GEOCHEMISTRY AND MINERALOGY OF THE ALTERATION HALO ASSOCIATED WITH THE THREE CROW ROLL-FRONT URANIUM DEPOSIT, NEBRASKA, USA

by

Julie Leibold
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Golden, Colorado
Date ________________

Signed: ________________________  Julie Leibold

Signed: ________________________  Dr. Thomas Monecke
Thesis Advisor

Signed: ________________________  Dr. Richard Wendlandt
Thesis Advisor

Golden, Colorado
Date ________________

Signed: ________________________  Dr. Paul Santi
Professor and Interim Head
Department of Geology and Geological Engineering
ABSTRACT

Roll-front uranium deposits are a significant source of uranium and a growing target for exploration. Despite their importance, there has been comparatively little research on roll-front deposits over the past decades. The present study refines the genetic model of roll-front uranium deposits and establishes new geochemical and mineralogical exploration vectors to ore by examining the mineralogy and geochemistry of the alteration halo associated with the Three Crow roll-front uranium deposit, Nebraska.

The deposit is hosted by arkosic sandstones of the late late Eocene Chamberlain Pass Formation. Uranium enrichment occurs along a redox boundary within the sandstone aquifer. The study of the accessory mineralogy of the sandstone showed that several distinct morphological types of pyrite and marcasite occur downstream of the roll-front. Framboidal diagenetic pyrite represents the only pre-ore sulfide mineral. Ore deposition was associated with extensive formation of ore-stage marcasite, implying a change in pH conditions during roll-front mineralization. In the oxidized zone upstream of the ore zone, goethite is predominant. There is little evidence for the oxidation of previous ore-stage pyrite or marcasite upstream of the current roll-front location.

Cathodoluminescence petrography showed that framework quartz grains of the sandstone were affected by radiation damage, causing extensive damage in the quartz crystal structure. The occurrence of widespread damage halos was found to be restricted to samples with elevated uranium contents (>100 ppm). Dosage calculations confirm that radiation damage visible in cathodoluminescence microscopy could not have developed from U-bearing groundwater, but record the presence of uranium in the sandstone matrix. The lack of extensive radiation damage upstream of the roll-front suggests that the now oxidized sandstone in the altered tongue has never hosted ore.

The framework grain mineralogy does not alter significantly across the roll-front with the exception of a slight increase in feldspar alteration in the oxidized zone. The mineralogical changes identified in this study are shown to influence the whole-rock geochemistry. Geochemical trends include elevated As and Mo proximal to the ore zone related to enrichment in ore-stage sulfides, depletion of C and S in the oxidized zone from the destruction of organic matter by oxidized groundwater, and some
redistribution of iron from the oxidized zone to the reduced zone from the alteration and dissolution of pre-ore sulfides. The mineralogical and geochemical changes in turn are a reflection of the Eh gradient from the oxidized upstream portion of the deposit to the reduced downstream zone.

The results of this research indicate that the ore-roll at Three Crow is not continuously moving within the host aquifer and has either been stagnant for a pronounced period of time or only moved periodically. Continuous movement of the ore-roll as required by the current deposit model does not appear to be a characteristic feature of all roll-front deposits.
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LIST OF ABBREVIATIONS

Element Abbreviations:

Ag  Silver
As  Arsenic
Au  Gold
Ba  Barium
Bi  Bismuth
C   Carbon
Cd  Cadmium
Co  Cobalt
Cr  Chromium
Cu  Copper
Fe  Iron
Ga  Gallium
Hg  Mercury
Mg  Magnesium
Mn  Manganese
Mo  Molybdenum
Ni  Nickel
Pb  Lead
REEs Rare earth elements
Rb  Rubidium
S   Sulfur
Sb  Antimony
Se  Selenium
Te  Tellurium
Th  Thorium
Tl  Thallium
U   Uranium
V   Vanadium
W   Tungsten
Zn  Zinc

Other abbreviations

Å   Angstrom
BSE Back-scattered electron
°C  Degrees Celsius
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>CCD</td>
<td>Charge-coupled device</td>
</tr>
<tr>
<td>CL</td>
<td>Cathodoluminescence</td>
</tr>
<tr>
<td>cm</td>
<td>Centimeter</td>
</tr>
<tr>
<td>EMP</td>
<td>Electron microprobe</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused ion beam</td>
</tr>
<tr>
<td>g</td>
<td>Grams</td>
</tr>
<tr>
<td>ISL</td>
<td>In-situ leach</td>
</tr>
<tr>
<td>ISR</td>
<td>In-situ recovery</td>
</tr>
<tr>
<td>Kα-line</td>
<td>K-alpha X-ray spectral line</td>
</tr>
<tr>
<td>kg</td>
<td>Kilograms</td>
</tr>
<tr>
<td>km</td>
<td>Kilometer</td>
</tr>
<tr>
<td>keV</td>
<td>Kilo-electron volt</td>
</tr>
<tr>
<td>LA-ICP-MS</td>
<td>Laser-ablation inductively couple plasma-mass spectrometry</td>
</tr>
<tr>
<td>Ma</td>
<td>Million years ago</td>
</tr>
<tr>
<td>m</td>
<td>Meters or molal, moles per kilogram</td>
</tr>
<tr>
<td>mg</td>
<td>Milligrams</td>
</tr>
<tr>
<td>mm</td>
<td>Millimeters</td>
</tr>
<tr>
<td>min</td>
<td>Minute</td>
</tr>
<tr>
<td>ms</td>
<td>Millisecond</td>
</tr>
<tr>
<td>mW</td>
<td>Milliwatt</td>
</tr>
<tr>
<td>nA</td>
<td>Nanoampere</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer</td>
</tr>
<tr>
<td>ppb</td>
<td>Parts per billion</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>s</td>
<td>Second</td>
</tr>
<tr>
<td>SE</td>
<td>Secondary electron</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscope</td>
</tr>
<tr>
<td>µA</td>
<td>Milliampere</td>
</tr>
<tr>
<td>µm</td>
<td>Micrometer, micron</td>
</tr>
<tr>
<td>wt.%</td>
<td>Weight percent</td>
</tr>
<tr>
<td>XRF</td>
<td>X-ray fluorescence</td>
</tr>
<tr>
<td>%</td>
<td>Percent</td>
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CHAPTER 1
INTRODUCTION

1.1 Uranium Deposit Types

Uranium deposits occur in a wide variety of geologic environments and can be classified based on the dominant mineralizing fluid source. This classification system results in three end-member categories, namely magmatic-hydrothermal-, metamorphic- and sedimentary basin-related uranium deposits (Skirrow et al., 2009). The dominant mineralizing fluid sources for these categories are magmatic-hydrothermal fluids, metamorphic fluids, and meteoric waters, respectively. Mixing of these fluids may result in a continuum of deposit types.

Magmatic-hydrothermal deposits include some volcanic and vein type deposits and intrusive deposits (Dahlkamp, 1993; Plant et al., 1999; IAEA, 2009). An essential element in these types of deposits is the enrichment of uranium in silicate melts and related hydrothermal fluids. Uranium enrichment results from a variety of magmatic processes, including: partial melting, fractional crystallization, wall-rock assimilation, magma mixing, and unmixing of aqueous fluids due to changes in pressure and temperature conditions. Key controls on uranium solubility in both melts and related hydrothermal fluids are temperature, redox state, and the content of fluorine and chlorine. It is rare for magmatic processes to enrich uranium concentrations to economic levels in orthomagmatic deposits. Most deposits in this group are interpreted to form from hydrothermal fluids related to magmatic intrusions (Skirrow et al., 2009).

Metamorphic deposits include some vein type deposits and metasomatic deposits (Skirrow et al., 2009). Deposits formed by metamorphic processes such as dehydration and partial melting are relatively rare compared to other deposit types (Plant et al., 1999). Metasomatic deposits form by the interaction of fluids with metamorphic rocks at elevated temperatures. The transport of uranium in these systems is dependent on many of the same factors as in magmatic-hydrothermal systems. However, by comparison the deposit forming processes are not as well
understood due to the lack of high-temperature thermodynamic data (Skirrow et al., 2009).

While both magmatic-hydrothermal- and metamorphic-related deposits can be significant sources of uranium, the majority of economic uranium deposits mined today are sedimentary basin-related. It is estimated that approximately 36 percent of the world’s uranium resources and 42 percent of world production is sourced from sedimentary-hosted deposits (OECD, 2012). This group of deposits includes sandstone, unconformity, quartz-pebble conglomerate, and calcrete uranium deposits. These deposits predominantly formed from fluids of meteoric origin and typically at low temperatures (Skirrow et al., 2009).

1.2 Roll-front Uranium Deposits

Roll-front and tabular uranium deposits are the main types of sandstone uranium deposits. Sandstone uranium deposits are defined as epigenetic concentrations of uranium minerals that occur as impregnations and massive replacements in continental sandstone formations within sedimentary basins (Finch and Davis, 1985). In general, these deposits form from uranium that is transported in low concentrations in oxidized groundwater and precipitated under reducing conditions within the host sandstones. Several factors influence uranium transport and its depositional processes and therefore the resulting type of sandstone deposit. These factors include host lithology and permeability, groundwater chemistry, aquifer hydrology, and depositional environment (IAEA, 2009).

1.2.1 Occurrence

Roll-front deposits typically occur in permeable fine- to coarse-grained arkosic to quartzitic sandstone aquifers interbedded with siltstone and mudstone within intramontane basins (Plant et al., 1999). Most roll-front uranium deposits in the world are hosted in rocks that are Upper Cretaceous or younger in age although examples occurring in older host strata are also known (Robertson et al., 1978; Finch and Davis,
1985). In active roll-front environments, the host sandstones are un lithified and range from completely unconsolidated to poorly consolidated (Fisher, 1974). Many roll-fronts develop within paleo-drainage patterns such as paleo-rivers as the nature and permeability of the host sediments exerts a critical control on groundwater flow (Finch and Davis, 1985).

Some of the largest roll-front deposits in the world are located in the United States, Australia, and Kazakhstan. Areas in the United States that contain significant roll-front deposits include the Powder River, Shirley, Wind River, and Great Divide Basins in Wyoming; the Crawford Basin in Nebraska; and the Southern Coastal Plain region in Texas (Finch, 1996; Dahlkamp, 2010). In Australia, important roll-front areas are located in the Frome Embayment; the Ngalia Basin; and the Grawler Craton and West Kimberley regions (Hou et al., 2007; McKay et al., 2010; Paladin Energy LTD, 2012). The uranium roll-fronts in Kazakhstan are primarily found in two southern basins, the Chu-Sarysu and Syrdarya Basins, with a few other deposits in the Ily Basin (Fyodorov, 2005; Dahlkamp, 2009).

1.2.2 Morphology

Roll-fronts are distinguished from tabular sandstone deposits by the crescent or roll-shape of the ore body in cross-section. The ore body cross-cuts sandstone bedding and extends vertically through the aquifer (Dahlkamp, 1993; IAEA, 2009). A single ore roll can range from less than one meter to tens of meters in thickness, but is typically not more than 20 meters thick. In plan-view, this deposit type typically appears sinuous along its length and can extend up to several kilometers along strike. The deposit width is also extremely variable and ranges from less than a meter to several hundred meters (Harshman, 1972; Galloway, 1978; Dahlkamp, 1993).

The roll-front ore zones are always closely associated with a redox boundary, an interface between oxidized and reduced zones, within the host sandstone which defines the trace of the deposit along its length (Fisher, 1970). As many basins contain multiple aquifers, each bound by confining mudstones and/or aquifers complexly interbedded
with mudstones, roll-fronts can develop within multiple sandstone layers, creating complexly stacked deposits (Min et al., 2005).

1.2.3 Uranium Sources and Transport

The source of the uranium contained in roll-front deposits is hitherto poorly constrained and several possibilities have been suggested in the past. As roll-front deposits are typically located close to the basin margins that are rimmed by areas of regional uplift (Melin, 1964; Adler, 1974; IAEA, 2009), creating a hydraulic gradient required for groundwater flow, it has been suggested that the uranium is sourced from exposed basement rocks adjacent to the intramontane basins. Because uranium is an incompatible element in silicate melts, felsic rocks in general have a higher uranium content than mafic rocks (Rogers and Adams, 1969). Therefore, felsic rocks exposed in the upland areas, such as granites, could represent a favorable source for the uranium (Finch, 1967).

In some basins of the western United States, volcanic ash beds form part of the sedimentary infill of the intramontane basins (Stanley and Benson, 1979; Baars et al., 1988). These ash beds can be laterally extensive and, in the case of the White River Formation, can reach a stratigraphic thickness of over 250 meters (Zielinski, 1983). As volcanic glass can readily alter, it has been suggested that regional ash beds can also represent a significant source of uranium (Hostetler and Garrels, 1962; Smith et al., 1982). In addition to these possible external sources, uranium could also be leached from the host aquifer by the groundwater flowing down the hydraulic gradient (Finch and Davis, 1985).

In low-temperature environments, uranium transport is primarily dependent on the redox conditions, pH, and availability of suitable ligands (Langmuir, 1978; Romberger, 2007; Skirrow et al, 2009). Under the oxidizing conditions prevailing in oxygenated groundwater, uranium occurs as $U^{6+}$, which is generally very mobile. The mobility of uranium in groundwater can be further enhanced by complexation with commonly occurring aqueous anions including carbonate, chloride, fluoride, hydroxide, phosphate, and sulfate (Hostetler and Garrels, 1962; Langmuir, 1978).
1.2.4 Uranium Deposition

Deposition of uranium in roll-front systems is dependent on the oxidizing and uranium-bearing groundwater crossing into a reducing environment. Under reducing conditions, U$^{6+}$ contained in the groundwater is reduced to U$^{4+}$, which is essentially immobile in the low-temperature environment. A reducing environment can be maintained by the presence of organic matter and/or sulfides in the host sandstone (Shawe and Granger, 1965; Reynolds and Goldhaber, 1983). Fixation of uranium can also be enhanced by sorption onto solid phases such as organic matter, zeolites, and clay minerals (Doi and Hirono, 1990; Yoshida et al., 1994; Metcalfe et al., 2006).

In some cases, roll-front deposits also appear to have formed in spatial association with faults (Jaireth et al., 2008; Hancock, 2012) that may allow upflow of reducing fluids such as hydrogen sulfide, hydrocarbons, or reducing brines (Spirakis, 1996; Hobday and Galloway, 1999). Many uranium roll-fronts develop in basins that also have oil and gas reserves. The Crow Butte uranium roll-front was discovered in part from a review of regional oil and gas drill hole logs (Collings and Knodel, 1984). Many of the intramontane basins in Wyoming also have significant oil and gas reserves in addition to uranium (Roberts, 2005). Some of the roll-front deposits in the Texas coastal plain region are spatially associated with faults that provided a conduit for saline reducing brines that carried organic acids and methane. These reductants fueled sulfate-reducing bacteria, producing pyrite which in turn reduced uranium (Goldhaber et al., 1983).

1.2.5 Ore and Alteration Mineralogy

The primary ore minerals in roll-front deposits are uraninite, UO$_2$, and coffinite, U(SiO$_4$)$_{1-x}$(OH)$_{4x}$. Alteration of the primary ore minerals can produce secondary minerals that include tyuyamunite, Ca(UO$_2$)$_2$(VO$_4$)$_2$·5-8H$_2$O, and carnotite, K$_2$(UO$_2$)$_2$(VO$_4$)$_2$·3H$_2$O (Granger et al., 1961; Harshman, 1968). Several deposits in Australia also contain brannerite, a uranium titanate with the ideal chemical formula UTi$_2$O$_6$, which does not dissolve by current leaching methods, limiting the uranium
recovery possible from mines with significant resources in brannerite (Zhang et al., 2003; Charalambous et al., 2011). The ore minerals occur as disseminated grains in the matrix of the host sandstones, as grain coatings, or as fracture filling in individual detrital grains (Fisher, 1970). In general, the highest grade mineralization is concentrated at the leading edge of the roll and decreases significantly upstream. Resources in roll-front deposits contain anywhere between a few hundred to several thousand tonnes of uranium. The average ore grades range between 0.05 to 0.5 % but can be as high as 1% U$_3$O$_8$ (McKay et al., 2010; OECD, 2012). In addition to uranium, the ore zones of roll-front deposits are commonly also enriched in arsenic, copper, iron, molybdenum, selenium, and vanadium (Granger et al., 1961; Melin, 1964; Fisher, 1970; Hansley et al., 1989). Typically only vanadium has been considered a desirable and recoverable element. However, some roll-front deposits have also produced molybdenum, rhenium, and selenium as a by-product (McGinley and Facer, 1976).

Authigenic non-ore minerals forming in association with roll-front deposits include calcite, goethite, hematite, pyrite, marcasite, and siderite (Granger and Warren, 1974; Goldhaber and Reynolds, 1979). The distribution of these non-ore minerals is closely related to changes in redox and pH across the roll-front. Pre-mineralization, the host sandstones are typically reduced and contain pyrite, calcite and, in some deposits, abundant organic matter. The host sandstones range from dark green-gray to light gray in color (Shawe and Granger, 1965). The reduced zoned is located downstream of the ore zone. Upon interaction with the oxidized uranium-bearing groundwaters, the host sandstone typically becomes bleached and sulfides such as pyrite and marcasite are oxidized to hematite and various iron oxides/hydroxides or undergo complete dissolution. Oxidized sandstones range in color from red to pink to yellow. The zones of oxidation upstream of the roll-front can be quite large and commonly extends several tens of kilometers back from the roll-front deposit and along its strike.

1.2.6 Exploration

Traditionally, exploration for roll-front uranium deposits largely focused on using sedimentological and stratigraphic analysis to define the geometry of potentially
mineralized aquifers. The data from these analyses was used to define likely zones of uranium precipitation. For instance, Dickinson (1993) used the spatial distribution of the sedimentary strata in the White River Group of South Dakota and Nebraska to define favorable areas warranting more detailed exploration. Exploration for paleochannel-hosted roll-front deposits has also utilized similar techniques but applied to defining the geometry of underlying bedrock, paleovalleys and paleochannels as well as the paleohydrology (Morgan, 1993; Jaireth et al., 2010). Increasingly, geophysical methods such as magnetic, gravity, and seismic are being used to define paleochannels in uranium roll-front exploration. The success of these methods is dependent on there being a measurable difference between the geophysical properties of the sediment and bedrock and, in the case of magnetic surveys, the presence of certain types of minerals in the rock (Hou et al., 2007; Hancock, 2012). Also used in targeting prospective uranium roll-front areas is the proximity to favorable source rocks such as uraniferous granites (Hou et al., 2007; Jaireth et al., 2010) and the recognition of uranium provinces (Hunter and Michie, 1988).

Once favorable areas are identified, exploration for roll-front uranium deposits largely relies on drilling and the use of various geophysical logging techniques, including gamma logging. Gamma logging was, for instance, instrumental in the discovery of the Crow Butte roll-front deposit (Collings and Knode, 1984), which is located immediately to the east of the Three Crow deposit investigated in the present study. The major problem with this exploration technique is that it measures the decay products of uranium and the signal does not correlate well to the actual uranium content if equilibrium conditions are not attained (Dickson, 1995; McKay et al., 2007). Issues with non-equilibrium conditions can be largely overcome through the use of prompt fission neutron logging. This technique is based on the emission of high energy neutrons from the logging tool that cause fission in the U-235 nucleus, sending out neutrons that are then counted to determine the uranium content (Killeen, 1997). The lowest uranium grade measurable with this technique is about 0.025 wt.% U₃O₈ (Skidmore, 2009). Due to the high capital cost, prompt fission neutron logging is comparably expensive.

Exploration drilling also yields useful information on the redox state of the host aquifer as sandstone color can be readily observed in cuttings or core. As previously
discussed, the oxidized zone upflow of the roll-front is readily distinguishable from the reduced zone downgradient of the roll-front by a characteristic change in color. The location of the redox-front can thus be mapped out simply by recording color of the host aquifer. In the past, airborne multispectral surveys have been used to map out these color changes over large areas of land to identify drilling targets (Peters, 1983). However, this type of remote sensing does not play a significant role in today’s exploration as exploration focuses on covered deposits located below the water table to allow in-situ mining. Although recording color has proven to be a useful tool in exploration, it is important to note that not every redox boundary is mineralized. In addition, processes of re-reduction can occur, modifying sandstone color in the oxidized zone upstream of the roll-front deposit (Cheney and Jensen, 1966; Adams and Smith, 1981).

1.2.7 In-Situ Mining

Before the development of in-situ mining techniques in the 1960’s, sandstone uranium deposits were mined using conventional open-pit and underground methods. With the rise in cost of open-pit mining in the early 1970’s and the depression of the uranium market, in-situ mining became the dominant way sandstone uranium deposits were mined (Davis et al., 1976; Davis, 1977). The basic mechanics for in-situ leach (ISL), also called in-situ recovery (ISR), mining involve pumping a solution capable of dissolving the uranium minerals into the host aquifer then, once the uranium is in solution, pumping it back out and recovering the uranium. In order to use ISL, the deposit must meet a number of conditions. One, the host sandstone must be permeable and have good hydraulic conductivity. Two, the host sandstone must be bounded by impermeable strata, such as clay or shale, but not contain more than 10 percent clay itself. Three, the ore zones must be located below the water table but not over 1000 m below surface. Four, the ore minerals must be amenable to leaching by non-toxic solutions (Dobrzinski, 1997; IAEA, 2001).

The differences in the ISL process between different deposits are typically in the type of leaching solution used and are determined by the mineralogy and geochemistry
of the ore zone. The leaching solutions are aqueous solutions that typically contain both a complexing agent (a lixiviant) and an oxidizing agent. In the United States, the presence of significant carbonate minerals and other acid reactive species necessitates the use of alkaline complexing agents, commonly carbonate salts such as carbonates and bicarbonates of sodium and ammonium (Tweeton et al., 1979; Bommer and Schecter, 1979). In Australia, the carbonate content is typically much lower than in the US so acidic leaching solutions using sulphuric, nitric and/or hydrochloric acids are used more commonly (Lambert, 2009; Mårten et al., 2011). Typical oxidizing agents include hydrogen peroxide, hypochlorite, oxygen, and iron(III). These agents are used in all mines except those in Kazakhstan which use highly acidic solutions (IAEA, 2001; Lambert, 2009). Acid solutions are more efficient at liberating uranium however their use can be of significant environmental concern.

In-situ leach mining has several advantages over other mining techniques such as: minimal surface disturbance of the environment, little dust generation from mining or processing, low capital and operational costs, reduced radiation exposure and capability of recovering low-grade ores (Dobrzinski, 1997; IAEA, 2001). In addition to the business advantages, ISL mining has far fewer environmental impacts than other mining techniques when developed properly. Current production from ISL mining accounts for approximately 43 percent of the world uranium production (OECD, 2012).

### 1.3 Statement of Problem

Although roll-front uranium deposits represent one of the principal sources of uranium and are a growing target for new exploration worldwide, comparably little research has been carried out on this deposit type in the past two decades. This not only limits the understanding of processes of uranium deposit formation in sedimentary basins, but also the development of new exploration methods and strategies that are tailored to today’s demand of finding deposits concealed beneath thick overburden or barren host rock strata.

To address these problems, a new look at and better understanding of the roll-front deposit model is needed. Previous research has largely focused on the geology
and geochemistry of the ore zones in roll-front deposits itself (Goldhaber and Reynolds, 1979; Stewart, 2002; Min et al., 2005). However, few detailed studies of the associated alteration halos have been carried out. The present work investigates the fluid-mineral interactions, alteration patterns, and geochemical gradients in a roll-front uranium deposit with the aim of describing the processes associated with ore formation and sandstone alteration using a range of state-of-the-art analytical techniques. This information is used to refine the current geologic model for roll-front uranium deposits and develop geochemical and mineralogical vectors for use in roll-front exploration.

Research has been carried out on the Three Crow roll-front uranium deposit, Nebraska. The Three Crow deposit is located in Dawes County in northwest Nebraska. It is part of a regional trend of deposits that includes the producing Crow Butte mine as well as the Marsland and North Trend deposits. Current indicated resources at Three Crow total 4.22 million pounds U\textsubscript{3}O\textsubscript{8} with an additional inferred resource of 1.14 million pounds at an average ore grade of 0.352 wt.% U\textsubscript{3}O\textsubscript{8}. Drill core was collected from the basal unit of the producing aquifer in the summer of 2008 and made available by Cameco for use in this study. The drill core covers the altered host rock, ore zone, and unaltered host rock of one of the ore rolls at Three Crow.

1.4 Thesis Organization

This thesis is presented as five chapters; an introduction, three journal papers and a conclusion. Each paper has either been submitted for publication in a peer-reviewed journal or is in final preparation for submission. The publication status of the papers is listed at the beginning of each associated chapter. The authors and roles of the authors for each paper are described here. Each paper focuses on different aspects of the entire thesis work. The first paper is contained in Chapter 2 and describes the accessory mineralogy of the roll-front halo. The second paper is presented in Chapter 3 and focuses on the cathodoluminescence study of detrital quartz. The third paper is presented in Chapter 4 and summarizes the results of the entire PhD project with a focus on the mineralogy and geochemistry of the alteration halo. A brief summary of the key findings of the research is provided in Chapter 5.
The authors for the first paper presented in Chapter 2 are Julie Leibold, Thomas Monecke, Nigel Kelly, and Alan Koenig. Julie Leibold is the primary researcher and author and a graduate student in the Department of Geology and Geological Engineering, Colorado School of Mines. Thomas Monecke and Nigel Kelly are Assistant Professors in the Department of Geology and Geological Engineering, Colorado School of Mines. Alan Koenig is a Research Geologist at the United States Geological Survey, Denver.

The authors for the second paper presented in Chapter 3 are Julie Leibold, Thomas Monecke, Brian Gorman, and Jens Götze. Julie Leibold is the primary researcher and author and a graduate student in the Department of Geology and Geological Engineering, Colorado School of Mines. Thomas Monecke is an Assistant Professor in the Department of Geology and Geological Engineering, Colorado School of Mines. Brian Gorman is an Associate Professor in the Department of Metallurgical and Materials Engineering, Colorado School of Mines. Jens Götze is a Professor at the Institute of Mineralogy, TU Bergakademie Freiberg, Germany.

The authors for the third paper presented in Chapter 4 are Julie Leibold, Thomas Monecke, Richard Wendlandt, and Nigel Kelly. Julie Leibold is the primary researcher and author and a graduate student in the Department of Geology and Geological Engineering, Colorado School of Mines. Thomas Monecke and Nigel Kelly are Assistant Professors in the Department of Geology and Geological Engineering, Colorado School of Mines. Richard Wendlandt is a Professor in the Department of Geology and Geological Engineering, Colorado School of Mines.
CHAPTER 2
ACCESSORY MINERALOGY OF SANDSTONE HOSTING THE THREE CROW ROLL-FRONT DEPOSIT, NEBRASKA: CONSTRAINTS ON PROCESSES OF URANIUM ENRICHMENT

Modified from a paper to be submitted to *Economic Geology*

Julie Leibold, Thomas Monecke, Nigel Kelly, and Alan Koenig

2.1 Abstract

The accessory mineralogy of the late Eocene to Oligocene sedimentary host rocks of the Three Crow roll-front uranium deposit, Nebraska, was studied to characterize the provenance of the detrital material and to better constrain the low-temperature processes of uranium enrichment. Detrital phases such as ilmenite, rutile, garnet, tourmaline, and zircon form euhedral to variably rounded grains with grain surface textures indicative of mechanical transport. The abundance of these phases does not depend on the oxidation state of the host rocks. The spectrum of accessory minerals encountered suggests a dominantly felsic igneous provenance. In contrast to the detrital phases, authigenic accessory minerals such as pyrite, marcasite, and goethite show delicate grain morphologies and grain surface textures. These authigenic minerals are characterized by pronounced variations in abundance across the roll-front. Pyrite and marcasite are most abundant on the reduced side of the oxidation front while goethite predominates in the oxidized upstream environment.

Grain morphology, internal textures, and trace element abundances suggest that multiple generations of authigenic pyrite and marcasite occur. Pre-ore framboidal pyrite, a product of diagenesis, is characterized by enrichment of Co, Ni, and Pb. Upstream oxidation of the diagenetic pyrite by groundwater flowing down the hydrological gradient resulted in the mobilization of chemical components, which were re-precipitated ahead of the oxidation front as ore-stage sulfide minerals showing elevated concentrations of As, Mn, and Mo. Coffinite precipitation under acidic to near-neutral conditions within the roll-front was accompanied by marcasite formation. As
upstream oxidation of pre-ore pyrite was nearing completion, a rebound to neutral or slightly alkaline conditions occurred, allowing growth of late ore-stage pyrite.

The observed textural relationships suggest that the roll-front at Three Crow has been stagnant in its current position for a prolonged period of time. This could only have been achieved if an external reductant was supplied to the host aquifer, for instance from a hitherto unrecognized fault intersecting the aquifer. Alternatively, it is possible that the roll-front migrated down the hydraulic gradient, but periodically rather than continuously.

2.2 Introduction

Roll-front deposits are an important type of sandstone-hosted uranium deposits that occur in sedimentary basins. Mineralization forms within permeable sandstone units acting as aquifers where U-bearing groundwater flowing down a hydrological gradient encounters an interface between oxidizing and reducing conditions, causing the precipitation of uranium minerals. This deposit type currently represents a growing target for exploration, primarily as the uranium ores are amenable to in-situ mining.

The dissolution and precipitation behavior of accessory minerals in the host sandstones exerts critical controls on the processes leading to the formation of roll-front uranium deposits in the low-temperature environment. Due to their influence on oxidation state, pyrite and marcasite represent particularly important components of the geochemical system (Granger and Warren, 1969; Goldhaber et al., 1978, 1983; Reynolds and Goldhaber, 1983; Min et al., 2005). Diagenetic pyrite is widespread in the reduced sandstone hosting most roll-front deposits. Consumption of the diagenetic pyrite on the oxidized side of the roll-front leads to the formation of metastable sulfur species that are subsequently transported downstream through the oxidation front where they are reduced and incorporated into ore-stage pyrite or marcasite that precipitate in the ore zone and up to several hundred meters further downstream (Granger and Warren, 1969; Reynolds et al., 1982; Reynolds and Goldhaber, 1983). Oxidation of diagenetic pyrite then results in the formation of goethite, giving the
sandstone on the oxidized side of the roll-front its characteristic reddish or orange colors.

In addition to pyrite and marcasite, the sandstone hosts of roll-front uranium deposits commonly contain other accessory phases such as ilmenite and magnetite (Reynolds and Goldhaber, 1978). Although quantitatively less important, these phases potentially provide important constraints on host-rock alteration during diagenesis and element mobility associated with the formation of roll-fronts. However, at present little is known on the stability of these accessory phases in U-bearing groundwater. Other accessory phases commonly present in the sedimentary rocks hosting roll-front uranium deposits include epidote, garnet, hornblende, staurolite, titanite, tourmaline, and zircon (Harshman, 1972; Hansley et al., 1989; Min et al., 2005). These minerals are likely of detrital nature and typically appear to be largely unaffected by alteration related to uranium enrichment.

The present study reports on the occurrence and distribution of accessory minerals in the sandstone host of the Three Crow roll-front uranium deposit, Nebraska. Heavy mineral separates were obtained from samples collected across the roll-front and subsequently analyzed for their mineralogical composition. A set of textural criteria was derived, allowing differentiation between detrital mineral grains and authigenic phases. Secondary phases that formed through diagenetic processes were distinguished from those minerals that precipitated from the U-bearing groundwaters as they evolved down the hydrological gradient. It is demonstrated that systematic variations in accessory mineralogy, trace element composition, and textural characteristics define regular zonation patterns with respect to the roll-front uranium enrichment.

2.3 Regional Geology

The Three Crow roll-front uranium deposit near Crawford in Dawes County, northwestern Nebraska, is located in the Crawford Basin, an approximately 1000 km² large sub-basin at the northern extent of the much larger Denver Basin (DeGraw, 1971), which covers large parts of eastern Colorado, southeastern Wyoming, western Nebraska, and northwestern Kansas (Fig. 2.1A).
Figure 2.1: Location of the Three Crow roll-front uranium deposit in Dawes County, Nebraska. A. Regional map showing the location of the Denver Basin and major regional uplifts. B. Paleogeographic reconstruction of western Nebraska, showing the location of major fluvial systems during the early Oligocene (modified from Swinehart et al., 1985). C. Map of the Crawford area and location of major roll-front deposits (modified from Crow Butte Resources, unpubl. data).

The Crawford Basin is composed of various Paleozoic and Mesozoic sedimentary strata that overlie the Precambrian crystalline basement rocks (Baars et al., 1988). The Pierre Shale, a dark gray to black marine shale that accumulated in the Late Cretaceous Interior Seaway of North America, represents the youngest Mesozoic deposit in the Crawford Basin. Deep oil drilling indicated that this highly impermeable
shale has a stratigraphic thickness of 350 to 450 meters in Dawes County (Collings and Knode, 1984). The top surface of the Pierre Shale marks a major unconformity (Retallack, 1983; Gjelsteen and Collings, 1988; Evans and Terry, 1994; Terry, 1998).

The Pierre Shale Formation is overlain by the late Eocene to Oligocene White River Group, which represents the oldest preserved phase of fluvial activity in the area following retreat of the Late Cretaceous Interior Seaway (Terry and Evans, 1994; Terry, 1998). The basal unit of the White River Group is the late Eocene Chamberlain Pass Formation (Fig. 2.2), which represents the host of Three Crow and other roll-front uranium deposits of the Crawford Basin. The Chamberlain Pass Formation is composed of sandstones and mudstones that represent channel and overbank facies of a large braided stream system (Fig. 2.1B). Within the immediate deposit area, the sandstones have a thickness ranging from 20 to 75 meters (Crow Butte Resources, unpubl. data 2010). The channel sandstone bodies are typically multistory, showing general fining-upward sequences (Evans and Terry, 1994; Terry and Evans, 1994). Overbank mudstone is massive and ranges up to three meters in thickness (Terry, 1998).

The Chamberlain Pass Formation is unconformably overlain by the late Eocene to early Oligocene Chadron Formation (Fig. 2.2). In northwestern Nebraska, the Chadron Formation is subdivided into the Peanut Peak and Big Cottonwood Creek Members (Terry, 1998). The Peanut Peak Member is dominated by bluish-green and gray hummocky mudstone (Terry, 1998), ranging from 10 to 30 meters in thickness (Collings and Knode, 1984). The Peanut Peak Member is overlain by the Big Cottonwood Creek Member, which consists of 25 to 50 meters thick (Collings and Knode, 1984) volcaniclastic overbank claystone, silty claystone, and siltstone with isolated tabular and lenticular channel sandstone bodies (Terry, 1998; Terry and LaGarry, 1998). Lacustrine limestone beds occur toward the top of the Chadron Formation (Evans and Welzenbach, 1998; Terry and LaGarry, 1998).

The Chadron Formation is overlain by the Brule Formation (Fig. 2.2), which has a total stratigraphic thickness of approximately 40 to 160 meters (Gjelsteen and Collings, 1988). The lower portion of the Brule Formation is dominated by fluvial, pale brown and brown volcaniclastic siltstone of the Orella Member, which contains zones of abundant
bluish-green nodules. Channel sandstones occur locally (Collings and Knodle, 1984; LaGarry, 1998). The overlying Whitney Member of the Brule Formation is dominated by eolian, pale brown, massive, and typically nodular siltstone with occasional thin interbeds of sandstone (LaGarry, 1998). A brown siltstone member is assigned to the top of the Brule Formation. The siltstone is composed of brown to pale brown, siltstone and fine sandstone, with minor reworked volcaniclastic siltstone and volcanic ash (Swinehart et al., 1985; LaGarry, 1998).

Figure 2.2: Schematic stratigraphic column for the Three Crow area. The column only shows relationships above the Late Cretaceous Pierre Shale. The Chamberlain Pass Formation represents the main uranium host at Three Crow. YMPE = Yellow Mounds Paleosol equivalent (modified after LaGarry, 1998).
The White River Group is unconformably overlain by the Oligocene to Miocene Arikaree Group (Fig. 2.2) that consists of 30 to 60 meters of predominantly fluvial volcaniclastic sandstone and 85 to 110 meters of eolian sandstone with carbonate-cemented concretions (Collings and Knode, 1984; Tedford et al., 1996). Quaternary alluvial and colluvial material represents the youngest sediment in the area, which is up to 10 m in thickness (Collings and Knode, 1984).

2.4 Deposit Geology

Three Crow forms part of a trend of roll-front deposits, which also includes Crow Butte, North Trend, and Marsland (Fig. 2.1C). All four roll-front deposits are hosted by the Chamberlain Pass Formation of the White River Group, which represents a regional aquifer that is confined between the Pierre Shale Formation and the fine-grained sedimentary rocks of the Chadron Formation (Gjelsteen and Collings, 1988). Crow Butte is currently the only operating roll-front deposit in northwestern Nebraska and has been continuously mined by in-situ leaching since 1991. The Three Crow, North Trend, and Marsland deposits are currently under permitting as expansion areas of the Crow Butte operation.

The Three Crow deposit is composed of five multi-story roll-fronts within the Chamberlain Pass Formation that are separated by thin mudstone layers. The ore zones are located 175 to 290 meters below surface and have an overall width of 640 to 1200 meters. Uranium grades in the ore bodies vary from less than 0.05 to greater than 0.5 wt.% U₃O₈, with the average grade being 0.352 wt.% U₃O₈. The deposit is composed of an indicated ore resource of approximately 4,220,000 pounds U₃O₈ with an additional inferred resource of 1.14 million pounds. Mining of the roll-front will be conducted by in-situ leaching with an expected annual production rate of approximately 600,000 pounds U₃O₈ (Crow Butte Resources Inc., unpub. data 2012).

The sandstone hosting the Three Crow uranium deposit is classified as a subarkose to sublitharenite, consisting of quartz (60 to 85%), feldspar (5 to 15%), and rock fragments (<1 to 10%). Rock fragments include chert, granite, and various metamorphic rocks. Detrital grains are subangular to subrounded and generally
Figure 2.3: Deposit geology of the Three Crow roll-front uranium deposit. A. Plan map of the western portion of the deposit showing the surface projection of the roll-front. The relative location of the five research drill holes are shown in red, other drill holes are shown as hollow circles. B. Schematic logs of the five research drill holes penetrating the lower portion of the Chamberlain Pass Formation. The position and numbers of the samples used for the present study are shown to the right of the logs. The drill holes intersect the ore zone at samples 1 and 2 of hole H161C. The roll is very thin at this location and does not have significant volume. The logs show grain size distribution and color of the sedimentary rocks.
moderately well sorted. The matrix of the sandstone consists of clay minerals including smectite and kaolinite, as well as minor authigenic calcite and pyrite. The redox state of the sandstone broadly correlates with rock color. Reduced sandstone occurring downstream of the roll-front is dark green to gray. Slightly reduced sedimentary rocks are typically light gray. Rocks sampled in transitional zones between the reduced and oxidized parts of the Chamberlain Pass Formation are grayish yellow. Upstream of the zone of roll-front uranium enrichment, the sedimentary rocks are oxidized and distinctly yellow to red.

2.5 Analytical Methods

The present study is based on drill core from five research holes that were drilled along a section across the lowermost roll-front at Three Crow, covering the host rocks located upstream and downstream of the roll-front as well as the ore zone itself (Fig. 2.3). Reverse circulation drilling was conducted in the upper parts of the drill holes while continuous coring was performed across sedimentary strata hosting the roll-front.

To study the accessory mineralogy of the variably altered sedimentary rocks, a total of fifty representative samples were collected from the cored intervals of the five research drill holes (Fig. 2.3). Initially, the samples were dried at 60°C in a drying oven over night to remove any moisture. Subsequently, the outer portion of the core was carefully removed as this part of the core showed evidence for contamination by drilling mud. The remaining core material was disaggregated with a mortar and pestle and split using a riffle splitter.

The sample split (~150 g) used for the present study was further crushed by hand and sieved through a one millimeter mesh. Gravity sedimentation was used to remove the <30 μm particle size fraction. For this, the crushed sample was weighed accurately and dispersed in a 0.004 M Na₄P₂O₇·10 H₂O solution. The suspension was then transferred to an Atterberg cylinder. After settling of the >30 μm fraction, the supernatant was drawn off and discarded. The process of gravity sedimentation was repeated until the supernatant was clear. After drying, the >30 μm fraction was passed through lithium metatungstate solution with a specific density of 2.95 g/cm³ in a
separatory funnel. All particles with a specific density greater than the threshold were considered heavy minerals and part of the accessory mineral fraction. After heavy liquid separation, the recovered accessory minerals were washed thoroughly and dried.

The obtained heavy accessory mineral fraction was then split using a rotary micro-riffle splitter. One half of the accessory mineral fraction was used for imaging of the grain morphologies and grain surface textures employing a JEOL JSM-7000F field emission scanning electron microscope equipped with an EDAX Genesis energy dispersive X-ray spectrometer at the Colorado School of Mines. The scanning electron microscope was operated under standard conditions of 20 kV at a working distance of 10 mm. Inspection of the grains was conducted by secondary electron imaging. Selected authigenic mineral grains were subsequently remounted and polished to image the internal textures of the grains. Backscatter electron imaging of the polished grains allowed correlation between the grain morphologies, grain surface textures, and textural relationships only visible in section. High-resolution backscatter images were collected at an accelerating voltage of up to 25 kV.

The second half of the obtained heavy mineral fraction was used for the determination of phase abundances by automated quantitative phase analysis. Standard 25 mm epoxy grain mounts were prepared following the procedure described in Appendix A and then analyzed using a QEMSCAN automated mineral scanning electron microscope system at the QEMSCAN Facility, Department of Geology and Geological Engineering, CSM. This technology is based on a Carl Zeiss EVO50 platform equipped with four Bruker X275HR silicon drift energy dispersive X-ray spectrometers for fast acquisition of X-ray signals. Data collection was controlled by the iMeasure software and analysis was controlled using the iDiscover software. The system was operated at 25 kV accelerating voltage, a specimen current of 5 nA measured on the Faraday Cup, and a working distance of 24 mm. The average analysis time for each epoxy mount was 30 minutes at an acquisition rate of approximately 1500 spot analyses per second. The stepping distance of the beam and its spot size were set to 10 μm to minimize analysis time while maintaining required resolution to identify smaller heavy mineral grains. At each step, the systems identified
the phase present using a predefined mineral definition that combines the back-scatter electron signal with the energy-dispersive X-ray spectrum.

Laser-ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) was performed at the Denver Region Office of the United States Geological Survey on representative pyrite and marcasite grains to determine the concentrations of trace elements. The analyses were performed using a Photon Machine analyte G2 laser (193 nm) coupled with a Perkin Elmer Elan DRC ICP-MS. The operating conditions included a spot size of 20 μm or 40 μm in spot analysis mode, a pulse frequency of 2 Hz, an energy density of close to 5 J/cm², and a He carrier gas flow of 0.8-0.95 l/min. Signals were calibrated using the USGS reference material MASS-1 (Wilson et al., 2002). The standard was analyzed 10 times at the start of an analytical session and monitored throughout for instrument drift. Element concentrations were determined using the off-line calculation protocol of Longerich et al. (1996). Fe was used as the internal standard for concentration calculations with the assumption that pyrite has a stoichiometric Fe content of 45 wt.%. 

Appropriate locations for LA-ICP-MS analysis were chosen using the backscatter electron images obtained on the grains. Depending on grain size and sulfide mineral, typically one to six spots were analyzed per grain. In general, the analytical spots were positioned away from mineral inclusions or grain edges recognized by backscatter electron imaging. However, heterogeneities were occasionally identified by noting changes in the time-resolved signals. These spot analyses were excluded from data analysis.

2.6 Results

2.6.1 Grain Morphologies and Grain Surface Textures

Scanning electron microscopy on the grain mounts showed that the sandstone samples from Three Crow contain a wide range of accessory phases (Table 2.1). Criteria outlined by Boggs (2009) were used to distinguish between detrital minerals and those of authigenic origin. In most cases, distinction could be made based on grain
morphology. Detrital minerals show grain morphologies indicative of mechanical transport. In contrast, authigenic minerals display well-developed crystal faces or intricate grain morphologies that would not survive transport in the sedimentary environment. Authigenic mineral grains display grain morphologies indicative of replacement, cementation, or overgrowth (Boggs, 2009).

Table 2.1: Accessory minerals recognized in the heavy mineral fraction of the sandstone host of the Three Crow roll-front uranium deposit, Nebraska.

<table>
<thead>
<tr>
<th>Detrital Mineral</th>
<th>Authigenic Mineral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ilmenite</td>
<td>Pyrite/marcasite</td>
</tr>
<tr>
<td>Rutile</td>
<td>Goethite</td>
</tr>
<tr>
<td>Garnet</td>
<td>Barite</td>
</tr>
<tr>
<td>Zircon</td>
<td>Gorceixite</td>
</tr>
<tr>
<td>Tourmaline</td>
<td></td>
</tr>
<tr>
<td>Titanite</td>
<td>Hematite</td>
</tr>
<tr>
<td>Staurolite</td>
<td>V-Goethite</td>
</tr>
<tr>
<td>Epidote</td>
<td>Sphalerite</td>
</tr>
<tr>
<td>Apatite</td>
<td>Chalcopyrite</td>
</tr>
<tr>
<td>Monazite</td>
<td>Celestine</td>
</tr>
<tr>
<td>Spinel</td>
<td></td>
</tr>
<tr>
<td>Amphibole</td>
<td></td>
</tr>
<tr>
<td>Andalusite/sillimanite/kyanite</td>
<td></td>
</tr>
<tr>
<td>Baddeleyite</td>
<td></td>
</tr>
<tr>
<td>Olivine</td>
<td></td>
</tr>
<tr>
<td>Pyroxene</td>
<td></td>
</tr>
</tbody>
</table>

As both detrital and authigenic minerals can display grain surface textures of chemical origin such as various types of etching pits, those types of grain surface textures cannot be used as distinguishing criteria. However, studies on detrital quartz grains have shown that certain grain surface textures are indicative of mechanical transport, such as conchoidal fractures, arcuate or linear steps, impact-V pits, and grooves (Krinsley and Danahue, 1968; Margolis and Krinsley, 1974; Higgs, 1979; Cater, 1984; Rimington et al., 2000; Pye, 2004). Cardona et al. (2005) demonstrated that different detrital accessory minerals contained in sandstone can show the same mechanical grain surface textures as quartz despite different mineralogical properties like hardness and density. Combined with grain morphology, the study of grain surface
textures, especially those of mechanical origin, permits unequivocal distinction between detrital and authigenic minerals.

2.6.2 Detrital Accessory Phases

Over fifteen different detrital accessory minerals were identified in the sedimentary rocks of the Chamberlain Pass Formation (Table 2.1). The most abundant detrital minerals recognized are ilmenite, rutile, garnet, zircon, and tourmaline.

Ilmenite represents the most abundant detrital accessory mineral (Fig. 2.4A). The grains range from 50 to 100 µm in size. Euhedral ilmenite grains commonly show conchoidal fractures, grain impressions (usually of smaller zircon grains), or irregular pits. Anhedral ilmenite grains can be rounded, sub-rounded, or angular (Table 2.2). The surfaces of these grains frequently display irregular pitting, chemical pitting, and impact V's (Table 2.3).

Table 2.2: Grain morphologies of common detrital minerals contained in the heavy mineral fraction of the sandstone host of the Three Crow roll-front uranium deposit, Nebraska. The table gives the number of grains and the relative abundance of the different grain morphologies.

<table>
<thead>
<tr>
<th>Detrital Mineral</th>
<th>Number of Grains</th>
<th>Grain Morphology (in %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Euhedral</td>
<td>Subhedral</td>
</tr>
<tr>
<td></td>
<td>Rounded</td>
<td>Sub-rounded</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>117</td>
<td>15</td>
</tr>
<tr>
<td>Rutile</td>
<td>77</td>
<td>1</td>
</tr>
<tr>
<td>Garnet</td>
<td>150</td>
<td>3</td>
</tr>
<tr>
<td>Zircon</td>
<td>186</td>
<td>58</td>
</tr>
<tr>
<td>Tourmaline</td>
<td>74</td>
<td>88</td>
</tr>
</tbody>
</table>

Rutile is the second most abundant detrital mineral (Fig. 2.4B). Although rutile grains are generally similar to those of ilmenite, there is much less variation in grain
Figure 2.4: Detrital mineral grains contained in the sedimentary host rocks of the Three Crow roll-front uranium deposit. The grains show evidence for mechanical transport. A. Euhedral ilmenite grain with grain impressions, conchoidal fractures, irregular pits, and impact V’s. Sample H150C-3. B. Anhedral, rounded rutile grain exhibiting evidence for extensive chemical etching. The grain surface texture is typified by irregular pits and linear steps. Sample T810C-4. C. Euhedral garnet grain. The grain surface shows impact V’s and chemical pitting. Sample T810C-6. D. Euhedral zircon crystal with minor impact V’s, cracks, irregular pitting, and grooves. Sample H150C-5. E. Euhedral tourmaline grain with impact V’s and irregular pits. Sample T792C-2 F. Anhedral titanite grain with impact V’s and extensive chemical pitting. Sample H161C-8. All images are secondary electron images obtained on a scanning electron microscope. Scale bar is 25 µm for all images.
morphology and grain surface texture (Tables 2.2 and 2.3). Rutile typically forms sub-rounded anhedral grains with linear steps, chemical and irregular pitting, and impact V's. The combination of linear steps and chemical pitting results in a distinctive lattice structure. Less common are subhedral, rounded, or angular rutile grains. Euhedral grains are very rare.

Garnet grains range from 20 to 150 µm in size (Fig. 2.4C). They are most commonly subrounded or angular (Table 2.2). The most prevalent grain surface textures are conchoidal fractures and chemical pitting. Botryoidal grain surface textures are common, which have not been observed on any other detrital accessory mineral grains from Three Crow. Less common grain surface textures on garnet include steps, impact V's, grain impressions, and irregular pitting (Table 2.3).

The heavy mineral separates also contain abundant zircon (Fig. 2.4D). The zircon grains are typically euhedral and on average 60 µm in size. Subhedral grains are somewhat common and anhedral grains are very rare (Table 2.2). Grain surface textures observed on zircon grains include conchoidal fractures, impact V's, groves, irregular pitting, and cracks. Chemical pitting is very rare (Table 2.3).

In addition to zircon, many samples from Three Crow contain detrital tourmaline, which ranges from 50 to 200 µm in size. Tourmaline typically forms euhedral grains with rare conchoidal fractures, impact V's, and irregular pitting (Fig. 2.4E). Subhedral grains are rare and anhedral grains are very rare (Table 2.2). Steps, grooves, cracks, and chemical pitting are grain surface textures that have been occasionally observed (Table 2.3).

In addition to the minerals described above, titanite, staurolite, apatite, epidote, and monazite were also identified. These minerals only occur in minor abundances. Titanite is generally subhedral with rounded edges and irregular pitting (Fig. 2.4F). Staurolite is euhedral with some pitting, grooves and impact V's (Fig. 2.5A). Apatite grains are angular and anhedral with chemical and irregular pitting (Fig. 2.5B). Epidote forms rounded grains that show few characteristic grain surface textures (Fig. 2.5C). Monazite grains are typically euhedral to subhedral, displaying grooves and linear steps (Fig. 2.5D).
Table 2.3: Grain surface textures of common detrital minerals contained in the heavy mineral fraction of the sandstone host of the Three Crow roll-front uranium deposit, Nebraska. The table gives relative abundances for samples of different color groups.

<table>
<thead>
<tr>
<th>Detrital Mineral</th>
<th>Conchoidal Fractures</th>
<th>Arcuate Steps</th>
<th>Linear Steps</th>
<th>Impact V’s</th>
<th>Grooves</th>
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Notes: xxxxx = very abundant; xxx = abundant; xxx = common; xx = rare; x = very rare.
Table 2.3: Grain surface textures of common detrital minerals contained in the heavy mineral fraction of the sandstone host of the Three Crow roll-front uranium deposit, Nebraska. The table gives relative abundances for samples of different color groups, cont’d.

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Notes: xxxxx = very abundant; xxxx = abundant; xxx = common; xx = rare; x = very rare.
Figure 2.5: Detrital mineral grains contained in the sedimentary host rocks of the Three Crow roll-front uranium deposit. The grains show evidence for mechanical transport. A. Twinned euhedral staurolite crystal with irregular pits, grooves, and impact V’s. Sample T792C-1. B. Subhedral apatite grain with grooves, impact V’s, and extensive chemical pitting. Sample H161C-7. C. Subhedral epidote crystal with conchoidal fractures, impact V’s, grooves, and chemical etching. Sample H161C-10. D. Subhedral monazite grain with conchoidal fractures, irregular pitting, and chemical pitting. Sample H150C-16. All images are secondary electron images obtained on a scanning electron microscope. Scale bar is 25 µm for all images.
2.6.3 Authigenic Accessory Phases

Pyrite and marcasite, goethite, barite and gorceixite are the main authigenic minerals identified. As pyrite and marcasite are polymorphs, distinction between them could not be made using energy dispersive X-ray spectrometry on the scanning electron microscope. In grain mounts, both minerals were primarily distinguished based on crystal shape, which reflects crystal system, as pyrite is cubic while marcasite is orthorhombic. Selected grains were remounted and polished to allow unambiguous distinction under reflected light.

Based on grain morphology, three distinct types of authigenic pyrite were distinguished: framboidal, small blocky, and large blocky pyrite. These types of pyrite also show distinct internal textures.

Samples collected from the reduced side of the oxidation front commonly contain framboidal pyrite. Individual framboids range from 5 to 25 µm in size. They are composed of pyrite crystals that are one or two µm in size and have cubic, dodecahedral, or octahedral shapes. The framboids can form composite aggregates that range up to 100 µm in diameter (Fig. 2.6A and B; 2.7A). These aggregates are generally quite porous. The cement between framboids is composed of either pyrite or marcasite and sometimes of both minerals. Pyrite cement is slightly more common than marcasite. The cementing pyrite or marcasite typically only displays minor compositional zoning. In some cases, replacement of organic material by framboidal pyrite can be identified based on relict cell structure and the fact that framboidal aggregates resembles small pieces of roots or twigs (Fig. 2.6C; 2.7B).

Small blocky pyrite grains were found in some samples. The grains range from approximately 100 to 500 µm in size. They are composed of intergrown aggregates of dodecahedral pyrite crystals that range up to 10 µm in size (Fig. 2.6D). Grain surfaces that were in contact with framework grains are flaky or platy and typically lack the otherwise characteristic intergrowth of small euhehedral pyrite grains. These grain surfaces are also typically concave and display cast shapes of detrital grains such as quartz or feldspar. In cross-section, the small pyrite crystals forming the small blocky pyrite grains are typified by oscillatory zoning from As substitution. Individual growth
Figure 2.6: Morphological types of pyrite in the sedimentary host rocks of the Three Crow roll-front uranium deposit.  

A. Aggregate of frambooidal pyrite with a thin coat of small blocky pyrite. The internal structure of the frambooids can be seen on the broken surfaces. Sample H161C-9. Scale bar is 50 µm. 

B. Aggregate of frambooidal pyrite coated with a single layer of small blocky pyrite. Sample H161C-9. Scale bar is 50 µm. 

C. Frambooidal pyrite replacement of detrital organic material. The shape of the organic fragment, probably a root or twig, has been well preserved. Sample T792C-1. Scale bar is 50 µm. 

D. Small blocky pyrite displaying slight dissolution pits on the surface. The small blocky pyrite is cementing detrital quartz. Sample H161C-10. Scale bar is 50 µm. 

E. Large blocky pyrite grain composed of intergrown octahedral crystals. Sample T792C-1. Scale bar is 50 µm. 

F. Close up of a concave grain surface of large blocky pyrite that was originally in contact with a rounded detrital grain. The pyrite has been affected by chemical etching. Sample T792C-4. Scale bar is 25 µm. All images are secondary electron images obtained on a scanning electron microscope.
Figure 2.7: Morphological types of pyrite in the sedimentary host rocks of the Three Crow roll-front uranium deposit. A. Cross-section of the framboidal pyrite aggregate shown in Fig. 2.6B, showing the internal structure of the individual framboids and the thin coat of small blocky pyrite. The phase with the high contrast is lithium metatungstate, which is an artifact of the sample preparation. Sample H161C-9. Scale bar is 25 µm. B. Cross-section of the pyrite grain shown in Fig. 2.6C. Framboidal pyrite is replacing organic material, resembling a root or twig. The phase with the high contrast is lithium metatungstate, which is an artifact of the sample preparation. Sample T792C-4. Scale bar is 100 µm. C. Cross-section of a grain composed of small blocky pyrite crystals displaying oscillatory zoning. This zoning results from varying As content of the pyrite. Sample H150C-5. Scale bar is 25 µm. D. Cross-section of the pyrite grain shown in Fig. 2.6E. The large crystals visible from the outside form a coating on pyrite framboids that are cemented by small blocky pyrite. Sample T792C-1. Scale bar is 50 µm. All images are backscatter electron images obtained on a scanning electron microscope.
zones are one \( \mu m \) or less in thickness (Fig. 2.7C). Oscillatory zoning is typically well developed in samples collected close to the roll-front and less pronounced in small blocky pyrite occurring in reduced samples further downstream of the ore zone. The small blocky pyrite grains are generally quite porous and can cement framboidal pyrite or may form an up to 15 \( \mu m \) thick overgrowth on the framboidal pyrite (Fig. 2.6B; Fig. 2.7A). The small blocky pyrite never coats authigenic marcasite. Some small blocky pyrite grains represent overgrowths on detrital mineral grains.

Large blocky pyrite grains are composed of equant pyrite crystals (Fig. 2.6E). Depending on the size of the blocky pyrite crystals, the grains consist either of a single crystal or several intergrown crystals. Where these grains were in contact with the framework grains, the grain surfaces of the otherwise blocky grains resemble casts of the framework grains and are smooth, rounded, or concave. The 10 to 50 \( \mu m \) large euhedral pyrite crystals forming the large blocky pyrite grains are most commonly octahedra or cubes. In cross-section, the large blocky pyrite grains were found to show little compositional zoning. Sometimes faint oscillatory zoning can be observed (Fig. 2.7D). The large blocky pyrite grains often contain cores of framboidal pyrite (Fig. 2.7D). The grains can also form an overgrowth on pyrite grains composed of small blocky pyrite crystals and can coat large blocky marcasite grains described below. Large blocky pyrite grains also occur as cement between framework grains such as quartz and feldspar or overgrow detrital accessory minerals such as rutile.

In transitional and oxidized samples, the different types of pyrite grains described above show grain surface textures indicative of dissolution, including chemical pitting and etching of grain surfaces (Fig. 2.6F). Pitting and etching are typically confined to the grain surfaces of euhedral grains that were presumably exposed to oxidizing groundwater. Grain surfaces interpreted to have been in contact with framework grains only rarely display such dissolution grain surface textures.

Three textural types of marcasite were identified: platy, granular, and large blocky marcasite. The three types of marcasite also display characteristic internal textures. Platy marcasite grains are composed of intergrown marcasite crystals that have a platy habit (Fig. 2.8A). Intergrowth of the platy crystals typically resulted in the formation of
Figure 2.8: Morphological types of marcasite in the sedimentary host rocks of the Three Crow roll-front uranium deposit. A. Platy marcasite grain composed of three intergrown spheres. Sample T810C-2. Scale bar is 50 µm. B. Granular marcasite coating a framboidal pyrite grain. Sample T810C-3. Scale bar is 50 µm. C. Close up of granular marcasite. Small equant euhedral crystals of marcasite coating pyrite with a slightly pitted surface. Scale bar is 10 µm. D. Close up of granular marcasite. The individual radiating crystals have an elongated crystal habit. Sample H150C-3. Scale bar is 10 µm. E. Large blocky marcasite grain with blocky platy crystal habit. Sample H161C-5. Scale bar is 50 µm. F. Large blocky marcasite grain composed of intergrown euhedral crystals. Sample T810C-2. Scale bar is 100 µm. All images are secondary electron images obtained on a scanning electron microscope.
Figure 2.9: Morphological types of marcasite in the sedimentary host rocks of the Three Crow roll-front uranium deposit. A. Cross-section image of the spherical platy marcasite grain shown in Fig. 2.8A. Sample T810C-2. Scale bar is 25 µm. B. Cross-section image of the marcasite grain shown in Fig. 2.8B. The granular marcasite coats an aggregate of framboidal pyrite. Sample T810C-3. Scale bar is 25 µm. C. Cross-section image of a framboidal pyrite grain with a granular marcasite coating. The granular marcasite, forming a slightly brighter rim, coats small blocky pyrite which is cementing framboidal pyrite. Sample T810C-3. Scale bar is 25 µm. D. Cross-section image of the marcasite grain shown in Fig. 2.8F. The intergrown marcasite crystals have inclusions of detrital quartz (dark areas within the grain). Sample H161C-7. Scale bar is 50 µm. All images are backscatter electron images obtained on a scanning electron microscope.
nearly spherical aggregates. Individual platy marcasite grains are on average 40 µm in size, with most of the grains being composed of two to four individual spherical aggregates. In cross-section, platy marcasite does not display pronounced zoning (Fig. 2.9A).

Granular marcasite grains are composed of small marcasite grains that are equant or acicular in shape (Fig. 2.8B-D). Individual acicular crystals in the granular marcasite grains are up to 10 µm in length and two µm in width. In most cases, the granular marcasite forms a coating on earlier framboidal pyrite (Fig. 2.8B; 2.9B). The thickness of the coating of granular marcasite varies, but is typically less than 10 µm. The granular marcasite can form a coating on the small blocky pyrite (Fig. 2.9C). In some cases, the granular marcasite is overgrown by large blocky pyrite, with the overgrowth appearing to have an interlocking texture with the underlying marcasite.

The large blocky marcasite grains have the same general textural characteristics as the large blocky pyrite grains. They form up to 500 µm large aggregates that are composed of euhedral marcasite crystals (Fig. 2.8E and F). These crystals do not display pronounced compositional zoning in cross-section. The large blocky marcasite frequently cements framework grains in the sedimentary host rocks (Fig. 2.9D). In some cases, the large blocky marcasite is intergrown with, and overgrown by, the large blocky pyrite.

Similar to pyrite, marcasite contained in transitional to oxidized sedimentary rocks has been affected by partial dissolution. Granular and large blocky marcasite grains show abundant dissolution surface textures such as pitting and etching while platy marcasite only rarely displays evidence for dissolution.

Many of the samples collected upstream of the oxidation front contain abundant goethite (mineral identified by XRD on pulverized grains). This phase occurs as grains that are interpreted to represent pseudomorphs after Fe sulfides, as anhedral grains, or grain coatings (Fig. 2.10). Three types of grain surface textures have been recognized: acicular, globular, and irregular (Fig. 11). The acicular grain surface texture is most commonly developed on pseudomorphs and anhedral grains, but can also be found on grain coatings of goethite. The globular grain surface texture is most common on anhedral grains and on grain coatings. The irregular grain surface texture can have
Figure 2.10: Morphological types of goethite grains in the sedimentary host rocks of the Three Crow roll-front uranium deposit. A. Goethite after pyrite that is intergrown with a detrital quartz grain showing evidence for chemical etching. Some of the replaced pyrite grains appear hollow. Sample T797C-5. Scale bar is 25 µm. B. Anhedral goethite cementing detrital quartz and feldspar grains. Sample H150C-15. Scale bar is 200 µm. C. Acicular goethite grains coating an octahedral pyrite grain. Sample H150C-13. Scale bar is 25 µm. D. Goethite with a globular texture coating a detrital feldspar grain. Sample H150C-9. Scale bar is 25 µm. All images are secondary electron images obtained on a scanning electron microscope.
Figure 2.11: Grain surface textures of goethite grains in the sedimentary host rocks of the Three Crow roll-front uranium deposit. A. Acicular grain surface texture developed on a pseudomorph of frambooidal pyrite. Sample H150C-11. Scale bar is 2 µm. B. Globular surface texture of goethite coating a detrital grain. Individual globules of goethite are composed of small radiating crystals. Sample H150C-15. Scale bar is 10 µm. C. Globular grain surface texture of goethite forming a coating on detrital quartz and feldspar. Sample H150C-9. Scale bar is 10 µm. D. Lattice surface texture developed on goethite cementing detrital quartz. Sample H150C-15. Scale bar is 10 µm. All images are secondary electron images obtained on a scanning electron microscope.
a lattice-like appearance at high magnifications and is found exclusively on pseudomorphs and anhedral grains.

Goethite displays a variety of textures in cross-section, in many cases preserving the internal textures of Fe sulfides they have replaced, but not their grain morphology (Fig. 2.12). For instance, replacement of pyrite frambooids is often seen as frambooidal textures in goethite grains. Rare goethite pseudomorphs formed after the large blocky pyrite grains. In some cases, especially where the grains are anhedral, the replacement is incomplete with a remnant core of the Fe sulfide grain being preserved. Like the Fe sulfides it replaces, the goethite grains can cement framework grains such as quartz and feldspar or form a distinct overgrowth on both framework grains and Fe sulfide grains. In general, goethite grains are highly porous in section.

Energy-dispersive X-ray spectroscopy has shown that rare goethite grains contained in samples close to the roll-front are distinctly V-rich. Grains of V-rich goethite are composed of radiating acicular crystals. The individual radiating crystals may be intergrown to form aggregates that are not more than 50 µm in size.

Barite was recognized as an abundant authigenic mineral in some samples, where it forms intergrown grains or grain coatings. Single grains of barite range from subhedral to euhedral and are 10 to 150 µm in size. The surfaces of barite grains are generally smooth with rare chemical and irregular pitting. The <100 µm thick grain coatings of barite are typically composed of euhedral crystals. They overgrow detrital minerals such as quartz and feldspar or other authigenic phases, including pyrite and marcasite.

In addition to barite, goorceixite (BaAl₃(PO₄)(HPO₄)(OH)₆) was recognized (mineral identified by XRD on a powdered grain at the USGS). Individual grains of gorceixite are on average 250 µm in size, but never smaller than 100 µm. The grains are anhedral and the surfaces of the grains are spongy and very irregular. Most grains also contain abundant mineral inclusions of quartz and K feldspar. The abundant occurrence of mineral inclusions made identification of this mineral difficult. Electron microprobe analysis of the mineral was inconclusive as it returned low totals.
Figure 2.12: Morphological types of goethite grains in the sedimentary host rocks of the Three Crow roll-front uranium deposit. A. Cross-section image of goethite cementing detrital quartz and feldspar detrital grains. A remnant Fe sulfide core is visible as the slightly brighter area at the center of the grain, indicated that the goethite replaced a sulfide grain. Sample H150C-15. B. Goethite with globular surface texture coating a detrital quartz grain. Sample H150C-15. C. Goethite replacement of a framboidal pyrite grain that is coated by small blocky pyrite. Pseudomorphs of both pyrite morphologies are clearly visible in the center of this grain. Sample H150C-15. D. Replacement of a Fe sulfide grain by goethite. The bright phase in the center of the grain is the remnant Fe sulfide. The goethite is quite porous. Sample H150C-15. All images are backscatter electron images obtained on a scanning electron microscope. Scale bar is 25 µm for all images.
The mineral was found to be highly sensitive to electron beam and was rapidly
damaged during analysis, presumably due to its volatile content. The goerceixite is
highly porous in section and contains abundant inclusions of quartz and potassium
feldspar. No replacement textures were recognized.

Several other authigenic minerals were identified, often only representing one or
two grains in the heavy mineral separates of a given sample. Hematite occurs as
subhedral crystals that are on average about 40 µm in size. The hematite can contain
small inclusions of detrital minerals. Sphalerite occurs as subhedral to anhedral grains
with an average grain size of 80 µm. In rare cases, the sphalerite cements quartz and
feldspar grains; however, it more commonly forms single crystals. Chalcopyrite was
found in only two samples. One grain was a single subhedral crystal. The other grain
was subhedral and composed of smaller crystallites. Celestine was found in a few
samples and occurs as subhedral to anhedral grains that are on average 50 µm in size.
The surfaces of celestine grains are typically highly pitted.

2.6.4 Trace Element Composition of Authigenic Pyrite and Marcasite

The different types of pyrite and marcasite were characterized chemically by LA-
ICP-MS analysis (Table 2.4). Although a large number of trace elements can be
analyzed using this technique, only six elements (As, Co, Mn, Mo, Ni, and Pb) could be
routinely detected in the various grain types at a level that allowed statistical analysis.
Of the six elements routinely detected, only As, Mo, and Mn showed significant variation
between the different types of grain morphologies. As the grain sizes of the platy and
granular marcasite grains were typically smaller than the spot size of the laser, only few
markasite grains of these types could be analyzed.

Trace element analysis showed that pyrite has on average higher As
concentrations than marcasite (Fig. 2.13). However, the highest concentrations of As
were encountered in two spot analyses of the platy marcasite grains. Of the other
sulfide grain types, the small blocky pyrite grains have the highest As concentrations.
Spot analysis confirmed that the zoning patterns of these grains visible in backscatter
electron images are related to the As content with the high contrast areas
Table 2.4: Trace element concentrations of pyrite and marcasite from the Three Crow roll-front uranium deposit, Nebraska. Analyses were performed by LA-ICP-MS analysis (all data in ppm; - = below detection limit).

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Table 2.4: Trace element concentrations of pyrite and marcasite from the Three Crow roll-front uranium deposit, Nebraska. Analyses were performed by LA-ICP-MS analysis (all data in ppm; - = below detection limit), cont’d.

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Figure 2.13: Box-and-whisker plot representation of trace element abundances in the different morphological types of pyrite and marcasite recognized in the sandstone host of the Three Crow roll-front uranium deposit, Nebraska. The box encloses the interquartile range (the values in the 2nd and 3rd quartiles) with the median displayed as a line. The vertical lines extending outside the box mark the minimum and maximum values that fall within the acceptable range (defined as 1.5 times the interquartile range). Individual points are considered to be outliers. All data were obtained by LA-ICP-MS analyses. The number of analyses are given in the figure.
corresponding to the highest As concentrations (Fig. 2.7C). Molybdenum concentrations, though lower on average than As, show a similar distribution pattern. Pyrite generally has higher average Mo concentrations than marcasite with the small blocky pyrite grains having the highest Mo concentrations on average. In contrast to As and Mo, Mn concentrations were generally higher in marcasite than in pyrite. The highest Mn levels were encountered in the blocky marcasite grains.

Although the concentrations of Co, Ni, and Pb are variable, no consistent trends were observed, linking grain morphology with the abundance of these trace elements. The pyrite framboids have the highest median concentrations of Co, Ni, and Pb while the large blocky marcasite and the large blocky pyrite grains have similar median concentrations of these three elements. The small blocky pyrite grains have the lowest median concentration of Co, Ni, and Pb (Fig. 2.13).

### 2.6.5 Distribution of Accessory Minerals Across the Roll-front

There are no systematic changes in the abundance of detrital minerals across the roll front (Table 2.5). Figure 2.14 shows the relative abundances of ilmenite, rutile (or anatase), garnet, zircon, and tourmaline in the different sample color groups. Ilmenite forms approximately 30 wt.% of the detrital minerals present in the samples from the Chamberlain Pass Formation while rutile is slightly less abundant in the different sample color groups. Garnet and zircon show broadly similar relative abundances. Tourmaline is a slightly less common accessory mineral, with the median values of the different sample color groups ranging from 12 to 15 wt.%.

In contrast to the detrital phases, the relative abundance of authigenic accessory minerals varies significantly across the roll-front (Fig. 2.14; Table 2.5). The mineralogical composition of the authigenic mineral fraction contained in strongly reduced dark green to gray and reduced light gray samples is dominated by pyrite and marcasite, with individual samples containing from 98 to 100 wt.% pyrite and marcasite. Goethite generally only occurs in traces. Small amounts of barite and gorceixite are present in most samples.
Table 2.5: Relative abundances of detrital and authigenic minerals in the heavy mineral fraction of the sandstone host of the Three Crow roll-front uranium deposit, Nebraska (in wt.% as determined by Qemscan).

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Table 2.5: Relative abundances of detrital and authigenic minerals in the heavy mineral fraction of the sandstone host of the Three Crow roll-front uranium deposit, Nebraska (in wt.% as determined by Qemscan), cont’d.

<table>
<thead>
<tr>
<th></th>
<th>Ilmenite</th>
<th>Rutile</th>
<th>Garnet</th>
<th>Tourmaline</th>
<th>Zircon</th>
<th>FeSulfide</th>
<th>Goethite</th>
<th>Barite</th>
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<tr>
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<td>6.2</td>
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</tr>
<tr>
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<td></td>
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</tr>
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<tr>
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<td>5.2</td>
<td>0.1</td>
<td>3.4</td>
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</table>
Table 2.5: Relative abundances of detrital and authigenic minerals in the heavy mineral fraction of the sandstone host of the Three Crow roll-front uranium deposit, Nebraska (in wt.% as determined by Qemscan), cont’d.

<table>
<thead>
<tr>
<th></th>
<th>Ilmenite</th>
<th>Rutile</th>
<th>Garnet</th>
<th>Tourmaline</th>
<th>Zircon</th>
<th>FeSulfide</th>
<th>Goethite</th>
<th>Barite</th>
<th>Gorceixite</th>
<th>Others</th>
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</thead>
<tbody>
<tr>
<td><strong>Yellow to red</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>H161C-5</td>
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<td>7.0</td>
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<td>0.7</td>
<td>1.3</td>
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</tr>
<tr>
<td><strong>Pierre Shale</strong></td>
<td></td>
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</tr>
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</table>
Figure 2.14: Box-and-whisker plot representation of the relative mineral abundances of detrital and authigenic minerals in the heavy mineral fractions of the sandstone host of the Three Crow roll-front uranium deposit, Nebraska. See Figure 2.13 for a description of the box-and-whisker plots. Number of samples in each category is shown in parentheses. A. Relative abundances of detrital minerals in samples belonging to different color groups. No significant differences between the different color groups. B. Relative abundances of authigenic minerals. Pronounced variations can be observed for samples belonging to different color groups.
Iron sulfides are distinctly less abundant in the grayish yellow samples that were sampled from the transition zone between the reduced environment downstream of the roll-front and the oxidized zone further upstream (Fig. 2.14). Pyrite and marcasite collectively account for 76 to 100 wt.% of the authigenic phases present. Goethite is more abundant, comprising <1 to 22 wt.% of the authigenic minerals contained in the samples. Barite is present in small concentrations. Only few grains of gorceixite occur in the samples of this color group.

The strongly oxidized, yellow to red samples upstream of the ore zone contain variable, but generally high amounts of goethite. The concentrations of this mineral in the samples ranges from 1 to 96 wt.%. Although pyrite and marcasite are abundant in some samples, the median Fe sulfide content is only 12 wt.%. Barite and gorceixite occur in significant concentrations in some oxidized samples.

Figure 2.15 shows how the different Fe-bearing authigenic minerals are distributed with respect to the zone of roll-front uranium enrichment at Three Crow. The pre-ore framboidal pyrite is finely dispersed throughout the matrix of the sedimentary rocks. It occurs in detectable quantities in the samples from the mineralized zone as well as the proximal and distal holes drilled on the reduced side of the roll-front. The abundance of pyrite framboids decreases significantly across the zone of uranium enrichment. Upstream of the roll-front, pre-ore pyrite is rare due to the nearly complete oxidation of the host rocks.

The small blocky pyrite occurs primarily in the central section of the mineralized hole. Comparably few small blocky pyrite grains have been identified downstream of the ore zone. In comparison to the framboidal pyrite and the small blocky pyrite, the platy and granular marcasite grains are not common at Three Crow. They typically comprise <10 % of the Fe sulfide minerals contained in reduced and transitional samples. Their highest abundances are registered in the samples from the mineralized hole and the two holes further down-stream.

Large blocky marcasite represents the most common type of marcasite. This type of marcasite occurs in close association with the roll-front ore zone. It is the most abundant Fe sulfide in samples also showing elevated U concentrations. This type of marcasite is also abundant downstream of the roll-front, although its relative
Figure 2.15: Distribution of pyrite, marcasite, and goethite in five research drill holes intersecting the host rock strata of the roll-front at Three Crow. The mineral abundances in the heavy mineral fractions were determined by automated quantitative phase analysis. Different morphological types of pyrite and marcasite were distinguished by reflected light microscopy on the same samples. The black lines give the relative abundance of these minerals in the heavy mineral fraction.
abundance decreases with increasing distance from the ore zone. Some of the reduced to transitional samples collected upstream of the roll-front also contain large blocky marcasite.

The distribution of large blocky pyrite across the roll-front is generally similar. However, there is no correlation with the whole-rock U content. The occurrence of large blocky marcasite and large blocky pyrite in the distal reduced drill hole suggests that that drill hole T810C was drilled too close to the roll front to represent truly unmodified background. It would be expected to find only minerals associated with diagenesis in unmodified sediments, such as diagenetic pyrite; however that is not the case here.

As expected, goethite grains are most commonly encountered upstream of the oxidation front. Goethite is the most abundant accessory mineral in oxidized samples, especially in highly permeable coarse-grained rocks of the Chamberlain Pass Formation.

2.7 Discussion

2.7.1 Timing of Accessory Mineral Formation and Alteration

The textural criteria used in the present study permitted unequivocal distinction between detrital and authigenic phases present in the sedimentary host rocks of the Three Crow deposit. Distinction was based on grain morphology and grain surface textures. Accessory mineral grains showing evidence for mechanical transport and rounding clearly represent detrital phases as delicate grain morphologies could not have survived transport in the sedimentary environment. Grain surface textures suggestive of impact and sedimentary transport such as conchoidal fractures, arcute and linear steps, impact V’s, and grooves provide further evidence for a detrital origin of accessory minerals such as ilmenite, rutile, garnet, zircon, and tourmaline. In addition to the textural evidence, the quantitative phase analysis showed that the relative abundance of these detrital phases does not vary significantly across the roll-front. As there is no direct correlation with sample color, the observed variations in mineral abundances between samples are probably related to depositional processes rather than post-
depositional modification. Although evidence for chemical etching of the detrital mineral grains has been observed, this process was quantitatively only of minor importance. Chemical etching may be related to diagenesis of the sedimentary rocks or possibly even the low-temperature processes of uranium enrichment.

Authigenic minerals lack evidence for transport in the sedimentary environment. The grains are often characterized by delicate grain morphologies and grain surface textures that would not have survived transport. Authigenic minerals commonly form a cement around detrital phases with casts of these grains being preserved. Textural relationships, combined with spatial constraints, suggest that the different authigenic minerals contained in the sedimentary rocks formed at different times with respect to the uranium enrichment. Authigenic minerals can be classified as having formed either pre-ore, most likely during the diagenesis of the sedimentary rocks, or syn-ore as a result of the roll-front formation. Changes in the oxidation state across the roll-front resulted in the development of pronounced variations in the distribution of authigenic minerals such as pyrite, marcasite, and goethite. There is no evidence for the formation of post-ore accessory minerals. The distribution of authigenic accessory minerals correlates with sample color, implying that re-reduction of the sedimentary rocks did not occur at Three Crow.

2.7.2 Constraints on the Provenance of the Sedimentary Rocks

The Chamberlain Pass Formation is likely of mixed provenance. The predominance of quartz, plagioclase, and potassium feldspar framework grains in the sedimentary rocks implies that the detrital material was largely derived from felsic sources. This is consistent with ilmenite, rutile, and zircon being among the most abundant detrital accessory phases. The sedimentary rocks also contain lithic fragments of chert, quartzite, and schist. Chert is the most common lithic fragment. A contribution from a metamorphic source is consistent with the presence of garnet, tourmaline, staurolite, and epidote as detrital accessory phases. Garnet and tourmaline may also be sourced from felsic intrusive rocks.
Variations in grain morphologies can be explained by the deviating mineralogical properties of the different detrital accessory phases. Ultrastable minerals such as zircon and tourmaline mostly form euhedral grains, with only a small percentage of the grains being fully rounded. Less stable minerals such as ilmenite, rutile, and garnet are more commonly subhedral or anhedral with a significant proportion of the grains being rounded or sub-rounded. Angular anhedral grains are common for garnet. Unstable detrital minerals include apatite, epidote, and monazite. All detrital minerals show a superimposition of grain surface textures of mechanical and chemical abrasion. Almost all apatite grains have been affected by chemical pitting and partial dissolution. Grain surface textures of chemical origin are also commonly developed on rutile and garnet.

Although differences in the grain morphologies can largely be accounted for by the mineralogical nature of the grains, it is important to note that there are some variations in grain morphologies and grain surface textures for individual minerals, implying different histories and possibly provenance for individual grains. For example, the majority of the observed grains of the mechanically ultrastable minerals zircon and tourmaline are euhedral. However, a small number of well rounded zircon and tourmaline grains have been observed. Rounding of these grains is probably a result of polycyclic transport. This implies that they originated from reworked sedimentary rocks (cf. Krynine, 1946) while the euhedral grains clearly did not undergo equally extensive reworking.

Previous reconstructions of the paleodrainage in the foreland of the Rocky Mountains during the late Eocene also suggest a mixed provenance for the sedimentary rocks of the Chamberlain Pass Formation. Swinehart et al. (1985), Evans and Terry (1994), as well as Terry (1998) showed that the up to 40 kilometers wide fluvial system depositing the sandstones of the Chamberlain Pass Formation stretched over a distance of at least 240 km from Wyoming in the northwest through Nebraska and Colorado in the southeast. The fluvial system entered present-day Nebraska in northwest Sioux County, turning southeast in the deposit area in western Dawes County (Fig. 2.1B), presumably because the Chadron arch to the east was a topographic high at the time (Swinehart et al., 1985; Gjelsteene and Collings, 1988). According to these reconstructions, the clastic material forming the sandstone of the Chamberlain Pass
Formation was most likely sourced from the Black Hills, which are composed of Precambrian igneous and metamorphic rocks and a carapace of Paleozoic to Mesozoic sedimentary rocks. However, it is possible that at least some of the detrital material was also derived from the Hartville Uplift or even the Laramie Mountains to the west (Stanley, 1976; Stanley and Benson, 1979; Seeland, 1985; Evans and Terry, 1994).

2.7.3 Diagenesis of the Sedimentary Rocks

The sedimentary rocks hosting the Three Crow deposit have undoubtedly been affected by diagenetic processes. The most important manifestation of diagenesis in the sandstones is the formation of calcite cementing the framework grains. Framboidal pyrite may also be of diagenetic origin. All other morphological types of pyrite and marcasite recognized at Three Crow overgrow framboidal pyrite or contain small cores of pyrite framboids, suggesting that framboidal pyrite formation was early in the paragenesis and presumably predated roll-front uranium enrichment in the Chamberlain Pass Formation.

Experimental studies have shown that framboidal pyrite can form through several different crystallization pathways (Sweeney and Kaplan, 1973; Wilkin and Barnes 1997; Butler and Rickard, 2000; Ohfuji and Rickard, 2005). While the exact mechanism for the development of the framboidal texture in sedimentary rocks such as those hosting the Three Crow deposit may not be easily identifiable, the pyrite framboids must have formed in an environment of extreme pyrite supersaturation where pyrite nucleation is greater than the rate of crystal growth (Wang and Morse, 1996; Butler and Rickard, 2000; Ohfuji and Rickard, 2005).

LA-ICP-MS analyses of the framboidal pyrite at Three Crow showed that the pre-ore pyrite is distinctly enriched in Co, Ni, and Pb in comparison to the other morphological types of pyrite and marcasite. Other detectable trace elements in the framboidal pyrite include As, Mn, and Mo. Similar element enrichment patterns of framboidal pyrite have been reported from other geological setting. Framboidal pyrite contained in carbonaceous mudstone and siltstone is commonly enriched in As, Co, Cu, Mn, Mo, Ni, Pb, V, and Zn (Guy et al., 2010; Large et al., 2007, 2009, 2012; Tuttle et al.,
Framboidal pyrite contained in coals of the Appalachian Basin show a depletion in As, Hg, and Se, but enrichment in Co, Cu, Ni, Pb, and Zn (Diehl et al. 2004, 2005, 2012).

The trace element content of diagenetic pyrite, especially elevated concentrations of As, Co, Cu, Mo, Ni, Pb, V, and Zn is a reflection of the concentration of these elements in sedimentary rocks that are rich in organic matter (Wood, 1996; Coveney, 2000; Algeo and Maynard, 2004; Rimmer, 2004). These elements are readily absorbed onto organic matter in anoxic environments and subsequently partition into pyrite formed during diagenesis (Raiswell and Plant, 1980). At Three Crow, framboidal pyrite is typically finely dispersed throughout the matrix of the sedimentary rocks, which contain 0.01 to 1.76 wt.% organic carbon. At least locally, framboidal pyrite formed through direct replacement of organic material such as small pieces of roots or twigs. This observation suggests that organic material played an important role as an initial reductant of sulfate contained in the pore water (cf. Spirakis, 1996). The low sulfur isotopic values (-12 to -27‰ $\delta^{34}$S) suggest that framboid formation in the host rocks of Three Crow involved microbial processes (A. Martin and M. Fayek, personal communication 2012).

### 2.7.4 Accessory mineral formation associated with roll-front mineralization

The study of the grain surface textures showed that detrital mineral phases have not been significantly influenced by chemical processes associated with roll front uranium enrichment. The abundance of grain surface textures of chemical origin does not vary systematically across the roll-front and the relative abundance of detrital phases in the sedimentary rocks does not correlate with rock color. Even ilmenite, a mineral that can undergo alteration in the roll-front environment (Reynolds and Goldhaber, 1978), does not show evidence for chemical alteration at Three Crow.

In contrast to the detrital minerals, the authigenic heavy minerals show significant variations across the roll-front in terms of relative abundance, grain morphology, and grain surface textures. Pyrite and marcasite are the most abundant authigenic minerals on the distal and proximal downstream side of the roll-front and within the ore zone
while goethite is predominant in the altered sandstone tongue upstream of the zone of uranium enrichment.

The occurrence of ore-stage pyrite and marcasite has been previously noted in a number of roll-front uranium deposits (Melin, 1964; Reynolds and Goldhaber, 1978, 1983; Reynolds et al., 1982; Min et al., 2005). It has been well established that marcasite represents a metastable mineral with respect to pyrite. Based on the work by Reynolds and Goldhaber (1983) and Murowchick and Barnes (1986), it is widely accepted that these minerals form under different pH conditions with different types of sulfur species being present. Formation of marcasite appears to be favored by acidic conditions, relatively high concentrations of elemental sulfur, and low concentrations or absence of polysulfide species. In contrast, pyrite formation more likely occurs in mildly acidic to basic environments that are typified by the predominance of polysulfide species.

The textural observations made at Three Crow suggest that the different types of pyrite and marcasite present in the sedimentary rocks of the Chamberlain Pass Formation formed at different times and locations with respect to the oxidation front. The overgrowth relationships imply that the formation of framboidal pyrite predated precipitation of all other types of pyrite and marcasite. As this type of pyrite was formed during diagenesis of the sedimentary rocks, it is likely that the framboidal pyrite was more or less evenly distributed throughout the sedimentary host rocks prior to fluid flow associated with the roll-front mineralization.

The framboidal pyrite is overgrown and cemented by the small blocky pyrite. This type of pyrite is most abundant in samples collected from the drill hole penetrating the roll-front, suggesting that the formation of the small blocky pyrite was related to the roll-front mineralization. Precipitation of the small blocky pyrite grains must have occurred in an environment of pyrite saturation, with the rate of crystal nucleation exceeding the rate of crystal growth. At the same time, the pyrite must have formed in a near neutral to slightly alkaline environment. Nutrients required for the formation of the small blocky pyrite must have been supplied from groundwater flowing through the aquifer as the small blocky pyrite is not replacing pre-existing detrital or authigenic minerals. It is likely that the groundwater causing formation of the small blocky pyrite
was initially oxidizing, causing oxidation of pre-ore framboidal pyrite upstream of the reduced conditions prevailing in the area where the small blocky pyrite deposited. Metals transported by the ground water were reincorporated into the small block pyrite, which is typified by high As and Mo concentrations. Experimental studies have shown that authigenic arsenian pyrite can indeed form at low-temperature conditions from ground waters having low As concentrations (Wolthers et al., 2005).

Formation of the small blocky pyrite was postdated by the formation of granular marcasite, which locally coats the small blocky pyrite. No conclusive textural relationships have been found allowing the establishment of the paragenetic relationships between the granular marcasite, the platy marcasite, and the large blocky marcasite. However, all three types of marcasite must have formed prior to the large blocky pyrite. In some cases, the large blocky marcasite is directly overgrown by large blocky pyrite, which is the youngest type of Fe sulfide formed at Three Crow. This textural observation suggests that the large blocky marcasite is the youngest type of marcasite.

The formation of marcasite in close spatial association with the zone of uranium enrichment implies that roll-front mineralization occurred under acidic conditions. The decrease in pH is probably related to the sustained oxidation of pre-ore pyrite upstream of the site of uranium enrichment, which would not only have brought iron and sulfur species into solution that re-precipitated as syn-ore marcasite, but would also produce acidity (Granger and Warren, 1969; Reynolds and Goldhaber, 1983).

The inferred pH conditions are consistent with solubility constraints of coffinite, which is the dominant ore mineral at Three Crow (A. Martin and M. Fayek, personal communication 2012) and the nearby Crow Butte deposit (Hansley et al., 1989; Stewart, 2002). Figure 2.16 shows the Eh-pH diagram for the U-Si-C-O-H system overlain with the stability fields of FeS$_2$ based on the Fe-S-O-H system and UO$_2$ of the U-O-H system (cf. Brookings, 1988). The plot illustrates that the stability of coffinite is highly dependent on the activity of silica in the groundwater. At high silica activity, coffinite is stable up to pH 9 under reducing conditions while the stability field is reduced to just below pH 7 at lower silica activity. Under the low pH conditions required for marcasite formation, coffinite can co-precipitate with marcasite, irrespective of silica activity.
Goldhaber et al. (1987) showed that surface adsorption reactions, leading to the precipitation of coffinite, are in fact favored under such conditions.

Figure 2.16: Eh-pH diagram for the system U-Si-C-O-H. Assumed activities for dissolved species are: U=10^{-8}, C=10^{-3}, Si=10^{-1} and 10^{-3.5}. The diagram also shows the stability of FeS_{2} in the system Fe-S-O-H. The assumed activities of dissolved species are Fe=10^{-6}, S=10^{-3} (modified from Brookins, 1988). The plot illustrates that coffinite and marcasite or pyrite could coexist under reducing conditions over a relatively wide range of pH values.

The grain size of the large blocky marcasite suggests that supersaturation of Fe sulfide minerals was not attained during uranium enrichment and that the rate of crystal
growth was larger than the rate of nucleation. Marcasite precipitation in association with the roll-front mineralization must have involved microbial processes as ore-stage Fe sulfides at Three Crow have $\delta^{34}S$ values that are as low as $-52$ to $-55\%$ (A. Martin and M. Fayek, personal communication 2012).

Over time, preexisting Fe sulfides must have been almost completely converted to goethite upstream of the mineralization within the altered sandstone tongue. In most cases, there are no remnant textures or pseudomorphs preserved. However, where present, goethite appears to replace pre-ore framboidal pyrite and possibly the early, small blocky pyrite. There is no evidence that the goethite have replaced marcasite.

Towards the end of the mineralizing event, the physicochemical environment of sulfide formation must have undergone another change. The large blocky pyrite was the last sulfide mineral that precipitated at Three Crow. This type of pyrite was never found to overgrow goethite, implying that its formation still occurred in association with the roll-front. This suggests that pH conditions returned to neutral to slightly alkaline conditions, presumably similar to modern groundwater that has a pH between 7.8 and 8.8 (Crow Butte Resources Inc., unpub. data 2010). The return to near neutral to slightly alkaline conditions suggests that sulfide oxidation upstream of the mineralization was nearly complete and that acidity was no longer produced by this process. At the same time, uranium precipitation was probably coming largely to a halt, which would also have contributed to the inferred rebound in pH. A decrease in available nutrients in the groundwater is suggested by the large size of the euhedral grains of the large blocky pyrite, implying that pyrite supersaturation could not be achieved late in the paragenesis as pyrite oxidation upstream of the mineralization was slowing down.

The youngest authigenic mineral found in the host aquifer of the Three Crow deposit is barite. Euhedral barite was observed as individual grains and forming overgrowths on quartz, pyrite, and goethite. Authigenic sulfate minerals such as barite and gorceixite occur in sedimentary rocks of different color, suggesting that the oxidation state of the rocks was not a primary control on the occurrence of these minerals.
2.7.5 Influence of Accessory Minerals on Whole-rock Geochemistry

The findings of the present study suggest that the heavy mineral fraction must exert important controls on the whole-rock geochemical signature of the sedimentary rocks at Three Crow and variations in chemical parameters across the roll-front.

Most notably, the detrital mineral content must influence the abundance of the high-field strength elements in the whole-rock samples. Zircon represents the only major Zr- and Hf-bearing mineral identified in the sedimentary rocks. Ilmenite and rutile are important carriers of Ti, Nb, and Ta while detrital phases such as apatite, garnet, monazite, and zircon contain abundant rare earth elements. Previous investigations by Bea (1996) have shown that these minerals also dominate the rare earth element patterns of felsic igneous rocks that are interpreted to be the primary source for the sedimentary rocks of the Chamberlain Pass Formation. As there are no systematic changes in the abundance of these detrital phases across the roll-front with chemical etching of these detrital phases being quantitatively unimportant, the high-field strength elements must largely behave as immobile elements in the low-temperature environment of roll-front formation.

These observations suggest that chemical vectoring to roll-front uranium enrichment is probably only possible using chalcophile or organophile elements in systems similar to Three Crow. The accessory mineral study implies that the bulk of the whole-rock sulfur content is contained in authigenic pyrite and marcasite although sulfate minerals may also be important in some samples. In the reduced dark green to gray rocks downstream of the roll-front and the light gray rocks of the ore zone, where pyrite and marcasite are most abundant, the Fe/S ratio must be low, but increase significantly in the oxidized grayish yellow and yellow to red samples upstream of the ore zone where most of the Fe sulfides have been converted to goethite. It can also be predicted that the total iron and sulfur contents of the whole-rock samples are highest in the reduced samples proximal to the ore zone that are typified by the presence of abundant authigenic pyrite and marcasite. Chemical analysis of the whole-rock samples showed that these relationships can indeed be observed at Three Crow.
LA-ICP-MS analysis of the authigenic pyrite and marcasite demonstrated that these minerals contain significant amounts of As, Co, Mn, Mo, Ni, and Pb. Diagenetic pyrite contains the highest amount of Co, Ni, and Pb, while syn-ore pyrite and marcasite are distinctly enriched in As, Mn, and Mo. Based on the distribution of pyrite and marcasite across the roll-front, it can be predicted that these elements are likely to show noticeable variations across the roll-front at Three Crow, potentially allowing their use as chemical vectors. It is also important to note that oxidation of the host rocks during in-situ mining could mobilize a significant amount of As, Co, Mn, Mo, Ni, and Pb from the ore zone due to oxidation of pyrite and marcasite. Trace amounts of Cu and Zn may also be mobilized, which are largely hosted by chalcopyrite and sphalerite.

2.7.6 Implications to the Roll-front Deposit Model

The results of the present study indicate that the oxidation front at Three Crow was essentially stagnant during deposit formation and has been since. Replacement relationships show that the goethite in the oxidized sandstone tongue upstream of the ore zone primarily replaced pre-ore framboidal pyrite. There is no textural evidence for extensive replacement of marcasite, which would be expected if the ore front would continuously move down the hydrological gradient due to progressive oxidation of the aquifer.

Two possibilities can be invoked to explain the observed relationships. Firstly, it is possible that the oxidation front has been fixed in its current position for a prolonged period of time. This would likely only be possible if an external reductant is supplied to the site of uranium precipitation as the total amount of organic carbon and pre-ore framboidal pyrite contained in the aquifer would probably not have been able to reduce enough groundwater to precipitate over 5 million pounds of uranium in a relatively small area. It is possible that the upflow of hydrocarbons from deeper parts of the basin along a hitherto unrecognized fault could have provided sufficient amounts of external reductant to the aquifer, allowing deposit formation along a stagnant oxidation front. Models invoking an external hydrocarbon source have been previously suggested for
some roll-front uranium deposits (Goldhaber et al., 1983; Jaireth et al., 2008; Hancock, 2012).

Alternatively, it appears possible that the roll-front at Three Crow may have indeed migrated down a hydrological gradient, but periodically rather than continuously. In such a case, the roll-front could have moved quickly during periods of high groundwater flow (i.e., climatic periods of increased precipitation), but may have become stagnant during periods of diminished groundwater flow (i.e., climatic periods of semiarid to arid conditions). If roll-front movement occurred periodically over significant distances within geologically short times, the location of the previous oxidation front would likely have been outside the current deposit area.

2.8 Conclusions

Over the past two decades comparably little research has been carried out on roll-front uranium deposits as mining low-grade uranium enrichments in sandstones has not been economically viable. As a consequence, few scientific studies employing modern analytical techniques have been conducted on these types of deposits. The present study, which is based on state-of-the-art scanning electron microscopic techniques, provided new insights into the mineralogy of accessory phases contained in the sedimentary host rocks of the Three Crow roll-front uranium deposit in Nebraska.

Detrital and authigenic accessory minerals were distinguished based on grain morphology and grain surface textures. It is shown that the authigenic accessory phases display a characteristic distribution pattern across the oxidation front and the zone of uranium enrichment. Classification of grain morphologies revealed that different types of pyrite and marcasite are present that formed at different times with respect to the roll-front mineralization. Establishing the paragenetic sequence between the different types of Fe sulfides allowed important conclusions on the processes of uranium enrichment at Three Crow. It is shown that pre-ore pyrite is typically framboidal in nature. Marcasite formation coincided with the precipitation of coffinite in the roll-front, implying that mineralization occurred under slightly acidic conditions. Rebound to near neutral or slightly alkaline conditions resulted in late ore-stage pyrite formation.
The different types of pre-ore and syn-ore pyrite and marcasite are characterized by different trace element compositions.

The textural evidence suggests that the roll-front at Three Crow was essentially stagnant throughout its formation, which is inconsistent with deposit models assuming that roll-fronts move gradually down a hydrological gradient. The present study also demonstrates that the study of accessory minerals can be used to test whether late re-reduction of the sedimentary host rocks must have occurred, which is critical in roll-front uranium exploration. At Three Crow, there is no textural evidence suggesting that the re-reduction of the host aquifer occurred after roll-front mineralization.
CHAPTER 3
RADIATION DAMAGE IN QUARTZ FROM THE THREE CROW ROLL-FRONT
URANIUM DEPOSIT, NEBRASKA

Modified from a paper submitted to *American Mineralogist*.
Julie Leibold, Thomas Monecke, Brian Gorman, and Jens Götze

3.1 Abstract

Cathodoluminescence microscopy of the sandstone host of the Three Crow roll-front uranium deposit, Nebraska, revealed that detrital quartz grains have been affected by extensive natural radiation-induced damage. Based on textural relationships, different types of radiation damage were distinguished, not all of which are related to the epigenetic roll-front uranium mineralization. In many detrital quartz grains, bright orange-yellow radiation damage halos visible in cathodoluminescence can be related to primary inclusions of zircon and monazite. The halos surrounding these inclusions are commonly circular to elongate and may show concentric rings caused by the different penetration depths of alpha particles originating from the uranium and thorium decay series. Damage halos surrounding entire quartz grains occur only in sandstone samples with elevated uranium contents (>100 ppm). The width of these halos corresponds to the penetration depth of alpha particles emitted by the uranium decay series, suggesting that damage halos surrounding entire grains formed in association with the roll-front mineralization.

Spectral investigations on the pristine and damaged portions of detrital quartz grains showed that the change in cathodoluminescence color is caused by an intensity increase of the ~650 nm emission band and a slight decrease in the intensity of the blue emission band, which is related to the generation of non-bridging oxygen hole centers during alpha particle bombardment of the quartz. Damage of the crystal structure within the radiation halos also resulted in peak broadening of the quartz Raman peak at 466 cm\(^{-1}\). Raman mapping of a radiation damage halo confirmed that the halo detected by cathodoluminescence microscopy corresponds to a zone of structural damage.
Transmission electron microscopy revealed the presence of abundant alpha tracks within these zones of structural damage.

The cathodoluminescence observations have important implications for the understanding of the ore-forming processes at Three Crow. As radiation damage halos surrounding detrital quartz grains have only been observed in mineralized samples, but not upstream of the roll-front in the oxidized aquifer, it is concluded that the roll-front is not slowly moving down-dip as predicted by the roll-front uranium deposit model. The lack of radiation damage outside the immediate ore zones is related to the fact that dosage accumulation from uranium-bearing groundwater is insufficient to produce radiation halos visible by cathodoluminescence microscopy, which is confirmed by a model dosage calculation. Damage halos around detrital grains can only develop in a stagnant ore zone. In roll-front uranium deposits, cathodoluminescence microscopy can, therefore, not be used to reconstruct the flow path of the uranium-bearing groundwater. However, this technique is capable of detecting former ore zones from which uranium has been remobilized.

3.2 Introduction

Roll-front uranium deposits are a globally important uranium resource and a growing target for new exploration worldwide due to their amenability to in-situ mining (Kyser and Cuney, 2008). The deposits form in laterally permeable sandstone units that act as aquifers within intramontane basins. Oxygenated groundwater flowing down the hydrological gradient oxidizes the sandstone aquifer and leaches metals such as uranium along its flow path. Uranium is precipitated when the groundwater encounters reduced conditions within the aquifer, forming crescent-shaped ore bodies along the redox boundary (Adler, 1964; Harshman, 1972). The reduced conditions in the sandstone outside the uranium roll are thought to be related to the presence of organic material and diagenetic pyrite that have not yet been oxidized (Adler, 1964; Spirakis, 1996). However, hydrocarbons introduced into the aquifer from deep basin faults may also have acted as the reductant in the formation of at least some uranium roll-front uranium deposits (Goldhaber et al., 1983; Jaireth et al., 2008; Hancock et al., 2011).
Previous research has shown that detrital quartz contained in the sedimentary host rocks of uranium deposits can be affected by radiation damage caused by alpha particle bombardment related to the radioactive decay of the uranium decay series (Meunier et al., 1990; Komuro et al., 1995; Götze et al., 2001; Vollbrecht et al., 2002; Botis et al., 2005, 2006; Hu et al., 2008; Kempe et al., 2012). Unlike minerals such as cordierite and biotite, where the radiation damage causes notable discoloration and strong pleochroism visible in plain polarized light (Nasdala et al., 2001, 2006 and references therein), radiation-induced structural damage in quartz is most easily visualized by cathodoluminescence (CL) microscopy. The damage halos show a distinct bright orange-yellow emission (Smith and Stenstrom, 1965; Owen, 1988; Götze et al., 2001; Komuro et al., 2002; Vollbrecht et al., 2002; Krickl et al., 2008; Götze, 2009; Procházka et al., 2011; Kempe et al., 2012). Large damage halos are only rarely recognizable by visible light observations (Rink and Odom, 1989; Odom and Rink, 1989).

The abundance and distribution of radiation damage in quartz contained in the host rock strata of uranium deposits can be studied to constrain the mechanisms of uranium transport and deposition. In a CL study of the sandstone-hosted uranium deposits of the Colorado Plateau, Meunier et al. (1990) observed radiation damage halos as rims around quartz grains that were surrounded by uranium minerals. Texturally identical rims on detrital quartz were also observed in sandstones lacking ore minerals, implying that the uranium had been remobilized. In the conglomerates of the Witwatersrand, South Africa, radiation damage halos around quartz grains were interpreted to have developed due to the presence of uraninite in the matrix of the conglomerate or the passage of uranium-bearing fluids through the sedimentary strata (Götze et al., 2001; Vollbrecht et al., 2002; Kempe et al., 2012). Similar radiation damage halos in detrital quartz grains (Botis et al., 2005, 2006) and drusy quartz (Hu et al., 2008) have also been recorded from the unconformity uranium deposits of the Athabasca basin in Saskatchewan, Canada. The observed radiation damage halos possibly formed from exposure to uranium-bearing fluids, suggesting that the study of radiation damage halos could aid in uranium exploration (Botis et al., 2006; Pan et al., 2006).
To test whether detrital quartz contained in the host rocks of roll-front uranium deposits is also affected by radiation damage related to uranium mineralization, sandstone samples collected across the ore zone of the Three Crow roll-front uranium deposit, Nebraska, were investigated. CL microscopy of the samples revealed that radiation damage is common in the detrital quartz. Based on textural criteria, several different types of radiation damage of the detrital grains were distinguished, not all of which are interpreted to be related to roll-front uranium mineralization. CL spectroscopy, Raman spectroscopy, and transmission electron microscopy (TEM) were conducted to better understand the link between the observed changes in CL emission and the radiation-induced structural damage of the quartz. It is shown that dosage accumulation from uranium-bearing groundwater is insufficient to cause observable radiation damage, implying that such damage can only originate in ore zones where uranium is present as a discrete mineral or adsorbed to other minerals such as clays. The findings of the present study have important consequences for the understanding of the roll-front uranium model and application of CL microscopy in uranium exploration.

### 3.3 Geological Setting

The Three Crow uranium deposit in Dawes County of western Nebraska is one of several roll-front uranium deposits within the northern Denver basin that are hosted by the Middle to Late Eocene Chamberlain Pass Formation (Fig. 3.1). This formation is composed of sandstone and tabular mudstone that represent the channel and overbank facies of a large, easterly-flowing fluvial system that stretched from Wyoming in the northwest through Nebraska and Colorado in the southeast (Swinehart et al., 1985; Evans and Terry, 1994; Terry and Evans, 1994; Terry 1998). The sandstones of the Chamberlain Pass Formation act as a regional aquifer and range on average from approximately 3 to 10 m in thickness (Collings and Knode, 1984; Evans and Terry, 1994; Terry and Evans, 1994).

Roll-front mineralization at Three Crow occurs at a depth of 175 to 290 meters below surface. The overall width of the mineralized area ranges from 640 to 1200 meters. Uranium grades in the ore body vary from less than 0.05 to greater than 0.5
wt.% $\text{U}_3\text{O}_8$, with the average grade being 0.352 wt.% $\text{U}_3\text{O}_8$. The deposit contains an indicated ore resource of 4,220,000 pounds $\text{U}_3\text{O}_8$ with an additional inferred resource of 1,135,500 pounds (Crow Butte Resources Inc., unpub. data 2012).

Figure 3.1: Location of the Three Crow roll-front uranium deposit, Dawes County, Nebraska. A. Geological map of the Denver Basin showing basement structures and contours of the top of the crystalline basin in hundreds of meters below sea level (modified from Baars et al., 1988). B. Roll-front uranium deposits near Crawford in Dawes County, Nebraska. The map shows the current Crow Butte mine permit boundary along with the boundaries of the proposed North Trend, Three Crow, and Marsland mine areas.

The present study is based on 46 poorly consolidated sandstone samples collected from five research drill holes intersecting the Chamberlain Pass Formation upstream and downstream of the roll-front. The fine- to coarse-grained sandstone samples are classified predominately as a sublithic arenite, consisting of quartz (65 to 85%), feldspar (5 to 10%), and rock fragments (5 to 15%). Rock fragments include
chert, granitic, and metamorphic rocks. Detrital grains are subangular to subrounded and generally moderately well sorted (Fig. 3.2A and B). Detrital accessory phases identified in thin section include muscovite, tourmaline, garnet, zircon, and monazite. The matrix of the sandstone consists of clays, dominantly muscovite, smectite, and kaolinite, as well as minor calcite and pyrite. The color of the sandstone varies from gray to greenish gray downstream of the roll-front to red and yellow upstream of the zone of uranium enrichment.

3.4 Analytical Methods

Initially, polished thin sections were prepared from the sandstone samples and inspected under an optical microscope. Subsequent CL microscopy was performed at the Colorado School of Mines using a HC5-LM hot-stage CL microscope by Lumic Special Microscopes. The microscope was operated at 14 kV and with a current density of ca. 10 μA mm⁻² (Neuser, 1995). CL images were captured with a high sensitivity, double-stage Peltier cooled Kappa DX40C CCD camera. CL spectra were collected over a wavelength range of 380 to 1000 nm using an Acton Research SP-2356 digital triple-grating spectrograph equipped with a Princeton Spec-10 CCD detector attached to the CL microscope by a silica-glass fiber cable. The CL spectra were measured under standardized conditions (acquisition time of 2 s and spot width of 30 μm). Wavelength calibration was performed with a Hg-halogen lamp.

Raman spectra of pristine quartz and quartz affected by radiation damage were collected on a WITec alpha500 confocal Raman microscope at the Colorado School of Mines. The 532 nm emission line of a semiconductor diode laser (100 mW) was used for excitation. Spot analyses and maps were collected with a software-controlled x-y stage and a 0.75 μm diameter spot size. The lateral resolution was approximately 1 μm. The spectral resolution was about 1 cm⁻¹. Processing of the Raman spectra was performed with the WITec Project 2.08 software.

Scanning electron microscopy on selected sandstone samples was conducted using a JEOL JSM7000F field emission instrument at the Colorado School of Mines operated at 15 kV and a beam current of ca. 70 μA. Electron microprobe element maps
of a representative quartz grain affected by radiation damage were collected on a JEOL 8900 electron microprobe at the United States Geological Survey equipped with five wave-length dispersive X-ray spectrometers. The instrument was operated at 20 kV and a beam current of 9.5 nA (measured on the Faraday cup). The spot size was approximately 1 µm. Elements analyzed included Na, Al, K, and Ti using TAP, PETJ and LIFH analyzing crystals respectively (TAP for both Na and Al). The dwell time was 1000 ms.

Lift-outs from two selected thin sections were prepared for TEM imaging with a FEI Helios NanoLab 600i DualBeam focused ion beam scanning electron microscope at the Colorado School of Mines. In each section, the region of interest was initially protected from ion beam damage by electron beam deposition of a thin strip of platinum on the surface. Standard specimen preparation routines including in-situ manipulation were employed to prepare nominally 200 nm thick specimens. Low energy 2 kV grazing incidence cleaning steps were performed on the final specimens to prevent damage from the Ga ion beam that would obscure the natural fission damage otherwise. TEM observations were conducted on a Philips/FEI CM200ST transmission electron microscope at the Colorado School of Mines operated at 200 kV.

3.5 Results

3.5.1 CL Microscopy

CL microscopy showed that the sandstone samples contain several distinct types of detrital quartz (Fig. 3.2C and D). The most common type of grains shows a bluish-violet CL. Some quartz grains, typically appearing cloudy in plane polarized light, are reddish brown under CL and may represent chert fragments. A third type of quartz is characterized by a short-lived bottle green CL. This CL emission fades almost immediately during electron bombardment, making it difficult to image. This quartz type has no long-lived CL. Quartz overgrowths on the detrital grains could be easily identified as the overgrowth lacks detectable luminescence.
Figure 3.2: Photomicrographs of the host sandstone of the roll-front uranium deposit.
A. Plane polarized light image of the poorly-sorted sandstone. Individual quartz grains are variably rounded. The matrix is rich in clay minerals. B. Plain polarized light image of a sandstone that is moderately well-sorted. The detrital quartz grains are well-rounded. The large quartz grain exhibits quartz overgrowth (arrow). C. Cathodoluminescence image of a sandstone sample. Both bluish-violet and red brown quartz occur. Feldspar grains show a bright blue cathodoluminescence color. D. Cathodoluminescence image of a sandstone sample. The large quartz grain hosts two small green apatite inclusions. The matrix of the sandstone is rich in blue kaolinite. Scale bars are 250 µm.
Figure 3.3: Cathodoluminescence images of different textural types of radiation damage in detrital quartz. A. Radiation damage halos surrounding zircon inclusions (arrows) in large blue-violet detrital quartz grain. The grain is dissected by a fracture containing calcite. Scale bar is 250 µm. B. Circular radiation damage halo surrounding a very small zircon grain. The damage halo shows concentric rings. Scale bar is 250 µm. C. Coalescent radiation damage halos surrounding two small zircon grains. Scale bar is 125 µm. D. Semicircular radiation damage halos (arrows) located at the grain boundary of a bluish-violet detrital quartz grain. Scale bar is 250 µm. E. Damage halo rimming detrital quartz grain (arrow). Scale bars are 250 µm.
Radiation damage of the detrital quartz grains is abundant in the sandstone samples. Based on CL microscopy, three textural settings can be distinguished. The most common type of radiation damage halos is associated with inclusions of zircon and monazite hosted by the detrital quartz grains (Fig. 3.3A). The halos surrounding these inclusions mimic the shape of the inclusions and consequently vary from round to oval. The bright orange-yellow halos typically enclose the entire mineral inclusion. In some cases, the halos are discontinuous, rimming only parts of the mineral inclusions. The radiation damage halos measure from approximately 10 to 40 μm in width, some of which display concentric rings (Fig. 3.3B). The radiation damage halos commonly coalesce in quartz grains that contain abundant mineral inclusions (Fig. 3.3C). Radiation damage associated with mineral inclusions is most abundant in the quartz grains having a bluish-violet CL but has also been recognized in the other quartz types.

In addition to halos surrounding mineral inclusions in the detrital quartz grains, semicircular zones and patches of radiation damage occur along the grain boundaries of some quartz grains (Fig. 3.3D). The semicircular damage halos can occur individually or as overlapping clusters along the quartz grain boundaries. Although these bright orange-yellow halos are commonly associated with mineral inclusions intersected by the grain boundaries, some of the semicircular zones and patches of radiation damage are not obviously related to radioactive minerals intergrown with the quartz or present in the adjacent matrix. Radiation halos surrounding entire mineral inclusions are most frequent in quartz grains having a bluish-violet CL.

Samples containing elevated concentrations of uranium (> 100 ppm) typically also contain a third type of radiation damage halo. In these samples, entire quartz grains or large portions thereof can be rimmed by a bright orange-yellow CL damage halo (Fig. 3.3E). The damage halos are usually uniform in intensity around a given detrital quartz grain and not wider than 20 μm. In rare occasions, the radiation damage extends along fractures intersecting individual quartz grains. Some smaller grains are altered to the point where the original CL is not apparent. These damage zones rim the entire grains and gradually fade in intensity toward the center of the grains. This type of radiation damage occurs in all types of quartz. However, the damage halos surrounding entire quartz grains appear to be somewhat rare in the reddish brown quartz grains.
This is probably related to the fact that the reddish brown CL emission masks the CL of the radiation damage halos.

Although CL anisotropy can occur in minerals (Walderhaug and Rykkje, 2000; Barbarand and Pagel, 2001), the CL color of the three texturally different types of damage halos appears to be independent of crystallographic orientation. No differences were noted between the randomly oriented quartz grains in the investigated sandstone samples. The damage halos are bright orange-yellow in color irrespective of the original color of the quartz grain. However, the intensity of the CL signal appears to vary slightly between grains, which may be related to variable irradiation doses (cf. Krickl et al., 2008). The intensity of the emitted CL signal overall is low and damage halos are typically barely visible in CL microscopy.

Image analysis of CL microphotographs taken on samples collected across the Three Crow roll-front deposit showed that there is no spatial trend for the damage halos surrounding mineral inclusions such as zircon and monazite. However, radiation damage associated with mineral inclusions appears to be most common in the coarsest-grained sandstone samples. Although the semicircular damage halos occurring along the grain boundaries of quartz are comparably rare, this type of radiation damage appears to be most common in samples from the ore zones. The damage halos forming rims around detrital grains were only observed in samples collected from the ore zones or proximal to ore. The abundance of radiation damage halos rimming entire detrital grains decreases rapidly upstream and downstream of the ore zone. As noted above, there appears to be a direct correlation between the uranium content of a given sample and the presence of radiation halos rimming entire quartz grains.

3.5.2 Spectral CL Characteristics

To characterize the spectral make-up of the emitted signal, CL spectra were collected on a representative detrital quartz grain showing a bluish-violet CL in the pristine parts of the grain and the bright orange-yellow CL within the damage halo. The CL spectrum of the undamaged quartz is characterized by broad emission bands in the
blue (~450 nm) and red (~650 nm) regions. The CL spectrum of the damage halo shows a significant intensity increase of the ~650 nm emission band and a slight decrease in the intensity of the blue emission (Fig. 3.4).

These results are consistent with previous spectral studies demonstrating a strong increase in the ~650 nm emission band in response to alpha-irradiation (Götze et al., 2001; Botis et al., 2005; Krickl et al., 2008). An increased emission of this band is possibly related to the presence of non-bridging oxygen hole centers (Siegel and Marrone, 1981; Stevens-Kalceff, 2009), which are produced by bond breaking during alpha particle bombardment (Götze et al., 2001). The intrinsic emission at ~450 nm observed in both the pristine and damaged zones of the quartz possibly relates to the recombination of self-trapped excitons (Stevens-Kalceff, 2009) that are formed by electron-phonon interactions (Fisher et al., 1990).

![Cathodoluminescence spectra comparison](image)

**Figure 3.4:** Cathodoluminescence spectra comparing the pristine portion of a blue-violet detrital quartz grain with its corresponding bright orange-yellow damage halo. Comparison of the spectra shows a significant intensity increase of the ~650 nm emission band and a slight decrease in the intensity of the blue emission at ~450 nm in response to natural alpha particle bombardment.
3.5.3. Chemical Composition of Radiation Halos

Secondary electron imaging has been performed on selected damage halos and adjacent zones of pristine quartz. No discernible differences in surface texture or porosity have been noted. The backscatter electron contrast is also identical between pristine areas in detrital quartz grains and the bright orange-yellow damage halos.

Electron microprobe element mapping was conducted on a blue-violet quartz grain that is partially rimmed by a radiation damage halo and also shows a damage halo developed along a fracture transecting the grain. The element mapping confirmed that there are no detectable differences in the concentrations of K, Na, Al, and Ti between the pristine portions of the quartz grains and the damage halo visible under CL (Fig. 3.5).

The findings suggest that the damage halos characterized by the bright orange-yellow CL are not chemically anomalous when compared to the pristine portions of the grains, at least not within the resolution of electron microprobe analysis. The lack of compositional gradients is to be expected as quartz at Three Crow only interacted with low-temperature ground waters. Under such conditions, element diffusion into zones of structural damage may be too slow to be of significance. However, previous investigations on minerals such as zircon, allanite, and titanite have shown that this may not be the case in high-temperature hydrothermal environments (Hawthorne et al., 1991; Geisler et al., 2001; Poitrasson, 2002 and references therein).

3.5.4 Raman Spectroscopy

Raman spectroscopy was conducted on the pristine blue-violet portions of detrital quartz grains and within the different textural types of bright orange-yellow damage halos identified by CL microscopy. The measurements showed that the full width at half maximum (FWHM) of the quartz A₁ peak at 466 cm⁻¹ broadens slightly within the damage halos (Table 3.1). At the same time, a slight increase in the background of the Raman spectra can be observed within the radiation halos. This increase is not systematic and varies from a few to over fifty counts per second. In cases where the
Figure 3.5: Compositional zoning in detrital quartz affected by natural alpha irradiation. The plain polarized light (PPL) and cathodoluminescence (CL) images show that the quartz grain is transected by a fracture. An extensive bright orange damage halo is developed along the fracture and rim of the quartz grain. The area characterized by element mapping on an electron microprobe is highlighted. The element maps of Na, Al, K, and Ti illustrate that there is no detectable compositional difference between the damage halo and the surrounding pristine quartz. Scale bars are 50 µm.

Table 3.1: Comparison of Raman spectroscopic measurements on pristine blue-violet CL quartz and bright orange-yellow CL radiation damage halo. The table lists the width at half maximum values of the quartz $A_1$ peak at 466 cm$^{-1}$ measured at different locations outside and inside the damage halo in different textural settings (data in cm$^{-1}$).

<table>
<thead>
<tr>
<th>Halo Type</th>
<th>Pristine quartz</th>
<th>Damage halo</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inclusion</td>
<td>9.18</td>
<td>11.02</td>
<td>-1.83</td>
</tr>
<tr>
<td>Rim</td>
<td>10.02</td>
<td>11.23</td>
<td>-1.21</td>
</tr>
<tr>
<td>Inclusion</td>
<td>8.93</td>
<td>10.43</td>
<td>-1.50</td>
</tr>
<tr>
<td>Inclusion</td>
<td>8.68</td>
<td>9.08</td>
<td>-0.39</td>
</tr>
<tr>
<td>Inclusion</td>
<td>8.73</td>
<td>10.19</td>
<td>-1.46</td>
</tr>
<tr>
<td>Rim</td>
<td>8.84</td>
<td>9.12</td>
<td>-0.28</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>9.06</strong></td>
<td><strong>10.18</strong></td>
<td><strong>-1.11</strong></td>
</tr>
</tbody>
</table>
background is high, only the 466 cm\(^{-1}\) peak is observed in the Raman spectrum. The change in the FWHM is attributed to the accumulation of point defects and possibly strain resulting from heterogeneous, irradiation-induced volume expansion (Krickl et al., 2008).

In one quartz grain, Raman spectra were also collected over an area covering a zircon inclusion and its radiation damage halo in the host quartz (Fig. 3.6A). A FWHM intensity map of the A\(_1\) peak at 466 cm\(^{-1}\) was constructed, showing an overall increase in the FWHM around the inclusion (Fig. 3.6B). The FWHM of the A\(_1\) peak is at maximum of about 10.0 cm\(^{-1}\) close to the inclusion and drops sharply approximately 5 µm out from the inclusion, after which it gradually decreases to the background level of about 8.4 cm\(^{-1}\) (Fig. 3.6C). The area of maximum FWHM corresponds to the most intense CL from radiation damage around the zircon inclusion. Typically only the most intense center of radiation damage will have a detectable change in the FWHM.

Figure 3.6: Raman analysis of a radiation damage halo surrounding a zircon inclusion. A. CL image showing a radiation damage halo enveloping a zircon inclusion hosted by a detrital quartz grain. The area used for Raman mapping is highlighted. B. Map of the full width half maximum of the Raman peak at 466 cm\(^{-1}\). The damage halo observed by CL is characterized by a slight increase in the full width at half maximum of the quartz A1 peak. Scale bar is 10 µm. C. Cross-section of the radiation halo showing the change in the FWHM of the quartz A1 peak over distance from the radiation source. The error bar is on the order of 0.1 cm\(^{-1}\) and represents the standard deviation over 10 measurements.
3.5.5 Transmission Electron Microcopy

TEM investigations were performed to conclusively demonstrate that the halos of bright orange-yellow CL are affected by structural damage related to alpha particle bombardment. Both a damage halo surrounding a zircon grain and a damage halo rimming a detrital quartz grain were selected. The TEM lift-outs were oriented parallel to the direction of irradiation, i.e. perpendicular to the grain boundary. The sample from the halo surrounding the zircon grain was cut out from the quartz at a distance of approximately 10 μm from the grain boundary with the inclusion. It had a length of 25 μm and reached to a depth of 15 μm below the thin section surface. The sample obtained from the damage halo rimming the quartz grain was cut out in such a way that a 15-μm-long profile from the grain boundary inwards could be studied. The lift-out reached the same depth below the thin section surface. As thin section preparation results in an amorphization of quartz close to the surface, all TEM investigations were performed on the deeper parts of the lift-outs.

TEM investigations of the radiation halos indicate considerable structural damage in both samples. A higher number of defects was noted in areas closest to the irradiation source compared to further away (Fig. 3.7A and B). Fewer defects were observed in the halo rimming the quartz grain than the halo surrounding the zircon inclusion. In addition to the alpha tracks, stacking faults were observed in the quartz samples (Fig. 3.7C). These could, however, be unrelated to the alpha particle bombardment. Although extensive damage to the quartz was observed in dark and bright field images, selected area diffraction patterns did not indicate that the quartz is amorphous (Fig. 3.7D). This suggests that the defect density is not high enough to visibly affect the electron diffraction patterns in the two naturally irradiated quartz samples.
Figure 3.7: Transmission electron microscope images of radiation damage halos in quartz. A. Dark-field image of a halo rimming a detrital quartz grain. The image was taken close to the grain boundary and shows the abundant occurrence of alpha tracks. Several dislocations can be noted. Scale bar is 500 nm. B. Dark-field image of the same sample, but located further away from the grain boundary. There are distinctly fewer alpha tracks. Scale bar is 500 nm. C. Bright field image of the radiation damage halo surrounding a zircon inclusion. A large stacking fault is noted. Radiation damage is extensive. Scale bar is 500 nm. D. Selected area electron diffraction pattern of the most damaged area identified in the radiation damage halo surrounding the zircon grain. The radiation damage is not extensive enough to cause amorphization of the crystal structure. Scale bar is 0.01 nm.
3.6 Discussion

3.6.1 Types of Radiation Damage

The results of the combined microscopic and spectroscopic investigations unequivocally demonstrate that the damage halos in detrital quartz from the Three Crow roll-front uranium deposit result from irradiation by alpha particles. The halos have the same CL characteristics as those observed in other types of uranium deposits as well as those of artificially irradiated quartz (Meunier et al., 1990; Komuro et al., 1995; Götze et al., 2001; Vollbrecht et al., 2002; Botis et al., 2005, 2006; Hu et al., 2008; Krickl et al., 2008; Götze, 2009; Kempe et al., 2012). The damage halos universally are of bright orange-yellow color. The occurrence of structural damage within the halos was indirectly verified by Raman spectroscopy. Transmission electron microscopy confirmed the occurrence of abundant alpha tracks within the CL damage halos.

The textural relationships indicate that many of the radiation damage halos observed in the detrital quartz grains are unrelated to roll-front mineralization. In particular, the radiation damage halos surrounding inclusions of zircon and monazite clearly formed in response to alpha particle emission from these radioactive mineral inclusions. This type of radiation damage is most abundant in bluish-violet quartz grains, which probably represent magmatic quartz grains derived from the erosion of felsic plutonic rocks (cf. Zinkernagel, 1978; Götze et al., 2001).

The halos have a maximum width of about 40 µm, which is consistent with the penetration depth of alpha particles sourced from both the uranium and thorium decay series (Owen, 1988). As alpha particles produced by these decay series have different energies and penetration depths in quartz, radiation damage halos surrounding small inclusions show concentric rings. The inner ring is brightest as most damage occurs in the immediate vicinity of the radioactive source (cf. Owen, 1988). Damage halos surrounding larger mineral inclusions do not show the same distinct rings as the alpha particles are not emitted from a point source in such cases.

Most of the semicircular zones and patches of radiation damage occurring along grain boundaries of detrital quartz grains probably also formed in association with
inclusions of zircon and monazite. The quartz grains were fractured during sedimentary transport, most likely along planes of weakness marked by the occurrence of mineral inclusions. The observation that this textural type of damage is particularly common in bluish-violet quartz grains supports the assumption that radioactive mineral inclusions originally present in the magmatic quartz grains are responsible for the radiation damage. However, in samples having elevated uranium concentrations (>100 ppm), the semicircular zones and patches of bright orange-yellow CL could also originate from radioactive point sources located in the matrix of the sandstone or at the grain boundary. As no radioactive minerals have been identified in the samples from Three Crow, a relationship between these damage halos and the roll-front mineralization cannot be established unequivocally.

Damage halos rimming entire detrital quartz grains must have formed after sedimentary transport and deposition as the halos are not truncated by grain boundaries. In situ formation of the bright orange-yellow CL halos is also suggested by the frequency distribution of this type of radiation damage across the roll-front. The damage halos rimming entire quartz grains are particularly abundant in samples having uranium concentrations above 100 ppm and are essentially absent upstream and downstream of the roll-front. The bright orange-yellow rims surrounding quartz grains tend to be of a fairly constant thickness of 20 µm or less.

No textural evidence was found directly linking the occurrence of the bright orange-yellow CL damage halos to uranium-bearing phases. As discrete uranium-bearing mineral phases such as coffinite are exceedingly rare in thin section (Martin and Fayek, pers. communication 2012; this study) and the overall uranium content of the investigated sandstone samples is not high (<1100 ppm), it appears possible that much of the observed radiation damage was caused by uranium adsorbed to grain surfaces such as those of clay particles abundant in the matrix of the sandstone. The relatively homogeneous distribution of quartz grains with damage halos in the mineralized sandstone samples further suggests that the radiation source is finely dispersed throughout the sandstone matrix.
3.6.2. Dosage Calculations

Previous studies on uranium deposits have suggested that radiation damage of detrital quartz grains can be caused by the passage of aqueous fluids containing dissolved uranium (Götze et al., 2001; Vollbrecht et al., 2002; Botis et al., 2005, 2006; Hu et al., 2008; Kempe et al., 2012). However, the absence of notable radiation damage outside the ore zones at Three Crow and the observed correlation between the abundance of damage halos and the bulk uranium content of the sandstone do not support this model of a mobile radiation source.

To test the empirical finding that groundwater cannot produce the radiation damage halos on the detrital quartz over geological times, an approximate dosage calculation can be easily carried out. Several factors need to be considered when determining the likely dosage of alpha particles emitted from uranium dissolved in groundwater, including the radionuclide concentration in water, the time of exposure, and the penetration depth of alpha particles in water. Systematic monitoring of the aquifer in the Chamberlain Pass Formation has shown that modern-day uranium concentrations in the groundwater at Three Crow are on average 8.7 μg/L (Crow Butte Resources Inc., unpub. data 2010). The maximum time of exposure is constrained by the depositional age of the sandstone, which is approximately 35 Ma. The maximum distance an alpha particle can travel in water is 300 μm, calculated with the program SRIM for a 4.4 MeV He ion.

Taking these constraints into account, it can be derived that an approximate number of 5.9·10^8 uranium atoms are located within a cube having a side length of 300 μm. At a half lifetime of 4.47·10^9 years, approximately one uranium atom would decay every ten years, producing about 10 alpha particles. This number is only approximate as alpha particles are produced by both the $^{238}$U and $^{235}$U series, yielding different numbers of alpha particles, each having different energies. Thus, a total of 34 million alpha particles would be produced in the cube of water over a period of 34 Ma. However, a maximum of one half (including those coming from the neighboring cubes) of all alpha particles would be emitted in such a way that they could impact on one side of the cube.
Artificial irradiation studies suggest that the minimum dosage to cause radiation damage visible by CL is on the order of one to ten million alpha particles per $\mu m^2$ (Komuro et al., 2002; Krickl et al., 2008). In the above scenario, a 1 $\mu m^2$ large surface area of a quartz grain bounding the water cube of 300 $\mu m$ side length would only be impacted by a maximum of 200 alpha particles in the last 34 Ma. As these particles would arrive with vastly different energies, depending on their travel distance through water, not all of these alpha particles would be able to penetrate deep enough into the quartz grain to cause radiation damage. Despite the simplifications made, it is clear from this model dosage calculation that the number of alpha particles emitted from groundwater was orders of magnitude too low to cause radiation damage in quartz that can be visualized by CL. This confirms the above empirical assumption that halos surrounding entire detrital grains must have formed in relationship to the uranium mineralization and cannot be the result of a mobile radiation source.

3.6.3 Implications to the Roll-front Deposit Model

The observations of the present study have several important implications to the roll-front uranium deposit model. The CL investigations showed that there is a relationship between the occurrence of radiation damage halos on detrital quartz grains and the uranium content of the sandstone. Extensive radiation damage was not recorded in the barren oxidized sandstone upstream of the roll-front, implying that the oxidized sandstone has not been exposed to the same radiation dosage as the sandstone hosting the ore. As radiation damage in quartz does not anneal at low temperatures, the lack of damage halos on detrital quartz grains upstream of the roll-front suggests that the now oxidized sandstone never hosted the roll-front. This contradicts the widely held perception that roll-fronts slowly, but continuously, migrate down dip through the aquifer over geological times due to successive oxidation of the host sandstone by the oxygenated groundwater.

The findings of the present study demonstrate that the roll-front at Three Crow has not been migrating continuously down the hydrological gradient. It appears possible that the roll-front has been stagnant in its current position for a prolonged
period of time. In such a case, abundant radiation damage of detrital quartz would not form on the oxidized side of the roll-front as the uranium content of the groundwater is too low to allow dosage accumulation. However, enrichment of approximately five million pounds of uranium oxide within the ore zone from groundwater having a very low uranium content (mean of 8.7 \( \mu \)g/L; unpublished data Crow Butte Resources Inc.) would require an enormous ground water throughput over geological times (2.2 \( \times 10^{11} \) m\(^3\) of water at 100% uranium precipitation). As a consequence, the ore zone could only have been stagnant in its current position if an external reductant is supplied to the host aquifer as the reducing capacity of the sandstone is insufficient to reduce such a quantity of water. An external reductant could be supplied to the site of mineralization through, for instance, hydrocarbon migration along a hitherto unrecognized fault intersecting the aquifer. Such a model has been previously invoked for some roll-front uranium deposits (Goldhaber et al., 1983; Jaireth et al., 2008; Hancock et al., 2011).

As an alternative to a stagnant roll-front, it appears plausible that the roll-front is indeed migrating down the hydraulic gradient, but periodically rather than continuously. The roll-front could move quickly during periods of high groundwater flow (i.e., climatic periods of increased precipitation) and become essentially stagnant during periods of diminished groundwater flow (i.e., climatic periods of semiarid to arid conditions). In the case of a rapid movement of the roll-front down the hydrological gradient, dosage accumulation along the flow path may be insufficient to cause abundant development of radiation damage halos on detrital quartz grains. In contrast, dosage accumulation causing radiation damage could be readily achieved within the ore zones when the roll-front is essentially immobile.

In contrast to previous studies on the Athabasca basin (Botis et al., 2005, 2006; Pan et al., 2006; Hu et al., 2008), the present study suggests that a reconstruction of the flow path of the uranium-bearing fluids in the roll-front environment is not readily possible using CL microscopy on the host sandstone. The concentrations of uranium in groundwater are too low to accumulate sufficient dosage along the groundwater flow path in these geologically young systems. Abundant damage halos on detrital quartz grains can only be detected within the ore zone of roll-front deposits such as Three Crow in Nebraska or possibly within former ore zones from which uranium has been
remobilized. As such, applicability of CL microscopy in exploration programs for this type of uranium deposits is likely limited.
CHAPTER 4
MINERALOGY AND GEOCHEMISTRY OF THE ALTERATION HALO ASSOCIATED WITH THE THREE CROW ROLL-FRONT URANIUM DEPOSIT, NEBRASKA

Modified from a paper to be submitted to Economic Geology
Julie Leibold, Thomas Monecke, Richard Wendtland, Nigel Kelly

4.1 Abstract

The present study provides new insights into the mineralogy and geochemistry of the host sandstone and alteration associated with the Three Crow roll-front uranium deposit, Nebraska, using state-of-the-art analytical techniques including CL microscopy, automated quantitative mineral analysis, and LA-ICP-MS. A model for the formation of Three Crow incorporating mineralogical and geochemical changes associated with mineralization is presented.

The Three Crow deposit is hosted by subarkosic sandstone and conglomeratic sandstone that were deposited in a large braided stream system during the late Eocene. The uranium deposit formed along a redox interface between oxidized and reduced conditions. Changes in the redox across this interface had only a minimal impact on the mineralogy of the detrital phases. The framework grains were essentially unaffected except for microcline and plagioclase which showed a slight increase in alteration with exposure to the oxidizing groundwater. Most detrital accessory minerals were also unaffected by the oxidizing groundwater.

In contrast to the detrital minerals, authigenic phases proved to be sensitive indicators of the redox conditions and changes in groundwater pH accompanying roll-front mineralization. The reducing and slightly basic conditions pre-mineralization favored the precipitation of smectite and diagenetic pyrite. Infiltration of oxygenated groundwater caused the oxidation of diagenetic pyrite which either converted to goethite in the oxidized zone or underwent complete dissolution and was transported to the reduced sandstone downstream of the roll-front. The alteration of diagenetic pyrite depressed the pH of the groundwater, which was instrumental in the formation of
marcasite, coffinite, and kaolinite. Later stages of mineralization coincided with a rebound to near neutral or slightly alkaline conditions and resulted in the precipitation of late ore-stage pyrite.

The differences in mineralogy are paralleled by systematic variation in whole-rock geochemistry. Whole-rock Fe and S abundances correlate with the pyrite and/or marcasite content of the samples. Other geochemical trends include higher total and organic carbon contents in the transitional and reduced rocks compared to the oxidized tongue upstream of the roll-front. Enrichment in trace elements, such as As, is most notable in the whole-rock data where host minerals, such as As-rich pyrite, are abundant. Evidence from CL microscopy on quartz and textural studies of the authigenic accessory minerals suggests that the roll-front at Three Crow has been essentially stagnant throughout its formation. This conclusion is inconsistent with the widely accepted deposit model that assumes roll-fronts continuously move down a hydrologic gradient.

4.2 Introduction

The central Rocky Mountain region between Montana and New Mexico is characterized by the occurrence of a number of sedimentologically isolated basins that formed in response to basement deformation during the late Cretaceous to early Tertiary Laramide orogeny (Baars et al., 1988). These intramontane basins host a large number of sandstone-hosted uranium deposits, which represent the principal source of uranium in the United States.

A significant number of past and present uranium producers in the central Rocky Mountain region are roll-front uranium deposits. These deposits form within sandstone aquifers where oxidized uranium-bearing groundwater flowing down a hydrological gradient encounter an interface between oxidizing and reducing conditions. Reduction of the groundwater causes uranium precipitation, typically as uraninite or coffinite, forming a roll-shaped ore body. Roll-front uranium deposits are typically low-grade, with average uranium grades ranging from 0.05 to 0.5 wt.% U₃O₈ (Gruner, 1956; Adler, 1963; Harshman, 1972; Harshman and Adams, 1981; Boberg, 2010).
Despite the low uranium grades, roll-front deposits currently are a growing target for uranium exploration in the United States as uranium enrichment in sandstone aquifers located below the present-day water table is amenable to low-cost in-situ recovery (cf. Collings et al., 1994; Stover, 2004). Since the increase of the uranium price in the early 2000s, significant exploration and development drilling has been conducted at a number of roll-front uranium deposits in the central Rocky Mountain region, in particular in Wyoming and Nebraska (Boberg, 2010).

The present paper presents the results of a comprehensive study of the mineralogy and geochemistry of the alteration halo associated with the Three Crow roll-front uranium deposit in Nebraska, which is currently in the permitting stage. Research drilling at Three Crow provided the unique opportunity to obtain samples upstream and downstream of the zone of uranium enrichment. As little research has been carried out on roll-front deposits over the past thirty years, the present study combines a range of state-of-the-art analytical techniques to better describe the alteration footprint of this deposit type. The findings of the present research are used to refine the current genetic model of roll-front uranium deposits.

4.3 Geological Setting

4.3.1 Regional Geology

The Three Crow roll-front uranium deposit is located within the Crawford Basin in northwestern Nebraska, an approximately 1000 km² large sub-basin at the northern most extent of the much larger Denver Basin (DeGraw, 1971). The Denver Basin represents a major intramontane basin that trends north to south along the eastern flank of the Laramie Mountains and the Front Range of the Southern Rocky Mountains, covering large parts of eastern Colorado, southeastern Wyoming, western Nebraska, and northwestern Kansas (Fig. 4.1).
The Precambrian crystalline basement of the Crawford Basin is overlain by various Paleozoic and Mesozoic sedimentary strata (Baars et al., 1988). The Pierre Shale, a dark gray to black marine shale deposited in the Late Cretaceous Western Interior Seaway of North America, represents the youngest Mesozoic deposit in the Crawford Basin. Deep oil drilling in Dawes County revealed that this highly
impermeable shale reaches a stratigraphic thickness between 350 to 450 meters (Collings and Knodle, 1984). The top surface of the Pierre Shale marks a major unconformity, which exhibits considerable paleotopography (DeGraw, 1971) and locally occurs as a paleosol, referred to as the Yellow Mounds Paleosol Equivalent (Retallack, 1983; Evans and Terry, 1994; Terry, 1998).

The Pierre Shale is overlain by the late Eocene to Oligocene White River Group, which is composed of clastic fluvial, eolian, and lacustrian strata (Terry, 1998). These sedimentary rocks contain a significant proportion of volcaniclastic material (Swinehart et al., 1985; Larson and Evanoff, 1998). The White River Group is laterally extensive, with a proven extent ranging from eastern Wyoming and northeastern Colorado through Nebraska, South Dakota, and southwestern North Dakota (Terry, 1998).

The late Eocene Chamberlain Pass Formation, the host of Three Crow and other roll-front deposits in northwestern Nebraska, represents the basal unit of the White River Group. The Chamberlain Pass Formation is composed of interbedded sandstones and mudstones that represent channel and overbank facies of a large braided stream system (Fig. 4.2). At Three Crow, the sandstones have a stratigraphic thickness of approximately 20 to 75 meters (Crow Butte Resources, unpubl. data). The channel sandstone bodies are multistory, showing general fining-upward sequences (Evans and Terry, 1994). The overbank mudstone is predominantly massive. Proximal overbank facies are up to 3 meters in thickness while distal overbank mudstone ranges from 0.8 to 1.8 meters in thickness (Terry, 1998).

The fluvial system depositing the Chamberlain Pass Formation was active in the late Eocene and represents the oldest preserved phase of fluvial activity in the area following retreat of the Late Cretaceous Interior Seaway of North America (Evans and Terry, 1994; Terry, 1998). The fluvial system depositing the sandstones of the Chamberlain Pass Formation was up to 40 kilometers wide and has been traced over a distance of at least 240 km from Wyoming in the northwest through Nebraska and Colorado in the southeast (Swinehart et al., 1985; Evans and Terry, 1994; Terry, 1998). The fluvial system entered the Crawford Basin in the northwest, turning southeast in the deposit area, presumably because the Chadron arch to the east was a topographic high at the time (Swinehart et al., 1985). The clastic material forming the Chamberlain Pass
sandstone was probably largely sourced from the Black Hills, which comprise Precambrian igneous and metamorphic rocks and a carapace of Paleozoic to Mesozoic sedimentary rocks. However, at least some of the detrital material may have been derived as far as the Hartville Uplift or even the Laramie Mountains to the west (Stanley 1976; Stanley and Benson 1979; Seeland 1985; Evans and Terry 1994).

Figure 4.2: Schematic stratigraphic column for the Crawford Basin showing relationships for units above the Pierre Shale. YMPE = Yellow Mounds Paleosol equivalent (modified after LaGarry, 1998).

The Chamberlain Pass Formation is unconformably overlain by the late Eocene to early Oligocene Chadron Formation (Fig. 4.2). The Chadron Formation is subdivided into four members, of which only the Peanut Peak and Big Cottonwood Creek Members
are observed in northwestern Nebraska (Terry, 1998). The Peanut Peak Member is dominated by bluish-green and gray hummocky mudstone (Terry, 1998) and ranges from 10 to 30 meters in thickness in Dawes County (Collings and Knode, 1984). The Peanut Peak Member is overlain by the Big Cottonwood Creek Member, which consists of 25 to 50 meters thick (Collings and Knode, 1984) volcaniclastic overbank claystone, silty claystone, and siltstone with isolated tabular and lenticular channel sandstone bodies (Terry, 1998; Terry and LaGarry, 1998). Lacustrine limestone beds are a volumetrically minor component and predominantly occur toward the top of the Chadron Formation (Evans and Welzenbach, 1998; Terry and LaGarry, 1998).

The Chadron Formation is overlain by the Brule Formation (Fig. 4.2), which has a total stratigraphic thickness of approximately 40 to 160 meters (Gjelsteen and Collings, 1988). The lower portion of the Brule Formation is dominated by fluvial, pale brown and brown volcaniclastic siltstone of the Orella Member, which contains zones of abundant bluish-green nodules and local channel sandstones (Collings and Knode, 1984; LaGarry, 1998). The overlying Whitney Member is dominated by eolian, pale brown, massive, and typically nodular siltstone that contains approximately 50% volcanic glass shards (Tedford et al., 1996). Rare interbedded sandstone beds occur (LaGarry, 1998). Several distinct fallout tuff layers of Oligocene age have been recognized in the Whitney Member of the Brule Formation (Larson and Evanoff, 1998), including the Lower and Upper Whitney Tuffs that yielded \(^{40}Ar/^{39}Ar\) biotite ages of 31.85 ± 0.02 and 30.58 ± 0.61 Ma, respectively (Swisher and Prothero, 1990). The top of the Brule Formation is assigned to the brown siltstone member that is composed of brown to pale brown, siltstone and fine sandstone, with minor reworked volcaniclastic siltstone and volcanic ash (Swinehart et al., 1985; LaGarry, 1998). The fluvial and eolian, brown siltstone member contains the Nonpareil Tuff that has a \(^{40}Ar/^{39}Ar\) biotite age of 30.05 ± 0.19 Ma (Swisher and Prothero, 1990).

The Oligocene to Miocene Arikaree Group unconformably overlies the White River Group. This group consists of 30 to 60 meters of predominantly fluvial volcaniclastic sandstone and 85 to 110 meters of eolian sandstone with carbonate-cemented concretions (Collings and Knode, 1984; Tedford et al., 1996). The youngest
deposits in the Three Crow area consist of Quarternary alluvial and colluvial material, which is up to 10 meters in thickness (Collings and Knode, 1984).

Faulting is widespread within the Crawford Basin. The most prominent structure is the White River Fault that strikes northeast-southwest with the upthrown side to the south. The total vertical displacement on this fault is 60 to 120 meters (Collings and Knode, 1984; Gjelsteen and Collings, 1988). Displacement of the Chamberlain Pass Formation suggests that faulting postdated deposition of the late Eocene sedimentary strata (Collings and Knode, 1984).

4.3.2 Deposit Geology

The Three Crow deposit is located near Crawford in Dawes County. It represents one of several roll-front uranium deposits in the Crawford Basin that are hosted by the fluvial deposits of the Chamberlain Pass Formation, which acts as a regional aquifer that is confined between the Pierre Shale Formation and the fine-grained sedimentary rocks of the Chadron Formation (Gjelsteen and Collings, 1988). Crow Butte, located approximately 10 kilometers to the west of Three Crow, is currently the only operating roll-front deposit in northwestern Nebraska and has been continuously mined by in-situ leaching since 1991 (Collings et al., 1994). In addition to Three Crow, the North Trend and Marsland deposits are currently under permitting as expansion areas of the operation at Crow Butte (Fig. 4.1).

The Three Crow deposit consists of five multistory roll-fronts that are separated by thin mudstone layers within the Chamberlain Pass Formation. The ore zones are located between 175 and 290 meters below the surface and have a width ranging from 640 and 1200 meters. Uranium grades vary from below 0.05 to greater than 0.5 wt.% U₃O₈, with an average uranium grade of 0.352 wt% U₃O₈. The total indicated resource of Three Crow is approximately 4,220,000 pounds U₃O₈. An additional inferred resource of 1,190,000 pounds U₃O₈ at a grade of 0.1 wt% U₃O₈ has been identified. In-situ leaching of the resource is expected to yield an annual production of approximately 600,000 pounds U₃O₈ (unpublished data, Crow Butte Resources Inc.).
The location of the roll-fronts coincides with changes in the redox state in the sedimentary host rocks that can be identified based on rock color. Reduced sandstone occurring down-stream of the roll-front is dark green to gray while slightly reduced sedimentary rocks are light gray. Rocks sampled in transitional zones between the reduced and oxidized zones of the sandstone are grayish yellow to yellow. Upstream of the zone of roll-front uranium enrichment, the sedimentary rocks are oxidized and distinctly yellow or red. Extensive drilling at Three Crow showed that there is a general correlation between redox state and sedimentological character of the sedimentary rocks of the Chamberlain Pass Formation. Within each drill hole, the most intense oxidation typically occurs in the most coarse-grained and poorly sorted sandstones and conglomeratic sandstones.

4.3.3 Research Drilling and Sampling

To study the alteration halo associated with the Three Crow roll-front uranium deposit, five research holes were drilled along a section across the lowermost roll-front at Three Crow. The research holes span the deposit from 305 meters upstream to 190 meters downstream of the zone of uranium enrichment (Fig. 4.3). Reverse circulation drilling was performed in the upper portion of the stratigraphy, while continuous coring was conducted across the lowermost sandstone unit of the Chamberlain Pass Formation.

A total of fifty representative samples (48 samples from the Chamberlain Pass Formation and two samples from the underlying Pierre Shale) were collected from the recovered core for the present study, with each sample representing an approximately 30-cm-long core interval. A small representative block of each sample was used for thin section preparation. Subsequently, the outer five millimeters of the core were removed to minimize possible contamination caused by the drilling mud. The remaining core was dried and disaggregated with a mortar and pestle. Homogenous sample splits for the mineralogical and geochemical studies reported in the present contribution were obtained by riffle splitting of the disaggregated material.
4.4. Results

4.4.1. Thin Section Petrography

Polished thin-sections were prepared from each sample to study the mineralogy and textures of the sedimentary rocks through standard optical microscopy. Four basic sedimentary rock types were identified; mudstone (>20 modal% matrix), sandstone (<20 modal% matrix and average framework grain size <2 mm), conglomeritic sandstone (<20 modal% matrix and average framework grain size >2 mm), and shale (>20 modal% matrix and fissile).
Sandstone and conglomeratic sandstone samples collected from the Chamberlain Pass Formation are primarily composed of framework grains of quartz (50-80 modal%), microcline (3-15 modal%), and plagioclase feldspar (0-4 modal%). Lithic fragments are common (0.5-15 modal%) and mostly comprise chert, quartzite, and granite with rare schist (Fig. 4.4). The framework grains account for 70-90 modal%. They are generally sub-angular to rounded and moderately well to poorly sorted. The samples range from framework supported to matrix supported, with the clay-rich matrix accounting for 2-20 modal%. The porosity of the sandstone and conglomeratic sandstone is high, ranging from 2-20 modal%. Using the sandstone classification of Folk (1974), the samples are classified primarily as subarkosic sandstone. A few samples are sublitharenite, arkose, and quartz arenite sandstones (Fig. 4.5).

Framework feldspar grains in the sandstone and conglomeratic sandstone samples typically are altered to clay along grain boundaries and twin planes. Some dissolution of feldspar was observed preferentially along twin planes; however this was very rare, alteration of feldspars was more common. The proportion of altered feldspar grains can vary from 5 to nearly 100 percent. Plagioclase is commonly more intensely altered than microcline. Feldspar alteration appears to be slightly more intense in the oxidized, yellow to red samples compared to the other color groups (Fig. 4.6).

The sandstone and conglomeratic sandstone samples from the Chamberlain Pass Formation also contain detrital white mica (up to 1 modal%). The white mica forms up to 2.5 mm large flakes. These are commonly bent and separate along cleavage planes. In addition to the white mica, garnet, pyroxene, tourmaline, and zircon have been identified in trace amounts. These minerals are likely also of detrital origin.

Authigenic minerals include calcite, goethite, pyrite, and marcasite. Calcite is present in trace amounts in most of the sandstone samples, but can occur at concentrations of up to 15 modal%. Calcite is commonly very fine-grained and present throughout the clay-rich matrix of the sandstone and conglomeratic sandstone samples (Fig. 4.7C). In several samples, mostly those that are dark green and light gray, calcite replaces feldspar grains or forms a cement with large (> 250 µm) euhedral grains being present (Fig. 4.7D). Iron oxide/hydroxide staining is noticeable only in sandstone samples.
Figure 4.4: Photomicrographs of the host sandstone of the Three Crow roll-front uranium deposit. A. PPL image of sandstone from the oxidized zone. The reddish color of the matrix is the result of sulfide alteration; remnant sulfide is visible as the opaque zones in the lower right portion of the image. Clay alteration of feldspar grains is abundant. Sample H150C-12. B. PPL image of conglomeritic sandstone from the oxidized zone. The detrital grains are variable rounded and very poorly sorted. The matrix is rich in clay minerals and the feldspars are partially altered to clays. Sample T797C-5. C. PPL image of the conglomeritic sandstone from the transitional/mineralized zone. The large grain in the center is chert. The detrital grains are variably rounded and poorly sorted and the matrix is somewhat patchy. Sample H161C-1. D. PPL image of the sandstone from the reduced zone (light gray in color). The detrital grains are generally rounded and well sorted. The matrix is clay rich and sulfides are present (small opaque grains). Sample T792C-1. E. PPL image of the sandstone from the reduced zone (dark green in color). Detrital grains are mostly rounded and moderately well sorted. Abundant frambooidal pyrite is present in the matrix (small opaque grains) and clay alteration of feldspars in sparse. Sample H161C-7. F. PPL image of the coarse sandstone from the reduced zone. Detrital grains are angular to somewhat rounded and poorly sorted. The matrix is somewhat patchy. Sample H161C-10. Scale bars are 0.25 mm.
Figure 4.5: Classification diagram of the sandstones and conglomeritic sandstones hosting the Three Crow roll-front uranium deposit (after Folk, 1974). The majority of the sandstones plot as subarkose. The conglomeritic sandstones contain more feldspar and lithic fragments so plot lower on the diagram than the majority of the sandstones. All data from thin section observations.
Figure 4.6: Box-and-whisker plot representation of the abundance of feldspar alteration to clay minerals of the different colors of the host sandstone of the Three Crow roll-front uranium deposit. This count includes both partially altered and completely altered grains. The boxes enclose the interquartile ranges and the median is displayed as a horizontal line. The vertical lines extending outside the boxes mark the minimum and maximum values that fall within the acceptable range. Individual points are considered outliers. Data from thin-section observations. The number of samples for each group are shown in the figure.
Figure 4.7: Photomicrographs of the host rock and confining units of the Three Crow roll-front uranium deposit. A. PPL image of a mudstone sample. The clay content is very high and the detrital grains are typically smaller than 0.25 mm. Porosity in the mudstones is also very low. Sample T797C-2. B. PPL image of the Pierre Shale, the lower confining unit of the deposit. The shale has abundant sulfides and clay minerals. Sample H161C-11. C. Cathodoluminescence image of the host sandstone with abundant fine-grained calcite disseminated in the matrix. The calcite is not visible in PPL but is readily apparent in CL due to its bright orange to pinky-red color. Sample H150C-8. D. Cross polarized light image of a sandstone where calcite has replaced detrital feldspar (upper left corner of the image). Sample H150C-15. Scale bar is 0.25 mm in all images.
that are yellow to red in color (Fig. 4.4A). Pyrite and marcasite can account for up to 4 modal% in reduced, dark green to gray samples. Framboidal pyrite is the most common iron sulfide mineral in the reduced samples although other morphological types of pyrite and marcasite have been noted (Fig. 4.4D and E).

The two mudstone samples from the Chamberlain Pass Formation have very similar detrital grain compositions to the sandstones and conglomeritic sandstones except that the framework grains account for less than 20 modal%, the remainder is composed of clay minerals (Fig. 4.7A). Quartz and potassium feldspar are the most common detrital grains, rock fragments are much less abundant (< 3 modal%) than in the sandstones, and white mica and plagioclase feldspar are very rare in the mudstones. The two shale samples from the Pierre Shale are distinguished from the mudstones by their fissile texture and color (Fig. 4.6B). The shales are very dark gray to black in color compared to the light tan to greenish gray color of the mudstones of the Chamberlain Pass Formation. Quartz and potassium feldspar account for less than 10 modal% of the shales and authigenic iron sulfide (both pyrite and marcasite) comprises between 1 and 5 modal%.

### 4.4.2 Cathodoluminescence Petrography

Cathodoluminescence (CL) petrography was performed on polished thin sections at the Colorado School of Mines using a HC5-LM hot-stage CL microscope by Lumic Special Microscopes, Germany. The microscope was operated at 14 kV and with a current density of ca. 10 μA mm⁻² (Neuser, 1995). A high sensitivity, double-stage Peltier cooled Kappa DX40C CCD camera was used to capture CL images.

Detrital quartz with several distinct CL signatures was identified in the sandstone samples using this technique, suggesting a mixed provenance for the sandstones of the Chamberlain Pass Formation. The CL color of the quartz grains varied from bluish-violet, reddish-brown to bottle green. The bluish-violet and reddish-brown CL colors of the quartz grains were found to be long-lived. In contrast, the bottle-green CL is short-lived, changing to a dark brown color within seconds of the electron bombardment, making it difficult to image. The three types of CL broadly correlate to the type of quartz
observed in plane polarized light. The bluish-violet quartz is typically monocrystalline with some mineral inclusions, most commonly zircon and rutile. The reddish-brown CL was found most commonly in chert fragments. The bottle-green CL is also typically monocrystalline, much like the bluish-violet CL quartz. While not definitive, CL color can be broadly correlated with source rock type (Götze et al., 2001). The blue-violet quartz is likely derived from intrusive igneous rocks while the reddish-brown quartz is sourced from metamorphic rocks. The short-lived green quartz is of hydrothermal or pegmatitic origin. The rare quartz overgrowth on detrital quartz grains recognized in optical microscopy was found to be non-luminescent.

Inspection of the thin section under the CL microscope also confirmed the presence of potassium feldspar in the samples, which has a very homogeneous bright blue luminescence. Plagioclase, which exhibits bright green, blue-violet, and violet CL, was also identified in some samples. Trace amounts of pale to bright yellow zircon and bright green apatite have been recognized. In addition, fine-grained calcite, characterized by a bright orange CL, was found in the matrix of many samples. This calcite is commonly not easy to recognize in plane polarized light due to its fine-grained nature and disseminated occurrence. In some samples the matrix exhibited bright blue CL, similar in color to the CL of potassium feldspar. This color is characteristic of Al-rich clays (Götze et al., 2002), which in this case is kaolinite.

CL petrography showed that many of the quartz grains contained in the sandstone show the effects of radiation damage caused by alpha particle bombardment of the quartz. Previous work has shown that radiation damage of sufficient dosage in quartz causes a visible color change. Damaged quartz has a distinct bright orange-yellow CL color (Owen, 1988; Götze et al., 2001; Krickl et al., 2008; Kempe et al., 2012, this study).

The detrital quartz grains contain abundant mineral inclusions of zircon and monazite that are typically surrounded by halos of bright orange-yellow CL. These halos are most common in conglomeratic sandstones and coarse-grained sandstones where quartz grains are coarse enough to contain mineral inclusions. The halos are circular to elongate in shape and can display concentric rings. The width of the halos is consistent with the penetration depth of alpha particles emitted by the uranium and/or
thorium decay series. In addition to the halos surrounding entire inclusions, bright orange-yellow halos are commonly also associated with mineral inclusions intersected by the grain boundaries. The fact that the radiation damage halos surround primary inclusions as well as the preferential occurrence of the radiation damage in quartz grains showing a blue-violet CL suggest that the development of these radiation damage halos is unrelated to the roll-front mineralization.

Sandstone samples having elevated uranium concentrations (>100 ppm U) were found to contain another texturally distinct type of radiation damage halos. In these samples, the bright orange-yellow CL occurs as halos riming entire quartz grains. These rims follow the grain boundaries and can be up to 20 micrometers in width. This type of radiation damage occurs in all types of quartz. The observed correlation between whole-rock uranium content and the occurrence of these damage halos suggests that the rims surrounding detrital quartz grains formed in association with the roll-front uranium enrichment whereby the source of the alpha particles must be located in the matrix between the framework grains.

4.4.3 Clay Mineralogy

Further information on the clay mineralogy of the sedimentary rocks was obtained by X-ray diffraction analysis after separation of the clay-sized (<2 µm) fraction. This was achieved by suspending ca. 10 grams of the sample material in a mixture of distilled water and sodium hexametaphosphate solution. After vigorous shaking, the suspension was centrifuged. The supernatant was drawn off with a syringe to reduce disturbance of the sediment at the bottom of the centrifuge bottle. The clay-sized fraction was then collected by centrifuging the supernatant at 4400 rpm for an hour. The clay was re-suspended in a small volume of water by sonication and subsequently freeze dried. Oriented mounts were prepared by filtering a small portion of clay suspended in sodium hexametaphosphate solution through a 0.45 µm Millipore filter using a vacuum filter apparatus (cf. Moore and Reynolds, 1997).

Clay identification was performed on XRD patterns collected at the Colorado School of Mines on a Rigaku diffractometer that was equipped with a Cu X-ray tube, a 2
mm divergence slit, a 0.2 mm receiving slit, and a monochromator. The samples were scanned from 1.5 to 30°2θ at a step width of 0.05°2θ per step and an acquisition time of 10 seconds per step. Samples were analyzed after air-drying, ethylene glycol saturation, and heating to 250°C and 550°C.

Smectite, muscovite, and kaolinite were identified in the <2 μm fractions of the sedimentary rocks from Three Crow. Smectite was identified by the presence of a broad 001 peak at 10.5 to 12 Å in the air-dried oriented mounts. Upon ethylene glycol-solvation, the peak position increased to 16.9 Å, while heating at 250°C resulted in a shift to 10 Å. The higher-order reflections of the smectite were usually not strong enough to be positively identified in the samples. Muscovite was identified by the presence of a sharp 001 peak at 10 Å in the air-dried oriented mounts. The peak position did not shift after ethylene glycol-solvation or heating to 250°C. Muscovite also has a less intense 002 peak at 5 Å and a 003 peak at 3.4 Å, the latter being commonly obscured by the presence of the quartz peak at 3.2 Å. Kaolinite was recognized by the presence of a sharp 001 peak at 7.1 Å in the air-dried oriented mounts that did not shift after ethylene glycol-solvation or heating to 250°C. Heating to 550°C resulted in the disappearance of this peak. The 002 reflection of kaolinite is located at 3.5 Å and showed the same behavior as the 001 peak. No chlorite, the 002 and 004 peaks of which are located very close to the 001 and 002 peaks for kaolinite, was detected in the samples from Three Crow (Fig. 4.8).

Several samples were also analyzed in a random powder mount to determine the type of smectite present. The samples were chosen based on minimal presence of quartz and feldspar because their peaks overlap with those of the smectite. Inspection of the 060 region revealed the presence of a broad peak centered at 1.5 Å, suggesting that dioctahedral smectite is dominant whereas trioctahedral smectite is either not present or only occurs in low concentrations. Extensive peak overlap prevented conclusive determination of the muscovite polytype.

Inspection of the XRD patterns confirmed that there are some general variations in clay mineralogy across the different color groups of samples. Smectite appears to dominate in the strongly oxidized yellow to red samples (Fig. 4.9A). In these samples, muscovite is generally more abundant than kaolinite. The grayish yellow transitional
Figure 4.8: Representative X-ray diffraction patterns of an oriented mount of the <2 µm separate from the host sandstone of the Three Crow roll-front deposit. Values shown are d-spacings in angstroms. S = smectite, M = muscovite, K = kaolinite, Q = quartz, EG = ethylene glycol, HT = heat treated.

samples contain variable concentrations of smectite, muscovite, and kaolinite (Fig. 4.9B). Most light gray samples contain muscovite as the dominant clay mineral (Fig. 4.10A). Kaolinite tends to be lower in concentration than both muscovite and smectite. Kaolinite occurs most abundantly in the dark green reduced samples with concentrations that usually exceed those of smectite (Fig. 4.10B). The relative abundance of muscovite is variable in this sample group.

In all color groups of samples, there is a general correlation between average grain size and clay mineral content. In the mudstone samples, smectite is the dominant clay mineral and the kaolinite abundance is usually low. The conglomeritic sandstone samples also tend to have less kaolinite and slightly more smectite. The proportion of
Figure 4.9: Representative X-ray diffraction patterns of the <2 µm fraction of the Chamberlain Pass Formation. A. Red to yellow oxidized samples. The smectite peak is the largest clay peak and muscovite and kaolinite are also present. Sample H150C-12. B. Yellow/gray transitional samples. Muscovite and kaolinite are the dominant clay minerals and smectite is also present. This sample also has significant contamination by quartz and potassium feldspar. The iron sulfate jarosite is also likely present. Sample H161C-3. S = smectite, M = muscovite, K = kaolinite, Q = quartz, F = feldspar, J = jarosite, EG = ethylene glycol, HT = heat treated.
Figure 4.10: Representative X-ray diffraction patterns of the <2 µm fraction of the Chamberlain Pass Formation. A. Light gray reduced samples. The smectite peak is the largest clay peak; significant muscovite and minor kaolinite are also present. Sample H150C-1. B. Dark green to gray reduced samples. Muscovite and kaolinite are the dominant clay minerals and smectite is also present. This sample also has significant contamination by quartz and potassium feldspar. Sample T810C-3. S = smectite, M = muscovite, K = kaolinite, Q = quartz, F = feldspar, EG = ethylene glycol, HT = heat treated.
the three clays in the sandstone samples is variable and corresponds closely to sample color. Muscovite is dominant in the shale samples which also contain some smectite and kaolinite.

4.4.4 Whole-Rock Mineralogy

Quantitative whole-rock mineralogy of the sedimentary rocks was determined using X-ray diffraction analysis. Whole-rock powders were prepared at the Colorado School of Mines with a vibratory McCrone micronizing mill. Crushed sample material was ground to <10 μm under ethanol. Homogeneous mixing was achieved in a vibratory mixer mill. Step-scan XRD data (5 to 80° 2Q, 0.03° 2Q step width, 8 s/step) were collected at TU Bergakademie Freiberg, Germany with an URD 6 Seifert-FPM diffractometer equipped with a diffracted-beam graphite monochromater and a variable divergence slit. A Co tube was used and operated at 40 kV and 30 mA. Qualitative phase analysis of the raw diffraction patterns was carried out by conventional search/match procedures. Subsequently, quantification of the phase abundances as conducted using the fundamental-parameter Rietveld program AutoQuan (Bergmann et al., 2001; Monecke et al., 2001; Kleeberg and Bergmann, 2002; Ufer et al., 2004).

The major minerals identified and quantified in the sedimentary rocks include quartz, microcline, albite, and muscovite (Table 4.1). It is assumed that much of the muscovite discussed in the above section is identified as muscovite here. The abundances of the major detrital minerals quartz, microcline, albite and muscovite do not vary systematically across the deposit. The redox sensitive (Fe-bearing) minerals change in abundance based on the redox state of the sandstone. Reduced samples contain pyrite and marcasite while oxidized samples can contain jarosite. In contrast to the major detrital minerals, the clay minerals do vary in abundance across the deposit (Figure 4.11). Smectite is the most abundant clay mineral in most samples and is consistently present in upstream of the mineralized zone. The abundance of smectite in the reduced zone downstream of the mineralization is more variable. Kaolinite is most abundant in the reduced zone of the deposit. While it occurs in the oxidized zone, its abundance is typically below 1 percent.
Figure 4.1: Down-hole plot of the clay mineral content in relative wt.% of total minerals. Muscovite content is relatively consistent across the deposit while smectite is variable. Kaolinite content is typically low in the oxidized drill holes (T797C and H150C) and is higher in the reduced drill holes (T792C and T810C).
Table 4.1: Minerals identified by Rietveld quantitative phase analysis sorted by average abundance.

<table>
<thead>
<tr>
<th>Minerals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
</tr>
<tr>
<td>Smectite</td>
</tr>
<tr>
<td>Microcline</td>
</tr>
<tr>
<td>Plagioclase Albite</td>
</tr>
<tr>
<td>Muscovite</td>
</tr>
<tr>
<td>Kaolinite</td>
</tr>
<tr>
<td>Calcite</td>
</tr>
<tr>
<td>Pyrite</td>
</tr>
<tr>
<td>Jarosite</td>
</tr>
<tr>
<td>Marcasite</td>
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<tr>
<td>Gypsum</td>
</tr>
</tbody>
</table>

4.4.5 Accessory Mineralogy

To study the accessory mineralogy of the sedimentary rocks, the heavy mineral fraction of the rocks was recovered. Initially, gravity sedimentation was performed to remove the <30 µm particle size fraction. The coarser-grained material was then dried and passed through lithium metatungstate solution with a specific density of 2.95 g/cm³ in a separatory funnel. The heavy mineral fraction recovered this way was split using a micro-riffle splitter. One sample split was used to study grain morphologies and surface textures of the heavy minerals on grain mounts using a JEOL JSM-7000 field emission scanning electron microscope at the Colorado School of Mines. The other sample split was used to determine relative mineral abundances by automated quantitative phase analysis using a QEMSCAN scanning electron microscope system (see Chapter 2 for detail).

The sedimentary host rocks of the Three Crow deposit contain a wide range of heavy minerals. Based on textural criteria such as grain morphology and grain surface textures, minerals of detrital origin were distinguished from authigenic phases. The detrital minerals show grain morphologies indicative of mechanical transport while authigenic phases display well-developed crystal faces or intricate grain morphologies that would not have been preserved during transport. In addition, grain surface textures
such as conchoidal fractures, arcuate or linear steps, impact-V pits, and groves are characteristic for detrital grains that have been mechanically transported (Krinsley and Danahue, 1968; Margolis and Krinsley, 1974).

Detrital minerals identified in the sedimentary rocks include ilmenite, rutile, garnet, zircon, and tourmaline (Table 4.1). The detrital minerals make up between 5 and 65 wt.% of the heavy mineral fraction of the samples analyzed. The relative abundance of these detrital minerals was found to vary little across the deposit. Grain morphologies and surface textures of the detrital phases do not show a correlation with sediment color or proximity to the ore roll, implying that the detrital minerals were chemically inert and largely unaffected by alteration related to uranium enrichment.

Table 4.2: Accessory minerals identified by Qemscan analysis sorted by average abundance. Samples above the line are above 1 wt% of the accessory minerals; samples below the line are below 1.0 wt% average abundance.

<table>
<thead>
<tr>
<th>Detrital minerals</th>
<th>Authigenic minerals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ilmenite</td>
<td>Pyrite/marcasite</td>
</tr>
<tr>
<td>Rutile</td>
<td>Goethite</td>
</tr>
<tr>
<td>Garnet</td>
<td>Barite</td>
</tr>
<tr>
<td>Zircon</td>
<td>Gorceixite</td>
</tr>
<tr>
<td>Tourmaline</td>
<td></td>
</tr>
<tr>
<td>Titanite</td>
<td>Hematite</td>
</tr>
<tr>
<td>Staurolite</td>
<td>V-Goethite</td>
</tr>
<tr>
<td>Epidote</td>
<td>Sphalerite</td>
</tr>
<tr>
<td>Apatite</td>
<td>Chalcopyrite</td>
</tr>
<tr>
<td>Monazite</td>
<td>Galena</td>
</tr>
<tr>
<td>Spinel</td>
<td></td>
</tr>
<tr>
<td>Amphibole</td>
<td></td>
</tr>
<tr>
<td>Andalusite/sillimannite/kyanite</td>
<td></td>
</tr>
<tr>
<td>Baddeleyite</td>
<td></td>
</tr>
<tr>
<td>Olivine</td>
<td></td>
</tr>
<tr>
<td>Pyroxene</td>
<td></td>
</tr>
</tbody>
</table>

The principal authigenic minerals identified are pyrite, marcasite, goethite, barite, and gorceixite. Sphalerite, chalcopyrite, galena, and celestine occur in trace.
abundances (Table 4.1). In contrast to the detrital phases, the concentrations of the authigenic phases vary substantially across the roll-front and correlate with sample color. Authigenic goethite is most abundant in the oxidized tongue of the roll-front while pyrite and marcasite are abundant in the reduced host rocks downstream of the ore zone. Both goethite and Fe sulfide minerals can be found in the transitional samples close to the mineralized zone (see Chapter 2).

As pyrite and marcasite cannot be distinguished by EDX analyses, distinction between both polymorphs in grain mounts relied on crystal habit. Selected grains were remounted and polished to confirm mineral identification and abundance by reflected light microscopy. Three morphological types of pyrite were distinguished: framboidal pyrite, small blocky pyrite, and large blocky pyrite. Morphologically, three types of marcasite were differentiated: platy, granular, and large blocky marcasite.

Individual pyrite framboids range from 5 and 25 micrometers in size while aggregates of framboidal pyrite can be up to 100 micrometers in diameter. Small blocky pyrite grains are aggregates of octahedral pyrite crystals that are around 5 micrometers in size. These aggregates range from 50 to 500 micrometers in diameter. The granular marcasite forms as a coating of needle-like marcasite crystals on framboidal pyrite and some small blocky pyrite overgrowths. The overgrowth layer of granular marcasite is typically not more than 10 microns thick and can be overgrown by large blocky pyrite. Platy marcasite grains are spherical and have a platy surface texture. Individual spheres are on average 40 micrometers in diameter. These marcasite grains can form larger aggregated grains that are composed of up to four individual spherical grains. In cross-section, it is apparent that the platy marcasite formed through overgrowth of framboidal pyrite resulting in the spherical grain shape. Large blocky marcasite grains are up to 500 microns in diameter. These grains are aggregates composed of euhedral marcasite crystals and can act as cement for framework grains. In some cases, the large blocky marcasite is overgrown by the large blocky pyrite. Large blocky marcasite never forms overgrowths on other types of sulfide. The large blocky pyrite crystals commonly act as cement for framework grains and can form a distinct overgrowth on framboidal pyrite, small blocky pyrite, granular marcasite, large blocky marcasite and detrital mineral grains.
The trace element contents of the different morphological types of pyrite and marcasite were determined by laser-ablation inductively coupled-plasma mass spectrometry (see Chapter 2). Due to the small grain size of the platy and granular marcasite, only few of these grains could be analyzed. The trace elements most commonly detected in the different types of pyrite and marcasite include As, Co, Mn, Mo, Ni, and Pb. Of these, only As, Mo, and Mn displayed significant differences between the different sulfide types. The highest As concentrations were recorded in the two spot analyses performed on platy marcasite. The small blocky pyrite showed the next highest As concentrations. On average, pyrite was found to have higher As concentrations than marcasite. Molybdenum displays a similar pattern to As although the concentration levels of Mo in pyrite and marcasite are lower than those of As. In contrast to As and Mo, Mn is slightly enriched in marcasite compared to pyrite with the highest Mn concentrations found in blocky marcasite.

The goethite grains present in oxidized samples display variable grain morphologies and grain surface textures. They occur as pseudomorphs after Fe sulfides, as anhedral grains, or as grain coatings on detrital grains or other authigenic phases. The most common type of goethite pseudomorphs formed through the replacement of framboidal pyrite and small blocky pyrite replacements also occur. In some cases, goethite grains contain a remnant core of pyrite. Unequivocal evidence for replacement of marcasite or the large blocky pyrite has not been observed. Rare goethite that is enriched in V has also been recognized. The V-rich goethite occurs as small (<50 micrometers) aggregates of radiating acicular crystals (see Chapter 2).

4.4.6 Whole-Rock Geochemistry

Whole-rock geochemical analyses were performed on homogenized sample fractions of the Three Crow core samples at Geoscience Laboratories, Ontario. In addition to the major and trace elements, the loss on ignition, the total sulfur, and total carbon contents were determined. The total inorganic carbon content of the samples was determined by coulometric analysis at the Colorado School of Mines. For details of the sample preparation and analytical procedures see Appendix A.
4.4.1 Chemical Classification of Sandstone

Several chemical classification schemes exist for clastic sedimentary rocks that can be used to estimate sandstone maturity. The Pettijohn (1972) classification (Fig. 4.11A) has no shale category. For this reason, shales typically fall within the arkose group. However, the majority of the samples are classified as subarkosic sandstone. According to the Herron (1998) diagram (Fig. 4.11B), the majority of the samples are classified as subarkosic sandstone, but several samples plot in the arkose and litharenite categories. One of the shale samples is also classified as a litharenite and several of the mudstone and more clay-rich sandstone samples are classified as wacke. Neither classification scheme differentiates between lithic arkose or feldspathic litharenite, which contrasts the petrographic classification scheme of Folk (1974).

4.4.2 Element Correlations

Uranium does not correlate with any element except for V and Mo. Samples that have an elevated U content (>100 ppm) also show high V concentrations (>200 ppm) (Fig. 4.12A). There is no strong correlation between U and V for samples that have lower U and V contents. Molybdenum shows a weak correlation with U in the dark green samples (Fig. 4.12B). Samples with lower U and Mo contents have generally been collected distal to the ore zone when compared to sandstone samples having higher U and Mo contents. No correlation between U and Mo is evident for samples from the other color groups.

In contrast to U, Fe and S show significant correlations with several elements, in particular the chalcophile elements. Fe shows strong positive correlations with Cr, Cu, Ni, and Zn. These elements also show strong correlations with each other. Cr, Cu, Ni, and Zn are also slightly positively correlated with S in all samples except for the oxidized yellow to red samples where S is distinctly low compared to the other samples. Fe strongly correlates with S in samples where FeS\textsubscript{2} is the dominant iron bearing mineral (Fig. 4.13A). Fe is also strongly correlated to Ti (Fig. 4.13B), likely due to significant amounts of ilmenite in the accessory mineral fraction of the sandstone.
Figure 4.12: Chemical clastic classification diagrams for the host rocks of the Three Crow roll-front uranium deposit. A. Pettijohn et al. (1972) sandstone classification. The fine-grained and clay rich shales and mudstones fall within the arkose category. Both types of sandstones fall within the arkose, subarkose and sublitharenite categories. B. Herron (1998) clastic classification. This classification scheme has a shale category however only two of the clay-rich shales and mudstones fall within this area. The other clay-rich rocks fall within the wacke category. The rest of the samples fall within the arkose, litharenite, and subarkose categories. It is interesting to note that, even though many of these samples contain significant sulfides and other Fe-bearing phases, none of the samples fall within the Fe-shale or Fe-sands categories. All data from whole-rock geochemical analyses.
Figure 4.13: Uranium correlations with vanadium and molybdenum. A. V plotted against U. There is a slight positive correlation. B. Mo plotted against U. Mo correlates with U in the reduced dark green to gray samples ($R^2 = 0.17$) but not in the red to yellow oxidized samples. All data from whole-rock geochemical analyses.
Figure 4.14: Diagram showing the relationships between whole-rock S, Ti, and Fe and Ba, Rb, and K. A. Relationship between Fe and S. While Fe is variable in the red to yellow samples, S is distinctly low. In the reduced samples, Fe and S are positively correlated. B. Relationship between Ti and Fe. Ti and Fe correlate in all samples, however there is a slight separation between the grayish yellow and dark green to gray samples and the red to yellow and light gray samples. C. Relationship between Ba and K. The correlation is high ($R^2 = 0.7$) for the samples without significant barite or other sulfates. D. Relationship between Rb and K. Rb and K correlate well in almost all samples, regardless of redox condition.
Other elements that show positive correlation are K, Ba, and Rb (Fig. 4.13C and D). K is strongly positively correlated with Ba and Rb, both of which can substitute for K in microcline and muscovite. Where Ba does not correlate with K, other Ba minerals such as barite form a significant proportion of the accessory mineral fraction.

4.4.6.3 Spatial Variations in Element Abundance

Most of the samples from the Chamberlain Pass Formation have U concentrations below 50 ppm. Only three samples, collected in close proximity to the roll-front, have U contents higher than 100 ppm. The highest U concentration of over 1000 ppm was noted for a mineralized sample from drill hole H161C. The average U content in the oxidized samples is slightly lower (9 ppm) than the average in the reduced samples (29 ppm in the light gray and 14 ppm in the dark green samples).

Several elements display systematic variations in abundance across the ore zone. Selenium shows a slight increase in abundance proximal to the ore zone, on the upstream side (Fig. 4.14). This is similar to the trend observed by Harshman (1974) although this trend seems to extend further upstream at Three Crow than at other deposits. Arsenic displays a similar trend. While whole-rock As concentrations are mostly below the detection limit in the sandstones of the Chamberlain Pass Formation, samples from the mineralized hole show significant As enrichment (Fig. 4.15). This As enrichment correlates with an elevated content of small blocky pyrite.

The concentration of sulfur and carbon also vary systematically across the roll-front (Fig. 4.16A). In the upstream oxidized yellow to red samples, total carbon and sulfur contents are low. Total carbon is generally below 500 ppm. The sulfur content is slightly more variable, ranging from 100 to 1500 ppm, presumably due to the presence of sulfate minerals such as barite in the oxidized sandstone. The total carbon and sulfur are slightly higher in the transitional grayish yellow and the light gray reduced samples, ranging from 200 to 1000 and 1000 to 10,000 ppm, respectively, than in the oxidized samples. The reduced dark green samples collected downstream of the ore zone have higher total carbon and sulfur contents of 500 to 4500 and 1300 to 16,000 ppm, respectively. Anomalously high total carbon (above 10,000 ppm) has been recorded in
Figure 4.15: Down-hole plot of Se content in parts per million. Concentrations above 1 ppm were above the detection upper detection limit. This plot shows that Se is enriched in the oxidized and transitional samples upstream and proximal to the ore zone (drill hole H161C).
Figure 4.16: Down-hole plot of As content in parts per million. As is below the detection limit for many samples but is distinctly enriched in hole H161C, below the mineralized samples. This zone is also where As-rich pyrite is abundant.
Figure 4.17: Diagram of the relationships between total carbon, total S, inorganic carbon, and organic carbon. A. Relationship between total carbon and S. Total carbon is low in the red to yellow oxidized samples upstream of the ore and higher in the dark green to gray and grayish yellow samples. B. Relationship between inorganic and organic carbon. In general, both inorganic and organic carbon are low, however in several samples, one or the other is much higher.
four samples, but there is no strong correlation with color or location within the deposit (Fig. 4.16A).

In general, the inorganic carbon content is less than 100 ppm except in the samples containing significant calcite as either disseminated grains in the matrix or as cement (Fig. 4.16B). The majority of these samples are dark green to light gray in color and from drill core T810C. Two other samples with high inorganic carbon are grayish yellow transitional samples. Organic carbon content is usually higher than the inorganic carbon content, especially in samples from drill cores H161C and T792C (Fig. 4.16B). While the average organic carbon content is about 1500 ppm, several samples have organic carbon contents as high as 17,600 ppm. Small preserved wood fragments were recovered from sample T792C-4 which has the highest organic carbon content of all samples.

4.4.6.4 Immobile Elements

A number of elements show no variation in their abundances across the roll-front. This is particularly the case for a number of high field strengths elements (the rare earth elements, Y, Th, Hf, and Zr). Other elements that behaved immobile include Cd and Pb. While the chalcophile elements (Cr, Cu, Ni, and Zn) are strongly correlated with each other as well as Fe, they also do not show any distinct variability in abundance across the roll-front. The behavior of these elements appears to be largely controlled by factors such as grain size and abundance of accessory minerals rather than the redox changes associated with U mineralization.

The behavior of Th is notable as it does not show a correlation with U. The U/Th ratio should remain constant with increasing U content if Th was coupled to U. However, at Three Crow the U/Th ratio increases with higher U content (Fig. 4.17). This indicates that Th content is essentially the same throughout the deposit and Th has not been mobilized. Thorium could be primarily contained in monazite and zircon, detrital accessory minerals that did not undergo dissolution in the roll-front environment (see Chapter 2).
The basic shape of the REE patterns is essentially the same for all samples (Fig. 4.18). The normalized light REEs (La through Sm) are steeply sloping with a slight upward curvature. The heavy REEs (Gd through Lu) have a slope that varies from slightly negative to slightly positive but is essentially flat. Europium displays a slight negative anomaly with Eu/Eu* values ranging from 0.6 and 0.9 (Taylor and McLennan, 1985). While the shape does not vary significantly between samples, the concentration of total REEs depends on the average grain size (Fig. 4.18). The shale and mudstone samples have the highest total REE content and the sandstone and conglomeritic sandstone samples have lower total REE contents. This trend is a reflection of the clay content of the samples and is typical for sedimentary rocks. Clay-rich sedimentary rocks tend to have higher concentrations of total REE than coarser grained sedimentary rocks (Cullers et al., 1987).

Figure 4.18: Uranium-thorium ratio plotted against uranium. The nearly linear relationship indicates the U/Th ratio is controlled by U. Th is interpreted to be decoupled from U and is immobile in this system. All data from whole-rock geochemical analyses.
Figure 4.19: Rare earth element (REE) plots for the host rocks of the Three Crow roll-front deposit. The vertical axis is the sample normalized to chondrite on a log scale (after Anders and Grevesse, 1989). The horizontal axis lists the REEs. A. Sandstone samples. B. Conglomeritic sandstone samples. C. Mudstone samples. D. Shale samples. All data from whole-rock geochemical analyses.
4.5 Discussion

4.5.1 Source of the Clastic Material and Environment of Deposition

Previous studies of the Chamberlain Pass Formation concluded that the sedimentary strata were deposited in a large braided stream system that extended from Wyoming through Nebraska to Colorado (Swinehart et al., 1985; Evans and Terry, 1994, Terry, 1998). These studies concluded that the source material for the Chamberlain Pass was of mixed provenance. Analysis of the framework grains and detrital accessory minerals conducted in this study confirms a mixed origin for the Chamberlain Pass Formation. The major detrital minerals are quartz, microcline, plagioclase, and muscovite. Lithic fragments include various felsic igneous and metamorphic rocks as well as chert and quartzite. The accessory mineralogy also points to felsic intrusive and metamorphic rocks as likely sources for the sedimentary rocks of the Chamberlain Pass Formation at Three Crow, with ilmenite, rutile, garnet, tourmaline, and zircon being the most abundant accessory phases.

In addition to igneous and metamorphic rocks, the grain morphology and grain surface textures of some of the detrital minerals indicate recycling of clastic material from a sedimentary source. For instance, non-luminescent quartz overgrowth on detrital quartz grains was observed under the CL microscope. As the quartz overgrowth was noticeably rounded and abraded, formation of the overgrowth must have predated transportation and deposition of the grains. Recycling of older sedimentary material is also supported by variable rounding of zircon and tourmaline grains. A small proportion of these grains was found to be exceptionally well-rounded. As these minerals are considered extremely stable in the sedimentary environment, the degree of rounding of these grains indicates they likely originated from reworked sedimentary rocks (Krynine, 1946).

The findings of the present study are consistent with paleoenvironmental reconstructions of the late Eocene, suggesting that the clastic material of the Chamberlain Pass Formation could have been primarily sourced from the Black Hills. The core of the Black Hills is comprised of Precambrian igneous and metamorphic
rocks that were capped by Paleozoic to Mesozoic sedimentary rocks prior to uplift (Terry, 1991; Evans and Terry, 1994; Evans, 1996; Evans, 1999).

**4.5.2 Sandstone Diagenesis**

The sedimentary strata of the Chamberlain Pass Formation have been affected by diagenesis following burial. Diagenesis of arkosic sandstone is known to form new clay minerals with the clay minerals forming being determined by the original detrital mineral composition, the burial depth, and the chemistry of the pore waters (Millot, 1970; Meunier, 2005). In the case of the Chamberlain Pass Formation, the original detrital components were primarily sourced from feldspar-rich igneous and metamorphic rocks. Alteration of these rocks results in the formation of secondary smectite and kaolinite. The alteration of volcanic ash, originally and important component of the Chamberlain Pass Formation, and detrital feldspars in an alkaline environment results in the formation of smectite (Moore and Reynolds, 1997; Guerel and Kadir, 2006). The kaolinite identified must have formed under slightly more acidic conditions (Moore and Reynolds, 1997), suggesting fluctuations in pore water pH during burial, diagenesis, and subsequent groundwater flow through the aquifer.

Muscovite was also identified as a major component of the clay-sized fraction of the Chamberlain Pass Formation. However, as these sedimentary rocks did not experience temperatures exceeding 100°C due to relatively shallow maximum burial, the muscovite identified is probably not a product of diagenesis (Abercrombie et al., 1994; Lanson, 2002; Monecke et al., 2007). Detrital white mica was identified during thin section petrography and quantitative whole-rock XRD analysis, supporting the assumption that much of the muscovite contained in the rocks is of detrital origin.

In addition to clay minerals, calcite and pyrite also formed during diagenesis. Although significant amounts of calcite cement were only found in a limited number of samples (H150C-8, H150C-17, T792C-8, and T810C-3,4, and 5), the occurrence of fine-grained disseminated calcite is widespread, mostly in samples that are dark green or light gray in color. Calcite cement, calcrete, and silcrete have been found in the Chamberlain Pass Formation and other sedimentary rocks of the White River Group.
across the region and have been attributed to pedogenic alteration and non-pedogenic processes (Lander, 1991; Evans and Terry, 1994; Terry and Evans, 1994). Diagenetic pyrite is almost exclusively frambooidal in nature. In some cases, the diagenetic pyrite replaces organic matter such as roots and twigs. The frambooidal pyrite occurs abundantly in the dark green to light gray reduced samples. A detailed discussion of the origin of diagenetic pyrite at Three Crow can be found in Chapter 2.

4.5.3 Sandstone Alteration Associated with Uranium Mineralization

After diagenesis, infiltration of oxygenated groundwater caused significant alteration of the host sandstones in conjunction with uranium mineralization. Alteration in the oxidized tongue was subtle. Most notably, feldspar was slightly more degraded and clay-altered in this zone. Alteration was most notable for redox sensitive authigenic minerals. Dissolution of diagenetic pyrite as well as the alteration of pyrite into goethite was extensive. This is evidenced by the distinct absence of pyrite in most strongly oxidized yellow to red samples and the presence of goethite pseudomorphs of diagenetic pyrite (see Chapter 2). The dissolution of microcline and the production of sulfate through pyrite oxidation also resulted in the precipitation of barite, which is most abundant in the yellow to red oxidized samples. Some kaolinite also precipitated in this zone.

Downstream of the oxidized zone in the still reduced sandstone, marcasite and pyrite precipitated. Initially, the small blocky pyrite formed, which coats diagenetic frambooidal pyrite or forms large aggregated grains. The small blocky pyrite is most abundant in the grayish yellow transitional samples proximal to the ore. Subsequent ore-stage sulfide formation involved the precipitation of marcasite and the late blocky pyrite. Kaolinite precipitation and calcite cement formation and grain replacement also occurred in the reduced zone.

Uranium enrichment occurred along the redox boundary between oxidized and reduced conditions, which is marked by the occurrence of light grey to grayish yellow sandstone colors. In the ore zone, uranium precipitated primarily as coffinite. As discrete coffinite grains are rare in the samples from the ore zone, it is possible that
uranium is also absorbed to earlier formed clay minerals or organic matter present in the sandstone. Uranium adsorption can be a major contributor to the total U contained in sandstone-hosted deposits (e.g., Bomber et al., 1986; Yoshida et al., 1994; Metcalfe et al., 2006) and may be important as a precursor step to the precipitation of discrete U ore minerals (Giblin, 1980; Goldhaber et al., 1987). Ore formation was accompanied by marcasite formation in the ore zone. Late blocky pyrite and calcite cement are also present in several samples.

The mineralogical changes described above correlate with significant changes in the whole-rock geochemistry. The most pronounced changes in elemental abundance between the oxidized and reduced zones of the deposit are for Fe, S, and C. Iron in the reduced zones is mostly contained in pyrite, marcasite, and ilmenite. This is reflected in the correlation of whole-rock Fe with Ti and Fe with S. In the oxidized tongue, Fe is contained in goethite phases. During oxidation, some Fe and S were mobilized upon dissolution of pre-ore pyrite and transported to the reduced zone of the deposit where they precipitated as ore-stage pyrite or marcasite. This change in mineralogy is reflected in the generally low Fe and S content of the oxidized samples and the equal or higher concentration of these elements in the reduced samples. A similar relationship exists between S and C. Oxidized samples have much lower concentrations of C and S than reduced samples, reflecting the destruction of organic carbon and dissolution of inorganic carbon and the precipitation of calcite at the redox interface. The sulfur content is variable in the oxidized samples due to the precipitation of the sulfates such as barite. The barium contained in barite is most likely sourced from the dissolution of potassium feldspar in the oxidized zone.

### 4.5.4 Deposit Model

The sedimentary host rocks of the Three Crow deposit were deposited in the late Eocene to early Oligocene. A large fluvial system stretching from Wyoming through Nebraska to Colorado created the multistory channel sandstones and overbank mudstones of the Chamberlain Pass Formation. Abundant organic material was incorporated into the sediments at the time because the prevalent tropical or semi-
tropical climate promoted dense vegetation (Dahlkamp, 2009). Burial of these sediments occurred with the deposition of the younger sediments of the White River Group, which included a significant volume of volcaniclastic material derived from the Absaroka volcanic field in northwestern Wyoming. Diagenesis of the Chamberlain Pass and overlying volcaniclastic rocks produced an anoxic slightly alkaline reducing environment conducive to the formation of framboidal pyrite and the preservation of detrital organic material. Framboidal pyrite formation likely required microbial mediation. This phase of diagenesis included the alteration of detrital feldspars and the precipitation of smectite.

These reducing conditions persisted until infiltration of oxygenated groundwater occurred along the basin margins. This oxidizing fluid moved through the Chamberlain Pass Formation altering diagenetic pyrite and carbonaceous material until equilibrium or near equilibrium conditions were established with the reduced host rock. This equilibrium zone became the redox interface and the zone of uranium precipitation. The main phase of mineralization began upon the establishment of this stable redox interface. The pH of the groundwater shifted to a more acidic character from the oxidization of upstream pyrite. Precipitation of coffinite could also have enhanced the acidity of the groundwater past the redox interface. The establishment of acidic conditions favored the precipitation of marcasite as the ore-stage sulfide in the reduced areas and the formation of kaolinite throughout the deposit. As the sulfides in the oxidized zone were consumed during the course of mineralization, acidic conditions could no longer be maintained and the pH rebounded to slightly alkaline. This prompted the precipitation of late ore-stage large blocky pyrite. No significant alteration post-mineralization occurred.

The model proposed for Three Crow differs from the established roll-front model with respect to the movement of the roll-front over time. The current deposit model summarized by Harshman and Adams (1981) and Cuney and Kyser (2008) assumes that the roll-front is dynamic throughout its lifetime. The roll migrates down a hydrologic gradient through perpetual oxidation along the leading edge of the oxidized tongue. The evidence from Three Crow implies that the roll-front was essentially stagnant, or alternatively moved only periodically over significant distances in a short period of time.
Ore-stage marcasite and pyrite has not been observed in the oxidized zone and no evidence for the replacement of these Fe sulfide minerals by goethite was found (see Chapter 2). This suggests that the formation of ore-stage pyrite and marcasite only occurred in the location of the present roll-front and that this roll-front has not continuously moved down the hydrological gradient. This finding is corroborated by the observations of the CL study that showed that significant radiation damage in quartz does not occur upstream of the current mineralized zone (see Chapter 3). If the ore zone had been located upstream and would have moved continuously across the drilled sandstone package, the uranium would have produced radiation damage in the now oxidized samples.

The concept of a spatially stable redox interface in the formation of uranium deposits has so far been limited to tabular type deposits. For tabular deposits, the mixing zone of two fluids, oxidized meteoric groundwater and deeper basin-derived reducing brine or hydrocarbon-bearing fluid, is the proposed origin of the redox interface. The coincidence of this interface with detrital organic matter or precipitated humic compounds can enhance uranium deposition (Granger et al., 1961; Sanford, 1992), however it is not strictly necessary to form tabular deposit (Xue et al., 2010). In all cases, concentrated uranium deposition only occurs with a spatially stable redox interface. A moving interface would result in a more disseminated ore body (Xue et al., 2010). This has also been proposed for redox interfaces in fractured basement rocks (Vogel et al., 1999).

Several factors present at Three Crow suggest that there is at least some sedimentological control on the location of the roll-front. All of the roll-fronts in the area are located within the channel sandstones and conglomeritic sandstones of the Chamberlain Pass Formation. This indicates that the paleochannel system acts as the aquifer for this mineralization system and that the surrounding sediments were not amenable to mineralization. The ore bodies are located along the flanks of the known extent of the Chamberlain Pass Formation at a bend in the paleochannel (Figure 4.1B). Reconstructions of the paleohydrology indicate that around the time of mineralization, the groundwater flowed within this channel also turning toward the south at the bend (Gjelsteen and Collings, 1988). Both the architecture of the sands and the
paleochannel created an ideal location for uranium mineralization by directing groundwater flow and concentrating detrital organic material, a likely initial source of reductant. As uranium concentration is low in the mineralizing groundwater, high volumes of water are required to form a deposit. Evidence indicates that the paleoclimate was significantly wetter than the current climate (e.g., Terry and Evans, 1994), producing the higher groundwater flow required.

As the sampling area was limited in this study, no detailed data on the mineralogical and geochemical conditions further away from the current roll-front position is available. Without data from further upstream in the paleochannel, there is no evidence to determine whether or not the roll-front was actually located further upstream at some time. If it is the case that the roll-front has moved to its current location from further upstream, then it would be expected to find mineralogical evidence of this. CL imaging would indicate the location of past mineralization. It is also likely that pseudomorphs of ore-stage pyrite and/or marcasite would also occur in the upstream zone if the Fe sulfides did not undergo complete dissolution. As these pseudomorphs are present at the current location, it is likely they would also be found at past locations of the roll-front.

The present work has also refined the understanding of geochemical gradients across roll-front deposits as established by Harshman (1974). Selenium is enriched in the yellow to red oxidized samples compared to the dark green to gray samples collected from the reduced side of the roll-front. While Harshman (1974) observed this trend typically within 5 to 10 meters of the redox interface, Se enrichment occurs several tens of meters away from the interface at Three Crow. Harshman (1974) also described the occurrence of V enrichment within reduced sandstones up to 10 meters from the redox interface. At Three Crow, V is higher in the oxidized sandstones up to 300 meters from the ore zone. Within the oxidized tongue, V is associated with goethite. Arsenic at Three Crow is enriched in a narrow zone in the grayish yellow samples proximal to ore. Elevated As concentrations are likely related to the presence of abundant small blocky pyrite in these samples. Molybdenum is enriched in the reduced sandstones within 100 meters of mineralization, similar to the distribution described by Harshman (1974).
The systematic zoning of these elements can be related to their redox potential and the redox gradient present across the roll-front. Initial Eh of the groundwater carrying U is around 0.2 to 0.3 V. This oxidizing groundwater comes in contact with reduced species, reacting and slowly the Eh falls to around -0.2 V. The distance over which this drop in Eh occurs is a function of the content of reducing species and the groundwater flow velocity, and is reflected in the minerals precipitated along this gradient. Figure 4.20 shows the approximate order in which the elements precipitate based on their redox potentials. V, having the highest redox potential, precipitates in a zone of relatively high Eh. Se also has a high redox potential so precipitates very near V. Both of these elements are found in the oxidized zone at Three Crow. The Fe-bearing minerals have varying redox potentials, therefore Fe minerals precipitate over a wide range of Eh conditions and over a greater distance in the deposit. The redox potential of As species fall within the same zone as Fe, therefore As precipitates in the same general area as Fe. At Three Crow, an As-rich pyrite is found close to the ore zone. Next to precipitate is U and then Mo, which has the lowest redox potential, precipitates downstream of U in the reduced zone. This same trend is observed in the geochemistry and mineralogy at Three Crow.

4.5.5 Exploration Implications

The present study has defined several mineralogical and geochemical gradients across the roll-front that could be used as vectors to ore during exploration for concealed roll-front deposits. Although the redox state of the sedimentary rocks provides a critical criterion during exploration, allowing explorers to identify redox fronts within the aquifer quickly, identification of additional gradients may be critical in some cases, especially where a re-reduction of the aquifer has occurred.

Feldspar alteration is more common in the oxidized and mineralized zones of the deposit where smectite is the dominant clay mineral. Goethite makes up a significant portion of the accessory minerals in the oxidized zone as well, giving the oxidized rock its characteristic color. Kaolinite is more abundant than other clay minerals downstream of ore in the reduced dark green to gray sandstones and less abundant than other clay
minerals in the red to yellow oxidized sandstones. Pyrite and marcasite are also abundant on the downstream side and very rare on the upstream side of the roll-front. These mineralogical changes are reflected in the whole-rock geochemistry. The Fe/S ratio is low in the reduced rocks where Fe sulfides are abundant and increases in the oxidized rocks where Fe sulfides have been converted to goethite. In addition to these major elements, trace element enrichment in authigenic Fe sulfides can be significant enough to influence the whole-rock trace element geochemistry. For example, As
enrichment in the whole-rock samples corresponds to the zone of the deposit with the highest proportion of As enrichment in authigenic pyrite.

The present study also suggests that, while not suitable for tracing the migration of uranium-bearing groundwater, CL microscopy could be used to identify the location of past or present uranium enrichment through the recognition of radiation damage in quartz. As notable radiation damage of quartz requires significant dosage accumulation, the application of CL techniques may be most useful to test whether uranium ores have been mobilized from a certain location, allowing reprecipitation down the hydrological gradient. At Three Crow, the use of this technique showed that the roll-front must have been stagnant for a pronounced period of time and did not continuously move down a hydrological gradient as previously assumed.

In addition to mineralogical and geochemical vectors, this study also suggests that sedimentology is an important factor in the formation of uranium roll-front mineralization. From an exploration standpoint, this means that defining paleochannel architecture is likely to be very significant in defining prospective locations for ore. Geophysical techniques such as seismic surveys will be critical to defining such locations.

4.6 Conclusions

The mineralogical and geochemical characteristics of the host sandstone of the Three Crow roll-front uranium deposit suggest that the redox interface and zone of uranium precipitation has remained essentially stable throughout its formation. Authigenic sulfide mineral paragenesis and alteration textures indicate that ore-stage sulfides were not present in the oxidized zone. Cathodoluminescence microscopy shows that radiation damage of detrital quartz grains only occurs in the mineralized zone. As the mineralizing fluids are not capable of causing the observed radiation damage, the lack of radiation damage upstream of the roll-front further supports a spatially stable redox interface. In addition, the mineralogical variations across the roll-front are reflected in the whole-rock geochemical analyses, most notably for the authigenic redox sensitive minerals such as goethite and the sulfide minerals pyrite and marcasite.
Zonation across the redox front for trace elements such as Se, As, V, and Mo closely match the expected zonation considering the Eh drop across the deposit and the relative redox potentials of the elements.
CHAPTER 5
CONCLUSIONS

This thesis aimed to describe the processes of sandstone alteration occurring in association with the formation roll-front uranium deposits, using the Three Crow uranium deposit in northwestern Nebraska as an example. A range of state-of-the-art analytical techniques including automated mineralogy, CL microscopy, LA-ICP-MS, and quantitative whole-rock XRD were used to expand current knowledge of alteration processes accompanying uranium enrichment and to develop new mineralogical and geochemical vectors to ore that could be used in the search for concealed roll-front deposits. The following sections summarize the key observations and interpretations and make recommendations for future work that would further improve the understanding of processes resulting in the formation of roll-front uranium deposits.

5.1 Key Findings

The key findings of the present study are:

1) The Three Crow deposit is located in the Crawford Basin in northwest Nebraska. Three other uranium roll-front deposits (North Trend, Crow Butte, and Marsland) are located in the vicinity of Three Crow and make up a trend of deposits extending from north of the town of Crawford southeast to the town of Marsland. All four deposits are hosted by the late Eocene Chamberlain Pass Formation of the White River Group. The sedimentary rocks of the Chamberlain Pass Formation are of mixed provenance and were most likely sourced from the Black Hills in South Dakota, with possible input of detrital material from the Hartville Uplift or the Laramie Mountains in Wyoming. Within the Chamberlain Pass Formation, there is a strong sedimentological control on the location of roll-front uranium enrichment. The ore zones occur within the channel sandstones and conglomeratic sandstones that acted as regional groundwater aquifers while
overbank mudstone deposits form important confining layers that were essentially impermeable to ground water flow.

2) Petrographic analysis of samples recovered by research drilling showed that the framework grains of the Chamberlain Pass sandstones and conglomeratic sandstones are composed of quartz, potassium feldspar, and plagioclase. Chert and other rock fragments are common. The mineralogy of the framework grains does not change dramatically across the roll-front although some subtle changes can be observed. Clay alteration of potassium feldspar is more strongly developed in the oxidized and mineralized zones of the Three Crow deposit when compared to the reduced zone downstream of the roll-front. Plagioclase is slightly more abundant downstream and can be almost completely altered on the oxidized side of the ore roll. The decrease in plagioclase abundance in oxidized sandstones and conglomeratic sandstones is related to replacement by clay minerals such as smectite and kaolinite.

3) XRD analysis of the clay-sized fraction identified several clay minerals, including dioctahedral smectite, dioctahedral white mica (muscovite), and kaolinite. No mixed-layered clay minerals were identified, presumably because diagenesis of the Chamberlain Pass Formation did not involve elevated temperatures due to the shallow burial depth. The relative proportions of these minerals appear to change slightly across the roll-front. Dioctahedral smectite, most likely a montmorillonite, is dominant in the oxidized interior of the ore roll while kaolinite is dominant in the reduced zone of the deposit. This could reflect systematic changes in pH conditions across the roll-front during uranium mineralization, which is also indicated by the distribution of the Fe sulfides pyrite and marcasonite.

4) SEM investigations on the accessory mineralogy of the Chamberlain Pass sandstones and conglomeratic sandstones showed that detrital accessory minerals such as ilmenite, rutile, garnet, tourmaline, and zircon were not significant contributors to the redox reactions occurring in the roll-front while the
authigenic minerals, specifically Fe-bearing phases such as pyrite, marcasite, and goethite, were important components of the geochemical system. The authigenic minerals are characterized by pronounced variations in abundance across the roll-front. Pyrite and marcasite are most abundant on the reduced side of the oxidation front while goethite predominates in the oxidized upstream environment. Other authigenic sulfide minerals occurring in trace abundances include chalcopyrite and sphalerite.

5) Several generations of iron sulfide were identified using grain morphology, internal textures, and trace element abundances. Framboidal pyrite represents the only pre-ore sulfide mineral and is primarily preserved in reduced rocks downstream of the roll front. Framboidal pyrite was found to be enriched in Co, Ni, and Pb. Ore-stage sulfide minerals included both pyrite and marcasite, which show elevated concentrations of As, Mn, and Mo. The presence of both pyrite and marcasite indicates that the groundwater geochemistry changed over the course of mineralization. Initial neutral to slightly alkaline conditions favored the precipitation of diagenetic pyrite and early ore-stage pyrite. Coffinite, the principal uranium ore mineral found at Three Crow, precipitated under acidic to near-neutral conditions which promoted ore-stage marcasite precipitation. Late ore-stage pyrite was precipitated as the pH of the groundwater rebounded to near neutral or slightly alkaline conditions. The shift in acidity is likely a result of acid generation upstream of the roll-front, caused by the oxidation of diagenetic pyrite by the oxidizing groundwaters.

6) Natural radiation-induced damage of detrital quartz is widespread within the sedimentary rocks of the Chamberlain Pass Formation. Based on their distinct bright orange-yellow CL, damage halos could be easily identified under CL. The link between this characteristic CL color and structural damage caused by alpha particle bombardment was established through Raman spectroscopy and TEM investigations. The textural context of the damage halos was used to establish that damage halos riming entire detrital quartz grains developed in association
with the roll-front mineralization. These halos were only observed in samples having elevated uranium contents. Dosage model calculations showed that visible radiation damage of quartz grains cannot be caused by the passage of uranium-bearing groundwater. This suggests that the distribution of radiation damage halos is a direct reflection of the present or past distribution of uranium-bearing minerals in the matrix of the sedimentary rocks.

7) Whole-rock geochemical investigations revealed that a number of elements showed systematic variations in their abundances across the roll-front. Most notably, As was found to be enriched proximal to the mineralization, which is probably related to the incorporation of As into ore-stage pyrite. Molybdenum was found to be enriched proximal to the ore zone, but only downstream of the ore roll. The whole-rock Fe and S abundances correlate well with the pyrite and/or marcasite content of the samples. The total and organic carbon contents are higher in the transitional and reduced zones of the deposit than the oxidized side. The distribution of most other elements analyzed is unrelated to uranium roll-front mineralization and mostly governed by sedimentological variations. For instance, the normalized REE patterns of the sedimentary rocks correlate primarily with grains size and accessory mineral content.

8) The Three Crow roll-front uranium deposit was found to share many similarities with other deposits of the same deposit type. This includes the zonation of redox sensitive elements and the distribution of goethite and sulfide minerals across the roll-front. Although the presence of marcasite has been previously reported from roll-front deposits, the occurrence of ore-stage pyrite and marcasite is not universal in roll-front deposits. Most notably, the observed paragenetic relationships between the different morphological types of Fe sulfides can only be explained by a model that assumes that the roll-front did not continuously move down the hydrological gradient as implied by the roll-front deposit model. This conclusion is in agreement with the findings of the CL microscopy that showed that radiation damage of quartz grains directly correlates with present
uranium content, which should not be the case if the roll-front would gradually move downstream in response to the consumption of the reductant in the aquifer. The findings suggest that the roll-front must have been essentially stagnant for a significant period of time, or alternatively, moved periodically down the hydraulic gradient as opposed to continuously. Although no direct evidence points to an external source of a reductant, a possible structural control on deposit formation must be invoked whereby hydrocarbons migrating up a deep-seated fault act as an external reductant or where mixing of groundwaters of different chemical composition controls the deposit location.

5.2 Recommendations for Future Work

Based on the findings of the present thesis, several areas for future work are recommended. More detailed research in those areas may not only help to better constrain the processes that led to the formation of the roll-front deposit at Three Crow, but may also yield new information on uranium roll-front deposits in general. The following recommendations are made:

1) Current and past drilling operations by uranium companies in the region have produced a significant amount of drill hole data. Records from historic drilling for oil and gas resources as well as various types of geophysical data may also be available. Digitizing these records and assembling them into a regional GIS-based database would allow for the creation of a detailed regional geology model for the sedimentary strata overlying the Pierre Shale. Development of such a 3D model incorporating all available information of the subsurface in the northwestern portion of the Crawford Basin would undoubtedly provide a wealth of new information. This could include new constraints on the correlation between sedimentary facies and roll-front uranium deposits as well as possible structural controls on uranium mineralization. Development of such 3D knowledge cubes for entire intramontane basins or portions thereof may also prove to be a stepping stone in regional exploration for this deposit type.
Sophisticated 3D modeling software is available today and already widely used in exploration for other ore deposit types and energy resources.

2) The study of sediment provenance conducted as part of the present thesis could be enhanced through a detrital zircon study. Zircon is a mineral that is mechanically and chemically highly stable during transport, deposition, and diagenesis. Radiometric dating of a large number of zircon grains could be conducted to fingerprint the age spectrum of the source of the detrital material. As there are likely several sources for the sedimentary rocks of the Chamberlain Pass Formation, analyses of the age spectrum of zircons may provide important new constraints that could be combined with currently existing reconstructions of the paleodrainage pattern in the foreland of the Rocky Mountains during the late Eocene. Isotopic analysis of zircon grains would most likely be conducted by laser ablation techniques to allow rapid analysis of a large number of zircon grains.

3) In addition to a more detailed provenance analysis, it could be advantageous to conduct paleontological studies on the sedimentary rocks hosting the uranium roll-front deposits in the Crawford Basin to better constrain their depositional ages. At present, paleontological work has been generally limited to the study of large land mammal fossils. Along with limited radiometric age dating, such fossil findings have been used to constrain the depositional age of the sedimentary rocks on a regional scale. It is possible that the sedimentary host rocks of the uranium deposits contain microfossils (e.g., diatoms, pollen, and charcoal) that could be used to further constrain their biostratigraphic ages. In particular, the fine-grained overbank deposits could contain microfossils while the coarser rocks deposited within the high-energy, fluvial environment are less likely to yield microfossils. In addition to their use in biostratigraphy, microfossils are also characteristic of past environmental conditions (e.g., temperature and precipitation), which would shed further light on the depositional conditions of the sedimentary host rocks. If microfossils could be recovered from core samples,
paleontological analysis may also be used for stratigraphic correlation between drill holes at the scale of individual deposits.

4) The present study focused primarily on the characteristics of the alteration halo associated with the Three Crow roll-front deposit. If new core material would become available, it is recommended to conduct a study of the ore zone itself. Of particular interest would be a very detailed analysis of the uranium mineralogy. So far, only coffinite has been identified as a discrete uranium mineral at Three Crow. However, coffinite is very rare in the mineralized samples used for this study, indicating that discrete uranium minerals may not be the only host of uranium in roll-front deposits or that uranium-bearing phases are exceedingly small, making them even hard to find under the SEM. CL imaging conducted as part of the present research suggests that the source of alpha particles is finely dispersed in the matrix of the sedimentary rocks and not restricted to individual large mineral grains. It is well known that uranium can be strongly adsorbed to clay minerals as well as organic material under the prevailing pH-Eh conditions. A uranium deportment study should test whether adsorption of uranium is quantitatively important. Knowledge on the speciation of uranium is clearly critical for future in-situ recovery mining operations, especially as uranium contained in minerals such as brannerite cannot be recovered by in-situ leaching. It is recommended to study the ore prior and after in-situ leaching, which could ultimately help in increasing recovery through adjustments to the chemistry of the production fluid.

5) The research conducted on the accessory mineralogy of the host rocks of the Three Crow deposit has shown that different types of pyrite and marcasite can be distinguished through their grain morphologies. It is recommended to conduct a sulfur isotopic study on the identified types of pyrite and marcasite, preferably through laser ablation analysis. Although a sulfur isotopic study on samples from Three Crow has been conducted recently at the University of Manitoba (A. Martin and M. Fayek), this study did not focus on testing for a potential correlation.
between sulfur isotopic signature and grain morphology although a distinction between diagenetic and authigenic Fe sulfides was made. It is possible that such a sulfur isotopic study focusing on the different morphological types of pyrite and marcasite would provide important constraints on the role of microbial processes in roll-front uranium deposit formation and the recycling of sulfur during the process of upstream oxidation of Fe sulfides and the associated downstream reduction and precipitation of ore-stage pyrite and marcasite.

6) Future studies should focus on the geochemistry of goethite. Detailed investigations should be performed to better constrain mode of trace element incorporation (i.e., structural versus absorption). As goethite is present within the zones that will undergo in-situ mining, it would be crucial to better understand the role goethite plays as a geochemical source or sink of toxic elements during in-situ leaching (e.g., Cu, Mo, Pb, Se, and V). It appears possible that changes to the chemistry of the production fluid may reduce the amount of metals liberated from the sedimentary rocks by promoting metal absorption to goethite.

7) Detailed geochemical modeling of the system is also recommended. The current work proposed several mechanisms by which this deposit remains stagnant, one of which invokes an outside source for reductant. Geochemical modeling incorporating the detailed mineralogical work done in this study would assist in determining if the host sandstone has the reductive capacity to reduce the volume of groundwater needed to form a uranium deposit of this size or not.

8) The CL microscopy study conducted as part of this work should also be conducted on several other roll-front deposits in various geological settings to test the conclusions drawn from this study. While there is no evidence that the oxidized sandstone within the study area at Three Crow ever hosted mineralization, this might not be the case at other deposits. In addition, the area of study should be expanded to capture more distal areas of the deposits. Without data further from
the roll-fronts, it is not possible to definitively say whether or not these deposits move periodically, continuously, or are completely stagnant.

Based on the present study, two recommendations are made to further improve the analytical procedures used.

1) The sample preparation procedure for the accessory mineral separates could potentially be optimized to include grains that have smaller particle sizes. The procedure used in this thesis recovered only mineral grains larger than 30 micrometers. However, petrographic analysis of thin sections showed that pyrite and marcasite can occur at grain sizes of less than 10 micrometers. As this size fraction was not recovered, the morphology and chemistry of the smallest Fe sulfide grains could not be studied. Systematic experiments should be carried out to optimize recovery of smaller grain sizes although the use of heavy liquids clearly imposes limits to the minimum size of particles that can be separated by this method.

2) The clay-sized mineral fraction investigated by XRD contained quartz and feldspars, which caused substantial peak overlap in random powder mounts. It should be attempted to optimize sample preparation procedure to optimize clay mineral recovery. In the present study, the clay-sized mineral fraction was prepared after coarse crushing of the sedimentary rocks, which was required to disaggregate the material and to obtain homogeneous subsamples for further laboratory analysis. Coarse crushing may have modified particle size distribution, resulting in the generation of quartz and feldspar particles that are <2 micrometers in size. Systematic experiments should be carried out to test whether other types of sample disaggregation could be devised that produce lower quartz and feldspar contents in the clay-sized mineral fraction.
REFERENCES


The supplemental electronic files provide the data that was collected and analyzed for the preceding thesis. The files are organized into folders of related analyses and presented in the general order they are encountered in the thesis. The accessory mineral images and data are discussed in Chapters 2 and 4. The sulfide images and LA-ICP-MS data are also discussed in Chapters 2 and 4. Thin-section microscopy is discussed in Chapters 3 and 4. The microprobe analyses are discussed in Chapters 3 and 4. The Raman data and TEM images are discussed in Chapter 3. The X-ray diffraction data and whole-rock geochemistry are discussed in Chapter 4.

<table>
<thead>
<tr>
<th>Folder or File Name</th>
<th>Description and File Types</th>
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<tbody>
<tr>
<td>Accessory Mineral SEM Images and Data</td>
<td>Folder contains SEM images of the accessory minerals organized by drill hole and sample number. Individual image files are in JPEG format. Folder also contains the raw Qemscan data in a Microsoft Excel 2010 file named Accessory_Min_Abundances.xlsx that contains two sheets.</td>
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<tr>
<td>Sulfide SEM Images and LA-ICP-MS Data</td>
<td>Folder contains SEM images of iron sulfides in cross-section and of the surface (subfolders SEM_CrossSection and SEM_Surface respectively). Individual image files are in JPEG format. Folder also contains the raw LA-ICP_MS data in a Microsoft Excel 2010 file named Sulfide_LA-ICP_MS_Data.xlsx which contains 3 sheets.</td>
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<tr>
<td>Thin Section Microscopy</td>
<td>Folder contains cathodoluminescence (CL), plane polarized light (PL), and cross-polarized light (CPL) microscopy images from thin-section organized by drill hole and sample number. Individual images are in JPEG format. Folder also contains descriptions of the CL observations in a Microsoft Excel 2010 file named CL_Descriptions.xlsx which contains two sheets and a summary of the thin-section descriptions in a Microsoft Excel 2010 file named Thin_Section_Descriptions.xlsx which contains three sheets.</td>
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<td>X-ray Diffraction Data</td>
<td>The folder contains the raw XRD data from both clay mineral separates and whole-rock powders. The clay mineral data is presented in the folder Clay Mineral XRD. Each drill hole is presented in a separate Microsoft Excel 2010 file. The whole-rock powder XRD data is in the Microsoft Excel 2010 file named WR_XRD_Data.xlsx which contains five sheets. The file Gorceixite_powderXRD.pdf contains the powder XRD tracing for gorceixite in PDF format.</td>
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<tr>
<td>Whole-rock Geochemistry</td>
<td>The folder contains the analytical procedures and raw data for the whole-rock geochemical analysis. The sample preparation and analytical procedures are contained in the PDF format file named WRGeochemProcedures.pdf. The raw data is presented in the Microsoft Excel 2010 file named WR_GeoChem_RawData.xlsx which has six sheets.</td>
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