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Obsidian Sourcing by PIXE Analysis at AURA2

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ABSTRACT

The technique of Proton Induced X-ray Emission is a suitable method for the elemental analysis of obsidian samples and artefacts. By comparing the elemental composition of obsidian artefacts with those of known sources of obsidian and identifying similarities, the likely origin of the sample can be discovered and information about resource procurement gained. A PIXE facility has now been established at the Auckland University Research Accelerator laboratory, AURA2. It offers a rapid, multi-element, non-destructive method of characterisation of obsidian samples ranging from small chips to large pieces. In an extensive survey of Mayor Island obsidian, a discrimination has been made between the different locations of obsidian deposits on the island. In addition, using the database developed at AURA2, artefacts from the site of Opita, Hauraki Plains, have been sourced.

Keywords: PIXE, OBSIDIAN, AURA2, SOURCING, ELEMENTAL ANALYSIS, MAYOR ISLAND, PCA, OPITA.

INTRODUCTION

Many techniques have been employed to study the elemental composition of obsidian originating from different geographical sources, with the underlying intention of provenancing obsidian artefacts. Most of the simpler and cheaper characterisation methods have lacked sufficient accuracy in that some sources could be easily distinguished while others could not. Other methods required destruction of the sample and were usually prohibitively expensive for routine sourcing of artefactual samples.

One early method involved measurement of the optical refractive index (Green 1962), but this did not distinguish the sources sufficiently. Another non-destructive method was that of density determination by flotation (Reeves and Armitage 1973), but it was shown to be of limited use in New Zealand. Emission spectroscopy (Green *et al.* 1967), atomic absorption spectroscopy (Armitage *et al.* 1972) and neutron activation analysis (Gordus *et al.* 1971) were more successful in their ability to distinguish between sources, but required destruction of the sample. In New Zealand the most frequently used method has been X-ray fluorescence analysis (XRF) (Ward 1974a, 1974b, 1974c), but this generally involves trade-offs between destruction of the sample and accuracy of analysis (cf. Bollong 1983; Seelenfreund and Bollong 1990).

The visual sourcing of obsidian using the physical characteristics (Moore 1988) of colour, lustre, fracture, translucency and flow banding has proved to be very useful for some sources. This technique requires familiarity with the various physical characteristics of obsidian and access to adequate reference materials from known source deposits. It is particularly difficult to identify the source of very small flakes in this way since the procedure relies on the presence of distinguishing characteristics and not on their absence.

The ideal method of elemental analysis would be one that is not destructive or damaging. It would require the minimum of sample preparation, be applicable to samples of a variety of sizes and shapes, capable of determining elemental concentrations for a wide range of elements, sufficiently precise in the results produced, and able to distinguish between different source deposits. It would be reasonable in its cost and availability and, finally, because of the large number of obsidian artefacts available for study, it would also be fast in analysis.

Elemental analysis by proton induced x-ray emission (PIXE) satisfies all these requirements. The technique uses a beam of protons to eject inner-shell electrons from atoms in the target material, and does no damage to the sample. When outer-shell electrons fill these resulting vacancies in the inner-shell, characteristic x-rays are emitted. These x-rays have energies which identify the particular atom in the material, and it is therefore possible to calculate the elemental concentrations in the material by detecting and counting these characteristic x-rays. Previously, the nearest available facility performing PIXE analysis on obsidian was at Lucas Heights in Australia, but now such a facility has been established in New Zealand at the Auckland University Research Accelerator laboratory AURA2, and this should reduce the cost and improve availability for New Zealand based users.

This paper presents information on the development of the AURA2 PIXE database of New Zealand obsidian sources, along with results obtained by application of PIXE to samples from an archaeological site in the Hauraki Plains, approximately 70 km southeast of Auckland. Samples weighing from 0.15 g to 247.07 g and of a variety of shapes have been analysed, and a discrimination has been made among samples originating from Mayor Island. These results demonstrate the advantages of obsidian characterisation with elemental analysis by PIXE.

DESCRIPTION OF THE SYSTEM

A 2.5 MeV proton beam from the AURA2 Van de Graaff accelerator is used to irradiate the obsidian samples which are positioned in the target chamber as shown in Figure 1. The samples are first loaded on to a target holder outside the chamber. They are washed with AR-Methanol to remove any minor surface contaminations and each is inspected to find the best surface to be irradiated, ideally the least conchoidally fractured surface without any irregularities such as spherulites. They are then positioned behind face plates made of tantalum on the target holder and held by a clamping screw at the rear of the sample. The target holder is about 1 m in length and normally holds 27 targets at a time, of maximum dimensions 27 mm x 40 mm x 30 mm and with a minimum diameter of 15 mm. However, accommodations can be made to mount smaller diameter pieces (to a minimum of approximately 3 mm in diameter), larger ones (of the order of 120 mm in diameter) and irregularly shaped ones. The holder is then placed inside the arm of the target chamber perpendicular to the beam direction, and engages on a stepping motor, which allows the user to control the position of the targets while the chamber is under vacuum.
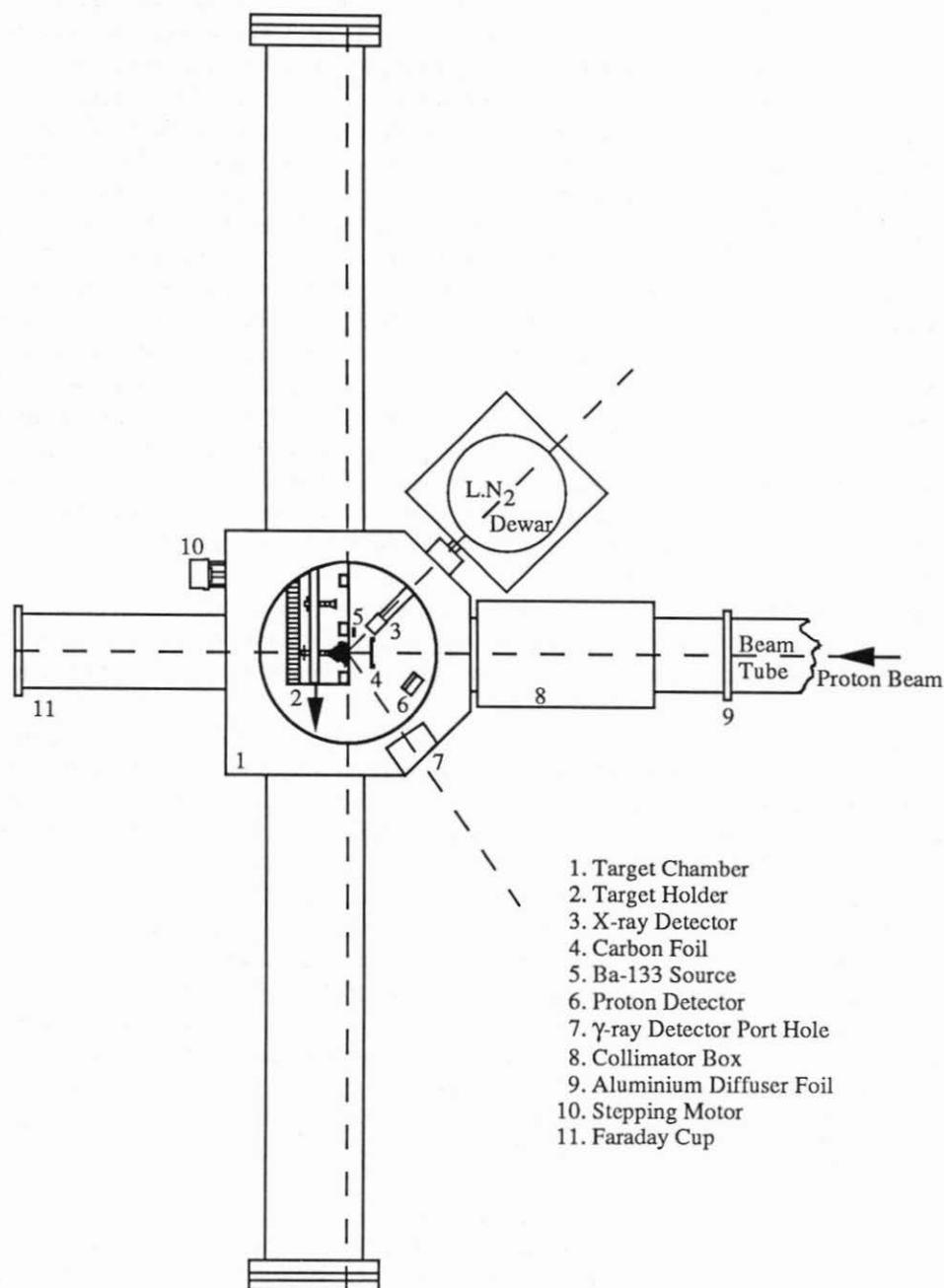
Figure 1: Schematic layout of the PIXE/PIGME target chamber at AURA2 (as viewed from above).

The proton beam enters the target chamber first through a thin aluminium diffuser foil, which gives the beam an even intensity across its cross-section, and then through a collimator which defines the size of the beam to be about 3 mm in diameter and the intensity to be a few tens of nanoamps (corresponding to about 1011 incident protons per second). It then passes through a thin carbon foil 25 mm in front of the target, which monitors the number of protons incident on the target by detecting those which are backscattered into a small silicon detector. The carbon foil also eliminates charging up of the obsidian. The beam then strikes the target at an angle of 90 degrees to its face (unless a different angle has been chosen). The x-rays emitted from the target are detected with a lithium-drifted silicon detector Si(Li) at 135 degrees to the incoming beam and about 58 mm from the target. The x-ray spectra associated with each sample are acquired using Camac modules in conjunction with a Macintosh IIcx computer and locally written acquisition software. Each spectrum is stored as a 1024 channel histogram, and the associated parameters that are needed for the analysis are recorded. This information is then analysed using a computer program which first extracts individual spectrum peak areas and then converts these to elemental concentrations. The program was originally the PIXAN PC analysis package (Clayton 1986), but we have subsequently redeveloped it to suit the needs of the AURA2 facility and to eradicate its various 'bugs' and it now runs on the Mac IIcx. A typical analysis time is 100 seconds for an obsidian spectrum with 15 elemental concentrations being calculated.

The elements which are of particular interest in obsidian characterisation are K, Ca, Ti, Mn, Fe, Rb, Sr, Y and Zr, whose K x-rays range in energy from 3.31keV to 15.74keV. A typical x-ray spectrum obtained from obsidian is shown in Figure 2. It was accumulated in ten minutes.

After the elemental concentrations have been calculated, statistical and graphical techniques are used to recognise patterns within the data set so that source identification can be made. Principal components provide useful source discrimination which can be readily presented in plots of the major principal components. Although our results for the elemental concentrations of New Zealand sources of obsidian lie in or near the ranges stated in the Lucas Heights obsidian composition catalogue (Duerden et al. 1987), we prefer to use the eight elemental ratios K/Fe, Ca/Fe, Ti/Fe, Mn/Fe, Rb/Fe, Sr/Fe, Y/Fe and Zr/Fe as the data set. This reduces the effects of uncertainties in the angle of the target face, of the distance from the target to detector (which arise from the irregular shapes of some samples), and of the varying pulse rate through the electronic system, each of which is common to the calculation of each elemental concentration. For each batch of samples that is analysed, we also include a piece of obsidian from Wekwok, Lou Island, Papua New Guinea. This is used as a standard for obsidian and is analysed at least once during each of the batches. A check of its composition consistency between batches allows the equipment performance to be monitored.

Because of the general homogeneity of obsidian and the fact that the samples are irradiated with a beam spot of at least 3 mm diameter, one measurement on each sample is thought sufficient. This is actually desirable if PIXE's speed in analysis is to be fully utilised. However, if anomalous results are obtained then further measurements are made on different parts of the sample surface. Samples with a weathered surface or severe contamination (which cannot be removed by gentle washing with AR-Methanol) give variable results and sometimes no conclusion can be made about the source of the artefact until more thorough cleaning is performed.
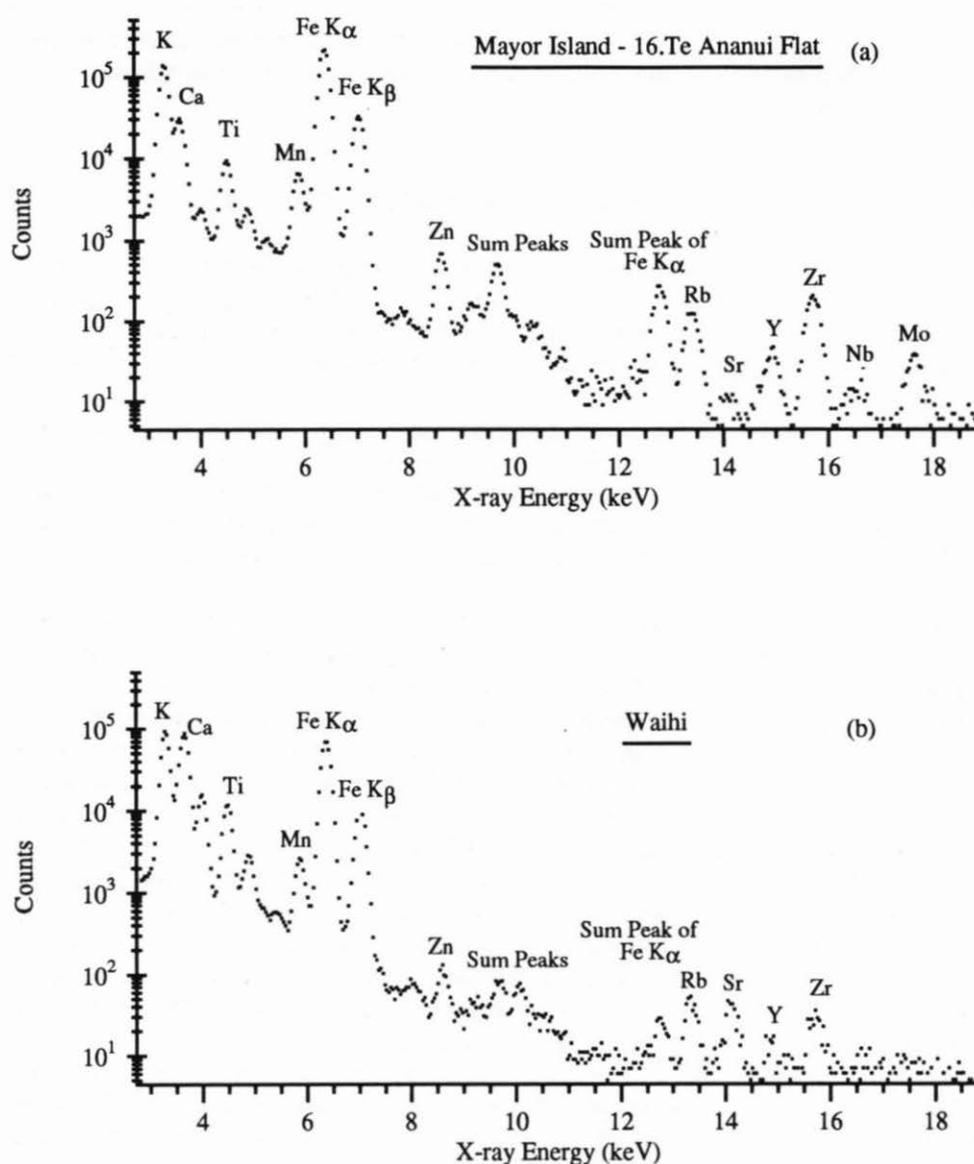
Figure 2: PIXE spectra of two pieces of obsidian. a, Mayor Island; b, Waihi.

We have found PIXE sufficient for the characterisation of obsidian sources, but the technique of proton induced gamma-ray emission or PIGME will be simultaneously employed at AURA2 in the future so that information on F, Na and Al, which is not accessible by PIXE, can be obtained. Sodium and aluminium are major constituents of obsidian. Fluorine is a trace element and has been shown to vary between sources (Bird *et al.* 1978; Duerden *et al.* 1987). With the PIXE set-up already available, the extra effort required to perform gamma-ray measurements is rather small.

At present the AURA2 PIXE facility is manually controlled, but automation of the target transport and data collection and storage system is underway so that the elemental analysis will be able to proceed basically unattended, which should increase the sample throughput rate of the system.

RESULTS OF ANALYSIS OF NEW ZEALAND OBSIDIAN SOURCES

To be able to say an artefact was from a particular source we first needed to analyse obsidian from the known sources in New Zealand (see Fig. 3 and Appendix 1) to build up a database of their elemental compositions. Particular attention was paid to obtaining broad coverage of the Mayor Island source in an effort to discriminate between subsources on the island.

The samples from the various sources which were used in the construction of the database were obtained from the reference collection of the Anthropology Department, University of Auckland, from the collection of the University of Otago, or collected from the actual sources by one of the authors. Unfortunately, samples from some sources were not available for PIXE analysis, but at least three samples from each of the more important major sources were generally obtained.

For each batch of samples analysed, a piece of obsidian from a block which had been retrieved by Ambrose from Wekwok, Lou Island, Papua New Guinea, was also included in the analysis. It has the virtue of being fairly homogeneous to look at and is by inference chemically homogeneous. The obsidian is referred to as Wekwok #2000. It has often been used as a standard in obsidian analysis and has been analysed by a variety of techniques, namely PIXE, XRF and EMP. The results obtained by these different methods are internally fairly consistent; however, on the whole there is a larger variation for some of the element concentrations, which could raise the question of compatibility between the methods. The results for Wekwok #2000 obtained in this work are in agreement with the ranges stated in the Lucas Heights obsidian composition catalogue (Duerden *et al.* 1987), with the absolute concentrations quoted at approximately ±20% and the concentrations relative to Fe at ± 10%. However, it is only the eight elemental ratios to Fe that are of interest in this work. It is this data set as a whole which is used in the investigation of source identification, as it is a definitive 'finger print' of the sample being analysed.

The results given in Table 1 are in terms of parts per million (mg/kg) and are the mean values for each source. Standard errors for the elements K to Fe are around the 5% level. The elements Rb to Zr are trace elements, depending on the source, and have larger standard errors due to poorer statistics. A large standard error can also be an indication of the chemical variability within the particular source, Burgess Island being one example. There is a greater variability than can be accounted for by poor statistics in the results for the major elements Ca, Ti and Fe.

The Mayor Island obsidian deposit has long been regarded as important in the study of prehistoric New Zealand as it is a major source of artefactual obsidians found in New Zealand archaeological sites. In an extensive survey of the island, 16 distinct locations were sampled, as shown in Figure 4, to see if individual deposits could be distinguished. A minimum of four samples were collected at each location. The results obtained are given in the first half of Table 1. By looking at these results in terms of the elemental concentrations in ppm, it is not immediately apparent that one could discriminate between the different source locations on the island. If, however, a comparison of the sources is

1. Weta
2. Waiare
3. Pungaere
4. Huruiki
5. Burgess Island
6. Fanal Island
7. Awana
8. Te Ahumata
9. Cooks Bay
10. Purangi
11. Hahei
12. Tairua
13. Whangamata
14. Maratoto
15. Waihi
16. Mayor Island
17. Maketu
18. Lake Tarawera
19. Lake Rotoiti
20. Lake Rotokawau
21. Lake Okataina
22. Ngongotaha
23. Whakarewarewa
24. Hemo Gorge
25. Maraetai
26. Whakamaru
27. Ongaroto
28. Ben Lomond
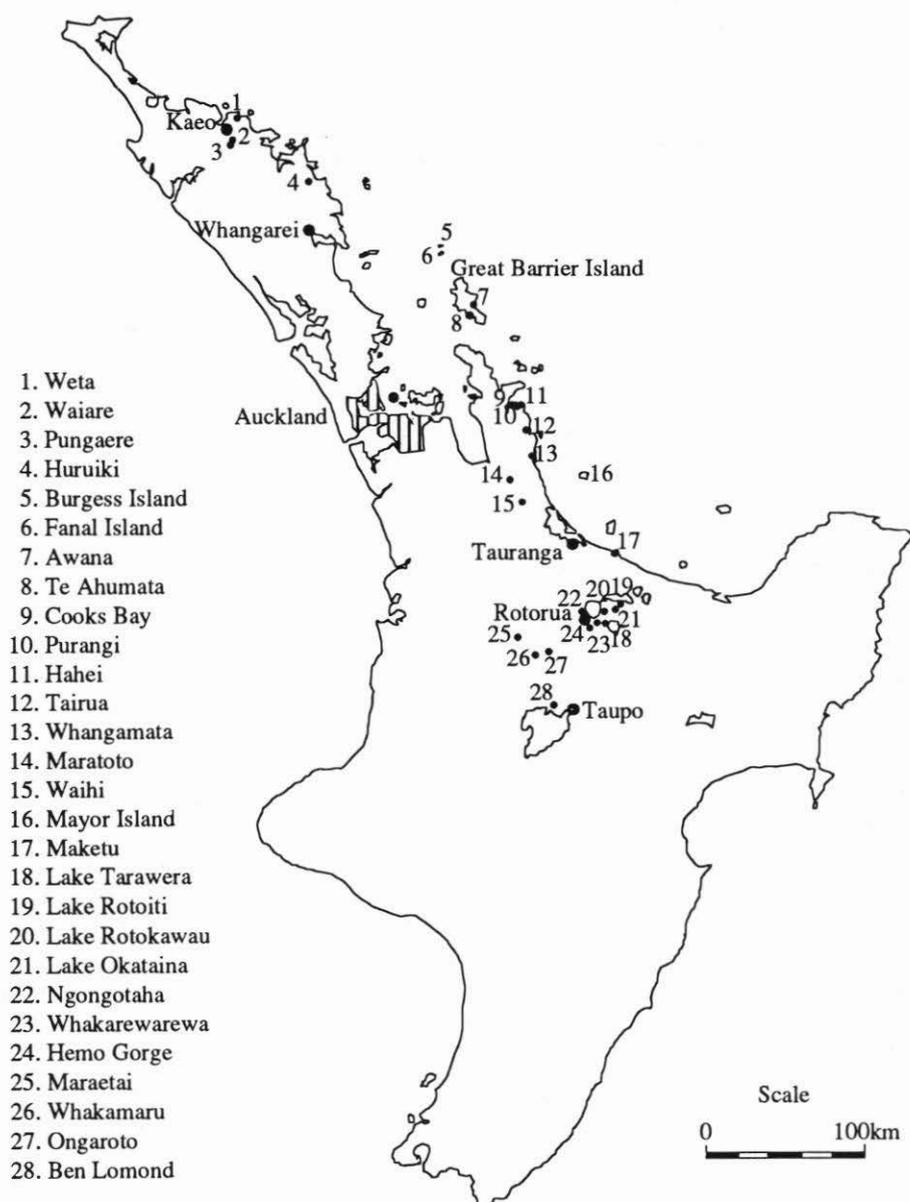
Figure 3: North Island obsidian sources.

made by considering their elemental ratios to iron, as seen in Table 2, it is initially possible to separate the Mayor Island source into two groups which approximately correspond to the western and eastern sides of the island. This distinction is made even more obvious (as seen in the following), when the statistical technique of principal components analysis is applied to the data set of elemental ratios. This technique reduces the original eight-dimensional data

set into principal components which can be plotted in a two- or three-dimensional display, but which still retain most of the information contained in the original data.

TABLE 1

THE AVERAGE ELEMENTAL CONCENTRATIONS (IN PPM) AND STANDARD ERRORS FOR OBSIDIAN SOURCES WHICH HAVE BEEN ANALYSED AT AURA2

(sample sizes in brackets)

Source	K	Ca	Ti	Mn	Fe	Rb	Sr	Y	Zr
Lou Island, PNG									
Wekwok	39900	8300	2000	560	17900	160	80	30	380
(1)	±2%	±2%	±2%	±2%	± 2%	±2%	± 3%	±9%	±2%
Mayor Island Group (1)									
1 Taumou Beach	42100	1200	1400	890	39000	130	20	150	1300
(4)	±2%	±4%	±3%	±10%	±7%	±12%	±42%	±8%	±1%
2 Taumou Beach	45500	1500	1500	940	40500	150	20	150	1420
(4)	±5%	±10%	± 5%	±6%	± 5%	±6%	± 20%	±7%	±4%
3 Taumou Pa	45000	1600	1500	870	38900	140	<10	160	1350
(4)	±4%	±10%	± 3%	±3%	± 2%	±6%	± 44%	±4%	±1%
4 Staircase	43700	1300	1400	820	36500	130	10	140	1290
'Quarry' (4)	±4%	±3%	±4%	±11%	±1%	±5%	± 18%	±7%	±3%
6 Oira Bay N	44700	1300	1500	890	37800	130	10	160	1330
(4)	±4%	±2%	±3%	±2%	± 1%	±9%	± 15%	±7%	±5%
11 Staircase	46300	1500	1600	930	40000	130	20	160	1360
'Honey' (4)	±4%	±4%	±3%	±3%	± 3%	±9%	± 40%	±6%	±2%
Mayor Island Group (2)									
5 Oira Bay S	38100	1200	1300	1100	46900	140	10	150	1540
(4)	±7%	±8%	±4%	±5%	± 4%	±8%	± 29%	±21%	±5%
7 Raumata Pt	43200	1300	1400	1100	46200	110	10	170	1490
(4)	±4%	±4%	±3%	±3%	± 2%	±4%	± 69%	±9%	±3%
8 Otiora Bay	44100	1400	1400	1100	47100	130	20	190	1570
NW (4)	±4%	±3%	±4%	±5%	± 5%	±13%	±16%	±8%	±6%
9 Otiora Bay	39900	1300	1300	1000	43500	130	10	150	1390
SE (4)	± 2%	±4%	±2%	±3%	± 2%	±13%	±14%	±5%	±2%
15 Opuhi Spring	44400	1400	1400	1200	49800	150	30	180	1600
(4)	±2%	±4%	±3%	±3%	± 2%	±10%	±15%	±4%	±2%
16 Te Ananui	45200	1400	1400	1200	49800	150	20	170	1600
Flat (4)	± 3%	±3%	±4%	±3%	± 4%	±6%	± 33%	±9%	±4%
Mayor Island Group (3)									
13 Opo Bay	44900	1500	1600	1000	41700	130	10	160	1350
(4)	±3%	±4%	±3%	±3%	± 2%	±4%	± 9%	±4%	±2%
14 Te Matawhero	44300	1400	1600	970	41500	130	10	150	1330
Pt (4)	±2%	±5%	±3%	±2%	± 2%	±11%	±46%	±7%	±3%
Mayor Island Group (4)									
10 Halls Pass	43200	1600	1500	1300	51600	120	30	160	1390
(4)	±4%	±3%	±2%	±2%	±2%	±8%	± 17%	±5%	±1%
12 Te Paritu	41300	2300	1400	1300	48400	120	30	160	1340
(4)	±3%	±19%	± 4%	±6%	±2%	±7%	± 6%	±4%	±3%

TABLE 1 Continued

Northland

Waiare	40100	810	850	690	36900	700	<10	230	2460
(4)	±3%	±4%	±2%	±2%	±1%	±1%	± 38%	±2%	±1%
Pungaere	44100	930	950	740	40600	750	<10	280	2550
(5)	±2%	±3%	±1%	±1%	±2%	±3%	± 40%	±1%	±2%
Huruiki	38600	5500	620	230	10500	140	30	30	160
(4)	±2%	±2%	±1%	±1%	±1%	±5%	± 10%	±14%	±8%

Great Barrier

Fanal Island	47800	6600	1200	180	10400	240	70	30	170
(7)	±5%	±4%	±3%	±2%	±2%	±2%	± 11%	±13%	±5%
Burgess Island	52700	5900	1500	440	26700	150	40	80	570
(3)	±3%	±8%	±13%	± 7%	±5%	±7%	± 24%	±17%	±8%
Te Ahumata	48300	5100	690	220	10700	240	30	20	130
(6)	±2%	±3%	±3%	±3%	±2%	±2%	± 14%	±18%	±6%
Awana	46900	5100	680	330	11700	210	30	60	190
(4)	±1%	±1%	±4%	±8%	±4%	±4%	± 7%	±22%	±4%

Coromandel

Cooks Bay	33300	6800	860	480	10800	140	70	30	130
(4)	±3%	±7%	±3%	±2%	±2%	±1%	± 4%	±7%	±4%
Purangi	34400	6700	900	500	11700	140	60	30	150
(4)	±3%	±3%	±3%	±2%	±1%	±5%	± 11%	±19%	±17%
Hahei	33200	7100	660	460	12200	150	90	20	160
(2)	±5%	±5%	±5%	±4%	±4%	±2%	± 8%	±40%	±16%
Tairua	31300	10500	1400	410	12600	120	120	30	180
(4)	±2%	±2%	±2%	±1%	±1%	±3%	± 3%	±21%	±2%
Onemana/	37200	5300	730	350	10700	150	40	50	180
Whangamata (4)	±4%	±3%	±3%	±3%	±2%	±3%	± 10%	±9%	±19%
Waihi	29400	17000	1900	450	16300	140	170	<10	130
(6)	±3%	±3%	±2%	±2%	±2%	±4%	± 2%	±25%	±4%
Maratoto	44200	4300	550	340	7400	210	30	10	70
(1)	±6%	±6%	±6%	±7%	±5%	±4%	± 19%	±43%	±4%

Central North Island

Rotorua	32500	7500	1000	450	9900	140	90	20	150
(10)	±3%	±5%	±6%	±6%	±3%	±4%	± 9%	±15%	±10%
Taupo	34200	8500	1300	400	11400	140	90	20	170
(10)	±2%	±2%	±1%	±2%	±1%	±2%	± 3%	±19%	±4%
Mangakino	38300	6700	950	360	9200	150	90	<10	90
(3)	±2%	±8%	±8%	±4%	±3%	±1%	± 3%	±60%	±6%
Maraetai	37300	7000	1000	390	9200	160	90	10	130
(5)	±4%	±3%	±3%	±7%	±3%	±3%	± 8%	±55%	±12%
Ongaroto	41300	8500	1200	400	10200	160	100	10	150
(2)	±1%	±4%	±2%	±2%	±1%	±4%	± 10%	±42%	±13%

TABLE 2

THE AVERAGE ELEMENTAL RATIOS WITH RESPECT TO IRON AND STANDARD ERRORS USED IN OBSIDIAN CHARACTERISATION

(sample sizes in brackets)

Source	K/Fe	Ca/Fe	Ti/Fe	Mn/Fe	Rb/Fe	Sr/Fe	Y/Fe	Zr/Fe
Lou Island, PNG								
Wekwok	2.23	.467	.113	.031	.009	.0043	.0019	.021
(1)	±0.3%	±0.3%	±0.3%	±0.4%	±1%	± 2%	±8%	±1%
Mayor Island Group (1)								
1. Taumou Beach	1.17	.033	.038	.022	.004	.0005	.0039	.036
(4)	±1%	± 1%	± 1%	± 0.1%	±8%	± 38%	± 3%	±4%
2. Taumou Beach	1.12	.035	.038	.023	.004	.0005	.0038	.035
(4)	±1%	± 1%	± 0.3%	±2%	± 5%	± 23%	± 3%	±1%
3. Taumou Pa	1.16	.040	.038	.022	.004	.0002	.0040	.035
(4)	±2%	± 9%	± 1%	± 1%	± 8%	± 42%	± 3%	±1%
4. Staircase	1.15	.036	.038	.023	.003	.0003	.0037	.034
'Quarry' (4)	± 1%	± 6%	± 1%	± 1%	± 5%	± 17%	± 4%	±1%
6. Oira Bay N.	1.14	.033	.037	.024	.003	.0003	.0040	.034
(4)	±1%	± 3%	± 1%	± 1%	± 7%	± 16%	± 3%	±2%
11. Staircase	1.16	.036	.040	.023	.003	.0004	.0039	.034
'Honey' (4)	±1%	± 1%	± 1%	± 1%	± 6%	± 38%	± 9%	±1%
Mayor Island Group (2)								
5. Oira Bay S.	.87	.030	.029	.025	.003	.0003	.0032	.033
(4)	±1%	±6%	± 3%	± 7%	± 12%	±26%	± 15%	± 1%
7. Raumata Pt.	.94	.029	.029	.024	.002	.0002	.0036	.032
(4)	±2%	±2%	± 1%	± 0.5%	±3%	± 65%	± 7%	±2%
8. Otiora Bay	.94	.029	.030	.024	.003	.0004	.0039	.032
N.W. (4)	± 2%	±2%	± 1%	± 1%	± 9%	± 11%	± 4%	±2%
9. Otiora Bay	.92	.030	.029	.024	.003	.0003	.0035	.032
S.E. (4)	±1%	±5%	± 1%	± 1%	± 10%	±9%	±7%	±1%
15. Opuhi Spring	.92	.028	.029	.024	.003	.0005	.0036	.032
(4)	±2%	±2%	± 1%	± 1%	± 8%	± 13%	± 6%	±1%
16. Te Ananui	.91	.028	.029	.024	.003	.0004	.0035	.032
Flat (4)	±1%	±1%	± 1%	± 1%	± 3%	± 31%	± 6%	±2%
Mayor Island Group (3)								
13. Opo Bay	1.08	.035	.039	.024	.003	.0003	.0038	.032
(4)	±1%	±2%	± 1%	± 2%	± 4%	± 11%	± 5%	±1%
14. Te Matawhero	1.07	.035	.039	.024	.003	.0003	.0037	.032
Pt. (4)	± 1%	±3%	± 1%	± 1%	± 9%	± 43%	± 7%	±2%
Mayor Island Group (4)								
10. Halls Pass	.84	.031	.029	.025	.002	.0006	.0031	.027
(4)	±3%	±1%	± 1%	± 0.4%	±8%	± 19%	± 4%	±3%
12. Te Paritu	.85	.047	.029	.026	.003	.0007	.0034	.028
(4)	±1%	±18%	±2%	± 6%	± 4%	± 14%	± 5%	±3%
Northland								
Waiare	1.09	.022	.023	.019	.019	.0002	.0064	.067
(4)	±2%	±3%	± 1%	± 1%	± 2%	± 40%	± 4%	±1%
Pungaere	1.09	.023	.024	.018	.018	.0001	.0068	.063
(5)	±2%	±2%	± 1%	± 1%	± 2%	± 42%	± 3%	±1%
Huruiki	3.66	.524	.059	.022	.013	.0027	.0026	.015
(4)	±1%	±1%	± 1%	± 1%	± 4%	± 10%	± 14%	± 9%
Great Barrier								
Fanal Island	4.41	.637	.117	.017	.023	.0056	.0029	.017
(7)	±2%	±3%	± 1%	± 1%	± 2%	± 1%	±14%	± 6%

TABLE 2 Continued

Burgess Island	1.98	.223	.058	.017	.006	.0017	.0030	.021
(3)	±3%	±7%	± 14%	±7%	± 5%	± 28%	± 14%	± 10%
Te Ahumata	4.54	.476	.065	.021	.022	.0027	.0021	.013
(6)	±2%	±1%	± 1%	± 1%	± 3%	± 14%	± 19%	± 6%
Awana	4.01	.438	.058	.028	.018	.0024	.0054	.015
(4)	±3%	±3%	± 2%	± 7%	± 6%	± 7%	±22%	± 5%
Coromandel								
Cooks Bay	3.07	.627	.079	.044	.013	.0065	.0026	.012
(4)	±2%	±6%	± 2%	± 0.3%	±1%	± 4%	±8%	±5%
Purangi	2.94	.569	.077	.043	.012	.0049	.0022	.012
(4)	±2%	±2%	± 2%	± 1%	± 7%	± 11%	± 19%	± 4%
Hahei	2.73	.582	.054	.037	.012	.0071	.0012	.013
(2)	±1%	±2%	± 1%	± 0.4%	±2%	± 8%	±37%	± 12%
Tairua	2.48	.832	.108	.032	.009	.0092	.0022	.014
(4)	±1%	±1%	± 1%	± 1%	± 3%	± 3%	±22%	± 2%
Onemana/	3.49	.496	.068	.033	.014	.0037	.0041	.016
Whangamata (4)	±4%	±1%	± 1%	± 1%	± 3%	± 9%	±9%	±18%
Waihi	1.85	1.068	.114	.028	.008	.0102	.0005	.008
(6)	±2%	±2%	± 1%	± 1%	± 5%	± 3%	±29%	± 5%
Maratoto	5.96	.585	.074	.045	.028	.0035	.0020	.010
(1)	±2%	±2%	± 2%	± 2%	± 0.5%	±20%	± 40%	± 8%
Central North Island								
Rotorua	3.33	.766	.106	.046	.014	.0096	.0021	.015
(10)	±4%	±5%	± 6%	± 6%	± 3%	± 10%	± 14%	± 6%
Taupo	2.99	.743	.113	.035	.012	.0081	.0018	.015
(10)	±1%	±1%	± 1%	± 1%	± 2%	± 2%	±21%	± 4%
Mangakino	4.16	.723	.103	.039	.017	.0094	.0005	.010
(3)	±1%	±5%	± 5%	± 1%	± 4%	± 7%	±62%	± 5%
Maraetai	4.05	.757	.111	.042	.017	.0092	.0012	.014
(5)	±4%	±2%	± 1%	± 8%	± 2%	± 8%	±54%	± 11%
Ongaroto	4.03	.828	.115	.039	.016	.0098	.0011	.015
(2)	±1%	±3%	± 1%	± 1%	± 3%	± 9%	±22%	± 14%

When the Mayor Island results are included with the North Island obsidian results and a principal component analysis performed, the splitting of the Mayor Island source group is readily observed, as seen in Figure 5a, along with the distinct clustering of the other source groups. However, if a principal component analysis is performed on the Mayor Island results by themselves, it is observed that the source in fact separates out into four distinct groups, as shown in Figure 5b. There are two smaller groups which are composed of only two sample locations each, in close proximity to one another (Fig. 4). One of the groups (3) contains the Opo Bay (13) and Te Matawhero Pt. (14) locations at the southern point of the island, and the other group (4), comprises Halls Pass (10) and Te Paritu (12), which are located on the crater rim on the eastern side of the island. The other two groups are composed of six sample locations each. The first (1) contains the five locations on the eastern side, Taumou Beach (1 and 2), Taumou Pa (3), Staircase 'Quarry' (4), and Staircase 'Honey' (11), together with Oira Bay North (6), which is on the western side. The other group (2) contains two sample locations from the northern part of the island, Opuhi Spring (15) and Te Ananui Flat (16), and the remaining four locations on the western point, Oira Bay South (5), Raumata Pt. (7), Otiora Bay NW (8) and Otiora Bay SE (9). The grouping of Oira Bay North with the eastern locations in group (1) is somewhat unexpected and additional sampling in this region will probably be required to explore this characteristic further. It is likely that further research will show that elemental variation in obsidian on the island correlates with the age of lava flows.
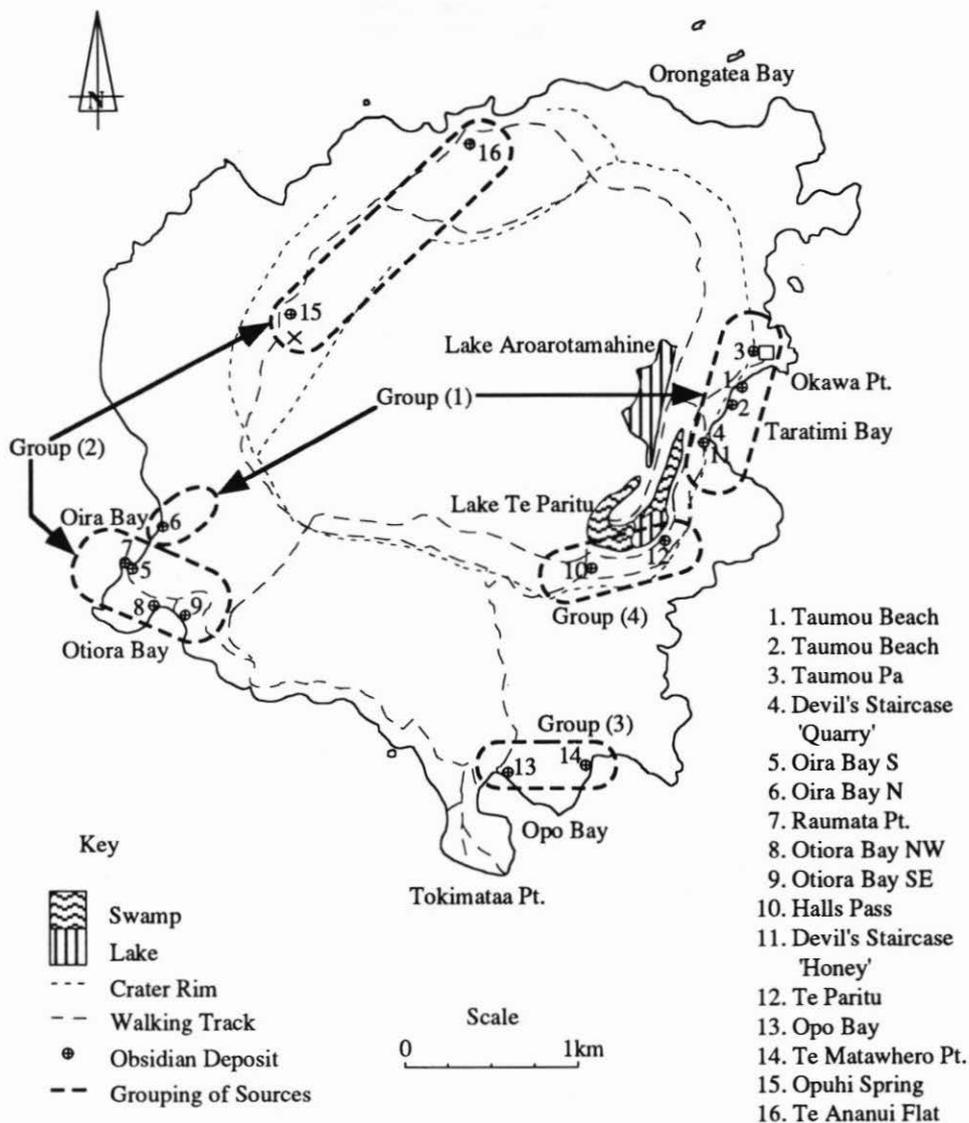
Figure 4: Locations of Mayor Island obsidian samples.

In Figure 5a, the clustering of the source groups is easily seen, but this two-dimensional representation is rather a poor substitute for a real three-dimensional plot, in which the clustering is far more apparent than is indicated here. The ability to animate the three-dimensional plot, by rotating the axes around in real time (which can be performed in a Macintosh software application such as Data Desk by Data Description Inc.), allows the clustering to be viewed from any perspective, and makes the source distinction very striking. Most of the source groups occupy a small region in this three-dimensional principal

(a)

1. ✿ Pungaere/Waiare
2. ✳ Huruiki
3. ■ Fanal Island
4. ○ Burgess Island
5. + Te Ahumata
6. ✳ Awana
7. ◆ Cooks Bay
8. ▲ Purangi
9. ✳ Hahei
10. ▸ Tairua
11. ● Onemana/Whangamata
12. ✰ Waihi
13. + Maratoto
14. ▼ Rotorua
15. ● Taupo
16. ◆ Maraetai/Mangakino
17. ● Ongaroto
18. ▪ Mayor Island
19. ▪ Wekwok (PNG)

(b)
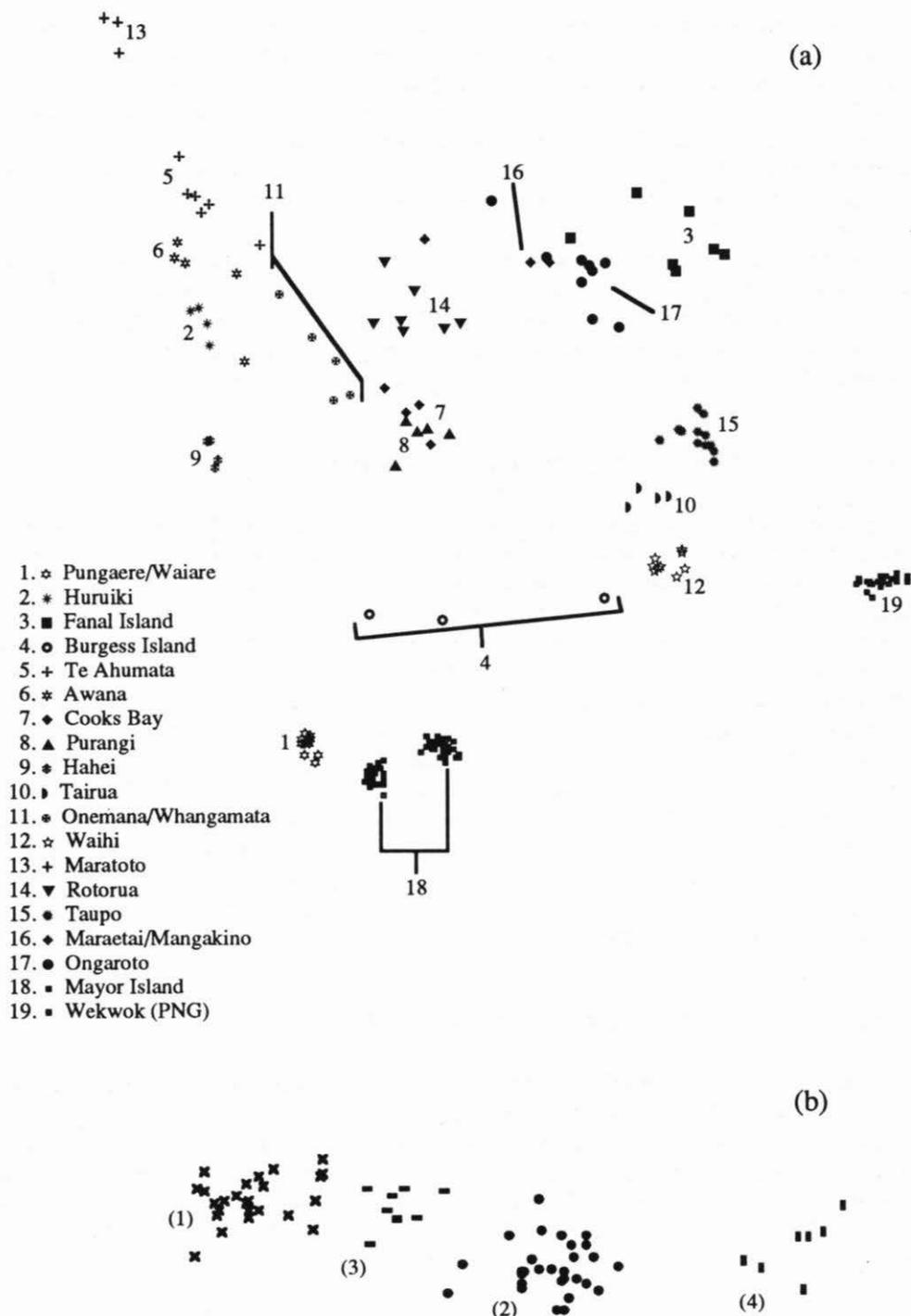
Figure 5: A plot of the first three principal components of the data set. a, Discrimination of New Zealand obsidian sources; b, Discrimination of Mayor Island obsidian.

component space, that is they are a close cluster. But there are a few sources which are spread over a larger region. The source groups of Rotorua, Taupo, Fanal Island, Awana and Onemana/Whangamata are not as tightly grouped as the others, which indicates that there is a larger chemical variability within them. Because of this larger span and the fact that a limited number of samples from these particular sources has been used in the analysis, there might be more difficulty in assigning the provenance to a particular artefact, especially if its results place it in the region between these groups. Extra source sampling may therefore be needed in the future.

The visual similarity of the Pungaere/Waiare and Mayor Island sources is matched by their close proximity in principal component space, as seen in Figure 5a, which indicates their similar chemical composition. The two Northland sources are a close clustering group. They are the only other source groups in the vicinity of the Mayor Island group, but they are quite distinct and there is no problem in identifying Mayor Island samples.

APPLICATION TO ARCHAEOLOGICAL OBSIDIAN

The sourcing of artefacts enables the creation of data on material distribution and source use which may be used in the investigation of processes of spatial distribution. This ability to source obsidian by its chemical composition is also of importance in obsidian hydration dating (OHD), which requires an accurate match between the artefact and the obsidian used for the determination of the hydration rate. For any given temperature and geochemistry, the diffusion of water into the surface of freshly fractured obsidian occurs at a constant determinable rate, creating over time a hydration layer which can be observed and measured. However, hydration rates vary between sources, because of the inter-source geochemical variation (Stevenson *et al.* 1993). Leach (Leach and Naylor 1981) suggested that the variation in the amount of fluorine may cause significant variation in hydration rates. A successful application of obsidian hydration dating would enable inexpensive absolute dating of many New Zealand sites. The combination of PIXE and PIGME analysis makes it possible to identify the geological source of obsidian artefacts, and also to identify any anomalies (e.g., the fluorine variation) in the elemental compositions of the artefacts which could influence hydration rates.

CASE STUDY: OPITA (T13/324, T13/788, T13/789)

The first use of the PIXE facility at Auckland University to source archaeological obsidians was to look at artefacts from the late prehistoric to early European contact site of Opita near Paeroa on the Hauraki Plains (Fig. 6). The obsidians from the excavations on this site had been previously sourced (Holroyd 1991) on the basis of physical characteristics using the guidelines set out by Moore (1988). They were either attributed to one of three well known sources (Mayor Island, Waihi or Great Barrier Island) or left unsourced under the category of 'grey'.
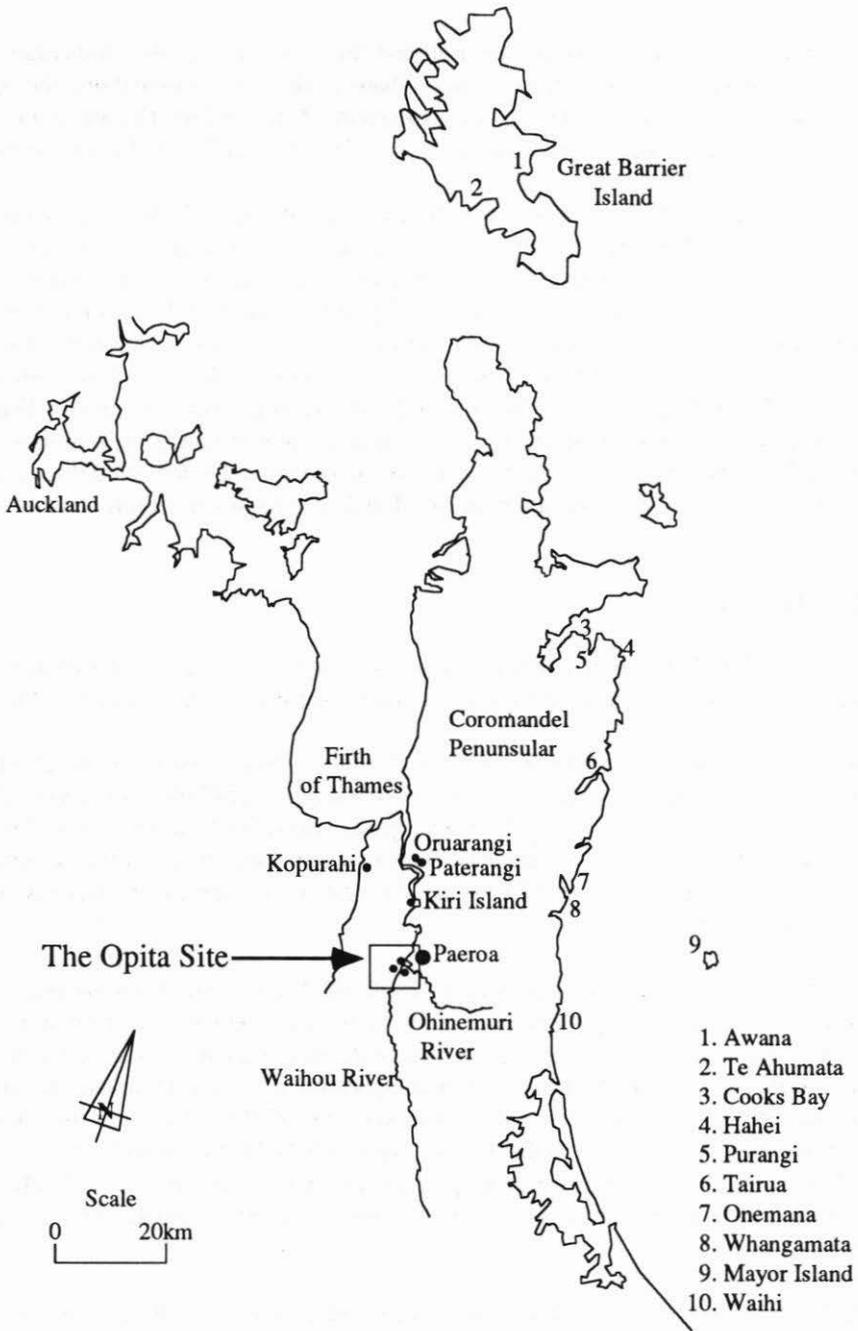
Figure 6: The location of the Opita site.

SITE HISTORY

Opita was one of three swamp *pā* clustered around the confluence of the Ohinemuri and Waihou Rivers, 40 km by river from the Firth of Thames. The area encompassing the Opita *pā* was the subject of an excavation by students from the Anthropology Department of the University of Auckland under the direction of Harry Allen and Caroline Phillips in February 1991.

The area on which Opita *pā* was built was probably first occupied in the late eighteenth or early nineteenth century. The first European reference to actual settlement at Opita was in 1839 when the land was bought by L. McCaskill. When the site was occupied, the Waihou River flowed from west to east past the Opita settlement, and was joined by the Ohinemuri River 500 m downstream. The Opita *pā* was constructed between a former Ohinemuri channel and the Waihou River. Because of the site's low relief and minimal height of around 4 m above sea level, flooding of the area occurred fairly frequently. During the late nineteenth and early twentieth century, sludge from goldmining operations in the headwaters of the Ohinemuri River caused extensive flooding which deposited thick layers of rockflour over much of the area and gradually filled up the old Ohinemuri channel with silt.

EXCAVATION AREAS

The confines of the old Ohinemuri channel were investigated by a series of trenches and small excavations, with the area being divided into three separately numbered sites (Fig. 7).

T13/788: This encompassed the western end of the survey area. Two excavations which were carried out on either side of Trench T uncovered a series of postholes probably relating to a hut and cooking area. The lack of European goods suggested a pre-1820 date. Trench T was 226.6 m long and ran almost due east–west in a direct line between the designated sites of T13/788 to the west and T13/324 to the east. Few features or artefacts were recovered from this area.

T13/324: This was the estimated location of the Opita *pā*. The site encompassed Trench U, and Trench B for approximately 50 m from the western end. A number of obsidian pieces were found in these regions in what appeared to be defensive ditches associated with the site. Three of these pieces, taken from Trench B, appeared to be core remnants, including by far the largest piece found on the site, which weighed 247.07 g. However, the lack of a large number of small flakes implied that core preparation had not been undertaken in this vicinity. It was therefore suggested that the pieces may have fallen into the ditch after the *pā* was abandoned, or been dumped as part of farming fill-in of ditches or ploughing procedures.

T13/789: This site spanned the southern bank of the old course of the Waihou River, and consisted of a 20 m trench dug into the top of the river bank (C), two adjacent area excavations (F and H), the eastern 70 m of Trench B and the small area excavation (M) at the eastern limit of the site. This site was of particular significance in that it was the only excavated area to have a complete, and relatively undisturbed, sequence of occupation. The possible sequence of events as proposed by Phillips (pers. comm. 1993) is shown in Table 3.
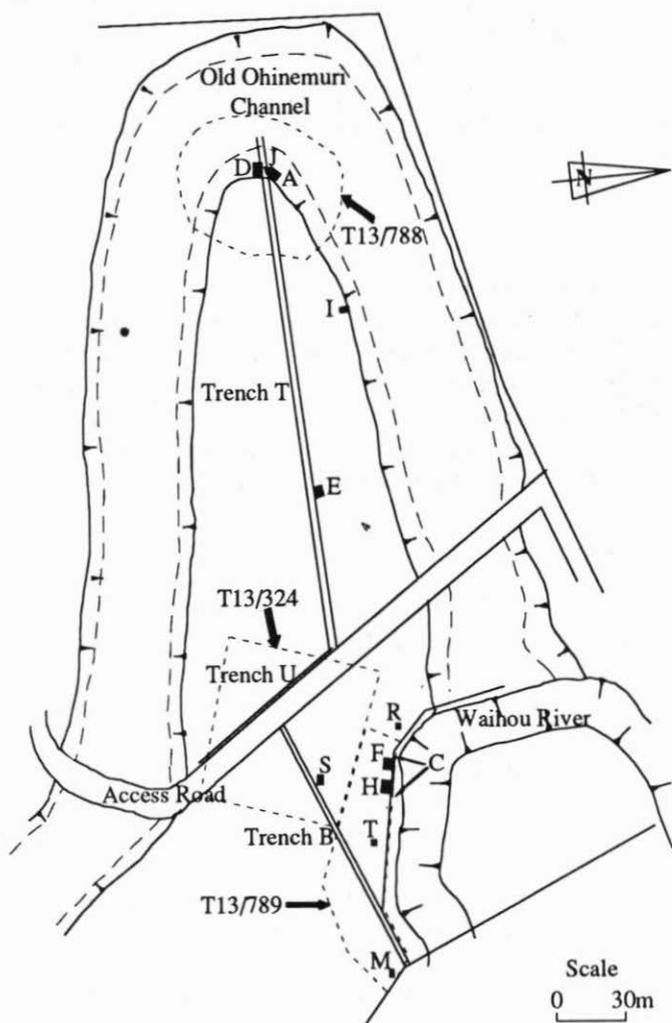
Figure 7: The Opita site map (OP/91).

ORIGINAL SOURCING RESULTS

Using physical characteristics, 97 artefacts were sourced to Mayor Island, 55 to Waihi and 8 to Great Barrier. Seven 'grey' pieces could not be accurately sourced. This method was found to be difficult because of the lack of an accurate reference collection. Mayor Island obsidian was distinctive because of its green colour in transmitted light; however there was some uncertainty because of the wide variety of translucency and greenness of Mayor Island pieces and the fact that Waihi and Pungaere/Waiare obsidians could also be green, although green material from these sources was not represented in the reference material available.

The Waihi source was distinguished by strong black/grey flow banding. On comparison with reference material, some pieces were attributed to Great Barrier on the basis of a slight brownish/purple tinge apparent on more translucent pieces. It was thought that all pieces sourced as Great Barrier were probably from Te Ahumata, as this was flake quality material, whereas that from Awana is not. The remaining artefacts were black in reflected light and grey in transmitted light and could have originated from a number of Coromandel, Rotorua and Taupo sources.

RESULTS BY PIXE ANALYSIS

Seventy-six of the artefacts recovered from the Opita site were analysed using PIXE. They ranged in size from one that weighed 0.15 g and had approximate dimensions of 15 mm x 8 mm x 1 mm, to one that weighed 247.07 g with dimensions of 80 mm x 60 mm x 50 mm. The remaining artefacts were beyond the size limits previously stated and were not able to be analysed with any confidence with the beam of 3 mm diameter being used at the time. The elemental analysis and final sourcing of the artefacts were completed in five working days (the process had not been automated at that time).

TABLE 3

SUMMARY OF ALL OBSIDIAN ARTEFACTS RECOVERED FROM T13/789,
DIFFERENTIATED BY PHASE OF OCCUPATION[3]

Phase	Layer	Date	No. Flakes
I	8	Pre-occupation land surface	0
	7	*C*. pre-1800 not necessarily pre-European	37
	6	Midden layer immediately on top of layer 7 also *c*. pre-1800 not necessarily pre-European	33
II	5	*C*. 1810–20 similar to late occupation at Raupa and Waiwhau (Phillips 1986)	6
III	4	Midden layer immediately on top of layer 5 1840s–50s associated with Opita *pā* occupied 1842–6	10
IV	3	1880s European artefacts only	0

[3]Excluding Square M and Trench B (i.e., including Square F, Square H and Trench C). Area R to the north-east of Area F, and Area T south of Area H (Fig. 7) contained no obsidian.

The pictorial results of the principal component analysis, performed on the elemental ratios of the Opita artefact data set, are shown in Figure 8. Elemental results and ratios to Fe are given in Tables 4 and 5. The majority of the artefacts were sourced to either Mayor Island or Waihi, with a smaller number to Coromandel sources. None of the artefacts appear to originate from Te Ahumata or Awana on Great Barrier. Of the eight artefacts visually sourced to Great Barrier, six have now been sourced to the Onemana/Whangamata region and two to Waihi. The Onemana/Whangamata artefact points in Figure 8a encompass a larger region than artefacts from other sources, indicating that they have a more varied chemical composition.

Of the 27 artefacts originally sourced to Waihi, 26 were confirmed as coming from that source and one was sourced to Onemana/Whangamata. On rechecking, this piece was shown to have been misrecorded in the original analysis as it was clearly of similar appearance to the other material. The seven 'grey' artefacts were all sourced to the Coromandel region: three to Onemana/Whangamata, two to Waihi and two to Cooks Bay/Purangi.

TABLE 4

THE ELEMENTAL CONCENTRATIONS (IN PPM) OF THE OPITA ARTEFACTS

Artefact	K	Ca	Ti	Mn	Fe	Rb	Sr	Y	Zr
Analysis of Standard									
Wekwok	39000	8100	2000	540	17300	160	70	40	350
	2%	2%	2%	2%	2%	3%	10%	16%	4%
Cooks Bay/Purangi									
106b	37900	7200	940	510	12000	140	80	50	120
339	30000	5800	770	450	10400	140	70	30	140
Onemana/Whangamata									
102e	41300	5700	770	360	11000	140	50	50	180
103	43500	5400	700	370	11400	160	40	50	150
338	35800	5600	730	370	10900	130	40	30	150
365c	23600	3700	490	260	8000	140	30	50	120
414a	37600	4700	650	350	10600	180	30	30	120
414b	32300	4300	600	360	10200	170	30	10	100
427a	32100	4100	570	330	10000	160	40	50	130
452a	39300	6000	800	380	11600	160	40	50	160
472d	41100	5100	690	360	11000	170	40	40	110
475	36000	4800	670	340	10600	170	40	30	140
Waihi									
4	35500	20100	2200	510	18400	150	230	<10	130
21	32700	18600	2000	500	17900	120	150	20	180
38	33900	19300	2100	520	18300	150	190	10	140
44	34000	19300	2100	490	18100	130	180	20	150
70	36600	21000	2200	540	19000	190	190	<10	140
87	26800	15100	1700	400	15100	120	150	20	140
98	24400	14000	1500	550	14200	120	150	30	110
116	34000	19500	2100	480	17500	170	200	20	130
117	33800	19100	2100	510	17700	160	180	20	120

TABLE 4 Continued

124	27100	15600	1700	440	16100	140	180	<10	140
130	26400	15300	1700	450	16100	110	170	10	200
146	32400	18400	1900	480	17100	160	180	<10	110
287	28700	16900	1800	480	16900	130	170	20	170
366a	27900	16200	1800	440	15700	120	160	30	120
366b	30000	17500	1900	440	16000	160	180	<10	90
367a	26400	15400	1700	420	15200	120	160	10	130
378	32900	18600	2000	470	16800	160	160	<10	130
394a	31900	18400	1900	450	16100	140	180	<10	100
395	26200	17700	1900	630	17000	100	230	<10	190
408c	23900	13800	1500	410	14400	120	140	10	130
440	28500	15600	1700	440	15600	120	160	<10	130
446c	34900	20000	2100	500	18100	160	170	<10	110
446f	29000	16800	1800	460	16300	160	180	20	160
452b	28300	16300	1800	490	17200	120	170	<10	150
470	31900	18100	2000	510	17100	150	190	<10	140
472c	26900	17300	1900	670	17400	140	220	10	150
472e	29600	17500	1900	480	17400	120	180	<10	140
472g	34500	19800	2100	520	18200	160	190	<10	130
477	32300	18600	1900	500	17200	170	170	10	110
513a	29200	16700	1800	490	17000	140	200	<10	150

Mayor Island Group (1)

12	47200	1300	1600	900	40900	130	<10	210	1400
46	44800	1300	1500	920	40400	170	10	110	1400
47	46100	1300	1500	930	41300	130	10	150	1400
51a	41900	1200	1400	840	35900	150	<10	140	1300
66	50600	1300	1600	1100	44900	170	<10	140	1500
77	48000	1400	1600	930	40000	140	<10	150	1300
119	42100	1300	1500	880	39200	150	<10	170	1400
322	45700	1200	1500	790	36500	130	<10	140	1300
337	44300	1300	1500	840	37400	140	20	160	1200
365a	30700	960	1100	700	31900	120	<10	140	1300
365b	34700	1000	1200	740	33500	140	10	130	1200
411	43000	1300	1400	850	37100	110	<10	140	1200
416	36900	1100	1300	770	34800	130	<10	130	1200
441	44700	1300	1400	840	37200	150	10	120	1200
446a	32500	970	1200	710	33000	130	<10	140	1300
446b	47100	1400	1600	880	39900	140	<10	150	1500
446d	43700	1200	1500	840	37700	110	10	140	1200
446e	44800	1600	1600	890	38800	120	<10	150	1300
446g	42800	1200	1400	860	38000	140	<10	130	1300
471b	45300	1200	1500	890	37900	120	20	150	1200
472b	44200	1300	1500	890	39200	160	20	160	1300
472f	50800	1400	1600	950	40400	140	20	170	1300
502	46900	1300	1600	940	41000	130	<10	160	1500
508	43600	1200	1400	920	39500	160	30	170	1400
509	41600	1200	1300	820	35600	110	<10	170	1100

TABLE 4 Continued

511a	47100	1400	1500	960	40800	120	<10	170	1400
511b	51100	1500	1700	1000	43100	170	10	150	1400
393a	94100	1200	1200	720	31900	250	10	140	1700
Mayor Island Group (2)									
2	48100	1500	1500	1200	51800	160	10	210	1600
414c	42400	1200	1300	1100	44100	110	20	170	1400
417	44700	1300	1400	1100	47500	140	10	170	1500
418	39500	1100	1200	1000	44700	140	10	220	1500
472a	49300	1500	1600	1200	50300	140	10	180	1500
472h	39500	1200	1300	1100	45700	130	10	180	1500

TABLE 5

THE ELEMENTAL RATIOS WITH RESPECT TO IRON
OF THE OPITA ARTEFACTS

Artefact	K/Fe	Ca/Fe	Ti/Fe	Mn/Fe	Rb/Fe	Sr/Fe	Y/Fe	Zr/Fe
Analysis of Standard								
Wekwok	2.25	.469	.113	.031	.009	.0040	.0020	.020
	0.2%	0.2%	0.3%	0.5%	2%	8%	15%	4%
Cooks Bay/Purangi								
106b	3.15	.598	.078	.043	.012	.0066	.0037	.010
339	2.88	.560	.074	.043	.013	.0065	.0032	.013
Onemana/Whangamata								
102e	3.74	.515	.070	.033	.013	.0048	.0041	.016
103	3.81	.472	.062	.032	.014	.0034	.0044	.013
338	3.27	.508	.066	.033	.012	.0038	.0025	.014
365c	2.95	.459	.062	.032	.017	.0037	.0058	.015
414a	3.56	.440	.062	.033	.017	.0026	.0031	.011
414b	3.16	.422	.058	.035	.016	.0032	.0014	.010
427a	3.23	.409	.057	.033	.016	.0037	.0051	.013
452a	3.39	.513	.069	.032	.014	.0034	.0047	.014
472d	3.74	.463	.063	.032	.015	.0032	.0040	.010
475	3.39	.454	.063	.032	.016	.0037	.0024	.013
Waihi								
4	1.93	1.096	.117	.028	.008	.0124	.0003	.007
21	1.83	1.039	.113	.028	.007	.0085	.0014	.010
38	1.85	1.055	.114	.028	.008	.0106	.0007	.008
44	1.87	1.065	.114	.027	.007	.0100	.0011	.008
70	1.94	1.115	.117	.029	.010	.0102	<.0001	.008
87	1.77	1.001	.111	.026	.008	.0100	.0010	.009
98	1.72	.991	.107	.039	.008	.0102	.0020	.008
116	1.94	1.112	.118	.027	.010	.0112	.0013	.007
117	1.91	1.079	.116	.029	.009	.0100	.0009	.007
124	1.68	.971	.108	.027	.009	.0114	<.0001	.009
130	1.64	.950	.105	.028	.007	.0103	.0008	.012

TABLE 5 Continued

146	1.89	1.079	.114	.028	.009	.0106	.0001	.007
287	1.70	1.000	.106	.028	.007	.0100	.0009	.010
366a	1.78	1.034	.113	.028	.008	.0101	.0017	.008
366b	1.88	1.099	.116	.027	.010	.0110	.0002	.006
367a	1.74	1.014	.110	.028	.008	.0108	.0008	.009
378	1.96	1.110	.116	.028	.010	.0097	.0002	.008
394a	1.97	1.139	.118	.028	.008	.0109	<.0001	.006
395	1.54	1.045	.111	.037	.006	.0133	.0001	.011
408c	1.66	.956	.101	.029	.008	.0100	.0007	.009
440	1.82	.995	.107	.028	.008	.0103	<.0001	.008
446c	1.93	1.107	.118	.028	.009	.0093	<.0001	.006
446f	1.78	1.031	.110	.028	.010	.0113	.0010	.010
452b	1.65	.947	.107	.029	.007	.0097	.0002	.009
470	1.86	1.056	.118	.030	.009	.0110	<.0001	.008
472c	1.55	.993	.109	.038	.008	.0128	.0007	.009
472e	1.70	1.004	.109	.028	.007	.0101	<.0001	.008
472g	1.90	1.089	.116	.028	.009	.0102	<.0001	.007
477	1.88	1.080	.112	.029	.010	.0097	.0006	.007
513a	1.72	.984	.106	.029	.008	.0116	<.0001	.009
Mayor Island Group (1)								
12	1.17	.033	.039	.023	.003	<.0001	.0051	.034
46	1.11	.032	.038	.023	.004	.0001	.0028	.034
47	1.11	.032	.037	.023	.003	.0003	.0037	.034
51a	1.17	.033	.038	.024	.004	<.0001	.0038	.035
66	1.13	.030	.037	.023	.004	<.0001	.0031	.033
77	1.20	.035	.040	.023	.003	<.0001	.0037	.033
119	1.07	.034	.037	.022	.004	<.0001	.0043	.036
322	1.25	.034	.040	.022	.003	.0001	.0038	.035
337	1.18	.034	.039	.022	.004	.0004	.0042	.033
365a	.96	.030	.034	.022	.004	<.0001	.0043	.040
365b	1.03	.031	.036	.022	.004	.0002	.0038	.037
411	1.16	.035	.038	.023	.003	<.0001	.0039	.032
416	1.06	.031	.036	.022	.004	<.0001	.0038	.035
441	1.20	.035	.038	.023	.004	.0004	.0032	.033
446a	.98	.029	.035	.022	.004	<.0001	.0042	.038
446b	1.18	.035	.039	.022	.003	<.0001	.0038	.037
446d	1.16	.033	.039	.022	.003	.0003	.0038	.033
446e	1.15	.041	.042	.023	.003	<.0001	.0040	.034
446g	1.13	.032	.038	.023	.004	<.0001	.0035	.034
471b	1.20	.033	.038	.024	.003	.0004	.0039	.032
472b	1.13	.034	.038	.023	.004	.0006	.0040	.034
472f	1.26	.036	.040	.023	.003	.0005	.0041	.031
502	1.14	.032	.038	.023	.003	<.0001	.0038	.036
508	1.10	.031	.036	.023	.004	.0007	.0042	.035
509	1.17	.032	.038	.023	.003	.0002	.0047	.032
511a	1.15	.035	.038	.024	.003	.0001	.0041	.034
511b	1.19	.034	.038	.023	.004	.0003	.0036	.032

TABLE 5 Continued

393a	2.95	.037	.036	.022	.008	.0004	.0044	.037
Mayor Island Group (2)								
2	.93	.028	.029	.024	.003	.0002	.0040	.031
414c	.96	.028	.030	.024	.003	.0005	.0037	.032
417	.94	.028	.030	.024	.003	.0003	.0036	.031
418	.88	.025	.027	.023	.003	.0003	.0048	.033
472a	.98	.031	.031	.024	.003	.0003	.0036	.031
472h	.86	.026	.027	.024	.003	.0003	.0040	.032

Of the 34 artefacts originally sourced to Mayor Island, 33 were confirmed as coming from that source. The majority, 27, were sourced to the group (1) region, 6 to the group (2) region and none to the group (3) or (4) regions (Fig. 8b). Initially no firm conclusion could be made about one of the Mayor Island artefacts, which appeared to suffer from either surface weathering or a severe surface contamination. It had a much higher concentration of the element K than normal Mayor Island obsidian. However, it was possible to determine the probable Mayor Island source of this artefact by considering the elemental ratios of Ca/Fe, Ti/Fe, Mn/Fe and Zr/Fe which were similar to normal Mayor Island obsidian trends, as seen in Table 5. This artefact was therefore sourced to the Mayor Island group (1) region.

These results translate to the locations on Mayor Island as follows. None of the artefacts were found to be from the southern point or crater rim on the eastern side of the island. However, there are two possibilities for the source of the artefacts from groups (1) and (2). This is due to the unexpected grouping of the Oira Bay North sample location on the western side in group (1) with the locations on the eastern side of the island. Thus it is possible that the artefacts are either all from the western regions of the island, or else from locations on both western and eastern sides.

In conclusion, the Opita obsidian artefacts were shown to be from Cooks Bay/Purangi, Onemana/Whangamata, Waihi and the specified regions on Mayor Island, all of which are in close proximity to Opita. The general characteristics of the obsidian recovered from the site and analysed at the AURA2 PIXE facility are summarised in Tables 6 and 7. In Table 6, the sources of the obsidian from Square F, Square H and Trench C in T13/789 have been differentiated by the phase of occupation previously proposed. Table 7 indicates the distribution and frequency of artefacts from the different obsidian sources throughout all excavation areas of the site. Mayor Island and Waihi were the major sources of the obsidian artefacts found in the site. The latter was prevalent mainly in the Phase I occupation and the former was somewhat more prevalent in Phase I and to a lesser extent in Phase III.

1. ✧ Pungaere/Waiare
2. ✳ Huruiki
3. ■ Fanal Island
4. ○ Burgess Island
5. + Te Ahumata
6. ✳ Awana
7. ◆ Cooks Bay
8. ▲ Purangi
9. ✳ Hahei
10. ▸ Tairua
11. ✳ Onemana/Whangamata
12. ☆ Waihi
13. + Maratoto
14. ▼ Rotorua
15. ✳ Taupo
16. ◆ Maraetai/Mangakino
17. ● Ongaroto
18. ▪ Mayor Island
19. ▪ Wekwok (PNG)
    ▪ Opita Artefact
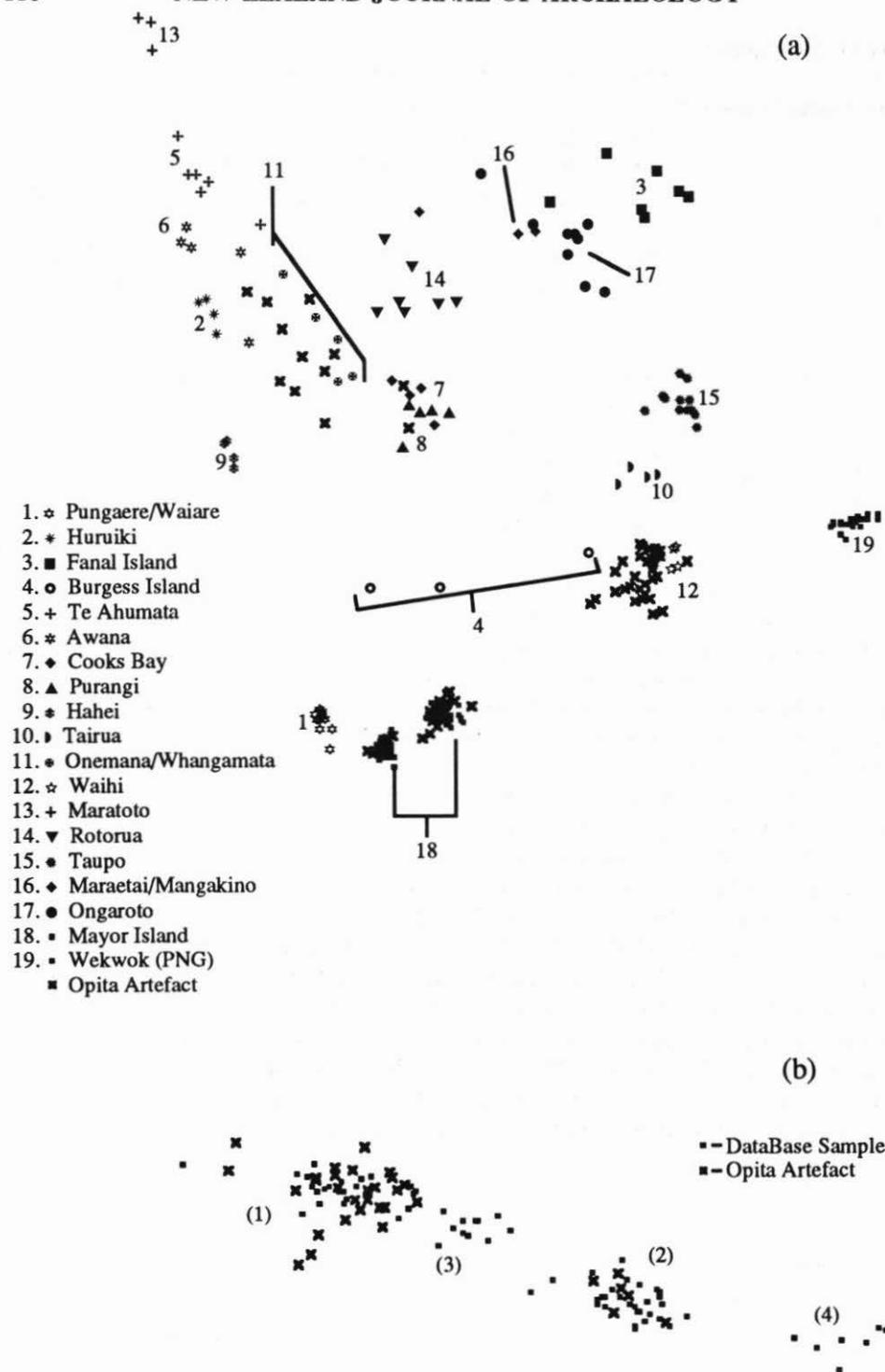
Figure 8: A plot of the first three principal components of the data set. a, Determination of the source of the artefacts from the Opita site; b, Discrimination of the Opita artefacts which had been sourced to Mayor Island.

TABLE 6

THE SOURCES OF THE ARTEFACTUAL OBSIDIAN RECOVERED FROM
SQUARE F, SQUARE H AND TRENCH C IN T13/789,
ACCORDING TO PHASE OF OCCUPATION

Weights are in g

Phase	Layer	Mayor Island		Waihi		Cooks Bay/ Purangi		Onemana/ Whangamata		Total for Layer	
		No.	*wt.*	*No.*	*wt.*	*No.*	*wt.*	*No.*	*wt.*	*No.*	*wt.*
I	7	11	32.35	8	33.18	0	0	3	6.02	22	71.55
	6	4	5.84	3	5.93	0	0	3	2.42	10	14.19
II	5	1	1.75	2	5.66	0	0	0	0	3	7.41
III	4	4	7.98	0	0	1	1.03	1	0.15	6	9.16
Total		**20**	**47.92**	**13**	**44.77**	**1**	**1.03**	**7**	**8.59**	**41**	**102.31**

TABLE 7

THE SOURCES OF THE ARTEFACTUAL OBSIDIAN RECOVERED
FROM THE SITE AREAS

Weights are in g

Excavation Area	Mayor Island		Waihi		Cooks Bay/ Purangi		Onemana/ Whangamata		Total for Site	
	No.	*wt.*	*No.*	*wt.*	*No.*	*wt.*	*No.*	*wt.*	*No.*	*wt.*
T13/788	4	16.21	8	14.68	1	0.22	0	0	13	31.11
Trench T	1	1.22	4	17.05	0	0	0	0	5	18.27
T13/324	5	345.21	0	0	0	0	2	1.74	7	346.95
T13/789	24	69.17	18	61.39	1	1.03	8	9.03	51	140.62
Total	**34**	**431.81**	**30**	**93.12**	**2**	**1.25**	**10**	**10.77**	**76**	**536.95**

CONCLUSION

The PIXE facility at the Auckland University Research Accelerator laboratory, AURA2, has
been set up and has been used for provenance studies on archaeological obsidian artefacts.
It has been shown to be of value in terms of its rapid, non-destructive, discriminative ability.
A database for obsidian from the North Island of New Zealand has been developed and will
be extended to include other South Pacific sources. Similar studies involving the application

of the PIXE analysis method will be applied to other artefact materials such as basalts. The correlation of elemental variation with hydration rates will be investigated, particularly for Mayor Island obsidian.

APPENDIX 1

The locations and reference numbers of the obsidian source samples used in the construction of the AURA2 PIXE database of New Zealand obsidian sources.

Area/Source	Auckland University	Otago University	Holroyd	Dept. of Conserv.
Mayor Island				
Taumou Beach 1	-	-	1	-
Taumou Beach 2	-	-	2	-
Taumou Pa	-	-	3	-
Staircase 'Quarry'	-	-	4	-
Oira Bay S.	-	-	5	-
Oira Bay N.	-	-	6	-
Raumata Pt.	-	-	7	-
Otiora Bay N.W.	-	-	8	-
Otiora Bay S.E.	-	-	9	-
Halls Pass	-	-	10	-
Staircase 'Honey'	-	-	11	-
Te Paritu	-	-	12	-
Opo Bay	-	-	13	-
Te Matawhero Pt.	-	-	14	-
Opuhi Spring	-	-	15	-
Te Ananui Flat	-	-	16	-
Northland				
Waiare	-	-	1802	-

	-	-	1805	-
	-	-	1809	-
	-	-	1811	-
Pungaere	-	24	-	Pung/1,2,3,4
Huruiki	-	-	1701	-
	-	-	1701a	-
	-	-	1701b	-
	-	-	1701c	-
Great Barrier				
Fanal Island	2949/1,2,3,5	33	-	-
Burgess Island	1685/7,9,10	-	-	-
	1688	-	-	-
Te Ahumata	680/3,6,7	-	-	-
	2935/7	-	-	-
	TeA_May93	-	-	-
	TeA_Nov92	-	-	-
Awana	679/7,13,16,17	-	-	-
Coromandel				
Cooks Bay	304/4	4/1,2,?	-	-
Purangi	917/1,4,6a,6b	-	-	-
Hahei	-	28=Ward#42	-	-
	-	28a	-	-
Tairua	-	-	1901	-
	-	-	1902	-
	-	-	1903	-
	-	-	1904	-
Onemana/Whangamata	-	-	2001	-
	-	-	2004	-
	-	-	2005	-
	-	-	2006	-
Waihi	3553/1,5,10	29	-	-
	Waihi 'Red'	30=Ward#44	-	-
Maratoto	-	32	-	-
Central North Island				
Rotorua				
Whakarewarewa	1627/1	14/1=Ward#25	-	-
	2942	14/2=Ward#24	-	-
	1496/1	14/3,4a,4b	-	-
Unspecified	-	15	-	-
Hemo Gorge	-	12=Ward#23	-	-
Taupo				
Ben Lomond	237	18/1a,b=Ward#28		-
	West_Taupoa	18/2a,b=Ward#29		-
	West_Taupob	18/3=Ward#30	-	-
	-	18/4=Ward#31	-	-
	-	18/5=Ward#32	-	-
Mangakino	253	-	-	-
	25	-	-	-

	307	-	-	-
Maraetai	673/2,3,4,6	17/6	-	-
Ongaroto	-	17/8a,8b	-	-

REFERENCES

Armitage, G.C., Reeves, R.D. and Bellwood, P. 1972. Source identification of archaeological obsidians in New Zealand. *New Zealand Journal of Science* 15: 408–20.

Bird, J.R., Russell, L.H., Scott, M.D. and Ambrose, W.R. 1978. Obsidian characterisation with elemental analysis by proton induced gamma-ray emission. *Analytical Chemistry* 50: 2082–84.

Bollong, C.A. 1983. Automated isoprobe analyses of New Zealand and oceanic volcanic glass. Unpublished M.A. thesis, Anthropology, University of Otago.

Clayton, E. 1986. *PIXAN: The Lucas Heights PIXE analysis computer package*. Australian Atomic Energy Commission.

Duerden, P., Clayton, E., Bird, J.R., Ambrose, W. and Leach, B.F. 1987. Obsidian composition catalogue. *In* W.R. Ambrose and J.M.J. Mummery (Eds), *Archaeometry: Further Australasian Studies*. Australia National University.

Gordus, A.A., Griffin, J.B. and Wright, B.A. 1971. Activation analysis identification of the geologic origins of prehistoric obsidian artefacts. *In* R.H. Brill (Ed.), *Science and Archaeology*. Symposium on Archaeological Chemistry, 4th, Atlantic City 1968.

Green, R.C. 1962. Obsidian: its application to archaeology. *New Zealand Archaeological Association Newsletter* 5 (1): 8–16.

Green, R.C., Brooks, R.R. and Reeves, R.D. 1967. Characterisation of New Zealand obsidians by emission spectroscopy. *New Zealand Journal of Science* 10: 675–82.

Holroyd, S. 1991. Analysis of obsidian from the Opitau excavation (OP/91). [T13/324]. Unpublished manuscript, Department of Anthropology, University of Auckland.

Leach, B.F. and Naylor, H. 1981. Dating New Zealand obsidians by resonant nuclear reactions. *New Zealand Journal of Archaeology* 3: 33–49.

Moore, P.R. 1988. Physical characteristics of New Zealand obsidians and their use in archaeological sourcing studies. Unpublished manuscript, New Zealand Geological Survey (now IGNS), Lower Hutt.

Phillips, C.A. 1986. Excavations at Raupa Pa (N53/37) and Waiwhau Village (N53/198), Paeroa, New Zealand, in 1984. *New Zealand Journal of Archaeology* 8: 89–113.

Reeves, R.D. and Armitage, G.C. 1973. Density measurements and chemical analysis in the identification of New Zealand archaeological obsidians. *New Zealand Journal of Science* 16: 561–72.

Seelenfreund, A. and Bollong, C.A. 1990. The sourcing of New Zealand archaeological obsidian artefacts using energy dispersive XRF spectroscopy. *In* D. Sutton (Ed.) *Saying So Doesn't Make It So: Essays in Honour of B. Foss Leach*, pp. 168–89. New Zealand Archaeological Association Monograph 17.

Stevenson, C.M., Knaus, E., Mazer, J.J. and Bates, J.K. 1993. Homogeneity of water content in obsidian from the Coso Volcanic Field: Implications for obsidian hydration dating. *Geoarchaeology* 8 (5): 371–84.

Ward, G.K. 1974a. Sources of obsidians from the Motutapu undefended site N38/37. *Records of the Auckland Institute and Museum* 11: 13–14.

Ward, G.K. 1974b. A systematic approach to the definition of the sources of raw material. *Archaeometry* 16 (1): 41–53.

Ward, G.K. 1974c. A paradigm for sourcing New Zealand archaeological obsidians. *Journal of the Royal Society of New Zealand* 4: 47–62.