Vineyards and soil mineralogy: Analytical approach to assessing clay minerals and correlations with soil's properties

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Keywords: geology, soil, mixed-layer clays, terroir, wine.

Abstract

The terroir is largely influenced by the soil, and so a precise knowledge of its mineralogical features and functions is imperative for quality management and vineyard productivity. The presence of clays, for example, is highly important, with certain great wines produced on clay soils. The scientific analysis of this consolidated evidence can be implemented by assessing qualitative and quantitative mineralogical data, which make soil mineralogy and vineyards comparable worldwide. This information is essential for understanding which types of clay minerals are most important, and in what quantities they are significant for both a vine's ecophysiology and its grapes' quality. A multi-technique analytical approach was developed and tested on soil samples taken from vineyards around the world to produce a precise and comparable database of all the soils' mineral components. This research allowed us to distinguish and measure a specific type of clay, the so-called mixed-layer clay minerals (e.g. illite/smectite), which in several vineyards represents the soil's most distinctive mineral element. We measured the relevance of these minerals for the soil's fertility, e.g. their impact on the cation exchange capacity, and found that mixed-layer clays are central to a vineyard's quality characters and soil-related terroir parameters thanks to the high fertility and moderate swelling behaviour they lend to the soil.

Introduction

The terroir is an interactive ecosystem that influences the quality and typicality of wine (Seguin, 1988) and can only be interpreted by separating out the natural environmental factors that have an ecophysiological effect on the vine. Among the abiotic factors that compose the terroir, the soil is a fundamental, albeit complex, element that influences the behaviour of the vine in different ways (Van Leeuven et al., 2018). To facilitate an interdisciplinary comparison of the nature of the soil and the quality of the wine, it is advisable to separate and catalogue the various soil components in a precise and comparable way. Then, it is possible to scientifically assess their ecological weight based on the physiological effect that the soil's sub-factors can have on the plant. For example, by analysing the mineral phases in the soil, we can obtain information on its pH, pedo-climate, soil stability, water availability and mineral exchange, and also frame minerals and biological interactions (Velde and Barré, 2010; Biget et al., 2021). Bulk geo-mineralogical soil analysis with precise qualitative and quantitative data on the soil composition can be of great help for this purpose. Combining many different soils' data into a global, detailed and comparable database makes it then easier both to identify outstanding minerals that uniquely characterise the vineyards and to link certain mineral soil components, i.e. their ecological potential in the form of abiotic stress promoters, with the wine quality.

The clay mineral component is known to be an important ecological factor in viticulture since clays are the most reactive inorganic components of soils and control the nutrients available for plant uptake. Yet, the nitrogen nutrition is weaker the greater the clay content of the soil because negatively charged ions are susceptible to leaching losses in soil solutions. As Van Leeuwen and Seguin (2006) stated, a low nitrogen supply as a result of soil parameters is a significant quality factor in red wine production, for example, ensuring the concentration of grapes' phenolic compounds.

Thus clay minerals are to all intents an important soil-related terroir parameter that deserves specific attention and extensive studies. Focusing on clays as a pivotal terroir sub-factor, to add new information on how a wine terroir works on the vine, we must take into account at least three fundamental aspects:

1. *There is a substantial difference in soils between the clay fraction and clay minerals:*

   Classical soil analysis based the agronomic distinction of the clay fraction on texture classification (Hillel, 2008); therefore, as Churchman (2018) stated, clay minerals in the soil were commonly construed to include all the secondary inorganic compounds of clay (< 2µm size) in the soil, regardless of their crystalline or nanocrystalline order, or their degree of disorder. Thus, they included oxides, hydroxides and oxyhydroxides of Fe, Al, Mn and other metals.

   Qualitative and quantitative soil analysis for the scientific study of the terroir must, however, move beyond this generic assessment based on texture alone. Greater accuracy of 'soil' models can be achieved by studying clay minerals as specific crystalline phases and noting their agronomical behaviour.

2. *A qualitative-quantitative approach to soil's clay mineralogy is essential to assessing a vineyard's quality:*

   Clay minerals are electron acceptors and/or donors in organic ion-exchange reactions, where the inorganic exchangeable cation of layered silicates belonging to clay minerals can be replaced by organic cations. The surface charge of clay is responsible for the ability to adsorb water and nitrogen and transport mineral colloidal phases through soil (Aboudi Mana et al., 2017), as well as retaining significant anions, which bolster complex chemical properties that have important implications for solute transport (Bertsch and Seaman, 1999). As a result, clay minerals influence the vegetative, productive and qualitative expression of the crop (Velde and Barré, 2010), thus constituting an important component of the soil system, related to their ability to adsorb water, cations and nitrogen. In this context, knowledge of their role in soil fertility is imperative for sustainable soil management and productivity (Kome et al., 2019).

   The cation exchange capacity (CEC) of soils varies according to the soil pH, amount of organic matter, clay percentage and type of clay or phyllosilicate, meaning these minerals have different CECs depending on the characteristics of their crystal lattice (Parfitt et. al., 2008).

3. *Clay minerals are of different types and very differently affect the soil's properties:*

   The clay fractions in each soil should be dominated by one of the four main common groups (Grim, 1953): kaolinite, illite, smectite or vermiculite. Yet, certain problems in identifying, classifying or defining clay minerals arise as those phyllosilicates in soils are often less well-ordered and more complex than those from geological deposits (Churchman, 2018). As measured in this study, a particular kind of clay, called "mixed-layer clay", is often present in vineyard soils. This contains intermediate crystalline phases between the more classical clay groups mentioned above, whereby different types of clay layers alternate, e.g. illite and smectite, reducing the swelling behaviour of the mixed-layer system (Ghasemi and Sharifi, 2021) and more stable soil aggregate conditions.

   Mixed-layer clays may be formed by the uptake of cations (e.g. K) or the removal of hydroxide interlayers, and they may represent an intermediate stage in the formation of swelling minerals from non-swelling minerals, or vice versa (MacEwan and Ruiz-Amil, 1975; Sawhney, 1989).

No references were found in the scientific literature on the mixed-layer topic to better explain and predict the functioning of these clays in vineyard soils. This gave rise to the need for a new codified analytical procedure, taking a Rietveld-Quantitative Phase Analysis (QPA) approach, to obtain precise and globally comparable mineralogical information, useful to classify not only the terroir but also the geopedological identity of each vineyard.

Materials and methods

The many studied soil vineyards represent varied geographical contexts worldwide but are located mainly in the South Tyrol region of northern Italy, supported by soil samples from renowned vineyards of winegrowing areas in Burgundy, Chablis and Bordeaux (France), California (USA) and Tuscany (Italy). A total of 35 vineyards were studied by analysing 50 soil samples.

Geological aspects related to these vineyards were analysed with the intent of explaining and documenting the natural variability of abiotic stress, which might be related to the natural geological environment. To study geological features, the Vineyard Geological Identity (VGI) method for the analysis of vineyards with different geopedological conditions was carried out (Ferretti, 2019).

Geo-mineralogical analyses were performed to investigate the sediment origin, soil mineralogy and bulk soil chemistry. The following analyses were conducted to explore the site-specific mineralogical characteristics of each vineyard, representative of different geological environments and soil parent materials. Thermogravimetric analysis (TGA/DTG), differential thermal analysis (DTA) and geo-mineralogical microanalysis of the soil composition using X-ray diffraction (XRD) and X-ray fluorescence (XRF) were also performed on all soil samples. The analysis procedure was designed to calculate the petrophysical properties of the soils, studied by combining the calculation of the structural formulae of variable composition minerals with a statistical analysis of the distribution of trace elements for all the minerals present in the sample set. Application of the accurate Rietveld-QPA method allowed the large, mixed mineralogy of vineyard soils to be fully quantified. Bulk-rock analysis was normalized to 100 wt.%. The wt.% of organic matter (OM), meanwhile, was not combined with the bulk quantitative results; it refers to the whole soil sample.

Agrochemical soil tests are conventionally used to classify soils and land plots. Therefore, additional soil classification parameters like the texture, pH, organic matter content (as determined using elemental analysis) and cation exchange capacity (CEC) were determined for all samples.

Results and discussion

The raw data underwent statistical analysis to identify the most consistently significant scores for a given parameter. The correlation between CEC and the soil's composition was evaluated using multivariate linear statistical analysis, which best suited our study case with multiple dependent variables. The correlation revealed no significant relationships between CEC and most mineral phases of phyllosilicates. Specifically, we found no significant relationships between CEC and the following silicate mineral phases: mica, kaolinite, clinochlore-chamosite and montmorillonite-vermiculite, nor was a relationship found with the total amounts of phyllosilicate measured in the soils.

Yet, statistical analysis revealed a large correlation between CEC and mixed-layer clay minerals (Figure 1a). A strong relationship between the two variables is expressed by the linear regression with estimated model $y = 0.5341\ x + 2.0107$, Pearson's $r = 0.67$ and $p < 0.001$. We observed that the impact of mixed-layer clay minerals on CECs was statistically more significant than the sole physical component, i.e. the soil's textural clay fraction, where the linear correlation between CECs and the clay fraction was $r=0.56$, $p < 0.001$. The research measured the importance of distinguishing between soils' clay fraction and clay minerals, which very differently affect soil fertility indicators.

According to our findings, the mineral phase most closely related to CECs is that of the mixed-layer clay minerals, which should thus be carefully considered in terroir studies. This mineral component of the soil is even more important than its physical counterpart, the clay fraction. The results and scatter points in Figure 1a are consistent with the findings of other studies on mixed-layer clays (Saidian et al., 2016). This typical dispersion greatly depends on the highly variable mineral and physical features of the soil's many parent materials, originating from widely ranging geological locations worldwide.

The effect of the clay content on CEC data cannot be interpreted without considering the effect of organic matter (OM). Our results show that the effect of OM on the CEC is more profound than that of clay ($r=0.79$ at $p < 0.001$), but it is known to decrease with the OM content in the soil; thus, the role of minerals is always important and should never be neglected during soil quality assessment in a vineyard. A separate analysis of the samples with the lowest OM contents (OM <1.5%) revealed a significant, moderate relationship between phyllosilicate minerals and the CEC ($r=0.67$, $p < 0.005$). For samples with the least OM (OM <1.0%), the impact of phyllosilicate minerals on the soil's fertility was most evident, and the linear relationship with CEC became stronger ($r=0.76$, $p < 0.05$).

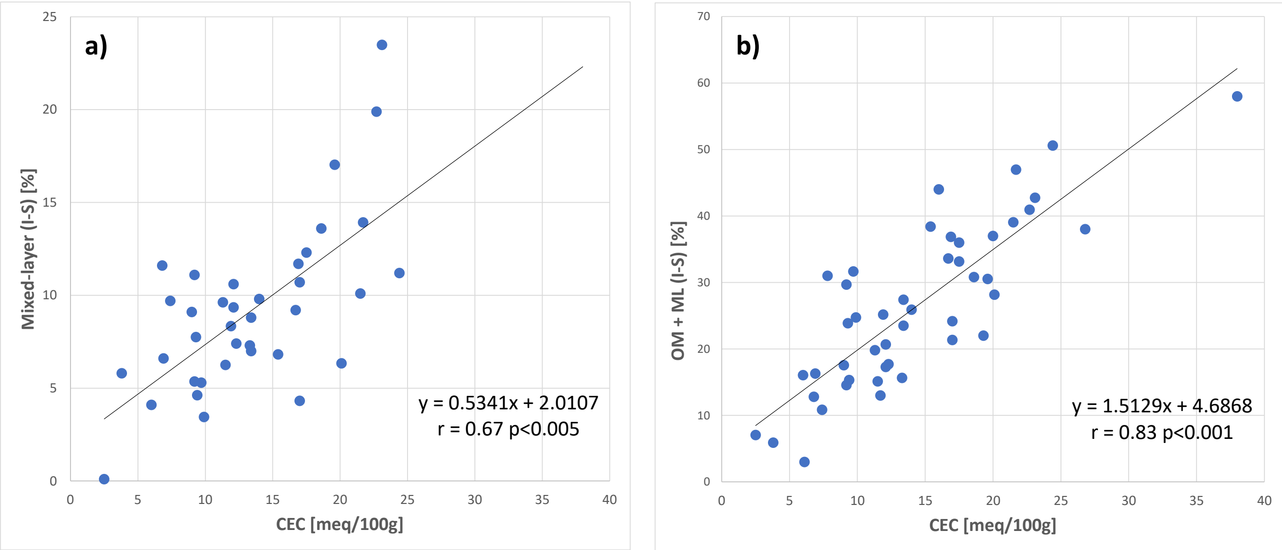

Figure 1. Cross plot and Pearson's correlation tests of (a) cation exchange capacity (CEC) and mixed-layer clays; (b) CEC and organic matter (OM) + mixed-layer clays. The data of graph (a) were cleaned to remove irrelevant outliers associated with intense biodynamic fertilisation and a rare mineralogical condition of the vineyard, which is distinguished by hydrothermal volcanic soil.

To better assess the importance of mixed-layer illite/smectite (I-S) on the vineyard soil's fertility, we tested a weighted contribution to CEC of the I-S clays added to the OM through a process of dataset correlation curve fitting. Mixed-layer I-S has a CEC in the range of 10–150 meq/100 g (Grim, 1953; Gunderson et al., 2000), which at its highest is nearly half that of OM, ranging from 150 to 400 meq/100 g (Brady and Weil, 2008). In our search, the line of best fit ($r=0.83$ $p<0.001$) that best expressed the relationship between the measured CEC and soil components OM + mixed-layer I-S was obtained by assigning mixed-layer clays a weighted exchange capacity about half that of organic matter (Figure 1b).

Research has revealed the important influence of mixed-layer clays on certain soil's fertility attributes. These clays in the past, were often misclassified in clay's illite group, which is a less reactive inorganic materials. Overcoming such misclassification, mixed-layer clays detection in soils could now, for example, explain the quality of certain wines from vineyards with very low soil clay fractions (<10%).

Conclusion

This research has documented how to obtain important new information on terroir sub-factors through accurate Rietveld-QPA of soil's mineral phase fractions, which allowed us to fully quantify the mineralogy of vineyard soils in a globally comparable manner. Modelling mixed-layer clays (e.g. illite/smectite) using a Rietveld-QPA approach showed these minerals are found in significant amounts in many vineyard soils worldwide. The importance of mixed-layer clays for the soil's fertility, specifically its CEC, was demonstrated as about 50% of that typical of soil organic matter. At the same time, clay's wettability and soil aggregate stability are steadier as there is less swelling behaviour of the I-S system. Mixed-layer clays should thus be measured and considered in soil quality assessment studies as specific predictive indicators of terroir quality.

Acknowledgements

The authors acknowledge S. Febbroni for data analysis and statistical survey, GIR Geo Identity Research for the soil sample and geographical data. This work was supported by the Autonomous Province of Bolzano/Bozen [grant number 256/2020].

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