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Article abstract

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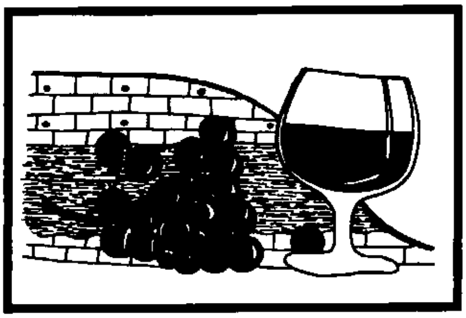
SERIES



Geology and Wine 5. Provenance of Okanagan Valley Wines, British Columbia, Using Trace Elements: Promise and Limitations

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SUMMARY

The trace element compositions of 52 Okanagan wines from 26 vineyards were examined to test for correlations between wine and soil/bedrock composition, and to estimate total variability in Okanagan wine composition. Trace element concentrations in wines analysed are shown to provide verification of vineyard of origin, indicating that trace element compositions are influenced by vineyard geology, although geologic and environmental/climatic influences could not be clearly differentiated from possible wine processing influences in this reconnaissance study. Cluster analysis of Okanagan white wines using Al, Mn, V, Sr, Rb, Mo, Sb, Co, Zn, and U groups wines from the same vineyard, as well as showing a general north-south trend in wine chemistry related to vineyard location within the valley.

RÉSUMÉ

La composition en éléments-traces de 52 vins de l'Okanagan provenant de 26 vignobles a fait l'objet d'une étude visant à mesurer les corrélations entre la composition des vins et celle de la rochemère ainsi que la variabilité totale de la composition des vins de l'Okanagan. Les concentrations en éléments-traces des vins analysés démontrent qu'elles peuvent servir à vérifier le vignoble d'origine, ce qui indique que les concentrations en éléments-traces sont influencées par la géologie du vignoble, quoiqu'il n'a pas été possible dans le cadre de cette étude préliminaire, de différencier clairement entre les influences de nature géologique, environnementale ou climatique, et des influences possibles reliées aux procédés de vinification utilisés. L'analyse typologique de vins blancs de l'Okanagan quant à leur teneur en Al, Mn, V, Sr, Rb, Mo, Sb, Co, Zn, et U permet de regrouper les vins par vignoble, et de démontrer l'existence d'une grande tendance nord-sud dans la composition chimique des vins liée à la localisation des vins dans la vallée.

INTRODUCTION

The Okanagan Valley has been a wine grape growing region since the 1860s, with extensive plantings near Kelowna in the 1920s (Schreiner, 1994). Until the mid-1970s, most vines in the Valley were *Vitis labrusca*, a North American grape species resistant to cold winters, but which yields wines with a strong musky flavour and aroma. Three great pullout programs (1979, 1984, and 1988) saw most *labrusca* replaced by *Vitis vinifera* by 1990 (Schreiner, 1994). The major grape varieties now grown in the valley are Chardonnay, Merlot, Pinot Gris, Cabernet Sauvignon, and Pinot Noir to the south; and Pinot Blanc, Pinot Noir, Pinot Gris, Riesling, and Gewürztraminer in the middle and northern Okanagan Valley (Schreiner, 1998).

Various studies indicate that trace element patterns can be used to "fingerprint" wines and that these patterns, at least in part, reflect the provenance, or site of origin, of wines (Baxter *et al.*, 1997; Danzer *et al.*, 1999). Preliminary studies of Okanagan Valley wines indicated that wines could be fingerprinted by vineyard (Greenough *et al.*, 1996, 1997). Given that many countries, including Canada, have labelling requirements that certify the geographic origin of grapes used in wine, fingerprinting may have both legal and regulatory uses.

Fingerprinting involves determining the concentrations of multiple elements in wines followed by statistical analysis. Okanagan Valley vineyards and wineries from which wines were sampled are listed in Table 1, along with grape variety, geographic subregion, and geologic classification (bedrock, glacial sediment, and soil). The strong influence of bedrock composition and soil chemistry on wine composition is supported by the discrimination of wines by subregion of origin, although viticultural practices and processing methods also have an impact. Okanagan vineyards are underlain by a wide variety of bedrock lithologies (Fig. 1a) and surficial geology (Fig. 1b), and there is a significant change in soil types (Fig. 1c) and climate, from relatively wet and cool in the north to more arid and hot in the south. Wines and vineyard soil samples from the Okanagan Valley (Fig. 1a) were collected in April 1999 and analysed later that year, to try to decipher geochemical influences on trace element composition of wine.

SUMMARY OF OKANAGAN VALLEY GEOLOGY

Bedrock

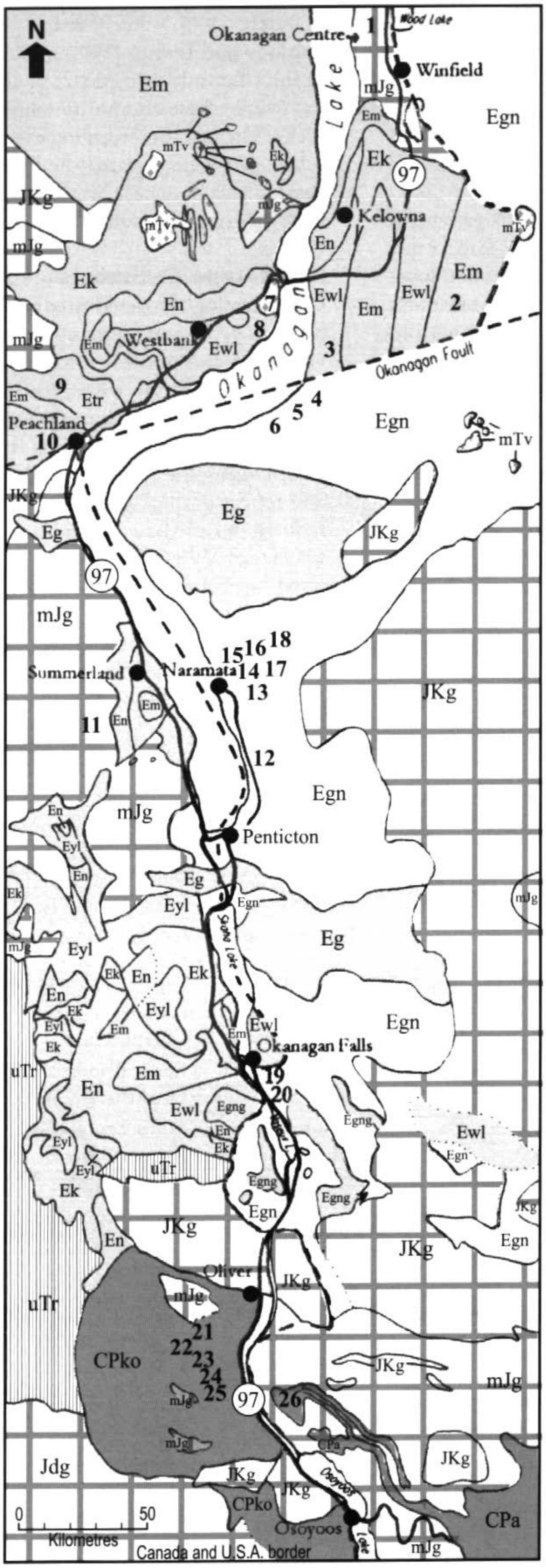
The Okanagan Valley is underlain by rocks of the Quesnellia terrane, which consists dominantly of upper Paleozoic and lower Mesozoic volcanic and sedimentary rocks accreted to North America and intruded by "granites" during the Mesozoic (Monger *et al.*, 1991). Six of the studied vineyards near Oliver (southern Okanagan, vineyards 21 to 26, Fig. 1a) are underlain by some of this terrane's oldest rocks, the Carboniferous or older, mafic metavolcanic rocks of the Anarchist and Kobau Groups. Three other vineyards (labelled 1, 10, and 11, north half of Fig. 1a) have Jurassic granites as bedrock. Of these nine vineyards, only one (26) lies on the east side of what is perhaps the most fundamental structural feature of Okanagan Valley geology: a major, low-angle, normal fault that runs from north to south the length of the valley, with the west side the down-thrown block (Fig. 1a; Tempelman-Kluit, 1989; Roed *et al.*, 1995). The oldest rocks east of the fault tend to be Early Paleozoic orthogneisses that were last deformed during an Eocene mountain-building event. These gneisses underlie 12 of the 26 Okanagan vineyards studied (Fig. 1a). Eocene gneiss deformation was accompanied, on the surface, by intermediate to felsic volcanism represented by basins bearing volcanic rocks and volcanic-rich caldera-fill sediments west of the fault at Kelowna, Summerland, and Okanagan Falls (Church, 1973, 1980, 1981, 1982; Bardoux and Irving, 1988). At least three of the vineyards studied (2, 3, and 9, Fig. 1a) overlie these compositionally variable rocks. The last rock-forming event in the Okanagan Valley created the Pleistocene basaltic lava flow near Westbank that underlies one vineyard (7, Fig. 1a).

Pleistocene Sediments

Complicating the determination of the bedrock geology underlying many of the vineyards, and possibly mitigating the effect of bedrock on wine geochemistry, are glacial sediment deposits (Fig. 1b), which locally approach 100 m in thickness. During the Pleistocene, the advance and retreat of thick glaciers (3 km) scoured out the base and sides of the Okanagan Valley, deepening it to as much as 640 m below sea level (Eyles *et al.*, 1990). When the last ice sheet melted ~10,000 years ago, thick fluvioglacial and colluvial (glacial lake silt and clay) deposits formed along the sides of the

Table 1 Grape variety, subregion and geology of Okanagan vineyards sampled

Vineyard	Number (Fig. 1)	Grape Variety	Subregion	Bedrock (Fig. 1a)	Sediment (Fig. 1b)	Soil (Fig. 1c)
Gray Monk	1	Rotberger	Vernon	mJg	Morainal	Eutric Brunisolic
House of Rose	2	Verdelet	Kelowna	Em	Fluvioglacial	Gray Luvisolic
Pinot Reach	3	Riesling	Kelowna	Ewl	Alluvial	Gleysolic
Summerhill	4	Chardonnay	Kelowna	Egn	Fluvioglacial	Chernozemic
St. Hubertus	5	Riesling	Kelowna	Egn	Fluvioglacial	Chernozemic
Cedar Creek	6	Chardonnay	Kelowna	Egn	Fluvioglacial	Chernozemic
Slamka	7	Riesling	West Side	QPI	Morainal	Eutric Brunisolic
Quail's Gate	8	Riesling	West Side	Ewl	Morainal	Eutric Brunisolic
Hainle	9	Treminor	Peachland	Etr	Colluvial	Eutric Brunisolic
McKenzie	10	Pinot Blanc	Peachland	mJg	Fluvioglacial	Eutric Brunisolic
Scherzinger	11	Gewurztraminer	Summerland	mJg	Fluvioglacial	Chernozemic
Hillside	12	Muscat	Naramata	Egn	Colluvial	Eutric Brunisolic
Irvine	13	Chardonnay	Naramata	Egn	Fluvioglacial	Chernozemic
Lake Breeze	14	Pinot Blanc	Naramata	Egn	Fluvioglacial	Chernozemic
Kettle Valley	15	Chardonnay	Naramata	Egn	Fluvioglacial	Chernozemic
Red Rooster	16	Chardonnay	Naramata	Egn	Colluvial	Eutric Brunisolic
Lang	17	Riesling	Naramata	Egn	Colluvial	Eutric Brunisolic
Nichol's	18	Syrah	Naramata	Egn	Colluvial	Eutric Brunisolic
Wild Goose	19	Gewurztraminer	Okanagan Falls	Egn	Colluvial	Eutric Brunisolic
Stag's Hollow	20	Chardonnay	Okanagan Falls	Egn	Colluvial	Eutric Brunisolic
Tin Horn Creek	21	Gewurztraminer	Oliver	CPko	Morainal	Eutric Brunisolic
Gehringer Bros	22	Verdelet	Oliver	CPko	Morainal	Eutric Brunisolic
Hester Creek	23	Pinot Blanc	Oliver	CPko	Morainal	Eutric Brunisolic
Inniskillin	24	Pinot Blanc	Oliver	CPko	Morainal	Eutric Brunisolic
Gersighel	25	Pinot Blanc	Oliver	CPko	Morainal	Eutric Brunisolic
Inkameep	26	Riesling	Oliver	CPa	Fluvioglacial	Chernozemic



Geology Legend

Miocene to Pleistocene

mTv	Plateau and valley basalts	Basalt

Eocene

Egng	Skaha formation	Brecciated greenstones and cherts in fault sheets overlying the White Lake Formation
Ewl	White Lake Formation	Volcanic breccia, pyroclastic rocks, immature, Volcanic-rich clastic sedimentary rocks
Em	Marama Formation	Dalcite
En	Nimpit Lake Member	Amygdaloidal trachyandesite
Ek	Kitley Lake Formation	Trachyte to trachyandesite
Eyl	Yellow Lake Formation	Mafic phonolite
Etr	Trepanier Rhyolite	Rhyolite
Eg	Eocene Granodiorite	Mostly granodiorite in this map area

Jurassic to Cretaceous

JKg	Okanagan Batholith and Intrusives	Granite and granodiorite
mJg	Nelson Plutonic Rocks	Granodiorite
Jgd	Kruger Syenite	Syenite

Ordovician to Upper Iriassic

uTr	Undivided	Greenstones and cherts

Carboniferous or older

CPa	Anarchist group	Amphibolite, greenstone, chlorite schist, minor sepentinite
CPko	Kobau Group	Amphibolite, greenstone, mica schists, minor marble

Precambrian to Cenozoic

Egn	Okanagan Gneiss	Gneiss, last deformation Eocene, diverse protoliths but Okanagan Batholith dominant

Vineyard Legend

1. Gray Monk
2. House of Rose
3. Pinot Reach
4. Summerhill Estate
5. St. Hubertus Estate
6. Cedar Creek
7. Slamka Cellars
8. Quail's Gate
9. Hainle Vineyard
10. McKenzie
11. Scherzinger Vineyard
12. Hillside Estate
13. Irvine
14. Lake Breeze
15. Kettle Valley
16. Red Rooster
17. Lang Vineyard
18. Nichol Vineyard
19. Wild Goose
20. Stag's Hollow
21. Tin Horn Creek
22. Gehringer Bros.
23. Hester Creek
24. Inniskillin Vineyards
25. Gersighel Wineberg
26. Inkameep

Figure 1a Bedrock geology and vineyards of the Okanagan Valley (adapted from Tempelman-Kluit, 1989).

valley and adjacent to short-lived Glacial Lake Penticton, the larger and deeper precursor to present-day Okanagan Lake (Nasmith, 1981; Vanderburgh and Roberts, 1996).

Soils

Okanagan soils are glacially derived, sandy in the south Okanagan, and tend to have a higher clay content in the north of the valley. Soils in a number of the Okanagan vineyards are Eutric Brunisols (Fig. 1c), meaning that they have undergone moderate physical, chemical, and biological weathering, which has changed the morphology of the parent material, but no major translocations or transformations have occurred (Valentine and Lavkulich, 1999). In several of the central Okanagan vineyards (*e.g.*, 11, 13, 14, 15, Fig. 1a) soils are Dark Brown Chernozems, which are characterized by a dark organic matter in the topsoil, and an accumulation of carbonates in the lower horizons owing to high soil evaporation rates. Soils in two of the Kelowna vineyards (2, 3, Fig.1c), are Gray Luvisolic and Gleysolic, respectively, which form in areas having more precipitation than do the Chernozemic or Brunisolic soils, causing a greater amount of weathering in the upper horizons (Valentine and Lavkulich, 1999).

POSSIBLE EFFECTS OF WINE PROCESSING ON TRACE ELEMENT COMPOSITION OF WINE

The Okanagan Valley wine and vineyard soil samples obtained were analysed to test for correlations between wine and soil composition, and to estimate total variability in Okanagan wine composition. There are, however, other factors that may influence the trace element composition of wines as follows.

Methods of wine processing affect the inorganic composition of wines, and concentrations of certain elements are expected to be controlled by processing more than by geological and plant uptake factors. The addition of sulphite is a common practice, in which K or Na metabisulphite is added to the grapes just before crushing. This process is meant to inhibit the growth of microbes by the release of SO_2 gas (Vine, 1982). The precipitation of "wine diamonds" (calcium tartrate crystals) during wine storage is expected to control Ca concentration in wine, and is likely to co-precipitate other trace elements. Storage in stainless steel has been shown to increase Ni and Fe concentrations in wine (Muryani and Papp, 1997). Aging in oak is a source of tannins and phenols and also a possible source of trace elements, which would be expected to vary with oak species, barrel conditioning, and cooperage size (Jackson, 1994). Clarification by fining agents and/or filtration also may affect element concentrations in wine. The use of bentonite as a fining agent has been shown to increase the concentration of rare earth elements in wine (Jakubowski *et al.*, 1999), and is likely to affect other element concentrations. Casein (a milk protein) and egg albumin are also used to adsorb tannins in wines, and may affect trace element composition in wines. In red wine production, the macerate (crushed grapes, including seeds and skin) is fermented, but in white wine produc-

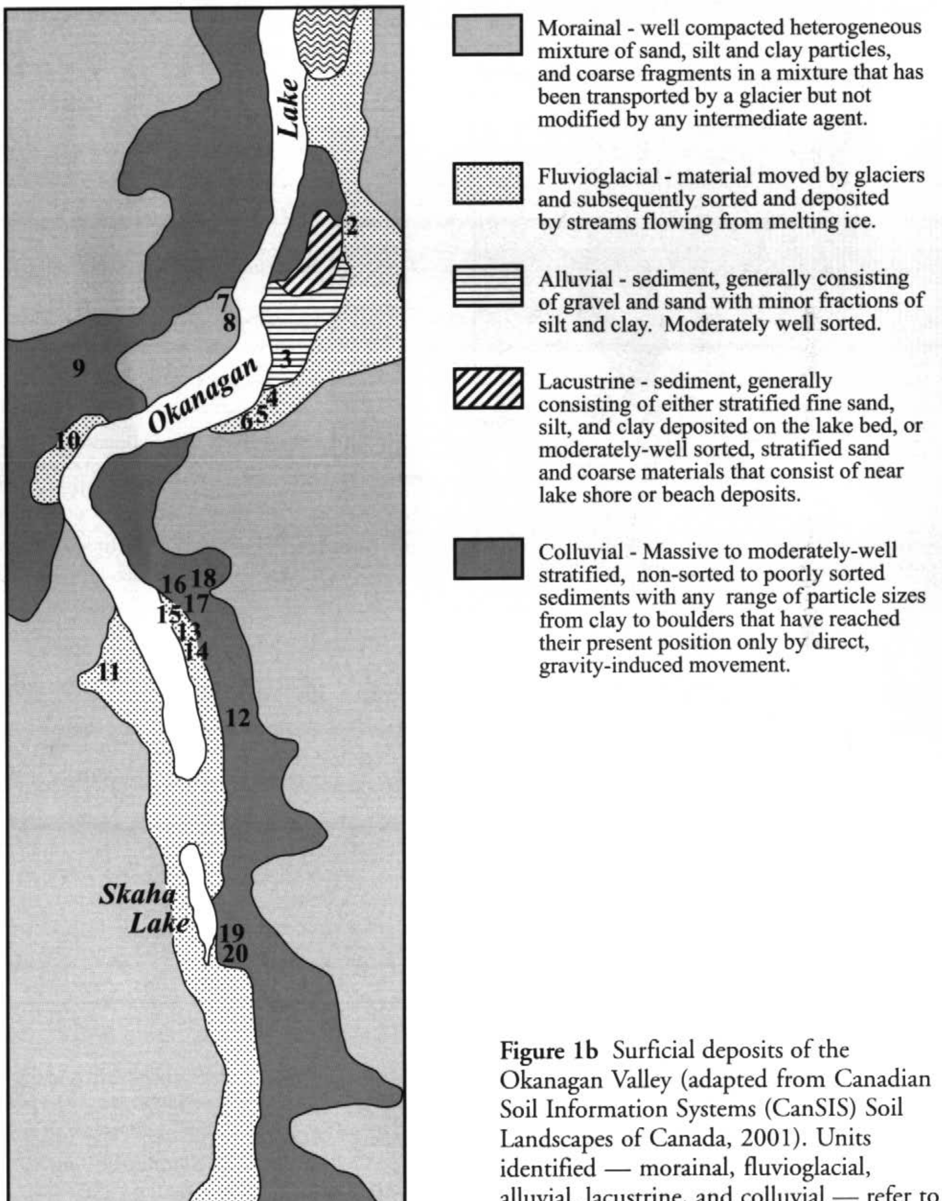
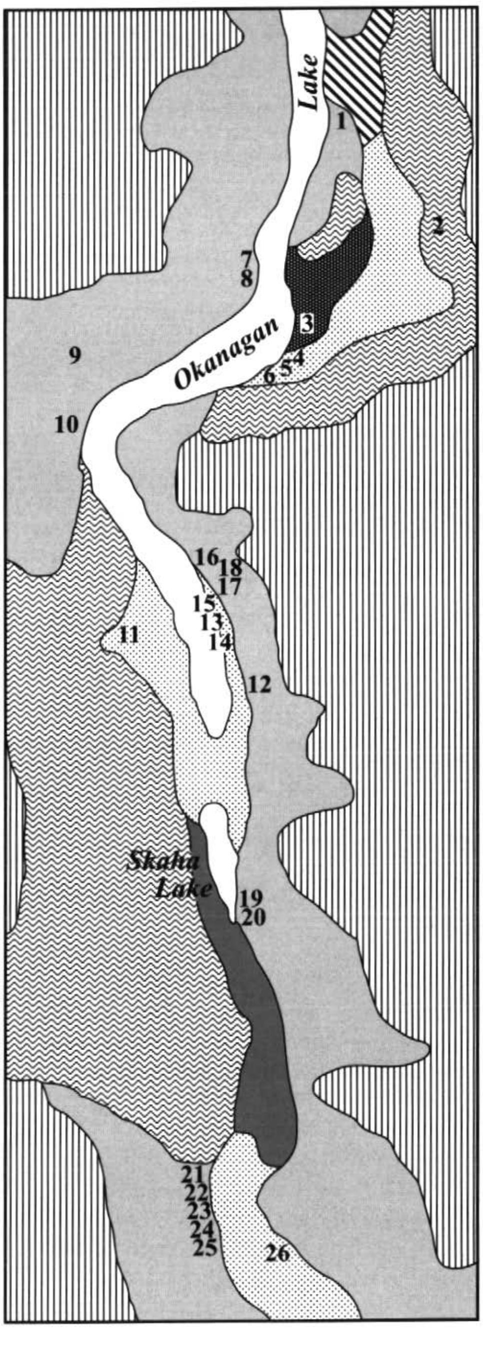


Figure 1b Surficial deposits of the Okanagan Valley (adapted from Canadian Soil Information Systems (CanSIS) Soil Landscapes of Canada, 2001). Units identified — morainal, fluvioglacial, alluvial, lacustrine, and colluvial — refer to the parent material mode of deposition (PMDEP) used in the National Soil Database of Agriculture and Agri-Food Canada. Unit descriptions given here are abbreviated from those given in the National Soil Database (see CanSIS, 2001).

tion, the skins and seeds are usually removed immediately by pressing, and the juice is fermented (Jackson, 1994). Red and white wines have been shown to be distinguishable by their trace element concentrations (Baxter *et al.*, 1997; Greenough *et al.*, 1997).

For this study, there are too many variables in wine processing, and insufficient data at the 26 vineyards/wineries from which wines were analysed to permit assessment of the significance of processing techniques in affecting the trace element compositions of the wines studied. Accordingly, this work should be regarded as a reconnaissance study of trace element compositions in the wines analysed.



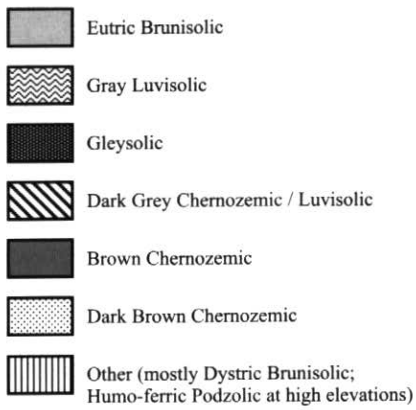


Figure 1c Soil classification of the Okanagan Valley (adapted from National Soil DataBase, Soil Landscapes of Canada, CanSIS, 2001).

SAMPLING AND ANALYTICAL METHODS

Sampling and Sample Preparation

Soils

Between five and eight soil samples were taken from a depth of 0.3 m to 0.6 m for each specific vineyard plot that produced a particular bottle of wine. Normally, this depth sampled the subsoil, which is less affected by microbial alteration and the addition of fertilizers than the topsoil. All Okanagan vineyards are irrigated (British Columbia Wine Institute, personal communication, 2000), and some have been tilled, which alters the soil horizons and chemical properties from natural soils of the area. Soils were sieved to <2 mm grain size and combined by weight to form a composite sample of each vineyard plot. A sub-sample was then sieved (unground) to a grain size of less than 0.074 mm (200 mesh) for each vineyard. This fine-grained fraction (<0.074 mm) was analysed for all vineyard soils, as trace elements are expected to be most concentrated in this silt and clay fraction, making differences in concentrations between soils more noticeable. To ensure that a bias was not given to vineyard soils with a high clay content, the <2 mm fraction was also analysed for the soils of 10 vineyards. Samples of both grain sizes were prepared as pressed pellets, and analysed by X-ray fluorescence for 28 elements/oxides as noted below.

Wines

All wines included in this study were produced from grapes grown on a single vineyard plot. White wines from the major *Vitis vinifera* varieties (Riesling, Chardonnay, Pinot Blanc, Gewürztraminer) were chosen preferentially, but were not always available. Previous studies of Okanagan wines indicated that wines from different vineyards can be distinguished chemically (Greenough *et al.*, 1997). As a further assessment of this finding, multiple (at least four) wines were obtained and analysed from five different vineyards. Sampling and analysis was also undertaken to permit evaluation of the effect of vintage on wine composition: five of the six wines from the House of Rose vineyard (Verdelet, 1992 to 1996 vintages), as well as five Wild Goose vineyard wines (Gewürztraminer, 1993 to 1997), and four Quail's Gate wines (Rieslings, 1995 to 1998) are from different vintage years. Also, five Rieslings sampled from Lang Vineyard are from the 1995 to 1997 vintage years, and of these two are late harvest wines (1995 and 1997) and one is an ice wine (1997). In order to determine variability in a single type of wine from one winery in one year, three Lake Breeze samples were taken from different vats of the same batch of wine, and three were taken from the top, middle, and bottom of one of these vats. The Summerhill and McKenzie wines were also sampled from vats, whereas all other samples were taken from bottled wines.

Analysis

Soils

The pressed pellets of both grain sizes were analysed by X-ray fluorescence for the following 28 elements/oxides: Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, S, Cl, K_2O, CaO, Sc, TiO_2, V, Cr, MnO, Fe_2O_3, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, Ba, Ce, Pb, Th, and U, according to the procedure in 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%. This method of soil analysis determines total element concentrations, not plant-available element concentrations, and was chosen to examine differences in the total soil composition, derived from underlying sediments and parent rock. At present there is no single (*i.e.*, applicable to all elements), simple and reliable method of determining plant-available trace element concentrations in soils (Dr. Gerry Nielson, Summerland Research Station, British Columbia, personal communciation, 1999).

Wines

These were diluted 1:1 with 0.2 M HNO_3 and analysed for 34 elements using ICP-MS following a procedure similar to Baxter *et al.* (1997). Replicate analyses of two in-house reference wines indicated precision over a 5-month period, and five water reference materials [t-123, t-127, t-129 and t-135 (USGS) and AMW-3(DFC)] were matrix matched to the wine samples (0.1 M HNO_3 and 6% ethanol) to indicate precision and accuracy as follows: <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.

RESULTS

Soils

Element concentrations were determined for each vineyard soil, and as found previously (Greenough *et al.*, 1996), little chemical variation exists between Okanagan vineyard soils. The mean concentration and standard deviation of the two measured particle-size fractions in all vineyard soils sampled are shown in Table 2. The fine-grained soil fraction (<0.074 mm) tends to contain similar or slightly higher concentrations of analytes than the <2 mm fraction, presumably reflecting the stronger sorption properties and higher surface area of electrostatically charged clay particles (Kabata-Pendias and Pendias, 1984). The use of soils as a direct indicator of bedrock composition is problematic because of glacial mixing, and because soil characteristics are highly dependent on climate (Krauskopf and Bird, 1995). Soils in the Oliver area (vineyards 21-25, Figs. 1a,c) were found to have the highest concentrations of Ni, Cu and Ba (see Table 3).

Wines

Mean trace element concentrations in wines from various Okanagan subregions, and in all Okanagan wines sampled, are given in Table 4. The large variation in element concentration within each group is partly due to the difficulty in defining subregions, as groups of wines become extremely small when subregions are defined by bedrock and overburden, making data from each group difficult to interpret. The data in Table 4 show that no one element can be used to discriminate wine regions, and as with other studies, the data were examined using multivariate analyses. Because multivariate statistical methods assume a

Table 2 Mean concentrations (in wt% for oxides, ppm for elements) and standard deviations of soils from 10 Okanagan vineyards (House of Rose, Pinot Reach, Slamka Cellars, McKenzie, Nichol, Irvine, Wild Goose, Inniskillin, Gersighel Brothers, and Inkameep).

Element	Mean 2 mm	SD	Mean 0.074 mm	SD
Al_2O_3	13.60	1.10	14.40	1.20
CaO	3.40	0.90	4.00	1.80
TiO_2	0.66	0.10	0.63	0.23
MnO	0.11	0.03	0.10	0.03
Fe_2O_3	5.10	1.00	6.60	4.70
Cl	158.00	72.00	200.00	113.00
V	97.00	23.00	96.00	18.00
Ni	17.90	18.70	18.40	18.10
Cu	21.80	10.10	27.20	10.20
Zn	33.30	8.70	50.20	8.50
As	8.90	5.10	16.40	9.20
Rb	70.00	9.00	70.00	9.00
Sr	456.00	130.00	459.00	83.00
Ba	1155.00	219.00	1026.00	156.00
Ce	47.00	24.00	63.00	32.00
Pb	18.30	18.00	27.60	21.30
Th	5.00	2.10	10.20	3.20
U	1.18	2.08	3.09	4.12

Table 3 Concentrations (ppm) of Ni, Cu and Ba in Oliver vineyard soils (Fig. 1, vineyard nos. 21-25) compared to all other Okanagan vineyard soils sampled Fig.1, vineyards nos. 1-20 and 26).

Element	Okanagan (except Oliver)	SD	Oliver	SD
Ni	10.5	7.7	47.0	8.1
Cu	22.0	7.0	52.0	12.0
Ba	998.0	313.0	1459.0	536.0

normal data distribution, and are easily skewed by outliers (Statsoft, 1999), element concentrations in wines were log transformed to better fit a normal distribution, and reduce the extremity of outliers. Log transformation also reduces the relative distribution of data, so that elements of higher abundance are brought into the same range as elements of lower abundance, which is important when elements of different abundance are included in the same analysis.

Elements with low analytical uncertainty were emphasized in comparing and "fingerprinting" wines, and those likely to be most affected by processing were eliminated, as follows. Elements which are important for discriminating wine provenance were determined by graphical analysis, and by F-statistics (between-group over within-group variability, where groups of wines were defined first by subregion, then by vineyard). The elements determined to be important to fingerprinting were Al, V, Mn, Co, Zn, Rb, Sr, Mo, Sb, and U. Exploratory cluster analysis was used as a method of visualizing data, by grouping objects (wine samples) into clusters so that objects in the same cluster are more similar to each other than to objects in other clusters (Hair, *et al.*, 1987). Cluster analysis of Okanagan white wines, using the 10 elements most important in fingerprinting wines as noted above, illustrates overall relationships among white wines from throughout the valley (Fig. 2). The analysis was found to group wines by vineyard of origin to a high degree, and there is an overall trend grouping wines from the north and south of the valley. Red and ice wines were not included in the cluster analysis due to the differences in fermenting and processing.

Variance within a batch of wine and wines from the same vineyard plot are compared in Fig. 3. The relative standard deviation (RSD) of element

Table 4 Mean trace element concentrations in wines (in ppb, except for the elements Mg, P, Cl, and Ca which are in ppm) and standard deviations (SD) for trace elements in North Okanagan (labelled N,1-8 in Fig. 1), Middle Okanagan: Peachland/Summerland (labelled MP, 9-11 in Fig. 1), Middle Okanagan: Naramata (labelled MN, 12-18 in Fig. 1), Middle Okanagan: Okanagan Falls (labelled MO, 19-20 in Fig. 1), South Okanagan (labelled S, 21-26 in Fig. 1) and for all wines analyzed in the Okanagan.

	Mean N	SD	Mean MP	SD	Mean MN	SD	Mean MO	SD	Mean S	SD	Mean Okanagan	SD
Li	9.20	7.90	3.30	2.30	6.20	3.20	8.00	2.40	4.90	2.50	7.20	5.70
Be	0.09	0.10	0.10	0.10	0.52	0.26	0.38	0.27	0.37	0.32	0.27	0.27
Mg	61.00	27.00	62.00	19.00	59.00	30.00	60.00	64.00	55.00	18.30	60.00	23.90
Al	146.00	114.00	205.00	37.00	593.00	365.00	254.00	158.00	391.00	279.00	309.00	286.00
P	131.00	122.00	140.00	55.00	96.00	38.00	93.00	28.00	114.00	55.00	116.00	84.00
Cl	12.90	6.80	18.90	12.40	17.20	16.30	21.90	23.40	11.80	6.30	15.40	12.90
Ca	72.00	30.00	80.00	64.00	86.00	61.00	65.00	13.00	75.00	33.00	76.00	41.00
Ti	5.50	3.20	6.80	4.60	6.40	4.20	10.90	8.70	8.40	4.90	6.90	4.90
V	6.80	8.90	3.10	2.30	8.60	13.60	3.60	2.90	26.00	46.60	9.20	19.90
Mn	678.00	216.00	896.00	629.00	631.00	272.00	712.00	214.00	697.00	367.00	692.00	300.00
Fe	1008.00	953.00	1611.00	390.00	1106.00	825.00	1178.00	850.00	890.00	374.00	1089.00	809.00
Co	1.68	0.59	1.64	1.03	3.34	1.24	1.78	0.61	2.60	1.73	2.23	1.22
Ni	17.90	8.70	69.30	85.90	18.20	9.10	10.00	4.30	18.50	7.20	21.60	28.50
Cu	45.00	61.00	95.00	85.00	67.00	125.00	39.00	41.00	56.00	52.00	56.00	80.00
Zn	456.00	291.00	743.00	479.00	322.00	164.00	415.00	156.00	555.00	446.00	457.00	311.00
As	1.90	1.40	2.00	1.40	5.20	3.90	1.80	0.90	3.50	2.90	2.90	2.70
Se	1.87	2.42	0.63	0.24	1.82	0.93	0.77	0.35	1.27	0.85	1.53	1.68
Br	166.00	81.00	203.00	77.00	198.00	79.00	168.00	30.00	197.00	59.00	182.00	72.00
Rb	367.00	161.00	376.00	102.00	504.00	145.00	765.00	141.00	372.00	133.00	451.00	194.00
Sr	764.00	424.00	721.00	395.00	796.00	271.00	791.00	171.00	687.00	198.00	761.00	329.00
Mo	4.79	2.91	27.01	21.18	9.75	7.20	3.79	1.09	4.54	2.19	7.80	9.45
Ag	0.01	0.01	0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Cd	0.38	0.41	1.57	2.82	0.28	0.11	0.44	0.45	0.42	0.21	0.47	0.89
Sb	0.32	0.18	0.24	0.13	0.36	0.29	0.30	0.16	0.80	0.58	0.39	0.33
I	1.60	0.70	2.90	2.10	3.70	1.60	1.00	0.20	2.40	1.30	2.30	1.50
Cs	0.81	0.46	1.08	0.57	1.77	1.09	1.83	0.70	1.31	0.62	1.27	0.82
Ba	132.00	128.00	217.00	79.00	131.00	56.00	113.00	12.00	156.00	94.00	140.00	97.00
La	0.24	0.41	0.69	1.17	0.35	0.32	0.47	0.41	0.26	0.19	0.34	0.48
Ce	0.46	0.75	1.32	2.17	0.91	0.84	0.96	0.89	0.54	0.40	0.72	0.95
Tl	0.07	0.03	0.06	0.02	0.21	0.13	0.11	0.01	0.10	0.05	0.11	0.09
Pb	7.80	6.40	12.40	7.50	8.90	4.10	21.10	13.20	19.40	10.00	11.70	9.10
Bi	0.14	0.18	0.15	0.16	0.15	0.11	0.40	0.31	0.26	0.21	0.19	0.20
Th	0.05	0.07	0.06	0.08	0.16	0.16	0.23	0.15	0.09	0.11	0.11	0.13
U	0.20	0.19	0.50	0.80	0.24	0.29	0.87	0.54	1.97	2.85	0.57	1.22

concentrations for six wines from the same batch of 1998 Lake Breeze Pinot Blancs; and for white wines from the same vineyard plot but from different vintage years (Quail's Gate Riesling, 1995-1998; Wild Goose Gewürztraminer, 1993-1997; House of Rose Verdelet, 1992-1996), are compared to the RSDs of element concentrations of all wines sampled in the valley (Fig. 3).

DISCUSSION

Soil Composition

Soils in the Oliver region have higher concentrations of Ba, Ni, and Cu than other Okanagan vineyard soils (Table 3), which may reflect the influence of climate on soil composition. In arid areas, metals can become enriched in the soil due to adsorption onto illuviated clay materials (Aubert and Pinta, 1977). The high Ni and Cu content may reflect derivation from bedrock of the Kobau Group amphibolites and greenstones that underlie other Oliver region vineyards. With the possible exception of basalts beneath the Slamka Cellars vineyard, these are the most mafic rocks known in the study area, and mafic rocks commonly have high Ni and Cu concentrations.

Despite some clustering of wines according to geography (Fig. 2), the correlation between wine and soil element concentrations is weak. The relationship between As (arsenic) in soil and wine reported by Greenough *et al.*, (1997), appears to be fortuitous when re-examined with the present, larger, data set. Similarly, element ratios (examined to account for variable element dilution in wine) yielded no strong correlations between wine and soil. Most of the Okanagan vineyards are underlain by deep glacial deposits, and soils formed from these parent materials were found to be fairly uniform in composition. Wine compositions possibly reflect bedrock rather than soil compositions, as the field of biogeochemical prospecting uses vegetation rather than soil samples in exploring for bedrock ore deposits (*e.g.,* Dunn, 1995). Grape roots, especially in arid areas (*e.g.,* southern Okanagan), can grow deep enough that they intersect the watertable, which tends to interact chemically with bedrock. Another factor mitigating a relationship between wine and soil composition is that plants do not

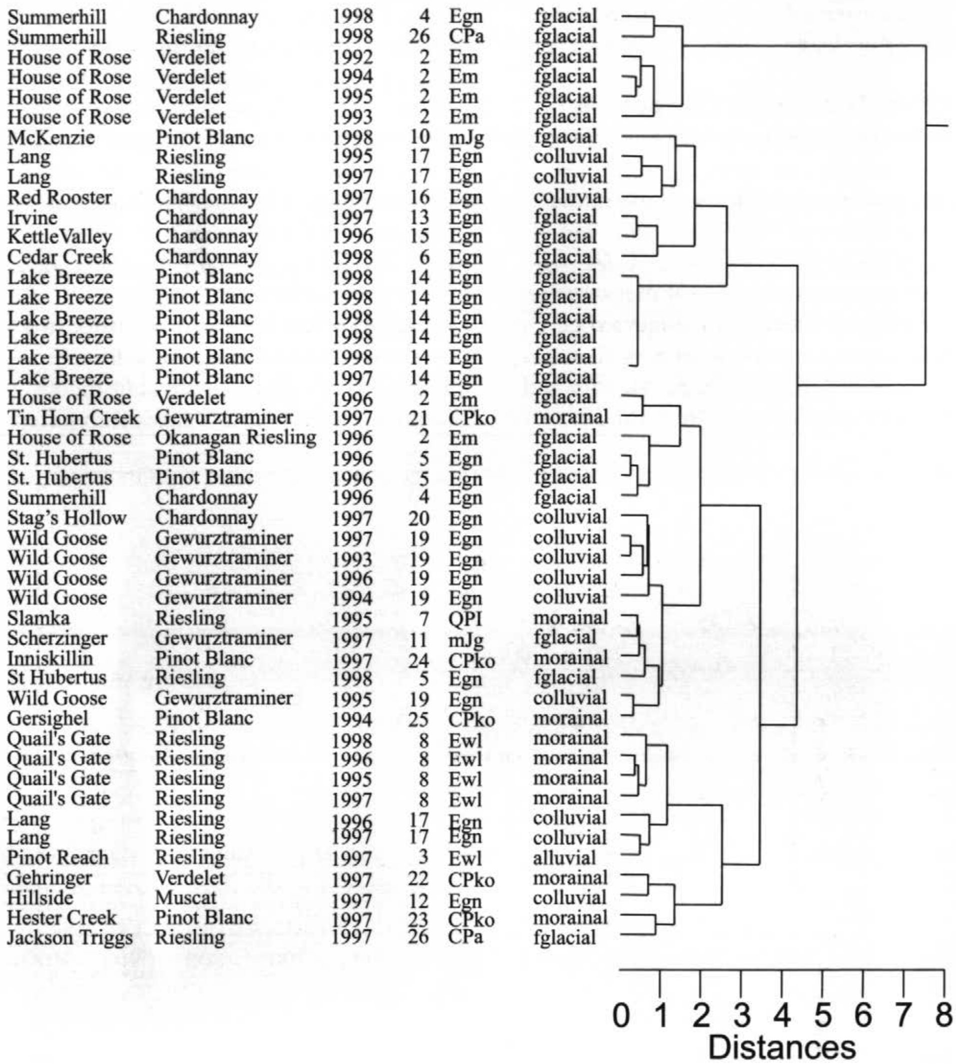


Figure 2 Cluster analysis of log transformed concentrations of Al, V, Mn, Co, Zn, Rb, Sr, Mo, Sb, and U in white Okanagan wines, using Euclidean distances and linkage by Ward's method. Wines are labelled by winery, grape variety, vintage year, vineyard number (see Fig. 1), bedrock type, and surficial geology.

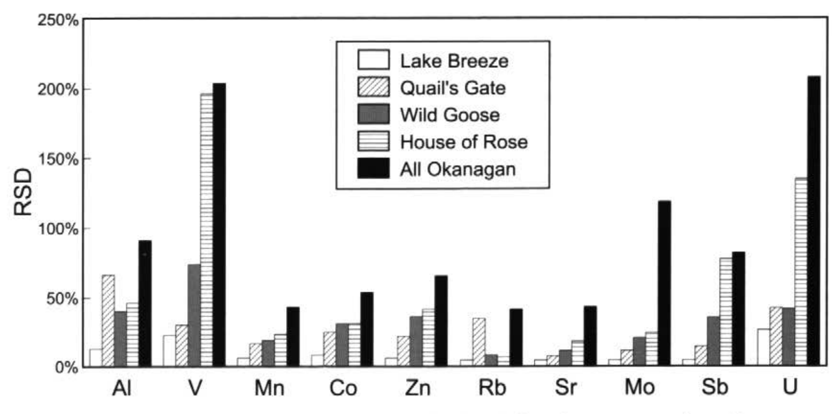


Figure 3 Percent relative standard deviation calculated for elements used to discriminate Okanagan wines by vineyard. Bars represent variance (RSD) in element concentrations for six wines from the same batch of 1998 Lake Breeze Pinot Blancs; Quail's Gate Riesling (1995-1998); Wild Goose Gewürztraminer (1993-1997); House of Rose Verdelet (1992-1996); and all Okanagan wines.

uptake essential nutrients at a constant rate (Kovalevsky, 1995).

Controls on Wine Composition

Although correlations between wine and soil chemistry are weak, it seems likely that geochemical factors influence the composition of Okanagan valley wines, based on trends seen in the cluster analysis results (Fig. 2). Okanagan wines are grouped according to vineyard of origin using the discriminating elements Al, V, Mn, Co, Zn, Rb, Sr, Mo, Sb, and U. For example, wines from the House of Rose, Lake Breeze, Wild Goose, and Quail's Gate vineyards form distinct groups. The two St. Hubertus 1996 Pinot Blancs were made from grapes from the same vineyard, but one was aged in oak for eight months and the other processed in a steel tank. That they plot together suggests that the different processing methods did not substantially affect trace element concentrations. The two Inkameep wines (vineyard 26) from two producers (Summerhill and Jackson-Triggs) do not plot together, but the Jackson-Triggs wine associates with other wines whose grapes originated in southern Okanagan vineyards. There is a tendency for north and northwestern Okanagan wines (Kelowna, Westbank, Peachland, and Summerland; vineyards 2-11 in Fig. 1a) to plot at the top of Figure 2, and southern Okanagan wines (vineyards 19-26) to fall in the lower half of the plot. This result suggests that wine composition might also reflect subtle changes in climate and its impact on soil chemistry.

The composition of irrigation water or variations in precipitation from year to year do not appear to affect wine composition, as wines of several vintage years from the same vineyard group together (Fig. 2) and have a low RSD of concentrations of the 10 fingerprint elements compared to wines from throughout the valley (Fig. 3). The wines from Quail's Gate, House of Rose, and Wild Goose vineyards/wineries represent several vintage years of the same wine, whereas the wines from Lake Breeze are from different processing tanks of the same batch, and show that within-batch variability is low for a single vintage year. Variability (RSD) in these individual vineyard wines is consistently lower than that of all wines sampled from the Okanagan. (Fig. 3). In spite of the fact that wine makers and their methods, supplies, and equipment might change from year to year and lead to variable compositions between vintages, the similarity in the trace element compositions of these wines suggests that vineyard of origin — including soil, bedrock composition, and possibly the long-term effects of climate on soil — affects the composition of wines more than the processing or viticultural methods used.

Fingerprints of Individual Okanagan Vineyards

Trace element fingerprinting studies of wines in other regions have used Cd, Cr, Cs, Er, Ga, Mn, and Sr to discriminate English and Spanish wines (Baxter *et al.*, 1997), and Al, B, Ba, Ca, Cr, Cu, Fe, Mg, Mn, P, Pb, Si, Sr, V, and Zn to group wines from six regions of Germany (Danzer *et al.*, 1999). In addition, wines from Galicia, Spain were classified using Li and Rb (Latorre *et al.*, 1994). These studies of other regions demonstrate both the success of wine fingerprinting analysis, and the necessity of using multiple

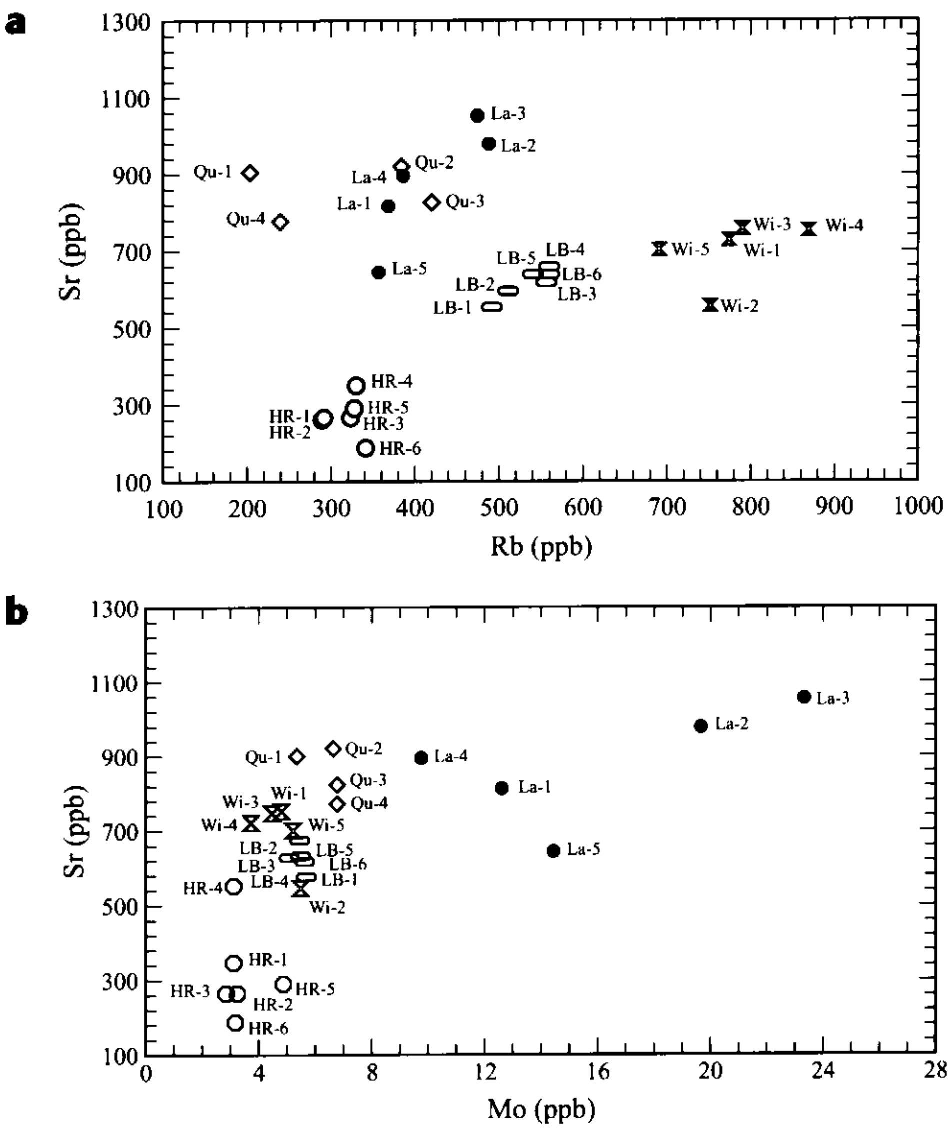


Figure 4(a)(b) Concentrations, in ppb, of Sr *versus* Rb and Sr *versus* Mo, used to discriminate wines from the same vineyard, but different vintage years (House of Rose Verdelet 1992 to 1996 (HR-1 to HR-5) and Okanagan Riesling 1996 (HR-6), Lake Breeze Pinot Blancs 1998: 6 different samples from the same batch (LB-1 to LB-6), Lang Riesling 1995 to 1997 (La-1 to La-5), including a late harvest (La-4) and an icewine, (La-3), Wild Goose Gewürztraminer 1993 to 1997 (Wi-1 to Wi-5) and Quail's Gate Riesling 1995 to 1998 (Qu-1 to Qu-4).

elements.

In this study, cluster analysis using 10 elements (Fig. 2) indicates that there are natural patterns in the data that enable correlation of trace element composition with vineyard of origin. Wines from Quail's Gate, House of Rose, and Wild Goose wineries show variance of select elements in wines from several vintage years to be consistently lower than the relative standard deviation (RSD) for all Okanagan wines (Fig. 3). The RSD of element concentrations in the Lake Breeze samples is low, and indicates that element concentrations are fairly uniform within different processing tanks of the same batch of wine. This low RSD has implications for fingerprinting individual wines from particular vintages.

Vineyards with four or more wine samples (House of Rose, Quail's Gate, Wild Goose, Lake Breeze and Lang) were used in discriminant analysis experiments, which relied on both multivariate statistics and graphical analysis. Elemental Sr/Rb plots differentiated vineyards (Fig. 4a), except for overlap between the Lang and Quail's Gate vineyards. Wines from the Lang vineyard were completely discriminated from the other four vineyards using an Sr/Mo plot (Fig. 4b), however. The high discriminating power of Sr and Rb may reflect element mobility in the environment, defined by ionic charge and ionic radius (Greenough *et al.*, 1996), which determines Sr to be a moderately mobile element, and Rb a more mobile element. The mobility of Mo depends on its oxidation state, but tends to be high in soil.

The ability to distinguish among these wines even when grown over several vintage years implies that geology and vineyard environment have a strong influence on wine composition, and that Sr and Rb are important discriminating elements. Isotopic ratios of Sr have been used as a natural tracer between soil and wine, where wines grown on basaltic, mixed, and granitic soils could be differentiated (Barbaste *et al.*, 2002). As the Sr isotopic ratios between wine and soil are similar, we suggest that there is little addition of Sr during wine processing. This experiment provides further evidence that individual vineyards can be fingerprinted, but many more vineyards (wines) will have to be multiply sampled in order to determine the precision/certainty of the fingerprinting process and the possible degree of overlap in trace element composition among wines from different vineyards.

Multi-element analysis was unsuccessful at grouping wines by grape variety, colour (red or white), or vintage year. Greenough *et al.*, (1997) and Baxter *et al.*, (1997) were able to accurately discriminate wine chemically by colour, but in this study there were only six red wines, an insufficient number for statistical significance.

Discrimination of wines by vineyard geology was examined using the discriminating elements Sr and Rb. Plots of Sr/Rb ratios *versus* vineyard latitude (Fig. 5a,b) for one wine from each of the 26 vineyards sampled, show no strong trends relating wines to latitude, bedrock or surficial deposit. The variability of Sr and Rb concentrations may reflect the heterogeneity of the bedrock, particularly the Okanagan Gneiss (Egn), and/or the complexity of the wine-geology relationship.

SUMMARY

Trace element composition of wines was found to group wines by vineyard, to show some trends with geographic location, and to discriminate wines by vineyard. This preliminary study suggests that multi-element analysis may be a useful addition to current Canadian certification parameters. Although the relationship between geology and wine composition is complex, the success in verifying vineyard of origin, and the low variance in element concentrations in several vintage years of the same wine, indicates a correlation between vineyard environment and wine composition, although there are limitations to deciphering provenance. In order to further examine the relationship between wine and geology, a study of the effects of

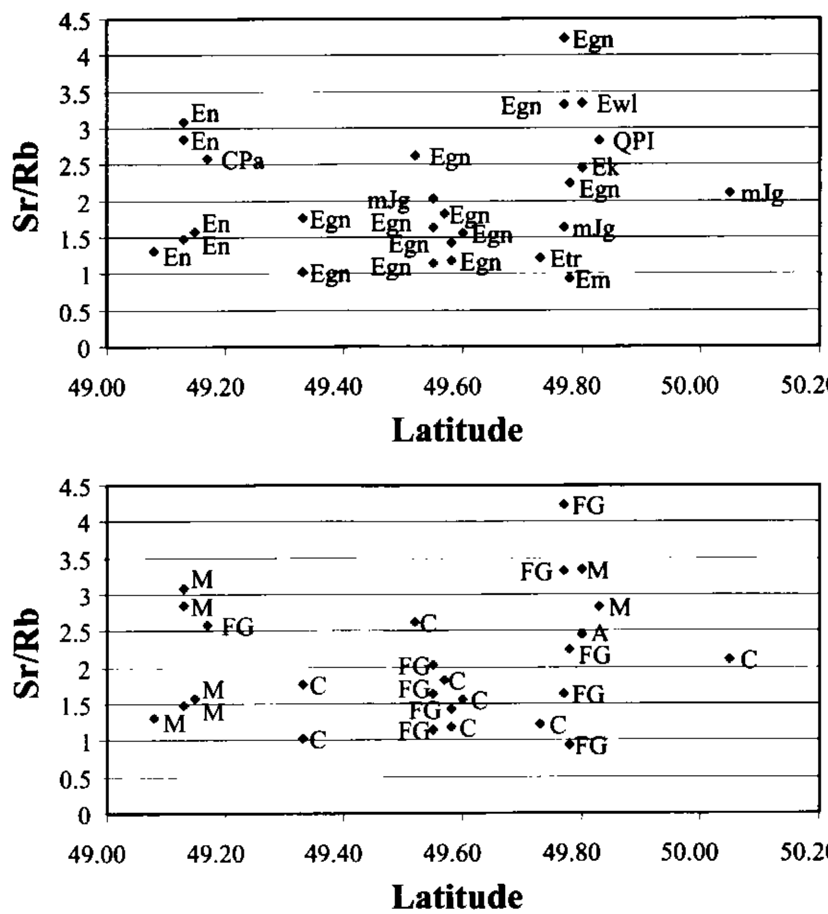


Figure 5 Plots of Sr/Rb concentrations in wine *versus* latitude, showing a bedrock geology (where bedrock abbreviations correspond to those of Figures 1a, b surficial geology (where M = morainal, C = colluvial, FG = fluvioglacial, and A = alluvial).

different wine production methods on wine composition is suggested.

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