

CLAY MINERALOGY OF FINGER LAKES VINEYARDS

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INTRODUCTION

The Finger Lakes region of New York State has been a producer of fine wines for many decades. Several factors, summarized by the French word *terroir*, influence the quality of grapes and wine: the climate, geologic setting, topography, and soil.

This project focused on clay mineralogy as a specific element of the terroir of the vineyards in the Finger Lakes region of New York. Clay mineralogy can have a significant affect on grape nutrient availability.

METHODS

Sample Collection, Preparation, and Analysis

Samples were collected from five vineyards in the Finger Lakes region of New York State including Shalestone Vineyard, Standing Stone Vineyard, Fox Run Vineyards, Sheldrake Point Vineyards and Dr. Konstantin Frank's Vinifera Wine Cellars. Samples at Shalestone and Standing Stone were taken roughly in the middle of ~1 m augers holes that averaged 30 cm in diameter. Samples from the other three vineyards were supplied by students working on those vineyards. Bedrock samples also were collected from outcrops at each of the vineyards.

Samples were disaggregated in water and centrifuged to 1 μ m. Oriented clay slides were prepared using the Millipore[©] Filter Transfer Method, also known as the Vacuum Pump Method (Moore and Reynolds, 1997).

Samples were analyzed with an XDS 2000 X-Ray Diffractometer (XRD) with Cu K alpha

radiation using a Nickel filter. Air-dried samples were scanned from 2 to 32 degrees 2 theta at a step size of 0.01 degrees 2 theta. One sample, 6JulySa, was also saturated in potassium chloride overnight in order to test for expansion indicative of vermiculite. Following the air-dried analysis each sample was placed in a desiccator over ethylene glycol for 24 to 48 hours. The samples were then analyzed by XRD using the same operating conditions as the air-dried samples. Subsequent to this analysis, the slides were heated in an oven at 350 °C for one hour and then scanned again in order to measure the degree of collapse due to dehydration. Finally, the slides were heated a second time at 500 °C for one hour and scanned once more to detect any further collapse. The resulting XRD scans were the main means of identifying the clay minerals. Scan peaks were identified and compared to those in the literature, primarily Moore and Reynolds (1997).

Cation Exchange Capacity Exchangeable Bases

To measure exchangeable bases of the clay minerals, samples were saturated with ammonium chloride so that the exchangeable bases (calcium, magnesium, potassium and sodium) were replaced by ammonium ions. The exchanged bases in the solution were then measured using the Büchner Funnel Procedure (Page et al., 1982). Because pH of the solutions did not need to be controlled, ammonium chloride was used instead of ammonium acetate (Page et al., 1982). Solutions to be analyzed for calcium and

magnesium were diluted by 20 percent with 5 percent lanthanum chloride to reduce interferences with dissolved silica oxide.

Base cation concentrations were analyzed with a Perkin Elmer Model 3030 Atomic Adsorption spectrophotometer. Absorption mode was used for measuring calcium and magnesium whereas sodium and potassium were measured by emission. Calibration standards for each of the cations were made in 1 mg/L, 2 mg/L, 5 mg/L and 10 mg/L concentrations and the values (in mg/L) were calculated in relation to the standards (Equation 1). The samples had to be diluted with deionized water by a factor of 10 to find the exchangeable potassium, by a factor of 20 to find the exchangeable magnesium and a factor of 50 to find the exchangeable calcium. Equations 2 and 3 show how the dilutions and the lanthanum chloride dilutions were taken into account in calculating the exchangeable bases. No dilutions were necessary to determine the exchangeable sodium.

Equation 1: Calculating exchangeable base concentration (meq/100g)

$$\text{meq/100g} = [(\text{Extract volume (mL)}) / (\text{Soil weight (g)} * 0.1 * \text{mg/L})]$$

Equation 2: Calculating concentration with Lanthanum dilution

$$\text{Ca and Mg meq/100g} = 0.8 * (\text{meq/100g})$$

Equation 3: Calculating concentration based on dilutions

$$\text{X:1 dilution} = \text{X} * (\text{meq/100g})$$

Exchangeable Acidity

Exchangeable acidity was measured by titration using sodium hydroxide. The Potassium Chloride Method was used to obtain the total exchangeable acidity (Page et

al., 1982). The results were then converted to meq per 100 grams (Equation 4).

Equation 4: Calculating Exchangeable Acidity

$$\text{Total Acidity (meq/100g)} = [(\text{mL NaOH in sample} - \text{mL NaOH blank}) * \text{Normality NaOH} * 100] / \text{sample weight (g)}$$

RESULTS

X-Ray Diffraction Images

With few exceptions, all the samples from the vineyards had the following peaks (determined from the glycol treated samples): 14, 10, 7, 5, 4.7, 3.5, and 3.3 angstroms, varying only by a few tenths of an angstrom in either direction. The intensities varied from peak to peak; however, the 14, 10, 5 and 3.3 peaks showed the most intensity. It is also interesting to note that the ratios of peak intensity vary from graph to graph. This difference can be seen most clearly in a comparison of Figures 1 and 3. The intensity of the 5.0 peak in Figure 1 is higher than the 4.7 peak, whereas in Figure 3 both the 5.0 and 4.7 peak are of roughly equal intensities.

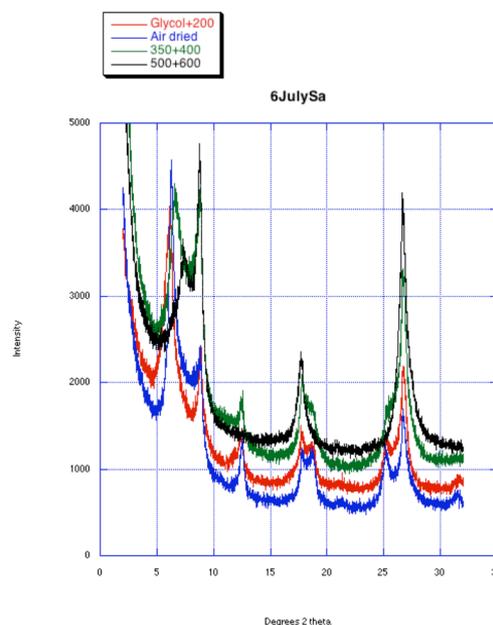


Figure 1. Sample 6JulySa from Shalestone vineyard. Sample was scanned air-dried, treated in glycol, and heated to 350 and 500 °C.

The Penn Yan bedrock scan shows typical bedrock clay peaks at 14, 10, 7, 5, 4.7, 4.5, 4.2, 3.5, and 3.3 angstroms (Fig. 4). These peaks are much narrower than the soil sample scans with no overlapping or broad peaks.

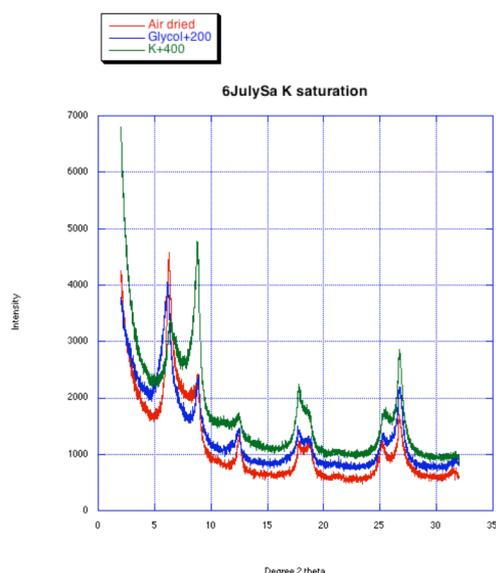


Figure 2. Sample 6JulySa from Shalestone vineyard. Graph shows the effects of K-saturation on vermiculite (peaks 14, 7, 4.8, 3.5 angstroms).

Cation Exchange Capacity Exchangeable Bases

Calcium dominated the exchangeable bases, whereas the amounts of sodium and potassium were very low. The magnesium content was also quite low, although it was noticeably higher than sodium and potassium (Fig. 5). The total exchangeable bases varied significantly from site to site in the same vineyard, as illustrated by the differences of 6JulySB, 10JulySa and 10 JulySc, all from Shalestone Vineyard. 10JulySc has the lowest amount of exchangeable bases, while 10JulySa has the highest and yet these samples were taken within the same acre.

The total exchangeable acidity was extremely low for each vineyard (Table 1) and therefore does not contribute significantly to the total cation exchange capacity of the minerals present.

INTERPRETATIONS

Clay Mineralogy

Each vineyard contains a mixture of soil vermiculite and illite, which is to be expected because illite is present in the bedrock and vermiculite is a common weathering product of chlorite, and New England tills are relatively rich in illite, chlorite and vermiculite (Chamley, 1989). The ratios of vermiculite to illite vary from sample to sample; however, they are fairly consistent from vineyard to vineyard (Figs. 1-4).

Additional evidence for the presence of illite and vermiculite comes from the peak positions of the samples treated in ethylene glycol. Peak positions at 14.0, 7.4, 4.83, and 3.55 angstroms are indicative of vermiculite and were present in all soil samples (Moore and Reynolds, 1997). In addition to the peak positions, Figure 2 also indicates the presence of vermiculite by the significantly diminished 001 peak at 14 angstroms and the expansion of 10 angstrom peak, which shows the collapse of vermiculite to illite (Moore and Reynolds, 1997).

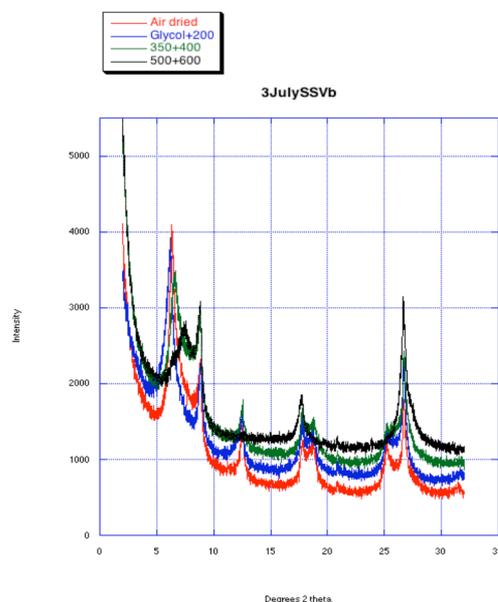


Figure 3. Sample 3JulySSVb from Standing Stone vineyard. Sample was scanned air-dried, treated in glycol, and heated to 350 and 500 °C.

Illite was identified based on peak positions and relative intensities. Pure illite has peaks at

10, 5 and 3.3 angstroms with the first and third peaks being the most intense (Moore and Reynolds, 1997). This can be seen in the air-dried and glycol treated samples (Figs. 1-4).

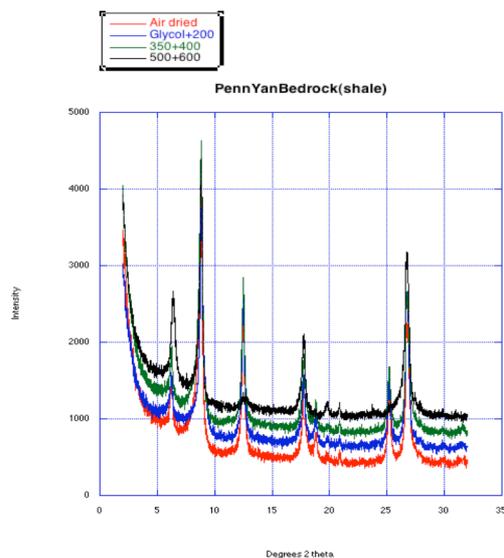


Figure 4. Bedrock sample from Shalestone and Standing Stone vineyard. Sample was scanned air-dried, treated in glycol, and heated to 350 and 500 °C.

Sample	Total Exchangeable Acidity
B27	0.55
10JulySc	0.45
8JulySSVe	0.00
J8-6	0.00
Ben9	0.00

Cation Exchange Capacity

The observed exchangeable base results are not unexpected, as the abundance of available calcium and magnesium is generally higher than sodium and potassium (White, 2003). Calcium, magnesium and potassium are all important macronutrients for grape vines; calcium plays an important role in the cell structure, magnesium is needed for chlorophyll function and potassium affects grape ripening and pH (White, 2003). Without these nutrients, the vines may suffer from such ailments as chlorosis and the yellowing and ultimate death of leaf margins

(White, 2003). According to the owners of Shalestone and Standing Stone Vineyards, there were no major nutrient deficiencies in the grapes, consistent with the observed presence of clay minerals. Shalestone has the largest range in exchangeable bases, but it is not known if this is related to wine quality.

The low exchangeable acidity of the clay minerals may also be beneficial to the grape vines, as the soil is not so acidic that it leaches nutrients out of the soil (White, 2003).

CONCLUSION

The vermiculite and illite in the soil are a result of the weathering of the chlorite and illite in the calcareous shale bedrocks of the region. The cation exchange capacity of these clays provides nutrients such as calcium, magnesium, potassium and sodium to the grape vines. The high clay content of the soils means that clay may play a significant role in grape vine nutrient availability and ultimately for wine quality.

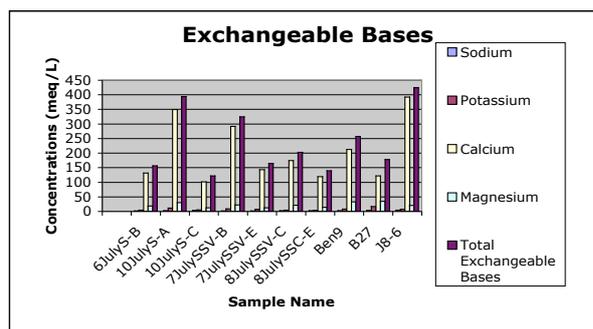


Figure 5. Graph of Exchangeable Bases

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