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ORIGIN OF SELECTED SOIL
PARENT MATERIALS AND SEDIMENTS
IN NORTH ISLAND, NEW ZEALAND

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ABSTRACT

In this thesis the origin of soil parent materials in the North Island of New Zealand was investigated. The parent materials varied from basaltic, andesitic and rhyolitic volcanics to quartzose beach sands and quartzofeldspathic sedimentary rocks. Oxygen isotope and grain size analysis show that quartz from global aerosolic dust (represented by the 5 - 2 μm size fraction), interregional loess (represented by the 63 - 20 μm size fraction) and intraregional sand (represented by the >63 μm size fractions) can be identified in soils formed from these materials. In addition, high temperature quartz from Central North Island rhyolitic tephras is identified in basaltic soils in Northland.

The presence of locally derived quartz in the aerosolic dust fraction is demonstrated in the basaltic Kiripaka soil from Northland. In this soil a low temperature quartz component with a $\delta^{18}\text{O}$ value of circa 26 ‰ (in contrast to the aerosolic quartz $\delta^{18}\text{O}$ value of 12 - 13 ‰) was derived from nearby Tertiary marine shales by erosion and wind transport.

In all of the soils examined, no evidence of pedogenic α -quartz was obtained. In particular, quartz from the highly siliceous albic horizon of a Wharekohe soil, a "kauri podzol", is of detrital rather than authigenic origin.

Aerosolic quartz accumulation in soils developed on a series of surfaces of known age in southern North Island shows a correlation between age and the amount of quartz accumulated. Thus within a region, relative ages of surfaces can be estimated from quartz accumulation.

In an Egmont soil from Taranaki, an increased rate of quartz accumulation is noted in the lower part of the soil profile. This is

correlated with a late glacial climate prior to the circa 11,000 year B.P. post-glacial rise in sea-level. During this time tephric loess with a substantial (30%) detrital quartzofeldspathic component accumulated. After the sea-level rise cut off the source of the tephric loess, only tephra accumulated to form the upper part of the soil profile, in which the detrital quartzofeldspathic component is small.

The chronosequence concept could not be directly applied to a development sequence of basaltic soils in Northland. Only one soil, the Kiripaka, accumulated fast enough for the glacial/post-glacial change in quartz accumulation to be detected. The remaining basaltic soils, Whatitiri, Waiotu, Kerikeri, Ruatangata and Okaihau, accumulated slowly on old surfaces and in some cases were subject to erosion.

In a mineralogical examination of the sand and silt fractions of the basaltic soils, four distinct components are recognised:

1. Basaltic component - comprising minerals inherited from primary basalt tephra or lava. These include calcic plagioclase, magnetite, augite and, rarely, olivine.
2. Secondary component - glaeboles of gibbsite, goethite and lesser amounts of clay minerals and hematite.
3. Rhyolitic component - abundant in the surface horizons of all six soils and comprising rhyolitic glass shards and pumice, sodic plagioclase, hypersthene, hornblende, augite, biotite, titanomagnetite, quartz, zircon and rare sanidine.
4. Detrital component - comprising predominantly quartz < 125 μm in size and largely derived as loess and aeros^olic dust. Other minerals occurring are muscovite, plagioclase and rarely microcline and tourmaline.

Through the soil development sequence the basaltic component rapidly

becomes unimportant while the secondary component increases in significance to a level where the soil grain size characteristics are largely controlled by the distribution of gibbsite and goethite glaebules.

In a further study of quartz accumulation with time, a core of marine sediment from off the east coast of the southern North Island is examined. Core P69 contains five tephras, Whakatane Ash, Rotoma Ash, Waiohau Ash, and Kawakawa Tephra, which have been radiocarbon dated from terrestrial sequences. Interpolation and extrapolation of sedimentation rates in core P69 allowed estimates of the ages of four further rhyolitic tephras from the Central North Island, for which no reliable radiocarbon dates are available:

Okareka Ash	17,100 years B.P.
Te Rere Ash	19,100 years B.P.
Poihipi Tephra	20,300 years B.P.
Okaia Tephra	21,200 years B.P.

Quartz accumulation decreases abruptly from a high Otiran (glacial) to a low Aranuiian (post-glacial) rate at circa 14,700 years B.P. This is matched by a similar abrupt change in both biogenic silica and carbonate accumulation. The changes are interpreted as reflecting a southward shift of a strong westerly wind system at the end of the Otiran. The decreased wind intensity, coupled with forest expansion led to a reduction in erosion and reduced transport of quartz. The biological components also decreased at this time, probably due to changes in ocean currents and upwelling of cold, nutrient-rich water, as a result of the decreased wind intensity.

Compared with aerosolic dust accumulation in the southern North Island chronosequence, far greater amounts of aerosolic quartz accumulated in core P69 over a similar time period. This indicates that local contributions to the 5 - 2 μm size fraction can cause much larger variations

in quartz accumulation than those caused by rainfall variations reported in the literature.

The following late Otiran - Aranuian chronology is suggested, based on the evidence in core P69:

23,000 - 19,200	cold, glacial
19,200 - 18,500	glacial, slight amelioration
18,500 - 16,200	glacial, maximum cold
16,200 - 14,700	climatic amelioration, maximum aeolian transport and erosion, little forest cover
14,700 - 14,400	southward migrating circumpolar currents and westerly wind systems leave area of core P69, rapid expansion of forest cover
14,400 - 9,500	ameliorating climate, early post-glacial
9,500 - present	post-glacial.

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List of Symbols Not Defined in the Text

B.P.	before present (1950)
$^{\circ}\text{C}$	temperature, degrees celsius
^{14}C	carbon isotope, atomic number 14
g	gram
mg	milligram
μg	microgram
K/Ar	Potassium/Argon
km	kilometre
l	litre
M	Molar
m	metre
mm	millimetre
μm	micron
my	million years
U/Th	Uranium/Thorium
>	greater than
<	less than
$\phi = -\log_2 \text{mm}$	arithmetic grain size measure
Folk and Ward Grain Size Parameters	
M_z	Graphic Mean
σ_I	Inclusive Graphic Standard Deviation
Sk_I	Inclusive Graphic Skewness
K_G	Graphic Kurtosis

CHAPTER 1

CHAPTER 1

INTRODUCTION

Dust in the Atmosphere.

The long distance transport of dust in the atmosphere has been well established. Sirocco winds carry dust from northern Africa across the Mediterranean into Europe (Rex and Goldberg, 1962; Pitty, 1968; Bain and Tait, 1977). In the North Atlantic the trade winds also contain large concentrations of dust (Prospero, 1968; Chester and Johnson, 1971), largely derived from equatorial African soils and the Sahara Desert (Aston, et al., 1973). These winds deposit their dust load as far west as North Carolina (Syers et al., 1969), Barbados, Bermuda (Parkin et al., 1967; Delany et al., 1967) and South America (Prospero et al., 1981). Sediment transport from North America to the North Atlantic by wind, and in particular by large dust-storms, is also thought to be an important contribution to the present accumulation of marine sediment (Windom and Chamberlain, 1978).

Atmospheric dust transport is also well documented in the South Pacific. Red dust from the arid, central regions of Australia has been recorded in soils and snow from the temperate regions of eastern Australia (Walker and Costin, 1970) and New Zealand (Mokma et al., 1972). The occurrence in New Zealand of 'red dust' from Australia has frequently been observed (Marshall, 1903; 1929; Kidson, 1929; 1930a; 1930b).

In the Northern Hemisphere the desert regions of Asia have been the source of both the extensive Chinese loess deposits (Barbour, 1927) and dust which has been recognised as being deposited across Japan to the

North Pacific (Futi, 1939; Rex and Goldberg, 1962). In the equatorial eastern Pacific the southeast trade winds carry large dust loadings. These dusts show the effect of concentrated volcanic activity along the eastern margin of the Pacific by containing a higher volcanic component than dusts from elsewhere (Rex and Goldberg, 1962; Prospero and Bonatti, 1969). These observations are in contrast to the westerly winds in the South Pacific which carry highly quartzose dust largely derived from Australia (Rex and Goldberg, 1962; Windom, 1969).

Dust Generation and Transport.

Most episodes of dust generation are a result of storm activity, particularly gusty, irregular winds with low humidity rather than persistent prevailing winds (Yaalon and Ginzbourg, 1966; Jackson et al., 1973; Fan and Disrud, 1977). The interaction of an upper level jet stream, coupled with strong surface heating, giving rise to dust-generating winds is described in detail by Jackson et al. (1973). Solar heating in arid regions causes a deep layer of mixing of air. Horizontal and vertical winds that are generated erode soil, to carry particle concentrations in the order of $600 \mu\text{g m}^{-3}$ of air to altitudes of 4 - 10 km. At these heights dust can affect diabatic cooling of the mid-troposphere, possibly leading to increased air subsidence and aridity. Jet streams associated with large cyclonic storms enter this mixed volume and produce strong wind gusts which break up soil aggregates to produce transportable silt-sized particles (Jackson et al., 1973). These are less than about $20 \mu\text{m}$ in size because larger grains have too high a sedimentation velocity for long distance transport (Gillette, 1974; 1977; Gillette et al., 1978). The lower size limit is at about $1 \mu\text{m}$ as clay-size particles are not easily separated from aggregates (Smalley, 1970; Gillette et al., 1972).

The advent of nuclear explosions has allowed the study of movement of atmospheric dust over long distances (Rex and Goldberg, 1962). Nuclear fallout from the troposphere is generally restricted to a band $\pm 10^\circ$ latitude from source and is distributed throughout the band within a period of 14 days (Karol and Malakov, 1965). Dust is transported largely by jet streams in the troposphere and, because these travel parallel to latitude, dust tends to be deposited in the same latitudes as the dust sources (Rex and Goldberg, 1958; 1962). Trans-equatorial transport in the troposphere also appears to be slight as atmospheric nuclear explosions near the equator give rise to little fallout in the other hemisphere (Jackson et al., 1973). In contrast, radioactive material injected at any latitude into the stratosphere tends to be deposited in mid-latitudes (Eisenbud, 1963).

The residence time of dust in the atmosphere is variable but is of the order of 5 - 30 days (Jackson et al., 1973). However, climate change may also influence residence time (Junge, 1963). Deposition of dust is primarily caused by precipitation scrubbing (Wilkins, 1958; Rex and Goldberg, 1962; Yaalon and Ginzbourg, 1966; Rex et al., 1969; Jackson et al., 1971; 1973), although inertial mechanisms such as impaction and gravitational settling may also be involved (Jackson et al., 1973).

Dust Composition.

The composition of atmospheric dust can include wind eroded soil, volcanic ash and extraterrestrial matter (Jackson et al., 1973), although on a present global basis volcanic ash and extraterrestrial contributions have been negligible (Hidy and Brock, 1970). However, on a local scale the volcanic ash component can predominate. For example, in the north-west Pacific, ash is a significant component of pelagic sediments in some

areas (Nayudu, 1964; Horn et al., 1969; Ninkovich and Robertson, 1975) while in the South Pacific ash in pelagic sediments can be traced a considerable distance to the east of New Zealand (Huang et al., 1973; 1975; Watkins and Huang, 1977). A high volcanic ash content in the dusts of the South Pacific has contributed to an overall lower proportion of quartz in Southern Hemisphere dusts (Aston et al., 1973). The composition of atmospheric dusts has been correlated with dusts from soils and sediments in specific continental areas (Griffin et al., 1968; Windom and Chamberlain, 1978; Prospero et al., 1981). The broad correspondence of fine-grained mineralogy of aeolian terrigenous sediments with the types of continental climate and weathering has also been demonstrated in the sediments of world oceans (Griffin et al., 1968; Griffin and Goldberg, 1970; Diester-Haass and Chamley, 1978).

In general, chlorites appear to be associated with polar regions while kaolinite is more common in sediments of low latitude where it is associated with tropical weathering (Griffin et al., 1968). Montmorillonites are most abundant in pelagic sediments of the Southern Hemisphere but this is thought to be due to the greater occurrence of volcanic ash in the sediment (Griffin et al., 1968). In detail, however, correlation of mineralogical changes with past climatic variations is not always found (Griffin and Goldberg, 1963; Biscaye, 1965; Piper and Slatt, 1977). For example, the sediment load of major river systems may mask any specific mineralogical climatic indicators in deep-sea sediments (McManus, 1970).

Quartz is a useful marker mineral in determining aeolian and other modes of sediment transport because it is present in a much wider range of particle sizes than other minerals present in deep-sea sediments (Beltagy et al., 1972) and it is almost exclusively derived from continental regions (Kolla et al., 1979). It is easily determined

quantitatively (Syers et al., 1968) and has been used extensively to trace dust additions to pelagic sediments (Radczewski, 1939; Delany et al., 1967; Beltagy et al., 1972; Ellis and Moore, 1973; Parkin and Shackelton, 1973; Bowles, 1975; Windom, 1975; Diester-Haass, 1976).

In atmospheric dust two components may be present, one local and concentrated in the coarser size fractions, the other global and concentrated in the finer size fractions. A bimodal size distribution has been found for particulate matter in permanent snow fields, from Greenland, North America, New Zealand and Antarctica, confirming two sources of aeolian material in the atmospheric dust (Windom, 1969). In a study of basaltic soils of Victoria, Australia, two aeolian quartz components have also been identified. One was "flotssand", intermediate in grain size between dune sand and loess and of local origin. The other component was attributed to aerosolic dust (Jackson et al., 1972). Aeolian components (flotssand of 250 - 20 μm size, loess of 50 - 10 μm size and aerosolic dust of 10 - 1 μm size) form widespread additions to soils and sediments in the South Pacific region (Mokma et al., 1972). Both loess and aerosolic dust quartz sources have also been recognised in soils from the southeastern United States to the Bahamas (Syers et al., 1969), attesting to the widespread multiple nature of the source of atmospheric dust.

Aerosolic Dust.

Stable tropospheric aerosols have a size range of 20 to 0.1 μm in which the insoluble fraction comprises mainly silicates (Junge, 1963). The size distribution of this silicate fraction of aerosolic dust is generally found to be 10 - 1 μm , with a mode at 4 μm (Rex and Goldberg, 1962; Walker and Costin, 1970; Jackson et al., 1971; 1973) and is distinct from the 10 μm to about 70 μm size distribution of loess (Ruhe, 1969; Jackson et al., 1971).

Quartz is a major component of atmospheric dust (Parkin et al., 1970; Folger, 1970; Chester and Johnson, 1971; Chester et al., 1972). Atmospheric quartz is a major constituent of pelagic sediments of the eastern equatorial Atlantic (Biscaye, 1965; Beltagy et al., 1972; Bowles, 1975; Parkin and Padgeham, 1975; Diester-Haass, 1976; Johnson, 1979). The decreasing grain size and abundance of quartz in deep-sea sediments with distance from Africa (Biscaye, 1965; Beltagy et al., 1972; Parkin and Padgeham, 1975) is consistent with fallout of quartz over the Atlantic, clay minerals $<2 \mu\text{m}$ in size reaching the Caribbean (Delany et al., 1967; Parkin et al., 1970; Prospero et al., 1981).

Quartz in the $10 - 1 \mu\text{m}$ size range is not readily generated by many sedimentary processes but is thought to be produced by two main mechanisms, glacial grinding to form "cold" loess (Smalley, 1966; Smalley and Vita-Finzi, 1968; Smalley et al., 1978) and aeolian impact of grains in deserts ("hot" loess) producing quartz of predominantly $5 - 1 \mu\text{m}$ size (Smalley et al., 1978). However, large volumes of dust are transported from regions in which neither of these processes appear to have operated, indicating additional sources of aerosolic dust-sized quartz. Such sources have been found in soils on marine shales, which can act as a reservoir for aerosolic quartz (Sridhar et al., 1975; Churchman et al., 1976).

Aerosolic dusts have been reported as being deposited in a wide range of environments, including glacial ice (Mokma et al., 1972; Thompson et al., 1975), permanent snowfields and alpine soils (Windom, 1969; Walker and Costin, 1970), soils (Rex et al., 1969; Syers et al., 1969; Mokma et al., 1972) and deep-sea sediments (Rex and Goldberg, 1958; 1962; Rex et al., 1969; Clayton et al., 1972; Mokma et al., 1972). In order to trace the origin of aerosolic dusts the oxygen isotope abundance of aerosolic quartz has been used extensively and successfully. Studies of quartz isolated from soils in the Hawaiian Islands have shown an $^{18}\text{O}/^{16}\text{O}$ ratio and size

distribution consistent with derivation from an aerosolic source, similar to quartz in the surrounding deep-sea sediments (Rex et al., 1969; Jackson et al., 1971). The $^{18}\text{O}/^{16}\text{O}$ ratios were incompatible with either an igneous or authigenic origin, as had been previously suggested by Sherman et al., (1964). K - Ar dates on micas in both Hawaiian soils and Pacific deep-sea sediments give ages of between 47 my and 155 my, much older than the age of the Hawaiian Islands themselves (Hurley, 1966; Dymond et al., 1974) but consistent with ages of micas from continental rocks (Jackson et al., 1971). This evidence strongly supports an aerosolic origin (Rex et al., 1969) rather than a pedogenic origin (Juang and Uehara, 1968) for the quartz and micas in the soils and sediments of Hawaii. In a further study of soils from the Bahamas and North Carolina it was found that quartz and other minerals had been transported as aerosolic dust from North Africa via the Caribbean - Sahara circulation system (Syers et al., 1969) to these localities, attesting to the wide-spread distribution of aerosolic dust.

In the South Pacific region an aerosolic origin has been demonstrated for quartz in a range of environments. In deep-sea sediments the $^{18}\text{O}/^{16}\text{O}$ ratios of aerosolic quartz decrease with increasing latitude (Clayton et al., 1972; Le Roux et al., 1980), in contrast to the North Pacific where quartz $^{18}\text{O}/^{16}\text{O}$ ratios are higher but show no consistent latitudinal variation (Clayton et al., 1972). This distribution of oxygen isotope composition is thought to be due to the occurrence of more rock strata containing low temperature quartz in the Northern Hemisphere, giving rise to higher $^{18}\text{O}/^{16}\text{O}$ ratios, whilst in the Southern Hemisphere an increasing abundance of high temperature quartz in source rocks with increasing latitude has led to decreasing $^{18}\text{O}/^{16}\text{O}$ ratios (Mokma et al., 1972; Jackson et al., 1973).

Aerosolic quartz is recorded in sequences of basaltic soils in both Australia and New Zealand (Jackson et al., 1972; Mokma et al., 1972). The $^{18}\text{O}/^{16}\text{O}$ ratios of the quartz from the New Zealand soils was found to be similar to that of deep-sea sediments of equivalent latitude, suggesting a similar source (Mokma et al., 1972; Clayton et al., 1972). Increasing abundance of quartz in the surface horizons with increasing soil development in the New Zealand soils was interpreted as showing increasing aeolian quartz accumulation with time (Mokma et al., 1972). Quartz of aerosolic dust size was also present in a series of soils developed in quartzofeldspathic parent materials in south Westland, New Zealand, but could not be distinguished isotopically from coarser, locally-derived quartz (Mokma et al., 1972). The $^{18}\text{O}/^{16}\text{O}$ ratios of quartz in shales and soils has been used elsewhere in quartz provenance studies. $^{18}\text{O}/^{16}\text{O}$ ratios of 10 - 1 μm quartz in shales from North America were found to be intermediate between high and low temperature quartz and the shales were suggested as a reservoir of mixed origin quartz which became the source of aerosolic material during glacial, fluvial, aeolian and weathering processes (Churchman et al., 1976), as has been previously discussed. Wind erosion of the fine silt fraction of sandy soils was also found to contribute to aerosolic dusts (Gillette et al., 1978; Sridhar et al., 1978).

The intermediate temperature of formation of aerosolic quartz indicated by its oxygen isotope ratios is due to the mixed origin of the quartz, including both high and low temperature material from diverse sources (Mokma et al., 1972; Sridhar et al., 1975). The presence of chert particles, comprising a low temperature component, has been demonstrated in shales by both selective dissolution in HF and by direct observation by Scanning Electron Microscope (SEM) (Sridhar et al., 1975). Intermediate $^{18}\text{O}/^{16}\text{O}$ ratios of quartz in the 50 - 20 μm size fraction of a soil developed on cherty dolomite were clearly shown to be derived from

mixing of low temperature cherty aggregates from the dolomite and higher temperature quartz from loess (Sayin and Jackson, 1975). In general, aerosolic quartz is derived from more diverse sources than quartz in coarser size fractions and consequently has a higher $^{18}\text{O}/^{16}\text{O}$ ratio since it contains a higher proportion of low temperature quartz.

Atmospheric Dust in Deep-Sea Sediments.

The accumulation of atmospheric dusts in deep-sea sediments was first investigated in the equatorial Atlantic (Radczewski, 1939). Subsequent studies of the existing distribution of minerals in deep-sea sediments has been in relation to current climatic zones (Biscaye, 1965; Griffin et al., 1968; Griffin and Goldberg, 1970; Piper and Slatt, 1977). Of the minerals derived by aeolian transport, only quartz shows a systematic variation with climate (and time), the remainder being more closely related to soils and lithological changes in source areas (Bowles, 1975; Piper and Slatt, 1977; Prospero et al., 1981).

Much of the quartzose component of pelagic and hemipelagic sediments can be attributed to dust transport (Windom, 1969; Johnson, 1976; Windom and Chamberlain, 1978; Prospero et al., 1981). The distribution of this quartz component appears to show a concentration in the trade wind belts and westerly wind systems of both hemispheres (Chester and Johnson, 1971; Johnson, 1976). For example, in the eastern equatorial Pacific, an increased abundance of quartz was demonstrated in sediments from the same latitude as the westerly wind system at about 30°N . This was considered to indicate that quartz was transported in the tropospheric westerly jet stream of this region (Rex and Goldberg, 1958).

In the southwest Pacific the transport of large amounts of dust from the arid and semi-arid regions of Australia by tropospheric winds has been reported (Marshall, 1929; Kidson, 1929; 1930a; 1930b; Mokma et al., 1972;

Thompson et al., 1975; Rognon and Williams, 1977). Here, the distribution of quartz in Holocene pelagic and hemipelagic sediments shows a pattern of abundance extending in a broad zone southeast of Australia, at about 40°S , consistent with the present tropospheric wind system. However, at 18,000 years B.P. (the height of the last glacial) a narrower zone of aeolian quartz distribution extended a further 20° longitude east than at present and was centred further north at about 30°S . This indicates a northerly shift of an intensified westerly tropospheric wind system (Thiede, 1979). Such intensification of wind systems, together with their expansion from present locations towards the equator, have been previously suggested from changes in biological and detrital components in deep-sea sediments (McIntyre et al., 1972; 1976; Ruddiman and McIntyre, 1973; CLIMAP, 1976) and from atmospheric modelling (Lamb, 1972; Lamb and Woodruff, 1970; Gates, 1976).

Lateral shifts in quartz deposition with climate changes are also apparent in Atlantic sediments (Molina-Cruz, 1977; Molina-Cruz and Price, 1977; Diester-Haass and Chamley, 1978). Such shifts are confirmed by the changes in abundance of quartz identified as "desert" quartz, correlated with glacial and interglacial fluctuations (Diester-Haass, 1976). Similar changes in the pattern of quartz distribution with changes in the position and strength of the monsoon winds through glacial and interglacial periods has been found in the northern Indian Ocean (Olausson and Olsson, 1969; Kolla and Biscaye, 1977).

In marine sediments at high latitudes, coarse detritus from glacial processes dominates sedimentation. This is attributed to ice rafting in both the Arctic and Antarctic regions (Conolly and Ewing, 1965; Kent et al., 1971; Ruddiman and McIntyre, 1976; Ruddiman, 1977a; 1977b; Anderson et al., 1980). The limits of ice-rafted particles is believed to correspond to the limits of sea ice at its maximum extent (Mullen et al.,

1972; Ruddiman and McIntyre, 1976; Ruddiman, 1977b; Kolla et al., 1978). Ice rafting is therefore an additional factor in transporting coarser material to high latitude deep-sea sediments.

If areal changes in aeolian quartz distribution in deep-sea sediments occurs between glacial and interglacial periods, then variations in quartz accumulation rates with time at any one location must occur. Such variations were detected in sediment cores from the eastern equatorial Atlantic where high quartz/illite ratios are correlated with glacials and low ratios with interglacials (Bowles, 1975). Similar increases in dust accumulation in ice cores from Antarctica occur in stratigraphic positions which can be correlated with major global glaciations (Thompson et al., 1975).

Authigenic Quartz in Soils.

The neoformation of quartz in soils has been the subject of much debate. In records of such occurrences in the literature the term "quartz" is sometimes applied to all forms of crystalline silica, including chalcedony, cristobalite and quartz (Eswaran, 1972; Eswaran and Stoops, 1979). Authigenic silt- and sand-sized quartz was reported from a soil developed on quartz free norite in Georgia, U.S.A. (Robinson, 1980). The quartz was thought to have been formed in the soil because of its association with Fe hydroxides as inclusions and coatings, an interpretation suggested by experiments showing an association of amorphous metal hydroxides with quartz crystallization at earth-surface conditions (Harder and Flehmig, 1970). However, evidence presented by Robinson (1980) to discount a wind-blown origin for the quartz, with a possible source in quartzo-feldspathic metamorphic rocks surrounding the norite pluton, is not sufficiently strong. Without corroborating evidence, such as that of quartz oxygen isotope analysis, an authigenic origin for the

quartz must be considered not proven.

Silica crystallisation has been recorded in basaltic soils. Chalcedony spherules were reported from a poorly-drained basaltic soil in Australia (Craig and Loughnan, 1964). Various forms of silica, all described as quartz, have been reported from tropical soils on basalts (Eswaran and de Coninck, 1971; Eswaran, 1972) and in saprolites on more siliceous rocks (Eswaran and Stoops, 1979). However, identification of quartz was made by XRD and this is not able to distinguish α -quartz from forms such as chalcedony (e.g. Fieldes, 1952). Quartz, in Hawaiian basaltic soils, previously thought to be authigenic, (Juang and Uehara, 1968) has been shown to be derived from tropospheric aerosolic dust by its grain size distribution and oxygen isotope composition (Rex et al., 1969; Jackson et al., 1971).

A range of forms of silica have been recorded from many New Zealand soils (Fieldes and Swindale, 1954; N.Z. Soil Bureau, 1968; Mokma et al., 1972; Claridge and Weatherhead, 1978). Authigenic quartz has been postulated to have formed the siliceous, albic horizons of Northland Kauri podzols, formed under intensive acid leaching beneath individual Kauri (Agathis australis) trees (Fieldes et al., 1956; Smidt et al., 1977).

Another form of silica of low structural order, termed chalcedonite, has been described from New Zealand soils, particularly those formed in siliceous parent materials (Fieldes, 1952; Fieldes and Swindale, 1954; Fieldes and Williamson, 1955; Fieldes et al., 1956). Chalcedonite is thought to be an intermediate stage between colloidal silica and α -quartz. The XRD properties are similar to those of α -quartz but the refractive index is reported as lower than that of chalcedony and the thermal properties are anomalous (Fieldes and Swindale, 1954; Fieldes and Williamson, 1955).

Oxygen Isotope Fractionation

As a result of initial work on the thermodynamics of isotopic systems, it was predicted that variations in temperature of precipitation of CaCO_3 from water should lead to measurable variations in the $^{18}\text{O}/^{16}\text{O}$ ratio of carbonate and therefore measurements of the $^{18}\text{O}/^{16}\text{O}$ ratio of fossil carbonate would allow determination of past ocean temperatures (Urey, 1947). Prior to this, variations in $^{18}\text{O}/^{16}\text{O}$ ratios in natural, terrestrial materials were known but the relationship to temperatures of formation had not been elucidated.

After the advent of sensitive mass spectrometers suitable for measuring small mass differences (Nier, 1947; McKinney *et al.*, 1950), extension of the studies of oxygen isotopic fractionation in carbonates led to the establishment of a paleotemperature scale (McCrea, 1950; Urey *et al.*, 1951; Epstein *et al.*, 1953). Carbonate paleotemperatures were subsequently used in a number of important studies on past climates and, based on the work of Emiliani (1955a; 1955b; 1957; 1966), oxygen isotope paleotemperature curves are now used as a standard means of correlating deep-sea cores (Shackleton and Opdyke, 1973).

Studies were also carried out on the oxygen isotope geology of silicates and silicate rocks (Silverman, 1951). Detailed investigations followed on oxygen isotope geochemistry of igneous (Taylor and Epstein, 1962 pt 1; Taylor, 1968), metamorphic (Taylor and Epstein, 1962 pt 2; Garlick, 1966; Garlick and Epstein, 1967) and sedimentary rocks (Savin and Epstein, 1970a; 1970b).

In calculating temperatures of formation from mineral-water pairs, the oxygen isotope composition of both phases must be known. However, if two oxygen-bearing mineral phases coexist in isotopic equilibrium with water in a system, then oxygen isotope analysis of both phases make temperature determinations possible without the necessity for assuming a

composition for water (Clayton, 1963). It has been shown that large isotopic fractionations do exist between some pairs of minerals in igneous, metamorphic and hydrothermal rocks which vary systematically with geologically inferred crystallisation temperatures (Clayton and Epstein, 1958; Engel et al., 1958), and much subsequent work has been directed towards calibration of such "mineral pair geothermometers" (O'Neil and Epstein, 1966; O'Neil and Taylor, 1967; Epstein and Taylor, 1967; Bottinga and Jarvov, 1973; Blattner and Bird, 1974).

Oxygen isotope fractionation in the system quartz-water has also been extensively studied (O'Neil and Clayton, 1964; Epstein and Taylor, 1967; Clayton et al., 1972; Bottinga and Jarvov, 1973). This temperature relationship has been extended in a qualitative way to indicate provenance of quartz in a range of sedimentary and soil environments (Rex et al., 1969; Syers et al., 1969; Savin and Epstein, 1970a; 1970b; Jackson et al., 1971; 1972; 1973; Clayton et al., 1972; Mokma et al., 1972; Sayin and Jackson, 1975; Sridhar et al., 1975; 1978; Churchman et al., 1976; Le Roux et al., 1980).

Oxygen isotope fractionation occurs through isotope exchange reactions. The extent of reaction is dependent on molecular vibrations which are in turn dependent on the masses of the atoms involved. The reaction rate is an increasing function of temperature, pressure effects being negligible. At high temperatures, thermal energy negates the mass differences between isotopes and fractionation approaches zero. In contrast, at low temperatures the heavier isotope (^{18}O) exchanges less readily than the lighter isotope (^{16}O) and ^{18}O will be preferentially enriched in the phase with the strongest oxygen bonding. In general, the more polymerised the silicate, the greater the ^{18}O enrichment.

In hydroxyl-bearing minerals, such as hornblende and biotite, hydroxyl oxygen exchanges more readily than lattice oxygen and this results

in anomalous fractionation values (Taylor and Epstein, 1962a; 1962b). In a pure silicate mineral such as quartz, which has crystallised in equilibrium with water, the isotope fractionation will reflect both the temperature of crystallisation and the isotopic composition of the water. If the latter is known then crystallisation temperatures can be determined.

In many instances, the isotopic composition of water in the system is not known. However, in general low ^{18}O fractionation indicates high temperatures of formation while low temperatures are shown by high fractionation values. Intermediate values are found in metamorphic rocks but are also found in clastic sediments where quartz of mixed origin occurs (Savin and Epstein, 1970a; 1970b).

Notation

Oxygen isotope ratios are reported as differences from an arbitrary standard, rather than as absolute ratios. The differences are reported as δ -values (Epstein, 1959) and are defined as:

$$\delta^{18}\text{O} = \frac{^{18}\text{O}/^{16}\text{O}_{\text{sample}}}{^{18}\text{O}/^{16}\text{O}_{\text{standard}}} - 1 \quad \times 1000$$

expressed as parts per mil ($^{\circ}/\text{oo}$).

Common standards used are Standard Mean Ocean Water or SMOW (Craig, 1961), a fossil carbonate PDB - 1 (Urey et al., 1951) and NBS - 120 (Solenhofen limestone distributed by the U.S. National Bureau of Standards). For oxygen isotope analysis of silicates, SMOW has been generally adopted as a standard.

Objectives of this study.

The primary objectives of this research were:

1. To investigate the accumulation of aerosolic dust, loess, and other materials in New Zealand soils, particularly those developed in volcanic ash, using the mineralogy of sand and silt fractions and the oxygen isotope composition of the marker mineral quartz.
2. To determine if neoformation of α -quartz is a process which is active in New Zealand soils and to determine if it was responsible for the formation of albic horizons in kauri podzols.
3. To investigate the accumulation of aerosolic quartz with time in soils and on surfaces of known age and to investigate the potential of using aerosolic dust accumulation to determine the stratigraphy of accumulating soils on undated surfaces.
4. To determine the accumulation of aerosolic quartz in a marine sediment core, dated by the presence of known tephras, which has a complete and regular sedimentary record preserved.

Methods

The samples were processed according to the methods of Jackson (1956). Soil samples were treated with 1M NaOAc-HOAc buffer at pH 5 to remove carbonates and 30% H_2O_2 to remove organic matter. Amorphous, ^{and some crystalline} short-range order/iron oxides and hydroxides were removed by citrate-bicarbonate-dithionite (CBD) at 80°C. This was followed by washings with saturated NaCl and acetone. The dispersed samples (dispersed with NH_4OH , not calgon as described by Jackson, 1956) were fractionated at 63 μm by wet sieving, 20 μm by sedimentation, and 5 μm and 2 μm by centrifugation. Dispersion with NH_4OH was found by experiment to be more successful for dispersing samples with a high allophane content.

For rock and marine sediment samples the NaOAc-HOAc treatment was omitted. Carbonate was removed by treatment with 3M HCl and the CBD

treatment omitted since the amorphous and short-range order iron oxide content of these samples was very low.

To isolate quartz for oxygen isotope analysis the procedure of Syers et al., (1969), as modified by Sridhar et al., (1975), was followed. Approximately 200 - 400 mg of sample was fused with 12 g of powdered $\text{Na}_2\text{S}_2\text{O}_7$. Where this was not available, 20 g of NaHSO_4 was used. The cooled melt was dissolved in 50 ml of 3M HCl then transferred to a 100 ml tapered glass centrifuge tube, washed once with 3M HCl and 3 times with distilled water. The sample was then transferred to a 20 ml polypropylene tube and 10 ml of H_2SiF_6 added. The H_2SiF_6 had been stored under refrigeration in contact with ground 63 - 20 μm quartz to remove free HF. The quartz was reacted with H_2SiF_6 at 19°C for 3 days, with a minimum of twice daily mixing. It was found that frequent mixing was required over the first six hours to prevent the sample from caking in the bottom of the tube.

At the end of three days the sample was centrifuged, washed once with 0.1M HF and 4 times with H_2O . Purity of the isolates was then checked by XRD. Cristobalite was often found to be present after one, three-day treatment but could be removed by 2 or 3 and rarely 4 X 3-day treatments with H_2SiF_6 . Once the XRD pattern indicated a sample free of feldspar and cristobalite, it was treated overnight with 5 ml of saturated boric acid, washed 4 times with H_2O , dried at 105°C and weighed (Sridhar et al., 1975). For observations of particle morphology with a scanning electron microscope, quartz particles were mounted on aluminium stubs and coated with Au/Pd.

Oxygen was extracted from quartz by reaction with BrF_5 (Clayton and Mayeda, 1963). In a modification of the original technique of Clayton and Mayeda, the oxygen is purified and converted to CO_2 in 10 - 15 minutes using one Toepler pump (Blattner and Bird, 1974). The oxygen isotopic

compositions were determined on an NAA 6-60 RMS, 15 cm radius, 60° sector double-collecting mass spectrometer. Isotopic composition is reported relative to Standard Mean Ocean Water (SMOW of Craig, 1961).

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CHAPTER 2

CHAPTER 2

EVALUATION OF THE NEOFORMATION
OF α -QUARTZ IN SELECTED SOILS AND SEDIMENTS,
NORTH ISLAND, NEW ZEALAND

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ABSTRACT

Quartz was extracted from selected size fractions of a range of soils and sediments from the North Island of New Zealand. Most of the quartz in soils developed primarily from volcanic ash was found to be in the 63 - 20 μm size fraction and of detrital, aeolian origin with $\delta^{18}\text{O}$ values of 12 - 14 $^{\circ}\text{oo}$. Small amounts of aerosolic dust, represented by the 5 - 2 μm size fraction quartz with a $\delta^{18}\text{O}$ value of 13 - 15 $^{\circ}\text{oo}$, was found in all the soils examined. Coarse grained quartz (>125 μm), found in some basaltic soils and composing many Northland Beach sands, shows $\delta^{18}\text{O}$ values of 8.2 - 8.7 $^{\circ}\text{oo}$, comparable with quartz obtained from rhyolitic tephra such as the Ohinewai Tephra, which has a $\delta^{13}\text{O}$ value of 8.4 $^{\circ}\text{oo}$ and is clearly of high temperature origin. High temperature quartz, with a $\delta^{18}\text{O}$ value of 9.0 - 9.3 $^{\circ}\text{oo}$, was also found in a soil developed from rhyolite in Northland and confirms previously published data on the oxygen isotope composition of quartz from this soil. Quartz from the albic horizon of a Wharekohe

silt loam was shown to be detrital and not pedogenic, since $\delta^{18}\text{O}$ values of 12.8⁰/oo and 13.4⁰/oo were obtained for the 63 - 20 μm and 5 - 2 μm size fractions respectively. Low temperature quartz was found in two North Island marine shales. In the Cretaceous Whangai Formation quartz has a $\delta^{18}\text{O}$ value of 25.6 - 26.6⁰/oo and is present largely as chert grains inherited as clastic material from pre-existing rocks. In the Tertiary Mangakahia Group shale SEM studies show quartz with overgrowths most abundant in the 5 - 2 μm size fraction (with a $\delta^{18}\text{O}$ value of 25.7⁰/oo) and none in the 63 - 20 μm size fraction (with a $\delta^{18}\text{O}$ value of 12.0⁰/oo). In both shales low temperature quartz formation appears to be due to geological processes. Although previous work has shown the presence of chalcedonite, a form of chalcedony, in soils with siliceous parent materials, the $\delta^{18}\text{O}$ values obtained for quartz in this study shows that neoformation of α -quartz is not a process operating in the soils examined.

INTRODUCTION

The crystalline forms of silica found in nature are quartz, cristobalite, tridymite, coesite and stishovite (Fron del, 1962). Coesite and stishovite are high pressure polymorphs which are formed by high pressure shock events on the earth's surface, such as meteorite impacts. They are not considered further in this paper. Non-crystalline forms of silica are amorphous silica and an hydrated form, opal (biogenic opal if formed by plants and animals).

Of the crystalline forms, quartz is the most abundant and is found in a wide range of rocks. Because of its resistance to both physical and chemical weathering it is the most abundant mineral found

in sediments. Tridymite and cristobalite are less common than quartz but are widely distributed in volcanic and biogenic sedimentary rocks.

Both quartz and cristobalite have very fine grained (crypto-crystalline) phases of lower structural order, referred to as chalcedony and low cristobalite respectively. These phases are found in low pressure and temperature environments and mark the early stages in crystallisation from amorphous silica and opal to quartz. They have been reported from both soils (Craig and Loughnan, 1964; Wilding et al., 1977) and sediments (Mizutani, 1970; Kastner et al., 1977).

PROPERTIES AND BEHAVIOUR OF SILICA

Quartz, tridymite and cristobalite should all have an ideal composition of 100% SiO_2 (opal = $\text{SiO}_2 \cdot n\text{H}_2\text{O}$). However, due to the decreasing density (as a result of increasing microporosity with decreasing crystallinity) from quartz to opal, increasing amounts of impurities are found (Wilding et al., 1977). The most common impurity is Al^{3+} , with lesser substitution of other ions (Deer et al., 1966). The more open framework of tridymite and cristobalite allows much freer entry of impurities and this may be the reason for the metastability of these silica polymorphs below their phase equilibrium conditions of pressure and temperature. The opal structure is so open that a range of impurities may be present, including N and C (Jones and Beavers, 1963), and the composition is often only 85 - 95% SiO_2 (Wilding et al., 1977).

Silica Solubility

The solubility of silica is related to the degree of long range crystal order with the most dense, crystalline phases being the least soluble. The order of solubility is:

amorphous silica > opal > cristobalite > quartz

(Wilding et al., 1977). Most values for the solubility of quartz lie between 3 and 7 mg l⁻¹ Si (Krauskopf, 1959) and approximately 3 mg l⁻¹ Si is thought to be most probable (Wilding et al., 1977). Because the activation energy involved in altering the Si - O - Si bond is high (Stober, 1967), at room temperature and pressure quartz equilibration is very slow and concentrations of 3 mg l⁻¹ Si can be maintained for long periods in solution in contact with quartz before reaching equilibrium (Wilding et al., 1977).

Quartz which has been freshly ground or continuously agitated in suspension shows a much higher solubility than unground quartz (Morey et al., 1962; McKeague and Cline, 1963b; Henderson et al., 1970). This is thought to be due to the formation of a disturbed surface layer, believed to be amorphous (Nagelschmidt et al., 1952). The thickness of the disturbed layer is thought to be a function of grinding time or, in natural samples, the environmental conditions the quartz has been subjected to; however, 0.03 μ m is commonly reported (Nagelschmidt et al., 1952; Gordon and Harris, 1955). This layer can be removed by treatment with HF, H₂SiF₆ or NaOH (Henderson et al., 1970). The solubility of quartz is therefore a function of temperature, pH, grain size and structural modifications to the surface layers of the quartz grains. However, quartz solubility is independent of temperature up to 145°C and is therefore not affected by temperature in soils (Krauskopf, 1959; Lidstrom, 1968). The solubility of both quartz and amorphous silica is independent of pH below pH 9, that is, in the pH range of most soils (Alexander et al., 1954; Krauskopf, 1956; 1959; 1967; White et al., 1956; McKeague and Cline, 1963a; Jones and Handreck, 1967; Lidstrom, 1968). There is a strong relationship between increasing quartz solubility and decreasing grain size

(Iler, 1955; Lidstrom, 1968). In one experiment there was virtually no solubility in water of quartz 250 - 500 μm in size after 200 days while grains $<5 \mu\text{m}$ in size resulted in concentrations of 3 mg l^{-1} in solution after 43 days (Siffert, 1967). There is a rapid increase in solubility as grain size decreases below $0.01 \mu\text{m}$ (Lidstrom, 1968).

The solubility of opal is more variable (Krauskopf, 1959; Lewin, 1961; Siffert, 1967). Geological opal commonly has a solubility of $10 - 15 \text{ mg l}^{-1} \text{ Si}$ and plant opal has much higher solubility, similar to that of amorphous silica (Wilding et al., 1977). Old plant opal in soils is possibly more resistant and a decrease in solubility of this material with time may be expected (Huang and Vogler, 1972). The variability of the structure, occluded crystal content and organic C content of plant opal will also affect solubility (Wilding et al., 1977).

The solubility of amorphous silica at room temperature and pH 7 lies within the range $50 - 65 \text{ mg l}^{-1}$ (Alexander et al., 1954; White et al., 1956; Krauskopf, 1956; 1959; 1967; Morey et al., 1962; Iler, 1973). Amorphous silica precipitates more rapidly than quartz from supersaturated solutions and even though it is more soluble than quartz, the equilibrium is still very slow (Krauskopf, 1959). The solubility of amorphous silica increases linearly with temperature from 0°C (Alexander et al., 1954; Krauskopf, 1959; Lidstrom, 1968).

Silica Mineral Stability

Several factors have been shown to affect the dissolution of silica in natural systems. The presence of polyvalent metal oxides and hydroxides, particularly those of Al, has been shown to depress the solubility of silica (Krauskopf, 1959; Lewin, 1961; Beckwith and Reeve, 1963; Jones and Handreck, 1963; Lidstrom, 1968; Iler, 1973).

This is thought to be a result of the formation of an Al surface layer and even a 5% coverage of Al would reduce the amount of soluble Si in amorphous silica (Iler, 1973). In systems containing particulate metal oxides, adsorption of solution Si increases the dissolution of silica, particularly between pH 8 - 10 (Jones and Handreck, 1963; McKeague and Cline, 1963c; Beckwith and Reeve, 1964). It is unlikely that quartz will be affected by this mechanism unless it has a disturbed surface layer, because quartz has such a low solubility and precipitation rate. Silica in solution will then probably be controlled by iron or aluminium silicate surfaces (Wilding et al., 1977).

The dissolution of biogenic silica is more variable. Alkali dissolution of plant opal from tree leaves and grasses ranges from 35 - 80% during a 2.5 minute digestion in boiling 0.5 M NaOH (Wilding and Drees, 1974). In contrast, only 33% of biogenic opal from a grass-land soil was dissolved during a 20 minute digest under the same conditions (Jones, 1969). The difference was attributed to the rapid dissolution of the more soluble forms of biogenic silica which had occurred in the soil. Organic carbon and anisotropic crystal phases occluded within the opal can also decrease silica solubility (Wilding and Drees, 1973; 1974).

The concentration of silica in groundwaters lies in the range of 5 - 30 mg l⁻¹ Si (Krauskopf, 1967). The low concentration in natural waters is attributed to the rapid dilution by infiltration relative to slow rates of silica dissolution (Krauskopf, 1959). In soil solutions, the concentration lies in the 1 - 40 mg l⁻¹ Si range (Jones and Handreck, 1963; 1967; McKeague and Cline, 1963b; Elgawhary and Lindsay, 1972), with 15 - 20 mg l⁻¹ being most common at field capacity (Jones and Handreck, 1967). The concentration of silica in soils lies between the equilibrium solubility of quartz and amorphous silica. In this

situation quartz should precipitate and amorphous silica dissolve, with the equilibrium silica concentration falling eventually to that of quartz (Wilding et al., 1977). This is not often the case. The probable factors controlling the soil silica concentration are phases with solubilities intermediate between amorphous silica and quartz (Elgawhary and Lindsay, 1972), weathering of primary minerals (Keller and Reeseman, 1963; Kittrick, 1969; Routson et al., 1977), equilibrium with clay minerals (Kittrick, 1969; 1971; Marion et al., 1976) and adsorption/desorption by metal oxides (McKeague and Cline, 1963c; Beckwith and Reeve, 1963; 1964). Leaching and plant uptake also affect silica levels in the soil solution (Kittrick, 1969) and it is likely that equilibrium concentrations are reached in soil solutions only in exceptional circumstances (Wilding et al., 1977).

Amorphous silica also plays a role in controlling silica concentrations in soil solution. Oversaturation with respect to silica leads to polymeric silica formation and the stability of amorphous silica for long periods (Harder and Flehmig, 1970). Oversaturation could easily arise in the situation where wetting and drying occurs and precipitation of silica proceeds faster than adsorption by metal oxides. Once dried, the amorphous silica has a lower solubility than undried gel, leading to lower silica levels in solution (Elgawhary and Lindsay, 1972; Harder, 1977). Changes in moisture status are therefore thought to influence silica concentration in solution faster than other processes while sorption/desorption reactions lead to equilibration faster than the very slow solution/precipitation reactions (Wilding et al., 1977).

Silica Mineral Synthesis

The synthesis of silica minerals at elevated temperatures has been studied extensively in both the laboratory and the field (e.g.

Fenner, 1913; Tuttle and Bowen, 1958; Morey et al., 1961; 1962; Chesworth, 1975; Fournier and Rowe, 1977). However, because of the slow rate of attaining equilibrium at room temperature (25°C), there is only sparse evidence for the direct precipitation of quartz at low temperatures. Morey et al., (1962) inferred that quartz precipitated because of the decrease in silica concentration of a solution over a 30 day period but did not record the formation of quartz. Direct precipitation of quartz onto the surfaces of quartz grains from sea water has been recorded. Quartz grains were free of sorbed material and the silica steady state concentration was approximately $2 \text{ mg l}^{-1} \text{ Si}$ at 20°C (MacKenzie and Gies, 1971). Precipitation in natural environments was thought to be inhibited by the presence of organic and metal oxide coatings (MacKenzie and Gies, 1971).

Quartz synthesis has been reported from solutions undersaturated with respect to amorphous silica; at higher concentrations the precipitates remain amorphous (Harder and Flehmig, 1970; Harder, 1977). Quartz synthesis can also occur by sorption of silica from quartz undersaturated solutions onto amorphous hydroxides of Al, Fe and Mg (Harder, 1971).

Tridymite and cristobalite have generally been considered as late crystallisation phases in igneous rocks, particularly lavas and pyroclastics (Deer et al., 1966; Mizota and Aomine, 1975). However, the presence of cristobalite in bentonites, deep sea cherts, claystones and lacustrine clays suggests a low temperature paragenesis (Peterson and von der Borch, 1965; Henderson et al., 1971; Wise et al., 1972; Weaver and Wise, 1972; 1974; Wise and Weaver, 1973; 1974). Both tridymite and cristobalite have been suggested as precursors of quartz in the conversion of either biogenic opal or amorphous silica to quartz (Deer et al., 1966; Ernst and Calvert, 1969; Mizutani, 1970;

Buurman, 1972) and this is thought to explain the virtual absence of tridymite and cristobalite from rocks older than Cretaceous.

Crystallisation of Silica in Natural Environments

The ageing of silica hydrogels is usually regarded as being the process by which quartz forms under earth surface conditions (Wilding et al., 1977). The sequence:

opal -----> chalcedony -----> quartz

has been reported for duripans and silica-cemented soils (Flach et al., 1969; Brewer et al., 1972). Other pathways are:

opal -----> tridymite -----> quartz

in fossilised wood (Buurman, 1972), and:

amorphous silica -----> cristobalite -----> quartz

(Ernest and Calvert, 1969; Mizutani, 1970).

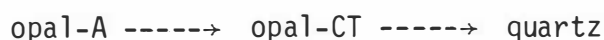
Although the transformation of biogenic opal to chalcedony/quartz has been suggested (Beavers and Stephen, 1958), later work has shown that the birefringent phases in plant opal are coprecipitated with the opal (Wilding and Drees, 1974) and are also partially an artifact of dry ashing and wet acid-digestion methods of analysis (Wilding et al., 1977). The opal to chalcedony transformation is given a time scale of millions of years (Mizutani, 1970), suggesting that this may not be an important pathway in soils (Wilding et al., 1977).

Under geological conditions, precipitation of quartz is facilitated because:

- (i) neoformation of quartz occurs under conditions of elevated temperature and pressure which increase reaction rates
- (ii) in highly siliceous rocks, such as quartzites, the equilibrium concentration of silica is likely to be low, controlled by the

dissolution of quartz rather than amorphous silica. Under such conditions of low silica concentration in solution, quartz precipitation is facilitated (Harder and Flehmig, 1970). In contrast, where there are sufficient aluminosilicates present to maintain a higher silica concentration than the quartz equilibrium concentration, cementation with opal or amorphous silica will occur rather than with quartz. This has been reported from silcretes in Australia where amorphous silica cement is associated with claystones, while quartzose cements are associated with Tertiary quartz sandstones (Watts, 1978). A similar relationship between lithology and type of silica precipitated was noted in surficial materials in the Sahara desert (Millot, 1970).

In deep sea sediments, transformations of opal-A (biogenic opal) to opal-CT (disordered low cristobalite with tridymite domains) to chalcedony, or cryptocrystalline quartz (chert), have been recognised (Heath and Moberly, 1971; Kastner et al., 1977). A number of factors affect the sequence, such as presence of clay minerals, carbonate, and ions such as Mg^{2+} . At higher temperatures opal-CT recrystallises to quartz (Weaver and Wise, 1972). The silica concentration relative to the equilibrium solubility of opal-CT is an important control on the form of silica crystallisation, in that quartz can only crystallise from solution if the silica concentration is less than the equilibrium solubility of opal-CT (Murata and Levson, 1975). Because in most siliceous oozes the concentration of silica is greater than this (Gieskes, 1975), opal-CT is the stable phase and the sequence



predominates (Heath and Moberly, 1971).

Silica in New Zealand Soils

A range of forms of silica have been reported from many New Zealand soils (Fieldes and Swindale, 1954; N.Z. Soil Bureau, 1968; Mokma et al., 1972; Claridge and Weatherhead, 1978). Authigenic quartz was postulated to have formed in the highly siliceous albic horizons of the Northland Kauri podzols, formed under intense acid leaching beneath individual kauri (Agathis australis) trees (Fieldes et al., 1956; Smidt et al., 1977). This quartz was thought to have been reworked to form some of the quartz in Northland beach sands (Schofield, 1970).

Another form of silica of low structural order, termed chalcedonite, has been described from New Zealand soils, particularly those formed in quartzose parent materials (Fieldes, 1952; Fieldes and Swindale, 1954; Fieldes and Williamson, 1955; Fieldes et al., 1956). Chalcedonite is thought to be an intermediate stage between colloidal, or amorphous silica and α -quartz. The X-ray diffraction (XRD) properties are similar to those of α -quartz but the refractive index is reported as lower than that of chalcedony and the differential thermal analysis (DTA) patterns are anomalous (Fieldes and Swindale, 1954; Fieldes and Williamson, 1955). A silica phase with similar properties has been described from fossil wood (Keith and Tuttle, 1952).

Relatively young rhyolitic and andesitic tephras constitute a significant component of many of the soil parent materials in the North Island of New Zealand. The rate of release of silica during weathering of such tephras in temperate to tropical climates can be rapid, being due largely to weathering of the volcanic glass component (Hendricks and Whittig, 1968; Ruxton, 1968; Neall, 1977). This leads to high concentrations of silica in solution which favour the precipitation of amorphous silica. The presence of amorphous silica

plates has been reported in both New Zealand (e.g. Kirkman, 1977) and Japanese soils (Shoji and Masui, 1969a; 1969b) without the formation of quartz (Stewart et al., 1977). Chalcedonite is also absent from soils developed in young volcanic ashes (Fieldes, 1955) and basaltic parent materials (Fieldes et al., 1956).

In soils developed from basaltic parent materials weathering is often very rapid and the weathering sequence:

primary minerals ----> montmorillonite ----> kaolinite ----> gibbsite

has frequently been recorded in well-drained soils (Craig and Loughnan, 1964; Singer, 1966). This process involves progressive desilication and leaching of silica. In poorly drained basaltic soils the weathering sequence is less well developed because silica is not removed from the system by leaching to the same extent as in the well-drained case. Pedogenic chalcedony has been recorded from a soil in such an environment in Australia (Craig and Loughnan, 1964).

The purpose of this paper is to report on an investigation into the likely origin of quartz in a range of soil parent materials from the North Island of New Zealand using the oxygen isotope abundance of the marker mineral quartz.

MATERIALS AND METHODS

A wide range of North Island soils and soil parent materials were examined for this study (Table 2.1). A kauri podzol (Wharekohe series) was first investigated because these soils were reported as evidence of pedogenic quartz crystallisation during podzolisation (Fieldes et al., 1956; Smidt et al., 1977). Soils

Table 2.1 Oxygen isotope abundance of quartz from selected size fractions of some New Zealand soil parent materials and sediments.

Sample	Size Fraction (μm)	* $\delta^{18}\text{O}$ (‰)
Mangakahia Group (shale)	63 - 20	12.0
	5 - 2	25.7
Whangai Formation (shale)	63 - 20	25.6
	5 - 2	26.6
Ohinewai Tephra Formation (rhyolitic tephra)	1000 - 500	8.4
	63 - 20	8.4
Waimamaku (quartzose beach sand, west coast, Northland)	500 - 250	8.7
Rarawa (quartzose beach sand, east coast, Northland)	250 - 125	11.7
	125 - 63	11.5
Te Aute Limestone (Coquina)	63 - 20	13.9
	20 - 5	14.5
	5 - 2	15.3

* Relative to Standard Mean Ocean Water, SMOW (Craig, 1961).

developed in basalt, andesite and rhyolite were examined to cover a range of volcanic parent materials from low to high silica content respectively. Some non-volcanic parent materials (shale, quartzose beach sands and limestone) were also included (Table 2.2).

Soil samples were treated with 1M NaOAc-HOAc (pH 5) and H_2O_2 to remove carbonate and organic matter (Jackson, 1956). The Te Aute Limestone sample was treated with 1M HCl to dissolve the shell material. Mangakahia Group and Whangai Formation shales were disaggregated by gentle crushing with mortar and pestle, care being taken to avoid grinding. The quartzose beach sands were treated with 6M HCl to remove carbonate and any iron oxide coatings present, were then dry sieved and quartz grains were hand picked from the size fractions for analysis. All other samples were size fractionated by sieving, sedimentation and centrifugation (Jackson, 1956). Quartz was isolated from the samples by $\text{Na}_2\text{S}_2\text{O}_7$ fusion and H_2SiF_6 digestion (Jackson, 1956; Sridhar et al., 1975). H_2SiF_6 was found to remove chalcedonite and, with repeated treatments, most cristobalite from these samples. This is probably a result of both the very fine grain size and the lower degree of structural order of these two phases relative to quartz.

For oxygen isotope analysis, oxygen was liberated from the quartz by reaction with BrF_5 (Clayton and Mayeda, 1963). Isotope ratios were determined with a double collecting mass spectrometer and are reported as $\delta^{18}\text{O}$ parts per thousand ($^{\circ}/_{\text{oo}}$) relative to Standard Mean Ocean Water, SMOW (Craig, 1961).

Table 2.2 Oxygen isotope abundance of quartz from selected
size fractions of a range of New Zealand soils.

Soil Series	Depth (m)	Horizon	Size Fraction (μ m)	*δ ¹⁸ O (‰)
Parahaki	0 - 0.1	Ap	63 - 20	9.0
			5 - 2	9.3
	0.1 - 0.2	Bw	63 - 20	9.2
			5 - 2	9.1
Wharekohe		E	63 - 20	12.8
			5 - 2	13.4
Te Kopuru		E	> 63	8.9
			63 - 20	10.9
			5 - 2	14.2
Kara	0.2 - 0.3	E	63 - 20	12.1
			5 - 2	15.6
	0.35 - 0.45	Btg	63 - 20	12.0
			5 - 2	15.1
Egmont	0.4 - 0.5	Bw1	63 - 20	13.9
			20 - 5	14.0
			5 - 2	15.0
	1.1 - 1.2	2Cu2	63 - 20	13.9
			20 - 5	14.5
			5 - 2	15.2
Northland Basaltic Soils	(mean of 2 soils)		> 125	8.2
	(mean of 6 soils)		63 - 20	12.0
	(mean of 5 soils)		5 - 2	13.9
Ruatangata	0.2 - 0.3	Bt	2 - 1	13.6

* Relative to SMOW.

RESULTS AND DISCUSSION

The results of oxygen isotope analysis are summarised in Table 2.1 and 2.2. The $\delta^{18}\text{O}$ values for 63 - 20 μm and 5 - 2 μm quartz from the albic horizon of the Wharekohe silt loam indicate intermediate temperature or mixed origin, detrital quartz (Table 2.2). Scanning electron microscope (SEM) examination shows both fractions to consist of angular quartz grains with no evidence of secondary quartz. This clearly suggests that the quartz in the Wharekohe silt loam is not authigenic and that quartz crystallisation has not been a significant process during podzolisation.

The Te Kopuru sand is another podzol from Northland, that has an albic horizon strongly cemented with silica. The $\delta^{18}\text{O}$ values for selected size fractions from the albic horizon (Table 2.2) show that the quartz in the sand fraction and part of the silt size fraction is of high temperature origin. Quartz in the 5 - 2 μm size fraction is of lower temperature origin and has $\delta^{18}\text{O}$ values similar to those obtained for quartz from this size fraction in a range of other soils and sediments (Table 2.1; 2.2; Mokma et al., 1972). A thin section from a cemented horizon within a Te Kopuru sand shows that it consists predominantly of angular quartz grains in a largely silica matrix. Silica precipitation in the Te Kopuru sand appears to be largely in the form of amorphous silica and crystallisation to quartz has not occurred.

The subsoil of a soil belonging to the Kara series, a gleyed podzol, was also investigated. The parent material is a siliceous, Holocene lacustrine sediment. The $\delta^{18}\text{O}$ values of the quartz in these samples indicate that there may be a small component of low temperature quartz present only in the 5 - 2 μm size fraction where

$\delta^{18}\text{O}$ values of 15.1‰ and 15.6‰ were obtained, these being higher than those obtained from the same size fraction of other soils in the same region (Table 2.2). This could be a result of quartz containing a low temperature component being derived from Cretaceous marine shales which occur in the lake catchment, rather than pedogenic quartz forming in the soil.

Two marine shales were analysed, these showing the highest $\delta^{18}\text{O}$ values of all the samples examined (Table 2.1). The 5 - 2 μm size fraction of the Tertiary Mangakahia Group shale, from Northland, appears to have a large component of low temperature quartz. However, the 63 - 20 μm size fraction shows quartz grains that are almost entirely angular, detrital monocrystalline fragments, which show markedly lower $\delta^{18}\text{O}$ values (Table 2.1). These values are similar to other $\delta^{18}\text{O}$ values of quartz in similar size fractions from Northland soils (Table 2.2). In contrast, the Cretaceous Whangai Formation shale, from Hawkes Bay, appears to have predominantly low temperature quartz in all of the size fractions analysed (Table 2.1). Thin section examination does show some detrital quartz present, which is most common in the coarser size fractions. This would explain the slightly lower $\delta^{18}\text{O}$ values obtained for the 63 - 20 μm size fraction (Table 2.1). Most of the grains, however, consist of detrital chert in a weakly to moderately cemented matrix. The Whangai Formation shale clearly had a predominantly chert-bearing source, the chert being responsible for the high $\delta^{18}\text{O}$ values, similar to those found for cherts elsewhere (Churchman *et al.*, 1976). The Whangai Formation is widespread, extending from East Cape in the north to Marlborough in the south. It is likely that several source areas contributed to the sediments mapped within the Formation and not all of these may have been chert-bearing. As a result, some geographic

variation in the $\delta^{18}\text{O}$ values for quartz within the Formation is expected.

Quartz in the acid-insoluble residues from the late Pleistocene Te Aute Limestone has $\delta^{18}\text{O}$ values indicative of a detrital origin (Table 2.1). The grain size characteristics of the residue (well-sorted, predominantly coarse silt to very fine sand material) are similar to other limestones from the North Island (Nelson, 1977). The quartz in the 5 - 2 μm size fraction has a $\delta^{18}\text{O}$ value of 15.3 $^{\circ}\text{oo}$, which may well indicate the presence of aerosolic dust in this marine sediment, as has been suggested for quartz in pelagic sediments of the Pacific Ocean (Rex and Goldberg, 1958; Clayton et al., 1972).

The $\delta^{18}\text{O}$ values for the quartz from the Northland basaltic soils are reported as mean values for the size fractions investigated (Table 2.2). Details of oxygen isotope analysis of quartz from each individual soil are presented in Chapter 4. Quartz in the sand fraction is clearly of high temperature origin with a $\delta^{18}\text{O}$ value of 8.2 $^{\circ}\text{oo}$. In contrast, the $\delta^{18}\text{O}$ values for the silt fractions are similar to values obtained for quartz in other soil and sediment silt fractions in New Zealand, for which a detrital origin has been postulated (Mokma et al., 1972). The 2 - 1 μm size fraction of one of the older basaltic soils (Ruatangata series) has a $\delta^{18}\text{O}$ value of 13.6 $^{\circ}\text{oo}$, indicating that the quartz is not of low temperature origin, and is similar to the mean value of the 5 - 2 μm size fraction for the basaltic soils of 13.9 $^{\circ}\text{oo}$ (Table 2.2). This suggests that the two size fractions have similar origin and are probably part of a 10 - 1 μm tropospheric aerosolic dust fraction (Rex et al., 1969; Syers et al., 1969; Mokma et al., 1972; Jackson et al., 1973). No quartz was found in the < 1 μm size fractions of these soils, compatible with the 1 μm lower limit for aerosolic dust. In one of the soils there is clear

evidence of low temperature quartz present in the 5 - 2 μm size fraction but this was shown to be due to local additions of material from a Tertiary marine shale, indicating that the 5 - 2 μm size fraction does not consist exclusively of tropospheric aerosolic dust (Chapter 4).

The absence of chalcedony or chalcedonite (Fieldes et al., 1956) is probably due to the free draining nature of the basaltic soils examined. In a free-draining basaltic soil, leaching of the initially low-silica parent material is thought to rapidly remove silica released during weathering (Craig and Loughnan, 1964). Some silica in solution is thought to react with alumina to form halloysite (Fieldes et al., 1956). XRD analyses of the Northland basaltic soils show the presence of halloysite, in addition to kaolinite, goethite and gibbsite, confirming that this reaction is possible. Under these free-draining conditions the formation of quartz or chalcedonite is considered unlikely. Recent studies of soils developed on basic volcanic rocks overseas have also reached this conclusion (Jackson et al., 1972; Singer and Navrot, 1977).

No evidence of pedogenic quartz formation was found in the andesitic Egmont soil from Taranaki, New Zealand, all quartz being of aeolian origin (Stewart et al., 1977).

The Ohinewai Tephra Formation is a rhyolitic tephra erupted from the central North Island (Vucetich et al., 1978). The $\delta^{18}\text{O}$ value of 8.4‰ for quartz from this tephra (Table 2.1) is typical of high temperature igneous quartz (Churchman et al., 1976) and is similar to the values of 9.0 - 9.3‰ obtained for quartz in a soil developed from a Parahaki rhyolite (Table 2.1; Mokma et al., 1972). The slightly higher $\delta^{18}\text{O}$ value for the rhyolite quartz probably reflects different cooling rates of rhyolite lava versus tephra, the more slowly cooled rhyolite recording a lower temperature oxygen isotope fractionation than the more rapidly cooled tephra.

CONCLUSIONS

The origin of quartz in soils and sediments can often be determined by its oxygen isotope composition. In particular, the presence of low temperature quartz formed in sedimentary or soil environments can be determined by its high $\delta^{18}\text{O}$ values. In this study we have shown that pedogenic α -quartz was not present in the range of soils examined. The rapid release of silica during weathering leads to the precipitation of amorphous silica in andesitic and rhyolitic volcanic ash. In free draining basaltic soils leaching of silica and reaction with alumina to form halloysite probably accounts for most of the silica released during weathering. Only in highly quartzose parent materials is the concentration of silica in solution apparently low enough to form the chalcedonite reported in the literature. Low temperature quartz from the Tertiary Mangakahia Group and Cretaceous Whangai Formation shales is clearly of geological origin.

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CHAPTER 3

CHAPTER 3

PARENT MATERIAL STRATIGRAPHY OF AN
EGMONT LOAM PROFILE, TARANAKI, NEW ZEALAND

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ABSTRACT

The Egmont loam of Taranaki, New Zealand, is regarded as a classic andosol developed in andesitic tephra (a yellow-brown loam in the N.Z. genetic soil classification or an entic dystrandept in the U.S. Soil Taxonomy). Variations in grain size distribution and mineralogy within a representative profile show it to consist of two distinct units, an upper unit of andesitic tephra and a lower unit containing up to 30% quartz, which is interpreted as a tephric loess. Correlation of peaks in andesitic glass distribution within the profile with eruptions from Mt Egmont suggest an accumulation period of circa 10,000 years for the tephra unit, while the presence, in places conducive to its preservation, of the Aokautere Ash, a rhyolitic ash of widespread distribution in the central North Island, dates (NZ1056A) the base of the profile at less than 19850 ± 310 years B.P. Peaks in distribution of the minor rhyolitic glass component in the tephra unit

are correlated with three major post-glacial rhyolitic eruptions from the central North Island; the Taupo eruption of 1840 ± 50 years B.P. (NZ1548A), the Waimihia eruption of 3440 ± 70 years B.P. (NZ2A), and the Rotoma eruption of 7330 ± 235 years B.P. (NZ1199A).

Variations in the rate of quartz accumulation in the silt fraction of the Egmont profile are correlated with climatic changes, a higher rate of quartz accumulation occurring during the colder climate of the last stadial, in contrast with a lower rate of quartz accumulation occurring during the warmer climate of post-glacial time.

INTRODUCTION

The volcanic ash soils of Taranaki, New Zealand, are typical andosols of the Circum-Pacific region (Fitzpatrick, 1971). Their dark topsoil overlying a yellow-brown subsoil, high allophane content, friable consistency, high porosity and high permeability show a strong similarity to representative andosols of Japan (Ministry of Agriculture and Forestry, 1964). A classical andosol in Taranaki is the Egmont loam, a yellow-brown loam in the New Zealand genetic soil classification (Taylor, 1948) or an entic dystrandept in the U.S. Soil Taxonomy (Soil Survey Staff, 1973). Traditionally it has been considered to have developed in 'Egmont Ash' (Fleming, 1953), a late Quaternary volcanic ash mantle which covers much of the southern part of the Taranaki region. This ash originated as a series of andesitic eruptions from Mt. Egmont, a 2518m high stratovolcano situated in the centre of Taranaki province (Fig. 3.1).

The Egmont loam was first recognized by Grange and Taylor (1933) in southern Taranaki and mapped as two soil types on the basis of the topsoil colours. Within 4 km of the coast, black topsoils predominate due to an initial native scrub vegetative cover, largely comprising

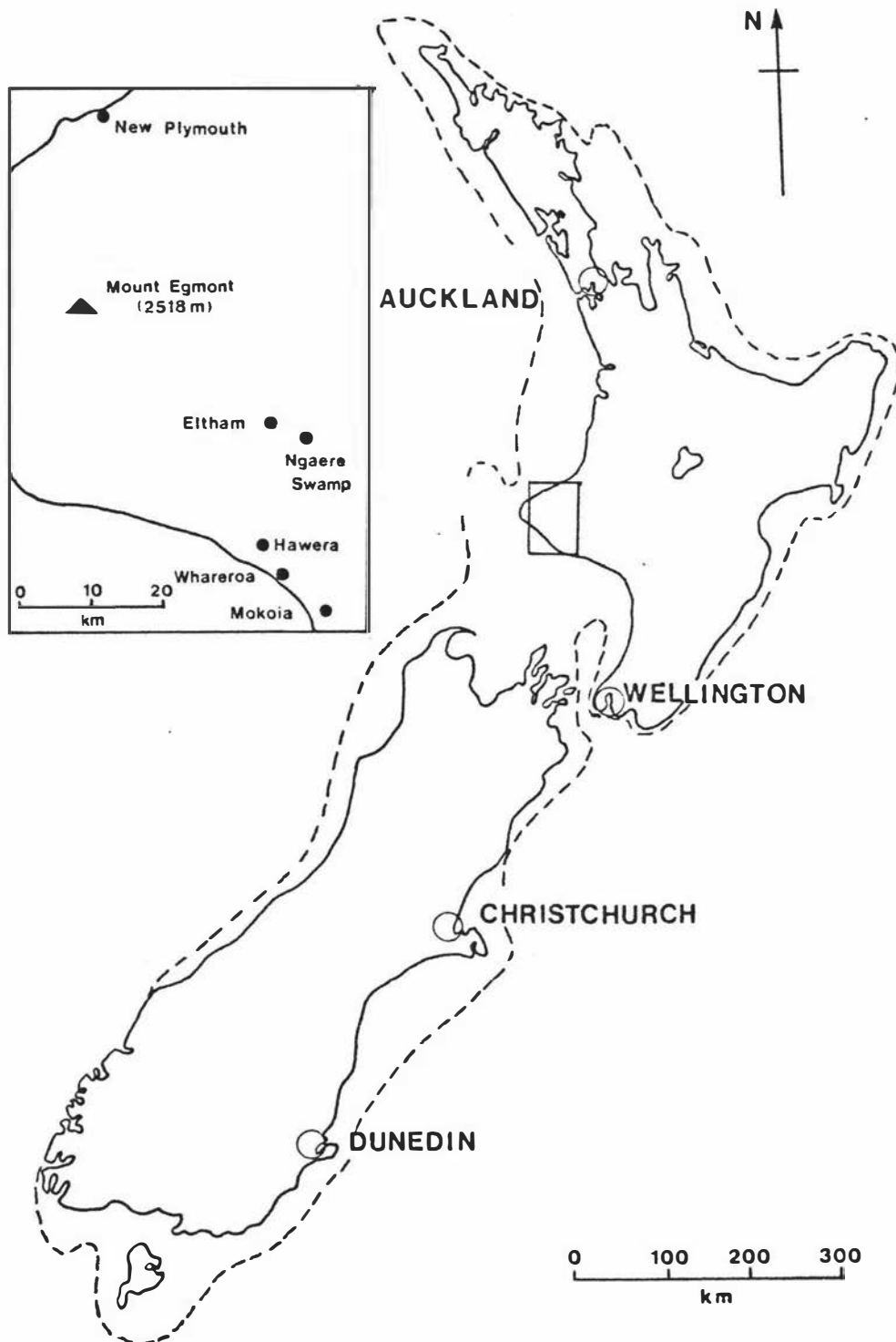


Figure 3.1 Location map for the South Taranaki region.

Phormium tenax and Pteridium aquilinum var. esculentum, prior to the nineteenth century European occupation of New Zealand. Inland of this zone predominantly brown topsoils were formed under a Podocarp-Hardwood forest cover. The Egmont loams occur on a terrain that slopes gently towards the coast and consists of easy-rolling surfaces constructed from terrestrial sand, lignite, tephra, loess and alluvium overlying a sequence of late Quaternary uplifted marine benches (Fleming, 1953). Post-glacial andesitic volcanism has spread a 2-5m thick ash cover over all but the youngest terrestrial deposits. Small rivers, many with their headwaters on the south-eastern slopes of Mt Egmont, are incised within steep-walled, box-shaped gullies as they cross the Egmont loam landscape, particularly near the coast. Rainfall varies both with altitude and position relative to Mt Egmont, from 1020 mm year⁻¹ at the coast to 7000 mm year⁻¹ at 900m altitude. Mean annual temperatures are 11-12°C in the south Taranaki region.

Several studies on the Egmont loam have been concerned with the unusually high allophane content of the soil and its associated physical and chemical properties (Birrell, 1951; Birrell and Fieldes, 1952; Saunders, 1956; 1963; New Zealand Soil Bureau, 1968). However little research has been directed towards determining the age and provenance of the Egmont loam parent materials.

This paper describes a detailed stratigraphical and mineralogical study of a representative Egmont loam profile.

MATERIALS AND METHODS

A representative sample site, located 7 km south of Hawera (Fig. 3.1), was selected for detailed study. The site is on the Ngarino uplifted marine bench (Dickson et al., 1974) and consists of a 4m high road section in which the stratigraphic relationships of the

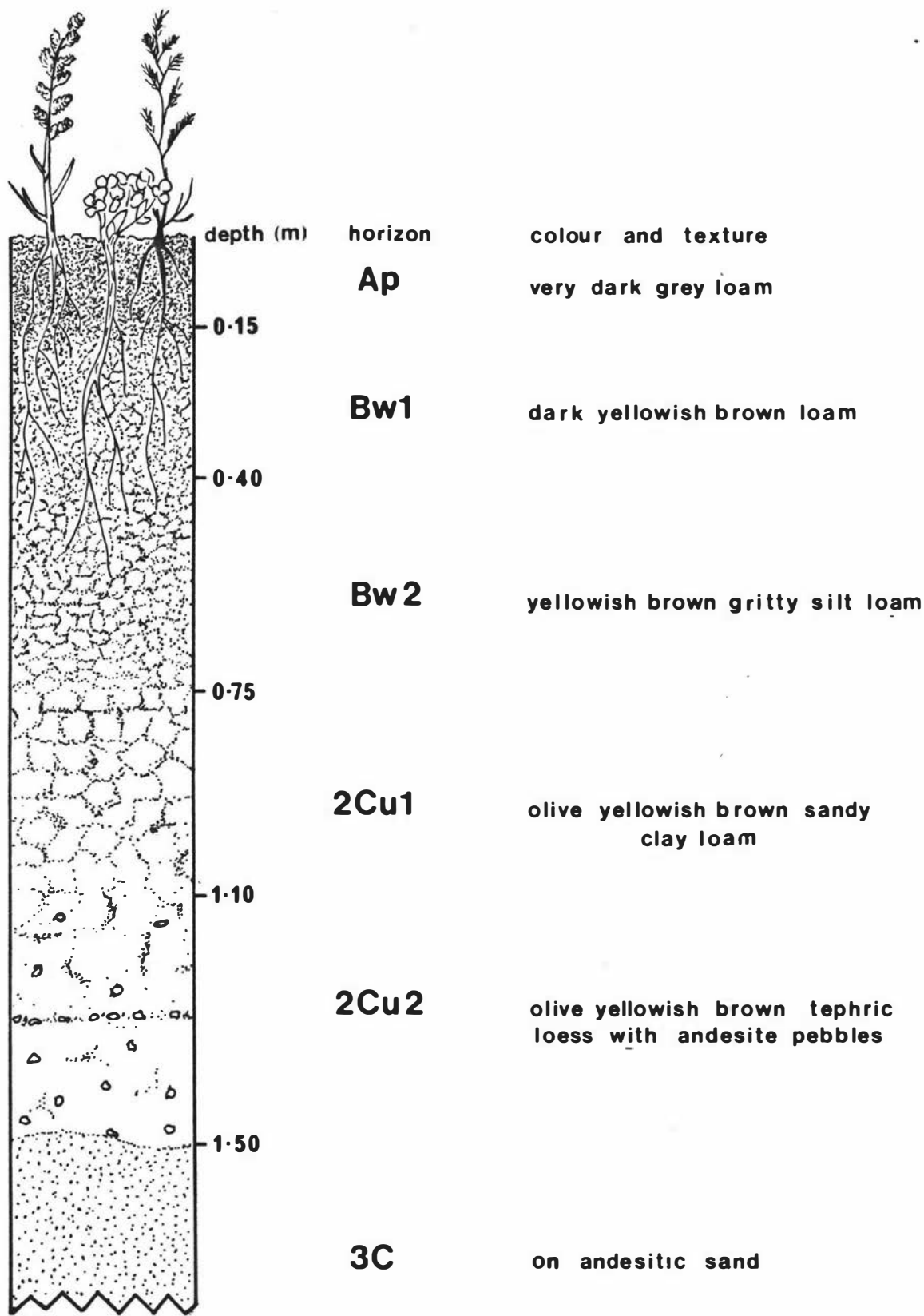


Figure 3.2 Stratigraphic and pedologic horizons within the Egmont black loam. Soil horizon nomenclature is according to the FAO-UNESCO (1974) system.

cover beds are clearly displayed, together with a profile pit in an adjoining paddock. Samples were collected at 10 cm intervals from the surface to the underlying dune sands. The profile is described fully in Appendix 1.

Three grain size parameters are used to distinguish grain size changes with depth, and therefore with time, in the accumulating Egmont loam parent materials. These parameters are the graphic mean (M_z), inclusive graphic standard deviation (σ_I) and graphic kurtosis (K_G) of Folk, (1968). The sand fraction size limits ($> 63 \mu\text{m}$ or 4ϕ) are those of Wentworth, (1922). However, coarse, medium and fine silt fraction size limits are those defined in Jackson, (1956).

Mineralogical data were obtained by point counting grain mounts of the very fine sand and coarse silt fractions. The distribution and amount of quartz in the profile was determined as an aid to tracing the non-andesitic component in the soil parent materials. Quartz size distribution was obtained by the quartz isolation methods of Syers et al., (1968), as modified by Sridhar et al., (1975).

EGMONT LOAM: STRATIGRAPHY

The 'Egmont Ash' overlies a range of parent materials, from aeolian dune sands near the coast to loess on the uplifted marine benches and older tephras further inland. The 'Egmont Ash' is common to all sections examined and is considered to be the material in which the Egmont loams have developed. Two lithological units within the 'Egmont Ash' are here recognized and referred to as the upper and lower units. The Ap, Bw1 and Bw2 horizons of the Egmont loam are developed within the upper unit, whilst the 2Cu1 and 2Cu2 horizons are developed in the lower unit (Fig. 3.2). The upper unit thickens considerably

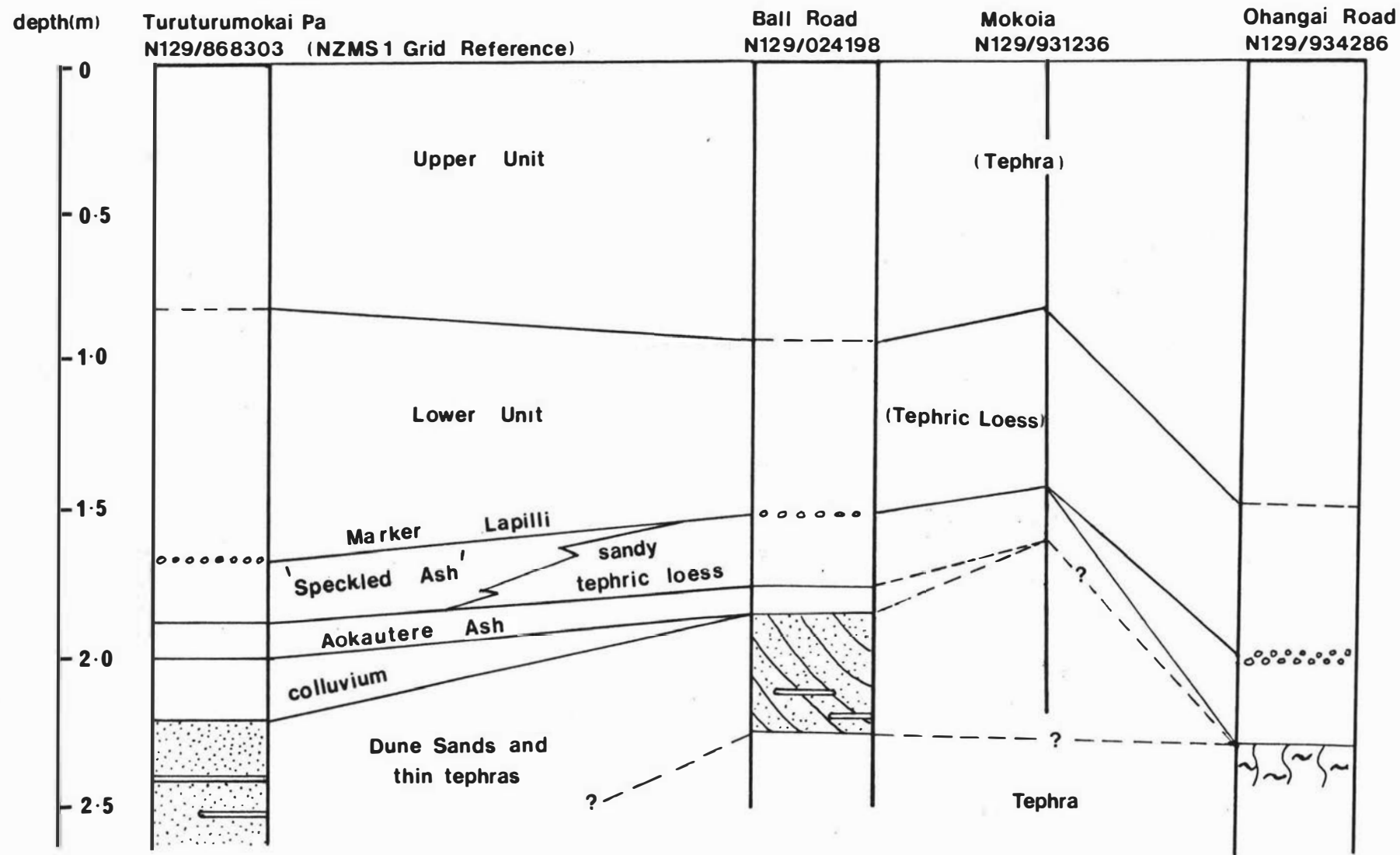


Figure 3.3 Stratigraphic columns demonstrating lithologic relationships of soil-forming parent materials on uplifted marine terraces near Hawera. The columns show (i) the consistent upper and lower units and marker lapilli throughout the region, (ii) localities where the 20,000 year B.P. Aokautere Ash is preserved and (iii) the widespread occurrence of underlying dune sand near the coast, as shown at Turuturumokai Pa, Ball Road and Mokoia.

towards Mt Egmont, accompanied by an increasing abundance and size of lapilli. The lower unit does not appear to thicken appreciably towards Mt Egmont. Few lapilli occur within the lower unit, except for an unnamed lapilli preserved at the base of the unit, which is an important marker horizon throughout the Hawera region (Fig. 3.2).

This marker lapilli rests on a 2m thick 'speckled ash' near Mt Egmont, which thins rapidly towards Hawera (Fig. 3.1) and is absent from the sample site south-east of Hawera. Here the marker lapilli rests on loess-like material which becomes increasingly more sandy towards the underlying dune sand. It is within this sandy material, (and under the 'speckled ash' where present) that the Aokautere Ash dated (NZ1056A) at 19850 ± 310 years B.P. is preserved (Fig. 3.3). The presence of the Aokautere Ash shows that accumulation of the underlying cold climate dune sands ceased approximately 20,000 years ago in the Hawera region. Relatively thin tephra and loess units within the dune sands indicate that there may have been several dune sand advances before 20,000 years B.P. Wood, identified as either Podocarpus totara, P. halli or Dacrycarpus dacrydioides, from a lignite beneath the dune sands, has been dated (NZ3970B) at $> 43,900$ years B.P.

The dune sands are absent from the old marine terraces, and the marker lapilli rests on either a thin unit of 'speckled ash' or loess which in turn overlies a < 1 m thick paleosol (Fig. 3.3).

Parameter Variation With Depth

Variations in the grain size parameters with depth (Fig. 3.4) confirm the existence of the two lithological units recognized on macroscopic physical features. Parameter values remain uniform throughout the upper unit to 75 cm depth. Below 75 cm depth there is a marked change in parameter values across the boundary into the lower unit where mean grain-size decreases, sorting improves and kurtosis

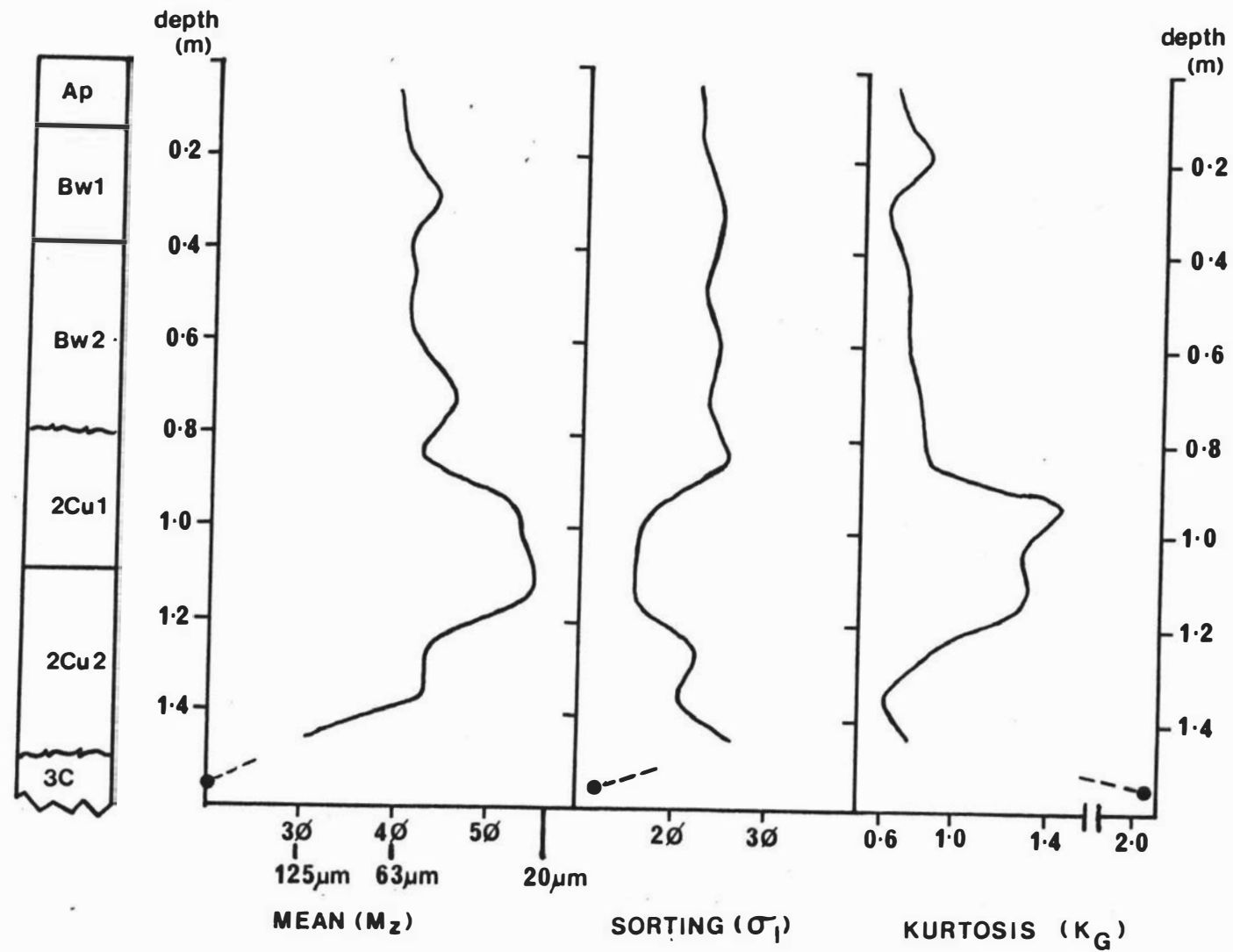


Fig. 3.4 Variation in grain size parameters for the Egmont loam profile as a function of depth. Values for the underlying dune sand are plotted near the base of each column.

values become much higher. In the lowermost 30 cm of the lower unit, there is evidence of mixing with the coarser, underlying dune sand to produce a poorly sorted end-product with a distinctly bimodal character shown by the much lower kurtosis values.

The cumulative curves for samples from the upper and lower units and the dune sand are compared, together with curves from a North American and a New Zealand loess in Fig. 3.5. A representative cumulative curve for the lower unit (curve B) is similar in shape to both loess curves (C, D) and the dune sand curve (E), indicating their cognate aeolian origin. In contrast, the representative cumulative curve for the upper unit (A) shows that it is much more poorly sorted, is polymodal and has a coarser grain size more consistent with near-source volcanoclastic deposits such as, for example, the Inglewood Tephra (curve F), a 4000-5000 years B.P. tephra-fall from Mt Egmont.

Quartz

Total quartz contents within the Egmont profile varied from 30% in the lower unit to 3% in the upper unit. There was a marked change in quartz abundance in the silt fractions across the boundary between the two units (Fig. 3.6). The boundary is interpreted as reflecting a change from conditions of relatively abundant inter-regional quartz supply during the accumulation of the lower unit to a very restricted inter-regional quartz supply during the accumulation of the upper unit.

In contrast to the silt fractions the very fine sand fraction showed no marked change in quartz abundance and this was uniformly low, <1% (Fig. 3.6). Quartz was rare or absent in the coarser sand fractions. These data suggest that the sand-size fractions have been continuously incorporated into the profile from an intra-regional, quartz deficient source, probably andesitic tephra dominated.

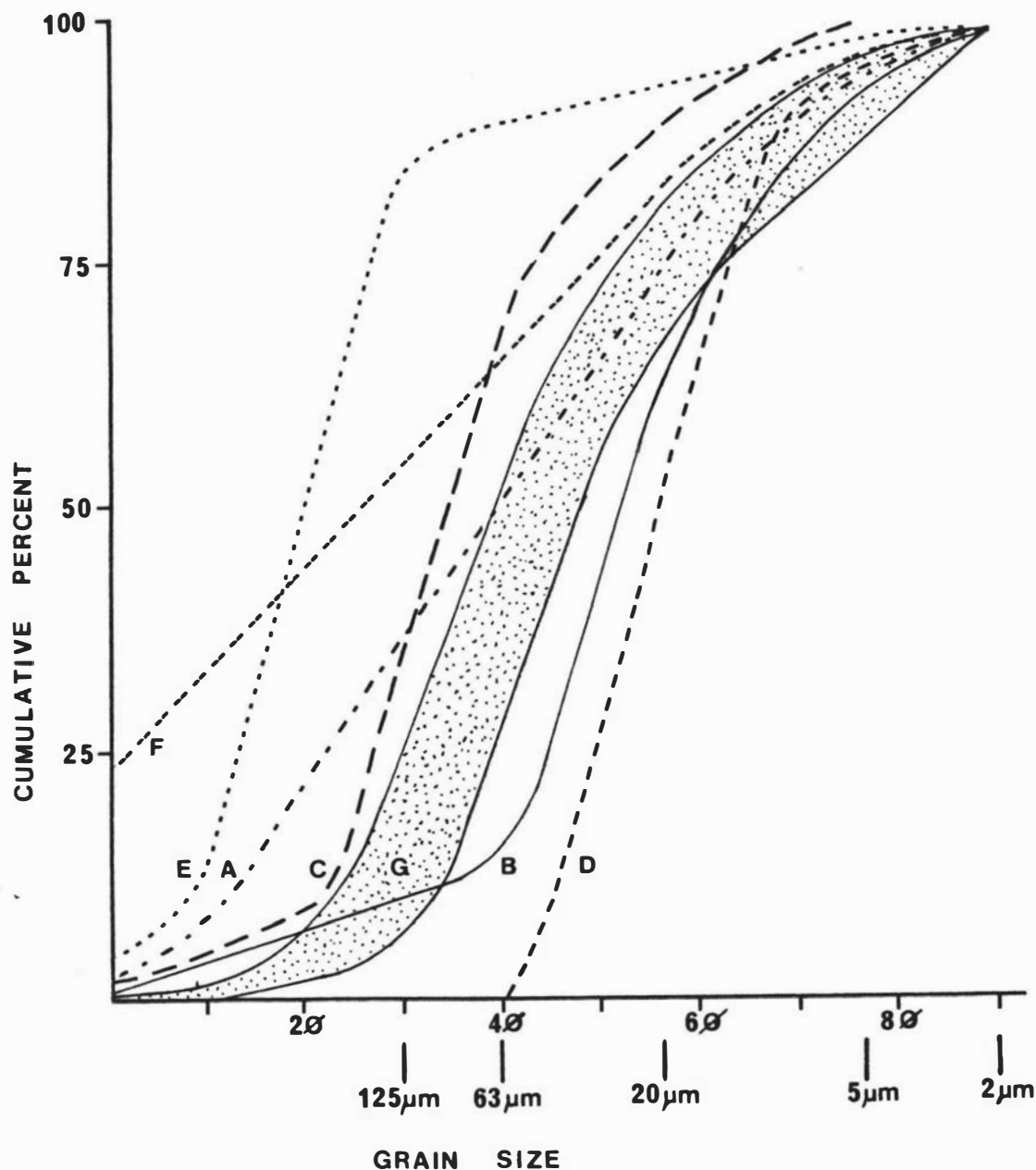


Fig. 3.5 Grain size cumulative curves for:
 A, Egmont upper unit (tephra); B, Egmont lower unit (tephric loess); C, Tokomaru silt loam 1Cwg horizon (after Pollok, 1975); D, North American loess (after Smith, 1942); E, Aeolian dune sand from beneath the Egmont profile; F, Inglewood Tephra. The hatched area represents the range of quartz cumulative curves from the Egmont profile. Curves are calculated on a clay free basis.

The quartz grain-size cumulative curves for all samples from the Egmont profile fell within a narrow field (curve G, Fig. 3.5). They are similar in shape and show a similar grain-size distribution to the loess curves, indicating that the quartz was transported into the profile by aeolian processes. The similarity of all quartz cumulative curves throughout the profile show that this transport mechanism operated unchanged during the accumulation of the entire profile, being independent of both the volcanic influences and changes in quartz supply.

Oxygen Isotope Abundance and Quartz Provenance

Oxygen isotope abundance of quartz from representative samples of the upper and lower units was determined in an attempt to define the provenance of the quartz in the profile. Similar $\delta^{18}\text{O}$ values were obtained for the coarse and medium silt fractions in both samples (Table 3.1). The principal difference occurs between the fine silt

Table 3.1 Oxygen isotope abundance of quartz isolated from selected size fractions, Egmont loam

	Upper unit (tephra) $\ast\delta^{18}\text{O} \text{ }^{\circ}/_{\text{oo}}$	Lower unit (tephric loess) $\delta^{18}\text{O} \text{ }^{\circ}/_{\text{oo}}$
Coarse silt	13.6 ± 0.3	13.9 ± 0.3
Medium silt	13.9 ± 0.3	14.0 ± 0.3
Fine silt	14.5 ± 0.3	15.0 ± 0.3
Quartz from Parahaki rhyolite (volcanic)	9.6	
Cretaceous chert (authigenic)	32	

$\ast$ Relative to standard mean ocean water.

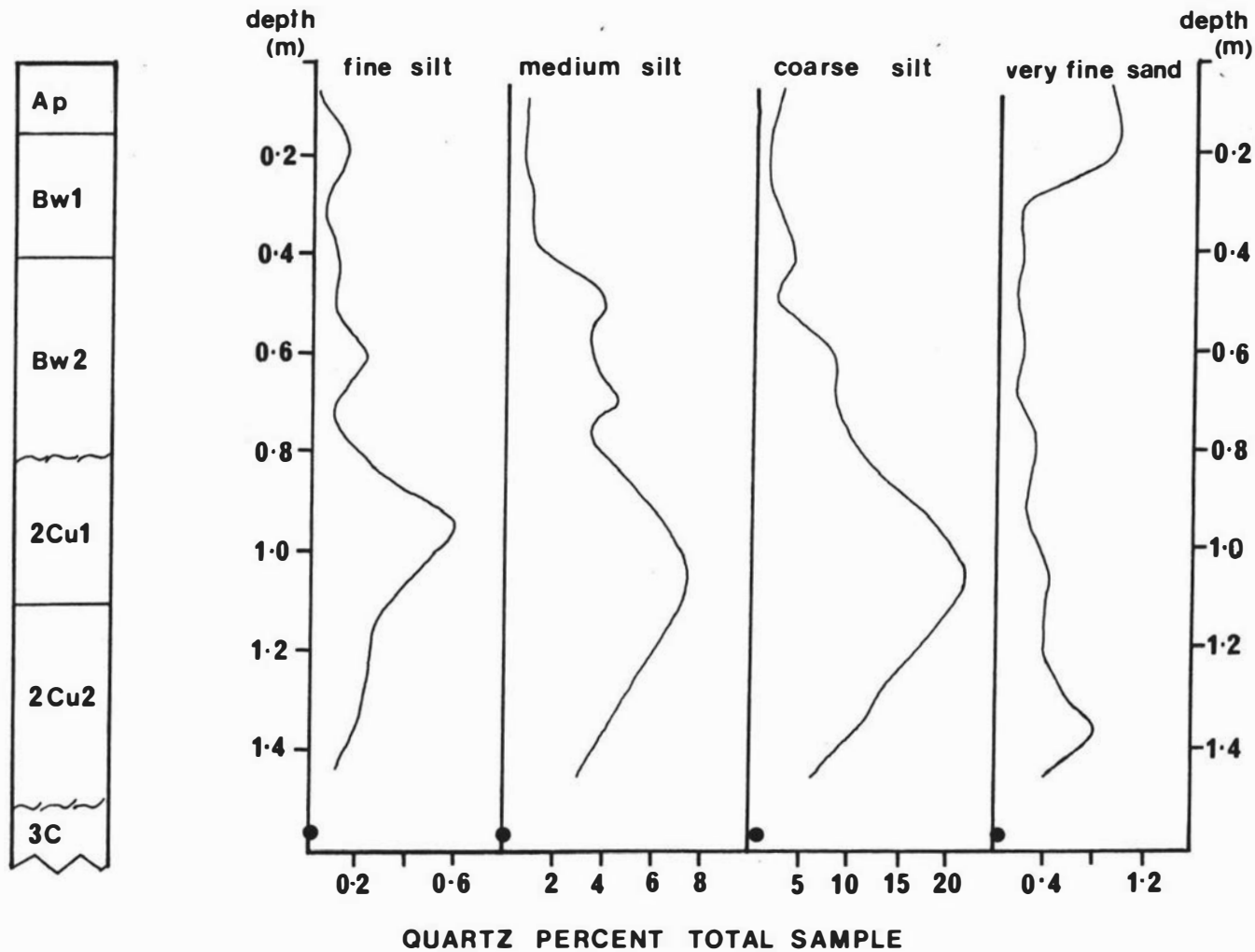


Figure 3.6

Distribution of quartz in particle size fractions as a function of depth. The quartz content of the underlying dune sand is shown at the base of each column.

fraction and the other two silt fractions. The data suggest that the fine silt fraction, a minor component of the quartz content of the profile, is of aerosolic origin (Rex et al., 1969), while the coarse and medium silt fractions are predominantly derived from more restricted regional sources, reflected in the lower $\delta^{18}\text{O}$ values.

The oxygen isotope abundance data show that the quartz in all size fractions analysed has neither an igneous (cf. Parahaki rhyolite, Table 3.1), nor an authigenic (cf. Cretaceous chert, Table 3.1) origin. This precludes the quartz being either derived from andesitic tephra or by in situ formation in the soil.

Feldspar

Most of the feldspar present is a calcic andesine, probably derived from Mt Egmont. The coarse silt fraction shows fluctuations in feldspar content in the upper unit rising to a higher, uniform level in the lower unit (Fig. 3.7). The peaks in the upper unit are suggestive of major andesitic eruptive episodes. The less variable feldspar content in the lower unit indicates little material being directly incorporated from eruptions.

In the very fine sand fraction there is little feldspar variation with depth, indicating, as in the quartz, that this fraction was derived intra-regionally and incorporated at a steady rate into the profile.

Andesitic Glass

'Andesitic glass' within the Egmont profile consists of microlites of feldspar, mafic minerals and titanomagnetite in a glassy matrix. It approximates to the groundmass in andesitic rocks.

Andesitic glass abundance in the lower unit is at a consistently low level (Fig. 3.7). In the upper unit there is a steady increase in abundance overprinted by major peaks in both the coarse silt and very

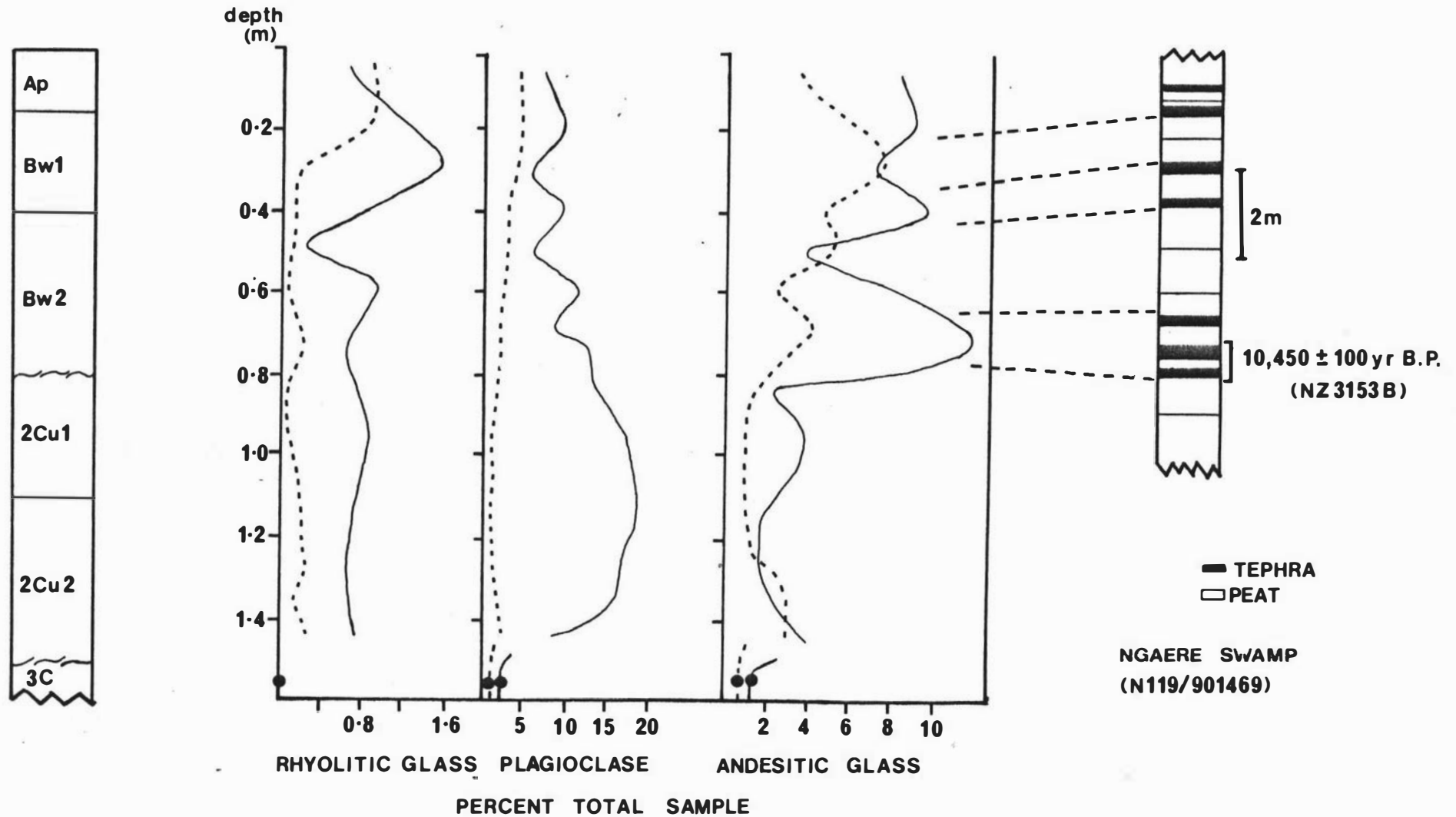


Fig. 3.7

Distribution of rhyolitic glass, plagioclase feldspar and andesitic glass as a function of depth. The solid lines represent the coarse silt fraction and the broken lines the very fine sand fraction. Dune sand values are plotted at the base of each column.

fine sand fractions (Fig. 3.7), which represent specific eruptive episodes. Differences in peak positions between the two size fractions probably reflect variation in grain size distribution of erupted materials. A point on the axis of tephra dispersal would tend to be dominated by coarser tephra, ^{rather} ^{one on} than the lateral and terminal margins of dispersal.

Mafic Minerals

Three mafic minerals occur in significant amounts; augite, hornblende and hypersthene. In the coarse silt fraction both augite and hornblende show a higher abundance in the lower unit, probably as a result of higher resistance to weathering relative to andesitic glass in the source area prior to the accumulation of the lower unit. Both minerals show only one major eruptive peak in the upper unit (Fig. 3.8), corresponding to the lowermost peak in the feldspar and andesitic glass abundances. Augite and hornblende show little variation in the very fine sand fraction. Hypersthene has a similar distribution pattern to the andesitic glass (Fig. 3.8).

Rhyolitic Glass

Rhyolitic glass is a minor component of the minerals present, but its variation with depth is a record of the influence of rhyolitic tephras from the Central North Island. Two rhyolitic glass abundance peaks occur in the coarse silt fraction, both within the upper unit, whilst only one peak is present, at the top of the upper unit, in the very fine sand fraction (Fig. 3.7).

Minor Mineral Constituents

Apart from quartz, several minor (< 1%) minerals occur which are foreign to andesitic rocks and are significant indicators of provenance.

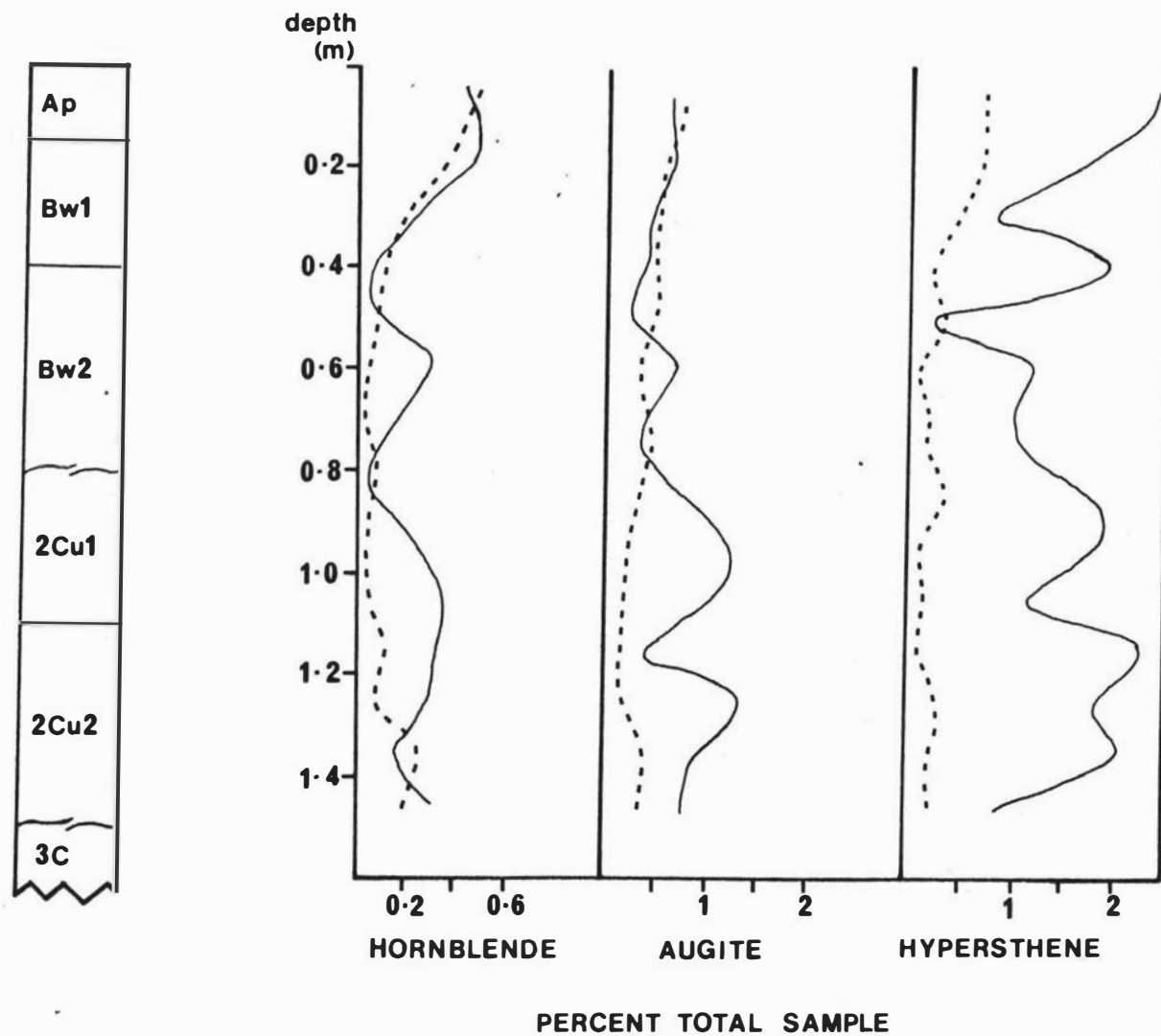


Fig. 3.8

Distribution of mafic minerals with depth.

The solid lines represent the coarse silt fraction and the broken lines the very fine sand fraction.

The most abundant mica present is muscovite. It may form up to 5% in some of the sand fractions, but it is present in only small amounts in the silt fractions of the lower unit and is absent from silt fractions of the upper unit. The most common sediment forming materials in the Hawera region, after andesitic tephra, are Pliocene mudstones, which contain abundant muscovite and biotite. These may be supplying some material to the sand fractions, but appear to contribute little to the silt fractions. Biotite is rare in the Egmont profile but may have altered to chlorite, which is present in greater amounts. Chlorite is also more abundant in the silt fractions of the lower unit than those of the upper unit.

Minerals of the epidote group present are epidote, clinozoisite and zoisite. All are present in the lower unit but are rare in the upper unit. Epidote and clinozoisite have a similar paragenesis. Both are common in igneous rocks, where they form as deuteric or late magmatic phases, and in metamorphic rocks, where they occur in the epidote-amphibolite facies of regional metamorphism. They may also form from the sausseritization or hydrothermal alteration of plagioclase (Deer et al., 1969). However, the coarseness of the grain size, together with grain rounding and absence of evidence of sausseritization of associated plagioclase, suggest that the epidote group minerals in the profile are detrital. Zoisite has a more restricted paragenesis, being formed only in metamorphic rocks.

Microcline occurs in trace amounts throughout the lower unit, but is virtually absent from the upper unit. Because microcline is not known to occur in volcanic rocks as a primary mineral, its presence indicates that one of the ultimate sources of the non-andesitic material was in an acid plutonic or high-grade metamorphic terrain, foreign to the Taranaki region.

DISCUSSION

The stratigraphic column of unnamed eruptions from Mt Egmont preserved within peat in the Ngaere Swamp (Fig. 3.1), 21 km NNW of the Egmont loam sample site, shows all the major post-glacial tephras erupted to the east and south-east of Mt Egmont (Fig. 3.7). A radio-carbon age (NZ3153B) from near the base of the column dates a major series of eruptions at 10450 ± 100 years B.P. This series of eruptions is correlated with peaks in the andesitic glass, feldspar and mafic mineral abundances at the base of the upper unit in the Egmont profile (Figs. 3.7 and 3.8). This indicates an age of 10-11,000 years B.P. for the boundary between the two units.

Paleoclimatic and paleogeographic evidence suggests a similar age for the upper to lower unit boundary. The change from accumulation of predominantly loessic to predominately tephric material across the boundary indicates a major environmental change at this time. Prior to 10-11,000 years B.P. sea level was some 90 m lower than at present and evidence from offshore Taranaki suggests that not only did the Egmont ring plain extend well beyond the present shoreline, but also that there was a land bridge (Fig. 3.1) extending from north-west Nelson to Taranaki at this time (Lewis and Eade, 1974). Such an area is a likely source for the lower unit. Tephra falling on this land bridge was subjected to weathering before being transported and deposited in the southern Taranaki region by aeolian processes. Evidence for redeposition is shown by the grain rounding and the concentration of mafic minerals relative to primary andesitic material in the upper unit. The decreased abundance of andesitic glass in the lower unit and the increased abundance of feldspar, show that glass was being preferentially removed in the source area, in contrast with

the abundance of andesitic glass and feldspar in the upper unit which vary sympathetically, indicating that both are being incorporated directly from eruptions. In addition, quartzose sediments from the predominantly granitic and high-grade metamorphic Nelson area carried north along the western shoreline of the land bridge probably supplied the substantial non-andesitic component of the lower unit. At circa 10-11,000 years B.P. the post-glacial rise in sea level inundated this area and eliminated the continental shelf region as a source of aeolian material.

The occurrence of the Aokautere Ash dates the base of the profile at approximately 20,000 years B.P. The boundary between the upper and lower units is dated at approximately 10,000 year B.P., showing that the two units have each accumulated over a 10,000 year period. Since the two units are of equal thickness at the Mokoia site, a similar mean rate of accumulation is implied for both units.

The mineralogical evidence is interpreted to indicate a change from (1) loessial material having a substantial quartz component and a major reworked tephra component, hereafter referred to as the 'tephric loess unit', to (2) a material consisting almost entirely of airfall tephra, hereafter referred to as the 'tephra unit'. Because both units appear to have a similar mean rate of accumulation, despite the removal of the loess source by the post-glacial rise in sea level, it follows that to compensate for the decrease in the loess component there must have been a corresponding increase in the amount of tephra accumulating in the upper unit (Fig. 3.7). This in turn suggests that tephra emission from Mt Egmont has increased during the Holocene.

Although inputs of major components to the tephra unit, particularly andesitic glass, are episodic (Fig. 3.7), a mean rate of accumulation can be derived. Within the limits of the resolution of

the sampling intervals approximate maximum ages for peaks in the rhyolitic glass abundance can be assigned. The inferred maximum age for the peak in the very fine sand fraction is 2000 years B.P., while those for the upper and lower peaks in the coarse silt fraction are 3500 years and 7500 years B.P. respectively (Fig. 3.7). These inferred ages agree remarkably well with radiocarbon ages of the three largest post-glacial rhyolitic eruptions in the central North Island: the Taupo eruption of 1840 ± 50 years B.P. (NZ1548A), the Waimihia eruption of 3440 ± 70 years B.P. (NZ2A) and the Rotoma eruption of 7330 ± 235 years B.P. (NZ1199A).

CONCLUSIONS

1. On the basis of the mineralogical data presented in this paper two units within the Egmont profile can be characterized. The upper unit, or 'tephra unit', consists of successive increments of andesitic tephra from Mt Egmont, with a minor component, particularly in the sand fraction, derived intra-regionally and a small inter-regional rhyolitic component from the central North Island.
2. The lower unit or 'tephric loess unit' also has a large (70%) andesitic component, but this is probably reworked material derived from pre-existing tephra deposits. The lower unit in the Egmont profile has a significant (30%) inter-regional quartz component, probably derived as loess from sediments of metamorphic and plutonic origin which formed a land bridge linking Taranaki and north-west Nelson. However, the reworked tephra component is sufficiently large to warrant calling the lower unit a tephric loess unit.
3. Variations in the rate of quartz accumulation in the silt fractions of the Egmont loam profile can be correlated with climatic

changes, a high rate of quartz accumulation occurring during the colder climate of the last stadial, while a low rate of quartz accumulation occurred during the warmer climate of the post-glacial period.

4. Peaks in rhyolitic glass abundance with depth are correlated with three major rhyolitic eruptions from the central North Island.

ACKNOWLEDGMENTS

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APPENDIX 3.1

SOIL PROFILE DESCRIPTION;
EGMONT BLACK LOAM

Location	Mokoia, in a paddock beside State Highway 3, 7 km south of Hawera. NZMS 1. N129/931237.
Parent Materials	Post-glacial andesitic tephra over tephric loess, on aeolian sands
Slope	1 ⁰
Elevation	61 m
Topography	Gently undulating tephra covered, uplifted marine terrace (Ngarino Terrace).
Drainage	Well drained
Vegetation	Present: pasture comprising perennial ryegrass (<u>Lolium perenne</u>), cocksfoot (<u>Dactylis glomerata</u>), Yorkshire fog (<u>Holcus lanatus</u>), white clover (<u>Trifolium repens</u>), red clover (<u>Trifolium pratense</u>), and various flatweeds. Past: coastal scrub, largely native flax (<u>Phormium tenax</u>) and bracken fern (<u>Pteridium aquilinum</u> var. <u>esculentum</u>).
Climate	Humid-temperature climate; mean annual rainfall: 1016 mm. Mean annual temperature: 10-12.5 ⁰ C. Prevailing wind: westerly. Frost: 10-20 screen frosts per year.

Profile

Ap	0-15 cm	Between very dark grey (10YR3/1) and very dark greyish brown (10YR3/2) loam; very friable; strongly developed fine nutty and very fine crumb structure; abundant roots; sharp, even boundary
Bw1	15-40 cm	Dark yellowish brown (10YR3/4) loam: friable; weakly developed medium blocky, breaking down to fine crumb structure; many roots; indistinct relatively even boundary
Bw2	40-75 cm	Dark yellowish brown (10YR4/4) silt loam with gritty component; friable-firm. moderately developed coarse blocky, breaking down to fine crumb structure; few roots; fairly distinct and even boundary in profile but revealed as wavy in adjoining roadside cutting
2Cu1	75-110 cm	Between yellowish brown (10YR5/4) and light olive brown (2.5Y5/4) sandy clay loam with a few andesitic pebbles appearing below 100 cm; firm; weakly developed coarse blocky tending to massive structure, breaking to fine blocky then to fine crumb; indistinct boundary
2Cu2	110-150 cm	Between yellowish brown (10YR5/4) and light olive brown (2.5Y5/4) sandy clay loam with scattered andesite pebbles; firm; weakly developed coarse blocky tending to massive structure, breaking to fine blocky then to fine crumb; distinct, wavy boundary
3C	onwards	Aeolian andesitic sands.

CHAPTER 4

CHAPTER 4

OCCURRENCE AND SOURCE OF QUARTZ
IN SIX BASALTIC SOILS FROM
NORTHLAND, NEW ZEALAND

ABSTRACT

The amount, distribution and oxygen isotope abundance of quartz from six basaltic soils in a soil development sequence from Northland, New Zealand, were determined. Monomineralic quartz in the $>250\ \mu\text{m}$ size fraction of two of the soils, Kiripaka and Ruatangata, have mean $\delta^{18}\text{O}$ values of 8.2 ‰ , indicative of a high temperature origin. Quartz in the $250 - 125\ \mu\text{m}$ size fraction of the Ruatangata soil had a $\delta^{18}\text{O}$ value of 8.1 ‰ and 8.4 ‰ , also indicating a high quartz crystallisation temperature. The sand sized quartz is thought to be derived from both airfall rhyolitic tephra from the central North Island, such as Kaharoa Ash, or by aeolian redeposition from the quartzose beach sands of the west coast of Northland. The latter have a $\delta^{18}\text{O}$ value of 8.7 ‰ , also indicating their probable derivation from central North Island rhyolitic volcanics. Beach sands from the east coast of Northland have a lower $\delta^{18}\text{O}$ value of 11.7 ‰ , indicating the presence of a significant component of lower temperature, locally derived quartz.

Quartz in the $63 - 20\ \mu\text{m}$ size fraction of the soils had a mean $\delta^{18}\text{O}$ value of 12.0 ‰ , more typical of a sedimentary origin. This size fraction represents a loessial component, the lower $\delta^{18}\text{O}$ values

indicating the mixed nature of local sources of this material, probably from both Mesozoic and Tertiary sediments. Quartz in the 5 - 2 μm size fraction has a higher mean $\delta^{18}\text{O}$ value of 13.9 ‰ in the basaltic soils, similar to that of aerosolic dusts previously reported from this latitude of the South Pacific region.

The Kiripaka soil has anomalously high $\delta^{18}\text{O}$ values in its fine silt fraction of 17.3 ‰ and 19.6 ‰. This was due to an additional component, contributing approximately 50% of the fine silt fraction, of low temperature quartz originating from local Tertiary marine shales. This data shows that local source components occur in the 10 - 1 μm (aerosolic dust) fraction of soils and sediments in addition to tropospheric aerosolic dust.

INTRODUCTION

The presence of quartz in basaltic soils has been reported from many localities around the world, from as far apart as Israel (Singer, 1967), Australia (Nicholls, 1936; Simonett and Bauleke, 1963; Corbett, 1968; Jackson *et al.*, 1972; Mokma *et al.*, 1972), Hawaii (Sherman *et al.*, 1964; Rex *et al.*, 1969; Jackson *et al.*, 1971) and New Zealand (Swindale, 1966; Fieldes and Weatherhead, 1966; Campbell, 1971; Mokma *et al.*, 1972). The origin of the quartz has been widely attributed to deposition by aeolian processes (Nicholls, 1936; Gill, 1964; Fieldes and Weatherhead, 1966; Singer, 1967; Rex *et al.*, 1969; Briner and Jackson, 1970; Jackson *et al.*, 1972; Mokma *et al.*, 1972). However, it has been suggested that fluvial processes may also be involved (Gill, 1964; Corbett, 1968). To explain quartz found at depth in Australian basaltic soils, it has been postulated that quartzose material, once deposited on a soil surface, was washed down cracks that

originated from drying in fine textured soils (Nicholls, 1936), by mixing due to gilgai processes or by deposition in cracks between blocks on young basalt lava flows (Jackson et al., 1972).

In Hawaii an authigenic origin for the quartz in basaltic soils was postulated by Sherman et al. (1964). However, this quartz was subsequently shown to be largely a result of aerosolic dust deposition (Rex et al., 1969). Aerosolic dust is distributed by the tropospheric wind system and has a characteristic particle size distribution of $10\text{ }\mu\text{m} - 1\text{ }\mu\text{m}$ with a mode at approximately $4\text{ }\mu\text{m}$ (Jackson et al., 1971; Walker and Costin, 1971) and a distinctive oxygen isotope composition (Rex et al., 1969; Syers et al., 1969; Clayton et al., 1972). The oxygen isotope composition of aerosolic quartz has also been shown to vary with latitude in samples from pelagic sediments in the South Pacific Ocean but samples from the North Pacific Ocean do not appear to show a similar variation (Clayton et al., 1972).

Additions of aeolian quartz, including aerosolic dust, to a range of New Zealand soils was first demonstrated by Mokma et al. (1972; 1973). The surface horizons of two basaltic soils from Northland, representing the Ruatangata and Okaihau soil series, were shown to have greater amounts of quartz than the deeper horizons. The quartz particle size distribution suggested that it had been added to the soil largely as loess and it was presumed that the quartz had been derived from basement Mesozoic greywackes (Fieldes and Weatherhead, 1966). The $\delta^{18}\text{O}$ values for quartz in the $20 - 5\text{ }\mu\text{m}$ fraction of both soils indicated that the quartz was neither inherited from the parent basaltic parent material (Mokma et al., 1972), nor was it derived from accretions of rhyolitic tephra from the central North Island (Swindale, 1966). Significant amounts of quartz were also shown to be present in the $5 - 2\text{ }\mu\text{m}$ fraction, indicating presence of aerosolic dust in

these soils (Mokma et al., 1972). However, no quartz of aeolian origin was found in a nearby soil derived from rhyolite, the $\delta^{18}\text{O}$ values indicating that the quartz was inherited from the underlying parent material (Mokma et al., 1972).

These investigations draw attention to the anomalous presence of aerosolic and loessial quartz in the basaltic soils of Northland. The purpose of the present study was to further elucidate the specific origin of the quartz in a sequence of basaltic soils, of varying degrees of soil development, from Northland. The detailed mineralogy of these soils is reported in Chapter 5.

MATERIALS AND METHODS

Materials.

Six basaltic soils from a Northland basalt soil sequence were selected for this study (Fig. 4.1). Samples were collected of representative soil series that are considered important stages in a soil development "maturity" sequence (Williams, 1965; Williams and Walker, 1969), considered by some to form a chronosequence (Walker, 1965). All of the soils sampled were considered to have developed in basaltic parent materials. Sample sites were selected where soil erosion was thought to be minimal and the most complete stratigraphic history preserved. In addition, preference was given to sites near localities where radiometric dates on subsurface lava flows were available (Table 4.1). Consequently, of the previously published soil reference sites (N.Z. Soil Bureau, 1968), only the Kiripaka and Ruatangata sites suited these criteria. It should be noted that at most localities dated lava flows lie at considerable depth below the present ground surface and we consider the flows to be much older than the parent materials of the present soils.

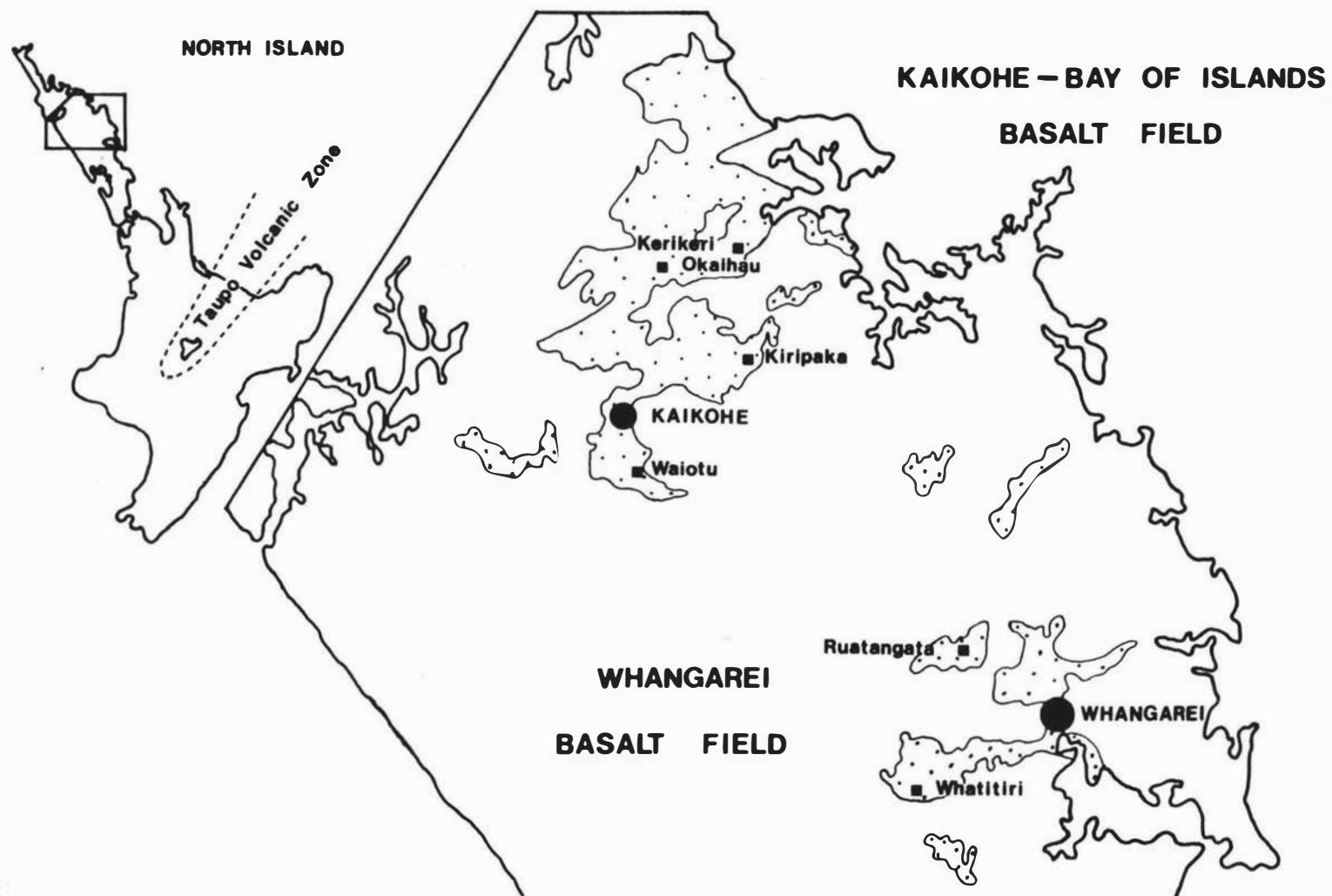


Figure 4.1 Map showing the distribution of basaltic soils in Northland and the locations at which the six soils were sampled. The location of the source of rhyolitic tephra, the Taupo Volcanic Zone, is shown on the inset.

Table 4.1 Radiocarbon and K/Ar ages of lava flows considered to be associated with each soil series.

Soil Series	Basalt Formation	Age
Kiripaka	Taheke	Kawiti, 21,600 ± 380 yr B.P. (NZ390A)
		Whangarei, 35,500 ± 2600 yr B.P. (NZ1721A)
Whatitiri	Horeke	Edge's Quarry, 0.521×10^6 yr B.P.
Waiotu	Horeke	Kaikohe Quarry, 1.27×10^6 yr B.P.
Kerikeri	Horeke	*
Ruatangata	Horeke	*
Okaihau	Horeke	*

* No date available.

Methods.

Approximately 80 g samples were treated with 1M NaOAc - HOAc at pH 5 and then 30% H_2O_2 to remove organic matter (Jackson, 1956). Free iron oxides were removed with citrate - bicarbonate - dithionite (CBD). Samples were then washed with saturated NaCl, followed by distilled water, and dispersed at pH 10 with NH_4OH . The sample was split at 63 μm by wet and dry sieving, and the sand fractions dry sieved at 1 ϕ intervals ($\phi = -\log_2 \text{mm}$, Krumbein and Pettijohn, 1938). The silt and clay fractions were split at 20 μm , 5 μm and 2 μm by a combination of sedimentation and centrifugation (Jackson, 1956).

Quartz was isolated from selected size fractions by fusion with $\text{Na}_2\text{S}_2\text{O}_7$ and treatment with H_2SiF_6 (Syers et al., 1968; Sridhar et al., 1975). Oxygen was liberated from the quartz by reaction with BrF_5 , converted to CO_2 and analysed by a double-collecting mass spectrometer (Clayton and Mayeda, 1963).

RESULTS AND DISCUSSION

Values for $\delta^{18}\text{O}$ for three size fractions were determined; a sand fraction ($>125 \mu\text{m}$), a coarse silt fraction (63 - 20 μm) and a fine silt fraction (5 - 2 μm). These represent locally-derived intraregional materials, interregionally-derived loess, and aerosolic dust respectively (Syers, et al., 1969; Stewart et al., 1977). No significant differences were found between $\delta^{18}\text{O}$ values for quartz of a given size fraction from different depths in any one profile.

Quartz was present in the $>125 \mu\text{m}$ fraction of only two of the soils, the Kiripaka and the Ruatangata (Table 4.2). The $\delta^{18}\text{O}$ values of this quartz have a mean of 8.2 ‰ (Table 4.3), similar to $\delta^{18}\text{O}$ values of 6 - 10 ‰ for quartz of high temperature origin (Churchman et al., 1976).

Table 4.2 Oxygen isotope abundance of quartz from selected size fractions of six Northland basaltic soils.

Size fraction (µm)	Soil series	Depth (m)	Soil horizon	% size fraction in sample	% Quartz in size fraction	δ ¹⁸ O * (‰)
>250	Kiripaka	0-0.3	Ah1-Ah2	composite	- - -	8.2
	Ruatangata	0-0.1	Ah	9	n.d.	8.2
250-125	Ruatangata	0.2-0.3	Bt1	1	12	8.1
	Ruatangata	0.6-0.7	Bt2	0.6	18	8.4
63-20	Kiripaka	0.2-0.3	Ah2	9	14	11.8
	Kiripaka	0.7-0.8	BC	4	46	11.6
	Whatitiri	0.3-0.4	Bw1	3	49	12.2
	Whatitiri	0.6-0.7	Bt	2	29	12.3
	Waiotu	0.4-0.5	Bw2	2	36	11.7
	Waiotu	0.7-0.8	Bw3	3	6	11.8
	Kerikeri	0.2-0.3	Bw1	5	9	12.2
	Ruatangata	0-0.1	Ah	9	59	12.7
	Ruatangata	0.6-0.7	Bt2	3	54	11.9
	Okaihau	0.2-0.3	Bcs	6	74	12.2
5-2	Kiripaka	0.2-0.3	Ah2	6	6	17.3
	Kiripaka	0.7-0.8	BC	8	21	19.6
	Whatitiri	0.3-0.4	Bw1	2	23	14.3
	Whatitiri	0.6-0.7	Bt	2	8	13.7
	Waiotu	0.4-0.5	Bw2	3	16	13.9
	Kerikeri	0.2-0.3	Bw1	7	4	13.4
	Ruatangata	0-0.1	Ah	3	37	14.6
	Ruatangata	0.6-0.7	Bt2	2	14	13.7
	Okaihau	0.2-0.3	Bcs	2	17	13.4
2-1	Ruatangata	0.2-0.3	Bt1	n.d.	7	13.6

* δ¹⁸O/δ¹⁶O ‰ relative to Standard Mean Ocean Water (SMOW).

NBS - 28	10.0 ‰.
R4150 (Institute of Nuclear Sciences Standard)	8.5 ‰.
M1 (Massey University Quartz Standard)	12.2 ‰.

It may have originated as direct airfall material from central North Island rhyolitic tephras (Swindale, 1966) or from beach sands on the west coast of Northland, presumed to be at least in part ultimately derived from central North Island volcanics (Schofield, 1970; Ricketts, 1979).

Quartz is present in the silt fractions of all the soils examined. In the coarse silt fraction, $\delta^{18}\text{O}$ values are quite uniform (Table 4.2) but have a mean value of 12.0 ‰ which is greater than that of the sand fraction (Table 4.3), indicating quartz of significantly lower temperature formation. These $\delta^{18}\text{O}$ values are indicative of quartz of mixed origin from sedimentary rocks (Jackson *et al.*, 1971; 1973; Churchman *et al.*, 1976).

In the fine silt fractions, still higher $\delta^{18}\text{O}$ values were obtained (Table 4.2) with a mean for five of the soils of 13.9 ‰ (Table 4.3). This is consistent with values obtained for quartz in aerosolic dusts in other New Zealand soils (Mokma *et al.*, 1972) and pelagic sediments of the South Pacific Ocean (Clayton *et al.*, 1972). $\delta^{18}\text{O}$ values for quartz in the fine silt fraction of the Kiripaka soil are exceptionally high (Table 4.2) and the reason for these high values is discussed later.

ORIGIN OF THE QUARTZ

There are four possible origins for the quartz found in the basaltic soils examined in this study. They are:

- i) as an original constituent of the parent basalt or basaltic tephra, either as a primary phase or as inclusions
- ii) as an authigenic mineral crystallising in the soil from silica released during weathering of the parent materials
- iii) as direct airfall material from rhyolitic tephras originating from the central North Island

Table 4.3 Oxygen isotope abundance of quartz from selected
Northland soils and sediments.

Sample	Size Fraction (μm)	$\delta^{18}\text{O}$ *
Basalt Soils	> 250 (mean)	8.2
	63 - 20 (mean)	12.0
	5 - 2 (mean)	13.9
Mangakahia Group shale	63 - 20	12.0
	5 - 2	25.7
Beach Sands, west coast	500 - 250	8.7
east coast	250 - 125	11.7
Ohinewai Tephra Formation	1000 - 500	8.4
	63 - 20	8.4
Rangiora Soil **	20 - 5 (0 - 10cm depth)	15.3
	<150 (3.3 m depth)	15.4
	<150 (18 m depth)	15.0

* Relative to Standard Mean Ocean Water (SMOW).

** Mokma et al., 1972.

- iv) as detrital material brought into the profile by aeolian or fluvial processes.

Each of these alternatives is considered in turn.

i). The predominant rock types in the Whangarei and Bay of Islands basalt fields are olivine basalt and olivine-bearing augite basalts (Heming, 1980). It has been shown that magnesian olivine and quartz do not coexist in equilibrium in a melt at low pressure (O'Hara, 1968). Furthermore, the $\delta^{18}\text{O}$ values of quartz in the silt fractions of these soils indicate that it formed at too low a temperature to have been an equilibrium phase in a basalt lava. Xenoliths of quartzofeldspathic material have been reported from basalts in the Northland and Auckland regions and these are commonly polycrystalline, and show reaction rims of pyroxene (Searle, 1962; Mulheim, 1973; Rafferty, 1977; Heming, 1980). Quartz from a xenolith in basalt from the South Auckland basalt field was found to have a $\delta^{18}\text{O}$ value of 13.9 ± 0.05 ‰ (Rafferty, 1977). The quartz was therefore interpreted as crustal contamination (Heming, 1980). This value is lower than the $\delta^{18}\text{O}$ values of 15.0 - 15.4 ‰ obtained for quartz from a Northland soil developed in Mesozoic greywacke (Mokma *et al.*, 1972). If quartz in the basaltic soils examined were derived from either xenoliths or loess derived from greywacke, then oxygen isotope composition would not differentiate their transport mechanism into the soil. However, $\delta^{18}\text{O}$ values of the coarse silt fraction from the basaltic soils are consistently lower than that obtained for the xenolith and the greywacke, suggesting a more uniform source, such as mixing in a loessial environment. The angular morphology of the quartz particles in the soils also suggests a detrital, aeolian origin. Quartz in the xenoliths tends to have reaction rims of pyroxene or glass and tends to become rounded as

reaction advances (Searle, 1962), contrasting with the angular quartz in the basaltic soils.

Geomorphic evidence also suggests that the quartz was not derived from the basalts. To achieve the concentration of quartz found in the soils, weathering of the basalts would require considerable landscape lowering and leaching of the basalt weathering products. While such a process may be argued for the surfaces on which the pedologically well developed soils have formed, the least developed soils (Kiripaka and Whatitiri) also contain abundant quartz in their sand and silt fractions. These latter soils are directly underlain by unweathered basalt and occur in the vicinity of well preserved cones and other volcanic features which show little evidence of advanced weathering or erosion (Kear, 1961). Highly weathered materials sampled beneath the well-developed soils in most cases have little or no quartz in them, further suggesting that residual concentration of quartz from basalt as a result of intense weathering is unlikely.

ii). The $\delta^{18}\text{O}$ values show that all the quartz is clearly not authigenic (Table 4.2). The only exception is the Kiripaka profile, which has unusually high $\delta^{18}\text{O}$ values of 17.3 and 19.6 ‰ for fine silt quartz from two depths within the profile (Table 4.2). These $\delta^{18}\text{O}$ values indicate the presence of a significant component of low temperature quartz. Scanning electron microscope (SEM) examination of the fine silt fractions shows that two morphologically distinct types of quartz are present. The first type (Plate 4.1) comprises clean surfaced, angular fragments, similar to those found in aerosolic dusts from a wide range of environments (Jackson *et al.*, 1971), whereas grains of the second type are irregular with surface overgrowths (Plate 4.1). This suggests that the two types of quartz are from separate sources. The irregular quartz was not found in any of the other soils and is

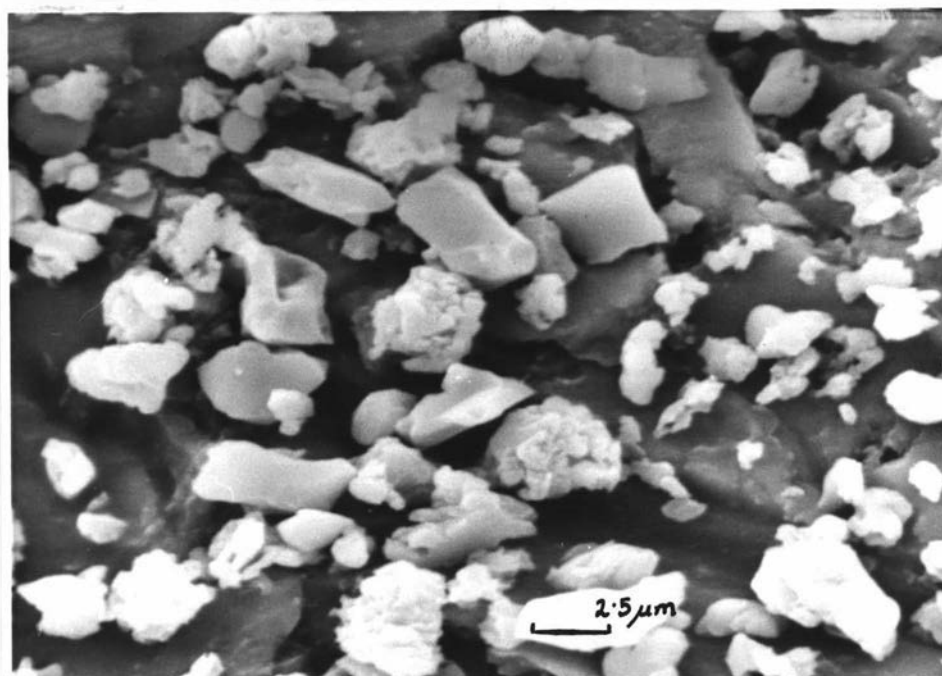
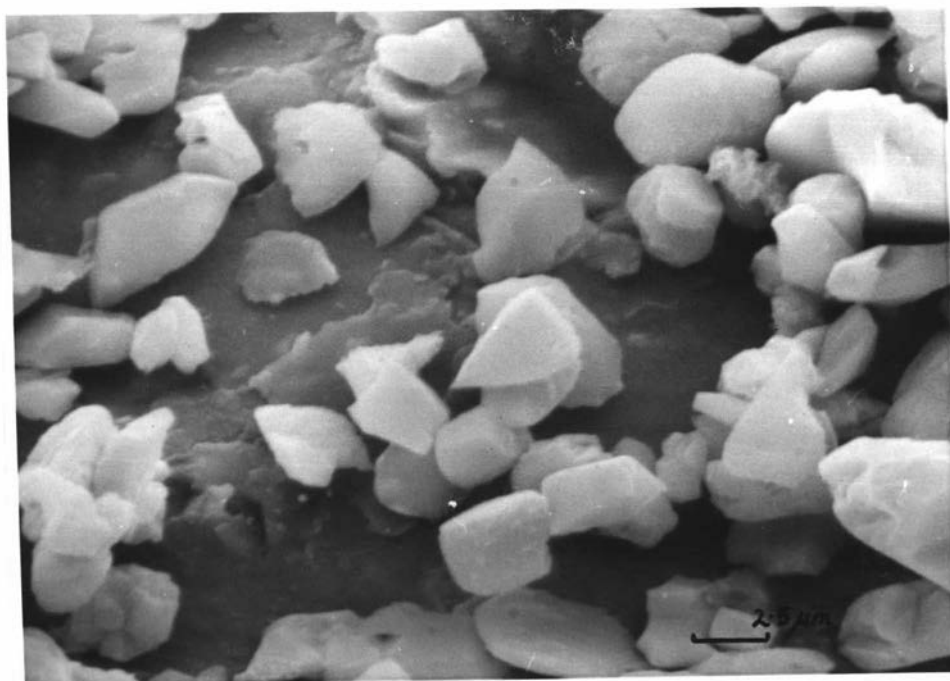
**a****b**

Plate 4.1 SEM photomicrograph of quartz in the Kiripaka soil;
a) 5-2 μm size fraction showing the presence of both
angular quartz and quartz grains with overgrowths.
b) 5-2 μm size fraction from the Okaihau soil
comprising angular particles with no overgrowths.

therefore thought to be of local origin. A re-examination of the area in the vicinity of the Kiripaka profile site resulted in the location of outcrops of a Tertiary marine shale belonging to the Mangakahia Group (Kear and Hay, 1961) within 0.5 km of the sample site. Quartz grains in the fine silt fraction of the shale exhibit a similar morphology to the irregular quartz grains in the Kiripaka (Plate 4.3). A $\delta^{18}\text{O}$ value of 25.7 ‰ for the fine silt-sized quartz separated from the shale confirms its low temperature crystallisation (Table 4.3). Visual estimates from SEM photographs indicate approximately equal amounts of the two types of quartz in the Kiripaka fine silt fraction (Plate 4.1). If an oxygen isotope composition for the irregular quartz of 25.7 ‰ is assumed and a value of 13.9 ‰ for the angular quartz is assumed (these are values obtained for the quartz in the shale and the mean of the fine silt quartz fractions in the other basaltic soils examined respectively), then equal amounts of both types of quartz would give a resultant composition of 19.8 ‰. This is very similar to the $\delta^{18}\text{O}$ values obtained for the quartz in the two fine silt fractions of the Kiripaka and is strong evidence in support of the two proposed sources of quartz.

Medium silt and coarse silt fractions of the Kiripaka were also examined by SEM. There is a marked decrease in the irregular quartz with increasing grain size and only a trace remains in the coarse silt fraction (Plate 4.2). The $\delta^{18}\text{O}$ values decrease from 17.3 ‰ and 19.6 ‰ in the fine silt fractions to 11.8 ‰ and 11.6 ‰ in the coarse silt fractions, respectively, in good agreement with the visual evidence from the SEM. It is also noted that a similar decrease in $\delta^{18}\text{O}$ values occurs in the marine shale from fine silt (25.7 ‰) to coarse silt (12.0 ‰). Contamination of fractions coarser than fine silt with quartz from the shales cannot therefore be distinguished.

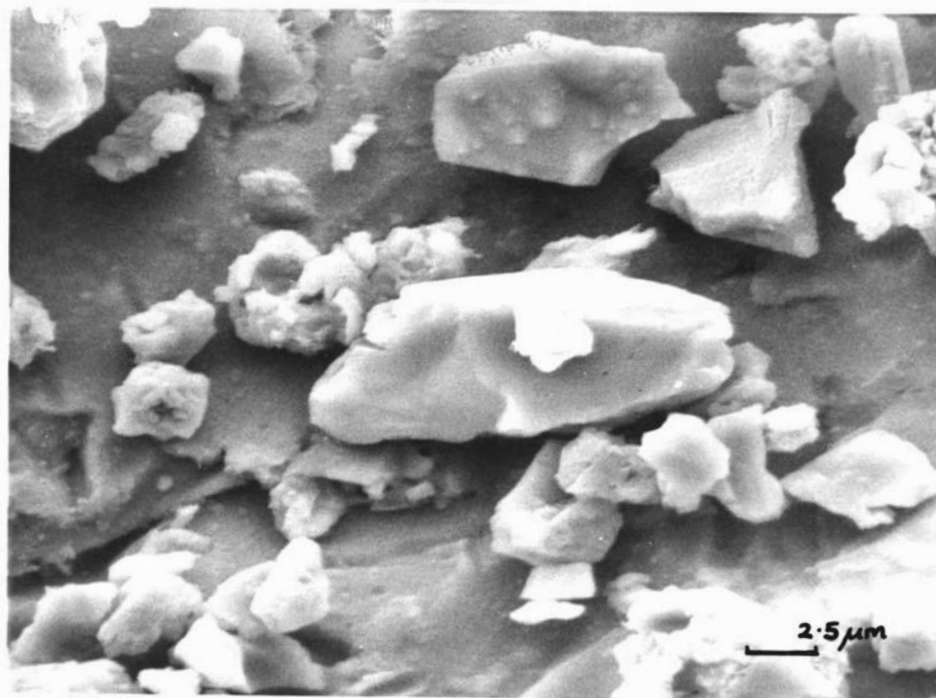
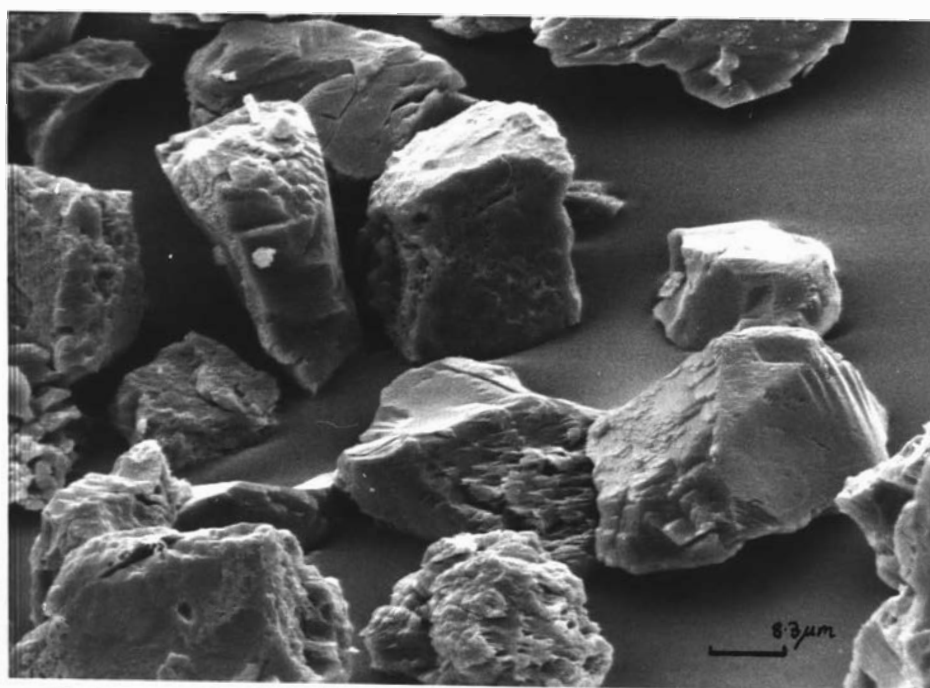
**a****b**

Plate 4.2 SEM photomicrographs of quartz a) in the 20-5 μm size fraction and b) the 63-20 μm size fraction of the Kiripaka soil. Irregular grains in these size fractions appear to have resulted from chemical etching rather than quartz formation.

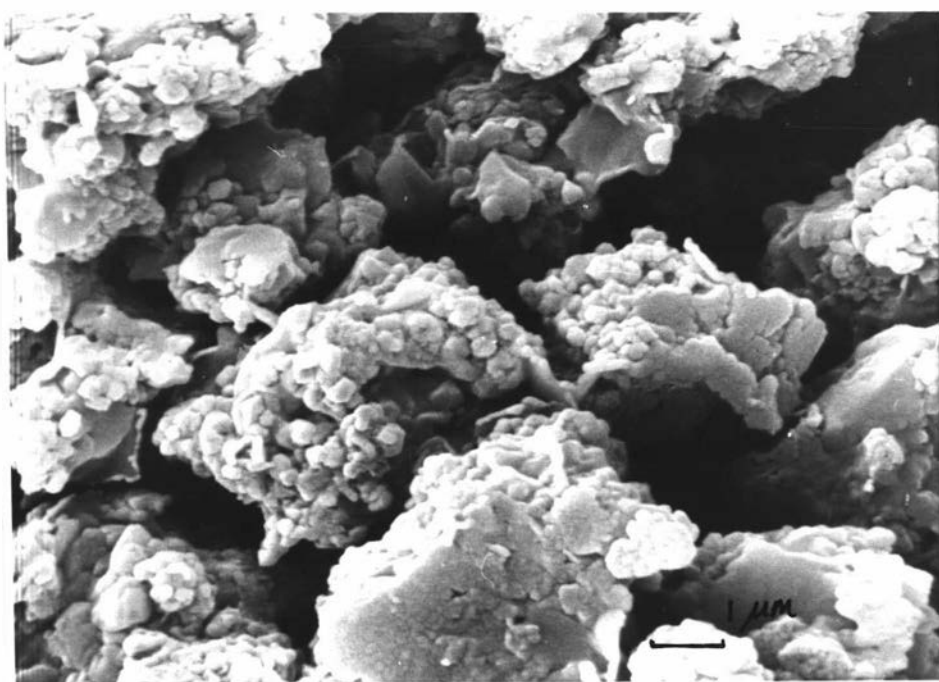
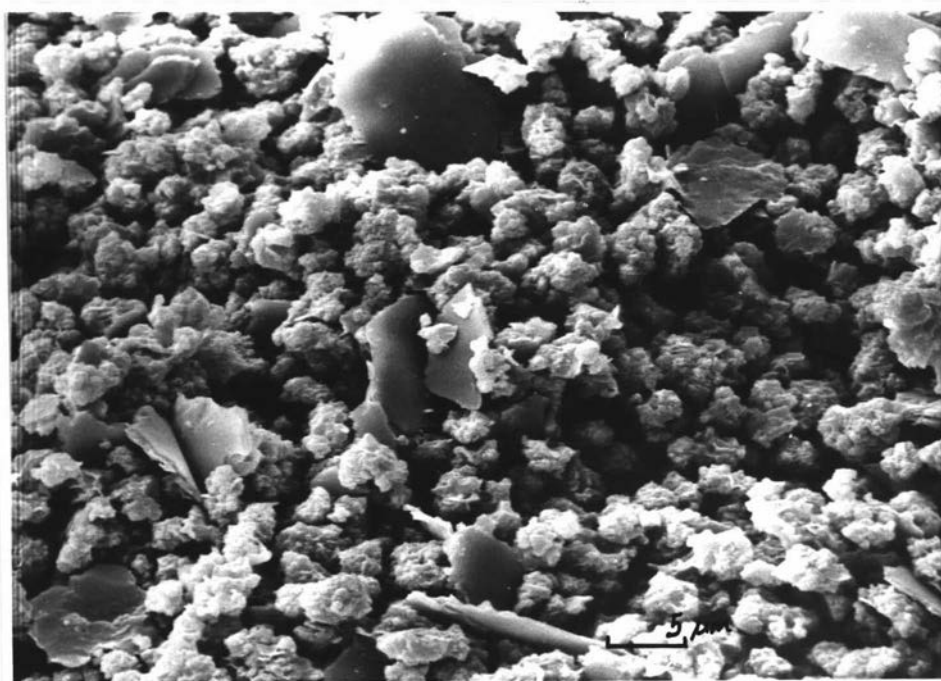


Plate 4.3 SEM photomicrographs of the 5-2 μm size fraction of Mangakahia shale. Quartz overgrowths are well-defined as terminated crystals on surfaces of larger grains.

Particles $>125\text{ }\mu\text{m}$ in size are absent from the shale.

Quartz has been reported from the clay ($< 2\text{ }\mu\text{m}$) fraction of Northland basaltic soils but because it was found to be largely restricted to the $2 - 1\text{ }\mu\text{m}$ particle size range the absence of smaller particles was attributed to dissolution (Fieldes and Williamson, 1955). A similar distribution of quartz in the $< 2\text{ }\mu\text{m}$ fraction was found in the soils examined in this study (Chapter 5, this thesis). The $2 - 1\text{ }\mu\text{m}$ size fraction of a Ruatangata soil contained 7% quartz with a $\delta^{18}\text{O}$ value of $13.6\text{ }^{\circ}\text{oo}$, not significantly different from the $\delta^{18}\text{O}$ values of $13.7\text{ }^{\circ}\text{oo}$ and $14.6\text{ }^{\circ}\text{oo}$ obtained for the quartz from the $5 - 2\text{ }\mu\text{m}$ size fractions of the same soil (Table 4.2). We consider that the $2 - 1\text{ }\mu\text{m}$ quartz is therefore part of the $10 - 1\text{ }\mu\text{m}$ aerosolic dust component (Jackson *et al.*, 1971) and is clearly not authigenic.

iii). Quartz is present as clean, angular grains, sometimes as bipyramids, in the $>250\text{ }\mu\text{m}$ fraction of the soils from the Kiripaka and Ruatangata series. The $\delta^{18}\text{O}$ values in both soils of $8.2\text{ }^{\circ}\text{oo}$ is similar to that of quartz phenocrysts in the rhyolitic Ohinewai Tephra ($8.6\text{ }^{\circ}\text{oo}$) and indicates a high temperature origin. This quartz may have originated as direct airfall material, because it is known that rhyolitic tephras from the central North Island were deposited in Northland in late Quaternary time. Not all contain quartz but the Kaharoa Ash, known to contain quartz phenocrysts (Cole, 1970), is well recorded in Northland (Pullar *et al.*, 1977). Further, biotite is a characteristic mineral in the Kaharoa Ash ferromagnesian mineral assemblage and the presence of biotite was noted in the surface horizons of both the Kiripaka and Ruatangata soils. It therefore seems likely that this quartz was derived in part from the Kaharoa Ash (Chapter 5, this thesis).

In the remaining soils the largest quartz grains occur in the

125 - 63 μm size fraction. Some of these are non-frosted and angular and others appear frosted. In the Ruatangata soil, quartz in the 125 - 63 μm fraction is largely non-frosted and the $\delta^{18}\text{O}$ value of 8.1 ‰ indicates it is similar to the coarser grained quartz. The frosted quartz grains indicate a long period in a weathering environment and are probably of more local origin. Possible local sources are the extensive quartzose beach sands in Northland. It has been suggested that the quartz in the beach sands has been derived in part from central North Island rhyolitic volcanics, carried to the coast by rivers and dispersed northwards by coastal currents (Schofield, 1970). The sands may have subsequently provided a source of quartz in many Northland soils and sediments. $\delta^{18}\text{O}$ values of west coast beach sands of 8.7 ‰ indicate a high temperature origin and confirm a probable central North Island rhyolitic source. The $\delta^{18}\text{O}$ values are also similar to those of the sand sized quartz in the basalt soils and some of the quartz, particularly the frosted grains, may have ultimately come from this source, lying windward from the basalt soil sites investigated with respect to the prevailing westerly winds of the region (Fig. 4.1).

It is interesting to note that a $\delta^{18}\text{O}$ value of quartz from beach sands on the east coast of Northland of 11.7 ‰ is considerably higher than sand sized quartz in west coast beach sands and in the basaltic soils (Table 4.3). The higher $\delta^{18}\text{O}$ value is consistent with multiple quartz sources, some local, as suggested by Ricketts (1979).

iv). Most of the quartz in the basaltic soils examined lies in the silt fractions. The particle size distribution (λ) of much of the quartz is similar to that of loess deposits (Smith, 1942; Swineford and Frye, 1945; Ives, 1973). The $\delta^{18}\text{O}$ values of quartz in the coarse silt fraction indicate that it is not of high temperature origin (Table 4.2) whilst being lower than $\delta^{18}\text{O}$ values of quartz from a

soil developed in greywacke parent materials (Mokma et al., 1972). This probably reflects the multiple sources of loessial materials within the region.

Quartz from the fine silt fractions of these soils has $\delta^{18}\text{O}$ values similar to that of fine silt sized quartz from a wide range of soils and sediments in the New Zealand region (Clayton et al., 1972; Mokma et al., 1972; Stewart et al., 1977). The similarity of $\delta^{18}\text{O}$ values for the fine silt quartz, both amongst the soils examined (Table 4.2) and with published data, supports the view of a common origin for quartz in this size fraction, being largely derived from globally transported aerosolic dusts. This has been demonstrated for soils and sediments throughout the Pacific (Rex et al., 1969; Clayton et al., 1972; Mokma et al., 1972).

CONCLUSIONS

The results of this study have shown that in all the basaltic soils examined from Northland there is a distinctive mineralogical component of non-basaltic origin, best indicated by the presence of the marker mineral quartz. Three populations of quartz have been distinguished by oxygen isotope abundance, SEM and grain size distribution. The first is a high temperature quartz in the sand fractions originating from rhyolitic tephras from the central North Island such as Kaharoa Ash. Some frosted quartz grains possibly originate from the west coast beach sands of Northland which have isotopically similar quartz, indicative of ultimate derivations from rhyolitic volcanics of the central North Island. The second population consists of loess-sized material of mainly local origin brought into the profiles by aeolian transport and represented by the coarse silt fraction

in this study. The third population is an aerosolic dust population, represented by the fine silt fraction, derived largely from globally circulating tropospheric dusts. Anomalous $\delta^{18}\text{O}$ values in the fine silt fraction quartz from the Kiripaka soil are due to aeolian contamination with low temperature quartz from nearby Tertiary marine shales and indicate that material from local sources may be present in this size fraction as well.

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CHAPTER 5

CHAPTER 5

SAND AND SILT MINERALOGY OF A BASALTIC SOIL
DEVELOPMENT SEQUENCE FROM NORTHLAND, NEW ZEALAND

INTRODUCTION

The mineralogy of the sand and silt fractions of most soils consists of primary minerals. In youthful soils, unstable primary minerals may dominate but in the majority of soils the sand and silt fractions commonly contain minerals resistant to weathering, and these are frequently quartzofeldspathic. Often these minerals are inherited from the soil parent material, although aerial or downslope additions (the "drift regime" of Taylor and Pohlen, 1962) may also be present.

Soils developed from rocks of basaltic composition usually contain minerals which are unstable in a weathering environment and from studies of primary minerals within basaltic soils, weather in the following order of olivine > labradorite > augite (Smith, 1957), olivine being therefore absent from all but the most recent of basaltic soils. With time these primary minerals rapidly weather to clay minerals and iron and aluminium oxides. These weathering products frequently form aggregates which are difficult to disperse and may occur in all size fractions (Smith, 1957). The aggregates contribute significantly to the chemical activity of a soil and a significant proportion of the cation exchange capacity of some basaltic soils is due to these aggregates in the non-clay fraction (McConaghy and McAleese, 1957; McAleese and McConaghy, 1957).

Where more than one component has contributed to soil parent materials, sand and silt mineralogical studies are paramount in determining the provenance of the components, providing they are distinguishable (Singer, 1967; Marchand, 1970; Stewart et al., 1977). Studies of soils developed in basaltic parent materials have shown that non-basaltic components are commonly present (Smith, 1957; Singer, 1967; Rex et al., 1969; Jackson et al., 1972; Mokma et al., 1972). The most common of these non-basaltic components is quartz, a mineral highly resistant to weathering. Provenance of much of this quartz can be determined, by both grain size and oxygen isotope analysis, to be "aeolian dust" (Singer, 1967; 1978) which may comprise tropospheric aerosolic dust (Rex, et al., 1969; Mokma et al., 1972) and/or wind-blown silt and sand (Jackson et al., 1972). Quartz from these sources has also been identified in non-basaltic soil parent materials (Syers et al., 1969; Jackson et al., 1973; Stewart et al., 1977). The abundance of quartz in basaltic soils has been shown to be time dependent. In basaltic soils from Israel the aeolian quartz component increases with time until it becomes the major component of the sand and silt fractions of very old, "senile" soils (Singer, 1967). A similar increase in quartz content with inferred age was discovered in the surface horizons of the basalt soils of Northland, New Zealand (Mokma et al., 1972), consistent with the concept of a chronosequence in these soils (Walker, 1965).

Climate change is a further influence on the accumulation of aeolian quartz in soils and sediments. In deep-sea sediments it has been recognised that greater amounts of quartz accumulated during Quaternary glacials than during interglacials (Bowles, 1975). On land, in a soil from Taranaki, New Zealand, greater amounts of aeolian quartz

have been shown to have accumulated during last glacial (Otiran Stage) times than in post-glacial (Aranuian Stage) time (Stewart et al., 1977).

Rhyolitic tephra in non-rhyolitic soil parent materials is one widespread process which has been shown to contribute primary minerals to existing soils in America (Marchand, 1970) and Europe (Juvigne, 1977). In New Zealand, additions of rhyolitic tephra to a wide range of soils are known (Cowie, 1964; Fieldes and Weatherhead, 1966; Vucetich and Kohn, 1973; Pullar et al., 1977; Stewart et al., 1977). In Northland, Kaharoa Ash, dated (NZ872A) at 850 ± 54 years B.P. occurs in peat swamps and as sea-rafterd pumice in coastal sand dunes, the latter in association with Taupo Pumice, dated (NZ1548A) at 1840 ± 50 years B.P. (Wellman, 1962; Pullar et al., 1977). Previous attempts have been made to identify the source of rhyolitic glass in soils from Northland by means of microelement composition but no positive identifications could be made (Rankin, 1973). Where positive correlations can be made on mineralogical or chemical evidence, the tephras become valuable time markers for determining rates of soil forming processes and sediment accumulation.

The purpose of this study was to determine the kind and origin of the various components present which made up the parent materials of six soil series developed in basaltic materials in Northland, New Zealand, from the sand and silt mineralogy of each soil. The six soils are thought to form a soil development sequence (Williams, 1965; Williams and Walker, 1969) of increasing weathering with age (Walker, 1965).

MATERIALS

Sample site locations for the six basaltic soils studied are shown in Fig. 5.1. Details of soils and sample sites are as follows:

Kiripaka silt loam, compact subsoil variant (Typic Dystrandept)

This soil was sampled at the N.Z. Soil Bureau reference site (N.Z. Soil Bureau, 1968). The site is located near the present margin of a vesicular basalt lava flow, the soil being developed in 1.1m of basaltic tephra and weathered basalt on the flow surface. The flow is a member of the Taheke Basalt Formation, within the Kaikohe - Bay of Islands basalt field and falls within the porphyritic basalt group of Heming (1980). The surface of the flow is not intensely weathered. Scoriaceous, gravel-sized pieces of basalt, consisting of unaltered rock with a thin weathering rind, are scattered throughout a zone within 0.15m from the underlying flow surface. A distinctive stratigraphic boundary at 0.4m depth is visible in the field and separates a lower, more compact horizon from an upper friable horizon. The upper horizon is more susceptible to erosion when exposed, leading to the formation of a distinct ledge at 0.4m depth in road cuttings.

Whatitiri silt loam (Typic Dystrandept)

This soil was sampled from a profile in a road cutting developed in 1.1m of surficial material overlying a lava flow of the Horeke Formation on the flanks of the Whatitiri volcano in the Whangarei basalt field (Heming, 1980). Weathering is evident in the rounding of basalt boulders at the base of the profile and subdued surface features on the flow. There is little physical evidence of differentiation within the profile but at 0.8m depth there is an horizon in which pockets of moa cropstones occur. This horizon can be traced laterally along the road

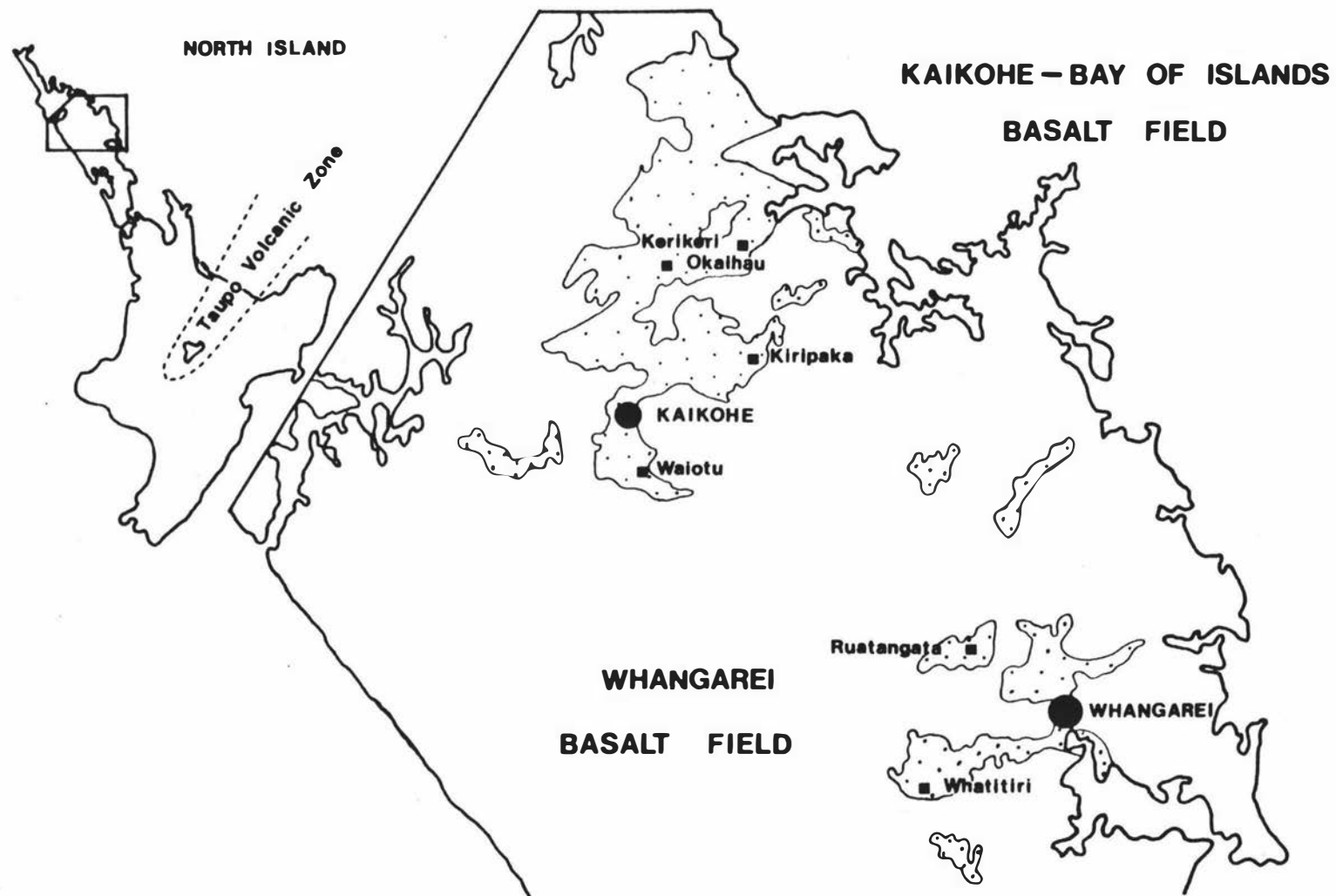


Figure 5.1 Map showing the distribution of basaltic soils in Northland and the location of sites sampled. The inset shows the location of the Bay of Islands - Whangarei region relative to the Taupo Volcanic Zone, the source area of rhyolitic tephras.

cutting in a similar stratigraphic position. The stones consist of rounded, polished silicified siltstone, an exotic lithology within the basaltic soil parent material.

Waiotu friable clay (Typic Haplohumult)

This soil was sampled from a planar surface on basalt lava flows of the Horeke Formation in the Kaikohe - Bay of Islands basalt field. At the sample site there is approximately 30m of layered Quaternary accumulations that overly the olivine basalt flows which have been K - Ar dated at 1.27×10^6 years B.P. (Stipp and Thompson, 1971). The profile was sampled to 1.3m depth and two further samples were taken at 1.5m and 2.4m depth. No rock fragments were found in the profile, all material being strongly weathered. Clay, gibbsite and iron oxide glaeboles are present, the first two increasing in frequency towards the base of the profile. No other visible textural changes were evident in the profile.

Kerikeri friable clay (Typic Haplohumult)

This soil was sampled on a basaltic lava flow of the Horeke Formation in the Kaikohe - Bay of Islands basalt field. The soil profile was sampled to 0.8m depth, where saprolite was encountered. No unweathered basalt was found above 0.8m but some occur between 1 - 2m depth. There is a gradual increase in clay and gibbsite glaeboles with depth to the saprolite but no systematic variation was noted within the saprolite. The soil has a silt loam texture to 0.4m but below this depth it becomes more compact with a clay loam texture.

Ruatangata friable clay (Typic Haplohumult)

This profile is located on a surface formed on the older basalt lava flows of the Horeke Formation in the Whangarei basalt field.

None of the flows were encountered during sampling to 1.5m depth. Marked weathering of the soil parent material is evident. Textural differentiation of horizons is not pronounced but there are marked colour differences between horizons. Gibbsite and goethite glaebules are present, the former predominating. Goethite glaebules are most abundant near the surface and decrease in abundance with depth, while the abundance of gibbsite glaebules increases with depth.

Okaihau gravelly clay (Orthoxic Palehumult)

This soil was sampled from a profile located on a surface overlying deeply-weathered olivine basalt lava flows of the Horeke Formation in the Kaikohe - Bay of Islands basalt field. In a nearby road cutting, isolated olivine basalt boulders are seen to be spheroidally weathering from an apparently originally continuous lava flow. The soil parent material is extremely weathered and within the profile there is a marked accumulation of goethite glaebules in the Bcs horizon from 0.1m to 0.4m depth (Grange, 1934). Below 0.4m there is a decrease in goethite glaebules and an increase in gibbsite glaebules.

METHODS

All profiles were continuously sampled over 0.1-m intervals, with spot samples taken at greater depths where necessary. Samples were treated with NaOAc-HOAc at pH 5, organic matter removed with H_2O_2 , and free iron oxides removed with citrate - bicarbonate - dithionite (Jackson, 1956). Size fractionation was carried out by wet sieving at $63\ \mu\text{m}$ and dry sieving of the sand fractions. Silt and clay fractions were determined by a combination of sedimentation and centrifugation. Sand and silt mineralogy was determined by optical microscopy and X-ray

diffraction. Quartz was isolated from the various size fractions by pyrosulphate fusion and digestion with H_2SiF_6 (Syers *et al.*, 1968; Sridhar *et al.*, 1975). Optical analysis was carried out in detail on the very fine sand (125 - 63 μm) and coarse silt (63 - 20 μm) size fractions as representing sand and silt, respectively, with supplementary examination of other size fractions, where appropriate.

Grain size distribution on a clay-free basis was measured using two of the parameters of Folk and Ward (1957) for characterisation. They were;

Graphic Mean (M_z) as a measure of mean grain size, and

Inclusive Graphic Standard Deviation (σ_1) as a measure of sorting.

For each profile these parameters were plotted as a function of depth to investigate differences between horizons and compared amongst soil profiles in order to relate changes in texture with the degree of soil development.

Size fraction intervals are at 1 ϕ intervals for the most part and, although this is not considered sufficiently close for statistical work, it was felt that the sampling interval was sufficient for the purpose of this study.

RESULTS

Mineralogy

Quartz - - This occurs in all six profiles and is most abundant in the silt fractions. It consists predominantly of angular, monocrystalline grains which are rarely stained or rounded. Some grains occurring in the $> 250 \mu\text{m}$ size fraction have crystal faces and have a bipyramidal form while others are occasionally sub-rounded with frosted surfaces (Plate 5.1).

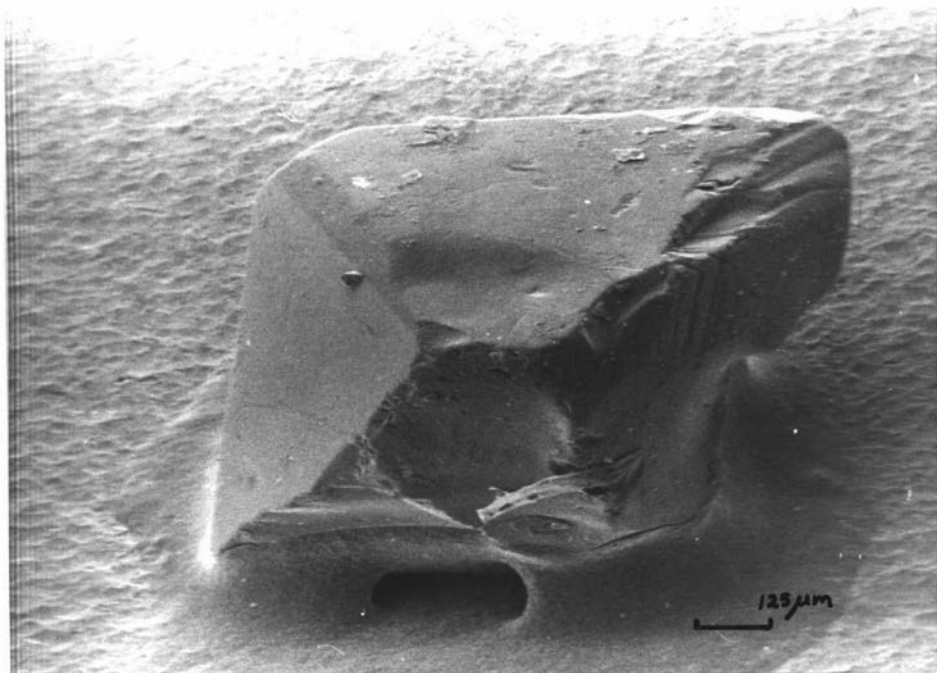
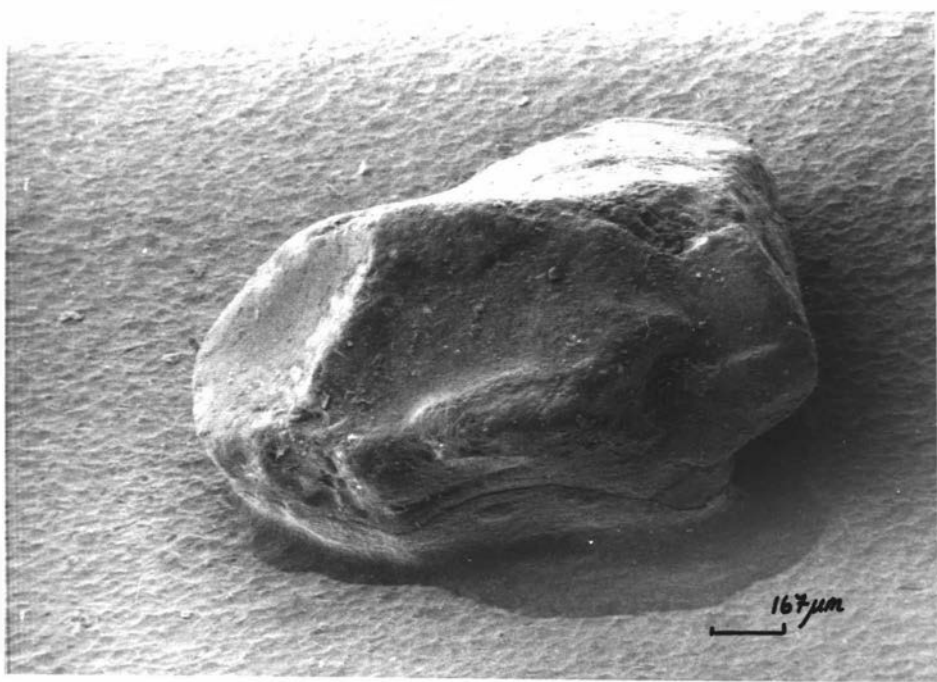
**a****b**

Plate 5.1 SEM photomicrograph of a) a quartz bipyramid from the Ruatangata soil. The occurrence of quartz in this form indicates crystallization at temperatures greater than 573°C. b) surface of large detrital quartz grain of a similar size to that in a), showing a rounded grain shape and surface frosting.

Plagioclase feldspar - - Two populations of plagioclase feldspar with differing degrees of susceptibility to weathering are recognised:

- a. a calcic plagioclase, generally labradorite, and
- b. a sodic plagioclase, generally oligoclase.

The calcic plagioclase is zoned with calcic cores and most grains have been weathered with rectangular etch pits, controlled by cleavage directions, on their external surfaces. The degree of weathering increases with both depth in the profile and increasing soil development. The etching increases to a point where the grains become skeletal (Plate 5.2) and eventually weather completely.

In contrast, the sodic plagioclase is frequently strongly zoned and occasional grains have rhyolitic glass selvages. Grains are generally unstained, show little sign of etching and are most abundant in the surface horizons of each profile. In the highly-weathered soils this may be the most abundant feldspar present. Only in the Okaihau profile, the most developed in the sequence, does the sodic plagioclase appear to show evidence of increased weathering with depth in the profile.

Rhyolitic glass - - This forms a major component of the sand and silt fractions in the upper 0.3m of all six profiles. It consists of both shards and fine pumice. Weathering becomes more pronounced with depth, preferentially removing highly vesicular grains. Below 0.5m depth, grains are predominantly rounded by weathering and have a low vesicle density. Inclusions common in the rhyolitic glass were hypersthene and plagioclase with lesser amounts of augite, hornblende, biotite, sanidine, magnetite, and rare quartz.

Magnetite - - This term is used to describe all opaque, magnetic iron oxides. Magnetite occurs in all six profiles and shows more pronounced

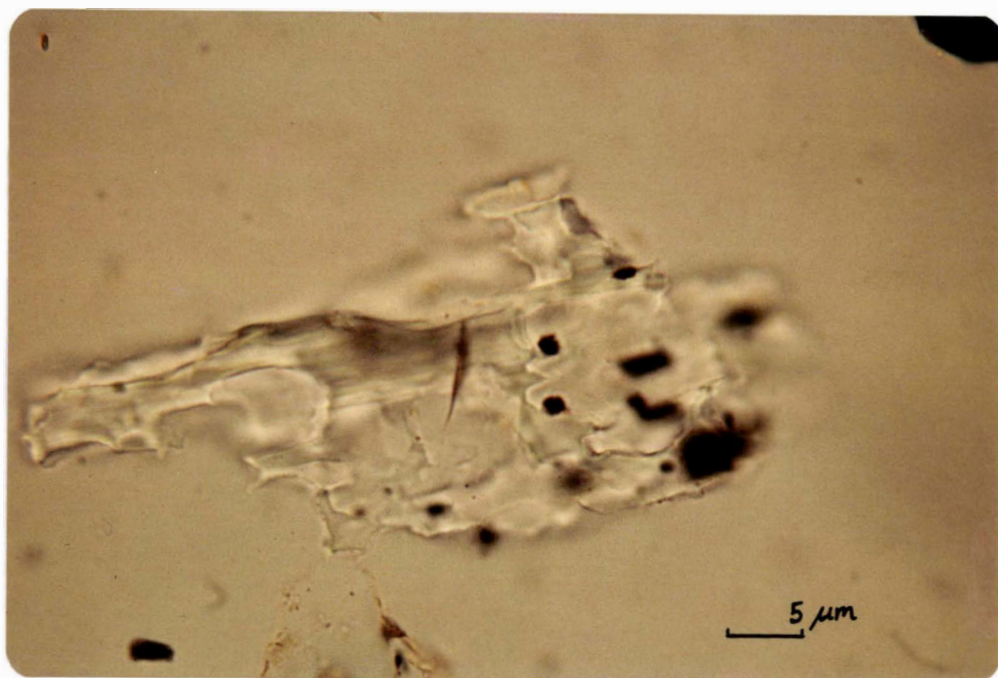
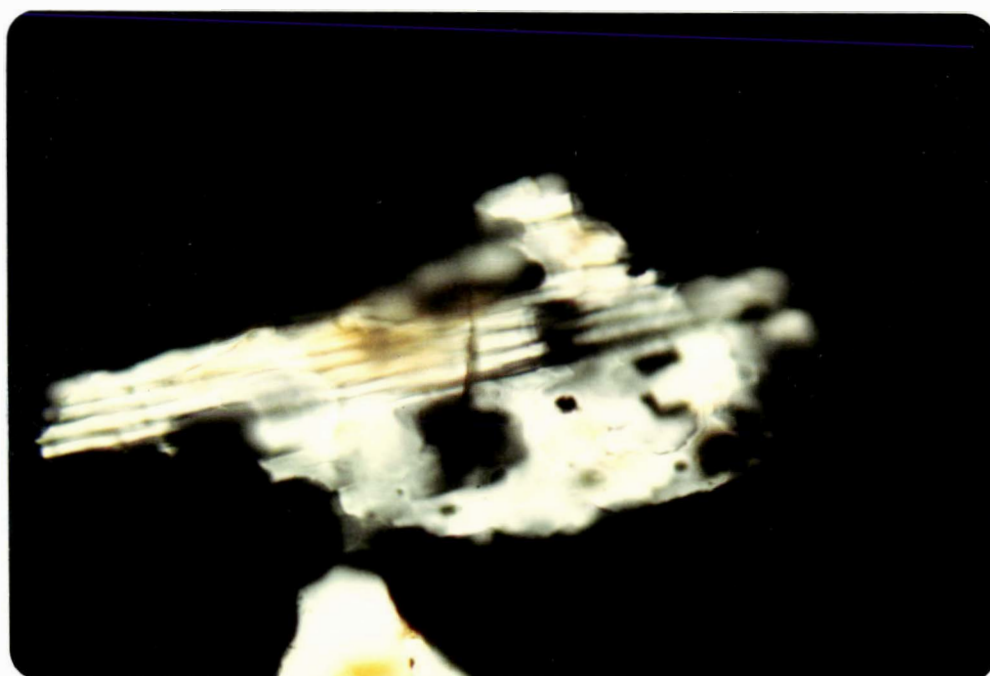
**a****b**

Plate 5.2 Form of weathering of plagioclase feldspars in the basaltic soil sequence a) plane polarised light, b) cross polarised light. Note the square etch pattern which follows cleavage directions.

weathering with depth as the degree of soil development increases. Magnetite of basaltic origin in these soils occurs as silt-sized, irregular or skeletal grains. Euhedral to subhedral magnetite grains, occasionally with rhyolitic glass selvages, are most abundant in the sand fractions.

Augite - - This occurs in all profiles, mainly as rounded and weathered grains in which the degree of etching increases with depth in the profile. Relatively fresh augite occurs in the uppermost 0.3m of the Whatitiri profile, where it forms part of an olivine - augite - calcic plagioclase - rock fragment assemblage. Euhedral and subhedral augite is more common in the sand fractions and rarely has rhyolitic glass selvages. In the more developed soils this is the only form of augite present.

Hypersthene - - This is present in small amounts in all six profiles and it usually forms euhedral, prismatic crystals which are often broken and, rarely, subrounded. There is little evidence that the grains have undergone chemical weathering in contrast to the often severely etched, coexisting augite. Some hypersthene grains have rhyolitic glass selvages and it is one of the most common inclusions found in rhyolitic glass.

Hornblende - - Green hornblende occurs in trace amounts in all profiles and is generally most abundant in the sand fractions. It also occurs as rare inclusions in rhyolitic glass and its distribution is similar to that of the glass, indicating a common derivation.

Olivine - - This mineral is only present in the Whatitiri profile, to a depth of 0.3m. It is most abundant at the surface and forms part of an unweathered olivine - calcic plagioclase - rock fragment assemblage, occurring both as discrete grains and as a constituent of the rock

fragments. In the remaining soils no olivine is present, due to its instability in strong weathering environments.

Biotite - - This is present in the surface horizons of the Kiripaka, Kerikeri, Ruatangata and Okaihau soils, occurring as flakes and inclusions in rhyolitic glass, and is attributed to the presence of Kaharoa Ash.

Rock fragments - - These are present mainly in the less-weathered Kiripaka and Whatitiri profiles. The grains consist of plagioclase feldspar and magnetite, with or without augite and olivine.

Other primary minerals - - Minerals occurring rarely are tourmaline, epidote, microcline, and muscovite, probably derived along with the quartz as loess from older Tertiary and Mesozoic rocks in the region.

Secondary minerals - - These include clay minerals, gibbsite and goethite in the form of glaebules which form a large part of the sand and silt fractions of the more-weathered soils. Most of the glaebules consist of (i) gibbsite with a trace of goethite and (ii) goethite with traces of hematite, gibbsite and quartz. A small proportion of the goethite glaebules are magnetic and contain unaltered or partially altered magnetite.

Profile Mineralogy and Particle-Size Distribution

Kiripaka This soil is the least weathered in the development sequence and gibbsite and goethite glaebules are rare. There is some basaltic material present but it shows the greatest degree of weathering of the parent materials present and is increasingly weathered with depth.

Rhyolitic glass forms the major non-basaltic component of the sand

and silt fractions in the upper part of the profile. Above 0.3m it forms up to 40% of each size fraction but below this depth, abundance decreases rapidly to fall below 1% at 0.5m (Fig. 5.2).

Quartz forms the second most important non-basaltic component of the sand and silt fractions throughout the profile, only decreasing markedly in abundance immediately above the basal lava flow (Fig. 5.2). Most of the quartz lies in the silt fraction but angular, monocrystalline grains, up to 3 - 4mm in size with some crystal faces, are present in the coarser sand fractions.

Gibbsite glaeboles are the most abundant secondary materials in the sand and coarse silt fractions, increasing in abundance with depth. Gibbsite was detected in the clay fraction ($< 2\mu\text{m}$) of this soil, from XRD, but is more abundant in the silt and sand fractions (Fig. 5.3). Gibbsite appears to form early during weathering in the Kiripaka soil but either nucleates on grains coarser than clay size or forms discrete grains coarser than clay size and is therefore a significant component of non-clay size fractions. Under the petrological microscope gibbsite glaeboles appear to be intergrowths of gibbsite crystals rather than aggregates (Plate 5.3) and therefore are likely to resist most means of disaggregation short of partial chemical dissolution.

Biotite occurs in the top 0.3m of the profile as flakes and, rarely, as inclusions in rhyolitic glass particles. These inclusions are evidence for the biotite being part of the mafic mineral assemblage of a rhyolitic tephra.

The part of the profile showing the largest mean grain size and poorest sorting is from 0 m to 0.3m depth corresponding to the Ap horizon (Fig. 5.2). This is due to three factors; the presence of a rhyolitic tephra which contributes glass to most size fractions and some

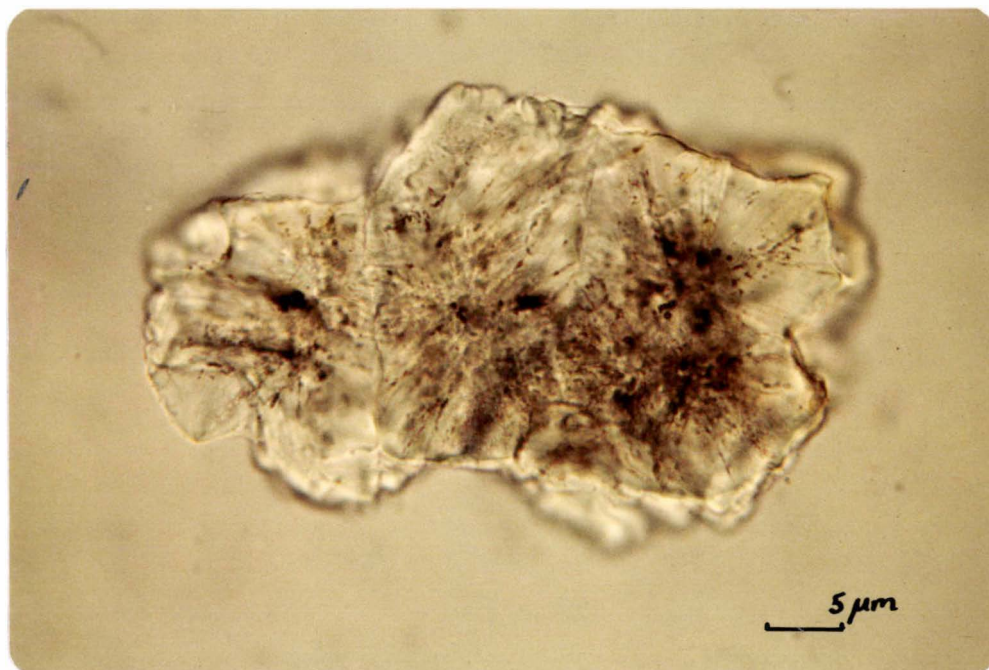
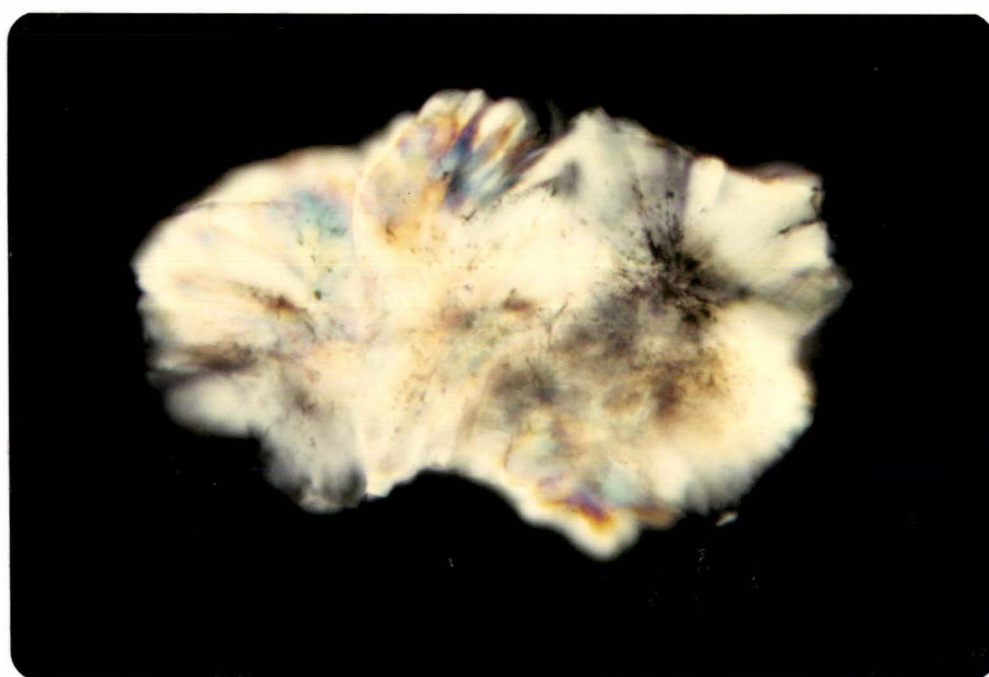
**a****b**

Plate 5.3 Gibbsite glaeboles in a) plane polarised light and b) cross polarised light. The gibbsite occurs as high relief, highly birefringent, fibrous, interlocking crystals which form grains stable to most forms of disaggregation.

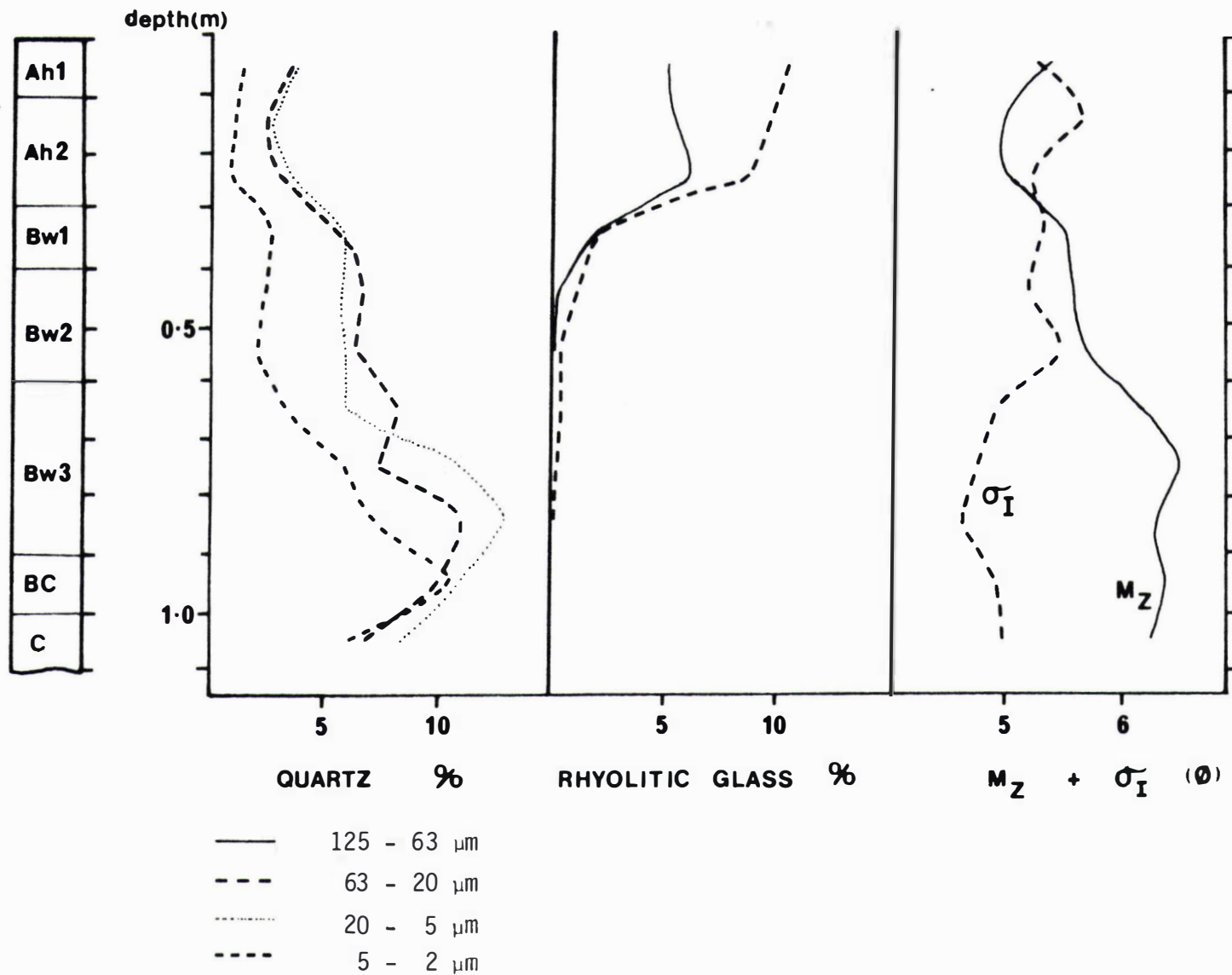


Figure 5.2 Kiripaka soil - distribution of quartz and rhyolitic glass, and variations in grain size parameters, with profile depth. Mineral contents are expressed as % of the non-clay fraction of the soil.

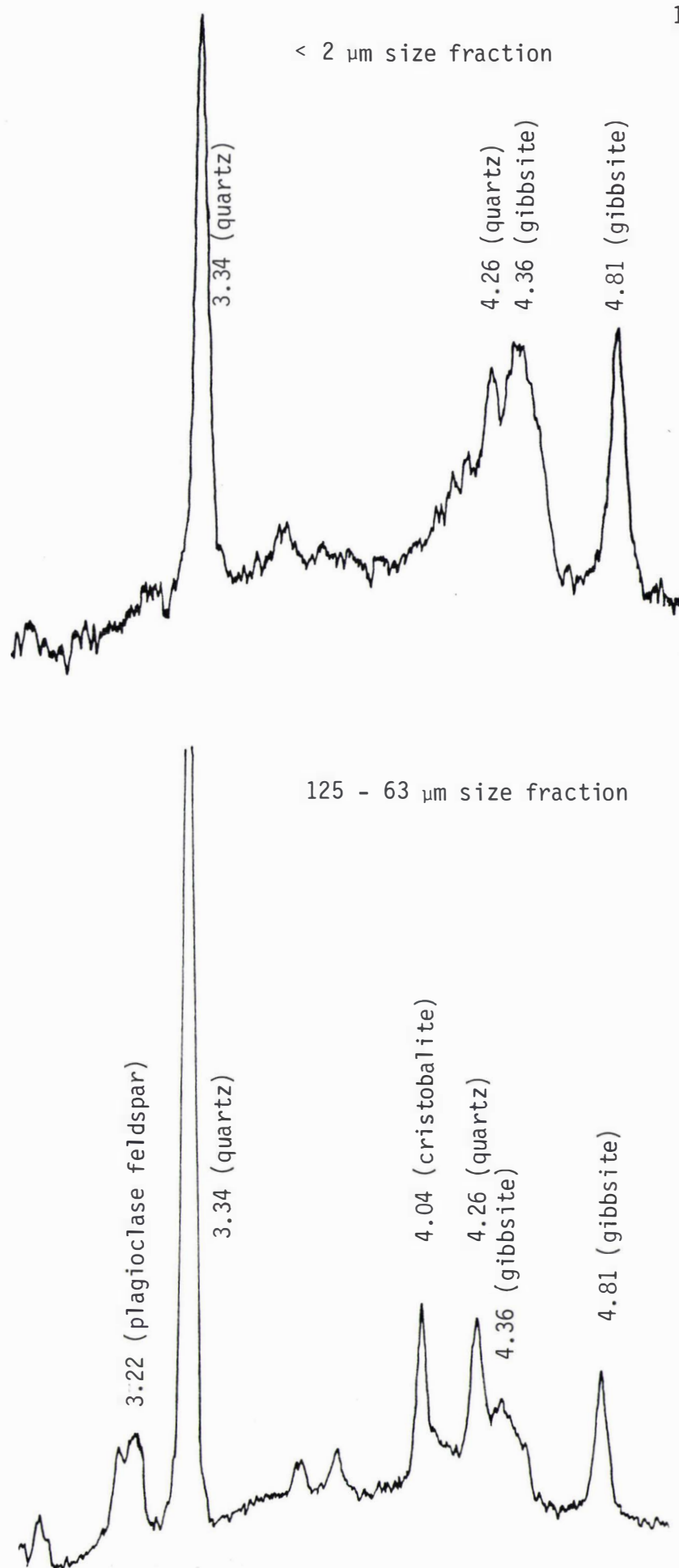


Figure 5.3

XRD patterns of minerals in Kiripaka <2 μm (clay) and 125 - 63 μm (very fine sand) size fractions. d-spacings are in Angstroms (Å). Quartz and gibbsite occur in all size fractions in this soil.

quartz to the sand fractions, the presence of detrital quartz and rock fragments, and the presence of glaeboles. All three components, of differing grain-size characteristics, have led to a coarser particle-size distribution and poorer sorting than the rest of the profile.

From 0.3 to 0.6m, mean grain size is lower, and sorting is better, than in the upper 0.3m (Fig. 5.2). This is associated with a rapid decrease in rhyolitic glass and an increase in quartz content below 0.3m depth, indicative of a major change in parent material provenance at this depth. Below 0.6m there is a marked decrease in mean grain size and an increase in sorting (Fig. 5.2). Here the quartz content is highest and rhyolitic glass is absent. The quartz, being of predominantly aeolian origin (Mokma *et al.*, 1972; see Chapter 4, this thesis) has a well-sorted particle size distribution with a mean in the silt fraction (Singer, 1967; Stewart *et al.*, 1977). Therefore, as the quartz content of the soil parent material increases the grain size distribution of the soil begins to approach that of the quartz component.

Whatitiri Of the six soils investigated this soil is unique because it is the only one containing olivine. This mineral is most abundant in the upper 0.2m of the profile and is virtually absent below 0.3m depth (Fig. 5.4). Other minerals associated with the olivine are augite, labradorite, and magnetite, also occurring as composite rock fragments. Below 0.3m depth, basaltic minerals are markedly weathered, suggesting that the olivine assemblage in the surface horizons was derived from a different source to the basaltic component in the lower part of the profile.

Rhyolitic glass is one of the most abundant non-basaltic components in the uppermost 0.3m of the profile (Fig. 5.4). A small increase in

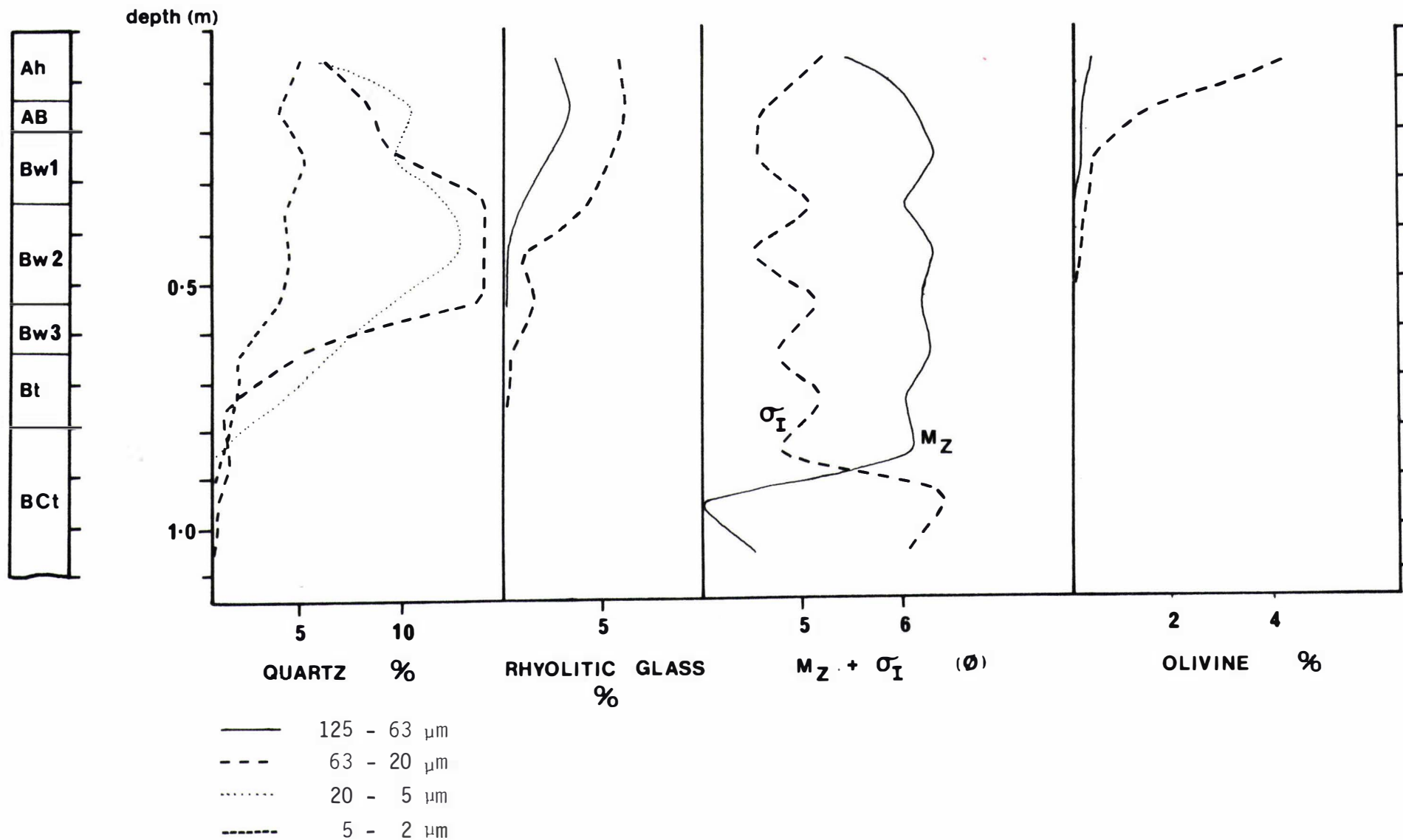


Figure 5.4

Whatitiri soil - distribution of quartz, rhyolitic glass and olivine, and grain size parameter variations, with profile depth. Mineral contents are expressed as % of the non-clay fraction of the soil.

the amount of glass in the coarse silt fraction was noted at 0.7m depth but this was not reflected in the sand fraction (Fig. 5.4).

Quartz is the most abundant of non-basaltic minerals and occurs throughout most of the profile. It is abundant in both sand and silt fractions to 0.8m depth, below which it decreases to a low level (Fig. 5.4). In the uppermost 0.3m of the profile the quartz content is slightly lower than in the immediately underlying Bw horizon, although still remaining relatively high. Associated detrital minerals found in trace amounts were microcline and tourmaline. Gibbsite, clay mineral, and goethite glaeboles are present in all size fractions. Calcic plagioclase has almost entirely been weathered, particularly below 0.8m depth, with one exception and that is the relatively fresh labradorite associated with the olivine assemblage in the surface horizons. At 0.8m an horizon occurs in which moa crop stones (J.E. Cox, pers. comm.) are distributed. This horizon also is thought to separate an overlying soil parent material containing non-basaltic components from underlying material with a very low abundance of non-basaltic minerals.

The presence of rhyolitic tephra, basalt tephra, and quartz in the surface horizons of the profile has resulted in an increased mean grain size and decreased sorting values relative to the lower part of the profile (Fig. 5.4). Below 0.2m there is little change in grain-size parameters, except that the presence of weathering basalt rock fragments has resulted in an increase in mean grain size and decreased sorting.

Waiotu In this soil the basaltic component has largely been weathered to gibbsite, goethite, and clay minerals. As a result, the sand and silt fractions are dominated by non-basaltic components, mainly rhyolitic glass, quartz, and glaeboles. Plagioclase feldspars of basaltic origin

have largely been weathered, leaving only slightly-weathered, sodic plagioclase of rhyolitic origin in the upper part of the profile.

Rhyolitic glass is most abundant to 0.2m depth, decreasing to be absent below 0.7m (Fig. 5.5). The glass becomes increasingly weathered with depth, grains with a low vesicle density being the most resistant. There is no evidence of discrete tephra events.

Quartz is most abundant in the uppermost 0.7m of the profile where it forms approximately 40 to 50% of the sand and silt fractions but it then decreases to 1.1m depth (Fig. 5.5).

Gibbsite and clay mineral glaebules increase in abundance with depth but goethite glaebules are more abundant near the surface. Weathering has been ^{greatest} below 1.0m with the only non-basaltic primary mineral present being traces of quartz.

The rhyolitic tephra and detrital quartz components in this soil are small and hence there is little correspondence between changes in grain size parameters and changes in these components. Of greater influence is the increasing glaebule component. The absence of a distinctive difference in mean grain size and sorting between the surface horizons and the underlying part of the profile (Fig. 5.5) indicates that there is only relatively minor goethite glaebule development and that gibbsite and clay mineral glaebules are evenly distributed. Below 0.9m increase in mean grain size is due to an increased abundance of gibbsite and clay mineral glaebules.

Kerikeri This soil is developed in surficial material over weathering olivine basalt. The basalt component is extremely weathered; almost all of the plagioclase feldspar present is sodic and of rhyolitic origin.

The sand fraction mineralogy of this soil is dominated by rhyolitic glass. Maximum abundance of glass occurs at 0.3m depth, decreasing

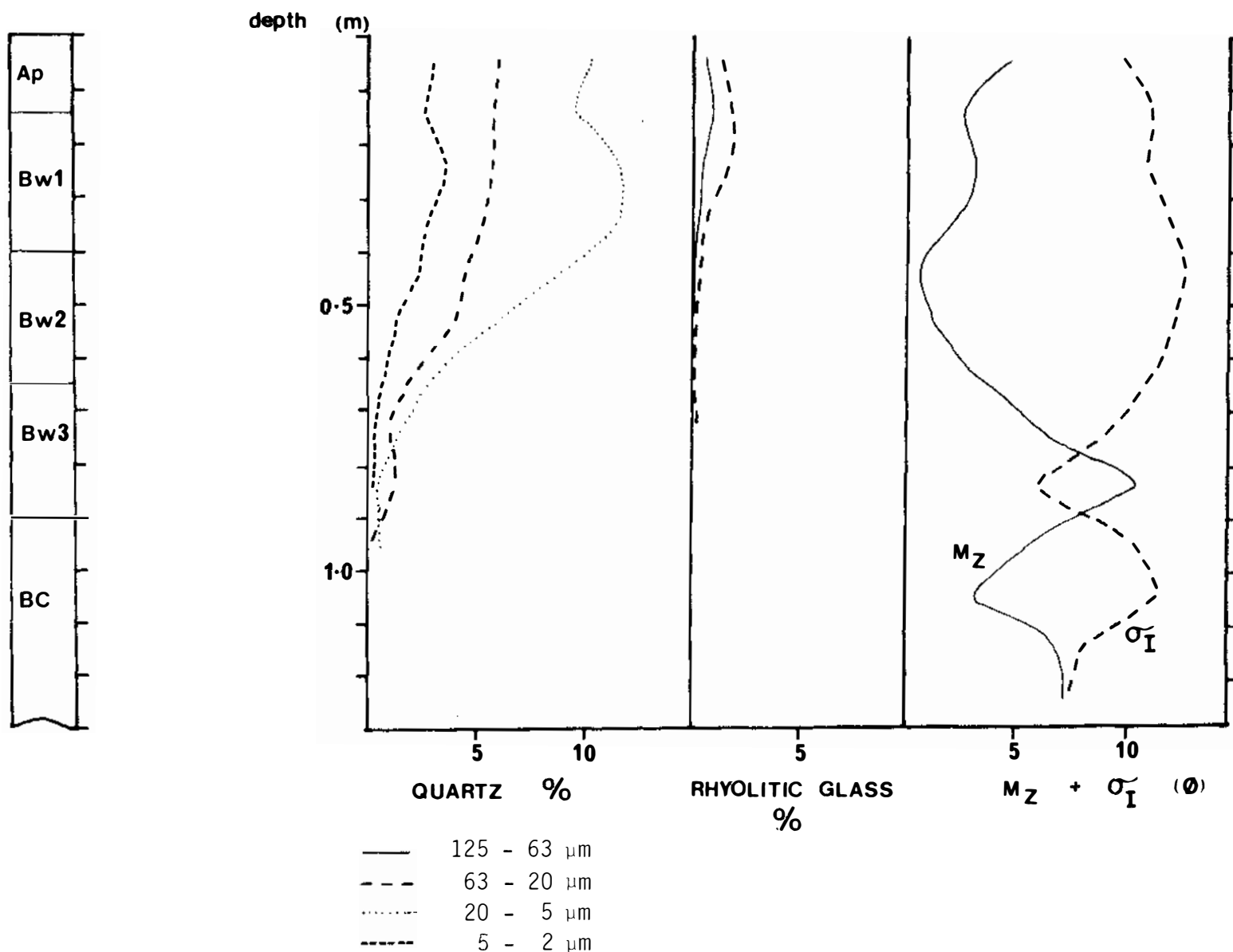


Figure 5.5

Waiotu soil - distribution of quartz and rhyolitic glass, and grain size parameter variations, with profile depth. Mineral contents are expressed as % of the non-clay fraction of the soil.

abruptly to become absent below 0.6m (Fig. 5.6).

In the silt fraction magnetite is the most abundant component with lesser amounts of rhyolitic glass and quartz. In contrast, only 1% - 2% of the sand fraction assemblage is magnetite.

Quartz occurs predominantly in the silt fraction but some rare, fractured grains were noted in the coarse sand fractions > 1 mm. The abundance of quartz is highest in the mid- to lower part of the profile, decreasing rapidly below 0.7 to be virtually absent below 0.8m (Fig. 5.6).

Gibbsite, clay mineral and goethite glaebules are abundant in the sand fraction, the first two types increasing in abundance towards the base of the profile. Mafic minerals present are hypersthene, hornblende, biotite, and augite, all attributed to a rhyolitic tephra origin.

The glaebules in this soil profile are one of the main factors governing the grain size parameter variations. The relatively coarse-grained, poorly-sorted nature of the parent material to 0.2m depth is due to the presence of goethite glaebules and rhyolitic glass. Below 0.2m quartz and magnetite, both mainly of silt size, increase in abundance and together are responsible for the decreased mean grain size and improved sorting in the lower part of the profile (Fig. 5.6).

Ruatangata The basaltic components in this soil have been weathered almost completely to clay minerals and iron and aluminium oxides. Traces of calcic plagioclase feldspar occur in the surface horizons but it has been weathered at depth. Most of the plagioclase present is sodic in composition and of rhyolitic origin.

Rhyolitic glass is abundant to 0.3m depth and is absent below 0.7m (Fig. 5.7). Associated with it are hypersthene, hornblende, augite, and in the surface horizon, biotite. The augite becomes increasingly

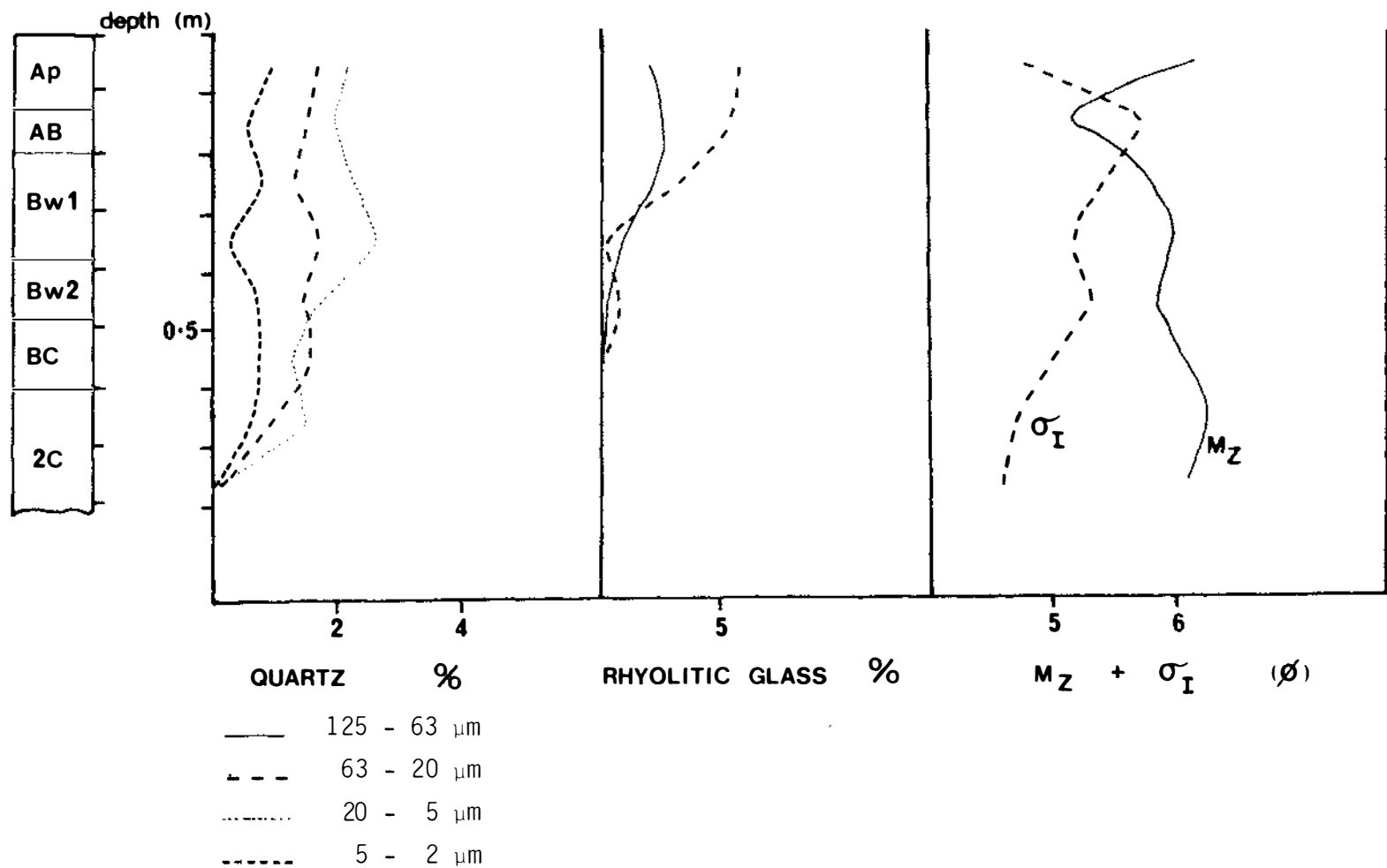


Figure 5.6 Kerikeri soil - distribution of quartz and rhyolitic glass, and grain size parameter variations, with profile depth. Mineral content is expressed as % of the non-clay fraction of the soil.

corroded with depth and by 0.4m depth has been completely weathered.

Quartz is most abundant between 0.3 and 0.7m depth (Fig. 5.7), occurring mainly in the silt fraction. Quartz content falls between 0.7 and 0.9m, then increases again below 1.0m. Continuous sampling ceased at 1.1m depth but a sample from 1.4m depth also contained quartz. Large quartz crystal fragments occur in the coarse sand fractions > 1 mm in the upper part of the profile.

Goethite glaeboles are abundant in the uppermost 0.2m of the profile and decrease in frequency with depth. Clay mineral and gibbsite glaeboles are present throughout the profile and increase in abundance to a maximum between 0.7m to 0.9m. Goethite glaeboles are the major control on grain size parameter variations in this soil. They are most abundant in the upper part of the profile and this reflects the coarser grain size and poorer sorting of the soil above 0.7m (Fig. 5.7).

The sand fraction content of the soil is very small below 0.7m depth and most of the silt-sized material consists of clay mineral glaeboles. The presence of a single, relatively uniformly sized component has given rise to the better sorted material of finer grain size in the lower part of the profile (Fig. 5.7).

Okaihau This soil is the end member of the soil development sequence. Almost all of the primary basaltic components are weathered. Calcic plagioclase is represented by rare, corroded grains in the upper part of the profile only, where they may be redeposited from younger basaltic material as part of a local aeolian component. Magnetite is partially weathered, the degree of weathering increasing towards the base of the profile.

Rhyolitic glass is most abundant in the uppermost 0.3m of the profile but decreases rapidly to be absent below 0.7m. It forms up to

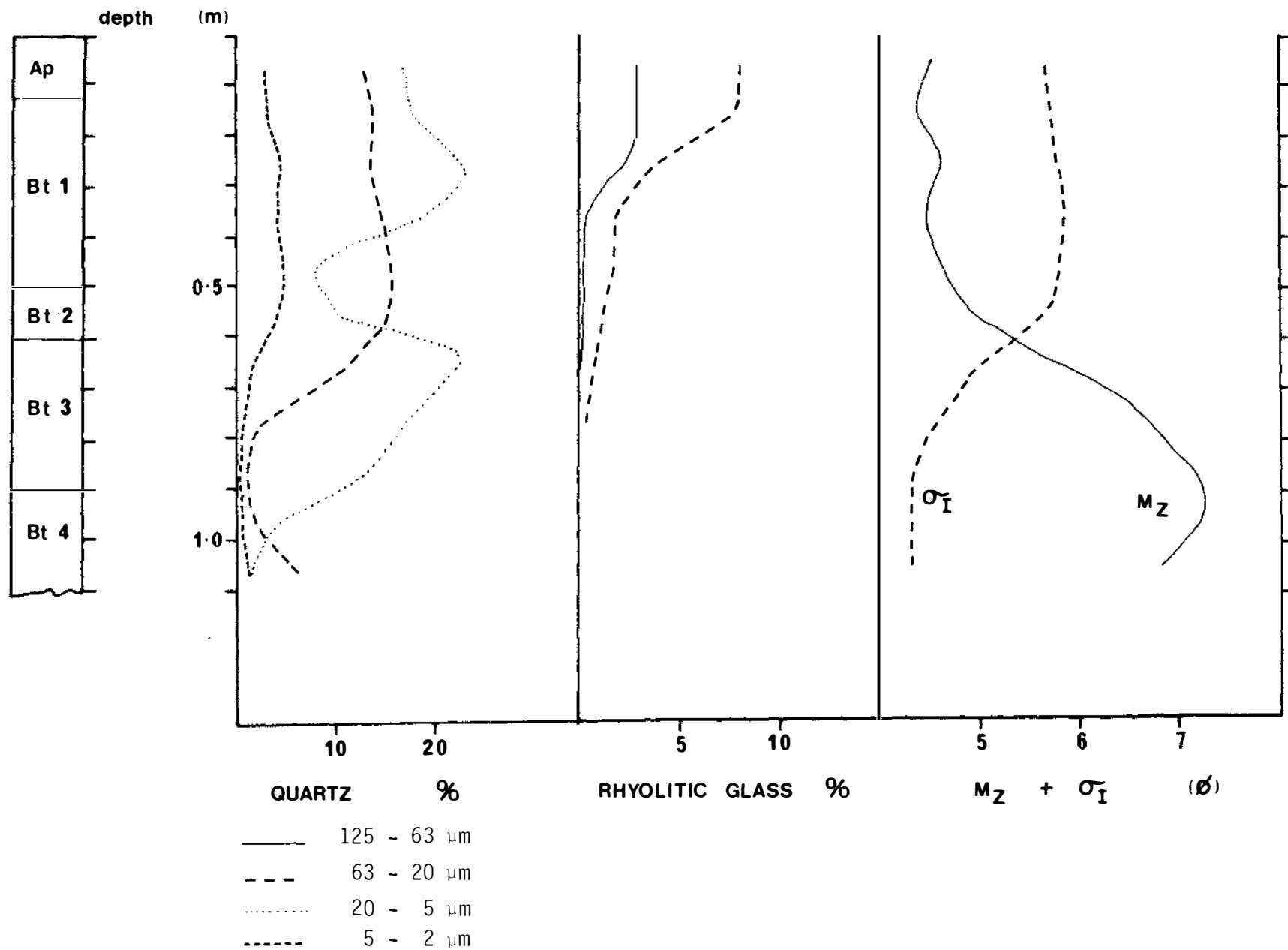


Figure 5.7 Ruatangata soil - distribution of quartz and rhyolitic glass, and grain size parameter variations, with profile depth. Mineral contents are expressed as % of the non-clay fraction of the soil.

60% of the very fine sand fraction to 0.3m depth (Fig. 5.8). Biotite and biotite inclusions in rhyolitic glass occur in small amounts to 0.3m depth.

Quartz is abundant in this profile to 0.7m depth, below which only trace amounts appear, and most of the quartz lies in the silt fraction (Fig. 5.8). The high quartz content and extreme weathering indicates a slow accumulation of surficial materials. The combination of this factor with the limited resolution of a 0.1m sampling interval and biological mixing have obscured stratigraphic relationships on all but a broad scale.

Goethite concretions are most abundant at 0.3m depth in the Bcs horizon and decrease in frequency towards the base of the profile. Gibbsite glaebules occur throughout the profile but are most abundant at depth. There is a marked increase in abundance of gibbsite glaebules in the very fine sand and coarse silt fractions below 0.8m.

This profile is extremely weathered and grain size distribution is controlled by the occurrence of glaebules. Quartz is abundant to 0.7m depth and rhyolitic glass to 0.3m depth, but neither appear to have more than a minor effect on grain-size distribution. This is clearly shown by the very coarse mean grain size and very poor sorting at 0.3 - 0.4m depth due to the presence of a distinct horizon of goethite glaebules, (Fig. 5.8).

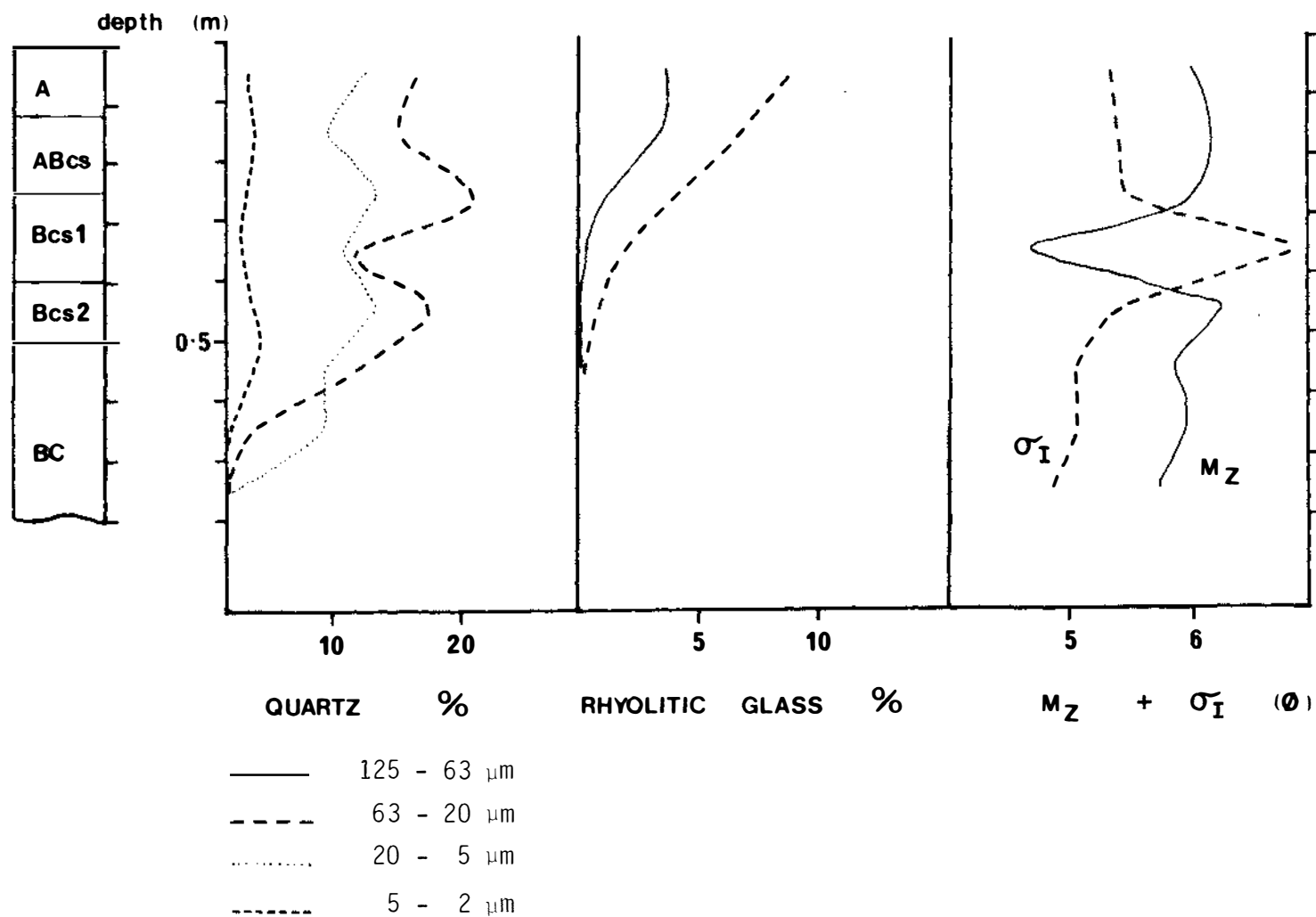


Figure 5.8 Okaihau soil - distribution of quartz and rhyolitic glass, and grain size parameter variations, with profile depth. Mineral contents are expressed as % of the non-clay fraction of the soil.

DISCUSSION

Mineralogy

The minerals present in the sand and silt fractions of these soils can be assigned to four components; basaltic, secondary, rhyolitic, and detrital. These are summarised in Fig. 5.9.

Basaltic component - - These minerals are recognised from their occurrence in unweathered basalt lava flows and tephras. Anhedral grains of augite are also included, with olivine and calcic plagioclase, as basaltic where the lack of crystal form is not due to weathering. Euhedral or weathered euhedral augite is classed as rhyolitic, because some of these grains have rhyolitic glass selvages. Fine-grained, usually silt-sized, skeletal magnetite is classed as basaltic and is most abundant in saprolite weathering from basalt.

Secondary component - - Secondary minerals include clay minerals, gibbsite, and iron oxides which form silt-, sand-, and gravel-sized particles in most of the basalt soils. XRD analysis of the gravel-sized iron oxide glaebules from the Okaihau soil show them to comprise goethite with traces of quartz, gibbsite, and hematite. A few glaebules were magnetic and in these magnetite was identified from the XRD patterns (Fig. 5.10). Gibbsite glaebules from the same soil consist of gibbsite with only a trace of goethite. The glaebules were the main components of the sand and silt fractions of the more weathered soils and strongly influence the particle size distribution of these soils, an influence which has been noted in strongly weathered soils elsewhere (Eswaran and Bin, 1978).

Rhyolitic tephra component - - Rhyolitic minerals are identified from

<u>BASALTIC</u>	<u>NON-BASALTIC</u>	
	<u>DETRITAL</u>	<u>RHYOLITIC</u>
Ca-plagioclase	quartz	glass
magnetite	muscovite	Na-plagioclase
augite	plagioclase	hypersthene
olivine*	microcline*	augite
	tourmaline*	hornblende
		sanidine*
		quartz
		titanomagnetite
		zircon
		biotite
	<u>SECONDARY</u>	
	gibbsite	
	goethite	
	kaolinite	
	halloysite	
	hematite	

* Minerals which occur infrequently or in trace amounts.

Figure 5.9 Mineralogy of the four components recognised
from the 125 - 63 μm and 63 - 20 μm size
fractions of the six Northland basaltic soils.

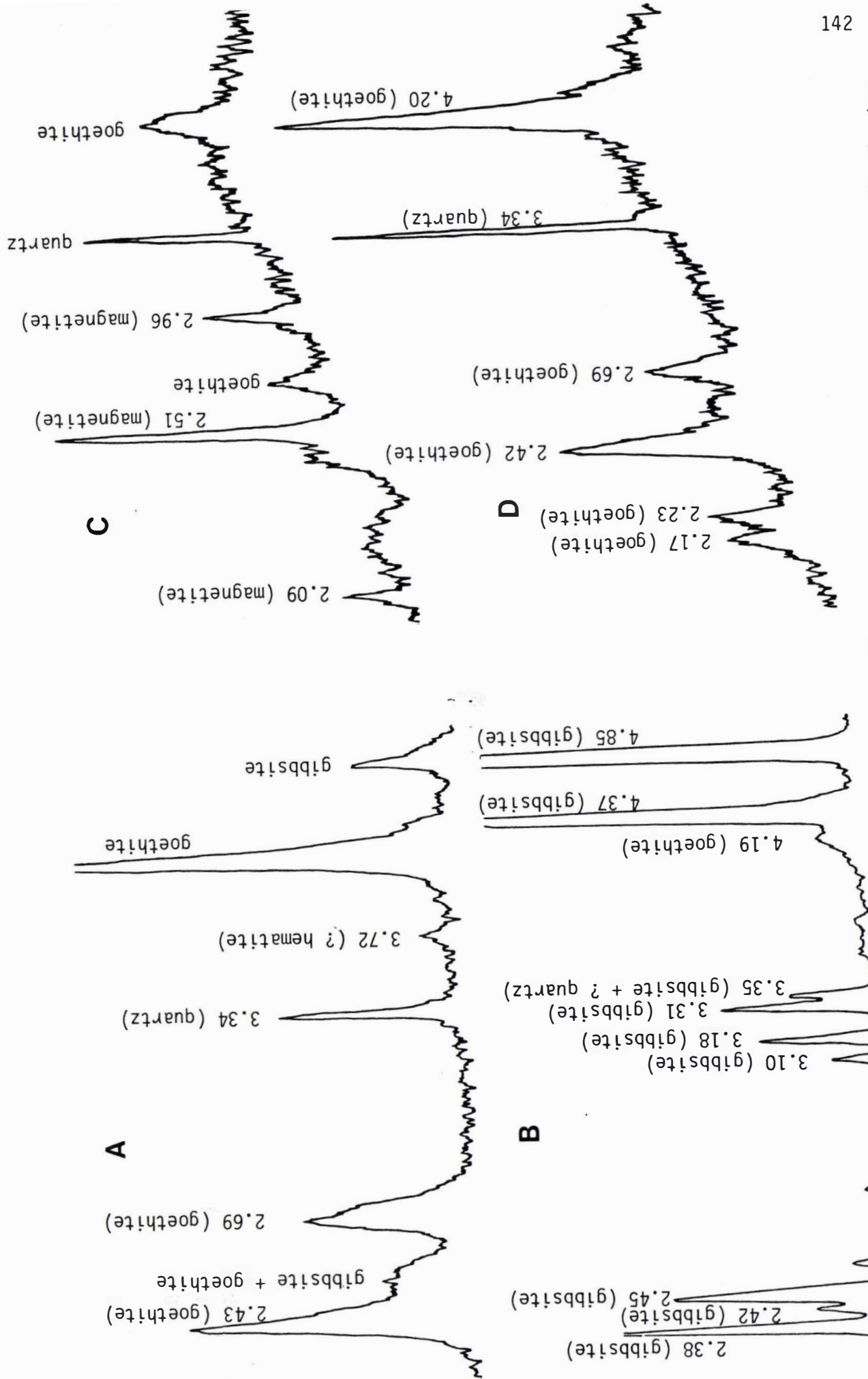


Figure 5.10

X-Ray diffraction patterns, units are in Angstroms (Å). A - iron oxide glaebule, Okaihau soil, showing it to comprise goethite, quartz, gibbsite and possibly hematite. B - gibbsite glaebule, Okaihau soil, showing it to comprise goethite, quartz, gibbsite and a trace of goethite. C - magnetic iron oxide glaebule, Ruatangata soil, showing the presence of magnetite, a mineral absent from non-magnetic glaebules in the same soil, shown in D.

their acid igneous character. Glass shards having a refractive index of 1.49 - 1.50 are consistent with a rhyolitic composition (Hodder, 1978). Oligoclase, hypersthene, calcic hornblende, augite, titanomagnetite, sanidine, and quartz all form phenocrysts in rhyolitic eruptives from the Taupo Volcanic Zone (Ewart, 1968). The rhyolitic origin of these minerals is confirmed by the presence of rhyolitic glass attached to all phenocrysts except quartz. However, oxygen isotope analyses of quartz grains in the > 250 μm size fraction indicate $\delta^{18}\text{O}$ values of 8.2 $^{\circ}\text{oo}$, consistent with a high temperature origin for this quartz (Chapter 4). In addition, bipyramidal forms after α -quartz indicate crystallisation at temperatures greater than 573 $^{\circ}\text{C}$ (Fronde1, 1962) and this quartz is accordingly included in the rhyolitic tephra component.

Detrital mineral component - - Quartz is the dominant detrital mineral present, accompanied by trace amounts of epidote, muscovite, tourmaline, and microcline. Oxygen isotope analysis of quartz has shown that the > 125 μm quartz is neither high temperature (igneous) nor low temperature (authigenic) but was probably derived from pre-existing sediments (Mokma et al., 1972; see Chapter 4). The remaining detrital minerals are more typical primary minerals in plutonic and metamorphic rocks but since these rock types are rare in Northland, it is more probable that the minerals have been recycled from existing Tertiary and Mesozoic sediments along with the quartz.

The occurrence of each mineral component in the basaltic soils is dependent on the environmental circumstances that led to their preservation or formation in these soils. The significance of these environmental circumstances varies, the rhyolitic and detrital components being the most useful. These two components preserve the record of any stratigraphic history and material additions at each soil site as well as showing the effects of subsequent soil-forming processes.

Significance of the Basaltic Component

Minerals of the basaltic component only occur in significant amounts in the Kiripaka and Whatitiri soils. In all of the remaining soils only traces of calcic feldspar remain. Olivine occurs only in the Whatitiri soil. The distribution of olivine, occurring in the uppermost 0.3m of this profile, makes it unlikely to have been derived from the underlying basalt. Within 2 km of the Whatitiri site is Maungatapere cinder cone, thought to be much younger because of its lesser degree of dissection than the Whatitiri cone (Kear, 1961). The eruption of Maungatapere is considered to be the most likely source of the olivine-bearing component in the surface horizons of the Whatitiri profile.

In the Kiripaka soil, augite and calcic plagioclase are common, sometimes within rock fragments. Olivine is absent. Given that olivine basalt is the main basalt type present in the region, olivine should be present in the sand and silt fractions. Its absence suggests that rapid weathering of olivine has occurred in this environment. An important implication of this observation is that although the Whatitiri soil is considered to be more developed than the Kiripaka, the surface horizons contain an influx of younger and less-weathered materials than the parent materials of the Kiripaka. This suggests that the Maungatapere cinder cone is much younger than the eruptions of the lava flows on which the Kiripaka soils have formed.

The Kiripaka and Whatitiri soils overly basalt lava flows. In both cases unweathered and partially-weathered basalt fragments are present in the base of the soil profiles. In the Kiripaka soil, quartz and other non-basaltic materials are common, even in the lowermost sample immediately above the flow surface (Fig. 5.2). In contrast, in

the Whatitiri soil a 0.3m zone extends up from the flow surface in which non-basaltic components are negligible (Fig. 5.4). This suggests that the parent materials of the Kiripaka soil are largely derived by redeposition of local material, derived from both basaltic and quartzose sources. In contrast, in the Whatitiri soil the detrital-free zone probably represents more rapid accumulation of basalt tephra on the flow during flow emplacement.

Both the Kerikeri and Okaihau soils have formed in a parent material over saprolite and here interpretation is ambiguous. In both cases there is a decrease in the detrital component of samples immediately above the saprolite. This could represent a thin ($< 0.1\text{m}$) tephra layer but it is more likely to represent incorporation of the quartz-free upper part of the saprolite in the basal soil horizons.

The remaining two soils, the Waiotu and Ruatangata, appear to have formed in a thick sequence of surficial materials overlying basalt flows at $>10\text{m}$ depth. Stratification apparent in the material underlying the Waiotu profile (Plate 5.4) suggests that it represents a long history of accumulation of basaltic and non-basaltic materials overprinted by intense weathering.

Significance of the Secondary Component

One of the notable features of this soil sequence is the development of gibbsite and goethite glaebules. Even in the least-weathered soils, the Kiripaka and the Whatitiri, small iron oxide glaebules occur in the finer-size fractions and iron-oxide coatings are formed on rock fragments throughout the profile. Gibbsite glaebules are not visible macroscopically in the Kiripaka but show increasing development through the rest of the soil development sequence. They have a marked effect on grain-size distribution such that in the older soils the grain-size



Plate 5.4 Section showing subsurface layering below the surface on which Waiotu soils occur. The lava flow, K/Ar dated at 1.27×10^6 years B.P., occurs at more than 30 m depth.

characteristics are largely determined by the presence and development of glaeboles. They occur through all grain size fractions $>2\text{ }\mu\text{m}$, and possibly smaller, and form the greater part of the most developed soils. Since they are glaeboles and not aggregates they are not easily dispersed into smaller particles. The overall grain-size distribution of the soil is therefore a reflection of the size distribution of the secondary component particles and does not simply represent a primary distribution. This also has implications for the chemical interactions in these soils. The presence of goethite and gibbsite glaeboles throughout all size fractions means that the silt and sand fractions will have a significant influence on the chemical reactivity of the soil (McAleese and McConaghy, 1957; McConaghy and McAleese, 1957).

Significance of the Rhyolitic Component

A similar distribution of rhyolitic glass was noted in all profiles. Most of the glass occurs within 0.2m of the soil surface. In the Kiripaka it persists in trace amounts to the base of the profile (Fig. 5.2) but in the remaining soils it seldom persists below 0.6m.

In the Kiripaka, Kerikeri, Ruatangata, and Okaihau soils biotite occurs in the top 0.2m. It is more abundant in the Kiripaka and Ruatangata than in the Kerikeri and Okaihau soils. Significant biotite in the mafic mineral assemblage of a rhyolitic tephra in New Zealand indicates a probable source in the Okataina Volcanic Centre (Ewart, 1968). Since the biotite occurs in the surface horizons of each soil, it is probable that it is from one of the more recent biotite-bearing tephras. The youngest tephra of this type is Kaharoa Ash, dated (NZ872A) at 850 ± 54 years B.P. More recent evidence suggests that the Kaharoa Ash may be even younger, having been erupted about 700 years B.P. (McGlone, 1981).

This tephra is known to occur elsewhere in Northland, preserved in peat swamps and coastal sand dunes (Pullar et al., 1977). Kaharoa Ash also contains quartz phenocrysts (Cole, 1970) and is therefore a likely source for the large quartz grains which are most abundant in soils containing the most biotite (Kiripaka and Okaihau). In contrast, no coarse-grained quartz was found in the surface horizons of either the Whatitiri or Waiotu soils, neither of which contain biotite.

Rhyolitic glass is common to all profiles, indicating that tephras other than Kaharoa Ash are also present. The large rhyolitic eruptions from the central North Island are shown in Table 5.1. Apart from Kaharoa Ash, Taupo Pumice, dated (NZ1548A) at 1840 ± 50 years B.P. was an eruption of "ultraplinian" proportions (Walker, 1980) of widespread distribution in the North Island of New Zealand (Vucetich and Pullar, 1973) and is present as sea-raftered pumice in coastal sand dunes in Northland (Wellman, 1962; Pullar et al., 1977). The mafic mineral assemblage of Taupo Pumice is not incompatible with the rhyolitic component of the surface horizons in the basaltic soils and is a probable source of some of the abundant rhyolitic glass.

Kawakawa Tephra is extremely widespread in distribution throughout the North Island and northern South Island. Its mafic mineral assemblage of hypersthene, hornblende, and augite (Howorth, 1980) is not distinctive and the possible presence of this tephra has been postulated in the surface horizons of the Okaihau soil (Rankin, 1973). The high quartz contents of both the Ruatangata and Okaihau soils suggests that they have accumulated slowly and Kawakawa Tephra could reasonably be expected to be found in their surface horizons. However, the remaining soils have much lower quartz contents and appear to have accumulated more rapidly. In this situation, evidence of the presence of Kawakawa Tephra would occur deeper in the profile, particularly in

Table 5.1 Major eruptions from the central North Island in the last circa 40,000 years

Tephra Formation	^{14}C Age	NZ ^{14}C No.	Mafic Mineralogy
Kaharoa Ash (O)	850 $\pm$ 54	NZ872A	biotite, hypersthene, augite
Taupo Pumice (T)	1870 $\pm$ 60	NZ1059A	hypersthene, augite, hornblende
Waimihia Ash (T)			hypersthene, augite, hornblende
Whakatane Ash (O)	4600 $\pm$ 90	NZ3948A	hypersthene, augite, hornblende, cummingtonite
Hinemaiaia Tephra (T)	4650 $\pm$ 80	NZ4574A	hypersthene, hornblende, augite
Motutere Tephra (T)	5370 $\pm$ 90	NZ4876A	hypersthene, hornblende, augite
Rotoma Ash (O)	9120 $\pm$ 130	NZ1945A	hornblende, hypersthene, cummingtonite
	9080 $\pm$ 100	NZ1943A	
Waiohau Ash (O)	11250 $\pm$ 200	NZ568A	hypersthene, hornblende
Rotorua Ash (O)	13450 $\pm$ 250	NZ1615A	hypersthene, hornblende, biotite
Rerewhakaaitu Ash (O)	14700 $\pm$ 200	NZ716A	biotite, hornblende, hypersthene
Kawakawa Tephra (T)	19850 $\pm$ 310	NZ1056A	hypersthene, hornblende, augite
Rotoehu Ash (O)	41700 $\pm$ 3500	NZ1126A	cummingtonite, hypersthene, hornblende

(T = Taupo Volcanic Centre, O = Okaitaina Volcanic Centre)

the Kiripaka and Whatitiri soils. Only in the Whatitiri is there evidence deep in the profile of an influx of rhyolitic glass (Fig. 5.4). This is preserved because:

- (i) this site is the southernmost sampled and is therefore likely to have received more rhyolitic ash than the more distant soils, and
- (ii) it is one of the younger soils and has accumulated rapidly enough for the record of eruptions to be differentiated. This is unlike the nearby, slowly-accumulating Ruatangata soil in which Kawakawa Tephra is more likely to be present in the surface horizons.

The fourth major tephra likely to have been recorded in Northland is Rotoehu Ash (Table 5.1), dated (NS1126A) at 41700 ± 3500 years B.P. This tephra has a distinctive mafic mineral assemblage, consisting predominantly of the amphibole cummingtonite (Kohn, 1970). Since cummingtonite was not found in any of the soils examined, it suggests that either:

- (i) deposition of Rotoehu Ash did not occur, or
- (ii) the cummingtonite has been weathered, or
- (iii) the surfaces on which the soils formed are either $< 40,000$ years old or have been eroded after the ash was deposited.

The Rotoehu Ash eruption distributed tephra in a broadly similar pattern to the Kaharoa Ash (Vucetich and Pullar, 1964) and, since the Rotoehu was the much larger eruption of the two, it would be unlikely for it to have not reached Northland. It would appear that both the Kiripaka and Whatitiri soils are probably on surfaces younger than 40,000 years B.P. However, the absence of Rotoehu Ash in the remaining soils is interpreted as either a result of weathering or erosion because these soils appear to be on surfaces $> 40,000$ years old. There is a decrease in rhyolitic glass content with depth in each soil which

suggests a weathering decay curve. This suggests, along with evidence of increasing weathering of glass particles with depth, that older rhyolitic glass has been entirely weathered in these soils.

The abundance of glass in the uppermost 0.2m of the younger soils is attributed to accumulation of primarily Holocene tephras, in particular Kaharoa Ash and Taupo Pumice. In the older soils, which have accumulated more slowly, the glass is partially attributed to older tephras which may also be present in the surface horizons.

Significance of the Detrital Component

as Evidenced by Quartz Accumulation

Grain size distribution - - More than 80% of the quartz in each profile lies in the $< 63 \mu\text{m}$ size fraction (Table 5.2). Only traces of quartz appear in the $< 2 \mu\text{m}$ size fractions of the soils and previous work has shown that in the Ruatangata soil all of the $< 2 \mu\text{m}$ quartz lay in the $2 - 1 \mu\text{m}$ size range. This quartz had an oxygen isotope abundance indistinguishable from the $5-2 \mu\text{m}$ quartz present in the same sample (Chapter 4) and is considered to be part of the $10-1 \mu\text{m}$ tropospheric aerosolic dust component in the soil.

Grain-size distribution curves for two samples from each profile are shown in Figs. 5.11 - 5.16. In three of the soils, Kiripaka, Kerikeri, and Ruatangata, the sample from near the surface contains a higher amount of sand-sized quartz. These three soils also show the highest amounts of biotite, presumably from the Kaharoa Ash eruption, in their topsoils. Further, large, fractured quartz grains also occur in the $> 250 \mu\text{m}$ size fraction of these three soils. It has previously been shown that this quartz is of high-temperature origin and is probably part of the Kaharoa Ash phenocryst assemblage (Chapter 4). In the

Table 5.2 Total amounts of quartz present in samples from
upper and lower parts of the profiles of the
six basaltic soils

Soil series	Depth (m)	% quartz, clay free	% quartz, total sample
Kiripaka	0.20 - 0.30	10.50	4.33
	0.70 - 0.80	26.61	7.07
Whatitiri	0.10 - 0.20	23.71	4.76
	0.70 - 0.80	9.22	1.57
Waiotu	0.20 - 0.30	22.90	5.32
	0.50 - 0.60	12.62	2.00
Kerikeri	0.10 - 0.20	4.76	1.82
	0.50 - 0.60	4.29	1.30
Ruatangata	0.20 - 0.30	47.21	14.28
	0.60 - 0.70	39.54	6.43
	1.30 - 1.42	13.04	1.48
Okaihau	0.10 - 0.20	31.45	10.83
	0.30 - 0.40	22.29	6.72

remaining soils there are only small amounts of quartz in the sand fractions. In the Whatitiri and Okaihau soils there is little difference in grain size distribution with depth for quartz. However, in the Waiotu soil the lower sample contains a higher proportion of sand-sized quartz (Fig. 5.13).

The total quartz content decreases with depth in all of the soils except the Kiripaka (Table 5.2). This is thought to reflect the slow accumulation of these profiles; any variations in quartz accumulation caused by factors such as climate change (Stewart *et al.*, 1977) cannot be resolved because the 0.1m sampling interval used is too coarse to detect them.

Quartz Accumulation - - In the soils sampled quartz accumulation and the presence of identifiable rhyolitic tephras allows some time constraints to be placed on soil forming processes. Where aeolian quartz accumulates over long periods of time, soils on older surfaces will show evidence of greater amounts of quartz than soils on younger surfaces. A rapidly accumulating profile should show a lower concentration of quartz than a more slowly accumulating profile of the same age but since it has accumulated to a greater depth it will still contain a similar amount of quartz. Factors which will cause changes in this pattern are erosion, overthickening, local changes in aeolian inputs, and chemical dissolution of quartz during weathering. All sites were chosen to minimise the first two factors. There is no evidence of either dissolution or pedogenic crystallisation of quartz in any of the soils and SEM photomicrographs show angular grains with no sign of etching typical of dissolution processes (Chapter 4). Therefore, for any given time period the main cause of variation in quartz accumulation should be factors relating to the local environment.

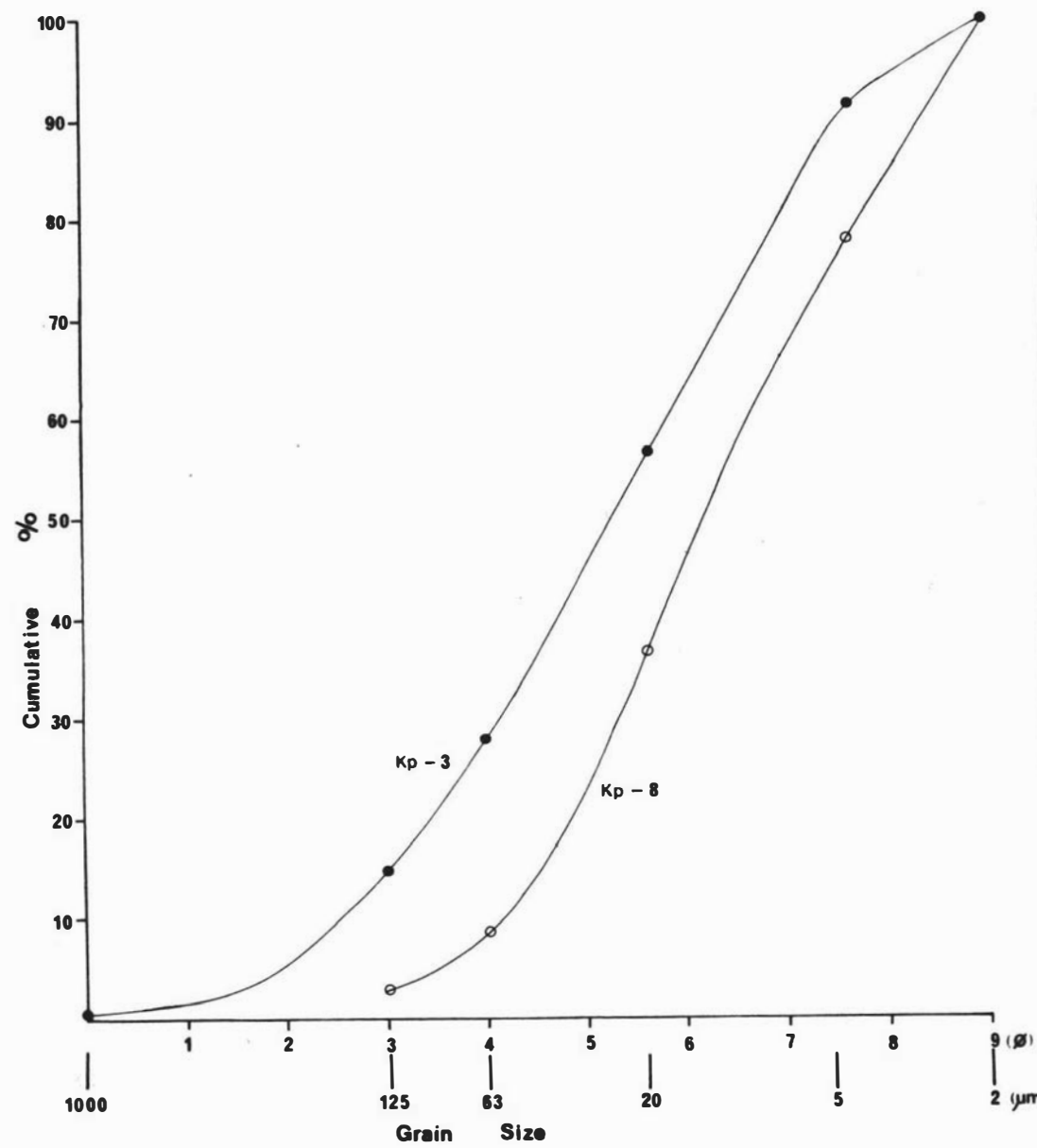


Figure 5.11 Kiripaka soil - grain size distribution of quartz at 0.2 - 0.3 m (Kp-3) and 0.7 - 0.8 m (Kp-8) depth. Grain size is expressed in ϕ units for arithmetic plotting. Size fractions in μm are also shown for comparison.

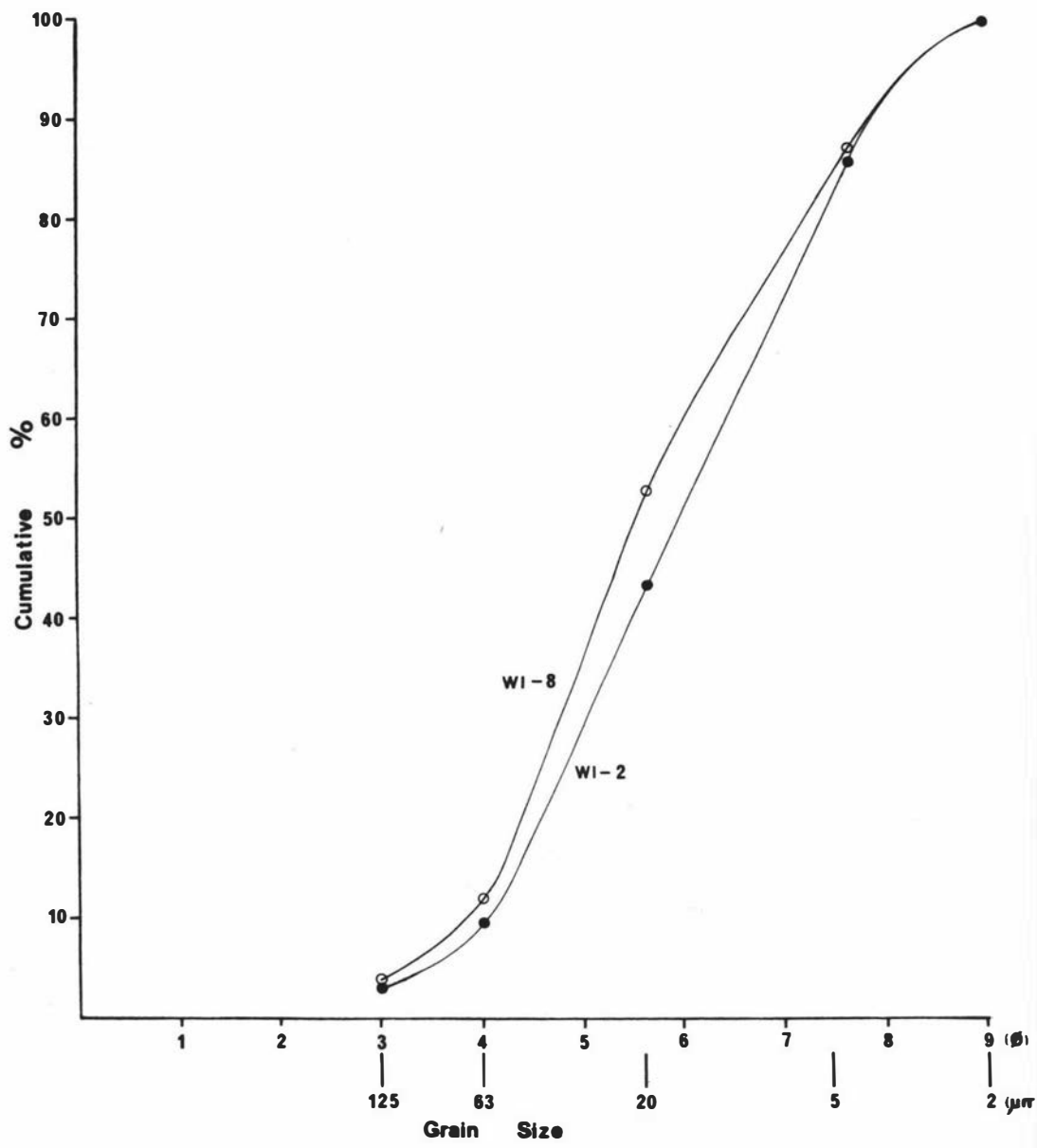


Figure 5.12 Whatitiri soil - grain size distribution of quartz at 0.1 - 0.2 m (WI-2) and 0.7 - 0.8 m (WI-8) depth. Grain size is expressed in ϕ units for arithmetic plotting. Size fractions in μm are also shown for comparison.

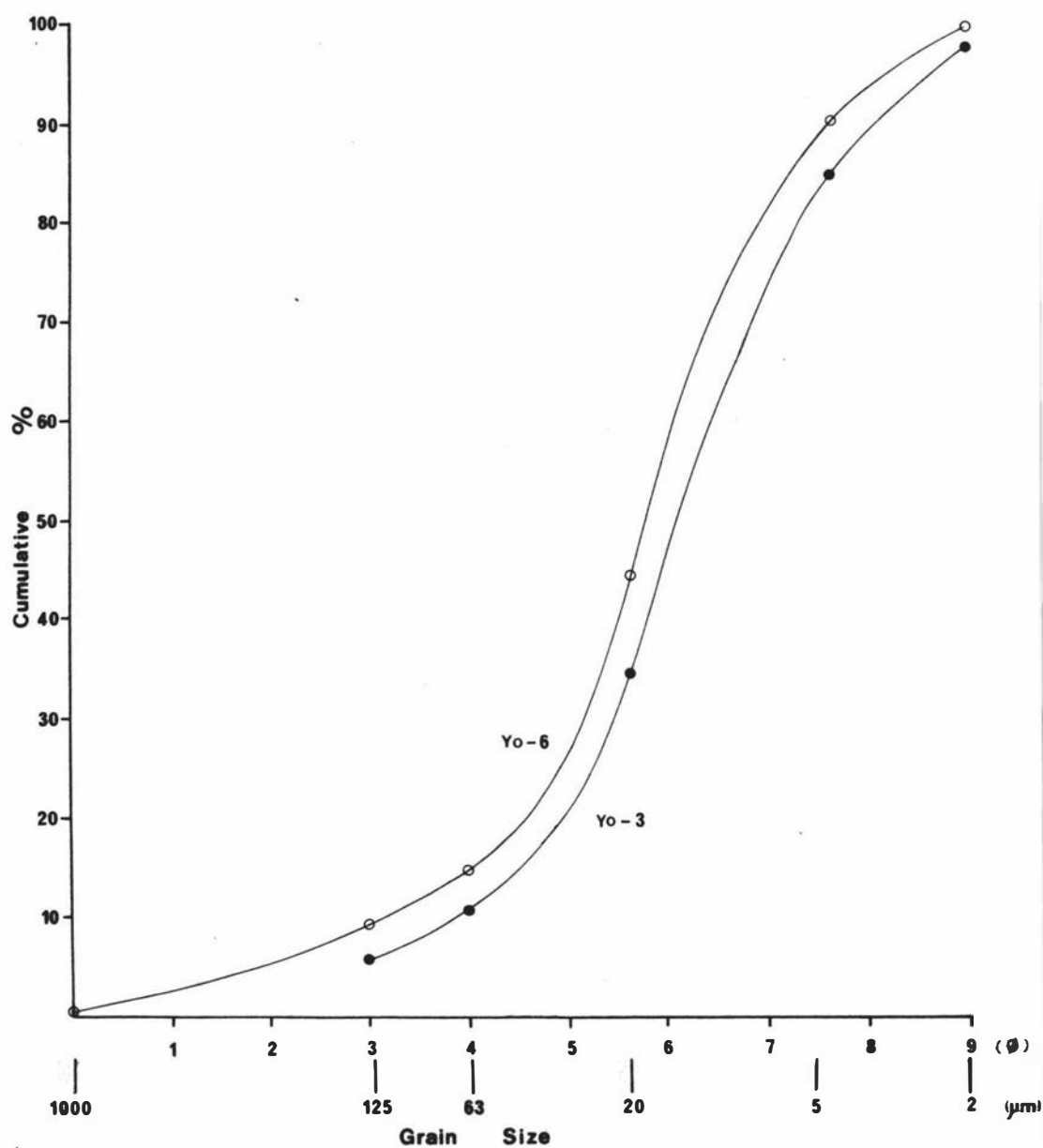


Figure 5.13

Waiotu soil - grain size distribution of quartz at 0.2 - 0.3 m (Yo-3) and 0.5 - 0.6 m (Yo-6) depth. Grain size is expressed in ϕ units for arithmetic plotting. Size fractions in μm are also shown for comparison.

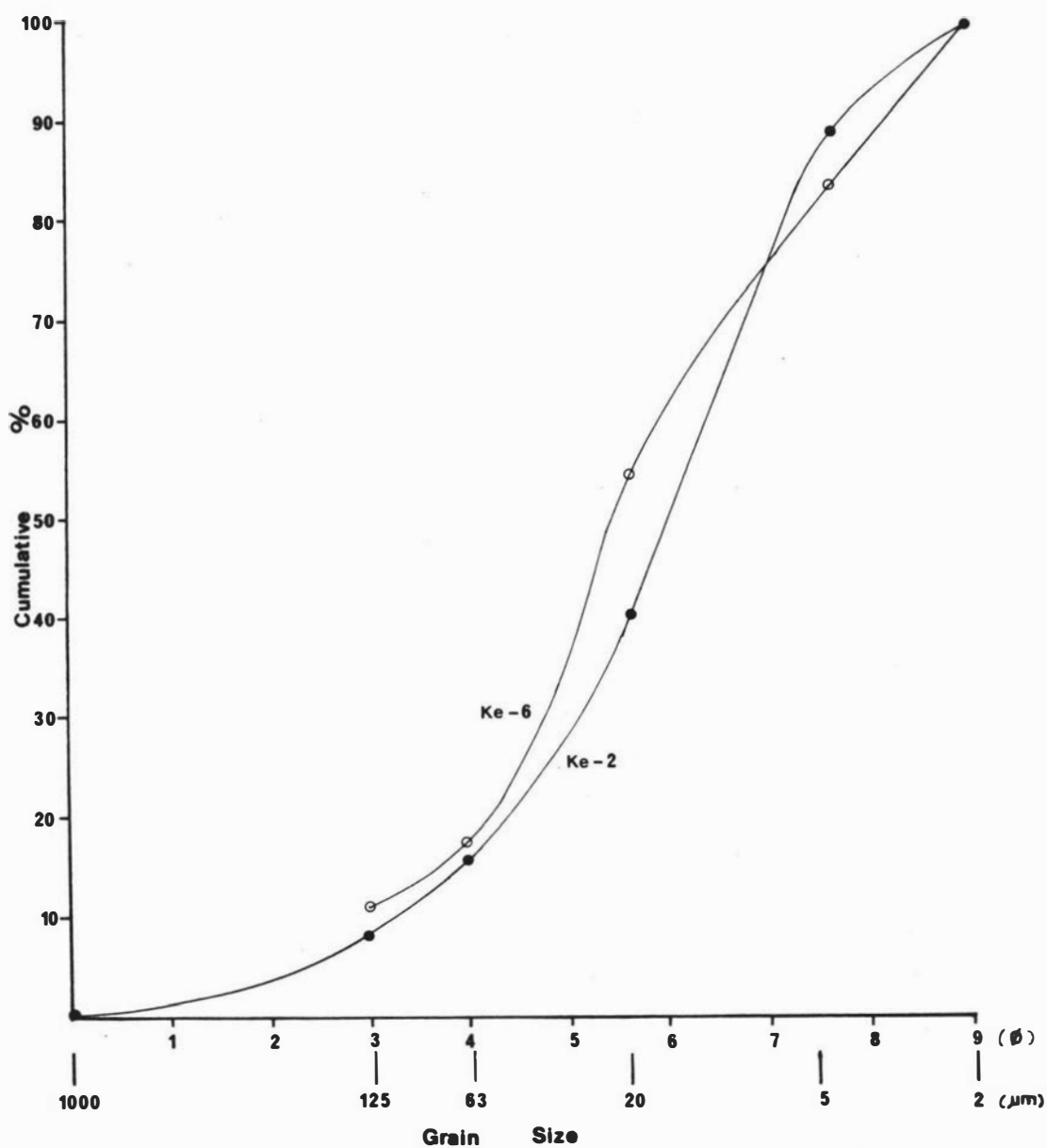


Figure 5.14

Kerikeri soil - grain size distribution of quartz at 0.1 - 0.2 m (Ke-2) and 0.5 - 0.6 m (Ke-6) depth. Grain size is expressed in ϕ units for arithmetic plotting. Size fractions in μm are also shown for comparison.

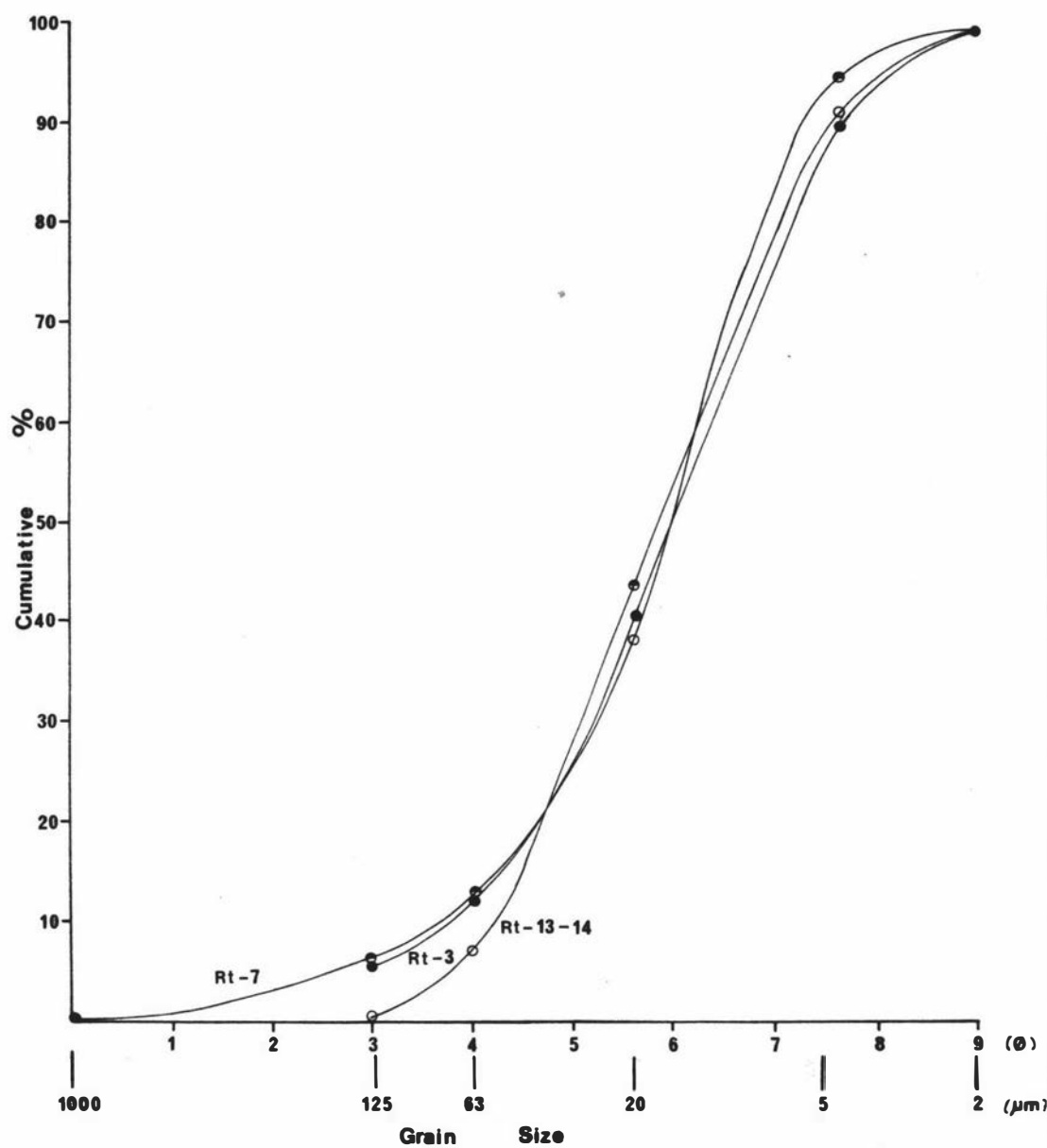


Figure 5.15 Ruatangata soil - grain size distribution of quartz at 0.2 - 0.3 m (Rt-3), 0.6 - 0.7 m (Rt-7) and 1.3 - 1.4 m (Rt 13-14) depth. Grain size is expressed in ϕ units for arithmetic plotting. Size fractions in μm are also shown for comparison.

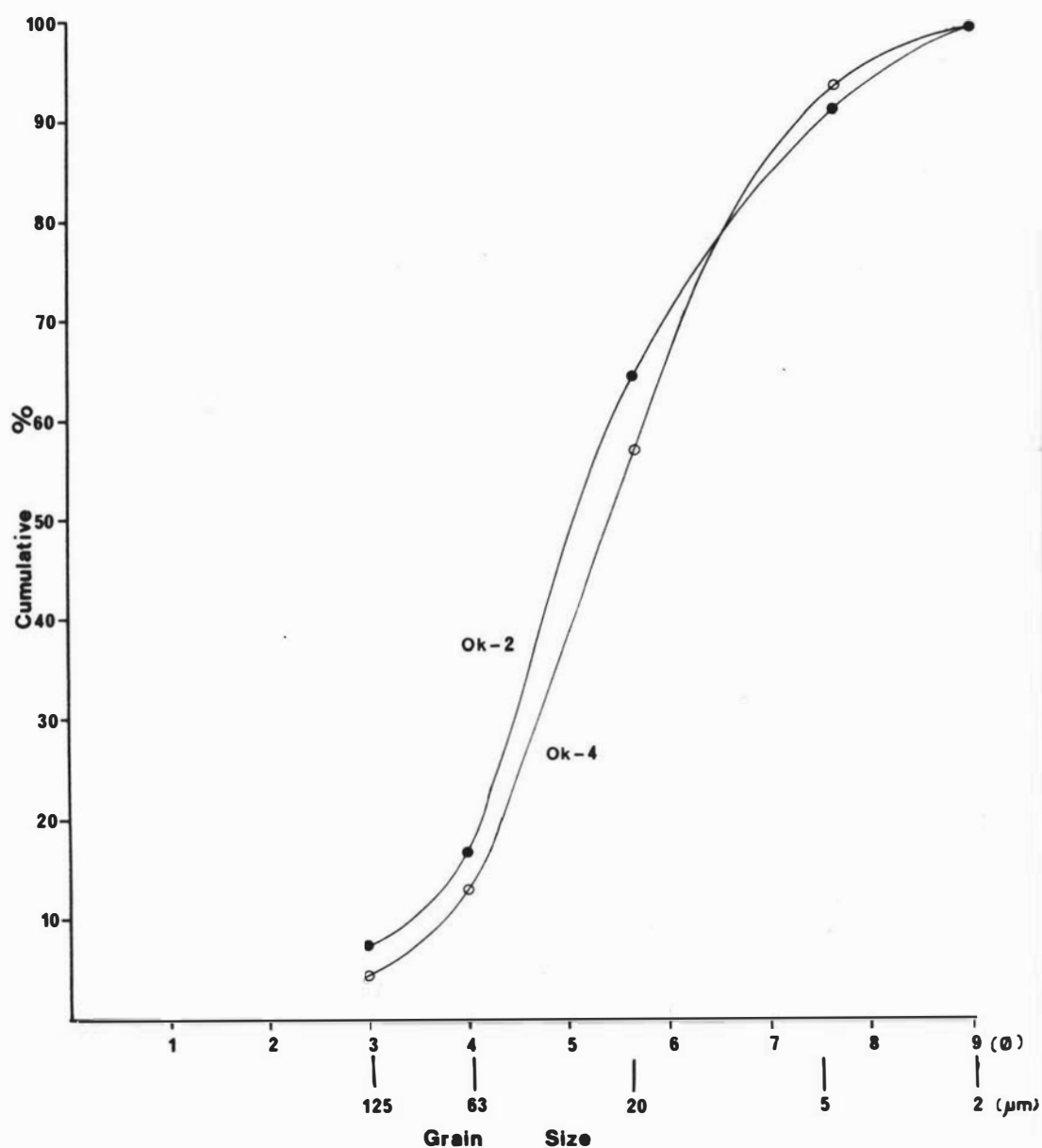


Figure 5.16

Okaihau soil - grain size distribution of quartz at 0.1 - 0.2 m (Ok-2) and 0.3 - 0.4 m (Ok-4) depth. Grain size is expressed in ϕ units for arithmetic plotting. Size fractions in μm are also shown for comparison.

Quartz accumulation with time has been shown to vary with climate change in deep-sea sediments (Bowles, 1975) and in an andesitic soil from Taranaki, New Zealand (Stewart et al., 1977). Lower rates of quartz accumulation have been shown to occur in post-glacial (Aranuian) time compared with glacial (Otiran) time. Of the Northland basaltic soils examined, only the Kiripaka shows a quartz distribution with depth consistent with this concept. However, in comparison with the Egmont loam profile (Stewart et al., 1977) there is a much higher amount of aerosolic quartz in the Kiripaka, this being attributed to an additional component of locally-derived quartz (Chapter 4).

The Kiripaka site lies on the down-wind edge of the Kaikohe basalt field (Fig. 5.1) and it also has the highest basalt component of any of the soils examined. However, all olivine has been weathered out so that an initial stage of weathering has been passed. This site appears to be one in which aeolian materials were remobilised from the rest of the basalt field to the west, along with non-basaltic material from local sedimentary rocks. This would explain the apparent rapid accumulation of this soil, in relation to the other basaltic soils studied.

The remaining soils are progressively more strongly weathered. Quartz contents are highest in the surface horizons, decreasing with depth. This implies very slow accumulation of material in the profile. Where such slow accumulation has occurred the 0.1m sampling interval has proved inadequate to show climate-induced changes in quartz accumulation, although evidence of variation on such a fine scale is also likely to be destroyed by mixing as a result of biological activity.

Inferred Relative Ages of Soil Parent Materials

It has been demonstrated that where there is a common origin for quartz within a region, it may be possible to determine the relative ages of soil profiles by the accumulation of aerosolic quartz (Chapter 3, 6). In the Taranaki region it was considered that quartzose source areas were restricted upwind of the depositional sites and most of the 5 - 2 μm quartz was of aerosolic dust origin. A similar situation was thought to exist in Northland. However, examination of the Kiripaka soil (Chapter 4) has shown the anomalous presence of a large component of 5 - 2 μm quartz from local siliceous sediments, derived as local aeolian material. It therefore appears that in the Northland environment locally-derived aerosolic quartz is considerably more abundant than in Taranaki. This is probably due to the large areas of Mesozoic and Tertiary sediments acting as an aeolian quartz source in relation to comparatively localised areas of basalt soils in Northland. The dominant material subject to wind erosion in Northland is probably highly quartzose. In contrast, in Taranaki the dominant surficial material is quartz-free andesitic ash and would thus be expected to dominate the soil parent materials of that region. Only small areas of possibly quartzose sediments can have existed upwind of Taranaki and thus the main source of 5 - 2 μm quartz there has been aerosolic dust.

The relative amounts of 5 - 2 μm quartz have been listed for each of the basalt soils (Table 5.3). It can be seen that although there is a general tendency for the most developed soils to have the greater amount of quartz (Ruatangata and Okaihau), there is no obvious relationship between aerosolic quartz content and soil development.

Kiripaka Accumulation of quartz in this soil is similar to that preserved

in the Egmont loam (Chapter 3) and which is interpreted as a record of post-20,000 years B.P. climate change. There is no influx of rhyolitic glass towards the base of the profile which could be attributed to the circa 20,000 years B.P. Kawakawa Tephra. This shows that either the Kawakawa Tephra did not contribute measurable quantities of glass to this profile or that it has largely been weathered out.

If the accumulation of 5 - 2 μm quartz in the Kiripaka soil is compared with that of the Egmont loam profile, it can be seen that the Kiripaka soil would have an estimated age of circa 64,000 years B.P. (Table 5.3). However, if the estimated 50% contamination with low-temperature quartz is considered, an estimated age of 32,000 years B.P. is obtained (Table 5.3). This is more consistent with previous radiocarbon ages for a similar basalt flow dated (NZ1721) at $35,000 \pm 2,600$ years B.P.

Whatitiri This soil does not contain demonstrable locally-derived quartz in the 5 - 2 μm size fraction. The only locally-derived additional material appears to be basaltic tephra in the surface horizons from the eruption of Maungatapere cinder cone. The presence of unweathered olivine in this material suggests a relatively young age for the eruption of Maungatapere.

The overall distribution of quartz in this profile shows an increase with depth (Fig. 5.4), possibly reflecting a paleoclimatic effect. Between 0.50 - 0.60m depth a small influx of rhyolitic glass is recorded. If the amount of 5 - 2 μm quartz accumulated to 0.5m depth is compared with that of the Egmont loam, an estimated age of 25,500 years B.P. was obtained for the rhyolitic glass influx. This is not inconsistent with the presence of Kawakawa Tephra, given that any contamination with non-aerosolic quartz will cause an overestimation of the age.

The total amount of 5 - 2 μm quartz present in the Whatitiri soil gives an estimated age of circa 39,000 years B.P. (Table 5.3), slightly older than that of the Kiripaka. The differences in soil development between the two soils are therefore likely to be due to factors in soil formation other than time. The Whatitiri soil parent materials appear finer grained than the Kiripaka (Fig. 5.2 and Fig. 5.4) and less scoriaceous. This may have led to increased weathering of the Whatitiri.

Waiotu This soil shows a decreasing quartz content with depth and this cannot be directly attributed to paleoclimatic change (Fig. 5.5). The soil also shows an unusually low rhyolitic glass content in the surface horizons of < 2% and < 1% in the 63 - 20 μm and 125 - 63 μm size fractions, respectively (Fig. 5.5), compared with approximately 6% and 3% for the corresponding size fractions in most of the remaining soils.

When the 5 - 2 μm quartz accumulation in the Waiotu soil is compared with the Egmont loam, and other basaltic soils, an estimated age of 38,000 years B.P. is derived, similar to that of the Whatitiri and only slightly older than the Kiripaka. However, the degree of development of gibbsite and goethite glaebules, together with the degree of weathering of primary mineral components in the profile, suggests a much longer period of soil development. No biotite-bearing glass was noted in the surface horizons and this suggests that Kaharoa Ash is not present. This is considered unlikely in an undisturbed profile as Kaharoa Ash was found in the Kiripaka, Kerikeri, and Okaihau soils, all located in the Kaikohe - Bay of Islands basalt field. Thus truncation of the profile is suggested that post-dates the Kaharoa Ash at circa 850 years B.P. It seems possible that this reference site on the boundary of an airfield has been truncated recently. It seems likely that this truncation occurred during construction of the airfield.

Kerikeri This soil is similar to the Waiotu in that it shows no variation in quartz content with depth which could be attributed to paleoclimatic change. It shows an anomalously low quartz content for the degree of soil development. The rhyolitic glass content of the surface horizons is, however, significantly higher than in the Waiotu (Fig. 5.6).

The 5 - 2 μm quartz content of this profile gives an estimated age of 18,000 years B.P. when compared with the Egmont loam (Table 5.3), much younger than would be anticipated from comparison with the Kiripaka and Whatitiri soils. Clearly some soil erosion has occurred here in the past. The presence of Kaharoa Ash and relatively abundant rhyolitic glass in the surface horizons shows that this erosion must have occurred prior to circa 850 years B.P. The degree of weathering in the B horizons of this soil is thus thought to be an inherited factor. The B horizons contain relatively large amounts of magnetite in the 63 - 20 μm size fraction, a similar size distribution to the magnetite in the underlying saprolite. This suggests that much of the present soil has weathered from basalt flow material and that a major disconformity exists in this profile. Loss of part of the stratigraphic record from the upper part of this profile would explain the unusually low 5 - 2 μm quartz content.

Ruatangata In this soil the 5 - 2 μm quartz content shows little consistent variation with depth (Fig. 5.7). If 5 - 2 μm quartz accumulation rates are extrapolated from the Egmont loam to this profile, then 0.2m of material would have accumulated in 20,000 years, suggesting that if the Kawakawa Tephra were present, it would be in the surface horizons. This means that post-20,000 years B.P. variations in quartz accumulation are not able to be resolved. The total 5 - 2 μm quartz

content of this soil is the greatest of the basaltic soils examined and by comparison with known rates in the Egmont profile would give this profile an estimated age of circa 95,000 years B.P. (Table 5.3).

Okaihau The concentration of 5 - 2 μm quartz in the surface horizons of this soil is similar to that in the Ruatangata. Thus there is also no resolution of events $\leq 20,000$ years B.P. The estimated age of this profile, from a comparison with the Egmont loam, is circa 83,000 years B.P. (Table 5.3). However, widespread erosion in the Okaihau soil terrain has been previously recognised (Grange, 1934). The relationship between quartz content and time can only presently be based on extrapolation of aerosolic quartz accumulation rates backwards into time. Until more detailed soil or marine core sections have been studied the accumulation rate prior to 20,000 years will be poorly understood. However, the much higher concentration of quartz in both the Ruatangata and Okaihau soils is indicative of their advanced stage of weathering.

Soil Parent Material Accumulation and Soil Development

The sedimentation rate for four of the soils based on estimated ages from quartz accumulation has been calculated (Table 5.4). Two of the soils (Waiotu and Kerikeri) appear to contain disconformities and are thus excluded from this calculation.

From Table 5.4 it can be seen that the degree of soil development is clearly related to the sedimentation rate, that is, the slowly accumulating soils undergo more intensive weathering than rapidly accumulating soils. One could speculate that, assuming there is no erosion in either profile, the Ruatangata soil is older than the Okaihau but has accumulated more rapidly and therefore does not show the same intense gibbsite and goethite glaebule development. Further, the clay

Table 5.3 Comparison of the aerosolic quartz ($5 - 2 \mu\text{m}$) in the Egmont loam with the Northland basaltic soils and age estimates based on the relative quartz contents

Soil	5 - 2 μm Quartz (gm cm^{-2})	Inferred Age [@] (years B.P.)
Egmont	0.18	20,000
Kiripaka	0.29	32,000
	0.58 (uncorrected)	64,000
Whatitiri	0.35	39,000
Waiotu	0.34	38,000
Kerikeri	0.16	18,000
Ruatangata	0.86	95,000
Okaihau	0.75	83,000

[@] Inferred age relative to the Egmont loam with 0.18 gm cm^{-2} quartz at 20,000 years B.P.

TABLE 5.4 Sedimentation rates for four soils of the basaltic soil sequence

SOIL	RATE (mm ka^{-1})
Kiripaka (least developed)	355
Whatitiri	289
Ruatangata	120
Okaihau (most developed)	99

mineralogy of the Ruatangata is predominantly halloysitic, particularly at depth, whereas that of the Okaihau is dominantly gibbsite and goethite. This suggests imperfect drainage in the Ruatangata which may also help explain the fewer and smaller gibbsite and goethite glaebules in this soil.

CONCLUSIONS

Four mineralogical components are recognised in the basaltic soils: basaltic, secondary, rhyolitic, and detrital.

1. Basaltic component - - This contains primary minerals similar to those occurring in unweathered basalt or basalt tephra. It is most abundant in the two least developed soils, Kiripaka and Whatitiri, but only traces are present in the remaining, highly-weathered soils. In the Whatitiri soil an olivine-bearing assemblage in the surface of the soil is a result of accretion of a very young (possibly less than 1000 - 2000 years B.P.) basalt tephra from the eruption of the nearby Maungatapere cone.
2. Secondary component - - This consists of glaebules of gibbsite, goethite, and clay minerals. These become increasingly abundant through the soil development sequence, reaching a peak expression in the Okaihau soil. They comprise over 50% of the sand and silt fractions of most soils and, in the deeper parts of the more developed profiles, may comprise > 90% of the non-clay fraction. The glaebules cannot be disaggregated by routine dispersion methods. Their presence controls the grain-size distribution characteristics of these soils.
3. Rhyolitic component - - In all soils this component is most abundant in the uppermost 0.2m of the profile. Biotite in four of the soils,

Kiripaka, Kerikeri, Ruatangata, and Okaihau, indicates the presence of Kaharoa Ash dated at circa 850 years B.P. However, the presence of abundant glass in the surfaces of the remaining soils with no biotite indicates that other tephras, particularly Taupo Pumice and Kawakawa Tephra, are also likely to be present. The presence of even older tephras, such as the circa 42,000 year B.P. Rotoehu Ash, is considered possible in some of the soils on older surfaces but no trace of them was found. This is interpreted as an indication they have been weathered out in the strong weathering environment of these soils.

4. Detrital component - - This component consists predominantly of the marker mineral quartz. Three soils with a significant biotite content in the rhyolitic component also contained fragments of quartz in the $>250\text{ }\mu\text{m}$ size fractions, some of which showed evidence of bipyramidal crystal form, indicating high temperature crystallisation. This correlation with the biotite abundance suggest the quartz is derived from phenocrysts in Kaharoa Ash and is part of the rhyolitic assemblage. However, most of the quartz present lies between 63 and $1\text{ }\mu\text{m}$. Two populations are recognised, (i) a loess population derived from regional quartzose Mesozoic and Tertiary sediments and (ii) a $10 - 1\text{ }\mu\text{m}$ aerosolic dust component, in part derived from tropospheric aerosolic dust.

Only in the Kiripaka soil was stratigraphic evidence of increased quartz accumulation during late glacial times detected, apart from post-glacial accumulation rates. This is due to the relatively rapid accumulation of the Kiripaka soil parent materials. In the remaining soils which have not been modified by erosion (Whatitiri, Ruatangata, and Okaihau), the accumulation has been too slow for change from glacial to post-glacial conditions to be resolved.

The accumulation of aerosolic quartz in each of the profiles was compared with that of the Egmont loam profile from Taranaki. A general trend was noted for the more developed soils to have greater amounts of quartz than the less-developed soils. However, two of the soils (Waiotu and Kerikeri) have anomalously low amounts of quartz for their degree of soil development. This is attributed to stripping of the surface material from the Waiotu site by man very recently, and pre-Kaharoa Ash erosion at the Kerikeri soil site.

In comparison with the Egmont aerosolic quartz accumulation, aerosolic quartz levels in the Kiripaka indicate an age of circa 32,000 years B.P., after correction for contamination with local quartz. This is consistent with the circa 35,000 years B.P. age of a radiocarbon dated flow considered to be of similar age to the flow underlying the Kiripaka soil sampled. The Whatitiri aerosolic quartz accumulation indicates an age of circa 39,000 years B.P., only slightly older than the inferred age of the Kiripaka. The difference in soil development, assuming no soil erosion, must therefore be due to soil-forming factors other than time. Using the inferred ages, the Whatitiri soil appears to have accumulated at a significantly lower rate than the Kiripaka. This may explain the pedological difference between the two profiles.

The Ruatangata soil shows the highest aerosolic quartz content of all the soils examined and in comparison with the Egmont, an age of circa 95,000 years B.P. was inferred. In comparison, the inferred age of the more developed Okaihau soil is circa 83,000 years B.P. This may reflect the increased likelihood of erosion at Okaihau soil sites in the past. Both the inferred accumulation rates and the clay mineralogy of the Ruatangata and Okaihau soils differ. The Ruatangata soil accumulated faster than the Okaihau, perhaps leading to less intense weathering differentiation. In addition, the Ruatangata

contains a significant proportion of halloysite and is evidence of a less well-drained profile than the Okaihau, where gibbsite is more common. This may have contributed to the fewer and smaller goethite and gibbsite glaeboles in the Ruatangata.

The previous concept of considering each soil as having largely developed from the underlying basalt flows has been re-interpreted as an accumulative succession of surficial increments of basaltic and non-basaltic additions to a succession of "accreting" soil profiles, each individually distinct for a number of differing site characteristics.

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CHAPTER 6

CHAPTER 6

THE ACCUMULATION OF QUARTZ IN A
CHRONOSEQUENCE OF ANDISOLS,
SOUTHERN NORTH ISLAND, NEW ZEALAND

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ABSTRACT

The quartz content of four Andisols, forming a chronosequence on andesitic ash in the Taranaki region of the North Island of New Zealand, shows that quartz accumulation in the soil profiles was much higher in glacial (Otiran) than in post-glacial (Aranui) time. Quartz is confined almost exclusively to the surficial material overlying the radiocarbon dated tephras and lahars, which form the surfaces on which the soils have developed.

The quartz grain size distribution, which is finer than $125\ \mu\text{m}$ with a mode in the silt fraction, suggests an aeolian origin for the quartz. In a soil from the central North Island, developed in rhyolitic tephra, quartz distribution is bimodal. Coarse grained quartz $> 125\ \mu\text{m}$ in size is considered to be phenocrysts from the parent material while quartz $< 125\ \mu\text{m}$ in size, is predominantly in the $\leq 20\ \mu\text{m}$ fraction, and appears to largely have an aerosolic dust origin, consistent with the location of this soil in a region in which little quartzose loess has accumulated since the parent tephra was deposited.

The content of aerosolic quartz in the soils, represented by the 5-2 μm size fraction, shows a systematic increase with increasing age of the surfaces on which the soils have developed, suggesting that in regional studies relative ages of soils can be estimated from the aerosolic quartz content of the accumulating material. However, in a marine sediment core, located 110 km to the east of the southern North Island, a much greater accumulation rate for aerosolic quartz in a corresponding time period was noted and this was attributed to additions of quartz of more local origin, its source being the extensive former aggradational river flood plains of the southern North Island. These have given rise to extensive loess deposits during glacial periods when quartzose dust was transported eastwards in the South Pacific by the prevailing westerly wind. In contrast, the local source area for quartz in the Taranaki soils investigated was more restricted and was largely inundated by the post-glacial rise in sea level at circa 11,000 years B.P. The magnitude of the effect of this local component on the aerosolic quartz flux is much greater than that of rainfall variations previously reported in the literature. It is therefore evident that using relative amounts of aerosolic quartz to estimate ages of accumulating soil parent materials can only be used within a region where there is some degree of constancy of quartz accumulation at a given time and that not all 10-1 μm quartz can be assigned to a tropospheric, aerosolic dust origin.

Quartz accumulation rate changes in both the soils and core indicate that the change from higher glacial aerosolic quartz accumulation rates to lower, post-glacial rates had ended by about 7,000 years B.P. The onset of this change is recorded only in the core, at circa 14,700 years B.P., because there was insufficient stratigraphic control on the soil data to show this change. Within the limits of

resolution of this information, it appears that late Pleistocene climate changes, as indicated by changes in aerosolic quartz accumulation rates, are recorded as synchronous events in both soils and marine sediment at these latitudes.

INTRODUCTION

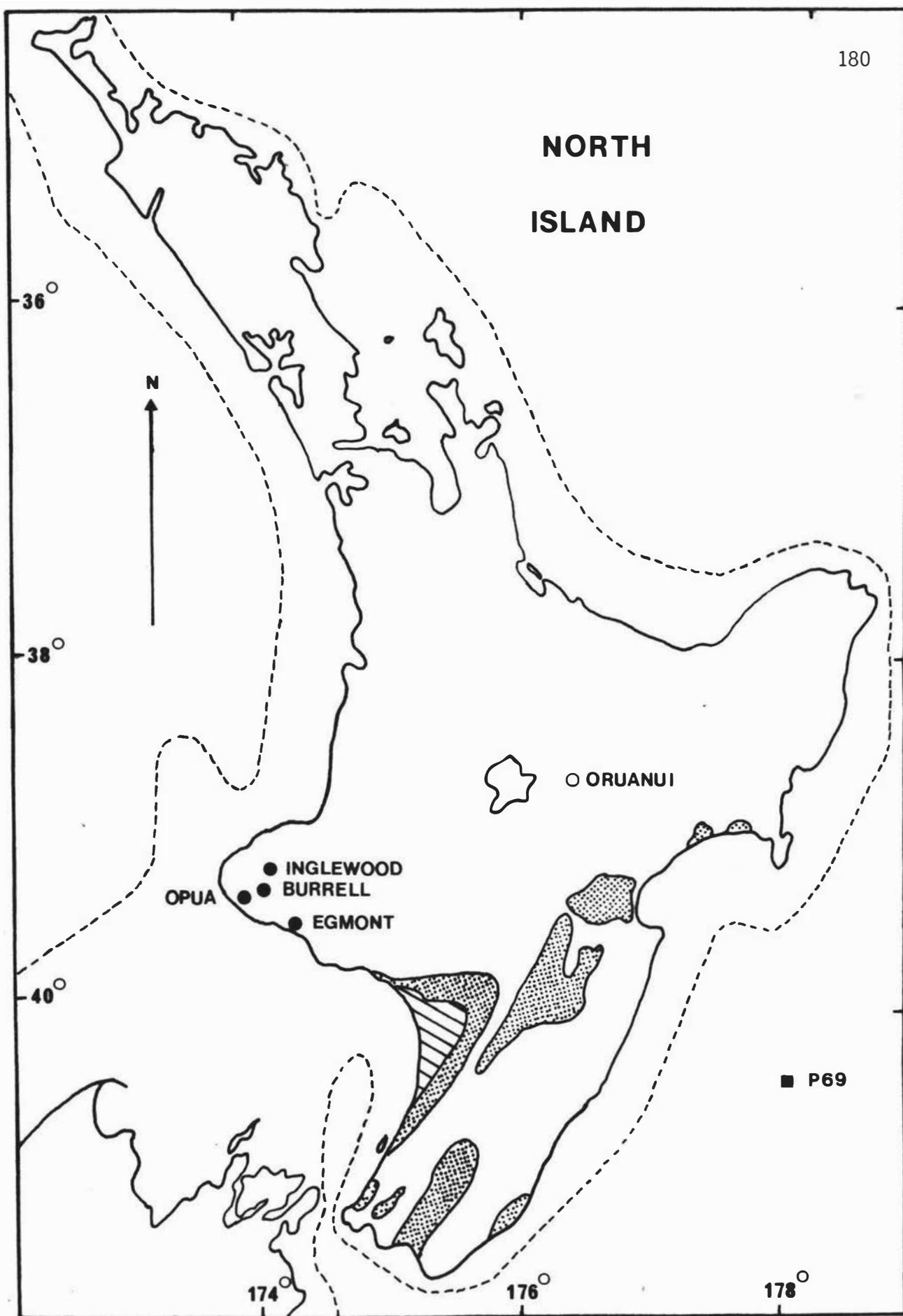
The addition of aeolian material to soils has long been established, the classic examples being the loess derived soils of North America, Europe, and China. Quartz is the most abundant constituent of these aeolian materials and as such is a useful marker mineral. It has also been noted that in Pacific Ocean pelagic sediments, quartz occurs with a characteristic grain size distribution of 20-1 μm , ascribed to tropospheric wind transport. Subsequently it has been shown that most of this quartz is 10-1 μm in size, with a mode at 4 μm (Clayton et al., 1972), and is part of the insoluble fraction of tropospheric aerosolic dust (Syers et al., 1969; Jackson et al., 1973).

Based on particle size distribution and oxygen isotope composition, the presence of quartz from aerosolic dust has been established in the 5-2 μm size fractions of basaltic soils in Hawaii (Rex et al., 1969), Pacific Ocean pelagic sediments (Clayton et al., 1972) and loess-derived soils in the central and eastern United States (Syers et al., 1969). In the South Pacific region, quartz from both local and aerosolic sources in basaltic soils is suggested while mainly aerosolic quartz has been added to pelagic sediments (Mokma et al., 1972; Clayton et al., 1972; Stewart et al., 1977).

Quartz accumulation in pelagic sediments has not remained constant with time and variations appear to reflect climatic oscillations; high levels of quartz corresponding to cold periods, low levels corresponding

with warm periods (Bowles, 1975). A similar correlation was noted in a detailed investigation of the parent materials of a Typic Dystrandept in Taranaki, New Zealand (Stewart *et al.*, 1977). There appear to be two causative factors. Firstly, although similar modes of quartz transport operate during glacial and non-glacial conditions, an increased intensity and expansion of global wind systems, coupled with increased aridity during glacial periods, leads to transport of greater amounts of quartz globally (Kolla *et al.*, 1979). Secondly, it has been suggested that the formation of particles of silt size is largely restricted to glacial environments (Smalley, 1966; Smalley and Vita-Finzi, 1969; Vita-Finzi and Smalley, 1970). Near source this material is deposited as loess but it may also be transported downwind of large land-masses to be deposited in the marine environment (Bowles, 1975; Kolla *et al.*, 1979). The 10-1 μm sized particles are injected into the tropospheric wind system, mainly by cold fronts (Jackson *et al.*, 1973) and are transported and deposited globally in a wide range of soils and sediments (Rex and Goldberg, 1958; Syers *et al.*, 1969). Consequently, the variation in quartz content in accumulating sediments and soils will reflect to a degree the climatic variations since the time of parent material formation or marine sediment deposition. This is best recorded where the rates of accumulation are high, and the sampling intervals are close.

In this paper we present the results of an investigation of the quartz contents of four soils developed in andesitic ash, from Taranaki and of one soil developed in rhyolitic ash from the central North Island. The first four soils form a chronosequence developed on volcanic (lahar and tephra) surfaces, the ages of which have been determined by radiocarbon dating. The objective of this paper is to show the degree of correlation between aerosolic quartz accumulation and both the age of the soil parent materials and the age of sediment



 Present extent of >1m loess cover, southern North Island. Much of the rest of the region has a discontinuous loess cover <1m thick.

 Coastal dune sands of Holocene and Upper Pleistocene age.

Figure 6.1 Location map.

The dotted line represents the shoreline at c 18,000 years B.P.

in a marine core from the New Zealand region.

MATERIALS AND METHODS

Profiles from four soil series (the Burrell, Inglewood, Opuā, and Egmont) in Taranaki and one from the central North Island (Oruanui series) were selected on the basis of differing ages of the surfaces on which they formed. Details of the soil samples (in the order of soil series, subgroup, according to U.S. Soil Taxonomy, and subgroup, according to Leamy *et al.* (1980), are as follows:

Burrell Series: Typic Vitrandept, Typic Vitrudand. A soil developed on andesitic, pumiceous Burrell Lapilli, an eruptive from Mt Egmont dated by dendrochronology at 1655 A.D. (Druce, 1966).

Oruanui Series: Typic Vitrandept, Entic Vitrudand. A soil developed on rhyolitic Taupo Pumice Formation, an eruptive from the central North Island radiocarbon dated (NZ1548A) at $1,840 \pm 50$ years B.P.

Inglewood Series: Typic Vitrandept, Typic Hapludand. A soil developed on the andesitic, pumiceous Inglewood Tephra, radiocarbon dated (NZ3352B and NZ3353B) at between $5,140 \pm 150$ years B.P. and $4,030 \pm 110$ years B.P., respectively.

Opuā Series: Typic Vitrandept, Typic Hapludand. A soil developed on laharic breccia (Opuā Formation) radiocarbon dated (NZ1761C) at 7320 ± 110 years B.P.

Egmont Series: Typic Dystrandept, Typic Hapludand. A soil developed in andesitic "Egmont Ash" and dated by the presence near the base of the soil profile of the rhyolitic Aokautere Ash

(Stewart et al., 1977) an eruptive from the central North Island which has been radiocarbon dated (NZ1056) at $19,880 \pm 310$ years B.P.

A marine sediment core, P69, was obtained from a site at latitude $40^{\circ} 23' S$, longitude $177^{\circ} 59.8' E$, 110 km to the east of southern North Island. The age of the core sediment was determined from the presence of rhyolitic tephras from the central North Island which have been radiocarbon dated in terrestrial sequences. A more detailed stratigraphy and interpretation of the core data is to be published elsewhere.

Particle size fractions were separated by decantation and centrifugation, after removal of organic matter with H_2O_2 and free iron oxides with citrate-bicarbonate-dithionite (Jackson, 1956). Quartz was isolated by $Na_2S_2O_7$ fusion and H_2SiF_6 digestion and the purity of the isolates monitored by XRD (Syers et al., 1968; Sridhar et al., 1975).

RESULTS AND DISCUSSION

The quartz in all the soils examined occurs in the surficial material overlying the dated surfaces. No $5-2 \mu m$ quartz, representing aerosolic quartz, occurs in underlying andesitic or rhyolitic tephra and only trace amounts occur in the underlying laharic materials (Table 6.1). Quartz is largely restricted to $<125 \mu m$ in size and most occurs in the $<63 \mu m$ fraction (Table 6.1). A similar quartz particle size distribution was previously noted in soil of the Egmont series, and was attributed to the effects of an aeolian transport mechanism (Stewart et al., 1977).

The amount of quartz in the $<63 \mu m$ fraction of the Egmont soil was found to be greater in the lower, tephric loess unit than the upper,

TABLE 6.1 Quartz distribution in chronosequence soils

Soil series	Depth (cm)	Quartz content % of size fraction (μm)					Quartz in size fraction (μm) as % Total quartz				
		> 125	125-63	63-20	20-5	5-2	> 125	125-63	63-20	20-5	5-2
Burrell	0 - 10	0	0.003	0.11	0.86	0.41	0	1.5	57.6	36.4	4.5
Oruanui	0 - 15	-	tr*	tr*	0.90	1.06	-	tr*	tr*	66.7	33.3
Inglewood	0 - 15	0	0.16	2.00	2.40	2.15	0	3.1	41.7	43.1	12.1
	15 - 25	0	0.26	1.10	1.20	0.08	0	5.0	51.9	42.4	0.7
Opua	0 - 10	0	0.1	3.3	1.6	0.91	0	0.7	48.0	42.7	8.6
	10 - 20	0	1.1	4.7	1.5	0.83	0	10.6	59.7	23.2	6.4
	20 - 30	0	0.2	4.1	1.3	0.96	0	9.4	40.9	40.0	9.7
	30 - 40	0	0.1	3.5	1.3	0.91	0	2.2	64.7	25.5	7.6
Egmont tephra (representative sample)	45 - 55	2	5.8	13.4	11.1	0.1	4.2	8.6	22.9	63.2	1.1
Egmont tephric loess (representative sample)	115 - 125	0.69	0.59	12.22	4.24	0.22	3.8	3.3	68.1	23.6	1.2
Pungarehu Formation	> 40					tr					

* H₂SiF₆ residue is mainly cristobalite.

tephra unit (Stewart et al., 1977). It has been postulated that this was due to the presence of a land bridge extending from northwest Nelson to western Taranaki during Otiran time (Lewis and Eade, 1974), providing a quartzose source area to the west of Taranaki. The subsequent rapid post-glacial rise in sea-level at circa 11,000 years B.P. (Cullen, 1967) covered this source and caused the rapid decline in quartz accumulation in the upper part of the Egmont soil. The remaining soils have all accumulated on surfaces less than 11,000 years old and their $<10\ \mu\text{m}$ quartz contents are similar to these previously obtained for the Egmont loam (Stewart et al., 1977). In one soil from the Oruanui series, there is only a trace of quartz in the coarse silt ($63\text{--}20\ \mu\text{m}$) fraction, most of the quartz lying in the $< 20\ \mu\text{m}$ fraction (Table 6.1). This paucity of coarse silt quartz is indicative of the lack of quartzose loess in the region of the soil site in the last 1,800 years, and any quartz present is therefore probably of tropospheric origin. Quartz crystals in the $>125\ \mu\text{m}$ size fraction are predominantly phenocrysts from the rhyolitic parent material.

The accumulation of aerosolic quartz with time, as shown by the quartz contents of soils in this chronosequence in Taranaki, is relatively uniform from 7,000 years B.P. to the present, in contrast to a higher accumulation rate prior to 7,000 years B.P. (Fig. 6.2). These data indicate that the change in aerosolic quartz accumulation from glacial to post-glacial times was complete by circa 7,000 years B.P. A higher rate of quartz accumulation occurs in the Egmont soil prior to 11,000 years B.P. but the soil data do not allow resolution of the commencement of post-glacial aerosolic quartz accumulation rates.

Aerosolic quartz accumulation in the Oruanui series soil, from the central North Island, is consistent with the amount of quartz predicted from the Taranaki chronosequence data over the last circa 1,800 years

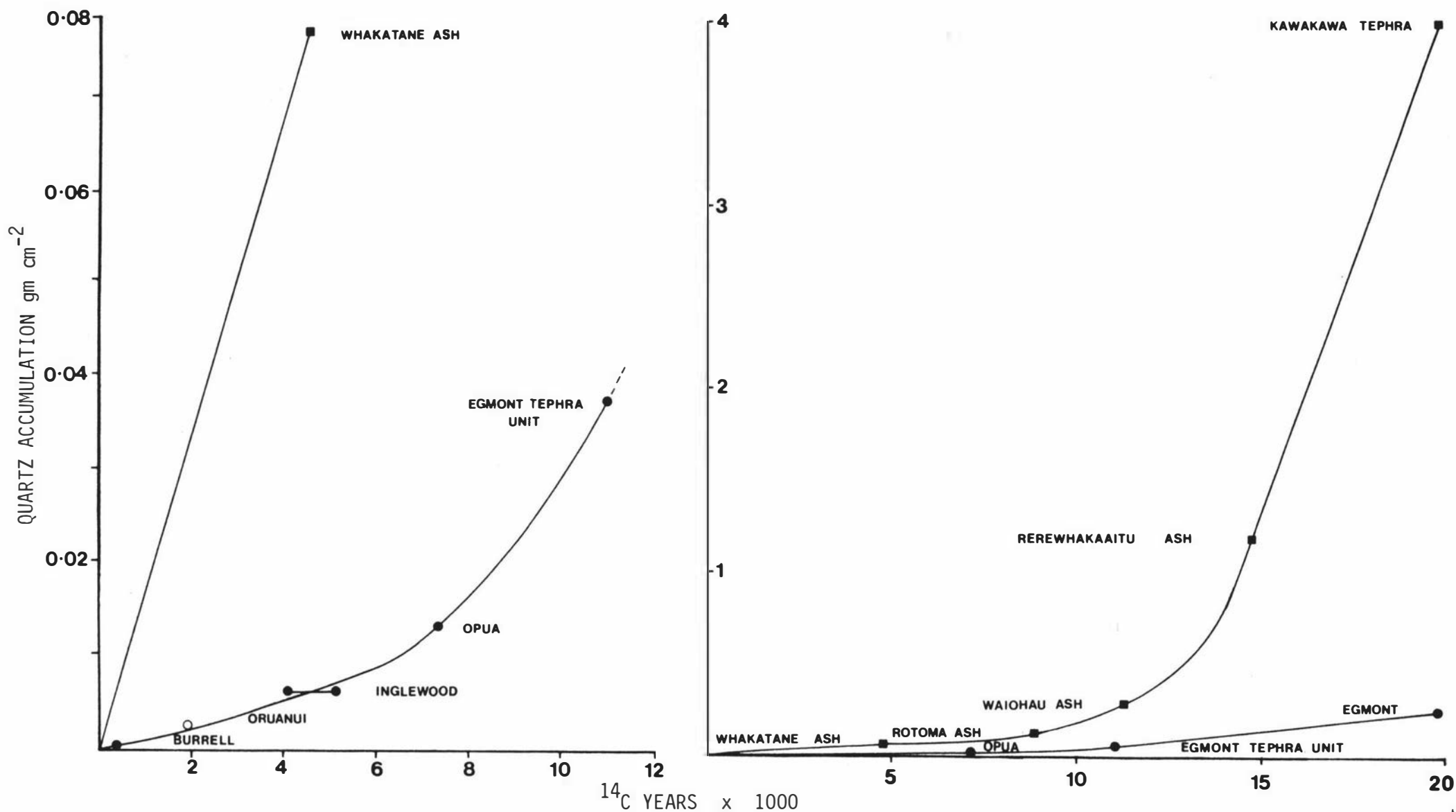


Figure 6.2 Quartz accumulation versus ¹⁴C age of tephras from Taranaki (closed circles), central North Island (open circle) and Core P69 (closed squares).

(Figure 6.2). The consistency of the data suggests that, within a general region in which rainfall regimes are similar, quartz accumulation rates can give an approximation of the relative ages of accumulating surficial materials. The effects of rainfall were not studied here but elsewhere have been shown to influence aerosolic quartz accumulation (Jackson *et al.*, 1971). The sites used in this study have similar rainfall and this has minimised variations caused by this factor.

The aerosolic quartz accumulation curve derived from the soil data has been compared with that recorded in the marine core (Fig. 6.2). The accumulation in the core is clearly much higher than that in the North Island soils over the same time period. This suggests either a real difference in globally derived tropospheric, aerosolic quartz or a large additional component of quartz from another, possibly local source. Because the core and the soils are from similar latitudes, it is unlikely that there would be so large a difference in the globally derived aerosolic quartz flux. The Taranaki region lies on the western side of the North Island while the core site lies to the east of the southern North Island (Fig. 6.1). Because the prevailing wind direction is westerly, any dust component of local origin is most likely to accumulate downwind, i.e., to the east, of any landmass. There are several large river flood plains in the southern North Island which have been the source of quartzose loess during glacial periods of the late Quaternary (Cowie, 1964; Milne, 1973). These areas are considered to be the most likely source of a local dust component carried downwind into the ocean sediments. In contrast, the soils of the North Island would record mainly the globally derived aerosolic dust accumulation with perhaps very local components from the relatively small quartzose source area to the west of the landmass (Fig. 6.1). Quartz accumulation in the Egmont soil for example, after the circa 11,000 years B.P. sea

level rise is considered to be almost entirely tropospheric in origin.

Additions of quartz from the southern North Island, transported by the prevailing westerly winds, are therefore considered to be the cause of the marked difference in aerosolic quartz accumulation between the soils and the marine core. This local effect on the pattern of distribution of aerosolic dust is additional to, and much larger than, the effects of variations in rainfall recorded in Hawaii by Jackson *et al.* (1971).

A rate of quartz accumulation approaching that of the present day is suggested from circa 9,000 years B.P. from the marine core and circa 11,000-7,000 years B.P. from the soil data (Fig. 6.2). In addition, the marine core data indicate that the decrease from glacial rates of quartz accumulation began at circa 14,700 years B.P. but lack of stratigraphic control in the soil data over this period has meant that no similar change in quartz accumulation rates has yet been observed. However, the limited data from the soils do indicate that there is a synchronicity of climate changes, as shown by variation in quartz accumulation, preserved in both terrestrial and marine environments.

CONCLUSIONS

1. The occurrence of only trace amounts of quartz in tephras and lahars underlying soils selected in this study indicate that much of the quartz content of the selected soils has accumulated in the surficial material in which the upper soil horizons developed. Grain size distribution of the quartz is consistent with an aeolian origin. In the Oruanui series soil, most of the quartz in the $<125\text{ }\mu\text{m}$ size fraction is $<20\text{ }\mu\text{m}$ in size, suggesting that the quartz is largely aerosolic dust. This is consistent with

the soil site being in a region where no quartz loess has accumulated post 1,800 years B.P.

2. Large amounts of aerosolic quartz were deposited in accumulating soil profiles prior to circa 11,000 years B.P., with a change to lower accumulation rates ending at circa 7,000 years B.P. Data from the marine core suggest that the onset of change from high glacial accumulation rates occurred at circa 14,700 years B.P. The timing of climate changes, as indicated by the variations in quartz accumulation rates, is similar in the soils and marine sediments, within the resolution of the available data.
3. Aerosolic quartz, as represented by the 5-2 μm size fraction, shows a systematic increase in abundance with increasing age of surfaces on which the soils are developed. This systematic increase indicates that, within a region, the aerosolic quartz content can be used to estimate relative ages of accumulating material.
4. A much higher rate of accumulation of aerosolic quartz in the marine sediment core is due to large additions of a locally derived quartz component, in addition to tropospheric, aerosolic dust. It is proposed that the source areas for this local component were the river flood plains of the southern North Island, which lie upwind of the core site. The quartzose source area for Taranaki soils of this age was much smaller and was inundated by the post-glacial rise in sea level.
5. The local effect of the southern North Island quartz source areas on quartz accumulation is additional to, and much greater than,

the effect of rainfall variations which have been previously noted in the literature. This suggests that attributing all 10-1 μm quartz in soils and sediments to an aerosolic dust origin should be approached cautiously, unless the absence of any local influence can be unequivocally demonstrated.

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CHAPTER 7

CHAPTER 7

TEPHROSTRATIGRAPHY AND PALEOCLIMATIC INTERPRETATION OF
CORE P69, OMAKERE DEPRESSION, NORTH ISLAND, NEW ZEALAND

INTRODUCTION

Inorganic components in marine sediments may record:

- (i) global climatic change, as indicated by the size, abundance, surface textures, and mineralogical composition of terrigenous materials;
- (ii) global dust deposition related to latitudinal atmospheric circulation zones, and
- (iii) tephra deposited down wind of active volcanoes providing unique marker horizons.

One of the principal inorganic components of hemipelagic and abyssal sediments is quartz. Quartz occurs predominantly in the <20- μ m size fraction of these sediments, with a substantial proportion being in the 1 - 10- μ m size fraction (Rex and Goldberg, 1958; 1962; Arrhenius, 1959; Rex et al., 1969; Mokma et al., 1972; Clayton et al., 1972). Quartz in this size range is thought to have been formed largely by glacial grinding (Smalley, 1966; Smalley and Vita-Finzi, 1968) and has subsequently been transported from terrestrial deposits to the oceans by tropospheric wind systems as a component of aerosolic dust (Rex and Goldberg, 1968; Windom, 1969; Clayton et al., 1972).

In sediment cores from the eastern equatorial Atlantic, a strong correlation has been established between increased amounts of largely silt-sized quartz and the colder periods of the Quaternary (Bowles, 1975).

A similar relationship has been found between the occurrence of dust in ice cores from Antarctica in stratigraphic positions correlated with major global glaciations (Thompson et al., 1975).

Mineralogical studies of deep sea sediments have tended in the past to deal mainly with the existing mineral distribution and how it relates to current climatic zones (Biscaye, 1965; Griffin and Goldberg, 1970; Piper and Slatt, 1977). The distribution of minerals with depth, and therefore time, has been the subject of more recent investigations (Bowles, 1975; Diester-Haass and Chamley, 1978; Kolla et al., 1979; Thiede, 1979). Of the principal sediment components, clay mineral production, transport and deposition does not appear to have been greatly affected by climatic changes in the Atlantic (Murray, 1970; Bowles, 1975; Piper and Slatt, 1977) but quartz contents vary in both areal distribution and depth, indicative of a climate-controlled origin (Biscaye, 1965; Bowles, 1975). Quartz in pelagic sediments off equatorial West Africa show a decrease in mean grain size and concentration with increasing distance from the African coast, strongly suggesting they have originated from the African continent (Biscaye, 1965; Delaney et al., 1967; Parkin et al., 1970; Beltagy et al., 1972). The highest concentrations of quartz are thought to be due largely, but not entirely, to increased intensity of the trade winds during cold periods (Bowles, 1975). In the Pacific lesser amounts of terrigenous material have been supplied to pelagic sediments than in the Atlantic (Hayes and Peruzza, 1972) and it appears that most of the quartz in Pacific deep-sea sediments is a result of aerosolic dust transport and deposition (Rex and Goldberg, 1958; Rex et al., 1969; Clayton et al., 1972). These dusts have been recorded from a wide range of environments, including glacial ice (Thompson et al., 1975), permanent snowfields (Windom, 1969), and soils (Rex et al., 1969; Mokma et al., 1972).

Organic components of marine sediments may also be particularly useful for determining paleoclimatic information. Deep sea organisms are insulated from conditions in the atmosphere by the overlying column of water. In contrast, surface-dwelling organisms (especially plankton) are sensitive to climatic change because their environment is controlled by the physical conditions in the atmosphere (McManus, 1970). Thus the planktonic organic detritus in deep sea sediments can be a good indicator of climatic change. The carbonate and silica tests of planktonic organisms make up a significant proportion of deep-sea sediments and may therefore be used to determine the productivity of ocean surface waters (Ellis and Moore, 1973; Molina-Cruz, 1977; Diester-Haass and Schrader, 1979). By measuring variations in carbonate and biogenic silica with depth, fluctuations in biological productivity may be determined, which are a record of environmental changes in surface waters with time (Ericson et al., 1961; Hays et al., 1969; Duncan et al., 1970; Hays and Perruzza, 1972; Sancetta et al., 1972; Prell et al., 1980).

The productivity of organisms forming carbonate tests is primarily a function of nutrient content, particularly phosphorus, in surface waters (Broeker, 1971; Molina-Cruz, 1977). During glacial periods the intensified wind systems and changed ocean current circulation patterns in middle to low latitudes resulted in a shift towards the equator of upwelling of cold, nutrient-rich bottom waters (CLIMAP, 1976). This resulted in enhanced surface water productivity at lower latitudes. Thus in cold periods, ocean sediments in lower and middle latitudes contain more carbonate than sediments deposited in warm periods (Adelseck and Anderson, 1978). This is classically shown in deep-sea sediments of the northern Pacific Ocean (Arrhenius, 1952), but in the Atlantic ocean

the situation is more complex. Unlike much of the Pacific, terrigenous sediment is a significant component in Atlantic sediments (Diester-Haass, 1976; Kolla et al., 1979). This leads to a dilution of the carbonate component and, because detrital input is greater during glacial periods, there is a resultant decrease in the concentration of carbonate in the sediments (Hays and Perruzza, 1972). Other factors that affect the biogenic carbonate and silica content of deep-sea sediments include dissolution of carbonate during settling below the carbonate compensation level (Bramlette, 1951), dissolution of both silica and carbonate during and after deposition and dilution by non-biogenic minerals (Thunell, 1976; Adelseck and Anderson, 1978; Volat et al., 1980).

Investigations of paleoclimatic variations in deep-sea sediments have largely been concerned with gross climatic changes from the Holocene back through the Pleistocene and into Tertiary times. The most detailed stratigraphic records are currently correlated on the basis of oxygen isotope variations in planktonic foraminifera and geomagnetic reversals (Emiliani, 1966; Shackleton and Opdyke, 1973; 1976). However, more detailed time control is difficult when intervals of time such as the Holocene are being examined. Radioisotope dating is of some use but diffusion by either bioturbation or redeposition limit the usefulness of ^{14}C and U/Th dating (Bowen, 1966; Berger and Johnson, 1978; Peng et al., 1979; Berger and Killingley, 1982). A more useful time stratigraphic marker is the occurrence of a unique chrono-horizon, such as a layer of tephra, deposited over a relatively short time period. In the New Zealand region, tephra layers are recorded in deep sea sediments and have been correlated with radiocarbon dated tephras in onshore sequences, allowing determination of sedimentation rates (Lewis and Kohn, 1973; Kohn and Glasby, 1978). This knowledge can allow

resolution of the timing of climatic events which should best be determined in areas with relatively high hemipelagic sedimentation, numerous interbedded and dated tephras, and minimal turbidity current erosion or deposition.

The purpose of this study was to examine the stratigraphy of a hemipelagic sediment core off the east coast of the southern North Island of New Zealand in which a sequence of Holocene and Upper Pleistocene rhyolitic tephras is preserved, so as to establish the nature of the quantitative relationship between aerosolic quartz accumulation and paleoclimatic variations. Most of the rhyolitic tephras erupted from the central North Island that are preserved in the core have been radiocarbon dated on land back to circa 40,000 years B.P. (Pullar and Heine, 1971). Although the tephrochronology on land is well established, the accumulation of surficial materials in the terrestrial environment is rarely continuous and is usually subject to erosion. The marine environment is therefore likely to have preserved a more complete sedimentary record over a similar time period. In order to more closely define established paleoclimatic fluctuations in the New Zealand region with time (ages determined by the presence of radiocarbon dated tephras), variations in total carbonate and biogenic silica were also determined.

MATERIALS AND METHODS

Core P69 was collected on 24 March, 1977, from the R.V. Tangaroa during New Zealand Oceanographic Institute (N.Z.O.I.) cruise no. 1059 - "Northland Plateau Sediments". The station was located at $40^{\circ} 23' S$, $177^{\circ} 59.8' E$, in the Omakere Depression to the east of the Wairarapa coast, North Island (Fig. 7.1). A 6.63 m core was recovered by a double length piston corer from 2195 m depth. The core was cut into four lengths

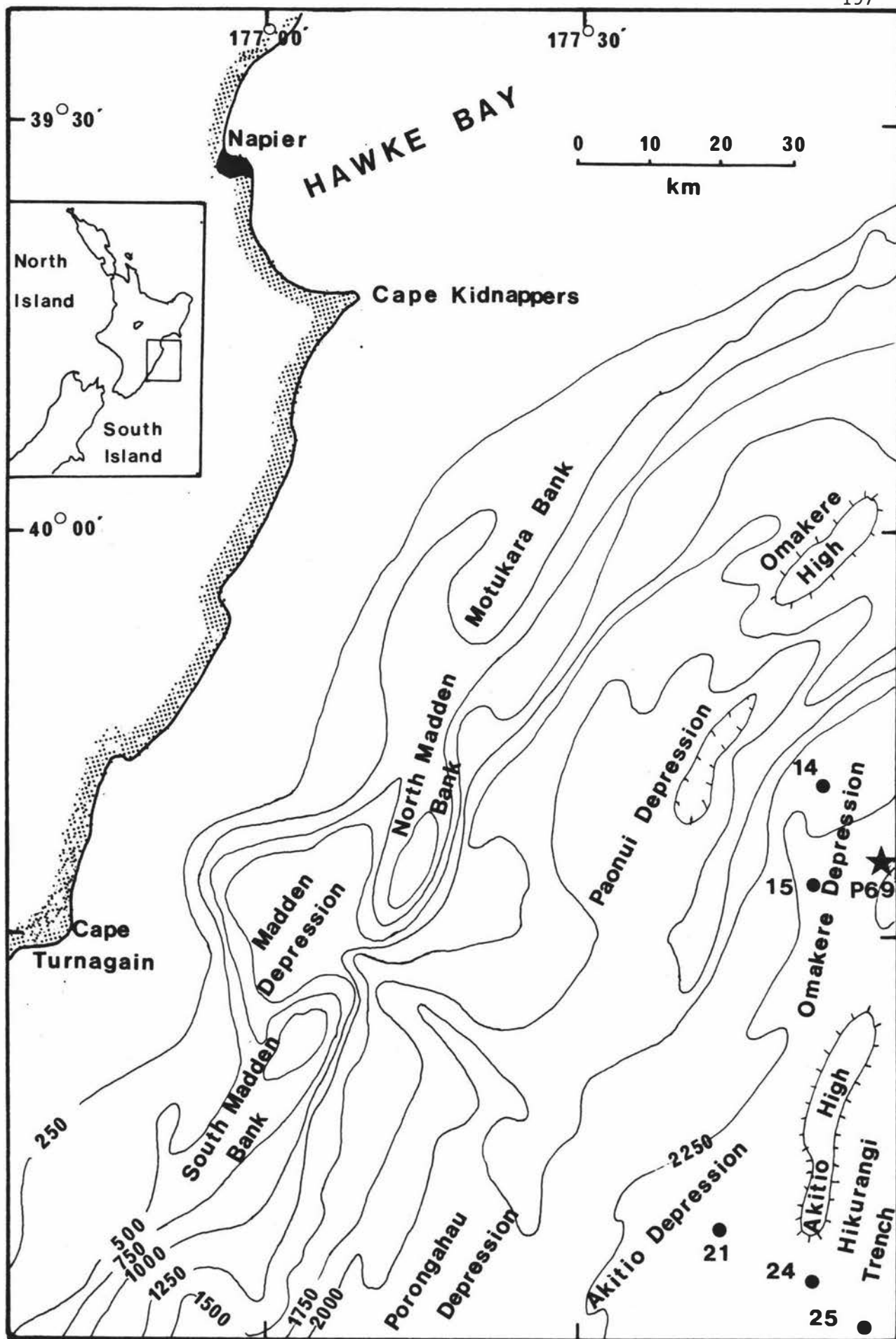


Figure 7.1 Map showing the location of core P69. Numbers 14, 15, 21 22 and 25 are cores investigated by Lewis and Kohn (1973). Depths shown are in metres.

and each length split longitudinally on board. One half of each length is retained by N.Z.O.I. for reference and the other half has been sampled for mineralogical and granulometric analysis, the results of which are the subject of this paper.

In the laboratory, the halved core lengths were split into two further longitudinal halves, one of these being cut into 0.10-m length samples. These samples were homogenised and subsampled for further work. Macroscopically visible tephras were sampled separately. Dry bulk density measurements were determined on all samples.

For mineralogical analysis and grain-size determination, samples were treated with H_2O_2 to remove organic matter. Grain size determinations were made on NH_4OH -dispersed samples by a combination of sedimentation and centrifugation (Jackson, 1956). Sand fractions were determined by dry sieving.

Quartz in selected size fractions was isolated using pyrosulphate fusion and fluorsilicic acid digestion (Syers et al., 1968; Sridhar et al., 1975). The oxygen isotope ratios in quartz from selected size fractions in selected samples were determined by the methods of Clayton and Mayeda (1963).

Mineral components in the sand fractions ($>63\ \mu\text{m}$) were determined by counting grain mounts (average 900 grains per mount). Mafic assemblages of visible tephras were determined by counting grain mounts (average 300 grains) of the heavy fraction after bromoform separation.

Total carbonate was determined by reaction with HCl and back titration with NaOH (van der Linden, 1968). Biogenic silica was determined by the XRD method of Ellis and Moore (1973). Diatomite was used as a standard to construct a cristobalite standard curve, using a calcite matrix. A known amount of CaCO_3 was added to the carbonate-free samples as an internal standard.

SEDIMENT CORE DESCRIPTION

The core was of a predominantly uniform texture, a clayey medium silt. However, sandy textures were encountered in proximity to tephras and, rarely in thin, fine sandy horizons comprising mainly quartzofeldspathic sediment. Colour, as determined in the freshly opened core, varied from moderately olive brown (5Y 4/4) in the uppermost 0.4 m through dark greenish grey (5GY 4/1), to greyish olive (10Y 4/2) below 1.5 m. No visible layering was evident in the sediment and there was evidence throughout the core of bioturbation by burrowing organisms. In the uppermost 0.3 m of the core, burrows were infilled with sediment slurry. This infilling was probably a result of slurring of the water-rich surface sediment during core collection and consequent infilling of open burrows near the sediment surface.

Very little evidence of turbidite deposition was visible in the core. At three levels, thin circa 50 mm zones containing non-tephric sandy sediment occur as small lenses which probably represent bioturbated thin distal turbidites. However, together these zones represent a negligible (< 3%) volume of the core.

Rhyolitic tephras are marked by discontinuous lenses of white to grey tephra, with little mixing of the surrounding sediment. The lensoid nature is thought to be due to the disruption of original ash layers by bioturbation (Kohn and Glasby, 1978). Some of the thin, fine-grained tephras are present only as infillings of fine (1 - 2 mm diameter) burrows over a 10 - 30 mm thick sediment interval. Additionally, there are intervals in which concentrations of 'pinhead' sized pumice occur but which cannot be identified as primary tephra.

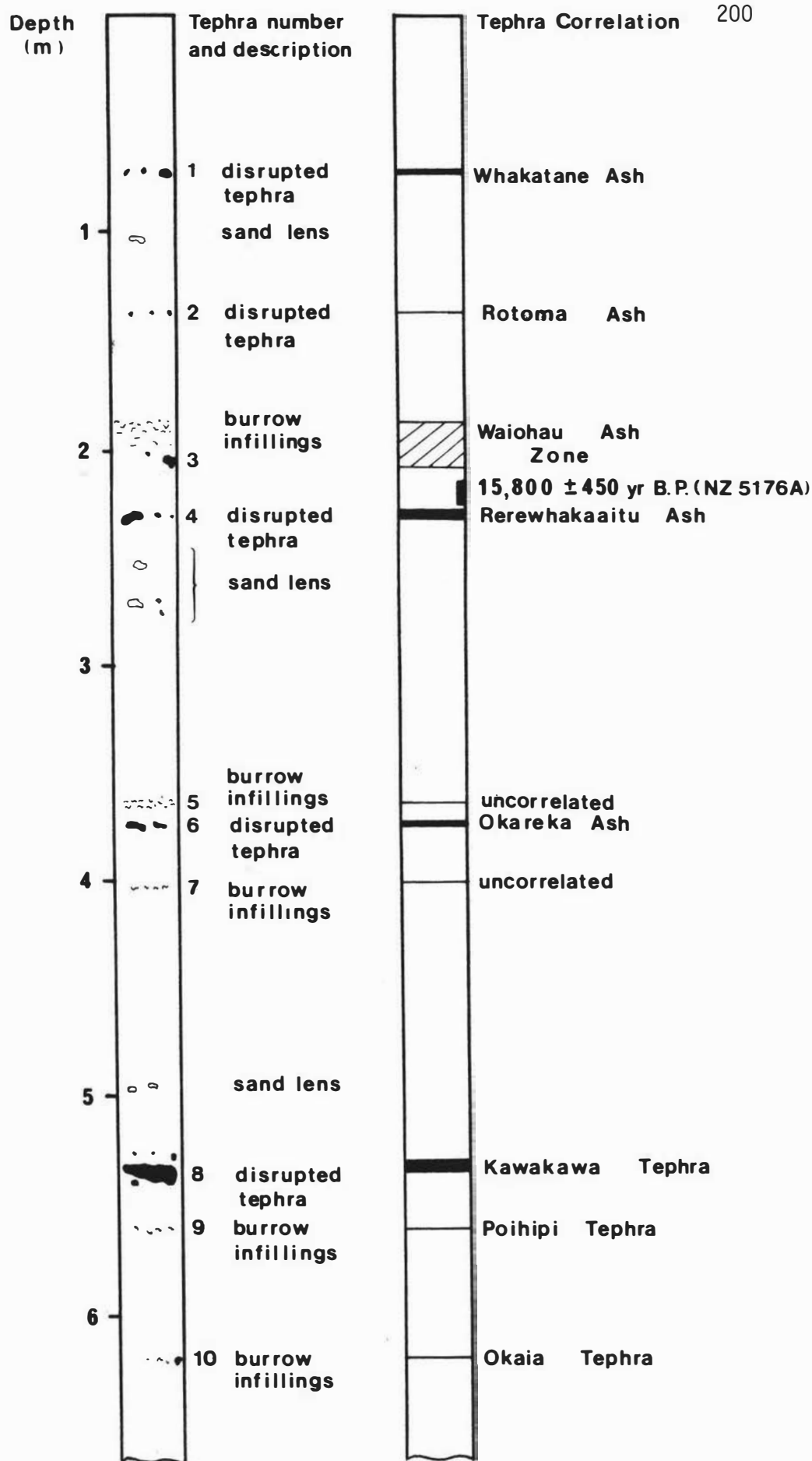


Figure 7.2 Appearance and stratigraphy of tephras in core P69. Radiocarbon date NZ5176A was determined from total carbonate in the sediment. Closed patches = tephra, open patches = quartzose sand.

TEPHRA IDENTIFICATION

The 500-250 μm ferromagnesian minerals in rhyolitic tephras erupted over the last 40,000 years from the central North Island (Table 7.1) can be divided into three dominant mineral assemblages (Ewart, 1966; Kohn, 1973; Kohn and Glasby, 1978):

- 1) hypersthene + augite
- 2) hypersthene + calcic hornblende + cummingtonite
- 3) biotite + hypersthene $\pm$ calcic hornblende

The ferromagnesian assemblages in Holocene tephras erupted from the Taupo Volcanic Centre (Taupo Subgroup - Healy, 1964) are of type 1, with additional rare biotite, amphibole, and olivine (Ewart, 1966). In contrast, the tephras from the Rotorua and Okataina Volcanic Centres (Healy, 1964) have predominantly assemblages 2 and 3 (Topping and Kohn, 1973; Kohn and Glasby, 1978). The most useful minerals for tephra identification are biotite, when it comprises more than 15% of the ferromagnesian assemblage, and the presence of cummingtonite (Kohn and Glasby, 1978).

Tephras 1 and 2 in core P69 (Fig. 7.2) contain significant cummingtonite (Table 7.2). Of the central North Island tephras containing cummingtonite, the Rotoehu Ash ferromagnesian assemblage is dominated by this mineral while Whakatane Ash and Rotoma Ash contain lesser amounts (Kohn, 1970). The low proportions of cummingtonite in tephras 1 and 2 and their relatively close occurrence high in the upper part of the core identifies them as Whakatane Ash and Rotoma Ash, respectively. These tephras have also been identified in sediment cores from the Bay of Plenty on this basis (Kohn and Glasby, 1978).

Tephra 8 is the largest tephra preserved in the core (Fig. 7.2). Its ferromagnesian mineral assemblage of hypersthene + hornblende + augite,

Table 7.1

Tephra Stratigraphy in the Taupo Volcanic Zone and Core P69, <25,000 years B.P.

Chronostratigraphic Units	Taupo and Maroa Volcanic Centres	Okataina and Rotorua Volcanic Centres	Age (^{14}C years B.P.)	Radiocarbon Number	Sedimentation Rate Ages, P69
Aranuian		Kaharoa Ash	656 $\pm$ 57	NZ4804A	
			780 $\pm$ 58	NZ4993A	
			937 $\pm$ 77	NZ5087A	
	Taupo Pumice		1840 $\pm$ 50	NZ1548A	
	Mapara Ash		2010 $\pm$ 60	NZ1068A	
			2150 $\pm$ 48	NZ1069A	
	Whakaipo Tephra		2670 $\pm$ 50	NZ1070A	
			2730 $\pm$ 70	NZ1071A	
	Waimihia Ash		3440 $\pm$ 70	NZ2A	
		Whakatane Ash	4600 $\pm$ 90	NZ3948A	
			4640 $\pm$ 90	NZ3949A	
	Hinemaiaia Ash		4650 $\pm$ 80	NZ4574A	
	Motutere Ash		5370 $\pm$ 90	NZ4846A	
		Mamaku Ash	c. 8000*		
	Opepe Tephra		8850 $\pm$ 1000	NZ185A	
		Rotoma Ash	9080 $\pm$ 100	NZ1943A	
			9120 $\pm$ 30	NZ1945A	
	Poronui Tephra		c. 9700*		
	Paparetu Tephra		9780 $\pm$ 160	NZ1372A	
	Karapiti Tephra		9910 $\pm$ 130	NZ4847A	
		Waiohau Ash	11250 $\pm$ 200	NZ568A	
		Rotorua Ash	13450 $\pm$ 250	NZ1615A	
		Rerewhakaaitu Ash	14700 $\pm$ 200	NZ716A	

Table 7.1 (continued)

Otiran	Tephra 5				16,900
		Okareka Ash	<u>c.</u> 17000*		17,100
	Tephra 7				17,600
		Te Rere Ash	<u>c.</u> 18000		19,100
	Kawakawa Tephra		19850 ± 310	NZ1056A	
	Poihipi Tephra		< 25000*		20,300
	Okaia Tephra		<u>c.</u> 25000*		21,200

*Estimated ages from Pullar (1980).

with a hypersthene:hornblende ratio of greater than 3:1 (Howorth et al., 1980), its size and its stratigraphic position identify this tephra as the Kawakawa Tephra Formation (Vucetich and Howorth, 1976a).

Of the known tephras erupted from the central North Island between circa 9000 years B.P. (Rotoma Ash) and circa 20,000 years B.P. (Kawakawa Tephra Formation), four contain significant amounts of biotite in their ferromagnesian mineral assemblages. These are the Rotorua Ash, Puketarata Ash, Rerewhakaaitu Ash, and Okareka Ash. Except for Puketarata Ash, an eruption from the Mairoa Volcanic Centre of limited distribution (Lloyd, 1972), all the tephras were erupted from the Okataina Volcanic Centre (Rotorua Subgroup). Rerewhakaaitu Ash and Puketarata Ash contain abundant (35 - 80%) biotite, whilst Rotorua Ash and Okareka Ash contain lesser (10 - 20%) amounts (Kohn and Glasby, 1978). Only tephra 4 (Fig. 7.2) in core P69 contains abundant biotite and is therefore correlated with the Rerewhakaaitu Ash.

Tephra 6 lies stratigraphically below the Rerewhakaaitu Ash in the core (Fig. 7.2) and its ferromagnesian mineral assemblage contains more than 15% biotite (Table 7.1). On this basis tephra 6 is correlated with the only known biotite-bearing tephra of this general age, the Okareka Ash (Table 7.1).

Tephra 3 (Fig. 7.2) has a ferromagnesian mineral assemblage of predominantly hypersthene with traces of hornblende and augite (Table 7.2). This assemblage is not distinctive and can be found in tephras of either the Taupo or Rotorua Subgroups (Topping and Kohn, 1973). However, no widespread tephra is known to have erupted from the Taupo Volcanic Centre which would give rise to a tephra in this stratigraphic position in the core (Vucetich and Pullar, 1973). Tephra 3 is therefore correlated with Waiohau Ash, from the Okataina Volcanic Centre. The ferromagnesian mineral assemblage of tephra 3 is compatible with that described for

Table 7.2 Ferromagnesian mineral assemblages of tephras from core P69
shown as % of total ferromagnesian assemblage.

Tephra	hypersthene	clinopyroxene	hornblende	cummingtonite	biotite
1. Whakatane Ash	68	2	15	15	-
2. Rotoma Ash	78	5	5	12	-
3. Waiohau Ash	93	5	2	-	-
4. Rerewhakaaitu Ash	26	4	15	-	55
5.	A	C	C	-	-
6. Okareka Ash	28	4	44	-	24
7.	A	C	C	-	-
8. Kawakawa Tephra	79	-	21	-	-
9. Poihipi Tephra	A	C	C	-	-
10. Okaia Tephra	A	C	C	-	-

Where insufficient sample could be obtained for analysis, relative abundances were estimated according to:

A >50%
a 30 - 49%
C 10 - 29%
c 5 - 9%
S 1 - 4%
R > 1%

Waiohau Ash (Cole, 1970).

Tephra 3 occurs in the core as a 30 - 40 mm block or lens of air fall tephra (Fig. 7.2). However, a large abundance peak in rhyolitic glass content in both 63 - 20- μ m and >63- μ m size fractions is located some 0.25 - 0.30 m above the tephra block, rather than in the same stratigraphic position (Figs. 7.2 and 7.3). It is probable that the block of tephra is infilling a burrow and that the true stratigraphic position of Waiohau Ash in the core is more accurately shown by the position of the peaks in rhyolitic glass abundance. The sedimentation rate calculated for the Rotoma Ash - Waiohau Ash sediment interval based on this assumption is more consistent with the post-Rotoma Ash sedimentation rate than the rate calculated assuming that the block of tephra marks the stratigraphic position of Waiohau Ash (Fig. 7.5). If the age of the Waiohau Ash is interpolated from the sedimentation rate calculated between the Rotoma Ash and the Rerewakaaaitu Ash, the peaks in rhyolitic glass abundance are more consistent with known ages of the Waiohau Ash than the age determined from the position of the block of tephra (Fig. 7.5). The position of the rhyolitic glass abundance peaks are therefore interpreted as showing the true stratigraphic position of Waiohau Ash in core P69.

There are fewer rhyolitic tephras recorded in terrestrial sequences between 25 - 15,000 years B.P. compared with the numerous rhyolitic tephras preserved in Aranuiian time. Characteristically, Otiran-age tephras are associated with tephric loess deposits which indicate considerable wind erosion and redeposition during the cold, dry Otiran climate (Cowie and Milne, 1973; Pullar and Kennedy, 1978). In terrestrial sequences it is the larger tephras that will tend to be preserved because the smaller tephras, particularly in distal areas, tend to be disrupted by soil-forming and erosional processes. Such erosion

is shown by the widespread occurrence of sedimentation breaks (unconformities) in terrestrial sequences at this time (Topping and Kohn, 1973; Vucetich and Howorth, 1976). In contrast, marine sedimentation in core P69 appears to have been continuous from circa 14,700 years B.P. to the base of the core and is more likely to contain a complete stratigraphic record of distal tephras.

In the core only Okareka Ash (tephra 6, Fig. 7.2) has been identified, as a visible tephra, from the Okataina Volcanic Centre during late Otiran time, consistent with it being the most significant eruption from Okataina Volcanic Centre of this general age. Two further small tephras occur in the core between the Rerewhakaaitu Ash and Kawakawa Tephra. Tephra 5 (Fig. 7.2) lies just above Okareka Ash and has a ferromagnesian assemblage of hypersthene + augite + hornblende. The relatively high augite content may indicate Taupo Sub-group affinities but may also reflect contamination with andesitic ash. No correlation can be made with any known tephra as none have been recorded of this general age (Table 7.1). Tephra 7 is stratigraphically below the Okareka Ash (Fig. 7.2) and its ferromagnesian assemblage of hypersthene + hornblende + augite also suggests a Taupo Volcanic Centre origin. Only Te Rere Ash, from the Okataina Volcanic Centre, is recorded lying between Okareka Ash and Kawakawa Tephra (Pullar, 1980) and no tephras are recorded from Taupo Volcanic Centre at this time. However, correlation of tephra 7 with Te Rere Ash is unlikely as Te Rere Ash lies immediately above or closer to Kawakawa Tephra than Okareka Ash in terrestrial sequences whereas tephra 7 lies close beneath Okareka Ash and well above Kawakawa Tephra in the core (Fig. 7.2). No positive identification of tephra 7 can be made at this time.

Small patches of tephra appear 0.10 - 0.15 m above Kawakawa Tephra but the ferromagnesian assemblage of hypersthene + augite + hornblende

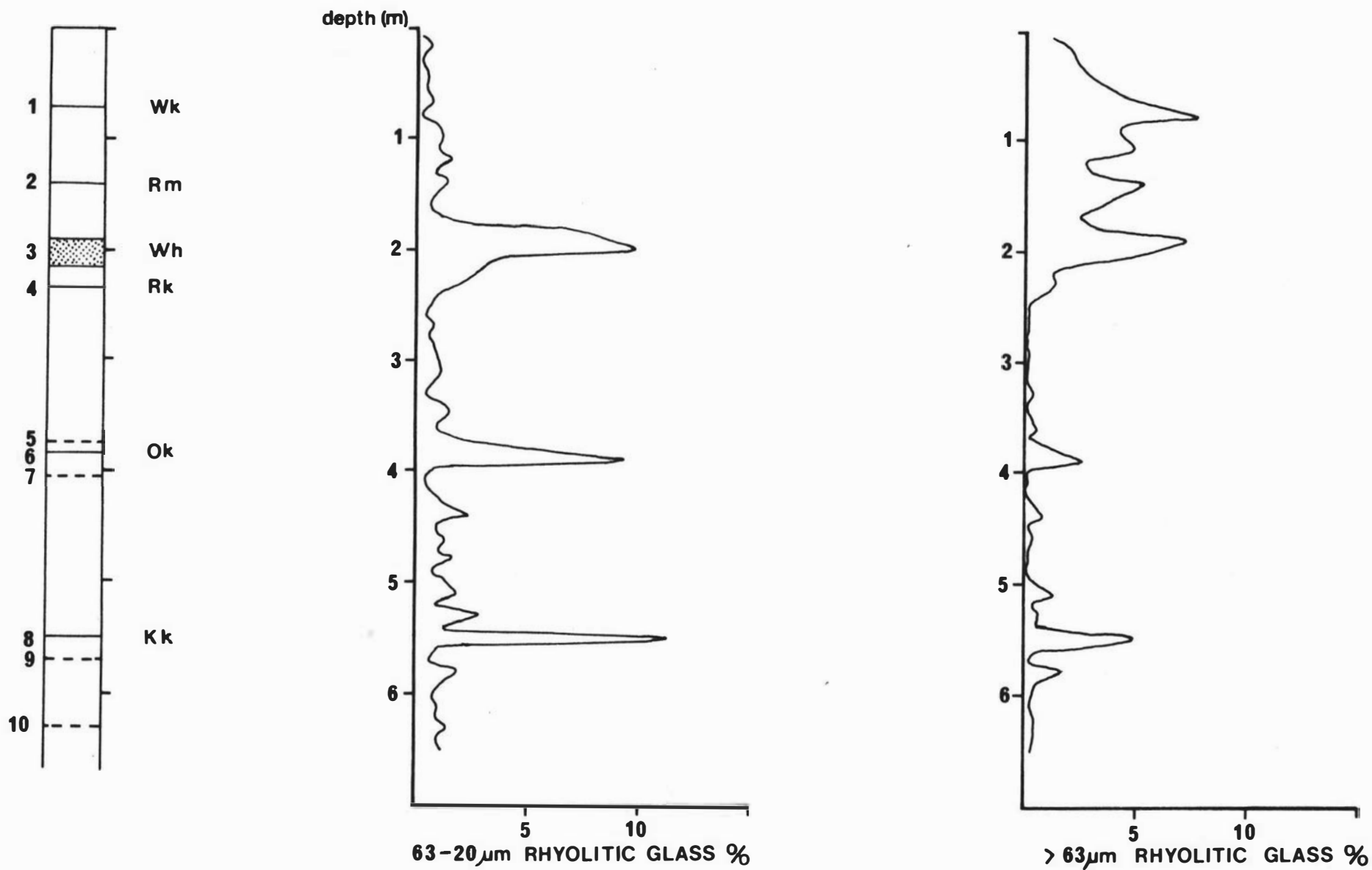


Figure 7.3 Abundance of rhyolitic glass in the $>63\ \mu\text{m}$ and $63\text{--}20\ \mu\text{m}$ size fractions, expressed as % of total sediment. See Fig. 7.6 for tephra symbols.

is consistent with that of Kawakawa Tephra. This material is therefore interpreted as redeposited Kawakawa Tephra.

Two tephra occur between the Kawakawa Tephra and the base of the core (tephras 9 and 10, Fig. 7.2). The two youngest pre-Kawakawa Tephra Formation tephra are the Poihipi Tephra Formation and the Okaia Tephra Formation (Vucetich and Howorth, 1976). The estimated age of the Okaia Tephra is circa 25,000 years B.P. (Pullar, 1980) with the younger Poihipi Tephra overlying it and separated in turn from the overlying Kawakawa Tephra by an erosion break on tephric loess (Vucetich and Howorth, 1976). Tephra 9 is therefore correlated with Poihipi Tephra and tephra 10 with Okaia Tephra, based on stratigraphic occurrence. The ferromagnesian assemblage of both tephra 9 and 10 was difficult to determine as only traces of both tephra were visible. However, in both cases hypersthene and augite appear to be characteristic, consistent with a Taupo Volcanic Centre origin.

As a check on the above stratigraphy, a sample of sediment was submitted for radiocarbon dating of the total carbonate content. The sample was selected from immediately above Rerewhakaaitu Ash and is dated (NZ5176A) at $15,800 \pm 450$ years B.P. This is slightly older than expected based on previous dates determined for the Rerewhakaaitu Ash (Table 7.1) but a slightly older date might be expected if there is contamination from older carbonate. Further, the 0.1 m interval sampled represents circa 330 years in this part of the core and bioturbation of the sediment above and beneath the tephra would be sufficient to cause a difference of the amount noted. Mixing of this magnitude has been previously described in deep sea cores (Berger and Johnson, 1978; Peng et al., 1979; Berger and Hillingley, 1982). The radiocarbon age confirms the mineralogical identification of the tephra stratigraphy.

Other evidence of tephras

Further tephras may have also been present in the core sediment but because they were very small, bioturbation obliterated any trace of a coherent tephra layer. However, components from those tephras would still be disseminated through the surrounding sediment. Three parameters, rhyolitic glass concentration, grain-size distribution and bulk density, were measured in an attempt to determine the presence of small, thin tephras.

1. Rhyolitic glass

Abundance of rhyolitic glass in the sand and coarse silt fractions was measured to check both for the presence of macroscopically invisible tephras and to investigate variations in background fluxes in indirectly derived rhyolitic glass (e.g., variations in tephric loess production). Curves of rhyolitic glass content vs depth of the sand and coarse silt fractions show peaks which can be correlated with all of the macroscopically visible tephras (Fig. 7.3). There is generally a "tailing off" effect of glass concentration above each tephra, indicating some mixing of ash in the overlying sediment but there is little evidence of mixing below each tephra. The pre-Rerewhakaaitu Ash tephras were deposited during a period of rapid sedimentation and they show evidence of lesser mixing with the overlying sediment than is the case with the younger tephras (Fig. 7.3). This indicates that more thorough bioturbation of the sediment occurs when sedimentation rates are low. Little mixing is evident above the Kawakawa Tephra (Fig. 7.3), indicating that this tephra may have been thick enough to inhibit bioturbation (Kohn and Glasby, 1978).

There is no distinct evidence for the presence of either Taupo Pumice or Waimihia Formation in the upper part of the core, both of which should

be present, given their widespread distribution in terrestrial sequences (Vucetich and Pullar, 1964). There are three possible explanations;

- i. the tephras were eroded by currents. However, there is no evidence of erosion in this core. Because the core site is on the top of a rise within a basin (Omakere Depression) it is elevated above the level of most turbidite activity (e.g., King, 1975, p.193).
- ii. the tephras were not deposited. Given the widespread distribution of both tephras in Hawkes Bay terrestrial and marine sequences (Vucetich and Pullar, 1964; Lewis and Kohn, 1973), it seems unlikely that at least one or other of the tephras is not present.
- iii. the tephras were mixed by bioturbation and slurring in the upper part of the core above the Whakatane Ash. Sedimentation rates are low in this part of the core, allowing an opportunity for intensified bioturbation, and the higher water content (lower bulk density, Fig. 7.4) has led to some sediment slurring and loss during core collection, obscuring stratigraphic relationships.

A significant concentration of rhyolitic glass in the $>63\text{-}\mu\text{m}$ size fraction, and to a lesser extent in the $63 - 20\text{-}\mu\text{m}$ size fraction, occurs between the Whakatane Ash and the Rotoma Ash (Fig. 7.3) but this is not matched by a visible tephra in the core. From known stratigraphic relationships on land, it is likely that this glass concentration correlates with Motutere Tephra, a widespread tephra erupted from the Taupo Volcanic Centre about 5,370 years B.P. (Froggatt, 1981).

The minor peaks in rhyolitic glass accumulation occur at 3.2 and 3.6 m depth, just above Okareka Ash (Fig. 7.3). The peak at 3.6 m

corresponds to the position of tephra 5 and there is no known correlative of either tephra in terrestrial sequences (Table 7.1).

Between Okareka Ash and Kawakawa Tephra two obvious peaks in rhyolitic glass accumulation occur. The peak at 4.20 - 4.30 m is in the vicinity of tephra 7 (Fig. 7.2) but the larger peak at 5.10 m depth has no visible correlative in the core. Only one tephra is known to have erupted during this time, the Te Rere Ash from Okaitaina Volcanic Centre (Table 7.1). This rhyolitic glass abundance peak is therefore tentatively correlated with Te Rere Ash.

Below Kawakawa Tephra only two abundance peaks are noted and these correspond to the positions in which the two tephras are correlated with Poihipi Tephra and Okaia Tephra (Tephras 9 and 10 respectively, Fig. 7.2).

2. Grain size parameter variations

Introduction of material into a sediment which has different grain size characteristics will always lead to changes in the grain size parameters of the resulting sediment, the magnitude of which will be related to the relative amounts and degree of difference between the two populations. The irregular occurrence of rhyolitic tephras at different depths in marine sediment should therefore appear as variations in grain size parameters when plotted as a function of depth. However, it should be noted that any coarser grained sediment influx, such as that resulting from turbidite activity, will also give a similar variation in grain size parameters of otherwise fine-grained hemipelagic sediment.

Grain size fractionation was made at 63, 20, 5, and 2 μm as quantitative yields of specific size fractions were required for further analysis. The sand fraction was not fractionated further as this rarely constituted >5% of the total sediment and was for the most part <3%, except immediately above and including tephras. Two parameters were

plotted, M_z and σ_I (Folk and Ward, 1957), as these showed the most consistent variations with depth in the core. All of the major tephras visible in the core and some of the minor ones are shown by an increase in mean grain size (M_z) in the vicinity of the tephra (Fig. 7.4). This effect is shown to occur in the sediment overlying each tephra where both have been mixed, but there is no evidence of mixing beneath the tephra (e.g., Kawakawa Tephra). Sorting (σ_I) appears to be less sensitive as a measure because only Whakatane Ash and Kawakawa Tephra are shown to have a distinct decrease in sorting relative to the surrounding sediment (Fig. 7.4).

The reason for the lesser effect of the smaller tephras on grain size distribution appears to be twofold. Firstly, the smaller amounts of tephra present have a reduced effect on overall grain size distribution and secondly, with greater distance from source the tephras would become progressively more fine grained and their grain size characteristics become more a function of the wind transport system they are in than of the original eruption. As a result the tephra may acquire grain size characteristics indistinguishable from the fine grained marine sediments in which they are finally deposited. Because of this, and the inability of grain size parameters to distinguish between tephras and turbidites, grain size parameters are seen as being of limited value in distinguishing tephras in marine sediments unless used in conjunction with other techniques.

3. Bulk density

Measurements of dry bulk density were made in an attempt to detect tephra-rich horizons. Rhyolitic glass has a lower density than most detrital minerals and this should be reflected in the bulk density of the whole sample. However, there is no systematic change in bulk density in

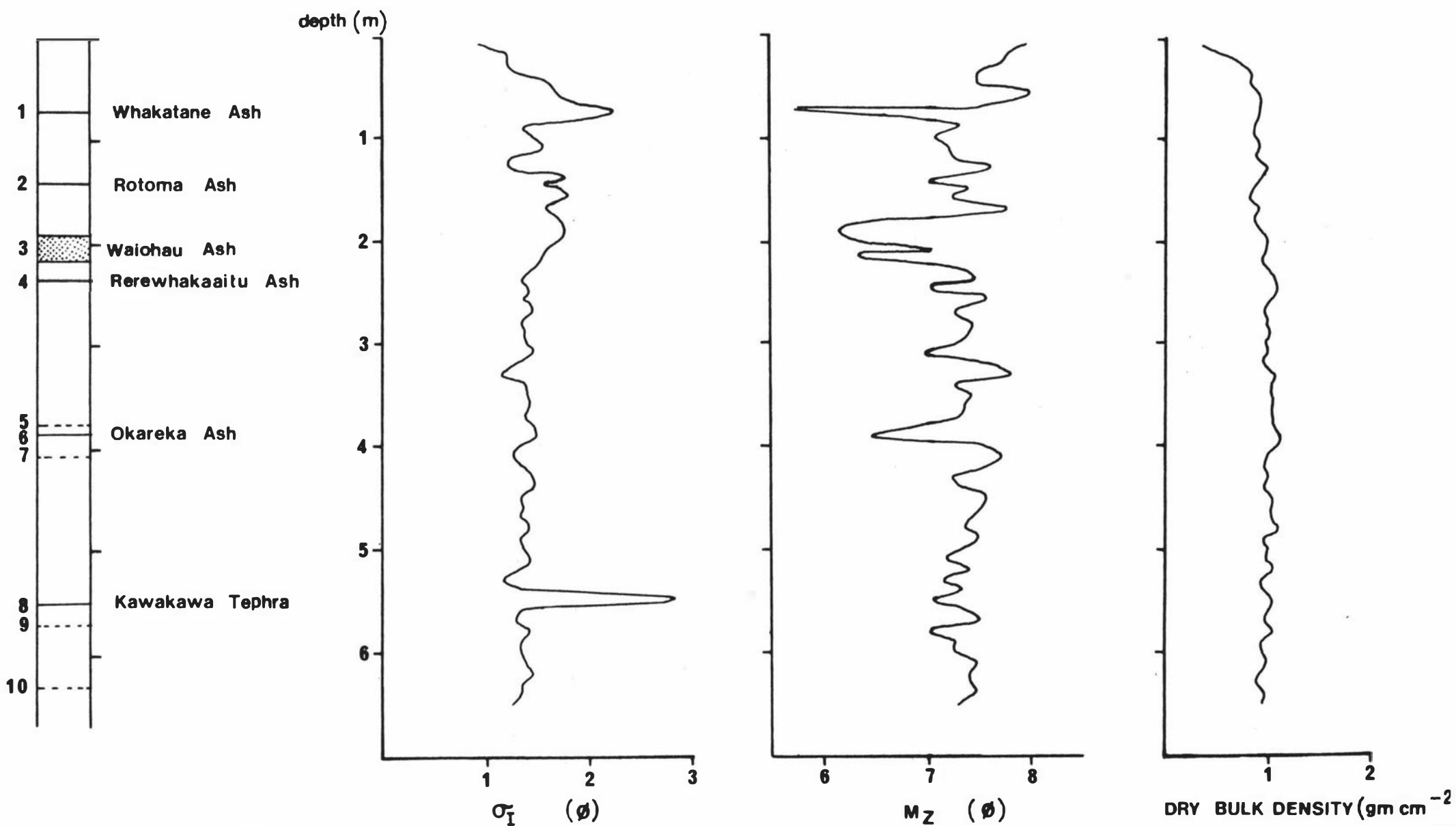


Figure 7.4

Variations with depth of M_z , σ_I and Dry Bulk Density.
Grain size parameters were calculated on a clay-free sediment basis.

the core which can be related to the presence of tephras (Fig. 7.4). The decreased bulk density of the uppermost 30 cm is a reflection of the water rich sediment at the surface.

SEDIMENTATION RATES

Sedimentation rates are determined from the thicknesses of sediment between identified tephras for which radiocarbon ages are known. The sedimentation rates in core P69 are shown in Fig. 7.5. There is a degree of uncertainty in the calculation of sedimentation rates because of the lack of precision in locating tephra depth in the core, particularly where it has been disturbed by bioturbation. The sedimentation rates give a mean figure for accumulation of sediment between dated tephras and take no account of accelerated sedimentation due to resorting and mixing of an underlying tephra. This factor must be considered in interpreting sedimentation rates derived from this core.

The mean sedimentation rate prior to 14,700 years B.P. (Otiran age sediments) of 594 mm ka^{-1} is markedly greater than that of the younger sediments (Aranuian age) of 156 mm ka^{-1} (Fig. 7.5). The Aranuiian sedimentation rate is similar to that obtained for sediments of this age in cores taken from greater than 1500 m depth in the Bay of Plenty (Kohn and Glasby, 1978). In the Hawkes Bay region, sedimentation rates have only been determined for post-Waimihia Formation sediments. These range from 0 - 360 mm ka^{-1} (Lewis and Kohn, 1973). Five cores from this study are of particular relevance to the interpretation of core P69 (Fig. 7.6). Cores 14 and 15 were located in the Omakere Depression, core 21 in the Akitio Depression and cores 24 and 25 in the Hikurangi Trench (Fig. 7.1). The post-Whakatane Ash sedimentation rate in core P69 is most similar to the post-Waimihia Formation rates recorded in

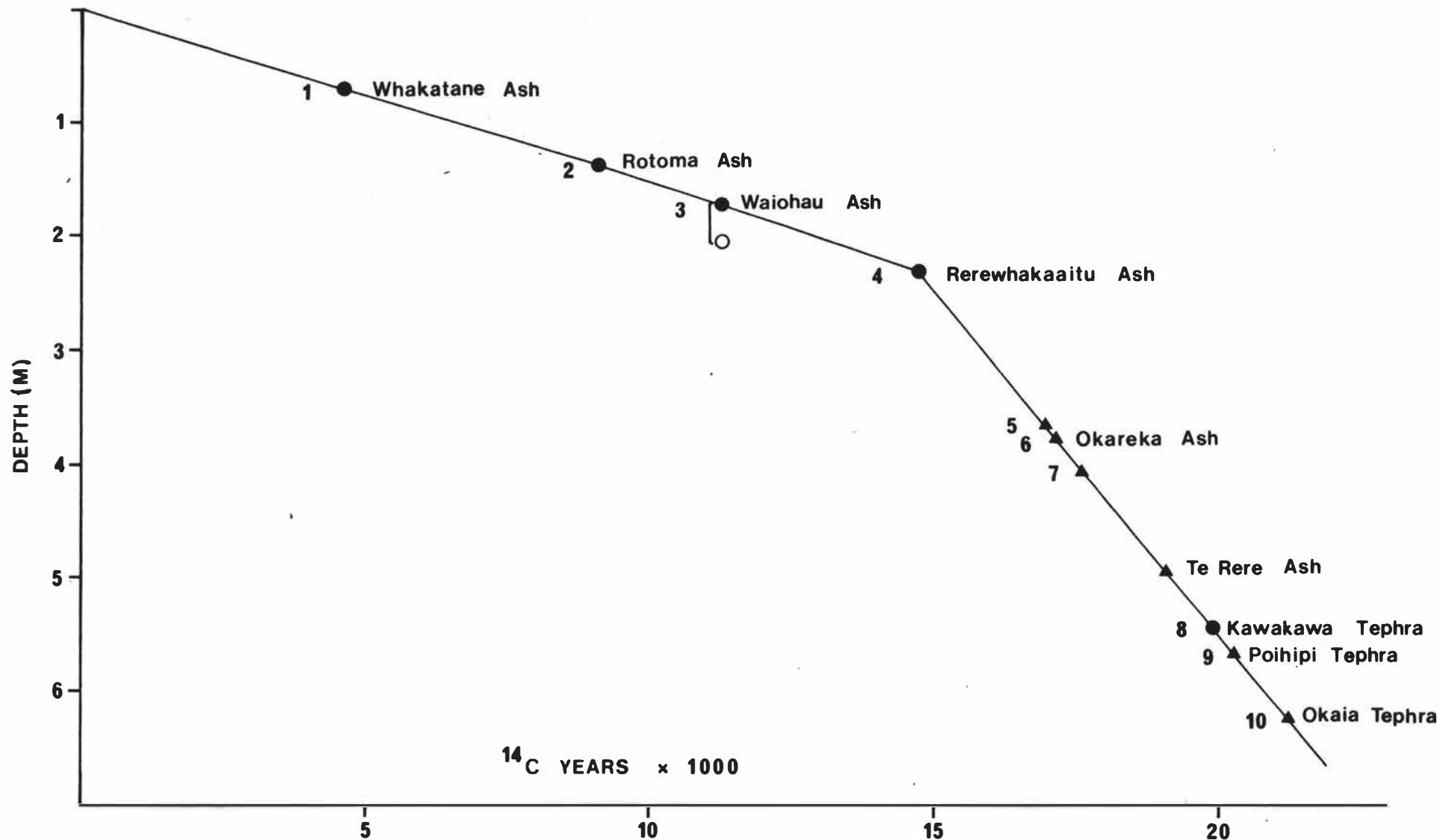


Figure 7.5 Depth versus ^{14}C age of tephras in core P69. Closed circles indicate tephras for which radiocarbon ages are known while closed triangles show tephras for which ages were estimated from the sedimentation rate curve. Numbers refer to tephras identified in Fig. 7.2. The open circle shows the depth which a block of Waiohau Ash occurs.

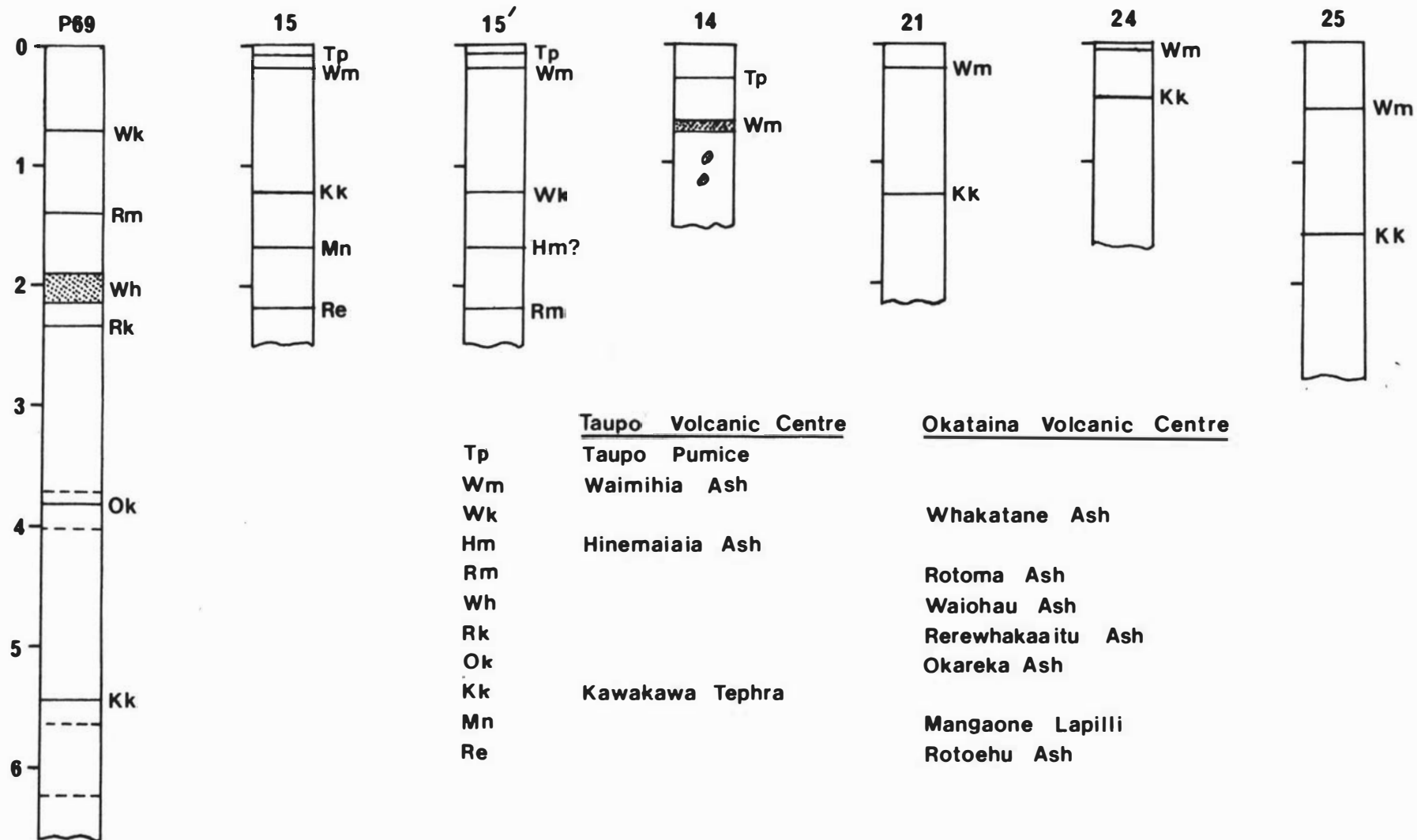


Figure 7.6 Diagrammatic sections of core P69 and cores 14, 15, 21, 24 and 25 from Lewis and Kohn (1973). 15' is 15 reinterpreted relative to the stratigraphy of P69.

cores 14 and 25, although these rates were thought to be high for Holocene sedimentation at such a distance from shore (Lewis and Kohn, 1973). There is wide variation amongst the sedimentation rates of the remaining cores (Table 7.3).

Because no tephras were identified by Lewis and Kohn (1973) between the Waimihia Formation and "Oruanui Ash" (Kawakawa Tephra), it is not possible to compare Aranuiian and Otiran sedimentation rates with those in core P69. However, in core 15 two tephras below their "Oruanui Ash" were identified as Mangaoni Lapilli and Rotoehu Ash (Lewis and Kohn, 1973). The Rotoehu Ash to "Oruanui Ash" (Kawakawa Tephra) sedimentation rate of 58 mm ka^{-1} determined for core 15 is very low in comparison with the $>14,700 \text{ year B.P.}$ rate of 594 mm ka^{-1} in core P69.

Two reasons are suggested for the wide variation in sedimentation rates interpreted from these cores:

1. the presence of turbidites, as shown by the occurrence of sandy, non-tephric horizons suggests either scouring of sediment and an underestimation of the regional sedimentation rate or more rapid deposition of coarse material leading to an overestimation of the regional sedimentation rate. Cores 21, 24 and 25 show evidence of varying effects of turbidites while cores 14 and 15 are almost unaffected (Lewis and Kohn, 1973). Core P69 shows evidence of little turbidite activity and shows sedimentation rates most similar to core 14 but quite different for core 15 (Table 7.3).
2. there may be an error in previous tephra identification, particularly in the case of core 15. If core 15 is reinterpreted in the light of the known stratigraphy of core P69 (Fig. 7.6), the sedimentation rate for post-Waimihia Formation sediments in core 15 is unchanged, remaining lower than the post-Whakatane Ash Rate

Table 7.3 Sedimentation rates in cores from the Omakere Depression region

Core Number	Sedimentation Rates (mm ka ⁻¹)			
	post-Waimihia	post-Whakatane	post-Rotoma	post-Kawakawa
25	158	-	-	81
24	at surface	-	-	25
21	61	-	-	63
15	58	-	-	60
15'	58	369	242	-
14	190	-	-	-
P69*	-	156	154	272

* This paper. The remaining cores are from Lewis and Kohn, (1973).

15' is core 15 reinterpreted in terms of the stratigraphy of core P69.

in core P69. However, if "Rotoehu Ash" in core 15 is reinterpreted as Rotoma Ash, a sedimentation rate is obtained which is more consistent with that of the post-Rotoma Ash sedimentation rate in core P69 (Table 7.3).

AGE DETERMINATIONS FROM SEDIMENTATION RATES

Radiocarbon ages are known for only five of the tephras positively identified in core P69 (Table 7.1). Four other tephras, Okareka Ash, Te Rere Ash, Poihipi Tephra, and Okaia Tephra, have estimated ages based on stratigraphic relationships with other, dated tephras (Table 7.1). On land erosion breaks are common, particularly in tephra sequences of Otiran age, making it difficult to estimate ages. In a non-eroded marine sediment sequence more precise estimates of ages of undated tephras are possible by using the sedimentation rate interpolated between tephras of known age. Where dated tephras are closely spaced in time and there is no evidence of non-uniform sedimentation, a reasonable level of accuracy in age estimation could be expected. This is, of course, very dependent on the accuracy of the Radiocarbon ages obtained for the tephras in terrestrial sequences.

Core P69 is considered to have good stratigraphic control and the ages of undated tephras based on inferred sedimentation rates are listed in Table 7.1. The sedimentation rate (SR) age for the Okareka Ash of 17,100 years B.P. is similar to original estimates from terrestrial sequences of circa 17,000 years B.P. (e.g., Pullar, 1980) and is consistent with its observed stratigraphic position in tephric loess units between Rerewhakaaitu Ash and Kawakawa Tephra.

Little is known about the age of Te Rere Ash but it is thought to be circa 18,000 years B.P. (Pullar, 1980). The SR age of circa 19,100 B.P. determined from core P69 is slightly older than this published

estimate but appears consistent with the stratigraphic position of Te Rere Ash within tephric loess overlying Kawakawa Tephra.

The two pre-Kawakawa Tephra eruptives, Poihipi Tephra and Okaia Tephra, are thought to be less than 25,000 years old (Pullar, 1980). The SR ages of 20,300 years B.P. and 21,200 years B.P. respectively suggest ages much closer to the time of the eruption of Kawakawa Tephra.

Sedimentation rates have been also used to date tephras which cannot currently be correlated with known tephras in terrestrial sequences. These estimated ages are presented in Table 7.1. These uncorrelated tephras appear to have been erupted during the later part of the Otiran when terrestrial sequences in the central North Island contain widespread tephric loess and erosional breaks. On the basis of current work, it is interpreted that tephras 5 and 7 are small tephras which have not yet been identified in terrestrial sequences as separate eruptive events.

QUARTZ ACCUMULATION RATES

Within core P69, there is a marked variation in quartz accumulation rates in both 63 - 20 and 5 - 2 μm size fractions (Figs. 7.7 and 7.8). Prior to the eruption of Rerewhakaaitu Ash at circa 14,700 years B.P., quartz accumulation rates reflect a much higher flux of quartz into the marine depositional environment in late Otiran time. At circa 14,700 years B.P. there was a rapid and substantial decrease in quartz accumulation rates that levelled to a uniform Holocene rate (Fig. 7.7).

Several conclusions can be drawn about paleoclimatic and paleoenvironmental changes from the quartz accumulation data. The high quartz accumulation in Otiran time reflects widespread aeolian sediment transport during glacial conditions. Changes in quartz accumulation

would therefore be related to mechanisms which directly affect the availability of quartz in the source areas and to aeolian sediment transport mechanisms rather than directly to inferred global temperature changes. Two mechanisms affecting the availability of quartz are changes in vegetation, both in cover and type, and a rise in sea level inundating coastal river flood plain source areas. The post-glacial rise in sea level is thought to have occurred at circa 11,000 years B.P. (Broeker et al., 1960; Cullen, 1967) but because there is no evidence in core P69 of a change in accumulation rate at this time (Fig. 7.7), other mechanisms must be involved.

One of the main stabilising influences against erosion is vegetation. It is known that circa 18,000 years B.P. much of the central and southern North Island had a grassland and shrubland vegetative cover (McGlone and Topping, 1973; 1977), in contrast to the Aranui forests. In river valleys aggradational river terraces were built up over wide areas and were the source of extensive loess deposits (Cowie and Milne, 1973; Selby, 1975). The highest rate of quartz accumulation recorded in core P69 occurs between circa 16,200 - 14,700 years B.P. (Fig. 7.7). It has been suggested previously that the last glacial maximum occurred in New Zealand at circa 18,000 years B.P. (e.g., Suggate and Moar, 1970), some 1800 - 2000 years earlier than the highest quartz accumulation rates in the core. The period 16,200 - 14,700 years B.P. is interpreted as representing a time in the southern North Island when there was maximum erosion coupled with a strong westerly wind system that transported aeolian sediment offshore. If the circa 18,000 years B.P. glacial maximum is correct then with a slight amelioration in climate after this time, a gradual increase in precipitation and attendant increased erosion is most likely (Tonkin et al., 1974). If the strong westerly wind system, thought to have existed during the glacial

maximum is maintained (Thiede, 1979), the combination of increased sediment supply and strong winds would post-date the glacial maximum and give rise to a higher quartz flux which is evidenced from 16,200 - 14,700 years B.P. in core P69. Rapid accumulation at the end of a glacial period has been previously postulated for the extensive loess deposits of the South Island, New Zealand as a result of climatic fluctuations and resultant changes in vegetation cover (Ives, 1973; Tonkin et al., 1974).

Alternatively, the possibility must be considered that the maximum quartz accumulation rates in core P69 indicate that the glacial maximum in the North Island was between 16,200 - 14,700 years B.P. However, there is no unequivocal evidence to support such an hypothesis known at present.

The rapid decrease in quartz accumulation at circa 14,700 years B.P. is seen as the result of two factors. Firstly, the intensity of strong westerlies must have decreased at this time, thus decreasing the amount of aeolian sediment eroded and transported. Secondly, stabilisation of the source areas is indicated and this is evidenced by the rapid expansion of forest cover over much of the area (McGlone and Topping, 1973; 1977). This is consistent with the southward movement of the westerly wind system as the polar wind and ocean circulation systems contracted to higher latitudes at the end of Otiran time (Lamb and Woodroffe, 1970; Gardner and Hays, 1976).

CARBONATE AND BIOGENIC SILICA ACCUMULATION RATES

The carbonate distribution in core P69 shows a higher concentration in sediments of post-glacial age than in Otiran-aged sediments (Fig. 7.7). However, the post-glacial carbonate accumulation is lower than that during

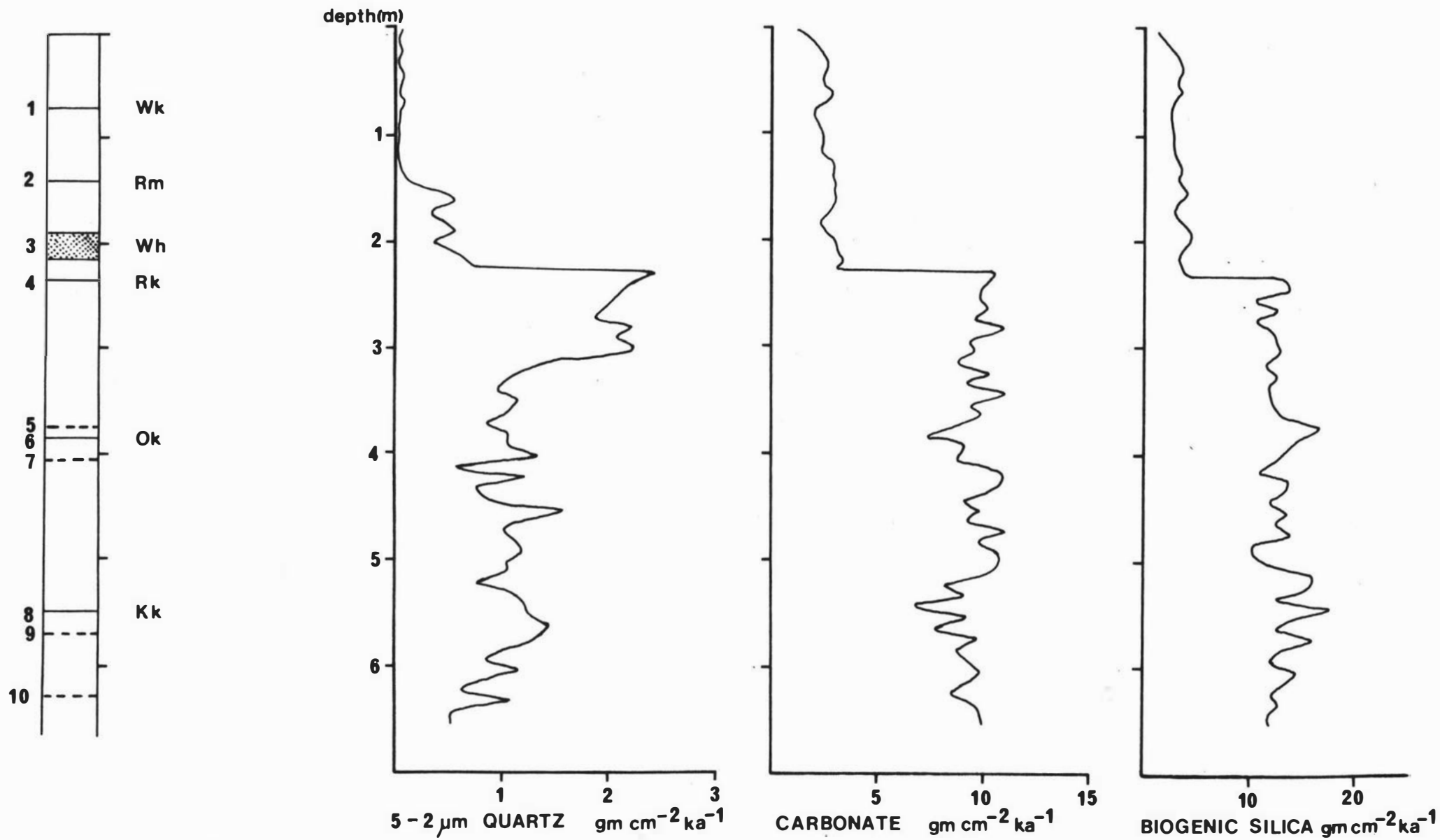


Figure 7.7

Accumulation rates of 5 - 2 μm quartz, carbonate and biogenic silica in core P69. Symbols for tephras are as in Fig. 7.6.

Otiran time due to the markedly lower post-glacial sedimentation rates. A similar distribution of carbonate has been recorded from Atlantic deep-sea cores where dilution of carbonate by a high influx of detrital sediment occurred during glacial periods (Hays and Perruzza, 1972). Dissolution of carbonate is considered to be unimportant in core P69 because of the relatively shallow depth (2195 m is above the carbonate compensation depth) and lack of evidence of foraminiferal test corrosion.

The causes of change in the productivity of biogenic silica are similar to those for biogenic carbonate (Molina-Cruz, 1977) and this is reflected in the close similarity of the two accumulation rate curves (Fig. 7.7). The accumulation rates at the beginning of Aranuian time are clearly shown to have decreased markedly from the Otiran rates.

There is a suggestion that increased amounts of biogenic silica occur in portions of the core in proximity to the tephra horizons (Fig. 7.7). This may imply increased biological activity but alternatively it may reflect a small component of cristobalite either contained within the rhyolitic material, or cristobalite forming from rhyolitic glass during heating for biogenic silica determination. No cristobalite was detected in the samples prior to heating, indicating that, if present, the amount of inherited cristobalite is small.

Carbonate and silica productivity during the Otiran Stage, as indicated by the accumulation rate curves, appears to have been relatively uniform (Fig. 7.7). The decrease in accumulation rate at the end of the Otiran commences at circa 14,700 years B.P. and falls to a relatively uniform post-glacial level at circa 12,000 years B.P. (Fig. 7.7). The change occurs more rapidly than the time span indicated by the quartz accumulation rates (Fig. 7.7). The reason for this lies in the differing

response of the respective production mechanisms to climate change. Quartz is largely generated on land from either outwash or river flood plains and may continue to be transported long after climatic changes have occurred. On the other hand, the biogenic silica and carbonate is dependent on physical and chemical factors relating to the nutrient supply at a given location. Nutrient rich waters are brought to the surface by upwelling, the intensity of which is directly proportional to wind intensity in a given period of time (Quinn, 1971; Molina-Cruz, 1977; Valencia, 1977a; 1977b; Diester-Haass and Schrader, 1979). Increased biological productivity in such nutrient rich waters is recorded by an increase in the biological component of sediments accumulating beneath (Burckle, 1972; Ellis and Moore, 1973; Diester-Haass, 1976; Molina-Cruz, 1977; Adelseck and Anderson, 1978; Diester-Haass and Schrader, 1979).

New Zealand is at present situated in the northern part of the westerly wind belt of the Southern Hemisphere and the Subtropical Convergence lies approximately across the centre of New Zealand (Heath, 1975). It is believed that the central gyres in the subtropical Atlantic, Pacific and Indian Oceans have remained stable in position and temperature and that in the Pacific the Subtropical Convergence has not shifted appreciably (CLIMAP, 1976). This has led to a compression of the area of Subantarctic water by expansion of the polar front and an increase in wind velocity due to the steeper thermal gradient in the atmosphere (CLIMAP, 1976; Gates, 1976). Evidence of increased wind velocities in the southwest Pacific is reported from Australia (Bowler, 1978) and from quartz distributions in the Tasman Sea and New Zealand regions (Thiede, 1979) circa 18,000 years B.P.

The synchronous decrease of similar magnitude in both carbonate

and biogenic silica accumulation in core P69 (Fig. 7.7) suggests a common causative factor, a change in nutrient supply being most probable. Biologically productive zones tend to be elongate parallel to the zones of upwelling of nutrient rich water (Ellis and Moore, 1973). For example, a 5° shift in latitude for a latitudinally elongate zone would be sufficient to cause a 5-fold decrease in accumulation of opal (estimated from the data of Ellis and Moore, 1973). The abrupt decrease in the accumulation rates of both carbonate and biogenic silica in core P69 is therefore seen as resulting from the southward migration, and probable decrease in intensity, of the westerly wind system in late glacial and post-glacial time.

The biological components show no increased accumulation in the period circa 16,200 - 14,700 years B.P. as shown by quartz accumulation (Fig. 7.7). This confirms the suggestion that the increased quartz accumulation was due to processes in the source area rather than in the wind transport system, because increased wind velocities would result in increased oceanic upwelling and resultant biological productivity. No evidence for increased biological activity during this time period was found in core P69.

Biological activity may also influence the accumulation of fine-grained particles in deep-sea sediments. A problem arises in sedimenting fine particles through a water column kilometers deep without wide dispersal. It has been suggested that these particles are incorporated into faecal pellets by zooplankton and nekton in surface waters and thereby more rapidly deposited (Delany et al., 1967; McCave, 1975; Honjo and Roman, 1978; Scheidegger and Krissek, 1982). Such a mechanism influencing deposition in core P69 would contribute to the sharp decrease in quartz accumulation at 14,700 years B.P. In addition, if biological

activity was responsible for the transfer of fine particles to the sea floor, then the increase in quartz accumulation between 16,200 - 14,700 years B.P. is clearly independent of biological productivity and is further evidence for changes in the quartz source areas being the main control on quartz accumulation at this time.

RHYOLITIC GLASS ACCUMULATION RATES

The rhyolitic glass component in the core has a completely different origin from the quartz and biogenic components. Obvious large inputs of rhyolitic glass coincide with each tephra horizon (Fig. 7.8), but the low background glass accumulation rates show no response to known paleoclimatic changes. The $>63\text{ }\mu\text{m}$ rhyolitic glass background accumulation apparently increases throughout post-glacial sediments but this is considered to be due to the increased influence of tephra during slow sedimentation and hence less dilution by terrigenous material.

The non-carbonate component of the $>63\text{ }\mu\text{m}$ size fraction in the core is largely volcanic-derived, apart from rare, sandy, probably distal turbidite layers (Fig. 7.2). The volcanic-derived grains could have been deposited either as direct air fall material, by the eventual sinking of floating particles, or by offshore current transport. The latter seems unlikely, given the lack of turbidite activity evident in the core. The coincidence of accumulation peaks in both the $>63\text{ }\mu\text{m}$ and $63 - 20\text{-}\mu\text{m}$ size fractions of rhyolitic glass suggests similar transportation and time of deposition for both fractions; if the coarser particles floated for a time an out of phase relationship would be expected. Within the tephras themselves, the lack of admixed hemipelagic sediment indicates rapid sedimentation of volcanic material with no redeposition.

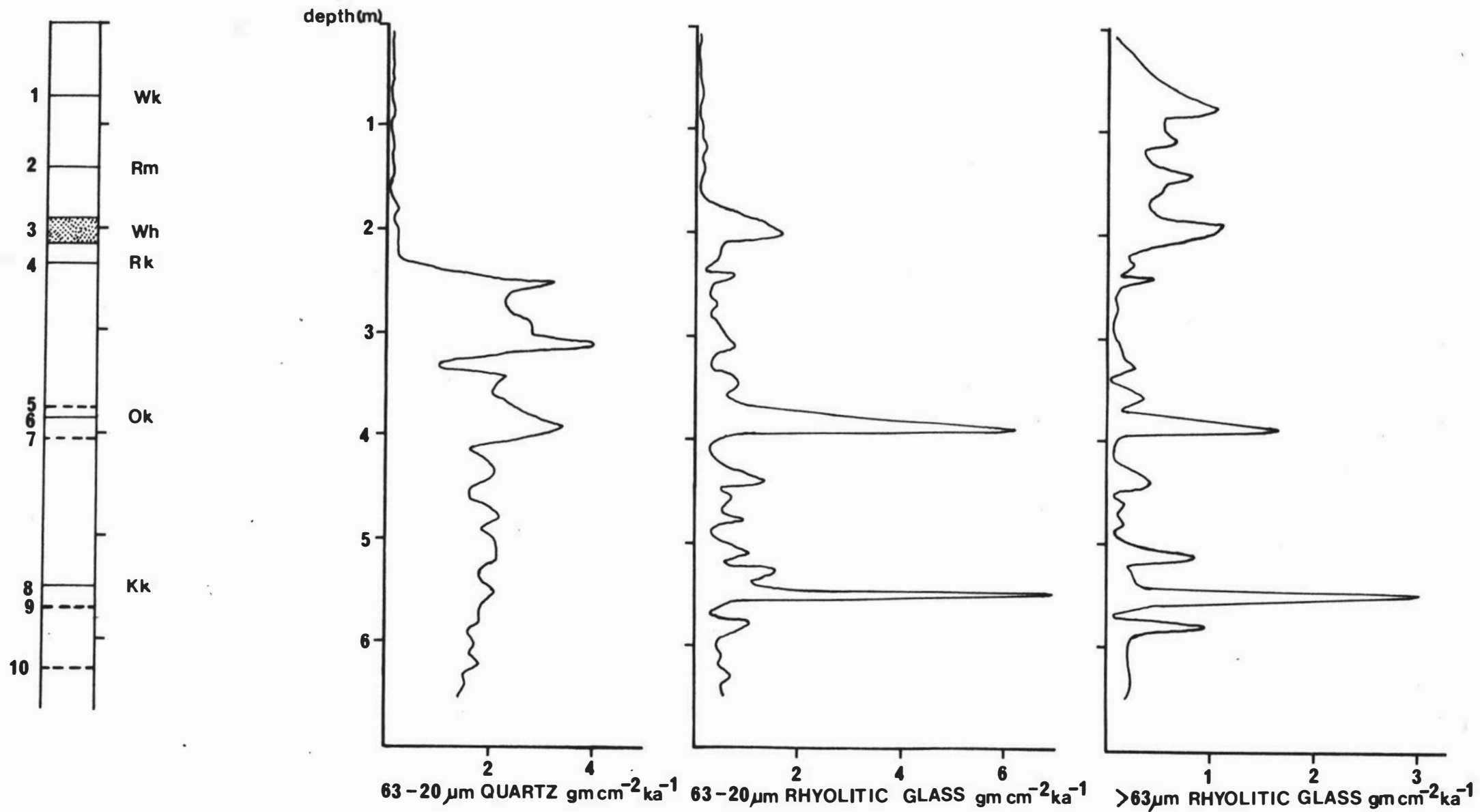


Figure 7.8

Accumulation rates of 63 - 20 μm quartz and rhyolitic glass, and >63 μm rhyolitic glass. Tephra symbols are as in Fig. 7.6.

The lack of response to paleoclimatic changes shown by the 63 - 20 μm rhyolitic glass accumulation rate indicates that this was not a major component of loessial additions to the sediment in late Quaternary time. Tephric loess has been described from the central North Island (Cowie and Milne, 1973; Pullar and Kennedy, 1978) during the Otiran Stage and its absence from the loess component here is surprising. However, core P69 is sited just to the south of the latitudes in which tephric loess is abundant in the central North Island and, given the prevailing west to north-west winds of the region, is downwind of the major greywacke river flood plains of the southern North Island (Fig. 7.1). In this situation the input of volcanic material other than directly from an eruption would be low.

QUARTZ OXYGEN ISOTOPE ABUNDANCE

The oxygen isotope abundance of quartz from both the 63 - 20 μm (representing loessial quartz) and 5 - 2 μm (representing aerosolic quartz) size fractions was determined at selected intervals from core P69 (Table 7.4). There was no consistent difference amongst $\delta^{18}\text{O}$ values with depth in either size fraction. The $\delta^{18}\text{O}$ values of 5 - 2 μm quartz of 13.6 - 14.8 $^{\circ}\text{oo}$ are consistent with those previously determined for aerosolic quartz from pelagic sediments in similar latitudes in the Pacific (Clayton et al., 1972; Mokma et al., 1972). The $\delta^{18}\text{O}$ values of 63 - 20 μm quartz range from 12.2 - 13.3 $^{\circ}\text{oo}$ and are similar to those of quartz from the same size fraction in a soil from Taranaki, located in a similar latitude (Stewart et al., 1977), and to quartz from this size fraction in other soils and sediments in New Zealand (Mokma et al., 1972; see Chapter 4).

Table 7.4 Quartz oxygen isotope data from core P69

Sample	Depth (m)	+ $\delta^{18}\text{O}$ (‰)	
		63 μ - 20 μ	5 μ - 2 μ
1/4/6	0.5 - 0.6		14.8
1/4/13	1.2 - 1.3		13.4
2/4/4	1.9 - 2.0	12.2	
2/4/6	2.1 - 2.2		14.6
2/4/12	2.7 - 2.8	12.9	
2/4/16	3.1 - 3.2		13.6
3/4/3	3.4 - 3.5	13.1	14.6
3/4/11	4.2 - 4.3	13.3	14.6
4/4/5	5.2 - 5.3	13.3	15.0
4/4/16	6.3 - 6.4	13.2	14.0
* mean		13.0 $\pm$ 0.42	14.3 $\pm$ 0.58

+ relative to SMOW

* means were significantly different ($P < 0.001$)

A systematic variation in $\delta^{18}\text{O}$ with grain size has been established previously. In North Pacific sediments $\delta^{18}\text{O}$ values of quartz ranged from about 16‰ for grains $>12\text{ }\mu\text{m}$ in diameter to 19‰ for grains $<2\text{ }\mu\text{m}$ in diameter (Clayton *et al.*, 1972). However, the $\delta^{18}\text{O}$ values of quartz of comparable grain size from the South Pacific is lower than that of quartz from the North Pacific and there is an established relationship between decreasing $\delta^{18}\text{O}$ and increasing latitude in the South Pacific (Clayton *et al.*, 1972; Mokma *et al.*, 1972). Thus although the $\delta^{18}\text{O}$ values of quartz in core P69 exhibit a similar increase with decreasing grain size to the North Pacific quartz, the $\delta^{18}\text{O}$ values themselves are consistent with those previously obtained for quartz in the South Pacific. These results are an indication of the homogeneity of the oxygen isotope composition of quartz in the various size fractions, particularly the 5 - 2 μm size fraction, in the source materials of aeolian sediment in the North Island of New Zealand.

CONCLUSIONS

This study has demonstrated the value of hemipelagic sediment sequences, in which tephras of known age are preserved, for paleoclimatic interpretation. Most of the major tephras erupted from the central North Island since circa 23,300 years B.P. are present in the core.

1. The oxygen isotope composition of loessial and aerosolic quartz in core P69 is consistent with that determined for quartz in similar size fractions from a similar latitude in both terrestrial and marine environments.
2. A major decrease in the accumulation rates of quartz, carbonate, and biogenic silica occurs at circa 14,700 years B.P., the time of

eruption of Rerewhakaaitu Ash. The accumulation of quartz depends on changes in both source area, as it affects supply of aeolian material, and changes in the transport mechanism. The increased accumulation between circa 16,200 years B.P., just after the Otiran glacial maximum, and circa 14,700 years B.P. is interpreted as showing increased erosion. This is attributed to availability of quartzose sediment in the source area due to increasing rainfall with climatic amelioration prior to the establishment of forest vegetation and the southward migration of the westerly wind system. The southward movement of the westerly wind belt resulted in a decrease in wind intensity and frequency, reducing the transport of terrestrial material and allowing the expansion of forest over much of the quartzose source areas. The circa 11,000 years B.P. rise in sea level may have further reduced the size of the source areas of aeolian material, although this must have been a minor effect as there is only a small change in quartz accumulation about this time. The abrupt change in quartz accumulation at circa 14,700 years B.P. indicates a short period, perhaps 300 - 500 years, during which the strong glacial westerly wind system moved southwards and caused a marked decrease in wind intensity. This was coupled with a rapid expansion of forest cover which stabilised the aeolian sediment source areas against further large-scale wind erosion.

3. The abrupt decrease in both carbonate and biogenic silica accumulation at circa 14,700 years B.P. is also interpreted as reflecting a major change in the wind system at this time. Decreased wind intensity resulted in decreased upwelling of nutrient-rich water and a corresponding decrease in biological productivity.

There was no change in biological productivity between 16,200 - 14,700 years B.P., when quartz accumulation reached a maximum, indicating that changes in the quartz source areas were the prime cause of the quartz variation rather than changes in wind intensity at this time.

4. The background accumulation of rhyolitic glass shows no evidence of an increase in Otiran time. This shows that the source areas for the aeolian sediment in core P69 therefore did not extend north to the extensive areas where tephric loess was deposited prior to circa 14,700 years B.P.
5. The following sequence of events is proposed for the period from circa 23,000 years B.P. to the present in the southern North Island, based on data from core P69.

23,000	-	19,200	cold, glacial
19,200	-	18,500	slight amelioration, glacial, little change in total vegetation cover but perhaps some expansion of forest in protected areas
18,500	-	16,200	maximum cold, glacial
16,200	-	14,700	climatic amelioration, maximum quartz flux implies maximum aeolian sediment transport but no major forest development
14,700	-	14,400	southward-migrating circumpolar water leaves area of core P69, concurrent with decreasing wind intensity and rapid expansion of forest cover
14,400	-	9,500	ameliorating climate, early post-glacial
9,500	-	present	post-glacial.

6. Sedimentation rates in core P69 also show a marked decrease from Otiran to Aranuiian time. Interpolation of sedimentation rates between dated tephras allowed estimates to be made of the ages of four Otiran tephras for which no radiocarbon dates were available. These are:

Okareka Ash	17,100 years B.P.
Te Rere Ash	19,100 years B.P.
Poihipi Tephra	20,300 years B.P.
Okaia Tephra	21,200 years B.P.

These estimated ages are similar to previous estimates for Okareka Ash and Te Rere Ash but are younger than a previously estimated age of circa 25,000 years B.P. for Okaia Tephra.

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CHAPTER 8

CHAPTER 8

SUMMARY AND CONCLUSIONS

1. This study has shown, by oxygen isotope analysis, that authigenic quartz has not formed during pedogenesis in selected soils derived from a range of parent materials. These parent materials included rhyolitic tephra, andesitic tephra, basaltic tephra and basaltic lava and quartzose sands and sediments. Quartz in the albic horizon of a Wharekohe soil, or "kauri podzol", was shown to be of detrital rather than pedogenic origin.
2. Two stratigraphic units are recognised in an Egmont loam soil from Taranaki. The upper (tephra) unit is dominated by primary andesitic tephra while the lower (tephric loess) unit is characterised by a large quartzofeldspathic component and redeposited tephra. Within the quartzofeldspathic component, three sources of quartz are recognised, based on oxygen isotope and grain size analysis:
 - (i) a sand fraction, represented by the 125 - 63 μm size fraction, derived from local (intraregional) sources
 - (ii) a "loess" fraction, represented by the 63 - 20 μm size fraction, from more distant (interregional) sources, and
 - (iii) an aerosolic dust fraction, represented by the 5 - 2 μm size fraction, from tropospheric aerosols.

An additional component of rhyolitic tephra is present in the profile. Peaks of rhyolitic glass abundance with depth are tentatively correlated with Taupo Pumice, Waimihia Ash and Rotoma Ash from the Central North Island. Kawakawa Tephra is known to occur at the base

of the profile in the South Taranaki region and places a maximum age of circa 20,000 years B.P. on the soil parent materials.

3. The change from a high rate of quartz accumulation in the tephric loess unit to a low rate in the overlying tephra unit is correlated with the circa 11,000 year B.P. post-glacial rise in sea level. This is thought to have inundated a land bridge area to the west (windward) of the South Taranaki region, covering the source area of quartzose sediment and tephra.
4. The anomalous presence of quartz was examined in six Northland basaltic soils belonging to the Kiripaka, Whatitiri, Waiotu, Kerikeri, Ruatangata and Okaihau series. Quartz in the $>125\ \mu\text{m}$ size fraction of these soils has an oxygen isotope composition consistent with that of high temperature quartz, an observation confirmed by the presence of bipyramidal quartz in this size fraction. This quartz is either derived directly from air-fall rhyolitic tephras, and in particular the Kaharoa Ash, from the Central North Island or indirectly from the same source area as sediment carried down the Waikato River and transported by ocean currents to the west coast beaches of Northland. Quartz in the coarse sand from these beaches has a similar oxygen isotope composition to that of quartz from similar size fractions in the basaltic soils. However, quartz oxygen isotope composition in beach sands from the east coast of Northland shows a larger, low temperature component and indicates quartz of mixed origin, with a larger component from local sedimentary rocks.

5. Quartz in the 63 - 20 μm size fraction of the basaltic soils has an oxygen isotope composition consistent with quartz of mixed origin, considered to be largely derived from local Mesozoic and Tertiary sediments. This is consistent with interregional loess derived from a number of sources.
6. Quartz in the 5 - 2 μm size fraction of the basaltic soils has an oxygen isotope composition similar to that of other aerosolic dusts previously reported from both soils in this region and marine sediments from a similar latitude in the South Pacific. This confirms the presence of aerosolic dust in these soils. In the 5 - 2 μm size fraction of the Kiripaka soil, anomalously high $\delta^{18}\text{O}$ values were obtained. These unusual values are attributed to the presence of authigenic quartz from nearby marine shales transported into the local profile by wind. This observation indicates that quartz of local origin may occur in the fine silt fraction of a soil in addition to aerosolic quartz.
7. Four mineralogical components can be recognised in the basaltic soils; basaltic, secondary, rhyolitic and detrital.
 - (i) Basaltic component - this comprises minerals remaining unweathered from the original basalt tephra or lava. These are most abundant in the youngest basalt soils and even here show evidence of rapid weathering. In the soil development sequence examined, olivine is only present in the Whatitiri soil, where it occurs in the topsoil as a result of contamination with tephra from the eruption of a much younger, nearby cinder cone.

- (ii) Secondary component - this consists of glaebules of gibbsite, goethite and lesser amounts of clay minerals, mainly of the kaolinite group. These become increasingly abundant through the soil development sequence with goethite glaebules accumulating in surface horizons and gibbsite predominating at depth. These glaebules cannot be disaggregated by conventional methods and in soils such as the Okaihau may comprise up to 90% of the non-clay fraction. Their presence controls the grain size distribution of these soils.
- (iii) Rhyolitic component - this is most abundant in the surface horizons of all profiles. The occurrence of biotite in four of the soils indicates the presence of Kaharoa Ash but the presence of glass in the remaining soils indicates that other tephras, probably Taupo Pumice and Kawakawa Tephra in the oldest soils, occur as well. The absence of Rotoehu Ash suggests that older tephras have been weathered out in the strong weathering environment of these soils.
- (iv) Detrital component - this comprises almost entirely quartz and the grain size of this component is restricted to 125 - 1 μm , the coarser quartz being of rhyolitic origin. Within the 125 - 1 μm size range, two populations of quartz are recognised, the same as those determined from oxygen isotope analysis.

A loess population of >10 μm is recognised as being derived from quartzose Mesozoic and Tertiary sediments. An aerosolic dust component of 10 - 1 μm size is recognised as being derived in part from tropospheric aerosols and in part from local sediments.

8. Only in the Kiripaka soil was a quartz abundance distribution determined which indicated increased accumulation during Otiran time. In the remaining soils the rate of parent material accumulation was too slow for the change from glacial to post-glacial accumulation to be detected.
9. The accumulation of aerosolic quartz in the basaltic soils does not indicate a consistent sequence of soil development although a general trend is evident for the less developed soils to have lower amounts of aerosolic quartz than the more developed soils. Two of the soils, Waiotu and Kerikeri, have anomalously low quartz contents for their inferred degree of soil development. This is attributed to recent stripping of the Waiotu site by man and pre-Kaharoa Ash erosion at the Kerikeri site.
10. For the remaining soils, the following estimations are made of profile age, based on a comparison of aerosolic quartz content with that of the Egmont loam:

Kiripaka	32,000 years B.P.
Whatitiri	39,000 years B.P.
Ruatangata	95,000 years B.P.
Okaihau	83,000 years B.P.
11. The basaltic soil development sequence is seen as an accumulation of increments of surficial basaltic and non-basaltic additions to a succession of "accreting" soil profiles, each individually distinct for a number of differing site characteristics and not a result of soil development on in situ weathering basalt.
12. In a chronosequence of soils developed in andesitic and rhyolitic tephra on surfaces of known age, the aerosolic quartz contents

showed a systematic increase with increasing profile age. Thus within a region of youthful soils the amounts of aerosolic quartz accumulation in each soil can be used for relative age dating. The grain size distribution of the quartz is consistent with a loessial and aerosolic dust origin.

13. In both the chronosequence and marine core P69 from off the east coast a change from high glacial rates of quartz accumulation to low post-glacial rates is evident. However, a much greater quartz accumulation rate is evident in the core relative to that in the chronosequence. The additional material in the core is thought to have been derived as loess from river floodplains and sediments in the southern North Island which lie upwind of the core site. In contrast, the quartzose source area for the chronosequence soils was much smaller, even during glacial times. The effect of local additions on the accumulation pattern of aerosolic dust is additional to, and may be far greater than, that exerted by differences in rainfall previously reported.
14. In marine core P69, the results of oxygen isotope analysis of quartz are consistent with those determined for quartz in similar size fractions from similar latitudes in both terrestrial and marine deposits.
15. Quartz accumulation decreases abruptly from a high glacial (Otiran) to a low post-glacial (Aranuian) rate at 14,700 years B.P., the time of eruption of Rerewhakaaitu Ash. The change in quartz accumulation is thought to be due to two factors:
 - (i) a decrease in intensity of the westerly wind system due to the southward migration of the westerly wind belt and

(ii) stabilisation of source areas by forest expansion.

The circa 11,000 year B.P. post-glacial rise in sea level is thought to have had little effect as no major changes in quartz accumulation occur at this time.

16. The abrupt change in carbonate and biogenic silica accumulation, also at 14,700 years B.P., is thought to reflect a change in wind intensity at this time. Decreased wind intensity led to a decrease in upwelling of nutrient-rich water and a corresponding decrease in biological activity. There was no change in biological productivity between 16,200 and 14,700 years B.P., when quartz accumulation reached a maximum, indicating that changes in the quartz source areas were the prime cause of the quartz variation at this time rather than a change in wind intensity.
17. The source of aeolian material deposited in core P69 did not include the extensive areas of tephra in the central North Island. This is shown by the absence of an increase in background accumulation of rhyolitic glass during Otiran time.
18. Sedimentation rates in core P69 also show a marked decrease from Otiran to Aranuiian time. Interpolation of sedimentation rates between dated tephras also allows the following estimates to be made of the ages of four Otiran rhyolitic tephras from the Central North Island for which no reliable radiocarbon dates are available:

Okareka Ash	17,100 years B.P.
Te Rere Ash	19,100 years B.P.
Poihipi Tephra	20,300 years B.P.
Okaia Tephra	21,200 years B.P.

19. The following late Otiran - Aranuian chronology is suggested, based on the evidence in core P69:

23,000 - 19,200	cold, glacial
19,200 - 18,500	glacial, slight amelioration
18,500 - 16,200	glacial, maximum cold
16,200 - 14,700	climatic amelioration, maximum aeolian transport and erosion, little forest cover
14,700 - 14,400	southward migrating circumpolar currents and wind systems leave area of core P69, rapid expansion of forest cover
14,400 - 9,500	ameliorating climate, early post-glacial
9,500 - present	post-glacial.

APPENDICES

APPENDIX I.Oxygen Isotope Analysis Results

Sample	Size Fraction (μm)	$\delta^{18}\text{O}/^{16}\text{O}$ ($^{\circ}/\text{oo}$)
E 11	63-20	13.6
E 4	63-20	13.9
Te Aute limestone	63-20	13.9
R4150 (Institute of Nuclear Sciences standard)		
E 11	20-5	13.9
E 11	5-2	14.5
E 4	5-2	15.0
Te Aute limestone	5-2	15.3
R4150		7.7
Te Aute limestone	20-5	14.5
E 4	20-5	14.0
R4150		7.8
R4150		7.8
Te Aute limestone	20-5	14.5
E 4	5-2	15.0
R4150		8.0
NBS-28 (International $\delta^{18}\text{O}$ standard)		9.8
P-1 (Massey standard)		10.7
R4150		8.4
Whangai shale	63-20	23.0
Whangai shale	20-5	23.1
Whangai shale	5-2	24.2
Rt 1-3	> 250	9.0
Kp 1-5	> 250	8.2
Ok 3	63-20	11.9
Ok 3	5-2	14.0
R4150		10.7

Sample	Size Fraction (μm)	$\delta^{18}\text{O}/^{16}\text{O}$ ($^{\circ}/\text{oo}$)
Ok 3	63-20	12.3
Ok 3	5-2	12.1
Rt 1-3	> 250	8.2
R4150		12.1
Kp 3	63-20	11.5
Y0 5	5-2	14.0
Rt 7 (HF treated)	> 250	7.2
R4150		6.4
WI 4	5-2	12.9
Kp 3	5-2	17.8
Kp 8	5-2	18.2
Rt 3 (HF treated)	> 250	8.3
R4150		7.1
Ok 3	5-2	13.9
Whangai shale	5-2	26.8
Kp 3	5-2	15.7
Y0 5	5-2	12.7
Ke 3	5-2	13.4
Whangai shale	63-20	22.3
WI 4	5-2	12.9
Kp 3	63-20	13.3
R4150		8.0
Kp 3	63-20	12.0
Ke 3	5-2	14.0
Kp 8	5-2	18.7
P-1		9.4
R4150		8.0
Rt-7 (HF treated)	> 250	8.4
Whangai shale	5-2	26.6
Y0 5	5-2	13.2
Kp 3	5-2	17.1
P-1		9.4

APPENDIX I contd.

Sample	Size Fraction (μm)	$^{18}\text{O}/^{16}\text{O}$ ($^{\circ}/\text{oo}$)
Kp 8	63-20	11.6
Kp 3	5-2	16.6
Kp 8	5-2	18.5
P-1		11.0
Kp 3	63-20	12.3
Ke 3	63-20	12.0
Kp 3	5-2	17.6
P-1		10.8
R4150		8.0
Kp 8	5-2	19.6
WI 4	63-20	12.1
WI 4	5-2	12.7
Kp 8	63-20	11.7
P-1		10.2
WI 4	5-2	13.6
WI 7	5-2	14.1
WI 4	63-20	11.0
WI 7	63-20	11.4
P-1		10.9
WI 7	63-20	12.2
Ok 3	5-2	12.9
WI 7	5-2	13.9
Ok 3	63-20	11.9
P-1		10.1
Y0 8	63-20	10.8
Y0 5	5-2	14.0
Y0 5	63-20	10.8
P-1		10.0
R4150		7.4

APPENDIX I contd.

Sample	Size Fraction (μm)	$^{18}\text{O}/^{16}\text{O}$ ($^{\circ}/\text{oo}$)
Y0 5	5-2	13.7
Y0 8	63-20	11.8
Y0 5	63-20	11.6
Ke 3	63-20	12.3
P-1		10.3
Y0 5	63-20	12.2
"	"	12.0
Y0 5	5-2	14.1
"	"	13.8
"	"	13.9
WI 4	63-20	12.2
"	"	12.3
WI 4	5-2	14.1
"	"	14.8
"	"	13.9
WI 7	63-20	12.6
"	"	12.5
"	"	12.1
Rt 7	63-20	12.1
"	"	12.1
"	"	11.4
Rt 7	5-2	13.4
"	"	14.2
"	"	13.6
Rt 1	63-20	12.0
"	"	13.4
"	"	12.6
Rt 1	5-2	14.6
Whangai shale	63-20	25.6
NBS-28		10.0
R4150		8.5
M-1 (Massey standard)		12.2

APPENDIX I contd.

Sample	Size Fraction (μm)	$\delta^{18}\text{O}/^{16}\text{O}$ ($^{\circ}\text{oo}$)
Putahi (0 - 0.1 m)	5-2	9.3
"	63-20	9.0
Putahi (0.1 - 0.2 m)	5-2	9.1
"	63-20	9.2
Wharekohe E horizon	5-2	13.4
" "	63-20	12.8
Kara (0 - 0.1 m)	5-2	15.6
	63-20	12.1
Kara (0.2 - 0.3 m)	5-2	15.1
"	63-20	12.0
Te Koperu sand	5-2	14.2
" "	63-20	10.9
" "	> 63	8.9
Mangakahia Group shale	5-2	25.7
" " "	63-20	12.0
Ohinewai Tephra	63-20	8.4
" "	1000-500	8.4
Waimamaku beach sand	500-250	8.7
Rarawa beach sand	250-125	11.7
" " "	125-63	11.5
Core P69 1/4/6	5-2	14.8
" 1/4/13	5-2	13.4
" 2/4/4	63-20	12.2
" 2/4/6	5-2	14.6
" 2/4/12	63-20	12.9
" 2/4/16	5-2	13.6
M-1		11.6

APPENDIX I contd.

Sample		Size Fraction (μm)	$\delta^{18}\text{O}/^{16}\text{O}$ ($^{\circ}/\text{oo}$)
Core P69	3/4/3	5-2	14.6
"	3/4/3	63-20	13.1
"	3/4/11	5-2	14.6
"	3/4/11	63-20	13.3
"	4/4/5	5-2	15.0
"	4/4/5	63-20	13.3
"	4/4/16	5-2	14.0
"	4/4/16	63-20	13.2
Rt 3		2-1	13.6
NBS-28			9.8
R4150			8.3
M-1			11.7

Results recorded in Appendix I are of raw data and analyses from runs in which standards varied significantly from normal were disregarded.

APPENDIX II. Egmont silt loam-grain size and point count data, key to sample nomenclature

1. Grain Size Distribution (gm).

	Size Fractions (μm)									
	>2000	2000-1000	1000-500	500-250	250-125	125-63	63-20	20-5	5-2	<2
E 0-0.15	0.07	0.04	1.46	4.84	5.97	4.20	9.25	8.73	2.37	9.29
E 0.15-0.25	0.24	0.53	2.14	5.37	5.77	5.10	9.88	7.18	1.97	9.79
E 13	0.05	0.60	2.32	4.39	4.62	4.27	5.50	8.94	1.32	8.20
E 12	0.06	0.42	1.77	3.29	4.02	2.07	6.51	5.71	1.25	4.75
E 11	0.05	0.43	2.11	3.91	4.68	3.03	3.47	11.57	1.48	6.38
E 10	0.04	0.40	1.82	2.62	3.19	1.59	8.43	8.72	2.69	8.69
E 9	0.11	0.48	2.03	2.43	3.31	2.19	8.70	10.52	2.02	7.95
E 8	0.21	0.81	2.96	2.43	2.60	1.99	10.64	9.07	1.62	12.60
E 7	0.97	3.47	2.12	2.06	0.96	11.52	8.00	1.90	9.55	0.35
E 6	-	0.16	1.30	1.47	1.60	0.58	15.83	8.30	2.24	9.39
E 5	-	0.05	0.46	0.92	1.39	1.09	17.05	9.95	1.65	11.29
E 4	-	0.05	0.58	0.94	1.66	0.85	15.50	9.75	1.97	10.87
E 3	-	1.95	1.06	1.71	2.82	1.17	11.83	9.90	1.39	8.09
E 2	-	0.09	1.66	2.54	4.43	1.97	9.34	8.57	1.27	8.91
E 1	0.22	5.00	3.32	4.17	7.60	2.39	8.08	6.24	1.24	5.40
Dune Sand	0.33	0.86	4.97	17.64	20.22	0.68	1.59	1.85	0.31	0.62

APPENDIX II. contd.

2. Grain Size Parameters (calculated on a clay-free basis).

	<u>$M_z(\phi)$</u>	<u>$\sigma_I(\phi)$</u>	<u>Sk_I</u>	<u>K_G</u>
E (0-0.15)	4.0	2.3	+ 0.04	0.75
E (0.15-0.25)	4.1	2.3	+ 0.03	0.88
E 13	4.4	2.4	- 0.19	0.70
E 12	4.1	2.4	+ 0.04	0.76
E 11	4.1	2.3	- 0.01	0.80
E 10	4.7	2.5	- 0.11	0.81
E 9	4.6	2.4	- 0.19	0.85
E 8	4.6	2.4	- 0.23	0.87
E 7	4.2	1.6	- 0.29	0.88
E 6	5.3	1.7	+ 0.05	1.48
E 5	5.4	1.5	+ 0.14	1.29
E 4	5.5	1.6	+ 0.11	1.34
E 3	4.6	2.2	- 0.20	0.93
E 2	4.5	2.0	- 0.08	0.72
E 1	3.1	2.6	+ 0.11	0.83
Dune Sand	1.95	1.13	+ 0.14	2.00

APPENDIX II. contd.

3. Quartz Grain Size Distribution (gm)

	Size Fraction (μm)							
	>500	500-250	250-125	125-63	63-20	20-5	5-2	< 2
E (0-0.15)	nd	nd	nd	nd	0.76	0.23	0.01	-
E (0.15-0.25)	nd	nd	nd	nd	0.45	0.26	0.04	-
E 13	nd	nd	nd	nd	0.38	0.31	0.01	-
E 12	0.02	0.01	0.24	0.38	0.94	0.23	0.02	-
E 11	tr	0.04	0.03	0.13	0.40	1.08	0.02	-
E 10	tr	0.01	0.08	0.08	2.10	0.66	0.06	-
E 9	tr	0.03	0.02	0.10	1.01	1.24	0.02	-
E 8	-	0.08	0.05	0.14	2.52	0.87	0.03	-
E 7	tr	0.01	0.03	0.08	3.50	1.16	0.08	-
E 6	tr	tr	0.06	0.08	5.18	1.73	0.17	-
E 5	tr	tr	0.10	0.24	6.15	2.02	0.11	-
E 4	tr	0.02	0.23	0.22	5.21	1.76	0.14	-
E 3	0.01	0.04	0.32	0.14	3.72	1.42	0.07	-
E 2	0.01	0.04	0.65	0.23	2.79	1.20	0.05	-
E 1	0.01	0.01	1.22	0.15	1.96	0.88	0.02	-
Dune Sand	nd	nd	nd	nd	nd	tr	tr	-

APPENDIX II. contd.

4. Egmont Loam Point Count Data. A. 125-63 μm size fraction (counts)

	Augite	Hypersthene	Hornblende (green)	Hornblende (brown)	K- feldspar	Plagioclase	Quartz	Andesitic glass	Rhyolitic glass	*Others	Total counts
E (0-0.15m)	21	16	12	1	-	121	18	211	28	12	340
E (0.15- 0.25m)	21	20	12	1	-	143	28	197	32	17	471
E 13	14	14	6	-	-	115	13	228	5	8	403
E 12	39	14	8	-	-	161	12	311	10	8	563
E 11	20	15	4	-	-	94	8	169	4	5	319
E 10	26	8	4	-	-	191	15	188	7	8	447
E 9	22	13	2	-	-	82	5	209	9	10	352
E 8	27	7	5	-	-	129	18	188	12	14	400
E 7	21	19	3	-	-	133	25	134	4	24	363
E 6	36	20	6	1	1	200	55	129	15	20	483
E 5	31	18	5	-	-	119	37	72	13	13	308
E 4	24	9	12	3	-	115	43	89	19	22	336
E 3	17	20	9	-	-	118	31	104	21	18	338
E 2	26	11	15	1	-	92	49	190	9	32	425
E 1	19	9	9	1	-	120	17	125	14	12	316
Dune Sand	21	17	9	3	-	206	10	137	-	30	433

* Includes titanomagnetite, epidote group minerals, biotite, muscovite, chlorite, zircon.

APPENDIX II. contd.

4. Egmont Loam Point Count Data. B. 63-20 μm size fraction (counts)

	Augite	Hypersthene	Hornblende (green)	Hornblende (brown)	K- feldspar	Plagioclase	Quartz	Andesitic glass	Rhyolitic glass	*Others	Total counts
E (0-0.15m)	11	40	8	-	-	136	32	143	13	32	415
E (0.15- 0.25m)	17	44	12	-	-	241	34	237	32	58	675
E 13	15	29	8	-	-	177	28	242	58	60	617
E 12	6	31	1	-	-	150	31	153	14	21	407
E 11	14	13	3	1	-	262	35	191	11	46	576
E 10	13	24	6	-	-	223	69	163	18	29	547
E 9	10	27	4	-	1	218	87	325	22	52	746
E 8	5	15	1	-	-	174	63	160	9	26	453
E 7	13	33	1	-	-	248	254	38	14	74	675
E 6	11	17	1	1	-	160	186	25	8	42	451
E 5	12	12	4	-	-	203	259	27	9	46	572
E 4	3	21	3	-	1	172	180	16	7	51	454
E 3	18	24	4	-	1	227	158	22	9	42	495
E 2	12	28	1	1	2	220	100	26	9	26	425
E 1	18	25	6	2	1	224	130	107	21	37	571
Dune Sand	3	8	-	-	1	191	9	106	1	8	327

* Includes titanomagnetite, epidote group minerals, biotite, muscovite, chlorite, zircon.

APPENDIX II. contd.

5. Egmont loam, key to sample nomenclature.

<u>Sample</u>	<u>Depth (m)</u>
E (0-0.15)	0-0.15
E (0.15-0.25)	0.15-0.25
E 13	0.25-0.35
E 12	0.35-0.45
E 11	0.45-0.55
E 10	0.55-0.65
E 9	0.65-0.75
E 8	0.75-0.85
E 7	0.85-0.95
E 6	0.95-1.05
E 5	1.05-1.15
E 4	1.15-1.25
E 3	1.25-1.35
E 2	1.35-1.45
E 1	1.45-1.55
Dune Sand	> 1.55 m

APPENDIX III. Kiripaka silt loam - grain size and point count data, key to sample nomenclature.

1. Grain Size Distribution (gm)

	Size Fraction (μm)										
	>4000	4000-2000	2000-1000	1000-500	500-250	250-125	125-63	63-20	20-5	5-2	< 2
Kp 1	-	0.08	0.19	0.34	0.82	1.65	2.17	4.75	6.85	2.27	26.09
Kp 2	-	1.23	0.52	0.59	1.23	2.55	3.30	5.55	7.67	3.09	28.17
Kp 3	-	0.56	0.35	0.50	1.01	2.17	2.93	4.95	7.86	3.42	32.30
Kp 4	-	0.33	0.28	0.36	0.76	1.26	1.45	3.18	6.93	2.90	39.18
Kp 5	-	0.16	0.21	0.40	0.75	1.25	1.51	3.65	7.06	2.97	43.38
Kp 6	-	0.88	0.22	0.34	0.59	1.10	1.50	3.90	8.26	3.66	41.24
Kp 7	-	0.19	0.21	0.29	0.44	0.71	1.13	4.44	8.56	4.07	50.00
Kp 8	-	0.05	0.19	0.31	0.30	0.36	0.61	3.04	8.50	5.26	51.45
Kp 9	-		0.17	0.28	0.26	0.30	0.51	2.98	8.64	2.55	57.70
Kp 10	-	0.09	0.24	0.33	0.31	0.29	0.53	2.86	7.61	3.30	54.27
Kp 11	-	0.06	0.26	0.47	0.56	0.62	0.72	3.60	9.05	4.18	54.02

APPENDIX III. contd.

2. Grain Size Parameters (calculated on a clay-free basis)

	$M_z(\phi)$	$\sigma_I(\phi)$	Sk_I	K_G
Kp 1	5.33	2.23	- 0.24	1.01
Kp 2	4.93	2.61	- 0.44	1.02
Kp 3	4.98	2.19	- 0.29	0.92
Kp 4	5.50	2.30	- 0.33	0.94
Kp 5	5.55	2.16	- 0.26	0.97
Kp 6	5.67	2.43	- 0.37	1.15
Kp 7	6.12	1.90	- 0.26	1.04
Kp 8	6.50	1.74	- 0.34	1.16
Kp 9	6.30	1.60	- 0.35	1.26
Kp 10	6.37	1.99	- 0.38	1.40
Kp 11	6.25	1.96	- 0.34	1.19

3. Quartz Grain Size Distribution (gm)

		Size Fraction (μm)						
		>1000	1000-125	125-63	63-20	20-5	5-2	< 2
Kp 1	nd	nd	nd	0.69	0.71	0.27	nd	
Kp 2	nd	nd	nd	0.63	0.65	0.25	nd	
Kp 3	0.002	0.36	0.31	0.70	0.84	0.21	tr	
Kp 4	nd	nd	nd	0.82	1.03	0.45	nd	
Kp 5	nd	nd	nd	1.21	1.05	0.44	nd	
Kp 6	nd	nd	nd	1.30	1.23	0.44	nd	
Kp 7	nd	nd	nd	1.67	1.21	0.67	nd	
Kp 8	-	0.14	0.26	1.39	2.05	1.10	tr	
Kp 9	nd	nd	nd	1.75	2.02	1.15	nd	
Kp 10	nd	nd	nd	1.56	1.72	1.64	nd	
Kp 11	nd	nd	nd	1.34	1.66	1.20	nd	

APPENDIX III. contd.

4. Point Count Data.

	125-63 μm		63-20 μm	
	Rhyolitic glass	Total	Rhyolitic glass	Total
Kp 1	171	389	139	336
Kp 2	139	338	148	338
Kp 3	171	364	150	380
Kp 4	95	386	42	377
Kp 5	10	302	22	399
Kp 6	8	339	9	417
Kp 7	4	347	8	379
Kp 8	7	441	5	372
Kp 9	4	355	4	391
Kp 10	4	311	4	327
Kp 11	1	397	3	377

5. Key to Sample Nomenclature.

	<u>Depth (m)</u>
Kp 1	0-0.1
Kp 2	0.1-0.2
Kp 3	0.2-0.3
Kp 4	0.3-0.4
Kp 5	0.4-0.5
Kp 6	0.5-0.6
Kp 7	0.6-0.7
Kp 8	0.7-0.8
Kp 9	0.8-0.9
Kp 10	0.9-1.0
Kp 11	1.0-1.1

APPENDIX IV. Whatitiri Silt Loam - Grain Size Data

1. Grain Size Distribution (gm)

	Size Fraction (μm)										
	<4000	4000-2000	2000-1000	1000-500	500-250	250-125	125-63	63-20	20-5	5-2	> 2
WI 1	-	0.77	0.51	0.27	0.26	0.51	1.17	6.40	7.04	2.45	41.20
WI 2	-	0.02	0.10	0.14	0.17	0.35	0.64	2.45	6.23	1.71	46.96
WI 3	-	0.04	0.04	0.09	0.09	0.20	0.39	2.11	5.18	1.95	55.12
WI 4	-	-	0.04	0.80	0.11	0.13	0.30	1.74	5.00	1.50	52.50
WI 5	-	-	0.09	0.09	0.12	0.13	0.25	1.61	4.35	1.28	57.90
WI 6	-	0.32	0.10	0.11	0.14	0.18	0.28	1.65	3.89	1.65	57.31
WI 7	-	-	0.17	0.15	0.18	0.24	0.39	1.43	5.25	1.60	55.27
WI 8	3.56	0.30	0.21	0.23	0.29	0.42	0.54	2.14	6.10	2.83	42.36
WI 8a	-	0.51	0.13	0.20	0.25	0.33	0.51	2.15	6.34	2.09	60.99
WI 9	-	0.10	0.24	0.39	0.49	0.65	1.03	3.25	11.20	2.68	46.71
WI 10	4.26	0.36	0.41	0.53	0.82	1.29	1.60	4.34	13.32	2.29	37.83
WI 11	-	4.42	0.76	0.90	1.19	1.61	2.12	5.30	15.42	2.94	32.42

APPENDIX IV contd.

2. Grain Size Parameters (calculated on a clay-free basis)

	$M_z(\phi)$	$\sigma_I(\phi)$	Sk_I	K_G
WI 1	5.42	2.22	- 0.19	1.56
WI 2	6.13	1.66	- 0.26	1.21
WI 3	6.35	1.55	- 0.21	1.06
WI 4	6.02	2.07	- 0.38	1.38
WI 5	6.32	1.51	- 0.25	1.18
WI 6	6.22	2.11	- 0.39	1.49
WI 7	6.30	1.75	- 0.39	1.43
WI 8	4.07	3.78	- 0.53	1.61
WI 8a	6.05	2.16	- 0.46	1.55
WI 9	6.10	1.80	- 0.51	1.39
WI 10	3.98	3.43	- 0.60	0.92
WI 11	4.53	3.08	- 0.57	0.98

3. Quartz Grain Size Distribution (gm)

	Size Fractions (μm)						
	>1000	1000-125	125-63	63-20	20-5	5-2	< 2
WI 1	nd	nd	nd	1.07	1.04	0.50	nd
WI 2	-	0.08	0.19	0.95	1.19	0.39	tr
WI 3	nd	nd	nd	0.97	0.94	0.46	nd
WI 4	nd	nd	nd	0.84	1.16	0.34	nd
WI 5	nd	nd	nd	0.68	0.97	0.30	nd
WI 6	nd	nd	nd	0.69	0.74	0.26	nd
WI 7	nd	nd	nd	0.41	0.55	0.13	nd
WI 8a	-	0.04	0.09	0.46	0.40	0.15	tr
WI 9	nd	nd	nd	0.18	tr	0.07	nd
WI 10	nd	nd	nd	0.07	tr	0.02	nd
WI 11	nd	nd	nd	0.04	tr	0.01	nd

APPENDIX IV. contd.

4. Point Count Data.

	125-63 μ m			63-20 μ m		
	Rhyolitic glass	Olivine	Total	Rhyolitic glass	Olivine	Total
WI 1	109	9	261	70	51	409
WI 2	223	2	366	91	23	313
WI 3	200	-	370	109	5	428
WI 4	105	-	417	79	2	323
WI 5	15	-	241	47	1	360
WI 6	8	-	255	25	-	320
WI 7	2	-	329	5	-	270
WI 8	1	-	331	2	-	314
WI 8a	2	-	411	6	-	376
WI 9	1	-	354	-	-	336
WI 10	-	-	360	3	-	380
WI 11	-	-	390	2	-	362

5. Key to Sample Nomenclature

	Depth (m)
WI 1	0-0.1
WI 2	0.1-0.2
WI 3	0.2-0.3
WI 4	0.3-0.4
WI 5	0.4-0.5
WI 6	0.5-0.6
WI 7	0.6-0.7
WI 8*	0.7-0.8
WI 8a	0.7-0.8
WI 9	0.8-0.9
WI 10	0.9-1.0
WI 11	1.0-1.1

* Contains moa crop stones.

APPENDIX V. Waiotu friable clay - grain size and point count data, key to sample nomenclature.

1. Grain Size Distribution (gm)

	Size Fraction (μm)										
	>4000	4000-2000	2000-1000	1000-500	500-250	250-125	125-63	63-20	20-5	5-2	<2
Y0 1	-	0.64	0.78	0.98	0.60	0.38	0.35	2.26	6.91	2.31	43.62
Y0 2	-	1.00	1.28	1.35	0.64	0.37	0.39	2.09	6.24	2.35	45.20
Y0 3	-	0.75	1.14	1.08	0.59	0.32	0.30	1.90	6.04	2.20	47.31
Y0 4	-	1.60	0.63	0.91	0.57	0.29	0.24	1.73	5.68	1.91	45.57
Y0 5	-	1.70	0.86	0.82	0.54	0.32	0.23	1.48	4.12	1.71	50.27
Y0 6	-	1.22	0.71	0.60	0.44	0.26	0.18	1.05	3.87	1.42	51.67
Y0 7	-	0.62	0.64	0.51	0.42	0.26	0.16	1.15	4.01	1.64	50.69
Y0 8	-	0.35	0.61	0.48	0.45	0.31	0.21	1.69	4.86	2.19	49.24
Y0 9	-	0.15	0.39	0.43	0.44	0.34	0.25	1.83	6.17	2.67	45.33
Y0 10	-	1.41	0.59	0.49	0.56	0.50	0.44	2.46	7.27	3.51	43.44
Y0 11	-	2.32	0.75	0.68	0.75	0.71	0.75	3.22	7.32	3.71	40.80
Y0 12	-	3.59	0.59	0.73	0.79	0.77	0.98	3.15	8.13	3.49	40.61
Y0 13	-	0.45	0.58	0.90	1.06	1.07	1.30	3.94	9.71	3.61	38.94
Y0 140-150	-	1.74	1.46	1.75	1.80	1.76	1.82	4.47	7.57	3.12	32.76
Y0 240-250	-	0.87	1.36	1.49	1.79	2.69	4.07	7.78	11.75	3.88	25.10

2. Grain Size Parameters (calculated on a clay-free basis)

	$M_z(\phi)$	$\sigma_I(\phi)$	Sk_I	K_G
YO 1	4.95	3.00	- 0.55	1.22
YO 2	4.53	3.27	- 0.53	0.65
YO 3	4.63	3.22	- 0.56	0.78
YO 4	4.44	3.42	- 0.58	0.68
YO 5	4.10	3.58	- 0.51	0.62
YO 6	4.30	3.49	- 0.56	0.63
YO 7	4.78	3.24	- 0.57	0.79
YO 8	5.30	2.86	- 0.52	1.32
YO 9	6.13	2.22	- 0.38	1.48
YO 10	5.17	3.07	- 0.53	1.25
YO 11	4.63	3.34	- 0.50	0.87
YO 12	5.42	2.65	- 0.46	1.18
YO 13	5.45	2.49	- 0.43	1.09
YO 140-150	4.30	3.12	- 0.30	0.78
YO 240-250	4.87	2.57	- 0.28	0.96

3. Quartz Grain Size Distribution (gm)

	Size Fractions (μm)						
	>1000	1000-125	125-63	63-20	20-5	5-2	<2
YO 1	nd	nd	nd	0.91	1.53	0.43	nd
YO 2	nd	nd	nd	0.88	1.49	0.40	nd
YO 3	-	0.18	0.15	0.80	1.65	0.42	0.07
YO 4	nd	nd	nd	0.72	1.57	0.36	nd
YO 5	nd	nd	nd	0.53	1.03	0.27	nd
YO 6	0.01	0.11	0.07	0.37	0.56	0.12	tr
YO 7	nd	nd	nd	0.17	0.26	0.06	nd
YO 8	nd	nd	nd	0.10	0.16	tr	nd
YO 9	nd	nd	nd	0.13	0.05	tr	nd
YO 10	nd	nd	nd	0.06	0.08	tr	nd
YO 11	nd	nd	nd	0.01	0.01	tr	nd
YO 12	nd	nd	nd	tr	0.02	tr	nd
YO 13	nd	nd	nd	0.01	0.01	tr	nd
YO 140-150	nd	nd	nd	tr	tr	tr	nd
YO 240-250	nd	nd	nd	tr	tr	tr	nd

APPENDIX V. contd.

4. Point Count Data.

	125-63 μm		63-20 μm	
	Rhyolitic glass	Total	Rhyolitic glass	Total
Y0 1	76	321	34	434
Y0 2	102	270	67	517
Y0 3	66	290	30	337
Y0 4	28	391	19	463
Y0 5	13	430	18	507
Y0 6	8	360	10	617
Y0 7	-	355	2	520
Y0 8	5	380	3	493
Y0 9	-	420	-	414
Y0 10	-	404	-	378
Y0 11	-	231	-	394
Y0 12	-	350	-	418
Y0 13	-	322	-	373
Y0 150-160	-	275	-	432
Y0 240-250	-	359	-	349

5. Key to Sample Nomenclature.

	Depth (m)
Y0 1	0-0.1
Y0 2	0.1-0.2
Y0 3	0.2-0.3
Y0 4	0.3-0.4
Y0 5	0.4-0.5
Y0 6	0.5-0.6
Y0 7	0.6-0.7
Y0 8	0.7-0.8
Y0 9	0.8-0.9
Y0 10	0.9-1.0
Y0 11	1.0-1.1
Y0 12	1.1-1.2
Y0 13	1.2-1.3
Y0 150-160	1.5-1.6
Y0 240-250	2.4-2.5

APPENDIX IV. Kerikeri friable clay - grain size and point count data, key to sample nomenclature.

1. Grain Size Distribution

	Size Fraction (μm)										
	>4000	4000-2000	2000-1000	1000-500	500-250	250-125	125-63	63-20	20-5	5-2	<2
Ke 1	-	-	0.10	0.50	0.58	0.77	0.73	3.31	9.62	3.77	29.86
Ke 2	-	0.65	1.48	1.04	0.55	0.44	0.87	3.52	10.91	3.44	36.93
Ke 3	-	0.83	0.95	0.56	0.38	0.33	0.62	2.93	9.75	4.20	39.83
Ke 4	-	0.64	0.85	0.62	0.42	0.28	0.34	2.60	10.31	3.11	44.60
Ke 5	-	1.00	0.67	0.63	0.44	0.27	0.22	2.08	10.98	3.52	52.23
Ke 6	-	0.49	0.60	0.62	0.44	0.30	0.25	2.96	10.13	3.37	43.97
Ke 7	-	0.12	0.33	0.48	0.43	0.32	0.29	4.60	10.00	4.05	44.22
Ke 8	-	0.06	0.23	0.37	0.45	0.53	0.61	7.30	12.29	4.02	45.62

APPENDIX VI. contd.

2. Grain Size Parameters (calculated on a clay-free basis).

	$M_z(\phi)$	$\sigma_I(\phi)$	Sk_I	K_G
Ke 1	6.23	1.83	- 0.40	1.28
Ke 2	5.20	2.78	- 0.56	1.27
Ke 3	5.83	2.49	- 0.51	1.49
Ke 4	6.07	2.24	- 0.50	1.70
Ke 5	5.90	2.38	- 0.61	1.85
Ke 6	6.15	2.04	- 0.51	1.58
Ke 7	6.35	1.75	- 0.30	1.36
Ke 8	6.18	1.63	- 0.23	1.11

3. Quartz Grain Size Distribution

	Size Fractions (μm)						
	>1000	1000-125	125-63	63-20	20-5	5-2	<2
Ke 1	nd	nd	nd	0.32	0.42	0.17	nd
Ke 2	tr	0.09	0.08	0.35	0.45	0.12	tr
Ke 3	nd	nd	nd	0.27	0.47	0.15	nd
Ke 4	nd	nd	nd	0.33	0.50	0.04	nd
Ke 5	nd	nd	nd	0.29	0.34	0.13	nd
Ke 6	-	0.09	0.05	0.30	0.24	0.13	tr
Ke 7	nd	nd	nd	0.18	0.30	0.11	nd
Ke 8	nd	nd	nd	0.05	tr	tr	nd

APPENDIX VI. contd.

4. Point Count Data.

	125-63 μm		63-20 μm	
	Rhyolitic glass	Total	Rhyolitic glass	Total
Ke 1	187	342	170	497
Ke 2	223	329	190	541
Ke 3	242	331	115	544
Ke 4	180	369	22	316
Ke 5	44	272	38	565
Ke 6	9	263	10	592
Ke 7	2	307	1	382
Ke 8	2	307	-	397

5. Key to Sample Nomenclature

	Depth (m)
Ke 1	0-0.1
Ke 2	0.1-0.2
Ke 3	0.2-0.3
Ke 4	0.3-0.4
Ke 5	0.4-0.5
Ke 6	0.5-0.6
Ke 7	0.6-0.7
Ke 8	0.7-0.8

APPENDIX VII. Ruatangata friable clay - grain size and point count data, key to sample nomenclature.

1. Grain Size Distribution (gm)

	Size Fraction (μm)										
	>4000	4000-2000	2000-1000	1000-500	500-250	250-125	125-63	63-20	20-5	5-2	< 2
Rt 1	-	0.11	0.53	3.09	1.77	1.06	1.49	5.40	9.24	2.05	38.14
Rt 2	-	-	0.93	3.34	1.39	0.82	1.45	5.19	8.45	1.82	43.23
Rt 3	-	0.01	1.01	2.59	1.25	0.64	1.14	4.10	8.52	1.20	46.63
Rt 4	-	0.08	1.25	2.66	1.46	0.61	0.80	3.83	8.05	1.85	52.15
Rt 5	-	0.15	0.92	2.35	1.42	0.59	0.78	3.99	7.91	2.05	49.65
Rt 6	-	0.06	0.37	1.46	1.17	0.58	0.79	3.55	6.81	2.02	51.35
Rt 7	-	-	0.07	0.60	0.46	0.40	0.58	2.11	5.68	1.35	57.88
Rt 8	-	-	0.02	0.09	0.19	0.49	0.82	2.97	7.82	5.67	59.92
Rt 9	-	-	-	0.01	0.03	0.19	0.53	1.19	6.32	5.45	55.24
Rt 10	-	-	-	-	0.01	0.06	0.19	0.74	3.47	3.13	58.77
Rt 11	-	-	-	-	0.02	0.05	0.11	0.75	2.20	1.41	61.27
Rt 130-142	-	-	-	-	0.01	0.06	0.15	0.84	3.90	2.31	56.88

APPENDIX VII. contd.

2. Grain Size Parameters (calculated on a clay-free basis)

	$M_z(\phi)$	$\sigma_I(\phi)$	Sk_I	K_G
Rt 1	4.50	2.60	- 0.38	0.79
Rt 2	4.36	2.68	- 0.37	0.74
Rt 3	4.57	2.74	- 0.47	0.81
Rt 4	4.47	2.78	- 0.45	0.68
Rt 5	4.58	2.76	- 0.46	0.74
Rt 6	4.94	2.54	- 0.43	0.98
Rt 7	5.66	2.04	- 0.40	1.21
Rt 8	6.51	1.50	- 0.38	0.97
Rt 9	6.92	1.20	- 0.42	1.10
Rt 10	7.03	1.10	- 0.47	1.03
Rt 11	6.70	1.22	- 0.31	0.87
Rt 130-142	6.88	1.09	- 0.31	0.95

3. Quartz Grain Size Distribution (gm)

	Size Fractions (μm)						
	>1000	1000-125	125-63	63-20	20-5	5-2	<2
Rt 1	nd	nd	nd	3.20	4.20	0.75	nd
Rt 2	nd	nd	nd	3.26	4.23	0.79	nd
Rt 3	tr	0.53	0.66	2.87	3.85	0.96	0.02
Rt 4	nd	nd	nd	3.04	1.69	0.89	nd
Rt 5	nd	nd	nd	3.16	1.89	0.99	nd
Rt 6	nd	nd	nd	2.53	2.53	0.71	nd
Rt 7	-	0.26	0.24	1.14	2.57	0.19	0.03
Rt 8	nd	nd	nd	0.53	3.13	0.11	nd
Rt 9	nd	nd	nd	0.16	1.82	0.06	nd
Rt 10	nd	nd	nd	0.16	0.35	0.04	nd
Rt 11	nd	nd	nd	0.30	0.09	0.06	nd
Rt 130-142	-	tr	0.06	0.35	0.44	0.09	tr

APPENDIX VII. contd.

4. Point Count Data.

	125-63 μm		63-20 μm	
	Rhyolitic glass	Total	Rhyolitic glass	Total
Rt 1	150	305	204	471
Rt 2	147	308	121	350
Rt 3	132	347	73	376
Rt 4	33	298	38	385
Rt 5	14	338	36	451
Rt 6	18	442	23	479
Rt 7	6	260	13	370
Rt 8	4	344	5	327
Rt 9	-	430	2	355
Rt 10	-	276	-	411
Rt 11	-	358	-	281
Rt 130-142	-	326		375

5. Key to Sample Nomenclature.

	Depth (m)
Rt 1	0-0.1
Rt 2	0.1-0.2
Rt 3	0.2-0.3
Rt 4	0.3-0.4
Rt 5	0.4-0.5
Rt 6	0.5-0.6
Rt 7	0.6-0.7
Rt 8	0.7-0.8
Rt 9	0.8-0.9
Rt 10	0.9-1.0
Rt 11	1.0-1.1
Rt 130-142	1.3-1.4

APPENDIX VIII. Okaihau gravelly clay - grain size and point count data, key to sample nomenclature.

1. Grain Size Distribution (gm)

	Size Fraction (μm)										
	>4000	4000-2000	2000-1000	1000-500	500-250	250-125	125-63	63-20	20-5	5-2	<2
Ok 1	0.41	0.21	0.89	0.94	0.46	0.30	0.67	3.52	5.14	1.32	13.67
Ok 2	8.14	0.76	5.98	2.93	1.55	1.24	2.37	10.48	16.30	5.44	49.07
Ok 3	7.83	6.89	4.45	0.85	0.34	0.23	0.53	2.60	4.12	0.98	12.90
Ok 4	3.74	11.63	2.34	0.61	0.24	0.14	0.32	1.78	3.18	0.85	10.06
Ok 5	4.26	5.21	2.66	1.07	0.46	0.31	0.51	2.94	4.70	1.53	16.22
Ok 6	1.91	0.68	0.95	0.64	0.33	0.24	0.41	2.68	4.58	1.55	17.90
Ok 7	2.73	0.37	0.36	0.30	0.23	0.21	0.27	2.08	3.68	1.55	18.81
Ok 8	1.83	0.47	0.30	0.31	0.24	0.20	0.26	1.67	3.14	1.50	17.87
Ok 9	2.64	2.18	2.18	1.22	0.59	0.34	0.21	1.80	2.28	1.18	17.71

APPENDIX VIII. contd.

2. Grain Size Parameters (calculated on a clay-free basis)

	$M_z(\phi)$	$\sigma_I(\phi)$	Sk_I	K_G
Ok 1	6.02	1.32	0.009	0.91
Ok 2	6.17	1.40	- 0.10	0.85
Ok 3	6.05	1.44	- 0.95	0.95
Ok 4	4.65	2.87	- 0.49	0.66
Ok 5	6.28	1.39	- 0.09	0.85
Ok 6	5.85	1.03	- 2.63	1.56
Ok 7	5.98	1.04	- 2.09	1.28
Ok 8	5.75	0.04	0.82	1.40
Ok 9	5.83	0.85	0.84	1.18

3. Quartz Grain Size Distribution (gm)

	Size Fractions (μm)						
	>1000	1000-125	125-63	63-20	20-5	5-2	< 2
Ok 1	nd	nd	nd	1.77	1.29	0.21	nd
Ok 2	-	0.83	1.04	5.39	3.05	1.01	tr
Ok 3	nd	nd	nd	1.93	1.06	0.17	nd
Ok 4	-	0.10	0.20	1.05	0.86	0.14	tr
Ok 5	nd	nd	nd	1.73	1.27	0.23	nd
Ok 6	nd	nd	nd	1.16	0.84	0.23	nd
Ok 7	nd	nd	nd	0.25	0.68	0.04	nd
Ok 8	nd	nd	nd	0.06	0.05	0.01	nd
Ok 9	nd	nd	nd	-	tr	-	nd

APPENDIX VIII. contd.

4. Point Count Data.

	125-63 μm		63-20 μm	
	Rhyolitic glass	Total	Rhyolitic glass	Total
Ok 1	206	345	166	315
Ok 2	187	352	136	581
Ok 3	97	373	69	472
Ok 4	45	354	33	360
Ok 5	9	350	15	451
Ok 6	3	334	5	345
Ok 7	1	211	-	337
Ok 8	-	281	-	366
Ok 9	-	267	-	323

5. Key to Sample Nomenclature.

	Depth (m)
Ok 1	0-0.1
Ok 2	0.1-0.2
Ok 3	0.2-0.3
Ok 4	0.3-0.4
Ok 5	0.4-0.5
Ok 6	0.5-0.6
Ok 7	0.6-0.7
Ok 8	0.7-0.8
Ok 9	1.1-1.2

APPENDIX IX. Southern North Island Chronosequence - Grain size data and key to sample nomenclature.

1. Grain Size Distribution (gm)

Size Fraction (μm)	Burrell	Inglewood (0-0.15)	Inglewood (0.15-0.25)	Opua (0-0.1)	Opua (0.1-0.2)	Opua (0.2-0.3)	Opua (0.3-0.4)	Pungarehu Formation	Oruanui
> 16000	2.38	-	3.91	-	-	-	-	nd	-
16000-8000	24.00	11.96	6.77	-	-	-	-	nd	-
8000-4000	40.58	11.41	8.87	-	-	-	-	nd	-
4000-2000	37.74	9.72	12.25	-	-	-	4.81	24.85	0.94
2000-1000	63.16	16.17	19.22	0.01	0.03	-	0.32	14.15	0.63
1000-500	66.96	22.01	17.92	0.04	0.09	0.02	0.50	24.09	1.86
500-250	8.49	22.35	16.20	0.50	1.35	2.80	10.67	24.43	3.58
250-125	13.27	26.92	17.44	6.23	7.50	10.77	22.73	11.90	5.34
125-63	18.08	21.92	15.36	12.41	8.85	11.35	20.37	7.56	7.89
63-20	30.15	34.85	23.21	17.77	11.51	2.29	22.32	7.18	8.82
20-5	27.22	30.03	17.39	32.58	13.99	7.07	23.66	5.58	7.36
5-2	4.66	6.19	2.65	7.50	4.47	1.49	6.53	1.65	1.00
< 2	6.12	11.80	7.32	32.57	17.72	27.09	39.86	7.33	1.10

APPENDIX IX. contd.

2. Grain Size Parameters (calculated on a clay-free basis)

	$M_z(\phi)$	$\sigma_I(\phi)$	Sk_I	K_G
Burrell	- 0.2	3.3	- 0.20	1.10
Inglewood (0-0.15)	2.5	3.3	- 0.05	0.94
Inglewood (0.15-0.25)	1.9	3.2	+ 0.01	0.86
Opuā (0-0.1)	5.4	1.7	- 0.13	0.79
Opuā (0.1-0.2)	4.9	1.9	+ 0.08	0.74
Opuā (0.2-0.3)	4.1	1.9	+ 0.47	0.95
Opuā (0.3-0.4)	4.1	2.2	+ 0.20	0.91
Pungarehu Formation	0.96	2.4	+ 0.12	1.21
Oruanui	3.87	2.2	- 0.01	0.98

3. Key to Sample Nomenclature.

	Depth (m)
Burrell	0-0.15
Inglewood	0-0.15
Inglewood	0.15-0.25
Opuā	0-0.1
Opuā	0.1-0.2
Opuā	0.2-0.3
Opuā	0.3-0.4
Pungarehu Formation	> 0.4
Oruanui	0-0.15

APPENDIX IX. contd.

4. Quartz Grain Size Distribution (gm)

	Size Fractions (μm)					
	>125	125-63	63-20	20-5	5-2	< 2
Burrell	-	tr	0.03	0.23	0.02	-
Inglewood (0-0.15)	-	0.05	0.70	0.72	0.20	-
Inglewood (0.15-0.25)	-	0.02	0.25	0.21	tr	-
Opua (0-0.1)	-	0.01	0.59	0.52	0.10	-
Opua (0.1-0.2)	-	0.10	0.54	0.21	0.06	-
Opua (0.2-0.3)	-	0.02	0.09	0.09	0.02	-
Opua (0.3-0.4)	-	0.03	0.78	0.31	0.09	-
Pungarehu	-	-	-	-	tr	-
Oruanui	-	tr	tr	0.07	0.01	-

APPENDIX X. Core P69 Data Summary.

1. Grain Size Distribution (gm)

Sample	Size Fraction (μm)				
	>63	63-20	20-5	5-2	< 2
1/4/1	0.49	0.05	7.60	2.22	6.17
1/4/2	0.69	0.36	8.53	2.50	7.14
1/4/3	0.75	0.30	9.07	2.34	7.38
1/4/4	0.97	0.33	10.04	1.92	8.59
1/4/5	1.20	0.27	10.89	2.14	8.88
1/4/6	1.36	0.34	11.04	4.70	8.21
1/4/7	1.78	0.46	11.30	3.34	9.96
1/4/8	2.18	0.26	10.80	1.59	11.24
1/4/9	1.32	0.77	10.64	2.18	10.17
1/4/10	1.31	0.59	9.45	1.29	11.71
1/4/11	1.48	0.46	11.69	1.68	10.09
1/4/12	1.07	1.03	10.70	2.07	10.53
1/4/13	0.96	0.39	11.02	2.49	9.80
1/4/14	1.56	0.44	10.36	1.80	9.37
1/4/15	1.25	0.33	9.24	1.96	8.84
1/4/16	1.27	0.33	8.61	1.53	10.26
2/4/1	1.76	0.49	8.68	3.29	7.80
2/4/2	1.38	2.93	6.73	3.12	8.00
2/4/3	2.03	4.04	7.07	2.90	7.80
2/4/4	1.68	3.79	6.88	2.93	7.70
2/4/5	0.98	2.11	6.54	2.89	7.99
2/4/6	0.66	3.42	6.04	2.76	7.27
2/4/7	0.56	1.87	6.50	2.91	7.66
2/4/8	0.42	2.86	9.21	4.03	8.97
2/4/9	0.58	4.04	9.02	3.74	9.15
2/4/10	0.16	3.02	7.53	3.89	9.09
2/4/11	0.29	4.11	7.61	3.84	9.05
2/4/12	0.22	3.28	7.92	3.84	9.31
2/4/13	0.15	3.62	7.37	3.79	8.95
2/4/14	0.23	3.82	7.74	3.82	9.32
2/4/15	0.17	2.90	4.06	2.06	3.87
2/4/16	0.21	2.32	7.23	3.51	6.11
3/4/1	0.36	1.51	9.80	3.71	9.06
3/4/2	0.31	3.58	7.82	3.65	9.50
3/4/3	0.31	3.28	7.65	3.83	9.62
3/4/4	0.36	2.87	6.94	3.39	8.81
3/4/5	0.22	3.86	7.77	3.86	9.45
3/4/6	0.51	4.74	7.33	3.67	8.75
3/4/7	0.95	6.56	8.19	3.52	7.76
3/4/8	0.17	3.39	8.53	4.39	9.90
3/4/9	0.18	2.52	8.95	4.20	10.08
3/4/10	0.18	2.90	7.52	3.79	8.90
3/4/11	0.37	3.26	7.03	3.39	8.75
3/4/12	0.33	3.67	7.30	3.84	9.37
3/4/13	0.28	2.70	7.92	3.89	9.99
3/4/14	0.20	3.05	7.81	3.93	9.77
3/4/15	0.25	3.04	7.93	3.69	9.84
3/4/16	0.32	3.47	7.41	3.80	9.70

APPENDIX X. contd.

Sample	Size Fraction (μm)				
	> 63	63-20	20-5	5-2	< 2
4/4/1	0.19	3.06	8.17	3.83	9.50
4/4/2	0.29	3.23	7.91	3.60	9.00
4/4/3	0.55	3.34	8.10	3.60	8.80
4/4/4	0.23	3.09	8.21	3.64	8.00
4/4/5	0.27	3.28	10.26	3.00	7.80
4/4/6	0.34	3.10	7.87	3.53	8.50
4/4/7	2.21	6.49	8.33	3.23	7.40
4/4/8	0.38	3.08	8.42	3.61	8.70
4/4/9	0.17	2.88	7.99	3.61	8.93
4/4/10	0.86	3.12	8.63	3.28	9.67
4/4/11	0.37	3.00	8.16	3.23	9.07
4/4/12	0.34	3.15	8.15	3.25	8.48
4/4/13	0.32	3.03	7.78	3.89	9.55
4/4/14	0.23	1.94	4.43	2.31	5.99
4/4/15	0.33	3.08	8.08	3.79	10.26
4/4/16	0.33	2.96	8.46	3.90	10.72
4/4/17	0.31	2.87	8.74	3.25	10.20
Catcher	0.31	2.96	7.99	3.03	9.50
Cutter	0.30	2.92	8.14	3.29	9.50
1/4/8T	1.70	0.60	7.24	0.84	5.59
1/4/14T	0.37	0.62	2.35	0.95	3.64
2/4/5T	0.59	2.87	3.20	1.60	4.11
2/4/8T	0.13	2.03	3.62	1.58	3.76

APPENDIX X. contd.

2. Grain Size Parameters (clay-free) and Bulk Density.

	$M_z(\phi)$	$\sigma_I(\phi)$	Sk_I	K_G	B.D. (gm cm ⁻³)
1/4/1	6.99	0.93	- 0.10	1.25	0.39
1/4/2	6.90	1.20	- 0.19	1.62	0.57
1/4/3	6.87	1.22	- 0.22	1.78	0.75
1/4/4	6.75	1.35	- 0.27	2.19	0.86
1/4/5	6.75	1.63	- 0.32	2.80	0.83
1/4/6	7.01	1.70	- 0.28	2.25	0.91
1/4/7	6.78	1.90	- 0.32	2.74	0.72
1/4/8	6.40	3.18	- 0.51	5.86	0.90
1/4/9	6.66	1.38	- 0.24	1.95	0.86
1/4/10	6.55	1.46	- 0.29	2.37	0.87
1/4/11	6.61	1.57	- 0.32	2.73	0.91
1/4/12	6.65	1.24	- 0.19	1.62	0.88
1/4/13	6.81	1.25	- 0.24	1.89	1.00
1/4/14	6.62	1.77	- 0.33	2.92	0.91
1/4/15	6.71	1.74	- 0.32	2.79	0.86
1/4/16	6.64	1.81	- 0.33	3.03	0.81
2/4/1	6.90	1.58	- 0.24	1.96	0.91
2/4/2	6.36	1.71	- 0.09	1.07	0.89
2/4/3	6.08	1.76	- 0.07	1.03	0.94
2/4/4	6.18	1.72	- 0.06	1.03	1.00
2/4/5	6.53	1.59	- 0.12	1.17	0.99
2/4/6	6.43	1.52	0.03	0.98	0.93
2/4/7	6.70	1.42	- 0.07	1.12	1.05
2/4/8	6.74	1.32	- 0.02	1.04	1.09
2/4/9	6.54	1.40	0.01	0.99	1.09
2/4/10	6.79	1.36	0.05	0.94	1.01
2/4/11	6.63	1.43	0.08	0.92	0.97
2/4/12	6.72	1.36	0.04	0.95	1.00
2/4/13	6.71	1.38	0.09	0.90	1.02
2/4/14	6.66	1.39	0.07	0.92	0.98
2/4/15	6.50	1.45	0.15	0.92	1.00
2/4/16	6.81	1.32	0.00	0.99	0.92
3/4/1	6.90	1.13	- 0.06	1.13	1.08
3/4/2	6.64	1.38	0.04	0.95	1.03
3/4/3	6.71	1.40	0.03	0.96	1.02
3/4/4	6.69	1.42	0.01	0.98	1.04
3/4/5	6.67	1.39	0.08	0.92	1.02
3/4/6	6.49	1.49	0.10	0.94	1.04
3/4/7	6.24	1.50	0.13	0.96	1.11
3/4/8	6.79	1.35	0.05	0.94	1.09
3/4/9	6.86	1.26	0.00	1.00	0.98
3/4/10	6.78	1.35	0.04	0.95	0.97
3/4/11	6.63	1.43	0.03	0.96	1.00
3/4/12	6.67	1.45	0.06	0.94	0.96
3/4/13	6.79	1.35	0.00	0.99	1.01
3/4/14	6.77	1.36	0.04	0.95	1.03
3/4/15	6.72	1.34	0.02	0.97	1.04
3/4/16	6.68	1.43	0.05	0.94	1.08

APPENDIX X. contd.

	$M_z(\phi)$	$\sigma_I(\phi)$	Sk_I	K_G	B.D. (gm cm ⁻³)
4/4/1	6.75	1.32	0.03	0.96	0.92
4/4/2	6.68	1.36	0.03	0.97	0.99
4/4/3	6.60	1.42	- 0.01	1.01	0.99
4/4/4	6.71	1.31	0.02	0.97	1.05
4/4/5	6.58	1.17	- 0.01	1.01	0.91
4/4/6	6.67	1.36	0.01	0.98	0.95
4/4/7	6.31	2.81	- 0.51	3.08	1.04
4/4/8	6.67	1.34	0.00	1.00	0.99
4/4/9	6.75	1.29	0.03	0.96	0.95
4/4/10	6.51	1.43	- 0.07	1.09	1.02
4/4/11	6.63	1.32	- 0.01	1.01	0.92
4/4/12	6.62	1.32	0.01	0.99	0.92
4/4/13	6.74	1.39	0.02	0.98	0.97
4/4/14	6.70	1.45	0.03	0.97	0.93
4/4/15	6.71	1.37	0.01	0.98	0.89
4/4/16	6.74	1.34	0.00	1.00	0.96
4/4/17	6.65	1.26	- 0.01	1.02	0.92
Catcher	6.61	1.29	0.00	1.00	0.92
Cutter	6.66	1.30	0.00	1.00	nd
1/4/8T	5.84	2.22	0.56	2.98	nd
1/4/14T	6.52	1.59	0.16	1.27	nd
2/4/5T	6.18	1.63	0.14	0.97	nd
2/4/8T	6.53	1.37	0.09	0.93	nd

APPENDIX X. contd.

3. Quartz distribution, biogenic silica and carbonate contents.

	*Quartz (gm) 63-20 μ m	*Quartz (gm) 5-2 μ m	Biogenic silica (%)	Carbonate (%)
1/4/1	0.01	0.04	25	18
1/4/2	0.05	0.03	22	19
1/4/3	0.06	tr	26	19
1/4/4	0.03	0.04	22	19
1/4/5	0.04	0.02	24	18
1/4/6	0.05	0.05	23	17
1/4/7	0.06	0.04	22	19
1/4/8	0.01	0.02	27	17
1/4/9	0.08	0.05	24	18
1/4/10	0.07	0.02	24	19
1/4/11		0.02	25	19
1/4/12	0.14	0.03	24	19
1/4/13	0.05	tr	26	19
1/4/14	0.04	tr	29	20
1/4/15	0.03	0.02	27	21
1/4/16	0.01	0.04	30	21
2/4/1	0.02	0.32	27	20
2/4/2	0.33	0.34	26	18
2/4/3	0.20	0.26	28	15
2/4/4	0.22	0.27	28	16
2/4/5	0.23	0.27	24	17
2/4/6	0.98	0.21	22	19
2/4/7	0.24	0.27	19	18
2/4/8	0.60	0.38	20	16
2/4/9	1.31	0.36	21	15
2/4/10	0.96	0.33	17	16
2/4/11	1.51	0.34	21	17
2/4/12	0.98	0.31	17	16
2/4/13	1.10	0.36	20	18
2/4/14	1.19	0.36	21	16
2/4/15	0.87	0.19	21	16
2/4/16	0.88	0.27	21	16
3/4/1	0.39	0.18	19	16
3/4/2	0.94	0.16	19	15
3/4/3	0.85	0.21	20	18
3/4/4	0.73	0.17	20	15
3/4/5	1.01	0.18	22	16
3/4/6	1.13	0.15	26	14
3/4/7	1.37	0.17	22	11
3/4/8	1.12	0.17	21	14

APPENDIX X. contd.

3.

	*Quartz (gm) 63-20 μ m	*Quartz (gm) 5-2 μ m	Biogenic silica (%)	Carbonate (%)
3/4/9	0.69	0.24	21	15
3/4/10	0.77	0.01	19	18
3/4/11	0.80	0.18	23	18
3/4/12	0.85	0.13	23	18
3/4/13	0.68	0.27	20	16
3/4/14	0.65	0.25	22	16
3/4/15	0.79	0.19	20	15
3/4/16	0.86	0.16	22	17
4/4/1	0.83	0.26	20	18
4/4/2	0.87	0.24	19	18
4/4/3	0.85	0.21	20	18
4/4/4	0.79	0.20	25	16
4/4/5	0.85	0.18	29	15
4/4/6	0.73	0.23	22	17
4/4/7	0.94	0.24	28	11
4/4/8	0.79	0.20	24	14
4/4/9	0.75	0.31	21	14
4/4/10	0.73	0.30	26	16
4/4/11	0.72	0.23	23	16
4/4/12	0.72	0.19	21	17
4/4/13	0.69	0.23	24	17
4/4/14	0.49	0.11	24	17
4/4/15	0.70	0.15	23	16
4/4/16	0.69	0.26	22	17
4/4/17	0.66	0.13	21	18
Catcher	nd	0.20	20	18
Cutter	nd	0.25	19	17
1/4/8T	0.10	0.07	nd	12
1/4/14T	0.08	0.08	nd	17
2/4/5T	0.71	0.09	nd	17
2/4/8T	0.50	0.15	nd	14

APPENDIX X. contd.

4. Point Count Data. (counts)

	125-63 μm		63-20 μm	
	Rhyolitic glass	Total	Rhyolitic glass	Total
1/4/1	807	1985	336	1583
1/4/2	607	1080	217	770
1/4/3	649	1169	73	756
1/4/4	554	917	165	979
1/4/5	697	1045	127	345
1/4/6	667	843	145	601
1/4/7	266	303	190	459
1/4/8	305	336	75	542
1/4/9	640	804	161	506
1/4/10	511	632	239	554
1/4/11	612	716	382	741
1/4/12	527	816	261	742
1/4/13	624	811	215	452
1/4/14	318	396	397	588
1/4/15	465	651	226	354
1/4/16	432	749	123	342
2/4/1	623	1334	299	651
2/4/2	395	764	222	682
2/4/3	672	804	536	1082
2/4/4	694	867	446	744
2/4/5	620	1042	221	701
2/4/6	284	706	152	961
2/4/7	424	901	176	794
2/4/8	273	1096	55	574
2/4/9	74	869	18	476
2/4/10	135	869	16	515
2/4/11	127	1138	21	472
2/4/12	55	613	19	515
2/4/13	69	656	25	591
2/4/14	152	1117	21	361
2/4/15	151	987	31	554
2/4/16	208	952	22	408
3/4/1	212	898	30	425
3/4/2	152	812	56	650
3/4/3	273	1003	71	688
3/4/4	251	790	41	566
3/4/5	242	1038	68	617
3/4/6	530	814	118	485
3/4/7	944	1318	154	399
3/4/8	173	878	28	434
3/4/9	106	699	13	320
3/4/10	188	986	28	594
3/4/11	249	804	49	565
3/4/12	815	1451	64	416
3/4/13	126	959	31	415

APPENDIX X. contd.

	125-63 μm		63-20 μm	
	Rhyolitic glass	Total	Rhyolitic glass	Total
3/4/14	232	706	48	549
3/4/15	132	768	24	375
3/4/16	160	824	67	537
4/4/1	138	751	21	441
4/4/2	356	908	31	450
4/4/3	406	659	56	453
4/4/4	283	859	42	602
4/4/5	440	1013	131	633
4/4/6	451	1254	63	414
4/4/7	811	1327	180	376
4/4/8	519	1149	38	550
4/4/9	227	954	20	452
4/4/10	547	1168	54	375
4/4/11	367	1203	35	391
4/4/12	309	1143	20	381
4/4/13	303	1136	37	509
4/4/14	385	1431	32	496
4/4/15	261	910	55	476
4/4/16	289	1038	48	624
4/4/17	198	742	56	611
Catcher	143	649	nd	nd
Cutter	189	680	nd	nd

APPENDIX X. contd.

5. Tephra Ferromagnesian Mineral Assemblages - Point Count Data (counts)

Tephra	Hypersthene	Clinopyroxene	Hornblende	Cummingtonite	Biotite	Total counts
1. Whakatane Ash	139	3	31	31	-	204
2. Rotoma Ash	271	17	19	40	-	347
3. Waiohau Ash	545	32	12	-	-	589
4. Rerewhakaaitu Ash	93	14	55	-	201	363
5. unidentified	6	2	2	-	-	10
6. Okareka Ash	38	5	59	-	32	134
7. unidentified	5	2	2	-	-	9
8. Kawakawa Tephra	382	-	99	-	-	481
9. Poihipi Tephra	8	2	2	-	-	12
10. Okaia Tephra	4	2	1	-	-	7

APPENDIX X. contd.

6. Key to Sample Nomenclature.

Sample	Depth (m)	Sample	Depth (m)
1/4/1	0-0.10	3/4/1	3.15-3.25
1/4/2	0.10-0.20	3/4/2	3.25-3.35
1/4/3	0.20-0.30	3/4/3	3.35-3.45
1/4/4	0.30-0.40	3/4/4	3.45-3.55
1/4/5	0.40-0.50	3/4/5	3.55-3.65
1/4/6	0.50-0.60	3/4/6	3.65-3.75
1/4/7	0.60-0.70	3/4/7	3.75-3.85
1/4/8	0.70-0.80	3/4/8	3.85-3.95
1/4/9	0.80-0.90	3/4/9	3.95-4.05
1/4/10	0.90-1.00	3/4/10	4.05-4.15
1/4/11	1.00-1.10	3/4/11	4.15-4.25
1/4/12	1.10-1.20	3/4/12	4.25-4.35
1/4/13	1.20-1.30	3/4/13	4.35-4.45
1/4/14	1.30-1.40	3/4/14	4.45-4.55
1/4/15	1.40-1.50	3/4/15	4.55-4.65
1/4/16	1.50-1.56	3/4/16	4.65-4.73
2/4/1	1.56-1.66	4/4/1	4.73-4.83
2/4/2	1.66-1.76	4/4/2	4.83-4.93
2/4/3	1.76-1.86	4/4/3	4.93-5.03
2/4/4	1.86-1.96	4/4/4	5.03-5.13
2/4/5	1.96-2.06	4/4/5	5.13-5.23
2/4/6	2.06-2.16	4/4/6	5.23-5.33
2/4/7	2.16-2.26	4/4/7	5.33-5.43
2/4/8	2.26-2.36	4/4/8	5.43-5.53
2/4/9	2.36-2.46	4/4/9	5.53-5.63
2/4/10	2.46-2.56	4/4/10	5.63-5.73
2/4/11	2.56-2.66	4/4/11	5.73-5.83
2/4/12	2.66-2.76	4/4/12	5.83-5.93
2/4/13	2.76-2.86	4/4/13	5.93-6.03
2/4/14	2.86-2.96	4/4/14	6.03-6.13
2/4/15	2.96-3.06	4/4/15	6.13-6.23
2/4/16	3.06-3.15	4/4/16	6.23-6.33
		4/4/17	6.33-6.45
		Catcher	<u>Circa</u> 10 cm
		Cutter	<u>Circa</u> 10 cm

Tephrae were recorded as sample numbers with the suffix T, e.g. 2/4/5T.