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ZEOLITE FACIES ALTERATION OF SANDSTONES IN THE SOUTHLAND SYNCLINE, NEW ZEALAND

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ABSTRACT. Studies in a 10.4 km sequence of Mesozoic sediments in the Southland Syncline adjacent to the Taringatura district indicate that individual mineral ranges overlap even more than previously described. Laumontite, heulandite, and albite occur throughout the section, and prehnite extends from the base to within 1.5 km of the present top; analcime does not occur more than 7 km below the present top. Stratigraphically high occurrences of laumontite and prehnite are believed to have formed at temperatures as low as 50° to 100°C and 90° to 130°C respectively. Stratigraphically high occurrences of prehnite are associated with heulandite. The incoming of pumpellyite may be a useful indicator of more advanced burial metamorphic conditions, as it formed at temperatures estimated as greater than 190°C, although a case has been made for its formation at significantly lower temperatures in another area.

Sphene contains 4 to 7 wt percent Al_2O_3 and appreciable Fe_2O_3. Substantial iron is present in new-formed prehnite (up to 6 percent Fe_2O_3 on an anhydrous basis) and pumpellyite (up to 15 percent). Analyzed chloritic minerals are estimated to contain up to 20 percent interlayered dioctahedral clays. Both authigenic albite and albitized plagioclase are nearly pure albite ($Ab_{99}An_1$). Albitization in the coarser grained sandstones (avg grain size greater than 0.3 mm) tends to be more advanced with increasing depth but is also more extensive than in finer-grained rocks, irrespective of depth of burial, presumably as the result of greater porosity and permeability.

Laumontite, heulandite, prehnite. pumpellyite, calcite, interlayered chloritic minerals, and sphene are associated mainly with rocks of andesitic parentage, whereas quartz, albite, and K-feldspar characterize rocks of rhyolitic to dacitic parentage. There is evidence of mass transfer, particularly of sodium and calcium, on a microscopic and sometimes larger scale.

The zeolite facies is best regarded as a mineral facies bridging the transition from diagenesis to metamorphism and including mineral assemblages produced by processes that may be regarded as diagenetic, metamorphic, and hydrothermal. The complexity of mineral distribution patterns is attributed to the interplay of many factors, including the effects of parent materials which include glass and less highly unstable mineral relics, incomplete reactions, permeability, ionic activity ratios in stratal waters, P_{CO_2}, relationship of P_{fluid} to P_{total} in undisturbed beds and in occasional fractures, and the effects of rising temperature following deep burial. Thus heulandite has altered to laumontite and to prehnite at single outcrops, where different reaction paths were probably controlled by differences in fluid composition which are correlated with features of the host sediments. On a regional scale, complex mineral distributions can result from fluid pressure gradients increasing rapidly over short stratigraphic intervals. Assemblages of newly formed minerals in more than a quarter of the sandstones and most of the siltstones contain no zeolites and are non-diagnostic of mineral facies.

INTRODUCTION

The zeolite facies was defined by Fyfe, Turner, and Verhoogen (1958) and burial metamorphism was defined by Coombs (1961), mainly on the basis of observations by Coombs (1954) in the Taringatura Hills, Southland, New Zealand. Since then numerous discussions of burial metamorphism have appeared (for examples, see summaries by Coombs, 1971; Zen, 1974a). Judging from difficulties in mineral distributions in different areas and from the variety of interpretations that have been put forward, it is clear that burial metamorphism and the development of the zeolite facies are complex processes.

Many interpretations of the zeolite facies have stressed the importance of temperature, load pressure, and differences between load

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pressure and fluid pressure (for example Coombs and others, 1959; Seki, 1969) as well as μCO_2 (Zen, 1961; Coombs, Horodyski, and Naylor, 1970) in controlling the mineral assemblages. More recently, factors such as the activity of ions in the pore fluids have been emphasized (Surdam, 1973; Boles and Coombs, 1975; B. F. Houghton, in preparation). Reaction rates, nucleation kinetics, and irreversible reactions (compare Helgeson, 1968) are almost certainly important and will probably be better recognized in the future as experimental data become available. In this paper we will show that most of these factors have played a role in the development of the zeolite facies in the Southland Syncline, New Zealand (fig. 1).

Zeolite facies terrains throughout the world are frequently compared with the Taringatura Hills, largely because that area is one of the few stratigraphically thick sections described that is well exposed, has a relatively simple structural history, and lacks *in situ* igneous rocks. Thus

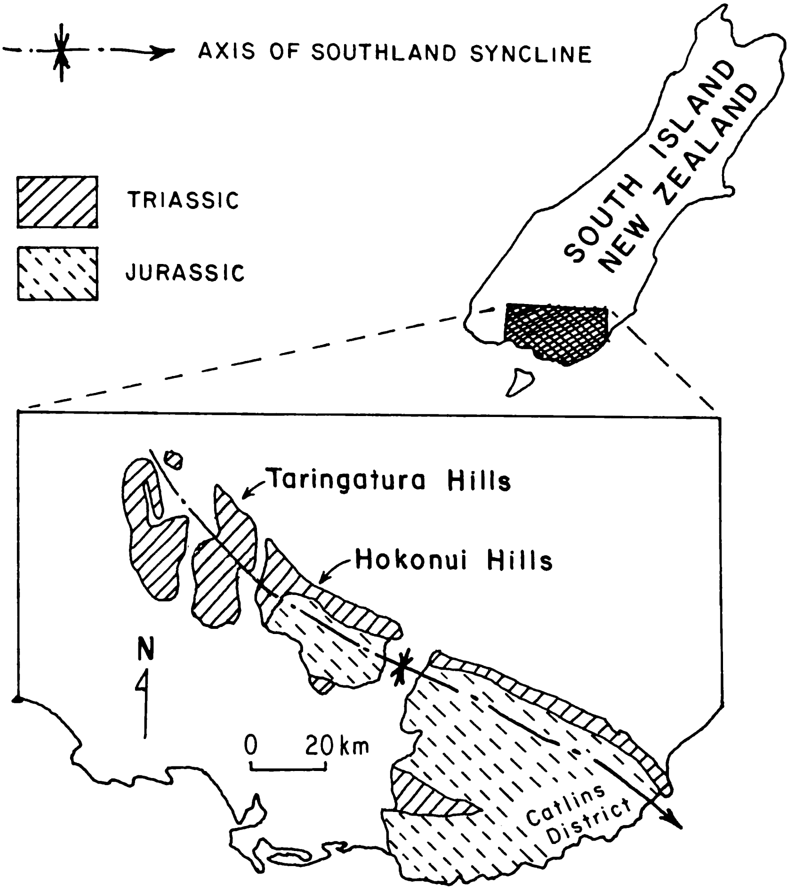


Fig. 1. Location map of Southland Syncline area, New Zealand.

temperature and pressure variations to which the section has been subjected are largely a function of initial depth of burial.

In this paper we expand the work in Taringatura to more easterly parts of the Southland Syncline in the Hokonui Hills (Boles, ms) and to a less extent in the Catlins district (Speden, 1971). These areas allow an examination of the upper part of the section not preserved in Taringatura and add considerably to knowledge of diagenesis and metamorphism in the Southland Syncline. We have recently described alteration of tuffs in the Hokonui Hills area (Boles and Coombs, 1975), and our emphasis in the present paper is on sandstones. Processes that we believe occurred at temperatures not differing materially from those of sedimentation, we will refer to as diagenetic, and those we believe occur in response to temperatures differing appreciably from those of sedimentation, we will refer to as metamorphic (Coombs, 1961).

GEOLOGIC SETTING

The Southland Syncline is an asymmetrical southeast-plunging fold in which the north limb is steeply dipping and relatively well exposed. Triassic and Jurassic rocks of the Syncline belong to the Murihiku Supergroup (Campbell and Coombs, 1966), consisting largely of detritus derived from an active volcanic arc (Landis and Bishop, 1972; Force, 1974; Coombs and others, 1976). Structure, petrochemistry, and lithologic sections of the Hokonui Hills have recently been described by Boles (1974).

The Triassic sequence thins from about 9.3 km in the Taringatura Hills to about 4.8 km in the eastern Hokonui Hills (Coombs, 1950; Watters, 1952; Boles, 1974). In contrast Jurassic strata are absent today in Taringatura, but 2.0 km, 3.2 km, and 4.6 km are preserved respectively in the western Hokonui Hills, eastern Hokonui Hills, and the Catlins district (Watters, 1952; McKellar, 1969; Speden, 1971).

The Murihiku rocks of the Hokonui Hills are composed entirely of clastic sediments of which largely volcanogenic sandstones and siltstones each make up 40 to 45 percent of the sequence with pyroclastic units and conspicuous but quantitatively minor conglomerates making up the remainder. Field relations and paleontologic evidence suggest that the depositional environment was mainly or entirely marine, except locally in mid-Jurassic times when shoaling occurred, especially in Catlins, vegetation being preserved in growth position. Local disconformities have been recognized by Wood (1956), McKellar (1969), and Force and Campbell (1974).

PETROGRAPHY OF THE SANDSTONES

The term "sandstones" will be used throughout this paper for rocks of appropriate grain size, even though some samples would be classified as "graywacke" in many classifications. Descriptions of such sandstones in the Southland Syncline are given by Coombs (1950, 1954), Watters (1952), Dickinson (1971), Speden (1971), Boles (1974), and Force (1974). The sandstones are composed mainly of volcanic rock fragments and plagioclase clasts together with subordinate K-feldspar, minor sedimentary and plutonic igneous rock fragments, and commonly some devitrified glass shards. Detrital quartz usually makes up less than 15 percent of the mode and in many samples is less than 5 percent. Clastic calcite as fossils or fossil fragments is locally important, and other detrital phases include augite, especially in andesitic volcanic sandstone, hornblende, and biotite particularly in the more acidic derivatives, and many others in accessory amounts (Brothers 1959).

Coombs (1950, 1954) and Watters (1952) recognized that volcanic clasts in some Southland rocks are markedly more "acidic" than others. Boles (1974) has shown (fig. 2) that andesitic detritus strongly predominates in sandstones of the North Range Group (lower and middle Triassic), whereas dacitic to rhyolitic detritus predominates in many rocks in the lower and middle portions of the Taringatura Group (middle and upper Triassic). Andesitic detritus again predominates in most rocks from the upper part of the Taringatura Group and in the Jurassic.

Sandstones of the Southland Syncline contain a diverse suite of new-formed minerals which occur as cements, fine-grained matrix, replacement of detrital minerals and glass shards, and as occasional joint-fillings and veins. New-formed minerals include the Ca-aluminosilicates heulandite (mostly replacing glass), stilbite (as veins), laumontite, prehnite, and pumpellyite; the Na-aluminosilicates analcime and albite; K-feldspar; phyllosilicates including smectites, chlorite, celadonite, sericite, and mixed-layer varieties; calcite and siderite; quartz, apatite, sphene, pyrite, and secondary iron oxides. Alteration is very incomplete. Except where

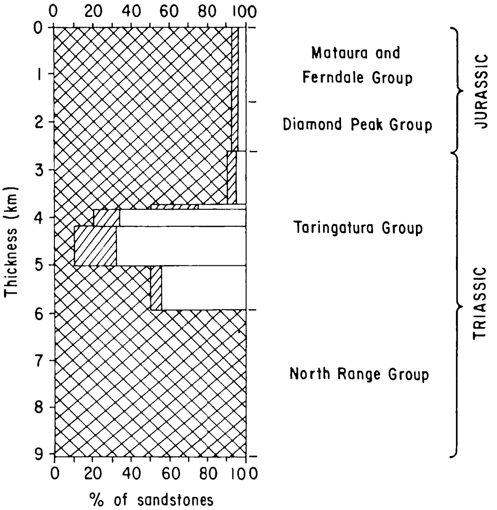


Fig. 2. Relative proportion of basic to intermediate and acidic volcanic clasts in Hokonui sandstones. Cross hatch = clasts predominantly of basic to intermediate composition; diagonal hatch = approximately equal proportions of intermediate and acidic type clasts; open area = clasts predominantly of acidic composition. Thicknesses are averaged from four sections given by Boles (1974); in the east the upper part of the section is about 1.5 km thicker than shown, and the lower part is thicker in the west.

plagioclase is thoroughly albitized, or where laumontite is particularly abundant, new-formed phases commonly make up less than 20 percent of the rock.

Quartz-lined cavities or pore spaces filled with subhedral authigenic twinned albite crystals and sometimes K-feldspar are common in Hokonui sandstones of all parentages but are particularly abundant in the more felsic sandstones. In many such cases relatively large (up to 100 μm) grains and aggregates of new-formed sphene occur on the edge of the filled cavities. Some of the "cavities" may in reality represent dissolved glass shards.

A number of andesitic sandstones have a mottled appearance in hand specimen, owing mainly to unequal distribution of chloritic and laumontite cements (Boles, 1974). In some cases dark mottles of chlorite are concentrated about argillite chips rich in iron oxides (pl. 1). Mottled sandstones have been widely recognized in volcanogenic sediments elsewhere in the world (Hoare, Condon, and Patton, 1964; Martini and Vuagnat, 1965; Horne, 1968; Madsen and Murata, 1970).

Plagioclase grains in laumontite-rich sandstones generally are albitized. However, in some of the stratigraphically highest laumontite-rich sandstones, both fresh and albitized plagioclase are present, and fresh plagioclase grains are sometimes partially replaced by laumontite (Boles, 1974, no. 12261, table 2) without albitization.

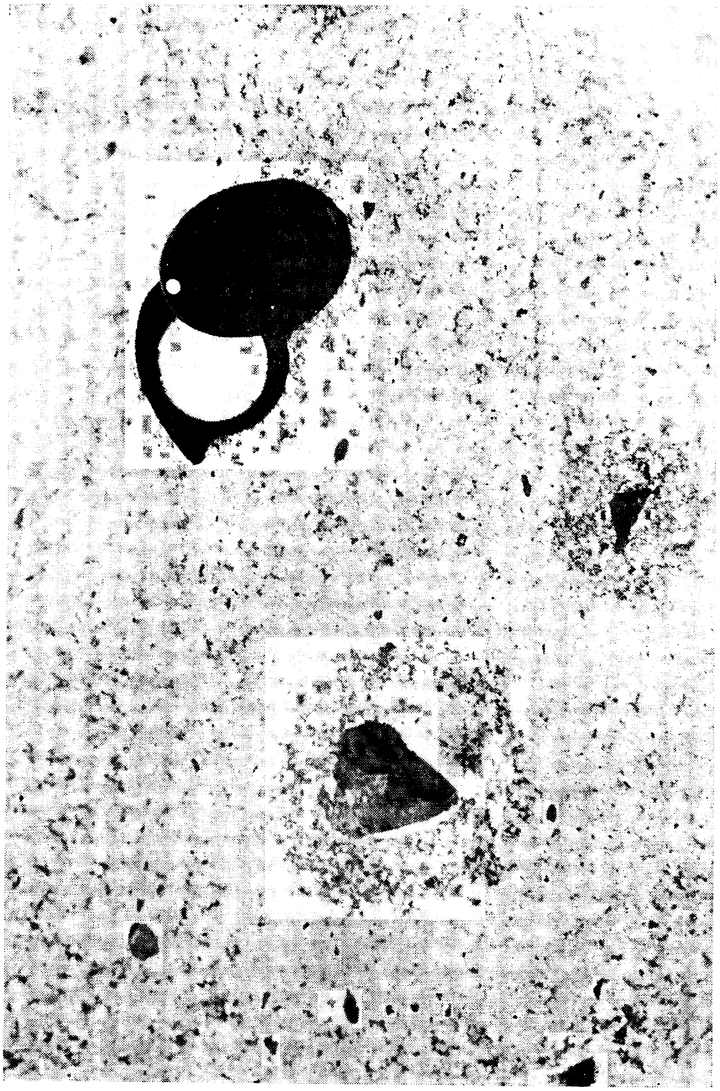
MINERAL DISTRIBUTION

In the Taringatura Hills, Coombs (1954) recognized a sequence of new-formed minerals which appeared to be related to depth of burial and hence presumably to increasing temperature. With increasing depth, first analcime, then heulandite disappear, and albitized plagioclase becomes more abundant. Laumontite, with minor prehnite and pumpellyite, is the dominant Ca-aluminosilicate below about 5.5 km but also occurs sporadically high in the section.

Much as in Taringatura, analcime does not occur more than 7 km below the top of the present section in the Hokonui area (fig. 3), pumpellyite occurs only below 5.5 km, and in sandstones of a given grainsize there is a tendency for increased albitization toward the base of the section. On the other hand, heulandite is more common in the lower (but not basal) part of the section in the Hokonui area than in Taringatura, whereas prehnite occurs higher than in Taringatura. Thus prehnite occurs in small quantities in a number of Jurassic and upper Taringatura Group andesitic sandstones only 1.5 to 3.0 km below the top of the section, and laumontite is very abundant right to the top (Griffen, ms; writers' observations) at stratigraphic levels not represented in Taringatura. Similarly in the Catlins district Speden (1971) reports veinlets of laumontite and quartz-prehnite in the False Islet Formation, the highest Jurassic unit recognized in the Catlins district.

There is a close relationship between the composition of the detrital clasts and the distribution of authigenic minerals (fig. 4). Thus new-

PLATE 1



Mottled laumontite-rich sandstone with dark mottles rich in chlorite surrounding argillite clast. Grid location S160/408726.

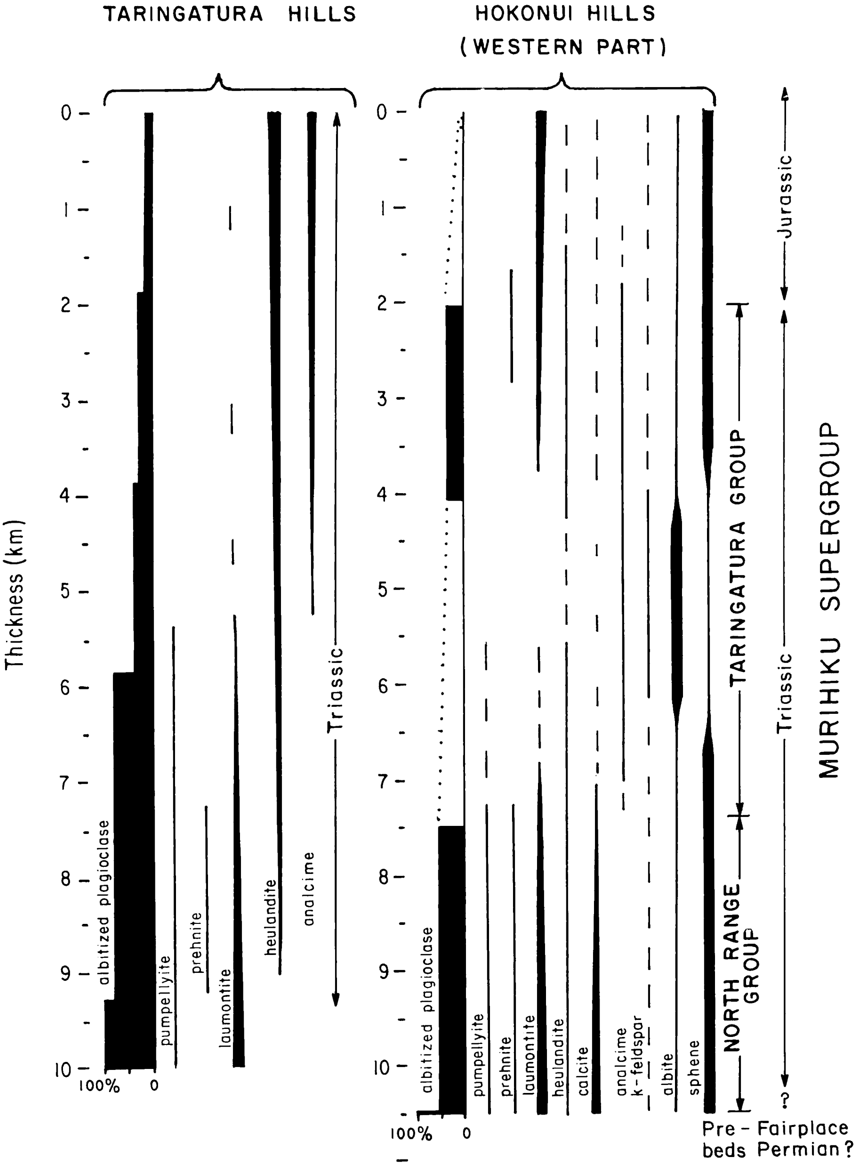


Fig. 3. Comparison of mineral distributions in Taringatura Hills (Coombs, 1954) and Hokonui Hills (this paper). Hokonui Hills "albitized plagioclase" dark area represents percentage of sandstones (0.2-0.5 mm avg grain size) with essentially all plagioclase grains albitized. Hokonui Hills "albite" refers to authigenic albite in cavities and as cement.

formed Ca-aluminosilicates, chlorite, and sphene are most abundant in sandstones rich in andesitic or basaltic clasts (Boles, 1974). Laumontite is similarly abundant in Jurassic andesitic sandstones of the Catlins district (Speden, 1971). In contrast sandstones rich in rhyolitic to dacitic clasts are characterized by abundant new-formed albite, K-feldspar, quartz, and minor chlorite and sphene. Rather similarly Stewart (1974, p. 1141) states that the presence of laumontite is closely controlled by the "presence of abundant intermediate and basic volcanic debris" in sandstones of the western Olympic Peninsula, Wash.

AUTHIGENIC MINERALOGY

The compositions of some Hokonui heulandites (Boles, 1972), analcime (Coombs and Whetten, 1967), and further heulandites and analcimes together with laumontites, "chlorites", and celadonites (Boles and Coombs, 1975) have already been described. The heulandites are of interest in ranging continuously from typical heulandite to relatively silica-poor, Ca- and K-rich clinoptilolites. In this section some additional mineral data will be presented.

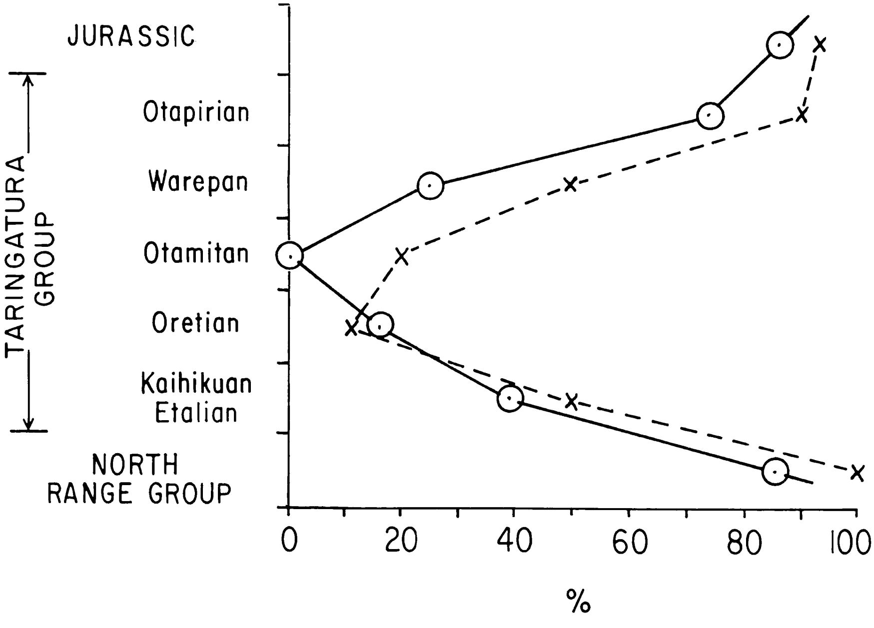


Fig. 4. Comparison between type of volcanic clast and occurrence of authigenic Ca-aluminosilicates in Hokonui sandstones. Open circles = percentage of sandstones in which predominant type of volcanic clast is basic to intermediate in composition in contrast to those in which felsic clasts predominate. Crosses = percentage of sandstones that contain one or more of the following: heulandite, laumontite, prehnite, pumpellyite. In the absence of a full set of established formational units within the Taringatura Group, counts in this part of the section have been averaged for each of the standard stages of New Zealand Triassic biostratigraphy; it is not to be inferred that sharp lithological changes occur at stage boundaries.

TABLE 1
Selected microprobe analyses of sphene,
Murihiku Supergroup, Southland Syncline

	OU30093		OU27608		OU8952
	A	B	A	B	
SiO_2	32.03	30.96	31.71	31.54	31.21
Al_2O_3	6.55	7.40	3.85	6.14	4.18
TiO_2	30.46	29.73	32.14	30.87	33.47
Fe_2O_3	0.13	0.14	1.57	1.12	2.97
MnO	0.00	0.02	0.00	0.00	0.10
MgO	0.00	0.02	0.00	0.00	0.00
CaO	28.48	27.70	27.39	28.01	27.22
Na_2O	0.00	0.07	0.02	.00	0.03
K_2O	0.02	0.03	0.01	.01	0.00
Totals	97.67	96.07	96.69	97.69	99.18
Atomic proportions, Si = 4					
Si	4.00	4.00	4.00	4.00	4.00
Al	0.97	1.13	0.57	0.92	0.63
Ti	2.86	2.89	3.05	2.94	3.23
Fe	0.01	0.01	0.15	0.11	0.29
Mn	0.00	0.00	0.00	0.00	0.01
Ca	3.81	3.83	3.70	3.81	3.74
Na	0.00	0.02	0.01	0.00	0.01
Σ cations	11.65	11.88	11.48	11.78	11.91

OU30093A,B	Stag Stream Formation, North Range Group, Hokonui Hills, Grid reference S169/647523.
OU27608A,B	Mataura-Ferndale Groups, Kelvin Peak area, eastern Hokonui Hills, S169/673434.
OU8952	Low in Taringatura Group, Wether Hill, Taringatura. S160/324754.

Sphene.—Sphene occurs as minute dusty granules in most rocks. Occasionally it forms larger crystals, 50 to 100 μm diameter, normally in association with pools of relatively coarsely crystallized authigenic albite. Such a rock is OU30093[1] from high in the North Range Group. Similarly large crystals occur very high in the Jurassic part of the section in a tuffaceous feldspathic volcarenite OU27608. The sphene is enclosed in plates of an unidentified zeolite, itself partially replaced by laumontite. Six or seven grains have been analyzed from both these rocks. Those showing upper and lower extremes of Al substitution in each case are given in table 1 together with one analysis from the Taringatura district. Sphenes of OU30093 are among the most aluminous that have been described but are unusually low in Fe. Substitution may be interpreted according to the formula $Ca(Ti,Al,Fe^{+++}) Si(O,OH,F)_5$ as discussed for sphenes of pumpellyite–actinolite facies assemblages in the Taveyanne Formation, European Alps (Coombs, Nakamura, and Vuagnat, 1976). On the arbitrary assumption of 4 Si per formula unit (table 1) the present data indicate a consistent deficiency of cations, the reason for which has not been determined. The analyses confirm that substitution of (Al,Fe^{+++}) for

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[1] OU numbers refer to catalogued specimens, Geology Department, University of Otago.

Ti, coupled with (OH) or (OH,F) for O, is characteristic of sphenes of very low grade rocks.

Pumpellyite.—Althought analyses of pumpellyite from Taringatura have not yet been published, optical data (Coombs, 1953) and unpublished microprobe data show that they are moderately to highly iron-rich. Judging from color and negative optic sign, Hokonui pumpellyites also are iron-rich varieties. Pumpellyite aggregates forming an important component of the groundmass of volcanic arenite OU30201 have been microprobed (table 2, fig. 5). Totals are erratic and in terms of cationic proportions calculated for an ideal Σ cations = 16 (Coombs, Nakamura, and Vuagnat, 1976) Si is consistently in excess of the ideal figure of 6, and Ca below the ideal 4. The latter effect might result from substitution of Fe^{++} for Ca, but the rather unsatisfactory analyses for these particular pumpellyites are probably related to the very fine-grained aggregate nature of the material analyzed. A range of pumpellyites from Taringatura and other Murihiku localities (Coombs and Kawachi, in preparation) is also plotted in figure 5. They are uniformly iron rich, and many show substitution of Fe for Al in the series trending toward julgoldite.

Values of total iron expressed as Fe_2O_3 ranging from about 10 to 23 percent (Surdam, 1969; Shimazu, Tabuchi, and Kusuda, 1971) are characteristic of the zeolite facies and perhaps of the prehnite–pumpel-

TABLE 2

Selected microprobe analyses of pumpellyite and prehnite from the Murihiku Supergroup, Hokonui Hills, Southland Syncline

	1	2	3	4	5	6
SiO_2	37.90	35.6 -38.6	46.51	44.93	43.68	43.81
Al_2O_3	20.72	19.33-21.41	17.78	19.96	20.05	21.06
TiO_2	—	0.04- 0.10	—	—	—	—
Fe_2O_3*	—	— —	1.19	3.21	5.52	5.31
FeO*	13.12	10.58-12.48	—	—	—	—
MnO	—	0.08- 0.14	—	—	—	—
MgO	3.07	2.23- 3.56	0.04	0.06	0.07	0.11
CaO	20.01	20.39-21.61	24.45	23.41	25.11	25.18
SrO	—	— —	<0.09	<0.09	<0.09	<0.09
Na_2O	0.11	0.01- 0.05	0.09	0.11	0.14	0.14
K_2O	0.02	0.02- 0.04	<0.02	<0.02	<0.02	<0.02
Total	94.95		90.06	91.68	94.57	95.61
Atomic ratios on basis of:						
	16 cations			22 oxygens		
Si	6.09		6.72	6.42	6.15	6.10
Al	3.93		3.03	3.36	3.33	3.45
Fe	1.76		0.13	0.35	0.59	0.56
Mg	0.74		0.01	0.01	0.01	0.02
Ca	3.45		3.79	3.58	3.79	3.75
Na	0.03		0.03	0.03	0.04	0.04

Analyses 1 and 2 (range in 5 other grains): pumpellyites in a volcanic sandstone OU30201, Glenure Formation, North Range Group, S160/498600.

Analyses 3 and 4: spongy prehnites; 5-6: clear prehnites; all from volcanic sandstone OU30010, North Peak Formation, North Range Group, S160/378718.

* Total iron expressed as Fe_2O_3 for prehnite and as FeO for pumpellyite.

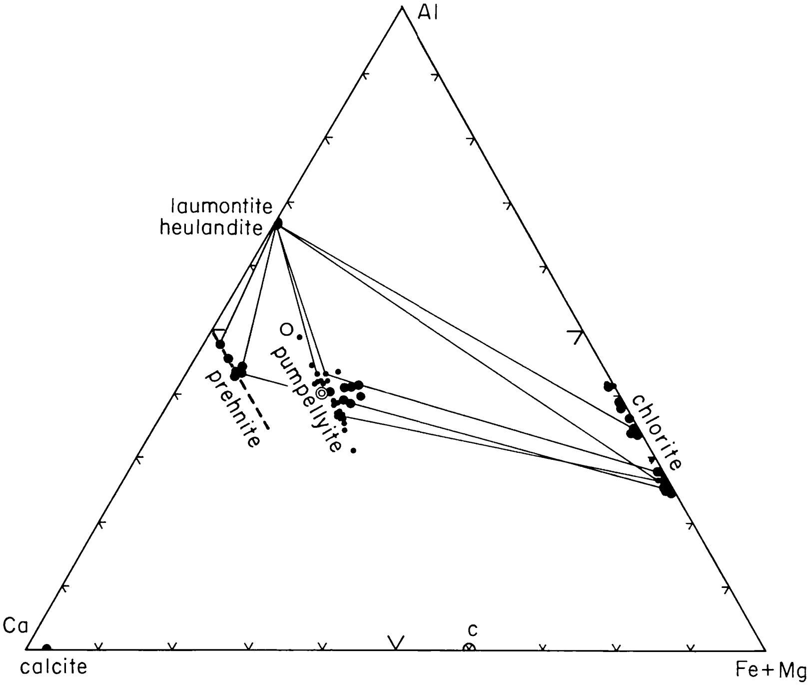

Fig. 5. Compositions of zeolite facies minerals of the Murihiku Supergroup in terms of relative atomic proportions Al:Ca: ($Fe^{2+}+Fe^{3+}+Mg$). Large filled circles: microprobe analyses, Hokonui Hills, (this study). Small filled circles: zeolite facies minerals from other Murihiku Supergroup localities (Coombs and Kawachi, in preparation). Dashed line: range of prehnite composition according to Surdam (1969). Open circle: pumpellyite—(Al) $Ca_4(Mg,Fe^{2+})AlAl_4Si_6O_{21}(OH)_7$. Double circle: pumpellyite—(Fe) $Ca_4(Mg,Fe^{2+})_{2-x}Fe_x^{3+}Al_4Si_6O_{20+x}(OH)_{8-x}$. C. Julgoldite—$Ca_4Fe_{2-x}^{2+}Fe_x^{3+}Fe_4^{3+}Si_6O_{20+x}(OH)_{8-x}$. Thin lines: typical tie lines between coexisting phases. Calcite coexists with all other minerals shown.

lyite facies in contrast to values of less than 10 percent in glaucophane-schist (for example Seki, 1961) and pumpellyite–actinolite facies (Kawachi, 1975; Coombs, Nakamura, and Vuagnat, 1976).

Prehnite.—Two varieties of prehnite are recognized in thin section of Hokonui rocks: (1) "spongy" (analyses 3 and 4, table 2) having an abundance of minute ($<1\mu m$) inclusions of low refractive index; and (2) "clear" (analyses 5 and 6, table 2) occurring as inclusion-free clusters of radiating crystals. Low summation and excess Si in analyses 3 and 4 suggest that the inclusions in the "spongy" type are in part fluid and in part silica.

Surdam (1969) and Zen (1974b) have shown that there is appreciable solid solution between the two ideal prehnite end members $Ca_2Al_2Si_3O_{10}(OH)_2$ and $Ca_2Fe_2Si_3O_{10}(OH)_2$ in low-grade metamorphic terrains. Surdam (1969) reports iron contents ranging from 0.5 to about 30 percent of the total atomic (Al + Fe) in prehnites from laumontite-, wairakite-, and pumpellyite-bearing rocks, and Zen (1974b) reports iron contents ranging from about 7 to 18 percent of the total atomic (Al + Fe) in rocks of the prehnite–pumpellyite facies from the Appalachians. The corresponding Hokonui figures are 4 to 9 percent for the spongy types and 14 to 15 percent for the clear types. Rather similar values were reported from Tanzawa Mountains by Shimazu, Tabuchi, and Kusuda (1971).

Both clear and spongy types occur as cavity fillings and as replacements of plagioclase in the Hokonui Hills. However prehnite which appears to replace heulandite, either in tuffs or in sandstones, is invariably of the spongy type, whereas prehnite occurring for example along cleavages of biotite (compare Moore, 1976) is of the clear type. The composition of these prehnites probably reflects the composition of their precursors. Alteration of heulandite or of laumontite to prehnite involves release of H_2O and silica (Boles and Coombs, 1975), and we believe that some of the H_2O and silica released was retained in the spongy prehnite as inclusions. Heulandites in the Hokonui area are relatively free of iron (Boles, 1972; Boles and Coombs, 1975) as are the spongy prehnites associated with them. On the other hand ferrian prehnites have probably acquired their relatively high iron content from iron-rich precursors or from pore solutions equilibrated with iron-bearing minerals.

Chlorite and Mixed-Layer Structures.—Analyses of chloritic minerals from the Hokonui and Taringatura Hills are given in table 3 and supplement data in Boles and Coombs (1975). Despite marked inhomogeneity within a single rock, the present and earlier analyses tend to show consistent features in each rock, for example high Al_2O_3, TiO_2, and K_2O in the "chlorites" of OU30093. As in the case of the earlier analyses appreciable CaO and in some cases K_2O and Na_2O, combined with low Σ cations and $Al^{VI}>Al^{IV}$, suggest the presence of about 5 to 20 percent interlayered dioctahedral clays. These are probably illite in K_2O-rich OU30093 and smectite or dioctahedral clorite in OU27562. The conclusion is supported by reconnaissance X-ray diffraction, glycolation, and thermal stability tests on clay fractions from a number of Hokonui rocks, mostly tuffs, which suggested that a wide range of irregular mixed layered and some regular mixed layered chlorite–smectites, chlorite–illites, and chlorite–celadonites occur throughout most of the section (Boles and Coombs, 1975). The name chlorite in this paper is to be taken as including these chloritic mixed layered structures.

Uniformly (—) optic sign, relatively high birefringence (often 0.010 to 0.025), and color which varies from light green to deep brownish green suggest that iron in the Hokonui "chlorites" is generally in part present as Fe^{+++}. However, the high birefringence must in part be due to interlayered smectites and clay micas. Thus in OU27562 the rims of the pore-fillings have higher birefringence and higher cation deficiencies, suggesting more interlayered smectite, than does the later-precipitated material which fills the cores of the voids.

OU27608, from conglomerate beds 50 m below the top of the section near Kelvin Peak. Plagioclase in this rock is partially albitized and partially replaced by laumontite, and there is an interstitial cement of impure cryptocrystalline silica. Microprobe analyses (avg of 3 grains) show SiO_2 59.36 percent, Al_2O_3 17.25, TiO_2 0.02, FeO 0.16, MnO 0.00, MgO 0.00, CaO 6.82, Na_2O 0.04, K_2O 2.00, total 86.65. This mineral possibly belongs to the stilbite group.

Calcite.—Microprobe analyses of calcite cement in volcanic sandstone OU27562 give average Ca:Fe:Mn:Mg = 96.6:0.8:2.0:0.5.

MINERAL REPLACEMENTS AND REACTIONS

We have already described a number of reactions in Hokonui tuffs that can be related ultimately to the alteration of volcanic glass (Boles and Coombs, 1975). These include hydration of glass to form clay minerals and heulandite (*sensu lato* including clinoptilolite) and dehydration and desilication of heulandite to analcime, albite, laumontite, prehnite, and calcite. Textural evidence indicates that the same reactions occurred in the sandstones. For example chlorite and less commonly heulandite occur as alteration products of the fine-grained, once glassy matrix of volcanic clasts; albite occurs as pseudomorphs after heulandite in filled cavities in a number of sandstones; a heulandite-cemented sandstone passes laterally within about 1 m into a laumontite-cemented sandstone at grid reference S169/379589, and at the same locality heulandite-filled cavities in a tuffaceous siltstone are partially replaced by prehnite + K-feldspar + quartz. Other reactions, including alteration of the voluminous clastic plagioclase and partial replacement of shell fragments are not immediately related to the former presence of glass. It is clear from the movements implied by these reactions that most ions were mobile, at least on a microscopic scale.

Albitization of clastic plagioclase.—Coombs (1954) recognized that plagioclase is more frequently albitized in coarse-grained than in fine-grained rocks. Speden (ms), Dickinson (1962), Martini (1968), and Dickinson, Ojakangas, and Stewart (1969) have also reported that albitization is inhibited by abundant matrix or calcite cement. In the Hokonui Hills there is a close relationship between the percentage of albitized grains per thin section and grain size, irrespective of stratigraphic position (fig. 6). Obviously in relating albitization to depth of burial only samples of similar grain size should be compared. The albitization reaction requires migration of Na^+ ions to the plagioclase crystal and release of Ca^{++} if no Ca-aluminosilicates form at the reaction site. The fine-grained samples presumably had relatively low initial permeabilities, and much of their original water and permeability may have been lost by compaction and/or cementation by the time albitization occurred in coarser-grained rocks.

Reactions producing laumontite.—Laumontite occurs (1) as a cement or groundmass replacement in sandstones containing completely albitized

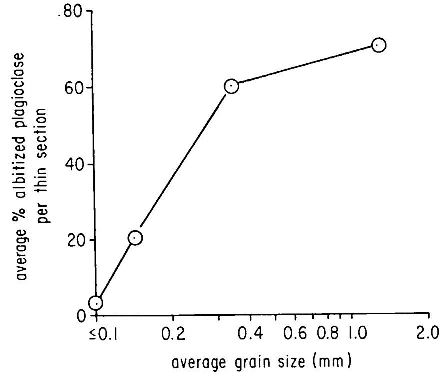

Fig. 6.

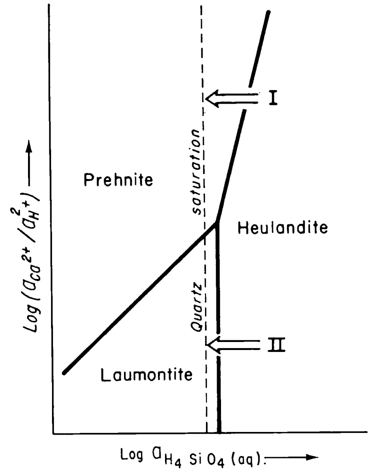

Fig. 7.

Fig. 6. Relationship between average grain size of sample and average percentage of albitized plagioclase within sample. Data from 118 thin sections of Hokonui rocks, divided into four groups according to grainsize.

Fig. 7. Activity diagram showing phase relations for laumontite, $CaAl_2Si_4O_{12}\bullet 4H_2O$; heulandite, $CaAl_2Si_7O_{18}\bullet 6H_2O$; and prehnite, $Ca_2Al_2Si_3O_{10}(OH)_2$. Arrows show direction of the most common reactions between the phases in Triassic–Jurassic rocks of the Southland Syncline.

plagioclase clasts; (2) as a component of laumontite–albite aggregates replacing calcic plagioclase; (3) jointly with finely divided quartz and authigenic Na-, K-feldspars replacing heulandite; (4) partially replacing fossil molluscs and brachiopods; (5) in occasional fracture zones where it is commonly accompanied by calcite; and (6) as a partial replacement of unalbitized feldspar clasts and/or as a cement in rocks containing unalbitized plagioclase. This latter type of occurrence, restricted to the uppermost parts of the stratigraphic column in the Hokonui Hills, appears to be relatively common in other parts of the world in sediments that have neither been metamorphosed nor particularly deeply buried, as in Eocene arkosic sandstones of the Spanish Peaks area, Colo. (Vine, 1969) and in the lower Tertiary Annick Group of the Te Anau basin of Southern New Zealand (Landis, 1974).

Replacement by laumontite of fossils and conceivably of calcite cement may be described by the reaction:

$$\begin{aligned} &CaCO_3 + 2Al^{+++} + 4SiO_2 + 7H_2O \\ &= CaAl_2Si_4O_{12}\bullet 4H_2O + CO_2 + 6H^+ \end{aligned} \tag{1}$$

Sources of Al are clay minerals and albite (as pointed out by Ivan Barnes, personal commun., 1976), the involvement of which will release Na^+ ions in solution.

In rocks where clasts of originally calcic plagioclase are partially albitized and partially replaced by laumontite, the probable reaction has the form:

$$\underset{\text{plagioclase}}{NaAlSi_3O_8{\cdot}CaAl_2Si_2O_8} + 2SiO_2 + 4H_2O$$
$$= \underset{\text{albite}}{NaAlSi_3O_8} + \underset{\text{laumontite}}{CaAl_2Si_4O_{12}{\cdot}4H_2O} \qquad (2)$$

By this reaction a volume V of plagioclase yields on equal volume of 1:1 albite–laumontite intergrowth plus 0.53V additional laumontite that is available to replace SiO_2 consumed in the reaction (0.22V if derived from quartz) together with pore space.

For those individual grains of plagioclase and larger volumes of rock in which complete albitization occurs, Na^+ ions must be received from solution and excess Ca^{++} ions are released into solution:

$$NaAlSi_3O_8{\cdot}CaAl_2Si_2O_8 + 3SiO_2 + 2H_2O + Na^+$$
$$= 2NaAlSi_3O_8 + 0.5CaAl_2Si_4O_{12}{\cdot}4H_2O + 0.5Ca^{++} \qquad (3)$$

In this case if the SiO_2 is provided by local replacement of quartz, pore space amounting to 18 percent of the volume of original plagioclase may be filled by laumontite or much more if the SiO_2 is introduced in solution. Such reactions can readily account for ratios of laumontite cement to albitized andesine approaching 1:2 in some Hokonui rocks. Production of laumontite may be expected to reduce drastically porosity and permeability in a rock and hence to impede any subsequent reactions requiring transport of ions in solution.

A considerable amount of sodium is required for reaction (3). Connate seawater, initially about 0.5 mol cm^{-3} Na^+, would have to be concentrated more than an order of magnitude to be the sole source of sodium in a closed system, but there is evidence that the stratal fluids were in fact mobile and further that sodium was released from volcanic glass altered to chlorite and calcic heulandite (Boles and Coombs, 1975). Involvement of albite in reaction (1) also releases Na^+, and there appears to be no difficulty in obtaining adequate quantities and concentrations of Na for the observed local metasomatism (Coombs, 1954).

Formation of laumontite plus quartz plus alkali feldspars by dehydration of heulandite solid solutions was described by Boles and Coombs 1975). Experimental data suggest that any heulandite–laumontite equilibrium is at a temperature not higher than 120° to 140°C at 2 kb, inferred negative slope possibly bringing the equilibrium to over 200°C at 1 kb (Thompson, 1971a), a temperature much higher that that at which laumontite is believed to have formed in the upper part of the Hokonui section. The transition does not appear to have been satisfactorily reversed experimentally (or on the basis of petrographic observations), and the existence of a true stability field of heulandite relative to laumontite plus quartz remains in some doubt.

As shown schematically in figure 7, laumontite could exist in equilibrium with a quartz-saturated fluid, while at the same T, P, heulandite could exist with solutions of higher a_{SiO_2}. Heulandite in the Hokonui and Taringatura sediments forms mainly from glass, and its silica content is a function of the silica content of the parent glass (Boles and Coombs, 1975). Laumontite cements high in the Hokonui section, like those in other areas referred to above, could perhaps form from quartz-equilibrated waters at quite low temperatures, similar to those at which clinoptilolitic heulandite formed in a high a_{SiO_2} environment controlled by glass. A similar case has been argued by Read and Eisbacher (1974) for the Sustut Group of British Columbia. Once formed, heulandite may perhaps persist metastably until its conversion to laumontite plus quartz and Na-, K-feldspars is activated by rising temperature or by lowered P_{H_2O}.

Formation of pumpellyite.—Possible closed-system reactions yielding pumpellyite in the presence of excess SiO_2 proposed by Coombs (1961, 1971) include:

$$\text{laumontite} + \text{calcite} + \text{chlorite} = \text{pumpellyite} + H_2O + CO_2 \tag{4}$$

$$\text{laumontite} + \text{chlorite} = \text{pumpellyite} + \text{clay mineral} + H_2O \tag{5}$$

$$\text{laumontite} + \text{prehnite} + \text{chlorite} = \text{pumpellyite} + H_2O \tag{6}$$

Such pumpellyite as has formed in Murihiku rocks appears to have done so largely at the expense of laumontite. Thus pumpellyite partially replaces chlorite–laumontite cement in sandstone OU30269. Celadonite is another potential source of the Mg, Fe^{++}, and Fe^{+++} in pumpellyite, and it is noticeable that pumpellyite is concentrated near the celadonite and chlorite-filled cavities in vesicular shards in quartz–albite–adularia–pumpellyite metasomatites in laumontite-rich tuffs from the North Range (Coombs, 1954). Unless the "chlorite" in eqs (4) and (5) has a high ratio $Fe^{+++}:Fe^{++}$ these equations are unrealistic for the pumpellyite compositions observed. The replacement of laumontite by pumpellyite may in fact be better represented by an open-system equation of approximate form:

$$\underset{\text{laumontite}}{2CaAl_2Si_4O_{12}\cdot 4H_2O} + 2Ca^{2+} + (Fe,Mg)^{++} + Fe^{+++} =$$

$$\underset{\text{pumpellyite-Fe}}{Ca_4(Fe^{++},Mg)Fe^{+++}Al_4Si_6O_{21}(OH)_7} + \underset{\text{quartz}}{2SiO_2} + 9H^+ \tag{7}$$

Bearing in mind the compositions of the phases revealed in the present study, reaction (6) above is also unrealistic. However, zeolite facies pumpellyite-Fe of composition closely approaching analysis 1, table 2, is chemically equivalent to ferrian prehnite plus a chloritic phase such as OU27562, table 3, according to the following equation with the proviso that the Fe++:Fe+++ ratios implied, while reasonable, are unknown:

$$\underset{\text{ferrian prehnite}}{6.6Ca_2Al_{1.6}Fe^{+++}{}_{0.4}Si_3O_{10}(OH)_2} +$$

$$\underset{\text{chloritic interlayer phase}}{Mg_{2.0}Fe_{2.6}Al_{2.0}Si_{3.2}O_{10}(OH)_8} + 1.61\ H_2O$$

$$= \underset{\text{pumpellyite-Fe}}{3.3Ca_4Mg_{0.61}Fe^{++}{}_{0.79}Fe^{+++}{}_{0.80}Al_{3.81}Si_6O_{20.6}(OH)_{7.4}} + \underset{\text{quartz}}{3.2SiO_2} \quad (8)$$

This reaction is a variant of the reaction:

$$\text{prehnite} + \text{chlorite} + \text{water} = \text{pumpellyite} + \text{quartz} \quad (9)$$

discussed by Glassley (1974) and Coombs, Nakamura, and Vuagnat (1976).

Pumpellyite would be favored in eq (8) by high P_{H_2O} and low temperature. The absence of pumpellyite and presence of prehnite high in the section might suggest a geothermal gradient dP/dT greater than that of the reaction curve or conditions $P_{H_2O} < P_{total}$. The equation potentially defines low T, low P boundary conditions for the incoming of pumpellyite in the zeolite facies. As no textural evidence for the reaction has been observed, whereas many occurrences of sparse prehnite + chlorite have been noted in the lower part of the column, further discussion will be withheld. In any case prehnite, chlorite, and pumpellyite of varying compositions can presumably coexist with quartz over a range of P,T,f_{O_2} conditions in the higher grade parts of the zeolite facies and prehnite–pumpellyite facies.

Pumpellyite is also occasionally found as small inclusions in albitized plagioclase; whether it formed directly from plagioclase during albitization or whether it replaces earlier laumontite in these rocks is not known.

Formation of prehnite.—Prehnite is perhaps most abundant in rocks of prehnite–pumpellyite facies, and its presence has sometimes erroneously been taken as definitive of that facies. However its association with zeolites is very common, and in the Hokonui Hills it occurs to within 1.5 km of the top of the preserved section, commonly in association with heulandite. Precursors of the prehnite are not always clear. However, at S169/379589 a laumontite-cemented sandstone high in the Taringatura Group contains scattered patches of heulandite and a few calcite concretions. A silty lens within the unit is cemented partly by heulandite and partly by laumontite and contains minor prehnite which is several times more abundant in the heulandite-cemented area than in the laumontite-cemented area. Underlying the sandstone is a 1 m thick, dark gray tuffaceous siltstone with numerous plant fragments, some of which are partially pyritized. The siltstone bed contains numerous tiny heulandite-filled vugs, some of which are partially or completely replaced by prehnite ± K-feldspar and quartz. Attention may also be drawn to prehnite–calcite–quartz concretions with minor heulandite in Jurassic Murihiku strata described by Speden (1971).

Differences in pore fluid composition may have played an important role in the distribution of phases at such outcrops. Following the methods of Korzhinskii (1957) and Helgeson (1967) and conserving Al in the equilibria,[2] Surdam (1973) has shown relative stability fields of prehnite, laumontite, and pumpellyite on a plot of log $[a_{\mathrm{Ca^{++}}}/(a_{\mathrm{H^+}})^2]$ versus log $a_{\mathrm{SiO_2}}$. Relative stability fields for prehnite, laumontite, and heulandite are shown similarly in figure 7 based on the following equations:

$$\underset{\text{heulandite}}{\mathrm{CaAl_2Si_7O_{18}{\cdot}6H_2O}} = \underset{\text{laumontite}}{\mathrm{CaAl_2Si_4O_{12}{\cdot}4H_2O}} + 3\mathrm{SiO_2} + 2\mathrm{H_2O} \qquad (10)$$

$$\underset{\text{heulandite}}{\mathrm{CaAl_2Si_7O_{18}{\cdot}6H_2O}} + \mathrm{Ca^{++}} = \underset{\text{prehnite}}{\mathrm{Ca_2Al_2Si_3O_{10}(OH)_2}} + 4\mathrm{SiO_2} + 4\mathrm{H_2O} + 2\mathrm{H^+} \qquad (11)$$

$$\underset{\text{laumontite}}{\mathrm{CaAl_2Si_4O_{12}{\cdot}4H_2O}} + \mathrm{Ca^{++}} = \underset{\text{prehnite}}{\mathrm{Ca_2Al_2Si_3O_{10}(OH)_2}} + \mathrm{SiO_2} + 2\mathrm{H_2O} + 2\mathrm{H^+} \qquad (12)$$

For more siliceous members of the heulandite series, the slope of the heulandite–prehnite boundary will be steeper than shown. Substitution of $\mathrm{Fe^{+++}}$ in prehnite should not affect the slopes of field boundaries defined by eqs (11) and (12) but will displace them, expanding the field of prehnite. Liou (1971a) pointed out that high $f_{\mathrm{O_2}}$ will expand the stability field of ferrian prehnite, but it is to be emphasized that the P–T field of prehnite overlaps with laumontite and heulandite independently of $f_{\mathrm{O_2}}$. From the common association of laumontite with authigenic quartz, the line of quartz saturation in figure 7 is presumed to pass through the laumontite field rather than that of heulandite.

Heulandite, initially formed from glass in a local environment of high $a_{\mathrm{SiO_2}}$, will, with falling $a_{\mathrm{SiO_2}}$, tend to convert to prehnite rather than laumontite if the activity ratio $a_{\mathrm{Ca^{++}}}/(a_{\mathrm{H^+}})^2$ is high.

In many of the pore fluids the ratio $a_{\mathrm{Ca^{++}}}/(a_{\mathrm{H^+}})^2$ may be buffered by calcite. At fixed T, P this ratio in a fluid in equilibrium with calcite is inversely related to $P_{\mathrm{CO_2}}$. Preservation of organic material and formation of pyrite suggests that pore fluids in the siltstones were relatively reducing compared to those in the sandstone, and thus $P_{\mathrm{CO_2}}$ may have been relatively low due to limited oxygen supply. Assuming that $a_{\mathrm{Ca^{++}}}/(a_{\mathrm{H^+}})^2$ was close to equilibration with calcite, then this ratio would have been higher in the siltstone than in the sandstone. Heulandite altered to prehnite (path "I", fig. 7) in the siltstone, whereas it altered to laumontite (path "II") in the sandstone. Relatively low permeabilities in the siltstone ap-

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[2] Although the common practice of conserving Al in such plots is followed here, it is to be noted that apart from relatively minor calcite and extremely sparse quartz, virtually all vein-forming minerals in the Murihiku rocks of the Southland Syncline are aluminosilicates: laumontite, stilbite, analcime, clinoptilolitic heulandite, albite, chlorite, prehnite, pumpellyite, in approximate order of decreasing abundance. Veins are admittedly a very minor phenomenon, but movement of Al in solution was evidently essential for their formation.

parently prevented P_{CO_2} from becoming homogenized with fluid in the overlying sandstone. Laumontite is less likely to alter to prehnite in the presence of waters saturated with quartz, except at higher temperatures than those prevailing in the upper part of the Hokonui section.

That stability of the heulandite–prehnite–quartz assemblage requires particularly low μ_{CO_2} relative to other low temperature calcium aluminosilicate assemblages is indicated in the μ_{H_2O}–μ_{CO_2} diagram of Coombs, Horodyski, and Naylor (1970). Thompson (1971b) calculated constraints on P_{CO_2} in very low grade metamorphism, and Ivanov and Gurevich (1975) have subsequently found that at 1 kb total pressure the maximum X_{CO_2} for laumontite stability is attained at a quartz–laumontite–prehnite–Ca-montmorillonite–calcite isobaric invariant point at 260°C, $X_{CO_2} = 0.023$. Lowering total pressure increases the equilibrium P_{CO_2}. Without giving experimental data, Ivanov and Gurevich plot four univariant curves about this invariant point and two other invariant points involving laumontite–montmorillonite–kaolinite–calcite (determined) and laumontite–heulandite–kaolinite–calcite (inferred). One of the curves plotted, laumontite + calcite = prehnite + quartz + H_2O + CO_2, is shown extending from the first invariant point to meet the temperature axis ($X_{CO_2} = 0$) at 250°C. To be topologically correct, however, this curve must curve down approaching the temperature axis asymptotically, intersecting the supposed heulandite–laumontite univariant curve to generate a further isobaric invariant point. This places very severe constraints on X_{CO_2} for the prehnite–heulandite–calcite assemblage, probably less than 0.006 at 1 kb.

MINERAL ASSEMBLAGES: APPROACH TO EQUILIBRIUM

Individual mineral grains in the Southland Syncline are of detrital, authigenic, and indeterminate origin. In addition, there is evidence that some of the authigenic minerals formed in a definite paragenetic sequence, and that coexistence may be due to incomplete reactions. Furthermore, it has been shown that in the case of heulandite, compositional variations reflect variations in the composition of the glass and pore solutions from which it formed, rather than from equilibration with other minerals (Boles and Coombs, 1975), and we have suggested in the present paper that variations in prehnite composition reflect local variations in composition of the reactants. Clearly, equilibrium has not generally been attained.

On the other hand, chemical variation of individual minerals between thin sections is commonly greater than in the one thin section, as for example in the case of the interlayered chloritic minerals described above, and it is noted that the few analyzed chloritic minerals coexisting with heulandite in the absence of prehnite are more aluminous than those coexisting with prehnite (fig. 4). Furthermore as will now be shown, assemblages of coexisting minerals are commonly rather simple. Such phenomena indicate an approach toward equilibrium, at least on the micro-domain scale.

The number of "coexisting" phases depends on the size of the domains chosen for consideration. For example in OU30331, the assemblage seen in thin section is albite–chlorite–sphene–quartz–laumontite–calcite–prehnite–pumpellyite. The dominant phases are albite (as albitized plagioclase), laumontite, and chlorite. Scattered patches of calcite are common, pumpellyite occurs in a few small patches, and prehnite as one or two grains. Thus if we examine an area substantially less than that of the thin section the most common assemblage of calcium-bearing minerals is laumontite alone or laumontite–calcite. In a few areas laumontite–pumpellyite, or laumontite–prehnite assemblages would be observed.

In analyzing prehnite–pumpellyite facies assemblages in the Appalachian belt, Zen (1974b) considered minerals to be coexisting if present in an area no larger than 1 mm diameter, showing no evidence of reaction relations, and which were not obvious relics. In general, the scale chosen for defining an assemblage of coexisting minerals should be large enough to include new-formed minerals which were in mutual communication with a uniform pore fluid but not so large as to include rocks of significantly different bulk compositions, or between which pore fluids had significant compositional gradients, or which were separated by different P–T regimes.

Bearing the above limitations in mind it is instructive to examine assemblages of coexisting minerals, where "coexisting" is used only to imply that the phases formed within the rock in question. It does not necessarily imply that the phases were in equilibrium. Our scale will be that of a conventional thin section (approx 2 × 3 cm area). On this basis we have recognized 24 assemblages of Ca-bearing phases in sandstones from the Hokonui Hills (fig. 8). Single-phase assemblages make up 55 percent of the occurrences, two-phase assemblages 31 percent, three-phase 12 percent, and four-phase 2 percent. Disregarding albite, sphene, and K-feldspar *or* celadonite which account for Na_2O, TiO_2, and K_2O respectively, assemblages with five phases or less, namely not more than 3 Ca-bearing phases + chlorite + quartz, make up 98 percent of the occurrences in these sandstones. Following Zen (1967) we may regard mixed layer structures as a single phase ("chlorite") for the purposes of this discussion. Clays are important in the tuffs and siltstones but are less important in the sandstones which are the subject of this paper. In terms of the phase rule, the phases concerned can be described by 8 components, CaO, MgO, FeO, Fe_2O_3, Al_2O_3, SiO_2, H_2O, and CO_2. Note that the low P_{CO_2} necessary for zeolite and zeolite–prehnite assemblages as discussed above in no way precludes calcite from zeolitic assemblages, and as shown in figure 8 calcite is a widespread though not especially abundant mineral in the Hokonui sandstones. Even if we assume that H_2O and CO_2 are mobile (boundary value) components, there are still 6 inert (initial value) components, which from the mineralogical phase rule, would allow up to 6 phases to coexist over a range of temperature and pressures. Thus most or all of the assemblages of new-formed minerals

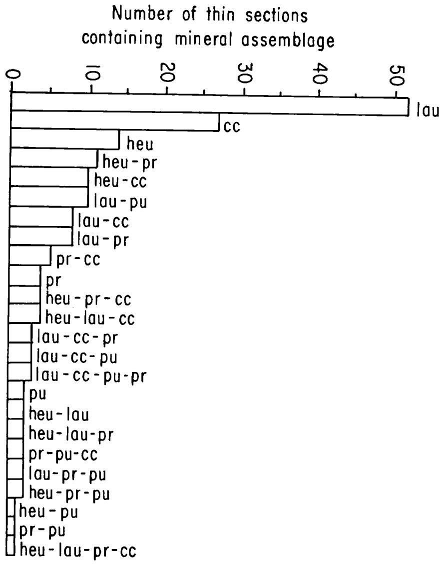

Fig. 8. Frequency of occurrence of selected mineral assemblages in Hokonui sandstones. Lau = laumontite, heu = heulandite, pr = prehnite, pu = pumpellyite, cc = calcite. Other phases include quartz, chlorite, sphene, and albite.

shown in figure 8 may represent divariant equilibrium, although some may represent buffered or incomplete reactions, and all are commonly developed in the presence of unstable relict detrital minerals.

Heulandite appears to be absent from the extreme base of the section, in which, however, vitric tuffs have not been found. One might have expected fine-grained plagioclase would have been more susceptible to albitization than coarse-grained plagioclase on account of greater surface area, but as shown above the opposite trend is observed. The supply of sodium ions to reaction sites in siltstones and very fine grain sandstones was severely limited by low permeabilities.

PHYSICAL CONDITIONS AND P_f, P_t RELATIONSHIPS

Allowing for removal of 1.5 km of overburden by erosion, we have previously shown from the lower limit of analcime occurrences that the thermal gradient in the area did not exceed about 25°C/km (Boles and Coombs, 1975). The maximum temperature for stability of analcime + quartz is taken as 190° to 200°C (Thompson, 1971a; Liou, 1971c). Our estimate of removed overburden is based on the fact that the youngest Jurassic strata (Temaikan Stage) in the Catlins district (Speden, 1971) are as much as 1 km thicker than those in the Hokonui area (McKellar, 1969), and we have also allowed for a possible additional 0.5 km. However the top of the section is eroded both in the Hokonuis and Catlins, and present evidence does not preclude the possibility of a few more kilometers of original section. But if more overburden was present, the temperature gradient was correspondingly less than 25°C/km.

The thickness of the present Mesozoic section is about 10.4 km, and the inferred maximum temperature at the base was less than 300°C, which is compatible with experimental data on the stability of laumontite (Liou, 1971b; Ivanov and Gurevich, 1975). *In situ* igneous rocks are absent, and thus the thermal gradient was probably relatively uniform throughout the area, the only likely perturbations being the result of exothermic reactions involving hydration alteration of volcanic glass, plagioclase, and pyroxene (compare Zen, 1974a) and localized enhanced transfer of heat by fluids produced during dewatering of the sedimentary pile (Norris and Henley, 1976) and moving up occasional fracture zones. Laumontite and stilbite were the most common phases to form in such fractures.

The absence of lawsonite suggests that pressures for the condition $P_{\text{fluid}} = P_{\text{total}}$ did not exceed about 3 kb (Liou, 1971b), equivalent to about 11 km depth of burial assuming an average density of 2.6g/cm³ for Hokonui rocks (Hatherton, 1966). Zen (1974a) has calculated that equilibrium for the reaction laumontite = lawsonite + 2 quartz + $2H_2O$ will be lowered at constant temperature of 200° from 2.9 kb where $P_f = P_t$ to about $P_t = 2$ kb where $P_f = 1.5$ kb. If the absence of lawsonite is not kinetically controlled, and if our measured thicknesses approximate to actual depths of burial, P_f must therefore have closely approached P_t toward the base of the section.

In the Hokonui area there are occasional cases where a phase less hydrous than that in the country rock has formed in a fracture, a phenomenon reminiscent of frequent prehnite–pumpellyite replacement of laumontite along fissures in the Taveyanne Formation of the Alps (Martini, 1968; Coombs, 1971). For example, a laumontite vein has partially replaced a heulandite vitric tuff at S160/498603; a pumpellyite vein has partially replaced a laumontite-cemented sandstone at S160/352708; an albite vein cuts an analcime vitric tuff at S169/528527. In fractures, where P_f was presumably less than P_t in impermeable neighboring rock, equilibrium could have been displaced to a less hydrous assemblage. As indicated above the heulandite–laumontite transition could also have resulted from the action of waters equilibrated with quartz, instead of with more highly soluble forms of silica, or from the heating effect of rising waters warmer than the country rock. More commonly stilbite veins cut laumontite, implying falling temperatures (Liou, 1971d).

Conditions where $P_f = P_t$ probably were attained only in the deeper parts of the section and in less deeply buried beds of low permeability. Conditions where P_f was less than P_t probably were maintained longest in relatively coarse beds of initially high permeability. In a modern analog of a regionally undeformed geosyncline, the Gulf Coast Geosyncline, fluid pressures vary widely. Essentially hydrostatic conditions ($P_f = 0.5\ P_t$) are found as deep as 5 km, but in some areas conditions where $P_f = 0.9\ P_t$ are found as shallow as 3 km (Dickinson, 1953; Jones, 1969). Fluid pressure gradients may increase gradually over a considerable depth interval, or they may increase rapidly from hydrostatic to lithostatic over a depth interval of not more than a few kilometers.

Consider a hypothetical low temperature reaction X = Y + H_2O for which equilibrium curves corresponding to P_f/P_t ratios of 0.5, 0.75, 0.87, and 1.0 respectively are as shown in figure 9. We will assume a thermal gradient of 25°C/km and that the fluid pressure gradient increases rapidly from a hydrostatic to a lithostatic gradient over a 2 km interval (path A). The change in equilibrium position as a result of changing P_f/P_t ratios could result in the following sequence: above 3.5 km, phase X; 3.5 to 5.6 km, phase Y + H_2O; 5.6 km to 7 km, phase X; and below 7 km, phase Y + H_2O. Phase X and Y could coexist stably at *three* temperatures corresponding to depths of 3.5 km, 5.6 km, and 7 km.

We conclude that during progressive burial of a sedimentary pile, gross overlap in mineral distributions may occur where dehydration reactions such as quartz + analcime to albite, and heulandite to laumon-

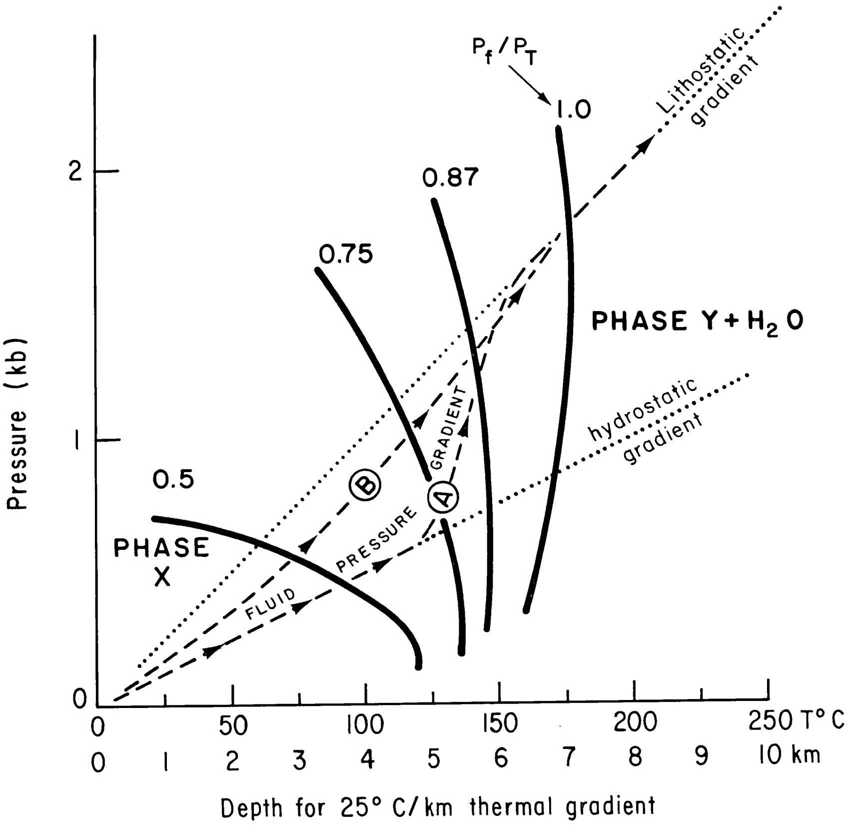

Fig. 9. Equilibrium curves for hypothetical reaction X = Y + H_2O at various P_f/P_t ratios. Also shown is a lithostatic gradient of 250 bar/km, a near-hydrostatic gradient of 125 bar/km, and two fluid pressure gradients (dashed curves A and B, see text).

tite, feldspar, and quartz, are sensitive to variations in P_f/P_t ratios, and where the fluid pressure gradient increases rapidly over a small depth interval. In cases where the fluid pressure gradient increases gradually with depth (curve B, fig. 9) overlapping equilibrium mineral distributions will not occur if the position of the equilibrium curve changes at a faster rate than the fluid pressure gradient. For curve B, phase Y + H_2O will become stable only at P_f/P_t ratio of 1.0. Obviously, if fluid pressure gradients vary from place to place, and from permeable to impermeable beds within a sedimentary basin, the resulting mineral distributions may be very complex, and furthermore fracturing, resulting in a lowered fluid pressure, may increase the complexity by promoting dehydration reactions.

Minimum temperatures of formation for laumontite, prehnite, and pumpellyite.—Laumontite occurs at the top of the Hokonui section and prehnite approaches within 1.5 km of the top. Laumontite has been reported at apparent shallow depths by Gill (1957), Otalora (1964), Hoare, Condon, and Patton (1964), Vine (1969), and Surdam (1973). However, in these cases the amount of removed overburden is not well known and/or the geothermal gradient was probably high. Seki and others (1969) report the occurrence and apparent formation of laumontite at 75 ± 5°C in the Katayama geothermal field, Japan. Castaño and Sparks (1974) describe the first appearance of laumontite at a depth of 3100 m, temperature 104°C, in Miocene to Eocene sediments in California, and at over 10 km, inferred temperature 130°C, at Cache Creek in the late Mesozoic Great Valley sequence. Merino (1975a, 1975b) reports its formation in the Kettleman North Dome, Calif., at a depth of 4 km, temperature 100°C. The coexisting stratal brines are essentially at hydrostatic pressure and are shown to be at or near equilibrium with quartz, albite, K-feldspar, mica, and montmorillonite.

Allowing for removal of 1.5 km of overburden in the Hokonui area, a mean surface temperature of 15°C, and a thermal gradient of 25°C/km laumontite, prehnite, and pumpellyite may have formed at a temperatures as low as about 50°, 90°, and 190°C respectively. As already discussed it is possible that more overburden has been removed and that the geothermal gradient was less than 25°C/km. On the other hand there seems to be no reason to suppose that the temperature of formation for the highest laumontite was any greater than the 100°C figures reported for the Californian occurrences.

It is also conceivable that the Hokonui minerals have formed at temperatures a little less than the figures given above, but we know of no good evidence that they have ever formed at surface temperatures. We consider it likely that laumontite commenced to form in the Hokonui section at temperatures in the range 50° to 100°C, prehnite 90° to 130°C, and pumpellyite at no more than about 200°C. As approximately 2 km of sandstones of rhyolitic to dacitic parentage overlie the highest pumpellyite observed, it is possible that its first appearance was retarded by relatively inappropriate whole-rock composition.

THE ZEOLITE FACIES CONCEPT

Turner's original definition of the "zeolite facies" (*in* Fyfe, Turner, and Verhoogen, 1958) was broadened by Coombs and others (1959, p. 91) and Coombs (1971, p. 324) from that of a metamorphic facies to a *mineral facies* (Eskola, 1920) so as to embrace all suites of coexisting assemblages which include various zeolite and quartz in those rocks of appropriate bulk composition, irrespective of the mode of origin, whether metamorphic, hydrothermal, or diagenetic. Some other writers following Turner, such as Winkler (1967) and Ivanov and Gurevich (1975), have preferred to restrict the concept to a metamorphic facies and have arbitrarily interpreted laumontite as "metamorphic" and diagnostic of the facies, and the heulandite group and analcime as "diagenetic" and to be excluded from the facies. We regard this distinction as overly simplistic, and we retain the broader concept.

Diagnostic assemblages of the zeolite facies are best developed in Murihiku sandstones of andesitic parentage. Intimately associated with rocks containing zeolites are other assemblages such as albite–"chlorite"–quartz–sphene ± prehnite, pumpellyite, calcite, without zeolites. Such slightly less aluminous assemblages (compare fig. 5) are compatible with the zeolite facies or with the prehnite–pumpellyite facies, or if prehnite and pumpellyite are absent, with the greenschist facies. Like the *faciès verte* of the Taveyanne Formation of the European Alps (Martini, 1968), these assemblages are non-diagnostic. Quartz–albite–K-feldspar–sphene assemblages without zeolites characterize many Murihiku sandstones of dacitic to rhyolitic parentage, although it is possible there were zeolitic precursors such as clinoptilolite and/or phillipsite. Such non-zeolitic, non-diagnostic assemblages have developed or persisted under conditions in which the diagnostic laumontite–"chlorite"–quartz assemblage was stable in interbedded rocks of appropriate composition. It is important to appreciate that even in the original zeolite facies terrain of the Southland Syncline, probably more than a quarter of the sandstones and most of the siltstones contain no zeolites.

CONCLUSION

The broadly overlapping distribution of analcime and albite and of heulandite and laumontite in the Hokonui section indicates that factors additional to temperature and pressure, as related to depth of burial, have controlled the occurrence of these phases. Incomplete reactions and alternative chemically equivalent assemblages suggest the importance of reaction kinetics and nucleation rates as controls on mineral assemblages in the diagenesis to very low grade metamorphism transition. Fluid pressure gradients are important as well as pore fluid chemistry, particularly in an open system where fluids are mobile, and in local domains in which, for example, volcanic glass may initially yield solutions of high a_{SiO_2}.

Initially, a sedimentary sequences is an open system in that pore fluids are expelled upward by continuing compaction. At this stage relatively large volumes of pore fluids can react with rock. The sedimentary pile approaches the condition of a closed system as compaction limits are reached and as cementation substantially reduces porosity and permeability. In such a closed or nearly closed system the fluid composition should eventually be buffered by the solid phases present (compare Greenwood, 1975). The system may once again become open upon fracturing, although if the rocks have very low permeability, the bulk of the fluid movement and hence potential mineralogical change will now be restricted to the fracture planes.

Hokonui rocks were at least locally open at times especially with respect to Na and Ca ions as indicated by the alteration of calcic heulandites to analcime or albite in tuffs (Boles and Coombs, 1975). Mobility of these ions is also required for the albitization of plagioclase and together with Si and Al, in the formation of vein minerals. Evidence for migration of K, Rb, Sr, and other minor elements was given by Coombs (1954). On the other hand, the fact that initial sandstone compositions, as inferred from the textures of volcanic clasts, can be related to the new-formed mineral assemblages, suggests that mass transfer was limited.

Attempts to define the zeolite facies mechanistically as a metamorphic facies characterized by the presence of laumontite, in distinction to a zone of diagenesis characterized by heulandite, are unrealistic. While some laumontite may form by reactions at temperatures of 200°C to perhaps 300°C that may generally be accepted as metamorphic, it may also form as a cement and partial replacement at temperatures as low as 50° to 100°C. We adhere to the view that the zeolite facies is best regarded as a mineral facies embracing assemblages of diagenetic, metamorphic, and hydrothermal origin.

Prehnite can form in sediments at inferred temperatures as low as 90° to 130°C; its presence virtually throughout the zeolite facies of Southland is to be emphasized. On the other hand the incoming of pumpellyite may prove to be a useful indicator of more advanced burial metamorphic conditions in the higher grade parts of the zeolite facies. In this study we estimate the lower temperature limit at which pumpellyite was formed by reactions involving laumontite and chloritic minerals to be about 190° to 200°C. Bishop (1972) estimates that pumpellyite formed at 50° to 130°C or less in sandstones of the Kyeburn Formation (Cretaceous), New Zealand. In this occurrence the pumpellyite may have recrystallized from detrital pumpellyite (Bishop, 1972, p. 249).

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