NEUTRON ACTIVATION ANALYSIS OF NEW ZEALAND OBSIDIAN

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PREFACE

The purpose of this work is the demarcation of New Zealand obsidian sources, primarily by examination of the chemical content. It follows the hypothesis of all characterisation studies. This proposes that by nature of the discreteness of a source, prehistoric worked evidence can be allocated to its origin, using a similar analysis. In this work the chemical element composition was determined by neutron activation analysis.

Once allocation of the archaeological obsidian can be confidently ascertained, the movement of this material from the source, to and between settlements contributes to the wider interpretation of the sphere of early lithic based societies, as New Zealand. Therefore, at the outset considerable time is spent constructing a template of the peculiarity of each source. This may be done by numerous scientific methods.

Generally, obsidian types differ only marginally by major element content (silicon, alumina). Alternatively, the trace and minor element composition provides a clearer and more accurate separation of obsidians. Neutron activation analysis permits the identification and measure of concentration of trace and minor elements to a sensitivity of less than one part per million. This analysis then is potentially an excellent method for the designation of New Zealand obsidian sources or source groupings.

However, for this method of analysis, high precision and low variability is essential, and it is desirable to remove as many systematic and random errors as is possible. The background of nuclear operating conditions reveals the difficulty of obtaining a constant energy range of neutrons during irradiation of the samples. Initially, it was not anticipated that any variations arising from variations in neutron flux would occur. In the first irradiation runs although standards were included, samples were not individually monitored for variations in flux. Subsequently, in the laboratory and during comparison of the data for the standards, severe flux variations were detected at a maximum of thirty-five percent across the diameter of the sample container. This variation, reflected in the analysis of the chemical elements, was likely to mask any attempts to characterise the New Zealand obsidian sources. Flux variations experienced in the original irradiations were determined by re-irradiating selected samples under known flux conditions, and comparing the data for certain selected elements.

As a result of the re-irradiation programme, the initial irradiation data had to be corrected for flux variation if the analysis (and subsequent archaeological implications) was to be valid. It should be mentioned that all the experimental irradiation work was carried out before it was decided that the present research be instigated. The first task of this work then was to assess the suitability of neutron activation analysis to New Zealand characterisation studies and hence to correct the raw analytical data on the basis of the estimates of flux variation determined by the re-irradiations. In this way, a correction constant for each sample was ascertained. The corrections and examination of the nuclear operating conditions (outlined in a technical discussion) constitutes an important factor for several reasons-

1. The New Zealand obsidian neutron activation analysis would be false without correction for the initial irradiations.

2. Any subsequent analysis by multivariate methods and later archaeological implications would be misleading if the raw data was not corrected.

3. With the advent of numerous characterisation programmes recently, and the popularity of neutron activation analysis to obtain trace element compositions, it is possible that the magnitude of flux variations have been underestimated by other workers and thus not always accounted for in later applications of the data. The detailed discussion is thus important for workers in this field.

The neutron activation results after subsequent correction aimed to provide a new body of data on New Zealand obsidian using multivariate analysis, which could later be applied to unprovenanced archaeological obsidians. If inter-source trace and minor element composition was shown (using multivariate analysis) to be greater than within a source, then the template of the uniqueness of each geological source (as originally proposed) has been constructed.

As the objective of characterisation studies in prehistory is the allocation of archaeological material to a raw source, a small programme using archaeological obsidian from Motutapu in the Great Barrier region (North Island) was incorporated in the neutron activation analysis.

The opportunity was also taken to consider several other properties of New Zealand obsidians which may be helpful to future characterisation studies. These include thin section and visual examinations of a selection of geological specimens in a consideration of the petrography of New Zealand obsidian. The major element composition was investigated using wavelength dispersive X-Ray fluorescence spectrometry and refractive index measurements. These methods were not able to justify themselves as a suitable alternative to neutron activation analysis (and hence as sourcing procedures) because it proved too difficult to separate the sources by major element composition. Therefore these lines of information have been separated from the main discussion which is focused on the characterisation of New Zealand obsidians by initially neutron activation analysis and secondly multivariate analysis.

Following the analytical data and its interpretation through multivariate statistics, the next step is to consider the feasibility of exchange systems and communication networks. Basically then two questions can be put to the student of New Zealand prehistory. To what extent do characterisation studies of New Zealand obsidian aid and clarify the economic prehistory of the two islands? Will provenance studies of raw materials as obsidian contribute to a knowledge of prehistoric lines of communication and exchange, given a relatively short time scale and a social system based on gift reciprocity ?

It is hoped that the above discussion will help the reader understand the important emphasis on several technical sections in this work.

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The geological samples for neutron activation analysis were brought to Bradford Laboratories by Dr. Foss Leach of the University of Otago, New Zealand, in 1976. I am grateful to Dr. Leach for valuable background information and for his continued interest in this work.

Additional to these samples were archaeological artifacts from Motutapu. For assistances with the technical details of the activation analysis and helpful discussions, I should like to thank Mr. John Crummett.

The Geology Department at the University of Nottingham provided me with excellent facilities and advice: Dr. Peter and Rael Harvey for the processing of the X-ray fluorescence analysis; Mr. John Eyett for technical assistance; Mr. Greg Lee with assistance in the preparation of the samples; Miss Maria Mackay for the visual and thin section examinations;Dr. Williams-Thorpe for the normative analyses.

I am especially appreciative to the following people at the University of Bradford: Dr. Keith Stoodley, David Sanderson, Frances Ibsen and Charles Braine. Throughout the research my supervisor Mr. Stanley Warren was most generous with his time and advice for which I am sincerely grateful.

The synthesis of the archaeological discussion and assessment of the analytical results was entirely my responsibility.

Throughout the research and even before it was begun, the moral support of my family was a constant source of inspiration. To them I dedicate this work as but a token of gratitude.

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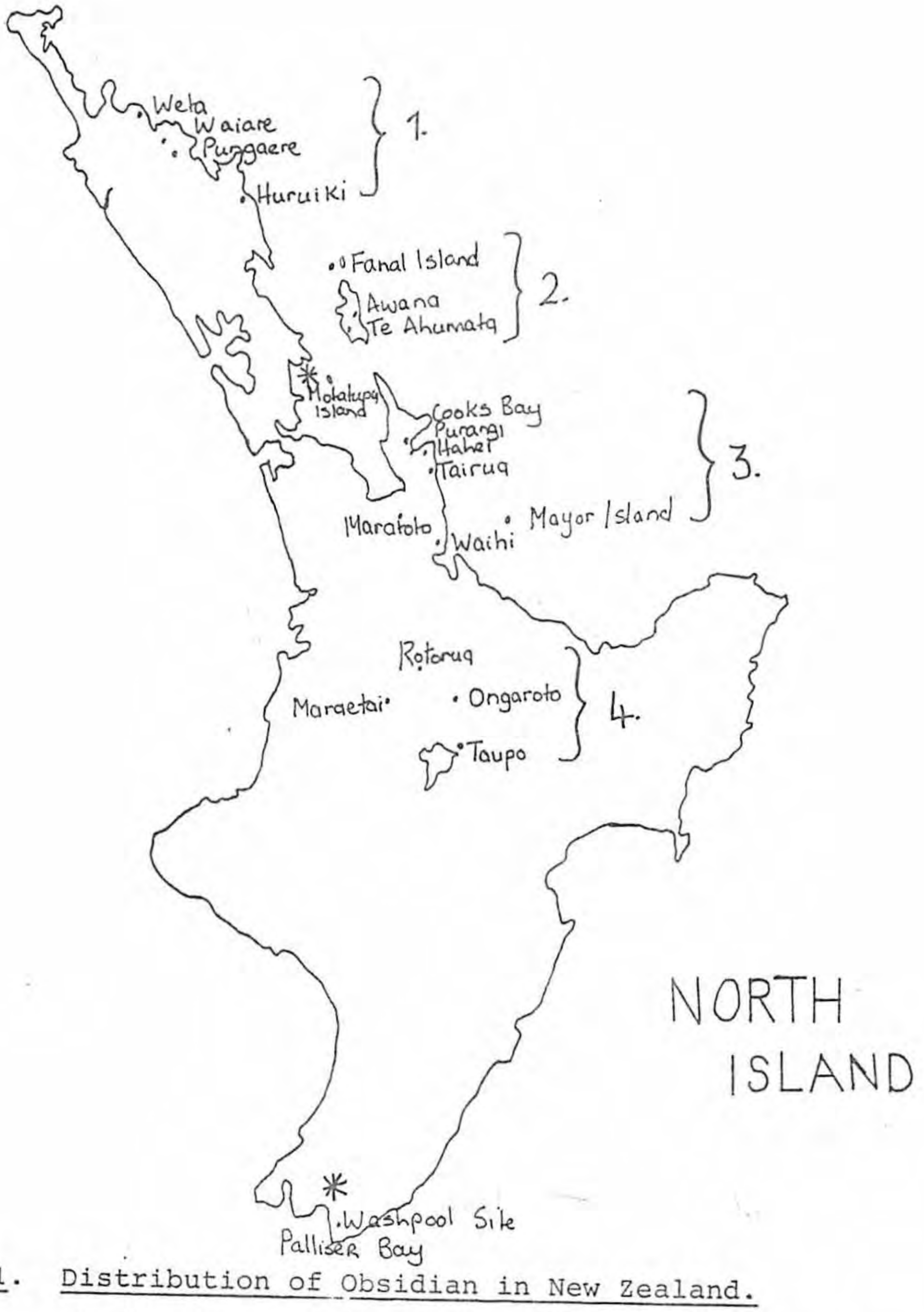


Figure 1. Distribution of Obsidian in New Zealand.

KEY: 1. Northland Region. 2. Great Barrier Area.
3. Coromandel Peninsula. 4. Central Inland Region.
* Denotes sites of archaeological obsidian.

PART A

NEUTRON ACTIVATION ANALYSIS OF NEW ZEALAND OBSIDIAN

CHAPTER ONE. INTRODUCTION

With the arrival of the Europeans to New Zealand in the mid eighteenth century, a full development of the Maori culture had taken place. This cultural period, referred to by Golson as 'Classic Maori' (Golson, 1959) was the outcome of over seven centuries of environmental adaptation from the earliest settlers from Eastern Polynesia. It became readily apparent to the new settlers that the social and economic structure of the society, together with abundant natural resources, provided a rich fund of material for ethnographers, anthropologists and natural historians. Later, excavation offered physical evidence towards the explanation of the origins of New Zealand prehistory. Today, nearly two hundred years after the first European settlers, and a considerable time lapse from the Polynesian immigrants, scientific principles are being applied to the growing documentary and material evidence available to the prehistorian.

This work considers in particular the application of one scientific technique, neutron activation analysis, to an important sector of the archaeological evidence. This is obsidian, found ubiquitously on New Zealand sites in varying proportions. Its utility as a tool, comparable to flint was recognised at an early stage in New Zealand. Coupled with the aceramic Maori culture and emphasis on lithic industries, a study of the distribution of obsidian in relation to natural sources may aid the reconstruction of the economic prehistory of New Zealand.

The social basis of Maori culture (and its predecessors) was integrally linked with the economic system. In this system, there is no parallel with the notion of market and trade, but instead a series of reciprocal exchanges.

Following a general introduction to the Maori economy in this chapter and a review of previous characterisation studies on New Zealand obsidian, the feasibility of exchange systems and communication networks linked to the movement of raw materials can be later assessed, if analysis should prove the discreteness of the sources.

The relative dating of New Zealand's prehistory may be divided into three phases: the earliest settlements; development to the Maori culture (arrival of the traditional 'fleet' from Central East Polynesia); and the influence of the European immigrants on the Maori society.

1.1 Moa Hunter, Archaic and Classic Maori

Early researches are attributed to Julius Haast. When he addressed the Philosophical Institute in Canterbury in 1871 (Haast, 1871) on 'Moas and Moa Hunters', it was proposed that there was 'ample evidence' for a previous race associated with the moa bird, before the settlement of the Maori. A cornerstone of this theory was the absence of the moa in Maori traditions, added to which the bird bones were discovered in separate context. This previous race was alternately named 'Moahunter'(Duff,1942); 'Archaic'(Golson, 1959); 'Waitaha I and II'(Adkin, 1960); and 'New Zealand Eastern Polynesian'(Green, 1963), and has been dated to 1200-1350 A.D.(Golson and Gathercole, 1962). The artifactual features of this settlement period are large quadrangular sectioned type adzes, moa bone bait hooks and necklaces and the absence of fortified camps. The coastal settlement sites are uniform in artifactual content, the early evidence of houses and burials displaying little variation. There was less mobility in the initial stages with manufacturing evidence on the site, suggesting that extensive trading took place to obtain raw materials. For example, the extensive coastal movement of obsidian. Later, specialised quarries developed indicating a divergence of population resulting from possible expansion and development of tribal awareness. Detailed studies of this period have been made(Duff 1947, 1959). Despite refutation (Aidkin, 1960) Golson defends the now widely used term 'Archaic' on the grounds that it represents the earliest phase akin in date and type to the Eastern Polynesian prototype(Golson, 1960).

Maori tradition accords the arrival of the First Fleet from Polynesia in about 1350 A.D. It has been suggested (Sharp, 1956) that the spread of the Maori arose from separate migrations to the North Island infiltrating to the South Island. The infusion of Maori traits may have arisen from the isolation of communities in the northern part of the north island together with the cultivation of the Kumara(sweet potato) throughout the southern areas, to gradually replace the original Polynesian culture (Green,1963).

Alternately, the Maori characteristics evolved from the Archaic of the tenth and eleventh centuries, as it has been argued (Groube, 1967) that the traditional features(for example, elaborately carved meeting houses and storehouses) have no precedent in Polynesia. Similarly, agriculture may have been introduced in the Archaic phase and heightened with the advent of the European. Groube proposes that the defended 'pa' habitations were most popular in the mid nineteenth century, descended from the earlier camp types.

Regional variations of this period, as the Auckland Maori Phase (Davidson, 1972) have been proposed to differentiate between Archaic and 'Classic Maori'. However, the Maori culture appears consistent and uniform in its relation to a tribal society throughout New Zealand.

1.2 The Maori Economy

The characteristics on which Maori society are based accords with the description of a primitive economy as given by Forde and Douglas (Dalton, 1967). Essentially there is a preoccupation with daily and seasonal food supply within the small village economic unit. Transport is limited, the canoe being the main carrier in coastal fishing expeditions and movement of goods on the extensive lake system. Specialisation is not common to the exclusion of sharing in communal tasks. Technology (tool industries) is dominated by lithic resources as obsidian, basalt and greywacke, and reached the Neolithic stage of development. Coastal regions exchange sea foods for the inland crop products and previous commodities as greenstone(predominantly in the South Island) were offered against craft goods. Two factors of Maori tribal society however are critical to the understanding of the economy. These are: first, economic relations cannot be divided from social relations or status. Secondly, the idea of the 'gift' between tribal members or across tribes is paramount to harmony and assured livelihood.

As there is no equivalent to modern concepts as trade or money in the early New Zealand economy, transactions may be seen in terms of utility and prestige. Transactions were either balanced, particularly on the utilitarian level and within the tribal sector - balanced reciprocity; informal and generous as between relatives - general reciprocity; or cautious dealings with other tribes - negative reciprocity(Sahlins, 1968). Common to all three categories is the reciprocal nature of the exchange essential to Maori protocol. However, transactions are not necessarily equal or utilitarian due to the importance of prestige in giving, as between tribal chiefs. The role of the tribal chief was to ensure the well being of his clan by redistributing from the collective pool of co-operative labour, and to subsidise craft production. He also sponsored ceremonies and initiated technical works(Sahlins, 1968). In return, the chief was accorded eminence in the social structure. Thus across the broad spectrum of Maori society from the household unit to the neighbouring or distant tribe, good communal relations meant healthy economic relations. War, an outcome of transgressing defined tribal territories and traditions, was a break down in the balance of giving and receiving through the normal channels of kinship distance. Defended settlements, pa , are witness to periods of invasion and unrest following the Archaic phase and may be seen as an adaptive response to increasing population and later pressures from the incoming Europeans.

Ethnographic data collected by Best (1924) was later indirectly integrated into the substantivist school of primitive economics (Sahlins, 1972). Sahlins attempts an explanation of exchange values in Stone Age societies, and examines the idea of the 'gift' originally proposed by Mauss(1970). He interprets "hau" (Best, 1924) to be the 'spirit of the thing given' and emphasises the strict obligations to give and receive. Here is the foundation of Maori custom. The worth of the gift is in proportion to the status of the recipient as well as the common interests of both donor and receiver - the exchange value.

1.3. Distribution of Obsidian in New Zealand

The mechanism whereby exchange took place leads to an investigation of the distribution patterns of regional resources. The early Maori or even 'Moa-hunter' travelled considerable distances to obtain essential raw materials. Obsidian sources are confined to the North Island although the material has been discovered in archaeological contexts throughout New Zealand.

The sources are clustered within four geographical areas: the Northland region, Great Barrier Area, Coromandel Peninsula and Central Inland Region (fig. 1). Within these regions, there are eighteen known localities of potential sources for artifact obsidian:-

1. Weta, Waiare, Pungaere, Huruiki. (Northland Region)
2. Fanal Island, Awana, Te Ahumata. (Great Barrier Area)
3. Cooks Bay, Purangi, Hahei, Tairua, Maratoto, Waihi and Mayor Island. (Coromandel Peninsula)
4. Rotorua, Maraetai, Ongorato, Taupo. (Central Inland Region

From a glance at fig. 1., it is evident that the distribution of sources in the Coromandel Peninsula and on Great Barrier Island are very close. The straight line distance from Weta to Taupo is in the order of 430 kilometres. Inter-regional distances average

The definition of eighteen sources (Ward,1974a.) was the outcome of numerous characterisation studies whereby the geological material is chemically 'fingerprinted' to isolate an element composition unique to each source. A brief review of these provenance studies on New Zealand obsidian reveals the variety of physical methods performed and their findings.

1.4. History of Research

The assumption that elemental variation between sources is greater than within one source, known as the Provenience Postulate, is fundamental to discrimination by chemical composition. This premise is the basis for all physical methods of analysis employed to discern the chemical makeup of raw materials. Obsidian displaying differences in trace element concentration has been examined frequently in an attempt to characterise secondary archaeological material.

Early research defined three broad geographical areas: Mayor Island, Taupo-Rotorua region, and the Whitianga rhyolite group (Coromandel Peninsula). The refractive indices and hydration thicknesses were measured (Green,1962) for major element variations and age determinations. Free flotation density methods identified six major sources of archaeological obsidians (Reeves,Armitage and Gaye,1973)'with a reasonable degree of confidence'. However, like the refractive indices, overlapping of sources was evident, even across regions. The density of Huruiki and Whitianga sources were classified within a range (2.356 - 2.375 g cm^{-3}) and did not provide a rapid method of characterising obsidian as proposed. Only the

130 kilometres from centre to centre.

Kaeo (Waiare) source with a density of above 2.400 g cm^{-3} proved distinct. Identification based on the evidence of colour was later found to be unreliable (Davidson, 1972; Reeves and Ward, 1976), owing to changes in colour across one source.

The ratios of line intensities of several elements recorded using emission spectroscopy - namely the relation between zirconium and manganese to beryllium and calcium - defined sources with more certainty than measuring absolute concentrations only (Green,Brooks and Reeves, 1967). Excepting the Northland sources - Kaeo and Huruiki - the results showed grouping of sources from the same geological province. Absolute concentrations of several elements from natural source obsidian were measured by two analytical techniques - atomic absorption spectroscopy and flame photometry - to determine the natural variations of concentrations within each source (Armitage and Reeves, 1972). By calculation of the co-efficient of variation, each element was considered to be normally distributed. The elements used were manganese, zinc and iron (atomic absorption) and potassium and sodium(flame photometry). The most significant result was the identification of 'at least' three separate geological flows on Mayor Island, supported by the analysis of the manganese concentrations of the archaeological obsidians.

The separation of sources by their fluorine/sodium ratio using a germanium lithium detector suggested that two flows - Maraetai and Taupo - located within a short distance of each other may have a common geochemical origin. Thus further sustaining the grouping of sources according to geological province.

A further aim of this analysis by the inelastic scattering of protons (Coote, Whitehead and McCallum, 1972) was to consider the effect of weathering and the possibility of sodium decrement from exposure. However, close correlation of the fluorine/sodium ratios was found between weathered and non-weathered surface of the same specimen measured at varying energies.

A major characterisation programme of obsidian employing X-ray fluorescence was undertaken by Ward(1974a)as a paradigm, for sourcing New Zealand archaeological obsidians. Five elements - zirconium, manganese, titanium, rubidium, and strontium - were analysed from fifty geographically discrete deposits to form eighteen petrographic source groups. Unlike previous analyses, the relation between the sources was conceptualised in more than two dimensions on the basis that delimitation of the sources according to degree of variation within a source could be best made using as many distinguishing variables as possible (Ward, 1974b). These distinguishing variables, the characterisation data available from the X-ray fluorescence geological determinations, were selected for analysis of archaeological obsidians, whereby a template was constructed and the probability of association to a particular source could be allocated. An examination of the sample size of the petrographic source groups highlights uneven representation, Mayor Island having the largest contingent with fifty-two samples, whereas the Great Barrier source groups reflect several subsources within the locality (Ward, 1974c). The most positive criterion for consideration of the variance between sources is the co-efficient of variation. The obsidian source characterisation data for the five elements if plotted in two dimensions shows a clustering of sources and underlines the necessity of a multivariate configuration.

Recent obsidian research has employed proton induced X-ray fluorescence (Bird, n.d.) to study the near surface layer, with relatively low background. Delayed neutron activation analysis (Wall, 1975) of short lived manganese and sodium as well as uranium (U^{235}) assay favours the precision of the manganese data and uniform major composition within flows. Detection of radioactive elements as uranium and thorium could provide a method of sourcing obsidian. Further the glow curve shapes produced by artificial thermoluminescence under standard conditions of beta irradiation have been proposed as a source identification scheme (Leach, n.d.). The sources selected for analysis followed Ward's groupings with extra subdivisions based on colour (as Waihi red and black) and the results indicated that intra-source variation was of a much lower order than those between sources.

Provenance studies undertaken on New Zealand obsidian have achieved the definition of geological sources by determination of trace element composition. Comparison of quantitative measurements is difficult, an assessment being made on the experimental conditions and the statistical confidence that variation between sources is greater than within a source. Separation of the sources into four broad natural geological provinces - Northland, Great Barrier Area, Coromandel and Central Inland Region (Leach, 1976) - aids general identification of archaeological material. However, to discern most clearly patterns of trade and communication in New Zealand prehistory, each individual source must produce a distinct chemical makeup as is possible. One way, as already discussed, is to use the maximum number of distinguishing elements through multivariate analysis. This method has been adopted in the present work.

1.5 Source Material Analysed

The source material used in the analysis of geological obsidians was collected by New Zealand archaeologists over a considerable time and documented by Ward (1973). Critical to the question of variation within each source is the size of the collection area and relation to the flow. Deposits from Rotorua and Maraetai are reported to feature as outcrops rather than part of a discrete flow. A distinction should be made between detrital source material and obsidian deposits acquired in situ. Detrital material would originally have derived from the primary flow but has been either exposed or weathered through modern agriculture, natural processes or road cuttings. Hence one must be wary to conclude in these circumstances that such localities were used in prehistoric times. The author did not personally collect the geological samples and the exact siting for each was not available.

Mayor Island and Taupo (Whangamata Fault) obsidian showed a direct relation to nearby flows. Volcanic bomb deposits occurred at Te Ahumata, Huruiki, Cooks Bay, Weta and Pungaere. It is interesting to note that the Waiare and Hahei sources are questioned as "correlating to artifact analysis" (Ward,1973) and this presents an interesting forethought for a later assessment of their validity in the previous list of obsidian sources. The majority of source localities are tabulated as being of flake quality (excepting Rotorua and some Maraetai deposits).

1.6 Background of Archaeological Material Analysed

Forty-five archaeological obsidian samples from Site N38/30 on Motutapu Island (fig 1) were incorporated in the neutron activation analysis programme.

Motutapu Island is situated in the Hauraki Gulf, north east of Auckland. Three separate excavations were carried out on the island between 1958 and 1971 on beach midden and undefended ridge occupation sites. Additionally a survey of all possible archaeological sites on the island was undertaken in 1963 directed by Davidson, Leahy and Nicholls (Davidson, 1970).

Site N38/30 located near Station Bay was excavated over two seasons, 1967/8 (Leahy, 1970) and 1970/71 (Leahy,1972), in conjunction with a nearby site - N38/37. Both sites are termed 'undefended' due to lack of defensive ditches, occupying terraced areas, Site N38/30 located above a swamp. The first excavation results of N38/30 suggested that the terrace contained a surface house structure and a semi-subterranean storage pit. A second stage in occupation was later identified, suggesting more intensive stone working and general activity area.

The chronology of the sites recorded on Motutapu has been aided by the deposit of a fine basaltic ash erupted from Rangitoto which has been dated by radiocarbon samples to between 600 ± 40 B.P. and 185 ± 71 B.P. at the other end of the scale (Davidson, 1972). Charcoal samples beneath the ash have been dated to approximately 1300 - 1500 A.D. which presents a problem when considering the Archaic artifacts that have been found in the same context and previously considered to be older. In a summary of the cultural sequence on Motutapu, Davidson describes Sites N38/30 and N38/37 as belonging to the Auckland Maori Phase. Characteristically there is a loss of many Archaic items and a continuation of working local greywacke stone (Davidson,1972). Analysis of the obsidian from these sites (Ward, 1974c) indicated sources on Great Barrier Island.

Seventy-eight obsidian pieces were found in layers 4 and 6 at Site N38/30(1967/8 season) together with stone flakes (majority of which were greywacke), hammer stones, stone adzes and associated midden. Layer 6 contained most of the artifacts found, including obsidian, which was reported to be of minor occurrence in the site rather than suggesting activity requiring a sharp cutting tool or scrapers. Stone working however was more common judging by the large cache of flakes (868), the presence of adzes and roughouts, all found in layer 6.

A large number of obsidian pieces were of a grey colour and of those recorded, fifteen showed evidence of use while thirty did not.

CHAPTER TWO. MINOR AND TRACE ELEMENT CHARACTERISATION

NEUTRON ACTIVATION ANALYSIS

Introduction

Neutron activation analysis of geological source obsidian and archaeological artifacts from New Zealand formed the central analytical technique in this characterisation programme. The results of the analysis and treatment of the data using multivariate statistical methods involved the major proportion of time and research in this work. This was further added to by the discovery from an independent study of flux variations that significant corrections of the neutron activation results were necessary.

As instrumental neutron activation is a routine analytical technique at Bradford Laboratories, previous analyses revealed that flux variations within one irradiation were generally in the order of six percent. Standards are always included with the samples in order to determine the specific activity (this will be discussed later). It was decided to conduct an investigation of the reactor operating conditions at the time of the New Zealand analyses. Therefore, several of the same samples were irradiated again in the same nuclear establishment, but this time, with included zinc monitors to assess the extent of flux variation present. The outcome proved to be more serious than normal routine analyses with flux variations up to 35 percent in the axial direction of the irradiation containers. Clearly then, because activity (and hence concentration) is proportional to flux, the results of the geological New Zealand material could not be considered without correction.

This correction was empirically determined by ratioing the concentrations of a few selected elements of the monitored and unmonitored samples. The details of the corrections are outlined in the technical discussion preluded by a consideration of the principles of neutron activation analysis. Also a report of the reactor operating conditions which attempts to explain why variations in flux occur.

I : EXPERIMENTAL METHOD

The geological samples were finely ground to a powder ranging from 110 mg to 170 mg by weight and packed into separate sealed polythene tubes which were wrapped in aluminium foil, along with United States Geological Survey granite standards. These tubes were then arranged in layers within a uniform irradiation container and sent to the Atomic Energy and Research Establishment at Harwell, United Kingdom. At Harwell, the containers were placed in either the Pluto or Dido reactors for a period of 72 hours (one irradiation:Run 572, the irradiation time was 66 hours). The samples were returned to the Bradford Laboratories, unpacked, and after a period of five days to allow for cooling and depression of background, the short half life isotopes were counted. These were:
^{24}Na , ^{42}K, ^{76}As, ^{82}Br, ^{140}La, ^{239}Np, ^{153}Sm and ^{175}Yb.

About four weeks hence when the interferences due to the short lived isotopes had decayed, it was possible to count the activity due to the long lived isotopes:
^{124}Sb, ^{59}Fe, ^{141}Ce, ^{46}Sc, ^{60}Co, ^{69}Zn, Sr, ^{86}Rb, Zr, ^{110m}Ag, ^{152}Eu, ^{160}Tb, ^{131}Ba, ^{134}Cs, ^{177}Lu, ^{181}Hf, ^{182}Ta, ^{233}Pa, ^{147}Nd.

The gamma activity was measured using a large volume lithium drifted germanium detector and a Hewlett Packard 1024 multichannel analyser. The analyser was calibrated within the energy range 0-1700 k.e.v.. Counting for 3000 seconds took place for short lived isotopes and 6000 seconds for long lived isotopes.

A Hewlett Packard 2 116B computer system is used in connection with the germanium lithium detector to produce computer analysis of the experimental data. The programme ABSOLUTE SPECT designed by S.E.Warren and J.G.Crummet at the Bradford Laboratories, converts the activity expressed in counts, to elemental concentrations in parts per million.

A further programme CORTEF by the same authors, corrects for sample geometry and flux variation and summarises the experimental data. The element and concentrations are tabulated together with energy and peak area of each sample. The ratio is then taken to a selected standard.

The standard used in the analysis was United States Geological Survey Granite Standard 2 (G2). The trace and minor element isotope data used in the processing of the standard is after 1972 values (Flanagan, 1972) for international geochemical reference samples. The data is listed in Appendix 1.

2.1 Advantages of Experimental Method

A major advantage of this analytical technique is that the neutrons are able to penetrate past the surface of the sample, so that any effects caused by weathering or mineral inclusions on the outer area will not bias a determination of the total volume, particularly for a homogeneous material as obsidian.

Further, activation analysis does not require destruction of the sample although geometric corrections need to be made if there is irregularity in length and shape. This may occur with archaeological specimens. These corrections have been discussed by Warren (1973) and calculation of the geometry factor for archaeological irradiation Run 579 is given below.

2.2 Archaeological Irradiation Run 579: Geometric Correction

The samples from archaeological irradiation Run 579 were counted at two distances from the detector. In the analysis of short lived isotopes, samples 1 to 34 were counted one inch from the detector window, and the remaining samples (35 to 52) at a distance of two inches.

The empiral correction made was dependant on the following principle.

The gamma rays produced by the active sample are emitted spherically into a solid angle (4π steradians). The fraction of this activity received by the detector depends on the solid angle subtended by the detector on the sample. For a fixed area detector, as used in the Bradford Laboratories, and a point sample, this fraction is inversely proportional to the distance between the sample and the detector, squared. Hence, if the distance is doubled, the intensity will be quartered. An empirical correction of three independent determinations (from granite (G2) standards irradiated with the samples) may then be applied to those samples whose position from the detector is increased.

This correction factor is equal to the value for the standard for all samples divided by the mean of three independent determinations.

II: TECHNICAL DISCUSSION

2.3 Principles of Neutron Activation Analysis

Neutron Activation Analysis permits the identification and measure of concentration of trace and minor elements to a sensitivity of less than one part per million for certain isotopes.

The principle rests on the basis of thermal neutrons causing gamma rays to be produced from the unstable radioactive elements. The gamma rays are emitted at discrete energies and differing intensities allowing the analysis to be both quantitative and qualitative. By counting the gamma rays emitted using a semiconductor lithium drifted germanium crystal, an estimate may be determined of the concentration of a given radioactive isotope.

The bombardment of neutrons produced by a nuclear reactor referred to as neutron flux is generally in the order of 10^{12} to 10^{14} neutrons cm.$^{-2}$sec.$^{-1}$. Neutron flux is proportional to the density of neutrons in the vicinity of the point of observation and to their velocity. The irradiation time can vary depending upon the elements chosen for analysis, and for the New Zealand source material was generally 72 hours. This irradiation period is treble that of analyses performed at the Herald reactor, Aldermasterton, owing to the aim to improve precision by irradiating for a long time to boost the total activity of short lived nuclides. During this continuous period, the radioactivity will increase according to the equation:

Activity = $N\sigma\phi(1-\exp(-0.693t/T\tfrac{1}{2})$

where N = total number of atoms per isotope

σ = thermal neutron capture cross section(barns)

ϕ = neutron flux (neutrons cm.$^{-2}$sec.$^{-1}$)

t = irradiation time

$T\tfrac{1}{2}$ = half life of isotope formed.

...equation 1.

As there are uncertainties in measuring the neutron capture cross section, neutron flux, and half life of the isotope formed, a sample and standard of known composition are irradiated together and compared according to the equation:

$$\frac{\text{specific activity of the sample}}{\text{specific activity of the standard}} = \frac{\text{concentration of sample}}{\text{concentration of standard}}$$

... equation 2.

Estimation of the concentration of elements in a sample are made by taking the ratio of the activity of the standard to the activity of the sample. The discrepancy between the amount of neutron dose received, the flux factor, is equal to:

$$\frac{\text{Activity of zinc in the standard}}{\text{Activity of zinc in the sample}}$$

... equation 3.

Variations in the neutron flux arise due to the position of the samples in the reactor and the size and composition of the sample.

At the outset of the irradiation of the samples at Harwell, flux variation was Supposed to be negligible in the axial direction of the sample container and very low in the radial direction. The expectancy was a flux radial variation of less than six percent over the full diameter of the container. For this reason, the flux received by each sample was not monitored (excepting the use of multielement standard rock samples). However, at a later date, the samples were re-irradiated with monitors and flux variations were found to be in the order of up to 35 per cent axial variation and 25 per cent in the radial direction. Adjustment would then need to be made to theoretically calculate the differences in activity received by each sample and to be allowed for in the estimation of element concentration.

To understand the variations in flux, it is necessary to consider the reactor conditions at time of initial irradiation.

2.4 Reactor Operating Conditions -Variations in Flux(Neutron Dose)

The nuclear reactor is composed basically of two regions: the core which contains the fuel elements and moderator surround (either graphite or heavy water), and the reflector region. (There may in fact be a further biological shield which acts as a protection against escaping radiation.) Low energy neutron production is mainly used for instrumental activation analysis because the cross sections of most elements are largest for slow neutrons.

However, as will be discussed, the neutrons in a reactor are not all of a low energy range (thermal) but some are 'epithermal' and others are 'fast'. The ratio of fast to slow neutrons in a reactor core depend on the type of fuel, moderator and the geometry of the system.

When assessing the activity of the radioisotopes produced, allowance should be made for the position of the samples in the reactor. The flux gradient is quite low in the core of the reactor but increases with distance towards the reflector region (fig. 3). Also the thermal neutron flux will be greatly depressed in the neighbourhood of fuel elements (fig. 2). Consequently, the advantage of higher flux associated with thermal neutron producing reactors (particularly in heavy water moderated reactors) must be balanced against the disadvantage of higher flux gradient outside the core.

Due to the very low probability of capture cross section, the number of thermal neutrons to which the sample is exposed is very high. The capture cross section(σ) may be defined as the probability of absorption of neutrons by the nucleus followed by emission of gamma rays.

Polythene was used to encapsulate the samples. This was chosen to scatter the neutrons effectively as it contains hydrogen and carbon, two light elements with a very high scatter cross section.

However the samples were entered into the reflector(outer) region of the reactor which scatters flux back to the outer regions of the core. Being in the outer region (at a neutron dose of between 5-5.6 times 10^{12}(Dido reactor) and 6-7.9 times 10^{12} (Pluto reactor)), there is a slow flux variation from the core to the reflector producing an enhanced fall off in the outer region. This is due to fast neutrons which enter the reflector and are slowed down there returning to the core as thermal neutrons. Coupled with the use and number of polythene tubs per layer, there is not sufficient compensation for scatterback, causing 20 to 30 per cent fall off of flux in the radial direction of the container.

Figure 2. Variation in thermal (—) and epithermal (--) neutron fluxes across a reactor core, showing depressions inside fuel rods. (Enriched uranium reactor, moderated with light water). After Bowen and Gibbons,1963).

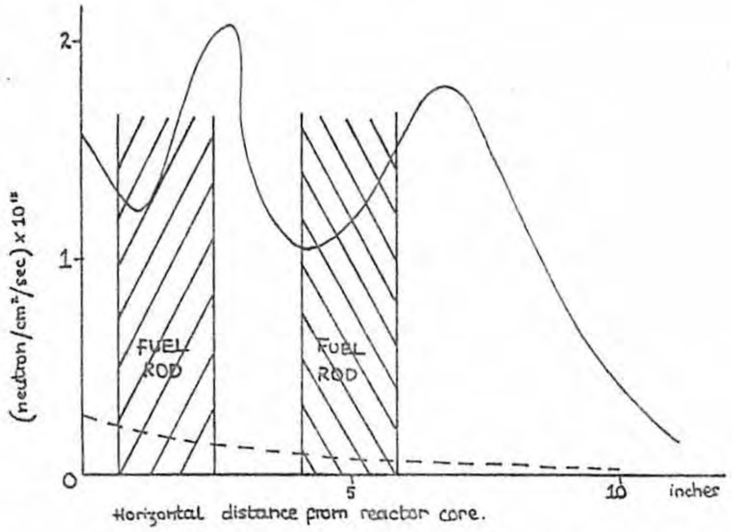
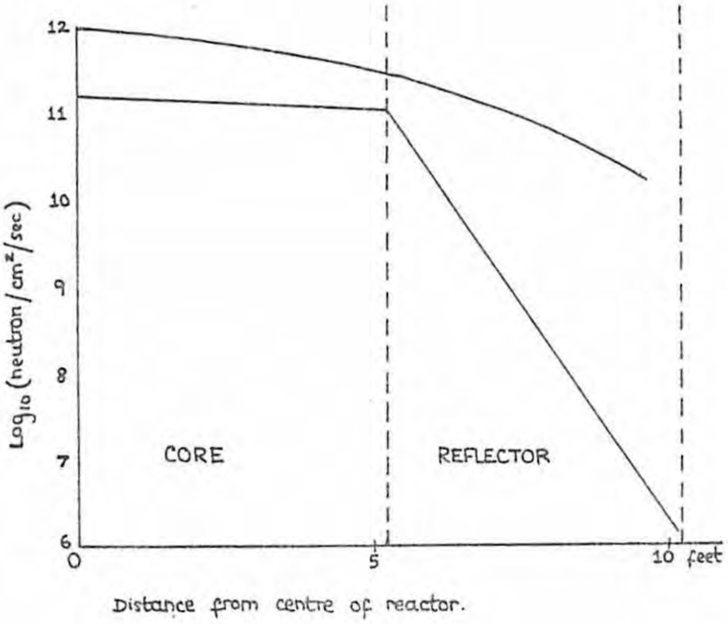


Figure 3. Neutron flux distribution in BEPO reactor, Harwell After Bowen and Gibbons,1963.



The outer region selected in the Dido and Pluto reactors does have the advantage that neutrons are of a thermal energy (up to .4 e.v.). The thermal neutron energy spectrum may be defined as neutrons in thermal equilibrium with the moderator atoms (Steinnes, 1970). The energy spectrum is not altered if only scattering of the neutrons occur off the light elements, as carbon or hydrogen, present in the moderator surround of the core. That is, the relative excitations of the different isotopes will not be changed. Nevertheless, materials which undergo neutron absorption in nuclear reactions are responsible for secondary radiation effects which will contribute to the radiation in the usual reactor field. It is possible to monitor variations in the thermal flux owing to this random process of distribution of neutrons and their velocity. This was done for irradiation Runs 555 and 572 using zinc pieces. The suitability of zinc as a monitor will be returned to.

The next energy zone is the epithermal flux region - .4 e.v. up to 1 m.e.v.. If the scattering of the neutrons due to the use of polythene, together with the position of the samples in the reflector region, alters the energy range by changing the activity, the activity measured will be a combination of epithermal and thermal fluxes.

The activity is dependant upon the neutron capture cross section of each isotope present and the absorption cross section of the material in contact with the incoming neutrons. Polythene absorbs neutron energy such that the layers closest to the incoming neutron dose will show higher flux dosage. (This is shown in the following section where figs. A and B illustrate that the lowest adjustment (flux factor) for activity of the samples coincides with the proximity to the incoming dose). As a result, the centre of the irradiation container will be preferentially depressed.

Neutron flux may also be disturbed by the size of the sample. If the sample is too large, the atoms in the centre may not receive the full neutron flux, termed self absorption. As successive layers of the sample (or across the diameter of the samples in the container) absorb particles, the residual flux becomes less. This results in the inside of the sample (or sample furtherest from the incoming neutron dose) becoming less active than the outside. As has been proposed(Bowen and Gibbons,1962) since the neutron energy spectrum in most reactors covers a wide energy range above the thermal energy region, and since many neutrons have much higher cross sections for reactions with these epithermal neutrons, the effective cross section for the assessment of self shielding can be quite high.

Hence it is necessary to use small enough samples so that self absorption is negligible while maintaining a balance with the specific activity. The sample size selected in the neutron activation analyses (about one centimetre) if in the thermal region, should not have errors greater than five percent arising from flux depression in the centre of the sample. The scatter cross section arising from the hydrogen content of the polythene in the samples irradiated was in the order of 200 to 300 barns, rather than 10 barns.

To monitor the cross section, care will need to be made on the particular choice of isotope. Some nuclides, such as ^{24}Na and ^{46}Sc will maintain the same activation rate in the epithermal region. Others however can reach high cross section values within small energy intervals in the low epithermal region and above (Steinnes,1970). Zinc was chosen because it has a relatively low cross section for n,γ, of 0.78 barns; readily available; and it has a long half life of 243 days, not affected by 72 hours of irradiation.

In the thermal neutron region, most nuclides follow the so called $\frac{I}{V}$ law: their activation cross section is inversely proportional to the neutron velocity. Hence, the higher the neutron velocity, the lower the activation cross section. While activation at higher energies tends to reduce the activity in a mixed element sample, there is a relative enhancement for certain isotopes with high activation (resonance) cross sections in the epithermal region. Otherwise, if irradiated in a thermal zone, the irradiation time will have to be increased, if the neutron flux is in the order of 6 to 7 neutron $cm.^{-2}sec.^{-1}x\ 10^{12}$ (compared with other reactors with a flux of 1.2 to 1.5 x 10^{12}). The ratio of epithermal to thermal flux is expressed through a term called the cadmium ratio.

2.5 The Cadmium Ratio

If the sample is covered with cadmium, which has a high capture cross section for thermal neutrons,the activity will be a measure of those neutrons with energies higher than about .4 e.v.. The thickness of the cadmium being approximately .7 mm.

The cadmium ratio is:

$$\text{ratio of: } \frac{\text{Activity in total flux (thermal and epithermal}}{\text{Activity in epithermal flux}}$$

... equation 4.

A measure of the practibility of using cadmium is the advantage factor. This is the ratio of the cadmium ratio of the interfering nuclide (the nuclide causing the background 'noise') to the nuclide being studied or:

$$F_a = \frac{(R_{cd})}{(R_{cd})} \text{ where } R_{cd} \text{ is the cadmium ratio.}$$

...equation 5.

(Steinnes,1970). If the interfering nuclide does not have a high epithermal cross section, whereas the nuclide wishing to be detected does, then it is advantageous to use a cadmium irradiation. (The cadmium ratio quoted by Harwell Atomic Centre is 10,000:1, in the 5×10^{12} neutrons $cm.^{-2} sec.^{-1}$ region. Therefore, there is virtually no epithermal flux component). Thus, the higher the advantage factor, the better use of cadmium shielding.

Preferential excitation may then be used to reduce errors in the determination of some nuclides by reducing the background. For example ^{238}U and ^{233}Pa. ^{239}Np arising from ^{238}U can only be detected in the present analysis with moderate precision due to the peaks being situated at the lower energy range of the gamma spectrum, where both high background and peak activity is present. However, other elements as ^{46}Sc, ^{59}Fe, ^{60}Co and ^{51}Cr, being dominant long lived isotopes would be much reduced in the epithermal gamma spectra.

2.6 Correction for Flux Variations

The differences in neutron flux received by each geological sample activated (irradiation Runs 533,534 and 535) was not measured at the time of initial irradiation. Owing to the reactor operating conditions, correction for flux variations was determined b

(1) Run 533 - calculation of the activity of one standard taken as the representative standard for two elements, lanthanum and

scandium.

(2) Runs 534 and 535 - re-irradiation of several samples from each batch in two later Runs 555 and 572 respectively, using a zinc flux monitor.

(i) Arrangement of the Samples

Generally the irradiation container held up to eight layers of seven samples. Each layer was arranged in a circle as illustrated in fig. 4 below. Standards were placed in the central position of the first three alternating layers and to the right of the centre for layer 8 in Runs 534 and 535. In Run 533, extra standards were located in the centre and to either side of the middle or fourth layer.

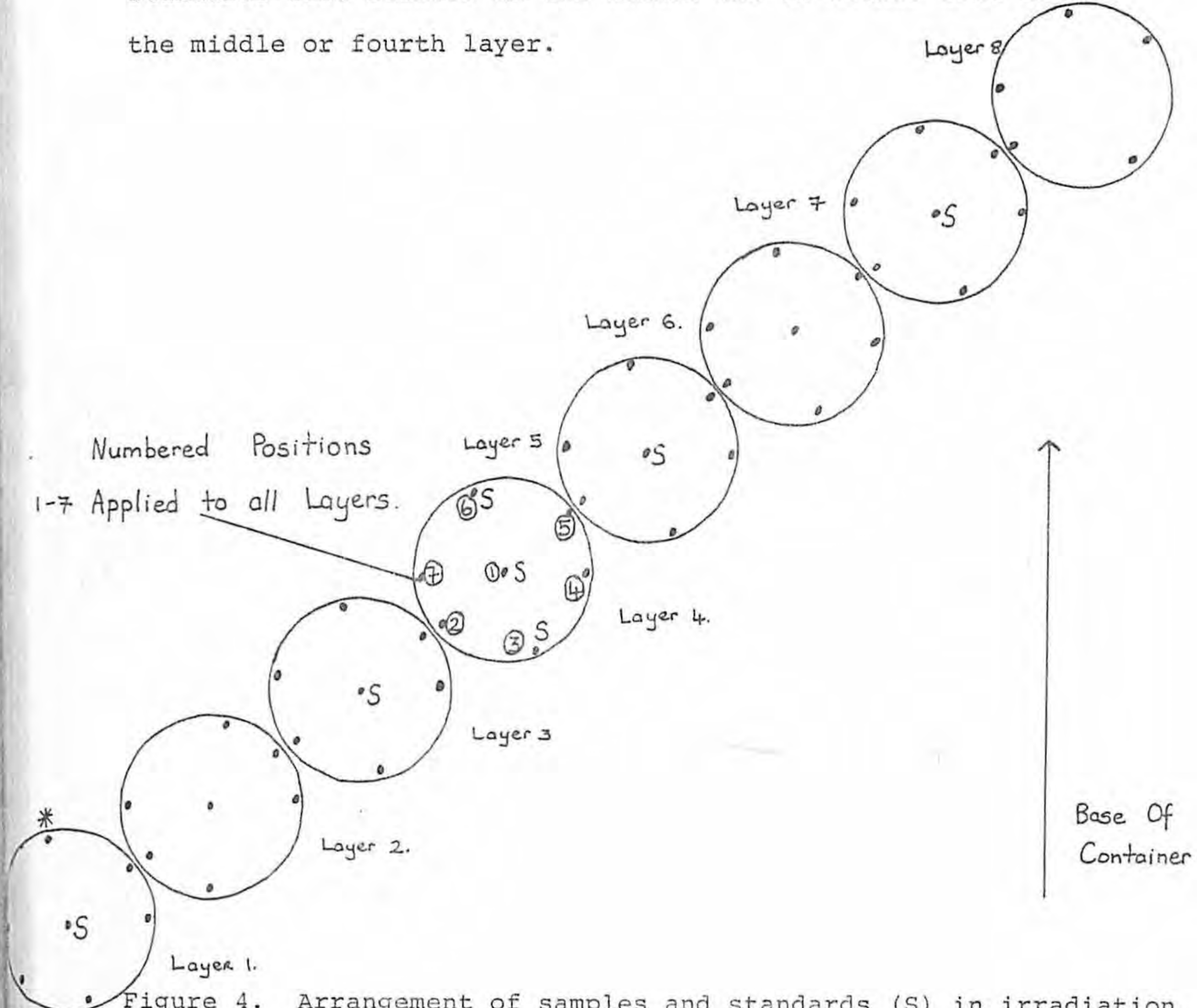


Figure 4. Arrangement of samples and standards (S) in irradiation container, Run 533. *Dots indicate a schematic arrangement for a close-packed hexagon of sample tubes approximately 8 mm in length.

(ii) Run 533

The irradiated Run 533 was investigated for variations in neutron dose by taking one standard G2 to be the standard for all the sample batch.

The activity for two elements, ^{140}La (short lived isotope) and ^{46}Sc (long lived isotope) was determined for all standards and ratioed to the representative standard. This gave a flux factor, a measure of horizontal variation from the base of the container to the top, as witnessed by deviations of the concentrations of the two elements.

The original assumption when the samples were irradiated is that sample positions (1 to 7, see fig. 4) will receive the same neutron flux. For example, positions 1 and 3 , and positions 4 and 6, display an equal variation in a vertical direction (fig. 5). This was calibrated from the placement of standards to either side of the centre as already outlined.

For seven layers, the flux count rate increased by 11.75 percent, extending to 13.44 percent variation for eight layers.

The maximum axial variation was 35 percent which is a significant increase over the lengthwise variation in the container. Lanthanum and scandium were chosen as internal monitors because they showed good peaks in the spectrum.

(iii) Runs 555 and 572

Six samples for Runs 534 and 535 were irradiated again at Harwell to form Runs 555 and 572. This formed a separate

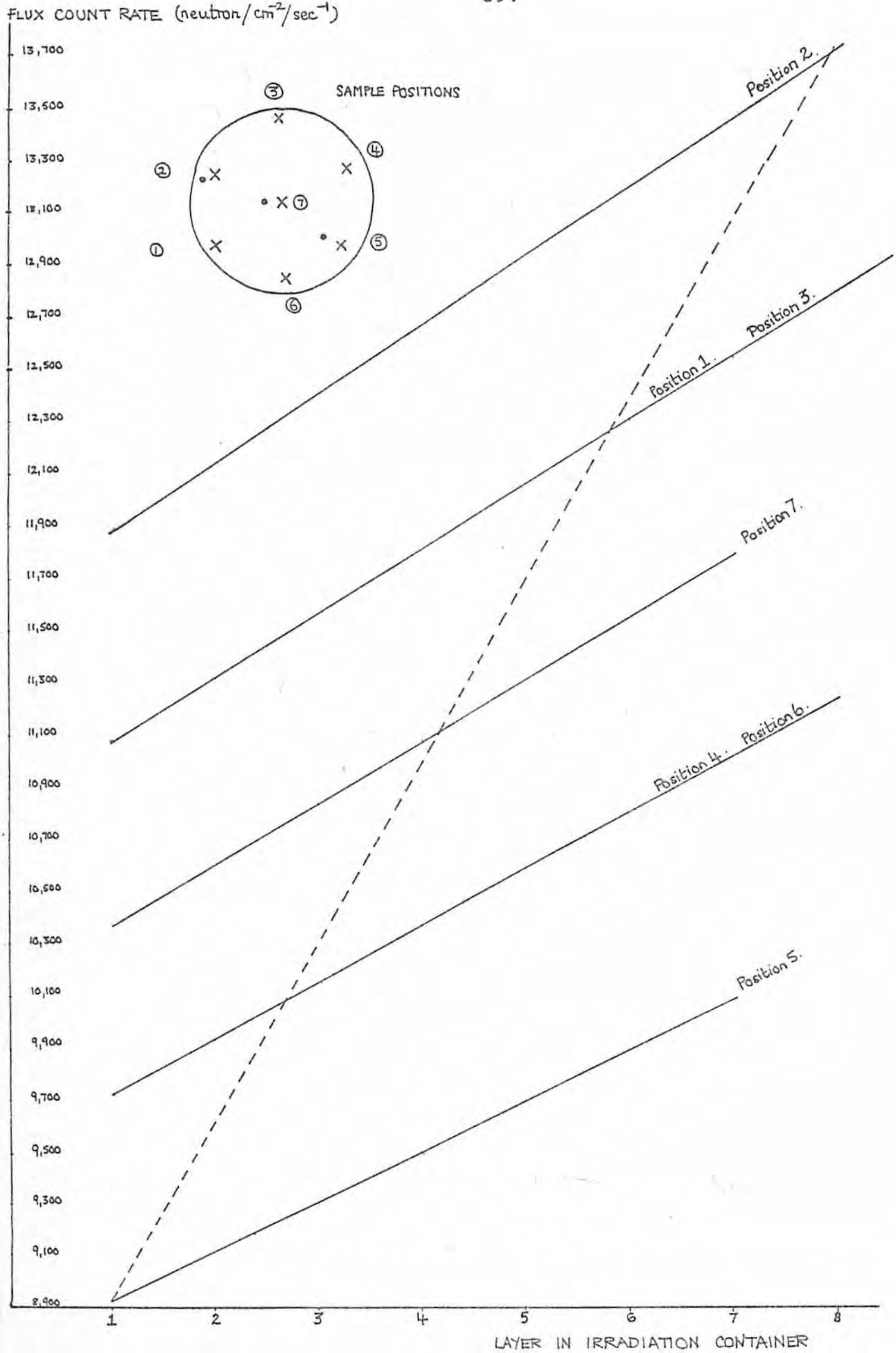


Figure 5. Vertical variation in flux count rate, irradiation Run 533. Over 7 layers it increased by 11.74 percent from base of container.

investigation of reactor operating conditions at Harwell, the purpose being to assess the extent of flux variation present by including zinc monitors in the irradiation containers. It was hypothesised that a determination of the flux variation trends in these later runs could be used to correct the source material element concentrations in the earlier runs where no monitors were included. As conditions within individual reactors differ, it should be noted that the Dido reactor was employed for Run 535 samples and the Pluto reactor for the same samples in Run 572.

A detailed study was made initially for vertical flux variations in the later runs. The variations are represented as systematic trends calculated by the least squares method of best fit (figs. 6 and 7). The average deviation for any sample from the calculated count rate was determined for positions 1 and 2 in Run 555 and found to be less than two percent. Fig. 7a illustrates the actual flux variation against the calculated trends (Run 572).

Table 1 summarises the flux variation trends for Runs 555 and 572 in a vertical direction over seven layers in the standard irradiation container.

The maximum diagonal variation ranges from 23 percent increase (Run 555) to 35 percent increase (Run 572). In both sample batches this is calculated from the sixth position in the first layer to the third position in the top layer. A significant change.

Figure 6. Run 555, vertical flux variation trends.The zinc flux monitor count rate (n.cm(-2)sec (-1)) was calculated for 8 layers in ascending order in the irradiation container. Axial variation is indicated by the dashed line. Inset showing numbered sample positions applies also to Run 572.

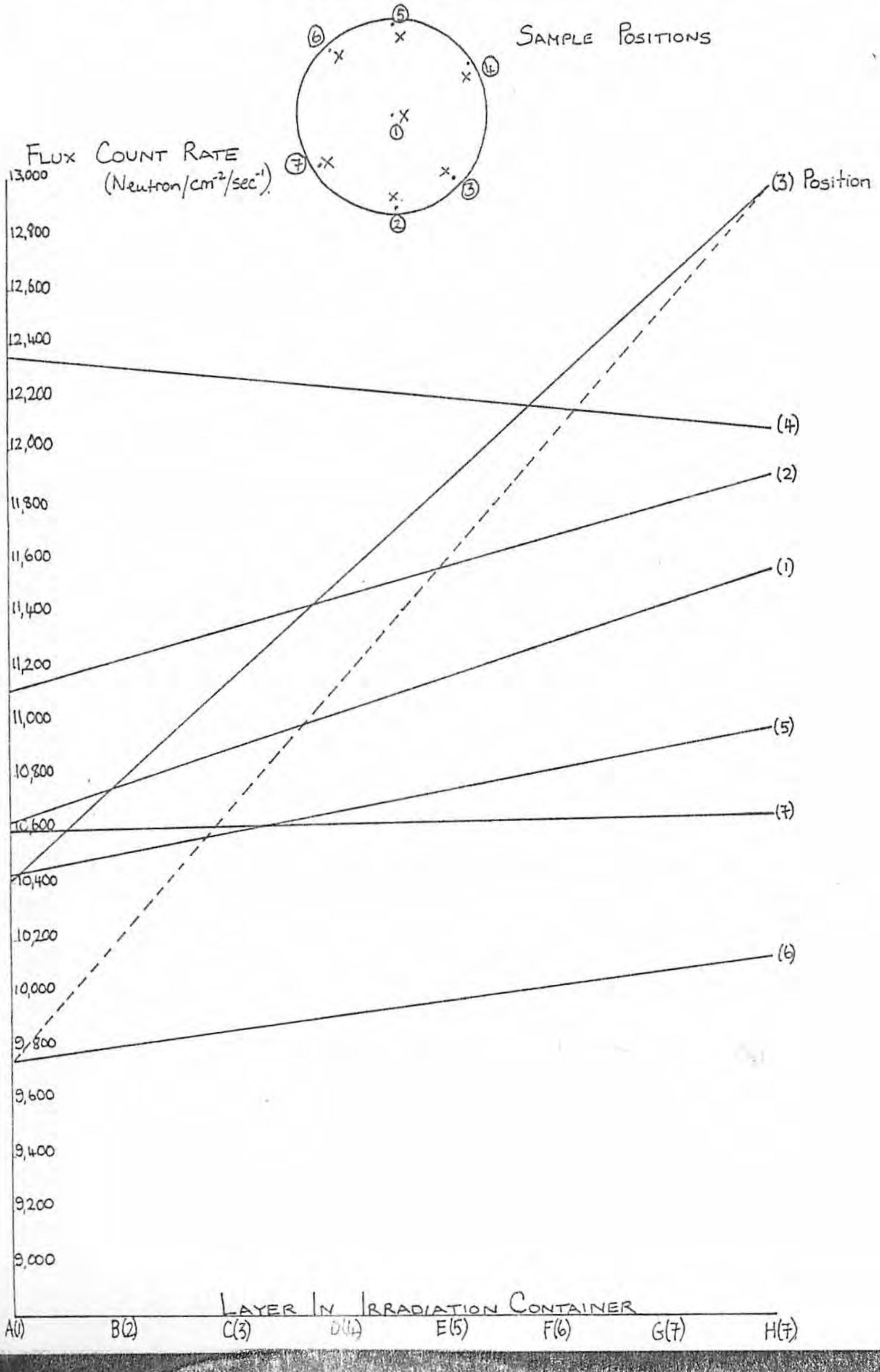


Figure 7. Run 572, vertical flux variations for 7 positions over 7 layers in the irradiation container. Layer 1 is the base and Layer 7 the top. (a) calculated variations; (b) measured variations. Note the almost uniform irradiation for position 7.

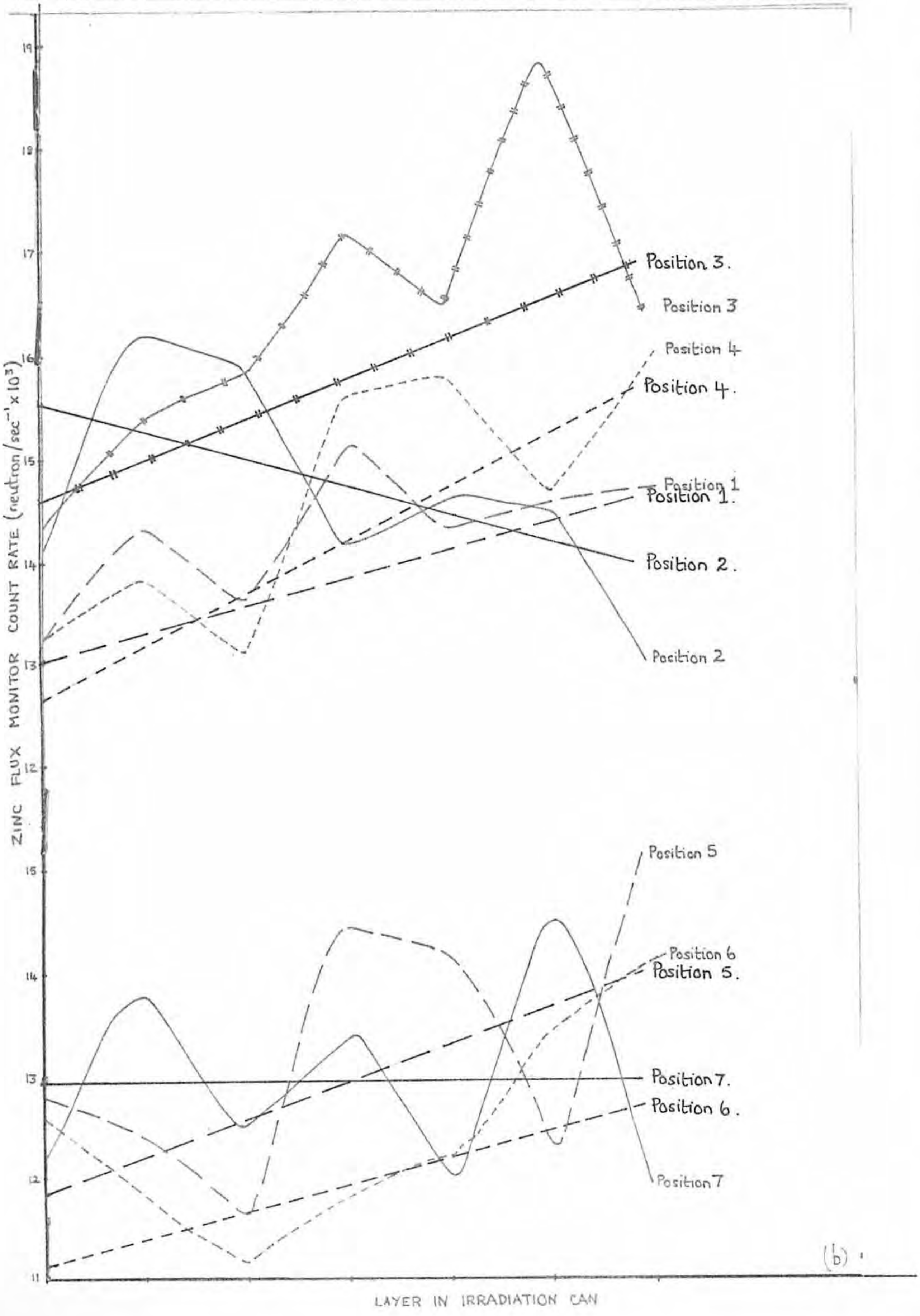


Table 1. Variation in zinc flux monitor count rate in the vertical direction from layer 1 (base) to layer 7 (lid) of the irradiation container, for Run 555 (Dido reactor) and 572 (Pluto reactor). + denotes increase; - denotes decrease; * denotes central position.

Sample position	Percentage Variation (Run 555)	Percentage Variation (Run 572)
*1	+ 6.82	+ 8.51
2	+ 5.60	-11.96
3	+13.52	+12.58
4	- 2.08	+18.76
5	+ 4.18	+15.40
6	+ 3.27	+16.29
7	+ 0.56	+ 0.28

It may be seen that the Pluto reactor displays more variation in flux (in the vertical trend) than the Dido reactor. The increase in flux for position 7 in both runs is insignificant relative to the other positions. Position 2 (Run 572) presents an anomaly in that there is a considerable decrease in flux over the length of the container suggesting that the direction of the neutron dose was highest near the lid and absorbed through the layers to the base.

Having determined the flux variation in the upward direction, a second investigation was made <u>radially</u> across the container of samples. Because the central position was occupied by a G2 standard in alternate layers, the zinc monitor count rate for the remaining positions was calculated relative to the centre (flux factor equal to 1).

$$\text{The flux factor} = \frac{\text{count rate of zinc monitor with standard}}{\text{count rate of zinc monitor with sample}}$$

... equation 6.

The proximity of the sample to the incoming neutron dose will be reflected in the region of lowest flux factor (or correction). Hence, it is possible to reconstruct the direction of the neutron flux across the container for each layer by the calculation of count rate of zinc monitor relative to the central position. This is illustrated in figs. A and B.

The average variation in flux across the diameter of the container was 25 percent for Run 572 and 23 percent for Run 555. The average flux factor for each position is shown in Table 2.

Table 2. The average flux factor for Runs 555 and 572 for sample positions 2 to 7, relative to the central position. Note that positions 2,3 and 4 are lowest, and suggest that side of the container to be nearest to the core of the reactor.

Sample Position	Average Flux Factor	
	Run 555 (8 layers)	Run 572 (7 layers)
2	0.981	0.955
3	0.924	0.885
4	0.928	0.971
5	1.044	1.081
6	1.125	1.149
7	1.067	1.110

(iv) Runs 534 and 535

Having assessed the flux variations present in the diameter

Figure B. Flux Variation across diamter of container, Run 572. Direction of neutron flux indicated by an arrow (relative to central position.)

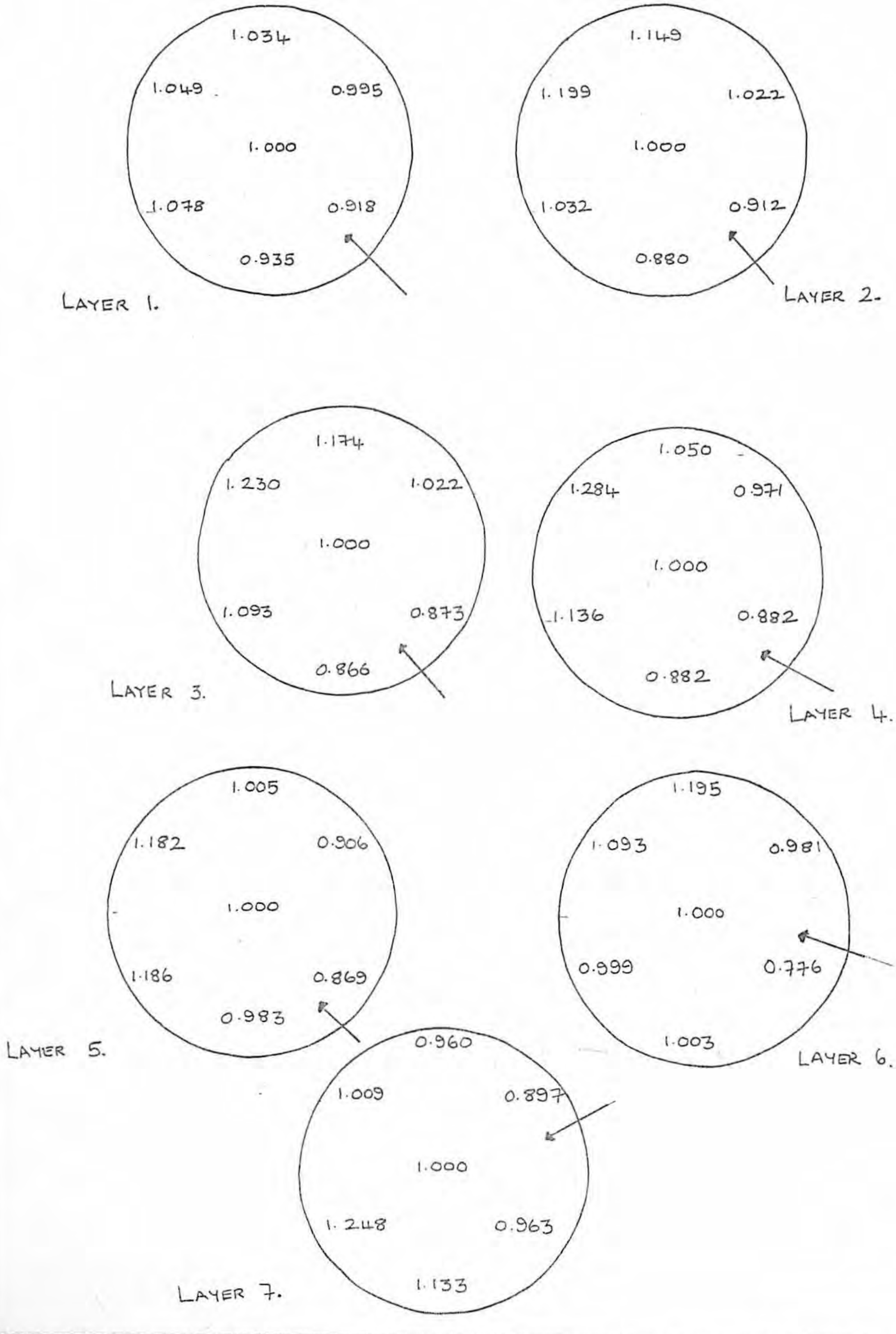
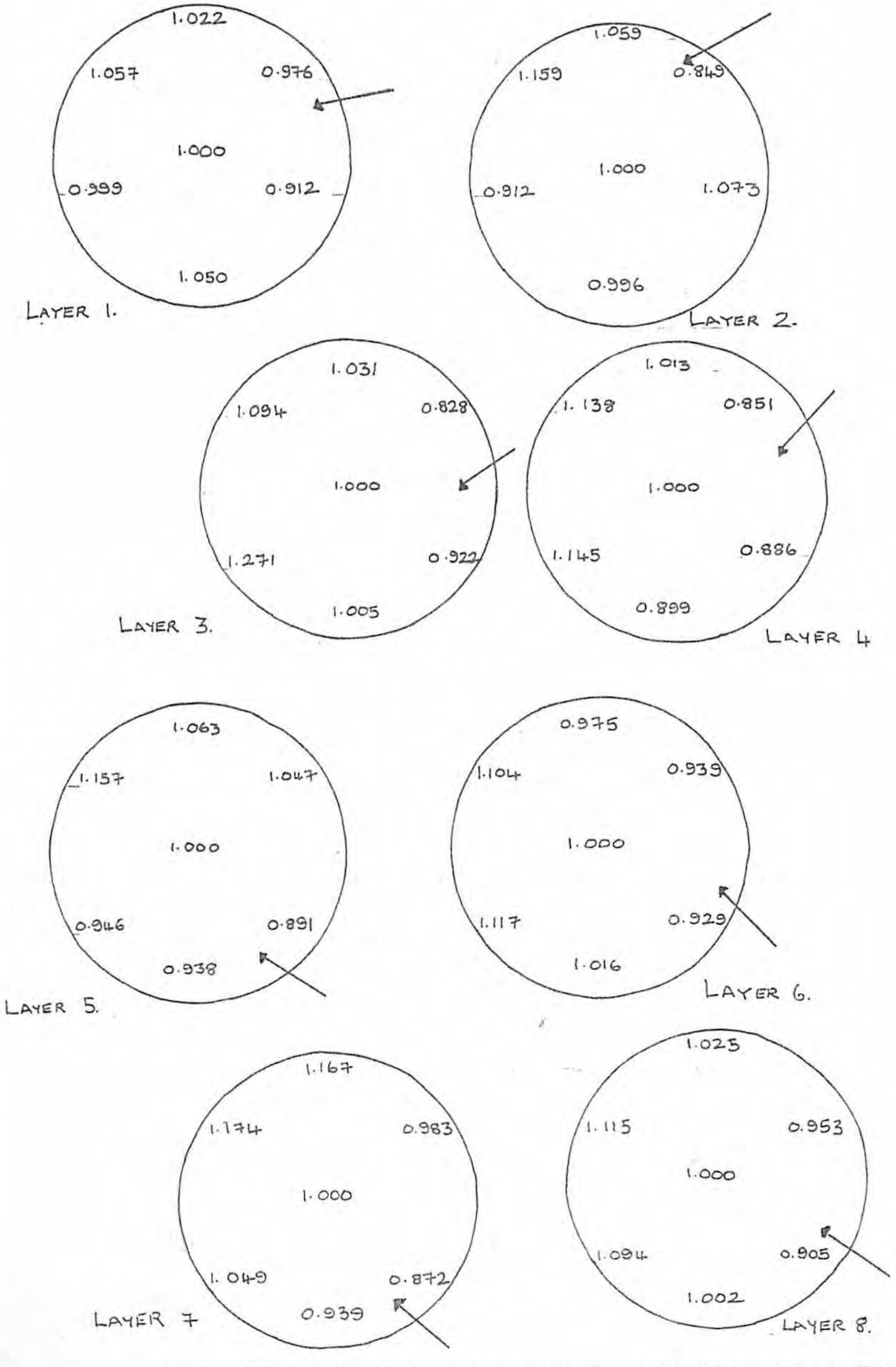


Figure A. Flux variation across diameter of container, Run 555. Direction of neutron flux indicated by an arrow.



and length of the irradiation containers in Runs 555 and 572, it is possible to return to the original premise of correcting for flux in Runs 534 and 535 which had not been monitored. It will be remembered that Activity = $N\sigma\phi$, proportional to the flux (ϕ). By determining a correction factor, for each sample from Runs 555 and 572, then,

Activity $\propto N_x f_x \phi$

where f_x =correction factor in a sample x
ϕ =neutron flux recorded
N_x =total number of atoms per isotope for a sample x.

...equation 7.

Given the activity, the concentration can then be determined.

As the samples were identical, the concentrations of two elements, ^{140}La and ^{59}Fe, were taken as representative of the short and long lived isotopes and corrected. To test the validity of using an average flux factor for all samples by position, the uncorrected concentrations for Runs 555 and 572 were multiplied (a) by the average flux factor, and (b) by the actual flux factor. The results (Table 3) show a favourable comparison.

The average flux factor (a) determined from the monitored runs was then applied to the source material. The ratio of concentrations for $\frac{\text{Run 534}}{\text{Run 555}}$ and $\frac{\text{Run 535}}{\text{Run 572}}$ provided finally an estimation of flux variation around a layer (Table 4). The mean of the ratios for lanthanum and iron was taken as the final flux factors for the unmonitored runs based on the assumption that this variation is valid for all layers.

The element concentrations of the data for Runs 534 and 535

Table 3. Concentrations of ^{140}La and ^{59}Fe for Runs 555 and 572. (a) average flux factor for bracketed position, times (uncorrected) concentration; (b) actual flux factor times (uncorrected) concentrations; (c) uncorrected concentrations.

(Note: Samples 11-16 are re-irradiations of Run 534.

Samples 38-43 are re-irradiations of Run 535.)

RUN 555			RUN 572		
Sample Number	^{140}La (ppm)	^{59}Fe (%)	Sample Number	^{140}La (ppm)	^{59}Fe (%)
	a) 24.16	0.605		a) 103.90	3.89
11	b) 26.11	0.643	38	b) 95.20	3.57
(5)	c) 22.70	0.560	(2)	c) 105.90	3.97
	a) 28.70	0.678		a) 80.90	2.96
12	b) 30.30	0.716	39	b) 86.90	3.18
(4)	c) 29.60	0.700	(7)	c) 75.80	2.78
	a) 26.80	0.879		a) 88.50	3.15
13	b) 27.60	0.906	40	b) 89.50	3.18
(3)	c) 30.30	0.993	(6)	c) 78.70	2.80
	a) 27.50	0.890		a) 87.10	3.20
14	b) 25.40	0.819	41	b) 84.60	3.11
(2)	c) 28.80	0.931	(5)	c) 83.50	3.07
	a) 27.00	0.933		a) 94.40	3.21
15	b) 25.10	0.867	42	b) 86.60	2.95
(7)	c) 24.40	0.840	(4)	c) 101.80	3.46
	a) 24.40	0.897		a) 90.60	3.53
16	b) 25.50	0.937	43	b) 86.90	3.39
(6)	c) 21.20	0.781	(3)	c) 98.00	3.82

Table 4. Ratio of Lanthanum and Iron Concentrations for Run 534/Run 555; Run 535/Run 572.

Sample Number	$\frac{^{140}\text{La}534}{^{140}\text{La}555}$	$\frac{^{59}\text{Fe}534}{^{59}\text{Fe}555}$	Sample Number	$\frac{^{140}\text{La}535}{^{140}\text{La}572}$	$\frac{^{59}\text{Fe}535}{^{59}\text{Fe}572}$
11/38	1.008	1.047	34/11	*	0.867
10/39	1.188	1.241	35/12	1.023	*
12/40	0.922	0.946	36/13	1.027	1.052
9/41	1.100	1.082	37/14	0.972	1.005
8/42	0.959	0.973	38/15	0.925	0.963
13/43	0.846	0.861	39/16	0.981	0.927
+26/51	1.000	0.988	+53/17	1.000	1.000

*Missing data +United States G2 standard

Table 5. Correction Factors for Flux Variation in Runs 534 and 535.

Position Number	Run 534	Run 535
1	1.000	1.000
2	0.966	0.989
3	0.854	1.040
4	0.934	1.023
5	1.028	0.863
6	1.215	0.954
7	1.091	0.944

were corrected by multiplying the uncorrected concentrations by the flux factor to get the new concentrations, each sample being defined as a position in the layer. The position numbers and corresponding factor multiplication are listed in Table 5 above.

The neutron activation data can now be considered as correct and an assessment of the results made. To determine the variation inherent in the data, as distinct from experimental variation, multivariate Cluster Analysis and Discriminant Analysis (chapter 4) were applied.

CHAPTER THREE. RESULTS

3.1 Presentation of Results

The results for the neutron activation analyses are presented in Tables 6 to 15. The concentrations have been corrected for flux variation as previously outlined, and now present a useable body of data for further statistical treatment. Concentrations are expressed in parts per million excepting sodium and iron which is given as a percentage. Each table represents one or part of an irradiation and the samples while grouped according to source are listed in the same order as they were entered for analysis. It could be argued that the sources be randomly distributed over two or more irradiations to examine the outcome from different reactor operating conditions. However, the application of multivariate analysis later proved more convenient using the present arrangement. Tables 13 to 15 are the results of the archaeological material. Where relevant the flux factor is stated.

3.2 Range of Elements Determined

The range of elements determined in the neutron activation analyses is closely correlated with the previous discussion of operating energy regions and scattering of neutrons in the reactor.

The practical resolution of the detector used places limitations on the range of elements analysed with precision. In this analysis, the gamma activity was measured using a large volume lithium drifted detector (resolution of approximately 2.5 k.e.v. at 1332 k.e.v.), and a Hewlett Packard 1024 multichannel analyser. The analyser was calibrated within the energy range 0-1700 k.e.v.. Counting for short lived isotopes was 3000 seconds and 6000 seconds for long lived isotopes.

Most sensitive elements are largely among the rare earths including lanthanum, cerium, samarium, terbium, ytterbium and lutetium. Most of the gamma peaks from these elements lie below 400 k.e.v. and the background in this region introduces problems in attaining good sensitivity. It has been proposed (Tomura,Higuchi,Miyayi,1968) that a sensitive determination of rare earth elements in rock samples can be achieved by removing interfering isotopes such as ^{24}Na, ^{46}Sc, ^{59}Fe and ^{60}Co from the samples before direct gamma ray counting.

^{181}Hf, ^{182}Ta and ^{233}Pa have intense photopeaks also below the 400 k.e.v. range.

3.3 Determination of Accuracy and Error Assessment

Measurements of radioactive disintegrations obey a Poisson frequency distribution for which the standard deviation on a mean, n, is given by the square root of n. Thus the percentage error in a count is:

$$\sigma\% = \frac{\sqrt{n}}{n} \times 100$$

...equation 8.

Hence to achieve an accuracy of one percent, a total count of 10,000 is necessary.

As has been previously discussed, the spectrum may be dominated in certain regions by the background produced by the Compton distribution. This effect results when a gamma photon is deflected by the orbital electrons. It can raise the background to levels that can lower the accuracy of determination of even the strongest peaks to a considerable extent. With the use of a multichannel analyser, the channel with the highest count rate in the peak (usually the centre) is determined and several channels to either side are counted. If the channels on either side are termed C_{-n} and C_{+n}, then the area of the peak will be equal to:

area above line C_{-n} to C_{+n} =

$$\text{area} = \sum_{m=-n}^{+n} A_m - (n + \tfrac{1}{2})\,(A_{-n} + A_{+n}),$$ (Bowen and Gibbons, 1963)

where A_m = number of counts in the mth channel.

... equation 9.

It may occur that the photopeak is assymetrical. In this event, if a low energy gamma ray has to be measured in the presence of a high energy one, where the former may coincide with the Compton distribution of the high energy gamma ray, then the peak area due to the low energy gamma ray is determined.

Flux inhomogeneities will occur according to the conditions described and add another consideration to the determination of accuracy.

During preparation of the samples, careful records were kept of weight and all possible precautions were taken to avoid contamination. This will be outlined more fully in the supplementary analyses undertaken by the author.

The use of known rock standards such as United States G2 are critical in order to calibrate the raw element results.

3.4 Element Variation within a Source

Calculations were made of the mean, standard deviation, co-efficient of variation and standard error of the mean for each element of the sixteen representative sources (Tables 16, 17 and 18 pages 54-56.). The co-efficient of variation determines the variability of one element relative to another, while the standard error measures the degree of uncertainty in the sample size. CV%

The variability of ^{59}Fe is seen to be quite high, as much as 54 percent for the Waihi source and 50 percent for the Rotorua source. For some sources, for example Purangi and Maratoto, the variation (in terms of co-efficient of variation) is approximately in concomitance across the element range.

In order to examine the discreteness of the source groups from an analysis of several elements, the large number of samples necessitates computer based statistical techniques. Discriminate Variate Analysis is able to select the most discriminating elements from all the sources, and linearly combine them to investigate the extent of intersource variation.

		^{175}Yb	^{24}Na	^{140}La	^{59}Fe	^{141}Ce	^{46}Sc	^{60}Co	^{152}Eu	^{160}Tb	^{134}Cs	^{177}Lu	^{181}Hf	^{182}Ta
Source		Short lived isotopes						Long lived isotopes						
Taupo	a.	3.49	2.81	20.71	0.92	38.90	4.17	1.35	0.58	0.59	4.86	0.32	3.92	0.64
	b.	0.50	0.38	3.07	0.14	5.40	0.62	0.18	0.09	0.11	0.63	0.04	0.53	0.08
	c.	14.33	13.52	14.82	15.22	13.88	14.87	13.33	15.52	18.64	12.96	12.50	13.52	12.50
	d.	0.19	0.14	1.16	0.05	2.04	0.23	0.07	0.03	0.04	0.24	0.02	0.03	0.63
Awana		6.28	2.62	37.77	1.01	68.70	4.46	1.05	0.59	1.16	9.03	0.52	4.86	0.94
		1.85	0.26	5.52	0.20	11.00	1.41	0.15	0.37	0.42	0.53	0.14	1.43	0.22
		29.46	9.92	14.61	19.80	16.01	31.61	14.29	62.71	36.21	5.87	26.92	29.42	23.40
		1.07	0.15	3.19	0.12	6.35	0.81	0.09	0.21	0.24	0.31	0.08	0.83	0.13
Pungaere		50.95	4.02	136.80	2.86	199.50	0.25	0.42	0.37	5.11	36.42	2.69	45.32	23.89
		3.89	0.17	6.24	1.12	16.32	0.03	0.02	0.05	0.33	2.35	0.19	2.71	1.70
		7.81	4.23	4.56	39.16	8.18	12.00	4.76	13.51	6.46	6.45	7.06	5.98	7.12
		1.99	0.09	3.12	0.56	8.16	0.02	0.01	0.03	0.17	1.18	0.60	1.36	0.85
Hahei		7.62	2.82	30.49	1.08	54.87	4.17	0.63	0.80	0.86	5.57	0.46	4.01	13.07
		0.56	0.21	2.52	0.11	4.00	0.36	0.08	0.06	0.11	0.57	0.05	0.40	1.10
		7.35	7.45	8.27	10.19	7.29	8.63	12.70	7.50	12.79	10.23	10.87	9.98	9.21
		0.21	0.08	0.95	0.04	1.51	0.14	0.03	0.02	0.04	0.22	0.02	0.15	0.03
Waihi		3.65	2.75	18.73	1.37	30.73	4.38	2.51	0.58	0.47	7.05	0.24	3.22	0.74
		0.36	0.15	1.10	0.74	1.91	0.23	0.14	0.04	0.06	0.41	0.02	0.18	0.08
		9.86	5.45	5.87	54.01	6.22	5.25	5.58	6.90	12.77	5.82	8.33	5.59	10.81
		0.13	0.05	0.39	0.26	0.68	0.08	0.05	0.01	0.02	0.14	0.01	0.06	0.03

Table 16. (a) Mean; (b) standard deviation (c) percentage coefficient of variation, and (d) standard error of the mean. Expressed in parts per million (a and b) excepting Na and Fe in percent.

	^{175}Yb	^{24}Na	^{140}La	^{59}Fe	^{141}Ce	^{46}Sc	^{60}Co	^{152}Eu	^{160}Tb	^{134}Cs	^{177}Lu	^{181}Hf	^{182}Ta
Source	Short lived isotopes						Long lived isotopes						
Purangi a.	7.53	3.02	28.98	0.94	50.45	5.19	0.72	0.78	0.81	3.64	0.46	3.81	0.92
b.	0.46	0.19	1.35	0.05	2.70	0.27	0.09	0.03	0.06	0.20	0.03	0.31	0.10
c.	6.11	6.29	4.66	5.32	5.35	5.20	12.50	3.85	7.41	5.49	6.52	8.14	10.87
d.	0.23	0.10	0.68	0.03	1.35	0.14	0.05	0.02	0.03	0.10	0.02	0.16	0.05
Maratoto	5.55	2.69	26.45	0.63	45.88	3.62	0.49	0.27	0.67	9.20	0.37	2.78	0.92
	0.34	0.03	1.12	0.01	1.27	0.03	0.04	0.01	0.05	0.20	0.01	0.03	0.05
	6.13	1.12	4.23	1.59	2.77	0.83	8.16	3.70	7.46	2.17	2.70	1.08	5.43
	0.20	0.02	0.65	0.01	0.73	0.02	0.02	0.01	0.03	0.12	0.01	0.02	0.03
Ongaroto	4.75	2.76	25.18	0.86	42.13	2.17	1.22	0.53	0.55	5.79	0.33	3.45	0.76
	0.21	0.14	1.23	0.05	1.76	0.26	0.13	0.02	0.06	0.27	0.02	0.20	0.08
	4.42	5.07	4.88	5.81	4.18	8.20	10.66	3.77	10.91	4.66	6.06	5.80	10.53
	0.09	0.06	0.50	0.02	0.72	0.11	0.05	0.01	0.02	0.11	0.01	0.08	0.03
Te Ahumata	7.81	2.83	37.59	0.87	64.06	4.06	0.76	0.39	1.09	11.38	0.53	4.05	0.89
	1.68	0.30	3.65	0.22	9.36	0.53	0.18	0.05	0.18	1.34	0.08	0.45	0.10
	21.51	10.60	9.71	25.29	14.61	13.05	23.68	12.82	16.51	11.78	15.09	11.11	11.24
	0.56	0.10	1.22	0.07	3.12	0.18	0.06	0.02	0.06	0.45	0.03	0.15	0.03
Huiriki	8.43	3.33	32.81	0.97	55.17	3.94	0.75	0.54	1.05	9.52	0.51	4.52	1.11
	1.01	0.35	3.54	0.30	6.34	0.73	0.16	0.07	0.15	1.12	0.06	0.52	0.22
	11.98	10.51	10.79	30.93	11.49	18.53	21.33	12.96	14.29	11.76	11.76	11.50	19.82
	0.34	0.12	1.18	0.10	2.11	0.24	0.05	0.02	0.05	0.37	0.02	0.17	0.07
Waiare	48.96	4.46	149.20	2.80	226.90	0.25	0.31	0.39	5.59	46.27	2.75	45.05	24.10
	5.70	0.48	17.10	1.10	26.91	0.03	0.04	0.06	0.75	5.31	0.31	8.36	2.74
	11.64	10.76	11.46	39.29	11.86	12.00	12.90	15.38	13.42	11.48	11.27	18.56	11.37
	1.90	0.16	5.70	0.37	8.97	0.01	0.01	0.02	0.25	1.77	0.10	2.79	0.91

Table 17. (a) Mean; (b) standard deviation (c) percentage coefficient of variation, and (d) standard error of the mean. Expressed in parts per million (a and b) excepting Na and Fe in percent.

		^{175}Yb	^{24}Na	^{140}La	^{59}Fe	^{141}Ce	^{46}Sc	^{60}Co	^{152}Eu	^{160}Tb	^{134}Cs	^{177}Lu	^{181}Hf	^{182}Ta
Source		Short lived isotopes						Long lived isotopes						
Cooks Bay	a.	5.90	2.95	28.07	0.91	46.99	4.91	0.56	0.77	0.76	3.96	0.42	3.47	0.79
	b.	0.74	0.37	4.04	0.13	6.36	0.58	0.07	0.12	0.10	0.55	0.06	0.48	0.10
	c.	12.54	12.54	14.39	14.29	13.53	11.81	12.50	15.58	13.16	13.89	14.29	13.83	12.66
	d.	0.28	0.14	1.53	0.05	2.40	0.22	0.03	0.05	0.17	0.21	0.02	0.18	0.04
Tairua		4.87	3.11	25.03	1.19	42.98	5.60	1.46	0.82	0.74	5.86	0.40	4.84	0.67
		0.97	0.49	3.90	0.21	7.44	0.95	0.45	0.13	0.20	0.80	0.06	0.89	0.13
		19.92	15.76	15.58	17.65	17.31	16.96	30.82	15.85	27.03	13.65	15.00	18.39	19.40
		0.40	0.20	1.59	0.09	3.04	0.39	0.18	0.05	0.08	0.33	0.02	0.36	0.05
Mayor Island		20.05	4.34	93.03	3.50	163.40	0.19	0.63	1.74	3.59	4.51	1.61	23.68	5.93
		3.44	0.79	17.01	0.60	24.18	0.04	0.12	0.35	0.60	0.73	0.25	3.79	0.97
		17.16	18.20	18.28	17.14	14.80	21.05	19.05	20.11	16.71	16.19	15.53	16.01	16.36
		0.95	0.22	4.72	0.17	6.71	0.01	0.03	0.10	0.17	0.20	0.07	1.05	0.27
Rotorua		4.26	2.93	28.27	0.85	48.67	5.52	1.12	0.75	0.77	4.81	0.38	4.11	0.75
		0.81	0.61	5.05	0.42	8.61	1.22	0.62	0.21	0.18	0.86	0.07	1.20	0.13
		19.01	20.82	17.86	49.41	17.69	22.10	55.36	28.00	23.38	17.88	18.42	29.20	17.33
		0.27	0.20	1.68	0.14	2.87	0.41	0.21	0.07	0.06	0.29	0.02	0.40	0.04
Maraetai		3.45	2.98	25.35	0.89	45.98	3.41	1.31	0.53	0.58	5.84	0.33	3.69	0.77
		0.61	0.50	3.68	0.18	7.37	0.69	0.34	0.12	0.10	0.95	0.06	0.70	0.13
		17.68	16.78	14.52	20.22	16.02	20.23	25.96	22.64	17.24	16.27	18.18	18.97	16.88
		0.22	0.18	1.30	0.06	2.61	0.24	0.12	0.04	0.04	0.34	0.02	0.25	0.05

Table 18. (a) Mean ;(b) standard deviation (c) percentage coefficient of variation, and (d) standard error of the mean. Expressed in parts per million (a and b) excepting Na and Fe in percent.

Table 6. Results of Neutron Activation Analysis, Irradiation Run 533.

Source/Sample No.		Yb^{175}	Na^{24}	La^{140}	Fe^{59}	Ce^{141}	Sc^{46}	Co^{60}	Eu^{152}	Tb^{160}	Cs^{134}	Lu^{177}	Hf^{181}	Ta^{182}	Pa^{233}
		SHORT LIVED ISOTOPES			LONG LIVED ISOTOPES										
TE AHUMATA	GS 114	8.80	3.13	43.00	1.05	78.07	4.58	0.845	0.484	1.15	12.65	0.627	4.30	0.994	24.24
	GS 130/2	8.33	2.90	39.54	0.94	69.43	4.10	0.737	0.431	1.11	11.20	0.530	3.89	0.897	21.52
	GS 130/1	7.48	2.54	34.18	0.84	62.85	3.62	0.711	0.340	0.935	10.21	0.489	3.70	0.731	19.33
	GS 139/1	6.81	2.42	32.61	0.78	59.61	3.40	0.718	0.329	0.997	9.65	0.468	3.46	0.776	18.29
	GS 140	7.09	2.62	36.05	0.87	65.49	3.78	0.764	0.354	0.925	10.72	0.535	3.83	0.842	20.38
	GS 143/1	8.70	3.03	41.79	1.02	75.22	4.45	0.819	0.411	1.14	12.33	0.573	4.46	0.928	23.38
	GS 146	10.92	3.23	36.02	1.01	66.93	4.91	0.486	0.448	1.49	12.64	0.708	4.78	1.04	22.53
	GS 147	7.95	3.01	39.97	1.05	70.71	4.23	1.15	0.374	1.13	13.19	0.509	4.38	0.989	22.32
	GS 148/1	7.42	2.66	36.29	0.84	52.55	3.64	0.717	0.372	0.985	10.53	0.487	3.73	0.766	19.42
	GS 149/1	6.32	2.45	33.15	0.79	58.52	3.46	0.616	0.325	0.854	9.56	0.453	3.61	0.806	18.28
HURUIKI	GS 151	7.76	3.06	30.01	0.88	53.12	3.42	0.716	0.473	0.940	8.83	0.484	4.05	0.969	11.20
	GS 167	9.12	3.57	35.19	1.01	61.91	3.98	0.746	0.602	1.14	10.32	0.558	5.13	1.16	13.12
	GS 188	9.30	3.89	38.28	1.10	67.12	4.32	0.766	0.570	1.31	11.02	0.586	5.07	1.32	14.30
	GS 222	8.58	3.57	35.03	1.01	50.24	3.97	1.34	0.555	1.13	10.19	0.549	4.60	1.23	12.88
	GS 232	7.39	3.06	29.38	0.84	61.26	3.30	0.588	0.479	0.904	8.84	0.466	4.05	1.06	10.92
	GS 237/2	7.30	2.79	27.45	0.77	47.31	3.06	0.562	0.439	0.872	7.47	0.425	3.70	0.887	9.93
	GS 258	7.32	3.15	31.24	1.51	53.17	3.64	0.696	0.530	0.900	9.29	0.491	4.46	1.04	11.61
	GS 371	8.72	3.62	35.72	1.07	63.13	4.16	0.944	0.618	1.09	10.70	0.566	5.08	1.25	13.52
	GS 400	8.98	3.52	35.16	1.01	61.55	3.97	0.704	0.377	1.15	10.18	0.561	4.68	1.18	12.82
	GW 260	9.99	3.26	32.79	1.03	57.88	5.54	1.06	0.342	1.19	9.09	0.614	4.42	0.739	12.83

Absolute p.p.m. excepting Fe and Na expressed as %

Table 7. Results of Neutron Activation Analysis, Irradiation Run 533.

Source/Sample No.		Yb^{175}	Na^{24}	La^{140}	Fe^{59}	Ce^{141}	Sc^{46}	Co^{60}	Eu^{152}	Tb^{160}	Cs^{134}	Lu^{177}	Hf^{181}	Ta^{182}	Pa^{233}
		SHORT LIVED ISOTOPES			LONG LIVED ISOTOPES										
TE AHUMATA	GS 114	8.80	3.13	43.00	1.05	78.07	4.58	0.845	0.484	1.15	12.65	0.627	4.30	0.994	24.24
	GS 130/2	8.33	2.90	39.54	0.94	69.43	4.10	0.737	0.431	1.11	11.20	0.530	3.89	0.897	21.52
	GS 130/1	7.48	2.54	34.18	0.84	62.85	3.62	0.711	0.340	0.935	10.21	0.489	3.70	0.731	19.33
	GS 139/1	6.81	2.42	32.61	0.78	59.61	3.40	0.718	0.329	0.997	9.65	0.468	3.46	0.776	18.29
	GS 140	7.09	2.62	36.05	0.87	65.49	3.78	0.764	0.354	0.925	10.72	0.535	3.83	0.842	20.38
	GS 143/1	8.70	3.03	41.79	1.02	75.22	4.45	0.819	0.411	1.14	12.33	0.573	4.46	0.928	23.38
	GS 146	10.92	3.23	36.02	1.01	66.93	4.91	0.486	0.448	1.49	12.64	0.708	4.78	1.04	22.53
	GS 147	7.95	3.01	39.97	1.05	70.71	4.23	1.15	0.374	1.13	13.19	0.509	4.38	0.989	22.32
	GS 148/1	7.42	2.66	36.29	0.84	52.55	3.64	0.717	0.372	0.985	10.53	0.487	3.73	0.766	19.42
	GS 149/1	6.32	2.45	33.15	0.79	58.52	3.46	0.616	0.325	0.854	9.56	0.453	3.61	0.806	18.28
HURUIKI	GS 151	7.76	3.06	30.01	0.88	53.12	3.42	0.716	0.473	0.940	8.83	0.484	4.05	0.969	11.20
	GS 167	9.12	3.57	35.19	1.01	61.91	3.98	0.746	0.602	1.14	10.32	0.558	5.13	1.16	13.12
	GS 188	9.30	3.89	38.28	1.10	67.12	4.32	0.766	0.570	1.31	11.02	0.586	5.07	1.32	14.30
	GS 222	8.58	3.57	35.03	1.01	56.24	3.97	1.34	0.555	1.13	10.19	0.549	4.60	1.23	12.88
	GS 232	7.39	3.06	29.38	0.84	61.26	3.30	0.588	0.479	0.904	8.84	0.466	4.05	1.06	10.92
	GS 237/2	7.30	2.79	27.45	0.77	47.31	3.06	0.562	0.439	0.872	7.47	0.425	3.70	0.887	9.93
	GS 258	7.32	3.15	31.24	1.51	53.17	3.64	0.696	0.530	0.900	9.29	0.491	4.46	1.04	11.61
	GS 371	8.72	3.62	35.72	1.07	63.13	4.16	0.944	0.618	1.09	10.70	0.566	5.08	1.25	13.52
	GS 400	8.98	3.52	35.16	1.01	61.55	3.97	0.704	0.377	1.15	10.18	0.561	4.68	1.18	12.82
	GW 260	9.99	3.26	32.79	1.03	57.88	5.54	1.06	0.342	1.19	9.09	0.614	4.42	0.739	12.83

Absolute p.p.m. excepting Fe and Na expressed as %

Table 8. Results of Neutron Activation Analysis, Irradiation Run 533.

Source/Sample No.		Yb^{175}	Na^{24}	La^{140}	Fe^{59}	Ce^{141}	Sc^{46}	Co^{60}	Eu^{152}	Tb^{160}	Cs^{134}	Lu^{177}	Hf^{131}	Ta^{182}	Pa^{233}
		SHORT LIVED ISOTOPES			LONG LIVED ISOTOPES										
WAIARE	GS 404A	44.14	4.12	136.23	2.93	206.16	0.221	0.302	0.377	5.26	41.82	2.47	43.26	21.90	90.14
	GS 410	44.99	4.07	134.46	2.89	210.54	0.228	0.289	0.342	4.45	42.19	2.56	43.41	21.97	91.21
	GS 415	54.91	4.96	167.59	3.63	255.34	0.285	0.301	0.424	5.63	52.25	3.05	53.52	26.73	112.23
	GS 427	51.86	4.72	158.43	3.42	236.71	0.275	0.335	0.360	6.30	49.60	2.86	50.42	26.48	104.99
	GS 428	45.68	4.12	138.48	2.96	199.84	0.223	0.257	0.413	5.18	41.86	2.55	43.48	22.01	89.73
	GS 433	41.24	3.79	126.33	2.73	191.35	0.225	0.241	0.373	4.85	39.09	2.38	40.26	20.31	83.55
	GS 441	43.45	3.95	133.15	2.85	199.75	0.218	0.312	0.321	5.05	41.15	2.44	41.85	21.30	87.82
	GS 443	51.54	4.66	156.58	3.42	240.92	0.274	0.342	0.404	6.25	49.28	2.99	50.71	25.63	105.52
	GS 463	57.75	5.17	174.75	N.D.	271.52	0.300	0.339	0.537	6.67	53.64	3.25	54.34	27.70	115.29
	GS 414	50.77	4.69	155.44	3.34	229.70	0.250	0.306	0.414	5.85	47.53	2.78	49.18	24.86	101.92
COOKS BAY	GS 537	5.54	2.79	26.04	0.83	43.28	4.61	0.541	0.683	0.710	3.74	0.395	3.17	0.762	11.14
	GS 545	4.75	2.57	23.92	0.78	40.65	4.29	0.491	0.650	0.679	3.33	0.360	2.95	0.670	10.31
	GS 549	6.31	2.85	27.12	0.88	46.56	4.91	0.519	0.737	0.729	3.91	0.399	3.36	0.758	11.89
	GS 568	7.17	3.47	33.84	1.09	55.87	6.09	0.635	0.935	0.921	4.73	0.474	4.08	0.951	14.37
	GS 575	6.97	3.47	33.55	1.09	56.01	6.05	0.672	0.927	0.875	4.71	0.506	4.19	0.914	14.36
	GS 589A	5.82	3.34	31.29	1.03	52.41	5.70	0.642	0.869	0.954	4.28	0.449	3.88	0.837	13.52
	GS 589B	5.86	2.90	27.00	0.88	45.26	4.88	0.580	0.750	0.712	3.85	0.397	3.38	0.780	11.54
	GS 591	5.69	2.63	25.01	0.81	42.17	4.53	0.496	0.672	0.693	3.54	0.362	3.13	0.703	10.73
TAIRUA	GS 632	5.37	3.01	24.19	1.13	40.72	5.35	1.15	0.807	0.700	6.44	0.389	4.45	0.673	11.79
	GS 635	4.36	2.58	20.67	0.95	34.60	4.57	1.00	0.655	0.609	5.45	0.325	3.75	0.512	9.97
	GS 630/1	4.53	2.45	20.32	0.95	34.43	4.47	1.02	0.693	0.554	5.59	0.333	3.69	0.516	9.81
	GS 634/1	5.14	2.94	24.23	1.13	39.68	5.29	1.18	0.809	0.755	6.48	0.386	4.51	0.667	11.59

Absolute p.p.m. excepting Fe and Na expressed as %

N.D. Not Detected

Table 9. Results of Neutron Activation Analysis, Irradiation Run 534.

Source/Sample No.		Yb^{175}	Na^{24}	La^{140}	Fe^{59}	Ce^{141}	Sc^{46}	Co^{60}	Eu^{152}	Tb^{160}	Cs^{134}	Lu^{177}	Hf^{181}	Ta^{182}	Pa^{233}	Flux Factor
		SHORT LIVED ISOTOPES			LONG LIVED ISOTOPES											
ROTORUA	GW 261	4.72	3.82	28.55	1.64	47.02	6.13	2.71	1.18	0.707	4.64	0.421	6.08	0.766	10.68	1.091
	GT 001	5.88	3.87	38.67	1.16	66.49	7.69	1.27	0.993	1.15	6.64	0.535	5.15	1.02	16.87	1.215
	GT 91	4.17	2.85	29.55	0.89	50.66	5.80	1.07	0.734	0.777	4.86	0.391	3.72	0.724	12.99	1.028
	GT 98	3.59	2.39	24.23	0.75	41.77	4.73	0.79	0.599	0.653	4.34	0.323	3.07	0.625	10.70	0.934
	GT 147/2	3.24	2.26	22.34	0.62	38.58	3.38	0.73	0.517	0.585	3.77	0.290	2.62	0.581	9.89	0.854
	GT 148	4.44	3.04	30.16	0.89	51.63	5.77	0.95	0.740	0.854	5.17	0.366	3.99	0.748	13.22	0.966
MARAETAI	GT 285	4.13	3.55	32.90	1.08	53.40	3.99	1.53	0.640	0.654	6.91	0.389	4.68	0.878	16.62	1.215
	GT 279	3.04	2.70	24.31	0.83	40.92	3.05	1.21	0.483	0.549	5.36	0.318	3.38	0.762	12.60	1.028
	GT 295	2.54	2.35	21.10	0.71	35.33	2.44	0.99	0.340	0.474	4.59	0.247	2.84	0.581	10.90	0.934
	GT 287	2.82	2.44	21.96	0.73	37.13	2.55	1.05	0.453	0.471	4.81	0.265	2.93	0.634	11.34	0.854
	GT 778	3.03	2.81	25.92	0.84	41.91	3.03	1.20	0.528	0.512	5.53	0.295	3.48	0.699	13.10	1.000
	GT 806	3.34	2.83	26.87	0.87	44.05	3.25	1.36	0.571	0.553	5.67	0.303	3.60	0.733	12.56	0.966
	GT 794	4.06	3.40	31.19	1.09	52.21	4.22	1.78	0.657	0.607	6.84	0.400	4.19	0.848	15.27	1.091
	GT 781	3.73	3.68	32.87	1.09	53.11	3.89	1.70	0.638	0.606	6.95	0.377	4.53	0.922	15.80	1.215
	GT 777	3.95	2.78	28.98	0.70	50.74	3.92	0.86	0.434	0.748	5.44	0.380	3.27	0.868	14.39	1.028
TAUPO	GT 432	3.02	2.50	20.94	0.82	35.49	3.71	1.24	0.531	0.516	4.40	0.300	3.54	0.577	9.34	0.934
	GT 453	3.04	2.47	20.24	0.80	34.38	3.65	1.23	0.513	0.471	4.25	0.278	3.45	0.534	9.88	0.854
	GT 529	4.10	3.15	26.77	1.05	43.82	4.72	1.54	0.652	0.703	5.45	0.356	4.43	0.693	12.60	0.966
	GT 539	4.26	3.52	29.16	1.15	47.52	5.16	1.67	0.732	0.697	5.97	0.405	4.89	0.822	13.85	1.091
	GT 544	4.28	3.52	29.79	1.16	48.86	5.31	1.66	0.747	0.775	5.98	0.406	4.89	0.798	14.12	1.215

Absolute p.p.m. excepting Fe and Na expressed as %

Table 10. Results of Neutron Activation Analysis, Irradiation Run 534.

Source/Sample No.		Yb^{175}	Na^{24}	La^{140}	Fe^{59}	Ce^{141}	Sc^{46}	Co^{60}	Eu^{152}	Tb^{160}	Cs^{134}	Lu^{177}	Hf^{181}	Ta^{182}	Pa^{233}	Flux Factor
		SHORT LIVED ISOTOPES			LONG LIVED ISOTOPES											
TAIRUA	GS 629	3.46	2.78	22.10	1.06	39.36	4.97	1.46	0.720	0.639	4.66	0.346	4.58	0.538	11.11	0.966
	GS 633/1	4.26	3.45	27.64	1.34	48.27	6.22	1.82	0.924	0.755	5.38	0.424	5.44	0.741	13.64	1.091
	GS 638/1	4.83	3.91	31.41	1.53	55.20	7.17	2.17	1.02	1.09	6.69	0.491	6.28	0.872	15.80	1.215
MAYORT	GS 672	27.18	4.53	103.81	4.09	184.37	0.212	0.680	2.20	4.11	4.37	1.87	27.10	6.95	N.D.	1.028
	GS 706	19.92	3.82	88.15	3.49	162.01	0.157	0.521	1.88	3.52	4.02	1.62	23.17	5.82	N.D.	0.934
	GS 716	17.35	3.35	77.37	3.04	139.44	0.173	0.473	1.65	2.93	3.78	1.38	20.09	5.07	14.18	0.854
	GS 734	19.63	4.05	91.71	3.22	168.29	0.163	0.594	1.48	3.39	4.40	1.60	22.96	5.76	16.30	1.000
	GS 739	22.96	3.89	87.50	3.02	159.83	0.155	0.555	1.41	3.26	4.04	1.49	21.60	5.42	15.65	0.966
	GS 844	26.15	4.90	104.60	3.78	N.D.	0.261	0.754	1.78	3.99	5.46	1.79	26.78	6.65	19.64	1.091
	GS 928	20.50	5.74	116.80	4.47	211.40	0.293	0.829	2.17	4.76	6.25	2.07	30.63	7.44	21.51	1.215
	GS 954	23.70	5.49	127.25	4.19	190.13	0.178	0.610	2.35	4.41	5.34	1.87	28.07	7.02	18.56	1.028
	GT 617	17.17	3.60	76.16	2.78	137.79	0.187	0.534	1.35	2.96	4.11	1.35	19.78	4.90	13.89	0.934
	GT 686	14.89	3.31	65.35	2.60	118.39	0.133	0.599	1.23	2.68	3.30	1.16	17.07	4.26	11.87	0.854
	GT 697	18.19	4.10	81.59	3.20	146.83	0.186	0.600	1.54	3.26	4.20	1.38	21.33	5.21	14.39	0.966
	GT 700	23.23	5.16	101.93	4.04	183.29	0.205	0.821	1.93	3.98	5.21	1.77	26.64	6.57	17.46	1.091
	GT 714	26.05	5.74	114.82	4.55	206.64	0.250	0.854	2.14	4.64	5.77	2.02	30.05	7.54	19.44	1.215
	GT 731	19.72	4.45	89.00	3.50	160.21	0.183	0.663	1.65	3.58	4.62	1.59	23.26	5.93	15.42	1.028
ROTORUA	GS 959	3.79	2.50	24.53	0.74	43.33	5.000	0.751	0.61	0.633	4.31	0.343	3.36	0.66	10.27	0.934
	GS 981	3.60	2.18	22.41	0.67	39.05	4.42	0.720	0.54	0.548	3.83	0.301	2.93	0.83	9.39	0.854
	GS 988	4.33	3.82	28.35	0.92	49.69	5.75	0.910	0.70	0.747	4.81	0.382	5.38	0.68	9.46	0.966

Absolute p.p.m. excepting Fe and Na expressed as %

N.D. Not Detected

Table 11. Results of Neutron Activation Analysis, Irradiation Run 534.

Source/Sample No.		Yb^{175}	Na^{24}	La^{140}	Fe^{59}	Ce^{141}	Sc^{46}	Co^{60}	Eu^{152}	Tb^{160}	Cs^{134}	Lu^{177}	Hf^{181}	Ta^{182}	Pa^{233}	Flux Factor
		SHORT LIVED ISOTOPES			LONG LIVED ISOTOPES											
TAUPO	GT 574	3.39	2.69	22.31	0.90	37.76	3.99	1.31	0.555	0.578	4.80	0.306	3.78	0.629	10.75	1.028
	GT 580	3.29	2.65	21.57	0.84	35.43	3.81	1.22	0.505	0.586	4.53	0.303	3.63	0.644	10.34	0.934
	GT 583	3.31	2.67	22.41	0.87	36.53	3.97	1.26	0.537	0.525	4.60	0.301	3.75	0.628	10.62	0.854
AWANA	GT 831/1	5.79	2.72	37.76	0.90	66.31	3.89	0.980	0.401	0.984	8.71	0.474	4.18	0.834	20.44	1.000
	GT 832/1	4.73	2.80	35.82	0.87	59.06	3.43	1.22	0.352	0.855	8.74	0.414	3.89	0.800	18.39	0.966
	GT 828	6.15	2.78	37.13	1.09	67.59	4.94	0.769	0.887	1.28	8.00	0.586	5.57	0.999	17.18	1.091
	GT 827	8.32	2.33	43.80	1.24	80.65	6.07	0.943	1.01	1.64	9.65	0.686	6.50	1.19	21.46	1.215
RUN 535																
PUNGAERE	GS 553/1	50.92	3.98	135.00	2.93	219.78	0.249	0.440	0.317	4.71	36.33	2.85	44.93	23.88	93.05	0.989
	GS 554	50.73	4.07	137.02	2.96	205.54	0.239	0.400	0.400	5.47	36.68	2.59	45.79	23.77	90.06	0.954
	GS 558/1	46.21	3.81	130.03	2.80	188.58	0.294	0.429	0.419	5.02	33.47	2.48	41.98	21.91	83.69	0.863
	GS 557/1	55.94	4.21	145.01	2.72	184.27	0.224	0.409	0.336	5.25	39.21	2.86	48.57	26.06	97.16	1.040
	GS 556/1	52.38	4.14	141.13	3.09	211.08	0.349	0.391	0.270	5.71	36.39	2.77	46.23	24.74	92.50	1.000
WETA	GW 373	20.12	2.80	14.88	0.72	37.55	2.05	0.327	N.D.	1.98	24.34	1.15	5.48	4.33	46.05	0.989
HAHEI	GS 466/1	7.51	2.74	29.77	1.03	54.10	4.04	0.642	0.777	0.850	5.10	0.452	3.74	0.762	12.82	0.944
	GW 365	7.97	2.92	31.60	1.09	56.58	4.26	0.621	0.803	0.945	5.79	0.465	3.97	0.753	13.40	0.954
	GW 363	7.52	2.76	29.89	1.04	53.33	4.05	0.599	0.768	0.862	6.47	0.435	3.92	0.756	12.74	0.863
	GW 364	8.22	2.99	34.33	1.24	62.72	4.82	0.734	0.915	1.062	6.32	0.543	4.54	0.872	14.93	1.023
	GW 369	7.67	2.93	32.61	1.26	59.50	4.68	0.792	0.853	0.960	6.19	0.538	4.75	0.848	14.51	1.040
	GW 370	6.48	2.44	25.62	0.91	47.57	3.54	0.510	0.704	0.663	4.59	0.402	3.48	0.649	11.06	0.989

Absolute p.p.m. excepting Fe and Na expressed as %

N.D. Not Detected

Table 12. Results of Neutron Activation Analysis, Irradiation Run 535.

Source/Sample No.		Yb^{175}	Na^{24}	La^{140}	Fe^{59}	Ce^{141}	Sc^{46}	Co^{60}	Eu^{152}	Tb^{160}	Cs^{134}	Lu^{177}	Hf^{181}	Ta^{182}	Pa^{233}	Flux Factor
		SHORT LIVED ISOTOPES			LONG LIVED ISOTOPES											
HAHEI	GW 368	8.05	2.85	30.67	1.08	54.30	4.17	0.630	0.791	0.774	5.68	0.435	4.02	0.713	12.94	0.944
	GW 367	8.11	3.09	33.28	1.14	58.73	4.47	0.619	0.882	0.937	6.14	0.499	4.17	0.841	14.00	0.954
WAIHI	GT 840/7	3.09	2.62	17.52	1.30	29.25	4.13	2.36	0.544	0.434	6.70	0.241	3.04	0.866	10.83	0.863
	GT 840/3	3.99	2.93	20.31	1.46	33.30	4.70	2.65	0.597	0.570	7.77	0.264	3.53	0.816	12.25	1.023
	GT 840/3	3.73	2.81	18.92	1.43	32.31	4.53	2.58	0.603	0.453	7.23	0.246	3.27	0.704	11.94	1.040
	GT 840/2	3.70	2.81	19.07	1.40	31.28	4.44	2.62	0.622	0.498	6.96	0.249	3.27	0.694	11.76	1.000
	GT 842/2	3.19	2.75	18.62	1.36	30.00	4.33	2.56	0.554	0.524	7.08	0.230	3.20	0.677	11.27	0.989
	GT 842/4	3.37	2.87	19.01	1.39	31.18	4.41	2.57	0.590	0.359	7.34	0.247	3.30	0.686	11.69	0.944
	GT 841/1	4.12	2.87	19.58	1.43	31.63	4.55	2.56	0.626	0.395	7.32	0.245	3.38	0.776	12.03	0.954
	GT 841/3	3.54	2.47	16.84	1.24	27.17	3.99	2.25	0.511	0.442	6.41	0.206	2.95	0.634	10.25	0.863
	GT 843/1	3.81	2.76	18.94	1.37	30.91	4.36	2.47	0.606	0.404	6.93	0.244	3.14	0.721	11.50	1.023
PURANGI	GT 844/1A	8.03	3.08	29.17	0.94	52.02	5.24	0.749	0.795	0.787	3.57	0.463	3.66	0.898	13.28	1.040
	GT 844/1B	7.04	3.03	28.85	0.92	50.36	5.17	0.698	0.792	0.753	3.38	0.457	3.72	0.854	12.82	0.989
	GT 844/1C	7.30	3.13	29.68	0.94	51.07	5.24	0.681	0.790	0.823	3.69	0.440	3.80	0.916	12.78	0.944
	GT 844/1D	7.78	3.14	30.03	1.00	52.23	5.45	0.834	0.807	0.892	3.88	0.495	4.25	1.06	13.43	0.954
	GT 844/1E	7.02	2.75	27.03	0.87	46.46	4.81	0.631	0.733	0.754	3.41	0.425	3.55	0.812	11.68	0.863
MARATOTO	GT 845/1A	5.90	2.70	25.78	0.64	45.31	3.64	0.448	0.257	0.725	9.39	0.369	2.77	0.927	16.22	1.023
	GT 847	5.22	2.67	25.82	0.63	44.99	3.62	0.523	0.260	0.660	9.20	0.380	2.82	0.956	16.07	1.040
	GT 848	5.91	2.79	26.40	0.63	45.77	3.70	0.621	0.295	0.657	9.42	0.368	2.78	0.940	16.37	1.000
	GT 845/1C	5.52	2.71	27.74	0.63	47.34	3.59	0.500	0.283	0.627	9.00	0.362	2.75	0.867	16.56	0.944

Absolute p.p.m. excepting Fe and Na expressed as %

Table 13. Results of Neutron Activation Analysis, Irradiation Run 535.

Source/Sample No.		SHORT LIVED ISOTOPES			LONG LIVED ISOTOPES											Flux Factor
		Yb^{175}	Na^{24}	La^{140}	Fe^{59}	Ce^{141}	Sc^{46}	Co^{60}	Eu^{152}	Tb^{160}	Cs^{134}	Lu^{177}	Hf^{181}	Ta^{182}	Pa^{223}	
ONGAROTO	GT 344	5.09	2.88	26.24	0.88	43.46	3.21	1.24	0.544	0.602	6.10	0.331	3.61	0.884	13.34	0.954
	GT 347	4.55	2.50	23.09	0.77	39.12	2.80	1.01	0.517	0.463	5.31	0.306	3.11	0.666	11.95	0.863
	GT 351	4.61	2.81	25.60	0.92	43.44	3.46	1.21	0.525	0.610	5.88	0.349	3.54	0.714	13.05	1.023
	GT 356	4.85	2.74	24.87	0.87	41.64	3.32	1.17	0.525	0.540	5.72	0.337	3.47	0.710	15.42	1.040
	GT 371	4.57	2.77	24.81	0.81	41.46	2.92	1.39	0.509	0.495	5.76	0.311	3.35	0.785	12.66	0.989
	GT 379	4.81	2.87	26.45	0.89	43.67	3.31	1.29	0.563	0.583	5.98	0.341	3.64	0.797	13.13	0.954
	GT 387	4.70	2.47	23.26	0.82	38.86	2.82	1.16	0.440	0.515	5.51	0.298	3.14	0.719	11.87	0.863
FANAL I	GW 258	5.83	2.20	22.30	0.76	39.46	2.63	1.71	0.294	0.712	9.91	0.358	3.42	0.824	15.33	1.000
	GW 259	7.61	2.84	28.27	1.01	49.14	3.39	2.40	0.380	0.849	13.80	0.462	4.44	1.13	19.31	0.989

Absolute p.p.m. excepting Fe and Na expressed as %

Table 14. Results of Neutron Activation Analysis, Irradiation Run 579.

Source/Sample No.

Yb^{175}	Na^{24}	La^{140}	Fe^{59}	Ce^{141}	Sc^{46}	Co^{60}	Eu^{152}	Tb^{160}	Cs^{134}	Hf^{181}	Ta^{177}	Pa^{233}
SHORT LIVED ISOTOPES			LONG LIVED ISOTOPES									
6.86	0.51	40.74	0.93	70.57	4.05	0.834	0.474	0.385	10.18	4.11	0.996	22.05
7.04	0.45	43.01	0.99	74.75	4.30	0.910	0.502	0.409	10.89	4.36	1.04	23.28
6.53	0.57	41.78	1.04	71.47	4.18	1.16	0.490	0.392	11.62	4.31	1.01	22.37
7.13	0.51	42.43	0.97	72.11	4.18	0.831	0.491	0.418	10.51	4.24	1.02	22.57
6.79	0.45	41.38	0.96	72.25	4.15	0.854	0.494	0.396	10.42	4.22	1.02	22.65
6.22	0.48	38.16	0.83	62.69	3.60	0.759	0.408	0.351	8.99	3.75	0.856	19.55
6.33	0.52	39.73	0.89	66.86	3.87	0.786	0.479	0.377	9.72	3.98	0.955	20.93
6.52	0.59	40.22	0.92	68.35	3.94	0.850	0.475	0.393	9.77	4.00	0.926	21.32
5.56	0.61	38.22	0.96	65.54	3.90	1.08	0.462	0.358	10.70	4.04	0.944	20.78
6.85	0.69	41.51	0.96	72.16	4.17	0.948	0.463	0.418	10.69	4.26	1.01	22.72
5.77	0.53	36.27	0.83	63.27	3.63	0.782	0.400	0.351	9.11	3.66	0.841	19.68
6.56	0.80	40.58	0.93	70.90	4.09	0.658	0.482	0.408	10.20	4.17	0.926	22.07
6.48	0.70	39.21	0.93	69.99	3.99	0.843	0.471	0.388	9.94	3.81	1.04	21.60
6.97	0.70	42.80	0.96	72.10	4.16	0.871	0.492	0.390	10.14	4.06	1.04	22.50
6.69	0.83	40.27	0.93	69.69	4.02	0.860	0.482	0.383	9.76	3.96	0.970	21.64
6.24	0.68	39.34	0.89	67.19	3.86	0.768	0.446	0.362	9.37	3.82	0.900	20.82
6.73	0.83	41.36	0.94	69.95	4.04	0.824	0.493	0.402	9.72	3.99	0.939	21.86
6.17	0.79	40.02	0.91	68.47	3.95	0.831	0.475	0.366	9.64	3.89	0.925	21.37
6.57	0.98	41.71	0.96	72.79	4.14	0.868	0.480	0.401	10.20	4.21	0.958	22.58
6.12	0.77	37.74	0.86	65.92	3.75	0.755	0.443	0.361	9.03	3.62	0.877	20.28

Absolute p.p.m. excepting Fe and Na expressed as %

Table 15a. Results of Neutron Activation Analysis, Irradiation Run 579.

Source/Sample No.	Yb^{175}	Na^{24}	La^{140}	Fe^{59}	Ce^{141}	Sc^{46}	Co^{60}	Eu^{152}	Tb^{160}	Cs^{134}	Hf^{181}	Ta^{177}	Pa^{233}
	SHORT LIVED ISOTOPES			LONG LIVED ISOTOPES									
	6.01	0.96	38.95	0.88	65.23	3.77	0.759	0.433	0.353	9.16	3.64	0.906	20.38
	5.56	0.88	40.33	0.92	68.78	3.95	0.832	0.473	0.382	9.55	3.85	0.949	21.41
	6.29	1.03	39.34	0.86	65.04	3.73	0.771	0.436	0.349	9.06	3.81	0.853	20.25
	6.04	1.06	39.68	0.89	67.53	3.86	0.800	0.449	0.370	9.19	3.85	0.913	21.08
	7.01	1.22	44.20	0.93	69.72	4.00	0.798	0.464	0.413	9.48	3.88	0.993	21.63
	6.71	1.19	42.39	0.94	70.68	4.05	0.813	0.500	0.398	9.75	3.99	1.03	22.03
	6.75	1.23	42.19	0.89	65.85	3.77	0.784	0.473	0.385	9.15	3.76	0.939	20.46
	6.11	1.27	39.82	0.89	66.11	3.80	0.748	0.457	0.379	9.07	3.79	0.932	20.64
	6.84	1.52	43.54	0.95	71.08	4.06	0.812	0.470	0.404	9.71	4.03	0.979	22.04
	8.33	1.62	38.00	0.97	65.61	4.66	0.603	0.514	0.488	10.24	4.43	1.18	21.97
	7.05	0.67	46.99	1.02	76.53	4.38	0.878	0.519	0.446	10.61	4.33	1.08	23.74
	6.08	1.28	38.76	0.88	66.65	3.75	0.793	0.436	0.379	8.89	3.79	0.921	20.59
	5.97	1.83	42.06	0.99	68.99	4.05	1.14	0.496	0.387	11.17	4.09	1.02	21.42
	6.25	1.58	42.46	0.91	67.56	3.94	0.838	0.474	0.374	10.02	3.95	0.922	20.77
	4.34	1.59	36.94	0.89	65.65	3.84	0.752	0.450	0.387	9.87	3.83	0.892	20.34
	3.84	1.53	35.12	0.92	62.82	3.75	1.11	0.433	0.353	10.32	3.75	0.931	19.47
	4.21	1.66	35.47	0.87	64.54	3.74	0.745	0.433	0.369	9.35	3.74	0.913	19.89
	4.22	1.73	36.40	0.88	66.21	3.84	0.763	0.455	0.388	9.55	3.82	0.908	20.29
	4.06	1.87	37.10	0.89	67.11	3.90	0.730	0.470	0.390	9.83	3.86	0.905	20.59
	4.61	1.44	38.19	0.94	69.88	4.00	0.782	0.466	0.408	9.44	3.96	0.904	21.74

Absolute p.p.m. excepting Fe and Na expressed as %

Table 15b. Results of Neutron Activation Analysis, Irradiation Run 579.

Source/Sample No.	Yb^{175}	Na^{24}	La^{140}	Fe^{59}	Ce^{141}	Sc^{46}	Co^{60}	Eu^{152}	Tb^{160}	Cs^{134}	Hf^{181}	Ta^{177}	Pa^{233}
	SHORT LIVED ISOTOPES			LONG LIVED ISOTOPES									
	4.19	0.67	34.37	0.85	63.84	3.63	0.709	0.431	0.362	8.81	3.61	0.867	19.74
	4.04	1.28	33.93	0.83	62.32	3.56	0.694	0.413	0.328	8.64	3.53	0.837	19.34
	5.06	1.83	42.51	1.04	77.51	4.43	0.831	0.523	0.437	10.27	4.42	1.04	24.08
	3.35	1.58	27.98	0.66	50.41	2.88	0.634	0.329	0.295	6.74	2.85	0.746	15.48
	7.55	1.59	60.25	1.76	124.57	4.92	0.410	2.49	1.48	2.76	8.45	11.24	15.48
	6.56	1.53	52.64	1.50	105.22	4.20	0.344	2.11	1.24	2.25	7.13	9.63	13.13
	5.87	1.88	48.68	1.38	97.52	3.92	0.354	2.00	1.13	2.24	6.65	8.70	12.03
	7.02	1.33	55.73	1.50	104.26	4.26	0.302	2.14	1.24	2.51	7.22	9.65	12.91

CHAPTER FOUR. APPLICATION OF TRACE ELEMENT DATA TO MULTIVARIATE ANALYSIS

OUTLINE OF APPROACH

The trace element data from the neutron activation analysis can be divided into two components: geological (Runs 533,534 and 535) and archaeological (Run 579).

When research on the experimental data was instigated, no previous studies had been formulated using neutron activation data of New Zealand obsidian. Previous characterisation programmes, notably Ward's petrographic groupings by the X-ray fluorescence technique (Ward,1974 b.) considered the application of trace element data to statistical methods. Thus the neutron activation results, after consideration and subsequent correction for flux variations, aimed to provide a new body of material whereby multivariate analysis could be applied to future relevant archaeological application. Therefore while irradiation Run 579 concerned archaeological artifact samples, emphasis was at the outset placed on the geological source groupings. This is further enhanced by subsequent analysis for possible major element variations related to refractive index measurements and X-ray fluorescence on geological samples. As will be seen, major element compositions do not yield differences significant enough to elucidate sourcing patterns.

Two methods of approach towards multivariate analysis were adopted to consider the discreteness of the sources. These are Cluster analysis and Discriminate Variate analysis.

As the term implies, multivariate analysis is the study of variables in more than one dimension. In early characterisation projects undertaken on New Zealand obsidian, frequently the ratio of two elements (for example fluorine and sodium (Coote, Whitehead and McCallum,1972)) or the relation between pairs of elements (Green,Brook and Reeves, 1967), measured the extent of variation between/within sources. Principal component analysis is another facet of two dimensional studies. It has been argued (Ward, 1974; Moroney,1951) that an increase in the number of variables (trace elements) that can be used simultaneously refines the sourcing procedure.

The eighteen petrographic source groups outlined by Ward (1972) and accepted in this work, were determined by analysing five elements. With the aid of computer facilities incorporating designed programmes, it is possible to consider a large number of variables and allow the programme to calculate the useful ones. Although fifteen variables may initially have the effect of a 'loose' classification, if the analysis is repeated using only the most discriminating variables, the classification will improve and be more significant. The purpose therefore is to be as objective as possible while retaining common sense.Bromine would not be analysed because the concentration could have been affected by contamination from the polythene containers. Scandium, on the other hand, shows little variation and is known to be an internal monitor (Hallam,Warren and Renfrew,1976).

Cluster analysis has seen numerous applications to archaeological differentiation problems (for example, Hodson,1969,1970,1971; Hammond et al, 1976). Stepwise discriminant analysis because it offers the researcher a versatile and powerful statistical technique for chemical characterisation of source groups and unknown artifacts has recently gained popularity. Amongst others, characterisation of obsidian sources in West Mexico employed this technique with success(Ericson and Kimberlin,1977). Both methods are adapted to a large number of cases and variables, indispensable to the present work, having 112 geological samples (48 archaeological samples) with 14 possible discriminating variables.

Several assumptions must be made before analysis, if a model of the sources in terms of their inter-relationships is to be valid. These are:-

1. The data represent independent observations from random samples of their populations.
2. The data is equally weighted - all observations and their measurements being of equal probability.
3. The observations form statistically representative groupings.
4. The measurements chosen to describe each observation correspond to the precision of the experimental technique.

The first assumption is consistent with the discussion of analysed material already given(Chapter One), although it should be acknowledged that resulting 'outliers' where misclassification to the original source occurred (for example, Taupo and Tairua) may be due to detrital deposits.

All measurements were entered into the analysis as part per million concentrations and given equal weighting to ensure that there is no bias towards variables which have large variances.

Two source groups - Weta and Fanal Island - were found to be statistically non-representative, having one and two samples respectively. These were excluded from analysis.

Fourteen elements from the short and long lived isotope data were initially selected. These were all included for cluster analysis but selectively reduced to five or six being the most discriminating in the discriminant analysis. These corresponded to the precision of the experimental technique. A large number was chosen in order that the maximum number of dimensions could differentiate the extent of intra-source variation between groupings.

The elements chosen and the sample size of source groups is listed in Table 19 below.

Table 19. (a) Source groupings of geological obsidian and the number per group of samples. The first column denotes the code entered into the analysis. (b) List of isotopes considered for multivariate analysis.

(a) Source Groups

Code No.	Source	Number of Samples
S(1)	Te Ahumata	10
S(2)	Huruiki	10
S(3)	Cooks Bay	8
S(4)	Tairua	7
S(5)	Rotorua	10
S(6)	Maraetai	9
S(7)	Taupo	8
S(8)	Awana	4
S(9)	Hahei	8
S(10)	Purangi	5
S(11)	Maratoto	4
S(12)	Ongaroto	9
S(13)	Mayor Island	14

Code No.	Source	Number of Samples
S(14)	Waihi	9
S(15)	Waiare	10
S(16)	Pungaere	5

(b) Short lived isotopes

^{175}Yb, ^{24}Na, ^{140}La, ^{233}Pa.

Long lived isotopes

^{59}Fe, ^{141}Ce, ^{46}Sc, ^{60}Co, ^{152}Eu, ^{160}Tb, ^{134}Cs, ^{177}Lu, ^{181}Hf, ^{182}Ta.

4.1. Cluster Analysis:Wards Method

Cluster analysis is a numerical technique whereby the data is ordered into relatively distinct groups, related to but separated from other groups (Hodson,1971). Several methods of partitioning the data are available, the merits of which have been extensively discussed elsewhere(Sokal and Sneath,1973; Everitt,1974). Ward's method of group clustering was adopted in this analysis in conjunction with the CLUSTAN 1C statistical package computer programme(Wishart,1975).

Ward's method uses a hierarchial clustering criterion whereby the distance between groups is a measure of the total sum of squared deviations of every sample from the mean of the cluster (group) to which it belongs (Ward,1963). The square of the distance between any two points, the Euclidean Distance (Error Sum of Squares) is equal to :

$$\sum_{i=1}^{n} x_i^2 - \frac{1}{n}(\Sigma x_i)^2,$$ where n=number of variables measured on each sample x.

...equation 10.

The method finds the minimum variance between spherical clusters, thus each cluster centre represents the constituent cases at a high level of similarity.

As a starting point, the maximum number of clusters, n, are chosen and the variables are standardised by dividing the score on each variable by its standard deviation. The data set is divided into n clusters according to input order. At each step of the reiterative procedure, two clusters which are most similar are fused. The fusion continues in a n-1 cycle until the optimum solution has been found. Each union is considered to be 'equal to or better than' that of the preceeding union. The aim is to achieve the identity of the 'best union' which is maintained throughout the sequence of comparisons (Ward, 1963). This may then be graphically illustrated on a two dimensional dendogram (or scattergram) showing the fusions which have been made at each successive level. The y axis records the measure of association. In this instance, the <u>dissimilarity</u> co-efficient of Euclidean distance.

Because the data was already classified into groupings (obsidian source groups) and no unknown observations were available, cluster analysis was used more to consider the question of inter-source variation, and to separate the dominant groups which tended to form exclusive clusters. Hence, five programmes were initiated on the arbitrary basis of irradiation runs with one overall programme considering the sixteen sources.

Each sample is prefixed by one or two letters indicating the source and numbered consecutively as they appear in the neutron activation results. The sample number is not cross-referenced to the original coding (for example, GS114), because the purpose is to discern patterns of dominance and separation within source groups rather than individual measures of similarity and dissimilarity.

Programme One: Run 533

Sources:	Te Ahumata	(Great Barrier Region)
	Huruiki	(Northland Region)
	Waiare	(" ")
	Cooks Bay	(Coromandel Peninsula)
	Tairua	(" ")

Forty-two samples representing three source regions formed two cluster groups (fig.8). Waiare formed one, and the remaining samples were tightly clustered. The degree of disassociation between cluster 1 and cluster 2 was 60.867. Within cluster 1, the sources fused at the same level of similarity for each grouping.

Programme Two: Run 533 Without Waiare

Sources: As Programme One excluding Waiare.

Waiare was removed from this programme to seek a division amongst the other source groupings (fig.9). As there were less samples in the analysis (32), and owing to the overall similarity of cluster 1 in the previous programme, the dissimilarity co-efficient was significantly lower being 22.805. Cooks Bay, Tairua and one sample from Huruiki (H20) formed a cluster, Te Ahumata and Huruiki samples the other. It is noticeable that there is a wider spread of association within a source group (for example, compare H11 and H16 with H14 and H17). This will be later paralleled with the distribution of samples about the centroid of the source group in discriminant analysis.

Programme Three: Run 534

Sources:	Tairua	(Coromandel Peninsula)
	Mayor Island	(" ")
	Rotorua	(Inland Region)
	Maraetai	(Inland Region)
	Taupo	(" ")
	Awana	(Great Barrier Region)

Forty-eight samples from three source regions formed again two cluster groups (fig.10). Excepting a slightly higher index of dissimilarity (65.899) between cluster 1 and cluster 2, the analysis produced a similar pattern to programme one. Mayor Island initiated its own cluster with the other five source groupings tightly clustered.

Programme Four: Run 534 Without Mayor Island

Sources: As Programme Three excluding Mayor Island.

An interesting feature of this analysis (fig.11) is the allocation of the Taupo, Maraetai and Rotorua sources into both clusters. The Awana and Tairua sources , considering their small representation (four and three samples respectively) exhibit a reasonable proportion of inter-source variation. Again the reduction of sample population (34) lowers the dissimilarity co-efficient between the two clusters to 26.230.

Programme Five: Run 535

Sources:	Pungaere	(Northland Region)
	Hahei	(Coromandel Peninsula)
	Waihi	(" ")

Purangi	(Coromandel Peninsula)
Maratoto	(" ")
Ongaroto	(Inland Region)

Each of the sources (excepting Hahei -Ha 12) partitioned into small groupings within a cluster (fig.12). The dissimilarity co-efficient for each source is very uniform suggesting a marked similarity of composition for these sources. This is not inconsistent with the predominance of the Coromandel Peninsula region, the Northland source, Pungaere, forming a separate cluster. The number of samples in this analysis was thirty-eight. 58.460 is the dissimilarity co-efficient between the clusters.

Programme Six: Overall Cluster Analysis

Sources: All sixteen sources.

One hundred and twelve samples taken from the previous programmes were analysed (fig.13). The most important contribution of this analysis is to illustrate the tight groupings of cluster 1 which includes thirteen sources. Mayor Island, Pungaere and Waiare form a separate cluster, a pattern of dominance that is repeated in discriminant analysis. Due to the large sample population, the distance co-efficient was 174.697.

<u>Figure 8. Programme One: Run 533</u>. The samples representing five sources formed two clusters. Cluster 1 above the dashed line, and Cluster 2 below. <u>Key</u>: TA=Te Ahumata; H=Huruiki; W=Waiare; CB= Cooks Bay; T=Tairua. The units of dissimilarity between samples and clusters are shown along the top axis.

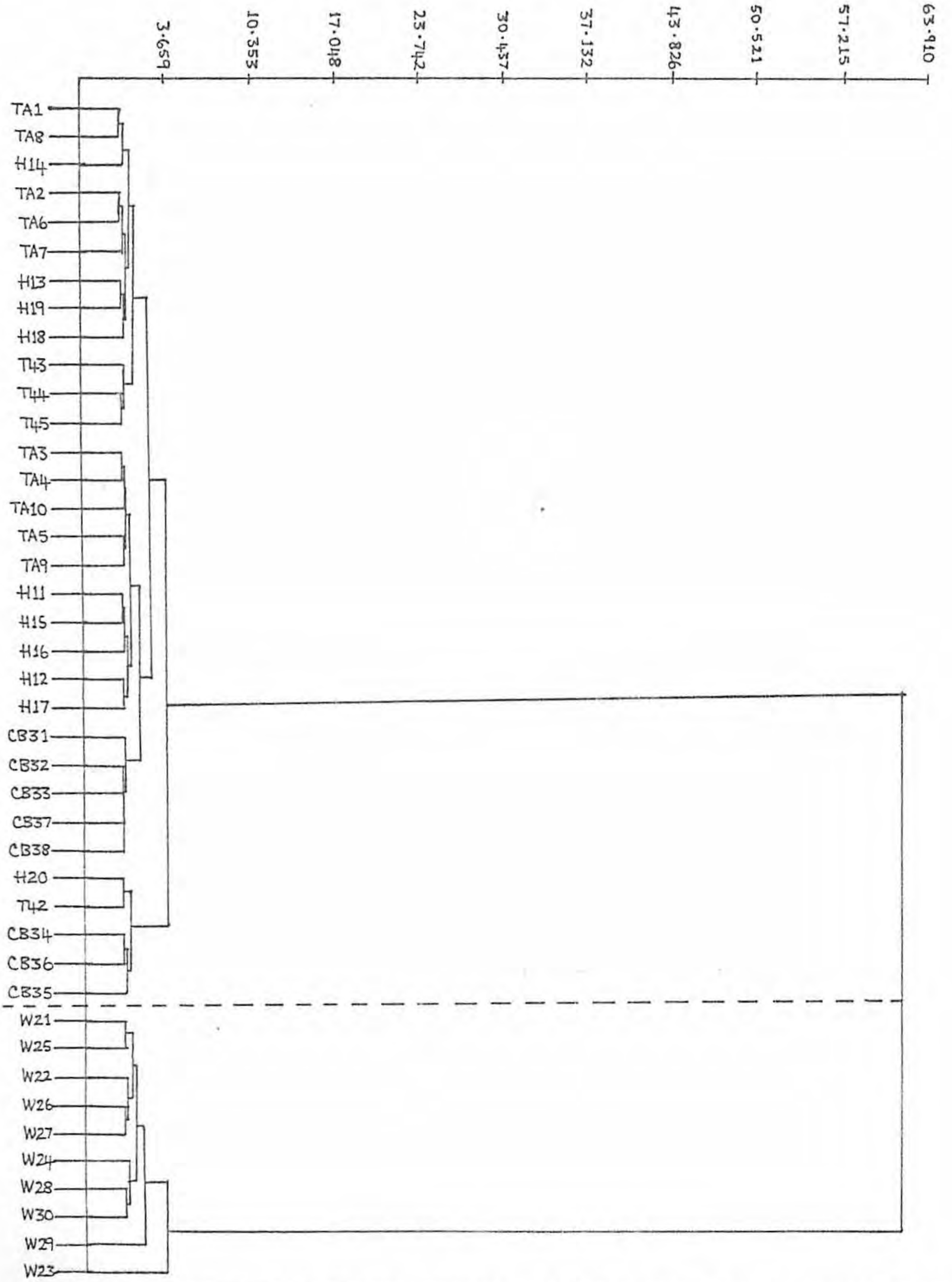


Figure 9. Programme Two: Run 533 Without Waiare. This dendogram illustrates the separation of the samples of Programme One when Waiare is removed. Accordingly, the dissimilarity index is lower. Key to the source prefixes as fig. 8.

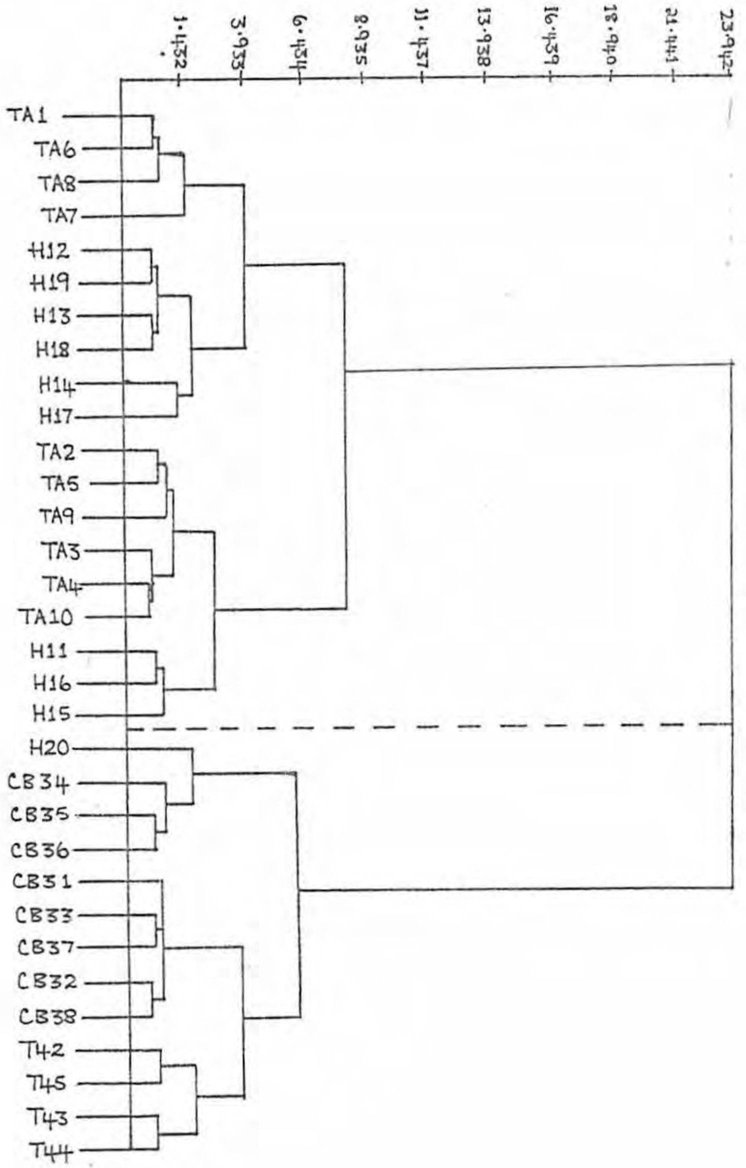


Figure 10. Programme Three:Run 534. A similar pattern of tight clustering of sources (cluster 1) as occured in fig.8. Mayor Island formed its own distinctive cluster. Key: TR=Tairua; AB32 - 37 and MA27-31=Maraetai; RA=Rotorua; AB38-41 and TO42-45= Taupo; MS=Mayor Island; AW=Awana.

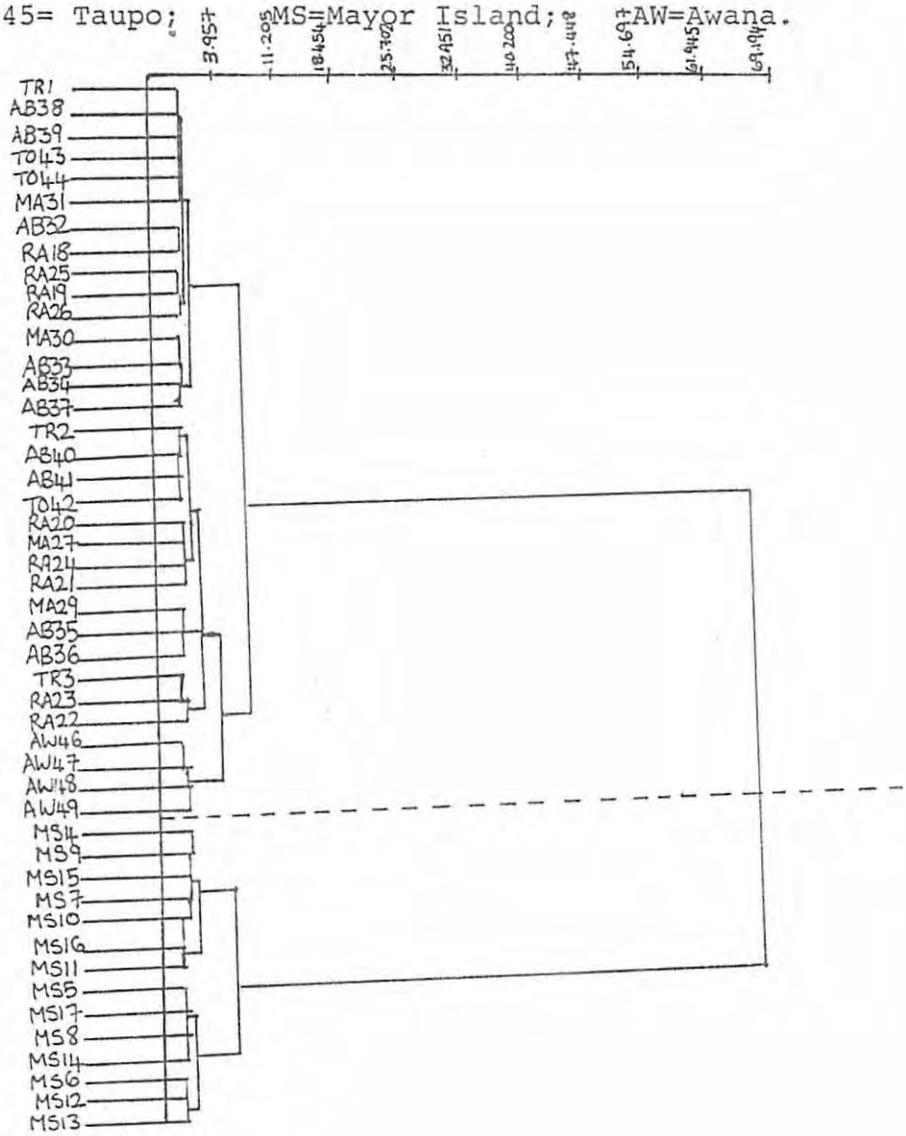


Figure 11. Programme Four:Run 534 Without Mayor Island.
The removal of Mayor Island causes the remaining source to re-allocate to two clusters. In the first cluster (above the dashed line), the successive fusion of each small group is the first indication that the inter-source variation will be greater than within the one source. Key as fig.10.

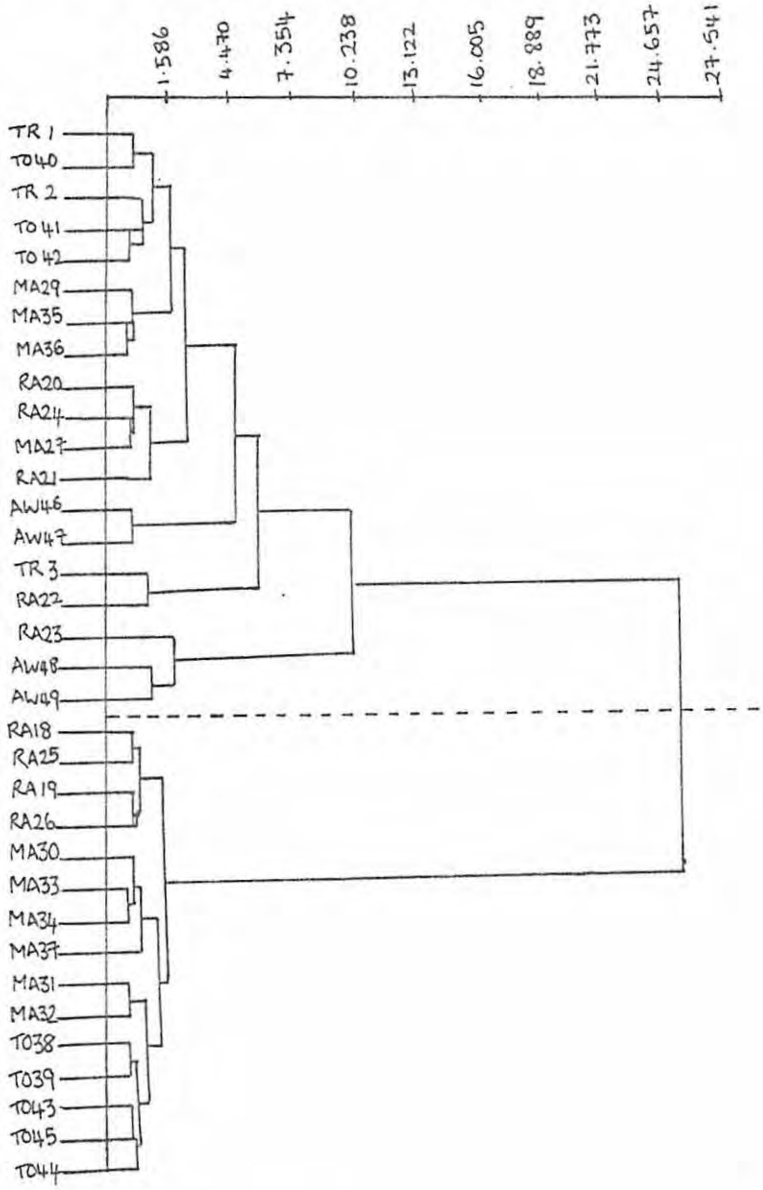


Figure 12. Programme Five:Run 535. The Ongorato samples (ON) are not markedly dissimilar from the Coromandel Peninsula sources. Pungaere(PU) situated in the Northland Region is distinct. Key: PU= Pungaere; HA=Hahei; PN=Purangi; ON=Ongaroto; MO=Maratoto; WH=Waihi.

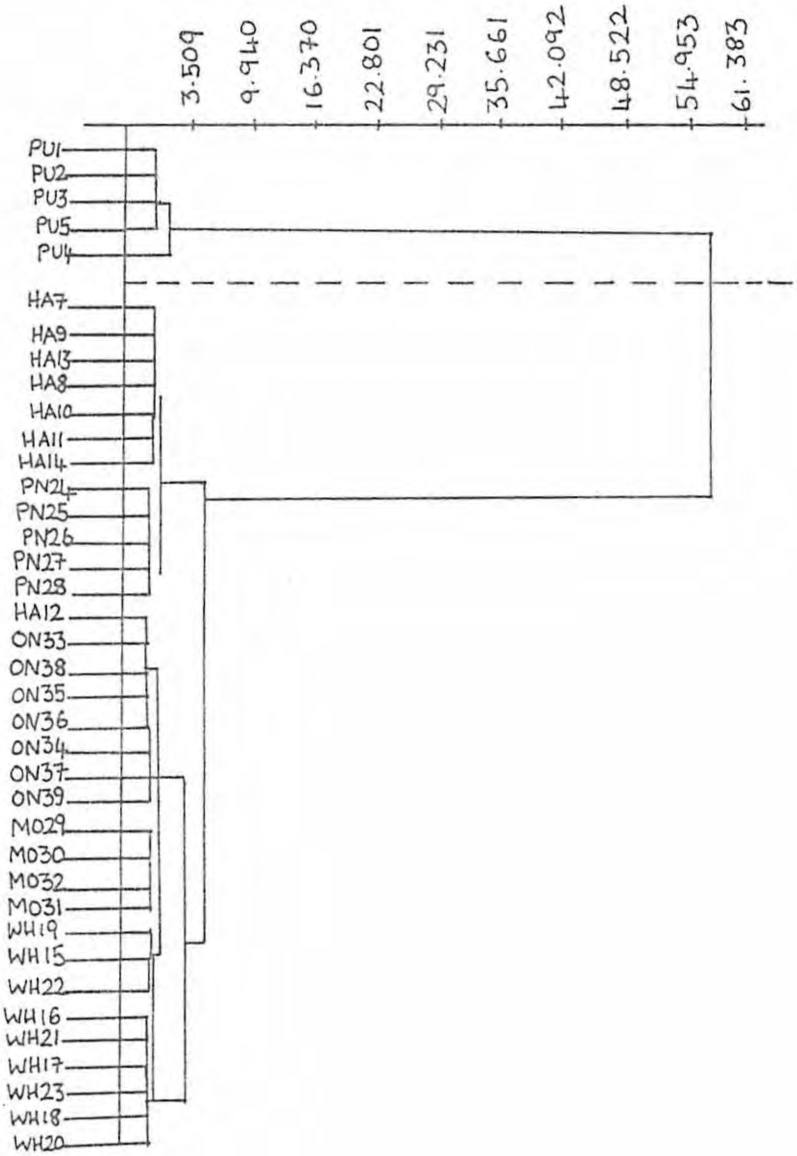
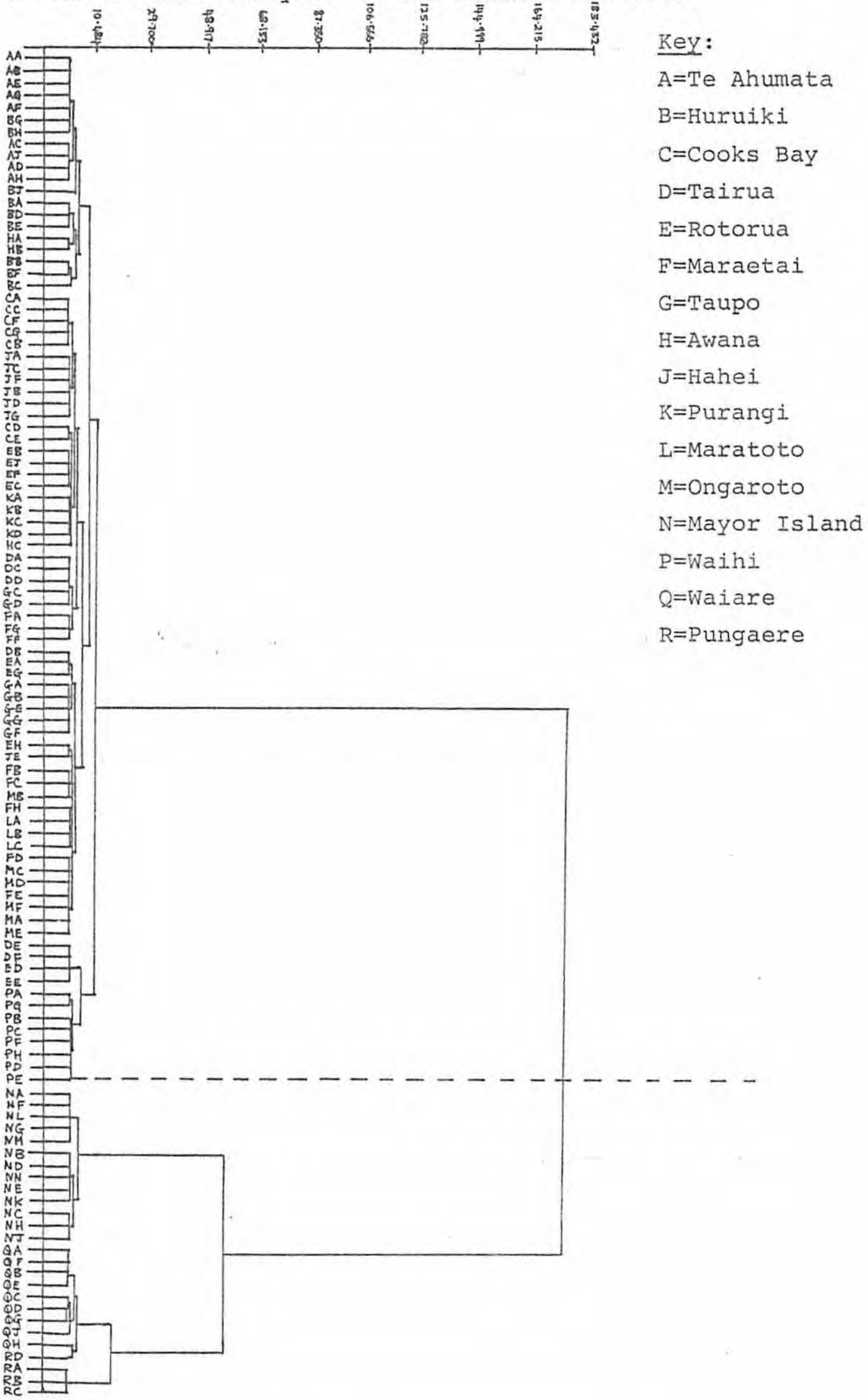


Figure 13. Programme Six:Overall Cluster Analysis. Dendogram of the cluster analysis of all sixteen sources.



Key:

A=Te Ahumata
B=Huruiki
C=Cooks Bay
D=Tairua
E=Rotorua
F=Maraetai
G=Taupo
H=Awana
J=Hahei
K=Purangi
L=Maratoto
M=Ongaroto
N=Mayor Island
P=Waihi
Q=Waiare
R=Pungaere

4.2 Discriminant Analysis

Discriminant analysis aims to statistically distinguish between two or more groups of cases on the basis of variables which measure the characteristics of those cases. It is assumed that the discriminating variables have a multivariate normal distribution. The mathematical objective is to weight and linearly combine the discriminating variables in order that the groups are forced to be as statistically distinct as possible. The discriminant function is equal to one or more linear combinations of the discriminating variables:

$$D_i = d_{i1}Z_1 + d_{i2}Z_2 + \ldots\ldots. + d_{ip}Z_p.$$

where D_i = score on discriminant function i

d_i = weighting co-efficient

Z = standardised value of the p discriminating variables used in the analysis.

(Klecka, 1975)

... equation 11.

In subprogramme DISCRIMINANT (Statistical Package for the Social Sciences) the discriminant score (D_i) represents the number of standard deviations a case is away from the mean for all cases on a given discriminant function.

The two major objectives of this technique are analysis and classification. If the discriminant functions are considered as orthogonal dimensions along which the location of one group relative to another (each group is measured by its centroid) can be described, then the analysis objective identifies the variables which maximise the separation of the groups along the respective dimensions.

Not all the variables entered in the analysis may cause maximum separation of the groups. To select the most useful, a stepwise procedure can be done. Initially, the single best discriminating variable is determined and at each step a variable is chosen to improve the value of the discrimination criterion in conjunction with the previous variable. The criterion may be either based on Wilks Lambda, Mahalonobis distance or Rao's V. The first was used in this analysis whereby the overall multivariate F ratio is the test of differences among group centroids. Accordingly, the variable which maximises the F ratio also minimises Wilks Lambda.

The second objective, classification, tests the validity of the original groupings using the discriminating variables found in the analysis stage. A separate linear combination of the discriminating variables for each group produces a probability of membership in the original group. The cases are then assigned to the group with the highest probability. Also, unknown cases may be entered and group membership sought. This last feature is a particular advantage allowing archaeological material to be classified to a source group.

To test the classification procedure, one sample was removed from each source grouping on a random allocation prior to analysis.

A graphical output of the relationship of the cases in respect to the first two discriminant functions is produced. Each case is plotted together with the group centroid facilitating an assessment of the distribution of each group.

(i) Validity of the Classification Procedure

Before discriminant analysis was used to consider the discreteness of the source groups, the validity of the classification objective was investigated. One sample from each group was entered as a subfile having no prior membership to any source. In this way the suitability of the data to discriminant analysis would be decided. If the variables chosen in the analysis are able to differentiate the source groups, then each sample of "unknown" membership would be expected to allocate to its original source. ("Unknown" in that there is no previous allocation.)

The sixteen samples were each classified to their respective sources, only the Taupo and Tairua cases having any noticeable affiliation with another source. The probability of 0.585 was quoted for Tairua membership , and 0.659 for Taupo, for the case taken from each. Of interest as well, is that several misclassifications from the known groups occurred summarised in Table 20 below.

Table 20. Misclassifications from discriminant analysis of 16 sources and "unknown" group (16 cases), based on the most discriminating trace elements: ^{134}Cs, ^{175}Yb and ^{141}Ce. The source group to which the sample has the highest probability of allocation is situated in Column 1, the second highest probability in Column 2.

Source	Sample Code No.	Highest Probability	Second highest Probability
Te Ahumata	GS 146	Huruiki (0.726)	Te Ahumata (0.246)
Rotorua	GW 261	Tairua (0.985)	Rotorua (0.008)
	GT 147/2	"Unknown"(0.432)	Taupo (0.251)
Maraetai	GT 287	Ongaroto (0.999)	Maraetai (0.421)

The discriminant analysis was repeated using the six most discriminating variables :- ^{134}Cs, ^{175}Yb, ^{141}Ce, ^{60}Co, ^{46}Sc and ^{182}Ta. There was a lowering of overall classification to 80 percent though fourteen out of the sixteen unallocated cases were correctly assigned (the Maraetai case was located in the Taupo source - probability 0.705, and the Taupo case was associated with Tairua -probability 0.510). In addition to the Te Ahumata and Rotorua cases in the previous analysis (Table 21), several other cases were misclassified.

Table 21. Additional misclassifications from repeated discriminant analysis of 16 sources and "unknown" group (16 cases). Note Sample GT777 is only weakly associated with the "unknown" group though less for the original allocation.

Source	Sample Code No.	Highest Probability	Second highest Probability
Te Ahumata	GS 149/1	Maratoto (0.534)	Te Ahumata (0.235)
Huruiki	GS 188	Te Ahumata (0.448)	Huruiki (0.438)
	GS 222	Maratoto (0.451)	Huruiki (0.339)
Tairua	GS 629	Taupo (0.448)	Tairua (0.358)
Maraetai	GT 777	"Unknown" (0.309)	Maraetai (0.245)
Taupo	GT 544	Tairua (0.493)	Taupo (0.324)

The significance of the misclassifications will be later discussed but at this juncture the classification procedure was believed to be valid for the data allowing analysis of the geological and archaeological trace element data to proceed.

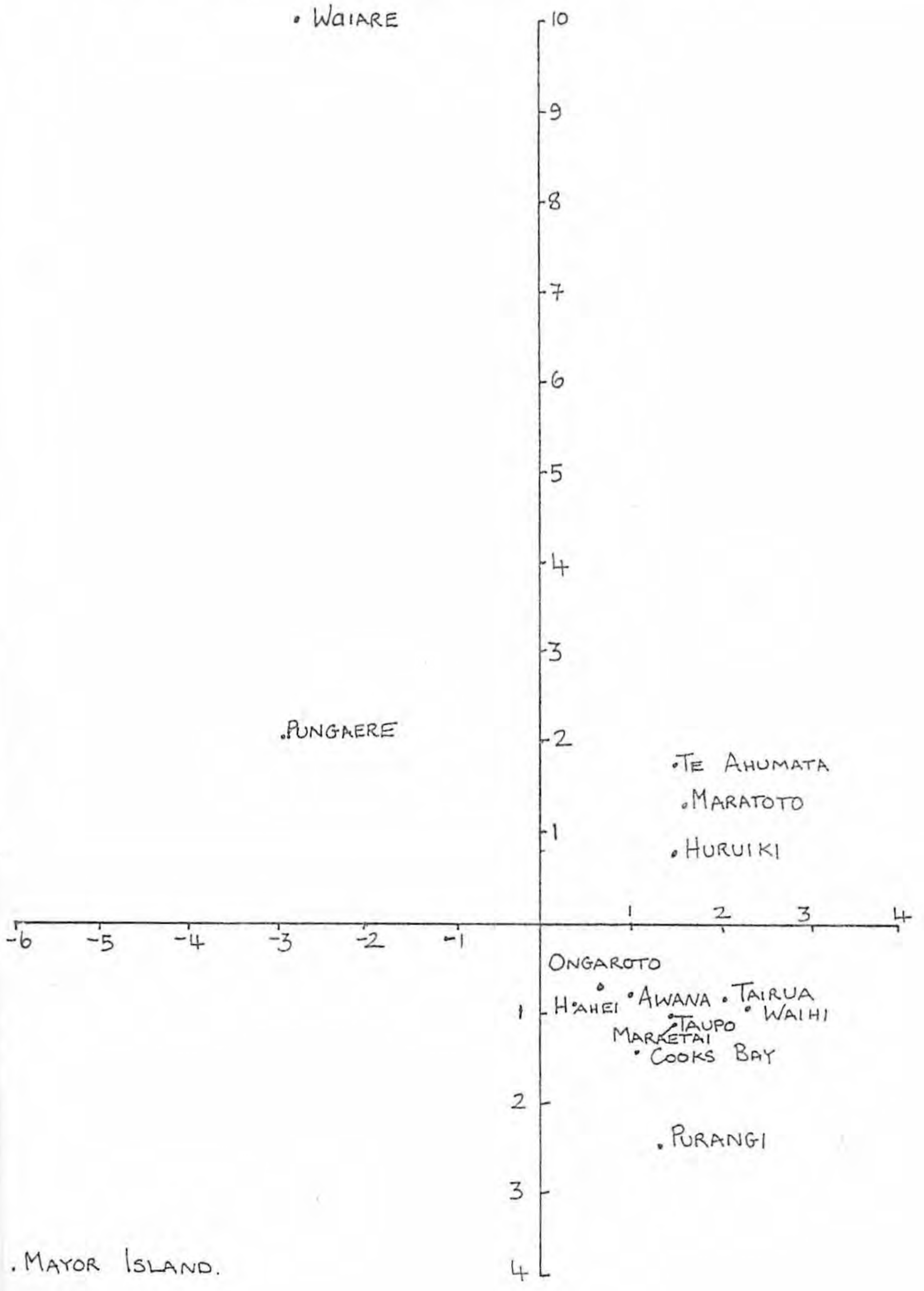
(ii) Analysis and Classification: Geological Data

The analysis of source groups was done in two stages. Initially a large range of elements were included without any a priori weighting but, nevertheless, standardised. When the analysis outlined the discriminating elements maximising separation of the groups, these were entered for analysis and the classification of cases to source groups was compared in both instances. As previously stated, the number of cases was reduced by 16 to 112 to allow for "unknown" group of cases to test the classification procedure. Although in the well represented sources as Mayor Island or Te Ahumata (Table 19), the removal of one case per group was not significant, Maratoto and Awana could be considered as borderline populations.

All sixteen sources were analysed and the discriminating elements in order were: ^{134}Cs, ^{175}Yb, ^{141}Ce, ^{60}Co and ^{46}Sc. These were computed from a larger range thus eliminating ^{24}Na, ^{152}Eu, ^{140}La, ^{160}Tb, ^{182}Ta and ^{181}Hf. The classification revealed a probability of 1.00 (maximum probability) that all cases from Mayor Island, Waiare, Pungaere and Waihi were in their own groups rather than another. Comparable to the results of the cluster analyses, the remaining source groups were situated in close proximity to each other on the two most discriminant score axes for the centroids of the groups (fig. 14). The plot clearly illustrates the separation of Mayor Island, Pungaere and Waiare (both from the Northland Region).

To clearly visualise the distribution of cases in the tightly knit grouping of sources, Mayor Island, Pungaere, Waiare and Waihi were excluded from the following analysis. Thus the total sample size was lowered to 78 cases. Thirteen trace elements were listed for analysis (again a large range owing to the possibility that removal of several sources may cause a differentiation of discriminating variables). The rare earths figured prominently with the highest F ratio to remove from the

Figure 14. Plot of the centroids of groups along the two most discriminant functions. The vertical axis represents the first discriminant score and the horizontal axis, the second discriminant score. These scores are computed from the linear combination of the most discriminating elements.



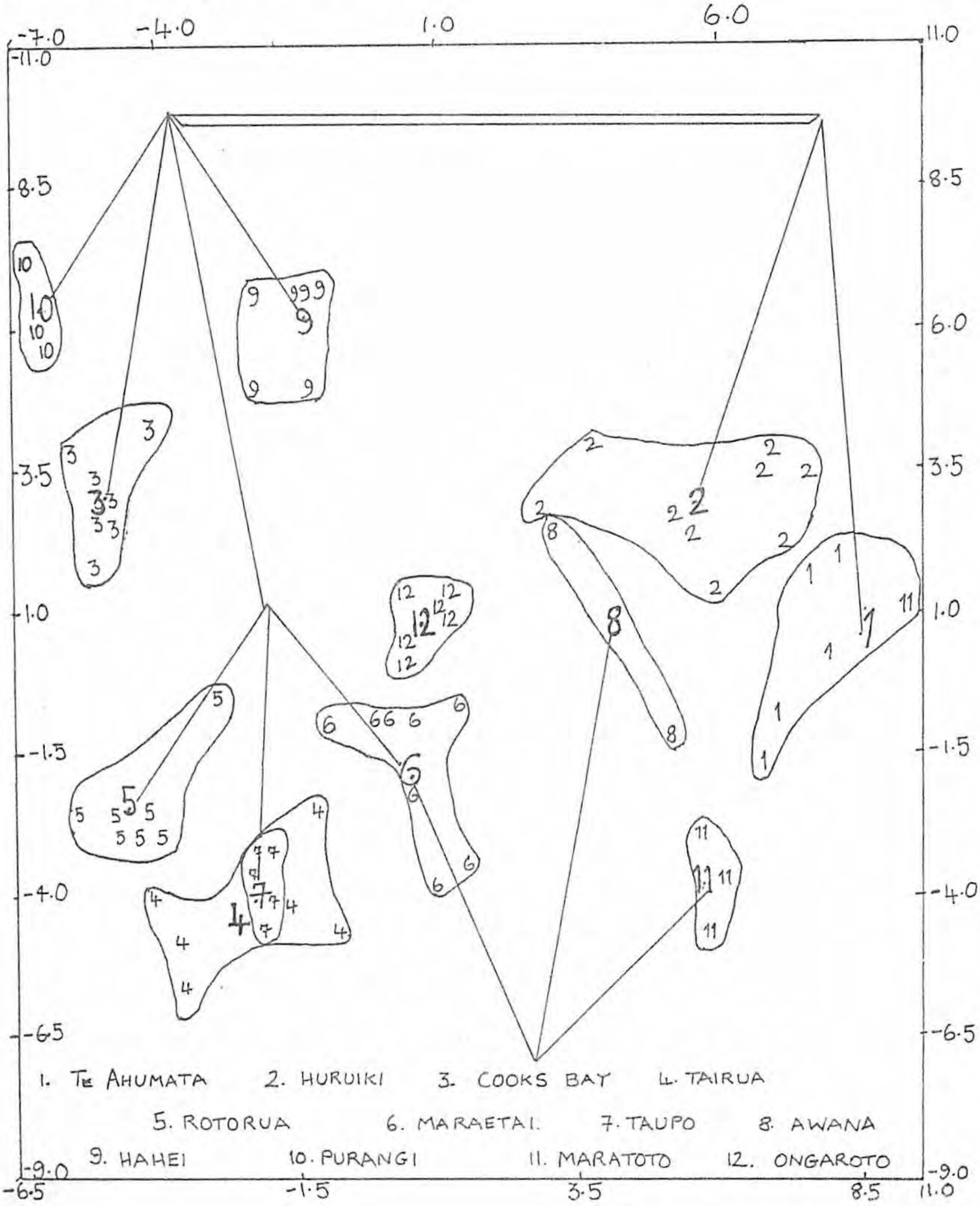


Figure 15. Plot of Discriminant Score 1 (Horizontal) vs Discriminant Score 2 (Vertical) for twelve sources. The larger figure indicates a group centroid, the other samples belonging to that source in lower case numerals. The boundaries of the source groups is an approximate indication of the spread of each group (the distance between centroids). Note the overlap of the Tairua and Taupo sources.

analysis: ^{134}Cs, ^{175}Yb, ^{141}Ce, ^{140}La and ^{24}Na. The results showed 100 percent of all cases correctly classified to the original source groups.

^{134}Cs, ^{175}Yb, ^{141}Ce, and ^{140}La reduced the classification to 97.4 percent when entered as a separate analysis. One case from Tairua had a higher probability of belonging to the Taupo source and similarly a case from Tairua was classified to the Taupo group. This is borne out in the plot of all cases in relation to the centroids of the respective groups (fig.14) where there is overlap of the two sources.

Fig. 15 finally demonstrates the separation and discreteness of each source which had previously not been possible to do. The distance between the centroids of the sources was measured (Table 22) showing a close correlation between the sources of the Inland Region. Generally, the Coromandel Peninsula and Inland Region sources feature nine out of a possible twelve sources and hence it is inadvisable to make assumptions on the inter-source distances with the most northern source regions. The greatest distances ('distance' being the separation of the groups on the basis of the most discriminating elements) are between Te Ahumata and Maratoto or Purangi. Central to any interpretation of the inter-source variation is the opposing factor of distribution of the cases within a source group.

Not all cases are plotted on fig. 15 because the programme is not able to differentiate two cases having a very similar score on the discriminant functions within the scale chosen. However, at least 85 percent of cases per source group are marked (the only exception being Taupo where overlapping causes the

Table 22. Distance between source groups 1-12 in units from the scale of two discriminant scores (x and y axis) in fig. 15.

(G) 1	1	2	3	4	5	6	7	8	9	10	11	12
(N) 2	3.90											
(C) 3	13.75	10.62										
(C) 4	12.03	10.94	7.81									
(I) 5	13.36	11.40	5.47	2.81								
(I) 6	8.36	7.03	7.03	3.98	5.00							
(I) 7	11.56	5.39	7.50	0.62	2.81	3.44						
(G) 8	4.53	2.50	9.29	3.98	9.22	4.53	7.89					
(C) 9	11.56	7.81	4.84	10.62	9.22	8.28	10.16	7.66				
(C)10	15.86	12.26	3.51	11.33	8.90	10.55	11.09	11.56	4.76			
(C)11	5.00	6.72	12.66	8.20	10.31	5.47	7.81	4.92	12.26	15.47		
(I)12	7.97	5.47	6.01	6.09	6.09	2.73	5.62	3.40	5.70	8.85	6.87	

Key: 1=Te Ahumata
2=Huruiki
3=Cooks Bay
4=Tairua
5=Rotorua
6=Maraetai
7=Taupo
8=Awana
9=Hahei
10=Purangi
11=Maratoto
12=Ongaroto
I=Inland Region
C=Coromandel Peninsula
N=Northland Region
G=Great Barrier Region

obscurity of two cases (70 percent of total group).

The measure of variation within a group in this technique is the classification details. Each case is calculated according to the highest and second highest probability of being in the group in which it was entered, or being in another group. For example, sample GS146(Te Ahumata had a probability of 0.543 of remaining in the original source and a probability of o.457 of being classifed to the Huruiki source. As 0.543 is greater than 0.457, this particular sample was predicted to have 100 percent membership with its own group. Similarly, for other cases at a distance from the centroid but proximate to another group could be considered as marginal classifications. The results (analysis and classification) produced from this consideration of 12 sources are best viewed in conjunction with a study of the standard deviations and co-efficients of variation for each source group (see Tables 17 and 18).

(iii) Analysis and Classification:Archaeological Data

A major goal of employing multivariate analysis in characterisation programmes is to allocate archaeological data to known sources. Once the geological configuration has been examined to satisfy that inter-source variation is greater than intra-source variation, artifact assignment can be made. The trace element data from Motutapu (Site N38/30, layers 4,6A and 6B) was available for analysis.

Motutapu (Run 579)

A large group of samples (forty-four) was put into the discriminant analysis programme together with the sixteen source groups previously described. There was a possibility that by excluding Weta and Fanal Island samples, the resultant allocations would be tentative. However, considering the small representations of these two latter sources, and that no previous research had suggested any associations, their exclusion seemed reasonable. It is unfortunate that the archaeological samples presented such a large group which could dominate the analysis, but without further documentation sub-groupings would be senseless.

Six elements were chosen for discrimination: ^{182}Ta, ^{134}Cs, ^{141}Ce, ^{60}Co, ^{140}La and ^{152}Eu. The first two proved to have the maximum power and then to a much lesser extent ^{140}La. As all the sources were entered as a subfile(If (Subfile Equals Source 1) Group=1), the archaeological data was listed as having no prior group membership. The source allocations are given in Appendix 2. 64 percent were classified to the Awana source (28 samples), 34 percent were classified to Te Ahumata (15 samples) and 2 percent (1 sample) to Maratoto. The layer context does not appear to be significant.

There is a good possibility that more than one flake originated from the same core and were scattered on the layer floor. In this event, the data would not represent independent observations.

The classification results are in agreeance with published reports (Davidson,1972; Ward,1974) indicating allocation to the Great Barrier Island source for Site N38/30. As only one sample related to the mainland Maratoto source, the significance cannot be established.

4.3 Discussion

The two different approaches to the analysis of the neutron activation results were selected to complement one another. That is to say, cluster analysis should be able to define the natural groupings and discriminant analysis then investigates the cause of the groupings. Both have a distinct advantage in their visual presentation.

However, the inherent weakness in employing cluster analysis as definitive of separating the sources, lies in the predetermined source allocations. If the data for a source is previously considered independent from another, then, at best, cluster analysis will confirm this independence. Nonetheless, the technique was useful in establishing the dominance of the Mayor Island, Pungaere and Waiare sources. They were presented as the maximum poles of separation and established a starting point to examine the distribution of the remaining sources. Analysis was based on irradiation runs in order that the large data block could be analysed in more detail, but validated by incorporating all the material into Programme Six. While other graphical displays are available (Wishart, 1975), the dendogram illustrates quite clearly the hierarchial fusion levels and the measure of similarity (dissimilarity) between samples on the principle of Euclidean distance.

Having defined the sources and confirmed their natural groupings, the problem becomes one of discrimination. The elements selected to be most discriminating in maximising the separation of the sources included the rare earths, notably ytterbium, cerium, and lanthanum. It has been proposed that there is a high correlation between the rare earths (Schroeder,1966) suggesting that one element could be representative of all three (Hawkins,1977). However, the homogeneity of obsidian and the precision of the neutron activation technique for these elements (Bowman et al, 1973), allows that each one be considered as discriminative in its own right.

Ultimately, the purpose of the classification procedure is to allocate archaeological data to the geological reference material. The choice of elements will depend not only on the multivariate statistical analysis but also the experimental technique. When X-ray fluorescence was used in conjunction with the eighteen petrographic source groups (Ward,1974a), zirconium, manganese, titanium, strontium and rubidium were selected for future archaeological source allocations.

The misclassifications that occurred when the"unknown" group was analysed with sixteen source groups, generally did not form strong associations with the new group. The placement of the Tairua and Taupo samples (GS544 and GS629, Table 21) accord with the overlap of these two sources (fig. 15). Geographically they form two distinct source regions. It is difficult to assess why these misclassifications should occur without further documentation of their geological origins. There is a likelihood that some may have been detrital deposits (Leach, pers.comm).

Overall the discriminant analysis in particular was able to clearly demonstrate the discreteness of the sources and hence to substantiate the original hypothesis. The distribution of samples within each source represented along the two most discriminant functions, has been achieved.

CHAPTER FIVE. ARCHAEOLOGICAL DISCUSSION

When defining a sequence of cultural events in prehistory, the archaeological evidence may be considered from its distribution in space and time. In the specific case of New Zealand, this sequence is hampered by a lack of continuity from one cultural period or 'phase' to the next. This is related to the presence of seasonal occupations at a site, intermittent warfare, and hence the lack of permanent settlements. A technology primarily based on function rather than form, and a fragmented tribal society, add to the difficulties in presenting a complete reconstruction of New Zealand's prehistory over the last one thousand years.

The transition period between the well documented early Archaic phase and the established Maori phase is uncertain. By tradition, the arrival of a fleet from Central Polynesia introduced Maori culture to New Zealand. The names of the various tribes are related to these ancestors. Alternatively, it has been proposed that by a gradual evolution of the characteristics of the Archaic phase, the Maori culture became prominent.

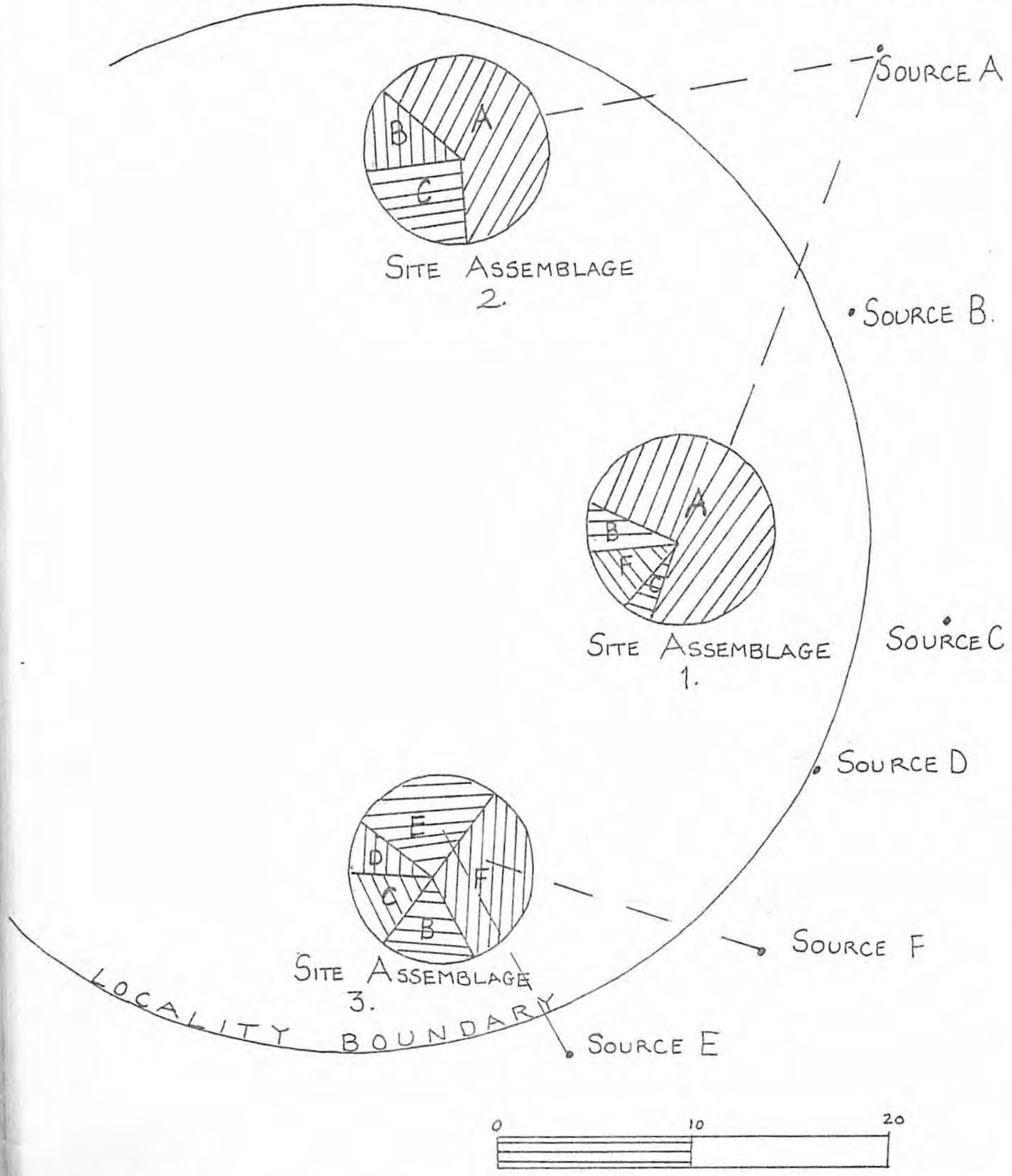
Distribution of archaeological evidence in time, apart from carbon 14 dating is largely dependant on relative methods of dating, Stratigraphy, artifact typology or dated geological and climatic events. There does not exist any single dated event or reference to a central political base that can be applied to the whole of New Zealand before the arrival of the Europeans. Hence the chronology of New Zealand prehistory has been determined from region to region. Common attributes, as the working of raw materials allows inferences to be made about the mobility of the population and settlement patterns.

Lithic flake assemblages on archaeological sites are derived from local deposits or were imported for working on the site. The spatial distribution of imported items is linked to the reconstruction of exchange mechanisms between the user and the source. The archaeological record reveals that the early Maori and also 'Moa-Hunter' travelled considerable distances to obtain essential raw materials. The proved quality of the source and the nature of relations with neighbouring or en-route communities were two important factors of the distribution patterns. Several possibilities can be suggested for the movement of goods from the expeditions of tribal chiefs to a network of exchanges operating on a territorial basis.

The concept of a network may be defined as a series of elements linked by specified exchanges of goods, behaviour and information (Plog,1977). The extent of interaction is determined by the proportion of local goods against imports at any one site. This can be measured by the exchange index: the relative degree of occurrence (rather than absolute quantity) of an imported item within the whole assemblage (Ericson,1977).

The system of exchanges between site and source and between sites on a regional basis forms the essential data for establishing the nature of inter-territorial social relations over time. Preference for one source may change throughout the history of the settlement in proportion to the total assemblage. An example of a hypothetical network model is given in fig. 16 below. Site assemblages 1,2, and 3, within a defined locality, represent three

Figure 16. Hypothetical Network Model represented by the proportion of source items at Site Assemblages 1,2, and 3. Pie diagrams for each assemblage show the sources utilised to a greater(dashed line),lesser extent or none at all. A distance scale is given(miles) to illustrate that closer sources may be by passed and hence the complexity of network analysis



chronological periods utilising different sources of the same item (A-F). In this model, the proportion of source A item is greater at Site 1 than Site 2, although the latter is closer to the source. The B source on the other hand, is better represented at Site 3, compared to Site 2, and not at all in the Site 1 assemblage. If the sources were considered to be obsidian, this model could be generally applied to distribution patterns in New Zealand. Notably, the Law of Monotonic Decrement, that raw materials become increasingly scarce as one moves away from the source [illegible] does not apply to the distribution of obsidian in New Zealand.

To apply network or graphic analysis (the abundance of a source material at a site against transportation factors) to the distribution of obsidian alone in New Zealand is difficult. It has been stressed (Leach and de Souza,1979) that it is essential that the whole suite of rock types being used by prehistoric people should be examined, before a communications network can be properly established. Additionally, the abundance of Mayor Island obsidian on archaeological sites on both North and South Islands, is related to its distinctive quality for tool making. This may lead to its preferential use compared to other sources of poorer flake quality. A group of archaeological sites recorded at Palliser Bay in the Cook Strait (fig.1) revealed that obsidian sources at a closer range were by passed. The proportion of obsidian at each site was expressed in the total percentage for lithic materials throughout four centuries (Leach,1977). This evidence was a primary consideration in constructing the hypothetical network model (fig.16). It presents a facet of the complexity of reconstructing exchange systems by source attribution in New Zealand. It is unlike the more spatial distribution of obsidian sources in the Near East, Americas and Mediterranean (Cann and Renfrew,1964; Renfrew, Dixon and Cann,1966; Gordus et al,1968; Aspinall and Feather,1972).

The Palliser Bay Washpool site lithic assemblage is in fact a good example of the variety of local and imported materials in use at any one time. The significant fall off in the latest level (about 1540 A.D.) of all types of rock, including local greywacke , accords with the general trend of specialised quarries or sites appearing at a later date and a move away from manufacturing on site. Whereas (imported) obsidian accounted for 32 percent of all rock types used on the site, and 40 percent of the imported materials, other sites as Motatupu, N38/30 which was situated geographically closer to the favoured Mayor Island and Great Barrier sources, identifies the appearance of obsidian as only a minor occurrence. The number of pieces found in the excavation was 78 compared to 868 stone flakes, the majority of which were local greywacke (Leahy,1970). However, Site N38/30 was classified into the small undefended domestic group sites involving seasonal occupation. The function and size of the settlement would determine the range of external relations with neighbouring and mainland communities.

The types of settlement fall into four categories. Fortified sites or pa; undefended pit or terrace sites; large/medium size complex undefended sites and single pits or domestic groups; and finally, middens. Nuclear centred pa appear to be a feature of the post Archaic, when the introduction of warfare called for defended sites. The period of occupancy at a site, whether seasonal, semi-permanent (a return to the site) or permanent,would necessarily involve temporary or permanent political relations with neighbouring communities.

Much of the study of the Maori, apart from ethnographic accounts, is centred on the "post-musket, post-white, potato Maori" (Groube,1967) when permanent villages afforded the opportunity to examine the social and economic system. The theory of reciprocity requires that both parties have something to exchange, if not in material value, then at least goodwill or protection. As a single unit, domestic groups like the occupants of Motatupu N38/30, may have needed the co-operation of other groups on the island to enter into any form of exchange with the mainland. However, if the community was self-sufficient as it appeared to be, utilising local greywacke for tools and the sea for food (also possibly agriculture), there would be little need to rely on external resources.

An estimation of the size of the population and the existence and quality of local resources is therefore related to the extent of interaction with outside parties. If the community is engaged in subsistence activities with a small population, exchange systems will not be as emphasised as if the site were specialised or needing to support a large population. Hence, it is important when considering the spatial distribution of raw materials to maintain a sense of perspective.

Characterisation studies have proved to be of singular priority for establishing the movement of raw materials. Analysis of trace element content of archaeological deposits matched with geological sources provides direct proof that transport of goods and materials from one region to another was taking place. To obtain the maximum benefit from analysis of the geological sources, the size of each group should be even. This work has shown that the source groups would be statistically more comparable had the sample sizes all been in the 9 to 10 range. It was unfortunate, therefore, that the Weta and Fanal Island sources had to be disregarded because of their inadequate numbers.

Provenience determinations of obsidian when placed in the context of other contemporaneous raw materials and the type of site where they are found will then contribute to a knowledge of prehistoric lines of communication in New Zealand. Whereas the emphasis previously has been on intensive research into the geological origins of New Zealand obsidian, attention must now be focused more on the archaeological material. Future work should consider the separation of the sources by geographical area rather than as individual units. Similarly, discriminate variate analysis could be employed for regional groupings to counteract the high number of souces in each geographical area. The overlapping of the Taupo and Tairua sources would benefit from further investigation to determine if the similarity is strictly geological, or if errors occurred in the sampling of the deposits. The theoretical calculation of the refractive indices of obsidians would serve to clarify an investigation that is currently unable to detect differences between sources to a significant degree using this method. A pooling of resources from enthnographic accounts, social anthropological work and continued excavation and analysis, will result in a more precise definition of the sequence of cultural events in New Zealand.

CHAPTER SIX. CONCLUDING REMARKS

The neutron activation analysis of geological sources of New Zealand obsidian, by the determination of trace element content, revealed that intra-source variation was greater than between sources. A selection of archaeological samples were also analysed to determine source allocation.

As discussed, the sequence of cultural events in New Zealand prehistory has been reconstructed from the archaeological evidence from separate regions of the two islands. The linking of this evidence to establish a chronological framework whereby the prehistory is divided into several phases- earliest settlements; Archaic and Maori - is dependant on the interpretation of the movement of raw materials. Because obsidian occurs frequently on New Zealand archaeological sites, aided by the geological terrain of the country, it was one of the first raw materials to be studied intensively. When the characterisation programmes began, and various types of analyses were undertaken to consider the most reliable methods to source obsidian, New Zealand archaeologists urgently requested that all geological reference samples be submitted (Green,1962). Two decades of research revealed that it was possible to discretely separate the sources. The neutron activation results in this work confirms the discreteness of sixteen geological obsidian sources. Now that a firm base for archaeological source allocations has been established, the emphasis is changing towards a greater volume of archaeological analyses, as well as, a consideration of the other raw materials available throughout New Zealand's prehistory.

A limitation of characterising New Zealand obsidian is that the majority of the sources are of a similar chemical and geological makeup. The multivariate analyses highlighted the close grouping of sources in terms of their distinguishing elements. Only by removing the dominant sources as Mayor Island, Pungaere, Waiare and Waihi, was it possible to clearly ascertain the separation of the others. Similarly, X-ray fluorescence major element determinations, highlighted the peculiarity of Mayor Island obsidian, a peralkaline type. An interesting result of the supplementary normative analysis, was that the Maratoto and Awana sources displayed higher major element ratios than was to be expected from the calcalkaline type.

It must be remembered that there is always the probability that new obsidian sources may be discovered. Although the geological study of the volcanic regions in New Zealand has been extensive, archaeological samples may reveal that allocation according to the present list of sources is not possible.

In conclusion, characterisation studies have proved to be of singular priority for establishing the movement of raw materials, in particular, obsidian. Analysis of trace element content of archaeological deposits with geological sources provides direct proof that transport of goods and materials from one region to another was taking place. Provenience determinations of obsidian when placed in the context of other contemperaneous raw materials, and the type of site where they are found, will contribute to a knowledge of prehistoric lines of communication in New Zealand.

APPENDIX ONE

CHEMICAL COMPOSITION OF UNITED STATES GEOLOGICAL SURVEY GRANITE STANDARD, G2, FROM THE PUBLISHED VALUES (FLANAGAN, 1973)

Major and Minor Constituents (percentage)

SiO_2	69.11
Al_2O_3	15.40
Fe_2O_3	1.08
FeO	1.45
MgO	0.76
CaO	1.94
Na_2O	4.07
K_2O	4.51
H_2O^+	0.55
H_2O^-	0.11
TiO_2	0.50
P_2O_5	0.14
MnO	0.034
CO_2	0.08

SUM = 99.73.

Trace Elements (parts per million)

Ag	0.049	Nd	60
As	0.25	Rb	168
Ba	1870	Sc	3.7
Br	0.30	Sm	7.3
Ce	150	Sr	479
Co	5.5	Ta	0.91
Cs	1.4	Tb	0.54
Eu	1.5	Th	24.2
Hf	7.35	Yb	0.88
La	96	Zn	85
Lu	0.11	Zr	300

APPENDIX TWO

SOURCE ALLOCATION OF ARCHAEOLOGICAL OBSIDIAN FLAKES FROM MOTATUPU, SITE N38/30(RUN 579).

The highest probability source is given with associated statistic (maximum=1) based on the discriminant analysis classification results.

Highest Probability Source	Probability Statistic	Sample Code No.	Layer Context
Maratoto	0.452	AR864-32	6A
Te Ahumata	0.740	AR792-3	6A
	0.989	AR361-4	6A
	1.000	AR782-5	6B
	0.945	AR812-6	6A
	0.887	AR812-7	6A
	0.989	AR782-11	6B
	0.971	AR782-12	6B
	0.916	AR782-14	6B
	0.796	AR773-20	6A
	0.933	AR812-33	6A
	0.999	AR855-35	4
	0.897	AR855-36	4
	0.556	AR855-37	4
	0.840	AR855-38	4
	0.364	AR782-41	4
Awana	0.583	AR863-45	6A
	0.910	AR812-8	6A
	0.568	AR812-9	6A
	0.557	AR782-10	6B
	0.825	AR782-13	6B
	0.693	AR782-15	6B
	0.507	AR782-16	6B
	0.782	AR782-17	6B
	0.858	AR782-18	6B
	0.702	AR844-19	6A
	0.743	AR832-20	6B
	0.886	AR773-22	6A
	0.916	AR803-23	6A
	0.866	AR803-24	6A
	0.924	AR734-25	6B
	0.949	AR734-26	6B
	0.921	AR734-27	6B
	0.557	AR782-43	6B
	0.580	AR782-44	6B
	0.831	AR859-28	6A
	0.943	AR859-29	6A
	0.943	AR859-30	6A
	0.769	AR743-31	6B
	0.962	AR855-32	4
	0.552	AR855-39	4
	0.520	AR855-40	4
	0.829	AR782-42	6B
	0.441	AR803-46	6A

GEOLOGICAL AND CHEMICAL COMPOSITION OF NEW ZEALAND OBSIDIAN : SUPPLEMENTARY INFORMATION

INTRODUCTION

Supplementary analyses were undertaken to investigate the geological and chemical composition of New Zealand obsidian. As the chemical composition is a reflection of the geological make up,it is reasonable that both should be discussed together. This investigation forms a secondary consideration to the characterisation of sources which were adequately separated by their trace element content.

The aim of this section was to determine if a similar programme could be initiated on the basis of chemical and geological composition. It was proposed that any inter-source variation evident from the percentage of major elements could be related to the two types of New Zealand obsidian, peralkaline and calcalkaline. As all the sources excepting Mayor Island have been classified to the latter type, it would be expected that little variation would be displayed. However, normative analysis based on the major element percentages obtained from X ray fluorescence illustrated that several sources deviated quite markedly from the others.

Wavelength dispersive X-ray fluorescence revealed a sympathetic variation of elements as sodium, iron, silica and alumina, while highlighting the several anamolous calcalkaline sources: Awana, Maratoto and Waiare. An explanation of the cause for the anamolies is beyond the scope of this work. However, it would be hoped that further investigations will clarify their relation to the calcalkaline type, and their subsequent relevance to archaeological obsidians.

A second step in the study of chemical composition was the measurement of refractive indices for several sources. The outcome emphasises the need for more study in this particular method. The maximum benefit for routine archaeological sourcing of obsidians may come from the theoretical calculation of indices from the predetermined chemical composition.

1. PETROGRAPHY OF NEW ZEALAND OBSIDIAN

1. Classification of New Zealand Obsidian

Type: As a class, obsidian belongs to the rhyolite group of glassy and volcanic rocks, and characteristically displays a conchoidal fracture (Whitten and Brooks,1972).

Within this class, two natural subdivisions are defined according to the molecular proportion of sodium and potassium oxides. These are peralkaline and calcalkaline and represent the two types of obsidian present in New Zealand. The pantellerites of peralkaline character peculiar to Mayor Island, as a type have more than 68 percent silica and less than 10 percent alumina (Smith,Ward and Ambrose, n.d.). The Coromandel Peninsula and Taupo Volcanic Zone are classified as being calcalkaline acid and intermediate obsidians, mineralogically similar to granites but appearing richer in silicon oxide.

New Zealand obsidian generally belongs to the Oceanic type (as opposed to Circum-Oceanic) together with the Central Pacific and Western Melanesia landforms(Smith,Ward and Ambrose, n.d.).

Colour: New Zealand obsidian varies in colour from black to dark green in reflected light, though other hues being red or pale brown. Ewart, Taylor and Capp in their detailed study of the pantellerites of Mayor Island (1968) consider the red colouration to be due to surface oxidation and the pale brown colour resulting from conversion of haematite to limonite after hydration. (Limonite being a range of mixtures of hydrated iron oxides and hydroxides). Visual examination in reflected light of North Island obsidian hand specimens from the Bradford reference collection, appeared as grey/black transparent or opaque, red or pale brown.

Despite the distinctive green appearance of Mayor Island obsidian which has often formed the basis for identification, characterisation of sources cannot rely on sole attribution by colour. This was borne out by the archaeological investigations on Motutapu Island where grey obsidian could not be reliably sourced without reference to an analytical technique(Davidson,1972).

Water Content: Obsidians generally contain about one percent water or less in the body of the rock. Additionally a hydration layer can form on the surface clearly visible in reflected light due to differences in refractive index for hydrated against unhydrated. Research of this surface phenomena has shown that the less water present at the outset, the slower will be the rate of perlite layer formation. Refractive Index measurements taken of some New Zealand sources (Section 2B) emphasise the importance of the initial selection of unhydrated fragments for analysis.

Conchoidal Fracture: Of particular importance to the study of archaeological obsidian, is the suitability of this material to the working of tools. The homogeneity of obsidian, having no definite cleavage pattern, and lacking a well defined structure, renders it possible to break along planes of fracture whose position can be more or less theoretically determined by the operator. The fracture, known as a conchoidal fracture, is produced by a force applied at one point which radiates symmetrically in all directions within a cone. The fragment produced has a concentrically rippled surface. (For further discussion: Bordaz,1970; Semenov,1964; Coles and Higgs,1969.)

The ringed scars are clearly visible in geological obsidian chipped from a large source or worked in an archaeological context.

Age: The ages of New Zealand silicic volcanic activity commenced in the Tertiary Period and extend to the Quaternary, the Taupo Volcanic Zone (Quartenary) continuing to the present day. In a recent study of the ages of Pacific obsidians from fission track analysis (Leach, Naser, Ward, in press), the three main areas of late silicic vulcanism were found to be predominantly of Pliocene to Holocene age. Fission track dates confirm the Cormomandel Peninsula obsidians to be the oldest. The petrogenesis of the Central Inland Region and Mayor Island has been comprehensively documented (Brothers,1957; Ewart and Stipp, 1968; Ewart and Healey,1965; Ewart, Taylor and Capp,1968).

2. Mineral Composition

The investigation of the mineralogical content of a representative sample of geological specimens was undertaken in two ways. The first by visual and thin section examination, and secondly, by normative analysis using the CPIW norm based on the chemical composition (as determined by X ray fluorescence). From this investigation, in accordance with the two main types of obsidian, the presence of alkali feldspars enriched in sodium and potassium and ferromagnesian minerals,differ in abundance and habitat for the sources.

These mineral inclusions grow within the glassy rock over time though at a slow rate initially. Devitrification appears in the formation of radial masses of microscopic crystals of feldspar, amphibole or pyroxene, termed crystallites and spherulites. Both were found to be common in the visual and thin section examinations. Flow banding may occur accentuated by alternate layers of glass and finely crystalline rock which may enclose phenocrysts of quartz and ferromagnesian minerals.

2.i. Hand Specimen and Thin Section Examinations

Sixteen sources were visually examined with a hand lens in terms of stratification, colour and vitreousness, with comments on weathering and obvious mineral inclusions where relevant (Table 23). Vitreousness was divided into three groups:- 1) highly vitreous-glass like; 2) less vitreous; 3) pitch like. Specimens which displayed layering or bedding were termed as stratified.

The majority of samples examined were highly vitreous. Mayor Island specimens were all of a green hue, although a pale brown ('honey') coloured type has been identified in this source (Leach, n.d.). The overlap of the grey/black appearance highlights the problem of sourcing by colour alone. Some samples showed evidence of working (9 GS 677, 21/4 GS 234, GS 160/1) and were suspected to be archaeological. Devitrification occurred in varying proportions over the total area of the specimen and spherials were present in either isolated masses or as flow banding. Even without thin sectioning, quartz and feldspar were clearly visible in the Rotorua, Cooks Bay and Hahei sources.

A more detailed study of the mineralogical content was done by thin section examination. A representative sample from eight sources was taken from the Bradford reference collection and thin sectioned. The report (see page 25) examines the varying extent of spherulitic inclusions and crystal habitats.

Table 23. Handspecimen Visual Examination of New Zealand Obsidians from the Bradford reference collection.

Source	Reference No.	Vitreousness	Stratification	Colour	Comments
TAUPO	18/3 GT539 (a)	1.	+	G/BT	
	18/5 GT579	2.	+	G/BT	Alternating bands.
	18/2 GT496 (a)	1.	-	G/BT	
	18/4 GT542	1.	+	G/BT	Stratifications perfectly horizontal
	18/1 GT440	1.	-	G/BT	
	18/3 GT539 (b)	1.	-	G/BT	Spherials range up to 4 mm diam.
	18/2 GT496 (b)	1.	-	G/BT	
ROTORUA	14/1 GS984	1.	-	Mottled Red-black	Weathered outer-surface. Red may be due to iron.
	15 GT148 (a)	1.	-	Black opaque	Spherulitic inclusions-up to 2mm diam.Quartz and feldspar and granular aggregates
	12 GS959	1.	+	Black opaque	As 15 GT148 (a)
	14/2 GS945	1.	-	Black	As 15 GT148 (a)
	14/3 GT91	1.	+	Light red	Fluctional arrangement of dark patches.

Table 23. Handspecimen Visual Examination.

Source	Reference No.	Vitreousness	Stratification	Colour	Comments
ROTORUA	15 GT148 (b)	1.	–	Black opaque	Weathered out spherulitic cavities showing iron staining.
ONGAROTO	17/8 GT345	1.	–	B/GT	Spherulitic
MARAETAI	17/6 GT278	2.	+	Light grey/ black opaque	Light grey on outer surfaces only.Spherials up to 1mm diam.
	22 GT777 (a)	1.	+	Light red/ with dark red and black.	Spherials
COOKS BAY	4/2 GS618	1.	+	B/GT	Spherials range up to 2mm diam. Alternating bands of quartose and feldspathic materials.
	14/1 GS543	1.	+	Light grey/ black	Spherials range up to 2mm diam. distinct light grey bands.
HAHEI	28 GS466/1	1.	+	G/BT	Spherials
	28a GW363	1.	+	G/BT	Alternating bands of quartose/ feldspathic layers

Table 23. Handspecimen Visual Examination

Source	Reference No.	Vitreousness	Stratification	Colour	Comments
TAIRUA	5 GS635	1.	+	Light grey /black	Alternating bands
MARATOTO	32 GT847	1.	-	G/BT	
WAIHI	30 GT843/1	2.	+	Light grey /black	Wax like.
	29 GT841/1	2.	+	Black	Mottled with red opaque.
MAYOR ISLAND	11 GS906	1.	+	Green	
	10 GS844	1.	+	Green	
	9 GS677	2.	+	Green	Weathered matt outersurface. Evidence of working
	6/1 GS640	2.	+	Green	
	7/1 GS766	2.	+	Green	
	6/2 GS716	2.	+	Green	
	19 GT617	1.	-	Green	
	21 GT745 (b)	1.	+	Green	Alternating layers of vitreous and non vitreous.
FANAL ISLAND	33 GW255	3.	-	Red	Weathered surface-spherials up to 1mm diam.

Table 23. Handspecimen Visual Examination

Source	Reference No.	Vitreousness	Stratification	Colour	Comments
FANAL ISLAND	20 GT684	2.	-	Buff/tan	
AWANA	23 GT830/1	1.	-	G/BT	
TE AHUMATA	1/1 GS147	1.	-	Black/ Grey	Pitted weathered matt outersurface
WAIARE	3/1 GS404A	2.	-	G/BT	
PUNGAERE	24 GS560/1	2.	-	Black	
HURUIKI	2/4 GS234	1.	-	Grey/	Pitted weathered outersurface. Evidence of working
	2/7 GS299	2.	+	Opaque	Weathered along stratified layers
	2/5 GS237/1	1.	+	Grey/ black	
	2/10 GS472	1.	+	Grey/ black	
	2/8 GS322	1.	-	Opaque	
	2/3 GW260	1.	-	G/BT	
	2/1 GS160/1	1.	+	Black/ opaque	Weathered along lines of stratification. Working evidence.

Table 23. Handspecimen Visual Examination

Source	Reference No.	Vitreousness	Stratification	Colour	Comments
HURUIKI	2/2 GS167/1	1.	+	Black/ opaque	As 2/1 GS160/1
	2/9 GS370	1.	+	Black/ opaque	As 2/1 GS160/1
	2/4 GS234	1.	+	Trans- parent	Transparent due to thickness of specimen

Key: G/BT-grey/black transparent.

+ -presence

- -absence

Obsidians from the Central Volcanic Region have been studied (Ewart,1971) to measure the extent of chemical changes accompanying spherulitic crystallisation in rhyolitic lavas. It was found that the phenocrysts included typically andesine, quartz, hypersthene, magnetite and biotite. The spherulites were enriched in Na_2O (from 4.19 percent (total rock) to 6.00 percent) and $Si\ O_2$ (from 73.48 percent (total rock) to 77.44 percent), but depleted in K_2O (3.10 percent (total rock) to 0.75 percent). Although these were present in varying proportions in the specimens examined, major devitrification had not occurred so as to leave no trace of the residual volcanic glass.

The presence of iron may be related to the colouration. Enrichment due to surface oxidation would not affect the internal chemical composition. As would be expected, the alkali feldspars and silicates (quartz,riebeckite,hornblende) feature prominently in all the specimens. Calcium trace minerals (anorthoclase, augite, and hornblende) were found in the Central Volcanic region sources classified as calcalkaline in type.

2.2. Normative Analysis

The normative variation in weight percent of albite, anorthite and orthoclase was determined from the chemical composition. Albite and anorthite belong to the plagioclase group of feldspars, the former being pure sodium and the latter, pure calcium. Both exhibity multiple lamellar twinning in thin section. Whereas albite (Ab) is associated with alkali rich rocks, anorthite (An) is related to basic rocks, and is subsequently present to a lesser extent than either of the other two minerals. Because of the depletion of calcium in the Mayor Island composition (Table 24), Only a minute amount of anorthite is present (effectively zero in percentage).

Orthoclase (Or) is a monoclinic potassium feldspar showing simple twinning.

The abundance of these three minerals in weight percent according to the CPIW norm is illustrated in fig.17 as a tertiary plot, for 10 New Zealand sources. It can be seen that the majority of the sources fall in the high albite and low anorthite range. The Awana obsidian displays a higher anorthite inclusion in correspondence with the enrichment of calcium (Table 24). Excepting the Maratoto source sample and half the Mayor Island samples, the normative variation displays greater albite representation than orthoclase for New Zealand obsidian.

This is closely related to the ratios of sodium, potassium and calcium. As would be expected from the normative analysis, there is a slightly higher sodium percentage than potassium and a low calcium content. Again the Waiare, Awana and Maratoto sources stand apart in the tertiary plot (fig. 18) from the majority. The ratios of sodium, potassium and calcium are presented in Table 24 below.

Because of the small quantities of iron visible in the thin section examination, the ratio of alkalis to iron and magnesium was determined. The separation of the calcalkaline sources according to increasing iron content is illustrated in fig. 19. Magnesium is present only in trace amounts excepting Awana and Maratoto sources.

Table 24. Chemical Ratios of K_2O, Na_2O and CaO in weight percent of New Zealand obsidian sources, where n= number of determinations and x is the average.

Source	n	$\frac{x\ K_2O}{K_2O+Na_2O+CaO}$	$\frac{x\ Na_2O}{Na_2O+K_2O+CaO}$	$\frac{x\ CaO}{CaO+K_2O+Na_2O}$
Mayor Island(1)	6	44	54	3
Maratoto (2)	1	54	27	19
Huruiki (3)	1	53	38	9
Tairua (4)	1	38	45	18
Purangi (5)	1	39	50	11
Cooks Bay (6)	1	42	47	11
Waiare (7)	1	33	38	29
Awana (8)	1	19	32	48
G2 Standard (9)	1	43	38	18
Taupo/Rotorua(10)	2/5 === 21 ===	41/ 45	46/ 45	14/ 11

Figure 17. Normative variation in weight percent of albite(Ab), Anorthite (An) and Orthoclase(Or). The position of the Tairua and Rotorua group (No 10) is the average.

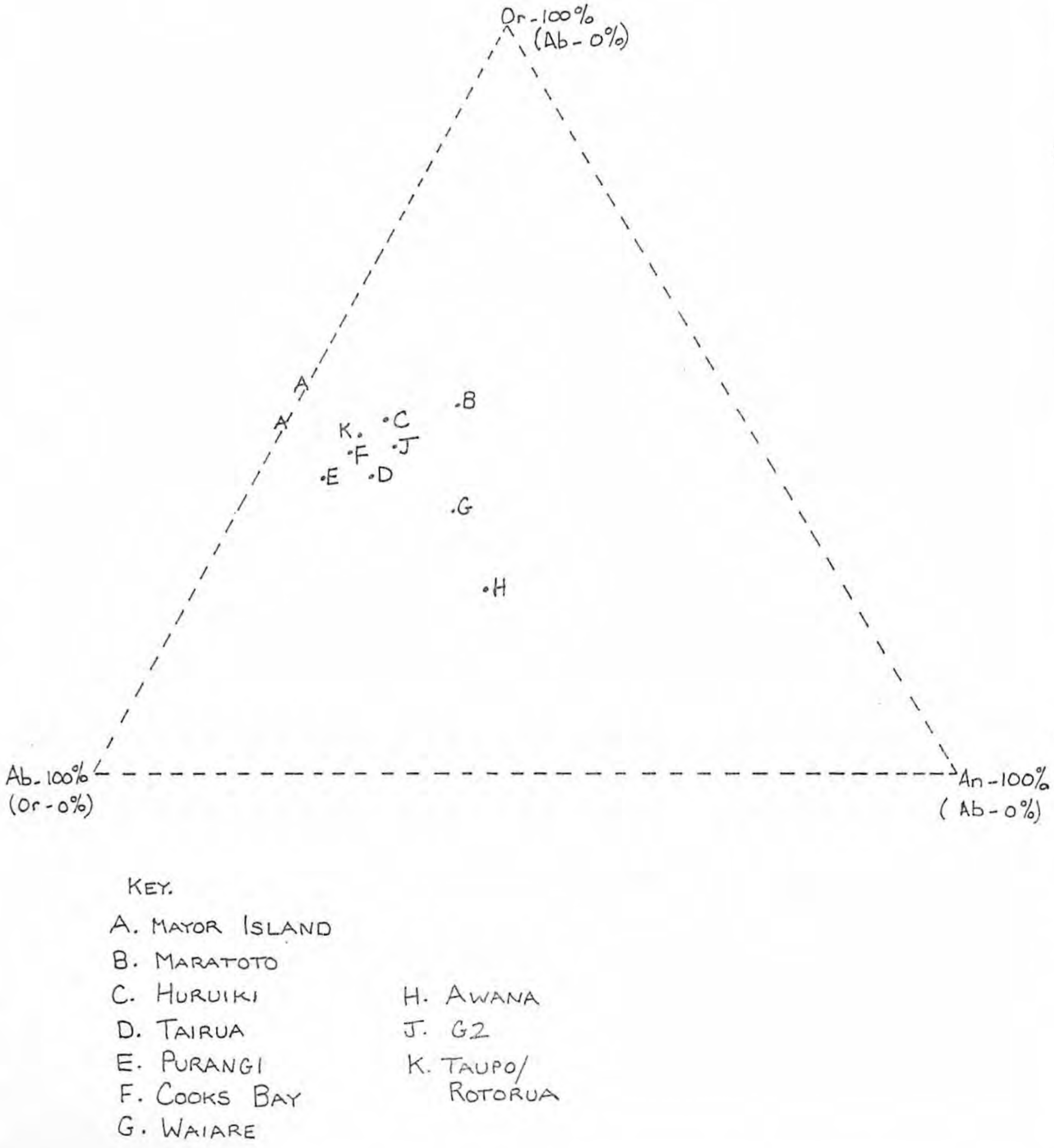


Figure 18. Chemical Variation in weight percent of Sodium (Na), Potassium(K) and Calcium (Ca).

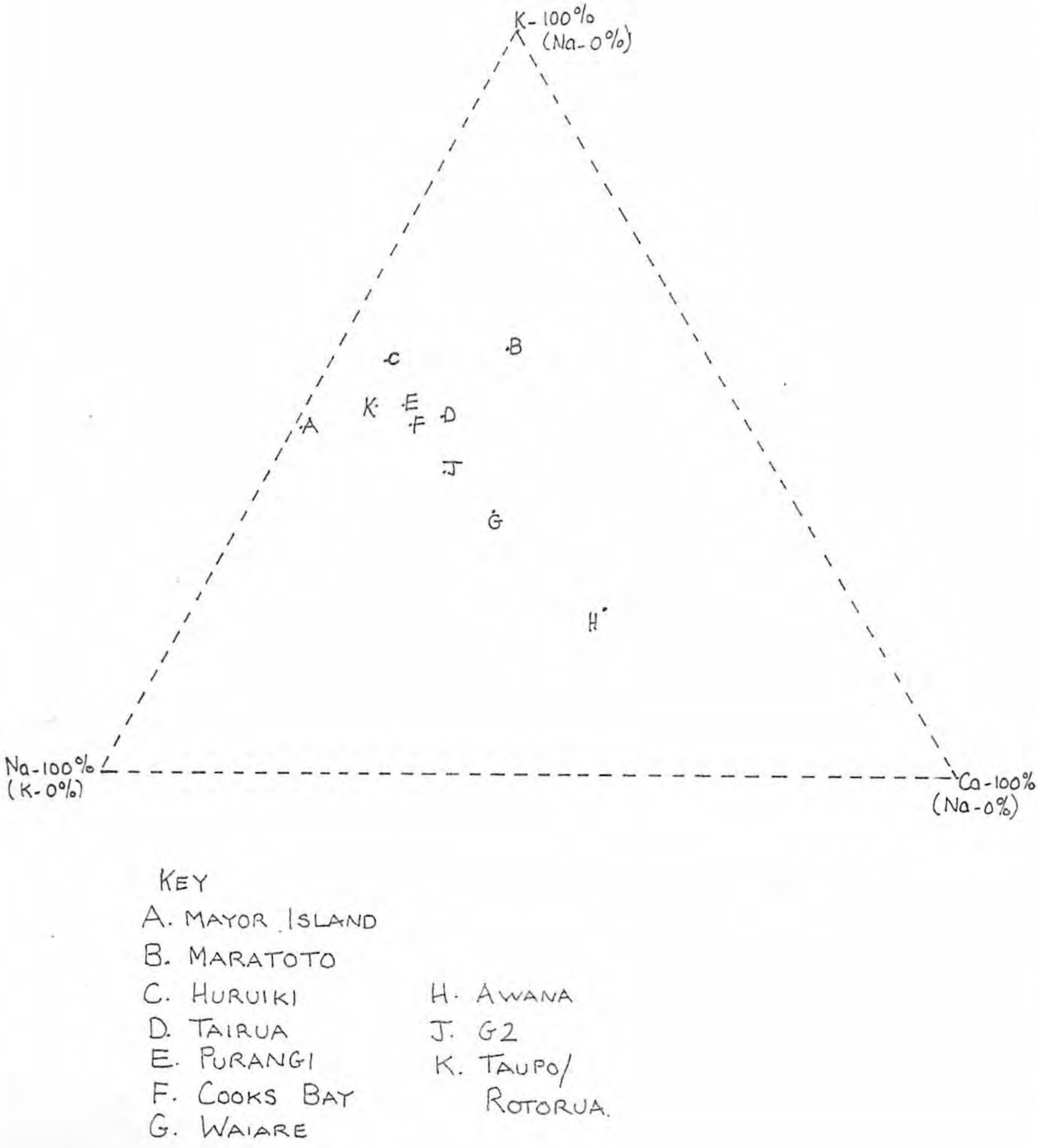
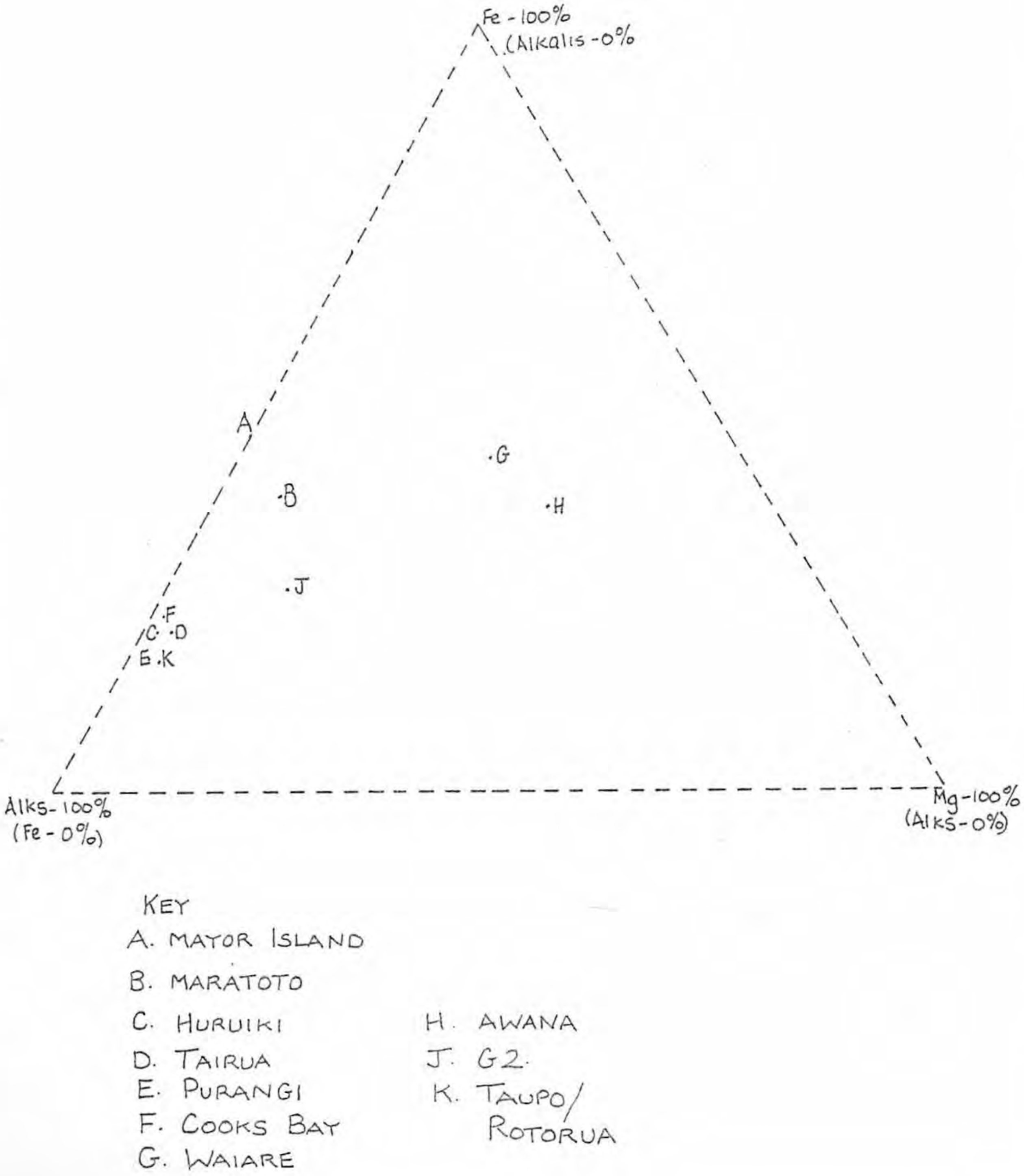


Figure 19. Chemical variation in weight percent of Magnesium (Mg), Iron (Fe) and Alkalis.



THIN SECTION EXAMINATION

Source-Cooks Bay; Reference Number:4/1 GS543

Radial microlites present forming spherules. Some show concentric lines which indicate interruptions at various stages of growth (maximum size 2mm diameter). Mineral composition of spherules:- radiate growths of alkali feldspar fibres with interstitial poikilitic quartz. The quartz occurs as granules packed in between the feldspars. The fibrous habitat suggests that spherules developed rapidly in a highly supersaturated viscous solution. The spherules in this particular obsidian have developed before the magma has come to rest. This is shown by the fact that the flow lines pass around them. ORTHOCLASE is attached to some spherules. $4((K,Na)(Al\,Si_3\,O_8))$. LIMONITE attenuation product present; Fe_2O_3 present as small stains on the boundaries.

Source-Taupo; Reference Number: 18/3(b) GT539

Completely vitreous excepting one sector of a spherule. Needle shaped microlites (belorites) are evidence of rapid quelching. Mostly are quartz and feldspar (alkali).

Source-Mayor Island; Reference Number: 10 GS844

One small tabular lath of ORTHOCLASE, zoned but still showing twinning. Twin crystals of RIEBECKITE present $Na_2\,Fe_3^{II}\,Fe_2^{III}\,(Si_8O_{22})(OH,F)_2$. The riebeckite may be associated with small green aegerines in this rock, but microlites are too small to determine.

Source-Rotorua; Reference Number: 14/3 GT91

Very distinct crystals of ANORTHOCLASE in this red obsidian (up to 1mm diameter): $4 ((Na, K) (Al Si_3 O_8))$ although anorthoclase does contain an arbitrary amount of Ca^{2+}. However, mostly sodic rich. Also twinned ORTHOCLASE, quartz crystals and limonite staining. Spherules range up to 1mm diameter. Overall haematitic staining of rock, perhaps evidence of surface oxidation.

Source-Rotorua; Reference Number: 14/2 GS945

Anorthoclase, ORTHOCLASE and QUARTZ present and again some minute RIEBECKITE crystals (distinctly pleochroic blue to violet). Possible magnetite or TITANIFEROUS MAGNETITE.

Source-Maraetai; Reference Number: 17/6 GT278

Zoned ANORTHOCLASE up to 1mm in diameter. Microspherulitic texture. Very distinct cross sections of the amphibole HORNBLENDE. $Ca_2 (Mg,Fe Al)_5 (OH_2 ((Si Al)_4 O_{11})_2$.

Source-Maraetai; Reference Number: 22 GT 777(b)

Microspherulitic, highly vitreous, cryptocrystalline texture. Haematitic staining on most of microlites preventing further identification. Magnetite abundant.

Source-Waihi; Reference Number: 29 GT 841/1

It is apparent that oxidation has occurred along the line of pre-existing fractures in the rock. The oxidation therefore would appear in this case to be surface value only. There appears to be a fluxional arrangement of feldspaths. Abundant magnetite.

Source-Waihi; Reference Number:30 GT843/1

Small crystallites of the sodic pyroxene AEGERINE present with distinct green pleochroism. Na Fe^{3+} (Si_2O_6). Aegerine contains an appreciable amount of zirconium and cerium. This rock is separated into bands of more coarse crystalline growth including alkali feldspars and quartz.

Source-Hahei; Reference Number: 28a GW363

Only ANORTHOCLASE crystals could be readily identified in a microcrystalline quartz - felspathic matrix crowded with circular microlites of aegerine and opaques.

Source-Ongaroto; Reference Number: 17/8 GT345

A more crystalline obsidian with distinct crystals of HORNBLENDE, QUARTZ, ORTHOCLASE, ANORTHOCLASE, AEGERINE, AUGITE and MAGNETITE. All ranging up to 1mm diameter. Spherules also range up to 1mm diameter. It would appear that the chemical environment has allowed good growth and form of the crystals.

2. SUPPLEMENTARY ANALYSES RELATED TO CHEMICAL COMPOSITION

A. X-RAY FLUORESCENCE

1. Outline of Technique

The sample is irradiated with primary X rays which cause displacement of the electrons from the inner orbits of the constituent atoms by the outer orbits. As a result, secondary radiation is produced in the form of fluorescent X-rays. These secondary X-rays have a discrete energy or wavelength characteristic of each element sensitive to the primary irradiation. As interaction occurs only on the surface of the sample it differs from neutron activation analysis in that only a thin surface layer will be analysed.

In the wavelength dispersive system, the secondary X-rays are channeled as a parallel beam through a collimator onto an analysing crystal which separates the different wavelengths and diffracts them into a radiation detector, typically a scintillation or gas proportional counter. At certain angles (θ) defined by the Bragg condition: $n\lambda=2d \sin\theta$

where n= an integer, the order, taking values 0, 1, 2, 3, etc.

λ= wavelength ... equation 12.

d= spacing between crystal lattices,

corresponding to each discrete wavelength present, a peak of radiation intensity is obtained. From a determination of the angle θ at which the peak occurs, each element in the sample can be identified and its concentration is approximately proportional to the measured intensity.

2. Sample Preparation

Obsidian chips with weights ranging from 2 to 8 grammes were crushed with a steel rod and pulverised in a Fritsch Pulverisette to achieve a particle size of 250 microns. The samples were then weighed accurate to the nearest 0.01 grammes. Organic resin (polyvinyl pyroladone) as a binder was added to the powder in the proportion of 2 drops to a gramme, and small pellets (less than 5 grammes) required a methyl cellulose backing. The powder was then compressed using a pump press to a maximum pressure of 10 tons per square inch and the pellets were dried for approximately one hour at a temperature of 100°C. Finally, pellets were loaded into the cyclic sample changer exposing the flat unpitted surface to the X-ray beam. The pellets were analysed in batches of six.

3. Apparatus

Wavelength dispersive X-ray fluorescence was undertaken by the Phillips X-Ray Spectrometry System PW1400. The samples were loaded automatically be means of a 72 position sample changer and analysed in a vacuum atmosphere. Primary radiation was generated by a rhodium anode, rated at 3 k.w. and up to 100 kV (50 kV applied). To ensure full wavelength range of the spectrometer, several analysing crystals are used -Li F 220, Li F 200, PE, TiAP, and Ge - aligned to a high precision crystal changer, attached to the theta shaft of the goniometer. Two types of proportional detectors are used in tandem. A scintillation detector for short wavelength radiation, and a gas flow detector for longer wavelength radiation. Angular reproducibility is better than 0.001° two theta.

4. Calibration

Calculation of concentrations were determined from straight line calibrations based on six international standards:

(1) G2 - Granite - United States Geological Survey
(2)GSP1 - Granodiorite - United States Geological Survey
(3)RGM1 - Glass Mt. Rhyolite - United States Geological Survey
(4)QLO1 - Quartz Latite - United States Geological Survey
(5)NIM6 - Granite - National Institute for Metallurgy, Republic of South Africa
(6) GA - Granite - Centre de Recherches Petrographiques et Geochemiquos, Nancy, France.

5. Results

Twenty-two samples were analysed from eleven different sources. A comparison of the results (Table 25) show reasonable agreement with published analyses of the Taupo and Mayor Island sources (Ewart,Taylor and Capp, 1968). The sodium and potassium oxide content however is lower, accounting for a smaller total percentage overall (Mayor Island samples). This is confirmed by an inspection of the values obtained for the G2 standard against the quoted percentage compositions (Flannagan, 1972). Specific comparative analyses for the five Coromandel Peninsula sources and the Great Barrier Region were not available.

The results may be divided into two groups according to their classification. Mayor Island is the only peralkaline type. The remaining sources are calcalkaline and appear very uniform in composition especially when there is more than one analysis per source. This would indicate that the chemical composition of a source area specifically and a classified type generally is homogeneous. For example, the standard deviation of aluminium oxide for the Taupo and Rotorua sources combined is a low 0.41 percent. Similarly, the silicon oxide content deviates 1.30 percent, and would be less if not for the unusually low percentage of the Awana sample.

Peralkaline obsidians, especially pantellerites, are reported to be high in sodium, iron, manganese and titanium content, and low in calcium, magnesium and phosphorus (Fleischer,McDonald and Bailey, 1973). An examination of the X-ray fluorescence results (Table 25) for the Mayor Island pantellerites shows a significantly higher content for iron than the Central Volcanic Region (Taupo and Tairua sources) and Coromandel sources. Alternately, these calalkaline obsidians are correspondingly rich in calcium and have higher alumina compositions. Potassium and sodium are expectedly lower.

It is considered that the scatter of silicon oxide values may result from variable quartz fractionation (Ewart,Taylor and Capp,1968). Chemical analyses from the Taupo Volcanic Zone (Ewart and Stipp,1968) report a variation from 70 to 77 percent SiO_2 though it was considered that rhyolites from this area were not highly fractionated. Water content is usually less than one percent (Williams .,1975).

6. Discussion

(i) Range of elements analysed

The element range is limited by the absorption of the X-rays which increases with increasing wavelength and lower atomic number. The rare earth elements are detected with difficulty, contrary to neutron activation analysis. Magnesium with an atomic number of 12 was detected in the present analysis. Generally, the technique is most suitable for major and minor elements. Trace elements as lanthanum, cobalt, zinc, thorium, rubidium and strontium may be analysed for part per million composition by X-ray fluorescence (Ward,1974a). Frequent investigations are carried out on geological samples to elucidate variations within flows from one source, as well as improving the range of elements capable of analysis (Leake, Hendry et al, 1970).

(ii) Determination of Accuracy

The concentrations were calculated from the count rate (counts per second) data as follows:-

(a) correction for background;

(b) correction for secondary absorption using a Compton Scatter Method (based on measurements of the rhodium K_β compton scatter peak for each sample);

(c) correction for major element absorption edges if the wavelength of such an edge lies between the wavelength of an analytical line and the wavelength of the compton scatter peak;

(d) calculation of concentrations from straight line calibrations based on international rock standards.

Detection limits were generally less than 2 parts per million for trace elements.

The chief likely sources of contamination are the grinding and crushing processes. As the samples were crushed with a steel rod, additional iron inclusions are possible, although every care was taken to clean all equipment between each sample to avoid cross-contamination.

Samples were selected from the Bradford reference collection as representative of the individual sources. Limitations on the number of samples that could be analysed favoured a large sample size from Mayor Island and Rotorua as these two source regions have been well documented. Where possible, specimens were chosen that were highly vitreous , although the majority showed evidence of flow banding. The purpose of the analysis was to determine 'average' major element compositions of homogeneous glassy obsidians. Therefore, depending on the original weight of the sample, it was occasionally necessary to effectively reduce the amount available for analysis to overcome devitrification effects. In particular, where radial masses of crystallites were visible. An investigation of chemical changes accompanying spherulitic inclusions revealed that the major element percentages differ from glassy rhyolites (Ewart,1971).

As with neutron activation analysis, the measurements follow a Poisson distribution where the standard deviation is the square root of the count rate.

(iii) Characterisation by X-Ray Fluorescence

The success of this analytical technique is dependant on the assumption that a sample is uniform in composition. For this reason, the specimen is ground to a powder to form a cylindrical pellet and problems that may occur with archaeological material like surface enrichment (Hall,1960) will be avoided. In this sense, the technique is not truly non-destructive, as it may be if energy dispersive methods were used. Nonetheless, the small quantities taken from the original specimen and the geological nature of the material validate the method.

Because the number of observations per source were limited and in seven cases were not greater than one, it was not possible to test statistically the significance of the results. To employ X-ray fluorescence to characterise the obsidian sources, further analysis for trace elements would be necessary, preferably using wavelength non-dispersive methods. However, the analysis was able to illustrate that there is a sympathetic variation of major elements within the peralkaline and calcalkaline types.

The problem of major element studies to aid the characterisation hypothesis is compounded in the subsequent refractive index measurements.

B. REFRACTIVE INDEX MEASUREMENTS

1. Principles of the Method

When light is passed through two different mediums, the ratio of the different velocities of light visible by the refraction at the interface, is termed the refractive index. The clarity or relief of the border is dependant on the magnitude of the differences between the respective refractive indices. Glasses (minerals or crystals) with low relief have refractive indices close to that of the medium in which they are mounted.

If the glass is immersed in oil (mounting medium), the boundary is observed with a medium to high power objective in parallel or weakly convergent light. As the lens is defocused by moving the microscope slowly upwards, a bright line (Becke Line) appears and is observed to move into the material of the higher refractive

Table 25. Percentage Major Element Composition of 12 New Zealand Obsidian Sources

Source	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	MnO	P_2O_5	Total %
Taupo												
GT440	75.33	13.02	0.18	0.41	1.09	0.22	1.05	3.56	3.10	0.05	0.02	98.03
GT579	75.20	13.08	0.18	0.42	1.12	0.20	1.04	3.48	3.11	0.05	0.02	97.90
+(	74.22	13.27	0.28	0.88	0.92	0.28	1.59	4.24	3.18	0.05	0.05	98.96)
Rotorua												
GT91	76.30	13.11	0.12	0.34	0.90	0.15	0.82	3.30	3.61	0.05	0.02	98.72
GS945	76.71	13.20	0.12	0.33	0.90	0.16	0.82	3.40	3.33	0.05	0.01	99.03
GS959	75.58	12.92	0.12	0.37	0.99	0.15	0.83	3.45	3.30	0.05	0.02	97.78
GT148	78.50	14.13	0.12	0.35	0.95	0.15	0.79	3.30	3.46	0.05	0.02	101.82
GS984	77.97	13.26	0.12	0.37	0.99	0.15	0.82	3.59	3.34	0.05	0.02	100.68
Maratoto												
GS847	68.13	18.27	0.66	1.04	2.79	1.14	1.91	2.79	5.51	0.04	0.30	102.58
Cooks Bay												
GS543	73.82	13.09	0.12	0.40	1.09	0.18	0.85	3.53	3.11	0.06	0.03	96.28
Hahei												
GW363	75.73	14.01	0.09	0.47	1.26	0.15	0.99	3.68	3.45	0.07	0.02	99.92
GS466	74.01	13.60	0.09	0.48	1.29	0.15	0.99	3.58	3.40	0.06	0.02	97.67
Tairua												
GS635	73.54	13.59	0.20	0.47	1.27	0.25	1.34	3.40	2.88	0.05	0.03	97.02
Purangi												
GT844	79.06	14.08	0.12	0.40	1.09	0.17	0.88	4.04	3.20	0.07	0.02	103.13
Fanal Is.												
GW255	77.52	15.55	0.29	0.51	1.36	0.28	1.12	3.77	4.00	0.04	0.04	104.48
Awana												
GT830	58.19	16.31	0.70	1.37	3.69	3.02	5.09	3.42	2.02	0.11	0.27	94.19
Mayor Is.												
GS777	70.47	9.11	0.23	1.63	4.40	0.09	0.23	4.67	3.76	0.14	0.12	94.85
GS766	74.45	10.27	0.23	1.37	3.69	0.09	0.21	4.73	3.82	0.11	0.02	99.03
GS906	72.80	10.31	0.25	1.39	3.75	0.09	0.24	4.67	3.87	0.11	0.02	97.50

Table 25. Percentage Major Element Composition of 12 New Zealand Obsidian Sources

Source	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	MnO	P_2O_5	Total %
Mayor Is.												
GS716	72.58	9.36	0.23	1.62	4.36	0.09	0.23	4.73	3.82	0.13	0.02	97.17
GS640	70.87	9.08	0.22	1.62	4.36	0.09	0.22	4.62	3.76	0.14	0.01	94.99
GT748	73.94	10.37	0.24	1.32	3.57	0.10	0.22	4.57	3.88	0.11	0.01	98.33
++ (	73.59	9.67	0.21	2.16	3.17	0.01	0.25	5.96	4.34	0.13	0.02	99.51)
Waiare												
GS404	64.64	15.22	0.65	1.15	3.11	0.66	2.98	3.96	3.46	0.10	0.22	103.23
G2	67.84	14.60	0.48	0.66	1.78	0.84	1.83	3.84	4.36	0.03	0.15	
+++ (	69.11	15.40	0.50	1.08	1.45	0.76	1.94	4.07	4.51	0.03	0.14	)

+,++ - chemical analyses (Ewart, Taylor and Capp,1968)
+++ - published G2 analysis (Flannagan,).

index. Similarly, when re-focussing, the line moves into the material with the lower refractive index. This method is called the Becke or Central Illumination Test.

This is explained by considering the properties of lenses. If it is assumed that the edges of a glass fragment are thinner than the centre, then the fragment will act as a convex lens when its refractive index is greater than that of the mounting medium, and as a concave lens when it has a smaller refractive index (Gay,1967).

With the single variation method, the wavelength of the monochromatic light source is kept constant while the temperature is varied. Immersion media as silicon oil possesses the property of a linear change in refractive index when subjected to heating or cooling. The refractive index of the glass, in this work being obsidian, is determined given the following information:-

d_o - the refractive index of the oil under sodium illumination;
T - the calibration temperature at which d_o was determined;
K - the temperature co-efficient or the rate of change of the refractive index per degree in temperature.

In the silicon oil used in the refractive index determinations, $d_o = 1.54493$, $T = 20^\circ C$, $K = -0.000377$.

The refractive index can then be calculated to be :-

$$\text{R.I.} = d_o - (\sigma M \times -K)$$
$$= d_o + (\sigma M \times K)$$

where σ = number of determinations per sample, thus denoting the average;

M = temperature at which the Becke line (between the fragment and the oil) disappears. That is, the refractive index of the oil is equal to that of the sample fragment.

...equation 13 .

The aim of the analysis was to consider the relation of refractive index to composition.

2. Sample Preparation

From the material available for analysis in the Bradford reference collection of geological obsidian, the number of suitable samples was found to be limited. A necessary condition is that the samples are not affected by weathering or hydration phenomena if there is to be any possibility of relating refractive index to composition.

Initially a wide range of samples (and sources) were inspected and fragmented for analysis. This was done originally by removing small chips during the grinding process of samples for X-ray fluorescence. However, these were found to be either too spherical or too large (approximately 2mm by 1 mm)and it was thus necessary to reduce them to minute flat fragments by using an aluminium rod and perspex base. Again care was taken to avoid cross-contamination by regular cleaning of the apparatus. It is essential to have flat pieces as light can easily be reflected off more than one plane of the fragment making it extremely difficult to define the Becke line. In routine mineralogical studies this problem is not present due to thin sectioning of appropriate specimens.

The wide range of samples was narrowed considerably by a trial analysis. Some samples were too dark to be observed with any precision (for example, Fanal Island) even with the use of neutral density filters across the light source. Others showed partial oxidation, where the Becke line was uncertain. Finally, a number of determinations were made on eight samples from four sources. Determinations were made from several different parts of a specimen to examine any possible variation. The Mayor Island source was best represented in the hope that later work could be done by taking this source as a standard and estimating the change for other sources, and to compare the differences in refractive index values.

3. Apparatus

The apparatus essentially comprises two units for temperature generation and control, and a viewing microscope with a monochromatic light source.

A Mettler FP 5 control unit acts as a visual display for recording by the operator (using a remote control hand held unit) the resultant temperature at which the Becke line appears, disappears and reappears. This is connected to a Mettler FP 52 unit which comprises two heating plates connected in parallel circuitry, a thermocouple for registering the temperature in the region of the sample, and a cooling fan which serves to lower the temperature when the current to the heater circuits is reduced.

The fragment is mounted on a slide in immersion oil (Dow Corning 710, silicone based) which remained stable throughout the temperature range. The slide is then placed between the two heating plates and may be moved vertically or horizontally by use of two finely adjusted screws. A further glass slide attached to the upper heating unit protects the sample from dust contamination. Within this framework, a sodium lamp (589.3 n.m.) is fitted. Owing to the different degrees of clarity of the obsidian fragments, it is helpful to apply neutral density filters to reduce the intensity of the light source viewed through the microscope. A Wratten 96 ND 0.90 filter was used in conjunction with the refractive indices determined.

The microscope used for viewing the samples was a binocular type. With the combination of a three times objective and twenty times eyepieces, sixty times magnification was achieved.

4. Results

For each fragment the temperature at which the Becke line disappeared (M) was recorded (Table 26). The refractive index was then determined according to the equation given. Three determinations were made for each measurement, as such, $\bar{M}$ is the average for each fragment.

The extent of variation for measurements on one sample is reflected by the standard deviation. Mayor Island GS716 has a co-efficient of variation of 18.54 percent with 10.70 being the standard error of the mean. If the sample was suitable, more than two fragments were selected for analysis. In a study of the physical properties of natural glasses (George,1924), the

Table 26. Refractive Index Measurements. M=temperature at which the Becke line disappears in celcius degrees; $\bar{M}$= average 'disappearance' temperature -the standard deviation (σ-1) is given in brackets; K=-0.000377; d_o=1.54493.

Source	M	$\bar{M}$	Refractive Index (=d_o + $\bar{M}$.K)
Mayor Island GS716	111.1 146.2 118.3	125.20 (± 18.54)	1.4977 ± 0.0070
Mayor Island	120.7 115.3 119.4 117.3	118.18 (± 2.37)	1.5004 ± 0.0009
Mayor Island GT745 (a)	123.6 119.2 122.2	121.67 (± 2.25)	1.4991 ± 0.0008
Taupo GT579	131.8 132.6 146.4 148.4	139.80 (± 8.82)	1.4996 ± 0.0033
Taupo Gt496	145.3 142.4	143.85 (± 2.05)	1.4907 ± 0.0008
Taupo GT539	139.2 151.8	145.50 (± 8.91)	1.4901 ± 0.0034
Rotorua GS959	149.0 153.0 153.1	151.70 (± 2.34)	1.4877 ± 0.0009
Tairua GS635	121.8 142.3 138.3 134.4	136.70 (± 4.59)	1.4934 ± 0.0017

reason for variation in a single specimen was thought to be due to weathering, partial oxidation and actual differences in chemical composition resulting from contact with local (soil) agencies.

5. Discussion

(i) Error Assessment and Accuracy

Unlike the fully automated apparatus of neutron activation and X-ray fluorescence analyses, human judgement plays a crucial role in refractive index determinations. An error may arise in the decision when the Becke line disappears which may be more pronounced if the outline is weak. The sodium lamp is an extremely bright background source and reproduction on the retina is possible. If a neutral density filter is used there has to be a careful balance between screening the light source and permitting an accurate definition of the Becke line.

Measurements were made accurate to 0.1 C and averaged to 0.01 C. The refractive index is calculated to four significant places in line with previous reported refractive indices of New Zealand obsidian(Green,1962). The standard deviation is given for the temperature and the refractive index. The average standard deviation is 6.83 C or 0.0026 refractive index. However, the resulting standard deviation on this average is high (± 5.94 C or 0.0023 refractive index) owing to the range of measurements for Mayor Island 716 and to a lesser extent GT579 and GT539.

(ii) Relation to Chemical Composition- Intersource Variation

The Mayor Island samples display a consistently higher refractive index within the experimental accuracy. The Taupo and Rotorua indices however are in close proximity within the range

1.4877 to 1.4996. As there is only one mainland source (and one sample), it is not relevant to discuss the significance of the result except to observe that the refractive index lies between the Central Volcanic Region sources and Mayor Island.

Early research attempted to relate the silica, potassium and iron oxide content to the refractive index of natural glasses (George,1924). Conversely, by a series of equations and constants, a method has been initiated to theoretically calculate the refractive index from the composition of silicate glasses (Huggins,1940). Continuing research at the Bradford Laboratories has shown that it is possible to determine the refractive index from the silicate composition, and hence likely differences in refractive indices arising from differences in compositions. The method of calculation has not been applied to this data because of the uncertainties arising from the estimates of the major element compositions (see Table 25).

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