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2009-2010 PROJECTS

SE ALASKA - EXHUMATION OF THE COAST MOUNTAINS BATHOLITH DURING THE GREENHOUSE TO ICEHOUSE TRANSITION IN SOUTHEAST ALASKA: A MULTIDISCIPLINARY STUDY OF THE PALEOGENE KOOTZNAHOO FM.

Faculty: Cameron Davidson (Carleton College), Karl Wirth (Macalester College), Tim White (Penn State University)

Students: Lenny Ancuta, Jordan Epstein, Nathan Evenson, Samantha Falcon, Alexander Gonzalez, Tiffany Henderson, Conor McNally, Julia Nave, Maria Princen

COLORADO – INTERDISCIPLINARY STUDIES IN THE CRITICAL ZONE, BOULDER CREEK CATCHMENT, FRONT RANGE, COLORADO.

Faculty: David Dethier (Williams) Students: Elizabeth Dengler, Evan Riddle, James Trotta

WISCONSIN - THE GEOLOGY AND ECOHYDROLOGY OF SPRINGS IN THE DRIFTLESS AREA OF SOUTHWEST WISCONSIN.

Faculty: Sue Swanson (Beloit) and Maureen Muldoon (UW-Oshkosh)

Students: Hannah Doherty, Elizabeth Forbes, Ashley Krutko, Mary Liang, Ethan Mamer, Miles Reed

OREGON - SOURCE TO SINK – WEATHERING OF VOLCANIC ROCKS AND THEIR INFLUENCE ON SOIL AND WATER CHEMISTRY IN CENTRAL OREGON.

Faculty: Holli Frey (Union) and Kathryn Szramek (Drake U.)

Students: Livia Capaldi, Matthew Harward, Matthew Kissane, Ashley Melendez, Julia Schwarz, Lauren Werckenthien

MONGOLIA - PALEOZOIC PALEOENVIRONMENTAL RECONSTRUCTION OF THE GOBI-ALTAI TERRANE, MONGOLIA.

Faculty: Connie Soja (Colgate), Paul Myrow (Colorado College), Jeff Over (SUNY-Geneseo), Chuluun Minjin (Mongolian University of Science and Technology)

Students: Uyanga Bold, Bilguun Dalaibaatar, Timothy Gibson, Badral Khurelbaatar, Madelyn Mette, Sara Oser, Adam Pellegrini, Jennifer Peteya, Munkh-Od Purevtseren, Nadine Reitman, Nicholas Sullivan, Zoe Vulgaropulos

KENAI - THE GEOMORPHOLOGY AND DATING OF HOLOCENE HIGH-WATER LEVELS ON THE KENAI PENINSULA, ALASKA

Faculty: Greg Wiles (The College of Wooster), Tom Lowell, (U. Cincinnati), Ed Berg (Kenai National Wildlife Refuge, Soldotna AK)

Students: Alena Giesche, Jessa Moser, Terry Workman

SVALBARD - HOLOCENE AND MODERN CLIMATE CHANGE IN THE HIGH ARCTIC, SVALBARD, NORWAY.

Faculty: Al Werner (Mount Holyoke College), Steve Roof (Hampshire College), Mike Retelle (Bates College)

Students: Travis Brown, Chris Coleman, Franklin Dekker, Jacalyn Gorczynski, Alice Nelson, Alexander Nereson, David Vallencourt

UNALASKA - LATE CENOZOIC VOLCANISM IN THE ALEUTIAN ARC: EXAMINING THE PRE-HOLOCENE RECORD ON UNALASKA ISLAND, AK.

Faculty: Kirsten Nicolaysen (Whitman College) and Rick Hazlett (Pomona College)

Students: Adam Curry, Allison Goldberg, Lauren Idleman, Allan Lerner, Max Siegrist, Clare Tochilin

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Keck Geology Consortium: Projects 2009-2010
Short Contributions – WISCONSIN

**THE GEOLOGY AND ECOHYDROLOGY OF SPRINGS IN THE DRIFTLESS
AREA OF SOUTHWEST WISCONSIN**

Project Faculty: *SUSAN K. SWANSON*: Beloit College
MAUREEN A. MULDOON: University of Wisconsin – Oshkosh

**LITHOSTRATIGRAPHIC CONTROLS ON GROUNDWATER FLOW AND
SPRING LOCATION IN THE DRIFTLESS AREA OF SOUTHWEST WISCONSIN**

HANNAH DOHERTY: Mount Holyoke College
Research Advisor: Al Werner

**ESTABLISHING PALEOCLIMATE VARIATION FROM MAJOR AND TRACE
ELEMENTS AND STABLE ISOTOPES IN A TUF A DEPOSIT, WISCONSIN**

ELIZABETH FORBES: Whitman College
Research Advisor: Kirsten Nicolaysen

**A COMPARISON OF TECHNIQUES FOR DETERMINING SPRING SOURCE
AREAS: CRAWFORD COUNTY, WISCONSIN**

ASHLEY KRUTKO: Capital University
Research Advisor: Terry Lahm

**WATER GEOCHEMISTRY OF TUF A-DEPOSITING SPRINGS IN THE
DRIFTLESS AREA, WISCONSIN**

MARY LIANG: Franklin and Marshall College
Research Advisor: Dorothy Merritts

**A CLIMATIC STUDY OF SPRING TUF A DEPOSITS USING STABLE ISOTOPES
AND MAJOR AND TRACE ELEMENT CONCENTRATIONS, SOUTHWESTERN
WISCONSIN**

ETHAN MAMER: Beloit College
Research Advisor: Susan Swanson

TEMPERATURE PROFILE MODELING OF A SMALL SPRING-FED STREAM

MILES REED: DePauw University

Research Advisor: Tim Cope

Funding provided by: Keck Geology Consortium Member Institutions and NSF (NSF-REU: 0648782)

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WATER GEOCHEMISTRY OF TUFA-DEPOSITING SPRINGS IN THE DRIFTLESS AREA, WISCONSIN

MARY LIANG

Franklin and Marshall College

Research Advisor: Dorothy Merritts

INTRODUCTION

The primary objective of this project is to investigate the occurrence of tufa deposition in the Driftless Area, in southwestern Wisconsin. Tufa is a sedimentary rock, formed by the precipitation of calcium carbonate from water (Kawai et al., 2006). Tufa deposition occurs at some spring orifices, but not others (Heller, 1988). The presence or absence of tufa is related to carbonate equilibrium in ground and surface water, and is used here to investigate interactions among geologic, hydrologic, and atmospheric processes.

Spring systems in Wisconsin have limited protection under the 2003 WI Act 310. This act gives the state the authority to evaluate the effects of high-capacity wells on springs. However, the act does not protect low-flow springs, which include those with spring water flow that is less than one cubic foot per second at least 80 percent of the time (2003 WI Act 310). Some low discharge springs can have significant impacts on the environment. Using water quality, this relation between low-flow springs and their local environment is investigated herein.

METHODS

There are numerous springs in the Driftless Area, but few deposit tufa. Springs at Potosi and Platteville tufa falls, located in Grant County, have tufa mounds. At Potosi Falls, three water samples were collected: one at the orifice, a second 10 m from the spring orifice (referred to as mid-stream), and a third at the drip face over the tufa into the Grant River. At Platteville Falls, two tufa spring sites were sampled. At the first, westerly spring, three samples were collected at the orifice, 5 m from the spring orifice (mid-stream), and at the drip face.

Further downstream along the Grant River, approximately 80 meters east from the first tufa spring site, is a second spring with a smaller tufa mound. Samples were collected at the orifice and tufa drip face. Two springs in Crawford County do not have tufa mounds. Water samples were collected at two orifices, referred to as Northeast and Southwest. In total, ten water samples were collected at five sites and three springs. This sampling procedure was carried out three times, for a total of thirty water samples collected for chemical analysis. Initial field analysis included temperature, pH, conductivity, and alkalinity tests.

All water samples were analyzed for major and minor ions using the Standard Operation Procedures of ICP - OES/MS at the University of Wisconsin Soil and Plant Analysis Lab. The results from the lab were evaluated and plotted using AqQa software to depict similarities and differences among samples. Additional graphs were generated using Microsoft Excel to examine relationships among variables, such as pH, carbon dioxide partial pressure, and calcite saturation.

RESULTS

Durov diagrams show that waters from the tufa falls in Grant County (the Potosi and Platteville tufa sites) are chemically similar (Fig. 1). Slight (<10%) differences in water chemistry are seen between the orifice and drip face samples. Cation composition is approximately fifty percent magnesium and fifty percent calcium cations, and close to ninety percent bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) anions (Fig. 1).

The chemistry of the Crawford County spring water

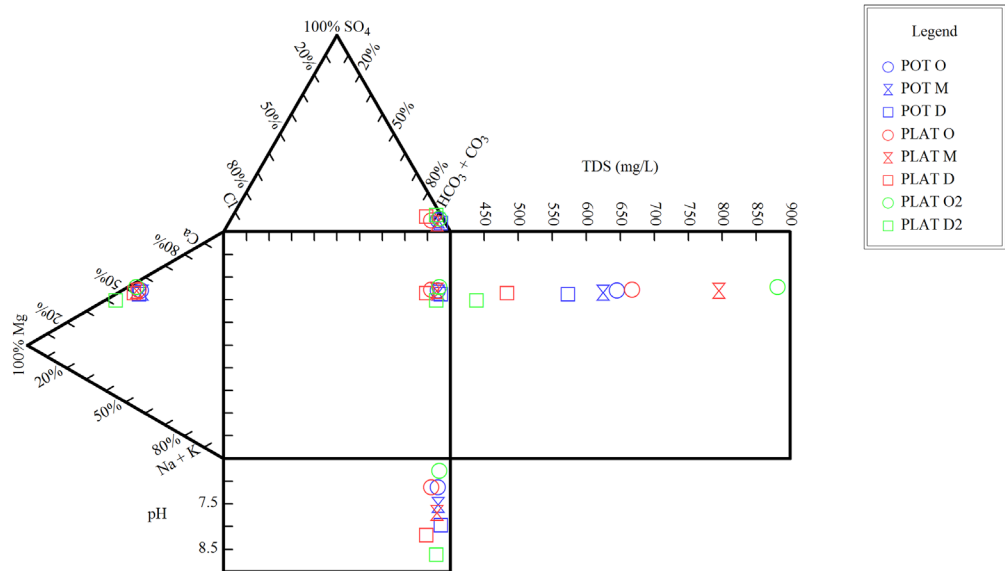


Figure 1. Durov diagram of Grant County tufa springs. The diagram represents the first sample taken from each of the three sites (orifice, midstream, drip face), tested on 7/21 at Potosi and 7/22 at both Platteville springs. The orifice values are represented as circles, midstream values as hourglasses, and drip sites as squares.

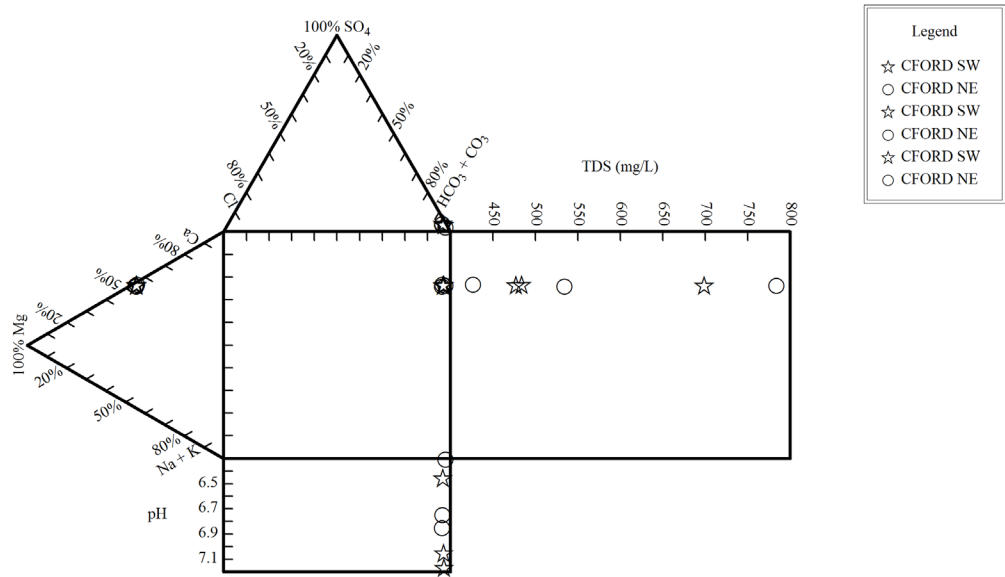
is very similar to that of the Grant County tufa spring water (Fig. 2). Water from the Crawford County springs, which produce no tufa, contains about 50 percent magnesium and 50 percent calcium cations. Water from these springs has a slightly higher percentage of bicarbonate (HCO₃⁻) and carbonate (CO₃⁻²) ions than the Grant County tufa springs (Fig. 2).

The partial pressure of carbon dioxide and pH vary with respect to distance from the orifice (Fig. 3) for the Grant County springs. The Grant County Durov diagrams also show TDS values decrease with distance from the spring orifice. The pH values are high and carbon dioxide partial pressure low for samples collected at the drip face with respect to samples collected at midstream sites. The partial pressure of carbon dioxide and pH values vary for the orifice sites at the Potosi and Platteville springs. The Potosi orifice site has a high carbon dioxide partial pressure (0.125), and low pH (6.56). The Platteville orifice site has a low carbon dioxide partial pressure (0.025), and high in pH (7.43) (Fig. 3), (Table 1). Generally, as the partial pressure decreases,

es, the pH increases, with a correlation coefficient of 0.546 (Fig. 3).

The partial pressure of carbon dioxide and calcite saturation values also vary with respect to the distance from the orifice (Fig. 3). Calcite saturation values are high and carbon dioxide partial pressure are low for samples collected at the drip face, with respect to samples collected at midstream sites. The partial pressure of carbon dioxide and calcite values differ for the Potosi and Platteville orifice sites. At the Potosi orifice, the calcite saturation value is low (-0.397) but the partial pressure is high (0.125). Conversely, at the second Platteville orifice site, the calcite saturation is mid-range (0.537), with a lower partial pressure (0.026) (Table 1). Generally, as the partial pressure decreases, the calcite saturation increases, with a correlation coefficient of 0.633 (Fig. 3).

The Crawford County spring site values are concentrated near each other with low pH and calcite saturation indices, and carbon dioxide partial pressure values between 0.04 and 0.06 (Table 1). There are



Legend
 ☆ CFORD SW
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Figure 2. Durov diagram of the Crawford County springs. The diagram represents all three samples taken at both spring orifices on three different dates.

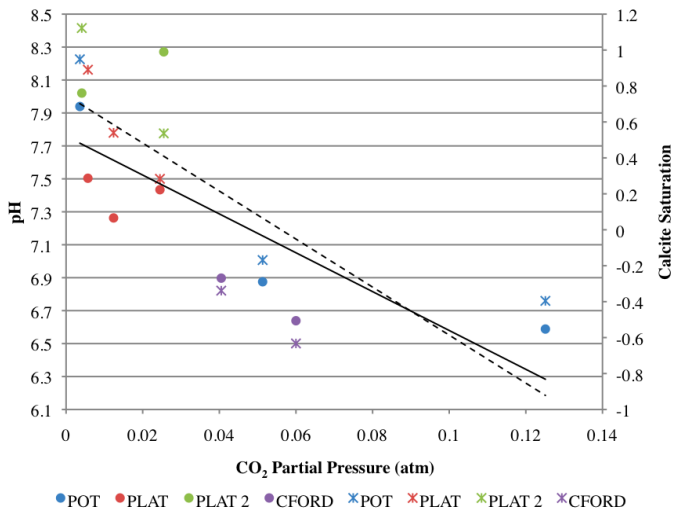


Figure 3. The relationships between the water's carbon dioxide partial pressure, pH, and calcite saturation. The colored circles with a solid line represent the water's CO₂ partial pressure and pH, with a correlation coefficient of 0.633. The crosses with a dashed line represent the water's CO₂ partial pressure and calcite saturation, with a correlation coefficient of 0.546. Values are plotted as means of three samples per site. See Table 1 for standard deviations.

noticeably lower values of calcium, magnesium, sodium, and sulfate in the Crawford Country Springs, than the Grant County Springs (Table 2).

DISCUSSION

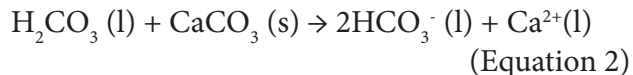
The bedrock geology of the Grant County springs (the Potosi and Platteville tufa falls) and Crawford County springs is very similar, consisting of sandstone, limestone, and dolomite. The Potosi and Platteville tufa springs originate from dolomitic limestone, while the Crawford County springs originate from dolomitic sandstone (Ostrom, 1967).

Carbonate equilibrium allows for tufa deposition at the Grant County springs. In the Potosi and Platteville limestone aquifer, the pH of the water is low. When rainwater enters the aquifer and reacts with carbon dioxide, produced by microorganisms in the soil, it forms carbonic acid (Equation 1). Immediately the carbonic acid dissolves the calcium carbonate from the limestone bedrock, and forms bicarbonate and calcium ions (Equation 2). The amount of hydrogen ions produced from the bicarbonate and carbonic acid reactions creates an acidic environment for the water in the aquifer.

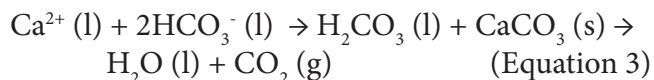


Sample Site	CO ₂ Partial		pH	Standard	Calcite	
	Pressure	Standard			Saturation	Standard
	Mean	Deviation	Mean	Deviation	Mean	Deviation
POT O	0.1251	0.1272	6.5883	0.55	-0.3956	0.567
POT M	0.0513	0.0415	6.8753	0.6139	-0.1686	0.7251
POT D	0.0036	0.0007	7.9393	0.0715	0.9489	0.0583
PLAT O	0.0245	0.0197	7.434	0.5821	0.2835	0.4438
PLAT M	0.0124	0.0088	7.2627	0.4664	0.5399	0.5794
PLAT D	0.0057	0.0081	7.5037	0.4392	0.8906	0.5328
PLAT O2	0.0255	0.0334	8.271	0.7348	0.5365	0.5644
PLAT D2	0.0041	0.0061	8.0207	0.6592	1.1225	0.6968
CFORD SW	0.0405	0.0374	6.8973	0.3821	-0.3387	0.3823
CFORD NE	0.06	0.0484	6.6387	0.2892	-0.6326	0.2776

Table 1. Carbon dioxide partial pressure, calcite saturation, and pH means for three samples from each site, and their corresponding standard deviations.



When water leaves the orifice, the reverse chemical reaction occurs. Calcium and bicarbonate ions in solution exit the orifice and produce carbonic acid in solution and calcium carbonate as a solid, which results in tufa deposition. The chemical reaction results in carbon dioxide degassing to the atmosphere and water (Equation 3).



This process is shown by the carbon dioxide partial pressure and pH values, as well as the deposition of calcium carbonate at the Potosi and Platteville tufa falls. Generally, at Potosi tufa falls, the pH of the water increases as it flows down the channel and over the tufa. When groundwater exits the orifice and flows into the spring channel, the water is acidic from carbonic acid and bicarbonate production. The release of carbon dioxide to the atmosphere raises the pH of water as the water reaches carbon dioxide equilibrium. When water leaves a closed system and enters an open system, the carbon dioxide partial pressure in the atmosphere is less than it was in the aquifer, and the carbon dioxide in the groundwater must exit the water to reach equilibrium. From the Durov diagrams, the correlation

coefficient for the linear relationship between CO₂ partial pressure and pH is 0.546. However, some samples have large standard deviations in carbon dioxide partial pressure and pH.

The carbon dioxide partial pressure standard deviation is high only for the Potosi orifice sample site seen in Fig. 3 because the site's partial pressure is very high with respect to the other sample sites (0.125). Drip sites have the lowest partial pressures, which is expected because the water has equilibrated with the carbon dioxide in the atmosphere, as it flows downstream.

There are large standard deviations for pH, specifically at the Potosi midstream site, and in the orifice and drip face sites at the second Platteville spring, as seen in Fig. 3. The results show the pH of water from the orifice site to be higher than the pH of water from the drip face site, although it was expected the opposite would occur. The pH should increase from the orifice to the drip face because hydrogen ions, previously present in the aquifer, are removed. Also, the pH of water from the drip face sample at the second Platteville spring, and the midstream sample at the Potosi spring have high pH standard deviations, which may be a result of field measurement quality. Multiple attempts to calibrate the pH meter may explain the variation in pH values in each spring site.

Sample No.	Sample Name	Date day-mo	Ca ppm	Mg ppm	Na ppm	SO ₄ ppm
1	POT O	20-Jul	95.06	45.72	5.54	19.48
2	POT M	21-Jul	93.17	45.09	5.74	19.66
3	POT D	20-Jul	86.09	44.3	5.45	14.38
4	PLAT O	22-Jul	94.66	47.08	7.82	20.81
5	PLAT M	22-Jul	91.39	47.48	7.81	20.68
6	PLAT D	22-Jul	85.08	47.08	7.89	21.23
7	PLAT O2	22-Jul	99.39	50.25	4.48	28.14
8	PLAT D2	22-Jul	61.68	48.68	4.39	22.4
9	CFORD SW	24-Jul	63.33	32.02	1.7	7.79
10	CFORD NE	24-Jul	65.93	33.24	2.18	9.12
11	POT O	28-Jul	92.35	45.73	5.46	20.54
12	POT M	28-Jul	92.56	46.34	6.14	20.24
13	POT D	28-Jul	86.29	45.84	6.68	19.32
14	PLAT O	25-Jul	86.18	45.29	7.17	20.15
15	PLAT M	25-Jul	90.32	47.52	7.56	21.19
16	PLAT D	25-Jul	84.37	47.12	7.55	16.03
17	PLAT O2	25-Jul	98.89	51.05	4.56	33.58
18	PLAT D2	25-Jul	65.43	48.65	4.46	28.44
19	CFORD SW	27-Jul	64.84	32.67	1.95	9.42
20	CFORD NE	27-Jul	65.75	33.41	1.66	4.8
21	POT O	31-Jul	92.83	46.08	5.5	20.46
22	POT M	31-Jul	92.1	45.9	5.47	17.87
23	POT D	31-Jul	88.16	45.75	5.48	21.06
24	PLAT O	30-Jul	94.24	48.46	8.11	20.37
25	PLAT M	31-Jul	92.78	48.81	8.25	23.05
26	PLAT D	31-Jul	85.39	48.25	8.15	22.81
27	PLAT O2	30-Jul	102.04	51.32	4.68	26.96
28	PLAT D2	31-Jul	64.32	49.71	4.68	29.73
29	CFORD SW	1-Aug	64.5	32.07	1.65	7.97
30	CFORD NE	1-Aug	67.27	32.96	1.61	6.54

Table 2. Selected water chemistry sample data, as analyzed by the University of Wisconsin- Madison Soil and Plant Analysis Laboratory.

The correlation coefficient between CO₂ partial pressure and calcite saturation is 0.633, and the moderately strong linear relationship is expected because as water exits the orifice and hydrogen ions bind with bicarbonate ions to produce carbonic acid and water, the calcium carbonate precipitates. Carbon dioxide partial pressure decreases as water flows downstream, and calcite, the end product, increases. Most of the sample sites follow this pattern, even though some sites have large standard deviation values such as at the midstream Potosi site, and the drip face at the second Platteville springs, seen in Fig. 3. The cause for the large standard deviations is unclear.

Although there is less tufa present at the base of the second Platteville spring, the value of calcite saturation is high. Similar water chemistry between the two Platteville springs suggests that water chemistry variations are not the reason why there is less tufa present in one spring relative to the other. Other variables might explain the smaller tufa size such as fractures, time, and seasonal rainfall (Kawai et al., 2006). There may be large or many fractures located at this specific aquifer location that allow water to percolate through the cracks, instead of out the

aquifer orifice; this would prevent the transportation of calcium carbonate to be deposited at the end of the spring.

The Crawford County springs discharge from a dolomitic sandstone aquifer (Ostrom, 1967). The water that flows out of both Crawford orifices is acidic, and as expected, there is high partial pressure of carbon dioxide at the orifices, because the system is approaching a state of equilibrium. The carbon dioxide partial pressures and pH values are comparable to the values at the Potosi orifice sites. There is no tufa deposition at the Crawford Country springs because the calcium content in the water sample is much less than the calcium content of the Grant County springs, 65 ppm and 92 ppm, respectively. It is possible that the Crawford springs did not deposit tufa because the waters did not have high amounts of free calcium ions when it exited the aquifer (Kawai et al., 2006). The sandstone aquifer at the Crawford springs is not conducive to tufa deposition, thus the calcite saturations are relatively low with respect to those at the Potosi and Platteville spring sites. It has been predicted that, in addition to aquifer geology, there must be a pH threshold for tufa deposition (Leybourne et al., 2009).

CONCLUSIONS

Tufa deposition occurs at the Grant County springs because water flowing through the dolomitic limestone aquifer extracts calcium carbonate that interacts with the atmosphere when water exits the aquifer, thus enabling tufa to precipitate. The high carbon dioxide partial pressure in the water relative to that of the atmosphere forces CO₂ to degass. Ultimately, the spring water precipitates calcium carbonate and generates water as a byproduct.

Water chemistry does not explain why tufa deposition is greater at the westerly spring, as opposed to the easterly spring, at the Platteville tufa site. The water chemistry from the two orifice locations at the Platteville site is very similar, so other variables must determine the differences in tufa mound size. Further research on the aquifer can be done to better understand the tufa processes in the region.

No tufa forms at the Crawford Spring sites because the dolomitic sandstone aquifers do not provide adequate calcium ions for water to extract and deposit tufa. Although carbonate equilibrium occurs, calcite does not precipitate from of the spring water.

Wisconsin. 2003 Wisconsin Act 310. 2003 Assembly Bill 926. Pub. 2004.

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REFERENCES

Heller, S., 1988, Seasonal geochemistry of two tufa-depositing Springs in southwestern Wisconsin. *Geoscience Wisconsin*, v. 12, p. 77-83.

Kawai, T., Kano, A., Matsuoka, J., and Ihara, T., 2006, Seasonal variation in water chemistry and depositional processes in a tufa-bearing stream in SW-Japan, based on 5 years of monthly observations, *Chemical Geology*, v. 232, p.33-53.

Leybourne, M.I., Betcher, R.N., McRitchie, W.D., Kaszycki, C.A. and Boyle, D.R., 2009, Geochemistry and stable isotopic composition of tufa waters and precipitates from the Interlake Region, Manitoba, Canada: Constraints on groundwater origin, calcitization, and tufa formation, *Chemical Geology*, v. 260, p. 221-233.

Ostrom, M.E., 1967, Paleozoic stratigraphic nomenclature for Wisconsin: Wisconsin Geological and Natural History Survey Information Circular 8.

University of Wisconsin-Madison Soil and Plants Analysis Lab. <http://uwlabs.soils.wisc.edu/madison/>