# CRYSTALLIZATION OF 'POCKET' BERTHIERINE FROM THE PULSIFER GRANITIC PEGMATITE, POLAND, MAINE, USA

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**Abstract**—A new occurrence of berthierine has been found in the Pulsifer granitic pegmatite, near Auburn, Maine. Berthierine was found in miarolitic cavities ('pockets') as aggregates of radial platy crystals with albite, as fracture-fillings in microcline and as fine-grained anhedral flakes with muscovite. Berthierine samples from all associations are depleted in Mg, but show variable enrichment in Mn. The textural relationships of the berthierine assemblage indicate that its formation is probably related to the dissolution of microcline in the presence of a low-temperature, neutral to alkaline, Fe-rich hydrothermal solution. This mode of occurrence is in direct contrast to the typical formation of berthierine in granitic pegmatites that is generally related to the alteration of cordierite-group minerals.

**Key Words**—Berthierine, Granitic Pegmatite, Miarolitic Cavity, Hydrothermal Fluids, Pulsifer, Maine.

## INTRODUCTION

Berthierine is an $Fe^{2+}$-rich trioctahedral member of the kaolin-serpentine group that is widespread in a variety of geological settings. Most berthierine is found in low-temperature sedimentary environments, although some igneous and metamorphic rocks may host minor quantities. Damyanov and Vassileva (2001) distinguished three genetic types of berthierine (marine, non-marine and hydrothermal) based on differences in their Mg/Fe and Al/Si ratios. In marine environments, berthierine is widely recognized as a significant component of shallow-marine sediments (Porrenga, 1967) and of oolitic ironstones (Bhattacharyya, 1983). Non-marine occurrences of berthierine include desert and lateritic soils (Kodama and Foscolos, 1981; Toth and Fritz, 1997), bauxite deposits (Klekl, 1979), brackish cold-water sediments (Rohrlich *et al.*, 1969), and coal measures (Iijima and Matsumoto, 1982). Hydrothermal-type berthierine has been observed in altered mafic rocks (Ruotsala *et al.*, 1964), volcanogenic massive sulfide deposits (Slack *et al.*, 1992), sedimentary exhalative siderite iron formations (Damyanov and Vassileva, 2001), as well as in granites and granitic pegmatites (Hogarth, 1972; Gottesmann and Förster, 2004).

Berthierine in granitic pegmatites is very uncommon and has mostly been identified as a fine-grained component of mineral assemblages that developed during the post-magmatic alteration of ferromagnesian silicates. Berthierine in pegmatites develops largely as an alteration product of cordierite (Povondra *et al.*, 1984; Abad-Ortega and Mieto, 1995; Jobin-Bevans and Černý, 1998) and sekaninaite (Guastoni *et al.*, 2004). Wise and Černý (1990) reported intermixed biotite and

berthierine as part of a metasomatic assemblage associated with microcline and triphylite-calcian beusite intergrowths. In the Hagendorf-Sud pegmatite, berthierine occurs as thin, dark green idiomorphic laths on pyrite and is believed to have formed by hydrothermal processes (Mücke, 1983). Berthierine (formerly called chamosite) occurs as part of a fine-grained mineral assemblage that includes kainosite, yttrian thorogummite and goethite that developed from the alteration of yttrian hellandite in the Evans-Lou pegmatite, Quebec (Hogarth, 1972). In altered pegmatites at Mont Saint Hilaire, berthierine is found as pseudomorphs after an unidentified mineral with a layered structure (Horvath and Gault, 1990).

During the field examination of granitic pegmatites in western Maine, crystal aggregates of an unknown sheet silicate mineral were discovered on alkali feldspars extracted from miarolitic cavities in the Pulsifer pegmatite. The unidentified mineral was originally suspected to be zinnwaldite; however, subsequent examination by X-ray diffraction (XRD), scanning electron microscopy-energy dispersive spectrometry (SEM-EDS) and electron microprobe analysis (EMPA) shows that the mineral is berthierine. The well formed crystals are unlike any other known pegmatite occurrence of berthierine and the associated mineral assemblage suggests a somewhat different origin from those summarized above. In view of the atypical textural features of the berthierine-bearing assemblage, this paper focuses on the chemistry, paragenesis and origin of berthierine crystals that crystallized in the Pulsifer pegmatite.

## GEOLOGICAL SETTING

The Pulsifer pegmatite is one of several rare-element granitic pegmatites that belong to the Sebago Pegmatite

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Group, located in the Oxford pegmatite field of western Maine (Figure 1). The Sebago Pegmatite Group constitutes a population of mineralogically primitive to highly evolved pegmatites enriched in Li, Rb, Cs, Be, Nb, Ta, Sn, B, F and P, and are generally considered to be late magmatic derivatives of the peraluminous and locally pegmatitic Sebago batholith (Wise and Francis, 1992). The Pulsifer and nearby pegmatites that are distributed along the eastern margin of the batholith show internal zonation that varies from poorly to well developed. Several of the pegmatites display advanced rare-element enrichment as is evident from the local presence of beryl, columbite-tantalite, cassiterite, spodumene, lepidolite and pollucite (Wise and Francis, 1992).

The Pulsifer pegmatite is a tabular body situated on the western flank of a small hill known locally as Mount Apatite. Five individually named pits (Keith, Pulsifer,

Wade, Dionne, Hole-in-the-Ground) have been opened in the pegmatite, which intrudes upper amphibolite-facies metapelites and schists that are locally interbedded with calc-silicate rocks. The geology observed within these pits indicates that the pegmatite is internally well zoned. From the hanging wall downward, there is first a zone of graphic microcline with biotite, followed by a zone of graphic microcline containing plumose muscovite, a zone of blocky albite containing miarolitic cavities ('pockets'), a nearly continuous layer of almandine garnet or 'garnet seam' and a zone of undetermined thickness consisting of graphic albite (Rose *et al*., 1997). The pegmatite was subjected to varying degrees of albitization by late-stage pegmatite-generated fluids. Albitization appears to have been a contributing factor in the formation of the gem-bearing pocket zone, which lies immediately above the 'garnet
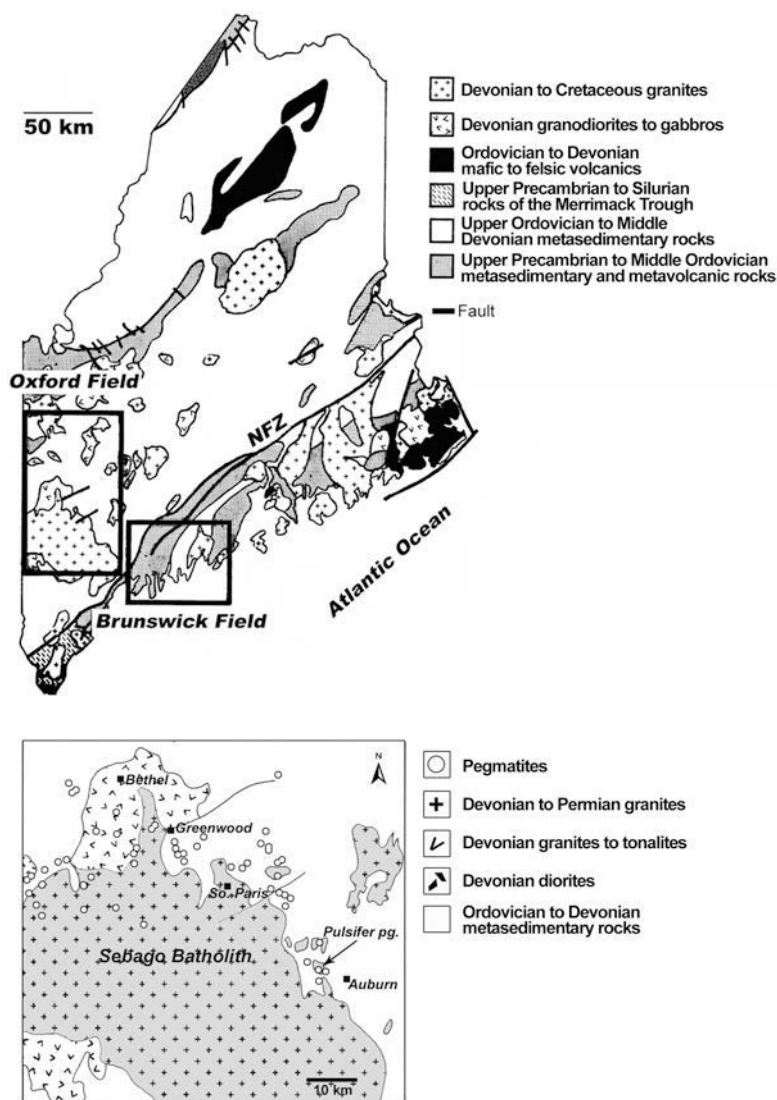


Figure 1. General geological map of the Sebago Pegmatite Group showing the location of the Pulsifer pegmatite.

seam'. The pockets are the primary source for gem- and specimen-grade elbaite, beryl, quartz, apatite, garnet and gahnite. Moreover, it is the only part of the pegmatite that contains berthierine.

The attitude of the pegmatite body could not be accurately determined due to lack of sufficient contact relationships with the country rock. Where visible, the pegmatite-country rock contacts were measured with dips of ~20º to the west. The true thickness is not known as mining operations have failed to encounter the footwall contact. Several near-vertical Mesozoic mafic dikes that strike 45−60º degrees intrude the pegmatite.

## SAMPLES AND EXPERIMENTAL METHODS

Berthierine was collected from the bottom of a single pocket in the Pulsifer pegmatite. The pocket mineralogy includes quartz with partially corroded microcline, coarsely bladed albite (cleavelandite) and minor amounts of muscovite. Berthierine crystals were found largely attached to albite, muscovite and microcline but some were also associated with rare crystals of pyrite and apatite, both typically ~1 mm across.

Based on examination of the pocket contents, the following sequence of mineralization is proposed for the berthierine assemblage. The earliest primary minerals to precipitate were quartz, perthitic microcline, medium-grained muscovite and coarse-grained cleavelanditic albite. Some perthitic microcline crystals are found partially corroded. Extensive corrosion resulted in the dissolution of the microcline component of the perthite and recrystallization of the albite lamellae. A later generation of fine-grained albite was deposited with quartz on the surfaces of the early generation of albite. Minor pyrite crystallized prior to the formation of berthierine which grew on the surfaces of both primary and recrystallized feldspars. A light brown clay-like mineral, which was identified by XRD as microcline, sometimes partially coats berthierine, pyrite and the fine-grained albite and represents the last stage of mineralization in the cavity.

Berthierine occurs in three types of textural assemblages: (1) as aggregates of radial platy crystals usually with recrystallized albite; (2) as veinlets of anhedral berthierine in microcline; and (3) as fine-grained anhedral flakes with muscovite. The aggregates of radial berthierine are composed of pale gray to gray-green, pseudohexagonal platy crystals typically 1 mm in diameter. The crystals cluster to form rosettes up to 3 mm across that are perched upon recrystallized albite with minor quartz and corroded microcline. A single specimen of coarsely platy albite crystals (cleavelandite) also contained berthierine rosettes on the albite blades. At the base of this specimen, fine-grained flakes of berthierine are intimately associated with an aggregate of fine-grained muscovite crystals. Texturally, it appears that muscovite crystallization post-dated that of berthier-

ine (Figure 2). One hand specimen contained a 1.5 cm wide band of fine-grained berthierine at the boundary of unaltered perthitic microcline and recrystallized albite. Extending from this band into the adjacent microcline, are fractures filled with fine-grained berthierine. Our SEM images show the presence of anhedral albite and trace amounts of apatite as part of the fracture-filling assemblage (Figure 2).

X-ray diffraction studies were performed on berthierine from all three assemblages and all gave similar diffraction patterns. Samples were finely ground, attached to a glass fiber and mounted on a Rigaku D/MAX-RAPID microdiffractometer system operating at 50 kV and 40 mA using MoKα radiation ($\lambda$ = 0.7093 Å). The X-ray beam was focused on the sample using a 0.3 mm collimator and an exposure time of 10 min. Samples were identified as berthierine using the search-match routine of the JADE program.

The major element chemistry of Pulsifer berthierine was determined using wavelength-dispersive analysis on a JEOL Model JXA-8900R electron microprobe operating at 15 kV and 20 nA using a beam diameter of ~1 μm. The counting time for background and peak determinations were 5−10 s and 15−40 s, respectively. Standards used for analyses were Kakanui hornblende (Si, Al, Mg, Ca), olivine (Fe) and manganite (Mn). No Na or K was detected during the analysis of multiple berthierine samples. The structural formula for berthierine was calculated on the basis of 28 oxygens.

## RESULTS

X-ray powder diffraction data of berthierine from the Pulsifer pegmatite are in good agreement with the 1$M$ polymorph structure reported from the literature (Figure 3). The patterns show a prominent 7 Å reflection, but lack the characteristic 14 Å reflection of chlorite (see Bailey, 1988 for criteria). The absence of the 14 Å reflection suggests that the Pulsifer material probably consists entirely of berthierine or at most, <10% admixed chlorite (Reynolds, 1988).

Electron microprobe analyses of the Pulsifer berthierine are presented in Table 1. The chemical analyses plot well within the field of berthierine compositions for all known geological settings (Figure 4). $SiO_2$ (~22−25 wt.%) and $Al_2O_3$ (~22−24 wt.%) show small variations compared to berthierine compositions reported by other studies. In the tetrahedral sites, ~30−36% of Si is substituted by Al and octahedral Al always exceeds tetrahedral Al. Total Fe (calculated as FeO) is consistent with most analyses found in the literature, although berthierine from the muscovite association tends to have slightly lower Fe contents than those associated with the alkali feldspars. The octahedral site is dominated by ~61−71% Fe. Berthierine associated with muscovite also has greater Mg contents and higher Mg/Fe values than berthierine
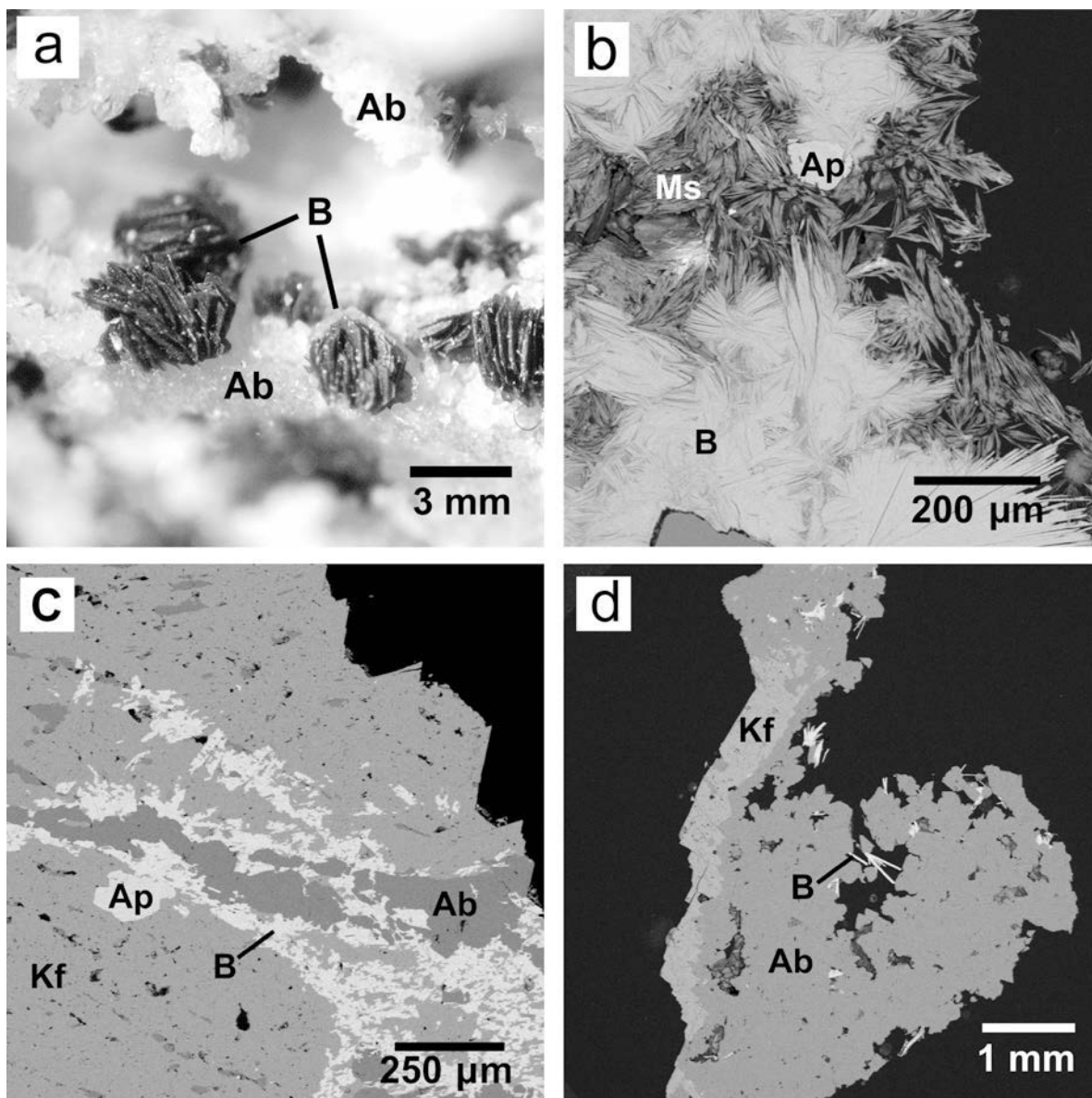
Figure 2. Textural relationships of berthierine and associated minerals in the Pulsifer pegmatite. (a) Euhedral crystals of berthierine. (b) Plumose aggregate of berthierine with muscovite. (c) Albite with berthierine fracture-filling in microcline. (d) Berthierine laths (white) in vuggy recrystallized albite. Kf − microcline, Ab − albite, B − berthierine, Ms − muscovite, Ap − apatite.

occurring with feldspars (Figure 5). However, with the exception of the muscovite association, the Pulsifer samples generally contain much smaller concentrations of MgO (0.41−0.63) compared to berthierine from most other geological settings (see examples of Brindley, 1982). Berthierine from pegmatites have been shown to exhibit elevated MnO contents that may reach as high as 2.7 wt.% (e.g. Guastoni *et al*., 2004). The MnO concentrations are typically <0.5 wt.% to absent in berthierine from most sedimentary environments, although a manganoan berthierine interlayered with manganoan chlorite was found to have manganese contents as high as 1.42 wt.% MnO (Coombs *et al*.,

2000). The Mn content of the Pulsifer samples is comparable to other pegmatite localities, varying from ~0.5−4.0 wt.% MnO with the highest values found in berthierine from the muscovite association.

The compositions of the Pulsifer berthierine are most consistent with a hydrothermal-type geological setting according to the Al/Si *vs*. Mg/Fe plot of Damyanov and Vassileva (2001). The '(Mg, Mn)-poor' berthierine plots within the 'ore' subfield (high-temperature in orebodies) of hydrothermal berthierine, while the '(Mg, Mn)-rich' composition bridges the gap between the 'ore' and 'pre-ore' (low-temperature zone of hydrothermal alteration around ore deposits) subfields (Figure 5).
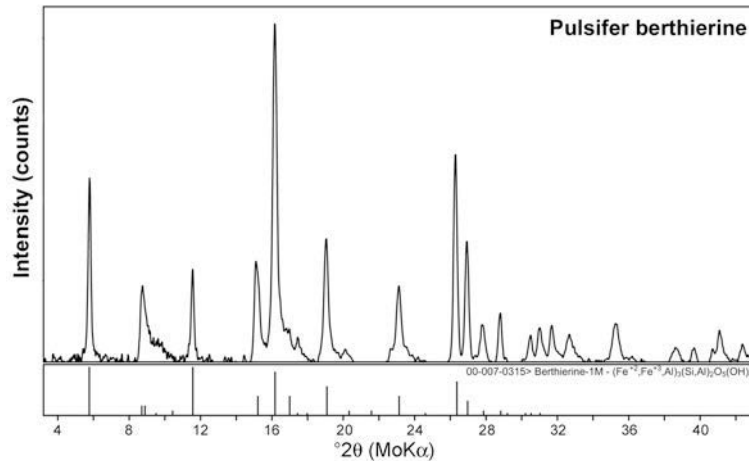
Figure 3. Powder XRD pattern for berthierine from the Pulsifer granitic pegmatite.

## ORIGIN OF BERTHIERINE IN GRANITIC PEGMATITES

The natural mineral assemblage hosting berthierine in this study is unlike that known from any sedimentary deposit or documented from other pegmatite occurrences and as such, raises questions about its genesis. In sedimentary rocks, berthierine originates: (1) as a chemical precipitate from solutions or gels; (2) *via* diagenetic transformation of pre-existing phases; and (3) as a hydrothermal replacement product of aluminous

Table 1. Representative electron microprobe analyses (wt.%) of berthierine from the Pulsifer pegmatite.

| | Rosette | | | | Fracture filling | | Muscovite association | | | Recrystallized albite | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 123 | 124 | 126 | 130 | 142 | 143 | 144 | 145 | 157 | 163 | 164 |
| $SiO_2$ | 22.96 | 25.07 | 23.24 | 24.03 | 21.99 | 22.64 | 25.51 | 23.71 | 23.27 | 22.18 | 22.46 |
| $Al_2O_3$ | 22.44 | 22.63 | 22.66 | 23.32 | 21.89 | 22.27 | 21.52 | 21.71 | 21.50 | 21.81 | 22.24 |
| $TiO_2$ | 0.03 | 0.04 | 0.00 | 0.00 | 0.01 | 0.02 | 0.05 | 0.00 | 0.02 | 0.00 | 0.00 |
| FeO | 43.25 | 38.08 | 44.66 | 43.32 | 43.42 | 44.04 | 39.52 | 39.40 | 38.09 | 41.91 | 42.00 |
| MnO | 0.81 | 2.79 | 0.45 | 1.00 | 0.83 | 0.50 | 1.15 | 2.57 | 3.83 | 1.76 | 1.57 |
| MgO | 0.48 | 0.62 | 0.58 | 0.55 | 0.41 | 0.48 | 2.63 | 3.14 | 2.91 | 1.22 | 1.17 |
| CaO | 0.11 | 0.42 | 0.03 | 0.08 | 0.09 | 0.00 | 0.20 | 0.13 | 0.01 | 0.02 | 0.02 |
| $Na_2O$ | 0.00 | 0.05 | 0.00 | 0.03 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 | 0.06 | 0.01 |
| $K_2O$ | 0.02 | 0.09 | 0.03 | 0.02 | 0.04 | 0.07 | 0.26 | 0.04 | 0.04 | 0.03 | 0.05 |
| Total | 90.11 | 89.79 | 91.65 | 92.35 | 88.70 | 90.02 | 90.84 | 90.74 | 89.70 | 89.00 | 89.55 |
| $Si^{4+}$ | 5.212 | 5.576 | 5.198 | 5.285 | 5.111 | 5.167 | 5.604 | 5.276 | 5.251 | 5.116 | 5.132 |
| $^{IV}Al^{3+}$ | 2.788 | 2.424 | 2.802 | 2.715 | 2.889 | 2.833 | 2.396 | 2.724 | 2.749 | 2.884 | 2.868 |
| $^{VI}Al^{3+}$ | 3.215 | 3.508 | 3.171 | 3.330 | 3.107 | 3.157 | 3.175 | 2.970 | 2.969 | 3.045 | 3.122 |
| $Ti^{4+}$ | 0.005 | 0.007 | 0.000 | 0.000 | 0.002 | 0.003 | 0.008 | 0.000 | 0.003 | 0.000 | 0.000 |
| $Fe^{2+}$ | 8.210 | 7.083 | 8.354 | 7.968 | 8.440 | 8.405 | 7.260 | 7.333 | 7.188 | 8.085 | 8.026 |
| $Mn^{2+}$ | 0.156 | 0.526 | 0.085 | 0.186 | 0.163 | 0.097 | 0.214 | 0.484 | 0.732 | 0.344 | 0.304 |
| $Mg^{2+}$ | 0.162 | 0.206 | 0.193 | 0.180 | 0.142 | 0.163 | 0.861 | 1.042 | 0.979 | 0.420 | 0.399 |
| $Ca^{2+}$ | 0.027 | 0.100 | 0.007 | 0.019 | 0.022 | 0.000 | 0.047 | 0.031 | 0.002 | 0.005 | 0.005 |
| $Na^+$ | 0.000 | 0.022 | 0.000 | 0.013 | 0.000 | 0.000 | 0.000 | 0.000 | 0.009 | 0.027 | 0.004 |
| $K^+$ | 0.006 | 0.026 | 0.009 | 0.006 | 0.012 | 0.020 | 0.073 | 0.011 | 0.012 | 0.009 | 0.015 |
| Total | 19.783 | 19.475 | 19.820 | 19.702 | 19.893 | 19.845 | 19.639 | 19.879 | 19.896 | 19.936 | 19.880 |
| Oct. vacancy | 0.252 | 0.670 | 0.197 | 0.336 | 0.146 | 0.175 | 0.482 | 0.171 | 0.129 | 0.106 | 0.149 |
| Fe/(Fe+Mg) | 0.981 | 0.972 | 0.977 | 0.978 | 0.983 | 0.981 | 0.894 | 0.876 | 0.880 | 0.951 | 0.953 |
| Mg/Fe | 0.020 | 0.029 | 0.023 | 0.022 | 0.017 | 0.019 | 0.119 | 0.142 | 0.136 | 0.052 | 0.050 |
| Al/Si | 1.152 | 1.064 | 1.149 | 1.160 | 1.173 | 1.159 | 0.994 | 1.079 | 1.089 | 1.159 | 1.167 |
| Mn/(Mn+Fe) | 0.019 | 0.069 | 0.010 | 0.023 | 0.019 | 0.011 | 0.029 | 0.062 | 0.092 | 0.041 | 0.036 |

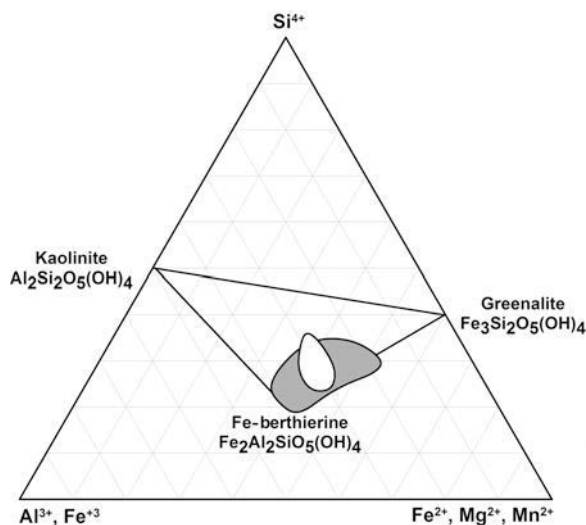Structural formula calculated on the basis of 28 oxygens. Total Fe as FeO.

Figure 4. Plot of berthierine compositions on the Si-(Al,Fe$^{3+}$)-(Fe$^{2+}$,Mg,Mn) ternary diagram (modified after Toth and Fritz, 1997). Open field: berthierine samples from this study. Shaded field includes berthierine compositions from pegmatites (Abad-Ortega and Mieto, 1995; Jobin-Bevans and Černý, 1998; Guastoni *et al.*, 2004) and non-pegmatitic settings (Damyanov and Vassileva, 2001).

phases. Under conditions of diagenesis, berthierine formation can occur within a very low-temperature range of ~50−130ºC (Velde, 1985; Iijima and Matsumoto, 1982). Aagaard *et al.* (2000) suggested that berthierine may be stable to temperatures ~200ºC, but above this temperature transforms to chlorite. The experiments of Zhou and Gunter (1996) indicate that berthierine is not stable in hydrothermal solutions at 250ºC, above which it transforms into Fe chlorite or Fe saponite, depending on the alkalinity of the hydrothermal solution. However, the occurrence of manganoan berthierine in metapelagites metamorphosed to the prehnite-pumpellyite facies suggests that Mn may help stabilize berthierine crystallization to temperatures of 250ºC (Coombs *et al.*, 2000). Slack *et al.* (1992) suggest that berthierine from the Kidd Creek volcanogenic massive sulfide deposit formed as a primary hydrothermal phase at ~350ºC. Furthermore, the experiments of James *et al.* (1976), Nikol'skaia *et al.* (1985), and Yau *et al.* (1988) show that berthierine can form under hydrothermal conditions at the relatively high temperatures of 300−400ºC.

The origin of berthierine in most granitic pegmatites is entirely different from sedimentary environments. The best documented cases attribute its formation to the interaction of post-magmatic fluids, presumably derived from the pegmatite, with primary cordierite-group minerals (*i.e.* cordierite and sekaninaite). The cordierite-group minerals crystallize as late-magmatic phases at temperatures estimated at ~550ºC under moderately low pressures (~3 kbar). Natural mineral assemblages and experimental work have shown that cordierite is strongly
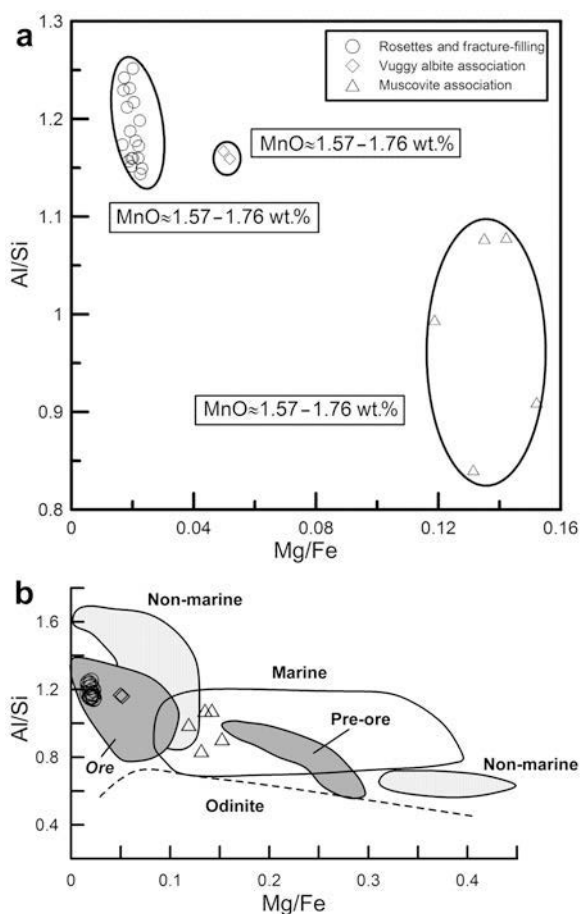


Figure 5. Plot of Mg/Fe *vs.* Al/Si for berthierine in (a) the Pulsifer pegmatite and (b) in different geological settings. Compositional fields for hydrothermal (ore and pre-ore), marine and non-marine settings are based on data compiled by Damyanov and Vassileva (2001).

susceptible to subsolidus alteration. The experimental work of Seifert and Schreyer (1970) and Seifert (1976) indicates that cordierite is unstable at low temperatures in the presence of $H_2O$ and alkali-bearing solutions. At temperatures of 500−450ºC, cordierite-group minerals alter to an assemblage dominated by muscovite and biotite. Relict grains of the precursor cordierite or sekaninaite, secondary beryl and quartz may exist as part of the replacement assemblage. Subsequent alteration of biotite may result in the generation of berthierine as a replacement product. The exact conditions at which this transformation takes place are uncertain; however, based on the cordierite-berthierine assemblage at the Greer Lake pegmatite, in southeastern Manitoba, the process probably takes place at temperatures significantly less than 450ºC (Jobin-Bevans and Černý, 1998). Similarly, berthierine derived from the hydrothermal alteration of sekaninaite in pegmatites of Feriolo and Baveno, Italy, presumably formed at temperatures below ~300ºC (Yates and Rosenberg, 1997; Pezzotta *et al.*, 1999; Guastoni *et al.*, 2004).

The replacement assemblage hosting berthierine typically forms very fine-grained to cryptocrystalline aggregates, in part pseudomorphing the precursor cordierite-group phase. Well formed macroscopic crystals of berthierine are rarely developed. Moreover, berthierine forming from the breakdown of cordierite-group minerals is commonly intermixed with other phyllosilicate minerals (*i.e.* muscovite, biotite and chlorite) and this sometimes leads to difficulty in obtaining reliable analytical results or conclusive identification of the berthierine phase.

Berthierine which originates in response to the reaction of residual pegmatite fluids on cordierite-group minerals typically inherits some of the chemical characteristics of its precursor (*e.g.* Mg/Fe ratio, elevated Mn content). Enrichment of the replacement products in elements such as Na, Be, Li, Rb, Cs and F provides further evidence of interaction of a cordierite-sekaninaite precursor with an evolved residual pegmatite fluid (cf. Gottesmann and Förster, 2004).

## GENESIS OF BERTHIERINE IN THE PULSIFER PEGMATITE

Although the actual conditions of berthierine formation in the Pulsifer pegmatite are uncertain, the restriction of berthierine to miarolitic cavities does place some constraints on its genesis. Miarolitic cavities are formed by the exsolution and build-up of a hydrous supercritical fluid triggered by: (1) vapor saturation due to the gradual accumulation of volatile components during progressive crystallization of the pegmatite-generating magma; (2) reduction of the confining pressure in the pegmatite magma; or (3) crystallization of minerals such as tourmaline, beryl, amblygonite and lepidolite which deplete the melt of components (B, F, P and Li) that enhance the solubility of water in the pegmatite melt (see London, 1986; London, 1992; Černý, 2000 and references therein). The exsolved aqueous fluid may cause metasomatic alteration of earlier-crystallized pegmatite assemblages in addition to forming pegmatitic pockets.

According to geological and experimental data, pocket development is estimated to occur within the temperature range 425−615°C and pressure range 2.4−3.5 kbar (Taylor *et al.*, 1979; Stern *et al.*, 1986; London, 1986, 1992; Peretyazho *et al.*, 2004). Feldspar geothermometry and fluid-inclusion studies of tourmaline and quartz, however, suggest that the crystallization temperatures of primary pocket minerals can be as low as 390−265°C (Zagorsky *et al.*, 1998; Morgan and London, 1999; Zagorsky *et al.*, 2003). Borocookeite, a boron-rich member of the chlorite group, was considered to have crystallized as a primary phase from an evolved residual solution in miarolitic cavities at temperatures near 265−240°C (Zagorsky *et al.*, 2003). The broad range of crystallization temperatures for miarolitic

cavities reported by the above studies easily overlaps the range of temperatures whereby berthierine is stable in igneous systems. Accordingly, it would not be unreasonable to consider the formation of the Pulsifer berthierine as a primary phase that crystallized from a moderate- to low-temperature fluid. However, the textural relationships of the pocket minerals point to an origin more consistent with crystallization subsequent to the alteration of a precursor silicate mineral.

The hydrothermal breakdown of cordierite-group minerals, biotite or muscovite may be viable mechanisms for the generation of berthierine in the Pulsifer pegmatite. However, cordierite-group minerals have never been observed in the Pulsifer pegmatite nor have they ever been reported from any of the granitic pegmatites in western Maine. This observation, in conjunction with the absence of relict cordierite or sekaninaite grains in the Pulsifer pegmatite, does not lend support to the idea of berthierine developing as a late alteration product of these minerals. Additionally, the small Mg content of the Pulsifer berthierine is inconsistent with the elevated Mg concentration typically observed in replacement berthierine from other pegmatite localities and further supports an origin that does not involve the breakdown of cordierite-group minerals.

In the absence of a cordierite-group precursor, an alternative explanation must be considered to account for the chemical features observed in the Pulsifer berthierine. The alteration of biotite or muscovite may serve as a more reasonable explanation for the formation of berthierine in the Pulsifer pegmatite. The crystallization of berthierine as a by-product of biotite alteration accompanying the breakdown of cordierite-group minerals has been addressed above and Slack *et al.* (1992) proposed that berthierine could form by the hydrothermal alteration of muscovite. Biotite and muscovite are relatively common in certain parts of the Pulsifer pegmatite, although muscovite is much more abundant than biotite. However, in the miarolitic cavity where berthierine is found, biotite is not present as primary crystals or relict grains, and muscovite, while prominent, shows no textural indication of replacement by berthierine (Figure 4).

Primary minerals that crystallize in miarolitic cavities of granitic pegmatites are susceptible to a variety of mechanical and chemical effects that occur contemporaneous with, or subsequent to, pocket formation. Crystals originally attached to the pocket roof and walls may become broken during pocket rupture (Foord, 1976). Chemical effects, which typically involve residual fluids enriched in Na, Li, B, F, $H_2O$ and $CO_2$, can be extremely destructive, and at times can significantly alter the original mineral assemblage of the pocket. Primary pocket minerals, particularly microcline, may be replaced by late micas or clay minerals, become overgrown by low-temperature minerals such as calcite,

zeolites, micas and Mn oxides, or undergo albitization (transformation of potassic feldspar to albite) or amazonitization (transformation of white or tan-colored microcline to blue-green microcline). Some minerals, including microcline, may become etched, sometimes resulting in 'boxwork' textures. All of the above phenomena provide evidence of mineral-fluid interaction that may exist during the final stages of pegmatite consolidation and pocket development. Based on the textural relationship of the berthierine-bearing assemblage, the origin of the Pulsifer berthierine appears to be best associated with the hydrothermal alteration of microcline and can be expressed as such by the general reaction:

$$4\text{microcline }_{(perthite)} + 5Fe^{2+} + 8OH^- \rightarrow$$
$$2\text{berthierine} + 2\text{albite} + 3\text{quartz} + 2K^+.$$
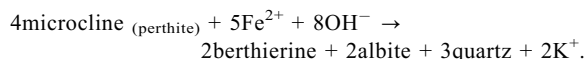
Portions of the perthitic microcline in the Pulsifer miarolitic cavities clearly show the effects of hydrothermal dissolution. Modest corrosion resulted in only minor K-feldspar dissolution, while the albite lamellae remained virtually unaffected. Where the hydrothermal alteration was more intense, complete dissolution of the K-feldspar portion of the perthite occurred while the albite lamellae merely recrystallized. Primary coarse platy albite crystals, on the other hand, were unaffected by the hydrothermal fluids. New K-dominant mineral species (*e.g.* muscovite, biotite, illite, chabazite-K) were not created at the time of berthierine crystallization, thus the K$^+$ liberated during the alteration of microcline may have been remobilized to other parts of the pegmatite, escaped to the surrounding country rock causing localized K metasomatism, or was removed from the fluid during precipitation of the clay-sized microcline following the crystallization of berthierine.

The general absence of berthierine in miarolitic cavities of granitic pegmatites suggests that unique conditions are required for its formation. Although fluid inclusion data for the Pulsifer pegmatite are unavailable at this time, the mineral assemblage of the berthierine-bearing pocket does provide some insight into the composition of the crystallizing fluid. The formation of berthierine in the Pulsifer pegmatite appears to have been favored by an Fe-enriched fluid having: (1) low oxygen and sulfur fugacities; (2) low pCO$_2$; and (3) small concentrations of B, Li and F. These conditions were generally not met in most miarolitic cavities within the Pulsifer pegmatite or in other chemically evolved pegmatites which may explain why berthierine is so uncommon. The occurrence of minor amounts of late pyrite and the absence of magnetite, hematite and goethite point to reducing conditions prior to and during berthierine crystallization. Carbonates are not present as part of the cavity assemblage, implying little CO$_2$ activity in the fluid. The berthierine-bearing pocket was devoid of tourmaline, beryl, lepidolite, spodumene, fluorite or topaz which demonstrates severe depletion of

the hydrothermal fluid in B, Be, Li and F. The absence of kaolinite clay and sericitic micas as alteration products of the pocket feldspars suggests that the precipitating hydrothermal fluid was probably not acidic in composition. More or less neutral to alkaline conditions appear to be conducive to berthierine formation (*e.g.* Fritz and Toth, 1997) and may also have existed during its precipitation in the Pulsifer pegmatite.

The source of Fe necessary to promote berthierine crystallization in the Pulsifer pegmatite is problematic. Small amounts of Fe$^{3+}$ can reside in the microcline structure and would become liberated during its breakdown. Fe-bearing microcline is typically pink, brick red or yellow in color and white to tan-colored feldspars are usually devoid of Fe. Locally, there exists some euhedral crystals of pink K-feldspar in the Pulsifer pegmatite, but mostly it is white. The absence of structural Fe in white microcline from the miarolitic cavities was confirmed by electron microprobe analysis, thus it was probably not the source of Fe for berthierine crystallization. The Fe necessary for the formation of berthierine may have come from the alteration of Fe-rich silicate minerals and subsequent remobilization of Fe. Schorl and almandine are abundant throughout the pegmatite, but only unaltered crystals were encountered near the pocket walls and no schorl or almandine were found in the pocket. Late-stage alteration of biotite to chlorite has been observed in parts of the Pulsifer pegmatite and could potentially release some Fe into late fluids (Rose, pers. comm.). However, no altered biotite was found in the immediate vicinity of the berthierine-bearing cavity. External sources of Fe (*e.g.* Fe-bearing metamorphic or metasomatic fluids, assimilation of Fe-rich country rocks) could have modified the chemistry of the hydrothermal fluid existing in the pocket; however, there is insufficient evidence to support the suggestion that such processes occurred in the Pulsifer pegmatite.

The most likely source of Fe appears to be the pegmatite-derived residual fluids. In chemically evolved pegmatites such as the Pulsifer, it is not uncommon for late fluids to be enriched in volatile components such as B, P and F. Crystallization of late sodic albite, lithian micas, zeolites and carbonate minerals in miarolitic cavities provide additional evidence for the existence of late-stage (Na, Li, Ca, CO$_2$)-enriched fluids. Additionally there is increasing evidence that not all of the Fe from the original pegmatite melt was consumed during the crystallization of early primary units. Late fluids enriched in Fe have been cited as the reason for the crystallization of schorl, green elbaite or foitite in miarolitic cavities that have not been breached by pocket rupture (*e.g.* Elba pegmatites, Pezzotta 2005). Granitic pegmatites derived from A-type granites may contain primary Fe-rich phases (*e.g.* hematite, siderite, goethite) in late miarolitic cavities or internal zones (*e.g.* Wausau Complex pegmatites, Falster 1981). The crystallization of abundant schorl in a late replacement unit of the

Black Mountain pegmatite was thought to have resulted from a shift towards a more primitive and less fractionated medium following normal rare-element enrichment of the melt (Brown and Wise, 2001). Those authors concluded that the composition of this late Fe-enriched medium was not modified by external sources. Thus, in the case of the Pulsifer pegmatite, it is possible that all of the Fe in the original pegmatite melt was not depleted during crystallization of primary units and some was preserved in residual fluids for the crystallization of berthierine. Similarly, the Mn-enriched nature of the Pulsifer berthierine is also probably the result of late Mn accumulation in the residual fluids that are typically the consequence of fractionation of highly evolved granitic pegmatite melts.

## CONCLUSIONS

Berthierine crystallized as a late-forming mineral with albite in miarolitic cavities within the Pulsifer pegmatite. The general absence of cordierite, biotite or chlorite within the pocket zone of the Pulsifer pegmatite lends support to the theory that berthierine did not form from the alteration of these minerals. Moreover, the berthierine that occurs within fractures and along cleavage planes of perthitic microcline provides further support for an origin dependent upon the migration of a late fluid phase. The concentration of berthierine at the interface of partially corroded microcline and 'planes' of recrystallized albite place the timing of berthierine formation subsequent to microcline crystallization and albite recrystallization. The Pulsifer berthierine does not appear to represent primary precipitation, but instead is the result of the replacive effect of pegmatite-derived, Fe-enriched, alkaline residual fluids at temperatures near $300-400°C$.

## ACKNOWLEDGMENTS

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