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The iron-rich blueschist facies minerals: 2. Howieite

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SUMMARY. The mineral howieite has a stability range that extends down to pressures at, or even below, those normally considered to represent blueschist facies metamorphism. Its structure, lying somewhere between a chain and a sheet silicate, can accommodate almost complete iron for manganese substitution as well as the more extraordinary ferrous iron for ferric iron substitution, that is tolerated by changes in the hydroxyl and water content of the unit cell. The ideal formula is $NaM_{12}Si_{12}(O,OH)_{44}$, where M is principally manganese and iron but may include limited amounts of aluminium and magnesium. Four new localities for howieite have been discovered by the author and the howieites from the eight localities that have been analysed here help complete the compositional spectrum. The most curious crystallographic feature of howieite is that although the structure seems capable of considerable chemical variation, it is only those howieites of approximate $NaMn_3Fe_8(AlMg)_1Si_{12}(O,OH)_{44}$ composition that are well crystallized, often growing to over 10 mm in length.

HOWIEITE is the second of the new minerals discovered by Agrell at the Laytonville Quarry, Mendocino County, California, and named as such in Agrell *et al.* (1965). Since that time it has been discovered at eight other localities, four of them found within the present study (see Table I).

TABLE I. *Howieite localities*

1. Laytonville Quarry, Mendocino Co., California (Agrell *et al.*, 1965)
2. Ward Creek, Cazadero, Sonoma Co., California (Coleman and Lee, 1966; unpubl.)
3. Panoche Pass, San Benito Co., California (Muir Wood, 1977)
4. Pacheco Pass, Santa Clara and Merced Cos., California (Muir Wood, 1977)
5. Covelo, Mendocino Co., California (Muir Wood, 1977)
6. Russian River, boundary of Sonoma with Mendocino Cos., California (Chesterman, unpubl.)
7. Powers Quarry, Coos Co., Oregon (Muir Wood, 1977)
8. Taneyama Mine, Kumamoto Prefecture, Japan (Aoki and Isono, 1968)
9. Brezovica, Jugoslavia (Schreyer and Abraham, 1977)

Although the chemical formula $NaM_{12}Si_{12}(O,OH)_{44}$ (where M is principally manganese and iron) and the structure have been determined, very little has been published concerning its range of chemistry and parageneses. Nearly 100 new howieite analyses were made by the author using an electron microprobe, during the course of a much more wide-ranging study of all the blueschist facies meta-ironstone localities. From these analyses it has been possible to show that the howieite structure can tolerate an extensive range of chemical substitution, the sort of range generally restricted to amphiboles. Soon after the original discovery of howieite it was recognized by Agrell that howieite, generally rich in ferrous iron, could exist as a fully oxidized ferric-iron-containing mineral termed 'oxy-howieite'.

Structure. The howieite structure is another adaptation to the problem of compatibility between octahedral and tetrahedral coordinated layers of ions, which becomes particularly critical for the high-pressure, low-temperature conditions of the blueschist facies. The elements of the structure can be considered as ribbons running parallel with the crystallographic *c*-axis that bear similarities to the chains of the amphibole and pyroxene structures, although the octahedral layers more closely resemble those of a sheet silicate. The silicate unit identified by Wenk (1973) is the same as that in deerite, Si_6O_{17}. The interdigitating octahedral and tetrahedral units lie on a series of parallel planes (unlike deerite). The detailed structure is presented in Wenk (1974) (see fig. 1). The octahedral ribbons are four cations wide and are cut off by the offset silicate ribbon at the same 'level'. As no single unit has continuity perpendicular to [001] there is an extra degree of flexibility and the silicate chain can demonstrate *some* plasticity in coping with varying size of octahedral ion compatibilities. Two-thirds of the interlayer alkali positions that would be present in the mica structure are missing leaving just one Na atom per twelve silicons, nestling between the eyes of the superimposed silicate rings. The closer bond-

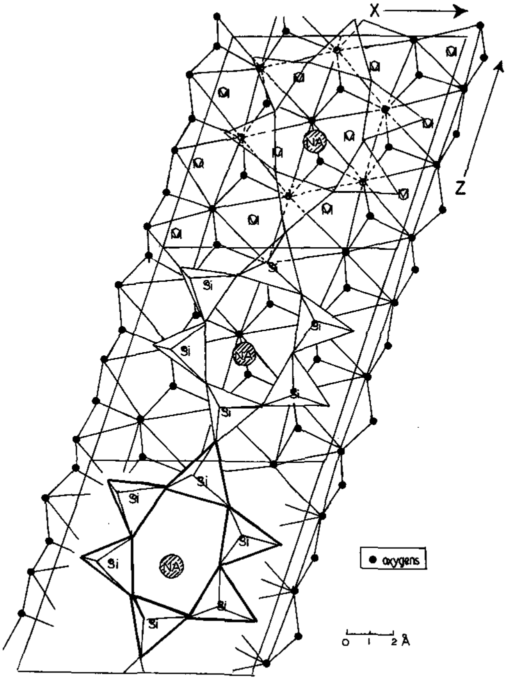


FIG. 1. Howieite structure: the silicate and octahedral ion ribbons.

ing afforded by the interdigitation allows the high-density (though not as high as deerite) and the high-water content that are features of these blueschist facies iron-rich silicates. As a result, the alkali site is too crowded for the larger potassium ion.

Howieite is triclinic; space group $P\bar{1}$ or $P1$. The high correlation factors combined with the asymmetry make detailed structural resolution very difficult. Wenk recognized variations in occupancy between the octahedral sites, but he could not detail these and the limits of solid solution remain the best measure of the limits of ionic substitution. Through lack of information on the sites, these are best considered in terms of the over-all octahedral ribbon size rather than as individual restrictions on specific cation site occupancy. The sodium and silicon contents are approximate constants, so it is only the octahedral ribbon with the allied charge balancing through trivalent and divalent cation substitution and the consequent hydroxyl content that are the variables.

Chemistry. The octahedral substitutions are principally those of ferric iron for ferrous and manganese for iron. The (OH) content of the formula unit cell is $15-(Fe^{3+}+Al)$, so that for the more reduced howieites some of the silicate oxygens must be hydroxyls. Thus $NaMn_3Fe_9^{2+}Si_{12}O_{29}(OH)_{15}$ (that has five silicate oxygens as hydroxyls) has an oxidized equivalent $NaMn_3Fe_9^{3+}Si_{12}O_{38}(OH)_6$. Due to this interdependence of hydroxyl content and oxidation state the ferric iron content cannot be retrieved from the analyses determined by the electron probe; the total anion charge is not independent of cations. (A similar but less formal variation is likely to operate within the deerite structure.) Thus, apart from three wet chemical analyses; two by Scoon (from Laytonville Quarry material) and a partial one by Aoki (on Japanese howieite) (pers. comm.), the bulk of the data has been recalculated on the basis of all iron ferrous, that produces a formula unit cell anion charge of 73. This neglects the presence of aluminium on octahedral or tetrahedral sites, which would affect the anion charge, in most cases insignificantly, Al being present only in trace quantities. A better recalculation could thus be for twenty-four cations neglecting the sodium, or twenty-five including it (this omission is justified through the poor accuracy for sodium on the electron probe).

Howieites in most assemblages are poorly crystallized, either in veins as interwoven fibres or as contorted knots of crystals radiating irregularly from a single nucleus. Where howieite crystals are well formed, they are often the largest crystals in the rock, up to 10 mm in length and easily visible in hand specimen as greasy black-bladed aggregates and rosettes on fracture surfaces and shear planes. The massive howieites possess a good (010) cleavage, a moderate (100), and a poor (210). In combination and in cross-section these resemble a cross-cut through a fibrous plant stem. The first two of these cleavages fit in well with anticipated planes of weakness inherent in the model structure, but (210) is unexpected, as is the absence of (110); (210) could even be a combination of (110) with (100) on a regular basis. These fracture directions are exhibited in fig. 2.

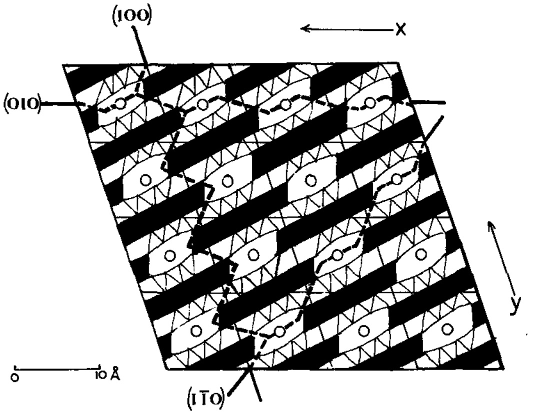


FIG. 2. Howieite structure: perpendicular to 'z', with superimposed cleavage traces.

The well-crystallized howieites are restricted to a narrow range of compositions; they are nearly always reduced ferrous-iron-rich, manganese-poor varieties. They are plentiful in many of the Laytonville Quarry assemblages, also in one rock from the Powers Quarry (Locality 6). (The compositions of the latter are slightly more iron-rich than those from the Laytonville Quarry, probably because they represent a lower pressure assemblage; the compressibility of octahedral ions within a structure is considered more significant than that of tetrahedral ions (Hazen, pers. comm.). The manganese ion is bigger than that of ferrous iron and hence will be favoured for higher pressures.) Well-formed crystals of oxy-howieite, rich in ferric iron, of identical crystal form have been found from stream material adjacent to the Laytonville Quarry and from one sample, PC53, from the Panoche Pass. The compositions of these lie in exactly the same range as the massive ferro-howieites and it is considered here that they represent secondary oxidations of earlier ferrous forms, rather than a primary crystallization. (Other minerals from these rocks also demonstrate very late stage oxidation.) Other oxy-howieites, that are demonstrably primary, occur in rocks that have not suffered secondary oxidation. They are, however, richer in manganese and invariably poorly crystallized. There is thus evidence that although the howieite structure can demonstrate flexibility in substitution behaviour, there is only a very limited range of compositions where the strain within the crystal is low enough to allow massive forms to grow. This is not just a function of the degree of crystallinity within an assemblage as at both Laytonville Quarry and Cazadero the size of howieites is variable while grain size of the rest of the assemblage is a relative constant. At Powers the grain size of the background assemblage is microcrystalline.

This relationship between composition and crystal form must depend on stacking strains and is analogous to similar behaviour in serpentines and zussmanites. The aggregates of radiating needles and foliated fibres are always elongated parallel to [001], along the ribbons of the structure. Increased substitution of Mn increases the size of the octahedral ribbon and thus the internal strain. Lower concentrations of Mn, as in material from Covelo, seem to have a similar affect. The ideal formula thus seems to be close to $NaMn_3Fe_9Si_{12}O_{29}(OH)_{15}$. With increased manganese concentrations compensatory ferric iron might be expected to substitute for ferrous. At the maximum manganese enrichment the solid solution series can be seen to swing towards more magnesium- and aluminium-rich compositions (as in fig. 5; howieite com-

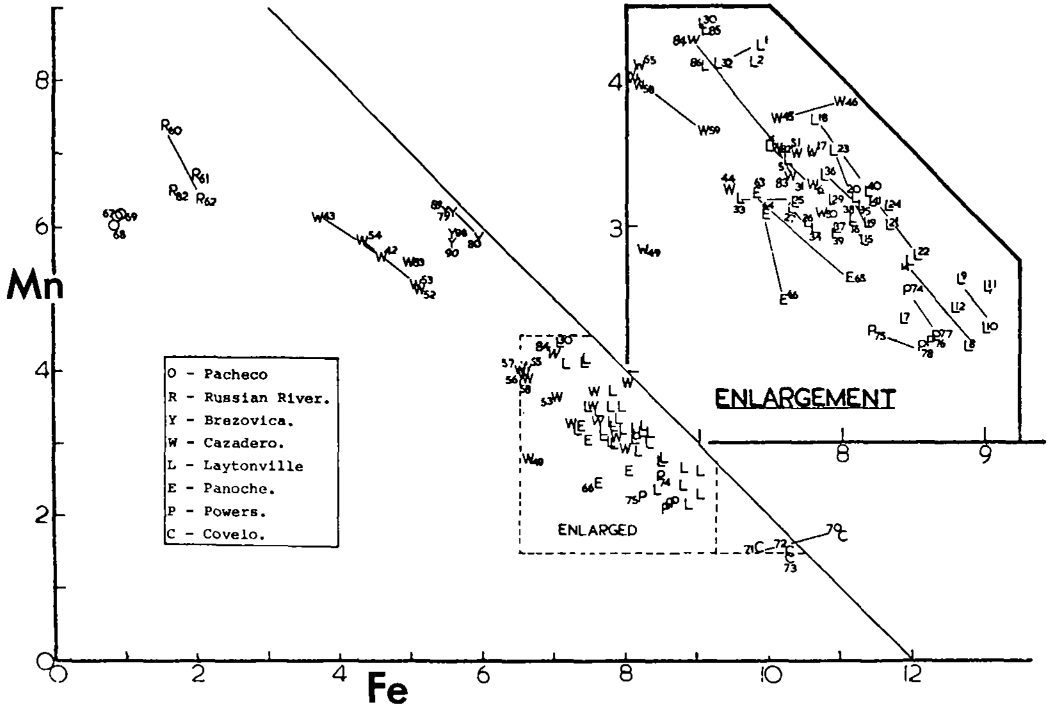


FIG. 3. Howieite chemistry: Mn v. Fe (cell contents).

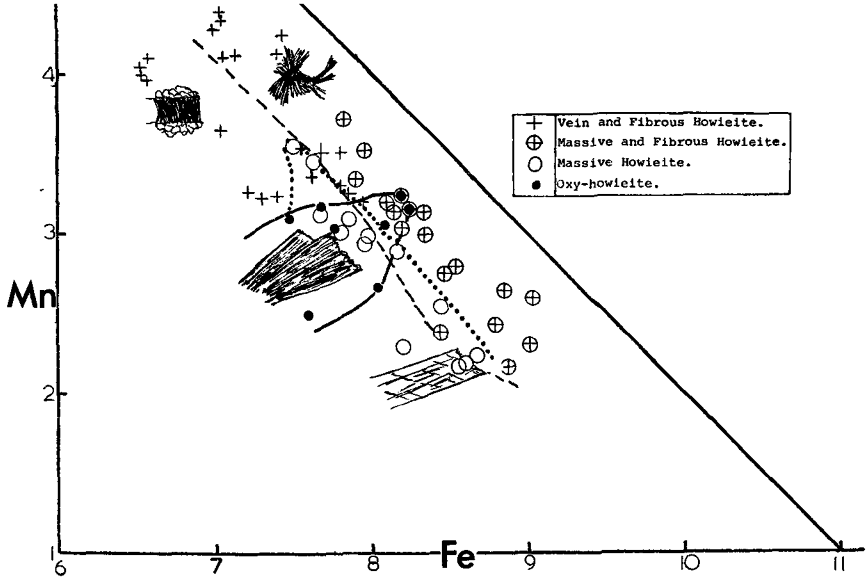


FIG. 4. The variation of morphology with chemistry for howieite crystals: Fe v. Mn (cell contents).

positions plotted within the Fe–Mn–Mg–Al tetrahedral system), apparently, again, on the grounds of structural balance.

The octahedral cation bond lengths (*M*–O) are smaller than those found in most normal silicates (see Shannon and Prewitt, 1969), another indication of the high-pressure nature of the mineral. Many of the individual radiating fibres of howieite in rocks from Cazadero and Laytonville Quarry are themselves bent, suggesting a mismatching of layers. As there is no bonding polarity perpendicular to the plane of the ribbons, this is likely to be curvature in this plane, but perpendicular to the ribbon elongation direction *c*. Intermediate oxidation state howieites can easily be mistaken for intermediate oxidation state stilpnomelanes. The straight-edged radiating clusters of stilpnomelane, however, have *c* perpendicular to the axis of elongation, whilst howieite has these characteristic bent acicular crystals.

The variation of composition for the recalculated formula unit cell is plotted in fig. 3 for Mn occupancy v. Fe occupancy. In fig. 4 the variation with crystal morphology is plotted for a part of the same system.

The variation in both absorption colour and

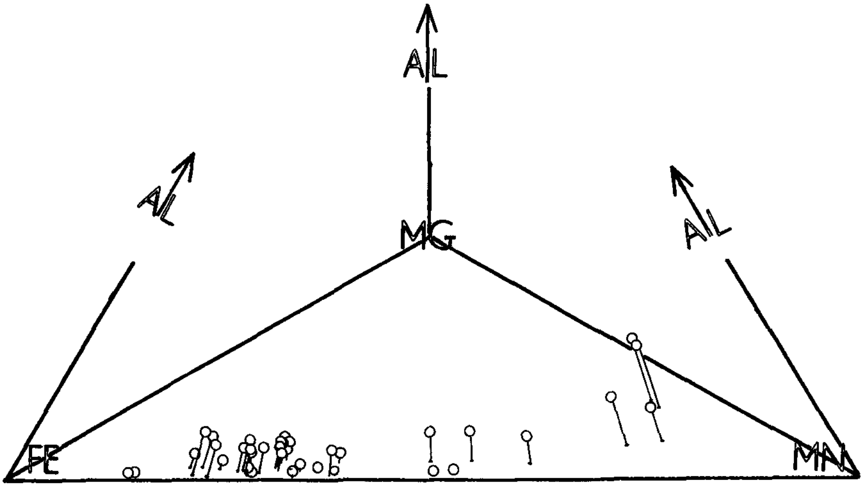


FIG. 5. Howieite chemistry: the Fe–Mn–Mg–Al quaternary system.

pleochroism of these howieites is dependent on both the manganese and the ferric iron content. The principal pigments and their absorption colours are: green—ferrous iron; red—ferric iron; and yellow—manganese. From such simple parameters the variation of colour with composition can be plotted, and a rough estimate of oxidation state obtained. Some details of such a colour chart are shown in fig. 6. The other optical properties for the howieites are difficult to obtain for all but the well-crystallized forms that have such a negligible variation in composition (see Agrell *et al.* 1965).

Paragenesis. Within the complex textures of these meta-ironstones howieite invariably appears very late in the assemblage variations, masking former mineral mosaics and often surrounding earlier more anhydrous minerals that are undergoing partial resorption. In some Laytonville Quarry assemblages howieite can be seen to be partially replacing both deerite and stilpnomelane, as well as the even earlier garnet, aegirine, manganese/iron carbonate material. At Cazadero howieite more often accompanies deerite as part of the mineralogy formed on the injection of fluid along fractures, with howieites forming the cores to the veins and deerites forming a sheaf of crystals that intrude into the surrounding garnet, aegirine, quartz, magnetite matrix.

The massive oxy-howieites from the stream bed adjacent to Laytonville Quarry were almost certainly once part of the rim of the exotic block and were eroded before quarrying began. They have suffered more alteration under metamorphic conditions than the material from nearer the centre of the exotic block, suggesting that the exotic block was still undergoing metamorphism after having left its parent conformable formation. The oxy-howieites are part of a very well-developed end-stage mineralogy that includes crocidolite and a new manganese-rich variety of zussmanite (see forthcoming zussmanite paper) and oxy-stilpnomelane. All of these appear to have suffered some degree of secondary oxidation.

Vein howieites from Laytonville Quarry are variably fibrous and intergrown with large vein quartz crystals. Small knots of orange howieite sometimes form late-stage aggregates growing from the edges of earlier massive howieites, or forming within deerite and manganese carbonate-rich layers. The partial oxidation of many of these tiny crystals seems likely to be secondary.

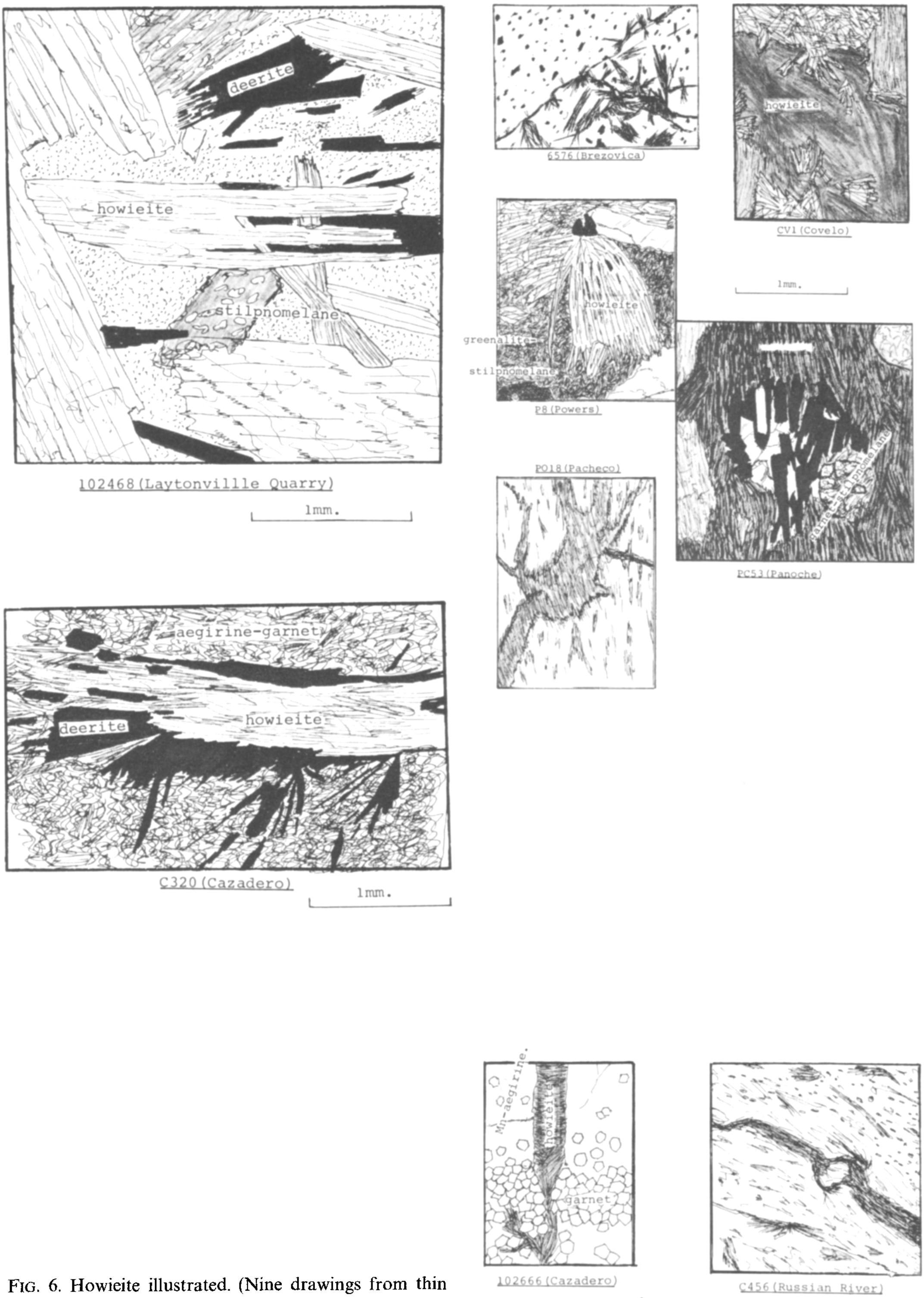
As mentioned above, howieite at Cazadero forms part of the vein assemblage, cross cutting, but not permeating the earlier mineralogy. When ferrous-iron-rich the crystals may be large; in the more manganous rocks they are small and fibrous. All the other howieite localities, with the exception of Powers and Panoche, contain only fine-grained veins or aggregates of howieite that are always somewhat oxidized and that are clearly formed as a result of the infusion of water into iron-manganese-rich rocks. Some of these forms of howieite from the various localities are illustrated in fig. 7.

The wide range of howieite compositions makes any attempt at delimiting the stability range somewhat indefinite. Although the principal localities of the mineral have all been within the blueschist facies, there is some reason for believing that this is because of the high activity and pressure of water within these rocks rather more than a strict high pressure of stabilization.

The manganese-rich assemblages differ from the iron-rich in the general lack of hydrated manganese silicates and the general anhydrous nature of the original manganese precipitates. Thus anhydrous decarbonation series can be mapped for high temperatures (Burt, 1973), but the low-temperature behaviour (see Roy, 1968 and Klein, 1974), because of the low initial water content, is irregular and the competing mineral stabilities cannot be arranged into a progressive sequence. The premiss with all attempts to quantify low-grade metamorphism is that the rock was initially saturated with water and will subsequently suffer dehydration. (Within many of the Franciscan blueschists it is the opposite process, hydration, that is a function of metamorphism.)

The lower-grade howieite localities all show the common development of veining and fluid entry into a rock that has previously been composed of amorphous manganese minerals, with no evidence of recrystallization prior to this hydration. This is even true of the core of the manganese nodule that is present within PC53 from Panoche. That howieite forms rather than other hydrated manganese silicates (such as manganpyrosmalite, bementite, or even parsettensite, which does occur with howieite in the rock from Russian River) does indicate some high-pressure restriction of stability. Howieite, so far, has not been discovered at any of the low-pressure manganese skarn deposits, with the possible exception of Brezovica, Jugoslavia. For although Schreyer and Abraham (1977) use the presence of howieite as an indicator of extremely high pressures, there is every reason for considering that the composition, texture, and mineralogy of the rocks is compatible with a low grade of metamorphism. The model they present for the assemblages they find, of subduction and very deep burial, is an exciting one, but one powered by speculation.

The rock P8 from Powers Quarry is clearly outside the stability range of deerite (as it contains ilvaite, greenalite, and quartz) and yet contains



102468 (Laytonvillle Quarry)

C320 (Cazadero)

6576 (Brezovica)

CV1 (Covelo)

P8 (Powers)

PO18 (Pacheco)

PC53 (Panoche)

102666 (Cazadero)

C456 (Russian River)

FIG. 6. Howieite illustrated. (Nine drawings from thin sections.)

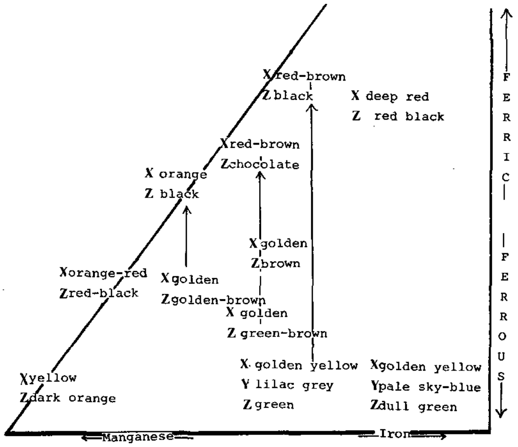


FIG. 7. Variation of absorption colours with composition.

abundant howieite. Associated assemblages suggest that this is 'blueschist'. Thus howieite extends its stability to lower pressure than deerite. At Laytonville Quarry, the early period of primary hydration has formed deerite without howieite, so evidently at some much higher pressure deerite has an extended stability. At Panoche and Cazadero, the formation of these two appears to coincide.

All the poorly crystallized lower-grade howieite assemblages are manganese-rich. It is likely that, parallel with other mineral species, manganese enrichment extends the stability to lower grades. The higher temperature stability is likely to be similar to deerite at around 400 °C.

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THE IRON-RICH BLUESCHIST FACIES MINERALS: 2. HOWIEITE

APPENDICES

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APPENDIX 1.

The analyses listed in Appendix 3 were obtained from two electron probes within the Department of Mineralogy and Petrology, Cambridge. These were a Cambridge Instrument Geoscan system, using analytical methods described by Sweatman and Long (1969), and the Energy Dispersive Microprobe based on the analytical procedure and processing discussed in Statham (1975).

Statham (P. J.), 1975. *Ph.D. Thesis*, Cambridge.
Sweatman (T. R.) and Long (J. V. P.), 1969. *J. Petrol.* 10, 332.

APPENDIX 2.

For howieite, the interdependence of the ferrous/ferric ratio and the hydroxyl content means that the normal procedure used for solving the oxidation state of iron within a known mineral structure from an electron probe analysis is inapplicable. Instead the analyses have been recalculated on the model of all iron ferrous, when there will be 36.5 oxygens in the half unit cell formula, with which the anions, neglecting hydrogen, must balance. This gives similar results to those obtained by assuming full cation occupancy (neglecting sodium) of 24.

APPENDIX 3.

Howieite analyses, weight per cent oxides. All iron considered as FeO. Recalculated cell contents. All iron Fe^{2+}. 36.5 oxygens

No.	Rock	SiO_2	TiO_2	Al_2O_3	V_2O_5	FeO	MnO	MgO	CaO	Na_2O	K_2O	Total	Si	Ti	Al	V	Fe	Mn	Mg	Ca	Na	K	No.
1	A2131	40.25	n.f.	0.20	n.f.	30.23	16.00	1.05	0.07	1.90	0.02	89.72	11.86	-	0.07	-	7.45	4.22	0.46	0.02	1.09	0.01	1
7	PA11	41.62	n.f.	1.69	n.f.	35.47	9.80	1.50	0.04	1.86	0.02	92.00	11.84	-	0.57	-	8.44	2.36	0.64	0.01	1.03	0.01	7
15	PA21/1	41.66	n.f.	1.17	n.f.	34.15	12.04	0.92	0.03	1.81	0.01	91.79	11.94	-	0.40	-	8.19	2.92	0.39	0.01	1.01	-	15
25	CG50	41.79	n.f.	1.46	n.f.	32.27	13.23	1.42	0.07	1.96	0.01	92.21	11.88	-	0.49	-	7.67	3.18	0.60	0.02	1.08	-	25
32	A2131	42.21	-	-	-	32.81	16.64	0.46	-	1.27	-	93.39	12.29	-	-	-	7.21	4.14	0.20	-	0.72	-	32
36	PA20	41.98	-	0.42	-	33.66	13.74	0.63	-	1.79	-	92.22	12.09	-	0.14	-	7.96	3.38	0.27	-	1.00	-	36
37	A2118	41.73	0.17	1.84	-	33.31*	12.29	1.06	0.06	1.85	-	92.31	11.96	0.04	0.62	-	7.98^{∇}	2.98	0.45	0.02	1.03	-	37
38	C653	41.45	0.14	1.41	-	33.70†	12.65	0.90	-	1.86	-	92.11	11.89	0.03	0.48	-	8.08^{o}	3.07	0.39	-	1.04	0.02	38
49	C313	45.74	0.11	0.88	-	29.78	12.45	4.07	0.16	1.94	-	95.13	12.20	0.02	0.28	-	6.66	2.83	1.62	0.05	1.01	-	49
50	C320	43.40	0.25	0.90	-	33.51	13.06	0.31	-	1.95	-	93.38	12.14	0.06	0.30	-	7.91	3.12	0.13	-	1.06	-	50
54	C307	43.73	-	1.89	-	18.61	25.06	2.01	-	2.16	-	93.46	12.03	-	0.62	-	4.28	5.84	0.83	-	1.16	-	54
55	WC7	41.82	-	0.87	-	27.50	16.89	2.00	0.14	1.93	-	91.15	11.99	-	0.30	-	6.59	4.11	0.85	0.05	1.07	-	55
60	C456	46.05	0.25	2.02	-	6.96	33.47	4.76	0.11	1.71	-	95.33	12.03	0.05	0.65	-	1.53	7.51	1.88	0.03	0.87	-	60
61	"	45.98	0.51	2.26	-	8.95	30.47	4.57	0.56	1.89	-	95.19	12.02	0.10	0.70	-	1.99	6.83	1.78	0.16	0.96	-	61
63	PC53	41.56	-	0.31	-	30.96	13.33	2.78	0.24	2.09	-	91.27	11.93	-	0.11	-	7.44	3.24	1.19	0.07	1.16	-	63
64	"	42.48	-	0.87	-	31.82	13.00	2.43	0.19	1.74	-	92.53	11.97	-	0.29	-	7.50	3.10	1.02	0.06	0.95	-	64
67	PO18	45.48	0.73	4.24	0.26	3.70	27.87	7.41	-	1.28	-	90.97	11.94	0.15	1.31	0.06	0.86	6.20	2.90	-	0.65	-	67
71	CV1	41.39	-	-	0.23	40.48	6.51	0.97	0.10	1.03	-	90.71	12.06	-	-	0.06	9.95	1.62	0.42	0.03	0.58	-	71
74	P8	41.86	-	1.86	-	35.61	10.62	0.32	0.17	1.57	-	92.01	11.96	-	0.63	-	8.50	2.58	0.14	0.05	0.87	-	74
75	"	42.85	-	2.73	-	35.16	9.63	0.35	-	1.94	-	92.66	12.01	-	0.90	-	8.23	2.29	0.15	-	1.05	-	75
79	BRZ	38.49	-	-	-	23.06	22.54	1.32	-	1.07	-	86.48	11.89	-	-	-	5.96	5.90	0.61	-	0.64	-	79
80	"	39.97	-	-	-	22.44	24.82	1.22	-	1.33	-	89.78	11.90	-	-	-	5.58	6.26	0.54	-	0.76	-	80

* $Fe_2O_3 = 7.30$, $FeO = 26.74$

† $Fe_2O_3 = 32.61$, $FeO = 4.32$

$^{\nabla}$ $Fe^{2+} = 6.41$, $Fe^{3+} = 1.57$

^{o} $Fe^{2+} = 1.04$, $Fe^{3+} = 7.04$

i) Laytonville Quarry
1, 32, (A2131) Ga,Ol-Ku,Q,Gr-R,D-Ek,S,St.
15 (PA21) Ga,Q,D,Ol-St,S,Ho.
36 (PA20) Q,Ol,A,D,Ga,-R,St,S,Ho.
38 (C653) Wet chemical - Scoon.
7 (PA11) Ga,A,Ap,Q,D-S,St,Ho.
25 (C650) Ga,A,Ap,Ol,-Ho,R,St,S.
37 (A2118) Wet chemical -Scoon.

ii) Ward Creek, Cazadero
49 (C313) Gr,Ho,Ga,S,Q.
54 (C307) Rh,MA,Ga,Q,Ho.
50 (C320) Q,A,Ga,Ho,D,R,Ol,S.
55 (WC7) A,Ga,D,R,S,Ho.

iii) Russian River
60, 61 (C456) Q,Pa,Ho.

iv) Panoche Pass
63, 64 (PC53) Mn nodule, Ga,Gr,Ho,S,D,Ap,A,Q.

v) Pacheco Pass
67 (PO18) Ho,Q,Ga.

vi) Covelo
71 (CV1) A,D,Ho,R.

vii) Powers Quarry
74,75 (P8) Ge,Q,S,Ho,Il,A,Ba,Py.

viii) Brezovica
79,80 (BRZ) (supplied by Schreyer) Ho,Q.

KEY A = aegirine, Ap = apatite, Ba = baryte, D = deerite,
Ek = ekmanite, Ga = garnet, Gr = grunerite, Ho = howieite,
Il = ilvaite, Ku = kutnahorite, MA = mangano-aegirine,
Ol = oligonite, Pa = parsettensite, Py = pyrite, Q = quartz,
R = riebeckite, Rh = rhodonite, S = stilpnomelane,
St = 'streichelite' (beta-zussmanite)