FINAL REPORT FOR ESF SHORT VISIT GRANT 5611:

Participation to the "Summer School on Speleothem Science", 28 July - 2 August 2013, Heidelberg, Germany

Valentina Vanghi
University of Burgos
E-mail: valentinavanghi@gmail.com

1. Purpose of the visit

The study of speleothems as paleoclimatological archives is of major interest for me since I have focused my MSc thesis over the last two years on a Holocene stalagmite record from the Basque Country (Spain). This is the reason why I decided to participate to the "Summer School on Speleothem Science" organized in Heidelberg. I had multiple objectives: (i) getting an updated overview of the state of the art in the investigation related to speleothems, (ii) learning more about the new cutting edge experimental techniques applied in speleothem research. (iii) meeting some of the world leading specialists in Speleothem Science, which could open me perspectives of future collaborations.

Speleothem science is a relatively new branch of paleoclimatology that has been increasingly investigated over the last decade, and for this reason the organization of this first summer school was a really good idea. Courses were given by outstanding researchers, and this school was expected to be a unique opportunity to discuss, confront ideas and address some specific issues by getting direct inputs from specialists.

2. Description of the work carried out during the visit

This summer school covered several fields of speleothem science, including an extended module about geochronology and palaeoclimatology. It provided an updated overview of the most recent and innovative experimental techniques applied to speleothem records, which are excellent archives for paleoclimate reconstructions, and are now widely considered as an appropriate support for Quaternary studies involving multidisciplinary approaches.

During the Summer School each course had a duration of about 45 minutes, followed by 15 minutes of discussion in which the lecturers could answer the questions from the participants or other professors. The group of participants was formed by ~50 people from all around the world, including mostly PhD students and Post-Doc researchers. 36 posters were prepared and presented in different poster sessions during the first three days of the Summer School courses. I presented my poster on Monday 29/07.

The participants were hosted in different guest houses. I was at the *Internationales Wissenschaftsforum Heidelberg* (IWH), a very nice place with comfortable rooms. Breakfasts were at IWH and lunches at the refectory of the University of Heidelberg. The food was always very good and we had a wide range of choice.

My work during this Summer School may be summarized as follows:

Sunday 28/07/2013

8:00 - 19:00 Field trip to the "Herbstlabyrinth" cave system

The Herbstlabyrinth is a 7 km long cave-system made of and 3 distinct levels open to public since 2009. It is located about 2h by bus from Heidelberg. Our guide was Simon Mischel (SM), a PhD student from the University of Mainz, who is monitoring and studying the cave. He introduced to us the geological context of the region. Herbstlabyrinth presents spectacular speleothemic formations, including stalagmites, flags,

flowstones and above all soda-straws. Two different stalagmite generations have been identified. The oldest one was inactive and brown colored, while the younger one (Holocene) was active, showed a clear-white coloration and was covering the first generation of stalagmites. SM is also currently studying a stalagmite that presents an extraordinary hiatus of 50.000 years, which really impressed me.

After this visit, we came back to Heidelberg for an ice-break dinner organized by the organizing committee, which gave the participants the opportunity to meet each other and the professors.

Monday 29/07/2013

9:45 – 10:30 "Petrography of speleothems" (Silvia Frisia, University of Newcastle)

Prof. Silvia Frisia's (SF) lecture was about the description of all the various crystalline fabrics that may be encountered in speleothems. She also detailed the variety of environments of crystallization corresponding to each fabric. This lecture was especially interesting for me because I could compare the crystalline fabrics that I found in my speleothem with the ones SF showed us.

11:00 – 11:45 "Geochemistry of trace elements provided by speleothems" (Ian Fairchild, University of Birmingham)

During this lecture, the professor told us about how trace elements are generally transported and incorporated into speleothems. He also explained the different climatic events that control these processes. This lecture was of special interest for me, since I performed XRF-core scanner and ICP-AES geochemistry analysis on my stalagmite for my two Master theses.

14:00 - 14:45 "Monitoring - key parameter, methods, sampling, equipment, developments" (Dave Mattey, University of London)

Monitoring a cave is very important because it provides key information about the rate of calcite precipitation and the capture of chemical proxies. These parameters vary from cave to cave and from place to place within a given cave. They also change with time. The lecturer gave us an interesting overview of all the different techniques and commonly used in cave monitoring.

15:00 – 15:45 "Trace metals in speleothems LA-ICP-MS vs. Synchrotron XRF techniques" (Andrea Borsato, the University of Newcastle)

Dr Andrea Borsato described the potential and limitations of these two different techniques, including specific aspects of sample preparation, analytical procedures, data reduction and detection limits. The lecture was very interesting especially because Synchrotron XRF is not an easily affordable technique and only a few researchers have the possibility to use it.

16:00 – 16:45 Workshop on speleothem petrography with Silvia Frisia

This workshop gave the opportunity to some participants to show and discuss their own thin sections on power point slides with Silvia Frisia. I got the possibility to show the crystalline fabrics of my speleothem to her and she gave me some helpful suggestion about the interpretation of their environmental conditions of formation.

17:00 – 18:00 1st Poster Session

During this poster session, I presented my work titled "*Non-destructive high resolution XRF-core scanner vs. ICP-AES techniques in stalagmite: preliminary results*". This was a great opportunity for me, I got many questions about my work. I also took the occasion to discuss with specialists in speleothem geochemistry. They gave me some specific advice about the evaluation and interpretation of the data that I have collected. A copy of my poster may be found hereafter, **and ESF support has been clearly acknowledged**.

Non-destructive high resolution XRF-CS vs. ICP-AES geochemistry in stalagmites: preliminary results

V. Vanghi[1], E. Iriarte[1], A. Moreno[2], A. Aranburu[3], V. Martínez-Pillado[3]
1: Human Evolution Laboratory, University of Burgos, Spain
2: Instituto Pirenaico de Ecología-CSIC, Spain
3: Petrology and Mineralogy Department, University of the Basque Country, Spain

Introduction

In this work we evaluate the potential of the X-ray fluorescence Core Scanner for the geochemical characterization of speleothems. This is a non-destructive technique that permits to obtain information about how the chemical composition changes along a rock or sediment sample.

The principle of XRF analysis is based on the excitation by incident X-rays radiation of electrons that consequently emit fluorescence energy (Weltje & Tjallingii, 2008).

This technique offers a very high spatial resolution (sub-mm scale) and allows the extraction of nearly-continuous records of element intensities from a sample core. Depending on the X-ray tube used, elements from Al to U can be detected with detection limits in the ppm range for most of them. Therefore, the XRF core scanning could potentially be an interesting tool to get a rapid evaluation of the geochemistry of speleothem samples. However, this technique has also some limitations. One problem is related with the conversion of the element intensities measured to element concentrations. Results obtained by XRF core scanning are indeed usually presented in the form of count rates (expressed as counts per time unit per unit area). For this reason, XRF core-scanner has to be considered as a semi-quantitative technique. Another weak point is that there is some uncertainty in the exact position of the sampling points, since it is complicated to precisely visualize it. (Weltje & Tjallingii, 2008; Löwemark *et al*., 2011; Ramsey *et al*., 1995, Jenkins, 1999; De Vries &Vrebos, 2002).

In order to evaluate the exact potential of the XRF core scanning for speleothem studies, the results are compared with those derived from inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis performed in parallel on a speleothem from Northern Spain (Fig. 1 and 2). Both techniques are potentially capable of determining an extensive suite of trace elements at low detection limits (Ramsey *et al*., 1995). First results are presented in this work.

Materials and methods

X-Ray Fluorescence core-scanner analysis (XRF-CS)

The speleothem was irradiated with an XRF core-scanner Avaatech at University of Barcelona. The step-size was set every 0.4 mm with a slit size of 0.4 mm x10 mm along the length of the sample and close to the central growth axis.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis

We collected a total of 74 powder samples (~0,003 g each) every 0.5 cm along the growth axis of the stalagmite. The elements were analyzed by a simultaneous dual ICP-AES (Thermo ICAP DUO 6300) at University of Oviedo (Stoll et al., 2012; Moreno et al., 2010).

Linear regression

XRF core-scanner and ICP-AES data were first normalized by Z-score standardization. Then, elements ratios results derived from each technique were plotted, and a linear regression was performed.

Principal component analysis (PCA)

We also performed a PCA for each analytical techniques data set. Then we compared the resulting principal components plots in order to find some similar trends.

For these studies we only considered Al, Ca, Fe, Mn, Ni, S, Sr and K, as these elements were measured by both XRF-CS and ICP-AES.

Main results and conclusions

These preliminary results highlight the apparent correspondence between some data sets derived from XRF and ICP-AES analysis, namely: Mn, Sr and Fe. For these three elements, the graphs of the two geochemical techniques display similarities in terms of trend (Fig. 3), especially obvious for the Phase 2. Their increasing tendencies, when getting closer to the tip of the stalagmite, are probably linked to an enhanced detrital content in the Phase 2 and to the fact that XRF-CS detection limits for Mn, Sr and Fe are the lowest within the group of elements analyzed. In addition, our data suggest that the Sr/Ca values could be used as a proxy to identify each phase, since data values below and above the phase transition surface are clearly different. For the remaining elements, we do not observe apparent affinities between the two techniques. XRF-CS data are somewhat scattered, very likely because elements concentrations are mostly close or below the detection limits of the XRF-CS. This will need to be further explored in the future.

We also checked a potential correspondence by comparing the two methods with a linear regression statistic. Results were negative for all the elements, showing a $R^2 << 1$. The only exception is for the Sr/Ca with R^2~0.5, demonstrating a possible stronger correlation than for the other elements, which is agreement with the observations from Fig.3. This affinity between the Sr/Ca ratios of the two techniques is also revealed by performing a principal component analysis (PCA). XRF-CS Factor 2 and ICP-AES Factor 3 graphs display a similar trend. These two factors indeed, are mostly controlled by Sr/Ca that has one of the higher loadings (Fig. 4). In addition, the Sr/Ca curves trends of both ICP-AES and XRF core-scanner reveal a clear similarity (Fig. 3).

To conclude, even if ICP-AES remains so far the most suitable technique for speleothem trace elements studies (since concentration values and sampling can be accurately controlled), XRF-CS may be of some interest for speleothem studies. This technique offer several advantages, by: (i) providing high resolution data, (ii) requiring only minor sample preparation, (iii) allowing rapid measurement and (iv) being non-destructive. Nevertheless, some aspects need to be further explored, since XRF-CS remains a semi-quantitative technique, and its potential for each element has to be precisely evaluated in regards with the specific detection limits of the equipment..

These preliminary and promising results definitely support the need of further investigation in order to see whether XRF-CS could offer the possibility of developing rapid scanning procedures for evaluating the potential of speleothem samples prior to any further analysis.

References

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Fig. 1A: Geographic location of Praileaitz cave (Basque Country, Spain).
Fig. 1B: The stalagmite in situ before the sampling

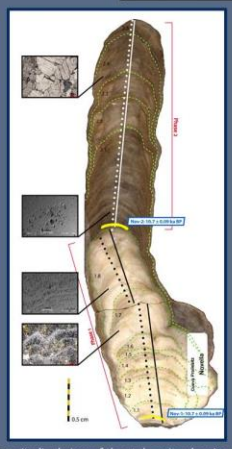


Fig. 2 : Longitudinal view of the stalagmite showing the U-Th ages, stratigraphical units and XRF core scanning (solid lines) and ICP-AES (dots) sampling, as well as petrologic characteristics. Phase 1 and Phase 2 are characterized by dendritic and columnar fabrics respectively.

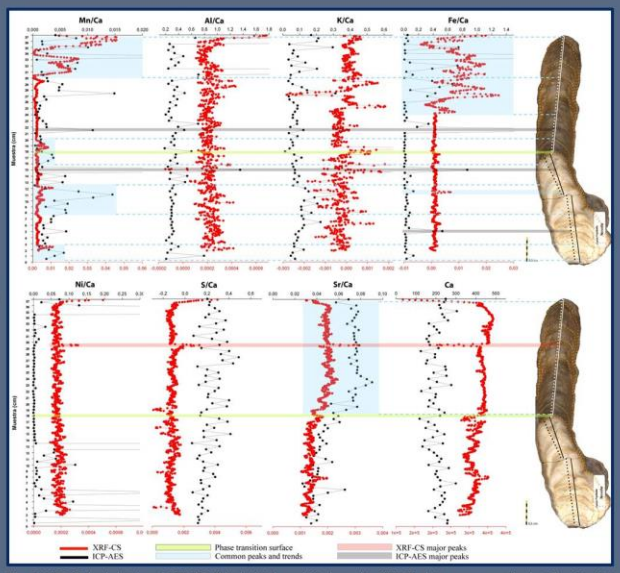
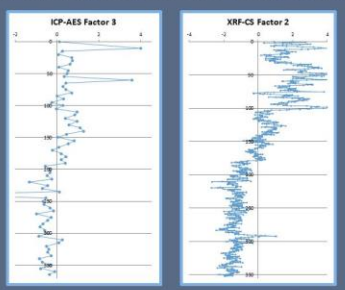


Fig. 3: XRF-CS (red data) and ICP-AES (black data) analytical results. XRF-CS data were smoothed with a 5-point running average. Common peaks and trends for both methods are hilighted by blue bands. Mn/Ca, Fe/Ca and Sr/Ca curves show similar trends, mainly in the Phase 2. XRF-CS and ICP-AES major peaks are indicated by red and black bands, respectively. ICP-AES and XRF-CS data are expressed in mmol/mol and counts per time unit per unit area, respectively. Some vertical shift might be sometimes observed between the peaks derived from each technique, which may be simply explained by the fact that the sampling was not performed at the exact same location.



ICP-AES loadings	Factor 1	Factor 2	Factor 3	Factor 4
Fe	**0,518111**	0,272147	0,0885052	0,22912
K	0,0731612	**0,438069**	-0,0213439	**-0,508745**
Mn	**0,475107**	**0,427794**	-0,152779	0,00467821
Ni	0,0699795	-0,121543	**-0,586216**	**-0,458065**
S	**0,592639**	-0,267839	-0,144566	-0,0549578
Sr	0,336874	-0,301219	**0,54453**	0,0343644
Al	0,00225481	0,00407939	**0,528384**	**-0,668758**
Ca	-0,176097	**0,611362**	0,167689	0,165524

XRF-CS loadings	Factor 1	Factor 2	Factor 3
Fe	0,123207	**0,77785**	-0,0424582
K	-0,0937113	-0,0687017	**0,880118**
Mn	0,192989	**0,460929**	0,366581
Ni	**0,693411**	-0,00937481	-0,181563
S	**0,68262**	0,239942	0,114678
Sr	-0,228095	**0,777252**	-0,0389956
Al	**0,55134**	0,101391	0,397357
Ca	**-0,84298**	0,33161	0,0147929

Fig. 4 PCA results for the XRF-CS and ICP-AES that yielded 3 and 4 factors, respectively. The cumulative variance explained for the principal XRF and ICP-AES factors were of 59.9% and 72.6% respectively. XRF core-scanner Factor 2 and ICP-AES Factor 3 graphs show a similar trend. Both factors are mostly controlled by Sr/Ca.

Acknowledgements

The participation to the Speleothem Summer School of the first author of this work was financed by a short visit grant from the **European Science Foundation** (EARTH-TIME Program). We would also like to thank Dr. Stoll who performed the ICP-AES analysis and Dr. Duval for his helpful comments.

Tuesday 30/07/2013

9:00 – 9:45 "Tracing carbon isotopes from the atmosphere into the cave" (Jens Fohlmeister, University of Heidelberg)

This lecture was an overview of the main processes influencing carbon isotope composition of speleothem $CaCO_3$. He talked about carbon isotope fractionation processes starting in the atmosphere to the cave system and radiogenic carbon isotope (^{14}C) as an alternative indicator for interpreting the isotopic composition of the carbonate.

10:00 – 10:45 "Processes determining the chemical evolution of DIC in drip water inside a cave: degassing, equilibration to the cave atmosphere, precipitation of calcite and isotopic signals" (Wolfgang Dreybrodt, University of Bremen)

Wolfgang Dreybrodt described the various physical processes involving drip water from the moment it enters into the cave until the precipitation of the calcite. He also showed the results of a laboratory experiment done under cave analogue conditions consisting on measuring pH and conductivity variations, to demonstrate that CO_2 degassing, chemical equilibration and precipitation of calcite happen at different times.

11:15 – 12:00 "Kinetic and equilibrium fractionation in speleothem carbonate 'clumped isotopes'" (Alan Matthews, the University of Jerusalem)

This lecture was about "clumped isotopes" a relative new branch of isotopic geochemistry in speleothems, which is based on the evaluation of the abundance of ^{18}O-^{13}C bonds in the carbonate lattice. Carbonate clumped isotopes may be used as paleo-thermometers, since they may potentially record the temperature of mineral growth. The lecturer compared this new approach with the most widely used $\delta^{18}O$ that, unlike clumped isotopes, may vary from calcite to aragonite or among biogenic carbonates.

14:00 – 15:45 "Processes – from the ocean to the cave (O isotopes)" + "Stable isotopes: sample preparation, standards, resolution, precision, developments" (Christoph Spötl, University of Innsbruck)

$\delta^{18}O$ is a proxy for atmospheric temperature and humidity. Variation in speleothem $\delta^{18}O$ is usually somewhat difficult to interpret because several factors are involved and closely connected, such as the ocean, atmosphere, soil, epikarst and cave system. The lecturer gave a brief introduction about oxygen isotope fractionation and then focused his lesson on the practical aspects, such as principles of mass spectrometric analysis, sampling, temporal and spatial resolution, Hendy test (method for evaluating the presence or absence of isotopic equilibrium in speleothems) and future developments.

16:00 - 18:00 2nd Poster session

Wednesday 31/07/2013

9:00 – 9:45 "Fluid Inclusions of speleothems I: H and O isotopes and noble gases temperatures" (Werner Aeschbach-Hertig, University of Heidelberg)

Thanks to fluid inclusions, one can access to the parent drip water of the calcite, which is of special interest for paleoclimatic reconstructions. These inclusions are formed when crystals start growing. The analyses of the isotopic composition of the water in the inclusions provide key information about palaeorainfalls and noble gas concentrations dissolved in the water of the inclusions yield useful information about palaeotemperature.

10:00 – 10:45 "Fluid Inclusions of speleothems II: fluid-gaseous homogenisation temperatures" (Ives Krüger, University of Bern)

Ives Krüger addressed the measurement of temperature of formation of fluid inclusions. This is usually done with a microscope heating/cooling stage, by measuring the liquid-vapor homogenization temperature that directly depends on the cave temperature at the time of formation of the inclusion.

11:00 – 11:45 "SIMS and other high resolution techniques in speleothem research" (Myriam Bar-Matthews, Geological Survey of Israel)

Myriam Bar-Matthews showed the importance of speleothem records to define the exact timing of main climatic events and to understand the response in continental environment from different parts of the world to rapid climatic changes. She also gave a brief introduction to SIMS, LA-ICP-MS and CLFM techniques and gave some examples of application at Soreq cave (Israel), one of the most studied cave of the world.

14:00 – 14:45 "U-series dating (sample preparation, standards, resolution, precision, developments)" (Dirk Hoffmann, CENIEH)

This lecture provided an overview on basics of U-series dating and techniques to measure U-series disequilibrium in speleothems. After a brief introduction about the method principles, Dirk Hoffmann provided practical advice about the sampling strategy (that is very important in order to produce reliable age results) and data interpretation.

15:00 – 15:45 "Age models" (Denis Sholz, University of Mainz)

During this lecture, Denis Sholz (DS) presented the currently used methods for the reconstruction of speleothem age models based on $^{230}Th/^{234}U$ ages (linear interpolation, splines and Bayesian statistics). Due to the low spatial resolution of U-series ages calculated from a given speleothem sample, it is usually crucial to better constrain the chronology between two successive U-series age results, which can be done by using an algorithm called StalAge, designed by Denis Sholz and colleagues for construction of speleothem age models.

16:00 – 16:45 Workshop with Denis Sholz

During this workshop DS briefly introduced the statistical software R and showed how to reconstruct age models with StalAge model.

17:00 – 18:00 3th Poster Session

Thursday 1/08/2013

Entire day "Time series analysis" (Manfred Mudelsee, Climate Risk Analysis)

During this course Manfred Mudelsee illustrated some statistical concepts like Monte Carlo method (bootstrap), regression and correlation. A workshop followed the lesson and we did some simple examples with R.

Friday 2/08/2013

9:00 – 9:45 "Frontiers of Speleothem Research" (Frank McDermott, University of Dublin)

The main objective of this lesson was to underline the need of collaboration with the oceanographers and with the climate modeling community in the framework of new frontiers in speleothem research. Frank McDermott gave some examples to demonstrate the real necessity of this approach in order to avoid oversimplified site-centered interpretations. He gave also some examples from his last research works about the interactions between the North Atlantic Oscillation (NAO), the East Atlantic Pattern (EA), the Scandinavian Pattern (SCA) and Sea level pressure (SLP) dipole.

10:00 – 10:45 "Speleothems in the context with other Palaeo-Climate archives" (Norbert Frank from the University of Heidelberg)

Norbert Frank described how carbonate archives of marine origin, like corals, can be related with the timing of continental carbonates itself.

11:00 – 11:45 "Potentials, challenges and threads of climate reconstruction in archaeology" (Thomas Meier, the University of Heidelberg)

In his lecture, Thomas Meier showed the role of climate changes in the course of the human history. He provided an original point of view by defending those cultural changes (i.e. falling/decline of societies, migrations etc…) were mostly caused by societal and economic reasons rather than climatic. This was a very interesting lecture, even if I personally did not fully agree with his conclusions.

14:00 – 14:45 "Frontiers of Palaeo-Climate Research" (Thorsten Kiefer, PAGES)

This lecture aimed to outline the state-of-the-art in paleoclimate science. Thorsten Kiefer reminded us to prefer quality over quantity of proxy records and to share research results with the scientific community. He also talked about the role of paleoclimate in the context of global-scale trends that yields ideas for future research priorities. He finally presented the PAGES review and policy and "Future Earth" program.

3. Description of the main results obtained

I think that this experience was very useful for me. I had the possibility to attend lectures given by some the most important specialists in speleothem science, which helped me to significantly improve my knowledge in that field. I felt very lucky to have the possibility to participate to this kind of event. It was also the first time for me where I could present the results of my investigation within the context of an international scientific meeting. I directly discussed with experienced researchers to address some specific issues related to my research work. In addition, I also had the possibility to meet other young researchers with who I will keep in contact and potentially collaborate in the future. Lastly, this summer school gave me the opportunity to get to know better Prof. Silvia Frisia who is supporting me for a PhD scholarship at the University of Newcastle.

The organizing committee of the Summer School was formed by PhD students from all around the world. They had the chance to demonstrate their ability to organize an international meeting with world leading specialists that have accepted to participate with great enthusiasm. I think they did a great job. During the last day, the committee met with the participants discussing the opportunity to repeat this event within the next couple of years. I think that it would be a good experience for me and a very good opportunity for my scientific development to join the organizing committee of the next meeting.

4. Projected publications / articles resulting or to result from the grant

During this Summer School, I presented a poster titled: "*Non-destructive high resolution XRF-core scanner vs. ICP-AES techniques in stalagmite: preliminary results*" (see p.3). These preliminary results derived from my MSc research work were promising, and I have the intention to keep working on these data and go further in their evaluation and interpretation thanks to the advice obtained during the Summer School. I am planning to prepare a manuscript based on this work, after my Master defense, for publication in an international peer reviewed journal. **The support from the ESF will be clearly acknowledged on that occasion.**

S^4 – Summer School on Speleothem Science: July 28th – August 2nd, Heidelberg, Germany

Organization Committee:

Laia Comas Bru (UDS School of Geological Science, University College Dublin, Ireland)

Mieghan Boyd (Stockholm University, Sweden)

Kerstin Braun (Geological Survey of Israel, Jerusalem, Israel)

Yuval Burstyn (The Geological Survay of Israel, Israel)

Michael Deininger (Heidelberg Academy of Science, Germany)

Anamaria Hauselmann (Bern University, Switzerland)

Simon Mischel (Johannes Gutenberg University Mainz, Germany)

Dana Riechelmann (Johannes Gutenberg University Mainz, Germany)

Andrea Schroder-Ritzrau (Heidelberg Academy of Science, Germany)

Sophie Winterhalder (Heidelberg Academy of Science, Germany)