Mineralogy of a Fertile Fluid Conduit Related to Unconformity-type Uranium Deposits in the Athabasca Basin, Saskatchewan

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Abstract

This report documents the occurrence and chemical variation of hydrothermal alteration minerals along the P2 fault, the structural host for the world-class McArthur River uranium deposit, in order to identify the mineralogical footprint of ore-forming fluids, define exploration criteria for fertile basement structures associated with this deposit type and infer the nature of the fluids. An assemblage of florencite (LREE-rich aluminum phosphate-sulphate; APS) and magnesio-foitite (alkali deficient Mg tourmaline) with sudoite and illite formed in the basement rocks along the P2 fault and is distinct relative to the alteration assemblages that formed in the basement rocks outside the fault. This assemblage occurs along the entire P2 fault, regardless of its proximity to the McArthur River uranium deposit and is interpreted to be the mineralogical footprint of ore-forming fluids. It may be useful when targeting fertile basement faults during exploration. Compositional zoning in APS minerals indicate that earlier fluids were SO_4^{2-}-rich and became P and LREE-rich through interactions with the basement rocks. The chemical composition of florencite and magnesio-foitite indicates that mineralizing fluids contained low Na and were enriched in REE, especially in the ore zone. High $\delta^{11}B$ values in magnesio-foitite are interpreted as being sourced from B dissolution by fluids from evaporitic rocks. The similar chemistry and occurrence of these minerals along the entire P2 fault, regardless of proximity to ore, indicate that the P2 fault was a conduit for mineralizing fluids and that the precipitation of uranium was selective to the location of the McArthur River deposit.

Introduction

The P2 fault is a reverse dip-slip structure situated in the southeastern Athabasca Basin, Saskatchewan, Canada. The fault is spatially associated with the McArthur River deposit, currently the world's largest high-grade uranium deposit (Fig. 1). The purpose of this TGI-4 supported project, which started in August 2012, was to examine alteration minerals in the basement rocks along the P2 fault in order to evaluate the role of this major structure in the uranium mineralization processes and define exploration criteria for fertile basement structures associated with this deposit type. Furthermore, the hydrothermal alteration of the basement rocks is not well studied compared to the Athabasca Group sandstones partly due to the more complex mineralogy and compositions of the basement rocks.

Early work of this study is described in Adlakha et al. (2014) and involved detailed sampling of representative rocks, mineral chemistry and the establishment of an alteration paragenesis in order to unravel the alteration history of the basement rocks. Currently, work is progressing on identification of the mineralogical signatures left by ore-bearing fluids. Here we describe alteration assemblages and their distribution along the P2 fault, and present the occurrence and chemical variation of aluminum phosphate-sulphate (APS) minerals and tourmaline[1] (magnesio-foitite) along the P2 fault. These minerals were studied as they are chemically complex and their chemistry reflects that of fluids (van Hinsberg et al., 2011). We also discuss APS minerals and magnesio-foitite as mineralogical footprints of ore-bearing fluids, the role of P2 fault during mineralization, and the nature and source of mineralizing fluids.

Geological context

The basement rocks below the eastern Athabasca Basin are part of the Wollaston domain and host the Zone 2 orebody of the McArthur River deposit. The Wollaston domain here consists of pelite, semipelite, arkose, calcsilicate and quartzite that were metamorphosed during the Trans-Hudson Orogeny (ca. 1.81.9 Ga; Lewry and Sibbald, 1980) under upper amphibolite facies conditions. Granitic pegmatite lenses intrude the metasediments and likely formed from local partial melting during peak metamorphism (Annesley et al., 2005). Substantial erosion during the exhumation of the basement rocks beginning at ca. 1.73 Ga (Kyser et al., 2000) resulted in weathering of the basement and the development of a weathering profile, a lower chlorite-dominated

[1] Hydrothermal tourmaline associated with uranium deposits of the Athabasca Basin is commonly referred to as "dravite"; however, it is noted here that the only true dravite in the study area is metamorphic in origin and found as relic grains in the basement or as detrital grains in the Athabasca Group. The hydrothermal tourmaline associated with uranium deposits is actually the species magnesio-foitite (alkali deficient dravite; e.g. Wasyliuk, 2002).

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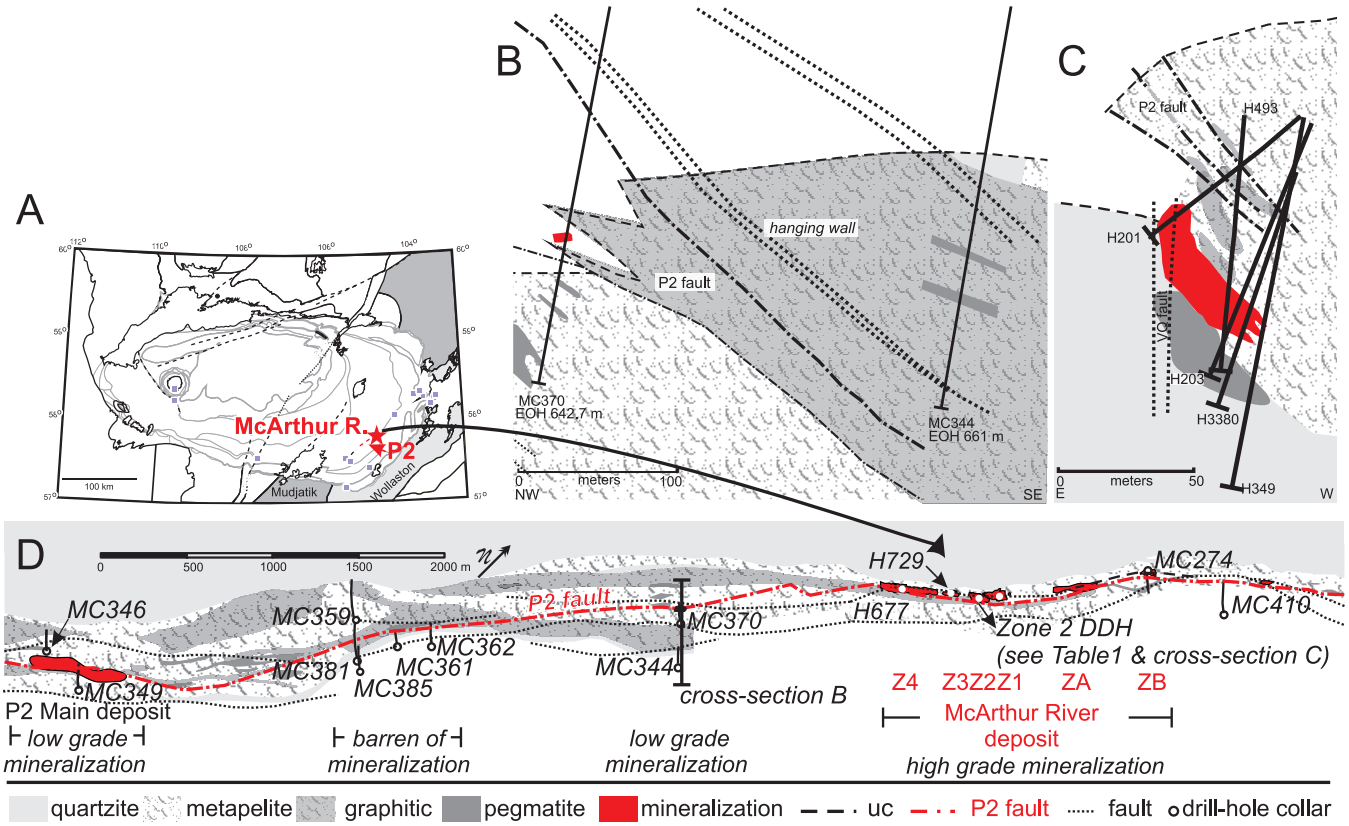

Figure 1: (A) A simplified map of the Athabasca Basin showing location of the P2 fault and McArthur River deposit (modified from Jefferson et al., 2007). (B) A schematic cross-section showing an example of a drill hole that intersected the P2 fault proximal to low-grade mineralization (DDH MC370) and a "background" drill hole that did not intersect the P2 fault (DDH MC344). (C) A cross-section of the Zone 2 basement hosted orebody showing sampled drill core which intersect the orebody and/or the alteration halo. (D) An interpreted geological strip map at the unconformity showing the P2 fault, the locations of sampled drill holes (italicized MC### or H###), ore bodies and the sites of the cross sections (B) and (C). Low-grade mineralization occurs along the middle and southeast (P2 Main deposit) portions of the P2 fault. The P2 fault is essentially barren in the southwestern part. Z1–4 = Zone numbers of orebody at the McArthur River deposit; uc = unconformity. Cross-sections (A) and (B) plan view map (D) and were modified from Cameco internal reports.

Green Zone and upper hematite and kaolinite dominated Red Zone (Macdonald et al., 1985), before deposition of the Athabasca Group conglomerate and sandstone sequences. The Athabasca Group comprises four major sequences, including the basal Read Formation, of dominantly fluvial to marine, quartz pebble conglomerate and quartz-dominated sandstone (99% quartz framework grains with minor K-feldspar + clay matrix), currently preserved at a maximum thickness of 1500 m in the centre of the basin (Ramaekers et al., 2007).

Above the McArthur River deposit, the thickness of the conglomerate-sandstone succession is approximately 500 m. Some conglomerate and sandstone units have been intensely silicified (Jefferson et al., 2007). During and after deposition of the Athabasca Group, diagenetic fluids extensively altered much of the stratigraphic section (except for the intensely silicified units), as well as the weathered basement rocks close to the unconformity. The alteration of the basement weathering profile at the unconformity formed what is known as the Bleached Zone and comprises illite with kaolinite (Macdonald, 1985). Subsequent hydrothermal activity further altered and brecciated the sandstone and basement rocks, particularly along intersecting faults that provided the fluid pathways during mineralization (McGill et al., 1993).

The P2 fault (045°/45–60°SE) developed in graphitic pelite in the metamorphosed basement rocks of the Wollaston domain below the basin and propagated as a number of splays into the overlying sandstone during fault re-activation (Figs. 1B, C). The P2 fault zone is a series of reverse faults with a strike length of approximately 13 km and has been traced seismically at least 2 km below the unconformity (McGill et al., 1993). In the basement, the several fault planes of the P2 fault are mostly constrained to graphite-bearing metapelite and trend parallel to the basement foliation (McGill et al., 1993). Reactivation of P2 faulting formed differences in the thickness of the basal conglomerate at the unconformity and broad fracture and breccia zones in the sandstones and the reverse movement of the P2 fault raised a wedge of basement rocks above the unconformity with the vertical displacement of up to 80 m (McGill et al., 1993; Figs. 1B, C).

While a few sub-economic (< 1 wt. % U_3O_8) uranium occurrences have been found along the P2 fault, the McArthur River deposit is the only high-grade deposit discovered to date. The McArthur River deposit comprises six main mineralized zones (Zones 1, 2, 3, 4, A, B). Current production at the McArthur River mine is from the Zone 2 ore lens which is almost entirely hosted in the basement rocks

Table 1: List of studied diamond drill holes (DDH). See Fig. 1 for the locations.

Area	DDH[a]	Samples[b]	Depth ranges[c]	Notes
least altered and alteration outside P2 fault	MC344	16	651.5 – 499.4 m	
	MC346	9	737.1 – 580.5 m	
	MC381*	4	660.5 – 603 m	
	MC385	8	686 - 652.2 m	
P2, unmineralized	MC359	7	626.1 – 491 m	
	MC361	26	652.9 – 493 m	
	MC362	15	643.9 – 520.2 m	
	MC381*			
P2, sub-ec (<1 wt% U3O8)	MC349	13	659 – 573 m	
	MC370	17	630.8 - 533.2 m	
	MC410	7	790.9 – 527.7 m	
P2, Z1	H729	20		
P2, Z2	H201	11		
	H203	7		
	H231	7		VQ fault
	H347	10		
	H493	7		
	MO227	5		
	H3380	5		2 ore samples
P2, Z3	H3559	2		
	H3576	1		
P2, Z4	H677	5		2 ore samples
P2, ZB	MC274	7	618.3 – 502.4 m; 93.1 m; 62.8 m	1 ore sample

Notes:
[a] exploration holes beginning with MC, underground collared drill holes are denoted H or MO;
[b] number of samples collected from respective DDH;
[c] depth ranges given for core lengths of exploration DDH collared at surface.

immediately below the unconformity (Fig. 1C). The Zone 2 orebody is bounded by the vertical quartzite (VQ) fault and ~140° trending cross faults in the basement rocks (Fig. 1D). The VQ fault is a steeply dipping structure located between the footwall quartzite and cordierite-bearing metapelite (Fig. 1C; McGill et al., 1993). The rocks adjacent to the P2 fault and below the Zone 2 orebody are highly brecciated and intensely altered. The five other ore bodies of the McArthur River deposit are hosted in the sandstones of the Read Formation immediately above the unconformity.

Sampling

This study commenced with examination and sampling of drill core from along 7 km of the P2 structure and within the McArthur River underground mine (Table 1; Fig,. 1B–D). A total of 209 drill core samples were collected that represent the least altered rocks outside the P2 fault (> 50 m from the fault plane and the unconformity), altered basement rocks outside the P2 fault (found within 50 m of the unconformity), P2 fault rocks in barren areas, P2 fault rocks below sub-economic mineralization, P2 fault rocks proximal to the Zone 2 orebody, VQ rocks proximal to Zone 2 orebody and P2 fault rocks associated with sandstone-hosted ore bodies, such as Zones 1, 3, 4 and B. Representative samples were chosen based on specific features, e.g. alteration style (green, red or bleached). Ore samples were collected from the Zone B, Zone 2, and Zone 4 ore bodies. Most samples are metapelite/pelitic gneiss and anatectic pegmatite from the basement, below the unconformity. Additionally, 18 samples of sandstone close to the unconformity were collected for comparison.

Methodology

Petrographic studies using plane-polarized and cross-polarized transmitted light microscopy on 151 polished thin sections were carried out for this study. Due to the fine-

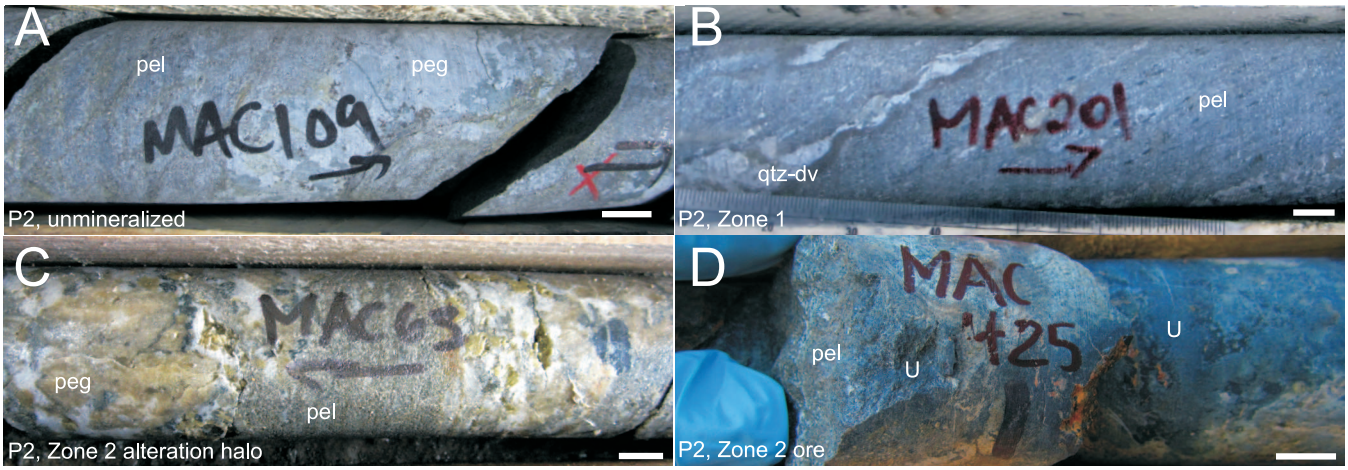

Figure 2: Drill core photographs of altered basement rocks from various areas of the P2 fault: (A) metapelite (pel) with pegmatite (peg) vein; (B) metapelite with quartz-dravite (qtz-dv) vein; (C) pegmatite and metapelite; (D) metapelite hosting uranium ore (U). Scale bars = 1 cm.

grained nature of alteration minerals, detailed textural analysis was carried out on carbon-coated polished thin sections using a JEOL 6610LV scanning electron microscope (SEM) at University of Ottawa. Energy-dispersive spectroscopy (EDS) was used to semi-quantitatively determine the compositions and identify minerals. Quantitative analysis of minerals for major and minor constituents was conducted at the University of Ottawa using a JEOL 8230 electron-probe microanalyzer (EMPA) with a wavelength-dispersive spectrometer (WDS).

Aluminum phosphate-sulphate minerals and tourmaline in polished thick sections were analyzed for trace elements by laser ablation inductively coupled plasma mass spectrometer (LA-ICPMS) at the Geological Survey of Canada, Ottawa. Ablation was performed using Photon-Machines Analyte193 excimer laser ($\lambda = 193$ µm) ablation system with Helex ablation cell and Agilent 7700x quadrupole ICP-MS. The reference National Institute of Standards and Technology (NIST610) was used as a calibration standard for APS mineral analysis and the concentration of Al (previously determined by EMPA) was used an internal standard to calculate trace element abundances. For magnesio-foitite, NIST GCD-1G was used as the calibration standard and the Mg (previously determined by EMPA) was used an internal standard.

The B isotopic composition of tourmaline was measured using a SHRIMP (sensitive high-resolution ion microprobe) II at the Geological Survey of Canada, Ottawa. Composition based instrumental mass fractionation was corrected using four tourmaline standards with known B isotope compositions. The results of the B isotopic analyses are reported in delta annotation (δ) as the variation in the $^{11}B/^{10}B$ ratios of sample compared to standard SRM NBS 951 as per mil (‰).

Results

Alteration mineralogy of P2 fault rocks

In general, rocks along the P2 fault (wall-rocks within 50 m of the fault plane) are moderately to highly altered. Samples with moderate alteration retain pseudomorphs of metamorphic minerals (Fig. 2), such as feldspar or cordierite. In intensely altered rocks, brecciation and veining destroy original mineral textures (Figs. 2C, D) with the exception of quartz and dravite (Mg-rich early tourmaline). Quartz and early dravite are associated. Strong degrees of alteration also produced an unconsolidated mixture of graphite and clay, especially immediately adjacent to ore. Rocks in the P2 fault are mostly green and graphitic (Figs. 2A, B) with patches of "bleached" alteration.

The alteration assemblage of competent rocks along the P2 fault comprises sudoite with varying amounts of illite, magnesio-foitite and APS minerals (Fig. 3). Sudoite forms needle-like crystals (< 2 µm in length) that are low-relief and colorless to very faint green in plane polarized light with anomalous blue birefringence (Figs. 3A-C, E–F). Illite occurs as colorless laths (usually < 2 µm in length, but can be up to 10 µm; Figs. 3A, B, D) that in thin section have high third order birefringence colours, typically light pink, blue and orange. Sudoite and illite are commonly found mixed in varying proportions. Magnesio-foitite is characterized as colourless, acicular aggregates (5 – 500 µm in length), overgrowths on dravite, in veinlets (up to 0.5 cm wide) or as disseminations in matrix of sudoite or illite. In ore samples, it is commonly coated with remobilized uraninite (Fig. 3D). Magnesio-foitite is distinguished from illite and chlorite by its second order birefringence (yellow, orange and purple; Fig. 3C), relatively high relief, and optically negative elongation. Small (typically <1 – 20 µm, rarely up to 40 µm), pseudo-cubic (rarely hexagonal) APS minerals are disseminated and/or clustered in fine-grained clay minerals (Fig. 3B). The textural relationships with surrounding clays suggest that they are in equilibrium. The APS minerals are commonly zoned, with darker cores and lighter rims in BSE-images (Fig. 3).

Hematite, kaolinite, clinochlore (Mg-rich chlorite) and chamosite (Fe-rich chlorite) are irregularly dispersed along the P2 fault. Hematite forms fine grained (< 2 µm) crystals and occurs with illite. Kaolinite forms aggregates or "books" of 2 µm thick stacked crystals.

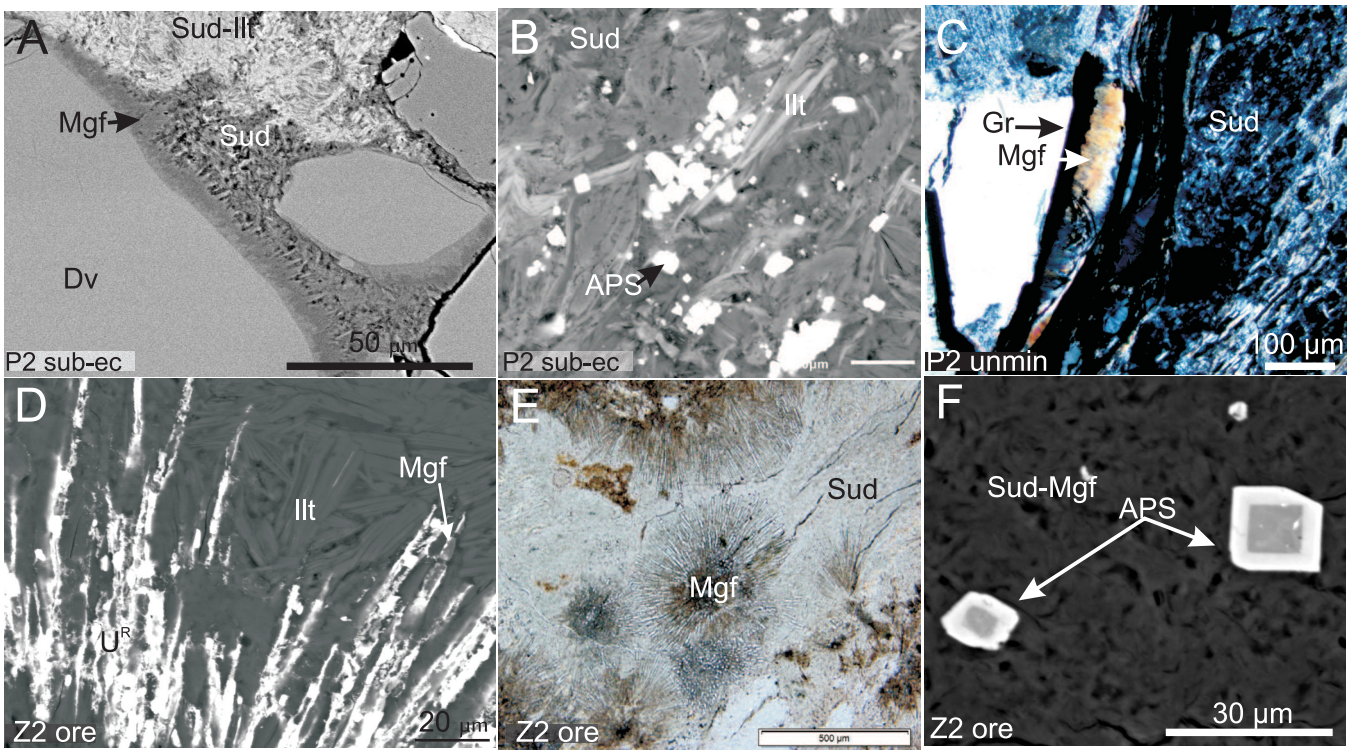

Figure 3: Photomicrographs (PPL = plane polarized light, XPL = cross-polarized light) and BSE images of alteration phases along the P2 fault: (A) relic dravite (Dv) overgrown by magnesio-foitite (Mgf) (BSE), (B) APS minerals surrounded by sudoite and illite (Ilt) (BSE), (C) magnesio-foitite with sudoite and relic graphite (Gr) (XPL), (D) magnesio-foitite occurring with illite and overprinted by remobilized uraninite (U^R) (BSE), (E) radial magnesio-foitite occurring with sudoite (PPL), and (F) zoned APS minerals surrounded by sudoite (Sud) and magnesio-foitite (BSE).

Quartz, dravite, graphite and pyrite are the only relic metamorphic minerals. Quartz grains are partially dissolved and are commonly replaced by sudoite or magnesio-foitite.

Distribution of alteration along the P2 fault

Samples from the unmineralized and sub-economic areas along the P2 fault (Table 1; Fig. 1D) are moderately to strongly altered. Unmineralized samples have a high proportion of illite to sudoite and low concentrations of magnesio-foitite. The APS minerals occur with illite. In sub- economic samples, illite and sudoite are of equal proportions (Fig. 3B). Magnesio-foitite is more common in sub-economic samples relative to barren samples and APS minerals occur with sudoite or kaolinite with magnesio-foitite.

Below the Zone 1 orebody, the P2 fault is strongly graphitic (> 5 modal % graphite) and contains abundant relic dravite. Sudoite and illite are the most abundant alteration minerals and magnesio-foitite forms overgrowths on relic dravite. The rocks below the Zone 3 orebody generally exhibit moderate degrees of alteration where the grains of cordierite are still discernable but replaced by sudoite-illite and biotite, which is then chloritized (Fe-Mg chlorite) or illitized. The APS minerals are mixed with sudoite and illite. Magnesio-foitite forms sporadic aggregates. Hematite is common and overprints biotite and illite laths.

Samples from the P2 fault in the Zone 2 alteration halo (Table 1; Fig. 1C) are strongly altered (Fig. 2C, D). Sudoite and magnesio-foitite are common alteration minerals and occur with pyrite and graphite. Sudoite is strongly associated with magnesio-foitite and can be intermixed with illite and APS minerals. Hematite occurs locally along fractures. Samples of Zone 2 ore contains magnesio-foitite, sudoite, sudoite-illite that is intermixed, and relatively coarse-grained illite (up to 10 µm long axis), APS minerals and minor sulphides (pyrite, galena etc.) and kaolinite. Primary uraninite (as per the characterization of Fayek and Kyser, 1995) occurs as masses while remobilized uraninite overprints sudoite, magnesio-foitite and illite (Fig. 3C).

Mineral chemistry – major elements

The chemical formula of tourmaline was calculated based on ideal formula $XY_3Z_6(T_6O_{18})(BO_3)_3V_3W$, which assumes 3 B atoms in the B-site, 18 O associated with the T-site and 3 OH in the V-site. For cation site assignment, the T-site was filled first with Si^{4+}, then Ti^{4+} and Al^{3+} to sum 6 cations. The Z-site was occupied by Al^{3+}, and the remaining Al^{3+} was assigned to the Y-site. The Y-site was filled by Fe^{2+} or Fe^{3+} and Mg^{2+}. All Ca^{2+}, K^+ and Na^+ are assigned to the X-site. The W-site accommodates F^-, OH^- and O^{2-}. The fraction of O^{2-} was calculated to compensate excess cation charges. Magnesio-foitite has an average composition of $(Na_{0.20}Ca_{0.02}K_{0.01})(Mg_{1.95}Fe^{3+}_{0.09}Al_{0.94})Al_6(Si_{6.02}O_{18})(BO_3)_3(OH_3)(F_{0.04}OH_{3.66}O_{0.30})$ and is alkali deficient where X-site vacancies range from 0.70 – 0.85 atoms per formula unit (apfu) (Fig. 6). X-site vacancies were calculated as 1 apfu subtract the sum of Na, Ca and K apfu.

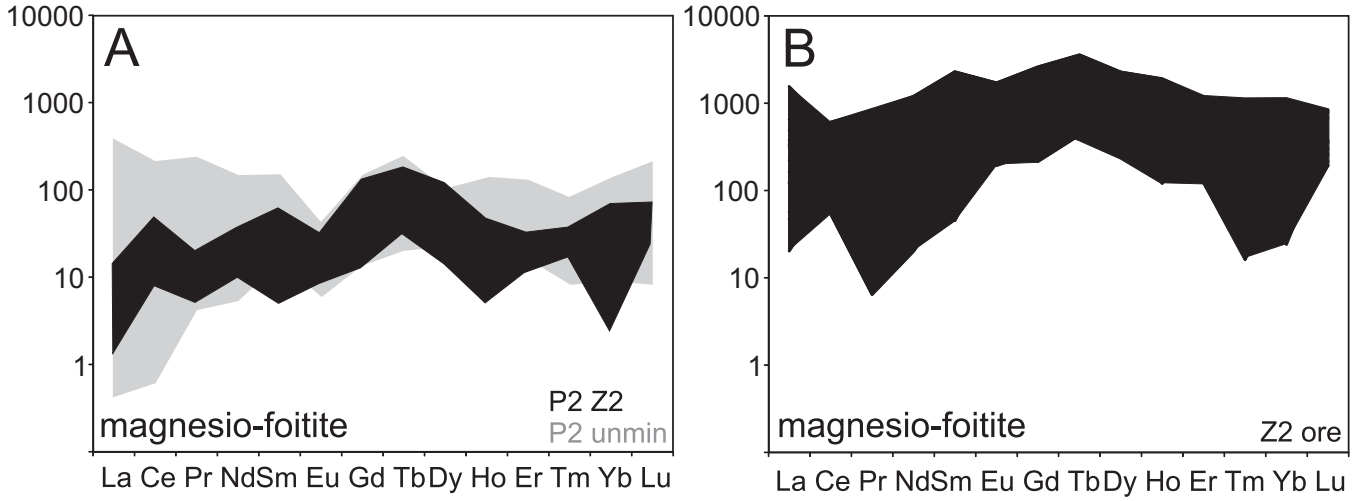

Figure 4: REE + Y plots (normalized to chondrite; McDonough and Sun (1995) of magnesio-foitite from the P2 fault: (A) in unmineralized areas of the basement (black) and sandstone (grey); and (B) near or in mineralization, including the alteration halo around Zone 2 orebody (grey) and in the Zone 2 and Zone B ore bodies (black).

The APS minerals show a range in composition (Adlakha and Hattori, in press; Fig. 5). The APS mineral formulae were calculated based on 6 cations as the ideal formula is expressed as $AB_3(XO_4)_2(OH)_6$, where A = mono-, di-, tri- or, more rarely, tetravalent cations (K^+, Na^+, Rb^+, Ca^{2+}, Sr^{2+}, REE^{3+}, Th^{4+} etc.); B = Al^{3+}, Fe^{3+}; and X = P^{5+}, S^{6+}, and As^{5+}. They contain high ΣLREE (0.35 – 0.58 apfu; LREE = La + Ce + Pr + Nd) relative to Sr (0.16 – 0.32 apfu) and Ca (0.18 – 0.28), and high PO_4^{3-} (1.70 - 1.97 apfu) relative to SO_4^{2-} (0.06 – 0.35 apfu) and AsO_4^{3-} (<0.01 apfu). Ce is high (0.15 – 0.27 apfu) relative to La (0.09 – 0.17), Pr (<0.01 – 0.03 apfu) and Nd (0.05 – 0. 12 apfu), showing [Ce]/[Ce]* of ~0.8 – 1.6. Compositional zoning in the APS minerals consists of cores enriched in Sr, Ca, and SO_4^{2-}, and rims high in LREE and P. Within the cores of APS minerals, Ca and P contents are inversely correlated with Sr and S contents.

Mineral chemistry – trace elements

Magnesio-foitite along the P2 fault has variable concentrations of REE. Magnesio-foitite from basement (DDH MC381 and MC361) and sandstone (DDH MC361) samples from unmineralized areas along the P2 fault contain low concentrations of ΣREE (avg. 0.7 ± 0.02 (1σ) and 0.4 ± 0.07 ppm, respectively; La – Lu). The data plot as a "bell-shaped" normalized REE pattern characterized by high HREE relative to LREE, with an average $[LREE]_N/[HREE]_N \approx 0.5$ and 0.4, respectively (Fig. 4A). Magnesio-foitite from the basement alteration halo near the Zone 2 ore body (DDH MO227) have low ΣREE contents (avg. 1.0 ± 0.3 ppm), plot as "bell-shaped" normalized REE patterns and contain high HREE relative to LREE, average $[LREE]_N/[HREE]_N \approx 0.6$ (Fig. 4B). Ore samples from Zones 2 and B ore bodies (DDH MC274 and H3380), magnesio-foitite contains relatively high concentration of ΣREE (avg. 15.0 ± 6.1 ppm), shows a "bell-shaped" normalized REE pattern with high HREE, $[LREE]_N/[HREE]_N$ value ≈ 0.7 (Fig. 4B).

Samples from the P2 fault located proximal to Zone 3 ore (DDH H729) have APS minerals containing appreciable U and Pb with a mean averages of 0.6 ppm) and 158 ppm, respectively. Similarly, APS from the Zone 2 alteration halo (DDH H201 and H493) have high U (avg. 5.7 ppm), and Pb (avg. 159 ppm) contents.

Boron isotope compositions

Magnesio-foitite from unmineralized and sub-economic mineralization areas of the P2 fault, and areas proximal to Zone 1 and Zone 2 ore bodies were analyzed. Magnesio-foitite has $\delta^{11}B$ values from +13.1 to +23.2 ‰, with a mean of +18.5 ± 1.9 ‰. Magnesio-foitite co-existing with uraninite has $\delta^{11}B$ values from +13.0 to +19.8 ‰. In low-grade areas along the P2 fault, magnesio-foitite has $\delta^{11}B$ values of +15.5 to +18.5 ‰ while in unmineralized samples range between +15.0 and +15.8 ‰.

Discussion

Mineralogical footprint of ore fluid and assessment of the P2 fault during mineralization

Sudoite, illite, magnesio-foitite and florencite are in textural equilibrium, which is consistent with contemporaneous crystallization (Fig. 3). Linked REE abundances of magnesio-foitite (Fig. 4) and florencite also imply co-precipitation, with high LREE contents in florencite (up to 0.58 apfu; Fig. 5) and lower the concentrations of LREE in magnesio-foitite reflecting precipitation of a common fluid. The occurrence of trace uranium in florencitic APS minerals and their proximity to ore suggest formation by a uranium-bearing fluid — indicating that magnesio-foitite and florencite are mineralogical footprints of ore-forming fluids.

The alteration assemblage of sudoite, illite, magnesio-foitite and APS minerals (florencite) is widely distributed in basement rocks along the P2 fault, being present in both mineralized and unmineralized areas of the fault (Fig. 3). This alteration assemblage along the P2 fault differs from that observed outside the fault, which is comprised predominately of illite and sudoite with no magnesio-foitite or florencite (Adlakha et al., 2014; Adlakha and Hattori, in press).

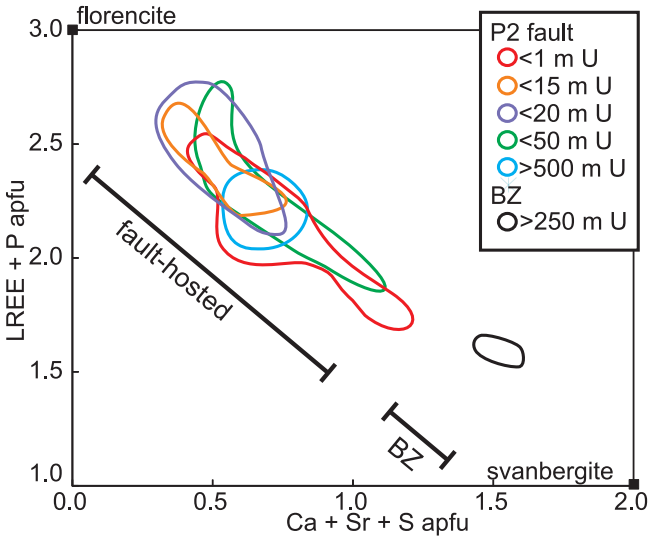

Figure 5: Cross-plot showing coupled substitution of Ca-Sr-S for LREE-P for APS minerals along the P2 fault (colored fields), and within the Bleached Zone (BZ) sample (black field). P2 fault samples are color coded with respect to distance in metre from the uranium mineralization (McArthur River deposit and low-grade): the red field represents samples < 1 m from U, the orange field represents samples < 15 m from U, the purple field represents samples < 20 m from U, the green field represents samples < 50 m from U and the blue field represents samples from unmineralized areas >500 m from U.

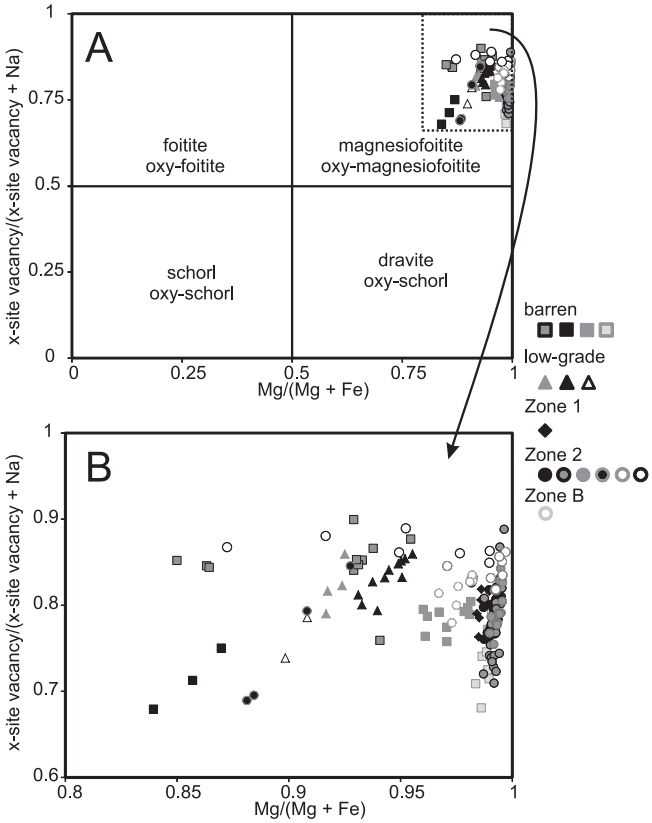

Figure 6: Cross–plots of magnesio-foitite data, Mg/(Mg + Fe) vs. x-site vacancy/(x-site vacancy + Na apfu), showing the alkali-deficiency of magnesio-foitite (after Henry et al., 2011). Cross-plot B shows a smaller range and therefore a larger amount of detail than cross-plot A. Data of magnesio-foitite from unmineralized areas are represented by squares, from low-grade areas by triangles, from Zone 1 by diamonds and from Zone 2 and B by circles. Magnesio-foitite from Zone 2 and B samples that contain uraninite are represented by open circles and show high x-site vacancies.

Therefore, magnesio-foitite and APS minerals may be useful in exploration programs when targeting fertile basement faults.

The widespread presence of this mineral assemblage along the P2 fault indicates that the P2 fault was a conduit for mineralizing fluids. Furthermore, it is evident that similar fluids travelled along the entire P2 fault, but ore was selectively precipitated (i.e. at the McArthur River deposit; Fig. 1).

Implication of APS mineral chemistry for nature of the fluid

The APS minerals along the P2 fault are florencitic in composition (ideal florencite is $CeAl_3(PO_4)_2(OH)_6$) with high LREE and P contents. These APS minerals are compositionally distinct relative to those of the Bleached Zone along the unconformity described by Adlakha and Hattori (in press; Fig. 5). The latter are closer to svanbergite-goyazite compositions ($SrAl_3(PO_4)(SO_4)(OH)_6$ - $SrAl_3(PO_4)_2(OH)_6$) (Fig. 5). Florencitic APS minerals along the P2 fault are also zoned with florencite rims and svanbergite-goyazite cores (Fig. 3F).

The composition of APS minerals along the entire P2 fault have a large range in concentrations of LREE and P (Fig. 5). For example, the (LREE+P)/(Ca+Sr+S) ratios of APS minerals close (<1 m) to ore range from 1.6–5.6, whereas APS minerals from unmineralized samples far from mineralization (>500 m) show moderate ratios of (LREE+P)/(Ca+Sr+S), from 2.8–4 (Fig. 5).

Gaboreau et al. (2005, 2007) found that APS minerals proximal to uranium deposits in the Athabasca and Kombolgie Basins contained high LREE+P relative to those in intermediate and distal areas. The data of this study shows that APS minerals less than 1 metre from low-grade mineralization have a larger range than that presented by Gaboreau et al. (2005, 2007) for APS minerals proximal to uranium deposits (Fig. 5). There is no significant difference in the APS mineral data from high-grade and unmineralized parts of the P2 fault (Fig. 5). The broad range in composition likely reflect the evolution of fluids that passed through the ore zone. The earlier fluids contained high Ca, Sr and SO_4^{2-}, and evolved to have high LREE and P contents (Adlakha and Hattori, in press).

Implication of magnesio-foitite chemistry for the nature and source of the fluid

Magnesio-foitite exhibits a large X-site vacancy (Fig. 6). The X-site vacancy likely reflects high H+/Na+ ratio of the fluid from which it crystallized. This indicates low pH or a fluid with low Na+ concentrations. A low pH fluid is consistent with the type locality of magnesio-foitite which formed by acidic fluid (Hawthorne et al., 1999) and recent fluid inclusion studies by Richard et al. (2012) on the genesis of the Athabasca deposits. A low pH fluid is inconsistent with thermodynamic modelling by Kister et al. (2005), who

reported that fluids responsible for the crystallization of magnesio-foitite, illite, and sudoite were slightly alkaline. A possible interpretation is that the tourmaline-crystallizing fluid contained low Na+ contents. This interpretation is consistent with previous studies that suggests mineralization associated alteration in the basement formed, in part, by Ca-rich, Na-poor brines (Derome et al., 2005; Richard et al., 2010). These brines have been found as quartz-hosted fluid inclusions in proximity to mineralization.

The REE chemistry of magnesio-foitite in unmineralized and mineralized areas of the P2 fault show similar LREE/HREE ratios and bell-shaped REE patterns (Fig. 4). One notable difference is that magnesio-foitite from mineralized samples contain much higher concentrations of REE than magnesio-foitite in barren areas (Fig. 4). This indicates that the mineralizing fluid contained higher REE, at least on a local scale.

The $\delta^{11}B$ values of magnesio-foitite along the P2 fault are high, ranging from +13 to +23 ‰. The $\delta^{11}B$ values of fluid are calculated using the fractionation factor between magnesio-foitite and fluid of Meyer et al. (2008) at ore forming temperatures (180 – 220°C; Kister et al., 2005), assuming that B is boric acid in the fluid. The $\delta^{11}B$ values for fluids range from +18 to +29 ‰.

High $\delta^{11}B$ values in the fluids indicate a contribution of evaporates or sea water because there is no other reservoir of B with such high $\delta^{11}B$ values. However, $\delta^{11}B$ values of Precambrian seawater are unknown which makes absolute interpretation on the source difficult. Based on B-isotope composition of tourmaline, microthermometry of high salinity fluid inclusions, and Cl and Br isotopes of fluid inclusions, many authors support the hypothesis of an evaporated sea water source fluid for tourmaline and uranium ore (Derome et al., 2005; Richard et al., 2010; Mercadier et al., 2012). As marine brines contain high Na^+/H^+ ratios, it is unlikely that an alkali deficient tourmaline would crystallize from a NaCl-rich fluid. It is possible that the evaporitic fluid evolved to the $CaCl_2$-rich brine through interactions with the basement, as suggested by the authors. A fluid with this composition could allow for precipitation of magnesio-foitite as suggested above. However, Na-rich phases such as albite which would have been produced through brine interaction with the basement (as suggested by Richard et al., 2010) are not preserved in the area (Adlakha et al., 2014). An alternative interpretation is that boron-bearing evaporitic rocks may have been dissolved by meteoric and diagenetic waters (Bray and Spooner, 1988; Kotzer and Kyser, 1995). Although evidence for evaporites in the Athabasca Basin is lacking, it is possible that they did exist at one time but were completely dissolved to form basinal brines or eroded. We support the latter hypothesis where fluids dissolved boron from carbonates and evaporites, as this interpretation is consistent with the Na+ deficient nature of tourmaline.

Summary

Sudoite, illite, magnesio-foitite and florencitic APS occur along the entire P2 fault. The relative amounts of these minerals differ depending upon the distance from ore: sudoite and magnesio-foitite are abundant close to the ore and illite is abundant in unmineralized areas. The presence of magnesio-foitite and florencite is restricted along the P2 fault. This study concludes that the assemblage of florencitic APS minerals and magnesio-foitite can be used as an exploration vector to identify fertile basement structures associated with uranium deposits.

An important conclusion in this study is that sudoite, illite, magnesio-foitite and florencite all crystallized from an uraniferous fluid. In particular, florencite contains appreciable uranium. These minerals were formed contemporaneously with uranium mineralization as they occur in equilibrium with each other and in high abundance proximal to uranium ore. The HREE enrichment of magnesio-foitite is coupled to the incorporation of LREE in APS minerals.

Low sodium contents in magnesio-foitite are consistent with fluids with low sodium concentrations. The high $\delta^{11}B$ values in magnesio-foitite are interpreted as being sourced from boron dissolution by fluids from evaporitic rocks. The REE chemistry of magnesio-foitite indicates that the fluid in the ore zone contained high concentration of REE but fluids in barren areas of the P2 fault contain lower REE. Compositional zoning in APS minerals are consistent with earlier SO_4^{2-}-rich fluid becoming to P- and LREE-rich through interactions with the basement rocks.

The alteration minerals of sudoite, illite, magnesio-foitite and florencite have similar chemistry along the entire 7 km strike length of the P2 fault studied, including areas barren of uranium mineralization. The uranium-bearing fluids likely passed along the entire P2 fault, but only precipitated uranium in localized areas where more reducing conditions prevailed.

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