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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

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Research Advisor: Al Werner

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ELIZABETH FORBES: Whitman College
Research Advisor: Kirsten Nicolaysen

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

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ETHAN MAMER: Beloit College
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TEMPERATURE PROFILE MODELING OF A SMALL SPRING-FED STREAM

MILES REED: DePauw University
Research Advisor: Tim Cope

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

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Whitman College
Research Advisor: Kirsten Nicolaysen

ABSTRACT

This study examines the paleoclimate from Middle to Late Holocene of southwest Wisconsin by analyzing the compositional and isotopic variation of a spring-deposited tufa mound. Two drill cores of 3.58 and 1.38 meters length were obtained and analyzed for major and trace elements and stable isotopes ($\delta^{13}C$, $\delta^{18}O$). Mg/Ca, Ba/Ca, Sr/Ca and $\delta^{13}C$ values within the tufa reflect the wetness or dryness of the climate, with high ratios and $\delta^{13}C$ values corresponding to dry periods. $\delta^{18}O$ values reflect the change in temperature, with high $\delta^{18}O$ indicating high paleotemperature. Results show that southern Wisconsin was dry and warm prior to ~4,500 YBP and has experienced a general increase in moisture and decrease in temperature for the past 6,000 years.

INTRODUCTION

Research on terrestrial sediments has become increasingly relevant in the context of extracting paleoclimatic information, as the debate surrounding anthropogenic climate change has grown. Several studies have shown that reliable paleoclimate data can be obtained from stable isotopes in tufa deposits (Andrews et al., 1994; Garnett et al., 2004; Andrews, 2006). Tufas can be useful in the study of Quaternary climate change as these deposits provide long, continuous records that can be accurately dated, while also providing paleoclimatic data, particularly changes in temperature and rainfall intensity (Ihlenfeld et al., 2003). Stable oxygen isotope composition reflects changes in temperature, with higher $\delta^{18}O$ ratios indicating higher temperatures, while $\delta^{13}C$ reflects changes in aquifer processes and vegetation. Ratios of metallic elements, present in trace quantities in tufas, have also been used (Ihlenfeld et al., 2003; Garnett et al., 2004) as indicators of wet and dry climates, but to a lesser extent. Mg/Ca ratios should indicate residence time within the aquifer, as short residence time results in preferential calcite dissolution over dolomite (Garnett et al., 2004).

Many studies on central North America Holocene climate have been conducted, mainly through analysis of speleothems (Dorale et al., 1992; Denniston et al., 1999) and pollen (Bartlein et al., 1983; Wright, 1992). These studies establish a Prairie Period in the Midwestern US, which is characterized by grasslands and a warm, dry climate. The age constraints of the Prairie Period are locally dependent, as the warm, dry prairie occurred earlier in Minnesota (8000 – 5000 BP) than it did in southern Wisconsin (6000 – 3000 BP). Southern Wisconsin is home to thousands of springs, several of which are tufa depositing, yet no tufas have been analyzed for paleoclimate data. Successful analysis of these tufa deposits can provide valuable high-resolution data on paleotemperature and paleorainfall in southwest Wisconsin.

This study aims to analyze and interpret the presence of major and trace elements within a tufa core sample, and determine how accurately these major and trace elements can be used in paleoclimate reconstruction. A 3.58 meter long core was obtained from a perched spring-line tufa in Grant County, Wisconsin, and analyzed for major and trace elements (Ca, Mg, Sr, Ba) and stable isotopes ($\delta^{13}C$, $\delta^{18}O$). By comparing our results with known regional climatic data from other sources, we will be able to constrain the age of the tufa deposit more precisely, and establish the effectiveness of metal analysis of a tufa as a paleoclimatic indicator.

SETTING

Tufa samples were collected in July 2009 from a spring-line tufa seven kilometers southwest of Platteville, Wisconsin. The source water for the tufa deposit is a small spring that emanates from the Sinnipee Group, which is comprised of limestone to dolomitic members (WGNHS, 2006). This tufa deposits on a hill slope above the Blockhouse Creek and has formed a large mound deposit roughly 9.5 meters high. The Platteville tufa was chosen because the tufa is well-exposed and actively depositing. This ensures that the upper most portion of the tufa is the youngest, and will allow for more accurate dating and determination of deposition rates. The tufa is asymmetrically shaped, as the spring channel migrates over the tufa. Thus, we can assume that the tufa is not always being evenly precipitated across the mound, creating some gaps in deposition and time. However, tufa deposits stratigraphically, so regardless of gaps in time, the upper most section of the tufa will be the youngest, and the deepest part will be the oldest.

METHODS

Core samples from the tufa were obtained using a handheld Tanaka 262DH Drill with a one-inch diameter, diamond-encrusted bit (Figure 1). Two cores, from boreholes PLC4 (3.58 meters length) and PLC5 (1.38 m), are the primary data source for this paper (Figure 2). PLC4 is the longer and more complete datum, while PLC5 is used to correlate the uppermost section of PLC4, which had less than 50% recovery in the first meter of drilling.

The recovered core was sampled at 10 cm intervals for metals concentration analysis, using a Dremel saw to slice 3-5 gram disks. Samples were sent to Washington State University and analyzed by XRF for 10 major and 19 trace elements abundances, with results having standard deviations equal or better than ± 0.03 weight percent. 50 mg samples were also taken every 20 cm for stable isotope analysis and analyzed for $\delta^{18}O$ and $\delta^{13}C$ at the University of Waterloo. Additionally, organic matter found at the

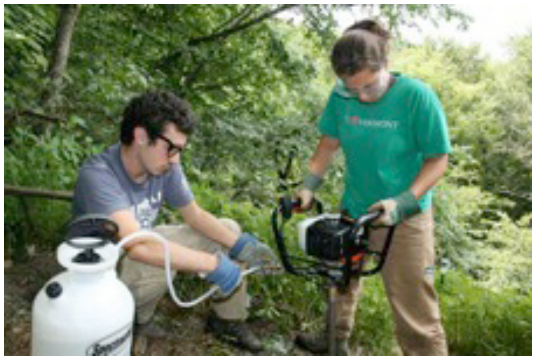

Figure 1. Ethan Mamer and Liz Forbes drilling at the tufa site to obtain core samples.

241 cm depth in core PLC4 was sent to the University of Arizona AMS lab for radiocarbon dating.

In addition to the core samples, a backwall rock sample and water samples were collected from the site. The rock sample was analyzed for major and trace elements to correlate the tufa chemistry with that of the host rock. The water sample was analyzed for stable isotopes to establish isotopic equilibrium with the tufa, in addition to on site testing of the spring water for alkalinity, pH, temperature, and conductivity.

Figure 2. Picture of the tufa core from PLC4, from approximately 36 to 41 cm depth.

RESULTS

XRF provides elemental concentrations for ten major elements and 19 trace elements, however only Ca, Mg, Sr, and Ba will be discussed here. Other elements have low concentrations (< 5 ppm) or show no distinguishable trends. Trace element results have a precision of ± 0. 03 wt %, and a triplicate test was run with most elements having <5.0% error. Molar ratios of Mg/Ca, Sr/Ca, and Ba/Ca trend similarly, all increasing with depth (Fig. 3).

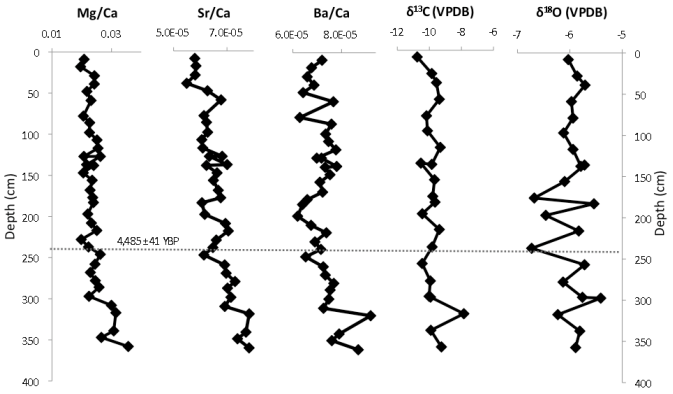

Figure 3. Trends of Mg/Ca, Sr/Ca, Ba/Ca, $\delta^{13}C$, and $\delta^{18}O$ versus depth, with the radiocarbon date to correlate. The molar ratios and $\delta^{13}C$ show similar trends, all increasing with depth, with the most significant increase occurring after ~4,500 yr BP. $\delta^{18}O$ shows a slight decrease in values at 4,500 yr BP.

$\delta^{18}O$ values range from -5.41 to -6.73‰ (VPDB), with an average value of 5.97‰. $\delta^{13}C$ values range from -7.85 to -10.76‰ (VPDB), with a mean value of -9.80. $\delta^{13}C$ shows more variability within the core, and shows an overall trend of increasing with depth. $\delta^{18}O$ shows less variability within the core sample. From the bottom of the core up, there is a slight decrease in values between 2.37 m to 1.56 m, where values jump to -6.73‰ with an average of -6.15‰, then a slight increase in the upper section, with values at the bottom of the core similar to values at the top, with averages of -5.82 to 5.91‰ respectively.

A single radiocarbon date from the tufa gives an age of 4,485 ± 41 yr BP at 241 cm depth. This is a calibrated age for the plant material within the tufa core. Despite a standard deviation of 0.5%, this result should be viewed with some skepticism, as it dates the plant material within the core, not the tufa itself. However, this date does provide context for the tufa core and places the timing of tufa formation within the Middle Holocene.

DISCUSSION

EQUILIBRIUM AND RADIOCARBON DATES

With $\delta^{18}O$ analysis from the top of PLC4 and water temperature measurements taken in July 2009, it is possible to determine if the top of the tufa is in isotopic equilibrium with the modern spring water. The Hays and Grossman equation (Andrews, 2006) was utilized to determine temperature from δ18O values:

$$T^{\circ}C = 15.7 - 4.36(\delta^{18}O_{CALCITE\ (VPDB)} - \delta^{18}O_{WATER(VSMOW)}) + .12(\delta^{18}O_{CALCITE(VPDB)} - \delta^{18}O_{WATER\ (VSMOW)})^2$$

Using this equation, the calculated water temperature was 9.1°C. The spring water temperature measured in July 2009 was 9.5°C, resulting in a 4.52% error between calculated and measured temperatures, establishing that the tufa is in isotopic equilibrium with the spring water.

From calibrated ^{14}C dating, an age of 4,485 ± 41 years yrs BP was calculated at 241 cm depth. From this date and the calculation determining isotopic equilibrium, we can make assumptions about deposition rates. Although deposition rates of tufa are variable (Rosen, et al., 2010), we will assume relatively constant deposition rates within this spring-fed tufa because of lack of other age constraints. Based on this assumption and the ^{14}C date recovered, deposition of the tufa is approximately 0.54 mm/year. If this is constant, then the bottom of the core represents approximately 6,500 yrs BP.

TRACE ELEMENTS

Trace elements of Mg, Sr, and Ba were examined by calculating molar ratios relative to the major constituent Ca to better correlate trends. The molar ratios generally increase with depth (Fig. 3). Mg/Ca ratios are linked to dissolution rates within a dolomite/calcite aquifer, with increased Mg/Ca reflecting increased dolomite dissolution (Fairchild et al., 2000; Ihlenfeld et al., 2003). Dolomite dissolution will increase with longer aquifer residence times, as dolomite will only begin dissolution after the water has reached saturation with respect to calcite (Garnett et al., 2004). Therefore, high Mg/Ca ratios are indicative of longer aquifer residence time. Long residence times are associated with dry climatic periods, thus high Mg/Ca ratios denote dry periods while low Mg/Ca ratios indicate a wetter climate.

Our data set trends suggest a dry maximum at the base of the core (6,500 yrs BP assuming constant deposition), with increasing moisture until the present. This differs slightly from the Prairie Period model presented by Wright (1992) and Dorale (1992), who both suggest that the Prairie Period occurred from around 6,000 to 3,000 yrs BP, with increased dryness and temperatures until 3,500-3,000 yrs BP, where there is a marked shift to increasing moisture and decreasing temperatures. Despite the age discrepancy, the data do agree that there was a distinct, drier and warmer period before 4,500 yrs BP. The difficulty in age correlating can be attributed to our lack of multiple radiocarbon dates.

Sr/Ca and Ba/Ca molar ratios both show a positive correlation to Mg/Ca ratios, where R_2 equals 0.33 and 0.38 respectively. These relationships suggest that the same process that controls Mg/Ca has an influence on Sr/Ca and Ba/Ca ratios. Since Mg/Ca is primarily controlled by residence time within the aquifer, we can assume that Sr/Ca and Ba/Ca are similarly affected by the residence time. This is in good agreement with several studies that observe that Sr and Ba concentrations within tufa are mainly controlled by changes in water chemistry (Huang and Fairchild, 2001; Ihlenfeld et al., 2003; Garnett et al., 2004). Therefore, Sr/Ca and Ba/Ca ratios further support that southwestern Wisconsin experienced a dry period prior to 4,500 yrs BP.

STABLE ISOTOPES: BULK TUFA $\delta^{13}C$

$\delta^{13}C$ change in tufa is influenced by the proportion of isotopically lighter CO_2 derived from soil organic matter to the isotopically heavier carbon derived from dissolution within the carbonate aquifer (Andrews et al., 1994; Garnett et al., 2004; Andrews, 2006). Therefore, an increase in $\delta^{13}C$ usually indicates an increase in calcite dissolution as a result of increased aquifer residence time. The $\delta^{13}C$ of soil CO_2 can also affect the changes in $\delta^{13}C$ in tufa deposits. CO_2 in soils is dependent on the proportions of C_3 (trees and shrubs) to C_4 (grasses) (Ihlenfeld et al., 2003; Andrews, 2006). Grassland environments have dominantly C_4 in the soil CO_2, resulting in higher $\delta^{13}C$ values. Hence, $\delta^{13}C$ variation within a tufa core can be the result of changes in residence time or changes in vegetation. However, if $\delta^{13}C$ is positively correlated with $\delta^{18}O$, this is usually an indication that the tufa was enriched in heavier $\delta^{13}C$ as a result of vegetation changes (Pazdur et al., 1988).

In this study, there is no significant correlation (R_2=0.006) between $\delta^{13}C$ and $\delta^{18}O$ in the core. This leads us to look at the relationship between $\delta^{13}C$ and Mg/Ca, which shows a stronger correlation (R_2=0.35). As Mg/Ca ratios are controlled predominantly by residence time, it is likely that $\delta^{13}C$ in the tufa is also controlled by residence time. Thus, $\delta^{13}C$ is most likely primarily controlled by residence time, with longer residence time resulting in dissolution of isotopically heavier carbon within the aquifer; however vegetation changes could still account for some of the variability within $\delta^{13}C$ values as indicated by Figure 4.

$\delta^{13}C$ values within the core record highest $\delta^{13}C$ values at the base of the core, and the lowest $\delta^{13}C$ at the top. This trend, based on the previous conclusion, suggests that from 6,500 yrs BP until the present, Wisconsin was increasing in moisture or changing from grasslands to forests, with the most significant spike at approximately 5,800 yrs BP. This correlates loosely with known climatic data (Fig. 5).

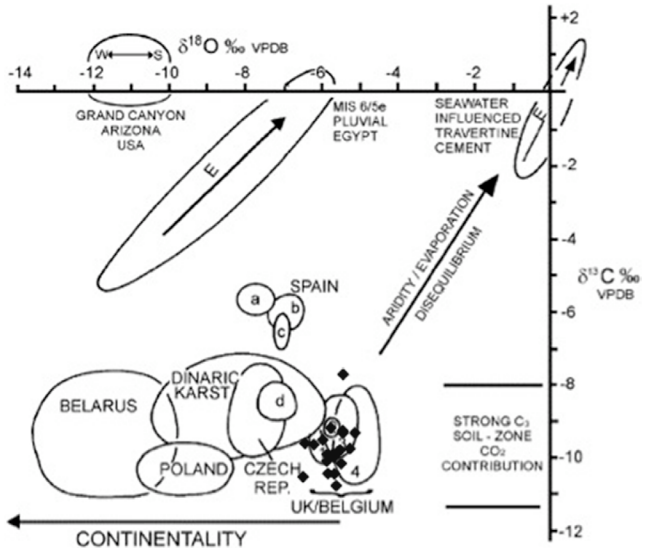

Figure 4. Graph from Andrews (2006) showing $\delta^{13}C$ and $\delta^{18}O$ data for Quaternary tufas. Data from the Wisconsin tufa is plotted in dark diamonds, and falls within the strong C_3 soil-zone CO_2 contribution, though a few points trend towards increased aridity/evaporation.

This change can be accounted for by the termination of the Prairie Period, and subsequent transition to a wetter and cooler climate and from grasslands to a spruce-dominated forest (Bartlein et al., 1983).

STABLE ISOTOPES: $\delta^{18}O$ INFLUENCES ON PALEOTEMPERATURE

$\delta^{18}O$ shows only small amounts of variation within the core, but some small trends are discernable, and even small changes in $\delta^{18}O$ reflect a temperature change of several degrees. It has been well established (Andrews et al., 1994; Ihlenfeld et al., 2003) that $\delta^{18}O$ in carbonate precipitates are directly linked with air temperature. Higher mean air temperatures correspond to higher $\delta^{18}O$ values (Ihlenfeld et al., 2003; McDermott et al., 2004; Andrews, 2006). The relationship between meteoric $\delta^{18}O$ values and air temperature is a function of condensation of water vapor from cooling, resulting in lower temperatures forming isotopically lighter water vapor (Andrews et al., 1994).

This translates to high mean air temperatures yielding higher $\delta^{18}O$ values in meteoric waters. Our data set shows a very small trend towards higher $\delta^{18}O$ with increasing depth, implying the temperature in Wisconsin has been gradually decreasing the last ~ 6,500 years. The small decrease in $\delta^{18}O$ values occurs at approximately 4,500 yrs BP, meaning lower temperatures and most likely marking the end of the Prairie Period.

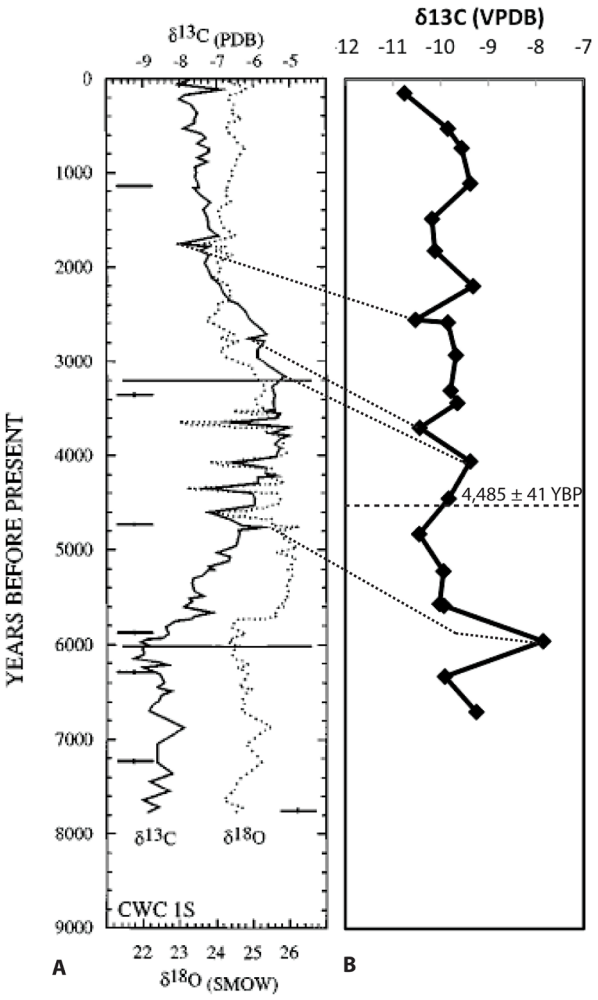

Figure 5. Comparison of $\delta^{13}C$ trends from Denniston et al., 1999 (A) and from this data set (B). The radiocarbon age of 4,485 yrs BP is shown at 241 cm depth; however, lines drawn show the more likely correlation between the two data sets.

CONCLUSIONS

This study demonstrates that molar ratios of Mg/Ca, Sr/Ca and Ba/Ca can be accurately used to establish climatic wet and dry periods. The results show that southwest Wisconsin was drier and warmer prior to ~ 4,000-4,500 yrs BP. This is in general agreement with other regional climatic studies. Additionally, positive correlation of Mg, Sr, Ba and $\delta^{13}C$ further supports the accuracy of paleoclimate data. $\delta^{13}C$ results further support the evidence for a drier climate prior to 4,000 yrs BP, as well as suggesting possible vegetation changes, namely a change from grasslands to forests. A shift to lower $\delta^{18}O$ values also marks the transition from a warmer climate to cooler at approximately 4,000 yrs BP. These results fit loosely with known paleoclimate data.

Overall, trace elements, $\delta^{13}C$, and $\delta^{18}O$ are roughly consistent with other paleoclimatic studies in the region, establishing the validity of tufa sampling as a method of determining paleoclimate. Stable isotopes were the primary data source in other studies, but promisingly, this case study verifies that trace elements can also be used as paleoclimate indicators, primarily as signals of wet or dry climatic conditions. To further establish the effectiveness of trace elements in paleoclimate studies, it would be recommended to obtain more radiocarbon dates to better constrain the age and deposition rates of the tufa.

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