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Visual and Geochemical Characterisation of Late Cretaceous-Eocene Cherts from Eastern New Zealand: A preliminary study

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ABSTRACT

Sedimentary chert from the eastern North Island and Marlborough region of the South Island, New Zealand (collectively referred to here as the Eastern Chert Province, ECP), was utilised by indigenous Māori communities from the 14th to 18th century. The chert is associated with Late Cretaceous-Paleocene siliceous shale of the Whangai Formation (*Whangai chert*) in the North Island, and the Late Cretaceous-Eocene Mead Hill Formation and overlying Amuri Limestone in Marlborough (*Kaikoura chert*). There is also an isolated occurrence at Tora, in south-eastern Wairarapa (*Tora chert*). Visual/petrographic attributes of these chert types are very similar, though some samples from Marlborough are calcareous and contain dolomite rhombs. Chemical analysis of geological samples, by wavelength-dispersive XRF (WDXRF) and portable XRF (pXRF), shows that the Whangai and Kaikoura cherts can be largely differentiated on the basis of Zr, Sr and Rb concentrations, but that the Tora chert is chemically indistinguishable from the Whangai chert. A separate group is recognised within the Kaikoura chert, characterised by higher Sr, Ca and Ba values, but there seems to be limited potential for the identification of specific sources within the ECP.

Keywords: chert; petrography; geochemistry; WDXRF; pXRF; New Zealand

INTRODUCTION

Chert is one of the more common lithic materials found on archaeological sites in Aotearoa New Zealand, particularly those dating to the early prehistoric period from the 14th to 16th century, where it was used primarily for cutting and scraping purposes as well as for drill points (e.g. Prickett 1979). Some adzes and chisels were also made from this material. There has been minimal research into the actual sources of the chert, although a few small-scale studies (Walls 1971, Leach 1977, Brassey 1985, Moore and Wilkes 2005, Moore 2019) have provided useful information. Progress has also been hampered to some extent by the limited geological knowledge of New Zealand cherts (Moore 1977, 1983).

The use of chemical analysis to identify the source of chert artefacts has been explored in a number of studies in various parts of the world (e.g. Sheppard 1996, Malyk-Selivanova *et al*. 1998, Speer 2014, Andreeva *et al*. 2014), but many of the analytical methods employed (wavelengthdispersive XRF (WDXRF), LA-ICP-MS, neutron activation) are sample-destructive and costly. Consequently, there has been growing interest in the application of inexpensive, readily available and non-destructive portable XRF (pXRF) to produce elemental data which are quantitative, accurate, and reproducible (e.g. Harrington and Farley 2015, Mehta *et al*. 2017, Newlander and Lin 2017, see also Frahm 2014). In this preliminary study, macroscopic and petrographic attributes, and WDXRF and pXRF analyses, are used to characterise sedimentary cherts from three different geologic formations in eastern New Zealand, and establish whether these could provide a reliable means, in future, of determining the provenance of chert artefacts.

GEOLOGICAL CONTEXT

There are significant occurrences of chert in two main areas of New Zealand: in the Northland–Auckland–Coromandel Peninsula region, provisionally termed the *Northern Chert Province*; and along the eastern side of the North Island and north-eastern part of the South Island, here referred to as the *Eastern Chert Province* (Figure 1). Chert is rare in the central-western part of the North Island, though the distinctive Raglan chert was widely utilised along the west coast (Moore and Wilkes 2005). Only sporadic chert occurrences are known in the southern half of the South Island (Moore 1977, 2019). The Eastern Chert province (ECP) can be conveniently divided into three separate regions or sectors: Gisborne-East Cape ('East Coast' *sensu strictu*), Southern Hawkes Bay-Wairarapa, and Marlbor-

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Figure 1. Extent of the Eastern Chert Province (darker shading), and location of other important sedimentary chert sources (open triangles).

ough, in the north-eastern South Island. Overall, the ECP extends for a distance of approximately 680km.

The main chert-bearing unit in the eastern North Island is the Whangai Formation, a widespread siliceous mudstone or shale of Late Cretaceous-Paleocene age (Moore 1983, 1988). It outcrops discontinuously from East Cape to southern Wairarapa, and is up to 500 m thick. Chert is relatively rare and generally occurs in the form of isolated nodules or lenses, though some bedded intervals have been recorded ranging from <1m to about 30 m in thickness (Moore 1988). The Mungaroa Limestone in south-eastern Wairarapa has, in the past, also been regarded as an important source of chert (Keyes 1970, Walls 1971). However, a recent geological study of this formation in the Tora area showed that it contains only rare nodules of chert, and that the main occurrence consists of exotic clasts within the Eocene Pukemuri Siltstone (Hines *et al*. 2013). The Mungaroa Limestone is a lateral equivalent of

the Amuri Limestone in Marlborough (Moore 1983, Lawrence 1989).

In Marlborough the main chert-bearing units are the Mead Hill Formation (of Late Cretaceous-Paleocene age) and overlying Amuri Limestone (Paleocene-Eocene). The Mead Hill, also referred to in some early reports as the 'Flint Beds' (Thomson 1916), consists of hard, greenish grey micritic limestone with abundant lenses and nodules of chert, and is locally up to 250m thick (Rattenbury *et al*. 2006). The chert is commonly associated with dolomite (Lawrence 1994). The more extensive Amuri Limestone is composed predominantly of hard, white siliceous micritic limestone and marl with only minor chert. A detailed petrographic and geochemical study of chert in the Mead Hill and Amuri formations was undertaken by Lawrence (1989, 1993, 1994).

There are other, older chert-bearing units in the eastern North Island and Marlborough (Moore 1977, 1983), but the

chert is generally of very poor flake quality and there is no indication that it was utilised to any extent by Māori. Known sedimentary cherts elsewhere, at Raglan (Moore and Wilkes 2005), Pahautane, and Gordon's Valley (Moore 2019) (Figure 1), all have visual characteristics which are quite distinct from ECP chert. The Pahautane and Gordon's Valley cherts are associated with bioclastic limestones of Oligocene age.

LOCATION AND NATURE OF CHERT OCCURRENCES

For the purposes of this study, occurrences of detrital chert in river and stream beds and on coastal beaches were specifically targeted, as this was believed to most closely reflect the strategy employed in prehistoric times. It was also expected that, on the whole, detrital material would be less fractured than samples obtained from outcrops, and provide a better indication of the range in variation of visual attributes. Some sample locations were previously known (e.g. Whangara, Tora, Waipapa Bay; Keyes 1970, Moore 1977, Jones and Moore 1985), but many have not been recorded before.

There are two important occurrences of detrital chert in the Gisborne-East Cape region, in the lower Mata River

and at Whangara (Figure 2). Chert nodules have also been found *in situ* within the Whangai Formation in the upper Mata River and elsewhere (Moore 1988). In southern Hawkes Bay-Wairarapa, chert beds, lenses and nodules have been recorded in the Whangai Formation at a number of localities (Moore 1988). Detrital material is also common in some rivers, streams and along parts of the coast, such as at Owahanga, the Mataikona River, and Orui. At Tora, chert occurs in several local streams, but appears to be less widely distributed than indicated in some earlier reports (Keyes 1970).

In Marlborough, there are sporadic outcrops of chert between Cape Campbell and Kaikōura, and in the upper Clarence Valley (Lawrence 1989, 1993, Figure 2), and some of the rivers and streams in this area contain common detrital material, particularly the Waima and Kekerengu rivers, though it is rare in others (e.g. Puhipuhi River). Chert is found *in situ* along parts of the coast at Ward Beach, Waipapa Bay, Kaikōura Peninsula and Oaro, but does not occur south of Haumuri Bluff. Although locally abundant, much of the chert in outcrops is highly fractured and incapable of yielding useable flakes (Figure 3). No obvious pre-European quarries have been identified.

Figure 2. Sample locations and other chert occurrences within the Eastern Chert Province.

Figure 3. Examples of ECP chert. a: Whangai chert, lower Mata River (locality EC1), showing conchoidal fracture; b: flake of Tora chert with white chalcedony veins, Tora (sample EC7/6); c: *In situ* nodule of highly fractured Kaikoura chert, Mead Hill Formation, Waipapa Bay (EC10); d: Cobble of good quality Kaikoura chert, Waipapa Bay (EC10).

DESCRIPTION OF CHERT TYPES

The recognition of different *chert types* is an important step in the sourcing of artefacts. Chert types are associated with particular geological formations or units (May 1981), and because of differences in the provenance, depositional environment and burial history of such formations, they are likely to have some distinctive visual, petrographic or geochemical characteristics (Malyk-Selivanova *et al*. 1998). Three main chert types are identified in the ECP.

Geological samples of chert were examined both macroscopically and under a binocular microscope, generally at 10× to 15× magnification. No thin-section petrography was undertaken. Colours were determined with reference to the Munsell Soil Color Chart (2000 version), in natural light (Table 1). The presence of carbonate (calcite) was tested with dilute HCl. Altogether 85 samples were studied.

Whangai chert

Forty five samples were collected from various locations in the Gisborne-East Cape and Wairarapa regions which are, or almost certainly, from the Whangai Formation. Some

were obtained *in situ* (Mara) or in close proximity to outcrops (Orui), while others consist of detrital material found in rivers (e.g. Mata River, Mataikona River) and along the coastline (e.g. Whangara, Owahanga, Figure 2).

The Whangai chert is predominantly grey to dark grey in colour (Table 1). Some is very dark grey and rarely bluish, greenish, or brownish grey; weathering rinds are usually light grey to white. Under low magnification some chert has a distinctive mottled appearance, due to abundant white to light grey blotches within a darker grey matrix (e.g. Mara). Other samples show vague to distinct bioturbation (produced by burrowing), which is often more evident in lighter coloured material (Figure 3). About half also contained rare to sparse spherical radiolarians, typically 0.1–0.2mm in diameter. Veins are relatively uncommon and generally composed of colourless chalcedony, though white to bluish white veins are present in some samples (e.g. Mataikona River, Mara).

Tora chert

Ten samples were collected from the Tora area (Awheaiti and Pukemuri streams), one of which came from an *in situ*

	Whangai chert	Tora chert	Kaikoura chert		
Colour	$(n=24)$	$(n = 6)$	$(n = 31)$		
Black			O		
Very dark grey	0 ₀	0 ₀	00000		
Dark grey	00000	000	00000		
Grey/medium grey	0000000000	O	000000000000		
Light grey			\circ		
Very light grey	\circ				
Bluish grey	o				
Light bluish grey	o				
Dark greenish grey			O		
Greenish grey			000		
Light greenish grey	\circ		O		
Olive grey	o				
Brownish grey	o				
Greyish brown	o		O		
Brown					
Pale brown			O		

Table 1*. Variation in colour of different chert types.*

block within the Pukemuri Formation. The chert is of good flake quality and predominantly dark to very dark grey in colour (Table 1); based on the Munsell chart none could be definitely described as black. Veins of white to bluish white chalcedony are relatively common (Figure 3). Some samples also show vague to distinct bioturbation, but no radiolaria were visible under the microscope.

Kaikoura chert

In the past, artefacts of chert (flint) from northern South Island sites have generally been attributed to the Amuri Limestone (e.g. Challis 1991, 1995) but, as noted above, the bulk of the 'Amuri' chert occurs within the Mead Hill Formation, and is relatively uncommon in the Amuri Limestone (Lawrence 1989, 1993). It would be difficult to establish with any certainty which formation detrital material found in rivers or along the coast was derived from, and therefore a more general name – Kaikoura chert – is used here. This is preferable to cumbersome descriptors like 'nodular limestone flint' (Challis 1995) and 'Marlborough limestone flint' (Jacomb 2000).

The Kaikoura chert is predominantly grey (medium to very dark grey), though some of that from the Waima River in particular is green or brown (Table 1, Figure 3). It typically has a waxy to dull-waxy lustre, and higher quality material tends to be slightly translucent. Much of the chert is bioturbated, some is finely layered (laminated), and a few samples include veins of white to clear chalcedony or calcite. Some of the chert is calcareous. Under a microscope, sparse to abundant spherical radiolaria (usually <0.1mm) are evident in many samples, along with relict

foraminifera, tiny flecks of organic matter, and rare pyrite. Probable sponge spicules were observed in two samples (from Waima River), and three others contained abundant dolomite rhombs (Waima and Kekerengu rivers). The presence of dolomite rhombs in Kaikoura chert is recorded by Thompson (1916) and Lawrence (1989, 1993). Radiolaria and sponge spicules were also observed by Lawrence (1989).

Distinction between chert types

It is evident from Table 1 that the predominantly grey colour of the Whangai, Tora and Kaikoura cherts would make it very difficult to differentiate between them in any simple visual analysis of archaeological assemblages. However, green and brown material is more common in the Marlborough area. The presence of bluish white to white chalcedony veins in some Whangai and Kaikoura cherts also means this is not an exclusive feature of Tora chert (cf. Walls 1971), though such veins are certainly more obvious in samples from the Tora area. Possibly the only factors that might be useful are the calcareous nature and presence of dolomite rhombs in some Kaikoura cherts. An association of dolomite and chert has been recorded at only one locality in the Whangai Formation (Mara, Moore 1989).

Cherts from the ECP can generally be distinguished from other chert types by a combination of their typically grey colour (compared to the predominantly red, brown or yellow colour of many volcanic cherts), presence of bioturbation and other sedimentary features, and relative abundance of radiolaria or foraminifera. The carbonate content and occurrence of dolomite rhombs in some Kaikoura cherts are also important distinguishing criteria.

GEOCHEMISTRY

There has been no dedicated geochemical study of chert from the Whangai Formation, but some qualitative data were obtained by Leach (1977) and three other analyses (major elements only) have been published (Moore 1988). Selected trace element concentrations for Tora cherts were reported by Walls (1971). More recently, 168 wavelengthdispersive XRF analyses were obtained by Lawrence (1989, 1994) for cherts from the Marlborough region, mostly from the Mead Hill Formation. These samples were pre-treated to remove all carbonate (calcite and dolomite), which limits comparisons with the analyses presented here. Nevertheless, Lawrence's data provide useful information on the range of variation in element concentrations, and overall composition of the Kaikoura cherts. Notably, he found little variation in chert geochemistry between different diagenetic zones within the Mead Hill Formation, or within individual nodules in those zones (Lawrence 1994:487).

Methods

Representative geological samples of all three chert types were selected for chemical analysis, by WDXRF and pXRF. These came from 13 different locations (EC1-13, Figure 2). Those subjected to pXRF analysis consisted of artificial flakes and pieces with at least one relatively flat side >1 cm² in area. Although most were un-weathered, some slightly weathered samples were also included. All samples collected from coastal situations were soaked in fresh water in order to remove any residual salt, and therefore potential contamination by Na and Cl. Only a few of the samples were obtained from or in close proximity to outcrops (EC4/1-2, EC12/1-3, EC13/1-2).

A small number of samples were analysed by WDXRF in order to provide some preliminary quantitative data on the composition of cherts from eastern North Island and Marlborough, particularly for those elements not measured by pXRF (Si, Na, Mg). Nine samples – four from the Whangai Formation, one of Tora chert, and four from the Kaikoura area (Table 2) were analysed using a Bruker S8 Tiger 1kW wavelength-dispersive X-ray fluorescence spectrometer at the University of Waikato, Hamilton. Major elements were analysed from fusion beads with 12:22 flux, and trace elements were measured using the pressed pellet method. USGS standard SCo-2 was run with each analysis. Although 26 trace elements were measured, concentrations for many of those were close to or below the Limit of Detection (LOD) and therefore not considered further.

Fifty nine samples were analysed by pXRF using a test stand-mounted Olympus Innov-X Delta series model (with 40 kV silver anode X-ray tube) known as the 'Delta Premium', at GNS Science, Lower Hutt, in November 2020. This instrument has two analytical modes, Soil and Geochem, and uses three different energy beams. Only the Soil Mode was used in this study, with X-ray beam energy levels of

50, 40 and 15 kV. All samples were scanned for 90 seconds, along with two powdered standards–pure silica and NIST 2710a (Montana 1 soil), and the results calibrated using the instrument's internal calibration software. Only single measurements were made on each sample. These samples included all except two of those (EC 2/3, 8/14) analysed by WDXRF (Table 2). Complete analytical data are provided in supplementary Table S1.

An earlier dataset of 45 analyses was obtained using a similar Olympus Delta-X spectrometer at the University of Waikato, in 2018. The samples included most of those subsequently analysed at GNS, but were scanned for 60 seconds on Geochem mode. Three standards (pure silica, Cody Shale SCo-1, 2 and granite GSP2) were also analysed at regular intervals. Although not reported here, this dataset provides a basis for comparison of the results obtained by different pXRF instruments under different operating conditions, as for example illustrated by Frahm (2014).

Accuracy and reliability of data

To check the accuracy and reliability (or reproducibility, Frahm 2014) of the GNS pXRF results, comparisons were made with the certified values for the standard NIST 2710a and the samples analysed by WDXRF. Mean pXRF values obtained for NIST 2710a are mostly in good agreement with the certified values, and generally within two standard deviations of the reported concentrations, except for Fe and Ca (Table 3). Comparison of the concentrations obtained for seven of the samples analysed by WDXRF with the same samples subjected to pXRF analysis shows that the pXRF values for Rb, Sr and Zr are consistently lower, by up to 10 ppm (mean 5–7 ppm). However, differences in values obtained by different methods are to be expected (see Frahm 2014), and it is not an issue here as the main focus of the study was to identify differences between chert types using the same analytical method.

Comparison of the values for Sr obtained by WDXRF and pXRF shows there is a good correlation $(R^2 = 0.9114,$ Figure 4). Similarly, Sr concentrations for the same samples analysed at GNS and Waikato University also have a high correlation, though slightly lower for Whangai samples $(R^2=0.9258)$ than the Kaikoura cherts $(R^2=0.987,$ Figure 5). On this basis it is considered the GNS results are reproducible.

Results

WDXRF analyses

Major element concentrations for the nine samples analysed (Table 2) show there is limited difference in composition between the three chert types, but considerable variation *within* the Whangai and Kaikoura cherts for certain elements. Samples EC2/3 and EC8/14 have higher values for Al and Mg in particular. By contrast, Ca values for Whangai

	Whangai chert				Tora	Kaikoura chert				
Sample	$EC1-1$	$EC2-3$	$EC3-2$	EC6-1	$EC7-1$	EC8-9	EC8-14	EC9-1	EC10-3	
$(Wt\%)$										
SiO ₂	95.23	92.35	95.5	96.59	95.78	95.37	93.07	94.72	96.63	
TiO ₂	0.08	0.16	0.08	0.06	0.07	0.04	0.07	0.05	0.02	
Al ₂ O ₃	1.71	2.97	1.57	1.20	1.40	0.89	1.94	0.96	0.30	
Fe ₂ O ₃	0.55	1.22	0.49	0.35	0.66	0.48	0.68	0.58	0.34	
MnO	< 0.01	0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	
MgO	0.21	0.34	0.18	0.17	0.16	0.07	0.38	0.26	0.01	
CaO	0.40	0.47	0.41	0.40	0.44	0.08	0.31	0.28	0.19	
Na ₂ O	0.30	0.37	0.30	0.10	0.26	0.17	0.22	0.14	0.10	
K ₂ O	0.30	0.52	0.28	0.20	0.19	0.19	0.42	0.20	0.06	
P_2O_5	0.05	0.06	0.06	0.05	0.06	0.03	0.10	0.03	0.04	
LOI	1.25	1.69	1.21	0.94	1.06	1.24	1.75	1.37	0.98	
Total	100.37	100.58	100.3	100.28	100.41	98.69	99.07	98.87	98.78	
(ppm)										
Ba	251	1071	282	528	237	415	883	360	177	
V	12	25	11	9	11	6	17	8	3	
Cr	8	15	15	27	13	22	5	45	42	
Co	72	18	48	71	109	69	84	56	80	
Ni	11	10	9	11	12	9	11	11	9	
Cu	8	10	6	8	$\overline{7}$	$\overline{7}$	10	$\overline{7}$	5	
Zn	11	14	12	12	15	15	21	19	10	
Rb	16	29	14	12	11	13	22	13	$\overline{7}$	
Sr	30	57	33	30	45	31	55	26	18	
Ζr	21	32	23	17	23	10	16	11	5	
Υ	3	3	3	$\overline{2}$	$\overline{2}$	$\overline{4}$	12	$\overline{4}$	$\overline{3}$	
Ce	11	8	15	14	21	10	14	20	15	
Pb	5	$\overline{4}$	3	3	3	$\overline{7}$	5	$\overline{7}$	$\overline{7}$	

Table 2*. WDXRF analyses of ECP cherts. LOI = Loss on ignition.*

Table 3*. Comparison of certified values for NIST 2710a and results obtained by pXRF analysis of this standard (n=6). All values in ppm.*

Element		Fe	Mn	Сa		Ba	Rb		
Certified value (mean)		3110 ± 70 43200 ± 800 2140 ± 60			9640±450 21700±1300	792 ± 36	117 ± 3	255 ± 7	$200*$
$pXRF$ mean (n = 6)	3342	50177	2136	6512	22150	782		273	195
SD	42	169	19	91	174	18	1.3	4.6	5.8

*not certified

cherts are remarkably consistent. Notably, concentrations for Mg, Ca, Na and K in the Tora sample are very similar to those of the Whangai samples, suggesting the Tora chert was probably derived from the Whangai Formation.

Trace element concentrations for the three chert types are quite similar, though the Whangai samples tend to have higher Zr concentrations, along with the one Tora chert (Figure 6). This reflects the more terrigenous nature of the Whangai Formation and likely presence of detrital zircon (Moore 1988: 36). For most other elements (e.g. Ni, Cu, Zn, Y, Pb) there is no significant difference between chert types. However, EC2/3 and EC8/14 have considerably higher Ba

and Sr values, two of the Kaikoura samples contain elevated Cr values, and the Co concentration (109 ppm) in the Tora chert is unusually high.

pXRF analyses (see supplementary Table S1)

Although a considerable number of elements are capable of being measured by pXRF, because of the high silica content (typically >90% $SiO₂$, as established from WDXRF analyses) values for many minor and trace elements are generally below the Limit of Detection (LOD). Meaningful data were obtained only for K, Fe, Ti, Mn, Ca, Ba, Rb, Sr and Zr, and

Figure 4. Comparison of WDXRF and pXRF Sr concentrations for selected ECP samples.

Figure 5. Correlation between Sr concentrations obtained by pXRF at GNS and Waikato University. The regression line is for Kaikoura chert samples.

Figure 6. Bivariate plot for different chert types, analysed by WDXRF.

to a lesser extent for Zn and V. Silica, aluminium, Na and Mg were not measured.

A bivariate plot of Zr-Sr shows a significant variation in Zr for Whangai cherts, but a limited range in Sr (Figure 7). Notably the Tora samples mostly plot within but at the lower end of the Whangai field. There is also some overlap with the Kaikoura cherts, which form two distinct clusters, one (Group K1) containing lower Zr values than most Whangai samples, the other (Group K2) having much higher Sr concentrations. Additionally, the Group K2 samples contain moderate to high Ca and Ba. This group also includes three other samples (8/6, 11/1, 13/2) with unusually high Sr values (106-386 ppm), which were excluded from the plot for practical reasons. Sample 8/6 has a particularly high Ca content (13,4035 ppm), equivalent to about 19% CaO, as well as an approximate silica value of only 57% (as determined by Waikato pXRF), and therefore could be almost classified as a siliceous limestone.

Strontium is often strongly correlated with carbonate (Luedtke 1992, Gauthier *et al*. 2012), and this seems to be the case for the small number of calcareous Kaikoura samples analysed (n = 5 , R² = 0.9465). However, there is no significant correlation between Sr and Ca overall. Lawrence (1989:138) also noted there was a general correspondence between Ba and Sr, and recorded higher concentrations for these elements in cherts from the Amuri Limestone. The Ba content of Kaikoura cherts is generally <500 ppm (Table S1), but there is a group of samples $(n = 7)$ with values >1000 ppm, and notably all of these are from the Waima and Kekerengu rivers, in the northern Kaikōura area (EC8, 9, Figure 2). There is also a stronger correlation between Sr and Ba for the Kaikoura samples $(R^2=0.7314)$ than Whangai (R^2 =0.4475). The samples with highest Sr and Ba values are all from Group K2.

There is a reasonably clear distinction between Whangai and Kaikoura cherts based on Zr-Rb (Figure 8),

Figure 7. Plot of Zr-Sr for cherts from different formations, showing two separate fields for Kaikoura cherts (Groups K1, K2).

Figure 8. Plot of Zr-Rb for cherts from different formations (field for Kaikoura cherts outlined).

with the Kaikoura samples showing a more linear trend. Again, the Tora cherts fall within the lower part of the Whangai field, and therefore cannot be distinguished from Whangai cherts on the basis of these elements alone. There is also a separate outlier of Whangai samples with much higher Rb values, all except one of which (EC3/1) are from Whangara near Gisborne. Some of these contain moderate to high Ca, Ba and Ti concentrations, but $EC₃/1$ has relatively normal values.

These analyses also provide some indication of the variation within specific outcrops or chert units. The two samples from Mara, for example $(EC4/1, 2)$, show very limited differences in the concentrations of Ti, Mn, K, Ba, Rb and Zr in particular. There is greater variation among the samples from Kaikōura Peninsula (EC12) and Oaro (EC13), except for K, Rb and Zr, and this is likely attributable to the incorporation of some limestone.

Importantly, the pXRF results closely match those previously obtained at Waikato University, which also showed reasonably clear differentiation of the Whangai and Kaikoura cherts, and inclusion of the Tora chert within the lower part of the Whangai compositional field. The separate Group K2 cluster was identified, though the isolated cluster of Whangai samples with higher Rb values was not so well defined. Average values for Rb, Sr and Zr for the Whangai and Kaikoura cherts were very similar to those obtained in this study, particularly for the latter. Overall, the Waikato pXRF analyses confirm the results obtained using the GNS instrument.

DISCUSSION

Compared to obsidian, the sourcing of chert has proved particularly challenging, mainly because of its multiple origins, wide natural distribution, highly variable visual attributes, and complex geochemistry (Luedke 1992, Malyk-Selivanova *et al*. 1998). Reliance on visual characteristics alone to identify specific sources for chert artefacts has often resulted in unreliable or incorrect results (e.g. Mehta *et al*. 2017), but this does not necessarily mean that visual attributes or petrographic observations have no place in sourcing studies. As shown in this study, there is a range of features that could be used to identify chert which originated from the ECP, including colour, sedimentary structures, and microfossils, as well as, in the case of some Kaikoura cherts, carbonate content. Nevertheless, it is considered that the most effective means of sourcing chert artefacts that likely originated from the ECP will be by using a combination of visual attributes and pXRF analysis, as demonstrated by Newlander and Lin (2017).

It would also appear from this study that the potential for identifying specific sources within the ECP on the basis of pXRF analyses is quite limited, and that in most cases the majority of chert artefacts could probably only be assigned to a general region (i.e. Eastern North Island or Marlborough). This may not be too much of a problem

for archaeologists in the South Island since the natural distribution of Kaikoura chert is restricted to a relatively small area. Clearly it is more of an issue in the North Island, although for the most part we could probably assume that chert artefacts were procured from the nearest suitable source, as for example at Whangara (Jones and Moore 1985).

CONCLUSIONS

This preliminary study has indicated that pXRF analysis is capable of differentiating between visually-similar cherts derived from sedimentary formations in the eastern North Island (Whangai Formation) and Marlborough region (Mead Hill + Amuri Limestone), but that the Tora chert is indistinguishable (chemically) from Whangai chert. The Whangai chert is distinguished, in particular, by higher Zr concentrations. A separate geochemical group, characterised by higher Sr, Ca and Ba values, is also recognised within the Kaikoura chert, although there would appear to be limited scope for identifying individual chert sources within the ECP. These findings are supported by an earlier dataset obtained on a different pXRF instrument, under different operating conditions, and demonstrate that the results are reproducible.

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