Zr
<hr/>										
< 2 μ m										
44-01	332	-	-	96	94	3340	374	110	178	1484
44-04	348	-	-	26	108	2902	572	140	104	1522
44-06	348	-	-	10	112	3618	806	166	82	1516
44-08	422	-	-	32	132	3244	1116	82	192	1576
44-11	224	-	-	4	118	1574	1540	30	98	1004
44-18	350	-	-	156	90	3938	3038	88	196	1722
49-12	520	-	10	384	138	6616	612	166	152	3644
49-13	250	-	-	36	98	2586	974	48	66	1000
53-02	174	262	-	8	62	850	48	46	60	268
53-14	224	244	6	236	76	154	248	86	108	578
53-15	176	164	-	180	74	284	612	76	42	356
57-02	182	-	20	170	50	1380	298	54	68	1024
60-02	302	-	-	20	104	2134	186	84	64	890
60-03	306	-	-	60	112	2888	806	158	114	1876
60-04	314	-	-	32	100	4412	294	130	116	1540
60-05	278	-	-	22	106	1902	458	106	120	850
60-06*	189	-	-	57	115	1222	240	106	137	929
60-07	204	-	4	84	104	934	464	70	108	686
60-08*	239	-	-	23	101	1608	424	94	95	1198
60-09	220	-	-	120	88	1224	500	216	96	1658
60-16	414	-	318	1690	934	156	2390	150	1714	1266
113-02	230	-	-	14	122	2134	704	180	150	2416
113-04	266	-	-	12	108	2290	252	108	84	1136

Table C.6 Continued

SAMPLE NUMBER	Ba	Cr	Nb	Ni	Rb	Sr	V	Y	Zn	Zr
< 2 μm										
118-03	210	-	-	260	86	2878	286	108	80	1590
118-06	232	-	-	154	84	4172	876	132	178	1536
119-30	232	-	-	9	82	1282	340	62	40	858
137-01	228	12	-	104	108	1440	394	84	52	704
139-12	220	206	-	-	92	418	286	24	-	290
139-18	160	190	-	164	116	112	76	52	34	422
2 - 5 μm										
44-11	246	20	8	46	96	1416	1006	30	96	452
60-05*	206	-	-	19	94	896	314	65	64	362
60-06	122	34	-	34	104	334	154	58	74	398
60-07	138	18	-	26	94	268	230	36	90	292
60-08	158	16	-	6	98	666	304	54	54	410
60-09	170	6	10	102	86	532	386	94	66	650
5 - 20 μm										
60-05	112	20	8	66	92	398	352	180	102	794
60-06	192	18	-	228	100	266	142	162	72	674
60-07	142	42	10	162	102	178	178	162	72	688
60-08	142	46	16	130	102	398	258	180	38	730
60-09	148	44	36	170	92	284	360	200	84	1070

C.2: FACTOR ANALYSIS

Principal component analysis was used to evaluate variability in the chemical data set. The factor method calculates eigenvectors (factors) and eigenvalues (intensity parameters of the eigenvectors) from a square (correlation) matrix produced by multiplying the data matrix by its transpose (Mellinger, 1984; Davis, 1986). This enables the variance - covariance matrices to be projected geometrically; the eigenvector determines the orientation of the principal axis of an ellipsoid and the eigenvalue represents its length (Davis, 1986). The more similar the variables, the smaller the angle between their eigenvectors (Taylor, 1977). The procedure is as follows:

In principal component analysis, it is assumed that only the variables account for the statistical variance; other factors are excluded. Eigenvectors are fitted to the array of data points to represent the maximum variance (Taylor, 1977). "Loadings" are calculated by summing each column in the correlation matrix to determine an aggregate correlation between each variable and all other variables. The loadings range from 0 to 1, with loadings near 1 considered to be significant, and those near 0 "non-correlated" or accounting for little variance in the data (Taylor, 1977). The factors are labelled, somewhat arbitrarily, using a term (e.g., clay mineralogy) that reflects the pattern of the variable loadings. Table C.7 lists the eigenvalues and the percentage variance for 15 factors. The factors with eigenvalues > 1 account for most of the variance of the data. The loadings of the variables on the first five factors are shown in Table C.8.

The factors can be represented in factor space on a dimensionless X-Y diagram. Further reduction of the data can be achieved by an iterative process in which the factor loadings are adjusted to ± 1 or near 0 to maximize the variance. By this technique, called varimax rotation, some loadings become higher but most lose significance (Davis, 1986). The results from this procedure are listed in Table C.9 and plotted in Figure 5.14. Based on these results, the

Table C.7: Eigenvalues and percentage of variance
by factor.

FACTOR	EIGENVALUE	VARIANCE (%)
1	6.795	45.3
2	1.945	13.0
3	1.412	9.4
4	1.182	7.9
5	1.163	7.8
6	0.773	5.2
7	0.553	3.7
8	0.513	3.4
9	0.327	2.2
10	0.171	1.1
11	0.109	0.7
12	0.035	0.2
13	0.014	0.1
14	0.006	0.0
15	0.002	0.0
		<hr/> 100.0

Table C.8: Loadings of each variable on the first five factors- factor matrix, principal component analysis.

	FACTORS				
	1	2	3	4	5
Al_2O_3	0.918	-0.005	-0.210	-0.050	0.029
K_2O	0.897	-0.082	-0.107	-0.164	-0.080
SiO_2	-0.893	-0.261	0.118	-0.188	0.183
TiO_2	0.832	-0.282	0.127	0.320	0.210
Zr	0.804	-0.459	0.095	0.009	-0.073
Nb	0.793	-0.367	0.098	-0.001	0.052
Rb	0.742	0.188	0.165	-0.401	0.080
Sr	0.741	-0.467	0.210	-0.087	0.003
V	0.550	-0.040	-0.210	0.156	-0.495
MgO	0.526	0.487	-0.474	0.073	0.276
CaO	0.367	0.674	0.517	-0.252	0.028
Ni	0.472	0.293	-0.570	-0.063	0.420
P_2O_5	0.510	0.378	0.535	-0.081	0.143
U	0.077	0.122	0.296	0.798	0.374
Fe_2O_3	0.286	0.489	0.017	0.324	-0.643

Table C.9: Loadings of each variable on the first five factors- rotated factor matrix, varimax rotation. High loadings for each factor are outlined in bold type.

	FACTORS				
	1	2	3	4	5
Zr	0.923	0.037	0.039	0.125	-0.010
Sr	0.895	-0.037	0.128	-0.008	-0.032
Nb	0.834	0.115	0.098	0.042	0.038
TiO ₂	0.845	0.216	0.105	0.077	0.396
K ₂ O	0.755	0.373	0.221	0.250	-0.188
Al ₂ O ₃	0.713	0.528	0.184	0.250	-0.069
Ni	0.142	0.880	0.030	-0.032	-0.025
MgO	0.080	0.862	0.167	0.187	0.088
CaO	-0.031	0.096	0.942	0.151	0.002
P ₂ O ₅	0.257	0.062	0.782	0.060	0.183
Rb	0.513	0.311	0.603	0.044	-0.236
Fe ₂ O ₃	-0.069	0.026	0.217	0.888	0.077
V	0.430	0.135	-0.086	0.630	-0.109
SiO ₂	-0.543	-0.471	-0.291	0.169	-0.101
U	0.018	0.025	0.070	0.017	0.939

factors responsible for most of the variance in the chemical data were labelled as: (1) detrital mineralogy (zircon, ilmenite, absence of quartz), illite and goyazite; (2) chlorite; (3) apatite; (4) Fe-oxides and (5) uraninite.

APPENDIX D

GEOCHEMISTRY - INAA

D.1 ANALYTICAL PROCEDURE - INAA

One to 2 g of each sample in a plastic capsule were irradiated for one hour in the Ecôle Polytechnique (Mont-réal) SLOWPOKE II reactor using a flux of 10^{12} n.cm⁻²s⁻¹. The samples were later counted for 3-hour periods using an Ortec 1000 low energy, photon spectrometer (LEPS) (resolution of 305 eV at 5.9 keV and 527 eV at 122 keV) after a decay time of 5-7, 20-25 and 50-60 days. After a decay time of 7-10 and 50-60 days, the samples were again counted using a Canberra Ge(Li) high energy detector (resolution 1.01 keV at 122 keV and 1.95 keV at 1332 keV) (Gariépy, 1980). Decay times and detector used for optimum data collection of the various isotopes are listed in Table D.1. Ludden (personal communication, 1989) estimated the precision to be $\pm 5\%$ for Co, Eu, La, Sc, Sm and Yb and $\pm 5-10\%$ for Ce, Hf, Ho, Lu, Nd, Ta and Tb. Table D.2 indicates the reproducibility for the REE data. Comparison of reported values for standards JB-1 and NIM-G with results from the Ecôle Polytechnique lab are shown in Table D.3.

Table D.1: Optimum time used to measure isotopes by INAA. X denotes the Ortec 1000 detector and Y is the Canberra Ge(Li) detector. Position 1, 2 or 3 indicates the height of the sample above the detector (G. Gauthier, Université de Montréal, personal communication, 1986).

Decay Time (days)	Detector and Height Position	Isotopes
5 - 7	X2	^{140}La , ^{153}Sm , ^{166}Ho , ^{175}Yb , ^{177}Lu , ^{239}Np
7 - 10	Y3	^{76}As , ^{122}Sb , ^{140}La , ^{153}Sm , ^{166}Ho , ^{175}Yb , ^{177}Lu , ^{234}Np
20 - 25	X1	^{51}Cr , ^{141}Ce , ^{147}Nd , ^{152}Eu , ^{160}Tb , ^{170}Tm , ^{181}Hf , ^{182}Ta , ^{233}Pa
50 - 60	X1	^{51}Cr , ^{141}Ce , ^{152}Eu , ^{153}Gd , ^{160}Tb , ^{169}Yb , ^{170}Tm , ^{181}Hf , ^{182}Ta , ^{233}Pa
50 - 60	Y2	^{46}Sc , ^{51}Cr , ^{134}Cs , ^{141}Ce , ^{152}Eu , ^{153}Gd , ^{160}Tb , ^{170}Tm , ^{233}Pa

Table D.2: Results (in ppm) of REE analysis by INAA
for duplicate sample 60-14.

	1	2	AVERAGE
La	45.2	46.0	45.6
Ce	53.4	51.3	52.4
Nd	68.0	70.2	69.1
Sm	22.9	22.2	22.6
Eu	3.20	3.20	3.20
Gd	16.8	20.3	18.6
Tb	2.20	2.30	2.25
Ho	1.40	1.60	1.50
Tm	0.40	0.40	0.40
Yb	2.30	2.90	2.60
Lu	0.50	0.50	0.50

Table D.3: Comparison of REE data (ppm) obtained at the Ecôle Polytechnique laboratory, Montréal to accepted values for JB-1 and NIM-G rock standards.

	1	JB-1 2	3	4	NIM-G 5	6
La	36.6	36.7	38.9	110	109	118.7
Ce	66.9	65.8	63.1	197	195	198.8
Nd	25.6	25.6	22.60	74.5	72	68.6
Sm	5.0	5.6	5.14	15.1	15.8	15.4
Eu	1.51	1.4	1.34	0.24	0.35	0.39
Gd	4.5	-	4.05	15.9	14	13.3
Tb	0.76	0.74	0.75	-	-	2.77
Ho	0.91	-	1.61	-	-	8.5
Tm	0.31	-	0.54	-	-	2.14
Yb	2.1	2.20	1.86	14.2	14.2	16.2
Lu	0.33	0.32	0.30	1.95	2	2.26

- 1 JB-1 values reported in Potts et al. (1981).
- 2 JB-1 values reported in Lajoie and Ludden (1984).
- 3 Average JB-1 values, Ecôle Polytechnique (J. Ludden, personal communication, 1989).
- 4 NIM-G values reported in Roelandts (1988).
- 5 NIM-G values reported in Hansen and Ring (1985).
- 6 Average NIM-G values, Ecôle Polytechnique (J. Ludden, personal communication, 1989).

TABLE D.4: Concentration (in ppm) of trace elements as determined by INAA.

SAMPLE NO.	As	Co	Cs ¹	Hf	Sb	Sc	Ta	Th	U	W
49-13	17.6	3.1	0.6	74.1	3.9	10.6	6.6	134	110	10.8
49-14	303	6.5	0.7	66.1	8.9	9.3	5.9	128	150	10.7
49-15	25.8	2.2	0.5	40.2	2.6	7.0	2.9	64.8	307	4.6
53-11	37.8	1.5	n.d.	37.3	1.4	5.6	2.1	40.8	53.5	6.6
53-12	27.8	2.2	0.7	27.5	3.4	5.4	1.9	31.5	35.6	n.a.
53-13	14.0	10.4	0.6	8.0	0.5	24.7	1.7	26.5	51.1	7.3
53-14	22.4	16.9	1.1	10.3	0.5	30.0	2.1	45.9	108	5.7
60-01	9.4	1.5	0.2	10.5	0.4	1.3	1.0	17.3	11.4	2.8
60-02	37.2	3.7	0.4	68.7	1.4	9.8	4.2	124	106	4.2
60-03	63.8	6.0	0.4	65.4	1.8	10.0	8.5	241	68.0	4.7
60-04	48.5	5.4	0.7	29.8	1.3	7.9	1.9	63.2	191	5.7
60-05	150	25.0	1.0	83.0	2.9	10.1	9.2	214	83.1	7.7
60-06	176	32.1	0.8	45.2	2.7	8.0	5.2	98.3	189	5.7
60-07	141	30.7	0.7	33.5	3.9	6.1	2.6	57.2	317	5.1
60-08	54.0	11.7	0.7	62.1	1.8	4.2	4.3	90.5	150	4.7
60-09	53.2	28.4	0.9	85.1	3.8	8.2	9.3	269	86.8	12.8
60-11	38.3	25.2	0.8	434	1.8	5.4	2.6	52.9	117	8.2
60-12	40.2	26.9	2.9	104	5.7	19.8	11.2	263	179	21.6
60-13	3.9	1.2	n.d.	1.5	0.7	0.6	0.1	2.5	23.4	1.1
60-14	113	11.1	0.9	29.5	0.8	3.9	1.9	40.9	133	n.a.
60-15	1110	119	1.3	32.7	9.6	4.2	2.3	57.4	130	n.a.
103-03	65.5	7.3	0.8	77.3	1.4	11.3	5.2	79.7	89.8	7.5
103-04	23.7	4.1	0.5	9.6	0.2	2.6	0.6	13.6	49.8	1.4
103-05	39.8	1.8	n.d.	15.7	1.3	2.8	1.0	21.6	54.3	1.7
103-04	55.7	3.8	0.7	54.5	1.2	9.2	4.5	117	96.2	8.1
103-05	46.7	22.7	0.7	63.4	1.5	11.2	3.7	101	246	6.7
119-30	36.7	3.4	0.7	132	1.6	8.8	12.9	357	141	8.3
119-31	21.6	1.8	0.4	51.8	1.0	6.0	3.2	71.7	54.0	4.8
119-32	32.4	7.3	0.6	60.0	2.4	7.2	3.1	53.1	70.7	7.8
119-33	46.4	24.3	0.9	16.3	1.1	28.1	1.8	57.6	214	6.2
126-01	86.5	5.6	0.7	81.6	1.9	10.1	5.0	117	70.4	6.0
126-03	647	123	0.6	54.3	2.0	7.1	3.4	59.8	29.0	6.8
137-10	27.2	1.0	0.6	63.8	1.3	8.2	4.4	74.6	103	6.6
137-11	35.5	1.8	0.3	42.0	7.6	6.8	2.8	56.9	49.9	7.8
139-17	10.8	26.0	1.3	21.0	0.2	27.4	2.6	38.2	13.2	6.4

¹ Cs counted at 50-60 day on Y2 counter. More accurate data available after 1 year of counting.
n.d. = non-detectable
n.a. = not analyzed

Table D.5: Concentration (in ppm) of trace elements as determined by INAA for sized fractions of $< 2 \mu\text{m}$, $2 - 5 \mu\text{m}$ and $5 - 20 \mu\text{m}$.

SAMPLE NUMBER	As	Co	Cr	Cs	Hf	Sb	Sc	Ta	Th	U	W
$< 2 \mu\text{m}$											
60-02	81	5.3	43	0.9	22	0.6	9.0	0.3	158	145	4.3
60-03	105	10.1	121	0.9	46	1.4	13.7	0.7	425	349	6.2
60-05	302	28	87	1.1	21	1.6	11.1	0.2	270	69	2.7
60-06	417	27	59	1.1	26	7.6	7.8	0.3	156	628	4.7
60-07	234	45	54	1.0	14	2.2	5.9	0.8	78	233	16
60-08	197	11	45	1.0	32	1.5	9.2	0.3	231	176	7.8
60-09	147	22	54	1.2	43	4.1	10.4	0.3	401	278	4.9
119-30	37	5.2	52	1.1	23	0.6	8.5	0.9	244	147	6.2
$2 - 5 \mu\text{m}$											
60-05	145	18.7	61	1.1	8.9	0.6	7.0	0.6	157	29	2.8
60-06	107	17	40	0.9	11	2.3	5.1	0.3	51	247	2.3
60-07	82	26	33	0.8	7.7	1.2	4.6	0.3	38	126	15
60-08	80	5.7	51	0.7	11	0.7	5.5	0.6	77	50	8.3
60-09	68	17	59	0.9	18	1.9	6.4	1.9	175	109	7.0
$5 - 20 \mu\text{m}$											
60-05	75	28	55	0.9	23	1.4	8.5	2.8	113	43	7.6
60-06	101	75	33	1.1	19	3.6	6.3	1.1	79	333	6.9
60-07	68	79	25	1.0	18	2.4	6.0	1.5	68	219	7.6
60-08	51	8.5	55	0.7	20	1.1	6.9	2.9	63	59	7.7
60-09	53	31	62	1.0	29	3.2	7.2	6.8	151	136	4.5

TABLE D-6: Concentration (in ppm) of rare earth elements as determined by INAA.

SAMPLE NO.	La	Ce	Nd	Sm	Eu	Tb	Ho	Tm	Yb	Lu
49-13	156	304	105	19.4	2.1	1.9	7.8	0.6	5.8	0.9
49-14	186	350	116	21.4	2.8	2.4	11.9	0.9	6.8	1.1
49-15	170	342	112	24.8	3.4	2.8	20.4	0.3	4.3	0.7
53-11	91	164	56	9.2	1.2	0.7	4.2	1.2	3.2	0.4
53-12	96	173	57	9.6	1.2	0.7	2.0	0.3	2.3	0.3
53-13	44	89	23.5	3.5	0.4	0.7	5.9	1.4	1.9	0.4
53-14	100	210	70	13.1	1.5	1.8	11.0	1.9	4.4	0.8
60-01	23.1	48.3	13.0	2.8	0.4	0.5	1.6	0.9	1.5	0.2
60-02	189	387	118	22.3	3.2	5.3	14.7	3.6	13.7	2.3
60-03	279	565	178	33.9	4.4	6.6	13.1	3.9	15.7	2.5
60-04	186	398	132	24.4	3.3	4.8	26.0	3.2	9.8	1.4
60-05	209	406	125	22.4	3.0	6.2	14.5	1.8	15.2	2.6
60-06	173	346	114	19.3	3.2	5.0	28.6	3.3	12.8	1.9
60-07	118	244	93	14.0	2.6	3.1	39.0	2.3	7.6	1.4
60-08	140	284	96	15.3	2.1	4.8	15.6	3.4	12.5	2.4
60-09	205	404	114	19.9	2.3	4.6	15.1	3.0	12.7	2.0
60-11	137	180	28.5	2.7	0.5	1.1	12.8	1.4	4.1	0.9
60-12	225	426	135	25.4	3.1	5.6	25.8	2.0	18.1	3.8
60-13	12.2	21.6	6.4	1.0	0.2	0.1	2.4	0.6	0.4	0.1
60-14	45.6	52.4	69.1	22.6	3.2	2.3	7.2	0.4	2.6	0.5
60-15	76.2	80.7	9.3	0.5	0.5	0.5	6.6	0.2	1.6	0.3
103-03	244	461	171	30.6	4.2	8.4	18.7	4.6	21.0	3.3
103-04	44.1	83.4	29.1	4.2	0.6	0.5	3.9	1.1	1.4	0.2
103-05	73.9	137	43.6	6.3	0.9	1.1	5.6	1.3	2.5	0.5
113-04	211	402	127	23.2	3.1	6.3	16.3	2.4	16.7	2.5
113-05	147	299	94.8	15.0	2.4	4.1	22.2	2.6	10.1	1.8
119-30	203	407	108	22.2	2.6	5.4	24.6	2.7	16.3	2.8
119-31	121	259	80.1	15.9	2.2	4.7	11.7	2.8	11.5	1.9
119-32	125	223	86.5	18.4	2.4	6.8	15.6	3.1	15.4	2.4
119-33	212	395	114	24.2	3.5	1.7	19.2	1.8	5.5	0.9
126-01	171	282	93.1	17.9	2.9	3.5	10.4	1.4	10.7	1.6
126-03	175	277	89.9	13.8	2.1	1.3	3.9	0.6	5.2	0.9
137-10	169	318	115	25.5	2.6	1.5	11.3	0.4	3.8	0.7
137-11	128	233	80.8	14.3	1.6	0.6	5.4	0.2	2.7	0.4
139-17	42.8	77.3	25.6	4.8	0.6	1.2	2.8	0.7	4.4	0.7

Table D.7 Concentration (in ppm) of rare earth elements as determined by INAA for sized fractions of < 2 μm , 2 - 5 μm and 5 - 20 μm .

SAMPLE NUMBER	La	Ce	Nd	Sm	Eu	Tb	Tm	Yb	Lu
< 2 μm									
60-02	428	898	269	48	5.7	3.5	2.9	5.4	0.7
60-03	544	1082	338	60	6.8	4.9	4.4	9.9	1.6
60-05	468	943	285	39	4.1	2.7	3.6	5.4	0.7
60-06	379	773	244	28	4.3	2.9	3.0	5.3	0.8
60-07	214	437	139	18	2.7	1.6	2.2	2.8	0.4
60-08	466	932	299	40	4.0	2.4	3.4	6.5	1.0
60-09	503	950	263	34	3.9	5.0	4.8	12	2.0
119-30	234	424	120	23	2.5	2.1	2.6	4.1	0.7
2 - 5 μm									
60-05	245	493	151	23	2.5	1.6	3.0	3.0	0.3
60-06	102	212	71	9.3	1.7	1.5	2.4	3.0	0.3
60-07	72	145	47	7.6	1.4	0.9	4.1	1.8	0.2
60-08	183	363	121	16	1.7	1.2	2.3	2.6	0.4
60-09	221	409	112	16	1.8	2.2	2.9	5.0	0.8
5 - 20 μm									
60-05	107	214	69	13	1.9	3.8	3.5	8.9	1.3
60-06	88	227	108	18	3.3	4.2	3.3	7.6	1.1
60-07	46	123	67	13	2.4	3.4	3.0	7.3	1.1
60-08	107	211	69	12	1.6	3.3	2.8	8.5	1.2
60-09	104	198	58	12	1.7	3.9	3.2	9.8	1.6

APPENDIX E

PARTIAL AND SEQUENTIAL EXTRACTION PROCEDURES

E.1 APPLICATION OF PARTIAL EXTRACTIONS TO URANIUM

Many investigations have examined the leachability of U by single extractant solutions. For example, leaching of U by strong acids (e.g., 1 M HNO_3) can be used to estimate the amount of soluble U present (Stalay and Samsoni, 1973). Van der Weijden et al. (1985a) used this approach to estimate U present in groundwaters through the natural process of weathering of granitoid rocks. Bailey et al. (1983) used an NH_4 -oxalate solution to leach U and Th from rocks of the Ilimaussaq intrusion, Greenland, to estimate the amount of leachable or "loose" U and Th present. Torma et al. (1985) used a sodium carbonate-bicarbonate leach to extract U and other radionuclides from low-grade U ore, in an attempt to produce environmentally safe tailings. Haque (1982) tested the efficiency of an aqueous-chlorine leach to remove U and Ra from Canadian U ores. The leach was effective, producing tailings that contained from 15 to 20 pCi $^{226}\text{Ra g}^{-1}$. Olade and Goodfellow (1979) used H_2O_2 - Na_2CO_3 to leach U and Th from stream sediments near the Tombstone Batholith in central Yukon. Their results suggested that U in stream sediments is readily leachable and likely occurs as mechanically-dispersed uraninite and hydromorphically-transported U precipitated on clays and organics.

E.2 PRELIMINARY EXPERIMENTS

E.2.1 Introduction

Sequential selective extractions were made to provide familiarity with established methods (see Chao, 1984), determine inherent technical problems and to assess selectivity for U. The procedure followed at Atomic Energy of Canada Limited (Walton and McLeod, 1984; Walton et al., 1984; Keizer, 1985) examined the relationship between various sorbed radionuclides and natural minerals. The sequence of reagents was designed to attack metals associated with: (1) exchangeable sites, (2) amorphous Fe-oxides, (3) crystalline Fe-oxides, and (4) residual silicates. The procedure was used on twenty-five powdered, bulk samples.

E.2.2 Method of Analysis

The following procedure (Walton and McLeod, 1984; Walton et al., 1984; Keizer, 1985) was used in the initial experiments.

(1) Exchangeable sites

20 mL 1.0 M MgCl_2 (pH 7, 1 hour at room temperature)

(2) Amorphous Fe-bound

20 mL 0.25 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ in 0.25 M HCl (30 minutes at 50 °C)

(3) Crystalline Fe-bound

20 mL 0.3 M Na-citrate, 2.5 mL 1.0 M NaHCO_3 ,
0.5 g $\text{Na}_2\text{S}_2\text{O}_4$ (15 minutes at 80 °C; 3 additions
of 0.5 g of Na-dithionite)

(4) Residual Silicates

13.3 mL conc. HNO_3 , 6.7 mL conc. HF (24 hours at
80 °C)

Step 3 was repeated until the red colour was removed from
the Fe-rich samples.

In the first experiment about 0.1 g of twenty-six
bulk, powdered samples were leached. Four samples were run
in triplicate and twenty-two in duplicate. All extractant
solutions from two samples (53-14 and 60-16) were analyzed
for U by high-performance liquid chromatography (HPLC). The
remaining samples were analyzed for U by inductively-coupled
plasma emission (ICP), except the residual extractant solu-
tions which were analyzed by the neutron activation analysis
(NAA)-delayed neutron counting (DNC) technique.

In a second experiment, sample weights were increased
ten-fold. The solutions, after extraction were evaporated
to dryness and brought up to volume (15 to 20 mL) with 4.0 M
 HNO_3 , suitable for fluorimetric analysis. Ward and Bondar
(1979) reported that U fluorescence can be suppressed by the
quenching effects of Fe and Mn. Samples containing chloride

react with the platinum dishes, so the fluorimetric technique was abandoned and some solutions sent out for NAA-DNC analysis.

E.2.3 Results

Results from the first experiment are shown in Table E.1. The HPLC results indicate that the U appears to be associated with an amorphous iron-bound or $\text{NH}_2\text{OH}\cdot\text{HCl}$ extractable phase. All solution extracts analyzed by high performance liquid chromatography (HPLC), were supposedly free of matrix interferences but generally less than 50% of the total U was determined (last column of Table E.1).

The remaining samples from the initial experiment were analyzed for U by ICP. Only two samples, out of 26, yielded measurable amounts of U. The ICP data show that for an Fe-rich sample (60-10, 11.3% Fe_2O_3), about one-half the extractable U was associated with the crystalline Fe phase extracted by DCB. However, relative to the total U content measured for the dry powdered sample, the ICP method yielded a higher value of total extractable U for 60-10 (2742 vs 2040 ppm), indicating matrix problems. For sample 60-16, however, slightly more than half of the total U determined by ICP was extractable and most U resided in the residual silicates ($\text{HF} + \text{HNO}_3$ -extractable) contrary to the HPLC results.

Table E.1: Concentration of U (ppm) extractable from powdered, bulk samples using a sequential extraction procedure (see Appendix E). Uranium determined by three analytical techniques: high performance liquid chromatography (HPLC), inductively-coupled plasma-atomic emission spectroscopy (ICP) and neutron activation analysis (NAA) using the delayed neutron counting (DNC) method. Total extractable U is the summation of U measured in each extractant. The last column indicates amount of U extracted by this procedure compared to total U of dry, bulk powders.

SAMPLE NO.	MgCl ₂ -Ext U ppm	NH ₂ OH.HCl-Ext U ppm	DCB-Ext U ppm	HF+HNO ₃ -Ext U ppm	TOTAL Ext U ppm	Ext U Tot U
HPLC						
53-14	25	27	2	2	52	0.46
60-16	125	45300	58	151	45634	0.33
ICP						
60-10	n.d.	680	1345	717 ¹	2742	1.34
60-16	13	567	14000	66150 ¹	80730	0.59
NAA						
49-15	n.d.	44	10	83	137	0.42
53-14	2	24	6	15	47	0.41
60-12	n.d.	13	36	28	77	0.56
DH-12	398	73	34	679	1184	0.66

¹ HF+HNO₃ extractable solutions measured by NAA-DNC technique.

² CANMET U standard with reported value of 1770 ppm (Ingles et al., 1977).
n.d. = non-detectable

Results from the second set of experiments are also shown in Table E.1. Uranium is associated with the $\text{NH}_2\text{OH} \cdot \text{HCl}$ and $\text{HF} + \text{HNO}_3$ extractable phases for samples containing low amounts of iron (49-15 and 53-14; 1.4%). For Fe-rich sample 60-12 (17.0%), U is associated more strongly with DCB and $\text{HF} + \text{HNO}_3$ extractable phases. The total U extracted is about half of the total U. The CANMET U standard, DH-1, showed U associated with MgCl_2 - and $\text{HF} + \text{HNO}_3$ -extractable phases. However, only 66% of the total U was measured.

Analysis of U in the washings made between the different extracting solutions indicated an additional 18%, 14% and 6% total U for samples 49-15, 53-14 and 60-12 respectively. The total extractable U, however, is still well below the total amount of U present.

Uranium concentration measured in samples that were totally digested by the $\text{HF} + \text{HNO}_3$ procedure are given in Table E.2. Uranium was analyzed by NAA-DNC. Concentration on a dry weight basis is given in ppm and the percent difference with the total U content, as measured by DNC, is shown on the right. In all cases but two, the percent difference is enormous - indicating analytical problems. Data for samples digested by HF combined with HClO_4 , evaporated to dryness and brought up to volume in 4.0 M HNO_3 , are also shown in Table E.2. The percent difference between U

Table E.2: Concentration of U in a total digestion of powdered bulk samples. The percent difference between total digestible and total U is also given.

SAMPLE NO.	HF+HNO ₃ Extractable U		HF+HClO ₄ Extractable U		Total U ppm
	ppm	% difference	ppm	% difference	
49-13	213	+94			110
49-14	199	+31			152
49-15	468	+43	341	+4	327
53-11	85	+55			55
53-12	62	+72			36
53-14			125	+10	114
60-05	175	+500			29*
60-08	245	+48			166
60-10	2132	+5			2040
60-11	188	+57			120
60-12	231	+67	146	+6	138
60-13	77	+208			25
60-14	226	+61			140
60-15	209	+60			131
60-16	142520	+4			137000
103-03	197	+110			94
103-04	84	+62			52
103-05	156	+156			61
DH-1			1755	-2.5	1800

* if the INAA value for this sample is used (83.1 ppm), a difference of + 111% results.

extracted and the total U is less than 10%, values within acceptable analytical errors.

E.3 RELIABILITY OF URANIUM ANALYSES

Quantitative analysis for U is difficult and the results in these investigations indicate unreliability of U analysis by some techniques. Uranium concentrations determined by DNC and INAA methods are plotted in Figure E.1. Excluding the two apparently spurious data points, the correlation coefficient of 0.99 indicates excellent agreement among results from these two techniques. The ICP and HPLC results, reported in Table E.1 for the preliminary experiments, did not agree with one another nor agree with the data obtained using other methods. Matrix interferences related to the extractant solutions are the probable cause.

E.4 EVALUATION OF PARTIAL EXTRACTION METHODS

E.4.1 Introduction

In order to determine the most suitable sequential extraction procedure for the Cigar Lake samples, it was necessary to evaluate some partial extraction methods on a smaller suite of samples. Following is a brief literature review of available partial extraction methods commonly used in exploration and soil studies. For further details see

Figure E.1: The relationship between total U determined on dry powders by the neutron activation analysis-delayed neutron counting (DNC) technique and by instrumental neutron activation analysis (INAA). The line indicates a correlation coefficient of 1.0.

Chao (1984). Results from the methods that were tested are included as part of this discussion.

XRD analysis of materials, before and after each extraction, was used to monitor the effects of the reagents on the clay and other minerals. Analysis of some major cations in the extractant solutions also served to verify any decomposition of the minerals. Aluminum, Fe, K and Mg were analyzed using a Perkin-Elmer model 703 Atomic Absorption/Flame Emission Spectrophotometer. Standards and blanks were prepared in the various extractant solutions according to routine procedures (D. Omond, personal communication, 1988). Atomic absorption was used to analyze for Al, Fe and Mg and flame emission for K. Al was analyzed using a nitrous oxide-acetylene ($\text{N}_2\text{O}-\text{C}_2\text{H}_2$) burner and Fe, K and Mg using an air-acetylene ($\text{air}-\text{C}_2\text{H}_2$) burner. Cleaning of the burners was required every few hours because of the high Na and organic salt contents of some reagents. Recalibration and auto-zeroing of the standard curve was conducted at the beginning and middle of the sample runs to ensure analytical accuracy.

E.4.2 Exchangeable Sites

Exchangeable metals can be extracted by neutral salt solutions. Reagents commonly used include MgCl_2 (Tessier et al., 1982; Ticknor et al., 1984), NH_4 -acetate (Gatehouse et

al., 1977; Sondag, 1981), NH_4 -citrate (Robinson, 1982), Na-acetate (Tessier et al., 1979) and $\text{Ca}(\text{NO}_3)_2$ (Miller et al., 1986). Any of these reagents will also extract water-soluble metals. Exchangeable and water-soluble metals normally account for only a small proportion of the total metals (Chao, 1984). Tessier et al. (1979) reported that NH_4 -acetate may attack carbonates.

The partial extraction for U associated with exchangeable sites using 1 M MgCl_2 (see section above) was abandoned as U was undetectable. Instead, a NaOAc partial extraction was introduced to leach U associated with carbonates and less resistant phases (see below).

E.4.3 Carbonates

Carbonates (calcite, dolomite, magnesite and siderite) may hold trace metals by surface adsorption, coprecipitation or isomorphous exchange (Chao, 1984). Acetic acid (Filipek and Owen, 1978; Filipek and Theobald, 1981), Na-acetate-acetic acid (pH = 5.0) buffer solutions (Gatehouse et al., 1977; Tessier et al., 1979, 1982) and NH_4 -acetate (Sondag, 1981) are effective reagents in removing most carbonates. This extraction would also remove exchangeable, water-soluble and easily-acid soluble forms, if not previously extracted.

Ten samples were extracted to test the NaOAc-HOAc procedure. This extraction should remove exchangeable, carbonate-bound and readily acid-soluble U. XRD analysis of the materials before and after extraction indicated no detectable attack on silicate minerals or siderite. Table E.3 lists the amount of U that was removed. The fraction extracted ranged from 1.2 to 44.2% of the total U present.

E.4.4 Sulphides

Metals associated with primary and secondary sulphides can be leached using a H_2O_2 -ascorbic acid method (Lynch, 1971; Peachey and Allen, 1977), a KClO_3 -HCl in HNO_3 leach (Chao and Theobald, 1976) or aqua regia. In a comparative study, Olade and Fletcher (1974) showed that reagents were effective in extracting Cu from sulphides in the order KClO_3 -HCl > H_2O_2 -ascorbic acid > aqua regia. The KClO_3 -HCl method does not attack silicates; H_2O_2 will attack organic matter and Mn oxides.

To test the $\text{H}_2\text{O}_2/\text{Na}_2\text{CO}_3$ procedure, which should extract U bound in uraninite, organics and sulphides, eight samples were extracted. XRD analyses of the materials before and after extraction indicated no degradation of clay mineral structures. The amount of U removed ranged from 32.5 to 92.7% (Table E.3) of the total U present. Uraninite peaks were only observed on the XRD chart of sample 60-16.

Table E.3: Concentration of uranium (in ppm) and percent of total U extracted from bulk samples using NaOAc and Na₂CO₃ partial extraction techniques.

SAMPLE NUMBER	NaOAc-Extractable Uranium	
	U (ppm)	U % Extracted
44-10	16.0	44.2
44-21	848	1.2
60-13	8.8	35.2
60-14	21.8	15.6
60-15	14.2	10.8
60-16	2.03%	14.8
60-16	2.03%	14.8
103-05	16.0	26.2

	Na ₂ CO ₃ -Extractable Uranium	
	U (ppm)	U % Extracted
44-10	1780	92.7
44-21	1143	52.9
60-15	54.6	41.7
60-16	7.77%	56.7
60-16	7.36%	53.7
103-05	19.7	32.3

E.4.5 Iron Oxides

Iron oxides commonly occur in clays, soils and sediments, as surface coatings on other minerals or as fine, discrete colloidal particles in clusters or aggregates (Jenne, 1968). The Fe-oxides include goethite (α -FeOOH), hematite (α -Fe₂O₃), lepidocrocite (γ -FeOOH), maghemite (γ -Fe₂O₃), magnetite (Fe₃O₄) and amorphous ferrihydrite (Fe(OH)₃.nH₂O). Amorphous Fe-oxides, although more reactive chemically than crystalline Fe-oxides (Chao and Theobald, 1976), cannot be detected by physical methods such as XRD analyses. Thus, numerous partial extraction methods have been developed to distinguish the various inorganic, organic and amorphous forms of Fe-oxides. Removal of Fe-oxides occurs through dissolution under acid and/or reducing conditions, usually followed by complexation of the reduced iron. Many of the methods may also selectively remove Mn-, Al-, and Si-oxides.

Acid ammonium oxalate (AAO) solution (Tamm's reagent) dissolves amorphous Fe-oxides when used under dark conditions (Borggaard, 1988). AAO only slightly attacks silicates, hematite and goethite (McKeague and Day, 1966; Chao and Zhou, 1983; Sheldrick, 1984) but selectively dissolves magnetite (Rhoton et al., 1981; Sheldrick, 1984). This solution is commonly used in studies of soil genesis (McKeague and Day, 1966; Blume and Schwertmann, 1969;

McKeague et al., 1971; Wang et al., 1987) and has been applied in sequential extraction schemes for exploration studies (Hoffman and Fletcher, 1981; Sondag, 1981).

Acidified hydroxylamine hydrochloride (HAH) solution, a weak reducing agent, has been used to dissolve Mn-oxides and amorphous Fe-oxides from soils and sediments in exploration studies (Chao and Theobald, 1976; Chao and Zhou, 1983; Chao, 1984). Changes in concentration of the HAH solution, acidified by variable concentrations of acetic, nitric or hydrochloric acids, make the method selective for Mn-, amorphous Fe- or crystalline Fe-oxides (Chao and Theobald, 1976; Gatehouse et al., 1977; Bogle and Nichol, 1981; Filipek and Theobald, 1981).

Wang et al. (1987) evaluated the effectiveness of AAO and HAH as extractants for Al, Fe and Si from Spodosols in Québec, and showed that, in general, AAO extracted more Al and Fe from the soil than HAH. However, AAO was more effective in extracting pedogenic amorphous material and less effective for ground materials than HAH. HAH is recommended as an alternative to AAO for soils containing magnetite (Ross et al., 1985; Wang et al., 1987).

A third method employs a complexing agent, Tiron. Under alkaline conditions (pH = 10.5) Tiron was found to be selective for amorphous Fe-, Al-, and Si-oxides in soils (Biermans and Baert, 1977). Kodama and Hayashi (1985)

reported that small amounts of Fe were extractable by Tiron from goethite, hematite and magnetite.

Partial extraction methods used to dissolve crystalline Fe-oxides include HAH in acetic acid (Chester and Hughes, 1967; Bogle and Nichol, 1981), AAO under ultraviolet light (Sondag, 1981; Cardoso Fonseca and Martin, 1986; Miller et al., 1986), oxalic acid (Taylor and Schwertmann, 1974; Chao and Zhou, 1983), hydrazine chloride (Gatehouse et al., 1979; Robinson, 1984) and variations of the dithionite-citrate-bicarbonate (DCB) method (Mehra and Jackson, 1960; Jackson, 1979). The DCB method and its variants are commonly used in soil studies (McKeague and Day, 1966; Webber et al., 1974) and have been used in sequential extraction schemes for exploration studies (Rose and Suhr, 1971; Gupta and Chen, 1975; Chao and Theobald, 1976; Hoffman and Fletcher, 1979; Learned et al., 1981).

In the DCB method, Fe^{3+} is reduced to Fe^{2+} by adding Na-dithionite (also known as Na-hyposulphite) with Na-citrate as a chelating agent (Chao and Theobald, 1976; Jackson, 1979). Sodium bicarbonate is used as a buffer to maintain the pH at the optimum conditions of 7 - 8. Solubility of Fe^{3+} decreases above pH 9 and Fe-sulphide and/or sulphur can be precipitated when pH is < 7 (Mehra and Jackson, 1960; Borggaard, 1988). Extractability of Fe by this method is dependent upon grain size. Large crystals of goethite,

hematite and magnetite are only partly dissolved (McKeague et al., 1971). Slight but detectable attack of Fe-bearing silicates also occurs (McKeague and Day, 1966).

Results from the Fe-oxide extraction tests are presented in Table E.4 and Figures E.2 and E.3. Of the three amorphous Fe-oxide extractants, AAO, HAH and Tiron, HAH consistently extracted the lowest amount of Fe_2O_3 , both for single and for multiple extractions. XRD analyses of the residues indicated that after multiple extractions by HAH, sudoite was slightly attacked, probably due to the acidic nature ($\text{pH} = 2$) of this reagent. There was no evidence of minerals being attacked by Tiron. In parallel tests on post-glacial marine clays, Tiron was the most aggressive reagent, possibly attacking biotitic-illite (Torrance and Percival, 1988). AAO was similar in its reactivity to HAH for the intermediate-Fe sample, but was more aggressive in the Fe-rich bulk sample. The large amount of HAH-extractable Fe in the Fe-rich bulk sample is surprising, as a very sharp hematite peak is present in XRD results (see Table 1, Appendix B). The high extractability may be the result of grinding.

Crystalline and amorphous Fe-oxides are readily leached using the dithionite-citrate (DC) technique. For the moderate Fe-bearing sample, most Fe was dissolved after 3 extractions whereas the Fe-rich sample required 5 extractions

Table E-4: Fe₂O₃ (in percent) extractable from a moderate-Fe sample (50-02) and a high-Fe (103-05) sample using acid ammonium oxalate (AAO), hydroxylamine hydrochloride (HAH), Tiron and dithionite-citrate (DC) partial extraction techniques. Fe₂O₃ data reported for first extraction and cumulative after ten extractions. U (in ppm) analyzed for sample 57-02 only. Both bulk sample (-B) and a particle-sized fraction (-2 = < 2 μ m; -5 = 2-5 μ m) were used.

SAMPLE NO.	AAO		HAH		TIRON		DC	
	Fe ₂ O ₃	U	Fe ₂ O ₃	U	Fe ₂ O ₃	U	Fe ₂ O ₃	U
57-02-B								
1st Ext.	0.28	0.01	0.23	n.d.	0.20	n.d.	12.37	0.03
10th Ext.	0.46	0.05	0.42	n.d.	1.01	n.d.	13.23	n.a.
57-02-2								
1st Ext.	0.39	0.03	0.26	0.03	0.24	0.07	34.80	0.08
10th Ext.	0.90	0.15	0.66	0.03	0.72	n.a.	35.05	n.a.
103-05-B								
1st Ext.	14.31	n.a.	5.95	n.a.	5.82	n.a.	31.40	n.a.
10th Ext.	38.18	n.a.	30.24	n.a.	31.47	n.a.	43.69	n.a.
103-05-5								
1st Ext.	4.11	n.a.	1.63	n.a.	1.79	n.a.	50.5	n.a.
10th Ext.	4.94	n.a.	4.08	n.a.	5.98	n.a.	80.9	n.a.

n.d. = not detectable

n.a. = not analyzed

Figure E.2: Cumulative amount of Fe_2O_3 extracted from a moderate Fe -bearing sample (57-02; 9.68% Fe_2O_3) with 10 extractions by each of acid ammonium oxalate (AAO), hydroxylamine hydrochloride (HAH), Tiron and dithionite-citrate (DC).

Figure E.3: Cumulative amount of Fe_2O_3 extracted from a high Fe-bearing sample (103-05; 55% Fe_2O_3) with 10 extractions by each of acid ammonium oxalate (AAO), hydroxylamine hydrochloride (HAH), Tiron and dithionite-citrate (DC).

(Figure E.3). This information was important in developing the final extraction scheme, as it established the number of repetitions that would be needed to remove the Fe-oxides in most samples.

Uranium was undetectable in some samples, and where detectable, was present in concentrations of less than 0.5 ppm. Data for sample 57-02, containing both crystalline and amorphous Fe-oxides from the bulk and clay-size fraction, suggest that U is not associated with Fe-oxides. In Fe-rich samples, however, association of U with Fe-oxides is more evident. In a similar study on weathered ore assemblages from a U deposit in the Alligator Rivers Uranium Province, Northern Territory, Australia, U was reported to be highly associated with amorphous and crystalline Fe-oxides (Airey et al., 1983; Airey, 1986).

E.5 RECOMMENDATIONS

Recommendations from this part of the study mainly concern the analysis for U. Uranium concentrations in the leachates were generally below the detection limits using DNC. The leachates had to be evaporated, then brought up to a minimum volume with nitric acid before U determination. The method for treating leachates outlined in Zielinski et al. (1983) would appear to be the best for concentrating the U. In this method, a 5 mL aliquot of leachate is combined

with 3 mL of concentrated HNO_3 and 1 mL of U-carrier solution containing 1 μg U. This mixture is shaken with 5 mL Tri-n-butyl phosphate (TBP) to extract the U into the organic phase. The TBP extract is then processed for neutron activation analysis. The addition of the U-carrier solution eliminates detection problems and should improve reproducibility in the analysis of leachates with low U concentrations.

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