Reconstruction of Brooksville Ridge Cave Temperatures from Speleothem Samples

Amor Elder
University of South Florida

Advisors:
Arcadii Grinshpan, Mathematics and Statistics
Connie Mizak, Geography
Philip van Beynen, Geography

Problem Suggested By: Philip van Beynen
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Abstract
A problem was proposed to use an adjusted version of Dorale's speleothem delta function to model the temperature fluctuations in the Brooksville Ridge Cave from the Medieval Warm Period to the present. The temperature values reconstructed by the model can be compared to the known temperature trend during the same selected time period. If the results matched the trend, it indicates that the cave's temperature was the dominant influence. If not, a different variable was the main influence of the cave.

Using δ¹⁸O values gathered from a speleothem, past temperatures of the cave were modeled. Results show that the model's temperature trend did not match the known temperature trend, indicating the main variable affecting the δ¹⁸O values is more likely rainfall than temperature. This conclusion corresponds with the cave's location in Florida. Reconstructions of past climates can be used in modeling future climate changes as well as helping to support or disprove current evidence of hazardous climate changes.

Keywords
Speleothem, Oxygen-isotoper ratio, Climate Change, Florida

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PROBLEM STATEMENT

Speleothems were gathered from Brooksville Ridge Cave (BRC) in Brooksville, Florida and analyzed for their ratio of O$^{16}$ and O$^{18}$ ($\delta^{18}O$) oxygen isotopes. The collected $\delta^{18}O$ values were used to model the change in Florida’s temperature from the Medieval Warm Period (MWP), 1000 years ago, to the present using the Dorale’s Speleothem Delta Function (SDF):

$$\delta^{18}O = e^{-\frac{2780}{(T+273.15)^2} - 0.00289} \times [0.475T + 986.4] - 1000. \quad (1)$$

Note that this model is dependent on temperature ($T$) alone. If the temperatures predicted by the model match the established temperatures for this specified time period, it is likely that the cave’s temperature held the largest influence on the speleothem growth.

MOTIVATION

I. MATHEMATICAL CONCEPTS

Dorale’s SDF (1) is the product of an exponential and linear function. To determine the past temperatures from the measured oxygen isotope concentration in the calcite, the inverse of Dorale’s SDF must be calculated numerically. Since the SF does not have a trivial inverse, the use of an approximate trial and error algorithm is utilized. Guessed temperatures are input into (1) and the resulting $\delta^{18}O$ SMOW values are compared with the $\delta^{18}O$ SMOW values collected in the sample. The guessed temperatures can be adjusted until the temperatures and SMOW values agree. This problem can be classified as an approximation algorithm.
II. **EXPERIMENT SETUP**

For this experiment, cave calcium carbonate deposits known as speleothems (specifically stalagmites) were collected from BRC and analyzed for their $\delta^{18}O$ values (van Beynen, 2009 Lecture). Stalactites form on the cave ceiling and form at a different rate than stalagmites, so they were excluded from this experiment. The $\delta^{18}O$ values of the stalagmites change over time, and depend on temperature and other factors. This change in $\delta^{18}O$ is known as fractionation, and can be used to reconstruct temperatures of caves and the areas above them.

Samples were taken from stalagmites which were cut in half lengthwise and dated using mass spectrometry (van Beynen, 2009 Lecture). Mass spectrometry is the use of magnets and electric fields to ionize samples, and then separate the molecules via composition and charge. Then smaller samples of speleothem dated using Uranium → Thorium measurements, evaluating the ratio of uranium and thorium in each sample. As time passes uranium decays to thorium and the ratio of these two elements allows for highly accurate dating of samples. After the samples were dated, continuous flow mass spectrometry was used to determine the $\delta^{18}O$ values, giving the data needed to begin the proposed problem (van Beynen, 2009 Lecture).

III. **PROJECT GOAL**

The purpose of this experiment was to explore the possibility of reconstructing the Holocene temperatures from the MWP to the present in the Brooksville Ridge Cave (BRC). To achieve this, temperatures were calculated by the algorithm to find the inverse function of the product of an exponential and linear equation. Data was compared against known temperature trends and analyzed for matching.
In this experiment, the Dorale model is used as a diagnostic tool. If the model matches the known temperature trends, it follows that temperature is the dominant factor of $\delta^{18}O$ concentrations in this cave. If the model’s temperature trend matches but the individual values disagree with established temperatures, the model can be recalibrated by adjusting the slope of the drip-water function in the SDF since different areas are subject to various climates. Such a modified SDF will be called the Adjusted Speleothem Delta Function (ASDF). However if the overall temperature trend of the ASDF model does not match the known temperature trend, then temperature alone does not account for the $\delta^{18}O$ ratio in the BRC and other factors such as rain may play an important role in the speleothem formation.

Calculating the past cave temperatures in the BRC is a way of reconstructing the temperatures above the cave, as a cave’s temperature tends to equal the temperature on the surface. Knowing the variations of past temperatures is valuable for predicting future climate changes. This information is also applied in modeling past amounts of rainfall. Collaboratively, these results are useful in the ongoing discussion over hazardous global climate change.

**MATHEMATICAL DESCRIPTION AND SOLUTION APPROACH**

Data was received in an Excel spreadsheet containing the known $\delta^{18}O$ coupled with the proper SDF (1) and ASDF

$$\delta^{18}O = e^{[\frac{2.760}{(T+273.15)^2} - 0.00289]}[0.475 T + 986.4] - 1000 \tag{2}$$

which is specifically calibrated for BRC. The $\delta^{18}O$ concentration values in the stalagmites were measured against the international standard PDB (Pee Dee Belemnite) concentrations. The SDF and ASDF are expressed in terms of SMOW (Standard Mean Ocean Water) ratios, so the data
was first converted. The conversion from PDB to SMOW is straightforward (see Appendix B). The ASDF is the built off of Dorale’s SDF with a different slope for the dripwater function (see Appendix B) to account for the regional meteoric water line (van Beynen, 2009 Lecture).

The inverses for both equations were solved via Excel, using a approximate trial and error algorithm. Initial temperatures were speculated and input into the ASDF. Knowing that the ASDF is monotonically increasing, if the $\delta^{18}O$ output of the guessed temperature was greater than the sampled value then the input of the next iteration was decreased slightly. Likewise, if the $\delta^{18}O$ output of the guessed temperature was less than the sampled value then the input of the next iteration was increased slightly till the guessed temperature matched the recorded $\delta^{18}O$ ratio. The SDF was calculated similarly, but will not be discussed further since the ASDF was calibrated specifically for the BRC site.

Though +1000 data values were supplied, specific years such as the LIA (Little Ice Age) and the MWP (Medieval Warm Period) were of greater relevance so a buffer of ±4 periods (≈ 6.17 years) around the LIA, MWP, and present time periods were analyzed first. Since the calculated trend established by the ASDF during these three time periods violated the known trend of past temperatures (see Figure 1), the remaining temperature readings were not calculated (see Appendix A).

**DISCUSSION**

Both the SDF and the ASDF contradicted the temperature trends in Figure 1 during the three tested time periods. The Little Ice Age period temperatures were calculated to be higher than both the Medieval Warm Period and the present day temperatures (see Appendix A). The
buffer years further confirmed that the temperatures around the key time periods do not match current trends.

Upon reviewing the results of Table 1 and considering the time-intensity of the approximation algorithm approach, it was decided that these contradictions established suitable evidence to refute that temperature alone dictated the formation of the stalagmites. Considering the cave’s location, it can be inferred that the BRC rainfall heavily affects the $\delta^{18}O$ ratio values.

If rainfall has been a dominant force in the BRC, the SDF and ASDF used in this study will be unable to give an accurate reconstruction of the cave temperatures and a different model will be necessary for reconstructing past temperatures in Florida. Nonetheless, the ASDF has been a valuable diagnostic tool in narrowing down the variables affecting the $\delta^{18}O$ values in BRC.
CONCLUSION AND RECOMMENDATIONS

The purpose of this experiment was to see if temperatures in Florida from the MWP to the present time period could reconstructed from the $\delta^{18}$O ratio in stalagmites from the BRC. However the known temperature trends did not match the speleothem formation predicted by the ASDF and it is hypothesized that rainfall has been affecting the model in the BRC. This hypothesis seems reasonable when the cave’s location is taken into account.

The results of this experiment have shown the ASDF to be a useful diagnostic tool in determining whether temperature dictates the $\delta^{18}$O ratio in a cave’s speleothem even though the ultimate goal of reconstructing the Holocene temperatures was not achieve. Using algorithms to diagnose significant variables has proven to be a valuable tool in determining climate change and could be applied to other areas where a system is modeled and prior data collected such as pollution build up or mineral loss.

Philip E. van Beynen suggests that a new equation be utilized to reconstruct the temperature of the BRC testing rainfall as the dependant variable (Elder, 8 December 2009). If the past the patterns of rainfall can be established, they could be compared with current weather patterns to further explore climate changes happening today.
# Nomenclature

| Abbreviation | Term                             | Notes                                      |
|--------------|----------------------------------|--------------------------------------------|
| ASDF         | Adjusted Speleothem Delta Function | See Appendix B                             |
| BRC          | Brooksville Ridge Cave           | Brooksville, Florida                       |
| $\delta^{18}$O | Ratio of $^{18}$O to $^{16}$O isotopes | Measured in parts per thousand (‰)         |
| LIA          | Little Ice Age                   | ~350 Years ago                             |
| MWP          | Medieval Warm Period             | ~1020 Years ago                            |
| PDB          | Pee Dee Belemnite                | A standard for $\delta^{18}$O             |
| SDF          | Speleothem Delta Function        | See Appendix B                             |
| SMOW         | Standard Mean Ocean Water        | A standard for $\delta^{18}$O             |
| T            | Temperature                      | Measured in Celsius (°C)                   |
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## Appendix A – Data Table

| Time Period        | Periods | Years Ago | Sampled $\delta^{18}$O Values | Calculated Temperatures (°C) |
|--------------------|---------|-----------|-------------------------------|-----------------------------|
|                    |         |           | PDB  | SMOW | SDF  | ASDF |
| Modern Isotopic Value | 1      | 1.2341    | -4.75 | 26.01311 | 11.2458 | 21.2799 |
|                    | 2      | 2.4682    | -4.59 | 26.18183 | 11.6050 | 21.9137 |
|                    | 3      | 3.7023    | -4.62 | 26.15053 | 11.5384 | 21.7964 |
|                    | 4      | 4.9364    | -4.68 | 26.08693 | 11.4030 | 21.5576 |
|                    | 5      | 6.1705    | -4.62 | 26.14790 | 11.5328 | 21.7865 |
|                    | ...    | ...       | ...  | ...  | ...  | ...  |
|                    | 280    | 345.5480  | -4.75 | 26.01160 | 11.2426 | 21.2743 |
|                    | 281    | 346.7821  | -4.66 | 26.10955 | 11.4512 | 21.6426 |
|                    | 282    | 348.0162  | -4.64 | 26.12491 | 11.4839 | 21.7002 |
|                    | 283    | 349.2503  | -4.56 | 26.21350 | 11.6724 | 22.0323 |
| Little Ice Age     | 284    | 350.4844  | -4.49 | 26.28246 | 11.8190 | 22.2902 |
|                    | 285    | 351.7185  | -4.60 | 26.16789 | 11.5754 | 21.8614 |
|                    | 286    | 352.9526  | -4.57 | 26.19950 | 11.6426 | 21.9799 |
|                    | 287    | 354.1867  | -4.53 | 26.24048 | 11.7298 | 22.1332 |
|                    | 288    | 355.4208  | -4.59 | 26.17352 | 11.5874 | 21.8825 |
|                    | 289    | 356.6549  | -4.60 | 26.16352 | 11.5661 | 21.8451 |
|                    | ...    | ...       | ...  | ...  | ...  | ...  |
|                    | 828    | 1021.835  | -5.01 | 25.74716 | 10.6782 | 20.2744 |
|                    | 829    | 1023.069  | -5.09 | 25.66420 | 10.5008 | 19.9591 |
|                    | 830    | 1024.303  | -5.03 | 25.72617 | 10.6333 | 20.1947 |
|                    | 831    | 1025.537  | -5.08 | 25.66920 | 10.5115 | 19.9781 |
|                    | 832    | 1026.771  | -5.09 | 25.65920 | 10.4901 | 19.9401 |
| Medieval Warm Period | 833    | 1028.005  | -5.14 | 25.61523 | 10.3960 | 19.7726 |
|                    | 834    | 1029.239  | -5.04 | 25.71518 | 10.6098 | 20.1530 |
|                    | 835    | 1030.474  | -5.03 | 25.72417 | 10.6290 | 20.1871 |
|                    | 836    | 1031.708  | -4.99 | 25.77015 | 10.7273 | 20.3617 |
|                    | 837    | 1032.942  | -4.92 | 25.84231 | 10.8814 | 20.6351 |
APPENDIX B – FORMULAS

CONVERSION FROM VPDB TO VSMOW:

$$\delta^{18}O_{SMOW} = 1.03091 \delta^{18}O_{PDB} + 30.91$$

DORALE’S SPELEOTHEM DELTA FUNCTION (SDF):

$$\delta^{18}O_c = e^{\left\{\frac{a}{(T_1+273.15)^2} - b\right\}} [F(T_2, t, g) + 10^3] - 10^3$$

where

- $\delta^{18}O_c$ : Oxygen-isotope composition of calcite (SMOW),
- $a, b$ : Constants governing the fractionation factor between the carbonate mineral and water,
- $F(T_2, t, g)$ : Dripwater function,
- $T_1$ : Cave Temperature (°C),
- $T_2$ : Surface Temperature (°C), commonly $T_2 = T_1$,
- $t$ : Time,
- $g$ : Geographical position of the site.

For this site,

$$\delta^{18}O_c = e^{\left\{\frac{2780}{(T_1+273.15)^2} - 0.00289\right\}} [0.695 T_1 + 986.4] - 1000.$$

ADJUSTED SPELEOTHEM DELTA FUNCTION (ASDF):

Calibration of the SDF for the Florida region is given by,

$$\delta^{18}O_c = e^{\left\{\frac{2780}{(T_1+273.15)^2} - 0.00289\right\}} [0.475 T_1 + 986.4] - 1000.$$  

(Note: the slope of the dripwater function changes from 0.695 to 0.475.)
APPENDIX C – GLOSSARY OF TERMS

$\delta^{18}O$ – An oxygen-isotope ratio denoting the difference between an international standard’s $^{18}O/^{16}O$ ratio (such as in PDB or SMOW) and a sample’s $^{18}O/^{16}O$ ratio.

**Fractionation** – The process which varies the $\delta^{18}O$ values of stalagmites over time depending on temperature and other factors.

**Holocene** – A geological epoch extending from 12,000 years ago to the present.

**Mass Spectrometry** – The use of magnets and electric fields to ionize samples in order to date their formation.

**Meteoric Water** – Water in the ground which originates from precipitation.

**Pee Dee Belemnite (PDB)** – A carbonate formation used as a standard for $^{18}O/^{16}O$ oxygen-isotope ratio testing.

**Speleothem** – A cave formation formed by mineral deposition.

**Stalagmite** – A speleothem which forms on the *floor* of a cave.

**Stalactite** – A speleothem which forms on the *ceiling* of a cave.

**Standard Mean Ocean Water (SMOW)** – A carbonate formation used as a standard for $^{18}O/^{16}O$ oxygen-isotope ratio testing.