

## Elemental Analysis of New Zealand Nephrite Jade (pounamu) for Forensic Purposes

G. P. Campbell<sup>1</sup>, G. M. Miskelly<sup>1</sup>, J. M. Curran<sup>1</sup>, S. A. Coulson<sup>2</sup>, G. M. Yaxley<sup>3</sup>

<sup>1</sup>The University of Auckland, Auckland, New Zealand; *gcam032@gmail.com*

<sup>2</sup>The Institute of Environmental Science and Research Ltd., Auckland, New Zealand

<sup>3</sup>Research School of Earth Sciences, Australian National University, Canberra, ACT, Australia

### Abstract

Pounamu (NZ jade), or nephrite, is a protected mineral in its natural form following the transfer of ownership back to Ngai Tahu under the Ngai Tahu (Pounamu Vesting) Act 1997. Any theft of nephrite is prosecutable under the Crimes Act 1961. Scientific evidence is essential in cases where origin is disputed. A robust method for discrimination of this material through the use of elemental analysis and compositional data analysis is required. Initial studies have characterised the variability within a given nephrite source. This has included investigation of both in situ outcrops and alluvial material. Methods for the discrimination of two geographically close nephrite sources are being developed.

**Key Words:** forensic, jade, nephrite, laser ablation, inductively coupled plasma mass spectrometry, multivariate analysis, elemental analysis, compositional data analysis

# 1 INTRODUCTION

Nephrite jade in its natural state is a privately owned resource in New Zealand. The Ngai Tahu (Pounamu Vesting) Act of 1997 (NZ) returned full ownership rights of all natural state nephrite in New Zealand to the indigenous Maori tribe, Te Runanga O Ngai Tahu, following settlement of grievance claims relating to injustices associated with the Treaty of Waitangi.<sup>1</sup> Due to this ownership any large-scale theft is punishable under the Crimes Act 1996 (NZ) with significant penalties, including imprisonment.

The lack of a database of appropriate nephrite samples with known provenance and the limited amount of provenance-directed research has caused problems in cases that have proceeded through the New Zealand courts. Without extensive sampling and a proven method, the ability to provenance nephrite jade is limited, at best, and this has led to major disputes in court proceedings.

Another significant issue in the New Zealand tourism industry is the misrepresentation of foreign nephrite as 'genuine New Zealand pounamu' (Anon 2004). This foreign material dominates the jade sold in New Zealand souvenir shops in all of the major centres, leaving it near impossible for the average tourist to acquire a piece of genuine stone ref!.

## 1.1 OPERATION ROAR

The New Zealand Police began Operation Roar to investigate alleged large-scale nephrite removal from the Cascade Plateau (an area known for nephrite). The theft was alleged to have happened in the period 1997 to 2003 and amount to somewhere in the order of \$500,000 to \$1M New Zealand dollars in value. Two separate court cases, involving four defendants, proceeded through the courts as a result of the operation. In one of the cases, helicopter pilot David Saxton and his son Morgan Saxton were charged with three counts each relating to large-scale pounamu theft from the Cascade Plateau between 1991 and 2004, a period involving Crown ownership (prior to 1997) and Ngai Tahu ownership (1997-present). There were many forms of evidence involved in the case including phone taps, video footage and financial records. However, one of the most contested pieces of evidence was the geochemical evidence pertaining to the origin of the stolen material.

The prosecution geochemical expert had undertaken geochemical analyses on rocks supplied by the New Zealand Police. His strategy of analysis was a targeted approach, to analyse the homogenous green material of the nephrite and exclude the inclusions. He applied X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) to the samples to determine the mineral and elemental content respectively. His evidence was a classification of the samples using  $K_2O$ ,  $Na_2O$  and Sr.

---

<sup>1</sup> The Treaty of Waitangi is the founding document of New Zealand. The Treaty was signed by Maori chiefs and the Crown as a document to lay down the terms of New Zealand's colonisation by Great Britain. Many of the terms set out in the document were not upheld by the Crown and New Zealand has been going through a lengthy grievance process whereby Maori tribes (iwi) are claiming reparations for losses incurred in, among other things, land during the colonisation process. Settlements from the Crown have been forthcoming and have included monetary compensation as well as the return of land and many culturally significant areas and resources to the original owners.

The defence expert disputed several points made by the prosecution. This expert stated that the targeted approach to the analysis was flawed, since by leaving out the inclusions was excluding the most distinctive quality of the rocks. Presumably the prosecution witness had decided to analyse only the green homogenous material since then he could compare like components, whereas the results of analysing the inclusions would be much more difficult. The small number of samples and lack of a database were also criticised by the defence. The most contested issue was the selection of  $K_2O$ ,  $Na_2O$  and Sr as discriminatory “probes”. The defence argued that these particular elements are considered mobile in metamorphic environments and because the alluvial nephrite boulders lie away from their host rocks (in situ sources), they are likely to have been infiltrated by water to a degree that would alter these elements in the samples. However, the courts found that although this may be true within in situ deposits during formation and on the weathering layer of a boulder, it would have little to no effect on the material deeper within the boulders – the source of the analysed samples. Finally the defence questioned the geochemical analysis carried out for the prosecution. They argued that a holistic approach involving visual, physical and mineralogical characteristics as well as geochemical data would be more appropriate for provenance. The courts concluded that this was outside the brief of prosecution witness.

The Saxtons were convicted on one count each of theft of pounamu from Te Runanga o Ngai Tahu to the value of just under \$1M NZD. David and Morgan Saxton were sentenced to 2 years 9 months and 2 years 6 months respectively.

What came to the fore during this case was that there was a lack of clear methodology for elemental analysis pertaining to provenance disputes for nephrite jade or similar materials and there was also uncertainty as to the significance of any results obtained through such analyses. Our research is attempting to reduce this gap in knowledge.

## 1.2 FORMATION AND CHEMISTRY

Jade is a term that covers two semi-precious materials, jadeite and nephrite. Although similar in appearance and physical properties, jadeite and nephrite are different in their chemical structure. Jadeite is a sodium aluminium silicate belonging to the pyroxine group and is found predominantly in Japan, Guatemala and Burma (Myanmar). Nephrite, on the other hand, resides within the spectrum of tremolite-actinolite amphibole minerals, being a calcium magnesium silicate with varying amounts of iron,  $Ca_2(Mg,Fe)_nSi_8O_{22}(OH)_2$ . Nephrite is more common throughout the world than jadeite and is found in Australia, Brazil, Canada, China, Germany, Italy, Korea, Mongolia, New Caledonia, Poland, Russia, Switzerland, Taiwan, USA, Zimbabwe and, New Zealand (Beck and Mason 2002).

The formation of nephrite is a two-stage process. Actinolite-tremolite is initially formed by metasomatic processes, and this is followed by a secondary mechanical process which develops the felted nephritic structure that is unique to this material (Adams et al. 2007, Finlayson 1909, Harlow and Sorensen 2001, Turner 1935). These processes are generally accepted to take place in metamorphic conditions involving high temperatures ( $450\pm 50$  °C) and comparatively low pressure (~2 kb) (Koons 1981).

The formation of nephrite (Fig. 1) is a complex process that is not entirely understood. Nephrite is believed to form as a ‘crust’ at the contact zone of metasedimentary (and metavolcanic) ‘knockers’ and ultramafic rocks, usually serpentinites or other ophiolitic rocks

(Adams et al. 2007). The other required factor for the formation of nephrite is association with fault action. In New Zealand, nephrite formation is intimately linked to the Alpine Fault that stretches down the West Coast of the South Island.

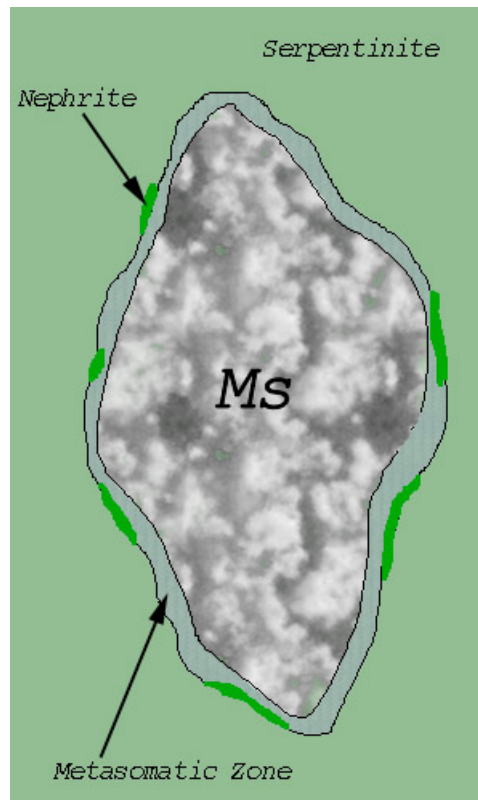


Figure 1 – Schematic diagram of a region where nephrite formation occurs. Ms = Metasediment. Adapted from (Coleman 1966).

## 1.2 SOURCE DISCRIMINATION

Early studies on New Zealand nephrite focused on the geological and mineralogical properties of traditional sources. These studies paved the way for future research with more advanced methods that were not then available (Coleman 1966, Finlayson 1909, Reed 1957, Skinner 1935, Turner 1933a, Turner 1933b, Turner 1935).

The first significant provenance study by Ritchie (1976) attempted to use elemental profiling to discriminate between the New Zealand sources. However, his work was inhibited by largely insensitive instrumentation and the small number of available samples (Ritchie 1976). This line of research was taken up again by Merrony (1985) who analysed samples from all of the New Zealand sources using Neutron Activation Analysis (NAA). The study again provided inconclusive results, being inhibited by the small number of available samples. Although these studies proved inconclusive they highlighted some important points including the need to undertake large-scale sampling at the sources due to the inhomogeneous nature of the material and the inherent variation in elemental concentrations.

Popham (2006) provided a brief geochemical analysis of pounamu from Scott Basin in the Wakatipu region of New Zealand. A comparison was made between the geochemical data of material sampled from Scott Basin and a sample set of nephrites from other New Zealand sources (including Big Bay, Caples, Cascade Plateau and North Westland) and also with some samples from overseas (including South Australia and British Columbia) (Popham 2006). This pilot investigation was inconclusive as to the ability to provenance nephrite from these regions, and the author noted that more work was required in this area.

Adams et al. (2007) wrote the most recent, and extensive, publication pertaining to New Zealand nephrite provenance (Adams et al. 2007). They attempted to determine the age of the nephrite by the Rb-Sr and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in their samples. Included in the study were nephrite samples, and their host rocks, from all over the South Island, New Zealand, covering the three major host geological terranes. Worldwide, and within New Zealand, nephrite is hosted in geological settings of different ages, and therefore age may be discriminatory. The method determines the initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio at the time of homogenisation and the Rb-Sr age is used to determine the time of recrystallisation during metamorphism. Unfortunately, the authors found that the Rb content of the nephrite samples was too low for precise analysis (<5 ppm), so they had to focus on the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio. Sr isolated from small drilled samples of the rocks was analysed, following sample preparation, by Thermal Ionisation Mass Spectrometry (TIMS). At a general level the data collected allowed separation of samples from each of the three major terranes, the Torlesse, the Caples and the Dun Mountain-Maitai. The work undertaken by these authors resulted in important advances in the provenance of nephrite. They commented on previous trace element targeted studies (Nichol 2000, Wilkins et al. 2003) saying that they showed that trace element signatures are potentially too variable to be a reliable sourcing mechanism. However, in our opinion none of the previous studies contained sufficient samples or was statistically robust enough to prove that trace element analysis cannot provide discriminatory information for nephrite. A combination of age techniques and trace elemental signatures may ultimately provide the discriminatory power required when dealing with samples of questioned source.

Here, and in ongoing work, we take up the challenge of attempting to source New Zealand nephrite based on elemental profiling, specifically using trace elements. The main features of this research include:

1. Assessing the intra-source variability of the elements.
2. Attempting to discriminate between the New Zealand sources based on multivariate statistical analysis of elemental profiling data.
3. Discriminating between New Zealand and foreign samples.

## **2 METHODS**

### **2.1 SAMPLE COLLECTION**

Two significant source areas have been sampled for this research project with a suite of additional samples covering the other important New Zealand sources being donated by others. The first site, Scott Basin, is located in the Wakatipu region of the South Island, an important, and recently rediscovered, area for traditional collection of nephrite by early

Maori. The Scott Basin area included in situ nephrite pods as well as a clear alluvial flow path where a number of samples were collected.

The second site of sampling was in the Westland area of the South Island, New Zealand's most significant site for the nephrite industry. Unfortunately, the in situ sources in the Westland area were not located even after extensive exploration. Thus, samples from this region were alluvial only.

Donated samples were from sites including the Livingstone Mountains (Southland), Routeburn (Otago), Slip Stream Dart Valley (another Wakatipu source), South Westland and other Westland sources, namely Jade Creek, Arahura, Marsden, Milltown and Kumara. All of these samples are of known origin as they were hand collected by the donating parties. Thus, we can assume that for all samples in this study, origin is known rather than inferred. Samples from foreign sources including Kobuk (Alaska), British Columbia (Canada), Karakash River (China), South Australia, Ospin (Siberia), USA and Siberia were donated (by Russell Beck).

## 2.2 ELEMENTAL ANALYSIS

All analyses were undertaken at the Research School of Earth Sciences, Australia National University, Canberra, ACT, Australia. Samples were crushed and small chips from each sample were mounted in epoxy resin. These were sanded so that polished faces of rocks were exposed for analysis. Elemental analysis of the nephrite samples were undertaken by Electron Microprobe Analysis (EMPA) for the 6 major elements Si, Al, Ca, Mg, Fe and Mn. Trace elements were analysed by Laser Ablation Inductively Coupled Plasma Mass-Spectrometry (LA-ICP-MS). The elements providing usable data (i.e. above detection limits) were  $^{45}\text{Sc}$ ,  $^{47}\text{Ti}$ ,  $^{51}\text{V}$ ,  $^{53}\text{Cr}$ ,  $^{59}\text{Co}$ ,  $^{58}\text{Ni}$ ,  $^{85}\text{Rb}$ ,  $^{88}\text{Sr}$ ,  $^{89}\text{Y}$ ,  $^{90}\text{Zr}$ ,  $^{91}\text{Zr}$ ,  $^{93}\text{Nb}$ ,  $^{137}\text{Ba}$ ,  $^{139}\text{La}$ ,  $^{140}\text{Ce}$ ,  $^{146}\text{Nd}$ ,  $^{147}\text{Sm}$ ,  $^{153}\text{Eu}$ ,  $^{157}\text{Gd}$ ,  $^{163}\text{Dy}$ ,  $^{165}\text{Ho}$ ,  $^{166}\text{Er}$ ,  $^{172}\text{Yb}$ ,  $^{175}\text{Lu}$ , and  $^{208}\text{Pb}$ . Calcium was used as an internal standard to allow for absolute values to be determined for the trace elements. This allows for combination of the major and trace datasets with confidence of the elemental ratios represented therein. No standard is available for nephrite, thus LA-ICP-MS analysis results in qualitative data only. However, since we are only interested in the ratios of the variables within these data this should not affect our analysis.

Each sample had three replicate analyses that were averaged to give an overall sample value. A 'sample' in this case is a small chip of rock (surface area exposed = approximately 1-4 mm<sup>2</sup>) taken from a rock slice. The rock slices are off-cuts of larger rocks collected from the source areas.

## 2.3 THE LOG-RATIO APPROACH TO COMPOSITIONAL DATA ANALYSIS

The data obtained from the analytical methods described in *section 2.2* is strictly compositional. Measurements from EMPA are in weight % form summing to 100% and measurements from the LA-ICP-MS instrument are in parts per million (ppm). Compositional data poses some challenges with data analysis and must be treated with care to avoid spurious statistical inference. The statistician John Aitchison has developed robust methods for the analysis of compositional data, focusing on the log-ratio approach (Aitchison 1981, Aitchison 1982, Aitchison 1983, Aitchison 1986, Aitchison 1999, Aitchison 1984, Aitchison et al. 2002, Aitchison and Kay 2004).

The log-ratio approach to compositional data analysis deals with the ratios between the components, not the raw values, since these ratios contain the compositional information (Aitchison 1986). In this research it was desired to use traditional multivariate statistical analyses and also to consider the impact of all of the elements on the data. Therefore, the centred log ratio (*clr*) transformation was used. This transformation involves taking the log of the concentration of each component ( $x_i$ ) over the geometric mean of concentrations of all elements determined in the sample ( $g(x)$ ):

$$clr(x) = [\ln(x_1 / g(x)), \ln(x_2 / g(x)), \dots, \ln(x_D / g(x))]$$

## 2.4 DATA PROCESSING

Major element data was converted from weight % values of the oxides into ppm of the element to allow combination with the trace element data.

When undertaking elemental analysis involving trace elements, zero values are commonly encountered. Log-ratio transformation requires that all data values are positive, thus a strategy for dealing with zero values is required. Martin-Fernandez et al (2003) discuss treatment of zero values obtained during elemental analysis. They refer to those values, where a component is present (or may be) but is below detection limits, as rounded zeros. In the current research, the LA-ICP-MS instrument returns a zero value (in the form of a “below limits of detection”) when the response does not rise above the background noise of the ICP-MS. The element is not necessarily absent; it is simply considered background noise and given a zero value. There are many strategies for replacement of rounded zeros (Martin-Fernandez et al. 2003). Some sit well with a statistician but not well with a chemist, e.g. replacement with a value of one. The strategy taken in this research is based on chemical analysis reasoning. Because the value does in fact exist, but is below detection levels, it is replaced with a value of half the detection limit for that element. Even when an element is detected its concentration may not be sufficiently high to meet the criteria of inclusion. That is they are below the 3 x Detection Limit range. In this circumstance, the measured value was used rather than replacement by a half detection level value. Elements that were not detected in a large number of the samples were removed from the data.

## 3 RESULTS

### 3.1 EXPLORATORY DATA ANALYSIS

#### 3.1.1 INTERNAL VARIATION

It is important to assess the internal variation of a region before attempts are made to discriminate between regions. The variation within small areas allows us to understand whether any discrimination we see in later analyses, or of new samples, is of significance.

The test sample suite to assess internal variation was collected from Scott Basin and its surrounding area, referred to below as Wakatipu. This site was chosen because a number of in situ pods of nephrite were located and sampled directly. Therefore, precise locality and the origin of each sample (i.e. in situ or alluvial) is known.

Following removal of extreme outliers, box plots for each of the elements analysed in the samples from the Wakatipu region (Figs 2 & 3) were used to evaluate the trends and variability of the data.

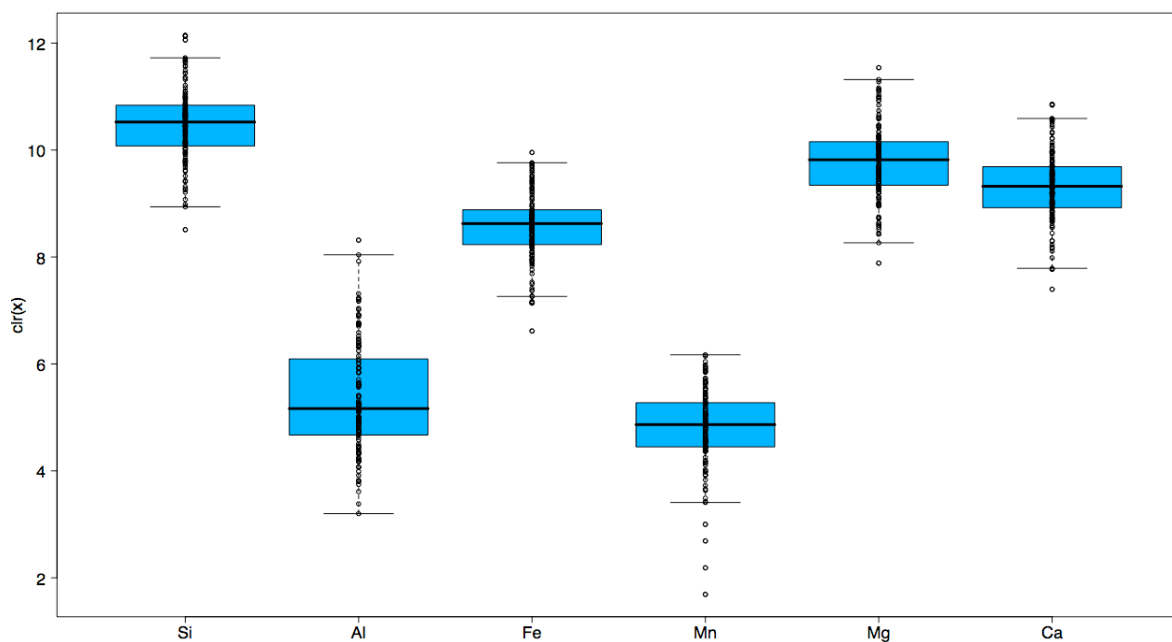


Figure 2 – Boxplot showing *clr* transformed major elements of New Zealand nephrite from the Wakatipu region, analysed by electron microprobe ( $n = 138$ ).

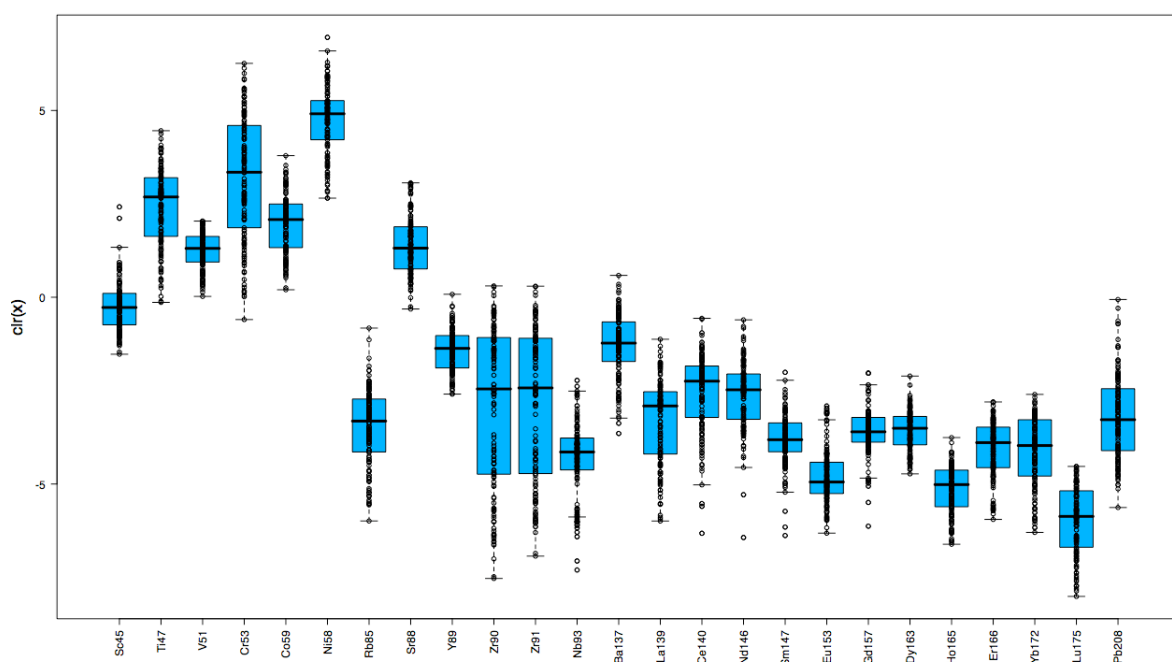


Figure 3 – Boxplot showing *clr* transformed trace elements of New Zealand nephrite from the Wakatipu region, analysed by LA-ICP-MS ( $n = 138$ ).

The major element that exhibits the most spread is Al with a spread approximately two times larger than any other major element. The trace elements all show differing levels of spread.



Some outliers are present, but overall the data is essentially symmetric for each element following the *clr* transformation.

During the initial data cleaning process samples consisting mainly of nephrite were specifically selected for based on the major elemental composition. This was to remove samples containing minerals that are similar in appearance to nephrite that were inadvertently collected and analysed. After this selection process there were 138 valid samples. The resulting major element data reflects this selection process with high correlations between the nephrite mineral elements. A Principal Components Analysis (PCA) biplot (Fig 4) shows the high correlation of Ca, Fe, Mg, and Si (oriented along Principal Component 1 (PC1), while Al and Mn are poorly correlated with these elements and affect PC2. The first two principal components represent 88% of the variation in the data. The majority of the variability in the data is shown in PC1 (68.5%), which is essentially a reflection of the variation in the nephrite mineral elements (Fe, Ca, Mg and Si). Another 19.5% variation is in PC2 that is predominantly controlled by Al. Levels of Mn influence both PC1 and PC2 to almost the same degree.

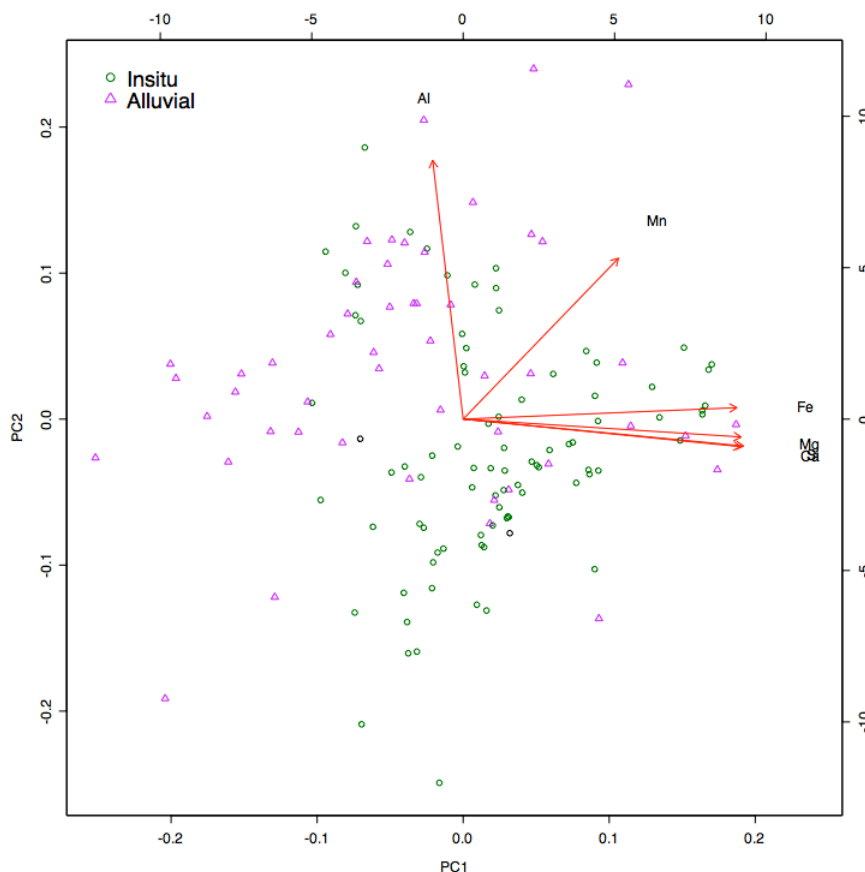


Figure 4 – PCA plot of the *clr* transformed major elements of New Zealand jade from the Wakatipu region, analysed by electron microprobe ( $n = 138$ ).

The in situ samples tend to show higher concentrations of the nephrite mineral elements (Si, Mg, Fe, Ca) compared to the alluvial samples, as shown by their tendency to be on the right of the above diagram. However, the in situ and alluvial samples show similar variability in Al and Mn as shown by the similar distributions over PC2. Figure 5 shows the same data as

Figure 4, but samples from each individual in situ nephrite outcrop are now identified to highlight any groupings due to the different elemental compositions within such outcrops (Fig 5).

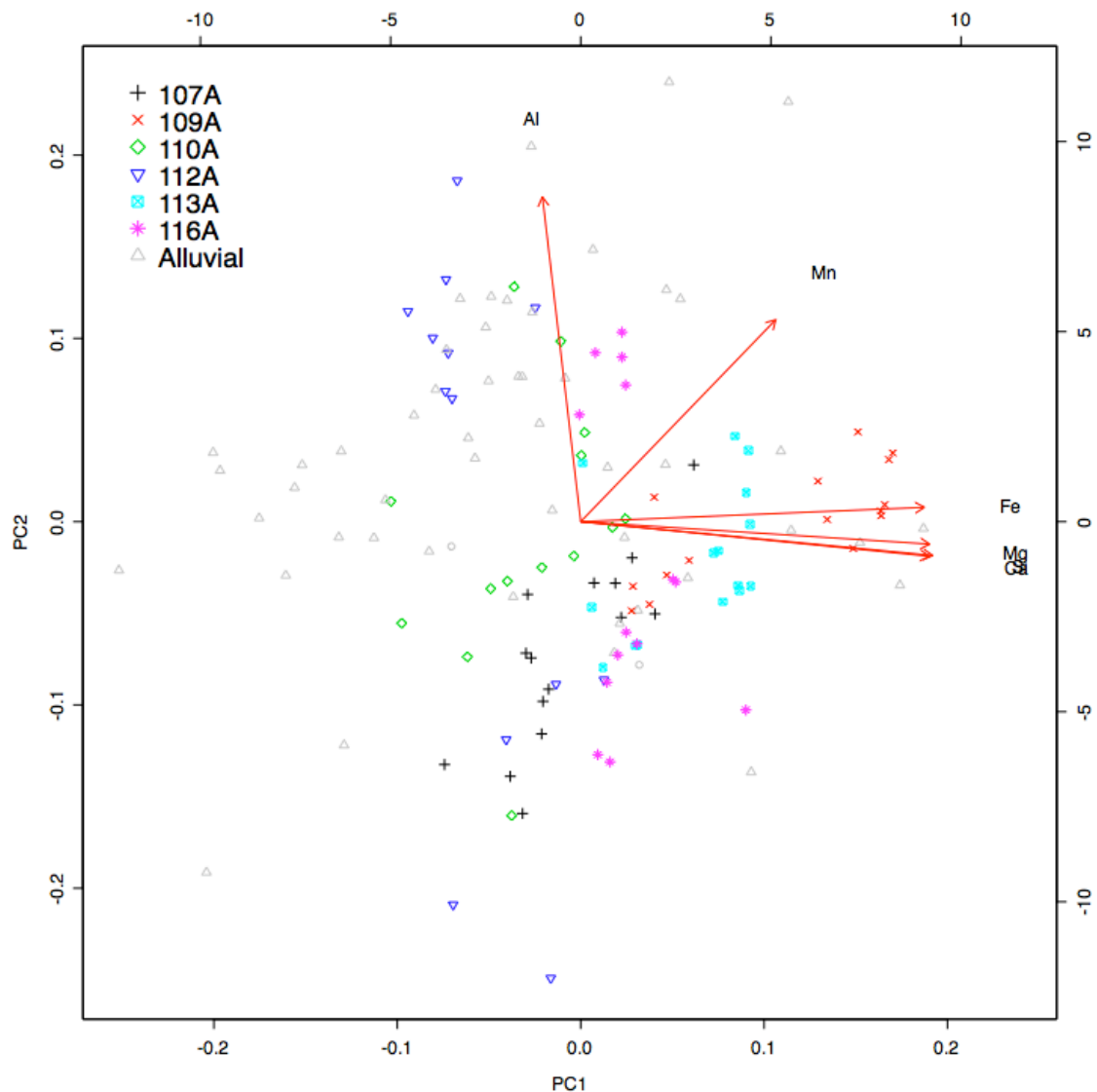


Figure 5 – PCA plot of the *clr* transformed major elements of New Zealand nephrite from the Wakatipu region, analysed by electron microprobe ( $n = 138$ ).

Some clustering of samples from a given outcrop can be observed in Figure 5, however no clear grouping is exhibited and overlap is obvious between the in situ groups based on their major elemental ratios.

Because of the behaviour of the nephrite mineral elements in the PCA plots, we can assume that the ratio of these elements is almost constant. This is reflected in high correlation coefficients between these elements – all are > 92% correlated with the highest being Si-Mg with 99% correlation. Al and Mn show little or no correlation with any of the nephrite mineral elements.

The Coefficient of Variation (CV) is used as a measure of standardised variability for each element. This was calculated by dividing the standard deviation ( $\sigma$ ) by the mean ( $\mu$ ) for each element of the Wakatipu ( $n = 138$ ) *clr* transformed dataset (Table 1).

Table 1 – Coefficient of Variation for the major and trace elements sorted from lowest to highest

Element	Coefficient of Variation	Element	Coefficient of Variation
Si	0.0643	<sup>85</sup> Rb	0.2922
Ca	0.0684	<sup>146</sup> Nd	0.3410
Mg	0.0714	<sup>139</sup> La	0.3431
Fe	0.0736	<sup>208</sup> Pb	0.3462
<sup>165</sup> Ho	0.1254	<sup>51</sup> V	0.3923
<sup>163</sup> Dy	0.1488	<sup>89</sup> Y	0.3930
<sup>175</sup> Lu	0.1498	<sup>59</sup> Co	0.4070
<sup>153</sup> Eu	0.1509	<sup>140</sup> Ce	0.4138
Mn	0.1547	<sup>47</sup> Ti	0.4325
<sup>157</sup> Gd	0.1675	<sup>53</sup> Cr	0.5131
<sup>147</sup> Sm	0.1782	<sup>88</sup> Sr	0.5511
<sup>166</sup> Er	0.1872	<sup>137</sup> Ba	0.6616
<sup>58</sup> Ni	0.1925	<sup>91</sup> Zr	0.7232
Al	0.1933	<sup>90</sup> Zr	0.7445
<sup>172</sup> Yb	0.2233	<sup>45</sup> Sc	2.6196
<sup>93</sup> Nb	0.2295		

The nephrite mineral elements show the least relative variation, which is partly due to the deliberate selection of samples dominated by nephrite. The other major elements, Mn and Al, are 2-3 times more variable than the nephrite mineral elements. As expected, the trace elements in the nephrite samples exhibit a significantly higher level of variability than the nephrite mineral elements. The element <sup>45</sup>Sc shows much larger relative variation than the other elements, and this may be due to interference from molecular ions such as <sup>28</sup>Si<sup>16</sup>OH<sup>+</sup> or <sup>29</sup>Si<sup>16</sup>O<sup>+</sup> (Nehring et al. 2008).

<sup>88</sup>Sr, <sup>58</sup>Ni, <sup>53</sup>Cr and <sup>47</sup>Ti were selected for further investigation because they are present in high levels and/or they exhibit a larger amount of relative variation, which could suggest that they are most likely to differentiate samples from different outcrops in the Wakatipu region.

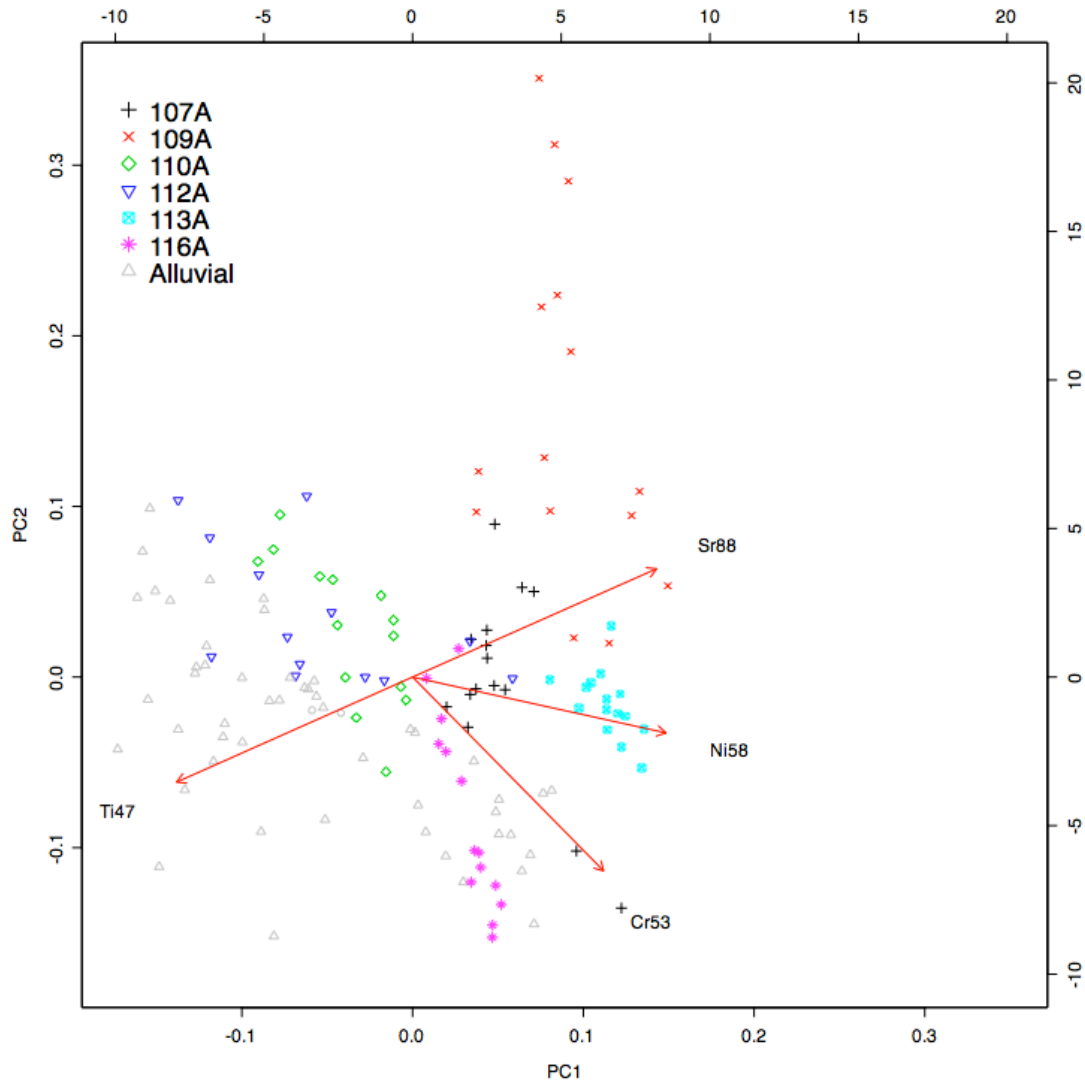


Figure 6 – PCA plot of selected *clr* transformed trace elements of New Zealand jade from the Wakatipu region, analysed by LA-ICP-MS ( $n = 138$ ).

The PCA biplot in Figure 6 represents 89.5% of the variation in the  $^{88}\text{Sr}$ ,  $^{58}\text{Ni}$ ,  $^{53}\text{Cr}$ , and  $^{47}\text{Ti}$  data, with PC1 and PC2 accounting for 69.2% and 20.4% of the variability respectively. More defined clustering of the in situ outcrops is seen in this figure compared to the case when only the major elements are considered (Fig. 5).

### 3.1.2 INTER-SOURCE DISCRIMINATION

The Wakatipu data were compared with a dataset of Westland samples ( $n = 128$ ). Those elements whose distributions exhibited the most intersource difference were selected using visual comparison of boxplots. For the analysis shown here, Al,  $^{53}\text{Cr}$ ,  $^{88}\text{Sr}$ ,  $^{89}\text{Y}$  and  $^{93}\text{Nb}$  were used since these variables showed the largest intersource differences in *clr* means. The data were analysed by PCA resulting in the biplot shown in Figure 7.

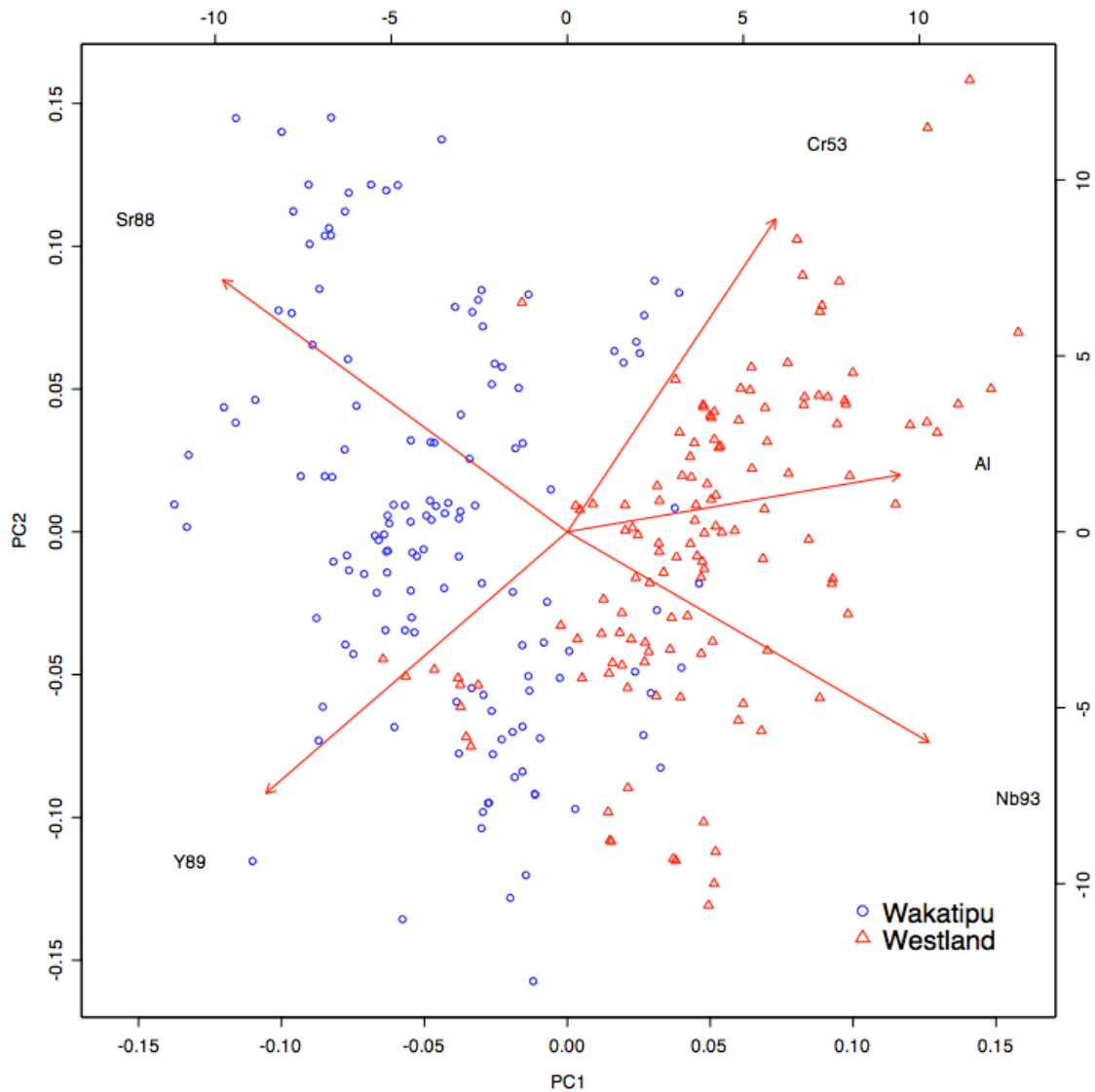


Figure 7 – PCA plot comparing the *clr* transformed Wakatipu ( $n = 138$ ) and Westland ( $n = 128$ ) Al,  $^{53}\text{Cr}$ ,  $^{88}\text{Sr}$ ,  $^{89}\text{Y}$  and  $^{93}\text{Nb}$  data.

The plot in Figure 7 represents 73.2% of the variation in the data with PC1 and PC2 representing 46.9% and 26.3% respectively.

The selected elements (Al, Cr, Sr, Y, and Nb) give reasonable differentiation between the two sources. Although overlap is present in the data, there is a clear tendency for samples from the two sources to be discriminated. Classification methods such as discriminant analysis may provide further power in source characterisation.

## 4 DISCUSSION

Previous attempts at using trace elemental analysis to discriminate between sources of nephrite material have given uncertain results due to a multitude of factors. With extensive sampling and the use of compositional data analysis, data reduction and classification methods, we believe that the analysis methods may yet provide an important tool for scientific

evidence in cases of disputed origin. There is still much more work to be completed on a number of additional data sets. This work is currently underway. Future work in this project will involve the analysis of more source data and intersource discrimination.

## 5 ACKNOWLEDGEMENTS

We would like to acknowledge the following groups and individuals, without whom this research would not have been possible: Dr Simon Cox, ESR Ltd, GNS Ltd, Te Runanga o Ngai Tahu, Te Runanga o Ngati Wae Wae, the Combined Otago/Southland Runanga, Charles Magee, Dr Val Orchard, Dr John Buckleton, Dr Jill Vintiner, Dr Douglas Elliot, the Physical Evidence Team, Tim Popham, Dr Hamish Campbell, Dr Chris Adams, The University of Auckland.

Financial assistance for this project has been kindly provided by The Institute of Environmental and Scientific Research (ESR) Ltd, The University of Auckland, GNS Science and the NZ Police. Financial support to attend the Codawork'08 Workshop was kindly provided by the Postgraduate Research Fund of The University of Auckland.

## 6 REFERENCES

- Adams, C. J., Beck, R. J. & Campbell, H. J. Characterisation and origin of New Zealand nephrite jade using its strontium isotopic signature. *Lithos* **97**, 307-322 (2007).
- Aitchison, J. A new approach to null correlations of proportions. *Mathematical Geology* **13**, 175-189 (1981).
- Aitchison, J. The statistical analysis of compositional data (with discussion). *Journal of the Royal Statistical Society, Series B (Statistical Methodology)* **44**, 139-177 (1982).
- Aitchison, J. Principal component analysis of compositional data. *Biometrika* **70**, 57-65 (1983).
- Aitchison, J. *The Statistical Analysis of Compositional Data* (Chapman and Hall Ltd, New York, 1986).
- Aitchison, J. Logratios and Natural Laws in Compositional Data Analysis. *Mathematical Geology* **31**, 563-580 (1999).
- Aitchison, J. The statistical analysis of geochemical compositions. *Mathematical Geology* **16**, 531-564 (1984).
- Aitchison, J., Barcelo-Vidal, C. & Pawlowsky-Glahn, V. Some Comments on Compositional Data Analysis in Archaeometry, in Particular the Fallacies in Tangri and Wright's Dismissal of Logratio Analysis. *Archaeometry* **44**, 295-304 (2002).
- Aitchison, J. & Kay, J. W. Possible Solutions of Some Essential Zero Problems in Compositional Data Analysis. *Compositional Data Analysis Workshop* <<http://ima.udg.es/Activitats/CoDaWoRk03/>>, (2004).
- Anon. Iwi Plans to Keep Control of Stone. *The New Zealand Herald* (Tuesday 21 September 2004). [http://www.nzherald.co.nz/section/1/story.cfm?c\\_id=1&objectid=3593207](http://www.nzherald.co.nz/section/1/story.cfm?c_id=1&objectid=3593207)
- Beck, R. J. & Mason, M. *Mana Pounamu New Zealand Jade* (Reed Publishing (NZ) Ltd, Auckland, New Zealand, 2002).
- Coleman, R. G. New Zealand Serpentinities and Associated Metasomatic Rocks. *New Zealand Geological Survey* **76**, 18-19, 78 (1966).
- Finlayson, A. M. The Nephrite and Magnesian Rocks of the South Island of New Zealand. *Quarterly Journal of the Geological Society of London* **65**, 351-381 (1909).

- Harlow, G. E. & Sorensen, S. S. Jade: Occurrence and Metasomatic Origin. *Australian Gemmologist* **21**, 7-10 (2001).
- Koons, P. O. A Study of Natural and Experimental Metasomatic Assemblages in an Ultramafic-Quartzofeldspathic Metasomatic System from the Haast Schist, South Island, New Zealand. *Contributions to Mineralogy and Petrology* **78**, 189-195 (1981).
- Martin-Fernandez, J. A., Barcelo-Vidal, C. & Pawlowsky-Glahn, V. Dealing With Zeros and Missing Values in Compositional Data Sets Using Nonparametric Imputation. *Mathematical Geology* **35**, 253-277 (2003).
- Nehring, F., Jacob, D. E., Barth, M. G. & Foley, S. F. Laser-ablation ICP-MS analysis of siliceous rock glasses fused on an iridium strip heater using MgO dilution. *Microchimica Acta* **160**, 153-163 (2008).
- Nichol, D. Two Contrasting Nephrite Jade Types. *Journal of Gemmology* **27**, 193-200 (2000).
- Popham, T. B. Characterisation and Resource Assessment; Scott Basin, Wakatipu, New Zealand. The University of Otago, New Zealand *The Department of Geology*, Master of Science- (2006).
- Reed, J. J. New Zealand Greenstone. *Australian Museum Magazine* **13**, 381-384 (1957).
- Ritchie, N. A. New Zealand Greenstone Sources. The University of Otago *Arts - Anthropology*, Masters of Arts Dissertation- (1976).
- Skinner, H. D. New Zealand Greenstone. *Transactions of the Royal Society of New Zealand* **65**, 211-220 (1935).
- Turner, F. J. The Metamorphic and Intrusive Rocks of Southern Westland: Part I. *Transactions of The New Zealand Institute* **63**, 178-236 (1933a).
- Turner, F. J. The Metamorphic and Intrusive Rocks of Southern Westland: Part II. *Transactions of The New Zealand Institute* **63**, 237-284 (1933b).
- Turner, F. J. Geological Investigation of the Nephrites, Serpentine, and Related "Greenstones" used by the Maoris of Otago and South Canterbury. *Transactions of the royal Society of New Zealand* **65**, 187-210 (1935).
- Wilkins, C. J., Craighead Tennant, W., Williamson, B. E. & McCammon, C. A. Spectroscopic and related evidence on the colouring and constitution of New Zealand jade. *American Mineralogist* **88**, 1336-1344 (2003).