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Characterisation of New Zealand Obsidian using PXRF

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Abstract:

New Zealand has some of the most active areas of rhyolitic volcanism in the world and this has produced numerous obsidian sources in the northern half of the North Island. In total archaeologists have recognized 27 named locations from which obsidian can be obtained scattered across 4 geological source regions. Shortly after colonization in the late 13th century AD Polynesian settlers began transporting this material some thousands of kilometers throughout the country and across the sea in small quantities to distant neighbors in the Kermadecs and Chatham islands. Although considerable research has been conducted on obsidian sourcing in New Zealand the complexity of geochemical source discrimination and the lack of a practical method of non-destructive geochemical analysis has hindered progress. We present the results of our use of PXRF to provide geochemical data on New Zealand obsidian sources and to compare the use of discriminant analysis and classification tree analysis to discriminate among sources and attribute archaeological samples to sources. Our research suggests that classification tree analysis is superior to discriminant analysis in sourcing studies. A large case study using an important settlement phase site (S11/20) from the Auckland region demonstrates the utility of the methods and the results support a model of high degrees of mobility and interaction during the early settlement of New Zealand.

Keywords: obsidian sourcing; New Zealand; classification tree; settlement

1. Introduction

Obsidian was of considerable economic and symbolic importance to the Maori inhabitants of New Zealand (Maning, 1875). It is found in archaeological sites throughout the country and geological sources are numerous in the North Island. Research into sourcing of obsidian has considerable antiquity in New Zealand with Roger Green first calling for work to begin in 1958 (Green, 1962). As recognized by Green, sourcing studies have considerable potential to contribute to our understanding of the process of colonization and settlement and to cultural transformation over time and space. Martin Jones (2002) has conducted the most recent comprehensive survey of source locations and his work summarizes earlier sourcing studies (Green, 1962, 1964, Holroyd, 1993, Leach, 1977, 1996, 1989, Moore, 1982, 1983, 1999, nd [1988], Neve, et al., 1994, Seelenfreund, 1985, Seelenfreund and Bollong, 1989, Ward, 1972, 1973, 1974a). Despite this body of work and much innovative research making use of a variety of geochemical and other sourcing methods (see review by Sheppard, 2004), there is still no well published comprehensive geochemical database of New Zealand obsidian obtained using an archaeologically practical non-destructive method of geochemical analysis which is routinely available. Most recent research has depended on visual sourcing using the method developed by Moore (n.d. [1988]) which uses a variety of physical attributes including color in reflected and transmitted light, presence of phenocrysts, and structure. Although this can be effective in the hands of skilled analysts with appropriate reference collections (Furey, 2002, Jones, 2002: Fig 7.1), it is hard to objectively assess the quality of results provided by different analysts. In this study we present in the first section, the results of our use of PXRF to develop a comprehensive geochemical database for New Zealand obsidian. We then use it to effectively source a large obsidian collection from an important early settlement phase site (S11/20) in the Auckland region. Comparison of classification using discriminant analysis and classification tree methods is made to develop robust assignments. The results are finally used to comment on models of trade/exchange and interaction at the time of New Zealand settlement and on the utility of our PXRF instrument for obsidian characterization.

2. Geology and Obsidian Sources

2.1 Geology

The term “source” as used here is equivalent to the “source area” defined by Moore (1988: 3) as “…a number of discrete obsidian deposits associated with a single rhyolitic eruption or series of closely related eruptive events (i.e. lava flows, lava domes, breccia or ignimbrite deposits)”. Moore defines a “source region” as consisting of “… source areas within a major zone of rhyolitic volcanism which contains obsidian with broadly similar physical and/or chemical characteristics”. In this study we will refer to a “geochemical source” as a source or set of geographically related sources which, based on current data, are geochemically similar (see also Nazaroff, et al., 2010, Summerhayes, et al., 1998).

New Zealand lies on the boundary of the Pacific and Australian tectonic plates. Subduction of the Pacific plate under the North Island has created a zone of volcanic activity which runs from the centre of the North Island north along the east coast. Obsidian is found in four distinct regions associated with Tertiary and Quaternary rhyolitic vulcanism: Northland, the Coromandel Volcanic Zone (CVZ), the Taupo or Central North Island Volcanic Zone (TVZ) and Mayor Island (called *Tuhua* or “obsidian” in Maori). Current evidence indicates the presence of some 27 named obsidian source locations in the upper half of the North Island (Figure 1). Many sources are easily accessible and found along the coast, however a number are located in the interior. Although there are many sources recorded most of these are small. Field observations suggest that at many of the identified source areas the amount of glass available today, and most probably in the past, is limited to a low-density scatter of cobbles over areas of variable but generally small size (*circa* 1 sq km to several hundred sq meters) and often occurring as detrital deposits in streams, in colluvium derived from in place rhyolitic formations upstream and inland, or possibly as volcanic bomb deposits (Bell and Clark, 1909:72, Ward, 1972:123-127, 172-173, Appendix 4). The major exception is Mayor Island, where very high quality completely isotropic obsidian without development of microlites or other phenocrysts is readily available throughout most of the island as massive seams, in pyroclastic fields and in beach deposits. It seems likely that the abundance, quality and accessibility of Mayor Island obsidian accounts for its role as the premier source in the country, as was noted by the earliest geologists to survey the island (Sladden, 1926, Thompson, 1926).

2.2 Mayor Island

Mayor Island is New Zealand's only extant peralkaline volcano (Houghton, et al., 1992) located 30 km off the east coast. The island is essentially circular, with a diameter of *circa* 4 km and is dominated by a central caldera whose walls attain a maximum height of 200 m. Although the only sheltered anchorage is found on the southwest corner of the island, access by canoe onto the many exposed sand and cobble beaches found around the island would be comparatively easy, giving rapid access to large amounts of obsidian. At Oira Bay, for example, massive flows (strictly flow selvages) of high quality obsidian up to 2 m in thickness are found at the southern point opposite a sand beach. In locations where cliffs rise above the sea (e.g. Taratimi Bay), the cobble beaches below contain large amounts of obsidian weathered from the numerous obsidian selvages which are exposed as layers in the cliffs (Jones, 2002:144-163). Although quarrying at some locations on Mayor Island has been suggested (Seelenfreund, 1985:163), evidence for such activity is equivocal (Sheppard, 2004). It seems probable that most obsidian was recovered in an unspecialized manner from the abundant cobbles on beaches and in pyroclastic detrital fields. Once people began gardening and living permanently on Mayor Island, some time after 1400 AD based on the palynological record (Empson, et al., 2002), access to this resource may have become more formalized. Prior to this, quick visits to cobble beaches would have provided all the obsidian needed. In this study we make use of 139 samples collected from 16 locations across the island.

2.3 Coromandel Volcanic Zone

Although Mayor Island is the major coastal obsidian source, many others are found along the east coast of the North Island providing easy access and transport opportunities. On the Coromandel Peninsula, located to the east and north of Mayor Island, obsidian is associated with the Pliocene age Minden rhyolites (Edbrooke, 2001, Moore, 1983) and is generally found as small weathered cobbles or pebbles in limited colluvial or alluvial deposits on or very near the coast, where the weathered rhyolite is exposed. The northern most deposits are found at Cooks Beach and extend south to Hahei, after which deposits are found at Tairua and from Onemana south to Whangamata (Edbrooke, 2001, Moore, 1999). The only other coastal source south of Whangamata is 75 kilometers south at Maketu, where the deposits of the Taupo Volcanic Zone extend northeast from the Central North Island to reach the coast. Interior Coromandel sources are found at Waihi and Maratoto which are inland occurrences of the Minden rhyolites found along the central Coromandel Peninsula. At these locations small pebbles and cobbles of obsidian are found in streams located 7 (Waihi) and 12 kilometers west of the coast.

The Minden rhyolites extend north 15 kilometers from the Coromandel onto Great Barrier Island and north again to the small Mokohinau and Poor Knights Islands (Edbrooke, 2001, Edbrooke and Brook, 2009, Thompson, 1960, 1961). Obsidian sources are found in the Mt Hobson (Awana) and Te Ahumata regions of Great Barrier Island and 20 kilometers northwest, poor quality (small pieces showing poor conchoidal fracture) obsidian is found on the tiny Fanal and Burgess Islands in the Mokohinau Group (Moore, 1986), where the rhyolite is capped by flow banded obsidian or an agglomerate of obsidian clasts (Edbrooke and Brook, 2009). Although *insitu* and detrital obsidian is found in the interior of Great Barrier, it can be found as pebbles and cobbles in coastal streams. Additional samples have been reported from Rakitu (Arid) Island off the east coast of Great Barrier, however it is not clear if these are geological (Ward, 1972) although the Minden rhyolites outcrop there.

2.3 Northland (Kerikeri Volcanic Group)

Edbrooke and Brooke (2009: 36) report a series of alkaline and peralkaline rhyolite domes “locally with obsidian” within the Kaikhoe-Bay of Islands Volcanic field which forms part of the Kerikeri Volcanic Group. These include exposures at Te Pene, Pungaere, Maungaparerua (west of Kerikeri) and Putahi (south of Lake Omapere). The rhyolites in these areas are commonly weathered to white halloysitic clays. To the south an additional rhyolitic remnant is reported (Edbrooke and Brook, 2009) within the Puhipuhi-Whangarei volcanic field at Paremata Hill.

The last coastal obsidian source of archaeological significance is found 110 km north of Great Barrier at Huruiki Hill, four kilometers inland overlooking Helena Bay south of the large Whangaruru harbour. Here detrital scatters are found extending along a ridge for three kilometers (Moore, 1982) and would appear to be lag deposits associated with the rhyolites exposed at Paremata Hill two kilometers to the northwest. The separation of coastal and inland obsidian sources is somewhat arbitrary in Northland, however the Kaeo source region within the Kaikhoe-Bay of Islands Volcanic field, located 60 kilometers north of the Huruiki source, is at a minimum 10 kilometers from the coast and there appears to be no obsidian in coastal streams. Although the source region has been named Kaeo, Jones (2002: Figure 3.10) reports finding four sources extending 11 kilometers south from Kaeo stream through Waiare to Pungarere. A much smaller source region is found near Weta 10 kilometers northeast of Kaeo. There Jones (Jones, 2002) reports two small detrital sources three kilometers inland of Matauri Bay.

2.4 Taupo Volcanic Zone

The major inland obsidian sources are located in the Taupo Volcanic Zone (TVZ) in the central North Island. There, a large zone of Quaternary aged volcanism extends 250 kilometers from Ohakune in the central North Island northeast to White Island and represents the most active centre of rhyolitic volcanism on earth (Challis, 1978, Smith, et al., 2005). Within the zone are found a considerable number of eruptive centers of rhyolitic lava and numerous obsidian sources are associated with two major regions: the Whangamata Fault located north of Lake Taupo and the Rotorua Caldera/Okataina Volcanic Centre. Obsidian flows and extensive detrital deposits associated with the Haparangi rhyolites are exposed by the Whangamata Fault in the Taupo Volcanic Centre and samples have been obtained from a series of sources (Ben Lomond, Maraetai, Whakamaru, Ongaroto). Seventy kilometers to the north obsidian is common in the Haparangi rhyolites surrounding Lake Rotorua, where it is found as flows and surface deposits (Jones, 2002). A number of sources are reported from this region and we include representative samples from three sources (Rotorua (Whakarewarewa), Lake Okataina, Lake Rotoiti). In general, the chemical composition of the rhyolites from the TVZ have been thought to be similar, however recent research suggests considerable variation resulting from evolution and mixing of magmas although individual eruptive events can be fingerprinted using glass chemistry (Smith, et al., 2005). It is as yet unclear to what extent this affects or is unrepresented in sampled obsidians of archaeological importance. In this study we have defined two geochemical source regions: Central North Island which includes the Taupo sources and Rotorua which includes all sources in that region. The closest of any of these sources to the coast is that at Lake Okataina in the Rotorua region which is 20 kilometers from the sea.

In total 434 geological source samples from 15 geochemical source areas have been characterized for this study (Table 1). Of those, the majority (353), were originally collected by Martin Jones as part of his research on obsidian hydration dating and are held in the Department of Anthropology at the University of Auckland. Details of that collection and sampling protocols can be found in Jones (2002) however Jones attempted to cover the range of color and structure in his survey which was directed at attempting to create a simple means of screening collections by source prior to OHD analysis. Additional samples from the departmental source reference collections (GS, GT and GW series) were included to increase sample sizes for some sources.

3. Analytical Method

Portable X-Ray Fluorescence (PXRF) has seen widespread use in the last 5 years, as it promises non-destructive inexpensive analysis of large numbers of samples both in the lab and in the field (e.g. Craig, et al., 2007). Comparison of the accuracy and precision of PXRF with other methods of lab based geochemistry has produced variable results, although it is argued that as long as precision is high, useful sourcing results can be obtained despite variable accuracy (Jia, et al., 2010, Nazaroff, et al., 2010). It needs to be remembered, however, that geochemical analysis of any kind can generate poor results if the equipment operating condition varies or the equipment is used incorrectly. Routine running of standards is a significant part of any geochemical analysis, which allows monitoring of operating conditions and on-going assessment of accuracy and precision. There is no such thing as generic PXRF and only the use of standards will allow assessment of different equipment as well as the same equipment over time. In this study geochemical analysis was conducted using an Innov-X Alpha series portable energy dispersive XRF system produced by Innov-X Systems (USA). This is an x-ray tube (Ag or W anode, 10-40 kV, 10–50 µA) based system powered by lithium ion batteries with results downloaded to a PDA. The Auckland system is configured to analyze 18 elements using the Standard Analysis Package and an additional 7 elements using the LEAP or Light Element Analysis Package. Our system is not currently configured to analyze some potentially useful elements such as Y and Nb. Detection limits for all the elements used in the analysis described below range from 10 to 100 ppm. Elements lighter than P can not be detected as the system has no vacuum capability. X-rays are detected by a Si PiN diode detector (<300 eV FWHM at 5.95 keV Mn K-alpha line) and calibration is achieved, in the soils analysis mode employed here, using the Fundamental Parameters method. We report here on results for 8 elements (Ti, Fe, Mn, Zn, Rb, Sr. Zr, Pb) which are regularly detected with adequate accuracy and precision in all samples, although

Mayor Island samples are distinguished from all other sources by Sr generally below detection limits (< 10 PPM). The elements Ti, Fe and Mn were determined using the LEAP package.

Standard analysis protocols used here involve placing clean flat (i.e. selecting the flattest face) surfaces of obsidian flakes on the detector window of the instrument, which is mounted in a test stand provided by the manufacturer. Samples were analyzed for 3 minutes using the standard analysis package and 3 minutes using the LEAP package (average live-time of 117 seconds). Generally only samples weighting more than 1 gm were analyzed to avoid effects produced by small samples which did not cover the instrument test window and which often included irregularly shaped lithic shatter. All runs regularly included the analysis of the NIST 2709 powder soil standard presented to the detector in a sample cup sealed with polyethylene film. This allows for monitoring of machine conditions over time and provides a basis for standardising analyses across projects and over the long term. Separate analyses of other appropriate standards are run as part of each project. In this project the NIST SRM-278 standard obsidian (powdered obsidian from Clear Lake, Newberry Crater, Oregon) was also regularly run, as well as our Mayor Island solid (MI 9.3) obsidian sample. Table 2 indicates degrees of accuracy and precision provided by current machine settings. NIST SRM-278 does not have certified values for zirconium, however there are a number of analyses by various methods which have been reported. These are 290±2 ppm, 285±16 (Crock, et al., 1983), 272±31 and 208±20 (Glascock and Anderson, 1993). Glascock and Anderson (1993) report good agreement with all elements in an earlier study except for zirconium (208±20), which was statistically different. Our analysis of Zr agrees with the 3 higher values.

Excellent precision, as shown by the coefficient of variation (CV), over the life of the project is shown for the NIST 2709 standard, while precision is less but still acceptable for the NIST SRM-278 values of Mn, Sr and Pb. As we were running solid flakes of source and artifactual material as opposed to powders, a solid flaked obsidian standard (Mayor Island 9.3) was run regularly to assess precision, which might potentially be affected by surface geometry and sample orientation. The same face was analyzed each time, however no attempt was made to standardize orientation or placement over the test aperture. The precision for the solid samples is systematically less than for the powders but did not exceed 13%.

As shown in Table 2 accuracy varies between elements and between standards. For the NIST 2709 standard PXRF values lie beyond 2 standard errors for Ti, Zn and Zr, while for NIST 278 Mn, Fe, and Zn fall outside those confidence intervals. Simple comparison of our values for those elements with those obtained by other methods should not be made, however the other elements used should compare well with other methods.

4. Results

4.1 Geological Source Characterization

Table 3 provides summary information on the geochemical sources studied. Separation of the far north sources Kaeo and Weta along with Mayor Island, from all other sources, can be made using Sr which is below detection limits (< 10 ppm) for Kaeo and Weta and only detected for 6 out of 139 samples run for Mayor Island. Those 6 samples have less than 13 ppm. Discrimination among these sources and their separation from the remainder of New Zealand sources is provided by a plot (Figure 2) of Rb by Zr.

Distinguishing among the remaining sources which, as is indicated in Figure 2, are geochemically very similar, is not easily accomplished using bivariate plots. Exploratory methods such as principal components were unable to pull apart the sources so they could be discriminated in a 2 or 3-d space. Multivariate methods, preferably with probabilistic sample assignments (Sheppard, 2004) are required. We have employed two different classification methods: discriminant analysis and classification tree analysis. Discriminant analysis is a widely available method for assigning unknowns to a set of known classes with considerable history of use in geochemical sourcing (Baxter, 1994). It assumes, however, that all classes are known and assigns all cases to the closest known; something which can be considered problematic. However all sourcing assumes all sources are known (Ward, 1974b) and discriminant analysis can have the advantage over visual discrimination in plots by providing a probability of assignment to the known sources for each sample. This results in systematic assignment of samples to sources with a known probability. Inspection of these probabilities can be used to evaluate the possibility of unknown sources, while misclassifications of knowns will inform on the degree to which sources can be discriminated.

Table 4 presents the results of discriminant analysis (SPSS 17) on the as yet undifferentiated sources using all 8 elements (Log10 transformed) in Table 3. Prior probabilities of groups (sources) were considered equal and all variables (elements) were entered into the analysis together. In total 91.8% of knowns were correctly classified to source, with Fanal/Burgess, Hahei, Maratoto, Huruiki, Onemana/Whangamata and Waihi 100% successful. Cross-validation using the leave-one-out method resulted in a total success rate of 87.2%. Inspection of misclassifications indicates that many are to neighboring sources, although there is a difficulty of discriminating among Great Barrier; its neighboring islands Fanal/Burgess and the Northland Huruiki source using the elements in this analysis. Similarly Cooks/Purangi has some overlap with its neighbor Hahei and further to the south with Maketu, which is also confused with Tairua. The large Central North Island group contains samples classified to Maketu, which is part of the same geological structure (TVZ), but also to Tairua on the Coromandel.

The possibility of unknown sources and considerable heterogeneity of some geochemical sources such as the Central North Island and Fanal/Burgess, suggests the need for a method which might allow additional partitioning of sources beyond the recognized geochemical sources defined here. Such a potential method is provided by the use of a classification tree methodology.

Although discriminant analysis is a useful method for systematically classifying unknowns, it assumes the data are derived from a multivariate normal distribution and it also looks for a holistic answer for the entire set of known classes given the complete set of selected classifier variables. Often, however, some classes or sources can be separated by one or a simple set of variables, while others require more complex solutions. In our case, for example, the values of Sr or Zr can discriminate all Mayor Island samples. This leads to a classification key or tree (Breiman, et al., 1984, De'ath and Fabricius, 2000) type approach where the problem is broken into a number of stages with division of the data at each stage, leading ultimately to definition of a known source or class. This has the advantage of being a familiar approach and specifying clearly in terms of values of specific variables or combinations of variables, the basis for each split in the tree. It also can accommodate situations where data is missing or unavailable (e.g. below detection limits) for some classes (Feldesman, 2002). The result can be represented as a tree diagram or a set of decision rules for classifying unknowns. This method is non-parametric, can make use of continuous or nominal data and makes no assumptions about normality within the data, Additionally, transformation of data has no effect on the result (Zuur, et al., 2007: 153). The difficulty is of course finding from all the possible combinations the best set of decision rules to minimize within group error (impurity) in classification. Research primarily in the field of machine learning has developed algorithms for performing this task and these methods are now routinely included in available statistical analysis packages such as SPSS or SYSTAT. In this study we have used the CRT (Classification and Regression Tree) approach implemented in SYSTAT, readers wishing an introduction to the subject should see Feldesman (2002).

Although classification tree methods have been available for some time, they appear to have seen little use in archaeology, although Baxter (2006, Baxter and Jackson, 2001) has discussed their potential for use both in investigating structure and in classification as a replacement for stepwise discriminant analysis. Using the SYSTAT routine we have employed the GINI index fitting method with a minimum split index value of 0.01 and a minimum improvement of proportional error (PRE) of 0.01. The maximum number of final nodes allowed was 20 with a minimum number of samples per node of 1. A total of 17 terminal nodes were generated with a final PRE obtained of 0.905.

Figure 3 presents the results of the classification tree analysis. Each node is labeled using the most common (mode) geochemical source found within the group. The impurity index indicates the degree of mixing or heterogeneity of the node. Impurity values of 0 indicate a pure node where all samples are from a single geochemical source. The values of the variables (elements) used to make each division are shown above the division to which the listed value applies. Therefore the first split is made using Rb+Zn <208, with samples in the node called Great Barrier having values greater than 208 and the node labeled Central North Island having values less than 208. Subsequently the Great Barrier node is divided from Fanal/Burgess on the values of Sr+Ti < 853, with Great Barrier having smaller values than Fanal/Burgess. The Great Barrier node is now a terminal node, although the impurity index indicates it still has samples from other sources. As can be seen in Table 5, which is a cross-tabulation of geochemical source against classification tree and discriminant analysis assignment, the Great Barrier classification tree grouping includes one sample from Maratoto. Further division of the Fanal/Burgess group is made to reduce the impurity value of that grouping to 0 by separating two outliers (one sample each from Great Barrier and Tairua) into a grouping which we have labeled Unknown-A. This illustrates the ability of this type of analysis to deal with outlier values. Similarly classification tree analysis can deal with multimodal distributions within sources, separating a source into a number of groups. Here Tairua, Cooks/Purangi and Central North Island have each been divided into two groups. The resulting misclassification rate is significantly improved over that from the discriminant analysis with 96% of cases correctly classified. As with the discriminant analysis, there remains some overlap among Tairua, Maketu and the Central North Island, although the Fanal/Burgess group is now perfectly separated. The least well defined groups based on the impurity index are Maketu and Tairua. Once the classification tree is produced SYSTAT generates a Basic programme which can then be run against unknowns to classify them.

4.2 Archaeological Case Study

The S11/20 site is located on Ponui Island in the Hauraki Gulf (Fig. 1). To the west of Ponui are sheltered islands of the Inner Gulf, while to the east are the deeper more exposed waters of the Firth of Thames. The island is well placed for coastal communications by canoe.

S11/20 was first excavated by V. Fisher (1956-1962) and subsequently by G. Irwin of the University of Auckland 1989-1992 (Irwin, et al., 1996, Nicholls, 1964, Wallace, nd). To the east of the stream which cuts the western side of the site, the cultural deposit lay as a dark greasy layer over natural shell and sandy gravel on a coastal flat just behind the current beach. Above the prehistoric Maori cultural horizon was an inverted topsoil buried by historic plowing and then a layer of disturbed cultural material of the same age, below modern topsoil. To the west of the stream, the cultural deposit was undisturbed and much thicker, consisting of several shell midden layers of Archaic age.

Palaeoenvironmental data conform to the pattern of the New Zealand settlement period. Analysis of charcoal data indicates a pristine forested landscape, prior to any substantial clearance (Wallace n.d.). The site also contains the bones of several species of bush birds and seabirds that went locally extinct soon after the arrival of people, and also of the tuatara, an endemic sphenodontid reptile. There was also a small amount of bone from a species of moa - a giant, extinct, wingless ratite - in the site. The overall archaeological evidence indicates a substantial hunting and fishing camp of a group of mobile and maritime people. Horticulture was present during the settlement period and Ponui would have been a climatically suitable location, however, there was no evidence for it here. C14 dates from the west of the stream are shown in Figure 4. Marine shell dates are corrected with a delta r of -7+_52 as recommended for the Hauraki Gulf by Fiona Petchy from the University of Waikato radiocarbon laboratory.

A total of 565 obsidian pieces out of 933 pieces examined were large enough to be analyzed by PXRF. Sourcing of the obsidian from the S11/20 site, which is located roughly in the centre of the distribution of New Zealand obsidian sources, provides a useful test of source preference and patterns of interaction during the settlement phase of New Zealand prehistory, and as the earliest large Archaic site excavated in the Auckland region it will serve as a baseline for future studies within the area.

4.3 Archaeological Sourcing Results

Figure 5 plots Rb by Zr with 95 % probability ellipses (MyStat v 12) for all sources and plots all archaeological samples. No archaeological samples fall into the Kaeo or Weta regions, however 382 samples, or 68% of the total sample, have the high Zr values which distinguish Mayor Island. All other samples have the low Zr (< 500 ppm) and Rb (<300 ppm) characteristic of the remainder of New Zealand sources.

Table 6 presents the results of discriminant analysis (SPSS 17) using all other sources to assign the remaining 183 archaeological unknowns using all 8 elements (Log10 transformed) presented in Table 2. Examination of the distribution of archaeological samples in a plot of their scores on the first two discriminant functions (Figure 6) shows the samples sourced to Fanal/Burgess do not cluster well together, forming a number of sub-groups. This suggests the presence of an as yet unknown geochemical source or sources which may be located in the Great Barrier/Hauraki Gulf region.

The strength of the discriminant assignments is illustrated by the plot of the distribution of probabilities of sample assignments to each source (Figure 7). The majority of unknowns (110) are assigned to Hahei with a very high probability, as are the Great Barrier and Waihi assignments. Many assignments to Fanal/Burgess, Maketu and Tairua are, in keeping with the misclassification rate for those sources, less certain. The sample assigned to the Central North Island is only marginally more like that source than another and should be questioned.

Table 6 presents the results of the classification according to the tree in Figure 3 and compares those results to that produced by the discriminant analysis. Figure 8 illustrates the effectiveness of the first 2 splits on the separation of the Great Barrier and Fanal/Burgess samples from the other sources. Although the basic pattern of source attributions remains there have been some significant changes in abundances. The 12 samples attributed to Fanal/Burgess have now reduced to only 2 with most samples re-assigned to Great Barrier or Maketu. Hahei remains the most common source, but the 110 samples assigned to it are reduced to 92 with the balance assigned to Great Barrier, Tairua and to Maketu which increases from 13 to 31 samples with the majority of re-assignments from Fanal/Burgess and Tairua. Of the marginally represented sources, the Northland Huruiki source is reduced to one sample and one additional sample is assigned to the Central North Island giving it two samples. As noted above the explanations for the changes in assignment relate primarily to situations where, in the case of discriminant analysis, source data may violate to some degree the assumptions of multivariate normality, as seems to be the case with the Fanal/Burgess source, and/or where outliers have a significant effect. In the classification tree method outliers may tend to fall into the wrong group as can be seen in Figure 8a where a Maratoto outlier falls above the split into the Great Barrier group.

5. Discussion

5.1 Characterization of New Zealand obsidian sources

Our research has shown that our PXRF system can provide sufficient precision on a useful range of elements to adequately discriminate among New Zealand obsidian sources in a fast and non-destructive manner. Separation of the major Mayor Island source and the Northland Kaeo and Weta sources can be easily accomplished using Sr, Rb and Zr, which are all determined with low detection limits and high precision. Differentiation of the remaining sources requires a multivariate approach, although as indicated by the classification tree, this could be reduced to a systematic series of biplots of elements and combinations of elements. Both discriminant analysis and classification tree analysis have produced good but not perfect separation of the geochemical sources used in this study, although the 96% success rate of the classification tree analysis is a considerable improvement over that produced by the discriminant analysis. Still there seems to be no other objective basis for choosing between these two somewhat different results, however the ability of the classification tree approach to reduce the impact of outliers and multi-modal source distributions which could adversely affect the discriminant analysis, would appear to favor that method.

Taken together, these analyses confirm the basic pattern of the importance of the Coromandel sources, in particular Hahei and very limited input from sources in Northland or Rotorua and the other inland Central North Island sources. The reduction of cases assigned to the Fanal/Burgess group by the classification tree would seem to be a reasonable outcome, both as the samples assigned by the discriminant analysis seemed very diverse (Figure 6) and the obsidian from the source is of poor quality and limited availability (Moore, 1986). Future work to assess the validity of the different outcomes could take advantage of the fact that classification tree analysis can incorporate nominal data into the analysis. This would allow the integration of both the geochemical data and data on physical properties such as color and structure, which have been used to source obsidian using the method developed by Moore (n.d. [1988]). The presence of some outliers among both the geological and archaeological samples suggests the need to look more closely at the possible effect of heterogeneity in composition created by microlites or spherulites, which are a feature of some sources and may dominate very small archaeological flake samples and also the possibility of some as yet unknown sources.

5.2. Obsidian Transport at Ponui

The Ponui (S11/20) site would appear to have been first occupied within the settlement phase of New Zealand prehistory. Although there has been considerable debate over the age of first settlement, research over the last decade has converged on a date close to 1300 AD based on proxy evidence from well dated pollen cores and dates of introduction of the Polynesian commensal, *Rattus exulans* (Hogg, et al., 2003, Wilmshurst, et al., 2008). Very shortly after arrival Polynesian sailors quickly explored most of the country as is shown by the widespread distribution of useful and attractive lithic materials from limited sources in the earliest sites of the North and South Island (Barber, 1996, Walter, et al., 2010). Although as migrants from the geologically impoverished central Pacific they would not have been familiar with obsidian, nephrite or meta-argillites, they soon readily appreciated their superior properties for the manufacture of flake cutting tools and adzes.

The presence of obsidian in many of the earliest Archaic Moa hunting sites throughout the South Island (Seelenfreund and Bollong, 1989) signaled to their early 20th century excavators that the inhabitants of these sites had long distance contacts, as obsidian was only found in the upper half of the North Island, a distance from the most southerly sites of over 1700 km by sea to the north. Systematic work on the characterisation and sourcing of obsidian in the mid 20th century showed that most of this long-distance transport was of the distinctive high quality glass from Mayor Island, which was green in transmitted light. Subsequent work has show that small amounts of Mayor Island obsidian were also carried across the open ocean beyond New Zealand 1000 km southeast to the Chatham Islands and northeast 1000 km to the Kermadecs (Anderson, 2000, Anderson and McFadgen, 1990, Leach, et al., 1986). Although the amounts of obsidian moved to the South Island were generally small, a few of the earliest sites at the bottom of the South Island had over 100 pieces recovered (e.g. Tiwai Point with 148) (Seelenfreund and Bollong, 1989: Table 3)). Study of the pattern of distribution of obsidian over time by Seelenfreund and Bollong (Seelenfreund and Bollong, 1989) showed that the early pattern of long-distance movement of obsidian changed over time and by 1600 AD obsidian was rarely transported to the South Island and in general the importance of the distinctive Mayor Island obsidian was reduced outside of the immediate hinterland of Mayor Island. Most recently it has been suggested that this change may have occurred as early as 1500 AD (Walter, et al., 2010). These changes are generally considered to be the result of increasing population density and the presence of more social barriers to trade/exchange. The pollen record from Mayor Island (Empson, et al., 2002) would support that argument as it is only after *circa* 1600 AD that we see evidence for gardening and by inference occupation of Mayor Island. Prior to that, Mayor Island, which sits 30 km off the coast, would have been an easy stop for any canoes moving along the east coast. Whether or not obsidian was being moved by means of down-the-line trade/exchange or direct procurement is hard to determine archaeologically and such movement should perhaps be best viewed as an index of interaction, however the Ponui data may make a contribution to that question given its location in the centre of the distribution of obsidian sources.

The closest obsidian source to Ponui Island is Great Barrier at 70 km to the north. Least effort models would suggest that most obsidian should come from that source, yet although the Great Barrier source was known and exploited, 67% of the obsidian pieces at Ponui come from Mayor Island requiring a journey north around the Coromandel Peninsula and then south along the coast and across to Mayor Island which is a sea distance of over 180 km. To travel from Ponui down the east coast of Coromandel meant passing through the Colville Channel at the northern end of the peninsula, which could be a difficult and sometimes dangerous passage for a canoe. Great Barrier Island, now as in the past, is a good place to stop, rest and wait for good weather before heading further south on the coast (Fig. 1). Using the classification tree results, Great Barrier actually ranks third in popularity after Mayor Island and Hahei. It is often suggested that the popularity of Mayor Island obsidian is explained by the superior quality of the material; it is highly vitreous has excellent conchoidal fracture and few inclusions or fracture planes. It is the best quality flaking obsidian in New Zealand, however it was rarely flaked in any demanding fashion other than simple free-hand percussion to produce sharp edges; most of the other sources could have served equally well. Yet even if the properties of Mayor Island obsidian were sought after, the east coast of the Coromandel was clearly an attractor for additional reasons given the importance of the Hahei and Tairua sources in the S11/20 assemblage.

There is a strong body of evidence to suggest that boats in this early period were stable and seaworthy twin-hulled canoes with a two-spar rig known as an Oceanic spritsail, which enabled them to steer courses across and with the direction of the wind (Finney, 2006, Irwin, 2008). The stretch of Coromandel coast in question is excellent for passage-making in good weather, but rocky and exposed in bad conditions. However, there were safe havens at intervals all the way down the coast to the Bay of Plenty to reach the obsidian source at Maketu and Mayor Island itself has a well sheltered harbour on its southwest coast. An interesting correspondence is found in the archaeological evidence because, in most places where a canoe could find good shelter on the coast or on offshore islands, there is a known Archaic site.

The Hahei source is on the south side of the Whitianga harbor, the largest harbor on the Coromandel with an extensive estuary along which there is considerable evidence of Archaic occupation. Similarly Tairua is the next harbor south of Hahei to have a large estuary and evidence of very early Archaic occupation, while the Maketu source is just beyond the last large harbor on that coast at Tauranga, opposite Mayor Island. It seems most probable that these resource rich areas attracted early populations of highly mobile people (Walter, et al., 2010, Walter, et al., 2006). Under the low population density conditions of the settlement phase, these people may have moved from one resource rich patch to the next. Under that scenario the obsidian at Ponui would have been directly procured at Mayor Island and along the Coromandel. Alternatively under low density conditions social networks would have been geographically large, bringing into touch distant populations focused on resource rich locations. Such networks may have exchanged materials over long distances. Of course a mixed model may have operated with both direct procurement and exchange operating. The presence of small amounts of material from Huruiki 200 km to the north or from the Central North Island indicates low level contacts into those most distant regions.

6. Conclusions

The development of portable XRF in the last decade has provided archaeology with a new tool suitable for use in the lab and field and requiring little technical or specialist support. Our experience at Auckland (Sheppard, et al., 2010) has shown that such instruments are able to provide useful geochemical data in a non-destructive manner on large datasets in comparatively short periods of time - something which was rarely possible when using earlier technologies located outside archaeological laboratories. Adoption of the sort of protocols around the use of standards and monitoring of machine performance which are standard in most geochemical laboratories, will allow archaeologists to compare results and assess precision and accuracy.

Generating geochemical data is however only half of the sourcing routine, as methods need to be created to discriminate sources and assign unknowns. Much of this has depended on the plotting of unknowns against clouds of source samples, either through simple plots of 2 or 3 elements or ratios or the plotting of data using principal components which summarize elemental variation. Although in many cases this can be all that is required, in others we may be left wondering how strong the assignment is and some statement of probability might be desired (Sheppard, 2004). Discriminant analysis provides a means of objectively assigning unknowns to classes. Different analysts using the same dataset will come to the same answer and the program can generate a probability of assignment which can be useful to the reader needing to assess the weight of the result. Unfortunately discriminant analysis makes assumptions about the nature of the data distribution and can remain something of a black box. Our experiment with the use of classification tree analysis has resulted in a significant improvement in our ability to discriminate sources. This approach makes no assumptions about the data distribution and generates a classification scheme which is easily understandable and verified. It is also able to accommodate a mix of data types and this will allow integration of geochemical data with other physical observations which may find substantial use in the sourcing of a variety of archaeological materials (e.g. mineralogical data with geochemistry).

Although obsidian sourcing in New Zealand has a long history, PXRF provides the first reliable easily accessible system for archaeological geochemical characterization. The results of our fine grained study of the obsidian from the early settlement period site on Ponui Islands in the Hauraki Gulf lends weight to the hypothesis that the early inhabitants of northern New Zealand were highly mobile (Walter, et al., 2010) or had broad networks of communication (Leach, 1978). Additional work looking at variation in source use through time and space in the Auckland region and the effects of demographic and economic change should shed light on how the regional communication or social field was structured (Rodseth, 1998).

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Table 6. Cross tabulation of archaeological sample sourcing comparing results of the discriminant analysis with those from the classification tree approach.

Table 1 Geochemical source samples. The numbers in brackets refer to size of sampled collection

	Collection		
Geochemical Source	Jones (2002)	Auckland Reference	Total
Great Barrier	49 (141)	10	59
Fanal/Burgess	4 (15)	6	10
Cooks/Purangi	10(10)	10	20
Hahei	10(10)	5	15
Huruiki	8(15)	5	13
Maketu	8(70)	0	8
Maratoto	2(39)	5	7
Onemana/Whangamata	8(8)	0	8
Central North Island	49(57)	10	59
Rotorua	5(19)	5	10
Tairua	16(16)	5	21
Waihi	22(22)	5	27
Mayor Island	131(921)	6	139
Kaeo	26(67)	10	36
Weta	2(10)	0	2
Total	352	82	434

Table 2 PXRF analysis of standards.and data quality controls.

	Quality Control				Standards											
	Mayor Island 9.3 Solid				NIST SRM 278 PXRF				Certified Values		NIST SRM 2709 PXRF				Certified Values	
ppm	N	Mean	Std	CV	N	Mean	Std	CV	Mean	Uncertainty	N	Mean	Std	CV	Mean	Uncertainty
Ti	51	1735.2	211.9	0.12	38	1497.6	56.8	0.04	1468.7	42.0	29	4466.9	135.2	0.03	3420.0	200.0
Mn	51	871.0	113.6	0.13	38	197.0	21.6	0.11	402.0	15.5	29	542.0	29.1	0.05	538.0	17.0
Fe	51	36942.0	2949.8	0.08	38	13360.3	321.0	0.02	14278.7	140.0	29	38151.6	605.1	0.02	35000.0	1100.0
Zn	51	194.2	24.0	0.12	38	38.7	2.3	0.06	55.00	Recommended	27	82.9	3.9	0.05	106.0	3.0
Rb	51	146.5	16.9	0.12	38	124.2	6.3	0.05	127.5	0.3	27	94.1	2.9	0.03	96.0	Recommended
Sr		< LOD			38	68.1	9.7	0.14	63.5	0.0	27	236.9	4.6	0.02	231.0	2.0
Zr	51	1146.9	131.3	0.11	38	268.4	20.4	0.08			27	130.7	3.2	0.02	160.0	Recommended
Pb	51	30.5	4.0	0.13	38	20.7	3.0	0.14	16.4	0.2	27	18.7	1.9	0.10	18.9	0.5

Table 3 PXRF results for geochemical sources.

Geochemical Source	N	Ti ppm Mean	Ti ppm Std	Mn ppm Mean	Mn ppm Std	Fe ppm Mean	Fe ppm Std	Zn ppm Mean	Zn ppm STD	Rb ppm Mean	Rb ppm Std	Sr ppm Mean	Sr ppm Std	Zr ppm Mean	Zr ppm Std	Pb ppm Mean	Pb ppm Std
Great Barrier	59	567.9	132.3	222.2	45.5	8,574.1	1,022.6	44.3	11.9	202.8	45.7	30.2	6.6	149.8	25.1	29.1	7.7
Fanal/Burgess	10	1,116.7	253.3	200.6	74.6	10,342.1	3,645.3	61.1	45.3	200.4	13.1	46.5	8.9	243.4	149.9	27.7	3.7
Cooks/Purangi	20	657.8	122.4	374.2	32.6	8,395.4	454.7	34.8	3.8	117.8	3.8	70.1	7.2	127.6	4.2	19.1	2.2
Hahei	15	573.0	84.2	403.1	27.6	10,238.7	421.5	40.0	3.5	132.7	3.9	93.4	2.6	134.7	6.0	24.5	2.0
Huruiki	13	645.2	125.0	193.4	30.9	7,960.1	194.3	36.8	3.2	137.1	2.6	38.1	1.9	145.4	3.9	21.4	2.1
Rotorua	10	777.4	239.9	323.5	82.3	7,383.0	474.7	34.2	6.1	119.9	16.5	87.1	20.6	120.7	7.4	23.2	3.2
Maketu	8	726.3	278.0	327.0	37.5	8,896.1	1,043.9	32.0	3.7	132.8	18.2	89.9	9.2	132.8	33.3	20.9	4.2
Maratoto	7	472.3	39.1	294.3	22.7	5,811.9	415.8	23.3	7.1	171.3	7.0	32.6	2.4	75.9	5.5	25.0	1.8
Onemana/ Whangamata	8	566.4	118.3	278.5	28.5	7,911.9	197.0	38.8	2.5	131.9	6.4	34.0	2.9	119.3	8.5	23.8	2.4
Central North Island	59	881.6	237.5	300.7	26.6	7,663.4	995.8	25.7	2.9	126.8	8.1	86.5	10.0	129.4	23.9	19.0	2.6
Tairua	21	1,141.4	262.2	320.3	37.6	9,861.5	921.0	33.0	3.0	119.6	20.2	122.7	52.6	168.6	21.5	19.5	3.7
Waihi	27	1,630.4	232.6	365.1	47.1	12,723.6	546.4	31.5	4.9	111.1	7.4	163.3	14.0	127.0	7.7	17.6	2.4
Mayor Island	139	1480.7	251.4	843.9	153.4	36,759.9	6115.4	189.3	21.2	137.1	8.4	5.7	3.4	1,103.7	96.8	28.5	4.2
Kaeo	36	990.2	210.1	674.0	63.0	34,727.5	927.5	295.0	11.6	654.3	15.3	<LOD	.	2,059.6	38.2	91.0	5.1
Weta	2	566.5	198.7	136.5	3.5	6,545.0	130.1	44.0	1.4	441.5	0.7	<LOD	.	117.5	0.7	44.5	2.1

Table 4 Results of discriminant analysis classification of geochemical sources. Cross validation is done only for those cases in the analysis. In cross validation, each case is classified by the functions derived from all cases other than that case;. 91.8% of original grouped cases were correctly classified and. 87.2% of cross-validated grouped cases were correctly classified.

		Predicted Group Membership												
	Geochemical Source	Great Barrier	Fanal Burgess	Cooks Purangi	Hahei	Huruiki	Rotorua	Maketu	Maratoto	Onemana Whangamata	Central North Island	Tairua	Waihi	Total
Original	Great Barrier	55	3	0	0	1	0	0	0	0	0	0	0	59
	Fanal/Burgess	0	10	0	0	0	0	0	0	0	0	0	0	10
	Cooks/Purangi	0	0	18	1	0	0	1	0	0	0	0	0	20
	Hahei	0	0	0	15	0	0	0	0	0	0	0	0	15
	Huruiki	0	0	0	0	13	0	0	0	0	0	0	0	13
	Rotorua	0	0	0	0	0	9	0	0	0	1	0	0	10
	Maketu	0	0	0	0	0	0	5	0	0	1	2	0	8
	Maratoto	0	0	0	0	0	0	0	7	0	0	0	0	7
	Onemana/ Whangamata	0	0	0	0	0	0	0	0	8	0	0	0	8
	Central North Island	0	0	1	0	0	4	1	0	0	49	4	0	59
	Tairua	0	0	0	0	0	0	1	0	0	0	20	0	21
	Waihi	0	0	0	0	0	0	0	0	0	0	0	27	27
Cross-validated	Great Barrier	54	4	0	0	1	0	0	0	0	0	0	0	59
	Fanal/Burgess	1	9	0	0	0	0	0	0	0	0	0	0	10
	Cooks/Purangi	0	0	18	1	0	0	1	0	0	0	0	0	20
	Hahei	0	0	0	14	0	0	1	0	0	0	0	0	15
	Huruiki	0	0	0	0	12	0	0	0	1	0	0	0	13
	Rotorua	0	0	0	0	0	7	0	0	0	2	1	0	10
	Maketu	0	0	1	1	0	0	2	0	0	1	3	0	8
	Maratoto	0	0	0	0	0	0	0	7	0	0	0	0	7
	Onemana/ Whangamata	0	0	0	0	0	0	0	0	8	0	0	0	8
	Central North Island	0	0	3	0	0	4	1	0	0	47	4	0	59

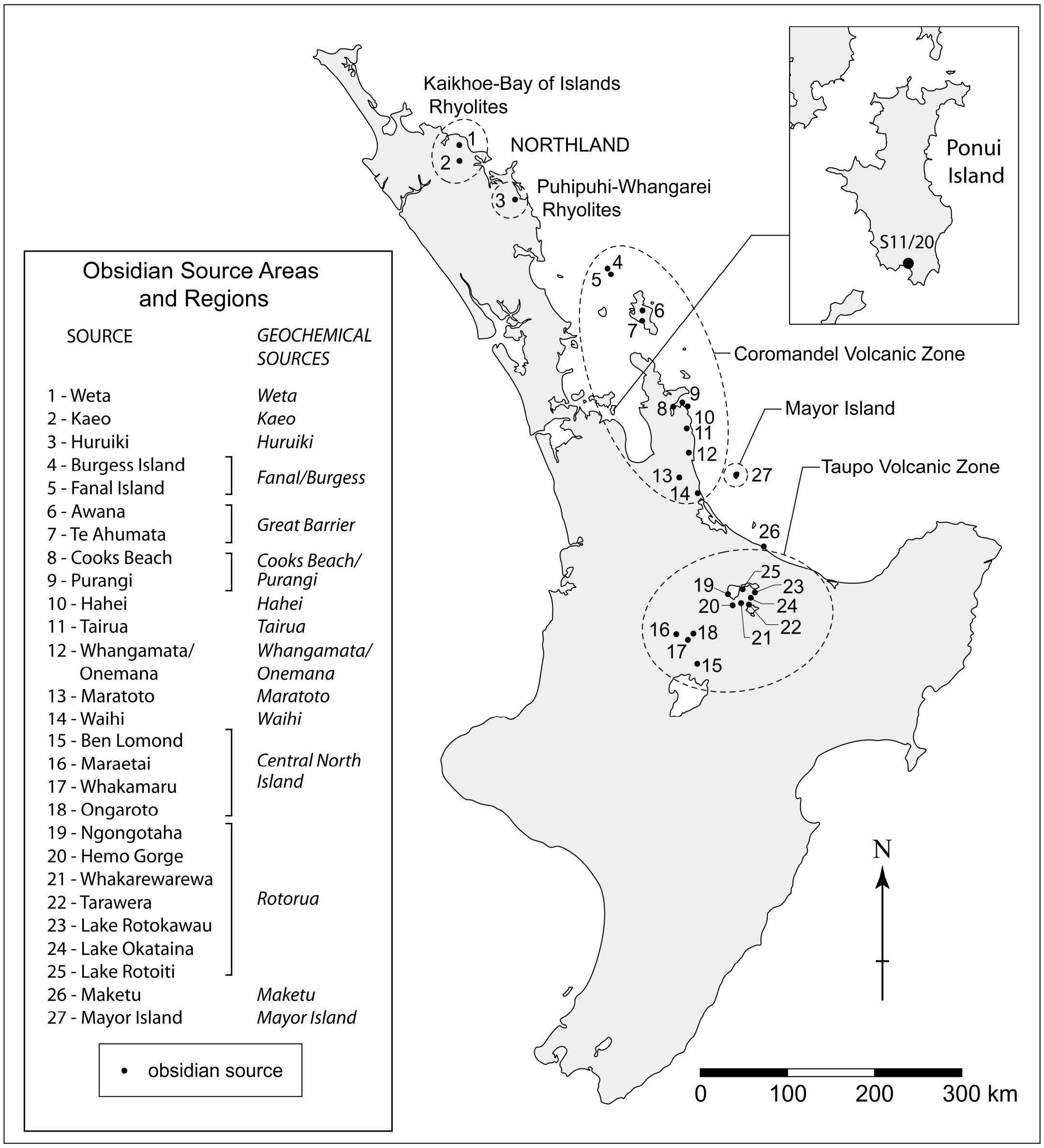
Tairua	0	0	0	0	0	1	1	0	0	0	19	0	21
Waihi	0	0	0	0	0	0	0	0	0	0	0	27	27

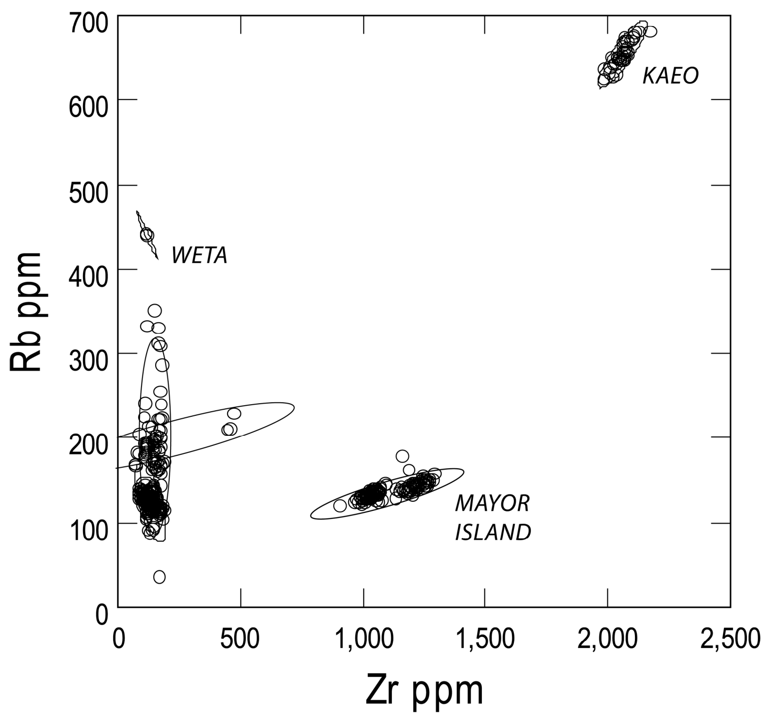
Table 5 Cross tabulation of geochemical sources comparing results of the discriminant analysis with those from the classification tree approach.

Discriminant Results	Classification Tree Results: Great Barrier	Fanal Burgess	Cooks Purangi	Hahei	Huruiki	Rotorua	Maketu	Maratoto	Onemana Whangamata	Central North Island	Tairua	Waihi	Total
Great Barrier	58	0	0	0	0	0	0	0	0	0	0	0	58
Fanal/Burgess	0	10	0	0	0	0	0	0	0	0	0	0	10
Cooks/Purangi	0	0	20	0	0	0	0	0	0	0	0	0	20
Hahei	0	0	0	15	0	0	0	0	0	0	0	0	15
Huruiki	0	0	0	0	13	0	0	0	0	0	0	0	13
Rotorua	0	0	0	0	0	5	0	0	0	3	0	0	8
Maketu	0	0	0	0	0	0	2	0	0	2	2	0	6
Maratoto	1	0	1	0	0	0	0	5	0	0	0	0	7
Onemana/Whangamata	0	0	0	0	0	0	0	0	8	0	0	0	8
Central North Island	0	0	0	0	0	0	0	0	0	59	0	0	59
Tairua	0	0	0	0	0	0	1	0	0	0	19	0	20
Waihi	0	0	0	0	0	0	0	0	0	0	0	27	27
Total	59	10	21	15	13	5	3	5	8	64	21	27	251

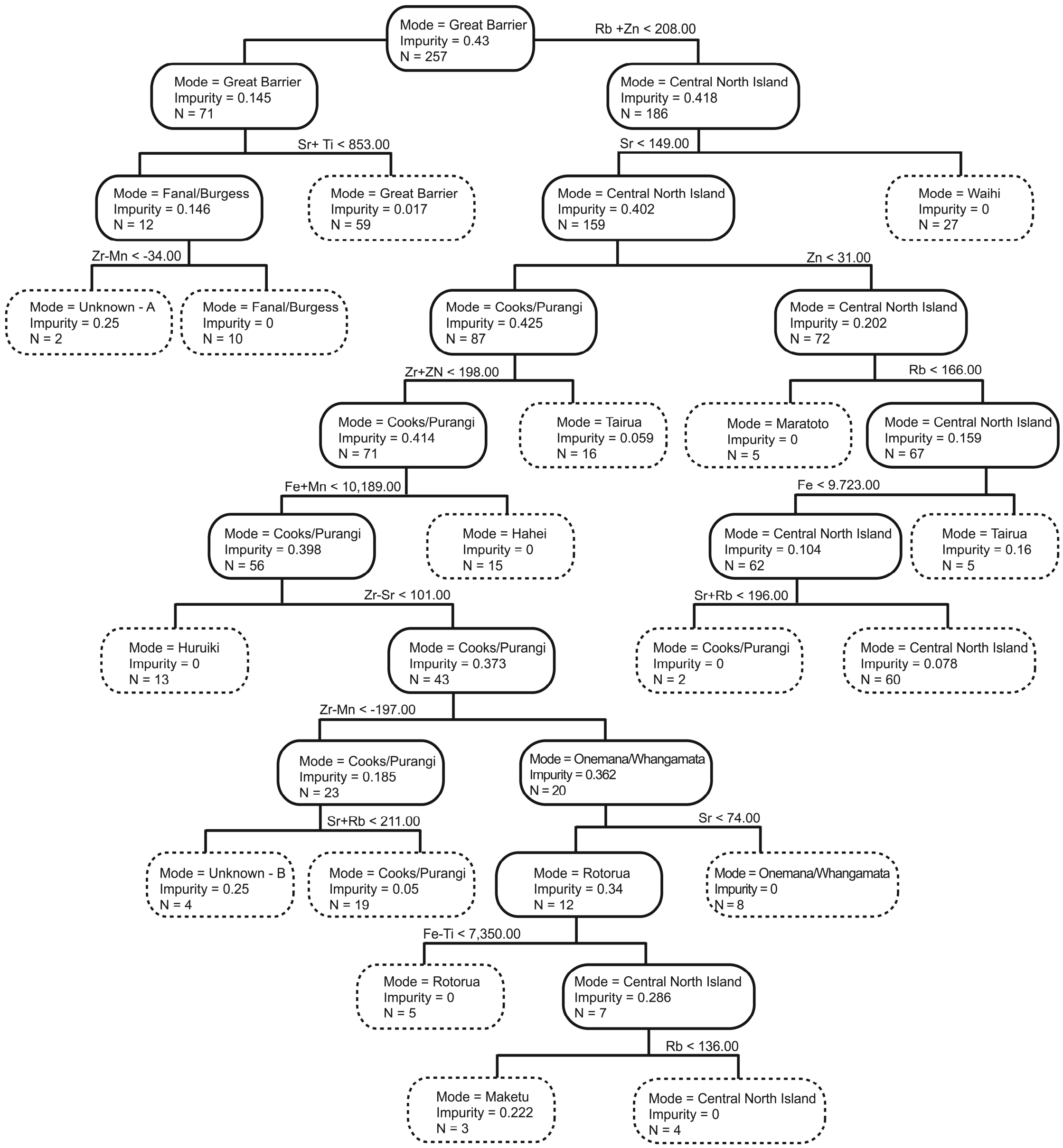
Table 6 Cross tabulation of archaeological sample sourcing comparing results of the discriminant analysis with those from the classification tree approach.

	Classification Tree Results										
Discriminant Results	Great Barrier	Fanal Burgess	Cooks Purangi	Hahei	Huruiki	Maketu	Onemana Whangamata	Central North Island	Tairua	Waihi	Total
Central North Island	0	0	0	0	0	0	0	1	0	0	1
Cooks/Purangi	0	0	4	0	0	0	0	1	0	0	5
Fanal/Burgess	4	2	0	0	0	6	0	0	0	0	12
Great Barrier	14	0	0	0	0	0	0	0	0	0	14
Hahei	13	0	0	89	0	4	0	0	4	0	110
Huruiki	1	0	0	0	1	1	1	0	0	0	4
Maketu	0	0	0	3	0	10	0	0	0	0	13
Tairua	2	0	0	0	0	7	0	0	0	0	9
Waihi	1	0	0	0	0	3	0	0	1	10	15
Total	35	2	4	92	1	31	1	2	5	10	183

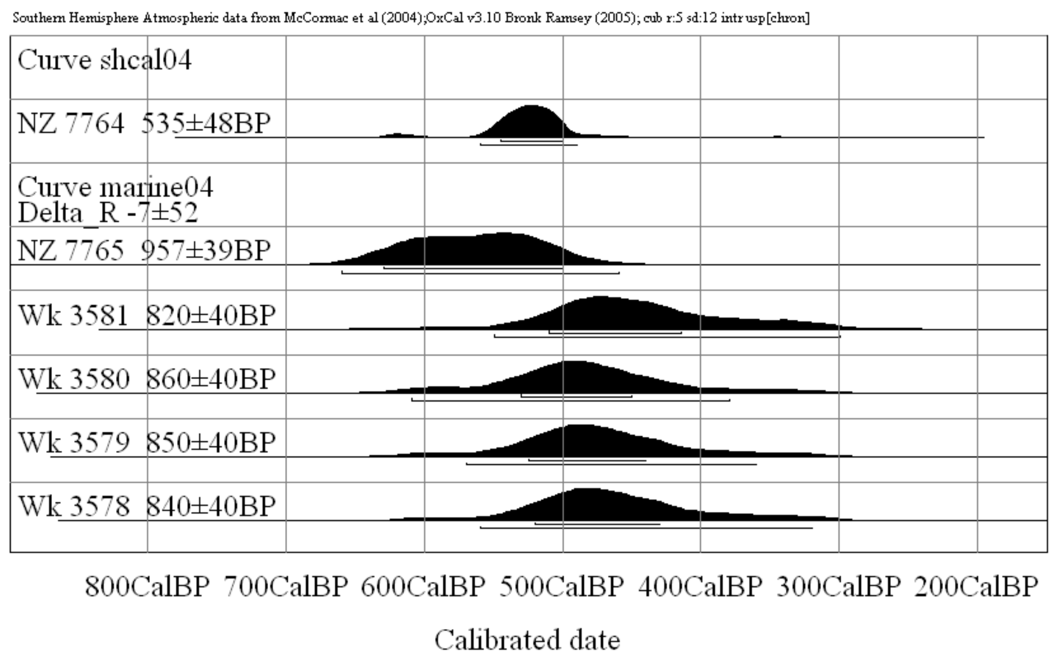

Kaikhoe-Bay of Islands
Rhyolites
NORTHLAND
Puhipuhi-Whangarei
Rhyolites
Coromandel Volcanic Zone
Mayor Island
Taupo Volcanic Zone
Ponui
Island
S11/20
Obsidian Source Areas
and Regions
SOURCE
GEOCHEMICAL SOURCES
1 - Weta
Weta
2 - Kaeo
Kaeo
3 - Huruiki
Huruiki
4 - Burgess Island
5 - Fanal Island
Fanal/Burgess
6 - Awana
7 - Te Ahumata
Great Barrier
8 - Cooks Beach
9 - Purangi
Cooks Beach/ Purangi
10 - Hahei
Hahei
11 - Tairua
Tairua
12 - Whangamata/ Onemana
Whangamata/ Onemana
13 - Maratoto
Maratoto
14 - Waihi
Waihi
15 - Ben Lomond
16 - Maraetai
17 - Whakamaru
18 - Ongaroto
Central North Island
19 - Ngongotaha
20 - Hemo Gorge
21 - Whakarewarewa
22 - Tarawera
23 - Lake Rotokawau
24 - Lake Okataina
25 - Lake Rotoiti
Rotorua
26 - Maketu
Maketu
27 - Mayor Island
Mayor Island
obsidian source
N
0
100
200
300 km



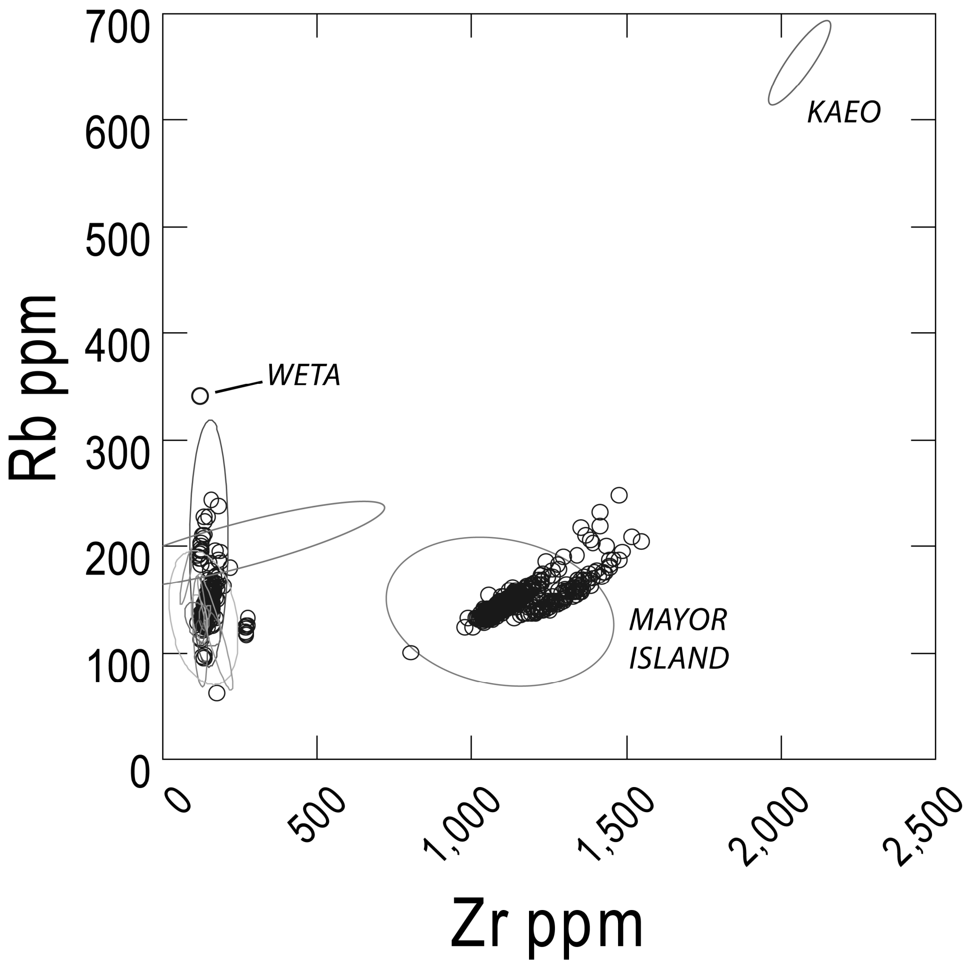
700
600
500
400
300
200
100
0
Rb ppm
0
500
1,000
1,500
2,000
2,500
Zr ppm
KAEO
WETA
MAYOR
ISLAND

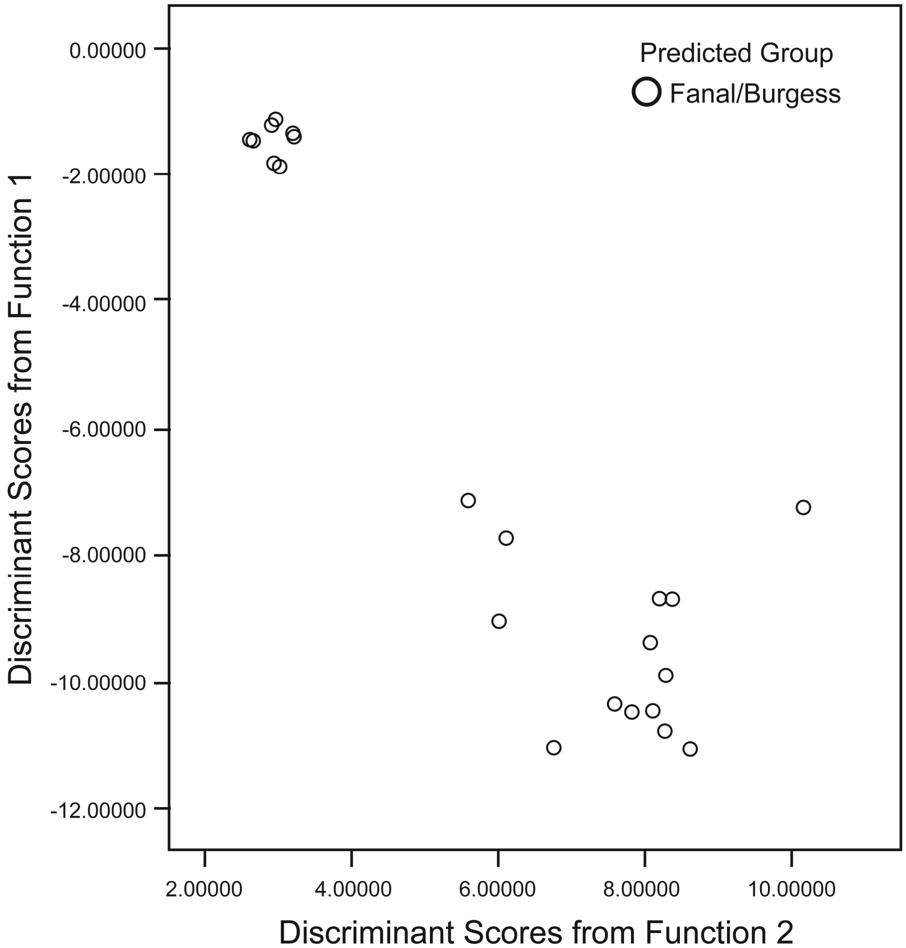


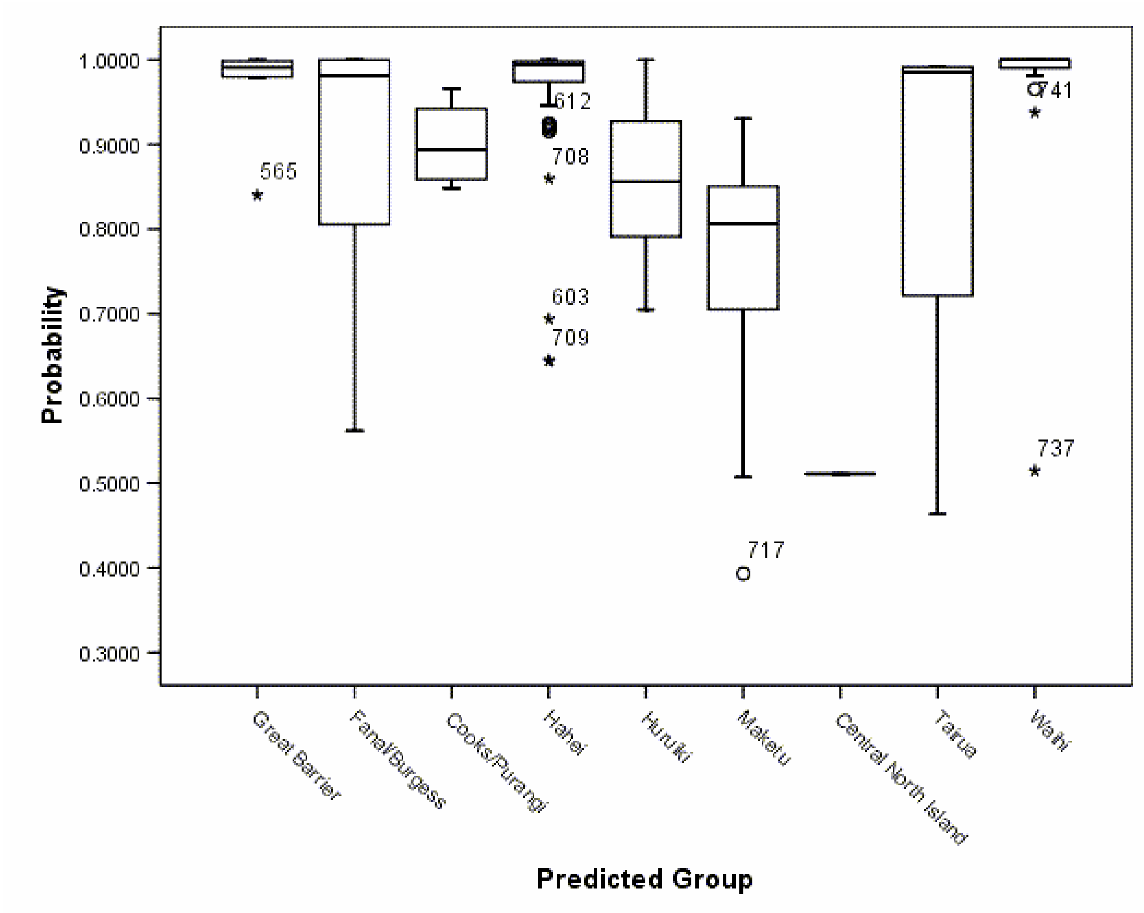
Mode = Great Barrier
Impurity = 0.43
N = 257
Rb +Zn < 208.00
Mode = Great Barrier
Impurity = 0.145
N = 71
Mode = Central North Island
Impurity = 0.418
N = 186
Sr+ Ti < 853.00
Sr < 149.00
Mode = Fanal/Burgess
Impurity = 0.146
N = 12
Mode = Great Barrier
Impurity = 0.017
N = 59
Mode = Central North Island
Impurity = 0.402
N = 159
Mode = Waihi
Impurity = 0
N = 27
Zr-Mn < -34.00
Zn < 31.00
Mode = Unknown - A
Impurity = 0.25
N = 2
Mode = Fanal/Burgess
Impurity = 0
N = 10
Mode = Cooks/Purangi
Impurity = 0.425
N = 87
Mode = Central North Island
Impurity = 0.202
N = 72
Zr+ZN < 198.00
Rb < 166.00
Mode = Cooks/Purangi
Impurity = 0.414
N = 71
Mode = Tairua
Impurity = 0.059
N = 16
Mode = Maratoto
Impurity = 0
N = 5
Mode = Central North Island
Impurity = 0.159
N = 67
Fe+Mn < 10,189.00
Fe < 9,723.00
Mode = Cooks/Purangi
Impurity = 0.398
N = 56
Mode = Hahei
Impurity = 0
N = 15
Mode = Central North Island
Impurity = 0.104
N = 62
Mode = Tairua
Impurity = 0.16
N = 5
Zr-Sr < 101.00
Sr+Rb < 196.00
Mode = Huruiki
Impurity = 0
N = 13
Mode = Cooks/Purangi
Impurity = 0.373
N = 43
Mode = Cooks/Purangi
Impurity = 0
N = 2
Mode = Central North Island
Impurity = 0.078
N = 60
Zr-Mn < -197.00
Mode = Cooks/Purangi
Impurity = 0.185
N = 23
Mode = Onemana/Whangamata
Impurity = 0.362
N = 20
Sr+Rb < 211.00
Sr < 74.00
Mode = Unknown - B
Impurity = 0.25
N = 4
Mode = Cooks/Purangi
Impurity = 0.05
N = 19
Mode = Rotorua
Impurity = 0.34
N = 12
Mode = Onemana/Whangamata
Impurity = 0
N = 8
Fe-Ti < 7,350.00
Mode = Rotorua
Impurity = 0
N = 5
Mode = Central North Island
Impurity = 0.286
N = 7
Rb < 136.00
Mode = Maketu
Impurity = 0.222
N = 3
Mode = Central North Island
Impurity = 0
N = 4



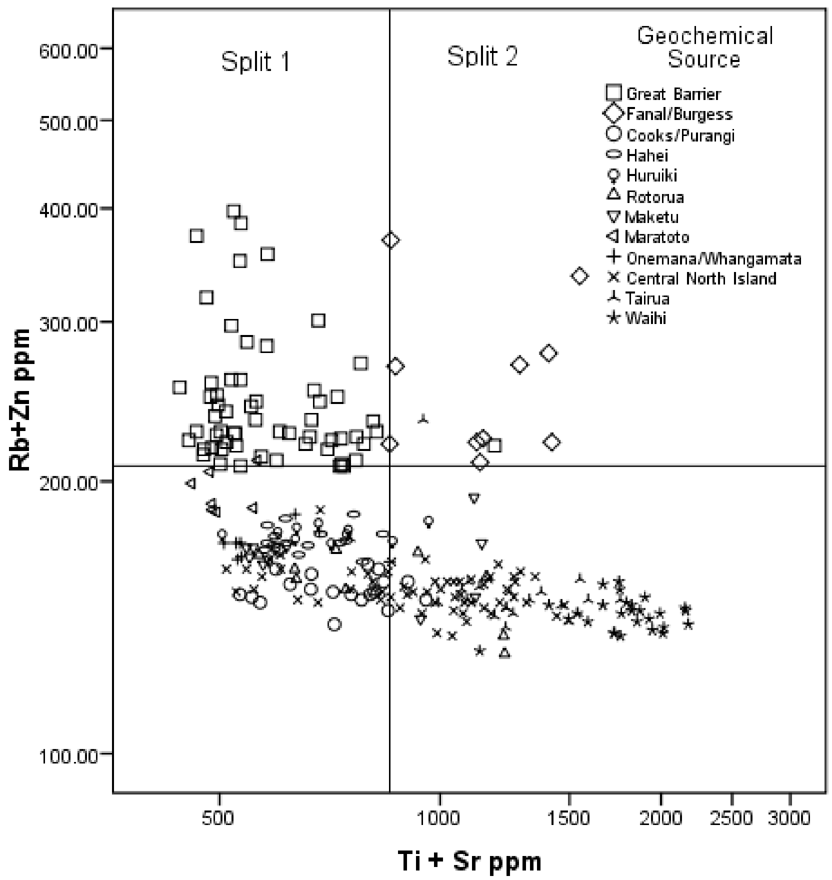
Southern Hemisphere Atmospheric data from McCormac et al (2004);OxCal v3.10 Bronk Ramsey (2005); cub r:5 sd:12 intr usp[chron]
Curve shcal04
NZ 7764 535±48BP
Curve marine04
Delta_R -7±52
NZ 7765 957±39BP
Wk 3581 820±40BP
Wk 3580 860±40BP
Wk 3579 850±40BP
Wk 3578 840±40BP
800CalBP 700CalBP 600CalBP 500CalBP 400CalBP 300CalBP 200CalBP
Calibrated date

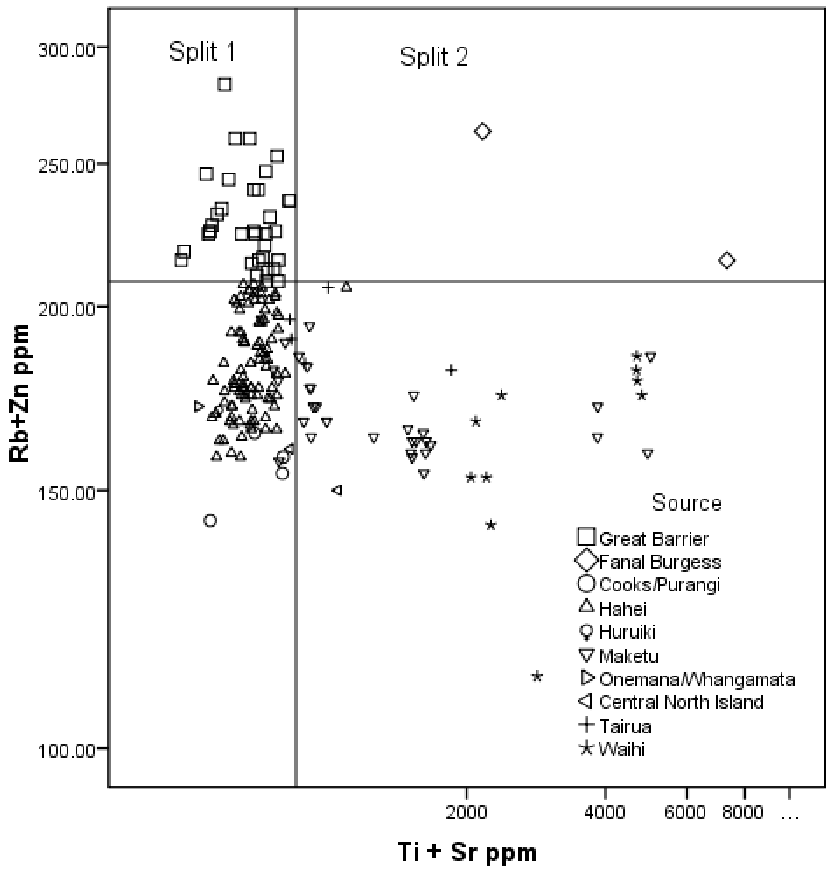

Rb ppm
700
600
500
400
300
200
100
0
0
500
1,000
1,500
2,000
2,500
Zr ppm
KAEO
WETA
MAYOR ISLAND


Predicted Group
Fanal/Burgess
0.00000
-2.00000
-4.00000
-6.00000
-8.00000
-10.00000
-12.00000
Discriminant Scores from Function 1
2.00000
4.00000
6.00000
8.00000
10.00000
Discriminant Scores from Function 2



1.0000
0.9000
0.8000
0.7000
0.6000
0.5000
0.4000
0.3000
Probability
565
612
708
603
709
717
741
737
Great Barrier
Fanal/Burgess
Cooks/Purangi
Hahei
Huruiki
Maketu
Central North Island
Tairua
Waihi
Predicted Group


Split 1
Split 2
Geochemical Source
Great Barrier
Fanal/Burgess
Cooks/Purangi
Hahei
Huruiki
Rotorua
Maketu
Maratoto
Onemana/Whangamata
Central North Island
Tairua
Waihi
Rb+Zn ppm
600.00
500.00
400.00
300.00
200.00
100.00
500
1000
1500
2000
2500
3000
Ti + Sr ppm



Split 1
Split 2
300.00
250.00
200.00
150.00
100.00
Rb+Zn ppm
2000
4000
6000
8000
Ti + Sr ppm
Source
Great Barrier
Fanal Burgess
Cooks/Purangi
Hahei
Huruiki
Maketu
Onemana/Whangamata
Central North Island
Tairua
Waihi