Canadian Mineralogist
Vol. 28, pp. 855-858 (1990)

HOWIEITE IN BLUESCHISTS, PINCHI LAKE, BRITISH COLUMBIA

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ABSTRACT

Lawsonite blueschist boulders from the Pinchi Fault Zone, British Columbia, locally contain howieite, stilpnomelane, and Na–Ca-amphiboles. These minerals have apparently crystallized late in the metamorphic history of the rocks. The howieite, of which this is the first reported occurrence in Canada, contains more Mg and Al and less Mn than is reported in howieite from other blueschist localities. It is possible that these minerals crystallized at relatively low temperature and pressure, compared to the high-pressure conditions of blueschists.

Keywords: howieite, stilpnomelane, winchite, blueschists, Pinchi Lake, British Columbia.

SOMMAIRE

Des blocs de schistes bleus à lawsonite dans la zone faillée de Pinchi, en Colombie-Britannique, contiennent ici et là l'association howieïte + stilpnomélane + amphiboles de Na + Ca. Ces minéraux auraient cristallisé tardivement dans l'évolution métamorphique de ces roches. La howieïte, dont c'est le premier exemple canadien, contient plus de Mg et de Al et moins de Mn que dans les autres localités de schistes bleus. L'association pourrait résulter d'un équilibre à pression et température relativement faibles, comparées aux conditions de pression élevée à l'origine des schistes bleus.

(Traduit par la Rédaction)

Mots-clés: howieïte, stilpnomélane, winchite, schistes bleus, lac Pinchi, Colombie-Britannique.

INTRODUCTION AND REGIONAL GEOLOGY

Howieite, a mineral with a crystal structure similar to both chain silicates and sheet silicates, was first described in blueschists from northern California (Agrell *et al.* 1965). It has since been described from other metamorphic belts, where it is typically associated with blueschists (Wood 1979). In this paper, we report the first occurrence of howieite from Canada, in blueschists from Pinchi Lake, British Columbia. A longer paper on the petrology and P–T history of these blueschists is in preparation.

The area in which the blueschists occur lies along the Pinchi Fault Zone, which separates rocks of contrasting geological history in the hinterland portion of the North American Cordillera; the area contains elongate fault-bounded blocks, including blueschists and ultramafic rocks near Fort St. James in central British Columbia (near 54°30′N and 124°W) (Paterson 1973, Paterson & Harakal 1974). The fault zone also contains boulders of glaucophane–lawsonite blueschist, in which the howieite occurs.

PETROGRAPHY

Howieite was identified in three samples of blueschist. The rocks are glaucophane–lawsonite granofelses, with no pronounced foliation. Small inclusions of garnet and clinopyroxene in lawsonite suggest replacement of an earlier garnet–clinopyroxene assemblage; the minerals in a given thin section may not have equilibrated at the same P and T. The mineral assemblages are: TLR–2: howieite – stilpnomelane – crossite – glaucophane – winchite – clinopyroxene ($Jd_{12-29}Ae_{10-28}Di$ + Hd_{60-72} – lawsonite – muscovite – garnet (Alm_{51-59} $Sps_{2-4}Prp_{11-19}Grs_{24-31}$) – titanite – quartz – Ba–Al-silicate (not yet identified); TLR–4: howieite – stilpnomelane – crossite – glaucophane (magnesioriebeckite cores) – clinopyroxene ($Jd_{27-30}Ae_{8-13}Di$ + Hd_{60-63}) – lawsonite – garnet ($Alm_{50-71}Sps_{1-2}Prp_{4-9}Grs_{24-33}$) – quartz – titanite – chlorite – apatite); TLR–6: howieite – stilpnomelane – crossite – clinopyroxene ($Jd_{24-33}Ae_{0-17}Di + Hd_{46-54}$) – lawsonite – garnet ($Alm\ _{59-70}Sps_{2-3}PrP_{4-19}Grs_{21-22}$ – quartz – titanite – rutile); TLR–1: (a similar rock, but without howieite) stilpnomelane – crossite – glaucophane – cummingtonite – clinopyroxene ($Jd_{16-32}Ae_{0-14}Di$ + Hd_{57-80}) – lawsonite – garnet ($Alm_{55-70}Sps_{1-16}Prp_{2-4}Grs_{23-27}$) – quartz – titanite – rutile). Abbreviations are after Kretz (1983) and Morimoto (1989).

Howieite occurs in aggregates or segregations, which could have formed late in the metamorphic history of these rocks. This texture is similar to that reported by workers in other areas, but there is one important difference, however. The Pinchi Lake howieite occurs in glaucophane–lawsonite rocks that are probably metamorphosed mafic igneous rocks. The howieite from many other blueschist localities occurs in metamorphosed ironstones. The howieite from Pinchi Lake occurs in elongate to round aggregates up to 6 mm in maximum dimension and locally in quartz-rich segregations. Crystals of howieite range from prisms up to 1.75 × 0.25 mm, some of which are bent, to fibers a few μm in size. Howieite crystals show no preferred orientation and commonly occur in radiating bundles. Pleochroic colors range from γ = dark green to nearly opaque and $\beta = \alpha$ = yellowish brown to brown. Stilpnomelane typically is associated with howieite and locally occurs without howieite (TLR–1). Stilpnomelane typically is reddish brown and attains 1.5 × 0.2 mm in maximum dimensions.

Howieite and stilpnomelane in these rocks are in sharp, regular contact with and locally completely surround glaucophane, lawsonite, and clinopyroxene. There is no evidence for replacement of the earlier blueschist minerals. In two samples, prisms of howieite occur within aggregates of fine-grained stilpnomelane. Textures suggest that howieite and stilpnomelane formed in fractures and small cracks by precipitation from solutions; possible precursor minerals could not be identified. Because the lawsonite replaces earlier garnet and clinopyroxene and appears to be stable with howieite, we infer that the howieite and stilpnomelane crystallized later in the metamorphic history of these blueschists.

X-Ray Diffraction

A small powdered sample was obtained by drilling out identifiable aggregates of howieite under a binocular microscope. Sample TLR–6 was chosen for X-ray diffraction because it is the only howieite-bearing sample in which we did not find coexisting stilpnomelane. An X-ray-diffraction pattern was obtained with 5-second counts at each 0.1° step over a scanning range of 7 to 76° 2θ (Fe$K\alpha$ radiation).

A search of the Mineral Powder Diffraction File Search Manual (Bayliss *et al.* 1986) indicated a close match between our pattern and a pattern for howieite (PDF 19–571). The data are presented in Table 1.

TABLE 1. X-RAY-DIFFRACTION DATA FOR HOWIEITE (PINCHI LAKE), COMPARISON WITH HOWIEITE (LAYTONVILLE, CALIFORNIA)

TLR6		19-571[1]	
d(A)	I	d(A)	I
9.02	VS[2]	9.18	VS
7.79	VS	7.91	VS
3.52	W	3.63	W
3.21	S	3.25	S
3.02	M	3.06	M
2.76	M	2.78	M
2.72	M	2.68	M
2.63	S	2.62	S
2.25	W	2.23	W
2.16	M	2.21	M

[1] Mineral Powder Diffraction File Card # 19-571 (Bayliss et al. 1986).
[2] VS=verystrong 80-100; S=strong 51-79; M=moderate 21-50; W=weak 20; (I <20 excluded for brevity); Fe $K\alpha$ radiation.

TABLE 2. REPRESENTATIVE CHEMICAL COMPOSITION OF HOWIEITE FROM PINCHI LAKE, AS DETERMINED BY ELECTRON–MICROPROBE ANALYSES

	TLR2 r	TLR4 r	TLR4 s	TLR6 r
SiO_2	45.19	44.83	44.97	44.26
TiO_2	0.74	0.52	0.83	0.86
Al_2O_3	4.53	3.37	4.20	4.23
FeO	28.98	31.87	30.34	32.33
MnO	1.72	1.89	1.55	0.63
MgO	8.47	8.54	8.71	8.27
CaO	<0.01	0.01	0.02	0.03
Na_2O	1.96	2.02	2.06	1.97
F	0.06	0.07	0.05	<0.05
Total	91.65	93.12	92.73	92.58
Tot-F	91.62	93.09	92.71	92.58
Number of ions on the basis of 73 anions in unit cell, 25 cations				
Si	12.121	11.910	11.931	11.816
Ti	0.149	0.103	0.165	0.178
Al	1.432	1.055	1.314	1.331
Fe	6.500	7.081	6.732	7.218
Mn	0.391	0.425	0.349	0.142
Mg	3.386	3.382	3.444	3.291
Ca		0.003	0.006	0.008
Na	1.020	1.041	1.060	1.020

r = rim, s = small crystals, Tot–F = Total minus oxygen equivalent of fluorine. BaO <0.10 wt.%, K_2O <0.01 wt.%. Oxides expressed in wt.%.

The chemical composition given for the howieite (PDF 19–571) is similar but not identical to that determined by electron–microprobe analysis for the howieite in the Pinchi Lake rocks [compare Agrell *et al.* (1965) with Table 2]. This difference in chemical composition may explain the observed small differences between these two X-ray patterns.

Mineralogy and Chemistry of Howieite from Pinchi Lake

The chemical formula for howieite is $NaM_{12}Si_{12}(O,OH)_{44}$, where M is principally manganese and iron (Wood 1979). The substitutions in the octahedral sites are principally those of ferric for ferrous iron, and manganese for iron. The hydroxyl content of the formula unit depends upon the oxidation state of iron and the amount of aluminum present. Because of these substitutions, one cannot estimate the ferric iron content from results of an electron-microprobe analysis. Wood (1979) suggested that compositions should be recalculated on the basis of 24 cations, neglecting sodium, or 25, including sodium. In this paper we have recalculated the analyses to 25 cations (Table 2). A complete set of electron-microprobe data for howieite, stilpnomelane and the Na–Ca amphiboles (expanded versions of Tables 2 and 3) have been deposited with the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

The howieite from three samples has been analyzed by electron microprobe. Analytical conditions and methods of data reduction are similar to those described in Nicholls & Stout (1988). We took particular care in the determination of Na_2O, K_2O and BaO, which are present in amounts less than 2 wt.%

in howieite and stilpnomelane. A list of the standards used is available from the authors. The Pinchi Lake howieite contains essentially no detectable K, Ba and Ca (Table 2). According to Wood (1979), the alkali site is too crowded for larger ions such as K. Agrell *et al.* (1965) and Schreyer & Abraham (1977) reported a small amount of Ca in substitution for Na. Compared to compositions of howieite reported by Wood (1979), the howieite from the Pinchi Lake area contains relatively low Mn and relatively high Mg and Al (Table 2). The number of Fe atoms per formula unit ranges from 6.5 to 7.2, and the number of Mn atoms per formula unit ranges from 0.08 to 0.42 (Table 2; *cf* Wood 1979, Fig. 3, p. 365). Wood (1979) demonstrated a correlation among crystal morphology, absorption colors and composition of howieite. Well-crystallized howieite is nearly always rich in ferrous iron and manganese-poor. Varieties rich in ferrous iron typically are green in thin section. Howieite from TLR-6 is well crystallized and has green absorption colors, which suggests a variety rich in ferrous iron. The yellowish brown color along α and β in some of the howieite suggests that some of the iron is oxidized (Wood 1979). Many compositions reported by Wood (1979), including those of Schreyer & Abraham (1977), contain little or no Al, whereas the howieite from Pinchi Lake contains 1.04–1.43 atoms per formula unit.

TABLE 3. REPRESENTATIVE CHEMICAL COMPOSITION OF WINCHITE, ACTINOLITE AND STILPNOMELANE, AS DETERMINED BY ELECTRON–MICROPROBE ANALYSES

	TLR2 win	TLR4 win	TLR2 act	TLR2 r stilp	TLR4 r stilp
SiO_2	55.11	54.57	54.38	45.50	44.80
TiO_2	0.04	0.06	0.05	<0.02	<0.02
Al_2O_3	3.95	2.87	1.83	5.84	5.78
FeO	18.24	17.96	16.41	24.14	27.36
MnO	0.39	0.35	0.19	4.60	4.73
MgO	11.80	11.13	13.52	6.73	5.37
CaO	3.82	6.07	8.64	0.12	0.27
BaO				0.80	0.76
Na_2O	4.32	3.53	2.10	<0.04	<0.04
K_2O				0.45	0.61
H_2O	2.07	3.22	2.05	11.54	9.91
Total	99.74	99.76	99.17	99.72	99.59
	Structural formula on the basis of				
	15 cat[1]	15 cat[1]	15 cat[1]	8 Si	8 Si
Si	7.840	7.928	7.848	8.000	8.000
^{IV}Al	0.160	0.072	0.152	1.211	1.217
^{VI}Al	0.503	0.419	0.159		
Fe^{3+}	0.840	0.634	0.570		
Ti	0.004	0.007	0.005		
Mg	2.502	2.410	2.908	1.763	1.429
Fe^{2+}	1.151	1.530	1.358	3.550	4.086
Fe^{2+}	0.179	0.018	0.053		
Mn	0.047	0.043	0.023	0.685	4.086
Ca	0.582	0.945	1.336	0.023	0.052
Ba				0.055	0.053
Na	1.192	0.994	0.588		
K				0.101	0.139

r=rim; win=winchite; act=actinolite; stilp=stilpnomelane; F <0.05 wt %.
[1] cat=cations. Oxides expressed in wt.%.

STILPNOMELANE

Stilpnomelane is associated with howieite in several samples (Table 3). Several workers have commented on the fact that howieite closely resembles stilpnomelane in thin section and that howieite may have been overlooked in earlier studies.

Stilpnomelane compositions have been recalculated on the basis of 8 Si atoms per formula unit (Table 3). This stilpnomelane is notable for the relatively high amounts of Ca, Na and Ba relative to K. We have not found comparable data in the literature.

Na–Ca AMPHIBOLES

Fibrous pale blue to pale green to colorless sodic-calcic amphibole (winchite) and calcic amphibole (actinolite) occur both as individual aggregates and within the larger aggregates of howieite and stilpnomelane. Grains range in size from a few μm to 100 μm in length and 10-15 μm in width. In TLR-4, the amphiboles appear to be intergrown with howieite and stilpnomelane. The amphiboles have been analyzed, and the compositions recalculated (Table 3). The amphiboles were normalized to 15 cations, excluding potassium, and classified according to the scheme presented by Leake (1978). H_2O contents were initially estimated by difference from 100 wt.% and reiteratively calculated according to the data-reduction methods outlined by Nicholls & Stout (1988). Compositions of the winchite and actinolite can be compared to those from blueschists reported by Evans (1986) from Siphnos, Greece. He inferred reactions between deerite and Na-pyroxene to produce ferri-winchite and actinolite. We found no evidence for precursor mineral(s).

INFERRED P–T CONDITIONS

Miyano & Klein (1989) have reviewed the phase relations of Al- and Fe-bearing silicates in the system K_2O–FeO–MgO–Al_2O_3–SiO_2–H_2O–CO_2–O_2 in the presence of magnetite and quartz. They used petrological data from Precambrian iron formations and blueschist-facies meta-ironstone from California. Integrating these data with geothermobarometry and limited experimental phase-equilibria, they estimated thermodynamic properties of several phases in this system. They calculated the phase equilibria involving the upper limits of stability of stilpnomelane, and suggested that stilpnomelane could persist to temperatures of about 430–470°C and pressures of 5–6 kilobars.

An experimental study of the stability relations of howieite was reported by Lattard & Schreyer (1981). They were unable to synthesize howieite, and used natural howieite and its breakdown products to evaluate its stability field. The stability of howieite is strongly dependent upon oxygen fugacity; with the iron–magnetite buffer, the limit of its stability is near 460°C, and with the nickel - nickel oxide buffer, it is higher than 480°C. The reactions could not be reversed, because growth of howieite could not be detected in the run products. In addition, howieite spontaneously decomposes at pressures above 10 kbar. The low-temperature limit of stability of howieite could not be determined, but the mineral is likely replaced by assemblages such as riebeckite - minnesotaite - magnetite - quartz. At higher temperatures, assemblages such as riebeckite - grunerite - magnetite - quartz or riebeckite - ferrosilite - magnetite - quartz are possibilities, but they are apparently not recorded in the literature. Although Lattard & Schreyer (1981) favored a low-temperature, high-pressure stability field for howieite, the parageneses observed suggest the possibility that howieite may be stable at lower pressures.

ACKNOWLEDGEMENTS

Ghent and Erdmer acknowledge financial assistance from NSERC (Operating Grant A4379 and A0750). The authors acknowledge the reviews of B.W. Evans, R.F. Martin, and E. Essene. Any remaining errors or murkiness are our doing.

REFERENCES

AGRELL, S. O., BOWN, M. G. & MCKIE, D. (1965): Deerite, howieite, and zussmanite, three new minerals from the Franciscan of the Laytonville District, Mendocino Co., California. *Am. Mineral.* **50**, 278 (abstr.).

BAYLISS, P., ERD, R. C., MROSE, M. E., SABINA, A. & SMITH, D. K. (1986): Mineral Powder Diffraction File, volume 2. Search Manual: JCPDS International Centre for Diffraction Data, Swarthmore, Pa.

EVANS, B.W. (1986): Reactions among sodic, calcic, and ferromagnesian amphiboles, sodic pyroxene, and deerite in high-pressure metamorphosed ironstone, Siphnos, Greece. *Am. Mineral.* **71**, 1118-1125.

KRETZ, R. (1983) Symbols for rock-forming minerals. *Am. Mineral.* **68**, 277-279.

LATTARD, D. & SCHREYER, W. (1981): Experimental results bearing on the stability of the blueschist-facies minerals deerite, howieite, and zussmanite, and their petrological significance. *Bull. Minéral.* **104**, 431-440.

LEAKE, B.E. (1978): Nomenclatue of amphiboles. *Can. Mineral.* **16**, 501-520.

MIYANO, T. & KLEIN, C. (1989): Phase equilibria in the system K_2O–FeO–MgO–Al_2O_3–SiO_2–H_2O–CO_2 and the stability of stilpnomelane in metamorphosed Precambrian iron-formations. *Contrib. Mineral. Petrol.* **102**, 478-491.

MORIMOTO, N., chairman (1989): Nomenclature of pyroxenes. *Can. Mineral.* **27**, 143-156.

NICHOLLS, J. & STOUT, M.Z. (1988): Picritic melts in Kilauea - evidence from the 1967–1968 Halemaumau and Hiiaka eruptions. *J. Petrol.* **29**, 1031-1057.

PATERSON, I.A. (1973): *The Geology of the Pinchi Lake Area, Central British Columbia.* Ph.D. thesis, Univ. British Columbia, Vancouver, British Columbia.

______ & HARAKAL, J.E. (1974): Potassium-argon dating of blueshists from Pinchi Lake, central British Columbia. *Can. J. Earth Sci.* **11**, 1007-1011.

SCHREYER, W. & ABRAHAM, K. (1977): Howieite and other high-pressure indicators from the contact aureole of the Brezovica, Yugoslavia, peridotite. *Neues Jahrb. Mineral. Abh.* **130**, 114-133.

WOOD, R. M. (1979): The iron-rich blueschist facies minerals. 2. Howieite. *Mineral. Mag.* **43**, 363-370.

Received December 3, 1989, revised manuscript accepted March 13, 1990.