Unorthodox compositional trends in columbite-group minerals from the Animikie Red Ace pegmatite, Wisconsin, USA

Neortodoxní trendy složení minerálů skupiny columbitu z pegmatitu Animikie Red Ace, Wisconsin, USA (Czech summary)

(6 text-figs)

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The 1.8 Ga Penokean age Animikie Red Ace pegmatite in Florence County, Wisconsin, is an example of an extremely fractionated granitic pegmatite system. The dike strikes in a northerly direction and dips at about 68 ° to the west. The pegmatite is strongly zoned with a thin border zone, a rubellite-bearing wall zone, 3 intermediate zones, a core margin, a core zone and several aplite and replacement units. The mineralogy is typical for a highly fractionated pegmatite; it includes Mn- and Ta-rich columbite-tantalite species, spodumene, lepidolite, elbaite, and several exotic minerals such as rhodizite, tantite, wodginite, and hambergite. Members of the columbite-tantalite group are geochemically evolved, with high Mn and Ta abundances in these minerals from the wall zone and the middle intermediate zone. Columbite-tantalite minerals from the other zones are still evolved, though not as highly as those from the wall zone and the middle intermediate zone. In general, there is a decrease in the value of Ta/(Ta+Nb) ratio from the wall zone to the core zone, which is the opposite of what is normally observed in highly evolved pegmatites. The high fractionation trends in the wall zone suggest that the pegmatitic magma may have been derived from an already geochemically evolved, much larger pegmatite body at depth.

Key words: Animikie Red Ace pegmatite, Hoskin Lake granite, Penokean, LCT-type pegmatite, columbite-group minerals

Introduction

LCT-family pegmatites (Černý 1992) are late fractionates of granitic parental magma. They are typically associated with orogenic activity and generally form during the final stages of an orogenic event. In most cases, the sources of these pegmatites can be linked to nearby granitic intrusions. LCT-family pegmatites are further subdivided into several types, for example the rare element type, which consists of several subtypes, the spodumene, amblygonite, and lepidolite subtypes (Černý 1991). This link, however, is more difficult to ascertain when we look at pegmatites from abyssal depths (Černý 1982). The source of NYF-type pegmatites is generally easier to establish, as they are often emplaced within their original plutonic source rocks (Simmons et al. 1987).

A pegmatite field with pegmatites of LCT-family signature surrounds the Hoskin Lake granite in Florence County, Wisconsin. Several hundred pegmatites ranging from approximately one m to several hundred m in maximum dimension have been discovered during exploration from 1985 to 1999. All pegmatites in this field contain spodumene as the dominant or sole Li-mineral. A few others carry lepidolite, spodumene, tourmaline, and lithian muscovite as Li-bearing species. The Animikie Red Ace pegmatite (Falster 1994, Falster et al. 1996) is a large thin dike with abundant lepidolite, tourmaline, var. rubellite, and spodumene. The King's X pegmatite which is subparallel to the Animikie Red Ace pegmatite contains abundant spodumene and amblygonite-montebrasite but only very scarce tourmaline and lepidolite (Richardson 1998). Columbite-group minerals (CGM) are widespread in the pegmatites of the Hoskin Lake field and occur in most pegmatites. In the Animikie Red Ace pegmatite, CGM occur in all zones and show unusual patterns of zonation within individual crystals as well across the zoned pattern of the entire pegmatite. Most notably, CGM in this pegmatite exhibits a reverse zoning with some of the most evolved compositions occurring in the wall zone, unlike the common trend where evolved CGM occur in the inner zones of pegmatites (Spilde – Shearer 1992, Černý et al. 1985). Therefore, we have undertaken a detailed investigation, the results of which should contribute to the understanding of the whole pegmatite, which is exotic in most aspects.

Geology

Regional Geology

The general geology of the Great Lakes region is relatively well known (Sims – Peterman 1976, Van Schmus 1976, Morey et al. 1982). The ancient Archean basement rocks of the southern Canadian Shield are overlain by metasedimentary and metavolcanic rocks of early Proterozoic age. The key element in the geology of the region is the existence of a northern and southern Archean crustal segment (Morey – Sims 1976, Sims – Peterman 1983). The northern segment consists of late Archean (2.75 to 2.6 Ga) greenstone-granite complexes (Sims – Peterman 1976), which are typical for most of the Superior Province. The southern Archean crustal segment is a complex terrain composed of gneisses, which range in age from 3.6 to 2.6 Ga (Sims 1981). The boundary between the two segments is offset by two major northwest trending strike-slip faults (Sims – Peterman 1983).

The most significant event in the formation of the early Great Lakes region was the Penokean orogeny, first defined by Blackwelder (1914). The orogeny occurred at about 1.8 to 1.9 Ga with a peak of activity at about 1.82 to 1.86 Ga (Card et al. 1972). Effects of the Penokean Orogeny can be traced from Minnesota to the Grenville Province, covering a distance of approximately 1400 km and outlining the southern margin of the Superior Province (Card et al. 1972, Sims – Peterman 1976, Van Schmus 1976).

Local Geology

Florence County is underlain by metasediments and metavolcanic rocks of the Quinnesec Formation (Dutton 1971). The age of the Quinnesec formation was determined from U-Pb dating (zircon) (Sims – Peterman 1976) and an age of 1.86 ± 0.39 Ga (Penokean) was obtained. The Quinnesec formation is separated from rocks of the Marquette Supergroup to the north by the Niagara fault (Greenberg – Brown 1983), which separates the two types of bedrock, namely the dominantly metavolcanic rocks of the Penokean belt and the dominantly metasedimentary rocks of the Marquette Range Supergroup. The dominant metamorphic grade in the study area ranges from greenschist facies to amphibolite facies in areas of more extensive deformation or plutonic activity. In the Penokean volcanic belt, greenschist facies metamorphism is common and lower amphibolite facies metamorphic rocks are encountered where areas of intense deformation or plutonic activity are found (Greenberg – Brown 1983). Amphibolite-grade metasedimentary and metavolcanic rocks are prevalent in the Hoskin Lake pegmatite field. The field extends several kilometers to the west and north to northwest of the outcrops of the Hoskin Lake granite.

The Hoskin Lake granite

The Hoskin Lake granite is gray to pink or white in color and can be mottled. It is coarse grained with abundant large microcline phenocrysts that range in size from 2 to 4 cm in maximum dimension. The Hoskin Lake granite consists of approximately 75 percent light buff to pink feldspars up to 1 cm in maximum dimension with phenocrysts up to 4 cm in length. Microcline is the dominant feldspar but in some parts plagioclase may exceed microcline making this rock a quartz-monzonite. Quartz is typically light gray in color, and is generally less than 5 mm in maximum dimension. Biotite is relatively uniformly distributed throughout most of the granite, and ranges from 1 mm to several mm in size in rare aggregates. The most abundant feldspar is microcline. The abundance of plagioclase is variable throughout the granite and as a result, some portions of the granite are actually a quartz monzonite. Plagioclase is typically oligoclase but ranges in composition from An_{0-8} to An_{43-53} (Dutton 1971). Both alkali feldspar and plagioclase may be cloudy and altered to sericite. Minor amounts of epidote-group minerals are present in the granite, as a result of sausseritization. Aplitic portions of the Hoskin Lake granite exist but are subordinate. The few outcrops of the Hoskin Lake granite form prominent rounded knobs with well-developed joints. No contacts between the granite and country rock have been observed in the field, and the general outline of the Hoskin Lake granite is based entirely on aeromagnetic surveys (Dutton 1971).

The Hoskin Lake pegmatite field

A large swarm of granitic pegmatites has intruded the country rock around the Hoskin Lake granite (Fig. 1). Pegmatites range from simple granitic types to complexly zoned rare-element types of the lepidolite, spodumene, or amblygonite subtypes and range in size from 1 m to 600 m in maximum dimension. Extensive replacement units exist in the more fractionated pegmatites, which are enriched in large-ion-lithophile elements and show extreme fractionation, evidenced by the presence of exotic and highly fractionated minerals such as rhodizite, tantite, and wodginite (Falster – Simmons 1989). These pegmatites are the first examples of rare-element pegmatites found in the Hoskin Lake pegmatite field and typically contain spodumene in the pegmatite cores. The Animikie Red Ace is the largest and most fractionated pegmatite described to date in the Hoskin Lake pegmatite field. The northern portion of the pegmatite intruded a gneissic quartz-muscovite schist, whereas the southern margin intruded amphibolite and hornblende schist. In the northern portion, the pegmatite intersects a small band of marble. Minor amounts of quartzite, graywacke, metatillite, biotite schist and banded iron formation are exposed in the vicinity of the Animikie Red Ace pegmatite (Dutton 1971, Greenberg – Brown 1983). Country rocks were metamorphosed to lower amphibolite facies gneisses and schists. In these metamorphic rocks, accessory almandine, hornblende, andalusite and cordierite occur. Thus, we see an assemblage typical for low to medium pressures in the range of 250 to 350 MPa, which is characteristic for Abukuma-type facies metamorphism. Černý (1982) suggests that rare-element pegmatites are typically confined to Abukuma facies metamorphic grade rocks. Rare-element pegmatites are late to post tectonic in relation to regional tectonic events (Černý – Meintzer 1988).

The Animikie Red Ace pegmatite

The Animikie Red Ace pegmatite is located in section 22, T 39 N, R 17 E (Fig. 1). Maximum dimensions of the pegmatite are approximately 600 m x 2.5 m. The GPS location for the most prominent part of the pegmatite cutting through a small hill is: N 45 ° 51.042', W 88 ° 21.182'. Along strike of the pegmatite, swamp, vegetation, and heavy soil obscure extensive sections of the dike. The foliation of the country rock dips to the southwest at 45–70 °. Isoclinal folds in the country rock surrounding the

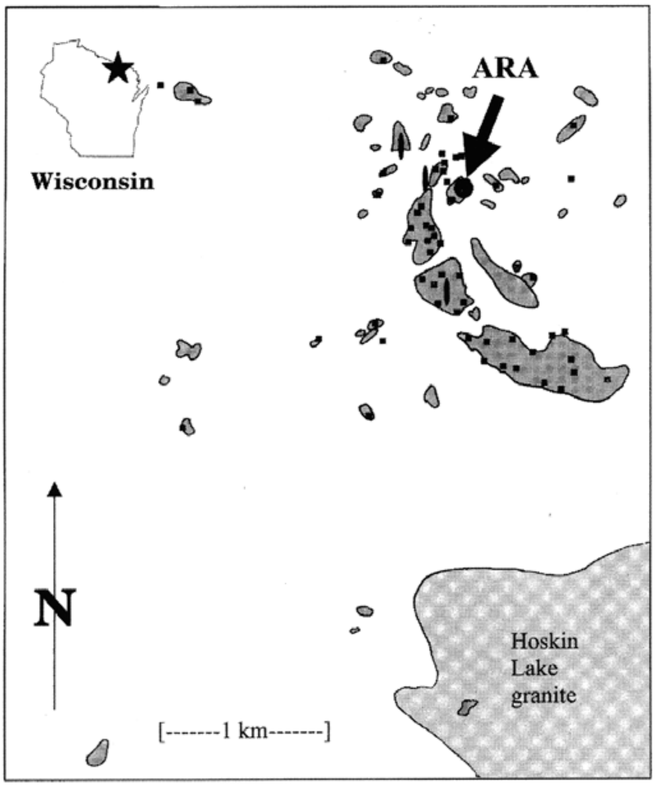

Fig. 1 The Hoskin Lake pegmatite field. Dark gray: bedrock exposures. Light gray: Northern and northwestern boundary of the Hoskin Lake granite. Black dots represent pegmatite exposures. ARA = Animikie Red Ace pegmatite. Insert shows the outline of the state of Wisconsin, star indicates map area.

pegmatite are abundant. Contacts are generally sharp and well defined. Intrusion into the country rock was parallel or subparallel to foliation and the pegmatite pinches and swells along strike suggesting a relatively ductile response of the country rock during pegmatite intrusion. A generalized sketch of the Animikie Red Ace pegmatite is shown in Fig. 2. Rafts of country rock are numerous and are typically heavily tourmalinized or almost entirely assimilated. The surrounding country rock shows the effect of exometasomatism, most mafic minerals were replaced by tourmaline and metacarbonate rocks have been altered to tremolite marble. Holmquistite was not observed in the metasomatized country rock.

Internal zonation of the Animikie Red Ace pegmatite is related to the type of country rock intruded. The two segments show somewhat different zonation patterns: Elbaite, variety rubellite, forms a comb structure that is continuous at the contacts of the pegmatite with the quartz muscovite schist and only discontinuous where amphibolite or hornblende schist makes up the country rock. Zonation in the southern segment is generally similar but tourmaline is less abundant. Pink feldspars are restricted to the southern segment. Tantite, rhodizite, hambergite and lithiophilite occur only in the northern segment, whereas griphite and helvite are restricted to the southern segment. In the Animikie Red Ace pegmatite, numerous continuous zones (such as the wall zone, the intermediate zones, the core margin, and the core zone)

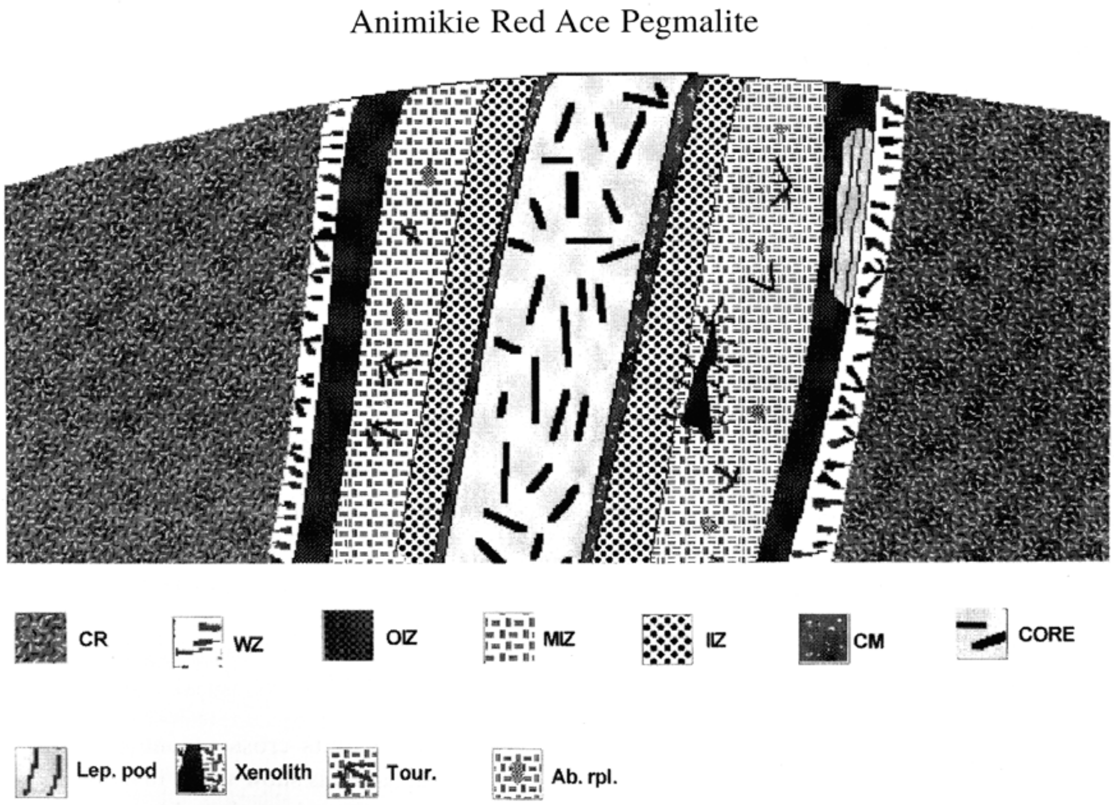

Fig. 2 Simplified cross section of the Animikie Red Ace pegmatite (northern segment). Surrounding country rock is represented as uniform gray; pegmatite zones and units are either subparallel bands or localized pods or units. Major zones are indicated as: WZ – wallzone, OIZ – outer intermediate zone, MIZ – middle intermediate zone, IIZ – inner intermediate zone, CMZ – core margin zone, CZ – core zone, AP – albite aplite, and the surrounding country rock as CR. Maximum width of the dike is 3.5 m.

and discontinuous, crosscutting or replacement units (such as aplites, lepidolite pods, albite and lepidolite replacement units) can be distinguished and are discussed in more detail below.

Border zone

The border zone is the thin, faintly foliated boundary between the pegmatite and country rock. It typically measures only 1–3 mm in thickness and consists of plagioclase (oligoclase), quartz, and the blue "roots" of rubellite, which form the comb structure in the wall zone.

Wall zone

This unit is remarkable for its abundance of deep red tapered elbaite crystals growing in a comb structure with the long dimension of the tourmaline crystals oriented perpendicular to the country-rock contact. Prior to this occurrence, the presence of an elbaite comb structure in a pegmatite wall zone has never been reported. The abundance of lepidolite is variable in the wall zone. Large pods of lepidolite tend to be associated with the footwall portions of the wall zone. These lepidolite pods show line-rock-like layering in the lower portions of the pods. A dearth of K-feldspar in this unit is noticeable although it occurs both in the country rock and in the outer intermediate zone. Rhodizite, pollucite, columbite-group minerals, tantite, and wodginite also occur in trace amounts in the wall zone. Deep blue manganoan apatite is abundant in this zone, which reaches a maximum thickness of 10 cm and grades into the outer intermediate zone. The Animikie Red Ace pegmatite wall zone is quite different compared to a more typical wall zone assemblage from similarly fractionated pegmatites consisting of dark blue schorl, feldspars, and quartz.

Outer intermediate zone

K-feldspar (maximum microcline) and quartz are very abundant in this unit. However, with the exception of columbite-group minerals, the rare accessory minerals found in the wall zone are absent. Tourmaline is generally absent in this unit, although it may occur as small nests comprised of a few crystals of bluish to greenish color. No rubellite has been found in this zone. Lepidolite is rare in the outer intermediate zone and occurs locally as interstitial stringers between feldspars. The zone has a pronounced gray color as the feldspars and quartz are both gray. Albitization of microcline is common. Typically, only the rims of large microclines are affected. This unit reaches a maximum thickness of 1 meter.

Middle intermediate zone

This zone is characterized by the re-appearance of abundant rubellite as well as bicolored green and red tourmaline that is associated with phosphate nodules. The phosphate nodules are mineralogically zoned with a core of apatite, a thick intermediate zone of lithiophilite, and a rim of a fillowite-like mineral and Mn-oxides. The nodules may attain 1–2 cm in maximum dimension but are more common in the mm range. Fracture planes in this unit are coated with large sprays of blue-black tourmaline up to 15 cm in diameter. This type of tourmaline is more common in the southern segment of the pegmatite. This unit reaches a maximum thickness of 25 cm.

Inner intermediate zone

Albite is more abundant in this zone than in any of the other zones, with the exception of the aplite and the albite replacement units. Albite is the dominant mineral, followed in abundance by potassium feldspar, lepidolite and quartz. Compared to the middle intermediate zone, tourmaline decreases in abundance and phosphate nodules disappear. Tourmaline from this zone is commonly greenish or bluish in color. This unit reaches a maximum thickness of 20 cm.

Core margin zone

This zone envelops the spodumene-quartz core and consists of altered spodumene, quartz, lepidolite, albite, minor potassium feldspar (maximum microcline), oxidized phosphate pods up to 1 cm in diameter, and crystals of columbite-group minerals which exhibit spectacular oscillatory zoning. The core margin grades gently into the core zone but has a sharp contact against the inner intermediate zone. This unit reaches approximately 5 cm in maximum thickness.

Core zone

The bulk mineralogy of the core zone is dominated by spodumene and quartz in approximately equal amounts. Spodumene may attain 12 cm in length in the northern segment and over 40 cm in length in the southern segment of the Animikie Red Ace pegmatite. Most spodumene is broken into fragments, which have been separated by a distance of several mm. Field evidence suggests fracturing in a melt moving from south to north. Accessory minerals include deep blue or gray-blue tourmaline, columbite-tantalite, and lepidolite. This zone attains 50 cm in thickness.

Other units

Albite aplite units

Albite aplite units crosscut one or more of the inner zones. The aplite is snow white in color and contains only a few other minerals such as blue tourmaline, blue apatite, and minor columbite-group minerals. This unit generally does not exceed 10 cm in thickness and the maximum lateral extent observed to date is 70 cm.

Albite replacement units

Albite replacement units typically occur in the intermediate zones where they may completely or partially replace pre-existing phases, particularly potassium feldspars. The replacing albite may be fine grained, almost felt-like in appearance, or it may form grains up to 5 mm in maximum dimension. Typically, the albite replacement occurs with, and may interfinger with, lepidolite replacement bodies.

Lepidolite replacement units

Lepidolite replacement units typically occur in the middle intermediate zone where they replace tourmaline. In some cases, only the cores of tourmaline crystals are replaced by coarse pink to lilac lepidolite aligned perpendicular to the c-axis of the host tourmaline. Albite in the middle intermediate zone also shows partial replacement by lepidolite. Lepidolite replacement rarely occurs in the core margin zone. In these rare instances, spodumene may be completely replaced by a mixture of lepidolite, albite, quartz, and other minerals.

Footwall lepidolite pods

Deep purple to lilac colored lepidolite occurs as discrete pods and extensive stringers in the footwall. These pods exhibit line-rock-like structures with bluish, purple, and blue-green color layers. The layers in this unit are primarily defined by the color of the lepidolite and not by local concentrations of tourmaline or garnet as is common in some of the San Diego County, California pegmatites. Layers in the lepidolite pods can be traced along strike of the Animikie Red Ace pegmatite for a distance of at least 120 m. Crosscutting relationships of several lepidolite generations suggest that in some cases intrusion of finer-grained lepidolite into coarser-grained lepidolite has occurred. Microlite is abundant in this unit as brown grains up to 3 mm in diameter, and can be intergrown with columbite-group minerals. Lepidolite pods and masses in the intermediate zones may be either yellow or purple in color and do not contain any microlite.

Table 1 Summary of mineral species identified in the Animikie Red Ace pegmatite.

Rock forming minerals	Minor minerals	Accessory minerals
Plagioclase (albite)	Fluorapatite	Bavenite
Microcline	Beryl	Bertrandite
Quartz	Hematite	Manganoan calcite
Lepidolite	Goethite	Cassiterite
Spodumene	Lithiophilite-triphylite	Chalcopyrite
Tourmaline, var. elbaite	Hureaulite	Cookeite
	Ferrocolumbite	
	Fillowite	
	Griphite	
	Hambergite	
	Helvite	
	Heterosite-purpurite	
	Lithian muscovite	
	Lőllingite	
	Manganocolumbite	
	Manganotantalite	
	Microlite	
	Pollucite	
	Pyrite	
	Rhodizite	
	Rynersonite	
	Sicklerite	
	Spessartine	
	Tantite	
	Varulite-alluaudite	
	Vayrynenite	
	Wodginite	
	Zinnwaldite	
	Zircon	

Mineralogy and Geochemistry

The mineralogy of the Animikie Red Ace pegmatite is comparable to that of other highly fractionated granitic pegmatites (Falster – Simmons 1989, Falster 1994, Falster et al. 1996). K/Rb ratios in microcline reach values of 5 and in lepidolite drop down to 3–4, K/Cs ratios reach values of 100 in microcline and 30 in lepidolite (Falster et al. 1996), Similarly, other elements and elemental ratios also indicate high geochemical fractionation of this pegmatite (Falster et al. 1996). The major differences, which make the Animikie Red Ace pegmatite unique, are the occurrence of some of the most fractionated mineral species such as rubellite, manganotantalite, wodginite, manganoan apatite, rhodizite, and hambergite, in the wall zone and not in the interior zones as is typical for this kind of geochemically evolved pegmatite. Table 1 shows a summary of the mineral species identified in the Animikie Red Ace to date. The presence of columbite-group minerals in all zones of the pegmatite is of particular interest, as it allows us to evaluate geochemical evolution in the pegmatite.

Columbite-group minerals and other Nb-Ta oxides

Typically, columbite-group (CGM) minerals are only found in the interior zones of many pegmatites. However, in the Animikie Red Ace pegmatite, CGM occur in all zones of the pegmatite, although they increase in abundance toward the interior zones. As the overall mineralogy and bulk chemistry of the zones change, there is a corresponding change in the CGM chemistry. The extent of zoning, from almost imperceptible to spectacular oscillatory banding, also changes from zone to zone. The size of the CGM grains attains a maximum of about 5 mm, the color ranges from black to deep red to tan. A composite of representative CGM samples from various zones is shown in Fig. 3. The widespread occurrence of CGM makes this mineral group an excellent indicator of geochemical evolution for this pegmatite. Within each zone, CGM has the following appearance:

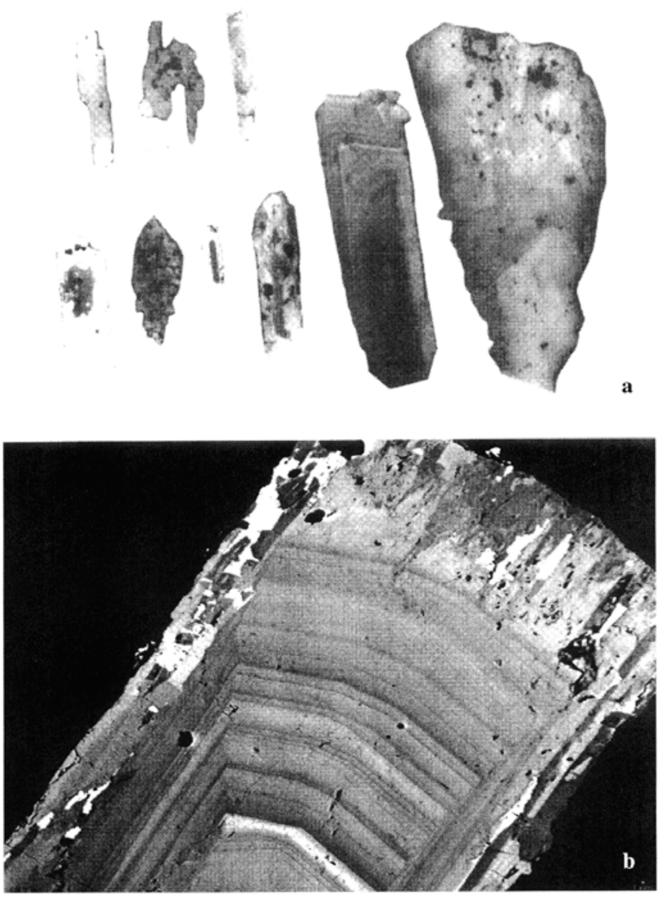

Fig. 3 a: Backscattered electron image of CGM from the zones in the Animikie Red Ace pegmatite. Samples are representative of each zone and are scaled the same.
Top row: CGM from the footwall lepidolite pods, the albite replacement units, and the albite aplite units. Bottom row: CGM from the wall zone, outer intermediate, middle intermediate, inner intermediate, core margin, and the core zone. Largest crystal measures 2 mm tall.
b: Close-up of a CGM from the core margin, showing pronounced oscillatory zoning pattern. Field of view is 2 mm wide.

Wall zone

CGM may reach 1 mm in maximum dimension and are distinctly zoned: under backscattered electron imaging the cores appear dark, the result of their overall lower average Z composition. There is a strong contrast between the core, which shows evidence of corrosion prior to deposition of the rim material, and the rim. The rim shows a remarkably brighter image in backscattered-electron imaging. Faint oscillatory zoning as well as irregular patchiness is evident in the rim portions of these CGM minerals in the wall zone. It is remarkable that wodginite, manganotantalite, and rynersonite have all been recovered from this unit.

Outer intermediate zone

CGM from this zone is about the same size as CGM from the wall zone. The color is typically black and zoning is much fainter than in CGM from the wall zone. Differences between core and rim compositions are minor and faint oscillatory zoning is evident throughout the crystals.

Middle intermediate zone

CGM from this zone attains 0.6 mm in maximum dimension and resembles that from the wall zone. The compositional differences between core and rim are very pronounced, however, there is no apparent corrosion of the core as there was in the wall zone. The color of CGM minerals in this zone is tan to deep red, with a black core. Wodginite is also found in this zone.

Inner intermediate zone

CGM from this zone attain a maximum dimension of 1.5 mm and is black in color. Zoning tends to be chaotic and shows at least in part oscillatory characteristics.

Core margin

CGM from the core margin attain up to 4 mm and is black in color. This zone yields the most spectacularly zoned CGM in the Animikie Red Ace pegmatite. Crystals are strikingly zoned in an oscillatory fashion.

Core zone

The core zone yields the largest CGM crystals in this pegmatite, up to 5 mm in maximum dimension, and of black color. Backscattered-electron imaging reveals higher average Z composition in the core rather than the rim, which is the reverse of CGM zoning in all other zones of the pegmatite except the core margin. Faint oscillatory zoning is evident in CGM from the core zone.

Albite aplite units

CGM from the albite aplite is very faintly zoned, with the rims being slightly brighter under backscattered electron imaging. Maximum size is about 1 mm and the color is deep brown.

Footwall lepidolite pods

CGM from the lepidolite pods is remarkably uniform in appearance under backscattered electron imaging: virtually no zoning is detectable. The maximum size is 1 mm and the color is dark brown. Microlite is fairly abundant in these pods.

Albite replacement units

CGM from the albite replacement units attains 1 mm in maximum dimension and shows evidence of intense corrosion; only irregular deep brown remnants have been found.

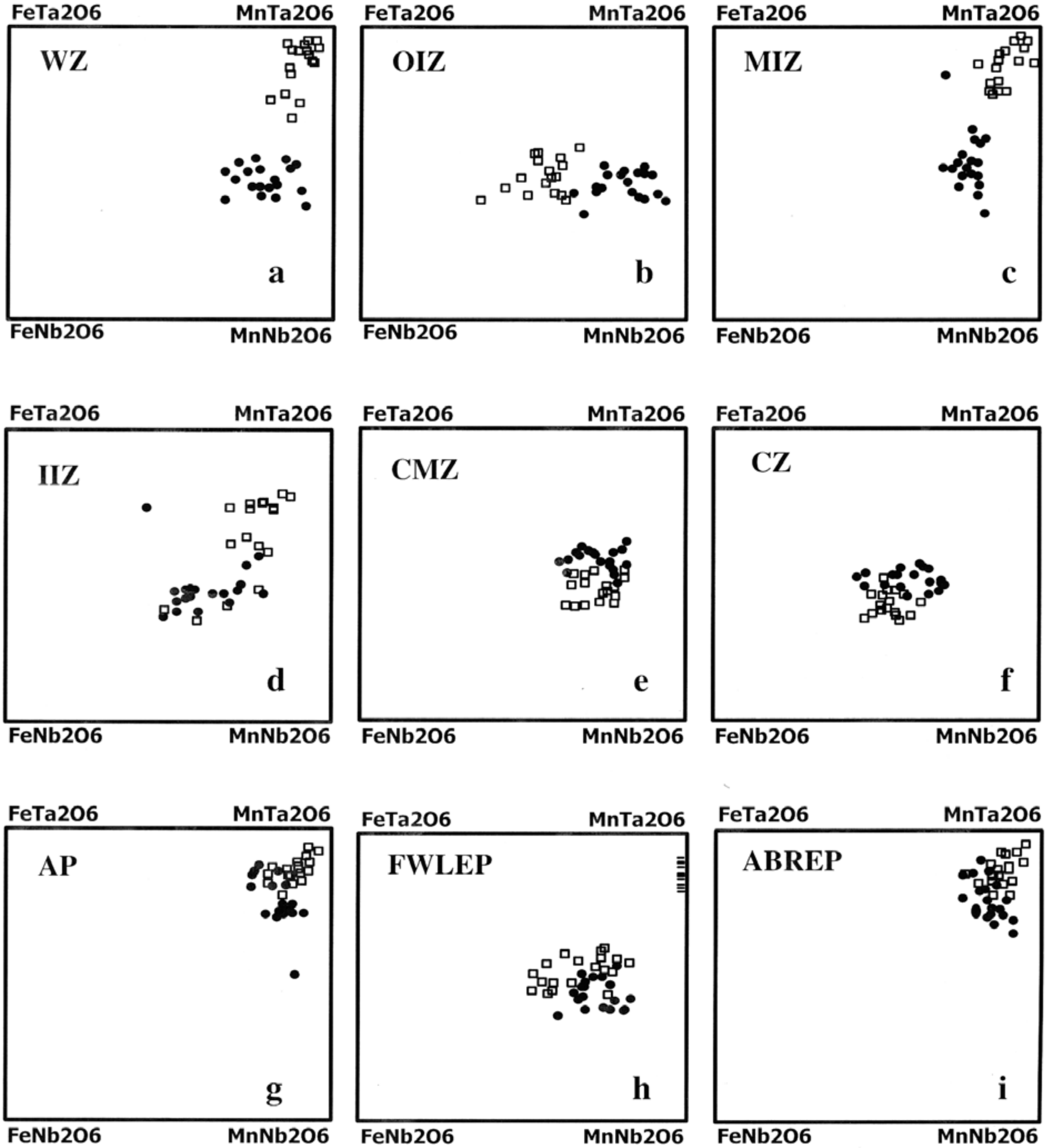

Fig. 4 Electron microprobe analyses of CGM from the Animikie Red Ace pegmatite, plotted in the columbite-tantalite quadrilateral. Core compositions are represented as solid circles, rim compositions as open squares; a) WZ: wall zone CGM; b) OIZ: outer intermediate zone CGM; c) MIZ: middle intermediate zone CGM; d) IIZ: inner intermediate zone CGM; e) CMZ: core margin zone CGM; f) CZ: core zone CGM; g) AP: albite-aplite unit CGM; h) FWLEP: footwall lepidolite pod CGM; i) ABREP: albite replacement unit CGM.

Methods

X-ray powder diffraction was performed on a SCINTAG XDS 2000 which was operated at 35 kV potential, 15 mA current with a scan range from 2 °2θ to 70 °2θ. The continuous scanning mode was used for the analyses. The scan rate was generally kept at 0.1 °2θ/minute. DMS (Diffraction Master System) software, which is an integral part of the SCINTAG X-Ray diffractometer, was used to process scans using moderate degrees of smoothing (3 to 5 point smoothing).

Scanning electron microscopy was performed on a digital AMRAY 1820 scanning electron microscope. Samples for energy-dispersive spectral analysis and backscattered-electron imaging were typically encased in epoxy, ground flat, polished with 1.0, 0.3, and finally 0.05 μm alumina grit. The samples were cleaned, rinsed, and coated with 250 Å of carbon. An acceleration voltage of 25 kV was used for both energy dispersive and X-ray mapping analysis.

An ARL Electron SEMQ Microprobe was used for quantitative analysis. Samples used for analysis were ei-

Table 2a Results of electron microprobe analyses of columbite-tantalite from the wall zone (1: core, 2: rim), outer intermediate zone (3: core, 4: rim), middle intermediate zone (5: core, 6: rim), inner intermediate zone (7: core, 8: rim).

	1	2	3	4	5	6	7	8
Ta_2O_5	45.62	80.00	32.31	35.30	34.82	68.92	33.54	46.55
Nb_2O_5	36.13	2.40	48.83	46.62	47.20	15.44	47.68	35.58
TiO_2	0.20	n. d.	0.34	0.28	n. d.	n. d.	0.03	0.20
SnO_2	0.66	1.10	n. d.	0.03	n. d.	0.02	n. d.	n. d.
Sb_2O_3	0.04	0.80	n. d.	n. d.	n. d.	0.02	n. d.	n. d.
Bi_2O_3	n. d.	1.00	n. d.	n. d.	n. d.	0.02	n. d.	n. d.
FeO	4.87	1.40	8.32	13.65	5.02	1.68	5.07	5.03
MnO	12.54	13.02	10.54	4.60	13.02	13.57	13.25	12.06
CaO	n. d.	n. d.	n. d.	n. d.	0.14	n. d.	n. d.	n. d.
Totals	100.06	99.72	100.34	100.48	100.20	99.67	99.61	99.42
apfu								
Ta	0.852	1.837	0.564	0.623	0.615	1.456	0.594	0.877
Nb	1.121	0.092	1.416	1.368	1.386	0.542	1.403	1.115
Ti	0.010	0.000	0.016	0.014	0.000	0.000	0.001	0.010
Sn	0.018	0.037	0.000	0.001	0.000	0.001	0.000	0.000
Sb	0.001	0.028	0.000	0.000	0.000	0.001	0.000	0.000
Bi	0.000	0.022	0.000	0.000	0.000	0.000	0.000	0.000
Fe	0.280	0.099	0.446	0.741	0.273	0.109	0.276	0.291
Mn	0.729	0.931	0.573	0.253	0.716	0.893	0.730	0.708
Ca	0.000	0.000	0.000	0.000	0.010	0.000	0.000	0.000
Sum A	1.008	1.030	1.019	0.994	0.999	1.002	1.006	0.999
Sum B	2.002	2.016	1.996	2.006	2.001	2.000	1.998	2.002

Table 2b Results of electron microprobe analyses of columbite-tantalite from the core margin (9: core, 10: rim), core zone (11: core, 12: rim), albite aplite units zone (13: core, 14: rim), footwall lepidolite pods (15: core, 16: rim), and from the albite replacement units (17: core, 18: rim).

	9	10	11	12	13	14	15	16	17	18
Ta_2O_5	39.54	33.31	36.13	27.73	50.98	76.44	30.87	33.32	60.34	69.33
Nb_2O_5	42.22	47.66	45.14	52.76	31.10	8.50	49.97	47.42	22.76	13.70
TiO_2	0.30	0.20	0.34	0.34	0.05	0.02	0.40	0.20	n. d.	n. d.
SnO_2	n. d.	n. d.	n. d.	0.10	0.40	0.76	n. d.	0.30	0.97	1.11
Sb_2O_3	n. d.	n. d.	n. d.	0.02	n. d.	n. d.	n. d.	n. d.	0.05	0.10
Bi_2O_3	n. d.	n. d.	n. d.	0.01	0.02	0.02	n. d.	n. d.	0.08	0.12
FeO	7.38	8.87	6.09	9.65	1.76	1.32	4.90	11.04	2.09	3.60
MnO	10.33	9.55	11.88	9.21	14.88	13.40	13.55	7.30	14.00	11.50
CaO	n. d.	n. d.	0.04	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.
Totals	99.77	99.59	99.62	99.88	99.19	100.46	99.69	99.58	100.29	99.46
apfu										
Ta	0.717	0.589	0.646	0.476	0.987	1.670	0.538	0.590	1.213	1.481
Nb	1.273	1.400	1.341	1.506	1.001	0.309	1.448	1.395	0.760	0.487
Ti	0.015	0.010	0.017	0.019	0.003	0.001	0.019	0.010	0.000	0.000
Sn	0.000	0.000	0.000	0.003	0.011	0.024	0.000	0.008	0.029	0.035
Sb	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.002	0.003
Bi	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.002
Fe	0.412	0.482	0.335	0.509	0.105	0.089	0.263	0.601	0.129	0.237
Mn	0.583	0.526	0.661	0.492	0.897	0.912	0.735	0.402	0.876	0.765
Ca	0.000	0.000	0.003	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sum A	0.995	1.000	0.999	1.002	1.002	1.001	0.998	1.003	1.005	1.002
Sum B	2.005	1.999	2.004	2.005	2.002	2.004	2.005	2.003	2.006	2.008

ther polished thin sections or samples encased in epoxy, which had been ground flat, and polished. The microprobe was operated at an acceleration potential of 15 kV and a beam current of 1.5×10^{-7} mA. Beam diameter was kept at about 2 μm for most analyses. Counting times ranged from 10 to 60 s per element. Raw data were processed using HAVOC and PDQ (a modified version of EMPADR) for ZAF corrections.

Standards used for electron microprobe analyses included: stibiotantalite, Mesa Grande, California (Sb, Ta); bismuthian stibiotantalite, Mesa Grande, California (Bi); manganotantalite, Rio Grande do Norte, Brazil (Mn, Ta); microlite, Harding pegmatite, New Mexico (Ca, Ta); titanium (IV) oxide, synthetic (Ti); uranium(IV) oxide, synthetic (U); hematite, Elba, Italy (Fe); cassiterite, synthetic (Sn); tantalum (V) oxide, synthetic (Ta).

Results

All CGM group minerals are highly evolved with elevated concentrations of Mn and Ta, particularly in the wall zone samples, where tantite, rynersonite, and wodginite also occur. A similar trend is found in CGM and wodginite from the middle intermediate zone. However, in this zone, tantite, wodginite, and rynersonite have not been found. Figs 4 a–i show representative chemical compositions of the core and rim CGM samples from the various zones. Representative CGM and other Nb-Ta oxide compositions can be found in Table. The calculated cell dimensions (for details see Falster 1994) indicate that CGM from the Animikie Red Ace pegmatite are at least partially disordered (Fig. 5). Within the pegmatite, several anomalous trends are apparent. Chemistry of CGM rims from the wall zone is unusual as the Ta/(Ta+Nb) and Mn/(Mn+Fe) ratios are the highest of all the pegmatite zones within the pegmatite, with the exception of the aplites and replacement units. Also, with the exception of the core margin and the core zone, CGM rims are generally more Ta-rich than the cores. The outermost rims commonly show an increase in Fe. Zoning in CGM (Fig. 3) shows a sharply defined core and rim, chaotic zoning, or very complex oscillatory zoning patterns.

Table 2c Results of electron microprobe analysis of microlite (19: core, 20: rim) from the footwall lepidolite pods, rynersonite from the wall zone (21), wodginite (22) from the wall zone and of tantite (23) from the wall zone.

	19	20	21
Ta_2O_5	72.16	70.99	76.98
Nb_2O_5	9.27	10.56	6.87
TiO_2	0.02	n. d.	n. d.
SnO_2	14.79	5.73	12.11
Sb_2O_3	0.02	0.06	0.55
Bi_2O_3	0.05	0.09	0.60
FeO	n. d.	2.27	n. d.
MnO	n. d.	8.31	n. d.
CaO	2.65	2.86	n. d.
Totals	98.96	100.87	97.11
apfu			
Ta	1.6478	1.476	1.696
Nb	0.3160	0.365	0.252
Ti	0.0010	0.000	0.000
Sn	1.1940	0.469	1.051
Sb	0.0010	0.004	0.037
Bi	0.0030	0.006	0.041
Fe	0.0000	0.336	0.000
Mn	0.0000	0.810	0.000
Ca	0.6310	0.691	0.000
Sum A	1.198	1.625	1.129
Sum B	1.795	1.841	1.948

	22	23
Ta_2O_5	71.95	96.47
Nb_2O_5	6.67	3.06
SnO_2	8.78	n. d.
TiO_2	0.01	n. d.
FeO	1.08	0.33
MnO	11.17	0.16
Totals	99.67	100.02
apfu		
Ta	8.480	1.889
Nb	1.307	0.100
Sn	1.517	0.000
Ti	0.003	0.000
Fe	0.391	0.020
Mn	4.100	0.010
Sum A	15.785	2.019

However, even in the simply zoned samples, a slightly chaotic zoning is evident in both core and rim. Replacement of columbite-tantalite by microlite is most common in interior pegmatite zones. Wodginite has only been found in the wall zone and in the middle intermediate zone. An interesting trend in Mn/(Mn+Fe) and Ta/(Ta+Nb) ratios is observed from wall zone to core zone (Fig. 6). Average CGM cores from the wall zone have a value of the Mn/(Mn+Fe) ratio of about 0.80, and a Ta/(Ta+Nb) ratio of about 0.48. However, the average rim compositions show a dramatic increase in both ratios to about 0.90. In the outer intermediate zone, CGM core compositions are not significantly different from those of the wall zone. However, the value of the Mn/(Mn+Fe) ratio of CGM rims decreases to about 0.50, with an accompanying increase in Fe-content. CGM from the middle intermediate zone has essentially the same composition as CGM from the wall zone. Inner intermediate zone CGM is chemically similar to both the wall zone and the middle intermediate zone CGM, although they do not quite reach the same level of Ta enrichment. Core margin zone CGM and core zone CGM show similar characteristics, both have core compositions comparable to CGM from the wall zone and the intermediate zone, but the CGM rim compositions tend to be slightly Fe-enriched and Ta-depleted. The albite aplite units have evolved CGM with high values of the Ta/(Ta+Nb) and Mn/(Mn+Fe) ratios in the cores. Rim compositions are only slightly more evolved with respect to these two ratios. The footwall lepidolite units contain CGM which

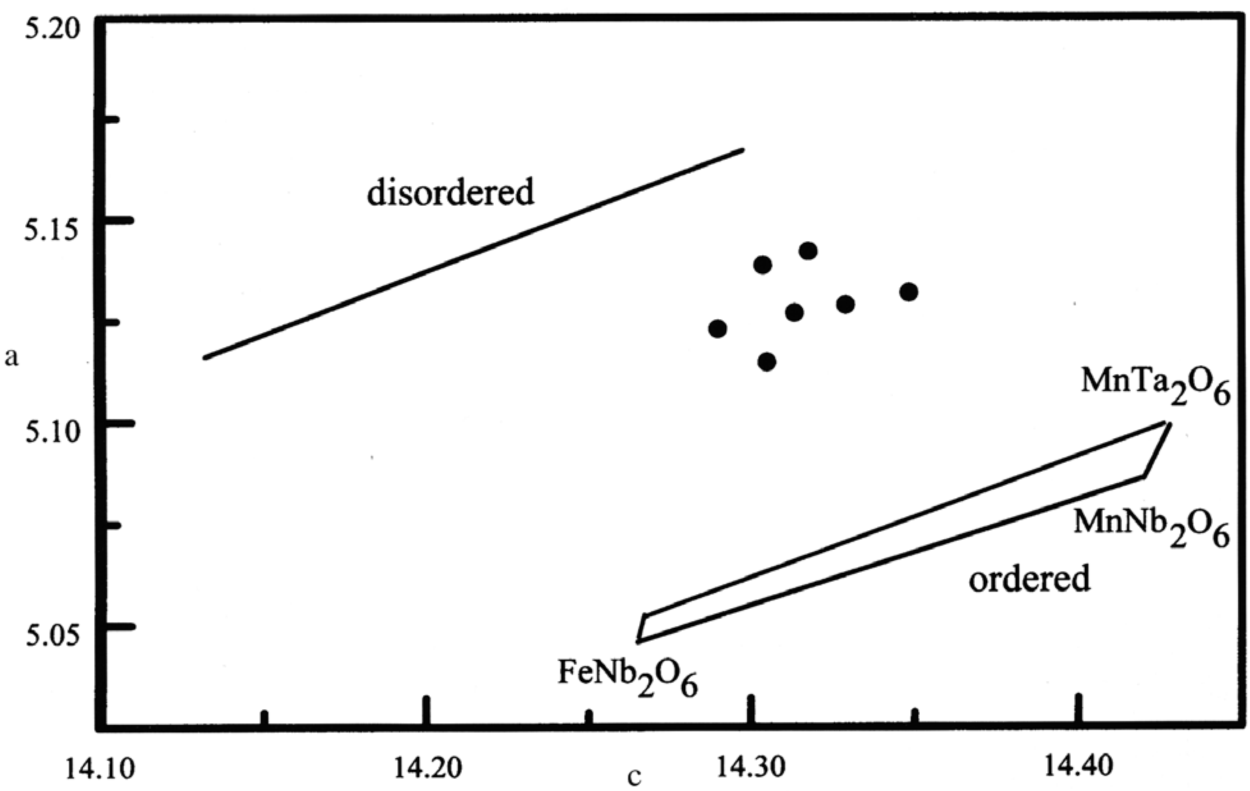

Fig. 5 The a–c diagram (in Å) of the columbite-tantalite minerals from the Animikie Red Ace pegmatite (*a* tripled for disordered phases). Based on Černý – Ercit (1995).

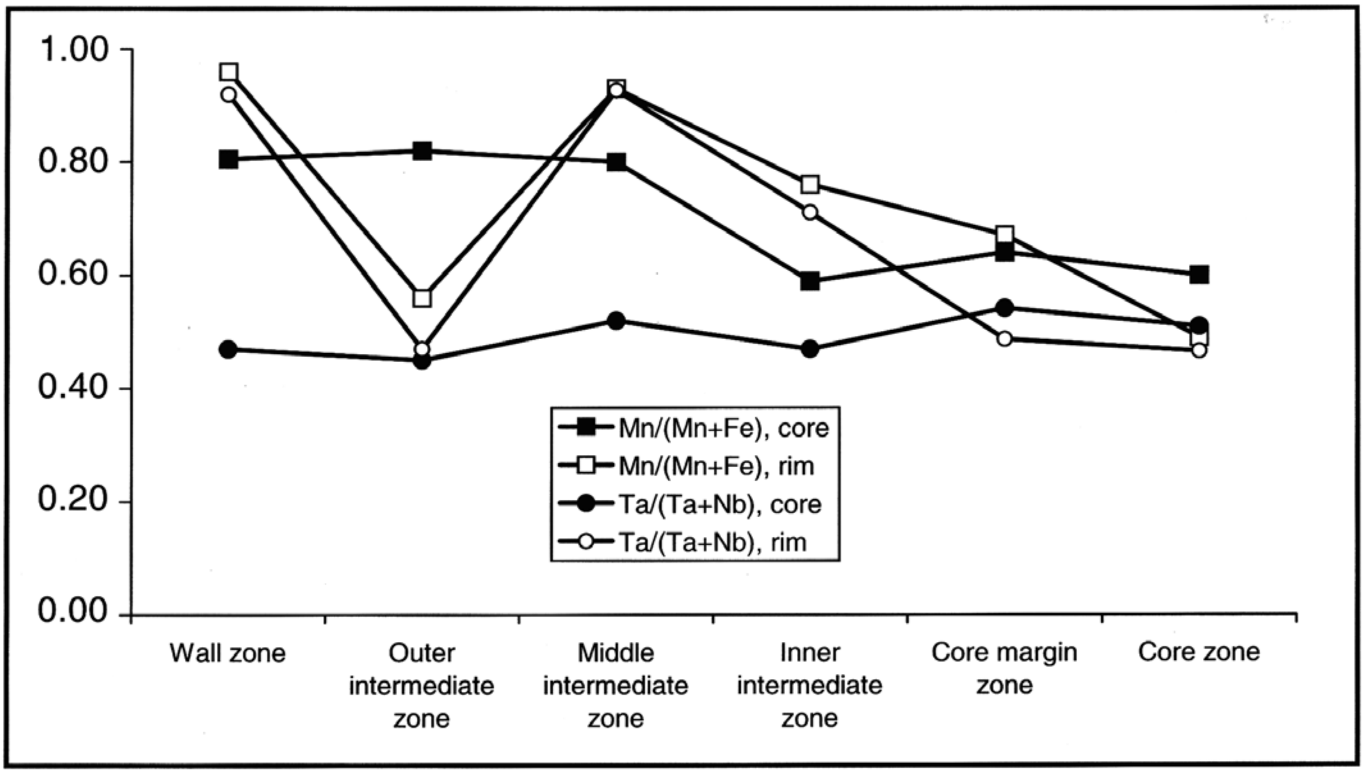

Fig. 6 Plot of Mn/(Mn+Fe) and Ta/(Ta+Nb) ratios for core and rim compositions of CGM group minerals in the Animikie Red Ace pegmatites across the continuous zones.

have core compositions similar to that of the other zones, the rim compositions are only slightly more Ta-rich with no change in the value of the Mn/(Mn+Fe) ratio. However, these pods contain a significant amount of microlite that is about three times as abundant as CGM. Microlite compositions from this zone are plotted in Fig. 4h. Thus, although there is as much Ta in this zone as in the albite aplite units, Ta is preferentially incorporated into microlite. The albite replacement units are very similar to the albite aplite units. There is an interesting correlation between the degree of fractionation of CGM minerals in the Animikie Red Ace and the zonal mineralogy: zones with high values of the Ta/(Ta+Nb) ratios tend to be either rich in lepidolite (wall zone, middle intermediate zone, and footwall lepidolite pods) or they are very late units (albite aplite and albite replacement units) (Falster 1994, Falster et al. 1996)

Discussion and Conclusions

In summary, CGM from the Animikie Red Ace pegmatite display the following characteristics:

1. All analyzed CGM in the Animikie Red Ace pegmatite are essentially tantalian manganocolumbite to manganotantalite.
2. They show no systematic fractionation trends within the zones in which they occur.
3. The concentration of Mn decreases from wall zone to core zone.
4. The value of Ta/(Ta+Nb) ratio of CGM core compositions is roughly the same from wall zone to core zone.
5. In the outer intermediate zone, core margin zone, and core zone, rim compositions are more Fe-rich than the CGM cores.
6. In general, there is a decrease in the value of Ta/ /(Ta+Nb) ratio from the wall zone to the core zone. This is the opposite of what is normally observed in highly evolved pegmatites.

The mineralogy of the Animikie Red Ace pegmatite indicates that this pegmatite is geochemically highly evolved with high abundance of Li, Rb, and Cs and high values of Mn/(Mn+Fe) and Ta/(Ta+Nb) ratios in CGM. A strong correlation exists between the enrichment of Ta and Mn in the CGM and the presence of F-rich lepidolite. The unusual chemistry of the wall zone may be related to the abundance of F in this zone. The middle intermediate zone also contains abundant F-rich lepidolite and CGM. The values of Ta/(Ta+Nb) and Mn/(Mn+Fe) ratios are similar to those of the wall zone. Evidently, F-complexes of Ta and Mn are responsible for the pronounced fractionation seen in these two zones, basically by increasing solubility of manganotantalite (Linnen – Keppler 1993). Zones with less abundant F-bearing phases contain CGM with noticeably lower values of the ratios of Mn/(Mn+Fe) and Ta/(Ta+Nb). The Animikie Red Ace pegmatite evidently cooled rapidly (Webber et al. 1997), as indicated by the pronounced comb-structure tourmalines in the wall zone, the generally small grain size of minerals in the pegmatite, the thin thickness of the pegmatite, and the oscillatory and chaotic zoning in the CGM.

Even the most primitive CGM in the Animikie Red Ace pegmatite is already tantalian manganocolumbite, ferrocolumbite is absent. The importance of high F activity on the high values of the Ta/(Ta+Nb) ratios is demonstrated by the strong correlation of this ratio with the occurrence of lepidolite. Thus, the earliest and the latest units such as the albite aplite and albite replacement units formed from a very highly evolved, pegmatitic magma that gave rise to highly evolved members of the CGM group.

A likely explanation for the observed characteristics is that CGM nucleated simultaneously throughout the pegmatite. In zones where there was abundant F, the crystals evolved to very Ta-rich crystal rim compositions and in zones where there was less F, there is less difference in the core-rim compositions. The observed complex or chaotic zoning in CGM crystals is consistent with the very rapid crystallization of the Animikie Red Ace pegmatite from a melt that was already highly evolved, derived perhaps from a larger pegmatite crystallizing at depth.

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Neortodoxní trendy složení minerálů skupiny columbitu z pegmatitu Animikie Red Ace, Wisconsin, USA

Pegmatit Animikie Red Ace z Florence County, Penokeanského stáří 1,8 Ga, je příkladem extrémně frakcionovaného pegmatitového systému. Žíla o rozměru asi 600 x 2,5 m má směr sever-jih a upadá ~ 68° k západu. Pegmatit je výrazně zonální s úzkou okrajovou zónou, následující rubelitovou zónou, třemi přechodnými zónami, zónou okraje jádra, vlastním jádrem a několika aplitickými a metasomatickými jednotkami. Mineralogie pegmatitu odpovídá vysoce frakcionovaným pegmatitům, zahrnuje Mn a Ta bohaté minerály skupiny columbit-tantalitu, spodumen, lepidolit, elbait a několik exotických minerálů jako jsou rhodizit, tantit, wodginit a hambergit. Minerály skupiny columbit-tantalitu jsou geochemicky frakcionované, vysoké koncentrace Mn a Ta jsou především v okrajové zóně a střední přechodné zóně. Columbit-tantalit z dalších zón není tak výrazně frakcionovaný jako v předešlých zónách. Lze pozorovat zřetelný pokles poměru Ta/(Ta+Nb) od okrajové zóny do jádra, což je opačný trend ve srovnání s ostatními vysoce frakcionovanými pegmatity. Trend vysoké frakcionace v okrajové zóně naznačuje, že pegmatitové magma bylo odvozeno od již geochemicky frakcionovaného a mnohem většího pegmatitového tělesa v podloží.