

Mineralogical and Geochemical Evolution of the Unconformity-Related McArthur River Zone 4 Orebody in the Athabasca Basin, Canada: Implications of a Silicified Zone*

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Abstract

The McArthur River unconformity-related uranium deposit, located near the southeastern margin of the Proterozoic Athabasca basin in northern Saskatchewan, Canada, contains both basement-hosted and sandstone-hosted orebodies, one of which is the sandstone-hosted Zone 4 orebody and its alteration system. Early pre-ore quartz cementation forming immediately above Zone 4 produced a 200-m-thick silicified zone within the lower Manitou Falls Formation. Late pre-ore oxidizing basinal fluids ($\delta^{18}\text{O} = 1.1\text{--}8.9\text{‰}$, $\delta^2\text{H} = -70$ to -34‰) formed zones of dickite, magnesiofioitite, and sudoite-rich alteration in the Manitou Falls Formation above the deposit. These zones were overprinted by an outer halo of illite and illite-chlorite mixed-layer clay that coincided with illite and clinocllore alteration of the Wollaston Group basement rocks. Circulation of basinal fluids into the fault zone, promoted by fault reactivation, created a reducing fluid ($\delta^{18}\text{O} = 3.9\text{--}7.8\text{‰}$, $\delta^2\text{H} = -62$ to -25‰) through basement interaction, which formed a narrow sudoite alteration halo near the faulted unconformity. Mixing of these two contrasting fluids initiated uranium mineralization at ca. 1600 Ma. Post-ore alteration caused isotopic resetting of primary uraninite, broadly coincident with the intrusion of the Mackenzie dikes into the basin, followed by alteration of uraninite to coffinite, poorly crystalline uraninite, and gummite during the Neoproterozoic. Cool (ca. 10°C), oxidizing, meteoric waters ($\delta^{18}\text{O} = -15.7$ to -13.2‰ , $\delta^2\text{H} = -120$ to -93‰) later infiltrated fractures, produced post-ore kaolinite, and caused partial oxidation of uraninite to uranophane.

The silicified zone at Zone 4 functioned as a physical barrier to fluid flow, creating favorable conditions for uranium mineralization by focusing basinal fluids into the fault zone, localizing reducing basement-modified basinal fluids, and enhancing ore preservation. However, the silicified zone limited the spatial extent of late pre-ore sudoite alteration and obstructed the post-ore mobilization of components such as radiogenic Pb and other pathfinder elements into the overlying strata.

Introduction

THE MCARTHUR River unconformity-related uranium deposit is situated near the southeastern margin of the Athabasca basin in northern Saskatchewan, Canada (Fig. 1). The deposit has an average grade of 21% U_3O_8 and combined proven and probable reserves of 332.6 million pounds U_3O_8 (Bronkhorst et al., 2009). The deposit comprises six orebodies, which occur near a faulted unconformity between Archean-Paleoproterozoic metasedimentary basement rocks and overlying Paleoproterozoic Athabasca Group sedimentary rocks (McGill et al., 1993). Ore zones 1, 3, 4, A, and B are hosted in the basement rocks, basal sandstones, and basal conglomerates (sandstone hosted), whereas Zone 2 is hosted entirely in the basement rocks (basement hosted) (Fig. 2a). As of 2009, Zones 2 and 4 were the active mine areas at McArthur River, with Zone 4 having greater combined proven and probable reserves and higher ore grades (Bronkhorst et al., 2009).

Genetic models for unconformity-related uranium deposits in the Athabasca basin (e.g., Wilson and Kyser, 1987; Kotzer and Kyser, 1995; Fayek and Kyser, 1997; Alexandre et al., 2005; Derome et al., 2005; Richard et al., 2011; Mercadier et al., 2012) are mainly modifications of the diagenetic-hydrothermal model originally proposed by Hoeve and Sibbald (1978). In this model, uranium mineralization formed during conditions of deep burial and peak diagenesis by the mixing of oxidizing basinal fluids with reducing fluids emerging from basement structures (Hoeve and Sibbald, 1978). Both the

Athabasca Group sandstones (Fayek and Kyser, 1997; Kyser et al., 2000) and the basement units (Hecht and Cuney, 2000; Cuney et al., 2003; Richard et al., 2010) have been proposed as the source of uranium. Although the diagenetic-hydrothermal model is generally applicable to deposits throughout the basin, mineralogical and geochemical differences at the deposit scale suggest that their origin and evolution may be related to locally unique factors. At McArthur River, extensive quartz cementation has created a silicified zone above the unconformity and surrounding the deposit. This overlying silicified zone is considered to have limited the spatial extent of hydrothermal alteration (McGill et al., 1993), although its role during the genesis of the deposit remains uncertain. Silicification of sandstones above other uranium deposits in the Athabasca basin has also been documented, including a dome-shaped silicified cap surrounding the Cigar Lake orebody (Cramer, 1986) and quartz-cemented breccias at Shea Creek (Lorilleux et al., 2002). However, unlike these other occurrences, the silicified zone at McArthur River formed during the early stages of basin diagenesis (Hiatt et al., 2007) and is not associated with fault reactivation or hydrothermal alteration.

Previous studies on McArthur River have examined the age and chemistry of U mineralization (Cumming and Krstic, 1992; Fayek et al., 2002; Alexandre and Kyser, 2005; Alexandre et al., 2009b; Mercadier et al., 2011), physical and chemical characteristics (e.g., isotopic and chemical composition, oxygen fugacity, pH, pressure, temperature) of the alteration and mineralizing fluids (Kotzer and Kyser, 1995; Derome et al., 2005; Kister et al., 2005; Richard et al., 2010, 2011, 2012), and mobility of radiogenic Pb (Holk et al., 2003). However,

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*A digital supplement to this paper is available at <http://economicgeology.org/> and at <http://econgeol.geoscienceworld.org/>.

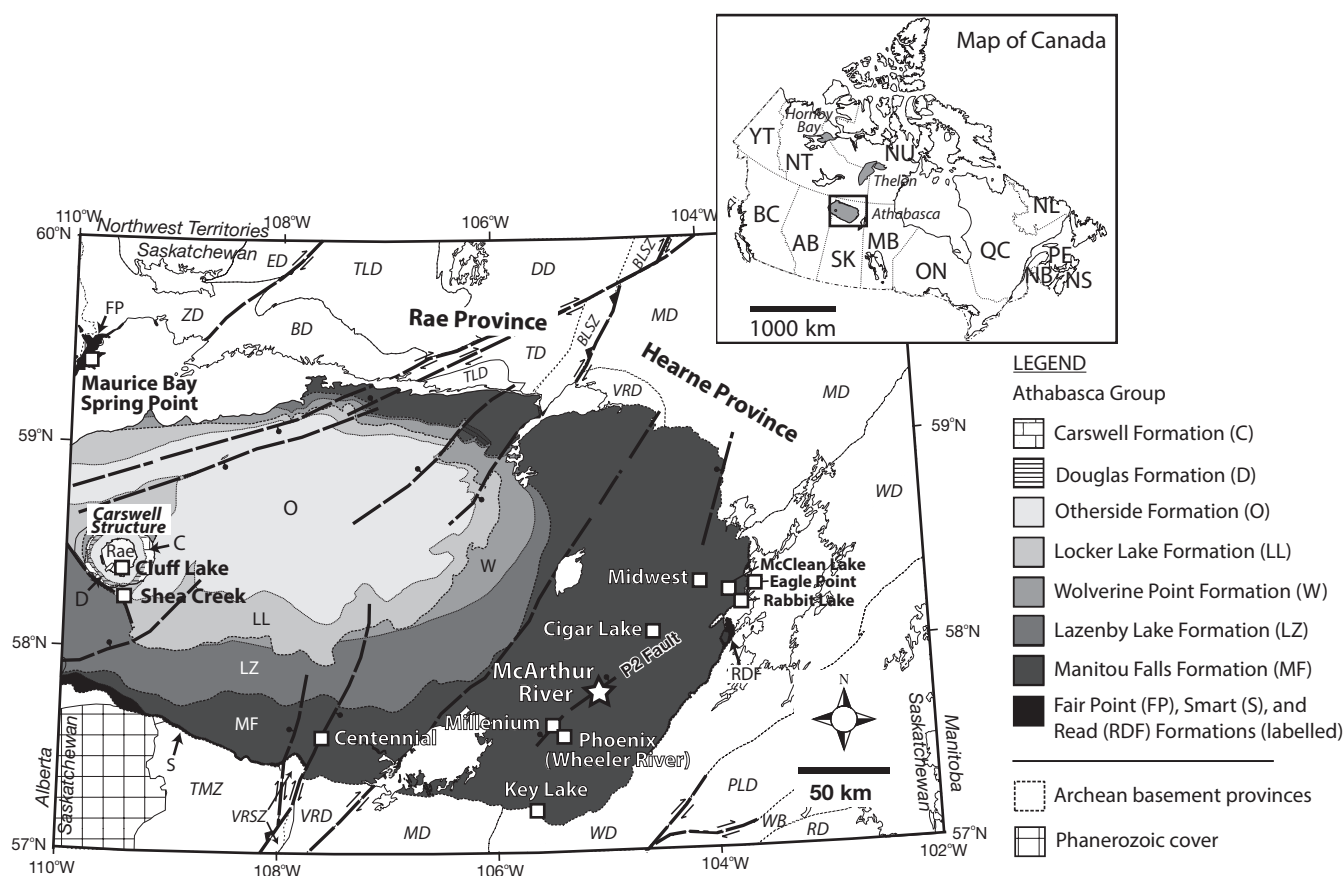


FIG 1. Generalized geologic map of the Athabasca basin, northern Saskatchewan, Canada, showing the major lithostructural basement provinces (bold), domains (italic), fault zones (dashed lines), stratigraphic divisions, and location of McArthur River (star) and other major unconformity-related uranium deposits (modified after Hoffman, 1989; Ramaekers et al., 2007). Domain abbreviations: BD = Beaverlodge, DD = Dodge, ED = Ena, MD = Mudjatik, ND = Nolan, PLD = Peter Lake, RD = Rottenstone, TD = Tantato, TLD = Train Lake, VRD = Virgin River, WB = Wathaman batholith, WD = Wollaston, ZD = Zemplak. Shear/magmatic zones: BLSZ = Black Lake shear zone, TMZ = Taltston magmatic zone, VRSZ = Virgin River shear zone.

these studies were mostly undertaken on the basement-hosted Zone 2 orebody (e.g., Alexandre et al., 2005; Derome et al., 2005), with the sandstone-hosted mineralized zones being less well understood.

The objectives of this study are to document the mineralogical and geochemical evolution of the sandstone-hosted McArthur River Zone 4 orebody and evaluate the genetic role of the silicified zone that overlies the mineralization. The structural and chemical composition of alteration and uranium minerals and their spatial and temporal distributions are characterized by petrography, X-ray diffraction, scanning electron microscopy, electron microprobe analysis, and short-wave infrared spectroscopy. The origin of the fluids responsible for forming the alteration minerals is determined by stable isotope chemistry and the absolute timing of uranium mineralization and post-ore alteration events are ascertained using isotopic and chemical U-Pb geochronology. Post-ore migration of elements and radiogenic Pb isotopes, which can be used as geochemical vectors for this type of deposit, into the surrounding environment of Zone 4 is assessed by the weak acid leach method of Holk et al. (2003). The results are integrated into a genetic evolution model and the implications of the silicified zone are evaluated.

Geologic Setting

Regional geology

The late Paleo-Mesoproterozoic Athabasca basin, located in northern Saskatchewan and Alberta, Canada, overlies the Archean-Paleoproterozoic Rae and Hearne structural provinces (Fig. 1). The Hearne province, located east of the Snowbird tectonic zone (Berman et al., 2007), is subdivided into the Peter Lake, Virgin River, Mudjatik, and Wollaston domains, the latter forming the basement rocks beneath McArthur River (Hoffman, 1988, 1989). The Snowbird tectonic zone beneath the Athabasca basin consists of the Virgin River and Black Lake shear zones.

The Wollaston Domain is an NE-striking fold belt that comprises an Archean granitoid basement overlain by Paleoproterozoic metasedimentary rocks of the Wollaston Group (Lewry and Sibbald, 1980; Ray and Wanless, 1980). These rocks underwent mid- to upper amphibolite-grade to local greenschist-grade metamorphism during the ca. 1.86 to 1.76 Ga Trans-Hudson orogeny (Ray and Wanless, 1980; Annesley et al., 2005).

Rapid exhumation of the Trans-Hudson orogen (Kyser et al., 2000) initiated the formation of the Athabasca basin

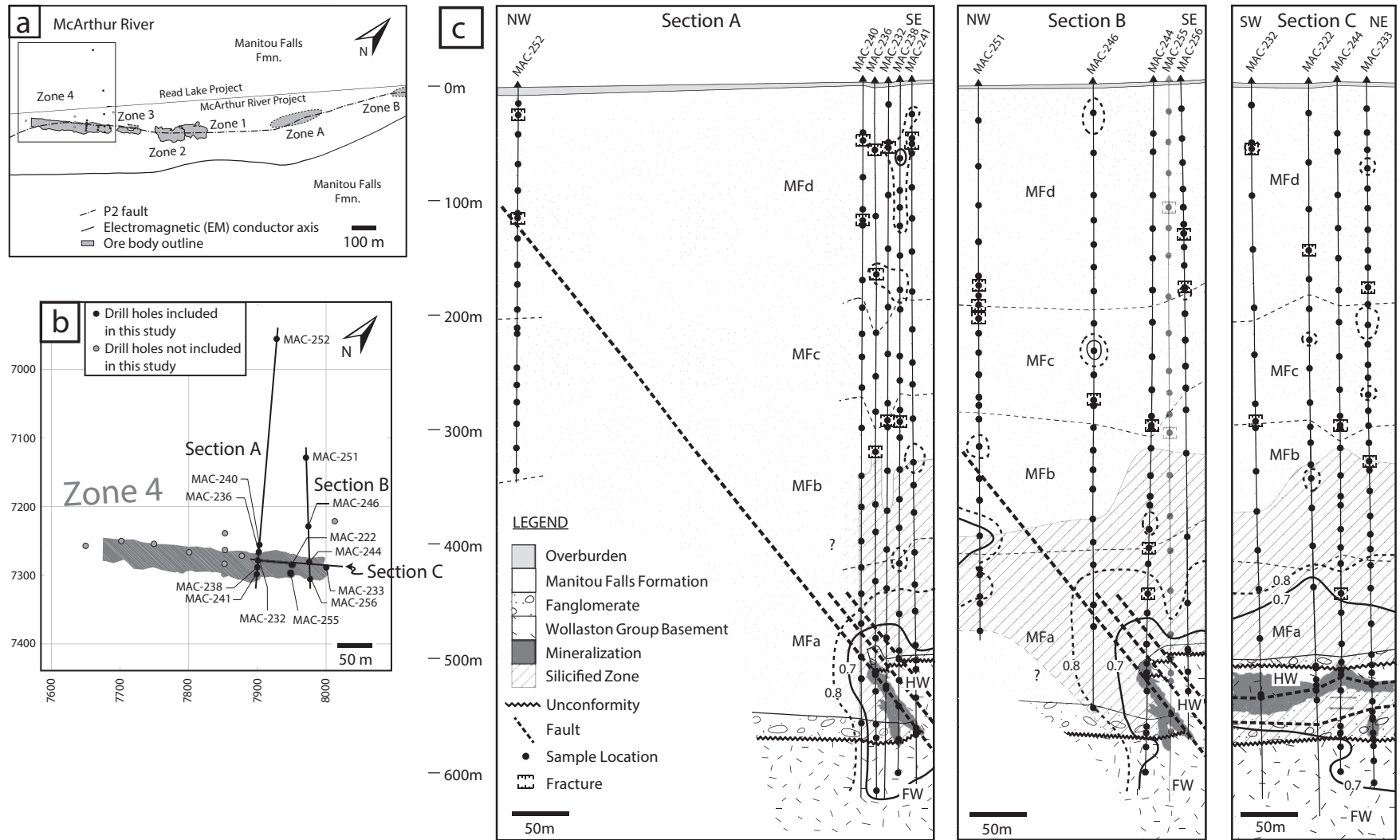


FIG. 2. a. Plan view of the McArthur River mine site with the ore zones projected onto surface. b. Plan view of the McArthur River Zone 4 orebody projected onto surface. The drill holes included in this study (black circles) delineate two NW-SE-oriented transects (lines A and B) and one SW-NE-oriented transect (Line C). c. Longitudinal cross sections (A, B, C) of McArthur River Zone 4 showing geologic structures, lithology, and location of drill core samples. Drill hole MAC-255 is projected onto section B. The spatial distribution of leachable $^{207}\text{Pb}/^{206}\text{Pb}$ ratios is shown as contour lines of 0.70 (solid line) and 0.80 (dashed line). Abbreviations: FW = footwall, HW = hanging wall, MF = Manitou Falls.

(ca. 1760 Ma), which collected sediments until ca. 1500 Ma (Ramaekers et al., 2007). Sediments filled three NE-SW-oriented subbasins, with the easternmost Cree subbasin hosting the majority of the sandstone-hosted deposits in the basin, including the McArthur River deposit. The basin fill consists mainly of sandstone with minor siltstone, conglomerate, mudstone, and dolostone, together constituting the Athabasca Group (Ramaekers, 1990; Ramaekers et al., 2001). The present-day thickness of the Athabasca Group is 1 to 2 km, but homogenization temperatures of fluid inclusions in quartz overgrowths suggest that it may have reached 5 to 7 km during the Mesoproterozoic (Pagel et al., 1980). NW-striking mafic dike swarms (Cumming and Krstic, 1992), emplaced during the 1267 ± 2 Ma Mackenzie thermal event (LeCheminant and Heaman, 1989), intrude the basin and underlying basement rocks.

Local geology

The six mineralized zones at McArthur River extend over a strike length of more than 1,700 m with variable widths along strike (Fig. 2a; Bronkhorst et al., 2009). The McArthur River Zone 4 orebody is located at a depth of 500 to 570 m and is partially hosted in the uplifted Wollaston Group basement hanging wall and adjacent Athabasca Group sedimentary rocks along a major reverse fault, the P2 structure (Fig. 2c). The Wollaston Group basement consists of pelitic, semipelitic, and arkosic gneissic rocks, with calc-silicate and quartzite units in the footwall and pegmatite veins in the hanging wall (McGill et al., 1993). There is a 25-m-thick sequence of graphite-bearing pelitic gneiss along the hanging wall of the P2 fault (McGill et al., 1993).

The P2 fault zone comprises a series of reverse thrust faults striking N45°E and dipping 40° to 45°SE (McGill et al., 1993). Displacement along the fault occurred along graphite-rich basement rocks and uplifted the hanging wall block by 60 to 80 m. The P2 structure, which may have initiated as a strike-slip fault plane during the Trans-Hudson orogeny (McGill et al., 1993), underwent multiple episodes of reactivation during sedimentation (Yeo et al., 2007). Three sets of steeply dipping transcurrent faults, striking 100° to 110°, displace the P2 fault and basement rock types (McGill et al., 1993).

The Athabasca Group at McArthur River is represented by the Manitou Falls Formation, which consists of a basal quartzite-bearing conglomerate (fanglomerate), overlain by a package of sandstones, pebbly sandstones, conglomerates, and siltstones (Ramaekers et al., 2001). To facilitate comparison with previously published work on McArthur River, this study maintains the usage of the original stratigraphy proposed by Ramaekers (1990), which subdivides the Manitou Falls Formation at McArthur River into four informal members (MFa, MFb, MFc, and MFD; Fig. 2c). The Manitou Falls a, b, and c members formed from clastic sediments that were deposited primarily within alluvial fans (MFa) and high-energy, proximal, braided streams (MFa, MFb, MFc). MFD is postulated to represent the distal portions of a braided stream system, an estuary, or a braided delta setting (Hiatt and Kyser, 2005).

The lower 200 m of the Manitou Falls Formation (MFa and lower MFb) at Zone 4 is intensely silicified (Fig. 2c). This silicification was intersected in multiple drill holes from the McArthur River and Read Lake areas, suggesting that it may

extend over all six McArthur River orebodies (McGill et al., 1993; Mwenifumbo et al., 2004). The silicification has been interpreted as originating either from early precompaction quartz cementation (Hiatt et al., 2007) or from silica remobilized from basement quartzite ridges prior to hydrothermal alteration and uranium mineralization (McGill et al., 1993). Alternatively, Derome et al. (2005) interpreted the silicified sandstones as the result of postdiagenetic, pre-ore pervasive silicification. Measurements of fluid inclusions trapped within quartz cements and euhedral quartz in veins document mixing between an NaCl-rich basinal brine (min. 190°C) and CaCl₂-rich basement-modified basinal brine (ca. 140°C) at McArthur River (Derome et al., 2005). Movement along the P2 fault caused extensive fracturing of the silicified sandstones, creating a 50- to 75-m fracture zone in the lower MFa (McGill et al., 1993; Mwenifumbo et al., 2004).

The alteration assemblage in the Manitou Falls Formation at McArthur River includes quartz cements, iron oxides, dravite, dickite, sudoite, and illite (McGill et al., 1993). Massive quartz dissolution is associated with the formation of chlorite-dravite solution breccias (Lorilleux et al., 2002; Derome et al., 2005). Kaolinite commonly occurs within fractures in the upper parts of the Manitou Falls Formation (MFc and MFD) and in sandstones proximal to the fault zone (Kotzer and Kyser, 1995). Basement alteration proximal to the fault zone is characterized by an inner illite-sudoite alteration and a distal clinocllore alteration. Dravite, apatite, and carbonate are present locally in the hanging wall (McGill et al., 1993; Alexandre et al., 2005). Uranium mineralization is spatially associated with intense hematite alteration.

Massive uranium mineralization occurs at the tip of the hanging-wall block (Bronkhorst et al., 2009). The Zone 4 orebody is essentially monometallic, containing uraninite as the principle ore of uranium, and minor quantities of galena, pyrite, chalcopyrite, and Ni-Co-As sulfides. Additional minor uranium phases include paragenetically late coffinite, poorly crystallized uraninite, and secondary uranyl minerals (McGill et al., 1993; Fayek and Kyser, 1997), which are all spatially related to primary uraninite.

Methodology

Thirteen diamond drill holes from the eastern half of Zone 4 were sampled (Fig. 2b). These drill holes delineate two subparallel NW-SE-oriented transects (Line A, Line B) and one SW-NE-oriented transect (Line C). Samples include fractured (28 in total) and unfractured sandstones and conglomerates (270 in total) from the Manitou Falls Formation, mineralized samples (17 in total), and basement rocks (25 in total; Fig. 2c). Fracture samples are drill cores that have rough broken surfaces or are highly friable; these contain elevated clay content, which suggests enhanced fluid flow along fracture permeability relative to porosity. The sampling interval was approximately 25 m, but with smaller spacing near mineralized and fractured samples. Samples are designated with their drill hole identifier followed by their depth in meters. The relative timing of minerals in the Manitou Falls Formation, Wollaston Group basement, and ore zone were discerned from examination of all samples in hand specimen and from petrographic analysis of polished thin sections under transmitted and reflected light.

Identification of alteration minerals in drill cores was performed by short-wave infrared (SWIR) spectroscopy using an Integrated Spectronics Pty PIMA SP instrument and pattern matching using the AusSPEC TSG™ and MinSPEC4™ spectral library. Mineral identification was aided by backscattered electron (BSE) images and energy-dispersive (EDS) spectra acquired using a FEI-MLA Quanta 650 scanning electron microscope (SEM).

Drill core samples were crushed and sieved to obtain four grain size fractions: >1.18 mm, 0.5 to 1.18 mm, 0.25 to 0.5 mm, and <0.25 mm. Alteration minerals were extracted from the >1.18-mm grains by ultrasonic disintegration and centrifuged into the 2- to 5- μ m and <2- μ m fractions. Air-dried oriented separates were analyzed by X-ray diffraction (XRD) using a PANalytical X'pert PRO MPD equipped with a CuK α target, Ni filter, 1/2° divergent slit, 1° anti-scatter slit, and 0.02-radian soller slits on both the incident and diffracted beam. Measurements were acquired at 45-kV accelerating voltage, 40-mA current, scan range of 5° to 75°2 θ , step size of 0.02°2 θ , and 20-s counting time. Mineral identification and estimation of modal abundances were performed by pattern matching using the PANalytical HighScore software and reference patterns from the ICDD database (2006).

Chemical compositions of detrital, alteration, and uranium minerals were determined by electron probe microanalysis (EPMA) using a JEOL JXA-8230 equipped with five wavelength-dispersive spectrometers (WDS). Acquisitions were made using a 15-kV accelerating voltage, 10-nA beam current, and 5- to 10- μ m-diameter defocused beam. Typical counting times were 10 s for major elements, 20 s for minor elements, and 30 to 40 s for trace elements. Analytical errors were generally <1% relative for major elements (>2 wt %) and 1 to 5% relative for minor elements (0.1–2 wt %). Background and matrix correction and conversion of X-ray measurements to oxide weight percentages were performed using a ZAF program in the JEOL software. The fine grain size, typically <1 μ m, for some phyllosilicate and tourmaline group minerals resulted in slightly low analytical totals. Mineral formulas were calculated based on anion normalization for illite (11 oxygen equivalents), chlorite (14 oxygen equivalents), and tourmaline (29 oxygen equivalents). A stoichiometric number of B³⁺ cations (three) was assumed for tourmaline. Chemical formulas for aluminum phosphate-sulfate (APS) minerals were calculated on the basis of six cations, assuming the general formula AB₃(XO₄)₂(OH)₆ (Gaboreau et al., 2007). Chemical ages for uranium minerals were calculated from EPMA data, following the U-Pb-Th method of Bowles (1990). The precision of the Pb analysis determined the error associated with each calculated chemical age and is typically ± 2 m.y.

Crystallization temperatures for illite were calculated from mineral chemistry using the regression curve of molar fraction pyrophyllite (X_{pyr}) versus temperature in Cathelineau (1988), with X_{pyr} calculated using K deficiency. Formation temperatures for chlorite were estimated from their aluminum tetrahedral occupancy (Al^{IV}) and Fe/Fe + Mg ratio, using the geothermometer of Zang and Fyfe (1995), which is a variant of that by Cathelineau and Nieva (1985). The illite and chlorite geothermometers have an uncertainty of $\pm 25^\circ\text{C}$ (Cathelineau and Nieva, 1985; Cathelineau, 1988; Zang and Fyfe, 1995). As published chlorite geothermometers are calibrated

for trioctahedral chlorites, their application to di-trioctahedral chlorites (e.g., sudoite) gives only approximate temperatures.

Elemental and Pb isotope compositions of mobile components from the 0.5- to 1.18-mm grain size fraction of crushed drill cores were determined using a 2% HNO₃ acid leach technique described by Holk et al. (2003). This partial-leach technique mainly targets elements that are weakly bounded onto surfaces of detrital minerals or adsorbed onto clay minerals. There may be minor contributions from elements contained within detrital (e.g., zircon) and clay minerals that were exposed as a result of crushing (Holk et al., 2003) or from partial dissolution (e.g., APS minerals). Forty-nine elements and four Pb isotopes (²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb) were measured using a ThermoFinnigan Element 1 and Element XR high-resolution inductively couple plasma-mass spectrometer (ICP-MS). Results were corrected for instrument drift, blank contributions, and isobaric interferences. Instrumental mass fractionation of Pb was corrected using a Tl spike and applying an exponential law correction (Rehkämper and Mezger, 2000). Element concentrations were quantified by external calibration and normalization to a 1-ppb In internal standard. Four in-house standards and NBS-981 (common Pb) and NBS-983 (radiogenic Pb) were used to monitor instrument accuracy and precision. Typical quantitation limits for the elements reported in this study are as follows: 50 ppb for As, Ce, Co, Cu, Ni, Mn, Pb, Th, U, V, Y, Zn, Zr; 75 ppb for Fe; 200 ppb for Mg; 500 ppb for Ca and P; and 5,000 ppb for Al.

Separates of monomineralic and bimodal mixtures, selected based on XRD results, were measured for their oxygen and hydrogen isotope compositions. Oxygen was extracted from silicate minerals following the BrF₅ method of Clayton and Mayeda (1963) and their isotopic compositions (¹⁸O/¹⁶O) measured using a dual-inlet Finnigan MAT252 isotope ratio mass spectrometer (IRMS). Hydrogen isotope ratios (²H/¹H) and water contents of alteration minerals were analyzed using a ThermoFinnigan thermal conversion elemental analyzer (TC/EA) linked to a Delta^{Plus} XP IRMS. Results for oxygen and hydrogen isotope ratios are expressed using conventional delta (δ) notation in units of ‰ relative to Vienna-standard mean ocean water (V-SMOW). Experimental reproducibility for oxygen extraction by the BrF₅ method is $\pm 0.2\text{‰}$, based on simultaneous measurements of the NBS-28 quartz reference standard ($\delta^{18}\text{O} = 9.6\text{‰}$). Instrumental reproducibility of the TC/EA method is $\pm 3\text{‰}$ as determined from replicate measurements of in-house standards and sample duplicates included with each analytical run. Oxygen isotope fractionation factors used were from Eslinger and Savin (1973) for illite-water, Wenner and Taylor (1971) for chlorite-water, Zheng (1993) for tourmaline-water, and Sheppard and Gilg (1996) for both kaolinite-water and dickite-water. Oxygen isotope fractionation factors between di-trioctahedral chlorites (e.g., sudoite) and water are not known. By assuming similar fractionation based on chemical composition and crystal structure comparable to trioctahedral chlorites, the chlorite-water oxygen fractionation factor of Wenner and Taylor (1971) was used to approximate for sudoite-water. Other oxygen isotope fractionation factors have also been used for chlorite-water in studies of uranium deposits in the Athabasca basin, including those of Yeh and Savin (1976) and Savin and Lee (1988), but without consensus on which is most appropriate.

At 200°C, $\delta^{18}\text{O}$ fluid values calculated using the Wenner and Taylor (1971) fractionation factor are ca. 1.7 to 3.0‰ higher than those determined using these other fractionation factors. Hydrogen isotope fractionation factors were after Kotzer et al. (1993) for tourmaline-water and Sheppard and Gilg (1996) for both kaolinite-water and dickite-water. The montmorillonite-water hydrogen isotope fractionation factor of Yeh (1980) was used to approximate illite-water fractionation. The hydrogen isotope fractionation factor by Marumo et al. (1980) was chosen for chlorite-water as it is most appropriate for chlorites forming between 130° and 250°C. Within this interval, hydrogen isotope fractionation is insensitive to temperature; rather, it decreases with increasing octahedral Fe content. Oxygen and hydrogen isotope fractionation factors for illite-chlorite mixed-layer clay were calculated from a 60:40 stoichiometric combination of the corresponding illite-water and sudoite-water fractionation factors; the proportion of illite and sudoite interlayers in McArthur River illite-chlorite mixed-layer clay was previously determined by XRD modeling (Quirt, 1999). For alteration minerals where monomineralic separates could not be obtained, their oxygen and hydrogen isotope compositions are determined by end-member extrapolation from plots of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ mineral values versus mineral proportion (wt %) for bimodal mixtures. The spread of the data determines the upper and lower limits in the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values for each end-member mineral.

Uranium minerals were dated by in situ U-Pb isotope ratios acquired by laser ablation on polished thin sections using a frequency-quintupled (213-nm) Nd-YAG (LUV-213 New Wave-Merchantek) laser system and measured using a ThermoFinnigan Neptune high-resolution multicollector ICP-MS (HR-MC-ICP-MS), following the method of Chipley et al. (2007).

Mineral Paragenesis

Four distinct paragenetic stages are recognized for McArthur River Zone 4: detrital, pre-ore alteration, ore stage, and post-ore alteration (Fig. 3). The Manitou Falls Formation consists predominantly of subangular to rounded, sand-sized detrital quartz and minor pebble-sized polycrystalline fragments; the basal fanglomerate unit contains mostly pebble-sized quartz. Minor detrital muscovite, occasionally occurring as 1- to 2-mm-thick muscovite-rich stylolite seams, and detrital tourmaline are present, but are typically altered by the pre-ore alteration clay assemblage. Detrital accessory minerals include rutile and zircon, which were also subsequently altered unless enclosed in quartz.

Pre-ore alteration

The earliest preserved alteration event is characterized by 10- to 250- μm -thick, hematite-bearing, optically syntaxial quartz (Q1) overgrowths around detrital quartz (Fig. 4a). This silicification is recorded in all units of the Manitou Falls Formation but is best developed within MFa and lower MFb. Strontium-rich aluminum phosphate sulfate (APS) minerals precipitated during the later stages of quartz cementation, forming 1- to 10- μm -sized, pseudocubic inclusions within the quartz overgrowths, and as clusters filling porosity (Fig. 4b). This is followed by a second stage of pre-ore quartz cementation (Q2), specific to the silicified zone in MFa and lower

MFb, which produced optically syntaxial, inclusion-free quartz cements (Fig. 4a). Triple junctions observed between these later-stage quartz cements suggest growth into open pores. Pre-ore Q1 and Q2 quartz cements in this study correspond, respectively, to precompaction Qa and compaction-related Q1 cements observed in the McArthur River silicified zone by Hiatt et al. (2007) and to diagenetic Qz1 and post-peak-diagenetic pre-ore pervasive Qz2 cements of Derome et al. (2005). Above the silicified zone, early pre-ore Q1 cement is less abundant owing to poor preservation as a result of quartz dissolution during continued burial diagenesis (MFb and lower MFc) or as the result of these units experiencing lower degrees of silicification (upper MFc and MFd). Early pre-ore Q2 quartz cements are followed by minor hematite, which occurs as rhombohedral to bladed crystals filling interstices and forming intergrowths with fine-grained rutile needles. This hematization imparts a dark red to maroon color to drill core in MFa and MFb. In the basal fanglomerate, rare dolomite crystals form overgrowths around inclusion-free quartz cements and are surrounded by later-forming clays filling interstitial porosity. Pre-ore alteration of detrital rutile produced brown leucoxene overgrowths with uncertain paragenetic timing due to the lack of crosscutting relationships.

Late pre-ore alteration of the Manitou Falls Formation is marked by quartz dissolution and formation of authigenic alteration minerals in secondary porosity and fractures. Within the silicified zone, coarse-grained dickite crosscuts earlier-formed clusters of Sr-rich APS minerals (Fig. 4b). Above the silicified zone, fine-grained kaolinite, which occurs contemporaneously with dickite, is replaced by a fibrous chlorite (C1), followed by acicular, occasionally spherulitic tourmaline (Fig. 4c). These tourmaline aggregates are common within the interstices of MFd sandstones and also occur as intergrowths with euhedral quartz (Q3) in fractures and veins in MFa (Fig. 4d). Euhedral Q3 quartz in this study corresponds to euhedral Q2 quartz breccias described by Kotzer and Kyser (1995) and to drusy Qz3 quartz veins of Derome et al. (2005). Late pre-ore alteration minerals are subsequently replaced by illite, which occurs as interlocking fibrous laths (Fig. 4b). Incomplete replacement of C1 chlorite by illite formed an illite-chlorite mixed-layer clay mineral which is spatially and temporally associated with illite. The illite-chlorite mixed-layer clay predominates within MFd and MFc sandstones but becomes absent with increasing depth toward MFb and MFa. This is followed by a pale green chlorite (C2), which replaces detrital muscovite and late pre-ore tourmaline and illite. This chlorite seals fractures crosscutting earlier-formed euhedral Q3 quartz in sandstone and fanglomerate near the faulted unconformity, suggesting it postdated brittle deformation (Fig. 4d).

Late pre-ore alteration of the Manitou Falls Formation occurred contemporaneously with illite and chlorite alteration of the Wollaston Group basement. Illite alters detrital muscovite and feldspars in basement rocks and displays a lath-like morphology similar to illite in the overlying sandstones. Chloritization of basement rocks occurs in two stages. An earlier chlorite (C1^{bsmt}) with anomalous green and purple interference colors (Fig. 4e) constitutes the matrix of altered metasedimentary basement rocks distal to the orebody (>25 m from ore zone). This chlorite occurs spatially with detrital mica flakes that have been pseudomorphously altered

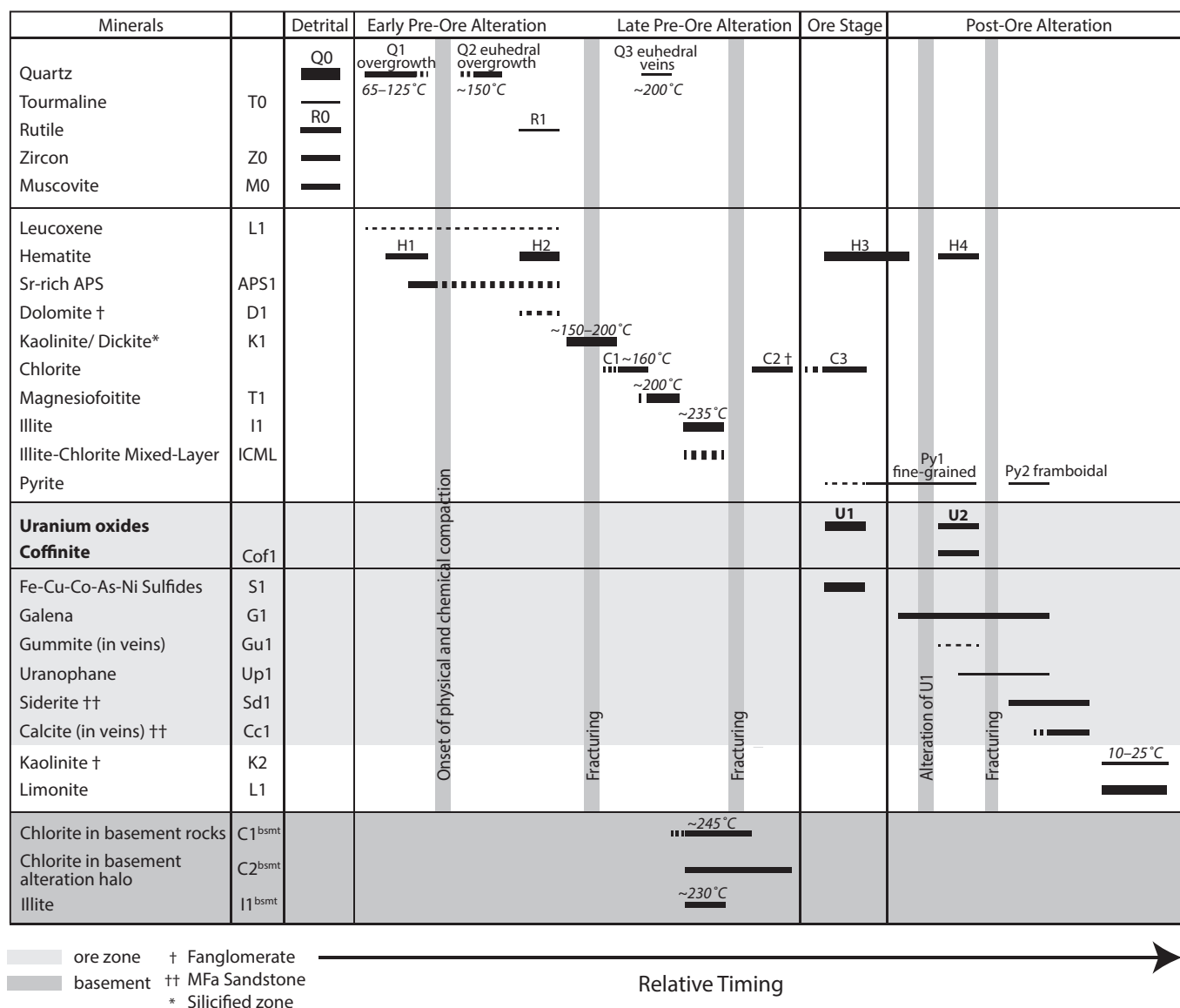


FIG. 3. Paragenetic sequence for the Manitou Falls Formation and ore zone at McArthur River Zone 4 indicating early- and late pre-ore alteration, ore, and post-ore alteration stages. Line thickness indicates relative abundance of each mineral and dashed line represents uncertainty in the timing of mineral formation. The formation temperature of K1 kaolin is constrained by homogenization temperatures of fluid inclusions in compaction-related quartz overgrowth and euhedral quartz (Q2 and Q3 in this study), determined by Kotzer and Kyser (1995). Basement paragenesis and remaining temperatures are discussed in text.

to blue chlorite, possibly representing the remnants of retrograde-altered biotite (Fig. 4e). However, the micaceous habit of these chloritized micas is destroyed by extensive alteration by C1^{bsmt} chlorite, suggesting the latter is a late alteration mineral unrelated to retrograde metamorphism. Earlier-formed C1^{bsmt} chlorite is replaced by a green-yellow fibrous chlorite (C2^{bsmt}), which forms the matrix of altered basement rocks proximal to the orebody and fault zone (<25 m, Fig. 4f). Based on crystal structure and chemistry, petrographic observations, and relative proximity of the alteration minerals to the ore zone and P2 fault, the paragenetic timing of basement illite and chlorite alteration was correlated with the basement paragenesis established for McArthur River by Kotzer and Kyser

(1995) and Alexandre and Kyser (2005; Fig. 3). The timing of illite alteration is used to relate the basin and basement paragenesis as illite crystallization in both host rocks is considered to have formed nearly synchronously (Laverret et al., 2006).

Ore stage

The main ore stage is characterized by the formation of uraninite within a polycrystalline syn-ore chlorite matrix, which is overprinted by intense fine-grained hematite (Fig. 5a). This uraninite forms clusters of massive, euhedral to subrounded crystals up to 0.5 cm (Fig. 5b), and finer-grained, pseudo-cubic crystals up to 100 μ m (Fig. 5a, c). Mineralization is coeval with a suite (<3%) of anhedral sulfides, which include

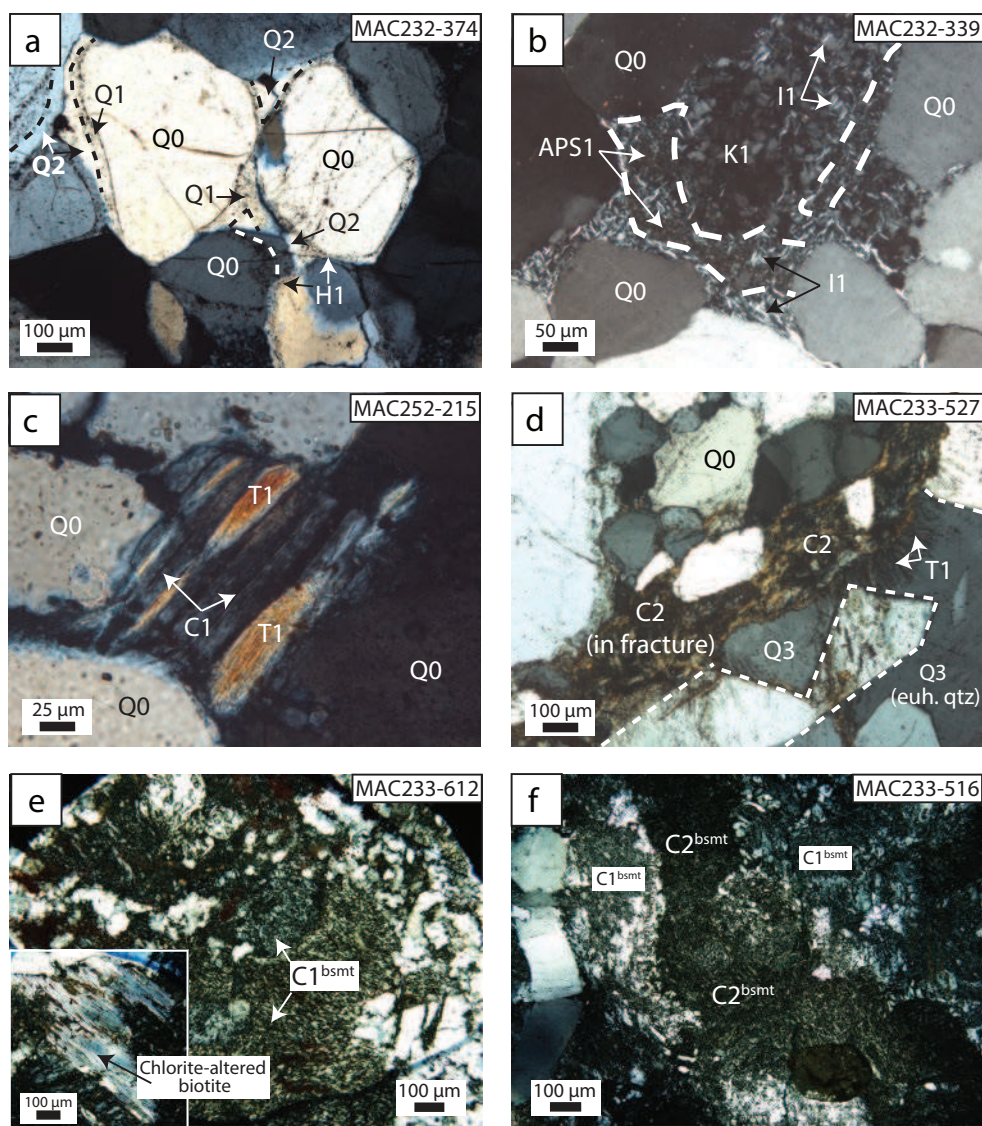


FIG. 4. Cross-polarized light photomicrographs of early to late pre-ore alteration features within the Manitou Falls Formation and Wollaston Group basement. a. Detrital quartz (Q0) surrounded by early quartz cement (Q1, outlined) with abundant hematite (H1) inclusions followed by inclusion-free euhedral quartz cement (Q2) filling residual porosity. b. Sr-rich APS clusters (APS1, outlined) crosscut by pore-occluding dickite (K1) and illite (I1). c. C1 chlorite, interpreted to have replaced a kaolinite grain, is altered by fibrous tourmaline (T1). Detrital quartz shows dissolved margins caused by clay alteration. d. C2 chlorite crosscutting euhedral quartz (Q3) vein and replacing acicular tourmaline (T1). e. C1^{bsmt} chlorite matrix in altered calc-silicate basement rock. Inset: Chlorite-altered mica flake, possibly representing retrograde altered biotite. f. C2^{bsmt} chlorite replacing earlier-formed C1^{bsmt} chlorite in altered pegmatite.

pyrite, chalcopyrite, Co-Fe sulfide, and Ni-Co-As sulfide, disseminated within the syn-ore chlorite matrix. Syn-ore chlorite replaces earlier-formed late pre-ore C2 chlorite locally at the ore zone and is differentiated by its association with sulfide and uranium minerals. Massive and pseudocubic uraninite are postdated by galena, which occurs as microscopic grains within its pits and fractures (Fig. 5b) and as euhedral to subhedral crystals within the clay matrix. Both uraninite and galena are rimmed by later-forming fine-grained pyrite.

Post-ore alteration

The post-ore stage is characterized by alteration and recrystallization of massive and pseudocubic uraninite in fractures,

voids, and veins. SEM images and EPMA analyses indicate that the altered uranium recrystallized as colloform coffinite (Fig. 5c) and blebby to botryoidal uraninite (U2, Fig. 5d). BSE images and EDS spectra reveal that massive uraninite is crosscut by anastomosing microveinlets; within these veinlets, the uraninite is partially altered to an amorphous micron-size Ca-U phase (Fig. 5b). This amorphous phase is classified as gummite based on its morphology and chemistry (Kotzer and Kyser, 1995; Fayek and Kyser, 1997). Fine-grained hematite forms colloform interbands with coffinite and with minor amounts (1–3%) of a green-yellow Ca-bearing uranium silicate, likely uranophane. Calcite postdates these alteration minerals, as observed by their sealing of remaining

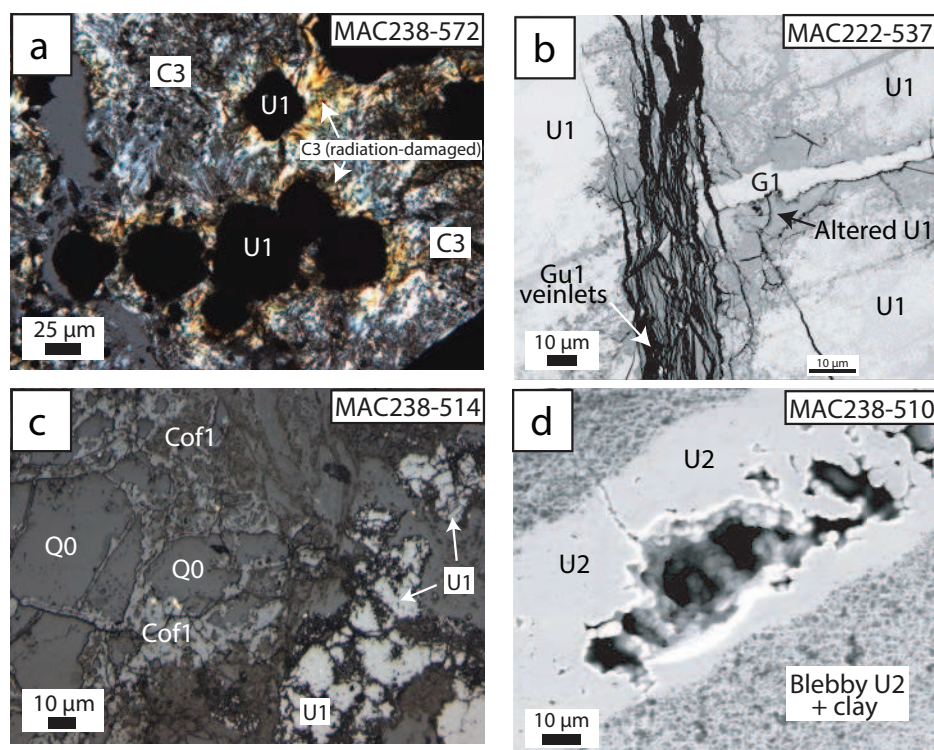


FIG. 5. Backscattered electron (BSE) images and photomicrographs of uranium minerals and syn- and post-ore alteration minerals from McArthur River Zone 4. a. Pseudocubic uraninite (U1) grains within a chlorite (C3) matrix (cross-polarized light). b. Variably altered U1 uraninite with galena (G1) filling fracture crosscut by anastomosing veinlets filled by Ca-U-bearing Gu1 gummite (BSE). c. Colloform-banded coffinite (Cof1) filling fractures within detrital quartz occurring near pseudocubic U1 uraninite (reflected light). d. Blebby-botryoidal-textured uraninite (U2) filling vug and overprinting clay matrix (BSE).

void space in fractures containing uranophane. Siderite and framboidal pyrite crystals form around massive and pseudocubic uraninite and fill fractures containing coffinite. Petrographic observations indicate that galena formed over a long duration after uranium mineralization, as indicated by galena grains crosscutting both ore stage and recrystallized uranium minerals.

Post-ore kaolinite is present in clay-rich samples proximal to the fault zone and in fractures, occurring as fine-grained polycrystalline clusters and coarse-grained vermicular aggregates, the latter representing recrystallized dickite. In hand sample, post-ore kaolinite occurs as massive blocks filling fractures near the fault zone and matches the description of late kaolinites found in altered sandstones near uranium mineralization by Kotzer and Kyser (1995). Pervasive yellow-orange limonite, which overprints MFc and MFd sandstones, is considered to occur late in the paragenesis as it stains surfaces of fractured drill core containing post-ore kaolinite.

Spatial Distribution of Alteration Minerals and Extent of the Silicified Zone

The spatial distribution of alteration minerals in the sandstone and basement rocks at McArthur River Zone 4 defines unique assemblages based on mineralogy and modal abundance that can be correlated across drill holes (Fig. 6). It is important to emphasize that these alteration features are related not only to the development of Zone 4 but to the evolution of the entire McArthur River ore system.

Detrital quartz normally composes 90 to 98% of the rocks throughout the Manitou Falls Formation, with the remainder being alteration minerals that constitute the matrix. Post-ore kaolinite is common near fractures within MFc and MFd, as observed in other sandstone-hosted alteration systems in the Athabasca basin (Wilson and Kyser, 1987; Kotzer and Kyser, 1995).

Pre-ore acicular tourmaline is the most abundant alteration mineral in MFd, above 180-m depth, where it occurs as mixtures with pre-ore kaolinite, illite, and lesser amounts of C1 chlorite and illite-chlorite mixed-layer clay (Fig. 6). Post-ore kaolinite is also present in MFd but occurs adjacent to fractures. This tourmaline-dominant alteration assemblage occurs in both mineralized and nonmineralized drill holes (e.g., MAC-251, MAC-252).

A C1 chlorite-rich alteration horizon occurs near the boundary between MFc and MFd (180–220-m depth) and can be traced to nonmineralized drill holes (Fig. 6). This unit has similar alteration mineralogy relative to the overlying MFd but differs by its greater abundance of pre-ore C1 chlorite. The occurrence of this C1 chlorite horizon coincides with the location of a sequence boundary in MFc identified by Hiatt and Kyser (2005). C1 chlorite is absent at depths below 240 m, where an assemblage of pre-ore illite and illite-chlorite mixed-layer clay, encompassing the mid to lower parts of MFc (240–290-m depth), becomes the dominant alteration in the matrix (Fig. 6). Below the illite-illite-chlorite mixed-layer alteration zone, and within upper MFb, a 40- to 60-m-thick

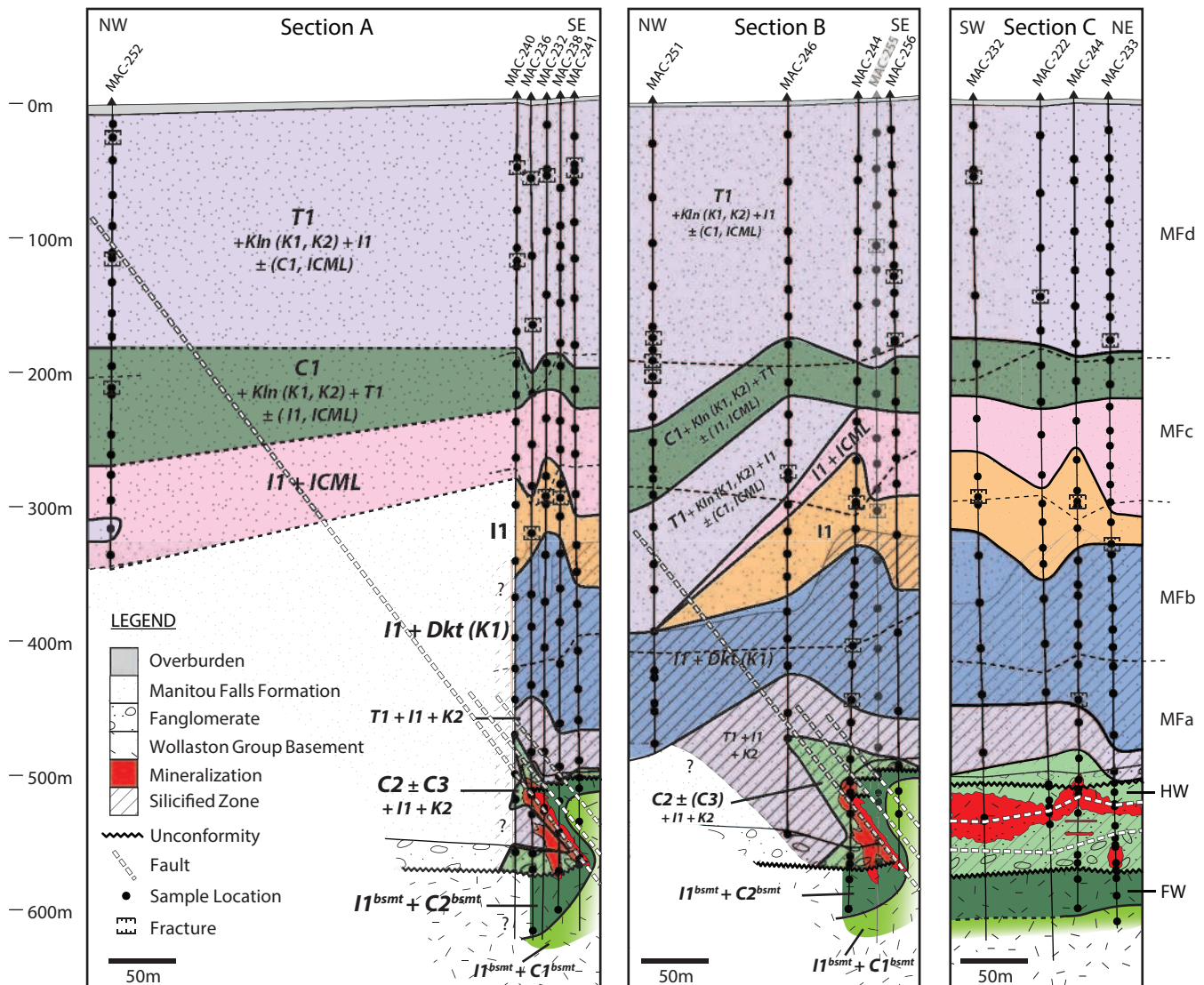


FIG. 6. Spatial distribution of alteration minerals within the Manitou Falls Formation and Wollaston Group basement at McArthur River Zone 4. Clay distribution based on XRD analyses of the $<2\text{-}\mu\text{m}$ size fraction from each drill core sample. Major alteration minerals occur in abundance greater than 5 wt %. Boundaries between alteration assemblages assigned based on changes in mineralogy and modal abundance. Basin: C1 = Mg sudoite, C2 = Mg-Fe sudoite, C3 = Fe-Mg sudoite, Dkt (K1) = dickite, ICML = illite-chlorite mixed-layer clay, I1 = illite, Kln (K1, K2) = kaolinite, T1 = magnesioferrite. Basement: C1_{bsmt} = clinocllore, C2_{bsmt} = Mg sudoite, I1_{bsmt} = illite.

illite-rich zone containing trace amounts of pre-ore tourmaline and kaolinite is present (Fig. 6). The illite-illite-chlorite mixed-layer and illite-rich alteration also marks zones of higher clay content (5–10%).

The silicified zone at McArthur River Zone 4 is a 200-m-thick package of quartz-cemented sandstones in the MFa and lower MFb that occurs at a depth below 320 m (Figs. 2c, 6). The lateral extent of the silicified zone is uncertain but its intersection in drill hole MAC-251 indicates that this paragenetically early feature extends at least 150 m from the strike of the Zone 4 mineralization (Figs. 2a, 2c). Its intersection in other McArthur River drill holes away from Zone 4 suggests that the silicified zone overlies the entire ore system (Mwenifumbo et al., 2004). Alteration mineralogy, porosity, and fracture permeability differentiate the silicified zone into

an upper and lower region. The upper silicified zone (lower MFb, upper MFa) occurs at a depth of ca. 320 to 440 m and is characterized by extensive early pre-ore quartz cementation (Fig. 4a), low porosity (ca. 1–3%), preservation of abundant pre-ore dickite (ca. 70%), and limited pre-ore illite alteration (ca. 30%) in the clay fraction (Figs. 4b, 6). The lower silicified zone (lower MFa, 440-m depth to fonglomerate) is differentiated from the upper silicified zone by its lower extent of early pre-ore quartz cementation, coarser detrital quartz grains, complex alteration assemblages (pre-ore illite, tourmaline, C2 chlorite, syn-ore chlorite, and post-ore kaolinite), higher porosity (ca. 5–7%), and greater fracture permeability (Fig. 6). Pre-ore C2 chlorite alteration delineates a 50-m-high by 100-m-wide halo that straddles the faulted unconformity and extends upward along fractures from the P2 fault (Fig. 6).

Pre-ore illite alteration occurs in both the hanging-wall and footwall basement rocks proximal to the fault zone, extending down to 40 m below the footwall unconformity (Fig. 6). Basement pre-ore chlorite alteration consists of distal (>25 m from ore zone) trioctahedral chlorite and proximal (<25 m from ore zone) di-trioctahedral chlorite (Fig. 6). Illite and chlorite alteration of the basement rocks is spatially rather than lithologically controlled, as both occur over multiple rock types, including (1) pelitic, semipelitic, and arkosic gneiss, (2) pegmatite, (3) calc-silicate, and (4) quartzite.

Mineral Chemistry and Crystallinity of Alteration Minerals

Pre-ore alteration of the Manitou Falls Formation

Pre-ore APS minerals have an average chemical composition of 11.4 wt % SrO, 30.0 wt % Al₂O₃, 21.9 wt % P₂O₅, and 6.1 wt % SO₃ with minor light rare earth elements (LREEs), Ca, and Fe (Table 1). The predominance of Sr and Al is consistent with the crandallite group mineral, goyazite (Jambor, 1999). Substitution of Ca and light rare earth elements (La, Ce, Pr, Nd) for Sr indicates an intermediate composition between crandallite (Ca) and florencite (LREE). Ba, Th, and U occur in trace amounts and Y is below detection limit. The Sr-rich composition of this APS mineral is consistent with that observed throughout the Manitou Falls Formation at Wheeler River Zone K (Cloutier et al., 2010) and in the regional barren metamorphic basement rocks and sandstones away from uranium deposits in the Athabasca basin (Gaboreau et al., 2007). LREE-rich APS minerals that are reported to be characteristic of mineralization, containing Σ LREEs between 0.5 and 0.75 apfu (Gaboreau et al., 2007), were not detected in the samples from McArthur River Zone 4.

Pre-ore C1 chlorite is characterized by an intense 006 basal reflection in XRD, consistent with di-trioctahedral chlorite (Percival and Kodama, 1989). This chlorite contains, on average, 31.9 wt % Al₂O₃, 10.4 wt % MgO, and 0.7 wt % FeO, respectively, and an octahedral occupancy of 4.63 cations per formula unit (O₁₀(OH)₈) (Table 2). It has an Fe/(Fe + Mg) ratio of 0.04 and a calculated formation temperature of 160°C (Table 2). The composition of C1 chlorite is similar to Mg-rich sudoite from the hydrothermally altered sandstones at Cigar Lake (Fig. 7), which follows illite paragenetically and is reported to be associated with uranium mineralization (Percival and Kodama, 1989).

Pre-ore tourmaline occurring in fractures and veins in MFa and interstices in MFd is compositionally similar and has an average chemical composition of 7.5 wt % MgO and 35.1 wt % Al₂O₃, with low contents of Na₂O and FeO (Fig. 8; Table 3). Its composition corresponds to the highly alkali deficient tourmaline, magnesiofoitite, in agreement with late-stage tourmalines associated with hydrothermal alteration described at other uranium deposits in the Athabasca basin (Rosenberg and Foit, 2006; Mercadier et al., 2012). In contrast, detrital tourmaline in the sandstones at McArthur River Zone 4 has chemical compositions that correspond to a slightly alkali deficient tourmaline with an intermediate composition between schorl and dravite (Fig. 8; Table 3), similar to detrital tourmalines in the sandstones of the Key Lake deposit (Rosenberg and Foit, 2006) and magmatic tourmalines in altered basement rocks of

TABLE 1. Electron Microprobe Analyses of Aluminum Phosphate-Sulfate (APS) Minerals at McArthur River Zone 4

Mineral	APS1	
	Avg. (n = 14)	$\pm 1\sigma$
Oxide (wt %)		
SrO	11.39	1.48
CaO	1.99	0.29
BaO	0.74	0.36
La ₂ O ₃	1.65	0.49
Ce ₂ O ₃	3.78	1.19
Pr ₂ O ₃	0.37	0.14
Nd ₂ O ₃	1.58	0.54
Y ₂ O ₃	<DL	-
ThO ₂	0.64	0.46
UO ₂	0.04	0.04
Al ₂ O ₃	29.97	1.00
Fe ₂ O ₃	1.35	0.79
P ₂ O ₅	21.86	1.19
SO ₃	6.08	1.14
Analytical total	81.45	1.21
H ₂ O*	10.69	0.29
Total	92.14	1.46
Atomic proportions on the basis of 6 cations		
<u>A-site</u>		
Sr	0.55	0.06
Ca	0.18	0.02
Ba	0.02	0.01
La	0.05	0.02
Ce	0.12	0.04
Pr	0.01	0.00
Nd	0.05	0.02
Y	0.00	-
Th	0.01	0.01
U	0.00	0.00
Sum	1.00	0.03
Σ LREEs	0.23	0.07
<u>B-site</u>		
Al	2.97	0.03
Fe ³⁺	0.09	0.05
Sum	3.06	0.06
<u>X-site</u>		
P	1.56	0.07
S	0.38	0.07
Sum	1.94	0.06
<u>Anions</u>		
OH	6.00	-

Notes: * = amount (wt %) of H₂O determined by stoichiometry; atomic proportion of OH calculated by subtraction; <DL = below detection limit; hyphens are used to indicate where a value is not needed or where assigning a value is inappropriate

the basement-hosted Eagle Point deposit (Mercadier et al., 2012). Detrital tourmaline serves as one possible source of Na, Mg, Fe, Al, and B for pre-ore tourmaline alteration within the upper Manitou Falls Formation. Alternatively, Mercadier et al. (2012) propose that Mg and B were primarily sourced from basinal brines originating from evaporated seawater. A formation temperature of 200°C is assigned to pre-ore tourmaline based on homogenization temperatures of fluid inclusions measured in coeval euhedral quartz (Q3) from several Athabasca basin sandstone- and basement-hosted deposits

TABLE 2. Electron Microprobe Analyses of Phyllosilicate Minerals at McArthur River Zone 4

Mineral	C1 chlorite Sandstone		C2 chlorite Sandstone, FAN		C1 ^{bsmt} chlorite Calc-silicate		C2 ^{bsmt} chlorite Pegmatite		C3 chlorite Ore zone		I1 illite Sandstone		I1 ^{bsmt} illite Pelite	
Oxide wt (%)	Avg (n = 9)	±1σ	Avg (n = 19)	±1σ	Avg (n = 11)	±1σ	Avg (n = 6)	±1σ	Avg (n = 16)	±1σ	Avg (n = 11)	±1σ	Avg (n = 9)	±1σ
SiO ₂	35.99	0.95	34.74	2.55	31.35	0.65	38.06	0.23	35.03	0.96	45.68	2.13	49.17	0.42
TiO ₂	<DL	-	0.02	0.02	0.01	0.02	0.01	0.01	0.02	0.02	0.02	0.01	0.22	0.18
Al ₂ O ₃	31.78	1.02	27.28	3.78	20.63	0.32	33.52	0.12	24.44	1.50	32.94	0.81	32.66	0.62
FeO	0.68	0.22	9.12	5.87	9.37	1.52	1.47	0.12	15.36	2.32	0.77	0.15	1.09	0.14
MnO	0.01	0.01	0.03	0.03	0.02	0.02	<DL	-	0.02	0.01	0.02	0.02	0.01	0.01
MgO	10.36	0.37	11.65	2.11	25.77	1.14	13.20	0.15	5.41	2.02	0.48	0.11	0.96	0.16
CaO	0.10	0.03	0.31	0.08	0.10	0.02	0.21	0.02	0.49	0.07	0.06	0.01	0.12	0.03
Na ₂ O	0.05	0.04	0.05	0.04	0.03	0.02	0.06	0.02	0.04	0.02	0.04	0.02	0.08	0.03
K ₂ O	1.16	0.12	0.29	0.11	0.18	0.13	0.73	0.11	0.11	0.03	8.83	0.55	9.23	0.25
Cl	0.02	0.01	0.17	0.05	0.01	0.01	0.02	0.01	0.02	0.01	0.02	0.01	0.03	0.01
F	0.20	0.14	0.31	0.21	0.28	0.12	0.07	0.05	0.70	0.26	0.21	0.09	0.14	0.04
Analytical total	80.36	1.28	83.96	1.46	87.74	0.69	87.34	0.28	81.61	1.56	89.04	3.09	93.70	0.85
H ₂ O*	12.33	0.27	12.09	0.55	12.35	0.11	13.42	0.03	11.21	0.45	4.17	0.19	4.42	0.05
O = Cl	0.00	0.01	-0.04	0.01	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.01
O = F	-0.09	0.06	-0.13	0.09	-0.12	0.05	-0.03	0.02	-0.29	0.11	-0.08	0.04	-0.06	0.02
Total	92.61	1.55	95.88	1.63	99.98	0.72	100.73	0.29	92.47	2.08	93.13	3.29	98.06	0.90
Anions (O, OH, Cl, F)	18		18		18		18		18		12		12	
<u>Tetrahedral sites</u>														
Si	3.47	0.05	3.39	0.12	3.01	0.05	3.39	0.01	3.64	0.07	3.21	0.04	3.28	0.02
Al ^{IV}	0.53	0.05	0.61	0.12	0.99	0.05	0.61	0.01	0.36	0.07	0.79	0.04	0.72	0.02
Sum	4.00	-	4.00	-	4.00	-	4.00	-	4.00	-	4.00	-	4.00	-
<u>Octahedral sites</u>														
Al ^{VI}	3.09	0.05	2.52	0.44	1.35	0.03	2.91	0.01	2.63	0.14	1.93	0.03	1.85	0.03
Fe	0.06	0.02	0.76	0.52	0.75	0.13	0.11	0.01	1.33	0.24	0.04	0.01	0.06	0.01
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-	0.00	0.00	0.00	0.00	0.00	0.00
Mg	1.49	0.07	1.70	0.32	3.69	0.15	1.75	0.02	0.83	0.29	0.05	0.01	0.10	0.02
Ti	0.00	-	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01
Sum	4.63	0.04	4.99	0.29	5.79	0.05	4.78	0.02	4.80	0.09	2.03	0.02	2.02	0.01
Vacancy	1.37	0.04	1.01	0.29	0.21	0.05	1.22	0.02	1.20	0.09	n.a.		n.a.	
<u>Interlayer sites</u>														
Ca	0.01	0.00	0.03	0.01	0.01	0.00	0.02	0.00	0.05	0.01	0.00	0.00	0.01	0.00
Na	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.01	0.00
K	0.14	0.02	0.04	0.01	0.02	0.02	0.08	0.01	0.01	0.00	0.79	0.05	0.79	0.02
Sum	0.16	0.02	0.08	0.02	0.04	0.02	0.11	0.01	0.08	0.01	0.80	0.05	0.80	0.02
Vacancy	n.a.		n.a.		n.a.		n.a.		n.a.		0.20	0.05	0.20	0.02
<u>Anions</u>														
Cl	0.00	0.00	0.03	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
F	0.06	0.04	0.10	0.07	0.08	0.04	0.02	0.01	0.23	0.09	0.04	0.02	0.03	0.01
OH	7.94	0.04	7.88	0.06	7.91	0.04	7.98	0.01	7.77	0.09	1.95	0.02	1.97	0.01
Sum	8.00	-	8.00	0.00	8.00	-	8.00	-	8.00	-	2.00	-	2.00	-
Fe/ (Fe + Mg)	0.04	0.01	0.28	0.13	0.17	0.03	0.06	0.00	0.62	0.11	n.a.		n.a.	
Temp (°C)	160		155		245		170		n.a.		235		230	

Notes: * = amount (wt %) of H₂O determined by stoichiometry; atomic proportion of OH calculated by subtraction; formation temperatures of illite and chlorite estimated from mineral chemistry after Cathelineau (1988) and Zang and Fyfe (1995), respectively; <DL = below detection limit; FAN = fanglomerate; n.a. = not applicable; hyphens are used to indicate where a value is not needed or where assigning a value is inappropriate

(Kotzer and Kyser, 1995). This temperature is in the upper range of that determined using fluid inclusion data and pressure-temperature reconstructions on similar euhedral quartz by Derome et al. (2005), which indicate formation temperatures of ca. 140° to 200°C. The lower temperatures determined by Derome et al. (2005) are attributed to anisothermal mixing of a higher-temperature diagenetic basinal brine with a

lower-temperature basement-modified basinal brine, whereas Kotzer and Kyser (1995) consider only a basinal brine of ca. 200°C to be involved in forming euhedral quartz.

Pre-ore illite is characterized by average K₂O contents of 8.8 wt % and MgO and FeO contents of 0.5 wt % and 0.8 wt %, respectively (Table 2). Its interlayer K of ca. 0.8 apfu and Si^{IV}/Al^{IV} ratio near 4, greater than that of ideal muscovite (Si^{IV}/Al^{IV}

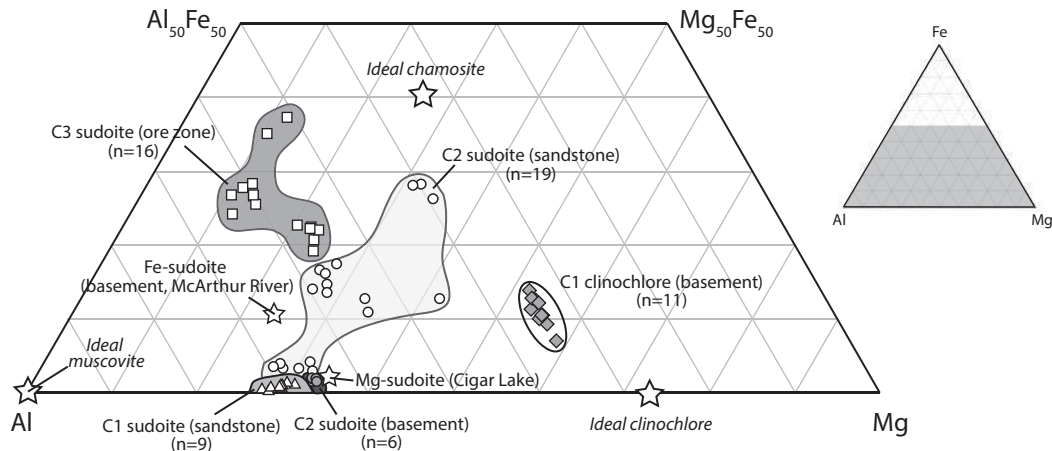


FIG. 7. Molar Fe-Al-Mg ternary plot of chlorite minerals from McArthur River Zone 4, showing composition of ideal chamosite, clinochlore, and muscovite (Deer et al., 1966). Composition of Fe sudoite in the basement of the McArthur River deposit reported by Billault et al. (2002) and Mg sudoite in sandstones at the Cigar Lake deposit (Percival and Kodama, 1989) are indicated.

= 3), are characteristic of illitic micas (Fig. 9). The presence of octahedral Mg may be a result of minor chlorite interlayers. Illite in the Manitou Falls sandstones has a calculated formation temperature of about 235°C (Table 2).

An illite-chlorite mixed-layered clay mineral, occurring spatially with pre-ore illite in the Manitou Falls Formation, was identified by XRD. Its diffraction pattern matched that of an illite-chlorite mixed-layer clay mineral reported near the upper parts of drill holes from the Close Lake-McArthur River area by Quirt (1999), which comprises interlayering of 60% illite and 40% sudoite.

Pre-ore C2 chlorite corresponds to a di-trioctahedral chlorite, based on XRD, and contains Al_2O_3 , MgO , and FeO contents averaging 27.3 wt %, 9.1 wt %, 11.7 wt %, respectively

(Table 2). C2 chlorite is an Mg-Fe-rich sudoite, as supported by the occurrence of one vacant octahedral site and variable $\text{Fe}/(\text{Fe} + \text{Mg})$ ratios that range between 0.09 and 0.47 (avg. 0.26; Table 2). C2 chlorite is distinguished from earlier-formed C1 chlorite by its greater Fe content (Fig. 7) and has a calculated formation temperature of about 155°C (Table 2). The lower formation temperatures recorded by C2 chlorite compared to earlier-formed pre-ore illite probably reflect the inaccuracy of the chlorite geothermometer for di-trioctahedral chlorites rather than a decrease in the fluid temperature. Zang and Fyfe (1995) noted that corrections for Al^{IV} made based on $\text{Fe}/\text{Fe} + \text{Mg}$ ratios may lead a large correction in Al^{IV} , which would cause lower calculated temperatures. Thus, the temperature of 155°C should be considered as a minimum

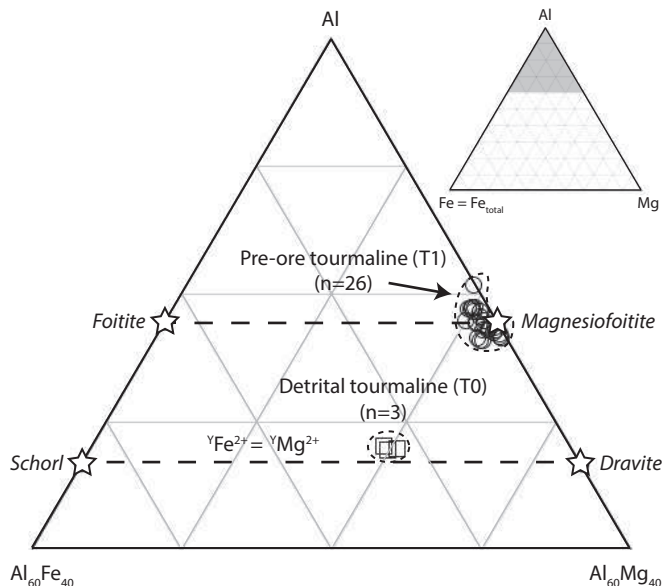


FIG. 8. Molar Al-Fe-Mg ternary plot of tourmaline group minerals from the Manitou Falls Formation at McArthur River Zone 4 and composition of end-member schorl, dravite, foitite (Deer et al., 1966), and magnesiofoitite (Rosenberg and Foit, 2006).

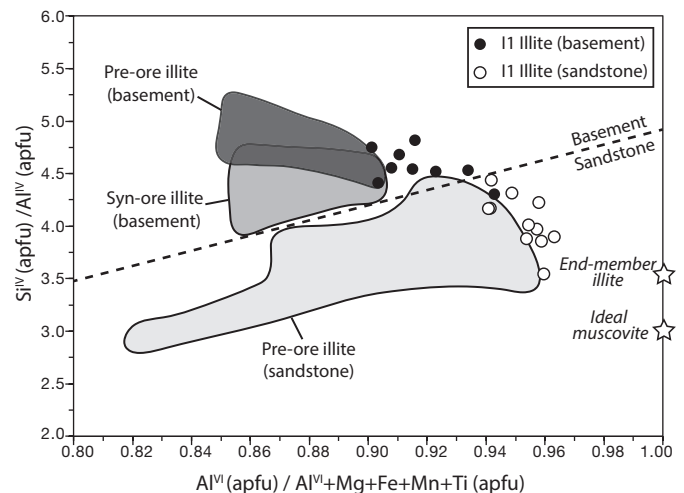


FIG. 9. Tetrahedral Si/Al ratio versus extent of substitution for octahedral Al in illite from McArthur River Zone 4. Both have lower degree of octahedral substitution for Al compared to sandstone and basement illite from other unconformity-related uranium deposits of the eastern Athabasca basin (shaded areas: data from Wilson and Kyser, 1987; Wilson et al., 1987; Percival et al., 1993; Alexandre et al., 2005; Cloutier et al., 2009, 2010, 2011). End-member illite composition defined using Rosenberg (2002); apfu = atoms per formula unit.

TABLE 3. Electron Microprobe Analyses of Tourmaline Group Minerals at McArthur River Zone 4

Mineral	T0 tourmaline		T1 tourmaline	
	Avg (n = 3)	$\pm 1\sigma$	Avg (n = 26)	$\pm 1\sigma$
Oxide (wt %)				
SiO ₂	35.36	0.24	36.09	0.78
TiO ₂	0.36	0.04	0.01	0.01
Al ₂ O ₃	30.12	0.06	35.14	1.15
FeO	7.62	0.25	0.67	0.34
MnO	0.03	0.00	0.02	0.02
MgO	6.99	0.16	7.54	0.30
CaO	0.91	0.04	0.12	0.03
Na ₂ O	2.08	0.13	0.69	0.18
K ₂ O	0.03	0.01	0.02	0.01
Cl	<DL	-	0.02	0.01
F	0.25	0.02	0.15	0.12
Analytical total	83.66	0.27	80.43	0.92
B ₂ O ₃ ^a	10.24	0.04	10.42	0.12
H ₂ O ^a	3.45	0.07	3.53	0.07
O = Cl	0.00	-	0.00	0.00
O = F	-0.07	0.06	-0.06	0.05
Total	97.28	0.31	94.33	1.07
Atomic proportions on the basis of 31 anions (O, OH, Cl, F)				
<u>Tetrahedral sites</u>				
Si	6.00	0.02	6.02	0.12
Al ^{IV}	0.01	0.01	0.04	0.08
Sum	6.01	0.02	6.05	0.06
B	3.00	-	3.00	-
<u>Octahedral Z sites</u>				
Al ^{VI}	6.00	0.01	6.00	0.00
Fe ²⁺	0.00	0.01	0.00	0.00
Mg	0.00	0.00	0.00	0.00
Sum	6.00	-	6.00	-
<u>Octahedral Y sites</u>				
Al ^{VI}	0.03	0.03	0.87	0.14
Ti	0.05	0.00	0.00	0.00
Mg	1.77	0.04	1.88	0.08
Mn	0.00	0.00	0.00	0.00
Fe ²⁺	1.08	0.05	0.09	0.05
Ca	0.08	0.04	0.02	0.01
Sum	3.00	-	2.86	0.10
<u>9-fold X site</u>				
Ca	0.09	0.03	0.00	0.00
Mg	0.00	0.00	0.00	0.00
Na	0.68	0.04	0.22	0.06
K	0.01	0.00	0.00	0.00
Sum	0.78	0.01	0.23	0.06
Vacancy	0.22	0.01	0.77	0.06
<u>Anions</u>				
Cl	0.00	-	0.00	0.00
F	0.09	0.08	0.07	0.07
OH	3.91	0.08	3.93	0.07
Sum	4.00	-	4.00	-

Notes: ^a = amount (wt %) of B₂O₃ and H₂O determined by stoichiometry; atomic proportion of OH calculated by subtraction; <DL = below detection limit; hyphens are used to indicate where a value is not needed or where assigning a value is inappropriate

formation temperature for this chlorite. Factoring in the large error margins of $\pm 25^\circ\text{C}$ for the chlorite geothermometer, the formation temperature of C2 sudoite could be near 200°C , which is typically assumed for the temperature attained at the floor of the basin (Hoeve and Sibbald, 1978).

Late pre-ore alteration of the Wollaston Group basement

Pre-ore illite from a pelite sample has an average chemical composition of 32.7 wt % Al₂O₃, 1.0 wt % MgO, and 1.1 wt % FeO (Table 2). Compared to illite in the Manitou Falls Formation, illite in the basement has a similar molar proportion of interlayer K, greater substitution of Mg and Fe for octahedral Al, higher Si^{IV}/Al^{IV} ratio (ca. 4.6), and similar formation temperatures (ca. 230°C ; Fig. 9; Table 2).

Pre-ore C1^{bsmt} chlorite occurring in a calc-silicate basement rock has an XRD pattern representative of trioctahedral chlorite with average Al₂O₃, MgO, and FeO contents of 20.6 wt %, 25.8 wt %, and 9.4 wt %, respectively (Table 2). This chlorite contains octahedral occupancy of about 5.8 apfu, close to the ideal number of six, for trioctahedral chlorite, and has a calculated formation temperature of about 245°C (Table 2). Its chemical composition is intermediate between chamosite and clinocllore, but is more similar to clinocllore (Fig. 7).

Pre-ore C2^{bsmt} chlorite from a basement pegmatite has an average chemical composition of 33.5 wt % Al₂O₃, 13.2 wt % MgO, and 1.5 wt % FeO and an Fe/Fe + Mg ratio of 0.06 (Table 2). It has an XRD pattern characteristic of di-trioctahedral chlorite, is compositionally similar to C1 chlorite, and has lower Fe content than C2 sudoite in the sandstone (Fig. 7). The calculated formation temperature of C2^{bsmt} chlorite is about 170°C , similar to C2 sudoite in the corresponding sandstone alteration halo (Table 2), which represents an estimate of its minimum formation temperature.

Syn-ore alteration

Syn-ore chlorite from the ore zone has an average chemical composition of 24.4 wt % Al₂O₃ and 5.4 wt % MgO and the highest iron content (FeO = 15.4 wt %) of all chlorites at McArthur River Zone 4 (Fig. 7; Table 2). Syn-ore chlorite is considered an Fe-Mg-rich sudoite based on the occurrence of about 1.2 octahedral vacancies per formula unit and Fe/(Fe + Mg) ratios ranging from 0.44 to 0.77 (avg. 0.62; Fig. 7; Table 2). Radiation damage of syn-ore chlorite caused by nearby uraninite, as recorded by their anomalous high birefringence in cross-polarized light (Fig. 5a), may be responsible for its aberrantly low calculated formation temperature of 70°C . Irradiation can cause amorphization of clays through creation of atomic defects (Allard and Calas, 2009), along with changes to the oxidation state of octahedral Fe (Drago et al., 1977; Gournis et al., 2000). Both may affect cation distribution, thus precluding the use of any chlorite geothermometer.

Crystal Chemistry of Uranium Minerals

The chemical compositions of uranium minerals are reported in Table 4, and their compositional variations illustrated in a UO₂-CaO-SiO₂ ternary diagram in Figure 10. All have very low ThO₂ contents of less than 0.05 wt %. Massive and pseudocubic uraninite, which formed during the main ore stage, is characterized by high, but variable, contents of UO₂ (77.28–87.79 wt %) and PbO (0.55–15.22 wt %), and

TABLE 4. Electron Microprobe Analyses and Calculated U-Pb Chemical Ages of Uranium Minerals at McArthur River Zone 4

Sample DDH-depth (m)	Mineral (morph.)	Oxides (wt %)											Chemical age (Ma)	
		Na ₂ O	MgO	CaO	FeO	TiO ₂	PbO	UO ₂	ThO ₂	SiO ₂	P ₂ O ₅	Y ₂ O ₃		Total (%)
MAC232-533 (n = 12)	U1 uran (massive)	0.10–0.30	0.02–0.06	0.87–2.56	0.15–0.42	0.19–0.30	7.55–14.73	77.90–84.09	<DL–0.01	0.04–0.59	0.04–0.18	0.13–0.22	94.33–97.16	633–1244
MAC222-528 (n = 13)	U1 uran (psdCubic)	0.03–0.11	0.01–0.05	0.33–1.94	0.01–0.27	0.27–1.11	0.84–13.98	80.23–87.79	<DL–0.03	0.10–3.04	0.05–0.26	0.16–0.36	92.24–96.37	72–1158
MAC222-537 (n = 6)	U1 uran (psdCubic)	0.17–0.36	0.03–0.04	1.22–2.26	0.30–0.70	0.15–0.19	7.71–9.58	82.69–84.32	<DL–0.02	0.21–0.64	0.10–0.18	0.41–0.46	94.96–96.76	643–789
MAC244-513 (n = 9)	U1 uran (psdCubic)	0.09–0.17	0.01–0.04	1.32–1.75	0.29–0.71	0.03–0.28	0.55–12.44	79.01–86.71	<DL–0.02	0.09–0.58	0.14–2.38	0.05–0.14	92.89–96.05	47–1034
MAC241-564 (n = 6)	U1 uran (psdCubic)	0.08–0.11	0.02–0.08	0.90–1.30	0.13–0.33	0.23–0.51	12.27–15.22	77.29–80.14	<DL–0.01	0.04–0.27	0.07–0.10	0.15–0.25	92.69–95.25	1033–1287
MAC236-510 (n = 9)	U2 uran (bleb-botry)	0.17–0.25	<DL–0.01	1.43–1.67	0.02–0.06	0.02–0.07	2.79–3.81	87.36–88.61	<DL–0.01	1.01–1.29	0.10–0.21	0.32–0.38	94.15–94.95	230–317
MAC241-564 (n = 3)	Cofl coff (colloform)	0.02–0.15	0.02–0.05	2.75–3.78	0.76–0.85	0.01–0.03	0.01–4.87	78.74–81.66	<DL	3.58–6.36	0.52–0.72	0.17–0.36	91.87–93.67	0–444
MAC222-537 (n = 4)	Gul gumm	0.14–0.67	0.02–0.05	5.52–6.22	0.73–2.42	0.10–0.12	1.06–3.41	79.08–80.68	<DL–0.02	1.46–3.75	0.16–0.33	0.42–1.09	92.30–92.97	98–314

Abbreviations: bleb-botry = blebby-botryoidal, coff = coffinite, DDH = diamond drill hole, gumm = gummite, morph. = morphology, n = number of analysis, psdCubic = pseudocubic, uran = uraninite

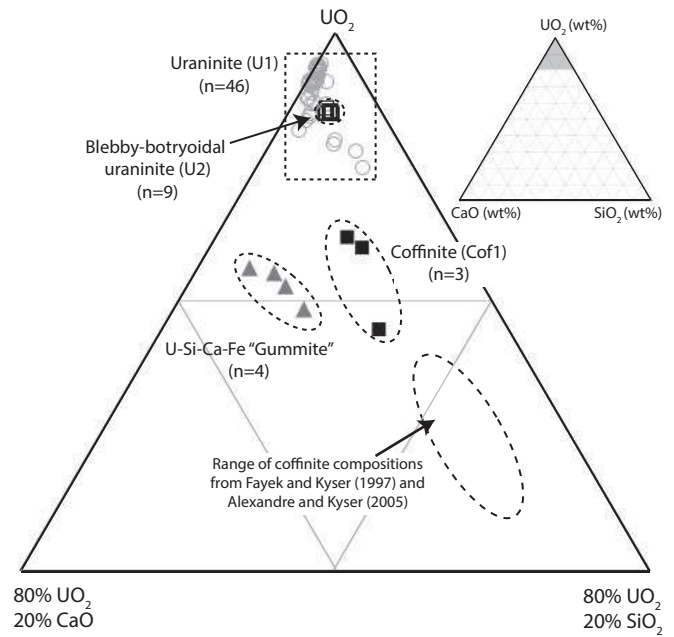


FIG. 10. Chemical variation (in wt %) of uranium minerals from McArthur River Zone 4 showing three compositional groups. See text for discussion.

moderate CaO (0.83–2.56 wt %) and SiO₂ (0.04–3.04 wt %), and low FeO contents (0.01–0.71 wt %; Table 4). There is a strong inverse correlation between U and Pb, Ca, and Si but a poor inverse correlation with Fe. The U-Pb chemical age of massive and pseudocubic uraninite varies widely from 47 to 1287 Ma as a result of chemical alteration, which appears as domains of variable brightness in BSE images (Fig. 5b; Fayek et al., 2002; Alexandre and Kyser, 2005). Darker regions, which typically occur along grain margins and fractures in uraninite, correspond to lower Pb and higher Ca, Si, and Fe contents, and record younger chemical ages (Table 4).

Blebby- to botryoidal-textured uraninite from one sample (Fig. 5d) is characterized by high UO₂ (87.36–88.61 wt %), low PbO (2.79–3.81 wt %), moderate CaO (1.43–1.67 wt %), and low FeO (<0.1 wt %) contents (Table 4). This uraninite has relatively young U-Pb chemical ages ranging from 230 to 317 Ma and is compositionally similar to massive and pseudocubic uraninite (Fig. 10).

Colloform-textured coffinite (Fig. 5c) is characterized by relatively low UO₂ (78.74–81.66 wt %) and PbO (0.01–4.87 wt %), and high CaO (2.75–3.78 wt %), FeO (0.76–0.85 wt %), and SiO₂ (3.58–6.36 wt %) contents (Table 4). Coffinite at Zone 4 has greater CaO and SiO₂ content than uraninite, forming a cluster displaced away from the UO₂ apex, and plots along a substitution trend defined by coffinite from Cigar Lake and the basement-hosted McArthur River Zone 2 orebody (Fig. 10; Fayek and Kyser, 1997; Alexandre and Kyser, 2005). Compared to coffinite from McArthur River Zone 2, Zone 4 coffinite has lower SiO₂ content, suggesting it may represent U1 uraninite that was only partly converted to coffinite. Coffinite from Zone 4 has young chemical ages (<450 Ma) similar to blebby-botryoidal uraninite (Table 4).

Gummite (Fig. 5b) is characterized by relatively low UO₂ (79.08–80.68 wt %) and PbO (1.06–3.41 wt %), moderate SiO₂ (1.46–3.75 wt %), and the highest CaO (5.52–6.22 wt %)

and FeO (0.41–2.42 wt %) contents among the uranium minerals at Zone 4 (Table 4). Gummite is distinguished from uraninite by its lower UO_2 content and from coffinite by its higher CaO content (Fig. 10). Calculated chemical ages are less than 315 Ma, similar to coffinite and blebby-botryoidal uraninite (Table 4).

Age of Mineralization

The initial age of uranium mineralization at Zone 4 can be estimated from a plot of $\text{SiO}_2 + \text{CaO}$ (wt %) versus chemical U-Pb age (Ma) (Fig. 11), following the method of Alexandre and Kyser (2005). Loss of radiogenic Pb in all uranium minerals is correlated with gains in Ca and Si (Fig. 11; Table 4). Extrapolation to an $\text{SiO}_2 + \text{CaO}$ content of 0 wt % for massive and pseudocubic uraninite gives a chemical age of 1601 ± 30 Ma, which represents the maximum age of uranium mineralization at McArthur River Zone 4, assuming that primary uraninite is pure UO_2 with no elemental substitution. This calculated age is similar to the age of ca. 1590 Ma interpreted to represent the timing of basin-wide mineralization in the Athabasca basin (Alexandre et al., 2009b). A similar regression line generated from coffinite and gummite data indicates a chemical age of 1376 ± 35 Ma, which is interpreted as the timing when the fluid altered the original uraninite to gummite and coffinite. The age of this alteration event coincides with the timing of a basin-wide resetting event at about 1330 to 1380 Ma that is recorded in several Athabasca basin uranium deposits (Cumming and Krstic, 1992).

The U-Pb isotope compositions of massive and pseudocubic uraninite, blebby-botryoidal uraninite, and coffinite define three discordant lines (group U1a, U1b, and U2) on a U-Pb concordia-discordia diagram (Fig. 12; Table 5). Group U1a consists of pseudocubic uraninite (Fig. 5a), with an upper intercept age of 1278 ± 47 Ma and a similar average

$^{207}\text{Pb}/^{206}\text{Pb}$ age of 1267 ± 32 Ma (Fig. 12; Table 5). Group U1b, comprising massive uraninite, has an upper intercept age of 1267 ± 140 Ma and a lower intercept age of 859 ± 150 Ma (Fig. 12). The poorer distribution of ages for massive uraninites compared to pseudocubic uraninites may be related to the former being less uniformly altered (Fig. 5b), resulting in fine scale variations in the amount of Pb loss. The $^{207}\text{Pb}/^{206}\text{Pb}$ ages for massive uraninite vary between about 950 and 1240 Ma. The oldest $^{207}\text{Pb}/^{206}\text{Pb}$ age, corresponding to the least altered uraninite, is similar to the upper intercept age of group U1a uraninites. Group U2, which includes coffinite (Fig. 5c), blebby-botryoidal uraninite (Fig. 5d), and gummite-altered (Fig. 5b) and siderite-altered uraninite, has an upper intercept age of 838 ± 40 Ma and an average $^{207}\text{Pb}/^{206}\text{Pb}$ age of 905 ± 157 Ma (Fig. 12). The lower intercept of Group U1b uraninites coincides with the upper intercept of Group U2.

Stable Isotopic Composition of Alteration Minerals and Fluids Involved in Sandstone and Basement Alteration

Pre-ore fluids

The oxygen and hydrogen isotope compositions of alteration minerals from the basin and basement, along with their calculated fluid values, are shown in Table 6. Pre-ore dickite, occurring in the upper silicified zone with pre-ore illite, has $\delta^{18}\text{O}_{\text{mineral}}$ values between 11.0 and 14.5‰ and $\delta^2\text{H}_{\text{mineral}}$ values between –88 and –64‰ (Table 6). Using a formation temperature of 200°C, as previously proposed for peak diagenesis in the Athabasca basin (Wilson and Kyser, 1987; Kotzer and Kyser, 1995), and consistent with the temperature of 235°C calculated herein for illite, the fluid in equilibrium with dickite has $\delta^{18}\text{O}_{\text{fluid}}$ values ranging from 5.4 to 8.9‰ and $\delta^2\text{H}_{\text{fluid}}$ values varying from –70 to –46‰ (Fig. 13; Table 6).

Pre-ore C1 Mg-rich sudoite occurs as mixtures with pre-ore kaolinite and dickite in MFc and MFd and has $\delta^{18}\text{O}_{\text{mineral}}$ values that range from 7.7 to 8.5‰ and $\delta^2\text{H}_{\text{mineral}}$ from –70 to –45‰ (Table 6). Using a formation temperature of 160°C, calculated based on Al^{IV} occupancy (Table 2), gives $\delta^{18}\text{O}_{\text{fluid}}$ values between 4.1 and 4.9‰ and $\delta^2\text{H}_{\text{fluid}}$ values between –68 and –43‰ (Fig. 13; Table 6), similar to those of dickite. Likewise, pre-ore illite from the illite-rich alteration zone has typical $\delta^{18}\text{O}_{\text{mineral}}$ values from 9.4 to 12.7‰ and $\delta^2\text{H}_{\text{mineral}}$ values from –78 to –57‰ (Table 6). A formation temperature of 235°C, calculated based on K deficiency (Table 2), indicates calculated $\delta^{18}\text{O}_{\text{fluid}}$ values for illite between 4.8 and 8.1‰ and $\delta^2\text{H}_{\text{fluid}}$ values between –64 and –43‰, similar to those of dickite and C1 chlorite (Fig. 13; Table 6). Illite-chlorite mixed-layer clays, which occur as mixtures with pre-ore illite in the sandstones, have $\delta^{18}\text{O}_{\text{mineral}}$ values between 9.0 and 12.0‰ and $\delta^2\text{H}_{\text{mineral}}$ values between –60 and –45‰ (Table 6). The fluid in equilibrium with illite-chlorite mixed-layer clay has $\delta^{18}\text{O}_{\text{fluid}}$ values between 4.8 and 7.8‰ and $\delta^2\text{H}_{\text{fluid}}$ between –51 and –36‰, similar to fluid values for illite (Fig. 13; Table 6).

Two pre-ore illite samples from the altered metasedimentary basement (quartzite and pelite) have $\delta^{18}\text{O}_{\text{mineral}}$ values of 9.5 and 9.7‰ and $\delta^2\text{H}_{\text{mineral}}$ values of –70 and –68‰ (Table 6). Using a formation temperature of 230°C determined by K deficiency (Table 2), the corresponding fluid has $\delta^{18}\text{O}_{\text{fluid}}$

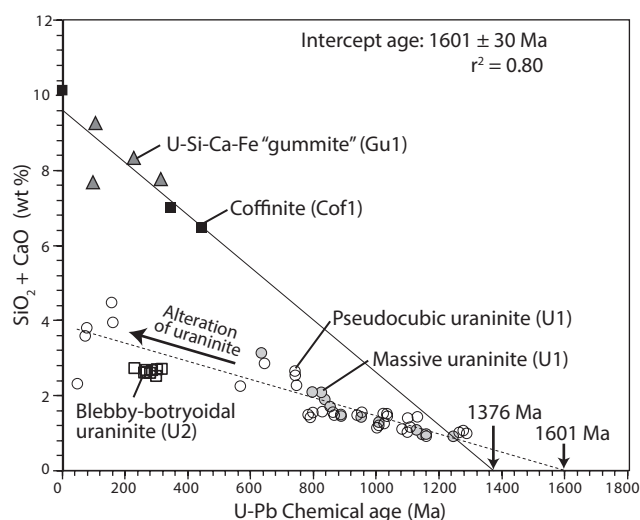


FIG. 11. Relation between $\text{SiO}_2 + \text{CaO}$ and chemical U-Pb age of uranium minerals from McArthur River Zone 4. Regression of massive and pseudocubic uraninite compositions to 0 wt % $\text{SiO}_2 + \text{CaO}$ intercepts the abscissa at 1601 ± 30 Ma, which is interpreted as the age of primary uranium mineralization at Zone 4. A regression line defined by coffinite and gummite intersects the abscissa at 1376 ± 35 Ma, corresponding to the timing of uraninite alteration. Absolute errors (1σ) associated with the $\text{SiO}_2 + \text{CaO}$ and chemical age for each data point are less than the size of the symbols.

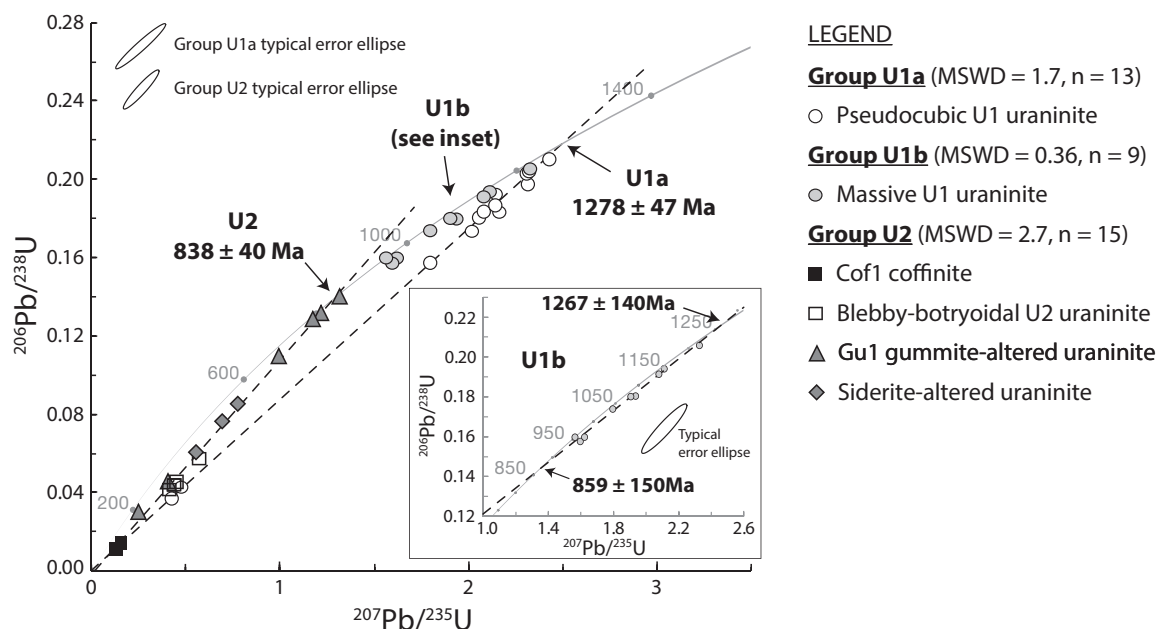


FIG. 12. U-Pb concordia diagram of uranium minerals from McArthur River Zone 4. Group U1a, U1b, and U2 uranium minerals are described in text. The upper and lower intercept ages of discordia lines (dashed) with the concordia curve are indicated. Upper intercept age for Group U1a calculated without the two data points near the lower intercept.

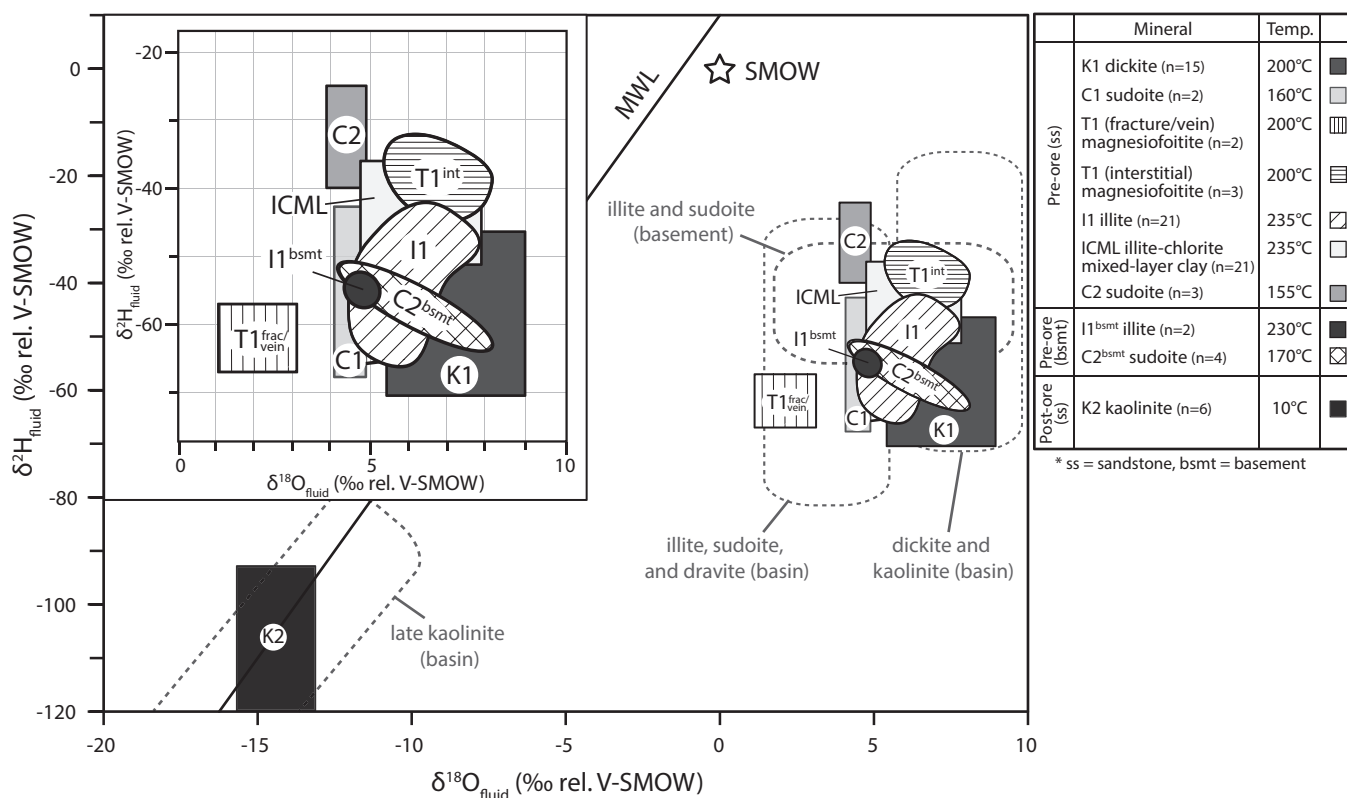


FIG. 13. $\delta^{18}\text{O}$ versus $\delta^2\text{H}$ for fluids in equilibrium with alteration minerals from the Manitou Falls Formation and Wollaston Group metasedimentary basement at McArthur River Zone 4. Fields for fluids in equilibrium with typical Athabasca basin alteration minerals (gray, dashed lines) calculated from $\delta^{18}\text{O}$ and $\delta^2\text{H}$ mineral values, formation temperatures, and mineral chemistry (for chlorite) data of Percival et al. (1993), Kotzer and Kyser (1995), Wasyluk (2001), Alexandre et al. (2005), and Cloutier et al. (2009, 2010, 2011). MWL = meteoric water line, SMOW = standard mean ocean water.

TABLE 5. U-Pb and Pb-Pb LA-HR-ICP-MS Isotope Data and Apparent Ages for Uranium Minerals from McArthur River Zone 4

													Apparent ages (Ma)							
Sample	DDH-depth (m)	No.	Group	Mineral (paragenesis)	$^{206}\text{Pb}/$ ^{204}Pb	% comm. Pb	$^{206}\text{Pb}/$ ^{238}U	$\pm 1\sigma$	$^{207}\text{Pb}/$ ^{235}U	$\pm 1\sigma$	ρ	$^{207}\text{Pb}/$ ^{206}Pb	$\pm 1\sigma$	$^{206}\text{Pb}/$ ^{238}U	$\pm 1\sigma$	$^{207}\text{Pb}/$ ^{235}U	$\pm 1\sigma$	$^{207}\text{Pb}/$ ^{206}Pb	$\pm 1\sigma$	Disc. (%)
Group U1a																				
MAC244-513	A-1	U1a	Pseudocubic U1 uran.	6,134	0.27	0.0370	0.0042	0.4243	0.0489	0.947	0.0826	0.0003	234	26	359	35	1261	6	81	
	A-2	U1a	Pseudocubic U1 uran.	32,624	0.05	0.1734	0.0074	2.0192	0.0868	0.963	0.0839	0.0001	1031	41	1122	30	1291	2	20	
	A-3	U1a	Pseudocubic U1 uran.	83,821	0.02	0.1831	0.0069	2.1631	0.0827	0.961	0.0851	0.0001	1084	38	1169	27	1319	3	18	
	A-4	U1a	Pseudocubic U1 uran.	9,733	0.17	0.0427	0.0066	0.4759	0.0731	0.889	0.0803	0.0003	270	41	395	52	1204	7	78	
MAC222-528	B-1	U1a	Pseudocubic U1 uran.	838,688	0.002	0.1922	0.0096	2.1482	0.1141	0.966	0.0812	0.0003	1133	52	1164	37	1226	7	8	
	B-2	U1a	Pseudocubic U1 uran.	212,496	0.01	0.1804	0.0028	2.0570	0.0311	0.961	0.0828	0.0001	1069	15	1135	10	1265	3	15	
	B-3	U1a	Pseudocubic U1 uran.	85,956	0.02	0.1836	0.0077	2.0794	0.0838	0.962	0.0823	0.0002	1087	42	1142	28	1252	5	13	
	B-4	U1a	Pseudocubic U1 uran.	199,380	0.01	0.2103	0.0122	2.4274	0.1383	0.956	0.0838	0.0002	1231	65	1251	42	1289	4	5	
MAC241-564	C-1	U1a	Pseudocubic U1 uran.	15,169	0.11	0.1974	0.0139	2.3128	0.1627	0.963	0.0850	0.0002	1162	75	1216	51	1316	6	12	
MAC238-572	D-1	U1a	Pseudocubic U1 uran.	120,874	0.01	0.2029	0.0070	2.3074	0.0802	0.963	0.0825	0.0001	1191	38	1215	25	1258	3	5	
	D-2	U1a	Pseudocubic U1 uran.	112,791	0.01	0.2038	0.0062	2.3205	0.0715	0.957	0.0827	0.0001	1195	34	1219	22	1261	3	5	
	D-3	U1a	Pseudocubic U1 uran.	4,455	0.37	0.1574	0.0189	1.7955	0.2149	0.950	0.0828	0.0003	942	106	1044	81	1264	7	25	
	D-4	U1a	Pseudocubic U1 uran.	25,004	0.07	0.1869	0.0145	2.1368	0.1669	0.961	0.0830	0.0002	1105	79	1161	56	1269	4	13	
Group U1b																				
MAC232-533	E-1	U1b	Massive U1 uran.	195,245	0.01	0.1945	0.0089	2.1096	0.0975	0.914	0.0785	0.0002	1146	48	1152	32	1159	5	1	
	E-2	U1b	Massive U1 uran.	266,640	0.01	0.1805	0.0082	1.9050	0.0918	0.933	0.0764	0.0004	1070	45	1083	33	1104	11	3	
	E-3	U1b	Massive U1 uran.	60,283	0.03	0.1603	0.0160	1.5646	0.1563	0.950	0.0707	0.0002	958	90	956	64	948	5	-1	
	E-4	U1b	Massive U1 uran.	81,561	0.02	0.1603	0.0089	1.6223	0.1080	0.957	0.0733	0.0009	958	50	979	43	1021	25	6	
	E-5	U1b	Massive U1 uran.	337,158	0.005	0.2062	0.0072	2.3272	0.0904	0.953	0.0817	0.0006	1208	39	1221	28	1238	14	2	
	E-6	U1b	Massive U1 uran.	101,817	0.02	0.1807	0.0068	1.9364	0.0843	0.957	0.0775	0.0006	1071	37	1094	30	1135	16	6	
	E-7	U1b	Massive U1 uran.	80,458	0.02	0.1581	0.0035	1.5969	0.0332	0.807	0.0733	0.0007	946	19	969	13	1021	19	7	
	E-8	U1b	Massive U1 uran.	122,054	0.01	0.1918	0.0059	2.0789	0.1123	0.926	0.0784	0.0021	1131	32	1142	38	1157	53	2	
	E-9	U1b	Massive U1 uran.	94,329	0.02	0.1742	0.0041	1.7956	0.0443	0.952	0.0746	0.0003	1035	22	1044	16	1057	8	2	
Group U2																				
MAC236-510	F-1	U2	U2 uran.	4,307	0.40	0.0572	0.0037	0.5722	0.0375	0.944	0.0726	0.0002	359	23	459	24	1002	5	64	
	F-2	U2	U2 uran.	4,945	0.35	0.0452	0.0011	0.4511	0.0105	0.909	0.0724	0.0002	285	7	378	7	998	7	71	
	F-3	U2	U2 uran.	5,138	0.34	0.0414	0.0011	0.4128	0.0110	0.936	0.0724	0.0002	262	7	351	8	997	6	74	
	F-4	U2	U2 uran.	5,080	0.34	0.0439	0.0027	0.4391	0.0270	0.921	0.0727	0.0003	277	17	370	19	1005	8	72	
MAC241-564	G-1	U2	Cofl coffinite	5,106	0.34	0.0114	0.0007	0.1283	0.0083	0.918	0.0814	0.0006	73	4	123	7	1232	15	94	
	G-2	U2	Cofl coffinite	6,131	0.28	0.0145	0.0017	0.1570	0.0184	0.915	0.0783	0.0006	93	11	148	16	1155	16	92	
MAC222-537	H-1	U2	Gummite-altered U1 uran.	67,407	0.03	0.1280	0.0092	1.1741	0.0855	0.961	0.0664	0.0001	777	53	789	41	820	3	5	
	H-2	U2	Gummite-altered U1 uran.	52,827	0.03	0.1398	0.0043	1.3152	0.0391	0.962	0.0682	0.0001	843	24	852	17	874	3	3	
	H-3	U2	Gummite-altered U1 uran.	196,936	0.01	0.1312	0.0103	1.2189	0.0960	0.965	0.0673	0.0001	795	59	809	45	848	4	6	
	H-4	U2	Gummite-altered U1 uran.	30,970	0.06	0.1092	0.0090	0.9940	0.0819	0.961	0.0660	0.0001	668	52	701	43	806	3	17	
	H-5	U2	Gummite-altered U1 uran.	2,418	0.72	0.0450	0.0051	0.4047	0.0470	0.923	0.0652	0.0013	284	31	345	35	780	43	64	
	H-6	U2	Gummite-altered U1 uran.	704	2.46	0.0296	0.0043	0.2476	0.0367	0.879	0.0607	0.0035	188	27	225	30	627	130	70	
MAC238-547	I-1	U2	Siderite-altered U1 uran.	33,636	0.05	0.0852	0.0046	0.7760	0.0438	0.942	0.0661	0.0003	527	27	583	25	811	10	35	
	I-2	U2	Siderite-altered U1 uran.	3,061	0.54	0.0764	0.0086	0.6938	0.0767	0.957	0.0660	0.0007	474	52	535	47	807	22	41	
	I-3	U2	Siderite-altered U1 uran.	2,832	0.59	0.0607	0.0064	0.5536	0.0629	0.938	0.0664	0.0009	380	39	447	42	818	29	54	

Notes: Common Pb correction for uranium minerals was not required as ^{204}Pb signal intensities were close to background; only positive ratios were used in the calculation of $^{206}\text{Pb}/^{204}\text{Pb}$; thus, the reported $^{206}\text{Pb}/^{204}\text{Pb}$ ratio represents a minimum for each measurement

Abbreviations: comm. Pb = percentage common Pb calculated from measured $^{206}\text{Pb}/^{204}\text{Pb}$ ratio and terrestrial lead from Stacey and Kramers (1975), Disc. (%) = percent discordances, <DL = below detection limit, uran. = uraninite, No. = analysis number, ρ = error correlation coefficient

TABLE 6. Oxygen and Hydrogen Stable Isotope Composition of Alteration Minerals and Calculated Fluids from McArthur River Zone 4

Sample DDH-depth (m)	Mineralogy %	Size μm	Mineral $\delta^{18}\text{O}$	$\delta^2\text{H}$	H_2O %	Temp. ($^{\circ}\text{C}$)	Fluid $\delta^{18}\text{O}$	$\delta^2\text{H}$	Sample DDH-depth (m)	Mineralogy %	Size μm	Mineral $\delta^{18}\text{O}$	$\delta^2\text{H}$	H_2O %	Temp. ($^{\circ}\text{C}$)	Fluid $\delta^{18}\text{O}$	$\delta^2\text{H}$
<u>Pre-ore illite (I1) in sandstone</u>									<u>Pre-ore illite (I1) and illite-chlorite mixed interlayer (ICML) clay in sandstone</u>								
MAC222-314	100 I1	1-2	11.0	-67	5.8	235	6.4	-54	MAC222-249	78 I1, 22 ICML	1-2	11.2	-70	6.3	-	-	-
MAC222-333	100 I1	1-2	13.9	-57	4.9	235	9.3	-43	MAC222-279	66 I1, 34 ICML	1-2	12.4	-63	5.6	-	-	-
MAC222-345	100 I1	1-2	10.4	-78	6.0	235	5.8	-64	MAC232-237	72 I1, 28 ICML	1-2	10.7	-67	6.1	-	-	-
MAC232-280	100 I1	1-2	11.6	-64	5.6	235	7.0	-50	MAC233-258	69 I1, 31 ICML	1-2	9.8	-68	6.3	-	-	-
MAC232-301	100 I1	1-2	14.9	-64	5.3	235	10.3	-50	MAC233-287	63 I1, 37 ICML	1-2	9.6	-65	6.1	-	-	-
MAC233-315	100 I1	1-2	12.7	-78	6.8	235	8.1	-64	MAC236-256	71 I1, 29 ICML	1-2	9.4	-60	6.7	-	-	-
MAC233-300	100 I1	1-2	9.6	-62	6.3	235	5.0	-49	MAC236-287	69 I1, 31 ICML	1-2	10.0	-66	6.9	-	-	-
MAC238-287	100 I1	1-2	9.4	-73	6.1	235	4.8	-59	MAC238-240	80 I1, 20 ICML	1-2	9.1	-78	7.2	-	-	-
MAC238-311	100 I1	1-2	11.1	-66	5.7	235	6.5	-52	MAC238-261	72 I1, 28 ICML	1-2	10.4	-74	7.0	-	-	-
MAC240-302	100 I1	1-2	10.3	-60	5.4	235	5.7	-46	MAC240-267	62 I1, 38 ICML	1-2	11.1	-69	6.8	-	-	-
MAC240-344	100 I1	1-2	12.1	-62	4.9	235	7.5	-48	MAC241-246	68 I1, 32 ICML	1-2	13.3	-59	6.3	-	-	-
MAC241-333	100 I1	1-2	10.9	-73	5.1	235	6.3	-60	MAC241-265	74 I1, 26 ICML	1-2	11.9	-60	6.2	-	-	-
MAC241-353	100 I1	1-2	10.6	-64	5.1	235	6.0	-50	MAC241-295	67 I1, 33 ICML	1-2	9.9	-68	6.9	-	-	-
MAC244-269	100 I1	1-2	9.8	-70	5.1	235	5.2	-57	MAC244-240	45 I1, 55 ICML	1-2	9.3	-65	8.1	-	-	-
MAC244-292	100 I1	1-2	9.8	-66	5.2	235	5.2	-52	MAC246-300	68 I1, 32 ICML	1-2	11.4	-63	6.4	-	-	-
MAC244-303	100 I1	1-2	11.0	-65	5.8	235	6.4	-51	MAC255-253	70 I1, 30 ICML	1-2	12.2	-68	6.3	-	-	-
MAC244-320	100 I1	1-2	10.4	-91	5.9	235	5.8	-77	MAC255-272	46 I1, 54 ICML	1-2	9.8	-61	7.9	-	-	-
MAC246-320	100 I1	1-2	9.6	-67	6.2	235	5.0	-53	MAC255-291	58 I1, 42 ICML	1-2	10.8	-63	7.1	-	-	-
MAC246-337	100 I1	1-2	11.1	-57	5.2	235	6.4	-44	MAC256-249	41 I1, 59 ICML	1-2	11.3	-62	7.8	-	-	-
MAC246-354	100 I1	1-2	11.2	-63	4.8	235	6.6	-49	MAC256-268	58 I1, 42 ICML	1-2	11.8	-65	7.3	-	-	-
MAC256-325	100 I1	1-2	11.0	-62	5.5	235	6.4	-48	MAC256-287	70 I1, 30 ICML	1-2	10.6	-60	6.3	-	-	-
									ICML	100 ICML (upper)	-	12.0	-45	-	-	7.8	-36
									ICML	100 ICML (lower)	-	9.0	-60	-	-	4.8	-51
<u>Pre-ore magnesiofioitite (T1^{interstitial}) in sandstone distal to ore</u>									<u>Pre-ore illite (I1) and dickite (K1) in silicified sandstone</u>								
MAC222-110	100 T1	2-5	11.8	-57	3.6	200	5.7	-34	MAC222-404	23 I1, 77 K1	<2	11.2	-63	8.6	-	-	-
MAC241-63	100 T1	2-5	12.7	-66	3.6	200	6.6	-43	MAC232-374	6 I1, 94 K1	<2	n.a.	-52	8.8	-	-	-
MAC241-184	100 T1	5-10	14.0	-62	3.3	200	7.8	-39	MAC232-408	15 I1, 85 K1	2-5	12.0	-62	8.5	-	-	-
									MAC233-422	27 I1, 73 K1	<2	13.7	-83	7.0	-	-	-
									MAC233-473	21 I1, 79 K1	<2	13.2	-96	8.1	-	-	-
<u>Pre-ore magnesiofioitite (T1^{fracture}) in sandstone proximal to ore</u>									MAC236-435	43 I1, 57 K1	1-2	11.5	-79	7.2	-	-	-
T1 ^{frac} Mg-Ft	100 T1 (upper)	-	9.3	-80	-	200	3.1	-57	MAC238-365	13 I1, 87 K1	<2	11.8	-87	8.4	-	-	-
T1 ^{frac} Mg-Ft	100 T1 (lower)	-	7.3	-90	-	200	1.1	-67	MAC240-447	61 I1, 39 K1	2-5	10.3	-63	7.7	-	-	-
									MAC241-440	19 I1, 81 K1	<2	13.1	-66	7.5	-	-	-
<u>Pre-ore chlorite (C1) in sandstone</u>									MAC241-463	10 I1, 90 K1	<2	10.2	-119	6.7	-	-	-
MAC252-215	35 K1, 65 C1	1-2	10.5	-62	15.6	-	-	-	MAC244-421	58 I1, 42 K1	2-5	11.8	-82	4.8	-	-	-
MAC251-252	33 K1, 67 C1	1-2	8.8	-61	14.5	-	-	-	MAC251-476	21 I1, 79 K1	2-5	10.8	-65	7.9	-	-	-
C1 Sud	100 C1 (upper)	-	8.5	-45	-	160	4.9	-43	MAC255-483	42 I1, 58 K1	<2	13.2	-79	7.1	-	-	-
C1 Sud	100 C1 (lower)	-	7.7	-70	-	160	4.1	-68	MAC256-398	11 I1, 89 K1	<2	n.a.	-70	10.7	-	-	-
									MAC256-456	22 I1, 78 K1	<2	14.1	-79	8.7	-	-	-
									K1 Dkt	100 K1 (upper)	-	14.5	-64	-	200	8.9	-46
									K1 Dkt	100 K1 (lower)	-	11.0	-88	-	200	5.4	-70
<u>Pre-ore illite and sudoite in fanglomerate (I1, C2) and basement (I1^{bsmt}, C2^{bsmt})</u>									<u>Post-ore kaolinite (K2) in basal sandstone and fanglomerate</u>								
MAC238-604	100 I1 ^{bsmt}	<2	9.5	-68	6.9	230	4.7	-54	MAC236-531	100 K2	1-2	14.3	-148	15.1	10	-13.4	-113
MAC233-593	100 I1 ^{bsmt}	<2	9.7	-70	5.2	230	4.9	-56	MAC233-500	70 K2, 30 T1	2-5	10.9	-135	15.9	-	-	-
MAC233-516	100 C2 ^{bsmt}	<2	11.0	-66	12.5	170	7.8	-62									

TABLE 6. (Cont.)

Sample DDH-depth (m)	Mineralogy %	Size μm	Mineral $\delta^{18}\text{O}$	$\delta^2\text{H}$	H_2O %	Temp. ($^{\circ}\text{C}$)	Fluid $\delta^{18}\text{O}$	Fluid $\delta^2\text{H}$
MAC241-569	100 C2 ^{bsmt}	<2	7.8	-56	13.3	170	4.5	-
MAC255-517	57 I ^{bsmt} , 43 C2 ^{bsmt}	<2	10.3	-63	12.9	-	-	-13.4 -110
MAC244-581	65 I ^{bsmt} , 35 C2 ^{bsmt}	1-2	8.1	-49	10.2	-	-	-15.7 -120
MAC240-560	43 I ^l , 57 C2	1-2	8.9	-53	13.2	-	-	-
MAC244-569	42 I ^l , 58 C2	1-2	9.0	-61	12.4	-	-	-
MAC236-572	53 I ^l , 47 C2	2-5	9.4	-53	10.9	-	-	-
C2 Sud	100 C2 (upper)	-	8.7	-50	-	155	4.9	-13.2 -93
C2 Sud	100 C2 (lower)	-	7.7	-65	-	155	3.9	-14.2 -117

Notes: Formation temperatures ($^{\circ}\text{C}$) and fluid $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values (‰) are reported for monomineralic separates and extrapolated end-members; "upper" and "lower" denote the upper and lower limits in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values for end-member minerals extrapolated from bimodal mixtures; hyphens are used to indicate where a value is not needed or where assigning a value is inappropriate. Abbreviations: Dkt = dickite, ill = illite, Kln = kaolinite, Mg-Ft = magnesiofioite, n.a. = not analyzed, Sud = sudoite.

values of 4.7 and 4.9 ‰ and $\delta^2\text{H}_{\text{fluid}}$ values of -56 and -54 ‰ (Fig. 13; Table 6), which are within the range of fluid values calculated for pre-ore clay alteration minerals in the basin.

Two populations of pre-ore magnesiofioite are distinguished on the basis of their oxygen and hydrogen isotope composition. Magnesiofioite occurring within the interstices of MFd sandstones has $\delta^{18}\text{O}_{\text{mineral}}$ values between 11.8 and 14.0 ‰ and $\delta^2\text{H}_{\text{mineral}}$ values between -66 and -57 ‰ (Table 6), whereas magnesiofioite occurring in veins and fractures of MFa sandstones has $\delta^{18}\text{O}_{\text{mineral}}$ and $\delta^2\text{H}_{\text{mineral}}$ values of 7.3 to 9.3 ‰ and -90 to -80 ‰ , respectively (Table 6). Assuming a formation temperature of 200 $^{\circ}\text{C}$ for magnesiofioite yields a fluid in equilibrium with interstitial magnesiofioite with $\delta^{18}\text{O}_{\text{fluid}}$ values between 5.7 and 7.8 ‰ and $\delta^2\text{H}_{\text{fluid}}$ values between -43 and -34 ‰ , and a fluid in equilibrium with vein- and fracture-filling magnesiofioite with $\delta^{18}\text{O}_{\text{fluid}}$ values between 1.1 and 3.1 ‰ and $\delta^2\text{H}_{\text{fluid}}$ between -67 and -57 ‰ (Fig. 13; Table 6). Thus, the latter equilibrated with a more ^{18}O and ^2H depleted fluid, in agreement with its occurrence in fractures (high water-rock ratios) and spatial relationship with post-ore kaolinite, suggesting later interaction with ^2H -depleted meteoric waters following crystallization.

The fluid forming the pre-ore alteration assemblage of dickite, C1 Mg-rich sudoite, illite, illite-chlorite mixed-layer clay, and magnesiofioite in the sandstones and pre-ore illite in the basement has $\delta^{18}\text{O}_{\text{fluid}}$ values between 1.1 and 8.9 ‰ and $\delta^2\text{H}_{\text{fluid}}$ between -70 and -34 ‰ . These isotopic values are within the range of values for basinal fluids producing similar alteration minerals in other Athabasca basin unconformity-related uranium deposits (Fig. 13). $\delta^2\text{H}_{\text{fluid}}$ values for these alteration minerals are typically greater than -70 ‰ , indicating minimal ^2H depletion caused by interaction with relatively recent meteoric waters.

Pre-ore C2 Mg-Fe-rich sudoite occurs as mixtures with pre-ore illite near the faulted unconformity and has $\delta^{18}\text{O}_{\text{mineral}}$ values from 7.7 to 8.7 ‰ and $\delta^2\text{H}_{\text{mineral}}$ values from -65 to -50 ‰ (Table 6). Assuming a formation temperature of 155 $^{\circ}\text{C}$, calculated based on Al^{IV} occupancy (Table 2), the fluid in equilibrium with this chlorite has $\delta^{18}\text{O}_{\text{fluid}}$ values ranging from 3.9 to 4.9 ‰ and $\delta^2\text{H}_{\text{fluid}}$ from -40 to -25 ‰ (Fig. 13; Table 6). Thus, the fluid that precipitated C2 sudoite has oxygen isotope compositions similar to the other pre-ore alteration minerals, but slightly higher $\delta^2\text{H}_{\text{fluid}}$ values. Pre-ore Mg-rich sudoite (C2^{bsmt}) from the proximal basement alteration halo has $\delta^{18}\text{O}_{\text{mineral}}$ values of 7.8 to 11.0 ‰ and $\delta^2\text{H}_{\text{mineral}}$ values of -66 to -56 ‰ (Table 6). Assuming a formation temperature of 170 $^{\circ}\text{C}$ for C2^{bsmt} sudoite, calculated based on Al^{IV} occupancy (Table 2), the fluid composition has $\delta^{18}\text{O}_{\text{fluid}}$ values between 4.5 and 7.8 ‰ and $\delta^2\text{H}_{\text{fluid}}$ values between -62 and -52 ‰ , which is similar to basement illite (Fig. 13; Table 6). The fluid precipitating late pre-ore sudoite alteration (C2, C2^{bsmt}) near the fault zone has $\delta^{18}\text{O}_{\text{fluid}}$ values between 3.9 and 7.8 ‰ and $\delta^2\text{H}_{\text{fluid}}$ values between -62 and -25 ‰ , which are isotopically indistinct from basinal fluids forming earlier pre-ore alteration minerals in the overlying sandstones.

Post-ore fluids

Post-ore kaolinite typically has high $\delta^{18}\text{O}$ (= 12.0–14.5 ‰) and low $\delta^2\text{H}$ (= -155 to -128 ‰) values, which cluster around the 10 $^{\circ}\text{C}$ kaolinite-meteoric water equilibration lines (Table 6;

Sheppard and Gilg, 1996). Using this formation temperature yields calculated $\delta^{18}\text{O}_{\text{fluid}}$ values from -15.7 to -13.2‰ and $\delta^2\text{H}_{\text{fluid}}$ values from -120 to -93‰ (Fig. 13; Table 6). Thus, the fluid in equilibrium with post-ore kaolinite is isotopically distinct from those forming pre-ore kaolinite and dickite and is consistent with recent meteoric fluids proposed by Kotzer and Kyser (1995).

Mobile Element Geochemistry

The Pb isotope ratios and select element concentrations of the weakly bound and absorbed components in drill cores from McArthur River Zone 4 were evaluated using a 2% HNO_3 acid leach technique (Table 7; digital Appendix A1). Mobile Pb isotopes have been used for vectoring toward uranium mineralization in other deposits of the Athabasca basin (e.g., Cigar Lake and McArthur River, Holk et al., 2003; Centennial, Alexandre et al., 2012). Samples can be divided into three populations on the basis of the $^{207}\text{Pb}/^{206}\text{Pb}$ ratios of leachable Pb. Samples are nonradiogenic if the $^{207}\text{Pb}/^{206}\text{Pb}$ ratios are greater than 0.80 (common Pb), weakly radiogenic if $^{207}\text{Pb}/^{206}\text{Pb}$ ratios are between 0.70 and 0.80, and radiogenic if the $^{207}\text{Pb}/^{206}\text{Pb}$ ratios are less than 0.70. Leachable element concentrations of U, Pb, Cu, Zn, Ni, Co, As, V, and Mn are measured, as they represent pathfinder elements for unconformity-related uranium deposits (e.g., Ruzicka, 1989). LREEs (e.g., Ce, Y) may indicate transport of elements from basement rocks (e.g., Gaboreau et al., 2007), trace elements (e.g., Th, P, Zr) are used for assessing detrital contributions of U and radiogenic Pb, and major elements (e.g., Al, Fe, Mg, Ca) reflect alteration and host-rock mineralogy. In the earlier study by Holk et al. (2003), only two drill holes from McArthur River were studied, both from Zone 4, with only Pb isotopes and U, Th, and Pb concentrations measured.

This study differs by its greater number of drill holes and drill cores sampled and additional elements analyzed. The close proximity of the drill holes in this study also enabled detailed mapping of the spatial distribution of mobile elements and Pb isotopes around Zone 4, which was previously untested.

The majority of sandstones and fractured sandstones from the Manitou Falls Formation at Zone 4 have nonradiogenic $^{207}\text{Pb}/^{206}\text{Pb}$ ratios (>0.80) and U concentrations typically between 50 and 2,500 ppb (Fig. 14). For the remaining sandstones and basement rocks, increasingly radiogenic Pb isotope ratios are generally correlated with increasing U concentrations (Fig. 14). This trend reflects variable mixing between a U-poor common Pb signature and a U-rich, highly radiogenic Pb signature ($^{207}\text{Pb}/^{206}\text{Pb} < 0.1$). Most of this U and radiogenic Pb likely originated from Zone 4, as it is the orebody closest to these samples (Fig. 2a). However, it is also possible there were contributions from the other McArthur River ore zones since the entire system was linked by the P2 fault, which would have facilitated transport of elements by post-ore fluids between ore zones.

Radiogenic Pb ($^{207}\text{Pb}/^{206}\text{Pb} < 0.70$) delineates a halo surrounding the Zone 4 orebody that extends up to 75 m above the hanging-wall unconformity and 75 m below the footwall unconformity (Fig. 2c). Sandstones with weakly radiogenic and radiogenic Pb occur only sporadically above the silicified zone (Fig. 2c), with some corresponding to fracture samples (Fig. 14; Table 7). Concentrations of Zr among these anomalous sandstones are typically low, suggesting that radiogenic Pb produced from in situ decay of U in detrital zircons had limited contributions to their Pb isotope ratio. Th and P detected in the Manitou Falls Formation are not derived from detrital monazite or apatite, two alternative sources of radiogenic Pb, as these are not observed in thin section. Rather, the

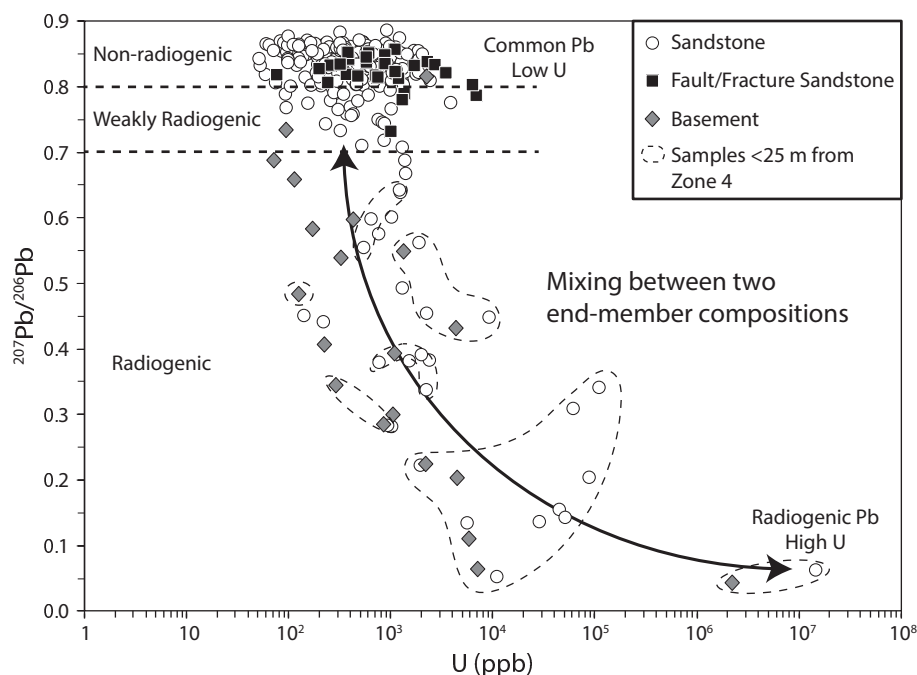


FIG. 14. Relationship between $^{207}\text{Pb}/^{206}\text{Pb}$ ratio and U concentration in leachable phases of McArthur River Zone 4 drill cores. There are two end-member compositions, one with lower U concentration and common Pb isotope ratios ($^{207}\text{Pb}/^{206}\text{Pb} > 0.80$) and another with higher U concentrations and highly radiogenic Pb isotope ratios ($^{207}\text{Pb}/^{206}\text{Pb} < 0.1$).

TABLE 7. Pb Isotope Ratios and Element Concentrations of Leachates

Sample no. DDH-depth (m)	Lith.	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁶ Pb	²³⁸ U/ ²⁰⁶ Pb	U (ppb)	Pb (ppb)	Cu (ppb)	Zn (ppb)	Th (ppb)	Ni (ppb)
MAC233-23	MFd	18.57	16	0.861	4.2	140	120	520	200	<QL	<QL
MAC233-44	MFd	19.29	15.5	0.803	1.5	200	480	1,020	370	<QL	<QL
MAC233-59	MFd	17.84	15.6	0.872	0.9	150	610	1,380	350	<QL	<QL
MAC233-75	MFd	21.23	15.9	0.751	9.2	740	290	1,250	610	70	<QL
MAC233-93	MFd	18.3	15.7	0.856	7.4	1,650	750	2,310	670	<QL	<QL
MAC233-110	MFd	18.59	15.6	0.841	8.6	370	160	1,910	490	100	<QL
MAC233-129	MFd	18.6	15.5	0.834	5.8	360	230	1,540	400	60	60
MAC233-147	MFd	18.39	15.5	0.845	20.8	570	100	1,270	360	<QL	<QL
MAC233-162	MFd	18.92	15.7	0.828	4.9	400	300	3,080	740	170	<QL
MAC233-179	FF	19.04	15.6	0.817	11.9	470	180	1,020	380	<QL	<QL
MAC233-194	MFd	19.86	16.1	0.81	25.4	1,270	220	1,580	580	50	<QL
MAC233-212	MFc	22.76	16.4	0.719	19.3	840	160	1,040	610	210	<QL
MAC233-229	MFc	19.48	15.6	0.803	9.6	530	200	2,110	540	60	<QL
MAC233-247	MFc	19.59	15.7	0.802	24.3	760	110	660	260	<QL	<QL
MAC233-258	MFc	18.57	15.4	0.83	5.1	240	170	1,420	730	70	<QL
MAC233-273	MFb	19.46	15.5	0.796	22.3	970	150	1,090	340	<QL	<QL
MAC233-287	MFb	19.32	15.9	0.821	13.4	400	110	1,000	620	<QL	<QL
MAC233-300	MFb	18.84	15.9	0.846	66.8	970	50	2,220	300	190	<QL
MAC233-315	MFb	18.85	15.8	0.837	32.9	900	120	1,290	450	60	<QL
MAC233-331	FF	18.63	15.6	0.839	51.5	2,230	210	2,010	340	<QL	70
MAC233-339	MFb	18.24	15.5	0.851	7.1	660	340	920	470	<QL	<QL
MAC233-357	MFb	20.23	16.3	0.807	4.8	200	160	1,200	440	160	<QL
MAC233-379	MFb	19.28	15.8	0.821	5.5	300	200	1,630	690	360	<QL
MAC233-395	MFb	18.56	15.7	0.844	1.7	100	220	1,330	360	<QL	<QL
MAC233-408	MFb	19.12	15.7	0.822	1.8	180	390	810	790	110	<QL
MAC233-422	MFa	19.8	15.9	0.79	2.2	90	140	1,390	530	100	<QL
MAC233-442	MFa	19.8	15.3	0.76	5.7	360	210	1,060	710	110	<QL
MAC233-473	MFa	24.94	16.1	0.64	13.5	1,220	290	1,470	610	<QL	<QL
MAC233-500	FAN	37.94	17.5	0.455	4.8	2,200	1,560	1,240	680	1,260	<QL
MAC233-509	FAN	51.07	17.7	0.339	3.9	2,180	1,890	2,920	2,170	170	6,800
MAC233-516	PEGM	64.43	18.4	0.283	2.2	1,000	1,530	1,530	950	230	1,090
MAC233-541	MFa	77.84	17.7	0.224	3.8	1,910	1,520	4,730	470	130	<QL
MAC233-550	FAN	89.32	18.5	0.205	45.3	86,100	8,080	337,000	1,420	550	1,490
MAC233-557	FAN	7057.1	457.2	0.064	198.9	14,300,000	280,000	15,500	330	15,800	1,240
MAC233-573	FAN	46.81	18.1	0.383	26.5	1,490	340	1,450	500	11,160	170
MAC233-580	SMPL	30.5	16.7	0.54	4.0	320	200	720	350	170	70
MAC233-593	FQZT	23.21	16.2	0.689	0.8	70	310	980	400	160	<QL
MAC233-612	CALC	26.07	15.5	0.584	3.4	170	160	1,040	400	1,400	180
MAC238-67	MFd	27.69	16.0	0.577	6.8	750	230	3,400	370	<QL	<QL
MAC238-95	MFd	19.77	15.6	0.788	3.1	590	580	3,160	580	<QL	<QL
MAC238-110	MFd	22.9	16.2	0.709	7.9	1,270	500	2,420	890	80	<QL
MAC238-126	MFd	20.24	15.6	0.77	3.2	390	370	1,420	520	<QL	<QL
MAC238-152	MFd	18.87	15.5	0.823	10.1	1,350	490	3,640	610	70	<QL
MAC238-182	MFd	21.2	15.8	0.747	8.7	810	240	1,940	440	110	<QL
MAC238-199	MFc	19.53	15.7	0.804	10.2	1,300	320	1,730	400	130	<QL
MAC238-240	MFc	19.23	15.6	0.81	11.1	1,000	240	2,920	520	<QL	<QL
MAC238-261	MFc	18.85	15.7	0.835	9.1	220	90	1,320	370	<QL	<QL
MAC238-287	MFb	18.76	15.8	0.845	4.5	470	340	1,310	360	<QL	<QL
MAC238-297	FF	18.56	15.1	0.816	41.0	730	<QL	2,460	170	<QL	<QL
MAC238-311	MFb	18.55	15.1	0.812	7.7	410	170	1,180	620	<QL	<QL
MAC238-339	MFb	18.57	15.5	0.834	2.7	210	270	810	320	<QL	<QL
MAC238-365	MFb	18.44	15.6	0.846	2.1	190	320	1,540	390	60	<QL
MAC238-390	MFb	18.65	15.5	0.834	1.3	120	300	1,490	400	80	<QL
MAC238-421	MFa	21.3	15.9	0.744	2.7	230	250	1,340	370	<QL	<QL
MAC238-465	MFa	18.5	15.8	0.841	2.2	240	360	1,190	400	70	<QL
MAC238-497	MFa	57.53	18.0	0.31	68.4	60,000	3,660	2,730	1,760	990	520
MAC238-505	FAN	51.22	17.7	0.342	385.9	107,500	1,120	6,100	8,800	5,110	1,610
MAC238-523	PELT	131	18.2	0.137	39.5	28,000	2,900	166,000	1,120	540	4,100
MAC238-604	QARK	24.11	16.0	0.66	1.2	110	320	680	430	260	87
MAC240-44	MFd	17.86	15.6	0.858	1.1	210	620	2,460	500	<QL	<QL
MAC240-51	FF	18.26	15.8	0.852	2.9	600	660	1,910	350	<QL	<QL
MAC240-83	MFd	18.16	15.9	0.869	1.2	520	1,480	4,250	1,170	90	<QL
MAC240-111	MFd	18.14	15.8	0.856	2.3	480	690	3,040	750	60	<QL
MAC240-121	FF	19.18	15.6	0.804	264.9	6,190	90	2,210	390	<QL	120
MAC240-125	MFd	17.98	15.8	0.868	1.2	330	930	3,590	880	<QL	<QL
MAC240-173	MFd	17.82	15.7	0.864	2.2	570	850	4,310	940	320	<QL
MAC240-197	MFc	18.25	15.7	0.845	3.6	850	750	3,000	710	<QL	<QL
MAC240-220	MFc	17.9	15.5	0.86	4.2	890	660	2,190	510	<QL	<QL

from Drill Core Samples for Select Drill Holes at McArthur River Zone 4

Sample no. DDH-depth (m)	Co (ppb)	Fe (ppb)	Mg (ppb)	V (ppb)	Mn (ppb)	As (ppb)	Ce (ppb)	Y (ppb)	Ca (ppb)	Al (ppb)	P (ppb)	Zr (ppb)
MAC233-23	<QL	700	1,600	<QL	<QL	<QL	<QL	<QL	3,220	3,800	<QL	<QL
MAC233-44	<QL	1,700	1,140	<QL	60	<QL	<QL	<QL	3,100	2,900	<QL	<QL
MAC233-59	<QL	3,400	4,000	50	210	<QL	<QL	<QL	6,400	6,100	<QL	<QL
MAC233-75	<QL	2,700	1,900	60	130	<QL	60	60	4,800	3,500	<QL	60
MAC233-93	<QL	4,800	19,700	290	210	<QL	<QL	110	21,200	10,700	<QL	<QL
MAC233-110	<QL	2,500	3,000	<QL	100	<QL	80	70	4,200	3,200	<QL	<QL
MAC233-129	<QL	4,300	9,200	<QL	70	<QL	50	120	11,800	7,300	8,000	<QL
MAC233-147	<QL	2,010	18,300	<QL	190	<QL	<QL	110	18,600	8,700	<QL	<QL
MAC233-162	<QL	3,000	5,200	<QL	<QL	<QL	<QL	60	6,300	4,700	<QL	<QL
MAC233-179	100	5,900	18,200	120	2,940	<QL	<QL	80	22,200	17,700	<QL	<QL
MAC233-194	<QL	4,460	6,800	460	750	<QL	<QL	110	7,900	7,600	<QL	<QL
MAC233-212	<QL	3,400	8,900	220	730	<QL	90	130	9,000	10,200	<QL	70
MAC233-229	<QL	3,800	3,600	190	850	<QL	60	70	4,300	4,400	<QL	<QL
MAC233-247	<QL	2,000	9,500	300	160	<QL	<QL	110	9,600	5,400	<QL	<QL
MAC233-258	<QL	1,600	9,100	<QL	70	<QL	<QL	60	9,000	6,000	<QL	<QL
MAC233-273	<QL	2,600	11,600	240	230	<QL	<QL	110	12,100	5,000	<QL	<QL
MAC233-287	<QL	6,900	14,600	<QL	220	<QL	<QL	<QL	14,800	6,900	<QL	250
MAC233-300	<QL	3,900	20,900	80	110	<QL	<QL	90	18,800	6,700	<QL	80
MAC233-315	<QL	4,300	15,500	100	890	<QL	<QL	120	14,000	8,800	<QL	<QL
MAC233-331	110	7,000	22,300	460	19,100	<QL	<QL	190	22,000	13,000	1,500	110
MAC233-339	<QL	13,000	30,900	<QL	370	<QL	<QL	<QL	27,300	13,000	<QL	<QL
MAC233-357	<QL	15,300	11,700	60	670	<QL	70	<QL	16,100	15,500	<QL	70
MAC233-379	<QL	14,600	4,800	110	900	<QL	80	50	6,500	5,900	<QL	60
MAC233-395	<QL	5,000	3,700	<QL	190	<QL	60	<QL	4,800	2,800	<QL	<QL
MAC233-408	<QL	8,900	4,100	<QL	200	<QL	90	<QL	5,600	12,700	<QL	90
MAC233-422	<QL	11,100	5,160	<QL	300	<QL	100	<QL	6,800	6,990	<QL	60
MAC233-442	<QL	4,000	3,030	<QL	420	<QL	130	50	4,800	18,100	<QL	80
MAC233-473	<QL	3,900	3,820	60	210	<QL	<QL	70	5,800	5,700	<QL	50
MAC233-500	<QL	7,500	6,000	90	540	<QL	180	420	10,300	7,700	<QL	70
MAC233-509	3,410	36,000	64,000	1,620	3,470	400	70	110	96,000	40,100	<QL	50
MAC233-516	1,970	229,000	166,000	90	13,500	200	560	1,050	320,000	155,000	133,000	<QL
MAC233-541	<QL	7,470	8,000	110	300	<QL	<QL	50	8,200	7,700	<QL	130
MAC233-550	2,140	49,000	26,800	1,510	2,440	190	100	810	29,300	46,500	3,100	410
MAC233-557	1,450	990,000	199,000	111,000	32,900	3,000	126,000	41,500	619,000	327,000	33,300	1,900
MAC233-573	100	1,480,000	96,000	4,140	11,000	60	1,220	280	120,000	99,000	44,000	90
MAC233-580	<QL	227,000	72,000	70	360	<QL	840	90	86,000	101,000	6,100	70
MAC233-593	<QL	37,000	30,000	<QL	180	<QL	350	<QL	46,300	30,800	4,900	200
MAC233-612	150	770,000	920,000	1,796	21,400	<QL	3,020	1,160	555,000	387,000	97,000	<QL
MAC238-67	<QL	5,600	<QL	<QL	150	<QL	<QL	<QL	3,200	<QL	1,020	130
MAC238-95	<QL	3,600	2,700	<QL	270	<QL	60	<QL	4,500	<QL	1,230	50
MAC238-110	<QL	4,700	5,700	370	680	<QL	50	140	8,800	9,500	1,560	<QL
MAC238-126	<QL	5,100	6,300	<QL	5,300	<QL	<QL	110	9,100	7,800	1,260	50
MAC238-152	<QL	6,500	7,700	<QL	660	<QL	70	140	8,100	17,700	1,500	250
MAC238-182	<QL	2,600	<QL	<QL	180	<QL	60	70	2,900	<QL	1,310	170
MAC238-199	<QL	4,000	5,100	<QL	350	<QL	50	90	6,800	7,800	1,370	140
MAC238-240	<QL	3,900	5,300	220	160	<QL	<QL	110	7,000	9,400	1,320	<QL
MAC238-261	<QL	16,600	9,300	<QL	270	<QL	<QL	140	10,100	22,000	9,300	<QL
MAC238-287	<QL	2,600	6,500	<QL	140	<QL	<QL	<QL	7,400	8,500	1,080	<QL
MAC238-297	<QL	4,300	15,600	200	10,700	<QL	<QL	120	16,300	15,800	1,650	<QL
MAC238-311	<QL	2,100	10,900	<QL	160	<QL	<QL	70	11,700	8,300	1,500	60
MAC238-339	<QL	2,041	9,900	<QL	110	<QL	<QL	<QL	10,800	9,100	2,180	<QL
MAC238-365	<QL	6,298	<QL	<QL	220	<QL	60	<QL	2,900	<QL	1,190	<QL
MAC238-390	<QL	5,711	3,600	<QL	700	<QL	<QL	<QL	3,900	7,200	770	<QL
MAC238-421	<QL	4,900	3,900	<QL	360	<QL	60	<QL	4,700	8,000	1,170	<QL
MAC238-465	<QL	2,200	2,500	<QL	110	<QL	70	<QL	4,100	<QL	<QL	60
MAC238-497	380	85,000	10,100	1,020	570	2,600	70	2,970	4,900	17,500	3,100	1,630
MAC238-505	1,080	135,000	27,500	1,700	2,080	490	230	1,180	15,200	53,100	<QL	1,120
MAC238-523	13,800	987,000	212,000	210	6,400	7,300	2,500	1,860	344,000	378,000	173,000	80
MAC238-604	<QL	63,000	89,600	80	380	<QL	1,080	150	109,000	77,700	10,000	80
MAC240-44	<QL	3,600	1,700	110	120	<QL	<QL	<QL	2,400	<QL	<QL	<QL
MAC240-51	<QL	16,000	12,100	550	440	<QL	<QL	120	16,600	14,000	<QL	<QL
MAC240-83	<QL	3,700	1,200	<QL	310	<QL	80	60	2,300	<QL	<QL	50
MAC240-111	<QL	1,500	1,400	<QL	270	<QL	70	<QL	2,300	<QL	<QL	60
MAC240-121	270	25,000	49,700	2,130	68,000	<QL	<QL	830	55,900	19,900	<QL	<QL
MAC240-125	<QL	1,900	8,700	<QL	<QL	<QL	<QL	80	9,400	8,000	<QL	<QL
MAC240-173	<QL	2,500	2,100	<QL	120	<QL	120	<QL	3,000	<QL	<QL	110
MAC240-197	<QL	3,100	7,500	90	620	<QL	<QL	<QL	7,100	6,600	<QL	140
MAC240-220	<QL	4,600	8,400	190	1,170	<QL	<QL	80	9,100	7,700	5,800	60

TABLE 7.

Sample no. DDH-depth (m)	Lith.	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁶ Pb	²³⁸ U/ ²⁰⁶ Pb	U (ppb)	Pb (ppb)	Cu (ppb)	Zn (ppb)	Th (ppb)	Ni (ppb)
MAC240-240	MFc	17.74	15.7	0.872	2.1	480	750	3,770	500	60	<QL
MAC240-267	MFc	18.68	15.8	0.833	13.1	1,530	340	2,280	420	<QL	<QL
MAC240-302	MFb	18.34	15.8	0.848	3.2	440	450	2,530	650	<QL	<QL
MAC240-344	MFb	17.79	15.6	0.863	4.2	960	710	3,300	560	<QL	<QL
MAC240-371	MFb	17.94	15.8	0.868	1.2	310	870	2,380	570	520	<QL
MAC240-401	MFb	17.99	15.7	0.865	0.4	110	920	2,890	690	60	<QL
MAC240-424	MFa	18.27	15.8	0.857	1.4	330	750	2,250	540	<QL	<QL
MAC240-447	MFa	18.39	15.7	0.845	3.0	560	600	2,050	490	150	<QL
MAC240-473	MFa	20.19	15.7	0.777	14.2	3,780	1,170	4,560	810	100	100
MAC240-502	MFa	122.19	19.1	0.156	39.0	43,900	760	47,500	2,290	350	3,800
MAC240-521	MFa	46.95	17.9	0.381	0.1	750	10,800	2,170	340	<QL	<QL
MAC240-560	FAN	20.31	15.8	0.776	0.6	150	850	2,990	630	380	170
MAC252-14	MFd	17.78	15.6	0.879	0.6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
MAC252-24	FF	19.29	15.8	0.819	0.2	80	1,380	280	970	<QL	<QL
MAC252-41	MFd	18.24	15.8	0.865	0.8	60	320	1,240	440	<QL	<QL
MAC252-67	MFd	17.76	15.5	0.871	1.0	80	310	1,360	530	<QL	<QL
MAC252-90	MFd	17.77	15.4	0.869	0.2	<QL	340	1,360	500	<QL	<QL
MAC252-110	MFd	18.09	15.6	0.861	0.5	<QL	300	1,210	490	<QL	70
MAC252-114	FF	18.65	15.6	0.839	16.0	570	120	450	770	<QL	<QL
MAC252-132	MFd	17.85	15.5	0.868	0.6	<QL	280	1,450	810	<QL	<QL
MAC252-155	MFd	17.84	15.5	0.869	0.9	100	400	1,230	500	<QL	<QL
MAC252-172	MFd	18.11	15.4	0.852	1.9	230	410	2,020	640	<QL	<QL
MAC252-194	MFd	18.67	15.9	0.851	1.7	<QL	110	2,000	310	<QL	<QL
MAC252-210	FF	18.68	15.6	0.836	4.8	310	230	680	690	<QL	<QL
MAC252-215	MFc	18.97	15.4	0.81	1.3	<QL	120	920	370	<QL	<QL
MAC252-245	MFc	18.09	15.5	0.856	1.7	70	160	1,020	440	<QL	<QL
MAC252-260	MFc	17.74	15.4	0.867	2.4	180	270	2,020	580	<QL	<QL
MAC252-275	MFc	18.11	15.4	0.848	3.1	130	150	910	710	<QL	<QL
MAC252-294	MFc	18.04	15.5	0.858	0.3	<QL	190	1,360	380	<QL	<QL
MAC252-315	MFc	18.43	15.4	0.834	0.6	50	330	2,030	710	<QL	<QL
MAC252-335	MFc	18.8	15.7	0.835	0.1	<QL	400	2,040	780	<QL	<QL

Note: Bold indicates upper silicified zone; italic indicates lower silicified zone

ARKS = arkose, CALC = calc-silicate, FAN = fanglomerate, FQZT = feldspathic quartzite, Lith. = lithology, MF = Manitou Falls, n.a. = not analyzed, PEGM = pegmatite, PELT = pelite, QARK = quartz-rich arkose, <QL = below quantitation limit, SMPL = semipelite

source of Th and P in the Manitou Falls Formation is likely from pre-ore APS minerals, which were partially dissolved by the 2% HNO₃ acid leach, but these do not contain significant U (Table 1). Some samples with weakly radiogenic and radiogenic Pb isotope ratios also contain elevated ²³⁸U/²⁰⁶Pb ratios, suggesting post-ore addition of U by fluids mobilizing components from the McArthur River ore system (Table 7).

Samples from the nonmineralized drill hole, MAC-252, located 300 m northwest of Zone 4, are considered to represent the background signature for the Manitou Falls Formation in the McArthur River area (Fig. 2a). Sandstones in this drill hole are nonradiogenic and have uniform leachable ²⁰⁷Pb/²⁰⁶Pb ratios of 0.81 to 0.87 (Fig. 15). Samples from two mineralized drill holes (MAC-238, MAC-233) and from a drill hole located 10 m from the ore zone (MAC-240) have common Pb values down to 450-m depth. Below this depth, samples become increasingly radiogenic toward the orebody, with ²⁰⁷Pb/²⁰⁶Pb ratios ranging between 0.04 and 0.84 (Fig. 15). This depth of 450 m coincides with the transition from the upper to lower silicified zone. Samples from the hanging-wall basement and basal fanglomerate overlying the unconformity are the most radiogenic but become progressively less radiogenic with increasing depth below the unconformity (Fig. 15). The hanging-wall block has radiogenic Pb signatures due to its close proximity to the zone of massive mineralization, whereas

the basal fanglomerates are radiogenic because they represent permeable pathways for post-ore fluids redistributing mobile elements from the McArthur River ore zones.

Basin and basement samples near the Zone 4 orebody have elevated leachable concentrations of uranium pathfinder elements, including U, Pb, Cu, and Zn (Fig. 15; Table 7), which are metals typically associated with sandstone-hosted uranium deposits (Ruzicka, 1989). The concentrations of these elements in the sandstones and fanglomerates in the lower silicified zone are much greater than background concentrations recorded in drill hole MAC-252 (Fig. 15). Concentrations of leachable Y, Mn, Ni, Co, As, and V, likewise, are elevated in samples near mineralization, but are typically below detection limit in sandstone samples (Table 7). As with ²⁰⁷Pb/²⁰⁶Pb ratios, the concentrations of uranium pathfinder elements in mineralized drill holes tend to be uniform to a depth of 450 m, but increase at the more permeable lower silicified zone (Fig. 15). As such, the geochemical signature of the uranium mineralization, represented by the dispersion of mobile pathfinder elements in the leachable phase, is subdued above the upper silicified zone. However, elevated concentrations of leachable Mn, Co, Zn, and U are recorded in some clay-rich fractures in sandstones, indicating a limited number of fractures were conduits for metals to ascend above the silicified zone (Fig. 15; Table 7).

(Cont.)

Sample no. DDH-depth (m)	Co (ppb)	Fe (ppb)	Mg (ppb)	V (ppb)	Mn (ppb)	As (ppb)	Ce (ppb)	Y (ppb)	Ca (ppb)	Al (ppb)	P (ppb)	Zr (ppb)
MAC240-240	<QL	2,500	14,200	70	140	<QL	<QL	90	12,700	8,200	<QL	<QL
MAC240-267	<QL	3,800	9,400	490	320	<QL	<QL	170	9,500	6,500	<QL	<QL
MAC240-302	<QL	1,300	9,200	<QL	70	<QL	<QL	60	9,000	5,600	<QL	<QL
MAC240-344	<QL	2,000	9,900	120	100	<QL	<QL	<QL	10,100	5,900	<QL	<QL
MAC240-371	<QL	5,100	2,500	<QL	210	<QL	70	<QL	3,700	<QL	<QL	50
MAC240-401	<QL	2,000	4,300	<QL	470	<QL	60	<QL	4,900	9,500	<QL	<QL
MAC240-424	<QL	1,800	4,600	<QL	710	<QL	<QL	<QL	5,200	11,100	<QL	<QL
MAC240-447	<QL	2,700	3,000	<QL	130	<QL	60	<QL	4,500	14,900	<QL	<QL
MAC240-473	110	6,600	4,400	70	490	<QL	90	140	<QL	7,900	610	260
MAC240-502	2,890	230,000	15,200	9,100	2,070	1,300	<QL	1,750	<QL	86,000	6,400	680
MAC240-521	<QL	3,000	4,000	180	350	<QL	<QL	90	<QL	<QL	<QL	<QL
MAC240-560	190	79,000	14,900	50	2,040	<QL	50	<QL	17,900	14,900	430	100
MAC252-14	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
MAC252-24	<QL	5,100	3,700	<QL	740	<QL	<QL	<QL	1,700	11,400	340	<QL
MAC252-41	<QL	2,500	7,400	<QL	110	<QL	<QL	<QL	2,200	6,400	650	<QL
MAC252-67	<QL	4,200	14,000	<QL	8,600	<QL	<QL	<QL	3,900	7,900	340	<QL
MAC252-90	<QL	5,800	5,900	<QL	1,830	<QL	<QL	<QL	1,300	4,300	470	<QL
MAC252-110	<QL	1,600	1,600	<QL	330	<QL	<QL	<QL	600	3,400	390	<QL
MAC252-114	<QL	15,000	25,600	<QL	3,970	<QL	<QL	<QL	6,800	7,900	810	90
MAC252-132	<QL	1,900	5,400	<QL	130	<QL	<QL	<QL	1,000	6,000	620	<QL
MAC252-155	<QL	1,600	2,400	<QL	1,450	<QL	<QL	<QL	700	3,700	710	50
MAC252-172	<QL	2,500	4,700	<QL	370	<QL	50	60	1,000	7,900	480	90
MAC252-194	<QL	3,900	3,700	<QL	1,290	<QL	<QL	<QL	700	4,200	440	<QL
MAC252-210	<QL	4,100	40,400	<QL	410	<QL	<QL	<QL	8,000	23,900	1,240	130
MAC252-215	<QL	700	27,600	<QL	330	<QL	<QL	<QL	5,100	10,400	300	60
MAC252-245	<QL	1,500	3,300	<QL	130	<QL	50	<QL	800	4,600	570	<QL
MAC252-260	<QL	1,800	3,700	<QL	90	<QL	<QL	<QL	1,200	4,900	860	160
MAC252-275	<QL	4,600	10,100	<QL	2,050	<QL	<QL	<QL	2,700	6,400	790	<QL
MAC252-294	<QL	9,800	4,600	<QL	530	<QL	<QL	<QL	1,400	7,000	1,260	<QL
MAC252-315	<QL	3,500	1,200	<QL	220	<QL	70	<QL	500	3,400	550	80
MAC252-335	<QL	60,000	12,400	<QL	1,680	<QL	<QL	<QL	2,900	6,900	<QL	<QL

Basal sandstones and fanglomerates near the faulted unconformity have elevated concentrations of leachable Mg, Fe, Ca, Al, Y, Ce, Zr, P, and Th relative to overlying sandstone and more distal samples (Fig. 15; Table 7). These elements were likely acquired by basinal fluids interacting with the paleoweathered basement rocks along the unconformity. Prebasin weathering would have caused decomposition of silicate and accessory minerals in the basement rocks, creating porosity and releasing major and trace elements, which subsequently sorbed onto clays in the regolith (Boiron et al., 2010).

Discussion

The objectives of this study were to reconstruct the mineralogical and geochemical evolution of the sandstone-hosted McArthur River Zone 4 alteration system and to assess the significance of the silicified zone on its genesis and preservation. This is characterized by mineral paragenesis, alteration mineralogy, crystal chemistry and crystallinity, isotopic and chemical U-Pb geochronology, and stable isotope chemistry. Based on these data, a model for the formation of the Zone 4 deposit at McArthur River is proposed.

Four alteration stages are recognized at McArthur River Zone 4, including early pre-ore alteration, late pre-ore alteration, ore stage, and post-ore alteration (Fig. 3). Early pre-ore Q1 quartz cement, corresponding to precompaction quartz

cement recognized by Hiatt et al. (2007), silicified the lower 200 m of the Manitou Falls Formation (Figs. 4a, 16a). Based on its oxygen isotope composition, Hiatt et al. (2007) determined that the early quartz cement precipitated at relatively low temperatures of 65° to 125°C and at shallow burial depths of 1.3 to 3.2 km. A proposed source of aqueous silica for this precompaction cement was from intensive weathering of paleosol horizons within MFa (Hiatt and Kyser, 2005). Kaolinitization of detrital feldspars by meteoric water may be another possible source of silica (Siever, 1957) as coarse-grained vermiform kaolinites, possibly representing relics of detrital feldspars, are preserved within the silicified zone. Preferential silicification of the lower 200 m of the Manitou Falls Formation may be related to a combination of factors, including the following: greater porosity within MFa and MFb compared to overlying sandstones, which allows for development of dense silicification; the low stratigraphic position of MFa and MFb, which are a sink for descending silica-saturated fluids; and the presence of silica source material.

As burial depth and basinal fluid temperatures increased due to basin subsidence, compaction caused dissolution of silica, which reprecipitated as inclusion-free Q2 quartz cement (Fig. 4a; Hiatt et al., 2007). Fluid inclusion homogenization temperatures measured on compaction-related quartz cements by Kotzer and Kyser (1995) indicate that basinal fluid

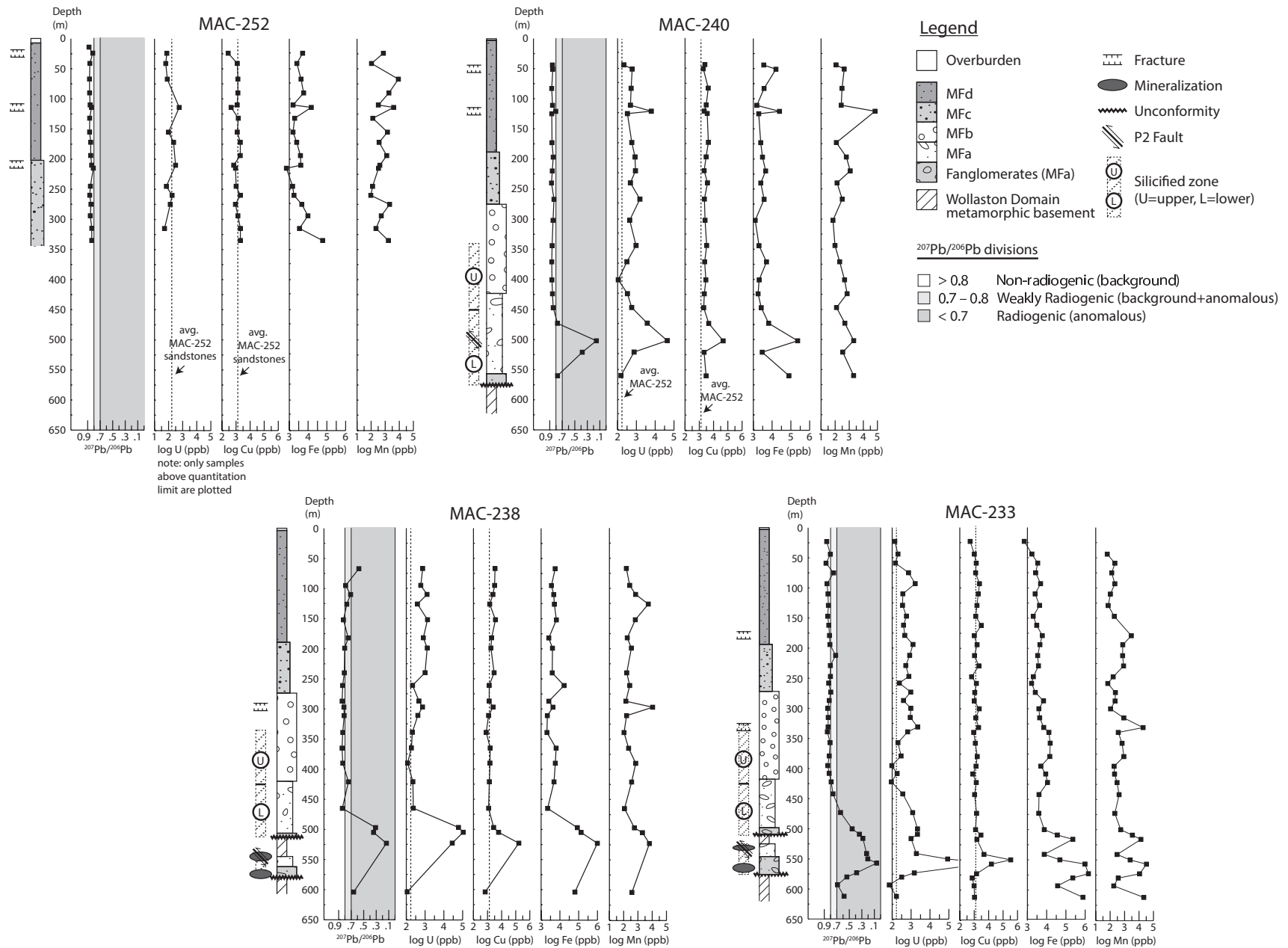


FIG. 15. Downhole plots of leachable $^{207}\text{Pb}/^{206}\text{Pb}$ ratios and select element concentrations for representative drill holes from McArthur River Zone 4. Samples are nonradiogenic ($^{207}\text{Pb}/^{206}\text{Pb} > 0.80$) and have leachable element concentrations close to the background drill hole, MAC-252, to a depth of 450 m. Below 450 m, Pb isotope ratios become increasingly radiogenic toward the orebody. U and pathfinder element (e.g., Cu, Mn) concentrations exhibit variations similar to those of Pb isotopes. Clay-rich fracture samples also show elevated Mn concentrations.

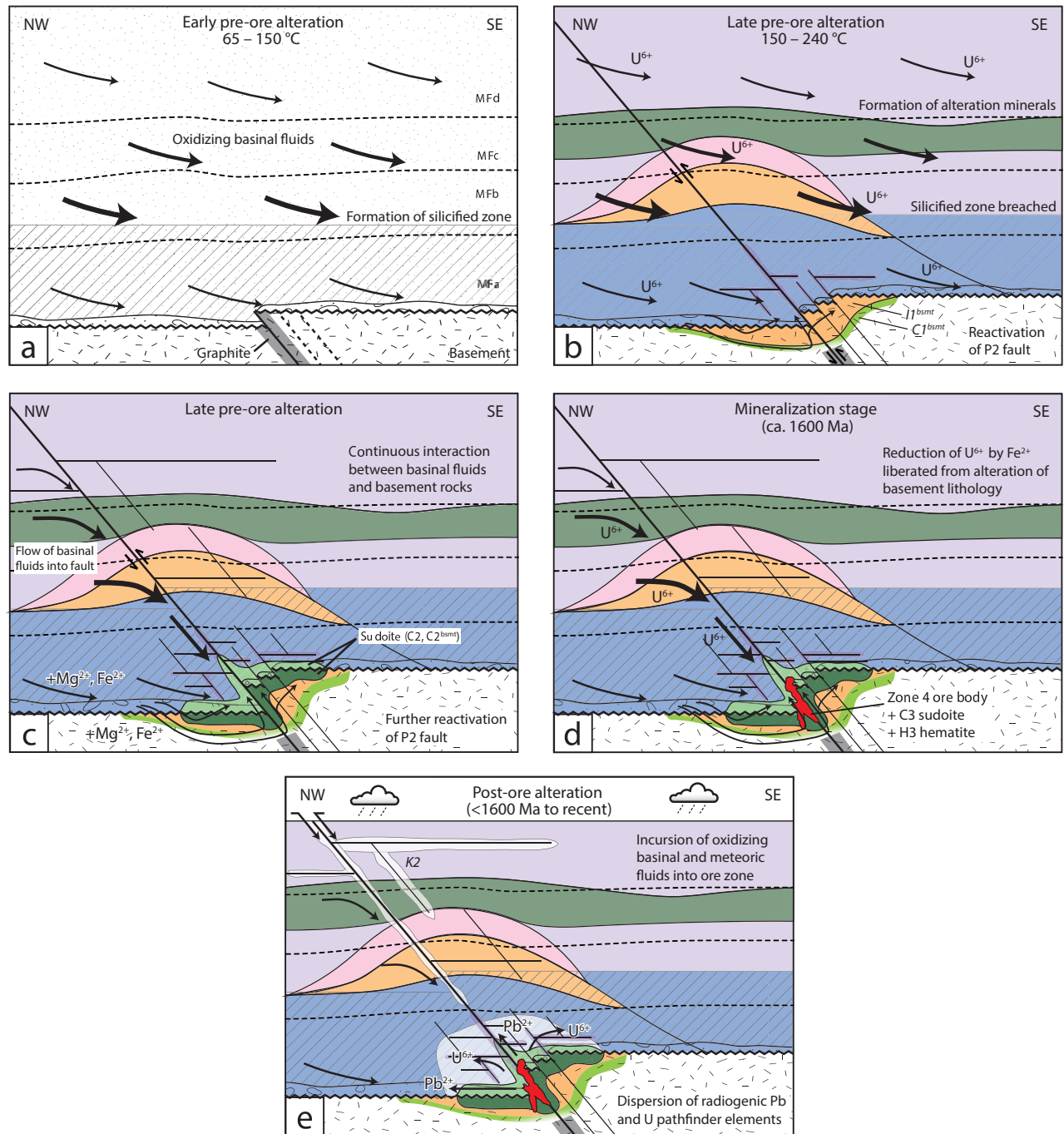


FIG. 16. Model for the evolution of the McArthur River Zone 4 orebody. Direction and thickness of arrows represent relative flow rate and direction of basal fluid flow within the Manitou Falls Formation (after Hiatt and Kyser, 2005) and basement. a. During early pre-ore alteration, oxidizing basal fluids produced early quartz cementation of the lower Manitou Falls (MFa and lower MFb), creating the silicified zone. b. During late pre-ore alteration, oxidizing basal fluids altered and leached uranium from detrital minerals and produced authigenic alteration minerals within the Manitou Falls Formation, forming zones of kaolinite/dickite, magnesiofioitite, and Mg-rich sudoite alteration, which were overprinted by a halo of illite and illite-chlorite mixed-layer clay (same color shading as Fig. 6). Circulation of basal fluids into the metasedimentary basement produced illite ($I1^{bsmt}$) and clinocllore ($C1^{bsmt}$) alteration of the basement rocks around the P2 fault. Fracturing of silicified sandstones, following reactivation of the P2 fault, resulted in euhedral quartz intergrown with magnesiofioitite above the faulted unconformity. c. Further reactivation of the P2 fault during the waning stages of late pre-ore alteration triggered additional influx of oxidizing basal fluids into the fault zone. Basal fluids interacting with basement rocks acquired Mg^{2+} and Fe^{2+} and formed a sudoite halo around the faulted unconformity. d. U-bearing basal fluids undergo a coupled redox reaction with Fe^{2+} and carbonaceous compounds liberated from alteration of basement rocks, leading to U deposition at about 1600 Ma. e. The silicified zone limited circulation of post-ore oxidizing basal and meteoric fluids, preventing significant remobilization of radiogenic Pb and U pathfinder elements from the ore zone.

temperatures reached 150° to 170°C during this time (Fig. 3). This second quartz cementation stage corresponds to diagenetic Qz1 quartz overgrowths of Derome et al. (2005), which formed from an NaCl-rich basinal brine (min. 190°C).

Varying degrees of quartz cementation compartmentalized the silicified zone into an upper, relatively impermeable region (upper MFa, lower MFb), and a lower region (lower MFa) characterized by greater porosity and fracture permeability. Although lower MFa underwent both stages of cementation, it occurred to a lesser degree, which enabled larger volumes of pore space to remain open. The greater abundance of quartz cement in upper MFa and lower MFb compared to lower MFa may be due to lithological variations related to depositional environment. Lower MFa, characterized by matrix-supported conglomerates, was deposited by debris flows associated with alluvial fans (Hiatt and Kyser, 2005). It is separated by a sequence boundary from the overlying upper MFa and lower MFb, which were deposited in a high-energy braided fluvial stream environment and characterized by grain-supported conglomerates (Hiatt and Kyser, 2005). As interstitial clay can inhibit quartz cementation (McBride, 1989), the lower abundance of interstitial mud in upper MFa and lower MFb allowed for greater silicification of this zone (Hiatt and Kyser, 2005). Additionally, the greater abundance of interstitial mud within the lower silicified zone (lower MFa) prevented significant compaction-induced cementation, which in the upper silicified zone (upper MFa, lower MFb) blocked remaining porosity. Thus, the basal ca. 100 m of the Manitou Falls Formation remained permeable to basinal fluids during subsequent alteration events.

Early pre-ore alteration basinal fluids were oxidizing, as evidenced by hematite inclusions within pre-compaction quartz overgrowths (Fig. 4a) and interstitial hematite. These oxidizing fluids would have caused dissolution of detrital monazite and pyrite in the sandstones, liberating U, P, REEs, Ca, Sr, and S, and forming early goyazite (Fig. 4b; Fayek and Kyser, 1997; Gaboreau et al., 2007). The Sr-rich nature of these APS minerals throughout the Manitou Falls Formation at Zone 4 is compatible with phosphates stable under slightly acidic, oxidizing, diagenetic basinal fluids of the Athabasca basin (Gaboreau et al., 2007). The absence of LREE-rich APS minerals detected at McArthur River Zone 4, unlike those described at Wheeler River Zone K (Cloutier et al., 2010) and near the Shea Creek (Anne deposit) and Cigar Lake deposits (Gaboreau et al., 2007), may reflect differences in hydrodynamics, with lower amounts of reducing LREE-enriched basement-derived fluids at Zone 4.

Prograde diagenesis of the Manitou Falls Formation resulted in progressively higher basinal fluid temperatures as recorded by the increasing formation temperatures of the pre-ore alteration mineral sequence. As basinal fluid temperatures climbed to about 200°C, alteration horizons consisting of dickite, kaolinite, Mg-rich sudoite, and magnesiofoitite developed (Fig. 3; Table 2). These were overprinted by a halo of illite and illite-chlorite mixed-layer clay surrounding the faulted unconformity (Figs. 6, 16b). The occurrence of magnesiofoitite within fractures intergrown with euhedral quartz suggests reactivation of the P2 fault following formation of the silicified zone (Fig. 16b). Illite alteration of the Manitou Falls Formation reflects peak diagenetic conditions

at temperatures of about 235°C (Fig. 3; Table 2). The fluid forming this late pre-ore alteration assemblage has calculated $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values consistent with the isotopic composition of basinal fluids forming similar diagenetic and hydrothermal alteration minerals at other unconformity-related uranium deposits in the Athabasca basin (Fig. 13). Detrital zircon and fluoroapatite would have been soluble in this peak diagenetic basinal fluid, which was also oxidizing ($\log f_{\text{O}_2}$ above hematite-magnetite buffer; Kister et al., 2005), saline (ca. 25 wt % NaCl, up to 14 wt % CaCl_2), and acidic (pH = 4–6; Kister et al., 2005; Fayek and Kyser, 1997), further liberating U into solution, resulting in their low concentrations in the Manitou Falls (Fayek and Kyser, 1997). As indicated by the formation temperature of illite in the sandstones, the peak diagenetic basinal brine attained temperatures residing within the “thermal leaching window” of ca. 150° to 250°C, which is favorable for efficient leaching of U from accessory minerals (Southgate et al., 2006). More recently, Richard et al. (2012) proposed that the pre-ore basinal fluid was more acidic, with pH of 2.5 to 4.5, which would further enhance the solubility of monazite and fluoroapatite (Ayers and Watson, 1991).

Basinal fluids flowing laterally along the unconformity permeated into the basement and produced illite and clinocllore alteration near the fault zone (Figs. 6, 16b). This is supported by similarities in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ fluid values, formation temperatures, and timing between basin and basement alteration minerals (Figs. 3, 13; Table 6). Basinal fluids infiltrated to at least 40 m below the footwall unconformity based on the occurrence of illite at this depth (Fig. 6). Interaction with the basement lithology enabled the basinal fluid to become chemically modified, acquiring Mg, Fe, Ca, and Al, as indicated by the occurrence of Mg-Fe-rich sudoite alteration in fanglomerates above the unconformity and in the elevated leachable concentrations of these elements in drill core (Figs. 15, 16c; Table 7).

During the waning stages of late pre-ore alteration, reactivation of the P2 fault, possibly triggered by the ca. 1.65 to 1.60 Ga Mazatzal orogeny (Karlstrom et al., 1990), caused further fracturing, which rejuvenated permeability previously sealed by quartz or clays (Lorilleux et al., 2003). This allowed circulation of oxidizing basinal fluids into the fault zone (Fig. 16c). Basinal fluids interacted with the uplifted hanging-wall basement or circulated into the P2 fault and interacted with deeper basement rocks. Interaction with the ferrous iron-, sulfide-, and graphite-bearing metamorphic basement caused the fluid to become reducing and chemically modified by alteration of ferromagnesian metamorphic minerals. This produced both Mg sudoite alteration of the basement rocks in the vicinity of the P2 fault and liberated ferrous iron, which became incorporated into the Mg-Fe-rich sudoite halo surrounding the faulted unconformity (Fig. 16c). The formation temperature of 155° to 170°C for sudoite in the alteration halo (C2 and C2^{bsmt}), which is cooler than peak diagenetic temperatures (ca. 235°–245°C), reflects the inaccuracy of the chlorite geothermometer for di-trioctahedral chlorites and does not signify cooling of the late pre-ore alteration fluids following peak diagenesis and prior to uranium mineralization (Fig. 3; Table 2). Circulation of this reducing basement-modified basinal fluid into the overlying sandstones would have caused quartz dissolution, increasing permeability along

fractures (Lorilleux et al., 2002, 2003), and also the porosity of silicified sandstones proximal to the faulted unconformity.

The basement-modified basinal fluid that produced late sudoite alteration (C2, C2^{bsmt}) has calculated $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values indistinct from fluids producing paragenetically earlier basin and basement alteration minerals (Fig. 13; Table 6). This suggests that the fluid evolution at McArthur River involved a single basinal fluid that became chemically but not isotopically modified by fluid-rock interaction with the Wollaston Group basement. Thus, the pre-ore evolution at McArthur River Zone 4 has a closer affinity to genetic models for basement-hosted deposits (Fayek and Kyser, 1997; Alexandre et al., 2005) that involve basinal fluids as the primary source of the sandstone and basement alteration without contribution of a distinct reducing basement-derived fluid, an idea similarly proposed by Cloutier et al. (2009) and Mercadier et al. (2012). This differs from the model proposed for typical sandstone-hosted deposits, which invokes mixing between a distinct basinal and basement-derived fluid (Wilson and Kyser, 1987; Fayek and Kyser, 1997). At Zone 4, uranium mineralization was initiated by the mixing of oxidizing basinal fluids with reducing fluids generated by basinal fluid-basement rock interaction, as inferred from mixtures of illite and Mg-Fe-rich sudoite.

Primary uranium mineralization at Zone 4 formed massive and pseudocubic uraninite (Fig. 5a, b) at about 1601 ± 30 Ma (Fig. 11, 16d), similar to the chemical age determined for initial mineralization at the basement-hosted Millennium deposit (ca. 1590 Ma; Cloutier et al., 2009), but slightly older than the 1520 to 1540 Ma U-Pb upper intercept age determined at other McArthur River orebodies (McGill et al., 1993; Fayek et al., 2002; Alexandre et al., 2009b). Uranium, as U^{6+} , was transported by oxidizing basinal fluids and reduced by ferrous iron (Fe^{2+}) liberated by clinocllore and Mg sudoite alteration of ferromagnesian minerals in the basement (Alexandre et al., 2005). The resulting U^{4+} was incorporated into uraninite, whereas Fe^{3+} was incorporated into late pre-ore Mg-Fe sudoite, syn-ore Fe-Mg sudoite, and syn-ore hematite.

U-Pb upper intercept ages of uranium minerals at Zone 4 record two episodes of resetting that affected the Zone 4 ore minerals, following primary uranium mineralization at ca. 1600 Ma (Fig. 12). The first occurred at ca. 1270 Ma and likely coincided with the intrusion of the Mackenzie dike swarms into the Athabasca basin (1267 ± 2 Ma; LeCheminant and Heaman, 1989). The second resetting event occurred during the Neoproterozoic (ca. 800–900 Ma) and is broadly coincident with the breakup of Rodinia (ca. 860–570 Ma; Li et al., 1999, 2008). Both events triggered circulation of fluids into structures that reached the ore zone. The former caused complete isotopic resetting of the ca. 1600 Ma primary uraninite and the latter led to recrystallization as blebby-botryoidal uraninite, coffinite, and gummite. The timing of these resetting events is comparable to the two U-Pb upper intercept ages (1247 ± 19 , 971 ± 27 Ma) measured at the basement-hosted McArthur River Zone 2 deposit, which were interpreted as recrystallization ages (Alexandre et al., 2009b). The near-origin lower intercepts of discordia lines are considered to represent a recent event causing variable radiogenic Pb loss, such as the incursion of meteoric waters in response to glacial unloading (Fig. 12). At Zone 4, the initial mineralization age

(ca. 1600 Ma) and a ca. 1380 Ma alteration event are inferred using the extrapolation method of Alexandre and Kyser (2005). The age of the ca. 1380 Ma alteration event broadly coincides with the 1300 to 1350 Ma regional metamorphism, deformation, and granitic intrusion associated with the East Kootenay orogeny southwest of the Athabasca basin (McMechan and Price, 1982). Disagreement between the chemical age (Fig. 11) and the upper intercept U-Pb isotope ages (Fig. 12) is explained by the former reflecting the timing when the chemical composition of the fluid changed (Alexandre and Kyser, 2005), whereas the latter indicates the timing when the U-Pb isotope system of the mineral was reset.

Circulation of post-ore fluids through the Zone 4 orebody caused dispersion of radiogenic Pb and uranium pathfinder elements (Mo, Zn, Cu, As, Ni, Co, Pb) into the surrounding host-rock environment (Figs. 2, 16e). Loss of radiogenic Pb is supported by discordant uranium minerals (Fig. 12), substitution of Si and Ca for Pb (Fig. 11), and formation of post-ore galena (Fig. 5b). The chemistry of the leachable phase indicates that dispersion of these fluids was primarily confined to sandstones within 50 to 75 m from the orebody (Figs. 2, 15) due to the low permeability within the overlying silicified zone caused by blocking of porosity by early pre-ore quartz cements. The distribution of radiogenic Pb indicates that late fluids interacting with the orebody were confined to the more permeable basal fanglomerate and fractures (Fig. 15; Table 7). Radiogenic Pb isotope ratios and elevated $^{238}\text{U}/^{206}\text{Pb}$ ratios are measured in some fracture samples above the silicified zone. This suggests that fractures which breached the silicified zone were potential conduits that enabled U pathfinder elements to reach above this impermeable barrier following primary uranium mineralization at ca. 1600 Ma.

Incursion of relatively cool oxidized meteoric fluids into the Manitou Falls Formation via fractures precipitated post-ore, ^2H -depleted kaolinite, recrystallized earlier-formed pre-ore dickite in the lower silicified zone, and caused limonite alteration in MFc and MFd (Fig. 13). The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of this fluid are consistent with relatively recent meteoric fluids ($<50^\circ\text{C}$) forming similar late-stage fracture- and fault-controlled kaolinite in other sandstone-hosted uranium deposits of the Athabasca basin (Kotzer and Kyser, 1995). Precipitation of post-ore siderite and calcite in the ore zone supports incursion of oxidizing fluids, which could explain the minor oxidation of the uranium ore to uranophane. A near-origin lower intercept in U-Pb concordia diagram for uranium minerals suggests that the incursion of this meteoric fluid into the ore zone caused loss of radiogenic Pb (Fig. 12).

Significance of the silicified zone and implications on the evolution of the Zone 4 orebody

Petrographical evidence, clay alteration patterns, and distribution of mobile elements indicate that the early pre-ore silicified zone functioned as a physical barrier to fluids at McArthur River Zone 4. It modified the mineralogical and geochemical evolution at Zone 4 during late pre-, syn-, and post-ore alteration.

Flow of oxidizing basinal fluids within the Manitou Falls Formation was likely restricted within the relatively impermeable upper silicified zone in upper MFa and lower MFb. Basinal fluids would have been channeled laterally along

the more permeable lower silicified zone of the basal 100 m of Manitou Falls Formation. Basinal fluids above the silicified zone would have only reached the base of the Manitou Falls Formation where fractures extending from the P2 fault breached the silicified zone (Fig. 16c). Basinal fluids flowing along the unconformity provided recharge of reductants, and fluids flowing along down the P2 fault provided a focused channel for oxidizing U-bearing basinal fluids to enter into the reduction zone (Fig. 16d). Evidence that these pathways were permeable to fluids is supported by radiogenic $^{207}\text{Pb}/^{206}\text{Pb}$ ratios in drill cores within the basal fanglomerate and along the extension of the P2 fault, indicating these samples were accessed by later fluids that mobilized Pb from the orebody (Fig. 2; Table 7).

Implications for exploration

Mobile pathfinder elements, such as U, Pb, Cu, Zn, Co, and Ni, are geochemical vectors to uranium mineralization. However, the occurrence of the silicified zone above the orebody obstructed the mobility of post-ore fluids that would have interacted with the Zone 4 orebody. This limited the dispersion of radiogenic Pb and U pathfinder elements into the overlying strata, resulting in nonradiogenic $^{207}\text{Pb}/^{206}\text{Pb}$ isotope ratios (>0.80) and low concentrations of U pathfinder elements such as Mn, Pb, Cu, Zn, Ni, Co, V, As, and Ni in sandstones above and within the upper silicified zone (Figs. 2c, 15; Table 7). The geochemical signature of the orebody is only obvious below 450-m depth, where greater porosity and fracture permeability, possibly aided by quartz dissolution associated with sudoite and magnesiofoitite alteration (Lorilleux et al., 2002, 2003), enabled post-ore fluids to ascend 50 to 75 m above the orebody (McGill et al., 1993; Mwenifumbo et al., 2004). A similar constraint on the upward migration of mobile Pb isotopes is observed at the Cigar Lake uranium deposit, where radiogenic Pb isotope ratios were confined to the sandstones below the quartz-cemented cap surrounding the orebody (Cramer, 1986; Percival et al., 1993; Holk et al., 2003). Thus, silicified barriers can contribute to concealing the geochemical signatures of underlying deposits.

The mobility of Mg-Fe-bearing reducing fluids, generated by basinal fluids interacting with basement rocks, was spatially limited by the overlying silicified sandstones. Therefore, only the sandstones within 50 m above and 100 m away from the faulted unconformity had interacted with this fluid, thus restricting the size of the late pre-ore Mg-Fe sudoite alteration halo (Fig. 6). Localization of the reducing fluid enabled uranium deposition to occur within a relatively confined area, leading to high-grade mineralization. In contrast, spatially extensive chlorite alteration halos are found in the apparently barren sandstone-hosted Wheeler River Zone K (Cloutier et al., 2010) and Spring Point (Quirt, 1986; Alexandre et al., 2009a) alteration systems, which do not have silicified zones.

Silicification of the lower Manitou Falls Formation by quartz cements is also a factor contributing to the preservation of the McArthur River Zone 4 orebody. As a barrier to fluids, the silicified zone aided in the preservation of the Zone 4 orebody by shielding it from significant interaction with oxidizing fluids from the upper parts of the Manitou Falls Formation, except along the P2 fault. Minimal oxidation of uranium ore

and limited uranium loss from the orebody are supported by the high oxide totals of uraninite (Table 4), low abundance of secondary uranyl minerals, and preservation of syn- and post-ore sulfides. Reducing conditions persisted in the ore zone for at least 800 m.y. following initial uranium mineralization at ca. 1600 Ma (Fig. 11), as indicated by the formation of blebby-botryoidal uraninite and coffinite at 838 ± 40 Ma (Fig. 12) and post-ore galena (Fig. 5b).

Summary

The genetic evolution of the McArthur River Zone 4 alteration system shares similar mineralogical and geochemical characteristics with other sandstone-hosted deposits in the Athabasca basin in terms of its alteration mineralogy, both spatially and temporally, alteration fluids, timing of uranium mineralization, and alteration events. McArthur River Zone 4 is a unique sandstone-hosted deposit, as its fluid evolution involves basinal fluids as the predominant source of sandstone and basement alteration without contribution of an isotopically distinct basement-derived fluid. Rather, the reducing fluid which precipitated the late pre-ore sudoite alteration halo and caused uranium deposition originated from basinal fluids that became reducing and chemically modified via interaction with the basement lithology. On this basis, the evolution model for the McArthur River Zone 4 orebody has closer affinity with genetic models for basement-hosted deposits (Fayek and Kyser, 1997; Alexandre et al., 2005). The occurrence of an early pre-ore silicified zone within the Manitou Falls Formation modified the flow of basinal fluids locally at McArthur River with basinal fluids transported laterally through porosity in lower MFa and downward via fractures that breached the silicified zone. Application of mineralogical and geochemical pathfinders, including sudoite alteration halos, U pathfinder elements, and radiogenic Pb isotopes, which have been demonstrated for other sandstone-hosted deposits of the Athabasca basin (Alexandre et al., 2009a, 2012), is hindered for McArthur River-type orebodies. This is because extensive silicification of the overlying sandstones restricted basement-modified basinal fluids precipitating sudoite and post-ore alteration fluids dispersing mobile elements from ascending above the silicified zone. However, silicified barriers may contribute to ore preservation by limiting the incursion of oxidizing basinal and meteoric waters into the ore zone. Lastly, exploration models for unconformity-related uranium deposits should consider silicified barriers as potentially concealing undiscovered orebodies.

Acknowledgments

This work benefited from field and financial support from Cameco Corporation and Natural Sciences and Engineering Research Council (NSERC) Collaborative Research and Discovery grants. Special thanks to Don Chipley, April Vuletich, Kerry Klassen, Allison Laidlow, and Steve Beyer at the Queen's Facility for Isotope Research for their academic and analytical support. Current and former Cameco Corporation geologists, notably Dan Jiricka and Donald Wright, are thanked for their field support. Brian Joy and Alan Grant of Queen's University are thanked for their help with electron microprobe and X-ray diffraction analyses. Antonin Richard and Kevin Ansdell are thanked for their detailed and constructive revisions,

which greatly helped in improving this manuscript. We would also like to thank Larry Meinert and Christine Brandt of *Economic Geology* for editorial handling and production of this manuscript.

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