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Research Advisor: Dr. James G. Mills, Jr.

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INFLUENCE OF CLIMATE AND LITHOLOGY ON SPRING CHEMISTRY IN THE UPPER DESCHUTES RIVER, OREGON

JULIA SCHWARZ
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Research Advisor: Cameron Davidson

INTRODUCTION

Knowledge of silicate mineral chemical weathering rates is important to the understanding of individual watersheds and the global carbon cycle. Silicate weathering creates bicarbonate from the uptake of atmospheric CO_2, and quantifying this process has major impacts for the global carbon cycle, as well as for rivers, which transport bicarbonate to the oceans (Walling and Webb, 1992a; Bluth and Kump, 1994; Suchet et al., 2003; Velbel and Price, 2007). Within watersheds, silicate rock weathering contributes an estimated 60% of major dissolved constituents (Ca^{2+}, Na^{+}, Si, etc.) to rivers (Walling and Webb, 1992b; White and Brantley, 1995). Clearer understanding of silicate mineral weathering rates will help quantify its role in the global CO_2 budget and to solute fluxes within watersheds.

This paper examines trace element chemistry in springs to determine relative weathering rates across the study area in order to explore factors that affect weathering rates of volcanic rocks in aquifers. The relative weathering rates are then compared to climate, lithology, and residence time.

What controls weathering rates?

Weathering rates are influenced by temperature, kinetics, residence time of water within the soil or rock body, and lithology (Walling and Webb, 1992b; Bluth and Kump, 1994; Bowser and Jones, 2002), since different mineral compositions will lead to variable weathering rates. Spatial variation in weathering rates can be due to elevation, air and water temperature (ambient and mean annual), precipitation, and topographic features (Walling and Webb, 1992b; Bluth and Kump, 1994).

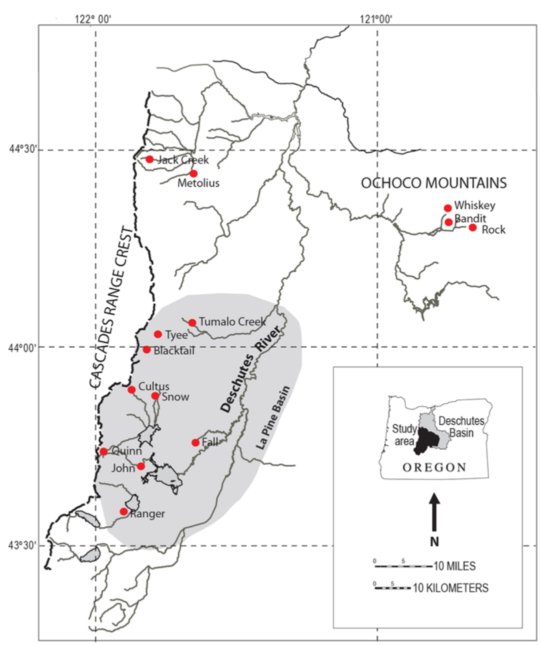
One of the most straightforward ways of quantifying weathering reactions is a geochemical mass-balance model, which helps to quantify fluxes in and out of the system and determine weathering rates of minerals by defining system inputs and outputs and accounting for the difference (Garrels and Mackenzie, 1967; Bricker and Jones, 2005; Velbel and Price, 2007). These models generally use concentrations (such as this study) or mass flux of solutes (Bricker and Jones, 2005). Studies based on concentrations are useful in determining the weathering reactions that are occurring, but they do not provide sufficient information to determine quantitative weathering rates. In this study, the idea of input-output budgeting is used to determine a relative weathering rate across the study area by using a simplified idea of weathering rates, specifically, that the weathering rate is approximately equal to the change in solutes in the system (output chemistry – input chemistry) divided by the residence time.

Watershed inputs include all processes that introduce minerals or elements into the watershed, such as precipitation and silicate weathering, which is influenced by rock composition (Bluth and Kump, 1994; Velbel and Price, 2007). Watershed outputs are measured by trace elements in spring water discharge. Rare earth elements (REEs) have been increasingly used in hydrologic studies, and the source of dissolved REEs in ground water is generally assumed to be weathering of the substrate rock (Garcia et al., 2007).

The residence time of water in the subsurface also plays an important role in mineral weathering. Since the 1930's, chlorofluorocarbons (CFCs) have been released into the atmosphere, where they last from 50 to 100 years. Waters exposed to the atmosphere have CFC concentrations corresponding to the year the water was last exposed (Phillips and Castro, 2005), so CFC concentrations are useful for dating young groundwaters, though the method is insensitive to dispersion and mixing of waters (Phillips and Castro, 2005).

GEOLOGIC SETTING

Waters within the Deschutes River watershed fall as precipitation on two main mountain ranges, the Cascades Mountains in the west, and the Ochoco Mountains in the east (Fig. 1). The precipitation chemistry is similar across the study area, but volume is higher in the west. Highly permeable igneous rocks allow precipitation to enter the subsurface and flow through the basin (Gannett et al., 2001). The Ochocos are made of predominantly Tertiary andesite, whereas the western part of the study area is predominantly Quaternary basalt. In particular, the Ochocos are composed of Oligocene, Eocene, and Paleocene clastic rocks and andesite flows, with some Cretaceous sedimentary rocks and Middle Tertiary tuffs; the Cascades crest is nearly all Quaternary basalt, basaltic andesite, Quaternary alluvium, and glacial deposits.



Central Oregon is part of the Oregon high desert, which averages less than 5 cm of rainfall per month, with June through August the driest months (NOAA, 2006). Precipitation is highest in the western half of the study area and lower in the Ochocos, but precipitation chemistry is similar across the study area. Precipitation chemistry shows the average pH is 5.31, and the average conductivity 58.5 µS, averaged from 1983 to 2009 (NADP). The mean annual temperature for the study area is 6.6 °C for the western half of the study area and 6.3 °C for the eastern half (Ochocos), averaged over a period of 1971-2000 (NOAA, 2006).

METHODS

This study is primarily concerned with the chemistry of 14 springs sampled in the headwaters of the Deschutes River. Eleven of these springs are within 30 km east of the Oregon Cascades crest, and three (Bandit, Rock, and Whiskey) are located in the Ochoco Mountains, over 100 km from the Cascade crest.

Spring samples were tested for dissolved oxygen (DO), conductivity, pH, temperature, alkalinity, chlorofluorocarbons (CFCs) and trace elements (PerkinElmer/Sciex Elan 6100 DRC at Union College in Schenectady, NY). DO and water temperature were collected by a YSI 58 Lab/Field Dissolved Oxygen meter. Conductivity was collected with a PCSTestr 35 conductivity probe. pH was recorded with a Thermo Orion 3 Star pH meter with a glass Orion Ross combination pH electrode. Samples for CFC dating were collected using USGS methods (Plummer and Busenberg, 2009) and tested at the Tritum Laboratory at the University of Miami. Alkalinity samples were tested using the Gran titration

.Figure 1. Schematic map of the study area with spring sample sites marked as red circles. The Cascades Range crest borders the study area on the west, and is the recharge area for springs on the west side of the study area. For the purposes of this study, springs are separated into two main groups, the Ochoco springs (Rock, Whiskey, and Bandit) and springs within 30 km of the Cascades crest. The La Pine Basin is a subsection of the Cascades springs area, and is shown on this map by a grey background. Map modified from Gannett et al. (2001).

method (Gran et al., 1981). All samples except for CFCs were filtered with a 0.45 micron nylon filter. ICP-MS and alkalinity samples were collected in 30mL HDPE bottles. ICP-MS samples were prepared with 5 drops of ultra pure nitric acid.

A USGS surface geologic map of Oregon (Walker and MacLeod, 1991; Sherrod and Smith, 2000; Lite and Gannett, 2002) and a groundwater flow map (Lite and Gannett, 2002) were used to approximate the different rock types within each spring drainage area. There is no data on subsurface composition in the Deschutes headwaters area, so this study uses surface lithology as a proxy for subsurface composition.

RESULTS

Trace element concentrations in spring waters are given in Table 1. Element concentrations are higher in springs within the Ochocos than in spring waters within 30 km of the Cascades crest. Rare earth elements (REE) were normalized to upper continental crust (UCC) values (Fig. 2) (Taylor and McLennan, 1985; Garcia et al., 2007). Springs in the Ochocos have higher concentrations of REEs than springs close to the Cascades crest (Fig. 2). All spring samples have higher concentrations of heavy rare earth elements (HREE) compared to light rare earth elements (LREE). Spring water residence times are given in years in Table 1. The residence times across the study area are similar, with the exception of the Metolius Spring.

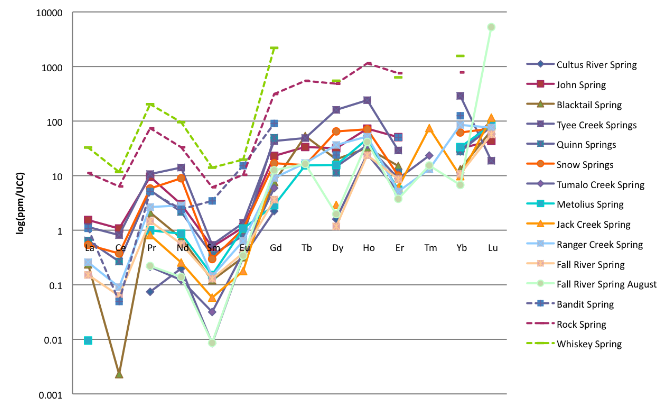


Figure 2. Plot of rare earth elements in spring samples, normalized to upper continental crust values (Taylor and McLennan, 1985). Ochoco springs are shown with dotted lines. REE concentrations in the Ochocos are higher than in the Cascades. All springs show higher concentrations of heavy rare earth elements (HREE) over light rare earth elements (LREE), which reflects the high HREE solubility in water. Comparing dysprosium (Dy) concentration to holmium (Ho) concentrations separates out two different types of weathering trends.

The average sampled water temperature in the Deschutes headwaters is 6.0 °C for springs. Water temperature in the Ochocos and the Metolius River was higher with an average of 12.0 °C. Conductivity was

	Li (ppm)	B (ppm)	Al (ppm)	Mn (ppm)	Fe (ppm)	Ni (ppm)	Co (ppm)	Cu (ppm)	Zn (ppm)	As (ppm)	Se (ppm)	Rb (ppm)	Sr (ppm)	Mo (ppm)	Cd (ppm)	Ba (ppm)
Cultus River Spring	1.418	0.752	0.931	0.024	3.934	0.056	0.016	0.133	0.790	0.085	bdl*	3.709	21.991	0.197	bdl*	1.160
John Spring	0.852	1.061	19.470	0.808	9.132	0.037	0.015	0.905	0.794	0.061	0.049	3.241	26.613	0.172	0.002	0.913
Blacktail Spring	1.662	1.569	2.509	0.204	4.142	0.049	bdl*	1.362	2.681	0.073	0.021	3.603	15.972	0.245	0.023	0.818
Tyee Creek Springs	15.780	4.574	14.973	1.695	4.347	0.417	0.007	2.375	16.896	0.481	bdl*	7.826	6.516	0.809	0.021	1.694
Quinn Springs	15.258	10.027	3.317	0.145	0.346	0.058	0.021	1.046	1.991	3.013	0.018	3.187	7.376	0.698	0.004	0.820
Snow Springs	2.438	2.525	8.342	0.472	5.537	0.129	0.001	0.423	4.364	0.251	bdl*	2.715	11.643	0.341	0.004	0.859
Rock Spring	0.884	3.075	19.537	1.076	24.123	0.141	0.013	0.773	5.372	0.138	bdl*	1.324	46.130	0.045	0.002	16.514
Whiskey Spring	0.993	1.960	63.120	9.988	44.863	0.259	0.039	4.344	4.685	0.145	0.079	1.398	25.043	0.020	0.003	14.350
Bandit Spring	0.863	12.391	0.426	0.251	124.591	0.263	0.049	1.951	6.456	0.094	0.063	0.973	476.977	0.262	0.003	63.958
Tumalo Creek Spring	2.094	1.759	1.038	bdl*	2.640	0.024	bdl*	bdl*	0.740	0.239	0.013	2.950	16.656	0.145	bdl*	0.753
Metolius Spring	4.650	50.289	4.325	0.106	7.519	0.058	0.015	8.166	6.081	1.315	bdl*	4.750	33.495	0.547	0.003	2.138
Jack Creek Spring	0.866	0.708	1.611	0.076	6.554	0.042	bdl*	0.118	0.734	0.061	bdl*	2.614	28.028	0.210	0.000	0.565
Ranger Creek Spring	2.356	1.594	2.202	0.087	4.777	0.034	bdl*	0.665	0.662	0.071	bdl*	2.684	25.511	0.154	0.001	1.337
Fall River Spring	1.819	3.307	3.986	0.211	7.153	0.067	0.001	7.288	1.903	0.202	bdl*	2.221	24.728	0.322	0.002	1.427
Fall River Spring Aug	1.776	3.017	1.967	0.069	5.922	0.020	0.002	0.065	0.188	0.193	0.047	2.072	24.146	0.326	-0.001	1.351

*below detection limit

Table 1. Trace Elements and recharge age for springsin the Deschutes River watershed

an average of 190.2µS in the Ochoco springs, higher than the average conductivity of 58.9µS in spring water near the Cascades crest. pH was slightly basic in 12 out of 14 samples, with a range from 6.4 to 7.8 and an average of 7.29. Tyee and Blacktail Springs showed a pH of less than 6.65. DO ranged from 73% to 110%.

Percent estimates of surface geology for each spring catchment is given in Table 2. Of the 11 springs sampled within 30 km of the Cascades crest, the primary surface formation is Quaternary basalt. Springs in the Ochocos have catchments of predominantly Tertiary andesite flows and clastic rocks from the Clarno Formation.

DISCUSSION AND CONCLUSIONS

An increase in precipitation and average spring discharge pH and conductivity indicate an addition of dissolved elements to waters within the watershed, primarily from inputs from silicate weathering. pH increases from 5.3 in precipitation to 7.29 in spring waters, and conductivity increases from 4.12 µS to 58.5 µS.

Rare Earth Elements (REEs)

All springs are heavy REE (HREE) enriched over light REEs (LREE) (Luucc/Ybucc) compared to the initial rock ratio, which was also weakly HREE enriched. This corresponds to trends of REE in river water, because HREE are more soluble in water than LREE (Gaillardet et al., 2005). Within the REE graph (Fig. 2), there are two trends of data for HREEs. Springs near the Cascades crest conform more closely with the distribution of HREE in the upper continental crust, though the concentrations may vary. Spring waters in the Ochocos are similar to each other but not as similar to the upper continental crust values.

Springs in the Ochocos have higher concentrations of REEs than springs close to the Cascade crest (Fig. 2). Dysprosium (Dy) concentrations seem to differentiate two types of springs. Many of the springs show about equal concentrations of Ho and Dy, but a few (the springs in the Ochocos and Tyee Spring) show a higher Dy and some a higher Ho concentration (Jack Creek, Fall River (both), and Cultus Springs). This may be due to a difference in the weathering minerals.

	QTmv† (%)	Qb1,Qb2§ (%)	Qb3/Qb4/Qb5# (%)	Qr** (%)	Tob†† (%)	Tca§§ (%)	Tr## (%)	Tct*** (%)	Ks††† (%)
Cascades crest									
Jack Creek Spring			100						
Metolius Spring	10		80		10				
Tumalo Creek Spring			30	70					
Tyee Spring		80	20						
Blacktail Spring		80	20						
Quinn Spring		60	40						
Snow Spring	20		80						
Cultus River Spring	20		80						
Fall River Spring	20	50	30						
John Spring	20		80						
Ranger Creek Spring			100						
Ochoco Mountains									
Rock Spring						90	10		
Whiskey Spring						90	10		
Bandit Spring						90		5	5

*Estimated percent ignores alluvial and glacial sediments

†Quaternary and Tertiary mafic vent deposits

§ Quaternary basalt, 0-25 k.y.

Quaternary basalt, 25 k.y. - 2 m.y.

** Quaternary rhyolite

†† Tertiary olivine basalt

§§ Tertiary clastic rocks and andesite

Tertiary rhyolite

*** Tertiary tuff, predominantly of the Clarno Formation

*Table 2. Estimated percentage of surface rock type by spring catchment, north to south**

Other Trace Elements

This paper concentrates on several elements that are of particular interest. These elements are either abundant in common rock-forming minerals or tracers of rock weathering (c.f. Gaillardet et al., 2005).

Fe, Al, and Mn all have strong positive linear correlations with each other, and waters in the Ochocos have higher concentrations of these elements than springs near the Cascades crest. The strong correlation between these elements suggests that they have a fixed weathering relationship, regardless of concentration. Sm and Nd are correlated to Fe and Al, suggesting that they are also tied up in similar rock weathering reactions.

Arsenic (As) is not correlated with DOC, water temperature, alkalinity, Fe, Al, Mn, Sm, Nd, or vanadium (V). Arsenic is common in fluids within magmatic systems, and is found in high concentrations in Quinn and Metolius Springs, suggesting that the flow path for these two springs may be closer to some deeper magmatic source. This is consistent with the theory postulated by James et al. (2000) that the Metolius Spring waters may be part of a deeper basin flow (James et al., 2000; Gannett et al., 2001; Lite and Gannett, 2002).

Vanadium (V) concentrations are not correlated to alkalinity, DOC, water temperature, pH, or any of the minerals addressed above. However, low vanadium concentration may act as a tracer for certain rock units, particularly Qb1, Qb2, and Tca.

Residence Time

CFC based residence times indicate that all springs except the Metolius River Spring are recharged within the same age range, though the age for Bandit Spring may be younger than the results suggest due to microbes in the water. A strong positive linear correlation between CFC residence times and spring water temperature (r^2=.855) for springs near the Cascades crest follows the theory of James et al. (2000) and Gannett et al. (2001) that springs with longer residence times, such as the Metolius Spring, are part of a deeper regional flow that accumulates heat from a deeper geothermal source.

The strong positive linear correlation between CFC age and alkalinity (r^2=.817) for spring waters with Cascade recharge suggests that waters flowing in the subsurface accrue elements at a constant rate. The Metolius Spring fits this linear trend even though Metolius Spring water has a longer residence time, which further suggests that spring water in the region does not reach saturation.

Relative Weathering Rates

Since the change in solutes is greater in the Ochocos but the residence time of water is similar, this suggests that the weathering rate is faster in the Ochocos than near the Cascades crest. The difference in weathering rates between the two different hydrogeologic units may be due to a difference in lithology, weathering rates, or to differences in water budgets, including less precipitation or greater evaporation. The age or composition of the lithology may contribute to the difference in weathering rates, because rocks in the Ochocos are older. Additionally, some areas are clastic rocks, which may be more susceptible to weathering due to easier water infiltration.

Influence of lithology on weathering rates

The difference in age and composition is a major factor in the high concentrations of trace elements in the Ochocos compared to the Cascades. Vanadium concentrations do not correspond to other elements mentioned above, but outlying data does correspond to different lithology types. Rock, Whiskey, and Bandit Springs all have low vanadium concentrations, and they also have the same percent of Tertiary age rocks, with about 70% Tertiary clastic rocks and andesite flows (Table 4). Tumalo Creek Spring has the highest concentration of vanadium, and it is the only spring catchment that is predominantly made up of rhyolite (80% Qr). Tyee and Blacktail Springs also have very low V concentrations, and these two springs have about the same percentage of the youngest Quaternary basalts (80% Qb1, Qb2). This may indicate a lack of vanadium in these rocks, or that minerals containing vanadium weather at a slower rate in these areas.

pH also corresponds to spring catchments with high percentages of Qb1and Qb2. Particularly, Tyee and Blacktail Springs are the only two springs in the study area that have a pH of less than 6.65 and a high percent of the youngest Quaternary basalts (Qb1, Qb2) (Table 2). One possible reason these springs may have a particularly low pH is that the very young basalts are weathering at a slower rate and thus contribute fewer elements to the subsurface water.

Temperature controls on weathering rates

Near the Cascades crest, spring water temperature is strongly correlated to concentrations of dissolved elements in spring water, as shown by correlations with alkalinity (r^2=.835) and conductivity (r^2= .733). This suggests that near the Cascades crest, temperature can control the concentrations of dissolved elements in the water (e.g. Walling and Webb, 1992a) because temperature controls the reaction rates of the mineral dissolution. Air temperature does not explain high spring water temperatures in the Ochocos, and there is no correlation between temperature and alkalinity or conductivity in the Ochocos. Instead, Ochoco spring temperatures are indicative of a shallow flow path, and water temperature does not control the concentration of dissolved elements.

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