THE IDENTIFICATION OF NEW ZEALAND OBSIDIANS

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ABSTRACT

Obsidian has proved to be a very valuable aid to archaeological investigations, especially in the area of prehistory. Its geological and archaeological occurrence is worldwide.

The aim of this investigation was to establish a satisfactory method of separating the eight known New Zealand sources of flake quality obsidian. Emission spectrography had been used with partial success but the maximum precision of this analytical method is ±5%. A more precise analytical method would enable the sources to be separated more readily.

A satisfactory method of sample preparation was developed which gave solutions in which iron, manganese and zinc could be analysed by atomic absorption spectrophotometry, and sodium and potassium by flame photometry.

Replicates of a representative sample from each source were analysed to establish the variation due to the method. This was found to be less than 2%, except when the zinc concentration was below 60 ppm. Analysis of a number of samples from six of the eight sources (Arid Island and Maraetai excluded), established that for these sources the variation in the concentration of at least one of the five elements, was greater between sources than within a source.

All sources, with the possible exception of Taupo and Arid Island, could be distinguished on the basis of the five named elements. Manganese was found to be the most useful element for characterization.

Only one Arid Island sample was available. In all properties it

was very similar to the Taupo pieces analysed, but it may not have been representative. The Maraetai samples available were not flake quality, therefore only one sample was analysed.

The densities of a number of samples from each source were determined by two methods, the hydrostatic weighing method and temperature variation free flotation method. The flotation liquid for the latter was a mixture of bromoform and 1-pentanol.

Successful separation by densities was limited because of extensive overlap between sources. Mayor Island and Kaeo samples were more dense and could be separated from the other six sources, but not from each other. The density method was useful, however, for pieces too small to be analysed chemically. It also had the advantages of being non-destructive and being more readily adaptable to the field.

The two methods of characterization, chemical analysis and density determination, were applied to obsidians from eight archaeological sites located in the following areas, Coromandel, Waikato, Kaipara, Auckland (3), Bluff and Manawatu. More than two hundred and fifty pieces were analysed and more than 95% were positively identified.

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CHAPTER I - INTRODUCTION

1. Occurrence and Use of Obsidian

Obsidian is a volcanic glass found in many areas of the world where igneous activity has occurred, such as North and South America, the Mediterranean, Iceland, Japan and Oceania. When viscous, silica-rich lava has cooled too rapidly to allow crystallization to occur obsidian is formed. It is typically a homogeneous, glassy material black or dark grey to reflected light. Viewed in transmitted light differences in colour become apparent. Some obsidians have a greenish hue, some are pale grey; internal banding and speckling may be visible. The degree of glossiness of freshly exposed surfaces varies and some obsidians have spherulitic inclusions throughout the glass.

The one property of obsidian which led to its worldwide use by Neolithic peoples is its conchoidal fracture. The material splinters readily to yield flakes with razor-sharp edges. These obsidian flakes were excellent cutting and scraping tools. Obsidian artifacts have been found at archaeological sites in Alaska[1], the United States[2,3], Mexico[4], and the Near East[5], the Mediterranean[6], New Guinea[7,8], Easter Island[9] and New Zealand[10].

The form which these artifacts took varied considerably. In some areas, such as New Zealand and New Guinea, there was little attempt to retouch the rude flakes produced haphazardly from the larger block of obsidian. Even here, however, deliberate shaping of tools was carried out to make blades and scrapers. With its property of furnishing razor-sharp edges obsidian was used for spear, arrow and lance heads[4,9,11]. In its

variegated colours the glass was treasured as a semiprecious stone and in Mexico was carved into delicate jewellery[12] and ornaments[13].

Except where obsidian occurred as well defined and easily recognized artifacts it was largely ignored by archaeologists. In New Zealand for example where adzes were carefully collected and documented, obsidian was ignored and no assemblages were made.

The possibility of using obsidian to establish trade relations and cultural contacts was first realised after examination of samples from archaeological sites in the Ancient World[14]. Often the archaeological site was many hundreds of miles from the known natural sources and examination of the obsidian present revealed that not all pieces were identical.

2. Characterization of Obsidians

The first attempts to characterize obsidians were on the basis of appearance. Even the earliest workers, however, found this method unsatisfactory[14]. Frankfort, the first to realise the possible value of obsidian studies in archaeology, noted that identification based on the presence or absence of inclusions could be misleading. For example it was believed that white spherulites indicated Liparian obsidian[15]. Chemical analyses have since shown this belief to be false.

Later investigators also found it was not possible to identify obsidians on appearance alone[5,16]. Examination of obsidian from twenty-one sources in the Mediterranean region in terms of six properties, (colour in transmitted light, colour in reflected light, fracture, translucency, transparency with internal structure and lustre), did not distinguish the

sources[5]. For satisfactory identification a given property must be constant for a wide range of specimens from a single source and different for all other sources. Much obsidian from Melos in the Aegean has a pearly lustre but specimens from the Lipari Islands off Italy can also have this characteristic[6]. Of the New Zealand obsidians examined, all those with a greenish colour in transmitted light have proved to be from the Mayor Island source but this is the only source which is distinguishable by appearance alone. Samples from a single flow at Obsidian Cliff, Yellowstone National Park, ranged in colour from clear to grey to black[3]. Neither opaqueness nor translucency is a constant property - the same source can produce both opaque and translucent obsidian. It is obvious from the foregoing that appearance can be useful only as a starting point for characterization.

When it was realised that appearance was not a satisfactory means of identification physical properties were examined. The refractive indices and densities of obsidians were measured by two investigators[14,17]. In the latter work, specimens from twelve provenances in the Mediterranean area were examined. The results were not promising. Nine of the pieces had densities of 2.37 and the refractive indices (1.485 ± 0.003) were very similar.

Attempts have also been made to distinguish New Zealand obsidians using the refractive indices of thin sections[18]. Obsidians from one hundred and seventeen archaeological sites in the North and South Islands were examined. The study established general patterns of trade but more detailed information could not be obtained because the refractive indices of the three geological provinces examined overlapped.

The results were:

1. Mayor Island. The range of refractive indices, 1.507 - 1.497, did not overlap with the other two provinces.

2. Taupo-Mangakino-Rotorua. Obsidians from the Whangamata Fault covered the range 1.4894 - 1.4867 and those from Maraetai covered a similar range, 1.4940 - 1.4866.

3. Whitianga Rhyolite Group. The refractive indices from Great Barrier Island, Fanal Island, Arid Island and the Mokohinau Islands were lower, 1.4873 - 1.4857, but still overlapped the second province.

Green[18] states that refractive indices have been used with some success to identify obsidian sources in the southwestern United States and in Japan.

Classical chemical analysis can be used to determine the concentrations of the major constituents of obsidian. The values cited by Washington[19] for a Mayor Island obsidian can be taken as representative. These are listed in Table I-1.

Table I-1 Analysis of a Mayor Island Obsidian

Element	% by weight
SiO_2	75.46
Al_2O_3	11.27
Fe_2O_3	1.17
FeO	2.05
MgO	0.27
CaO	0.53
Na_2O	3.45
K_2O	4.88
TiO_2	0.05
MnO	trace

Later analyses of obsidians from other sources have shown less than 0.06% P_2O_5[20,21,22].

Major constituent analyses of a large number of different samples have revealed significant concentration differences[19,20,21,22]. This method of characterization was subsequently tried for the Aegean sources of Melos, Antiparos and Giali[23], and for obsidians from Palmarolo, Lipari, Melos and Pantelleria[24]. In the former study, the three sources could be distinguished but the differences between Melos and Giali were only slight. Even though several classical analytical methods were tried in the latter study, the results were inconclusive.

Several difficulties are inherent in the use of classical analytical methods. In general, the use of the major element concentrations determined by these methods requires the analyses to be of very high precision. This is because obsidians from different sources often show quite small relative differences in the major element concentrations. Achieving the precision necessary to distinguish between obsidians with 74% silica and those with 75% silica is both difficult and time-consuming. In addition, several grams of sample are required.

By comparison, different obsidians show much greater relative differences in trace element concentrations. For example, two obsidians with 100 ppm and 200 ppm of a particular trace element can be easily and rapidly distinguished using modern instrumental methods.

Cann and Renfrew[6], using spectrographic analysis of sixteen trace elements, were able to characterize and distinguish successfully obsidians from twenty-one geological sources in the Mediterranean region and nearby areas. The elements determined were Ba, Sr, Zr, Y, Nb, La, Rb, Li, Mo, Ga, V, Pb, Sn, Ca, Fe and Mg. Barium and zirconium were the most useful, showing up to ten-fold variation of concentration. Obsidian from the Near East[5] has

been classified into eight groups on the basis of the concentrations of these two elements. The same workers have also applied emission spectrography to the characterization of Aegean obsidians[16].

Emission spectrography has been used to analyse seven New Zealand sources of obsidian[25]. The elements Mn, Be, Zr and Ca were studied. Absolute elemental concentrations were not computed, the ratios of intensities of emission lines compared to the intensity of the palladium internal standard being used. The confidence limit with which the seven sources could be distinguished was generally in excess of 90%.

The same method has established the source of New Guinea artifact obsidian[7]. Twelve elements, Ca, Mg, Fe, Mn, V, Ti, Nb, Zr, Sr, Ba, La and Cu were analysed.

Obsidians from three regions in California have been distinguished using X-ray spectroscopy[26]. The ratio of strontium concentration to rubidium concentration was determined by the ratio of the heights of the intensity peaks, no attempt being made to determine the actual amounts of these two elements. Even outcrops within an area were distinguishable. No further work has been done using this method of trace element analysis and for results of different workers to be compared the actual concentrations of Sr and Rb would have to be determined. The possibility of developing a non-destructive method of analysis of artifacts makes this method attractive. Weathered surfaces could not be examined because absorption of water produces structural and compositional changes, but small chips broken off from inconspicuous places could be powdered and used for analysis.

Neutron activation analysis has been applied with great success to the characterization of obsidian sources[2,27]. The initial study, the aim of which was to develop a satisfactory analytical method and establish the geochemistry of obsidian, involved the analyses of more than one thousand samples for Na, Mn, La, Fe, Rb, Sc and Sm. These samples were from forty-four locations in western U.S.A., four in Central America, two in South America, two in Alaska and a number in Europe and Asia. It was found that Mn, La, Sm and Sc were the most useful elements, having a mean minimum - maximum variation for sixty flows of more than ten-fold.

The method has been applied subsequently to obsidian from the Near East and Alaska[1,28]. Specimens were first analysed for Na and Mn and sub-groups established on the basis of these two elements. The concentrations of Sc, Fe, Rb, La and Sm were then found. Although it is unlikely for two sources to have identical concentrations of these seven elements, five other elements (Ba, Cs, Ir, Ta and Tb) were then measured.

The success and validity of trace element content as the basis for identifying the source of archaeological obsidian depends on two factors:

(i) Each flow or source must be of relatively constant composition. The homogeneity of a single source must be established by analysis of a large number of samples representing the whole area. Constant composition could be expected on geological grounds, as a single source originated from the same pocket of magma which was thoroughly mixed before ejection and cooling. Homogeneity has been demonstrated for the Lipari and both the Melian Sources[16]. For most of the obsidians studied by emission spectrography separation between sources was good. Groups established on the basis of trace element composition were in basic agreement with the petrological theory that rocks

from the same area have similar compositions[6].

Although there is up to a two-fold variation in the concentration of a given element from a single flow, the ten-fold variation between different sources ensures the usefulness of the method. It should also be pointed out that much of the two-fold variation may be inherent in the emission spectrographic method. For example, the molybdenum content was never greater than 10 ppm and in many samples was less than 3 ppm. Most samples analysed had vanadium concentrations of less than 5 ppm[5,6].

The variation within a single flow was less when obsidians were analysed by neutron activation analysis. The mean minimum - maximum variation for any element from the four flows examined was 30 - 40%[27]. For the elements La, Fe, Rb, Sc and Sm the precision is ±20%. Since part of this variation arises from the limitations imposed by the statistics of radioactive counting, the true variation must be somewhat less than that quoted.

Replicate analyses on a 5 x 5 x 2.5 cm block of obsidian were essentially the same as analyses on random samples from across the same flow. Elements appeared to be uniformly distributed throughout a flow and samples from one section could be assumed to be representative of the entire flow[2].

(ii) Variation in composition between sources must be greater than variation within a source. The initial study using neutron activation analysis[27], which involved the examination of more than one thousand samples from sixty single natural flows in different volcanic regions of the world, verified this requirement. Of the seven elements analysed, Mn, La, Sm and Sc had mean minimum - maximum variations of more than ten-fold. A similar variation was found for barium and zirconium in Mediterranean[6] and Near

East obsidians[5], and for strontium and rubidium in obsidians from three regions of California[26].

Thus the three methods so far employed for trace element analysis have established that several elements can often be found for which the variation between sources is greater than variations within a source. As stated previously much of the latter may in fact be a function of the analytical methods used. If this variation could be largely eliminated then finer concentration differences between sources could be used for characterization.

3. Obsidian Dating

As well as being used to establish trading routes, obsidian has been used for dating archaeological sites[29]. A freshly exposed surface undergoes gradual hydration and crystallization on contact with the atmosphere. The rate of diffusion of water into the obsidian is a function of temperature and therefore temperature, and to a lesser extent chemical composition, are the main factors to be considered. Obsidians in an equatorial region would hydrate forty times faster than those of similar age in an arctic region[30].

The hydration layer (usually a few microns thick) is clearly visible when a thin section is viewed under the microscope, but preparation of these sections requires time and skill.

The relation between time and the thickness of the layer has been established by correlation with objects of known ages, as determined by other dating methods such as carbon-14, ceramic analysis, dendrochronology

and written records. Knowing the effective temperature to which an obsidian artifact has been exposed its age can also be found by using the hydration equation of Friedman, Smith and Long[31]. Friedman and Smith[29] originally established seven different rates of hydration. Subsequent work has re-examined these rates and added new ones[32].

Initially the method was highly experimental and of doubtful reliability but the application of statistical tests has proven its accuracy and precision[32]. This dating method has found very wide application in the study of prehistory and has been applied to obsidian artifacts from Easter Island[9], Central California[30], Ecuador[33], Egypt, Iraq, Alaska and U.S.A.[29]. Hydration-rim dating has revealed that re-use of obsidian was widespread[30,33] and fake artifacts have been detected[9].

Obsidian dating has been applied in New Zealand. The relative chronology of eleven archaeological sites in the Auckland-Coromandel area and the range of time encompassed by each was determined[34]. On the assumption that the New Zealand climate has been static since Polynesian occupation one of the hydration rates for temperate climates established by Friedman and Smith[29] was used.

The thickness of the hydration rim for an artifact 2000 years old found in a temperate zone would be 3.3 - 3.6 microns[29]. This is not sufficient to change the composition significantly and therefore hydration does not have to be considered when trace element analyses are being carried out. Because of the widespread re-use of obsidian and the fact that there is a certain critical thickness for the hydration rim, (when the layer reaches a thickness of 50 microns it spalls off[30]), dating cannot be used to establish the source of artifact obsidian. It is useful, however, to

know the relative chronologies of each sequence of a stratified archaeological site as established by hydration-rim dating as well as the proportions of different obsidians in each sequence as established by trace element analysis.

4. New Zealand Obsidians

(i) Natural Sources

For obsidian to be of archaeological interest and significance it must be flake quality, i.e., it must fracture conchoidally to produce sharp-edged flakes. There are eight known sources of flake quality obsidian in New Zealand. All are in or near the North Island. They are listed below and are located in Fig.1.

1. Mayor Island
2. Kaeo
3. Huruiki
4. Great Barrier Island
5. Arid Island
6. Whitianga
7. Taupo
8. Maraetai

Other sources are known but these are non-flake quality, usually because of the presence of large numbers of spherulitic inclusions in the glass. Such obsidian has been found in a road cutting near Lake Rotoiti, in the Hemo Gorge (two miles south of Lake Rotorua) and on Mount Tarawera[18]. Fanal Island in the Mokohinau Islands north of Great Barrier Island is the source of a green-black obsidian which because of the presence of spherulites is not high flake quality[35]. The source has not been located exactly and

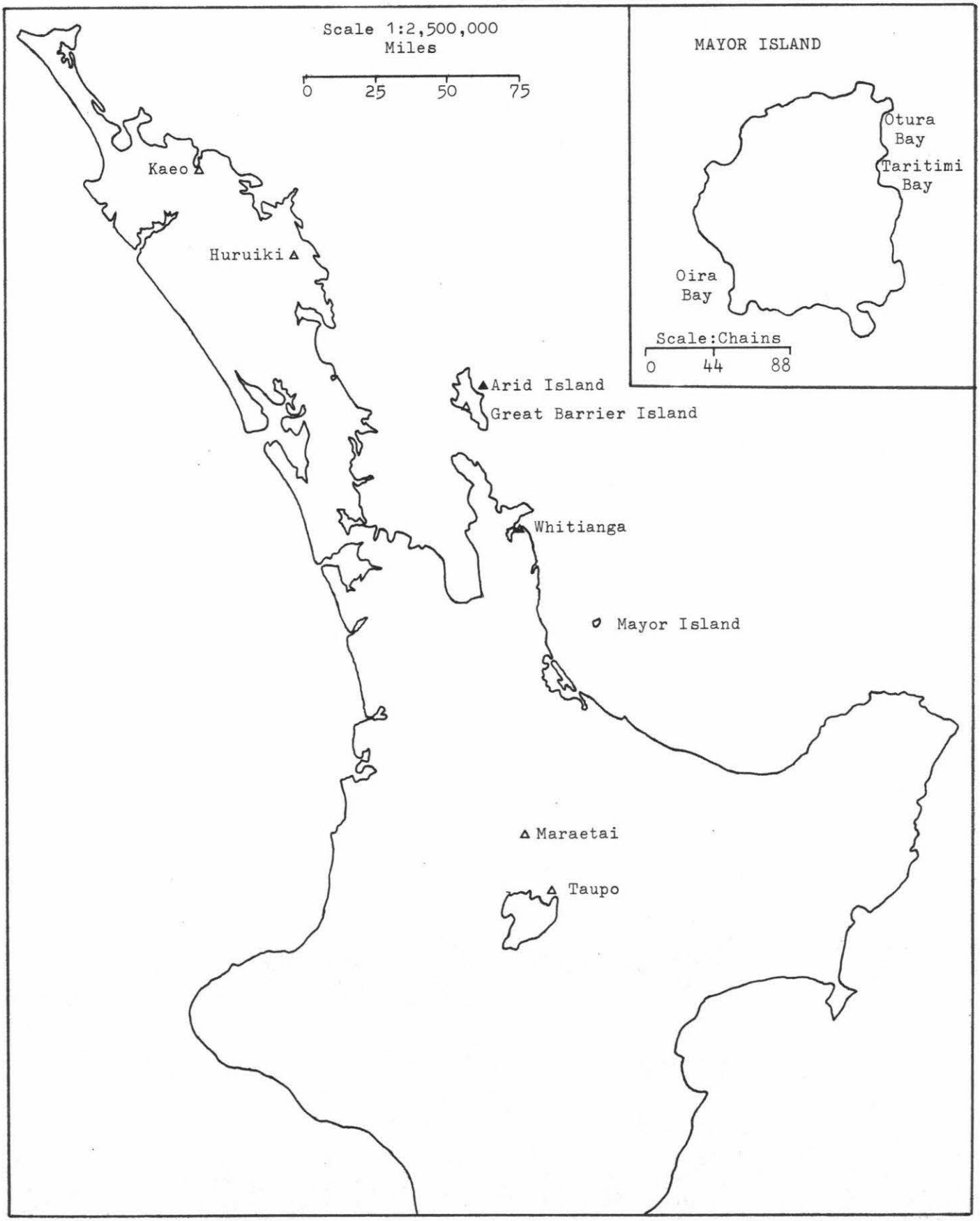

Fig.1 Natural Sources of Flake Quality Obsidian in New Zealand

no pieces were available for analysis. The Maraetai source also yields non-flake quality obsidian.

There are references in the literature to other sources of obsidian but these are not well documented[36]. A source in the Waikato is reported[37,38]. It is likely that the obsidian reported in the former reference was derived from the Taupo source, boulders being carried downstream by the Waikato River. Several outcrops of red flecked and red coloured obsidians have been reported from the Rotorua district[34].

No source of flake quality obsidian has been found in the South Island. Poor quality obsidian has been reported from Banks Peninsula[39]. Mayor Island has the most extensive deposits of obsidian in New Zealand, some of it in the form of great cliffs[40,41]. It was the main source of artifact obsidian and for this reason was important to the Maoris, being named Tuhua (obsidian) by them. The appearance of the obsidian varies but it is usually black or very dark green in reflected light with fairly numerous inclusions of quartz or feldspar[42]. Banding is a feature of some of the samples. Chemical analysis had shown that the alkali concentration was higher than that of mainland obsidian[42] and that lime and magnesia concentrations were lower[41]. These results have been verified by this and a previous study[25]. Obsidian from Mayor Island can be identified readily by its yellow-green or green colour in transmitted light. All identifications made in this way have been verified in this study by chemical analysis.

Not all Mayor Island obsidian is high quality and only three areas yielding high quality flake obsidian have been reported[43]. Only one of these has evidence of a real quarry. The three areas are:

1. Taritimi Bay. This is the site of the quarry, where obsidian has been obtained by tunnelling about six feet into a seam.
2. North Otura Bay. This source yields light, clear, slightly greenish obsidian.
3. Oira Bay. This obsidian is more opaque but still has a high gloss.

The existence and use of Mayor Island obsidian has been known since the first archaeological investigations in New Zealand[10]. The other sources, however, have been well documented only recently.

The Kaeo source was first documented in 1961 and it was noted that in some properties it closely resembled Mayor Island obsidian[34].

The Huruiki source was discovered in 1965[44] and clear light-grey obsidian from Arid Island was reported in 1962[18].

Old mining records indicated that Great Barrier Island had obsidian deposits and the names Te Ahumata (ahu - heaped up; mataa - obsidian) and Hirakimata (hira - abundant, widespread; mataa - obsidian) suggested a local source[45]. The first search did not lead to its discovery[46] but later, large boulders of clear, grey, flake quality obsidian were found on the Te Ahumata Plateau[45]. Mt Hobson - Hirakimata is reported to yield greenish obsidian (further details were not given). Poor quality crumby, spherulitic obsidian was also found[47].

The existence of obsidian deposits in the Taupo and Whitianga areas has been known longer[37,38]. Moa-hunter sites on the east coast of the South Island yielded grey obsidians which indicated that Mayor Island was not the

only source. This grey obsidian was assigned to either a Taupo or a Whitianga source. The grey-black obsidian which is common at Coromandel archaeological sites was suggested to come from a ridge behind Cook's Beach[48]. This has been confirmed by this work.

Outcrops scattered over a wide area constitute the Maraetai source.

(ii) Archaeological Usage

Obsidian was highly prized by the Polynesian inhabitants of New Zealand and it has been found at nearly every archaeological site investigated[34].

The uses to which the material was put were various. Flakes were used for cutting purposes. Hair was cut with sharp-edged obsidian flakes[49] and a Maori proverb refers to the cutting of moas with these tools[10]. It is reported that large blocks were thrown during warfare on Mayor Island[40]. Duff[10] states that obsidian may have been used for making drill points and cutting the eyes of the hei tiki. At one site obsidian was most common in the burial area[50].

At any site most of the obsidian is in the form of waste flakes. At Kauri Point Swamp 13,250 pieces of obsidian were counted and of these a large number were less than 0.5 cm long[51]. Examination of the size distribution of the flakes showed that no attempt had been made to produce special types of artifacts.

Very few formal tools have been found[34]. Some retouching or secondary working was done to shape knives, scrapers, saws[52] and the "mata" or blubber cutter[53]. A medium sized slab of obsidian was found at Wairau and a large block was found at a Moa-hunter camp at the mouth of the Hurunui River[10]. It has been suggested that obsidian from the north was bartered for

moas from the South Island[54].

Obsidian has been found from North Auckland to Stewart Island[10] and is present at the earliest archaeological sites. This demonstrates that contact between the North and South Islands dates from the very early days of Polynesian colonization. Mayor Island obsidian predominates in early sites even when there is a nearby local source[34]. Identification by appearance has shown that the ratio of green Mayor Island obsidian to local grey obsidian increases from top to bottom in sites in the Coromandel - Auckland area[55,56]. This observation has been suggested as evidence that the original landing point of the Polynesians was the Bay of Plenty[57]. These are some of the archaeological answers obsidian study has furnished but for elucidation of details of trading routes and cultural contacts, characterization of the natural sources has to be improved.

CHAPTER II - AIMS OF THE PRESENT INVESTIGATION

As stated previously, classification of New Zealand obsidians based on appearance or refractive index has not been successful except for Mayor Island obsidian. Its greenish colour in transmitted light and its high refractive index (1.507 - 1.497)[18] make it quite distinctive. Attempts to identify other sources using visual differences have not been very satisfactory.

Emission spectroscopy distinguished seven of the eight known New Zealand sources of flake quality obsidian with a confidence limit of the order of 90%[25]. To overcome the "matrix effect", which makes it difficult for different workers to obtain the same results, relative intensities of spectral lines were used for characterization. For completeness approximate absolute concentrations were also determined. Four elements, Be, Ca, Mn and Zr were used. These elements were chosen after preliminary arcing of a sample from each source had shown them to be the most useful for characterization. Use of the ratios Be/Ca, Zr/Mn and Zr/Ca gave the best separation of the seven sources.

This technique did not separate the Huruiki and Great Barrier obsidians, even at the 90% confidence level and the difference in the mean concentration of the four elements between the two sources was small. Both had Be concentrations of 3.0 ppm and the differences for Ca, Mn and Zr were 5.3%, 1.0% and 5.9% respectively.

Table II-1 Ratios of Relative Intensities of Various Line pairs with Corresponding Standard Deviations (s.d.) and Coefficients of Variation (C%)

Source	n	Zr/Ca	s.d.	C%	Be/Ca	s.d.	C%	Zr/Mn	s.d.	C%
Kaeo	8	19.5	5.5	28.2	10.6	2.2	18.9	1.98	0.81	40.1
Mayor Island	9	7.1	0.6	8.5	3.0	0.5	16.7	0.86	0.12	14.0
Huruiki	9	0.34	0.04	11.8	0.29	0.04	13.8	0.36	0.04	11.1
Great Barrier Island	9	0.28	0.03	10.7	0.28	0.04	14.3	0.26	0.05	19.2
Whitianga	9	0.25	0.02	8.0	0.19	0.03	15.8	0.15	0.03	20.0
Maraetai	3	0.18	*		0.12	*		0.17	*	
Taupo	9	0.23	0.01	4.4	0.14	0.01	7.1	0.23	0.02	8.7

* Standard deviation not computed because of small number of samples.

Because only three Maraetai samples were available for analysis the standard deviation was not calculated. It is possible that analysis of more samples would reveal overlap with other sources, especially Whitianga and Taupo. Archaeological obsidians, therefore, could not be identified with certainty using this method.

Table II-1 shows the large coefficient of variation, (standard deviation expressed as a percentage of the mean) obtained when eight or nine samples from each source were analysed. This large variation is due partly to the poor reproducibility of the emission spectrographic method and partly to the natural variation of any element within a source. The precision of the method is dependent on the experience of the analyst; $\pm$ 5% for an

experienced analyst and ± 10-15% for an inexperienced operator.

The contribution of the natural variation to the standard deviation must be known before obsidian characterization can be applied to archaeological material. Carrying out replicate analyses on a representative sample from each source would establish the standard deviation due to the method. The standard deviation could then be partitioned and the natural variation determined. If emission spectroscopy was used it is still possible that the variation of the analytical method would make the greater contribution to the standard deviation. This would preclude the use of finer differences in element concentration to distinguish the eight geological sources of obsidian. If the precision of the analytical method was ± 2-3% a difference of 5-10% in the concentration of an element would enable two sources to be distinguished.

Characterization of obsidian by other workers[2,6] has also indicated a large variation in element concentration within a source. In both studies the actual variation was thought to be less, much of the quoted variation being due to the analytical method. Although the use of relative spectral line intensities to characterize the seven sources did overcome the "matrix effect", it restricts the usefulness of the method. For interchange of results among workers reliable absolute concentrations must be known.

The aim of the present investigation was to find a method which did not have the limitations of emission spectroscopy and to use it to:

(i) establish accurately the absolute concentrations of several elements in obsidians from each source;

(ii) obtain a reliable indication of the natural variation of these concentrations within each source;

(iii) establish the variation due to the analytical method for these elements for each source;

(iv) apply chemical analysis for the first time to obsidians from New Zealand archaeological sites. Archaeological interpretation of these and future results should enable much to be learnt about the prehistory of New Zealand.

Neutron activation analysis has been applied very successfully to the identification of obsidian[2]. It is not suitable for the study of New Zealand obsidians, however, because a neutron source is not readily available and the equipment is expensive.

Atomic absorption spectrophotometry[58] and flame photometry[59] have been used to analyse a wide variety of materials including silicate rocks. They fulfil most of the requirements of a satisfactory analytical method.

(i) The precision during routine analysis is frequently better than 2%.

(ii) Accuracy, (as shown by analysis of standards, e.g., G-1 and W-1) is satisfactory. The degree of accuracy depends on the refinements included in the analytical method.

(iii) Interferences are either absent or can be overcome.

(iv) The methods are rapid.

(v) They are simple to carry out. An inexperienced analyst can obtain good precision during routine analysis.

(vi) Instruments are readily available throughout New Zealand.

Rapidity, simple instrumentation and availability are essential if the methods are to be of maximum use in archaeology.

In the present work an investigation was also made of the densities of New Zealand obsidians. Characterization of obsidians using densities has been attempted unsuccessfully[14,17]. The former work enabled densities to be measured with a precision of ± 0.4%. With very simple equipment a precision of ± 0.1% can be obtained and with a few modifications the precision can be as good as one part in 10^5 [60]. Because of differences in chemical composition, general appearance and refractive indices, differences in density would be expected. More precise measurements should enable density differences between the sources to be detected.

The method, if satisfactory, could be more readily adopted to the field. It is also very low cost. Although atomic absorption spectrophotometry and flame photometry are rapid methods of chemical analysis, it would take two or three days to analyse a set of samples. Density measurements could be carried out more rapidly. Even if complete separation of the sources was not possible densities could be used for preliminary identification. If the findings were interesting or ambiguous the archaeological material could be analysed chemically.

For chemical analysis pieces larger than 0.4g are needed whereas density measurements are possible on pieces weighing as little as 0.03g. Obsidian for chemical analysis must be in the form of a fine powder and the amount analysed is destroyed. The density method is non-destructive. This would be important if the archaeological fragment was small. If the chemical analysis results were inconclusive all chance of identifying the fragment would be lost. It is also possible that not even 0.4g of a larger specimen could be sacrificed.

The method also has the advantage of being simpler for nonchemists. The ideal method would be one that archaeologists themselves could use to distinguish unequivocally the New Zealand sources of flake quality obsidian.

CHAPTER III - DENSITY METHODS

The two main methods for measuring the density of solids are displacement methods and buoyancy methods[60]. Both depend on immersing the solid in a fluid of known density. The latter, which are more precise, reliable and simple, are an application of Archimedes Principle and are limited only by the existence of a suitable immersion liquid. This must not dissolve the solid and must be at least as dense as the solid. The upper limit of density for liquids is about 3.6 g cm^{-3}, e.g., aqueous barium mercuric iodide[60].

Buoyancy methods are of two types:

i) free flotation

ii) hydrostatic weighing

1. Free Flotation Method

When a solid neither sinks nor rises in a liquid the densities of the solid and the liquid are equal. The density of the liquid can be found by using a calibrated pycnometer. It is possible to determine the density of a solid very accurately by adding the less dense component to a liquid mixture until the solid is just suspended. Although precisions of the order of 5 parts in 10^6 are possible with strict temperature controls and precautions to prevent evaporation, this would not be practicable for large numbers of samples.

Alternatively a number of liquid mixtures with slightly different densities could be prepared. For a series of solids differing slightly in density, e.g., obsidians from different sources, the densities could be chosen so that each liquid was approximately the same density as one of the sources.

Preliminary experiments involved adding three or four different obsidians to a tube containing bromoform (Merck, 4% ethanol by weight). All floated. Acetone was added dropwise with shaking until one piece sank. Because each obsidian sank with the addition of different amounts of acetone it appeared feasible to distinguish the obsidian sources using density measurements. Fragments of headlamp glass have been distinguished by the flotation method. Bromoform diluted with xylene was used as the flotation liquid[61].

Another free flotation technique is the temperature variation method. Here the density of theflotation liquid is adjusted by changing the temperature. The fineness of the density difference that can be determined depends on the precision of the temperature control. With a temperature control of $\pm 0.02^{\circ}C$ specimens as small as 1.0 mg have been used for density measurements[60]. Freedom from vibration and convection is also important.

The temperature variation method was chosen for the study of obsidian densities for the following reasons:

i) For samples of nearly the same density it is the most precise. The temperature variation method could distinguish 50 pieces of headlamp glass in all but two instances[61]. A much finer adjustment of density could be made by using temperature rather than xylene to change the density of the bromoform-xylene flotation mixture.

ii) It is the most rapid. A number of samples can be examined together. The number is limited by the ability of the experimenter to distinguish similar obsidians in a tube. The preparation of a series of mixtures of nearly the same densities would be difficult and

time consuming. Adding the less dense component to the mixture until an obsidian was just suspended would also be slow, because for each obsidian, it would be necessary to determine the density of the final mixture using a calibrated pycnometer. With the temperature variation method, once the flotation liquid is prepared and its change of density with temperature determined, it can be used for all obsidian pieces without further adjustment or calibration.

One value for the specific gravity of Mayor Island obsidian was found in the literature, 2.40[62]. Specific gravities quoted for other obsidians were 2.390 and 2.372[20] and a density of 2.37 g cm^{-3} was given for a Russian obsidian[63].

(i) Preparation of Flotation Mixture

Bromoform has been widely used for separating ores and minerals with densities between 1.58 and 2.6 g cm^{-3} [64]. Pure bromoform has a density of 2.8905 g cm^{-3} at 20°C[65].

Several less dense organic liquids have been used as the second component, including carbon tetrachloride[64], benzene[66], ethanol and higher alcohols[67].

Unless bromoform contains 4% ethanol by weight (Merck's bromoform) it is unstable and decomposes to bromine and bromoparaffins. Ethanol was therefore chosen as the second component.

Bromoform was distilled at reduced pressure and the fraction boiling at 149.0°C collected. Its refractive index was 1.5970 at 20°C. (Timmermans[65], b.p. 149.5°C, n_D^{20} 1.5977).

Absolute ethanol was distilled twice at atmospheric pressure. The boiling point of the fraction collected was 78.0°C and the refractive index was 1.3618. (Timmermans, b.p. 78.32°C, n_D^{20} 1.3614.)

A flotation liquid was prepared with a density such that Kaeo and Mayor Island obsidians sank and the other obsidians floated at ambient temperatures. Bromoform (336.04 g) was weighed in a brown bottle with a ground-glass stopper and ethanol (41.42 g) was added using a pipette. The refractive index of the mixture was 1.5253 at 20°C. The literature value of the refractive index for a bromoform ethanol mixture of this composition is 1.5240 at 20°C [68].

With this flotation mixture consistent density measurements could not be obtained over a period of several weeks. The problem of a gradual increase in the density of the liquid appeared to be caused by the preferential evaporation of ethanol. The alcohol has a much higher vapour pressure than bromoform. (v.p. at 25°C 59.0 mm Hg and 9.4 mm Hg respectively[69]).

Measurement of refractive index was difficult for the same reason. The composition of a drop on the refractometer plate changed rapidly, until after two minutes the refractive index measured was almost that of pure bromoform.

An alternative second component was sought with the following properties:

i) comparable volatility to bromoform (v.p. 9.4 mm Hg at 25°C [69]) to minimize changes in composition over a period of time.

ii) stabilizing action on bromoform similar to that of ethanol.

These requirements excluded acetone, benzene and carbon tetrachloride. The higher alcohols, 1- pentanol and 1- hexanol have been found to prevent decomposition of bromoform by light and air and are a little less volatile than bromoform (v.p. 1- pentanol 2.8 mm Hg at 20°C[69]). Experiments in which oxygen was bubbled through various alcohol bromoform mixtures, with exposure to sunlight, showed that the higher alcohols were more effective stabilizers than ethanol[67].

1- pentanol was redistilled at atmospheric pressure using quick fit distillation apparatus. The fraction boiling at 137.8°C was collected and was found to have a refractive index of 1.4108 at 20°C. (Timmermans, b.p. 138.2°C, n_D^{20} 1.4100). The pure alcohol was stored in a glass-stoppered bottle until required.

Bromoform stabilized with ethanol (Reidel-de Haen, chem. pure) was redistilled at atmospheric pressure in a quick fit round-bottom flask using a heating mantle. The bromoform fraction collected was pale yellow and cloudy due to traces of bromine and moisture respectively. (Redistillation at reduced pressure did not overcome this problem.)

Attempts to remove bromine by bubbling nitrogen through the distillate were not successful. Bromine was removed by shaking the distillate with approximately 5 cm^3 0.880 ammonia solution per 100 cm^3 bromoform in a 250 cm^3 separating funnel. Ammonia reduces bromine as follows:

$$3\ Br_2 + 8\ NH_3 \longrightarrow 6\ NH_4^+ + 6Br^- + N_2 \uparrow$$

Periodically, after the stoppered funnel was inverted, the stop-cock was opened to allow nitrogen to escape. The products of the reaction were an upper aqueous layer containing reduced bromine and a denser, cloudy,

non-aqueous layer.

The non-aqueous layer was run off into a glass beaker. Moisture was removed by shaking with approximately 5 g each of anhydrous sodium sulphate and anhydrous calcium chloride. The purified bromoform was recovered when the non-aqueous layer was filtered through filter paper (Whatman No.40) containing a bed of anhydrous sodium sulphate and anhydrous calcium chloride. The latter, as well as acting as a drying agent, forms an addition compound with ammonia thus removing any ammonia present in the non-aqueous layer.

The final product was a clear, colourless, sweet-smelling liquid, boiling point 149.0°C and refractive index 1.5970 at 20°C. (Timmermans, b.p. 149.5°C, n_D^{20} 1.5977)

The pure bromoform was stored in a brown bottle with a ground-glass stopper, to prevent decomposition. With standing for twenty-four hours a small amount of a white solid formed at the surface of the liquid. It was removed by filtering. The solid was not characterized but was probably either the ammonia calcium chloride addition compound or ammonium bromide or a mixture of both. The fact that the measured boiling point and refractive index were slightly lower than the literature values may have been due to the continued presence of traces of impurities such as water, ammonia and bromoform decomposition products.

The flotation mixture was made up by adding 1- pentanol (7.36 g) to bromoform (85.55 g) to give a mixture of density at 5 - 10°C similar to that of Kaeo obsidians. The mixture was 92.06% bromoform by weight (80.25 mole%) and its refractive index was 1.5515 at 20°C.

(ii) Calibration of Pycnometer

The change of density of the flotation mixture with temperature was determined using a pycnometer calibrated in terms of the weight of water it held at temperatures between 7°C and 38°C. A Sprengel-Ostwald pycnometer with a small bulb above the graduation on one side-arm was used. This type of pycnometer can be filled without danger of loss of liquid by evaporation and it is therefore suitable for mixtures.

Deionized water was used to fill the pycnometer. A piece of rubber tubing, placed in a beaker containing deionized water and attached to one arm of the pycnometer, allowed water to be drawn up into the pycnometer when suction was applied to the other arm. Water was not allowed to enter the bulb on the side-arm. If air bubbles formed the vessel was refilled as this is the most frequent cause of large accidental errors in pycnometry. When less than ambient temperatures were used the liquid was cooled first, otherwise even when the pycnometer was filled to the side-arm bulb, there was not an excess of liquid when equilibration was reached.

The filled pycnometer was suspended, by a thin wire from a retort stand, into a thermostatically-controlled water bath. At each temperature the pycnometer was equilibrated for 15 minutes without the two caps. Temperatures could be read to ± 0.05°C. Before weighing the pycnometer was wiped with a tissue and dried with a stream of compressed air for 30 seconds. This procedure standardized any effect of adsorption of water on the outside of the pycnometer. The same piece of wire was not used to suspend the pycnometer in the water bath and to hold it in the balance case. The pycnometer was allowed to rest for one minute in the balance case before it was weighed to ensure equilibration with the atmosphere. No change in weight was observed after this time.

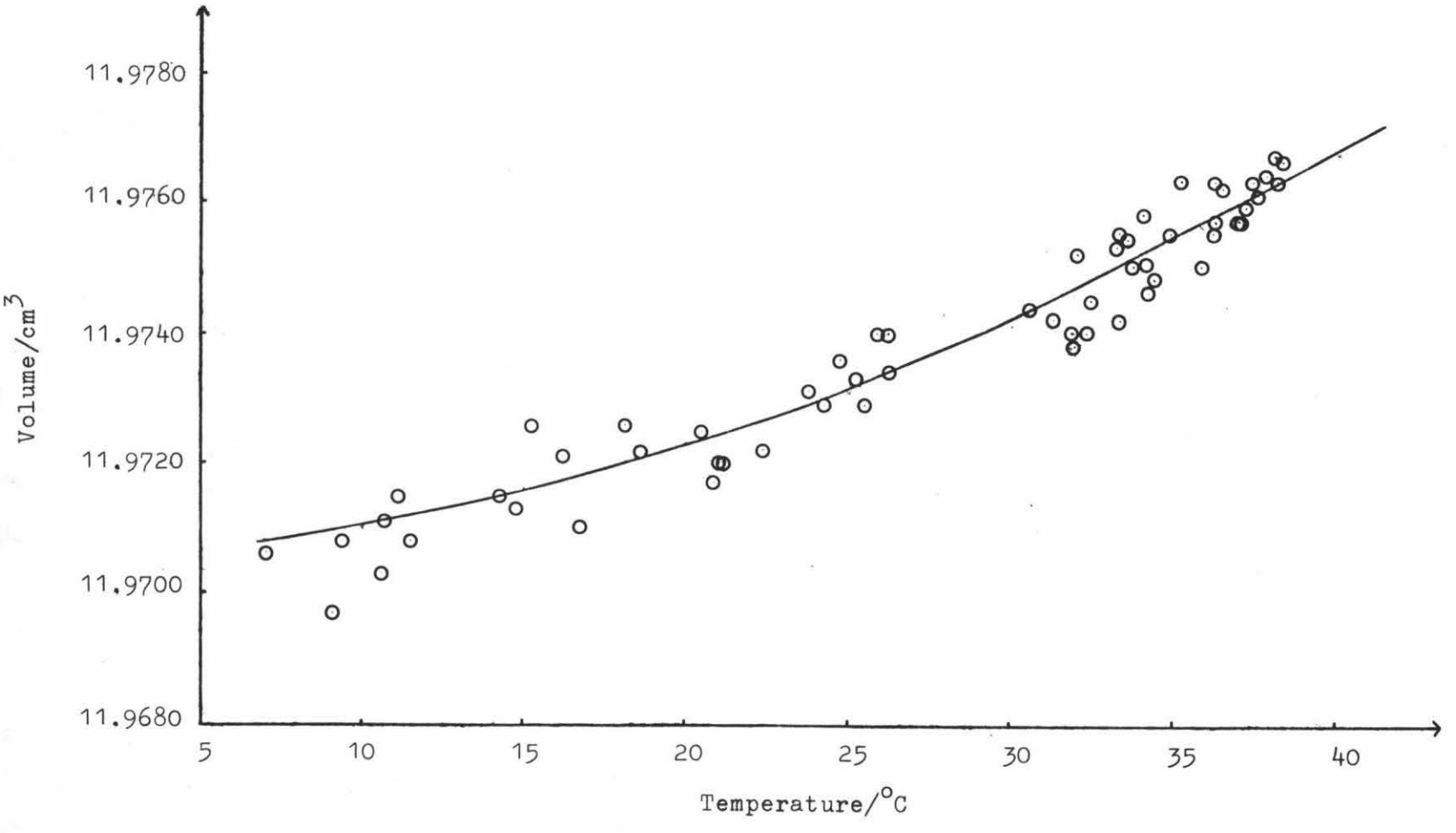

Fig.2 Volume of Pycnometer as f(T)

The results are recorded in Table III.1 and Figure 2.

TABLE III.1 - VOLUME OF PYCNOMETER AS f(T)

Temp./°C	Mass H_2O/g *	Density H_2O/(g cm^{-3})[69]	Vol./cm^3
7.05	11.9694	0.999900	11.9706
9.10	11.9670	0.999774	11.9697
9.40	11.9679	0.999751	11.9708
10.62	11.9661	0.999643	11.9703
10.70	11.9668	0.999635	11.9711
11.10	11.9667	0.999595	11.9715
11.52	11.9655	0.999551	11.9708
14.27	11.9619	0.999206	11.9715
14.77	11.9609	0.999133	11.9713
15.22	11.9614	0.999066	11.9726
16.20	11.9590	0.998910	11.9721
16.74	11.9568	0.998819	11.9710
18.12	11.9555	0.998572	11.9726
20.50	11.9498	0.998099	11.9726
20.87	11.9480	0.998020	11.9717
21.00	11.9479	0.997992	11.9720
21.16	11.9475	0.997957	11.9720
22.38	11.9444	0.997683	11.9722
23.76	11.9414	0.997355	11.9731
24.24	11.9398	0.997236	11.9729
24.74	11.9390	0.997110	11.9736
25.21	11.9372	0.996990	11.9733
25.47	11.9360	0.996922	11.9729
25.86	11.9359	0.996820	11.9740
26.19	11.9349	0.996732	11.9740
26.22	11.9342	0.996724	11.9734
30.53	11.9202	0.995485	11.9743
31.27	11.9174	0.995257	11.9742
31.84	11.9151	0.995077	11.9740
31.91	11.9146	0.995055	11.9738

(continued over page)

Table III.1 continued...

Temp./°C	Mass H_2O/g *	Density H_2O/(g cm^{-3})[69]	Vol./cm^3
31.98	11.9157	0.995033	11.9752
32.26	11.9135	0.994943	11.9740
32.41	11.9134	0.994895	11.9745
33.20	11.9111	0.994637	11.9753
33.28	11.9097	0.994611	11.9742
33.30	11.9109	0.994694	11.9755
33.55	11.9098	0.994521	11.9754
33.55	11.9097	0.994521	11.9753
33.70	11.9088	0.994472	11.9750
34.00	11.9084	0.994371	11.9758
34.36	11.9060	0.994250	11.9748
34.83	11.9047	0.994090	11.9755
35.17	11.9041	0.993982	11.9762
35.17	11.9042	0.993982	11.9763
35.79	11.9003	0.993758	11.9750
36.14	11.8993	0.993635	11.9755
36.20	11.8998	0.993613	11.9763
36.20	11.8992	0.993613	11.9757
36.44	11.8987	0.993528	11.9762
36.96	11.8960	0.993343	11.9757
37.03	11.8957	0.993318	11.9757
37.15	11.8954	0.993275	11.9759
37.38	11.8948	0.993192	11.9763
37.53	11.8939	0.993137	11.9761
37.77	11.8932	0.993050	11.9764
38.04	11.8923	0.992951	11.9767
38.09	11.8917	0.992932	11.9763
38.28	11.8912	0.992863	11.9766

*corrected to vacuum

Mass empty pycnometer + wire = 23.0527 g

The weighings are given in order of ascending temperature but were carried out in several ascending sequences. After each sequence the pycnometer was emptied, dried with acetone and compressed air and refilled with deionized water. At temperatures above 30°C water tended to condense in the bulb on the side-arm. This problem, which could not be overcome even when the bulb was submerged in the water bath, was probably responsible for a slight curvature of the volume-temperature graph. A best-fit curve was drawn through the experimental points and a quadratic equation derived for the volume of the pycnometer as a function of temperature.

The volume-temperature relation was written in the form

$$V = a + b\Theta + c\Theta^2$$

where Θ is the temperature (in °C). The coefficients a, b and c were determined by substitution of the following points from the best-fit curve:

i) $\Theta = 10$ $\quad V = 11.9710$

ii) $\Theta = 25$ $\quad V = 11.9731$

iii) $\Theta = 36$ $\quad V = 11.9756$

This gives $\quad a = 11.9705 \quad b = 2.0 \times 10^{-5} \quad c = 3.4 \times 10^{-6}$

and the equation is

$$V = 11.9705 + 2.0 \times 10^{-5}\Theta + 3.4 \times 10^{-6}\Theta^2$$

It was hoped that the occurrence of slight condensation in the side-arm bulb at higher temperatures would also occur in measurements of the flotation liquid. This was found to be the case, and the use of the quadratic equation appeared to be justified, as the final density-temperature relation for the flotation liquid was accurately linear up to 37°C.

As shown by Fig. 2 the precision with which the pycnometer was calibrated was greater than 1 part in 10^4, i.e., the volume was determined

to within 0.0010 cm^3. The least precise measurement was the mass of water. It was difficult to adjust the water level exactly to the graduation on the side-arm and at the same time ensure that the other arm was filled to the tip.

(iii) Density of Flotation Liquid as a Function of Temperature

The calibrated pycnometer was used to determine the density of the flotation liquid from 9°C to 45°C. The same method of filling the pycnometer was used. It was filled only once and all measurements were carried out in order of ascending temperature.

Exposure to air caused some yellowing of the liquid due to decomposition. The refractive index of the liquid was then 1.5512 at 20°C compared to 1.5515 when the liquid was first prepared. Work was continued with this liquid. After one week's use, which included heating the liquid to 45°C, the refractive index had fallen to 1.5504 at 20°C.

Table III.2 shows the variation of the density of the flotation mixture with temperature. The results are graphed in Fig.3.

The equation of the best-fit straight line was found to be

$$y + 2.21 \times 10^{-3}\theta = 2.4265$$

where θ is the temperature (in °C). The slope of the line gives the temperature-density coefficient for the liquid, 2.21×10^{-3} g cm^{-3} per °C.

As mentioned the density-temperature relation was accurately linear up to 37°C. The precision with which the density of the flotation liquid could be determined was better than ± 0.0005 g cm^{-3} (2 parts in 10^4). Above 37°C the precision was less and had halved at 45°C.

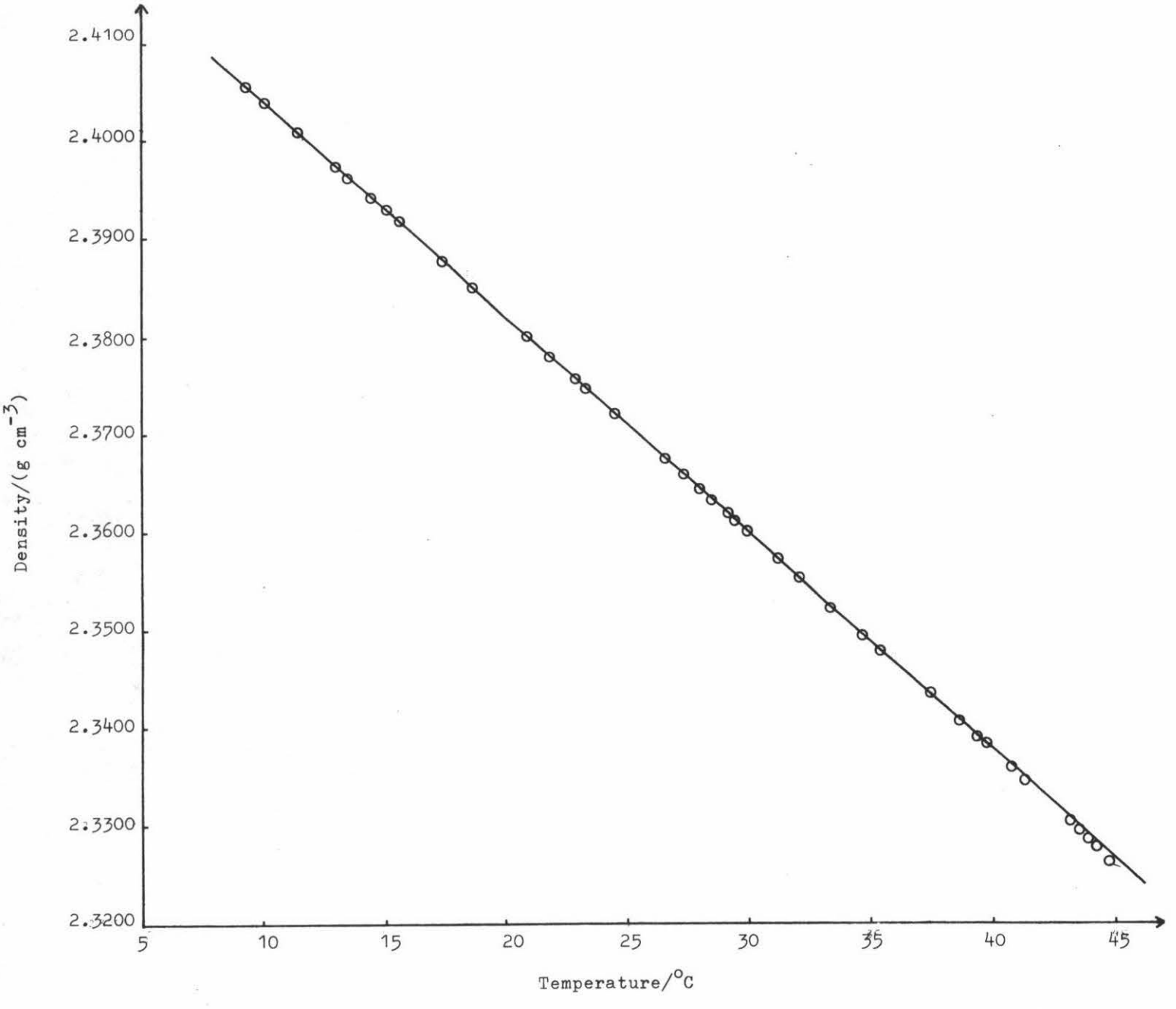

Fig.3 Density of Flotation Liquid as f(T)

TABLE III.2 - DENSITY OF FLOTATION LIQUID AS f(T)

Temp./°C	Vol. pycn./cm^3	Mass liquid/g *	Density/(g cm^{-3})
9.33	11.9709	28.7956	2.4055
10.10	11.9710	28.7772	2.4039
11,50	11.9712	28.7427	2.4010
13.00	11.9713	28.7011	2.3975
13.54	11.9714	28.6868	2.3963
14.45	11.9715	28.6633	2.3943
15.10	11.9716	28.6474	2.3930
15.60	11.9717	28.6339	2.3918
15.60	11.9717	28.6327	2.3917
17.40	11.9719	28.5582	2.3877
18.60	11.9721	28.5535	2.3850
20.90	11.9724	28.4948	2.3800
21.80	11.9726	28.4708	2.3780
22.88	11.9727	28.4429	2.3756
23.36	11.9728	28.4314	2.3747
24.50	11.9730	28.4016	2.3721
26.50	11.9734	28.3486	2.3676
27.28	11.9736	28.3285	2.3659
27.94	11.9737	28.3101	2.3644
28.41	11.9738	28.2984	2.3634
29.13	11.9739	28.2790	2.3617
29.41	11.9740	28.2719	2.3611
29.88	11.9741	28.2593	2.3600
31.10	11.9744	28.2273	2.3573
32.03	11.9746	28.2036	2.3553
33.31	11.9749	28.1693	2.3524
34.64	11.9752	28.1359	2.3495
35.35	11.9754	28.1165	2.3479
37.39	11.9759	28.0635	2.3433
38.57	11.9763	28.0318	2.3406
39.27	11.9765	28.0125	2.3390
40.72	11.9769	27.9766	2.3359

(continued over page)

Table III.2 continued.....

Temp./°C	Vol. pycn./cm^3	Mass liquid/g *	Density/(g cm^{-3})
41.28	11.9771	27.9607	2.3345
43.12	11.9776	27.9136	2.3305
43.52	11.9778	27.9021	2.3295
43.85	11.9779	27.8933	2.3287
44.20	11.9780	27.8838	2.3279
44.67	11.9781	27.8713	2.3268

*corrected to vacuum

Mass empty pycnometer + wire = 23.1587 g

Some of the deviation from linearity above 37°C would be due to water condensing in the bulb on the side-arm to a greater extent than the liquid. This would be expected as the vapour pressure of water is greater than that of bromoform (at 25°C 23.69 mm Hg and 9.4 mm Hg respectively[69]). As a result the value used for the volume of the pycnometer would be high.

(iv) Experimental Procedure for Density Measurements

A quick-fit tube (20 x 2.5 cm), fitted with a ground-glass joint and a thermometer calibrated every 0.20°C, was used. The tube, half-filled with the flotation liquid, was held immersed in the water bath. A perspex window in the water bath enabled the movement of the obsidians to be observed. During heating the liquid was agitated by moving the thermometer or the retort stand to ensure that surface tension effects did not cause the measured density to be low.

The temperature at which a piece of obsidian had sunk half way through the liquid was recorded. Temperatures could be determined to $\pm 0.05^{\circ}C$.

Pieces of obsidian weighing less than 0.05 g were not used so that viscosity and convection effects would be minimized. The upper limit on the size of pieces was determined by the size of the tube used to hold the flotation liquid.

2. Hydrostatic Weighing Method

This is a rapid method of measuring densities of a wide variety of samples. For large, homogeneous specimens it can give results with a greater accuracy (about 0.001%) than any other method[60]. The apparent loss in weight by weighing the solid first in air, then suspended in a liquid is used to calculate the density. For greater than 0.1% accuracy the observed weights must be corrected for the buoyant effect of water. The buoyancy correction amounts to about 0.1% for water, the liquid used.

(i) Buoyancy Correction:

Weighing in air -

Wt. in vacuo = wt. in air + wt. air displaced by obsidian - wt. air displaced by wts.

$$W_v = W_{air} + V_{ob} \cdot \rho_{air} - V_{wts}\,\rho_{air}$$

$$= W_{air} + \frac{W_v}{\rho_{ob}} \cdot \rho_{air} - \frac{W_{air}}{\rho_{wts}} \cdot \rho_{air}$$

$\rho_{wts} \doteqdot 8.4$ g cm^{-3} (brass weights); $\rho_{air} \doteqdot 0.0012$ g cm^{-3} (approximation valid for 4th decimal accuracy)

$$\therefore\ W_v = W_a \left(1 - \frac{0.0012}{8.4}\right) + \frac{W_v}{\rho_{ob}} \cdot 0.0012 \qquad (1)$$

Weighing in water -

Wt. in vacuo = Wt. in water + wt. water displaced by obsidian - wt. air displaced by wts.

$$W_v = W_{H_2O} + V_{ob} \cdot \rho_{H_2O} - V_{wts} \cdot \rho_{air}$$

$$= W_{H_2O} + \frac{W_v}{\rho_{ob}} \cdot \rho_{H_2O} - \frac{W_{H_2O}}{\rho_{wts}} \cdot \rho_{air}$$

$$= W_w \left(1 - \frac{0.0012}{8.4}\right) + \frac{W_v}{\rho_{ob}} \cdot \rho_{H_2O} \qquad (2)$$

Hence $$\frac{W_a}{W_w} = \frac{\rho_{ob} - \rho_{air}}{\rho_{ob} - \rho_{H_2O}}$$

or $$\rho_{ob} = \frac{W_a \cdot \rho_{H_2O} - W_w \cdot \rho_{air}}{W_a - W_w} \qquad (3)$$

A correction for the length of the wire immersed was necessary for each determination:

$$\frac{W_{wire,air}}{W_{wire,\,H_2O}} = \frac{\rho_{wire} - \rho_{air}}{\rho_{wire} - \rho_{H_2O}}$$

$$= \frac{7.8 - 0.0012}{7.8 - 1.0} \quad \div \quad \frac{7.8}{6.8}$$

$$= 1.15$$

$W_{wire,air}$ = 0.0574 g

Length wire = 22.0 cm

$\therefore$ W_{air} of ℓ cm = 2.60ℓ mg

W_{H_2O} of ℓ cm = 2.27ℓ mg

And weight loss of wire in water = 0.33ℓ mg, where ℓ cm are immersed.

(ii) Experimental Procedure for Density Measurements

Measurements were carried out using a four figure Mettler balance. A piece of obsidian was suspended by a fine steel wire in a beaker of water placed on a bridge over the balance pan. The weights in air and in water were determined to 0.1 mg and the temperature of water was measured to 0.1°C.

CHAPTER IV

INVESTIGATION OF NATURAL SOURCE OBSIDIANS BY DENSITY MEASUREMENTS

A total of 88 samples from the eight known New Zealand sources of flake quality obisdian were examined during this investigation. In Table IV.1 the samples are identified and details about location, occurrence and appearance outlined.

Sixty-two of these samples from seven of the natural sources were examined by the two density methods. (The Maraetai sample was not examined.) The densities of 20 of these were measured by flotation only, 15 by hydrostatic weighing only and 27 by both methods. The details are recorded in Table IV.2.

TABLE IV.2 - NATURAL SOURCE OBSIDIANS EXAMINED BY DENSITY METHODS

Source	Number of Samples		
	Total	Flotation	Hydrostatic Weighing
Mayor Island	14	11	8
Kaeo	12	12	7
Huruiki	10	6	7
Great Barrier Island	6	5	4
Arid Island	1	1	1
Whitianga	9	6	7
Taupo	10	6	8

TABLE IV.1 - NATURAL SOURCE OBSIDIANS EXAMINED BY DENSITY MEASUREMENTS AND BY CHEMICAL ANALYSIS

Source	Sample	Location and Occurrence	Grid Reference	General Description	Remarks
Mayor Island (20 samples)	115	Not recorded	Fig.1 between p.11 & 12	Green or yellow-green in transmitted light. High gloss, excellent flake quality. Some pieces banded and opaque. Powder green-grey.	Dull grey-green. Not flake quality
	PB/508/3	South of Oira Bay			
	PB/504/3	Edge of crater, Taritimi Bay			
	PB/505/6	Oira Bay			
	PB/1490/4	North Otura Bay			
	PB/1491/6	North Oira Bay			
	MT/M1	Oira Bay			
	MT/M2	Oira Bay			Banded, less shiny, poorer quality.
	GW/M1 - GW/M12	Quarry on "Staircase" ridge, Taritimi Bay. Samples from area about 3 meters sq.			
Kaeo (24 samples)	228	In slip, tributary of Opokorau Stream	N 11/346662	More opaque, less glassy than other sources. Some pieces had small inclusions. Powder grey.	
	GW/K1 - GW/K10	River-worn boulders from about 1000 metres of bed of Opokorau Stream.			
	GA/K1 - GA/K13				
Huruiki (11 samples)	2	Deeply pitted block on Trig Hill.	N 16/823313	Excellent flake quality. Grey, opaque, a few small inclusions. Powder dark grey.	
	GW/H1 - GW/H10	Samples from separate deposits 2000 metres along a ridge. Blocks weathered.			

(continued over page)

Table IV.1 continued.....

Source	Sample	Location and Occurrence	Grid Reference	General Description	Remarks
Great Barrier Island (8 samples)	GW/GB1 - GW/GB8	Extensive flat at end of Te Ahumata. Samples from narrow band about 50 metres long. Supply scanty and weathered.	N 30/926329	Excellent flake quality. Thin sections pale grey or purple-brown, very transparent. Powder pale grey.	GB6 - purple-brown banding. Powder brown-grey.
Arid Island (1 sample)	PB/A1	Not recorded.		Good flake quality, pale grey. Powder grey-white.	
Whitianga (12 samples)	GW/W1 - GW/W12	Ridge behind Cook's Bay. Samples from 2 deposits each about 75 metres across and less than 100 metres apart.	N 44/240605	Good flake quality. Grey, opaque with small inclusions. Powder grey.	
Taupo (11 samples)	JA/T1 GW/T1 - GW/T10	Outcrop along Whangamata Fault, Ben Lomond Station One outcrop, Whangamata Fault, 1 mile east Ben Lomond Station.	Not recorded N 93/436498	Good flake quality. Thin sections pale grey and very transparent. Powder pale grey.	Few inclusions Large pumice-like inclusions.
Maraetai (1 sample)	GW/Ma1	One outcrop 6 miles east Lake Maraetai.	N 84/384725	Not• flake quality. Crumbly, with many pumice-like inclusions and glassy bands. Powder grey-white.	

Flotation Method

Up to six pieces of obsidian, sufficiently distinctive to be identified individually, were examined at the same time. Pieces weighing between 0.07 g and 0.53 g (most weighed 0.10 - 0.25 g) and of regular dimensions were chosen. To minimise surface tension effects, very thin flakes were not used. A check was made that no air bubbles were trapped on the obsidians.

The density of each of the 48 pieces was measured in duplicate. For Table IV.3, the temperatures of flotation and the densities were averaged. The temperature was raised until all pieces in the tube sank; then the flotation liquid was cooled and the temperature raised again.

Hydrostatic Weighing Method

The 43 pieces examined weighed between 1 g and 30 g, (most weighed 4 - 8 g). The precision of the method decreased rapidly when samples weighing less than 1 g were used. Where possible smooth, regularly shaped pieces were chosen to avoid errors due to occluded air bubbles and surface inhomogeneties. Differences of the order of 0.010 g cm^{-3} were found between smooth specimens and pieces with rough or irregular surfaces.

After it was established that duplicate measurements of the density of a piece agreed to within $\pm$0.001 g cm^{-3} (the maximum precision of the method) each piece was examined only once. All density determinations using the second method were carried out by Dr R.D. Reeves.

Results for both methods are recorded in Table IV.3.

TABLE IV.3 - DENSITIES OF NATURAL SOURCE OBSIDIANS

Source	Sample	Temp. of Flotation/ °C	Density, /(g cm^{-3})	
			Flotation	Hydrostatic Weighing
Mayor Island	115	19.51	2.3830	2.384
	PB/508/3	1.6	2.4230	2.442
	PB/504/3	17.11	2.3883	2.391
	PB/505/6	14.10	2.3950	
	PB/1490/4	12.69	2.3981	2.398
	PB/1491/6			2.404
	MT/M1			2.395
	MT/M2			2.419
	GW/M3	10.80	2.4023	2.404
	GW/M4	11.13	2.4016	
	GW/M5	9.67	2.4048	
	GW/M6	10.63	2.4027	
	GW/M7	10.07	2.4039	
	GW/M10	23.04	2.3752	
	Range	2.375 - 2.442		
Kaeo	GW/K1	9.71	2.4047	2.403
	GW/K2	9.41	2.4055	2.405
	GW/K3	10.13	2.4037	
	GW/K4	3.62	2.4183	2.421
	GW/K5	10.35	2.4034	
	GW/K6	9.13	2.4060	2.405
	GW/K7	5.47	2.4142	2.415
	GW/K8	4.99	2.4174	2.419
	GW/K9	8.27	2.4079	
	GW/K10	8.36	2.4078	2.406
	GA/K3	7.46	2.4097	
	GA/K12	3.15	2.4195	
	Range	2.403 - 2.421		
Huruiki	GW/H1	29.97	2.3599	2.359
	GW/H2			2.363
	GW/H3	29.49	2.3630	2.363
	GW/H4			2.363
	GW/H5	28.42	2.3632	
	GW/H6			2.362
	GW/H7	28.17	2.3638	
	GW/H8			2.362
	GW/H9	29.02	2.3619	
	GW/H10	30.75	2.3582	2.357
	Range	2.357 - 2.364		

(continued over page)

Table IV.3 continued.....

Source	Sample	Temp. of Flotation/ °C	Density, /(g cm^{-3})	
			Flotation	Hydrostatic Weighing
Great Barrier Island	GW/GB2	41.31	2.3349	
	GW/GB3	33.68	2.3517	2.350
	GW/GB5			2.345
	GW/GB6	33.28	2.3526	2.356
	GW/GB7	33.23	2.3527	
	GW/GB8	32.89	2.3534	2.354
	Range	2.335 - 2.356		
Arid Island	PB/A1	36.25	2.3461	2.344
Whitianga	GW/W1			2.358
	GW/W2	31.18	2.3571	2.357
	GW/W4	33.93	2.3513	
	GW/W5			2.358
	GW/W6	32.95	2.3533	2.353
	GW/W8	31.04	2.3576	2.356
	GW/W9			2.352
	GW/W10	31.58	2.3564	
	GW/W12	32.85	2.3536	2.353
	Range	2.351 - 2.358		
Taupo	GW/T1	32.88	2.3535	2.353
	GW/T2			2.352
	GW/T3	32.93	2.3534	2.354
	GW/T4			2.353
	GW/T5	32.88	2.3535	
	GW/T7	33.04	2.3531	2.352
	GW/T8			2.353
	GW/T9	33.39	2.3523	2.352
	GW/T10	32.90	2.3534	
	JA/T1			2.346
	Range	2.346 - 2.354		

Results and Discussion

On the basis of the 62 natural source obsidians examined, density measurements divided the obsidians into three groups.

Sources	Density/(g cm^{-3})
1. Mayor Island, Kaeo	2.375 - 2.421*
2. Huruiki	2.357 - 2.364
3. Great Barrier Island, Arid Island, Whitianga, Taupo	2.335 - 2.358

* non-flake quality PB/508/13 excluded.

When archaeological samples from Skipper's Ridge were examined some Whitianga pieces were found to have densities in the same range as the natural source Huruiki samples. There were also four Mayor Island pieces with densities less than 2.375 g cm^{-3}.

If more natural source obsidians were examined it is probable that overlap between the sources would be even greater. The ten Taupo samples from the outcrop (GT/1-10) had very similar densities, 2.352 - 2.354 g cm^{-3}, but the sample from another outcrop (JA/T1) had a density of 2.346 g cm^{-3}. The latter was closer to and not significantly different from that obtained for the Arid Island sample.

On the basis of one sample the range of densities of the Arid Island source cannot be stated but it appears likely that overlap with other sources, especially Taupo and Great Barrier Island, will be extensive. If no pieces have a density greater than 2.350 g cm^{-3} Arid Island samples could be separated from Huruiki and Whitianga samples.

The agreement between the two flotation measurements varied but it was usually within 0.0003 g cm^{-3}. The precision depended on deciding when a particular piece of obsidian was sinking. Unless the liquid was agitated surface tension effects kept the sample floating even when its density was much more than that of the liquid (especially when the sample was disc-like).

Quantitative experiments were not made on the surface tension effects or the effects of convection and vibration. On a few occasions the effect of one piece sinking and "pulling" down another sample was noted. Neither was the effect of the shape and size of the sample on the measured density determined, because the overlap of densities between sources was so extensive.

The temperature of the flotation liquid was raised approximately 0.1°C per minute. Increasing the rate of temperature change would have decreased the density measured because the rate of sinking of the obsidian would have been less than the change of density of the mixture.

The accuracy of the method would have been improved if the temperature of floating as well as the temperature of sinking had been determined. A water bath on which the temperature could be lowered in a controlled manner would have been necessary for this.

Bromoform has been widely used as the main component of flotation liquids[64], but even when alcohols are present to stabilize it decomposition occurs on exposure to light and air. When a mixture of 1- hexanol, 1- pentanol and bromoform was used to determine the densities of lithium isotopes, the density of the mixture remained constant for several days only[67]. Gradual discolouration in sunlight was also noted.

The flotation mixture of bromoform and 1- pentanol was colourless when prepared but after standing for a week in a brown, glass-stoppered bottle it had discoloured very slightly. The refractive index had not changed significantly having decreased only 0.0001, from 1.5515 to 1.5514 at 20°C. As soon as the mixture was exposed to light and air when the calibrated pycnometer was filled it went quite yellow. This decomposition caused the refractive index to decrease to 1.5512 but there was no smell of bromine. The refractive index of bromine is 1.6637^{70} at 20°C compared to 1.5977 for bromoform but the refractive indices of the bromoparaffins arising from decomposition, e.g., dibromomethane (1.5420^{70}), are lower. As bromoform has a higher vapour pressure than 1- pentanol it could have evaporated preferentially and this would lower the refractive index of the mixture.

When the mixture was used for Mayor Island and Kaeo obsidians it was not subjected to temperatures greater than 23°C and yellowing was slight. Decomposition accelerated, however, when the mixture was used at temperatures greater than 30°C. This was accompanied by a greater decrease in the refractive index and in the density. After two weeks use the refractive index at 20°C was 1.5504 compared to 1.5515 when the mixture was prepared.

The density of GW/GB7 was measured on two occasions four days apart. The measured densities were 2.3528 g cm^{-3} and 2.3535 g cm^{-3} respectively and the refractive indices 1.5503 and 1.5500. Five natural source Mayor Island samples were examined ten days apart. The second measurements averaged 0.0012 g cm^{-3} higher than the first and the refractive index of the liquid had decreased 0.0004 in this time. Because the density of the flotation mixture had decreased the samples sank at lower temperatures and the measured densities were higher.

Agreement between the two density methods was good for the natural source obsidians, e.g., for seven Kaeo samples the mean density was 2.4106 g cm^{-3} by flotation and 2.411 g cm^{-3} by hydrostatic weighing. As the flotation liquid was used, however, agreement became less. When four Tiwai Point archaeological obsidians were examined the differences in the measured densities were 0.0033, 0.0042, 0.0020 and 0.0063 g cm^{-3}.

Clearly this decrease in accuracy is a problem. During the study of lithium isotopes the decomposition of the flotation mixture was overcome by checking the density using a "standard" crystal and making the necessary adjustments. If this flotation method was to be used routinely for identifying archaeological obsidian it would be necessary to either prepare the flotation liquid every few days or use another liquid with a similar temperature-density coefficient. Tetrabromoethane (Timmermans, b.p. 134°C, d_4^{25} 2.9529, n_D^{20} 1.63795) could be suitable. This has been used with carbon tetrachloride to separate ores and minerals[64].

The precision of the hydrostatic weighing method was $\pm$0.001 g cm^{-3} or approximately one part in 2.4 x 10^3. Two measurements made on the same piece of obsidian always agreed within 0.001 g cm^{-3}. The precision of the method decreased when samples weighing less than 1 g were used. Here the precision of weighing limited the reproducibility of the method. Conversely, the larger the piece of obsidian the more precise was the measurement of density.

The absolute accuracy of the method was not tested but for large homogeneous speciments this method gives the greatest accuracy (about 1 part in 10^5)[60]. Air bubbles occluded on the obsidian and rough surfaces were the greatest sources of inaccuracy, causing a lowering of the observed density.

The accuracy, therefore, should be comparable to the precision. Although good accuracy was desirable high precision was more important because the sources were separated by their relative densities.

This second method of density measurement was the more useful except for archaeological specimens weighing less than 1 g. Its precision was more reliable and its execution simpler and more rapid. Adaptation to the field would be simple - only a Mettler balance and a supply of distilled water being required.

CHAPTER V - CHEMICAL ANALYSIS METHOD

As stated in the aim of the present investigation, atomic absorption spectrophotometry has been widely and successfully applied to the analysis of silicate rocks.

1. Preliminary Experiments

These were carried out to determine which elements would be the most useful for the identification of New Zealand obsidian sources.

Firstly two or three samples from each source were analysed using the following method[72]. Concentrated reagent grade nitric and hydrofluoric acids (15 cm^3 of each) were added to approximately 0.4g of powdered obsidian contained in a 250 cm^3 teflon beaker. The acids were evaporated to dryness over a period of 2 - 3 hours using a hot plate. To the residue was added a further 15 cm^3 of concentrated nitric acid and this was reduced to dryness. The residue was taken up in 10 cm^3 of 2M nitric acid and after gentle warming the solution was filtered. This solution was diluted 1 : 5 with 2M hydrochloric acid, and Ca, Mg, Zn, Fe, Mn, Cu and Cr were analysed by atomic absorption spectrophotometry using an air-acetylene flame. With each set of analyses two blanks, containing the acids alone, were prepared.

The analysis of copper and chromium was not continued because the blanks contained as much of each element as the obsidian solutions. Even if metal-free acids were available the levels of these two elements would be too low for them to be detected by AAS. For copper, a value of 20 ppm is given in the literature[20].

Problems were encountered when calcium and magnesium were analysed. For the Mayor Island and Kaeo samples the amounts in the blanks were almost equal to the amounts in the samples. Green, Brooks and Reeves[25] obtained 2500 ppm and 2220 ppm respectively as the approximate concentrations of calcium in these two sources. For a Mayor Island obsidian Washington[19] reported 3800 ppm calcium and 1600 ppm magnesium.

Aluminium makes up 5 - 8% of obsidian and this element interferes with the determination of alkaline earth elements by forming stable molecular species with them[73]. At the temperature of the air-acetylene flame these compounds are broken down very little and the absorption by calcium and magnesium is severely depressed. This chemical interference has been overcome by adding lanthanum or strontium[74] to the analytical solutions. These two elements combine preferentially with aluminium thus releasing the alkaline earth elements. Silicon also interferes with the determination of calcium and magnesium and this interference can be overcome in a similar manner. Even when 2M hydrochloric acid containing 1000 ppm strontium (as strontium chloride) was used to dilute the original solutions there was not a significant improvement in the results obtained for these two elements.

Unless all fluoride is expelled from the residue calcium and magnesium are said to form complex or slightly soluble fluorides[75]. The presence of a precipitate suggested that this was causing the interference. To expel all fluoride both perchloric and sulphuric acids have been used, with evaporation carried out at 180°C and 250°C respectively[76].

The modified method used for all subsequent analyses did not produce a precipitate, which suggested that all fluoride was expelled. In these solutions, therefore, it appeared that aluminium would be the only

interferent. Again 2M hydrochloric acid containing 1000 ppm strontium was used to dilute the original solutions. (The diluted solutions contained approximately 20 - 28 ppm aluminium.) The solutions were analysed by atomic absorption spectrophotometry using an air-acetylene flame.

The results obtained for calcium were comparable with those obtained by emission spectroscopy[25], but like those for magnesium, were very variable. Thirteen Kaeo samples were analysed in duplicate and the following results obtained.

Element	Mean Concentration (ppm)	Standard Deviation	Coefficient of Variation (%)
Calcium	2505	379	15.1
Magnesium	170	88	51.8

The range of calcium values was 1870 - 3185 ppm and duplicates differed by as much as 580 ppm. The cause of the poor precision was not investigated further because it did not appear that these two elements would separate the obsidian sources any more satisfactorily than the elements chosen.

The preliminary experiments indicated that the concentrations of iron, manganese and zinc were sufficiently high and sufficiently different for these elements to be useful for the identification of obsidians. Also, their analysis by AAS was straight-forward. No interferences have been reported for iron in an air-acetylene flame[77] as long as the acid concentration of the standards and samples is the same[78].

Only silicon interferes with the determination of manganese[79] and zinc[80] in an air-acetylene flame. The complete dissolution of the residue (with the modified method) suggested that most, if not all silicon was expelled as silicon tetrafluoride.

The method used to remove silicon varies. Some workers have used a mixture of hydrofluoric and sulphuric acids[81,82], and others have used perchloric acid instead of sulphuric acid[83] and another has used both[76]. Billings, however, claims that silicon is removed by hydrofluoric acid alone[84].

During the initial experiments, when 2M nitric acid was used to dissolve the residue, a white precipitate remained. When dilute hydrochloric acid was substituted all the residue dissolved. This acid has been used in almost all analyses of silicate rocks traced in the literature[85,86].

A mixture of hydrofluoric and nitric acids has been used by a number of workers to decompose silicate rocks[87,88]. It has also been noted[88] that extraction with sulphuric acid - nitric acid and with hydrochloric acid - nitric acid was less effective. When hydrochloric acid - nitric acid was used to decompose obsidian almost no decomposition occurred. Hydrofluoric acid breaks down the silicate structure by reacting with silicon to form silicon tetrafluoride which escapes as a gas. Dissolution was incomplete if concentrated hydrochloric acid was not added <u>after</u> the nitric and hydrofluoric acids had been evaporated. Hydrochloric acid could not be added with these acids because it has a lower boiling point than hydrofluoric acid (110°C and 120°C respectively[69]) and evaporated before the silicate structure had been broken down. For example, the manganese concentrations determined for six Skipper's Ridge archaeological obsidians were 20% lower when hydrochloric acid was not added separately.

Sodium and potassium were also analysed during these preliminary experiments because all obsidians contain 2 - 5% of these elements. Both can be analysed by atomic absorption spectrophotometry but a flame cooler than an air-acetylene flame is needed. Because of a low ionization potential

one element supplies electrons to the other, increasing the number of ground state atoms and thus the absorption signal of the second element. An air-coal gas flame has a temperature of approximately 1800K, whereas an air-acetylene flame has a temperature of approximately 2350K[58]. Ionization will be less in the cooler flame.

Both elements can be analysed equally well by flame photometry and this method was chosen for several reasons. When the investigation was started only a Techtron AA-3 Atomic Absorption Spectrophotometer was available and the photomultiplier of this instrument was not sensitive at 7664.9 Å, the wavelength of the potassium absorption line. A Techtron AA-5 became available after the preliminary experiments and, although the above problem no longer existed, analysis of sodium and potassium was carried by flame photometry because the sodium-potassium hollow cathode lamp available was not sufficiently bright or stable to give satisfactory results.

Some ionization still occurs in an air-coal gas flame[89] and matching the alkali content of standards and samples has been considered necessary for accurate results[86]. The difference between standards containing just sodium or potassium and standards containing both elements was investigated. The enhancement of potassium by sodium was negligible and that of sodium by potassium only a few per cent; therefore composite standards were not considered necessary.

2. Experimental Procedure

Grinding: If available, approximately 3g of each obsidian sample was crushed using a percussion mortar. The crushed sample was transferred to an agate mortar and ground with an agate pestle to approximately 100-mesh.

Contamination from the percussion mortar could not be detected. A sample crushed with the percussion mortar had the same iron content as one powdered only with the agate mortar and pestle.

Sample contamination could have occurred before grinding, but it was more likely to occur during grinding. Emission spectroscopy has been used to determine contamination arising in this way [90]. When an agate mortar was used there was no contamination. Cross contamination was found to be the major source of contamination. This was avoided by cleaning the mortars and pestles between the grinding of different obsidian sources.

Dissolution: Samples of 200 $\pm$ 3mg, weighed to the nearest 0.1mg, were transferred to 50cm^3 polypropylene beakers. To each beaker 10cm^3 of concentrated nitric acid (69.5 - 71.5% w/w, "Pronalys", M & B) and 10cm^3 of hydrofluoric acid (40% w/w, "Analar", BDH) were added from a 25cm^3 teflon measuring cylinder. The uncovered beakers, held in a teflon rack, were evaporated to dryness over a boiling water bath. This took about three hours.

The residue was dissolved in 10cm^3 of concentrated hydrochloric acid (35.5 - 37.5% w/w, "Pronalys, M & B) added from a 10cm^3 measuring cylinder. The acid was added when the water bath was not boiling because otherwise the acid effervesced vigorously and cross contamination could occur. Evaporation to dryness took about two hours.

When the beakers had cooled 20 cm^3 of 2M hydrochloric acid was pipetted into each. (The 2M hydrochloric acid was prepared by diluting concentrated hydrochloric acid with deionized water.) After being weighed to $\pm$ 0.010g the beakers were warmed gently for about twenty minutes over a water bath to facilitate dissolution. During this time the volume of solution decreased about 2 cm^3. Each beaker, when cooled, was made up to volume by adding 2M hydrochloric acid from a pipette until the original weight (about 25g) was reached.

This procedure, although not as precise or accurate as one using volumetric flasks to make the solutions up to volume, introduced an error of less than $\pm$ 0.1% and was much more rapid. The loss of 2 cm^3 of solution caused the acid concentration to be greater than 2M but the increase was not sufficient to be a source of experimental inaccuracy.

With each set of analyses two blanks were prepared to determine the amount of each of the five elements in the three acids. The acids contained no detectable amounts of potassium, iron or manganese, but corrections had to be made for sodium and zinc.

Manganese and zinc were determined on these solutions. Diluted solutions were prepared for the analysis of sodium, potassium and iron. Two cm^3 of each solution was transferred by pipette to a 50 cm^3 volumetric flask and diluted with 2M hydrochloric acid

Standards: For each of the five elements 1000 ppm standards were prepared using "Specpure" (Johnson, Matthey & Co.) or "Analar" (M & B) chemicals. More dilute standards were prepared with each set of analyses to avoid the possibility of adsorption on to and leaching of cations from the glass. Dilution was done with 2M hydrochloric acid to prevent errors due to different atomization rates for the samples and standards.

For the 1000 ppm standards the required weight of chemical was weighed to ± 0.1 mg and dissolved in deionized water in a 100 cm^3 volumetric flask.

Sodium. "Specpure" NaCl (0.2543g) was used. The dilute standards were 1, 5, 10, 15 and 20 ppm.

Potassium. "Specpure" KH_2PO_4 (0.3481g) was used. The dilute standards were 5, 10, 15 and 20 ppm.

Iron. "Analar" $NH_4Fe(SO_4)_2.12\ H_2O$ (0.8634g) was used. The dilute standards were 2, 5, 10, 15 and 20 ppm.

Manganese. "Analar" $MnSO_4.7\ H_2O$ (0.4487g) was used. The dilute standards were 2, 5 and 10 ppm.

Zinc. "Specpure" $ZnSO_4.7\ H_2O$ (0.4551g) was used. The dilute standards were 0.5, 1.0, 2.5, 4.0 and 5.0 ppm.

Instrumentation: Atomic Absorption Spectrophotometry

TABLE V.1 - INSTRUMENTAL CONDITIONS FOR Fe, Mn, Zn

	Fe	Mn	Zn
Wavelength (Å)	2483.3	2794.8	2138.6
Current (mA)	6	7	7
Slit Width (μ)	50	50	50
Air pressure (p.s.i.)	15	15	15
Acetylene flow rate (meter reading)	3.2	3.2	3.2

A Techtron AA-5 Atomic Absorption Spectrophotometer was used. The burner height was adjusted each time to give maximum absorption, but this was a variation of only a few millimeters. Hollow cathode lamps were used as the spectral sources and a lean, non-oxidising air-acetylene flame was used throughout.

For all three elements sensitivity was decreased by rotating the burner rather than by diluting the solutions. The latter would have been time consuming and would have increased the risk of contamination. The instrument settings, e.g. burner rotation and gain, were adjusted each time so that minimum use of calibration graphs were required. For example, these were adjusted so that the 2, 5 and 10 ppm manganese standards gave absorbances of 0.10, 0.25 and 0.50 respectively.

Instrumentation: Flame Photometry

A Gallenkamp Flame Analyser FH-500, operated as outlined in the instruction manual, was used to analyse sodium and potassium. An air-coal gas flame was used for most analyses. An air-natural gas flame was used for the Foxton and Auckland archaeological obsidians because the gas supply was changed.

Some difficulty was encountered with drifting of signals on the flame photometer, necessitating frequent checking of the signals from the standards. Some sodium analyses were carried out using the Techtron AA-5 and an air-acetylene flame as a flame-emission instrument. The results obtained were about 4% higher than with the flame photometer, because of the higher flame temperature. Only a few sets of analyses were carried out with the AA-5, and the difference between the two instruments did not introduce a serious error in the obsidian identification.

Aspiration Procedure:

Both instruments were zeroed with 2M hydrochloric acid at the beginning of each set of analyses. For potassium, iron and manganese de--ionized water could be used thereafter because the dilute acid did not contain detectable amounts of these elements. The standards were aspirated

starting with the most dilute, followed by the samples. After each five samples had been aspirated the absorbance of at least one standard was checked. The two blanks were aspirated at the beginning and end of each set of analyses.

Calculation of Results:

The absorbances of the standards were graphed and the concentrations of each element in the samples and blanks read off. For sodium and zinc the blank contributions were then subtracted, before the results were corrected to allow for dilutions and the weight of powdered obsidian taken.

CHAPTER VI

INVESTIGATION OF NATURAL SOURCE OBSIDIANS BY CHEMICAL ANALYSIS

Samples from the eight known sources of flake quality obsidian were examined.

1. Mayor Island
2. Kaeo
3. Huruiki
4. Great Barrier Island
5. Arid Island
6. Whitianga
7. Taupo
8. Maraetai

The majority of samples were collected by Mr G.K. Ward, Department of Anthropology, University of Otago. These were designated "GW". Samples were also supplied by Mr P. Bellwood, Department of Anthropology, University of Auckland ("PB"), Mr M.H. Timperley ("MT"), Mr J.E. Armitage ("JA") and the author ("GA"). Samples not prefixed came from Dr R.C. Green, Auckland Institute and Museum and were used during the characterization of New Zealand obsidians by emission spectroscopy[25].

Details about the samples are given in Table IV, pages 39 and 40. Even though seventeen Maraetai samples were available only one piece was analysed, because non-flake quality obsidian was not used archaeologically. Flake quality obsidian is known to be present at the Maraetai source and three pieces were analysed by Green, Brooks and Reeves during their emission spectrographic study of New Zealand obsidians. In the following discussion

it was assumed that the chemical composition of the non-flake quality Maraetai samples did not differ significantly from that of flake quality obsidian from the same source.

Only one Arid Island piece, (supplied by Mr P. Bellwood) was available during this study, therefore the natural variation of this source could not be established.

The size of the samples varied, but whenever possible a piece weighing at least 3g was powdered and 0.2g of this used for each analysis.

1. Variation Due to the Analytical Method

One aim of the present investigation was to establish how much of the variation, obtained when different samples from the same source were analysed, was due to the variation of the analytical method. Two sources are not distinguished if the difference in chemical composition between them is accounted for by the variation of the method.

This was done by carrying out ten replicate analyses on a representative sample from each source, with the exceptions of Mayor Island sample 115 (nine replicates), Arid Island (eight replicates) and Maraetai (5 replicates). The replicates from each source were analysed consecutively, and with the exception of the two Mayor Island samples, all samples were analysed at the same time. Two Mayor Island samples, one with a manganese concentration about 680 ppm and one with a manganese concentration about 1000 ppm, were examined to determine whether the precision of the method was constant for all samples from this source. The experimental procedure outlined in the preceeding chapter was followed.

The results, expressed as mean element concentrations and standard deviations, are recorded in Table VI.1. In Table VI.2 the coefficients of variation (standard deviations expressed as percentages of the means)are recorded.

Results and Discussion

In general, the higher the mean concentration of an element the lower the standard deviation and the coefficient of variation, i.e. the variation was usually lower for the two Mayor Island pieces and the Kaeo piece. This was especially evident for zinc.

TABLE VI.1 - MEAN ELEMENT CONCENTRATIONS AND STANDARD DEVIATIONS OF REPLICATE ANALYSES OF SINGLE OBSIDIAN SAMPLES

Source	Sample	No. of analyses	Mean Element Concentrations and Standard Deviations									
			Na %	s.d.	K %	s.d.	Fe %	s.d.	Mn ppm	s.d.	Zn ppm	s.d.
Mayor I.(1)	115	9	4.68	0.04	3.62	0.03	n.d.		996	6	233	3
Mayor I.(2)	GW/M4	10	4.60	0.03	3.60	0.02	3.26	0.01	690	6	221	2
Kaeo	GW/K5	10	4.79	0.04	3.37	0.02	3.23	0.02	564	2	339	4
Huruiki	GW/H3	10	3.88	0.04	3.18	0.01	1.00	0.02	219	1	50	2
Great Barrier I.	GW/GB5	10	3.27	0.09	3.90	0.03	0.92	0.01	199	2	44	3
Arid I.	PB/A1	8	3.67	0.03	2.82	0.03	1.03	0.02	360	5	40	2
Whitianga	GW/W3	10	3.84	0.05	2.87	0.03	1.02	0.01	434	6	49	2
Taupo	GW/T9	10	3.68	0.04	2.88	0.03	1.01	0.01	354	3	41	1
Maraetai	GW/Ma1	5	3.35	0.04	3.12	0.03	.078	0.01	320	3	37	4

n.d. not determined

TABLE VI.2 - COEFFICIENTS OF VARIATION OF REPLICATE ANALYSES OF SINGLE OBSIDIAN SAMPLES

Source	Sample	No. of analyses	Coefficients of Variation (%)				
			Na	K	Fe	Mn	Zn
Mayor I.(1)	115	9	0.9	0.8	n.d.	0.6	1.3
Mayor I.(2)	GW/M4	10	0.7	0.6	0.3	0.9	0.9
Kaeo	GW/K5	10	0.8	0.6	0.6	0.4	1.2
Huruiki	GW/H3	10	1.0	0.3	2.0	0.5	4.0
Great Barrier I.	GW/GB5	10	2.8	0.8	1.1	1.0	6.8
Arid I.	PB/A1	8	0.8	1.1	1.9	1.4	5.0
Whitianga	GW/W3	10	1.3	1.0	1.0	1.4	4.1
Taupo	GW/T9	10	1.1	1.0	1.0	0.8	2.4
Maraetai	GW/Ma1	5	1.2	0.9	1.3	0.9	10.2

n.d. not determined

The precision of the method was high; better than 2% except for sodium in the Great Barrier Island sample and zinc in all but the Mayor Island and Kaeo samples.

The higher coefficient of variation (2.8%) for sodium in the Great Barrier Island sample reflected the fact that this sample had the lowest sodium content. It also reflected the difficulties encountered with drifting flame photometer readings. Although the drift was corrected as far as was possible by aspirating the standards, it did cause the variations of sodium results to be generally higher.

The concentration of zinc in the analytical solutions of all sources, except Mayor Island and Kaeo, was about 0.35 - 0.55 ppm. Standards were prepared in the range 0.5 - 5.0 ppm. Scale expansion and flame position were adjusted so that 5 ppm gave an absorbance of about ·60. With these conditions 0.5 ppm gave an absorbance of about·08. (The calibration curve was not linear above 1 ppm.) When the first two or three sets of analyses gave zinc results with high standard deviations the instrumental conditions were altered after the Mayor Island and Kaeo samples had been analysed. Reducing the amount of burner rotation, to increase the sensitivity, did not significantly improve the precision however, and the former conditions described above were used throughout the investigation.

The Maraetai sample had the highest coefficient of variation (10.2%) because it contained the least amount of zinc (37 ppm) and because only five replicates were analysed. The latter caused the standard deviations of this sample to be less reliable. If this sample was not considered the variation when the zinc concentration was below 60 ppm was better than 7%. Other workers have achieved similar variations for the

analysis of zinc in silicate rocks. Belt[91] obtained a precision of 9.7% for zinc at a concentration of 3 ppm, and a precision of 3.7% for 260 ppm.

A number of factors could have been responsible for the higher standard deviations of these zinc results. When the precision of atomic absorption spectrophotometry, during the analysis of geological material, was examined on a previous occasion it was found that an occasional determination was completely spurious[87]. Contamination during sample preparation or other errors in sample preparation were proposed as the causes. Anomalously high results were sometimes obtained for zinc in obsidian, as well as infrequently for other elements. When the obsidian solutions contained less than 1.0 ppm zinc contamination could have occurred quite easily.

The amount of zinc in the blank was a factor contributing to the high standard deviations. If the obsidian solution contained 0.40 ppm zinc a variation of 0.01 ppm in a blank contribution of 0.2 ppm represented a variation of 5% in the concentration of zinc per gram of obsidian.

Only a very small amount of zinc in the acids would lead to a blank contribution of 0.2 ppm. Assuming the density of the acids was 1.2g. cm^{-3}, 0.11 ppm zinc in each acid would cause this contribution. (Thirty cm^3 of concentrated acid was used and the final volume of the obsidian solution was 20 cm^3.)

At 2138.6 Å, the wavelength of the zinc absorption line, most flame gases absorb and for precise results flame conditions must be kept very stable. This was done as far as was practicable but it is not possible to achieve exactly the same conditions from one day to the next.

Variations in instrumental conditions, for example sample aspiration and flame and burner conditions, are indeterminate errors. The

precision of the apparatus and dilution errors also contribute to these errors.

As carried out, the experiment to determine the variation due to the method did not take account of indeterminate errors. It did, however, take account of variations arising from the dissolution of obsidian. It has been suggested that, even if flame parameters and standards were exactly reproducible, the precision of silicate analysis is limited by the difficulties of putting the samples into solution[86].

If the sample from each source had been analysed on ten different occasions the standard deviations would have been higher because of indeterminate errors. When the variation of chemical composition within a source was investigated these errors were measured because analyses on a sample were usually carried out at different times. As already mentioned, instrumental conditions were kept as constant as possible, but variations would still have arisen from slightly different aspiration and flame conditions.

Even if the variation due to the method was twice as high as that determined, it was much less than the variation of the emission spectroscopic method used in the former study of New Zealand obsidians. The method developed went a long way towards eliminating errors in the analysis itself and enabledthe sources to be characterized more precisely and separated with greater confidence.

2. Variation in Chemical Composition within a Source

Once the variation due to the experimental method had been established, the variation in chemical composition within a source could be determined. If the sources were to be distinguished chemically the variation within a source had to be less than the variation between sources. Also, the variation between sources had to be greater than the variation due to the analytical method.

For each source, excluding Arid Island and Maraetai, eight or more different samples were analysed at least in duplicate. Rather than set out the results of every analysis for each of the five elements in all sources, only the means were recorded in Table VI.3. The ranges of these means and their medians were also recorded in this table. The median of the average results for the samples, rather than the mean, was chosen to avoid undue weighting by high or low values. Because the number of analyses done on each sample was so variable (between two and eighteen), the median of all analysis was not recorded. For example, the median of the potassium values for the eleven Huruiki samples was 3.13%, whereas the median for all forty analyses was 3.18%. The sample with the highest potassium content, GW/H3, had been analysed eighteen times, compared to duplicate analyses for most of the other ten samples.

Results and Discussion

The manganese concentration was the most distinctive feature of any source, as Figures 4 - 8 show. On the basis of this element all sources except Taupo and Arid Island, and Huruiki and Great Barrier Island could be separated.

TABLE VI.3 - CHEMICAL ANALYSES OF NATURAL SOURCE OBSIDIANS

Source	Sample	No. of analyses	Mean Element Concentrations				
			Na %	K %	Fe %	Mn ppm	Zn ppm
Mayor Island (20 samples)	PB/504/3	2	4.61	3.62	3.26	692	224
	PB/505/6	2	4.67	3.58	3.26	693	227
	PB/1490/4	2	4.59	3.61	3.27	695	222
	PB/1491/6	2	4.70	3.63	3.44	737	223
	MT/M1	13	4.60	3.63	3.21	700	211
	MT/M2	10	4.45	3.69	3.37	748	213
	GW/M1	6	4.49	3.62	3.22	680	270*
	/M2	2	4.53	3.49	3.29	660	221
	/M3	2	4.57	3.54	3.29	667	217
	/M4	16	4.61	3.59	3.24	687	219
	/M5	2	4.73	3.55	3.21	655	215
	/M6	2	4.66	3.57	3.26	653	216
	/M7	2	4.58	3.52	3.28	660	214
	/M8	4	4.46	3.65	3.20	675	215
	/M9	2	4.72	3.55	3.24	671	217
	/M10	2	4.58	3.58	3.32	664	217
	/M11	2	4.45	3.67	3.28	673	215
	/M12	2	4.62	3.56	3.23	665	217
		Medians:	4.60	3.59	3.26	674	217
		Ranges:	4.45-4.73	3.52-3.69	3.20-3.44	653-748	211-270
	PB/508/3**	4	4.71	3.55	4.00	897	256
	115	16	4.82	3.59	4.40	1000	231

* Relatively large range of values averaged (259 - 300 ppm).

** Non-flake quality obsidian.

Table continued over page.....

Table VI.3 continued.....

Source	Sample	No. of analyses	Mean Element Concentrations				
			Na %	K %	Fe %	Mn ppm	Zn ppm
Kaeo (24 samples)	228	1	4.74	3.73		542	320
	GW/K1	2	4.84	3.43	3.03	607	326
	/K2	4	5.02	3.48	3.06	598	335
	/K3	2	4.81	3.46	3.02	599	326
	/K4	2	4.74	3.46	2.97	604	330
	/K5	16	4.79	3.43	3.23	574	338
	/K6	2	4.73	3.46	3.06	589	328
	/K7	4	5.00	3.48	3.08	601	338
	/K8	4	4.75	3.49	3.09	581	331
	/K9	2	4.62	3.49	2.94	607	326
	/K10	2	4.57	3.51	3.08	607	328
	GA/K1	4	4.53	3.50		593	317
	/K2	2	4.65	3.54		580	316
	/K3	2	4.83	3.62		596	326
	/K4	4	4.60	3.55		572	326
	/K5	2	4.69	3.60		578	330
	/K6	2	4.89	3.74		576	318
	/K7	2	4.61	3.62		580	318
	/K8	2	4.67	3.53		595	324
	/K9	2	4.70	3.56		576	307
	/K10	2	4.82	3.61		567	302
	/K11	2	4.49	3.52		564	308
	/K12	7	4.69	3.46		592	308
	/K13	2	4.44	3.49		550	314
		Medians:	4.72	3.50	3.06	585	326
		Ranges:	4.44-5.02	3.43-3.74	2.94-3.23	542-607	302-338

Table continued over page .....

Table VI.3 continued.....

Source	Sample	No. of analyses	Mean Element Concentrations				
			Na %	K %	Fe %	Mn ppm	Zn ppm
Huruiki (11 samples)	2	2	3.83	3.16	0.99	212	52
	GW/H1	2	4.09	3.12	1.06	225	55
	/H2	2	4.17	3.13	1.01	228	48
	/H3	18	3.90	3.23	1.00	221	50
	/H4	4	3.89	3.15	1.01	217	49
	/H5	2	4.01	3.10	1.03	219	48
	/H6	2	3.96	3.17	1.03	217	47
	/H7	2	3.90	3.12	0.99	224	48
	/H8	2	4.14	3.12	1.05	237	46
	/H9	2	4.01	3.13	1.03	226	47
	/H10	2	3.92	3.16	1.00	220	51
		Medians:	3.96	3.13	1.01	221	48
		Ranges:	3.83-4.17	3.10-3.23	0.99-1.06	212-237	46-55
Great Barrier Island (8 samples)	GW/GB1	2	3.33	3.80	1.06	220	44
	/GB2	2	3.32	3.88	1.05	207	46
	/GB3	2	3.28	3.90	0.97	202	48
	/GB4	2	3.40	3.96	0.96	209	52
	/GB5	18	3.33	3.92	0.94	200	43
	/GB6	7	3.29	3.92	0.95	200	45
	/GB7	2	3.27	4.00	0.99	208	46
	/GB8	2	3.30	3.95	0.99	205	44
		Medians:	3.31	3.92	0.98	206	46
		Ranges:	3.27-3.40	3.80-4.00	0.94-1.06	200-220	43-52
Arid Island (1 sample)	PB/A1	10	3.68	2.83	1.03	361	41

Table continued over page .....

Table VI.3 continued.....

Source	Sample	No. of analyses	Mean Element Concentrations				
			Na %	K %	Fe %	Mn ppm	Zn ppm
Whitianga (12 samples)	GW/W1	2	4.00	2.77	1.06	467	42
	/W2	6	3.84	2.84	1.04	453	42
	/W3	16	3.87	2.87	1.03	443	45
	/W4	2	3.82	2.71	1.01	461	43
	/W5	4	3.96	2.83	1.03	462	41
	/W6	2	3.77	2.75	0.99	449	38
	/W7	2	3.88	2.74	1.02	458	40
	/W8	2	3.90	2.69	1.02	449	44
	/W9	4	3.71	2.84	1.00	439	42
	/W10	2	3.77	2.68	1.01	451	45
	/W11	2	3.78	2.68	0.98	452	43
	/W12	2	3.71	2.71	1.00	469	42
		Medians:	3.83	2.74	1.02	452	42
		Ranges:	3.71-4.00	2.68-2.87	0.98-1.06	439-469	38-45
Taupo (11 samples)	JA/T1	13	3.48	2.83	1.07	360	37
	GW/T1	2	3.56	2.91	1.03	374	40
	/T2	2	3.60	2.97	1.07	363	43
	/T3	3	3.64	2.98	1.07	367	35
	/T4	6	3.50	2.89	1.05	359	36
	/T5	4	3.42	2.96	1.03	356	38
	/T6	2	3.57	2.95	1.06	372	39
	/T7	2	3.59	2.97	1.05	356	37
	/T8	2	3.53	2.90	1.08	363	36
	/T9	16	3.65	2.88	1.03	357	38
	/T10	2	3.49	3.00	1.08	353	35
		Medians:	3.56	2.95	1.06	360	37
		Ranges:	3.42-3.65	2.83-3.00	1.03-1.08	353-374	35-43
Maraetai (1 sample)	GW/Ma1	5	3.35	3.12	0.78	320	37

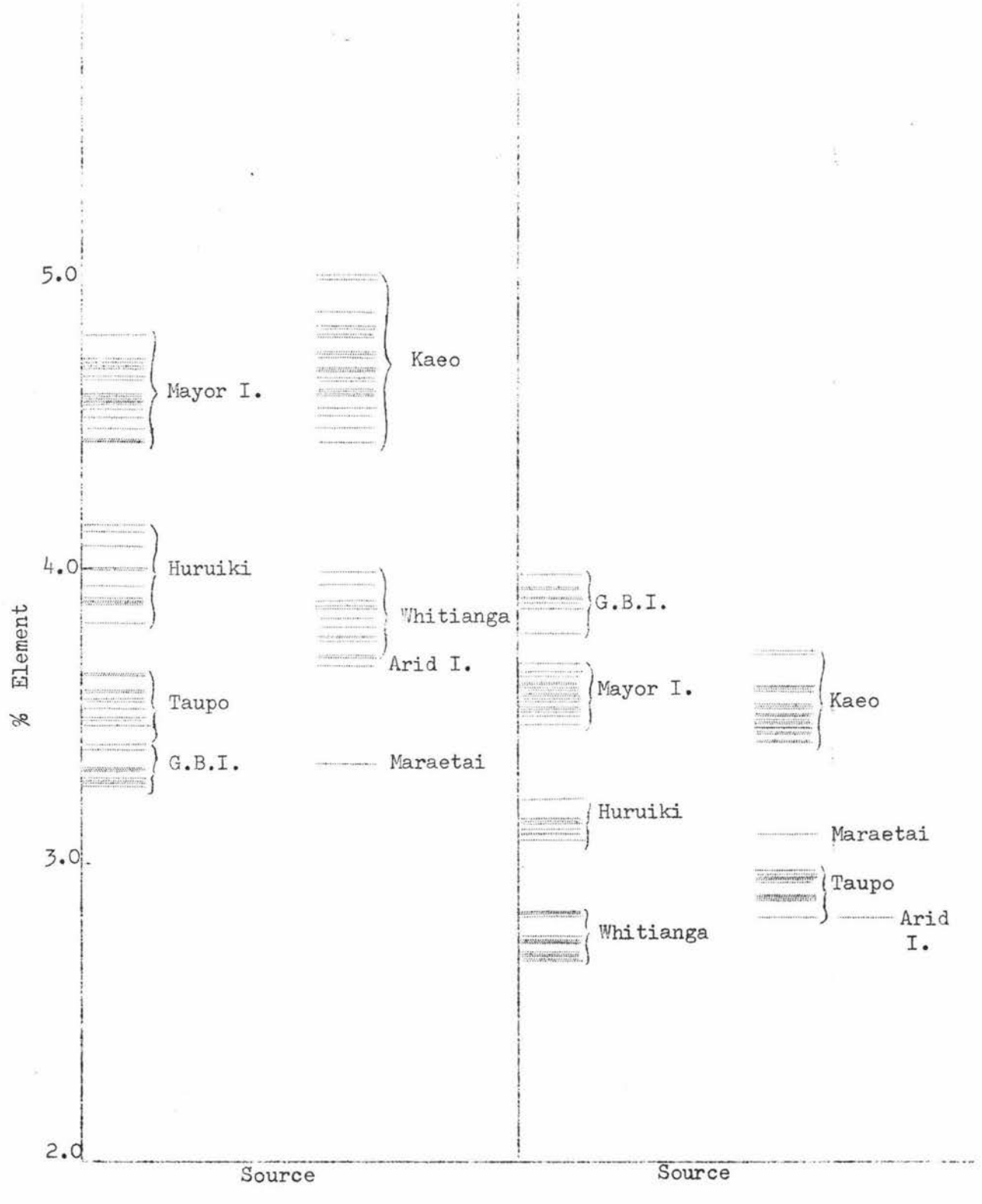

Fig. 4. Sodium In Obsidian

Fig. 5. Potassium In Obsidian

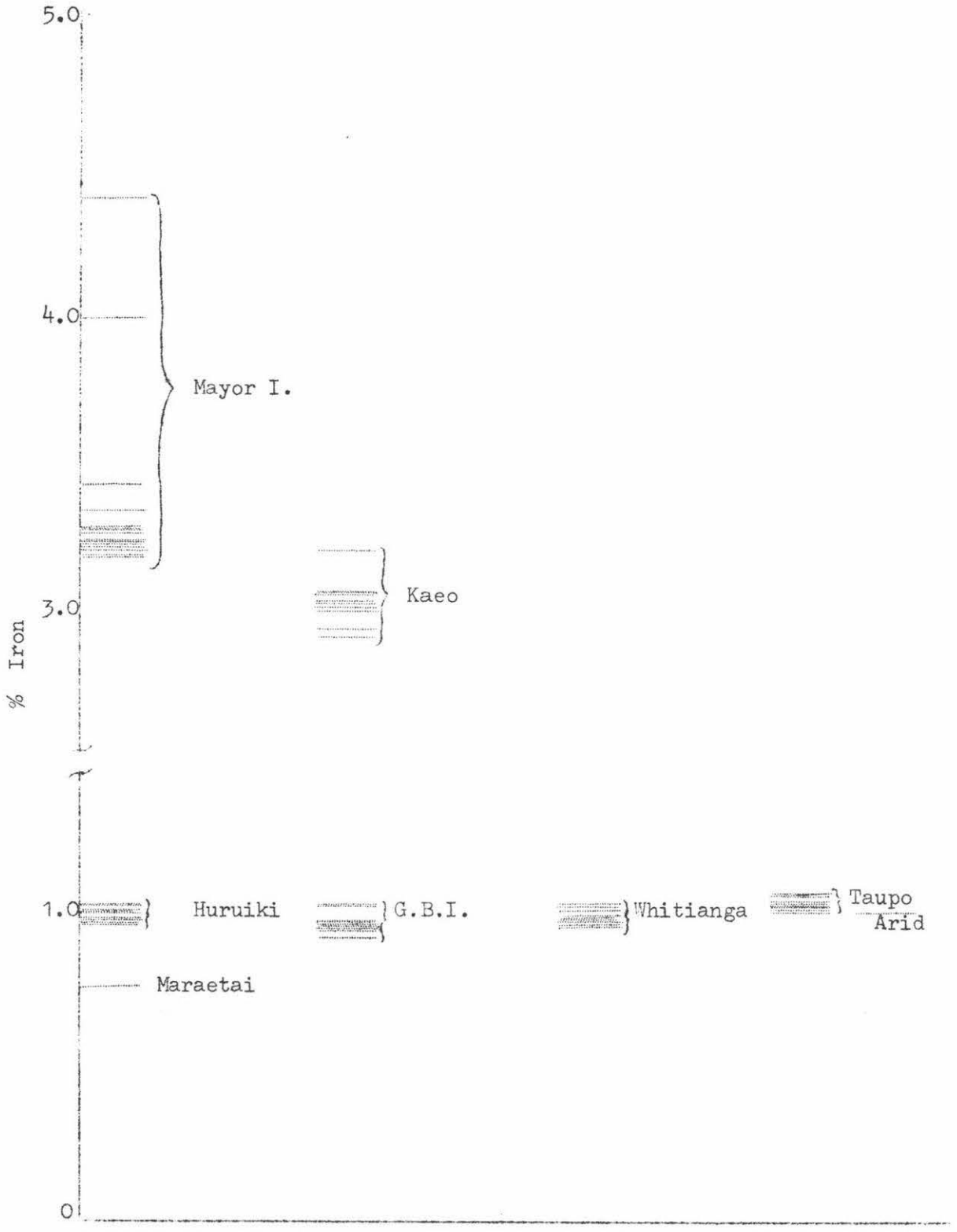

Fig. 6. Iron In Obsidian

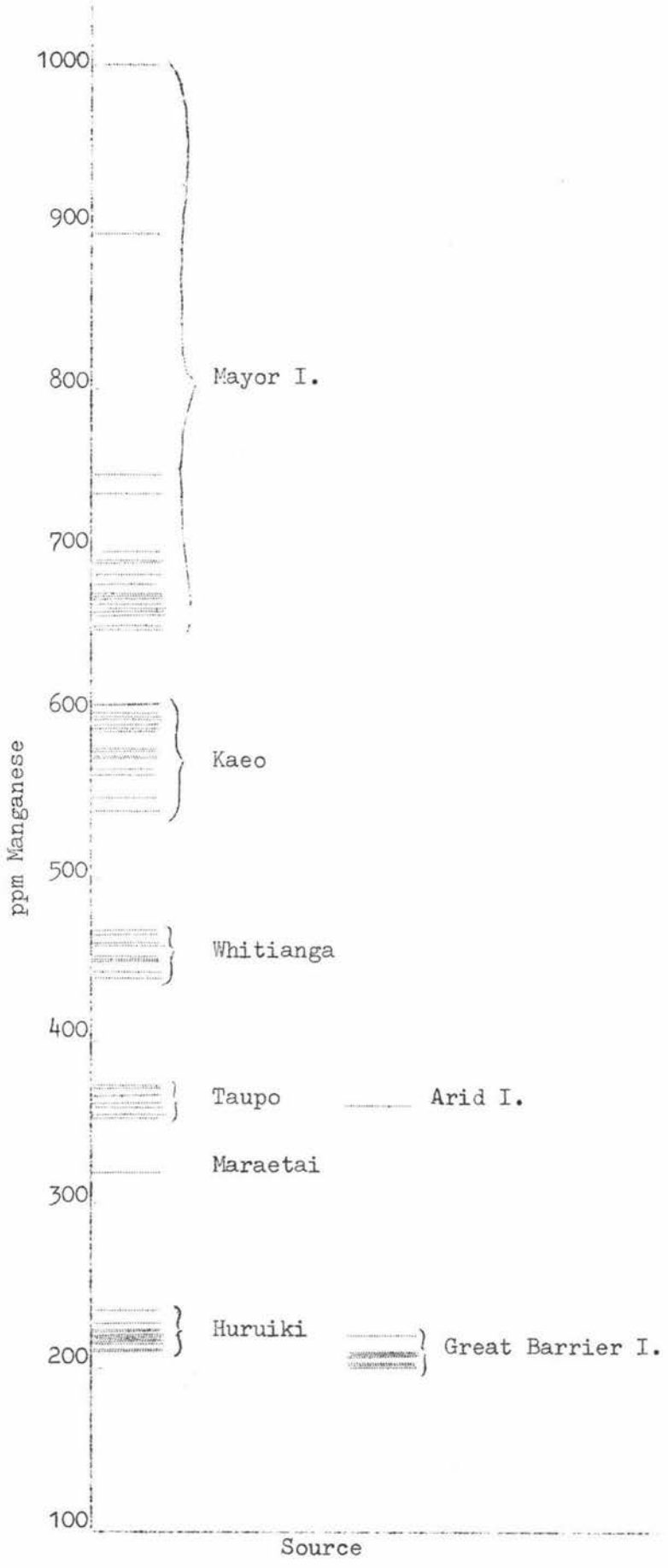

Fig. 7. Manganese in Obsidians

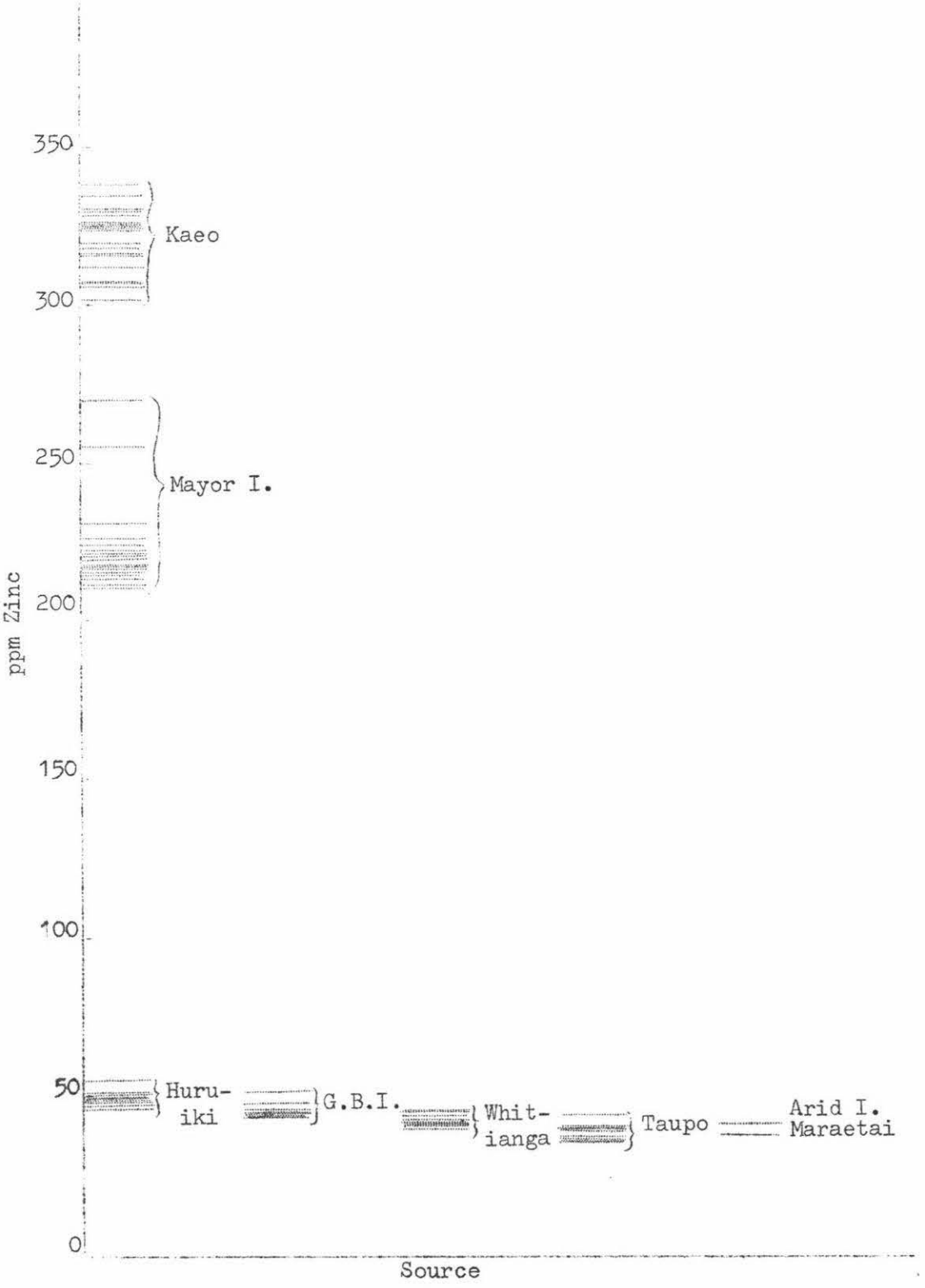

Fig. 8. Zinc in Obsidians

For the natural source obsidians, only one Great Barrier sample, GW/GB1, overlapped the Huruiki values. The median manganese concentration for the Huruiki obsidians was 221 ppm, whereas that for the Great Barrier obsidians was 206 ppm. However, two archaeological samples for Motutapu Island identified as Great Barrier obsidians had manganese concentrations greater than 210 ppm, and when the variation due to the analytical method was considered the two sources overlapped considerably.

Fortunately the potassium content of the two sources was quite different and any uncertainty could be resolved by analysing this element (see Fig.5). The median potassium concentration of the Huruiki samples was 3.16% and that of the Great Barrier samples was 3.92%.

The sodium content of the two sources was also different, being 3.96% and 3.31% respectively, but because of the lower precision of the sodium results it was more reliable to base characterization on potassium content.

Sodium was not of great use for characterizing any of the sources because no source had a distinctive sodium content (see Fig.4). This element was really only useful to confirm identification.

Iron and zinc concentrations also were less distinctive. Zinc identified only the Mayor Island and Kaeo sources (see Figures 6 and 8). If the variation of the method was as high as 5% then obsidians with manganese concentrations between 600 ppm and 650 ppm would need to be analysed for zinc. Otherwise, the determination of this element was not of great value.

Assuming the non-flake quality Maraetai sample was representative of flake quality obsidian from the same source, iron could be used to distinguish this source (see Fig.6). Depending on how representative was

this piece, it could be necessary to base identification of this source on iron rather than manganese content. (The difference in manganese content between this and the Taupo source was less than 10%.)

The only other sources which iron could be used to characterize were Mayor Island and Kaeo. There was some doubt whether this was possible because the iron content of one Kaeo sample overlapped the Mayor Island results. Only ten of the twenty-four Kaeo samples were analysed for iron and the confidence with which the two sources could be distinguished on the basis of this element would depend on how representative were the ten analyses. The higher iron content of these two sources caused their solutions to be quite yellow, compared with pale yellow for the other six sources.

Two Mayor Island samples, PB/508/3 and 115, had distinctively higher iron concentrations. These two samples also had higher manganese concentrations. Except for these two exceptions the variation of the five elements within each source was less than 20%. The manganese results especially, suggested that there were three subsources within the Mayor Island source.

The majority of samples, eighteen out of twenty, were characterized by a manganese concentration between 650 ppm and 750 ppm and an iron concentration between 3.20% and 3.45%. The median zinc concentration was 217 ppm but, as noted at the foot of Table VI.3, the zinc content of GW/M1 was much higher (270 ppm). All the sample was ground up so it was not possible to determine whether the variation of the results and the higher concentration were due to sample contamination.

Two of the eighteen, PB/1491/6 and MT/M2, had manganese concentrations greater than 730 ppm, compared with less than 700 ppm for the rest of the samples in this subsource. Some Skipper's Ridge archaeological obsidians also had manganese concentrations in this range, and of these some also had slightly higher zinc concentrations - greater than 230 ppm compared with about 220 ppm. These Skipper's Ridge obsidians did not fall unambiguously into a separate group because sometimes both manganese and zinc were higher, and sometimes only one was higher. Samples PB/1491/6 and MT/M2 had higher than average manganese concentrations but not higher zinc concentrations. Therefore, the obsidians with slightly higher manganese concentrations were not placed in a separate group.

The iron concentration of these two samples was also slightly higher, 3.44% and 3.37% respectively, compared with the median value of 3.26%. The Skipper's Ridge obsidians were not analysed for iron and it would have been statistically unsound to propose a fourth subsource on the basis of only two results.

The manganese content of sample PB/508/3 was 897 ppm, and the iron content 4.00%. The zinc content (256 ppm) was also higher than that obtained for eighteen samples of the first subsource. This sample was not flake quality but twelve Skipper's Ridge obsidians had manganese concentrations between 860 ppm and 923 ppm. Two archaeological obsidians from Foxton and one from Tiwai Point also had manganese concentrations in this range.

Sample PB/508/3 had the highest zinc concentration of the natural source Mayor Island obsidians, but the twelve Skipper's Ridge obsidians did not have distinctive zinc concentrations. Although higher than subsource one, they were not distinct from subsource three.

Sample 115, with a manganese concentration of 1000 ppm, an iron concentration of 4.40% and a slightly higher zinc concentration, represented the third subsource. Later analysis of Skipper's Ridge obsidians also supported the existence of this subsource; twelve of the pieces analysed chemically had manganese concentrations between 961 ppm and 1065 ppm.

The sodium content of sample 115 was also significantly higher than the sodium content of the other nineteen samples - 4.82% compared with the median value of 4.60%. As with zinc, the sodium contents of subsources two and three from Skipper's Ridge were higher, but not distinguishable. It appeared that an increase in manganese content was parallelled by an increase in sodium, iron and zinc.

A portion of sample MT/M2 had paler striations running through it. The clear and striated portions were ground up and analysed separately but no significant difference in the concentration of the five elements could be detected.

TABLE VI.4: ANALYSIS OF STRIATED AND UNSTRIATED OBSIDIAN FROM THE SAME SAMPLE, MT/M2

Sample	No. of analyses	Mean Element Concentrations				
		Na %	K %	Fe %	Mn ppm	Zn ppm
MT/M2, clear	3	4.42	3.61	3.36	752	209
MT/M2, striated	7	4.46	3.72	3.37	746	214

Unfortunately only one Arid Island sample was available during this study. Ten replicate analyses were carried out on this piece and the

results were not significantly different from those obtained for the eleven Taupo samples. Although the mean sodium content of the latter was 3.65%, individual analyses were greater than 3.68%, the average of the ten Arid Island analyses. Similarly, individual Arid Island results were less than 3.65%.

Nor did density measurements separate these two sources, but the density of the Arid Island sample was less than the densities of all but one Taupo sample. Depending on how representative of the whole source was this Arid Island sample, the two sources could be separated with greater or lesser accuracy. At least ten Arid Island samples would need to be analysed to establish the extent of overlap in composition. Even if the sources were indistinguishable on the basis of sodium, potassium, iron, manganese and zinc, the concentrations of other elements could be different. Alternatively, the Arid Island source may not have been used archaeologically.

The above conclusions have been made on the basis of the available natural source obsidians. Except for the Mayor Island, Kaeo and Huruiki sources, the areas over which these samples were collected were rather restricted (see Table IV.1, pages 39 and 40). It could be argued that the medians and ranges quoted were not necessarily correct. However, Huruiki and Taupo samples collected at different times from the majority of samples did not have significantly different chemical compositions.

Results obtained for Mayor Island samples PB/505/6, 1491/6 and 508/3, especially supported the validity of the quoted medians and ranges. These three samples were picked up from a small area but their chemical compositions were quite distinctive. (For the location see Table IV.1, pages 39 and 40, and Fig.1, between page 11 and page 12.) Sample PB/1490/4

came from the other side of the island but its composition was very similar to PB/505/6, and these two pieces were similar to samples PB/504/3 and GW/M1 - GW/M12 which came from another area again.

The existence of a small number of archaeological obsidians of unknown origin did suggest, however, that either the sampling had not revealed some subsources or that unknown sources exist.

Standard deviations were not determined because the number of analyses of each sample was so variable (between two and eighteen). If ten samples from each source had been analysed on ten different occasions and the order of the samples within each set had been different and random, standard deviations could have been calculated.

The eight sources, except possibly Arid Island and Taupo, could be separated unequivocally because the variation due to the method, for at least one element in each source, was less than half the variation in composition between sources; and the variation in composition within the sources was less than the variation between sources.

Clearly chemical annlysis was a much more satisfactory method of identifying New Zealand obsidians than density measurements. It was interesting that Mayor Island and Kaeo obsidians had the highest concentration of all five elements, (except potassium in Great Barrier obsidian) and the highest densities.

CHAPTER VII: INVESTIGATION OF ARCHAEOLOGICAL SITE OBSIDIANS

After it was established that it was possible to distinguish the New Zealand sources of flake quality obsidian the two methods were applied to the analysis of obsidians from eight archaeological sites. The sites were:

1. Skipper's Ridge, Coromandel.
2. Sunde Site, Motutapu Island, Hauraki Gulf.
3. Two Motutapu Undefended Sites.
4. Hamlins Hill, Auckland City.
5. Lake Mangakaware, Waikato.
6. Otakanini, South Kaipara Harbour.
7. Foxton Beach, Manawatu.
8. Tiwai Point, Bluff.

Depending on the size of the pieces of obsidian the entire sample or about 3 g were powdered and analysed chemically using the method described previously. With each set of analyses at least six geological samples were included to check that the analysis was reproducible. Many samples were analysed more than once and in the tables of results the mean element concentrations are given.

Densities were measured in some cases to confirm identification, and in some cases where the specimen was too small for chemical analysis, identification was based on density alone. The density results are quoted in the same tables as the analytical results. Each flotation density is the average of two consecutive determinations.

1. Skipper's Ridge Site

This site is a prehistoric Maori kumara storage area at Opito Bay some fifteen miles northeast of Whitianga. Approximately 300 flakes were recovered and many showed "use" marks. Carbon-14 dating has established the age of the site as early eighteenth century[92].

Mr P. Bellwood, Department of Anthropology, University of Auckland, submitted 232 samples for analysis. One sample, SR 541, was more like pumice than obsidian and was ignored for the purposes of this study.

Results and Discussion:

Of the 231 obsidians submitted 194 were examined, 140 by chemical analysis, 47 by density measurements and seven by both methods. The results are recorded in Table VII.1.

Chemical Analysis

Only three samples of the 147 examined by this method were not identified as Mayor Island (90) or Whitianga (54) obsidians.

TABLE VII.1 - SKIPPER'S RIDGE OBSIDIANS

Inscription	No.	Appearance	No. of analyses	Chemical Analysis				Density/(g cm^{-3})		Identification
				Na %	K %	Mn ppm	Zn ppm	Flotation	Hydrostatic Weighing	
SR67I(1)	301	Green	2	4.23	3.48	703	201			MI
"	302	"	1	4.58	3.42	894	223	2.4030		"
"	303	"	2	4.28	3.58	686	212			"
"	304	"	1	4.23	3.54	667	208			"
"	305	Green-grey, denser	2	4.58	3.50	1000	238			"
"	306	Grey, striations, fairly transparent	1	3.17	2.68	378	32			?
"	307	Grey, striations, fairly transparent	1	3.37	2.76	465	46			W
"	308	Green	5	4.74	3.59	996	232			MI
"	309	"	1	4.11	3.48	743	231			"
"	310	"	2	4.13	3.61	720	222			"
"	311	Grey, banded	3	3.31	2.91	441	43			W
"	312	Grey-green	1	4.59	3.42	744	239			MI
"	313	"	4	4.31	3.56	689	199			"
"	314	"	4	4.74	3.53	990	235			"
SR67I(1),83	315	Grey, inclusions	1		3.14	443	43			W
SR67I(1)	316	Grey	2	3.40	3.13	448	42			"
"	317	"	4	3.28	3.18	462	47			"
"	318	Green	1	4.42	3.38	901	339			MI
"	319	Grey, many inclusion								
"	320	Grey-green	4	4.23	3.50	722	222			"
"	321	Green	2	4.49	3.54	910	252			"

Continued over page .....

Table VII.1 continued.....

Inscription	No.	Appearance	No. of analyses	Chemical Analysis				Density/(g cm^{-3})		Identification
				Na %	K %	Mn ppm	Zn ppm	Flotation	Hydrostatic Weighing	
SR67I(1)	322	Grey	1	3.26	3.04	460	53			W
"	323	Grey-green								
"	324	Grey	2	3.25	3.20	457	47			"
"	325	Green	2	4.32	3.67	696	199			MI
"	326	Grey-green								
"	327	Grey	2	3.26	3.21	462	52			W
"	328	Green	2	4.09	3.58	685	196			MI
"	329	"	2	4.06	3.61	674	202			"
"	330	Grey	2	3.30	3.21	460	46	2.3630		W
"	331	Grey-green	1		3.44	646	206			MI
"	332	"	3	4.38	3.51	709	215			"
"	333	"	1		3.44	748	202			"
"	334	"	3	4.43	3.52	889	232			"
"	335	"	1		3.70	686	214			"
"	336	"	1		5.0	649	208			"
"	337	Green	1		3.60	678	226			"
"	338	"	1		3.61	684	217			"
"	339	"								
"	340	"	1		3.60	666	194			"
SR67I	342	Grey-green	1		3.56	719	262			MI
Ext(1)	343	Grey	3	3.32	3.24	454	45			W
"	344	"								
"	345	"	2	3.12	3.24	456	45			"
"	346	"	1		3.32	443	49			"
"	347	"	2	3.19	3.26	456	47			"
"	348	Grey-green	3	4.10	3.61	696	195			MI
"	349	Green	2	4.06	3.46	706	217			"
"	350	Grey-green, less shiny	3	4.24	3.73	692	226			"

Continued over page .....

Table VII.1 continued.....

Inscription	No.	Appearance	No. of analyses	Chemical Analysis				Density/(g cm^{-3})		Identification
				Na %	K %	Mn ppm	Zn ppm	Flotation	Hydrostatic Weighing	
SR67I(1)	351	Green	1		3.46	897	238			MI
"	352	"	4	4.27	3.60	679	221			"
"	353	Grey	3	3.17	3.16	453	49			W
"	354	Green	1		3.46	1032	269			MI
"	355	"	2	4.34	3.58	719	213			"
"	356	"	1		3.58	1017	260			"
"	357	"	1		3.54	923	267			"
"	358	Grey-green	3	4.20	3.57	718	214			"
"	359	"	1		3.54	696	227			"
"	360	Green	4	4.51	3.56	906	239			"
SR67N	362	Grey	1		2.88	437	39			W
Ext(1)	363	"	2	3.23	3.16	482	47			"
"	364	Green	1		3.62	732	218			MI
"	365	Grey	1	3.15	3.21	446	60			W
"	366	Grey-green	3	4.59	3.58	1017	222	2.3985		MI
"	367	"	4	4.43	3.50	902	258			"
"	368	"	2	4.36	3.61	670	223			"
"	369	"	2	4.23	3.61	703	205			"
"	370	"	4	4.34	3.61	687	209			"
"	371	Grey		3.09	3.17	471	48			W
"	372	"	6	3.15	3.21	458	48			"
"	373	"	4	3.12	3.17	444	50			"
"	374	"	1		3.14	464	51			"
"	375	"	2	3.18	3.32	462	54			"
SR67NExt(1), 94	376	Grey-green	2	4.19	3.68	710	223			MI
SR67NExt(1)	377	Grey	2	3.35	2.96	436	43			W
"	378	Grey-green	2	4.94	3.48	1065	238			MI

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Table VII.1 continued.....

Inscription	No.	Appearance	No. of analyses	Chemical Analysis				Density/(g cm^{-3})		Identification
				Na %	K %	Mn ppm	Zn ppm	Flotation	Hydrostatic Weighing	
SR67NExt(1)	379	Grey	3	3.33	2.98	435	40			W
"	380	Green-grey	3	4.34	3.63	702	204			MI
"	381	Grey	1		3.02	494	50			W
"	382	Green	3	4.28	3.65	696	194			MI
"	383	Grey	1		3.10	458	48			W
"	384	Green-grey	2	4.33	3.64	687	219			MI
"	385	Grey	1		3.18	447	47			W
"	386	"	5	3.22	3.35	302	42	2.3492		?
"	387	"	2	3.00	3.14	449	43			W
"	388	" , less shiny, banded	4	4.77	3.62	1038	242			MI
SR67Pitβ	390	Grey-green, banded	2	4.19	3.54	684	213			MI
SR67Pitγ	392	Grey	1		3.08	427	41			W
"	393	Green-grey	3	4.30	3.61	684	213			MI
"	394	"	1		3.58	689	217			"
"	395	"	2	4.27	3.60	676	209			"
"	396	"	2	4.24	3.60	677	213			"
SR67,76	398	Grey-green	3	4.29	3.57	697	212		2.400	MI
SR67,Te(1)	400	"								
"	401	"								
"	402	"	1		3.50	1029	250			MI
"	403	"								
Unlabelled	405	"	2	4.31	3.55	706	208			MI
"	406	"								

Continued over page .....

Table VII.1 continued.....

Inscription	No.	Appearance	No. of analyses	Chemical Analysis				Density/(g cm^{-3})		Identification
				Na %	K %	Mn ppm	Zn ppm	Flotation	Hydrostatic Weighing	
SR67(2),45	408	Grey, inclusions	3	3.23	3.07	447	45			W
SR67(2),31	409	Grey-green	2	4.01	3.54	708	213			MI
SR67(2),33	410	"	2	4.56	3.41	872	234			"
SR67(2)	411	"	4	4.30	3.50	714	221			"
"	412	Grey	3	3.18	3.09	429	48			W
"	413	"								
"	414	" , inclusions							2.369	W?
"	415	"							2.367	W
"	416	"						2.3650	2.371	W?
"	417	"						2.3658		"
SR67(2),38	418	"							2.362	"
SR67(2),35	419	"							2.357	"
SR67(2)	420	"						2.3669		"
"	421	"							2.363	"
"	422	Grey-green						2.4114	2.412	MI
"	423	"							2.386	"
"	424	"							2.418	"
"	425	"								
"	426	"							2.392	"
"	427	"								
"	428	"								
"	429	"								
"	430	Grey							2.364	W
"	431	"						2.3636		"
SR67(2),43	432	"						2.3563		"
SR67(2)	433	Grey-green								
"	434	"								
"	435	"							2.413	MI

Table continued over page .....

Table VII.1 continued.....

Inscription	No.	Appearance	No. of analyses	Chemical Analysis				Density/(g cm^{-3})		Identification
				Na %	K %	Mn ppm	Zn ppm	Flotation	Hydrostatic Weighing	
SR67(2)	436	Milky grey-green								
"	437	Grey-green							2.386	MI
"	438	Grey							2.365	W
"	439	"						2.3559		"
"	440	"							2.367	W
SR67(2),36	441	Grey-green							2.398	MI
SR67(2),41	442	"						2.3897	2.389	"
SR67(3),8	444	Grey	1	3.21	2.87	391	48			?
SR67(3),13	445	", banded	2	3.33	2.90	446	41			W
SR67(3)	446	"	1	3.17	3.02	467	53			"
"	447	"	1	3.44	3.02	469	45			"
"	448	"	3	3.83	3.19	467	48			"
"	449	"	20	3.24	3.25	464	51			"
"	450	", fairly transparent	1	3.32	2.69	456	43			"
"	451	Grey	2	3.36	2.79	434	41			"
"	452	"	2	3.18	3.11	445	54			"
"	453	"	1	3.39	3.14	459	47	2.3636	2.362	"
"	454	"	1	3.51	3.04	483	46			"
SR67(3),44	455	Grey(?)	1	3.37	3.17	448	76			"
SR67(3)	456	Green-grey	3	4.37	3.65	697	216			MI
"	457	"	1	4.39	3.37	730	202			"
"	458	"	1	4.35	3.56	672	192			"
"	459	"	2	4.51	3.62	861	241	2.4076		"
"	460	"	2	4.89	3.60	998	231			"
"	461	"	2	4.43	3.69	707	219			"
"	462	"	2	4.32	3.72	689	210			"
"	463	"	1	4.53	3.79	702	207			"

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Table VII.1 continued.....

Inscription	No.	Appearance	No. of analyses	Chemical Analysis			Density/(g cm^{-3})		Identification
				Na %	K %	Mn ppm	Zn ppm	Flotation	Hydrostatic Weighing	
SR67(3)	464	Green-grey								
"	465	"	1	4.34	3.36	712	217			MI
"	466	"	1	4.55	3.63	780	223			"
"	467	Green-grey (?)	2	4.61	3.64	971	235			"
SR67I(3),20	469	Green	4	4.32	3.61	706	222			"
SR67I(3)	470	"	2	4.63	3.62	899	246			"
"	471	"	1	4.42	3.85	714	222			"
"	472	"	1	4.43	3.57	697	225			"
"	473	Grey, inclusions	2	3.28	3.12	463	48			W
SR67I Ext(3),22	475	Grey						2.3665		W
SR67I Ext(3)	476	"							2.367	"
	477	"							2.362	"
"	478	"							2.367	"
"	479	"						2.3551		"
"	480	"							2.371	W?
"	481	"						2.3650		"
"	482	Grey-green							2.399	MI
"	483	"							2.388	"
"	484	"								
"	485	"							2.369	MI?
"	486	"								
"	487	"								
"	488	Grey	3	3.32	2.99	442	39			W
SR67I Ext(3),25	489	Green-grey	2	4.40	3.69	686	209			MI

Continued over page .....

Table VII.1 continued.....

Inscription	No.	Appearance	No. of analyses	Chemical Analysis				Density/(g cm^{-3})		Identification
				Na %	K %	Mn ppm	Zn ppm	Flotation	Hydrostatic Weighing	
SR67I	490	Grey-green	1		3.46	721	193			MI
Ext(3)	491	"	1		3.52	714	193			"
"	492	"	1		3.66	701	207			"
"	493	Grey	1	3.08	3.28	447	45			W
"	494	Grey-green	2	4.08	3.62	682	203			MI
"	495	"	2	4.17	3.52	744	223			"
"	496	Grey	2	3.17	3.22	439	46			W
"	497	Green-grey	1		3.62	694	212			MI
"	498	"	1		3.60	717	213			"
"	499	Green	1		3.62	860	233			"
"	500	Green-grey							2.402	"
"	501	"								
"	502	"								
"	503	Green								
"	504	Grey-green								
"	505	"								
"	506	"							2.370	MI?
"	507	"							2.374	"
"	508	Green-grey							2.397	"
SR67N Ext(3)	510	Grey, inclusions								
"	511	Grey								
"	512	Grey-green								
"	513	Green								
"	514	"							2.408	MI
"	515	Green-grey, less shiny							2.383	"
SR67N Ext(3),77	516	Grey-green							2.372	MI?
SR67N Ext(3)	517	Green-grey								

Table continued over page .....

Table VII.1 continued.....

Inscription	No.	Appearance	No. of analyses	Chemical Analysis				Density/(g cm^{-3})		Identification
				Na %	K %	Mn ppm	Zn ppm	Flotation	Hydrostatic Weighing	
SR67III(1), 63	519	Grey	4	3.19	3.13	444	40			W
SR67III(1)	520	"								
"	521	"	1		2.96	432	34			"
SR67III(1), 70	522	"	2	3.38	2.93	440	30			"
SR67III(1), 65	523	Green-grey	3	4.26	3.56	706	206			MI
SR67III(1)	524	Grey	2	3.25	3.11	452	44			W
"	525	"	1		2.90	452	36			"
"	526	"	1		3.08	451	41			"
"	527	Milky grey	2	3.52	2.90	432	36			"
"	528	Grey	3	3.34	3.00	440	38			"
"	529	Green	1		3.54	762	219			MI
"	530	Green-grey	2	4.26	3.52	730	211			"
"	531	Grey-green	1		3.58	961	243			"
"	532	"							2.406	"
"	533	"							2.394	"
"	534	"							2.394	"
"	535	Green								
"	536	Grey-green								
"	537	"								
"	538	Green								
"	539	" , less shiny						2.4174	2.420	MI
"	540	Green-grey							2.388	"
"	541	Pumice-like								

Table continued over page .....

Table VII.1 continued.....

Inscription	No.	Appearance	No. of analyses	Chemical Analysis				Density/(g cm^{-3})		Identification
				Na %	K %	Mn ppm	Zn ppm	Flotation	Hydrostatic Weighing	
SR67IV(1), 48	543	Grey							2.359	W
SR67IV(1), 50	544	Grey-green							2.381	MI
SR67IV(1), 53	545	"								
SR67IV(1)	546	Grey						2.3570		W

In Table VII.1 and Table VII.3 to Table VII.9 the following abbreviations have been used:

MI	Mayor Island
H	Huruiki
GB	Great Barrier Island
A	Arid Island
W	Whitianga
T	Taupo

Identification based on colour in transmitted light approximated to identification based on chemical analysis. All "green" obsidians were from Mayor Island, but one "grey, less shiny, banded obsidian", (SR 388) was also from Mayor Island. The other "grey" obsidians were from the Whitianga source, except three samples, 306, 386 and 444.

Samples 306 and 444 had manganese concentrations similar to Taupo and Arid Island obsidians, (378 ppm and 391 ppm respectively). But as there was only enough obsidian for one chemical analysis of each and there was none for density measurements, it would not be valid to identify them as Taupo or Arid Island obsidians.

Sample 386 had a manganese concentration closest to the Maraetai obsidian, (302 ppm and 320 ppm respectively). If iron had been analysed it would have been possible to identify this piece with more confidence. The density of this sample (2.349 g cm^{-3}) was determined by both methods, and it indicated Great Barrier Island, Taupo or Arid Island as the source.

Of the 90 samples shown by chemical analysis to be from Mayor Island, 12 were from the second subsource and 12 were from the third subsource. The range of manganese concentration for each was:

1) 646 - 762 ppm
2) 860 - 923 ppm
3) 961 - 1065 ppm

As mentioned with regard to the natural source Mayor Island obsidians, the zinc and sodium contents of (2) and (3) above were higher.

The agreement of the potassium, manganese and zinc results with those obtained for the natural source obsidians was good. Some zinc results

were about 10% lower, (approximately 200 ppm rather than 210 ppm), but this would be expected because of the greater number of samples analysed.

Sodium results were generally 10% lower. (This element was not always analysed because of the difficulty experienced in obtaining constant sodium readings.) Most analyses of Skipper's Ridge obsidians were carried out whilst the experimental method was being developed, when the conditions were not standardized. (These archaeological obsidians were the only samples available early in this investigation.) Changes in the degree of extraction and in flame conditions would affect the amount of sodium measured. The sodium results obtained for the Whitianga samples were also about 10% lower than the natural source obsidian results. Because the manganese results were unambiguous it was not considered worthwhile to analyse the samples again.

The occasional result was quite spurious, e.g. potassium in sample 336 (5.0%) and zinc in samples 318 (339 ppm) and 455 (76 ppm). These results were probably due to contamination.

Density Measurements.

These were carried out on 54 Skipper's Ridge obsidians to supplement the chemical analysis results. Only seven samples were analysed by both methods. Of the remaining 47, 21 were identified as Mayor Island obsidians and 20 were identified as Whitianga obsidians. The identification of the remaining six was not unequivocal.

Three "green" obsidians, 485, 506 and 516 had densities of 2.369, 2.370 and 2.372 g cm^{-3} respectively, and three "grey" obsidians, 414, 416 and 480 had densities of 2.369, 2.371 and 2.371 g cm^{-3}. One Mayor Island natural source obsidian, GW/M10, had a density of 2.375 g cm^{-3}, but the

highest density measured for the Whitianga natural source obsidians was only 2.358 g cm^{-3}. However, two "grey" obsidians (330, 453) identified chemically as Whitianga obsidians had densities greater than 2.362 g cm^{-3} which indicated that samples 414, 416 and 480 were probably from the Whitianga source. If time had permitted identification could have been confirmed (or refuted) by chemical analysis.

No "green" or "grey-green" obsidians have been identified as anything but Mayor Island so it can be stated with good confidence that samples 485, 506 and 516 were from this source.

TABLE VII.2 - SUMMARY OF SKIPPER'S RIDGE RESULTS

Method of Examination	Total No. examined	Identification		
		Mayor Island	Whitianga	?
Chemical Analysis	140	86	52	2
Density Measurements	47	21(3?)	20(3?)	
Both Methods	7	4	2	1
Total	194	111(114?)	74(77?)	3

Thirty-seven obsidians were not examined by either method. Thirty-one were "green" and were identified as Mayor Island obsidians. The remaining six "grey" obsidians were probably from Whitianga because the majority of "grey" obsidian were shown to be from this source. If these identifications are assumed and the six samples not unequivocally characterized by density measurements are taken to be similarly identified then:

Total No. analysed	Mayor Island	Whitianga	?
231	145	83	3

Because of the overwhelming predominance of Mayor Island and Whitianga obsidians at this site it was likely that the three unidentified "grey" obsidians were from an unknown local source.

2. Sunde Site N 38/24

Five samples from this site on Motutapu Island were submitted by Dr R.C. Green, Auckland Institute and Museum. Data on the excavations of this site have been published[93].

Motutapu Island is covered with Rangitoto ash and one piece of obsidian was found below this ash, which has been carbon-14 dated to about A.D. 1200. This piece was not available for analysis but it has been identified by handlens examination and refractive index measurements as a Mayor Island obsidian.

Pieces 1568/9, 1570/3A and 1574/4 were analysed chemically and the densities of all five pieces were determined by the flotation method. Pieces 1570/3B and 1572/4 could not be analysed chemically because each weighed only 0.3 g. Results are presented in Table VII.3.

TABLE VII.3 - SUNDE SITE OBSIDIANS

Sample	Appearance	No. of analyses	Chemical Analysis					Flotation Density/ ($g\ cm^{-3}$)	Identification
			Na %	K %	Fe %	Mn ppm	Zn ppm		
1568/9	very pale grey and very transparent	2	3.51	3.47	0.77	381	31	2.3459	?
1570/3A	grey, opaque, a few small inclusions	2	4.20	3.26	1.05	216	47	2.3608	H
1570/3B	green-grey, less shiny, striated							~ 2.418	MI
1572/4	pale grey, smoky							2.3648	H or W
1574/4	see 1570/3A	2	4.21	3.20	1.01	217	59	2.3609	H

Chemical analysis identified Huruiki as the source of two pieces, 1570/3A and 1574/4. This is the first time that the archaeological use of this source has been confirmed. The trace element concentrations obtained for piece 1568/9 did not place it in any of the eight sources analysed. The zinc content was lower than that found for any of the natural source obsidians. Maraetai could be the source on the basis of the iron content but the manganese content was higher. The latter was nearest to the Arid Island and Taupo sources but the iron content was too low and the potassium content too high for these sources.

Density measurements confirmed the identifications made on the basis of elemental concentrations. The result for 1568/9 of 2.3459 g cm^{-3} was in accord with results obtained for Arid Island and Taupo obsidians. The two pieces not analysed chemically, 1570/3B and 1572/4, were identified as Mayor Island and either Whitianga or Huruiki respectively. Notes made on appearance, before measurements were carried out, indicated that the latter was not from the same source as 1570/3A and 1574/4. It must be borne in mind, however, that appearance cannot be used as the only means of identification.

The exact density of 1570/3B was not determined, but as it sank when the flotation liquid was at about $4^{\circ}C$ it was identified as a Mayor Island obsidian. In appearance it was similar to MT/M2, being green-grey, banded and less shiny than other Mayor Island obsidians. Its characteristic green colour in transmitted light distinguished the piece from Kaeo obsidians which have similar densities.

3. Motutapu Undefended Sites N 38/30 and N 38/37

Motutapu is an island adjacent to Rangitoto Island in the Hauraki Gulf. Thirteen pieces of obsidian from two nearby undefended settlements were submitted by Dr R.C. Green. The first site had yielded 78 pieces of obsidian[94], whilst excavation of the second had produced 132 pieces of obsidian[95]. Twenty-eight of the latter were identified by their greenish tinge as Mayor Island obsidians. All but one (743C) of the thirteen pieces were analysed chemically and five were studied by the flotation density method, 743A, 743B, 743C, 782C and 810. Table VII.4 summarizes the results.

Chemical analysis identified all but three pieces as Great Barrier Island obsidian. Two pieces, 743C and 782C, were identified by density measurements as Mayor Island obsidian as was expected from their green-yellow colour in transmitted light. Chemical analysis confirmed Mayor Island as the source of the latter. The thirteenth piece was found to be from the Whitianga source.

Two of the Great Barrier Island pieces, 782E and 810, had slightly higher manganese concentrations compared to the other eight pieces from the same source. The former also had a slightly higher iron concentration, whilst the latter had a higher zinc concentration. None of these results, however, were significantly different from those obtained for the natural source Great Barrier Island obsidians.

TABLE VII.4 - MOTUTAPU UNDEFENDED SITE OBSIDIANS

Sample	Appearance	No. of analyses	Chemical Analysis					Flotation Density/ ($g\ cm^{-3}$)	Identification
			Na %	K %	Fe %	Mn ppm	Zn ppm		
743C	green-yellow							2.3889	MI
782C	"	3	4.52	3.57	3.20	702	222	2.3959	MI
743A	grey, milky	2	3.78	2.93	1.02	447	42	2.3529	W
743B	pale purplish, grey, very clear	1	3.39	4.03	0.98	199	44	2.3504	GB
761	pale grey very clear striated	2	3.37	3.97	0.96	196	43		GB
773B	pale grey, very clear	1	3.39	4.03	0.98	196	40		GB
782F	"	2	3.48	3.98	0.97	199	40		GB
855B	"	2	3.41	3.90	0.96	198	44		GB
882	" smoky	2	3.33	3.93	0.95	207	44		GB
773A	grey, opaque a few small inclusions	2	3.36	3.88	0.96	195	42		GB
782A	"	2	3.26	3.92	0.97	196	41		GB
782E	grey, cloudy	2	3.27	3.87	1.02	212	43		GB
810	see 782A	1	3.41	4.03	0.98	213	48	2.3607	GB

4. Hamlins Hill

This is a non-volcanic hill just north of Westfield, Auckland[96] (Grid reference: N 42/352520). The total number of obsidian fragments found was fourteen[97]. Two pieces submitted by Dr R.C. Green were analysed. Both were analysed chemically and the identification of one was confirmed by density measurements. The results obtained for the two pieces are given in Table VII.5.

TABLE VII.5 - HAMLINS HILL OBSIDIANS

Sample	Appearance	No. of analyses	Chemical Analysis					Flotation Density/ ($g\ cm^{-3}$)	Identification
			Na %	K %	Fe %	Mn ppm	Zn ppm		
2751	pale grey, smoky	2	3.46	3.91	1.01	214	39		GB
2756	"	2	3.40	3.90	1.00	214	39	2.3547	GB

The obsidians were identical in appearance, which corresponded with that of the Motutapu piece 822. Likewise, they were also identified as Great Barrier Island obsidians. The similarity of trace element content could indicate that both were derived from one larger block of obsidian.

5. Lake Mangakaware

This was the site of a strongly fortified pa fifteen miles south of Hamilton (Grid reference: N 65/731293). Excavations in 1968[98] revealed only three pieces of obsidian which were all submitted for chemical analysis by Mr P. Bellwood.

The densities of two pieces, MAN A6 and MAN A, were measured by the hydrostatic weighing method, the latter was also measured by the flotation method. Results for the three samples are recorded below in Table VII.6.

TABLE VII.6 - LAKE MANGAKAWARE OBSIDIANS

Sample	Appearance	No. of analyses	Chemical Analysis					Density/(g cm^{-3})		Identification
			Na %	K %	Fe %	Mn ppm	Zn ppm	Flotation	Hydrostatic Weighing	
MAN A6	green	1	4.46	3.51		691	226		2.395	MI
MAN A6 (1)	green	1	4.39	3.67		686	220			MI
MAN A	purple-brown, very transparent	3	3.34	2.90	1.00*	351	41	2.3518	2.352	T (or A)

* one analysis only.

Two of the three pieces, MAN A6 and MAN A6(1) were identified as Mayor Island obsidians. Their chemical compositions were sufficiently similar for it to be possible that they were flaked from the same larger block of obsidian.

Identification of the third piece on the basis of appearance as Great Barrier Island obsidian would have been incorrect. Both methods of characterization showed that either Taupo or Arid Island was the source.

6. Otakanini

This was also a pa site excavated by Mr P. Bellwood[98] (Grid reference: N 37/924868). Twelve pieces of obsidian were found, five stratified and seven unstratified (designated by "US"). The site has been carbon-14 dated to A.D. 1561 ± 48[99].

Seven pieces weighed less than 0.5 g and therefore only one chemical analysis could be carried out on each. Only two pieces, OT68 US and OT US, were large enough for a solid sample to be available for density measurements. For the former the flotation method was used, and for the latter the hydrostatic weighing method was used. A summary of the results obtained for the twelve samples is presented below in Table VII.7.

TABLE VII.7 - OTAKANINI OBSIDIANS

Sample	Appearance	No. of analyses	Chemical Analysis					Density/(g cm^{-3})		Identification
			Na %	K %	Fe %	Mn ppm	Zn ppm	Flotation	Hydrostatic Weighing	
OT68 K104	grey	4	3.60	3.26	0.94**	318	49			?
K104	grey	2	3.20	3.88	0.94*	205	45			GB
K104/1	grey, banded, non shiny	1	2.63	13.2		392	92			
L104	green	1	4.43	3.38		668	219			MI
L104/1	grey	1	5.61	7.66		387	134			
OT68 US	very pale brown-grey, very transparent	2	3.31	4.00	0.94*	204	42	2.3527		GB
OT US	pale grey, very transparent	2	3.22	4.05	0.95*	201	43		2.343	GB
US(1)	green	1	4.47	3.46		663	219			MI
US(2)	dark grey	4	3.80	3.22	1.04**	218	45			H
US/1	dark grey, less transparent than OT US	1	3.17	3.17		228	42			H
US/2	dark grey	1	3.48	3.22		225	45			H
US/3	dark grey, surface non-shiny	1	2.35	4.20		204	38			GB

* One analysis only ** Average of two analyses

K104. Three samples (designated K104) were found in one trench. One piece (K104) was identified by chemical analysis as Great Barrier Island obsidian but identification of the other two pieces was not possible.

OT68 K104 was analysed on four different occasions. Reasonable agreement was obtained except for sodium, when the results were 3.41, 3.38, 3.80 and 3.82%. The two higher values were obtained when a natural gas-air flame was the excitation source for flame photometry. All sodium results in this set of analyses were higher than those obtained previously when a coal gas-air flame was used. The sample did not conform to any of the natural sources analysed formerly. The manganese concentration (318 ppm) agreed with that obtained for the Maraetai non-flake quality sample, as did the sodium and potassium concentrations. The iron concentration was significantly higher, however, 0.94% compared with 0.78%. Skipper's Ridge sample 386 was very similar and the two may be from the same source.

The results obtained for K104/1 are quite different from any others, The potassium value especially, suggested that the analysis was invalid because of contamination. Unfortunately all the sample was used for this analysis making identification impossible.

L104. Two samples were found in another trench. L104 was from the most common Mayor Island subsource but the other, L104/1, could not be identified because the one available analysis was not reliable. The percentages of sodium and potassium could result only from contamination or incorrect dilution. Zinc contamination would be very easy at the 0.5 ppm level, the concentration present in most analytical solutions. This was probably the cause of the unusually high zinc concentration as compared with the manganese concentration. The manganese concentration (387 ppm) was very

similar to that obtained for K104/1 (387 ppm) and the Skipper's Ridge sample 444. The results of Na, K and Zn for the Skipper's Ridge sample were not unusual, but as stated, the results of these elements for the two Otakanini samples were too unreliable for much reliability to be attributed to the manganese results. If the latter were accurate, however, then these two samples came from either an unknown source or an unanalysed subsource.

US. (Unstratified) Two specimens, OT68 US and OT US were identified chemically and by density measurements as Great Barrier Island obsidians. Both were very transparent and a brown cast was noted for OT68 US. Objective observation as to whether a piece of obsidian was pale grey or purple-brown in transmitted light was not possible. Observations made on different days were often not consistent.

US(1) was from the main Mayor Island subsource, and three pieces, US(2), US/1 and US/2 were identified as Huruiki obsidians. The sodium concentrations of the Huruiki samples were not consistent. The result for US/1 was low but the manganese and potassium concentrations were consistent with the Huruiki source. No pieces were available for density measurements but the dark grey colour of the powdered obsidian was as expected for this source.

Most evidence pointed to Great Barrier Island as the source of US/3 also. The concentrations of potassium, manganese and zinc agreed with other results for this source but the sodium concentration was somewhat lower than usual. This source does, however, have the lowest sodium content. One feature was quite in opposition to all other Great Barrier Island obsidians - the dark grey colour of the solid and the powder. All others examined were pale and transparent and when ground up produced an almost white powder. Remembering that appearance is far from consistent within a source and

assuming the other elemental results were accurate, the piece was identified as Great Barrier Island obsidian.

Results obtained for this archaeological site were the least satisfactory. All were analyses for the first time before the density method was proposed and those pieces weighing less than 0.5 g could be analysed only once. If this analysis was inconclusive identification was not possible.

7. Foxton Beach

The samples, supplied by Mr B.G. McFadgen, Anthropology Department, University of Otago, were from a Moa-hunter site which has been dated to about A.D. 1300[100]. Twelve pieces of obsidian, nine of them weighing less than 1 g, were submitted for identification. Time did not permit the detailed examination of three of the pieces. Pieces 2, 5 and 10 were examined by the flotation density method as well as by chemical analysis. The results are set out below in Table VII.8.

TABLE VII.8 - FOXTON BEACH OBSIDIANS

Sample	Appearance	No. of analyses	Chemical Analysis					Flotation Density/ ($g\ cm^{-3}$)	Identification
			Na %	K %	Fe %	Mn ppm	Zn ppm		
2	pale grey, very transparent	1	3.40	2.94	1.00	346	38	2.3527	T (or A)
5	pale grey, cloudy	1	3.47	2.94	1.02	354	39	2.3512	"
10	grey, transparent	2	3.47	2.89	1.01	348	38	2.3559	"
4	yellow-green	2	4.42	3.65	3.11	675	214		MI
7	grey-green, cloudy	1	4.44	3.59	3.11	695	227		"
9	grey-green, banded	2	4.46	3.68	3.12	672	219		"
11	yellow-green	1	4.47	3.64	3.06	657	211		"
8	green, less shiny	1	4.63	3.60	3.77	867	244		"
12	yellow-green	2	4.70	3.58	3.80	864	247		"

The chemical composition of pieces 2, 5 and 10 was almost identical and indicated either Taupo or Arid Island as the source. The densities agreed well with those obtained for the Taupo natural source obsidians. It is

noteworthy, however, that although the concentrations of Na, K, Fe, Mn and Zn in the three samples were almost identical their densities were significantly different - 2.3527, 2.3512 and 2.3559 g cm^{-3} respectively. Again the observation could be made that within a source density was less consistent than chemical composition.

The other six pieces were shown to be from Mayor Island. Four (4, 7, 9, 11) corresponded with the main subsource and two (8, 12) were from the second subsource. The latter were very similar chemically and could have been flaked from the same block of obsidian.

The three pieces (1, 3, 6) not analysed chemically were all green in transmitted light. As all obsidians examined during this investigation which were described as green proved to be from Mayor Island these three pieces can reasonably be identified as Mayor Island obsidians.

8. Tiwai Point

This is the location of the Comalco Aluminium Smelter and archaeological material was discovered during preliminary clearing of the site[101]. The point is the end of an eight mile long peninsula between Awarua Bay and Foveaux Strait and is directly opposite Bluff.

The thirty-two obsidian samples submitted by Mr G.S. Park, Otago Museum came from two areas about fifty metres apart. These are not all the obsidians collected but are only representative. Samples 1 to 26 came from area B, 27 to 31 from area X and sample 32 was found in a bulldozed road about one kilometre away.

Sodium, potassium, manganese and zinc were determined for all samples but only seventeen were analysed for iron. Except for samples 1, 3, 19, 22, 23 and 32, which weighed more than 2 g, the entire piece was ground up. Of these, the densities of 1, 19, 22 and 23 were determined by both methods and 32 was examined by the hydrostatic weighing method only.

All pieces were greenish in transmitted light except 29 and 32 which were pale grey. The results of both chemical analysis and density measurements (recorded in Table VII.9) indicated that all samples except the two grey ones were Mayor Island obsidians.

The elemental concentrations of No.s 29 and 32 agreed with both the Taupo and Arid Island sources. Although identification cannot be based on appearance, No.32 bore little resemblance to the Taupo natural source obsidians. It was banded and less transparent.

TABLE VII.9 - TIWAI POINT OBSIDIANS

Sample	No. of analyses	Chemical Analysis					Density/(g cm^{-3})		Identification
		Na %	K %	Fe* %	Mn ppm	Zn ppm	Flotation	Hydrostatic Weighing	
TW/B2/1	2	4.64	3.69	324	687	219	2.4018	2.405	MI
TW/B2/2	1	4.68	3.57		688	211			"
TW/B2/3	2	4.62	3.58	3.18	667	221			"
TW/B2/4	1	4.21	3.55		662	226			"
TW/B2/5	2	4.62	3.53	3.19	670	220			"
TW/B32/6	1	4.35	3.52		661	217			"
TW/B32/7	1	4.39	3.55		679	223			"
TW/B32/8	1	4.37	3.47		673	219			"
TW/B32/9	2	4.59	3.55	3.21	663	221			"
TW/B32/10	1	4.54	3.52		682	221			"
TW/B32/11	2	4.65	3.63	3.21	700	216			"
TW/B42/12	2	4.71	3.55	3.18	700	228			"
TW/B7/1b/13	2	4.50	3.56	3.19	668	217			"
TW/B14/1b/14	3	4.56	3.62	3.16	686	219			"
TW/B332/15	3	4.56	3.58	3.19	679	219			"
TW/B39/1d/16	1	4.28	3.50		666	228			"
TW/B42 2/17	2	4.38	3.54	3.18	693	222			"
TW/B49/1c/18	1	4.58	3.47		691	228			"
TW/B51/2/19	2	4.48	3.56	3.15	676	214	2.3979	2.402	"
TW/B51/2/20	1	4.65	3.60		715	225			"
TW/B57/1b/21	2	4.78	3.43	3.91	858	257			"
TW/B60/1c/22	2	4.59	3.60		720	234	2.3900	2.392	"
TW/B61/2/23	2	4.58	3.60	3.19	687	220	2.3878	2.394	"

Table continued over page.....

Table VII.9 continued .....

Sample	No. of analyses	Chemical Analysis					Density/(g cm^{-3})		Identification
		Na %	K %	Fe* %	Mn ppm	Zn ppm	Flotation	Hydrostatic Weighing	
TW/B84/2/24	1	4.37	3.60		675	220			MI
TW/B86/25	2	4.77	3.67	3.20	683	220			"
TW/B87/2/26	1	4.46	3.68		651	226			"
TW/XJ21/2/27	1	4.53	3.63		657	230			"
TW/XL21/2/28	1	4.46	3.42		682	239			"
TW/XM21/2/29	4	3.37	2.87	1.02	350	40			T (or A)
TW/XQ23/2/30	2	4.35	3.65	3.18	659	212			MI
TW/XQ29/2/31	1	4.65	3.55		639	219			"
TW/32	5	3.32	2.82	1.03	353	37		2.350	T (or A)

* Only 1 analysis for each sample.

Only one Mayor Island sample, No.21, appeared to be significantly different. The higher concentrations of iron, manganese and zinc indicated that this piece was from the second Mayor Island subsource. In agreement with this the sodium concentration was higher and the potassium concentration lower than in the remaining samples. Pieces 20 and 22 had slightly higher manganese and zinc contents but these were still within the ranges for the first and major Mayor Island subsource.

In all instances density results confirmed identification based on chemical analysis. As mentioned previously agreement between the two methods was not as good as that obtained for the natural source obsidians.

Until 1956, Mayor Island was the only source proven to have been used by the Polynesian inhabitants of New Zealand.

Not until 1961 was the Kaeo source documented and the Great Barrier Island and Huruiki sources were documented in 1965. The other sources were also confirmed less than ten years ago.

This investigation has shown that not all "grey" obsidian is from the same source. The presence of obsidian at the Foxton site, which has been dated to A.D. 1300 shows that obsidian trade took place early in the prehistory of New Zealand.

The archaeological usage of Huruiki obsidian was confirmed when this source was shown to be present at the Sunde site and the Otakanini site. No Kaeo or Maraetai obsidian was found archaeologically. If the former was known, examination of Northland sites should reveal its presence. Analysis of flake quality obsidian from Maraetai would need to be carried out before archaeological obsidian could be assigned to this site.

A total of 270 archaeological obsidians were examined. Only 20 were not unequivocally identified, and of these 20, six were from Taupo or Arid Island. Six others were Skipper's Ridge obsidians that could be identified almost unequivocally, three as Whitianga and three as Mayor Island.

Another (Sunde 1572/4) was examined only by density measurements, which did not distinguish between the Whitianga and Huruiki sources.

This left seven samples that could not be assigned to any source, three from Skipper's Ridge, one from Sunde, and three from Otakanini. Two

of the Skipper's Ridge samples and two of the Otakanini samples could possibly have been identified if more than one analysis could have been carried out on each.

CHAPTER VIII: SUMMARY AND SUGGESTIONS FOR FURTHER WORK

Using the analytical method developed it was possible to identify and separate the eight known sources of flake quality obsidian in New Zealand, with the possible exception of Taupo and Arid Island. Manganese was found to be the most useful element for identification.

If the Arid Island source was used archaeologically then it will be necessary to separate this source from the Taupo one. Depending on how representative was the Arid Island sample, it may be possible to state with more or less confidence whether an archaeological obsidian is from Arid Island or Taupo. If there is no significant difference in the concentrations of Na, K, Fe, Mn and Zn or in the densities, it would be necessary to determine other elements or other properties of obsidian.

It may be possible to analyse calcium, magnesium and aluminium by atomic absorption spectrophotometry if the hotter acetylene-nitrous oxide is used.

Emission spectroscopy could be used to analyse barium and zirconium, the elements found most useful for characterizing Mediterranean and Near East obsidians[5,6]. Some of the less common trace elements such as Sm, Sr, Sc, Rb and La could be analysed by emission spectroscopy and X-ray spectroscopy. These elements were used in neutron activation analysis of obsidian[2] and the strontium and rubidium contents of Californian obsidians were different even for flows within a source[26].

Fission-track analysis could possibly be used as a means of identifying different obsidian sources. If the uranium contents or the

ages of the Taupo and Arid Island sources are different the two sources could be separated by this method.

The analytical method developed went a long way towards eliminating the problem inherent in the emission spectrography - variation due to the method. A reliable indication of the natural variation of Na, K, Fe, Mn and Zn within each source was obtained. This was found to be less than the variation between sources and greater than the variation due to the method.

The usefulness of density measurements was found to be limited. No obsidian source had a distinctive density. Examination of natural source obsidians indicated that Mayor Island and Kaeo obsidians could be separated from the other sources. When the Skipper's Ridge samples were examined, however, the densities of three Mayor Island and three Whitianga obsidians overlapped.

Density was a much more variable property than chemical composition, which was not affected significantly by inclusions or banding. It was decided, therefore, that measuring the density of the non-flake quality Maraetai obsidian would not indicate the density of flake quality material from this source.

The hydrostatic weighing method was more useful, being more readily adaptable to the field, quicker, simpler and more accurate. Only for samples weighing less than 1.0 g was the temperature variation flotation method useful, and this method was the only way by which samples weighing less than 0.3 g could be examined.

The analytical method was applied successfully to the identification of archaeological obsidian. Of the 270 samples analysed only seven could not be assigned to a natural source. The existence of these seven samples

suggests either unknown sources or unknown subsources. These are likely, especially in the Coromandel area, and a survey of the area to determine whether other sources exist would be valuable. To complete the chemical study of natural sources flake quality Maraetai obsidian needs to be analysed, as does obsidian from Fanal Island.

The Mayor Island samples were not documented precisely enough for the nature of the subsources to be defined. They do not appear to correspond to geographical areas. A detailed study of Mayor Island obsidian could be worthwhile. Obsidians from the three areas known to yield high quality flake obsidian[43] were analysed but no way was found to distinguish them.

The archaeological usage of Huruiki obsidian was confirmed but no Kaeo obsidian was found at any of the eight sites. Examination of obsidians from archaeological sites in Northland would indicate whether this source was used.

Most archaeological obsidians would be identified by application of the analytical method. To attain unequivocal identification of all samples, however, the Taupo and Arid Island sources would need to be separated and the origins of the unidentified samples would need to be found.

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