

Babingtonite and Fe-rich Ca-Al silicates from western Southland, New Zealand

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ABSTRACT. Babingtonite is a common constituent of calcareous volcanic detritus in the interstices of pillow lavas from an outcrop of the Takitimu Group, western Southland, New Zealand. Associated minerals include Fe-rich prehnite ($\text{Fe}/(\text{Fe} + \text{Al}) = 0.12 - 0.33$), Fe-rich epidote (Ps_{24-53}), grandite garnet (av. Andradite_{70} Grossular_{30}), quartz, calcite, chlorite, and pumpellyite. Babingtonite shows little departure from its ideal composition other than minor Mg, Mn, and Al and a trace of Na.

Textural evidence and microprobe data suggest that the babingtonite, Fe-rich epidote, calcite, and quartz formed from hydrothermal solutions by direct precipitation in open cavities and by replacement of higher-temperature silicate phases (in particular plagioclase and basaltic glass) in a shallow marine volcanic environment. During subsequent burial and low-grade metamorphism babingtonite was partially replaced by prehnite, less Fe-rich epidote, grandite, and chlorite.

KEYWORDS: babingtonite, prehnite, epidote, garnet, chlorite, pumpellyite, Southland, New Zealand.

BABINGTONITE ($\text{Ca}_2\text{Fe}^{2+}\text{Fe}^{3+}\text{Si}_5\text{O}_{14}(\text{OH})$), although relatively rare, has been recorded from numerous localities and in a number of parageneses (Burt, 1971a). Many occurrences are clearly hydrothermal in origin (skarn deposits and veins in granites, e.g. Verkaeren and Bartholome, 1979; Gole, 1981) but the derivation of others is more equivocal (veins in diabases and basic volcanics that have undergone low-grade metamorphism).

This paper describes an occurrence of babingtonite and associated Fe-rich Ca aluminosilicates in calcareous volcanoclastic material occupying the interstices of pillow lavas. Textural relationships provide valuable information on the origin and relative time of formation of the phases. Some data are also included for comparative purposes on another babingtonite locality in New Zealand in the Three Kings Islands (Battay, 1954).

Analyses were obtained on a Joel JXA-5A electron probe microanalyser using the techniques described by Nakamura and Coombs (1973).

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Geological setting

The pillow lavas form the northern part of a rocky knoll about 10 m high located immediately west of the main access road through the Woodlaw Forest 3 km south of Twinlaw Trig Station and 9 km southwest of Ohai in western Southland ($46^\circ 0.0' \text{ S}$, $167^\circ 53.5' \text{ E}$; fig. 1). The rock sequence comprises a southerly extension of the Takitimu Group, a homoclinal sequence of pyroclastics, volcanogenic sediments and some lava flows which reaches some 12 km in thickness in the main massif of the Takitimu Mountains about 30 km to the north (Houghton, 1981). Rocks in the Woodlaw-Twinlaw area contain abundant prehnite and pumpellyite. Laumontite is locally present which suggests metamorphic conditions transitional between the zeolite and prehnite-pumpellyite facies have prevailed. The Woodlaw-Twinlaw succession strikes approximately north-south with dips to the east of up to $40-50^\circ$. The lower (western) part is dominated by volcanoclastic arenites with subordinate lutite and rudite while the upper (eastern) part contains predominant volcanoclastic rudite (abundant angular to subrounded clasts of andesite up to 20 cm in diameter) with minor arenite. Small dykes and flows of basalt and andesite occur throughout the sequence. Although no detailed comparisons have been made these stratigraphic and lithologic features compare closely with the McLean Peaks Formation and overlying Elbow Formation which comprise the upper part of the Takitimu Group (Houghton, 1981).

At the babingtonite locality, which is located near the contact between the two units, pillow lavas appear to form a tongue sloping northward away from a small plug-like outcrop of massive basalt. Cuspate remnants of volcanoclastic sediments up to about 20 cm across occur between the pillows, which are exposed in both transverse and longitudinal section. Bedding preserved in the sediments is commonly strongly contorted, broken and chaotic in orientation, suggesting that the pillows were emplaced on, or perhaps immediately below,

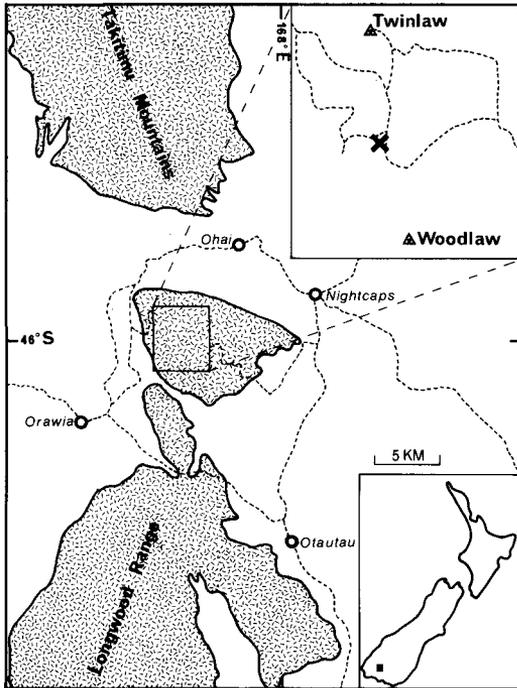


FIG. 1. Sketch map showing the location of the babingtonite occurrence in southern New Zealand. Permo-Triassic intrusives and Permian volcanics and volcanogenic sediments are shaded.

the sediment-water interface and resulted in severe disruption of the sediments. The tuffaceous sediments vary from very fine muddy material through to coarse clastic rocks composed of basaltic and andesitic fragments up to 10 mm in diameter. Prism-shaped grains of calcite preserved in the sediments represent fragments of the Permian bivalve *Atomodesma*. Casts of whole shells of *Atomodesma* occur in an outcrop 2 km north and along strike from the locality.

Apart from relict pyroxene grains, the original mineral assemblage of the pyroclastic fragments has been completely replaced by one or more of prehnite, babingtonite, epidote, grossular-andradite garnet (granite), calcite, quartz, pumpellyite, and chlorite.

Mineralogy

Clinopyroxene is the only major primary volcanic mineral in the tuffaceous material to survive post volcanic processes. It occurs as individual broken crystals and as relict phenocryst and groundmass grains in the altered volcanic fragments.

Phenocrysts (Table I, nos. 1, 2) are relatively magnesian (av. $\text{Ca}_{46}\text{Mg}_{49}\text{Fe}_5$) and poor in Al_2O_3 (< 2.0 wt. %) and TiO_2 (< 0.1 wt. %) relative to groundmass grains (Table I, nos. 3, 4) which are enriched in Fe (to $\text{Ca}_{38}\text{Mg}_{38}\text{Fe}_{14}$), Al_2O_3 (up to 4.7 wt. %) and TiO_2 (up to 1.0 wt. %). These compositions and trends are typical of clinopyroxene in subalkaline rocks.

TABLE I Analyses of pyroxenes and glass inclusion

O.U. No.	(1) 53132	(2) 53119	(3) 53132	(4) 53135	(5) 53132
SiO_2	53.54	50.79	59.47	48.83	49.70
TiO_2	0.10	0.35	0.73	1.00	0.98
Al_2O_3	1.16	2.89	4.42	4.74	14.93
Cr_2O_3	0.34	0.27	0.10	0.03	-
FeO^*	3.23	6.44	10.08	11.98	9.71
MnO	0.09	0.19	0.27	0.29	0.24
MgO	17.89	15.59	14.49	14.68	4.89
CaO	23.74	21.73	21.38	19.04	9.48
Na_2O	0.11	0.34	0.27	0.25	2.39
K_2O	-	-	-	-	0.62
Total	100.20	98.59	101.21	100.84	92.94
	Cation Proportions (O = 6)				CIPW Norm
Si	1.951	1.905	1.839	1.827	Gz 2.3
Al^{IV}	0.049	0.095	0.161	0.173	Or 3.7
Al^{VI}	0.001	0.033	0.032	0.036	Ab 20.2
Ti	0.003	0.010	0.021	0.028	An 28.2
Cr	0.010	0.008	0.003	0.001	Di 15.8
Fe	0.099	0.202	0.313	0.375	Hy 21.0
Mn	0.003	0.006	0.009	0.009	Il 1.9
Mg	0.972	0.872	0.803	0.819	
Ca	0.927	0.873	0.851	0.763	
Na	0.008	0.025	0.020	0.018	

1,2 Pyroxene - relict phenocrysts in babingtonite

3,4 Pyroxene - relict groundmass grains in babingtonite

5 Glass inclusion in pyroxene

* Total Fe as FeO

O.U. Numbers refer to collection numbers in the Otago University Geology Department collections

Further evidence of the original subalkaline character of the volcanic rocks is provided by inclusions of pale brown homogeneous isotropic glass up to 100 μm in diameter occurring within pyroxene phenocrysts. Microprobe analyses of these (Table I, no. 5) indicate compositions broadly appropriate to Mg-poor tholeiite. Modification of the glass composition after entrapment by precipitation on the walls of the host is likely, and this would mean that the original magma composition may have been rather more diopside-normative but nevertheless still saturated in SiO_2 .

Babingtonite is highly variable in abundance from one specimen to another and even over small distances within a single hand specimen. It is concentrated in zones of high permeability, namely in coarser layers of arenaceous sediments and in cavities up to 2 cm in diameter in porcelaneous material. In these cavities, which probably developed by hydrothermal leaching of carbonates, babingtonite forms stumpy euhedral crystals up to

5 mm in longest dimension often partially encrusted by epidote. Elsewhere it forms anhedral single grains and granular aggregates up to 20 mm in diameter. In many cases relict textures show that these have formed either as vesicle and pore fillings or by total replacement of one or more phases in volcanic fragments. In many of the latter cases, an original basaltic texture is still clearly evident in which phenocrysts and groundmass laths of plagioclase have been replaced by babingtonite which is commonly optically continuous over much of the original fragment and from one fragment to another. Pumiceous and glassy basaltic fragments totally replaced by babingtonite contain abundant round or oval outlines of dusty near-opaque material representing margins of vesicles. Areas not included within the oval outlines contain abundant clinopyroxene granules.

Babingtonite infilling vesicles is free of clinopyroxene inclusions but may include elongate euhedral quartz crystals. Rarely, babingtonite together with quartz has replaced olivine as indicated by relict crystal morphology and by inclusions of deep red to opaque chrome spinel commonly observed included in olivine phenocrysts elsewhere.

Representative analyses of babingtonite are given in Table II. As noted by several earlier authors (e.g. see Burt, 1971a) the babingtonites exhibit only minor deviation from the ideal composition (fig. 2). The principal substitutions are Mg and Mn for Fe^{2+} and minor Al for Fe^{3+} . Substitution of Al for Si in tetrahedral sites is negligible in most analyses. A trace of Na observed in some analyses probably substitutes for Ca. The near ubiquitous presence of micron-range garnet granules included in babingtonite prevented preparation of a sufficiently clean separate for determination of Fe^{2+}/Fe^{3+} . Consequently, in the structural formulae presented in Table II, Fe^{2+} and Fe^{3+} have been calculated on the basis of stoichiometry (9 cations and 14.5 oxygen atoms anhydrous).

For comparative purposes, an analysis of babingtonite from the other known New Zealand occurrence in the Three Kings Islands (Battey, 1954) is also presented in Table II. The babingtonite occurs within a spilitic volcanic rock in thin veinlets of quartz and albite. The specimen studied (6203) lacks Ca aluminosilicates although prehnite and epidote have been recorded in other specimens

TABLE II Analyses of babingtonites

O. U. No	(1) 53135	(2) 53125	(3) 53119	(4) 53133	(5) 53133	(6) 53136	(7)	(8)
SiO ₂	53.39	52.80	53.69	53.23	53.24	53.81	52.98	53.19
TiO ₂	0.01	0.02	-	0.02	0.04	0.01	0.03	-
Al ₂ O ₃	0.35	0.28	1.18	0.76	0.39	0.45	0.52	1.27
FeO*	20.58	21.49	20.31	21.71	21.13	21.46	21.41	20.13
MnO	1.15	1.68	1.19	0.81	1.31	0.64	0.96	2.42
MgO	1.91	0.92	1.02	1.02	0.99	1.49	1.24	0.34
CaO	19.87	19.63	20.18	20.04	20.32	19.82	19.74	19.62
Na ₂ O	0.05	0.03	0.04	-	-	0.07	0.05	0.17
K ₂ O	-	-	-	-	-	0.01	-	0.06
Total	97.31	96.85	97.61	97.59	97.42	97.76	96.93	97.20
Fe ₂ O ₃ **	13.99	13.61	11.96	12.98	13.34	13.14	13.44	12.31
FeO	7.99	9.24	9.55	10.04	9.12	9.64	9.31	9.05
Total	98.71	98.21	98.81	98.90	98.75	99.08	98.27	98.43
Cation Proportions (Cations = 9; O = 14.5)								
Si	4.992	5.002	5.018	4.991	5.004	5.021	4.996	5.012
Al ^{iv}	0.008	-	-	0.009	-	-	0.004	-
Al ^{vi}	0.031	0.031	0.013	0.075	0.043	0.049	0.054	0.141
Ti	0.001	0.001	-	0.001	0.003	0.001	0.002	-
Fe ^{3+***}	0.985	0.970	0.841	0.930	0.944	0.922	0.954	0.873
Fe ²⁺	0.625	0.732	0.746	0.773	0.717	0.752	0.735	0.714
Mn	0.091	0.135	0.094	0.064	0.104	0.051	0.077	0.193
Mg	0.267	0.130	0.142	0.143	0.138	0.207	0.174	0.048
Ca	1.991	1.993	2.021	2.014	2.046	1.982	1.995	1.981
Na	0.009	0.006	0.007	-	-	0.013	0.009	0.031
K	-	-	-	-	-	0.002	-	0.007

1,2 Babingtonite replacing volcanic glass

3,4 Babingtonite replacing plagioclase in volcanic fragment

5 Babingtonite - vesicle infilling with quartz

6 Babingtonite - cavity infilling with quartz

7 Average of 30 analyses of babingtonite from the Twinlaw locality

8 Babingtonite from Three Kings island; Auckland Museum specimen 6203

* Total Fe as FeO

** Fe₂O₃ and Fe³⁺ calculated assuming stoichiometry (cations=9; O=14.5)

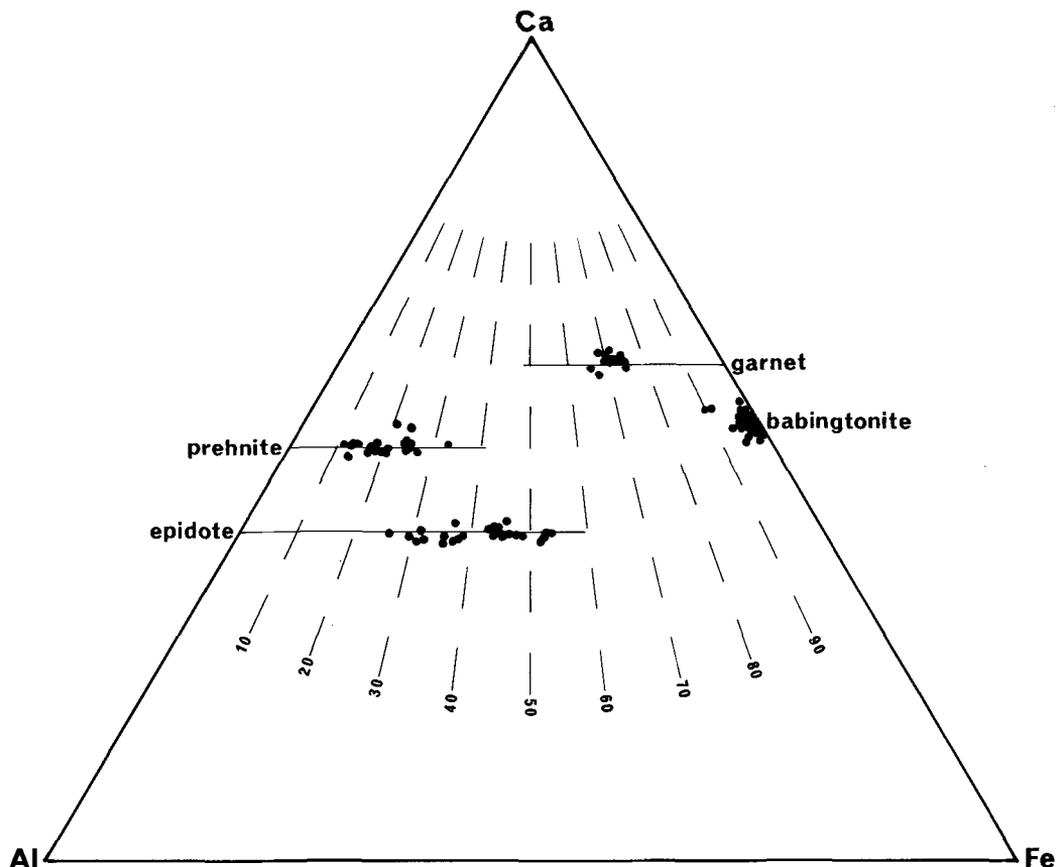


FIG. 2. Compositions of babingtonites, garnets, prehnites and epidotes in terms of Ca, Fe, and Al (atomic proportions). Dashed isopleths indicate $100\text{Fe}/(\text{Fe} + \text{Al})$ ratios.

by Battey. The principal compositional differences are significantly higher Al, Mn, and Na and lower Mg content relative to the Twinlaw babingtonite.

Epidote is fairly common as small euhedral or subhedral grains up to about 0.1 mm varying in colour from pale to very deep yellow in thin section. It frequently occurs as euhedral inclusions in babingtonite. Elsewhere it may be included in calcite or within aggregates of prehnite, quartz, and grandite.

Representative microprobe analyses of epidote are given in Table III. It varies from moderately to very Fe-rich with pistacite contents ($P_s = 100\text{Fe}/(\text{Fe} + \text{Al})$) extending from $P_{s_{25}}$ up to and beyond $P_{s_{50}}$ (figs. 2, 3) which exceeds the previously reported upper limit of Fe substitution (Tulloch, 1979; Nystrom, 1983). The maximum measured Fe content is $P_{s_{53}}$ (Table III, no. 1) representing the composition $\text{Ca}_2\text{Fe}_{1.58}\text{Al}_{1.42}\text{Si}_3\text{O}_{12}(\text{OH})$. Epidote grains included in babingtonite are either unzoned

or slightly sector zoned and relatively enriched in Fe ($> P_{s_{40}}$). Some epidote grains included in calcite have a characteristic zoning pattern in which a rather irregular heterogeneous and predominantly Fe-rich core ($P_{s_{35-50}}$; Table III, no. 3) is mantled by a more Al-rich, homogeneous overgrowth ($P_{s_{32}}$; Table III, no. 4), often with an euhedral outer margin (figs. 4a, 5). The boundary between the zones is irregular but quite sharp.

Commonly associated with the epidote are small irregular grains of chalcopyrite and an opaque or very dark red mineral tentatively identified by electron microprobe as delafossite (CuFeO_2). Where in contact with this mineral epidote is significantly depleted in Fe ($P_{s_{38}}$; Table III, no. 6) relative to neighbouring grains.

Epidote also occurs to a limited extent in the associated pillow lavas where it occurs as vesicle infillings, vein fillings and partially replacing feldspars. In this paragenesis it is relatively more

TABLE III Analyses of epidotes

O. U. No.	(1) 53135	(2) 53135	(3) 53125	(4) 53125	(5) 53132	(6) 53135
SiO ₂	36.07	35.78	36.78	37.56	36.15	36.88
TiO ₂	0.12	0.11	0.06	0.16	0.18	0.16
Al ₂ O ₃	14.08	14.79	18.08	21.81	17.80	19.06
Fe ₂ O ₃ [*]	24.96	21.40	21.48	23.21	22.73	21.81
MnO	-	0.02	0.01	0.03	-	0.06
MgO	-	-	0.15	0.02	0.01	0.01
CaO	21.93	21.40	21.48	23.21	22.73	21.81
Total	97.16	96.92	96.51	98.79	97.38	96.26
Cation Proportions (O = 12.5)						
Si	3.028	3.004	3.036	2.991	2.981	3.037
Ti	0.007	0.007	0.003	0.010	0.011	0.010
Al	1.393	1.464	1.759	2.047	1.730	1.849
Fe	1.577	1.568	1.240	0.959	1.272	1.134
Mn	-	0.001	0.001	0.002	-	0.004
Mg	-	-	0.006	0.003	0.001	0.001
Ca	1.973	1.925	1.900	1.981	2.008	1.924
$\frac{100\text{Fe}}{\text{Fe}+\text{Al}}$	53.1	51.7	41.3	31.9	42.4	38.0

1 Most Fe-rich epidote analysed
 2,5 Epidote included in babingtonite
 3 Epidote - core of zoned grain
 4 Epidote - rim of zoned grain
 6 Epidote adjacent to Fe-Cu oxide grains
^{*} Total Fe as Fe₂O₃

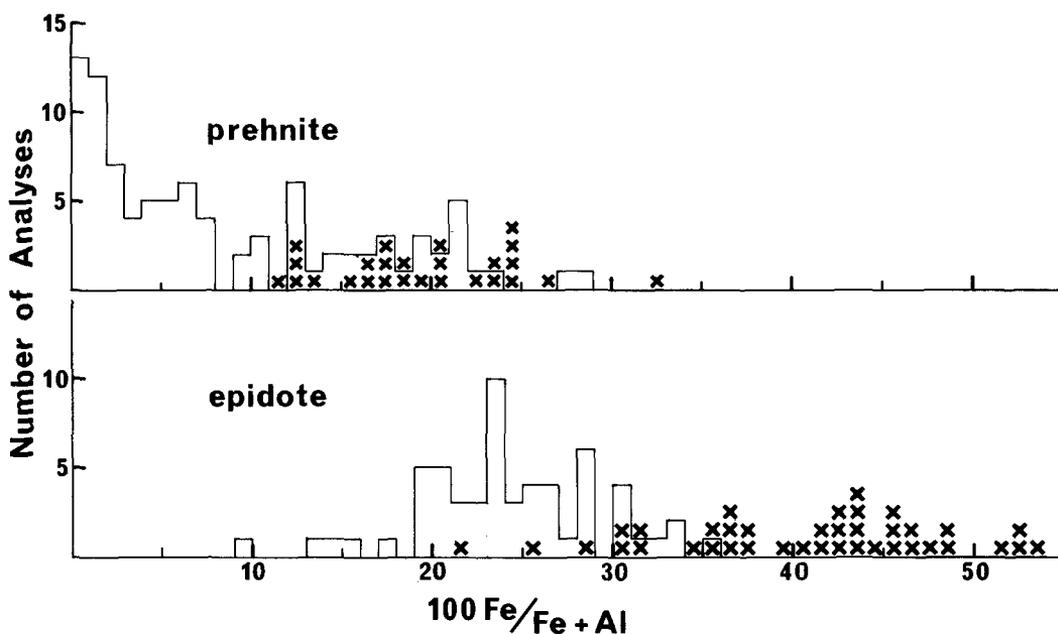


Fig. 3. Histograms showing range of substitution of Fe for Al in epidotes and prehnites. Crosses indicate analyses from this study. Other data from Evarts and Schiffman (1983).

Al-rich (Ps₁₅₋₃₀) and is closely similar to epidote elsewhere in the Takitimu Group (Houghton, 1982) and other low-grade metamorphic sequences (e.g. Evarts and Schiffman, 1983).

Garnet. Very small equant grains of garnet (av. 10

µm in diameter) are observed in almost every thin section and are locally abundant. In particular the grains are commonly dispersed through babingtonite, especially where textural features suggest that this has formed by replacement of volcanic

glass or plagioclase. It is rare in babingtonite filling former vesicles. Elsewhere garnet forms framboidal aggregates up to about 0.5 mm in diameter, usually totally enclosed in quartz.

TABLE IV Analyses of garnets

O.U. No.	(1) 53132	(2) 53132	(3) 53131	(4) 53135	(5) 53134
SiO ₂	33.40	36.20	33.42	34.96	37.15
TiO ₂	1.71	0.58	0.18	0.31	-
Al ₂ O ₃	5.86	6.45	5.41	7.07	6.70
Fe ₂ O ₃ *	21.14	20.73	23.71	22.26	23.30
MnO	0.12	0.07	0.09	0.13	1.39
MgO	0.22	-	0.20	0.19	0.28
CaO	33.72	34.68	33.83	33.31	30.92
Na ₂ O	0.01	0.02	0.04	0.06	-
K ₂ O	-	-	0.01	0.03	0.06
Total	96.18	98.73	96.89	98.32	99.80
Cation Proportions (O = 24)					
Si	5.719	5.976	5.725	5.821	6.056
Al	1.183	1.255	1.092	1.387	1.287
Ti	0.220	0.072	0.024	0.039	-
Fe	2.724	2.576	3.056	2.788	2.859
Mn	0.017	0.010	0.013	0.018	0.192
Mg	0.056	-	0.052	0.047	0.069
Ca	6.187	6.135	6.209	5.941	5.400
Na	0.003	0.005	0.013	0.019	-
K	-	-	0.002	0.007	0.011
100Fe Fe+Al	69.7	67.2	71.7	66.8	69.0

1, 2 Garnet in babingtonite

3, 4 Garnet in quartz associated with babingtonite, epidote and prehnite

5 Garnet with prehnite in altered pillow lava

* Total Fe as Fe₂O₃

Selected microprobe analyses are presented in Table IV. The garnets are essentially andradite-grossular solid solutions (c.95% andradite + grossular) with only trace amounts of other components. Compared with the other Ca-Al-Fe silicates these grandites display only a limited range of Fe-Al substitution (fig. 2) plotting in a relatively tight group around And₇₀Gro₃₀ ($X_{Fe} = 0.7$ where $X_{Fe} = Fe/(Fe + Al)$) which is intermediate between the groups of almost pure andradites and the andradite-grossular solid solutions ($X_{Fe} = 0.48-0.55$) reported for garnets in rocks of the zeolite to pumpellyite-actinolite facies in southern New Zealand by Coombs *et al.* (1977) and Tulloch (1979).

One notable feature of the garnet compositions is the TiO₂ content of grains embedded in babingtonite (TiO₂ up to 2.5%, av. 1.0%; Table IV, nos. 1, 2) compared with those in quartz (TiO₂ < 0.5%; Table IV, nos. 3, 4).

Most of the grandites have low analytical totals. This is common in garnets in low-grade metamorphic rocks and has been attributed to the presence of abundant sub-microscopic fluid inclusions in the crystals lowering X-ray intensities during microprobe analysis (Coombs *et al.*, 1977).

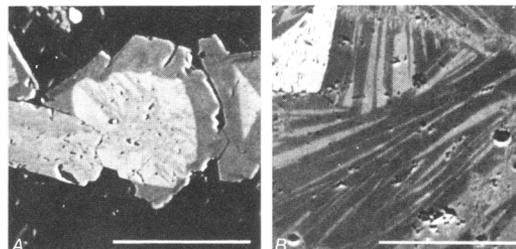


FIG. 4. Backscattered electron images of epidote (a) and prehnite (b) showing variations in substitution of Fe for Al. Darker tones indicate lower Fe/(Fe + Al) ratios. Scale bar is 100 μ m.

Prehnite is an abundant and ubiquitous constituent of all samples of interpillow material, where it has clearly replaced most of the feldspar and glass components of volcanic fragments and has partially replaced babingtonite except where this has been armoured by quartz and/or calcite.

The prehnite varies from extremely fine grained dusty aggregates containing some quartz (these appear to represent replacement of a muddy component) through to coarse grained sheafs and aggregates with individual crystals up to about 1.0 mm in length.

In coarser grained aggregates, prehnite displays a bladed habit. The blades are randomly oriented except where they have developed by partial replacement of babingtonite in which case the blades are oriented broadly normal to the original crystal margin.

TABLE V Analyses of prehnites

O.U. No.	(1) 53131	(2) 53132	(3) 53132	(4) 53132	(5) 53136
SiO ₂	42.11	40.98	43.16	43.61	42.27
TiO ₂	0.05	0.04	0.14	0.05	0.26
Al ₂ O ₃	15.42	21.67	17.73	21.17	18.69
Fe ₂ O ₃ *	11.52	4.36	9.16	5.01	7.70
MnO	0.05	0.01	-	0.03	0.04
MgO	0.01	0.01	-	0.11	0.11
CaO	25.26	27.43	26.67	26.39	26.42
Total	94.42	94.50	96.86	96.91	95.49
Cation Proportions (O = 22)					
Si	6.108	5.828	6.053	6.004	5.991
Ti	0.005	0.004	0.015	0.005	0.028
Al	2.636	3.633	2.931	3.522	3.122
Fe	1.257	0.467	0.967	0.519	0.821
Mn	0.006	0.001	-	0.003	0.005
Mg	0.002	0.003	-	0.022	0.024
Ca	3.925	4.180	4.008	3.892	4.012
100Fe Fe+Al	32.3	11.4	24.8	12.8	20.8

1 Most Fe-rich prehnite analysed

2 Most Fe-poor prehnite analysed

3 Fe-rich portion of same grain as analysis 2

4 Prehnite adjacent to pumpellyite

5 Prehnite replacing babingtonite

* Total Fe as Fe₂O₃

Representative analyses of prehnite are presented in Table V. Substantial and variable substitution of Fe^{3+} for Al is observed. X_{Fe} ($= \text{Fe}/(\text{Fe} + \text{Al})$) varies in the range 0.11–0.32, with much of this range often present in a single crystal (figs. 4b, 6). For example, three individual grains have measured X_{Fe} in the ranges 0.11–0.25, 0.18–0.24 and 0.12–0.23. The maximum measured Fe content ($\text{Fe}_2\text{O}_3 = 11.5$ wt.%; $X_{\text{Fe}} = 0.323$) is above the commonly accepted maximum substitution of $X_{\text{Fe}} = 0.3$ and represents the most Fe-rich prehnite so far reported. It should be noted that contrary to the statement of Liou *et al.* (1983, p. 340), Surdham (1969) and Everts and Schiffman (1983) have not reported prehnite with $X_{\text{Fe}} = 0.43$. The maximum X_{Fe} reported by Surdham (1969) is 0.30 while the value of 0.43 reported by Everts and Schiffman (1983, Table III and fig. 4) refers to the ratio $\text{Fe}/(\text{Fe} + \text{Al}^{\text{VI}})$ and excludes Al in tetrahedral coordination. In fact for this analysis $X_{\text{Fe}} = 0.21$ and on the same basis more Fe-rich prehnites have been reported by several authors including Zolotukhin *et al.* (1965), Tulloch (1979), Houghton (1982) and in this paper. The most Fe-rich prehnite reported here has $\text{Fe}/(\text{Fe} + \text{Al}^{\text{VI}}) = 0.63$. This correction appears to remove the difficulty of reconciling the co-existence of such Fe-rich prehnite and epidote as discussed by Liou *et al.* (1983).

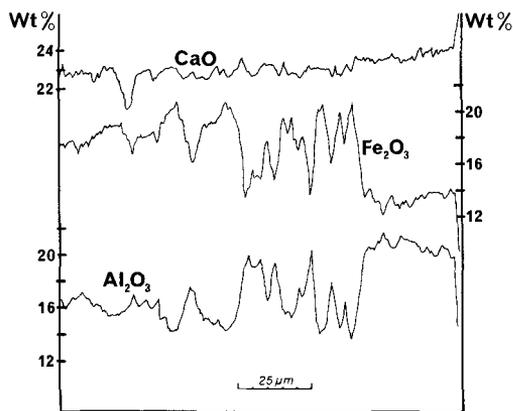


FIG. 5. Core to margin electron microprobe traverse for Ca, Fe, and Al of epidote grain shown in fig. 4a. Note homogeneous Al-enriched zone on right-hand side of diagram (outer portion of grain).

Pumpellyite. Where present, pumpellyite forms bladed aggregates of randomly oriented pleochroic green crystals. It is not particularly common in the tuffaceous interpillow material but is very common within the pillow units. In either environment

TABLE VI Analyses of pumpellyites and chlorite

O.U. No.	(1) 53134	(2) 53132	(3) 53135
SiO_2	34.09	36.58	27.62
TiO_2	0.07	0.07	-
Al_2O_3	17.12	18.01	17.61
FeO	18.58	13.81	27.53
MnO	-	0.06	0.36
MgO	2.12	2.00	16.10
CaO	21.71	22.89	0.20
Na_2O	0.03	0.02	0.06
K_2O	0.01	-	0.02
Total	93.73	93.44	89.50
	Cation Proportions**		
Si	5.660	6.033	5.770
Al^{IV}	0.340	-	2.230
Al^{VI}	3.010	3.501	2.106
Ti	0.009	0.009	-
Fe	2.580	1.905	4.818
Mn	-	0.009	0.063
Mg	0.524	0.491	5.103
Ca	3.862	4.046	0.045
Na	0.011	0.005	0.024
K	0.003	-	0.005

1,2 Pumpellyite replacing babingtonite

3 Chlorite replacing babingtonite

* Total Fe as FeO

** Cation proportions calculated on the basis of 16 cations (pumpellyite) and 20 oxygen atoms (chlorite) anhydrous

pumpellyite is enriched in Fe (total Fe as FeO = 13.2–19.9 wt.%; Table VI, nos. 1, 2) representing a high jugoldite component. Such a composition [pumpellyite-(Fe)] in the classification scheme of Passaglia and Gottardi (1973) is characteristic of the zeolite and prehnite-pumpellyite facies and contrasts with more Mg and Al-rich compositions [pumpellyite-(Mg)] typical of the pumpellyite-actinolite facies (Coombs *et al.*, 1976; Nystrom, 1983).

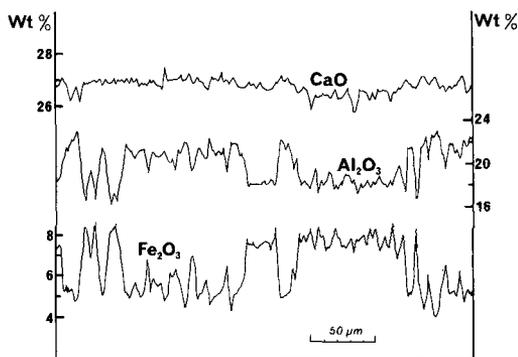


FIG. 6. Electron microprobe traverse for Ca, Fe, and Al across part of a prehnite aggregate showing variation in Fe and Al.

Some pumpellyite aggregates in the pyroclastic fragments contain rare ragged grains of babingtonite suggesting that pumpellyite as well as prehnite has formed at the expense of babingtonite.

Chlorite is a widespread but minor constituent of the interpillow material and may partially replace babingtonite, especially along cleavages and fractures. A microprobe analysis of the chlorite (pynochlorite after Hey, 1954) is presented in Table VI.

Discussion

The babingtonite-bearing mineral assemblage at Twinlaw has apparently developed in a two-stage process. The whole area has been subject to burial and heating leading to regional development of mineral assemblages appropriate to the prehnite-pumpellyite facies (Houghton, 1982). These assemblages are well developed in the pillows and massive basaltic lavas and in the surrounding terrane. It is clear that the prehnite, pumpellyite, chlorite and most likely garnet in the interpillow material formed at this time. These phases are all observed in the pillows and massive volcanics and all are characteristic mineral phases of the prehnite-pumpellyite facies in southern New Zealand. Furthermore, the pillows and massive basalts contain an abundance of relatively Fe-poor epidote similar in composition to rims sometimes developed as overgrowths on Fe-rich epidote in the interpillow material. These overgrowths probably also resulted from metamorphic overprinting.

Observations of replacement phenomena, specifically replacement of babingtonite by one or more of prehnite, pumpellyite, chlorite, and garnet, indicate that the babingtonite is most likely a product of an earlier event. Evidence for the nature and timing of this event is equivocal but it may represent either an early stage of the low-grade metamorphism or, more likely, hydrothermal activity associated with the shallow marine volcanism. The following observations and experimental data support the latter interpretation.

1. Geological observations suggest that the pillow lavas are immediately adjacent to the site of eruption in a shallow marine environment and therefore a likely site of sea floor hydrothermal vents.

2. Babingtonite is entirely absent within pillows. Instead it is restricted to pillow interstices where the pyroclastic material is more permeable to hydrothermal solutions. Within pillow interstices babingtonite is also concentrated in areas of higher permeability such as cavities and coarser grained fractions.

3. The interpillow material is completely purged

of alkalis (semiquantitative XRF determination indicates $\text{Na}_2\text{O} + \text{K}_2\text{O} = 0.2$ wt. %). Clearly there has been intense metasomatism in an open hydrothermal system such as might be found on or near the sea floor in a zone of submarine volcanism. Albite, absent from interstices, is abundant within pillows.

4. Although corroborative experimental data are meagre, multisystems analysis of the stability of babingtonite in the system Ca-Fe-Si-C-O-H by Burt (1971*b*) indicates that babingtonite stability relative to other Ca-Fe silicates is favoured by low a_{CO_2} and high $a_{\text{H}_2\text{O}}$. This is consistent with a submarine environment at or not far below the sediment-seawater interface. Epidote stability is also favoured by low a_{CO_2} (Storre and Nitsch, 1972) while entry of Fe^{3+} into epidote is favoured by high f_{O_2} (Liou, 1973; Liou *et al.*, 1983). Textural data show that at least the more Fe-rich epidote formed contemporaneously with babingtonite.

Experimental data on the stability of babingtonite are scarce. It was synthesized by Shvedenkov and Kalinin (1972) in the system $\text{CaCO}_3\text{-Fe}_2\text{O}_3\text{-6SiO}_2\text{-NaCl-H}_2\text{O}$ at $T = 500^\circ\text{C}$ and $P_{\text{total}} = 500$ atmospheres but nucleation of babingtonite in experimental studies has been difficult. Shvedenkov and Mazurov (1977) have shown that babingtonite is stable over a wide range of f_{O_2} (at least in the range defined by the Cu-CuO and the Fe- Fe_3O_4 oxygen buffers) and up to about $T = 550^\circ\text{C}$. They also report fluid inclusion homogenization temperatures in natural babingtonites in the range 450 to 480°C . The P - T stability fields of epidote and ferroactinolite overlap that of babingtonite. Increases in their Al and Mg contents respectively will enlarge their stability fields leading to a contraction and perhaps elimination of the babingtonite field. Babingtonite will therefore be restricted to very Fe-rich, Mg- and Al-poor environments and Shvedenkov and Mazurov suggest that this may account for its relative rarity in nature.

No data are available on the lower temperature stability limit of babingtonite but it is commonly observed in association with zeolites (Burt, 1971*b*; Birch, 1983). This suggests that it may also form at relatively low temperatures. Alternatively such occurrences may represent babingtonite formed at higher temperatures and preserved metastably at lower temperatures during zeolite crystallization. Data presented by Birch (1983) appear to be equally consistent with this interpretation.

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REFERENCES

- Batley, M. H. (1954) *Records Auckland Inst. Museum*, **4**, 263-6.
- Birch, W. D. (1983) *Mineral. Mag.* **47**, 377-80.
- Burt, D. M. (1971a) *Soc. Mining Geol. Japan Special Issue*, **3**, 375-80.
- (1971b) *Carnegie Inst. Washington Yearb.* **70**, 189-97.
- Coombs, D. S., Nakamura, Y., and Vaugnat, M. (1976) *J. Petrol.* **17**, 440-71.
- Kawachi, Y., Houghton, B. F., Hyden, G., Pringle, I. J., and Williams, J. G. (1977) *Contrib. Mineral. Petrol.* **63**, 229-46.
- Evarts, R. C., and Schiffman, P. (1983) *Am. J. Sci.* **283**, 289-340.
- Gole, M. J. (1981) *Can. Mineral.* **19**, 269-77.
- Hey, M. H. (1954) *Mineral. Mag.* **30**, 277-92.
- Houghton, B. F. (1981) *New Zealand J. Geol. Geophys.* **24**, 333-48.
- (1982) *Ibid.* **25**, 1-19.
- Liou, J. G. (1973) *J. Petrol.* **14**, 381-413.
- Kim, H. S., and Maruyama, S. (1983). *J. Petrol.* **24**, 321-42.
- Nakamura, Y., and Coombs, D. S. (1973) *Contrib. Mineral. Petrol.* **25**, 241-69.
- Nystrom, J. O. (1983) *Ibid.* **83**, 159-68.
- Passaglia, E., and Gottardi, G. (1973) *Can. Mineral.* **12**, 219-23.
- Shvedenkov, G. Yu, and Kalinin, D. V. (1972) *Dokl. Akad. Nauk SSSR*, **205**, 131-3.
- and Mazurov, M. P. (1977) *Ibid.* **232**, 178-81.
- Storre, B., and Nitsch, K. H. (1972) *Contrib. Mineral. Petrol.* **35**, 1-10.
- Surdham, R. C. (1969) *Am. Mineral.* **54**, 256-66.
- Tulloch, A. J. (1979) *Contrib. Mineral. Petrol.* **69**, 105-17.
- Verkaeren, J., and Bartholome, P. (1979) *Econ. Geol.* **74**, 53-66.
- Zolotukhin, V. V., Vasilyev, Yu. R., and Zyuzin, N. I. (1965) *Dokl. Akad. Nauk SSSR* **161**, 138-41.

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