# FRACTIONATION OF HFSE AND PETROGENETIC INDICATORS IN NYF-TYPE PEGMATITES

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**Summary**

NYF-type pegmatites are characterized by high F, FeO/MgO ratios, and high/economic concentrations of Nb, Y, Zr, Th, U, REE (except Eu), and Ga. F plays a critical role in the development of NYF-type pegmatite chemistry and mineralogy. In the presence of F, many high field strength elements (HFSE) such as Nb, Zr, Th and U, behave incompatibly and are thus strongly concentrated in highly differentiated NYF-type pegmatites in such phases as zircon, rutile, columbite-tantalite, samarskite and other REE minerals. It appears that many NYF-type pegmatites, such as those in the South Platte District, Colorado and Wausau Syenite Complex, Wisconsin, are genetically related to anorogenic, sub- to metaluminous (to peralkaline) granitoids, a major component of which is derived from F-rich, Proterozoic crustal sources depleted in Li, Cs, B, and P.

The degree of pegmatite fractionation has typically been evaluated using indicators such as K/Rb, K/Cs, and Fe/Mn. While this works well for LCT-type pegmatites derived from orogenic, I- or S-type granites enriched in Li, Cs, Ta, and B, these elements do not effectively measure the degree of fractionation in NYF-type pegmatites. NYF fractionation may be better evaluated using elements enriched in A-type granites i.e. Nb, Y, F, REE, Zr and Ga. The extreme concentration of REE+Y, Nb, and F in South Platte pegmatites suggests that they are just as evolved as their LCT-type counterparts.

Biotite composition in NYF-type pegmatites is distinctly different from that in LCT-type pegmatites. Compared to LCT-type biotites, NYF-type biotites crystallized under relatively reducing $f_{O_2}$ conditions and low $f_{H_2O}$, are annite-rich with high F and Ga/Al. Therefore, biotite composition can be used as a tectonic discriminant for pegmatites.

**Introduction**

A strong correlation between trace element abundances in granitoids and the tectonic regime prevailing during magma genesis was demonstrated by Pearce *et al.* (1984). This suggests that mineral compositions may be direct indicators of the tectonic regime prevailing during host granitoid magma genesis and thus pegmatite genesis.

This study investigates variations in mineral chemistry between anorogenic and orogenic tectonic settings. Biotites from four pegmatite districts were analyzed in order to compare and contrast the biotite chemistry from anorogenic and orogenic tectonic regimes. Anorogenic NYF-type pegmatite districts include the South Platte (SP) district in Colorado and the Wausau Syenite Complex (WSC) in Wisconsin. Orogenic pegmatite districts include the Trout Creek Pass (TCP) district, Colorado and pegmatites from southwestern Maine (ME) from the Oxford and Brunswick pegmatite fields. Biotite chemistry from this study was compared with analyses from other areas including biotites from the anorogenic Honeycomb Hills (HH) topaz rhyolites, Utah (Congdon and Nash 1991); siderophyllites from the eastern part of the anorogenic Arabian Shield (EAS; du Bray 1994); and biotite in late-orogenic rare-element granitic pegmatites in the southwestern Grenville Province (GP; Lentz 1992).

Compared to orogenic granites, anorogenic granites are characterized by high FeO/MgO ratios, high abundances of $SiO_2$, $K_2O + Na_2O$, F, Rb, Ga, Y, REE (except Eu), Zr, Th, Nb, U, and Zn and by low concentrations of CaO, MgO, $Al_2O_3$, Cr, and Ni as well as lower magmatic water content. Typically, NYF-type pegmatites, characterized by high F, FeO/MgO ratios, and high/economic concentrations of high field strength elements (HFSE) such as Nb, Zr, Th, and U, as well as Y, REE (except Eu), and Ga are hosted in A-type granites, whereas LCT-type pegmatites, derived from orogenic, I- or S-type granites, are enriched in Li, Cs, Ta, and B.

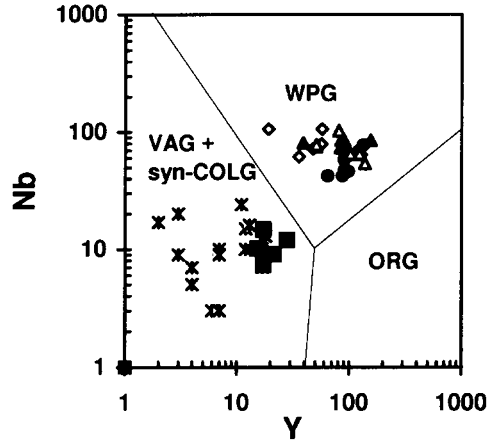


Figure 1: Nb vs. Y tectonic discrimination diagram of Pearce *et al.* (1984), showing the anorogenic within-plate signature for granitoids from SP (filled circles), WSC (open diamonds), HH (filled triangles), and EAS (open triangles). Granitoids from TCP (filled squares) and ME (stars) have an orogenic, syn-collisional signature.

**South Platte District, Colorado**

The South Platte (SP) pegmatite district is located in Jefferson County, Colorado in the Colorado Front Range. All the pegmatites are associated with the 1.0 Ga anorogenic, epizonal, composite Pikes Peak Batholith (Post Berthoud Suite). They are significantly enriched in F, REE, Nb and Y and exhibit well-developed internal zonation. SP granitoids are contained within the parental Pikes Peak batholith and are thus unambiguously genetically related to the Proterozoic A-type Pikes Peak Granite. SP granitoids can be classified as within-plate granites (WPG) using the Nb-Y discrimination diagram of Pearce *et al.* (1984) (Fig. 1). Geochemically, granitoids from the SP district have high Ga/Al ratios and high $K_2O + Na_2O$ compared to M-, S-, and I-type granites and plot in the A-type field of Whalen *et al.* (1987) and more specifically the $A_2$-type (postcollisional, postorogenic and anorogenic environments) granitoid field according to Eby (1992).

Pegmatites of the SP district constitute one of the world's classic NYF pegmatite districts. The district is located within the Precambrian core of the Rocky Mountain Front Range in central Colorado, near the northern margin of the Pikes Peak batholith.

More than 75 pegmatites belong to this district and all are enriched in Nb, Y and F. Samarskite-(Y) is abundant throughout the district and many tons were mined from several pegmatites. Synchysite-(Y) and xenotime-(Y) are abundant in several pegmatites and fluorite is abundant in most. Several contained mappable zones of fluorite. The whole pegmatite-granite system is extremely REE enriched and the pegmatites are well known for their contents of relatively abundant rare-earth minerals. Boron is virtually absent and beryllium is present only in rare gadolinite-(Ce) and -(Y), and rare samples of beryl. The mica is almost exclusively biotite and the feldspars are pink. The pegmatites are enriched in Fe and pods of metallic hematite occur in some pegmatites and there is abundant secondary hematite replacement. In addition to the common rock-forming minerals such as quartz, microcline, sodic plagioclase, and biotite, the following accessory minerals are prevalent: hematite, fluorite, zircon (cyrtolite), muscovite, siderite, calcite, pyrolusite, and widespread rare-earth minerals including yttrian fluorite, cerian fluorite, monazite-(Ce), xenotime-(Y), allanite-(Ce), samarskite-(Y), fergusonite-(Y), yttrotantalite-(Y), gadolinite-(Ce), gadolinite-(Y), molybdenite, thorite, thalenite-(Y), synchysite-(Y) and bastnaesite-(Ce). In some deposits one or more of these minerals may be very abundant in secondary units. Very rarely, minerals such as sellaite and autunite have been found.

The pegmatites are characterized by an extraordinarily well-developed internal zonation with biotite concentrated in the wall-zone units (biotite graphic granite) and sometimes in an outer-intermediate zone characterized by giant biotite crystals that exceeded 2.5 m in length.

**Wausau Syenite Complex, Wisconsin**

The Wausau Syenite Complex (WSC) is a Proterozoic (1.52-1.48 Ga) epizonal, anorogenic intrusive complex that forms part of a widespread belt of Proterozoic anorogenic activity that extends across the US from eastern Canada to the American southwest (Anderson 1983). It is age equivalent to the Silver Plume-Berthoud Plutonic suite in Colorado. Geochemically, samples from the WSC can be classified as within-plate granitoids (WPG) using the Nb-Y discrimination diagram of Pearce *et al.* (1984) (Fig. 1) and as $A_1$-type granitoids (rift, plume, hotspot environments) according to Eby (1992), consistent with the belt of anorogenic activity that extended across the US. Similar to other anorogenic complexes, the WSC contains relatively low levels of B; however, Li and Ga are considerably elevated compared to the SP district in Colorado.

The WSC consists of four distinct intrusive centers, the Stettin, the Wausau, the Rib Mountain, and the Nine Mile plutons. Within the Nine Mile pluton, a group of more evolved F-enriched pegmatites (Koss pegmatite group) has recently been found. Miarolitic pegmatites are found in all four intrusive centers and are enriched in REE, Nb, Y and F. Of the four, the syenitic Stettin pluton is the oldest and most alkalic. This pluton is roughly concentrically zoned with two nepheline syenite rings, one as the outermost unit, the other as a core margin around a pyroxene syenite core. The three other plutons, the Wausau, Rib Mountain, and Nine Mile, are progressively more silica-rich. The Nine Mile pluton consists of alkali granite and monzonite. Pegmatites in the Stettin pluton range from nepheline-bearing to pyroxene- and amphibole-bearing types. Minor minerals include magnetite, zircon, apatite, ilmenite, xenotime, cheralite, and titanite. Rare accessories include eudialyte, catapleiite, fluorite, pyrochlore, allanite, thorite, and thorogummite. Pegmatites in the Nine Mile pluton are characterized by feldspars, quartz and minor biotite (siderophyllite). Minor minerals include magnetite, hematite, anatase, brookite, rutile and siderite. Rare minerals include phenakite, bertrandite, cheralite, xenotime, zircon, and pyrite. Significantly, columbite-tantalite group minerals are virtually absent except in one localized area in the central Nine Mile pluton. Pegmatites of the Wausau and Rib Mountain plutons have characteristics between those of the Stettin and Nine Mile plutons. The intrusion of the Wausau Syenite Complex and the slightly younger Wolf River batholith to the east represent the last large-scale intrusive event in central Wisconsin.

**Trout Creek Pass, Colorado**

Three major Proterozoic intrusive episodes occurred in the Colorado Rockies. The Trout Creek Pass (TCP) pegmatite district, located in the Mosquito Range in Chaffee County, Colorado, is associated with the catazonal, orogenic, 1.7 Ga Denny Creek Granodiorite of the Routt Plutonic Suite, emplaced during the Boulder Creek Orogeny. Subsequent to this orogenic event, mesozonal granitoids of the Berthoud Plutonic Suite (Silver Plume equivalents) were emplaced as part of the Proterozoic anorogenic 1.4 to 1.45 Ga event. The youngest plutons in this area belong to the 1 Ga post Berthoud plutonic group, the largest of these being the anorogenic epizonal Pikes Peak granite. Geochemically, samples from the TCP can be classified as syn-collisional (Fig. 1).

TCP pegmatites are notably enriched in REE, Nb, Y and Ti, and depleted in F, and are simply zoned, composite-core pegmatites. Polycrase-(Y) is the dominant Nb mineral in the district. Even though the TCP district is associated with an orogenic event, the chemistry of the pegmatites suggests a close affiliation with NYF-type (or NY-type?) pegmatites. Regionally, the pluton ranges in composition from quartz monzonite to granodiorite with foliated biotite granite dominant in the TCP district. Pegmatites in this district are structurally well-zoned with a graphic granite wallzone, a composite quartz-microcline core and superimposed albite-rich replacement units. The overall composition is granodiorite to biotite quartz diorite. Intrusives can be foliated and are concordant with adjacent metamorphics. Biotite in the host foliated biotite granite occurs as centimeter-size, sub-parallel grains, which give the rock its foliated texture. Within the pegmatites, biotite is notably absent in wallzone graphic granite, but is found as centimeter- to 1.5 meter-size books along the core-wallzone contact.

**Southwestern Maine Pegmatites**

The granitic pegmatites of southwestern Maine (ME) are divided into the Brunswick and Oxford pegmatite fields. The Topsham series pegmatites within the Brunswick field possess both NYF- and LCT-type characteristics. They are moderately fractionated, rare-earth to beryl-columbite subtype pegmatites. The Oxford field pegmatites are typical LCT-type pegmatites with moderately to highly fractionated beryl-columbite, beryl-columbite-phosphate, spodumene and petalite subtypes. The Oxford pegmatite field is spatially related to the Sebago Batholith in southwestern Maine. Pegmatites are concentrated within and marginal to the pluton, which has intruded middle- to upper-amphibolite grade metasedimentary rocks. U-Pb data indicate that the age of the Sebago Batholith is 296 ± 3 Ma (Foord *et al.* 1995a). Geochemically, samples from southwestern ME can be classified tectonically as syn-collisional (Fig. 1). The Topsham series pegmatites are poorly zoned, contain no pockets and are characterized by biotite > muscovite, monazite, magnetite, beryl and columbite. Overall, they are characterized by REE, Be and Nb > Ta. Oxford field pegmatites are moderately well zoned and are pocket bearing. They are characterized by muscovite > biotite, beryl, columbite-tantalite, cassiterite, spodumene, lepidolite, petalite, and tourmaline.

### Honeycomb Hills Topaz Rhyolites, Utah

F- and Fe-rich biotite (siderophyllite) occurs in the 4.7 Ma anorogenic, peraluminous, highly evolved, Honeycomb Hills (HH) topaz rhyolites in west-central Utah (Congdon and Nash 1991). Rhyolites can be divided into two units, a pyroclastic sequence and overlying lavas that form a dome. HH micas occur as phenocrysts up to 1 mm in diameter throughout the eruptive sequence and as megacrysts in the topaz horizon of the dome. Some F has been lost from glassy samples selectively after eruption. HH was included in this study for comparison as Congdon and Nash (1991) suggest that chemically and mineralogically these rhyolites represent the extrusive equivalents of rare-element pegmatites. More specifically, we feel they are most characteristic of NYF-type pegmatites. Congdon and Nash (1991) suggest the pegmatitic magma was derived from F-enriched Proterozoic continental crust and subsequently differentiated within the upper reaches of a granitic magma cupola that was enriched in rare elements and F. HH rhyolites can be classified tectonically as within-plate granitoids (WPG) using the Nb-Y discrimination diagram of Pearce *et al.* (1984) (Fig. 1).

### Eastern Arabian Shield

Peraluminous, rare-metal enriched granitoids of the eastern part of the late Proterozoic Eastern Arabian Shield (EAS, du Bray 1994) were generated in anorogenic terranes. EAS granitoids can be classified tectonically as within plate granites (WPG) based on Nb and Y trace element data (Fig. 1). Micas included in this study were siderophyllites characterized by elevated abundances of $Li_2O$ and F and by low MgO abundances. According to du Bray (1994), the genesis of the highly evolved 590-565 Ma EAS granitoids involved fluorine-fluxed, second generation, anorogenic partial melting of a granulitic source or crustal partial melting of tonalitic to granodioritic compositions.

### Southwestern Grenville Province, Canada

Biotite occurs in late-tectonic rare-element granitic pegmatites in the southwestern Grenville Province (GP), Canada (Lentz 1992). The pegmatites intrude a complex sequence of supracrustal and mafic to felsic plutonic rocks of the Central Metasedimentary belt. The late-tectonic pegmatites are the largest in the Grenville Province and are enriched in U, Th, Mo, REE, Nb, and Be. Pegmatite samples can be classified tectonically as syn-collisional based on Nb and Y trace element abundances (Fig. 1). According to Lentz (1992) the late-tectonic Grenville pegmatites probably originated as $H_2O$ undersaturated, fractional partial melts from deeper crustal levels, generated by the introduction of fluids into volatile-undersaturated gneisses. These low temperature melts would begin fractionally crystallizing during ascent to their present level of emplacement. A trend of increasing chemical fractionation exists from unzoned to partially zoned to zoned pegmatites. The most fractionated biotites have high Fe/Fe+Mg, Al, Mn, Rb, Nb, Zn. High Al in part reflects the peraluminous character of the pegmatites.

### Biotite Data

Biotites from the SP, WSC, TCP, and ME pegmatites were analyzed by electron microprobe. All analyses were recalculated to 22 oxygens. The $Fe^{2+}/Fe^{3+}$ ratio was determined by titration. Biotites from all four areas are chemically distinct. Anorogenic biotites (siderophyllites) from SP and WSC pegmatites and granites have high Fe/Fe+Mg ratios ranging from 0.91 to 0.95 for the WSC and ~0.95 for the SP district (Fig. 2). HH (Congdon and Nash 1991) and EAS (du Bray 1994) biotites also have high Fe/Fe+Mg ratios. In contrast, orogenic biotite from TCP are more $Mg^{2+}$ rich with a Fe/Fe+Mg ratio of ~0.70, ME biotites have a ratio of about 0.6 to 0.8, and GP (Lentz 1992) biotites have a Fe/Fe+Mg ratio less than 0.6. Biotite $Al^{TOT}$ content is partially a function of the $Al_2O_3$ content of the biotite host rock. TCP and ME biotites have higher $Al^{TOT}$ than do the WSC biotites, consistent with the more peralkaline nature of the WSC versus the metaluminous nature of the SP and TCP districts and the peraluminous nature of ME, EAS, and HH.

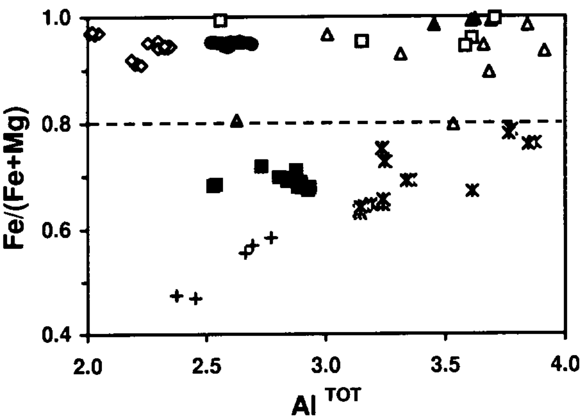


Figure 2: Fe/Fe+Mg ratio vs. $Al^{TOT}$ for biotites. Symbols are as follows: WSC (open diamonds), TCP (filled squares), SP (filled circles), ME (stars), HH (filled triangles), GP (plus signs), EAS (open triangles), Pikes Peak Li-Fe biotites (open squares; Foord *et al.* 1995b). Biotite analyses were recalculated on the basis of 22 oxygens. The dashed line separates higher Fe/(Fe+Mg) anorogenic biotites from lower Fe/(Fe+Mg) orogenic biotites.

Overall, F is noticeably higher (Fig. 3) in biotites from anorogenic suites (WSC, SP, HH, EAS) compared to those from orogenic tectonic environments (TCP, ME, GP). F varies from 2.5 to 4.0 wt % in WSC biotites, with the most F-rich biotites coming from the Koss granite and pegmatite. SP biotites have 3.0 to 3.75 wt % F, whereas TCP biotites have only 1.0 to 1.5 wt% F.

Interestingly, two discrete populations of biotite can be differentiated in the SP district on the basis of their $Al^{TOT}$ and $Si^{4+}$ contents (Fig. 4). The first group of biotites, which are found in topaz-bearing pegmatites are characterized by lower $Si^{4+}$ and $Al^{VI}$, and higher $Al^{IV}$, $Mn^{2+}$ and $Ti^{4+}$. The second group of biotites, characterized by higher $Si^{4+}$ and $Al^{VI}$, are from SP pegmatites that have little to no topaz. The Al-rich biotite population may be explained by the contamination of the pegmatitic melts by metasediments of the overlying Idaho Springs Formation, which produced local enrichments of aluminum as evidenced by the presence of topaz.

Biotite chemistry was also used to determine $f_{H_2O}$ for the pegmatite districts using the formula of Wones and Eugster

(1965). Consistent with the Fe/Fe+Mg biotite ratio at QFM, a temperature of 800 °C and log $f_{O_2}$ of −15 bars for TCP biotites and a temperature of 725 °C and log $f_{O_2}$ of −17 bars for both SP and WSC was used for the calculations. TCP had the highest $f_{H_2O}$ of $\sim 10^{3.8}$ bars. Both SP and WSC had lower $f_{H_2O}$ of $\sim 10^{3}$ bars.

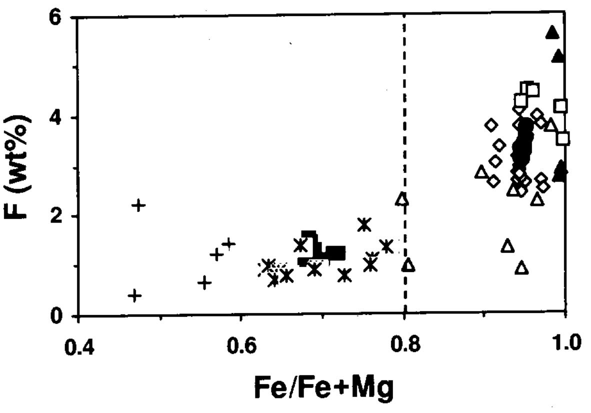


Figure 3: Weight percent F vs. Fe/Fe+Mg ratio for biotites. Symbols as in Fig 2. The dashed line separates higher Fe/(Fe+Mg) anorogenic biotites from lower Fe/(Fe+Mg) orogenic biotites.

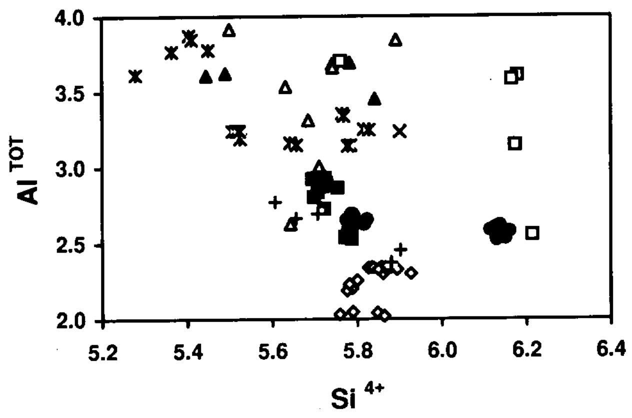


Figure 4: $Al^{TOT}$ vs. $Si^{4+}$ in biotites. Symbols as in Figure 2.

**Conclusions**

NYF-type pegmatites are characterized by high F, FeO/MgO ratios, and high/economic concentrations of HFSE (Nb, Zr, Th, U) Y, REE (except Eu), and Ga. F plays a critical role in the development of NYF-type pegmatite chemistry and mineralogy. In the presence of F, many HFSE behave incompatibly and are thus strongly concentrated in highly differentiated NYF-type pegmatites in such phases as zircon, rutile, columbite-tantalite, samarskite and other REE minerals. Many NYF-type pegmatites, such as those in the SP district, Colorado and WSC, Wisconsin, are genetically related to anorogenic granitoids, a major component of which is derived from F-rich, Proterozoic crustal sources depleted in Li, Cs, B, and P. Conversely, LCT-type pegmatites are derived from orogenic, I- or S-type granites and are enriched in Li, Cs, Ta, and B.

Biotites from NYF-type anorogenic pegmatites (SP, WSC, EAS) are distinctly different from those in LCT-type pegmatites. Compared to LCT-type biotites, NYF-type biotites crystallized under relatively reducing $f_{O_2}$ conditions and low $f_{H_2O}$, are characterized by high Fe/Fe+Mg ratios, and are F-rich. Interestingly, biotites from the F-rich HH topaz rhyolites are very similar to those from NYF- and not LCT-type rare-element pegmatites.

Biotite chemistry for orogenic biotites (TCP, ME, GP) is distinct and accurately reflects the appropriate tectonic setting. Even though the TCP district is enriched in REE, Nb and Y and thus has some chemical characteristics in common with anorogenic granitoids and NYF-type pegmatites, the biotite chemistry (lower Fe/Fe+Mg ratio, lower F, etc.) accurately reflects its orogenic tectonic setting. Biotites from the LCT-type pegmatites of the Oxford field plot along with other orogenic biotites from TCP and GP (Figs. 2-4). Interestingly, biotites from Topsham series pegmatites that display some NYF-type characteristics also plot with other orogenic biotites, which suggests an orogenic origin for the Topsham series.

In summary, biotite composition, particularly the Fe/Fe+Mg ratio and F content, is effective for discerning the appropriate tectonic regime associated with pegmatite genesis. This is particularly helpful for pegmatite districts that have "mixed" signatures with respect to mineralogy and chemistry.

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