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Geochemical characteristics of biotite from felsic intrusive rocks around the Sisson Brook W–Mo–Cu deposit, west-central New Brunswick: An indicator of halogen and oxygen fugacity of magmatic systems



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ABSTRACT

The Sisson Brook W–Mo–Cu deposit was formed by hydrothermal fluids likely related to the Nashwaak Granites (muscovite–biotite granite, Group I; and biotite granite, Group II) and related dykes (biotite granitic dykes, Group III); and a feldspar–biotite–quartz porphyry dyke, Group IV). Chemical data obtained using EPMA and LA-ICP-MS data of primary magmatic biotites were used to investigate magmatic processes and associated hydrothermal fluids.

Trace element features of biotite in the Group I two-mica granite suggest other magmatic processes along with a simple fractional crystallization. The K/Rb ratios and compatible elements (Cr, Ti, Co, V, and Ba) in biotite from Groups II, III, and IV decrease, whereas incompatible elements including Ta, Tl, Ga, Cs, Li, and Sn increase with magma fractionation. No correlation of Cu, W and Mo with K/Rb ratios is evident, suggesting that partitioning of Cu, W, and Mo into biotite may not be entirely controlled by magma fractionation.

Halogen fugacity of the parental magma of the Nashwaak Granites and related dykes, calculated from zircon saturation temperature shows that Group I has high *f*HF/*f*Cl ratios (broadly higher than 0), similar to the plutons at the Henderson porphyry Mo deposit. The *f*HF/*f*Cl ratios of the other groups are generally lower than 0, comparable to the Santa Rita porphyry Cu deposit. The *f*H₂O/*f*HCl and *f*H₂O/*f*HF ratios inferred from biotite in the Nashwaak Granites and related dykes range from 3 to 5 and from 4 to 5, respectively. The inferred oxygen fugacity shows that the dyke phases (Groups III and IV) have the oxygen fugacity around the nickel–nickel oxide buffer. The plutonic phases (Groups I and II) have the oxygen fugacity around the quartz–fayalite–magnetite (QFM) buffer at high temperatures and oxidized to nickel–nickel oxide buffer at lower temperatures. This oxidation process in the plutonic phases (Groups I and II) could be caused by H₂ release at or near H₂O vapor saturation at high H₂O/*f*e²⁺. The magma associated with the biotite dykes (Group III) is more likely the source of the hydrothermal fluids at the Sisson Brook deposit since it has the highest differentiation degree and seems to have formed in an oxidized setting, necessary for Mo to concentrate in the late stage fluids.

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1. Introduction

The Sisson Brook W–Mo–Cu deposit, situated in west-central New Brunswick, is hosted by the Cambro-Ordovician volcanic and sedimentary rocks of the Miramichi and Tetagouche groups (Fig. 1). Rennie (2012) defined this deposit as an intrusion-related, structurally controlled, bulk tonnage tungsten–molybdenum deposit whose hydrothermal features are generally similar to porphyry copper deposits. The Sisson Brook deposit is similar to other W–Mo deposits in New Brunswick, such as the Mount Pleasant (W–Mo–Bi and Sn–Zn–In, ca. 370 Ma, Re–Os molybdenite; Thorne et al., 2013), Burnthill (W–Mo–Sn), and Lake George (Sb–Au and W–Mo, ca. 412 Ma, U–Pb

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zircon, McLeod et al., 2003) deposits, as they are genetically linked to magmatic hydrothermal fluids exsolved from felsic batholiths and plutons formed during the Acadian Orogeny. These granitoids are metaluminous to peraluminous and have transitional I-type to A-type granite signatures, which are enriched in incompatible elements and are generally evolved (>65% SiO₂, Kooiman et al., 1986; MacLellan and Taylor, 1989; Yang et al., 2002, 2003; Inverno and Hutchinson, 2006). Enrichment of metallic elements may have resulted from a combination of crystal fractionation followed by aqueous phase saturation and separation, suggested by field and petrographic evidence including the presence of miarolitic cavities and myrmekite (Tucker et al., 1998; McLeod et al., 2003; Yang et al., 2008).

Chemical composition of magmatic biotite is sensitive to chemical and physical factors associated with crystallization of the magma (Munoz, 1992; Abdel-Rahman, 1994) and also to exsolved hydrothermal

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Fig. 1. Regional geological map showing the distribution of the Nashwaak Granites (scale: 1:50,000) and location of the Sisson Brook W–Mo–Cu deposit (Smith and Fyffe, 2006a, 2006b). Cambrian to Early Ordovician: $COTL_{gn}$ – Trousers Lake Metamorphic Suite, $COKB_{mc}$, – Miramichi Group; Ordovician: OLf_{in} – Little Clearwater Brook Granite, OMK_{in} – McKiel Lake Granite, OPBD, OHL_{fn} , OTU_{is} , OTM, OHL – Tetagouche Group; Silurian: SCR_{fc} , SBU_{mc} , STR_{mc} , SSM_{fc} , $SBOG_{ii}$; Devonian: DH_{fia} – Hawkshaw Granite, DBL_{mi} – Becaguimec Lake Gabbro, DHP_{ii} – Howard Peak Granodiorite, DNW_{fia} – Nashwaak biotite Granite, DNW_{fib} – Nashwaak two-mica Granite, Carboniferous: CCL_{cc} , CHRmv, CSN_{cc} – Mabou Group; CMO_{mc} – Pictou Group; - Fault, \bullet location of pluton samples, dyke samples are from star area around the Sisson Brook W–Mo–Cu deposit (see Fig. 2).

fluids (Siahcheshm et al., 2012). The interlayer cations (K⁺, Na⁺, Ca²⁺, Ba⁺, and Cs⁺) in biotite crystals could be leached out by later hydrothermal fluids and alteration processes (e.g., chloritization); the octahedral layer (Al⁶⁺, Mg²⁺, Fe²⁺, Fe³⁺, Li⁺, Ti⁴⁺, Mn²⁺, Zn²⁺, Cr³⁺, and V³⁺) and tetrahedral layer cations (Si^{4+} and Al^{4+}) are controlled by complex substitution mechanisms at different P-T-X conditions of a melt (magma) (Fleet, 2003). Abdel-Rahman (1994, 1996) suggested that the MgO, FeO, and Al₂O₃ contents of biotite are related to bulk composition of their host rocks. Munoz (1984, 1992) showed that the FeO/ (FeO + MgO) ratio of biotite is affected by oxygen fugacity (fO_2) of the system, which is a critical factor controlling partition behavior of W and Mo. In muscovite- and fluorite-free granitoid rocks, biotite contains between 70 and 90% of the F and Cl in the hydroxyl site with the remainder in apatite, amphibole and titanite (Speer, 1984). Chemical equilibrium between biotite and hydrothermal fluids percolating through the rock in the late stages of crystallization makes it possible to calculate the halogen composition of the fluids using composition of biotite (Zhu and Sverjensky, 1991, 1992). This method has been used to study the fluid composition of porphyry Cu (Mo, Au) deposits (Loferski and Ayuso, 1995; Selby and Nesbitt, 1997, 2000; Idrus et al., 2007; Ayati et al., 2008), intrusion-related Au deposits (Coulson et al., 2001; Yang and Lentz, 2005; Saravanan et al., 2009), and tungsten deposits (van Middelaar and Keith, 1990; Rasmussen and Mortensen, 2013). In this paper, the partition behavior of trace element into biotite during magma crystallization, as well as halogen and oxygen fugacity in the magmatic system associated with the Nashwaak Granites and related dykes will be investigated by analyzing composition of biotite in these rock units. The results of this study are helpful to identify the rock unit that is more likely to have exsolved the hydrothermal fluids associated with the W–Mo mineralization of the Sisson Brook deposit.

2. Geological setting

The rocks in the vicinity of the Sisson Brook deposit consist of a thick sequence of Cambro-Ordovician continental and marine volcanic and sedimentary rocks and younger mafic and felsic intrusive rocks (Nashwaak Granites, Howard Peak granodiorite and gabbro) (Fig. 1).

The oldest rocks are quartzose wackes interbedded with siltstones and shales of the Cambrian–Early Ordovician Miramichi Group, which occur in the core of a north-northeast-trending, southerly plunging anticline in the area (Lutes, 1981). These rocks are bound to the east and west by younger volcanic and sedimentary rocks of the Ordovician Tetagouche Group (Fig. 1). To the west, the Miramichi Group rocks are in fault contact with felsic crystal tuffs, mafic tuffs, and clastic sedimentary rocks of the Ordovician Turnbull Mountain Formation, and to the east, they are overlain unconformably by black shales, flow-banded felsic volcanic rocks and fragmental mafic volcanic rocks of the Ordovician Hayden Lake Formation.

The oldest intrusive pluton in the Sisson Brook area is the Howard Peak Granodiorite dated at 432.1 ± 1.9 Ma using U–Pb titanite geochronology (Bustard, 2013). This granodiorite is dark gray, medium- to coarse-grained, and consists primarily of plagioclase feldspar, with

25–35% hornblende, and 5% quartz. It also contains accessory potassium feldspar, hematized magnetite, titanite, apatite, and zircon (Rennie, 2012). The Howard Peak Granodiorite is foliated and marked by segregations of metamorphic biotite, which formed by intrusion of the Nashwaak Granites on its west margin. The Howard Peak Granodiorite grades eastward into, and becomes intermixed with dark gray, medium-grained ophitic gabbro. Its eastern contact with the Turnbull Mountain Formation is a vertical fault (Fyffe et al., 2008).

The Nashwaak Granites are the unfoliated Acadian granites in the Central Plutonic Belt of New Brunswick and covers an area of 250 km², extending from Spruce Peak northwards to McKiel Brook. On their east side, the Nashwaak Granites intrude the Miramichi Group, Tetagouche Group, and the Howard Peak Granodiorite. Andalusite and cordierite are present in sedimentary rocks up to 2 km from the contact. This constrains the level of exposure to approximately 10 km (Turner, 1981). To the north, they intrude the Cambro-Ordovician Trousers Lake Metamorphic Suite, which contains sillimanite within 1 km of the contact with the Ordovician McKiel Lake Granite. To the west, they intrude the Becaguimec Lake Gabbro. The contact between the Nashwaak Granites and Early Devonian volcanic rocks to the south is not exposed, but is likely intrusive. The Nashwaak Granites have two subfacies: (1) pink, coarse- to medium-grained, equigranular to subporphyritic biotite granite with a mineral assemblage of plagioclase, orthoclase, guartz, and minor biotite, that grades northward into (2) muscovite-biotite granite. In drill core, foliated, silicified and greisenized granite dykes containing xenoliths of gabbro crosscut the Howard Peak Granodiorite.

A gray, massive, unfoliated granite porphyry dyke was intersected in drill hole SSN26. The phenocrysts are plagioclase, biotite, and quartz. A U–Pb age of 364.5 \pm 1.8 Ma from zircon has been determined for this dyke (Fyffe et al., 2008).

The Sisson Brook deposit has three mineralized zones (Fig. 2), in which Zones I and II are structurally controlled and reach over tens of meters in width and about a hundred meters along strike. These zones contain W and Cu, but no significant Mo was observed. Zone III contains the main W and Mo resource for the Sisson Brook deposit. The latest mineral resource estimate shows this deposit has 387 Mt. of ore grading 0.067% WO₃ and 0.021% Mo in the measured-plus the indicated category, and 187 Mt. of ore grading 0.05% WO₃ and 0.02% Mo in the inferred category (Rennie, 2012).

3. Source of data, specimens and analytical methods

In fresh or least-altered Nashwaak Granites and related dykes, six samples of two-mica granite, seven samples of biotite granite, seven samples of biotite granitic dykes, and one sample of porphyry dyke, were collected and prepared for the biotite analysis by electron probe micro analysis (EPMA) at the University of New Brunswick. The samples were analyzed using a 15 kV accelerating voltage, 10 nA beam current, and a maximum 40 s counting interval. The analysis was conducted in wavelength-dispersion mode on a JXA JEOL-733 probe, equipped with dQant32 and dSpec automation from Geller Microanalytical Laboratories. Halogen elements F, and Cl of biotites from different groups were determined by EPMA. These samples were then analyzed at the same spots in each biotite grain by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) which was conducted using a Resonetics M-50-LR 193 nm Excimer laser ablation system coupled to an Agilent 7700× quadrupole ICP-MS also at the University of New Brunswick. The analysis used 64 µm beam size, 4.5 Hz pulse rate, 4 J/cm² energy. The Al content of each spot measured by EPMA was used with an internally-standardized data reduction scheme in order to obtain the most accurate trace element data (Appendix Table A).



Fig. 2. Geological map of the local area around the Sisson Brook W–Mo–Cu deposit (Fyffe et al., 2008). D_{NW} Devonian Nashwaak Granite, D_{HP} Devonian Howard Peak Diorite, D_G Devonian gabbro, O_{PB} Ordovician Push and Be Damned Formation, O_{HL} Ordovician Hayden Lake Formation, O_{TM} Ordovician Turnbull Mountain Formation, ϵ_{M} Cambro-Ordovician Miramichi Group, Dash line – fault. Zones I, II, and III of the deposit are noted.

The GOR128-G and NIST 612 glass were used as the reference material in order to confirm the precision and accuracy of the results of the LA-ICP-MS analysis. The relative standard deviations (%RSD) for the most of trace elements in GOR128-G and NIST 612 are lower than 4% (See Appendix Table B). The relative deviations for trace elements in them are generally within 10% (see Appendix Table B). Detailed analytical results and limits of detection are in Appendix Table C and D. Formula calculation of biotite is based on 22 atoms of oxygen by the EPMA data. Water contents were calculated by stoichiometry (cf. Yang and Lentz, 2005).

4. Petrography

The studied samples can be grouped based upon their geological occurrences and mineral assemblages. Group I is muscovite–biotite

phase of the Nashwaak Granites that is fine- to coarse-grained (0.5–7 mm), seriate textured, and is characterized by the presence of biotite with variable muscovite contents. Biotite (0.5–2 mm) is euhedral to anhedral, containing mineral inclusions of zircon and apatite. Apatite also occurs in feldspar with moderate to high relief and low birefringence (Fig. 3a). Microcline with predominantly patchy tartan twins is present. Plagioclase displays typical polysynthetic twinning and/or Carlsbad twins. Some small earlier formed plagio-clase with altered cores (not resorbed) and K-feldspar rims are contained in large perthite (Fig. 3b). Large (3 mm) euhedral crystals of plagioclase are zoned and are altered along the boundary of each growth zone (Fig. 3c). This concentric zoning of plagioclase consists of a core formed at a high temperature with enriched Ca and Al, and a rim crystallized at a lower temperature with more Na and Si,



Fig. 3. Representative photomicrographs of texture and mineralogy of the Nashwaak Granites and related dykes. a) muscovite and biotite cluster with a nearby apatite, plagioclase with altered core and magmatic rim, sample MBG5, cross polarized light (XPL); b) plagioclase inclusion in perthite, sample MBG5, XPL; c) plagioclase with zoning, sample MBG5, XPL; d) biotite inclusion in quartz grain, sample BG1, XPL; e) granophyre texture, sample BG1, XPL; f) relative fresh anhydral biotite occur with plagioclase, sample BGD11, XPL; g) skeletal or resorbed quartz phenocryst, sample PD, XPL; h) zoned plagioclase and biotite phenocryst, sample PD, XPL.

as determined by well-known experiments on plagioclase crystallization (Lofgren, 1974, 1980).

Group II is biotite granitic phase of the Nashwaak Granites, which is fine- to coarse-grained (0.5–6 mm). Biotite is abundant (approximately 20%, 0.5–1.5 mm) in the samples of Group II, associated with accessory minerals consisting of zircon, apatite, monazite, and opaque magnetite, and ilmenite. Zircon and apatite commonly occur in biotite clusters. Biotite inclusions are also found in large quartz grains (Fig. 3d). Anhedral quartz and alkali feldspar intergrowth formed granophyre texture suggests water saturation during crystallization (Fig. 3e; Yang and Lentz, 2005). Microcline with tartan twins is common and is consistent with water saturation and slow cooling. Plagioclase with altered cores and magmatic rims is present inside microcline or between quartz and feldspar grains, similar to that observed in the muscovite–biotite granite (Group I).

Biotite granitic dykes (Group III) crosscut the Howard Peak dioritegabbro observed in drill cores. These dykes range in width from several cm up to 12.2 m, generally exhibiting sharp contacts with the host although locally, irregular with angles from 20° to 80° to the core axis (holes drilled at a dip angle of 45° with a few at 55°) (Geodex Minerals Ltd. drill logs). The dyke samples are generally light greenish gray in color, fine- to coarse-grained (0.5-5 mm), allotriomorphic inequigranular and unfoliated. This group generally has the same mineral composition as the biotite granite with the exception of the presence of some secondary minerals (i.e., pyrite and chalcopyrite). Biotite is altered to chlorite along their rims and cleavages. Unaltered or relatively fresh biotite is anhedral (typically <1 mm) and is in contact with plagioclase that shows both Albite and Carlsbad twins (Fig. 3f). No plagioclase zoning was observed. Magmatic, anhedral quartz is more abundant than in the Group II samples, and equant subgrains in deformed quartz was also seen in several samples.

Group IV is a quartz-biotite-feldspar porphyry dyke that was intersected from 13.6 to 54.6 m in drillhole SSN-26. The granite

porphyry contains about 50% phenocrysts set in a fine-grained groundmass of alkali feldspar and quartz. The phenocryst population includes about 25% zoned plagioclase laths (An₃₄–An₁₅) up to 1 cm in length; 10% euhedral to subhedral (i.e. resorption texture with embayed outline or habits of ß-quartz polymorph, Fig. 3g) quartz crystals from 1 to 7 mm in width; 8% biotite laths ranging from 0.05 to 1 cm in length; and 7% alkali feldspar crystals from 0.2 to 1 cm in width (Mann, 1980; Nast, 1985; Nast and Williams-Jones, 1991). Plagioclase crystals are zoned and some have Albite twins. The biotite is euhedral and some have slight alteration along their rims (Fig. 3h).

5. Biotite mineral chemistry

5.1. Biotite classification

It is critical to be sure that biotite grains analyzed are of primary magmatic origin, so that their chemical composition may reflect magmatic conditions of crystallization. The Ti content of biotite is thermally controlled (Patiño Douce, 1993; Stussi and Cuney, 1996). Re-equilibrated and neoformed biotite grains, resulting from low temperature hydrothermal alteration, have less Ti than those of primary magmatic biotites. Most of the biotites from the Nashwaak Granites and related dykes plot in the primary biotite domain defined by Nachit et al. (2005) with the TiO₂ ranging from 1.76 to 4.55 wt.%. The Ti (*a.p.f.u*, atoms per formula unit) of the biotite from Group II (mean Ti = 0.42) and Group IV (mean Ti = 0.46) are generally higher than that of the biotite from Group I (mean Ti = 0.32) and Group III (mean Ti = 0.3) (Fig. 4a, Table 1). Aluminum content of biotite crystallized in equilibrium with a silicate melt reflects the peraluminosity of the melt (Stussi and Cuney, 1996) and it is commonly the host for the excess Al in peraluminous granitoids (Fleet, 2003). Therefore, biotite from the two-mica granite (Group I, whole rock aluminum saturation index > 1.1, Zhang, 2015) has higher Al (a.p.f.u > 3.1) than that of biotite from other groups



Fig. 4. Chemical compositional diagrams of biotite from the Nashwaak Granites and related dykes. a) Ternary TiO₂–FeO + MnO–MgO diagram after Nachit et al. (2005), b) Al–Mg diagram after Stussi and Cuney (1996), c) Fe/(Fe + Mg)–Al diagram after Rieder et al. (1998), d) Ternary MgO–FeO–Al₂O₃ diagram after Abdel-Rahman (1994) of biotite from Nashwaak Granites and related dykes. × two mica granite (Group I), \triangle biotite granite (Group II), \square biotite granite dykes (Group III), \blacksquare porphyry dyke (Group IV). Ann = annite, Sid = siderophyllite, Phl = phlogopite, Pol = polylithionite.

Table 1

Average chemical compositions of biotite from the Nashwaak Granites and related dykes analyzed by electron probe microanalysis (EPMA).

Sample	Two-mica granite 6		Biotite granit	e	Biotite graniti	c dykes	Porphyry dyke		
No. of samples			7		7		1		
No. of analyzed spots	30	30			18		5		
	Ave.	1σ	Ave.	1σ	Ave.	1σ	Ave.	1σ	
T _{Zr} (°C)	772	28.1	796	15.4	754	24.9	772	0.00	
SiO ₂	33.3	1.96	33.7	1.53	34.9	2.38	34.9	0.83	
TiO ₂	2.75	0.53	3.51	0.46	2.59	0.50	4.03	0.38	
Al ₂ O ₃	19.5	1.44	16.7	0.90	17.9	0.66	16.3	2.38	
FeO	23.8	2.04	22.7	2.61	22.1	2.47	22.7	0.48	
MgO	5.96	0.58	7.70	1.54	8.40	1.65	8.07	1.48	
MnO	0.51	0.11	0.35	0.07	0.32	0.12	0.29	0.06	
BaO	0.05	0.06	0.05	0.07	0.07	0.09	0.06	0.06	
CaO	0.12	0.16	0.05	0.06	0.18	0.40	0.04	0.02	
ZnO	0.08	0.04	0.06	0.03	0.04	0.03	0.03	0.03	
K ₂ O	8.73	1.43	9.27	0.90	7.64	1.96	8.78	0.47	
Na ₂ O	0.16	0.11	0.18	0.13	0.23	0.14	0.20	0.08	
Rb ₂ O	0.11	0.07	0.05	0.05	0.04	0.05	0.00	0.01	
F	0.51	0.16	0.35	0.11	0.49	0.16	0.51	0.15	
Cl	0.04	0.04	0.05	0.05	0.12	0.06	0.14	0.04	
H ₂ O	3.59	0.13	3.63	0.08	3.64	0.11	3.62	0.09	
O = F	-0.22	0.07	-0.15	0.05	-0.20	0.07	-0.22	0.06	
O = Cl	-0.01	0.01	-0.01	0.01	-0.03	0.01	-0.03	0.01	
Total	98.9	2.06	98.2	2.02	98.5	3.09	99.7	0.65	
Si	5.18	0.19	5.30	0.18	5.37	0.19	5.36	0.11	
Aliv	2.82	0.19	2.70	0.18	2.63	0.19	2.64	0.11	
Tsite	8.00	0.00	8.00	0.00	8.00	0.00	8.00	0.00	
Ti	0.32	0.06	0.42	0.05	0.30	0.06	0.46	0.04	
Alvi	0.75	0.25	0.40	0.11	0.62	0.13	0.32	0.33	
V	0.01	0.01	0.01	0.01	0.00	0.01	0.03	0.00	
Fe	3.10	0.31	2.99	0.36	2.86	0.39	2.92	0.09	
Mg	1.39	0.15	1.81	0.36	1.92	0.34	1.85	0.35	
Mn	0.07	0.01	0.05	0.01	0.04	0.02	0.04	0.01	
Zn	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	
Osite	5.65	0.21	5.67	0.14	5./5	0.25	5.63	0.11	
Ca K	0.02	0.03	0.01	0.01	0.03	0.07	0.01	0.00	
K	1./4	0.29	1.86	0.18	1.49	0.35	1.72	0.08	
Na	0.05	0.03	0.05	0.04	0.07	0.04	0.06	0.02	
F	0.25	0.08	0.17	0.05	0.24	0.07	0.25	0.07	
	0.01	0.01	0.01	0.01	0.05	0.01	0.04	0.01	
	3.74	0.08	3.81	0.05	3.73	0.07	3./1	0.09	
AI X	5.57	0.24	5.10	0.17	5.25	0.16	2.90	0.42	
A _{Mg}	0.25	0.02	0.52	0.00	0.55	0.00	0.55	0.06	
A _{Sid}	0.07	0.06	0.50	0.10	0.51	0.09	0.45	0.13	
A _{An}	0.09	0.05	0.18	0.04	0.15	0.05	0.22	0.10	
W(C)	1./3	0.10	2.05	0.25	1.90	0.10	1.07	0.00	
IV(U) Log(f = 0)/(f = 0)	- 2.77	0.54	- 5.00	0.42	- 5.52	0.20	- 5.02	0.24	
$\log(\pi_2 O)/(\pi C)$	4.15	0.13	4.34	0.24	4.32	0.10	4.23	0.09	
$LUg(\Pi_2U)/((\Pi U))$	4.50	0.50	4.10	0.57	0.56	0.25	0.59	0.19	
LUg(JIT/JIICI)	0.22	0.59	-0.16	0,55	-0.50	0.24	- 0.58	0.12	

Notes: Formula calculations are based on 22 oxygen. OH is calculated by OH = 4 - (Cl + F). Intercept values IV(F) and IV(Cl) and halogen fugacity are calculated by Munoz (1984, 1992). T_{zr} were calculated by Watson and Harrison (1983). Complete data see Appendix Table A.

(whole rock ASI < 1.1, Zhang, 2015) (Fig. 4b). In the International Mineralogical Association (IMA) classification diagram, the most of the biotites plot close to the siderophyllite-eastonite boundary (Rieder et al., 1998) with the Fe/(Fe + Mg) ratio between 0.49 and 0.74 (Fig. 4c). In the study of Abdel-Rahman (1994) on the composition of biotite from various igneous rock types, he concluded that biotites in alkaline anorogenic suites are mostly iron-rich, biotites in peraluminous (including S-type) suites are siderophyllitic in composition, and those in calc-alkaline, mostly subduction-related orogenic suites are enriched in Mg. In the $MgO-FeO + MnO-Al_2O_3$ diagram (Fig. 4d; after Abdel-Rahman, 1994), most of the biotites of Nashwaak Granites and related dykes plot on the border between calc-alkaline and peraluminous suites. This conclusion is supported by using plots of the inverse correlation between the Al and Mg a.p.f.u. contents of these biotites (Nachit et al., 1985). Stussi and Cuney (1996) explained that the most fractionated members of calc-alkaline magmas may become slightly to moderately peraluminous, although it is well-established that the origin of most peraluminous granites is known to be different than that of calc-alkaline magmas.

5.2. Trace-element characteristics

Tischendorf et al. (1997); Tischendorf et al. (2001) investigated the trace elements (Ti, Sn, Sc, V, Cr, Ga, Mn, Co, Ni, Zn, Sr, Ba, Rb, Cs) in micas of the system phlogopite–annite–siderophyllite–polylithionite (PASP) and divided the micas into seven varieties by the parameter *mgli* (=octahedral Mg minus Li). However, if the Ba, Mg, Fe, Ni, Co, Sc, V, Cr, Ti, Be/Rb and K/Rb all decrease in biotite, whereas Li, Rb, Cs, Tl, Be, Sn and Fe/Mg increase in biotite with magmatic fractionation as suggested by Gordiyenko (1975), then the parameter *mgli* may be substituted by K/Rb as an indicator of magma evolution as this ratio decreases with fractionation.

The K/Rb ratios of biotite from the Nashwaak Granites and related dykes decrease gradually from porphyry dykes (Group IV, 148 to 219), to the biotite granite (Group II, 74 to 163), the biotite granitic dykes (Group III, 92 to 108), and two-mica granite (Group I, 33 to 112) (Table 2, Appendix Table D, Fig. 5). The same trend is observed for the compatible elements (in felsic rocks) Cr (12 to 97 ppm), Ti (1.19 to

Table 2	2
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Average content of trace elements in biotite from Nashwaak Granites and related dykes analyzed by the laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS).

	MBG	Int2SE	LOD	BG	Int2SE	LOD	BGD	Int2SE	LOD	PD	Int2SE	LOD
wt.%												
Si	16.3	0.28	870	16.9	0.27	636	16.6	0.31	516	19.0	0.31	302
Ti	1.39	0.02	4.85	1.81	0.03	4.64	1.48	0.03	3.58	2.67	0.08	10.4
Fe	17.2	0.28	19.5	16.1	0.26	17.7	17.5	0.33	17.5	20.5	0.46	35.1
Mn	0.43	0.01	2.25	0.29	0.00	1.74	0.31	0.01	1.55	0.31	0.01	1.48
Mg	3.39	0.05	4.29	4.47	0.06	5.42	4.21	0.06	6.13	6.20	0.11	11.2
Ca	0.09	0.02	238	0.25	0.03	198	1.91	0.20	117	1.53	0.09	63.5
Na	0.05	0.00	10.0	0.11	0.00	8.26	0.09	0.01	4.70	0.11	0.00	2.33
K	8.03	0.13	10.8	8.55	0.14	13.6	6.37	0.11	9.09	7.55	0.14	23.4
ppm												
Li	766	12.5	2.98	198	4.44	2.51	281	6.76	1.21	217	4.42	0.11
Be	6.10	0.95	0.11	0.30	0.22	0.23	6.48	1.04	0.08	2.45	0.65	0.06
Rb	1270	22.8	0.60	728	13.0	0.45	632	10.9	0.22	423	8.04	0.14
Sr	4.89	0.32	0.08	2.63	0.25	0.06	14.1	0.87	0.02	13.0	0.36	0.00
Ba	329	6.26	0.46	407	6.88	0.39	67.2	1.59	0.15	1732	28.0	0.35
Cs	105	2.39	0.13	24.4	0.62	0.10	22.5	0.53	0.05	18.9	0.52	0.01
Ga	73.8	1.80	0.98	52.9	1.51	1.02	99.3	1.99	0.37	68.3	1.52	0.02
Tl	8.97	0.28	0.04	3.91	0.17	0.05	4.18	0.13	0.02	2.48	0.09	0.01
Ta	25.9	0.57	0.03	5.32	0.14	0.02	6.26	0.16	0.01	2.50	0.10	0.00
Sc	38.8	1.13	0.91	59.3	1.29	1.03	89.2	2.29	0.26	44.1	1.85	0.06
V	184	3.20	0.67	223	3.34	0.72	81.4	1.79	0.22	433	8.16	0.23
Cr	102	2.12	1.61	62.6	1.78	1.64	26.8	0.97	1.05	91.4	1.80	0.84
Со	35.0	0.92	0.49	44.5	1.11	0.50	29.4	0.79	0.15	48.9	1.15	0.02
Ni	41.6	2.16	2.52	38.9	2.28	2.85	24.7	1.28	0.80	31.7	1.12	0.08
Cu	6.35	0.68	0.59	7.08	0.67	0.67	6.66	1.17	0.22	5.13	1.42	0.04
Zn	828	14.9	1.85	584	11.1	1.52	514	62.3	0.76	276	4.18	0.18
Mo	0.27	0.47	1.21	0.30	0.35	0.94	0.09	0.16	0.38	0.60	0.04	0.00
Sn	60.9	1.53	0.23	23.5	0.89	0.19	75.8	4.58	0.10	15.2	0.47	0.04
W	2.86	0.16	0.06	2.39	0.13	0.05	4.18	0.27	0.01	4.05	0.28	0.00

Note: Stoichiometric Al content for each spot measured by EMPA is used for internal standardization. Int2SE is the analytical error. LOD is the limit of detection which is shown in ppm for all the elements. Complete data see Appendix Table D.

2.89 wt.%), Co (19 to 61 ppm), V (38 to 463 ppm), and Ba (30 to 2423 ppm) in Groups II, III, and IV. Group I deviates slightly from this trend with Cr contents values between 39 to 186 ppm, Ti from 0.9 to 1.9 wt.%, Co from 26 to 42 ppm, V between 96 and 309 ppm, and Ba of 12 to 1420 ppm. Nickel in those biotites is scattered and ranges from 6 ppm to 64 ppm. The incompatible elements, Ta (2–76 ppm), Tl (2–14 ppm), Ga (44–140 ppm), Cs (8–651 ppm), and Li (105–1282 ppm), show a reverse distribution pattern and increase continuously from the porphyry dykes, to biotite granite, biotite granitic dykes, and two-mica granite. Scandium is enriched in Group III (50–154 ppm) relative to the other groups (26–58 ppm). Metal elements Sn (8–128 ppm) and Zn (204–1480 ppm) increase with decreasing K/Rb. The concentration of other metallic elements, such as Cu (1–60 ppm), Mo (< 2 ppm), and W (<15 ppm) are independent of K/Rb (Fig. 5, Table 2).

6. Halogen chemistry of biotite

Most (70 to 90%) of the F content of muscovite- and fluorite-free granitoid rocks is contained in biotite (Grabezkev et al., 1979), with the remainder being in apatite and titanite. The range of F contents within biotites from the Nashwaak Granites and related dykes is from 0.11 to 0.83 wt.%. In contrast, because ionic radius of Cl⁻ is larger (1.81 Å) than that of F⁻ (1.31 Å) or OH⁻ (1.38 Å) (Munoz, 1984), the amount of Cl substitution in the OH site is less than that of F; it varies widely between 0.01 and 0.28 *wt.*% in these biotites. The extent of halogen replacement of hydroxyl in biotite is governed by its Mg/Fe ratio. Biotites with high Mg/Fe ratios tend to incorporate more F, and low Mg/Fe biotites contain more Cl, as noted by Munoz (1984). This correlation is caused by the crystal-chemical effect known as 'F-Fe avoidance" and "Mg–Cl avoidance" (Munoz, 1984). In order to calculate relative degree of halogen enrichment in biotite, intercept values, IV(F), IV(Cl), and IV(F/Cl), were developed by Munoz (1984) that have been

corrected by the effect of Mg/Fe ratios, and are given by the following equations

 $IV(F) = 1.52X_{phl} + 0.42X_{ann} + 0.20X_{sid} - log(X_F/X_{OH})$

 $IV(Cl) = -5.01\!-\!1.93X_{phl}\!-log(X_{Cl}/X_{OH})$

IV(F/Cl) = IV(F) - IV(Cl)

where $X_{phl} = Mg/sum$ of octahedral cations; $X_{sid} = [(3 - Si/Al) / 1.75](1 - X_{phl})$; $X_{ann} = 1 - (X_{phl} + X_{sid})$. The smaller intercept value representing higher degree of halogen enrichment in biotites.

The biotite from the two-mica granite (Group I) is distinct from the other groups by its low IV(F) (1.51 to 2.16, mean = 1.73) and high IV(Cl) (-3.56 to -2.13, mean = -2.77). The IV(F), IV(Cl), and IV(F/Cl) of biotite from other groups of samples are between 1.76 and 2.64, -4.11 and -2.03, and 3.89 and 6.51, respectively. The diagram of IV(F/Cl) and IV(F) shows that they have a positive correlation (i.e., IV(F/Cl) decreases with decreasing IV(F)) (Fig. 6). Loferski and Ayuso (1995) explained that the decrease of IV(F) value might be caused by crystal fractionation processes during which F concentrates in the late magmatic stage. The F/Cl intercept values for biotites from porphyry copper deposits, Mo-W-Sn-Be deposits (excluding Henderson) and the Henderson porphyry molybdenum deposit were plotted against IV(F) by Munoz (1984). In the IV(F/Cl) versus IV(F) diagram (Fig. 6), biotite from Groups I has more F enrichment (low IV(F)), which is similar to that of the Henderson porphyry Mo deposit. Biotite from Group II has wide range of IV(F/Cl) varying from 4 to 6.5. The overlap of the IV(F/Cl) ratio in biotite between Groups III and IV and those of the Sn-W-Be deposits indicates that the magma or fluids that were in equilibrium with those biotites had similar f(HCI)/f(HF) fugacity ratios (Table 1, Appendix Table A).

7. Halogen fugacity of associated fluids

The contents of fluorine and chlorine in biotite may be used to calculate the halogen fugacity in associated magma or fluids (Munoz, 1984, 1992; van Middelaar and Keith, 1990; Loferski and Ayuso, 1995; Selby and Nesbitt, 1997, 2000; Yang and Lentz, 2005; Ayati et al., 2008; Boomeri et al., 2009, 2010). Calculations can be made in terms of the following equations proposed by Munoz (1992) based on the revised coefficients for F–Cl–OH partitioning between biotite and the hydrothermal fluid (Zhu and Sverjensky, 1991, 1992).

$$\log(fH_2O/fHF)^{\text{fluid}} = 1000/T(2.37 + 1.1X_{\text{phl}}) + 0.43 - \log(X_F/X_{OH})^{\text{biotite}}$$

$$\log(fH_2O/fHCl)^{\text{fluid}} = 1000/T (1.15 - 0.55X_{\text{phl}}) + 0.68 - \log(X_{\text{Cl}}/X_{\text{OH}})^{\text{biotic}}$$



Fig. 5. (2 pages) Trace-element composition of biotite from the Nashwaak Granites and related dykes analyzed by LA-ICP-MS. See Fig. 4 for symbols used.





 $\text{Log}(\text{fHF}/\text{fHCl})^{\text{fluid}} = -1000/\text{T} \left(1.22 + 1.65 X_{\text{phl}} \right) + 0.25 + \left. \text{log}(X_{\text{F}}/X_{\text{Cl}})^{\text{biotite}} \right.$

where X_F , X_{Cl} , and X_{OH} are mole fractions of F, Cl, and OH in the hydroxyl site of biotite, respectively. T is the equilibrium temperature (in Kelvin) which could be estimated by the X_{phl} and X_{PDoxy} (Fe³⁺/sum

of octahedral ions) of hydrothermal biotites (Beane, 1974) or by the Ti content of biotite from graphitic-peraluminous-metapelites, which contain ilmenite or rutile (Henry et al., 2005). However, for biotites from igneous rocks, Yang and Lentz (2005) calculated oxygen fugacity of the associated magmas by using zircon-, apatite-, and (or) monazite-saturation temperatures (Watson and Harrison, 1983; Harrison and



Fig. 6. Intercept value IV(F/Cl) plots against IV(F) for biotite from the Nashwaak Granites and related dykes. Composition of biotite related to the typical porphyry Cu, Sn–W–Be, and porphyry Mo deposits are from Munoz (1984). See Fig. 4 for symbols used.

Watson, 1984; Montel, 1993). The zircon saturation temperatures of the Nashwaak Granites and related dykes vary from 719 to 819 °C (Zhang, 2015). The calculated $\log(fH_2O/fHF)$, $\log(fH_2O/fHCI)$, and log(fHF/fHCl) ratios of magmatic fluids in equilibrium with magmas (based on the equations mentioned above) are shown in Fig. 7. The fluids of Group I have higher log(fHF/fHCl) ratio (mean = 0.22) and lower $\log(fH_2O/fHF)$ (mean = 4.15) than that of the other groups. The fluids associated with Group II have similar or slightly higher $\log(fH_2O/fHF)$ (mean = 4.34), $\log(fH_2O/fHCI)$ (mean = 4.16), and $\log(fHF/fHCl)$ (mean = -0.18) than those fluids associated with Groups III and IV. The fluids of Groups III and IV are relatively waterrich (more than 3 orders of magnitude relative to halogen fugacity) and Cl-rich (log(fHF/fHCl) ratios are lower than 0), and are similar to the fluid composition associated with biotites from the porphyry-Cu deposits at Santa Rita, New Mexico, U.S.A (Munoz and Swenson, 1981). However, the fluids of Group I have more F than Cl (log(fHF/ *f*HCl) ratios higher than 0). Furthermore, the log (X_F/X_{OH}) vs. X_{Fe} and $\log (X_{Cl}/X_{OH})$ vs. X_{Mg} plots of the biotites formed under the same T, P, and fluid composition would form linear trends (Zhu and Sverjensky, 1992). These linear trends are not observed in the biotite of the Nashwaak Granites and related dykes. The variation of halogen fugacity calculated by zircon saturation temperature, and the scatter of the $\log (X_F/X_{OH})$ vs. X_{Fe} and $\log (X_{CI}/X_{OH})$ vs. X_{Mg} plots, could be explained by the possible continuous equilibration of biotites with fluids over a range of temperatures and of fluid composition. This is typical for magmatic fluids during cooling of granitic plutons, manifested by fHF/fHCl ratios of magmatic fluids that may progressively increase with differentiation (Yang and Lentz, 2005).

8. Oxygen fugacity

Oxygen fugacity (fO_2) exerts a control on the partitioning behavior of Mo and W between ferromagnesian phases and melts, and on relative efficiencies of removal of these metals from the magmas into associated ore-forming fluids. Ore systems with high W/Mo ratios are relatively reduced, whereas systems with low W/Mo are oxidized (Candela and Bouton, 1990). Blevin and Chappell (1992) explained that during fractionation of a magma, W and Mo are sequestered by Fe–Ti phases whose stability is normally fO_2 -dependent. Molybdenum is associated with oxidized felsic granites (Mengason et al., 2011), but W shows little dependence on redox conditions of a magma. However, besides the Fe³⁺/Fe²⁺ ratio of whole rocks, the Fe³⁺/Fe²⁺ ratio of biotite is also used to constrain oxygen fugacity of the associated magma system. Shabani et al. (2003) investigated the composition of biotites from the Gander zone of New Brunswick, which falls on or above nickel-nickel oxide (NNO) buffer in the Fe³⁺-Fe²⁺-Mg diagram of Wones and Eugster (1965). The latter authors demonstrated that biotite crystallizing from a magma that contains sanidine and magnetite may follow either an iron-rich trend or a magnesium-rich trend depending upon the fO₂ conditions during crystallization over cooling. Thus, the total Fe and Mg ratio of biotite is another useful quantitative tool that can be used to estimate fO_2 instead of Fe³⁺ and Fe²⁺, which cannot be measured directly by EPMA. In the fO₂ vs. T diagram (Fig. 8), biotites in Groups I and II samples are plotted along the quartz-fayalite-magnetite (QFM) buffer at high temperatures, and increase above the nickelnickel oxide buffer with cooling of magmas. The increase of fO_2 during magma evolution may be attributed to H₂ release at or near H₂O vapor saturation at high H₂O/Fe²⁺ (cf. Candela, 1986a; Lentz, 1992). The biotite from the dykes (Groups III and IV) plot around the nickelnickel oxide buffer, indicating that these dykes formed at relatively higher oxygen fugacity than that of plutonic phases (Groups I and II). The oxygen fugacity of all the samples is generally between 10^{-14} and 10⁻¹⁶ bars at between 719 to 819 °C estimated from zircon saturation geothermometer (Watson and Harrison, 1983). In these samples, Group I and some of Group II have the fO_2 values comparable with that of strongly contaminated reduced I-type granites of Ague and Brimhall (1988a, 1988b), whereas the fO_2 of Group III are close to oxidized I-type granites (Ague and Brimhall, 1988a, 1988b; Candela, 1989b).

On the other hand, magnetic susceptibility meter (KT-10) measurements (n = 3 for each sample) yielded average values that lie along the boundary of the magnetite series and ilmenite series granites (1 × 10^{-4} emu/g; Ishihara, 1981). This result is in accordance with the findings of Shabani et al. (2003), who demonstrated that the magnetite/ilmenite ratio in granites varies considerably in the Gander Zone of New Brunswick.

9. Discussion

9.1. Petrogenetic implications

On the \sum Al–Mg diagram of Nachit et al. (1985) and MgO– \sum FeO– Al₂O₃ diagram of Abdel-Rahman (1994), biotites from the Nashwaak Granites and related dykes are located in the peraluminous and calcalkaline fields, likely formed in a subduction and/or collisional setting. This conclusion is supported by their whole rock geochemistry (Zhang, 2015) with low Nb, Rb, and Y contents indicating a volcanic arc setting (Pearce et al., 1984). Also, this is consistent with the research of Whalen (1993) who plotted the composition of Siluro-Devonian granitic rocks from the Gander Zone in the diagrams of Pearce et al. (1984) and most of these granites straddle the boundary between volcanic-arc to within-plate granites. In these granites, negative correlation between Al and Mg of biotite are controlled by different substitution mechanisms as shown by Abdel-Rahman (1994); Stussi and Cuney (1996) and Fleet (2003). Average Al content is lower in biotite in calc-alkaline granites than that in peraluminous granites because of lower activity of Al₂O₃ in calc-alkaline magmas.

Almost all the F present in the continental crust resides in granitoids and their metamorphic counterparts. Thus, F contents in granitoids may be related to the nature of magma source rock and the melting processes involved. Whether F behaves as an incompatible or compatible element in magmas depends upon whether the resultant magmatic rocks contain anhydrous or hydrous mineral assemblages (Sallet, 2000). Ague and Brimhall (1988a, 1988b) studied regional variations in bulk chemistry and mineralogy in the batholiths of California. In those I-type granitoids, the F/OH value of biotite increases with the degree of crustal contamination and the biotites in strongly reduced I-type granitoids are enriched in iron. However, Loferski and Ayuso (1995) investigated the biotite composition from some plutons in Maine that do not display a systematic regional variation. Comparing to the biotite composition of I-type granitoid rocks in the Sierra Nevada batholith of



Fig. 7. a) Log(Cl/OH), log(F/OH), and log(Cl/F) vs. XMg for biotites from the Nashwaak Granites and related dykes. In each diagram, the relative log($fH_2O/fHCI$), log($fH_2O/fHCI$), and log(fHF/fHCI) reference lines are calculated at 750 °C. b) Detailed log($fH_2O/fHCI$), log($fH_2O/fHCI$),

California (Ague and Brimhall, 1988a, 1988b), biotites in the Nashwaak Granites and related dykes are plotted along the border between oxidized and reduced I-type granites with weak to medium crustal contamination. The crustal contribution to the Nashwaak Granites and related dykes as shown by the whole-rock $\delta^{18}O$ (9.3–10.9 ‰), $\epsilon_{Nd}(T)$ (-4.51 to -1.42), and the ${}^{206}Pb/{}^{204}Pb$, ${}^{207}Pb/{}^{204}Pb$, ${}^{208}Pb/{}^{208}P$ ²⁰⁴Pb values of 18.3, 15.6, and 38.3, respectively (Ayuso and Bevier, 1991; Zhang, 2015), implies that these Nashwaak granitoids originated from infracrustal sources (Bevier and Whalen, 1990; Whalen, 1993). Whalen et al. (1996) interpreted those granitic magmas to be derived from bulk assimilation of Mesoproterozoic Gondwanan basement \pm the overlying Gander Zone sedimentary prism, by enriched asthenospheric mantle-derived melts. In Fig. 9, the value of log $(X_{Mg}/X_{Fe}) =$ -0.21 was chosen as the dividing line between the reduced and oxidized rocks because of absence of muscovite, garnet, and tourmaline and the presence of titanite at higher values of log (X_{Mg}/X_{Fe}) in the batholiths of California (Ague and Brimhall, 1988a, 1988b). However, the experiment of Wones and Eugster (1965) indicated that the biotite with a constant Fe/Mg ratio represents more oxidized settings if it crystallized at lower temperatures (i.e. from CO_2-CH_4 buffer at 900 °C to Ni–NiO buffer at 700 °C). Ague and Brimhall (1988b) calculated oxygen fugacity based on the representative conditions of 800 °C for the batholiths of California and the $log(X_{Mg}/X_{Fe})$ of -0.21 was chosen to divide the oxidized and reduced granites. The Nashwaak Granites and related dykes crystallized at temperatures lower than 800 °C (Zhang, 2015). Thus the line of log (X_{Mg}/X_{Fe}) between oxidized and reduced granites should be lower than -0.21 (Fig. 9) for the Nashwaak Granites and related dykes and some of the points in the I-SCR area might represent the oxidized I-type granites (Fig. 9).

9.2. Metallogenic implication of volatiles

9.2.1. Water content in melts

Water vapor is a major volatile component in natural aluminosilicate melts, and controls the chemical and physical properties of magmas, such as phase relationships, viscosity, density and diffusivity (Holtz



Fig. 8. Temperature vs. oxygen fugacity diagram for biotite from the Nashwaak Granites and related dykes (see Candela, 1989b). See Fig. 4 for symbols used. Light gray pattern denotes contaminated I-type granite. Dark gray pattern represents strongly contaminated reduced I-type granitoids (after Ague and Brimhall, 1988b).

et al., 2001). In ore deposit-related melts, water content influences hydrothermal evolution behavior as shown by the model of Burnham (1979) and William-Jones and Heinrich (2005). This is because water promotes the segregation of metal elements from the melt to ore fluids (Candela, 1989a). The water content in granitic melts could be estimated using the method developed by Holtz et al. (2001) if the initial temperature and pressure are known. However, temperature estimation by using zircon saturation thermometer (Watson and Harrison, 1983) indicates that the Nashwaak Granites and related dykes are 'cold' granites ($T_{Zr} < 800$ °C, Zhang, 2015) as defined by Miller et al. (2003). The presence of inherited zircons in these magmas shows that zircon is saturated and thus T_{Zr} could represent the initial magma temperature at the source (Miller et al., 2003). At moderate crustal depths (equivalent to lithostatic pressures of 4–8 kbar), the melts forming the Nashwaak Granites and dykes contain ~4–5% water in the *P*–T–H₂O



Fig. 9. Classification of the Nashwaak Granites and related dykes according to the composition of their magmatic biotite composition (after Ague and Brimhall, 1988a). For comparison purposes, the biotites related to the Mo- and W-porphyry deposits are also shown after Brimhall and Crerar (1987). I-SC, strongly contaminated I-type; I-MC, moderately contaminated I-type, I-WC, weakly contaminated I-type, I-SCR, strongly contaminated and reduced I-type. See Fig. 4 for symbols used.

diagram of Holtz et al. (2001). This estimated water content is significantly higher than that of magmas resulted in scheelite skarn granitoids ranging from 2% to 4% as suggested by Newberry and Swanson (1986). Candela (1989a, 1989b) indicated that the ratio of the initial water concentration to the saturation water concentration in the melt is the important parameter when calculating the proportion of any given ore metal removed from the magma into an ore fluid. Tungsten (Mo) deposits usually have lower ratios than those of porphyry Cu deposits, since W (Mo) behave as incompatible elements and their enrichment needs a significant amount of crystallization before water content is increased to the saturation level. This could explain why large W skarn deposits are related to deep emplacement of H₂O-poor magmas (Newberry and Swanson, 1986; Keith et al., 1989; van Middelaar and Keith, 1990; Newberry, 1998; Rasmussen et al., 2011). In the H₂Opoor system, HF has essentially the same effect per unit mass as H₂O on melting relations according to the model of Burnham (1979), this suggests that magmas produced by partial melting of a source region with a high F/H₂O ratio will be impoverished in water, and will, therefore, experience a protracted crystallization history before vapor evolution, allowing W, Mo, and other incompatible elements to concentrate in the melt (e.g., Climax-type Mo deposits) relative to compatible elements such as copper (Candela, 1989b). For the Nashwaak Granites and related dykes, the water cannot be derived from dehydration melting of biotite and/or hornblende since the temperature is too low (T_{7r}<800 °C) (Patiño Douce and Harris, 1998) and therefore, fluid influx would be required.

9.2.2. Implication of halogen elements

Experiments of W and Mo partitioning behavior between melt and fluid show that the majority of dissolved tungsten species in hydrothermal solutions occur as tungstates and have the forms H₂WO₄, HWO_4^- , and WO_4^{-2} (Candela and Holland, 1984; Keppler and Wyllie, 1991; Samson, 1998; Wood and Samson, 2000). Molybdenum tends to be more easily reduced in nature than tungsten. Besides the similar species of H_2MoO_4 , $HMoO_4^-$, and MoO_4^{-2} as tungsten in the fluids, the MoO²⁺ and Mo(OH)³⁺ also possibly form under reducing conditions (Samson, 1998; Rempel et al., 2009). Molybdenum oxy-chloride complexes (i.e., MoO_2Cl^+) might only be present at highly acidic conditions (Bernard et al., 1990; Yokoi et al., 1993). Results of some experiments indicate that tungsten or molybdenum-chloride or -fluoride is not necessarily required for transporting significant W and Mo to form an ore deposit (Candela and Holland, 1984; Eugster, 1985; Wood and Vlassopoulos, 1989; Keppler and Wyllie, 1991; Gilbert et al., 1992; Wood, 1992; Samson, 1998; Wood and Samson, 2000).

Although W and Mo transported in the hydrothermal fluids is not directly combined with halogen elements, the ratio of F, Cl, and H₂O in a magmatic system is still worthwhile to be discussed since it could be one of W (Mo) mineralization vectors (Candela, 1989b; Rasmussen and Mortensen, 2013). However, the halogen composition of magma is dictated by the composition of source rock and the differentiation degree of magma (Keith et al., 1989; van Middelaar and Keith, 1990; Loferski and Ayuso, 1995; Christiansen and Keith, 1996; Sallet, 2000). The I-type magmas of the Nashwaak Granites and related dykes were derived from partial melting of lower crust, which could be the seismically defined Central Crustal Block that underlies the area (Keen et al., 1986; Marillier et al., 1989; Quinlan et al., 1992; Zhang, 2015). Partial melting of a dehydrated protolith (consisting of granulite-grade metamorphic rocks) would be rather rich in F occurring in the remaining hydrous minerals (Holloway, 1977; Burt et al., 1982; Ague and Brimhall, 1988a, 1988b; Loferski and Ayuso, 1995). As the magmatic system evolves, chlorine is strongly partitioned into fluids over melt when the volatile phase exsolves, whereas the fluorine displays the opposite behavior partitioning into minerals in the melt (Coulson et al., 2001; Rasmussen and Mortensen, 2013). Thus, the Cl/F and H₂O/F decrease with magma differentiation accompanied by volatile release from the magma system (Candela, 1986b; Keith et al., 1989;

van Middelaar and Keith, 1990; Loferski and Ayuso, 1995; Christiansen and Keith, 1996; Webster, 1997a, 1997b). Anomalously high HCl/HF and H₂O/HF ratios of biotites from highly differentiated granites might represent a build-up of volatiles (Cl, H₂O) as well as W and Mo within a magmatic system, and thus could be tungsten mineralization vectors (Rasmussen and Mortensen, 2013). However, the Nashwaak Granites and related dykes are all highly evolved granites and anomalous halogen activity ratios as those observed in Rudi and Lened pluton (Rasmussen and Mortensen, 2013) were not found. Except for the two-mica granite which has high F/Cl due to crustal contamination as discussed before, the other groups of rocks have the log(*f*HCl/HF) larger than 0.0, and the $log(fH_2O/HF)$ larger than 4.0 (cf. Fig. 7). The lack of extremely high Cl/F and H₂O/F ratios in the Nashwaak Granites and related dykes may indicates that a large granitic pluton as a source for mineralizing hydrothermal fluids at Sisson Brook deposits is not exposed (Rennie, 2012). Alternatively, the halogen ratios of biotites may not be able to effectively distinguish mineralized systems from barren systems (Munoz, 1984) and the granites associated with tungsten deposits have no restricted ranges of F/Cl ratios (Keith et al., 1989; van Middelaar and Keith, 1990).

10. Conclusions

The Sisson Brook W–Mo–Cu deposit formed, in part, by magmatic hydrothermal fluids inferred to be related to one of the four phases of the Nashwaak Granites and related dykes. Analysis results on primary magmatic biotites helped to investigate magmatic evolution processes and evaluate composition of related fluids. The compositions of biotites within the Nashwaak Granites and related dykes indicate that their magmas were emplaced in a subduction and/or collisional setting. According to the classification of I-type granitoids of Ague and Brimhall (1988a, 1988b), the biotite granite pluton (Group II) and dykes (Groups III and IV) are similar to the weakly to moderately contaminated I-type granite, whereas the muscovite–biotite granite (Group I) is similar to the strongly contaminated and reduced I-type granites.

The K/Rb ratio of biotite decreases with magma fractionation. The same trend is observed for compatible elements (in felsic rocks) Cr, Ti, Co, V, and Ba in Groups II, III, and IV, but Group I is slightly off this trend. The incompatible elements Ta, Tl, Ga, Cs, Li, and Sn show a reverse distribution pattern. Interestingly, Ni is scattered in those groups. Partitioning of W and Cu into biotite is not (or not entirely) controlled by magma fractionation (cf. Fig. 5) as no obvious correlation is evident. Molybdenum in these magmas is lower than 2 ppm.

Compared to Cl-rich magma systems related to porphyry Cu deposits, porphyry Mo deposits are more enriched in F. The high F/Cl ratio of magma in porphyry Mo systems could be inherited from their metamorphic source rocks or could be due to vapor exsolution during magma evolution that may have leached the Cl out of the system. The calculated halogen fugacity of magmas associated with the Nashwaak Granites and related dykes shows that Group I has undergone some degree of crustal contamination and thus has higher F/Cl than the other groups, and similar to those magmas associated with the Henderson porphyry Mo deposit. Groups II, III, and IV have their log(fHF/HCl) broadly lower than 0.0, and their log(fH₂O/HF) larger than 4.0. Anomalously high Cl/F and H₂O/F ratios which could be the W and Mo mineralization vectors (Rasmussen and Mortensen, 2013) were not found in the Nashwaak Granites and related dykes.

The Mo–W enrichment and mineralization are likely to form from slightly oxidized magmas (Blevin and Chappell, 1992), since Mo is more easily sequestered from the magma system in reduced settings. Tungsten shows little dependence on redox conditions of a magma although high grade W deposits are usually related to the reduced granites (Mahood and Hildreth, 1983; Candela and Bouton, 1990; Blevin and Chappell, 1992). In the Nashwaak Granites and related dykes, the dyke phases (Groups III and IV) have the oxygen fugacity around the nickel–nickel oxide buffers. The plutonic phases (Groups I and II) have the oxygen fugacity around the quartz–fayalite–magnetite (QFM) buffer at high temperatures and oxidized to nickel–nickel oxide buffer at lower temperatures. The oxidation process in the plutonic phases (Groups I and II) could be caused by H₂ release at or near H₂O vapor saturation at high H₂O/Fe²⁺ (cf. Candela, 1986a; Lentz, 1992). Although several other vital factors could control W and Mo mineralization, such as the ratio of initial water content to saturation water content in the magma, emplacement depth, the difference of those factors between each group is difficult to precisely determine. If only considering the evolution degree of magma and oxygen fugacity interpreted from the composition of biotite, the magmatic source of the biotite granitic dykes (Group III) is the plausible source of the hydrothermal fluids responsible for the Sisson Brook deposit mineralization since it has the highest differentiation degree and formed in an oxidized setting.

Conflict of interest

No conflict of interest exits in the submission of this manuscript, and manuscript is approved by all authors for publication. I would like to declare on behalf of my coauthors that the work described was original research that has not been published previously, and not under consideration for publication elsewhere, in whole or in part. All the authors listed have approved the manuscript that is enclosed.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.oregeorev.2016.02.004.

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