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Mineralogical and Paleoclimate Studies in Caves from the Trascău Mountains (Romania)

Doctoral Thesis
Summary

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Summary of the Main Sections of the Thesis

Part of the scope of the research that lead to this thesis was to establish the mineral paragenesis in a cave that hosts an alluvial deposit intermixed with bat guano and attempt to clarify the specific physical and chemical conditions under which the phosphate minerals precipitate and remain stable in a sedimentary cave deposit. The second endeavor was to implement trace elemental geochemistry of a stalagmite covering ca. 2000 years as a proxy for identifying historic Au-Ag-Cu mining and smelting activities in the "Golden Quadrilateral" of the Apuseni Mountains, as well as paleoclimate reconstruction. The focal sections of the thesis are chapters V.: Stability of Cave Phosphates: Case Study from Liliecilor Cave; VI. Historic gold mining in the Apuseni Mountains recorded in stalagmite geochemistry; and VII. Controls on stalagmite trace elements and their potential as paleoclimate proxies: case study from the Trascău Mountains.

Two neighboring cylindrical stalagmites (PF109 and PF111) of similar diameters and heights, with recent deposition on the apex were collected from Frumoasă Cave from Hăldăhaia Mică for a larger project that also includes paleoclimate work ($\delta^{13}C$ and $\delta^{18}O$ and trace elemental studies). Both speleothems were dated and it was subsequently decided that only PF109 was an appropriate candidate for the proposed twofold study: the reconstruction of paleoclimate variability and anthropic pollution for the past ca. 2000 years. Speleothem PF109 is a 32.7 cm tall, 7.9 cm thick (at the base) "*candle-stick*" shaped stalagmite, its shape suggesting a low drip rate with solutions having fairly constant supersaturation levels (Fairchild *et al.*, 2006). Ceiling height above PF109 is ca. 45 cm. The longitudinal section displays four thick (ca. 0.5 to 2.5-cm) clayey bands that probably coincide with either flood events or periods of undersaturated drip water. The rest of the stalagmite is made of visibly banded, compact, cream to yellowish calcite, with a number of mm-sized pores along the growth axis (mainly developed toward its base). The reason behind collecting a second speleothem is that we wished to replicate our results for a more solid dataset. Stalagmite PF111 is 316 mm tall and visibly banded. The top ca. 30 mm present a similar structure to PF109, in that it also contains discrete levels of mostly detrital material, but in this case they are very thin. The following 35 mm slightly gray laminated calcite, similar to the bottommost 20 mm of the speleothem, and the remainder of PF111 is made of cream-colored, dense calcite. Based on 6 U-Th dates, PF111 covers the time period from 2271 (17 mm DBT) to 10357 (270 mm DBT), thus indicating that it is not suitable for replication purposes.

In Liliecilor Cave four profiles (only one reaching the limestone bedrock) of various depths (30- 196 cm) were excavated (and subsequently filled back in) in the mixed sediment and guano deposit in the main passage. A total of 49 samples (nodules of various colors, pasty masses, earthy aggregates, hardened, weathered crusts and rinds etc.) were collected from: 1. the lower ca. 50 cm of the cave walls in the proximity of the profiles where the limestone bedrock is in direct contact with fresh bat droppings, 2. the reddish sediment within the paleokarst, and especially 3. profiles A – D.

A wide array of traditional and modern analytical techniques was implemented in order to extract the maximum amount of information from all collected samples and to provide a robust dataset, the basis for solid interpretations. The mineral samples collected from Liliecilor Cave were analysed by means of powder X-ray diffraction (pXRD), while pH and moisture were measured in sediment samples collected at 15 cm. Intervals in Profile D. Several gypsum samples from Liliecilor Cave were combusted in a Elemental Analyzer (EA) and stable sulphur isotopes measured by means of Isotope Ratio Mass Spectrometer (IRMS). Stalagmite PF109 was used to microdrill powder samples for U/Th dating by means of Multi Collector Inductivelly Coupled Plasma (MC-ICP-MS). A separate slab was used to produce petrographic thin sections and rectangular billets for Laser Ablation – Inductivelly Coupled Plasma (LA-ICP-MS). 21 trace elements were measured as a potential proxy for anthropic pollution and 6 for paleoclimate work.

Temperature, pH, and moisture ranges under which various mineral species precipitate and remain stable have been assessed in the field and then extensively studied under laboratory conditions (Neuberg and Grauer, 1957; Filipov, 1977; Vieillard *et al.*, 1979; Frost and Palmer, 2011; Frost *et al.*, 2012). These conditions are generally thought to apply to all occurrences (soil, surface sediment, or cave deposits); however, stability fields of various minerals in the cave itself have been less rigorously studied. Cave sediments and associated secondary minerals are useful indicators for the understanding of speleogenesis (Summers Engel *et al.*, 1997; Zupan Hajna *et al.*, 2008; Häuselmann *et al.*, 2010), reconstructing and dating the geomorphic evolution of karst (evolution of local and/or regional base levels, catchment areas; Krekeler *et al.*, 1997; Sasowsky *et al.*, 2003; Polyak *et al.*, 2008), and retrieving paleoclimate information (Zhang, 1998; Knapp, 1999; Häuselmann *et al.*, 2008). Numerous studies report on new phosphate species (new for the cave environment, or to science altogether; *e.g.*, Schadler, 1932; Balenzano *et al.*, 1976; Martini, 1978; Onac *et al.*, 2005), phosphate stratigraphy within cave sediment deposits (*e.g.*, Goldberg and Nathan, 1975; Onac and Vereş, 2003; Onac *et al.*, 2006), and also report geochemical (in addition to X-ray Diffraction -XRD) data on the phosphate species involved. Far fewer, though, tackle the connection between phosphate stratigraphy, associated mineral species, and sediment characteristics (*i.e.*, mineralogy, grain size, sorting, etc. *e.g.*, Karkanas *et al.*, 1999; Karkanas and Goldberg, 2010).

The phosphate succession identified in Liliecilor Cave is very similar to the one described by Murray and Dietrich (1956) from Big Hole Cave (Virginia, USA). At the base of the cave walls (up to a few tens of centimeters above the guano and sediment deposit) the Ca-rich mineral species are dominant. They form white to dark yellow and brown rinds and crusts, wherever bat excrements (source of PO_4^{3-}) are in contact with the limestone bedrock. In the sediment, Ca is provided by calcite/limestone (present down to ca. 70 cm in the sediment) and smectites (present in most sampled horizons). Species containing K and Al (provided by kaolinite, smectites, muscovite, and illite-group) are encountered at deeper levels within the profiles, seldom at the surface.

Some of the identified minerals are clearly not of secondary origin, thus not proper cave minerals (*e.g.* quartz, muscovite 2M1, ulvöspinel, hematite, illite-2M1, kaolinite-1A, and smectite (Ca)). They resulted either from dissolution of the bedrock, or were brought into the cave as constituents of the alluvium. The source of ulvöspinel $TiFe_2^{2-}O_4$ is the ophiolitic sequences that outcrop in the vicinity of the olistolith, rocks that could have been eroded and deposited in surface limestone outcrops – or reached the cave as alluvium during its vadose stage. These minerals are crucial components in the formation of some of the cave minerals – especially the phosphate group – through their ability to release important cations (*e.g.*, Na^+, Ca^{2+}, Mg^{2+}, K^+, Al^{3+}, Fe^{3+}, etc.) upon chemical weathering, thus making them available for uptake in newly formed minerals.

In the sediment, pH is inversely correlated to depth and to moisture content. Moisture content of sediment samples fluctuates between ca. 11 and 33%, whereas pH values range from 5.73 to 7.20. Differences in moisture levels were visible during sampling, as pasty levels/lenses alternated with earthy, crumbly ones. Sediment moisture is controlled by a number of parameters, mainly textural and mineralogical heterogeneity (especially clays), as well as water infiltration and organic content. Sediment sorting, grain size, and structure are also relevant parameters (Reynolds, 1970).

Phosphates (hydroxylapatite, brushite, ardealite, monetite, whitlockite, fluorapatite, and taranakite), one carbonate (calcite) and one sulfate (gypsum) make up the cave mineral assemblage in Liliecilor Cave; silicates (quartz, muscovite, illite and smectite group minerals, and kaolinite) and one oxide (hematite) represent important allochthonous species that contribute cations to the precipitation of cave phosphates. The occurrence of hydroxylapatite throughout the deposit is allowed by the presence of limestone fragments and smectite (providing Ca). Taranakite is restricted to the bottom third of the deposit (> 25 % moisture and $pH < 7.5$) where clay minerals (source of K and Al) abound. The succession of phosphate minerals in sediment is an indication that leaching of P and S-rich solutions from the uppermost, fresh layer of excreta is heterogeneous both on longitudinal and transversal transects through the deposit. It is clear that the heterogeneity of the sediment deposit (*e.g.*, different clay minerals, textures, organic content) causes (at least in part) the variation of pH and moisture. However, more than the sediment characteristics must dictate the observed steady inverse relationship between depth, pH, and moisture. Each autochthonous mineral that forms locally alters the pH and alkali content, thus controlling the subsequent phosphate species that can precipitate from the same solution. Further changes in pH (*e.g.*, from bacterial activity) and moisture (*e.g.*, changes in the infiltration rate) may induce phase changes resulting in minerals that are more stable under the newly (and likely metastable) formed conditions.

Phosphate minerals formed in caves give insight into the intricate physical and chemical processes occurring in large underground voids and can be a proxy for processes that take place in soil when PO_4^{3-} is added; depending on soil/sediment type and its chemical/mineralogical composition, different series of phosphate minerals form (Haseman *et al.*, 1950; Kittrick & Jackson, 1954; Vieillard et al., 1979). The long-term stability of underground environments allows for some of these minerals to be more stable than at surface, although even underground stability requirements are often violated, incurring phase changes. The $\delta^{34}S$ ratios of gypsum from this cave vary between 1.4 and 4.7‰ with a clear distinction between samples collected from the limestone walls. The sediment in Liliecilor Cave offers the possibility of dating Earth processes (*e.g.*, Carbonnel *et al.*, 1999), as well as reconstructing paleoclimate conditions (Bird *et al.*, 2007; Wurster *et al.*, 2008). Quartz from the terra rossa can be employed in dating the earlier phases of karst development in the region described by Bleahu (1972). Judging by its mineral components the sediment is mostly allochthonous, with some autochthonous input (derived from the bedrock and paleokarst infillings).

The focus of Chapter VI is represented by Au, Ag, and Cu mining and smelting activities located in the vicinity (< 30 km), upwind of the cave site, as probable sources for some of the trace elements documented within the speleothem. Historically, the most prominent localities where ores were processed in the area are in the vicinity of: Roșia Montană, Zlatna, and Abrud (Haiduc, 1940). Speleothem calcite can incorporate trace elements that are carried as aerosols by air masses or precipitation and then leached through soil, bedrock, and finally into the cave as colloids/particles or in solution. Similar studies have been successfully carried out in other parts of the world: Hungary (Siklósy *et al.*, 2009; Siklósy *et al.*, 2011), Italy and Austria (Wynn *et al.*, 2010), etc. In this contribution I present trace elemental concentrations (obtained by LA-ICP-MS) in a ca. 2000-year old stalagmite from the Trascău Mountains as a proxy for historical gold, silver, copper mining and smelting in the SE Apuseni Mts.

Mining and smelting activities release aerosols into the atmosphere and thus pollutants can be carried long distances downwind. Wet deposition is a result of scavenging of these aerosols via condensation and precipitation, while dry deposition occurs directly from the air masses (Loosmore and Cederwall, 2004). Lake sediments

(Laird and Campbell, 2000), ice caps (Kehrwald *et al.*, 2010a, b), and speleothems (Frumkin *et al.*, 2004) are exceptional repositories for these types of particulates, often allowing the retrieval of information (recorded by trace elemental concentration, rare earth elements, stable isotopic signatures, pollen, etc.) and reconstruction of paleoclimate, paleoenvironment, and ancient human activity. Signals produced by natural events (*e.g.* volcanic eruptions – Siklósy *et al.*, 2009) or human endeavors (Wynn *et al.*, 2008; Wynn *et al.*, 2010; Siklósy *et al.*, 2011) can be carried into a cave through either dripwater or cave aerosols and archived in the form of speleothems (Jochum *et al.*, 2012). In the "Golden Quadrilateral" technological advances allowed for ever-increasing amounts of material to be processed for ore extraction and at the same time, extraction processes involved larger amounts of toxic substances. The accumulation of heavy metals in soils is dependent mainly on hydrology, topography, lithology, climate, dominant winds, soil type and pedogenic processes, land use, and type of pollutant (Constantinescu, 2008).

Stalagmite PF109 (Frumoasă Cave) is made of cream to yellowish calcite, compact, with rare, mm-size pores developing along the growth axis at the base and near the top. It displays a complex stratigraphy with wide variations in texture, porosity, and color, with 4 tan-colored areas where significant amounts of siliciclastic detritus is incorporated. According to the constructed age model one of these areas represents a hiatus. Based on 4 U/Th dates, PF109 is 2,034 ± 48 years old at a depth below top (DBT) of 26.8 cm (total length 30.4 cm), the resulting estimated maximum growth rate being 132 μm/year (according to Fairchild *et al.*, 2001, typical growth rates for temperate climates ranges between 20-300 μm/year). An age-depth model was build based on these 4 dates following the mathematical approach of Scholz and Hoffmann (2011). According to the model, PF109 grew between 2136 and 332 years before present, with a ca. 300-year hiatus (ca. 1650-1350 AD).

The list of elements (U, Th, V, Sc, Mn, B, Ti, Au, Co, Cu, Ni, Mo, Sn, Pb, Ag, Te, Rh, Pt, Au, Cd, and Zn) to be measured by LA-ICP-MS was chosen based on the detection limits of the spectrometer, known elemental mass-interferences, and composition of aerosols (both dry- and wet-deposition) that one expected as a by-product of the mining and smelting of the Au-Ag-Cu ores.

Variations in the intensity of mining activities in the "Golden Quadrilateral" as presented in historic and archeological accounts generally agree with the observed oscillations in speleothem calcite geochemistry, potentially also indicating changes in mining and smelting processes and technological advances. Primary mining carried out by the Dacians was fairly primitive, and although impressive quantities of Au and Ag were extracted, wood burning was probably the primary source for aerosol transport. Romans benefitted from a larger workforce and improved smelting techniques, by some accounts already implementing Hg amalgamation (Haiduc, 1940). During the Migrations Period extraction was erratic and in Medieval times acclimated German and Saxon populations implemented more modern methods, probably resulting in a significant increase in pollutant output (although the Au and Ag production was modest compared to Roman and Dacian times). Toward the end of the Medieval Period and into the Modern Era ore smelting became more efficient, but at the same time resulted in significantly higher aerosol output (Haiduc, 1940). These changes, although mitigated by climate (through precipitations) – and possibly soil processes and PCP – can also be followed in trace elemental composition of PF109. Trace elemental concentrations in carbonate rocks of various ages show wide variations (function of location, depositional facies, diagenesis, age, etc.). Comparison of the speleothem calcite data to concentrations in soil in the surroundings of Zlatna (Pope *et al*., 2005) and carbonate rocks from various locations (Warren and Delavault, 1961; Barber, 1974; Madhavaraju and González-León, 2012) suggests that with the exception of Ti, the bulk of the trace elements were derived not from bedrock, but from atmospheric deposition controlled by upwind mining activities. Sudden rises in trace elemental concentrations as seen in PF109 may be the direct result of surges in mining and associated activities windward the cave site, or backed by an increase in precipitation, leading to a sudden leaching of particles accumulated in the soil and epikarst during drier periods.

Cave aerosol composition and significance to speleothem geochemistry is strictly site-dependent and dictated by numerous variables (*e.g.*, cave morphology, ventilation, and location). The morphology of the cave, its small single entrance, and the location of PF109 within the cave suggest that drip water is the overwhelming contributor to the trace elemental chemistry of the stalagmite. Trace elemental concentrations in stalagmite

PF109 are far too high to be explained by bedrock dissolution alone. Over the past ca. 2000 years, less than 30 km upwind of the cave site, historical mining for Au, Ag, Cu, Pb, Fe, and Hg took place. Activities such as mining and smelting of ores for the extraction of prized metals and the associated biomass burning undoubtedly produced abundant amounts of aerosols that were carried downwind and accumulated as wet or dry deposition. Leaching of the soil by precipitation remobilized and carried them as solute or particle/colloidal phase through the bedrock and into the cave. Unquestionably, the elements we measured interacted with both organic and inorganic matter in the soil and with the bedrock, but elemental concentrations observed throughout the speleothem are well above normal values for limestone bedrock to suggest that atmospheric input was the primary source.

In general there is a good correlation between the most significant concentration spikes of trace elements measured as proxies for anthropic activity (lithophiles, siderophiles, and chalcophiles) and those measured as proxies for climate variability (Mg, Sr, Ba, and P). This relationship is best explained by local and regional climate dynamics: aerosols generated above the mining/smelting areas accumulate downwind on the surface during drier intervals and are flushed into the caves during the wet periods. The trace elemental geochemical data set interpretation could be enhanced by an improved age model (additional U/Th dated samples), as well as by a comparison to similar data from bedrock, soil, clay accumulated within the cave, the "*soda straw*" stalactite feeding PF109, and ideally monitoring of drip water geochemistry at the site. Stable isotope data (*e.g.*, Pb) would be a valuable tool to fingerprint the provenance of trace elements found in PF109.

A series of major (Ca) and trace elements (Mg, Sr, Ba, P, and Ti) were measured on PF109 by means of LA-ICP-MS as potential paleoclimate proxies. An attempt was made to also determine the concentration of Si as a tool for monitoring terrigenous input (and indirectly precipitation variability) into the stalagmite (Klein and Walter, 1995; Hu *et al*., 2005), but the signal to noise ratio was too high and the calculated error for many of the data points was beyond the acceptable error range; as a result, Si was measured only for the top ca. 85 mm of PF109. Al (also a proxy for terrigenous input) was not determined because of contamination issues, as the sample billets were polished with

Al_2O_3 powder. Silicate impurities are concentrated in 4 discrete, tan segments of the stalagmite, but do not contribute to the overall lamination of PF109. The second such segment from the top down coincides with a growth hiatus indicated by the age-depth model. A band of fine, detrital, predominantly siliciclastic material, ca. 6 mm in thickness, was accumulated over a period of approximately 300 years (ca. 370 – 660 AD) of little to no deposition (ca. 2 μm/year).

All measured elements present rhythmic oscillations with a number of distinct spikes and troughs; Ti, P, and Mg show the largest amplitude oscillations. High-frequency variations – most pronounced in P and Ti–are superimposed on long-term trends. With few exceptions Ca concentration is very coherent and remains between 0.60 – 0.70 wt% ; as a result, when plotting either the pattern of an element (*i.e.*, Mg, Sr, Ba, and P) concentration vs. DBT, or its ratio to Ca vs. DBT, there is little to no distinction. Concentrations vary between 471.92 and 9447.04 ppm (average of 2379.14) for Mg, 15.35 – 1042.81 ppm (average 342.84) for Sr, 2.57 – 78.47 ppm (average 35.13) for Ba, 0.79 – 793.31 ppm (average 130.60) for P, 0.001 – 0.011 wt% (average 0.006) for Ti, and 0.43 – 0.80 wt% (average 0.64) for Ca.

Variations in Mg, Sr, and Ba concentrations show a good positive correlation, while P shows variable correlation patterns with respect to the general trend. Sr/Ca and Mg/Ca show a weak positive correlation, the same is valid for Ba/Ca and Mg/Ca, while Ba/Ca and Sr/Ca have a very good positive correlation; on the other hand there is a very weak positive relationship between P/Ca and Sr/Ca. If the same analysis is carried out on shorter segments of the stalagmite (*i.e.*, distinct highs or lows in concentration) the correlations become more evident, suggesting that the geochemistry of the speleothem calcite may be controlled by discrete processes at different timescales. Similar to the observation of Roberts *et al.* (1998), Sr and Ba are much better correlated with each other than either of them with Mg, pointing to a ionic radius dependent behavior (Sr^{2+} and Ba^{2+} are larger than Ca^{2+}, while Mg^{2+} is smaller). Ti shows good positive correlation with Mg, P, and especially with Ba and Sr, while it is weakly correlated with Ca.

Similarly to St. Michaels Cave (Mattey *et al.*, 2008), stalagmite PF109 from Frumoasă Cave shows P concentrations that are antipathetic with respect to covarying Mg, Sr, and Ba. This is at least in part explained by the fact that P (usually present in speleothem calcite as phosphate minerals) is a strong inhibitor for calcite precipitation (Burton and Walter, 1990), thus an increase in P supply would induce a drop in growth rate and a decrease in Sr uptake into calcite (Huang *et al*., 2001).

The extreme seasonal variations in Sr/Ca ratios displayed by PF109 indicate that Sr partitioning is determined by solution composition (Baker *et al*., 2001), as opposed to precipitation rate –which would have resulted in muted seasonal variations (Huang *et al*., 2001). Furthermore, when plotting Mg/Sr vs. Ba it becomes apparent that there is a bimodal distribution, indicating a mixing between two geochemically distinct sources (Albarède, 1996), *i.e.* the bedrock is predominantly limestone, but dolomite is also present, although minor. Calcite is predicted to display low Mg/Ca and high Ba, while dolomite would correspond to high Mg/Ca and low Ba (Roberts *et al*., 1999). Based on our data we infer that the water feeding the stalagmite interacted with geochemically distinct carbonate rocks in the epikarst above the cave, one of which was dolomitic.

Based on the correlation between measured elements we can infer that the concentrations of Mg, Sr, Ba, and Ti (all sourced primarily from the bedrock) are predominantly controlled by hydrologic conditions. The strong variations observed in Sr/Ca ratios in PF109 support the idea that Sr partitioning is controlled primarily by solution composition –as opposed to growth rate (Fairchild *et al*., 2001). On the other hand, P concentration (showing varying relation to Mg, Sr, and Ba) is generally accepted to be an indicator for biological productivity and its leaching from the soil has been associated with heavy rainfall. Mattey *et al*. (2008) in a high-resolution study of a speleothem with similar trace elemental behavior as PF109 inferred that high Mg/Ca and Sr/Ca (and low P) correspond to low discharge rates and $p\mathrm{CO}_2$ that lead to stronger supersaturation levels, while high P, low Mg and Sr calcite corresponds to higher water flows and/or cave $p\mathrm{CO}_2$ and lower supersaturation. Experimental work supports the proposition that Sr uptake in calcite increases with supersaturation (Wasylenki *et al*., 2005).

Our present age model shows that PF109 stopped growing at the end of the Little Ice Age (LIA; ca. 1688 AD) and also indicates the presence of a growth hiatus ca. 1350 – 1650 AD. Based on lamina thickness, we argue that the growth rate of the stalagmite remained relatively constant from the period predating LIA and throughout its duration.

On the other hand, the 300-year growth hiatus is confirmed by the stratigraphy of PF109, coinciding with a thin level of detrital deposition. There are 2 possible scenarios for the deposition of the 4 tan, clay-rich segments observed in the longitudinal cross-section: 1. They were deposited during wet intervals, when either a. due to heavy discharge the dripwater became undersaturated while also dislodging significant amounts of siliciclastic material from the bedrock, or b. the water table rose significantly flooding the passage and submerging the stalagmite, allowing for detrital material to settle down on the surface of the speleothem; 2. these segments could also have been deposited during dry intervals when the feeding drip showed significant fluctuations in both chemistry and rate, allowing for detrital particles to be incorporated into the stalagmite. For example, Hartland *et al.* (2012) found that during the lag that is frequently observed between rainfall maxima and significant changes in drip water chemistry, particulates and coarse colloids have shorter breakthrough times, being less prone to matrix diffusion than fine colloids.

It has been suggested that during drier periods low $p\mathrm{CO}^2$ air pockets form in fractures within the epikarst, promoting degassing of the percolating solutions that results in PCP (Fairchild *et al.*, 2000; Tooth and Fairchild, 2003; Baldini *et al.*, 2006; Johnson *et al.*, 2006); PCP enriches the solution in Mg, Sr, and Ba, enrichment that is evident in the geochemistry of the resulting speleothem. We believe this process to be valid for PF109 and that elevated Mg, Sr, and Ba concentrations in the calcite are the consequence of reduced recharge (*i.e.*, precipitation).

Geochemically, two discrete trends are observed during the period pertaining to LIA in the concentrations of Mg and Sr, in tune with P variations, but with a more subdued rising trend in Ba: one at the onset of LIA between ca. 1400 to 1450 AD, the second between 1550 and 1630 AD, both drier and colder relative to the time interval between the Medieval Climate Anomaly (MCA; 950 – 1250 AD) and LIA. The segment corresponding to the MCA shows drier and warmer conditions than observed during LIA. The ca. 300 years long hiatus (ca. 1350 – 1360 AD) corresponds to the highest concentrations in Mg, Sr, and Ba (positively correlated here with P) observed in the entire dataset – suggesting the driest interval in the timespan covered by the stalagmite – and is followed by a sharp drop in all elements – corresponding to the interval between ca. 760

– 860 AD (lowest concentrations of Mg, Sr, and Ba in the dataset). The bottom 3 dark, detritus-rich segments correspond to drier than average climate; in these areas Mg, Sr, Ba, and P are correlated. The Roman Climate Optimum (RCO; 200 BC – 100 AD) shows unusually high (compared to the rest of the data) P variability (also the lowest concentrations) and appears to be generally wetter than MCA, LIA, and any of detritus-rich segments.

Given that stalagmite PF109 was sampled from deep within the cave, where temperature is constant year-round, it is unlikely that Mg partitioning was controlled by temperature, but rather by fluctuations in recharge. Sr and Ba, which are partitioned independently of temperature, covary with Mg and as such must be controlled by the same driving force (recharge, residence time, supersaturation of the solution, etc.). As a result, the dataset presented here can be applied to the reconstruction of precipitation variability, but not temperature. P on the other hand, as an indicator of biologic productivity, could be a reliable proxy for temperature. Based on Ba vs. Mg/Sr it is probable that the limestone bedrock above the cave comprises minor dolomite and preferential dissolution of one over the other dictates changes in the chemistry of drip water. Although detrital non-carbonate input is evident in the stratigraphy of PF109, the high Si content measured in the calcite could be derived from anthropic-derived atmospheric input above the cave and as such not affect the concentration variation of the other elements. Based on the results of the present study trace elements in stalagmite PF109 can be a reliable proxy for climate reconstruction spanning the past ca. 2000 years.

Differences in paleoclimate reconstructions can result from either regional climate discrepancies, sensitivity of the chosen proxy, or interpretation of the proxy data. Certain interpretations presented here could be hindered by the large errors associated with the age model. A better understanding of growth rate variation through an improved age model calculation could be achieved by adding more U-Th dates (*e.g.*, immediately below and above the hiatus indicated by the age model and between the top 2 ages). Linking the measured trace elemental variability to a robust age model would considerably strengthen the function of PF109 as a climate archive. Additionally, statistical modeling of the whole dataset would be beneficial to extracting short and long-term trends in climate variability over the past 2000 years for this region, further allowing better comparison to other studied proxies. Comparing trace elemental concentrations with δ13C and δ18O ratios (sampled at the same resolution; awaiting analysis) from the same transect of PF109 will clarify the source of these metals and their behavior in the bedrock-dripwater-calcite system, while also helping to build a better constrained climate reconstruction.

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