1   **Revision 4: Compositional variation and timing of aluminum phosphate-sulfate minerals in**

2   **the basement rocks along the P2 fault and in association with the McArthur River uranium**

3   **deposit, Athabasca Basin, Saskatchewan, Canada**

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7   **Abstract**

8   The Athabasca Basin hosts world class uranium deposits, such as the McArthur River

9   deposit. This paper presents the occurrence of aluminum phosphate-sulfate (APS) minerals in the

10 metasedimentary rocks along the P2 fault, the main ore-hosting fault of the McArthur River

11 deposit. It compares the APS minerals along the P2 fault with those outside the fault, examined in

12 this study, and those from other deposits of the Athabasca Basin and from other Paleo- to

13 Mesoproterozoic basins worldwide.

14   APS minerals are common along the P2 fault, rare outside of the P2 fault zone in the

15 basement, and sparse along the unconformity between the Athabasca sandstones and the

16 basement. The APS minerals along the P2 fault occur with sudoite (± illite, magnesiofoitite) and

17 are zoned with Sr-, Ca- and S-rich cores (solid solution between svanbergite, crandallite and

18 goyazite) and LREE- and P-rich rims (close to florencite composition). APS minerals in the

19 Bleached Zone (altered rocks along the unconformity consisting predominantly of kaolin and

20 illite) are Sr-, Ca- and S-rich (high svanbergite component) and occur with kaolin. APS minerals

21 in the Red-Green Zone (mingled red hematitic and green chloritic basement rocks below the

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22   Bleached Zone) occur with sudoite and clinochlore. They contain relict cores of LREE- and As-

23   rich arsenoflorencite-(Ce), and rims of svanbergite-goyazite-crandallite solid solution.

24   The occurrence of svanbergite-crandallite-goyazite along the unconformity suggests their

25   formation by relatively oxidizing fluids during diagenesis of the overlying sandstones. The relict

26   cores of arsenoflorencite-(Ce) in the Red-Green Zone are interpreted to be the product of paleo-

27   weathering before the deposition of the Athabasca sandstones. Florencitic APS minerals are

28   found along the entire studied strike length (7 km) of the P2 fault, including the ore zone and

29   non-mineralized areas, but absent outside the fault zone. The florencitic APS minerals contain

30   low SO_4^{2-} in the ore zone, suggesting relatively reducing conditions during their crystallization.

31   Zoned APS minerals (with svanbergitic cores and florencitic rims) proximal to ore contain

32   elevated U (up to 16 ppm). These features suggest that diagenetic, oxidizing, and uranium-

33   bearing fluids travelled along the P2 fault and became relatively reduced, especially within the

34   ore zone. It also suggests florencitic APS minerals are contemporaneous with uranium

35   mineralization. The restricted occurrence of florencitic APS mineral along the P2 fault in the

36   basement suggests their use in identifying fertile basement structures associated with uranium

37   mineralization.

38   *Keywords:* hydrothermal alteration, APS, uranium mineralization, florencite, svanbergite,

39   arsenoflorencite, diagenesis, paleo-weathering, unconformity-type uranium deposits

40   **Introduction**

41   The Athabasca Basin hosts numerous large uranium deposits (Fig. 1), which are classified

42   as unconformity-related uranium deposits. The prevalent model for the mineralization was first

43   proposed by Hoeve and Sibbald (1978) and modified later by many researchers (e.g. Alexandre et

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44   al. 2005; Derome et al. 2005; Richard et al. 2011; Mercadier et al. 2012). This model suggests

45   that sea-water derived, uranium-bearing oxidizing brines (25-35 wt.% eq. NaCl) precipitated

46   uranium ore at the unconformity when it reacted with a reducing fluid of currently unknown

47   origin. Many deposits occur in the proximity of deformation zones in the basement and it is

48   suggested that re-activated basement faults served as conduits for uranium-bearing fluids

49   (Jefferson et al. 2007) or reducing basement fluids to reach the unconformity (McGill et al.

50   1993). The McArthur River deposit, the largest discovered high-grade (average grade of 16.46

51    $\%U_3O_8$; Bronkhorst et al. 2012) uranium deposit on Earth, is situated along the P2 fault, a 13 km

52   long reverse fault constrained to graphitic metapelite below the Athabasca Basin. Although

53   geophysical and structural studies have been carried out on the P2 fault (e.g., Hajnal et al., 2010),

54   the exact role of the fault in the mineralization remains uncertain.

55   In the Athabasca and Thelon basins of Canada, aluminum phosphate-sulfate (APS)

56   minerals (also known as alumino-phosphate sulfate) spatially associated with uranium deposits

57   have been reported (Quirt et al. 1991, Gaboreau et al. 2007, Riegler et al. 2014). APS minerals

58   occur in a variety of environments (Dill, 2001) and form many solid solution series with over 40

59   end-members (Jambor 1999; Stoffregen et al. 2000; Dill 2001). APS minerals have the general

60   formula: $AB_3(XO_4)_2(OH)_6$, where A = mono-, di-, tri- or, more rarely, tetravalent cations (K^+,

61   Na^+, Rb^+ , Ca^{2+}, Sr^{2+}, REE^{3+}, Th^{4+} etc.); B = trivalent cations (Al^{3+}, Fe^{3+}); and X = P^{5+}, S^{6+}, or

62   As^{5+}. Since incorporation of ions with different valences requires coupled substitution to

63   accommodate charge balance, compositional zoning of APS minerals is commonly well

64   preserved. This makes APS minerals excellent candidates for evaluating the chemical and

65   physical characteristics of fluids from which they formed (Dill 2001; Beaufort et al. 2005;

66   Gaboreau et al. 2005, 2007).

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67   The focus of this paper is to present the occurrence and compositional variation of APS

68   minerals in basement rocks along the P2 fault, discuss the role of the fault during mineralization

69   and the timing of APS mineral formation with respect to uranium mineralization. In addition, the

70   chemistry of APS minerals is compared with those along and outside of the fault zone in the

71   basement, from other APS minerals studied in Athabasca Basin (within deposits or not), and from

72   other Paleo- to Mesoproterozoic basins worldwide. The potential use of APS mineral in

73   exploration for unconformity-related uranium deposits is also discussed.

74   **Geological Setting**

75   **Regional Geology**

76   The basement rocks in the eastern Athabasca Basin area are part of the Wollaston and

77   Mudjatik Domains. The rocks of the Wollaston Domain consist of metapelite, metasemipelite,

78   meta-arkose, calc-silicate and quartzite (e.g., Annesley et al. 2005). They were metamorphosed

79   under upper amphibolite to lower granulite conditions during the Trans-Hudson Orogeny (ca.

80   1.8-1.9 Ga; Lewry and Sibbald 1980, McKechnie et al. 2012). Abundant granitic pegmatite

81   lenses intruded the metasedimentary rocks during peak metamorphism (Annesley et al. 2005;

82   Jefferson et al. 2007).

83   Alteration immediately below the unconformity is laterally extensive and consists of a

84   deeper Green Zone with sudoite (Al-Mg chlorite) and illite ± Fe-Mg chlorite, a transitional Red-

85   Green Zone with illite, sudoite and hematite, an upper Red Zone with hematite and kaolin ± illite,

86   and, locally, there is Bleached Zone of kaolin and illite, immediately beneath the unconformity

87   (Macdonald 1985; Quirt 2001; Adlakha et al. 2014). In addition to the Red-Green transitional

88   Zone, the Red and Green Zones are mingled in places. The origin of these Zones has been in

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89   discussion. Macdonald (1985) considered them as the products of paleo-weathering before

90   sandstone deposition, whereas Cuney (2003) proposed their formation after the deposition of

91   sandstones. Quirt (2001) and Adlakha et al (2014) pointed out extensive overprinting of alteration

92   minerals by subsequent hydrothermal fluids, which makes it difficult to determine the condition

93   of their initial crystallization. Rocks of the Bleached Zone are altered to white due to loss of

94   hematite and interpreted to be a reaction product of the Red Zone with late diagenetic fluids from

95   the overlying basin (Macdonald 1985; Quirt 2001). The least-altered metapelite occurs > 50 m

96   below the unconformity and away from faults.

97   The sedimentary rocks of the Athabasca Group are comprised of dominantly fluvial to

98   shallow marine, quartz pebble conglomerate and quartz arenite, with a preserved maximum

99   thickness of 1500 m in the centre of the basin (Ramaekers et al. 2007). Early diagenesis included

100   silica cementation on hematite-dusted detrital quartz grains (Hoeve and Quirt 1984; Jefferson et

101   al. 2007), alteration of kaolinite by dickite with minor illite and locally traces of sudoite (Quirt

102   2001; Laverret et al. 2006). Uranium deposits are localized near the intersection of the

103   unconformity and basement faults or down-dip along these faults into the basement. These

104   deposits are surrounded by alteration haloes of sudoite, illite and magnesio-foitite (alkali-

105   deficient dravite). Sandstone-hosted unconformity-type deposits show the inner halo of sudoite

106   with an outer alteration halo of illite (e.g., Hoeve et al. 1981; Hoeve and Quirt 1984; Alexandre et

107   al. 2012). Basement-hosted unconformity-type deposits are accompanied by the inner alteration

108   halo of illite and the outer halo of sudoite. The different proportions of sudoite and illite between

109   two types of unconformity-type deposits are considered to be related to differences in fluid

110   circulation (i.e. Ingress vs Egress; Hoeve and Quirt 1984).

111 **Structure and alteration of the McArthur River deposit and P2 fault**

112   The McArthur River deposit is comprised of six ore bodies, Zones 1-4 and Zones A and

113 B, which collectively have a strike length of approximately 1.7 km near the intersection of the P2

114 fault (~050°/45-60°) and the unconformity, ~500 m below surface (Fig. 2c) (McGill et al. 1993;

115 Alexandre et al. 2005; Bronkhorst et al. 2012). The total reserves of the McArthur River deposit

116 as of August 31, 2012, were 385.5 Mlbs U_3O_8 (Bronkhorst et al. 2012). All ore bodies are hosted

117 in the sandstone immediately above the unconformity except for the Zone 2 ore body which

118 occurs immediately below the unconformity and is bounded by the vertical quartzite (VQ) fault

119 and ~140° trending series of cross faults (Fig. 2b). Late minor remobilizations of uraninite

120 formed veinlets and fractures with pyrite, chalcopyrite and minor nickel-cobalt sulfarsenides

121 (McGill et al. 1993).

122   The P2 fault zone is a series of reverse faults with a strike length of approximately 13 km

123 (McGill et al. 1993) and has been traced seismically at least 2 km below the unconformity

124 (Hajnal et al. 2010). In the basement, the several fault planes of the P2 fault are mostly

125 constrained to graphite-bearing metapelite and trend parallel to the basement foliation (McGill,

126 1993). Reactivation of P2 faulting formed differences in the thickness of the basal conglomerate

127 at the unconformity and broad fracture and breccia zones in the sandstones and the reverse

128 movement of the P2 fault raised a wedge of basement rocks above the unconformity with the

129 vertical displacement of up to 80 m (McGill et al. 1993; Figs. 2a,b). The basement wedge is also

130 referred to as the "middle block" by workers (Bronkhorst et al. 2012) as it is offset by differential

131 movement of fault planes (Figs 2a,b). These offsets at the apex (or the "nose") commonly hosts

132 the uranium mineralization of McArthur River deposit and sporadic occurrences of low-grade (<1

133 $\%U_3O_8$) mineralization along the P2 fault (Fig. 2a). The P2 fault and basement rocks show minor

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134   lateral displacement by three sets of steeply dipping faults that strike 100 – 110° in the mine-site

135   area (Fig. 2b). These faults and offsets likely provided pathways for mineralizing fluids, but also

136   truncate high-grade zones, especially the Zone 2 ore body (Fig. 2b; McGill et al. 1993;

137   Bronkhorst et al. 2012).

138   Basement rocks along the P2 fault were intensely altered to form sudoite, illite, magnesio-

139   foitite, Fe-Mg chlorite, and sulfides (McGill et al. 1993; Adlakha et al. 2014). The hanging wall

140   basements rocks, including the ore-hosting wedge, commonly show intense alteration forming

141   sudoite and illite ± kaolin. Formation of illite and/or kaolin makes rocks creamy white in colour,

142   and this alteration is called "bleaching". Bleaching is common, especially in close proximity to

143   the fault, mineralization and the unconformity (McGill et al. 1993). The most intense alteration of

144   the basement rocks is found in close proximity to the Zone 2 ore body where sudoite and

145   magnesiofoitite are the dominate alteration minerals (Adlakha et al. 2014). In comparison, illite

146   with minor sudoite are the dominate alteration minerals in the moderately altered basement rocks

147   in unmineralized areas (the south-west portion of the P2 fault) and near the weakly mineralized

148   P2 Main deposit (Fig. 2b), that is "perched" higher in sandstones. APS minerals only occur in

149   highly altered rocks where primary metamorphic minerals and textures are altered.

Sampling

151   A total of 192 samples of metasedimentary rocks, predominately metapelites with fewer

152   pegmatite and quartzite, were collected from 27 different drill-holes along the P2 fault zone from

153   the McArthur River mine site to ~7 km southwest (Fig. 3). Of these, 139 samples were selected

154   for examination of APS minerals in thin sections. Out of the 139 samples, APS minerals were

155   found in only 17 samples. Among these 17 samples, APS minerals in 4 samples were too small

156   for quantitative analysis with electron microprobe analyzer (EPMA). Of these remaining 13

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157   samples (Table 1), nearly all were from metapelites located along the P2 fault (11 of 13) that

158   showed intense/pervasive alteration in which clay-sized minerals replaced most metamorphic

159   minerals and metamorphic textures were obliterated by alteration, fractures and/or veinings. In

160   this paper, samples collected within 50 m of the centre of the fault are considered to be associated

161   with P2 fault, as the fault is accompanied by splay structures and alteration extending outside the

162   fault zone.

163   The samples associated with the P2 fault were collected from varying distances to the

164   McArthur River uranium deposit (Fig. 2c; Table 1). MAC425 was collected within the Zone 2

165   ore body (Fig. 3A), MAC152 < 15 m from the Zone 2 ore body, MAC67 (Fig. 3b) and MAC85 <

166   20 m from the Zone 2 ore body, MAC63 < 50 m from the Zone 2 ore body, MAC43 and MAC44

167   <50 m from the Zone 3 ore body. MAC29 was within 1 m of low grade (< 1 wt% U_3O_8) uranium

168   mineralization disseminated within the sandstone (Fig. 2a), MAC404 was approximately 50 m

169   from low grade uranium mineralization within the sandstone. MAC117 and MAC35 are >500 m

170   away from low grade uranium mineralization in the sandstone, >1 km from the low grade P2

171   Main deposit and > 2 km from the McArthur River deposit.

172   Although 5 samples from the Bleached Zone were examined in detail, APS minerals were

173   found only in one sample (MAC17; Fig. 3c) of quartzite along the unconformity, > 250 m from

174   low grade mineralization and > 1 km from the McArthur River deposit (Fig. 2a,c). Twenty-two

175   samples of metasedimentary rocks of the Green, Red-Green and Red Zones outside the P2 fault

176   were examined and APS minerals were found only in one sample (MAC412) of strongly

177   hematized and chloritized metapelite from the Red-Green Zone in the footwall near the P2 Main

178   deposit (Figs. 2c, 3d). Here we use field terminology "Bleached Zone" and the "Red-Green

179   Zone" to reflect the samples position within the basement rocks as these terms were commonly

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180   used by geologists in the area. The Bleached Zone occurs along the unconformity and it refers to

181   a creamy-white colored zone where kaolin and illite predominate. The Red-Green Zone is a

182   physical mixture of hematitic Red Zone and chloritic Green Zone.

183   **Methods**

184   Thin sections were examined using an optical petrographic microscope with reflected and

185   transmitted light sources. Due to the very fine-grained nature of minerals in the samples, detailed

186   textural analysis was also carried out on carbon-coated polished thin sections using a JEOL

187   6610LV scanning electron microscope (SEM) at the University of Ottawa. Minerals were

188   identified using energy-dispersive spectroscopy with the spectrum acquisition time of 40 s and an

189   accelerating voltage of 20 kV.

190   Quantitative analysis for the major and minor elemental compositions of the APS

191   minerals was carried out using a JEOL 8230 EMPA at the University of Ottawa. APS minerals

192   were analyzed at an accelerating voltage of 15 kV, a beam current of 20 nA using a focused beam

193   of 5 μm (to account for alkali migration). Counting times were 20s on-peak and 10s off-peak for

194   all elements except for S (10s on and 5 s off), F (50s on and 25s off), Pr (20s on and 5s off) Cl

195   (25s on 12s off), P (10s on and 5s off), Si (10s on and 5s off) and As (20s on and 20 s off). The

196   mineral standards used were sanidine (Si, Al, K), hematite (Fe), apatite (Ca, P, F), albite (Na),

197   tugtupite (Cl), celestine (Sr, S), synthetic $NdPO_4$ (Nd), PrPO4 (Pr), $CePO_4$ (Ce), $LaPO_4$ (La),

198   ThO_2 (Th) and GaAs (As). The elemental concentrations were calculated after matrix interference

199   correction using ZAF. Elemental maps of selected APS grains were acquired at an accelerating

200   voltage of 10 kV with a 10 nA current at a counting time of 0.5 s per pixel with a total of 10000

201   pixels per image.

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202   APS minerals are small (mostly < 20 µm, rarely up to 40µm) and surrounded by quartz

203   and fine-grained alteration minerals (Fig. 4; Table 1-2), but it was necessary to use a broad

204   electron beam of 5 µm to minimize the loss of alkalis from APS minerals during the EPMA

205   analysis. This made it unavoidable for the surrounding minerals to contribute to the analytical

206   results. To evaluate the possible contributions of surrounding minerals in the chemical

207   composition obtained for the APS, their compositions were measured by EMPA. The contents of

208   SiO_2 were used to monitor the contribution of surrounding minerals because APS minerals rarely

209   contain Si. For the data showing Si, the amounts of K, Al, and Na of the surrounding phases were

210   subtracted from the analytical results. For example, for Al_2O_3 using the equation, Al_2O_{3APS}

211     $_{corrected}$= $Al_2O_{3APS\ analyzed}$ - $(SiO_{2APS\ analyzed}*Al_2O_{3matrix}/SiO_{2matrix})$. The remaining concentration

212   values were normalized to the original analytical total. Table 2 shows the contents of SiO_2 before

213   subtracting the contribution of surrounding minerals. The contribution of surrounding minerals

214   never exceeded 5% of the total.

215   Trace element contents in the APS minerals were determined using polished thick (>60

216   µm) sections by laser ablation inductively coupled plasma mass spectrometer (LA-ICP-MS) at

217   the Geological Survey of Canada, Ottawa, using a Photon-Machines Analyte193 ArF excimer

218   laser (λ = 193 µm) with Helex ablation cell and Agilent 7700x quadrupole ICP-MS. Helium gas

219   was used to transport ablated sample from the ablation cell and was mixed with Ar plasma (flow

220   rate of 1.05 mL/min) via a T-connector before entering the ICP. The detailed operating

221   conditions for the LA-ICP-MS instrument and the isotopes quantified are listed in Appendix

222   Table 1. During analysis, ~40 s of background signal with the laser turned off was collected and

223   then ablation was performed by a laser focused to 10 µm for a data acquisition time of ~60 s

224   (total time of 100 s for one analysis) for a total time of 100 s for one analytical cycle. The isotope

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225   counts were monitored during the analysis, and the acquisition time for the data of APS minerals

226   was adjusted (Appendix Fig. 1). Aluminum contents are similar among grains of APS minerals.

227   Therefore, the counts of these isotopes and their count ratios to Al in the sample and the reference

228   NIST610 (National Institute of Standards and Technology) were used to calculate the element

229   abundances (Longerich et al. 1996). There is no international standard that has the composition

230   similar to APS minerals. Therefore, the standard NIST610 was used as it contains high Al and it

231   is the most used standard. The elemental concentrations were obtained based on the count ratios

232   of elements to Al and the average Al contents in APS minerals of the sample determined by

233   EMPA (Table 2). The Al content was used because Al does not vary between the core and rim of

234   APS minerals (Table 2). The same grains could not be analyzed both by EPMA and LA-ICP-MS

235   because electron beam decomposes APS minerals (Appendix Fig. 2). EMPA and LA-ICP-MS

236   data is comparable (Appendix Fig. 3). One round of LA-ICPMS analysis consisted of seven

237   analyses of grains, bracketed by two analyses of the NIST610 reference and one analysis of the

238   BCR2G (Basalt, Columbia River) reference from USGS. The analysis of NIST610 shows that a

239   counting precision of > 98 % for all elements. Accuracy, determined by BCR2G, was > 90 % for

240   all elements except for Sc, Ti, Fe, Zn, Ce, Pr, Sm, Ho, Lu, Gd, Tb, Pb and Th which were > 85 %

241   and Cu, Y, Zr, Cr, Tm, Yb and Hf which were > 75%.

242   **Results**

243   **Mineral occurrence and distribution**

244   APS minerals were found in metapelites along the 7 km section of the P2 fault examined

245   (Fig. 2). APS minerals were found only in one sample from the Bleached Zone (sample MAC17

246   in quartzite) (Figs. 2a, 4i; Table 1). APS minerals are rare in the basement rocks distal from the

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247   unconformity and outside the P2 fault. They were found in only one sample (sample MAC 412)

248   in metapelite that contains hematite and chlorite alteration (Fig. 3d) in the footwall 100 m from

249   the P2 fault, 50 m below the unconformity and 100 m away from uranium mineralization (Fig.

250   4h; Table 1). APS minerals were not observed in samples along the VQ fault (Fig. 2b) or in

251   samples of the least-altered basement rocks.

252   APS minerals along the P2 fault occur together with fine-grained sudoite and/or illite

253   intergrown with magnesiofoitite (Adlakha et al. 2014; Figs. 4a-f). Less commonly, APS minerals

254   occur with kaolin and illite, or a mixture of clinochlore and sudoite. In the Bleached Zone

255   sample, APS minerals occur with kaolin and illite (Fig. 4i). APS minerals are rare in the

256   transitional Red-Green Zone and occur predominately with clinochlore (Fig. 4h).

257   APS minerals are small (mostly < 20 μm, rarely up to 40 μm), transparent, pseudo-cubic

258   (rarely hexagonal) crystals, disseminated and/or clustered in fine-grained clay minerals (Fig. 4).

259   There is no evidence of dissolution between APS minerals and surrounding clay minerals. The

260   texture suggest that they are in equilibrium (Figs. 4a-j,l). APS minerals are commonly zoned.

261   Zoning may be observed using plane polarized light microscopy as some cores show high relief.

262   SEM BSE-images commonly show darker cores with lighter rims (Fig. 4c), although grains with

263   lighter cores and darker rims are also observed (Fig. 4h). Darker parts in BSE images are due to

264   greater amounts of Sr and Ca, and brighter parts contain higher LREE.

265   In all samples, APS minerals commonly occur in contact and/or are spatially associated

266   with zircon (Figs. 4f,g), primary apatite (Fig. 4l), or sulfide minerals, such as pyrite (Fig. 4k) and

267   lesser chalcopyrite (Fig. 4d). Zircon grains associated with APS minerals are commonly fractured

268   and/or partially dissolved and rimmed by xenotime (cf. Quirt et al. 1991) (Fig. 4g). Apatite forms

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269   subhedral, rounded crystals and APS minerals also occur with small hydrothermal fluorapatite

270   crystals as disseminations or clusters. APS minerals commonly contain inclusions of sulfides or

271   Fe-oxide (Figs. 4h,k,l). APS minerals in the Zone 2 ore body are in close proximity (within the

272   same thin section) with uraninite.

273   **APS mineral chemistry – major elements**

274   The APS mineral formulae were calculated based on 6 cations (Table 2) as the ideal

275   formula is expressed as $AB_3(XO_4)_2(OH)_6$, where A = mono-, di-, tri- or, more rarely, tetravalent

276   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+}.

277   Cation charges were allocated using the following:

278   i.   the X-site was filled with P^{5+}, S^{6+}, As^{5+},

279   ii.   the B-site was filled by Al^{3+}, then Fe^{3+} to have 3 cations,

280   iii.   the A site was then filled by remaining cations.

281   High contents of trivalent cations in the A site create excess cation charges. To compensate for

282   this, $PO_3(OH)^{2-}$ is assigned for $(PO_4)^{3-}$, as has been used by previous researchers (e.g., Gaboreau

283   et al. 2007).

284   Along the P2 fault, APS minerals occur predominately with sudoite and lesser illite and

285   magnesiofoitite, in intensely altered metapelite and pegmatite. These APS minerals contain high

286   ΣLREE (0.35 – 0.58 apfu; LREE = La + Ce + Pr + Nd) relative to Sr (0.16 – 0.32 apfu) and Ca

287   (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-}

288   (<0.01 apfu) (Table 2). Ce is high (0.15 – 0.27 apfu) relative to La (0.09 – 0.17), Pr (<0.01 – 0.03

289   apfu), producing $[Ce]_N$ /$[Ce]_N$* of ~0.8 – 1.6, where $[Ce]_N$* = $\sqrt{([La]_N \cdot [Pr]_N)}$). Cores of zoned

290   grains are enriched in Sr-, Ca-, and S, and rims contain high LREE and P (Fig. 5a; Table 2).

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291 Within the cores, Ca and P contents are inversely correlated with Sr and S contents (Fig. 5a).

292 Narrow width of zoning and small size of grains prevented acquisition of quantitative

293 compositions of individual zones excluding coarse grains in MAC152 (Table 2). Therefore, most

294 data presented in Table 2 represents mixtures (referred to as mixed data) of compositional zones

295 identified in SEM-BSE.

296 APS minerals in the sample of Bleached Zone quartzite (sample MAC17) contain high Sr

297 (0.68 apfu) relative to Ca (0.16 apfu) and ΣLREE (0.13 apfu) and high SO_4^{2-}(0.54 apfu; Table 2).

298 APS minerals are abundant in the Red-Green Zone sample of the basement footwall

299 (MAC412) near the P2 Main deposit. APS minerals occur with clinochlore and sudoite and

300 contain high AsO_4^{3-}, ($\sim$ 0.63 apfu), Fe^{3+} (0.16 apfu), and Ce ($\sim$0.32 apfu) showing positive Ce

301 anomalies ([Ce]/[Ce]*) of up to 6. APS minerals from this sampl are also zoned with high-Ce

302 cores, and a Ca- and P-rich inner rim and Sr-rich outer rim (Fig. 5b). APS minerals in this sample

303 were relatively coarse-grained; therefore, individual core and rims were analyzed in two grains

304 (Table 2). The data shows that the cores contain high As (0.78 apfu) and low P (0.92 apfu)

305 relative to the rim (0.26 and 1.46 apfu, respectively; Table 2).

306 **APS mineral chemistry – trace elements**

307 LA ICP-MS analyses were conducted on relatively coarse-grained (>10 μm) APS

308 minerals proximal to the Zone 3 (sample MAC44) and Zone 2 ore deposits (samples MAC63 and

309 MAC85). Counts of all elements were monitored during the analysis to detect mineral inclusions

310 and contributions of surrounding minerals. Mineral inclusions should give sharp increases in the

311 counts of elements, but no such spikes were observed during the analysis, confirming the lack of

312 mineral inclusions. None of surrounding minerals contain any significant concentrations of

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313   elements described below. Counts of elements, such as U, Y, Pb and Th were at background

314   levels in surrounding minerals and only high when the laser beam hit APS grains. Unlike clays,

315   APS minerals show high counts of LREE, Sr, Ca and P (Appendix Fig. 1). This confirms that

316   these elements are in the APS crystal structure and were not incorporated from surrounding

317   minerals. Furthermore, different grains from individual sections yielded comparable

318   concentrations of minor and trace elements, suggesting that these trace elements originate from

319   APS minerals and that the values are minima since the dilution effects by the surrounding

320   minerals were not corrected. The dilution effects by surrounding minerals are confirmed by the

321   detection of a significant Si (48000 – 99000 ppm) during the ablation of the APS minerals.

322   APS minerals in P2 fault proximal to Zone 3 (MAC44) ore deposit contain appreciable Se

323   (130 ppm), U (0.39 – 0.88 ppm), Pb (160 - 180 ppm), and Th (1100 - 1600 ppm). Similarly, APS

324   from sample MAC63 (~50 m) from Zone 2 ore and ~ 20 m into the hanging-wall of the P2 fault)

325   show appreciable Se (100 – 160 ppm), U (1.7 – 4.2 ppm), Pb (82 – 190 ppm), and Th (1000 –

326   1400 ppm). Sample MAC85, from within 20 m of Zone 2 ore and directly within the P2 fault,

327   contains APS with relatively high U (16 ppm), Pb (260 ppm), and Th (2300 ppm); this sample

328   also contains high LREE (0.54 apfu; Table 2). Similar to samples MAC44 and MAC63, sample

329   MAC85 showed appreciable Se (130 ppm). Combined with the EPMA data of major elements

330   (La, Ce, Pr, Nd), these APS minerals from the P2 fault area contain high LREE relative to HREE

331   ($[LREE]_N/[HREE]_N$ = 800 – 2500; Fig. 6) and show low S/Se weight ratios, ranging from 100 –

332   150.

15

333 **Discussion**

334 **Major element compositions of APS minerals**

335 The following elemental relationships are observed:

336   i.   the P contents positively correlate with LREE and both inversely correlate with Sr and S

337   (Figs. 5a, 7c,d); the LREE inversely correlate with Ca (Figs. 5a, 7d);

338   ii.   the S contents positively correlate with Sr and inversely correlate with Ce (Figs. 5a, 7b).

339   iii.   high Ca correlates with high P (Figs. 5a,b);

340   iv.   the As contents inversely correlate with P;

341   v.   high As APS minerals contain high Ce relative to other REE (Fig. 7a).

342 The above relationships and cations in A-site and X-site (Fig. 8) suggest the presence of the

343 following end-members:

344   i.   high LREE and P contents correspond to high proportions of florencite

345         $(REE)Al_3(PO_4)_2(OH)_6$ (Figs. 8a-c);

346 high S and Sr contents correspond to high proportions of svanbergite $SrAl_3(PO_4)(SO_4)(OH)_6$ with

347 a minor goyazite component $SrAl_3(PO_4)_2(OH)_6$ (Figs. 8a-d);

348   ii.   high Ca contents correspond to high proportions of crandallite $CaAl_3(PO_4)_2(OH)_6$ (Figs.

349   8a,b,d);

350   iii.   high As and high Ce contents correspond to high proportions of arsenoflorencite (Ce,

351         $REE)Al_3(AsO_4)_2(OH)_6$ (Figs. 8a,b).

352 APS minerals show wide compositional variations, but all can be expressed using the above five

353 end members (crandallite, goyazite, svanbergite, florencite, arsenoflorencite).

16

Spatial, chemical and temporal variation of APS minerals and associated clay minerals

354

355   Along the entire studied range of the P2 fault, APS minerals occur with sudoite (± illite,

356   magnesiofoitite) in metapelite and pegmatite. The APS minerals are florencitic, but contain

357   significant Ca, Sr, and SO_4^{2-} reflecting a minor component of svanbergite, mainly as core (Fig.

358   9).

359   Gaboreau et al. (2005, 2007) found that APS minerals proximal to uranium deposits

360   contain high LREE and P relative to those in intermediate and distal areas (Fig. 9). The present

361   study found a large compositional variation of APS minerals even within the ore compared to the

362   range presented by Gaboreau et al (2005, 2007) and compositional variation do not correlate with

363   distance from uranium mineralization (Fig. 9). For example, the (LREE+P)/(Ca+Sr+S) ratios of

364   APS minerals near (<1 m) the uranium ore range from 1.6 to 5.6, whereas those from barren

365   samples far (>500 m) from mineralization vary from 2.8 - 4 (Fig. 9). We suggest that our data

366   reflects the evolution of fluids in the ore zone where the earlier fluids contained high in Ca, Sr

367   and SO_4^{2-}, and evolved to have high LREE and P. This proposed interpretation is supported by

368   compositional zoning of APS minerals with Ca, Sr and S -rich cores and LREE and P -rims (Fig.

369   5a).

370   APS minerals are abundant with kaolin and illite in one sample of the Bleached Zone

371   (MAC17) along the unconformity. These grains are Sr- and S-rich and similar in composition

372   within the sample but not with the APS minerals found along the P2 fault (Fig. 9). The average

373   composition   of   the   APS   minerals   is

374     $Ca_{0.16}Sr_{0.68}Ce_{0.05}La_{0.03}Nd_{0.04}Pr_{0.01})(Al_{2.96}{}^{III}Fe_{0.02})(PO_3O_{0.94}OH_{0.06})_{1.50}(SO_4)_{0.54}(AsO_4)_{0.01}(OH)_{6,}$

17

375   svanbergite$_{0.54}$-crandallite$_{0.16}$-goyazite$_{0.14}$-florencite$_{0.13}$. The data are comparable to APS mineral

376   compositions in distal sandstones by Gaboreau et al. (2007) (Fig. 9).

377   One Red-Green Zone sample of intensely altered metapelite (MAC412) footwall to the P2

378   fault, contain APS minerals with As- and Ce-rich cores and Ca, Sr, and S-rich rims together with

379   clinochlore and sudoite. The grains show similar Ca, Sr, and S contents with varying LREE and P

380   due to the presence of As that substitutes for P (Figs. 7a and 9). The average composition of these

381   grains   is $(Ca_{0.31}Sr_{0.22}Ce_{0.32}La_{0.04}Nd_{0.02}{}^{III}Fe_{0.15})(Al_{2.92}{}^{III}Fe_{0.08})(PO_3O_{0.83}OH_{0.17})_{1.11}(SO_4)_{0.18}$

382     $(AsO_4)_{0.68}(OH)_6$, arsenoflorencite(-Ce)$_{0.39}$-crandallite$_{0.31}$-svanbergite$_{0.18}$-goyazite$_{0.12}$. This is the

383   first documented occurrence of arsenoflorencite(-Ce) in Athabasca Basin.

384   APS minerals from the McArthur River deposit and the P2 fault show cores of

385   svanbergite-crandallite-goyazite rimmed by florencite (Figs. 4c-e,k,l, 5a). APS minerals from the

386   Red-Green Zone contain arsenoflorencite-(Ce) cores rimmed by svanbergite-crandallite-goyazite

387   (Figs. 4h, 5b, 8b). APS minerals of the Bleached Zone are svanbergite-crandallite-goyazite (Fig.

388   8). The zoning suggests the crystallization sequence of APS minerals in the study area. Early

389   crystallization of arsenoflorencite (Ce) was followed by svanbergite-crandallite-goyazite, and

390   finally florencite.

391   **Nature of fluids responsible for APS mineral formation**

392   APS minerals in the Bleached Zone sample contain high SO_4^{2-} contents, up to 0.59 apfu

393   (Figs. 7b,d, 8b-d), indicating relatively oxidizing conditions for their formation. These APS

394   minerals have close to svanbergite end-member composition (Fig. 10), with a minor goyazite and

395   crandallite component (Figs. 7b,d-f; 8a-d). The grains coexist with kaolin and illite (Fig. 4I),

396   which is the diagenetic assemblage in the Athabasca Group sandstones (Hoeve and Quit 1984;

397   Quirt 2001). Furthermore, the composition of the APS minerals is similar to those of diagenetic

398   origin reported in Athabasca and Kombolgie sandstones (Gaboreau et al. 2005, 2007), and other

399   sedimentary basins worldwide (Spötl, 1990; Gaboreau et al. 2005, 2007; Pe-Piper and Dolansky

400   2005; Gall and Donaldson 2006; Fig. 10). Therefore, the APS minerals of the Bleached Zone

401   along the unconformity most likely crystallized from an oxidizing, Ca-, Sr- and SO_4-rich,

402   diagenetic fluid of the overlying sandstones.

403   The oxidizing conditions of diagenetic fluids from sandstones are recorded as relict cores

404   of the APS minerals along the P2 fault in the basement (Figs. 4, 5a). These cores contain high Ca,

405   Sr and S and are similar in composition to diagenetic APS minerals in sandstones described

406   above. The S/P ratios of APS minerals as whole grains along the P2 fault are relatively low (<

407   0.16) compared to those of the Bleached Zone (0.36; Fig. 11). The lowest S/P ratios (< 0.06) are

408   found in areas of Zone 2 ore in the basement (Fig. 11b). The data shows that the SO_4^{2-} contents in

409   fluids decreased from the unconformity to the P2 fault and from non-mineralized areas along the

410   P2 fault to ore zone. This indicates the change from a relatively oxidized to a relatively reduced

411   environment. This modification of fluid chemistry may have taken place due to interaction of

412   fluids with graphite-rich basement rocks, as has been suggested by Gaboreau et al (2007).

413   Alternatively, it was caused by reduced fluids originated from the graphite-rich basement rocks

414   and supplied through faults. In either case, this redox change closer to the uranium ore is

415   consistent with the reduction of U^{6+} to U^{4+} necessary for the precipitation of uraninite. Therefore,

416   S/P ratios of APS minerals record the reduction of fluids associated with the uranium

417   mineralization

418   The spatial association of florencitic APS minerals with the McArthur River uranium

419   deposit (Fig. 2b) and their abundance within the deposit suggest the close relationship between

19

420   florencite and the uranium mineralization. This observation is consistent with that of Gaboreau

421   (2005, 2007). The APS minerals in metapelite and pegmatite along the entire 7 km of the P2 fault

422   studied are predominantly florencite with minor components of svanbergite-svanbergite-

423   crandallite-goyazite (Figs. 4d-e, 9). The alteration assemblage of sudoite, magnesiofoitite and

424   illite is also similar all along the P2 fault including the ore zone. The evidence suggests that

425   similar fluids passed along the entire P2 fault. These fluids were likely uranium-bearing because

426   APS minerals contain uranium (up to 16 ppm; Table 3).

427   The Red-Green Zone sample of metapelite (sample MAC412; Fig. 3d), 100 m laterally

428   away from the P2 fault contains As- and LREE-rich APS minerals (Figs. 7a,d, 8b; Table 2).

429   Arsenic in APS minerals occur as As^{5+}, replacing P^{5+} in the X-site of the crystal structure. These

430   As-bearing crystals show prominent zoning with cores of arsenoflorencite-(Ce) and rims of

431   crandillite-goyazite and svanbergite solid-solution (Figs. 5b, 7a,c; Table 2) with sharp

432   boundaries. The zoning suggests that arsenoflorencite-(Ce) formed earlier than the svanbergite-

433   goyazite of diagenetic origin. This arsenoflorencite-(Ce) may have formed in the very early stage

434   of diagenesis. If this is the case, As-rich APS minerals should be observed in sandstones.

435   However, there is no record of As-rich APS minerals in the Athabasca sandstone. Furthermore,

436   sharp boundaries between cores and with rims suggests that As-rich APS minerals formed before

437   the sandstone diagenesis. We suggest that, arsenoflorencite(-Ce) cores may have formed during

438   the paleo-weathering before the deposition of the Athabasca sandstones. This proposed

439   interpretation is further supported by the presence of As^{5+} in the APS minerals. Although As

440   contents are high in organic-rich shale (e.g., Ketris and Yudovich 2009), As is mostly fixed in

441   sulphide minerals (e.g., Ryan et al., 2013). For As to be incorporated in the APS minerals, it

20

442   must be oxidized to As^{5+}, which is stable in oxidizing, near-surface conditions (Smedley and

443   Kinniburgh 2002).

APS minerals related to uranium deposits and role of P2 fault

445   It has been suggested that APS minerals with florencitic compositions are

446   contemporaneous with uranium mineralization based on their occurrences within uranium

447   deposits (Quirt 1991; Gaboreau et al. 2005, 2007; Mercadier et al. 2011). Here we have shown

448   that APS minerals of florencitic composition are found along a 7 km strike length of the P2 fault,

449   even in areas barren of mineralization (Table 2; Fig. 9); although, as previously discussed, APS

450   minerals with the highest florencite component (reflecting relatively reducing conditions) are

451   found in proximity to ore (Figs. 9, 11). The APS minerals also contain elevated uranium contents

452   (Table 3; Fig. 6), suggesting that florencitic APS minerals crystallized from uranium-bearing

453   fluids that became reduced. The evidence supports that florencite was contemporaneous with

454   uranium mineralization.

455   Florencitic APS minerals are not found in the basement greater than ~50 m from the

456   centre of the P2 fault (Table 1; Fig. 9). The distribution of the APS minerals constrains the extent

457   of the fluid footprint, and suggests that the entire P2 fault was a conduit for an oxidizing

458   uranium-bearing fluid during mineralization. The P2 fault was also a site of redox change where

459   an initial oxidizing fluid became modified and relatively reducing.

Implication

461   APS minerals are very small in size, but ubiquitous in the altered metasedimentary rocks

462   along the P2 fault, which hosts the McArthur River uranium deposit. Previous researchers noted

463   the spatial association of florencitic APS minerals and uranium deposits and suggested their use

21

464   as an exploration vector (e.g., Gaboreau et al. 2007). Our study reveals that APS minerals record

465   the timing and characteristics of geological events, from paleoweathering, diagenesis to

466   uraniferous hydrothermal activity. We conclude that oxidizing diagenetic fluids travelled along

467   P2 fault and formed svanbergite-crandallite-goyazite. The fluid evolved to become reducing

468   through interaction with the basement rocks and formed florencite rims. Our study shows that

469   APS minerals are an excellent mineralogical tool to fingerprint fluid pathways. APS minerals

470   with similar chemistry (high florencite component) are found along a 7 km of strike length of the

471   P2 fault, including areas barren of uranium mineralization. This suggests that uranium-bearing

472   fluids likely passed along the entire P2 fault, but only produced uranium mineralization in

473   localized areas. This study confirms that APS minerals are good indicators in identifying

474   alteration related to uranium mineralization, thus they may be used, especially when having a

475   florencitic composition, to identify fertile structures associated with uranium deposits.

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612   **Figure Captions**

613   **Figure 1.** A map showing the location of the major uranium deposits (red squares), including

614   McArthur River deposit, and basement structures (dashed lines), including the P2 fault, in the

615   Athabasca Basin (modified from Jefferson et al., 2007). The south-eastern margin of the

616   Athabasca Basin is underlain by the basement rocks of the Wollaston and Mudjatik Domains of

617   the western Churchill Province. An insert shows the locations of the Athabasca basin relative to

618   other two Mesoproterozoic sedimentary basins: Hornby and Thelon basins. Major shear zones:

619   BB = Black Bay, BLSZ= Black Lake Shear Zone, CB = Cable Bay, GR = Grease River Shear

620   Zone, RO = Robbilard, VRSZ = Virgin River Shear Zone.

621   **Figure 2.** Schematic cross-sections **(a, b)** showing the distribution of APS minerals, some sample

622   locations (stars) and a geologic map **(c)** at the unconformity showing sample locations. **(a)** APS

623   minerals are found in the P2 fault proximal to low-grade mineralization (sample MAC29) and in

624   the Bleached Zone (BZ) in quartzite (sample MAC17); **(b)** APS minerals are found in the P2

28

625 fault proximal to the Zone 2 ore body (samples MAC63, 67, 85, 152, 425). APS minerals were

626 not found in samples from the footwall and hanging-wall (indicated ``No APS``) nor in samples

627 collected from the VQ fault. **(c)** An interpreted geological strip map at the unconformity showing

628 the P2 fault, the locations of sampled drill-holes and ore bodies, sample locations, and the sites of

629 the cross sections AB. The P2 fault is essentially barren in the southwestern part. Low-grade

630 mineralization occurs along the middle and southeast (P2 Main deposit) portions of the P2 fault.

631 APS minerals were found in one sample (sample MAC412) of the Red-Green Zone in the

632 footwall proximal to the P2 Main mineralization. Z1 - 4 = Zone numbers of ore body at the

633 McArthur River deposit; uc = unconformity.

634 **Figure 3.** Photographs of selected drill-core samples; **(a)** uranium ore of the Zone 2 ore body and

635 P2 fault (MAC425); **(b)** intensely sudoite-altered pegmatite from the P2 fault (MAC67); **(c)**

636 quartzite from the Beached Zone along the unconformity (MAC17); and **(d)** hematitized and

637 chloritized metapelite from the Red-Green Zone (MAC412). Sample locations are shows in Fig.

638 2.

639 **Figure 4.** Photomicrographs **(a, b, f)** and SEM BSE **(c-e, g-l)** images of APS minerals. **(a)**

640 Disseminated APS grains in fine-grained illite (Ilt) and with hematite (Hem); **(b)** Clustered APS

641 grains in contact with an aggregate of feather-textured, magnesiofoitite (Mgf) and a mixture of

642 sudoite+illite+magnesiofoitite (Sud/Ilt/Mgf); **(c)** Zoned APS grains in magnesiofoitite; **(d)**

643 Oscillatory zoned APS crystals disseminated in a mixture of clinochlore+illite+magnesiofoitite

644 (Clc-Ilt-Mgf) with chalcopyrite (Ccp); **(e)** Zoned APS crystals clustered in

645 magnesiofoitite+sudoite; **(f)** Zoned APS crystals, apatite, and magnesiofoitite in a mixture of

646 sudoite+illite; **(g)** Partially corroded zircon (Zrn) mantled by xenotime (Xtm) and APS grains; **(h)**

647 Aggregate of euhedral, zoned APS crystals in a clinochlore+sudoite matrix; **(i)** Disseminated,

29

648   sub-hedral APS grains in fine-grained kaolin (Kln); **(j)** A mixture of APS minerals and quartz

649   rimming coarse quartz grain; **(k)** APS grain in contact with pyrite (Py); **(l)** APS crystal with

650   inclusions of Fe-oxide in contact with apatite (Ap). Sample number and location are indicated at

651   the bottom left corner of each image. Qz = Quartz

652   **Figure 5.** X-ray maps of APS minerals showing zoning with respect to Ca, Ce, Sr, S and P

653   obtained by wave-length dispersive spectra of EPMA: **(a)** sample MAC425 from the P2 fault and

654   Zone 2 ore body and **(b)** sample MAC412 from the Red-Green Zone (locations shown in Fig. 2a

655   and 2b; Table 2 for quantitative chemical data).   svan-goy-crand = svanbergite-goyazite-

656   crandallite. Note that very dark areas in BSE images contain low mass elements and they are not

657   holes or other mineral inclusions.

658   **Figure 6.** Chondrite-normalized REE, U, Th, Pb and W for APS grains from sample MAC44

659   (along the P2 fault proximal to the Zone 3 ore body of the McArthur River deposit) and from

660   samples MAC63 and MAC85 (close to Zone 2 ore). The abundance of these elements was

661   obtained using EPMA (La, Ce, Pr and Nd) and LA-ICP-MS (Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm,

662   Yb, Lu, W, Pb, Th and U). Error bars are not shown in the diagram because the uncertainty of the

663   analysis (< 10 %) is smaller than the size of symbols. Sample locations are in Figure 2c and

664   Table 1. Each line represents one APS grain. Chondrite values from McDonough and Sun (1995).

665   **Figure 7.** Binary plots showing substitution and elemental relationships of APS minerals based

666   on EPMA data: **(a)** As vs P (black) and As vs. Ce (gray); **(b)** S vs. Sr (black) and S vs. Ce (gray);

667   **(c)** P vs Sr (black) and P vs. LREE (gray); **(d)** S vs. As (black) and S vs. P (gray); and **(e)** LREE

668   vs. Sr (black) and LREE vs. Ca (gray). Each data point represents one grain. P2 fault = P2 fault

669   samples (triangles). BZ = Bleached Zone sample (stars), RGZ = Red-Green Zone sample

670   (crosses).

30

671   **Figure 8.** Compositions of APS minerals plotted on ternary diagrams. End member minerals are

672   indicated at the apexes of the diagrams. **(a)** Ca-Sr-LREE; **(b)** P-S-As; **(c)** S-Sr-LREE; **(d)** S-Sr-

673   Ca. Each data point represents one grain. P2 fault = P2 fault samples (triangles). BZ = Bleached

674   Zone sample (stars), RGZ = Red-Green Zone sample (crosses).

675   **Figure 9.** Cross-plot showing coupled substitution of Ca-Sr-S for LREE-P for APS minerals

676   along the P2 fault (triangles), and within the Bleached Zone (BZ) sample (stars) and Red-Green

677   Zone (RGZ) (crosses). P2 fault samples are color coded with respect to distance in metre from the

678   uranium mineralization (McArthur River deposit and low-grade): red filled triangles represents

679   sample < 1 m from ore (MAC425 and MAC29), orange filled triangles were < 15 m from ore

680   (MAC152), purple filled triangles were < 20 m from ore (MAC67 and MAC85), open green

681   triangles were < 50 m from ore (MAC43, MAC44, MAC63 and MAC404) and open blue

682   triangles were of unmineralized areas >500 m from the ore (MAC117 and MAC135). Each data

683   point represents one grain. For comparison, the diagram shows the compositional ranges of APS

684   minerals determined by Gaboreau et al (2005, 2007) from the Athabasca Basin (fields with

685   various shades of gray) and Kombolgie Basin, Australia (field with various shades of blue).

686   **Figure 10.** An alunite-goyazite-crandallite [S-Sr-Ca] ternary plot showing compositions of APS

687   minerals from the P2 fault (P2; triangles), the Bleached Zone (BZ; stars) sample, and the Red-

688   Green Zone (RGZ; crosses) sample. Each data point represents one grain. For comparison, the

689   compositional ranges of diagenetic APS minerals from various sedimentary units are shown:

690   diagenetic APS minerals of the Athabasca and Kombolgie basins are represented by grey dotted

691   field (Gaboreau et al. 2005, 2007) and diagenetic APS minerals of the Chaswood Formation (Pe-

692   Piper and Dolansky, 2005), Hornby Basin and Thelon Basins (Gall and Donaldson, 2006) and

693   Mitterberg Formation (Spötl, 1990) are collectively represented by the grey field. APS minerals

694   associated with uranium deposits of the Athabasca and Kombolgie Basin (Gaboreau et al. 2005,

695   2007) are represented by the black dashed field.

696   **Figure 11:** Spatial variation of S/P ratios for APS minerals. The average S/P ratio (mixed data,

697   see Table 2) of APS minerals within a sample is expressed as a red, bold, italicized number next

698   to its corresponding sample ((a) and (b)) or drill-core (c) location.

Appendix

700   **Figure 1: (a)** A graph of the LA-ICP-MS analysis of an APS grain from sample MAC85

701   showing element counts (major and trace) vs. time in seconds. High counts of Y, Th and U

702   correlate with high counts of the major elements in APS minerals (eg., Ce, La, Al, and Sr). This

703   graph clearly shows that trace elements (such as Y, Th and U) are incorporated in the APS crystal

704   structure and were not present as inclusions or contributed by surrounding minerals of sudoite

705   (Sud) or illite (Ilt). **(b)** The same graph as shown in (a) but counts/sec of each element is

706   normalized to that of Sr.

707   **Figure 2:** An APS mineral **(a)** before EMPA analysis and **(b)** after analysis showing beam

708   damage. **(c)** A laser pit after LA ICP-MS analysis. (a) and (c) are BSE images and (b) is a

709   secondary electron image.

710   **Figure 3:** A binary plot comparing the average concentrations of Ca (green), Fe (red), Pr (cyan)

711   and Nd (blue) in APS mineral grains from samples MAC44 (diamonds), MAC63 (x), and

712   MAC85 (crosses) obtained with EMPA (Table 2) and LA ICP-MS (Table 3). Horizontal and

713   vertical bars represent one standard deviation of the data (Tables 2 and 3). LA ICP-MS data of

714   sample MAC85 is of one grain.

32

Table 1: Sample descriptions.

zone[a]	DDH[b]	sample	depth[c]	proximity to P2 fault[d]	proximity to uc[d]	proximity to U-min[d]
P2	MC370	MAC29	560.2 in the P2 fault zone		u/c (Fig. 2A)	<1 m from lg U-min in ss
	H729	MAC43	49.5 in the P2 fault zone		~15 m	<50 m from Z3 ore
	H729	MAC44	64.5 ~15 m laterally from P2 in fw		~15 m	<50 m from Z3 ore
	H201	MAC63	7.6 ~30 m laterally from P2 in hw		~20 m	<50 m from Z2 ore
	H201	MAC67	30.8 the P2 fault zone		~20 m	<20 m from Z2 ore
	H493	MAC85	17.7 in the P2 fault zone		~20 m	<20 m from Z2 ore
	H203	MAC152	62 in the P2 fault zone		~50 m	<15 m from Z2 ore
	MC410	MAC404	542.7 ~50 m laterally from P2 in hw		~15 m	~50m laterally from lg in ss
	H3380	MAC425	57.1 in the P2 fault zone		~50 m	Z2 ore
	MC361	MAC117	523.3 in the P2 fault zone		~25 m	>500 m from U-min
	MC362	MAC135	520.2 ~40 m above P2 in hw		~10 m	>500 m from U-min
GRZ	MC346	MAC412	669 ~100 m laterally from P2		~50 m	~100 m below P2 Main
BZ	MC344	MAC17	499.4 ~250 m laterally from P2 in hw		<1 m	>250 m from U-min

Notes:

[a]P2 = P2 fault sample; RGZ = Red-Green Zone sample; BZ = Bleached Zone sample

[b]DDH= diamond dril-hole number

[c]drillhole with the prefix H are collared underground, therefore sample depths are not from the surface

[d]U-min= uranium mineralization in the McArthur River deposit; fw= footwall; hw = hangingwall; lg = low-grade (<1 wt% U_3O_8); ss

[e]Ap = apatite; Clc = clinochlore; Dck = dickite; Drv = dravite; Fe-Mg chl = Fe-Mg Chlorite; fg = fine-grained; Gr = graphite; Ilt = illi

degree of alteration and rock-type[d]	APS occurrence	clay[e]	mineralogy[f]
moderately altered mp	isolated, 3-10 µm	Sud	Mgf, Xtm, Qz
green intensely altered graphitic mp	isolated, 3-10 µm	Sud/Ilt	Mgf, Gr, Py, Ap, Zrn, Xtm
red and white intensely altered peg	zoned, clustered, 5-20 µm	Sud/Ilt	Hem, Mnz, Zrn, Qz, Gr, Py
green intensely altered mp	zoned, clustered, fragmented, 1-20 um	Sud	Ilt, Rt, Ap, Fe-Mg Chl, Ilt, Py, Qz
green intensely altered peg	zoned, clustered, 5-20 µm	Sud	Mgf, Ilt, Py, Ap, Qz
intensely altered graphitic mp w/ peg boudins	zoned, disseminated, 5-20 µm	Sud/Ilt	Drv, Py
green-white intensely altered mp	zoned, disseminated, 5-30 µm	Sud/Clc	Mgf, Ill, Py, Qz, Ccp
red moderately altered mp w/ peg boudins	disseminated, < 1 µm	Kln	Hem, Ap
green intensely altered mp with U-ore	some cores missing, isolated, 3-10 µm	Mgf/Sud	U, Hem
white-green intensely altered peg	isolated, 3-10 µm	Ilt	Fe-Mg Chl, fg Qz, Qtz
red-green intensely altered peg	disseminated, < 1 µm	Ilt	Hem, Rt, fg Qz
red-green intensely altered mp	large clusters up to .5 mm, 10-40 µm	Sud/Clc	Hem
quartzite with bleached matrix	disseminated, < 1 µm	Kln	Ilt, Zrn, Qz

= sandstone; uc = unconformity; peg = pegmatite; mp = metapelite

ite; Mgf = magnesiofoitite, Py = pyrite; Qz = quartz; Rt = rutile sud = sudoite, U = uraninite; xtm = xenotime; zrn = zircon

Table 2: EMPA major element oxide data and atomic proportion formula units for APS minerals.

sample	MAC67	MAC85		MAC152 Sud/Clc		MAC404	MAC117	MAC425	MAC
a	Sud	Sud/Ilt				Kln	Ilt	Mgf/Sud	Ilt
b	Mixed	Mixed	Mixed	Core	Rim	Mixed	Mixed	Mixed	Mix
# grains	10 1σ	11 1σ	8 1σ	3 1σ	3 1σ	10 1σ	10 1σ	9 1σ	3
CaO	2.72 0.30	2.70 0.36	2.86 0.44	2.92 0.24	2.37 0.31	3.40 0.18	2.68 0.36	2.79 0.67	3.14
SO$_3$	1.68 0.77	1.69 1.29	2.06 0.53	2.58 0.44	1.14 0.30	0.94 0.37	3.70 0.46	3.43 1.48	3.40
Al$_2$O$_3$	28.96 1.56	31.26 1.30	32.01 1.08	32.30 0.31	31.26 0.63	31.13 1.25	32.22 1.07	32.37 1.10	29.49
Fe$_2$O$_3$	0.85 0.77	0.54 0.51	0.54 0.24	0.58 0.24	0.44 0.05	0.91 0.63	0.82 0.71	0.96 0.57	1.40
Nd$_2$O$_3$	3.26 0.44	3.29 0.79	2.77 0.50	2.44 0.33	3.80 0.47	4.26 0.37	2.16 0.42	2.20 0.36	1.41
Pr$_2$O$_3$	0.94 0.16	0.87 0.23	0.76 0.21	0.75 0.08	0.97 0.08	0.96 0.06	0.60 0.12	0.70 0.15	0.50
Ce$_2$O$_3$	8.67 1.21	8.33 1.09	7.81 0.78	7.74 0.37	9.44 0.54	7.50 0.48	7.85 0.80	7.50 1.78	8.81
La$_2$O$_3$	5.40 0.82	5.55 0.31	5.18 0.47	5.11 0.29	5.33 0.42	3.58 0.19	5.58 0.87	4.50 1.22	2.83
P$_2$O$_5$	25.84 1.71	26.76 1.17	27.10 0.58	26.66 0.64	28.20 0.27	28.85 1.43	25.24 0.73	25.71 1.17	26.65
SrO	3.14 0.64	3.17 1.08	3.73 0.62	4.09 0.37	2.64 0.25	3.65 0.74	4.38 0.45	5.49 1.64	5.95
ThO$_2$	0.51 0.29	0.27 0.38	0.16 0.05	0.15 0.09	0.11 0.07	0.15 0.10	0.04 0.02	0.13 0.09	0.27
As$_2$O$_5$	0.02 0.01	0.02 0.02	0.01 0.01	0.01 0.01	0.01 0.01	0.06 0.05	0.04 0.01	0.01 0.02	0.13
Total	81.98 2.61	84.46 1.99	84.98 0.92	85.34 0.96	85.70 0.76	85.40 0.89	0.04 1.40	85.78 1.45	83.97
SiO_2[c]	1.44 1.54	0.63 0.30	0.39 0.10	0.41 0.12	0.36 0.29	5.85 4.21	1.19 0.77	1.88 1.44	6.75
apfu									
Ca	0.25	0.24	0.25	0.25	0.21	0.29	0.23	0.24	0.28
Sr	0.16	0.16	0.17	0.19	0.13	0.17	0.21	0.25	0.28
Nd	0.10	0.10	0.08	0.07	0.11	0.12	0.06	0.06	0.04
Pr	0.03	0.03	0.02	0.02	0.03	0.03	0.02	0.02	0.02
Ce	0.27	0.25	0.23	0.23	0.28	0.22	0.23	0.22	0.27
La	0.17	0.17	0.16	0.15	0.16	0.11	0.17	0.13	0.09
Fe^{3+}		0.03	0.03	0.04	0.03	0.02	0.05	0.06	
Al		0.05	0.06	0.07	0.02		0.07		
Th	0.01								0.01

P2 fault (spans MAC404, MAC117, MAC425, MAC)

A	1.00	1.02	1.00	1.02	0.97	0.97	1.04	0.99	0.97
Al	2.95	3.00	3.00	3.00	3.00	2.96	3.00	3.06	2.86
Fe^{3+}	0.06					0.04	0.00	0.00	0.09
B	3.01	3.00	3.00	3.00	3.00	3.00	3.00	3.06	2.95
P	1.89	1.87	1.86	1.82	1.96	1.97	1.73	1.75	1.86
S	0.11	0.10	0.12	0.16	0.07	0.06	0.23	0.21	0.21
As									0.01
X	2.00	1.97	1.98	1.98	2.03	2.03	1.96	1.95	2.07
ΣLREE	0.58	0.54	0.51	0.47	0.58	0.48	0.48	0.44	0.41
Ce anomaly[d]	0.83	0.81	0.85	0.85	0.89	0.87	0.92	0.90	1.59
S/P	0.06	0.05	0.06	0.09	0.04	0.03	0.13	0.12	0.11

Notes:

Due to small grain size of APS minerals and the relatively large electron beam size (5 μm) for the analysis, it was difficult to obtain precise composition of individual compositional zones in grains, as some rims are narrower than 5 μm. Most cores are also smaller than 5 μm (Figs. 4,5). Therefore, most of the compositional data presented in Table 2 reflect mixtures of different zones. Rim and core anlysis was conducted on two samples containing relatively large APS (MAC152 and MAC412).

a: adjacent minerals, Ilt=illite, Sud=sudoite, Mgf = magnesiofoitite; Clc = clinochlore

b: Area of analysis in grains, ie. rim, core or mixed. Compositional zones are narrower than the beam size of 5 μm. The mixed area refers to the data from different compositional zones defined in SEM-BSE images

c: contribution of surrounding minerals in the analitical data was evaluating using SiO2 contents (see the Results for detailed description)

d: $[Ce]_N* = \sqrt{([La]_N \cdot [Pr]_N)}$

	135	MAC63	MAC29	MAC44	MAC43	GRZ MAC412			BZ MAC17
		Sud	Sud	Sud/Ilt	Sud/Ilt	Sud/Clc			Kln
	ed	Mixed	Mixed	Mixed	Mixed	Mixed	Core	Rim	Mixed
	1σ	7 1σ	4 1σ	14 1σ	2 1σ	10 1σ	2 1σ	2 1σ	3 1σ
	0.11	3.34 0.31	1.95 0.26	3.18 0.19	2.98 0.45	3.49 0.36	3.46 0.42	3.87 0.44	1.76 0.19
	0.28	4.49 0.35	3.14 0.83	4.80 0.71	5.86 1.33	2.84 0.24	2.89 0.17	3.27 0.53	8.41 0.85
	0.98	32.82 0.64	30.28 1.90	32.52 0.78	31.99 0.46	30.15 1.01	28.78 0.65	31.57 1.76	29.33 0.90
	0.56	0.23 0.11	1.90 0.87	0.50 0.19	0.31 0.14	3.49 1.66	5.85 2.02	3.37 2.99	0.34 0.11
	0.17	2.79 0.54	2.62 0.33	1.84 0.19	2.26 0.37	0.68 0.26	0.74 0.02	0.48 0.23	1.21 0.32
	0.12	0.71 0.16	0.76 0.09	0.58 0.12	0.46 0.17	0.12 0.09	0.25 0.08	0.19 0.07	0.31 0.25
	0.63	6.75 0.46	4.65 0.70	6.07 0.70	5.84 0.44	11.16 0.80	9.40 1.05	10.19 1.26	1.71 0.64
	0.27	3.78 1.01	4.08 1.33	3.95 0.47	3.28 0.25	1.32 0.39	1.56 0.52	1.26 0.74	1.01 0.36
	0.66	25.52 0.63	23.95 0.49	25.61 0.73	25.09 0.85	15.56 2.78	13.02 0.36	21.64 3.87	20.66 0.97
	0.74	5.01 0.61	6.27 0.68	6.77 0.79	7.01 1.59	4.52 0.58	4.51 0.23	5.18 1.69	13.70 0.74
	0.06	0.08 0.05	0.19 0.09	0.02 0.03	0.04 0.01	0.01 0.01	0.02 0.02	0.01 0.01	0.06 0.03
	0.05	0.02 0.02	0.05 0.03	0.01 0.01	0.05 0.03	15.72 4.32	17.85 0.79	6.04 5.16	0.24 0.06
	1.17	85.56 1.25	79.85 1.57	85.86 1.46	85.19 0.74	89.04 1.16	88.34 0.22	87.07 0.96	78.75 1.90
	1.47	*0.84 0.35*	*8.32 3.91*	*0.88 0.30*	*0.98 0.17*	*0.70 0.59*	*0.70 0.22*	*0.69 0.58*	*9.74 5.57*
		0.28	0.18	0.27	0.25	0.31	0.31	0.33	0.16
		0.23	0.31	0.31	0.32	0.18	0.22	0.24	0.68
		0.08	0.08	0.05	0.06	0.02	0.02	0.01	0.04
		0.02	0.02	0.02	0.01				0.01
		0.20	0.15	0.18	0.17	0.34	0.29	0.30	0.05
		0.11	0.13	0.12	0.10	0.04	0.05	0.04	0.03
		0.01	0.12	0.03	0.02	0.14	0.21	0.17	
		0.08		0.03	0.01				

1.01	**0.99**	**1.00**	**0.95**	**1.03**	**1.10**	**1.09**	**0.98**
3.00	3.06	3.00	3.00	2.92	2.84	2.96	2.96
0.00	0.00	0.00	0.00	0.08	0.16	0.04	0.02
3.00	**3.06**	**3.00**	**3.00**	**3.08**	**3.00**	**3.00**	**2.98**
1.72	1.74	1.71	1.70	1.08	0.92	1.46	1.50
0.27	0.20	0.28	0.35	0.18	0.18	0.19	0.54
				0.63	0.78	0.26	0.01
1.99	**1.94**	**2.00**	**2.05**	**1.89**	**1.88**	**1.91**	**2.05**
0.41	0.38	0.36	0.35	0.40			0.13
0.89	0.57	0.86	1.02	6.00	3.25	4.42	0.65
0.16	0.12	0.17	0.21	0.17	0.20	0.13	0.36

Table 3: LA-ICPMS data of APS (ppm).

Sample:	44		63		85	BCR2G[a]		precision	accuracy[b]
# grains	3	1σ	3	1σ	1		1σ	%	%
Li	150	19	190	16	150	9	0.97	1.3	0.78
Si	48000	12000	68000	12000	99000	247000	3900	1.11	2.5
Ca	15000	1000	13000	3000	18000	48000	540	1.2	6.8
Sc	8.1	1.7	4.9	0.80	<3	28	0.35	0.46	14
Ti	31	17	26	5.5	52	12000	83	1.13	13
V	20	10	20	7.5	13	400	1.43	1.08	4.7
Cr	31	12	16	3.6	<30	15	0.29	0.50	18
Mn	30	7.6	18	5.8	55	1560	2.11	0.27	2.9
Fe	7600	1600	6300	3100	3500	85000	1300	1.48	12
Co	4.0	0.42	70	96	3.7	36	0.05	0.46	2.4
Ni	21.43	1.21	49	43	<10	10	0.82	1.07	
Cu	5.4	0.53	5.7	0.79	72	16	0.12	0.67	16
Zn	4.4	0.19	9.0	4.7	<8	150	1.4	1.56	15
Se	130	2.6	120	20	130	<3		1.85	
Rb	17	11	2.0	0.23	5.0	46	0.45	0.40	4.9
Sr	42000	7000	23000	6300	24000	310	2.7	0.79	10
Y	57	7.6	38	2.7	60	28	0.025	1.16	23
Zr	1.1	0.66	7.0	2.1	7.1	160	0.87	0.35	17
Nb	0.28	0.16	0.15	0.04	<0.3	10	0.01	0.53	
Mo	3.4	1.3	8.3	9.5	<4	240	0.86	1.06	3.1
Sn	2.3	0.86	3.3	1.2	2	2	0.03	1.08	
Ba	630	63	250	74	440	620	9.6	0.72	9.9
La	20000	3500	24000	5300	34200	23	0.25	1.36	6.3
Ce	39000	8000	45000	9400	58000	50	0.97	0.70	11
Pr	3800	500	4600	840	5900	5.8	0.035	0.75	15
Nd	14000	1400	17000	3200	20400	26.0	0.74	1.21	7.3
Sm	2000	69	2200	440	2800	5.7	0.17	0.68	14
Eu	760	87	800	200	1300	1.8	0.059	0.67	9.0
Gd	820	68	450	69	810	6.0	0.42	1.05	11
Tb	43	7.6	17	1.5	40	0.9	0.012	1.28	15

Dy	64	10	28.63	2.3	60	6	0.01	0.99	
Ho	3.8	0.94	2.3	0.29	3.7	1.2	0.0095	0.84	10
Er	2.9	1.9	2.8	0.58	4	3	0.095	1.24	
Tm	0.25	0.11	0.148	0.017	0.27	0.40	0.02	1.37	28
Yb	0.94	0.34	1.4	0.45	1.7	2.8	0.21	0.77	18
Lu	0.13	0.033	0.14	0.081		0.41	0.032	0.75	20
Hf	0.91	0.40	0.30	0.099	<0.53	4.3	0.23	1.32	11
Ta	0.17	0.10	0.077	0.08	<0.161	0.6	0.007	1.56	
W	0.79	0.36	0.9	0.029	1	0.5	0.03	0.61	
Pb	160	10	120	39	260	10.3	0.005	0.92	12
Th	1300	200	1100	140	2300	5.4	0.035	0.91	13
U	0.62	0.19	2.4	1.1	16	1.7	0.065	1.46	1.9

[a]BCR2G from US Geological Survey
[b]based on the data of BCR2G provided by USGS
data is the average of anaylzed grains (# grains) in the sample (± 1 standard deviation)
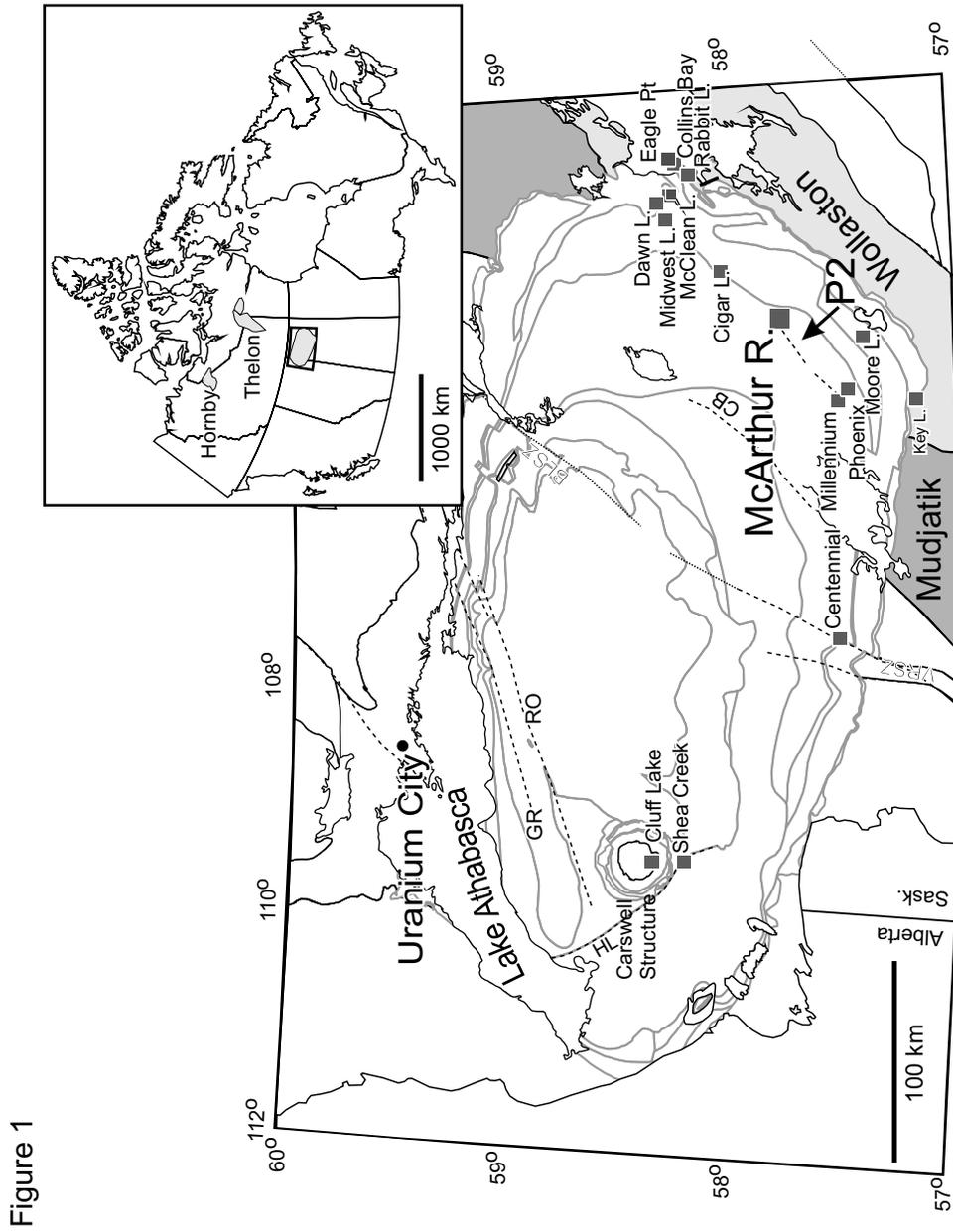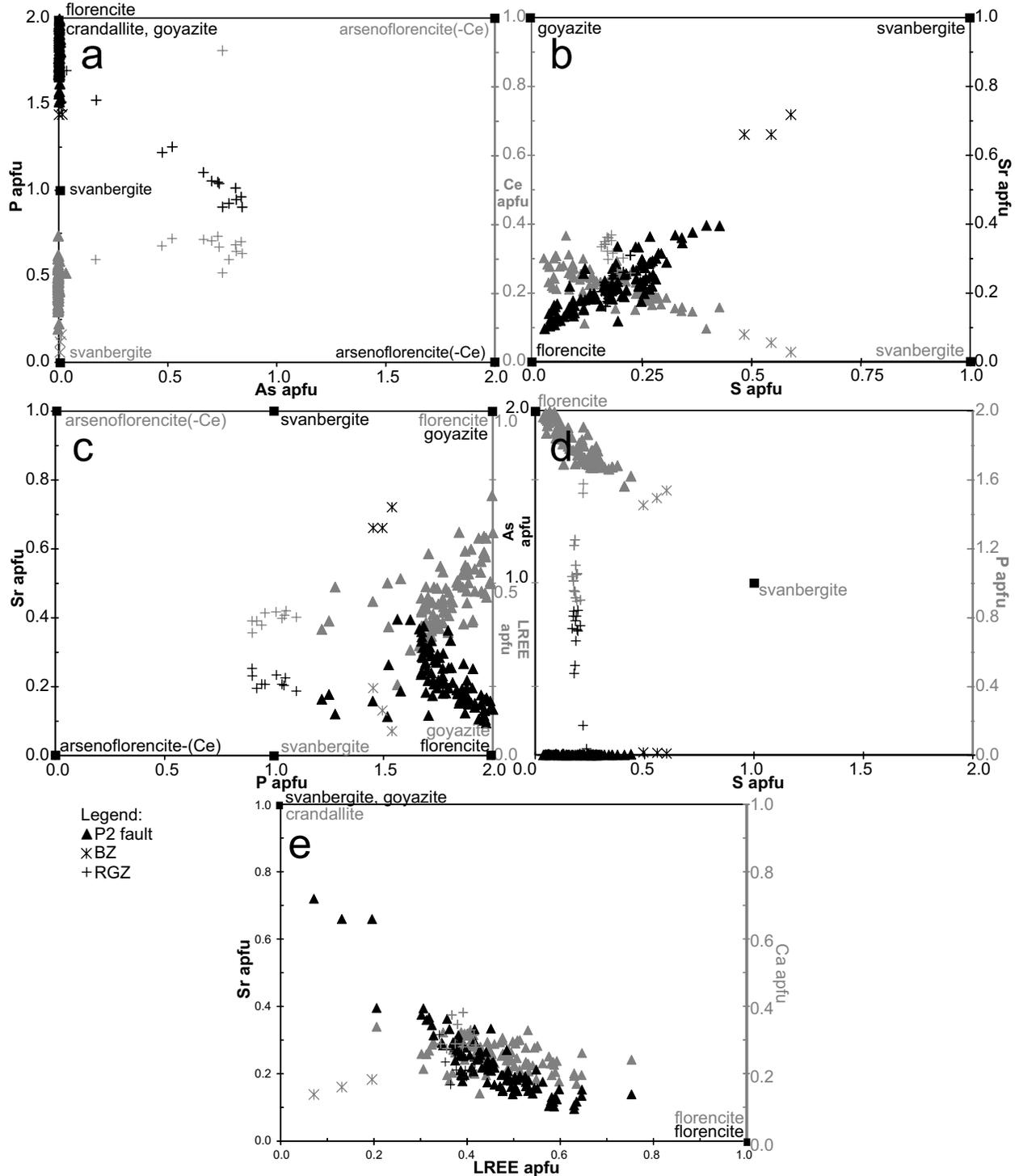
Figure 1
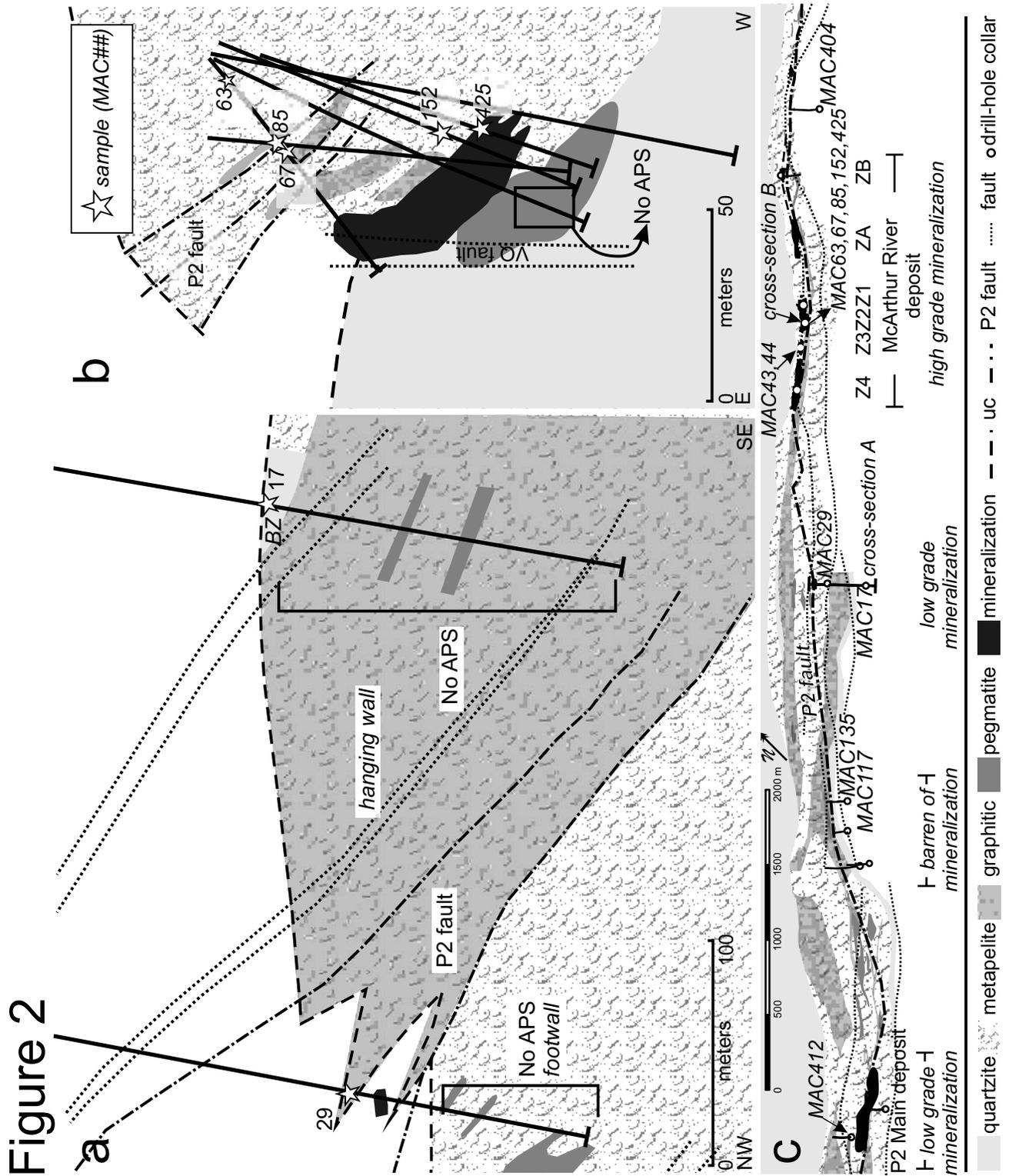
Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11