Using MicroCT to Improve Precision of Uranium-Thorium Dating in Speleothem Records

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Speleothems, MicroCT, Uranium-Thorium Dating

Avoiding impurities by using microCT to look below stalagmite surfaces leads to more precise age models and better climate records.

ABSTRACT. Isotopic and elemental proxy records from cave deposits (speleothems) provide crucial information for understanding past climate. However, to extract useful information from speleothems, proxy records must have precise, accurate chronologies. Speleothems can be accurately and precisely dated using established ^{230}Th/U techniques, but the dates are degraded if U- or Th-bearing foreign materials contaminate the analyzed carbonate. Such contaminants can be difficult or impossible to detect using conventional microscopic approaches when they are below the speleothem's surface. To address this problem, a 38 cm Holocene stalagmite from White Moon Cave in California was scanned using micro computed tomography (microCT) to identify clean, dense carbonate samples. The stalagmite contained sub-mm to mm-sized pockets of silicate detritus that, if sampled, would greatly reduce the precision of resulting ^{230}Th/U estimates, possibly rendering them unusable. These scans were used to select volumes to sample for analysis, and allowed for identification of the contaminating phases as mica and quartz, present in trace amounts in the cave's marble host rock. Using this strategy, the precisions of detritus-corrected ages were improved by about 30% relative to analyses where this screening method was not employed. This method shows promise for optimizing the selection of material for ^{230}Th/U or other proxy analyses and can thus help provide improved speleothem paleoclimate records.

INTRODUCTION.

The warming of the Earth's atmosphere due to the anthropogenic emissions of greenhouse gases is a global issue, the effects of which are already being felt, and will continue affect the planet [1]. Paleoclimatic research is required to document past climate patterns and predict future responses of Earth's climate system. Speleothems, mineral deposits usually consisting of calcium carbonate ($CaCO_3$) that form over time as groundwater precipitates in caves, are particularly useful in paleoclimatic research. These speleothems can be found in a variety of spatial and temporal ranges, including areas where people tend to live, unlike other paleoclimate archives such as ice cores, and can be dated to very high degrees of precision through established uranium-decay techniques.

One of the most significant climate events in the relatively stable Holocene epoch (the last ~11,000 years) was the 8.2 kyr event. This event, which occurred 8,200 years ago and lasted about 150 years, was likely caused by the dumping of cold, fresh, glacial lake water into the Atlantic Ocean after the glacial barriers holding it back melted. Paleoclimate records and models suggest this had global climate effects including large changes in temperatures and alterations in monsoon patterns [2-6]. While notable to study in the past, the 8.2 kyr event also relates to anthropogenic climate change in the future, in that if ice caps continue melting at the rates they are today, it is possible that an influx of freshwater akin to that of the 8.2 kyr event could be seen in the future [5]. Patterns of greater variability in weather and more intense winter storms as effects of the 8.2 kyr event are visible through chemical records from speleothems in several locations, including coastal California [2]. Though ice cores have been studied historically and were the proxy in which the 8.2 event was first identified [3], speleothems provide a unique lens to investigate past climate because they record at a high resolution and can be found in a wide variety of places [2,5,6]. A better understanding of the climatic effects of the 8.2 kyr event through speleothem records could help predict and prepare for similar events in the future.

In order to use information from cave deposits to infer paleoclimatic changes, the samples need to be precisely and accurately dated. Without accurate dates, it cannot be assumed that analysis of chemical changes in the speleothems correspond to any certain time, making global comparisons impossible. This has notable importance when considering events like the 8.2 kyr event, which occurred over a brief 150 years. High precision is needed to ensure that the event is actually being resolved, otherwise the errors on ages may be larger than the timespan of the event. Unfortunately, speleothems can be contaminated by other phases that reduce precision, such as particles from host rock that are incorporated into the speleothem as it grows. The method for dating by analyzing isotopes of uranium and thorium (^{230}Th/U dating) requires part of the sample to be drilled into a powder. A relatively large amount of powder is needed, compared to the thin age bands that exist in most speleothems. This large volume requires that drilling goes deep into the sample to collect the powder, into areas unseen from the surface of the cut stalagmite. Contaminating phases can be difficult to visually identify, leading to unexpectedly large dating uncertainties.

Developing a method to decrease uncertainty with ^{230}Th/U dating speleothems that is minimally destructive and less time consuming is necessary, especially for "dirty" samples that may contain high volumes of contaminants. ^{230}Th/U dating is one of the most well-developed dating methods for samples less than about 500,000 years old, as opposed to uranium-lead dating, which is more difficult because it requires even cleaner samples [7]. Thus, improving the precision ^{230}Th/U dating technique by avoiding unseen contaminants will improve the widely utilized technique as a whole. Understanding the internal characteristics of a sample before drilling allows a drilling path to be selected based on features other than surface appearance, so that pockets of mineral detritus and other irregularities can be avoided. Avoiding contaminants, and thus having precise dates, serves especially important when looking at major climate events because knowing it improves understanding of when within the event certain climate characteristics occurred. Having knowledge prior to the drilling process is far preferable to unknowingly basing a drilling path based on characteristics only visible from the surface. It also allows the visualization of variability in the growth bands. As growth bands propagate through a cylindrical sample, they curve to varying degrees. By using computed tomography (CT), samples can be drilled in such a way that avoids this.

The present study develops a method to identify clean, dense carbonate samples for ^{230}Th/U age dating that is non-destructive and rapid. This technique was applied to a speleothem collected from White Moon Cave on the coast of central California in 2012. Preliminary age dates for this sample indicate that it grew just after the 8.2 kyr event, giving it the potential to reveal more information about hydroclimate variability in CA, a hydrologically unstable and arid region that is densely populated today.

MATERIALS AND METHODS.

Sample Collection

The stalagmite used in study was collected from White Moon Cave (37°00'N, 122°11'W) in the Santa Cruz Mountains near Davenport, California. The cave entrance is located on the wall of an abandoned quarry. The 38 cm tall sample was collected by Dr. Jessica Oster in the summer of 2013. The top half of the speleothem was cut into quarters along the growth axis, and the bottom half was divided into six ~1.5 cm x 2 cm x 4.5 cm billets and encased in a grainy epoxy in order to make thin sections for additional analysis by Laser Ablation ICP-MS.

Scanning and Path Selection

A North Star Imaging microCT scanner was used to acquire a high-resolution 3D image of the speleothem's internal characteristics based on density variations within the sample. This, coupled with a 2D image of the visible sides of the speleothem, was used to plan a drilling path to collect powdered sample for ^{230}Th/U analysis (Figure 1). Areas of the speleothem that appeared free of irregularity from the CT scan were correlated to the visible surface of the sample where a path was selected. The chosen path was then translated onto a 2D image, which was used when drilling. Depth was also considered, in order to obtain the necessary amount of sample powder while avoiding pockets of detritus below the surface of the sample. Ten sites in total were selected, ensuring that one site was chosen as close as possible to the top and bottom of each billet in order to understand the total age range the sample spans.

Drilling and Dating

A Volvere Vmax hand drill (a dental drill) was used to acquire the powder from the sample, drilling using short, shallow strokes to dislodge calcite powder from the sample. Although it varies from speleothem to speleothem based on U content, around 200 mg was required for ^{230}Th/U dating in this sample. The 10 samples were dated using established ^{230}Th/U techniques, which involve dissolving the sample, chemically separating uranium and thorium, and measuring the concentrations of several isotopes of each using a mass spectrometer [2].

RESULTS.

Contaminating phases were identifiable in CT scans, showing up as large pockets of air or small dense pockets filled with detritus that could potentially cause an imprecise date, but are difficult to see from the surface of the billet (Figure 1). Closely examining a pocket like those that appear on CT scans reveals that it can potentially contain several types of detritus that would cause uncertainty in dating if included in the drilling sample. The following non-calcite materials were identified by thin section petrographic microscopy in the billet: quartz, mica, dolomite, and iron oxide (Figures 1b-c). These same non-calcite materials were also evident in host rocks found around the cave.

The age model based off usable dates [8], revealed that the speleothem had a period of older, slow growth followed by an increase in growth speed around 4000 years ago (Figure 2). Small error allows for the most accurate age model possible, in order to understand the growth of the speleothem.

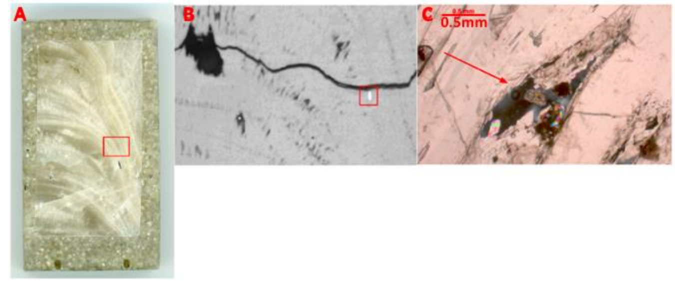

Figure 1. Comparison of a 2D scan (A) of a billet with visible features about 0.5 cm in from the surface on a CT scan (B) of the same billet. White spot in the highlighted area represents a pocket of dense non-calcite material. Example of a pocket of detritus seen in a thin section of the billet (C) [containing mica and other minerals] that could potentially cause an imprecise date, but that is difficult to see from the surface of the billet.

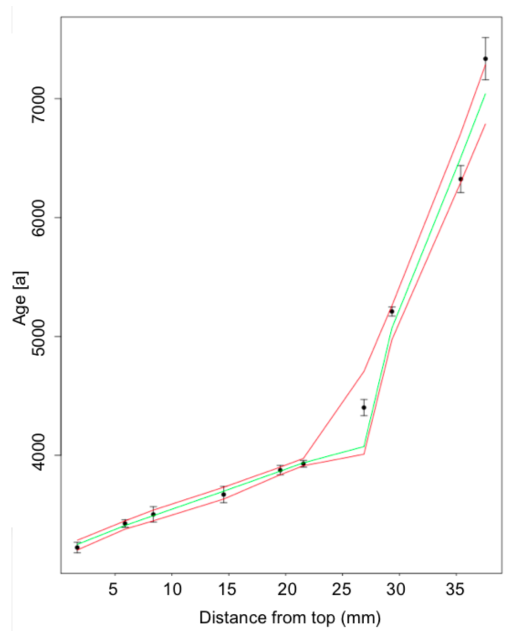

Figure 2. Final age model with original error. Age model determined based on dates analyzed from scanned and drilled samples. Small error allowed for an accurate age model that revealed a period of slow growth followed by a period of notable faster growth. Circles represent analyzed ages with error bars, red lines represent the outer bounds of what the growth model could look like based on ages, and the green line represents the average, or most normally distributed version of the growth model. The date from SC 2-A, the topmost site on the speleothem, was not included.

Dates with scanning method employed all had error small enough to be incorporated into the age model; none were discarded (Figure 3). Compared to dates obtained for the same stalagmite a few years earlier without the CT scanning before drilling, the new method procured dates that were 30% more precise. The average error of the old ages (not including the date with error so large it was unusable) was 97.59 years. The average error of new ages was 67.46 years. If the date from previously obtained ages with error so large it was unusable was considered, the average error is 392.13, and employing the scanning method improves precision by over 83%.

DISCUSSION.

Studying past climate change is imperative because it shows us how the Earth responded to different degrees of warming and cooling in the past. Knowing how these changes affected the Earth historically helps in predicting and understanding the effects that current and near-future climate change will have on the environment [9].

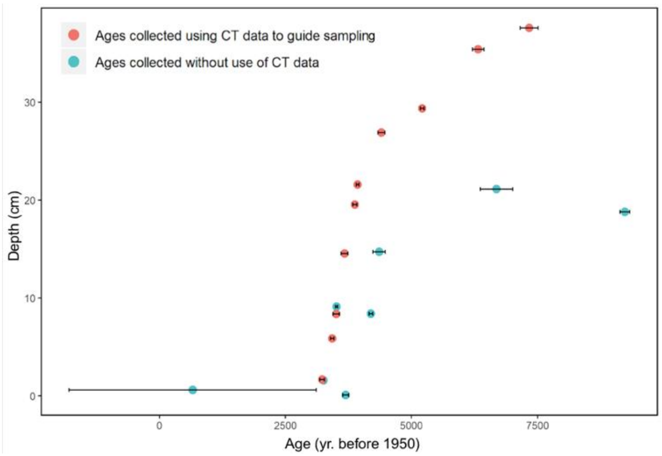

Figure 3. Comparison of newly acquired with CT data and old ages without CT data. The average error of the old ages (not including the date with unusable error) was 97.59 years. Average error of new ages was 67.46 years; error with the scanning method was decreased by 30%. In the old ages, several age reversals and out of sequence dates are seen. The growth model created by these ages would not make logical sense, and a date had to be discarded due to excessively large error.

Studying past major climate events, like the 8.2 kyr event, is also especially important because they could occur in a similar fashion in modern times, in this case if the Greenland ice sheet melted. Speleothem proxies serve as a high-resolution glimpse into the past, providing information about local climate change that could not be gleaned from other environmental clues. Understanding and preparing for the effects of global warming will be a necessity as we progress towards or exceed a 2 ℃ global temperature increase from greenhouse gas emissions [10]. Improving historic climate records by increasing precision of the process used to analyze proxies contributes to this goal. Small error allows for an accurate age model [8] that reveals the sample's variant growth speeds, from slower, old growth to a faster period of growth about 4000 years ago (Figure 2).

The idea of changing the very first step of the dating process, drilling material for analysis from the sample, serves the goal of making it more accurate and precise. Drilling in areas with little to no impurities will improve the accuracy and precision of the date of the sample. Qualitatively, major pockets of air and detritus were avoided when drilling the samples, and contaminating phases have been identified as mica particles from the cave's marble host rock [11]. These contaminants, if not avoided, cause ^{230}Th/U dating techniques to yield unusable dates because of large uncertainties [2]. This study reveals that avoiding contaminants and pockets based on density differences seen in microCT scans prior to uranium-series dating yields precise dates. The dates without employing microCT were 30% less precise, and were out of sequence in several cases, likely indicating that a pocket of detritus was sampled when drilling. The new dates acquired allowed for the creation of an accurate age model that represent the speleothem sample's growth. This microCT scanning methodology is translatable to drilling and has potential for continued development to improve age models, which are critical to understanding past climate change by providing a way to avoid impurities that otherwise could not be seen.

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REFERENCES

1. N. Oreskes, The Scientific Consensus on Climate Change. *Science*. **306**, 1686 (2005).
2. Jessica Oster, Warren Sharp, Aaron Covey, Janson Gibson, Bruce Rodgers, Hari Mix, Climate response to the 8.2 ka event in coastal California. *Scientific Reports*. **7**, 2045-2322 (2017).
3. R. Alley, P. Mayewski, T. Sowers, M. Stuviers, K. Taylor, P. Clark, Holocene climatic instability: A prominent, widespread event 8200 years ago. *Geoscience World*. **25,** 483-486 (1997).
4. B. Davis, A. Stevenson, The 8.2 ka event and Early-Mid holocene forests, fires, and flooding in the Central Ebro Desert, NE Spain. *Quaternary Science Reviews*. **26**, 1695-1712 (2012).
5. J. Wu, Y. Wang, H. Cheng, X. Kong, D Lui, Stable isotope and trace element investigation of two contemporaneous annually-laminated stalagmites from northeastern China surrounding the 8.2 ka event. *Climate of the Past*. **8**, 1497-1507 (2012).
6. E. Thomas, E. Wolff, R. Mulvaney, J. Steffensen, S. Johnsen, C. Arrowsmith, J. White, B. Vaughn, T. Popp, The 8.2 ka event from Greenland ice cores. *Quaternary Science Reviews*. **26**, 70-81 (2007).
7. S. Schmidt and J. K. Cochran, Radium and radium-daughter nuclides in carbonates: a brief overview of strategies for determining chronologies, *Journal of Environmental Radioactivity*. **101**, 530-537 (2010).
8. D. Scholz and D. Hoffmann, StalAge - An algorithm designed for construction of speleothem age models. *Quaternary Geochonology*. **6,** 369-382 (2011).
9. P. Braconnat, S. Harrison, M. Kageyama, P. Bartlein, Y. Zhaom Evaluation of climate models using paleoclimateic data. *Nature Climate Change*. **2**, 416-424 (2012).
10. J. Rogelj, Paris Agreement climate proposals need a boost to keep warming well below 2O C. *Nature Perspectives*. **534**, 631-639 (2016).
11. L.B. Railsback. "An atlas of speleothem microfabrics." (University of Georgia, 2010).

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