

Occurrence of Prehnite, Pumpellyite and Garnet in Biotite from Granitic Rocks of the Canadian Appalachians: A Mineral Chemistry Study Using Electron Microprobe

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Received: 18 August 2009 / Revised: 16 October 2010 / Accepted: 1 January 2011

Abstract

A particular feature of biotite grains from some of the Canadian Appalachian granitic rocks is the presence of lenses of Ca-Al silicates developed along cleavage planes. These from the more to less common are prehnite, pumpellyite and grandite garnet, an intermediate composition between andradite and grossular. Rarely all three minerals can be observed together in one single biotite grain. Microprobe analyses show that Al_2O_3 contents of prehnite vary from 17.52 to 24.55 and Fe_2O_3 from 2.38 to 8.88 wt. %, which can be reflected in a substantial and variable substitution of Fe for Al. Furthermore, a fairly positive correlation of MnO values of both prehnite and host biotite may indicate the role of biotite replacement by prehnite. Fe_2O_3 content in nine analyzed pumpellyite samples varies between 10 and 23 wt%. Fe_2O_3 contents of more than 10 wt% in pumpellyite are indicative of zeolite and prehnite-pumpellyite facies conditions.

Keywords: Prehnite; Pumpellyite; Garnet; Biotite; Appalachian orogen

Introduction

Prehnite can be found in different rock types. For instance, it usually occurs as a late-stage mineral in amygdaloids, cavities and veins in igneous rocks, particularly basic volcanic rocks (e.g., [64, 7, 19, 47, 52, 6 and 43]), hydrothermal alteration zones around ore bodies (e.g., [10]), and in metamorphic rocks of prehnite-pumpellyite facies as a diagnostic mineral (e.g., [17, 58, 44, 21, 64, 12, 39, 53, 16, and 54]).

In addition, occurrence of lens-like prehnite and pumpellyite within primary biotite of plutonic rocks

have attracted the attention of a number of authors (e.g., [29, 28, 61, 27, 49, 63, 38, 46, 40, 57, 8, 20, 31, 45, 4, 2, 33, 24, 23, 25 and 37]). The plutonic rocks in which biotite has been noted for its prehnite occurrence range from ultrabasic rocks (e.g., [28]), gabbro (e.g., [40]) diorites (e.g., [46 and 8]) to granites (e.g., [57, 25, and 37]). The importance of these mineral is that they can be used to constrain the P-T conditions of emplacement and cooling of plutonic rocks (e.g., [25]).

In this study we present for the first time the occurrence of prehnite, pumpellyite and andradite-grossular garnet as lens shape minerals in the biotites of

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the Canadian Appalachian granitic rocks from several plutons in New Brunswick and Newfoundland and document the detailed textural and mineral chemical characteristics of these overlooked secondary minerals. Chemical composition of 44 prehnite, pumpellyite and garnet and their host biotites were determined by wavelength-dispersive X-ray spectrometry method using electron microprobe.

Brief Geological Setting

Plutonic rocks comprise about one quarter of all exposed rocks in the Canadian Appalachians. These rocks are granitic in the broad sense, meaning that for the most part they are members of the tonalite to alkali-feldspar granite suite. Much of this granitic plutonism occurred during Middle Ordovician to Early Devonian times [59]. Details of the geological, petrological, geochemical and isotopic characteristics of these suites and plutons have been discussed elsewhere [59, 60, 30 and 13].

Materials and Methods

Electron Microprobe Analysis and Mineral Formula Calculation

Mineral analyses were obtained by wavelength-dispersive X-ray spectrometry for 11 elements (K, Na, Mg, Ca, Mn, Fe, Al, Ti, Si, F, and Cl) using the JEOL 8900 superprobe at McGill University. Typical beam operating conditions were 15 kV and 20 nA. ZAF method was applied for data correction.

Ca-Al silicate analyses were carried out simultaneously with the host biotite analyses. It turned out that 29, out of 44 secondary Ca-Al silicate mineral specimens analyzed by EPMA, were prehnite, 9 pumpellyite and 6 garnet samples. The number of analyses included in the mean of each analyzed sample varies from 1 to 4.

The general formula of prehnite can be written as $X_2YZ_4O_{10}(OH)_2$ where Y and Z are octahedral and tetrahedral sites respectively. The structural formula of prehnite was calculated on the basis of $O_{20}(OH)_4$ [25]. It is clear that the amount of hydroxyl ions, divalent and trivalent iron cations cannot be determined by electron microprobe analysis. Therefore, the obtained total iron was assumed to be Fe_2O_3 or ferric iron based on ^{57}Fe Mössbauer spectroscopy (MS) investigations of Akasaka et al., [3] and Artioli et al., [5] and water content was determined through calculation. Si and tetrahedral Al occupy the tetrahedral site and Fe^{3+} , Ti and octahedral Al the octahedral site. The X-site is

occupied mainly by Ca, but minor Mg and Mn may also be incorporated at the Ca position.

It is difficult to verify the quality of pumpellyite analyses because the numbers of OH and trivalent ions are variable and cannot be measured directly by microprobe. The structural formulae are calculated based on 16 cations per 24.5 oxygen atoms assuming the general mineral formula of pumpellyite, recommended by Yoshiasa and Matsumoto [62], as $(Ca)CaAl_2(OH)_2(Mg, Fe^{2+}, Al, Fe^{3+})[(OH), O]Si_4Si_2O_6(OH)$.

The structural formula of garnet can be written as $X_3Y_2ZO_{12}$ where X site is occupied by divalent cations and Y site by trivalent cations. Therefore, the mineral formula for the garnet was calculated based on 5 cations and 12 oxygen atoms proposed by Rossman and Aines [48].

Representative chemical compositions of prehnite, pumpellyite and garnet are presented in Table (1) along with their respective structural formulae.

Using chemical composition of biotite specimens, structural formulae were calculated based on 20 oxygen atoms and $(OH+F+C) = 4$. Contents of FeO and Fe_2O_3 for some of the specimens were determined by applying the $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ ratios determined by Mössbauer spectroscopy. For those samples not measured by MS, the above ratios were extrapolated from those of similar petrographic units [51]. Note that the complete data sets used in this study can be obtained from the author upon request.

Whole-Rock XRF Analyses

Whole-rock major, minor and trace elements were determined by sequential wavelength-dispersive X-ray fluorescence (XRF) with a Philips PW2400 automated spectrometer. Major, minor and trace element analyses were performed on glass discs of fused rock samples.

Results and Discussion

Several post-magmatic Ca-Al silicates can be observed exclusively within non-to-partly altered biotite in all plutonic rocks of the Canadian Appalachians based on EPMA data. These from the more to less common minerals, are prehnite, pumpellyite and garnet. The rocks containing these secondary Ca-Al silicates range in composition from biotite-muscovite to biotite granite/granodiorite and biotite-hornblende tonalite and granite to hornblende-biotite quartz diorite, diorite and biotite-hornblende/pyroxene gabbro. Textures exhibited by these rocks are generally defined as either foliated or non-foliated.

Table 1. Representative electron microprobe analyses of prehnite, pumpellyite and garnet with their related structural formulae from the Canadian Appalachian granitic rocks

Prehnite				Pumpellyite			Garnet		
sample	NF-102	SNF-2	NB-52	sample	NF-26	NF-45	sample	NB-199	SNF-25
average	2	4	2	average	1	1	average	2	4
SiO ₂	43.16	41.16	42.73	SiO ₂	39.12	36.74	SiO ₂	34.45	34.44
TiO ₂	0.10	1.14	0.03	TiO ₂	19.20	16.76	TiO ₂	1.08	2.48
Al ₂ O ₃	21.33	20.12	24.55	Al ₂ O ₃	2.17	4.46	Al ₂ O ₃	7.05	10.43
Fe ₂ O ₃	3.83	7.20	1.07	Fe ₂ O ₃	11.32	10.14	Fe ₂ O ₃	20.90	18.53
MnO	0.06	0.10	0.03	MnO	0.19	0.16	MnO	0.21	0.15
MgO	0.42	1.89	0.05	MgO	2.43	4.47	MgO	0.05	0.75
CaO	25.93	23.37	26.75	CaO	19.62	19.98	CaO	35.26	32.33
Na ₂ O	0.03	0.04	0.02	Na ₂ O	0.04	0.01	Total	98.99	99.12
K ₂ O	0.05	0.06	0.03	K ₂ O	0.70	0.19			
F	0.01	0.11	0.09	Total	94.78	92.90			
Cl	0.01	0.02	0.00						
H ₂ O *	4.24	4.13	4.28	Si	6.24	6.02	Si	2.86	2.80
Total	99.14	99.28	99.60	OH	0.00	0.00	Z	2.86	2.80
				Z	6.24	6.02			
Si	6.09	5.89	5.93						
Al (IV)	1.91	2.11	2.07	Al (VI)	3.61	3.24	Al (VI)	0.07	0.15
Z	8.00	8.00	8.00	Ti	0.26	0.55	Ti	0.69	1.00
				Fe ³⁺	0.13	0.21	Fe ³⁺	1.31	1.13
Al (VI)	1.64	1.29	1.94	Y	4.00	4.00	Y	2.06	2.28
Ti	0.01	0.12	0.00						
Fe ³⁺	0.45	0.86	0.12	Fe ³⁺	1.23	1.04	Mn	0.01	0.01
Y	2.09	2.15	2.07	Mn	0.03	0.02	Mg	0.01	0.09
				Mg	0.58	1.09	Ca	3.14	2.81
Mn	0.01	0.01	0.00	OH	0.16	0.00	X	3.16	2.91
Mg	0.09	0.40	0.01	X	2.00	2.15			
Ca	3.92	3.59	3.98				pyrope	0.18	3.12
Na	0.01	0.01	0.00	Ca	3.36	3.51	grossular	33.22	42.23
K	0.01	0.01	0.01	Na	0.01	0.00	spessartine	0.47	0.36
X	4.04	4.15	4.00	K	0.14	0.04	andradite	62.88	47.89
OH *	3.99	3.94	3.96	W	3.51	3.55	Ca-Ti Gt	3.24	6.40
F	0.00	0.05	0.04	OH	0.16	0.00			

Prehnite

Prehnite characteristically forms colorless lenticular patches of moderate relief accommodated within the cleavages of biotite. It displays a habit of lens form parallel to the host biotite cleavage that might or might not be deformed and show a birefringence of about 0.03. Biotite cleavages locally bow around the podlike

outline of the prehnite. The {001} cleavages of the prehnite are subparallel to the lens elongation but are usually curved and appear to branch outward from the middle of each lens (Fig. 1).

A plot of Fe₂O₃ versus Al₂O₃ displays a fair correlation indicating a substitution between ferric iron and aluminum (Fig. 2). This is the only significant compositional variation observed in prehnite. The Fe₂O₃

content varies from 2.14 to 7.99 wt% approaching the 10 % limit suggested by Liou [35]. Al_2O_3 content ranges from 17.52 to 24.55 wt%. As it is clear from Figure (2), no discrimination can be revealed among prehnites from different rock types, implying the lack of rock compositional influence upon the prehnite composition. According to Liou et al., [36] and Schiffman and Liou [50] the $Fe_2O_3 - Al_2O_3$ variation among prehnite may imply its formation over a significant temperature range.

Figure 3 displays a fairly positive correlation of MnO values of both prehnite and host biotite despite some scattered points. Such a correlation for the rest of the analyzed elements is rarely found between prehnite and host biotite.

Pumpellyite

Its habit is essentially the same as that of prehnite and forms lenses in the biotite often causing slight bending in the mica (Fig. 1). Total Al as Al_2O_3 and Fe as FeO vary from 13.51 - 20.85 and 9.13 - 21.11 respectively. Although Fe^{2+}/Fe^{3+} has not been determined, it is assumed that Fe assigned to the Y sites is Fe^{3+} whereas that in the X sites, arbitrarily treated as Fe^{2+} may include Fe^{3+} [57 and 15].

A Fe_2O_3 total content of nine analyzed pumpellyite samples varies between 10.14 and 23.46 wt %. According to Schiffman and Liou [50] a Fe_2O_3 total content of pumpellyite of more than 10 wt % indicates zeolite and prehnite-pumpellyite facies conditions.

Garnet

Lens shape garnet occurs also parallel to the biotite cleavage within biotite. It forms more rounded lenses than prehnite or pumpellyite and shows anomalous gray colors between crossed nicols.

Structural mineral calculation shows that the garnets are composed of 47.7 to 62.9 % andradite and 32.8 to 42.2 % grossular; therefore, the composition of garnet lies between the andradite and grossular end member (Table 1). This intermediate grossular-andradite garnet was called "grandite" by Tulloch [57]. TiO_2 content is up to 4.2 wt%, which is most likely inherited from its host biotite. Comparison of our garnet data exhibits that their compositions are similar to those of garnets reported by Tulloch [57] from Victoria Range granitoids in New Zealand and by Freiburger et al., [25] from Hercynian granitoid complex of Charroux-Civray in France and Fichtelgebirge in Germany.

Working on the P-T-X conditions of the late magmatic to early postmagmatic crystallization history of the Hercynian granitoid complex of Charroux-Civray

in France and Fichtelgebirge in Germany, Freiburger et al., [25] demonstrated that the main period of the early postmagmatic stage is characterized by the crystallization of Ca-Al silicates like hydrogarnet, Pumpellyite, prehnite, pistacite and laumontite occurring as lenses within biotite. Hydrogarnet is most likely formed first, followed by prehnite and Pumpellyite and finally some less common laumontite. Hydrogarnet is stable at temperatures of more than ~ 340 °C independent of pressure [36]. Prehnite may begin to form at ~ 370 °C, however, the development of prehnite and pumpellyite

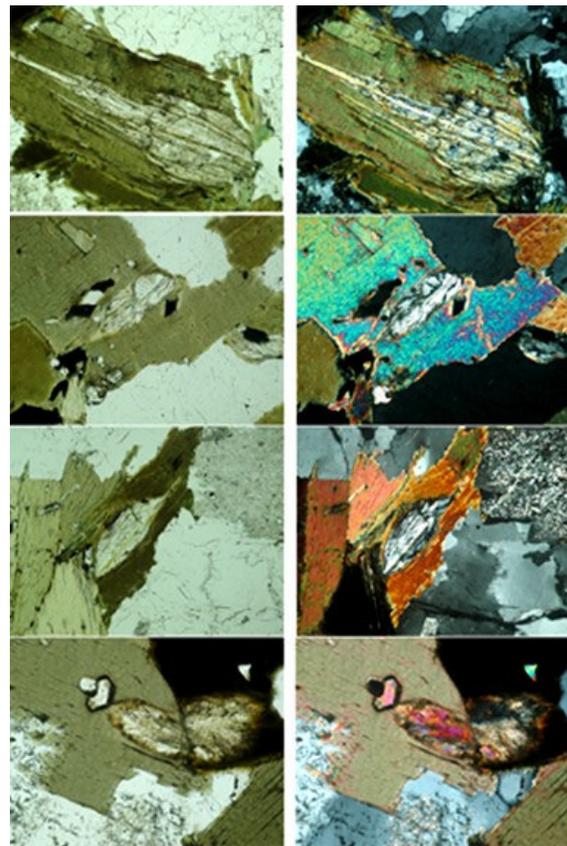


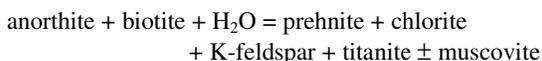
Figure 1. Microphotographs showing the typical lens shape occurrences of prehnite and pumpellyite along the cleavages of biotite from granitic rocks of the Canadian Appalachians.

The left pictures taken with parallel nicols and the same pictures in the right with crossed nicols. A), cleavages in the right portion of the biotite flake slightly bend around the curved outline of the prehnite lens B), prehnite shows a so-called bow-tie structure C), sericitized plagioclase in contact with biotite containing prehnite D), pumpellyite lenses; it seems that the host biotite in the right portion is replaced entirely by pumpellyite. Note yet again the seritization of plagioclase here.

paragenesis may indicate a relatively narrow temperature range of 200 to 280 °C and pressures of 2 to 3 kbar [26]. According to her interpretation the formation of Ca-Al silicates in Charroux-Civray granitoids occurred during successive cooling instead of a later metamorphic or hydrothermal overprint. This is different from models proposed by Tulloch [57], Alderton [4], AlDahan [2] and Leake [33] in which Ca-Al silicate formation in biotite resulted from a secondary hydrothermal overprint after cooling of the granitic pluton.

Likewise, there has been a debate on the origin of these secondary Ca-Al silicates that typically occur as lenses parallel to the cleavages of biotite. Our comprehensive literature survey indicates that two main ideas have been generally presented so far. One idea considers the growth of prehnite within the biotite as a secondary process without replacing its host biotite. For instance, Phillips and Rickwood [46] and [40] argue that the lens-like form of the prehnite with curved cleavage of biotite around it suggests that prehnite forced the biotite apart along (001) indicating that there has been an increase in the total volume. They concluded that biotite cleavage simply forms a suitable structural site or chemical environment for prehnite to crystallize from a fluid foreign to the immediate locality of the biotite probably as a result of deuteritic reactions i.e., biotite represents a local chemical trap for the Ca-Al silicates and replacement does not occur; i.e., biotite remains stable and intact. Most recently, in this way some writers debate on the catalytic effect of biotite that induces crystallization of prehnite (e.g., [9 and 42]). Based on this argument, it is assumed that the lattice defects inside the structure of biotite (e.g., Al^{3+} and Si^{4+}) which cause incipient leaching of K^+ ions from the cleavage structure surface, lead to an attraction of H^+ onto the negative charged biotite cleavage surface. This creates a local decrease in H^+ concentration in the pore water (increase in pH) and induces crystallization of Ca-Al silicates [9].

The other idea considers the occurrence of prehnite within the biotite as result of replacement of biotite [57]. It is clear that the formation of Ca-Al silicates within Ca-free biotite requires Ca to be intruded by a fluid phase. Tulloch [57] argued that the source of Ca was from a later, post-magmatic process, like sericitization caused by meteoric fluids or late-magmatic (deuteritic) fluids connected with the parental magma during post-magmatic cooling. He proposed the following reaction in which prehnite is replacing its biotite host:



To support his proposed reaction, Tulloch [57] found only a positive correlation between Fe_2O_3 values of prehnite and its corresponding values in host biotite from Victoria Range granitoids from New Zealand and reached to the conclusion that the biotite was replaced by prehnite. Although, our microprobe data do not support his finding, instead a fairly positive correlation between MnO values of prehnite and corresponding host biotite takes the place of Tulloch's correlation (Fig. 3).

According to Tulloch [57] and Freiberger et al., [25] the occurrence of secondary Ca-Al silicates are restricted to the rocks whose bulk CaO content exceeds 1%. Our data of whole rock does not support their results, because the CaO content in some of our prehnite bearing rock samples is slightly less than 1 wt %.

In low calcium granitoid rocks of the Victoria Range, biotite compositions with Fe/Fe+Mg ratios greater than 0.7 do not allow Ca-Al silicates to develop [57]. Whereas, our biotite grains containing prehnite have Fe/Fe+Mg ratio of maximum 0.76 which is slightly higher than those of the Victoria Range biotite.

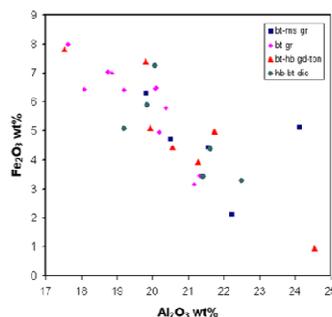


Figure 2. A plot of Fe_2O_3 versus Al_2O_3 contents of the investigated prehnite from the Canadian Appalachian granites showing a substitution between ferric iron and aluminum. (bt: biotite, ms: muscovite, hb: hornblende, gr: granite, gd: granodiorite, ton: tonalite, dio: diorite).

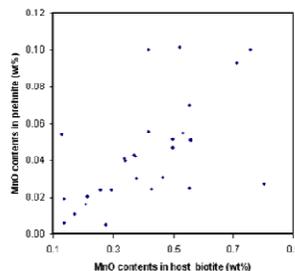


Figure 3. A plot of MnO contents of the investigated prehnite versus those of its host biotite from the Canadian Appalachian granites.

Seritization of plagioclase is probably considered as the main source of Ca [57] as hornblende can not be the supplier of Ca because it is not ubiquitous in all samples and where it occurs it is rarely altered. This is consistent with our petrography observation of the rock samples studied in this work which confirms that the occurrence of Ca-Al silicates is accompanied with the seritization of plagioclase; however, alteration of plagioclase which directly corresponds to the occurrence of Ca-Al silicates is not established in the Hercynian granitoid complex of Charroux-Civra [25].

Comparison of the abovementioned results obtained for this study with those reported from other distinct spots may imply that each granitic pluton or complex has its own post-magmatic evolution processes probably due to different physico-chemical conditions. Therefore, because of this diversity in physico-chemical states, a common and unique genetic model for the occurrence of Ca-Al silicates within biotite is unexpected. However, the absence of prehnite in muscovite flakes in our muscovite-biotite granite samples may suggest that the crystallization preference of the Ca-Al silicates within biotite is most likely because of catalytic effects in combination with particular structural features of the host biotite. On the other hand, the positive correlation of MnO values of both prehnite and its host biotite cannot be either ignored or considered as a coincidence.

Similarly, it is not easy to determine whether the occurrence of Ca-Al silicates within biotite of the Canadian Appalachian granitic rocks caused during successive cooling of a pluton or after the cooling of a pluton during a later or a secondary hydrothermal overprint or during a later separate metamorphic phase with its own P-T-time regime. The latter possibility might also be applicable since regional deformation and metamorphism have affected the Canadian Appalachian rocks at the Silurian (e.g. [59 and 11]). In addition, the Fe₂O₃ contents of pumpellyite, as mentioned earlier, are more than 10 wt% indicating zeolite and prehnite-pumpellyite facies conditions.

Acknowledgement

Funding for this study was provided by the Ministry of Sciences, research and technology of Islamic Republic of Iran and the Natural Sciences and Engineering Research Council of Canada. Glenn Poirier, McGill University, is thanked for access to Electron Microprobe laboratory.

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