

Tourmaline, Phosphate Minerals, Zircon and Pitchblende in the Athabasca Group: Maw Zone and McArthur River Areas, Saskatchewan¹

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Anomalously high abundances of several incompatible-element-rich minerals have been found in the Helikian Athabasca Group sandstone and conglomerate in the McArthur River-Wheeler River area (Assessment Files 74H-0006, -0010, -0011). Dravite, hematite, phosphate minerals, clay minerals and euhedral quartz occur in alteration halos surrounding Athabasca unconformity-type $U \pm Ni \pm Co \pm As \pm Cu \pm S$ mineralization in this area (Hoeve and Quirt, 1984; Kotzer and Kyser, 1990a). A similar alteration assemblage of xenotime, dravite and euhedral quartz occurs in altered sandstones hosting heavy rare earth element (HREE), yttrium-rich phosphate mineralization at the Maw Zone, near Brook Lake (Agip Canada Ltd., 1985; MacDougall, 1990).

The objectives of the present investigation are:

- 1) to illustrate and characterize the variety of rare earth element (REE)-bearing minerals found in the basal portion of the Athabasca Group;
- 2) to document the geochemical composition of the dravite; and
- 3) to determine whether the quartz-dravite alteration assemblages evident in both the unconformity-type uranium mineralization and the HREE-yttrium phosphate mineralization have formed from similar fluids and processes.

To determine 3), the chemical and REE compositions of diagenetic phosphates and tourmalines in the altered sandstones hosting the HREE-yttrium phosphate mineralization are compared to the chemical and REE compositions of phosphates, tourmalines and uraninite from areas of high grade uranium mineralization at McArthur River (P2 Main, BJ, P2 North) where the fluid history and mineral paragenesis is known. Results of these comparisons will then be used to; 1) ascertain which minerals are hosting the rare-earth elements and yttrium, 2) constrain the origin and timing of fluids associated with the HREE-yttrium phosphate mineralization relative to the fluids related to the unconformity-type uranium deposits and, 3) suggest sources of the REE and

mechanisms for the transport and fractionation of REE into the various minerals.

Throughout the course of this study, diagenetic and detrital tourmalines and diagenetic phosphate minerals in samples of silicified and tourmalinized Manitou Falls Formation sandstones from the Maw Zone and the McArthur River area were examined by transmitted light microscopy. Their major element compositions were determined with an electron microprobe; REE compositions in dravite, pitchblende, phosphate and clay minerals were determined by electron microprobe and ICP-MS.

1. Geological Setting and Alteration

The Athabasca Group is composed primarily of first cycle fluvial and marine quartz sandstone and conglomerate. In the southeastern portion of the Athabasca Basin (the location of the study area) the basal sequence of the stratigraphic column consists of the fluvial Manitou Falls Formation. All sandstones hosting the tourmaline and phosphate minerals analyzed in this study are from this formation. It is composed of permeable, medium- to coarse-grained conglomerate and pebbly sandstone, overlain by sandy braided stream and wadi deposits. Mineral grains in these rocks are sub-rounded to well rounded detrital quartz.

Diagenetic minerals present in the sandstone include kaolinite, illite, hematite, goyazite, tourmaline and quartz (Hoeve and Quirt, 1984). Hematite is ubiquitous giving purple to reddish to pink colouration to the rock. Superimposed diagenetic chemical reduction has resulted in zones having a bleached or mottled appearance. Goyazite, a Ca-Sr-LREE-phosphate, is found in trace quantities throughout the Athabasca Group. Diagenetic Mg-tourmaline (dravite) is found in pore spaces as wispy tufts of radiating needles originating from surface defects on detrital quartz grains and as oriented overgrowths on detrital tourmaline grains. Detrital heavy mineral bands are common and are characterized by hematite, rutile, zircon, and minor tourmaline and monazite.

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Maw Zone samples consist of pinkish and variably-bleached hematitic sandstones, sandstone-euhedral quartz breccias, and silicified emerald green sandstone. Petrographically, alteration of the sandstones consists of quartz overgrowths, radially-textured clear to green aggregates of interstitial acicular dravite, euhedral quartz, altered brownish-green detrital tourmaline, granular xenotime, phosphate-rich altered detrital zircon, and fractured, detrital zircons rimmed by xenotime. Negligible amounts of illite and kaolinite are present. In the highly brecciated silicified sandstones, the matrix consists mainly of euhedral quartz and radially textured dravite surrounding altered sandstone blocks.

The Athabasca Group in this area is underlain by Wollaston Domain, Archean granitoid gneisses and Aphebian Wollaston Group metasediments. The northeast-trending metasediments comprise an interbedded sequence of meta-quartzite, feldspathic meta-quartzite, and pelitic to psammopelitic to psammitic gneiss, with minor amphibolite and pegmatite. A sub-Athabasca paleoridge associated with meta-quartzite is spatially associated with the uranium mineralization at McArthur River and the REE mineralization at the Maw Zone. The basement rocks have undergone several episodes of folding followed by several episodes of ductile to brittle thrusting and faulting, commonly localized along contacts of graphitic gneiss with the Archean granitoid. The faults have remained active to recent times (Wilson and Kyser, 1987; Annesley, 1989; Annesley and Madore, 1988, 1989; Kotzer and Kyser, 1991). Peak metamorphic conditions are interpreted as being middle amphibolite to lower granulite grade.

a) McArthur River

Highly altered hematitic and bleached sandstones and euhedral quartz sandstone breccias near uranium mineralization from the McArthur River area (P2 main, P2 North, BJ) contain significant amounts of euhedral quartz and tourmaline. They are petrographically similar to those of the Maw Zone, consisting of an alteration assemblage of quartz overgrowths, varying amounts of euhedral quartz and dravite, goyazite intergrown with dravite and illite in pore spaces, fractured detrital zircons, hematite and rutile.

At the unconformity between the Athabasca Group and the sub-Athabasca lithologies is a well developed paleoweathering profile. This profile consists of kaolinite with hematite at the top grading downwards, through less altered rocks containing kaolinite-illite, to mildly altered rocks with a chlorite-illite assemblage to fresh rock.

Several episodes of mixing of fluids from the basement with fluids in the sandstones have produced and modified the unconformity-type uranium mineralization (Hoeve and Sibbald, 1978; Hoeve and Quirt, 1984; Sibbald, 1985; Wilson and Kyser, 1987; Kotzer and Kyser, 1990a). Associated with these fluid mixing events was neoformation of minerals such as illite, Al-Mg chlorite, dravite, euhedral quartz, and hematite, which overprint the diagenetic mineral assemblages. A later retrograde assemblage of kaolinite with chemically and isotopically altered illite and chlorite overprints the

diagenetic and prograde mineral assemblages in the vicinity of fault and fracture zones (Wilson and Kyser, 1987; Kotzer and Kyser, 1991).

b) Maw Zone

The Maw Zone is expressed on surface by a silicified, dravitized, brecciated, faulted, and anomalously radioactive sandstone outcrop. Outcrop geology has been described and mapped by Agip Canada Ltd. (1985) and MacDougall (1990). REE mineralization was discovered in 1982 by Agip Canada Ltd., who subsequently obtained yttrium values greater than 2.0 percent, boron values up to 2.5 percent, and total rare earth oxide (REO) values up to 8.1 percent.

MacDougall (1990) interpreted the brecciated sandstone to be a result of clastic depositional processes that fragmented the sediments soon after deposition or somewhat later when more consolidated. The brecciated zone is not only present at surface but can be traced downwards through the sandstone below the outcrop.

Detailed logging of core from Agip drill hole ZQ-10-83 (Quirt, unpublished data; Agip Canada Ltd., 1985) indicates that zones of strong brecciation and sandstone blocks, up to 5 m in thickness, with rotated bedding extend from surface to nearly 200 m downhole. The breccia zones are commonly healed by dravite and illite. Below this depth, to within about 10 m of the unconformity (at 256.3 m), bedding is locally highly disturbed, folded and faulted. In addition to the brecciation, fracturing of the sandstone is ubiquitous, both on the outcrop as noted by MacDougall (1990), and in drill core. The upper 170 m of this drill core is pervasively silicified and fractured, the fractures commonly being open and lined with euhedral quartz. Those fractures not lined with euhedral quartz are healed with silica and dravite. The large vertical extent and restricted horizontal extent (Agip Canada Ltd., 1985) of the brecciation and fracturing at the Maw Zone indicates that the process responsible is more likely one of intense hydrothermal activity, as has been described for the McArthur River uranium deposit (Hubregtse and Sopuck, 1987; Kotzer and Kyser, 1990a, 1991), than one of syn- to early post-depositional fragmentation.

The Maw Zone is on the east side of a northeast-trending reverse fault, that dips to the southeast. The fault is believed to occur at the contact between Archean granitic gneiss (to the northwest) and Wollaston Group pelitic to psammopelitic graphitic gneiss. The fault is on the north(west) side of the basement topographic high, formed by meta-quartzite and psammopelitic to pelitic gneiss, that underlies the Maw Zone (Agip Canada, 1985). This sub-Athabasca ridge was interpreted to be an eroded pre-Athabasca thrust block. Diamond drilling indicates that the ridge is 150 m or more above its surroundings and extends for approximately 8.5 km, the presumed extent of the meta-quartzite unit and the fault. The peak of the ridge is about 0.5 km in length, in the region of the Maw Zone.

Post-Athabasca thrusting was not considered by Agip Canada Ltd. (1985), therefore, no note was made of the

possibility of the presence of thrust slices or interleaving of basement lithologies with the Athabasca sandstone. Preliminary petrographic, mineralogical, and geochemical examinations of two clay mineral-rich and hematite-rich intervals in drill hole ZQ-10-83 indicate that regolithic Wollaston Group gneiss may be present as thrust slices in the Athabasca sandstone below the Maw Zone.

2. Petrography and Chemistry

a) Diagenetic dravite

Unique to the Maw Zone is the presence of 'emerald' dravite which imparts a light green to olive green to emerald green colour to the sandstone and siltstone. MacDougall (1990) noted the presence of olive green quartz grains, however, this coloration is commonly due to the presence of 'emerald' dravite as a matrix mineral. In outcrop, only patchy zones of greenish sandstone are found (cf map in MacDougall, 1990). In drill core, greenish to bluish-green dravite is most prevalent as a fracture filling and as breccia matrix within pinkish to pinkish-buff to bleached-white sandstone in the upper 125 m of the core (i.e. more than 130 m above the unconformity). Within this interval, extensive development of pale green to emerald-green pervasive dravite is restricted to relatively thin zones of less than 5 m in width. Below this interval, variably pervasive dravite of the sandstone, plus dravite fracture fillings and breccia matrix, imparts a pale blue to bluish-grey colour to the rock.

Diagenetic tourmaline in the euhedral quartz-breccias and altered hanging-wall sandstones from the McArthur River area (Plate 1- typical of P2 main, P2 north, BJ) and from the euhedral quartz-sandstone breccias and emerald-green sandstones from the Maw zone (Plates 2 and 3) have Fe/Mg ratios and Al_2O_3 contents (#1 in Table 1) corresponding to an alkali-free dravite (Deer *et al.*, 1982). 'Emerald' dravite in the silicified emerald-green sandstone from the Maw Zone, however, is significantly enriched in Cr_2O_3 (#2 - Table 1). Based on

chromium and magnesium content, it can be classified as chrome dravite (Dunn, 1977).

Chemical compositions were determined for detrital tourmalines that display various degrees of alteration. Petrographically and chemically unaltered areas on the greenish-brown detrital tourmalines have Fe/Mg ratios and Al_2O_3 contents corresponding to a schorl-dravite (#3 - Table 1; Deer *et al.*, 1982). No significant amounts of Cr_2O_3 were detected. Altered detrital schorl-dravites, which appear as darker coloured areas (Plate 4), are substantially different with Fe, Mg and Al concentrations (#4 - Table 1) similar to the diagenetic alkali-free dravites in the pore spaces. Altered areas on the detrital schorl-dravites from the silicified emerald-green sandstone have similar Fe, Mg and Al contents as the altered schorl-dravites found elsewhere; however, they also contain elevated amounts of chromium (#5 - Table 1).

b) REE Mineralization

The REE mineralization at the Maw zone is microscopic in nature. It is not directly associated with the open fracturing or highly dravitized zones, but is contained within the zone of brecciated sandstone (Agip Canada Ltd., 1985). All samples containing REE mineralization are anomalously dravitic. Partial whole-rock geochemical analyses are presented in Table 2. In thin section the mineralization is indicated by the presence of xenotime, a Y-HREE-phosphate, as microcrystalline-granular, yellowish red-brown grains surrounded by acicular dravite, interstitial to quartz. Dravite appears to be intimately intermixed with the xenotime (Plate 2). In samples containing xenotime, Y, P, and REE are also found in significant quantities in altered detrital zircon.

Partial microprobe analyses of xenotime, zircon, and detrital monazite are presented in Tables 3 and 4. It is assumed that the difference between 100 percent and the oxide total is due to water and that other light elements that may be present in trace quantities (Deer *et al.*, 1962; Smith *et al.*, 1991).

The Y_2O_3 content of Maw Zone xenotime is approximately 40 weight percent, somewhat lower than for Alpine xenotime (Table 3). Water contents appear to be high (4.5 to 10.1 weight percent) as compared to the nearly stoichiometric Alpine xenotime (weight percent). The atomic ratio $100Y/(Y+REE)$ is almost constant at about 78 percent, falling within the upper range of reported values (Table 3; Jefford, 1962; Fleischer, 1989; Demartin *et al.*, 1991). Individual REO contents are almost constant and total around 19 weight percent (Table 3). Maw Zone xenotime is notably enriched in HREE, especially Dy, Gd, Er, and Yb, and, in addition, the distribution of the individual REO is distinctly different from those reported for fracture filling in the Alps (Table 4).

c) Altered zircon

Microprobe analyses of altered detrital zircon in samples that contain discrete xenotime indicates that significant quantities of Y, P, H_2O , and to a lesser extent U, Al, and

Table 1 - Chemical Compositions of Tourmaline from the Maw Zone and the McArthur River Area.

group	#1	#2	#3	#4	#5
n	4	1	3	2	1
SiO ₂ (%)	37.89	38.54	38.07	37.74	37.96
Al ₂ O ₃ (%)	37.44	36.73	31.82	37.46	37.71
TiO ₂ (%)	0.01	0.01	0.89	<0.01	0.02
FeO (%)	0.70	0.74	6.18	1.18	0.79
MnO (%)	0.02	0.02	0.02	<0.01	0.04
MgO (%)	8.58	8.31	8.23	8.28	7.95
Cr ₂ O ₃ (%)	0.03	1.68	0.01	<0.01	1.19
CaO (%)	0.17	0.13	1.24	0.15	0.22
Na ₂ O (%)	0.85	0.80	1.94	0.70	0.51
K ₂ O (%)	0.02	0.01	<0.01	<0.01	0.01
NiO (%)	0.01	0.01	0.05	0.01	<0.01
Fe/Mg	0.11	0.12	1.01	0.19	0.13

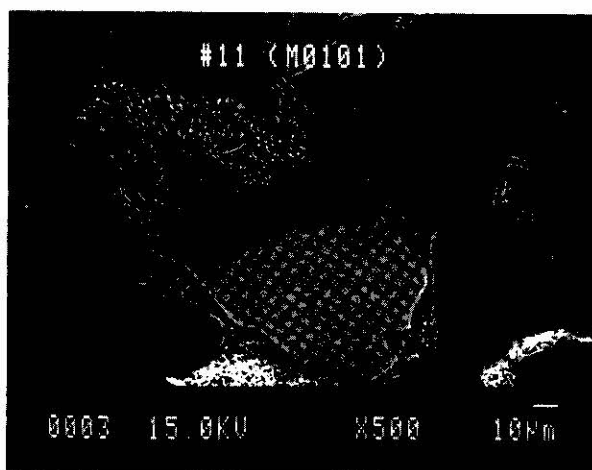
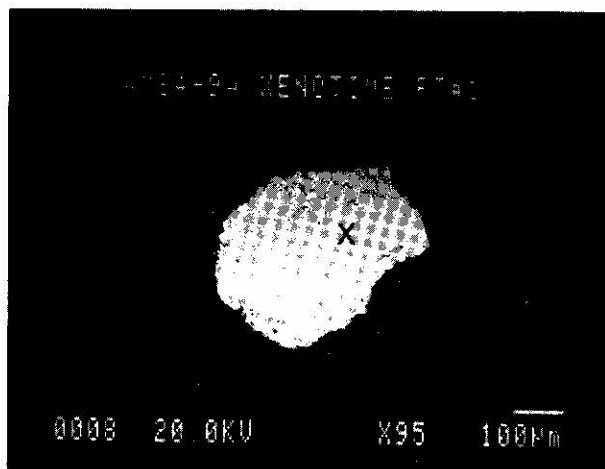
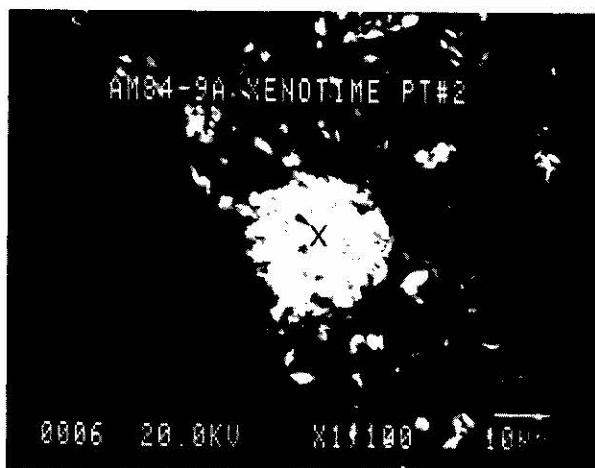
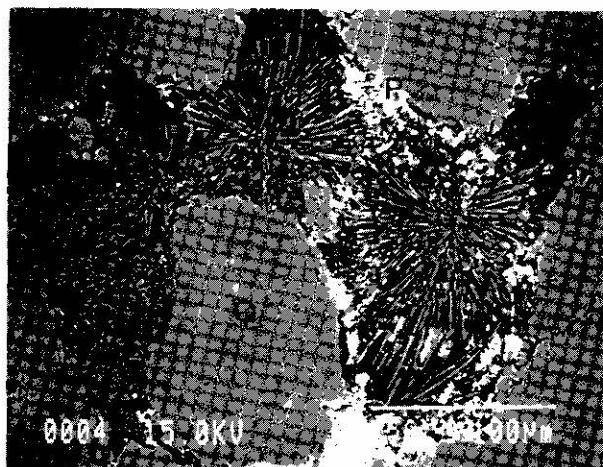


Plate 1 (upper left) - Back-scattered electron image of rosettes of acicular diagenetic tourmaline (dravite) in sandstone, McArthur River area. Q, quartz; P, goyazite; T, alkali-free dravite. Plates 2 (upper right) and 3 (lower left) - Back-scattered electron images of dravite and xenotime in sandstone, Maw Zone. Q, quartz; X, xenotime; T, dravite. Plate 4 (lower right) - Back-scattered electron image of altered detrital tourmaline in sandstone, Maw Zone. Q, euhedral quartz; Tsd, detrital schorl-dravite; Tc, chrome dravite.

Ca, are present (Table 3). The calculated amount of H₂O reaches 13 weight percent and the contribution of elements other than Zr, Si, and Hf range from 7 to 70 weight percent. Unaltered zircons from the Maw Zone area contain, near-stoichiometric proportions of Zr and Si, and low quantities (consistently less than 1.1 percent and commonly near zero) of the additional elements. Altered zircons vary from being indistinguishable from unaltered zircon (Plate 5) to being turbid and obviously altered (Plate 6), much like the granular xenotime.

The compositional information obtained from Maw Zone xenotime and zircon indicate the degree to which the zircon structure can incorporate foreign ions. In the altered zircons, Zr is mainly replaced by Y, REE, U, Ca, whereas Si is mainly replaced by P, H₂O, and, to some extent, Al. Zircon commonly contains Y due to the isostructural relationship of xenotime and zircon (Palache *et al.*, 1951; Deer *et al.*, 1962, 1982). Appreciable quantities of water may also be accommodated by the zircon structure (cyrtolite; Deer *et al.*, 1962, 1966,

1982). A general correlation appears to be present between water content and Y + P + REE content (Table 3; Deer *et al.*, 1962, 1982).

Unaltered detrital zircon and monazite (Tables 3, 4) are found within and surrounded completely by unfractured detrital quartz grains. Altered detrital zircon is found within fractured quartz grains (Plates 5 and 7) or as discrete detrital grains (Plate 8). The progression from unaltered zircon, with near-stoichiometric proportions of Zr, Si, and Hf, through increasingly altered zircon, with significant proportions of Y, P, and HREE, to xenotime is displayed in samples from the Maw Zone. The zircon analysis that returned sub-equal proportions of Zr, P, and Y, with some Si (Table 3, M-0101c), may represent an intergrowth of host zircon and replacement xenotime.

Table 2 - Selected Chemical and Mineralogical Analyses: Maw Zone and Wheeler River Area. Oxides in percent, elements in ppm; 1 RA- and ZQ-series data from D. Quirt, S.R.C. unpublished data file, (1984); Agip Canada Ltd. (1985); 2 samples courtesy of Cameco Corp.

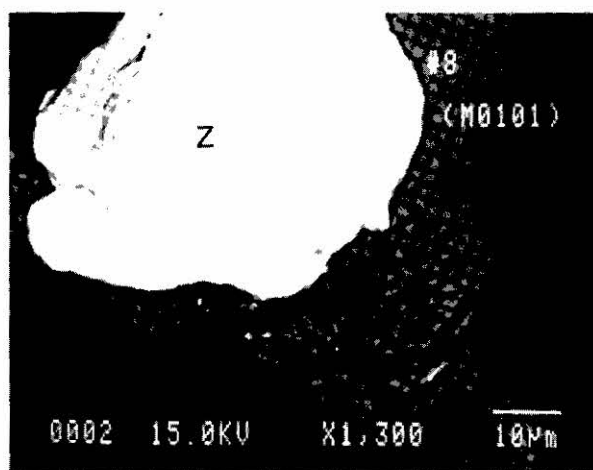
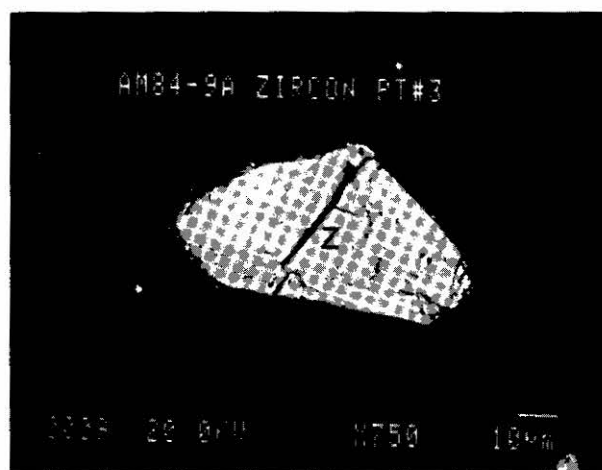
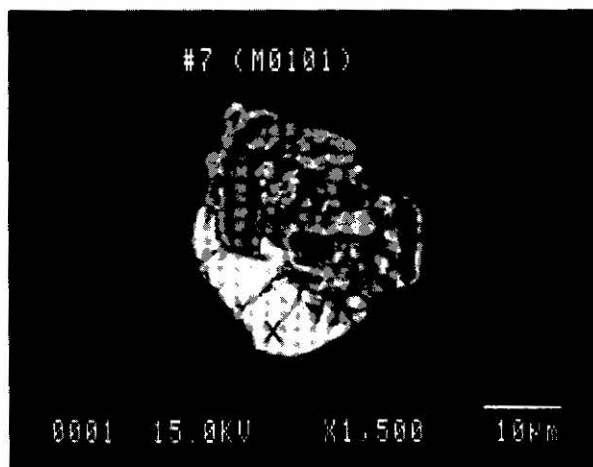
sample #	description	I+C+K=100			clay min.	dravite (0 to 6)	xenotime	Fe ₂ O ₃ (t)	P ₂ O ₅	TiO ₂	U	Ni	As	B	Sr	Zr	V	Au (ppb)	Y	La	Ce	Nd	Yb	sum REE	Yb/Ce ratio
		Illite	Chl.	Kaol.																					
AM-84-01	silicified sst.	0	0	100	yes	2	no	0.03	0.02	0.03	0.4	3	0.2	170	28	69	7	16	1	10	18	4	0.4	38	0.02
AM-84-02	clay pebble	0	0	100	yes	4	no	0.03	0.02	0.01	1.0	6	0.2	840	24	33	23	9	7	8	11	1	0.6	26	0.05
AM-84-03	'emerald' sst.	100	0	0	yes	2	no	0.02	0.02	0.02	0.8	4	0.3	420	28	34	14	4	3	10	13	4	0.3	31	0.02
AM-84-04	silicified sst.				no	2	no	0.09	0.02	0.02	2.2	251	33.0	260	22	58	10	38	2	21	17	5	0.4	47	0.03
AM-84-05	silicified sst.	0	36	64	yes	1	no	0.02	0.02	0.02	1.6	5	0.5	30	21	33	5	6	4	13	12	5	0.3	36	0.03
AM-84-06	'emerald' sst.				no	3	no	0.04	0.02	0.03	1.2	4	0.3	880	31	114	24	4	3	5	18	4	0.6	32	0.04
AM-84-09	dravitic sst.	0	0	100	yes	5	yes	0.10	0.07	0.02	5.4	6	0.8	3500	27	143	36	4	381	7	20	7	15.0	138	0.75
AM-84-10	dravitic sst.				no	3	no	0.04	0.02	0.03	1.0	3	0.8	700	38	82	10	5	9	13	24	6	0.8	50	0.03
AM-84-11	silicified sst.	0	45	55	yes	1	no	0.02	0.02	0.02	1.6	3	0.3	60	16	29	6	3	4	11	11	4	0.3	31	0.03
AM-84-12	'emerald' sst.				no	3	no	0.03	0.02	0.04	0.4	7	0.3	490	32	35	14	6	7	11	19	8	0.6	44	0.03
AM-84-13	regolith?	7	0	93	yes	1	no	3.02	0.29	1.09	8.6	11	3.7	100	962	2216	38	35	25	162	396	153	4.9	738	0.01
AM-84-14	regolith?	68	0	32	yes	5	no	0.91	0.19	0.63	6.6	23	1.6	12000	470	553	18	7	38	160	363	176	5.5	734	0.02
AM-84-15	'emerald' breccia				no	3	no	0.05	0.02	0.01	1.8	2	0.3	590	25	30	8	4	3	8	17	5	0.4	36	0.02
RA-1-83 ¹	silicified sst.	0	0	100	yes	4	yes	0.57	0.30	0.06	220.0	27	16.2	1570	39.1	442	72		36400	60.0	80	55	1100.0	7896	13.75
RA-2-83	clay-altered sst.						yes	0.49	0.12	0.03	420.0	36	12.5	599	17.2	208	62		19900	10.0	40	19	600.0	4763	15.00
RA-3-83	silicified sst.						yes	0.80	0.13	0.03	9.1	40	5.5	260	14.2	173	67		4000	6.7	14	8	110.0	957	7.86
RA-4-83	silicified sst.						yes	0.99	<0.01	0.02	16.4	55	1.8	213	17.1	33	78		500	8.1	19	9	1.7	52	0.09
RA-5-83	clay-altered sst.						yes	0.45	0.49	0.08	41.2	24	15.0	696	19.6	619	62		14600	9.0	32	8	400.0	3849	12.50
RA-6-83	sst. breccia						yes	0.46	0.24	0.04	70.4	25	20.0	400	10.8	311	67		14300	10.0	39	18	370.0	3527	9.49
RA-7-83	silicified sst.	4	0	96	yes	5	yes	0.47	0.51	0.07	160.0	19	23.8	3410	22.6	579	123		67600	70.0	100	35	1700.0	14245	17.00
ZQ-10-83-CA-02	silicified sst.	0	0	100	yes	2	no	0.53	0.02		6.0	9	2.3	797					105						
ZQ-10-83-CA-04	silicified breccia	0	0	100	yes	2	no	0.54	0.02		0.4	8	0.8	645					12						
ZQ-10-83-CA-06	silicified sst.	53	0	47	yes	2	no	0.66	0.02		0.7	17	1.5	519					14						
ZQ-10-83-CA-08	silicified sst.	99	0	1	yes	1	no	0.61	0.02		0.5	12	1.0	329					<1						
ZQ-10-83-CA-10	silicified sst.				no	3	no	0.62	<0.01		0.3	13	1.5	2470					3						
ZQ-10-83-CA-12	silicified sst.				no	2	no	0.50	<0.01		<0.2	11	2.1	924					<1						
ZQ-10-83-CA-14	silicified sst.	100	0	0	yes	4	yes	0.58	0.05		0.6	10	4.0	5430					445						
ZQ-10-83-CA-16	sst.	99	0	1	yes	1	no	0.79	0.05		1.2	11	7.6	489					4						
ZQ-10-83-CA-18	dravitic sst.	100	0	0	yes	2	no	0.67	0.05		0.6	9	2.5	1070					6						
ZQ-10-83-CA-20	siltstone	38	0	62	yes	1	no	0.59	0.15		3.4	7	10.3	483					24						
ZQ-10-83-CA-23	dravitic sst.	57	0	43	yes	4	no	0.77	0.14		11.9	9	4.0	5440					66						
ZQ-10-83-CA-25	silicified sst.	41	0	59	yes	4	no	0.68	0.03		0.2	11	1.7	3600					38						
ZQ-10-83-CA-27	silicified siltstone	31	11	58	yes	1	no	0.67	0.02		0.7	14	1.7	652					3						
ZK8D/345 ²	dravitic sst.	15	14	71	yes	4	no	0.36	0.03	0.08	1.8	6	0.7	700	83	138	8	4	10	40	16	4	0.8	82	0.05
ZK8D/366	dravitic regolith?	37	0	63	yes	6	no	0.35	0.97	0.50	30	31	7.5	30000	3200	986	407	3	283	3200	1100	3	21.8	5654	0.02
HL8D/1717	dravitic sst.	32	67	1	yes	4	no	0.50	0.03	0.10	1.8	14	1.2	850	66	221	8	23	8	32	10	23	0.8	62	0.08
HL8D/1718	dravitic sst.	47	49	4	yes	4	no	0.39	0.04	0.15	2.8	9	0.9	600	99	280	7	19	8	38	13	19	0.9	74	0.07
MC6D/4840	dravitic sst.	59	0	41	yes	5	no	0.29	0.04	0.08	2.4	3	1.2	1200	124	232	11	2	5	60	30	2	0.8	126	0.03
MC6D/4846	dravitic sst.	20	0	80	yes	5	no	0.38	0.03	0.06	1.2	8	0.7	2100	80	124	5	3	3	46	17	3	0.5	91	0.03

Table 3 - Partial Microprobe Data: Maw Zone Data and Comparison with other published data. nc, not calculated; nd, not detected; 1 Demartin et al. (1991).

mineral	sample	condition	SiO ₂ wt. %	ZrO ₂ wt. %	U ₃ O ₈ wt. %	ThO ₂ wt. %	P ₂ O ₅ wt. %	CaO wt. %	Al ₂ O ₃ wt. %	Y ₂ O ₃ wt. %	H ₂ O(c) wt. %	sum Y ₂ O ₃ +REO wt. %	sum REO wt. %	Y/(Y+REE) at. %
zircon	AM-84-13a	unaltered	32.8	65.0	0.1	0.0	nd	0.0		0.0	0.9	0.1	0.0	68.6
	AM-84-13b	unaltered	33.5	65.3	nd	nd	nd	nd		nd	0.0	0.1	0.1	nc
	AM-84-9a	mod. altered	30.0	62.1	nd	0.1	1.0	0.3		0.9	4.1	1.1	0.1	91.3
	AM-84-9b	mod. altered	27.9	60.4	0.2	0.1	2.0	0.5		1.6	5.7	1.7	0.1	95.1
	M-0101a	mod. altered	32.6	58.0	0.1	0.1	3.3	0.7	1.0	0.6	2.7	1.0	0.4	68.2
	AM-84-9c	altered	23.4	56.8	0.1	0.0	4.4	0.8	1.0	1.8	7.1	2.8	1.0	75.5
	M-0101b	altered	19.0	54.5	0.3	0.1	7.1	1.1		1.3	13.1	3.2	1.9	51.8
	AM-84-9d	altered	20.2	52.5	0.4	0.1	6.4	1.1		3.3	12.3	3.5	0.3	95.0
xenotime	M-0101c	altered edge	8.1	21.5	0.4	0.3	24.0	1.0	0.5	25.5	6.2	37.7	12.2	77.5
	Maw Zone	avg. (n=3)	0.6	nd	0.6	0.1	32.5	0.5	0.2	39.6	6.7	58.7	19.0	77.6
detrital monazite	Alpine ¹	avg. (n=82)	0.1	<0.01	1.0	0.4	35.1	0.1	<0.1	46.5	<0.1	63.9	17.4	81.8
	avg. (n=2)	unaltered	0.2	nd	2.5	6.8	25.0	2.0	nd	1.8	5.9	57.5	55.7	4.6

Table 4 - REO Data Recalculated to 100 percent REO: Maw Zone data and comparison with other published data. nc, not calculated; nd, not detected.

mineral	sample	condition	Y ₂ O ₃ wt. %	Y/(Y+REE) at. %	Ce ₂ O ₃ /REO %	Eu ₂ O ₃ /REO %	Gd ₂ O ₃ /REO %	Tb ₂ O ₃ /REO %	Dy ₂ O ₃ /REO %	Ho ₂ O ₃ /REO %	Er ₂ O ₃ /REO %	Yb ₂ O ₃ /REO %	Lu ₂ O ₃ /REO %
zircon	AM-84-13a	unaltered	0.03	68.6									
	AM-84-13b	unaltered	<0.01	nc									
	AM-84-9a	mod. altered	0.94	91.3	0.0								
	AM-84-9b	mod. altered	1.61	95.1	83.3								
	M-0101a	mod. altered	0.57	68.2	16.3	<0.1	<0.1	2.3	<0.1	23.3	16.3	25.6	<0.1
	AM-84-9c	altered	1.83	75.5	1.0	<0.1	22.7	1.0	33.0	4.1	14.4	11.3	<0.1
	M-0101b	altered	1.26	51.8	5.7	<0.1	9.8	1.0	15.0	14.5	17.1	22.8	2.6
	AM-84-9d	altered	3.25	95.0	48.0								
xenotime	M-0101c	altered edge	25.47	77.5	0.5	<0.1	19.1	2.8	32.5	17.9	12.5	9.5	1.6
	Maw Zone	avg. (n=3)	39.64	77.6	0.3	nd	16.4	2.4	36.1	7.7	16.7	15.9	2.4
	Demartin et al. (1991)	avg. (n=82)	46.49	81.7	nd	0.23	10.57	3.44	29.38	6.00	22.34	24.18	3.13
	Jefford (1962)			68.5		nd	3.4	1.8	18.9	2.4	18.4	44.4	3.6
	Fleischer (1989)	avg. (n=54)		67.7		0.5	11.6	2.8	21.8	4.7	19.5	22.3	4.4
detrital monazite	Maw Zone	unaltered avg. (n=2)	1.85	4.6	51.2	nd	2.3	nd	1.1	0.7	<0.1	<0.1	<0.1



Plates 5 (upper left) and 6 (upper right) - Back-scattered electron images of altered zircon with xenotime rim at the Maw Zone. Q, quartz; Z, altered zircon; X, xenotime. Plate 7 (lower left) - Back-scattered electron image of altered zircon with a xenotime rim located at margin of fractured quartz grain in sandstone at Maw Zone. Q, quartz; Z, altered zircon; X, xenotime; T, dravite. Plate 8 (lower right) - Back-scattered electron image of discrete altered detrital zircon with a xenotime rim in sandstone at Maw Zone. Q, euhedral quartz; Z, altered zircon; X, xenotime; Tc, chrome dravite.

3. REE Mineral Chemistry

Rare earth element concentrations in xenotime (YPO_4) from the Maw Zone indicate a significant HREE enrichment. Similar HREE enrichments occur in uraninites and pitchblendes from unconformity-type uranium mineralization at Collins Bay, McArthur River, Key Lake and the Pine Creek Geosyncline (Figure 1; McClenahan and Taylor, 1979; Fryer and Taylor, 1987) along with significant quantities of yttrium in uranium minerals from Key Lake and McArthur River (~3000 ppm). Concentrations of the REE in xenotime (170,000 ppm) are significantly higher than in the uranium minerals (2000 to 18,000 ppm) with the LREE/HREE ratios in xenotime and uraninite being about .01 and .10 to .16, respectively.

In contrast, illite containing varying amounts of goyasite and dravite from the alteration halos surrounding the unconformity-type uranium mineralization at McArthur

River, Key Lake and Midwest Lake and dravite intergrown with xenotime in the alteration halo at the Maw Zone have a LREE enrichment with LREE/HREE ratios between 1.1 to 39.6 (Figure 1). In the unconformity-type uranium deposits, anomalous amounts of Sr in illite positively correlate with increasing goyasite content and concentration of LREE, suggesting that the LREE resides in the goyasite rather than the illite. Generally, illite with stoichiometric amounts of Sr has a flatter REE pattern with a LREE/HREE ratio slightly greater than 1.

4. Controls on REE and U Mobility in the Athabasca Basinal Fluids

The HREE and LREE contents in Maw Zone xenotime and dravite are similar to those in dravite, goyasite, clay minerals and uraninite from unconformity-type uranium deposits (Figure 1). These minerals have apparently formed from the same fluid processes, such that the

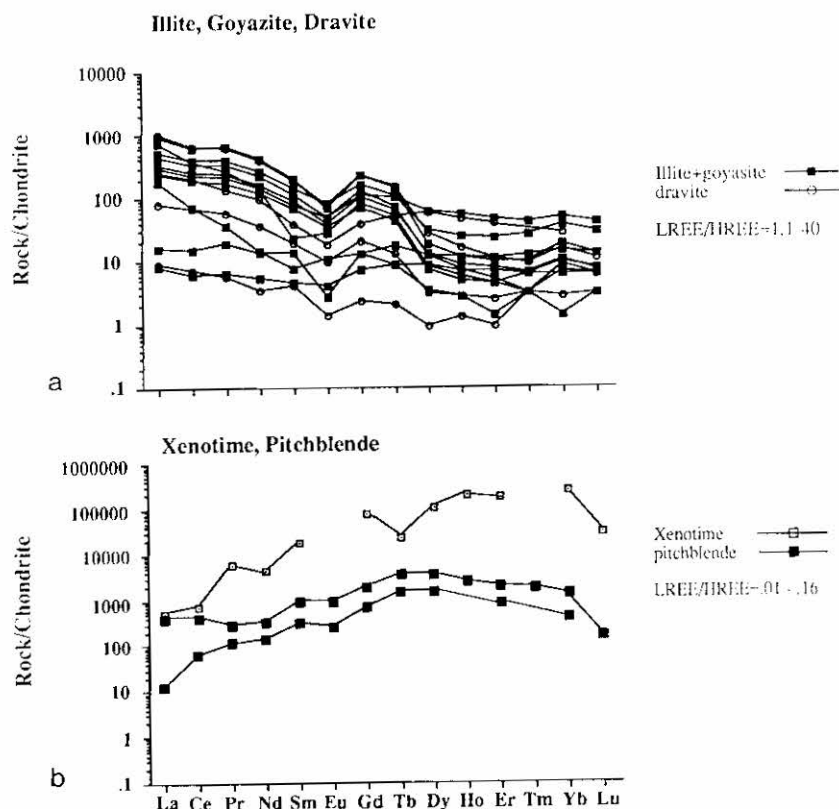


Figure 1 - Chondrite-normalized REE patterns for (a) illite, goyazite, dravite, and (b) xenotime and pitchblende minerals; $LREE/HREE = (La + Ce + Nd)/(Dy + Er + Yb)$.

high REE concentrations and consistent REE patterns implies relatively homogeneous controls, for the transport and fractionation of REE, in areas of hydrothermal alteration throughout the basin. Similar Eu anomalies in all the minerals possibly suggests that the redox state was similar in the fluids responsible for hydrothermal alteration and uranium and HREE-yttrium mineralization.

Microthermometric analyses of fluid inclusions in gangue silicates and carbonates indicates that the Athabasca sandstones were altered by hot, highly saline, oxidizing basin fluids (Kotzer and Kyser, 1990b). These chloride-rich, basin brines are believed to have been the major source of the REE, uranium and precious and base metals. Experimental and empirical studies on the fluid transport of Au, U, PGE, yttrium and REE indicate they are highly mobile in chloride-rich brines similar to Athabasca Basin fluids (Michard, 1989; Wilde *et al.*, 1989; Wood, 1990). In the Athabasca Basin, anomalous REE, Y and U concentrations within the hydrothermal alteration haloes are compatible with high mobility of these elements in the chloride-dominated fluids which formed the Athabasca unconformity-type uranium deposits.

Studies of REE fractionation in various mineral groups (Burt, 1989; Mariano, 1989) along with empirical data on

REE in hydrothermal fluids indicate that both Y and HREE tend to be mobile with, and concentrated in, xenotime and uranium relative to goyazite, dravite and illite, which tend to concentrate LREE. In the Athabasca unconformity-type uranium deposits, the HREE and Y enrichment in pitchblende and the LREE enrichment in the associated gangue and phosphate minerals are a consequence of the minerals which formed from the REE-enriched fluids. At the Maw Zone, formation of a Y-HREE-phosphate mineral (xenotime) possibly results from insignificant formation of pitchblende, which normally appears to deplete the basinal fluids of their HREE and Y content in the unconformity-type uranium deposits. Although whole-rock P_2O_5 contents of Maw Zone samples are, in general, comparable to background values for the Athabasca Group (Quirt, 1985), the conspicuous lack of goyazite in the Maw Zone area may indicate that this mineral was replaced by xenotime. However, individual samples contain phosphate contents up to 10 times background indicating that moderate phosphate enrichment is associated with the REE-Y mineralization process.

5. Sources of REE in the Athabasca Basin

Alteration of the Athabasca sandstones at the Maw Zone and McArthur River is due to mixing of fluids from the basin with those issuing from the basement along fault zones. Enrichments of REE in the fluids may have come from sources in either the underlying metamorphic rocks or the sandstones themselves. In sandstone environments, enrichments of heavy detrital minerals such as zircon can substantially alter the initial REE concentrations of the sediments, which generally tend to be low and LREE-dominated (McClennan, 1989). Garnets in the underlying garnet-bearing Wollaston Group gneisses and detrital zircons in the Athabasca sandstones, both enriched in HREE (McClennan, 1989), are sources for HREE in the basinal and basement fluids. At the Maw zone, textural relationships between the altered zircons and the HREE-enriched xenotime, coupled with the ability for the chloride-rich basinal brines to transport REE, indicates that the zircons were the more likely source for HREE in this area.

6. Phosphate Paragenesis in the Athabasca Basin

High mobility of phosphate is suggested from empirical and experimental studies on phosphate-clay assemblages which indicate that apatite dissolution and crandallite mineral precipitation can readily occur in neutral to low pH fluids from which illite and kaolinite can also form (Weaver and Wampler, 1972; Nriagu, 1976; Spotl, 1990). Mineralogical evidence from Athabasca Group sandstones indicates that the saline basin fluids were in equilibrium with illite and kaolinite, thus suggesting that phosphate mobility was possible. Phosphate mobility is also indicated by: early diagenetic apatite formation ca. 1650 to 1700 Ma (Cumming *et al.*, 1987); goyasite intergrown with illite and dravite ca. 1250 to 1500 Ma (Kotzer and Kyser, 1990a,b); and a very recent mixture of crandallite minerals with late-formed kaolinite (Hoeve and Quirt, 1984; Wilson, 1985; Kotzer and Kyser, 1990a). Broad correspondence of these phosphate ages to U-Pb, Rb-Sr, K-Ar and paleomagnetic ages on uraninite, diagenetic illite and hematite, which formed from regional high temperature fluid diagenesis (Kotzer and Kyser, 1990b), is compatible with the interpretation that the phosphate minerals also underwent continual destruction and reprecipitation by large scale fluid movements in the Athabasca sandstones.

7. Interpretation of Detrital and Diagenetic Dravite Compositions

Kotzer and Kyser (1990a) suggested that dravite formation in the alteration halos surrounding the unconformity-type uranium deposits resulted from mixing of a saline, oxidizing, boron-bearing, basin fluid with a reducing, Mg-rich basement fluid in the fault zones hosting the uranium deposits. The chemical and textural similarity of dravites from both the Maw Zone and unconformity-type uranium deposits and the alteration of detrital schorl-dravite indicate that the enclosing sandstones in both areas were altered by a basement-sandstone fluid mixing event involving a significant Mg component (Figure 2).

Slight chemical variations of the basement fluid are reflected by dravite compositions from the Maw Zone and unconformity-type uranium deposits. At the Maw Zone, formation of chrome dravite in pore spaces and in altered areas on the schorl-dravites, indicate elevated chromium concentration in the basement fluids. The sporadic occurrence of chrome dravite in close spatial association with a chrome-poor, alkali-free dravite implies that the basement fault zones penetrated rocks of distinctly different lithologies and that the basement fluids emanating from these fault zones had elevated chromium contents. The association of chrome dravites with ultramafic rocks (Dunn, 1977; King and Kerrich, 1989) suggests that along certain parts of the fault conduits the basement fluids possibly interacted with ultramafic rocks in the underlying Wollaston Group.

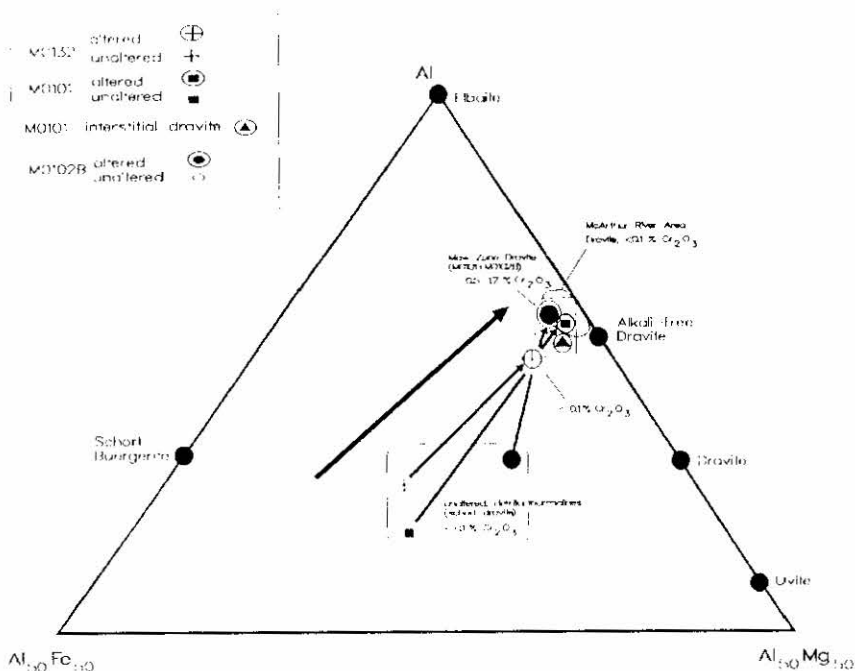


Figure 2 - Ternary plot (Fe-Mg-Al) of tourmaline compositions at McArthur River and the Maw Zone. Diagenetic dravite in pore spaces is an alkali-free dravite with variable amounts of chromium. Detrital tourmalines at the Maw Zone are schorl-dravites. Altered areas on detrital schorl-dravites have similar compositions to the interstitial alkali-free dravites. Arrows indicate trend of magnesium enrichment in the compositions of the tourmaline as a result of hydrothermal alteration.

8. Conclusions

In both the unconformity-type uranium deposits and the HREE-yttrium phosphate mineralization, similar spatial and textural associations between phosphate, silicate and clay minerals, common assemblages of euhedral quartz-dravite and similarities in the chemical compositions of dravite and REE concentrations in dravite, phosphates, clay minerals and uranium indicate a similar paragenesis and fluid history.

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