



Development and optimization of microbeam X-ray fluorescence analysis of Sr in speleothems



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ABSTRACT

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

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

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1. 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

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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.

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

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

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

Prior to $\mu\text{-XRF}$ analysis, samples were cut in half along the stalagmite growth 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 $\mu\text{-XRF}$ 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 s (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.

2.1. Test scans

Analyses of speleothems were undertaken at tube settings in the range of 40–50 kV and 500–600 μA , with a variable count time from 5 to 120 s 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 $\text{K}\alpha$ (for Sr counts only) and Ca $\text{K}\alpha$ (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 $\mu\text{-XRF}$ in this study are reported as Sr/Ca to allow easier inter-method comparison.

2.2. Counting statistics and optimization of analysis

A series of test scans was performed in order to assess the applicability of $\mu\text{-XRF}$ to speleothem trace-metal analysis. Of principal concern to the authors was to determine the ability of $\mu\text{-XRF}$ 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

Table 1
Sample and instrument setting information for speleothems scanned using $\mu\text{-XRF}$ in this study.

Sample name	Location	Coordinates	Transects no.	kEv	μA	Count time (s)	Spot distance (mm)
BCC-002 ^b	WV, USA	37°58'33.45"N/80°23'58.87"W	5	50	500	10	0.2
BCC-020	WV, USA	37°58'33.45"N/80°23'58.87"W	Area	50	500	10	0.5
BCC-025	WV, USA	37°58'33.45"N/80°23'58.87"W	13	50	500	10	0.06
CCC-001	WV, USA	37°56'08.40"N/80°25'23.88"W	13	40	500	30	0.5
CCC-003	WV, USA	37°56'08.40"N/80°25'23.88"W	Area	40	500	5	0.06
CCC-003	WV, USA	37°56'08.40"N/80°25'23.88"W	16	50	600	10	0.06
CCC-003	WV, USA	37°56'08.40"N/80°25'23.88"W	2	50	600	120	0.25
CCC-007 ^a	WV, USA	37°56'08.40"N/80°25'23.88"W	3	50	600	10	0.1
CCC-007 ^a	WV, USA	37°56'08.40"N/80°25'23.88"W	14	50	600	60	0.2
CCC-007 ^a	WV, USA	37°56'08.40"N/80°25'23.88"W	2	50	600	120	0.2
SAN-5	YUC, MEX	20°44'29.00"N/89°17'28.00"W	Area	40	500	15	0.03
TN-MOR02-1	TN, USA	36°27'27.79"N/82°13'37.96"W	3	50	600	120	0.33

^a Results from CCC-007 $\mu\text{-XRF}$ scans shown in Figs. 2–4.

^b Results from BCC-002 $\mu\text{-XRF}$ scans shown in Fig. 5.

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