PARAGENESIS AND FLUID HISTORY OF THE KARKU UNCONFORMITY-URANIUM DEPOSIT, PASHA-LADOGA BASIN, WESTERN RUSSIA

by

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Abstract

The Karku unconformity-type uranium deposit is located in the Proterozoic Pasha-Ladoga Basin in western Russia. The deposit is located in basinal sandstones near a reverse fault that offsets the unconformable contact with underlying graphite-bearing biotite schist basement rocks. Meteoric water-sourced diagenetic fluids altered sandstones outside mineralized zones, producing clay assemblages of interstratified illite-smectite with minor dickite and Fe-rich chlorite, and fluid isotopic compositions of $\delta^{18}O = 3.3\%$ to $6.0\%$ and $\delta D = -55\%$ to $-44\%$ at $130^\circ C$. Altered sandstones within zones of mineralization include a clay mineral assemblage of Fe-rich chlorite with minor illite, and fluid isotopic compositions of $\delta^{18}O = 6.0\%$ to $12.7\%$ and $\delta D = -8\%$ to $-4\%$ at $210^\circ C$, caused by seawater-derived fluids related to ore formation. In addition, a Mg-chlorite occurring with uraninite in the mineralized lenses was identified. Dating of Karku uraninite using U/Pb isotope systematics from LA-MC-ICP-MS, LA-HR-ICP-MS, and SIMS gave upper-intercept ages of $1467 \pm 39$ Ma, $1459 \pm 74$ Ma, and $1302 \pm 150$ Ma respectively. The lower-intercept age of all methods was around $300$ Ma.

A formation model for the Karku uranium deposit is proposed based on the results of this study and incorporating previously published. Early, low-temperature diagenesis resulted in cementation of distal, basin-marginal sandstones by mixed-layer illite-smectite clays, preventing later, higher-temperature diagenetic alteration in this unit. Sandstones towards the centre of the basin allowed the circulation of higher-temperature basinal fluids that later flowed along the unconformity to the graphitic schist unit. A fault intersecting this unit facilitated the mixing of basement and basinal fluids, causing uraninite to precipitate at the unconformity.
Co-Authorship

The journal papers in this thesis were co-authored by Dr. T. Kurt Kyser and Dr. Don Chipley.
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Chapter 1

Introduction

Since the discovery of the first unconformity-type uranium deposits in Canada and Australia thirty years ago, they have come to constitute 33% of the world’s uranium resources (World Nuclear Association, 2010) and Canada’s mining of unconformity-type uranium alone accounted for 21% of global production in 2008 (OECD and IAEA, 2010). Because of the uniquely high grades and large reserves, they are one of the major exploration targets for uranium in the world today (World Nuclear Association, 2010).

The Athabasca Basin in Saskatchewan, Canada, and the Kombolgie Basin in the Northern Territory, Australia, have been studied extensively since their discovery and were used to define the genetic model for unconformity-type uranium as they host the only deposits of this type currently being mined (World Nuclear Association, 2010). The model has been refined through a number of investigations into alteration mineral assemblages, mineral chemistry, and fluid-rock interactions (e.g. Cloutier et al., 2011; Kyser and Cuney, 2009; Kyser, 2007; Alexandre et al., 2005; Polito et al., 2005). According to the Athabasca and Kombolgie model, this deposit type occurs in Paleoproterozoic sedimentary basins near or at the unconformity between basal sandstones and underlying Archean to Early Proterozoic crystalline basement rocks, or just below the unconformity in fractures and faults (Fig. 1-1). Sedimentary units hosting deposits in these basins generally consist of mature quartz arenites (Hoeve and Sibbald, 1978; Gustafson and Curtis, 1983) with characteristic diagenetic clay mineral assemblages of illite/sericite and minor dickite (Gustafson and Curtis, 1983; Polito et al., 2004; Beaufort et al., 2005) and, in the case of the Athabasca Basin, dravite, illite and kaolinite clay minerals (Hoeve and Sibbald, 1978; Wilson and Kyser, 1987; Kotzer and Kyser, 1995).
Figure 1-1. Unconformity-type uranium deposit formation model.

Paleoproterozoic quartz arenites unconformably overlie Archean crystalline basement rocks. Brines carrying U in solution circulate through the basin and interact with reducing basement fluids at faults, causing U to crystallize into uranium ore minerals. Faults related to mineralization are developed at the boundary between weak, graphite-bearing units and stronger rocks. Modified after Kotzer and Kyser (1995).
Sudoite occurs sporadically in sandstone close to the unconformity and in the basement rocks (Gustafson and Curtis, 1983; Kotzer and Kyser, 1995). Uranium-bearing, oxidizing diagenetic fluids circulating through the basin at temperatures in excess of 200ºC encounter chemically- and isotopically-distinct reducing fluids moving along faults and fractures from the basement, causing uranium to precipitate out of solution and form minerals such as uraninite and coffinite (e.g. Kotzer and Kyser, 1995; Alexandre et al., 2005; Beaufort et al., 2005; Polito et al., 2005; Cloutier et al., 2011). Several sources for the uranium have been suggested, including the regolith at the unconformity (Pagel, 1991), hydrothermally altered detrital minerals such as fluorapatite and zircon in the sedimentary rocks (Fayek and Kyser, 1997) and hydrothermally altered monazite (Hecht and Cuney, 2000) or garnet (Fayek and Kyser, 1997) in basement rocks. Paleoproterozoic basins of similar age and character have been the focus of recent investigation (Kyser and Cuney, 2009).

In 1989, the Karku uranium deposit was discovered in the 150km-wide Pasha-Ladoga Basin in northwestern Russia. Located just north of St. Petersburg on the northeastern shore of Lake Ladoga, Karku has been classified as an unconformity-type deposit (Velichkin et al., 2005) but differs from the Athabasca and Kombolgie basins in several key aspects. The Pasha-Ladoga basin is younger, having formed during the Mesoproterozoic after 1530 Ma at the earliest (Andreeva and Golovin, 2005; Amelin et al., 1997). The sedimentary rocks that host mineralization in the Karku area are immature, feldspathic, clay and lithic-rich sandstones and conglomerates with significant amounts of calcite in the cement, quite different from the mature arenites of the Athabasca (Ramaekers, 1981) and Kombolgie (Sweet et al., 1999; Polito et al., 2006) basins. Previous work on Karku focused mainly on the deposit in the context of the geology and geochemistry of the immediate surroundings (e.g. Lobaev et al., 2003; Shurilov et al., 2003; Velichkin et al., 2005; Andreeva and Golovin, 2005; Kuptsova et al., 2011). The second chapter of this thesis characterizes the fluids causing alteration and mineralization at Karku. The third chapter
presents a comparison of three different *in-situ* mass spectrometry techniques used to date the uranium ore at Karku. Together, these studies allow for the evaluation of results in the context of Pasha-Ladoga basin evolution and its implications for the unconformity uranium exploration model.
Chapter 2
Paragenesis and Fluid History of the Karku Unconformity-Uranium Deposit,
Pasha-Ladoga Basin, Western Russia

Co-authored by Kurt Kyser. Submitted to Economic Geology.

2.1 Introduction

In 1989, the Karku uranium deposit was discovered on the northeast shore of Lake Ladoga (Fig. 2-1) located near St. Petersburg, Russia. It is a small deposit, with 3,100t of measured uranium resources (Thomas, 2004), compared to 457,500t U proven resources at the McArthur River deposit, Athabasca basin (Cameco, 2011). Karku has been classified as unconformity-type (Velichkin et al., 2005) but differs from the traditional deposit model (Hoeve and Sibbald, 1978) in several key aspects. The age of the host Pasha-Ladoga Basin is Mesoproterozoic (Amelin et al., 1997; Kuptsova et al., 2011), whereas the Athabasca and Kombolgie basins formed in the Paleoproterozoic (Kyser et al., 2000; Rainbird et al., 2003; Polito et al., 2006). The sedimentary units in the area of Karku are lithic subarkose to arkose sandstones and conglomerates (Kuptsova et al., 2011), which contrasts with the quartz arenites hosting unconformity-uranium deposits in other basins (Ramaekers et al., 2007). Previous work on Karku focused mainly on the deposit in the context of the geology and geochemistry of the immediate surroundings (e.g. Lobaev et al., 2003; Shurilov et al., 2003; Velichkin et al., 2005; Andreeva and Golovin, 2005). This study characterizes the fluids causing alteration and mineralization at Karku, and to evaluate the results in the context of Pasha-Ladoga basin evolution.
Figure 2-1. Geological map of the Pasha-Ladoga Basin, located in the Bothnia-Ladoga rift zone. Modified after Velichkin et al., 2005.
2.2 Regional Geology

The Pasha-Ladoga Basin is located on the border between the southeast margin of the Archean Baltic Shield and the Palaeoproterozoic Fennoscandian crustal region (Bogdanova et al., 2008), all part of the East European Craton (Fig. 2-1). The small intracratonic rift basin sits in the Ladoga graben (Bogdanova, 1996) and is mostly covered by Lake Ladoga, lying underneath glacial cover where it extends past the lake margins.

The basement rocks (Fig. 2-2) consist of Archean granite-gneiss domes and troughs filled with Ladoga Supergroup metasedimentary and metavolcanic units dated at 2100-1880 Ma by U-Pb isotopes in various minerals (Matrenichev et al., 2006; Kotova et al., 2009). All lithologies were metamorphosed up to granulite facies (Kotova et al., 2009) and folded during the 1910-1820 Ma Svecofennian orogeny (Velichkin et al., 2005; Nironen, 1997). The Salmi rapakivi anorthosite-mangerite-charnockite-granite (AMCG) pluton lies at the northeast edge of the basin, intruded into basement rocks (Bogdanova, 1996). The pluton is dated at 1547-1530 Ma (U-Pb) by TIMS on zircon (Amelin et al., 1997). A sharp angular unconformity, gently dipping to the southwest and marked by regolith development from a few centimetres to 30m thick, overlies both the metamorphic and rapakivi granite basement rocks (Velichkin et al., 2005). The Ladoga graben was developed sometime after the emplacement of the Salmi pluton during a period of intracratonic rifting on the Baltic Shield (Bogdanova, 1996; Amelin et al., 1997).

The Pasha-Ladoga Group basin rocks (Fig. 2-2) consist of several unmetamorphosed volcano-sedimentary packages. The basal units are complicated by multiple faults and fractures, formed due to subsidence and post-depositional tectonic movement occurring with the Danopolitan orogeny ca. 1500-1460 Ma (Bogdanova et al., 2008). The Pasha-Ladoga Group is comprised of the basal Priozersk Formation with lower conglomerate to sandstone and upper flood basalt members, the Salmi Formation with lower sandstone and upper flood basalt members, and the sandstone and siltstone Pasha Formation
which is intruded by the Valaam gabbro-monzonite sill (Kuptsova et al., 2011). The Salmi flood basalt has been dated at 1499 ± 68 Ma by Sm-Nd isochron (Andreeva and Golovin, 2005) and the Valaam sill was dated at 1457 ± 3 Ma (U-Pb) on baddeleyite by thermal ionization mass spectrometry (TIMS; Ramo et al., 2005). The area is covered by a thick succession of unconsolidated Quaternary glacial sediments, ranging from 24 to 85m thick (Velichkin et al., 2005).

2.3 Deposit Geology

The Karku uranium deposit is located over a block in the Pasha-Ladoga Basin called the Central Horst, uplifted by 200-300m from surrounding basement rocks (Velichkin et al., 2005). Only the Priozersk Formation and lower part of the Salmi Formation are present over the Central Horst (Velichkin et al., 2005; Kuptsova et al., 2011). The basement directly under Karku (Fig. 2-3) consists of Archean granite-gneiss domes with graphitic biotite schists occupying the surrounding synformal troughs. The western margin of the Salmi rapakivi granite pluton occurs on the deposit property (Velichkin et al., 2005; Kotova et al., 2009). The basal Priozersk Formation preserved at the Karku deposit is characterized by arkosic conglomerates and sandstones with matrix-supported quartz pebbles and poorly sorted, angular clasts characteristic of basement uplift close to the source (Kuptsova et al., 2011). The sandstone matrix is clay-rich, with chlorite, mixed-layer and swelling clays forming the bulk of the sample matrix. There is localized kaolinite reported towards the unconformity (Andreeva and Golovin, 2005). Three uranium ore zones occur around the margin of a granite-gneiss dome, above the unconformable contact with graphitic schist and particularly above areas highly enriched in graphite and sulphides. High-grade ore zones ranging from 0.3% up to 19% U occur within larger low- to medium-grade ore zones in the sandstone directly at the unconformity, with some mineralization up to 20m above and 10m into the basement along faults. Mineralization is associated with intense fracturing, more than what is normally present along the unconformity (Velichkin et al., 2005).
Figure 2-2. Generalized stratigraphic section of the Pasha-Ladoga Group in the vicinity of the Karku uranium deposit.

Modified from Kuptsova et al., 2011. Isotopic dates are reported in Ramo et al., 2005, Andreeva and Golovin, 2005, and Amelin et al., 1997.
Figure 2-3. Map of basement lithologies at Zone Three, Karku deposit.

Extent of alteration and low to high grade ore in Zone Three at the Karku deposit, including the location of drill hole #627 and measured and inferred fault structures. Other drill holes are in this area but their exact locations are unavailable. Modified after Velichkin et al., 2005 and Thomas, 2004.
Matrix clays have been identified as illite-kaolinite-smectite (Lobaev et al., 2003) and illite-smectite (Velichkin et al., 2005) mixed-layer minerals. Widespread Fe-rich chloritization along the unconformity (Lobaev et al., 2003; Velichkin et al., 2005; Andreeva and Golovin, 2005) is accompanied by carbonates, pyrite, and fluorite (Velichkin et al., 2005; Shurilov et al., 2003). Several generations of uraninite have been identified, with the earliest dated at 1405 ± 76 Ma (U-Pb) by secondary ion mass spectrometry (SIMS) (Shurilov et al., 2006).

2.4 Methods

A total of thirty-seven barren samples from four drill holes (Fig. 2-4) sampled by David Thomas of Cameco Corp. in 2004 and three thin sections from mineralized sandstone provided by Andre Khudoley from St. Petersburg State University were examined in detail in this study. Drill holes #770, #871 and #C1001 are from within the Karku deposit property. Drill hole #627 and the three mineralized thin sections are located within a high-grade ore zone (Fig. 2-3). This drill hole intersects uranium ore at the unconformity, none of which was available for sampling.

Clays were initially identified in situ with a portable infrared mineral analyzer (PIMA II) to aid in choosing a representative subset of samples for further investigation. Clay fractions were prepared from nine barren sandstone samples by crushing, centrifuging to size fractions of >5µm, 2-5µm and <2µm, and air drying. The <2µm size fractions were analyzed as oriented, air-dried, unaltered mounts on glass slides and subjected to progressive heating and glycolation for more exact determination of interstratified clay mineralogy using movement of characteristic peaks (USGS, 2001). X-ray diffraction was done with a PANalytical X’Pert x-ray diffractometer with a cobalt tube and the HighScore Plus identification software.
Figure 2-4. Logs of drill holes sampled at the Karku deposit showing location of samples used in this study.
Sections are modified after Thomas, 2004.
Oxygen isotope analysis used the BrF₅ method (Clayton and Mayeda, 1963) and a Finnigan MAT 252 isotope ratio mass spectrometer (IRMS) on the <2µm clay size fraction. Hydrogen isotope analysis was done with a ThermoFinnigan thermal-conversion elemental analyzer (TC/EA) and a ThermoFinnigan Delta⁺PLUS XP IRMS. All values are reported in ‰ notation relative to V-SMOW. Precision was ± 3‰ for δD and ± 0.2‰ for δ¹⁸O. The oxygen and hydrogen isotope illite-water fractionation factor equations used are those of Sheppard and Gilg (1996) and Capuano (1992), and chlorite-water fractionation factor equations are those of Cole and Ripley (1998) and Taylor (1974).

Chemical compositions of chlorite and uraninite from one barren and three mineralized thin sections were determined using a Camebax MBX electron microprobe at Carleton University, operating at 15kV accelerating potential and 20nA beam current. Backscattered photomicrographs were taken using the electron microprobe and an Amray scanning electron microscope at Queen’s University.

Uranium-lead isotopic dating was done on three mineralized thin sections with laser ablation multi-collector inductively-coupled plasma mass spectrometers (LA-MC-ICP-MS). A NewWave Research UP-213 laser ablation system operating at 60% power and 3Hz with a 100µm spot size was used in conjunction with a Thermo Neptune MC-ICP-MS. An in-house davidite standard was used and analyses were corrected for ²⁰⁴Hg interferences and for ²⁰⁴Pb where applicable (Chipley et al., 2007). Isoplot 3.2 (Ludwig, 2003) was used to generate all U-Pb concordia diagrams. Errors (1σ) in ²⁰⁷Pb/²³⁵U and ²⁰⁶Pb/²³⁸U are calculated from RSD on each analysis. Error (1σ) in ²⁰⁷Pb/²⁰⁶Pb is calculated and ranges from ± 4 Ma to ± 15 Ma. All error correlations in the ratios were assumed to be 0.9.

Leachable Pb was determined on 23 <2µm clay size fractions using the method of Holk et al. (2003). A 0.5g sample was digested in a polyurethane tube in 5mL ²¹⁵In-spiked 2% HNO₃ with trace HF, placed in a sonic bath for 120 minutes, and centrifuged. One gram of digested solution was diluted with 50g of 2% HNO₃ and measured with a Thermo Element XR high resolution (HR) ICP-MS using in-house
standards with low and high uranium content. Lead isotopic ratios were determined using signal intensities in counts per second, with 1% uncertainty on repeat analyses. Blank subtractions and $^{204}\text{Hg}$ interference and mass bias corrections were applied.

### 2.5 Paragenesis

All thin sections were examined with transmitted- and reflected-light microscopy. The modal mineralogy and cross-cutting relationships were documented and photographed. Infrared spectroscopy, x-ray diffraction and electron microprobe analysis were done on selected sedimentary rock samples to determine the mineralogy and composition of various phases. Petrographic observations and crystal chemistry studies were compiled into a paragenetic relationship between post-deposition minerals and features in the basement and sandstones (Fig. 2-5).

The overlying amygdaloidal flood basalts in the ore zone (hole #627) have a subophitic texture, composed of about 50% plagioclase laths with varying amounts of glassy material, olivine, pyroxene, and some sulphide minerals. The voids are filled with calcite and chlorite. Chlorite and hematite occur in fractures but do not pervasively alter the unit.

The basal sedimentary rocks of the Priozersk Formation, located above the unconformity, are arkosic clay-rich sandstones and conglomerates. Original clasts include 20-50% quartz ($Q^6$), 10-35% potassium feldspar as microcline and orthoclase, detrital zircons and muscovite grains, and highly corroded lithic fragments including plagioclase and pyroxene clasts. All sandstone samples have 5-30% fine-grained clay minerals (I/S, I) and chlorite ($C^1$) occurring in the matrix. Detrital quartz ($Q^6$) shows hematite rims (H) and euhedral quartz cement ($Q^1$) on original grain boundaries, with corrosion of the euhedral cement by matrix clays (I/S, I) (Fig. 2-6A). Calcite ($Ca^1$) replaces matrix clays (I/S, I), particularly in the sandstones near the basalt contacts, but shows corrosion by matrix clays in the middle of the sandstone units (Fig. 2-6B), suggesting that the two were forming around the same time and
overprinting each other. A dark green to black chlorite (C₂) occurs at the unconformity and corrodes matrix clays and calcite (Ca₁) (Fig. 2-6C). Large orthoclase clasts show cracking and alteration inside the grains as well as on the edges, and plagioclase and pyroxene clasts are mostly replaced by matrix clays (I) and chlorite (C₁). Microcline (Ksp) grains appear to be almost unaltered with only slightly corroded grain edges, although they are also cracked (Fig. 2-6D).

The Archean basement samples are comprised of biotite-graphite schists containing 30-45% plagioclase, 5-15% graphite, 10-40% biotite, small amounts of quartz, amphibole and sulphides, and about 30% chlorite alteration. One basement sample is rapakivi granite comprised of 60% alkali feldspar with untwinned plagioclase rims and 30% quartz, with biotite partially altered to chlorite as the remainder.

Ore samples contain quartz (Q₀) and potassium feldspar clasts that are replaced by a dark greenish-brown chlorite (C₃) with small pyrite inclusions (Fig. 2-6E). Uraninite (U) occurs as complete replacement of matrix minerals, and is corroding the chlorite crusts (C₃), indicating that the chlorite formed prior to the uraninite. Reflected light microscopy reveals considerable inhomogeneity within the uraninite, including many small euhedral cubes of galena (G) scattered throughout representing post-ore alteration that mobilized radiogenic lead and added sulphur to the system, also responsible for the pyrite grains in the chlorite. Post-ore calcite veinlets (Ca₂) cut through the uraninite (Fig. 2-6F).
Figure 2-5. Paragenesis of Karku deposit-area basin lithologies.
Temperatures are inferred from illite/smectite temperature window and chlorite geothermometry. Age calculated from U-Pb dating on uraninite.
Figure 2-6. Photomicrographs of sedimentary rocks from the Karku area

(A) Hematite (H) rim inside quartz overgrowth rim (Q') corroded by illite (I) and chlorite (C'), plane polarized light, section KAR-9 hole #627. (B) Illite/smectite (I/S) corroding calcite (Ca') in matrix, cross-polarized light, section KAR-35 hole #1001. (C) Dark green chlorite (C') overprinting calcite matrix (Ca') and quartz (Q') and lithic clasts near unconformity, cross-polarized light, KAR-14 hole #627. (D) Large microcline grain (Ksp) with calcite infilling cracks (Ca') and chlorite (C') in the matrix, plane polarized light, KAR-16 hole #627. (E) Brown chlorite (C') replacing clasts in the ore zone with uraninite (U), plane polarized light, KAR-#1. (F) Uraninite (U) with galena (G) inclusions, corroding brown chlorite (C') that is replacing detrital clasts, and is cut by a calcite veinlet in upper left (Ca'), reflected light, KAR #3.
2.6 Mineral Chemistry

Karku alteration zones in the Priozersk Formation inferred from mineral chemistry and petrography are shown in Fig. 2-7. Infrared spectroscopy was used for identification of the clay matrix minerals. Generally, in samples from zones B and C, the matrix contains 10-85% smectite and illite with rare to common dickite (10-55%). Samples from zone A on Fig. 2-7 consist of 40-100% chlorite and 10-65% muscovite. On the basis of petrographic examination and infrared spectroscopy results, four samples from zones A and B and five samples from zone C were selected for clay separation and x-ray diffraction (Fig. 2-8). In zone C, mixed-layer illite-smectite (I/S) dominates while more illite (I) is present in zone B, along with ubiquitous minor quartz and chlorite (C1). Any kaolinite present is in small amounts, as the intensities of the peaks are low and often obscured by chlorite. In zone A, clays in the <2µm size fraction consist of 100% chlorite (C2).

Fluid inclusion studies conducted by Velichkin et al. (2005) reported that calcite cement (Ca1) had homogenization temperatures of 130-190ºC, consistent with relatively low-temperature early diagenesis, whereas calcite syngenetic with uraninites (not seen in the samples from this study) had homogenization temperatures of 170-240ºC, indicating that the fluids causing mineralization were heated to in excess of 200ºC.

The chlorite crystal chemistry of KAR-15, an unmineralized sample located in zone A, and KAR #1, a mineralized sample, were determined by electron microprobe. The Fe-rich chlorite (C2) present in zone A is chemically distinctly different from the ore-related Mg-rich chlorite (C3) replacing detrital clasts in the mineralized samples, confirming their distinct paragenesis (Fig. 2-9). Two chlorite geothermometers, Kranidiotis and MacLean (1987) and Zang and Fyfe (1995), were considered with the chlorite chemistry results due to their normalization of Al(IV) content with Fe, a significant component of both chlorite minerals. For the Fe-rich chlorite (C2), the composition falls within the calibration ranges of
both thermometers and the temperature of the fluid was between 190ºC and 240ºC (Table 2-1), similar to fluid inclusion temperatures from the syn-ore calcite. This confirms the Fe-rich chlorite (C²) is the result of hotter fluids flowing along the unconformity before mineralization. However, the composition of the Mg-rich chlorite (C³) falls outside of the calibration ranges for each of the three methods, and meaningful temperatures cannot be obtained from this sample using chlorite geothermometry.

A method described by Arkai (1991) for measuring formation temperatures of illite using crystallinity, or full width at half maximum of the 001 peak of an x-ray diffraction pattern, was used on the <2µm size fraction of samples containing illite. This technique gives temperatures of 190-300ºC, a level of heating at which smectite layers in the interstratified clays should have been completely destroyed (Freed and Peacor, 1989). Because the crystallinity method is calibrated for pure illite with no interstratification, temperatures calculated with this geothermometer was used as an estimate only.
Figure 2-7. Schematic diagram of alteration zones around uranium mineralization.

Zone A: Fe-rich chlorite (C²); Zone B: Illite (I), chlorite (C¹); Zone C: Illite/smectite (I/S), detrital clays; black pod, mineralization.

Figure 2-8. XRD patterns of KAR-23, hole #770 after heating at 400°C, 550°C and glycolation.

Interpretation of peaks was done using the USGS clay identification flowchart (USGS, 2001). This sample contains mixed-layer illite-smectite and minor kaolinite-group and chlorite minerals.
Figure 2-9. Chlorite composition from electron microprobe data.

Pre-ore Fe-rich chlorite ($C^2$) and syn-ore Mg-rich ($C^3$) chlorite plotted with typical compositions of chamosite and clinochlore by Deer et al. (1992) and sudoite by Lin and Bailey (1985). Dashed grey lines indicate composition field for chlorites associated with early alteration in the Athabasca Basin basement units (Alexandre et al., 2005) and the dashed black line indicates chlorite associated with peak diagenesis in the McArthur Basin sandstone units (Polito et al., 2006).
Table 2-1. Electron microprobe data and chlorite geothermometry temperatures.
Sample #1, or KAR #1, is mineralized and contains brown Mg-rich chlorite (C³). Sample #15, or KAR-15, is from Zone A and contains dark green to black Fe-rich chlorite (C³). Errors in calculated temperature are ± 25°C. <DL indicates value below detection limit.

<table>
<thead>
<tr>
<th>Sample</th>
<th>#1-1</th>
<th>#1-2</th>
<th>#1-3</th>
<th>#1-4</th>
<th>#1-5</th>
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<th>15-6</th>
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<tbody>
<tr>
<td><strong>Oxide Wt %</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>SiO₂</td>
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<td>38.12</td>
<td>35.31</td>
<td>35.98</td>
<td>35.74</td>
<td>35.68</td>
<td>37.06</td>
<td>21.87</td>
<td>24.43</td>
<td>25.00</td>
<td>24.32</td>
<td>22.07</td>
<td>25.10</td>
<td>25.83</td>
<td>26.18</td>
</tr>
<tr>
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<td>0.12</td>
<td>0.04</td>
<td>0.19</td>
<td>0.12</td>
<td>0.14</td>
<td>0.20</td>
<td>0.02</td>
<td>0.01</td>
<td>0.02</td>
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<td>0.26</td>
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<td>0.99</td>
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<td>Cr₂O₃</td>
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<td>0.02</td>
<td>0.01</td>
<td>&lt;DL</td>
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<td>0.05</td>
<td>0.03</td>
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<td>0.48</td>
<td>0.32</td>
<td>0.33</td>
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<td>MnO</td>
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<td>1.83</td>
<td>1.58</td>
<td>1.86</td>
<td>1.71</td>
<td>1.83</td>
<td>0.25</td>
<td>0.47</td>
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<td>0.25</td>
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<td>MgO</td>
<td>18.16</td>
<td>21.90</td>
<td>19.18</td>
<td>18.86</td>
<td>18.73</td>
<td>18.97</td>
<td>18.63</td>
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<td>3.40</td>
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<td>&lt;DL</td>
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<td>&lt;DL</td>
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<td>0.14</td>
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<td>0.08</td>
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<td>0.05</td>
<td>0.03</td>
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<td>87.40</td>
<td>83.73</td>
<td>84.57</td>
<td>83.25</td>
<td>83.37</td>
<td>85.36</td>
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<td>83.18</td>
<td>82.33</td>
<td>74.68</td>
<td>87.73</td>
<td>86.89</td>
<td>87.92</td>
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<td>Zang &amp; Fyfe 1995</td>
<td>223</td>
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<tr>
<td>Kranidiotis &amp; MacLean 1987</td>
<td>193</td>
<td>188</td>
<td>190</td>
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</table>
2.7 Stable Isotopes

Oxygen and hydrogen isotopic compositions relative to V-SMOW of matrix clays were measured from the <2µm size fraction of four samples in zones A and B and five samples in zone C. The δ¹⁸O values range from 8.9‰ to 9.1‰ in zone A and 11.2‰ to 15.5‰ in zone B, whereas δD ranges from -58‰ to -46‰ through both zones. In zone C, δ²⁰⁶O ranges from 14.6‰ to 16.9‰ and δD ranges from -72‰ to -62‰ (Table 2-2). A formation temperature of 210ºC was used to calculate isotopic compositions of the fluids in equilibrium with chlorite in zones A and B, taken from the average of fluid inclusion homogenization temperatures in syn-ore calcite (not seen in this study; Velichkin et al., 2005) and from calculated formation temperatures of chlorite obtained in this study. A temperature of 130ºC was used in Zone C, based on the smectite-illite transition identified in Pollastro (1993), and the lower bound of fluid inclusion homogenization temperatures from calcite syn-genetic with matrix cement (Ca¹) reported in Velichkin et al. (2005). These calculated δ¹⁸O values of the fluids range from 6.0‰ to 12.7‰ and δD from -8‰ to 4‰ in zones A and B, and δ²⁰⁶O ranges from 3.3‰ to 6.0‰ and δD from -55‰ to -44‰ in zone C (Table 2-2; Fig. 2-10).

The O and H isotopic compositions of fluids calculated from pre-ore illite-smectite and syn-ore chlorite indicate that both fluids evolved from pore waters in the original sediment, but these pore waters were distinct in time, temperature and origin. The ~3‰ increase in δ¹⁸O and ~40‰ increase in δD from pre-ore to syn-ore fluids reflect the distinct origins of these fluids, with the values for pre-ore fluids consistent with basinal fluids derived from low-latitude meteoric waters and the values for the syn-ore fluids consistent with modified seawater. Both have become more ¹⁸O-rich as a result of interaction with rocks over time, which would have minimal effect on the δD values if molar water-rock ratios were <0.1. (Kyser and Kerrich, 1991).
Table 2-2. Oxygen and hydrogen stable isotopic compositions for clay minerals and formation fluids.

From selected samples with pre-ore illite/smectite (Zone C) and syn-ore chlorite (Zones A and B.) Temperature used for pre-ore fluid isotopic composition is 130°C and for syn-ore fluid composition, 210°C. Precision is ±0.2‰ for δ\(^{18}\)O and ±3‰ for δD.

<table>
<thead>
<tr>
<th>Sample</th>
<th>δ(^{18})O min. %o</th>
<th>δD min. %o</th>
<th>δ(^{18})O fluid %o</th>
<th>δD fluid %o</th>
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<td>Pre-ore Illite/Smectite</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KAR-21 (C)</td>
<td>14.2</td>
<td>-72</td>
<td>3.3</td>
<td>-55</td>
</tr>
<tr>
<td>KAR-22 (C)</td>
<td>16.8</td>
<td>-62</td>
<td>5.8</td>
<td>-44</td>
</tr>
<tr>
<td>KAR-23 (C)</td>
<td>16.9</td>
<td>-64</td>
<td>6.0</td>
<td>-46</td>
</tr>
<tr>
<td>KAR-26 (C)</td>
<td>16.8</td>
<td>-62</td>
<td>5.9</td>
<td>-44</td>
</tr>
<tr>
<td>KAR-35 (C)</td>
<td>14.6</td>
<td>-64</td>
<td>3.7</td>
<td>-46</td>
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<tr>
<td>Syn-ore Chlorite</td>
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</tr>
<tr>
<td>KAR-8 (B)</td>
<td>15.5</td>
<td>-50</td>
<td>12.7</td>
<td>0</td>
</tr>
<tr>
<td>KAR-9 (B)</td>
<td>11.2</td>
<td>-57</td>
<td>8.4</td>
<td>-7</td>
</tr>
<tr>
<td>KAR-10 (A)</td>
<td>8.9</td>
<td>-58</td>
<td>6.0</td>
<td>-8</td>
</tr>
<tr>
<td>KAR-11 (A)</td>
<td>9.1</td>
<td>-46</td>
<td>6.2</td>
<td>4</td>
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</table>
Isotopic composition of fluids are calculated from syn-ore chlorite at 210°C and pre-ore illite-smectite at 130°C. Syn-ore temperature from chlorite geothermometry summarized in Table 2-1 and calcite fluid inclusion homogenization temperatures (Velichkin et al., 2005). Pre-ore temperature from illite-smectite crystallinity and transition temperature (Pollastro, 1993) and calcite cement fluid inclusion temperatures (Velichkin et al., 2005). Composition windows of basin and basement fluids during peak diagenesis in unconformity-uranium deposits in Canada and Australia are from Kotzer and Kyser (1995). Values of SMOW and the global meteoric water line (GMWL) are plotted for reference.
2.8 Uranium and lead isotopes

2.8.1 U-Pb dating

Uranium and lead isotope ratios collected from uraninite grains LA-MC-ICP-MS (Table 2-3) indicate an upper intercept U-Pb age of 1467±39 Ma (Fig. 2-11a). The lower intercept on the concordia diagram is 230±150 Ma, which in conjunction with the high MSWD (Mean Standard Weighted Deviation) and points above concordia indicate variable resetting as a result of redistribution and loss of Pb from the uraninite. This is supported by the presence of galena within uraninite grains, as well as variable backscatter intensities of the uraninite under the scanning electron microscope. The Pb-Pb ages calculated from the isotope ratios reveal a number of resetting events, which can be related to specific tectonic events (Fig. 2-11b) and indicate a maximum age of 1505±20 Ma (Table 2-3), similar to the U-Pb age deduced from the upper intercept.

Chemical compositions of the uraninites (Table 2-4) from the electron microprobe range from 791 Ma to 1960 Ma using the equation in Powers (1985) and assuming a closed system with no gain or loss of U or Pb. Average error in the chemical ages is ±12 Ma. No correlation exists between cation content and calculated chemical age (Fig. 2.12), indicating that uraninite alteration to pseudosecondary minerals does not vary with age (Alexandre and Kyser, 2005). Discordance in the U-Pb isotopic ages in conjunction with the visible evidence that Pb has been redistributed in the uraninite and lack of correlation between crystal chemistry and age indicate the calculated chemical ages have no temporal significance (Kotzer and Kyser, 1993).
Figure 2-11. Uranium-lead isotopic dating results.

(a) U-Pb concordia diagram of Karku uraninite by in situ LA-MC-ICP-MS. Ellipses are proportional to 1σ error. Pb-Pb ages for each spot are indicated beside ellipses. (b) $^{207}\text{Pb}-^{206}\text{Pb}$ age histogram for mineralized sections from Karku, with key regional events and their ages identified (Bogdanova et al., 2008). Additional Pb data is included and reported in Chapter 3.
Table 2-3. Pb/U isotope ratios and Pb/Pb isotope ages for Karku uraninite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{207}$Pb/$^{235}$U Abs. Error (1σ)</th>
<th>$^{206}$Pb/$^{238}$U Abs. Error (1σ)</th>
<th>$^{207}$Pb/$^{206}$Pb Ages</th>
<th>Abs. Error (1σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1-1</td>
<td>2.479 0.042</td>
<td>0.215 0.004</td>
<td>1302 ±6 Ma</td>
<td>±6 Ma</td>
</tr>
<tr>
<td>#1-2</td>
<td>2.810 0.046</td>
<td>0.229 0.003</td>
<td>1389 ±11 Ma</td>
<td>±11 Ma</td>
</tr>
<tr>
<td>#1-3</td>
<td>1.159 0.224</td>
<td>0.090 0.018</td>
<td>1505 ±9 Ma</td>
<td>±9 Ma</td>
</tr>
<tr>
<td>#1-4</td>
<td>3.537 0.076</td>
<td>0.267 0.004</td>
<td>1484 ±13 Ma</td>
<td>±13 Ma</td>
</tr>
<tr>
<td>#1-5</td>
<td>2.993 0.047</td>
<td>0.230 0.003</td>
<td>1499 ±9 Ma</td>
<td>±9 Ma</td>
</tr>
<tr>
<td>#2-1</td>
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<td>0.123 0.007</td>
<td>1465 ±11 Ma</td>
<td>±11 Ma</td>
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<tr>
<td>#2-2</td>
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<td>0.326 0.005</td>
<td>1443 ±13 Ma</td>
<td>±13 Ma</td>
</tr>
<tr>
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<td>0.276 0.002</td>
<td>1444 ±5 Ma</td>
<td>±5 Ma</td>
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<td>0.209 0.005</td>
<td>1439 ±7 Ma</td>
<td>±7 Ma</td>
</tr>
<tr>
<td>#3-2</td>
<td>1.202 0.073</td>
<td>0.113 0.005</td>
<td>1253 ±15 Ma</td>
<td>±15 Ma</td>
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<tr>
<td>#3-3</td>
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<td>0.272 0.005</td>
<td>1328 ±9 Ma</td>
<td>±9 Ma</td>
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<tr>
<td>#3-4</td>
<td>3.223 0.069</td>
<td>0.258 0.005</td>
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<td>±5 Ma</td>
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<tr>
<td>#3-5</td>
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<td>0.081 0.005</td>
<td>1384 ±5 Ma</td>
<td>±5 Ma</td>
</tr>
<tr>
<td>#3-6</td>
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<td>1426 ±6 Ma</td>
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<td>0.266 0.008</td>
<td>1379 ±9 Ma</td>
<td>±9 Ma</td>
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<tr>
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<tr>
<td>#3-9</td>
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<td>1433 ±5 Ma</td>
<td>±5 Ma</td>
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<td>#3-10</td>
<td>3.667 0.093</td>
<td>0.281 0.007</td>
<td>1492 ±8 Ma</td>
<td>±8 Ma</td>
</tr>
</tbody>
</table>
Table 2-4. Uraninite chemical data from electron microprobe and calculated U-Pb chemical ages.

<DL indicates value below detection limit. Error in uraninite chemical age is ± 12 Ma.

| Sample | #2-1 | #2-2 | #2-3 | #2-4 | #2-5 | #3-1 | #3-2 | #3-3 | #3-4 | #3-5 | #3-6 | #3-7 | #3-8 | #3-9 | #3-10 | #3-11 | #3-12 |
|--------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| Wt. %  |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| Si     | 0.73 | 0.86 | 3.00 | 3.24 | 1.23 | 3.77 | 0.81 | 7.86 | 1.02 | 3.69 | 3.15 | 3.61 | 3.52 | 3.33 | 0.93  | 0.74  | 0.87  |
| U      | 66.82| 67.96| 58.19| 61.06| 69.23| 61.99| 64.12| 50.73| 64.46| 59.85| 61.66| 61.51| 65.41| 58.27| 66.25 | 65.53 | 66.92 |
| Pb     | 10.81| 10.60| 16.00| 10.58| 8.01 | 7.93 | 13.25| 9.34 | 11.97| 11.21| 9.18 | 10.15| 7.26 | 15.17| 11.69 | 12.43 | 11.29 |
| Fe     | 0.59 | 0.66 | 0.32 | 0.28 | 0.39 | 0.12 | 0.47 | 0.10 | 0.46 | 0.10 | 0.12 | 0.23 | 0.20 | 0.19 | 0.41  | 0.65  | 0.63  |
| Al     | 0.04 | 0.07 | 0.21 | 0.27 | 0.09 | 0.38 | 0.05 | 0.22 | 0.10 | 0.41 | 0.34 | 0.39 | 0.27 | 0.19 | 0.07  | 0.04  | 0.06  |
| S      | <DL  | 0.04 | 1.77 | 0.98 | 0.10 | 0.39 | 0.35 | 0.72 | 0.14 | 0.64 | 0.37 | 0.67 | 0.52 | 1.38 | 0.24  | 0.08  | 0.06  |
| Ca     | 2.73 | 2.28 | 1.38 | 1.41 | 2.66 | 1.67 | 3.13 | 2.17 | 2.95 | 1.65 | 1.88 | 1.25 | 1.21 | 1.32 | 2.77  | 2.64  | 2.62  |
| Total  | 94.49| 95.44| 98.05| 93.69| 95.05| 91.77| 95.70| 90.57| 94.40| 93.55| 91.62| 93.68| 93.88| 96.66| 95.78 | 95.10 | 95.53 |
| Chemical Age | 1153 | 1111 | 1960 | 1235 | 824  | 912  | 1472 | 1312 | 1323 | 1334 | 1060 | 1176 | 791  | 1855 | 1257  | 1352  | 1202  |
Figure 2-12. Relationship between calculated chemical ages of uraninite and cation content.
2.8.2 Pb isotopes

Core samples from Karku, including basement and basin rocks, were leached with 2% HNO₃ and measured with HR-ICP-MS (Holk et al., 2003) to detect radiogenic lead dispersed from a uranium deposit by late-stage fluid circulation. Samples with $^{206}$Pb/$^{204}$Pb values greater than 30 have a relatively high proportion of radiogenic lead, given the average crustal value of ca. 19. Of the 23 samples analysed (Table 2-5), 18 have ratios within error of the average crustal ratio. In hole #627, which contains mineralization, two sandstone samples (KAR-12, KAR-15) and one basement sample (KAR-17), all within 5m of mineralization, have $^{206}$Pb/$^{204}$Pb ratios above 100. Two samples 24m apart from hole #770 (KAR-20, KAR-24) have radiogenic ratios of 197 and 45.

2.9 Discussion

A formation model for the Karku deposit can be constructed on the basis of the data collected in this study in combination with published results (Fig. 2-13). The basal sandstone unit of the Priozersk Formation (<1530Ma, Amelin et al., 1997) at Karku represents the distal edge of an alluvial fan. Sediment comprised of detrital clasts and pore-filling mud developed early swelling clays during low-temperature diagenesis (<100°C), forming a diagenetic paleo-aquitard. The fluid had isotopically light δD values, consistent with low-latitude meteoric water. In deeper portions of the basin, pore fluids derived from seawater as seen in the near-0‰ values of δD continued to interact with the basin fill during burial. Only 80m of basal sedimentary rock is preserved in the Karku area, but it is up to 320m thick in drill holes elsewhere in the basin (Kheraskova et al., 2006). These fluids circulated through the deeper parts of the basal paleo-aquifer, leaching U into solution and evolving through interaction with basin and basement rocks. During peak diagenesis, these fluids flowed along the unconformity due to a shift in hydraulic gradient caused by the 1500-1460 Ma Danopolonian orogeny (Bogdanova et al., 2008).
Table 2-5. Lead isotope data for drill core samples from 2% HNO₃ leach.

Alteration zone location is indicated in brackets beside sample number. (Bs) indicates flood basalt and (Ar) is Archean basement. Asterisks * indicate highly radiogenic isotope ratios.

<table>
<thead>
<tr>
<th>Sample</th>
<th>206Pb/204Pb RSD %</th>
<th>207Pb/206Pb RSD %</th>
<th>208Pb/206Pb RSD %</th>
<th>207Pb/204Pb RSD %</th>
<th>208Pb/204Pb RSD %</th>
</tr>
</thead>
<tbody>
<tr>
<td>KAR2 (Bs)</td>
<td>18.90 2.66</td>
<td>0.81 2.43</td>
<td>2.04 2.09</td>
<td>15.37 2.86</td>
<td>38.62 2.12</td>
</tr>
<tr>
<td>KAR4 (C)</td>
<td>27.24 3.66</td>
<td>0.58 2.61</td>
<td>1.71 2.22</td>
<td>15.84 3.64</td>
<td>46.42 2.91</td>
</tr>
<tr>
<td>KAR5 (C)</td>
<td>24.53 5.65</td>
<td>0.64 3.20</td>
<td>1.86 3.12</td>
<td>15.58 5.10</td>
<td>45.67 5.19</td>
</tr>
<tr>
<td>KAR6 (C)</td>
<td>25.67 4.74</td>
<td>0.60 1.50</td>
<td>1.87 1.90</td>
<td>15.39 5.04</td>
<td>48.04 5.17</td>
</tr>
<tr>
<td>KAR7 (C)</td>
<td>24.27 3.28</td>
<td>0.64 1.63</td>
<td>1.66 1.68</td>
<td>15.64 3.33</td>
<td>40.24 3.33</td>
</tr>
<tr>
<td>KAR12 (A)*</td>
<td>132.92 2.42</td>
<td>0.14 1.19</td>
<td>0.34 1.19</td>
<td>18.51 2.82</td>
<td>45.47 2.96</td>
</tr>
<tr>
<td>KAR14 (A)</td>
<td>26.56 1.00</td>
<td>0.60 0.69</td>
<td>1.45 0.77</td>
<td>15.81 1.16</td>
<td>38.49 1.14</td>
</tr>
<tr>
<td>KAR15 (A)*</td>
<td>122.06 1.03</td>
<td>0.15 0.72</td>
<td>0.32 0.92</td>
<td>18.83 1.00</td>
<td>39.26 1.16</td>
</tr>
<tr>
<td>KAR17 (Ar)*</td>
<td>233.80 1.34</td>
<td>0.10 0.73</td>
<td>0.16 1.03</td>
<td>23.98 1.47</td>
<td>38.44 1.74</td>
</tr>
<tr>
<td>KAR18 (Ar)</td>
<td>20.34 1.00</td>
<td>0.78 0.91</td>
<td>1.81 1.08</td>
<td>15.84 1.15</td>
<td>36.81 1.15</td>
</tr>
<tr>
<td>KAR19 (Ar)</td>
<td>21.45 1.19</td>
<td>0.73 1.05</td>
<td>1.79 1.24</td>
<td>15.76 1.45</td>
<td>38.38 1.60</td>
</tr>
<tr>
<td>KAR20 (C)*</td>
<td>197.65 1.65</td>
<td>0.14 1.16</td>
<td>0.20 1.18</td>
<td>26.98 1.82</td>
<td>38.95 1.96</td>
</tr>
<tr>
<td>KAR24 (A)*</td>
<td>45.54 1.63</td>
<td>0.37 1.08</td>
<td>1.34 1.17</td>
<td>17.02 1.45</td>
<td>61.24 1.52</td>
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<tr>
<td>KAR25 (Ar)</td>
<td>17.36 0.92</td>
<td>0.91 1.16</td>
<td>2.10 1.27</td>
<td>15.77 1.25</td>
<td>36.55 1.59</td>
</tr>
<tr>
<td>KAR27 (C)</td>
<td>19.93 3.79</td>
<td>0.76 1.94</td>
<td>2.16 2.08</td>
<td>15.05 3.44</td>
<td>43.07 3.18</td>
</tr>
<tr>
<td>KAR28 (B)</td>
<td>21.96 5.56</td>
<td>0.71 2.13</td>
<td>2.03 2.46</td>
<td>15.54 5.82</td>
<td>44.54 5.68</td>
</tr>
<tr>
<td>KAR29 (B)</td>
<td>18.50 4.15</td>
<td>0.83 12.37</td>
<td>2.16 4.20</td>
<td>15.39 13.34</td>
<td>39.97 5.47</td>
</tr>
<tr>
<td>KAR30 (B)</td>
<td>16.38 1.33</td>
<td>0.92 1.14</td>
<td>2.19 1.14</td>
<td>15.02 1.40</td>
<td>35.86 1.38</td>
</tr>
<tr>
<td>KAR31 (B)</td>
<td>19.48 4.15</td>
<td>0.79 2.37</td>
<td>2.04 5.30</td>
<td>15.47 3.71</td>
<td>39.75 5.02</td>
</tr>
<tr>
<td>KAR33 (B)</td>
<td>17.25 1.34</td>
<td>0.87 0.91</td>
<td>2.10 1.24</td>
<td>15.05 1.33</td>
<td>36.24 1.67</td>
</tr>
<tr>
<td>KAR36 (C)</td>
<td>22.62 2.85</td>
<td>0.68 1.30</td>
<td>2.06 1.59</td>
<td>15.43 3.22</td>
<td>46.48 2.44</td>
</tr>
<tr>
<td>KAR38 (B)</td>
<td>18.56 1.36</td>
<td>0.83 0.97</td>
<td>2.10 1.22</td>
<td>15.41 1.45</td>
<td>38.96 1.78</td>
</tr>
<tr>
<td>KAR39 (Ar)</td>
<td>20.53 1.56</td>
<td>0.74 0.92</td>
<td>2.39 1.23</td>
<td>15.24 1.54</td>
<td>49.02 1.60</td>
</tr>
</tbody>
</table>
Figure 2-13. Formation model for the Karku deposit.

Fluids sourced from depth in the basin were forced along the unconformity until they met structures developed over graphite-rich basement units and precipitated uraninite without appreciably altering the early-cemented units at the edge of the alluvial fan.
When these fluids encountered the paleo-aquitard unit preserved at Karku, the flow was forced into structures near the unconformity, some of which were developed as the result of preferential fracturing and movement in weak graphite-rich units on the margin of a granitic gneiss dome. The cemented nature of the paleo-aquitard prevented any infiltration of fluid and high-T (>200°C) destruction of swelling clays. Interaction of the U-bearing basin fluids with reduced basement fluids flowing through structures on the weak graphitic units caused precipitation of uranium ore at 1467±39 Ma.

The evolution of the fluids causing the uranium mineralization is enigmatic. Assuming a geothermal gradient of 40°C/km and a mineralizing temperature of 220°C, the fluids would have been sourced from ca. 5 km depth. However, highly elevated (>50°C/km) palaeogeothermal gradients have been documented under continental rifts (e.g. Berg et al., 1989). In general, rifting and magmatism were widespread in the Baltic Shield around 1500 Ma due to plate margin reorganization within Columbia (Lubnina et al., 2010) and magmatic activity leading to the emplacement of the Salmi pluton and several generations of flood basalts at ca. 1550-1450 Ma (Amelin et al., 1997; Andreeva and Golovin, 2005; Ramo et al., 2005) were ongoing at Karku.

Late post-peak diagenesis resetting events shown by recurrent $^{207}\text{Pb}/^{206}\text{Pb}$ dates (Fig. 2-11b) also reflect major regional geological events in the region, such as magmatism related to rifting and extension from 1400-1200 Ma and the Sveconorwegian orogeny around 1150 Ma (Bogdanova et al., 2008). The lower-intercept on the concordia diagram (Fig. 2-11a) gives a date of around 250 Ma, which we interpret as representing reactivation of old fault structures caused by far-field effects of the Caledonian orogeny (Shurilov et al., 2003). Resetting events can be similarly related to tectonic processes in the Athabasca and Kombolgie basins (e.g. Polito et al., 2005; Alexandre et al., 2009). Radiogenic lead was prevented from large-scale migration out of the deposit due to early cementation of wall rocks, instead remaining mostly within the ore as galena. Some movement of radiogenic lead did occur during resetting events, but
this was confined to fractures, as seen by the sporadic positive results for radiogenic lead across four drill holes.

In comparison with other unconformity-type uranium deposits in Canada and Australia, Karku exhibits many similarities as well as significant differences. In all of the uranium-bearing basins, mineralization occurs through focusing of basinal brines into structures with reducing material and precipitation of high-grade uranium ore minerals near the unconformity. Temperatures in the Karku ore zone recorded by clay minerals and fluid inclusions, as well as the oxygen and hydrogen isotopic composition of the circulating fluids, are similar to the deposits of the Athabasca and Kombolgie basins. The major difference is the lack of wide-scale circulation of fluids in the units proximal to the deposit. The immature, clayey nature of the Priozersk Formation rocks acted as an effective paleo-aquitard, isolating it from fluid movement during diagenesis. Instead, arenitic sandstones deeper in the basin allowed circulation and leaching of uranium from detrital minerals, and mineralizing fluids were forced along the unconformity to the edge of the basin where the Karku deposit formed. In addition, the $\delta^D$ and $\delta^{18}O$ values of diagenetic (pre-ore) fluids at Karku are similar to early diagenetic fluids in the Kombolgie and Athabasca basins, but the ore-forming fluids at Karku are isotopically distinct because they reflect evolved marine waters that have experienced much lower water/rock ratios during their evolution. This may be caused by the different paleolatitudes of the basins within the Arctica/Nena continents and thus a different point of origin along the meteoric water line (MWL), similar to the evolution of brines off the MWL in the Gulf Coast Basin pore waters as compared to the Western Canada Basin (Taylor, 1974).

2.10 Conclusions

Karku has expanded the unconformity-uranium model to include Mesoproterozoic basins, but the mineralogical and apparent geochemical differences from the Athabasca and Kombolgie type model serve to illustrate the need for holistic basin analysis when exploring for uranium or other base metals in
sedimentary basins. The Karku deposit was found through prospecting, and the basin would have ranked low on a list for potential of unconformity-uranium deposits based on a few samples from the sandstones. Hydrologic pathways to basement structures that allow fluids to infiltrate through the unconformity are the major control on location of mineralization in the unconformity-uranium model, in addition to the nature of circulating fluids and whether they have leached enough uranium to make an economic deposit.
2.11 References


Chapter 3

Comparison of In-situ Mass Spectrometry U-Pb Dating Techniques


3.1 Introduction

In-situ chemical and isotopic analysis of geological materials offer distinct advantages over sample digestion techniques, such as avoiding difficulty with acid digestion of resistive minerals and the low-level contamination issue inherent to fluxes used in total fusion methods. The development of laser ablation as a sample introduction system to the inductively coupled plasma mass spectrometer (LA-ICP-MS) in the 1980s (Gray, 1985) allowed several improvements over previous in-situ techniques, such as secondary ionization mass spectrometry (SIMS). These improvements include significantly faster analysis and lower cost overhead; however, reduced precision is a drawback of the method. The application of laser ablation to U-Pb geochronology was put forth in the early 1990s (e.g., Fryer et al., 1993). This technique is now widely used for measuring U-Th-Pb isotopes in a variety of minerals, including zircons (Jackson et al., 2004), uranium ore minerals (Chipley et al., 2007) and carbonates (Hoffmann et al., 2009; Eggins et al., 2005). SIMS and LA-ICP-MS results have been compared using U-Pb dating of zircons (Kosler et al., 2002), but have not previously been compared for uraninite dating. This study compares three in-situ methods of U-Pb isotopic analysis of uraninite: SIMS, high-resolution ICP-MS (HR-ICP-MS, also called the sector field ICP-MS) coupled with laser ablation, and multi-collector high resolution ICP-MS (MC-ICP-MS) coupled with laser ablation. Uraninite from the Karku unconformity-type uranium deposit in western Russia, with a reported age of 1405 ± 76 Ma by SIMS (Shurilov et al., 2003), was used to compare these in-situ techniques.
3.2 Methods

Uranium-Pb isotopic dating was done on three mineralized thin sections: KAR #1, KAR #2, and KAR #3 from the Karku unconformity-related deposit in Russia (Velichkin et al., 2005; Kuptsova et al., 2011). Ore mineral identification and backscattered electron microphotography was done using the Camebax MBX electron microprobe at Carleton University, operating at 15kV accelerating potential and 20nA beam current.

An Nd:YAG NewWave Research UP-213 laser ablation system operating at 60% power and 3Hz with a 100µm spot size was coupled to a Thermo Neptune multi-collector ICP-MS at the Queen’s Facility for Isotope Research (QFIR). An Nd:YAG NewWave Research LUV-213 laser ablation system operating at 50% power and 2Hz with a 50 µm spot size was used with a Thermo Element high-resolution ICP-MS at QFIR. The larger spot size used for the MC-ICP-MS relative to the HR-ICP-MS analyses reflects the difference in sensitivity between these two instruments. An in-house davidite standard was used for reference on both instruments (Chipley et al., 2007). Laser ablation ICP-MS analyses were corrected for $^{204}$Hg interferences and for common lead Pb using $^{204}$Pb where applicable. A Cameca IMS 7f SIMS at the University of Manitoba was used with 10nA and 2nA beam currents, only on KAR #3. Pb/U ratios obtained from the SIMS were corrected using a mass discrimination factor determined from an in-house uraninite standard (Fayek et al., 2002). Isoplot 3.2 (Ludwig, 2003) was used to generate all U-Pb concordia diagrams. Errors (1σ) in $^{207}$Pb/$^{235}$U and $^{206}$Pb/$^{238}$U analysed on the MC-ICP-MS are calculated from RSD on each analysis. Error (1σ) in $^{207}$Pb/$^{206}$Pb is calculated and ranges from ± 4 Ma to ± 15 Ma. Errors (1σ) in $^{207}$Pb/$^{235}$U and $^{206}$Pb/$^{238}$U for the HR-ICP-MS are 3% and 1%, and 2% and 1% for the SIMS, respectively. Error (1σ) in $^{207}$Pb/$^{206}$Pb amounts to ± 20 Ma. All error correlations in the ratios were assumed to be 0.9.
3.3 Results

Data are summarized in Table 3-1. Upper intercept U-Pb concordia dates are: 1467 ± 39 Ma for LA-MC-ICP-MS (Fig. 3-1A); 1459 ± 74 Ma for LA-HR-ICP-MS (Fig. 3-1B); and 1302 ± 150 Ma for SIMS (Fig. 3-1C). $^{207}\text{Pb} / ^{206}\text{Pb}$ ages for all methods range from 1118 Ma to 1587 Ma. For comparison, Shurilov et al. (2003) report an upper-intercept age on the U-Pb concordia curve of 1405 ± 76 Ma using a Cameca IMS 3f SIMS for uraninite from the same mineralized zone at the Karku deposit. Ore mineralogy consists of variably-altered uraninite with small galena inclusions throughout (Fig. 3-2).

3.4 Discussion

3.4.1 Heterogeneity of uraninite at Karku

The upper intercepts on U-Pb concordia plots are interpreted to represent the age of formation of uraninite in each sample (Fig. 3-1). All data points falling above concordia represent gain of radiogenic Pb or loss of U, whereas points falling below concordia represent loss of Pb or gain of U from the uraninite. The lower intercept on concordia represents the age of the most recent intense fluid event to variably reset the uraninite.

A backscattered electron image of the mineralized samples (Fig. 3-2) indicates the highly heterogeneous nature of the uraninite grains and provides further evidence of the character of resetting events that affected the ore zone at Karku. Concordant ages, or those clustered around the upper-intercepts on the concordia curves, are represented by light grey, relatively pristine uraninite. Discordant ages or those falling along the line below concordia are represented by medium or darker grey uraninite where Pb has left the uraninite crystal structure and lighter ions such as Si, Fe, Ca and Mg have entered, thus lowering the mean atomic weight and causing it to appear darker than the surrounding uraninite.
Table 3-1: Summary of U-Pb isotope ratios and Pb-Pb ages from Karku uraninites.

<table>
<thead>
<tr>
<th></th>
<th>KAR #1</th>
<th>KAR #2</th>
<th>KAR #3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^{207}$Pb/$^{235}$U</td>
<td>$^{206}$Pb/$^{238}$U</td>
<td>Pb/Pb Age</td>
</tr>
<tr>
<td>MC-ICP-MS</td>
<td>2.479</td>
<td>0.215</td>
<td>1302</td>
</tr>
<tr>
<td></td>
<td>2.810</td>
<td>0.229</td>
<td>1389</td>
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<tr>
<td></td>
<td>1.159</td>
<td>0.090</td>
<td>1505</td>
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<tr>
<td></td>
<td>3.537</td>
<td>0.267</td>
<td>1484</td>
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<tr>
<td></td>
<td>2.993</td>
<td>0.230</td>
<td>1499</td>
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<tr>
<td>HR-ICP-MS</td>
<td>1.395</td>
<td>0.118</td>
<td>1118</td>
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<td></td>
<td>1.938</td>
<td>0.167</td>
<td>1132</td>
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<td></td>
<td>1.836</td>
<td>0.153</td>
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<td>SIMS</td>
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Figure 3-1: Uranium-lead isotopic dating results from Karku uraninites.

Concordia plots for results from (a) MC-ICP-MS; (b) HR-ICP-MS; (c) SIMS. Error ellipses are proportional to 1σ error magnitude. Numbers beside error ellipses are $^{207}\text{Pb}/^{206}\text{Pb}$ ages for each data point. (d) $^{207}\text{Pb}/^{206}\text{Pb}$ histogram for all data.
Figure 3-2: Backscattered SEM image of uraninite from Karku.

Mottled grey uraninite (U) in the matrix surrounding quartz (Q) indicates variable alteration, where darker areas (U') have lost lead and gained major cations. Euhedral galena cubes (G) of various sizes within the ore indicates that lead lost from uraninite did not move far from the source.
Some of the radiogenic Pb that has left the uraninite structure makes up the very bright, small, euhedral galena crystals dispersed throughout the uraninite grains. The amount of alteration varies considerably over a small scale as shown by the mottled appearance of the uraninite. The apparent Pb gain shown by the data points above concordia is accounted for by comparing the size of the laser ablation pits with the size of the galena crystals. If the laser beam samples uraninite and galena simultaneously, the Pb/U ratios will be much higher so that Pb appears to have been added to the system and ages plot above concordia. Under these circumstances, Pb-Pb dates can still reflect the true age of the radiogenic Pb in the uraninite and the galena.

3.4.2 Laser ablation and high-resolution ICP-MS

The MC-ICP-MS is an excellent high-precision, low abundance analytical method for isotopic ratios. However, a larger spot sampling size is required for the MC-ICP-MS (Fig. 3-3a) because of its lower sensitivity relative to the HR-ICP-MS (Arevalo et al., 2010). A larger sampling area will not be able to detect the heterogeneity of the uraninite as reset uraninite and galena are more likely to be sampled simultaneously, resulting in more consistent ages, albeit with a higher mean square of weighted deviates (MSWD). Thus, fewer individual analyses are required to date the uraninite. The smaller spot size used with the more sensitive HR-ICP-MS results in a wider range of discordant ages and a lower MSWD, but the upper intercept age is still within error of the MC-ICP-MS results. However, care must be taken to ensure enough individual spots have been measured to eliminate random sampling bias.

3.4.3 SIMS

The SIMS measured only discordant ages, with a very high MSWD compared to the ICP-MS measurements. The sampling spot size on the SIMS is smaller than laser ablation with ICP-MS, at around 20µm (Fig 3-3b) and the depth sampled is significantly less. Sampling bias due to uraninite heterogeneity
is pronounced in the SIMS results, but very fine-scale changes may be detected with the SIMS that cannot
with laser ablation, such as diffusion of Pb towards the edges of uraninite grains. The large MSWD from
SIMS must be taken into account when attempting to date the formation age of a uranium deposit because
it may be difficult to find a concordant age when targeting uraninite that has experienced loss of Pb,
thereby requiring a large number of individual analyses to establish a reliable upper intercept age. Pb-Pb
ages can qualify U-Pb dating from the SIMS, as shown by the range of Pb-Pb ages older than the upper
intercept on the SIMS concordia.

Figure 3-3. Spot sizes of each in-situ technique.
(a) MC-ICP-MS (larger red circle) and HR-ICP-MS (smaller red circle) spot sizes on thin section in
reflected light microscopy; (b) red arrow pointing to SEM image of SIMS spots.
3.5 Conclusions

Fluid resetting events of variable intensity can redistribute, add, or remove U or Pb from uranium ore minerals and complicate their dating. Sampling spot size required for in-situ analysis is dictated by the sensitivity of the mass spectrometer, which will in turn control the accuracy and precision of the results. In general, SIMS is most useful for very fine-scale analysis, but one grain must be analyzed many times to obtain a meaningful date and Pb-Pb ages should be taken into account when determining an earliest age for the mineralization.

The large spot size used with the MC-ICP-MS can more easily include a wider spectrum of the heterogeneity within a mineral grain. HR-ICP-MS with laser ablation provides a balance between high sensitivity and manageable errors in results, but enough individual analyses must be carried out to mitigate against sampling bias. An understanding of the intra-grain heterogeneity of U and Pb content in uranium ore minerals is crucial to the interpretation of U-Pb dates obtained from these techniques.
3.6 References


Chapter 4

Summary

Through the application of holistic basin analysis and systematic investigation of barren, altered and ore zone paragenesis, it is possible to identify the key characteristics of a basin that allow and promote the formation of mineral deposits and to separate these characteristics from the background noise of tectonics and time. The Karku deposit challenged the accepted formation model for unconformity-style uranium deposits when it was discovered, but it can be shown that the key ways in which Karku differs from the model may be explained with mineral chemistry, sedimentology and structural geology. The key features required for an unconformity-style uranium deposit are: a) a sedimentary basin that was buried or otherwise heated with pore fluids in some portion of it available to circulate for a long period of time; b) a source of uranium in the basin or the basement rocks for the fluids to scavenge; c) a tectonic regime active enough to stimulate circulation of pore fluids and creation of structures in the basin and basement rocks that are pre-, syn- and post-mineralization; and d) a redox boundary to cause precipitation of uraninite, such as reduced basement-derived fluids or a lithological unit to act as a reductant. Such conditions are restricted to the unique configuration and timing of tectonic activity, and lack of land plants to allow braided fluvial systems in the Paleo- and early Mesoproterozoic (Kyser, 2007). Using these generalized terms, the Pasha-Ladoga Basin fits the model and the unusual location of Karku in a paleo-aquitard can be explained in the greater context of the basin and the tectonic processes that affected it. In the future, as the average grade of new mineral deposit discoveries decrease and their depths from surface increase, careful consideration of the entire system contributing to their formation must be examined with a cross-disciplinary focus.
References


