Analytical approaches to wine authenticity

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IN **BRIEF**

- The ability to verify the origin of wines through analysis would bring greater transparency to the international wine market.
- To do this requires parameters that uniquely reflect the conditions where grapes are grown and are not altered during winemaking.
- Models were developed to identify Australian wines based on statistical analysis of isotope ratios of naturally-occurring elements and trace element concentrations.
- The models could successfully identify Australian wines across different vintages and varieties.
- Region of origin of Australian wines could also be identified with a lower classification success rate.
- Insights were gained as to why some methods that have been previously promoted as tools for identifying provenance have not been successful.

A Wine Australia-funded project at the AWRI set out to use analysis of isotope ratios to verify the geographic origin of Australian wines. Multi-dimensional statistical tools were employed and a model developed using data from 292 Australian and 94 international wines. The model had a successful classification rate of 98% for Australian wines with the main drivers of the model being isotopic ratios of boron, oxygen and strontium. Identification of the region of origin of Australian wines was also achieved with a classification success rate of approximately 60%.

BACKGROUND

While there are a number of existing and emerging technologies to support wine authenticity claims, situations will still arise within the international wine market where it is necessary to use chemical analysis to verify the origin of wine. Examples could include cases where 'refilling' of authentically labelled bottles is suspected, or if a wine of unknown origin is labelled as an Australian product after having originated from a bulk shipment. Analytical authentication is not a simple task, as the analytical parameters chosen must both uniquely identify grapes' place of origin and remain unaltered by winemaking processes, transport and maturation. Many methods proposed in the past have later been shown to be unsuitable for authentication of wine samples.

Building on earlier work, AWRI researchers set out to identify analytical parameters based on stable isotope ratios to verify the geographic origin of Australian wines within the framework of the international packaged and bulk wine trade.

The overall objectives for the project were to:

- measure the isotope ratios of boron, lithium, oxygen and strontium as well as trace metal concentrations in a wide selection of red and white commercial wines from across Australia, drawn from most of the wine-producing zones over several vintages
- determine which parameters, if any, were able to discriminate Australian wines from those produced overseas, using multi-dimensional statistics
- ensure vintage variation was within acceptable limits
- investigate any obvious confounding factors that might render these analytical parameters redundant such as grape cultivar, the use of bentonite or the use of

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glass bottles produced overseas.

RESULTS

A set of 292 Australian (from 16 production zones) and 94 international wines of known provenance (from Europe, South America, Canada, New Zealand, South Africa and USA) were sourced with support from Wine Australia. When choosing wines the focus was on Shiraz, Chardonnay, Cabernet Sauvignon and Merlot, which represent the top four cultivars grown in Australia. Isotope ratios of boron, lithium, strontium and oxygen and trace metal concentrations were determined in the wines in conjunction with collaborators at CSIRO. The data generated were then analysed using multi-dimensional statistical tools, in particular Orthogonal Projection of Latent Structure-Discriminant Analysis (OPLS-DA) (Figure 1).

A discriminant model was developed using the data set of Australian and international wines. The model had a successful classification rate of 98% for Australian wines, with a successful classification rate of 90% on average for all wines analysed. The main drivers of the model were isotopic ratios of boron, oxygen and strontium with the trace metal concentrations not significantly contributing to achieving these levels of discrimination. Identification of the region of origin of Australian wines, mostly through the impact of the underlying soil and geology on strontium isotopes, was also achieved with a classification success rate of approximately 60%. The success rate for regional identification is strongly linked to the underlying similarity of geology that contributes to the subsoil composition of many Australian grapegrowing regions. This information will provide important baseline data for any future studies of analytical methods to determine regional origin of Australian wines.

INVESTIGATION OF CONFOUNDING FACTORS

Several potentially confounding factors were investigated as a key aspect of the project.

Vintage variation was measured using a vertical series of three single-vineyard wines from very different regions across Australia produced over a period of 10 years. This temporal variance was tested against that measured for all study samples and found to be smaller for all isotopic parameters with the exception of two lead isotope ratios. This allowed the majority of isotope ratios to be used in the final model.

Grape variety variation was tested in 10 cultivars, both red and white, grown in several locations of South Australia subjected to controlled micro-vinification. Differences in the isotope ratios of Li, O and Sr differed by below 10% due to grape cultivar and were therefore useable.

Neither vintage nor variety showed a significant negative effect on the use of the models to classify if a wine was of an Australian origin.

Bottle source and type were investigated to understand if they have the potential to influence the boron isotopic ratios found in packaged wine. However, analysis demonstrated that the bottle did not make a significant contribution compared to the differences introduced by wine origin.

Bentonite fining is a common winemaking practice that can introduce trace amounts of lead into wine above the typical background levels from soils. This fact makes the use of lead isotopic ratios unsuitable for classification of white wines (which are commonly treated with bentonite). Analysis demonstrated that the lead isotope ratios were more useful at indicating the regional source of the bentonite used, an internationally traded commodity, than the wine's origin and, hence, these isotope ratios were excluded from the models.

UNDERSTANDING THE LIMITATIONS OF EARLIER METHODS

The project also made important strides in understanding why some isotopic and elemental analyses, which have been previously promoted as tools for identification of provenance, have not been successful. A specific example is the use of lead isotopic ratios, which were clearly shown in this project to be unsuitable for classification of white wines due to the significant amounts of lead introduced by the use of bentonite during winemaking. Similar influences were noted for efforts to use relative trace metal concentration ratios to identify the provenance of Australian wines. Overall, it was clear from the statistical analysis of the data for trace metal concentrations that they did not contribute significantly to differentiation of wines from Australia and other wine-producing regions from around the world, despite these being the basis of a number of earlier programs to determine the provenance of wines and their success in other food and beverages. It is recommended that before any authentication approach is adopted, it should not only show a reasonable correlation with origin for the calibration data set (through

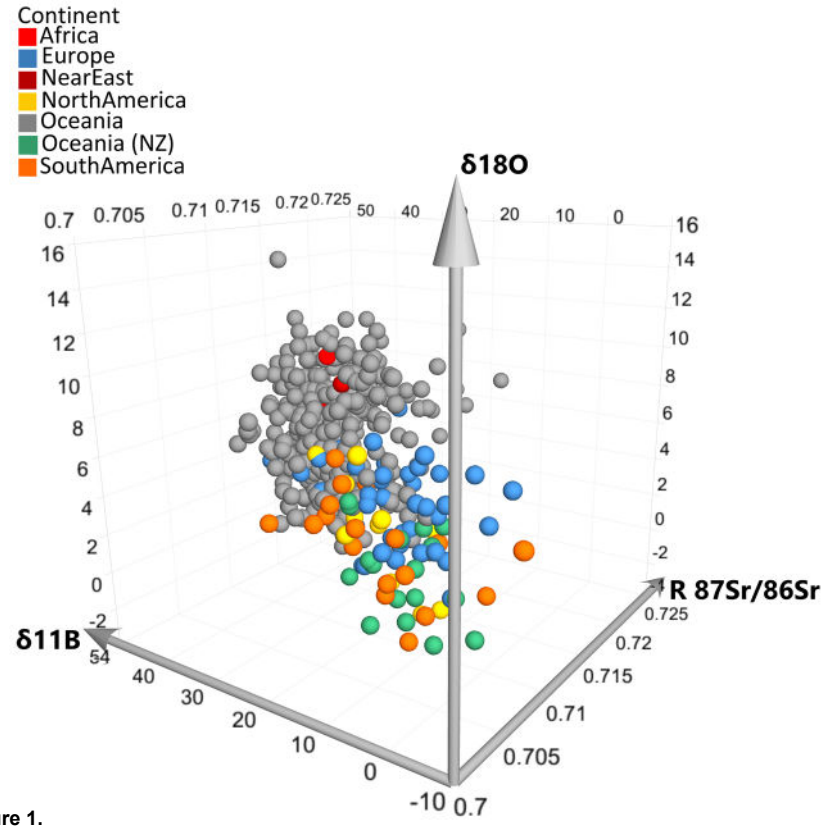

Figure 1.
Example of how isotope ratios can be used to differentiate the continent of origin of wine samples.

methodologies such as cross validation), but also demonstrate that it can achieve similar results with a significant number of blind samples that are not part of the original sample set. Such an approach is necessary to ensure that confidence in the technology is well founded and that unseen biases are not introduced.

APPLICATION IN WINE MARKETS

The success of this project in using combined isotopic ratios and statistical analysis to categorise a wine's origin will allow the provenance of a wine that claims to be Australian to be analytically determined. While by its nature this technique is not suitable for rapid in-market applications, it will provide an important addition to technologies such as smart labelling and methods that compare direct retention samples of known wines. Significantly, unlike many other technologies used in the authentication of wine, the use of isotopic ratios can link a wine's provenance to the underlying physical attributes of its place of origin irrespective of the processes used in its production, its age or the environmental condition of its storage and maturation. This is important in cases where rather than being a direct forgery of an existing Australian product, a wine is simply making claims of Australian provenance. Such cases can expose the consumer to, at best, a disappointing quality outcome and, at worst, possible health impacts from the use of unapproved additive or ingredients, with additional obvious negative outcomes for the reputation of all Australian wines.

FUTURE OPPORTUNITIES

The publication of the most effective isotope ratios identified in this work and the underlying data describing their typical content in Australian wines compared to wines from outside Australia will allow the adoption of this approach, in conjunction with the statistical protocols identified, by any organisation with appropriate equipment and capabilities to carry out the testing.

While this work identified the overall potential of using a combined group of isotopic ratios to provide information on wine origin, further work is needed to clarify the nature of the links between the final values of these components in wine and the underlying sources in the geology, soil, water and air. Such an understanding will allow the much larger data sets compiled in environmental and geological studies to be used in the determination of the provenance of wine as well as other agricultural products.

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