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Assimilation and metamorphism at a basalt-limestone contact, Tokatoka, New Zealand

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SUMMARY. Small-scale assimilation of limestone during the intrusion of an olivine basalt feeder dyke into an Eocene argillaceous, siliceous biomicrite in the Tokatoka area has resulted in the incorporation of large amounts of calcium into the parent magma. Initial effects of assimilation have caused partial resorption of the early-formed igneous mineralogy and the precipitation of calcic, iron-rich clinopyroxenes (ferrosahlite to hedenbergite), wollastonite, schorlomite, and pyrrhotine. Pyroxene compositions show a trend of strong enrichment in Ca-tschermak and ferrosilite components. Derivative hydrothermal solutions, rich in Ca, Si, Al and alkalis have precipitated and altered anhydrous phases to tobermorite, thomsonite, prehnite, pectolite, cebollite, hydrogrossular, gismondine, analcime, Sr- and Ba-bearing zeolites, and calcite.

Modelling of the basalt-limestone assimilation process by least-squares mixing methods has shown that the observed chemical variation can largely be accounted for by the dilution of the basalt with up to 30 wt.% decarbonated limestone. Desilication of the liquid, a result of this dilution effect, has been accommodated in the chemistry of the early-formed mineralogy rather than by the crystallization of minerals characteristic of an undersaturated rock type.

Contemporaneous with the intrusion of the basalt was the high-temperature contact metamorphism of the limestone. This produced assemblages of rankinite, kilchoanite, larnite, spurrite, grossular, and tobermorite. Subsequent injection of the basalt and hybrid phases into fractures has resulted in the alteration of the primary metamorphic assemblage to wollastonite, scawtite, foshagite, hydrogrossular, calcite, and vaterite.

IN the Tokatoka district, about 150 km north of Auckland, a series of shallow intrusive plugs and dykes of basaltic and andesitic composition cut an Eocene argillaceous limestone sequence. The first record of high-temperature calcium silicates developed in contact metamorphic rocks in this area was made by Mason (1957) who described larnite, scawtite, and hydrogrossular from an andesite-limestone contact near Rehia, 3 km south-east of Tokatoka. Later, during a regional investigation of the igneous geology of the area, Black (1964) recognized several other localities where the intrusion of basalts into limestones had caused extensive development of calcium silicates and recorded the occurrence of rankinite and kilchoanite from Golden Gully, 1 km north of Tokatoka (Black, 1969).

Associated with the contact rocks in Golden Gully are narrow veins of finely crystalline basaltic rock containing wollastonite as a phenocryst phase (Black, 1964). This is the only recorded find of wollastonite-bearing basaltic rock in the area. Exposure in Golden Gully is poor as a result of deep weathering of the basalt. However the development of refractory calcium silicates has made the contact between basalt and marble very resistant. Two exposures about 3 m in diameter are probably in place; other samples were obtained from loose blocks.

Because of the finely crystalline nature of the rocks thin-section identification of minerals was often difficult. Most identifications were made using X-ray diffraction data. Chemical analyses were obtained using X-ray fluorescence after the method of Norrish and Hutton (1969) and supplemented with wet chemical analysis of the alkalis, Fe^{II}/Fe^{III}, H_2O and CO_2. Mineral compositions were determined by electron probe microanalysis using polished thin-sections. After removal of instrument drift, dead time, and background effects, data were corrected using the method of Bence and Albee (1968) and Albee and Ray (1970).

Petrography of the uncontaminated igneous suite

No basalts completely free from alteration were found. Typically the basalts are strongly porphyritic and contain phenocrysts, up to 2 mm in diameter, of plagioclase, clinopyroxene, and olivine. These occasionally occur together as glomerophenocrysts.

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Phenocrystal plagioclase is found as zoned crystals with corroded rims and cores. Core compositions range from An_{70} to An_{80}, and show a decreasing anorthite component towards the rim. Smaller phenocrysts are generally less calcic (An_{50-75}). In addition, crudely twinned, oscillatory zoned, anorthite crystals (An_{90-94}) occur as individual subhedral phenocrysts up to 0.5 mm diameter and sometimes as overgrowths on the less calcic phenocrysts.

Pyroxene phenocrysts fall into two size groups. The larger (1–1.5 mm diameter), associated with olivine in clots or as single euhedra, often show colour zonation. The second are medium-sized euhedra, 0.1 to 0.5 mm in diameter. Both groups give core to rim analyses of approximately $Wo_{33}En_{38}Fs_{12}CaTs_{8}Rem_{9}^{*}$ to $Wo_{40}En_{38}Fs_{13}CaTs_{1}Rem_{8}$ (analyses, Table IV).

Unaltered olivines are found rarely. They have compositions around Fo_{75} and are surrounded by reaction rims of magnetite. Most commonly olivine is completely altered to chlorite and serpentine. The opaque mineralogy consists dominantly of titanomagnetite, but some of the more coarsely crystalline basalts contain, in addition, phenocrysts of pyrite or pyrrhotine.

The groundmass assemblage consists of colourless calcic augite subhedra ($Wo_{38}En_{29}Fs_{14}CaTs_{0}Rem_{19}$), plagioclase laths ($An_{40-56}$), abundant titanomagnetite, and chlorite. Biotite is an uncommon groundmass constituent.

Major, minor, and trace element composition of the basalt is given in Table II, analysis I.

TABLE I. *Chemical analyses of the limestone and calc-silicate hornfels*

	I	II	III
SiO_2	17.75	32.54	40.99
TiO_2	0.15	0.31	0.33
Al_2O_3	2.65	5.05	5.64
Fe_2O_3	0.13	0.83	2.08
FeO	0.82	1.19	0.27
MnO	0.02	0.07	0.07
MgO	0.4	0.2	0.6
CaO	42.24	58.2	44.8
Na_2O	0.18	0.12	tr.
K_2O	0.4	0.04	tr.
P_2O_5	0.12	0.23	0.17
S	0.09	0.42	0.15
CO_2	33.15	0.65	0.33
H_2O^+	1.52	0.42	4.29
Total	99.62	100.27	99.72
Ba	192	53	19
Cr	17	49	36
Cu	26	68	61
Ni	33	42	50
Pb	9	12	5
Rb	17	3	4.3
S	876	4210	1510
Sr (ppm)	1190	1300	811

I. Eocene limestone (argillaceous, siliceous biomicrite).

II. Larnite-hydrogrossular-grossular-calcite hornfels.

III. Wollastonite-hydrogrossular hornfels.

Contact metamorphism

The country rock limestone. The closest exposures of unmetamorphosed limestone to the Golden Gully basalt-limestone contact are deeply weathered, but limestone in a small quarry 500 m to the east appeared similar to that at Golden Gully. The biomicrite is composed of planktonic foraminifera, often infilled with pyrite, and subangular rock fragments, quartz, opaque minerals, and clays, set in a micritic matrix. At this locality the limestone is highly sheared and shows indistinct bedding. A chemical analysis is given in Table I.

The contact metamorphic rocks. The rocks have a dark, flinty appearance, and consist of almost monomineralic patches of rankinite, kilchoanite, larnite, and spurrite with ubiquitous grossular. This is cut by a network of narrow wollastonite-grossular-scawtite veins and hydrothermal precipitates of tobermorite and calcite, with lesser amounts of afwillite, gismondine, and foshagite. In only one outcrop is the parental olivine basalt seen in contact with the metamorphosed limestone. In this case the limestone has been altered to an 11 Å tobermorite–grossular assemblage with subsequent hydrothermal alteration to wollastonite, scawtite, and vaterite (Baker, in prep.). Calc-silicate mineral compositions are shown schematically in fig. 1.

Formation of high-temperature, contact metamorphic calc-silicates has been discussed by Joesten (1974) who evaluated the experimental data of Zharikov and Shmulovich (1969) in light of the Christmas Mountains paragenesis.

From these studies the following conclusions can be drawn:

1. Larnite is stabilized with respect to spurrite and rankinite at low f_{CO_2}. (X_{CO_2} of fluid phase

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* Pyroxene analyses have been recalculated using the method of Hess (1949). The remainder (Rem) is the sum of the jadeite, acmite, and CaTi pyroxene components.

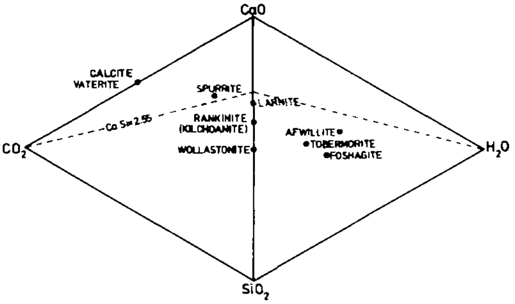

FIG. 1. Schematic representation of calc-silicate mineralogy in terms of CaO-SiO_2-H_2O-CO_2 (in mole %). Dashed line shows ratio of Ca to Si for the analysed Eocene Limestone.

less than 0.8 at 1000 °C; less than 0.2 at 900 °C, for 0.3 kb)

$$\underset{\text{larnite}}{4Ca_2SiO_4} + CO_2 = \underset{\text{spurrite}}{Ca_5Si_2O_8CO_3} + \underset{\text{rankinite}}{Ca_3Si_2O_7}$$

2. Spurrite is stabilized with respect to tilleyite (which is absent at Tokatoka) at reduced X_{CO_2}: less than 0.8 at 960 °C.

$$\underset{\text{spurrite}}{Ca_5Si_2O_8CO_3} + CO_2 = \underset{\text{tilleyite}}{Ca_5Si_2O_7(CO_3)_2}$$

3. The occurrence of rankinite in the absence of spurrite also implies relatively low X_{CO_2} of the fluid phase.

$$\underset{\text{spurrite}}{Ca_5Si_2O_8CO_3} + \underset{\text{wollastonite}}{4CaSiO_3} = \underset{\text{rankinite}}{3CaSi_2O_7} + CO_2$$

4. Kilchoanite represents a lower temperature, retrograde phase of rankinite. The polymorphic transition has been measured by Speakman *et al.* (1967) at about 625 °C, varying little with pressure. This is lower than previous estimates of Roy (1958) at 800-850 °C and Agrell (1965) at 700 °C.

5. The occurrence of grossular places an upper limit on the temperature of formation. Experimental work of Gordon and Greenwood (1971) shows that at about 880 °C, 2 kb total pressure and X_{CO_2} up to 0.4 grossular breaks down to anorthite, wollastonite, and gehlenite.

Bulk analyses of the wollastonite-garnet and larnite rocks (Table I) have been recalculated to a weight percentage norm using theoretical mineral compositions. A deficiency of silica occurs if pure grossular is used in the calculation. This can be allowed for by assuming that the garnet species is hydrogrossular, with a substitution of 4OH for one Si. The proportions of the normative minerals are for analysis II: larnite, 76.1 %, hydrogrossular, 20.8, and calcite, 3.1; and for analysis III: wollastonite, 73.4 % and hydrogrossular, 26.6 (in wt. %).

Fig. 1 delineates the ratio of Ca to Si for the analysed argillaceous biomicrite (Ca:Si = 2.55) which, during isochemical metamorphism, could produce a spurrite-bearing rock. For the formation of rankinite and larnite the introduction of silica is necessary. It is uncertain whether these compositions were attained by variation in parent-rock chemistry or by silica metasomatism.

Associated with the localized injection of the hybrid basalt liquid into fractures in the high-temperature calc-silicate rocks is a second metamorphic phase involving further addition of silica to produce the predominantly wollastonite-hydrogrossular assemblage as the result of the following reactions:

$$\underset{\text{rankinite}}{Ca_3Si_2O_7} + SiO_2 = \underset{\text{wollastonite}}{3CaSiO_3}$$

$$\underset{\text{spurrite}}{Ca_5Si_2O_8CO_3} + 3SiO_2 = \underset{\text{wollastonite}}{5CaSiO_3} + CO_2$$

$$\underset{\text{rankinite}}{4Ca_3Si_2O_7} + SiO_2 + H_2O = \underset{\text{foshagite}}{3Ca_4Si_3O_9(OH)_2}$$

The more refractory larnite remained relatively unaffected by the hydrothermal solutions.

The igneous hybrid phases

Veins of basalt and basalt-limestone hybrid up to 3 cm wide penetrate the calc-silicate country rocks along rectilinear fractures (fig. 2). The wider portions of the vein are composed largely of a basalt similar to the pristine rock type. Phenocrystal olivine, augite, and plagioclase show strong corrosion textures, with olivine displaying reaction rims of magnetite. The groundmass, in addition to titanomagnetite and feldspar, consists of aggregates of green, calcic clinopyroxenes. Chemical analysis (Table II, analysis II) reveals that a small amount of limestone has been incorporated by the parent basalt to produce this rock type.

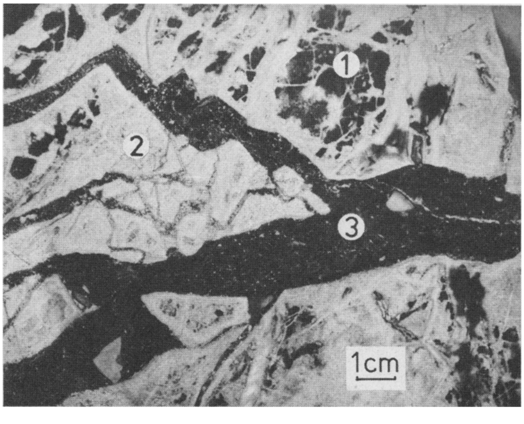

FIG. 2. Rankinite-kilchoanite-grossular hornfels (1) and alteration assemblage of wollastonite-grossular (2) cut by a wollastonite-schorlomite bearing basalt-limestone hybrid (3), Tokatoka, New Zealand.

TABLE II. *Chemical analyses of the igneous suite*

	Ia	Ib	II	III	IV
SiO_2	47.16	47.16	45.05	43.81	42.94
TiO_2	1.06	1.06	1.03	0.85	0.97
Al_2O_3	15.65	15.65	14.36	8.71	11.01
Fe_2O_3	5.74	4.55	4.81	3.38	2.67
FeO	5.08	6.29	5.87	5.64	5.03
MnO	0.14	0.14	0.18	0.15	0.13
MgO	5.17	5.17	5.7	4.77	2.28
CaO	11.8	11.8	14.53	27.85	28.11
Na_2O	2.37	2.37	1.5	0.97	1.22
K_2O	1.39	1.39	1.8	0.32	0.53
P_2O_5	0.2	0.2	0.19	0.37	0.31
S	0.07	0.07	0.42	0.18	0.26
CO_2	0.1	0.1	1.66	0.2	0.53
H_2O^+	4.4	4.4	2.8	2.43	3.28
Total	100.33	100.35	99.90	99.63	99.27
Ba		362	1660	597	1730
Cr		72	63	97	51
Cu		88	112	163	124
Ni		58	53	61	47
Pb		12	11	11	19
Rb		48	65	34	43
S		716	4220	1770	2680
Sr		726	893	3590	11000
(ppm)					
MOLECULAR NORM					
qz	0.67	—	—	—	—
or	8.68	8.67	11.12	—	—
pl	52.04	51.98	46.46	19.52	24.54
lc	—	—	—	1.60	2.67
ne	—	—	—	5.52	7.01
wo	—	—	—	22.25	32.99
di	24.44	24.41	28.25	38.66	22.64
hy	5.50	5.32	0.45	—	—
ol	—	2.27	5.77	—	—
cs	—	—	—	5.95	3.36
mt	6.34	5.02	5.26	3.73	2.98
il	1.56	1.56	1.50	1.25	1.44
ap	0.44	0.44	0.42	0.82	0.69
py	0.06	0.06	0.38	0.17	0.25
cc	0.27	0.27	4.39	0.53	1.43

I. Parent olivine basalt. Ia = Fe^{II}/Fe^{III} as analysed; Ib = Fe^{II}/Fe^{III} = 1.5.

II. Basalt showing initial effects of lime contamination.

III. Wollastonite-plagioclase-ferrosahlite intermediate hybrid.

IV. Wollastonite-ferrosahlite-schorlomite hybrid.

Approaching the vein walls, wollastonite and abundant groundmass clinopyroxene appear, largely at the expense of primary plagioclase. This zone of coexisting wollastonite and plagioclase gradually widens as the vein tapers.

In the narrower sections of the vein little remains of the primary mineral assemblage: plagioclase is absent; olivine and augite show strong resorption textures and are mantled with a second generation of clinopyroxene. The hybrid mineral assemblage consists dominantly of calcic clinopyroxene, Ti-rich andradite, and wollastonite set in a matrix of hydrous silicates.

On this basis, segments of the hybrid rock types were selected for chemical analysis and have been characterized by the following mineral assemblages and mineral chemistry. It must be emphasized that the change from parent basalt to hybrid is entirely gradational.

Wollastonite-plagioclase intermediate hybrid (chemical analysis III, Table II). The initial effects of assimilation are reflected in the pyroxene chemistry. The normally colourless or weakly coloured calcic augite is overgrown by green sahlite with compositions ranging from $Wo_{36}En_{41}Fs_2CaTs_{18}Rem_3$ to $Wo_{28}En_{30}Fs_4CaTs_{33}Rem_5$ (analyses 7–12, Table IV). The proportion of pyroxene increases at the expense of plagioclase and groundmass titanomagnetite. Close to the contact with the metamorphosed limestone, within these wider portions of the vein, laths of phenocrystal and groundmass wollastonite appear and the groundmass of the resulting hybrid is crowded with massive accumulations of green clinopyroxene subhedra ($Wo_{41}En_{37}Fs_9CaTs_9Rem_4$). The appearance of wollastonite coincides with the disappearance of all groundmass plagioclase. Phenocrystal plagioclase appears reduced in volume. However, any resorption textures have been masked by subsequent hydrothermal alteration of the feldspar rims to tobermorite.

Wollastonite-Ti-andradite-bearing hybrid (chemical analysis IV, Table II). Hybrids from the narrower veins show an increased influence of limestone assimilation. The original magmatic augite and olivine phenocrysts, still occasionally intergrown as glomeroporphyritic clots (plagioclase is notably absent) are overgrown by a strongly coloured ferrosahlite ($Wo_{32}En_{10}Fs_{21}CaTs_{24}Rem_{13}$) showing marked enrichment in the Ca-Tschermak and ferrosilite components. Olivines within the overgrowths are small (*c.*0.5 mm) and are separated from the ferrosahlite by a symplectic reaction intergrowth of magnetite and magnesioferrite. Newly crystallized pyroxenes show similarly strong zoning with pale green to green pleochroic cores ($Wo_{43}En_{24}Fs_{17}CaTs_6Rem_{10}$) and green to brown pleochroic rims ($Wo_{35}En_{13}Fs_{22}CaTs_{20}Rem_{10}$) (analyses 13–18, Table IV). Enrichment in iron to almost hedenbergite compositions at approxi-

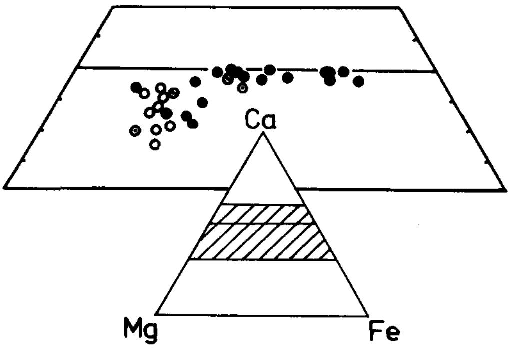

FIG. 3. Ca–Mg–Fe diagram (in atomic %) showing the iron enrichment trend of Tokatoka clinopyroxenes from the parent basalt and basalt-limestone hybrids. Symbols = ○ pyroxenes from parent basalt; ⊙ from wollastonite-plagioclase-bearing intermediate; ● from wollastonite-schorlomite-bearing hybrid.

mately constant calcium content is illustrated in terms of Ca–Mg–Fe in fig. 3. They are intergrown with each other and show morphologies ranging from subequant to almost acicular. Crystal faces are finely serrated and in places deeply embayed from incorporation of inclusions. Elongate pyroxenes may show simple twinning and hourglass and sector zoning. These features, combined with high frequency oscillatory zoning (observed in the larger crystals), suggest that crystallization was rapid and took place under conditions of local disequilibrium (cf. Nakamura, 1973). Strongly corroded and hydrothermally altered relics of plagioclase remain although these disappear in the extreme hybrids.

Wollastonite occurs occasionally as tabular phenocrysts up to 2 mm in diameter but dominantly it is found as small (*c.*1 mm) elongate laths. The iron content of the wollastonite varies considerably (analyses 1–3, Table V). Some may contain nearly 2 % iron although commonly it is less than 1 %, in contrast to wollastonite of metamorphic origin which contains less than 0.1 %. Rarely ferrosahlite exsolution lamellae of similar composition to the coexisting pyroxenes are observed within low-iron wollastonite, growing parallel to the (001) crystal face.

Crystallizing as an additional phase, the titanium-bearing andradite, schorlomite (analysis 4, Table V) forms discrete crystals and is found intergrown with wollastonite and ferrosahlite. Within wollastonite accumulations marginal to the vein walls, strongly corroded Ti-poor andradite garnets occur (analysis 5) in minor quantity. The schorlomite is rimmed with colourless hydrogrossular (analysis 6), and adjacent to the vein wall both the garnet and partially resorbed relics of wollastonite are enclosed within massive aggregates of finely crystalline hydrogrossular. The opaque mineralogy, which had up to this stage consisted of mainly magnetite and titanomagnetite, shows replacement by a sulphide assemblage of pyrrhotine and chalcopyrite.

Forming a groundmass for the pyroxene, wollastonite, and schorlomite of the hybrid basalts are a number of hydrous calcium silicates, including 11 Å tobermorite, pectolite, prehnite, cebollite, thomsonite, analcime, hydrogrossular, and possibly gismondine. Electron microprobe analyses of these minerals are given in Table V. These are largely primary late-stage hydrothermal precipitates from solutions rich in the alkalis, CaO, SiO_2, and Al_2O_3. The most abundant of these minerals is tobermorite which occurs dominantly as pale brown, low birefringence fibres, and also as plumose aggregates. It is found as monomineralic patches, bordered with small sahlite pyroxenes, indicating pseudomorphic replacement of an earlier-formed mineral (plagioclase and ?wollastonite). Pectolite and cebollite intergrow in small micaceous laths associated with tobermorite and partially replacing wollastonite. Prehnite is pseudomorphous after plagioclase and also as a direct hydrothermal precipitate. It occurs mainly as xenomorphic interstitial plates, sometimes simply twinned, and also in a fibrous, radiating form. Prehnite also appears to be in a reaction relationship with the microcrystalline tobermorite. A calcium zeolite, tentatively identified as gismondine, forms large (1 mm diameter), low relief plates and is often intergrown with thomsonite and analcime. Aggregates of grossular, rimmed with weakly birefringent hydrogrossular are found as inclusions within the gismondine. Sr- and Ba-rich zeolites (harmotome and brewsterite?) and calcite are found interstitially.

Petrochemistry

The over-all chemical trends in the Tokatoka rocks can be explained simply by diluting the original basaltic composition with appropriate amounts of siliceous limestone. A mixing programme using the least squares method of Wright and Doherty (1970) was used to combine the parental basalt composition with the intruded Eocene limestone. The results are given in Table III together with the difference between the calculated and actual composition. In many cases these differences are less than 10 % of the amount of each component of the derivative rock. High residuals exist amongst the other elements, which suggests that such an approach may be oversimplified. Difficulty in obtaining a representative sample of vein

TABLE III. *Least-squares combination of olivine basalt (analysis I, Table II) and limestone (analysis I, Table I) using the method of Wright and Doherty* (1970) *to give hybrid basalts*

	1	D	2	D	3	D
SiO_2	47.69	-2.07	42.48	2.20	42.28	2.69
Al_2O_3	15.54	-1.00	12.61	-3.72	12.49	-0.96
FeO	11.28	0.42	8.77	0.81	8.68	-0.31
MgO	5.09	0.68	3.95	0.92	3.90	-1.51
CaO	15.26	-0.55	28.04	0.37	28.53	0.91
Na_2O	2.33	-1.27	1.81	-0.82	1.79	-0.51
K_2O	1.39	0.43	1.20	-0.87	1.19	-0.63
TiO_2	1.05	-0.04	0.84	0.03	0.83	0.18
P_2O_5	0.21	-0.02	0.20	0.67	0.20	0.12
MnO	0.14	-0.04	0.11	0.27	0.11	0.03

D is difference between actual and calculated composition. All analyses recalculated to 100%. All iron as FeO.

1. Combination of 94.28 wt.% parent basalt (analysis I, Table II) with 5.72 wt.% limestone, calculated CO_2 free, approximating basalt, analysis II, Table II.
2. Combination of 70.12 wt.% parent basalt with 29.88 wt.% limestone, CO_2 free, approximating hybrid, analysis III, Table II.
3. Combination of 69.19 wt.% parent basalt with 30.81 wt.% limestone, CO_2 free, approximating hybrid, analysis IV, Table II.

hybrids or variation in the chemistry of the assimilated limestone could explain discrepancies between the real and calculated compositions. These effects would be further modified by localized fractionation of the earlier-formed mineralogy during intrusion and also by the subsequent hydrothermal episode. Nevertheless application of such a method serves to illustrate the effect of diluting a magmatic composition with the assimilated siliceous limestone. SiO_2 and Al_2O_3 show a strong depletion as the result of their expulsion into the contact marbles during emplacement of the hybrids. TiO_2 shows consistently low residuals and this probably best reflects the dilution effect. The mineralogy indicates that titanium has been relatively immobile, i.e. as the titanomagnetite was resorbed, TiO_2 was precipitated either as a pyroxene component or as schorlomite garnet. Table III also shows the calculated proportions of decarbonated limestone (analysis I, Table I) needed to produce the calculated hybrids. The amounts range from 5.7% approximating analysis II, Table II to 30.8% to generate the extreme hybrid, analysis IV, Table II.

Chemical differences exist, particularly between the two hybrid types. This reflects the strong remobilization of elements during the formation of the hybrid mineral assemblages. The alkalis and alumina are enriched in the last-formed wollastonite-schorlomite hybrid (analysis IV), relative to the wollastonite-plagioclase intermediate hybrid (analysis III) reflecting the compositions of the late-stage hydrothermal mineralogy. TiO_2 is also higher in the extreme hybrid (analysis IV), concentrated in the schorlomite and pyroxene.

Transition metal trace elements show a slight enrichment in the wollastonite-plagioclase basalt, and a strong depletion in the wollastonite-schorlomite hybrid. This reflects the relative modal proportion of pyroxene (and chalcopyrite). Notable exceptions to the dilution trend are Sr and Ba. Sr, in particular, has been strongly concentrated in the late-stage hybrid liquids, probably by a process of preferential exclusion from early-formed calcium silicates. Ba must have been mobile in the very late stage solutions because the least contaminated basalt (analysis II) shows a five-fold concentration compared to the parent basalt. Cu shows slight enrichment in the hybrid rocks, concentrated as chalcopyrite.

Discussion

Early petrologists were well aware of the influences of country rock assimilation on the composition of magmas. Wyllie (1974) has reviewed the historical aspects of the limestone assimilation theory, proposed by Daly in 1910 to account for the generation of undersaturated alkaline magmas. The hypothesis drew little support (e.g. Shand, 1930; Schuiling, 1964), and current petrologic and experimental evidence indicates that it is an unlikely process.

Bowen (1922) warned of the danger of assuming wholesale melting of country rock for, in order to accomplish this, considerable amounts of energy must be released from the igneous body. It is unlikely that magmas are ever superheated much above their liquidus temperatures. Crystallization is usually an exothermic process, and for a closed system Bowen proposed that accompanying any solution of country rock (an endothermic reaction), there must be a corresponding crystallization with the magma. The effects of the addition of calcium to the magma will initially be compensated for by the solid-solution of the crystallizing mineral phases, for example, pyroxene, so that '... the addition of sedimentary inclusions adds nothing that is not already present' (Bowen, 1922).

Watkinson and Wyllie (1969) have proposed a model for the progressive assimilation of limestone from the experimental system albite-calcite-H_2O. It involves initially the precipitation of plagioclase and wollastonite, followed by the resorption of plagioclase, precipitation of nepheline, and finally

Table IV Representative electron microprobe analyses of clinopyroxenes from the parent olivine basalt (1-6), the plagioclase - wollastonite intermediate hybrid (7-12) and the wollastonite - schorlomite bearing hybrid from Tokatoka.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
SiO_2	51.30	51.52	52.21	53.02	52.31	53.79	46.17	44.42	42.03	43.62	50.17	48.00	50.74	41.00	45.07	40.24	49.76	45.03
TiO_2	0.85	0.82	0.75	0.80	0.84	0.72	0.82	0.92	2.06	1.45	0.64	0.96	0.65	2.64	0.62	2.23	1.54	2.06
Al_2O_3	3.98	3.26	3.02	2.40	2.49	2.49	4.67	6.03	7.63	6.84	1.74	3.61	2.58	5.99	4.36	7.66	1.80	5.14
FeO*	9.91	8.35	7.88	7.04	8.55	7.10	10.82	14.36	14.72	14.16	10.08	13.40	5.68	22.16	13.32	22.81	12.10	19.52
MnO	0.27	0.28	0.20	0.15	0.28	0.42	0.22	0.20	0.11	0.22	0.51	0.24	0.17	0.28	0.20	0.25	0.27	0.25
MgO	13.17	13.98	13.17	13.73	13.71	12.42	13.90	8.22	0.16	8.39	13.40	9.74	15.61	3.94	10.39	3.49	9.83	4.44
CaO	19.48	20.28	21.78	21.84	21.09	21.75	23.88	24.75	23.12	23.90	23.50	23.18	22.96	22.84	23.98	22.32	23.66	22.61
Na_2O	0.5	0.55	0.60	0.80	0.75	1.01	0.50	0.51	0.18	0.19	0.18	0.17	0.61	0.65	0.45	0.61	0.66	0.60
Total	99.46	99.04	99.61	99.78	100.02	99.70	100.98	99.41	99.01	98.77	100.22	99.30	99.00	99.50	98.39	99.61	99.62	99.65
Structural formulae on basis of 6 oxygen atoms																		
Si	1.92	1.93	1.94	1.96	1.94	1.99	1.76	1.75	1.66	1.72	1.90	1.86	1.90	1.68	1.78	1.65	1.91	1.80
Ti	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.06	0.04	0.02	0.02	0.02	0.08	0.02	0.07	0.05	0.06
Al	0.18	0.14	0.13	0.10	0.11	0.11	0.21	0.28	0.36	0.32	0.08	0.17	0.11	0.29	0.20	0.37	0.08	0.24
Fe	0.31	0.26	0.24	0.22	0.27	0.22	0.34	0.47	0.49	0.47	0.32	0.44	0.18	0.76	0.44	0.78	0.39	0.65
Mn	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	-	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Mg	0.73	0.78	0.73	0.76	0.76	0.69	0.79	0.48	0.54	0.49	0.76	0.56	0.87	0.24	0.61	0.21	0.56	0.26
Ca	0.78	0.81	0.87	0.87	0.84	0.86	0.97	1.03	0.98	0.01	0.95	0.96	0.92	1.00	1.01	0.98	0.98	0.97
Na	0.04	0.04	0.04	0.06	0.05	0.07	0.04	0.04	0.01	0.01	0.01	0.01	0.04	0.05	0.03	0.05	0.05	0.05

*All iron as FeO

1-4 Augite-salite phenocryst, core to rim.
5 Salite phenocryst, rim.
6 Groundmass salite.

7, 8 Salite phenocryst, core and rim.
9,10 Small salite phenocryst, core and rim.
11,12 Groundmass salite.

13,14 Salite-ferrosalite phenocryst, core and rim.
15,16 Salite-ferrosalite phenocryst, core and rim.
17,18 Small salite-ferrosalite phenocryst, core and rim.

TABLE V. Representative electron microprobe analyses of wollastonite, ugrandite garnets and the hydrous mineralogy from hybrid igneous phases and calc-silicate hornfels.

	1	2	3	4	5	6	7	8	9	10	11	12
SiO_2	49.96	50.16	50.11	24.39	38.52	38.45	45.65	44.42	31.07	35.18	36.89	42.97
TiO_2	0.09	0.01	0.05	14.68	0.44	1.21	-	-	-	-	-	-
Al_2O_3	0.01	0.05	0.26	3.08	13.57	16.12	4.39	7.67	18.48	31.18	32.50	24.86
Fe_2O_3	-	-	-	25.31	10.51	4.00	-	-	-	-	-	-
FeO	1.74	0.67	0.08	0.22	0.42	-	0.01	0.06	1.36	0.03	0.02	0.11
MnO	0.32	0.16	0.10	0.01	0.05	0.09	-	-	-	-	-	-
MgO	0.28	0.31	0.06	0.15	0.38	2.69	-	-	-	-	-	-
CaO	46.87	47.70	48.62	32.68	36.85	36.76	34.75	37.02	41.06	11.16	14.02	28.99
Na_2O	-	-	-	-	-	-	8.41	0.83	0.28	4.09	3.09	0.27
H_2O (by diff.)	-	-	-	-	-	1.68	6.70	10.80	7.75	18.36	12.68	2.80
Total	99.27	99.06	99.28	100.52	100.28	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Structural formulae based on 6(0)				24(0)	24(0)	24(0)	18(0)	18(0)	18(0)	64(0)	30(0)	24(0)
Si	5.87	5.90	5.89	4.17	6.09	5.66	4.92	4.49	3.37	11.11	15.34	6.04
Ti	0.01	0.01	-	1.88	0.05	0.14	-	-	-	-	-	-
Al	-	0.01	-	0.62	2.49	2.87	0.56	0.91	2.36	11.61	15.94	4.12
Fe^{III}	-	-	-	3.26	1.23	0.46	-	-	-	-	-	-
Fe^{II}	0.15	0.06	0.01	0.03	0.06	-	0.01	0.01	0.12	0.01	0.01	0.01
Mn	0.03	0.02	0.01	-	0.01	0.01	-	-	-	-	-	-
Mg	0.05	0.05	0.01	0.04	0.07	0.61	-	-	-	-	-	-
Ca	5.90	6.02	6.14	5.99	5.99	5.95	4.02	4.01	4.77	3.78	6.25	4.36
Na	-	-	-	-	-	-	1.76	0.01	0.06	2.50	3.14	0.07
H_2O	-	-	-	-	-	1.69	4.82	7.28	5.60	38.66	35.17	2.63

Fe^{II}/Fe^{III} in analyses 4-6 have been allocated on the basis of deficiencies in the R^{3+} site. Otherwise iron is calculated as FeO.

All minerals from wollastonite-schorlomite hybrid, unless indicated.

1, 2. Wollastonite phenocrysts. 3. Wollastonite from hydrothermally altered rankinite hornfels. 4. Schorlomite.
5. Grossularite-andradite. 6. Hydrogrossular. 7. Pectolite. 8. Tobermorite. 9. Cebollite. 10. Gismondine.
11. Thomsonite. 12. Prehnite.

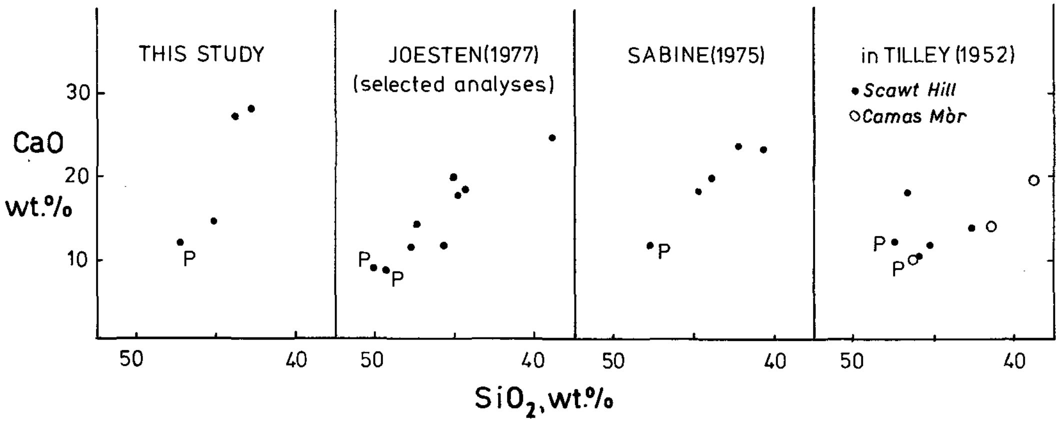

FIG. 4. Plot of CaO against SiO_2 for the Tokatoka parent basalt and basalt-limestone hybrids. Data from similar occurrences are included for comparison: Christmas Mountains (Joesten, 1977), Carneal (Sabine, 1975), Scawt Hill, and Camas Mòr (Tilley, 1952). P denotes parental igneous composition.

the solidification of a nepheline-wollastonite bearing rock.

Much of the early work on limestone syntexis was carried out by Tilley: at Scawt Hill (Tilley and Harwood, 1931), Camas Mòr (Tilley, 1947), and Ardnamurchan (Agrell, 1950). More recently, examples from Carneal (Sabine, 1975) and Christmas Mountains, Texas (Joesten, 1977) have been examined in detail. These occurrences are all associated with plutonic or hypabyssal intrusives. The Tokatoka intrusives are a high-level volcanic feeder complex and in such a dynamic system the heat flux would be expected to be constant for some length of time. Hydrostatic load during the formation of the Tokatoka hybrids was probably less than 0.5 kbar. Formation of the extreme basalt-limestone hybrids is unlikely to have occurred during the injection of basaltic liquid along fractures in the country rock. While this mechanism may be valid in the formation of the wollastonite-plagioclase intermediate hybrid, where calcic phases have crystallized marginal to the vein wall, the angular character of the fractures and xenoliths (fig. 2) suggests that little solution of the enclosing rock has taken place. To produce a hybrid rock containing as much as 30 % decarbonated limestone, it is probable that much of the calcium was incorporated prior to introduction of the hybrid into the fracture system. The shallow depth of emplacement allowed the development of a circulating hydrothermal system within the volcanics and the formation of the late-stage hydrous mineral assemblage.

Mineralogically the major difference between the Tokatoka basalt hybrids and the examples cited is that in the other cases nepheline has been reported as a late-stage mineral in association with wollastonite-bearing gabbros and pyroxenites. Fig. 4 illustrates the variation of CaO and SiO_2. The Tokatoka hybrids show the strongest enrichment in CaO and this chemical composition suggests that nepheline should occur. This is reinforced by the fact that both hybrids (analyses III and IV, Table II) show significant proportions of normative nepheline, yet the mineral is not observed in any of the rocks. Comparison of the five localities using the normative components qz-ab-ne-ks-lc (fig. 5) shows that the trend of desilication is at least comparable to the Camas Mòr and Christmas Mountains occurrences. However the undersaturated nature of the Tokatoka rocks must be accommodated by means other than the precipitation of nepheline.

Instead of recasting analysis IV (Table II) using normative components, proportions of normative minerals with compositions based on the actual mineralogy of the hybrids can be calculated. These

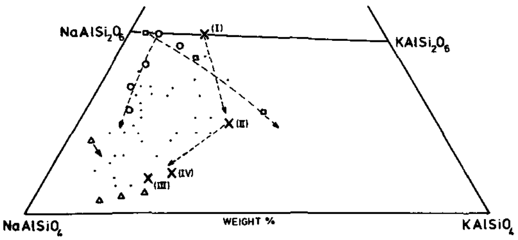

FIG. 5. Trends of increasing limestone assimilation (shown by arrows) as reflected by the normative components qz–ab–ne–ks–lc of bulk rock analyses. Symbols: × Tokatoka (subscripts refer to analyses, Table II), • Christmas Mountains (Joesten, 1977), △ Carneal (Sabine, 1975), ○ Scawt Hill, and □ Camas Mòr (Tilley, 1952).

are: schorlomite ($Ca_{5.99}Fe_{3.29}Mg_{0.04}Al_{0.62}Ti_{1.88}Si_{4.17}O_{24}$); 'average' pyroxene ($Na_{0.03}Ca_{0.98}Mg_{0.29}Fe_{0.69}Al_{0.37}Si_{1.61}O_6$); pyrrhotine, wollastonite, orthoclase, albite, anorthite, and quartz, in normal stoichiometric proportions. Although the latter four minerals are not found in the hybrid rocks they provide a simple representation of the complex hydrous assemblage. The calculation involves initially allocating all the Ti to schorlomite, plus appropriate amounts of Ca, Fe, Mg, Al, and Si. Likewise all the remaining Mg is allocated to pyroxene (with proportional amounts of Fe, Ca, Na, Al, and Si). The remaining amount of Fe equates with the proportion of sulphur, as pyrrhotine. Calculation of the remainder is in the order: albite, orthoclase, anorthite, wollastonite, quartz. This gives the following normative proportions (in wt. %): schorlomite, 11.0 %, pyroxene, 17.0, pyrrhotine, 1.6, albite, 5.9, orthoclase, 1.9, anorthite, 11.3, wollastonite, 46.5, quartz, 2.7. This method of recasting the analysis, although approximate and oversimplified, reveals that this rock contains an excess of SiO_2, although the molecular norm shows it to be otherwise.

According to the model of Watkinson and Wyllie (1969) the initial stages of limestone assimilation result in the precipitation of wollastonite and the resorption of plagioclase. As shown by Joesten (1977) the $CaAl_2Si_2O_8$ component is incorporated in the pyroxene rather than in the crystallization of an anorthite-rich plagioclase. This reaction can be summarized as:

$$\underset{\text{An component of plagioclase}}{CaAl_2Si_2O_8} + \underset{\text{component of pyroxene}}{2CaFeMgSi_2O_6} + 2CaO = \underset{\text{aluminous pyroxene}}{2CaFe^{II,III}MgAlSi_{1.5}O_6} + \underset{\text{wollastonite}}{3CaSiO_3} + \tfrac{1}{2}O_2$$

and involves a desilication of the primary igneous phases, yet does not require the precipitation of nepheline. Substitution of aluminium in tetrahedral sites in pyroxenes at the expense of silicon effectively enriches the coexisting liquid in silica, thus forming the saturated component of the hybrid. The inverse relationship of the two elements is illustrated in fig. 6*a*. The upward deviation from the line Si = Al reflects the high activity of alumina in the liquid from which the pyroxene was crystallizing. Replacement of titanomagnetite by pyrrhotine and chalcopyrite under conditions of high f_S released significant proportions of titanium and iron, again reflected in the changing composition of the clinopyroxene. The lack of coherency between Ti and Al in the hybrid pyroxenes (fig. 6*b*), in contrast to the work of Verhoogen (1962) and Joesten (1977), may be explained by rapid disequilibrium crystallization and local variations in liquid composition.

The crystallization of clinopyroxene in the early stages confirms Bowen's thesis that mineralogies will not change if chemical imbalance can be

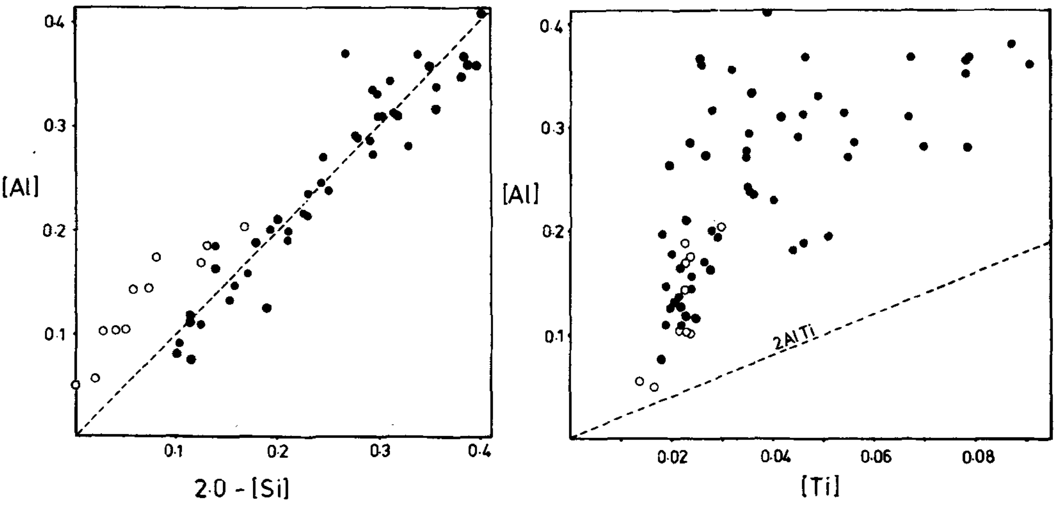

FIG. 6 (*a, left*). Plot of mineral formula proportions of Al against tetrahedral deficiency for Tokatoka igneous and hybrid clinopyroxenes, showing strong enrichment in Al in the hybrid rock types. Dashed line shows Al = 2.0-Si. (*b, right*). Plot of mineral formula proportions of Ti against Al for Tokatoka parent olivine basalt and hybrid clinopyroxenes. There is a general trend of increasing Al and Ti (at the expense of Si) with increasing assimilation. Dashed line shows the ratio of Al and Ti in the Ti-Tschermak component. Symbols = ○ clinopyroxene from parent olivine basalt, ● from basalt-limestone hybrids.

accommodated within a solid solution. The point at which chemical imbalance could not be incorporated is marked by the crystallization of other phases, notably wollastonite and garnet.

At this stage the temperatures were probably slightly submagmatic (*c.*900–1000 °C), conditions under which wollastonite can accommodate significant amounts of iron in solid solution. Subsolidus reactions result in the observed ferrosahlite exsolution lamellae in the phenocrystal wollastonite. Experimental studies of Rutstein (1971) and Matsueda (1974) conclude that below about 800–860 °C an immiscibility gap exists between hedenbergite and wollastonite. Values of 100 Fe/(Fe + Ca) for the Tokatoka wollastonite are generally low (less than 2 %) suggesting that the bulk of the wollastonite-pyroxene association equilibrated below this temperature. According to the data of Rutstein, wollastonite (analyses 1, 2, Table V) with 1.7 % FeO could form in equilibrium with hedenbergite at approximately 800 °C; wollastonite with 0.7 % FeO could crystallize at about 650 °C.

Increase in a_{CaO} and $a_{Al_2O_3}$ of the liquid is reflected both by the precipitation of aluminous calcic pyroxene and by the formation of the titanium-rich andradite. The intergrown and replacement textures of the pyroxene, garnet, and wollastonite can be represented in terms of end-members:

$$\underset{\text{titanomagnetite}}{Fe^{II}TiO_4\cdot(Fe^{II,III})_3O_4} + \underset{\text{hedenbergite}}{CaFeSi_2O_6} + \underset{\text{wollastonite}}{CaSiO_3} + CaO + 4H_2S = \underset{\text{schorlomite}}{Ca_3Fe^{III}TiSi_3O_{12}} + \underset{\text{pyrrhotine}}{6FeS} + 4H_2O + O_2$$

According to this reaction schorlomite is stabilized by low f_O. Subsequent to the crystallization of the primary hybrid minerals the hydrous calcium and sodium-aluminium silicates form a late-stage, low-temperature mineralogy. Finely crystalline, these minerals are probably the product of rapid crystallization during injection of the partly solidified liquid along fractures in the contact marble.

11 Å tobermorite, containing more than 7 % alumina, occurs as both an alteration product of remnant plagioclase and wollastonite and also as a direct precipitate from Ca-, Si-, and Al-bearing solutions. The alteration reactions can be summarized as:

$$\underset{\text{bytownite}}{10Ca_{0.7}Na_{0.3}Al_{1.7}Si_{2.3}O_8} + 7CaO + 2SiO_2 + 23H_2O = \underset{\text{tobermorite}}{Ca_8Al_2Si_{10}O_{16}(OH)_2\cdot 4H_2O} + \underset{\text{thomsonite}}{3NaCaAl_5Si_5O_{20}\cdot 6H_2O}$$

Other reactions observed within the hydrothermal assemblage are:

$$\underset{\text{prehnite}}{Ca_2Al(AlSi_3O_{10})(OH)_2} + 2Na^+ + 6H^+ = \underset{\text{gismondine}}{CaNa_2Al_2Si_2O_8\cdot 4H_2O} + Si^{4+} + Ca^{2+}$$

$$\underset{\text{tobermorite}}{Ca_5Si_6O_{18}(OH)_2\cdot 4H_2O} + 6Na^+ + 6Al^{3+} + 3H^+ = \underset{\text{gismondine}}{3CaNa_2Al_2Si_2O_8\cdot 4H_2O} + 2Ca^{2+} + 11H_2O$$

$$\underset{\text{tobermorite}}{Ca_5Si_6O_{18}(OH)_2\cdot 4H_2O} + Ca^{2+} + H_3O^+ + 4Al^{3+} = \underset{\text{hydrogrossular}}{2Ca_3Al_2Si_2O_8(OH)_4} + 2Si^{4+} + 2H^+$$

Notably absent in the Tokatoka rocks is the chemical analogue of tobermorite, xonotlite, which is commonly associated with higher pressure environments. Experimental relationships are indefinite however Mitsueda (1970) shows that xonotlite will form from tobermorite at 170–180 °C in saturated steam, while Taylor (1959) demonstrates the reaction at 380 °C and 0.25 kb under anhydrous conditions. This puts some constraints on the conditions of hydrothermal precipitation in the Tokatoka case.

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