Diagenesis in Early Miocene Waitemata Group sediments, Upper Waitemata Harbour, Auckland, New Zealand(MEMORIAL VOLUME TO THE LATE PROFESSOR TERUHIKO SAMESHIMA)

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Diagenesis in Early Miocene Waitemata Group sediments, Upper Waitemata Harbour, Auckland, New Zealand

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Abstract The Waitemata Group in the Upper Waitemata Harbour area is a turbidite sequence with interbedded volcaniclastic sandstones, rhyolitic granule-sand and tuff horizons, and conglomerate lenses containing metamorphic, volcanic, plutonic and sedimentary clasts. Clastic debris in the sediments is little altered except for devitrification of volcanic glass. Zeolites and clay minerals encrust clastic grains and fill pores. There is a strong lithologic control on diagenetic assemblages. Lithic-rich sandstones poor in volcanic debris have calcite cement. Volcaniclastic sandstones have zeolite cement with the paragenetic sequence clinoptilolite (+ mordenite) → chabazite and/or erionite, and finally rare analcime. Rhyolitic granule-sand horizons contain the paragenetic sequence analcime → clinoptilolite → chabazite and/or erionite. Conglomerate horizons, which frequently lack any vitric debris, have analcime cement. In rhyolitic tuff only mordenite occurs crystallising directly from devitrified glass shards. Clay minerals present are smectite and illite, and chlorite in highly altered volcaniclastic sediments. Interbedded mudstones sealed fluids into volcaniclastic sandstone and tuff horizons and diagenesis occurred in a closed hydrologic system. The original pore fluid, believed bicarbonate-rich, precipitated calcite cement in the absence of vitric debris. In volcaniclastic and vitric rocks devitrification of glass liberated alkalies and silica into pore fluids leading to crystallisation of zeolite. Conglomerates filling channels cut into other sediments were an open hydrologic system and analcime crystallised from Na-saturated fluids flowing through them.

Key words: zeolites, analcime, rhyolitic tuffs, volcaniclastic sediments, Waitemata Group, New Zealand.

INTRODUCTION

Early Miocene Waitemata Group clastic sediments outcrop over large areas of the Auckland Region (Fig. 1A). They rest unconformably either on the Northland Allochthon (Ballance & Spörli 1979) or on the basement rocks of the North Island – the Permian to Jurassic metagreywackes and enclosed ocean floor material of the Waipapa terrane. The Waitemata Group sediments are all marine and are believed to have been deposited in a rapidly subsiding extensional basin in an intra-volcanic arc environment (Ballance 1974; Hayward 1979, 1993; Ricketts *et al.* 1989). They also represent the last significant period of Tertiary sedimentation and in the Northland – Auckland region are stratigraphically overlain only by sediments of Quaternary age.

The stratigraphy (Ballance 1976), sedimentology (Ballance 1974; Ricketts *et al.* 1989) and the heavy mineral content (Hayward & Smale 1992) of the Waitemata sediments are now well known. Basal and early sediments appear to have been derived entirely from the local Waipapa Group basement rocks. However, study of the clastic material contained in the Waitemata sediments (Hayward & Smale 1992) has shown that the bulk of the succession was largely derived from two main sources: (i), allochthonous rocks of Cretaceous-Oligocene age (Tangihua Volcanics and sedimentary rocks of the Northland; Allochthon) which outcrop over much of central Northland; and (ii), the contemporaneous and largely andesitic arc volcanism (Fig. 1A). The predominant sediments in the older part of the Waitemata sequence are flysch type and derived largely from the older allochthonous rocks. Locally, rhyolitic tuffaceous and pumiceous horizons occur interbedded in the sedimentary sequence. Basic-intermediate volcanic-derived sedi-

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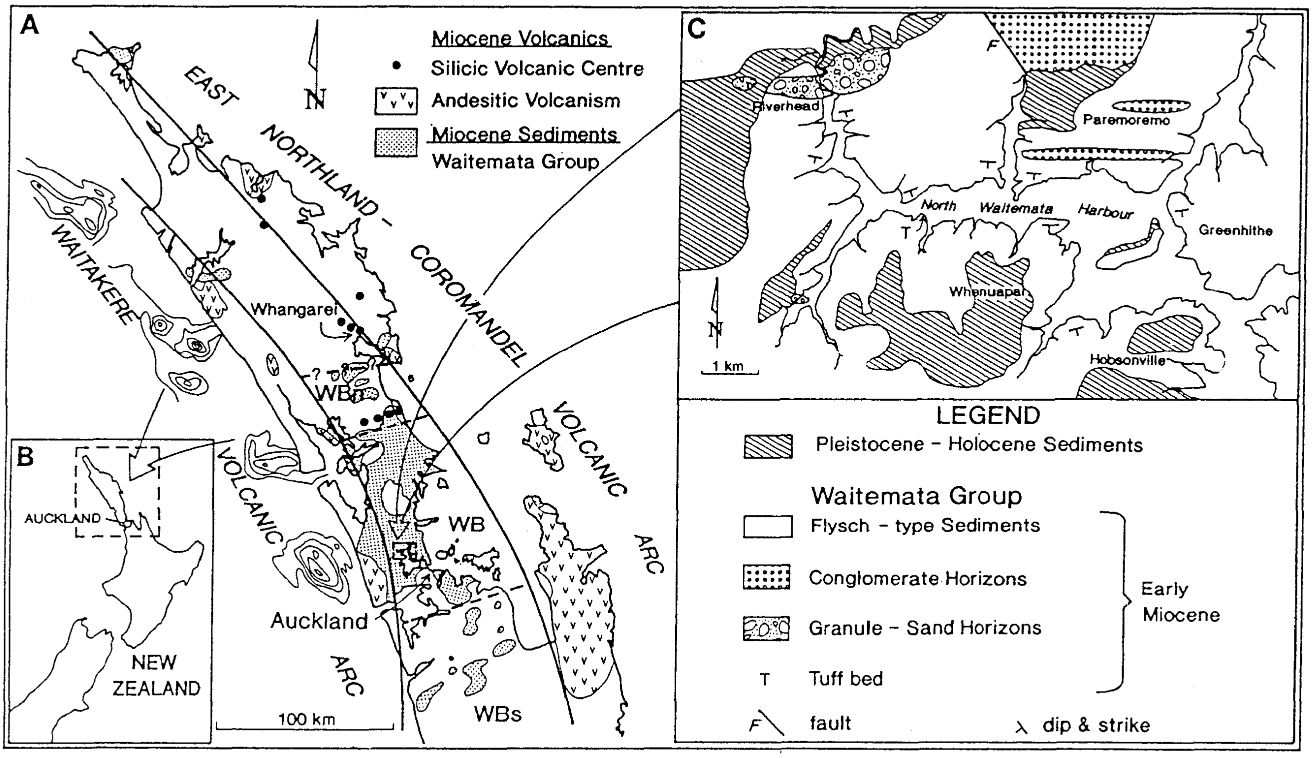

Fig. 1 1A = Map showing distribution of early to mid Miocene rocks in northern New Zealand including the positions of the parallel volcanic arcs. Lines indicate the eastern and western limits of volcanics belonging to the Waitekere and Northland-Coromandel Volcanic arcs respectively. Offshore contoured positive magnetic anomalies (Davey 1974) delineate probable centres of the Waitekere Volcanic Arc. The Waitemata Basin is an elongate interarc basin with northern (WBn) and southern (WBs) shelf facies separated by a deeper water facies (WB). 1B = inset map showing location of Fig. 1A. 1C = simplified geology of the Upper Waitemata Harbour area.

ments, apparently sourced in the west (Waitakere Group Volcanics), interdigitate with and later overstep the typical flysch sediments and airfall tuff layers. The Waitemata Group sediments have been subjected to two syn-basinal phases of thrusting and folding, a post-basinal phase of gentle regional tilting and a late block faulting phase (summarised in Hayward 1993). They show negligible burial "metamorphic" effects and indeed lack evidence for any major postdepositional compaction but, as may be expected for a young volcanogenic sequence, most of the sediments are diagenetically altered.

Professor Teruhiko (Terry) Sameshima was the first to systematically investigate diagenetic minerals in the Waitemata Group. He recognised and described the widespread occurrence of zeolites in the volcaniclastic and tuff horizons of the Waitemata succession and published a paper recording and presenting mineralogical and chemical data for analcime, clinoptilolite, chabazite, erionite, mordenite and phillipsite (Sameshima 1978). In this paper Terry also highlighted some unusual features of the Waitemata Group zeolitisation which included the first records of chabazite and erionite in marine sediments. He also noted that all the zeolites were, in general, Si-poor varieties of the individual mineral species. The characterisation and potential uses of the zeolitised Waitemata tuff horizons remained one of his major research interests during his Auckland years.

In this paper we examine the diagenetic processes in a variety of Waitemata Group sediments in the Upper Waitemata Harbour area with particular emphasis on understanding the distribution of diagenetic minerals and the paragenetic relations between the zeolite minerals. The study was part of a Masters thesis (Davidson 1990ms). During the course of the thesis Terry Sameshima gave considerable help with X-ray diffraction methods and identification of zeolites and the clay mineralogical techniques used were those had been developed by him. This paper is dedicated to the memory of Terry Sameshima as an acknowledgement of his work and the stimulation he provided which encouraged others to work on zeolites and zeolitised tuff horizons in the Auckland-Northland area.

WAITEMATA GROUP SEDIMENTS OF UPPER WAITEMATA HARBOUR AREA

There are no basement rocks exposed in the upper Waitemata Harbour area. The rocks outcropping are Waitemata Group sediments belonging to the Paremoremo Facies of Schofield (1989). They are believed to have a thickness of the order of 4000 m (Schofield 1989) and are stratigraphically overlain only by Pleistocene sands, peats, ashes and muds which form terrace deposits on the Miocene sediments. The Waitemata Group sequence is stratigraphically upright with a broad regional tilt to the south.

Waitemate Group strata in the Upper Waitemate Harbour area can be divided into five distinct lithofacies:

(i) A well bedded flysch sequence composed of alternating thin sandstones and mudstones which are interpreted as a marine turbidite facies (Ballance 1974). The turbidite sandstones are largely litharenites composed dominantly of clasts of sedimentary (argillaceous) debris but with variable amounts (0 to 60%) of volcanic lithic material which is typically a fine-grained basaltic andesite. The inter-turbidite siltstones are mineralogically very similar, differing only in that they are laminated and have carbonaceous matter concentrated in the laminations. The turbidite sequence is considered by Hayward & Smale (1992) to have been largely derived from Tangihua Volcanics and sediments of the Northland Allochthon.

(ii) Interbedded with the more usual sedimentary lithic-rich and mixed turbidites are occasional thin (<0.5 m thick) poorly sorted, ungraded medium to coarse grained volcanic sandstones. Lithologically they are composed of angular, highly altered basaltic to andesitic clasts and detrital mineral grains removed from them. The source of the volcanic material is believed to be the Manukau Volcanic Centre of the Waitakere Volcanic Arc which is situated approximately 15 km to the west (Davidson 1990).

(iii) A 100 m thick series of well cemented, laterally extensive, granule-sand beds, usually individually no more than 300 mm thick. This horizon is localised in the Riverhead area (Fig. 1C). The dominant lithic clast in the granule-sand beds is rhyolite (60-80%) with minor siliceous mudstone and biotite as the major detrital mineral constituent. A petrographic survey of all known mid to late Tertiary silicic volcanics has shown that only the rhyolite domes in the Brynderwyn-Mangawhai area (Pukeroro Dacites of Hayward 1993), 30 km south of Whangarei (Fig. 1A), contain abundant phenocrystal biotite and since sedimentary structures also indicate an origin for the rhyolitic debris from the north (Davidson 1990), we presume that the Brynderwyn-Mangawhai rhyolite domes are the source of the silicic volcanic debris.

(iv) Massively bedded conglomerates which occur in distinct horizons in the lower (north) parts of the stratigraphic sequence (Fig. 1C). They belong to the Albany Conglomerate facies, the oldest of three conglomerate facies recognised in the Waitemata Group (Hayward 1993). Each conglomerate horizon in the Upper Waitemata Harbour area has its own distinctive lithologic constitution. Two of the conglomerates were studied in detail – the Paremoremo and Riverhead conglomerates (Fig. 1C). The Paremoremo conglomerate outcrops as a series of crosscutting channel infillings composed of unconformably bedded lenses, each of which has a width along strike of up to 20 m and a maximum thickness of 1 m. The lenses contain pebble to boulder sized clasts of andesitic material (>80%) with minor (<5%) rhyolitic clasts, <5% material derived from the Waipapa Group and rare diorite and scoriaceous basalt fragments. The Riverhead conglomerate horizons are contained within the rhyolitic granule-sand horizon as channel fills of pebble-size clasts of weakly to low grade metamorphosed (greenschist) basic volcanics and dolerite derived from Tangihua Volcanic massifs.

(v) Although silicic vitric tuff horizons are known in many areas of Waitemata Group and are particularly notable in the Kaipara region (Sameshima 1978), only one has been recorded in the Upper Waitemata Harbour region. This tuff occurs as a discrete, 0.8 m thick, fine grained, cemented horizon conformably interbedded with flysch beds in the estuary south-east of Riverhead (Fig. 1C). The tuff is highly sorted and is composed of silicic glass shards and feldspar grains and also contains foraminifera.

In the section exposed around the Upper Waitemata Harbour, rhyolitic debris is concentrated in the stratigraphically lowest part of the section (Riverhead region) while volcaniclastic sandstones are increasingly abundant in the upper parts of the succession, interbedded with normal flysch sandstones and mudstones, and apparently thicken to the west (Davidson 1990). The observed stratigraphy is compatable with known age relations of volcanic source rocks and allows an estimation of the age of the sediments. The Brynderwyn-Mangawhai domes, believed to be the source of the rhyolitic debris, have been K-Ar dated as 18-20 Ma (Doi 1993ms; Hayward 1993), older than the Manukau Volcanic Centre of the Waitakere Volcanic Arc which is 15 km to the west and for which K-Ar dates cluster at 16-18 Ma (Doi 1993; Hayward 1993). We conclude that the Waitemata Group sediments in the Upper Waitemata Harbour area were deposited during the time interval 18 to 20 Ma BP.

The sedimentary succession exposed in the Upper Waitemata Harbour area represents a microcosm of Waitemata Group lithologies and as such is important in providing information about the diagenetic processes which led to their cementation.

Methods

Fifty-seven Waitemata Group sediment samples were first examined by thin section to determine the nature and degree of diagenetic alteration in the framework (clastic) grains, the presence of cementing material and the location of deposits of diagenetic minerals. Because most of the diagenetic changes involve minerals of very small size which also occur in very minor amounts the diagenetic minerals had to be separated and concentrated. Thirty-six samples from a range of representative lithologies were selected and the clay mineral constituents were concentrated by dispersing the sample in water and separating the clay size fraction by settling techniques. The resulting clay fraction was then pipetted onto a glass side and allowed to air dry and sediment overnight. This provided an oriented air-dried sample for X-ray diffraction examination. After this sample was examined it was treated with glycol and then heated to 550°C with X-ray diffractograms being run after each treatment. The zeolite fraction was concentrated by gently crushing the rock and hand picking the zeolites. These techniques allowed the identification of the diagenetic phases.

Twelve samples were also examined with a Philipps 505 Scanning Electron Miroscope fitted with an EDAX system which allowed qualitative analysis of the phases present and their paragenetic relations. Samples were prepared for SEM study by first breaking the airdried sample to provide a fresh fracture surface. The samples were then mounted on an aluminium stub and evacuated for 24 hours to remove any remaining moisture. The sample was then blown with compressed air, and dipped for several seconds in an ultrasonic bath filled with freon to remove any loose particles.

Fig. 2 Subequal amounts of clinoptilolite and smectite lining framework clasts in a porous sandstone. Hair-like fibres are mordenite. Authigenic growth of these minerals is considered to be contemporaneous. (Sample AU 42032)

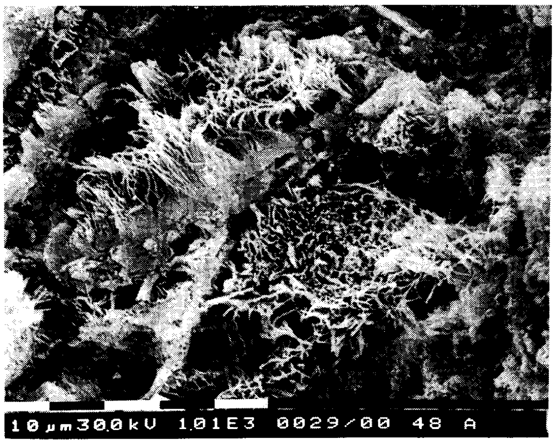

Fig 3 Mordenite "beards" growing from rhyolitic glass shards in Riverhead tuff horizon. (Sample AU 42056)

DIAGENESIS IN WAITEMATA GROUP SEDIMENTS

In all the unweathered Waitemata Group sediments studied, feldspars, mafic minerals and most lithic clastic grains show little sign of alteration. In contrast, the volcanic glass shards and rhyolitic debris are extensively devitrified and overgrown by clays and zeolites (Fig. 2).

Five clay minerals (smectite, illite, chlorite, kaolinite and halloysite) have been recorded in the Waitemata Group sediments. The most widespread and abundant is smectite which is concentrated in volcaniclastic sediments and rocks with high permeability. Thin sections show it to be a matrix mineral except in the volcanic sandstones where it is occasionally seen to pseudomorph volcanic glass in lithic clasts. Smectite is notably absent from the strongly cemented rhyolitic granule-sand horizons at Riverhead. Illite occurs in most sediments but never in major amounts. Little chlorite is present and is confined to highly altered volcaniclastic sediments. The position of kaolinite and halloysite is uncertain. The amount of the kaolin group minerals increases with the degree of weathering and there is an inverse relationship between the amounts of smectite and kaolin which also suggests that the kaolins are the products of terrestrial weathering.

As already noted by Sameshima (1978), zeolites are widespread in the Waitemata Group sediments occurring chiefly in volcaniclastic and tuffaceous beds. In the Upper Waitemata Harbour area zeolites, often with clay minerals, commonly coat clastic grains, fill pores (Fig. 2), and have nucleated on precursor volcanic glass (Fig. 3). Zeolites do not replace the framework grains instead they occur most commonly as a cement. The most intensive zeolitisation is in the rhyolitic granule-sand horizons enclosing the

Fig. 4 Clinoptilolite plates (on edge) lining pores in siltstone. Later phase chabazite forms pseudo-cubic crystals in open pores. (Sample AU 42046)

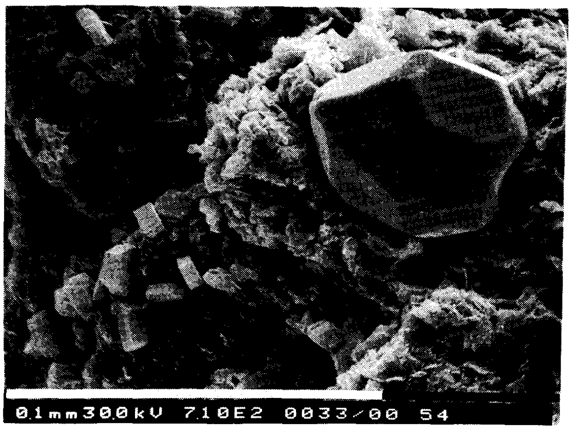

Fig 6 Well formed analcime crystal in the matrix of siltstone. Tabular crystals of clinoptilolite can be seen growing on the grain to the lower left. Clean crystal faces suggest the analcime may be later than the clinoptilolite. (Sample AU 42060)

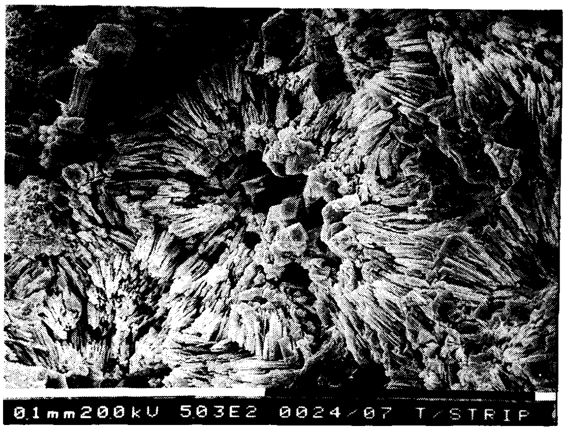

Fig 5 Hexagonal bundles of erionite fibres in centre of clinoptilolite rimmed pores in siltstone. Chabazite (pseudo-cubic crystals) also occur in centre of pores. (Sample AU 42046)

Riverhead conglomerates. Boundaries between intensively zeolitised horizons and underlying and overlying flysch sediments are sharp and zeolite cements rarely extend further than 0.1 m into these strata.

Five zeolites have been recorded in this study of the Waitemata Group sediments. The most abundant, clinoptilolite, occurs in almost all lithologies as 2 to 40 μm long plates and laths with coffin-shaped terminations; these are randomly oriented in samples with low concentrations (Fig. 2) but become more stacked as their abundance increases (Figs. 4 and 5). Chabazite is also ubiquitous but occurs most abundantly in sediments with high volcaniclastic content. Chabazite crystals are particularly small (varying in width from less than a micron to several microns) and while they are not able to be discerned in thin section their characteristic habit makes them easy to recognise with the SEM.

Erionite is the zeolite with the most restricted occurrence in that it occurs only in association with highly altered andesitic clastic material. It occurs in closely packed hexagonal bundles of acicular crystals (Fig. 5) visible in thinsection. Chabazite and erionite both crystallise later than clinoptilolite (Figs. 4 and 5) and are commonly seated on the latter mineral in open cavities.

Mordenite is a very minor constituent of some volcaniclastic sediments where it occurs in clinoptilolite-rich specimens as scattered, thin curved fibres, a few tenths of a micron in diameter, bridging gaps between larger grains (Fig. 2). Mordenite is the dominant zeolite in the silicic vitric tuff bed and grew directly from glass (Fig. 3).

Analcime is rare in the flysch samples with trace amounts being found in only two samples; here it forms large crystals which appear to have crystallised late in the zeolite paragenesis (Fig. 6). In contrast analcime is widespread and was the first zeolite to crystallise in the Riverhead granule-sand horizons where it forms a thin (2-10 μm) coating on framework clasts in many samples. Following the deposition of analcime, clinoptilolite crystallised, often completely filling pore spaces, and finally chabazite clusters lined remaining voids. Analcime is usually the only zeolite cement in the conglomerate horizons where it forms characteristic cubo-octahedral and trapezoidal crystals lining and infilling cavity spaces.

Sameshima (1978) recorded phillipsite with smectite in the matrix of the Parnell Grit, a fine conglomeratic horizon which although similar to those in the Upper Waitemata Harbour area contains basaltic and not rhyolitic debris; phillipsite has not been recorded in the Upper Waitemata Harbour area.

Authigenic carbonate minerals are common as cements in some sediments but zeolite and carbonate cements are mutually exclusive. Calcite cements are common but confined to a very limited range of sediment types – i.e., lithic rich sandstones that are very poor in volcanic debris (<6%). The calcite cementation is evenly distributed both horizontically and vertically resulting in some packets of sediments being more resistant than others. A less common carbonate cement found in the Upper Waitemata Harbour sediments is siderite which forms isolated concretionary nodules.

DISCUSSION

Sameshima (1978) concluded that the zeolitisation in the Waitemata sediments was the result of hydrothermal alteration accompanying widespread hotspring activity related to volcanic activity. However, this seems unlikely for the following reasons: the observed alteration is nonpervasive; zeolitisation is confined to specific lithologic units; individual zeolite and other alteration mineral parageneses are lithologically controlled; only vitric clasts are altered and the observed alteration is devitrification rather than replacement with secondary minerals growing on rather than in framework clasts.

The paragenetic succession of zeolites observed in the Upper Waitemata Harbour area is clinoptilolite (+ mordenite) → chabazite + erionite. The crystallisation of individual zeolite species are determined by many factors, including the activities of silica and aluminium ions, concentration and ratios of alkalies in both the start materials and the reacting solutions (Barth-Wirsching & Höller 1989).

Sameshima (1978) pointed out that the clinoptitolite-chabazite-erionite association and other zeolite assemblages recorded in the Waitemata Group sediments were those most commonly associated with lacustrine (i.e., closed hydrologic systems) rather than marine sedimentary environments. The low-Si content of individual zeolites in the Waitemata Group also suggests formation in an alkaline environment rather than the near neutral conditions more typical of marine sediments. Further evidence for a closed system environment comes from the strong lithologic control of diagenetic mineral assemblages in the Upper Waitemata Harbour sediments. Probably the alternating sandstone mudstone sequence typical of the dominant sediment type in the Waitemata Basin (turbidite) effectively sealed each individual sandstone so that diagenetic reactions proceeded as if in a closed hydrologic system. In those horizons containing vitric material interpore fluids reacted with volcanic glass becoming more alkaline and crystallising zeolites while in lithic-rich sandstones lacking volcanic material carbonate and other cements occur. Crystallisation of cements reduces porosity and ultimately restricts fluid flow which then leads to a decrease in the rate of alteration as well as changes in fluid composition. The changing cation contents of zeolites in the clinoptilolite -> chabazite ± erionite sequence are considered to reflect changes in pore fluid chemistry.

Analcime has an inconsistent position in the sequence. The paragenetic sequence of clinoptilolite followed by analcime is the usual one in volcaniclastic and tuffaceous rocks (summarised in Gottardi & Galli 1985) and is generally related to increasing temperature or depth of burial. In the andesitic volcaniclastic sediments of the Upper Waitemata Harbour area analcime is uncommon and crystallises after clinoptilolite. However, in the rhyolitic granule-sand horizons analcime crystallises before clinoptilolite. The crystallisation of analcime rather than clinoptilolite is controlled by the amount of Na in solution (Smyth 1982) and by the activity of dissolved silica (Bowers & Burns 1990). In silica saturated environments where there are abundant alkali ions clinoptilolite is the stable zeolite (e.g., Iijima 1978; Bowers & Burns 1990) but clinoptilolite is very susceptible to further diagenetic reactions and is known to transform to analcime at low temperatures (Bowers & Burns 1990); the rare late crystallisation of analcime in the volcaniclastic sandstones of the Upper Waitemata Harbour area may represent such diagenetic alteration of clinoptilolite. At temperatures of less than 100℃ analcime will form instead of clinoptilolite from any start material provided the solution is Na-saturated and slightly alkaline (Iijima 1978; Barth-Wirsching & Höller 1989).

The rhyolitic granule-sand horizons, which contain more than 50% vitric rhyolitic debris, are notable for their strong zeolite cementation (up to 20% in some samples) and also for lacking smectite. Devitrification of the abundant glass, which liberates Si and alkalies, is considered to have been an essentual precursor to the formation of zeolites in the granule-sand horizons as little or no alteration has occurred since zeolites crystallised. Na is the most mobile element in natural glasses and experiments have shown that because of the rapid release of Na and Si from natural glasses, analcime is common in zeolite assemblages which crystallise in the first stages of devitrification reactions (Barth-Wirshing & Höller 1989). We conclude that the thin analcime rims preceeding clinoptilolite on some clasts could have originated in such a fashion. The lack of smectite could be due to the rapid reduction in permeability as the result of the devitrification and consequent zeolitisation. Additionally, the alkalinity of the initial analcime-producing solution and the high levels of alkali ions liberated later into solution by the alteration of the abundant silicic glass could have inhibited the formation of smectite which is stabilised by near neutral conditions.

The occurrence of analcime is, however, not confined to horizons with tuffaceous material. Analcime is the dominant cement in all the conglomerate horizons in the region north of Auckland, where it may be very abundant (Sameshima 1978, recorded up to 30% analcime in an Albany Conglomerate horizon). The occurrence of analcime cannot be correlated with a particular lithology as each conglomerate horizon appears to contain its own unique set of clasts (Bartrum 1924; Bunting 1970ms) and most conglomerate horizons do not contain glassy rocks (e.g., the Riverhead conglomerate which contains weakly to low grade metamorphosed material). Similar occurrences of analcime cements in marine sediments and conglomerates that lack volcaniclastic material have been described (e.g., Obradovic 1988) and all cases the analcime appears to have crystallised from Na-saturated alkaline interpore solutions. Na-rich fluids are relatively common in nature (Drever 1988) and often have evolved from sea water but natural brines always have very low levels of Al which is also required for the crystallisation of analcime. The origin of Na-saturated solutions is uncertain but they appear to have occurred in all Albany Conglomerates in the region. The conglomerates would have had the highest primary permeability of the Waitemata Group sediments and from the widespread occurrence of analcime cement must also have had a very high fluid through flow for sufficient Al to have been provided to allow precipitation of analcime. Analagous precipation of calcium aluminium silicates from fluids with very low Al ion concentrations occurs commonly in pipes in geothermal fields (e.g., Browne *et al.* 1989).

It is our conclusion that the zeolite and other mineral cements in the Upper Waitemata Harbour area are the products of low-temperature diagenetic changes at temperatures of probably not more than 100℃. Mudstone layers in the turbidite sequence essentually sealed fluids into the interbedded sandstones and tuffs. The interpore fluid was probably a normal bicarbonate-rich water which precipitated calcite cement in the absence of vitric debris. In those lithologies containing volcanic glass, devitification liberated Si and alkalies into the interpore fluid and resulted in the crystallisation of zeolites under essentually closed hydrologic conditions. The highly permeable conglomerate horizons, which occur in channels cut into the sedimentary sequence are, in contrast, open hydrologic systems and analcime crystallised from Na-saturated interpore waters flowing through them.

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