A NEW TECHNIQUE FOR TRACE ELEMENTAL ANALYSIS OF SPELEOTHEMS USING μ-XRF

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ABSTRACT

Trace element ratios in speleothems (Sr/Ca, Mg/Ca, Ba/Ca) have been used to interpret the hydrogeochemical processes in the epikarst zone as well as the partitioning that occurs at the calcite-water interface. During periods of low rainfall, trace element ratios generally increase as a result of the longer residence time of water in the soil and epikarst zones. High-resolution time series analyses of these elements in speleothems provide evidence for changing paleohydrological and geochemical conditions.

The conventional methods of trace metal analysis of speleothems- Laser Ablation Inductively-Coupled Plasma Mass Spectrometry (LA-ICPMS) and Inductively-Coupled Plasma Optical Emission Spectroscopy (ICP-OES) have yielded many high-quality data sets. However, these methods can be expensive, time-consuming and require the destruction – either by ablation, micro-milling, or powdering – of speleothem samples. The many caveats of these conventional methods have led to the search for a viable alternative – one that will provide the same high-resolution results, but that is affordable, rapid, and non-destructive.

Presented here are preliminary results using μ-X-ray Fluorescence Spectrometry. The Brüker-AXS ARTAX μ-XRF spectrometer permits a multi-element analysis from Na to U with a spatial resolution of 70 μm. The method is non-contact and non-destructive, therefore preserving the sample for additional analyses (e.g. stable isotopes). A simple calibration method for Sr/Ca using pressed mixed powders is described.

It is demonstrated that μ-XRF is an important tool in trace element analysis of speleothems and a viable alternative to conventional methods. Sr/Ca ratios were obtained for multiple speleothems and serve as a preliminary test of μ-XRF suitability. Analyses of variable count times, temporal and spatial reproducibility along transects, and a comparison between μ-XRF spectra and ICP-OES spectra for the same transect of a speleothem growth axis are presented. In addition, ARTAX multi-transect area-mapping demonstrates trace element abundances along both calcite bands and the growth axis.

METHODS

The Brüker ARTAX μ-XRF was used to scan multiple speleothems for Sr/Ca trace elemental abundances along their growth transects. Individual analyses were conducted at various settings of count time and sample increment in order to establish a methodology for the technique and determine its applicability to the study of trace elements in speleothems.

Instrument settings
Beam size: 70 μm
X-ray tube: Pt
Voltage: 50 kV
Current: 600μA
Filter: Al-Ti-Cu
Conditions: Air
Ca and Sr Lines: Kα

The full range of uninterrupted transect scanning distance is approximately 4 cm, requiring that multiple transect ratios be pieced together.

FIGURE 2: A) Brüker ARTAX μ-XRF system, scanning stalagmite in lab.
B) Close-up view of ARTAX during scanning. Tube is attached to an x-y-z stage that can be programmed to account for a slanted stalagmite surface.
C) Digital onboard camera view of scanning mode. Laser pointer indicates location of XRF beam during analysis. If desired, a digital snapshot of each analysis point can be collected.

CALIBRATION

A simple calibration method was created for the ARTAX system using weighed mixtures of pure metal carbonate powders purchased from Alfa Aesar. Mixtures of 99.9999% pure CaCO3 and SrCO3 powders were made, pressed into small cylindrical molds, and scanned.

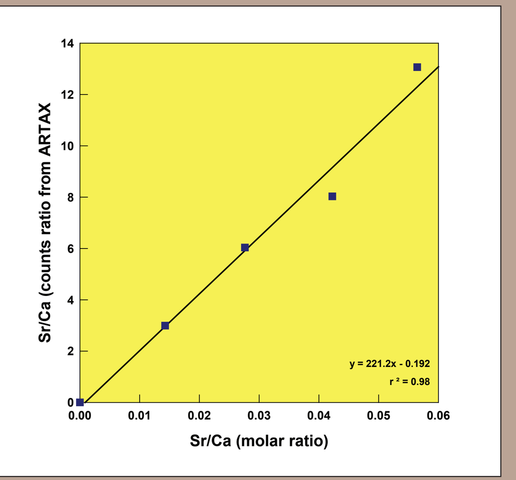


FIGURE 1: Calibration line for Sr/Ca in stalagmites.

EVALUATION OF ANALYSIS CONDITIONS

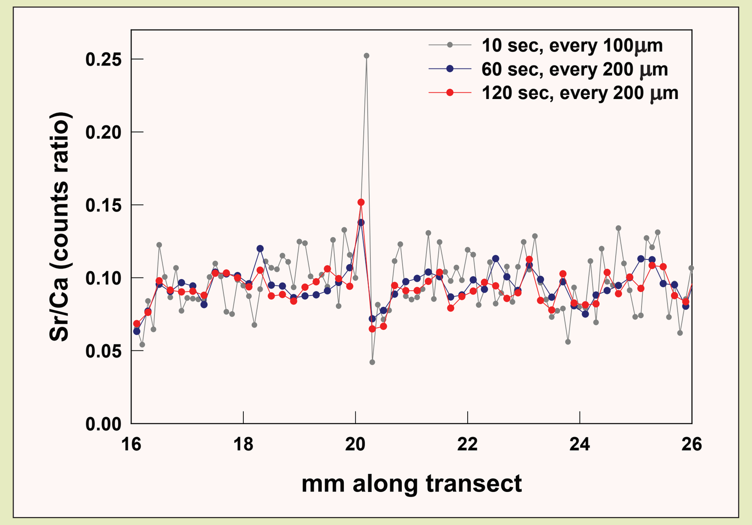


FIGURE 3: Demonstration of effects of count time on reproducibility of Sr/Ca record. The same transect was analyzed at 10, 60, and 120 seconds. Note how, despite the "jumpiness" of the record, the transect from the 10-sec count time largely reproduces the results obtained from transects with longer count times.
Each stalagmite will need to be evaluated, and will be analyzed according to the needs of the study. However, even with low count ratios (~0.1), and short count times (10-20 sec), a useful record of down-axis changes in Sr/Ca can be generated.

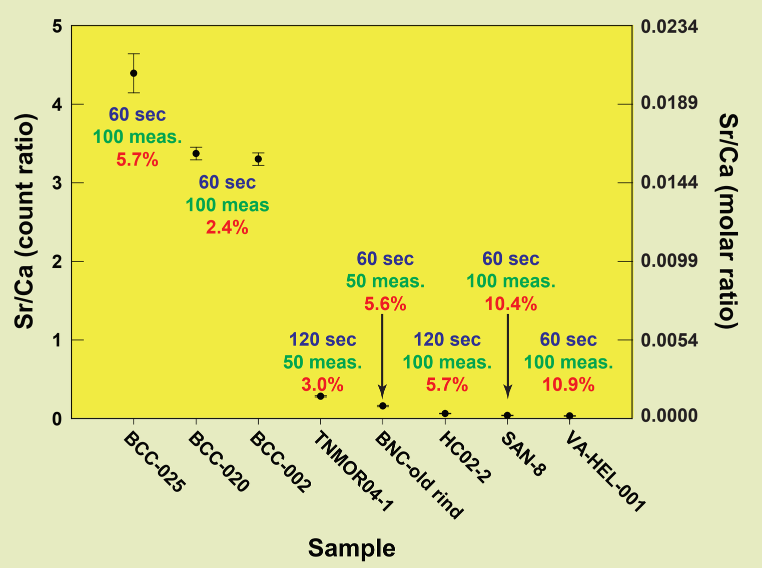


FIGURE 4: Demonstration of the reproducibility (1σ) of the same point, given different stalagmites with different Sr/Ca ratios.

Analysis time is given in blue.
Number of measurments is given in green.
Std. dev. of counts ratio is expressed as % in red.

BCC samples are from Buckeye Creek Cave, WV.
TNMOR sample is from Morrels Cave, TN.
BNC sample is from Bone Norman Cave, WV.
HC02 sample is from Harr Cave, WV.
SAN-8 sample is from San Eduardo Cave, MX.
VA-HEL sample is from Helictite Cave, VA.

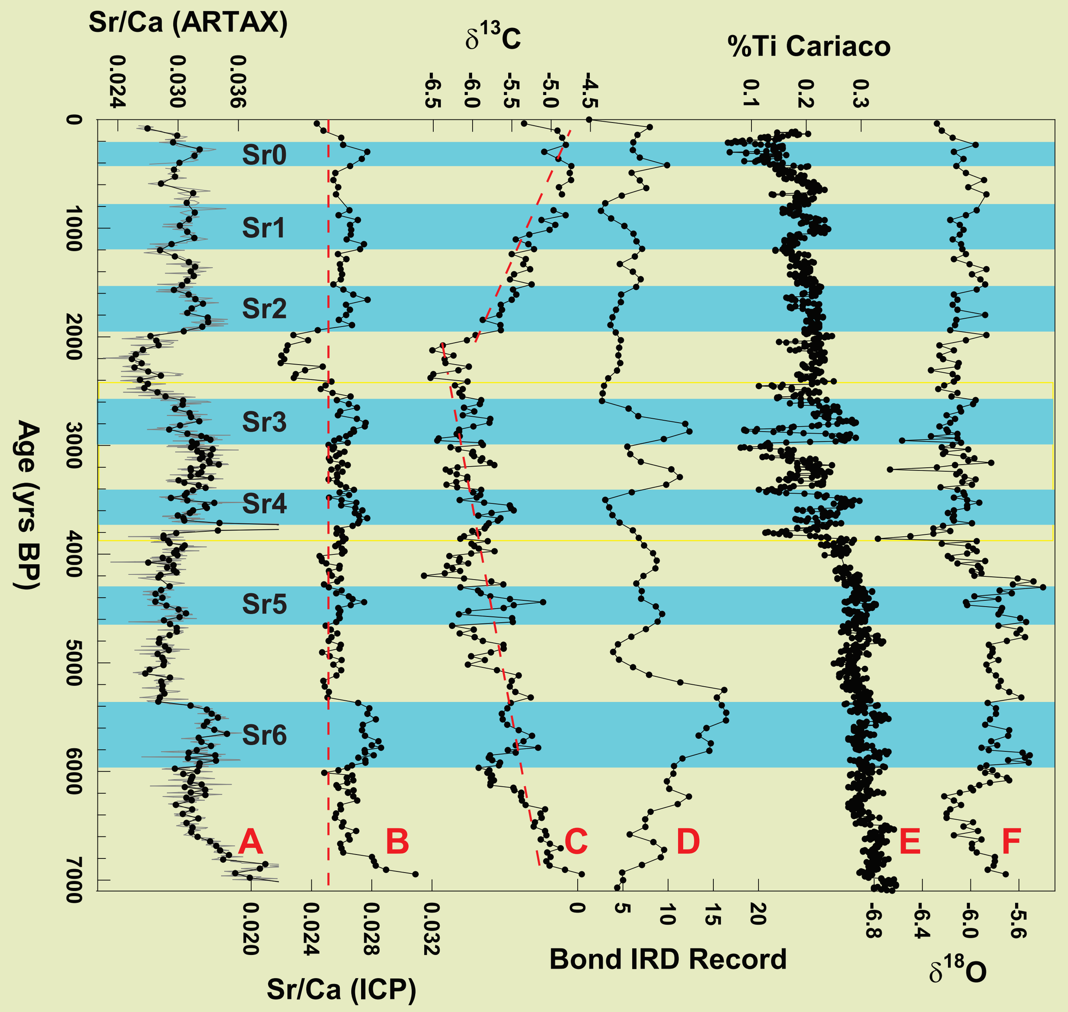


FIGURE 5: Comparison of ARTAX μ-XRF analysis (A) with traditional ICP-OES analysis of Sr/Ca (B), and $\delta^{13}C$ of calcite (C) for BCC-002, a Holocene stalagmite from Buckeye Creek Cave, West Virginia. Note similarities between ICP- and ARTAX-generated record. Blue bars denote peaks in Sr/Ca that have been previously attributed to Bond ice-rafted detritus episodes (D) in the North Atlantic (Bond et al., 2001; Springer et al., 2008). Also shown are the Cariaco Basin %Ti record (E) (Haug et al., 2001) and the record of $\delta^{18}O$ of calcite (F) for BCC-002 (Hardt et al., 2010). BCC-002 age chronology has been updated (Hardt et al., 2010).

APPLICATIONS OF μ-XRF IN SPELEOTHEM RESEARCH: Appalachian Paleoclimates

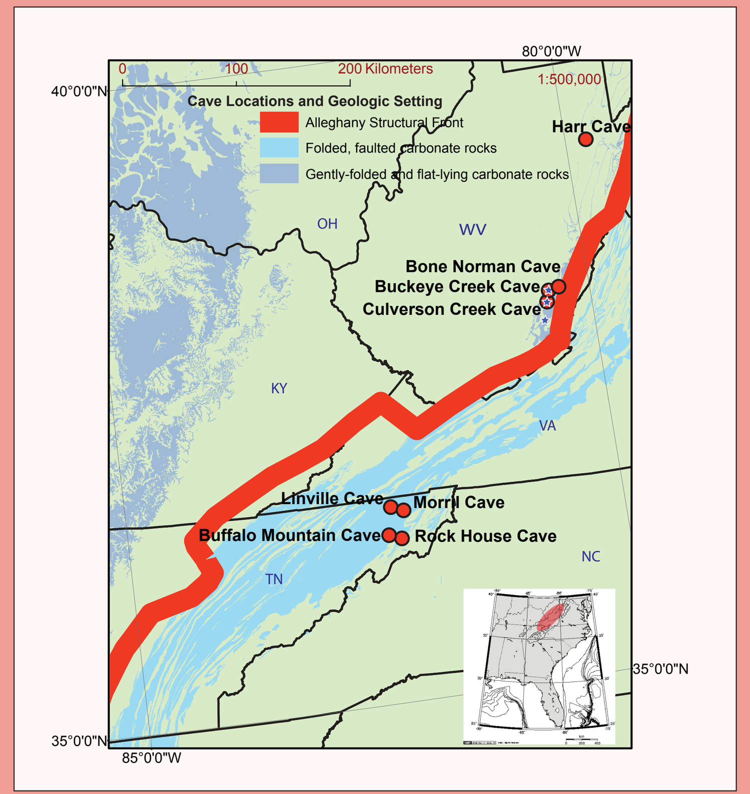


FIGURE 6 (above): Stalagmite CCC-003 (pictured on the right) was collected from a humid cave passage, more than a kilometer from the closest known entrance in Culverson Creek Cave, southeastern West Virginia. It was sawed, polished, and sampled contiguously at a 0.5-mm increment along its growth transect for stable carbon and oxygen isotope composition. The sample was subsequently analyzed at a 100-μm increment for Sr/Ca using the ARTAX system.

FIGURE 7 (below): The polished face of CCC-003 showing the growth transect and the locations of samples taken for ^{230}Th age-dating. The ARTAX transect was undertaken using the "isotope transect" half of CCC-003.

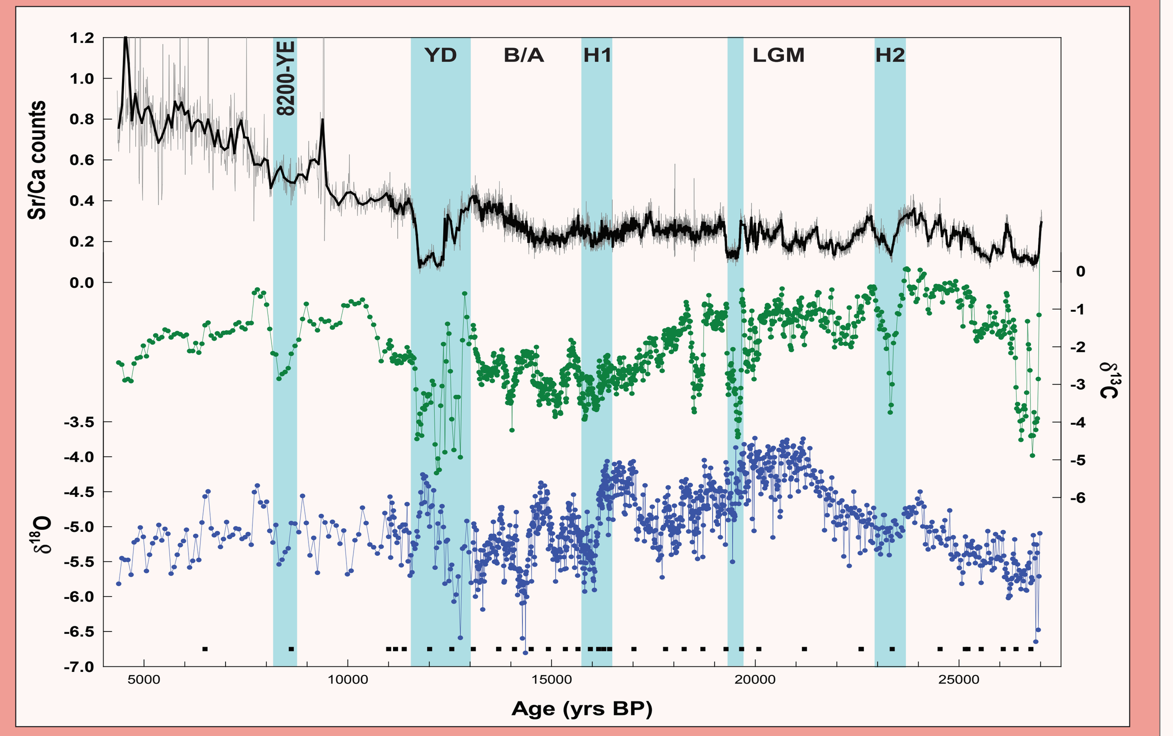


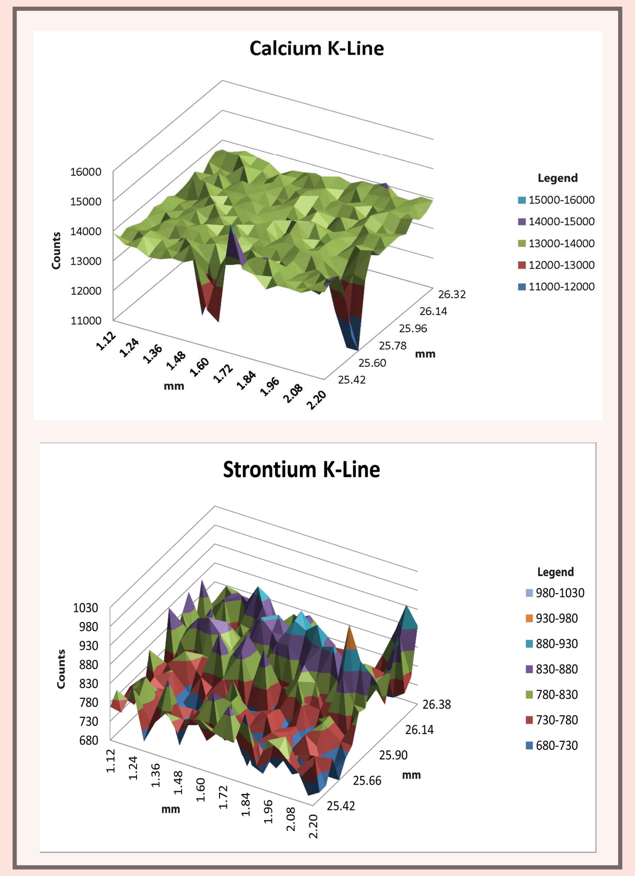
FIGURE 8: The stable isotopic ($\delta^{18}O$, $\delta^{13}C$) and Sr/Ca record from stalagmite CCC-003, Culverson Cave, WV. The black curve in Sr/Ca is a 11-point average of the raw (gray) results.
The stalagmite has been age-dated using the ^{230}Th method at the University of Minnesota. The 37 ^{230}Th ages are shown as black squares at the bottom of the graph. Ages were generated using the NEPTUNE MC-ICP-MS.
H1, H2, and H3 are Heinrich events, and LGM, B/A, and YD are the Last Glacial Maximum, Bolling/Allerod, and Younger Dryas, respectively. The 8200-Year Event is also indicated.
It can be observed that large-scale changes in Sr/Ca occured contemporaneous with H3, H2, the YD, with smaller changes occuring at H1 and the 8200-YE. The mid-Holocene drying trend is most apparent in Sr/Ca.

AREA SCANS

A multi-directional area scan can be generated using the ARTAX system. Each valley or peak in the 3-dimensional plot to the right corresponds to an individual scan spot. This allows for a high resolution analysis of trace elements---not only along the growth transect, but also laterally, which may be useful for understanding lateral variations in stalagmite chemistry and growth banding.

FIGURE 9 (right): Area scans of stalagmite CCC-003 from Culverson Creek Cave, West Virginia, showing the Calcium Kα-line (above) and Strontium Kα-line (below) of a ~1-cm² area.

Settings: Al-Cu filter, 40 KV, 500 μA, 5 seconds count time, 70-μm beam size.



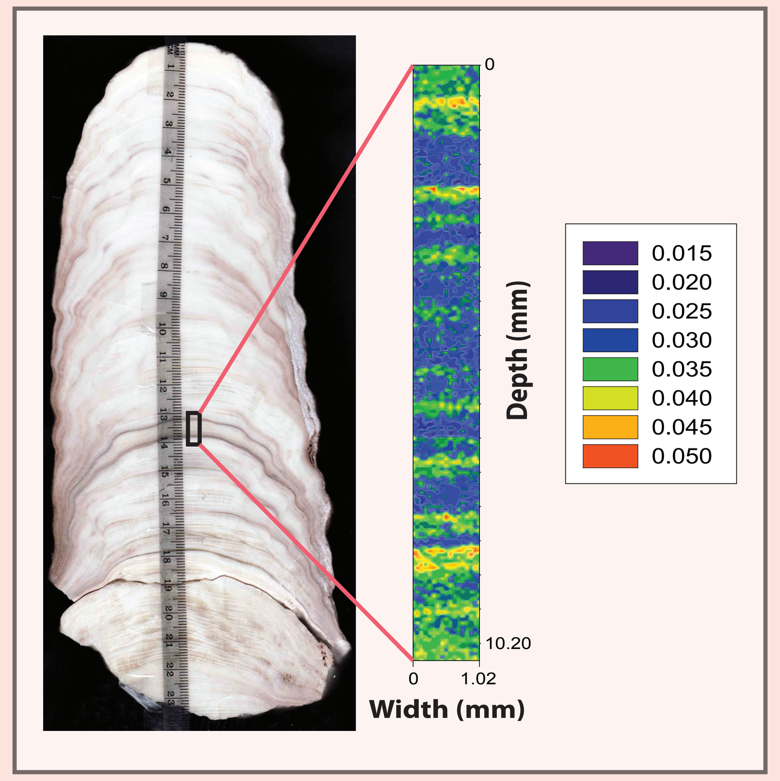


FIGURE 10 (left): Area scan of stalagmite SAN-8 from San Eduardo Cave, Estado Yucatán, Mexico, showing the Sr/Ca count ratio in a ~1 mm x 10 mm area.

Note the well-defined banding in the scanned stalagmite to the left, and the corresponding variations in the Sr/Ca banding observed on the right. The Sr/Ca ratios in stalagmites from shallow caves in the Yucatán are generally very low, but variations in the ratios are detectable and interpretable using the ARTAX system.

Settings: Al-Cu filter, 50 KeV, 500 μA, 60 seconds count time, 70-μm beam size.

FUTURE WORK

Further develop the strategy for analysis time, based on Sr content and the full range of the Sr/Ca ratio in samples.
Develop the calibration and analysis of Mg in stalagmites---this will only be possible in high-Mg samples.
Develop applications on additional rock types.

ACKNOWLEDGEMENTS

We acknowledge the generous instrument support and technical interaction provided by Brüker AXS, and especially, the kind, respectful interaction with Dr. Bruce Kaiser. We also appreciate discussions with Harry B. Rowe regarding statistical analysis of the Sr/Ca results.

This work is an offshoot of NSF-P2C2 grant (#0903071), entitled *"Global Change and the Terrestrial Paleoclimate Record from Eastern North America: 600,000 years BP to Present"*. Furthermore, this work would not be possible without the award of NSF-EAR-IF#0949384 to Rowe, entitled "Acquisition of a Bruker AXS Handheld X-ray Fluorescence Unit for Chemostratigraphic Studies", which allowed initial work and interaction with Brüker AXS.

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