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

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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)

Keck Geology Consortium Franklin & Marshall College PO Box 3003, Lancaster Pa, 17603 Keckgeology.org

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

ETHAN MAMER

Beloit College Susan Swanson

INTRODUCTION

The focus of this study is to explore Holocene climate variation of the Driftless Area of southwestern Wisconsin using a tufa mound found 7 km southwest of the city of Platteville (Fig. 1). In this area, there are several tufa-depositing springs that were potentially active during or soon after glaciation (Heller, 1988). The groundwater that feeds the springs flows through the Sinnipee Group, an Ordovician age group of rocks made up of limestones, dolomites, and shale (Ostrom, 1967).

The field of climate science has been expanding rapidly as methods of extracting paleoclimate information are advancing. Through the use of stable isotope records preserved in terrestrial carbonates such as tufa, our understanding of Quaternary environments has greatly expanded. Because stable isotopes of carbon and oxygen, as well as molar ratios of major and trace elements are preserved at the time of deposition, an area's climate in terms of temperature and moisture conditions can be determined (Andrews, 1993).

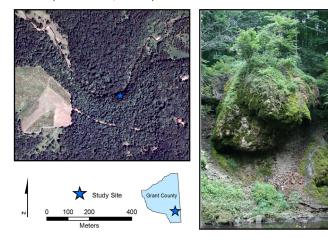


Figure 1: Location of the Platteville tufa mound in Grant County (Left), and a picture of the Platteville tufa mound (Right).

Tufa is a terrestrial carbonate that can record rough climate records preserved in stable isotope values and major and trace element ratios. Tufa is precipitated when water discharged from carbonate-rich bedrock comes in contact with the atmosphere, slowly recording a record stratigraphically. Distinguishable from other carbonates, tufa deals exclusively with ambient temperatures and is often found in the presence of plants (Pentecost, 1996).

Holocene Climate History

The study area is not only significant because of its presence in the Driftless Area. Throughout the early and middle Holocene, the Pacific air mass slowly extended its influence across the modern day Dakotas and Minnesota, reaching its maximum extent around 5600 yr B.P. in western Wisconsin (Fig. 2). As the Pacific air mass crosses the Rocky Mountains it loses most of its moisture resulting in a drying, or rain shadow effect. As the dry air advanced eastward, Boreal forests of the Upper Midwest retreated northward and gave way to vast grasslands, known as the Prairie Peninsula. After approximately 5600 yr B.P. the Pacific air mass began to retreat allowing the Arctic and Gulf air mass to move into the area. The moist air began to influence the area, allowing Boreal forests to move back into the area. The location of the study area is particularly interesting as it is very close to what may be the Prairie Peninsula's farthest eastward extent (Fig. 2) (Bartlein et al., 1984; Denniston et al., 1999).

Tufa Deposition

Studies performed on a British tufa revealed that degassing of carbon dioxide is responsible for 70-



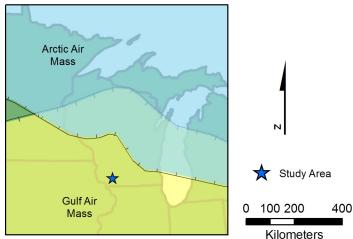


Figure 2: Extent of the Pacific air mass from 9000 to 6000 yr B.P. (Left) and the Gulf and Arctic air masses 6000 yr B.P. to today (Right) (Bartlein et al., 1984).

80% of tufa deposition, 10-20% is deposited through evaporation, and 6-12% through photosynthesis (Pentecost, 1996). Rainwater reacts with atmospheric CO₂ and passes through an organic rich soil layer. This forms bicarbonate, which dissolves the calcite from the limestone aquifer. As the calcitesaturated spring water is discharged, it returns to atmospheric pressures. This decrease in pressure, as well as the pull to reach equilibrium, forces calcite to precipitate from solution. As a result, carbon dioxide is released and tufa is precipitated (Equation 1)(Hori et al., 2007).

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO^{3-}$$

(Equation 1)

Mosses found on some tufa mounds have also been determined to play a large role in the deposition of tufa due to photosynthesis. As the calcium bicarbonate-rich water flows over mosses growing on tufa, they absorb carbon dioxide during photosynthesis, aiding the degassing process described earlier. The moss also facilitates precipitation passively as the water is allowed to stagnate on the moss fibers and eventually evaporate. These fibers create an excellent base on which the carbonate deposition can take hold (Pentecost, 1996).

Stable Isotopes

The majority of oxygen isotopes consist of ¹⁸O and

 16 O. The ratio of the two at a given location can reveal the area's climate in terms of temperature. Because of its two extra neutrons, 18 O is heavier, which makes it more sensitive to condensing at lower temperatures. Therefore, δ 18 O will be lighter, or more negative, when the climate is colder (Andrews and Pedley, 2000).

The climate analysis for carbon is measured using δ^{13} C values. The carbon, which will eventually be locked into the calcium carbonate (tufa), starts as carbon dioxide. Carbon dioxide originating from organic matter or the atmosphere has a lighter (more negative) δ^{13} C value, while carbon derived from the dissolution of aquifer limestone has a heavier (less negative) δ^{13} C value. Thus, in a dry period when the water has longer residence time in the aquifer, greater dissolution of the aquifer may occur. The heavier (less negative) δ^{13} C is thus recorded in the tufa during these times (Andrews and Pedley, 2000).

Major and Trace Elements

Molar ratios of major and trace elements are also indicators of moisture conditions. Because the primary aquifer that feeds the tufa springs is composed of limestone and dolomite, Mg and Sr are present and have the chance of being dissolved and precipitated as well as Ca. In the same way that $\delta^{\rm 13} C$ values become heavier (less negative) the longer they are in

contact with the aquifer, Mg/Ca and Sr/Ca ratios increase the longer the groundwater is in contact with the aquifer materials (Garnett et al., 2004).

METHODSSite Survey

Upon first visiting the study site, a stream reconnaissance was performed to better understand the area. This was conducted 75 m up and downstream of where the tufa-depositing spring feeds into Blockhouse Creek. Next a comprehensive spring survey was conducted of the tufa mound and its spring orifice using the Springer 2009 spring classification protocol (Springer and Stevens, 2009). A site sketch was made noting important sample locations as well as distinctive geographic markers in the site (Fig. 3).

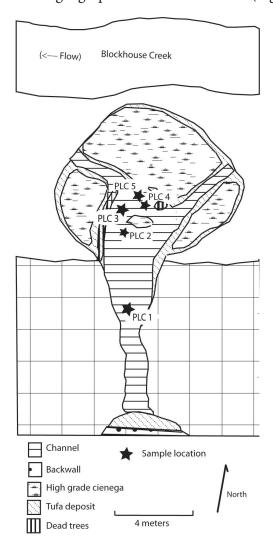


Figure 3: Plan view of the Platteville tufa mound.

Drilling

Five cores in total were drilled on the tufa mound using a Tanaka double-stroke rotary coring drill (PLC 1-5). This study describes results of PLC 3, which was collected 12.5 m from the spring orifice. Each run would last approximately 2-3 minutes during which an average of 30 cm of tufa was collected (Fig. 4). The length of the retrieved sample would then be measured, as well as the actual depth range from which the sample was collected. The sample was then briefly described and labeled before being packaged. Notes were also taken concerning the drilling process (i.e., how much resistance there was, peculiar drops or jams). The drilling consisted of 15 separate runs, collecting a total of 4.0 m of tufa over drilling depth of 4.1 m (97% recovery). A water sample was also collected at the drilling site to ensure that the mound was in isotopic equilibrium with the spring water.



Figure 4: Drilling of tufa (Left) and tufa core being described (Right).

Laboratory Analysis

Once the samples were returned to the laboratory, the core was laid out in full and carefully examined. The core was then photographed and sketched in great detail. Along with the sketch, an in-depth description of the core's wet color, porosity, density, and other physical attributes were recorded. A thorough search for organic matter that could be used for radiocarbon dating was performed as well, though the only sample found was not significant enough to be analyzed.

50 mg samples were then drilled every 10 cm and

sent to the University of Waterloo Environmental Isotope lab to test for stable isotopes of oxygen and carbon. 20 g samples were collected every 20 cm and sent to the Washington State University GeoAnalytical lab for analysis of major and trace elements by X-ray fluorescence analysis.

RESULTS Site Survey

The spring that feeds the tufa mound emerges from the north-facing slope of a stream-cut valley. Located approximately 15 m above the creek surface, the spring emerges sub-aerially by gravity where the valley slope intersects a bedding plane contact or fracture. Water is discharged from multiple orifices on a small portion of exposed bedrock. The backwall is made up of limestone rich in brachiopods from the Guttenberg Member of the Decorah Formation. The backwall faces north with an aspect of 350 degrees. The discharged water flows into a channel that is approximately 1 m wide and 2 cm deep. The channel descends steeply directly down-slope 9 m until it reaches the tufa mound where it levels out. The mound today is approximately 10 m in diameter. On the mound, the flow turns into a high-gradient cienega as it flows over tufa that is covered in moss and Jewel Weed (Impatiens capensis, sp.). It then flows over the drip-face, falling approximately 9 m into Blockhouse Creek (Fig. 3).

Carbon 14 Dating

Although a small sample of organic matter was found in PLC 3, unfortunately there was not enough material to analyze. However, a specimen (AA86991) was found at a depth of 241 cm in adjacent core (PLC 4). It was analyzed by the NFS-Arizona Accelerator Mass Spectrometry Laboratory and found to be $4,485 \pm 41$ yr B.P. (Forbes, this issue). Assuming current and continuous deposition this suggests a deposition rate of approximately 0.5 mm/year.

Stable Isotopes

Before isotope or metals ratios can be analyzed with

regard to climate it must first be established that the modern tufa is in isotopic equilibrium with the water from which it precipitates. To determine current deposition, as well as prove isotopes measured represent the source, the Hays and Grossman (1991) equation for isotopic equilibrium was used. This was done by sampling the δ^{18} O of the water, as well as the δ^{18} O of the uppermost tufa deposit. The recorded temperature at the time of sampling was 9.6° C and the following equation found the temperature of deposition to be 8.1°- 9.1° C.

$$\begin{split} T^{o}C &= 15.7 - 4.36 \big(\delta^{18}O_{\text{calcite(PDB)}} - \delta^{18}O_{\text{water(SMOW)}}\big) \\ &+ 0.12 \big(\delta^{18}O_{\text{calcite(PDB)}} - \delta^{18}O_{\text{water(SMOW)}}\big)^2 \end{split}$$

Samples for stable-isotope analysis were collected at 10 cm intervals along the length of the core. Fluctuations in the $\delta^{\scriptscriptstyle 13} C$ and $\delta^{\scriptscriptstyle 18} O$ records indicate a subtle shift in the region's climate. The δ^{18} O values throughout the core vary from -7.7 ‰ at lightest to -5.4 ‰ at heaviest. There is little variation from the core's deepest measurements of 4.1 m up to 2.6 m. These values remain consistent around -6 % with two minor variations at 3.5 m and 3.3 m where values become lighter, or more negative. At 2.6 m however there is a very abrupt shift in the isotope value, as it becomes lighter, or more negative, approaching -8 % for approximately 20 cm of core. The values become heavier, or less negative, at 2.3 m at which point they remain fairly consistent until they attain their heaviest, or least negative, value of -5.4 ‰ at the depth of 1.9 m. Throughout the remaining core there are several minor variations in the δ 18O values. These include peaks of lighter, more negative, values at 1.7 m, 1.4 m, 1 m, and 0.2 m (Fig. 5). δ13C values varied from -10.8 ‰ to -8.2 ‰. From the cores deepest measurement of 4.1 m to 2.8 m the δ13C values slowly increase, or become less negative (-10.7 ‰ to -8 ‰). Then the values decrease to more negative values. This persists until 2.1 m where there is a short 40 cm spike in the data of heavier, or less negative, values. Once again the δ^{13} C values shift to lighter, or more negative, values from 1.6 m to 1.0 m. At 1.0 m however there is a brief shift to lighter values that then gradually becomes heavier until 0.5 m. The final 0.5 m of core show heavier values from -10.7 ‰ up to -9.0 ‰ at the top

of the core (Fig. 5).

The molar ratios of the major and trace elements (Mg, Sr) to calcite (Ca) were used to determine trends in moisture. δ^{13} C also is a indicator or precipitation, and the trends recorded in elemental ratios are similar to those observed for δ^{13} C (Fig. 5).

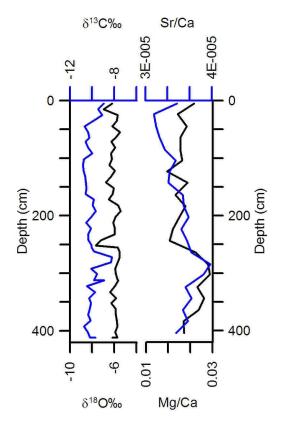


Figure 5: Graphs displaying the records of stable isotopes, $\delta^{13}C$ and $\delta^{18}O$, as well as major (Mg/Ca) and trace (Sr/Ca) elements ratios with depth in the PLC 3 tufa core.

DISCUSSION

The variations preserved in the $\delta^{13}C$ values and the ratios of major and trace elements are used to determine general trends in moisture that took place in the area. From 4.1 m through 2.9 m there appears to be a drying trend that reaches its maximum at 2.8 m. At 2.6 m the area's moisture conditions shift back to values similar to before the deeper shift. This wet period persists until 1 m, at which point the data shift, suggesting modern moisture conditions are drier than in the recent past.

The δ^{18} O record serves as an indicator of paleotem-

perature. The temperature in this area seems to have been fairly consistent with a few periods of extremes. There is a cold shift from 2.6-2.4 m. The cores warmest period occurs shortly after these temperatures stabilize at 1.9 m. Throughout the rest of the core temperature remains fairly stable.

One element this study still lacks is more accurate age constraints. The data collected in this study correlate well with that of PLC 4 and 5, which do have one radiocarbon age that can be inferred (Forbes, this issue). Based on the fact that the PLC 3 records correlate with PLC 4 and 5, we might assume that the depth of 1.5 - 2.0 m on PLC 3 has an age of approximately 4,500 yrs BP. Using this correlation, the spikes seen in the δ^{13} C record and the major and trace element ratios indicate a period of drying prior to approximately 4,500 yrs BP. This correlation also indicates that the cold shift recorded in the δ^{18} O record occurred just before 4,500 yrs BP.

There are several climate studies conducted in the area that also focus on the Holocene climate (Denniston et al., 1999; Baker et al., 1996; Bartlein et al., 1984; Knox and Kundzewicz, 1997). Methods such as speleothem data from northeastern Iowa, as well as pollen analysis from several lakebed sediments in the area have been used to help determine the area's climate. In general, the studies show three main stages. The first stage is labeled as pre-prairie. During this time, moisture conditions were similar to and temperature conditions were colder than modern conditions. This period may be represented in PLC 3 in the deepest parts of the core. Stage two is the Prairie period. During this time, moisture conditions were much drier and temperature conditions were warmer compared to modern conditions. This period may be represented in PLC 3 up to 2.6 meters. While speleothem data show this stage persisting for a large portion of the Holocene (Denniston et al, 1999), PLC 3 data indicate the Prairie period may have played a much smaller role just 100 miles to the east. This may indicate that the furthest extent of the Pacific air mass is just a short distance east of the tufa mound's location as the area was only briefly affected before the prairies began to retreat westward. The third and final stage is a record of post-prairie

climate. During this time, moisture conditions were wetter and temperature conditions were colder compared to Prairie period conditions. This period may be represented in PLC 3 from 2.6 to 0 meters.

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