The role of soil chemistry in wine grape quality and sustainable soil management in vineyards

D.E. Mackenzie and A.G. Christy
Department of Earth and Marine Sciences, The Australian National University, Canberra ACT 0200, Australia (E-mail: Doug.Mackenzie@ems.anu.edu.au; andyc@ems.anu.edu.au)

Abstract This study aimed to establish if there is any evidence that soil mineralogical and/or chemical composition influence the composition and quality of wine grapes. In the initial phase of the study, soils and grapes were sampled in two riesling vineyards in South Australia. Soils were analysed for a wide range of total major and trace elements; soil cation extracts and grape juices were analysed for 27 trace elements by ICP-MS and ICP-AES. The results show that grape juice properties such as Baume and titratable acidity (TA) are clearly correlated with several plant-available trace elements in the soil. Most notable of these are Ca, Sr, Ba, Pb and Si. Soil clay content also plays a (lesser) role. The cations Ca, Sr, Ba and Pb are closely similar to one another in their relationships to Baume and TA, strongly indicating that the correlations are real. It is evident from our results that soil cation chemistry does indeed have an influence on wine grape composition. Such knowledge has the potential to be used in better tailoring grape varieties to soils, and in managing – or modifying – soils for optimum viticultural results and better wines in a more sustainable way.

Keywords Chemistry; grapes; influence; soil; terroir; wine

Introduction

Over many centuries, European vignerons have established how best to match the various wine-grape varieties to soil types. They found that planting grape vines in the “right” soil can literally make the difference between a great wine and a vin ordinaire. Some soils produce better wine grapes than others, and various wine-grape varieties produce the best results in particular soil types. This vine–soil relationship is a fundamental part of the concept of terroir, a concept born in the “Old World” and being adopted, albeit reluctantly in some parts, by the “New World”.

The concept and role of terroir in viticulture may be well known, but the underlying science is only beginning to be understood. The purpose of our research is to better understand the role of soil in terroir by investigating the basic geochemical factors that may affect grape vines and the development of their fruit. This understanding can then be used to help guide the siting of new vineyards, to help in the making of decisions on the varietal make-up of existing vineyards, and to help provide a proper scientific basis for the sustainable management of soils in vineyards.

Previous research

The renowned French researcher Gérard Seguin wrote: “As our knowledge stands at the moment, it is impossible to establish any correlation between the quality of wine and the soil content [sic] of any nutritive element . . . If there were such a correlation it would be easy, with the appropriate chemical additives, to produce great wine anywhere” (Seguin, 1986). Since this was written, very little of significance has been published on research into the influence of soil chemistry on wine-grape quality or composition; Seguin was influential indeed.
More recently, research into the trace-element composition of wine (e.g., Baxter et al., 1997; Greenough et al., 1997; Peña et al., 1999) indicates that individual vineyard areas have unique isotopic and/or trace-element “signatures” that allow identification of the provenance of wine. High-sensitivity measurement of isotopic compositions of wines (e.g. Martin et al., 1999) has allowed further refinement of these signatures with isotopic ratios of oxygen, hydrogen and carbon. Similar results have been obtained with potatoes (e.g., Anderson et al., 1999), honey (e.g., González Paramás et al., 2000), and other produce.

The existence of isotopic and/or trace-element signatures in wine suggests that trace elements could play some role in determining the subtle characteristics of wines that distinguish wines of one area from those of another. They may also play a part in determining the “quality” of a wine – factors such as Baumé/Brix, pH, total acidity and phenolic content, as well as the distinctive but difficult-to-quantify flavours of the wine: the so-called goût de terroir. This project set out to determine whether or not the chemical composition of soil in a vineyard has any influence on the measurable composition of wine grapes produced.

**Methods**

The white variety riesling was chosen for the initial, trial phase of the project, principally because of its observed sensitivity to geographic location (factors other than climate) and soil type. Two premium riesling vineyards, “Heggies” and “Pewsey Vale” in the Eden Valley area of South Australia, were selected. Sampling included sections that consistently produce the best (in the judgement of the winemakers) riesling fruit, as well as sections that produce lesser-quality fruit.

Soil profiles in each vineyard were sampled using a 15 cm-diameter Jarret hand auger at two (in some cases three) levels throughout the vine root zone: an “A” sample from about 30–35 cm; a “B” sample from about 60–65 cm; and, where a significant number of vine roots were evident below about 70 cm, a third (“C”) sample was collected from about 90–100 cm below the surface.

Approximately 1.0 g of each 40 g air-dried, sieved (2 mm Teflon) sub-sample was dried overnight at 45°C and extracted with 15 ml of 1-molar ammonium acetate, centrifuged, and filtered into 50 ml of ultrapure water. 1 ml of internal standard (20 ppm Be, Sc, Y, In and Tl) and 1 ml of 12% H₂O₂ was added and the solution made up to 100 ml with 2% nitric acid.

Grapes from the vine nearest each soil sample site were crushed by hand in a stainless steel cone crusher. Sulphur dioxide and pectic enzyme were added to the samples during crushing, and solids were allowed to settle before centrifuging and transfer to inert sample containers for determination of total titratable acidity (TA), pH, Baumé and glycosyl glucose (GG) content. Grape-juice samples were prepared for trace-element analysis by centrifuging 50 ml at 3,000 rpm for 20 minutes, adding 1.0 ml sample of the liquid to approximately 50 ml of ultrapure water, adding 2.0 ml of concentrated nitric acid, and making up to 100 ml with ultrapure water.

Bulk soil samples were analysed for total contents of the following elements by X-ray fluorescence spectrometry (XRF): Si, Ti, Al, Fe (total, as Fe³⁺), Mn, Mg, Ca, Na, K and P (all expressed as oxides); Ag, As, Ba, Bi, Br, Cd, Ce, Co, Cr, Cs, Cu, Ga, Ge, Hf, I, In, La, Mo, Nb, Nd, Ni, Pb, Pr, Rb, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Tl, U, V, W, Y, Zn and Zr (as elements).

Soil cation extracts and grape juices were analysed by inductively coupled plasma mass spectrometry (ICP-MS) for the elements Al, As, B, Ba, Bi, Cd, Ce, Co, Cr, Cs, Cu, Er, Ga, La, Li, Mn, Mo, Ni, Pb, Rb, Sb, Sn, Sr, Ti, V and Zn; samples were diluted for analysis of the more abundant elements such as Ba, Fe, Mn, Rb and Sr. ICP atomic emission spectrometry (ICP-AES) was used in the analysis of undiluted soil extract and grape juice samples for the elements B, Ca, Cr, Fe, K, Li, Mg, Mn, Na, P, Si, Ti, V and Zn.
**Results and discussion**

Analysis of the results revealed a pattern of correlations between concentrations of plant-available cations in the soils studied and the compositions of the grapes grown in them. Few of the correlations are strong (the sample size is statistically small), but they are consistent between elements (e.g., Ca, Sr and Ba) and from one grape-juice parameter to another. Relationships between soil cations and grape juice composition are generally much less clear for the Heggies vineyard than for the Pewsey Vale vineyard, chiefly because of the small sample size from the former. Part of the Heggies vineyard (J Block) is planted on Ramsey rootstocks. This results in a larger leaf area than vines on their own roots, more photosynthetic activity, and, with cropping rates controlled, greater production of sugars. This probably explains why samples from Heggies J Block tend to plot separately (e.g., higher Baumé) from the other samples.

Error bars in Figures 1–16 are as follows: Baumé $\pm 0.3\%$; TA $\pm 0.35\%$; pH $\pm 0.3\%$; metal cations $\pm 1\%$; clay content $\pm 5\%$.

**Baumé**

Grape juice Baumé level in the Pewsey Vale vineyard generally *increases* with increasing concentrations of plant-available sodium, at least in low-Na$^+$ soils (Figure 1). The “outlier” point (lower right) represents a soil with several properties that are significantly different from the others, including the presence of unweathered biotite. It is therefore not unexpected that Na in this sample is “anomalously” high relative to Baumé. Baumé also increases with increasing content of plant-available silicon (Figure 2); the two “outlier” samples (lower right) are very sandy loams that contain abundant partly weathered and unweathered mica as well as some chlorite.

Grape juice Baumé level shows a consistent pattern of *decrease* with increasing concentrations of Ca (Figures 3 and 4), Sr (Figures 5 and 6), Ba, and Pb cations in both “A” and “B” soil levels. Significantly, these cations are geochemically related to one another, and in the rocks beneath these vineyards are all found chiefly in the mineral plagioclase. Also significantly, there is no correlation between calcium cation content and pH of the soils studied.

The relationship between Baumé and calcium cations in the “A” soil samples (Figure 3) is negative overall, but there is a considerable degree of scatter. Four of the five samples from one part (J Block) of Heggies vineyard, along with three samples from particularly...
Figure 2  Relationship between juice Baume and silicon cation content of soil “A” samples from the Pewsey Vale vineyard

Figure 3  Relationship between grape Baume and calcium cation content of soil “A” samples from Heggies and Pewsey Vale vineyards

Figure 4  Relationship between grape Baume and calcium cation content of soil “B” samples from Heggies and Pewsey Vale vineyards
sandy soil profiles in Pewsey Vale vineyard, have apparently anomalous high Ca and/or Baumé values.

A negative correlation between Baumé and soil Ca content is also apparent in the “B” samples (Figure 4), but, again, three samples from Heggies vineyard J Block appear to be anomalously high in Ca and/or Baumé.

Strontium cation content, particularly in the soil “B” samples (Figure 5), is strongly correlated with decreasing Baumé levels; again, three samples from Heggies vineyard J Block appear anomalously high in Baumé. Pewsey Vale and Heggies vineyard soil “A” samples appear to form two separate trends (Figure 6), suggesting that the rate of decrease in Baumé with increasing Sr content is more rapid in the Pewsey Vale vineyard than in the Heggies vineyard. The Heggies sample that plots with Pewsey Vale samples is from a thick soil profile with an unusually high readily available water capacity.

Baumé also decreases as barium cation content of the soil (both “A” and “B” samples – Figures 7 and 8) increases, although, again, there is considerable scatter. In both cases, the sample points that deviate most from the main trend represent soils with particularly high readily available water capacities.

Figure 5 Relationship between grape Baumé and strontium cation content (log scale) of soil “B” samples from Heggies and Pewsey Vale vineyards

Figure 6 Relationship between grape Baumé and strontium cation content in soil “A” samples from Heggies and Pewsey Vale vineyards
There are also indications of a negative correlation between grape juice Baume and lead cation content of both the “A” and the “B” soil samples, although the degree of scatter is considerable. However, because of the much more definite correlations seen between Baume and Ca, Sr and Ba, and the close geochemical relationship that exists between Pb and these elements, it is likely that the Baume–Pb correlation is real.

Baume levels are generally higher in grapes grown on the more clay-rich soils than in sandier soils (cf. Seguin, 1986), although correlations between Baume and clay contents are not strong.

**Titratable acids (TA)**

Grape juice TA *increases* with increasing soil calcium cation content (Figures 9 and 10). There is no immediately apparent reason why three Pewsey Vale “A” samples plot below the main trend (high Ca\(^{2+}\) and/or low TA); a fourth Pewsey Vale site that falls above the main trend is from a particularly kaolinite-rich, mica-poor soil profile on granitic gneiss. The soil “B” sample from this last site also plots above the main group in Figure 12.
Patterns in the correlation plots for strontium (Figures 11 and 12) are similar to those for Ca, but with less overall scatter. This indicates, inter alia, that the correlations are neither coincidences nor artefacts of the data. Two of the four points that fall above the main trend in Figure 11, and the point that falls well below the main group in Figure 12 represent sites in J Block of Heggies vineyard, the last representing a particularly sandy soil profile. The other two points that plot above the main group in Figure 11 are also “anomalous” in the TA–Ca plots (Figures 9 and 10).

Barium behaves similarly to calcium and strontium with respect to TA: there is a general (although not strong) positive correlation in both “A” and “B” soil levels (Figures 13 and 14). In Figure 13, the three Heggies samples that plot above the main group are all from J Block; in Figure 14, two Heggies J Block samples again plot above the main group, along with the kaolinite-rich, mica-poor soil sample from Pewsey Vale. The samples that plot below the main trend are from a very sandy soil profile (high readily-available water capacity) and from a moderately sandy, kaolinite-rich, mica-poor soil profile.

There are some indications that juice TA decreases with increasing soil concentrations of titanium cations, and also with increasing Al, Fe, Ni, K, Mn, Si, Sn and Zn, but correlations are generally poor, and none is consistent between “A” and soil “B” samples or between vineyards.
Figure 11  Relationship between titratable acid and strontium cation content of soil “A” samples from Heggies and Pewsey Vale vineyards

Figure 12  Relationship between titratable acid and strontium cation content of soil “B” samples from Heggies and Pewsey Vale vineyards

Figure 13  Relationship between titratable acid and barium cation content of soil “A” samples from Heggies and Pewsey Vale vineyards
There is a broad positive relationship between grape juice TA level and the soil clay content of soil “A” samples (Figure 15); the correlation with respect to “B” samples is weaker.

**pH and glycosyl glucose**

Grape juice pH and glycosyl glucose (GG) levels generally show modest to weak correlations with soil cation concentrations. Grape juice pH appears to be negatively correlated with soil concentrations of Cu, Cr (Figure 16), and Pb cations; there also appears to be a negative correlation with soil clay content. Glycosyl glucose (GG) content of the grapes is positively correlated with soil Na and Mg cation contents, and possibly with Sr$^{2+}$; several other cations – notably K and Ti in soil “A” samples – are correlated positively with GG, but these correlations are not observed with respect to both soil levels.

**Relationship between soil and grape juice metal cation contents**

Many cations, including Si, Na, K, Mn, B, Rb, Cr, Cu, Sn, As, Pb and V are strongly concentrated in the grape juices relative to their concentrations in both the soil “A”-level and “B”-level samples; such concentration is a well known phenomenon in plants. On the other
hand, concentrations of several cations, including Ca, Sr, Ba, Cs, Ni and Zn, are lower in the grapes than in the host soils. It may be highly significant that the first three of these elements are those that show the strongest evidence of having an influence on grape organic composition.

The exact nature of the role of Ca, Sr and Ba is at present unknown. It is known, however, that calcium accumulates in grapevine leaves in the form of insoluble calcium oxalate (e.g., Webb et al., 1995). Sr, Ba and Pb, because of their chemical similarity to and affinity with Ca, will similarly be held, as highly insoluble oxalates. It is possible that in non-carbonate-bearing soils with relatively low plant-available Ca contents, such as those of the Heggies and Pewsey Vale vineyards, more calcium (along with strontium, barium and lead) is passed on to the fruit than in soils with greater levels of plant-available Ca, which are commonly carbonate-bearing. Calcium is also known to have functions in plant cell walls and in cell membrane permeability, and is an enzyme co-factor (e.g., Howe et al., 2002). In this way, it could be that Ca (and Sr, Ba and Pb) influence cell reactions (such as formation of sugars) by affecting the cell membrane ion exchange process and enzyme reactions.

Conclusions
The results summarized above indicate that soil cation chemistry does appear to affect grape composition in the vineyards studied. Baumeé levels appear to be negatively influenced by increasing levels of plant-available Ca, Sr, Ba and Pb in particular; Ca, Sr and Ba also appear to be involved in elevating TA levels in grapes. It is highly significant that Ca, Ba, Sr and Pb all form large divalent cations closely related to one another in geochemical behaviour. This similarity supports the observed correlations being real rather than simply coincidence. On the other hand, increasing clay content appears to not only influence Baumeé, but also decreases pH and increases TA, possibly reflecting the water-providing properties of clays (cf. Seguin, 1986).

Stage two of our research, now under way, involves studying the composition of cabernet sauvignon grapes (Baumeé, TA, pH, total polyphenols and total anthocyanins) grown in soils that range from low carbonate, low plant-available Ca types to high plant-available Ca soils formed on limestone. We envisage that the results presented above, when augmented by the results of this second stage, will be a significant advance in the scientific understanding of the role of soil in terroir, will be useful in developing “rules” to “tailor”
wine-grape varieties to vineyard sites, and will assist in managing vineyard soils for optimum performance and quality.

Standard methods of vineyard soil amelioration commonly involve the use of superphosphate and synthetic chemicals, as well as agricultural lime, dolomite and gypsum. Superphosphate and some of the synthetic additives are known to have long-term harmful effects on the soil. Our future research, building on the results reported here and those of stage two, is planned to establish which naturally occurring additives are best suited to improving the viticultural performance of soils by providing chemical nutrients in a balanced form to which plants are adapted, and doing this in a sustainable way, without risking long-term detriment to the soil and the vineyard.

References