1 **Development and optimization of microbeam x-ray fluorescence analysis of Sr in**
2 **speleothems**

3 **Authors**

4 Jessica Buckles^{1*}

5 Harold D. Rowe²

6

¹Corresponding author at: Department of Geological Sciences, University of Texas at San Antonio, San Antonio, TX, USA, 78249.

Email address: jessica.buckles@utsa.edu

² Bureau of Economic Geology, University of Texas at Austin, Austin, TX, USA, 78712.

6

6

7 **ABSTRACT**

8 Trace-metal abundances and ratios (Sr/Ca, Mg/Ca, Ba/Ca) in speleothems can
9 be indicators of the hydrogeochemical processes active in overlying epikarst and serve
10 as valuable proxies for precipitation amount and source, water residence time, and
11 vegetation cover. However, conventional methods of trace element acquisition can be
12 expensive, time-consuming, and destructive. A semi-portable μ -XRF system is
13 compared to other methods, as it is non-destructive, rapid, and has the capacity to
14 provide high quality datasets. A suite of test scans was performed in order to define the
15 appropriate methodology for the application of μ -XRF in trace metal analysis of
16 speleothems. Statistical analyses were performed on an experimental dataset in order
17 to assess the precision with which data were obtained and determined that there is no
18 evidence for time-dependent behavior within the data and there is no evidence that the
19 data do not follow a Poisson distribution. The optimal count time varies from sample to
20 sample, as it was determined to be a function of the desired level of analytical
21 uncertainty.

22 Sr results for a speleothem obtained through LA-ICP-OES show a high degree of
23 comparability to results obtained through μ -XRF and demonstrate the suitability of this
24 non-destructive method. Sr counts can also be converted to concentration [ppm] via X-
25 ray-tube-dependent calibration curves.

26 **Keywords:** speleothem; strontium; XRF; paleoclimate

INTRODUCTION

Speleothem trace metal abundances and ratios have been used to provide invaluable insights into past climates and paleohydrological regimes and aid in the interpretation of stable isotopic results (Fairchild et al. 2006; Springer et al. 2008). The ability to accurately date such records using U-series chronologies has heightened interest in such records because they offer better time-control and, commonly, higher resolution than many other continental paleoclimate records, such as those from fluvial and lacustrine deposits, and from paleosols.

Trace-metal (Mg, Ba, and Sr) concentrations and variations are reflections of hydrogeochemical processes in the epikarst, in addition to possible partitioning at the depositional interface. The concentrations indirectly record surface climate as they are influenced by the amount of precipitation and moisture present in the soil and epikarst. During periods of low rainfall, trace-element concentrations 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 the changing paleohydrological and geochemical conditions over time (Fairchild et al. 2006; Fairchild and Treble 2009).

Numerous analytical techniques have been employed in the analysis of trace metal concentrations in speleothems: laser-ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) and optical-emission spectroscopy (LA-ICP-OES) (Roberts et al. 1998; Treble et al. 2003); secondary ionization mass spectrometry (SIMS) (Huang et al. 2001; Treble et al. 2007); and synchrotron X-ray microprobe (Frisia et al. 2005; Borsato et al. 2007). These conventional methods of trace-metal analysis of

speleothems have been shown to produce high-resolution, high-quality datasets. However, these methods can be expensive, time-consuming in both sample preparation and machine time, and generally require the destruction of irreplaceable speleothem samples.

X-ray fluorescence spectrometry, which measures the elemental abundances as secondary X-rays from sample material that has been bombarded with high-energy primary X-rays, has been used in a variety of disciplines (West et al. 2014). There are many different instruments and methods utilized in XRF spectrometry, with specific geologic applications. We present Sr results obtained through the rapid and non-destructive method of μ -X-ray fluorescence spectrometry (μ -XRF) using the semi-portable Bruker ARTAX system and compare them with data obtained using conventional methods. Due to the energy ranges of Mg and Ba, as well as interference peaks, only Sr could be precisely measured using this method. However, our results demonstrate that the same high-quality Sr values can be obtained using μ -XRF as with the conventional analytical methods and may serve as a preliminary method of optimizing additional speleothem geochemical analyses. To our knowledge, there is no reported hard detection limit for Sr using this instrument, as the number of characteristic X-rays that reach the detector is influenced by several factors including the type of X-ray tube and filtering of dominant Ca as well as the count-time parameter.

METHODS

A semi-portable microbeam x-ray fluorescence unit (Bruker ARTAX) was utilized to develop down-axis geochemical cross-sections of Ca and Sr in several stalagmite

73 samples from eastern North America and the Yucatán Peninsula of Mexico.

74 The ARTAX system is comprised of a motor-driven, tripod-supported x-y-z axis
75 with a spot size of 70-650 μm , depending on the interchangeable element tube as well
76 as a variety of filters. Rh microfocus (70 μm) and W (650 μm) X-ray tubes were utilized
77 in this study. The sample is subjected to an X-ray beam that excites, and subsequently
78 emits, secondary X-rays along a spectrum of known wavelengths that allow for the
79 identification and concentration of atoms present in the sample. Therefore the terms
80 “count” and “count time” refer to the number of atoms of a particular element detected
81 and the amount of time an individual measurement was exposed to the incident beam.
82 Speleothem carbonate samples require the use of an Al-Ti-Cu filter, which serves to
83 block much of the Ca wavelength emissions and thereby allows the identification and
84 quantification of secondary (trace) elements, such as Sr.

85 The spatial sensitivity of the system allows for a minimum step increment of 5
86 microns, ultimately allowing for resolution down to spot-size overlap. Because the beam
87 is non-contact and non-destructive, scans can be performed at a variety of count-times
88 and resolutions, thereby conserving speleothem materials for additional or future
89 analyses. The maximum long-axis range of an individual scan is 4 cm, requiring that
90 long speleothem transects be pieced together. Once a scan is programmed and
91 initiated, ARTAX is fully-automated and requires no further manipulation. Additionally,
92 the mount is equipped with a camera that records pictures of measurement locations,
93 which aids in piecing together the analyzed transects.

94 Prior to $\mu\text{-XRF}$ analysis, samples were cut in half along the stalagmite growth
95 axis using a continuous-rimmed diamond blade affixed to a wet-saw and polished to a

smooth, flat surface with a hand-held, water-spray polisher. The importance of acquiring a very smooth polish on the cut surface will be discussed in the Results section.

Calibration curves were created in order to convert Sr counts obtained through μ -XRF to concentrations [ppm] ([mg/kg]). Weighed mixtures of 99.9999% pure CaCO_3 and SrCO_3 powders from Alfa Aesar were pressed into small cylindrical molds and scanned over time settings of 30, 60, 90, and 120 seconds (See Supplemental Material for calibration data and expanded methodology).

The stalagmite test samples analyzed as well as their scanning parameters are shown in Table 1. A wide variety of settings was utilized in order to understand the optimal settings to rapidly acquire the most useful data for stalagmites exhibiting different growth properties.

Test scans

Analyses of speleothems were undertaken at tube settings in the range of 40-50kV and 500-600 A, with a variable count time from 5 to 120 seconds per measurement. The increment of analysis (step) varied from 0.1 to 1 mm, depending upon the desired temporal and spatial resolution. Growth-axis transects up to 4 cm in length were assembled piecewise in order to develop continuous records. A typical spectrum for an individual measurement is shown in Fig. 1. The Sr $K\alpha$ (for Sr counts only) and Ca $K\alpha$ (for Sr/Ca value) peaks are the pertinent values reported. Rh elastic and inelastic peaks are present in this spectrum due to the use of a Rh X-ray tube. Many of the results obtained through μ -XRF in this study are reported as Sr/Ca to allow

easier inter-method comparison.

Counting Statistics and Optimization of Analysis

A series of test scans was performed in order to assess the applicability of μ -XRF to speleothem trace-metal analysis. Of principal concern to the authors was to determine the ability of μ -XRF to produce accurate and reproducible results.

In order to test for instrument consistency, a suite of statistical analyses was utilized (Supplementary Material). A 'spot test' was performed for 30 individual measurements of the same point location in order to obtain the means and standard deviations of Ca and Sr counts. For Ca, a mean of 2383 and standard deviation of 59.1 was computed and for Sr, a mean of 7742 and standard deviation of 99.7. In order to test the hypothesis that the sample data are drawn from a Poisson distribution, a Kolmogorov-Smirnov test was applied, which resulted in values of 0.8365 and 0.6169, respectively. These values indicate that there is no reason to conclude that the data do not follow a Poisson distribution.

In order to test larger sample sizes, R statistical software was utilized to construct a set of 1000 samples (one for both Ca and Sr), each a set of 30 values, which was drawn from a Poisson distribution about the computed means of 2383 and 7742, respectively (Supplemental Material). Results for Ca will be discussed henceforth, though the same statistical tests were also performed for Sr. For Ca, 95% of the standard deviations fell between 36.8 and 61.2, bracketing the calculated standard deviation of 59.1. This further indicates that we cannot reject the hypothesis that the

sample is drawn from a Poisson distribution. In order to test for time-dependency, a lag test for autocorrelation was performed. With a correlation coefficient of -0.353, there is no evidence for time-dependent behavior within the data. The Sr/Ca ratio utilized in paleoclimate reconstructions using speleothems is derived from two random variables, and therefore no new variation should be introduced beyond those inherent in the Ca and Sr counts data.

Results and Discussion

The reproducibility of a sample transect was tested using the same settings and transect line for three individual scans, at 60s count time (Fig. 2). Whereas there is some noticeable variation between the three curves, the overall trend of the data is apparent in the three scans. The importance of count time of measurements in obtaining similar results was tested through the scanning of a 10-mm transect with three different count times: 10s, 60s, and 120s at a step increment of 0.2mm (Fig. 3). The lower count times resulted in greater variation between adjacent values. These data, as plotted in Fig. 4, show less variability in measurements with increasing count times. The regression line between the two higher count times is plotted to demonstrate the increasing linearity with increased count times. Finally, Sr/Ca results of a μ -XRF analysis of a speleothem is compared with LA-ICP-OES results (Fig. 5). The time-series displayed in Fig. 5 demonstrate the comparability of both methods. However, at approximately 3700 years BP, an abrupt spike in the Sr/Ca measured by ARTAX is not observed in the ICP results. This is likely due to the presence of a visible crack in the calcite at this depth in the speleothem. It was determined that any imperfections in the

polish of the sample, cracks, or voids potentially impact the analysis of calcium specifically, presumably because the characteristic X-rays emitted from the lighter elements are generated from the shallowest depths of the sample. Thus, surficial scratches have a definite and uncorrectable impact on the analysis. Because of the different depths at which the Ca and Sr atoms are excited, and because of the potential for microscopic cracks or voids that may influence one element over the other, it is therefore beneficial when utilizing this method to report the results as “Sr counts” instead of Sr/Ca ratio values.

Calibration curves, such as those presented in Fig. 6, allow for the conversion of measured Sr counts to concentration [ppm] values. Counts-to-concentration curves at typical count times of 30, 60, 90, and 120 seconds are shown. Because of differing beam sizes of different-element X-ray tubes and slight variations between same-element tubes, calibrations are specific for individual X-ray tubes.

Also obtained from the experimental dataset is a determination of the optimal count time, as a function of the quantification of the uncertainty of a measurement. The optimal count time can be thought of as a function of the desired measurement uncertainty level as we have shown that the accuracy increases with count time. Statistical analysis of the experimental dataset yields a quantification of the measurement uncertainty (Fig.7), where three sigma limits of a measurement are given by $\lambda \pm 3 \cdot \sqrt{\lambda}$ where λ is the measured value in counts. Given as a fraction of the measurement, this is calculated as

$$\pm \frac{3}{\sqrt{\text{counts}}}.$$

For example, if a maximum uncertainty of 0.1 is desired, the counts for the scan must be ≥ 900 . Therefore, given the wide range of Sr concentrations in speleothems, the optimal count time would be a result of the desired uncertainty value. In the case of 0.1 uncertainty, the count time would be how long it takes to obtain at least 900 counts. For high-Sr samples, this would likely take only a few tens of seconds per measurement.

Conclusions

Variations in trace-metal abundances in speleothems have been shown to be valuable paleoclimate proxies. Trace element concentrations have been quantified through a variety of methods, many of which are costly and at the same time consume sample material.

Statistical analysis of a 'spot test' revealed that there is no evidence to reject a Poisson distribution for measured values as well as no evidence for time-dependence within the data. Some variation between identical transect scans was observed, although overall patterns were replicated. Count time appears to be an important factor, because higher counts times per measurement have less variability between adjacent values (less noise). The optimal count time will vary greatly from sample to sample, as it was determined to be a function of the desired level of analytical uncertainty.

The inter-method comparison of Sr in speleothems demonstrates a high degree of comparability. However, variations between Sr curves highlights the importance of matrix effects in μ -XRF of speleothem material. Surficial imperfections and/or

subsurface voids may complicate the results obtained by μ -XRF by the incorporation of erroneous values. Therefore, the investigator should show due diligence in obtaining a smooth, flat, highly-polished sample surface prior to analysis and should note the presence of any surficial imperfections that should be avoided.

Both Sr and Ca count values are obtained during μ -XRF analysis, so either Sr counts or Sr/Ca values can be reported from the same dataset. However, the utilization of Sr counts is the most appropriate for those values obtained through μ -XRF, because the sample material is excited at different depths for the two elements.

The use of μ -XRF for Sr analysis in speleothems has many advantages to other methods. The μ -XRF results obtained prior to costly determination of U-Th age dates or stable isotope analysis could aid in the identification of samples of focus. We propose that this type of analysis would ultimately allow an investigator to rapidly identify and prioritize the best speleothem samples in order to optimize both time and resources in paleoclimate reconstructions using geochemical methods.

References

- Borsato, A., Frisia, S., Fairchild, I. J., Somogyi, A., and Susini, J. (2007). "Trace element distribution in annual stalagmite laminae mapped by micrometer-resolution X-ray fluorescence: implications for incorporation of environmentally significant species." *Geochim.Cosmochim.Acta*, 71(6), 1494-1512.
- Fairchild, I. J., Smith, C. L., Baker, A., Fuller, L., Spötl, C., Matthey, D., and McDermott,

229 F. (2006). "Modification and preservation of environmental signals in speleothems."
 230 *Earth-Sci.Rev.*, 75(1), 105-153.
 231

232 Fairchild, I. J., and Treble, P. C. (2009). "Trace elements in speleothems as recorders of
 233 environmental change." *Quaternary Science Reviews*, 28(5), 449-468.
 234

235 Frisia, S., Borsato, A., SPÖTL, C., VILLA, I. M., and Cucchi, F. (2005). "Climate
 236 variability in the SE Alps of Italy over the past 17 000 years reconstructed from a
 237 stalagmite record." *Boreas*, 34(4), 445-455.
 238

239 Huang, Y., Fairchild, I. J., Borsato, A., Frisia, S., Cassidy, N. J., McDermott, F., and
 240 Hawkesworth, C. J. (2001). "Seasonal variations in Sr, Mg and P in modern
 241 speleothems (Grotta di Ernesto, Italy)." *Chem.Geol.*, 175(3), 429-448.
 242

243 Roberts, M. S., Smart, P. L., and Baker, A. (1998). "Annual trace element variations in a
 244 Holocene speleothem." *Earth Planet.Sci.Lett.*, 154(1), 237-246.
 245

246 Springer, G. S., Rowe, H. D., Hardt, B., Edwards, R. L., and Cheng, H. (2008). "Solar
 247 forcing of Holocene droughts in a stalagmite record from West Virginia in East-Central
 248 North America." *Geophys.Res.Lett.*, 35(17), L17703.
 249

250 Treble, P., Shelley, J., and Chappell, J. (2003). "Comparison of high resolution sub-
 251 annual records of trace elements in a modern (1911–1992) speleothem with

instrumental climate data from southwest Australia." *Earth Planet. Sci. Lett.*, 216(1), 141-153.

Treble, P., Schmitt, A., Edwards, R., McKeegan, K., Harrison, T., Grove, M., Cheng, H., and Wang, Y. (2007). "High resolution Secondary Ionisation Mass Spectrometry (SIMS) $\delta^{18}\text{O}$ analyses of Hulu Cave speleothem at the time of Heinrich Event 1." *Chem. Geol.*, 238(3), 197-212.

West, M., Ellis, A. T., Potts, P. J., Strelt, C., Vanhoof, C., and Wobrauschek, P. (2014). "2014 Atomic Spectrometry Update—a review of advances in X-ray fluorescence spectrometry." *J. Anal. At. Spectrom.*, 29(9), 1516-1563.

Acknowledgements

The authors would like to thank Dr. Bruce Kaiser and Bruker AXS, Inc, for their assistance in instrument access, maintenance and application, Harry B. Rowe, Jr. for his help with statistical analysis, and Gregory S. Springer and Yongli Gao for the acquisition of speleothem samples utilized in this study and Chris Ray for his assistance. We would also like to thank the University of Texas at Arlington for supporting the doctoral dissertation research and the University of Texas at San Antonio for supporting the postdoctoral research of Jessica Buckles. The research was supported by NSF grant EAR 0903071 to HDR.

Figure 1

Figure 1. Sample spectrum for single spot scan using ARTAX μ -XRF with Al-Ti-Cu filter. Ca and Sr $K\alpha$ and $K\beta$ peaks and Rh elastic and inelastic peaks (from X-ray tube) have been labeled.

Figure 2

Figure 2. The reproducibility of Sr/Ca results for a 40-mm transect of sample CCC-007.

Figure 3

Figure 3. Depth comparison of Sr/Ca values and count times of 10, 60, and 120 seconds for a 10 mm transect of sample CCC-007. Note the importance of longer count times to more closely approximate the true value.

Figure 4

Figure 4. Measured Sr/Ca values for count times of 10 and 60 seconds, compared to 120 seconds.

Figure 5

Figure 5. ARTAX μ -XRF Sr/Ca results compared to ICP-OES results previously obtained for the same section of stalagmite BCC-002.

Figure 6

Figure 6. Calibration curves for W tube and Al-Ti-Cu filter at settings of 30s, 60s, 90s, and 120s. Calibration methods described in Supplementary Materials.

Figure 7

Figure 7. Measurement uncertainty versus count time for Sr analysis in speleothems using μ -XRF.

Table 1 12-21-15

Sample Name	Location	Coordinates	Transects r	kEv	μA	Count time (s)
BCC-002 ²	WV, USA	37°58'33.45"N/80°23'58.87"W	5	50	500	10
BCC-020	WV, USA	37°58'33.45"N/80°23'58.87"W	area	50	500	10
BCC-025	WV, USA	37°58'33.45"N/80°23'58.87"W	13	50	500	10
CCC-001	WV, USA	37°56'08.40"N/80°25'23.88"W	13	40	500	30
CCC-003	WV, USA	37°56'08.40"N/80°25'23.88"W	area	40	500	5
CCC-003	WV, USA	37°56'08.40"N/80°25'23.88"W	16	50	600	10
CCC-003	WV, USA	37°56'08.40"N/80°25'23.88"W	2	50	600	120
CCC-007 ¹	WV, USA	37°56'08.40"N/80°25'23.88"W	3	50	600	10
CCC-007 ¹	WV, USA	37°56'08.40"N/80°25'23.88"W	14	50	600	60
CCC-007 ¹	WV, USA	37°56'08.40"N/80°25'23.88"W	2	50	600	120
SAN-5	YUC, MEX	20°44'29.00"N/89°17'28.00"W	area	40	500	15
TN-MOR02-1	TN, USA	36°27'27.79"N/82°13'37.96"W	3	50	600	120

Table 1. Sample and instrument setting information for speleothems scanned using μ -XRF in this study. ¹Results from CCC-007 μ -XRF scans shown in Figures 2-4. ²Results from BCC-002 μ -XRF scans shown in Figure 5.