2007-2008 PROJECTS:

**Tectonic and Climatic Forcing of the Swiss Alps**
John Garver (Union College), Mark Brandon (Yale University), Alison Anders (University of Illinois), Jeff Rahl (Washington and Lee University), Devin McPhillips (Yale University)
Students: William Barnhart, Kat Compton, Rosalba Queirolo, Lindsay Rathnow, Scott Reynhout, Libby Ritz, Jessica Stanley, Michael Werner, Elizabeth Wong

**Geologic Controls on Viticulture in the Walla Walla Valley, Washington**
Kevin Pogue (Whitman College) and Chris Oze (Bryn Mawr College)
Students: Ruth Indrick, Karl Lang, Season Martin, Anna Mazzariello, John Nowinski, Anna Weber

**The Árnes central volcano, Northwestern Iceland**
Brennan Jordan (University of South Dakota), Bob Wiebe (Franklin & Marshall College), Paul Olin (Washington State U.)
Students: Michael Bernstein, Elizabeth Drewes, Kamilla Fellah, Daniel Hadley, Caitlyn Perlman, Lynne Stewart

**Origin of big garnets in amphibolites during high-grade metamorphism, Adirondacks, NY**
Kurt Hollocher (Union College)
Students: Denny Alden, Erica Emerson, Kathryn Stack

**Carbonate Depositional Systems of St. Croix, US Virgin Islands**
Dennis Hubbard and Karla Parsons-Hubbard (Oberlin College), Karl Wirth (Macalester College)
Students: Monica Arienzio, Ashley Burkett, Alexander Burpee, Sarah Chamlee, Timmons Erickson
Andrew Estep, Dana Fisco, Matthew Klinman, Caitlin Tems, Selina Tirtajana

**Sedimentary Environments and Paleoeconomy of Proterozoic and Cambrian “Avalonian” Strata in the United States**
Mark McMenamin (Mount Holyoke College) and Jack Beuthin (U of Pittsburgh, Johnstown)
Students: Evan Anderson, Anna Lavarreda, Ken O’Donnell, Walter Persons, Jessica Williams

**Development and Analysis of Millennial-Scale Tree Ring Records from Glacier Bay National Park and Preserve, Alaska (Glacier Bay)**
Greg Wiles (The College of Wooster)
Students: Erica Erlanger, Alex Trutko, Adam Plourde

**The Biogeochemistry and Environmental History of Bioluminescent Bays, Vieques, Puerto Rico**
Tim Ku (Wesleyan University) Suzanne O’Connell (Wesleyan University), Anna Martini (Amherst College)
Students: Erin Algeo, Jennifer Bourdeau, Justin Clark, Margaret Selzer, Ulyanna Sorokopoud, Sarah Tracy

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INTRODUCTION

The Walla Walla Valley American Viticultural Area (AVA) is a wine-producing area in eastern Washington state. Within this AVA, the region west of Milton-Freewater is a location with a distinctive terroir. Terroir, a viticultural term, describes the sense of place captured in the grape that shows through in the flavor of the wine. This sense of place is a characteristic of the location where the plant is grown and the result of all of the interactions that take place within the “critical zone.” All life on the planet exists within this zone at the Earth’s surface that extends from the upper reach of vegetation to the lower limits of groundwater (Brantley et al., 2007). Geologic, atmospheric, biologic, and anthropogenic inputs are all key aspects of the critical zone (Amundson et al., 2007), and their interactions form the terroir.

One way that terroir may be expressed is through the chemistry of the vines. Their chemistry is a function of the interaction of geologic, atmospheric and anthropogenic variables, both as sources of elements and determinants of element availability and uptake. An analysis of the rock chemistry, soil chemistry, and plant chemistry at different vineyards can help to quantify the relative contributions of these different aspects of the critical zone. These three characteristics were measured at nine vineyards in the region to the west of Milton-Freewater, Oregon (Fig. 1).

GEOLOGIC SETTING

All of the sampled vineyards near Milton-Freewater are located on an alluvial fan that was formed by an ancestral channel of the Walla Walla River earlier in the Holocene (Meinert and Busacca, 2000). These alluvial sediments consist of a mixture of slackwater deposits and weathered Columbia River flood basalt. The slackwater deposits are associated with outburst floods from glacial Lake Missoula. This 7800 km² glacial lake in Montana flooded more than 30 times between 15,300 and 12,700 years ago, releasing 2500 km³ of water in each flood that rushed through eastern Washington and Oregon and picked up sediment as it traveled. This sediment has a granitic character. The water was temporarily dammed by a narrow canyon, so much of the sediment
fell out of suspension. The slackwater sediments were deposited, forming graded beds called the Touchet beds (Carson and Pogue, 1990). The basalts were weathered by the river, and many basalt fragments remain cobble-sized based on relative close proximity to their source. The resultant soil is an Entisol and is characterized by a bimodal size distribution of silt and rounded cobbles. In the present day, the windblown transportation and deposition of fine sediment as loess is common in this area, and loess also has the potential to contribute to the chemistry of the soil.

**METHODS**

Three samples were collected from each of nine vineyards distributed across the alluvial fan. At eight of the vineyards, an approximately 50 cm-deep soil pit was dug at the base of a grapevine in its root zone. From this pit, an integrated soil sample was collected through the entire soil profile. Sampling was done in such a way as to exclude cobble-sized material. Cobbles were collected separately at three of the sample sites. Samples of leaves, with the stems removed, were collected from the vine immediately adjacent to the hole. At the ninth vineyard site, only soil samples were collected, as this was a new vineyard, and grapevines had not yet been planted.

Major and trace element analyses were performed on bulk soil samples from each soil sample site and on cobble samples from the three cobble sample sites. Sample preparation followed the methods described by Rhodes (1996). Major elements (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P) were analyzed using a Siemens MRS-400 multi-channel, simultaneous X-ray spectrometer. Trace elements (Nb, Zr, Y, Sr, Rb, Th, Pb, Ga, Zn, Ni, Cr, V, Ba, Ce, and La) were analyzed using a Philips PW2400 sequential spectrometer. For soil samples, loss on ignition (LOI) was used to determine the percent mass of organic carbon and calcium carbonate. The samples were heated to 550°C for 2.5 hours to measure organic carbon and to 950°C for 2 hours to measure the amount of calcium carbonate using the method described by Heiri et al. (2001).

Cation exchange capacity was determined for all soil samples using a KCl extraction for the acid cations and an NH₄Cl extraction for the base cations. The concentration of acid cations (H⁺ and Al³⁺) was measured using titration with NaOH and back titration with HCl after the addition of KF. The concentration of the base cations (Ca²⁺, Mg²⁺, Na⁺, and K⁺) was measured in the extracts using a Perkin Elmer model 2020 atomic absorption spectrometer. To determine the plant chemistry, leaves were first washed, dried, ground, and ashed for seven hours at 480°C after a gradual increase in temperature. Samples were prepared using the method described by Radojevic and Bashkin (1999). A filtered HNO₃ acid leach of the ash was analyzed using ICP spectrometry. Plant samples were analyzed for Ca, Mg, Na, K, Sr, Mn, Ba, Zn, and Pb.

**RESULTS**

**Major and Trace Element Chemistry of Soils and Cobbles**

Silica is the most abundant element in both the soils and cobbles. The soils contain higher amounts of Si, Al, Zr, Pb, Zn, Ni, and Cr. The cobbles contain higher amounts of Ti, Fe, Mn, Mg, Ca, Na, K, P, Nb, Y, Sr, V, and Ba. The soils and cobbles had overlapping values of U, Th, Ga, Ce, and Li (Table 1). Lead and Zn in the soils are the only two elements that show large amounts of variation both between and within vineyards. They have high standard deviation values. Zn, with an average of 191ppm in the soils has a standard deviation of 157.4ppm. The average value of lead, 148ppm, is less than the standard deviation, 166.0ppm.

**Exchangeable Soil Chemistry**

The cation exchange capacity in these soils is relatively low (Eby, 2004) with an average value of 19.2 meq/100g. The exchange sites in all samples were dominated by base cations, and the soils had an average base saturation of 99.7%. Of the two acid cations, H⁺ and Al³⁺, H⁺ had low quantities averaging around 0.06 meq/100g, and no Al³⁺ was measured in any of the soils. The most abundant
exchangeable ion was Ca$^{2+}$ with an average value of 13.12 meq/100g. Magnesium was the second most abundant ion (average 4.25 meq/100g), potassium was the third (average 1.68 meq/100g), and sodium was the fourth (average 0.088 meq/100g) (Table 1). No significant trend in quantity of exchangeable elements was present between the vineyards.

**Plant Chemistry**

Of the eight elements analyzed, the average sequence from greatest to least abundant was: Ca, K, Mg, Na, Sr, Mn, Ba, Zn, Pb (Table 1). The amount of calcium was about three times larger than any of the other elements. Although Ca (average 33.6 mg/g), K (average 11.41 mg/g), and Mg (average 4.26 mg/g) had higher values, none of the other elements at any of the locations had values greater than 0.3 mg/g. There were large variations of Zn, Na, and Pb both within and between the different vineyards.

**DISCUSSION**

Elemental trends and relative quantities change between the cobbles, soils, and plants. This is partially a result of selection processes in the weathering of the cobbles, the exchange sites of the soil, and the uptake of the plants. The soil and cobbles chemical analyses all measured a lower value of K than Mg. This relationship is reversed in the plant. The higher values of K could be the result of the fact that K$^+$ is more easily transported in the plant than Mg$^{2+}$ (Larcher, 1995). The amount of Na$^+$ also changes its relative abundance as it travels from the rock, to the soil, to the plant. Sodium is lower than Ca and Mg but is higher than K in the total cobbled and soil analyses. In the exchangeable portion of the soil, Na$^+$ has the lowest value. Na$^+$ is very soluble, and it is also the cation with the least tendency for absorption (Larcher, 1995). It is likely that sodium has been leached out of the soil.

The only soil element of the four measured for both total chemistry and exchange that shows a significant relationship between these two values is K (Fig. 2). This suggests either that most of the potassium in the soil is exchangeable or that most of the potassium that weathers out of the soil immediately occupies the exchange sites. It appears that plant uptake and weathering of potassium occur at a similar rate.

The values of Mg, Ca, and Sr in the plant are positively related. These three elements are all alkaline earth elements with a charge of $2^+$, so that could be responsible for the similar tendency for absorption and transportation by the plant.

![Figure 2: The amount of exchangeable soil K is directly related to total soil K.](chart)
There is a significant positive relationship between the cation exchange capacity and the amount of organic C (Fig. 3). Organic material in the soil has a slight negative charge and can therefore act as an exchange site, so when there is more organic material, the soil will be able to hold more cations.

Some variation in the chemistry between the soils and cobbles appears to be caused by more than just selective weathering and exchange. There is much more Pb in the soils than the cobbles (as much as 30 times more in some of the soils), so this suggests that there is an outside source for lead. This source could be atmospheric or anthropogenic. Because...
the lead values vary greatly between the different vineyards and even within the same vineyard, it is unlikely that the source is atmospheric. At the scale of the vineyards in this study, atmospheric deposition should be fairly consistent across the entire area. Anthropogenic deposition of lead on the vineyards through agriculture is highly possible because there is a long history of orchards in the area. One source of Pb in agriculture is in pesticides. Pesticides used in orchards in the early 1900s contained Pb and As, and the use of these pesticides for a number of years can lead accumulation of lead and arsenic in the soil (Newton et al., 2006). Another possible source of Pb is aerosol deposition from vehicle use of leaded gasoline, although there is no correlation between vineyards high in lead content and close proximity to roads. Lead is also the only element that shows a significant positive correlation between the total soil chemistry and the plant chemistry.

Chemical variation between vineyards provides evidence that the vineyard management influences the chemistry. The total soil chemistry shows that soil Zn and Pb vary between vineyards, and plant analyses found that plant Zn, Pb, and Na chemistries vary between vineyards. The fluctuations between the vineyards are more pronounced in the plants than the soils (Fig. 4). The vineyard specific concentrations suggest that management does have the ability to influence the chemistry of the soil and the plants. Management potentially has a larger influence on the plants than the soils.

CONCLUSION

Interactions in the critical zone shape the chemistry of the plants. Weathering of the cobbles and the soil releases ions for exchange, but in the transition to exchange sites, only potassium has a direct relationship with the soils. Processes, including leaching of Na, change the composition of the ions. Selective uptake of ions by the plant also changes the relative composition in the plant, and only Pb shows a direct relationship between the soil and the vine. Anthropogenic inputs into the critical zone appear to have added elements, including Pb, to the soil. Anthropogenic management of a vineyard also influences uptake of ions by the plant. These critical zone interactions that rely upon the location's geology, atmosphere, climate, and management shape the chemistry of the plant and therefore shape the terroir of the wine.

REFERENCES


Newton, K., Amarasiriwardena, D., Xing, B., 2006. Distribution of soil arsenate species, lead and arsenic bound to humic acid molar mass fractions in a contaminated apple orchard: Environ-
mental Pollution, v. 143, p. 197-205.
