TRACE ELEMENT FINGERPRINTING OF CANADIAN WINES

VIVIEN TAYLOR

TRACE ELEMENT FINGERPRINTING OF CANADIAN WINES

by

Vivien Taylor

A thesis submitted to the School of Graduate Studies in partial fulfilment of the requirements for the degree of Master of Science

Department of Environmental Science
Memorial University of Newfoundland

October, 2001

St. John's, Newfoundland

Abstract

Wines from Canada's two major wine grape growing regions, the Niagara Peninsula, Ontario and the Okanagan Valley, British Columbia, were fingerprinted with 100% correct classification, using the elements Al, V, Mn, Co, Zn, Sr, Rb, Mo, Sb, and U, for the purpose of verifying region of origin. Wines were diluted 2:1 with 0.2 M HNO_3 and element concentrations in wine were determined by inductively coupled plasma mass spectrometry (ICP-MS), with precision <5% for Cd, Sb, Ba, Tl, Pb, and U; <10% for As, Rb, Sr, Mo, Cs, La, Ce, and Th; <15% for V, Mn, Fe, Cu, Zn, Ag, and Bi; <20% for Mg, Al, Ca, Co, Ni, and Br; and <25% for Li, Be, Ti, Se, and I; and 27% for Cl and P. Element concentrations were log transformed to give a better evaluation of the consistency of the data given the assumptions evolved in parametric statistical models. Graphical analysis and multivariate statistics were used to discriminate wine by region, and the element Sr was found to have the highest discriminating power. Analysis of vineyard soils by X-ray fluorescence also revealed that Sr, as well as Ca, Ba, and Ti, can be used to discriminate soils from the two regions unequivocally. Note the relationship between soil and wine concentrations was not linear. Elements in wine grouped by principal component analysis showed agreement with elements grouped by ionic potential, suggesting element mobility has a strong influence on element concentrations in wine. Discriminant and cluster analysis of the Okanagan wines grouped wines made from grapes from the same vineyard to a high degree, suggesting individual vineyards could be fingerprinted for this region. The Niagara wines were grouped to a lesser extent by these statistical procedures, possibly due to the more homogeneous geology and climate of the Niagara region.

Acknowledgments

The author would like to thank Prof. Henry Longerich for advice and encouragement, as well as for monetary support and the opportunity to attend two conferences. Dr. John Greenough provided room and board during field work, as well as monetary support, and gave much needed explanations of geology. Lakmali Hewa, Mike Tubrett, and Pam King were extremely generous with their time and advice in the laboratory. I thank my academic committee, Dr. Paul Sylvester and Dr. Moire Wadleigh, who gave helpful advice, and Dr. Niall Gogan, for overseeing the course work portion of my degree. The School of Graduate Studies and Prof. Henry Longerich provided a fellowship for two years of financial support.

Table of Contents

List of Tables

List of Figures

List of Abbreviations and Symbols Used

Acid mine water ..... AMW

Atomic mass units ..... amu

British Columbia ..... B.C.

British Columbia Wine Institute ..... BCWI

Chemical Rubber Company ..... CRC

Counts per second ..... cps

Denver Federal Centre ..... DFC

Electrical Conductivity. ..... E.C.

F-statistic to evaluate variance between two groups ..... F

gram ..... g

High-efficiency particulate air. ..... HEPA

Inductively Coupled Plasma Mass Spectrometer. ..... ICP-MS

Less than detection ..... LD

Limit of detection ..... LD

Limit of quantization ..... LOQ

Litres l

Metres. ..... m

milli Siemens ..... mS

Millimetres. ..... mm

Minute ..... min

Mol per litre. ..... M

Most probable value ..... MPV

Parts per billion ..... ppb

Parts per million ..... ppm

Pearson's correlation coefficient ..... R

Picometres ..... pm

Principal Component Analysis. ..... PCA

Probability value ..... P

Radio frequency ..... RF

Recommended value ..... RV

Relative Standard Deviation ..... RSD

Scanning electron microscope ..... SEM

Standard Deviation ..... SD

T-statistic evaluate differences between two groups ..... T

United States Geological Survey ..... USGS

United Kingdom Earth Science Courseware Consortium ..... UKESCC

Vintner's Quality Alliance ..... VQA

Volts V

Watts ..... W

Weight percent ..... wt%

X-ray Fluorescence. ..... XRF

Chapter 1 Introduction

1.1 Fingerprinting wines

Fingerprinting wines to show region of origin has been examined for the purpose of verifying authenticity, and is of interest in Canada due to the recent growth and increased regulation of the wine industry. A fingerprint is an identifying pattern, and in this study refers to a pattern in trace element concentrations which identifies a wine, a vineyard, or a wine region. Trace element fingerprints are deciphered in wine by the determination of multiple element concentrations followed by statistical analysis of the concentrations. Studies of fingerprinting wines from other grape growing regions have used trace element concentrations (Baxter *et al.*, 1997; Danzer *et al.*, 1999), isotope ratios (Horn *et al.*, 1993; Day *et al.*, 1994; Eschnauer *et al.*, 1994), and organic compounds (Moret *et al.*, 1994). Baxter *et al.* (1997) analysed 48 trace elements in wine and were able to discriminate between English and Spanish wines with 95% correct classification, and between wines from 3 regions within Spain unequivocally. Individual vineyards in the Okanagan valley were identified with 100% correct classification using trace element composition (Greenough *et al.*, 1997). Wines from six different German wine producing regions were analysed for inorganic and organic constituents, and statistical analysis showed five of the regions could be fingerprinted, with 90% correct classification (Danzer *et al.*, 1999). These preliminary studies indicate that trace element concentrations show good potential for fingerprinting wine.

Bedrock composition, soil chemistry and viticultural practice are thought to have a strong influence on trace element composition of wine. Bedrock is weathered to form soil, and elements are taken up from the soil by grape plants from which wine is produced.

Wine processing can also enrich or deplete some element concentrations in wine. However, the proven ability to discriminate wines by region of origin suggests that regional environmental factors and viticultural practice have a controlling influence on element concentrations. The addition or depletion of some elements in wine differs with wine processing and winemaking technologies (Muryani and Papp, 1997; Eschnauer, 1982), for example the use of stainless steel storage tanks have been shown to increase Cr and Ni concentration in wines (Eschnauer, 1982). Wine processing methods and conditions differ with wineries and wines, therefore it is expected that element concentrations which are strongly influenced by viticulture or processing will have greater within region variability than between region variation. Wine processing practices can change from year to year, so using elements which have concentrations that are strongly affected by processing will create an unstable fingerprint, especially if it is to be applied to wines outside the sample population. For fingerprinting a specific wine, elements which are influenced by processing are useful unless processing practices change significantly between vintage years.

1.2 Major wine regions in Canada

The Niagara Peninsula and the Okanagan Valley are considered to be cool climate grape growing areas, due to their northerly latitude compared to other grape growing regions, and their cold winters. The Okanagan Valley spans 160 km, and many of the vineyards are located on the sloped sides of the valley on well drained soils of glacial and post glacial origin. Climate is governed by the region's location in the lee of the Coast Mountain range. The south end of the valley is Canada's only classified desert, receiving less than 10 cm of precipitation per year, whereas the north end is slightly less arid,

receiving less than 26 cm precipitation per year (BCWI, 2000). All the vineyards in the Okanagan are irrigated, with more water being required in the arid south end of the valley (BCWI, 2000). More detailed discussion of the geology and climate of the two regions are given in Chapter 5. Grape production in the region has rapidly expanded from 2500 acres of vineyard land in 1995 to 4200 acres in 1999 (BCWI, 2000).

The climate of the Niagara Peninsula is governed by its proximity to Lake Ontario and Lake Erie, as these large bodies of water store and release heat, moderating the temperature of the region from cold winter air masses (Haynes, 2000). The topography of the area is flat compared to the Okanagan, and soils are also of glacial origin, but are poorly drained due to a subsoil accumulation of clay (Chesworth and Evans, 1982). The major differences in viticultural practice between the two grape growing regions are that few of the vineyards in the Niagara region are irrigated, but many have been re-graded and had sub-drains added to improve drainage (Haynes, 2000).

1.3 Grape growing in Canada

Grape growers have become increasingly aware of the importance of which grape variety grows where, creating an interest in defining wine subregions, or appellations (Wilson, 1999). Grape variety has a defining influence on wine flavour, and hundreds of grape varieties exist. Most of the wine grape varieties produced today are members of the single species *Vitis vinifera*, the only vine which originated from Europe (Robinson, 1996). *Vitis vinifera* species are damaged by winter temperatures reaching below -20°C (Haynes, 2000), so there is a risk to growing *vinifera* varieties in Canada's cold climate. North American vine species, of which there are several, are better suited to the cool Canadian climate, but many, particularly *Vitis labrusca*, produce wines with a marked

musky flavour, making them less popular to consumers than wines made from the European grapes (Robinson, 1996). Hybrids are vines bred from more than one species, and vines bred from two or more North American species are termed American hybrids, whereas vines bred from *Vitis vinifera* and American species, are termed French hybrids. Hybrids have been produced both to suit climatic conditions of grape growing regions, and to combat mildew and pests. The American vines are resistant to phylloxera, a louse which attacks vine roots and has been termed "the great vineyard scourge", as it killed off many of the vineyards in Europe in the 1860's. Most *Vitis vinifera* vines are now grafted onto the roots of a *phylloxera* resistant American species, or onto specially bred rootstocks (Robinson, 1996). Both the Niagara and Okanagan regions went through a "rebirth" in the late 1980's and early 1990's when most of the North American vine species were pulled out and vineyards were replanted with *Vitis vinifera* grapes (Schreiner, 1994; Haynes, 1998).

1.4 Wine production in Canada

In Canada, most grapes are harvested in September, with the exception of grapes for late harvest wines and icewines, which are harvested as late as the end of November. Grapes are stemmed immediately after picking, to remove the stem, leaves, and grape stalks, and crushed, which is done either by pressing the grape against a perforated wall or passing the fruit through a set of rollers. Sulfite compounds are sometimes added to grapes immediately after harvest, to prevent microbial contamination before crushing (Jackson, 1989). Maceration is the breakdown of grape solids by crushing, allowing extraction of compounds from the seeds and skin into the juice. In red wine production, the macerate (crushed grapes, including seeds and skin) is fermented, but in white wine

production, the skins and seeds are usually removed immediately by pressing, and the juice is fermented (Jackson, 1989). To produce rose or blush wines, fermentation of the macerate is much shorter than for red wines. Maceration can involve a short exposure to high temperature, and then sulfur dioxide is usually added to the juice to prevent microbial contamination. Sulfur dioxide prevents microbial growth while not affecting most wine yeasts (Jackson, 1989). Trace elements which adsorb to the grape skin are expected to be more concentrated in red wines. Trace element concentrations were used to discriminate red and white wines (Greenough *et al.*, 1996); and to discriminate red, rose and white wines with 100% accuracy (Baxter *et al.*, 1997).

Dejuicing is accomplished first by allowing the juice to run out from the macerate under its own weight, followed by pressing, where pressure, spread out over a large surface area, is applied to the crushed grapes (Jackson, 1989). Fining, which is the removal of suspended solids, can be accomplished by adding the adsorbant clay, bentonite; by adding diatomaceous earth, or by filtration. The use of bentonite as a fining agent causes enrichment in rare earth elements in wine (Jakubowski *et al.*, 1999).

Sugar content of juice is measured as total soluble solids (in °Brix), and determines the capacity of the juice to support alcohol production. In cool climate grape producing areas such as Canada, cane sugar can be added near the end of the fermentation process if the juice °Brix is insufficient to generate the desired alcohol content (Jackson, 1989). Yeast cause fermentation to produce alcohol, where glucose and fructose are metabolised producing ethanol as one of the products. Wine is fermented and stored in large tanks or vats, usually made of oak, stainless steel, or fibreglass. During storage, crystals can form from tartrate and oxalate, and precipitate out Ca and other elements (Jackson, 1989).

Wines are usually bottled and corked in the spring following grape harvest, so wine processing takes about 8 months.

1.5 Wine Labelling

Fingerprinting wine by its trace element concentrations has applications for detecting fraudulent wines. Wines in Canada are labelled by grape variety, geographical region, and vintage year, which is the year in which the wine grapes were harvested. Wine production in British Columbia (B.C.) is governed by the British Columbia Wine Institute (BCWI), which enforces regulations on winemaking and labelling, and by the Vintner's Quality Alliance (VQA), which also sets standards for the wine industry, but to which membership is currently optional. Membership in the VQA of Ontario became mandatory on June 29, 2000, but the Ontario VQA is currently separate from the British Columbia VQA (Wine Council of Ontario, 2001). The Ontario and British Columbia VQA are in the process of joining to form VQA Canada, to make industry standards the same for both regions, and as a consequence labelling laws of Canadian wine are undergoing change in both areas.

At the time of sampling, there were slight variations between labelling and wine producing standards in the two regions, but the use of geographic and varietal designations are similar. Varietal wines are made from *Vitis vinifera* grapes or approved *Vitis vinifera* hybrids, where at least 85% of the grapes used are of the variety on the label. Geographical designation requires that wines be made from grapes exclusively from a given region. Wines which are labelled with a vineyard designation must be made from grapes grown only on that vineyard. Wines which are labelled "Estate Bottled" must be

made from 100% grapes owned or controlled by the winery in a viticultural area (BCWI, 2000).

1.6 Objectives and outline of the study

The primary purpose of the study was to determine if it was possible to differentiate the two wine-growing regions of Canada by trace element concentration, and to determine which elements are important to fingerprinting wine. Fingerprinting of subregions and individual vineyards was also examined within each region, and the source of the fingerprint elements in wine was studied by analysing the soils and examining the geology of the two regions. The ability to distinguish wines from the same vineyard within a region, and to fingerprint wines from which several vintage years were sampled, was also examined. Samples were taken to try to explain variability in element composition of wine caused by grape variety, regional environmental effects, differences in viticulture and processing.

A sample set of 95 Canadian wines, 59 from the Okanagan Valley and 36 from the Niagara Peninsula, were analysed by inductively coupled plasma mass spectrometry (ICP-MS) for 35 elements. Wines taken for the study were made from grapes grown on a single plot of land, and a soil sample was taken from the vineyard plot. To reduce the effects of varietal differences, wines made from the most popular varieties of *Vitis vinifera* grapes were chosen preferentially, because these were the most frequently available in both wine producing regions. *Vitis vinifera* grape varieties which were sampled were Riesling (29 samples, 2 of which were icewines, and 2 of which were late harvest), Chardonnay (16 samples), Pinot Blanc (12 samples), Gewurztraminer (9 samples), Pinot Noir (7 samples), and Pinot Gris (2 samples), as well as one wine each from the varieties Merlot, Muscat,

Rotberger, Sauvignon Blanc, Syrah, Traminer, and Viognier. Also sampled were the varieties Baco Noir (3 samples), Vidal (2 samples), Marechal Foch (1sample), and Okanagan Riesling (1 sample), which are French hybrids. Of the wines sampled, only 13 of the 95 were red, being from the grape varieties Baco Noir, Marechal Foch, Merlot, Pinot Noir, and Syrah. Rotberger grapes have a pale flesh and a dark skin, and wine made from these grapes is fermented on the skin, as are red wines, giving the wine a rose colour. The ability to discriminate wine variety and colour using trace element composition was also examined.

From within the Okanagan region, samples from 4 or 5 vintage years of the same wine were taken from 4 wineries, for the purpose of fingerprinting individual wines and vineyard plots. Samples from the upper, middle and lower part of a tank of wine, and from 3 different tanks containing the same wine, were sampled to determine the variability within a batch of wine. Two icewines were also analysed, and the effects of icewine production on trace element composition were examined.

From the Ontario region, wines made from 3 to 5 grape varieties, from grapes grown on the same vineyard, were sampled to fingerprint individual vineyards. Three wines processed at the same winery but made from grapes grown on different vineyards were sampled, to compare variability with wines which are processed at different wineries. The variability of element concentration in wine samples which were made from grapes grown on the same vineyards, but processed in two different wineries, were also compared.

Chapter 2 Analytical Methodology

2.1 Wine sampling

All samples were taken in the Okanagan Valley and the Niagara Peninsula in April-May, 1999, then transported to Memorial University of Newfoundland. The majority of the samples were taken from corked bottles of wine, except for 16 of the samples which were taken from processing tanks at wineries. Corks were removed from bottled wines and wine was poured into labelled 100 ml Nalgene bottles until completely full. The bottles were previously cleaned by soaking overnight in 2 M HNO_3, then rinsed with Nanopure water and dried in a high-efficiency particulate air (HEPA)-filtered air cabinet, which filters air to reduce contamination from particle deposition. For the 16 samples taken from tanks, the wine was either poured off through a spout on the tank or sampled with a pipette into a 100 ml bottle. The sample bottles were filled to the top and then capped to eliminate air bubbles and minimize the effects of oxidation during storage. The samples were transported to Memorial University of Newfoundland, and kept in cold storage (4°C) before analysis. The effects of storage on wine was examined by Baxter *et al.* (1997) and was shown to have no effect, although the amount of time from beginning to the end of the study was unspecified. Wine samples in this study were stored for three to five months before analysis, and relative standard deviation (RSD) was found to be similar for samples analysed on three consecutive days as three samples analysed several weeks apart (Fig. 2.1).

2.2 Wine analysis

Wines were analysed for 36 trace elements by ICP-MS (Li, Be, B, Mg, Al, P, S, Cl, Ca, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, As, Br, Se, Rb, Sr, Mo, Ag, Cd, Sb, I, Cs, Ba, La, Ce, Tl, Pb, Bi, Th, and U). Samples were analysed in duplicate or triplicate to monitor reproducibility of the analytical method.

2.2.1 Reagents and solutions

Solutions were prepared using distilled HNO_3. Equal volumes of Fisher Reagent Grade ACS concentrated acid and Nanopure type 1 grade water (17 MΩcm) were mixed and distilled in a sub-boiling quartz still (Quartz and Silice, France), and the distilled 8 M acid was collected in a Nalgene 201 polyethylene carboy (Longerich, 1993). Ethanol was Anhydrous Ethyl Alcohol from Commercial Alcohols Inc. (Brampton, Ontario).

2.2.2 Sample preparation

All sample tubes and standard bottles were cleaned prior to use by soaking overnight in 2 M HNO_3, then rinsing with Nanopure water and drying in a HEPA-filtered air cabinet. Wine samples were diluted by accurately weighing approximately 5 g of wine and 5 g of 0.2 M HNO_3 into 16 mm by 101 mm polypropylene tubes (Sarstedt, Germany). This method of sample preparation, as discussed by Baxter *et al.* (1997), gives the advantage of diluting the amount of ethanol from 10-12% in the wine to 5-6% in the sample, and thereby diminishes matrix effects associated with ethanol. All of the elements in gaseous state in the spray chamber are transported to the plasma, whereas only 1-2% of sample in liquid state reaches the plasma. Organic solvents often have a higher volatility than water and therefore in mixed aqueous-organic solutions, more of the sample solution

reaches the plasma, causing plasma instability (Montaser *et al.*, 1998). By reducing the amount of ethanol to 5-6% in the sample, the plasma loading is reduced causing a more stable plasma (Boorn and Browner, 1982). The 1:1 dilution maintains most trace element concentrations above detection limits of the ICP-MS, and the 0.1 M HNO_3 sample matrix maintains element stability in solution.

2.2.3 Calibration standards and reference materials

Four external calibration standards were used for the wine analysis. Standards were made up in 250 ml Nalgene bottles from laboratory stock solutions which were prepared using SPEX Plasma-Grade standard kit powders. Standard solutions were matrix matched to the wine samples by diluting with 0.1 M HNO_3 and adding ethanol to a final solution of 6% w/w. Element concentrations in the standards are given in Table 2.1.

Water reference materials T-123, T-127, T-129, T-135 (United States Geological Survey(USGS)) and Acid Mine Water (AMW-3; Denver Federal Centre (DFC), Colorado) were matrix matched to the wine solutions by diluting 10 ml reference material with 84 ml 0.1 M HNO_3, and 6 ml ethanol, to give a final solution of 6% ethanol. These reference materials were then analysed as unknowns to monitor the accuracy and precision of the analyses.

2.2.4 Instrumentation

The inductively coupled plasma mass spectrometer (ICP-MS) was a Hewlett Packard 4500 Series ICP-MS which uses a quadrupole as the mass analyser, an Ar plasma source and a concentric nebuliser. Samples are nebulised into a Scott double pass spray chamber, where larger droplets (>10 μm) are deposited on the walls of the spray chamber

then fall into a drain, and the finer droplets, as well as the molecules in gas phase, are transported to the plasma by the carrier gas (Montaser *et al.*, 1998). The instrument laboratory is supplied with two air conditioners in order to minimise instrument fluctuations. A Neslab CFT-75 Refrigerated Recirculator cools deionised water flowing to the Peltier cooling device, which in turn cools the spray chamber to 2°C. Water from the cooler is also passed through the copper tubing of the load coils, and through cooling water lines to the sample interface, the turbo molecular pump at the ion lens chamber, and the radio frequency (RF) amplifier, to prevent overheating (HP 4500 ChemStation Operator's Manual, 1997).

2.2.5 Operating conditions

The tuning parameters for the instrument are given in Table 2.2. The instrument was tuned for maximum sensitivity and uranium oxide ion formation of less than 2%, according to HP 4500 ChemStation Operator's Manual Ch. 2. A tuning solution of 10 ppb Co, Y, Rh, Cs, Tm, and U was made up to 0.1 M HNO_3 and 6% ethanol and used to optimise sensitivity throughout the mass range. Optimal operating conditions, particularly the ion lens settings (Longerich *et al.*, 1985), are different for low and high mass elements, so tuning for the entire mass range compromises the sensitivity (count rate per unit concentration).

The instrument was operated at a radio frequency (RF) power of 1500 W (increased from 1200 W usually used for solution analysis) to accommodate the dilute ethanol (5-6%) content of the samples (Longerich, 1989). Because of the increased plasma loading caused by the ethanol in the samples, the RF power was raised to ensure a stable plasma. A high RF power increases plasma tolerance to organic solvents and creates

a hotter plasma with higher ionisation (Boorn and Browner, 1982). Plasma temperature, which is decreased by the introduction of volatile solvents into the spray chamber, can be increased by 1) increasing RF power (Lichte, 1987), 2) decreasing Ar gas flow (carrier, auxiliary, and nebuliser gas), and 3) decreasing sample uptake. The plasma gas cools the outer torch tube, so because of the increased torch temperature resulting from the high RF power, a high plasma gas flow-rate (14 l/min) was used to cool the torch and ensure plasma stability.

Once sensitivity was optimised, the conditions for low oxide ion formation, without loss of sensitivity, were found by aspirating the tuning solution and measuring the ion intensities for $^{238}U^{+}$ and its oxide $^{238}U^{16}O^{+}$. The oxide ratios (254 / 238 amu) were approximately 1%, and did not exceed 2%. The formation of oxides decrease with an increase in plasma temperature, as more bonds break (bonds break when heat energy is greater than bond energy), and equilibrium shifts from MO^{+} to $M^{+} + O$, reducing polyatomic species formation in the plasma. The operating conditions determined for optimal sensitivity with low oxide ion formation are given in Table 2.2.

Nebuliser gas flow has a strong effect on the ion signal intensity (Longerich, 1989). The effect of nebuliser gas flow on signal intensity, oxide formation, argide formation and double ion formation was examined for a number of elements. The data acquisition software was programmed to count each of the desired ion intensities for 10 s, with the nebuliser gas flow-rate set at 0.5 l/min. The nebuliser gas flow-rate was then increased by 0.1 l/min and the ion intensities were acquired again. This was repeated over the range of nebuliser gas flow-rates from 0.50 to 1.50 l/min, and ion signal intensity was then plotted as a function of nebuliser gas flow-rate (Figs. 2.2 to 2.5). Thorium ($^{232}Th^{+}$) is a good indicator of polyatomic ion formation because it forms the strongest oxide bond

(204 Kcal/mol) of all the elements except carbon (CRC Handbook of Chemistry and Physics, 1983), and therefore provides a "worse case scenario" for oxide formation for a given set of operating parameters. Fig. 2.2 shows optimal ion intensity, with low oxide ion interference, occurs at a nebuliser gas flow-rate of 1.0 l/min. The background signal, monitored at 227 amu, was stable throughout the range of nebuliser gas flow-rates. Although Co forms much weaker oxide bonds than Th (88 Kcal/mol, CRC Handbook of Chemistry and Physics, 1983), ion intensity and oxide formation as a function of nebuliser gas flow-rate were examined in Fig. 2.3 to show a nebuliser gas flow-rate of 1.0 l/min gave high sensitivity and low oxide ion formation for a low mass element.

The effect of nebuliser gas flow-rate on the sensitivity of ^{140}Ce was examined, as well as oxide formation ($^{140}Ce^{16}O^{+}$), and doubly charged ion formation ($^{70}Ce^{++}$) (Fig. 2.4). The signal intensity was found to be optimal at a nebuliser gas flow-rate of 1.1 l/min, with oxide formation decreasing with decreasing gas flow, and a high sensitivity and low oxide formation occur at 1.0 l/min gas flow rate. Doubly charged ion formation, which usually decreases with increasing gas flow, was found to be low throughout the range of nebuliser gas flows. The nebuliser gas flow-rate was therefore set to 1.0 l/min as a comprimise between high sensitivity and low oxide formation.

Because the hotter plasma associated with running at an RF power of 1500 W causes a higher temperature torch box, the water cooler was found to be inadequate at keeping the cooling water at 20°C. Temperature drift in the water cooling the loading coils of the torch can create instability in the plasma conditions. The cooling water temperature was set to 25°C, to keep the water temperature stable and the torch conditions constant.

Because many of the low mass elements were important to this study, and have higher backgrounds as well as more interferences than do high mass elements, the nebuliser gas flow-rate was further examined, where the low mass elements were optimised in terms of maximum signal intensity (Fig. 2.5). Optimal signal intensity was found to occur at 1.1 l/min nebuliser gas flow-rate. While the signal intensities for ^{55}Mn and ^{65}Cu decreased for gas flow-rates greater than 1.1 l/min, the signal at 42 amu remains above 100,000 cps. This is due to an increase in argide formation at higher gas flow-rates, and the signal at 42 amu becomes enhanced by the presence of $^{40}Ar^{1}H_2$. The signal at 43 amu is also enhanced, though to a lesser extent, by the tail of $^{12}C^{16}O_2$, and the formation of $^{40}Ar^{2}H^{1}H$ and $^{40}Ar^{1}H_3$. Argide formation, along with all polyatomic ion formation, is minimised by lowering the gas flow-rate, but is accompanied by a loss of sensitivity. Setting the nebuliser gas flow-rate to 1.0 l/min compromises a high sensitivity with low argide formation.

2.2.6 Background ion intensities

The formation of polyatomic argides, hydrides, oxides, nitrides and carbides in the plasma causes high background intensities, especially in the low mass range. The high ion intensities for the 6% ethanol blank, as compared to the 0.2 M HNO_3 and H_2O blank solutions, resulted in high detection limits for several of the low mass elements due to the formation of polyatomic species. The spectrum for the lower mass range of a 6% ethanol blank is compared to the spectra of 0.2 M HNO_3 and H_2O in Fig. 2.6. The low mass spectra of 2 wine samples, Irvine Chardonnay and De Sousa Baco Noir, are plotted with the spectra of the 6% ethanol blank, in Fig. 2.7, to show ion intensities in wine compared to those in the calibration blank (background intensities). For ions where the concentration

of the analyte in the sample is below or close to the background intensity, which is high due to high backgrounds from polyatomic ion formation, quantitative analysis is not possible. Elements which were below detection limit in most wines were ^{28}Si, due to the occurrence of $^{12}C^{16}O$ at 28 amu, ^{45}Sc, due to the occurrence of $^{12}C^{16}O^{16}O^{1}H$ at 45 amu, and ^{52}Cr and ^{53}Cr, because of the formation of $^{40}Ar^{12}C$ and $^{40}Ar^{12}C^{1}H$. The polyatomic species $^{40}Ar^{13}C$ is also present at 53 amu, but its abundance is relatively low compared to that of $^{40}Ar^{12}C^{1}H$.

In addition, analytical data for B and S were discarded. The element, ^{10}B, was below detection in most wines and all reference materials, due to high backgrounds. The element, B, has a low mass and a high ionization potential so quantization by ICP-MS is expected to be poor. The use of boric acid in sample preparation for rock samples analysed by the HP 4500 Series ICP-MS may also cause memory effects for this element. Backgrounds were also high for ^{34}S, causing high detection limits and poor precision. Because metabisulfite is used to prevent bacterial growth in wine processing and in storage equipment, high variability in S concentrations may occur between wines from the same vineyard and different batches of the same wine, and therefore S is not expected to be a useful element for discriminating wine by region.

2.2.7 Choice of isotopes

For elements where two or more isotopes exist, analyte ions can be chosen by examining the spectra for masses with high analyte isotope abundance and low interferences and backgrounds. The isotope ^{35}Cl was measured due to the high background on ^{37}Cl caused by $^{36}Ar^{1}H$. Both ^{42}Ca and ^{43}Ca were measured, but the determination of ^{43}Ca was used in the data analysis, because despite the higher isotopic

abundance of ^{42}Ca, the occurrence of $^{40}Ar^{2}H$ at 42 amu causes a high background. The other isotopes of Ca were not used for the determination due to the presence of Ar at 40 amu, $^{12}C^{16}O^{16}O$ at 44 amu and the isobaric interferences with Ti at 46 and 48 amu. Three isotopes of Fe were measured, at 54, 56, and 57 amu. Determination of the isotope ^{57}Fe was used as a high background occurred at 56 amu from $^{40}Ar^{16}O$, a high background occurred at 54 amu due to $^{40}Ar^{14}N$, and Cr causes an isobaric interference at 54 amu. The two isotopes ^{77}Se and ^{82}Se were measured, with high backgrounds occurring due to $^{40}Ar^{36}Ar^{1}H$ and $^{40}Ar_{2}{}^{1}H_{2}$, and interferences occurring from $^{40}Ar^{37}Cl$ and $^{81}Br^{1}H$. The determination of ^{82}Se was used for the data analysis although the detection limits of the two isotopes are similar. Determined concentration of these two Se isotopes showed good agreement, which is evidence for good background and interference correction.

2.2.8 Analog calibration

The Hewlett Packard 4500 Series ICP-MS has two modes of detection: a pulse counting mode, which measures ions in counts per second (cps), and an analog mode, which measures a current signal, and is cross calibrated with the pulse counting mode to produce an equivalent cps. The pulse counting mode is used for low ion intensities, up to about 1,000,000 cps, and the analog mode, which overlaps the upper range of the pulse counting mode, can be used for signals above 10,000 cps, but is better not used until required (at 1,000,000 cps), as pulse counting has less noise. Calibration of the analog current to equivalent cps is performed once a week according to the procedure in the HP4500 ChemStation Operator's manual, using tuning solutions made up in 0.1 M HNO_3 and 6% ethanol, to give signals with low RSD in both modes.

2.2.9 Data acquisition

The elements ^{103}Rh and ^{187}Re were used as internal standards because they are not present in significant quantities in wine. An internal standard containing 2 ppm Rh and Re in 0.2 M HNO_3 is introduced to the sample tube by a y-connector, to give a sample solution containing approximately 0.1 ppm internal standard. Both the sample uptake and the internal standard uptake are controlled by a peristaltic pump, and the sample solution reaches the nebuliser at a rate of 0.4 ml sample/min and 0.02 ml internal standard/min. The use of two internal standards allows the interpolation or extrapolation of a matrix correction throughout the mass range (Longerich, 1990).

A wash cycle with 0.5 M HNO_3 for 180 s was performed between each analysis. Two flush samples were placed at the beginning of each run in order to allow the uptake of internal standard solution to reach the y-connector.

Samples were run in sets of 14, in which there are four calibration standards (solutions containing known amounts of specific elements (HP 4500 Chemstation Operator's Manual)), a flush sample (a solution used to rinse out residual analytes caused by high concentrations in the samples), a calibration blank (a solution used to determine background concentrations for the calibration solutions; a reagent blank is a blank for the sample solutions, but was not used in this study because samples and calibration solutions were matrix matched), six unknown wine samples and two reference materials. Two wine samples, Irvine Chardonnay and Inniskillin Chardonnay, were used as in-house reference materials and one of these samples was analysed in every run, to monitor long term reproducibility. Cycles of 14 tubes (data acquisition for 1 cycle takes 170 min) were used to provide frequent re-calibration and drift correction. Because of the increased volatility of the 6% ethanol samples compared to aqueous solutions, evaporation is more of a

concern as it alters concentration. To reduce evaporation effects, runs were no longer than 3 cycles and the tubes were kept covered until immediately before the run commenced. Calibration standards, which are usually measured repeatedly from 500 ml bottles throughout many runs, were poured into tubes for analysis, to ensure that evaporation effects are the same for samples and standards. Using larger vessels for repeated measurements and runs may allow evaporation of ethanol over time, altering the concentration of the standards and causing a difference in matrix between the samples and standards.

2.3 Calculation of unknown element concentrations

The wine standards and samples were analysed by ICP-MS, using the operating parameters given in Table 2.2. The ion intensities are recorded as cps (counts per second), and the unknowns are then calculated as concentrations in parts per billion (ppb) according to the procedure described in detail in Appendix 1, which was written as a Lotus 1-2-3 (Release 5) spreadsheet, Wine.wk4.

The data was reduced first by matrix correction, then blank correction. Interference corrections were made for Cl on ^{49}Ti, ^{51}V, and ^{77}Se; Br on ^{82}Se; and Ca on ^{57}Fe, ^{59}Co, ^{60}Ni, and ^{65}Cu, for which ion intensities of interfering species are shown in Fig. 2.8 and 2.9. Also shown in Fig. 2.9 is the ion intensity of the interference caused by Cl on ^{75}As, which was negligible and therefore not corrected. Sensitivity (cps/ppb) of analytes throughout the mass range, normalized to isotopic abundance, is given in Fig. 2.10 (calculation for sensitivity given in Appendix A). Ion intensity (in cps), was divided by sensitivity and by dilution factor to give concentrations (in ppb) of analytes in wines.

2.3.1 Detection limits and precision (as RSD) calculated for each element

Detection limits (DL) and limits of quantization (LOQ) for the method are calculated for quality assurance and to allow interpretation of the uncertainty of the data, especially for analytes with concentrations near or below the DL. The DL is defined as the lowest concentration that can be determined to be statistically different from a blank (Douglas, 1992). The solution detection limit was calculated as 3 times the standard deviation of the mean count rate of the analyte in the calibration blank, divided by its sensitivity in ppb/cps. The sample detection limit is calculated for each analyte of each unknown sample, by dividing the element detection limit by the sample dilution factor. If the sample detection limit for an element is greater than the concentration calculated for that element, then the precision of the analysis is poor as the percent relative standard deviation (RSD) for that concentration is greater than 33%. Confidence in the apparent analyte concentration increases as the analyte signal increases above the DL (Keith *et al.*, 1983). Limit of quantization (LOQ), calculated from 10 times the standard deviation of the blank divided by sensitivity, gives a more rigorous parameter for detection. The LOQ is defined as the level above which quantitative results may be achieved with a certain degree of confidence (Keith *et al*, 1983). Table 2.3 gives mean sample DL and LOQ's for the method, calculated as the solution DL or LOQ divided by the mean sample dilution factor.

The reproducibility of the method was determined by analysing each of the wine samples in duplicate or triplicate. Precision, as RSD for each analyte, calculated as the mean RSD of the samples with concentrations above LOQ, is reported in Table 2.3.

The detection limits for many of the lower mass elements were high for wines measured by this procedure due to high backgrounds from polyatomic ion formation, but

none of the wines analysed had concentrations below LOQ for the elements Li, Be, Mg, Al, Ca, Ti, V, Mn, Fe, Co, Ni, Cu, or Zn were below LOQ.

Poor precision was found for the halogens, Cl, Br, and I, which also have high detection limits associated with them because of their high ionization potential, and also due high backgrounds for Cl and Br (Section 2.2.7). High analytical backgrounds for these elements occur in St. John's, where the wines were analysed, due to high atmospheric concentrations from road salt and sea spray. Of the halogens, I has the lowest detection limit due to the low background at 127 amu, which is only continuum as there are no polyatomic species causing high background at this mass. It is also monoisotopic and has the lowest ionization potential of the halogens, although it is also the lowest crustal abundance halogen.

The detection limit and RSD of the element P was also high, due to high backgrounds and low sensitivity due to a low ionisation potential (Douglas, 1992). Low ionisation potential as well as polyatomic background and interfering species also cause poor precision for Se, and concentrations in most wines are below LOQ (but above DL). Several determined concentrations of the elements Ag and Bi were below detection limit.

2.3.2 Accuracy of the method

The mean measured concentrations of elements in the five waters reference materials (USGS and DFC) are compared to the recommended values (RV) for the reference materials, and most probable values (MPV's) compiled from past runs on the instrument (HP 4500 Series at Memorial University of Newfoundland), which are used as in-house reference values (Table 2.4). The MPV's compiled at Memorial University of Newfoundland have been found to be consistently and significantly different than RV's for

some values, which is thought to be due to RV's being compiled from a large data base with high variability. Where concentrations compiled from past runs were found to be significantly different from recommended values, MPV's are given, and were used as "most probable" values instead of the recommended values. Because the waters reference materials were diluted 10 times, the sample detection limits of these materials are approximately 5 times higher than those of the wines, although the solution detection limits remain the same as for the wine samples.

There is poor agreement between the MPV and the measured concentration for Zn in reference T-123, because the MPV is below the LOQ. The concentration of Zn in this reference material is well below the range of concentrations of Zn in the wine samples, and the measured values for Zn show good agreement with MPV's in the other reference materials, which contain higher concentrations.

None of the halogens determined (Cl, Br, and I) had MPV's available for the reference materials, so the accuracy of their determination could not be assessed. Concentrations of I were found to be highly variable between wines, suggesting it may be of use in discriminating wines. In the environment, I exists in several oxidation states. In highly oxidizing environments, I is in the form of IO_3^-, which is a mobile and stable species. In its most reduced form, I^-, it is also mobile, but can be oxidized to the volatile species I_2. Wines are a reducing environment, as the alcohol-producing yeast use up the oxygen creating an anaerobic environment, and I is therefore expected to exist in its reduced form, I^-. The wine samples were diluted to 0.1 M HNO_3, so it is possible that I^- was oxidised to I_2. When the samples are analysed by ICP-MS, the I_2 would easily convert to a gas upon nebulisation, and a signal enhancement would occur as gas is transported from the spray chamber to the plasma with 100% efficiency, whereas only 1-2% of the

solution reaches the plasma. The oxidation state of I in the calibration standard is different from that of the samples, as paraperiodic acid is acidified with 0.2 M HNO_3, so I is in an oxidized state as IO_3^-, and will not be volatilised in the spray chamber. The uncertainty in the speciation of I in solution also creates uncertainty in the accuracy of the wine analysis. The inclusion of elements in the fingerprint analysis is further discussed in Section 2.6. The elements P, Cl, and Br, for which accuracy and precision are suspected to be poor, were left out of the analysis, whereas for the elements Se, Ag, I and Bi, concentrations in wine were examined relative to other elements, but were not included in the regional fingerprint.

2.4 Icewines

Icewines are made from grapes which are naturally frozen on the vine at -8°C or lower (VQA Icewine Factsheet, 2000). Grapes are harvested for icewines much later than other wine grapes, often in late November, so these grapes left on the vine have more time to bioaccumulate trace elements. Grapes also wither and shrink when they are left on the vine this late, which may cause element concentrations in the fruit to become more concentrated. Grapes are harvested and pressed while frozen, and most of the water in the grape cells remains in the press as ice, so the juice is extremely concentrated and has a high sugar content (Jackson, 1994). Due to the high concentration of sugar in the icewine juice, the wine is left with a residual sugar concentration of greater than 100 g/l after fermentation (which converts sugar to ethanol and CO_2). This high sugar content in icewines caused these samples to be poorly matrix matched to the calibration standards and blanks, and high backgrounds and interferences were suspected due to the higher C content of these samples. To determine the accuracy of the analysis, and the high

backgrounds caused by the sugar content, full mass spectra were collected for a solution of 6% ethanol in 0.1 M HNO_3 (calibration blank), a solution of 6% ethanol in 0.1 M HNO_3 also containing 100 g/l fructose, a solution of 6% ethanol in 0.1 M HNO_3 containing 180 g/l fructose, and two icewines (Lang and Summerhill Riesling Icewines). Sugar in wine is actually approximately 50% fructose ($C_6H_{13}O_6$) and 50% glucose ($C_6H_{12}O_6$), but the two molecules are expected to have similar spectra due to their similar formula and structure. High backgrounds in the fructose solutions, compared to the calibration blank, are due to polyatomic species containing C, H, and O. Fructose has a molecular weight of 180 amu, and the fructose solutions have higher ion intensities at this mass than does the calibration blank, indicating that a small percentage of the fructose molecules are not atomised in the plasma. The fructose molecule (Fig. 2.11) breaks in the plasma to form the species CH_2OH-C=O at 59 amu, causing a high background for Co, and $(CHOH)_3CH_2OH$ at 121 amu, causing a high background for Sb (Figs. 2.12 and 2.13). Several hydrocarbon species form in the intermediate mass range, some of which are CH_2OH-COH at 60 amu which causes a high background for Ni, O=COH-CHOH at 75 amu which causes a high background for As, and O=C-$(CHOH)_2$ causes a high background at ^{88}Sr (Fig. 2.13).

2.5 Wine digests

Ten of the wine samples were prepared for analysis by a digestion procedure, used by Greenough *et al.*, (1996 and 1997), as well as by the dilution method described above. This study served two purposes: 1) the comparison of the digested sample data with the dilution method and 2) the removal of interferences caused by ethanol carbon in the

diluted wine samples, which especially effects the elements Si and Cr due to high backgrounds from the formation of CO and ArC.

2.5.1 Digestion procedure

From each wine sample, 20 g of wine was weighed accurately into a 30 ml Teflon digestion jar. The flasks were placed on a hotplate at 90°C and the sample volume was reduced to a few mls. Approximately 2-3 ml of 8 M HNO_3 was added and the wines were taken almost to dryness. The residual was then dissolved in approximately 20 g of 0.2 M HNO_3 (Greenough *et al.*, 1997).

2.5.2 Analysis by ICP-MS

The wines were analysed by a Hewlett-Packard Series 4500 ICP-MS for the elements Li, Be, B, Mg, Al, Si, P, S, Cl, Ca, Ti, Cr, Fe, Mn, Co, Ni, Cu, Zn, As, Br, Se, Rb, Sr, Ag, Cd, Sb, I, Cs, Ba, La, Ce, Tl, Pb, Bi, and Th. Because the ethanol was removed from the samples, the wines were analysed as waters with an RF power of 1200 W and a nebuliser gas flow of 1.0 l/min. The calibration standards were made up in 0.2 M HNO_3, and contained the same elements as those used for the wines (Table 2.1), except for the exclusion of Th from Standard A, as it was used as an internal standard. A solution of 2 ppm ^{45}Sc, ^{103}Rh, ^{187}Re and ^{232}Th in 0.2 M HNO_3 was used as an internal standard, and all count rate data was corrected for matrix effects, background and drift, as with the data reduction procedure for the wine samples. The only element with a mass greater than ^{232}Th was ^{238}U, and for this element matrix effects were linearly extrapolated from the internal standards. Linear interpolation from the internal standard data, was used for elements with masses between ^{45}Sc and ^{232}Th. For elements with masses less than ^{45}Sc,

the matrix effects were linearly extrapolated, which is different from the data reduction of the wine samples prepared by the dilution method, where matrix/drift correction factor was not extrapolated (but kept constant) for elements lighter than ^{103}Rh. For the wines prepared by the dilution method, a low mass internal standard could not be used due to high backgrounds from the ethanol in the samples, and extrapolation from 103 amu was determined to cause extreme correction factors in the low mass range. Blanks were subtracted and known interferences, which for the digested samples were Cl with ^{51}V, ^{75}As, and ^{77}Se; Ca with ^{57}Fe, ^{59}Co, and ^{60}Ni; and Br with ^{82}Se, were corrected for mathematically. Sensitivity and concentration were then calculated using the four external standards, as with the diluted wines. The disadvantages of the digestion method compared to the dilution method are that volatile elements (especially Cl, Br, and Se) are lost upon evaporation of the sample, the additional reagents used for the digestion increase the risk of contamination, and sample preparation is more time consuming. The problem of polyatomic carbides causing high backgrounds is considerably reduced in the digestion method by the evaporation of ethanol, but significant C concentrations were still present due to C in the Ar gas supply and C entrained from the atmosphere. The removal of ethanol lowered the detection limits for Cr and Si enabling them to be quantified, as high backgrounds obscured these elements from being determined by the dilution method. The results from the digested wine show good agreement with those prepared by the dilution method (Fig. 2.14) for the analytes Mg, Al, P, Ca, Ti, V, Fe, Mn, Co, Ni, Cu, Zn, As, Rb, Sr, Mo, Cd, Sb, Cs, Ba, La, Ce, Tl, Pb, and U.

2.6 Multivariate analysis

Multivariate analyses are statistical methods used to identify patterns in multivariate data sets (Statsoft, 1999), which are data sets with multiple random variables which are interrelated in such a way that their different effects cannot be interpreted separately (Hair, 1987). Multivariate statistics are useful to identify patterns in large data sets (Statsoft, 1999), and have been used for chemical fingerprinting in environmental studies which rely on a large amount of chemical data (Urdal *et al.*, 1986; Van Dobben *et al.*, 2001; Vogt, 1997). Because no individual element was found to completely discriminate wine by region, and the large number of values of data available to fingerprint wines (35 analytes for 95 wines), multivariate statistics were applied to reduce and analyse the data. Other multi-element studies of wine classification have used multivariate statistical methods for deciphering patterns of recognition for different regions and showing structures in the relationships between elements (Danzer *et al.*, 1999; Baxter *et al.*, 1997; Soleas *et al.*, 1997; Greenough *et al.*, 1997 and 1996; Moret *et al.*, 1994 and 1984; Latorre *et al.*, 1994). All of the multivariate techniques rely heavily on computer software. For this study Systat Version 6.1 was used, along with Minitab 12 for creating normality plots (Section 2.6.2).

2.6.1 Application of statistics to chemical data

Data from chemical analysis presents certain difficulties when applying statistical methods. Analytical uncertainty can not be accounted for in multivariate methods, so errors can occur by including analytes with concentrations close to detection limit in statistical methods as the RSD associated with them is high. Small data sets and outliers cause results to be skewed and have low significance, and the multivariate methods used

assume the variables are normally distributed (a normal distribution would assume that for each element, 68% of the determined concentrations are within 1 standard deviation (SD) of the mean, 95% of the concentrations are within 2 SD, 99% are within 2.5 SD).

2.6.2 Considerations for analytical uncertainty

All of the statistical methods used were parametric, meaning the methods assume certain population parameters, usually a normal distribution and equal variance about the mean. Data values which are below detection limits are difficult to account for in parametric statistical methods, because for most statistical procedures, ordinal values (values which are greater or less than a value, such as concentrations below detection limits) can not be included even though they have some quantitative meaning. Concentrations below detection limit in this study were not discarded because they have meaning relative to concentrations in other wines, however, elements for which there are several wines with concentrations below detection limit were excluded from the fingerprint analysis. Concentrations which are less than the detection limit are sometimes calculated to have small negative values. ICP-MS, along with most analytical methods, has a non-zero background which is subtracted from the gross signal to give the net signal. For a set of samples with a mean concentration of zero, half the samples will be calculated to have positive values and half will have negative values.

2.6.3 Graphical examination of the data

Before any statistical procedures were applied to the data, descriptive statistics were used to examine characteristics of the data set. Box plots were created for each of the elements in wine, to provide a visual summary of the data (Fig. 2.15). The median of

the data set splits an ordered batch of numbers in half (50th percentile), and the quartiles split each half of the data in half, marking the 25th and 75th percentiles. The interquartile range, which is the range between the quartiles, is represented as the height of the box, so the box outlines the extent of the central half of the data, and the median is marked as a line dividing the box into halves (Wilkinson, 1996). The upper whisker of the plot extend to the largest value that is less than or equal to 1.5 times the interquartile range, and the lower whisker extends to the smallest value that is less than or equal to 1.5 times the interquartile range. Values outside the range of the whiskers are marked with an asterix. Box plots were created for each of the elements, and examination of these plots shows the median, spread or overall distribution, skewness (symmetry about the mean) and the presence of outliers.

Because a normal distribution is an assumption of the statistical methods used, each element was also plotted on a normality plot, in which variables are plotted against a theoretical normal distribution with the same mean and standard deviation as the data.

Fulfilment of the assumption of normal distribution in a sample set decreases with the number of samples. The wine sample set has 95 samples, and Monte Carlo studies have shown that violations to the assumption of normal distribution are not as serious as expected, especially with large numbers (greater than 100) of samples (StatSoft, 1999).

2.6.4 Multivariate methods

The multivariate techniques which were used to classify wine samples are principal component analysis (PCA), cluster analysis, and discriminant analysis. A combination of these methods was used for the fingerprinting of wines, to fully explore the data and diminish restrictions that may be put on the analysis by any particular technique.

Relationships between element concentrations were first examined using PCA and cluster analysis, then discriminant analysis was used to determine a fingerprint to distinguish wines by their region of origin.

2.6.5 Principal component analysis

The behaviour of elements in Canadian wine was examined using principal components analysis. Principal component analysis (PCA) is a data reduction technique, in which the interrelationships between large numbers of variables are analysed and classified in terms of common underlying dimensions or factors (Hair, 1987). This approach condenses a large number of variables into a smaller set of dimensions with a minimum loss of the information which they contain.

The first step in factor analysis is the derivation of a Pearson correlation matrix for element concentrations in wine, in which Pearson's R correlation coefficients determine the extent to which values of the two variables are proportional to each other. Pearson's R range from +1 to -1 and because of the linear relationship there is an assumption that the variables are normally distributed in the population. A normal distribution assumes that outliers are highly unlikely and therefore meaningful, having a large influence on correlation coefficients. The robustness of the Pearson R values were examined by plotting each analyte against every other analyte in a simple *x*-*y* scatter plot, and also by determining a probability value associated with each correlation. The probability value (p) is the probability that an observed relationship occurred by pure chance, so for $p = 0.05$, there is 95% confidence that the relationship can be reproduced (StatSoft, 1999). The correlation matrix is then examined for high values expressing similarity between variables. If two variables are highly correlated, it is indicated they will give the same information,

and one of them can therefore be discarded, as a ratio of 4 or 5 observations relative to variables is recommended to produce a stable model, although a ratio as low as 2 observations relative to one variable is allowed by the method (Hair, 1987).

Unrotated components give the best linear combination of variables, meaning the combination of variables which accounts for more of the variance than any other combination (Hair, 1987). The component loadings range from 0 to 1, and are ideally high for a few variables and low for all other variables in the analysis, showing a clear grouping of variables. The number of components in PCA is initially derived by the latent root criterion, then adjusted experimentally. With the latent root criterion only factors which have eigenvalues greater than 1 are included. Eigenvalues are the column sum of squares for a component, and represent the amount of variance accounted for by that component (Hair, 1987). The criterion is based on the rationale that if a factor is to be retained it should at least account for the variance of a single variable. Another determinant is the scree plot derived by Systat as part of the PCA, in which the eigenvalues are plotted against the number of factors in their order of extraction, and a cutoff point is determined from the shape of the graph. The plot begins as a steep slope then slowly becomes a horizontal line. The cutoff point for the number of factors to be used can be taken as the point at which the slope begins to straighten out (Wilkinson, 1996).

Rotation of the component matrix redistributes the variance to achieve a different component pattern. Orthogonal rotation is accomplished by rotating the factors clockwise so that the primary factor passes close to a cluster of variables, while the second factor remains at a 90° angle to it (Hair, 1987). Varimax rotation was used to maximize the variance of the component loadings by rotating the initial factor so that a variable loads high on one factor and as low as possible on all other factors (Hair, 1987). The

components determined by PCA are labelled by the elements they group, and the total variance explained by each component is determined by converting the eigenvalue to a percent value.

2.6.5.1 Elements discarded from the PCA

Examination of the PCA reveals simple data structures, but a high proportion of variables to samples has been determined to make the PCA less reproducible (Hair, 1987), so several elements were removed, also making the analysis easier to interpret. Elements were excluded from the analysis if they did not load high on any of the components, a high analytical uncertainty associated with them, and if concentrations are expected to be strongly influenced by processing, which would make the element a poor discriminator of region. The elements, Cl and Br, loaded moderately high in several components and were removed from the analysis. As well as having high analytical uncertainty associated with them (Section 2.6.2), these halide elements can be introduced into wine from the use of antiseptics such as monochloracetic acid, and improperly cleaned ion exchangers through which wines are sometimes passed to remove suspended material affecting taste, odour, and clarity of the wine (Amerine *et al.*, 1982). Concentrations of these elements were variable in wines from the same vineyard, as well as between vineyards, which is thought to be because concentrations of these elements are strongly influenced by wine processing, and not by regional environment. The concentration of Fe in wine can be increased by processing in stainless vats (Latorre, 1994). This element was removed from the statistical analysis as it did not load high in any of the components, possibly due to the high RSD associated with it, and because it is likely that concentrations are determined by processing. Concentrations of Ca in wine are affected by processing, where crystallization

of calcium tartrate or calcium oxalate occurs both in tanks and after bottling (Jackson, 1994; Latorre, 1994), and Ca was also removed from the PCA, as it did not load high in any of the components. Calcium carbonate is often added to wine for deacidification. During aging, Ca precipitates from wine as the crystals calcium tartrate and calcium oxalate, termed "wine diamonds". Tartrate is a secondary metabolite formed in grapes, and calcium tartrate crystals are believed to precipitate with aging due to the slow conversion of L-calcium tartrate to the insoluble D-isomer (Jackson, 1994). The precipitation of the crystal nuclei (nucleation) takes more free energy than crystal growth, and nucleation is therefore the limiting factor in calcium tartrate stability. Once the nucleus has formed, crystal growth is rapid. Nucleation is temperature dependent, so crystals can be precipitated in storage tanks, prior to bottling, by bringing the wine down to a temperature near freezing. Scanning electron microscope images of calcium tartrate crystals taken from Scherzinger's Pinot Noir are shown in Figs. 3.2a) and b), and are recognizable by their dodecahedral (rhombic), prismatic form. Calcium oxalate crystals occur less frequently than the tartrate crystals, but can occur when tartaric acid is converted to oxalic acid in must or wine. The redox potential of most wines stabilizes oxalic acid as a metal complex, such as ferrous oxalate, which can be converted to the unstable ferric oxalate, and then dissociates and bonds with Ca, precipitating calcium oxalate as small cubic crystals (Jackson, 1994).

2.6.6 Cluster analysis

Cluster analysis is a method of visualizing data, by grouping objects into clusters so that objects in the same cluster are more similar to each other than to objects in other clusters. Partitioning of the clusters can be determined from a number of similarity measures. Pearson's R correlation was used as a distance measure, along with agglomerative hierarchical clustering, which creates a tree-like structure, in which each sample starts out as its own cluster. The two most similar clusters are then joined, and this is repeated in a step-wise manner. The clustering method used was Ward's method, in which distance between two clusters is the sum of squares between two clusters summed over all variables (Wilkinson, 1996). This procedure tends to combine clusters with a small number of observations. Cluster analysis of element distributions was used to examine structures in the data set, to show element groupings found by PCA are not method specific, and wines were also clustered by their element concentrations to examine wines which cluster together.

2.6.7 Discriminant analysis

Discriminant analysis can be applied to data sets where the dependent variable is categorical (a grouping variable, such as Okanagan or Niagara) and the independent variables are metric (continuous numbers), and derives linear combinations of the two or more variables that will discriminate best between the defined groups, by maximizing between-group variance relative to within-group variance. The equation takes the form:

$$Z = W_1X_1 + W_2X_2 + \ldots + W_nX_n \qquad (2.2)$$

where W is the discriminant weight and X is the independent variable (Hair, 1987). By averaging the discriminant scores for all the individuals within a given group, a group mean is derived, referred to as the centroid.

There are several assumptions which must be fulfilled for discriminant analysis, including a normal distribution and equal variance for the independent variables, and an unknown dispersion of the groups. Violations of these assumptions have less effect with large sample sets (StatSoft, 1999), which is the case for the regional fingerprint as there were 95 wines. The volatile elements Se and I, which have poor precision, and the elements Ag and Bi, for which several concentrations were below detection limit, were included in the PCA, but not the discriminant analysis.

Discriminant analysis performs the tasks of 1) determining statistically significant differences between average score profiles of predefined groups; 2) establishing procedures for classifying statistical units into groups on the basis of their scores on several variables; and 3) determining the importance of the independent variables for accounting for differences between groups (Hair, 1987).

Two classification matrices are examined, the first classifies each case into a group where its classification function is largest, and the second is a Jackknifed classification table, which is a more robust bootstrapping method where classification functions are computed from all the data except the case being classified (Systat, 1996). The most important components for discriminating the regions were determined by examination of the F-statistics, which are the between group variance over the within group variance. Discriminant analysis using a high proportion of variables to samples creates an unstable model, and analysis is also weakened by the inclusion of correlated elements. The tolerance of the variables measures the correlation of each component with other

components in the model (Systat, 1996). Multivariate analysis of variance statistics are included in the discriminant analysis. Wilks' lambda, Pillai's Trace, and Lawley-Hotelling trace are given, along with their values converted to approximate F-statistics. These statistics are largely affected by sample size, and provide only an enforcement of the strength of the model determined by the classification table.

2.7 Soil sampling and analysis

The objective of sampling the vineyard soils was to take a representative sample of the soil from a plot of land from which all the grapes used to make a varietal wine were grown. The soil was then analysed to examine relationships between concentrations of elements in the soil and in the wine produced from grapes grown on the plot.

2.7.1 Vineyard soil sampling

To get a representative sample of a specific plot, five or more samples were taken, then combined before analysis. For plots with a uniform topography and soil texture, samples were taken in a systematic pattern, approximately equal distances apart. As many of the vineyards were highly irregular in shape and topography, judgmental sampling was done to best represent spatial variability in the topography and soil characteristics. Samples were not taken from the rows near the edge of the plot, as dust or contamination from roads may cause anomalies in the element concentrations of these samples.

Soil was sampled from the B horizon, which is the layer of soil formed immediately below the A horizon, or topsoil. The A horizon contains organic matter mixed with the mineral fraction, whereas the B horizon is dominated by the obliteration of much of the original rock structure and contains an accumulation of silicate clay (Fanning and Fanning,

1989). Because the soil was analysed to study regional geochemical composition and compare it to wine composition, the B horizon was analysed to represent the parent bedrock material from which the soil was formed. Samples were taken from approximately 0.3 to 0.5 m in depth, and placed in paper soil sample bags. A shovel was used to dig a small pit, then a sample of approximately 200 g was taken from the bottom of the pit, avoiding any material which had been in contact with the shovel. Many of the vineyards, particularly in Ontario, had been tilled or re-graded, so the soil samples did not represent a true B horizon, but taking samples from a lower horizon did minimize the effects of atmospheric deposition and fertilizers which may have been applied to the surface of the soil.

2.7.2 Soil sample preparation

The collected soil samples were air dried in soil sampling bags to prevent contamination from dust, and the sample bags were hung to dry the same day the soils were collected to reduce chemical change caused by microbial action in wet soils (Kalra and Maynard, 1991). The dried samples were then shipped to the laboratory.

Large clumps of soil were broken up in a clean porcelain mortar and pestle. The soil was passed through a 2 mm stainless steel sieve, to separate out a fine earth (< 2 mm particle size) subsample. Each of the five or more subsamples from a vineyard were weighed out in equal proportion and combined, to give a representative vineyard sample. In the case of five vineyards (Lang, Slamka, Kettle Valley, Scherzinger, and Gray Monk), the samples were combined into two vineyard samples, to represent the upper and lower vineyard. This was done in vineyards where the wine being analysed was grown on two

plots on the same piece of property, or in the case of Lang and Slamka, where the soil was markedly different in composition at the top and bottom of a sloped plot.

The pH and conductivity of the soil were then measured on the fine earth fraction samples (procedure given below). For the five cases where two vineyard samples were taken, pH and conductivity were measured on each sample, then the two samples were combined in proportion to the approximate fraction of grapes which were grown on each plot.

2.7.3 Measurement of soil pH

Soil pH is measured potentiometrically in a saturated paste which is in equilibrium (Kalra and Maynard, 1991). A saturated paste is used as opposed to a measured volume of water to minimize the amount of water in the soil, as an increase in the amount of water added to the soil will cause an increase in pH (Hendershot *et al.*, 1993).

A 100 ml plastic beaker is filled approximately 1/3 full with the dried, fine earth fraction (< 2 mm) of the vineyard soil samples. Deionised water is added until the entire soil sample is just wet. The sample is stirred and more water added until saturation, at which point a paste forms, but there is no free water on the surface of the sample. The saturated soil paste is then allowed to sit for 30 min to equilibrate, then more water is added if the soil is not completely saturated.

A pH electrode is calibrated with two buffer solutions (pH 4 and 7). The electrode is inserted into the saturated paste, allowed to stabilise, then raised and lowered to get a representative reading from different parts of the sample (Kalra and Maynard, 1991).

2.7.4 Measurement of soil conductivity (E.C.)

Electrical conductivity (E.C.) of an aqueous soil extract is taken as an estimate of the total soluble salts in the soil (Kalra and Maynard, 1991). Approximately 10 g of dried soil and 20 g of deionised water were weighed into 50 ml plastic beakers. The beakers were placed on a mechanical shaker for 15 min, then allowed to sit for 15 min to settle the soil so the extract could be sampled. The E.C. electrode is calibrated with 0.01 M KCl, then rinsed 3 times with deionised water, and once with the soil extract. The electrode is filled with soil extract without disturbing the settled soil, and the conductivity is recorded in mS/cm.

2.7.5 Soil chemical analysis

Soil chemical analysis is usually carried out on the < 2 mm soil fraction, as materials greater than 2 mm in grain size are not soil constituents, but rock fragments (Tan, 1996). The use of the < 2 mm soil fraction for chemical analysis is an internationally accepted convention, making soil data accumulated all over the world comparable. Because this study was focussed on the differences in geochemical composition between grape growing regions and their effects on wine chemistry, and not on the chemistry of the soil itself, a finer grained fraction (< 0.074 mm) of the soil was analysed, as trace elements adsorb in the fine grained fraction of soils because of the larger particle surface area for adsorption and the surfaces of clay particles are charged. The vineyard soil samples were passed (unground) through a 200 mesh sieve (0.074 mm) for analysis by XRF. This grain size represents the silt and clay fractions of the soil, eliminating most of the sand fraction (sand: 2.0 - 0.05 mm (Tan, 1996)). The silt and clay fractions are a mixture of aluminosilicate clay minerals with lesser amounts of quartz, feldspars, oxides, and

hydroxides. Sorption properties of the mineral part of soil material are associated principally with the clay and silt-size fractions (Kabata-Pendias and Pendias, 1984). This finer fraction was therefore used for the elemental analysis to attempt to provide a stronger correlation between element concentrations in soil and wine. Because analysing only the clay and silt fractions of the soil may cause a regional bias if clay content is significantly different between the Niagara and Okanagan regions, the < 2 mm particle size of 10 soils from each region were ground to < 200 mesh, then analysed by XRF for regional comparison.

Soils were analysed for major and minor elements by X-ray fluorescence. All of the sieved (< 200 mesh) vineyard soil samples, plus the 20 ground soil samples, were analysed as pressed pellets. Ten samples were also fused to form a metaborate/tetraborate glass bead and analysed for major elements to check the accuracy of the pressed pellet analysis. The analysis of homogeneous fused glass beads is very accurate for the light major elements (Na, Mg, Al, Si, and P), whereas the determination of these elements in pressed pellet is less accurate and dependent on grain size of the powdered material (Longerich, 1995). Pressed pellet analysis provides accurate determination of the middle x-ray energy elements, as does the glass bead analysis. High emission energy elements are not measured on fused glass beads, as pressed pellet analysis gives lower detection limit due to the higher concentration of sample (Longerich, 1993b).

Pressed pellets were prepared and analysed according to Longerich, 1995. Into 100 ml glass jars were weighed 5.00 g of soil and 0.70 g of BRP-5933 Bakelite phenolic resin (Bakelite Thermosets, Brampton, Ontario, Canada). Two 0.8 cm diameter stainless steel ball-bearings were added, the jar was capped with a plastic lid and the soil was mixed with the resin on a roller mixer for 10 min. Each sample was then pressed into a pellet,

using 20 tonnes for 5 s, with a Herzog (Germany) pellet press. The pellets were then baked at 200°C for 15 min.

Lithium borate fused glass beads were prepared by first igniting 2 g of each soil sample in a CanadaWide Scientific porcelain crucible in a muffle furnace at 1050°C for 4hrs. Loss on ignition was then calculated as weight loss (weight before minus weight after ignition) relative to weight before ignition. Ultrapure, high density lithium metaborate (6 g) and lithium tetraborate (1.5 g)(Ultrapure, High Density, Corporation Scientifique Claisse) and ignited soil (1.5 g) were weighed into vials, and mixed. Half of the mixed powder was then transferred to a clean platinum crucible and three drops of 250 g/l LiBr were added to each sample as a wetting agent. The samples were then fused by heating at 850°C for 8.5 min followed by 11.5 min at 1050°C in a Leco fluxer. Fused samples are then cast into a platinum mould, cooled and analysed by XRF.

Pressed pellet samples were analysed on a Fisons /ARL (Mississauga, Ontario, Canada) model 8420 + sequential wavelength-dispersive x-ray spectrometer, using the operating conditions described in Longerich (1995). Gross count rates were background and interference corrected. The corrected intensities of Mg and Si, elements which vary greatly in concentration between rocks, were transformed by a quadratic equation, which passed through the origin (equivalent to a background-corrected blank), and which contains constant values determined from two reference materials. Sensitivity of the elements was determined from the mean of four measurements acquired on six reference materials. Matrix correction were applied to the intermediate-energy elements, using two iterations of the Lachance-Traill correction, and to the high-energy elements using the Compton matrix correction algorithm (Longerich, 1995). Precision and accuracy were monitored with geological reference materials (AGV-1(andesite, USGS), DNC-1 (diabase,

USGS), JG-2 (granite, JGS), and BCR-1 (basalt, USGS)) and are better than +/-2% for most elements except Cl, As, and Pb, which are better than +/-5%. Fused discs were analysed by XRF under the same conditions. Background and interference corrections are applied to the gross count rate data, followed by two iterations of the Lachance-Traill matrix correction (Longerich, 1993b). Precision for the major oxides Na_2O, MgO , Al_2O_3, and SiO_2 was better than +/-0.5% , and better than +/-2% for P_2O_5 for samples analysed as fused beads.

The mean concentrations, with standard deviation, for each soil fraction, along with the relative difference between the mean concentration of each fraction, are given for ten Okanagan and ten Niagara vineyard soils in Table 2.5. While some differences in element concentration were apparent for the different grain size fractions, particularly for the elements Zr, Pb, Th and U, the relative difference in mean concentrations between fractions is similar for both regions. While data from both size fractions was examined for correlating wine and soil element concentrations (Chapter 5), analyses of the smaller fraction (0.074 mm), which was done for all soil samples, does not heavily bias one region. Comparison of pressed pellet and fused bead analyses for the major elements of 10 soil samples shows there to be uncertainty in the accuracy of the methods for the major elements Na and Mg, likely due to inhomogeneous grain size within the <200 mesh fraction, and these elements were left out of the analysis. There was good agreement between the two methods for other major and intermediate elements (Table 2.6).

Table 2.1 Element concentrations in calibration standards for wine analysis.

Standard A	Co, Ag, Bi, Th	5 ppb
	V, Mn, Rb, Sr, Mo, Sb, Cs, La, Ce, Tl, Pb, U	10 ppb
	Li, Be, Al, Ti, Ni, Cu, Zn, As, Ba	20 ppb
	Cd	30 ppb
	B, Mg, Se	50 ppb
	Fe	100 ppb
Standard B	Ca	16 ppm
Standard C	I	10 ppb
	Br	160 ppb
	Cl	20 ppm
Standard D	S	7 ppm
	P	600 ppb

Table 2.2 Operating parameters for analysis of wine samples.

RF Power	1500 W
Carrier Gas (inner)	1.00 l/min
Auxiliary Gas (intermediate)	0.82 l/min
Plasma gas flow (outer)	14 l/min
Peristaltic Pump (liquid sample uptake)	0.4 ml/min
Spray chamber temperature	2°C
Extract 1	-220 V
Extract 2	-98 V
Einzel 1,3	-100 V
Einzel 2	-38 V
Quadrupole Focus	9 V

Table 2.3 Limit of detection, limit of quantization, and RSD for elements determined in wine samples.

Element	LD (ppb)	LOQ (ppb)	RSD
Li	0.017	0.057	22%
Be	0.002	0.007	21%
Mg	10	33	20%
Al	1.4	4.7	19%
P	150	500	27%
Cl	2500	8333	26%
Ca	56	187	18%
Ti	0.24	0.80	21%
V	0.03	0.10	13%
Mn	0.08	0.27	13%
Fe	4.3	14.3	14%
Co	0.002	0.007	18%
Ni	0.16	0.53	16%
Cu	0.26	0.87	12%
Zn	0.45	1.50	11%
As	0.046	1.53	10%
Br	0.76	0.33	16%
Se	0.10	2.53	23%
Rb	0.08	0.27	8%
Sr	0.013	0.043	8%
Mo	0.031	0.103	10%
Ag	0.013	0.043	13%
Cd	0.004	0.013	4%
Sb	0.005	0.017	4%
I	0.09	0.30	21%
Cs	0.005	0.017	6%
Ba	0.046	0.153	5%
La	0.0004	0.0013	10%
Ce	0.0005	0.0017	10%
Tl	0.002	0.007	4%
Pb	0.03	0.10	5%
Bi	0.008	0.027	13%
Th	0.001	0.003	9%
U	0.001	0.003	3%

Table 2.4 Recommended values (RV), most probable values (MPV) and mean determined element concentrations (mean) with standard deviations for waters reference materials (all concentrations in ppb). (ld=less than detection limit)

	T-123				T-127				T-129			
	RV	MPV	Mean	SD	RV	MPV	Mean	SD	RV	MPV	Mean	SD
Li	9.68	8.42	9.2	1.3	24		23.6	4.2	18		17.2	1.5
Be	8.1		8.1	1.0	14		14.2	2.3	0.12	0.03	0.027	0.004
Mg	1800		1771	202	2000		2007	389	5830		5686	475
Al	10		11	4	85		85	13	50		49	6
P			ld				ld				ld	
Cl			26313	4439			133082	18702			23701	8428
Ca	9100		9142	640	8800		9278	1255	21100		21766	984
Ti			ld				ld				ld	
V	4	3.4	3.7	0.4	10.2		10.7	1.2	1	0.1	ld	
Mn	13.6		15.4	3.6	5.4		7.0	3.3	25.2		26.1	1.4
Fe	57.5		53	15	135		136	25	10.4		ld	
Co	5.27		5.3	0.6	11.6		12.0	2.0	0.74	0.1	0.135	0.021
Ni	4.3		5.3	0.8	9		10.2	2.0	1.7	1.36	3.4	1.9
Cu	10.2		10.7	2.4	42		42	5	2.7		2.59	0.74
Zn	6	10	13.5	6.3	32.9		36	6	72	79	78	5
As	20.2		20.3	0.7	4.4		4.3	0.5	0.55	0.15	0.33	0.27
Se	5.23		5.5	0.3	7.38		7.6	0.7	1.6		ld	
Br			12.9	2.4			22.1	3.9			10.5	2.0
Rb			2.53	1.19			1.63	0.94			10.8	1.5
Sr	48.6		49.1	1.2	51.1		52	4	181		188	7
Mo	9.2	7.8	7.7	0.4	1.25	0.6	0.65	0.10	20.3		17.8	0.6
Ag	1.44	1.22	1.02	0.48	2.71		1.66	1.06	0.37	0	ld	
Cd	5.86		5.6	0.2	8.34		8.5	0.5	0.34		0.31	0.02
Sb	6.99		6.7	0.2	5.15		4.9	0.3	0.55	0.22	0.208	0.009
I			4.9	2.8			2.78	2.38			3.7	2.6
Cs			ld				ld				0.99	0.08
Ba	7.65		7.6	0.3	20.6		20.3	0.9	34		34	1
La			0.031	0.007			0.56	0.02			0.140	0.005
Ce			0.049	0.015			0.84	0.04			0.214	0.007
Tl			ld				ld				ld	
Pb	9.8		11.2	2.3	3.25		3.3	0.1	1	0.2	0.30	0.24
Bi			ld				ld				ld	
Th			0.008	0.003			0.04	0.01			ld	
U			0.272	0.009			0.79	0.02			4.6	0.2

Table 2.4 (continued)

	T-135				AMW-3			
	RV	MPV	Mean	SD	RV	MPV	Mean	SD
Li	73.7		70	7	35		38	9
Be	59		57	6	12		13.5	3.0
Mg	2000		1973	175	114000		114652	20826
Al	10.5	12.5	10.9	3.8	21000		21244	3131
P			ld				ld	
Cl			35827	7903			19802	5910
Ca	10400		10505	767	320000		354593	74243
Ti			ld				18.2	3.9
V	52.8		53.0	2.7	15	4	5.0	0.8
Mn	423		405	25	82800		66455	38468
Fe	228		219	17	142650		141217	8547
Co	40		42	6	133		156	36
Ni	65.6		65	7	206		256	77
Cu	62		62	12	4670		4648	683
Zn	48.2		57	25	41450	42000	44458	3124
As	10		10.1	0.4		72.5	86	11
Se	10		11.0	0.5			2.78	0.39
Br			13.5	2.5			184	35
Rb			1.21	0.34			25.0	3.1
Sr	46		48	2	1474		1546	79
Mo	63		56	2			1.15	0.85
Ag	9.81		9.4	1.2	0.8	0.16	0.123	0.036
Cd	50.5		50	1	121		119	11
Sb	76.3		76	2	2.7		2.58	0.20
I			4.4	2.2			3.6	0.6
Cs			ld				6.7	0.5
Ba	67.8		67	2	4.5	3.7	4.0	0.3
La			0.028	0.007			151	10
Ce			0.036	0.014			326	21
Tl			ld				0.38	0.01
Pb	103		106	4	17.8		18.1	0.3
Bi			ld				0.058	0.008
Th			0.006	0.002			12.7	1.2
U			0.24	0.01			66	2

Table 2.5 Mean concentrations (in wt% for oxides, ppm for elements) and standard deviations of soils from ten Niagara and ten Okanagan vineyards; and mean ratio of concentration from 2 mm fraction to 0.074 mm fraction for each region.

Element	Niagara					Okanagan				
	2 mm		0.074 mm			2 mm		0.074 mm		
	Mean	SD	Mean	SD	Ratio	Mean	SD	Mean	SD	Ratio
Na_2O	0.99	0.16	1.17	0.24	85%	1.72	0.24	2.03	0.25	85%
MgO	2.52	0.60	2.58	0.49	98%	2.96	0.95	2.99	0.80	99%
Al_2O_3	13.9	1.6	14.6	1.0	96%	13.7	1.1	14.5	1.2	95%
SiO_2	65	3	68	4	96%	61	2	64	3	95%
P_2O_5	0.159	0.064	0.167	0.092	95%	0.200	0.071	0.215	0.075	93%
K_2O	2.51	0.53	2.38	0.48	105%	2.44	0.21	2.36	0.20	103%
CaO	1.81	1.09	1.57	0.91	116%	3.38	0.95	3.98	1.84	85%
TiO_2	0.90	0.07	0.99	0.21	90%	0.66	0.10	0.63	0.23	105%
MnO	0.108	0.029	0.085	0.025	127%	0.111	0.028	0.104	0.029	107%
Fe_2O_3	5.8	1.3	5.6	1.1	103%	5.1	1.0	6.6	4.7	76%
S	301	106	333	150	90%	456	414	428	340	107%
Cl	105	24	98	28	107%	158	72	200	113	79%
Sc	11.4	4.2	16.2	4.0	70%	11.6	3.3	12.8	5.0	91%
V	97	21	94	20	103%	97	23	96	18	101%
Cr	76	11	64	13	119%	133	49	99	47	135%
Ni	11.9	7.8	13.6	5.4	87%	17.9	18.7	18.4	18.1	97%
Cu	22.6	8.0	24.2	6.3	93%	21.8	10.1	27.2	10.2	80%
Zn	35	12	45	5	77%	33	9	50	9	66%
Ga	14.6	3.1	15.5	2.6	94%	14.1	1.8	15.7	1.8	90%
As	6.8	5.1	8.6	5.7	80%	8.9	5.1	16.4	9.2	54%
Rb	80	24	83	19	96%	70	9	70	9	100%
Sr	163	23	138	12	118%	456	130	459	83	100%
Y	25.9	5.5	30.7	9.6	84%	15.9	2.3	22.0	2.9	72%
Zr	365	160	697	795	52%	177	17	298	57	59%
Nb	15.7	2.1	20.6	6.4	76%	13.6	1.9	17.6	1.8	77%
Ba	521	44	471	72	111%	1155	219	1026	156	113%
Ce	83	24	103	34	80%	47	24	63	32	75%
Pb	11.0	4.4	17.7	5.0	62%	18.3	18.0	27.6	21.3	66%
Th	5.6	1.5	9.8	2.7	56%	5.0	2.1	10.2	3.2	49%
U	1.6	0.9	4.1	2.7	38%	1.2	2.1	3.1	4.1	38%

Table 2.6 Ratio of element concentrations of 10 soils analysed by fused bead analysis relative to concentrations from pressed pellet analysis (%).

Element	Fused bead / pressed pellet
Na_2O	128%
MgO	62%
Al_2O_3	91%
SiO_2	105%
P_2O_5	97%
CaO	99%
TiO_2	106%
V	97%
Cr	98%
MnO	101%
Fe_2O_3	101%
Ba	97%
Ce	102%

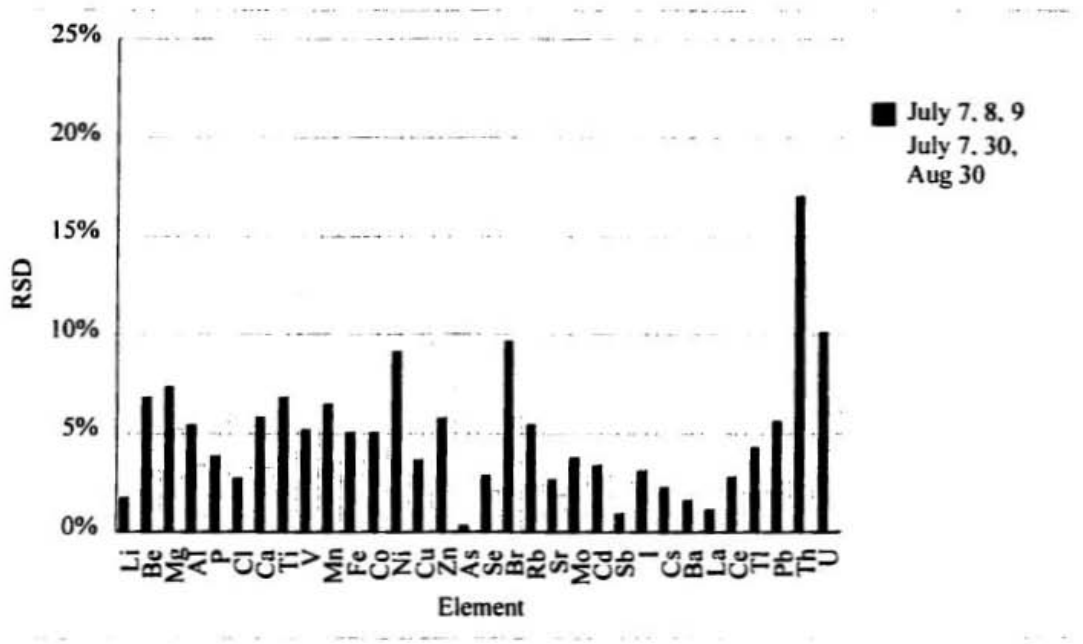

Fig. 2.1 RSD of determined element concentrations in Irvine Chardonnay from July 7, 8, and 9 analyses, and from July 7, July 30 and August 30 analyses.

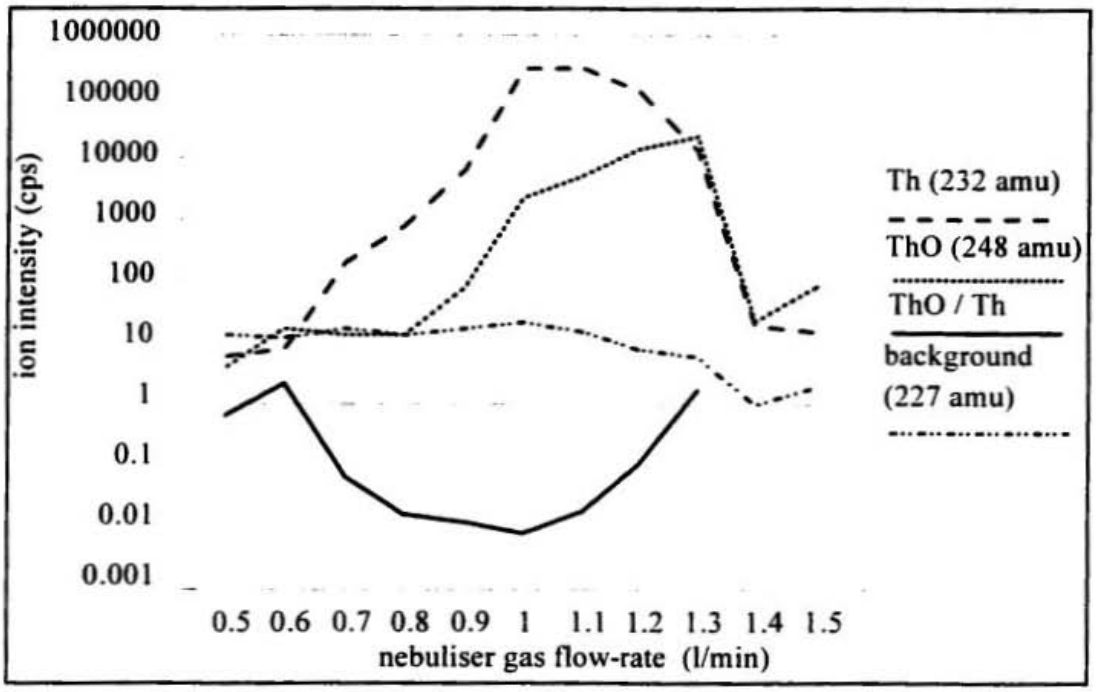

Fig. 2.2 Oxide formation as a function of nebuliser gas flow-rate (l/min) for Th.

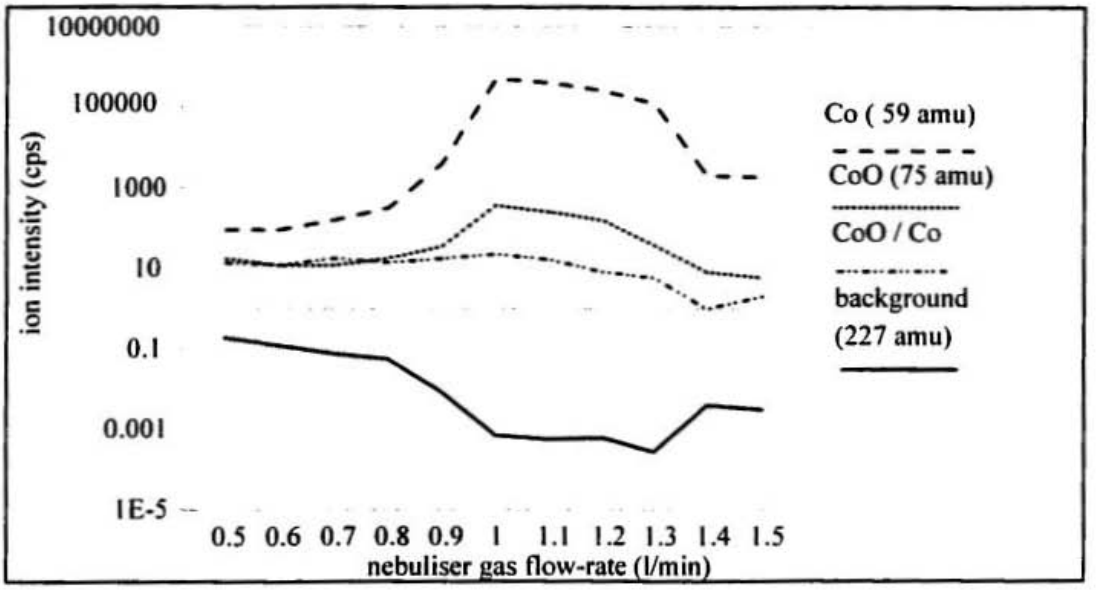

Fig. 2.3 Oxide formation as a function of nebuliser gas flow-rate (l/min) for Co.

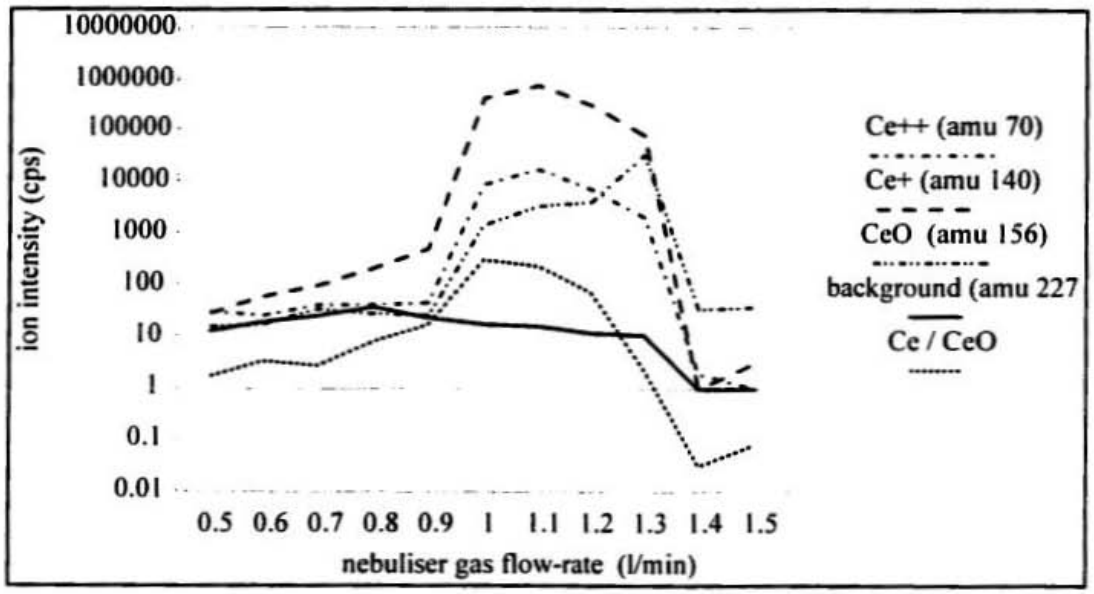

Fig. 2.4 Oxide formation and double-charged oxide formation as a function of nebuliser gas flow-rate for Ce.

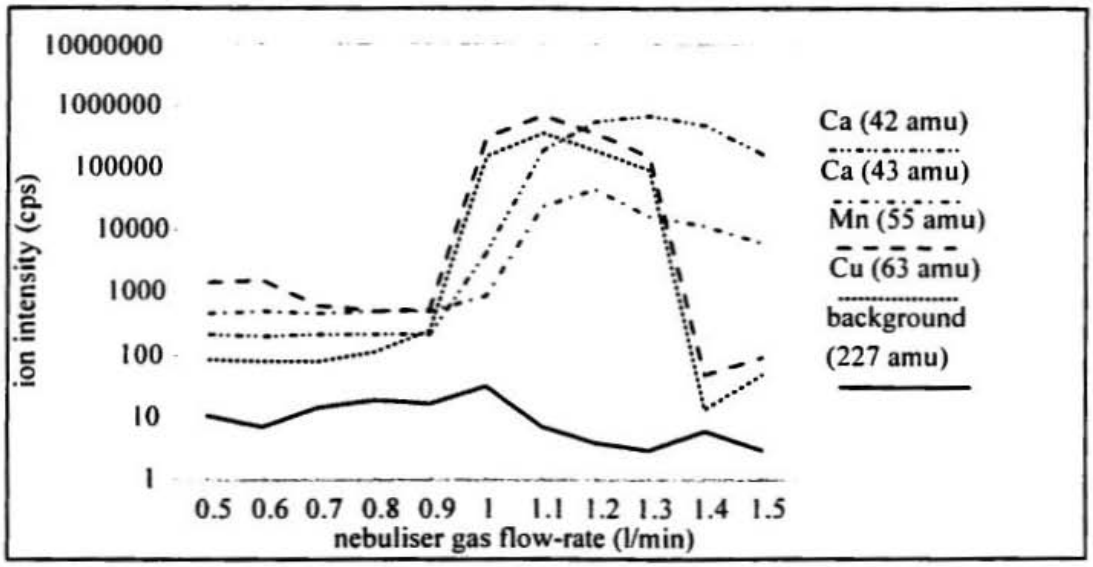

Fig. 2.5 Ion intensities for low mass elements (Ca, Mn, Cu) as a function of nebuliser gas flow-rate (l/min).

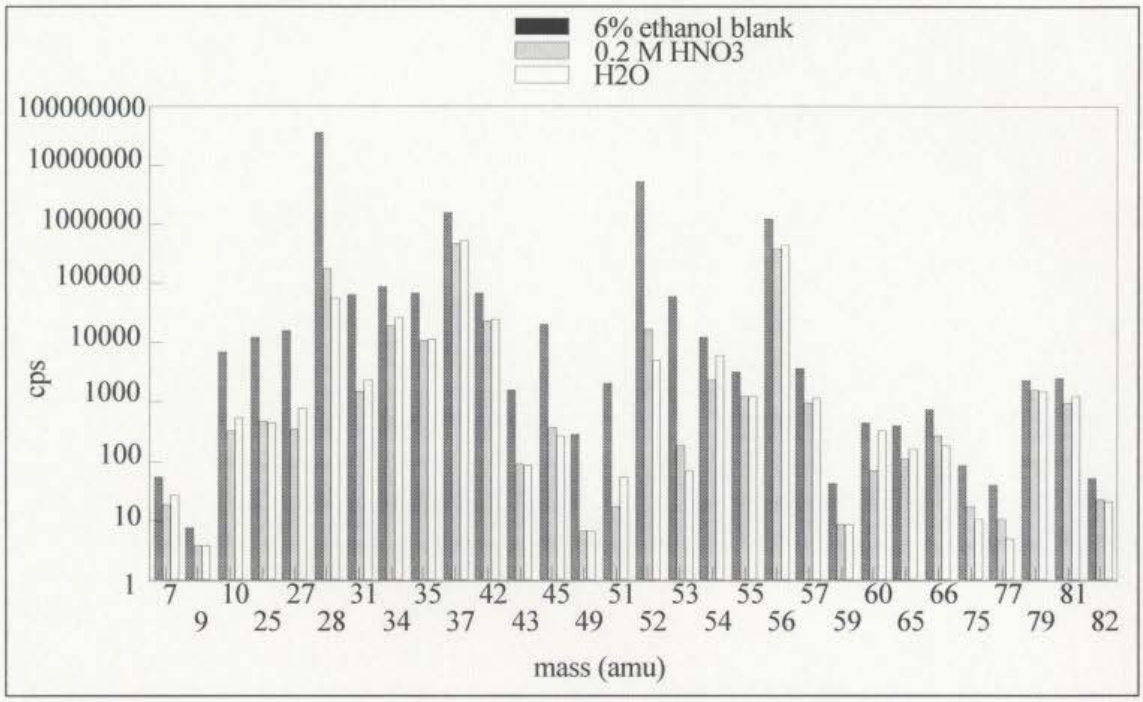

Fig. 2.6 Low mass range ion intensities (cps) determined for blank solutions of 6% ethanol (in 0.1 M HNO_3), 0.2 M HNO_3 and H_2O (distilled and deionised).

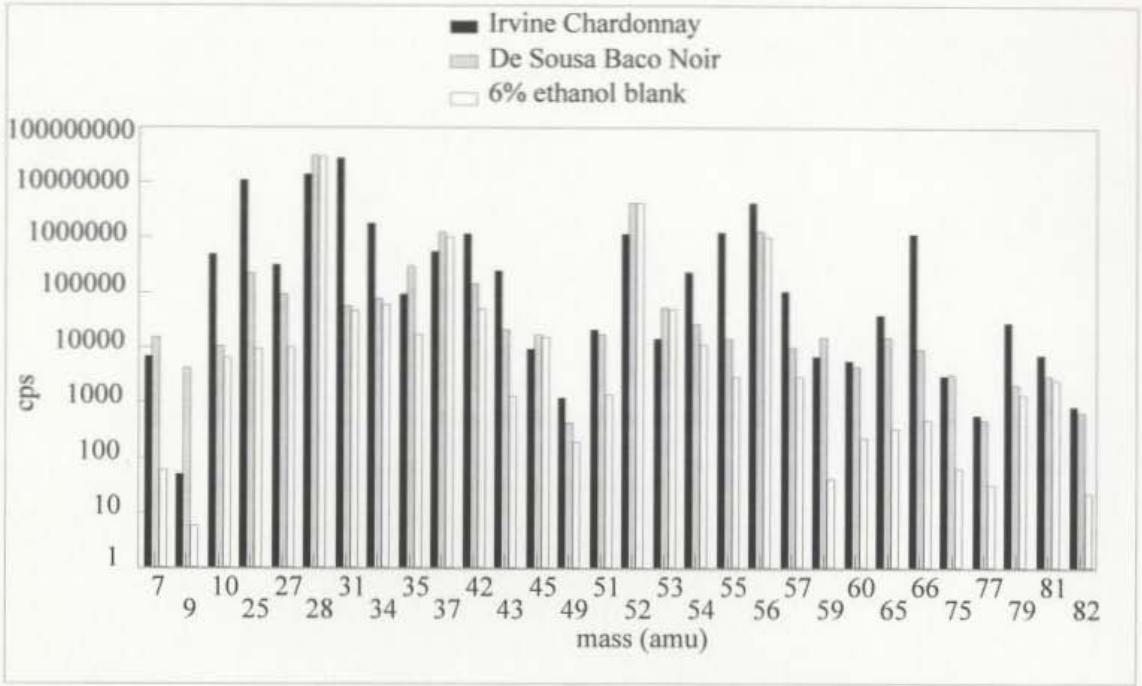

Fig. 2.7 Ion intensities (cps) for low mass elements in two wines (Irvine Chardonnay and De Sousa Baco Noir) and 6% ethanol blank solution, all diluted to 0.1 M HNO_3.

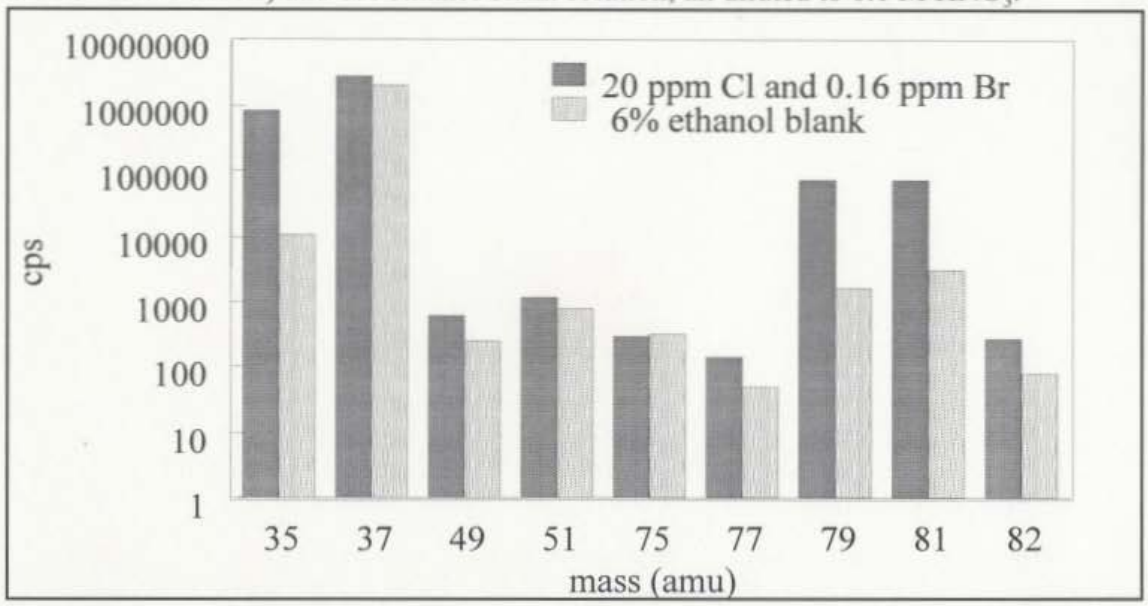

Fig. 2.8 Ion intensities of 20 ppm Cl (35 and 37 amu) and 0.16 ppm Br (79 and 81 amu) and the polyatomic species $^{12}C^{37}Cl$ (49 amu), $^{35}Cl^{16}O$ (51 amu), $^{40}Ar^{35}Cl$ (75 amu), $^{40}Ar^{37}Cl$ (77 amu), and $^{81}Br^{1}H$ (82 amu) compared to the blank solution.

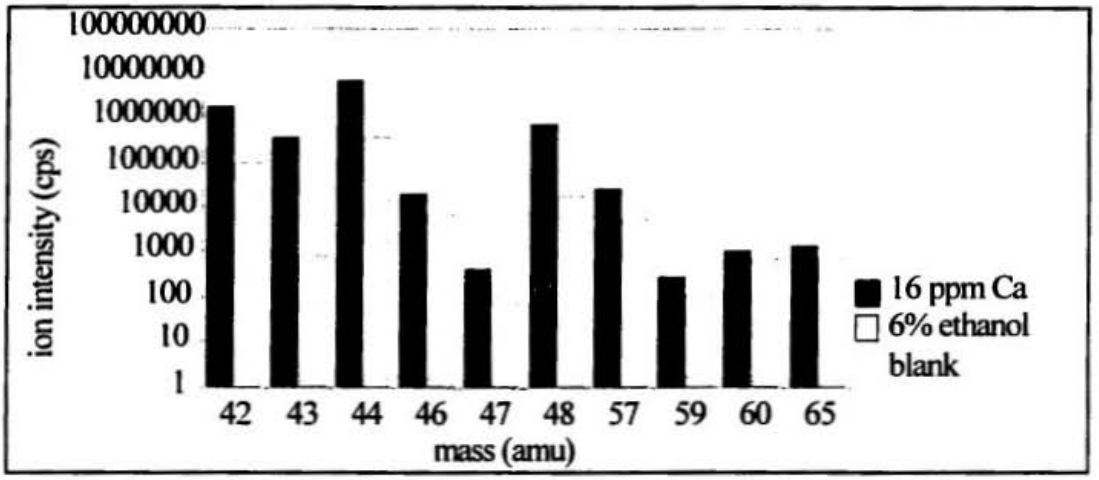

Fig. 2.9 Ion intensities (in counts per second) of 16 ppm Ca and the polyatomic compounds it forms at 57, 59, and 65 amu, as compared to a 6% ethanol blank.

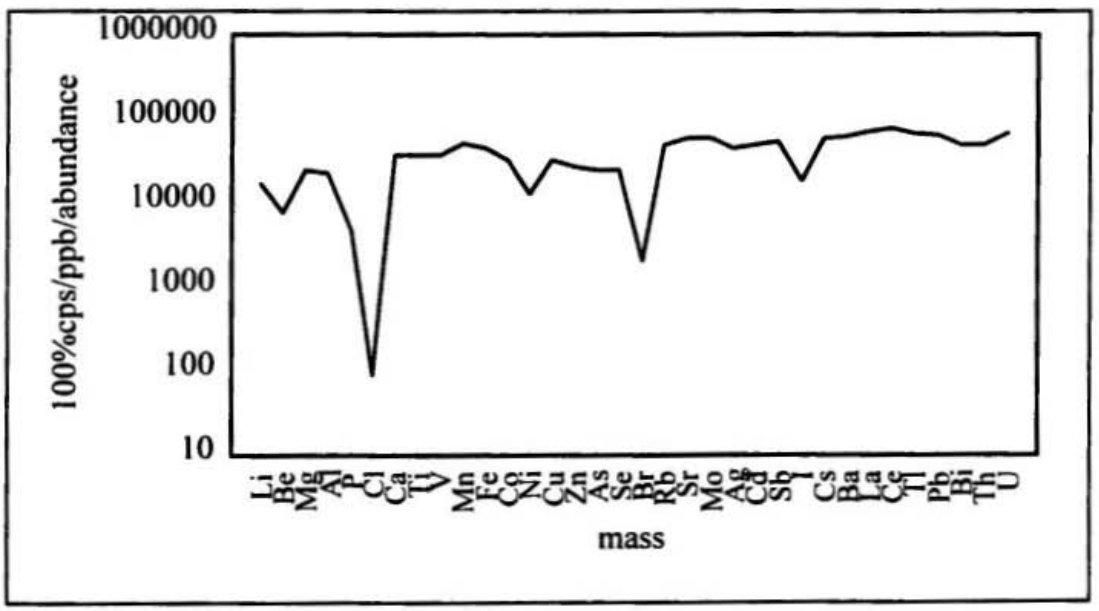

Fig. 2.10 Normalised sensitivity calculated as 100%*cps/concentration/isotopic abundance.

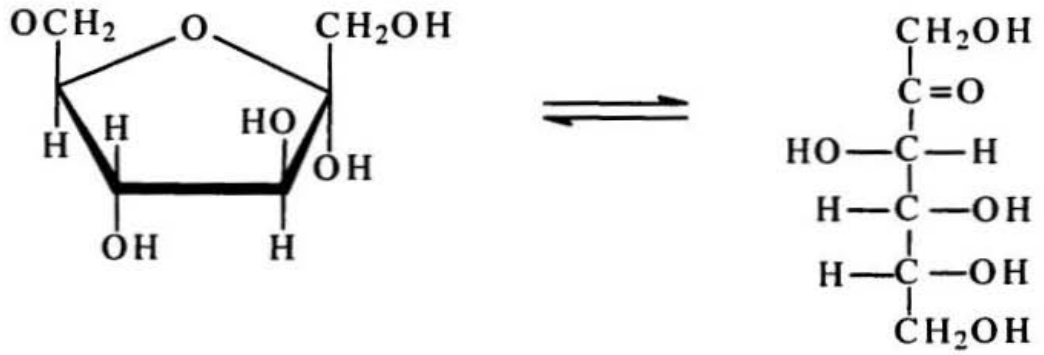

Fig. 2.11 Two isomers of the fructose molecule: α-D-(-)- fructose and D-(-)-fructose.

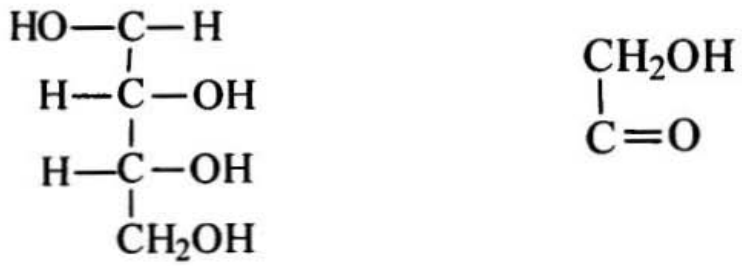

Fig. 2.12 Fractionation of fructose to form molecules with mass 121 amu and 59 amu.

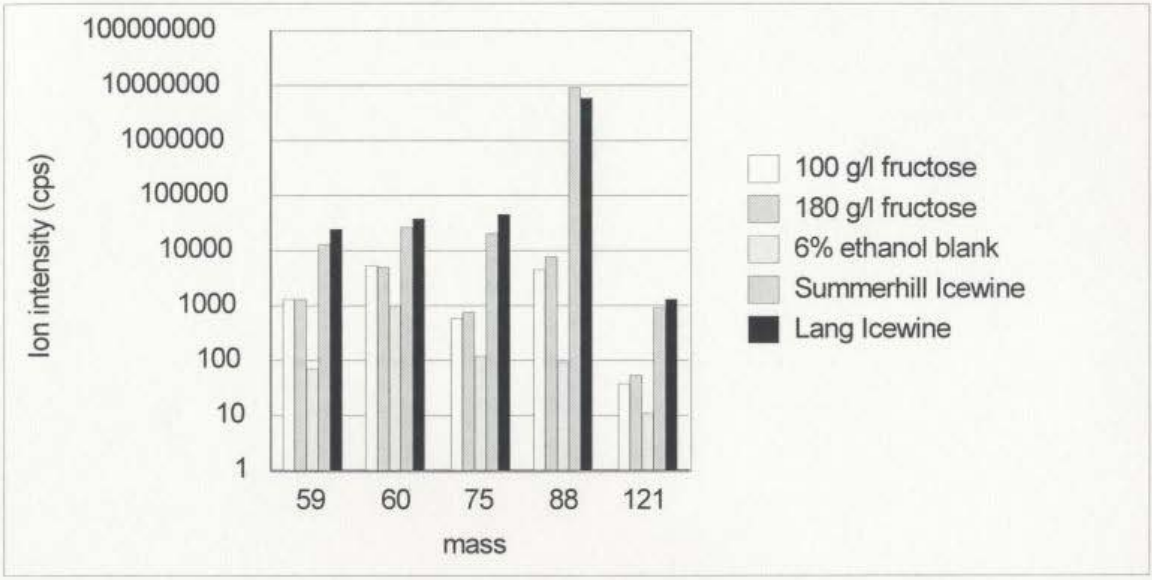

Fig. 2.13 Ion intensities of 100 g/l fructose, 180 g/l fructose, 6% ethanol and Lang and Summerhill icewines.

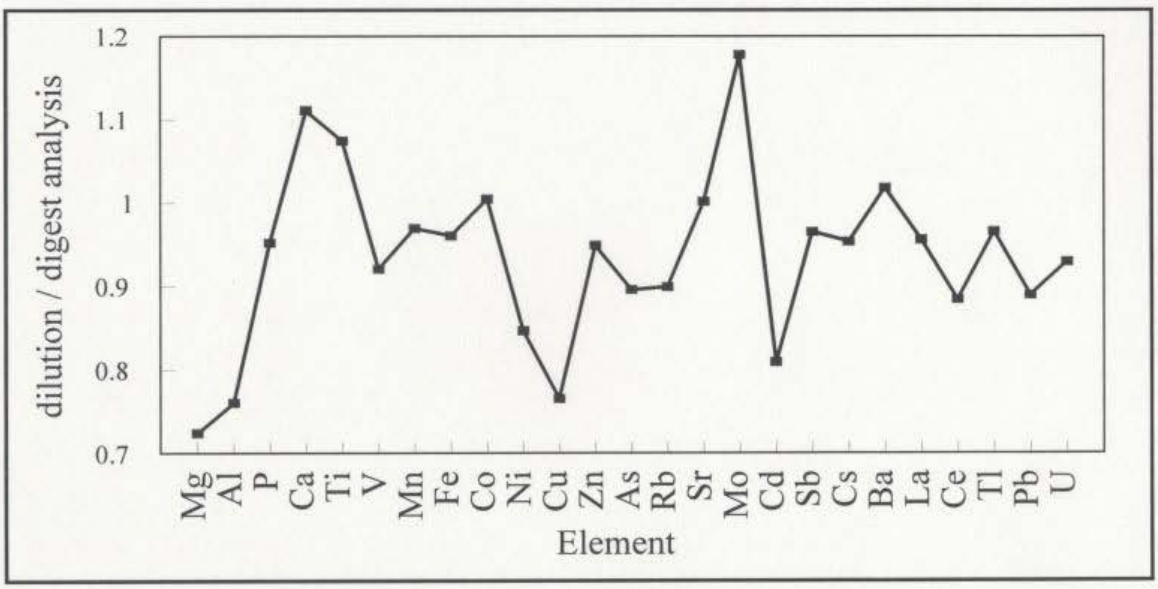

Fig. 2.14 Comparison of concentration determined by dilution method relative to concentration determined by digestion method for elements throughout the mass range, (where a value of 1 represents agreement).

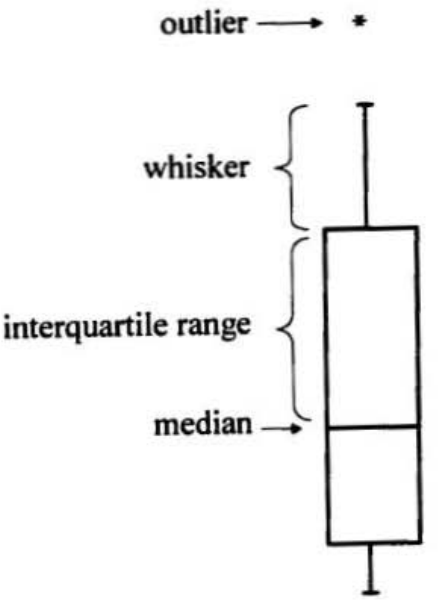

Fig. 2.15 Key for a box plot.

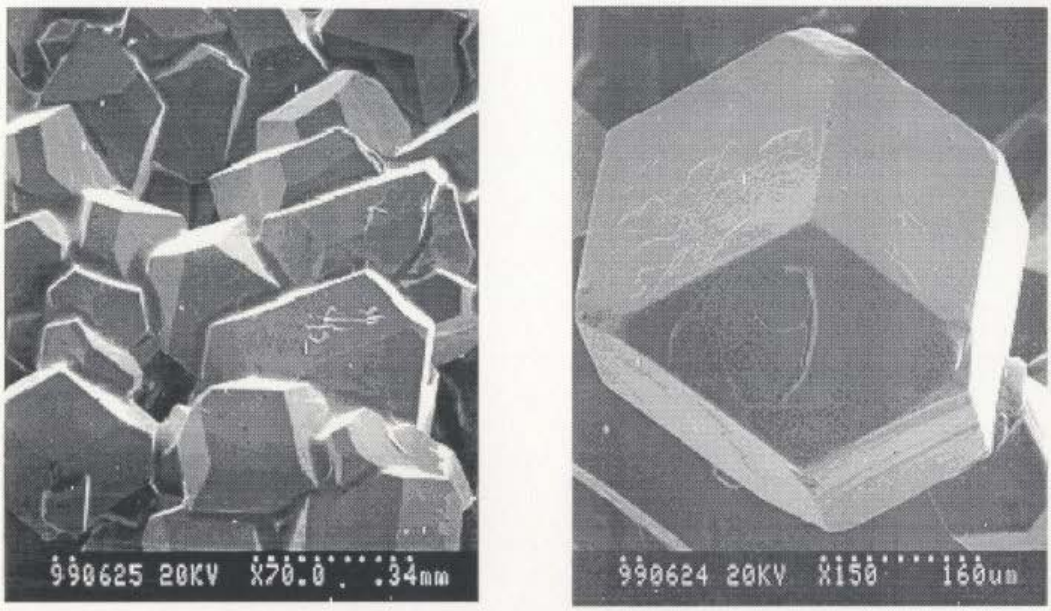

Fig. 2.16 a) and b) Backscattered electron photographs of calcium tartrate crystals from Scherzinger's Pinot Noir, 1997, at magnification of X70(a) and X150(b). Crystals were removed from wine by filtration, coated with carbon and imaged using a scanning electron microscope (SEM) with a working distance of 23μm, a takeoff angle of 30°, and an accelerating voltage of 20kV.

Chapter 3 Results of analyses

3.1 Determined concentrations of elements in wines

The measured concentrations for individual Canadian wines, as well as 10 store-bought French wines which were analysed for comparison of chemical composition with the Canadian wines, are given in Appendix 2. The concentration ranges for elements determined in the wine samples are compared to the maximum acceptable concentration in Canadian drinking water (Canadian Drinking Water Guidelines, 1993), in Table 3.1, showing that concentrations of Mn, Fe, Cu, Se, Cd, and Pb in very few wines were above the acceptable level defined as the concentration above which an element may cause deleterious health effects. Concentrations of elements in ten wines determined by the digestion method described in Chapter 2, Section 5 are given in Appendix 3.

3.2 Log transformation

Examination of box plots and normality plots for each element suggested that a log transformation of the concentrations of all the elements determined in wine made the data better fit a theoretical normal distribution, which is assumed by the statistical analyses. An example is given in Figs. 3.1a-f, where plotting the determined concentrations of Co against a theoretical normal distribution (Fig 3.1a) produces a curved line showing positive skewness, and a boxplot of the concentrations of Co shows unequal variance about the mean (Fig. 3.1b). A scatter plot of Co *vs.* Al concentrations (Fig. 3.1c), creates a curved line, whereas Pearson's R correlation coefficient determines a straight line through the data. By log transforming the data (taking natural logarithms of the concentrations), the normality plot becomes a straight line, meaning the data fits a normal

distribution (Fig. 3.1d). The distribution shown by the boxplot becomes more symmetrical about the mean, and the extremity of outliers is reduced (Fig 3.1e). The scatter plot of Co *vs.* Al becomes more linear and more evenly distributed with the log transformed data (Fig. 3.1f). The log transformation also has a standardising effect, bringing elements of high abundance into a similar range with elements of low abundance. Application of the log transformation is suited to analytical data, as the assumption that SD is constant (in a normal distribution) is changed to the assumption that RSD is constant (through propagation of errors, relative error becomes absolute error when a natural logarithm is taken), which is true for determined concentrations significantly above DL.

Three wines were determined to have negative concentrations of the element Ag: St. Hubertus Oak Bay Pinot Blanc, De Sousa Vidal, and De Sousa Riesling, which can occur for concentrations below detection limit (Chapter 2). Because values of zero or less can not be log transformed, and the multivariate methods do not allow for missing data, the concentrations for Ag for these three cases were set to half the value of the detection limit (0.0065 ppb), which is an arbitrary low value that does not create an outlier when log transformed, as do values closer to zero. The element, Ag, was included in the PCA, to determined structures in the data, but not the discriminant analysis used to determine a regional fingerprint.

3.3 Principal component analysis

Log transformed element concentrations were analysed by PCA to examine underlying structures in the data set. The principal components were then plotted to determine their ability to discriminate between wine regions.

3.3.1 Pearson's R correlation matrix

A Pearson's R correlation matrix, along with probability values, was derived for the data set (Appendix 4). In this study element concentrations in wine were log transformed so the Pearson correlation matrix determines linear relationships between log transformed variables. Distributions of the Pearson's R correlations were examined in scatter plots (Appendix 5), which show even distribution of the log transformed data.

3.3.2 Derivation of principal components

An unrotated PCA was first derived for the data set, and eigenvalues were plotted in a scree plot (Fig. 3.2). The latent root criterion determined 7 components were significant, but the scree plot showed no clear break. The eigenvalues of the 8^{th}, 9^{th}, and 10^{th} components were 0.90, 0.83, and 0.73, respectively, and these components were retained for analysis as they showed clear element grouping (where component loadings were high for a few elements and low for all other elements). The VARIMAX rotation was then applied, and the results are given in Table 3.2. The components are also listed in Table 3.3, showing the elements grouped, which are the elements which load high in a component, and the percent total variance explained by the component. In a few cases, elements load high in more than one component (Sr, Bi, Pb), as some overlap usually does occur between components in PCA (McCuen, 1993).

Components were plotted against each other to see their importance in regional separation. Plots of Component 4 *vs.* Component 5, and Component 4 *vs.* Component 8 (Figs. 3.3 and 3.4) were determined to be the most important in separating wines according to region, although collectively they only represent 22% of the overall variance. Although component 1 represents 21% of the overall variance, it groups 11 elements, and may obscure the discriminating ability of individual elements.

3.4 Cluster analysis

Cluster analysis of the element data using Pearson's R correlations as a distance measure, and Ward's method of clustering (Fig. 3.5), provides another means of examining structures in the data. Some elements which form clusters that correspond with the PCA are Zn and Cd (Component 2), Sr and Ba (Component 5), and Tl, Cs, and Rb (Component 4). Similar relationships between elements are apparent in the clustering methods and PCA, indicating groupings are not method specific.

3.5 Regional fingerprint

Discriminant analysis of the two regions was applied to both principal components and to element concentrations to determine the best method of differentiating between regions. Classification matrices, between-group F-statistics and tolerance, and multivariate analysis of variance statistics are reported to determine the discriminating ability of each analysis.

3.5.1 Discriminant analysis of the principal components

Discriminant analysis of the two regions using the principal components as variables showed components 6, 7, 9, and 10 to have little discriminating power. These components were discarded and regions were classified with a 98% success rate (1 Niagara and 1 Okanagan wine were misclassified in both the classification matrix and the Jackknifed classification) using the discriminant function given in equation 3.1 (Table 3.4).

Discriminant Function: (component = cpt)

$$0.65(\text{cpt } 1) + 0.84(\text{cpt } 2) - 0.65(\text{cpt } 3) + 1.12(\text{cpt } 4) + 0.75(\text{cpt } 5) + 1.40(\text{cpt } 8) \qquad (3.1)$$

The components with a high discriminating power, determined as F-statistics (Table 3.5) were components 4 and component 8. None of the tolerance values (Table 3.5) are low, meaning none of these components make the classification model unstable. Examination of the multivariate analysis of variance statistics (Wilk's lambda, Pillai's trace, and Lawley-Hotelling trace) indicate the group means for the two regions to be significantly different (Table 3.6).

3.5.2 Discriminant analysis of element concentrations

Discriminant analysis was repeated using log transformed element concentrations as variables, because a large number of elements, which may be individually useful to the fingerprint, were grouped in Component 1of the PCA. The discriminating ability of elements was first examined graphically using boxplots and scatterplots (Appendix 5). Elements which were found useful to separating wine by region were Sr, Rb (Fig. 3.6),

Co, Mn (Fig. 3.7), Mo, V (Fig. 3.8), U,Sb (Fig. 3.9), Cd, Al (Fig. 3.10), Ba and Zn (Fig. 3.11). Important discriminating elements were then identified by examining the between-group F-statistic and tolerance, which in this case determine the amount of regional variance explained by each element. The elements Ba and Cd were excluded from the discriminant analysis because of high correlations between Sr and Ba (R=0.57), and between Zn and Cd (R=0.60) (from Appendix 4), causing low tolerances for these elements. A discriminant function (equation 3.2) was derived which classified Niagara and Okanagan wines with a 100% success rate (Fig. 3.12, Table 3.7). The important elements for discriminating between regions were determined to be Sr, Rb, Mn, V, Mo, Al, U, Co, Zn, and Sb (Table 3.7), where Sr is the most discriminating element. Test statistics for the discriminant analysis, converted to approximate F-statistics (Table 3.8), as well as the classification matrix, determine the Okanagan and Niagara wines to be significantly different using this statistical model.

Discriminant function: $14.09 + 0.54U - 0.54V - 0.90Al - 0.70Sb + 1.01Co - 0.82Zn + 1.94Sr - 1.32Rb + 0.49Mo - 1.24Mn$ (3.2)

Another element which has a high discriminating ability between regions is iodine (I), but due to the uncertainty of its speciation upon analysis (Chapter 2), it was left out of the fingerprint. By including I in the discrimination, the regions were discriminated with 100% correct classification by both the classification matrix and the Jackknifed classification matrix, and the F-statistic for I was 45 with a tolerance of 0.61.

3.6 Inclusion of French wines in the fingerprint

The regional fingerprint was further examined by including 10 French store-bought wines into the statistical analysis, to determine whether Okanagan and Niagara wines could be discriminated from wines from other regions. The French wines did not meet the criteria of the other samples of being made exclusively from grapes from a known vineyard of origin, and this creates a problem with the statistical analysis as there is not enough known about these wines to classify them together as a group.

3.6.1 Inclusion of French wines in the PCA

The inclusion of wines from another region into the sample set was first examined by PCA, and graphical analysis of the discriminating elements. The Okanagan, Niagara, and French wines are plotted using PCA Components 4, 5 (Fig. 3.13) and 4, 8 (Fig. 3.14), and show that there is overlap between the French and Niagara wines.

3.6.2 Discriminant analysis of French, Niagara and Okanagan wines

Plotting the individual elements Sr and Rb, which have a high discriminating power for wine region, was found to separate the Okanagan and Niagara wines to a high degree in Fig. 3.15, but the French wines were again found to overlap with the Niagara wines by this method.

The inclusion of the French wines in the discriminant analysis was examined first by applying the discriminant function of the two Canadian regions (equation 3.2) to the samples. This equation was derived to discriminate between the two Canadian wine regions, and therefore may not maximise differences between the three groups. The application of the equation is given in Fig. 3.16, in which the French wines can be seen to

plot overlapping from the Niagara region, but are completely differentiated from the Okanagan wines.

The discriminant analysis was then repeated in which functions (equations 3.3 and 3.4) were derived to differentiate between all three regions (Fig. 3.16 and Tables 3.10-3.12).

Factor (1) : -14.68 + 0.88Al + 0.56V + 1.11Mn - 1.05Co + 0.82Zn + 1.43Rb - 1.85Sr - 0.48Mo - 0.54U + 0.69Sb (3.3)

Factor (2) : 0.46 + 0.57Al - 0.55V + 1.04Mn + 0.52Co + 0.06Zn - 1.38Rb - 0.15Sr - 0.32Mo + 0.20U + 0.12Sb (3.4)

The classification matrices (Table 3.10 and Fig. 3.16) show the Okanagan and Niagara wines, and Okanagan and French wines, cluster separately, but there is overlap between the Niagara and French wines. The same elements were found to be important to this analysis as the discriminant analysis for the two Canadian regions, with Sr being the most discriminating element, as determined by F-to-remove statistics (Table 3.11). The robustness of this analysis is very difficult to assess, as not enough is known about the French samples to expect them to form one group. If these 10 wines were made from grapes grown in extremely diverse vineyard environments, as the French wine growing regions are reported to be (Wilson, 1998), statistical analysis may be more meaningful if the wines were divided into 2 or more groups. Due to the small number of French wines sampled, results of the discriminant analysis are not highly significant. The purpose of the inclusion of the French wines, however, was to assess the application of the fingerprint to wines from outside the two regions, and the statistical analysis of the French wines show

that the Okanagan and French wines are distinguishable, and suggest that wines from other regions could be discriminated by fingerprinting.

3.7 Fingerprinting individual vineyards

Multivariate statistics were used to examine trace element patterns within each of the regions. Fingerprints for individual vineyards were derived to see if classification could be repeated on a smaller geographic area. Sample size becomes much smaller when looking at each region individually, making statistical models more unstable and results more difficult to validate.

3.7.1 Fingerprints of individual Okanagan vineyards

The vineyards from which 4 or more wines were sampled were analysed by discriminant analysis. The wine samples from each vineyard came from grapes from the same plot of land, but represent several vintage years. The wines from Lake Breeze were all from the 1998 Pinot Blanc, but were taken from 3 different tanks; the samples from Wild Goose were Gewurztraminer from 5 different vintage years (1993 to 1997); Quail's Gate wines were Riesling from four vintage years; the wines from Lang were all Riesling, but taken from 3 different vintage years (1995 to 1997) and include an icewine and a late harvest wine; the samples from House of Rose were Verdelet from five vintage years (1992 to 1996) as well as one Okanagan Riesling. Because of the small sample size (20 degrees of freedom), the number of variables that could be used without weakening the analysis was low. Five elements (Sr, Rb, Mn, Mo, and U) were found to classify the vineyards with 100% accuracy and 4 factors (Fig. 3.18 and Table 3.13), where the variability accounted for by each factor is represented by an eigenvalue. The group mean

of each vineyard in each of the factors is given in Table 3.14, and the classification matrices in Table 3.15. As with the regional discrimination, Sr, was the most discriminating element, as determined by F-statistics and tolerance (Table 3.16). The stability of the model is assessed by Wilk's lambda, Pillai's trace, and the Lawley-Hotelling trace (Table 3.17), which show wines from these vineyards to be significantly different.

The RSD of the concentrations of discriminating elements in wines from each of the vineyards in the fingerprint is plotted in Fig. 3.19. The RSD for each vineyard is less than the total RSD for wines in the Okanagan valley, for all ten elements, which suggests the use of these elements in fingerprinting Okanagan vineyards is robust. Examination of the RSD of element concentrations in wines from each region shows the Lake Breeze wines, which are all from one batch but from different tanks, to have the lowest variability for all elements. Variability is similar to analytical uncertainty for these wines.

Two of the Okanagan wines sampled were icewines (Summerhill Riesling Icewine and Lang Riesling Icewine), and wines made from Riesling grapes were also sampled from both of these vineyards. The high backgrounds from the high sugar content of the icewines (Chapter 2) causes a much higher analytical uncertainty in the icewine analyses. Two late harvest wines made from Riesling grapes were sampled from Lang, and these are wines made from grapes left on the vine much longer than usual, and have a higher sugar content due to concentration of the juice when grapes wither, but are not harvested or pressed frozen. These samples allowed a comparison of trace element concentrations in wines made from grapes harvested at the usual time (September), late harvest wine made from grapes left on the vine (an extra 1-2 months), and icewine made from grapes harvested and processed while frozen (Table 3.18). The icewines from Lang and Summerhill had much higher concentrations of many of the trace elements than the Lang and Summerhill

Riesling samples. The Late Harvest Rieslings from Lang do not have significantly elevated trace element concentrations. The highly concentrated grape juice from pressing the grapes while frozen, rather than the longer growing season of ice wines, is the likely cause of the high element concentrations in icewines. The concentration factor between wines and ice wines is difficult to distinguish, as it varies considerably between elements.

3.7.2 Cluster analyses of all Okanagan wines sampled

Element concentrations in wines were examined by cluster analysis to determine whether wines made from grapes grown on the same vineyard group together, and also to determine if wines cluster according to vineyard location within the Okanagan. The icewine samples were not included in this analysis as they have significantly different concentrations of some elements than other wines from the same vineyard. Cluster analysis of Okanagan wines using the elements Al, V, Mn, Co, Zn, Sr, Rb, Mo, Sb, and U, with Pearson's R as distance measures, and Ward's method of clustering, groups wines from the same vineyard to a high degree (Fig. 3.20). Wines are labelled by colour, vintage year and winery, and red wines from Stag's Hollow, Summerhill, Scherzinger and Inniskillin plot higher than white wines from the same vineyard.

3.7.3 Fingerprints of individual Niagara vineyards

Discrimination of wines according to vineyard within the Niagara region was less successful than the discrimination of Okanagan vineyards (Fig. 3.21). Using the discriminant functions in Table 3.19, the vineyards were discriminated (Table 3.20) by the elements Al, V, Co, Sr, and Mo, but tolerance values associated with these elements were extremely low (Table 3.21), indicating the elements are highly correlated. The discriminant

functions were found to classify Niagara wines 100% correctly (Table 3.22), but due to the low tolerance values, the model is unstable. This analysis is therefore not considered robust, but removal of any of the variables causes much lower correct classification. Test statistics for the discriminant analysis are given in Table 3.23, and are much lower than for the discrimination of the Okanagan vineyards. The small number of samples in the data set makes the significance of the model difficult to assess.

A plot of the RSD for highly discriminating elements in wines from each vineyard shows concentrations for individual vineyards to be comparable to those for the entire region (Fig. 3.22). Only the three wines from Cave Spring have a relatively low variability compared to the variability for the whole region Niagara, for all ten discriminating elements.

3.7.4 Cluster analysis of all Niagara wines sampled

Cluster analysis using the ten highly discriminating elements was also applied to Niagara wines (Fig. 3.23). Wines from Cave Springs vineyards were found to cluster together, but wines from De Sousa, Joseph's, Reif, and Pilliterri did not plot close together in the analysis.

3.8 Discrimination of colour and variety

The data set was examined for the statistical separation of wines according to colour and grape variety. Because the samples were selected for the primary purpose of examining regional chemical trends, the data set was not robust for fingerprinting colour, where only 13 of the 95 samples were red wines. Attempts at statistically separating colour and grape variety by trace element patterns were unsuccessful.

3.9 Determined concentrations of elements, pH, and conductivity of vineyard soils

Vineyard soils were prepared as pressed pellets and analysed by XRF for 28 elements according to the procedure described in Chapter 2. Determined concentrations of elements in soil are given in Appendix 6, along with pH and conductivity measurements. Element concentrations in soil were correlated to concentrations in wine, to further examined the source of the fingerprint.

3.9.1 Correlations between elements in soils and wines

A table of Pearson correlations relating the total concentrations of elements in soil and wine (Appendix 7) along with probability coefficients, were examined for high correlation coefficients. Correlations were also examined for soils and wines within each region, and for the larger size fraction of soil, to ensure the correlation data is robust. The strongest correlation between the soil and wine concentrations was for Sr, which was also found to be an element highly discriminating of wine region. A Pearson correlation coefficient of 0.63 (Appendix 7) with an associated probability of less than 0.008 was determined for Sr. When examined graphically, this relationship was found to have a major discontinuity between the Niagara and Okanagan regions (Fig. 3.24), and that the relationship between the elements is not linear. Correlation coefficients were determined for Sr between soil and wine for each region individually, and were found to be lower ($R = 0.27$, $p = 0.18$ for the Okanagan; $R = 0.32$, $p = 0.21$ for Niagara) than for the whole data set, indicating the high correlation for both regions was a result of the discontinuity. The soil-wine correlation for Sr was also found to be negligible when the < 2 mm fraction of soil was used, as opposed to the < 0.074 mm fraction, which was used for most of the soil analyses.

While no other positive correlations were found between element concentrations in soil and wine, concentrations of Ti were found to be consistently higher in soil from Niagara (Fig. 3.25), whereas Ba concentrations (like Sr), were found to be consistently higher in soil from the Okanagan (Fig. 3.26), causing a similar distribution between soil and wine as with the Sr data.

3.9.2 Correlations between element ratios in soils and wines

Because wines may have an uneven dilution effect during processing, correlations between element ratios in soil and wine were determined. Wine can evaporate upon storage in tanks and water is sometimes added to adjust sugar content (Jackson, 1989). The loss and addition of water is probably minimal in terms of its effect on trace element concentration, but examination of element ratios minimizes any variability in dilution. The elements in wine which were also present in the soil analysis, were each divided by other elements to create element ratios. The same ratios were derived for the soil element concentrations, and correlations between these ratios were then examined. Strong correlations were found between wines and soils for the element ratios Ti/Sr, Ti/Ba, Mn/Sr and Zn/Sr (Table 3.24), where the relation between these ratios is likely due to the positive relationship between Sr, Ti, and Ba in soil and wine. Because the relationship between Sr, Ti, and Ba soil and wine concentrations is caused by a discontinuity between the two regions, and is not a linear relationship (Figs 3.23-3.25), the element ratios were examined for each region individually, and no positive correlations were found.

3.10 Summary

Element concentrations in wines were determined, and the data was examined graphically. A log transformation applied to element concentrations in wine made the data better fit the assumptions of parametric statistical methods. Structures in relationships between elements were examined using PCA and cluster analysis. Discrimination of the major wine regions of Canada using concentrations of Sr, Rb, Mn, Mo, Al, V, Co, Zn, Sb, and U achieved 98% correct classification. Niagara and Okanagan wines can be discriminated with 98% accuracy, and the wines from 5 vineyards from the Okanagan were classified correctly according to origin. The wines from the Niagara region could not be classified correctly according to vineyard.

Element concentrations in soil were determined by XRF, and correlations between elements in soil and wine were derived. A significant positive correlation was determined for Sr in soil and wine, although there is a discontinuity between data from the Niagara and Okanagan which causes the positive correlation. This element also has the highest discriminating ability for wine region.

Table 3.1 Minimum and maximum concentrations (ppb) of elements measured in this study of Canadian wine compared to Canadian Drinking Water Guidelines, 1993. (n.s. = not specified).

Element	Minimum	Maximum	Canadian Water Standard
Li	0.74	33	n.s.
Be	0.005	1.80	n.s.
Mg	26900	149000	n.s.
Al	16.5	2080	n.s.
P	29400	490000	n.s.
Cl	2430	119000	250000
Ca	31000	240000	n.s.
Ti	1.44	46.2	n.s.
V	0.239	206	n.s.
Mn	207	4700	50
Fe	15.0	6900	300
Co	0.61	9.3	n.s.
Ni	4.0	164	n.s.
Cu	3.1	1200	1000
Zn	130	2960	5000
As	0.55	24.7	25
Br	86	900	n.s.
Se	0.20	10.9	10
Rb	190	1250	n.s.
Sr	176	1920	n.s.
Mo	0.87	67	n.s.
Ag	<0.001	0.155	50
Cd	0.098	6.6	5
Sb	0.038	5.2	n.s.
I	0.54	16.0	n.s.
Cs	0.165	8.0	n.s.
Ba	45	675	1000
La	0.002	8.6	n.s.
Ce	0.002	17.4	n.s.
Tl	0.034	0.62	n.s.
Pb	1.55	93	10
Bi	<0.008	3.09	n.s.
Th	0.005	1.02	n.s.
U	0.002	8.7	100

Table 3.2 Principal component analysis for elements in wines using 10 components and VARIMAX rotation.

Element	Component									
	1	2	3	4	5	6	7	8	9	10
U	0.92	0.11	-0.02	0.01	-0.10	0.11	-0.05	-0.00	-0.01	-0.05
Ce	0.85	0.07	-0.05	0.23	0.15	0.01	0.09	-0.01	0.09	-0.01
Th	0.85	-0.04	0.01	0.07	0.01	0.00	0.04	-0.15	-0.03	-0.14
Ti	0.74	0.19	0.21	0.30	0.08	0.35	-0.02	0.20	0.09	0.05
Be	0.68	-0.33	0.17	0.29	0.05	0.08	0.15	0.10	0.31	0.07
V	0.64	0.19	0.04	0.15	0.19	0.49	0.17	0.26	0.06	0.12
Bi	0.60	-0.28	0.14	0.02	0.06	0.02	0.04	-0.04	0.07	-0.55
Al	0.60	0.01	0.04	0.45	-0.05	0.19	0.30	0.20	0.34	0.14
Sb	0.59	0.18	0.10	0.17	0.13	0.54	0.08	0.18	0.26	0.04
Pb	0.56	0.22	-0.01	0.14	-0.08	0.19	-0.04	0.07	0.44	-0.40
Co	0.55	0.06	0.17	0.47	0.09	0.19	0.24	0.10	0.35	0.26
Zn	-0.03	0.83	-0.01	0.18	0.07	0.06	-0.04	0.14	0.19	0.11
Cd	0.16	0.79	0.02	0.12	-0.07	0.02	0.27	-0.02	0.22	-0.07
Li	0.15	-0.12	0.86	0.02	0.03	0.20	0.15	-0.07	-0.03	-0.16
Mg	0.04	0.13	0.84	0.10	-0.30	0.01	-0.01	0.12	0.11	0.15
Sr	-0.16	-0.04	0.53	-0.13	-0.65	-0.01	0.28	-0.10	-0.16	-0.16
Tl	0.24	0.03	-0.07	0.85	-0.05	0.07	0.11	0.15	0.16	0.14
Cs	0.22	0.16	0.02	0.85	-0.04	0.09	0.10	0.05	-0.03	0.02
Rb	0.08	0.17	0.15	0.80	0.06	0.00	-0.05	0.02	-0.17	-0.37
Ba	-0.08	0.01	0.11	0.09	-0.91	0.11	-0.09	0.12	0.16	0.07
Mo	0.08	0.03	0.10	0.02	-0.19	0.88	0.10	-0.07	0.15	-0.10
As	0.39	-0.08	0.15	0.42	0.04	0.60	0.11	0.11	0.32	0.10
Se	0.09	0.13	0.23	0.09	0.04	0.08	0.87	-0.11	0.02	-0.03
I	0.19	0.10	-0.17	0.39	-0.10	0.31	0.54	0.29	0.22	0.09
Mn	0.12	0.15	0.06	0.28	-0.09	0.08	-0.07	0.78	0.31	0.04
Ag	0.37	0.04	0.14	0.06	0.08	0.39	-0.03	-0.51	0.51	0.17
Cu	0.13	0.18	0.10	-0.06	-0.13	0.18	-0.08	0.16	0.77	0.12
Ni	0.03	0.25	-0.11	0.05	-0.01	0.11	0.22	0.09	0.71	-0.18

Table 3.3 Elements grouped by principal components and the percent of the total variance each component explains (%).

Component	Elements grouped	Total variance explained (%)
1	U, Ce, Th, Ti, Be, V, Bi, Al, Sb, Pb, Co	21
2	Zn, Cd	6.8
3	Li, Mg, Sr	7.4
4	Tl, Cs, Rb	11
5	Ba, Sr	5.6
6	Mo, As, Sb	8.2
7	Se, I	5.6
8	Mn	4.8
9	Ag, Cu, Ni	8.8
10	Pb, Bi	3.4

Table 3.4 Group means and classification matrices of wine regions discriminated by principal components (equation 3.1).

Region	Group means	Classification	Jackknifed classification
Okanagan	-1.63	98	98
Niagara	2.66	97	97

Table 3.5 Discriminating power, as F-to-remove statistics and tolerance, of PCA components used to discriminate wine region.

	F-to-remove	Tolerance
Component 1	30.53	0.79
Component 2	50.61	0.71
Component 3	31.12	0.79
Component 4	90.59	0.61
Component 5	40.99	0.75
Component 8	145.17	0.54

Table 3.6 Test statistics for discriminant analysis of wine region using PCA components.

Statistic	Approximate F-statistic	probability value
Wilk's lambda	64.84	< 0.001
Pillai's trace	64.84	< 0.001
Lawley-Hotelling trace	64.84	< 0.001

Table 3.7 Group means and classification matrices for discriminant analysis of Niagara and Okanagan wines using element concentrations (equation 3.2).

Region	Group mean	Classification	Jackknifed classification
Okanagan	-1.848	100	98
Niagara	3.029	100	97

Table 3.8 Discriminating power, as F-to-remove statistic and tolerance, of elements used to discriminate Niagara and Okanagan wine.

Element	F-to-remove statistic	Tolerance
U	20.78	0.37
V	14.25	0.32
Al	18.37	0.36
Sb	9.00	0.35
Co	7.68	0.39
Zn	13.56	0.85
Sr	63.97	0.69
Rb	24.90	0.80
Mo	9.38	0.57
Mn	21.52	0.87

Table 3.9 Test statistics for discriminant analysis of Niagara and Okanagan wines.

Test Statistic	Approximate F-statistic	Probability value
Wilk's lambda	48.9	< 0.001
Pillai's trace	48.9	< 0.001
Lawley-Hotelling trace	48.9	< 0.001

Table 3.10 Group means and classification matrices for discriminant analysis of Niagara, Okanagan, and French wines (equations 3.3 and 3.4).

Region	Group means (Factor 1)	Group means (Factor 2)	Classification	Jackknifed classification
Okanagan	-2.19	-0.05	100%	98%
Niagara	2.60	0.44	75%	67%
France	3.57	-1.31	90%	80%

Table 3.11 Discriminating power, as F-to-remove statistics and tolerance, of elements used to discriminate Okanagan, Niagara, and French wines.

Element	F-to-remove	Tolerance
Al	9.89	0.36
V	10.72	0.33
Mn	10.78	0.88
Co	4.75	0.39
Zn	7.08	0.86
Rb	21.54	0.82
Sr	31.02	0.73
Mo	5.15	0.56
U	12.05	0.38
Sb	5.12	0.37

Table 3.12 Test statistics for discriminant analysis of Niagara, Okanagan, and French wines.

Test statistic	Approximate F-statistic	Tolerance
Wilk's lambda	18.86	<0.001
Pillai's trace	10.53	<0.001
Lawley-Hotelling trace	30.56	<0.001

Table 3.13 Discriminant functions and associated eigenvalues for classifying wines from 5 Okanagan vineyards.

	Discriminant Functions	Eigenvalues
Factor 1	10.04 + 2.03Rb - 7.84Sr - 1.00Mo + 5.71Mn + 0.60U	25.41
Factor 2	-44.49 + 3.62Rb + 8.00Sr - 4.52Mo - 2.99Mn + 0.99U	18.61
Factor 3	15.21 + 3.13Rb - 1.12Sr +1.65Mo - 4.79Mn - 0.57U	4.57
Factor 4	-24.57 + 4.26Rb -4.17Sr +2.19Mo +3.27Mn - 0.29U	2.00

Table 3.14 Group means for discriminant functions of wines from 5 Okanagan vineyards.

Vineyard	Group means			
	Factor 1	Factor 2	Factor 3	Factor 4
Lake Breeze	-2.219	2.668	2.707	-1.011
Wild Goose	3.622	5.642	-1.027	1.366
Lang Vineyards	-6.416	-3.273	-0.200	1.540
Quail's Gate	-2.144	0.159	-3.343	-1.902
House of Rose	5.977	-4.748	0.544	-0.142

Table 3.15 Classification matrices for discrimination of wines from 5 Okanagan vineyards.

Vineyard	Classification (% correct)	Jackknifed classification
Lake Breeze	100	100
Wild Goose	100	100
Lang Vineyards	100	100
Quail's Gate	100	100
House of Rose	100	100

Table 3.16 Discriminate power, as F-to-remove statistics and tolerance, for elements used to discriminate wines from 5 Okanagan vineyards.

Element	F-to-remove Statistic	Tolerance
Rb	15.48	0.85
Sr	42.85	0.34
Mo	35.18	0.43
Mn	28.33	0.33
U	6.60	0.54

Table 3.17 Test statistics for the discriminant analysis of wines from 5 Okanagan vineyards.

Test statistic	Approximate F-statistic	Probability
Wilk's lambda	41.21	< 0.001
Pillai's trace	22.57	< 0.001
Lawley-Hotelling trace	39.20	< 0.001

Table 3.18 Concentrations of select elements in icewines, late harvest wines and Rieslings from Lang Vineyards and Summerhill Estates.

Wine	Mn	Co	Ni	Zn	Rb	U
Lang Riesling 1997	620	3.2	15.1	400	360	0.164
Lang Late Harvest 1997	860	3.0	14.7	280	390	0.052
Lang Icewine 1997	1080	5.5	32	820	471	0.39
Summerhill Riesling 1998	440	1.35	7.7	680	370	0.273
Summerhill Icewine 1998	1046	3.1	19.1	390	205	0.014

Table 3.19 Discriminant functions and associated eigenvalues for wines from four Niagara vineyards.

Factor	Discriminant function	Eigenvalue
1	-12.63 + 3.45V - 6.83Al + 3.79Co + 6.24Sr - 6.49Mo + 2.15Mn	36.66
2	-28.71 + 1.19V + 3.04Al - 6.17Co - 2.18Sr + 0.20Mo - 3.67Mn	5.91
3	1.60 + 1.45V - 1.02Al - 0.66Co - 0.31Sr + 0.10Mo + 0.47Mn	1.62

Table 3.20 Group means of discriminant functions for wines from four Niagara vineyards.

Vineyard	Group mean		
	Factor 1	Factor 2	Factor 3
Cave Spring	-6.08	-3.81	0.39
Joseph's	0.71	0.37	-1.71
Reif	-3.86	2.47	0.80
De Sousa	8.50	-0.68	0.84

Table 3.21 Discriminant power, as F-to-remove statistics and tolerance, for elements in discriminant analysis of Niagara wines.

Element	F-to-remove	Tolerance
V	19.13	0.06
Al	15.54	0.06
Co	10.99	0.14
Sr	13.53	0.12
Mo	75.70	0.05
Mn	5.26	0.21

Table 3.22 Classification matrices for discriminant analysis of wines from 5 Niagara vineyards.

Vineyard	Classification (% correct)	Jackknifed classification (%correct)
Cave Spring	100	100
Joseph's	100	100
Reif	100	80
De Sousa	100	100

Table 3.23 Test statistics for the discriminant analysis of wines from 5 Niagara vineyards.

Test statistic	F-statistic	Probability
Wilk's lambda	11.60	< 0.001
Pillai's trace	7.37	< 0.001
Lawley-Hotelling trace	16.36	< 0.001

Table 3.24 Positive Pearson's R correlation coefficients between wines and soils determined for concentration ratios of elements.

Element ratio	Pearson R	Bonferroni probability
Ti / Sr	0.73	<0.001
Ti / Ba	0.52	0.055
Mn / Sr	0.65	<0.001
Zn / Sr	0.56	0.015

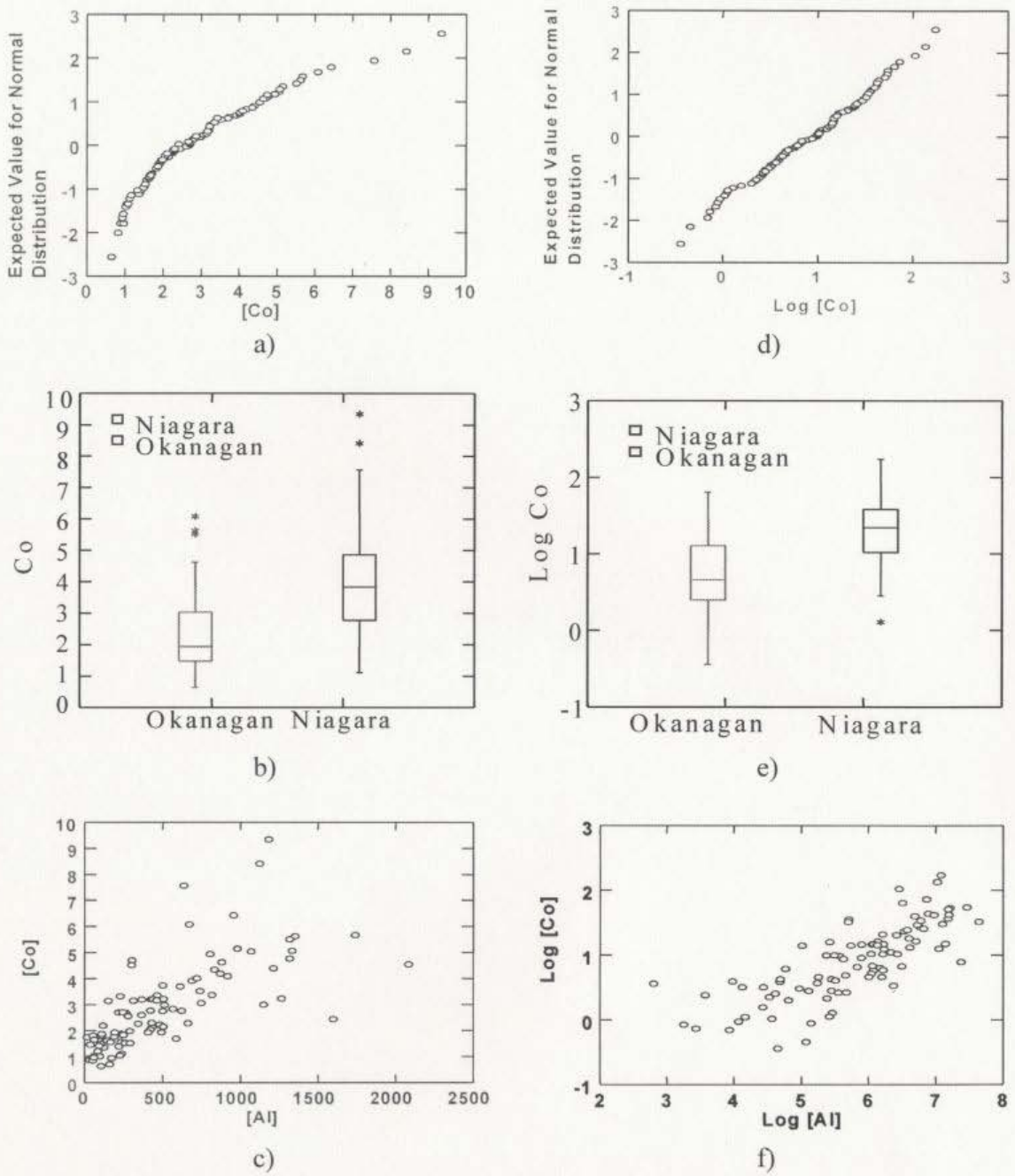

Fig. 3.1a) to f) Normality plot (a) and boxplot (b) of concentrations of Co, and scatter plot of concentrations of Co and Al (c); normality plot (d) and boxplot (e) of log transformed concentrations of Co, and scatterplot of log transformed concentrations of Co and Al (f).

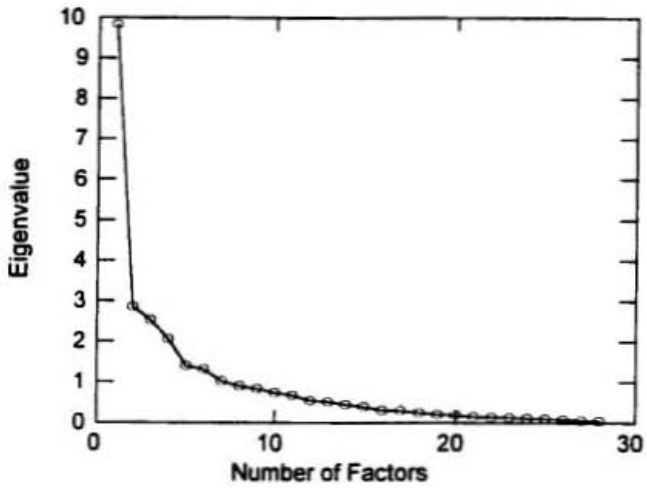

Fig. 3.2 Scree plot for PCA of elements in wine, in which factors are plotted against their eigenvalues to determine the number of factors needed in the analysis.

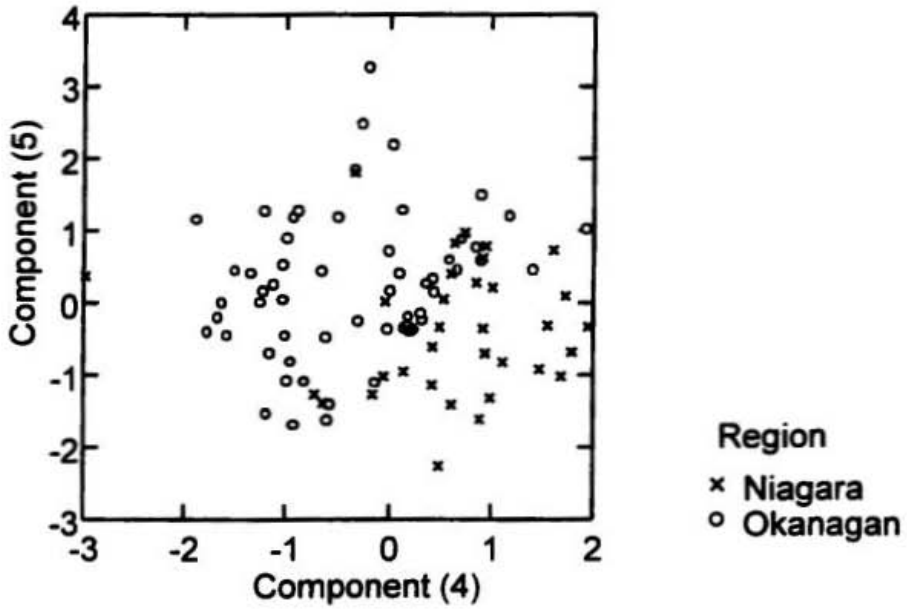

Fig. 3.3 Plot of PCA Component 4 *vs.* Component 5 for element concentrations in wines.

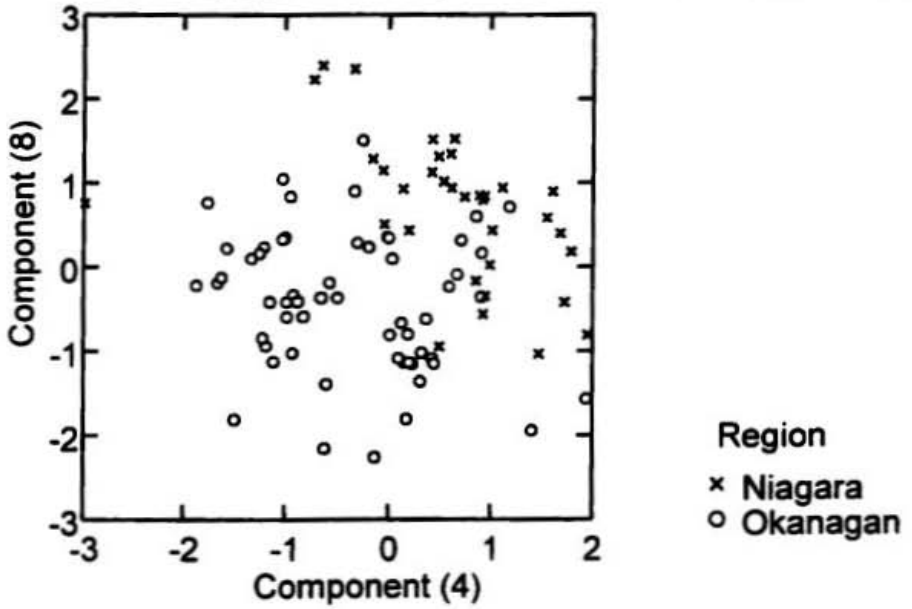

Fig. 3.4 Plot of PCA Component 4 *vs.* Component 8 for element concentrations in wines.

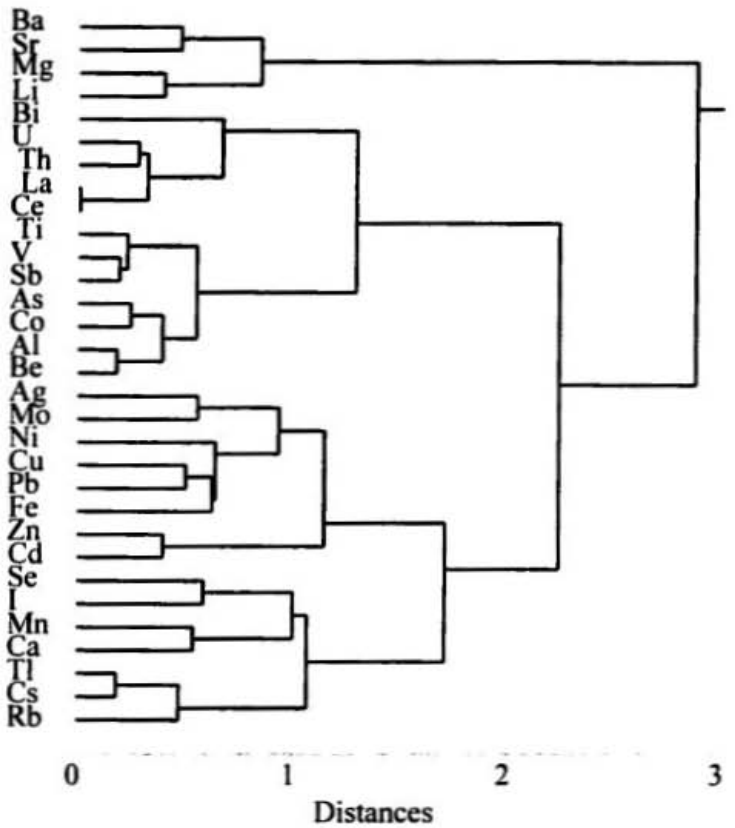

Fig. 3.5 Cluster analysis, using Pearson's R correlation coefficients and Ward's clustering method, showing element association in Okanagan wines.

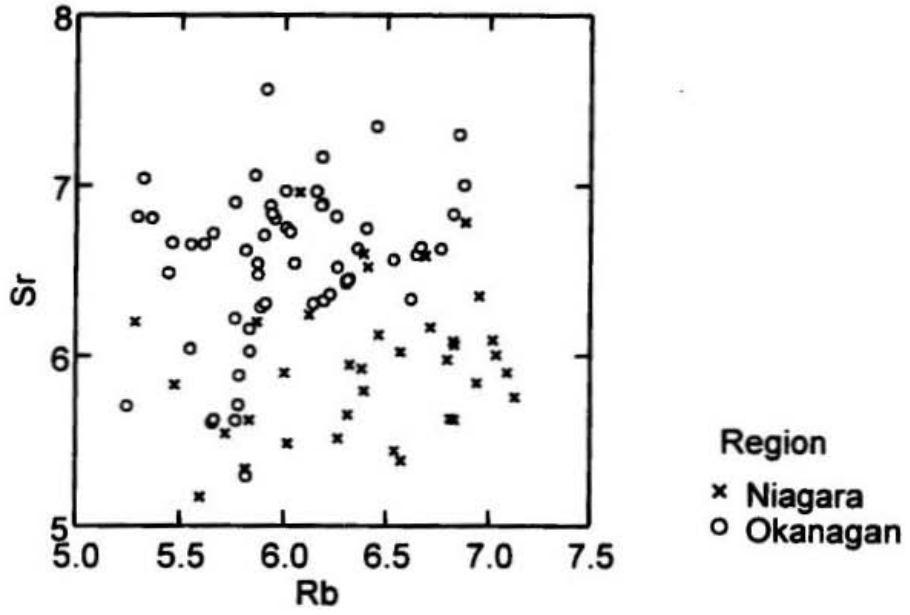

Fig. 3.6 Log transformed concentrations of Sr and Rb for Niagara and Okanagan wines.

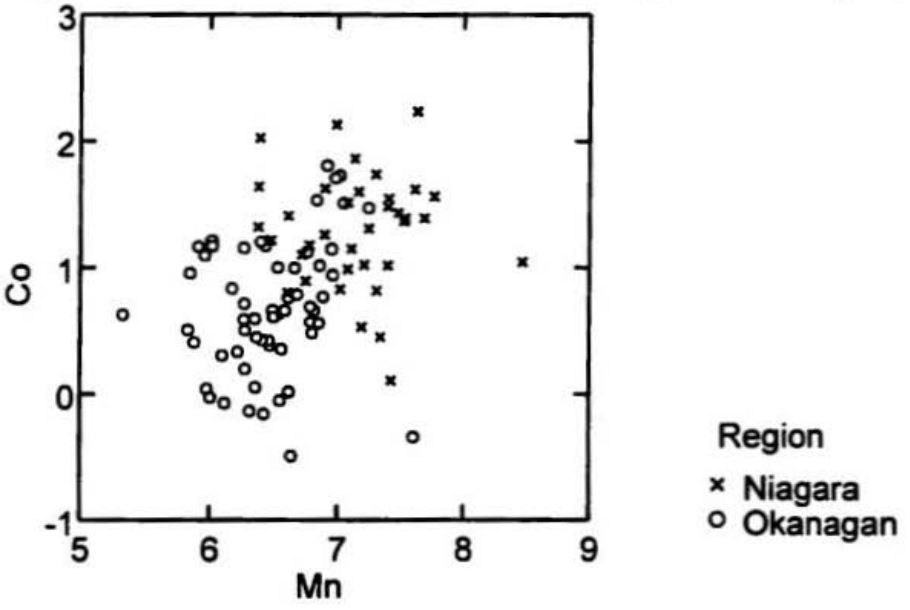

Fig. 3.7 Log transformed concentrations of Co *vs.* Mn in Niagara and Okanagan wines.

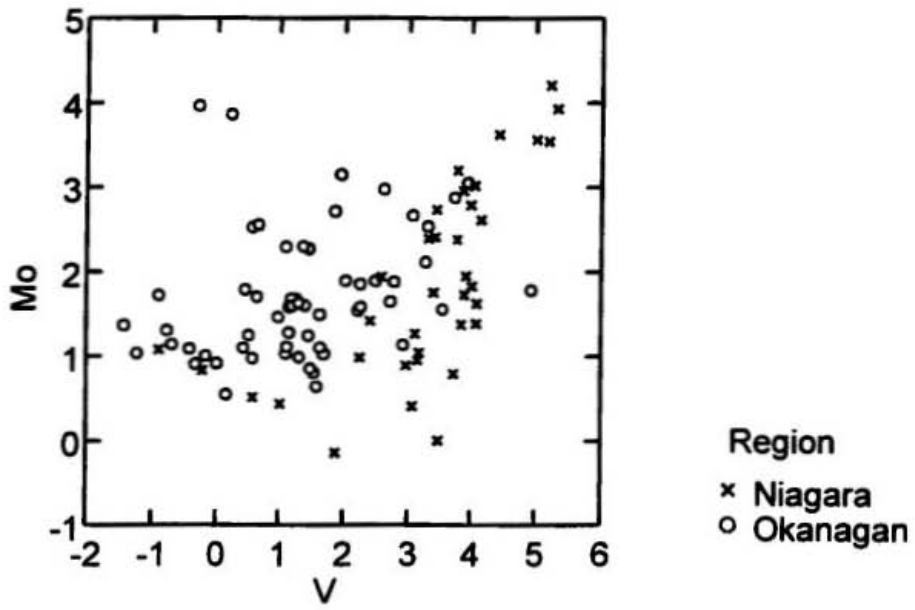

Fig. 3.8 Log transformed concentrations of Mo *vs.* V in Niagara and Okanagan wines.

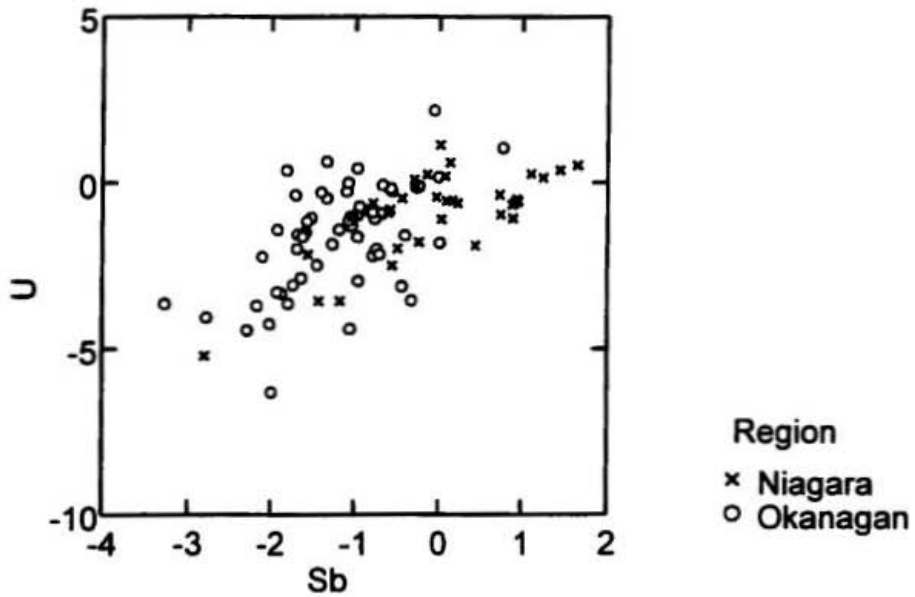

Fig. 3.9 Log transformed concentrations of Sb *vs.* U in Niagara and Okanagan wines.

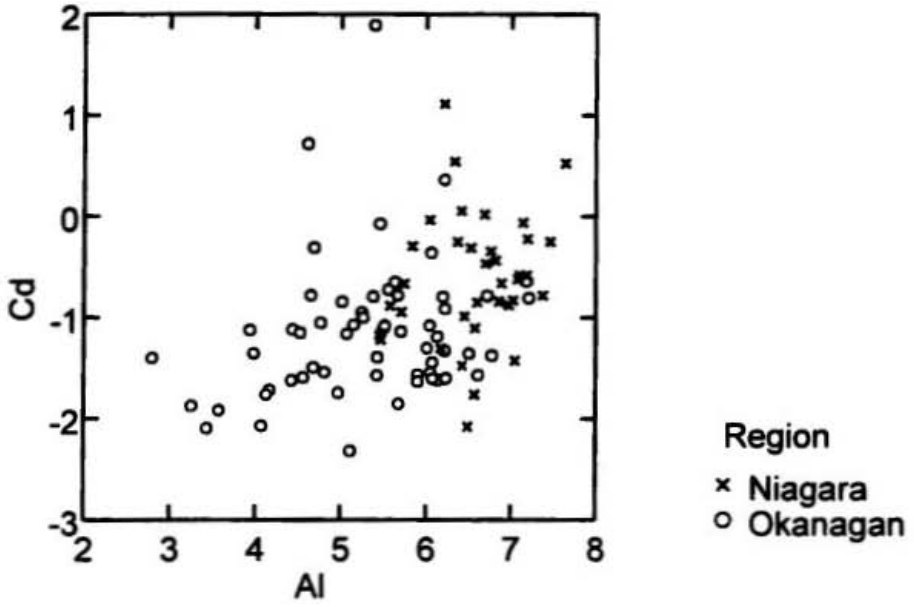

Fig. 3.10 Log transformed concentrations of Cd *vs.* Al in Niagara and Okanagan wines.

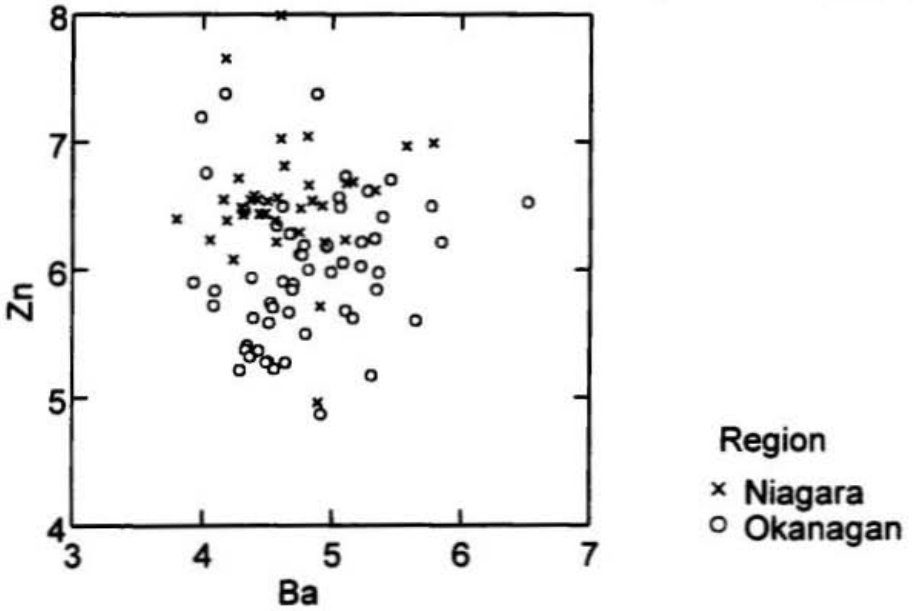

Fig. 3.11 Log transformed concentrations of Zn *vs.* Ba in Niagara and Okanagan wines.

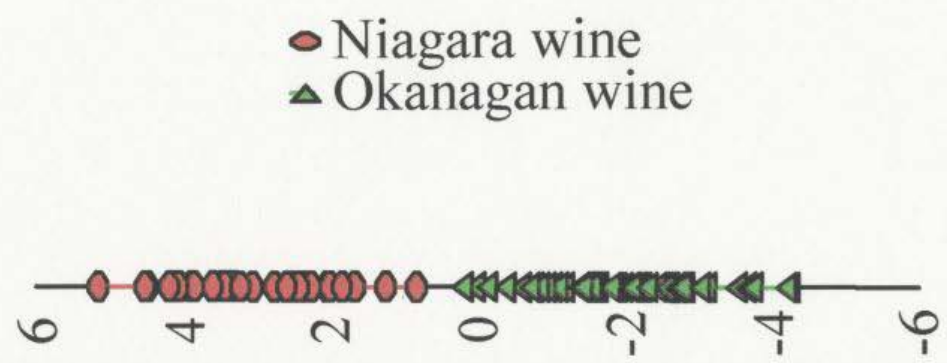

Fig. 3.12 Plot of discriminant function (equation 3.4), grouping Okanagan and Niagara wine.

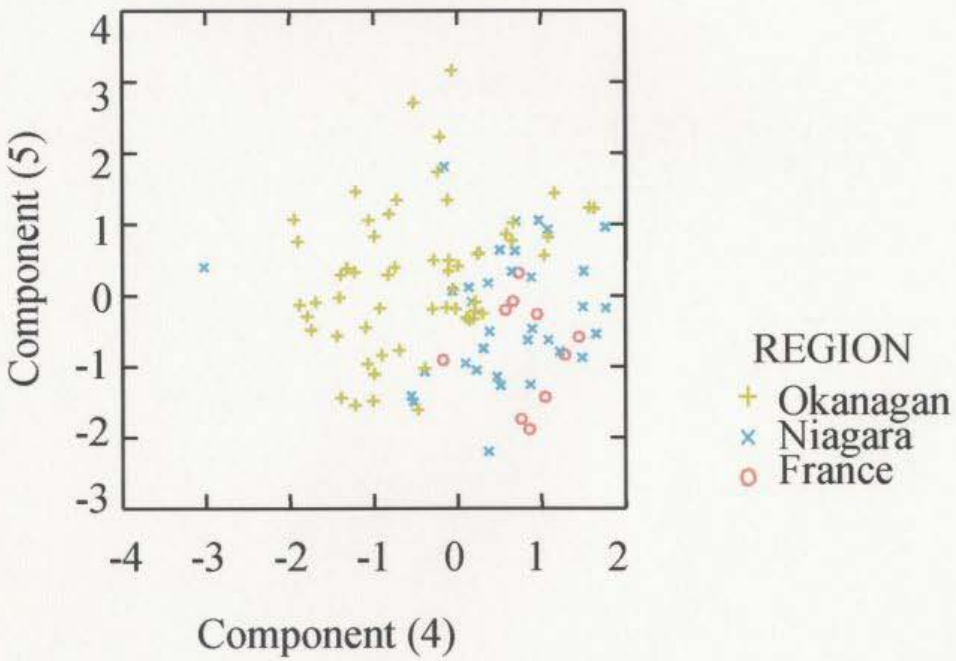

Fig. 3.13 Component 4 *vs.* Component 5 for Okanagan, Niagara, and French wines.

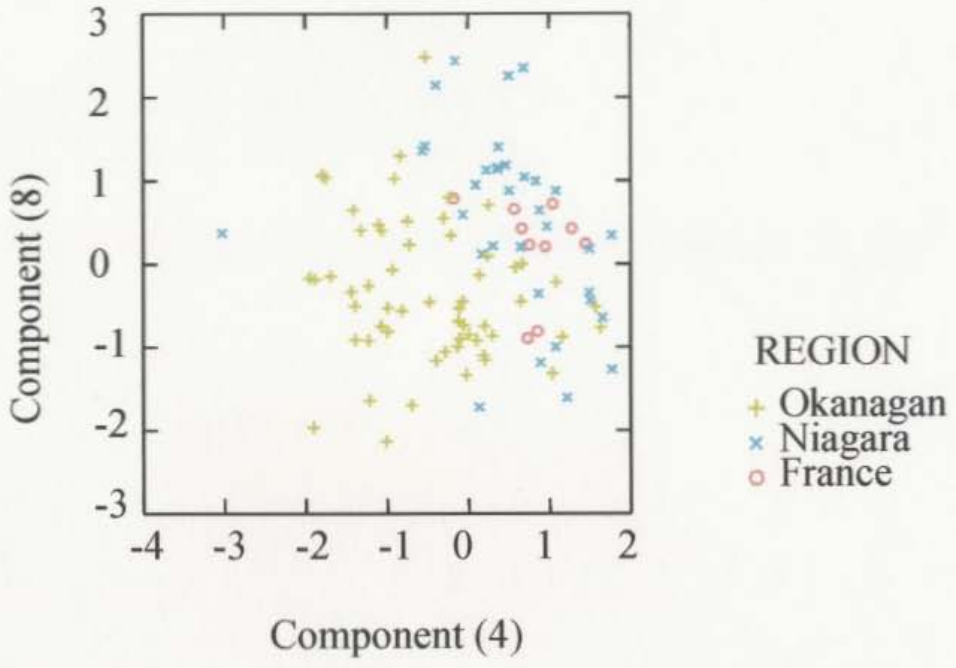

Fig. 3.14 Component 4 *vs.* Component 8 for Okanagan, Niagara, and French wines.

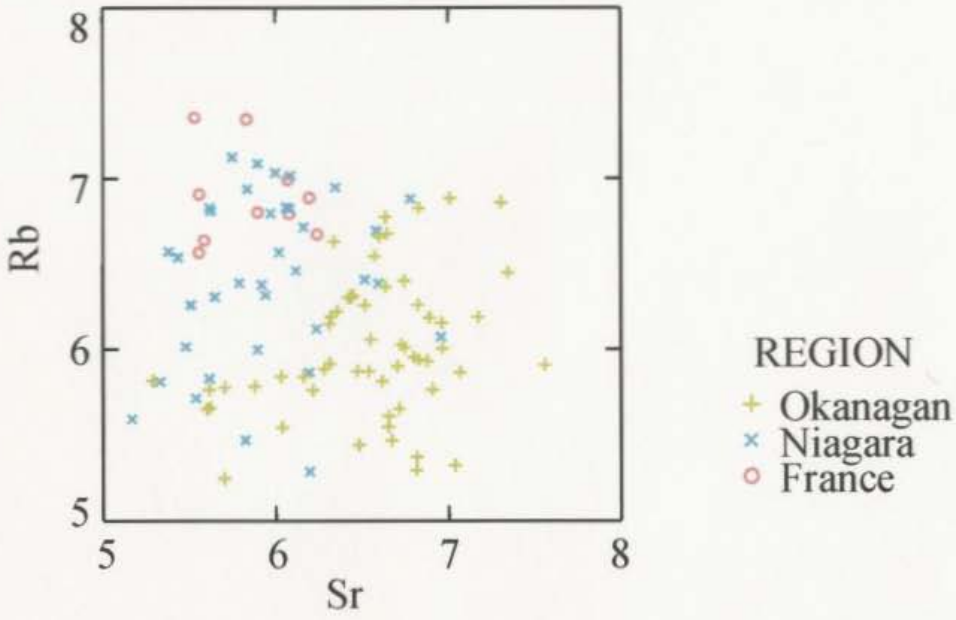

Fig. 3.15 Log transformed concentrations of Sr *vs.* Rb for Okanagan, Niagara, and French wines.

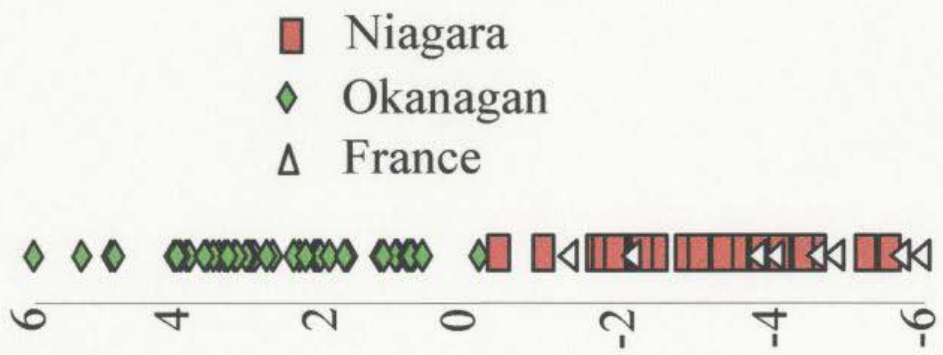

Fig. 3.16 Application of the discriminant function (equation 3.4) to the Niagara, Okanagan, and French wines.

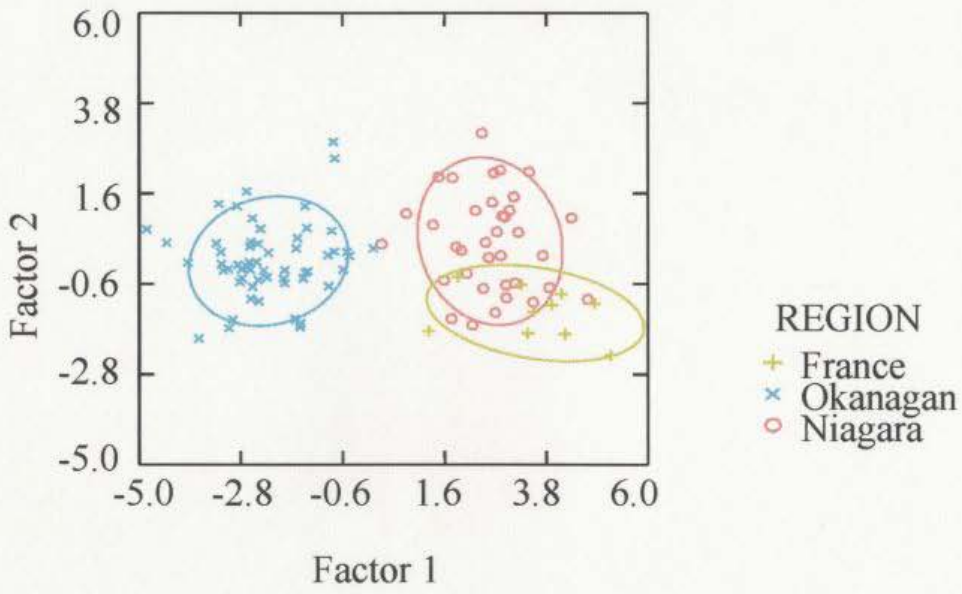

Fig. 3.17 Plot of discriminant functions (equations 3.5 and 3.6) grouping wines from France, the Okanagan, and Niagara regions.

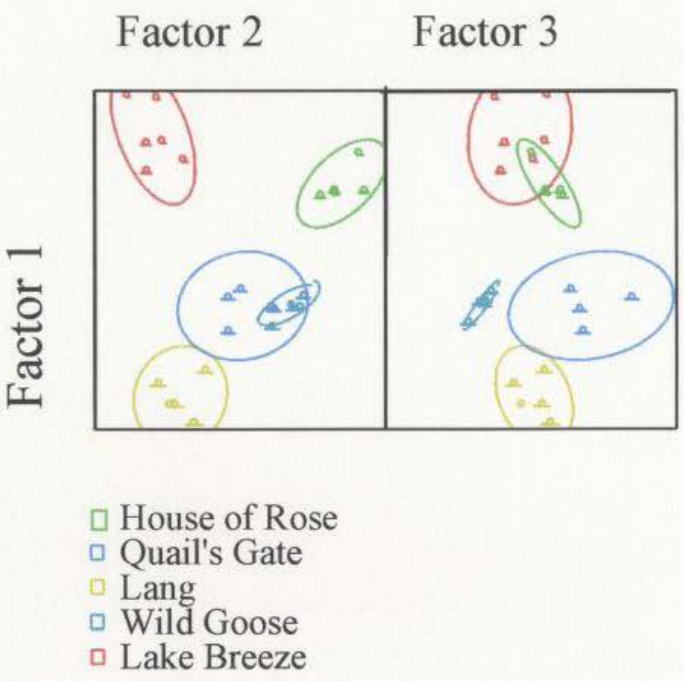

Fig. 3.18 Plot of discrimination functions classifying wines from 5 Okanagan vineyards.

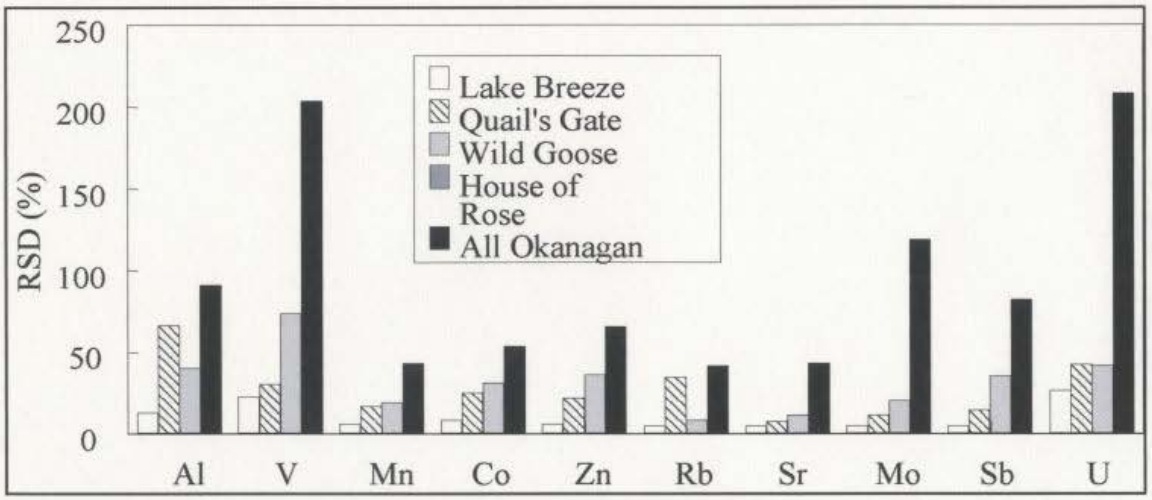

Fig. 3.19 Percent RSD calculated for elements used to discriminate Okanagan wines by vineyard. Bars represent variance (RSD) in element concentrations for 6 wines from the same batch of 1998 Lake Breeze Pinot Blancs; Quail's Gate Riesling (1995-1998); House of Rose Verdelet (1992-1996); and all Okanagan wines.

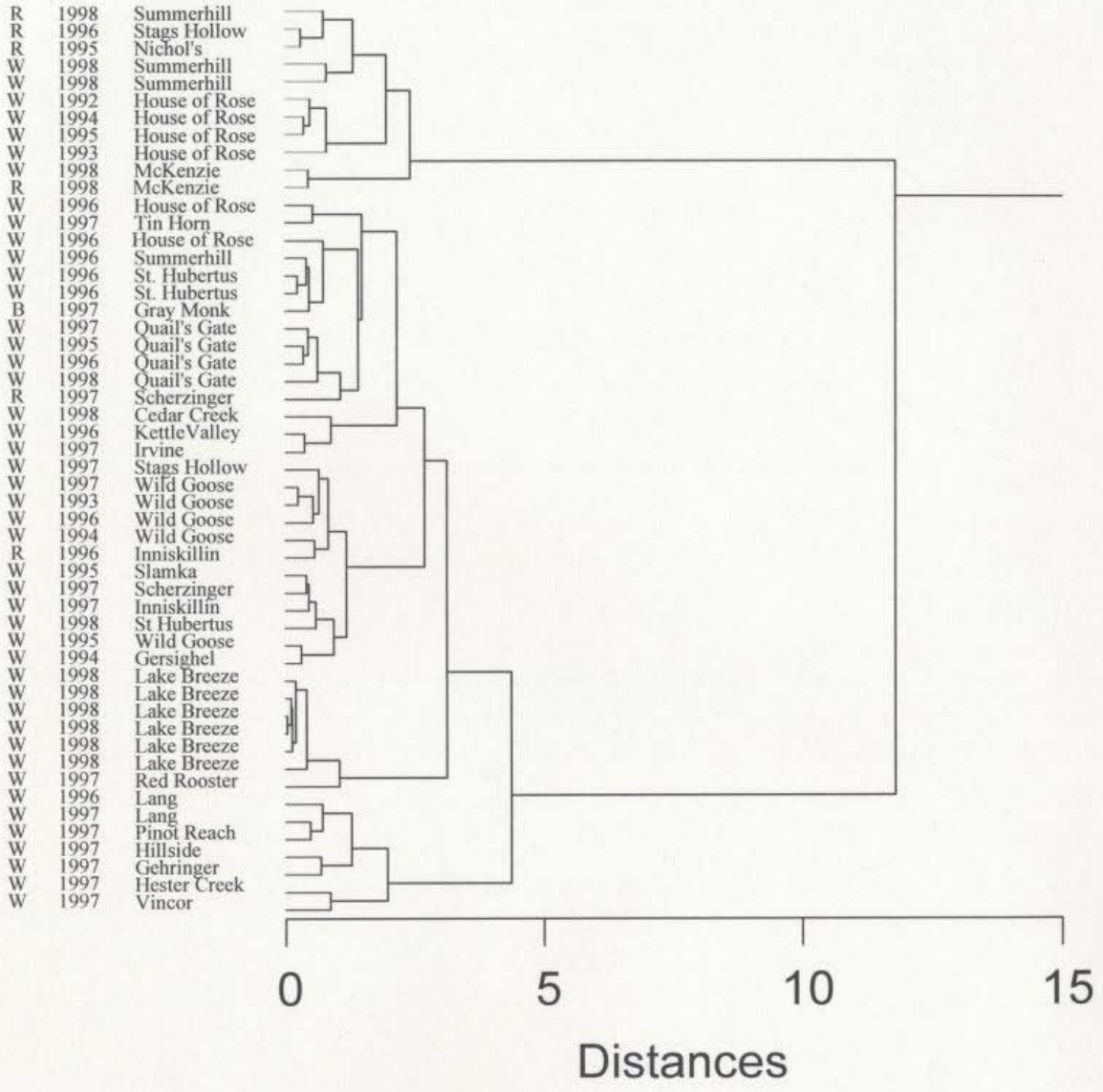

Fig. 3.20 Cluster analysis of log transformed concentrations of Al, V, Mn, Co, Zn, Rb, Sr, Mo, Sb, and U, in Okanagan wine, using Pearson's R correlations as distance measures and clustering by Ward's method. Wines are labelled by colour (R=red, W=white, B=blush /rose), vintage year, and winery name.

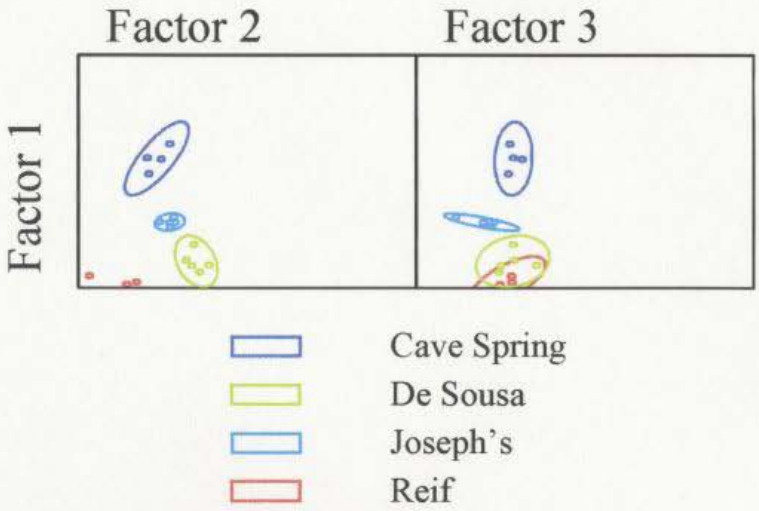

Fig. 3.21 Discriminant analysis of wines from four vineyards in Niagara.

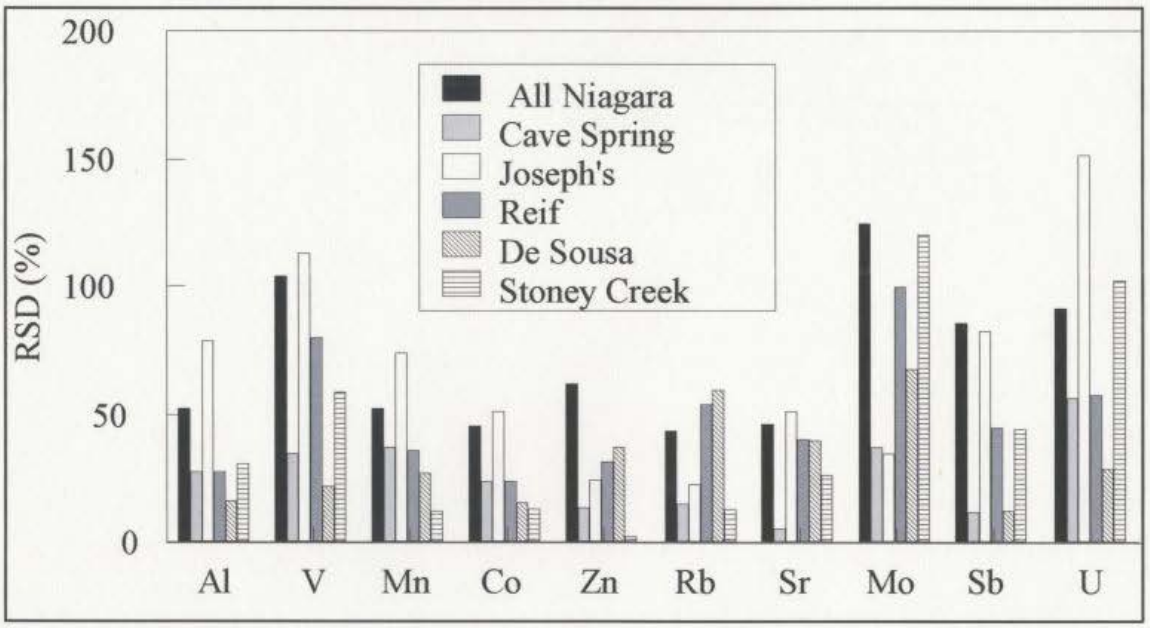

Fig. 3.22 Comparison of RSD for 10 discriminating elements in Niagara wines. The samples from Cave Spring, Joseph's, Reif, and De Sousa are wines made from different varieties of grapes from the same vineyard, and the Stoney Creek samples are 3 Pinot Blancs from grapes grown on different vineyards, but processed at the same winery.

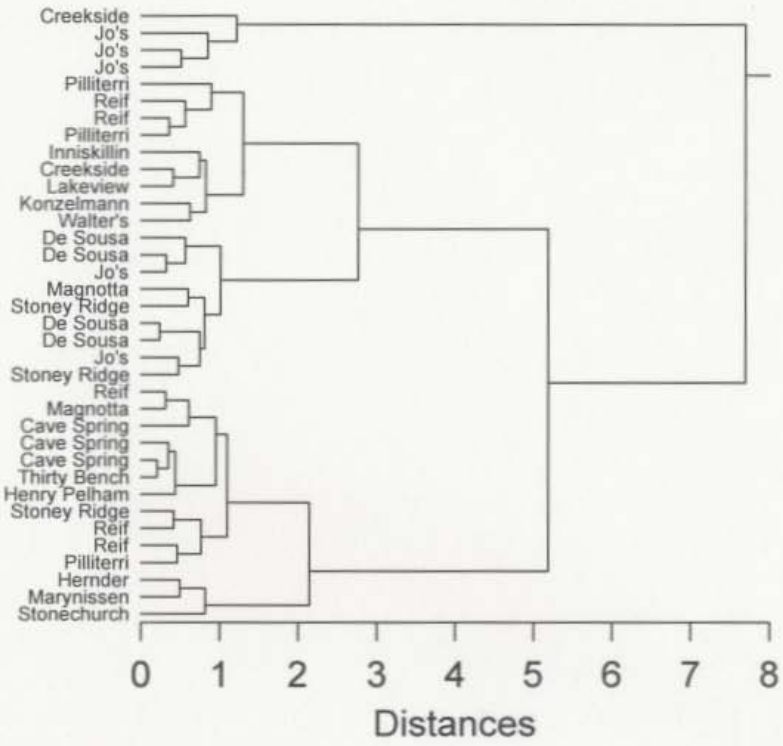

Fig. 3.23 Cluster analysis of log transformed concentrations of Al, V, Mn, Co, Zn, Rb, Sr, Mo, Sb, and U, in Niagara wines, using Pearson's R correlations as distance measures and clustering by Ward's method.

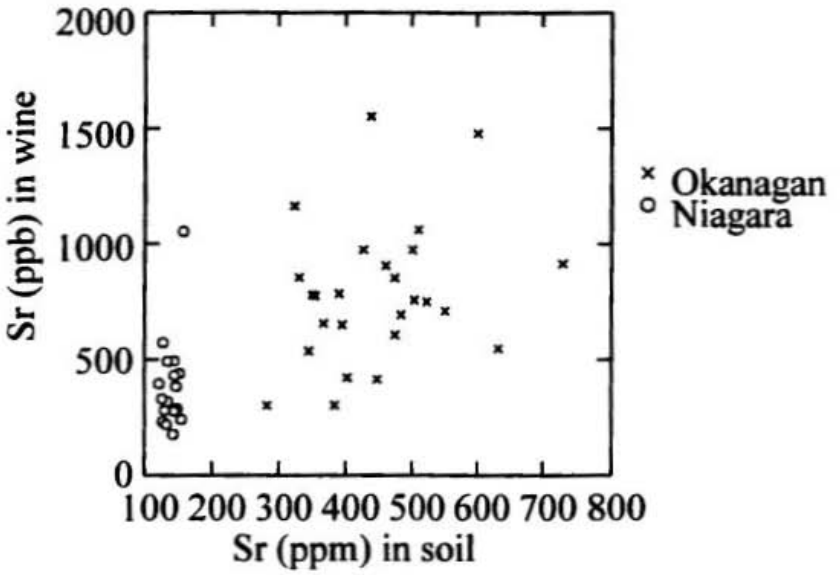

Fig. 3.24 Concentration of Sr in wines (ppb) *vs.* concentration of Sr in vineyard soils (ppm) for Okanagan and Niagara wines and vineyards.

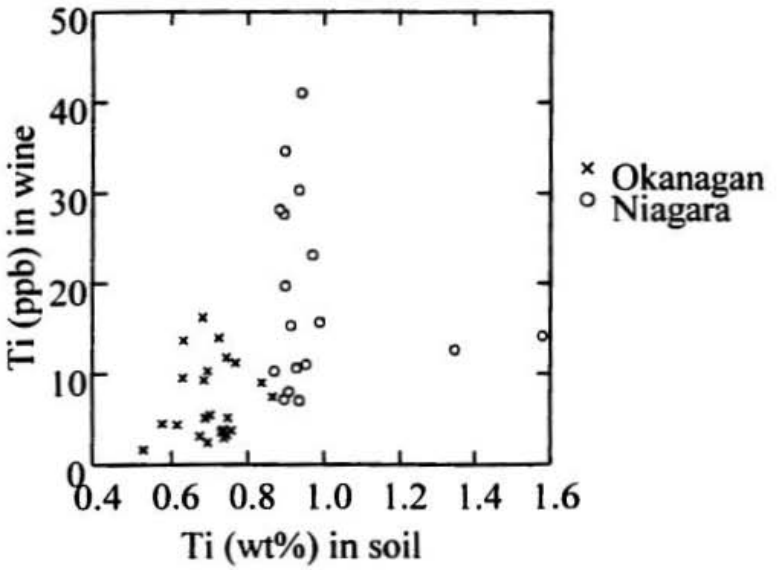

Fig. 3.25 Concentration of Ti in wines (ppb) *vs.* concentration of Ti in soils (wt%) for Okanagan and Niagara wines and vineyards.

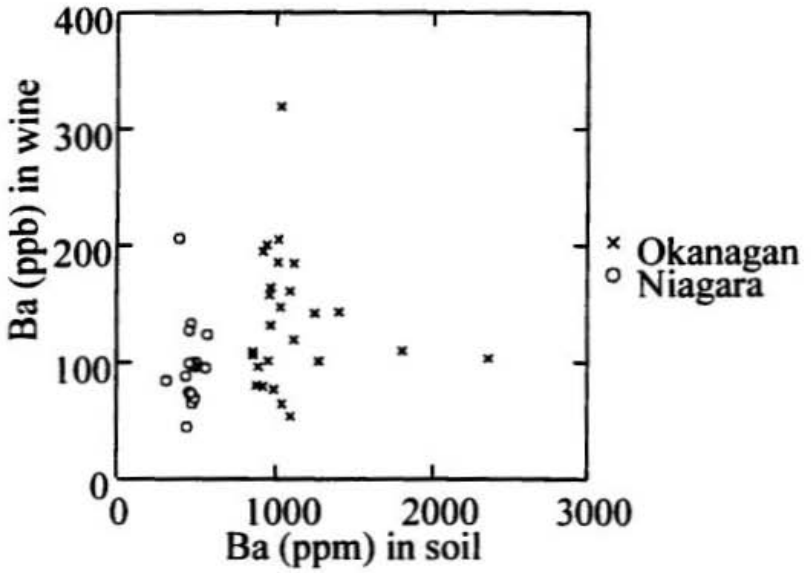

Fig. 3.26 Concentration of Ba in wines (ppb) *vs.* concentration of Ba in soils (ppm) for Okanagan and Niagara wines and vineyards.

Chapter 4 Fingerprinting of Canadian wines

4.1 Introduction

To interpret the fingerprint analysis, the elements grouped by the PCA are compared to the grouping of elements with similar chemical properties, according to periodic law and ionic potential. The agreement of element association in wine with associations between elements with similar chemical properties suggests that element mobility influences concentration in wine to a high degree, and the effects of differential plant uptake and wine processing are minimal. Elements which were found to have discriminating power of wine region are discussed in terms of possible sources and their mobility in the environment.

4.2 Ionic potential of elements

According to periodic law of the elements, elements in the same groups, or columns, of the periodic table, have the same valences and structure, and therefore tend to have similar physical and chemical properties (Faure, 1998). Elements in the same periodic group display geochemical coherence in their distribution in nature (Faure, 1998). Element mobility is influenced by the ionic potential of an element, which is quantified as the ratio of the valence, or positive ionic charge, to the ionic radius, in picometres (pm) (Rollinson, 1993). Elements of low ionic potential (< 0.03 pm^{-1}) can be related, at least theoretically, to a tendency to go readily into solution, whereas ions with an intermediate ionic potential (0.03-0.12 pm^{-1}) have a strong tendency to precipitate as hydroxides (UKESCC, 2000). The relationship of ionic potential to the tendency of an ion to remain in solution, or precipitate as a hydroxide, can be applied to elements which form highly ionic bonds, but

is complicated by the tendency of elements, particularly from the middle of the periodic table, to form covalent bonds (Krauskopf and Bird, 1995). Often a single ionic potential for an element can not be defined, because many elements exist at more than one ionic charge, which determines valence and affects ionic radius. Ionic radius is determined from the distances between ions in crystals, and is therefore dependent on the coordination number of the ion in the crystal in which it is measured (Faure, 1998). Elements which were analysed in wine samples, and which are expected to form highly ionic bonds due to a low electronegativity (Krauskopf and Bird, 1995), were plotted by their valence and ionic radius in Fig. 4.1, using the radii of ions for a coordination number of 6, except for Be for which a radius associated with a coordination number of 4 was used (Krauskopf and Bird, 1995). From this plot, elements are grouped as soluble cations and insoluble hydroxides, using the ionic potential of 0.03 pm^{-1} as a boundary (UKESCC, 2000). The plot shows elements from Group 1A and 11A on the periodic table (Li, Rb, Cs, Mg, Ca, Sr, and Ba), with the exception of Be, to have low ionic potential, and are classified as soluble cations. The ions Tl^{1+} and Pb^{2+}, have a highly ionic character and are predicted to be soluble by low ionic potentials (Fig. 4.1), but have less ionic character and are less mobile as Tl^{3+} and Pb^{4+} (Krauskopf and Bird, 1995). The elements Be, Ti, and V were predicted to exist as insoluble hydroxides by their ionic potential. The element, Mn, exists in both groups, depending on valence (UKESCC, 2000). The behaviour of transition elements, which readily form covalent bonds, and the halogens, which can exist as anions, are not well predicted by this plot. Periodic law still applies for these elements, and predicts that the chemical properties of Cd are similar to those of Zn, a far more abundant element (Faure, 1998).

4.3 Interpretation of PCA

Elements grouped in each component from PCA, along with the % variance they represent were summarised in Table 3.3. The elements in Component 3(Li, Mg, Sr), Component 4(Tl, Cs, Rb) and Component 5(Ba, Sr) are all classified as soluble cations by their ionic potential, and are therefore expected to be mobile in the environment. With the exception of Tl, these elements belong to Group IA and IIA of the periodic table, and therefore have similar chemical and physical properties. The elements Be, Ti and V, which are predicted to be immobile by their ionic potential (Table 4.1), are in Component 1 of the PCA analysis, but eight other elements are also included in this component. Examination of the Pearson's R correlations (Appendix 4) shows strong correlations between Be and Ti (R=0.54), and Ti and V (R=0.67). The only element which loads high in Component 8 is Mn, which is a mobile cation as Mn(II), and an insoluble hydroxide as Mn(III).

The elements Zn and Cd are grouped in Component 2, and are transition metals from group IIB on the periodic table, and Component 9 groups the transition metals Ni, Cu and Ag. The elements Se and I are grouped in Component 7, and can exist as anions or cations.

The grouping of elements with similar ionic potential in some of the Components (3,4,and 5), suggests the mobility of these elements in the environment, as defined by their ionic potential, is not obscured by factors such as differential plant uptake, differences in soil chemistry, or addition of elements during wine processing. The elements grouped in Components 4 and 5, which were shown to be good discriminators of region (Fig. 3.3), were elements which are predicted to be mobile cations. The only element which loaded high in Component 8 was Mn, which can behave as a soluble cation or an insoluble

hydroxide depending on its ionic charge (UKESCC, 2000). The discriminating ability of this element suggests there are differences in its mobility and abundance in the two wine producing regions.

In plants, Cd is a toxic element, whereas Zn is an essential plant nutrient. A study of uptake of Cd by strawberry plants shows Cd is most mobile in acid soils and is readily plant available in soluble form (Cielinski *et al.*, 1996), but there is disagreement as to whether the uptake of Zn is passive or active in plants (Kabatas-Pendias and Pendias, 1984). The Zn-Cd interaction has been reported to be both antagonistic and synergistic in plants, where Zn has been reported to compete with Cd for binding sites but also to increase Cd solubility and translocation from roots to plants (Kabatas-Pendias and Pendias, 1984). The positive correlation (R=0.60, Appendix 4) between these elements in wines suggests that differential plant uptake does not occur, and concentrations of these elements in wine is determined by similar chemical properties.

The plot of ionic potential predicted Pb^{2+} to be soluble and therefore mobile in the environment, but Pb did not group with other mobile elements in the PCA. This may be due to the presence of Pb^{4+}, which is not predicted to be soluble, and also to other sources of Pb in wine. Increased lead concentrations in wine have been attributed to faulty cork capsules. Cork capsules are the film of plastic or foil which sometimes covers the cork, and some types of foil capping have a high lead content, although high aluminum content foils have largely replaced those containing lead alloys (Roses, 1997). Fertilizers and wine-making equipment (Gulson *et al.*, 1992; Rosman *et al.*, 1998), and atmospheric deposition on vineyards near major highways (Eschnauer, 1982) have also been attributed to increasing lead concentration in wines.

4.4 Discrimination of region

Fingerprinting the two major wine regions was successful using ten elements (Al, V, Mn, Co, Zn, Rb, Sr, Mo, Sb and U). Inclusion of French wines in the fingerprint, and the cluster analysis of wines from the same vineyard in the Okanagan region suggests these elements are useful for discriminating wine by geographic origin. Elements included in the fingerprint were found to have different mobilities in the environment, particularly the mobile elements Sr and Rb, and the insoluble element, V, as predicted by their ionic potential.

The most important regional discriminator was determined to be Sr by graphical analysis and examination of the F-statistics. A study of Sr isotope ratios in wine to uncover regional fraud related Sr isotope ratios in wine were found to relate to those in soil for various geologic regions (Horn *et al.*, 1993). The addition of Sr to wine from processing with fining bentonites is thought to be minimal, as a significant contribution of Sr from bentonites to wine is expected to alter the isotopic ratio of Sr in wine, making it indistinguishable from that of the soils of the region (Horn *et al.*, 1998). The element Sr is easily weathered and mobile, and can easily taken up by plants (Kabata-Pendias and Pendias, 1984). Other studies have found Sr to be a useful discriminating element (Baxter *et al.*, 1997; Danzer *et al.*, 1999). Another mobile element, Rb, was found to be a good regional discriminator by this study and by Latorre *et al.* (1994). A plot of Sr and Rb was found to separate wines by region to a high degree (Fig. 3.6), and in the discriminant analysis, these elements are weighted heavily and opposite to each other (Sr is weighted with a value of +1.94 and Rb with a value of -1.32), so this relationship is enhanced (equation 3.1).

Other studies have found Mn to be a useful element for fingerprinting region (Danzer *et al.*, 1999; Baxter *et al.*, 1997), as well as Zn and V (Danzer *et al.*, 1999). The uptake of discriminating elements Mo, V, Co, and U into plants are sometimes used for mineral exploration of underlying bedrock (Brooks *et al.*, 1995), which suggests there is a relationship between concentration in plants and in bedrock. The mobility of Mo is dependent on its speciation which is controlled by its oxidation state, but tends to form soluble complexes (Krauskopf and Bird, 1995).The element, U, is easily mobilized from bedrock with weathering, and is soluble over a large pH range, making U soil concentration a good indicator of bedrock U concentration. High clay content in soil causes sorption of U, but the soluble fraction of U is readily available to plants (Kabatas-Pendias and Pendias, 1984), which explains the regional discriminating power of U as its abundance and mobility are variable with bedrock and soil type. The highly discriminating element, Al, is a major constituent of clay minerals. The total Al content of soils is weathered from parent rock, but the plant available fraction is largely determined by soil acidity (Kabatas-Pendias and Pendias, 1984). Except in very acidic or very basic solutions, Al, has a very low solubility; its dissociation from aluminosilicate clay minerals only occurs at very low or high pH (Krauskopf and Bird, 1995). Unlike Al, there is a low crustal abundance of Sb, but when in soluble form it is easily taken up from the soil by plants (Kabata-Pendias and Pendias, 1984). Using ten elements to discriminate wine region enables the inclusion of elements with different abundances and mobilities in the regional environments.

4.5 Composition of Okanagan wines

Discriminant analysis of Okanagan wines (Fig. 3.18) suggests that wines from the same vineyard from within the Okanagan can be differentiated by their trace elements. The low variability of element concentrations in Lake Breeze wines (Fig. 3.19) shows that samples from the same batch, but different parts of a tank, and from different tanks, are fairly uniform in concentrations of these ten elements. Variability in wine concentrations for several vintage years is consistently low for all vineyards for Mn and Sr, which suggests that concentrations of these elements are not strongly affected by differences in climate, viticultural practice, or wine processing which may have occurred over several vintage years. The apparent concentration of some elements during icewine production (Table 3.19) suggests these wines cannot be reliably grouped with other wines for trace element fingerprinting.

Cluster analysis using the ten discriminating elements (Fig. 3.20) shows wines made by the same winery over several vintage years to group together to a high degree. The two Pinot Blanc samples from St. Hubertus, which were made from the same grapes, but one was processed in an oak barrel and the other in a stainless steel tank, cluster together suggesting these different processes do not strongly affect the fingerprinting elements.

While insufficient samples were available to determine whether red and white wines can be differentiated by trace element composition, the red wines from four wineries plotted apart from white wines from the same wineries, suggesting that colour does affect trace element composition. Baxter *et al.* (1997) and Greenough *et al.*, (1997) were able to discriminate colour using trace elements, which suggests that discrimination of wine region may be more successful in a larger data set if red and white wines were analysed

separately. Red wines are processed on the skin, and heavy metals (Pb, Cu, Zn and Cd) have been found to be more concentrated in grape skin than in pulp (Angelova *et al.*, 1999), so red wines are likely to have higher concentrations of these elements.

There is some tendency for wines from the same location of the valley to group together. Wines from the Oliver vineyards Hester Creek, Inkameep (Vincor wine), Gehringer Brothers, and Gersighel Wineberg group together towards the bottom of the graph, the Naramata vineyards Lang, Red Rooster, Irvine, Kettle Valley, and Lake Breeze are found in the centre of the plot, and the Kelowna vineyards House of Rose, Summerhill and Quail's Gate are near the top of the plot. This trend shows some agreement with vineyard location, and may reflect environmental influences.

4.6 Composition of Niagara wines

Discriminant analysis of Niagara wines by vineyard of origin was less successful than Okanagan wines, and variability in concentrations for the entire region were found to be similar to the variability for the region (Fig. 3.22). The wines from Cave Spring, Joseph's, Reif and DeSousa are made from different grape varieties, but are from the same vintage year, whereas multiple samples taken from Okanagan vineyards were from different vintage years, but the same grape variety. While grape variety may cause this increased variability in element concentrations, there have been no reports of successful differentiation of wine varieties using trace elements. For this type of discrimination, organic constituents such as terpenes (Danzer *et al.*, 1999) and polyphenols (Soleas *et al.*, 1997) have been used. The Stoney Creek winery makes three different Reserve Pinot Blancs, meaning each wine is made exclusively from grapes grown on a single vineyard, but all three are processed at the same winery. The RSD of these wines was found to be

low for the elements Al, Mn, Co, Zn, Rb, and Sr, (Fig. 3.22), but comparable to the variability for entire region for the elements Mo and U. These wines did not group together in the cluster analysis, which suggests that winery practices have a strong influence on the concentrations of some of the discriminating elements. The fingerprint was re-examined using cluster analysis with the ten discriminating elements (Fig. 3.23), and only the wines from Cave Springs were found to group together, although the wines from De Sousa formed two groups close to each other.

4.7 Relationship between element concentrations in soils and wines

The positive correlations between soil and plant concentrations of Sr was not found to be robust, but examination of Fig. 3.23 shows the Niagara soils sampled to have consistently lower Sr concentrations than Okanagan soils, and Sr has been shown to be the strongest discriminating element in wine. Concentrations of Ba are also consistently lower in Niagara soils (Fig. 3.24), and this element correlates strongly with Sr in wine and soil. The alkaline earth elements, Sr, and Ba, are highly soluble elements due to low ionic potential, whereas Ti is determined to be an immobile element by its ionic potential. Concentrations of Ti are consistently higher in Niagara soils than Okanagan soils, and have a greater range of concentrations in Niagara wines (Fig. 3.25).

Few reports are available which relate the concentrations of elements in fruits and vegetables to those of associated soils. No simple relationship exists between the amount of a particular element in the soil and the amount that is absorbed by the plant. Determining plant availability is difficult due to the complexity of soil chemistry and the physiological processes characteristic of different plants (Shaklette, 1980). Trace element concentrations in a plant can depend on the species and strain of plant, the part of the

plant, the time of year and the climate, and the soil type and pH. Relationships between soil and wine element concentrations are further complicated by wine processing.

Because the soil data is based on total concentration and not plant-available concentration, it is likely that the speciation of many of the elements in soil is not suitable for plant uptake. Elements which are chemically bonded to the soil solid phase can be tightly bound and not soluble (Sparks, 1995). There is also the possibility of active element uptake, in which plants will absorb nutrient elements from the soil preferentially over non-nutrient or toxic elements (Brooks *et al.*, 1995) Further complications to the soil-wine element relationship are that the roots of grape vines tend to reach extreme depths, and because soil was sample from within the top 0.3-0.5 m of the vineyard, it is not a highly accurate representation of where the plants absorb nutrients. Depending on the age of the plant and the depth and nature of the overburden, it is possible that the plant roots are in fact reaching bedrock. The effects of groundwater, and in some cases irrigation water, are also difficult to quantify. The overall soil-plant interaction is highly complex, and soil-wine element relationships are further complicated by wine processing effects.

4.8 Summary

Elements grouped by PCA were found to show good agreement with elements grouped by mobility in the environment, defined by ionic potential, which suggests that chemical properties of elements have a stronger effect on element concentrations than differential plant uptake, anthropogenic inputs and wine processing.

Statistical analysis of element concentrations in wines determined that Canadian wines can be fingerprinted by the elements Sr, Rb, Mn, Mo, Al, V, Co, Zn, Sb, and U.

Using these elements the Niagara and Okanagan wines can be discriminated with 98% accuracy, and the wines from 5 vineyards from the Okanagan were classified correctly according to origin, whereas the wines from the smaller Niagara region could not be fingerprinted according to vineyard. These elements are thought to be useful to fingerprinting region of origin of wines because of variable abundances and solubilities in vineyard environments.

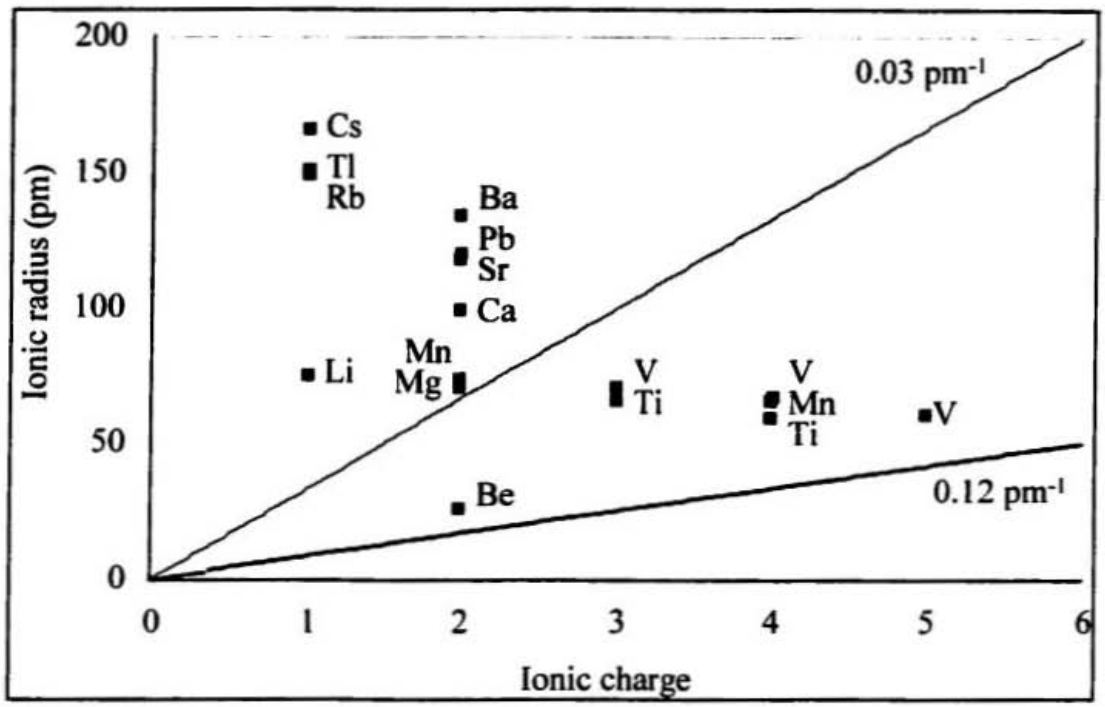

Fig. 4.1 Plot of ionic radius (in pm) *vs.* ionic charge for commonly occurring ions of elements which form bonds with a high ionic character, as predicted by electronegativity. Ionic potentials which are used as boundaries to define element solubility, are labelled as $0.03pm^{-1}$ and $0.12pm^{-1}$. Ionic radii are for a coordination number of 6, except Be for which a radius for a coordination number of 4 was used. Elements which commonly exist at more than one oxidation state are included for each existing ionic charge. All radii were taken from Krauskopf and Bird, 1995; boundary definitions are from UKESCC, 2000.

Chapter 5 Soil, geology and wine

5.1 Introduction

Elemental concentrations in wine have been attributed to geology, soil chemistry, climate, and processing, the effects of each being difficult to dissociate from the others. Geology, climate, and chemical composition of the vineyard soils sampled from each region were compared for the two regions, to further examine influences on wine composition.

5.1.1 Overview of the geology of the Okanagan Valley

The Okanagan wine growing region (Fig. 5.1) transects two major physiographic regions: the Thompson Plateau from Vernon down to Penticton, and the Okanagan Highlands to the east of Kelowna and the areas below Penticton. The Thompson Plateau was formed during the tectonic plate convergence of the North American and Pacific plates during the Mesozoic era (245 to 66 million years ago), and was later intruded by magma which formed granites (Roed, 1995). The Okanagan Highland is a more mountainous region than the Thompson Plateau, dominated by Precambrian rocks (from over 570 million years ago) known as Okanagan Gneiss. The gneiss, a banded metamorphic rock which is thought to have been a part of the Precambrian Shield, has been deeply buried and chemically altered over time by heat and pressure, then thrust to the surface during the Eocene (58 to 37 million years ago) and Oligocene (37 to 24 million years ago) epochs (Roed, 1995). Intrusions of Jurassic to Cretaceous granite and diorite rocks occur in the gneiss causing them to be highly variable in composition (Tempelman-Kluit, 1989; Roed, 1995).

The Okanagan fault can be traced along the length of the Okanagan Valley, and has been determined by geophysical studies to be 20 km deep (Roed, 1995). The initial movement along the fault is believed to coincide with the volcanic activity of the Eocene epoch. These volcanoes deposited lavas and pyroclastic rocks (Church, 1978), and four calderas were formed at Kelowna, Summerland, Penticton, and Vernon when gases building up in underlying magma caused a large eruption, which blew away most of the volcano. When volcanism of the Eocene period ceased in the region, a huge river system developed that deposited sediments into the calderas (Church, 1980). These fluvial sediments, intercalated with the volcanic debris, formed the Marama, White Lake, and Marron formations (Bardoux and Irving, 1988).

The river system which developed in central B.C. at the end of the Tertiary Era mobilized uranium from some of the underlying granite or volcanic rock. The groundwater then percolated through the fluvial sediments of the Eocene formations, and precipitated high concentrations of uranium in deposits which were then immobilised by basalt from lava flows of the Miocene (24 to 5 million years ago) and Pliocene (5 to 2 million years ago) volcanoes (Church, 1982).

When the climate cooled in the Pleistocene Era (1.6 million to 10,000 years ago), ice over 3 km thick accumulated above the base of the valley. The advance and retreat of glaciers scoured out the base and sides of the Okanagan valley, deepening it up to 640 m below sea level (Roed, 1995), as well as depositing thick layers (up to 700m) of transported material (Vanderburgh and Roberts, 1996). The Late Wisconsinan glaciation (25 to 10 thousand years ago), which eroded deposits from earlier Pleistocene glaciations deposited glacial till, and glaciofluvial and pluvial sediments. Till is unsorted material which was deposited by a glacier; glaciofluvial materials are sands and gravels that were

deposited by glacial meltwater streams, and pluvial deposits are fine grained materials from lakes formed by rainwater during a period of glaciation.

Global warming following the ice age occurred approximately 15,000 years ago, although the final melting of the Fraser Glacier did not occur until 10,000 years ago (Roed, 1995). Soil formation and growth of vegetation occurred in the Holocene period (10 thousand years ago until present) with these climatic changes (Roed, 1995).

5.1.2 Overview of the geology of the Niagara Peninsula

The bedrock of the Niagara wine growing region (Fig. 5.2) is from the Upper Ordovician and Silurian periods (445 to 420 million years ago) (Tovell, 1992). Compared to the Okanagan Valley, in which rocks are from the Paleozoic through to the Quaternary period, this is a short geologic time span. The physiography and pedology of the area was formed from erosion and glaciation in the Quaternary era.

The Niagara region is located on the western side of the Appalachian basin (Haynes, 1998). The region was covered by a shallow subtropical sea in the Ordovician era, which then became deltaic during the Taconic Orogeny (mountain building) of the Late Ordovician-Early Silurian periods (Haynes, 2000), during which a range of mountains in the place of the Appalachian range existing today, fed an immense delta with runoff from a series of rivers. Calcareous sediments were deposited and reefs grew, later forming the sedimentary rocks underlying the region today (Tovell, 1992).

The Upper Ordovician Queenston Formation is composed of clastic shales with layers of siltstone, and small amounts of hematite, giving it a red colour (Tovell, 1992). During the Early Silurian epoch, a shallow sea developed from which the carbonate sandstones and shales of the Medina or Cataract Group were deposited (Haynes, 2000).

The shales and dolostones of the Clinton Group were then formed, followed by the dolomitic reefal and algal carbonates of the Lockport Formation (Haynes, 2000). The Lockport Formation is a dolostone, containing over 50% dolomite ($CaMg(CO_3)_2$). This formation was likely formed from the calcareous sediments and reefs of the Paleozoic delta, which were then altered by waters carrying magnesium compounds (Tovell, 1992). The Lockport dolostone forms an erosion resistant cap at the top of the escarpment.

The Quaternary period has been an ongoing period of erosion, forming the present land forms of the region. A series of glaciers carved out the bedrock and deposited till during the advance and retreat of the ice front. Because of the erosive power of each of these continental glaciers, usually only the results of the Late Wisconsinan glaciation are visible (Haynes, 2000). As the ice front retreated north from the Escarpment, a series of lakes formed between the ice and the Escarpment, with deposition of glaciolacustrine (glacial lake) clays and silt over the till on the terraces. A large glacial lake, Lake Iroquois formed 12,000 years ago and eroded the earlier glacigenic sediments, forming a shore bluff as a prominent ridge of beach deposits at the base of the escarpment (Haynes, 1998). Below the shore bluff are lacustrine deposits of stratified sand, silt, and clay forming the Lake Iroquois plain (Haynes, 2000).

The water drained from Glacial Lake Iroquois as the ice retreated, causing erosion which carved out much of the present physiography of the Niagara Escarpment. Two lakes lay to the south of the escarpment, Lake Tonawanda, which drained over the escarpment at three spillways, and Lake Wainfleet, which drained water from Lake Erie (Haynes, 2000). Differential uplift following the retreat of the ice caused northeastward-flowing waters crossing the Niagara Peninsula to reverse and flow west.

The pre-glacial gorge through which the Niagara river flowed then became filled with sediments, causing the river to cut a new path over the Escarpment (Haynes, 1998).

5.1.3 Differences in climate between the two regions

The effects of climatic conditions on grape growing are measured by two parameters: solar radiation and growing degree days. The amount of solar radiation received decreases with increasing slope (Davis *et al.*, 1984), which refers to the degree of incline of a surface. Growing degree days are the number of days during a growing season in which the mean temperature is above 10°C, where the growing season begins in the spring on the first of five consecutive days with a mean temperature above 10°C, and ends in the fall when there is no longer five consecutive days with a mean temperature above 10°C (Davis *et al.*, 1984). Growing degree day accumulation is affected by topography and proximity to large lakes. Due to its more southerly latitude than the Okanagan valley (the Niagara Peninsula is at 43° north latitude compared to the 49° to 50° north latitude of the Okanagan Valley), the Niagara region receives more solar radiation and a higher number of growing degree days per year. The average number of growing degree days in the Niagara region is 1426 (Ziraldo, 1994), compared to 1359 degree days measured in Osoyoos (southern Okanagan) and 1049 degree days measured in Okanagan Centre (northern Okanagan) (Davis *et al.*, 1984).

5.1.4 Soils of the Okanagan Valley and Niagara Peninsula

The vineyard soils in the Okanagan are brown chernozems formed on pluvial, glaciofluvial and glacial till (Wittneben, 1986). Chernozemic soils are influenced by the processes of calcification, which causes the subsoil accumulation of secondary calcium

carbonate (Fanning and Fanning, 1989). These soils are well drained, and salts are eluviated (the removal of constituents from a soil horizon or layer by leaching with water) from the surface soil, to accumulate in the deeper part of the soil.

The soils of the Niagara region are luvisolic due to the calcareous nature of the Paleozoic rocks (Chesworth and Evans, 1982). The major pedological process occurring with luvisols is the downward movement of clay from the surface soil to the subsoil (Chesworth and Evans, 1982). This accumulation of clay in the subsoil forms a layer of low permeability, keeping available water in the upper soil, so vineyards in the Niagara region do not require irrigation most years. Because grapes grow best on well drained soils, sub-drains have been installed in many of the vineyards (Haynes, 2000), causing soils to retain less water, and vineyards have been regraded from their natural topography, to improve drainage.

5.2 Examination of the soil and wine data

5.2.1 Comparison of Niagara and Okanagan soils

Chemical soil analyses from the Okanagan and Niagara regions were examined for overall regional differences. The soils from the two regions could be completely differentiated by the elements Ca, Ti, Sr, and Ba, and concentrations of Ca, Sr and Ba were higher in Okanagan soils, whereas Niagara soils have higher Ti concentrations.

5.2.2 Composition of Okanagan soils

Soil composition within each region was fairly uniform, presumably due to glacial mixing of soil parent material in both regions. Some differences in element concentrations were observed in Okanagan soils, which is a larger region with more variation in bedrock

composition and climate. Cluster analysis of concentrations of Ba in Okanagan soil grouped vineyard soils by their subregion (Fig. 5.3). Kelowna and Westbank soils, which are from the north Okanagan (Fig. 5.1), are found towards the bottom of the plot. Naramata, Peachland and Summerland soils are found near the centre of the plot, and soils from the southern Oliver and Okanagan Falls areas plot near the top of the figure. The groupings are not exact, but a trend between vineyard location and Ba concentration in apparent. Soils from vineyards in the Oliver region are also completely distinguishable by high concentrations of Cr, Ni, and Cu compared to other Okanagan vineyard soils in the study (Figs. 5.4-5.6).

5.2.3 Element concentrations in Okanagan wines and soils

Element concentrations in soil and wine were examined for anomalous high concentrations and for trends linking wines with subregion. Trends in concentration of U, As and Pb were studied in Okanagan wines with respect to soil concentrations, geology, climate, and anthropogenic sources. Possible sources of anomalous high concentrations of Mo, Cr, and Ni in wine were explored. Two adjacent vineyards, which were found to produce wines with strikingly different chemical compositions, were further examined.

5.2.3.1 Concentrations of U in Southern Okanagan Valley wines

Examination of U concentrations in Okanagan wine revealed all wines to have extremely low concentrations, although several southern Okanagan wines to have high U concentrations compared to wines from the rest of the valley (Fig. 5.7). Of the Okanagan vineyards, only the soil from the Oliver vineyard, Gersighel Wineberg, has a detectable concentration of U (11 ppm, Appendix 5).

5.2.3.2 Concentrations of elements in Peachland wines

Anomalously high concentrations of Mo and Ni were found in two wines from McKenzie's vineyard in Peachland (Fig. 5.8). McKenzie's Pinot Blanc also contains high concentrations of Zn and Cd, and McKenzie's Pinot Noir was found to have a high concentration of Cu (Fig. 5.9). Soil concentrations of these elements were not found to be elevated compared to other Okanagan vineyards sampled.

5.2.3.3 Concentrations of As and Pb in wines and soils

A positive correlation between As concentration in Okanagan wine and soil was reported by Greenough *et al.*, 1997, but found to be fortuitous when re-examined with the present, larger sample set (R= 0.028; Appendix 6). Of four of the vineyards sampled which were reported to be on land previously used as an apple orchard, three of these vineyards were found to contain high concentrations of As and Pb in the soil, suggesting the presence of pesticide residue (Table 5.3). The soils from House of Rose, Lang Vineyards and Gersighel Wineberg have high As and Pb concentrations, whereas the soil from Slamka Cellars, which was also an orchard, shows no evidence of pesticide use. There is no strong correlation found between As and Pb in wine and in soil, and the wine from Slamka Cellars, which has a low soil Pb concentration, has an elevated wine Pb concentration from some other source.

5.2.3.4 Concentrations of elements in wines and soils from Okanagan Falls

Wines from the two Okanagan Falls vineyards, Wild Goose and Stag's Hollow, were found to have strikingly different concentrations of Pb, Bi, Th, and U in wines (Table 5.4). Concentrations of U are variable in the five vintage years of wine from Wild Goose

and the two vintage years from Stag's Hollow. The concentrations of the elements Pb, Bi, and Th are considerably higher in the five vintage years of Gewurztraminer from Wild Goose than in the Chardonnay and Pinot Noir from Stag's Hollow.

5.3 Discussions

The geology of the Niagara and Okanagan regions have been determined on a large scale, and due to the amount of glacially deposited overburden in both areas, the presence of intrusions and anomalies are largely unknown. The chemical composition of wines and soils are discussed with possible geologic interpretations.

5.3.1 Interpretation of soil analyses

Soils have characteristics determined by a combination of soil parent material and pedogenic (soil forming) factors including climate, organisms, topography, and time (Fanning and Fanning, 1989). Soil at several metres of depth, is relatively unaltered by soil forming factors, whereas topsoil contains organic matter and is where most plants get there nutrients (Fanning and Fanning, 1989). There is ambiguity as to the depth of soil to be sampled for determining a biogeochemical fingerprint, where information is needed on both plant available element concentrations and regional geology. Soil analysis is generally not a good indicator of bedrock composition, because soil characteristics depend chiefly on climate during soil formation, and the nature of the bedrock makes little difference, unless it is of extreme composition such as an ultramafic rock or salt bed (Krauskopf and Bird, 1995).

The higher concentrations of Ca, Sr, and Ba in the Okanagan soils than the Niagara soils (Table 5.1), is likely due to their chernozemic nature. The Okanagan Valley is a more

arid region than the Niagara Peninsula, and water reaching the surface of the soil does not percolate down, so clay minerals and hydrated exchangeable cations are not transported downwards from the surface layer (Fanning and Fanning, 1989). In Niagara, the upper horizons of soil are well drained, but underlain by a layer of clay. Eluviation of clay particles from the surface soil may cause transport of mobile cations from the upper soils, to the lower clay layers where they adsorb (Fanning and Fanning, 1989). The more calcareous nature of the bedrock of the Niagara region (Tovell, 1992) than the Okanagan, would likely cause soil parent material to have higher concentrations of these elements, but soils have been chemically altered during soil formation. Concentrations of Ca, Sr, Ba, and Ti in soils from the Okanagan have a greater variability than in the Niagara soils, which is probably due to a more variable climate in the larger Okanagan region.

5.3.2 Soil composition in the Okanagan Valley

Although there is little variability in soil chemical concentrations throughout the Okanagan Valley, the influence of climate on soil composition is evident in the variation of Ba concentrations in soil. The mobility of Ba in soil is influenced by climate, and Ba accumulates in soil in warm, dry regions, but migrates in cooler climate soils (Kabatas-Pendias and Pendias, 1984). This is evident in Fig. 5.1, where cluster analysis groups the soils from the hotter, more arid Oliver vineyards, which have higher Ba concentrations, towards the top of the plot, and soils from the cooler northern vineyards cluster towards the bottom.

The elevated concentrations of Cr, Ni and Cu in the Oliver area are also likely due to soil forming processes in the semi-arid climate rather than bedrock composition in this area. The soils of the Oliver area vineyards are well drained glacial till (Davis *et al.*, 1994).

The five vineyards are located on the southwesterly slope in the south of the valley, and receive the most solar radiation and have the highest number of growing degree days of the Okanagan vineyards (Davis *et al.*, 1984). The hot, dry microclimate of these vineyards is likely the cause of the elevated concentrations of Cr, Ni, and Cu (Figs. 5.4-5.6), as in arid areas these elements become enriched due to adsorption onto illuviated clay materials (Aubert and Pinta, 1977), and due to the arid environment, most of the water reaching the soil surface does not percolate down to the lower layers, so element leaching is minimal. The pH of these vineyard soils are neutral (pH 7.2 - 7.5; Appendix 4), causing the metals to be strongly adsorbed and immobile (Sparks, 1995). The concentrations of the metals Cr, Ni, and Cu in the Oliver wines are not notably high, as are the soil concentrations. The immobility of these elements in neutral soils makes them largely unavailable for plant uptake (Aubert and Pinta, 1978).

5.3.3 Element concentrations in Okanagan soils and wines

While bedrock composition is not the major factor controlling soil composition, soils are used in geochemical prospecting because anomalies in bedrock composition are often evident in overlying soils. Geochemical dispersion in glacial soils is a result of both syngenetic dispersion, which is principally mechanical or particulate and took place during glaciation, and epigenetic dispersion, which is chemical or mechanical and has occurred since glaciation (Bolviken and Gleeson, 1979). Dispersion of glacial material can be quite complex because glaciers advanced and retreated several times leaving several layers of deposit, but soil analysis of areas that have been glaciated is an important tool in geochemical prospecting as anomalous concentrations in parent material can cause enriched concentrations in the soil (Bolviken and Gleeson, 1979).

Plants tissues are also analysed in geochemical prospecting as they are sometimes better indicators of chemical anomalies in underlying rock than are soils, especially in arid, well drained soils, such as those in the Okanagan (Brooks *et al.*, 1995). The use of plants for mineral exploration suggests that plants will better reflect bedrock composition than soil because plant roots can reach to several metres of depth, which is true of grape plants. In such cases, a correlation between the metal content of soil and plant often does not occur, particularly in areas where bedrock is covered with a thick layer of glacial deposit. Some plant species also hyperaccumulate metals making them better indicators of mineral deposits than are soils (Brooks *et al.*, 1995). There is very little research in which fruit are used for biogeochemical prospecting. Treetops and leaves are frequently sampled, and represent new growth of a plant, as does the fruit, but different organs of the plant have different barriers to metal uptake (Brooks *et al.*, 1995).

5.3.3.1 Uranium deposits

Distribution of U concentrations in Okanagan wine and soil were examined to reveal possible relationships with reported U deposits in the area. Along the west side of the valley from Summerland to Oliver is a zone of U concentration where extremely high anomalous concentrations of U (0.6 - 17.9 ppm) have been reported in alkali ponds (Church, 1979), and in peat bogs (623 ppm) (Church *et al.*, 1990). Ash deposits associated with calderas left from the Eocene era are thought to provide source material and suitable traps for U (Tilsley, 1988). High U concentrations in ponds are anomalous within the Summerland area, and associate with highly alkaline water (Church, 1979). A several-fold increase in U concentration was reported near the mouth of Trout Creek, near Summerland, where a groundwater input occurs (Church, 1980). Climatic conditions are

also partly responsible for the high U concentrations as high evaporation rates concentrate U in ponds.

Concentrations of U were extremely low in all wines sampled, but the highest concentrations were found in wines from the Oliver vineyards, Hester Creek and Inkameep, along with wines from the Wild Goose vineyard in Okanagan Falls (Fig. 5.7) and Hainle in Peachland. A study of uptake of radionuclides near the Summerland U deposit by eight plant species native to the Okanagan showed some species to accumulate U, but the relationship between soil and vegetation is complex due to the soil chemistry of U (Mahon and Matthews, 1982). These south Okanagan vineyards, with the exception of Inkameep, are located on the west side of the valley, where the high U alkaline ponds exist, so it is possible that U from the deposits is being accumulated in the grape plants.

5.3.3.2 Possible sources of Ni, Mo, Zn, Cd, and Cu in Peachland wines

There is a Cu - Mo deposit currently being exploited by Brenda Mines, 32 km northwest of Peachland (Dayton, 1981), and anomalous high concentrations of Mo, Zn, Cd, and Cu in McKenzie's wines made from grapes grown in the Peachland area were observed (Figs. 5.8-5.9). The element, Mo, has been identified as a good element for biogeochemical prospecting in Canada where a majority of plant species have a low barrier or no barrier to Mo uptake (Bolviken and Gleeson, 1979). It is an essential micronutrient and therefore can be scavenged and concentrated in certain plants, making it a more useful element than Cu for indicating the presence of Cu-Mo deposits. High concentrations of these elements have been attributed to processing in stainless steel vats, but McKenzie's wines were processed in polyurethane, and were not filtered or fined. Soil concentrations of

these elements are not exceptionally high for the region and the soil pH is slightly basic (7.9), causing soil elements to have low mobility.

In a study of Cu in soils from Highmont Valley, another Cu-Mo deposit in southern B.C. which is overlain by glacial till (60 km northeast of Kamloops), Cu was found to be leached in well drained soils over mineralized bedrock, but concentrations of Cu were markedly higher in poorly drained soils, where Cu accumulates in organic rich topsoil (Horsnail, 1975). Much less variation in Mo concentrations occurred in soil profiles near the deposit. While glaciers have dispersed larger rock fragments, the fine-grained fraction of till was found to have elevated concentrations of Mo near the ore deposit due to hydromorphic dispersion, which is when elements are dissolved in groundwater, transported to a new location, and precipitated (Horsnail, 1975). Anomalous dispersion of Cu, Mo, and Zn also occurs in stream sediments near the ore forming bodies (Horsnail,1975). Although some of the vineyards of the Okanagan are in close proximity to the ore deposit, soils are all well drained, which may explain why Cu does not accumulate in soils from the Peachland area.

5.3.3.3 Anthropogenic sources of Pb and As in soils and wines

Soils and wines with high As and Pb concentrations were found in vineyards which were previously apple orchards (Table 5.3). In the 1940's lead arsenate pesticides were applied to orchards in the Okanagan valley, and there is evidence that these elements remain at elevated concentrations in the soil for several decades (Peryea and Creger, 1993). Elevated concentrations of As also occur in some ore deposits, and therefore As accumulated in wine grapes may be from either a geologic or anthropogenic source. The majority of the vineyards in the valley have soil arsenic concentrations below detection

limit, however those vineyards which show significant arsenic levels may be linked with past use of the land as orchards. Acid lead arsenate ($PbHAsO_4$) was applied to individual trees with a handgun sprayer as an aqueous slurry, causing its distribution patterns in soil to be highly variable (Hanson, 1984). It has been reported that As is depleted in contaminated soils relative to Pb (Peryea and Creger, 1993), but also that the use of lead arsenate pesticides has been linked to significant contamination of wines with Pb to a greater extent than As (Hanson, 1984). While some elevated concentrations of Pb remain in the soil in vineyards that are believed to have once been treated with lead arsenate, elevated concentrations of As and Pb are not consistently evident in wines made from grapes grown on these soils.

5.3.3.4 Geologic heterogeneity of the Okanagan Falls area

Two vineyards from Okanagan Falls were sampled: Stag's Hollow and Wild Goose. These vineyards are underlain by the heterogenous Okanagan Gneiss (Tempelman-Kluit, 1989), although there are deposits of the Eocene White Lake Formation in close proximity, and numerous faults dominate the geology of the area (Meyers and Taylor, 1988). The vineyard soils are glacial tills and changes in sand and clay content of the soil in different parts of the vineyard were observed upon sampling. The concentrations of heavy elements in wine are strikingly different for these adjacent vineyards (Table 5.4), and this may be caused by the heterogeneity of the bedrock, or by different groundwater sources in the vineyards. There are three gold-silver prospects located in the Eocene deposits surrounding Okanagan Falls, one of which was mined between 1969 and 1975 (Meyers and Taylor, 1989), and the presence of these fracture-controlled vein deposits is further evidence that the geology of this area is highly heterogenous. Uranium concentrations in ponds in the

region can also be erratic due to groundwater passing over a source rock, or adsorption on clay deposits (Church, 1980), so the high U concentration in the Wild Goose soils may indicate an undocumented nearby U anomaly in the bedrock.

5.8 Summary

Differences in soil chemistry between the Niagara Peninsula and the Okanagan Valley were evident. The upper soil layers have been chemically altered by pedogenic processes, and in many cases tilled. Climate appeared to have a strong influence in soil composition, compared to bedrock. The heterogenous geology of the Okanagan Valley may be the source of anomalous high concentrations of elements in wine, but the soil samples were not conclusive as to the origin of the source of these anomalies, probably due to the necessity for sampling from throughout a greater depth, to represent the material from which plants get water.

Table 5.1 T-test statistics (using separate variance T-test) and associated probabilities for soil analytes which are significantly different between the Okanagan and Niagara regions, as well as mean concentrations of each analyte in the two regions.

Element	T statistic	Probability	Okanagan mean concentration	Niagara mean concentration
CaO	6.7	< 0.001	3.8 +/-1.5	1.47 +/-0.80
TiO_2	-5.5	< 0.001	0.62 +/-0.24	0.98+/-0.19
Sr	15.1	< 0.001	450 +/-104	138 +/-11
Ba	9.8	< 0.001	1104 +/-324	465 +/-58

Table 5.2 T-test statistics (using separate variance T-test) and associated probabilities for Sr and Ti in Okanagan and Niagara wines, as well as mean concentrations with SD for each region.

Element	T statistic	Probability	Okanagan mean concentration	Niagara mean concentration
Sr	6.5	< 0.001	766 +/-325	419 +/-193
Ba	1.6	0.112	140 +/-96	115 +/-57
Ti	-5.7	< 0.001	7.1 +/-5.0	18.3 +/-11.0

Table 5.3 Concentrations of As and Pb in soil (in ppm) and wine (in ppb) of vineyards known to have once been apple orchards.

Vineyard	As (soil)	Pb (soil)	As (wine)	Pb (wine)
House of Rose	31	66	2.03	6.0
Slamka Cellars	14	13	1.48	17.1
Lang Vineyards	38	78	4.3	6.2
Gersighel Wineberg	22	55	6.2	12.2
Mean Okanagan concentration	14	27	2.97	11.7

Table 5.4 Mean concentration and standard deviation of the elements U, Pb, Bi, and Th in the Okanagan Falls wines, Wild Goose and Stag's Hollow.

Element	Wild Goose (n = 5)	Stag's Hollow (n = 2)
U	1.07 +/- 0.45	0.38 +/- 0.52
Pb	28.1 +/- 6.6	3.37 +/- 1.36
Bi	0.53 +/- 0.27	0.074 +/- 0.003
Th	0.31 +/- 0.09	0.036 +/- 0.013

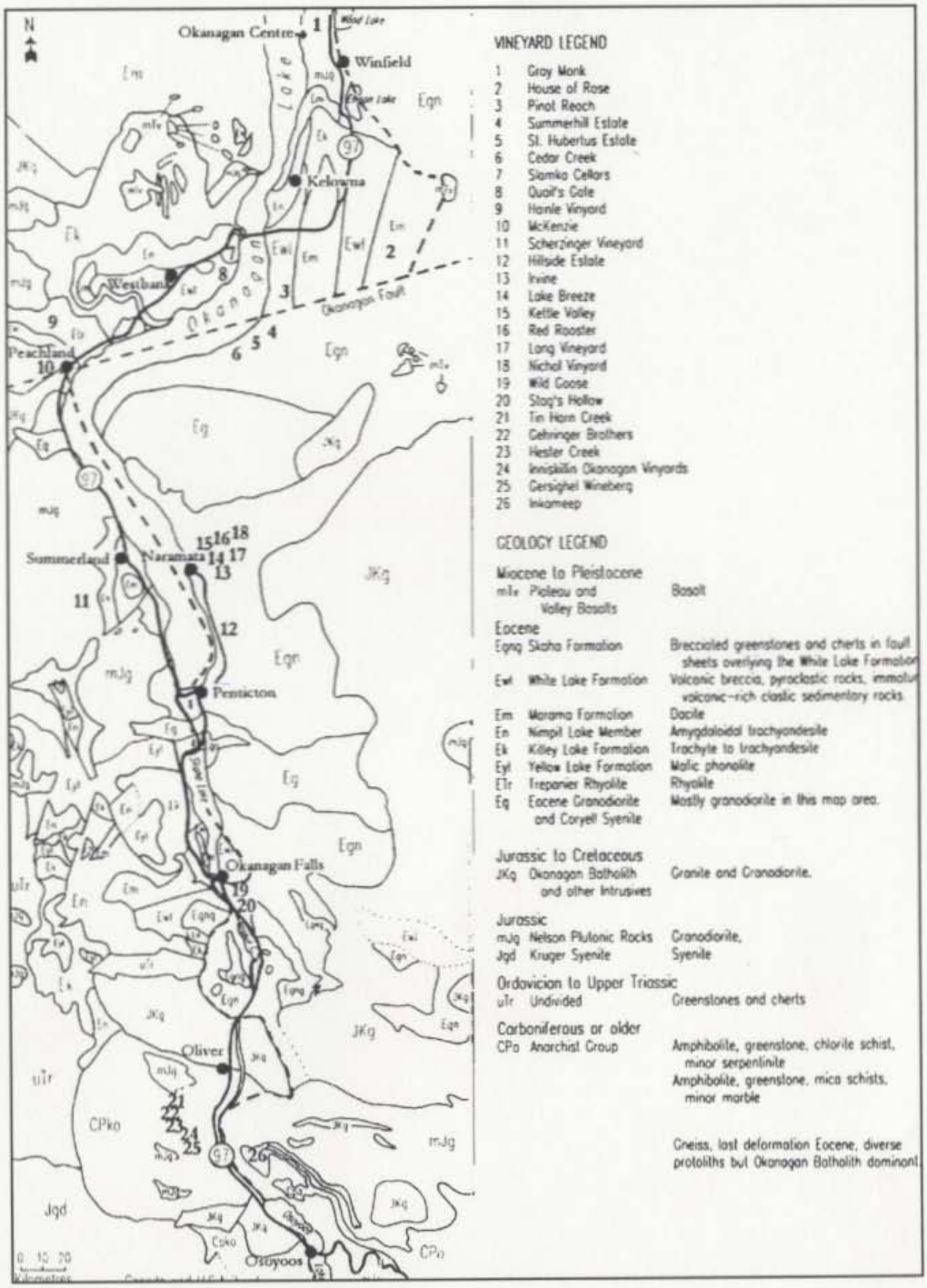

Fig. 5.1 Vineyards and geology of the Okanagan valley (adapted from Tempelman-Kluit, 1989).

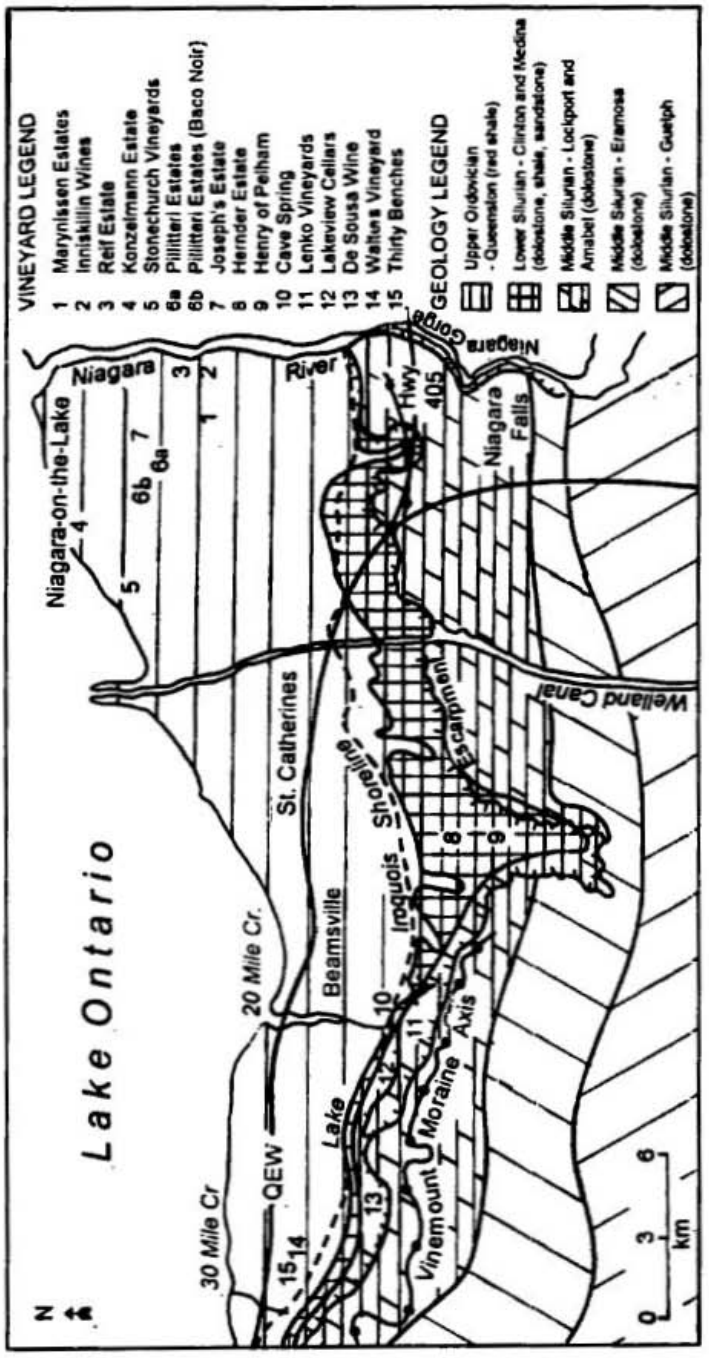

Fig. 5.2 Vineyards and geology of the Niagara Peninsula (adapted from Haynes, 2000).

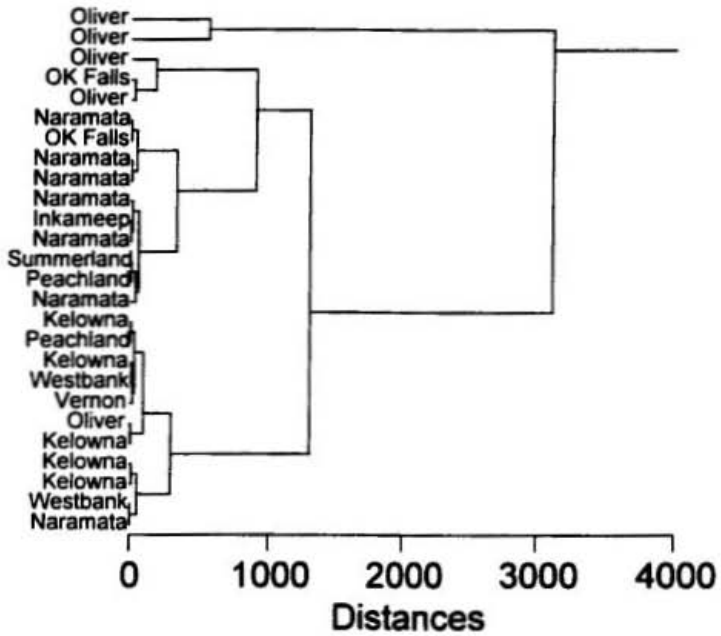

Fig. 5.3 Cluster analysis of Ba concentrations in Okanagan vineyard soils, where soils are labelled by the subregion of the vineyard (OK Falls = Okanagan Falls).

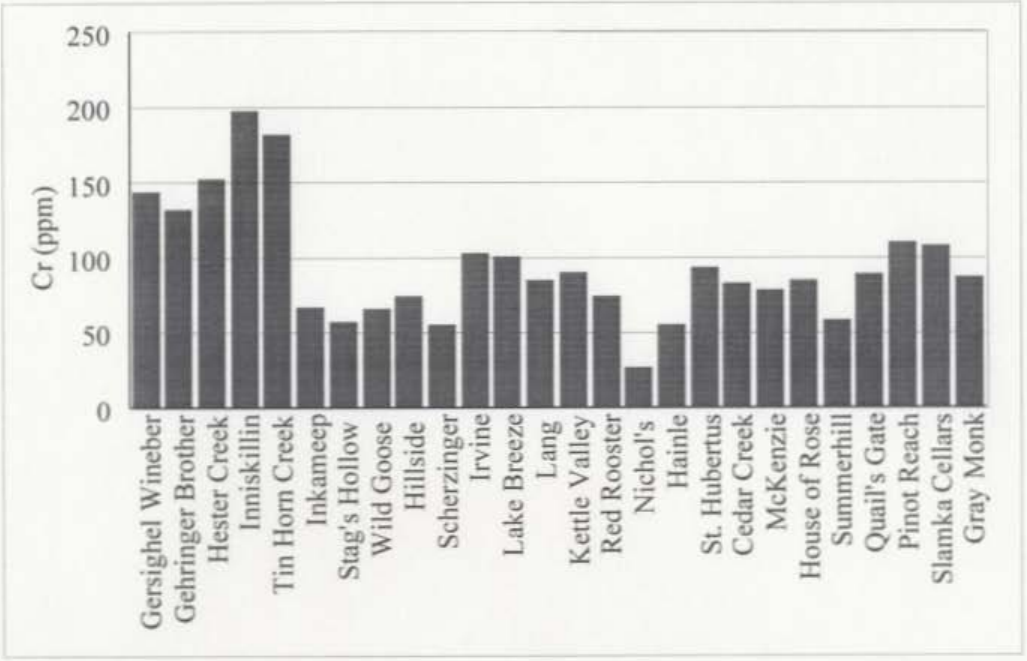

Fig. 5.4 Concentrations of Cr in Okanagan vineyard soils, (vineyards are arranged from south to north).

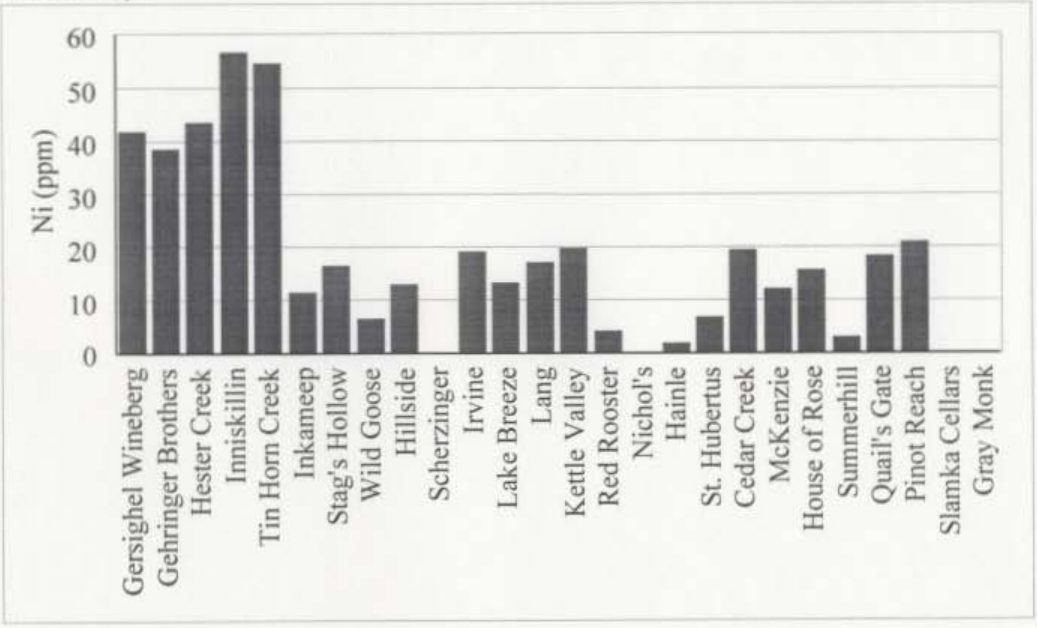

Fig. 5.5 Concentrations of Ni in Okanagan vineyard soils (vineyards arranged from south to north).

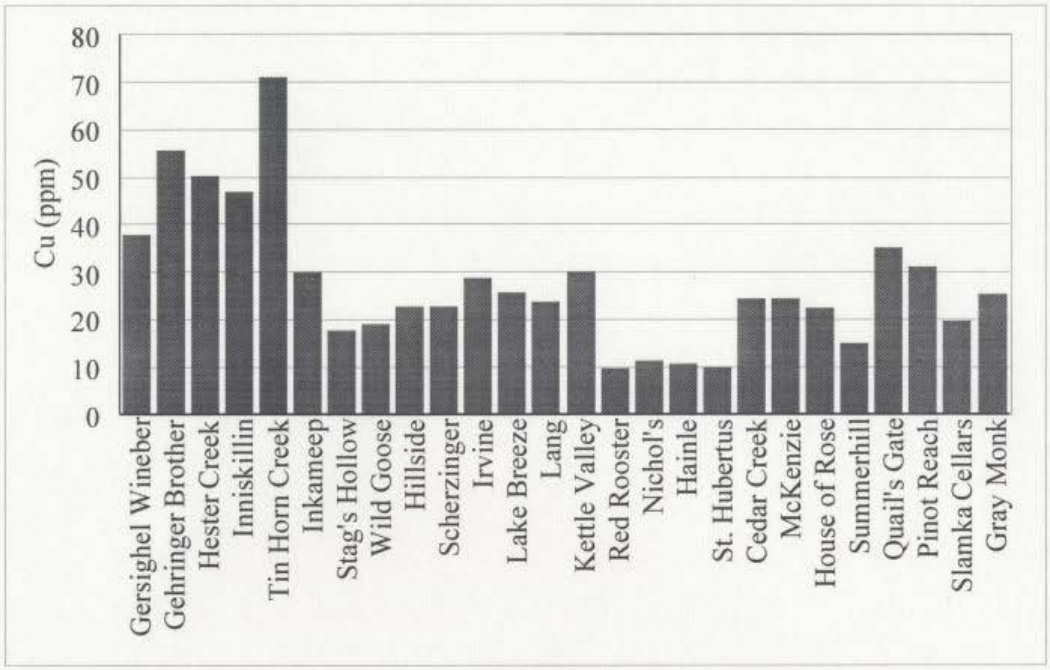

Fig. 5.6 Concentrations of Cu in Okanagan vineyard soils (vineyards arranged from south to north).

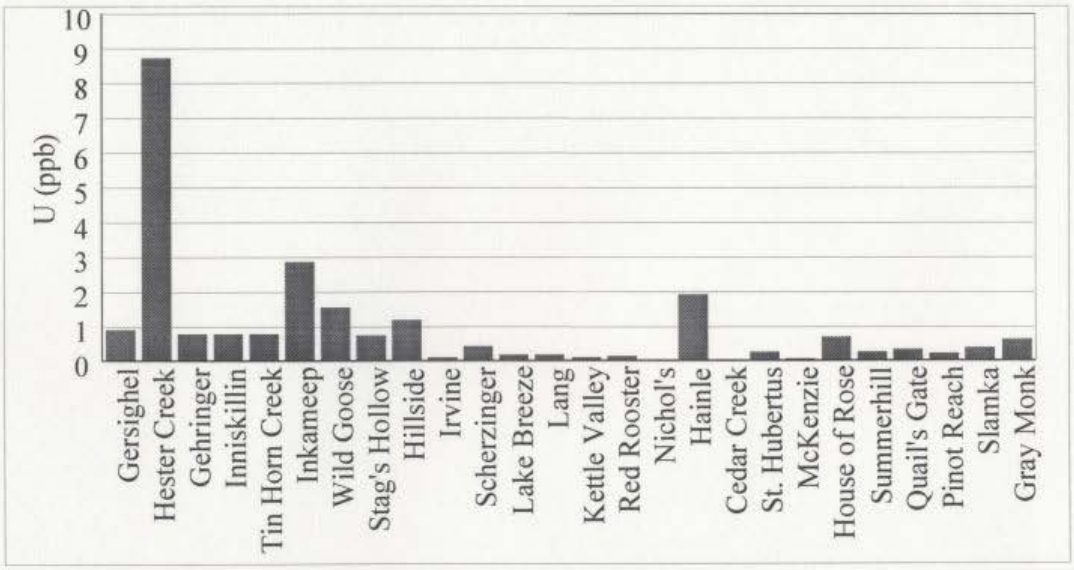

Fig. 5.7 Concentrations (in ppb) of U in Okanagan wine. Vineyards are arranged from north to south, and where more than one sample was taken, the most recent vintage year of the wine sampled was plotted.

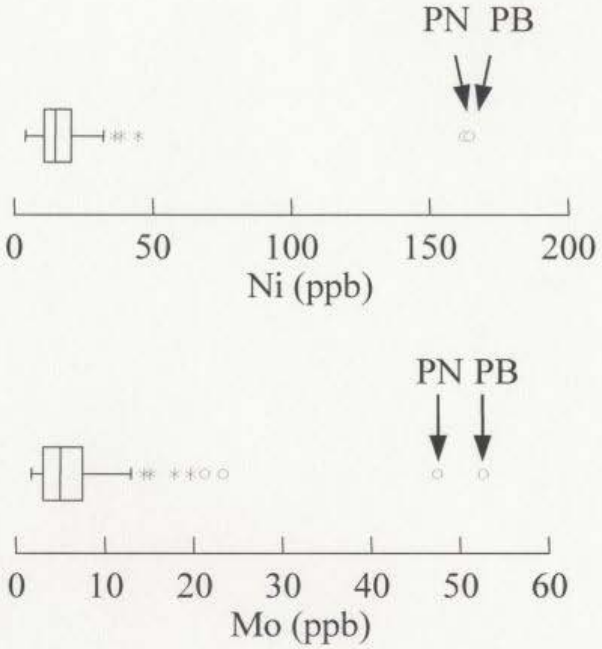

Fig. 5.8a) and b) Box plots of Mo and Ni concentrations (in ppb) in Okanagan wine, showing McKenzie's wines to be extreme high outliers (PN=McKenzie's Pinot Noir; PB=McKenzie's Pinot Blanc).

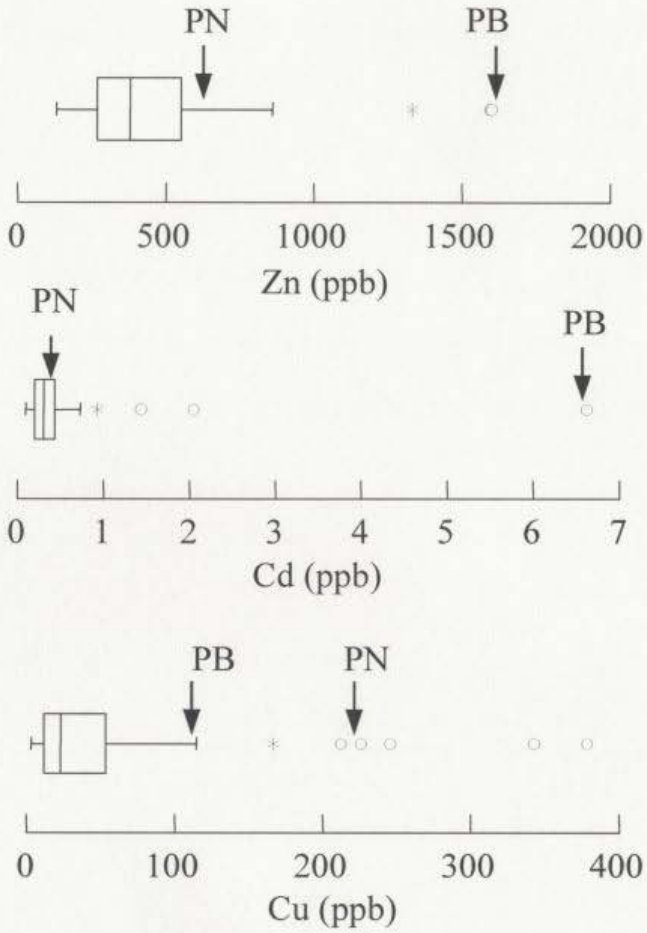

Fig. 5.9 a-c) Boxplots of Zn, Cd, and Cu (in ppb), showing the concentrations of McKenzie's wines relative to other Okanagan wines. (PN=McKenzie's Pinot Noir; PB=McKenzie's Pinot Blanc).

Chapter 6 Conclusions

6.1 Summary of fingerprinting results and implications

Analysis of wine samples which were diluted 1:1 with 0.2 M HNO_3 by ICP-MS determined 35 elements with good precision and accuracy, and is an efficient method of analysis, which is an important consideration when determining the applicability of a method to standardised testing. The two major Canadian wine regions, the Okanagan Valley and the Niagara Peninsula, were discriminated with 100% accuracy using ten trace elements. The element most discriminating of wine region was found to be Sr, which was also found to be an important fingerprint element in other studies (Baxter *et al.*, 1997; Danzer *et al.*, 1999; Horn *et al.*, 1993). Individual vineyards in the Okanagan were also fingerprinted, but wines from the Niagara region showed less discrimination by vineyard, possibly due to the more homogenous geology and climate of this region. The high correct classification rate of the trace element fingerprint suggests this method could be applied to wine certification testing, along with standardised taste testing methods currently in effect.

6.2 Sources of the fingerprint and suggestions for further study

The source of the trace element fingerprint in wines could not clearly be defined, as no strong correlations were found between soils and wines. Correlations between elements in wines showed good agreement with elements associated by ionic potential, suggesting mobility of elements in the environment has a strong influence on concentration.

The influence of climate on grape growing has long been attributed to the suitability of varieties to specific areas, and to sugar content and acidity of the grapes at

harvest (Jackson, 1989). The effect of climate on soil composition was evident in the Okanagan, where soil concentrations of Ba, a mobile element, increased from north to south, and the elements Cr, Ni, and Cu were concentrated in the desert soils of Oliver. Despite the carbonate parent material of the Niagara soils (Tovell, 1992), the soils of the Okanagan vineyards, had higher concentrations of Ca, Sr, and Ba, due to concentration of these elements in chernozemic subsoils. The effect of climate on trace element uptake by plants is suggested by the more successful fingerprinting of Okanagan vineyards compared to Niagara vineyards, because the Okanagan region has both a marked difference in climate between the south and north, and a more mountainous topography than Niagara which creates microclimates due to the effects of slope and aspect on solar radiation reaching the ground (Davis *et al.*, 1994). A study of the bedrock geologies of both areas also showed bedrock from the Okanagan to be heterogenous compared to the Niagara region, so vineyard environments in the Okanagan are expected to be much more diverse.

It is suggested that a useful and feasible continuation of this study would be to analyse the grapes, macerate, juice, and wine for trace elements to examine the effects of the wine-making process on element concentrations in the wine. The analysis of soils as an indicator of regional geology was found to be of limited use, because of the controlling influence of climate on soil composition as well as glacial mixing of the parent material. Determining the composition of the bedrock underlying each vineyard, for the purpose of correlating the wine trace element concentration to the regional geology, would be an extremely difficult study due to the large depth of overburden (> 700 m in some parts of the Okanagan Valley (Vanderburgh and Roberts, 1996)). Because grape plants are absorbing elements from the overburden, the soil, and the groundwater, and plant uptake may be differential to some elements (Brooks *et al.*, 1995), it would probably be difficult

to link the determination of the exact bedrock composition of each vineyard to the trace element fingerprints of wine, although it would provide useful information on the vineyard environment and on vineyards from which wines have anomalous high concentrations. Analysis of the plant available fraction of elements in soils involves extractions with different solvents, but the accuracy of these methods is uncertain as uptake is species dependent, and affected by such things as soil chemistry, climate, and water availability (Brooks *et al.*, 1995). The plant available fraction of soil could be more accurately, as well as more efficiently, determined by analysing the grape plant. Because grape plants have roots reaching to a great depth and grow in arid areas, they meet the criteria of plants which are useful to biogeochemical prospecting, and therefore analysis of the plants would also be of interest for this application. Particularly in the Okanagan region, where ore deposits concentrated in U and Cu-Mo exist, and where anomalous concentrations of metals were found in wine, analysis of grape plants may indicate the sources of these anomalies, or at least rule out the effects of wine processing.

Sampling for this study was completed in the month of May, before vines had started producing fruit, and before irrigation of the vineyards was commenced, so although these things were considered for this study, they were not feasible due to time constraints. It is suggested that the study of the wine making process, from the grapes to must to wine, would be a useful and interesting project to better understand the source of the wine fingerprint.

6.3 Conclusions

The fingerprinting of wine was successful in discriminating between regions of Okanagan and British Columbia, as well as between individual vineyards of the Okanagan

region. These results suggest that trace element analysis could be used along with taste test parameters for certification processes, as well as to protect individual vineyards from counterfeiting. The success of fingerprinting Canadian wines, along with results of fingerprinting in other regions, also verifies the accuracy of the method, and its application to showing provenance and authenticity of wine.

References

Amerine, M.A., Kunkee, R.E., Ough, C.S., Singleton, V.L., and Webb, A.D., 1982. The Technology of Wine Making, 4th Edition. Avi Publishing Company Inc. Westport, Connecticut. pp.234-236.

Angelova, V.R., Angel, S.I., and Braikov, D.M., 1999. Heavy metals (Pb, Cu, Zn and Cd) in the system soil-grapevine -grape. Journal of the Science of Food and Agriculture. 79. pp. 713-721.

Aubert, H. and Pinta, M., 1977. Trace Elements in Soils. Elsevier Scientific Publishing Company, New York. 395pp.

Baxter, M.J., Crews, H.M., Dennis, J.M., Goodall, I., Anderson, D. 1997. The determination of the authenticity of wine from its trace element composition. Food Chemistry. 60. pp. 443-450.

Bolviken, B. and Gleeson, C.A., 1979. Focus on the use of soils for geochemical exploration in glaciated terrain. *In* Geophysics and geochemistry in the search for metallic ores. Geological survey of Canada, 31. Ottawa, Ontario. pp. 295-326.

Boorn, A.W. and Browner, R.F., 1982. Effects of organic solvents in inductively coupled plasma atomic emission spectrometry. Analytical Chemistry, 54. pp.1402-1410.

British Columbia Wine Institute Factsheet., 2000. British Columbia Wine Institute (BCWI).

Brooks, R.R., Dunn, C.E. and Hall, G.E.M. (Editors), 1995. Biological Systems in Mineral Exploration and Processing. Ellis Horwood, Toronto. 538pp.

Brownlow, A.H., 1996. Geochemistry, 2nd Ed. Prentice-Hall Inc., Toronto. pp. 283-285.

Canadian Council of Resource and Environment Ministers Task Force of Water Quality Guidelines, 1993. Canadian Water Quality Guidelines, The Council, Ottawa.

Chatfield, C., 1991. Avoiding Statistical Pitfalls. Statistical Science. 6. pp. 240-268.

Chesworth, W. and Evans, L.J., 1982. Field Excursion Guide Book 10A: Weathering, soil formation and land use in South and Central Ontario. International Association of Sedimentologists. McMaster University, Hamilton, Ontario. 66pp.

Church, B.N., 1977. Tertiary stratigraphy in South Central British Columbia. Geological Fieldwork, 1977-1, pp .7-11.

Church, B.N., 1979. A survey of Cenozoic magnetostratigraphy in South-Central British Columbia. Geological Fieldwork, 1979-1, pp. 9-23.

Church, B.N., 1980. A survey of Cenozoic magnetostratigraphy in south-central British Columbia. British Columbia Ministry of Energy, Mines and Petroleum Resources, Geological Fieldwork 1979, Paper 1980-1, pp. 9-10.

Church, B.N., Jessop, A.M., Bell, R., 1990. Tertiary outlier studies: recent investigations in the Summerland Basin, South Okanagan area, B.C.. Geological Fieldwork, 1990, pp.163-169.

Cieslinski, G., Neilsen, G.H. and Hogue, E.J., 1996. Effects of soil cadmium application and pH on growth and cadmium accumulation in roots, leaves and fruit of strawberry plants. Plant and soil, 180. pp.267-276.

Chemical Rubber Company (CRC) Handbook of Chemistry and Physics, 81st Edition. 2000. CRC Press, Cleveland, Ohio.

Danzer, K., De La Calle Garcia, D., Thiel, G., and Reichenbacher, M., 1999. Classification of wine samples according to origin and grape varieties on the basis of inorganic and organic trace analysis. American Laboratory. 31. pp. 26-33.

Davis, R., Chilton, R., Ottenbreit, L., Scheeler, M., Vielvoye, J., Williams, R., and Wittneben, U., 1984. Atlas of Suitable Grape Growing Locations in the Okanagan and Similkameen Valleys of British Columbia. Agriculture Canada. Association of British Columbia Grape Growers. Kelowna. 139pp.

Day, M.P., Zhang, B-L., Martin, G.J., 1994. The use of trace element data to complement stable isotope methods in the characterization of grape musts. American Journal of Enology and Viticulture, 45. pp. 79-85.

Dayton, S.H., 1981. Brenda; a vision of moly as a copper co-product. E & MJ, Engineering and Mining Journal, 182. pp.215 - 216.

De Kimpe, C.R., 1993. Soil Separation for Mineralogical Analysis. *In* Soil Sampling and Methods of Analysis. Carter, M.R. (Editor) Lewis Publishers, Ann Arbor. pp. 711-735.

Douglas, D.J., 1992. Properties of the Inductively Coupled Plasma as an Ion Source. *In* Inductively Coupled Plasmas in Analytical Atomic Spectrometry, 2nd Edition. Montaser, A. and Golightly, D.W. (Editors) VCH Publishers, New York. pp. 613-650.

Eschnauer, H., Holzl, S., and Horn, P., 1994. Isotope signatures of heavy elements as a parameter of characterizing wine. Wein-Wissenschaft, 49. pp125-129.

Eschnauer, H., 1982. Trace elements in must and wine: primary and secondary contents. American Journal of Enology and Viticulture, 4. pp. 226-230.

Fanning, D.S. and Fanning, M.C.B., 1989. Soil: Morphology, Genesis and Classification. John Wiley and Sons, Toronto, 395pp.

Faure, G. 1998. Principles and Applications of Geochemistry 2nd Edition. Prentice-Hall Inc., Upper Saddle River, New Jersey, 600p.

Greenough, J.D., Longerich, H.P., and Jackson, S.E., 1996. Trace Element Concentrations in Wines by ICP-MS: Evidence for the Role of Solubility in Determining Uptake by Plants. Canadian Journal of Applied Spectroscopy, 41. pp. 76-80.

Greenough, J.D., Longerich, H.P., and Jackson, S.E., 1997. Element Fingerprinting of Okanagan Valley wines using ICP-MS: Relationships between wine composition, vineyard and wine colour. Australian Journal of Grape and Wine Research, 3. pp.75-83.

Gulson, B.L., Lee, T.H., Mizon, K.J., Korsch, M.J. and Eschnauer, H.R., 1992. The application of lead isotope ratios to determine the contribution of the tin-lead to the lead content of wine. American Journal of Enology and Viticulture, 43. pp.180-190.

Hair, J.F., Anderson, R. E., and Tatham, R. L. 1987. Multivariate Data Analysis 2nd Edition. Macmillan Publishing Company, New York. 449pp.

Hanson, P.D., 1984. Lead and arsenic levels in wines produced from vineyards where lead arsenate sprays are used for caterpillar control. Journal of the Science of Food and Agriculture, 35. pp. 215-218.

Haynes, S.J., 2000. Geology and Wine 2. A geological foundation for terroirs and potential sub-appellations of Niagara Peninsula wines, Ontario, Canada. Geoscience Canada, 27. pp.67-87.

Haynes, S. J., Grant, E.B., Haynes, V.S., 1998. Geology of Niagara Falls and Niagara's Vineyard and Wines International Geological Society 1998, Field Trip B7: Guidebook, 10pp.

Hendershot, W.H., Lalande, H., Duquette, M., 1993. Soil Reaction and Exchangeable Acidity. *In* Soil Sampling and Methods of Analysis. Carter, M.R. (Editor) Lewis Publishers, Ann Arbor. pp. 711-735.

Horn, P., Holzl, S., Todt, W., and Matthies, D., 1998. Isotope abundance ratios of Sr in wine provenance determinations, in a tree-root activity study, and of Pb in a pollution study on tree-rings. Isotopes in environmental and health studies, 34. pp.31-42.

Horn, P., Schaaf, P., Holbach, B., Holzl, S., Eschnauer, H., 1993. ^{87}Sr / ^{86}Sr from rock and soil into vine and wine. Zeitschrift fuer Lebensmittel-Untersuchung und Forschung, 196. pp. 407-409.

Horsnail, R.F., 1975. Highmont Cu-Mo deposits, British Columbia. Journal of Geochemical Exploration, 4. pp. 67-72.

HP 4500 ChemStation Operator's Manual, 1997. Yokogawa Analytical Systems Inc. Ch.2.

Jackson, R.S., 1994. Wine Science : Principles and Applications. Academic Press, Toronto. pp. 227 - 332.

Jakubowski, N., Brandt, R., Stuewer, D., Eschnauer, H.R., and Gortges, S., 1999. Analysis of wines by ICP-MS: Is the pattern of the rare earth elements a reliable fingerprint of provenance? Fresenius Journal of Analytical Chemistry, 364. pp. 424-428.

Kabata-Pendias, A. and Pendias H., 1984. Trace Elements in Soils and Plants. CRC Press, Inc. Boca Raton. 315pp.

Kalra, Y.P. and Maynard, D.G., 1991. Methods manual for forest soil and plant analysis Forestry Canada. Northwest Region Information Report NOR-X-319. Forestry Canada. pp. 17-38.

Keith, L.H., Libby, R.A., Crummett, W., Taylor, J.K., Deegan, J., and Wentler, G., 1983. Principles of Environmental Analysis. Analytical Chemistry. 55. pp. 2210-2218.

Krauskopf, K.B. and Bird, D.K., 1995. Introduction to Geochemistry, 3rd Edition. McGraw-Hill, Inc., Toronto. pp.534-557.

Latorre, M.J., Garcia-Jares, C., Medina, B., and Herrero, C., 1994. Pattern Recognition Analysis Applied to Classification of Wines from Galicia (Northwest Spain) with Certified Brand of Origin. Journal of Agriculture and Food Chemistry. 42. pp. 1451-1455.

Lazar, A.C. and Farnsworth, P.B., 1997. Characterization of an Inductively Coupled Plasma with Xylene Solutions Introduced as Monodisperse Aerosols Analytical Chemistry, 69. pp. 3921-3929.

Lichte, F.E., Meier, A.L. and Crock, J.G., 1987. Determination of the Rare-Earth Elements in Geological Materials by Inductively Coupled Plasma Mass Spectrometry. Analytical Chemistry 59 pp. 1150-1157.

Longerich, H.P., 1995. Analysis of Pressed Pellets of Geological Samples Using Wavelength- Dispersive X-Ray Fluorescence Spectrometry. X-Ray Spectrometry, 24. pp. 123-136.

Longerich, H.P., 1993. Oxychlorine Ions in Inductively Coupled Plasma Mass Spectrometry: Effect of Chlorine Speciation as Cl^- and ClO^+. Journal of Analytical Atomic Spectrometry, 8. pp. 439-444.

Longerich, H.P., 1993b. Application of a New Treated LiF200 Crystal to X-Ray Fluorescence Analysis of Geological Samples X-Ray Spectrometry, 22. pp.114-118.

Longerich, H.P., Jackson, G.A., Friel, J.K., Chen, Z. and Frimpong, A., 1993. Progress of the determination of trace elements using solution nebulization ICP-MS. 1993 European Winter Conference on Plasma Spectrochemistry, Granada Spain, January 10-15, 1993.

Longerich, H.P., 1989. Effect of Nitric Acid, Acetic Acid and Ethanol on Inductively Coupled Plasma Mass Spectrometric Ion Signals as a Function of Nebuliser Gas Flow, With Implications on Matrix Suppression and Enhancements. Journal of Analytical Atomic Spectrometry, 4. pp.665-667.

Longerich, H.P., Strong, D.F. and Kantipuly, C.J. 1985. Progress in evaluation of instrumental and other parameters affecting chemical and isotopic analysis by inductively coupled plasma-mass spectrometry (ICP-MS). Canadian Journal of Spectroscopy, 31. pp.111-121.

Mahon, D.C. and Mathewes, R.W., 1983. Uptake of naturally occurring radioisotopes by vegetation in a region of high radioactivity. Canadian Journal of Soil Science, 63. pp.281-290.

McCuen, R.H., 1993. Microcomputer Applications in Statistical Hydrology. Prentice Hall, Engelwood Cliffs, New Jersey. 306pp.

Meyers, R.E. and Taylor, W.A., 1989. Metallogenic studies of lode gold-silver occurrences in south-central British Columbia, a progress report. *In* Geological fieldwork 1988; a summary of field activities and current research. Ministry of Energy, Mines and Petroleum Resources, Province of British Columbia, 1989-1. pp. 355-363.

Middlemost, E.A.K., 1986. Magmas and magmatic rocks; an introduction to igneous petrology. Longman Group, London, U.K. pp.79.

Montaser, A., McLean, J.A., Liu, H., and Mermet, J-M. 1998. An introduction to ICP spectrometries for elemental analysis. *In* Inductively coupled plasma mass spectrometry. Montaser, A.(Editor) Wiley-VCH, Toronto, pp.1-32.

Moret, I., Scarponi, G., Cescon, P. 1994. Chemometric characterization and classification of five Venetian white wines. Journal of Agriculture and Food Chemistry, 42. pp.1143-1153.

Moret, I., Di Leo, F., Giromini, V., and Scarponi, G. 1984. Multiple discriminant analysis in the analytical differentiation of Venetian white wines. 4. Application to several vintage years and comparison with the *k* nearest-neighbour classification. Journal of Agriculture and Food Chemistry

Muranyi, Z. and Papp, L., 1997. ICP-AES metal content analysis of wines made with different technologies. Acta Chimica Hungarica-Models in Chemistry,134. pp.529-537.

Peryea, F.J. and Creger, T.L., 1993. Vertical distribution of lead and arsenic in soils contaminated with lead arsenate pesticide residues. Water, Air and Soil Pollution, 78. pp.297-304.

Potts, P.J., 1987. A Handbook to Silicate Rock Analysis. Blackie Academic and Professional, New York, pp. 242-285.

Robinson, J., 1996. Guide to Wine Grapes, Oxford University Press, New York, 232pp.

Roed, M.A., 1995. Geology of the Kelowna Area and Origin of the Okanagan Valley British Columbia. Kelowna Geology Committee, Kelowna, B.C.

Rollinson, H.R., 1993. Using geochemical data: evaluation, presentation, interpretation, Longman Scientific & Technical, New York. pp.102-105.

Rosman, K.J.R., Chisholm, W., Jimi, S. Candelone, J-P., Boutron, C.F., Teissedre, P-L., and Adams, F.C., 1998. Lead concentrations and isotopic signatures in vintages of French wine between 1950 and 1991. Environmental Research, Section A. 78. pp.161-167.

Schreiner, J., 1994. The wineries of British Columbia. Orca Book Publishers, Victoria, B.C., 218pp.

Seeber, R., Sferlazzo, G., Leardi, R., Serra, A.D., and Versini, G. 1991. Multivariate data analysis in classification of musts and wines of the same variety according to vintage year. Journal of Agriculture and Food Chemistry, 39. pp. 1764-1769.

Shaklette, H.T., 1980. Elements in fruits and vegetables from areas of commercial production in the conterminous United States. Geological Survey Professional Paper 1178.

Shaw, T.B., 1994. Climate of the Niagara region *in* Niagara's Changing Landscapes Gaylor, H.J. (Editor), Carleton University Press, Ottawa, Ontario. pp.111-138.

Soleas, G.J., Dam, J., Carey, M., and Goldberg, D.M. 1997. Toward the fingerprinting of wines: cultivar-related patterns of polyphenolic constituents in Ontario wines. Journal of Agriculture and Food Chemistry, 45. pp. 3871-3880.

Sparks, D.L., 1995. Environmental Soil Chemistry. Academic Press Inc., San Diego, California. 265 pp.

Stroh, A., Brueckner, P. and Vollkopf, U., 1994. Multielement analysis of wine samples using ICP-MS. Atomic Spectroscopy, 15. pp. 100-106.

StatSoft, Inc. 1999. Electronic Statistics Textbook. Tulsa, OK. (www.statsoft.com/textbook/stathome.html)

Systat, 1996. Statistics: Systat 6.0 for Windows. Chicago, Illinois. 751 pp.

Tan, K.H., 1996. Soil Sampling, Preparation and Analysis. Marcel Dekker, Inc., New York. pp. 73-75.

Telford, P.G., 1978. Silurian Stratigraphy of the Niagara Escarpment, Niagara Falls to the Bruce Peninsula. *In* Field Trips Guidebook, Annual Meeting, Geological Association of Canada, Toronto, pp. 28-42.

Tempelman-Kluit, D.J., 1989. Geology, Penticton, British Columbia; Geological Survey of Canada, Map 1736A, scale 1:250 000.

Tilsley, J.E., 1988. Genetic considerations relating to some uranium ore deposits. In: Ore Deposit Models. Eds. Roberts, R.G. and Sheahan, P.A. Geoscience Canada Reprint Series 3, Ottawa.

Tinkler, K.J., 1992. Field Guide: Niagara Peninsula and Niagara Gorge Printing Services, McMaster University, Hamilton, Ontario. 24pp.

Tovell, W.M., 1992. Guide to the Geology of the Niagara Escarpment Niagara Escarpment Commission and Ontario Heritage Foundation Ashton-Potter Concord, Ontario. 159pp.

United Kingdom Earth Science Courseware Consortium, 2000. Department of Earth Sciences, University of Manchester. Basic Geochemistry Section 5 Subsection 5.2. (www.people.man.ac.uk/~ukescc)

Urdal, K., Vogt, N.B., Sporstol, S.P., Lichtenthaler, R.G., Mostad, H., Kolset, K., Nordenson, S., and Esbensen, K.1986. Classification of Weathered Crude Oils Using Multimethod Chemical Analysis, Statistical Methods and SIMCA Pattern Recognition. Marine Pollution Bulletin, 8. pp.366-373.

Van Dobben, H.F., Wolterbeek, H.T., Wamelink, G.W.W., and Ter Braak, C.J.F., 2001. Relationship between epiphytic lichens, trace elements and gaseous atmospheric pollutants. Environmental Pollution, 112. pp. 163-169.

Vanderburgh, S. and Roberts, M.C., 1996. Depositional systems and seismic stratigraphy of a Quaternary basin: north Okanagan Valley, British Columbia. Canadian Journal of Earth Science, 33. pp.917-927.

Vogt, R.D. 1997. Soil and stream water chemistry in a pristine and boggy site in mid-Norway, Hydrobiologia, 348. pp.19-38.

Wilkinson, L., Blank, G., and Gruber, C. 1996. Desktop Data Analysis with Systat. Prentice -Hall, Inc. NJ.

Wilson, J.E., 1998. Terroir: the role of geology, climate, and culture in the making of French wines. University of California Press, Berkeley. 336pp.

Wine Council of Ontario, 2001. Wineroute (www.wineroute.com)

Wittneben, U., 1986. Soils of the Okanagan and Similkameen Valleys, MOE Technical Report 18. B.C. Ministry of the Environment, Victoria, B.C.

Ziraldo, D.J.P., 1994. Anatomy of a winery: the art of wine at Inniskillin. (www.inniskillin.com/tours/anatomy.html)

Appendix 1: Calculation of element concentration (ppb) from signal intensity (cps) for wines analysed by ICP-MS

A-1 Data imported from the ICP-MS

The count rates from each run on the ICP-MS are collected and saved in a Lotus 1-2-3 format, (WK1). The file is then combined with the Lotus 1-2-3 spreadsheet, wine.wk4, for conversion of count rates to concentrations.

A-2 Calculation of matrix/drift correction

Samples are matrix/drift corrected first, then blank corrected. It is also possible to do the blank correction first, although this was tested for comparison on several runs and was shown to have an insignificant effect on the final concentration.

The sensitivity (count rate/ppb) of an element can be suppressed or enhanced by the sample matrix, and also varies with time as a result of changes in instrumental parameters (Longerich *et al.*, 1990). Matrix effects are mass dependent, with light elements more significantly affected by matrix than heavier elements (Longerich *et al.*, 1990). The correction factors for matrix effects and drift are calculated for each of the analytes, using the internal standards as explained below.

The mean count rates of Rh and Re measured in standard A of each cycle throughout a run are calculated ($I_{Rh(meun)}$ and $I_{Re(meun)}$). Matrix/drift correction factors (md_{Rh} and md_{Re}) are then calculated for the internal standards in each of the samples, standards and blanks of a run, using equations 1 and 2, where I_{Rh} and I_{Re} are the count rates for the internal standards in each tube.

$$md_{Rh} = \frac{I_{Rh(mean)}}{I_{Rh}} \quad (1)$$

$$md_{Re} = \frac{I_{Re(mean)}}{I_{Re}} \quad (2)$$

Matrix/drift correction factors (*md*) are then calculated for each analyte in the unknown wine samples. For elements with a mass less than 103 amu (Rh), *md* is calculated by equation 3.

$$cf_x = cf_{Rh} \quad (3)$$

For elements with a mass between 103 amu and 187 amu, *md* is linearly interpolated by mass, using equation 4, where $mass_x$ is the atomic mass of the element, *x*.

$$md_x = md_{Rh} + \frac{(md_{Re} - md_{Rh})}{(mass_{Re} - mass_{Rh})}(mass_x - mass_{Rh}) \quad (4)$$

For elements with mass greater than 187 amu, *cf* is given by equation 5.

$$md_x = md_{Re} \quad (5)$$

Matrix/drift correction factor (*md*) vs. element mass is plotted for every sample for quality assurance, to show possible anomalies in the matrix (see Fig. 2.8). The count

rate, i_x of each analyte is multiplied by its matrix/drift correction factor, md_x, for all unknown wines, blanks and standards.

A-3 Blank correction

Time interpolated blank correction is used to account for drift and background. The count rate of the matrix/drift corrected calibration blanks are interpolated by sample tube, then subtracted from the count rate of each sample and standard, according to equation 6. There are 14 tubes in a cycle, x is the number of samples from the last blank, *blank1* is the blank preceding the unknown sample, and *blank2* is the blank after the unknown sample.

$$I_x = i_x - \frac{(14-x)(i_{blank1}) + x(i_{blank2})}{14} \qquad (6)$$

A-4 Interference correction

Ratios of ThO^+/Th^+ are calculated for Standard A in each run to estimate the degree of polyatomic ion formation. The ratio, ThO^+/Th^+, is used as a measure of oxide and other polyatomic ion formation as a response to plasma conditions. It has been shown that metal to metal oxide ratios respond similarly to plasma conditions for elements throughout the mass range (Lichte, 1987). The element Th was chosen because it forms the strongest M-O bond of any element except C, and because 232 and 248 amu have no isobaric interferences and can be measured accurately (Lichte, 1987). Oxide formation was low (around 1.5% for ThO^+/Th^+), due to the high plasma temperature (Lichte, 1987).

The following polyatomic ions caused interferences which were significant and were corrected mathematically: $^{12}C^{37}Cl$ on ^{49}Ti, $^{35}Cl^{16}O$ on ^{51}V, $^{40}Ar^{37}Cl$ on ^{77}Se, $^{81}Br^{1}H$ on ^{82}Se, $^{40}Ca^{16}O^{1}H$ on ^{57}Fe, $^{43}Ca^{16}O$ on ^{59}Co, $^{44}Ca^{16}O$ on ^{60}Ni, and $^{48}Ca^{16}O^{1}H$ on ^{65}Cu.

The oxide, hydroxide, argide or carbide of the lower mass element occurs at the same atomic mass as the heavier element.

Interferences are corrected mathematically by equation 7 and 8, where CF_x is the interference correction factor for analyte x, and I_x is the count rate at the amu of the analyte, x, in the sample. The background corrected count rate in the standard, $I_{f(std)}$, is determined for the element, f, which forms a polyatomic interferent, $I_{x(std)}$, at the same amu as the analyte, x. *Std1* is the standard preceding the unknown sample, and *std2* is the standard after the sample. For example, the carbide of ^{37}Cl interferes with ^{49}Ti. Standard C contains Cl but not Ti, so the count rate of the interferent $^{12}C^{37}Cl$ can be measured at 49 amu, as $I_{Ti(Std\,C)}$, and the count rate of Cl in the standard would be $I_{Cl(Std\,C)}$. In this case, I_{Ti} would be the count rate of the analyte plus its interferent in the sample, both at 49 amu. Ion intensities of Cl and Br, as well as the intensities of polyatomic species formed at 49, 51, 77, and 79 amu, are shown relative to a 6% ethanol blank in Fig. 2.9. The formation of $^{40}Ar^{35}Cl$ at 75 amu is negligible compared to the background (blank) intensity, even for the standard solution containing 20 ppm Cl, which is higher than the concentration in most of the wine samples. The polyatomic ion formation is low in this method (determined to be 1-2% from ThO^- formation) and interference of ArCl with As was determined to be negligible. Fig. 2.10 shows the ion intensities of a 20 ppm Ca solution and the interfering species it forms at 57, 59, 60, and 65 amu, as compared to a 6% ethanol blank solution. The interference factor of the polyatomic species formed by Cl, Ca, and Br are used to subtract interferences in unknown samples, according to equation 7.

$$CF_x = \frac{I_{x(std1)} + I_{x(std2)}}{I_{f(std1)} + I_{f(std2)}}(I_f) \qquad (7)$$

The interference factor, CF_x, is then subtracted from the count rate of the analyte.

A-5 Calculation of sensitivity

Standards are collected and averaged, and standard deviation (SD) is calculated for the standards. The solution sensitivity, in cps/ppb, of each element is calculated for each cycle according to equation 8.

$$S_x = \frac{I_{x(std)}}{ppb_{x(std)}} \tag{8}$$

Sensitivity normalized to abundance is calculated for each analyte by equation 9, where N_x is the normalised sensitivity, and IA is the isotopic abundance of the analyte.

$$N_x = \frac{S_x}{IA} \tag{9}$$

N_x *vs.* amu is plotted to show the sensitivity of analytes over the mass range (see Fig. 2.11), and to identify elements which have anomalous sensitivity. The degree of ionization of an element is a function of its ionization potential, the free electron temperature and the ratio of the electronic partition function of the ion over that of the atom (Douglas, 1992). Non-metal elements with high ionization potentials (P. S, Br, and Cl) show low sensitivity. This plot is also useful to observe anomalous data.

A-6 Calculation of interference factor and error of interference factor

Interference factors are calculated for quality assurance. Interference factors, *IF*, are calculated for each of the analytes identified in section 2.7.5. The factor, *IF*, is calculated according to equation 10, where $I_{x(std)}$ is the mean count rate of the interfering polyatomic species in the standard, and $I_{y(std)}$ is the mean count rate of the analyte in the standard. For example, the interference factor for $^{35}Cl^{16}O$ on ^{51}V would be the intensity of the signal at 35 amu relative to the signal intensity at 51 amu would be measured in standard C, in which Cl is present but V is not, to monitor the relative intensity of $^{35}Cl^{16}O$ formation, as the interference factor, *IF*.

$$IF = \frac{I_{x(std)}}{I_{y(std)}} \qquad (10)$$

A-7 Conversion of net count rates to ppb

Sensitivity, *S*, (cps/ppb) of each analyte is calculated for each cycle, then time interpolated and used to convert count rates to concentration (equation 2.11). The equation converts count rates, I_x, to concentration, C_x, for each analyte, *x*, in the unknown wine samples, where *cycle1* is the set of standards preceding the sample and *cycle2* is the set of standards after the sample. Time interpolation accounts for drift in the standards, which is not corrected by the internal standards, especially in the lower mass elements, which show more drift and more matrix.

$$C_x = \frac{14I_x}{(x)S_{cycle1} + (14-x)S_{cycle2}} \qquad (2.11)$$

A-8 Calculation of dilution factors

Dilution factors, *DF*, are calculated for each of the unknown wine samples according to equation 2.12, where M_s is the mass of the sample and M_d is the mass of the diluent.

$$DF = \frac{M_s}{M_s + M_d} \qquad (2.12)$$

The analyte concentrations in each sample solution are then divided by the dilution factor to give the determined concentrations, in ppb, of the wines. Dilution from the online internal standard addition does not need to be corrected for because addition is constant and therefore the same for calibration standards and samples, but does affect the calculated sensitivity because the signal intensity is dependent on the concentration of sample reaching the plasma.

Appendix 2: Element concentrations (ppb) in wines

Name	Winery	Vineyard	Region
30B_R	Thirty Bench	Thirty Bench	Niagara
In_C	Inniskillin	Inniskillin	Niagara
Cave_G	Cave Spring	Cave Spring	Niagara
Cave_R	Cave Spring	Cave Spring	Niagara
Cave_C	Cave Spring	Cave Spring	Niagara
Mag_C	Magnotta	Lenko	Niagara
Mag_Vg	Magnotta	Lenko	Niagara
Creek_PN	Creekside	Pillitteri	Niagara
Creek_S	Creekside	Pillitteri	Niagara
Pil_BN	Pillitteri	Pillitteri (Baco Noir)	Niagara
Pil_C	Pillitteri	Pillitteri	Niagara
Pil_PG	Pillitteri	Pillitteri	Niagara
Sto_R1	Stoney Ridge	Pleka	Niagara
Sto_R2	Stoney Ridge	Butler's Grant	Niagara
Sto_R3	Stoney Ridge	Puddicombe	Niagara
Hen_R	Henry of Pelham	Henry of Pelham	Niagara
Wal_C	Walter's	Walter's	Niagara
Her_R	Hernder	Hernder	Niagara
Lak_C	Lakeview	Lakeview	Niagara
Jo_Vi	Joseph's	Joseph's	Niagara
Jo_PG	Joseph's	Joseph's	Niagara
Jo_C	Joseph's	Joseph's	Niagara
Jo_R	Joseph's	Joseph's	Niagara
Jo_BN	Joseph's	Joseph's	Niagara
Rei_R	Reif	Reif	Niagara
Rei_PN	Reif	Reif	Niagara
Rei_T	Reif	Reif	Niagara
Rei_M	Reif	Reif	Niagara
Rei_C	Reif	Reif	Niagara
Mar_R	Marynissen	Marynissen	Niagara

Appendix 2: Element concentrations (ppb) in wines

Name	Winery	Vineyard	Region
Stn_C	Stonechurch	Stonechurch	Niagara
Kon_R	Konzelmann	Konzelmann	Niagara
De_F	De Sousa	De Sousa	Niagara
De_Vi	De Sousa	De Sousa	Niagara
De_R	De Sousa	De Sousa	Niagara
De_BN	De Sousa	De Sousa	Niagara
Ket_C	Kettle Valley	Kettle Valley	Okanagan
HR_OK	House of Rose	House of Rose	Okanagan
HR_V1	House of Rose	House of Rose	Okanagan
HR_V2	House of Rose	House of Rose	Okanagan
HR_V3	House of Rose	House of Rose	Okanagan
HR_V4	House of Rose	House of Rose	Okanagan
HR_V5	House of Rose	House of Rose	Okanagan
LB_start	Lake Breeze	Lake Breeze	Okanagan
LB_mid	Lake Breeze	Lake Breeze	Okanagan
LB_end	Lake Breeze	Lake Breeze	Okanagan
LB_T1	Lake Breeze	Lake Breeze	Okanagan
LB_T2	Lake Breeze	Lake Breeze	Okanagan
LB_T3	Lake Breeze	Lake Breeze	Okanagan
La_R95	Lang	Lang	Okanagan
La_R96	Lang	Lang	Okanagan
La_R97	Lang	Lang	Okanagan
La_R97S	Lang	Lang	Okanagan
La_R97I	Lang	Lang	Okanagan
Don_PB	McKenzie	McKenzie	Okanagan
Don_PN	McKenzie	McKenzie	Okanagan
Geh_V	Gehringer	Gehringer	Okanagan
Su_C1	Summerhill	Summerhill	Okanagan
Su_C2	Summerhill	Summerhill	Okanagan
Su_R1	Summerhill	Inkameep	Okanagan

Appendix 2: Element concentrations (ppb) in wines

Name	Winery	Vineyard	Region
Su_R2	Summerhill	Inkameep	Okanagan
Su_PN	Summerhill	Summerhill	Okanagan
Haw_G	Hawthorne		Okanagan
Pin_R	Pinot Reach	Pinot Reach	Okanagan
Hes_PB	Hester Creek	Hester Creek	Okanagan
Vin_R	Vincor	Inkameep	Okanagan
Gra_Ro	Gray Monk	Gray Monk	Okanagan
In_PN	Inniskillin (Okanagan)	Inniskillin (Okanagan)	Okanagan
In_PB	Inniskillin (Okanagan)	Inniskillin (Okanagan)	Okanagan
Hil_M	Hillside	Hillside	Okanagan
Tin_G	Tin Horn Creek	Tin Horn Creek	Okanagan
Sla_R	Slamka Cellars	Slamka Cellars	Okanagan
Qu_R1	Quail's Gate	Quail's Gate	Okanagan
Qu_R2	Quail's Gate	Quail's Gate	Okanagan
Qu_R3	Quail's Gate	Quail's Gate	Okanagan
Qu_R4	Quail's Gate	Quail's Gate	Okanagan
Hai_Tr	Hainle	Hainle	Okanagan
Nic_Sy	Nichol	Nichol	Okanagan
Stg_C	Stag's Hollow	Stag's Hollow	Okanagan
Stg_PN	Stag's Hollow	Stag's Hollow	Okanagan
Red_C	Red Rooster	Red Rooster	Okanagan
Wi_G1	Wild Goose	Wild Goose	Okanagan
Wi_G2	Wild Goose	Wild Goose	Okanagan
Wi_G3	Wild Goose	Wild Goose	Okanagan
Wi_G4	Wild Goose	Wild Goose	Okanagan
Wi_G5	Wild Goose	Wild Goose	Okanagan
St_PB1	St. Hubertus	St. Hubertus	Okanagan
St_PB2	St. Hubertus	St. Hubertus	Okanagan
St_R1	St. Hubertus	St. Hubertus	Okanagan
St_R2	St. Hubertus	St. Hubertus	Okanagan

Appendix 2: Element concentrations (ppb) in wines

Name	Winery	Vineyard	Region
Ge_PB	Gersighel	Gersighel	Okanagan
Sc_G	Scherzinger	Scherzinger	Okanagan
Sc_PN	Scherzinger	Scherzinger	Okanagan
Ce_C	Cedar Creek	Cedar Creek	Okanagan
Bar_C	Irvine	Irvine	Okanagan
Ro	Rothschild		France
Bo	Bouchard Aine		France
Ch	Chateau Peruchet		France
Sic	Siche Bordeaux		France
For	Fortant de France		France
Lou	Louis Latour		France
CdC	Chateau de Courteillac		France
Cou	La Cour Pavillon		France
Bar	Barton and Guestier		France
Ale	Alexis Lichine		France

Appendix 2: Element concentrations (ppb) in wines

Name	Subregion	Variety	Vintage Year	Name
30B_R	Beamsville Bench	Riesling	1997	30B_R
In_C	Niagara-on-the-Lake	Chardonnay	1996	In_C
Cave_G	Beamsville Bench	Gewurztraminer	1997	Cave_G
Cave_R	Beamsville Bench	Riesling	1997	Cave_R
Cave_C	Beamsville Bench	Chardonnay	1997	Cave_C
Mag_C	Beamsville Bench	Chardonnay	1997	Mag_C
Mag_Vg	Beamsville Bench	Viognier	1996	Mag_Vg
Creek_PN	Niagara-on-the-Lake	Pinot Noir	1998	Creek_PN
Creek_S	Niagara-on-the-Lake	Sauvignon Blanc	1998	Creek_S
Pil_BN	Niagara-on-the-Lake	Baco Noir	1997	Pil_BN
Pil_C	Niagara-on-the-Lake	Chardonnay	1998	Pil_C
Pil_PG	Niagara-on-the-Lake	Pinot Gris	1998	Pil_PG
Sto_R1	Niagara-on-the-Lake	Riesling	1996	Sto_R1
Sto_R2	Niagara-on-the-Lake	Riesling	1996	Sto_R2
Sto_R3	Niagara-on-the-Lake	Riesling	1996	Sto_R3
Hen_R	Beamsville Bench	Riesling	1997	Hen_R
Wal_C	Beamsville Bench	Chardonnay	1998	Wal_C
Her_R	Beamsville Bench	Riesling	1997	Her_R
Lak_C	Beamsville Bench	Chardonnay	1997	Lak_C
Jo_Vi	Niagara-on-the-Lake	Winter Vidal	1996	Jo_Vi
Jo_PG	Niagara-on-the-Lake	Pinot Gris	1997	Jo_PG
Jo_C	Niagara-on-the-Lake	Chardonnay	1998	Jo_C
Jo_R	Niagara-on-the-Lake	Riesling	1998	Jo_R
Jo_BN	Niagara-on-the-Lake	Baco Noir	1998	Jo_BN
Rei_R	Niagara-on-the-Lake	Riesling	1997	Rei_R
Rei_PN	Niagara-on-the-Lake	Pinot Noir	1997	Rei_PN
Rei_T	Niagara-on-the-Lake	Trollinger Riesling	1996	Rei_T
Rei_M	Niagara-on-the-Lake	Merlot	1997	Rei_M
Rei_C	Niagara-on-the-Lake	Chardonnay	1996	Rei_C
Mar_R	Niagara-on-the-Lake	Riesling	1997	Mar_R

Appendix 2: Element concentrations (ppb) in wines

Name	Subregion	Variety	Vintage Year	Name
Stn_C	Niagara-on-the-Lake	Chardonnay	1997	Stn_C
Kon_R	Niagara-on-the-Lake	Riesling	1997	Kon_R
De_F	Beamsville Bench	Marechal Foch	1997	De_F
De_Vi	Beamsville Bench	Vidal Blanc	1997	De_Vi
De_R	Beamsville Bench	Riesling	1997	De_R
De_BN	Beamsville Bench	Baco Noir	1997	De_BN
Ket_C	Naramata	Chardonnay	1996	Ket_C
HR_OK	Kelowna	Okanagan Riesling	1996	HR_OK
HR_V1	Kelowna	Verdelet	1992	HR_V1
HR_V2	Kelowna	Verdelet	1993	HR_V2
HR_V3	Kelowna	Verdelet	1994	HR_V3
HR_V4	Kelowna	Verdelet	1995	HR_V4
HR_V5	Kelowna	Verdelet	1996	HR_V5
LB_start	Naramata	Pinot Blanc	1998	LB_start
LB_mid	Naramata	Pinot Blanc	1998	LB_mid
LB_end	Naramata	Pinot Blanc	1998	LB_end
LB_T1	Naramata	Pinot Blanc	1998	LB_T1
LB_T2	Naramata	Pinot Blanc	1998	LB_T2
LB_T3	Naramata	Pinot Blanc	1998	LB_T3
La_R95	Naramata	Riesling (Late Harvest)	1995	La_R95
La_R96	Naramata	Riesling	1996	La_R96
La_R97	Naramata	Riesling	1997	La_R97
La_R97S	Naramata	Riesling (Late Harvest)	1997	La_R97S
La_R97I	Naramata	Riesling (Icewine)	1997	La_R97I
Don_PB	Peachland	Pinot Blanc	1998	Don_PB
Don_PN	Peachland	Pinot Noir	1998	Don_PN
Geh_V	Oliver	Verdelet	1997	Geh_V
Su_C1	Kelowna	Chardonnay	1996	Su_C1
Su_C2	Kelowna	Chardonnay	1998	Su_C2
Su_R1	Oliver	Riesling (Icewine)	1998	Su_R1

Appendix 2: Element concentrations (ppb) in wines

Name	Subregion	Variety	Vintage Year	Name
Su_R2	Oliver	Riesling	1998	Su_R2
Su_PN	Kelowna	Pinot Noir	1998	Su_PN
Haw_G	Penticton	Gewurztraminer	1997	Haw_G
Pin_R	Kelowna	Riesling	1997	Pin_R
Hes_PB	Kelowna	Pinot Blanc	1997	Hes_PB
Vin_R	Oliver	Riesling	1997	Vin_R
Gra_Ro	Kelowna	Rotberger	1997	Gra_Ro
In_PN	Oliver	Pinot Noir	1996	In_PN
In_PB	Oliver	Pinot Blanc	1997	In_PB
Hil_M	Penticton	Muscat	1997	Hil_M
Tin_G	Oliver	Gewurztraminer	1997	Tin_G
Sla_R	Kelowna	Riesling	1995	Sla_R
Qu_R1	Kelowna	Riesling	1995	Qu_R1
Qu_R2	Kelowna	Riesling	1996	Qu_R2
Qu_R3	Kelowna	Riesling	1997	Qu_R3
Qu_R4	Kelowna	Riesling	1998	Qu_R4
Hai_Tr	Peachland	Traminer	1997	Hai_Tr
Nic_Sy	Naramata	Syrah	1995	Nic_Sy
Stg_C	Okanagan Falls	Chardonnay	1997	Stg_C
Stg_PN	Okanagan Falls	Pinot Noir	1996	Stg_PN
Red_C	Naramata	Chardonnay	1997	Red_C
Wi_G1	Okanagan Falls	Gewurztraminer	1993	Wi_G1
Wi_G2	Okanagan Falls	Gewurztraminer	1994	Wi_G2
Wi_G3	Okanagan Falls	Gewurztraminer	1995	Wi_G3
Wi_G4	Okanagan Falls	Gewurztraminer	1996	Wi_G4
Wi_G5	Okanagan Falls	Gewurztraminer	1997	Wi_G5
St_PB1	Kelowna	Pinot Blanc	1996	St_PB1
St_PB2	Kelowna	Pinot Blanc	1996	St_PB2
St_R1	Kelowna	Riesling	1998	St_R1
St_R2	Kelowna	Riesling	1998	St_R2

Appendix 2: Element concentrations (ppb) in wines

Name	Subregion	Variety	Vintage Year	Name
Ge_PB	Oliver	Pinot Blanc	1994	Ge_PB
Sc_G	Peachland	Gewurztraminer	1997	Sc_G
Sc_PN	Peachland	Pinot Noir	1997	Sc_PN
Ce_C	Kelowna	Chardonnay	1998	Ce_C
Bar_C	Naramata	Chardonnay	1997	Bar_C
Ro		Chardonnay	1997	Ro
Bo		Chardonnay	1996	Bo
Ch	Bordeaux	Sauvignon	1996	Ch
Sic	Bordeaux		1997	Sic
For		Chardonnay	1997	For
Lou		Chardonnay	1997	Lou
CdC	Bordeaux		1997	CdC
Cou	Bordeaux	Merlot	1997	Cou
Bar	Bordeaux		1997	Bar
Ale	Bordeaux		1997	Ale

Appendix 2: Element concentrations (ppb) in wines

Name	Li	Be	Mg	Al	P	Cl	Ca	Ti	V
30B_R	13.2	0.66	65929	955	147626	22057	103925	34.6	48.5
In_C	4.6	0.57	54636	481	123562	17723	71741	8.0	6.5
Cave_G	13.1	1.05	79521	1124	144793	24115	91597	30.3	57.6
Cave_R	28.7	0.95	68830	979	110444	26123	122851	23.1	27.7
Cave_C	5.8	0.69	69888	636	150335	24175	142821	30.9	44.0
Mag_C	8.4	0.29	57657	817	108754	47625	107779	13.9	43.7
Mag_Vg	2.5	0.42	46536	1211	101486	52259	62800	15.3	50.5
Creek_PN	0.9	0.03	30255	236	150471	12499	93033	2.4	0.4
Creek_S	1.4	0.43	48544	869	96248	9078	63344	12.6	19.4
Pil_BN	2.2	0.08	64999	311	211083	50962	96075	11.0	30.6
Pil_C	0.8	0.10	34787	263	110250	10010	48184	5.8	9.4
Pil_PG	1.1	0.18	40824	420	486377	30316	228527	14.2	63.8
Sto_R1	12.1	0.63	59225	1316	95137	22482	101066	46.2	59.7
Sto_R2	17.1	0.33	60191	687	193911	31187	102122	20.6	150.8
Sto_R3	14.4	0.51	49943	1068	107164	35731	96814	16.0	59.3
Hen_R	11.7	1.24	54994	1182	64770	20252	111801	28.1	54.4
Wal_C	3.0	0.25	65814	499	127793	15760	75360	7.1	21.5
Her_R	27.2	0.72	65697	2083	83310	64477	104364	30.3	181.4
Lak_C	7.0	0.13	72128	302	116793	53899	64312	15.6	23.8
Jo_Vi	4.9	0.57	65983	1739	118265	42774	115590	23.4	22.3
Jo_PG	1.4	0.52	32194	1332	33450	10288	76374	18.4	23.2
Jo_C	1.3	0.18	51296	342	102373	7294	49332	7.0	2.8
Jo_R	1.3	0.12	45185	233	96803	11989	87627	7.5	1.8
Jo_BN	0.7	0.09	64768	564	108881	41964	85181	4.5	0.8
Rei_R	6.3	1.28	52964	662	79249	18095	82438	10.3	11.1
Rei_PN	2.1	0.24	48321	620	65792	17041	77752	38.3	83.9
Rei_T	4.1	0.76	47970	718	83849	16545	80809	10.3	13.2
Rei_M	3.5	0.37	46240	1149	80595	19895	73898	22.1	49.1
Rei_C	5.0	0.55	45797	719	58172	16107	99081	12.3	31.3
Mar_R	7.1	0.19	52784	1263	137830	16206	81724	27.6	206.5

Appendix 2: Element concentrations (ppb) in wines

Name	Li	Be	Mg	Al	P	Cl	Ca	Ti	V
Stn_C	5.0	1.80	56009	1598	66362	13623	80360	41.0	186.1
Kon_R	6.2	0.07	45777	585	92979	15373	83046	10.6	29.8
De_F	6.4	0.22	60081	612	57917	91623	50585	11.1	55.2
De_Vi	1.9	0.32	56270	739	43604	27662	52528	12.7	32.4
De_R	2.4	0.34	45492	916	63883	23171	76654	19.7	41.4
De_BN	4.1	0.26	66288	804	150167	118727	88998	14.7	46.9
Ket_C	3.7	0.04	48203	101	80284	19763	44108	2.9	3.0
HR_OK	2.9	0.02	35544	85	85307	15482	34485	10.7	3.1
HR_V1	1.6	0.01	26888	36	52453	12177	55146	1.4	1.8
HR_V2	2.0	0.05	36593	65	102390	9665	55302	3.2	0.5
HR_V3	3.1	0.02	46397	26	123006	17727	55948	3.8	0.8
HR_V4	2.1	0.03	38041	31	85907	18939	49607	3.7	0.7
HR_V5	1.0	0.01	42134	54	91426	14524	41117	9.3	34.4
LB_start	5.6	0.60	47235	463	78994	6027	58069	5.2	4.1
LB_mid	5.4	0.58	46705	425	81043	6492	56915	5.3	3.6
LB_end	5.9	0.61	48795	437	83613	6709	59266	5.6	3.6
LB_T1	4.7	0.50	38669	365	66741	7582	56826	5.2	3.3
LB_T2	4.2	0.48	34907	364	70536	4224	49320	4.8	1.9
LB_T3	4.7	0.55	41103	510	70859	5714	52731	4.6	3.2
La_R95	7.2	0.37	57071	434	120747	21702	43856	3.1	1.8
La_R96	6.3	0.81	76254	1351	127426	44052	127913	5.7	13.6
La_R97	3.0	0.26	41981	504	74810	14784	96229	5.1	21.4
La_R97S	6.9	0.36	79096	747	160013	26940	195657	7.3	4.3
La_R97I	15.7	0.73	148926	1316	170510	59783	239631	17.7	7.0
Don_PB	2.0	0.02	47501	218	97859	4699	39387	2.4	0.7
Don_PN	1.8	0.02	39458	172	74415	19880	55404	1.9	1.2
Geh_V	6.8	0.54	38470	671	81834	23801	105593	14.0	139.2
Su_C1	11.9	0.05	83117	233	102699	15749	65613	10.8	4.7
Su_C2	32.9	0.07	99251	62	170983	18875	49059	3.8	0.7
Su_R1	11.6	0.03	111050	151	-210	27567	75891	11.7	1.9

Appendix 2: Element concentrations (ppb) in wines

Name	Li	Be	Mg	Al	P	Cl	Ca	Ti	V
Su_R2	9.0	0.13	61289	123	68929	3508	58724	1.9	1.7
Su_PN	6.7	0.02	85244	105	455108	24882	60421	3.3	0.5
Haw_G	10.8	0.42	69521	216	51737	17295	68488	13.3	41.8
Pin_R	15.8	0.03	88154	243	71963	10148	100560	11.8	27.3
Hes_PB	3.9	0.19	65971	491	122714	11354	75176	9.0	26.4
Vin_R	9.3	0.94	80269	831	112866	15167	132704	10.3	5.5
Gra_Ro	5.3	0.18	37622	144	29419	9243	93682	4.4	5.2
In_PN	2.0	0.03	56086	96	97974	13404	38482	3.3	1.0
In_PB	4.0	0.61	61534	421	134238	13031	71313	7.4	3.3
Hil_M	8.4	0.32	48132	461	89445	13607	67848	13.7	51.7
Tin_G	3.8	0.20	35617	84	57111	2431	54773	3.7	18.5
Sla_R	8.0	0.23	40646	258	87598	3886	99644	7.6	1.6
Qu_R1	17.0	0.34	61860	278	80037	8847	85297	4.7	15.1
Qu_R2	12.3	0.26	75874	189	114966	14431	125428	6.0	16.1
Qu_R3	18.2	0.23	81990	502	476648	10896	103992	7.1	12.0
Qu_R4	7.1	0.14	44272	92	81509	9161	60696	3.3	7.6
Hai_Tr	2.4	0.17	62846	227	158481	13725	31192	11.2	6.4
Nic_Sy	5.8	0.01	37535	51	34675	8086	41420	1.6	0.3
Stg_C	5.3	0.05	66314	108	148797	7626	76666	4.5	4.9
Stg_PN	5.2	0.00	56589	59	97171	16412	61503	2.5	0.2
Red_C	2.6	1.10	78251	879	111047	15878	58862	4.4	1.2
Wi_G1	7.7	0.53	58271	192	84803	15800	42383	9.5	3.2
Wi_G2	7.7	0.34	48104	226	59170	8902	55098	9.5	1.5
Wi_G3	12.3	0.66	65897	500	93698	15223	65737	29.2	9.2
Wi_G4	9.1	0.69	63397	406	76508	74497	78751	11.3	2.7
Wi_G5	8.5	0.37	62635	288	94268	15121	74033	9.5	3.7
St_PB1	3.1	0.08	37201	291	111847	3639	80865	4.1	3.7
St_PB2	3.7	0.10	40537	166	118948	3996	158368	2.8	4.3
St_R1	10.2	0.01	57387	16	88642	5273	54386	3.1	0.4
St_R2	16.6	0.21	102333	299	172367	12514	80710	14.6	5.1

Appendix 2: Element concentrations (ppb) in wines

Name	Li	Be	Mg	Al	P	Cl	Ca	Ti	V
Ge_PB	6.9	0.42	74001	428	233653	6799	86620	16.2	9.5
Sc_G	7.3	0.24	81622	247	214004	17510	86314	11.6	3.0
Sc_PN	3.1	0.05	80927	159	157583	38630	188391	6.7	4.0
Ce_C	22.8	0.04	120351	117	335745	17951	40888	5.4	9.6
Bar_C	2.8	0.01	31509	109	69053	8459	36244	3.6	4.4
Ro	6.2	0.40	49696	950	98838	10882	88668	41.5	153.7
Bo	3.2	0.39	51008	586	110877	9529	73861	31.2	70.7
Ch	4.3	0.36	45354	451	70199	18733	75393	21.6	37.2
Sic	4.1	0.15	39365	489	88516	16530	79549	31.1	102.5
For	3.8	0.29	49888	453	104930	9735	88397	16.4	12.5
Lou	2.2	0.09	45940	270	120225	3598	56440	10.1	13.8
CdC	5.2	0.09	48202	372	115988	26670	53424	34.6	44.8
Cou	2.6	0.08	47301	399	135276	24420	55694	43.8	80.7
Bar	3.8	0.31	38942	865	88687	22146	80662	85.2	120.6
Ale	3.9	0.72	39334	1018	83346	25735	80409	121.6	184.7

Appendix 2: Element concentrations (ppb) in wines

Name	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Br	Se
30B_R	1256	3068	6.43	22.9	312	502	16.5	1.41	197	1.33
In_C	742	586	2.23	11.3	7	658	2.0	0.74	188	0.67
Cave_G	1084	2411	8.42	29.8	165	540	19.5	1.46	178	1.40
Cave_R	592	1403	5.15	19.1	40	709	15.5	1.74	201	1.69
Cave_C	596	1173	7.57	26.5	33	653	15.4	1.49	365	1.37
Mag_C	650	1497	3.37	21.8	25	509	8.5	1.80	420	1.65
Mag_Vg	1639	1500	4.40	20.5	29	436	4.3	1.35	279	1.20
Creek_PN	1684	1240	1.11	14.6	13	499	0.7	1.04	619	0.81
Creek_S	1778	762	4.19	24.7	23	752	2.2	0.89	217	0.85
Pil_BN	1222	5741	3.15	15.6	22	621	6.9	0.95	647	0.78
Pil_C	1189	980	2.68	11.5	38	593	1.7	1.00	232	0.91
Pil_PG	1356	693	2.77	14.6	17	625	5.9	1.15	848	1.06
Sto_R1	2372	2477	4.77	21.4	49	665	6.3	1.09	205	1.00
Sto_R2	1864	1344	3.92	15.4	8	698	8.0	1.12	218	1.09
Sto_R3	2032	1731	5.05	22.9	28	690	6.5	0.91	350	0.76
Hen_R	2069	1503	9.35	29.9	74	782	24.7	1.55	148	1.49
Wal_C	589	2544	3.74	29.1	108	2960	1.9	0.79	157	0.68
Her_R	1191	2074	4.54	38.8	104	1125	15.3	3.86	369	3.87
Lak_C	1648	3330	4.70	67.9	73	601	4.6	0.91	258	0.84
Jo_Vi	1487	5879	5.67	47.5	23	1059	7.0	3.49	445	3.33
Jo_PG	995	6894	5.07	31.4	73	794	6.4	2.09	291	2.01
Jo_C	1497	597	2.26	17.6	31	626	1.5	1.33	208	1.30
Jo_R	1543	1879	1.57	12.9	25	699	1.4	0.98	228	0.91
Jo_BN	4737	3929	2.84	53.3	638	1087	5.7	2.66	653	2.40
Rei_R	1118	4023	2.29	28.6	433	721	3.6	0.59	155	0.57
Rei_PN	1635	3803	2.76	33.4	14	802	22.2	1.65	289	1.45
Rei_T	2192	5252	4.02	26.2	1207	827	21.0	0.85	171	0.76
Rei_M	829	2634	3.00	23.3	51	303	4.2	1.32	262	1.26
Rei_C	1879	3181	4.02	23.4	130	701	9.7	1.02	178	1.01
Mar_R	879	2901	3.24	21.3	57	693	12.5	1.50	202	1.49

Appendix 2: Element concentrations (ppb) in wines

Name	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Br	Se
Stn_C	855	3885	2.44	21.9	305	143	10.6	2.16	291	2.13
Kon_R	1329	1170	1.70	14.8	15	2109	2.6	1.57	167	1.59
De_F	1403	2639	3.70	30.3	71	910	2.8	1.87	357	1.78
De_Vi	992	2165	3.52	18.3	244	509	1.8	0.97	200	0.92
De_R	745	2077	4.09	19.8	227	592	2.1	1.09	187	1.07
De_BN	1295	2844	4.94	30.4	72	1146	2.4	1.10	895	0.94
Ket_C	357	884	1.50	11.2	5	1331	1.2	10.76	362	10.89
HR_OK	341	2445	1.66	20.2	11	365	1.3	0.64	136	0.55
HR_V1	646	1046	1.46	14.6	18	641	1.3	0.31	131	0.24
HR_V2	395	936	1.04	10.4	40	860	3.1	0.45	135	0.38
HR_V3	453	1058	0.93	12.5	10	342	1.3	0.45	146	0.37
HR_V4	552	1016	0.87	15.9	25	311	1.2	0.57	162	0.48
HR_V5	574	1457	1.81	19.4	23	569	2.0	0.27	119	0.20
LB_start	410	784	3.35	38.3	12	211	2.7	1.38	128	1.30
LB_mid	405	770	3.21	30.6	9	223	2.8	1.69	127	1.64
LB_end	411	790	3.22	12.4	6	214	2.8	1.41	131	1.38
LB_T1	369	773	3.20	17.3	8	216	2.7	1.49	127	1.50
LB_T2	346	764	2.60	9.1	3	184	2.6	1.52	125	1.48
LB_T3	387	874	2.99	10.5	6	204	2.8	1.36	126	1.34
La_R95	745	1076	2.14	11.6	38	292	5.8	0.69	291	0.49
La_R96	1116	1106	5.62	19.5	378	345	8.0	2.05	302	1.98
La_R97	623	689	3.22	15.2	39	396	4.3	1.60	211	1.54
La_R97S	864	625	3.06	14.7	50	275	8.5	1.30	295	1.16
La_R97I	1077	1446	5.51	32.1	343	816	16.7	3.00	336	2.85
Don_PB	502	961	1.39	164.3	115	1595	0.7	0.81	118	0.76
Don_PN	700	1720	0.95	162.5	226	609	1.3	0.79	320	0.58
Geh_V	1011	972	6.08	20.2	55	361	9.5	1.51	294	1.41
Su_C1	687	292	1.87	16.5	20	305	1.2	3.20	181	3.18
Su_C2	532	15	1.66	8.5	22	276	1.0	2.07	175	2.00
Su_R1	1046	4449	3.14	19.2	212	683	7.7	0.83	444	0.51

Appendix 2: Element concentrations (ppb) in wines

Name	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Br	Se
Su_R2	445	31	1.35	7.7	20	394	1.4	0.65	86	0.62
Su_PN	765	679	0.61	12.1	9	130	0.6	0.83	196	0.72
Haw_G	784	993	2.70	14.5	52	534	4.7	1.23	115	1.24
Pin_R	686	1850	2.71	20.2	13	659	1.8	5.49	156	5.50
Hes_PB	660	584	1.94	12.4	166	483	2.8	1.44	168	1.37
Vin_R	1403	1700	4.35	26.1	39	664	2.9	0.86	137	0.88
Gra_Ro	898	1361	1.62	36.1	40	176	1.9	1.40	154	1.34
In_PN	750	775	1.02	20.9	91	270	0.6	0.56	225	0.36
In_PB	529	488	2.04	21.4	39	486	2.7	0.73	170	0.61
Hil_M	527	3873	3.17	12.0	26	289	6.1	3.82	224	3.75
Tin_G	533	734	1.22	13.8	7	195	1.8	1.17	127	1.07
Sla_R	640	1029	1.52	24.0	22	345	1.5	1.99	134	1.98
Qu_R1	1056	788	2.56	20.8	40	266	2.1	1.26	87	1.25
Qu_R2	888	701	1.77	20.8	77	214	2.0	1.72	150	1.68
Qu_R3	980	1027	2.16	44.6	61	300	2.5	5.10	141	5.03
Qu_R4	707	458	1.42	14.9	245	367	2.0	1.49	108	1.43
Hai_Tr	601	1714	3.32	8.7	90	499	2.7	1.08	186	0.91
Nic_Sy	617	824	0.85	12.5	13	426	3.6	3.62	195	3.57
Stg_C	528	210	1.80	12.6	24	662	1.3	1.39	164	1.26
Stg_PN	405	1267	0.97	7.9	9	456	0.6	1.10	232	0.91
Red_C	932	1095	4.63	19.5	12	414	3.3	1.63	151	1.53
Wi_G1	725	727	1.93	8.8	22	453	2.6	0.40	150	0.33
Wi_G2	577	491	1.05	6.4	12	196	1.0	0.63	160	0.48
Wi_G3	953	2743	2.76	18.7	88	403	3.1	0.70	153	0.59
Wi_G4	912	1689	1.94	7.7	9	244	1.9	0.63	173	0.65
Wi_G5	885	1117	1.99	7.9	106	489	2.4	1.27	141	1.17
St_PB1	608	464	1.53	11.0	22	196	2.0	1.08	156	1.00
St_PB2	582	1024	1.56	10.3	13	186	2.1	0.77	176	0.70
St_R1	947	83	1.75	26.0	17	745	1.4	1.06	124	1.02
St_R2	1147	825	4.52	19.3	16	711	2.3	0.99	101	0.91

Appendix 2: Element concentrations (ppb) in wines

Name	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Br	Se
Ge_PB	480	1034	2.30	27.0	10	379	6.2	1.52	196	1.31
Sc_G	665	2011	1.84	7.1	40	514	4.1	0.72	162	0.64
Sc_PN	2013	1652	0.71	4.0	4	499	1.1	0.39	229	0.25
Ce_C	800	93	2.20	14.2	76	838	1.9	2.04	166	1.92
Bar_C	207	830	1.87	6.0	38	1599	1.4	3.19	262	3.16
Ro	923	2757	2.75	17.6	37	656	16.2	1.28	266	1.21
Bo	991	2687	3.71	21.5	18	648	14.4	0.68	194	0.64
Ch	714	1270	3.18	21.0	47	698	9.9	0.76	223	0.72
Sic	1237	2115	2.70	18.8	126	735	7.2	0.47	228	0.42
For	911	1964	2.61	21.1	64	709	7.5	0.73	303	0.64
Lou	641	1990	2.51	15.7	55	577	1.9	0.41	159	0.33
CdC	1196	7307	3.90	26.4	171	1077	5.2	1.49	448	1.33
Cou	1057	4241	2.80	23.1	120	933	6.5	1.43	402	1.26
Bar	1308	2660	5.03	25.2	20	894	17.3	0.68	275	0.61
Ale	1315	4304	4.61	23.3	63	886	14.4	0.59	368	0.49

Appendix 2: Element concentrations (ppb) in wines

Name	Rb	Sr	Mo	Ag	Cd	Sb	I	Cs	Ba
30B_R	1245	316	19.3	0.025	0.43	2.44	3.7	6.19	96
In_C	693	231	0.9	0.020	0.27	0.46	3.0	1.85	73
Cave_G	1198	366	20.4	0.033	0.43	2.52	3.6	6.24	115
Cave_R	896	394	11.0	0.064	0.51	3.03	4.9	5.03	97
Cave_C	1136	405	24.5	0.031	0.37	2.43	5.8	6.50	116
Mag_C	1033	344	10.9	0.012	0.62	1.18	9.1	4.75	164
Mag_Vg	269	176	7.0	0.031	0.55	1.07	5.1	5.98	69
Creek_PN	589	374	2.9	0.001	0.30	0.06	4.5	0.75	140
Creek_S	550	285	2.4	0.016	0.70	0.37	4.1	5.24	206
Pil_BN	1044	572	11.1	0.007	0.51	0.57	10.3	2.12	74
Pil_C	335	207	2.7	0.005	0.41	0.79	3.7	1.70	66
Pil_PG	411	241	13.7	0.038	0.96	0.97	14.0	1.76	84
Sto_R1	826	477	5.1	0.018	0.56	1.01	4.6	2.42	137
Sto_R2	927	277	35.2	0.009	0.73	2.56	2.8	2.54	79
Sto_R3	713	413	4.0	0.023	0.41	2.60	4.1	1.50	90
Hen_R	922	439	16.3	0.039	0.53	2.09	9.1	6.60	124
Wal_C	928	430	1.5	0.017	3.05	0.36	2.8	2.41	99
Her_R	434	1053	34.5	0.018	1.68	4.28	16.0	3.85	100
Lak_C	909	279	2.8	0.006	0.39	0.54	2.4	1.58	45
Jo_Vi	455	513	3.5	0.014	0.77	1.26	4.0	4.65	263
Jo_PG	404	365	2.6	0.033	0.80	1.14	2.8	7.99	166
Jo_C	716	218	1.5	0.004	0.74	0.21	2.6	2.69	88
Jo_R	524	248	1.7	0.007	0.31	0.24	2.3	2.52	64
Jo_BN	594	733	2.3	0.004	1.72	0.31	5.8	0.45	324
Rei_R	304	255	4.1	0.005	0.13	0.61	2.8	0.95	81
Rei_PN	607	680	37.5	0.009	0.23	2.12	4.4	4.26	174
Rei_T	341	276	6.9	0.014	0.17	1.57	3.4	1.01	72
Rei_M	1116	442	5.6	0.006	0.24	1.10	9.1	3.40	135
Rei_C	640	456	15.4	0.006	0.33	1.03	5.8	2.27	83
Mar_R	596	328	51.0	0.155	0.94	3.50	2.3	2.66	127

Appendix 2: Element concentrations (ppb) in wines

Name	Rb	Sr	Mo	Ag	Cd	Sb	I	Cs	Ba
Stn_C	198	492	67.4	0.087	0.46	5.23	8.6	0.17	133
Kon_R	555	382	5.8	0.001	0.77	0.56	2.6	1.28	65
De_F	976	884	6.2	0.018	1.05	0.74	7.3	2.76	102
De_Vi	238	340	1.0	-0.006	0.43	0.64	3.6	1.83	58
De_R	353	491	2.2	-0.005	0.64	0.87	3.4	2.69	95
De_BN	807	725	4.0	0.001	1.02	0.76	15.5	2.98	123
Ket_C	602	853	2.8	0.005	2.05	0.24	1.7	1.67	54
HR_OK	336	199	3.0	0.007	0.33	0.22	1.6	0.37	51
HR_V1	285	272	2.6	0.009	0.15	0.15	0.5	0.49	75
HR_V2	287	277	3.1	0.049	0.18	0.64	0.6	0.34	56
HR_V3	319	276	2.7	0.004	0.15	0.11	0.6	0.33	60
HR_V4	325	359	3.0	0.006	0.12	0.20	0.7	0.36	92
HR_V5	324	302	4.7	0.007	0.26	0.18	0.7	0.33	96
LB_start	545	627	5.0	0.008	0.20	0.21	4.7	1.26	80
LB_mid	545	618	5.3	0.012	0.21	0.21	3.3	1.19	77
LB_end	553	633	5.3	0.010	0.20	0.20	4.0	1.21	78
LB_T1	489	557	5.4	0.006	0.21	0.19	2.5	1.17	76
LB_T2	503	578	5.5	0.010	0.20	0.19	2.2	0.82	73
LB_T3	549	629	4.9	0.010	0.20	0.20	2.3	1.08	78
La_R95	366	820	12.5	0.004	0.23	0.15	1.6	2.01	164
La_R96	485	983	19.6	0.040	0.44	0.45	4.3	3.11	209
La_R97	355	650	14.4	0.009	0.40	1.01	2.5	3.07	147
La_R97S	385	901	9.7	0.017	0.21	0.38	3.9	1.89	174
La_R97I	471	1057	23.2	0.045	0.52	0.50	6.6	3.54	232
Don_PB	256	421	52.6	0.023	6.62	0.18	1.5	0.61	132
Don_PN	318	502	47.4	0.054	0.34	0.17	3.8	0.63	218
Geh_V	360	536	5.9	0.034	0.26	0.57	2.6	2.17	110
Su_C1	354	694	2.2	0.018	0.93	0.15	1.5	1.09	59
Su_C2	334	749	2.5	0.013	0.17	0.14	1.8	0.53	80
Su_R1	369	1923	12.9	0.023	0.43	0.35	2.7	0.99	675

Appendix 2: Element concentrations (ppb) in wines

Name	Rb	Sr	Mo	Ag	Cd	Sb	I	Cs	Ba
Su_R2	205	1142	3.5	0.003	0.21	0.13	2.7	0.45	212
Su_PN	922	926	3.7	0.003	0.46	0.04	1.3	1.79	136
Haw_G	285	828	17.8	0.012	0.45	0.76	4.2	0.74	107
Pin_R	632	1552	12.6	0.004	0.33	0.66	1.5	1.22	158
Hes_PB	273	778	8.3	0.017	0.45	0.94	2.0	0.58	142
Vin_R	377	974	2.8	0.011	0.45	2.17	2.1	2.02	319
Gra_Ro	407	855	3.0	0.006	0.17	0.27	1.3	0.97	201
In_PN	522	678	2.5	0.002	0.20	0.56	1.7	1.59	282
In_PB	257	776	5.0	0.026	0.34	0.56	2.4	0.66	143
Hil_M	406	1061	21.2	0.035	0.30	0.99	2.3	0.43	106
Tin_G	190	300	3.1	0.002	0.20	0.33	1.4	0.70	104
Sla_R	231	655	6.0	0.015	0.48	0.38	2.1	0.71	109
Qu_R1	200	913	5.2	0.008	0.52	0.38	1.6	0.58	91
Qu_R2	379	929	6.5	0.009	0.38	0.35	1.5	1.04	84
Qu_R3	415	835	6.6	0.007	0.26	0.47	2.5	0.84	94
Qu_R4	235	784	6.6	0.017	0.32	0.47	2.8	0.65	101
Hai_Tr	342	414	15.1	0.020	0.25	0.27	6.1	0.76	186
Nic_Sy	947	1478	2.8	0.003	0.32	0.10	6.6	3.42	161
Stg_C	518	914	1.9	0.008	0.22	0.25	1.1	1.58	101
Stg_PN	969	1099	3.9	0.003	0.13	0.06	1.1	3.34	116
Red_C	465	547	1.7	0.022	0.25	0.28	4.8	0.54	185
Wi_G1	771	731	3.6	0.017	0.37	0.34	0.7	1.21	118
Wi_G2	751	563	3.0	0.006	0.21	0.16	0.9	1.65	90
Wi_G3	787	763	4.7	0.029	1.43	0.51	1.1	1.61	123
Wi_G4	867	755	4.3	0.002	0.27	0.43	1.1	1.96	121
Wi_G5	689	709	5.1	0.027	0.46	0.38	0.9	1.46	119
St_PB1	341	472	2.7	0.003	0.16	0.31	2.1	1.35	89
St_PB2	368	548	3.5	-0.002	0.10	0.34	1.6	1.61	95
St_R1	214	906	5.6	0.006	0.25	0.35	1.9	0.52	195
St_R2	317	992	4.4	0.004	0.32	0.39	2.3	1.09	156

Appendix 2: Element concentrations (ppb) in wines

Name	Rb	Sr	Mo	Ag	Cd	Sb	I	Cs	Ba
Ge_PB	576	756	6.4	0.015	0.69	0.78	1.4	1.43	79
Sc_G	482	975	10.0	0.013	0.34	0.45	1.4	1.83	205
Sc_PN	484	1294	10.0	0.001	0.31	0.12	1.6	1.56	346
Ce_C	350	1164	4.9	0.020	0.35	0.72	1.6	0.53	164
Bar_C	424	693	2.3	0.010	0.73	0.49	5.4	1.32	65
Ro	1091	435	35.8	0.069	0.50	2.63	6.7	3.39	126
Bo	766	268	16.2	0.007	0.34	4.56	5.6	4.55	58
Ch	1002	261	4.9	0.010	0.31	0.94	5.4	2.37	58
Sic	712	260	15.0	0.013	0.44	1.06	6.7	1.46	78
For	792	515	7.4	0.010	0.32	1.22	7.0	3.27	89
Lou	981	492	5.1	0.020	0.12	0.32	3.4	3.11	33
CdC	1555	342	6.8	0.014	0.51	0.51	11.8	5.12	118
Cou	1572	253	7.6	0.012	0.27	0.62	11.0	4.17	103
Bar	893	438	13.6	0.028	0.49	1.48	8.0	2.12	116
Ale	902	365	14.0	0.019	0.51	1.40	9.4	1.95	106

Appendix 2: Element concentrations (ppb) in wines

Name	La	Ce	Tl	Pb	Bi	Th	U
30B_R	1.26	2.32	0.27	55.8	0.116	0.160	0.34
In_C	0.48	0.95	0.18	13.4	0.129	0.029	0.54
Cave_G	0.60	1.12	0.31	45.4	0.182	0.137	0.56
Cave_R	2.68	5.50	0.25	37.6	0.415	0.231	1.31
Cave_C	1.23	2.36	0.32	40.3	0.316	0.103	0.52
Mag_C	0.90	1.74	0.35	18.4	0.235	0.066	0.58
Mag_Vg	1.11	2.22	0.20	7.6	0.067	0.350	1.22
Creek_PN	0.02	0.06	0.19	5.0	0.036	0.010	0.01
Creek_S	0.91	2.08	0.62	10.1	0.125	0.023	0.38
Pil_BN	0.07	0.13	0.13	7.6	0.057	0.007	0.08
Pil_C	0.70	1.08	0.20	4.6	0.035	0.018	0.17
Pil_PG	0.37	0.67	0.23	9.2	0.047	0.060	0.65
Sto_R1	8.62	17.42	0.21	27.0	0.692	1.017	3.12
Sto_R2	0.99	1.85	0.25	10.6	0.245	0.072	0.60
Sto_R3	1.29	3.03	0.18	58.1	0.533	0.062	0.58
Hen_R	2.05	3.76	0.31	26.8	0.372	0.552	0.70
Wal_C	0.84	1.29	0.18	13.8	0.027	0.032	0.35
Her_R	2.47	4.22	0.22	50.7	0.139	0.173	1.46
Lak_C	0.96	1.96	0.19	10.6	0.197	0.127	0.40
Jo_Vi	1.83	3.51	0.29	27.8	0.036	0.103	0.54
Jo_PG	2.29	4.39	0.33	28.1	0.098	0.228	1.84
Jo_C	0.07	0.17	0.24	7.1	0.081	0.011	0.12
Jo_R	0.05	0.11	0.11	7.4	0.104	0.013	0.03
Jo_BN	0.06	0.10	0.14	18.2	0.065	0.029	0.03
Rei_R	0.29	0.54	0.10	12.5	0.040	0.038	0.14
Rei_PN	1.55	2.46	0.27	16.5	0.247	0.076	0.38
Rei_T	0.31	0.73	0.10	35.1	0.070	0.059	0.15
Rei_M	1.89	3.59	0.15	36.8	0.151	0.100	0.58
Rei_C	0.16	0.22	0.18	13.0	0.091	0.089	0.33
Mar_R	1.31	1.95	0.21	30.8	0.104	0.173	1.16

Appendix 2: Element concentrations (ppb) in wines

Name	La	Ce	Tl	Pb	Bi	Th	U
Stn_C	1.31	2.51	0.03	93.0	0.201	0.308	1.69
Kon_R	0.08	0.17	0.16	8.3	0.043	0.030	0.44
De_F	1.45	2.86	0.28	58.6	0.529	0.144	1.09
De_Vi	1.22	2.51	0.17	35.4	0.150	0.121	0.62
De_R	4.74	9.42	0.25	53.9	0.115	0.417	1.27
De_BN	1.62	3.22	0.30	80.6	0.104	0.139	0.90
Ket_C	0.23	0.42	0.07	3.4	0.119	0.029	0.08
HR_OK	1.63	2.84	0.07	4.2	0.021	0.234	0.35
HR_V1	0.09	0.16	0.06	6.4	0.038	0.014	0.04
HR_V2	0.05	0.12	0.08	26.1	0.121	0.008	0.04
HR_V3	0.02	0.06	0.05	2.7	0.062	0.010	0.02
HR_V4	0.09	0.17	0.04	3.4	0.083	0.021	0.06
HR_V5	0.80	1.48	0.05	6.0	0.027	0.183	0.68
LB_start	0.76	1.66	0.12	8.1	0.108	0.199	0.32
LB_mid	0.50	1.29	0.11	8.0	0.150	0.175	0.23
LB_end	0.47	1.25	0.11	7.2	0.117	0.162	0.21
LB_T1	0.52	1.37	0.11	7.4	0.105	0.162	0.21
LB_T2	0.50	1.25	0.10	7.2	0.310	0.479	0.14
LB_T3	0.40	0.94	0.11	7.5	0.142	0.336	0.20
La_R95	0.01	0.01	0.18	9.5	0.051	0.008	0.04
La_R96	0.01	0.05	0.50	3.7	0.014	0.005	0.11
La_R97	0.09	0.28	0.32	6.2	0.133	0.013	0.16
La_R97S	0.07	0.15	0.32	5.0	0.066	0.008	0.05
La_R97I	0.45	1.39	0.40	12.6	0.160	0.419	0.39
Don_PB	0.01	0.02	0.04	20.8	0.047	0.008	0.05
Don_PN	0.01	0.02	0.05	19.2	0.041	0.015	0.03
Geh_V	0.35	0.74	0.17	10.3	0.268	0.040	0.77
Su_C1	0.21	0.47	0.05	4.4	0.073	0.047	0.24
Su_C2	0.01	0.03	0.06	2.5	0.046	0.018	0.00
Su_R1	0.05	0.17	0.14	7.8	0.036	0.015	0.27

Appendix 2: Element concentrations (ppb) in wines

Name	La	Ce	Tl	Pb	Bi	Th	U
Su_R2	0.00	0.00	0.05	5.2	0.019	0.018	0.01
Su_PN	0.01	0.02	0.08	2.6	0.009	0.005	0.03
Haw_G	0.32	0.68	0.09	19.7	3.094	0.038	0.86
Pin_R	0.32	0.74	0.07	7.4	0.055	0.056	0.20
Hes_PB	0.41	0.78	0.06	19.1	0.237	0.337	8.74
Vin_R	0.42	0.97	0.12	27.9	0.174	0.076	2.86
Gra_Ro	1.12	2.34	0.13	17.7	0.846	0.224	0.63
In_PN	0.07	0.14	0.13	40.1	0.046	0.020	0.80
In_PB	0.36	0.75	0.08	18.2	0.172	0.057	0.84
Hil_M	1.07	2.88	0.10	17.4	0.178	0.239	1.18
Tin_G	0.02	0.04	0.06	12.4	0.547	0.023	0.77
Sla_R	0.39	0.61	0.08	17.1	0.315	0.113	0.38
Qu_R1	0.04	0.10	0.06	13.7	0.357	0.017	0.20
Qu_R2	0.06	0.17	0.06	10.0	0.201	0.014	0.35
Qu_R3	0.06	0.13	0.07	7.4	0.181	0.017	0.13
Qu_R4	0.06	0.14	0.05	10.7	0.246	0.017	0.34
Hai_Tr	2.72	5.01	0.08	8.1	0.314	0.196	1.90
Nic_Sy	0.01	0.03	0.25	17.4	0.089	0.005	0.01
Stg_C	0.23	0.42	0.13	4.3	0.076	0.045	0.75
Stg_PN	0.01	0.01	0.10	2.4	0.072	0.026	0.02
Red_C	0.08	0.19	0.12	8.2	0.432	0.049	0.16
Wi_G1	0.03	0.06	0.10	27.5	0.910	0.233	0.99
Wi_G2	0.45	0.88	0.09	18.9	0.567	0.344	1.45
Wi_G3	0.60	1.12	0.13	34.7	0.253	0.221	0.92
Wi_G4	1.05	2.22	0.12	34.3	0.294	0.322	0.43
Wi_G5	0.91	2.01	0.10	25.4	0.640	0.437	1.53
St_PB1	0.16	0.27	0.11	1.9	0.113	0.035	0.25
St_PB2	0.04	0.06	0.11	1.7	0.149	0.028	0.32
St_R1	0.00	0.01	0.06	1.6	0.036	0.014	0.01
St_R2	2.03	3.89	0.07	5.1	0.105	0.111	0.48

Appendix 2: Element concentrations (ppb) in wines

Name	La	Ce	Tl	Pb	Bi	Th	U
Ge_PB	0.46	0.90	0.14	12.3	0.581	0.168	0.90
Sc_G	0.72	1.53	0.09	10.7	0.349	0.076	0.41
Sc_PN	0.01	0.00	0.05	3.3	0.018	0.016	0.11
Ce_C	0.02	0.03	0.08	15.3	0.017	0.007	0.03
Bar_C	0.01	0.01	0.04	15.1	0.019	0.026	0.12
Ro	1.44	2.88	0.23	29.5	0.997	0.411	1.65
Bo	0.92	1.96	0.26	25.2	0.212	0.058	0.13
Ch	0.21	0.43	0.14	16.1	0.633	0.030	0.32
Sic	0.58	1.08	0.12	20.7	0.252	0.114	0.41
For	0.59	1.14	0.24	27.4	0.514	0.050	0.27
Lou	0.23	0.48	0.09	6.8	0.079	0.026	0.08
CdC	0.31	0.53	0.17	26.2	0.180	0.060	0.13
Cou	0.55	1.01	0.15	18.7	0.093	0.059	0.17
Bar	2.31	4.41	0.22	28.6	1.187	0.097	0.95
Ale	1.95	3.36	0.23	25.9	0.246	0.570	0.78

Appendix 3: Element concentrations in wines prepared by the digestion method

Winery	Variety	Name	Li ppb	Be ppb	Mg ppb	Al ppb	Si ppb
Hernder	Riesling	Her_R	35.66	0.90	77108	2216	12131
Cave Spring	Riesling	Cave_R	43.62	1.31	82732	1133	8535
Joseph's	Chardonnay	Jo_C	2.06	0.35	65738	381	10914
Lakeview	Chardonnay	Lak_C	10.11	0.22	81757	296	6985
Pillitteri	Pinot Gris	Pil_PG	2.38	0.39	62898	570	4549
Scherzinger	Gewurztraminer	Sc_G	13.02	0.46	111501	330	14615
Gehringer	Pinot Blanc	Geh_V	16.04	1.19	65005	1073	8571
Nichol	Syrah	Nic_Sy	15.37	0.06	79048	145	8267
Lake Breeze	Pinot Blanc	LB_T3	9.23	0.99	60380	534	6910
St. Hubertus	Riesling	St_R1	22.04	0.30	105353	310	7954

Name	P ppb	Cl ppb	Ca ppb	Ti ppb	V ppb	Cr ppb	Mn ppb
Her_R	82301	17210	105928	20.7	166.9	33.1	1062
Cave_R	116175	5213	104576	20.7	25.3	14.0	515
Jo_C	106234	3312	53896	5.7	2.7	10.6	1285
Lak_C	110625	10399	67055	13.9	22.2	10.2	1527
Pil_PG	222420	2985	77135	14.2	74.0	17.5	1635
Sc_G	275722	8506	118424	12.3	3.7	10.8	709
Geh_V	119287	7117	115271	13.6	158.6	10.1	1100
Nic_Sy	68814	5026	59135	3.3	0.5	11.9	787
LB_T3	93911	1789	59741	4.2	3.3	10.2	397
St_R1	325023	3450	79580	8.5	4.5	18.3	992

Appendix 3: Element concentrations in wines prepared by the digestion method

Name	Fe ppb	Co ppb	Ni ppb	Cu ppb	Zn ppb	As ppb	Br ppb
Her_R	1880	4.2	36.6	112	1017	16.0	147
Cave_R	1281	4.7	25.0	51	648	14.5	86
Jo_C	557	2.1	16.3	42	559	1.4	138
Lak_C	2431	4.6	66.5	94	604	5.1	161
Pil_PG	837	3.2	17.3	<38.63	708	7.1	149
Sc_G	2511	2.0	16.9	73	596	5.3	169
Geh_V	1126	6.0	22.3	73	387	10.6	206
Nic_Sy	951	0.8	16.3	<36.00	478	4.2	139
LB_T3	774	2.7	13.0	<36.21	226	2.7	81
St_R1	920	3.8	18.6	<39.36	662	2.5	77

Name	Rb ppb	Sr ppb	Mo ppb	Ag ppb	Cd ppb	Sb ppb	I ppb
Her_R	412	985	27.6	0.04	1.85	4.02	17.22
Cave_R	890	349	8.3	0.12	0.66	2.95	3.42
Jo_C	684	180	1.3	<0.03	0.94	0.20	1.93
Lak_C	1021	276	2.5	<0.04	0.50	0.56	1.67
Pil_PG	506	267	12.0	0.05	1.16	1.04	2.87
Sc_G	585	1118	10.6	<0.05	0.49	0.57	0.79
Geh_V	393	506	4.6	0.12	0.33	0.54	1.91
Nic_Sy	1125	1573	2.1	0.00	0.40	0.10	1.94
LB_T3	516	537	3.9	<0.04	0.23	0.18	1.50
St_R1	359	906	3.7	0.04	0.32	0.41	1.78

Appendix 3: Element concentrations in wines prepared by the digestion method

Name	Cs ppb	Ba ppb	La ppb	Ce ppb	Tl ppb	Pb ppb	Bi ppb	U ppb
Her_R	3.61	85	2.33	4.31	0.23	48	0.11	1.46
Cave_R	4.69	89	2.53	5.60	0.26	36	0.19	1.35
Jo_C	2.53	79	0.07	0.17	0.22	8	0.04	0.11
Lak_C	1.65	47	0.94	2.10	0.18	12	0.11	0.39
Pil_PG	1.95	84	0.37	0.73	0.23	11	0.03	0.75
Sc_G	2.44	251	0.92	2.06	0.12	15	0.28	0.48
Geh_V	2.22	95	0.05	0.11	0.16	9	0.12	0.77
Nic_Sy	3.24	146	0.01	0.04	0.25	18	0.04	0.01
LB_T3	1.09	66	0.41	1.17	0.10	9	0.16	0.22
St_R1	1.13	156	2.10	4.30	0.07	7	0.08	0.54

Appendix 4: Pearson's R correlation coefficients between element concentrations in wines

	Li	Be	Mg	Al	P	Cl	Ca	Ti
Li	1.00							
Be	0.20	1.00						
Mg	0.59	0.12	1.00					
Al	0.20	0.68	0.14	1.00				
P	0.20	-0.13	0.38	-0.05	1.00			
Cl	0.13	0.11	0.30	0.40	0.10	1.00		
Ca	0.18	0.24	0.35	0.38	0.34	0.28	1.00	
Ti	0.27	0.54	0.16	0.71	-0.02	0.25	0.28	1.00
V	0.21	0.34	-0.05	0.61	0.01	0.27	0.19	0.67
Mn	-0.01	0.13	0.10	0.36	0.05	0.35	0.29	0.29
Co	0.24	0.61	0.24	0.71	-0.04	0.35	0.35	0.62
Ni	-0.07	-0.02	-0.03	0.11	-0.04	0.08	-0.04	0.02
Cu	-0.04	0.29	0.12	0.25	-0.08	0.12	0.10	0.10
Zn	-0.05	-0.11	0.05	0.15	-0.03	0.19	0.00	0.08
As	0.26	0.54	0.19	0.61	-0.02	0.21	0.41	0.69
Br	-0.16	-0.07	0.05	0.25	0.26	0.63	0.37	0.16
Se	0.23	-0.02	0.13	0.14	0.05	0.03	0.04	0.04
Rb	0.11	0.16	0.11	0.22	0.10	0.35	0.11	0.39
Sr	0.36	-0.17	0.55	-0.18	0.02	0.07	0.12	-0.18
Mo	0.11	0.28	0.08	0.38	0.00	0.07	0.17	0.47
Ag	0.15	0.35	0.09	0.43	0.04	0.03	0.17	0.43
Cd	-0.05	-0.09	0.01	0.10	0.01	0.10	-0.06	0.03
Sb	0.33	0.57	0.06	0.70	-0.01	0.20	0.25	0.75
I	0.06	0.28	0.03	0.54	0.13	0.57	0.33	0.39
Cs	0.08	0.33	0.04	0.60	-0.04	0.30	0.30	0.55
Ba	0.02	-0.04	0.43	0.06	-0.08	0.11	0.20	0.01
La	0.14	0.26	-0.02	0.51	-0.11	0.20	0.06	0.67
Ce	0.15	0.27	-0.01	0.49	-0.12	0.20	0.07	0.65
Tl	0.00	0.29	0.10	0.60	0.00	0.39	0.39	0.39
Pb	0.13	0.48	0.01	0.55	-0.15	0.44	0.04	0.60
Bi	0.14	0.16	0.03	-0.02	-0.14	-0.01	-0.03	0.14
Th	0.11	0.40	0.00	0.40	-0.17	0.10	0.06	0.53
U	0.03	0.18	0.04	0.26	-0.06	0.03	0.04	0.30

Appendix 4: Pearson's R correlation coefficients between element concentrations in wines

	V	Mn	Co	Ni	Cu	Zn	As	Br
V	1.00							
Mn	0.19	1.00						
Co	0.38	0.33	1.00					
Ni	0.02	0.13	0.07	1.00				
Cu	0.04	0.43	0.19	0.20	1.00			
Zn	0.09	0.21	0.16	0.26	0.13	1.00		
As	0.51	0.32	0.71	0.06	0.40	0.09	1.00	
Br	0.21	0.41	0.20	0.10	0.11	0.20	0.17	1.00
Se	0.10	-0.06	0.06	-0.01	-0.03	0.17	0.07	0.11
Rb	0.15	0.19	0.40	-0.05	-0.09	0.14	0.34	0.24
Sr	-0.17	-0.11	-0.17	-0.11	-0.06	-0.09	-0.10	-0.01
Mo	0.64	0.02	0.17	0.48	0.16	0.08	0.48	0.10
Ag	0.57	-0.03	0.28	0.17	0.12	0.03	0.43	0.06
Cd	0.09	0.08	0.02	0.58	0.06	0.60	-0.03	0.12
Sb	0.80	0.21	0.51	0.04	0.18	0.10	0.68	0.14
I	0.45	0.28	0.43	0.09	0.11	0.19	0.40	0.69
Cs	0.28	0.20	0.69	0.01	-0.02	0.15	0.59	0.22
Ba	-0.11	0.26	0.04	0.12	0.14	0.02	0.07	0.22
La	0.34	0.21	0.42	0.01	-0.01	0.09	0.25	0.05
Ce	0.31	0.21	0.42	0.00	-0.00	0.06	0.23	0.04
Tl	0.24	0.31	0.63	0.00	0.08	0.15	0.48	0.36
Pb	0.50	0.17	0.40	0.13	0.27	0.12	0.37	0.26
Bi	0.08	-0.01	0.05	-0.08	-0.09	-0.12	0.05	-0.15
Th	0.20	0.10	0.34	-0.06	0.01	-0.12	0.24	-0.10
U	0.23	0.02	0.12	-0.08	0.02	-0.02	0.06	-0.03

Appendix 4: Pearson's R correlation coefficients between element concentrations in wines

	Se	Rb	Sr	Mo	Ag	Cd	Sb	I
Se	1.00							
Rb	0.03	1.00						
Sr	0.30	-0.07	1.00					
Mo	0.06	0.00	-0.02	1.00				
Ag	0.03	0.02	-0.13	0.63	1.00			
Cd	0.17	0.04	-0.06	0.33	0.10	1.00		
Sb	0.10	0.22	-0.17	0.63	0.57	0.05	1.00	
I	0.12	0.28	-0.06	0.28	0.14	0.11	0.43	1.00
Cs	0.08	0.56	-0.18	0.13	0.20	0.04	0.43	0.37
Ba	-0.08	-0.09	0.57	0.11	0.05	0.00	-0.03	0.01
La	-0.01	0.21	-0.18	0.08	0.13	0.03	0.34	0.28
Ce	-0.01	0.20	-0.17	0.05	0.11	0.01	0.31	0.26
Tl	0.02	0.41	-0.14	0.10	0.18	0.02	0.28	0.41
Pb	-0.02	0.29	-0.11	0.35	0.33	0.13	0.67	0.45
Bi	-0.05	0.02	0.04	0.03	0.02	-0.06	0.06	-0.01
Th	-0.02	0.18	-0.11	0.07	0.19	-0.06	0.21	0.12
U	-0.03	-0.04	-0.01	0.07	0.16	-0.01	0.26	0.07

	Cs	Ba	La	Ce	Tl	Pb	Bi	Th
Cs	1.00							
Ba	0.03	1.00						
La	0.33	-0.04	1.00					
Ce	0.32	-0.04	1.00	1.00				
Tl	0.75	0.14	0.26	0.26	1.00			
Pb	0.31	-0.01	0.40	0.40	0.22	1.00		
Bi	-0.05	-0.07	0.14	0.15	-0.06	0.14	1.00	
Th	0.21	-0.10	0.73	0.75	0.12	0.29	0.21	1.00
U	0.06	0.05	0.36	0.36	-0.01	0.27	0.17	0.47

Appendix 5: Element concentrations in vineyard soil

vineyard (0.074 mm fraction)	pH	Conductivity mS/cm	Na2O % w/w	MgO % w/w	Al2O3 % w/w	SiO2 % w/w
Hainle	7.3	25	2.71	2.52	15.6	66
Gray Monk	6.3	61	1.82	2.60	15.9	66
Gehringer Brothers	7.5	130	1.54	3.23	13.5	63
Hester Creek	7.3	108	1.57	4.01	13.8	64
Tin Horn Creek	7.2	262	1.25	3.54	12.1	59
Inkameep	7.3	39	2.14	2.19	15.3	64
Lake Breeze	6.6	857	2.18	3.50	14.8	63
Lang	6.2	60	1.93	2.74	15.9	67
Red Rooster	8	117	2.61	2.48	14.2	62
Nichol	6.9	151	2.32	2.91	13.1	66
Kettle Valley	7.4	180	2.28	3.86	16.2	63
Irvine	7.9	1020	2.21	3.51	14.6	63
House of Rose	6.5	42	2.01	2.29	13.6	68
Gersighel Wineberg	7.4	122	2.02	3.73	12.8	63
Inniskillin	7.2	87	1.61	4.55	13.9	63
St. Hubertus	7.5	48	2.17	1.96	14.8	65
Summerhill	7.4	68	2.58	2.02	14.7	71
Slamka	7.5	69	1.93	2.71	16.2	67
McKenzie	6.7	67	2.00	2.36	15.4	64
Cedar Creek	7	87	1.74	2.65	15.6	67
Hillside	8	102	2.37	4.05	15.1	69
Stag's Hollow	7.5	45	2.70	2.47	15.9	64
Pinot Reach	7.4	157	1.69	3.49	13.7	58
Scherzinger	6.5	128	2.02	2.33	16.0	66
Quail's Gate	7.4	93	1.91	3.16	15.8	65
Wild Goose	7.4	75	2.39	2.17	15.9	64
Konzelmann	6.7	53	1.44	1.94	13.2	73
Stonechurch	7.2	87	1.22	2.22	13.6	70
Pillitteri	6.1	34	1.54	2.12	14.1	67

Appendix 5: Element concentrations in vineyard soil

vineyard (0.074 mm fraction)	pH	Conductivity mS/cm	Na2O % w/w	MgO % w/w	Al2O3 % w/w	SiO2 % w/w
Pillitteri (Baco Noir)	6.6	76	1.18	2.17	15.2	70
Creekside (Pilliterri plot)	5.9	37	1.30	1.73	13.7	66
30 Bench	7.2	201	1.02	2.93	14.8	65
Marynissen	7.4	116	1.12	2.19	15.0	67
Reif	7.6	137	1.18	2.52	13.6	68
Lenko	6.7	119	1.14	2.48	13.9	71
Hernder	7.3	129	1.01	3.30	15.4	65
Inniskillin	7.4	67	1.25	2.23	13.8	70
De Sousa	6.7	81	0.98	2.76	14.6	65
Cavespring	6.4	57	0.99	2.81	15.2	68
Henry of Pelham	7.6	162	0.89	3.17	16.4	62
Walter's	7.1	285	1.22	2.56	13.9	70
Joseph's	6.7	164	1.48	1.99	13.1	70
Lakeview	7.2	275	1.21	2.58	14.0	73
Detection limit			0.02	0.02	0.01	0.01

Appendix 5: Element concentrations in vineyard soil

vineyard (0.074 mm fraction)	P2O5 % w/w	K2O % w/w	CaO % w/w	TiO2 % w/w	MnO % w/w	Fe2O3T % w/w
Hainle	0.08	2.58	3.01	0.77	0.089	4.8
Gray Monk	0.20	2.68	2.29	0.01	0.051	17.4
Gehringer Brothers	0.35	2.30	4.21	0.72	0.132	5.8
Hester Creek	0.35	2.22	3.05	0.84	0.184	6.2
Tin Horn Creek	0.37	2.19	6.85	0.76	0.157	6.7
Inkameep	0.19	2.34	2.85	0.69	0.123	4.9
Lake Breeze	0.24	2.63	5.04	0.75	0.097	5.4
Lang	0.21	2.58	2.56	0.69	0.102	5.1
Red Rooster	0.28	2.34	4.64	0.62	0.084	4.5
Nichol	0.23	2.31	4.41	0.53	0.095	4.0
Kettle Valley	0.22	2.85	4.91	0.74	0.098	5.8
Irvine	0.22	2.69	5.79	0.73	0.094	5.4
House of Rose	0.28	2.04	2.88	0.68	0.108	5.1
Gersighel Wineberg	0.36	2.13	3.96	0.68	0.144	5.3
Inniskillin	0.27	2.28	3.03	0.87	0.150	6.5
St. Hubertus	0.19	2.39	2.78	0.67	0.081	4.7
Summerhill	0.25	2.29	3.57	0.74	0.078	4.2
Slamka	0.12	2.60	2.70	0.01	0.053	19.8
McKenzie	0.14	2.37	2.75	0.69	0.090	4.9
Cedar Creek	0.15	2.69	2.18	0.70	0.127	5.8
Hillside	0.22	2.99	4.42	0.63	0.093	4.6
Stag's Hollow	0.27	2.40	3.82	0.58	0.099	4.5
Pinot Reach	0.21	2.45	8.42	0.74	0.101	5.7
Scherzinger	0.17	2.25	3.02	0.01	0.048	6.6
Quail's Gate	0.15	2.92	2.83	0.74	0.118	5.5
Wild Goose	0.14	2.43	3.06	0.63	0.084	4.7
Konzelmann	0.17	2.10	1.07	0.93	0.076	3.9
Stonechurch	0.22	2.17	1.28	0.94	0.074	4.6
Pillitteri	0.42	1.67	1.71	1.58	0.135	7.3

Appendix 5: Element concentrations in vineyard soil

vineyard (0.074 mm fraction)	P2O5 % w/w	K2O % w/w	CaO % w/w	TiO2 % w/w	MnO % w/w	Fe2O3T % w/w
Pillitteri (Baco Noir)	0.09	2.36	0.77	0.95	0.049	5.4
Creekside (Pilliterri plot)	0.24	1.49	1.24	1.35	0.102	5.7
30 Bench	0.14	2.72	2.19	0.90	0.119	6.0
Marynissen	0.12	1.97	1.22	0.90	0.049	5.1
Reif	0.24	2.36	2.71	0.87	0.090	4.6
Lenko	0.29	2.44	1.02	0.91	0.089	4.8
Hernder	0.15	2.86	3.85	0.94	0.081	6.1
Inniskillin	0.19	2.17	1.13	0.91	0.078	4.6
De Sousa	0.14	2.63	0.85	0.90	0.082	5.6
Cavespring	0.11	2.69	0.73	0.97	0.078	6.0
Henry of Pelham	0.13	3.04	1.02	0.89	0.089	6.8
Walter's	0.13	2.37	1.16	0.90	0.097	5.0
Joseph's	0.18	1.78	1.53	0.94	0.073	4.5
Lakeview	0.11	2.39	1.52	0.99	0.067	4.7
Detection limit	0.005	0.003	0.003	0.003	0.002	0.005

Appendix 5: Element concentrations in vineyard soil

vineyard (0.074 mm fraction)	S ppm	Cl ppm	Sc ppm	V ppm	Cr ppm	Ni ppm	Cu ppm	Zn ppm	Ga ppm
Hainle	142	366	13	96	55	2.0	10.7	44	15.9
Gray Monk	395	249	15	93	87	0.0	25.4	52	16.3
Gehringer Brothers	660	103	8	120	133	38.6	55.5	64	14.1
Hester Creek	897	200	15	118	153	43.5	50.4	60	12.5
Tin Horn Creek	968	143	35	135	182	54.7	70.9	72	13.7
Inkameep	300	152	10	90	67	11.6	30.1	63	14.8
Lake Breeze	511	103	15	118	101	13.4	25.7	47	15.9
Lang	370	252	17	100	85	17.1	23.9	53	18.6
Red Rooster	162	133	13	90	75	4.3	9.7	37	16.7
Nichol	330	362	6	72	27	-0.4	11.2	39	15.5
Kettle Valley	254	101	15	123	90	19.7	30.2	54	17.2
Irvine	604	93	18	110	103	19.2	28.9	41	15.4
House of Rose	345	245	11	86	85	15.7	22.4	56	15.8
Gersighel Wineberg	1232	374	9	86	145	41.7	37.7	63	15.5
Inniskillin	731	104	14	126	198	56.7	46.9	54	13.7
St. Hubertus	133	166	10	83	93	6.9	10.1	33	13.6
Summerhill	173	213	10	75	59	3.2	15.0	33	14.4
Slamka	200	184	14	95	108	0.0	19.8	48	16.3
McKenzie	198	146	9	102	79	12.3	24.4	49	17.8
Cedar Creek	262	217	14	99	83	19.5	24.4	70	17.7
Hillside	340	419	19	87	74	13.0	22.6	58	19.0
Stag's Hollow	266	201	17	88	58	16.6	17.5	37	17.1
Pinot Reach	176	53	24	117	111	20.8	31.2	43	12.6
Scherzinger	341	178	14	100	56	0.0	22.8	53	14.9
Quail's Gate	333	154	19	98	89	18.3	35.2	63	16.9
Wild Goose	163	288	12	74	66	6.5	19.1	46	19.0
Konzelmann	417	88	9	68	46	4.8	20.6	41	14.1
Stonechurch	354	90	11	77	65	8.1	13.3	41	12.9
Pillitteri	672	169	17	120	84	9.7	14.8	48	11.5

Appendix 5: Element concentrations in vineyard soil

vineyard	S	Cl	Sc	V	Cr	Ni	Cu	Zn	Ga
(0.074 mm fraction)	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Pillitteri (Baco Noir)	355	103	13	88	60	8.4	24.5	26	15.6
Creekside (Pilliterri plot)	572	114	16	93	81	6.4	12.6	42	11.9
30 Bench	197	92	14	107	63	16.1	35.5	46	14.8
Marynissen	436	82	16	95	53	9.6	17.6	40	13.5
Reif	459	111	18	66	57	9.4	35.3	65	13.1
Lenko	378	136	16	73	62	11.5	33.3	51	13.8
Hernder	241	115	22	99	77	20.2	21.2	43	19.4
Inniskillin	414	83	16	76	48	10.3	24.3	47	13.0
De Sousa	222	97	15	91	53	11.5	27.5	39	15.2
Cavespring	299	71	11	91	72	16.0	26.9	54	18.4
Henry of Pelham	212	95	19	126	81	22.3	24.9	48	19.1
Walter's	337	96	15	81	58	11.6	26.0	54	13.5
Joseph's	408	70	18	71	57	10.1	31.1	47	14.2
Lakeview	231	103	20	74	54	15.9	22.1	41	14.5
Detection limit	24	44	10	9	10	7	6	4	4

Appendix 5: Element concentrations in vineyard soil

vineyard (0.074 mm fraction)	As ppm	Rb ppm	Sr ppm	Y ppm	Zr ppm	Nb ppm	Ba ppm	Ce ppm	Pb ppm
Hainle	-1.2	84	447	18	282	15.4	1013	65	8
Gray Monk	37.3	83	331	20	235	15.4	943	98	97
Gehringer Brothers	21.4	65	345	21	211	17.5	1799	4	11
Hester Creek	19.9	62	351	20	215	16.6	1249	57	12
Tin Horn Creek	14.2	64	282	19	163	16.2	2353	112	24
Inkameep	17.4	71	501	23	329	17.4	1031	93	16
Lake Breeze	13.3	78	474	27	369	19.7	987	90	16
Lang	38.7	81	395	22	286	17.0	1030	92	78
Red Rooster	1.9	63	633	20	390	19.1	1116	88	16
Nichol	26.8	57	602	19	352	15.6	1090	79	53
Kettle Valley	14.2	88	474	21	233	19.1	1095	64	25
Irvine	2.0	81	483	27	361	21.1	1039	52	18
House of Rose	31.8	62	384	25	344	16.9	889	95	66
Gersighel Wineberg	22.5	58	504	18	200	16.2	919	67	55
Inniskillin	14.9	65	355	19	211	20.1	1400	31	11
St. Hubertus	-2.3	69	460	20	350	16.6	917	90	11
Summerhill	-3.1	66	523	21	378	17.1	879	51	11
Slamka	12.2	79	368	25	326	17.9	856	113	14
McKenzie	14.9	75	402	22	305	15.4	966	6	16
Cedar Creek	10.7	86	324	21	185	15.4	966	56	12
Hillside	24.6	81	510	18	224	14.4	855	51	54
Stag's Hollow	-3.5	62	730	18	287	18.4	1273	100	15
Pinot Reach	17.0	78	437	22	289	18.2	959	45	16
Scherzinger	-0.5	73	426	22	287	15.4	1016	66	21
Quail's Gate	13.3	87	390	20	244	18.9	952	47	17
Wild Goose	3.9	70	551	20	265	17.3	1115	49	11
Konzelmann	14.4	67	146	29	719	18.7	473	65	22
Stonechurch	4.4	74	143	31	733	19.9	467	92	13
Pillitteri	6.4	48	154	55	2925	38.4	312	177	21

Appendix 5: Element concentrations in vineyard soil

vineyard	As	Rb	Sr	Y	Zr	Nb	Ba	Ce	Pb
(0.074 mm fraction)	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Pillitteri (Baco Noir)	-12.5	87	127	20	497	19.5	455	77	13
Creekside (Pilliterri plot)	-4.5	45	148	48	2559	30.9	390	153	18
30 Bench	13.4	90	134	30	365	17.3	494	97	12
Marynissen	13.9	74	126	23	438	18.6	455	102	14
Reif	8.4	74	143	28	427	17.6	466	91	40
Lenko	3.2	78	142	22	463	18.7	490	84	19
Hernder	1.4	102	157	28	294	18.2	499	114	19
Inniskillin	3.7	77	126	28	437	18.0	469	85	30
De Sousa	8.0	94	134	27	424	19.1	557	61	13
Cavespring	6.0	99	121	25	366	20.5	478	109	16
Henry of Pelham	15.8	108	151	37	329	16.3	569	131	15
Walter's	14.4	82	144	26	426	18.4	456	112	32
Joseph's	7.1	62	132	31	664	18.9	434	96	29
Lakeview	-0.9	84	130	21	444	20.2	441	82	16
Detection limit	21	2.1	1.9	1.9	1.9	2.2	33	58	7

Appendix 5: Element concentrations in vineyard soil

vineyard (0.074 mm fraction)	Th ppm	U ppm
Hainle	7.6	3.71
Gray Monk	10.1	0.68
Gehringer Brothers	9.1	-1.51
Hester Creek	6.8	3.00
Tin Horn Creek	5.3	-1.88
Inkameep	11.0	7.19
Lake Breeze	13.2	3.00
Lang	15.0	1.96
Red Rooster	10.6	6.43
Nichol	9.5	-0.70
Kettle Valley	11.1	0.30
Irvine	16.5	3.11
House of Rose	9.4	-0.15
Gersighel Wineberg	7.7	11.15
Inniskillin	4.8	2.18
St. Hubertus	7.2	2.24
Summerhill	9.3	6.37
Slamka	12.0	0.80
McKenzie	12.3	1.69
Cedar Creek	10.4	-2.13
Hillside	11.7	-0.65
Stag's Hollow	10.3	0.58
Pinot Reach	11.2	-1.54
Scherzinger	11.2	2.80
Quail's Gate	12.2	2.56
Wild Goose	7.6	7.14
Konzelmann	8.1	5.02
Stonechurch	6.4	3.91
Pillitteri	8.7	8.86

Appendix 5: Element concentrations in vineyard soil

vineyard	Th	U
(0.074 mm fraction)	ppm	ppm
Pillitteri (Baco Noir)	9.6	3.15
Creekside (Pilliterri plot)	14.4	8.09
30 Bench	6.5	1.07
Marynissen	8.2	4.18
Reif	8.9	3.48
Lenko	9.1	1.71
Hernder	15.1	5.80
Inniskillin	7.2	3.69
De Sousa	9.3	6.71
Cavespring	11.1	1.89
Henry of Pelham	11.0	1.36
Walter's	6.8	4.81
Joseph's	7.6	1.25
Lakeview	12.7	5.26
Detection limit	5	6

Appendix 5: Element concentrations in vineyard soil

Vineyard (2 mm fraction)	Region	Na2O wt%	MgO wt%	Al2O3 wt%	SiO2 wt%	P2O5 wt%	K2O wt%	CaO wt%	TiO2 wt%	MnO wt%
Cave Spring	ON	0.76	2.32	13.4	61	0.10	2.60	0.76	0.94	0.113
Henry of Pelham	ON	0.79	3.39	16.8	62	0.14	3.26	1.08	0.94	0.116
Marynissen	ON	0.90	2.03	13.1	62	0.11	1.96	1.24	0.82	0.059
De Sousa	ON	0.92	2.87	15.0	64	0.15	2.82	0.89	0.92	0.131
Herndner	ON	0.93	3.22	15.3	63	0.15	3.07	4.31	0.98	0.107
Thirty Bench	ON	0.96	2.95	15.2	66	0.14	2.94	2.43	0.92	0.169
Lakeview	ON	1.07	2.69	14.2	71	0.13	2.56	1.98	0.99	0.101
Joseph's	ON	1.07	2.24	12.2	65	0.17	2.04	2.67	0.79	0.105
Pilliterri	ON	1.22	1.52	11.5	66	0.33	1.66	1.60	0.84	0.090
Konzelmann	ON	1.24	2.00	12.9	71	0.18	2.16	1.17	0.82	0.085
Inniskillin (BC)	BC	1.35	4.57	13.2	61	0.25	2.31	2.87	0.84	0.155
Pinot Reach	BC	1.46	3.55	14.7	58	0.20	2.82	4.40	0.77	0.115
Slamka	BC	1.54	2.52	14.4	62	0.12	2.60	2.44	0.69	0.110
House of Rose	BC	1.66	2.06	12.8	63	0.24	2.04	2.57	0.61	0.102
Gersighel	BC	1.70	4.38	12.1	60	0.36	2.23	4.01	0.73	0.165
Inkameep	BC	1.73	1.94	13.5	61	0.16	2.41	2.37	0.57	0.098
McKenzie	BC	1.74	2.27	15.0	62	0.15	2.47	2.64	0.68	0.102
Irvine	BC	1.82	3.23	13.2	58	0.16	2.54	5.06	0.59	0.083
Nichol	BC	2.01	2.78	12.6	62	0.21	2.44	4.09	0.49	0.085
Wild Goose	BC	2.17	2.27	15.3	60	0.15	2.53	3.36	0.62	0.096

Appendix 5: Element concentrations in vineyard soil

Vineyard (2 mm fraction)	Fe2O3T wt%	S ppm	Cl ppm	Sc ppm	V ppm	Cr ppm	Ni ppm	Cu ppm	Zn ppm	Ga ppm
Cave Spring	6.9	306	83	11	101	76	13.8	26.2	46	16.2
Henry of Pelham	7.5	206	101	19	129	94	21.7	28.4	44	18.7
Marynissen	5.0	350	87	12	88	71	4.3	14.6	24	11.9
De Sousa	6.5	253	120	11	107	88	15.1	26.7	43	16.5
Herndner	7.1	195	91	13	119	80	21.7	26.7	44	18.0
Thirty Bench	6.7	180	92	16	114	79	19.1	33.3	42	15.7
Lakeview	5.5	228	154	12	92	66	12.0	25.3	39	15.5
Joseph's	4.4	388	91	6	78	69	8.5	18.6	26	10.6
Pilliterri	4.2	487	138	5	77	55	0.1	5.8	11	10.0
Konzelmann	3.8	420	93	9	62	80	2.6	20.3	26	12.7
Inniskillin (BC)	6.7	673	97	15	138	236	52.3	42.4	40	13.1
Pinot Reach	6.4	124	124	13	126	145	24.2	25.6	37	15.8
Slamka	5.1	158	97	15	81	113	14.8	17.9	31	14.8
House of Rose	4.3	300	199	9	76	107	9.1	11.2	31	15.4
Gersighel	6.2	1323	278	15	111	203	48.7	35.2	52	12.1
Inkameep	4.1	199	99	10	83	92	4.9	18.7	32	11.7
McKenzie	4.9	227	143	12	97	113	9.3	18.2	35	14.8
Irvine	4.6	1019	102	13	100	132	14.6	20.5	25	11.8
Nichol	3.5	361	280	7	65	91	-4.1	10.1	21	15.0
Wild Goose	4.9	177	163	7	90	99	5.5	18.3	30	16.4

Appendix 5: Element concentrations in vineyard soil

Vineyard (2 mm fraction)	As ppm	Rb ppm	Sr ppm	Y ppm	Zr ppm	Nb ppm	Ba ppm	Ce ppm	Pb ppm	Th ppm	U ppm
Cave Spring	-1.9	92	128	25	287	17.1	573	77	14	7.1	2.96
Henry of Pelham	13.0	110	158	36	263	17.3	576	125	6	6.7	1.51
Marynissen	4.8	64	163	19	313	13.5	510	100	8	4.9	1.66
De Sousa	9.6	94	155	28	343	17.0	541	98	6	5.0	1.05
Herndner	0.2	108	156	31	241	18.0	515	63	13	6.2	0.98
Thirty Bench	5.6	92	155	31	291	16.2	550	74	11	8.4	1.60
Lakeview	9.8	82	149	21	328	17.5	454	40	14	4.5	0.79
Joseph's	7.8	55	194	22	349	12.0	520	78	17	5.0	0.91
Pilliterri	5.6	39	211	23	792	14.3	448	99	7	3.3	1.02
Konzelmann	14.0	60	165	23	437	13.9	521	72	16	4.3	3.40
Inniskillin (BC)	10.8	59	312	17	158	17.1	1619	13	3	3.3	-0.11
Pinot Reach	7.7	85	370	19	200	16.0	1068	56	11	5.9	0.81
Slamka	10.7	78	356	17	174	13.5	929	50	9	6.8	-0.73
House of Rose	15.1	67	411	18	181	13.1	974	63	50	6.3	0.45
Gersighel	17.6	62	455	15	158	14.7	1030	66	44	4.6	6.72
Inkameep	3.2	70	445	13	163	10.7	1104	87	6	2.8	1.86
McKenzie	8.2	74	396	15	165	11.5	1085	12	5	2.2	1.25
Irvine	1.2	79	446	16	177	13.9	1024	55	9	6.7	0.75
Nichol	9.1	58	714	12	206	12.3	1370	34	37	3.3	0.78
Wild Goose	4.9	66	659	16	190	13.3	1351	37	9	8.3	0.06

Appendix 6: Pearson's R correlation coefficients between element concentrations in wines

	Mg	Al	P	S	Cl	Ca	Ti	V	Mn	Fe	Ni
Mg	1.00										
Al	0.09	1.00									
P	0.56	0.08	1.00								
S	0.13	0.50	0.49	1.00							
Cl	0.30	0.48	0.31	0.48	1.00						
Ca	0.07	0.54	0.20	0.55	0.34	1.00					
Ti	0.21	0.77	0.23	0.52	0.55	0.57	1.00				
V	-0.06	0.65	0.10	0.42	0.52	0.50	0.80	1.00			
Mn	0.12	0.46	0.08	0.26	0.45	0.44	0.48	0.35	1.00		
Fe	-0.21	0.58	-0.19	0.20	0.31	0.31	0.55	0.53	0.27	1.00	
Ni	-0.01	0.25	-0.16	0.08	0.01	0.15	0.14	0.10	0.35	0.26	1.00
Cu	0.09	0.34	-0.03	-0.02	0.25	0.10	0.38	0.33	0.32	0.31	0.24
Zn	0.11	0.04	0.21	0.22	0.21	-0.07	-0.04	0.00	0.06	0.07	0.15
As	0.04	0.65	0.07	0.40	0.53	0.55	0.74	0.65	0.48	0.55	0.12
Br	-0.08	0.29	0.35	0.62	0.62	0.35	0.34	0.43	0.21	0.25	-0.12
Rb	0.22	0.22	0.10	0.23	0.37	0.20	0.24	0.10	0.20	0.31	-0.02
Sr	0.29	-0.35	-0.15	-0.20	-0.19	-0.05	-0.33	-0.33	-0.43	-0.25	-0.20
Ba	0.23	-0.03	-0.09	-0.17	-0.30	0.06	-0.09	-0.21	0.07	-0.10	0.03
Ce	0.08	0.68	-0.00	0.36	0.45	0.45	0.76	0.60	0.29	0.58	0.09
Pb	-0.03	0.64	-0.17	0.13	0.18	0.33	0.57	0.46	0.20	0.57	0.25
Th	0.01	0.50	-0.11	0.17	0.25	0.33	0.66	0.47	0.12	0.43	0.04
U	-0.10	0.59	-0.01	0.27	0.17	0.43	0.61	0.62	0.15	0.55	0.03

	Cu	Zn	As	Br	Rb	Sr	Ba	Ce	Pb	Th	U
Cu	1.00										
Zn	0.09	1.00									
As	0.39	-0.11	1.00								
Br	-0.08	0.09	0.36	1.00							
Rb	-0.12	0.34	0.31	0.24	1.00						
Sr	-0.12	-0.10	-0.20	-0.18	-0.08	1.00					
Ba	0.07	-0.20	-0.09	-0.37	-0.25	0.42	1.00				
Ce	0.28	-0.15	0.52	0.14	0.25	-0.23	-0.00	1.00			
Pb	0.62	-0.05	0.56	0.03	0.08	-0.08	0.10	0.48	1.00		
Th	0.27	-0.29	0.44	-0.05	0.00	-0.14	-0.04	0.81	0.46	1.00	
U	0.24	-0.12	0.36	0.05	-0.07	-0.21	0.08	0.74	0.51	0.73	1.00