

AUTOMATED ISOPROBE ANALYSIS OF  
NEW ZEALAND AND OCEANIC VOLCANIC GLASSES

by

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## ABSTRACT

The problem identified is the lack of a functional analysis facility for the routine characterization of obsidian artefacts. In over twenty years and no fewer than 12 different projects, a dedicated system for the analysis of New Zealand and Oceanic archaeological obsidian by prehistorians themselves has yet to be established. An attempt is made to remedy the situation, and a program of research and development is initiated which utilizes  $^{241}\text{Am}$  radioisotope gamma-ray induced X-ray fluorescence analysis. An automated analysis and sample changing facility capable of up to 50 artefacts per run is amalgamated with microcomputer controlled data reduction and inspection.

Experiments are performed to determine the excitation source emission characteristics as well as sample specific effects inherent in physically non-destructive fluorescence analysis. Minimum system detection limits are explored with the use of glass standards. Volcanic glass source samples from Melanesia, New Zealand and Central and Eastern Oceania are examined and distinct source-region groups established. Sources best distinguished by this technique include Mayor Island and Northland within New Zealand, in addition to Central and Eastern Pacific volcanic glasses. Lesser discrimination ability is attained between the New Zealand source regions of Inland, Coromandel and Great Barrier with the Melanesian groups. Artefact allocation is based upon a rejection configuration which clearly shows the level of source

discrimination achieved.

Allowance is made for the addition of an X-ray tube excitation source, and recommendations to improve the isoprobe system's performance are proposed.

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## CHAPTER ONE

### OBSIDIAN SOURCING AND ARCHAEOLOGY IN THE PACIFIC

#### INTRODUCTION

Archaeologists have long recognized the potential information to be gained from the study of artefactual obsidian. In a recent paper describing the prehistoric exploitation of obsidian sources in Melanesia, Ambrose *et al.* (1981:1-2) present an outline of the value of obsidian in archaeological contexts in the Pacific region. Their main points may be summarized as follows:

1. Obsidian was sought after for the razor sharp edge which could be produced from it. However, because of its fragility, the response of the edge to different cutting operations varies. Microscopic use-wear analysis has proven useful in utilization studies of obsidian implements.
2. The formation of obsidian is a relatively rare geologic occurrence, being generally confined to localized flows. Subsequent distribution of the material over wide areas has provided a good base for the study of exchange and contact.
3. Obsidian is very durable in archaeological deposits. The weathering of obsidian is basically a hydration process. Under favourable conditions the obsidian hydration rate can be calculated to produce an estimate of the time since the production of the flaked surface.
4. Obsidian has a short use-life as a cutting implement. As artefacts of the area in which they are found, small useless but used flakes should be fairly reliable indicators of activity areas.
5. A particular flow of obsidian is a geologically instantaneous event with a high degree of chemical homogeneity frozen into its composition. Obsidian used for artefacts should be chemically representative of its parent flow at the time of formation.
6. The homogeneity of an individual flow means that even very small artefacts or flakes should be chemically consistent with the composition of the parent flow.

Thus, when geographically discrete obsidian deposits are reliably characterized by a given technique, and artefactual material derived from the deposits is related back to its source, patterns of exchange or changing circles of communication through space and time can be studied. Archaeologists can thereby gain information about the activities of populations which exploited this resource.

#### AN OVERVIEW OF THE PROBLEM IDENTIFIED IN THIS THESIS

Over the past two decades there have been no fewer than 12 attempts to establish a characterization method which would allow New Zealand obsidian artefacts to be allocated to their geographic source. Similarly, Oceanic obsidians have been subject to nearly the same degree of characterization analysis. Relevant details of this work will be reviewed in the next chapter. At this point it is sufficient to note that the full complexity of the problem has only recently emerged, with the results of the analyses showing varying degrees of success.

The present research was begun out of a sense of dissatisfaction with previous characterization work, particularly with the general absence of a follow-through stage whereby answers to archaeological questions are produced. This thesis is aimed at breaking the apparently never-ending cycle of characterization research which ends before being useful to the archaeologist.

In the Pacific region, setting up a viable identification technique for New Zealand obsidian alone is a difficult task. Obsidians from specific geographic localities have been shown

to have a high degree of chemical similarity across broad regions (Leach and Warren 1981:64). Those sources from the Coromandel Peninsula through to the inland region of Rotorua/Taupō have a closely related form of mantle petrogenesis, and this is reflected in their composition (Ewart and Stipp 1968).

Additionally, however, there are distinct similarities between some New Zealand obsidians and others thousands of kilometers distant. For example, it has been shown that some artefacts from the Middle East sites of Harman Tepe and Taskin have a strong geochemical resemblance to the New Zealand sources at Huruiki and Te Ahumata (Leach and Manly 1982:103). In a comparison of neutron activation analysis results, it was found that there were significant differences in concentration for a maximum of only three elements of some 23 that were tested (ibid.). While more extensive analyses of the Middle East material may indicate that the differences are sufficient for source discrimination, the predominant similarity of these sources is notable.

Nonetheless, an archaeologist would immediately discount such a resemblance as creating any problem in allocating artefacts from either area to their 'true source'. This is because an archaeologist has access to knowledge in addition to geochemistry when considering the prehistoric movement of materials. Culture-historical information for instance, demonstrates that prehistoric contact between the Middle East and New Zealand is extremely unlikely, despite the impressions formed by some 18th and 19th century European writers (noted by Sorrenson 1979:14-17).

The existence of an obsidian source in the Middle East which bears a strong chemical resemblance to New Zealand obsidian types is therefore not a cause for alarm to archaeologists, though it may be a point of interest to geochemists. While it is hoped that this degree of similarity would be an infrequent occurrence, studies employing restricted analyses (which consider only a few elements) might expect poorer discrimination capabilities. Regarding the aforementioned example, it should be noted that values were not reported for either strontium or yttrium. Both of these elements have been shown to be important indicators in geological composition studies (see for example, Ewart 1968; Smith *et al.* 1977; Johnson *et al.* 1978).

In cases of chemically similar yet geographically distinct sources, the possibility must always be considered that alternative methods of analysis will reveal differences in composition not presently known about (Stross *et al.* 1976:240 ff.; Leach 1977a:13-16; Leach and Warren 1981:155-164). Smith *et al.* (1977) in consideration of this point state, "there are substantial reasons for accepting that potential sources of volcanic glasses throughout Oceania can be uniquely differentiated by the process of chemical characterization" (1977:174). It should be realised, however, that a formal identification system based solely on a selection of trace elements might in some instances be inadequate. Recourse to additional information such as major or minor element constituents may be required for judging the origin of artefact material (Smith *et al.* 1977:188-193; Leach 1977a:15-16).

A somewhat different situation can arise in the case of



an 'unknown source' as identified by Leach and Manly (1982: 104). It was determined that the trace element concentrations for two of fourteen obsidian artefacts recovered in the Chatham Islands were similar to, but could be distinguished from Rapanui material. Moreover, these two artefacts showed a closer similarity with, but could not definitely be ascribed to, known Mayor Island sources. While twelve other artefacts from the Chathams could be allocated to the Mayor Island source with conviction, their elemental compositions were still not especially close to the centroids of variation for that source (ibid.). Leach and Manly noted the particularly low coefficients of variation for these artefacts, atypical of Mayor Island obsidian, and suggested that this could be explained if they were all derived from a single large block which made its way to the Chathams from New Zealand. The two unallocated artefacts may have been derived from an as yet unsampled source, and their origin as determined from the present data would have to remain as 'unknown' (ibid.).

Determining the actual source of the artefactual obsidian, or perhaps the most likely region where the source might be located is of considerable importance. Studies by Smith *et al.* (1977:174 ff.) and Ambrose *et al.* (1981:5-13) considering unknown obsidian sources in Melanesia which appear to have been utilized prehistorically, underline the point. This type of situation taken together with a slight possibility that an obsidian source might even occur in the Chathams itself (Leach 1973:104-105), emphasizes the complexity of the problem. There is still a need to carry out geographic surveys in potential

source regions, as well as to expand our knowledge of the chemical compositions of various obsidians already recognized.

Over the same period, while sourcing methods have developed the complexity of the statistical treatment of the data for making the source allocations has also grown. This is primarily a response to the increasingly detailed data which are being generated for a growing number of known sources. It is also a response to archaeologists demanding to know not only from which source an artefact may have derived, but also with what certainty the allocation has been made. This question too will be considered in detail later. It can be noted here that there has been reasonable success in the statistical differentiation of the 18 major source groups now known to exist in New Zealand.

In spite of the great progress in this field, however, there has yet to be seen the 'routinization' of analysis coined by Green in 1975 (Leach 1977a:6). Indeed, Mayor Island obsidian, long noted for its ubiquitous distribution and occurrence in all periods of New Zealand prehistory (Green 1964:138-141; Leach and de Souza 1979:44; Davidson 1981:113-114), is still occasionally being identified on the basis of visual inspection alone (Fox 1982:208). This technique was shown by Ward (1972:52) to be unreliable. Green obsidian has been identified not only on Mayor Island, but also near Kaeo and Huruiki in Northland as well as Cooks Bay (Ward 1974a:59). It may be mentioned though, that the Huruiki allocations of green colouration have recently come under some question (Moore 1982:245).

In addition, the characteristic of showing green colouration in transmitted light is by no means exclusive to New Zealand. Rapanui obsidian also displays this trait and thereby emphasizes the dubious value of the visual method of source identification.

#### DISCRIMINATION OF NEW ZEALAND AND OCEANIC OBSIDIANS

That there is a need to differentiate New Zealand obsidian types from other Oceanic sources must be seriously considered. The first and foremost reason lies with the seafaring nature of the ancestral New Zealand population.

It is quite likely that part of the tool-kit brought by Polynesians reaching New Zealand was obsidian. It is now widely believed that multiple contacts to New Zealand from Polynesia occurred. There is therefore a good chance that non-New Zealand obsidian may exist in an archaeological context. As noted, this highly valued material has been found in Pacific archaeological sites vast distances from its source (Ambrose and Green 1972:31; Ambrose 1978:330-331).

With the earliest movements of the Lapita pottery making peoples from the Bismark Archipelago over 3,000 years ago, obsidian was being spread by seaward transportation (Green 1979:33). Obsidian from the New Britain source of Talasea for example, was exploited for at least 6,000 (Ambrose 1976a: 367), and perhaps as long as 11,000 years (White *et al.* 1978: 877; Sprecht *et al.* 1981). Also, obsidian from the Admiralties source of Lou Island, has been found as far away as the Santa Cruz Islands in the Solomons and Malo Island in the New Hebrides.

In the latter case, the obsidian has been moved a straight-line distance of some 2,700 km from its source (Ambrose 1978:331).

This is not to suggest that people regularly took part in such long distance transfer. Most movements would have taken place by 'archipelago hopping'. That is, by moving up or down strings of islands until the desired destination had been reached.

New Zealand, however, was settled without the benefit of potential interim stop-over points and thereby raises the question of just how the journey was accomplished. As would have been the case in locating new islands for settlement across the major water-gaps of Central and Eastern Polynesia, the first people to reach New Zealand would have had little prior evidence (besides a possible world view of an ocean filled with islands or by observance of the migratory birds) to suggest that these southernmost islands in the Polynesian triangle existed at all (Levinson *et al.* 1973:64; Lewis 1978:19).

Levinson, Ward and Webb (1973) utilized computer simulation in an attempt to generate data on this problem. Specifically, they state that "The process simulated is that of drift and navigated voyaging in the Pacific Ocean, and the distribution to be explained by the processes adopted is that of Polynesian peoples and culture" (*ibid.*:11). Drift voyaging is defined as movement before wind and current, while navigation "implies setting a course or sequence of courses and is a conscious activity directed to some goal, whether that goal

is a known landfall or the search for possible homelands across a stretch of unknown ocean" (ibid.:11).

Indefinite results were obtained throughout Central and Western Polynesia where a high percentage of the simulated voyages, both drift and navigated, reached land. For other regions, consistent landfalls were achieved only in navigated voyages, with none of the simulated drifts reaching the areas under investigation. Levinson *et al.* consider an outer arc region from Hawaii through Easter Island to New Zealand where "a drift hypothesis cannot be sustained; intentionally navigated, though perhaps only one-way, voyages must have been necessary" (1973:59-60). Further, voyaging to New Zealand would have required "just the right combination of well found canoe, skilled crew and favourable conditions" (Finney 1979: 349).

Nonetheless, the computer simulations indicated that even if the prehistoric craft were able to sail no closer than  $90^{\circ}$  to the wind (and they were probably able to sail a good deal closer, perhaps as near as  $75^{\circ}$ ), a sizeable number of navigated voyages would have been able to reach New Zealand from Rarotonga in the Southern Cook Islands given the prevailing winds and currents. Levinson *et al.* state, "no less than 453 of 732 [simulated] voyages [originating at Rarotonga] reached New Zealand" (ibid.:60).

Return drift voyages from New Zealand to Central Polynesia are considered more likely to have occurred. Subsequently this could have been the means whereby the knowledge of New Zealand and its associated zenith stars reached tropical Polynesia

(ibid.:56). What seems quite certain is that New Zealand was not colonized as a result of a canoe drifting before wind and tide. Such a craft "had no chance of reaching ... New Zealand from other parts of Polynesia" (ibid.:42).

The likelihood of long distance navigated voyages involving New Zealand is supported by recent archaeological findings in East Polynesia. As well as the close similarity in the material culture of early populations in the whole region, dates of initial settlement are within the same general time-frame for the Marquesas, the Society Islands and New Zealand. The recent discovery of whalebone and wooden patu at Vaito'otia on Huahine in the Societies adds further force to the suggestion of close contact between New Zealand and East Polynesia during the early stages of settlement in the eastern Pacific (Sinoto 1974; Sinoto and McCoy 1975; Sinoto 1979). Further, obsidian recovered from both the Chatham Islands and the Kermadecs was shown to definitely have been derived from Mayor Island (Leach *et al.* n.d.), distances of 939 km and 1037 km respectively from the source.

Taken together, these two points suggest that 'Archaic East Polynesia' was inhabited by a remarkable group of seafarers. However, this view has not generally been advanced in the literature by archaeologists. Green (1979:45-47) for instance, argued for a much more restricted range to effective two-way voyaging, placing the maximum distance at about 600 km. The identification of Mayor Island obsidian at far greater distances would seem to indicate what the true capabilities of these early seafarers were. Such data supply hard evidence

for extensive cultural contact in the eastern Pacific. Schemes to identify obsidian must give due recognition to this by making sure that when 'foreign' obsidian occurs in archaeological sites it can be accurately identified as such.

To date, no method of obsidian identification has been developed that is reliable in the sense described by Leach and Manly (1982:107), which could be counted on to recognize non-New Zealand obsidians in New Zealand archaeological sites. Similarly, no method has been set up which would identify New Zealand obsidians should they occur in Pacific Island archaeological contexts, although Smith *et al.* (1977) compare available data. A central aim of this thesis, therefore, is to develop such a system.

#### A PROBLEM OF APPLICATION

Of equal importance in the quest to identify obsidian artefacts is the fact that no method has yet been developed which can be routinely applied by archaeologists to archaeological problems. Although little has been published on this point, there is widespread disillusionment and frustration amongst archaeologists in the Pacific region, in that few 'final and reliable' artefact identifications have been made, despite the 20 years of intensive research noted above (for discussion of the reliability of artefact source identification, see Leach and Manly 1982).

The view is offered here that until a technique is put directly in the hands of archaeologists, little long term progress can be expected which will serve to assist culture-

historical research. The point must be made that archaeologists are motivated by culture-historical questions, physicists by quite different issues. The history of obsidian sourcing in the Pacific and New Zealand has been cyclical in nature - successive rounds of development followed by abandonment. The two main reasons for this are the changing research interests of physicists and geochemists, and the lack of a suitable applied research facility for sourcing which archaeologists themselves can use.

The primary cause of this inability on the part of archaeologists is the general complexity in application of techniques which have been shown capable of discrimination. Operation by and large requires skills far too specialized for the average archaeologist to quickly obtain. Worse, techniques such as neutron activation analysis, or fluorescence analysis utilizing the inelastic scatter of protons (PIXE-PIGME), require rare and extremely expensive equipment which is almost exclusively committed to other problems. This situation can no longer be tolerated.

The following two problems can therefore be identified as the prime concerns of this thesis:

1. To develop an obsidian characterization method, largely centred on the Central and Eastern Pacific regions of Oceania as well as New Zealand, which is as reliable as possible, and to reveal where the strengths and weaknesses of the method are.
2. To develop an identification facility employing this technique which is both sophisticated enough



to cope with the characterization problem, yet simple enough for archaeologists themselves to operate, so that attention at long last can be directed to meaningful questions about prehistory in the Pacific, and matters of geochemistry and mathematics abandoned.

The next chapter will identify a research strategy which will attempt to solve these two problems. At a later point in this thesis, a culture-historical problem will be addressed, utilizing the method and facility developed.

## CHAPTER TWO

## DEVELOPMENT OF RESEARCH STRATEGY

## INTRODUCTION

Fundamental in the development of a research strategy is to review previous work in the field. A study involved with the characterization of Oceanic and New Zealand obsidians is no exception. As noted in Chapter One, there have been some 20 years in which sourcing related studies have been applied. The volume of these works constitute a major body of literature, and represent a fair contribution to the geochemical knowledge of the Pacific Basin as well as to its archaeology. A review of relevant aspects of this material should supply a good basis for the development of the present research.

Nonetheless, this thesis has goals beyond the simple (or complex) characterization of obsidian, though this is obviously a main issue. There are some specific requirements regarding both the type of analysis to be employed as well as the use of the developed facility. These should be clearly stated before a survey is undertaken. With such criteria established, the suitability of previous work to the present research needs can be evaluated. It is hoped that an optimal solution to the problem of routine obsidian analysis can be found.

Before the analysis requirements of this thesis are defined, the petrologic characteristics of obsidian should be discussed. The chemical nature of obsidian is a result of the mode of its formation. The first section of this chapter will therefore consider obsidian as a geological material.

Subsequently, the present research requirements will be specified, followed by a review of the relevant literature. An analysis technique which best suits these requirements will be determined and its application developed in Chapter Three.

#### THE PETROLOGY OF OBSIDIAN

" ... exact reports which I have received about the occurrence of obsidian (Iceland agate, lavaglass) in Iceland and pieces of similar, in fact nearly the same, rock which I received from the region of Tokai in upper Hungary and Madagascar have made it very doubtful that this rock is of volcanic origin; in fact, I am almost completely convinced of the contrary"

(Werner 1786:87-88).

Despite this description published in 1786 by Abraham Gottlob Werner (a 'Neptunist' who believed that all important rocks which made up the earth's crust were either chemical precipitates or mechanical sediments), obsidian is indeed a naturally occurring glass of volcanic origin. Obsidian was utilized by prehistoric peoples for its glassy nature and characteristic conchoidal fracture, which allowed extremely sharp edges to be produced from it. This glass-like condition is the result of many factors which must successfully interact, and hence, obsidian is a rare geological occurrence.

An extrusive igneous rock, obsidian is generally acid in composition, containing greater than 66 percent silica as  $\text{SiO}_2$ . Most often produced from rhyolite magmas (>66% silica and >2/3 feldspar), obsidian can also be produced from dacite (>66% silica and 1/8 - 1/3 feldspar) and trachyte (52 -- 66% silica and 2/3 feldspar) compositions (Williams *et al.* 1954:

93-128).

It should be noted here that the descriptions given apply in only the broadest sense. More detailed classification schemes abound which employ various other compositional ratios (Williams *et al.* 1954:25-35; Barker 1981). It is common in geological classification that several terms may be applied to the same 'rock'. Hard and fast designations are generally eschewed in favour of less restrictive terms which incorporate compositional ranges. Rhyolites as much as any other igneous rock show a wide range of variation and "classification of these rocks remains a major problem" (Barker 1981:10131).

Lavas of lower silica content such as basalts, when appropriately chilled, may also produce thin selvages with glassy texture. Most frequently, these occur as the skin of deep sea lava flows (Carmichael 1979:237). Tachylyte, a glassy form of basalt, is found on Mauna Kea in Hawaii and was utilized in the manufacture of tools (Kirch 1971:229; Barrera and Kirch 1973:176).

How the magma is deposited is as important to glass formation as is composition. Both holocrystalline (all crystal) granites and holohyaline (all glass) obsidians can be derived from the same parent magma under different conditions. For example, rhyolitic magma intruded at a depth of 5 kilometers can remain at 80% of its initial temperature for a million years, allowing extensive crystallization to occur and ultimately, granite to be produced. Glass can result from the extreme undercooling of the same magma in surface or near

surface extrusions which thereby impedes the formation of crystals (Ericson *et al.* 1976:36).

While some glasses may be totally holohyaline, "glass completely devoid of crystals is rare" (Carmichael 1979:233). The cooling rate required to prevent crystal formation has been shown to depend upon the composition of the magma. Obsidian flows derived from rhyolitic magmas can occur in thicknesses of ten meters or more and cool over months or years in surface environments (for example the 'Obsidian Cliffs' of Wyoming). Basaltic magmas are quenched to glass only if cooled in seconds or hours. Hence tachylite is formed in thin selvages and generally only where direct contact with water or ice has occurred (Stewart 1979:339).

Crystalline inclusions take the form of spherulites or phenocrysts and can develop either during or after the extrusion of the lava. Most frequently occurring in siliceous lavas, radial aggregates of acicular and fibrous minerals can form spherical or polygonal inclusions within the glassy matrix. The composition of spherulites varies from feldspar to quartz. They are produced from the devitrification of the glass around scattered nuclei. Phenocrysts represent the fractional crystallization of lavas as a result of prolonged cooling. The presence of either in obsidian impair its ability to fracture conchoidally and, in extreme cases, rule out its use in the manufacture of tools.

Pumice is formed where rapidly effervesced magmas are inflated to foam by gases released across the pressure gradient between the magma chamber and the extrusion surface. It is

estimated that water contained within the magma increases its volume 1067 times. This expansion contributes to the tremendous energy required for surfacial extrusion (Bayley 1958: 371). Resultant ejecta, showing the characteristic spongy or pumiceous texture is, in effect, extremely vesicular glass. Obsidian too, when ejected as 'bomb' deposits generally appears externally as vesicular lumps while retaining a vitreous internal matrix. The physical structure of flows can be affected by rapid degassing, and rhyolitic deposits with an upper pumiceous surface grading through vesicular and finally non-vesicular glass occur (Friedman *et al.* 1963:6534).

Colour in obsidian varies as much as texture. Parker Cleaveland (1822) noted, "its color is black, either deep and pure, or tinged with green, brown, blue, or grey, and sometimes passes to green, blue, brown, or grey, or is even yellow, or red. The darkest colors often discover a tinge of green by transmitted light" (Cleaveland 1822:307 In:Johannsen 1932:277). This colouration is attributed to the inclusion of microlites and crystallites arranged in a more or less fluid manner, and some obsidian in thin section is wholly transparent (Johannsen 1932:278).

New Zealand obsidians for example, show a wide range of colouration between various localities. Perhaps none are as striking as those found on Mayor Island.<sup>1</sup> Gradations from dark green through to tan or 'honey', to yellow or tan with

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1. The author was able to visit Mayor Island during May/June 1982 as part of a site survey project directed by A. Seelenfreund of the University of Otago Anthropology Department (see Seelenfreund 1982).

grey speckles occur in several places where obsidian outcrops on the island. Particularly impressive to the author, are patches and nodules of obsidian in a flow at the southern tip of Crater or Taratimi Bay. Here, where the still hot obsidian extrusion apparently reached the sea, it displays a skin of pale green metallic lustre covering the more common dark green translucent interior.

Mainland North Island sources of New Zealand obsidian are predominantly black or grey, though red and brown obsidian is found in the inland region (Maraitai, Rotorua); on the Coromandel Peninsula (Purangi); and in Northland (Weta) (Ward 1972:Appendix 4). As noted in Chapter One, green obsidian has been described from Northland sources as well.

Perlites and pitchstones differ from obsidian only in their water content. By definition, "these are called obsidians if they contain less than 1 percent water; if they carry water up to a few percent and have abundant perlitic cracks they are known as perlites; glasses with still more water (up to about ten percent) and with a dull, resinous lustre in hand specimens are termed pitchstone" (Williams *et al.* 1954:122).

The reason for the variation in water contained by these glasses is not fully understood. Siliceous magma when extruded has a temperature of between 600°C. and 850°C., and because of this contains only a little water in solution. Subsequently, many such magmas chill to produce obsidian. Perlites and pitchstones on the other hand, take up additional water by absorption as they cool, and "many pitchstones which must

have erupted with only a small amount of water (0.09 - 0.29%) now contain large amounts of water, perhaps 2 - 7 percent by weight" (Carmichael 1979:241). Generally perlites and pitchstones are intermingled with holocrystalline deposits, presumably because they absorbed water from the more slowly cooled crystalline component (Williams *et al.* *ibid.*).

As supercooled liquids, volcanic glasses therefore are not static, but subject to chemical and morphologic change. Williams *et al.* note an example in Iceland where a rhyolitic dike contains anorthoclase phenocrysts which could not have crystallized from a melt with the composition of the surrounding glass. The selvage it seems not only absorbed water, but enriched in potash at the expense of soda during cooling (*ibid.*:122).

All glasses tend to devitrify with time and, ultimately, may be converted to micro- and cryptocrystalline aggregates. Devitrification may also yield micrographic intergrowths or secondary spherulites (*ibid.*:122-123). As noted by Cann and Renfrew, nearly all obsidians of pre-Tertiary age (greater than 65 million years old), have lost their glassy properties (1965:111). Most notably, they no longer retain the characteristic ability to fracture conchoidally, for which they were primarily valued. While this alteration limits the obsidians which could be used prehistorically, the archaeologist can rest assured that those that were utilized will retain their petrologic characteristics within an archaeological context for many hundred thousand years to come (Mason, *pers. comm.*: 1983).



Obsidians as well as perlites and pitchstones absorb meteoric water. As mentioned at the beginning of Chapter One, the rate of hydration has been employed as a basis for the dating of obsidian artefacts. Pioneered by Friedman and Smith (1960), hydration studies have since been applied to a large number of archaeological problems where artefactual obsidian occurs (see summary in Taylor 1976, and more recently, Leach and Naylor 1981).

The study of obsidian hydration as a dating technique per se, however, is not strictly germane to this thesis and will not be treated in detail. Nonetheless, it has been shown that hydration rates are affected by the particular chemical composition of the obsidian being studied. For instance, sodium and potassium have a positive effect on hydration, while iron and calcium slow the hydration rate (Ambrose 1976b: 83). Further work by Ericson and Berger (1976:61) indicates that the most important variable affecting obsidian hydration is the silicon/oxygen ratio.

Many obsidian sets derived from archaeological contexts contain specimens from different sources (and hence of different compositions), which may thereby hydrate at different rates. The hydration rate constants derived from such material must therefore be suspect (Kimberlin 1976:77). Source identification of obsidian artefacts destined for hydration analysis is indicated as a preliminary step (Ericson *et al.* 1976:43; Leach 1977c:136). The importance of establishing source specific hydration rates has most recently been demonstrated by Michels *et al.* (1983), in a study of East African

obsidian artefacts.

Not only does the chemical composition of obsidian contribute to the rate at which hydration takes place, but more important to this thesis, the chemical composition of the obsidian is in turn effected by the weathering process of hydration. Ion-exchange constants experimentally determined from the interaction of obsidians with meteoric waters indicate that for a wide range of glass compositions, a gain in potassium and water, and a loss of sodium, calcium and magnesium occurs (Ambrose 1976b:83, Truesdale 1966 In: Stewart *et al.* 1979:343). Hydrated obsidian depletions in potassium (21%), lithium (56%), sodium (31%) and a few percent of calcium and magnesium, with a 300% enrichment of hydrogen were reported by Tsong *et al.* (1978:340).

While the depletion of alkaline earths (Ca and Mg) is perhaps more consistent with the deficiencies in alkaline ions that have been measured in hydrated layers, the conflicting results in potassium exchange with those of Ambrose and Truesdale are somewhat disconcerting. Undoubtedly, the diffusion kinetics involved are highly complex, and "chemical composition plays an important role in the hydration process" (Tsong *et al.* 1978:341).

Hydration rinds in archaeologically derived samples have been observed over ten microns in depth (Meighan 1976:114), and up to 30 microns deep on some East African pieces (Michels *et al.* 1983:365). This degree of chemical alteration is potentially significant where surface and near-surface techniques

of analysis are employed (Cox and Pollard 1977:50).

Of the various petrographic characteristics of obsidian that have been discussed so far, none have been as important to sourcing studies as chemical composition. In this respect, basic to all elemental characterization work are the requirements:

1. that intrasource chemical variation is sufficiently low to allow artefactual material to be related back to its source, and,
2. that elemental variation between flows is sufficient to allow the reliable characterization of each.

It has already been noted that some obsidian flows separated by large distances show a high degree of similarity in certain chemical concentrations (Leach and Warren 1981; Leach and Manly 1982). Similarly, Stross *et al.* (1976:241) determined a high degree of overlap in certain elements between widely dispersed sources in Central America. Bowman *et al.* (1973a,b) studied the compositions of some Californian obsidian flows and also found different degrees of intrasource variability.

While the Napa County flow was determined to be highly uniform in composition, the Borax Lake obsidian was shown to be heterogeneous. The Mt. Konocti flow, on the other hand, was found to contain only small degrees of variation. The compositional variations observed, however, occurred in highly systematic fashions. Correlations of samples to flow regions

were as reliable as if the flows had been uniform (*ibid.*: 316-326). All three sources were found to be chemically distinct from each other (*ibid.*:317-318). Similar variation has been noted for the Lou-Pam obsidian by Smith *et al.* (1977: 193). Moreover, New Zealand obsidians display a wide range of elemental variation as shown by Leach and Manly (1982:88, Table 1).

Thus, some degree of intrasource variation is acceptable providing it is well sampled and documented. The corollary suggested by Stross *et al.* (1976:240) is that for any unknown source, multiple analyses should be made to test the possibility that it may be heterogeneous as was found in the Californian and New Zealand obsidians.

From this discussion of obsidian petrology, there are several points to make which are relevant to this thesis. Firstly, the volcanic glass obsidian is formed only under some very specific conditions which relate both to the environment into which the lava is extruded and the composition of the parent magma source. This limits its geological occurrences.

Secondly, the suitability of obsidian as a tool making material can be effected by spherulites, phenocrysts, devitrification and the process of hydration, during and after its formation. Most pre-Tertiary obsidians are no longer useful for tool manufacture.

Thirdly, hydration proceeds at different rates for obsidians of different compositions, and alters the chemical composition of hydrated layers during the process. Sodium, hydrogen, potassium, lithium, calcium and magnesium appear to be

the most affected elements. Caution is therefore needed where surface-analysis characterization techniques are employed.

Finally, obsidian flows vary in chemical homogeneity and compositional uniqueness from one region to another. Nonetheless, detailed sampling of sources and extended ranges of elemental analysis have enabled effective characterization. By and large, characterization research continues to "confirm the expectation of the unique and identifiable composition of potential sources of artefact glass" (Smith *et al.* 1977:193).

#### RESEARCH REQUIREMENTS

It is the goal of this thesis to develop an obsidian characterization technique which is not only capable of distinguishing between New Zealand and Oceanic sources, but further, which can be used by non-technically trained personnel, notably field archaeologists. The requirement regarding the ability to discriminate between sources is distinct from the actual technique which is used, as several methods of analysis may have the same ability to differentiate sources. Moreover, while several techniques may be able to characterize obsidian sources to the same degree, a quite separate consideration is the matter of which of the techniques require the least specialized skills for routine operation.

Clearly, a highly discriminative technique is of little practical value to archaeologists if its use requires either an elaborate and expensive facility or high technical skill. Similarly, an extremely simple and rapid technique (such as

colouration in transmitted light) is of little functional value if the results produced are ambiguous over broad regions.

The history of obsidian sourcing studies to date has seen the application of analysis techniques ranging from relatively simple tests of colouration and refractive index such as employed by Green (1962:1964), and density (Reeves and Armitage 1973), to highly sophisticated procedures such as neutron activation analysis (Leach and Warren 1981) and PIXE (proton induced X-ray emission) or PIGME (proton induced gamma-ray emission) analysis (for example, Coote *et al.* 1972; Bird *et al.* 1978). A single technique which is both highly discriminative yet readily applicable by archaeologists has yet to be established as a permanent facility in New Zealand.

It is quite likely that these two criteria will involve a trade-off, one against the other - that is, some loss of precision in source discrimination might have to be accepted in the interests of establishing a readily usable method. Assuming that a less-than-perfect solution might have to be adopted, it is important that a clear statement is made on the relative status given to these two criteria. These priorities will provide a yardstick whereby previous characterization research can be evaluated.

One of the foremost considerations of the present study is that the technique to be developed should be applicable by non-technically trained personnel - that is, the field archaeologist. Ward (1972) felt that the suitability of any technique to application by those with non-specialist knowledge was "perhaps most important ... so that the archaeologist could

have control over the production of the data" (Ward 1972:94). This opinion has been echoed recently by Leach (1977a:10; 1977b:2), and Leach and Warren (1981:152); it has already been noted, however, that such a technique has not yet been developed. In fact, the total number of New Zealand obsidian artefacts actually analyzed has been estimated at something less than one thousand pieces (Leach and Warren 1981:164). This can only be attributed to the lack of an appropriate facility, and not the lack of artefacts requiring analysis.

Not all who are involved with the characterization of lithic material, however, share this ordering of priorities. The geologists Shotten and Hendry in *The Journal of Archaeological Science* state,

"... it would be a disservice to the archaeologist not to point out that it is unlikely that he can perform these analyses himself and that he needs the co-operation of a specialized analyst with complex equipment at his control" (1979:78).

The consequences of this sort of reasoning were described in Chapter One. It is the opinion of the present author (in strict agreement with Ward, Leach and Warren) that a technique directly applicable by archaeologists is of primary concern. The main problem therefore will be in finding a level of source discrimination acceptable to archaeologists, since this will be the real trade-off in the interests of solving problems relating to prehistory.

An additional, though in no way subordinate requirement of this study is that the technique should be capable of distinguishing between New Zealand and Oceanic obsidians. The reasons for this requirement were discussed at some length

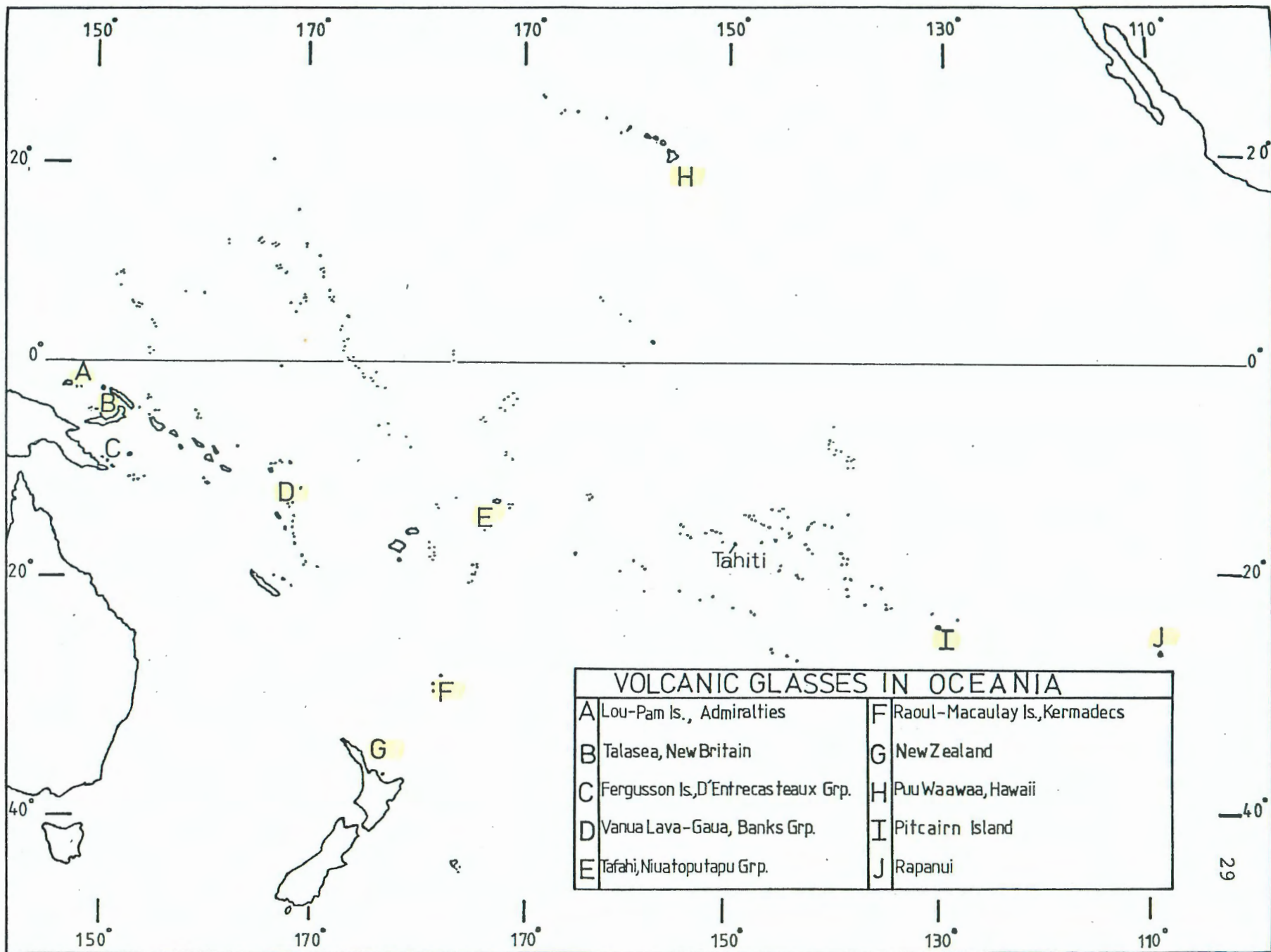
in the previous chapter. Again, the question arises as to what confidence level this discrimination is required. It is argued here, that for most archaeological purposes, it should be quite sufficient to be able to identify broad regions of origin. That is, the technique should be able to identify all of the major Polynesian sources (see Map 1), and if necessary sacrifice discrimination at the level of a particular flow.

For example, although Rapanui has been identified as having three main regions which were exploited prehistorically (Smith *et al.* 1977:179-180; Michels *et al.* 1981:2), it is considered satisfactory here to be able to identify Rapanui obsidian as a single regional source. At this level, New Zealand obsidians would need only be identified as such, though it is expected and desired more detailed differentiation would be achieved in practice.

The New Zealand situation does warrant special consideration. Unlike anywhere else in Oceania, the prehistoric inhabitants of New Zealand had access to a particularly abundant supply of obsidian within a reasonably restricted geographic area. Ward (1972:123-127), after identifying no less than 42 separate localities from which obsidian could be obtained, was finally able to group these into 18 major source regions (on the basis of chemical similarity) within the confines of the North Island of New Zealand. Not surprisingly, these 18 major source groups are themselves situated within a few main regions. Regarding this, Leach and Warren note, "although desirable, it is not considered necessary to distinguish



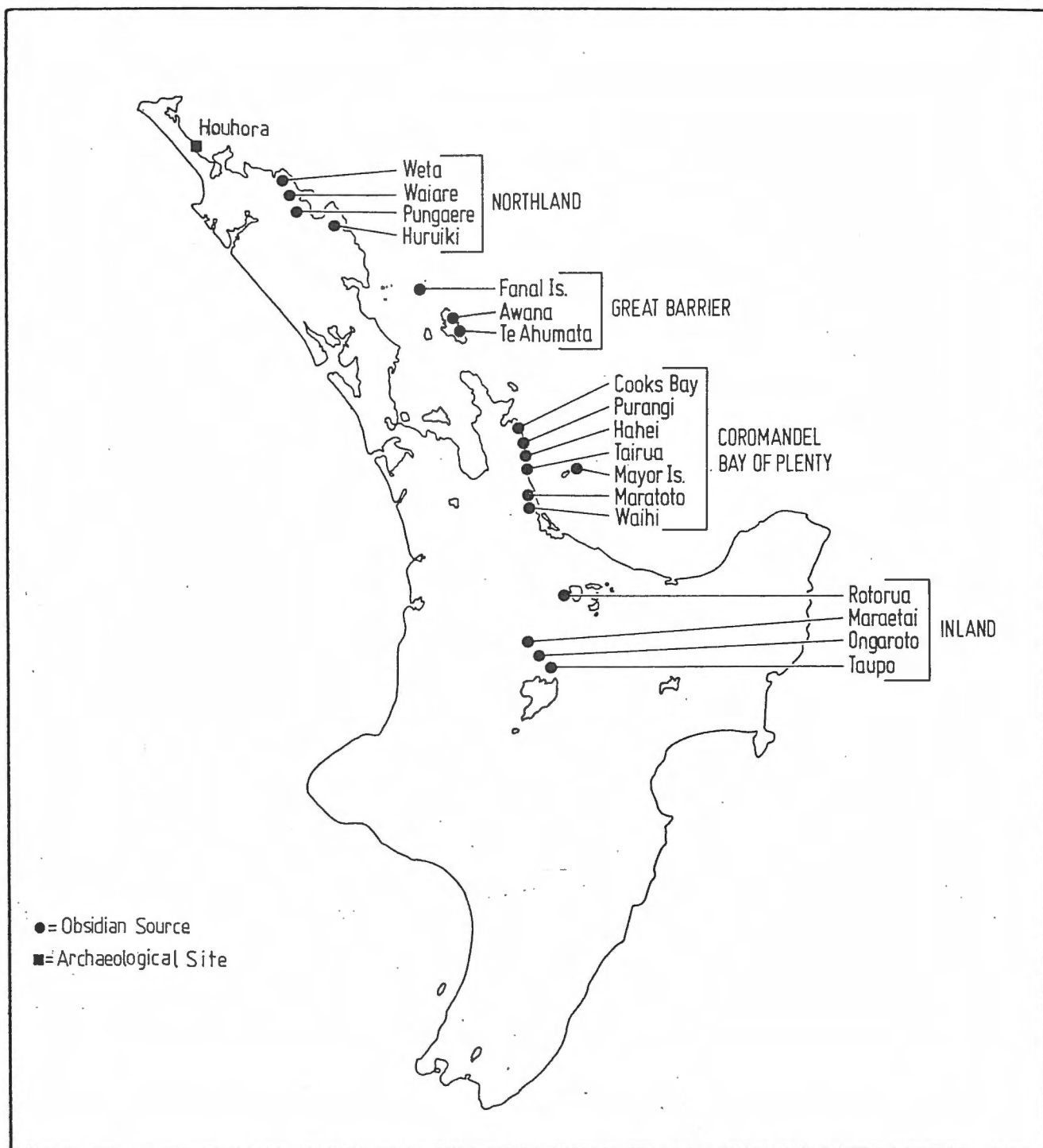
MAP 1: Sources of volcanic glasses in Oceania (after Smith *et al.* 1977).



between all 18 of the New Zealand sources" (1981:64). Rather, they would consider it sufficient to be able to reliably allocate artefacts to one of the four major regions which they have defined (Map 2). This is not to imply that definition of the 18 sources is considered superfluous, but that it may not be strictly required by archaeologists.

One proviso to this 'source region' approach should be added. Mayor Island obsidian must be considered as a separate region by itself. The particular importance of this source in New Zealand prehistory has been discussed, and it is felt that this justifies precise and unambiguous identification of Mayor Island obsidian in whatever context it occurs (for instance, see Leach *et al.* n.d.). Of course, the primary reason that Mayor Island obsidian's importance has been recognized, is due to the fact that it has a certain physical and chemical distinctiveness when compared to other New Zealand sources, albeit with some ambiguity as discussed above (see also, Leach and de Souza 1979:42-43). A programme of source discrimination must acknowledge this importance.

A further requirement within the context of this study is that the adopted technique should be as minimally destructive as practical. An issue infrequently dealt with in the literature is the potential for residual effects upon the sample from nearly all types of analytical techniques. While powdering a portion of an artefact is an obvious injury, the effects of ostensibly 'non-destructive' techniques are not generally discussed. Irradiation of an artefact by X-rays or gamma-rays as in energy dispersive XRF analysis will almost



MAP 2: Obsidian sources and source regions in New Zealand (after Leach and Warren 1981).

certainly alter the ESR (electron spin resonancy) and TL characteristics of the sample. Neutron flux irradiation in whole sample NAA has additional effects on fission track characteristics, as well as the residually induced radioactivity. Even the sun's ultraviolet rays can have a deleterious influence, as is evidenced by the purple colouration induced in old bottles.

A worthwhile exercise at this point, is to define some terms of reference relating to levels of destructiveness as used in this thesis:

Totally destructive	- use of entire sample for powdering
Semi-destructive	- use of 0.5 to 5.0 gm for powdering
Macroscopically destructive	- use of 50 to 500 mg for powdering
Microscopically destructive	- irradiation processes such as X-rays, gamma-rays, proton beams or neutrons etc.
Absolutely non-destructive	- detection of natural sample emissions ( $\alpha$ or $\beta$ ), density analysis or colour analysis etc.

In evaluating the analysis techniques for general suitability to routine application, the above list of potential artefact 'impacts' should be kept in mind. A technique which is at worst only microscopically destructive is desired. Analysis which does not require the mechanical destruction of the artefact has two specific advantages, both of which are considered essential.

Firstly, a non-mechanically destructive technique permits

valuable cultural property to be analysed. While some methods of analysis require only minute samples to be removed from the artefact (for instance, atomic absorption spectroscopy as employed by Michels 1981 utilizing approximately 200 mg of sample), that particular sample can never be re-run. There is also the danger of additional samples being required if procedural mistakes are made during analysis.

Semi-destructive techniques such as wavelength dispersive X-ray fluorescence, which do not actually consume the sample, still require that it be ground to a fine powder for quantitative results. Although the samples themselves are not destroyed by analysis, the original artefact area which they represent is, and negates the possibility of subsequent use-wear or form/function analysis (for example, Leach 1973: 105). This is particularly true where smaller lithics are concerned.

Secondly, exacting sample preparations can create problems in reproducibility, especially where multiple, untrained users of the facility are expected (the reader is referred to Michels 1982:116 for a more detailed discussion of the atomic absorption sample preparation to illustrate the procedural complexity). Laborious sample preparation also increases the handling time for each specimen, and consequently, the total analysis time invested per sample. This relates to the last major requirement to be specified, regarding the analytical rapidity of the technique.

In order for any regularly operated system to be of value in data production such that "statistically significant

numbers of samples" (Stevenson *et al.* 1971:17) can be run, it must be able to handle a certain minimum number within a given amount of time (see also, Leach 1977a:8-10). While these are subjective quantities, it is hoped that something on the order of one thousand samples per month as suggested by Leach (1977b:3) could be processed by the facility. This rate of analysis would make it of practical use to archaeologists who may be concerned with hundreds or even thousands of artefacts from a single excavation (for example, Prickett 1975: Appendix 4). To optimise throughput the analysis should be automated, permitting samples to be run continuously day and night.

To review the requirements outlined, in order of importance:

1. The technique should be applicable by non-technically specialized personnel.
2. It should be able to distinguish New Zealand and Oceanic sources on a broad level, including some greater detail within New Zealand.
3. It should be largely non-destructive, to allow analysis of valuable cultural material and to minimize preparation and handling time per sample.
4. The technique should be reasonably fast, and able to perform on the order of one thousand analyses per month in full-time operation, within an automated format.

## OBSIDIAN CHARACTERIZATION TECHNIQUES: AN EVALUATION

Bearing in mind these criteria, the majority of the characterization techniques which have been applied to New Zealand and Oceanic obsidians are quite unsuited to archaeologists. Detailed reviews of these studies have been made by Ward (1972:47-95), Reeves and Ward (1976:264-276) and Smith *et al.* (1977:176-177, 188-197). Leach (1977a; 1977b) reviewed potential characterization techniques that had yet to be extensively evaluated with New Zealand or Oceanic materials. A tabulated survey of New Zealand obsidian characterization studies has recently been made by Leach and Warren (1981:154). A similar format is adopted here to list the New Zealand and Oceanic characterization work applied to date (Table 1).

The techniques listed, as well as others used in the analysis of geological materials, have been well described for the non-specialist by Reeves and Brooks (1978) and specifically for the archaeologist by Goffer (1980). These texts supply clear and concise descriptions of the theory and use of the various techniques listed, in addition to extensive bibliographic references of experimental applications. For this reason, the theoretical background to methods discussed will not be elaborated upon here.

In considering which technique might closely approximate the objectives of this thesis, however, the findings of previous reviews are of interest. Ward (1972:95) concluded,

"The only one of these methods [up to 1972] which fulfilled the ... criteria adequately, and appeared to be among the simpler and more reliable forms of analysis within the operating ability of the archaeologist was the X-ray fluorescence spectrographic method."

TABLE 1. Summary of analysis techniques applied to New Zealand and Oceanic obsidians for archaeological characterization.

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NEW ZEALAND ;

Physical Properties

Refractive Index

- Green, 1962.

Density

- Reeves and Armitage, 1973.

Element Analysis

Emission Spectrography

- Green *et al.*, 1967.

Atomic Absorption/Flame Photometry

- Armitage, 1971; Armitage *et al.*, 1972.

Wavelength Dispersive XRF

- Ward, 1972; 1974a; 1974b; 1974f; Leach, 1973; 1976; Leach and Anderson, 1978; Chidgey, 1981.

PIGME

- Coote *et al.*, 1972; Bird *et al.*, 1978.

Thermoluminescence

- Leach and Fankhauser, 1978.

Radioactive Properties

- Leach *et al.*, 1978.

Energy Dispersive XRF (TEFA)

- Leach, 1977a; 1977b; McCallum *et al.*, 1979.

Energy Dispersive XRF (SEFA)

- Leach, 1977a; 1977b.

Neutron Activation Analysis

- Leach and Warren, n.d.; 1981; Chidgey, 1981.

PIXE - PIGME

- Duerden *et al.*, 1979; 1980; Bird *et al.*, 1981a.

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TABLE 1. (cont.)

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PAPUA NEW GUINEA

Physical Properties

Density

- Ambrose, 1976a.

Element Analysis

Emission Spectrography

- Key, 1968; 1969; Ambrose and Green, 1972.

Wavelength Dispersive XRF

- Smith, 1974; Ambrose, 1976a; Smith *et al.*, 1977.

Neutron Activation Analysis

- Ambrose, 1976a; Wall, 1976; Leach and Warren, n.d.; 1981.

PIGME

- Bird and Russell, 1976; Bird *et al.*, 1978; 1981b.

Natural Radioactivity

- Leach *et al.*, 1978.

PIXE - PIGME

- Duerden *et al.*, 1979; 1980; Bird *et al.*, 1981a.

CENTRAL/EASTERN PACIFIC

Element Analysis

Wavelength Dispersive XRF

- Ward, 1974b; 1974c; Smith *et al.*, 1977.

PIXE - PIGME

- Duerden *et al.* 1979; 1980; Bird *et al.*, 1981a.

Natural Radioactivity

- Leach *et al.*, 1978.

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Wavelength dispersive XRF such as was used by Ward (1972; 1974a; 1974b; 1974c; 1974d) is, as discussed, a 'semi-destructive' technique that requires the sample to be ground to powder, though the material itself is neither consumed nor chemically altered. For the reasons previously stated, this is considered to be unsuitable in the present context. Similarly, other destructive techniques such as refractive index, emission spectroscopy, atomic absorption, flame photometry and thermoluminescence are considered unsatisfactory. Even though much smaller samples are required, the process of sample preparation is considered problematic.

Reeves and Ward (1976) review only New Zealand characterization studies, and make no clear recommendations for 'best suited' techniques. They do, however, note that those which employ physical characteristics of the samples (such as density measurements made by Reeves and Armitage, 1973) are generally poor discriminators and "the confidence with which assignments could be made is very much less than that given by chemical analysis for appropriate elements" (1976:286).

PIGME analysis is described to some extent by Reeves and Ward (1976), though at that time no artefact samples had been analysed (1976:271). The minimally destructive aspect of the method is noted as being particularly attractive to archaeological applications. In New Zealand, following the initial study by Coote *et al.* (1972) at the Institute of Nuclear Sciences, further work regarding the characterization of obsidian was abandoned as changing interests focussed the use of the accelerator on other research topics (Coote pers. comm.,

1983).

The proton source employed by Bird and Russell (1976), Bird *et al.* (1978; 1981a; 1981b) and Duerden *et al.* (1979; 1980), is generated by the Australian Atomic Energy Commission's Lucas Heights Van de Graaf accelerator. A major drawback of this technique still remains for archaeologists, in that these are very expensive and complicated facilities and are generally in demand for a wide range of research applications (see for instance, Nelson *et al.* 1977). As such they are clearly limited to 'specialist' operation. Any archaeological application will have to queue for attention, with charges proportional to the value of analysis time.

Smith *et al.* (1977) are more specific in their recommendations, noting that mechanically non-destructive techniques are preferable for archaeological applications (1977:197). The mechanically non-destructive NAA as applied by Wall (1976) and Ambrose (1976), was considered to be a type of analysis which "met the archaeological requirements most completely", though the relative inaccessibility of the user to neutron activation facilities was noted (*ibid.*). It should be recalled, however, that from the aspect of sample alteration at the atomic level, NAA probably has the most serious effects. PIXE - PIGME analysis, while described as "potentially most useful", is not discussed in terms of its accessibility, though this has also been mentioned above. An advantage of PIXE - PIGME is the very restricted beam size employed. Subsequently only a small area of the artefact is affected.

Minimally destructive energy dispersive X-ray tube

excitation XRF (TEFA), initially employed by Nelson *et al.* (1975) to the characterization of Pacific Northwest Coast obsidians in North America, was considered useful by Smith *et al.* (1977). This was qualified, however, in that detection limits of the system were not low enough for many trace elements in volcanic glasses to be measured. While the elemental range is not as broad as the PIXE - PIGME analysis, TEFA does present the advantage of greater instrument availability, and a broader range of elements than reported in the NAA work of Ambrose and Wall.

Leach (1977a; 1977b) applied the TEFA energy dispersive technique to New Zealand obsidians and obtained favourable results, stating, "it is able to produce absolute concentrations for about twenty elements to the precision required in about ten minutes" (1977a:12). Such a system would have negligible running costs and "only about 1 hour instruction is needed for a person of average intelligence to use it effectively" (1977b:18). Certainly a technique's ability in characterizing New Zealand obsidians can be considered a rigorous test of its merit and, if successful, a fair recommendation.

Additionally, Leach (1977a) investigated a second form of energy dispersive XRF which utilized a small radioactive source to produce the secondary fluorescent X-rays in the sample. SEFA (Source Excitation Fluorescence Analysis) or alternatively 'isoprobe' (Hall *et al.* 1973), refers to the use of a radioactive isotope 'probe'. It was applied by Leach to New Zealand obsidians with some surprising results

regarding the characterization of Mayor Island source material.

Employing a small quantity of the radioactive isotope Americium ( $^{241}\text{Am}$ ), elements of the rare earth suite far above the range of conventional TEFA XRF can be detected. It was found that the elements barium, lanthanum and cerium varied markedly between Mayor Island obsidian and all other sources (1977a:13-14). Most similar to Mayor Island obsidian was the source material near Kaeo in Northland, although this too was distinguished.

As Leach noted, a method of quickly identifying Mayor Island obsidian would greatly reduce the subsequent characterization load in New Zealand archaeology, almost regardless of what its further capabilities were. The preponderance of Mayor Island obsidian in archaeological contexts throughout New Zealand prehistory has already been mentioned. Leach also determined that the natural radioactivity of the obsidians north of the Bay of Islands was an order of magnitude greater than for any other New Zealand source. A potential screening technique utilizing a Beta-particle counter to detect this radioactivity was suggested (*ibid.*:14-15). Additional techniques such as thermoluminescence, remnant magnetism and magnetic susceptibility were given cursory evaluation.

It was concluded by Leach that a routine obsidian sourcing facility could be oriented around a two-stage analysis system. This would include a rapid screening process for Mayor Island obsidian (such as SEFA), followed by TEFA application to characterize the remaining material (*ibid.*:16).

Extended work on obsidian characterization by thermoluminescence was carried out by Leach and Fankhauser (1978). Their results indicated that good separation of New Zealand obsidians could be obtained, and 22 petrographic source groups were defined. Obsidian samples are required to be powdered for TL analysis, however, and final sample preparation is an exacting procedure. Additionally, the thermoluminescence technique is not easily applied and requires experienced operation for reliable results to be obtained (Fankhauser, pers. comm., 1983).

Natural radioactivity of New Zealand and Oceanic obsidians was further explored by Leach *et al.* (1978), but only the sources near Kaeo in Northland demonstrated any clearly distinctive values.

Energy dispersive X-ray tube excitation XRF has more recently been applied to New Zealand obsidians by McCallum *et al.* (1979). Success in distinguishing Northland, Mayor Island and Taupo region sources was reported. Characterization work is proceeding (see Moore 1982), but artefact allocation data have yet to be published. Being a microscopically destructive technique with analysis times on the order of five minutes (*ibid.*:4), and reasonably straight-forward application (Wallace 1974), it would seem in these respects to comply with the earlier stated requirements. The availability of this facility for routine sourcing of New Zealand obsidians has not eventuated, although the technique was considered suitable for mass sourcing of artefacts (McCallum *et al.* 1979:1).

Leach and Warren (1981) review the history of characterization studies applied to New Zealand obsidians. They note that of those techniques shown capable of fully distinguishing New Zealand sources (wavelength dispersive XRF, thermoluminescence, neutron activation analysis and PIXE - PIGME), all have serious drawbacks in being either physically destructive, laborious, expensive or unavailable for routine application to archaeological problems (ibid.:152). It is recognised that energy dispersive XRF equipment is generally more available for potential archaeological use, but also that it is less discriminative than the physically destructive wavelength dispersive technique.

In the hope that a simple technique or set of techniques could be found which had the capability of reliably allocating obsidian artefacts, Leach and Warren undertook a program of neutron activation analysis in 1976 (ibid.:155). This work corresponds with Leach's "1st generation" method of determining elements suitable for source characterization (Leach 1977b:4). The study produced data on 23 elements for 33 sources of volcanic glass in New Zealand and greater Oceania (Tables 2 and 3) and demonstrates the difficulties which can arise from a limited range of elemental analysis when wide-ranging geographic sources are considered (see Chapter One).

Acknowledging the restricted availability of NAA facilities to New Zealand archaeologists, yet the need for analysis of extended ranges of elements, Leach and Warren propose the adoption of analytical technique 'sets' with which to characterize obsidian on a broad scale. With the provision that each

TABLE 2: NAA SOURCE AND ELEMENT KEY (AFTER LEACH AND WARREN 1981).

SOURCES	ISOTOPES	UNITS
1 Weta	1 $^{24}\text{Na}$	%
2 Waire	2 $^{46}\text{Sc}$	ppb
3 Pungaere	3 $^{59}\text{Fe}$	%
4 Huruiki	4 $^{60}\text{Co}$	ppb
5 Burgess Island	5 $^{76}\text{As}$	ppm
6 Awana	6 $^{82}\text{Br}$	ppb
7 Te Ahumata	7 $^{86}\text{Rb}$	ppm
8 Cooks Bay	8 $^{95}\text{Zr}$	ppm
9 Purangi	9 $^{124}\text{Sb}$	ppb
10 Hahei	10 $^{131}\text{Ba}$	ppm
11 Tairua	11 $^{134}\text{Cs}$	ppm
12 Maratoto	12 $^{140}\text{La}$	ppm
13 Waihi red	13 $^{141}\text{Ce}$	ppm
14 Waihi black	14 $^{147}\text{Nd}$	ppm
15 Mayor Island green	15 $^{152}\text{Eu}$	ppb
16 Mayor Island honey	16 $^{153}\text{Sm}$	ppm
17 Mayor Island yellow	17 $^{160}\text{Tb}$	ppb
18 Rotorua red	18 $^{175}\text{Yb}$	ppm
19 Rotorua black	19 $^{177}\text{Lu}$	ppb
20 Maraetai red	20 $^{181}\text{Hf}$	ppm
21 Maraetai black	21 $^{182}\text{Ta}$	ppm
22 Ongaroto	22 $^{233}\text{Pa}$ ( $^{232}\text{Th}$ )	ppm
23 Taupo	23 $^{239}\text{Np}$ ( $^{238}\text{U}$ )	ppm
24 Admiralty Islands		
25 Puu Waawaa (Hawaii)		
26 Maunga Orito (Easter Island)		
27 Motu Iti (Easter Island)		
28 Te Mamavai (Easter Island)		
29 Rano Kau (Easter Island)		
30 Pitcairn Island		
31 Otago glass		
32 Canterbury pitchstone		
33 Fanal Island		



TABLE 3: NAA DETERMINED MEAN ELEMENT CONCENTRATIONS (AFTER LEACH AND WARREN 1981).

Sources	ISOTOPE																						
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
1	3.3	2178	0.8	314	23	0	490	151	1286	239	27	16	34	29	0	9	1873	19	1159	6	4	48	12
2	4.5	267	3.2	317	56	0	661	1557	1906	498	46	151	225	132	423	24	5327	49	2734	48	24	100	28
3	4.4	243	3.2	469	13	703	656	1650	2075	491	39	145	213	123	348	26	5057	51	2801	48	25	96	21
4	3.4	4225	1.0	795	13	563	148	122	257	566	10	33	57	31	547	6	1024	8	530	5	1	12	3
5	1.3	7721	1.7	840	11	0	267	336	383	1900	12	47	80	38	1108	12	1289	12	812	12	1	14	3
6	2.7	4218	0.9	833	90	2815	190	158	204	675	9	37	62	34	538	6	1066	6	514	5	1	18	4
7	2.9	4285	0.9	750	6	845	212	122	0	524	11	39	69	34	401	7	1070	8	538	4	1	22	5
8	3.1	5435	1.0	588	5	878	123	106	0	731	4	29	49	25	785	5	778	6	423	4	1	13	3
9	3.7	5594	1.0	687	7	1674	134	122	147	813	4	32	51	26	850	5	782	7	485	4	1	13	3
10	3.1	4514	1.2	624	4	1794	142	161	231	936	6	33	58	28	857	6	873	8	501	4	1	14	2
11	3.0	5560	1.2	1354	11	2790	122	168	280	1032	6	34	40	15	818	4	725	5	380	5	1	11	3
12	3.2	3777	0.6	420	25	1084	185	83	395	947	10	27	44	20	303	4	633	5	370	3	1	16	4
13	3.0	4604	1.4	2536	4	1016	125	128	231	761	7	20	30	13	576	3	462	3	251	3	1	12	3
14	3.3	4564	1.4	2308	8	924	133	36	169	773	7	20	29	20	591	3	329	3	240	3	1	12	3
15	4.2	142	3.6	489	17	6322	143	960	247	54	5	95	163	103	1871	22	3576	21	1608	24	6	17	4
16	4.6	121	3.6	631	0	7915	139	1019	280	39	5	90	162	106	1688	20	3633	20	1588	24	6	16	4
17	4.1	106	3.2	523	0	0	139	975	200	53	4	91	166	107	1465	20	3382	19	1595	23	6	16	4
18	2.7	5576	0.9	804	27	2997	135	104	261	797	5	27	45	22	693	5	702	5	345	3	1	12	3
19	3.0	5660	0.9	1037	19	2933	131	146	235	851	5	28	47	26	763	5	666	5	376	4	1	12	2
20	2.9	3432	0.9	1260	0	5178	143	141	241	859	6	27	45	20	527	0	574	3	338	4	1	14	3
21	2.7	2991	0.8	1082	127	4531	140	141	212	859	6	24	40	17	492	3	506	3	308	3	1	13	3
22	3.1	3386	0.9	1144	40	1461	144	117	245	932	6	27	42	19	536	4	594	5	342	4	1	14	3
23	2.9	4251	0.9	1285	238	4178	124	166	205	683	5	24	38	22	602	4	571	4	323	4	1	11	3
24	3.3	3952	1.3	1439	0	3790	150	312	262	713	2	43	72	23	1030	0	1043	10	581	7	3	11	2
25	6.8	8790	3.3	107	0	1363	133	875	106	282	1	83	115	65	2821	11	1969	15	915	21	10	8	1
26	4.1	471	2.1	112	0	1866	70	800	240	495	1	96	179	101	3847	25	4667	32	1796	23	8	11	2
27	4.1	682	2.1	70	0	1927	61	634	231	459	1	89	155	93	3845	23	4339	29	1616	18	7	8	2
28	4.5	505	2.3	110	0	3042	80	797	256	509	1	105	181	110	4155	27	4991	35	1923	23	9	9	3
29	4.2	256	1.9	50	0	2008	79	743	257	466	1	106	185	109	3459	26	4740	34	1764	22	9	10	3
30	5.2	13601	4.8	1526	0	3378	89	729	344	2038	1	97	136	71	6003	18	2572	13	722	16	8	12	3
31	0.1	41952	0	323	0	0	66	0	0	287	8	28	55	40	1910	7	1698	18	0	2	0	5	8
32	3.1	7119	9.1	15199	0	541	99	714	177	789	1	137	155	120	6013	20	2484	14	0	14	11	15	0
33	2.9	3369	1.0	2174	1	0	205	118	596	378	14	29	49	20	364	0	878	8	475	4	1	20	1

technique adhere to requirements similar to those specified in this thesis (techniques that would allow 'hands-on' operation by archaeologists), a 'stratified' sourcing scheme is suggested (ibid.:162). Primary analyses are assigned to SEFA/TEFA techniques, supplemented by natural radioactivity detection in one stage (ibid.:163).

While development of TEFA XRF has proceeded since the investigation by Leach (1977a; 1977b) in the work of McCallum *et al.* (1979), SEFA has received no further attention within the context of this problem. If a routine obsidian sourcing facility as suggested by Leach and Warren (and specified as essential within the field of source characterization by this thesis) is to be realized, a fundamental requirement would seem to be the refined development of the SEFA technique.

Within this chapter, four main requirements are specified with which to evaluate a prospective analytical technique. SEFA should now be judged by these criteria. While the ability of the technique to discriminate between New Zealand and Oceanic obsidians cannot be fully estimated until after it has been applied, a good idea of the effective range of  $^{241}\text{Am}$  induced XRF can be gained from the published literature.

Figure 1 indicates some appropriate fluorescence applications of  $^{241}\text{Am}$  SEFA (after Anon. 1975:1). As can be seen,  $^{241}\text{Am}$  not only has the ability to excite barium, but additionally, can induce fluorescence in elements as low as iron when the americium by-product Np X-rays are employed. Thus zirconium, strontium, and rubidium appear to be within the analytical

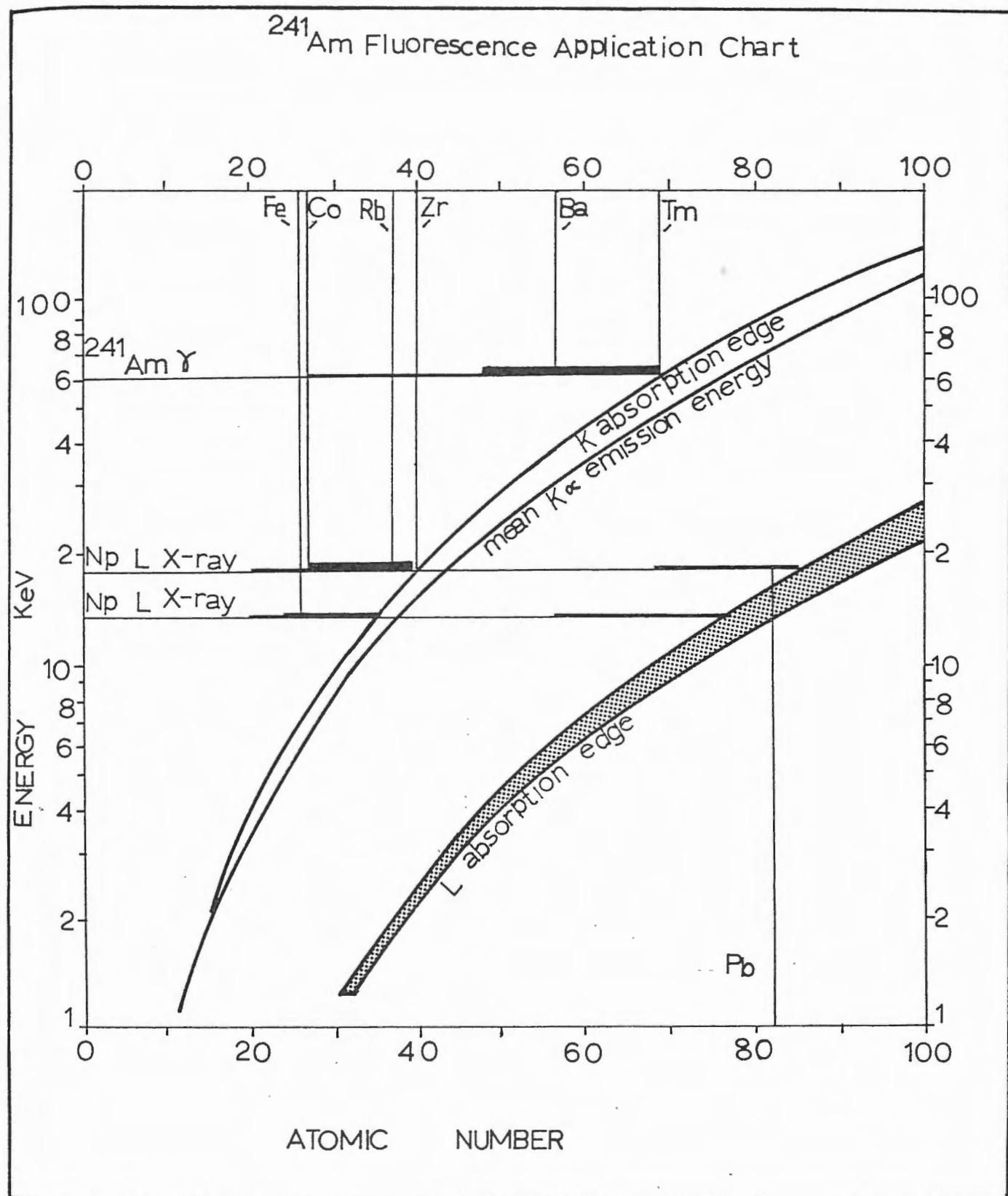


FIGURE 1: Fluorescence efficiency/application chart. Relative thicknesses of horizontal bars indicate most efficient fluorescence regions (after Non. 1975:1).

range of this technique.

Ward's (1972) definitive wavelength dispersive study utilized zirconium, rubidium, and strontium as three of five elements employed to discriminate between the 18 petrographic regions of New Zealand obsidian which were established (1972: 138, 143). Reference to Leach and Warren's NAA data in Table 3 shows that rubidium, zirconium, and barium have good variation throughout New Zealand and Oceanic sources. Of particular note is the difference in barium concentrations reported for Easter Island (Rapanui) obsidians and that from Mayor Island. Indeed, the value of barium in discriminating Mayor Island obsidian from all other examined sources would seem to be very high.

In theory, therefore,  $^{241}\text{Am}$  SEFA appears to have a reasonable potential for obsidian differentiation. Only controlled application within a standard facility will produce the final answer.

Concerning the requirement that the proposed technique be readily applicable by non-technically specialized personnel, SEFA has the potential to exceed even energy dispersive TEFA analysis in simplicity. In the case of SEFA, the radioactive source needs only to be fixed in position relative to sample and detector. Monitoring of beam current or X-ray tube vacuum as noted by Wallace (1974:9-13) is not necessary. Further, while excitation of the sample is greatly simplified, detection of the fluoresced X-rays is no more difficult than in TEFA. Indeed, the same detection equipment is employed.

As with TEFA, isoprobe fluorescence is only microscopically

destructive. Nelson *et al.* (1975) limited sample preparation for their TEFA analysis to "a thorough scrubbing in distilled water with a stiff brush" (1975:89). Similarly, McCallum *et al.* (1979) performed no special cleaning before analysis, though care was taken not to irradiate any labels or accession numbers written on the specimen (1979:4).

Speed of analysis is one other parameter which is hard to estimate prior to the actual application of the technique. Leach and Warren mention that source excitation can take some time (due to low count rates), but that the differences in concentrations of some elements (for instance barium) are large enough that "qualitative assessment can be made within a few minutes" (1981:164). Higashimura *et al.* (1981), employing two radioactive sources ( $^{109}\text{Cd}$  and  $^{55}\text{Fe}$ ) for SEFA characterization of sanukite implements in western Japan, reported that they are able to analyse 24 samples within a full day (1981:123). While this rate would only produce about 720 artefact characterizations per month, this figure alone equals the published total of artefacts which have been allocated in New Zealand to date. Thus, SEFA would appear to be sufficiently rapid.

It has been shown here that the technique of radioactive source excitation fluorescence analysis fulfills most of the main criteria established within this thesis. Judging from published literature, SEFA should produce sufficient information on New Zealand and Oceanic obsidians to allow reasonable discrimination to the source-region level.

Once developed, a functional system employing SEFA analysis

could be easily amalgamated with TEFA instrumentation as required. Such a 'dual-source' arrangement has been employed by Hall *et al.* (1973), and demonstrates the complementary nature of these techniques. Additionally, alternative radioactive source isotopes may also be employed.

In summary, it is argued that development of a SEFA facility is a necessary objective for the characterization of New Zealand and Oceanic obsidian artefacts; both on a routine basis and as a technique capable of being applied by archaeologists.

Chapter Three will explore the more technical details of establishing a SEFA facility. The remainder of the thesis will be concerned with the development, application, and evaluation of this technique for obsidian analysis in light of the four criteria discussed above (pp.25 - 34).

## CHAPTER THREE

## DEVELOPMENT OF ANALYSIS FACILITY

## PRINCIPLES OF X-RAY FLUORESCENCE ANALYSIS

Texts which discuss the principles and applications of XRF are numerous and vary a good deal in their level of presentation. Those essentially for the layperson, such as Reeves and Brooks (1978) or Goffer (1980), provide only the most cursory introduction to the technique. Advanced texts, such as by Dyson (1973) and Bertin (1975), provide comprehensive theory, but may be inaccessible to the social scientist. The description of XRF fundamentals presented here follows that of Woldseth (1973) which is a well rounded exposition of the energy dispersive method of analysis.

The basis of X-ray fluorescence as a technique for elemental analysis is an interaction with the inner electrons of atoms. In considering the atomic configuration, it will be sufficient for the purposes of this chapter to present the atom as a spherical shell structure (the Bohr model).

Negatively charged electrons may be thought of as bound to the positively charged nucleus by an electrostatic force in a series of discrete orbits or shells. In an electromagnetically stable atom, the number of electrons and protons are equal. The energy associated with a given shell is related to the charge of the nucleus. The shells are numbered from the inner shells outwards according to the principle quantum number  $n$ . These are designated by letter with the innermost K shell ( $n=1$ ) followed by the L ( $n=2$ ), M ( $n=3$ ), N ( $n=4$ ) shells

and so on. Each shell may hold a maximum number of electrons equal to  $2n^2$ .

Shells are characterized by a specific binding energy for the electrons which they contain. The binding energy is the minimum energy required for an irradiating photon or particle to free an electron from its orbit. The strength with which an electron is held within its normal orbit is related to the number of protons in the nucleus (the atomic number  $Z$  of the element); therefore, specific elements will have particular binding energies associated with each shell. This energy increases with the  $Z$  of the element.

Shortly after an electron is removed from its orbit by an interaction with a photon or particle of sufficient energy, fluorescence is produced. The fluorescence represents the movement of an electron from an outer to inner orbit. Atomic electrons are replaced on the order of  $10^{-12}$ - $10^{-14}$  seconds after excitation occurs (Bertin 1975:21). With this transition there is an effective loss of energy to the atomic system, and it is characterized by the emission of a photon from the atom. This photon has the energy equivalent to the difference in binding energy between the two shells involved. While certain 'radiationless transitions' (Dyson 1973:78) may also take place, they are not significant events within the confines of this discussion.

The emitted photon is labelled according to the shell from which the initial vacancy was created, as well as the shell from which the vacancy was filled. Thus, detection of a K-alpha ( $K_{\alpha}$ ) photon indicates the removal of a K shell



electron, and replacement by an L shell counterpart. Some further inner shell transitions are indicated in Figure 2. The proportionate line thicknesses indicate the relative frequencies of the transitions.

Generally, where the  $K_{\alpha}$  transition intensity is assumed to be equal to 100, K-beta ( $K_{\beta}$ ) transitions will achieve only a small proportion (1-30%) of the  $K_{\alpha}$  series (Woldseth 1973: Appendix D; Dyson 1973:83). Major transition/fluorescence energies for the elements considered in this study are shown in Table 4.

By definition, photons emitted from inner shell transitions are X-rays (gamma rays are only emitted from nuclear reactions, while outer electron transitions produce photons in the ultraviolet and visible range of the electromagnetic spectrum). XRF is concerned with the detection of inner electron events. As XRF analysis interacts only with the atomic electrons, the nucleus remains unaltered by the process.

X-ray fluorescence analysis, therefore, involves the irradiation of a sample with photons of sufficient energy (either X-rays or gamma-rays) to cause the removal of inner electrons from elements in the range of interest. By determining the energies of the detected fluorescence peaks, elemental identifications are made.

An additional effect which must be considered in XRF analysis, especially when radioisotope excitation is employed, is the scattering of the primary radiation within the sample and subsequent detection as part of the analytical spectrum. The phenomenon has two main components known as Rayleigh

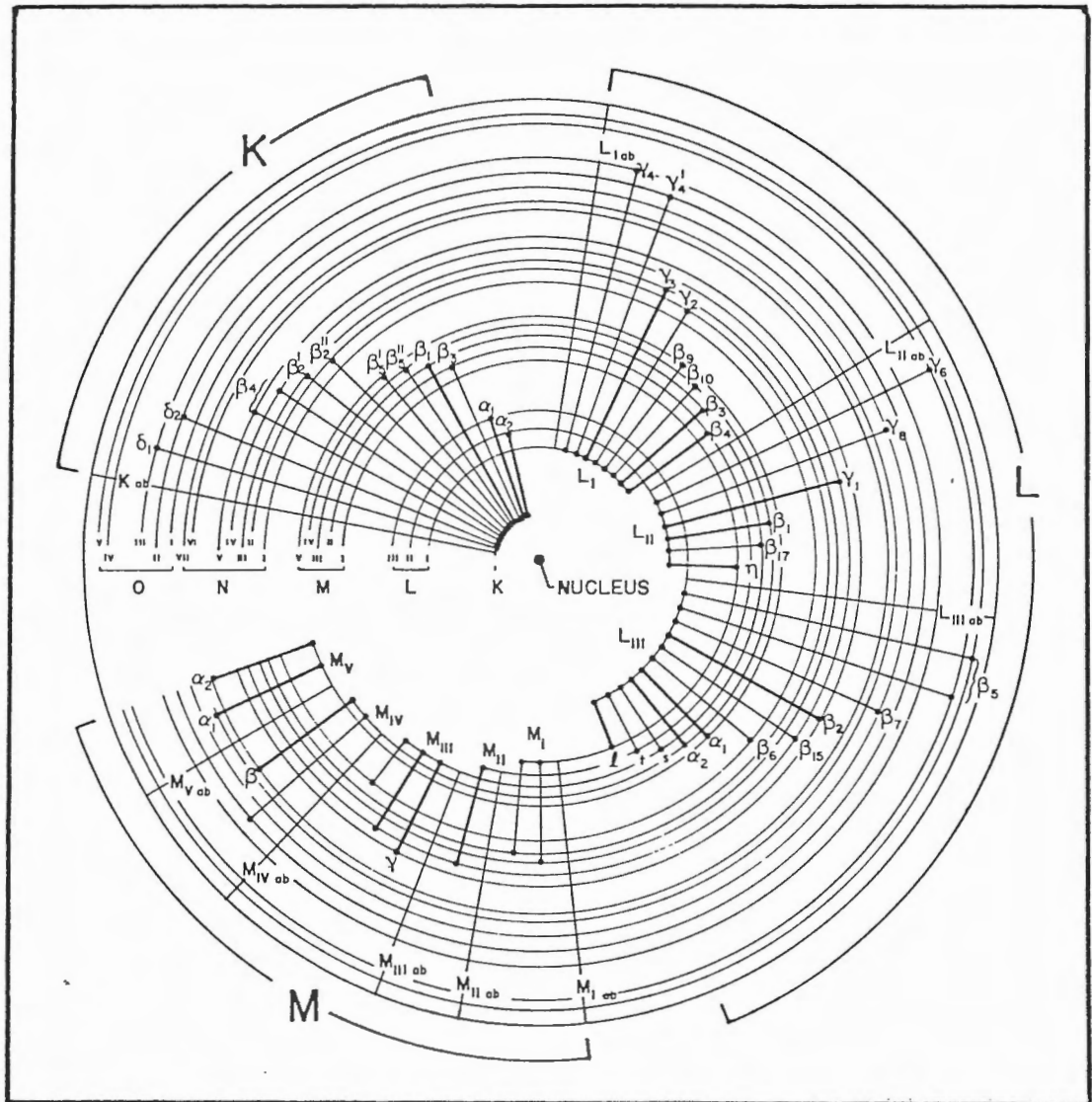


FIGURE 2: Atomic model, showing some transitions that may follow electron vacancies. Transitions are labelled with conventional notation for associated emission lines (after Woldseth 1973).

TABLE 4: ASSOCIATED K SERIES TRANSITION ENERGIES (in KeV)  
 FOR SPECIFIC ELEMENTS CONSIDERED IN THIS STUDY  
 (AFTER WOLDSETH 1973:APPENDIX D).

Element	Symbol	$K_{\alpha 1}$	$K_{\alpha 2}$	$K_{\beta 1}$	$K_{\beta 2}$
Iron	Fe	6.403	6.390	7.057	-
Rubidium	Rb	13.393	13.333	14.959	15.183
Strontium	Sr	14.163	14.095	15.833	16.082
Yttrium	Y	14.956	14.880	16.735	17.013
Zirconium	Zr	15.772	15.688	17.665	17.967
Barium	Ba	32.188	31.812	36.372	37.251
Lanthanum	La	33.436	33.028	37.795	38.723
Cerium	Ce	34.714	34.273	39.251	40.226

(elastic or coherent) and Compton (inelastic or incoherent) scatter.

Rayleigh scatter can be conceived as the perfectly elastic scatter of the excitation radiation within the sample. Thus, it is detected in the fluorescence sample spectrum at exactly the same energy as it was emitted from the source. Compton scatter, on the other hand, represents the less-than-perfectly elastic rebounding of the primary photon within the sample, and is emitted at lower energy.

The probability of inelastic as opposed to elastic scatter is proportional to the average atomic number of the sample (Woldseth 1973:1.14). The Compton/Rayleigh ratio can therefore provide valuable diagnostic information on material composition (see for example, Kunzendorf 1972; Cesareo 1981; Cesareo *et al.* 1982). The probability for Compton scatter is also dependent upon the angle of the primary radiation relative to the sample and detector, with a characteristic minimum between  $90 - 100^{\circ}$  (Woldseth 1973:1.16). Mean scatter angle determines the amount of energy loss detected. The absolute energy loss increases with the scatter angle as well as with the energy of the primary photon. The maximum energy shift occurs at  $180^{\circ}$  (backscatter) (*ibid.*:1.15).

The implication for XRF analysis is that the analyst must be fully aware of the emission characteristics of the excitation source being employed. Particular attention must be given to Compton or Rayleigh peaks which may interfere with elements of analytical interest (see *ibid.*:2.45). The parameters of these effects must therefore be identified in the development

of the SEFA programme.

At this point it should be noted that some workers refer to the form of analysis employed in this study as 'non-dispersive' XRF (for example, Rhodes 1966; Cesareo *et al.* 1972; Hall *et al.* 1973; McKerrell 1974; Higashimura and Warashina 1975). Some confusion may arise for the layperson due to the use of two terms to describe this technique. Both 'energy dispersive' and 'non-dispersive' are applied to the same form of analysis, and refer to the ability of the semi-conductor Si(Li) detector to discriminate between different energies in the fluorescent radiation.

Bertin (1975:162) makes a clear distinction between these two methods, however, and maintains that the term non-dispersive should only be applied where the spectral lines are not separated on the basis of either wavelength or energy. Potential discrimination, monochromatic excitation, differential excitation, selective filtration and gas discrimination detection techniques are cited as truly non-dispersive methods.

The technique applied in this study is energy dispersive. While the Si(Li) detector receives the undispersed fluorescent radiation comprising all excited lines of specimen elements, the detector output is subjected to pulse-height selection. Resulting pulse distributions arising from several detected wavelengths are separated on the basis of their average pulse heights, i.e., on the basis on the photon energies of the corresponding incident X-ray lines (Bertin 1975:356-357).

## RADIOISOTOPE SOURCE INDUCED XRF

Excitation of characteristic X-rays utilizing radioactive isotope sources has been employed for nearly fifty years (Rhodes 1966:683). Experiments involving the analysis of metals and rare-earth oxides using  $^{241}\text{Am}$  in conjunction with a lithium drifted silicon or Si(Li) detector, were performed by Bowman *et al.* (1966). Even at that time, the potential for "the routine analysis of samples" was recognized (1966:568).

Archaeological/historical applications of SEFA were proposed by Frierman *et al.* (1968), McKerrell and Stevenson (1972) and Cesareo *et al.* (1972). These developments were primarily due to the refinements in instrumentation, particularly Si(Li) detectors (referred to as 'Sillies'), and fast pulse processing electronics, notably ADC (analogue to digital converters) and super linear amplifier systems. This capacity for physically non-destructive multi-element analysis had some of its first social science applications in the examination of ancient coinage and paintings (McKerrell and Stevenson 1972; Cesareo *et al.* 1972).

Hall *et al.* (1973) employed a dual-source system for the analysis of ancient Chinese ceramics. A miniature X-ray tube was used in conjunction with the  $^{241}\text{Am}$  source to expand the total range of elemental analysis. The distinct advantage of using  $^{241}\text{Am}$  to excite the K series lines from elements above copper in the periodic table was noted (Hall *et al.* 1973:74).

McKerrell (1974), employing radioisotope excitation, emphasized the physically non-destructive nature of the technique stating that it "would be no exaggeration to say that

this technique seems potentially one of the most generally useful analytical methods yet applied to museum objects" (1974:3). Specimens studied included Anatolian bronzes, British and Cypriot faience and North British bronze age metallurgy. Thus, both technological development (in metallurgy) and prehistoric trade and commerce (in faience) were explored with the technique (*ibid.*:10-11). Debasement of currency in Anglo Saxon and Early Mediaeval silver was also traced, and authenticity evaluations of ancient coinage and Egyptian relics were made (*ibid.*:12-15). The extreme versatility of the energy dispersive analysis is well demonstrated by this work.

The application of SEFA to source characterization of stone implements was developed by Higashimura and Warashina (1975), Warashina *et al.* (1978) and Higashimura *et al.* (1981). Japanese sanukite (a hypersthene andesite) was characterized using  $^{55}\text{Fe}$  and  $^{109}\text{Cd}$  radioisotope excitation sources. Peak ratios for K/Ca, Ti/Ca, Rb/Sr, Y/Sr and Zr/Sr were measured and eight Western Japan sources identified. Automatic sample changing and data collection allowed up to twenty-four samples to be analysed within a full day (Higashimura *et al.* 1981).

The use of peak ratios partly overcomes difficulties with variation of fluorescence due to surface texture variation. Similar procedures for the analysis of obsidian artefacts by tube excitation XRF have been applied by Nelson *et al.* (1975) and McCallum *et al.* (1979). In addition to problems with surface texture, it was shown by Hall *et al.* that the sample-to-detector distance is equally important for quantitative

analysis (1973:76). Again, peak ratio measurements partly obviate these problems (*ibid.*: Figure 12). While absolute quantitative results are problematical to obtain with energy dispersive XRF in its crude form, it is argued that source characterization studies do not strictly require this level of data treatment (see Nelson *et al.* 1975; Higashimura and Warashina 1975; McCallum *et al.* 1979).

In summary, applications of radioisotope excitation have been widely utilized in the study of archaeological and historical objects. The potential for routine analyses has been successfully incorporated within automated facilities. The problems in obtaining absolute quantitative measures in both SEFA and TEFA were shown to offer no hinderance in source characterization research.

An additional asset of the technique frequently noted in the literature is the potential portability of analysis systems which employ radioisotope excitation (for example, Bowey *et al.* 1964; Frierman *et al.* 1968; Cesareo *et al.* 1972; 1976; McKerrell 1974). Leach (1977a) presented the point of view that a laboratory system developed with this technique might be easily modified to an 'on site' facility for use in the field (1977a:14).

The long-lived radioisotope  $^{241}\text{Am}$  (half-life 458 years) has been a particularly popular excitation source. One of the advantages of this source is its ability to fluoresce intermediate to high Z elements. While Rb, Sr, Y and Zr are within the capabilities of most X-ray tube energy dispersive systems, americium allows the  $K_{\alpha}$  fluorescence of additional



elements up to lanthanum and cerium, with a theoretical capability up to thulium,  $Z=69$  (as demonstrated by Fig. 1). A system employing this radioisotope was developed for the programme of obsidian characterization in this thesis.

#### $^{241}\text{Am}$ EXCITATION SOURCE PARAMETERS

The radioisotope used in this research is a 50 mCi americium-oxide source ceramic with an active diameter of 6.4 mm. This gives a standard activity of  $155.4 \text{ mCi/cm}^2$  (Anon. 1975:2).

$^{241}\text{Am}$  decays by alpha emission. When a nucleus has a neutron/proton ratio too low for stability, one of the ways in which it decreases the excess number of protons is by alpha decay. This consists of the expulsion of a  $\text{He}^{2+}$  nucleus from the parent at high energy (Adams and Gasparini 1970:4). The total decay sequence for  $^{241}\text{Am}$  is very complex, involving many daughter transitions (see Lederer *et al.* 1967:430). For the purposes of XRF, however, only a few of the dominant decay emissions are of interest.

Table 5 lists the major decay emissions of  $^{241}\text{Am}$ . Of primary interest is the 59.57 KeV gamma which represents 36% of the emission yield per disintegration. It is this radiation which makes americium suitable for mid to high Z-alpha fluorescence.

Figure 3 shows a spectrum from  $^{241}\text{Am}$  source radiation when presented directly to the Otago laboratory detector. Appropriate peaks are labelled. In some  $^{241}\text{Am}$  sources, the Np L series X-rays are filtered out within the radioisotope

TABLE 5: PRINCIPLE UNSHIELDED  $^{241}\text{Am}$  RADIATIONS (AFTER  
LEDERER *ET AL.* 1967:146).

Energy (KeV)	Source	% Yield
59.57	$^{241}\text{Am}$ gamma	36
33.21	$^{241}\text{Am}$ gamma	1
26.4	$^{241}\text{Am}$ gamma	3
20.8	Np $L_\gamma$ X-ray	5
17.8	Np $L_\beta$ X-ray	18
13.9	Np $L_\alpha$ X-ray	14

N.B.:  $^{241}\text{Am}$  alpha-decay particles at 5.63 KeV are filtered. Their contribution to the radiation output has been ignored.

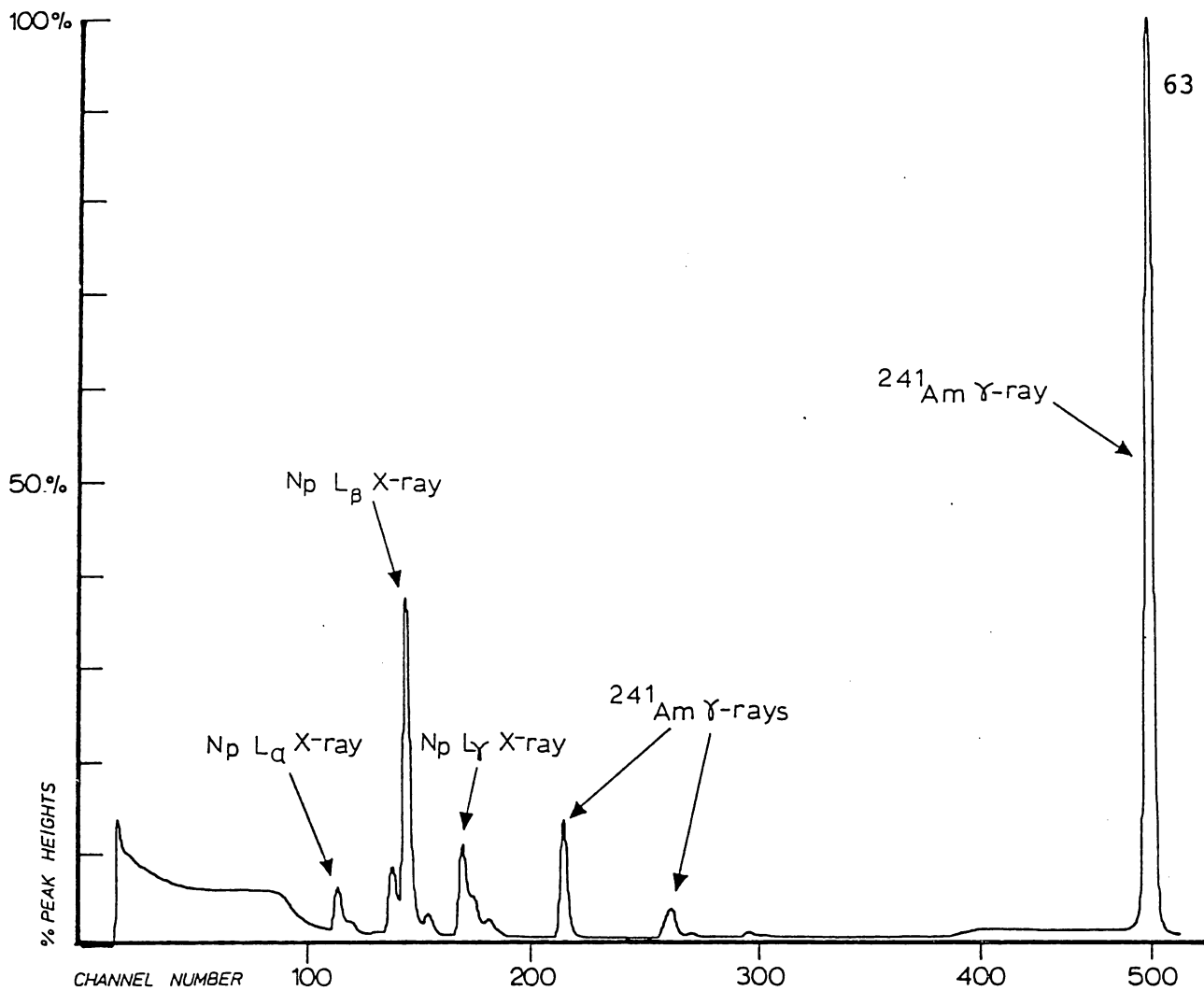


FIGURE 3: Proportionate  $^{241}\text{Am}$  emissions from isoprobe source when presented directly to Si(Li) detector. Compare with associated energies in Table 5. Full horizontal scale = 512 channels. Detection range is approximately 4-60KeV.

source capsule (Woldseth 1973:2.41; Anon. 1977:39). By utilizing these radiations, the fluorescence responses of the lower Z elements of interest in this study (Fe, Rb, Sr, Y and Zr) are enhanced to some degree.

#### CONTAINMENT AND COLLIMATION OF THE RADIOISOTOPE

The americium source is housed within a lead collimation/container arrangement (Plate 1). A cross-section diagram of the container body and source is shown in Figure 4. The interchangeable collimation inserts are made from aluminium alloy and capped with 4 mm of lead shielding. The lead is necessary to prevent the transmission of uncollimated 59.57 KeV gamma radiation which would otherwise pass through the straight aluminium insert. A 1 mm perspex alpha particle filter is mounted outermost, and also serves to protect the softer lead shielding. The collimators produce beams of 4 mm and 2 mm diameters respectively at point of exit. Initial experiments showed that these were likely to give satisfactory target area/fluorescence count rates within the system design. Beam target area is, of course, a function of the sample distance from the source/collimation assembly. Figure 5 shows the sample beam target areas achieved with the two collimators and the polished standard sample count rate associated with each.

The radioisotope apparatus is entirely portable, self-contained, and easily adaptable to a variety of experimental requirements. An automatic sample changing facility was designed to incorporate this radioisotope excitation source.



PLATE 1:  $^{241}\text{Am}$  source container and collimation assembly. The 4 mm collimator is in place and the 2 mm collimator is visible at left.

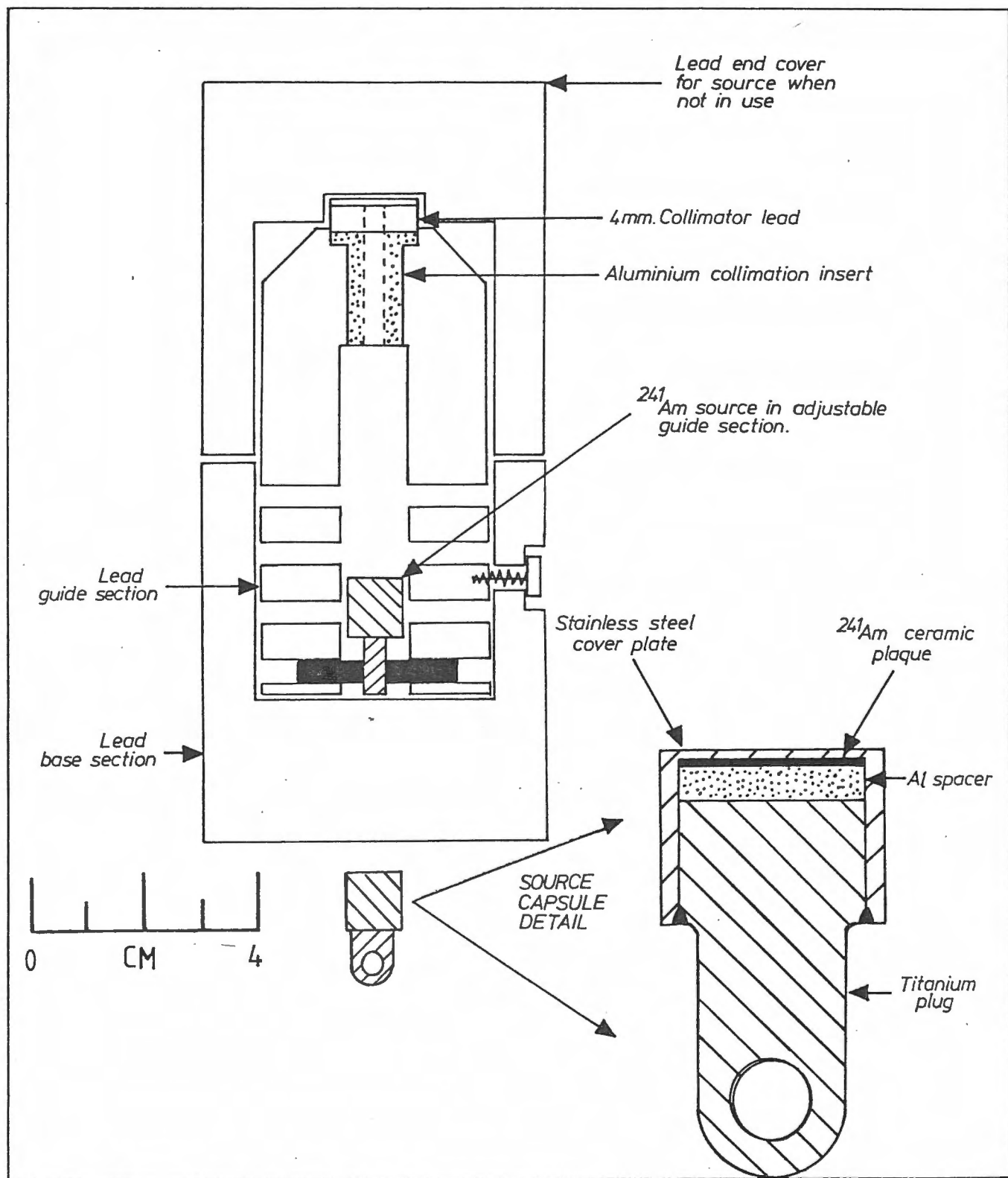


FIGURE 4: Cross-section diagram of  $^{241}\text{Am}$  source and source container. Compare with Plate 1.

## COLLIMATION PARAMETERS




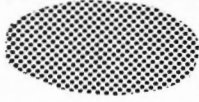
2mm	4mm
EXIT BEAM 	EXIT BEAM 
TARGET AREA  23mm <sup>2</sup>	TARGET AREA  72mm <sup>2</sup>
COUNT RATE 3.5 cts/sec	COUNT RATE 13.0 cts/sec

FIGURE 5: Fluorescence target areas and count rates associated with 2 mm and 4 mm collimators.

## SEFA ANALYSIS APPARATUS

The analysis equipment constructed for the SEFA project was developed specifically for the purpose of handling large numbers of source and artefact samples under controlled conditions. To minimize unnecessary fluorescence variations, its design centred around the desire to strictly control the position of each sample relative to the irradiating source and the detector, while being flexible enough to accommodate samples of irregular shape and size. Also, the apparatus was designed to be amenable to either computerized or manual operation to allow for both overnight and 'spot placement' runs.

Another consideration during the planning of this facility was that it should have the potential to incorporate the use of an X-ray tube excitation source (see Hall *et al.* 1973). While the present research is concerned with the development of the SEFA technique, allowance was made for the implementation of a TEFA unit.

As a starting point, the ideal configuration for sample irradiation and fluorescence detection was determined. From this calculation came the design for the dual-source/detector block.

The core of the system is a machined, high purity, cast aluminium block. This block houses both the americium radioisotope and the X-ray tube excitation sources (Plate 2). As mentioned, a proto-type form of the dual-source arrangement was developed by Hall *et al.* (1973), but was only used for single sample alignment. It was not associated with a sample



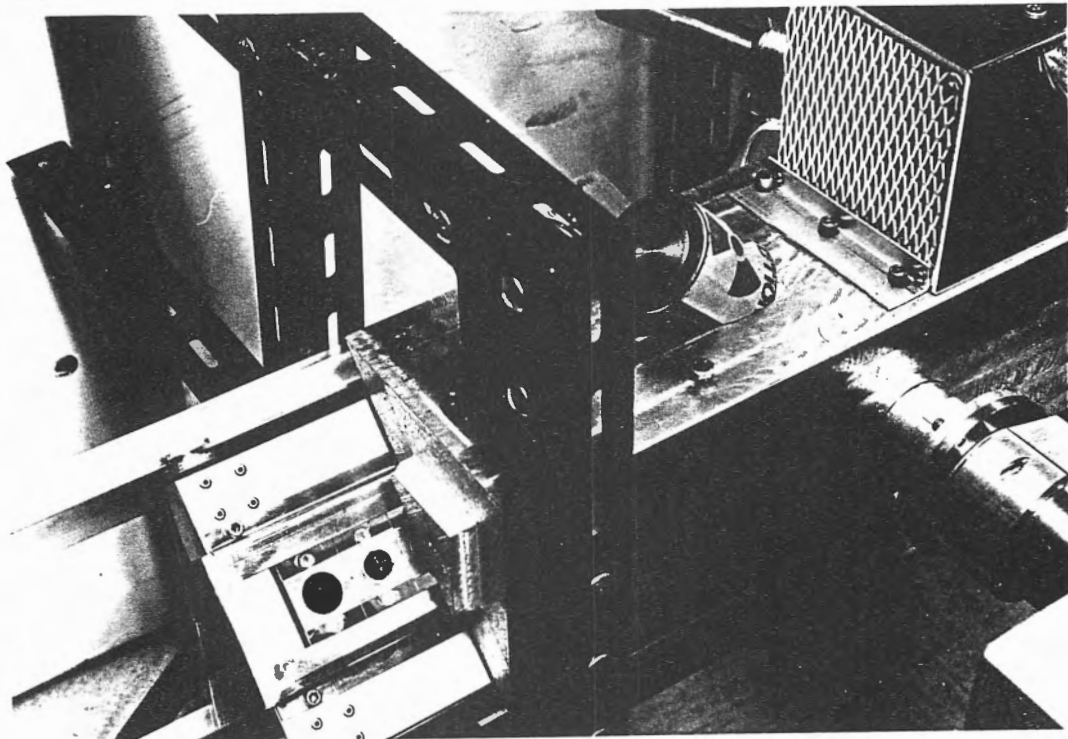


PLATE 2: Aluminium dual-source detector block.  $^{241}\text{Am}$  source is positioned in socket and X-ray tube housing is visible at upper right. Si(Li) detector exits from block at lower right. Portion of sled which has passed analysis region is visible at left.

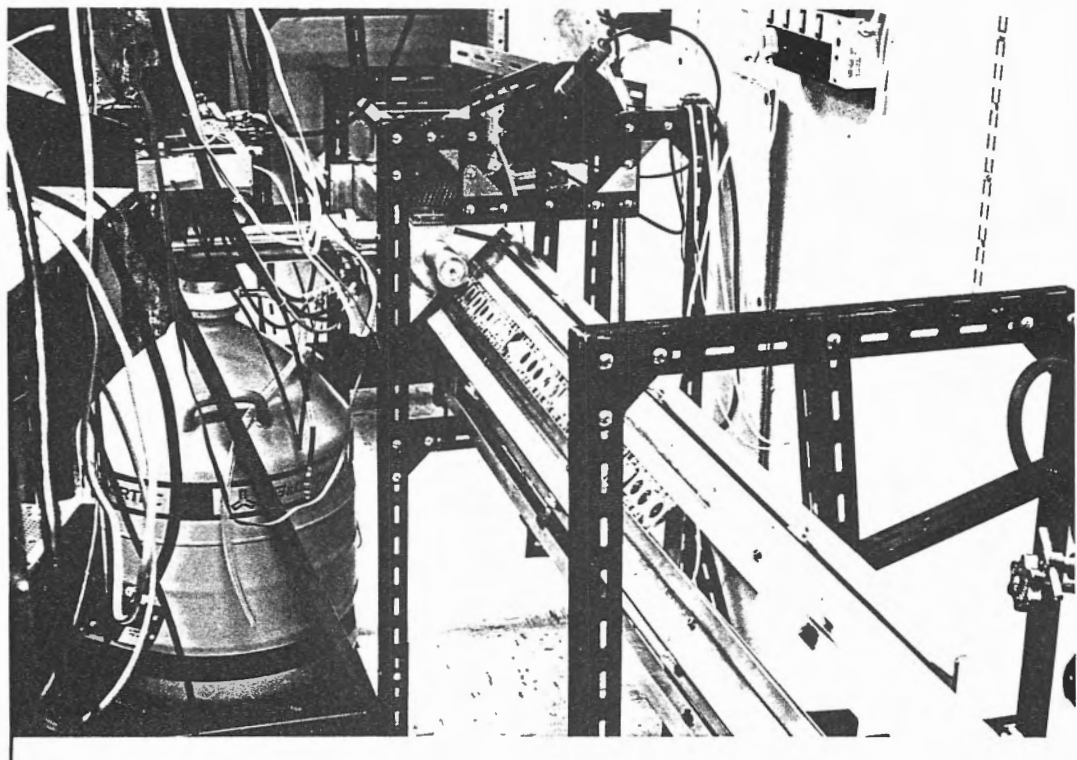


PLATE 2a: Automatic sample changer assembly. X-ray tube is at top centre. Si(Li) detector liquid nitrogen dewar is at left.

changing system.

As seen in Plate 2, the  $^{241}\text{Am}$  container fits into a corresponding socket milled into the top surface of the aluminium block. The X-ray tube is mounted across from the radioisotope assembly.

The  $^{241}\text{Am}$  is easily removable from the block to facilitate safe storage when not in use, or when TEFA is in progress. The system is therefore adaptable to other radioactive sources in similar containers (for example  $^{109}\text{Cd}$ ) and so is ready to meet changing analysis requirements as they occur in the future. The intersection of the source-to-detector angles is at the same sample position for both excitation sources, though the solid angle employed by each is slightly different ( $90^\circ$  for  $^{241}\text{Am}$  and  $100^\circ$  for the X-ray tube). These angles are optimal in minimizing inelastic or Compton scatter into the detector with the best fluorescence yield (Woldseth 1973: 1.16; Bertin 1975:70). The automatic sample changing system was designed to incorporate the characteristics of this analysis unit.

#### THE SAMPLE CHANGING APPARATUS .

Based loosely on the Lucas Heights PIGME - PIXE sample changing system, the Otago facility utilizes a rack or sled onto which individual samples are placed. Samples are sequentially brought into the detector/irradiation position by advancement of the sled. Movement of the sled is achieved via the controlled rotation (switched either manually or by computer) of a threaded shaft. A closely fitted sleeve

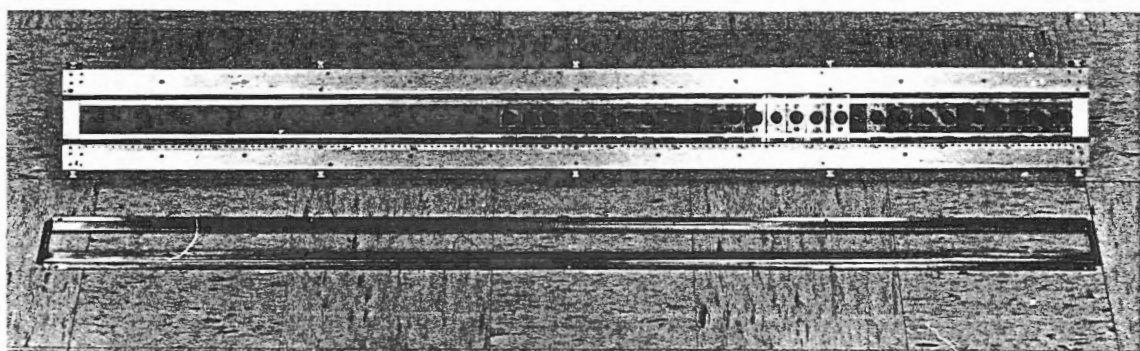
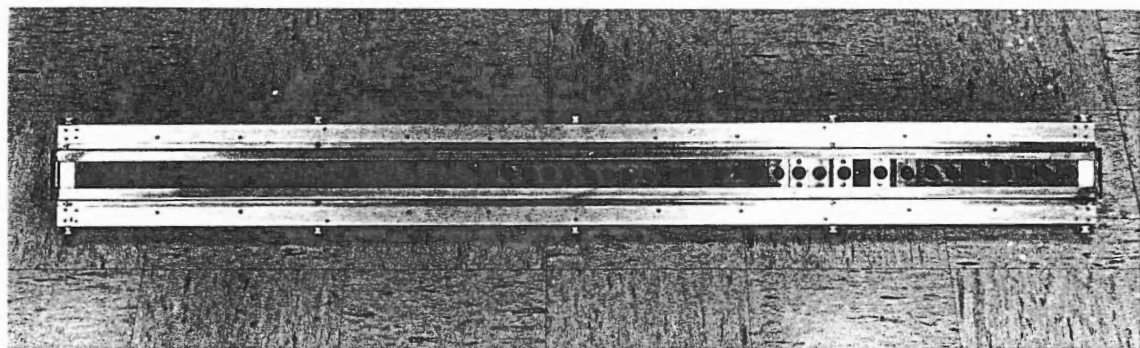
travels along the length of the shaft, and the attached sled moves accordingly (see Plate 2a).

The shaft has been turned at sixteen threads to the inch, or approximately 1.59 mm traverse per single rotation of the shaft. It is connected to a 'slow sync motor' which can be controlled to within 1/16 of a rotation. This gives a controlled horizontal movement of the sled to within 0.02 mm. After an automatic full length run of the 1500 mm sled, comprising some 50 separate movements or computer-commands, the cumulative error is within 1 mm. Manual operation achieves equal precision.

The sled is connected to the drive mechanism by four hex-key bolts and is easily removed for positioning of samples. Once detached from the drive mechanism, the sled's stainless steel cover plate is clearly visible (Plate 3a). The cover plate has the dual function of securing the individual sample holders as well as providing a positive contact surface to roller bearings which are recessed into the face of the detector block. The positive contact serves to control the sample-to-detector distance without restricting the horizontal movement of the sled. A cross-sectional diagram of the sample changer/block arrangement is shown in Figure 6.

Once the cover plate is removed from the detached sled, the exposed sample holders can be freely exchanged with others awaiting analysis (Plate 3b).

When deciding upon the basic sample holder design to be used in the obsidian analysis programme, it was necessary to adopt a standard size that would accommodate the 'average



PLATES 3a and 3b: Multiple sample sled with 26 holders in position. Coverplate in place (a) and removed (b).

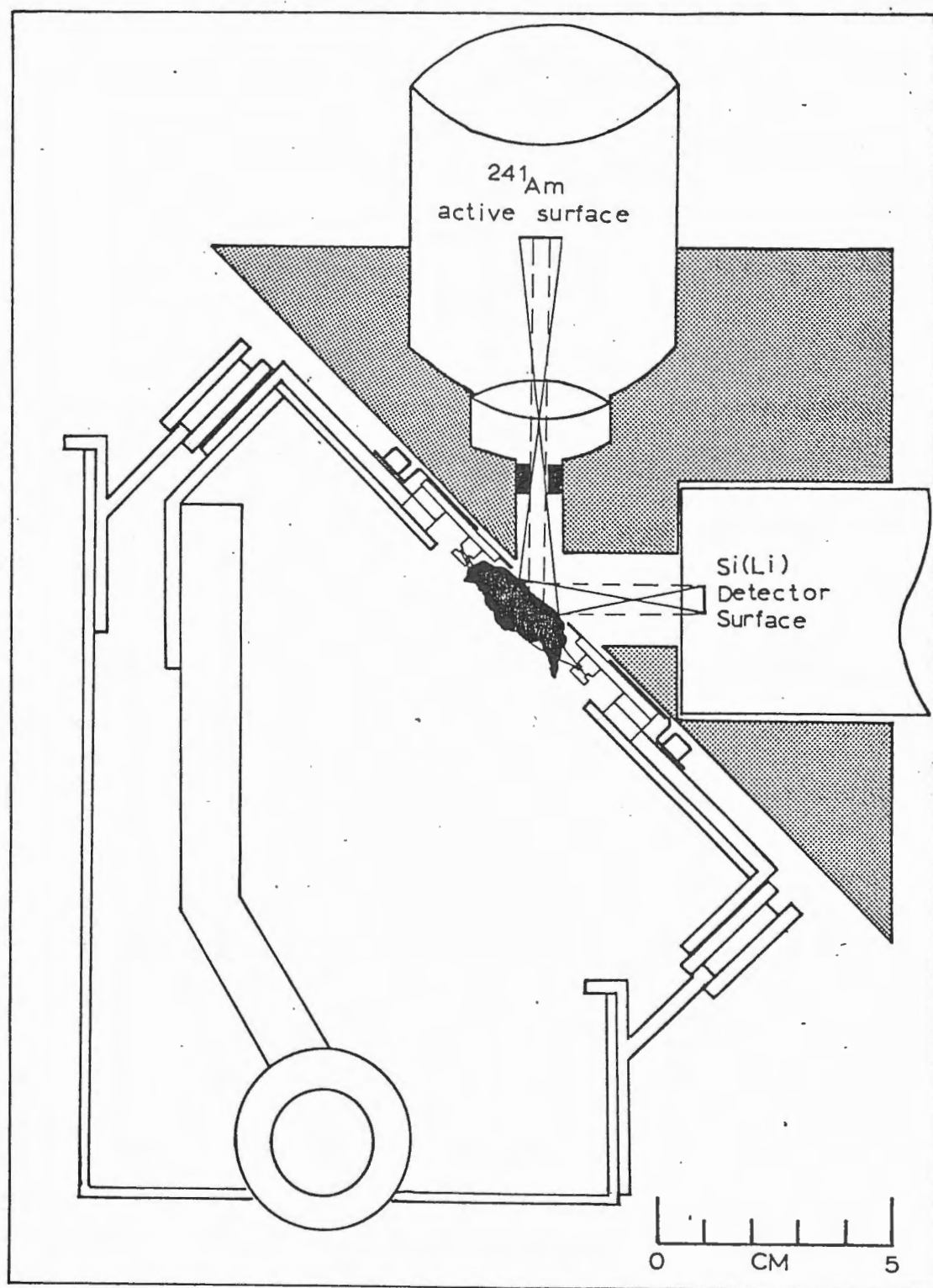


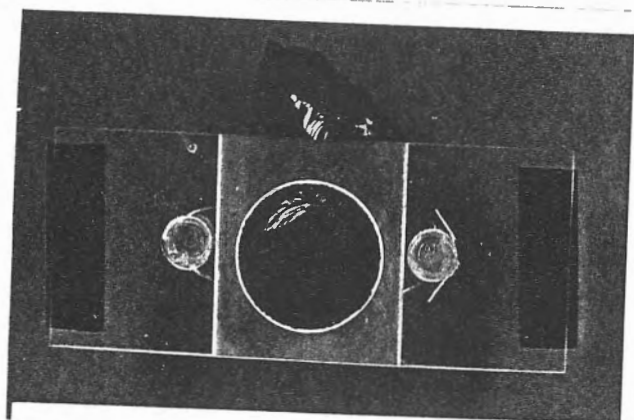
FIGURE 6: Cross-section diagram of sample changer/analysis block arrangement. Mean source to sample distance = 106 mm. Mean sample to detector distance = 35 mm.

obsidian flake' as might be encountered in an archaeological context. Archaeologists will quickly realize that there is a broad range of potential flake sizes possible. It was hoped nonetheless that a general purpose holder could be developed to contain the various types.

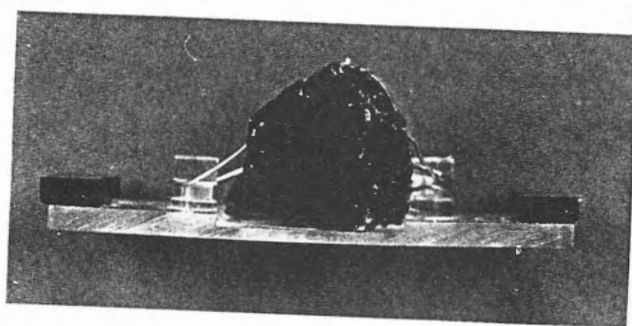
In an attempt to determine the optimal sample holder dimensions, several assemblages under analysis by A. Seelenfreund of the Otago Anthropology Department were observed. It was decided that a general exposure area of approximately 15 - 20 mm diameter would be sufficient to handle most pieces. Considerable latitude was provided so that small flakes as well as large core fragments could be mounted on the same holder. The type developed is shown with a mounted flake in Plates 4a, 4b and 4c.

Of some concern during the development of the sample holder was the material from which it was to be made. Due to the source activity being employed and the form of collimation being used, it was felt that there was some chance of the holder occasionally being irradiated by the primary beam. For this reason, it was important to choose a material of low yield for the elements potentially of interest.

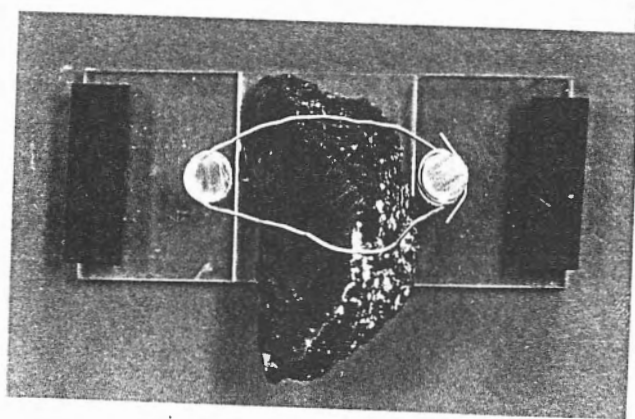
With X-ray tube analysis anticipated in the system, elements between potassium and cerium might potentially be examined. The construction materials left for consideration in this context were therefore quite limited. For example, the remaining metals above or below this elemental range are either too soft to be practicable, or not readily available in the purities required. Synthetic materials were therefore considered



4a



4b



4c

PLATES 4a, 4b, and 4c: Perspex sample holder design. Magnetic strips are visible at each end of holder. Fuse wire wrapped between posts secures flake. Actual size.

as a possible solution.

It was decided to examine a wide range of commercially available plastics including PVC, ABS (acrylonitrile/buradiene/styrene), polycarbonate, polypropylene and a selection of three brands of perspex (cast acrylic). To establish the presence/absence of low Z elements, TEFA was performed by Gavin Wallace of the DSIR Institute of Nuclear Sciences, Lower Hutt.

Not surprisingly, all of the coloured plastics showed considerable quantities of titanium and zinc (their oxide components are used in white pigments). The clear PVC and polycarbonate samples contained chlorine and bromine respectively, in significant amounts. The three perspex samples, however, showed no appreciable elements within the entire range of TEFA, nor did they reveal any potential interferents under subsequent isoprobe examination.

Perspex has the added advantage of being readily available commercially. It is also easily worked with regular power tools. The material used is brand named 'Clarex' and is manufactured by Nitto Jushi Kogyo Co. Ltd, Japan. Several hundred standard holders were produced within a few days' time and a jig-system devised for efficient production line manufacture.

Attachment of samples to their holder is a simple operation. It involves the use of common 20 amp fuse wire wrapped between two posts fixed on either side of the analysis region (see Plates 4b and 4c). Neither the attachment wire nor the glued posts enter the irradiation area, thus there is no



peripheral contamination of analysis spectra. The solvent glue used to fix the acrylic posts was also examined and showed no significant interference peaks.

Once the sample is attached, the holder unit can be freely positioned on the sled. Movement of the individual holders before mounting of the cover plate is prevented by short lengths of plastic magnetic strip fixed to each end of the holder. The unit is held to the sled by corresponding magnetic strips which run the sled's entire length. The magnet to magnet contact is quite secure, and allows the sled to be moved during the placement of the samples without any shifting of the holders occurring. Again, the magnetic stripping is situated well clear of the irradiation and analysis region.

The specific location of each sample on the sled is determined by reading off the horizontal distance of the particular holder centre from a scale mounted alongside the sled's magnetic strip (Plate 5). This position is recorded during the placement of the holder unit and is later keyed into a computer reference file for the automatic sample changing run. The sled can be advanced in non-iterative units to suit any irregular positioning of samples. As noted, the sled may be manually switched and samples moved into the analysis region by reference to an external scale. The sled is returned to its starting point solely from the manual control station.

Single samples can be positioned for analysis simply by withdrawing the sled and inserting a small perspex mount (Plate 6). The sample is visually sighted down the gamma ray beam pathway before emplacement of the collimated isoprobe

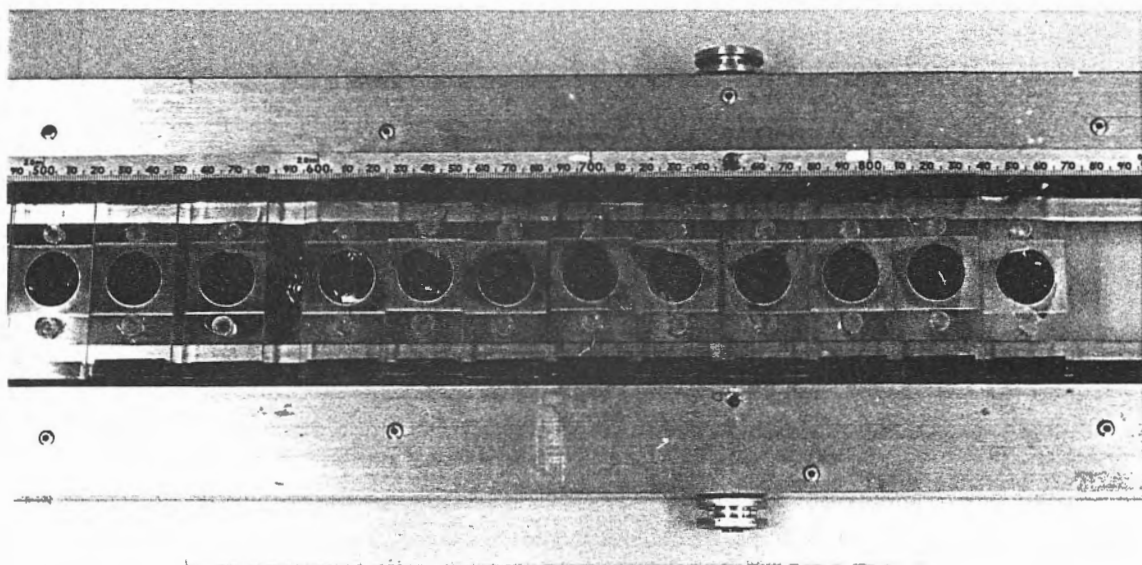


PLATE 5: Sample location scale on sled. Divisions are in millimeters.

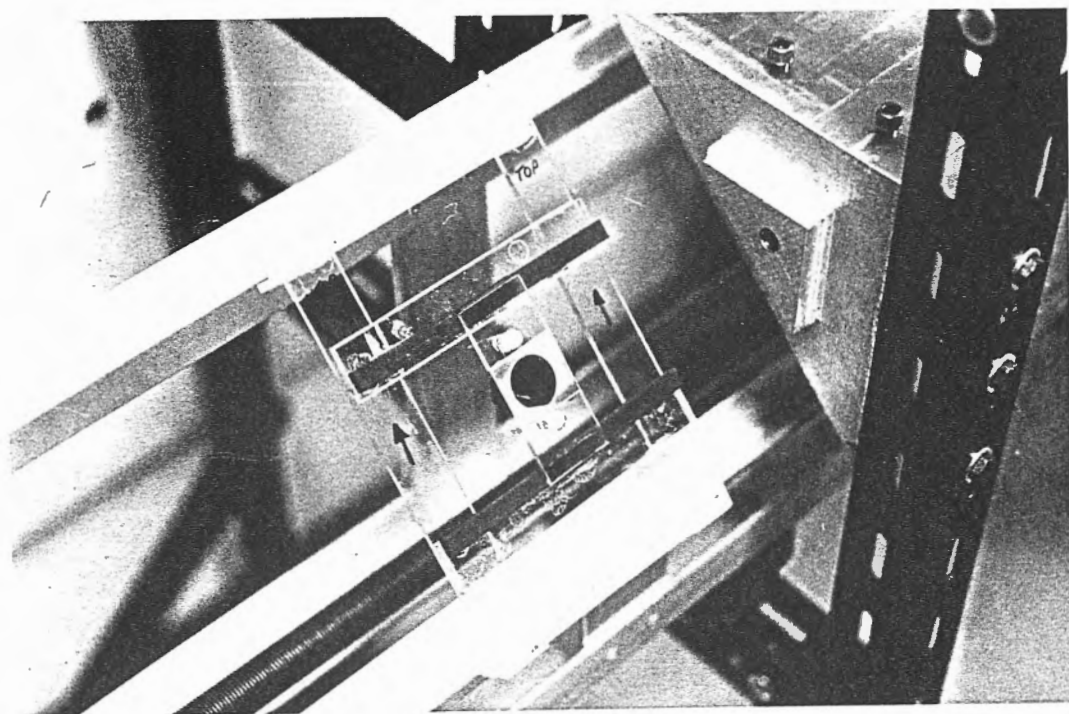


PLATE 6: Single sample mount on sled rails.

source. Thus, accurate orientation is quickly achieved.

The sample changing system devised is flexible and able to accommodate a wide array of potential sample sizes, either singularly or as multiples on the motor-driven sled. A true test of its capabilities, however, is its application in the analysis of an actual archaeological assemblage. The results from such a test should indicate its suitability for routine use.

#### FLUORESCENCE DETECTION INSTRUMENTATION

Fluorescent X-rays are detected with an ORTEC model 7113-06175 - S Si(Li) detector. It has an active diameter of 6 mm, and a sensitive depth of 5 mm. A 0.05 mm beryllium window separates the detector diode from the atmosphere (Anon. 1980:v). It is operated at 1500 V negative bias polarity with an ORTEC 459 5kV detector bias supply. This is run in series with an ORTEC 729A liquid nitrogen level monitor. The detector has a resolution of 174eV FWHM and 320eV FWTM at 5.9 KeV (ibid.). It is connected through an ORTEC 117B pre-amp to an ORTEC 572 amplifier with a gain setting of 0.61 X 100 and 1  $\mu$ sec shaping time. The analysis range is 0 - 60 KeV.

The unipolar output is connected to a Norland Ino-tech 5300 MCA, and spectra are collected on 1024 channels. Accumulated spectra are dumped from the MCA into the 64K RAM of a hybrid S100, Z80 based microcomputer. The 1024 channels represent a resolution beyond the useful limits of the present research. In the interests of maximizing available storage space, adjacent channels are averaged to yield a 512 channel

spectrum. This in turn is recorded on DSDD (double sided, double density) 1200 kilobyte floppy disks.

The MDL microcomputer is run under a CP/M operating system with ANSI standard FORTRAN 80 and Z80 assembler. Associated output facilities include a 12 inch 4-shade graphics monitor, JJ instruments XY plotter, and a Texas Instruments OMNI 800 line printer. A block diagram of the instrumentation system is shown in Figure 7.

#### SPECTRA ANALYSIS SOFTWARE

A significant portion of the SEFA programme is related to the computerized operation of the facility. Both multiple-sample analyses via the automated sample changer as well as subsequent examination of collected spectra are performed by the microcomputer link. All software was developed at the University of Otago Archaeometry Laboratory and is retained in floppy disk and printout form. The following section will briefly outline the major computer programs used in this study.

Transfer of collected spectra from the MCA to the MDL is facilitated in one of three ways. For single sample analyses, FORTRAN program MCA dumps the spectrum into the RAM (random access memory) of the MDL, converts the 1024 channels into 512 by a moving means averaging process, and, finally, writes the spectrum onto floppy disk. The spectrum is displayed on the graphic monitor during this process, permitting the analyst to make a cursory visual inspection. Program MCA allows the operator to record a literal description (up to 80 characters) and checks the run number assigned to the

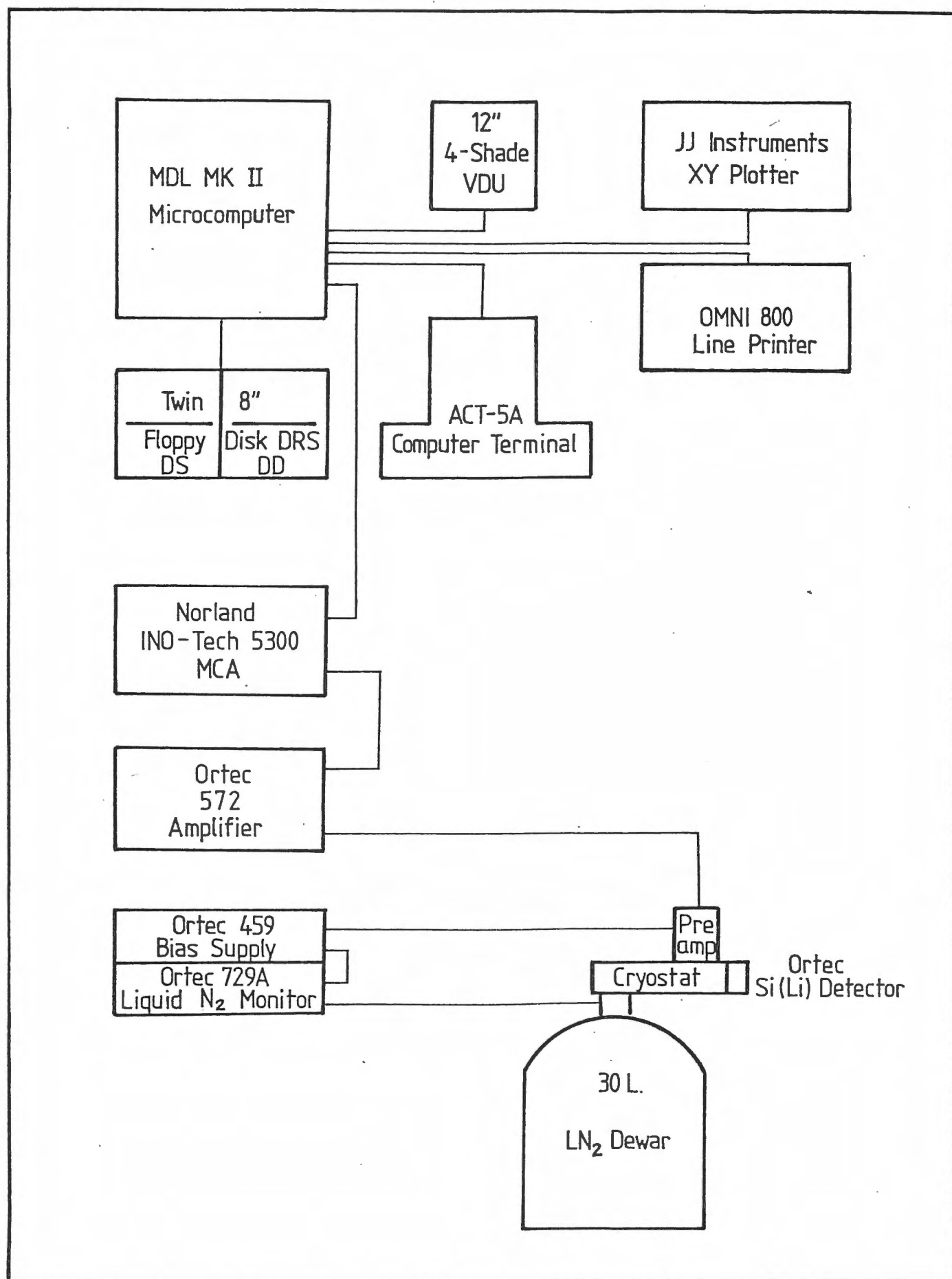


FIGURE 7: Block diagram of analysis instrumentation.

sample (as entered by the operator) against possible duplication of the file name with those already present on the destination disk. In this way, both the literal entry and disk file check help ensure the unique labelling of each spectrum.

For multiple analyses utilizing the automatic sample changer without any data treatment beyond recording the reduced 512 channel collected spectra onto disk, program NIGHT is employed. The program functions in a similar manner to MCA, but incorporates the use of a prepared data file for the operation of the automatic sample changing system.

As was noted in the description of the sample changing apparatus, samples are located on the sled by reference to a mounted scale (see Plate 5). The data file created by FORTRAN program CHANGER records this information. Any number of samples from one to a sled maximum of fifty can be automatically advanced into the analysis region and have the collected spectrum written onto disk. Extensive testing of NIGHT has proven its reliability in automatic spectra collection.

Where analyses of the obsidian spectral data are required in addition to sample changer operation, FORTRAN program SOLO is employed. SOLO performs the added function of selected window analysis of the collected obsidian spectrum and compares the obtained values with recorded source-group parameters. The program attempts to reject the unknown spectrum as having come from each source in the reference group file

at a given level of certainty based on the group dispersion characteristics. A detailed discussion of the sourcing algorithm will be presented in Chapter Four.

Spectra are stored on disk by SOLO as with program NIGHT, but with the addition of an output data file. The output file records the selected element window values that have been calculated for each of the analyzed spectra. Each window group is identified by the run number from the parent spectrum. A list file of the sources unable to be rejected is also created, in addition to an 'as processed' printer output. The operator is thereby able to retain a disk file of the sourcing allocations ascribed to each artefact.

For spectra already recorded on disk, two programs are available for analyst interactive inspection. FORTRAN program AMSPEC searches for an operator specified spectrum file on the data disk drive. Through a series of interactive prompts, AMSPEC allows the operator to display all or a portion of the designated spectrum on the graphics monitor. Analysis options include: graphing the spectrum (or portion) on the XY plotter, determining the energy of a particular region or peak, integrating window areas (an accessory light pen is employed for these last two functions) and producing a counts per channel printout of the displayed spectrum region.

Sourcing of previously collected obsidian spectra is performed by program SCREEN. This program utilizes the same sourcing parameters as SOLO, but permits the operator to select the obsidian spectrum file to be examined. An output file of the generated element values for each spectrum is also produced.

This flexible software package permits obsidian spectra analyses to be performed in either interactive or automatic modes. Additional software available to the computer system allow basic statistical treatment of the data output to be performed. All programs are easily adaptable to changing analysis requirements.

Chapter Four will develop the application of the SEFA facility to the characterization of New Zealand and Oceanic obsidians. The analysis parameters employed and the method of artefact source allocation will be discussed.



## CHAPTER FOUR

APPLICATION OF ISOPROBE ANALYSIS  
TO OBSIDIAN CHARACTERIZATION

## DEFINITION OF ISOPROBE SYSTEM RESPONSE

Before the developed SEFA facility could be applied to obsidian characterization, it was necessary to establish some basic response characteristics of both the system and the material under study. General XRF response factors such as routine background and fluorescence peak/energy calibration as well as characteristic Compton/Rayleigh peaks specific to the excitation system had to be determined. Sample-specific effects to fluorescence response such as thickness and surface texture also needed to be explored. Experiments were designed to identify these parameters.

The theoretical ability of  $^{241}\text{Am}$  to induce  $K_{\alpha}$  fluorescence in elements as high as thulium in the periodic table (see Fig. 1) is quite separate from the ability of a system to detect the fluorescence generated. Additionally, as noted in Chapter Three, effects of Compton and Rayleigh scatter from the primary americium emissions may interfere with the detection of certain elements. The sensitivity of the system to the detection of given fluorescence emissions and minimum element detection levels required evaluation.

To calibrate the Otago system to elements of particular interest in this study, standard pellets of zirconium silicate and barium sulphate were prepared. The pellets allow the

system to be quickly checked against known fluorescence peak locations. Detector/amplifier stability is easily verified by the consistency with which known fluorescence peaks occur at specified channels.

While the ORTEC 572 amplifier was used as a dedicated component in the system and its settings locked during the course of the study, weekly fillings of the Si(Li) detector liquid nitrogen dewar required the bias supply voltage to be turned to zero. Upon re-applying the detector voltage, brief analyses of the standard pellets allowed rapid system calibration. All system checks confirmed its stability regarding energy/peak location.

Calibration checks of collected obsidian spectra were easily made with program AMSPEC. After reading the appropriate spectrum from disk, element windows can be displayed on the graphics monitor and specific channel energies identified by light-pen. Examination of the barium  $K_{\alpha}$  peak, for example, should indicate an associated energy of 32.191 KeV. Failure to do so is an indication of a calibration shift for the collection of that spectrum. Again, the analytical stability of the system regarding the location of discrete elemental transition peaks for obsidian spectra was consistently verified:

As noted earlier, the radioisotope employed in this study,  $^{241}\text{Am}$ , is relatively long-lived as compared with other commonly used radioactive sources. By comparison,  $^{55}\text{Fe}$  has a half-life of 2.7 years, while for  $^{109}\text{Cd}$  the value is on the order of 453 days. Iron and cadmium radioisotopes were

employed by Higashimura and Warashina (1975), Warashina *et al.* (1978) and Higashimura *et al.* (1981) in the study of Japanese sanukite implements, as discussed in Chapter Two.

To overcome the effects of source decay, element ratios were utilized. While the total fluorescence emission of the samples was reduced through time, the relative element responses remained proportionately consistent (Higashimura and Warashina 1975:173). Thus, even with comparatively short-lived radioisotope sources, changes in excitation flux did not impair analytical results. Due to the long half-life value associated with  $^{241}\text{Am}$  (458 years), source-decay effects are considered to be analytically insignificant within the context of this thesis.

A primary concern with the excitation mode used was to determine the Compton and Rayleigh contributions to the analytical spectrum. Figure 3 demonstrates the rather complex emission characteristics of the Otago  $^{241}\text{Am}$  source. Identification of the americium Compton and Rayleigh scatter component in obsidian spectra was a fundamental task. Figure 8 shows the typical Compton/Rayleigh peaks determined in the obsidian analysis. The particular spectrum illustrated displays low element values except for a singularly large barium  $K_{\alpha}$  peak at 32.191 KeV (channel 260). It was chosen to allow clearer identification of the individual scatter peaks. These same scatter peaks are present in all obsidian spectra in this study.

As indicated by Figure 8, the complex americium primary emissions are passed on to the fluorescence spectrum. Inelas-

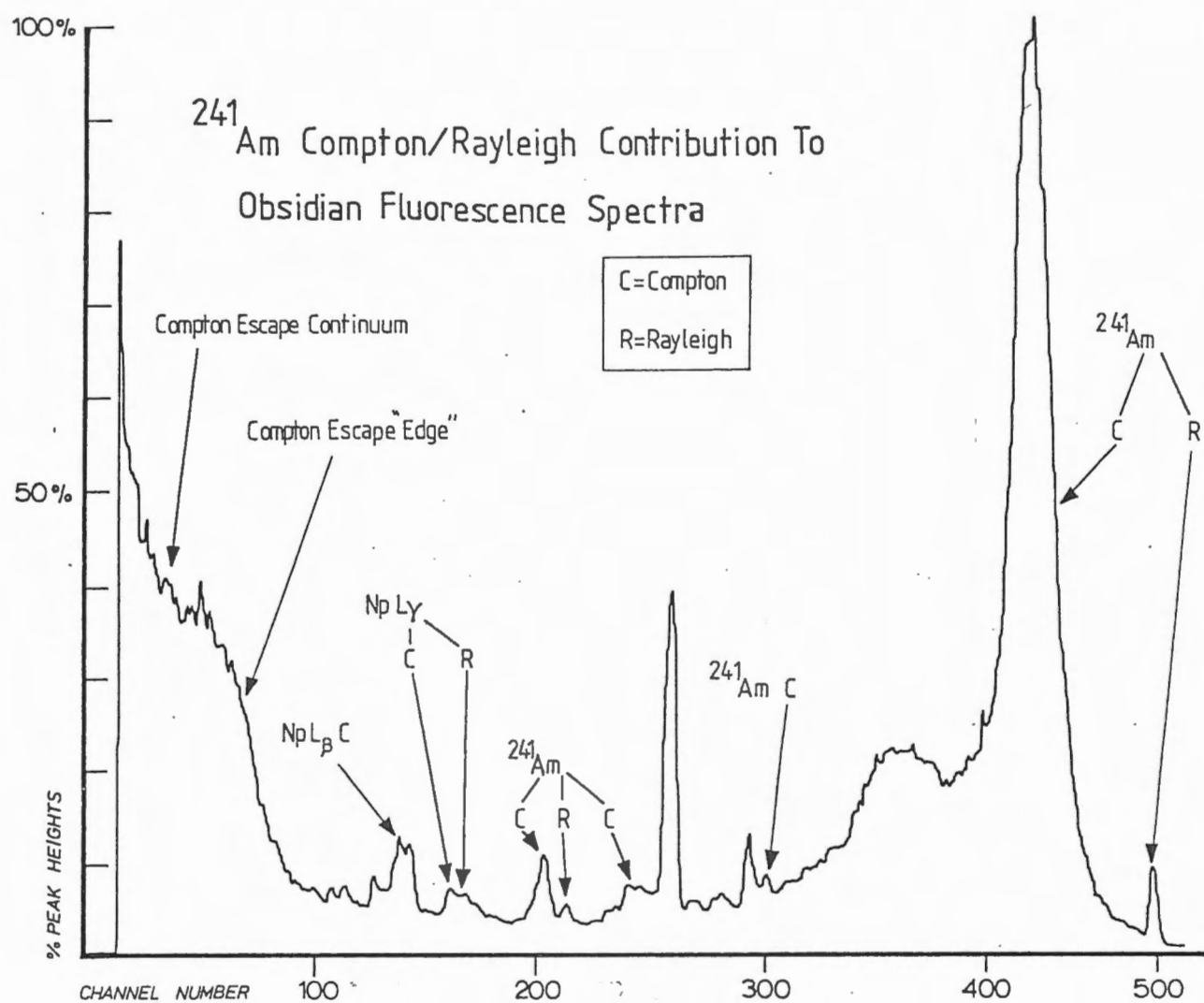


FIGURE 8: Compton/Rayleigh contributions to  
obsidian fluorescence spectrum.

tic scatter dominates in the low Z composition of the obsidian. The largest Compton peak at around 52 KeV (channel 423) represents the  $90^{\circ}$  inelastic scatter of the 60 KeV gamma radiation within the sample. The primary radiation is also represented by an elastic scatter (Rayleigh) component at its emission energy of 60 KeV (channel 498). Scattered Np X-rays are also present in the analytical spectrum, predominantly as Compton peaks.

With the excitation source emission characteristics established, sample specific effects of the analytical spectrum were explored. Thickness and surface texture were identified as the main sample variables which would be encountered.

#### SAMPLE TEXTURE EFFECTS

The effects of sample surface texture on fluorescence response has been broadly discussed by Higashimura and Warashina (1975) as well as Nelson *et al.* (1975) and McCallum *et al.* (1979). Detailed analysis of surface texture effects is made by Bertin (1975:728-734). The effect of surface roughness was shown to be directly related to the "critical thickness" associated with the particular elements of interest (*ibid.*:729).

Critical thickness is the maximum depth from which fluorescent lines excited within a sample can escape to the detector. Thus, "effective layer thickness is determined not by the depth to which the primary radiation penetrates, but by the depth from which fluorescent X-rays can emerge" (*ibid.*:

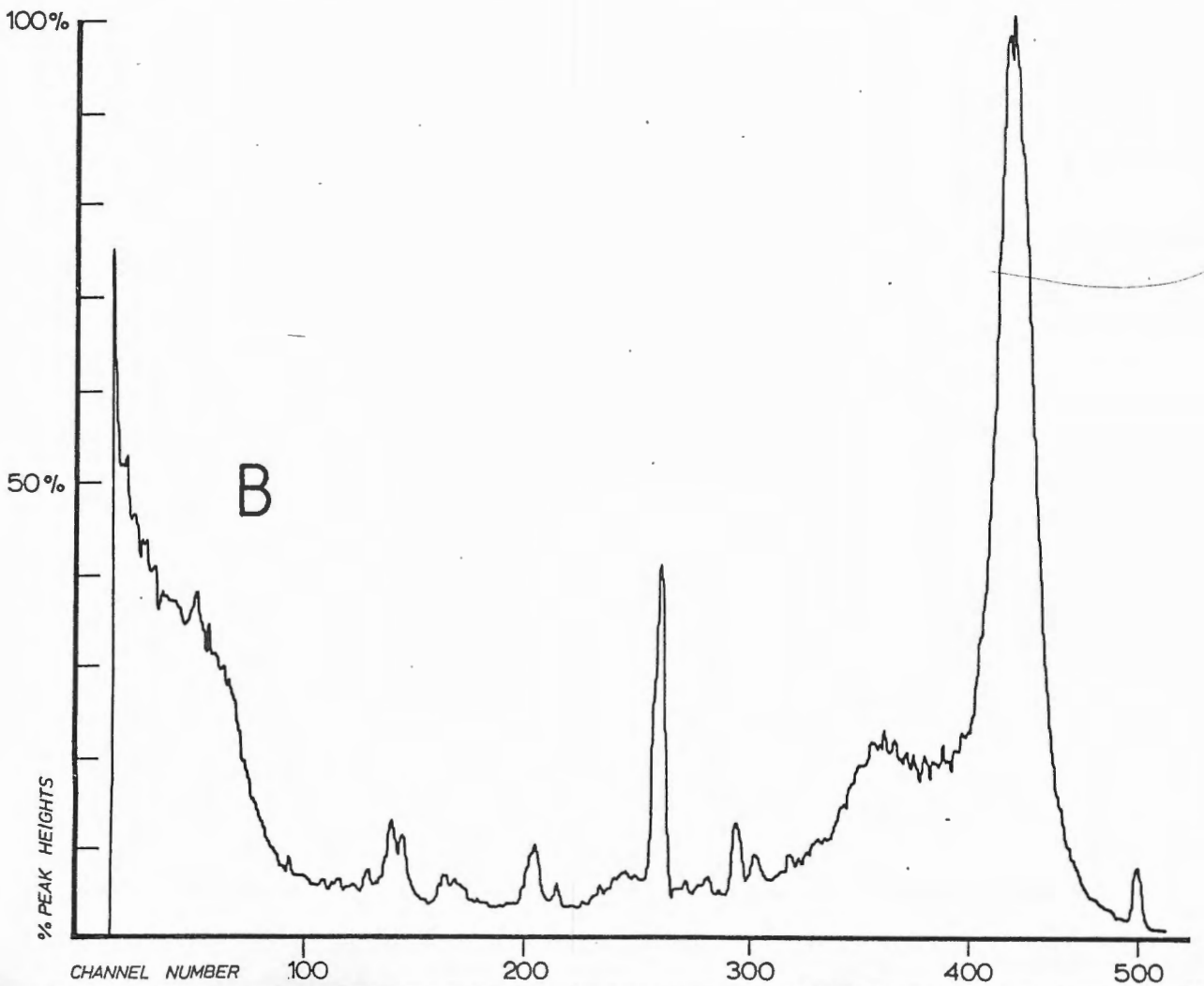
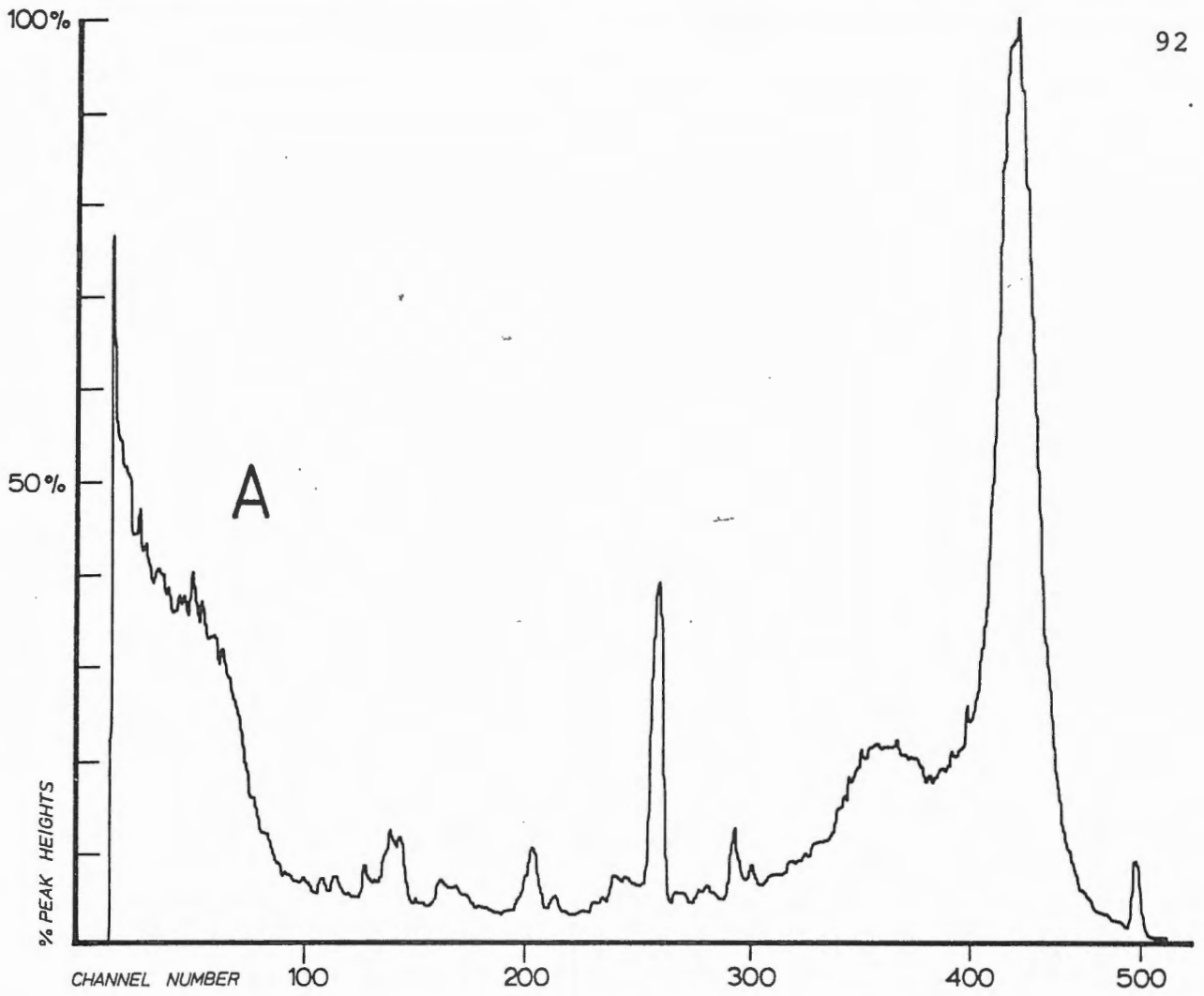
717). Therefore, in consideration of specimen surface texture, where the physical roughness exceeds the effective depth of fluorescent X-rays, a damping effect results. Low-Z elements (with their associated lower effective depth) are more sensitive to texture effects than elements of higher atomic number. Where Si fluorescence can be reduced by 50% by altering surface texture from polished to 160  $\mu\text{m}$  grooved roughness, Sn fluorescence shows less than 10% reduction in response (Bertin 1975:730, Figure 16.6).

As the present study is concerned with the analysis of totally unmodified artefact surfaces, knowledge of potential effects from surface texture variation was required. Figure 9a-d shows the analysis spectra of a series of 30 mm x 30 mm x 10 mm thick samples made from a contiguous piece of Taupo obsidian. A total range of surface texture variations from 'roughly flaked' through 80, 200, 400, 600, 1000 grit and finely polished flat surfaces were examined, though only four interspersed samples are shown.

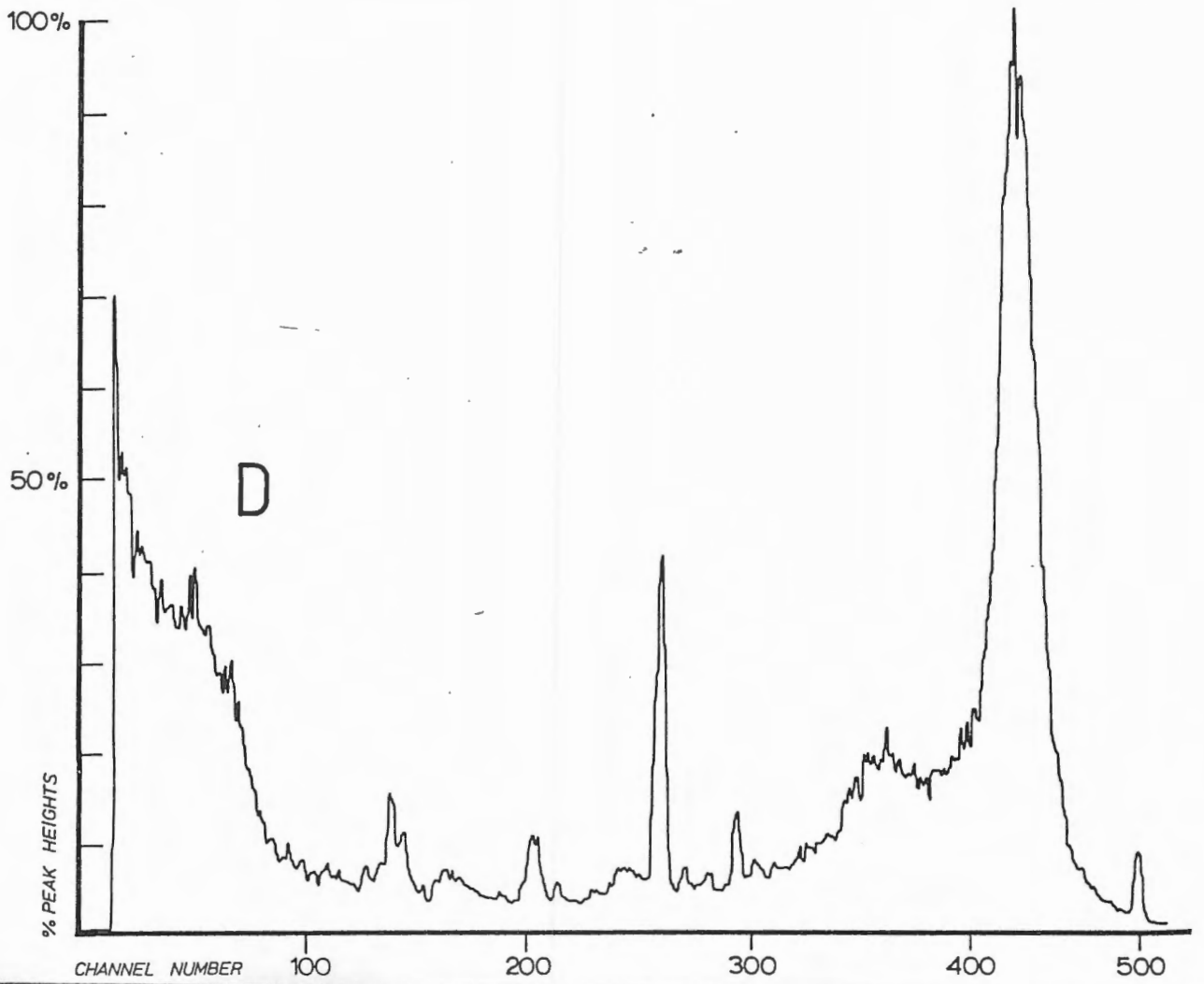
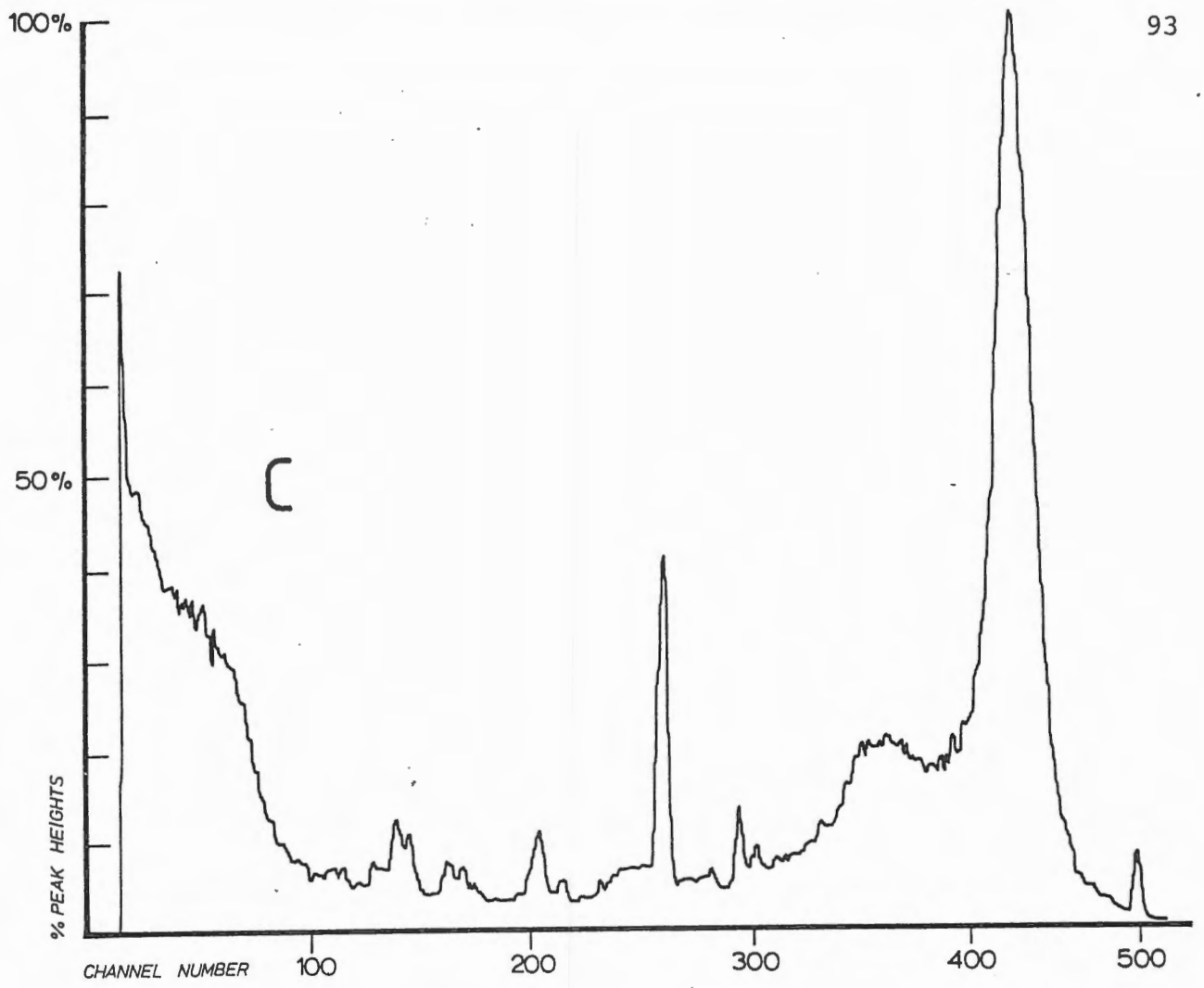
The Taupo sample was chosen because of its widely divergent elemental concentrations in both high and low-Z elements. Placement of the included overlays shows that as surface texture is taken from finely polished (9a) through to 80 grit (9c) the low concentration, low-Z elements Rb, Sr and Zn are swamped by background 'noise'. Conversely, there is little or no marked change in the high-Z elements (Ba, La and Ce) either in high or low concentrations. The effect described by Bertin is therefore confirmed.

As might be expected, there is a slight but distinct

FIGURE 9: Effects of surface texture on fluorescence response  
A- Taupo finely polished; B- Taupo 400 grit;  
C- Taupo 80 grit; D- Taupo flaked surface.







increase in the overall 'roughness' of the accumulated spectrum with increasing surface roughness. This is a result of the increased scatter angles and hence increased Compton energy dispersion generated by the various facets.

Of particular note, however, is the response obtained from the ostensibly 'roughly flaked' specimen (9d). Not only are the high-Z low concentration elements clearly defined as in the polished sample, but the low-Z elements (particularly Fe) are enhanced as well. This might be explained in that the actual flake surface may be equivalent to a fine polish, albeit 'bumpy'. It appears that when surface irregularities exceed a certain dimension, that is, when granular becomes more generally curvilinear - as with many flake artefacts - fluorescence response approximates that of a polished face.

#### SAMPLE THICKNESS EFFECTS

Having isolated the general fluorescence response to changes in sample surface texture, the effects of variation in sample thickness were observed. As with variation in surface texture, it was expected that distinct changes in the fluorescence spectrum would occur as sample thickness was reduced.

Higashimura and Warashina (1975) examined samples from 0.3 to 1 cm in thickness but do not specify the "shape effect" beyond noting that it can be overcome by the use of peak ratio measures (1975:174-175). Even less specific references are made by Warashina *et al.* (1978) and Higashimura *et al.* (1981). More instructive mention of the effects of sample thickness

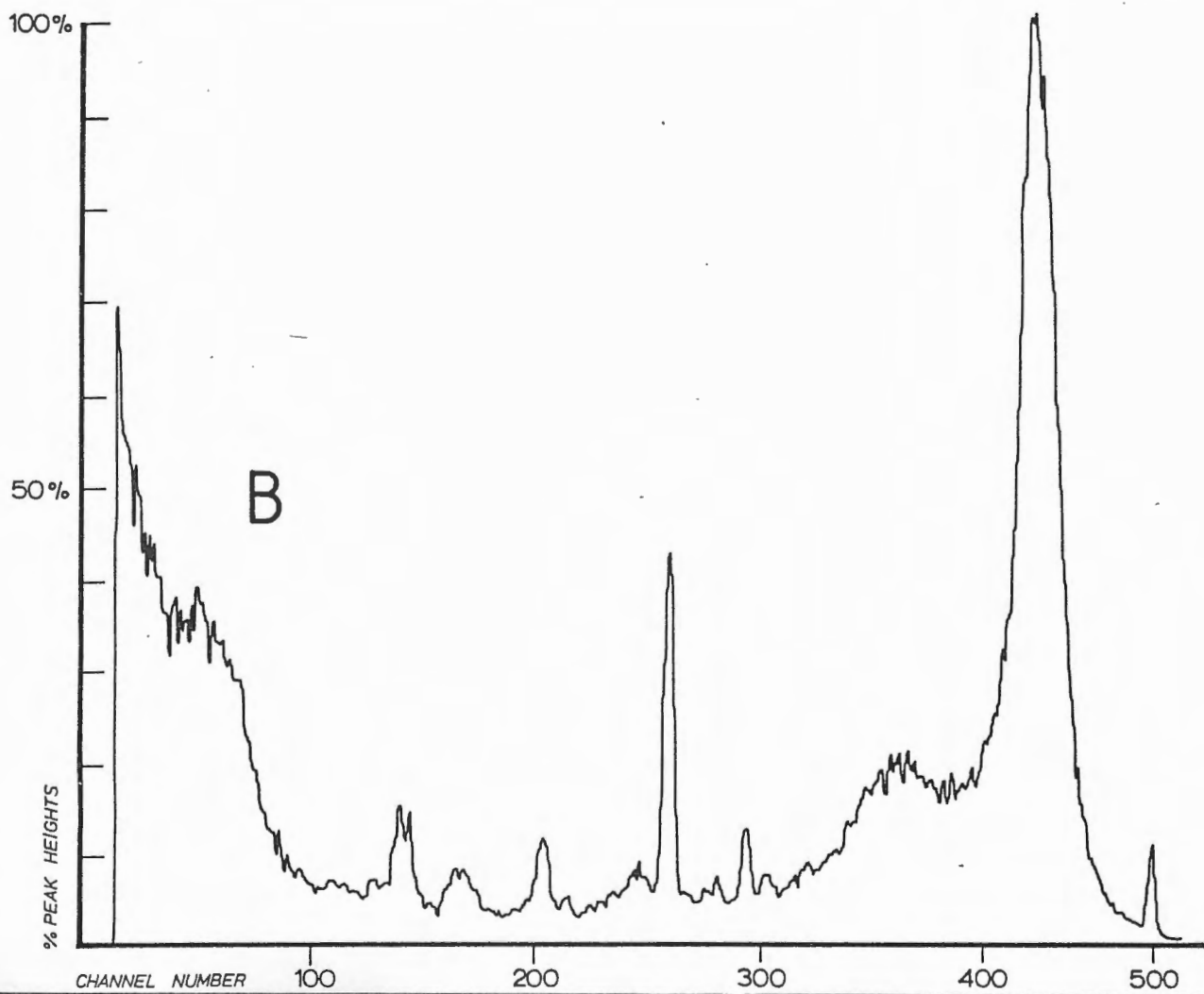
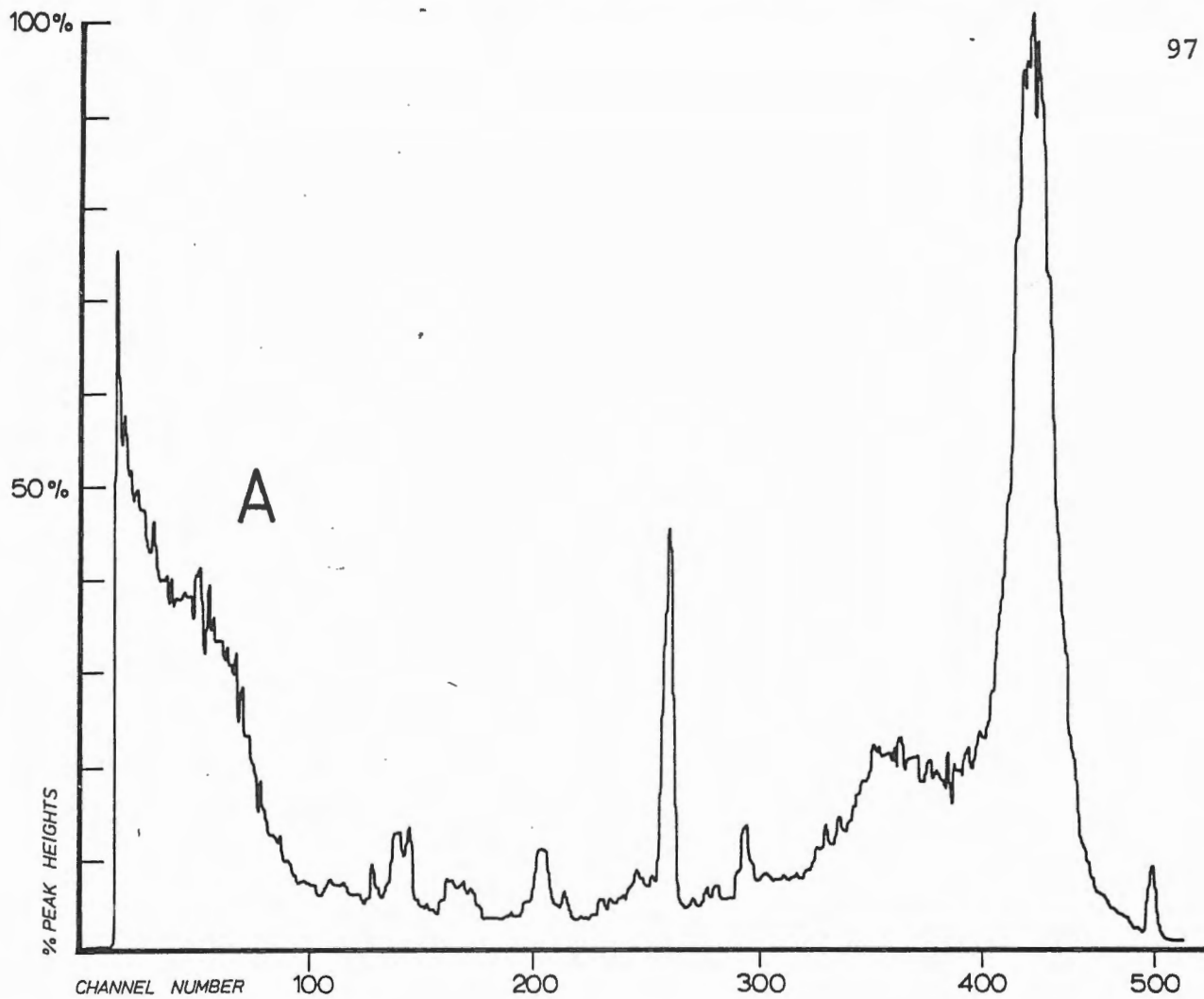
to fluorescence response is made by Nelson *et al.* (1975). Concerned with the physically non-destructive analysis of obsidian artefacts, it is noted that "in those extreme cases in which a specimen of thickness 1mm is to be analysed, one should expect an increase in the response to the low-Z elements relative to that for the high-Z elements" (Nelson *et al.* 1975:89). As in the Japanese study, Nelson *et al.* report that sample shape effects are almost completely eliminated by measuring the relative responses of the system to the various elements in the sample (*ibid.*:88). This same observation is made by McCallum *et al.* (1979:7).

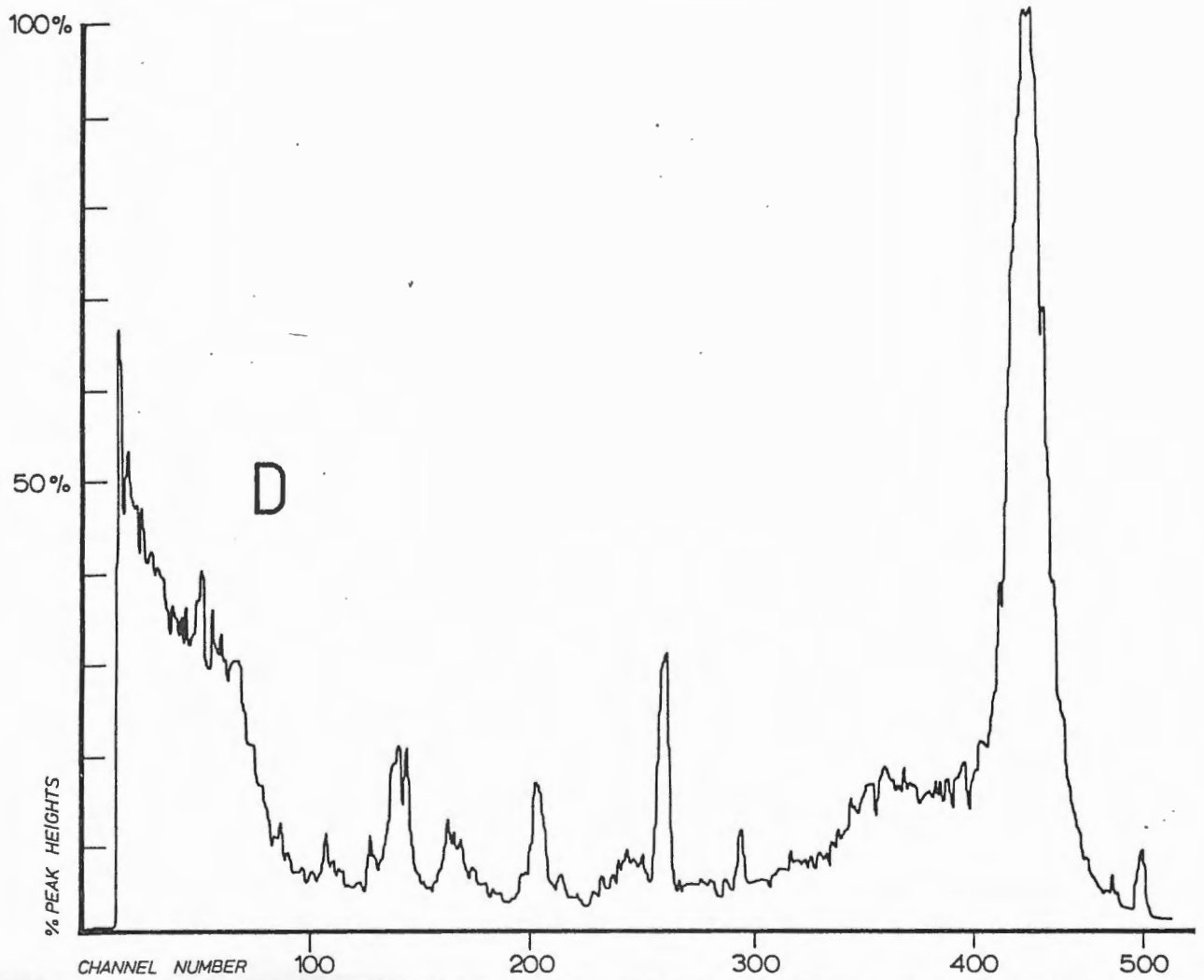
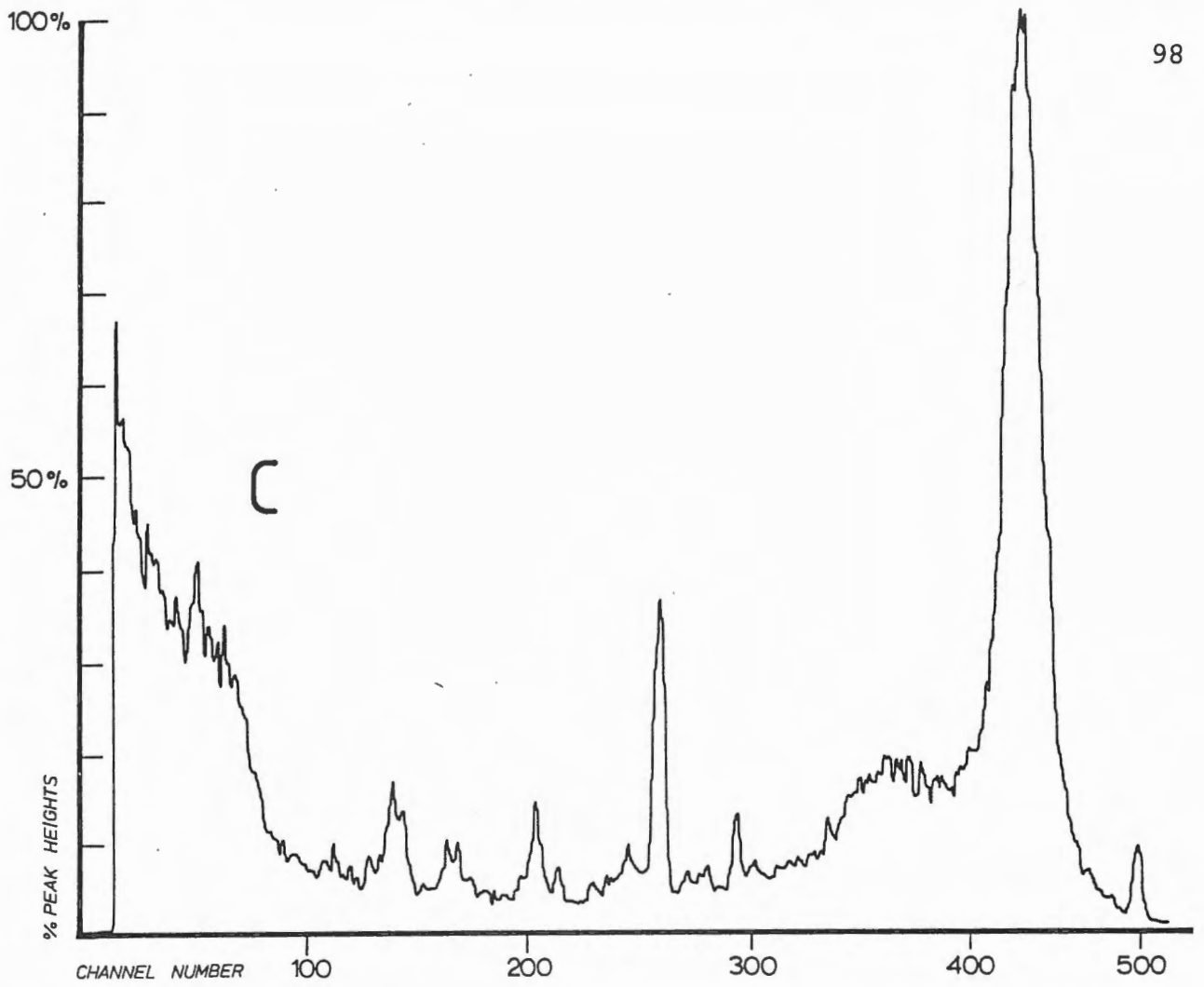
To test for the effects of obsidian sample thickness fluorescence response in the isoprobe facility, a 'thickness series' was made in the same manner as the 'texture series' previously run. The same course material was used, and the samples were again cut from a contiguous block. The results of the analyses are graphed in Figure 10a-d and represent sample thicknesses of 10 mm, 5 mm, 3 mm and 1.5 mm respectively.

As samples are reduced in thickness, there is an apparent increased response of the low-Z elements (as predicted by Nelson *et al.*). Also, there is a marked decrease in the proportional response of the high-Z elements.

It should be recalled that the total fluorescence contribution of the high-Z elements is generated from a greater cumulative depth in the sample. Conversely for the elements of lower Z, the fluorescence is basically a surface response. Thus, as sample thickness decreases, the total fluorescent volume for the high-Z elements is concomitantly reduced. It

FIGURE 10: Effects of sample thickness on fluorescence response for Taupo obsidian.  
A- 10 mm; B- 5 mm; C- 3 mm; D- 1.5 mm.





remains functionally unchanged for elements of low-Z.

A second effect observed in these spectra is the increased relative contributions of the mid-to-lower energy scatter peaks. The increased proportionate response (with decreasing thickness) is essentially due to the same phenomenon as described for the lower Z elements; being derived from surface and near surface regions. Both element and scatter peaks show increased response relative to background because the background itself has been reduced. As sample thickness decreases, the general scatter in the sample and detector as created by the 60 KeV gamma is lowered. This is reflected in the collected spectrum. With the reduced volume there is a lower overall 'noise' effect from the high-energy radiation scatter.

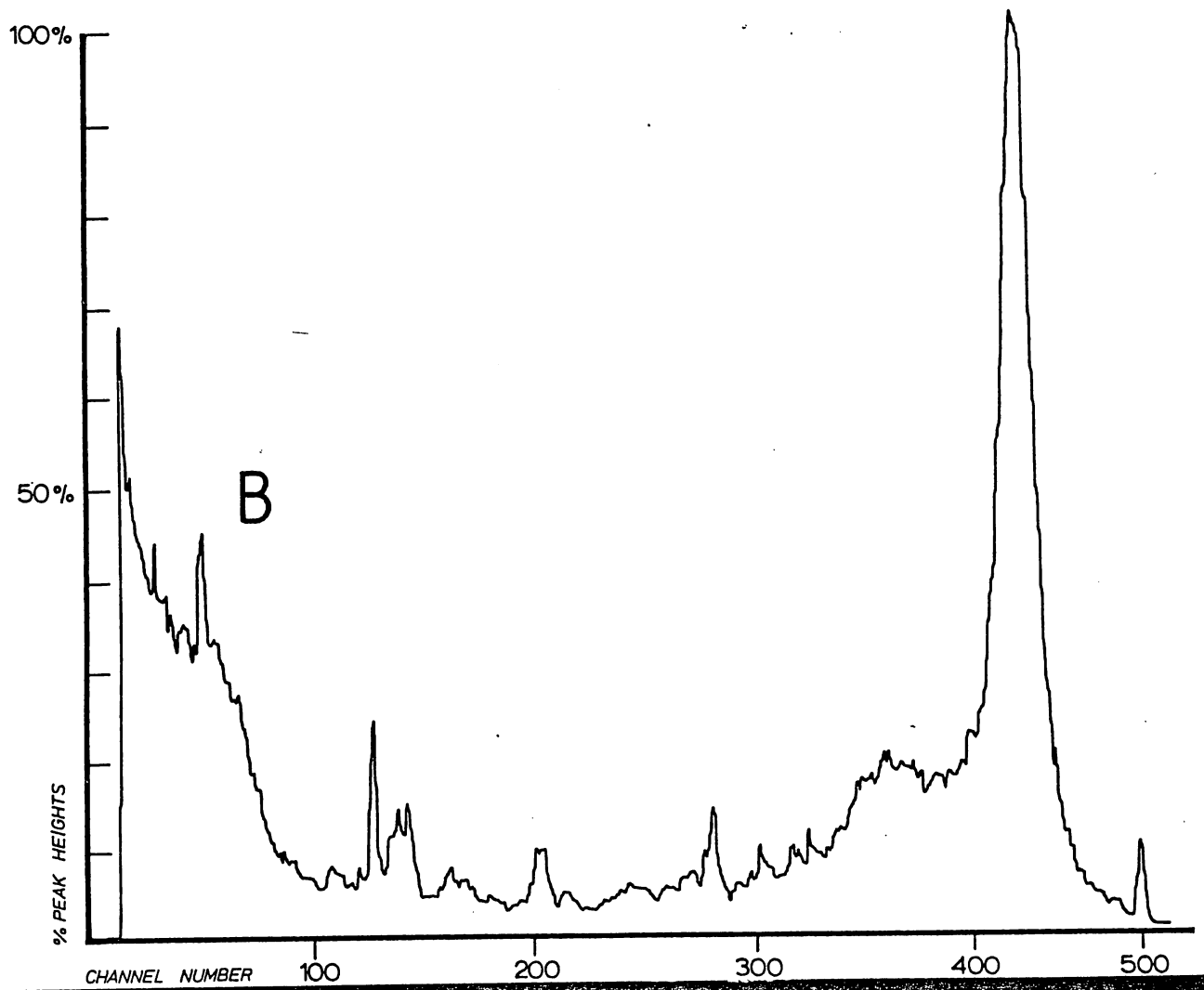
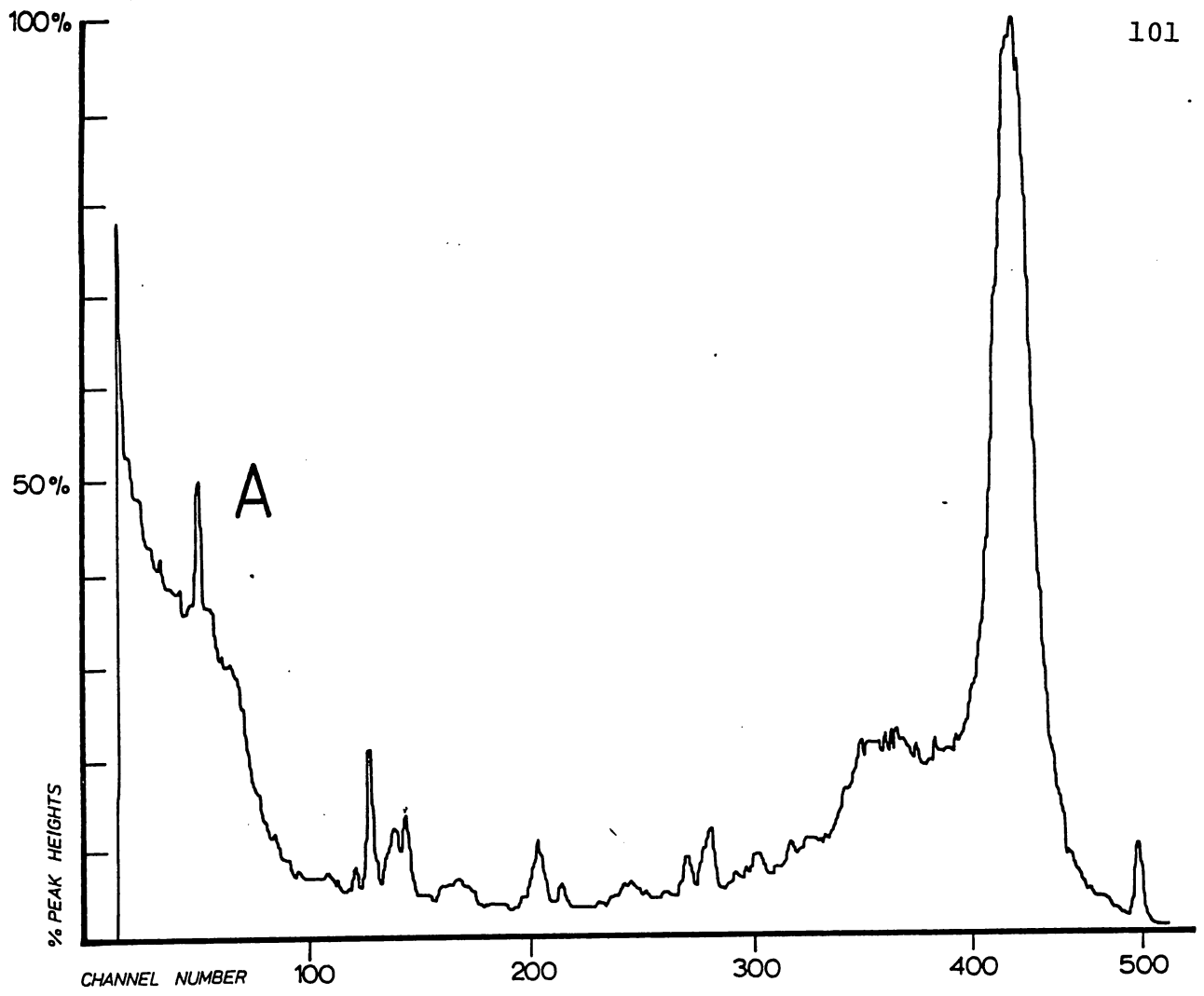
To better exemplify the changed apparent response of the low-Z elements, the thickness experiment was repeated with a sample of Mayor Island obsidian (Mayor Island source sample catalogue no. AL380). This is shown in Figure 11a-d. Here, the exaggeration of the low-Z response is amplified due to the absolutely larger concentrations contained by the Mayor Island material (see Tables 2 and 3). Note also, that as described by Higashimura and Warashina (1975) and Nelson *et al.* (1975), the relative proportions of the low-Z peaks remain consistent between themselves.

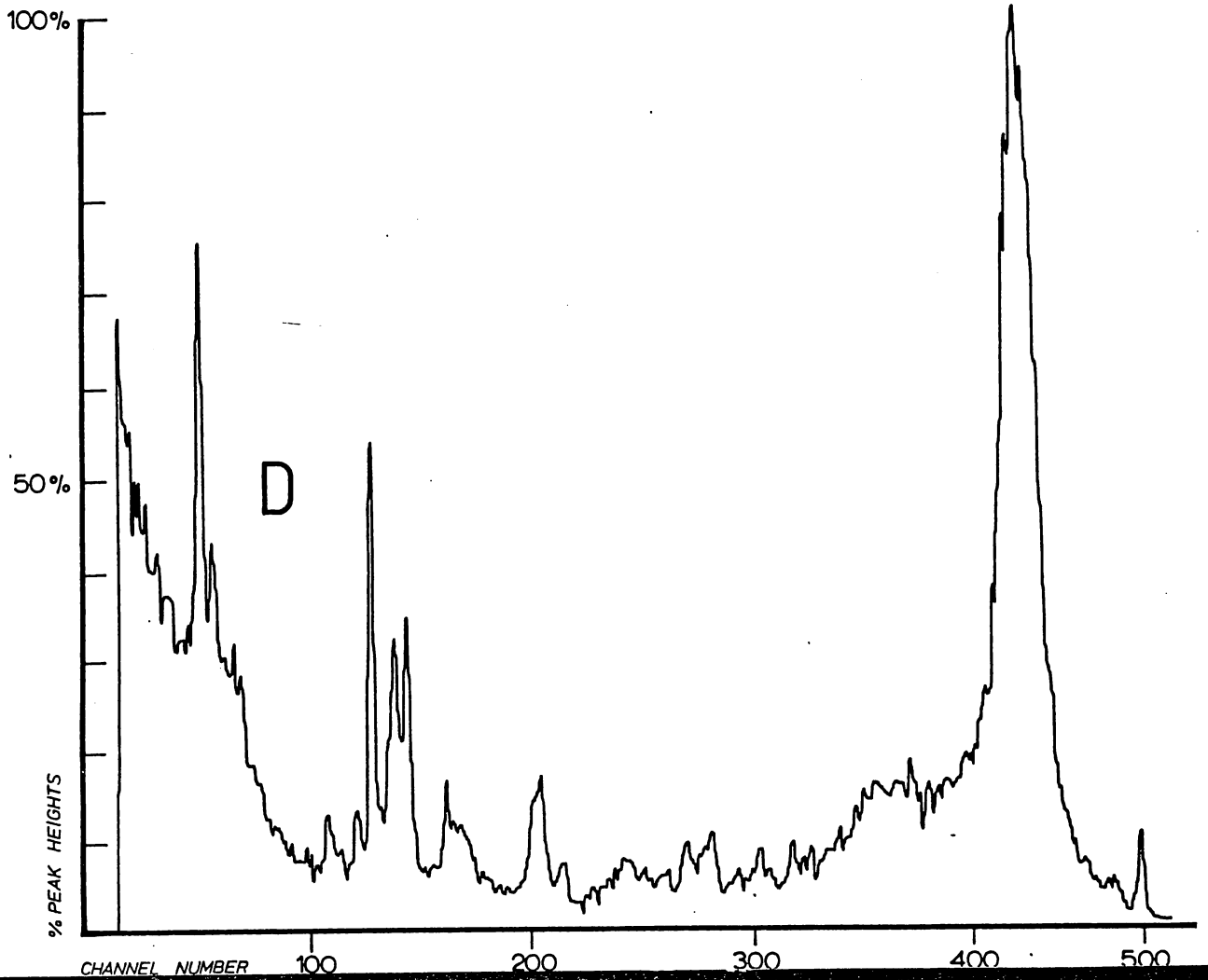
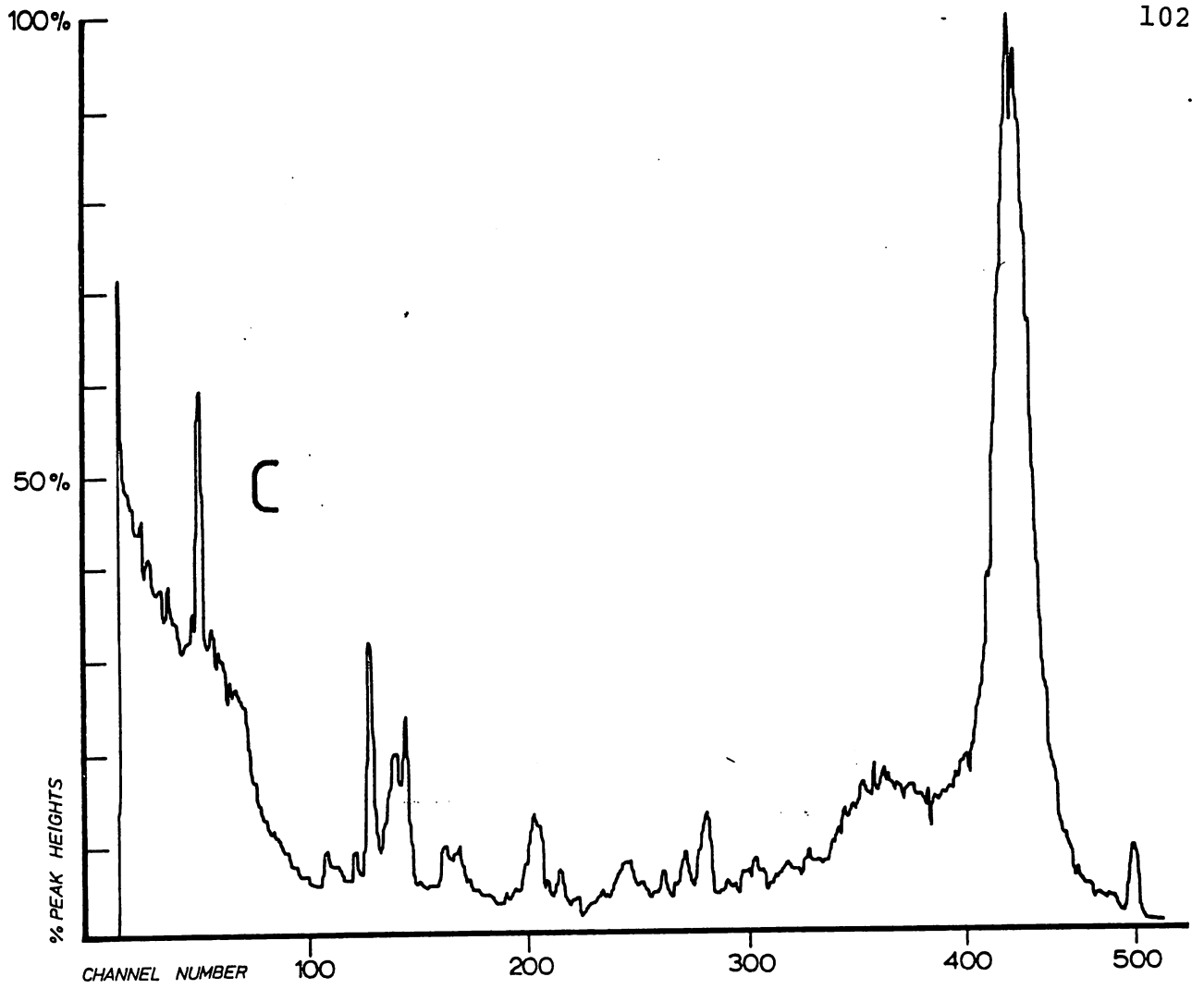
From these experiments, it was established that both surface texture and sample thickness affect fluorescence detection from samples. A programme of physically non-destructive analysis of obsidian artefacts (which may be

FIGURE 11: Effects of sample thickness on fluorescence response for Mayor Island obsidian.

A- 10 mm; B- 5 mm ; C- 3 mm ; D- 1.5 mm.







expected to vary a good deal in thickness) has to allow for these phenomena in calculation of element values.

#### DETECTION SENSITIVITY OF THE ISOPROBE UNIT

In examination of fluorescence effects from variations in texture and thickness, the examples illustrated were evaluated by subjective means. Up to this point, little discussion has been given to any sort of objective method by which to measure the performance or sensitivity of the system. Spectral peaks can be broadly compared to the ppm values of the published NAA data (Tables 2 and 3), but this is not the same as measuring the response of the system from an actual sample with closely verified elemental concentrations. Use of the G2 granite, as by Ward (1972), is one such method, although in unpowdered form the matrix effects of such a highly crystalline material may be expected to produce different elemental responses than that from a holohyaline obsidian.

In an effort to obtain an objective calibration of the system's sensitivity, two U.S. National Bureau of Standards glass wafers (nos. 610 and 612) were analysed. The standard wafers are cut from a glass rod 'doped' with certified concentrations of 61 specified elements ranging from Bi ( $Z=3$ ) to U ( $Z=92$ ). The fundamental matrix of the glass is 72%  $\text{SiO}_2$ , 12%  $\text{CaO}$ , 14%  $\text{NaO}_2$  and 2%  $\text{Al}_2\text{O}_3$ . The trace elements are represented in 50 ppm (wafer 612) and 500 ppm (wafer 610) nominal concentrations (Anón. 1970).

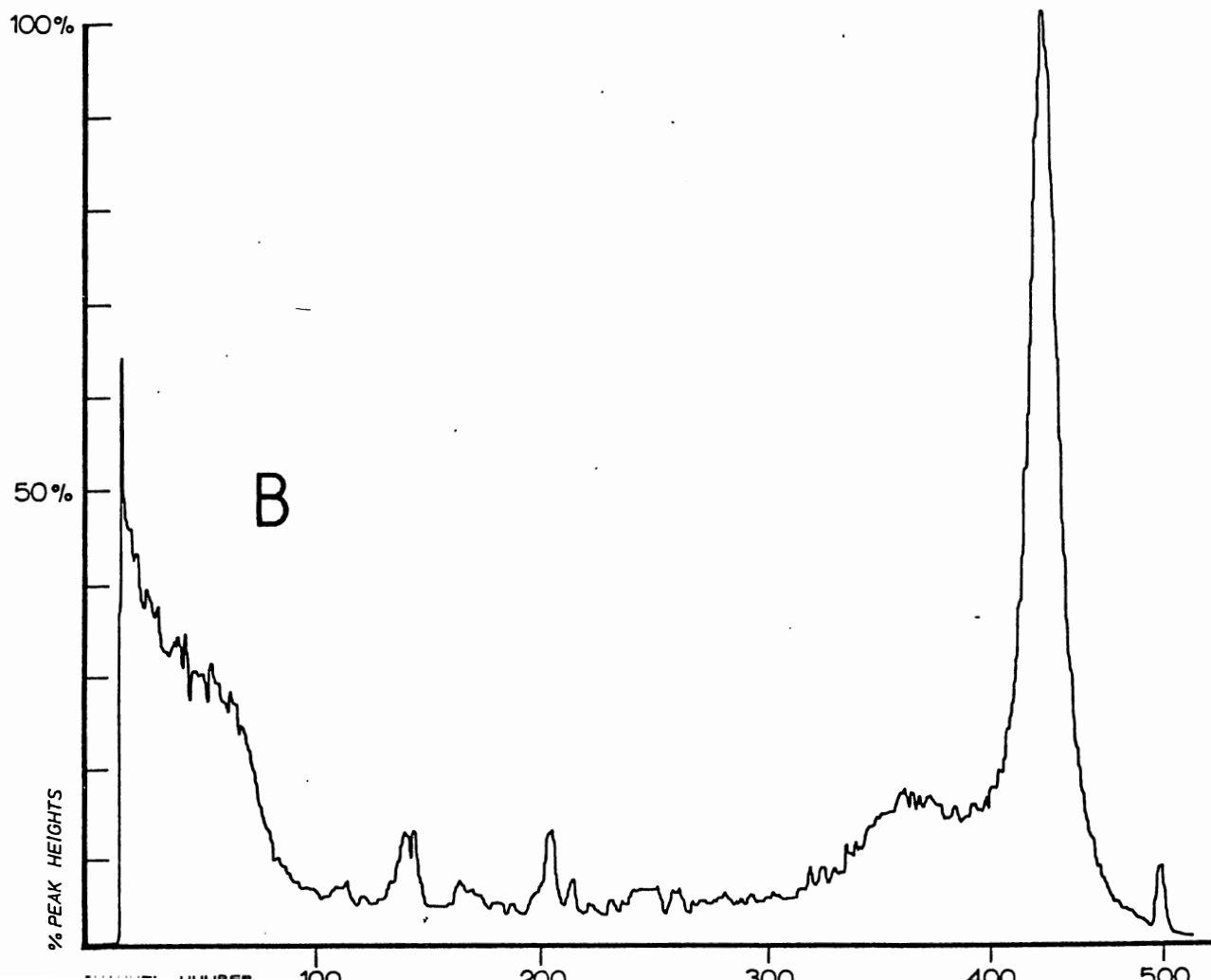
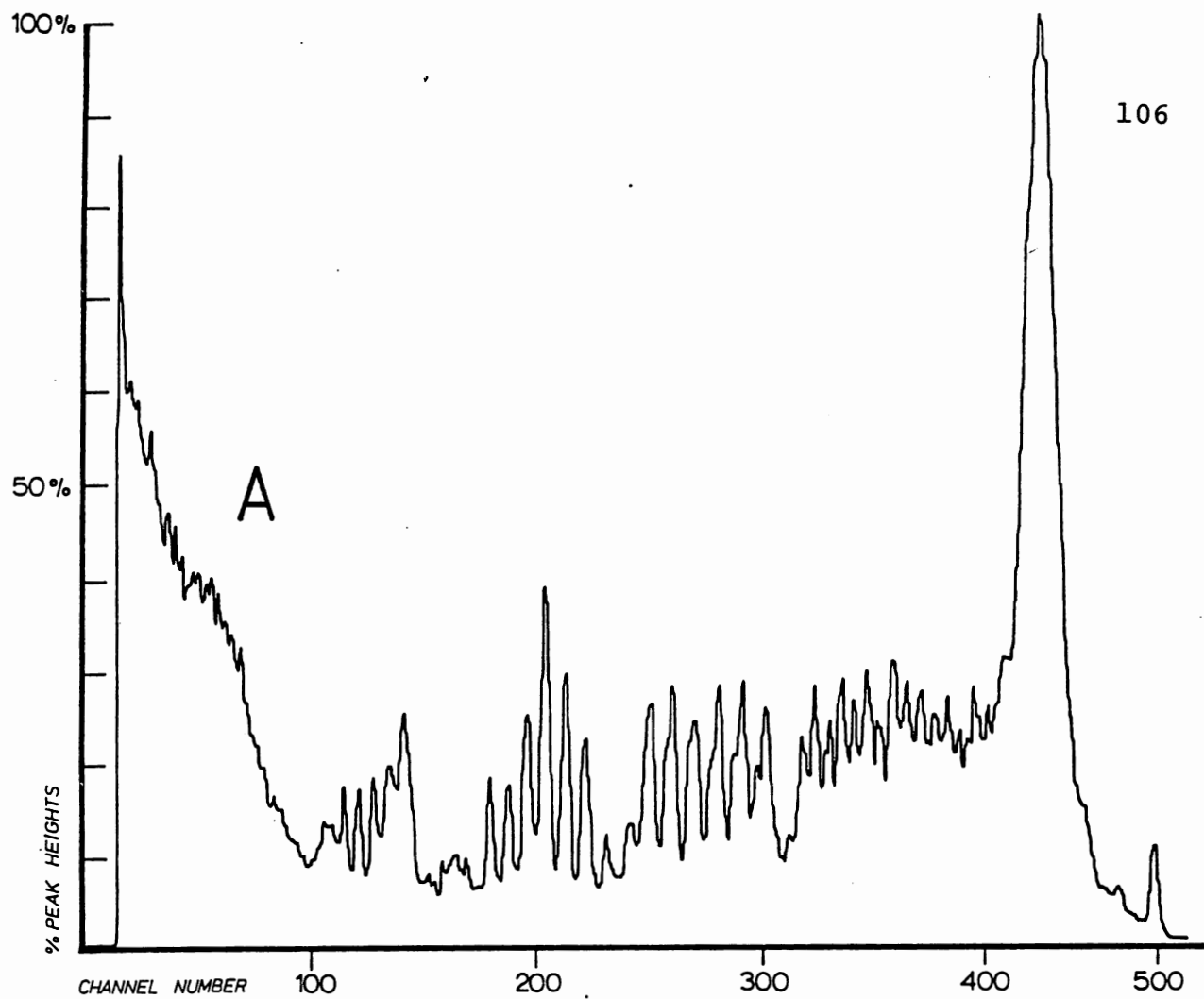
The matrix of the glass wafers (15 mm diameter x 3 mm

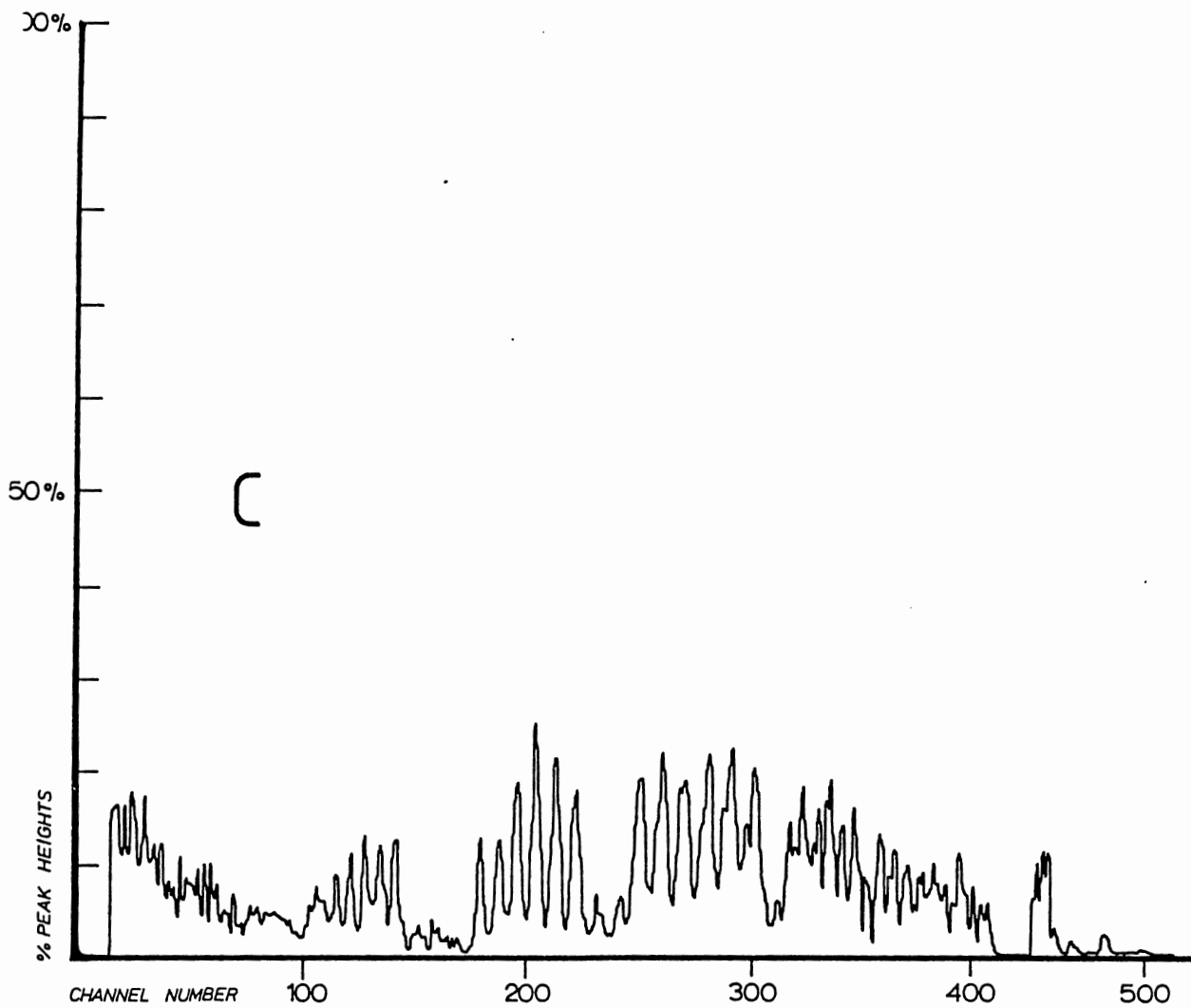
thick) is therefore a close approximation of the natural glass obsidian. They are as a result, excellent specimens to test with the isoprobe facility. The spectra generated by each of these wafers are illustrated in Figure 12a-b. Particular peaks of interest in this study are identified by the overlay charts. One point which becomes immediately apparent is that the minimum concentrations detectable in a glass matrix of moderate thickness by this system are on the order of 50 ppm (Figure 12b).

Figure 12a shows an additional characteristic of XRF spectrographic analysis; being the variable response in fluorescence yield of low and high-Z elements present in equal concentrations (compare Rb, Sr, Y, and Zr with Ba, La, and Ce). Also, there is preferential matrix absorption of low-Z emissions as compared with higher energy fluorescence. This is better illustrated in Figure 12c which shows the net area difference between Figures 12a and 12b.

Discussed in great detail by Bertin (1975:82-84, 501-527), the probability of photoionization increases with atomic number as about  $Z^4$  for constant excitation energy. It is well represented by Figure 12c which shows a third hindrance to low-Z fluorescence detection, that is, the preferential absorption of lower energy X-rays in the air path between the sample and detector. One further effect represented in Figure 12c is the Si(Li) detector efficiency 'roll off' for transition energies above 20 - 30 KeV (Anon. 1980:4). This is evidenced by the reduced above background peak heights for those elements above barium ( $K_{\alpha}=32.191$  KeV). Also, it

FIGURE 12: SEFA analysis of standard glass wafers  
A- 500 ppm; B- 50 ppm; C- Net response.





should be noted that the  $^{241}\text{Am}$  26.4 KeV gamma-ray Compton peak is overlapped by a Sn  $K_{\alpha}$  peak. For this reason that element appears to be more prominent than those peaks to either side (at approximately channel 205).

Further complications to spectrum interpretation are effects such as excitation efficiency of the primary radiation for elements of given  $Z$  (see Fig. 1 and also Woldseth 1973: Figures 2.23-2.24), and complex element enhancement/absorption effects competing within the sample itself (Bertin 1975:501-524, 648-651). Derivation of absolute quantitative measures for obsidian samples by interpolation from only two standards is obviously no easy task. The spectra do, however, give an idea of the overall efficiency of the isoprobe unit.

Nonetheless, some measure is required to determine analytical values for specified elements in the obsidian spectra. Ratio measures as employed by aforementioned workers would seem to be a suitable course to take. A problem with utilizing elemental ratios in this study, however, is that for the sample 'universe' considered, each of the likely elements (i.e. Fe, Zr or Ba) occur as detectably 'zero' for a particular source or group. Their use as a constant denominator for other element activities is therefore ill advised.

Consequently, it was decided to utilize a ratio measure within the sample spectra which was independent of trace element concentration. Such a measure has been employed by Cormie (1981) and Cormie and Nelson (n.d.). The method in this instance is to generate element ratios by taking calcu-



lated element peak values over a Compton or Rayleigh scatter value for the spectrum.

Cormie's (1981) work with the characterization of the glass fractions from volcanic tuffs utilized a secondary target TEFA system as described by Nelson *et al.* (1975). The scatter peaks occur at the high energy end of the spectrum as the secondary target excitation is purely monochromatic (and thus the highest energy represented). These high-energy scatter peaks were found to be particularly variable with changes in sample thickness using the  $^{241}\text{Am}$  source, that is, as the effective scatter volume is decreased.  $^{241}\text{Am}$  does however produce an additional scatter peak (referred to here as the 'mid-Compton') which is derived from the 26.4 KeV gamma. This was found to produce a more balanced response with fluorescence variation. Element window values were therefore generated as ratios against the mid-Compton peak.

Net peak areas above background were calculated by designating upper and lower channel positions for the  $K_{\alpha}$  peak of particular elements. By arithmetically 'drawing a line' between the background channels on either side of the element peak and assuming linearity of background profile between the measured adjacent background channels, the remaining area above the line was taken as the net peak value (Bertin 1975:386). All peak values, including the mid-Compton peak area, were generated in this manner.

The net element peaks were then taken as a ratio against the net mid-Compton value, and the ratio assigned as a measure of the proportionate element presence. All element values

reported in this thesis were calculated accordingly.

#### COUNT TIMES AND SYSTEM REPRODUCIBILITY

Determining the sample analysis time required for this study proved a difficult task for two main reasons. Firstly, low count rates (as shown in Figure 5) indicated that much longer counting times would be required to achieve analytical precision in the counting statistics. For a single measure of  $N$  counts, the inherent error in the measurement follows a Poisson distribution. Over a series of repeated measurements this will generate a standard deviation in certainty equal to  $\sqrt{N}$  (Bertin 1975:472-474). Therefore as  $N$  becomes larger (by extending the count time) the proportionate error associated with the measurement is reduced.

Secondly, while cursory evaluation of general differences between the various source groups indicated at least an order of magnitude variation in some elements, other regions showed very similar compositions over the range of elements analyzed. Deciding upon a standard count time would have to consider the value of increased discrimination against the reduction in sample throughput.

It has been mentioned that an analysis rate of approximately a thousand samples per month was desirable. This is equivalent to approximately 2000 seconds of analysis time per sample, allowing for interspersed handling and data transfer. Preliminary evaluation of counting statistics indicated that this would be insufficient to produce reliable source characterization on a broad level.

A compromise between discrimination efficiency and sample turnover was imposed, and the basic counting time for full source reference comparison was set at 4000 seconds. It is felt that this count time provides a good approximation of the isoprobe system's overall ability in source discrimination though at some expense of sample throughput. This rate allows some 20 samples per day to be analyzed and recorded under full-time operation, and is on the same scale as that achieved by Higashimura *et al.* (1981).

The system reproducibility obtained by this count time was determined by running a series of 10 non-consecutive 4000 second analyses on a standard piece of Taupo obsidian. The piece was arbitrarily included with source group material during the program of basic data collection. The raw data are given in Table 6 and the basic statistics in Table 7. The elements included are those which were found to occur in any source in detectable amounts. The Compton/Rayleigh ratio (CR) is the value of the 60 KeV inelastic/elastic scatter in the sample. It has been shown by Cormie and Nelson (n.d.) to have some discriminative value for volcanic glass.

Table 7 shows that while there is less than 20% variation (at one standard deviation) for the major barium peak and the CR ratio, lesser element peaks which at best are marginally detectable have a greatly increased proportionate uncertainty (see also Figure 9a-d). Nonetheless it was judged that the range of differences in these elements between various source groups would aid discrimination in some instances and that it was best to include them as reference elements. These data are

TABLE 6: RAW DATA FROM TAUPO REPRODUCIBILITY TEST.

ANALYSIS SYSTEM REPRODUCIBILITY DATA:						TAUPO STANDARD N=10		
Fe	Rb	Sr	Y	Zr	Ba	La	Ce	CR
.136943	.060510	.159236	.000000	.009554	4.797771	.007962	.130573	18.875431
.393082	.191824	.056604	.000000	.176101	5.761006	.011006	.154088	20.624149
.110063	.144654	.272013	.007862	.141509	5.790880	.234277	.311321	16.926647
.179856	.129496	.178657	.125899	.095923	4.350120	.000000	.103118	18.150818
.442073	.018293	.018293	.000000	.265244	5.269817	.025915	.231707	20.534023
.303371	.075843	.117978	.000000	.196629	4.023876	.089888	.266854	26.314722
.137615	.000000	.033639	.000000	.128440	5.126912	.201835	.192661	18.946903
.091644	.000000	.072776	.057951	.064690	4.711590	.270889	.336927	16.742332
.407855	.093656	.160121	.087613	.277946	4.978852	.000000	.268882	24.728394
.253264	.067885	.118799	.010444	.271540	4.523499	.139687	.362924	19.030254

TABLE 7: REPRODUCIBILITY RESULTS OF 10 NON-CONSECUTIVE ANALYSES OF TAUPO STANDARD SAMPLE

VARIABLE= FE				VARIABLE= ZR			
MEAN	=	.25 +-	.04	MEAN	=	.14 +-	.03
STANDARD DEVIATION	=	.13 +-	.03	STANDARD DEVIATION	=	.09 +-	.02
SKEWNESS(G1)	=	.31 W1=	.54	SKEWNESS(G1)	=	-.14 W1=	.25
KURTOSIS(G2)	=	1.51 W2=	-1.25	KURTOSIS(G2)	=	1.89 W2=	-.75
VARIABLE= RB				VARIABLE= BA			
MEAN	=	.08 +-	.02	MEAN	=	4.93 +-	.18
STANDARD DEVIATION	=	.06 +-	.01	STANDARD DEVIATION	=	.58 +-	.13
SKEWNESS(G1)	=	.33 W1=	.56	SKEWNESS(G1)	=	.13 W1=	.22
KURTOSIS(G2)	=	2.12 W2=	-.45	KURTOSIS(G2)	=	2.10 W2=	-.47
VARIABLE= SR				VARIABLE= LA			
MEAN	=	.12 +-	.02	MEAN	=	.10 +-	.03
STANDARD DEVIATION	=	.08 +-	.02	STANDARD DEVIATION	=	.11 +-	.02
SKEWNESS(G1)	=	.50 W1=	.87	SKEWNESS(G1)	=	.51 W1=	.88
KURTOSIS(G2)	=	2.57 W2=	.16	KURTOSIS(G2)	=	1.65 W2=	-1.06
VARIABLE= Y				VARIABLE= CE			
MEAN	=	.03 +-	.01	MEAN	=	.24 +-	.03
STANDARD DEVIATION	=	.05 +-	.01	STANDARD DEVIATION	=	.09 +-	.02
SKEWNESS(G1)	=	1.24 W1=	2.14	SKEWNESS(G1)	=	-.09 W1=	.16
KURTOSIS(G2)	=	3.00 W2=	.73	KURTOSIS(G2)	=	1.73 W2=	-.96
VARIABLE= CR				VARIABLE= CR			
MEAN	=			MEAN	=	20.09 +-	1.00
STANDARD DEVIATION	=			STANDARD DEVIATION	=	3.16 +-	.71
SKEWNESS(G1)	=			SKEWNESS(G1)	=	.97 W1=	1.68
KURTOSIS(G2)	=			KURTOSIS(G2)	=	2.75 W2=	.40

a fair measure of the analytical uncertainty involved with this technique in the present facility.

Perhaps the most significant finding at this stage of the investigation is the rather limited sensitivity that has been achieved with this particular application of the  $^{241}\text{Am}$  SEFA technique. A minimum detection limit of some 30 - 50 ppm, with up to 100% variance (at one standard deviation) at that level, will greatly impede the ability of the system to differentiate some sources (see for example, Tables 2 and 3, and Ward 1972: Appendix 3.2). Given that the variance has been measured using the same sample, and that the particular specimen was prepared with a flat, smooth surface - in short, an ideal analyte - the associated error that will be incurred with multiple source samples may only be expected to increase. Clearly, the level of applicability of this technique will be defined by the minimum detection limit that has been achieved.

Despite shortcomings, some order-of-magnitude differences could be identified between sources. The subsequent application of SEFA to the analysis of New Zealand and Oceanic obsidians was aimed at specifically identifying these regions.

#### SOURCE GROUP ANALYSIS

Having established a method of quantifying the spectra, a program of analysis of the obsidian reference collection held by the Otago Archaeometry Laboratory was initiated. The Oceanic sources represented are: Rapanui (3 sites), Pitcairn Island (1 site), Puu Waawaa (1 site), Tafahi (1 site),

Kermadec Islands (2 sites), Banks Island Group (2 sites), Talasea (1 site), Fergusson Island (1 site) and Lou Island (1 site). A selection of Mauna Kea (Hawaii) basalt was also included in this group for reference. The New Zealand obsidian sources examined were derived from the reference collection assembled by Ward (1972), including samples of Canterbury pitchstone and Otago 'glass'. The Mayor Island material was supplemented with additional samples collected by the author. All samples were analyzed for a minimum of 4000 seconds. Where small sample size required the use of the 2mm collimator, 8000 second analyses were made.

Sample preparation was minimal and entailed no more than washing in technical grade ethanol and distilled water. This was applied to minimize the possibility of any surface contamination which might have occurred during storage. Surface textures varied, as would be expected with archaeological specimens, and while some samples were ground flat to facilitate maximum target surface and mounting ease, others were analyzed on raw flaked surfaces. As evidenced by the texture experiments, the effects of sample surface texture are minimal within the overall sensitivity achieved by the technique.

Additionally, samples were analyzed in thicknesses greater than 3mm where possible to reduce sample thickness effects to proportionate fluorescence response. This factor was shown in the thickness tests (Figures 10a-d and 11 a-d) to alter relative peak heights between low and high-Z elements, and while it was not anticipated that this in itself would hinder source characterization to a significant degree, a general minimum

sample thickness limit was imposed for analysis of source material.

#### SOURCE REGION EVALUATION

A representative catalogue of source group spectra is presented in Appendix A. The included overlays identify element and scatter peak regions. The raw data for the source localities examined are included in Appendix B. At the outset of this section, it should be noted that while the raw data for New Zealand obsidians have been retained in their original source locality groupings (following the 18 major regions established by Ward 1972) in Appendix B, some major groupings were made for all characterization and 'sourcing' procedures. Specifically, the sources of Rotorua, Taupo, Ongoroto and Maraetai have been grouped as Inland; the sources of Cooks Bay, Purangi, Hahei, Tairua, Maratoto and Waihi have been grouped as Coromandel; and Waiare and Pungaere have been grouped as Northland (the Northland source of Weta remains uncharacterized due to the lack of source samples). Great Barrier Island has been defined as a single source region (combining Awana and Te Ahumata) as have the sub-groups of Mayor Island, Huruiki, and Fanal Island. Canterbury pitchstone has been included in the reference source data as well as samples of unconfirmed provenience identified as Otago 'glass'.

Oceanic sources are presented as identified at the beginning of the previous section with Rapanui, the Kermadecs, and the Banks Island Group sources being considered as single source regions respectively. Mauna Kea basalt was retained as separate on both the basis of composition and petrologic



type.

The justification for these primary groupings is based upon the preliminary results obtained which reflect the quality of data being produced by the technique. For instance, the similarity of the Inland and Coromandel source regions to each other as well as between their composite localities is striking, both in the raw data and plotted spectra. Likewise, the high degree of similarity of the other grouped sources amongst their combined groups made them functionally indistinguishable with the present facility. Table 8 shows the element means and standard deviations for the working groups used in the characterization program. The values indicated are based on the raw data presented in Appendix B.

Cursory examination of Table 8 shows some broad similarities even beyond the groupings already performed. These reflect macro-similarities of the sources related to their location in terms of plate tectonics. The main division of obsidians is between so-called oceanic and circum-oceanic types (see for example, Smith *et al.* 1977:177-189; and Johnson 1979). Those obsidians which contain high proportions of barium and much smaller amounts of Fe, Rb, Sr, Y, Zr, La, and Ce are typically circum-oceanic as analyzed in this study. The volcanic glasses of Pitcairn, Rapanui, and Hawaii are oceanic, and show the characteristic abundance of many elements besides barium. Tafahi and Kermadec types appear transitional to circum-oceanic, and Mayor Island/Northland show distinct oceanic affinities.

## A BASIC CHARACTERIZATION TEST

To determine the degree of separation between sources that can be discerned from these data, it was decided to employ a simple test of element overlap. Most recent sourcing studies of New Zealand and Oceanic obsidians have been concerned with complex measures of 'similarity' between sources and unknowns (see for example, Ward 1972:161; Duerden *et al.* 1979; McCallum *et al.* 1979; Leach and Warren 1981; Leach and Manly 1982) which employ either the  $D^2$  statistic of Mahalanobis (1930) and Rao (1948) or as with McCallum *et al.*, derivation of the mean Euclidean distance (M.E.D.).

In light of the data generated by the facility, it was felt that a more basic test of source separation was required, such as can be determined by attempts at source rejection. Ward (1977) concisely expressed the fundamental difference of this approach with measures of similarity as they specifically apply to archaeological problems of sourcing. He summarizes that,

"geochemical or petrographic similarity is insufficient argument for a similar source; but characterizational dissimilarity is a good argument for the difference in geographic source. In other words, the 'identification' of sources of material can be made suggestively but not absolutely; confidence in such tentative identification is gained from rejection of the other possible identifications that can occur within a universe of possibilities which is sometimes difficult to delimit"

(1977:192).

It was with this intention that a method of screening

which tried to reject an unknown spectrum as having been potentially derived from any given source group in the reference configuration was used. This more closely follows a test applied by Nelson *et al.* (1975) and refined by Cormie and Nelson (n.d.).

The basis for the screening strategy is to compare the value generated for each element of the unknown spectrum against the 2 and 3 standard deviation dispersion value for that element in a given source. If the value of the unknown exceeds or is below  $\pm 2$  or  $3\sigma$  for that element in the compared source, then it is rejected at that level of certainty (i.e. 95 or 99%). By reference to Table 8 it is obvious that a fair degree of overlap exists between many of the sources at the 2 and  $3\sigma$  level. The chances of rejecting the majority of Inland spectra as having been derived from the Coromandel source region are very small indeed with this technique. A sobering point, for archaeologists interested in unambiguously identifying the originating source of an artefact, is that for many Oceanic and New Zealand sources the ability to unequivocally reject either a given source sample as having been derived from the other's region can be extremely limited.

In an attempt to improve this screen, an additional set of ratios between certain elements was generated in the hope that this would increase the ability to reject inappropriate sources. As mentioned in the beginning of this chapter, some source spectra record zero values for elements which might otherwise be quite suitable denominators. For this reason it was necessary to segregate the ratio tests applied to the

TABLE 8: ELEMENT MEANS AND STANDARD DEVIATIONS FOR THE  
REFERENCE SOURCE MATRIX.

SOURCE GROUP ELEMENT MEANS AND STANDARD DEVIATIONS

N	(MEAN VALUES)	Fe	Rb	Sr	Y	Zr	Ba	La	Ce	C/R
9	NORTHLAND	.92	.54	.08	.29	2.32	.08	.65	1.38	17.64
62	MAYOR ISLAND	1.00	.22	.08	.16	1.40	.25	.58	1.03	19.60
9	FANAL ISLAND	.20	.17	.19	.08	.16	2.03	.18	.25	21.44
30	HURUIKI	.31	.24	.18	.14	.21	3.25	.18	.40	22.00
13	GREAT BARRIER IS.	.37	.16	.10	.10	.10	3.10	.20	.40	20.66
26	COROMANDEL PENIN.	.33	.11	.11	.08	.14	5.38	.22	.29	19.90
56	INLAND	.24	.17	.15	.12	.18	5.11	.23	.33	21.29
8	TALASEA	.13	.09	.20	.06	.10	3.05	.14	.18	20.97
8	LOU ISLAND	.44	.16	.13	.07	.44	5.07	.11	.44	20.63
5	FERGUSSON ISLAND	.30	.13	.08	.04	.38	5.45	.09	.40	18.77
13	BANKS GROUP	1.00	.15	.11	.04	.24	5.73	.13	.39	19.69
7	PITCAIRN ISLAND	1.23	.06	.06	.10	.72	9.50	.25	.81	18.89
8	TAFahi	1.41	.05	.29	.05	.10	2.29	.05	.12	17.82
8	KERMADEC IS.	1.23	.10	.15	.10	.08	1.72	.09	.14	19.06
11	RAPANUI	.66	.07	.07	.22	1.20	2.50	.31	.96	17.85
10	PUUWAAWAA HAWAII	.98	.18	.10	.10	1.18	2.03	.36	.87	19.06
8	MAUNA KEA HAWAII	4.35	.10	.51	.04	.42	2.93	.23	.61	14.76
8	CANTERBURY PITCH.	3.23	.10	.25	.10	.55	5.78	.57	1.19	14.83
8	OTAGO GLASS	.10	.10	.35	.14	.18	2.37	.19	.40	12.81
N	(S.D. VALUES)	Fe	Rb	Sr	Y	Zr	Ba	La	Ce	C/R
9	NORTHLAND	.25	.12	.04	.09	.42	.04	.20	.27	1.60
62	MAYOR ISLAND	.50	.11	.04	.08	.36	.13	.22	.31	2.74
9	FANAL ISLAND	.14	.13	.08	.10	.14	.49	.13	.16	3.20
30	HURUIKI	.20	.13	.09	.08	.16	.68	.14	.16	3.80
13	GREAT BARRIER	.23	.10	.05	.05	.09	.75	.12	.16	3.60
26	COROMANDEL PENIN.	.16	.08	.08	.05	.09	.99	.12	.16	3.05
56	INLAND	.12	.09	.08	.07	.09	1.09	.12	.17	3.16
8	TALASEA	.14	.09	.10	.03	.10	.73	.10	.18	5.54
8	LOU ISLAND	.17	.08	.07	.08	.14	.79	.10	.12	2.81
5	FERGUSSON ISLAND	.20	.08	.07	.05	.14	.36	.13	.16	2.10
13	BANKS GROUP	.25	.09	.09	.02	.15	1.26	.13	.20	2.37
7	PITCAIRN ISLAND	.33	.08	.09	.10	.29	1.41	.13	.24	3.91
8	TAFahi	.59	.05	.05	.05	.05	.39	.05	.08	1.23
8	KERMADEC IS.	.36	.07	.07	.05	.09	.49	.11	.07	2.14
11	RAPANUI	.12	.04	.04	.11	.35	.60	.09	.23	1.72
10	PUUWAAWAA HAWAII	.26	.09	.05	.06	.30	.44	.18	.29	3.40
8	MAUNA KEA HAWAII	.79	.06	.19	.02	.15	.58	.16	.23	1.46
8	CANTERBURY PITCH.	.78	.10	.22	.06	.29	1.20	.29	.28	1.44
8	OTAGO GLASS	.08	.05	.14	.09	.16	.40	.19	.14	1.00

unknown spectrum depending upon how it had survived the initial screen. For instance, while the other sources display reasonable barium values, it is frequently measured as zero in Mayor Island and Northland spectra. While this in itself is a good way to discriminate Mayor Island and Northland from all other sources (a major success of this technique), it is useless to proceed to attempt in identifying the spectrum as Mayor Island or Northland by taking a ratio over the barium peak. For this reason, different ratios were set up to be applied to the unknown spectrum depending upon how it survived the primary element screen. These ratios (with the associated standard deviation ranges applied to each) are shown in Tables 9 and 10.

Note that on the basis of the initial barium test that is made (Table 8), no known spectrum which survives being rejected from either Mayor Island or Northland on the basis of element values can possibly be anything else but either Mayor Island or Northland.

As the screen is actually applied within the program, the unknown spectrum has the nine window values generated for it, and then each reference source in turn is compared element by element with the values of the unknown. If any value of the unknown spectrum is beyond the range being tested, that source is rejected and the program moves on to the next source in the reference matrix. Once completed, the program retains the identity of those sources which have not been rejected at the  $2\sigma$  level and then proceeds to compare the ratio values in Table 9 or 10 for just those sources which have not been

TABLE 9: SOURCE GROUP RATIO MEANS AND STANDARD DEVIATIONS  
FOR MAYOR ISLAND AND NORTHLAND.

SOURCE GROUP RATIO MEANS AND STANDARD DEVIATIONS			
MEAN VALUES	Fe/Zr	Rb/Zr	(Compton/Rayleigh)/Zr
NORTHLAND	.36	.22	7.83
MAYOR ISLAND	.61	.10	14.27
S.D. VALUES	Fe/Zr	Rb/Zr	(Compton/Rayleigh)/Zr
NORTHLAND	.06	.03	1.71
MAYOR ISLAND	.31	.09	3.97

TABLE 10: SOURCE GROUP RATIO MEANS AND STANDARD DEVIATIONS  
CONTINUED.

## SOURCE GROUP RATIO MEANS AND STANDARD DEVIATIONS

MEAN VALUES	Fe/Ba	Zr/Ba	(Compton/Rayleigh)/Ba
FANAL ISLAND	.12	.12	10.39
HURUIKI	.13	.10	7.85
GREAT BARRIER	.14	.08	7.21
COROMANDEL PENIN.	.06	.04	4.06
INLAND	.06	.04	4.35
TALASEA	.09	.06	7.40
LOU ISLAND	.09	.10	4.71
FERGUSSON ISLAND	.06	.07	3.46
BANKS GROUP	.16	.04	3.59
PITCAIRN ISLAND	.13	.08	2.01
TAFahi	.80	.06	7.89
KERMADECS	.73	.06	12.54
RAPANUI	.26	.38	8.30
PUUWAAWAA HAWAII	.49	.60	9.92
MAUNA KEA HAWAII	1.50	.14	5.25
CANTERBURY PITCH.	.57	.10	2.71
OTAGO GLASS	.09	.07	5.61
S.D. VALUES	Fe/Ba	Zr/Ba	(Compton/Rayleigh)/Ba
FANAL ISLAND	.08	.06	1.95
HURUIKI	.07	.05	1.96
GREAT BARRIER IS.	.09	.04	1.66
COROMANDEL PENIN.	.04	.02	.88
INLAND	.04	.02	1.03
TALASEA	.06	.03	2.40
LOU ISLAND	.03	.02	.85
FERGUSSON ISLAND	.04	.03	.45
BANKS GROUP	.06	.03	.84
PITCAIRN ISLAND	.04	.03	.43
TAFahi	.29	.03	.93
KERMADECS	.24	.06	3.77
RAPANUI	.08	.10	1.85
PUUWAAWAA HAWAII	.12	.13	3.10
MAUNA KEA HAWAII	.18	.04	1.33
CANTERBURY PITCH.	.08	.05	.66
OTAGO GLASS	.05	.05	1.25

rejected after the first screen. Clearly there is little value in testing against a source already rejected on previous grounds.

With the  $2\sigma$  screen applied and results recorded, those sources which could not be rejected are recorded on disk and printed out. The process is then repeated with a 3 standard deviation dispersion being calculated for each of the source elements and compared with the unknown. At the  $3\sigma$  level one can expect a greater degree of overlap to occur. This is verified by the results obtained.

To test the degree of overlap (or conversely 'separation') found between the various sources by this technique, the source spectra were run through the screening procedure. The results of the  $2$  and  $3\sigma$  tests are presented in Tables 11 and 12. Note that the intersection of a source with itself records the total number of source spectra which could not reject it's own source and at least one other.

#### SOURCE SCREEN RESULTS

As an overview of the results obtained, each source has been considered individually. The proportion of other sources which could not be rejected, in addition to the actual source of that spectrum, have been calculated and the list presented in Appendix C. This information fills out the data presented in Tables 11 and 12, and helps to indicate the 'nearest neighbour' generally associated with a given source spectrum by this technique at either level of uncertainty.

A point to be emphasized is that at both  $2$  and  $3\sigma$ , each



TABLE 11: 2 SIGMA DISTRIBUTIONS OF SOURCE DISCRIMINATION  
BY PROGRAM SCREEN.

	n	SOURCE ONLY	NORTHLAND	MAYOR ISLAND	FANAL ISLAND	HURUIKI	GREAT BARRIER	COROMANDEL	INLAND	TALASEA	LOU ISLAND	FERGUSSON ISLAND	BANKS ISLAND GRP	PITCAIRN ISLAND	TAFAHI	KERMADECS	RAPANUI	PUU WAAWAA	MAUNA KEA	CANTERBURY PITCHSTONE	'CLASS', OTAGO	
NORTHLAND	9	9																				
MAYOR ISLAND	62	62																				
FANAL ISLAND	9	6			3	3	2			1												
HURUIKI	30	9			12	21	18		2	15												
GREAT BARRIER	13	0			3	12	13		2	3												
COROMANDEL	26	5				7	7	21	16	4	2	5	2									
INLAND	56	4				21	17	47	52	23	4	7										
TALASEA	8	3			3	3	1	1	2	5												
LOU ISLAND	8	3				5	1				5											
FERGUSSON ISLAND	5	1						1			2	4	1									
BANKS ISLAND GRP	13	12						1			1	1	1									
PITCAIRN ISLAND	7	7																				
TAFAHI	8	6													2	2						
KERMADECS	8	7													1	1						
RAPANUI	11	5															6	6				
PUU WAAWAA	10	9															1	1				
MAUNA KEA	8	8																				
CANTERBURY PITCHSTONE	8	8																				
OTAGO 'CLASS'	8	6								2												2

	n	SOURCE ONLY	NORTHLAND	MAYOR ISLAND	FANAL ISLAND	HURUIKI	GREAT BARRIER	COROMANDEL	INLAND	TALASEA	LOU ISLAND	FERGUSSON ISLAND	BANKS ISLAND GRP	PITCAIRN ISLAND	TAFahi	KERMADECS	RAPANUI	PUU WAAWAA	MAUNA KEA	CANTERBURY PITCHSTONE	OTAGO 'GLASS'	
NORTHLAND	9	9																				
MAYOR ISLAND	62	62																				
FANAL ISLAND	9	1			8	8	4		1	5						2						
HURUIKI	30	1			25	29	24	5	10	21	5		2			4						
GREAT BARRIER	13	0			9	13	13	5	5	9	2	1	1			7						1
COROMANDEL	26	0				18	18	26	23	16	15	19	15	3								
INLAND	56	0			5	46	46	55	56	43	36	30	12	1								
TALASEA	8	0			5	8	6	3	4	8						3						
LOU ISLAND	8	0				7	2	2	2	3	8	2	4			8						
FERGUSSON ISLAND	5	0				2	1	3	3	1	5	5	3									
BANKS ISLAND GRP	13	1				4	6	3		1	6	4	12	5								
PITCAIRN ISLAND	7	4												3	3							
TAFahi	8	1														7	6			2		
KERMADECS	8	5				2	2									1	3					
RAPANUI	11	2															9	9				
PUU WAAWAA	10	8															2	2				
MAUNA KEA	8	8																				
CANTERBURY PITCHSTONE	8	8																				
OTAGO 'GLASS'	8	2			3	6	2		1	3												6

TABLE 12: 3 SIGMA DISTRIBUTION OF SOURCE DISCRIMINATION  
BY PROGRAM SCREEN.

of the source spectra have always been unable to reject their own source group. That is, 100% of spectra which defined each source group are unable in turn to reject that portion of the comparison matrix. This situation would not have occurred if the strict standard deviations as calculated were used in the source matrix. The reason is that in calculating the mean value and standard deviation of a normally distributed group of values, a few of those values may lie outside the  $2\sigma$  or  $3\sigma$  range of that group. It is held to be untenable in this exercise that any source spectra which created a particular set of matrix values should itself be able to reject those values.

To prevent this occurrence, the pertinent standard deviation values were modified so that all spectra which contributed to a particular source matrix set would be unable to reject that matrix at  $2\sigma$ . Invariably this entailed increasing the  $\sigma$  value for those matrices where a contributing source spectrum would have rejected its own source. As all spectra would be 'caught' at the  $2\sigma$  level, they would therefore always include their own source at  $3\sigma$  as well.

In effect, spectra which do reject a given source matrix at either the  $2\sigma$  or  $3\sigma$  level are slightly further away from the group mean than the  $\sigma$  value indicates. The result was a reduction in the ability of the screen to separate sources, but with the advantage of always including source spectra with their own matrix. An added justification for this artificial 'widening' of the dispersion range is that those samples analyzed may be considered by and large to be ideal specimens,

generally displaying minimum variation in surface texture and thickness within a specified range. One would not expect to be so fortunate with archaeological specimens. This added robustness should reduce the possibility of an archaeological specimen subsequently rejecting its own source upon analysis.

In evaluating the relative success or failure of the screen and thereby the SEFA technique, there are some general observations to be made. Of particular note is the strong clustering and overlap between most of the New Zealand obsidians and with some Oceanic sources. This is most readily apparent in Table 12 where  $3\sigma$  values have been applied. Amongst the non-Northland/Mayor Island New Zealand obsidians the best separation at  $2\sigma$  was achieved by the Fanal Island source (Appendix C). Even here, however, only 67% of the Fanal Island spectra were unambiguously identified.

Huruiki was somewhat less successful, being unequivocally identified in only 30% of its source spectra. Great Barrier, Coromandel and Inland fared even worse in terms of being uniquely partitioned as demonstrated in Appendix C. While Great Barrier spectra are most frequently unable to reject Huruiki as well as their actual source (at least retaining a Great Barrier region affiliation), the Coromandel and Inland spectra were often associated with Huruiki and Great Barrier sources in addition to rarely being able to discriminate between themselves at the  $2\sigma$  level. Of the Oceanic sources associated with New Zealand spectra by this method, the New Britain source of Talasea figures most prominently.

Indeed Talasea spectra are unable on occasion to reject Inland, Coromandel and Great Barrier sources as well as Huruiki and Fanal Island. The Coromandel and Inland spectra are also periodically unable to reject the Admiralties source of Lou Island, the D'Entrecasteaux Group source of Fergusson Island or the Banks Island Group sources. Conversely, in Oceania the Lou Island source spectra sometimes cannot reject Huruiki and Great Barrier matrix values while the Banks Island Group - Fergusson Island - Lou Island spectra are intermittently grouped between themselves (as well as with the odd Coromandel inclusion).

Better separation is achieved at the  $2\sigma$  level by Pitcairn Island material (100%), Tafahi (75%) and the Kermadec Islands (87%) with all of these spectra being able to reject the whole of New Zealand sources. Rapanui obsidian shows some affinities with the Hawaiian Puu Waawaa (and to a lesser extent the reverse), while the Mauna Kea basalt spectra remain uncompromised as do those of the Canterbury pitchstone. The unprovenanced Otago 'glass' is unable to reject Talasea for 25% of its spectra though Talasea spectra are all able to reject the Otago reference group.

The average separation achieved by source spectra deteriorates markedly at the  $3\sigma$  level. Notable exceptions are the Mauna Kea basalt and Canterbury pitchstone source spectra which remain uniquely separated even at  $3\sigma$ .

A result of the screen not yet discussed is its unambiguous separation of the Northland and Mayor Island spectra from all other sources in the reference group including between

themselves at both the 2 and 3 $\sigma$  levels. While the success of the screening matrix is gratifying, it is not without some concern about the basis on which Northland obsidian along with Mayor Island was separated from all other sources.

Reference to Tables 2 and 3 (after Leach and Warren 1981) indicates barium values among the 23 elements measured for each of the 33 sources. According to the NAA data, the Northland sources have been determined to contain nearly 500 ppm of barium for each of Waiare and Puŋaere. This is roughly equivalent to that of the NBS standard 610 wafer as represented in Figure 12a. It is the finding of this study that such is almost certainly not the case for the Waiare and Pungaere obsidians (combined here as Northland).

Appendix A and Appendix B support the finding of low barium for the Northland source region. Indeed, the compiled barium values in Table 3 are even lower for the Northland group than for Mayor Island (though this could be a function of the smaller Northland sample size, which is possibly a skewed representation).

Upon discovery of this anomaly, the Northland samples were re-examined against the possibility of system error. During the same analysis session, samples of Huruiki and Rapanui obsidian were also examined. These latter sources have NAA barium values on the same order as those which were reported for Waiare and Pungaere. It was found that while the Huruiki and Rapanui samples were in mutual agreement and consistent with NAA and SEFA, the Northland material confirmed earlier results: the barium concentrations of these obsidians.

is at the very limit of minimum system sensitivity - on the order of 50 ppm. It must be emphasized that all other reported NAA results are in general agreement with SEFA data.

An explanation of this divergence is not easily made. If the NAA study was not suited to barium measurement, it might be expected that other differences with the present SEFA programme would emerge as well, but this has not been found. A more recent analysis of New Zealand obsidians employing the same facility has not, however, included barium measurements (Chidgey 1981). Barium is a clearly detected element by the isoprobe unit and is not subject to overlap or masking. It is advised therefore that a much reduced barium value be allotted to the Northland group. Re-examination of the Northland material by a highly quantitative technique is required so that an accurate determination can be made.

This is especially important for those techniques which measure the barium L series transitions (as, for example, with PIXE) in that the  $Ti K_{\alpha}$  emissions overlap with these peaks. Titanium values are reported in PIXE analysis (Duerden *et al.* 1980:450; Bird *et al.* 1981a:36). The proportionate contribution of the relatively weak barium peaks must be closely estimated to achieve accurate determination of both elements. The advantage of Ba  $K_{\alpha}$  fluorescence is well illustrated by this point.

In summary, it was demonstrated that a reasonable degree of success has been achieved in the development and application of an automated SEFA facility. The particular strengths of the analysis technique within New Zealand are in the iden-

tification of Mayor Island and Northland obsidians, with a reduced ability to differentiate the remaining sources. Canterbury pitchstone as well has been uniquely identified.

Amongst the Oceanic obsidian sources there are additional successes, including clear separation of Central and Eastern Oceanic source spectra from New Zealand types.

As a case study of the facility, it was decided to apply SEFA to an archaeological assemblage which might best utilize the strengths of this technique in the differentiation of Mayor Island and Northland obsidian. Chapter Five will evaluate the analysis of the Mount Camel site material, and its implications for the further application of the technique.



## CHAPTER FIVE

## ARCHAEOLOGICAL APPLICATION OF THE ISOPROBE FACILITY

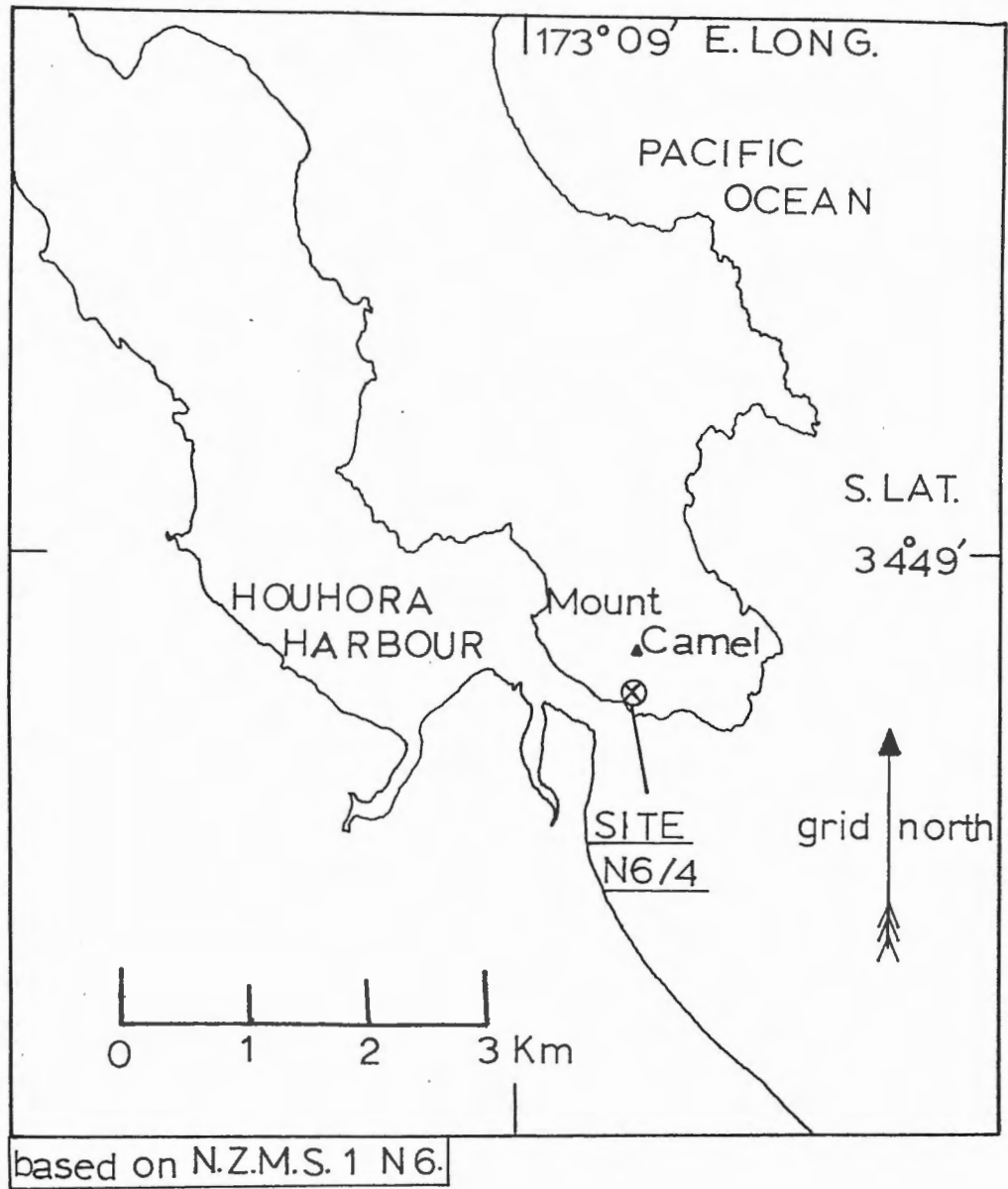
## THE MOUNT CAMEL SITE

Based on the conditional success of the isoprobe facility in discriminating New Zealand and Oceanic obsidians, an archaeological application of the technique was the next step. Within New Zealand, the SEFA technique has shown its greatest strength in identifying Mayor Island and Northland obsidians. Therefore an application which exploits this ability is appropriate. To this end, the obsidian assemblage of the Houhora or Mount Camel site (N6/4) was examined.

Situated on a low coastal platform at the mouth of Houhora Harbour, the site is located at the foot of Mount Camel (see Maps 2 and 3). The two radiocarbon dates associated with the lower Archaic occupation are A.D. 1154  $\pm$  56 and A.D. 1260  $\pm$  44 (Shawcross 1972:603-605). The excavation and site analysis have been discussed by Shawcross and Roe (1966) and Roe (1967) and the considerable lithic assemblage was studied by Best (1975; 1977).

## THE ORIGINS OF MOUNT CAMEL OBSIDIAN: IMPLICATIONS

The obsidian component of the assemblage is extensive, with some 3,150 flakes recovered (Best 1975:22). These were described by Roe as being comprised mostly of "primary flakes without secondary retouch. Some of the larger obsidian flakes had secondary flaking along the edges, but this could have resulted from use. One obsidian core . . . was excavated



MAP 3: Detail of Mount Camel site location (after Shawcross 1972).

from Cl3" (1967:63).

It was suggested by Best that based on the identification of stone resources utilized at the site, close ties with the Coromandel region existed (Best 1975:24-25). In his analysis of the obsidian, Best sorted the recovered flakes according to colour in transmitted light, i.e., as 'green/not-green'. Of these, 2,990 were classified as 'green'.

Best notes that obsidian identification on the basis of colour has been shown to be somewhat unreliable (citing Leach and Anderson n.d., which was later published as Leach and Anderson 1978). Approximately 4.2% of the obsidian designated as Mayor Island on the basis of its green colour (in the Palliser Bay study), was determined by XRF to actually have been derived from Northland. In an attempt to limit misclassification, Best therefore applied an additional test of specific gravity (after Reeves and Armitage 1973) to his 300 specimen grab sample of green flakes. Oddly enough, Reeves and Armitage state that Northland and Mayor Island obsidian, while separable from all other New Zealand sources on the basis of density, are separable from each other simply "by the fact that all known Mayor Island obsidian shows a greenish colour in transmitted light" (1973:565). That is, Reeves and Armitage suggest that Mayor Island and Northland obsidians are best separated not on the basis of specific gravity, but on the basis of colour!

Nonetheless, Best concluded after tests of specific gravity and colour that 93.5% of the flakes were derived from Mayor Island material, 1.5% were derived either from Mayor

Island or Northland (Kaeo), and 5% from either Great Barrier, Whitianga (Cooks Bay, Ward 1972:110), Taupo or Huruiki. His opinion at the time was that it was "reasonable to expect that results obtained from the above procedures will be confirmed by more sophisticated analysis, such as X.R.F. and trace element study" (Best 1975:23).

Davidson (1982:19) argues against Best's cultural interpretation of the lithic evidence, noting that the presence of local Northland material in the site possibly indicates a more general geographic affiliation. This is in contrast to the interpretation suggested by Shawcross (1972:611) of the Mount Camel site representing the first settlement of a virgin region. Davidson proposes that Mount Camel is probably far from unique in Northland, and instead represents a typical early Polynesian settlement in the far north - the summer hunting-fishing camp (Davidson 1982:19). Artefacts of material culture not known from the Coromandel, yet present at Mount Camel (such as biperforate lure points and broad tattocing chisels) support this argument.

While Davidson does not deny that regular contact with more southern regions existed (as is most certainly reflected in the Tahanga basalt and Nelson meta-somatized argillite, see Best 1975:17-21, 26 ff.), she suggests that the culture at Mount Camel was more distinctly that of a northern group than Best has allowed. She concludes that "influences and ideas probably flowed both ways" and that "the end result was a society and culture which had distinctive features, but which shared many characteristics with other regions"

(Davidson 1982:26).

Were a study of the Mount Camel obsidian to confirm Best's identifications based on colour and specific gravity, Davidson's interpretation (which accepts Best's lithic allocations) would not necessarily be compromised because of the additional cultural features to which she refers. However, if an analysis were to produce results which were significantly different from those assigned by Best, a changed perspective of the site may be gained, and the argument for more substantial northern affinities strengthened. Thus, in light of the potential value of such a study, a research program of isoprobe analysis was undertaken.

#### SAMPLING THE ASSEMBLAGE

As noted at the opening of this chapter, the obsidian assemblage of Mount Camel is represented by over 3,000 flakes. Analysis of the total assemblage would be within the capabilities of the system (albeit requiring nearly five months running under present running conditions), but would also be a misuse of facility time. Secure sampling methods have been developed for large populations and were justifiably invoked here. The first problem of analysis, therefore, was to define the null hypothesis to be tested. From this statement the sample size required to test its premise was derived.

Observations of workers involved with obsidian characterization in New Zealand indicate that quite possibly the percentage of Northland obsidian present in the Mount Camel assemblage is different from the 1.5% assigned by Best -

perhaps as high as 30% (Leach pers. comm. 1982). If so, this would indicate a much more generalized awareness of the stone resources by the inhabitants of the Mount Camel site. Concomitantly, the argument for an identifiably northern culture (which had developed this awareness through time) would gain support.

The null hypothesis may therefore be stated as: "The proportion of Northland/not-Northland obsidian identified by the isoprobe analysis is not significantly different (within 95% certainty) from that determined by Best, i.e., 1.5% to 98.5%". The sample size required to test this hypothesis can be generated accordingly. However, if it is suspected that Northland obsidian could be as high as 30%, and therefore that 95 percent confidence limits are required for sampling this proportion, the sample size will change. This is demonstrated by Snedecor and Cochran (1980:441-443, Formula 21.6.2) where  $n$  (the sample required) is generated by:

$$n=4(p)(q)/L^2$$

where  $p$  equals the proportion of one trait (i.e., Northland),  $q$  equals the proportion of not- $p$  (i.e., not-Northland) and  $L$  equals the confidence limit required (e.g.  $\pm 5\%$ ). If the proportion to be determined is 1.5% to 98.5%, within 95% certainty, the sample size required is:

$$n=4(1.5)(98.5)/25$$

or 24 flakes. However, if the population to be tested is 30% to 70%, the sample size increases to:

$$n=4(30)(70)/25$$

or 336 flakes to be randomly sampled in order to identify

this proportion within 95% confidence limits. Snedecor and Cochran note, however, that where the calculated sample exceeds 10% of the population  $N$  being tested, a revised estimate of  $n$  can be made which takes proper account of the finite population where:

$$n' = n / (1 + n/N)$$

or

$$n' = 336 / (1 + 336/3150)$$

(ibid.).

In other words, with a finite population of 3,150 flakes, a random sample of 303 is needed to adequately test the 30% versus 70% estimation.

A further modification can be made to this estimate because of the fact that the Mount Camel site represents two major occupation phases. The point being considered here is whether or not the Lower, Archaic population was exploiting a higher percentage of the Northland source. Roe (1967:96) states that "the layer under the turf, layer 2a contains a few artefacts disturbed by cultivation . . . The layers below 2a contained the assemblage . . . which is typical of Maa-hunter assemblages". For this reason, the upper agriculturally disturbed layers may be excluded from the sample population. The portion of the recovered assemblage which should be sampled therefore, is that below the agricultural zone; layers 2b and below.

Observation of the Mount Camel obsidian collection indicated that perhaps a few hundred flakes are associated with level 2a and above. This therefore reduces the estimated

sample size required to test the 30/70 hypothesis. Nevertheless, because of the relative efficiency of the isoprobe system, and as a slightly more rigorous test of the system's flexibility, it was felt that a 10% sample of the total assemblage (approximately 300 pieces) drawn from below the 2a layer would not be an unreasonable fraction to take. Three hundred flakes would satisfy the theoretical sampling requirement as well as being directly comparable to Best's grab sample evaluation.

The method of sample selection was to lay out the Mount Camel obsidian assemblage according to square and separated by level. The flakes were then selected on the basis of randomly generated numbers. The excavation grid layout was adopted except that the north-south co-ordinates were changed from letters to numbers during the selection process. A random numbers table was employed (Thomas 1976:482-486, Table A.2) and samples located by allocating portions of five-digit groups.

The first two digits defined the north-south co-ordinate, the second two digits the east-west co-ordinate, and the last number (either odd or even) determined whether the upper or lower half of the levels below 2a were to be sampled. The number of levels below 2a varied depending upon square. Some squares contained a 2b layer only, while others went to level 4, which was defined as "natural" (Roe 1967:6). The final flake selection was made as a grab sample from the remaining one or two level 'clump'.

It is possible that some limited sampling bias of the



levels below 2a occurred with this method (in vertical representation) but it is not considered serious within the context of the problem at hand.

#### ARTEFACT SPECTRUM ANALYSIS

During the course of the present characterization research, it was discovered that some source spectra were quite distinctive upon visual inspection. This phenomenon has been recognized by other workers. For instance, in a series of preliminary studies designed to determine the feasibility of sourcing various New Zealand lithic materials using a low power TEFA system, Leach (1977b) achieved some highly encouraging results.

Regarding the examination of argillites, Leach states that after "about 1 to 2 minutes of counting, the visual differences in the spectra are so striking that source allocation can be made without further ado" (1977b:10). In the analyses of indurated limestones, Leach found that "total spectrum shape is very distinctive in each case and may be matched by eye in the manner suggested for the argillites" (ibid.:12).

While less successful results from the analysis of cherts indicated that some form of simple mathematical manipulations were required for sourcing this lithic type, Leach concluded that for "the routine analysis of argillites and indurated limestones, simple visual inspection is all that is necessary for sources to be determined" (ibid.:18).

McCallum *et al.* (1979) made similar observations during

their TEFA analysis of obsidian. They state,

"Fortuitously the X-ray spectra of Mayor Island obsidians are so characteristic that flakes from this source can be identified by visual inspection of the pulse-height analyser display. As Mayor Island is by far the most common source of obsidian flakes in New Zealand archaeological sites, most samples do not in fact demand the detailed analysis described ..."

(McCallum *et al.* 1979:2).

Similarly, Mayor Island obsidian has proven itself distinct under isoprobe analysis, along with Northland material, and both of these sources produce visually unique spectra with the technique. Foremost is the lack of barium described in Chapter Four. Low barium content is a trait shared by Northland, and these sources may be immediately partitioned from all others examined after as little as two hundred seconds counting with the SEFA technique.

Differences between Mayor Island and Northland are not as visually blatant as the barium value discussed; but indeed, absolutely larger Rb, Y, and Zr peaks and a proportionately distinct Fe/Zr abundance easily separates Northland from the Mayor Island source. To securely determine the differences between these spectra on a visual basis, something on the order of 1000 to 2000 second count-times are required. Note that this is insufficient time to make any clear visual identification of spectra which are neither Northland nor Mayor Island.

Inspection of the Mount Camel assemblage therefore, provided a two-way examination for the analysis technique:

firstly, by securely establishing the identity of the green obsidian component in 2000 second counts; and secondly, by evaluating the ability of the facility to routinely and reliably analyze a large sample of archaeological material.

Samples were mounted on the standard perspex holders after being lightly washed in distilled water to remove any adherent surface dirt. Flakes too small to be mounted were not encountered, though on several occasions large fragments required more extensive use of the fuse wire to be secured. Where possible, care was taken to orient the flake in such a way that the flattest surface was presented for analysis. All flakes were analyzed however, and none rejected as being 'too rough' or otherwise unsuitable.

Brief descriptions of the flakes (approximate thickness, surface texture, matt or glassy matrix, and colour in transmitted light) were recorded in the analysis log along with the square and level from which each was obtained. Individual run numbers were assigned to each flake. The site designation, square and level were also entered into the computer as the literal component in program CHANGER and the run number assigned as the filename for the spectrum. Samples were automatically analyzed by program NIGHT with 2000 second collection times. Accumulated spectra were recorded onto disk as per normal operation (see Appendix D for raw data).

Due to the presence of a few 'over-sized' flakes, the maximum number of samples per sled run was approximately 45. Seven runs were made in total, over a period of 11 days. The turn-around time required to reload the sled was the major

cause for delay between runs. This is presently being rectified with the construction of a second sled that will permit sample mounting while analysis of another group is underway.

Collected spectra were inspected with program SCREEN in non-sourcing mode as a method of generating low count-time element values during visual inspection. Source identification was made visually, with allocations of either Mayor Island, Northland or 'other' being made. All non-green flakes were found to be other than Mayor Island or Northland material. Non-green flakes taken in the random sample were not assumed to be other than Mayor Island or Northland prior to analysis, though this was confirmed.

Colour could not be determined during the selection of artefacts and so no sampling bias of this sort could occur. The percentage of non-green flakes in the random sample was a good check of the overall sampling procedure as the total non-green component was actually determined by Best to be 5% (approximately 160 flakes) (Best 1975:22).

## RESULTS

In the section which dealt with sample size, the number of flakes to be sampled was derived from the initial estimation of the proportion of Northland/not-Northland obsidian being tested for. This ensured that a representative sample would be obtained within specified confidence limits as long as the sampling procedure was random.

Best's estimation of the number of 'grey' as opposed to

'green' flakes contained in the assemblage has been accepted as an accurate description. This level of colour distinction should be a reliably determined visual judgement. This is not considered to be the case where shades of colour, e.g., 'pale green', are involved. As no discrimination on the basis of colour was possible during the sampling procedure (all flakes appeared as dark and opaque), it would be expected that approximately 5% of the isoprobe sample would also be grey. The results obtained are shown in Table 13.

TABLE 13: PROPORTION OF GREY TO GREEN OBSIDIAN IN ISOPROBE SAMPLE

	Grey	Green	Total
Number of flakes	11	289	300
% of sample	4	96	100

The question then asked was whether or not the proportion of grey obsidian obtained in the isoprobe sample was significantly different from the population proportion determined by Best. This was found by using the nonparametric chi-square test (after Thomas 1975:264-283; Snedecor and Cochran 1967: 215-219). The statistical hypothesis formed was:

$$H_0 : p = 0.05$$

where  $p$  is the proportion of grey flakes obtained in the random sample. A significance level of .05 for a two-tailed (non-directional) test with 1 degree of freedom was set.

Chi-square was calculated as:

Outcome	Observed Value $O_i$	Expected Value $E_i$	$(O_i - E_i)$	$(O_i - E_i)^2$	$(O_i - E_i)^2/E_i$
Grey	11	$300(.05)=15$	-4	16	1.0667
Green	289	$300(.95)=285$	4	16	.0561
	300	300		$\chi^2 = 1.123$	

and  $\chi^2_{0.005} = 3.841$ .

The derived chi-square value does not fall beyond the critical region (3.841) and  $H_0$  cannot be rejected. The isoprobe random sample does not represent a significant departure from the predicted values with a known population of 5% grey and 95% green. This indicates that the random sample obtained is a fair representation of the Mount Camel assemblage.

The next step was to determine whether or not the proportion of Mayor Island to Northland obsidian as identified by the isoprobe analysis was significantly different from those proportions assigned by Best. The isoprobe identifications and those of Best are shown in Table 14.

TABLE 14: COMPARISON OF MAYOR ISLAND/NORTHLAND OBSIDIAN IDENTIFICATIONS BY ISOPROBE ANALYSIS AND AFTER BEST (1975:22-23)

Analysis Method	Green Obsidian Identification		
	Mayor Island	Northland	Sample Total
Isoprobe	236 (81.7%)	53 (18.3%)	289
Green colour/specific gravity	295 (98.3%)	5 (1.67%)	300

In this instance the tested hypothesis is slightly different as the real population proportions are not known; the comparison involves two sample populations. In other words, is the apparent tendency specious, due mainly to chance errors in sampling, or does a real difference in sample proportions exist?

The chi-square statistic in this case was calculated as:

Cell	O <sub>i</sub>	E <sub>i</sub>	(O <sub>i</sub> -E <sub>i</sub> )	(O <sub>i</sub> -E <sub>i</sub> ) <sup>2</sup>	(O <sub>i</sub> -E <sub>i</sub> ) <sup>2</sup> /E <sub>i</sub>
a	236	260.54	-24.54	602.21	2.311
b	53	28.4	24.54	602.21	21.160
c	295	270.4	24.54	602.21	2.227
d	5	29.6	-24.54	602.21	20.386

$$\chi^2 = 46.0843$$

E<sub>i</sub> is calculated as: 
$$\frac{(\text{COLUMN TOTAL} \times \text{ROW TOTAL})}{(\text{GRAND TOTAL})}$$
 from Table 12.

Chi-square is highly significant in this instance with  $p < .001$ , again with 1 degree of freedom. The  $H_0$  hypothesis that there is no difference beyond that found between random samples can be strongly rejected. There is a statistically significant difference between those results obtained by iso-probe analysis and the proportions assigned by Best. It is argued here on the basis of the previous chapter that the iso-probe sample results are an accurate representation of the Mount Camel obsidian proportions. The total Mount Camel green obsidian component is most probably 18.3% Northland and 81.7% Mayor Island instead of Best's 1.67% and 98.3% split.

The overall obsidian proportions of the Mount Camel assemblage as found by this analysis (and allowing Best's 5% grey identification to stand) are: 17.4% Northland, 77.6% Mayor Island, and 5% other (Huruiki, Coromandel, etc.).

Regarding the 11 grey obsidian pieces, it was judged appropriate to attempt further source definition beyond simple allocation to sources other than Mayor Island or Northland. For this reason, the 11 artefacts were re-analyzed for the standard 4000 sscond count time. The spectra were run through program SCREEN and the results obtained. As an example of the standard output format of the sourcing program, the SOURCE.LST and OUTPUT.DAT files are presented in Tables 15 and 16.

A point well illustrated by Table 15 and discussed in Chapter Four, is the difficulty which the program has in separating some Oceanic and New Zealand sources based on the data generated by the system. This is most apparent at the  $3\sigma$  level, although Oceanic sources were not rejected by four spectra in the  $2\sigma$  range. Combinations of Inland and/or Coromandel sources occur in seven spectra analyses as the only regions not rejected at the  $2\sigma$  level. This probably does reflect the affinities of the obsidians examined. In 2 spectra (R820876 and R820872), low barium values - which nonetheless are still an order of magnitude higher than found in either Mayor Island or Northland obsidians - possibly indicate a more northern origin for the pieces in question. However, as shown by the source table, the present analysis procedure is unable to determine just how far north this might be;



TABLE 15: SOURCE.LST file after 4000 second

## analysis of Mount Camel grey obsidian.

R820862 DAT  
 AT THE 2 SIGMA LEVEL, CANNOT REJECT  
 INLAND.,  
 AT THE 3 SIGMA LEVEL, CANNOT REJECT  
 COROMANDEL PENIN., INLAND, LOU IS. ADMIRALTIES, PITCAIRN ISLAND,

R820863 DAT  
 AT THE 2 SIGMA LEVEL, CANNOT REJECT  
 COROMANDEL PENIN., INLAND,  
 AT THE 3 SIGMA LEVEL, CANNOT REJECT  
 COROMANDEL PENIN., INLAND, WEST FERGUSSON IS.,

R820864 DAT  
 AT THE 2 SIGMA LEVEL, CANNOT REJECT  
 COROMANDEL PENIN., BANKS ISLAND GROUP,  
 AT THE 3 SIGMA LEVEL, CANNOT REJECT  
 COROMANDEL PENIN., INLAND, BANKS ISLAND GROUP, PITCAIRN ISLAND,

R820865 DAT  
 AT THE 2 SIGMA LEVEL, CANNOT REJECT  
 COROMANDEL PENIN., INLAND,  
 AT THE 3 SIGMA LEVEL, CANNOT REJECT  
 COROMANDEL PENIN., INLAND, BANKS ISLAND GROUP,

R820866 DAT  
 AT THE 2 SIGMA LEVEL, CANNOT REJECT  
 COROMANDEL PENIN., INLAND,  
 AT THE 3 SIGMA LEVEL, CANNOT REJECT  
 COROMANDEL PENIN., INLAND,

R820867 DAT  
 AT THE 2 SIGMA LEVEL, CANNOT REJECT  
 FANAL ISLAND, HURUIKI, GREAT BARRIER IS., TALASEA,  
 AT THE 3 SIGMA LEVEL, CANNOT REJECT  
 FANAL ISLAND, HURUIKI, GREAT BARRIER IS., KERMADEC ISLANDS, TALASEA,

R820868 DAT  
 AT THE 2 SIGMA LEVEL, CANNOT REJECT  
 COROMANDEL PENIN., INLAND,  
 AT THE 3 SIGMA LEVEL, CANNOT REJECT  
 GREAT BARRIER IS., COROMANDEL PENIN., INLAND, BANKS ISLAND GROUP, WEST FERGUSSON IS.,

R820869 DAT  
 AT THE 2 SIGMA LEVEL, CANNOT REJECT  
 COROMANDEL PENIN., INLAND,  
 AT THE 3 SIGMA LEVEL, CANNOT REJECT  
 COROMANDEL PENIN., INLAND, WEST FERGUSSON IS.,

R820870 DAT  
 AT THE 2 SIGMA LEVEL, CANNOT REJECT  
 COROMANDEL PENIN., INLAND,  
 AT THE 3 SIGMA LEVEL, CANNOT REJECT  
 COROMANDEL PENIN., INLAND, WEST FERGUSSON IS.,

R820871 DAT  
 AT THE 2 SIGMA LEVEL, CANNOT REJECT  
 COROMANDEL PENIN., INLAND, TALASEA,  
 AT THE 3 SIGMA LEVEL, CANNOT REJECT  
 HURUIKI, GREAT BARRIER IS., COROMANDEL PENIN., INLAND, TALASEA,

R820872 DAT  
 AT THE 2 SIGMA LEVEL, CANNOT REJECT  
 HURUIKI, GREAT BARRIER IS., INLAND, LOU IS. ADMIRALTIES, TALASEA,  
 AT THE 3 SIGMA LEVEL, CANNOT REJECT  
 HURUIKI, GREAT BARRIER IS., COROMANDEL PENIN., INLAND, LOU IS. ADMIRALTIES,  
 TALASEA,

TABLE 16: OUTPUT.DAT file after 4000 second  
analysis of Mount Camel grey obsidian.

FILE NAME SUPPLIED=...OUTPUT DAT ...

820862 DAT								
.295302	.000000	.015101	.226510	.251678	6.110738	.000000	.442953	18.138891
820863 DAT								
.007634	.141221	.139313	.068702	.290076	5.839695	.000000	.072519	21.010416
820864 DAT								
.502203	.022026	.000000	.028634	.000000	6.825991	.246696	.414097	17.137056
820865 DAT								
.423581	.157205	.082969	.000000	.131004	6.930131	.458515	.467249	24.553400
820866 DAT								
.313653	.143911	.169742	.173432	.000000	6.837638	.228782	.413284	23.096296
820867 DAT								
.323129	.159864	.017007	.000000	.020408	2.091837	.217687	.248299	19.363905
820868 DAT								
.378723	.051064	.019149	.031915	.000000	5.321276	.185106	.446809	19.652632
820869 DAT								
.075758	.015152	.207071	.068182	.005051	5.939394	.219697	.388889	23.993631
820870 DAT								
.035088	.216374	.000000	.020468	.000000	6.076023	.266082	.485380	20.424049
820871 DAT								
.023333	.093333	.070000	.000000	.100000	4.355000	.000000	.066667	17.857143
820872 DAT								
.150000	.082353	.000000	.095588	.194118	3.561765	.030882	.308824	21.012346
END OF FILE FOUND - END								
STOP								

Talasea on New Britain and Lou Island in the Admiralties are retained in the unrejected list.

Given the present capabilities of the analysis system it would still be up to the archaeologist to exclude the Oceanic groups. The Melanesian sources may be considered far beyond any stretch of culture-historical contact, as with the Middle East sources discussed in Chapter One, but as the universe of potential sources grows smaller, the justification for rejecting them out of hand must also be reduced (see Ward 1977). A subjective interpretation of the data is that two of the grey pieces originated in either the Great Barrier or Huruiki region and that the remainder were derived from either Inland or Coromandel sources.

#### DISCUSSION

Having re-ordered the obsidian source proportions of the Mount Camel assemblage, it remains to discuss the implications of the findings. A statistically significant change in the proportion of Northland obsidian must be judged as moving in support of Davidson's interpretation of the site, but the question remains to what degree. The greatest amount of obsidian was still derived from Mayor Island, which is at least six times as far away from Mount Camel as the nearest Northland source. Additionally, seventeen percent Northland obsidian is still short of the thirty percent intimated earlier in the Chapter.

Detailed discussion of exchange mechanisms and patterns is beyond the scope of the present thesis. It will remain

for others to utilize available equipment and determine on a broader scale the factors which influenced transfer of obsidian in New Zealand.

Nonetheless, a very real problem with the sourcing of lithic materials is how to interpret the information provided. Determining at what point the percentage of one source type of obsidian becomes significant in relation to another is made more difficult in New Zealand simply due to the number of sources available. No all encompassing answers can be given, especially when the identification of a single flake from a given source (as for instance if Mayor Island obsidian were found on New Caledonia or Rarotonga) might provide the initial link whereby archaeologists can investigate stronger ties. Clearly, none of this is possible without first being able to acquire the basic data.

Considering the site of Mount Camel, if additional analysis of the grey component of the obsidian assemblage finds that a percentage has indeed been derived from the Huruiki region, the argument for an awareness of the Northland region beyond that allowed by Best can only be strengthened. By securely identifying the Mayor Island and Northland component at Mount Camel, a majority of the obsidian work has already been done.

#### THE 2000 SECOND ANALYSIS: ADDITIONAL DISCUSSION

Subsequent to the analysis of the Mount Camel obsidian sample, an attempt was made to establish an automatic screening procedure for 2000 second analyses. A subroutine called

COARSE was inserted into the main program SCREEN in an effort to quantify the obvious visual differences which are apparent between Northland and Mayor Island spectra in 2000 and even 1000 second counts. Using the data output from the Mount Camel material, as well as that derived from 2000 second analyses of Mayor Island and Northland source samples, data groups were calculated in the same fashion as for the regular SCREEN parameters.

The most obvious result of this study was that as the count-time was reduced from 4000 to 2000 seconds, the smaller element peaks as well as the mid-Compton peak began to demonstrate increased variation as determined by the present peak stripping procedure. In that allelement peaks are normalized against the mid-Compton, the variation of the large peaks as well as the small was amplified. A wide degree of overlap was generated between Mayor Island and Northland sources by this data - far beyond what visual inspection of the spectra could justify.

At 4000 seconds the system had no difficulty whatsoever in uniquely partitioning each of these sources into mutually exclusive groups, yet the ability largely deteriorated with 2000 second analyses. As the source characteristics themselves did not change, it appears that it is the data extraction ability of the analysis program which is inadequate. The counting error is undoubtedly increased, but this would not explain the wholly reduced discrimination of the program between the two sources.

Leach and Manly (1982:78) recognize that a routine system

of obsidian characterization cannot rely upon visual identification alone. As they note, the statement "I can see from the shape of the spectrum of this artefact that it comes from Mayor Island" is not acceptable as a means for the regular allocation of artefacts. While it may be in fact true that spectra can be reliably identified by visual inspection, at least for some sources, the ability to recognize the distinctive traits of particular obsidian spectra is not easily transferred to inexperienced workers. A facility designed for the routine analysis of obsidian from a wide variety of sources must be capable of reliably identifying obsidian sources in non-subjective terms.

For this reason, until such time as an improved method of spectrum reduction is incorporated into the isoprobe facility, the minimum count-time which can be justifiably employed for *automatic* sample characterization is 4000 seconds.

In summary, the analysis of the Mount Camel assemblage has provided some valuable information about the isoprobe technique, as well as the composition of the assemblage. The proportion of Northland obsidian has been found to be significantly different than previously indicated, to the support of Davidson's interpretation of the site.

Further, results of an attempt to quantify the data obtained from 2000 second analyses have shown that the present method of spectrum reduction is inadequate for the task. The importance of accurately assessing background counts and determining peak centres has been emphasized recently by Cox

and Pollard (1981) and undoubtedly, a peak searching routine such as employed by Bird *et al.* (1981) or McCallum *et al.* (1979) is required if a 2000 second count time is to be instituted with the present system.

The closing chapter will review the programme of research and development applied to the SEFA technique as a means for the characterization of obsidian. Evaluation of the technique's potential and recommendations for the improvement of the system's capability will be made.

## CHAPTER SIX

## CONCLUSION

## EVALUATION

At the end of Chapter One, two main research goals were identified as fundamental to the development of routine and reliable obsidian characterization in Pacific archaeology. Subsequent chapters have attempted to develop an analysis technique which embodies the research plans set forth. Through the review of previous work in the field of obsidian source characterization, the essence of these problems which have seen numerous false-starts towards their solution was defined. In reviewing the findings of this thesis, the answer as to whether or not (or to what degree) the study has succeeded in solving them will be expressed.

The first goal identified, was to develop an obsidian characterization method (which included Oceanic as well as New Zealand sources) that was as reliable as possible, and to explicitly reveal what the strengths and weaknesses of the technique were. The selection of the SEFA method encompassed many considerations, not the least of which was its ability to determine the presence of high-Z elements. The analysis of barium, lanthanum and cerium in addition to iron, rubidium, strontium, yttrium and zirconium has provided data for the unambiguous separation of Central and Eastern Pacific volcanic glasses from their New Zealand counterparts.

Discrimination of obsidians within New Zealand is less successful between the Inland, Coromandel, and Great Barrier



regions, although a clear separation of Mayor Island and Northland material has been achieved. This in itself will serve as a valuable tool for archaeologists, by enabling the accurate determination of Mayor Island obsidian proportions in large assemblages analyzed by the facility. The ability of the technique to handle large numbers of artefacts has been demonstrated in the archaeological example of the Mount Camel assemblage.

The characterization framework is based on the logical concept of conjecture and refutation as described by Ward (1977) and Leach and Manly (1982) after the writings of Sir Karl Popper (1969). The system is explicit in its mode of potential source allocation (through the inability to reject) and thereby clearly displays both its weaknesses and strengths in the output which is produced. Where only one source remains unrejected from the reference source group, the archaeologist may well take this to mean (and with some justification) that the particular artefact in question was derived from that source. It must be strongly emphasized, however, that while rejection of all sources but one may be good evidence of that particular source allocation being correct, it is not proof. It remains for the archaeologist to accept that no other potential source (of similar composition) might actually be represented by the flake.

Where more than one source remains unrejected by the screening procedure, the archaeologist must define the specific universe of sources which are being considered as potentially having produced the artefact. In the case of two sources

such as Talasea and Huruiki remaining unrejected after the analysis of an artefact excavated in Auckland Province, a problem for the archaeologist may not exist. Where the unrejected sources include Huruiki as well as Great Barrier Island, Coromandel and Inland groups, the selective interpretation of data is not so easily made. Under present facility capabilities, application to problems which hinge upon the distinction of the latter sources will be less useful, and supply little information beyond determination of which source groups are amongst those which may have produced the artefact. A TEFA addition to the isoprobe analysis unit will undoubtedly increase the rejection capability of the system as a direct result of the broadened elemental comparisons permitted. Thus, the present facility has laid the foundation of equipment for sample analysis and data processing. With the augmentation of TEFA it may well display a discrimination ability on the order of that presently achieved by nuclear reactor and accelerator facilities. In a very real sense, the system can only be improved.

The second problem identified by this thesis goes beyond a statement of 'how well the system works'. Specifying that the technique to be developed must not only be sophisticated enough to cope with the characterization problem at hand, but must also be simple enough to use so that archaeologists themselves can operate the facility, presupposes that the problem will permit such a solution. While the present research and previous studies indicate that energy-dispersive XRF (both SEFA and TEFA) can supply the answers to problems

of obsidian characterization, archaeologists should not feel that at last a 'black box' has been created which removes their own responsibility for the data generated.

It is the belief of the author that although the process of artefact analysis has been largely simplified by the implementation of the isoprobe apparatus, its intention has not been to release the archaeologist from the need to understand just what it is being measured. No analytical system is totally without sources of error (both from equipment and operation). This is especially true when numerous variables such as sample thickness, texture, presentation within analysis region, and system calibration all affect the reliability of the analysis results. Unless the researcher is aware of what can go wrong during the process of obsidian artefact source identification, he/she will have little basis for understanding what is 'right' about the final product. One of the purposes of this thesis therefore has been to explore the various problems to be considered during the analysis of artefactual material. If spurious results are produced, some understanding of the why's of their occurrence may be gained by reference to this work.

A question not as yet dealt with, is the response of the characterization program SCREEN (or SOLO) to the encounter of a specimen from an unknown source. It should be clear at this point that within the structure of the artefact allocation system, there are two possible results, depending upon the composition of the unknown source. Either the general chemical resemblance of the unknown will be unable to reject

other sources within the reference configuration (and its identity as an unknown will go undetected), or some particular elemental abundance will permit the rejection of all known sources within the reference configuration and thereby mark it for the archaeologist as a peculiar specimen. Again, the archaeologist must understand the nature of the data which is being generated. If an unknown specimen is encountered and total rejection of the source configuration occurs, personal inspection of the data can be made to identify the cause. An example of this situation was encountered during the process of the present research when samples of a material tentatively identified as 'Santa Cruz glass' were analyzed (see also, Duerden *et al.* 1980:450; Bird *et al.* 1981:38). The spectrum is included at the end of Appendix A.

Clearly, there is something 'wrong' about the nature of the spectrum obtained from this material when compared to the other source groups examined. The huge elemental peaks (which, incidentally, occur at the energy of the mid-Compton and mid-Rayleigh peaks) approximate those of Sn, an effect which has already been noted in Chapter Four (pp.

It is not possible for these peaks to be a scatter response, however, because of their disproportionate presence relative to the other excitation source peaks. They would appear in this case to represent huge quantities of tin. Further examination of this material revealed that in fact it has a radioactivity far above the natural radiation produced from even those obsidians with relatively high uranium/thorium concentrations (see Northland sources of Waiare and Pugnaere in

Table 3). The spectrum rejects all reference sources upon examination by program SCREEN.

Visual inspection of the 'glass' shows that it very closely resembles a slag produced from smelting operations. Such slag may have been employed as ship ballast, and it is possible that the recovered material has been derived from this type of 'source'. Were the analyst not prepared to inspect and question data, anomalous results such as these may be passed off as merely strange; possibly representing a rogue geological specimen. Analysts must be prepared to review the spectra, and the facility must be flexible enough to allow them to do so. The present isoprobe facility via program AMSPEC permits this form of interactive analysis to be made.

In this sense, even if a particular assemblage is analyzed and allocated without difficulty, it is still advised that some form of detailed visual inspection of spectra be employed. The stated objective at the end of Chapter One to be able to "abandon matters of geochemistry and mathematics" must be viewed as referring to their development for source characterization. This does not imply that one should remain unaware of their role in the programme of research applied..

Thus, in review of the goals proposed in this thesis, the results can be judged as having provided the basic framework for development of a more fully comprehensive system. Even at its present level, the facility will enable archaeologists to deal with some of the basic problems associated

with understanding distribution of obsidian in New Zealand. The large scale identification of Mayor Island obsidian in archaeological sites will enable accurate determination of its distribution and finally, perhaps some understanding of its role in the culture of the people it represents. Central and Eastern Pacific sources as well have been characterized. The system's application to the problems of these sources' exploitation is awaited.

#### RECOMMENDATIONS

Through the course of developing the isoprobe analysis unit, two major restrictions to analysis efficiency were identified. The first of these stems from the particular source strength being employed. As described in Chapter Three, the 50 mCi americium source presently in use has a standard loading of  $155.4 \text{ mCi/cm}^2$ . This is far below the saturation loading point, calculated as nearly  $900 \text{ mCi/cm}^2$  (Anon. 1975:2). Increased source activity to approximately 200 mCi (as employed by Cesareo *et al.* 1982) on the same active diameter would provide a loading of  $621 \text{ mCi/cm}^2$ , which is over 80% of the saturation level (op. cit.). The present source only achieves 30% of this output. Greater activity will largely reduce the count-time required, and thereby improve the isoprobe efficiency.

The second recommendation for the system is an improvement in the spectrum reduction process as identified in Chapter Five. This will enable greater accuracy in data generation, and in all likelihood serve to reduce the total

system error currently encountered.

In conclusion, the research and development of a functional isoprobe facility for the characterization of New Zealand and Oceanic obsidians as performed in this thesis should supply the means whereby answers to culture-historical questions are forthcoming. The emplacement of the system within the University of Otago Archaeometry Laboratory ensures its permanent application to archaeological problems. The job of clearing the immense backlog of unsourced obsidian can be initiated at last.

## ADDENDUM

## ANALYSIS OF TAHITIAN BASALTIC GLASS

## INTRODUCTION

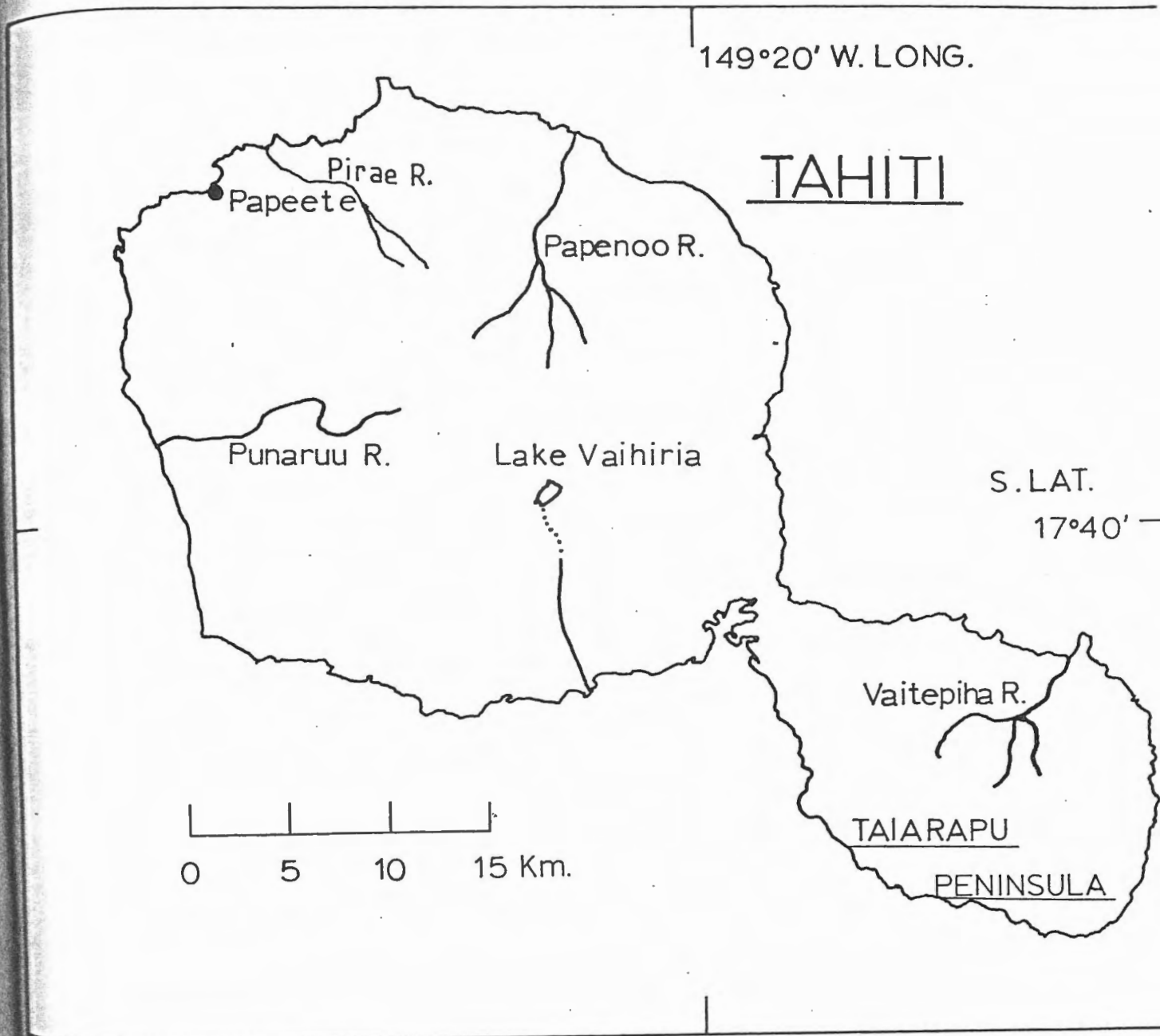
After the body of work for this thesis was completed, a small cobble of Tahitian basaltic glass (accession number AN 837) was supplied to the Otago Archaeometry Laboratory.<sup>2</sup> The specimen was collected from the Vaitepiha Valley on the Taiarapu Peninsula (see Map 4). In hand specimen the material is totally opaque, with a black, waxy sheen on freshly flaked surfaces. Comparison with Pitcairn Island and Puu Waawaa material has shown it to be indistinguishable in general macroscopic examination. The cobble (approximate size: 14 x 7 x 6 cm) appeared roughly water rolled and coarsely-grained, grey/brown on its external surface. The vitreous internal matrix was exposed upon breaking the cobble apart. Irregular internal planes within the cobble caused it to fracture irregularly, but 4 x 5 x 3 cm fragments were recovered which are wholly vitreous. Flakes of reasonable quality were obtained from these pieces.

Williams (1933) carried out a broad geological survey on Tahiti, including a detailed description of the Vaitepiha Valley. He identified basaltic glass or "basanitoids" (*ibid.*: 37) from several locations throughout the island. Specifically, Williams notes, "among the dikes outside Papanoo

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2. The author and the Otago Archaeometry Laboratory are indebted to Maeva Navarro of the Department de Archaeologie, Papeete, Tahiti for making this material available for analysis.





MAP 4: Tahiti, showing regions of basaltic glass identification (after Williams 1933).

Valley, all but a few are dark grey or black, glassy, or very fine grained rocks devoid of any crystals" (ibid.:30). Also, there was found "near the southern shore of Lake Vaihiria ... crags of black glassy lava..." and further, "black glassy lavas which outcrop in Pirae Valley, about 4 miles from the mouth" (ibid.:30, 37). In the bed of the Punaruu River there were found many boulders which "vary from coarsely ophitic to glassy" (ibid.:38).

Of the Vaitepiha Valley in particular, it was noted that "the tributaries of the Vaitepiha, the Vainia intersecting on the right bank and the Vaitia on the left, bring down none but volcanic detritus ..." (ibid.:27). Regarding the rock suite represented, Williams comments that "it is likely that all these rocks would be classed together in the field as glassy or aphyric basalts" (ibid.:30). As noted, the author has found little that would distinguish the particular example of this material from that which has been obtained from the Pitcairn or Hawaiian sources; to which Williams pertinently comments,

Manifestly, therefore the series is an "Atlantic" one. It is indeed merely a part of a large "Atlantic province" that comprises most of the South Sea Islands, sharply distinguished from the circum-Pacific province of andesites and diorites

(ibid.:41).

It has been indicated to the author that some dark, glassy material is being recovered from archaeological excavations proceeding on the island, suggesting that this lithic resource was being exploited prehistorically (Seelenfreund pers.

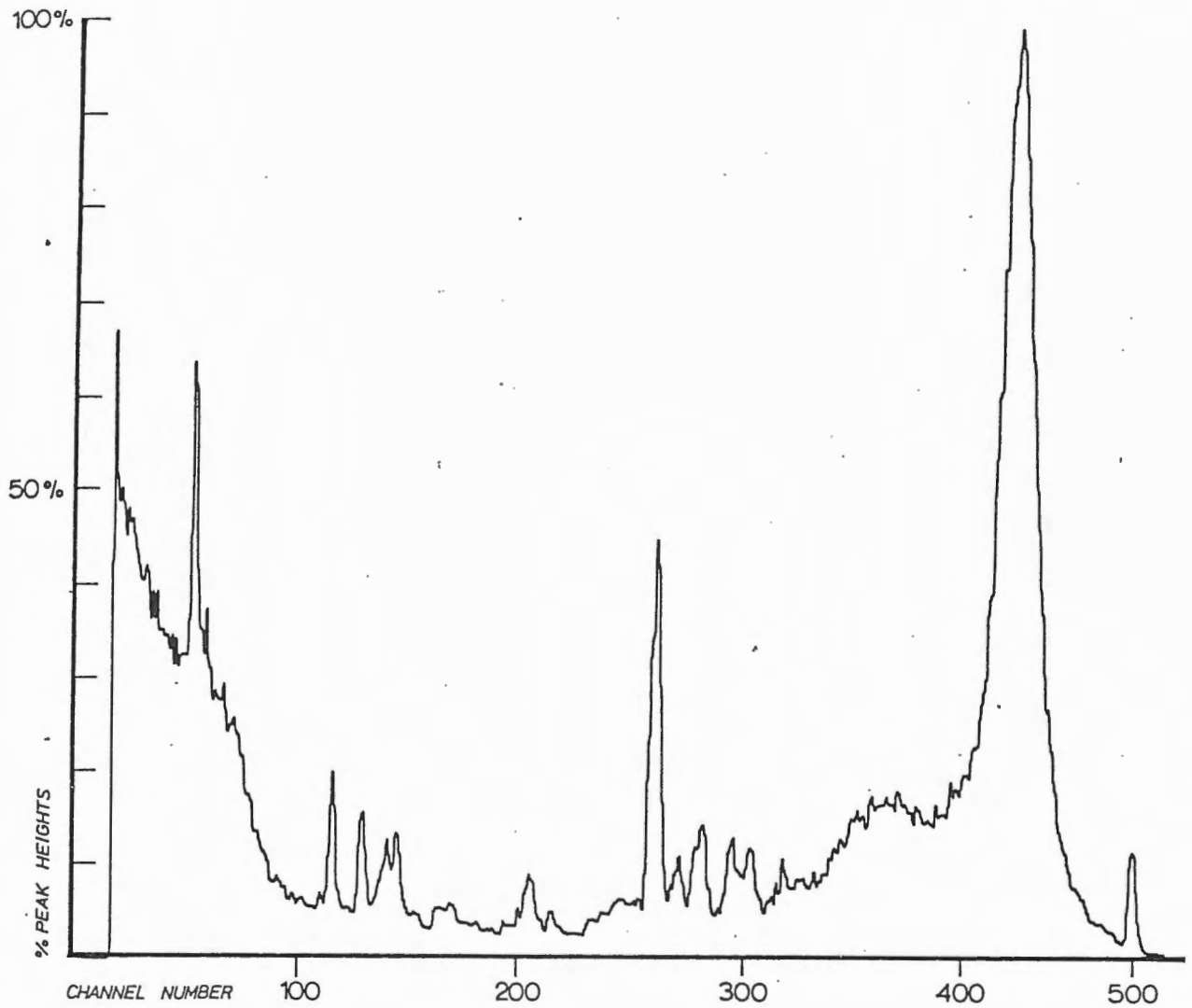


FIGURE 13: Typical spectrum of Tahitian basaltic glass.

TABLE 17: Mean element values of Tahitian glass.

N=5									
MEAN VALUES FOR TAHITIAN BASALTIC GLASS									
ELEMENTS	Fe	Rb	Sr	Y	Zr	Ba	La	Ce	C/R
MEANS	3.20	.03	1.72	.09	1.46	7.50	.93	2.17	13.82

comm. 1983 ). Clearly a test of this material was warranted by the isoprobe facility. No Tahitian volcanic glass had been included within the reference source matrix, and indeed, to the author's knowledge Tahitian glass has not been previously identified as a potential source of artefact-grade material.

#### ANALYSIS

Five pieces of the cobble were subjected to standard 4000 second analyses in the isoprobe facility. The mean values generated are shown in Table 17. A typical spectrum of the Tahitian glass is shown in Figure 13.

Upon running the collected Tahitian spectra through program SCREEN, all were able to reject the entire reference source group at both 2 and 3 $\sigma$ . Primary distinction from most other sources is due to the high Fe values. These immediately reject all sources but Mayor Island, Tafahi, Mauna Kea and Canterbury on the basis of that element alone; even at 3 $\sigma$ . Rubidium as well is not rejected from these sources at the 3 $\sigma$  level, after the initial screening on the basis of iron. Nonetheless, even these sources are easily rejected on the basis of the third element to be tested; strontium. Moreover, all other volcanic glasses which are presently contained within the reference matrix can be separated from the Tahitian glass on the strontium value alone.

#### DISCUSSION

This analysis must be classified as an unqualified success for the isoprobe facility in general, and the screening matrix in particular, in identifying the 'unknown source'.

It also recalls the point made in Chapter One (p.4) on the importance of strontium as a geological indicator. Further, the need to continue surveys in potential source regions (pp. 5-6) has been well illustrated by this example. Work is presently underway to include the Tahitian glass in the reference source matrix, but additional samples of material from other localities on the island (as identified by Williams) are also required to better delimit the range of chemical variation which might be present.

The geographical location of Tahiti between the Cook Islands to the west, as well as the Marquesas to the north and the Pitcairn Group to the east, may well make the characterization of this source (and others which possibly exist) critical in understanding patterns of prehistoric communication. A basic problem still remains in identifying all possible sources and obtaining data on the material by which to compare. The point can be made, however, that the facility with which to make these measurements is now in existence.

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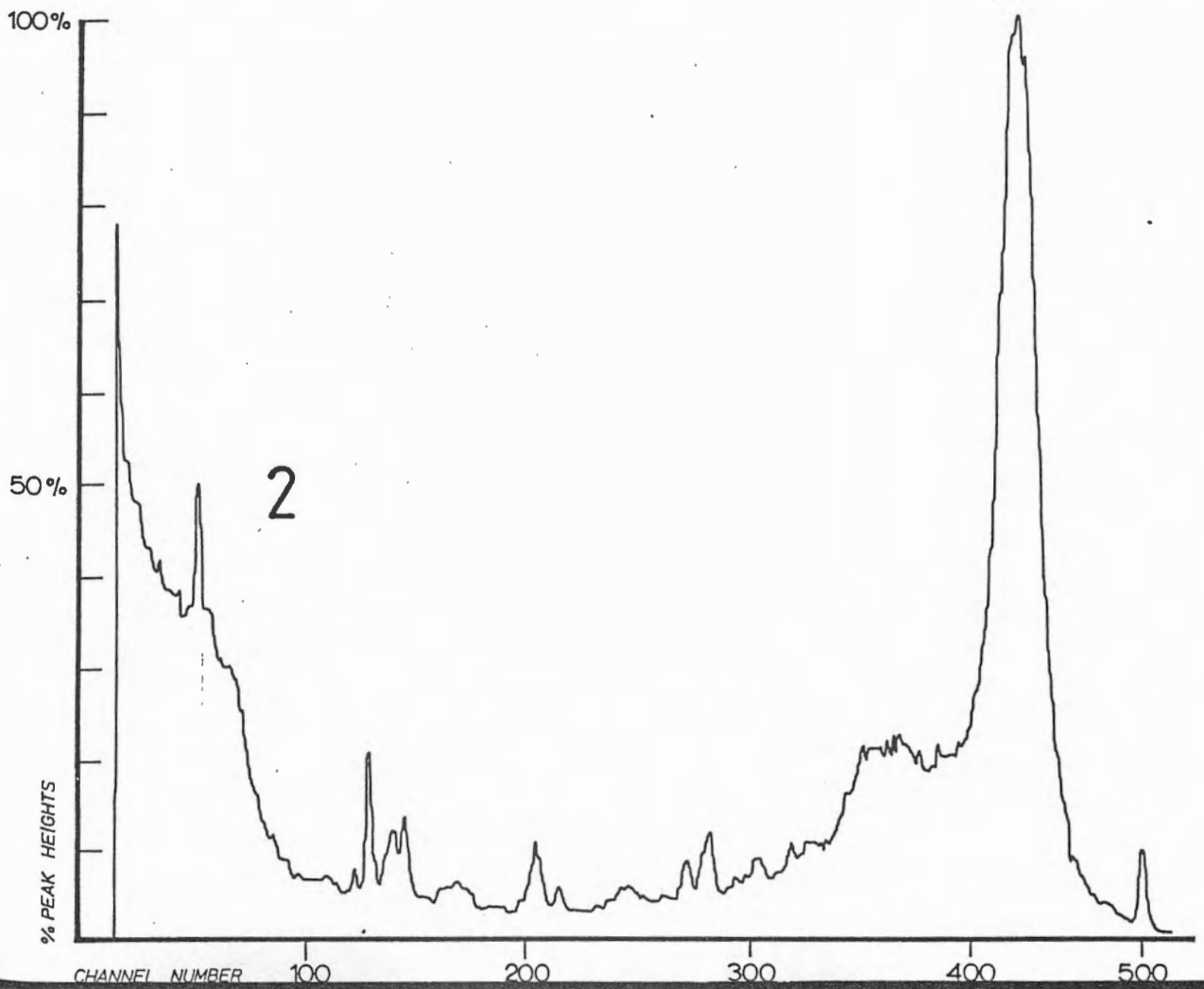
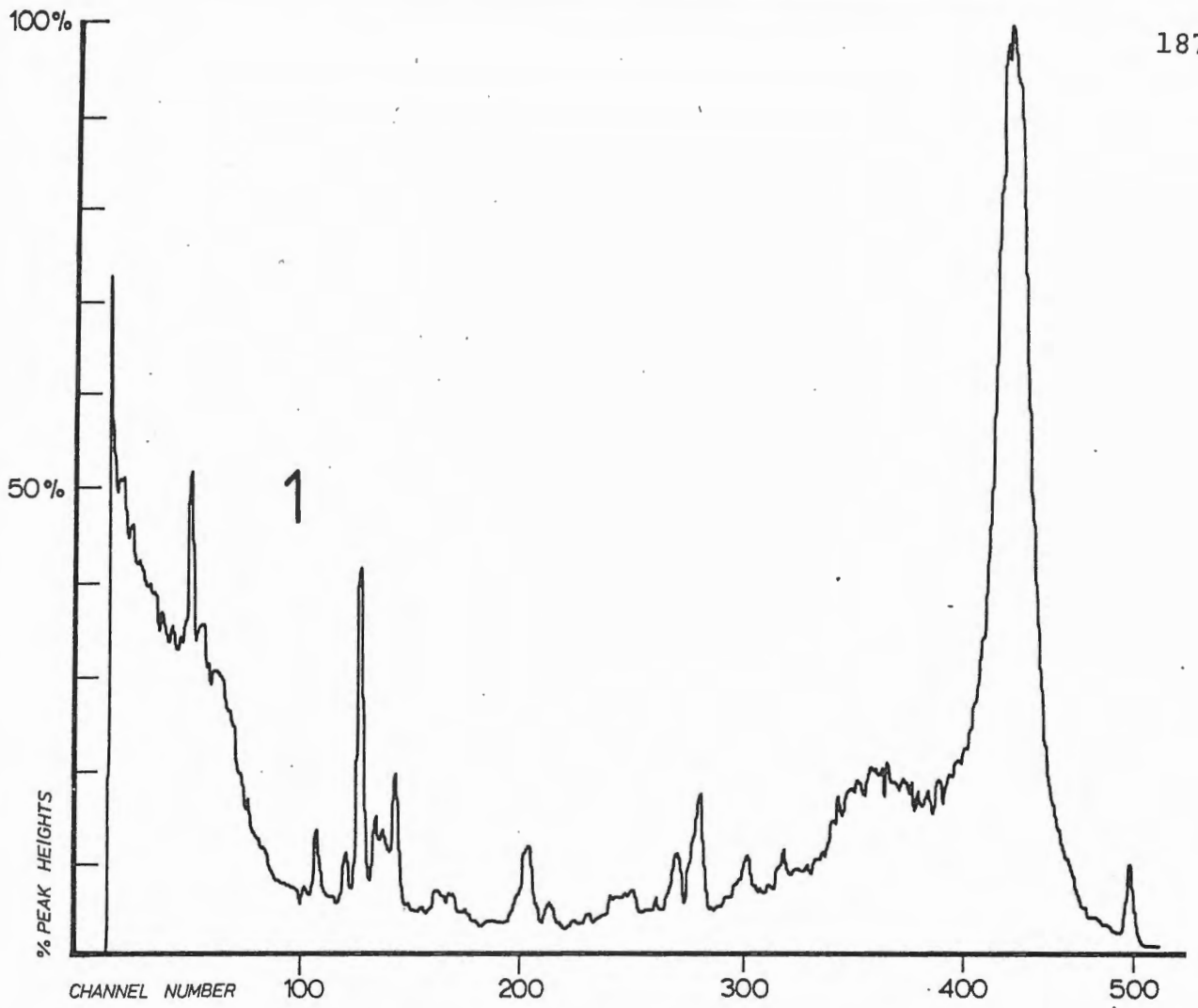
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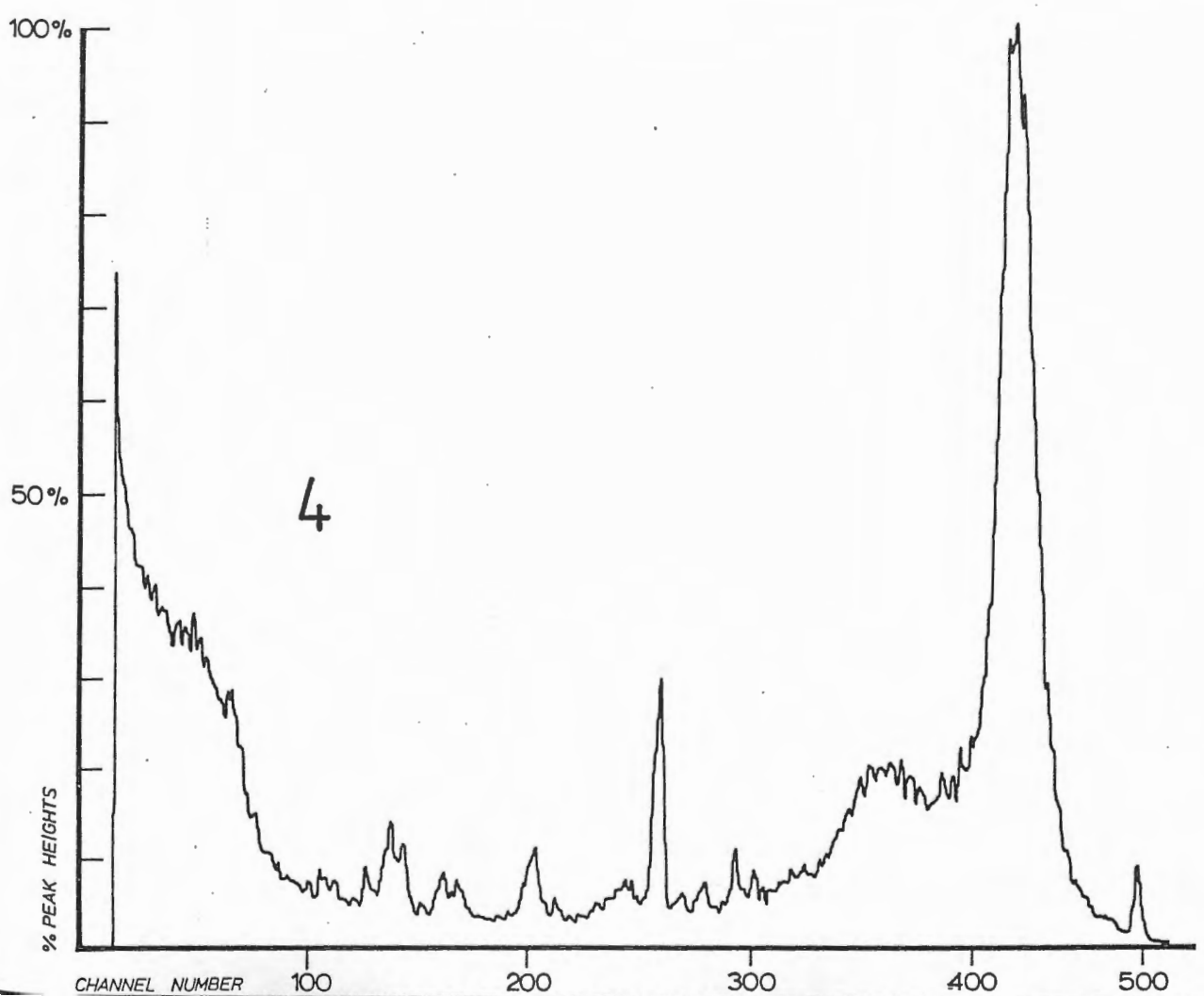
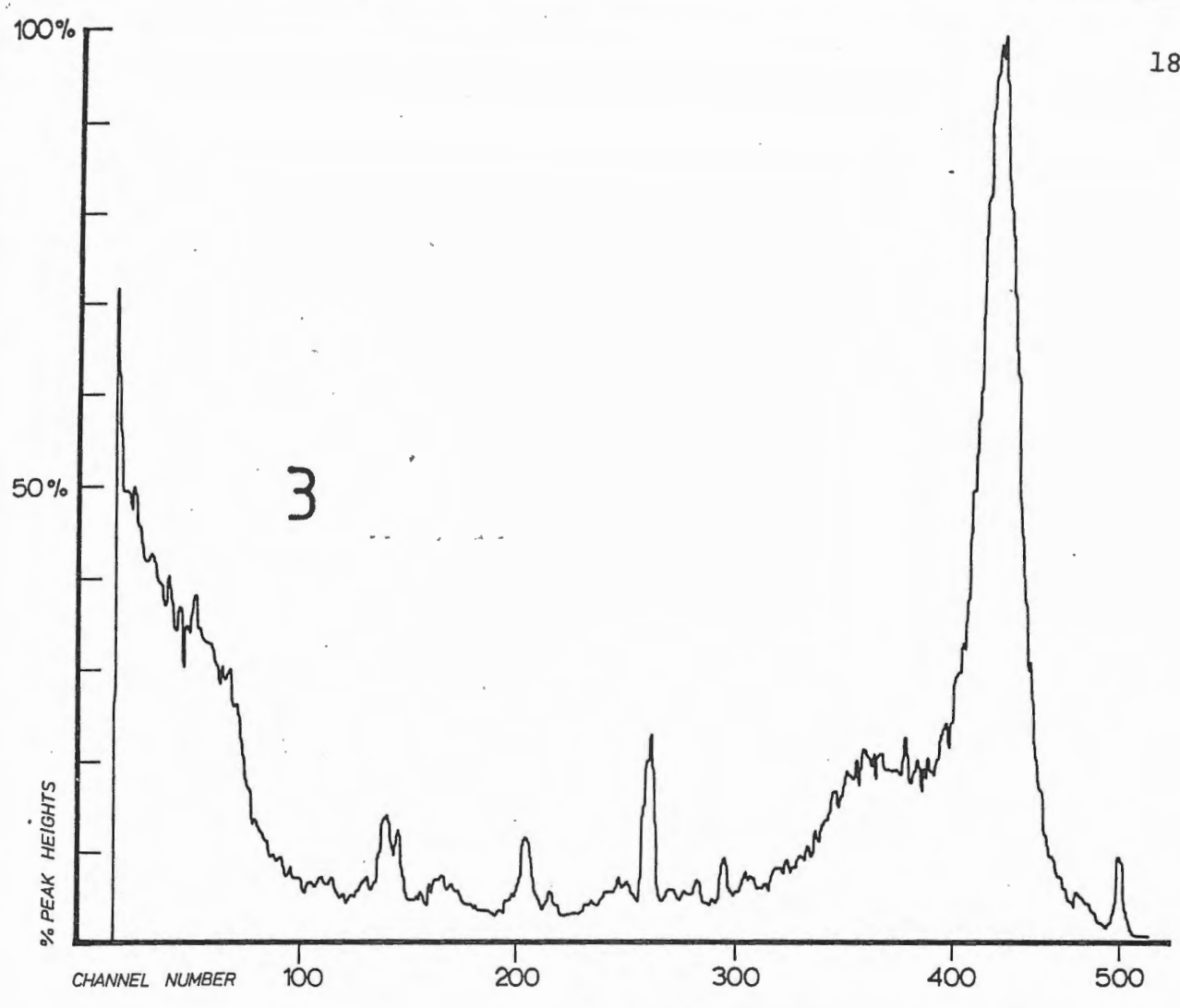
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## APPENDIX A

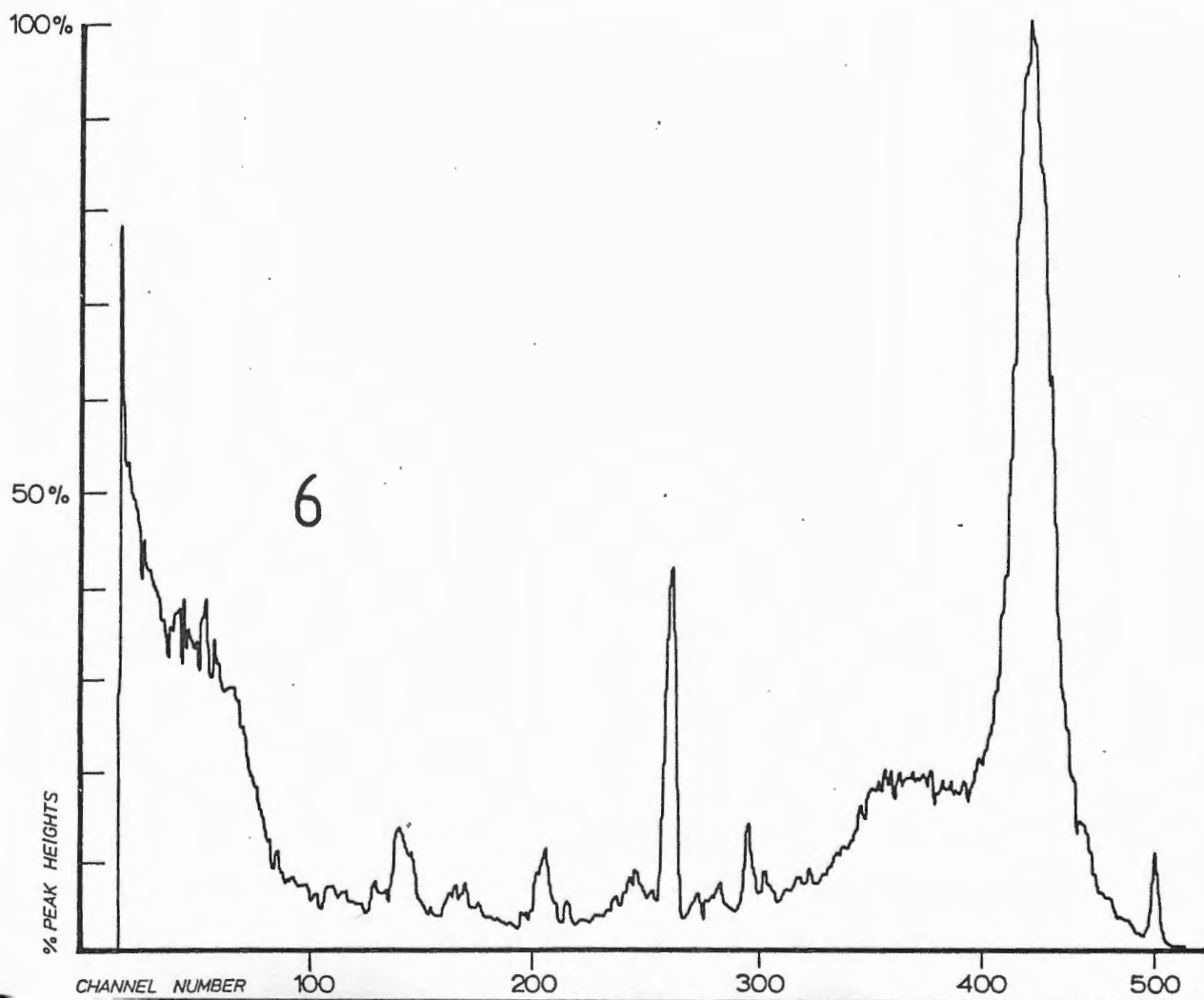
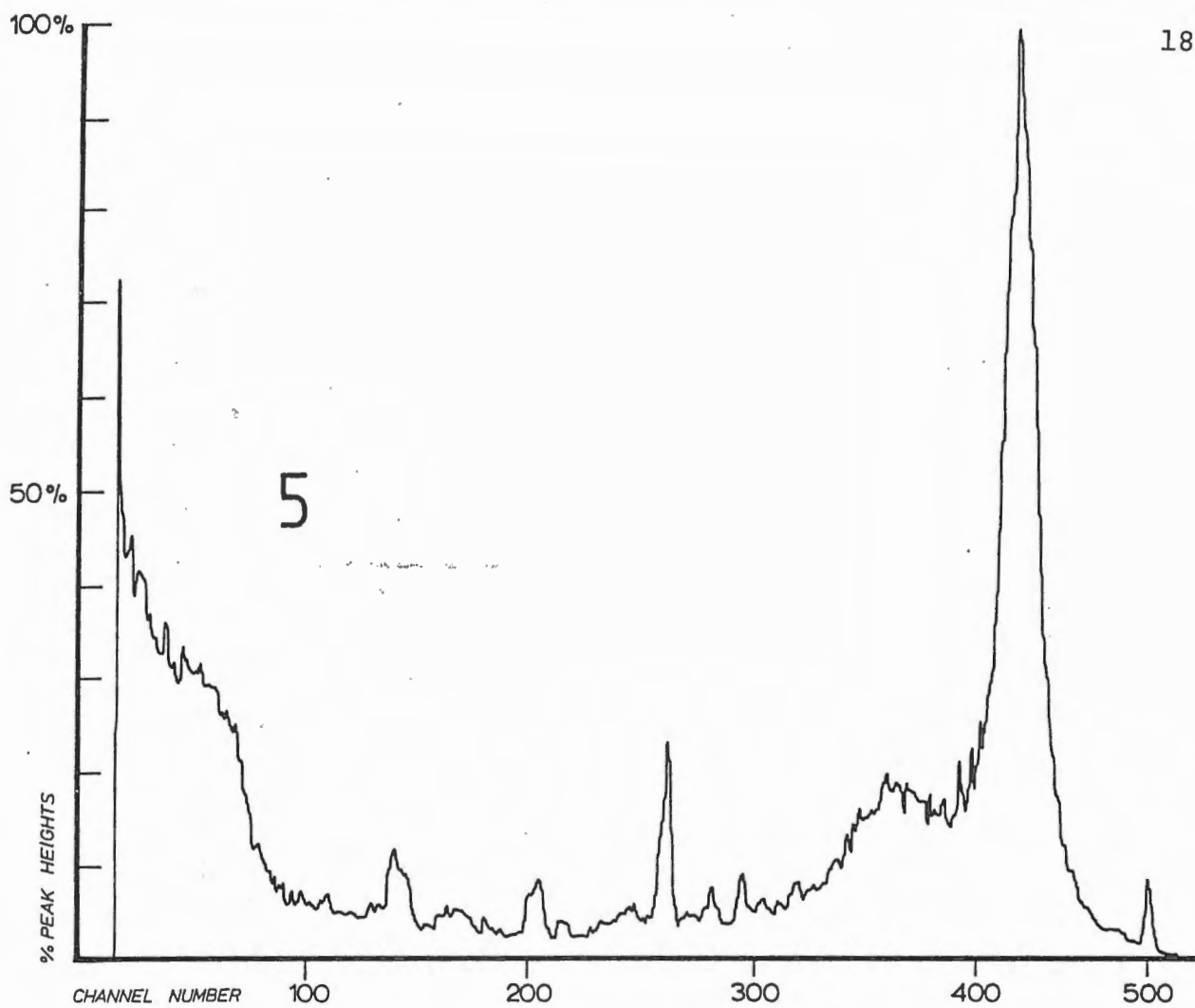
## TYPICAL SOURCE GROUP SPECTRA

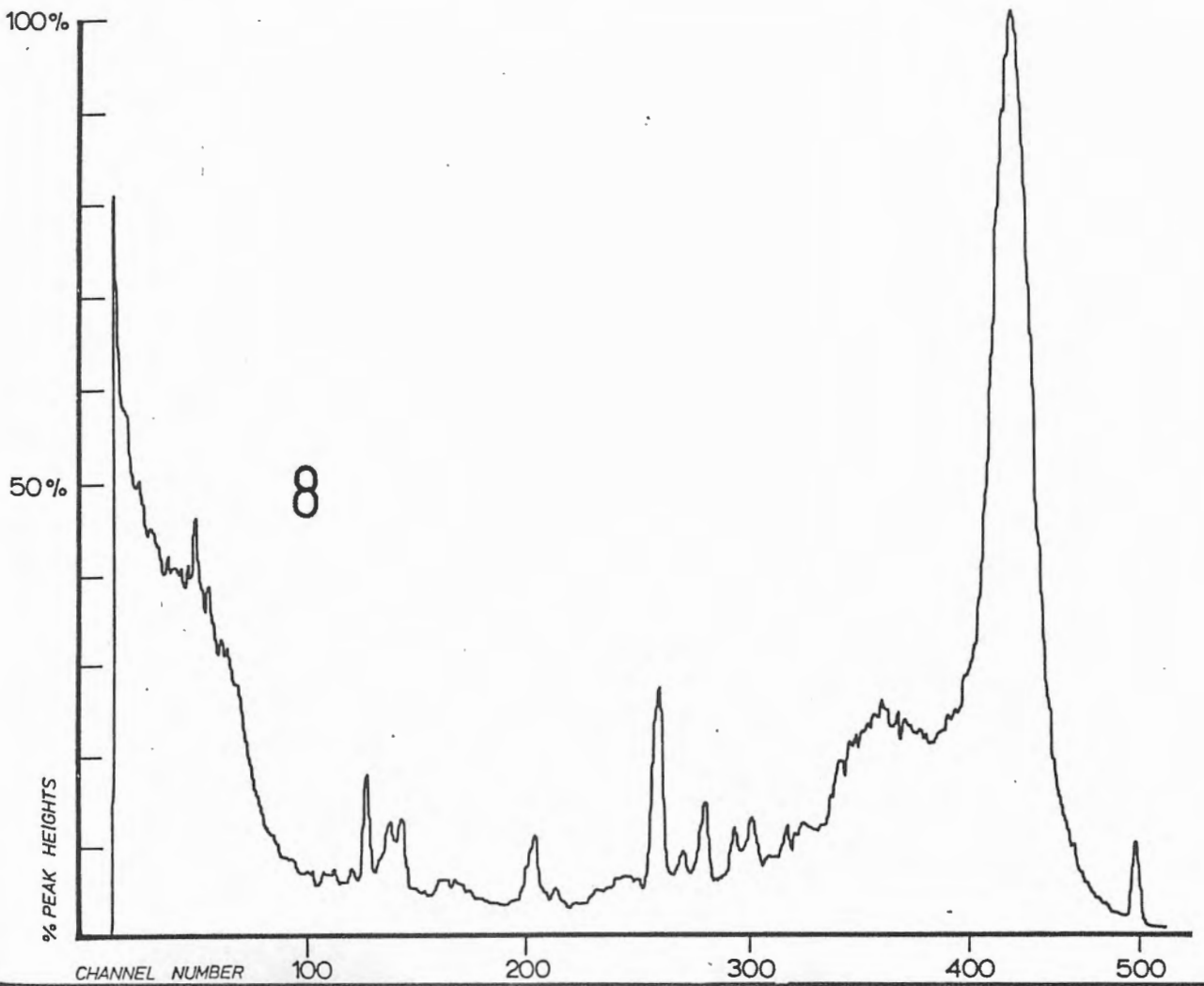
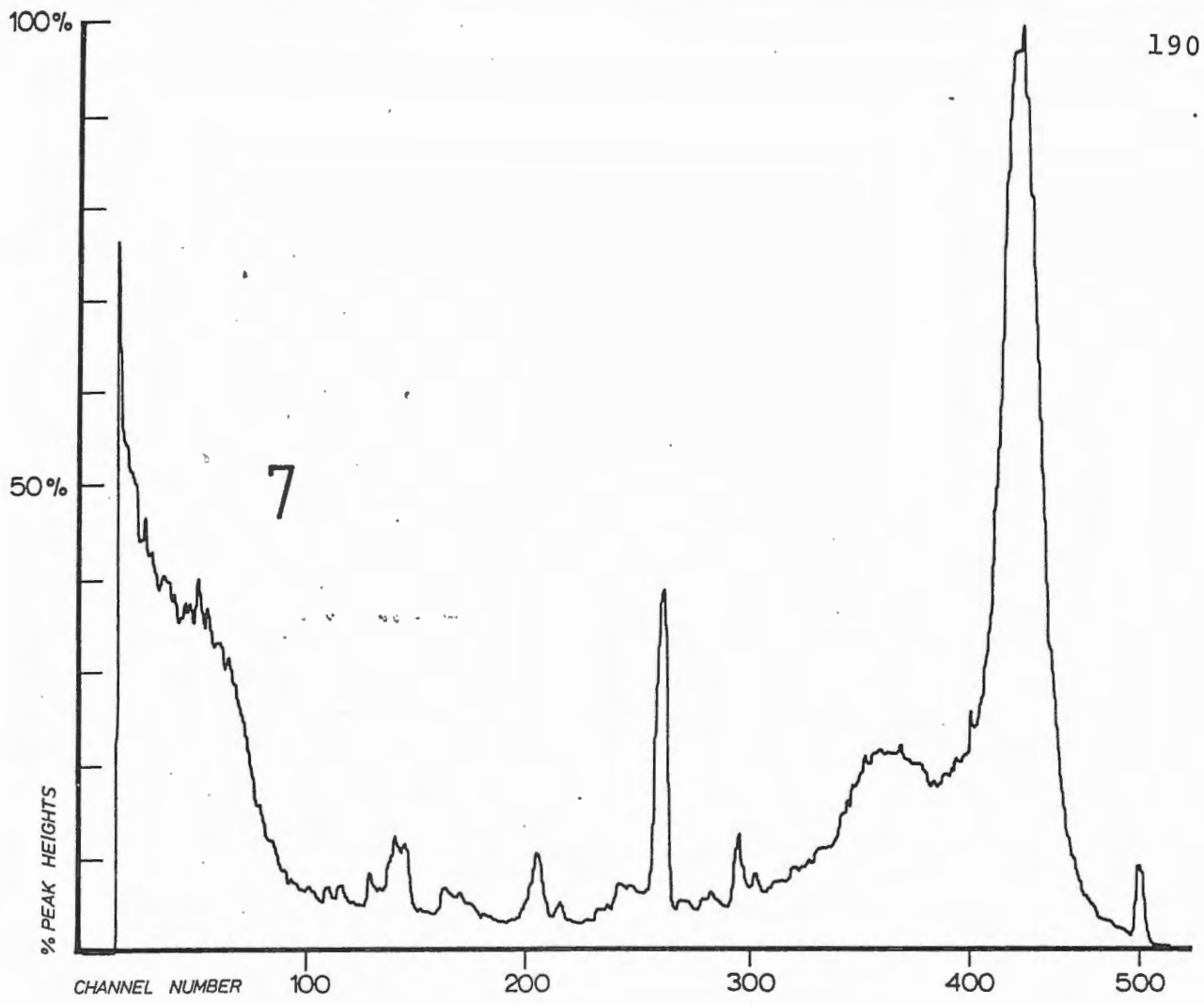
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2. Mayor Island
3. Fanal Island
4. Huruiki
5. Great Barrier Island
6. Coromandel Peninsula
7. Inland
8. Rapanui
9. Tafahi
10. Kermadecs
11. Lou Island, Admiralties
12. Puu Waawaa, Hawaii
13. Mauna Kea, Hawaii
14. Banks Island Group
15. Talasea, New Britain
16. Pitcairn Island
17. Fergusson Island, D'Entrecasteaux Group
18. Canterbury pitchstone
19. Otago 'Glass'
20. Santa Cruz 'Glass'

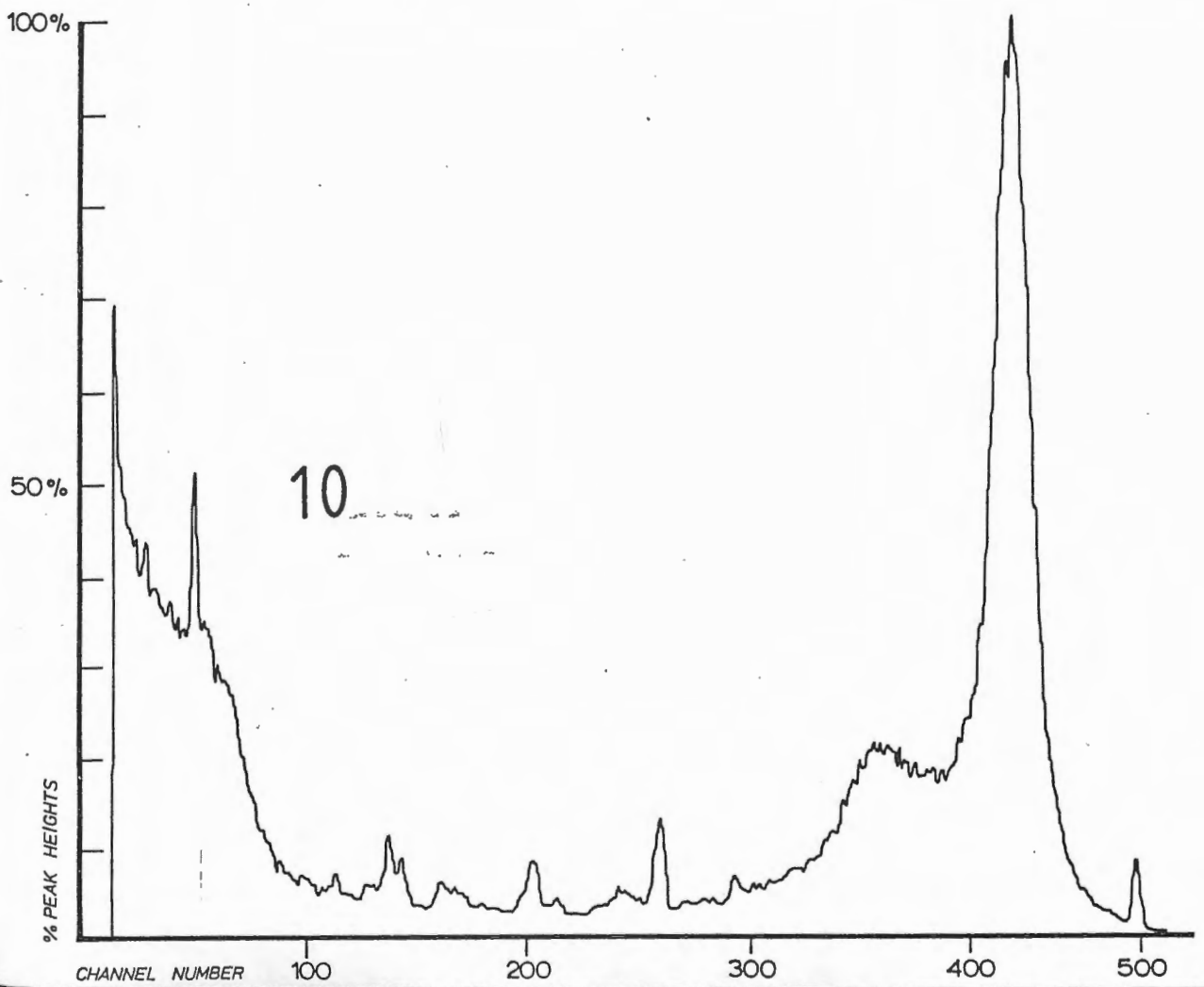
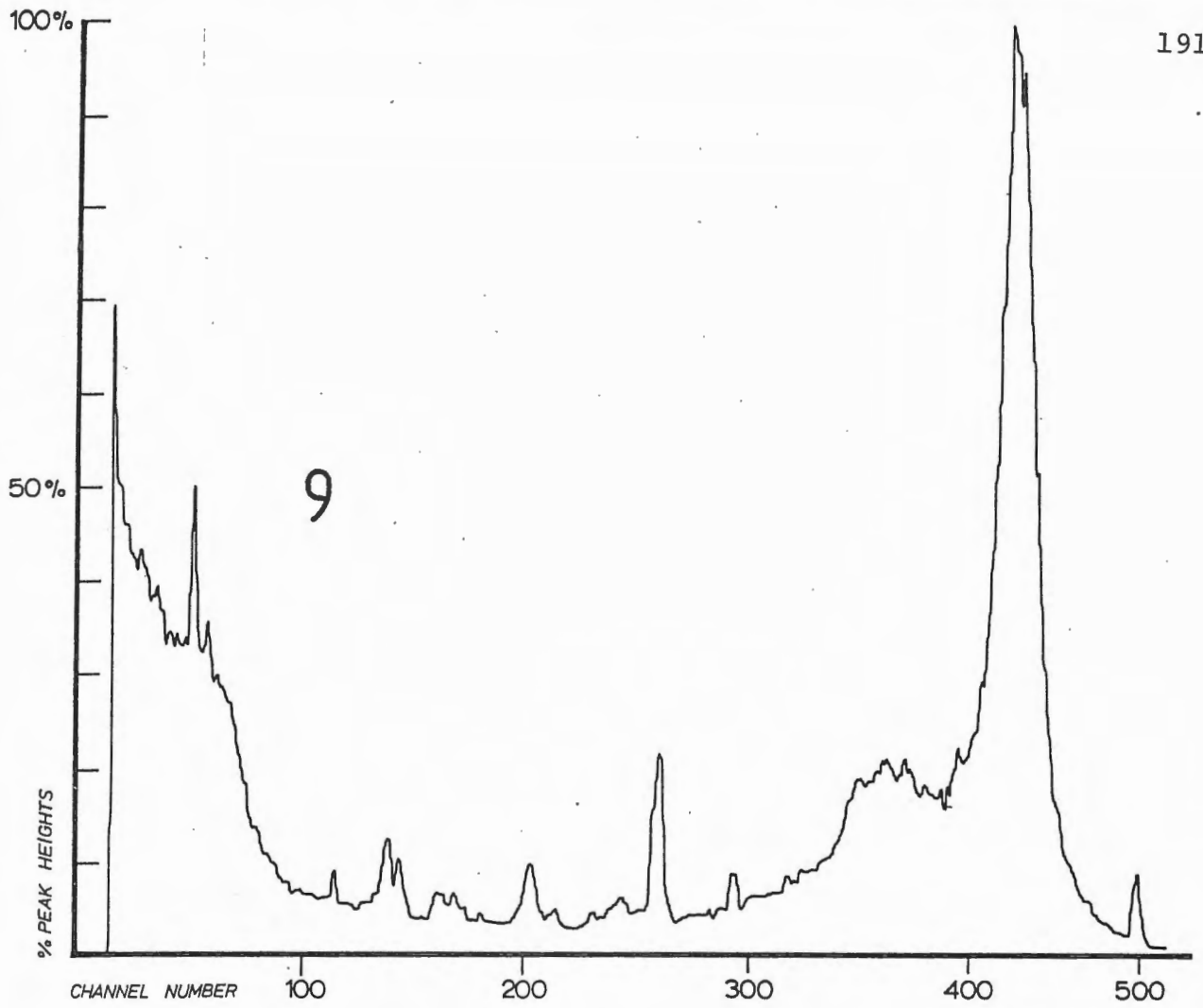


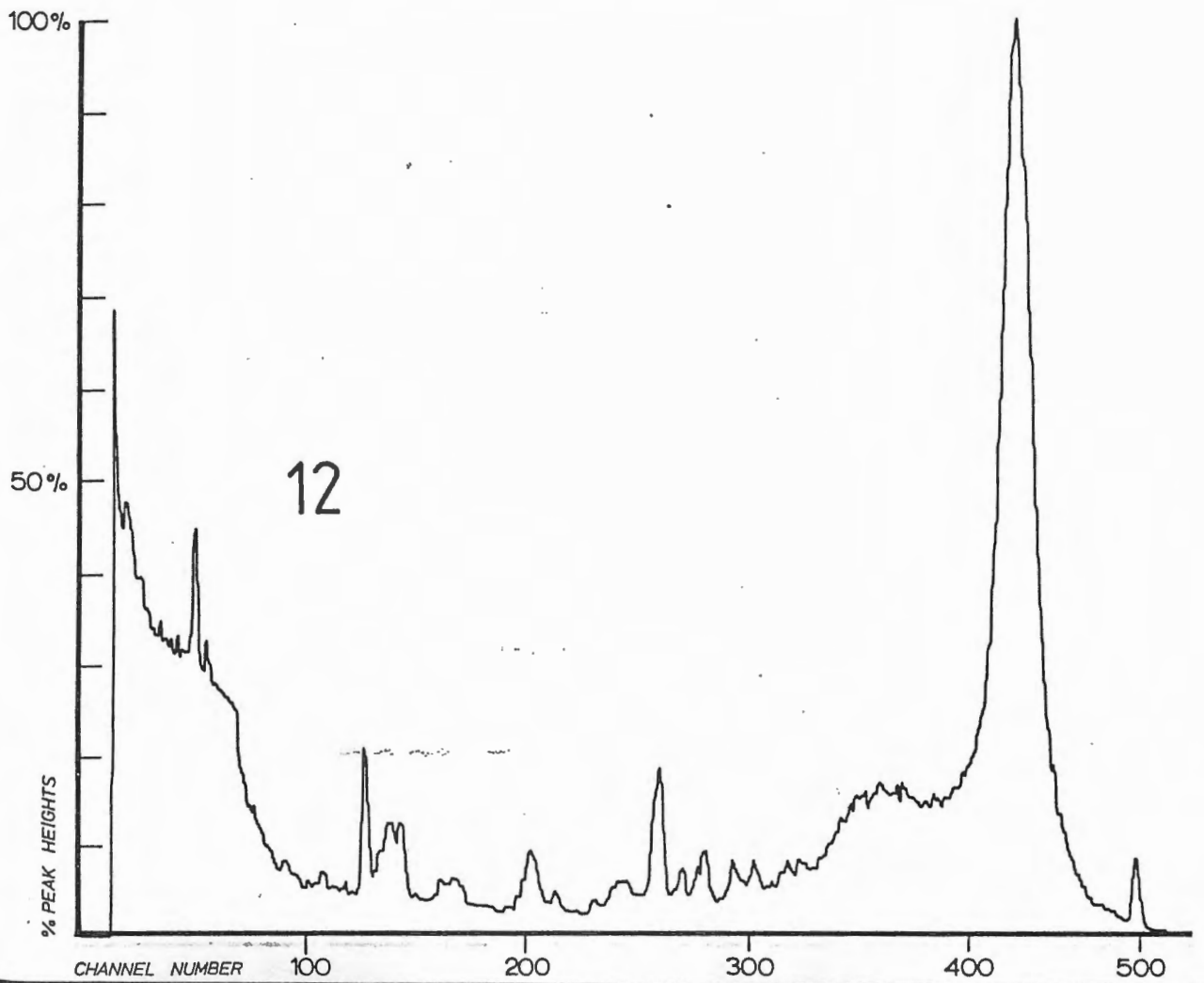
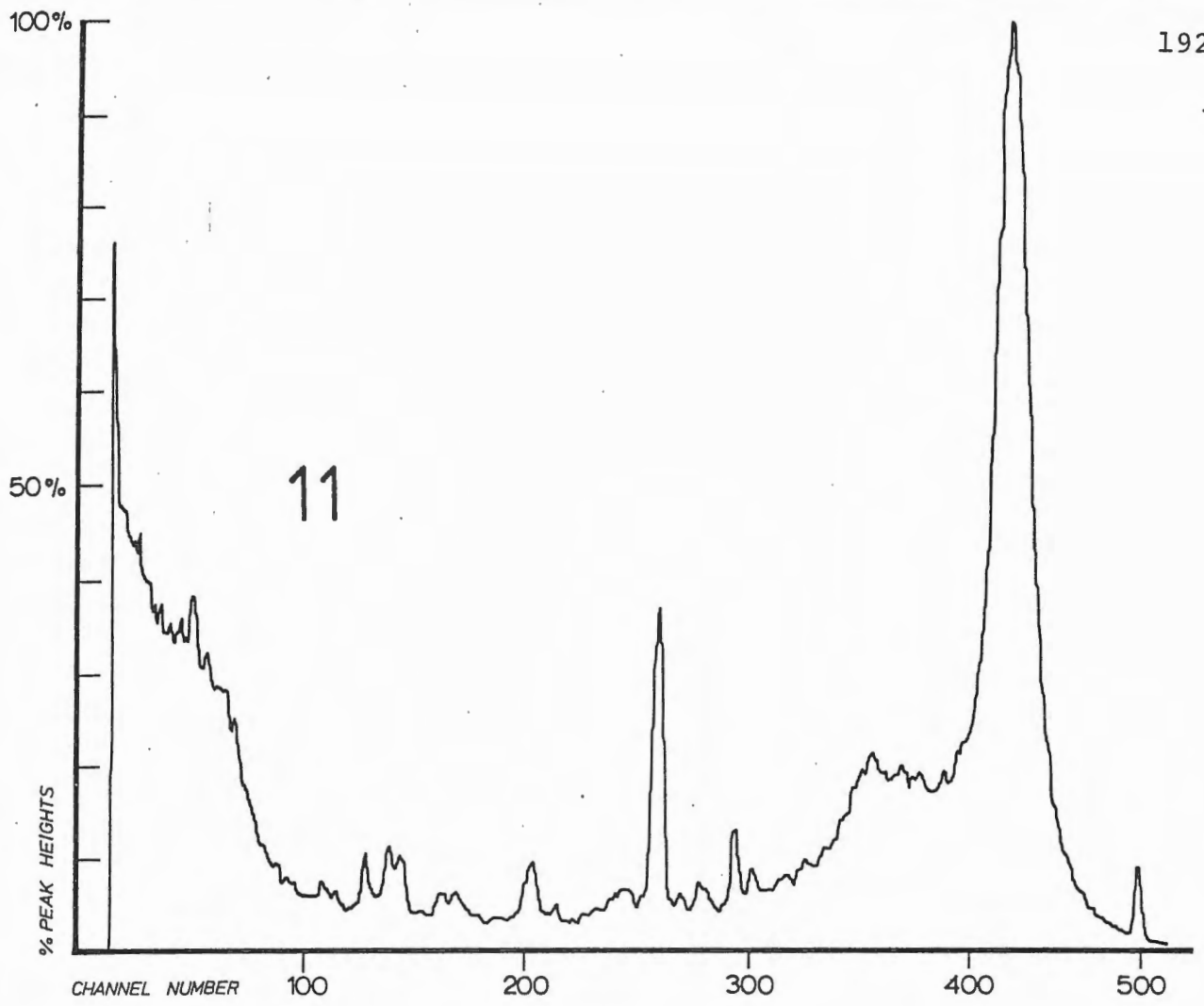


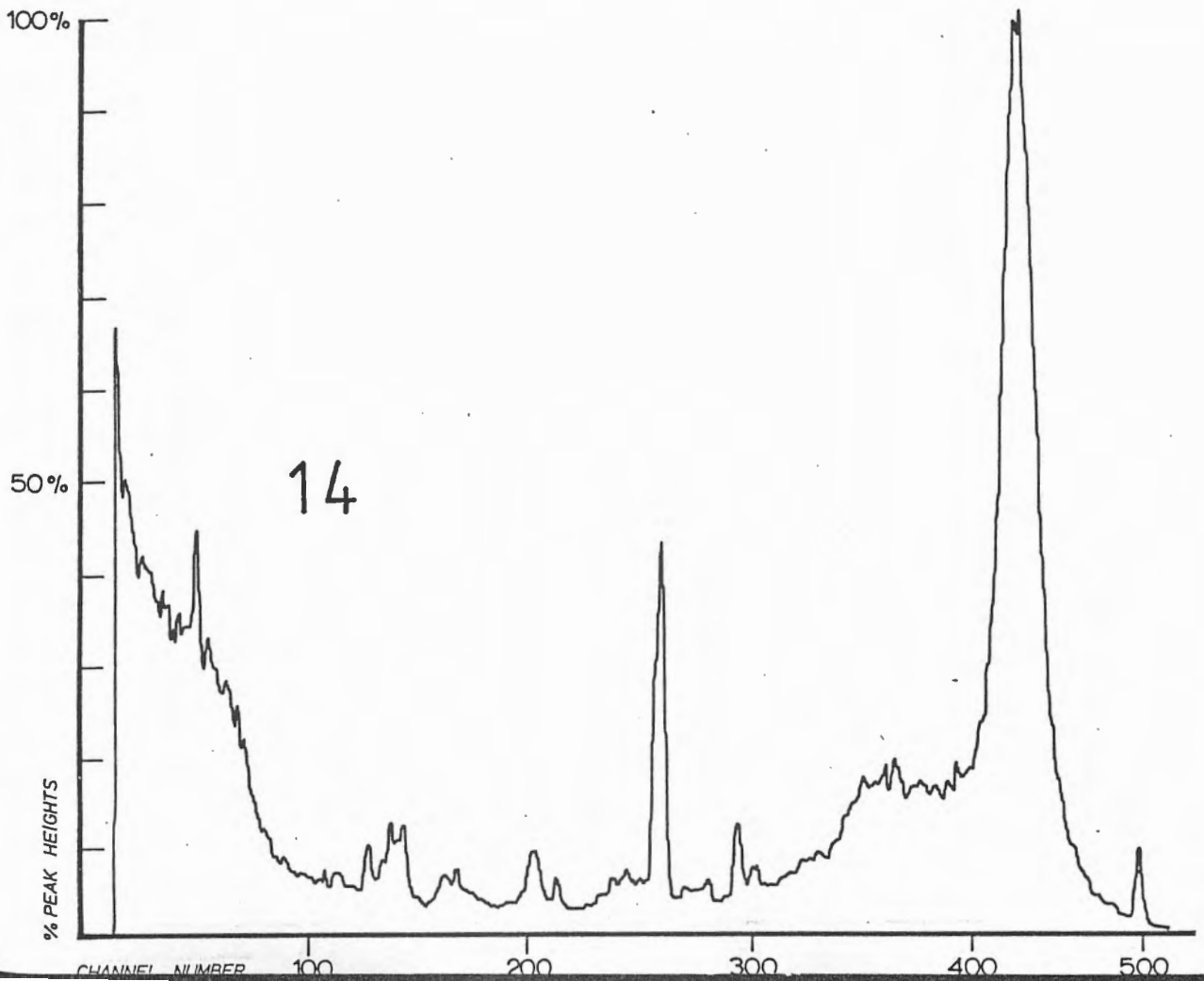
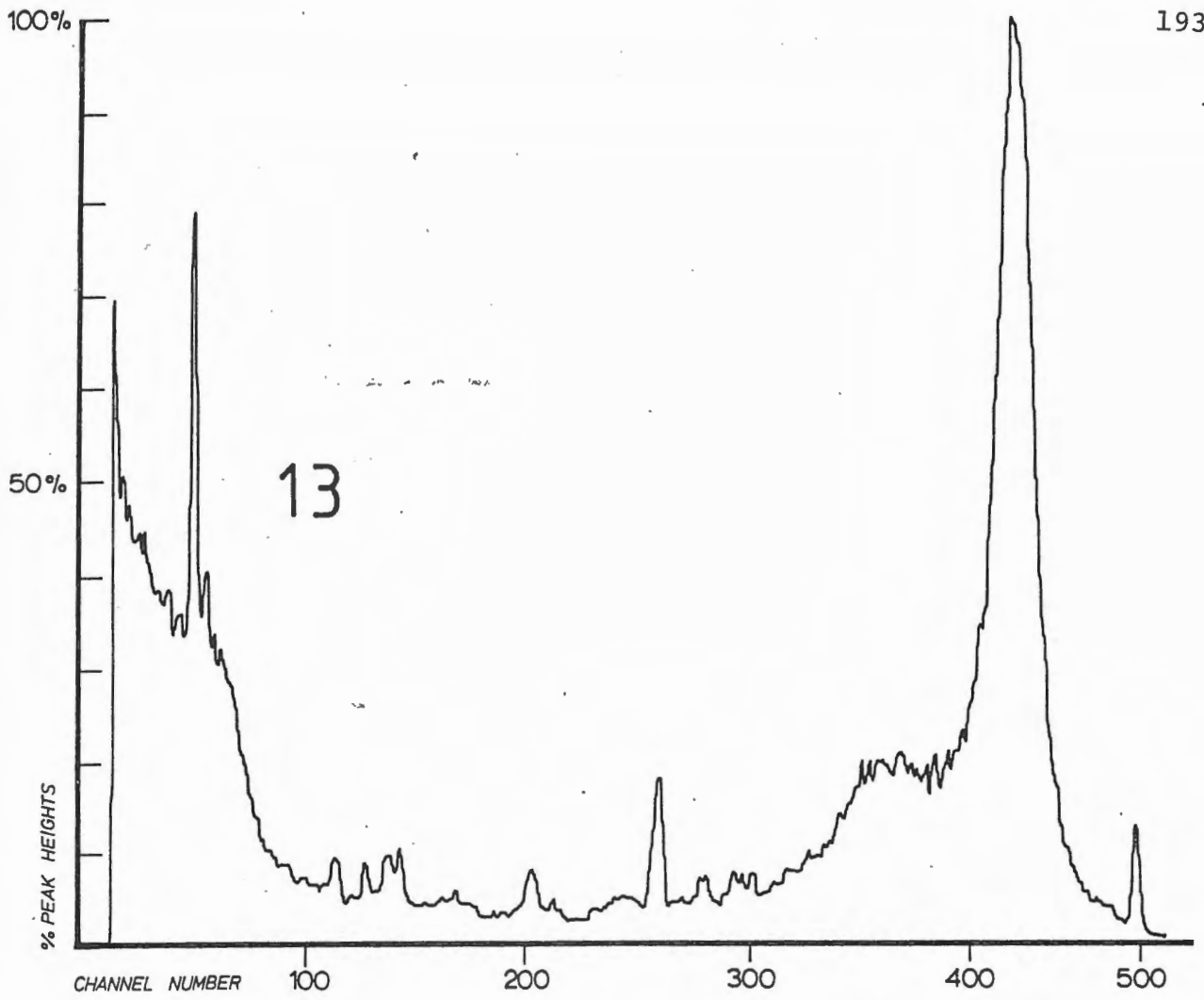


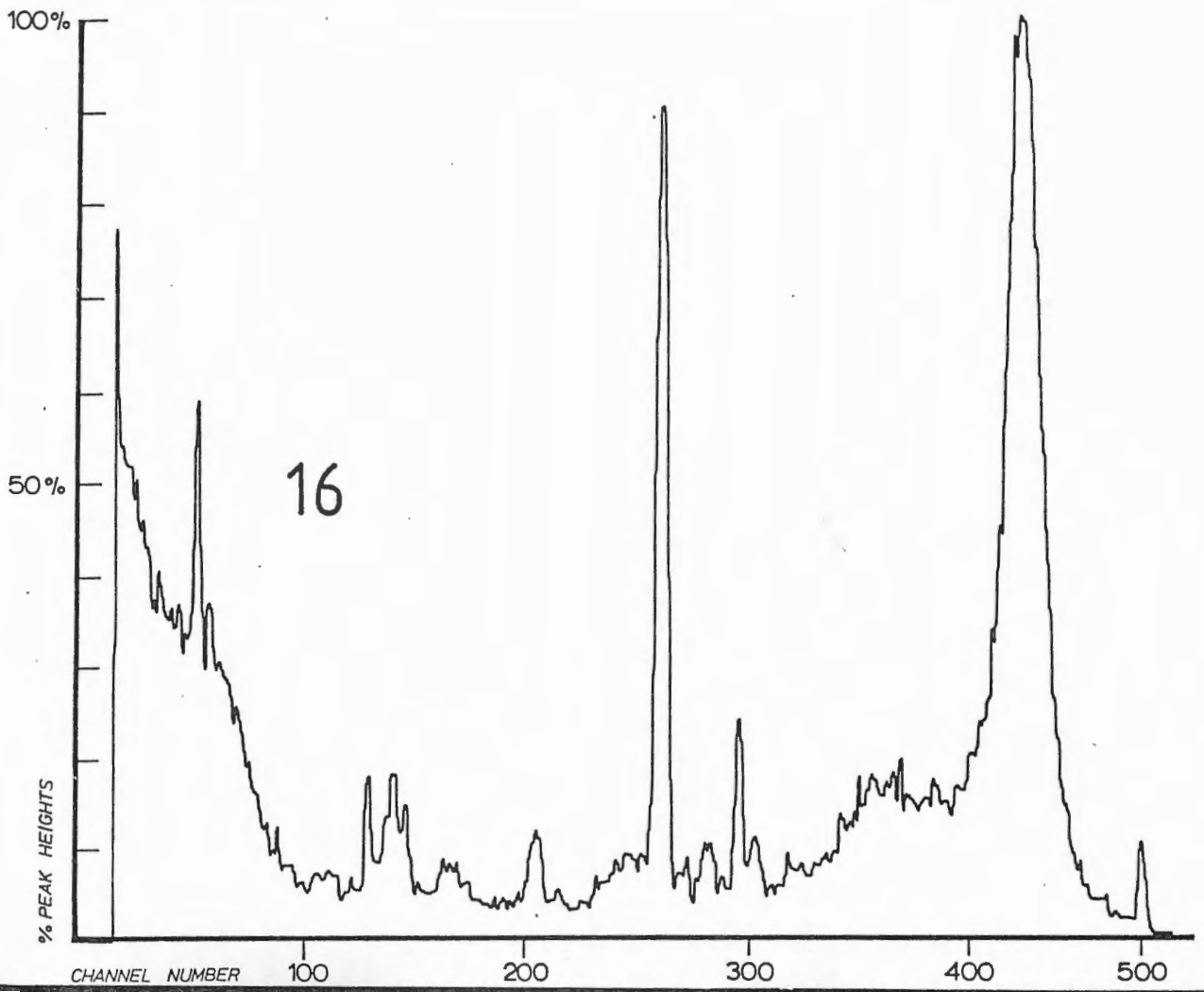
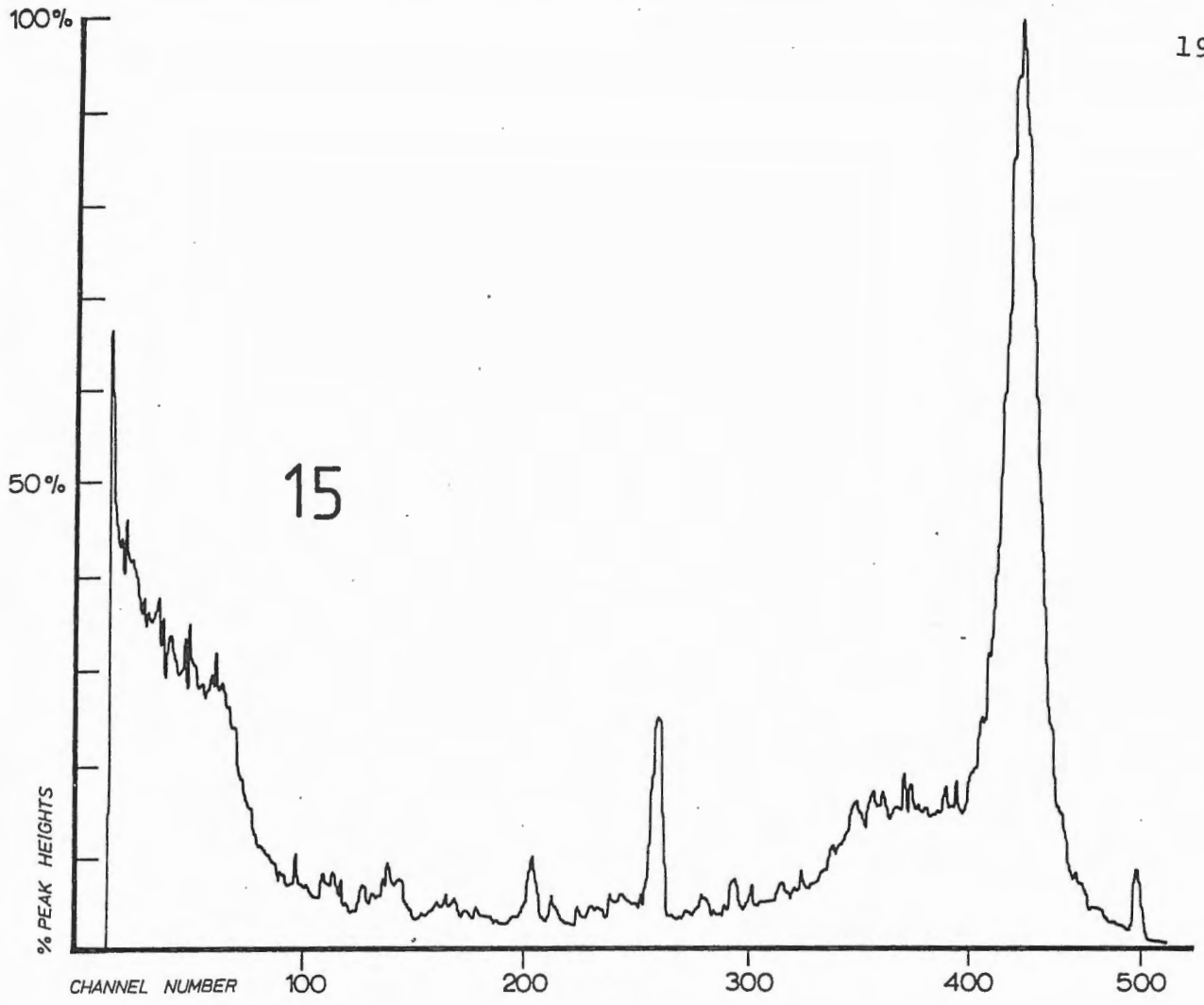


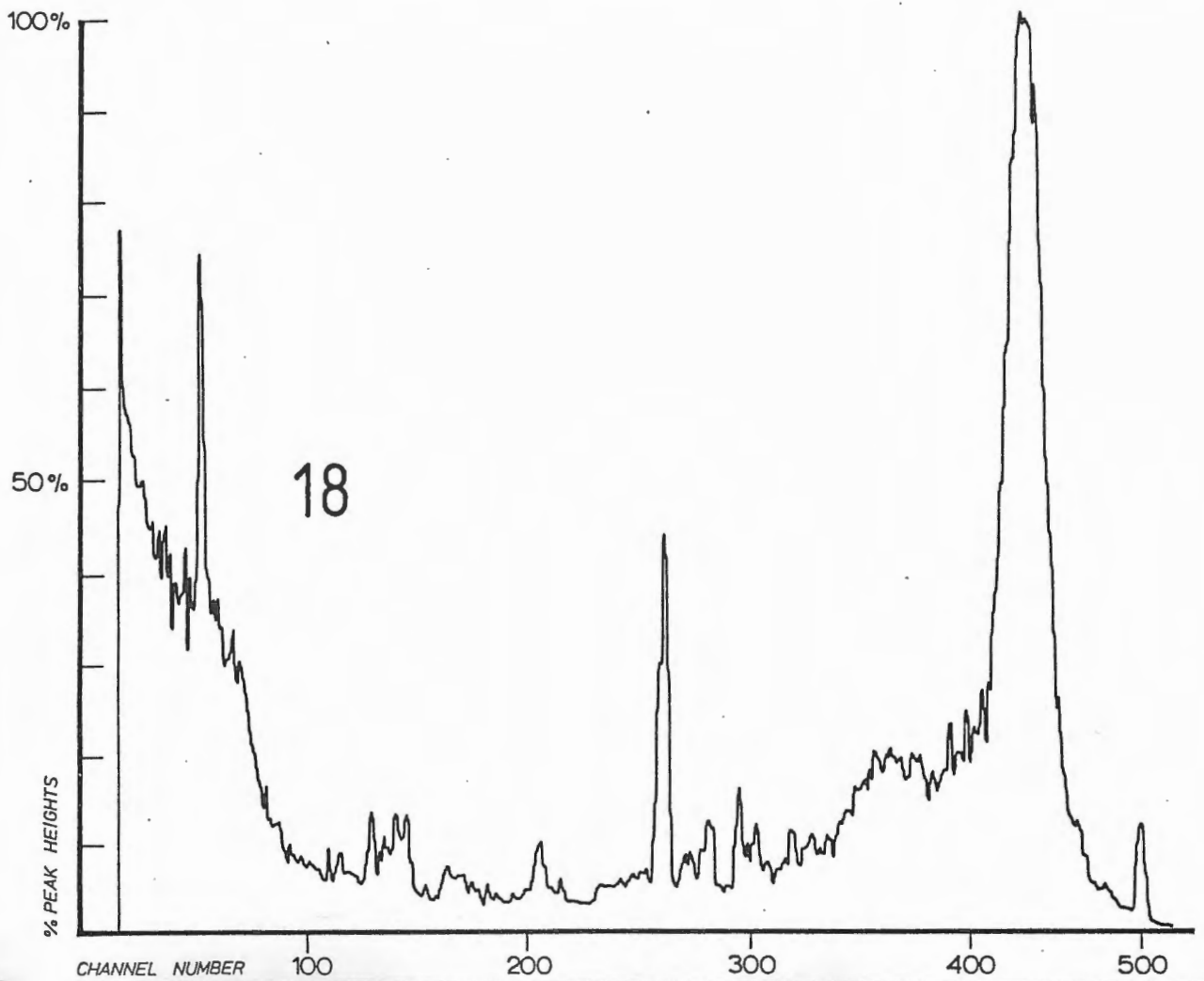
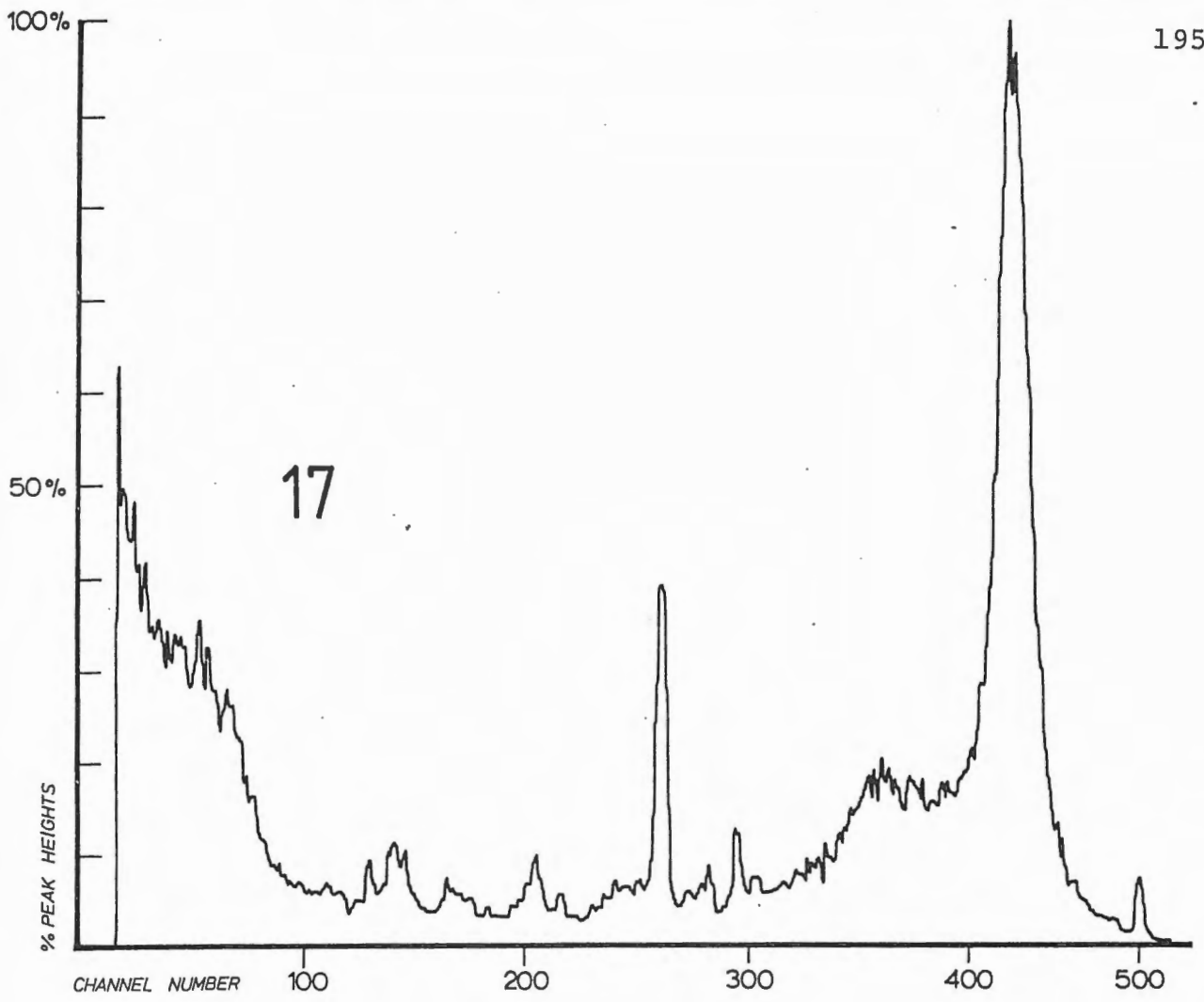


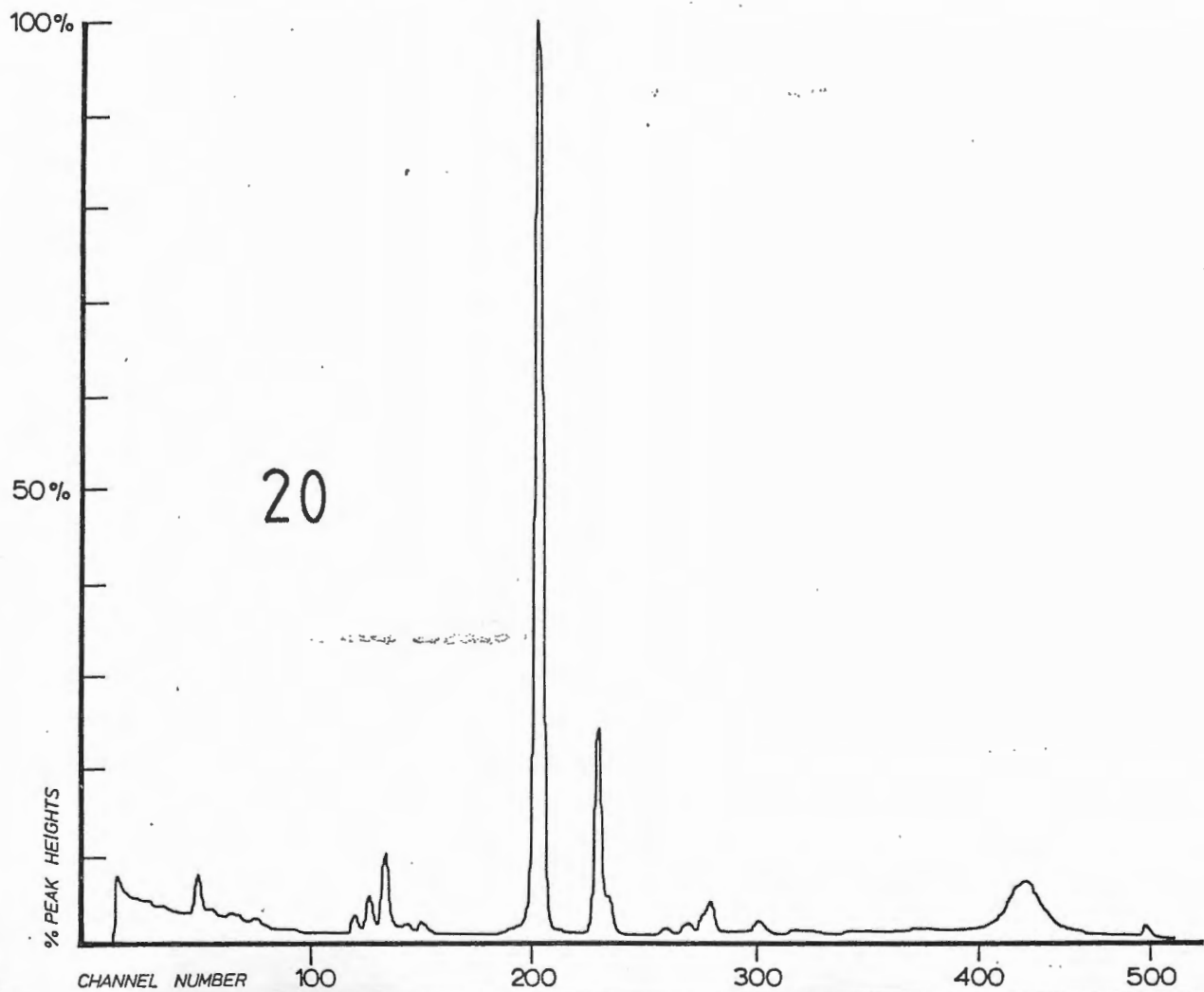
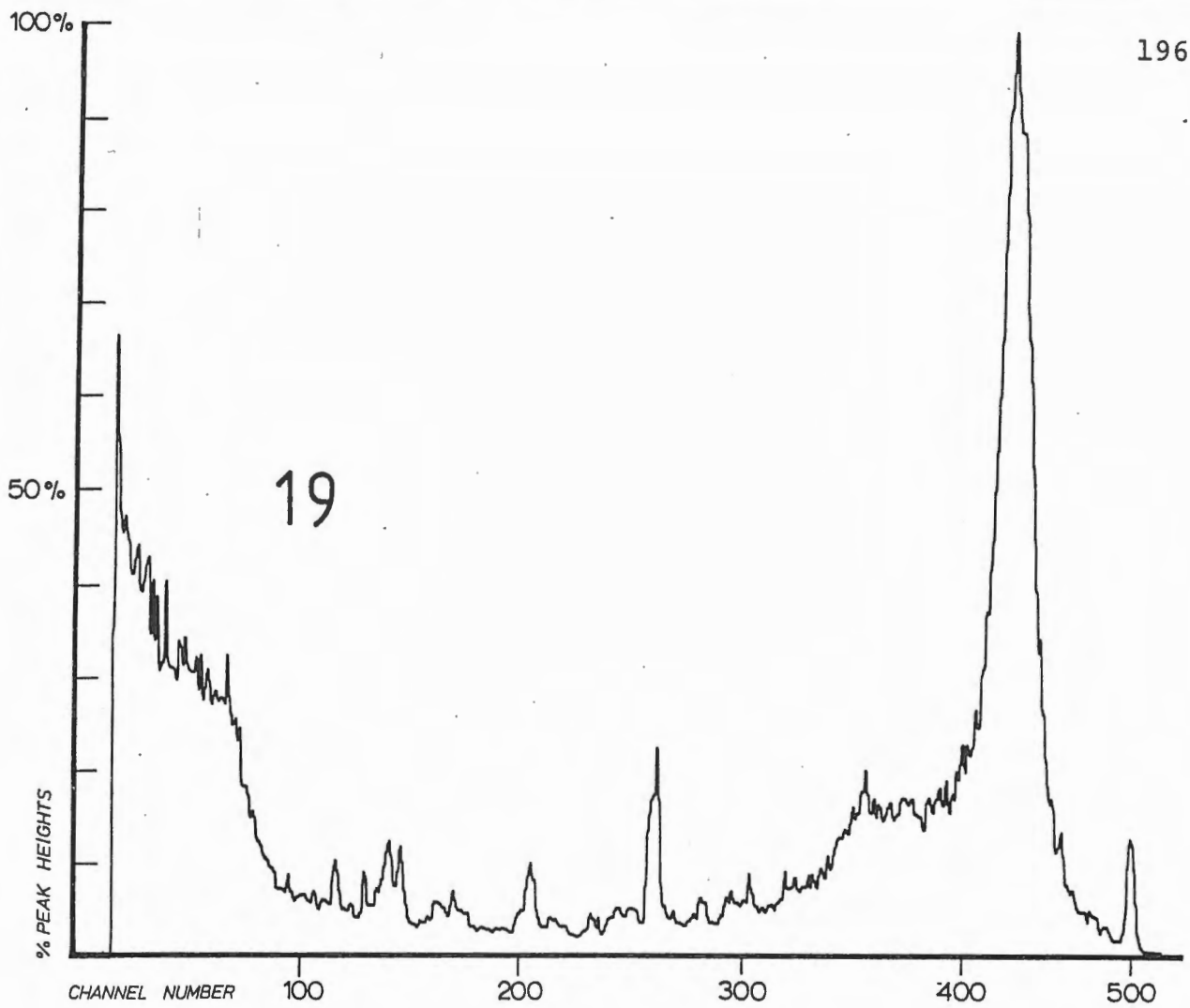














## APPENDIX B

## REFERENCE SOURCE GROUPS

## RAW DATA

FILE NAME SUPPLIED=...WAIARE DAT ...

820157 DAT

.945371	.463497	.000000	.357355	2.421052	.000000	.676570	1.393888	15.196516
---------	---------	---------	---------	----------	---------	---------	----------	-----------

820249 DAT

.823782	.404011	.023639	.240688	1.868125	.000000	.624642	1.213467	18.947840
---------	---------	---------	---------	----------	---------	---------	----------	-----------

820270 DAT

.742588	.425876	.000000	.232480	1.894879	.000000	.372642	1.193288	18.490124
---------	---------	---------	---------	----------	---------	---------	----------	-----------

820251 DAT

.832378	.429799	.000000	.275072	2.355301	.000000	.515759	1.223496	14.964749
---------	---------	---------	---------	----------	---------	---------	----------	-----------

END OF FILE FOUND - END  
STOP

FILE NAME SUPPLIED=...PUNGAEREDAT ...

820150 DAT

.467391	.459627	.000000	.210404	1.911491	.121118	.447981	.972050	17.895832
---------	---------	---------	---------	----------	---------	---------	---------	-----------

820252 DAT

.385470	.558974	.000000	.169231	2.475214	.067521	.996581	1.526496	18.984825
---------	---------	---------	---------	----------	---------	---------	----------	-----------

820253 DAT

1.416822	.771963	.128037	.408411	3.063551	.000000	.820561	1.771963	16.853401
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820254 DAT

1.041308	.588640	.059380	.426850	2.822720	.000000	.788296	1.764200	19.006226
----------	---------	---------	---------	----------	---------	---------	----------	-----------

820255 DAT

.839580	.454273	.050225	.254123	2.112444	.000000	.608696	1.386807	18.393259
---------	---------	---------	---------	----------	---------	---------	----------	-----------

END OF FILE FOUND - END  
STOP

820195 DAT

1.014901 820196 DAT	.200331	.000000	.100461	1.022179	.119377	.435430	.937001	18.804406
.901216 820274 DAT	.039514	.000000	.067629	1.042553	.039514	.356393	1.080547	18.562763
1.155594 820275 DAT	.083916	.000000	.227273	1.540210	.093531	.555944	1.232517	19.910858
.892009 820277 DAT	.125270	.000000	.022678	1.287257	.112311	.331533	.939525	17.399441
.694505 R820282 DAT	.000600	.034066	.124176	.993604	.180220	.159341	.421978	16.665627
1.563596 820295 DAT	.131579	.004336	.144737	1.618421	.217105	.399123	1.008772	16.669470
.860384 820296 DAT	.197208	.054101	.176265	1.396160	.071553	.418348	1.092496	17.119747
1.260442 820297 DAT	.130221	.009828	.232187	1.783784	.058968	.500000	1.484030	18.588097
.777056 820298 DAT	.012987	.000000	.135281	1.593073	.231602	.521645	1.203463	19.860189
.751323 820299 DAT	.235450	.000000	.160053	1.690476	.407407	.707672	1.134921	24.547297
1.197092 820300 DAT	.109855	.000000	.136511	1.222940	.218094	.638126	1.098546	18.732559
1.119601 820301 DAT	.039867	.058140	.066445	1.018272	.142027	.493355	.863787	18.599190
1.047203 820302 DAT	.013986	.027972	.154720	1.650349	.107517	.428322	.994755	17.408859
1.146639 820303 DAT	.114053	.000000	.253564	1.486762	.186354	.741344	1.496945	19.472103
.899691 820304 DAT	.016975	.000000	.101080	1.458333	.274691	.509259	1.246914	20.329863
.835329 820305 DAT	.095808	.000000	.097305	1.074850	.116018	.401198	.727545	21.546295
1.277887 820306 DAT	.174168	.030333	.263209	1.485323	.055773	.477495	1.307241	19.099548
.812741 820307 DAT	.148649	.000000	.100386	1.181467	.227799	.621622	1.088803	20.379900
1.222011 820308 DAT	.051233	.030361	.095325	1.388994	.000000	.347249	1.058823	16.918552
1.108992 820309 DAT	.057221	.000000	.099455	.918256	.226158	.456403	.841962	19.587769
1.189602 820310 DAT	.000000	.037462	.115443	1.188073	.177370	.574159	1.003058	21.993563
1.248963 820311 DAT	.076763	.000000	.154564	1.632780	.105809	.668050	1.114108	16.709940
1.161702 820312 DAT	.151064	.008511	.121277	1.748936	.115957	.720213	1.644681	19.565638
1.181675 820313 DAT	.251135	.101106	.177723	1.251185	.105845	.389415	.984202	19.155478
1.089985 820314 DAT	.119013	.000000	.116110	1.137881	.000000	.373004	.962264	21.153347
.719388 820315 DAT	.039116	.022109	.032313	.920068	.047619	.530612	.904762	19.318087
1.155361 820316 DAT	.129103	.003282	.165208	1.765864	.283340	.510941	1.588621	18.877319
.957389 820317 DAT	.167411	.000000	.176339	1.352679	.171875	.400670	.939732	19.027353
1.044993 820318 DAT	.100145	.047896	.106853	1.271403	.177794	.543541	1.123367	17.336842

.570755 820317 DAT	.196319	.000000	.102781	.704788	.100000	.136150	.912577	13.924209
1.373873 820320 DAT	.029724	.000000	.100467	1.407777	.000000	.000000	1.024741	10.181857
.747826 820321 DAT	.000000	.013043	.193913	1.003261	.189565	.307321	.763478	16.110628
.931783 820322 DAT	.055814	.000000	.087597	1.200000	.000000	.279045	.831009	16.665209
.303982 820323 DAT	.122511	.000000	.122511	1.468606	.172282	.482009	.943338	17.174917
.896435 820324 DAT	.073005	.000000	.000000*	1.280136	.040747	.375212	1.275043	17.533733
1.430605 820325 DAT	.250890	.000000	.300712	1.508897	.183274	.642349	1.336299	16.717550
1.153571 820326 DAT	.042857	.020536	.134821	1.166072	.000000	.405357	1.080357	17.501957
.998527 820327 DAT	.126657	.064065	.168630	1.097202	.234904	.521355	1.219440	15.447807
1.022770 820328 DAT	.092979	.000000	.074953	1.470583	.000000	.651803	1.299810	20.182377
.938255 820329 DAT	.158389	.012081	.227517	1.330201	.164430	.412081	1.033557	15.444128
1.390909 820331 DAT	.203636	.000000	.237273	1.750909	.207273	.659091	1.298182	16.031424
.858569 820332 DAT	.119800	.006656	.167221	1.522462	.074875	.511647	1.212978	22.529182
.901869 820333 DAT	.151090	.000000	.135514	1.302181	.031153	.505452	.981308	17.238907
.588342 820334 DAT	.065574	.000000	.291439	1.422586	.161202	.370674	.794171	18.702271
1.014199 820335 DAT	.103448	.062880	.240365	1.561866	.000000	.414807	1.160243	20.876984
1.267552 820336 DAT	.098672	.015180	.260911	1.527514	.484820	.589184	.939279	21.456570
1.997758 820337 DAT	.094170	.000000	.093049	1.636771	.205157	.689462	1.401345	17.137810
.739130 820338 DAT	.164855	.082428	.146739	1.333333	.000000	.286043	.788043	16.679157
.863481 820339 DAT	.136519	.007679	.091297	1.390785	.083618	.368225	.885666	19.930549
1.050769 820340 DAT	.095385	.047692	.133077	1.092308	.147692	.547692	1.012308	19.616388
1.245378 820469 DAT	.100840	.068908	.135294	1.363025	.014286	.394118	.877311	17.975073
.837288 R820472 DAT	.000000	.000000*	.240678	1.223729	.271186	.522034	.881356	19.779219
.983784 820473 DAT	.129730	.048649	.281081	2.070270	.000000	.502703	1.108108	18.162264
1.139394 R820476 DAT	.212121	.000000	.236364	1.721212	.363636	.157576	.963636	20.346354
.398340 820477 DAT	.000000	.000000*	.024896	1.319502	.147303	.809129	1.219917	16.406639
.501845 820478 DAT	.265683	.118081	.190037	1.151291	.138376	.437269	1.014760	22.644230
1.123967 820479 DAT	.000000	.000000*	.065116	1.433471	.000000	.407025	.938017	17.928228
.668750 820480 DAT	.218750	.114063	.164063	1.109375	.000000	.146875	1.109375	15.583943
.992806 820481 DAT	.122302	.026978	.035971	1.179856	.000000	.393885	.848921	20.146757
1.325123 820482 DAT	.103448	.007389	.206897	1.719212	.096059	.729064	1.172414	17.643552
1.303777 820484 DAT	.221519	.000000	.000000*	1.060759	.056962	.303797	1.500000	21.176630
.905903	.000000	.000000*	.182336	1.116309	.000000	.122507	.946718	17.073364

FILE NAME SUPPLIED=...FANAL DAT ...

820434 DAT

.357664	.014599	.047445	.124088	.120438	1.428032	.127787	.113139	16.303225
820441 DAT								
.311787	.395437	.000000	.00000*	.00000*	2.939163	.174905	.357414	20.412754
820442 DAT								
.000000	.269504	.039007	.028369	.063830	1.746454	.000000	.171489	21.721394
820443 DAT								
.337302	.000000	.095238	.075397	.150794	2.664683	.299603	.428571	24.295336
820444 DAT								
.325260	.183391	.084775	.159170	.093426	2.055363	.259516	.276817	16.906250
820445 DAT								
.239645	.094675	.226331	.275148	.224652	1.855029	.244083	.375740	23.609846
820446 DAT								
.305344	.270992	.188931	.101145	.011450	2.193206	.365496	.461332	27.028250
820447 DAT								
.214058	.201278	.110224	.000000	.00000*	1.698083	.127794	.456869	21.146790
820448 DAT								
.000000	.091803	.000000	.00000*	.436066	1.742623	.000000	.019672	21.497652

END OF FILE FOUND - END  
STOP

GRTBAR DAT

FILE NAME SUPPLIED=...GRTBAR DAT ...

820194 DAT

.360825	.160530	.000000	.037555	.000000	2.401325	.000000	.325479	19.541153
820435 DAT								
.475177	.156028	.000000	.102837	.000000	2.671986	.276596	.205674	21.131887
820436 DAT								
.700521	.059896	.067708	.074219	.151042	2.819010	.113281	.276042	23.727119
820437 DAT								
.639896	.225389	.000000	.00000*	.028197	2.727979	.400259	.370466	19.020761
820438 DAT								
.171875	.071875	.154688	.132813	.175000	2.978125	.160938	.443750	20.299595
820439 DAT								
.049479	.312500	.039062	.000000	.101562	4.541667	.197917	.718750	21.555172
820389 DAT								
.154762	.000000	.043155	.130952	.139881	3.147321	.220238	.467262	26.581920
820889 DAT								
.188755	.301205	.000000	.00000*	.00000*	3.130522	.212851	.566265	17.319195
820390 DAT								
.540909	.304545	.000000	.084091	.004545	3.081818	.015909	.304545	18.562763
820891 DAT								
.605263	.162281	.000000	.078947	.276316	2.471491	.184211	.149123	21.959257
820892 DAT								
.154589	.072464	.000000	.00000*	.00000*	2.601449	.115942	.338164	13.752403
820893 DAT								
.639706	.069353	.000000	.119485	.000000	2.472426	.000000	.327206	25.843538
820894 DAT								
.162996	.118943	.000000	.00000*	.00000*	3.145375	.050661	.198238	17.342106

END OF FILE FOUND - END



.000000 820403 DAT	.251813	.178102	.000000	.110727	4.161818	.091777	.269091	22.577477
.145570 820402 DAT	.000000	.028681	.009494	.025316	3.131329	.047051	.215190	19.958933
.134004 820410 DAT	.235194	.140931	.007333	.203333	3.704657	.000000	.132353	17.095318
.203704 820411 DAT	.055556	.065344	.063786	.232310	2.957819	.000000	.100823	17.609196
.373333 820412 DAT	.063333	.098333	.000000	.136667	5.778334	.000000	.116667	19.402222
.314356 820413 DAT	.032178	.049505	.037129	.000000	4.150790	.210396	.413366	19.125971
.116477 820414 DAT	.071023	.000000	.00000*	.036932	4.518466	.093750	.062500	19.955645
.072254 820415 DAT	.182081	.078035	.023121	.101156	4.864162	.004335	.563584	19.908045
.000000 820416 DAT	.018088	.018088	.074935	.033592	5.059432	.038760	.136951	16.347179
.141827 820417 DAT	.137019	.013221	.000000	.00000*	3.156250	.000000	.165865	18.544600
.000000 820418 DAT	.00000*	.050546	.023224	.000000	4.087432	.000000	.120217	15.884616
.308989 820419 DAT	.143258	.068820	.061798	.000000	3.497191	.147472	.081461	16.747574
.333333 820385 DAT	.003175	.180952	.141270	.282540	4.052381	.047619	.485714	19.010754
.051643 820386 DAT	.215962	.258216	.000000	.145540	6.286385	.124413	.211268	16.487703
.204489 820387 DAT	.087282	.000000	.00000*	.087282	4.401496	.061097	.246883	17.758553
.194690 820379 DAT	.005900	.104720	.000000	.00000*	5.081121	.000000	.206490	27.553648
.290541 820380 DAT	.000000	.057432	.000000	.060811	5.856419	.074324	.266892	20.341797
.216560 820381 DAT	.054140	.050955	.081210	.251592	6.708599	.152866	.210191	16.461096
.069054 820382 DAT	.184143	.135550	.031969	.053708	4.516624	.000000	.381074	23.650862
.050992 820383 DAT	.000000	.100567	.135977	.101983	4.762040	.114731	.283286	21.838461
.098551 820384 DAT	.121739	.131884	.073913	.133333	4.923188	.037681	.168116	18.040598
.257511 820420 DAT	.163090	.148069	.100858	.047210	4.881974	.000000	.025751	24.868055
.235437 820421 DAT	.218447	.157767	.040049	.046117	4.104369	.000000	.434466	21.688211
.103261 820422 DAT	.089674	.084239	.039402	.057065	4.629076	.000000	.317935	18.809989
.127796 820423 DAT	.073482	.193291	.142173	.025559	4.944090	.000000	.159744	16.568001
.132716 820505 DAT	.197531	.177469	.004630	.040123	5.203704	.000000	.219136	18.847015
.504273 820495 DAT	.150997	.000000	.009972	.074074	4.606837	.042735	.193732	18.720585
.272727 820506 DAT	.340909	.190341	.247159	.244318	7.281250	.142045	.250000	17.165255
.103560	.148067	.252427	.014563	.000000	5.491910	.000000	.365696	20.505281

END OF FILE FOUND - END  
STOP

820191 DAT								
.211781	.032749	.016830	.002505	.072805	3.006957	.129617	.298738	17.242447
820348 DAT								
.244352	.121665	.053111	.008653	.058670	2.613301	.153753	.343676	10.560397
820349 DAT								
.704434	.305419	.177340	.000000	.108374	3.036246	.024631	.142857	22.836009
820350 DAT								
.154186	.025714	.000000	.041429	.000000	2.273571	.220000	.420000	24.215593
820351 DAT								
.205314	.108696	.055556	.062802	.185990	2.500000	.099034	.490338	16.064598
820352 DAT								
.000000	.225895	.044077	.115702	.143251	2.712121	.119835	.432507	25.942461
820353 DAT								
.152000	.152000	.156000	.184000	.456000	3.098000	.104000	.216000	17.800480
820354 DAT								
.173913	.236025	.068323	.000000	.158335	2.697205	.180124	.475155	18.559927
820355 DAT								
.033654	.389423	.350962	.254808	.182692	4.579327	.295673	.461538	18.262777
820356 DAT								
.331230	.094637	.025237	.000000	.000000	2.621451	.238170	.394322	18.398340
820357 DAT								
.444840	.341637	.199288	.126335	.131673	2.884342	.128114	.476868	22.334999
820358 DAT								
.116000	.160000	.216000	.138000	.100000	3.202000	.088000	.104000	27.580379
820359 DAT								
.508152	.230978	.073370	.028533	.000000	2.911685	.072011	.171196	27.189871
820360 DAT								
.193651	.190476	.101587	.025397	.260317	3.114286	.319048	.380952	21.758333
820361 DAT								
.103797	.159494	.032911	.055696	.174684	2.192405	.011392	.270886	21.535521
820363 DAT								
.289963	.208178	.087361	.076208	.000000	2.641264	.269517	.486939	15.831839
820366 DAT								
.296073	.314199	.193353	.072508	.051360	2.509063	.028701	.178248	17.158590
820367 DAT								
.386973	.222222	.011494	.026820	.141762	3.459770	.287356	.398467	26.631945
820368 DAT								
.219512	.410569	.162602	.266260	.134146	3.121951	.091453	.646341	18.111940
820369 DAT								
.451505	.344482	.138796	.078595	.143813	2.961538	.209030	.438127	16.243986
820370 DAT								
.374622	.495468	.209970	.102719	.229607	2.531722	.191843	.462236	29.521471
820371 DAT								
.000000	.039216	.039216	.000000	.277778	2.736928	.107843	.388889	23.407768
820372 DAT								
.293210	.064815	.037037	.109568	.000000	2.083333	.070988	.376543	23.147961
820373 DAT								
.486842	.282395	.062500	.138158	.526316	2.822368	.177632	.430921	22.597610
820374 DAT								
.057307	.045845	.134670	.031519	.128940	2.446291	.217765	.406877	20.458622
820375 DAT								
.230126	.284519	.100418	.121339	.041841	3.282427	.156904	.292887	20.314919
820376 DAT								
.070652	.396739	.157609	.040761	.239130	3.625000	.355978	.646739	21.499998
820377 DAT								
.204327	.000000	.021635	.012019	.040865	2.152644	.014423	.120192	23.619049
820378 DAT								
.111111	.154882	.085859	.291246	.043771	3.580908	.346001	.653199	27.352823
820500 DAT								
.625000	.354167	.172917	.222917	.037500	4.193750	.241667	.608333	21.099369





820213 DAT

1.000000	.022133	.134105	.012072	.000000	1.011066	.094567	.219316	19.762354
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820214 DAT

1.287457	.000000	.188153	.057491	.222997	1.335366	.000000	.033101	17.105263
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820215 DAT

1.497890	.200422	.200422	.000000	.000000*	1.453586	.172270	.210970	20.712210
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820216 DAT

1.453815	.000000	.186747	.134503	.046185	2.016064	.265060	.168675	18.524694
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820217 DAT

1.286995	.000000	.154709	.000000	.000000*	1.466368	.190583	.100897	20.136011
----------	---------	---------	---------	----------	----------	---------	---------	-----------

820218 DAT

.863544	.071283	.035642	.000000	.150713	2.505092	.000000	.107943	16.851116
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820219 DAT

1.789568	.000000	.193345	.104317	.071942	1.982014	.000000	.066547	16.713285
----------	---------	---------	---------	---------	----------	---------	---------	-----------

820220 DAT

.693295	.000000	.045649	.000000	.161198	2.029244	.000000	.186876	22.682617
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END OF FILE FOUND - END  
STOP

FILE NAME SUPPLIED=...LOUIS DAT ...

820259 DAT

.412387	.084592	.085347	.011329	.522659	4.459214	.105740	.528701	22.455883
---------	---------	---------	---------	---------	----------	---------	---------	-----------

820260 DAT

.305882	.117647	.160504	.058824	.608403	4.412605	.024370	.341176	16.785198
---------	---------	---------	---------	---------	----------	---------	---------	-----------

820236 DAT

.563050	.258065	.126833	.096041	.458944	4.342376	.022727	.642229	18.347677
---------	---------	---------	---------	---------	----------	---------	---------	-----------

820237 DAT

.752273	.070455	.056818	.000000	.550000	6.364773	.082955	.479545	21.020794
---------	---------	---------	---------	---------	----------	---------	---------	-----------

820238 DAT

.159944	.147427	.097357	.039638	.390821	3.828929	.068846	.276773	18.758865
---------	---------	---------	---------	---------	----------	---------	---------	-----------

820501 DAT

.421405	.280936	.030100	.000000	.187291	4.219064	.078595	.351171	18.122406
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820502 DAT

.179402	.142857	.265781	.222591	.521595	4.916944	.000000	.441860	21.989001
---------	---------	---------	---------	---------	----------	---------	---------	-----------

820503 DAT

.448276	.158046	.140805	.000000	.301724	4.018679	.306034	.433908	25.659752
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END OF FILE FOUND - END  
STOP

FILE NAME SUPPLIED=...TALASEA DAT ...

820233 DAT	.000000	.197279	.370748	.000000	.000000	2.074150	.275519	.353742	14.329700
820234 DAT	.000000	.066116	.208673	.026840	.000000	4.000000	.179752	.491736	16.719425
820493 DAT	.000000	.255319	.129433	.019504	.205674	2.625886	.177305	.017750	14.826087
820835 DAT	.358871	.012097	.104839	.082661	.169355	2.453629	.120968	.153226	21.380436
820836 DAT	.159817	.095890	.228311	.000000	.000000*	2.152968	.000000	.159817	24.608107
820877 DAT	.254630	.050926	.145833	.000000	.000000*	2.791667	.236111	.000000	22.337502
R820879 DAT	.250000	.073770	.110656	.000000	.086066	2.670082	.141393	.229508	30.791208
820884 DAT	.027027	.000000	.285714	.069498	.239382	3.801158	.000000	.007722	22.785389

END OF FILE FOUND - END  
STOP

FILE NAME SUPPLIED=...BANKSGRPDAT ...

820248 DAT	.872340	.027079	.278530	.026112	.261122	7.000967	.000000	.295938	17.521194
820263 DAT	.982721	.000000	.185745	.046436	.393089	6.220302	.000000	.287257	18.574795
820264 DAT	.521739	.013913	.147826	.027826	.240000	4.806087	.013043	.323478	20.104624
R820828 DAT	.739645	.177515	.032544	.000000	.147929	7.505917	.168639	.775148	22.105526
820829 DAT	1.049383	.119342	.002058	.006173	.329218	5.004115	.331276	.320988	22.280104
820837 DAT	1.260000	.000000	.110000	.000000	.000000*	7.736666	.000000	.653333	17.224138
820838 DAT	.854922	.051813	.220207	.059585	.481865	6.595855	.186529	.580311	18.523254
820895 DAT	.779343	.061033	.000000	.000000*	.450704	5.626761	.000000	.178404	18.589520
820896 DAT	.848777	.000000	.000000*	.000000*	.250859	4.005155	.000000	.206136	19.082569
820897 DAT	.729034	.302789	.019920	.000000	.143426	4.778885	.258964	.119522	18.849056
820898 DAT	1.022013	.034591	.110063	.029874	.179245	3.954402	.080169	.323699	16.265217
820899 DAT	1.426901	.000000	.169591	.046784	.000000	6.204678	.283626	.520468	23.540232
820900 DAT	.803828	.105263	.143541	.035885	.229665	5.031100	.196172	.449761	23.250000

END OF FILE FOUND - END

FILE NAME SUPPLIED=...TAFahi DAT ...

820265 DAT

.949477	.000000	.317944	.017422	.156537	2.968815	.022648	.073171	19.815836
820266 DAT								
1.038585	.049839	.327974	.089228	.000000	2.020900	.000000	.135048	17.061539
820267 DAT								
1.269682	.045226	.241206	.000000	.000000*	2.278057	.000000	.018425	18.434015
820268 DAT								
1.226087	.084783	.372826	.052174	.034783	2.961957	.000000	.058696	18.322332
820269 DAT								
1.328094	.000000	.312377	.030452	.051081	2.585462	.000000	.151277	17.869478
820270 DAT								
2.259174	.000000	.244266	.019495	.050459	1.772936	.000000	.272936	15.979555
820271 DAT								
2.367580	.084475	.267123	.000000	.152968	2.146119	.114155	.050228	18.467117
820492 DAT								
.807971	.115942	.219203	.000000	.038855	2.023551	.000000	.072464	16.584507

END OF FILE FOUND - END  
STOP

FILE NAME SUPPLIED=...PITCARN DAT ...

820491 DAT

1.076471	.014706	.000000	.010294	.685294	9.048530	.247059	.911765	19.865803
820830 DAT								
.952096	.000000	.000000*	.022455	.497006	8.326347	.287425	.745509	16.611874
820832 DAT								
1.105085	.000000	.000000*	.047458	.450847	9.238899	.344068	.610170	16.834906
820833 DAT								
.976471	.188235	.211765	.019608	.509804	10.358824	.000000	.819608	22.537033
820875 DAT								
1.821839	.017241	.163793	.281609	1.258621	12.195403	.339080	1.264368	16.441177
820876 DAT								
1.558139	.148837	.058140	.000000	.972093	9.318604	.318605	.813953	25.447155
820873 DAT								
1.142857	.050193	.000000	.000000*	.698642	7.998417	.179537	.501931	14.526317

END OF FILE FOUND - END  
STOP

FILE NAME SUPPLIED=...CANTERB DAT ...

820229 DAT									
2.228980 820347 DAT	.096601	.016100	.007156	.597496	3.837209	.367621	.030631	14.195163	
4.384106 820348 DAT	.000000	.655629	.000000	.367550	7.625828	.400662	1.417219	15.239494	
2.414530 820349 DAT	.119658	.241453	.042735	.034188	4.329060	.083333	1.012820	14.578389	
4.171053 820350 DAT	.000000	.256579	.082237	.828947	6.250000	.796053	1.480263	17.210257	
3.404255 820301 DAT	.000000	.156028	.000000	.879433	7.815603	.968085	1.609929	13.508959	
3.013699 820902 DAT	.287671	.160959	.000000	.520548	5.657534	.530822	.945205	15.990244	
2.784211 820903 DAT	.000000	.023684	.076316	.389474	4.323684	.547368	1.047368	12.607091	
3.469136	.104938	.453704	.160494	.697551	6.432099	.842593	1.160494	15.285023	

END OF FILE FOUND - END  
STOP

FILE NAME SUPPLIED=...OTAGPEN DAT ...

820230 DAT									
.016598 820843 DAT	.000000	.325726	.056017	.085062	2.040456	.158714	.479253	11.077260	
.000000 820844 DAT	.00000*	.218000	.132000	.072000	2.210000	.098000	.408000	12.308909	
.000000 820845 DAT	.00000*	.559859	.250000	.246479	2.816901	.285211	.619718	14.039569	
.061538 820846 DAT	.000000	.361538	.182051	.000000	1.838462	.005128	.261538	13.286386	
.221154 820906 DAT	.000000	.298077	.103365	.000000	1.661058	.055298	.509615	13.261575	
.000000 820907 DAT	.00000*	.248677	.002646	.306878	2.473545	.497354	.206349	11.145329	
.070175 R820910 DAT	.000000	.222222	.192982	.385965	2.970760	.435672	.573099	14.138578	
.000000	.00000*	.567308	.237179	.346154	2.980769	.000000	.467949	13.204981	

END OF FILE FOUND - END  
STOP

FILE NAME SUPPLIED=...PUNAWA DAT ...

820239 DAT

1.160998	.253968	.017007	.010204	1.390023	2.535117	.090023	.904762	18.002029
820240 DAT								
1.142857	.202703	.000000	.018340	1.166023	1.926641	.418919	.866795	13.992351
820487 DAT								
1.441767	.020080	.000000	.010040	1.105141	2.409759	.441767	1.257023	17.946886
820488 DAT								
.878205	.038462	.043269	.201923	1.275641	1.514423	.000000	.660256	18.090910
820489 DAT								
.892473	.078853	.091398	.130824	1.075269	2.087813	.548387	.942652	18.688053
820459 DAT								
1.131148	.036885	.063525	.043033	1.331967	1.911835	.221311	.467213	20.542599
820490 DAT								
.846575	.161644	.120548	.057534	.742466	1.486301	.300000	.597260	20.432314
R820881 DAT								
.801749	.110787	.093294	.058309	.842566	1.688047	.406706	.862974	25.857141
820882 DAT								
1.021277	.212766	.000000	.007979	1.755319	2.784575	.643617	1.398936	16.833899
820883 DAT								
.504615	.000000	.00000*	.024615	.956923	1.884615	.238462	.732308	20.115881

END OF FILE FOUND - END  
STOP

FILE NAME SUPPLIED=...MANAKEA DAT ...

820256 DAT

4.791925	.173913	.624224	.000000	.574534	2.875777	.310559	.447205	15.625925
820257 DAT								
5.027682	.000000	.660900	.000000	.543253	3.837370	.368512	.937716	13.116498
820258 DAT								
3.780980	.000000	.291066	.010086	.149856	2.139770	.000000	.602305	15.629777
820460 DAT								
4.040000	.034286	.428571	.000000	.531429	3.168571	.277143	.468571	15.739256
820885 DAT								
3.209945	.000000	.328729	.000000	.270718	2.256906	.000000	.392265	14.953975
R820911 DAT								
4.034246	.000000	.541096	.044521	.513699	2.863014	.356164	.458904	16.726294
820887 DAT								
5.711864	.000000	.347458	.000000	.347458	3.516949	.148305	.313559	13.721992
820888 DAT								
4.226027	.054795	.849315	.058219	.445205	2.787671	.383562	.315068	12.533505

END OF FILE FOUND - END  
STOP

FILE NAME SUPPLIED=...WESFERG DAT ...

820261 DAT

.423140	.138843	.149587	.043302	.373554	5.212397	.000000	.361963	18.240248
820839 DAT								
.551570	.210762	.154709	.000000	.206278	5.762331	.123318	.663677	21.750002
820840 DAT								
.064639	.129278	.007605	.026517	.418251	5.891635	.007605	.285171	16.272909
820841 DAT								
.339100	.186851	.000000	.003460	.591695	5.083045	.000000	.276817	19.839130
820842 DAT								
.125402	.000000	.086817	.118971	.299035	5.295820	.308682	.395498	17.755320

END OF FILE FOUND - END  
STOP

FILE NAME SUPPLIED=...RAPANUI DAT ...

820221 DAT

.528716	.032095	.059966	.168074	.760135	1.626689	.308277	.778716	19.351893
820222 DAT								
.583591	.078947	.019350	.103715	.882353	2.514706	.424923	.772446	16.129629
820223 DAT								
.894009	.110599	.080645	.218894	.946236	2.308756	.199693	.869432	16.882978
820224 DAT								
.555215	.073620	.000000	.437117	1.898773	3.674847	.217791	1.337423	18.030661
820225 DAT								
.517119	.000000	.00000*	.102125	.769776	1.913813	.338253	.752066	18.428840
820241 DAT								
.564112	.066978	.000000	.140966	.683801	1.869159	.258318	.677570	14.816038
820242 DAT								
.721884	.120061	.082067	.139818	1.045593	2.018997	.227964	.802432	16.081797
820243 DAT								
.642393	.015605	.105332	.127438	.919376	2.531209	.419376	1.189857	17.715729
820244 DAT								
.439101	.104905	.050409	.120572	.918256	2.954360	.297003	1.087193	19.795225
820245 DAT								
.449052	.041469	.054502	.031991	.513033	2.636256	.333531	1.202607	18.777435
820246 DAT								
.568398	.063536	.109807	.229972	.917127	3.109116	.452348	1.087017	20.317667

END OF FILE FOUND - END  
STOP

## APPENDIX C

RESULTS OF SCREENING PROCEDURE AS  
APPLIED TO SOURCE GROUP SPECTRA



## NORTHLAND N=9

At  $2\sigma$ :

100% were able to reject every other source but Northland

At  $3\sigma$ :

100% were able to reject every other source but Northland

## MAYOR ISLAND N=62

At  $2\sigma$ :

100% were able to reject every other source but Mayor Island

At  $3\sigma$ :

100% were able to reject every other source but Mayor Island

## FANAL ISLAND N=9

At  $2\sigma$ :

67% could not reject Fanal Island only

33% could not reject Fanal Island and at least one other source

33% could not reject Huruiki

22% could not reject Great Barrier

11% could not reject Talasea

At  $3\sigma$ :

11% could not reject Fanal Island only

89% could not reject Fanal Island and at least one other source

89% could not reject Huruiki

56% could not reject Talasea

44% could not reject Great Barrier

22% could not reject Kermadecs

11% could not reject Inland

## HURUIKI N=30

At 2 $\sigma$ :

- 30% could not reject Huruiki only
- 70% could not reject Huruiki and at least one other source
- 60% could not reject Great Barrier
- 50% could not reject Talasea
- 40% could not reject Fanal Island
- 7% could not reject Inland

At 3 $\sigma$ :

- 3% could not reject Huruiki only
- 97% could not reject Huruiki and at least one other source
- 83% could not reject Fanal Island
- 80% could not reject Great Barrier
- 70% could not reject Talasea
- 33% could not reject Inland
- 17% could not reject Coromandel
- 17% could not reject Lou Island
- 13% could not reject Kermadecs
- 7% could not reject Banks Island Grp

## GREAT BARRIER N=13

At 2 $\sigma$ :

- 0% could not reject Great Barrier only
- 100% could not reject Great Barrier and at least one other source
- 92% could not reject Huruiki
- 23% could not reject Fanal Island
- 23% could not reject Talasea
- 15% could not reject Inland

At  $3\sigma$ :

- 0% could not reject Great Barrier only
- 100% could not reject Great Barrier and at least one other source
- 100% could not reject Huruiki
- 69% could not reject Fanal Island
- 69% could not reject Talasea
- 54% could not reject Kermadecs
- 38% could not reject Coromandel
- 38% could not reject Inland
- 15% could not reject Lou Island
- 8% could not reject Banks Island Grp
- 8% could not reject Fergusson Island
- 8% could not reject Otago 'Glass'

COROMANDEL N=26

At  $2\sigma$ :

- 19% could not reject Coromandel only
- 81% could not reject Coromandel and at least one other source
- 62% could not reject Inland
- 27% could not reject Huruiki
- 27% could not reject Great Barrier
- 19% could not reject Fergusson Island
- 15% could not reject Talasea
- 8% could not reject Lou Island
- 8% could not reject Banks Island Grp

At  $3\sigma$ :

- 0% could not reject Coromandel only
- 100% could not reject Coromandel and at least one other source
- 88% could not reject Inland

73% could not reject Fergusson Island  
 69% could not reject Huruiki  
 69% could not reject Great Barrier  
 61% could not reject Talasea  
 58% could not reject Lou Island  
 58% could not reject Banks Island Grp  
 11% could not reject Pitcairn Island

INLAND N=56

At  $2\sigma$ :

7% could not reject Inland only  
 93% could not reject Inland and at least one other source  
 84% could not reject Coromandel  
 41% could not reject Talasea  
 38% could not reject Huruiki  
 30% could not reject Great Barrier  
 12% could not reject Fergusson Island  
 7% could not reject Lou Island

At  $3\sigma$ :

0% could not reject Inland only  
 100% could not reject Inland and at least one other source  
 98% could not reject Coromandel  
 82% could not reject Huruiki  
 82% could not reject Great Barrier  
 77% could not reject Talasea  
 64% could not reject Lou Island  
 54% could not reject Fergusson Island  
 21% could not reject Banks Island Group

9% could not reject Fanal Island

2% could not reject Pitcairn Island

TALASEA N=8

At  $2\sigma$ :

38% could not reject Talasea only

62% could not reject Talasea and at least one other source

38% could not reject Fanal Island

38% could not reject Huruiki

25% could not reject Inland

13% could not reject Great Barrier

13% could not reject Coromandel

At  $3\sigma$ :

0% could not reject Talasea only

100% could not reject Talasea and at least one other source

100% could not reject Huruiki

75% could not reject Great Barrier

63% could not reject Fanal Island

50% could not reject Inland

38% could not reject Coromandel

38% could not reject Kermadecs

LOU ISLAND N=8

At  $2\sigma$ :

38% could not reject Lou Island only

62% could not reject Lou Island and at least one other source

62% could not reject Huruiki

13% could not reject Great Barrier

At  $3\sigma$ :

- 0% could not reject Lou Island only
- 100% could not reject Lou Island and at least one other source
- 87% could not reject Huruiki
- 50% could not reject Banks Island Grp
- 38% could not reject Talasea
- 25% could not reject Great Barrier
- 25% could not reject Coromandel
- 25% could not reject Inland
- 25% could not reject Fergusson Island

FERGUSON ISLAND N=5

At  $2\sigma$ :

- 20% could not reject Fergusson Island only
- 80% could not reject Fergusson Island and at least one other source
- 40% could not reject Lou Island
- 20% could not reject Coromandel
- 20% could not reject Banks Island Group

At  $3\sigma$ :

- 0% could not reject Fergusson Island only
- 100% could not reject Fergusson Island and at least one other source
- 100% could not reject Lou Island
- 60% could not reject Coromandel
- 60% could not reject Inland
- 60% could not reject Banks Island Group
- 40% could not reject Huruiki
- 20% could not reject Great Barrier
- 20% could not reject Talasea

## BANKS ISLAND GROUP N=13

At  $2\sigma$ :

- 92% could not reject Banks Island Group only
- 8% could not reject Banks Island Group and at least one other source
- 8% could not reject Coromandel
- 8% could not reject Lou Island
- 8% could not reject Fergusson Island

At  $3\sigma$ :

- 8% could not reject Banks Island Group only
- 92% could not reject Banks Island Group and at least one other source
- 46% could not reject Great Barrier
- 46% could not reject Lou Island
- 38% could not reject Pitcairn Island
- 31% could not reject Huruiki
- 31% could not reject Fergusson Island
- 23% could not reject Coromandel
- 8% could not reject Talasea

## PITCAIRN ISLAND N=7

At  $2\sigma$ :

- 100% were able to reject every other source but Pitcairn Island

At  $3\sigma$ :

- 57% could not reject Pitcairn Island only
- 43% could not reject Pitcairn Island and at least one other source
- 43% could not reject Banks Island Group

## TAFahi N=8

At  $2\sigma$ :

75% could not reject Tafahi only

25% could not reject Tafahi and at least one other source

25% could not reject Kermadecs

At  $3\sigma$ :

13% could not reject Tafahi only

87% could not reject Tafahi and at least one other source

75% could not reject Kermadecs

25% could not reject Mauna Kea

## KERMADECS N=8

At  $2\sigma$ :

87% could not reject Kermadecs only

13% could not reject Kermadecs and at least one other source

13% could not reject Tafahi

At  $3\sigma$ :

63% could not reject Kermadecs only

37% could not reject Kermadecs and at least one other source

25% could not reject Huruiki

25% could not reject Great Barrier

13% could not reject Tafahi

## RAPANUI N=11

At  $2\sigma$ :

45% could not reject Rapanui only

55% could not reject Rapanui and at least one other source

55% could not reject Puu Waawaa



At  $3\sigma$ :

18% could not reject Rapanui only

82% could not reject Rapanui and at least one other source

82% could not reject Puu Waawaa

PUU WAAWAA N=10

At  $2\sigma$ :

90% could not reject Puu Waawaa only

10% could not reject Puu Waawaa and at least one other source

10% could not reject Rapanui

At  $3\sigma$ :

80% could not reject Puu Waawaa only

20% could not reject Puu Waawaa and at least one other source

MAUNA KEA N=8

At  $2\sigma$ :

100% were able to reject every other source but Mauna Kea

At  $3\sigma$ :

100% were able to reject every other source but Mauna Kea

CANTERBURY PITCHSTONE N=8

At  $2\sigma$ :

100% were able to reject every other source but Canterbury Pitchstone

At  $3\sigma$ :

100% were able to reject every other source but Canterbury Pitchstone

## OTAGO 'GLASS' N=8

At  $2\sigma$ :

75% could not reject Otago 'glass' only

25% could not reject Otago 'glass' and at least one other source

25% could not reject Talasea

At  $3\sigma$ :

25% could not reject Otago 'glass' only

75% could not reject Otago 'glass' and at least one other source

75% could not reject Huruiki

38% could not reject Fanal Island

38% could not reject Talasea

25% could not reject Great Barrier

13% could not reject Inland

APPENDIX D .

HOUHORA ARTEFACTS

2000 SECOND COUNT

RAW DATA

FILE NAME SUPPLIED=...OUTPUT DAT ...

820518 DAT

2.188679	.207547	.358491	.188679	2.339622	.311321	.867925	2.849057	20.371134
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.824242	.212121	.133333	.221212	1.381818	.027273	.348485	1.066667	23.608334
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.470588	.222222	.150327	.000000	.00000*	5.392157	.000000	.163399	26.892857
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.955357	.178571	.107143	.071429	1.625000	.794643	.678571	.651786	23.086958
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.894309	.089431	.000000	.178862	1.357724	.065041	.288618	.495935	15.609650
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.949275	.644928	.228261	.242754	2.579710	.358696	.434783	1.268116	18.227642
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.971429	.257143	.000000	.125000	1.114286	.414286	.342857	.771429	17.704082
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1.604478	.358209	.037313	.350746	2.485075	.000000	.578358	1.462687	23.534882
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.675497	.536424	.000000	.076159	2.483444	.039735	.887417	1.364239	20.836365
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1.632184	.080460	.000000	.218391	1.264368	.632184	.540230	.747126	19.305264
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.313187	.285714	.189560	.000000	.00000*	4.848901	.000000	.00000*	14.806251
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.731481	.138889	.013889	.342593	1.111111	.041667	.236111	1.027778	18.752941
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.978261	.717391	.286232	.503623	2.260869	.000000	.659420	1.115942	19.266666
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1.111111	.111111	.059829	.346154	1.564103	.089744	.743590	1.051282	32.905659
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1.050000	.650000	.000000	.350000	2.390000	.000000	.815000	1.560000	26.769840
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1.117647	.137255	.000000	.075163	1.065359	.003268	.660131	.941176	23.197672
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.210526	.057416	.100478	.239234	.741627	.000000	.229665	.688995	20.643679
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1.211382	.406504	.000000	.207317	1.626016	.101626	.662602	1.203252	14.589042
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.744318	.187500	.014205	.343750	1.340909	.267045	.443182	1.017045	18.488806
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1.756757	.486486	.304054	.229730	1.770270	.000000	1.087838	2.067568	15.388887
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.595238	.273810	.101190	.000000	1.523810	.017857	.922619	1.464286	21.257145
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.962733	.322981	.012422	.062112	1.701863	.198758	.965838	1.521739	19.525423
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1.202247	.522472	.000000	.393258	2.022472	.000000	.418539	1.292135	15.598640
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.777070	.000000	.00000*	.00000*	.777071	.000000	.194713	.821655	17.764421
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1.799474	.289474	.289474	.013158	.986842	.230263	.585526	1.013158	19.944445
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.753623	.144928	.007246	.286232	1.688406	.000000	.079710	1.159420	17.293104
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.960938	.593750	.000000	.308594	2.210937	.351563	.859375	1.226562	16.349398
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1.305785	.256198	.157025	.223141	1.388430	.000000	.309917	1.363636	14.833333
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1.020202	.343434	.000000	.303030	2.080808	.151515	.944444	1.767677	22.037593
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820615 DAT	.886076	.000000	.075949	.139241	1.645570	.278491	.329114	.443038	21.854166
820616 DAT	.722222	.085859	.055556	.141414	1.015152	.083333	.126263	.454545	52.787041
820617 DAT	.326923	.355769	.076923	.086538	1.798077	.000000	.360577	1.028846	24.474682
820618 DAT	.426829	.560976	.189024	.000000	1.402439	.000000	.128049	1.365854	38.842106
820619 DAT	.246479	.000000	.000000*	.073944	1.338028	.003521	.000000	.359155	19.126215
820620 DAT	.835052	.123711	.000000	.000000*	1.577320	.000000	.010309	.587629	42.666664
	.053435	.496183	.000000	.175573	2.496183	.057252	.198473	.572519	22.352942

END-OF-FILE-FOUND---END  
STOP

FILE NAME SUPPLIED=...OUTPUT DAT ...

820621 DAT

820622 DAT	.516393	.000000	.012295	.000000	.688525	.090164	.385246	.778688	39.777779
820623 DAT	1.485437	.427184	.000000	.155340	1.951456	.432039	.334951	.650485	27.488096
820624 DAT	.124183	.281046	.003268	.179739	1.437908	.000000	.013072	.267974	231.250015
820625 DAT	.686667	.000000	.000000*	.000000*	1.033333	.070000	.286667	.893333	26.830359
820626 DAT	.545455	.157025	.000000	.000000*	1.107438	.152893	.500000	.834711	54.931377
820627 DAT	.437500	.150000	.000000	.275000	1.937500	.000000	.443750	1.200000	51.275005
820628 DAT	.415842	.000000	.000000*	.207921	2.000000	.158416	.500000	.554455	25.962769
820629 DAT	.446154	.492308	.223077	.000000	2.676923	.276923	.330769	1.569231	65.333336
820630 DAT	.097902	.125874	.111888	.055944	1.062937	.272727	.524475	.755245	26.088234
820631 DAT	1.147727	.511364	.159091	.295455	1.977273	.221591	.278409	.295455	58.926838
820632 DAT	.091743	.064220	.114679	.009174	1.073395	.000000	.000000*	.284404	64.187500
820633 DAT	.507042	.161972	.000000	.000000*	.464769	.000000	.000000*	.274648	24.797102
820634 DAT	.221429	.150000	.067857	.000000	1.564286	.000000	.232143	1.242857	28.166666

820635 DAT	.642458	.530726	.000000	.075419	2.039106	.000000	.324022	.675978	37.347225
820636 DAT	1.353536	.737374	.015152	.363636	2.929293	.242424	.217172	1.383839	29.141792
820637 DAT	.447154	.211322	.000000	.00000*	.894309	.003130	.398374	.634146	33.961540
820638 DAT	.356061	.356061	.064394	.321970	3.409091	.140152	.575758	1.257576	15.849055
820639 DAT	1.911111	.600000	.988889	.922222	3.377777	.566667	.788889	1.244444	20.119659
820640 DAT	.438202	.370787	.000000	.044944	2.056180	.280899	.674157	1.011236	60.151512
820641 DAT	.481203	.443609	.000000	.300752	1.676692	.165414	.000000	.458647	84.093750
820642 DAT	.642857	.238095	.218254	.206349	1.841270	.000000	.396825	.912698	29.500000
820643 DAT	.629630	.177778	.203704	.181481	1.170370	.196296	.044444	.400000	32.807693
820644 DAT	.677419	.814516	.044355	.471774	3.322581	.000000	.504032	1.104839	26.421877
820645 DAT	2.391954	.804598	.120690	.367816	4.609196	.000000	.448276	1.103448	29.203884
820646 DAT	.460000	.333333	.056667	.000000	1.206667	.160000	.686667	.486667	40.666676
820647 DAT	.444444	.055556	.005051	.060606	.747475	.000000	.313131	.601010	30.755322
820648 DAT	.611651	.126214	.053398	.000000	1.320388	.000000	.257282	1.359223	38.238094
820649 DAT	.639785	.053763	.000000	.032258	1.327957	.088710	.002683	.581398	39.693882
820650 DAT	.606061	.000000	.00000*	.080808	2.090909	.186869	.181818	.939394	22.561949
820651 DAT	.318841	.239130	.000000	.105072	.630435	.590580	.594203	.655072	33.277779
820652 DAT	.713043	.026087	.239130	.017391	.034783	5.634783	.000000	.156522	31.774195
820653 DAT	.070513	.358974	.054487	.035256	.916667	.169872	.112179	.115385	22.048386
820654 DAT	.301508	.386935	.067839	.037688	1.095477	.000000	.256281	.758794	38.809093
820655 DAT	.264957	.333333	.000000	.00000*	.897436	.000000	.418803	.974359	30.436365
820656 DAT	.183099	.154930	.000000	.239437	1.014084	.359155	.091549	.783732	18.488096
820657 DAT	.58182	.204545	.000000	.039773	1.943182	.409091	.159091	.227273	28.586958
820658 DAT	.382637	.076923	.000000	.137363	1.340659	.302198	.148352	.494505	30.840910
820659 DAT	.400000	.257143	.000000	.250000	1.471429	.342857	.207143	1.171429	44.779068
820660 DAT	.475000	.087500	.140625	.071875	.512500	.000000	.031250	.181250	25.064516
820661 DAT	.400000	.000000	.00000*	.00000*	1.800000	.270000	.340000	.630000	23.023529
820662 DAT	.511628	.186047	.027132	.000000	.829457	.000000	.170543	.542636	26.166670
820663 DAT	.609929	.581560	.000000	.00000*	2.397163	.485816	.336879	.836879	46.175003
820664 DAT	.585540	.116788	.000000	.361314	1.489051	.000000	.014599	.226277	31.459999
820665 DAT	.325571	.135714	.000000	.00000*	1.021429	.135714	.285714	.885714	32.794872
820666 DAT	.107527	.354839	.000000	.188172	1.752688	.177419	.543011	.935484	31.792685



820657 DAT	.494118	.341177	.000000	.000000*	2.176471	.000000	.411765	.029412	22.613335
820658 DAT	.907801	.283688	.085106	.000000	.439716	.000000	.219858	.475177	48.733334
820659 DAT	.217822	.000000	.000000*	.000000*	.000000*	4.252475	.000000	.504950	27.048613
820670 DAT	.166667	.650000	.483333	.175000	.466667	6.758334	.000000	.550000	31.610170
820671 DAT	.385714	.014286	.053571	.139286	1.100000	.000000	.385714	.642857	32.885719
820672 DAT	.538462	.083333	.000000	.000000*	.993590	.211538	.368590	.589744	36.850002
820673 DAT	.371212	.295455	.000000	.064394	1.659091	.000000	.522727	1.477273	20.095505
820674 DAT	.422414	.060345	.000000	.047414	1.060345	.258621	.521552	.939655	40.785717
820675 DAT	.034014	.000000	.034014	.105442	1.170068	.255102	.282313	.863946	27.696970
820676 DAT	.296053	.000000	.082237	.000000	.486842	.381579	.713816	.835526	30.000002
820677 DAT	.538462	.261539	.000000	.061538	1.184615	.000000	.292308	1.046154	19.551725
820678 DAT	.453237	.230216	.000000	.201439	1.517936	.000000	.014388	.187050	27.445944
820679 DAT	.190217	.000000	.000000*	.078804	.875000	.263587	.282609	.413043	25.796297
820680 DAT	.427350	.000000	.213675	.000000	1.384615	.000000	.726496	.948718	37.359150
820681 DAT	.333333	.085106	.000000	.000000*	1.042553	.056738	.517731	1.198582	29.389610
820682 DAT	.000000	.590909	.136364	.121212	1.772727	.106061	1.234848	1.606061	35.810349
820683 DAT	.849558	.061947	.000000	.000000*	.973451	.172566	.349557	.247788	45.636379
820684 DAT	.221476	.006711	.000000	.030201	.966443	.000000	.204698	.724832	13.870968
820685 DAT	.868217	.054264	.000000	.127907	1.248062	.000000	.368217	1.279070	37.964909
820686 DAT	.932836	.208955	.000000	.059701	1.291045	.000000	.171642	.910448	23.234568
820687 DAT	.683544	.107595	.079114	.000000	.860759	.246835	.227848	.556962	22.529068
820688 DAT	.053333	.100000	.030000	.000000	1.166667	.000000	.120000	.786667	36.000000
820689 DAT	.488889	.229630	.000000	.000000*	1.088889	.281481	.259257	.362963	23.163364
820690 DAT	.797101	.188406	.000000	.000000*	.920290	.000000	.000000*	.000000*	27.360291
820691 DAT	.532609	.586957	.027174	.070652	1.554348	.000000	.315217	1.239130	30.412504
820692 DAT	.466165	.135338	.097744	.172932	2.353384	.000000	.259393	.699248	28.007351
820693 DAT	.179487	.000000	.000000*	.000000*	.880342	.239316	.363248	.726496	23.403847
820694 DAT	.208333	.000000	.000000*	.101852	.875000	.164352	.000000	.518519	32.779068
820695 DAT	.403846	.096154	.067308	.153846	1.807692	.269231	.581731	.596154	31.620693
820696 DAT	.857742	.274194	.000000	.000000*	1.661290	.403226	.532258	.338710	34.351067
820697 DAT	.198473	.000000	.000000*	.000000*	1.175573	.000000	.000000*	.603053	20.921740
820698 DAT	.000000	.195122	.000000	.000000*	1.414534	.000000	.000000*	.593496	34.684612

387007 820700 DAT	.446237	.029570	.159533	1.519753	.072381	.456189	.397849	23.395603
.941176 820701 DAT	.424837	.111111	.032680	.973836	.000000	.052288	.751634	28.451614
.000000 820702 DAT	.00000*	.00000*	.539474	3.303632	.000000	.427632	2.013158	24.676545
.414966 820703 DAT	.000000	.010204	.044218	.707483	.000000	.255102	.496599	19.452829
.898876 820704 DAT	.000000	.039326	.067416	1.269663	.466292	.522472	1.539326	34.375000
.000000 820705 DAT	.273437	.195312	.097656	.007812	4.449218	.000000	.539062	23.603260
.669291 820706 DAT	.220472	.000000	.00000*	1.181102	.000000	.047244	.960630	34.171432
.412844 820707 DAT	.100917	.013761	.316514	1.394496	.000000	.385321	.954129	31.744680
.932203 820708 DAT	.152542	.000000	.050847	3.576271	.542373	1.067797	2.508475	30.846941
1.047619 820709 DAT	.019048	.000000	.00000*	.771429	.395238	.519048	.904762	38.612904
.437158 820710 DAT	.000000	.00000*	.065574	1.109290	.568306	.745902	.874317	23.882610
.520000 820711 DAT	.140000	.000000	.236667	1.806667	.190000	.506667	.433333	49.719299
.696429 820712 DAT	.267857	.281250	.000000	1.053571	.000000	.218750	.562500	27.221518
.710692 820713 DAT	.075472	.000000	.242138	1.119497	.000000	.292453	.465409	28.360762
.990654 820714 DAT	.448598	.000000	.257009	2.906542	.000000	.509346	1.915888	26.767122
.923810 820715 DAT	.047619	.000000	.085714	1.400000	.133333	.190476	.571429	40.510414

.526316 820716 DAT	.388158	.000000	.00000*	.822368	.016447	.427632	.342105	40.020832
.345588 820717 DAT	.330882	.102941	.290441	1.279412	.000000	.183824	.654412	33.129211
1.024390 820718 DAT	.085366	.256098	.000000	1.475610	.000000	.579268	.768293	135.875000
.217742 820719 DAT	.000000	.00000*	.00000*	1.298387	.000000	.262097	.830645	56.796375
.425373 820720 DAT	.149254	.018657	.044776	.962687	.097015	.305970	.658209	33.809856
.415584 820721 DAT	.123377	.000000	.022727	1.058442	.000000	.029221	.084416	29.932928
.369369 820722 DAT	.144144	.000000	.00000*	1.252252	.216216	.441441	.900901	37.694916
END OF FILE FOUND END STOP								

FILE NAME SUPPLIED=...OUTPUT DAT ...

820722 DAT								
.304813 820723 DAT	.401069	.000000	.002674	1.235294	.010695	.344920	.732620	43.156864
.000000 820724 DAT	.000000*	.000000*	.113475	1.432624	.269504	.507092	.319149	22.626123
.049724 820725 DAT	.000000	.000000*	.135359	1.066298	.016575	.193370	.751381	26.322580
.919355 820726 DAT	.274194	.000000	.000000*	1.370968	.094774	.274194	.943548	27.021276
.477778 820727 DAT	.261111	.000000	.000000*	.533333	.141667	.066667	.183333	44.414635
.496552 820728 DAT	.000000	.006897	.272414	1.158621	.000000	.082759	.393103	21.966215
.694030 820729 DAT	.044776	.000000	.070896	1.402985	.000000	.220149	.447761	35.712971
.528662 820730 DAT	.433121	.031847	.149682	1.420382	.000000	.031847	.535032	27.378376
.354545 820731 DAT	.136364	.000000	.031818	1.609091	.304545	.072727	.109091	45.777775
1.081818 820732 DAT	.027273	.000000	.390909	1.436364	.313636	.468182	.590909	21.125000
.625000 820733 DAT	.200000	.000000	.000000*	1.658333	.079167	.129167	.783333	23.745283
.684210 820734 DAT	.245614	.000000	.000000*	2.254386	.065789	.846491	1.447368	24.800001
.710145 820735 DAT	.000000	.231884	.188406	2.260870	.000000	.855072	1.231884	17.117977
.382716 820736 DAT	.425926	.000000	.206790	1.648148	.000000	.305556	.697531	32.103893
.222222 820737 DAT	.202614	.000000	.000000*	.784314	.245098	.238562	.339869	31.103447
.792453 820738 DAT	.037736	.000000	.377358	3.264151	.433962	1.349057	2.075472	27.825844
.291339 820739 DAT	.015748	.244094	.204724	1.511811	.437008	.338583	.716535	36.034481
.603960 820740 DAT	.237624	.000000	.108911	1.217822	.000000	.000000*	.683168	29.012663
.407895 820741 DAT	.000000	.000000*	.000000*	.980263	.000000	.000000*	.013158	32.259262
.000000 820742 DAT	.653226	.084677	.000000	1.387097	.000000	.120968	.338710	18.117645
1.200000 820743 DAT	.052632	.000000	.000000*	2.094737	.294737	.738842	.463158	27.145161
.381443 820744 DAT	.185567	.082474	.010309	1.938144	.350515	.000000	.257732	38.337662
.590062 820745 DAT	.074534	.217391	.288820	.807453	.298137	.220497	.509317	56.650005
.000000 820746 DAT	.265625	.000000	.000000*	1.023437	.000000	.003906	.492187	23.553846
.953846 820747 DAT	.023077	.000000	.011538	.961538	.146154	.707692	.630769	36.458336
.397849 820748 DAT	.494624	.193548	.209677	2.870968	.016129	.543387	1.451613	33.195118
.000000 820749 DAT	.267717	.003937	.000000	1.070866	.000000	.299213	.645669	23.311319
.523438 820750 DAT	.210937	.027344	.148437	1.031250	.000000	.011719	.328125	25.397963
.896226 820751 DAT	.000000	.000000*	.155660	1.679245	.363208	.344340	1.320755	34.094597



2.037975 820784 DAT	.000000	.000000*	.010767	2.240506	.335443	.373418	1.455686	17.626747
1.100000 820785 DAT	.250000	.012500	.333333	2.641667	.000000	.329167	1.466667	17.022522
.646667 820786 DAT	.286667	.000000	.046667	2.346667	.000000	.486667	.890000	11.008620
.985507 820787 DAT	.471015	.000000	.347326	2.130435	.014493	.677536	1.528986	20.306665
.536842 820788 DAT	.231579	.178947	.021053	.873684	.431579	.047368	.347368	35.448978
.386905 820789 DAT	.267857	.065476	.154762	.940476	.059524	.273810	.940476	19.816900
.27241 820790 DAT	.000000	.000000*	.081897	.693276	.443965	.349138	.560345	18.670885
.390977 820791 DAT	.150376	.041353	.011278	1.060150	.315789	.439850	1.007519	16.943298
2.562500 820792 DAT	.875000	.218750	.656250	2.625000	.260417	2.020833	2.958333	36.392151
5.695648 820793 DAT	1.173912	1.304347	1.978260	8.695646	.000000	2.565216	4.782605	18.421431
1.090909 820794 DAT	.298701	.000000	.246753	2.038961	.324675	.753247	1.584416	19.196201
.549020 820795 DAT	.071895	.009804	.133987	.954248	.000000	.509804	1.326797	20.999998
.991667 820796 DAT	.258333	.000000	.233333	1.583333	.220833	.366667	.541667	21.375000
1.375000 820797 DAT	.090909	.284091	.426136	1.693182	.295455	1.090909	1.704545	17.888889
.823944 820798 DAT	.098592	.000000	.267606	1.070422	.000000	.218310	.570423	24.458761
1.776471 820799 DAT	.011765	.235294	.182353	2.400000	.052941	1.011765	1.800000	21.068628
1.033333 820800 DAT	.050000	.000000	.233333	1.516667	.000000	.641667	1.075000	25.560438
5.838709 820801 DAT	.000000	.000000*	.580645	5.451613	.338710	3.241935	5.677420	27.559999
.981595 820802 DAT	.000000	.000000*	.177914	.748466	.098160	.662577	.975460	24.181818
.896552 820803 DAT	.048276	.000000	.041379	1.041379	.000000	.362069	.731035	19.217392
.766667 820804 DAT	.373333	.093333	.356667	1.540000	.203333	.446667	.893333	22.495968
3.750000 820805 DAT	1.678571	.160714	.571429	8.357142	2.017857	3.339286	4.642857	28.511904
.694737 820806 DAT	.157895	.178947	.252632	1.242105	.000000	.231579	.526316	16.430769
.972477 820807 DAT	.110092	.096330	.256381	1.550459	.541284	.600917	.633027	13.784723
.456897 820808 DAT	.672414	.198276	.525862	2.353448	.181034	.831897	1.396552	17.183908
.680851 820809 DAT	.340426	.005319	.425532	1.723404	.430851	.351064	.617021	22.089041
1.537500 820810 DAT	.537500	.043750	.268750	1.975000	.043750	1.143750	1.375000	18.299999
1.083333 820811 DAT	.541667	.027778	.000000	1.361111	.000000	.097222	1.125000	21.957628
.553442 820812 DAT	.766234	.000000	.824675	2.610389	.000000	.162338	1.246753	15.738635
1.046667 820813 DAT	.106667	.000000	.016667	1.066667	.120000	.050000	.646667	21.222826
1.148936 820814 DAT	.297872	.000000	.132979	1.500000	.095745	.898936	1.148936	19.843748
1.515790 820815 DAT	.147368	.000000	.000000*	1.157895	.000000	.000000*	.863158	12.240908

1	1.595238	.535714	.196429	.041667	1.214236	.297619	.517857	1.404762	22.422413
2	820816 DAT								
3									
4	.921260	.031496	.059055	.283465	1.055118	.031496	.220472	.748031	14.992159
5	820817 DAT								
6									
7	1.532609	.380435	.059793	.353261	2.202609	.000000	.663043	.793478	18.050505
8	820818 DAT								
9									
10	.372340	.021277	.053191	.393617	1.670213	.696809	.861702	1.542553	21.747313
11	820819 DAT								
12									
13	1.326087	.181159	.152174	.010670	1.159420	.384058	.590580	.710145	19.362745
14	820820 DAT								
15									
16	.376471	.100000	.032353	.305882	.905882	.064706	.323529	.741176	19.901234
17	820821 DAT								
18									
19	.977941	.007353	.128676	.224265	1.154412	.352941	.360294	.588235	11.815535
20	820862 DAT								
21									
22	.295302	.900000	.015101	.226510	.251678	6.110738	.000000	.442953	18.138891
23	820863 DAT								
24									
25	.007634	.141221	.139313	.068702	.290076	5.839695	.000000	.072519	21.010416
26	820864 DAT								
27									
28	.502203	.022026	.000000	.028634	.000000	6.825991	.246696	.414097	17.137056
29	820865 DAT								
30									
31	.423581	.157205	.082969	.000000	.131004	6.930131	.458515	.467249	24.553400
32	820866 DAT								
33									
34	.313653	.143911	.169742	.173432	.000000	6.837638	.228782	.413284	23.096296
35	820867 DAT								
36									
37	.323129	.159864	.017007	.000000	.020408	2.091837	.217637	.248299	19.363905
38	820868 DAT								
39									
40	.378723	.051064	.019149	.031915	.000000	5.321276	.185106	.446809	19.652632
41	820869 DAT								
42									
43	.075758	.015152	.207071	.068182	.005051	5.939394	.219697	.388889	23.993631
44	820870 DAT								
45									
46	.035088	.216374	.000000	.020468	.000000	6.076023	.266082	.485380	20.424049
47	820871 DAT								
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