AUTHIGENIC PREHNITE, LAUMONTITE AND CHLORITE IN THE LOWER CRETACEOUS SEDIMENTS OF SOUTH-EASTERN ALEXANDER ISLAND

By R. R. HORNE

ABSTRACT. The formation of authigenic prehnite, laumontite, chlorite and epidote resulting from chemical re-organization during diagenesis in a thick sequence of tuffaceous, feldspathic marine sediments of Lower Cretaceous age in south-eastern Alexander Island is described. The development of these authigenic silicates bears no regular relationship to the structural or stratigraphic position of the host rock, but it appears to be controlled by the initial composition of the parent material (such as volcanic glass and plagioclase feldspar) and by the composition and mobility of pore solutions.

THE tectonics, slump structures and mass-flow deposits, and petrology of a thick sequence of marine clastic sediments of Lower Cretaceous age in south-eastern Alexander Island have been described (Horne 1967, 1968*a*, *b*). Certain observations made by Taylor (1966) in the Fossil Bluff area (Fig. 1) have been made available for inclusion in this paper. The highly immature arkosic and tuffaceous detrital marine sediments and associated intermediate pyroclastic rocks are post-orogenic, back-deep trough deposits associated with an early Mesozoic orogenic phase. The formation of authigenic prehnite, laumontite, chlorite and epidote in these sediments during diagenesis was widespread but both stratigraphically and geographically irregular. In some localities the complete alteration of highly tuffaceous or feldspathic horizons has resulted in the formation of almost pure prehnite and laumontite deposits.

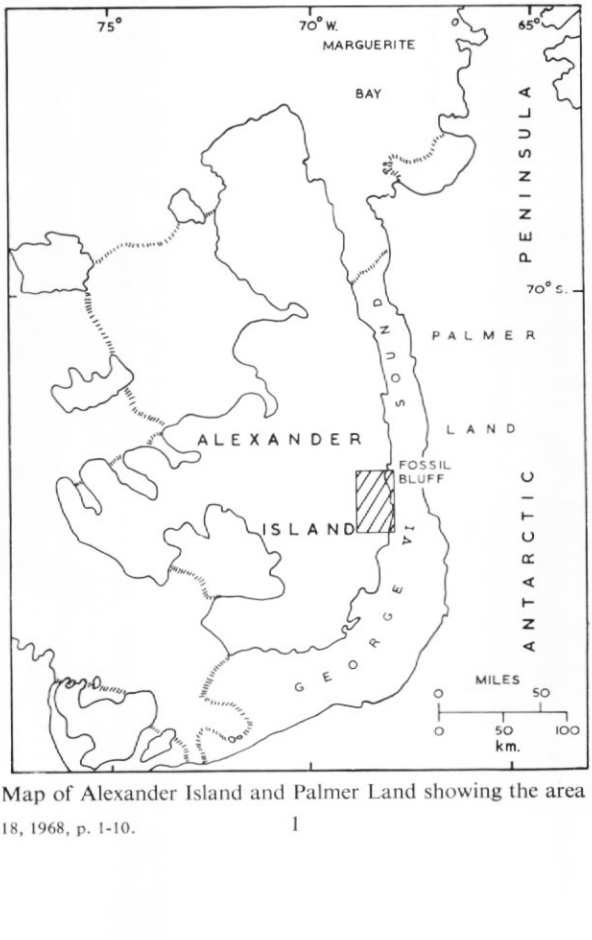

Fig. 1. Map of Alexander Island and Palmer Land showing the area studied.

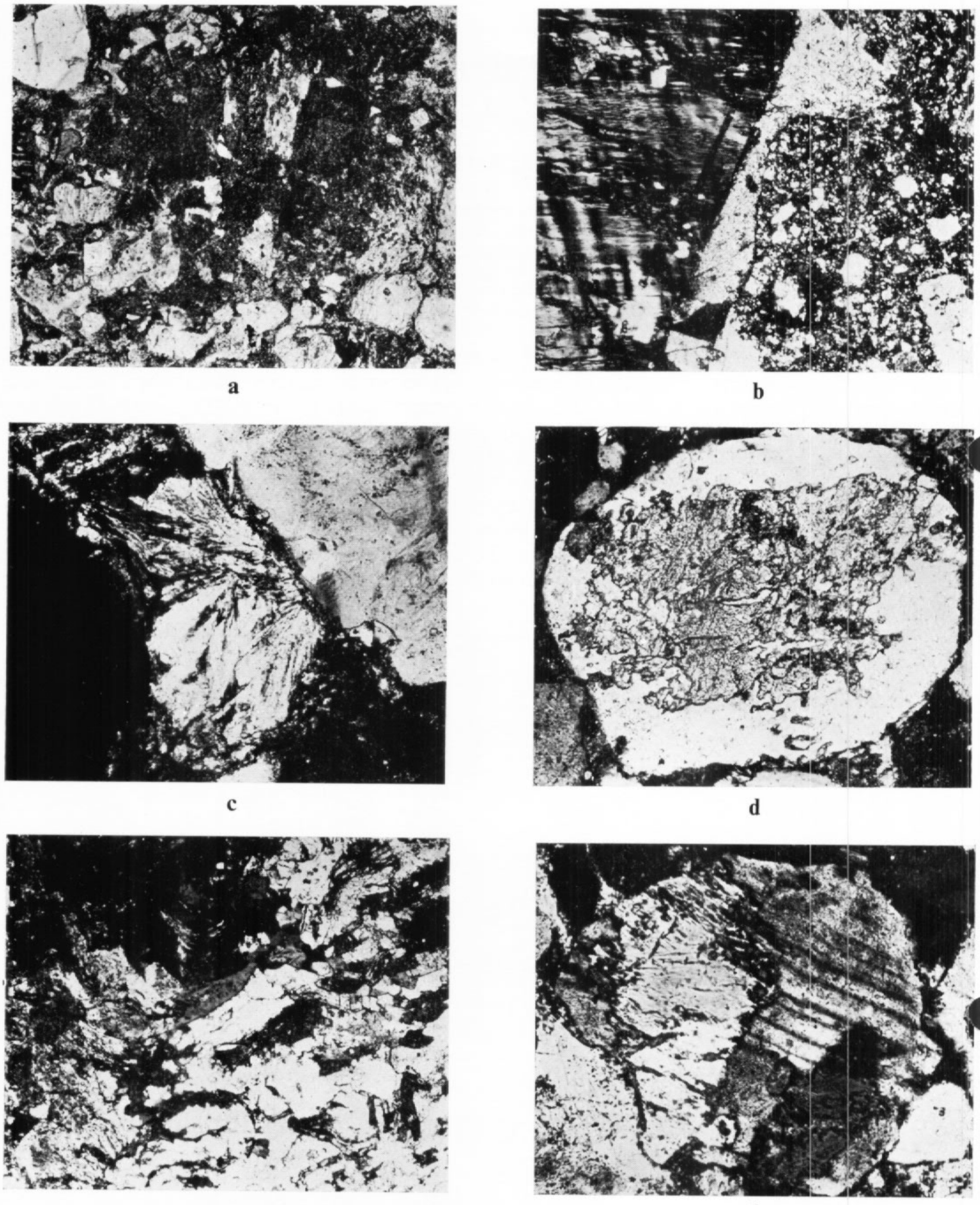

Fig. 2. a. Granular prehnite in an arkosic sandstone (KG.61.4; ordinary light; ×40).
b. Prehnite in an intergranular space (KG.78.1; X-nicols; ×40).
c. Radiating prehnite in a pore space (KG.50.2; X-nicols; ×120).
d. Optically continuous prehnite in the core of a plagioclase grain (KG.53.1; ordinary light; ×40).
e. Prehnite-biotite-quartz rock (KG.63.2; X-nicols; ×60).
f. Laumontite in a plagioclase grain (KG.70.13; X-nicols; ×120).

AUTHIGENIC MINERALS

Prehnite

Prehnite is widely distributed through the arkosic sandstones. It occurs as diffuse granular patches (Fig. 2a), in intergranular spaces (Fig. 2b), in radiating groups in pore spaces (Fig. 2c) and also as grains within plagioclase crystals (Fig. 2d). Where prehnite has formed within a plagioclase clast, it is often restricted to the more calcic cores of grains showing normal zoning (Fig. 2d), a relationship also noted by Hay (1966). Taylor (1966) observed prehnite replacing glass shards. Prehnite has also been re-deposited in narrow veinlets cutting the bedding structures of the sandstones and siltstones, and extensively within fault-breccia zones.

Although it is widely dispersed, prehnite generally forms only a small fraction of the bulk of these sediments, but one horizon that was sampled is composed of 66 per cent of a coarsely crystalline intergrowth of prehnite, 28 per cent of biotite and 4 per cent of quartz (Fig. 2e). The biotite shows little chemical alteration apart from slight bleaching in places and a tendency for its margins to be somewhat diffuse. The flakes are strongly curved, and they have been expanded and disrupted by the penetration and crystallization of prehnite along the cleavage planes. This rock probably resulted from the complete alteration of a feldspathic tuffaceous sandstone.

Whereas laumontite and calcite appear to have a broad antipathetic relationship, the association of calcite and prehnite is common. Taylor (1966) has described a pale green rock composed entirely of calcite and prehnite. Taylor (1967) also observed these minerals infilling *Zoophycus* structures.

Laumontite

Zeolite is abundantly developed in arkosic sandstones containing tuffaceous material.

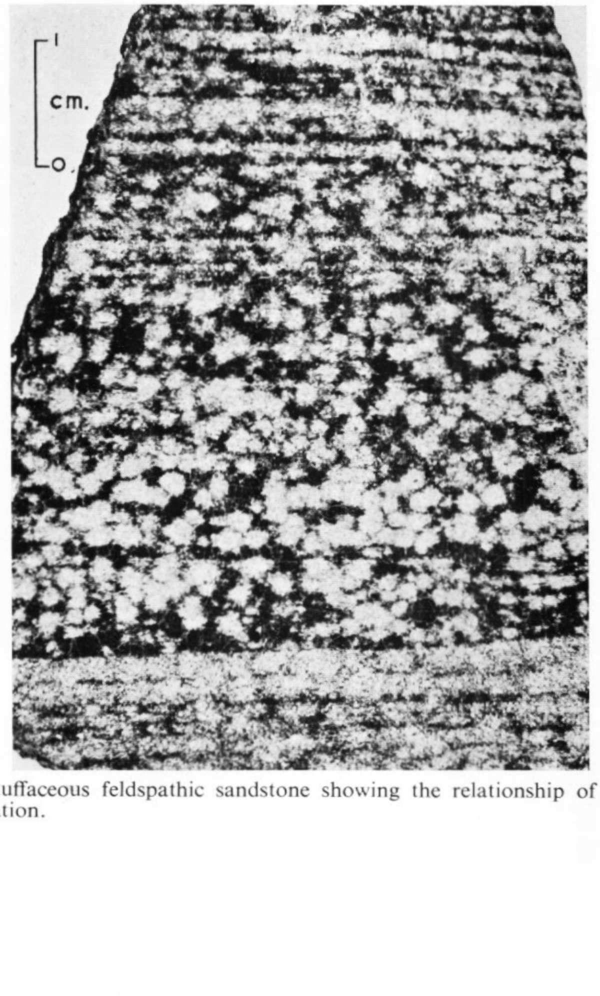

Fig. 3. Laumontitized tuffaceous feldspathic sandstone showing the relationship of the strongly zeolitized areas to the lamination.

Table I. Comparison of *d* spacings and intensities for laumontite from the Cretaceous sediments of Alexander Island and other localities

Alexander Island						*Laumontite*				*Leonhardite*	
Laumontite in zeolitized tuff (KG.72.2)		*Laumontite in mottled tuffaceous sandstone* (KG.72.7)		*Laumontite in zeolite-cemented sandstone* (KG.70.9)		Kaley and Hanson, 1955		Coombs, 1952		Coombs, 1952	
3·32	vs	—		—		3·32	vs	3·35	w+	3·36	w
4·15	s	4·15	m	4·15	m	4·16	vs	4·18	vs	4·18	vs
3·49	s	3·50	s	—		3·49	s	3·53	s	3·52	vs
3·02	mw	3·02	mw	3·02	w+	3·02	m	3·08	m	3·04	m+
2·86	w+	2·88	w+	2·86	vw	2·87	w+	2·89	w+	2·88	w+
1·810	w+	—		1·810	vw	1·808	mw	1·785	vw	1·796	vw
2·43	w+	2·43	vw	—		2·42	m	2·45	m	2·44	m
3·19	w	3·18	vs	3·20	s	3·20	vvw	3·21	mw	3·21	mw
2·56	w	2·57	w+	2·57	vw	2·56	vvw	2·60	w	2·58	m
4·72	w	4·72	vw	—		4·73	vvw	4·77	w	4·75	vw
1·548	vw	—		1·542	vw	1·536	mw	—		1·544	vvw
—		2·51	w	2·57	vw	2·52	vvw	2·51	vw	2·52	w
—		3·64	mw	3·66	mw	3·67	vw	3·67	m+	3·67	m+
—		—		1·371	w	1·37	mw	1·375	vw	1·375	vvw

Only one zeolite species has been recognized in these rocks and it has been identified on its optical properties and by X-ray analysis as laumontite (Table I). It occurs both as diffuse patches between and around volcanic fragments and as areas with sutured boundaries within plagioclase grains (Fig. 2f). In general, the degree of zeolitization seems to be related to the amount of volcanic material present. The mottling of the tuffaceous sandstones has resulted from the localization of zeolite into discrete patches (Fig. 3). Zeolitic alteration of glass is typically a solution phenomenon rather than a process of devitrification or hydration in the solid state (Hay, 1966). The zeolite is therefore located in pore spaces rather than as replacement patches in volcanic fragments. Although the reactions in which pore solutions are both actively and catalytically involved are complex, volcanic material and plagioclase appear to have been affected and altered, in the former case by total or selective solution and in the latter by substitution. It is now generally agreed that pore solutions are the agents of extensive mineralogical re-organization. This is supported by the observation that rocks, in which the porosity (and hence the mobility of these solutions) is inhibited by a fine-grained matrix or cement of early formation, have a restricted development of authigenic silicates. This effect is particularly apparent in those tuffaceous sandstones which have an abundant calcite cement.

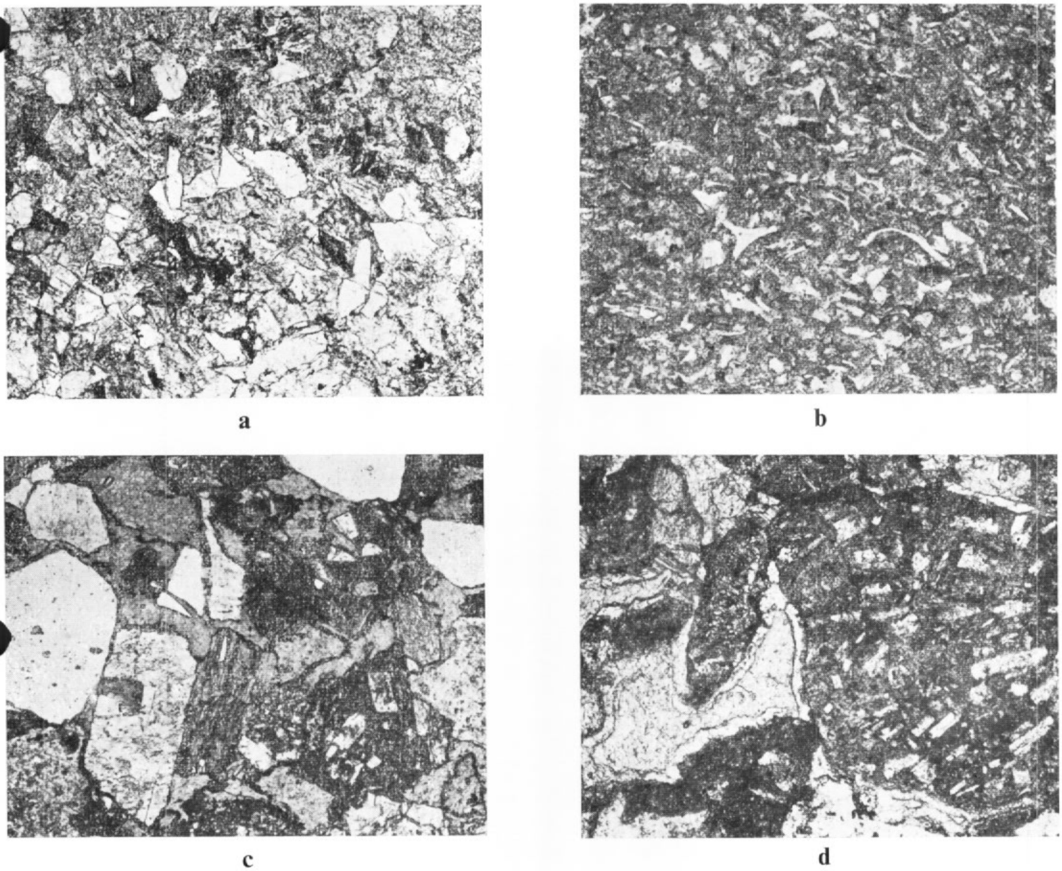

Fig. 4. a. Feldspathic sandstone with a laumontite cement (KG.70.9; ordinary light; ×53).
b. Laumontitized shard deposit (KG.72.2; ordinary light; ×53).
c. Chlorite cement in a tuffaceous feldspathic sandstone (KG.72.13; ordinary light; ×53).
d. Pore spaces in a tuffaceous sandstone infilled by rims of calcite and cores of pale green chlorite. A typical partly rounded andesitic fragment is visible at the right-hand side of the photograph (KG.71.2; ordinary light; ×60).

Hay (1966, p. 66) and Hoare and others (1964) have recorded other examples of a broad inverse relationship between authigenic silicates and calcite cement.

In a number of specimens of yellow friable sandstone from Alexander Island which are free from volcanic material the zeolite cement may be secondary (Fig. 4a).

It has already been observed that the mottling of tuffaceous sandstones has resulted from the localization of zeolite in regularly dispersed diffuse spots throughout the rock (Fig. 3). Where angular fragments of mudstone or laminated siltstone are enclosed as xenoliths in these mottled rocks, they are invariably surrounded by a lighter-coloured aureole in which the sandstone is enriched in zeolite (Fig. 5). This concentration of a secondary mineral in the rock adjacent to the xenolith may be a consequence of the dilatant effect of the xenolith on the surrounding sand, resulting in a reduction of pore pressure and the migration of zeolite-bearing interstitial solution towards the xenolith; alternatively, the rock fragment may have supplied material to the reactions forming zeolite. Identical structures have been recorded by Brown and Thayer (1963) in tuffaceous, zeolitized, marine Mesozoic sediments in Oregon. They have described "chips, slivers and slabs of black shale which are surrounded by poorly-defined, light-coloured haloes of laumontite". From the Cumberland Bay Series of South Georgia, Trendall (1959) described "bleached aureoles surrounding mudstone fragments in tuffaceous greywacke in which the tuff is more abundantly prehnitized than that outside".

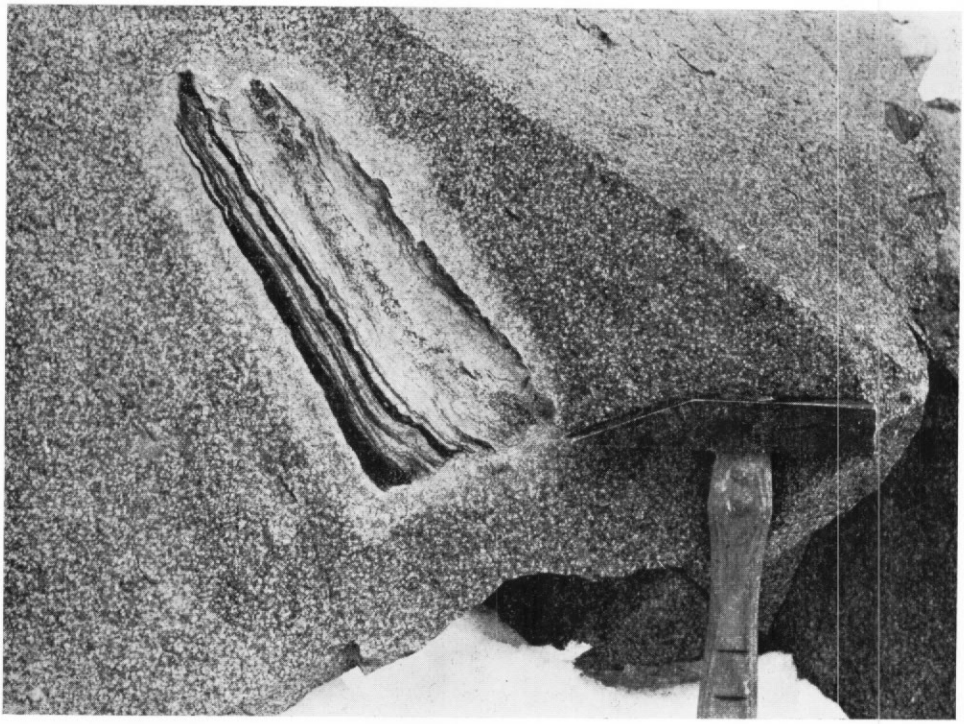

Fig. 5. A laumontite-rich aureole surrounding a contemporaneous sedimentary fragment in a zeolitized tuffaceous sandstone. The hammer shaft is marked in 2·5 cm. units.

Laumontite horizons

Although few horizons containing more than 50 per cent of prehnite were recorded, beds composed largely of zeolite are comparatively common in south-eastern Alexander Island. They are quite thin, laterally persistent beds which have a light grey colour when fresh but on weathering they develop a typical powdery chalk-like crust. These exceptional rocks are composed of small laumontite crystals which pseudomorph partly broken or cuspate glass shards, indicating that the zeolite has been produced by diagenetic alteration of a pyroclastic vitric shard deposit (Fig. 4b). The powdery white alteration product of laumontitic rocks is the dehydrated variety, leonhardite.

Similar, thin persistent beds of fine white material occur throughout the circum-Pacific post-orogenic troughs but, although they are similar in morphology and origin, they differ in mineralogy. Some are composed of montmorillonite or other clay minerals (bentonite), or various types of zeolite, or combinations of these minerals in the same beds (Mason and Sand, 1960; Iijima, 1961; Shepard, 1961; Schultz and Wright, 1963). These authors have regarded both the bentonites and the zeolite horizons as the products of diagenetic alteration of vitric tuffs in a probably alkaline, marine or non-marine environment at low temperatures and pressures. The difference in the mineralogical compositions does not depend on the difference in the physico-chemical conditions during diagenesis but on the difference in the initial chemical composition and on the influence of pore solutions.

Chlorite

In Alexander Island, authigenic chlorite is abundant in several sandstone horizons as an alteration product of both detrital hornblende and of volcanic glass and ferromagnesian minerals (Fig. 4c). Biotite appears to be very stable chemically and it rarely shows alteration to chlorite. One unusual rock which is black in the hand specimen contains almost 50 per cent of chlorite as an intergranular cement or matrix between volcanic fragments (Fig. 4d).

Epidote

In several sandstone horizons small grains of weakly pleochroic lemon-yellow epidote are developed within and around plagioclase grains.

Pumpellyite

Pumpellyite, a common mineral in other prehnitized sedimentary sequences in the circum-Pacific region, has not yet been recognized in any of the Alexander Island sediments that have been studied.

ZEOLITE FACIES

In their memoir on metamorphic reactions and metamorphic facies, Fyfe and others (1958) observed that "with decreasing temperature and pressure metamorphic crystallization should theoretically merge into diagenesis of sediments". They have suggested that rocks characterized by minerals which are stable at low temperatures in an aqueous environment, such as zeolites, adularia, albite and quartz, should be grouped under the term "zeolitic facies". They recognized, however, that regional zeolitization is only achieved "under exceptionally favourable circumstances". Sediments bearing authigenic mineral assemblages typical of this facies had previously been described in outline by Coombs (1954) from Southland, New Zealand. A comprehensive account of this proposed facies, transitional between cementation and the greenschist facies of metamorphism, was based on field investigations in the Taringatura District, Southland, New Zealand, and on a laboratory study of glasses and oxide mixes of appropriate composition (Coombs and others, 1959). Although admitting the "profound influence of starting materials on reaction products in hydrothermal synthesis", a progressive replacement of successive assemblages of hydrous calcium silicates with increasing temperature and pressure as a consequence of low-grade, isochemical load metamorphism was proposed. These assemblages were defined in terms of zeolites such as laumontite and heulandite, and analcite, prehnite, pumpellyite and epidote. They include a lowest-grade heulandite-analcite-quartz assemblage which is succeeded downwards by a laumontite-albite-quartz assemblage. These are underlain in turn by prehnite-quartz or pumpellyite-quartz assemblages which are transitional into the greenschist facies.

The significance of this concept of a zeolite facies defining a restricted grade of regional metamorphism at low temperatures and pressures has required modification as a result of recent studies in other areas, and the concept of sub-facies defined by different authigenic mineral assemblages has been completely abandoned. Factors such as the close correlation with depth in the succession, i.e. with limited pressure-temperature conditions, the apparently minor influence of bulk composition and the inferred approximation to bulk equilibrium, which were in evidence in the New Zealand rocks, have been found lacking to a greater or lesser degree in other areas of regional zeolitization and prehnitization, particularly in a number of circum-Pacific after-deep troughs.

In the Koyukuk geosyncline of western Alaska, a sequence of tuffaceous sediments of Cretaceous age with a composite thickness of 8,000 m. has been extensively laumontitized, the detrital feldspar being totally albitized (Hoare and others, 1964). Despite thicknesses and bulk lithology corresponding to those of New Zealand, no prehnite-bearing facies is in evidence here. Similar contrasts were observed by Brown and Thayer (1963) in late Triassic to early Jurassic sediments in the Aldrich Mountains of Oregon. They concluded that, although the albitization of plagioclase appears to have a distinct correlation with depth in the succession, the "distribution of laumontite, prehnite and pumpellyite seems to be governed much more by the initial composition of the rocks than any other obvious factors". Just to the south-west of the Aldrich Mountains, in the Izee District, Grant County, Oregon, 5,800 m. of Jurassic, tuffaceous marine sediments, stratigraphically overlying the Aldrich Mountains sequence, contain an intermingled authigenic assemblage of prehnite, pumpellyite, heulandite, laumontite, chlorite, and both albitized and unaltered plagioclase (Dickinson, 1962). In this case equilibrium has not been achieved in a bulk sense and Dickinson emphasized the controlling influence of interstitial water. The tuffaceous sandstones of the late Mesozoic Yahgan Formation of Navarino Island, southern Chile, which has a thickness of about 3,000 m., show extensive development of prehnite and the albitization of calcic plagioclase, but no zeolites have been formed (Watters, 1965).

Similarly, in the Cretaceous sediments of south-eastern Alexander Island no regular relationship exists between the development of authigenic silicates and the stratigraphical and structural environment of the host rock. Both vertically and laterally, prehnite and zeolite occur together throughout the upper 3,000 m. of the succession studied so far. In both the New Zealand and Alexander Island successions, prehnite and laumontite have a broadly antipathetic relationship. In New Zealand, however, the prehnite- and laumontite-bearing facies have developed at different levels in the succession, whereas in Alexander Island the horizons with prehnite and those with laumontite alternate irregularly throughout the succession, indicating that oscillatory compositional variation rather than regionally gradational pressure-temperature conditions controlled the distribution of these minerals. In Alexander Island no acidification of intermediate plagioclase is recognized even in andesine crystals which are themselves partly altered to prehnite or laumontite.

DEVELOPMENT OF ZEOLITES AND PREHNITE

As a result of these and numerous other recent studies, the literature on zeolitization and prehnitization of tuffs and tuffaceous sediments has become very extensive and the data presented are often confused and somewhat conflicting. Nevertheless, a number of factors controlling the formation of authigenic silicates, consistent with the observations in Alexander Island, is becoming generally accepted.

At low temperatures and pressures, authigenic hydrated calcium silicates, such as zeolites, prehnite, analcite, epidote and clay minerals, are common alteration products of tuffaceous feldspathic sandstones which lack an extensive clay matrix. Pure, pumiceous, basic vitric tuffs are most susceptible to this form of alteration. From a tabulation of recorded occurrences of authigenic minerals in tuffaceous sediments by Deffeyes (1959), it can be seen that the interplay of controlling factors is very critical and the resulting rock can be composed of one of several zeolite species (clinoptilolite, laumontite, heulandite, etc.), or one of several clay mineral species (montmorillonite, illite, etc.), or any combination of these in association with prehnite and unaltered tuff. In the literature there are also records of the alteration of pyroclastic material to glauconite, stilpnomelane, apophyllite, etc.

The porous, friable and intimately mingled nature of the components of tuffs and tuffaceous sandstones accelerates the otherwise slow reactions at low temperatures. High rates of sedimentation, such as occurred in this and other after-deep troughs in which great thicknesses of tuffaceous zeolitized sediments have accumulated, enhance reactivity due to high porosity and freedom of circulation of connate pore solutions.

Prehnite and zeolites can form at all temperatures below approximately 300–350°C, at which value they are theoretically superseded by assemblages typical of the greenschist facies. They appear to be stable up to pressures of at least 3,000–4,000 bars (Fyfe and others, 1958).

Influence of the Parent Material

A close relationship appears to exist between the composition of the host rock and authigenic assemblages in marine and fresh-water tuffs that have not been deeply buried (Hay, 1966, p. 65). However, in more deeply buried sequences which are inferred to have been subjected to higher temperatures and pressures, and in strongly saline lake environments, mobility and reactivity of the various phases are more significant and the influence of initial composition is less obvious.

The preferential prehnitization of the calcic cores of zoned plagioclase grains in the Alexander Island sediments emphasizes the critical influence of initial mineral and pyroclast composition in this sequence. Prehnite, laumontite and epidote are authigenic silicates coexisting with quartz but favoured neither by silica deficiency nor silica saturation (Coombs and others, 1959, p. 75). The Cretaceous sandstones of south-eastern Alexander Island have quartz : feldspar ratios of the order of 1 : 4 (Horne, 1968*b*), and hence quartz is neither abundant nor deficient.

Influence of Connate Solutions

The hydrothermal alteration of volcanic glass by solutions of varying compositions and concentrations has been studied experimentally by Sudo and Matsuoka (1959). Digestion of glass in solutions of sodium chloride and sodium hydroxide at normal temperatures and pressures resulted in the formation of sodalite and a zeolite mineral. At a higher salinity, proportionally more sodalite than zeolite formed. Hay (1966) recognized the possibility of a relationship between the salinity of a depositional basin and the formation of authigenic albite. In a discussion of the diagenetic alteration of the Belly River Formation in the Rocky Mountains foothills in Alberta, Lerbekmo (1963) stated that "restriction of the albitization to the lower and upper parts of the formation is believed due to the availability of sodium . . . the lowest and highest sandstones of the formation were probably deposited in at least brackish water while the middle part of the formation was probably laid down in more nearly fresh water."

Evidence will be presented in a subsequent paper to show that the salinity of the offshore shelf area of the Alexander Island depositional trough was reduced by the influx of river currents. The entrapped connate water in the sediments, therefore, would be low in sodium but relatively rich in calcium, conditions favouring the formation of a calcic zeolite but inhibiting the albitization of plagioclase.

Conclusions

The development of prehnite, laumontite, chlorite and epidote in the tuffaceous feldspathic sediments of south-eastern Alexander Island is a result of the diagenetic alteration of intermediate to basic plagioclase, tuffaceous fragments and ferromagnesian minerals. The distribution of these authigenic mineral species appears to be controlled by the composition of the parent material and by the composition of the connate solution phase. Reduced salinity of the marine environment, the abundance of calcic plagioclase and free calcium carbonate, the lack of quartz and the intermediate to basic composition of the volcanic material favoured the development of a silica-deficient calcic zeolite (laumontite) and prehnite, but inhibited the formation of sodic zeolites and the albitization of plagioclase.

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