

APPLICATION OF HIGH-RESOLUTION X-RAY COMPUTED TOMOGRAPHY IN DETERMINING THE SUITABILITY OF SPELEOTHEMS FOR USE IN PALEOCLIMATIC, PALEOHYDROLOGIC RECONSTRUCTIONS

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The isotopic and elemental compositions of speleothems can be used as proxies to elucidate past climate changes. Speleothem material is precious, however, and its use in such climate studies must be balanced against the need to preserve fragile cave environments. Accordingly, accurate assessment of the internal speleothem stratigraphy can provide insight into: 1) Overall sample quality for paleoclimate studies, and 2) the position of the central growth axis of the sample prior to destructive sample preparation, which involves bisecting by sawing the sample along its growth axis. Chemical and isotopic samples taken along the growth axis have the greatest potential to reflect the composition of the water from which the speleothem precipitated. The growth axis of speleothems cannot be reliably determined by visual inspection of uncut specimens, and incorrect bisections may compromise their applicability as geochemical climate proxies.

High-resolution X-ray computed tomography (HRXCT) is a non-destructive technique that can identify the position of the growth axis in speleothems by detecting subtle changes in calcite density between growth bands. HRXCT imagery of these variations can be animated as 'stacks' of slices and rendered in three dimensions. Such imagery can be used to identify the best plane along which the speleothem should be sectioned for sampling. These images may also reveal samples that have been extensively altered during their history, making them unsatisfactory for climatic studies. Additionally, HRXCT imagery can be used to determine the volume and location of large fluid inclusions for use in reconstructing the H and O isotopic composition of paleoprecipitation.

The use of isotopic and trace element compositions of speleothems (i.e., secondary cements found in caves such as flowstones, stalagmites, and stalactites), has grown with the increased interest in climate change studies. Speleothems are effective proxies in paleoclimate studies for several reasons, including the following: 1) they contain trace element and isotopic tracers that have been used to infer changes in paleotemperature, paleovegetation and paleoprecipitation (Hendy & Wilson 1968; Dorale *et al.* 1992; Winograd *et al.* 1992; Banner *et al.* 1996; Baker *et al.* 1998; Genty *et al.* 1998); 2) they may be continuously deposited over thousands of years and have thin growth bands that can be precisely dated using U-series dating methods (Musgrove *et al.* 2001); 3) growth rates of these bands may provide proxies for environmental parameters such as aquifer recharge rates (Proctor *et al.* 2000; Polyak & Asmerom 2001; Tan *et al.* 2003), and 4) speleothems form in a wide variety of locations where other high-resolution climate records may be absent. Although the potential value of speleothems in climate studies is clear, geochemical sampling is destructive, such that speleothem use should be balanced with the need to conserve fragile cave environments and material.

A speleothem is usually prepared for sampling by slicing the specimen, with a rock saw, along the growth axis and polishing the slabbed surface. The elemental and isotopic compo-

sition of speleothems may change away from the growth axis due to changes in water chemistry caused by progressive CO₂ degassing, evaporation and calcite precipitation (Hendy & Wilson 1968; Hendy 1971; Gonzalez & Lohmann 1988). Specifically, off-axis samples are more subject to non-equilibrium fractionation effects that are not regular or predictable. In addition, recent studies have attributed paleo-environmental significance to changes in speleothem growth band thickness (Proctor *et al.* 2000; Polyak & Asmerom 2001; Tan *et al.* 2003). Growth bands in speleothems thin away from the growth axis. For these reasons, acquisition of the most reliable paleo-environmental information requires that speleothems be sectioned to intersect the growth axis. Unfortunately, the growth history of speleothems is often complex (Fig. 1), making external visual identification of the growth axis difficult or impossible. A mistake during slabbing wastes valuable speleothem material and may limit data quality.

Computed tomography (CT) is a non-destructive technique for creating images of the interior of solid opaque objects (Ketcham & Carlson 2001). Rather than conventional X-radiography, in which an X-ray cone beam is projected through an entire sample onto film, CT images are created by directing a planar fan beam at an object from multiple angular orientations. The resulting images are termed slices because they correspond to what would be observed if the object were cut open

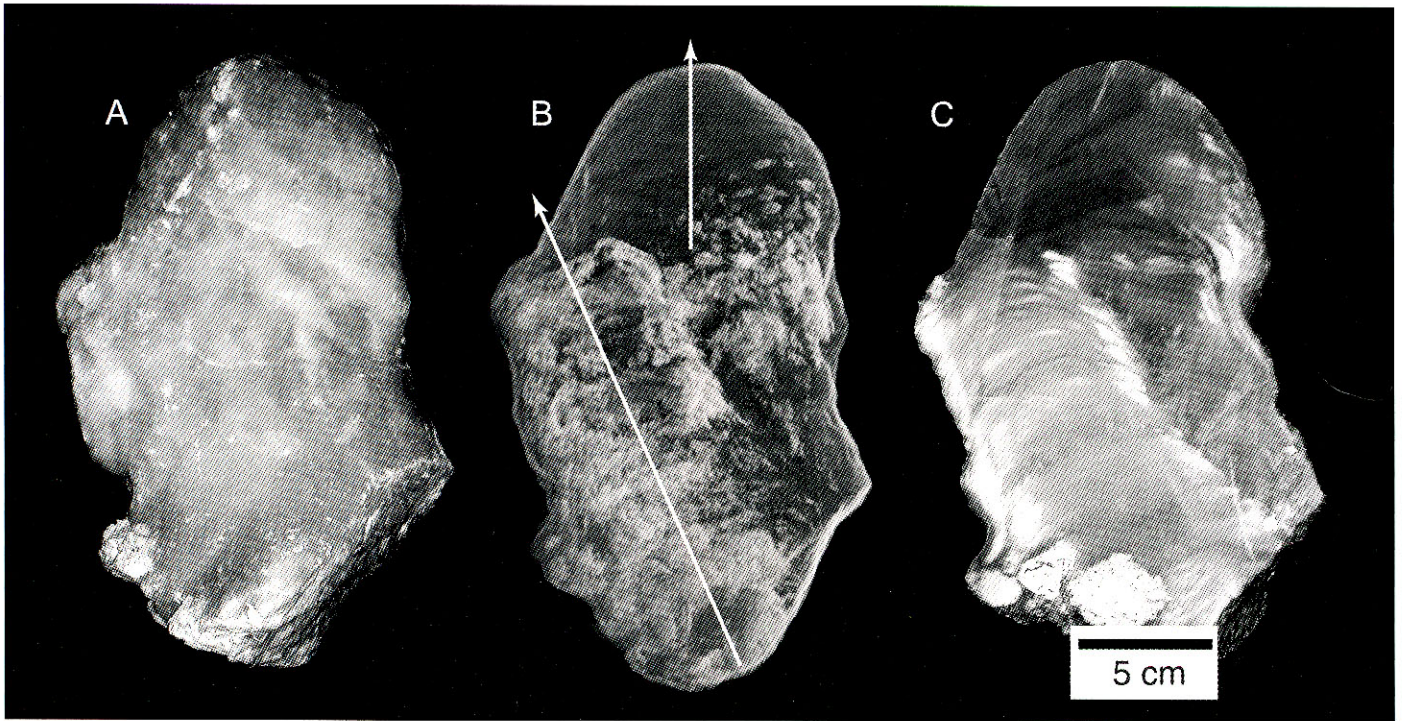


Figure 1. A. Photograph of the unsliced, unpolished side of stalagmite sample AH-M. Note that no internal structure is visible. B. Three-dimensional volume rendering of AH-M with solid material rendered transparent and inclusions rendered in lighter grays. Solid arrows indicate two different growth axes easily visible in the HRXCT data. The speleothem apparently leaned to one side during its growth, shifting the locus and apparent direction of precipitation. These images are available as a complete animation at: <http://www.ctlab.geo.utexas.edu/pubs/mickleretal/mickleretal.htm>. C. Photograph of the sliced and polished stalagmite AH-M. Note how the internal stratigraphy identified by HRXCT scanning prior to the slicing of the sample matches the stratigraphy of the polished specimen. The scan was used to identify the plane that intersected both growth axes.

along the image plane. The grayscales in these images correspond to relative X-ray attenuation, which is a function of elemental composition and density. By obtaining a series of contiguous slices for an object, a complete three-dimensional volume can be imaged. Because the fan beam has a thickness determined by the X-ray spot size and detector vertical pitch or collimation, the pixels in CT images are called voxels, or volume elements. Resolution in CT images is partly determined by the voxel dimensions, and partly by properties of the features being imaged.

High-resolution X-ray CT (HRXCT) is an industrial adaptation of standard medical CT or CAT scan. It differs in that it can use higher-energy X-rays, finer detectors, and longer imaging times, allowing it to penetrate denser objects and achieve 1-3 orders of magnitude better resolution than medical devices (Ketcham & Carlson 2001). The scanner at The University of Texas at Austin can image objects up to 500 mm in diameter, with a height of up to 1500 mm. Slice thickness on large objects (in excess of 75 mm in diameter or 150 mm high) can be as low as 0.25 mm. For smaller objects, the minimum slice thickness is approximately 1/1000 of the cross-sectional diameter, and can be as low as 5 μm .

HRXCT provides a non-destructive means to image the internal stratigraphy of speleothems, as it can detect density contrasts within the calcite growth bands. CT slices of these 'stratigraphic' variations can be animated as 'stacks' of slices, as well as rendered as a three-dimensional (3D) volume. The resulting imagery can serve as a guide to determine the most appropriate plane for sample sectioning and the overall suitability of the sample for study.

MATERIALS AND METHODS

SPECIMENS

Stalagmite AH-M was collected at the Apes Hill Quarry, Barbados, West Indies (Fig. 1 and 2). The stalagmite was unearthed from a cavity during quarry operations and subsequently donated to the University of Texas as part of an ongoing study of paleoclimatic and paleohydrologic reconstruction. The stalagmite is approximately 24 cm in height and 12 cm in diameter and consists of dense, optically clear calcite crystals. Like most speleothems, its shape and texture do not allow its internal stratigraphy to be ascertained.

Stalagmite ANY-01 (Fig. 3) was collected from Anyway Cave, Hays County, Texas for use in an ongoing study of pale-



Figure 2. HRXCT slice through AH-M showing density variations. Higher densities are indicated by lighter gray scale values. Two sets of concentric growth bands are visible. The upper set was apparently deposited before subsidence of the speleothem. The lower set indicates the location of the new growth axis on the flanks of the previously deposited speleothem material. A plane that bisects both growth axes is easily determined (dashed line A). A large void, near B, may be filled with air or the water from which this speleothem precipitated.

oclimatic and paleohydrologic reconstruction. The stalagmite is approximately 33 cm in height and 20 cm in diameter. Dark staining on the outside of the stalagmite, plus the reasons given above for AH-M, made determination of the internal stratigraphy impossible. Both stalagmite samples were CT scanned prior to sample preparation.

CT SCANNING

The specimens were scanned at the High-Resolution X-ray Computed Tomography (CT) Facility at The University of Texas at Austin (UTCT). The facility and typical scanning procedures and parameters are described in detail by Ketcham and Carlson (2001). Scanning parameters were optimized for fast

acquisition of slices, to minimize scanning time and costs. For sample AH-M, X-ray energy was set to 420 kV and 4.7 mA, with a focal spot size of 1.8 mm. X-rays were pre-filtered to reduce beam-hardening artifacts (artificial brightening of the edges compared to the center of the images caused by preferential attenuation of soft X-rays through dense objects) using two brass plates with a total thickness of 3.175 mm. X-ray intensities were measured using a 512-channel cadmium-tungstate solid-state linear array, with a horizontal channel pitch of 0.31 mm. Each slice was acquired using 808 views (angular orientations), each view having an acquisition time of 32 ms. The resulting acquisition time was approximately 34 seconds per slice. The speleothem was scanned in a 160% offset mode (Ketcham & Carlson 2001), with a slice thickness and inter-slice spacing of 1.0 mm. The image field of reconstruction was 180 mm, and the reconstructed image was created as a 512×512 16-bit TIFF file, resulting in an in-plane pixel resolution of 0.35 mm. Image reconstruction parameters were calibrated to maximize usage of the 12-bit range of grayscales available in the output images. Two hundred thirty nine images were obtained, with a total scanning time of approximately 2.25 hours.

For sample ANY-01, scanning parameters were changed slightly to accommodate the different sample dimensions. The differences were that the offset mode was 130%, there were 1000 views per slice, slice thickness and spacing were 2.0 mm and the field of reconstruction was 155 mm. One hundred fifty three slices were acquired, and the total scan time was approximately 1.75 hours.

Overall costs were \$200-\$300 per sample scanned. While not trivial, such amounts are small compared to the time and expense of field work and geochemical analysis, in addition to the larger issues of data quality and preservation of cave material. It should also be emphasized that data with better clarity and resolution than those presented here can be obtained with the equipment used for this study, if greater detail is required for a particular research objective.

IMAGE PROCESSING

Animations of the original CT serial sections were made using QuickTime™. Two techniques were used to study the data in three dimensions. First, images were 'resliced' along orthogonal planes using ImageJ© creating a series of images that can be animated. This software program can be downloaded from the National Institutes of Health (NIH) web site (<http://rsb.info.nih.gov/ij/>). Second, a technique known as volume rendering was used to create visualizations of the entire data volume in three dimensions. Volume rendering consists of allocating to each voxel grayscale value a color and opacity, allowing some materials to be transparent while leaving others partially or fully opaque, while also retaining the density information in the images. The entire data set can be rendered, or a part can be cut away along an arbitrary plane to reveal any internal surface. These renderings were accomplished using VG Studio Max™ software (Volume Graphics GmbH, Heidelberg, Germany).

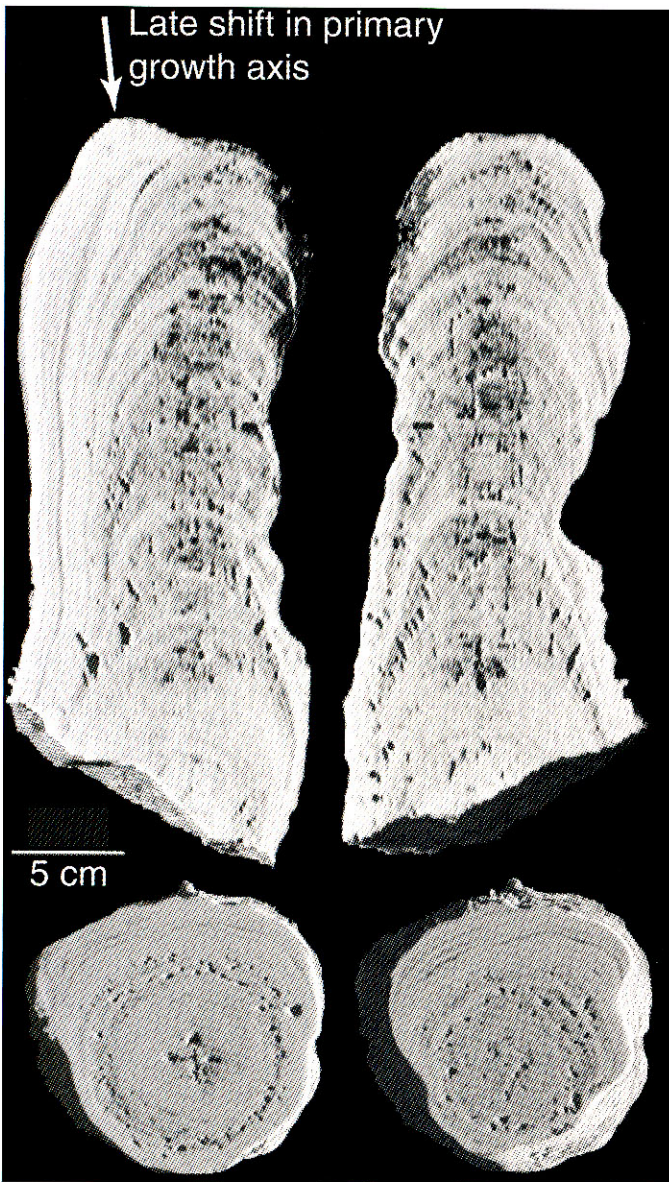


Figure 3. Volume renderings of ANY-01. Cutaways reveal a late shift in the primary growth axis and significant internal porosity around the growth axis. Calcite deposited after the shift in the growth axis has a significantly lower porosity and higher density than calcite near the core of the speleothem. This calcite drape further complicates the visual inspection of the speleothem by obscuring the highly porous central core.

RESULTS AND DISCUSSION

CT scanning of the speleothems reveals complex internal stratigraphies that can not be identified by visual inspection of the uncut specimens. For sample AH-M, CT scanning revealed that the locus of deposition changed significantly at least three times as the stalagmite leaned to one side during its growth (Fig. 1). This stratigraphy likely resulted from deposition on a soft substrate that settled during formation of the stalagmite.

Similar to AH-M, CT scanning of ANY-01 reveals that the latest stage of growth took place off the main axis (Fig. 3). Additionally, the late stage calcite is denser than the previously deposited calcite and formed a drape on the outside of the stalagmite, which obscures the porous nature of the underlying calcite. CT scanning reveals the multiple growth axes of these stalagmites and the planes that intersect these axes (Fig. 2).

In addition to aiding in the identification of the growth axes, CT scanning also reveals the volume and location of large voids within the stalagmite, which may be filled with air or water (Fig. 2). Researchers have recently analyzed water from large fluid inclusions in speleothems for use in paleoprecipitation stable-isotope reconstructions (Genty *et al.* 2002). The dramatic density contrast between calcite and pore space (either water- or air-filled) allows easy identification of voids that fall within the scan's scale of resolution. A more time-intensive scanning protocol with detailed calibration could potentially allow discrimination between fluid-filled and air-filled voids, although this was not undertaken in this study because the primary objective was inexpensive inspection for growth axis determination.

The scanning reveals that AH-M is comprised of dense calcite with an occasional isolated void. In contrast, the calcite around the primary growth axis of ANY-01 varies greatly in density and contains many large and small voids (Fig. 3). Porous calcite around the growth axis of a speleothem may allow both post-depositional alteration of calcite through isotopic and elemental exchange with cave water, and emplacement of pore-filling calcite cements. Such processes will alter the primary isotopic and elemental composition of a speleothem, rendering it unsuitable for paleoclimate studies. For these reasons, ANY-01 was not sliced for sampling. Where feasible such samples can be returned to the location within the cave from which they were collected.

Another feature of CT imagery is that it can be easily disseminated via the Internet, both as a record of the work done and potentially as an educational or archival resource. Web-based images allow remote users to view CT data animations, isolate individual slices, and view rendered 3D volumes from any orientation. Scans and image processing of the samples used in this study are available on the World Wide Web at: (<http://www.cflab.geo.utexas.edu/pubs/mickleretal/mickleretal.htm>).

ACKNOWLEDGEMENTS

We would like to thank the management at Williams C. O. Asphalt and Quarries LTD. for providing access to Apes Hill Quarry, Barbados, West Indies and Dr. George Veni and Mr. David Buie for providing the sample ANY-01 from Anyway Cave, Hays County, Texas, USA. We thank Dominique Genty, an anonymous reviewer, and Earth Science Editor Dr. Ira D. Sasowsky for constructive comments.

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