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Micro-X-ray studies of the Godarville speleothems

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Introduction

It was observed some decades ago that the predominantly calcite material of speleothems (stalagmites, stalactites and similar cave forms) preserves climatic information "forever". This is connected with the controlled involvement of some elements (Mg, Sr, Ba) and isotopes (^{18}O, ^{13}C) into the calcite matrix. Speleothems are now estimated to be one of the richest sources of climatic data over millennia.

Many calcitic materials are known to be sensitive to involvement of some elements into a crystallographic structure in a way that is dependent on the temperature. Magnesium is an example of such an element and its process of involvement is thermodynamically steered. Similarly, strontium involvement, although, theoretically, this should be controlled only by steric effects, is dependent on the temperature as a result of some indirect processes. But the problem within caves that are well isolated is somewhat more complicated, due to the fact that the cave temperatures are more or less constant throughout the year. Thus, speleothems in these caves should be insensitive in respect of external temperature changes. However, in many studies of chemical elements in the speleothems, it has been discovered that elements such as Mg, Sr, Ba and sometimes others are involved in a way dependent on the season of the year. To explain this apparent contradiction, several hypotheses have been proposed. In one, the dependence of the stalagmite growth and the Mg or Sr involvement on the temperature results from the dependence on the "water excess" (the effective amount of water that penetrates the soil: the total evaporation and transpiration subtracted from the monthly precipitation), which is clearly seasonal in many countries. Since the seasons of the year are temperature related, then in turn the stalagmite growth is indirectly temperature dependent. Another hypothesis emphasises the role of water stagnation and relevant residence time in the pores. This stagnation is also seasonal and during this time, the water is in equilibrium with the stone/soil material. When water starts to flow again, its mineral content is not in equilibrium with the environment. The role of CO_2 degassing and preferential precipitation of the carbonates of heavier elements (here, strontium) is also emphasised.

Another advantage resulting from deciphering of climatic data fixed in the speleothems is the possibility of attributing these data to chronology. If attributed to particular years, and even seasons of years, we have deterministic links between the time and climatic parameters. This deterministic dating is in principle different to the probabilistic dating that is derived from isotopic measurements. However, both the scales should be convergent at some key points, e.g. at their end points.

Significance of the Godarville tunnel

In general, speleothems are formed in natural caves. The only point that can be dated for certain is at the very surface of a growing speleothem—we know the time and conditions for the formation of that location. The Godarville tunnel in Belgium, close to Charleroi, was constructed by man and the conditions for speleothem growth were controlled in two ways—first, from the start of formation in 1948, then from the moment of evolving the fully shaped annual rings in 1960 (the date of the tunnel closing) up to the end, i.e., the time of sampling the fragments in 1992. The laminations of annual growth were clearly observed in the optical image of the speleothem and counting gave the exact number of rings, corresponding to the periods mentioned. Having such a rigorous annual chronology, we tried to make it even more detailed, with attribution to sub-annual details. The ultimate aim was to extract and differentiate as small as possible increments in the sample, which coincided with time, in order to attain the highest time resolution. Simultaneously, complete climatic data had been collected at the nearby (kilometres distance) meteorological station at Houdeng–Aimeries. The relevant data cover the temperature, precipitation and so-called water excess.

The interest in the Godarville speleothems has continued over many years, due to their unique position among speleothems.[1,2]

Samples

Several samples were studied. The speleothem marked God-stm2 was analysed by synchrotron-based X-ray fluorescence analysis (at LURE) along its whole

length (33 mm). It presented a specific structure, with short and generally dark lamina formed soon after the conditions at the cave enabled crystallisation (1948–1960), followed by a zone of very well-shaped annual layers, widespread during the period 1961–1992. The first, basal area was relatively short and dark grey, with the annual layers being very thin. The total number of layers in this zone was about one dozen. It corresponded to the earlier period of initial zonation, from 1948 to 1960. The much wider neighbouring region was composed of relatively bright calcite, organised in clear annual couplets composed of dark compact and bright porous layers. Strictly speaking, approximately one half of the bright area plus the whole dark zone and half of the next bright area formed a one-year long lamina.

The fragment was cut off at the very end of 1992. The strict chronology could be attributed to the stalagmite growth during three periods: (i) 1948 to the very beginning fragment, (ii) 1960/1961 to the full-contrast boundary in between generally dark and bright zones, and (iii) December 1992 to the end of the last layer. The latter data gave a possibility of attributing part of the stalagmite to the actual month. This made attributing some zones of the stalagmite to the seasons of year easier. The annual lamination was clear everywhere.

Another sample was used for electron microprobe measurements. It also covered nearly the whole range of the speleothem growth. This auxiliary sample was used just to analyse all the low-*z* elements that could not be detected in the LURE measurements. The observation of magnesium was especially important, because the element is considered as an essential geochemical indicator in calcite materials and could not be analysed by the LURE microprobe, due to its ambient atmosphere environment. Some parts of that sample were chemically destroyed in the process of preparation for the atomic absorption spectroscopy measurements. These measurements enabled the quantitative estimation of the results from the X-ray microprobe. Also, they gave a possibility of cross-calibration of the results from the electron microprobe that were only semi-quantitative.

Instrumentation

The X-ray microprobe at Laboratoire pour l'Utilisation du Rayonnement Électromagnétique, Orsay—LURE (Orsay, Paris), now closed, was an essential tool for making the linear scans carried out in the X-ray microfluorescence mode. The microprobe was installed as a D15 end station in a frame of the D1 bending magnet beamline at the DCI storage

ring. The conditions for the beamline were: 1.85 GeV positron energy and 300 mA current with 70 h half-life. The construction of the microfluorescence and microdiffraction facilities have been described by Chevallier *et al.*[3,4] The monochromatisation and partial focussing of the beam was done by the graphite double crystal and Bragg Fresnel Multilayer Lens (BFML), to give bundles of X-rays with energies about 15.5 keV. The input pinhole regulated the diameter of the focal spot to approximately 20 µm, which was adjusted to the size of minor details on the samples. As a consequence, the seasonal variations (e.g., within the annual increments that are roughly 1.0 mm) were well recognised and the ultimate time resolution could be estimated as corresponding to approximately one-week periods. However, we assumed in our calculation the uniform growth rate of the speleothem during a year, which was rather unrealistic.

Since the patterning of the speleothem was naturally set perpendicular to the growth axis of the object, the reasonable (although, not the only possible) direction of potential scans was along this axis. To carry out a scan along the measured direction, a set of four computer-controlled step motors were used.

The characteristic X-ray signals were collected by the use of Si(Li) detector, with a working area of 13 mm^2 and energy resolution of 160 eV (for the MnKα line). All the measurements were carried out in an ambient air atmosphere. A relatively long measurement time of 100 s for each measurement point was selected, to compensate for rather poor photon flux and to ensure statistical reliability. The particular X-ray spectra were recorded by the use of the multichannel analyser card. These were then identified and fitted with WAPI3 and EPAIS programs.[5] The unresolved Rayleigh and Compton components of the scattered radiation were also recorded as auxiliary signals. All these signals were always related to the optical signal from the microscope, collected in parallel.

The supplementary measurements were made using the scanning electron microscope LEO 1430 VP (Chemistry Department at KUL). A Röntec Si(Li) detector with an energy resolution of 180 eV (for the MnKα line) allowed the microscope to function as a microprobe and enabled the detection of elements, especially the lighter ones. The measurement parameters of the microprobe were: voltage 20 keV, adjusted to detect both the light and heavy elements in one scan; the beam current was 0.7 nA. The semi-quantitative determination of the elemental content was possible by the use of a standardless system of quantification, built into the software of the instrument.

Backscattered electron images along a vertical profile of the speleothem were made periodically, along the scan direction, with the aim of collecting images over the whole length of the speleothem. To analyse these images, the image analysis program Micro Image 4.0 was applied for the extraction of the linear grey-scale profile along the line of the scan. This profile was then compared with the optical image and the elemental profiles measured by the Si(Li) detector.

The atomic absorption method was applied to establish the mean level of elemental concentrations in the samples. The method was used to overcome the inability of accurate determination of the concentrations by either the X-ray or electron microprobes. Only the auxilliary sample was analysed in this way, since the analysis is destructive. A Hitachi polarised Zeeman atomic absorption spectrophotometer, Model Z-8200, working in flame mode was used in the experiments. Precisely weighed small fragments of the speleothems were dissolved in spectrally pure hydrochloric acid in the Maxidigest MX 4350 microwave digester, manufactured by Prolabo, France. Two cycles of digestion at 1000°C were performed. After cooling, the samples were diluted to a specific volume and analysed. The multiple standard addition method was applied for quantitative estimation.

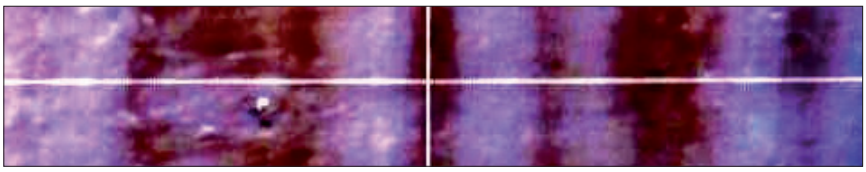

Figure 1. Fragment of the analysed speleothem (rotated 90° so that the vertical axis lies horizontally). The horizontal line shows the direction of the chemical analysis scan. The left-hand portion of the figure (containing half of the bright zone with the whole of the dark zone and half of the next bright zone) is a 1986-year lamina. The length of the scan is 6665 µm.

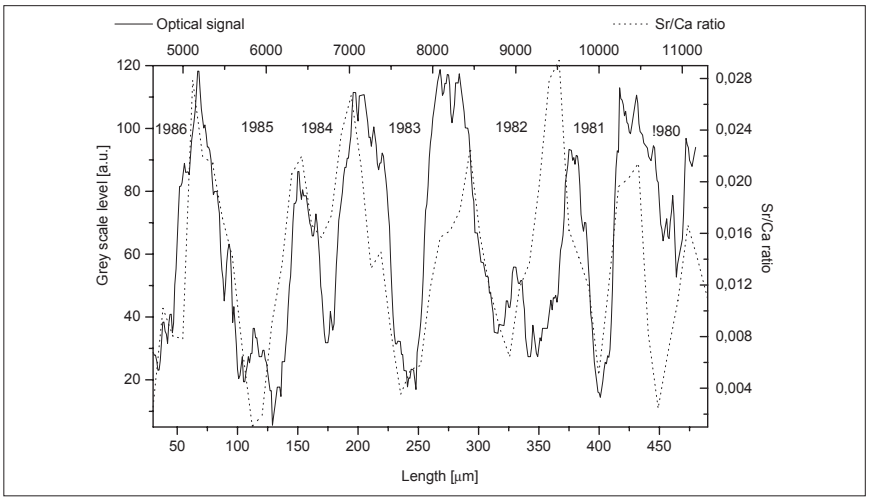

Figure 2. Optical profile along the line of scan in Figure 1 with superimposed results of Sr/Ca ratio, as determined by the synchrotron-based X-ray microfluorescence. The full chronology of the sample is shown.

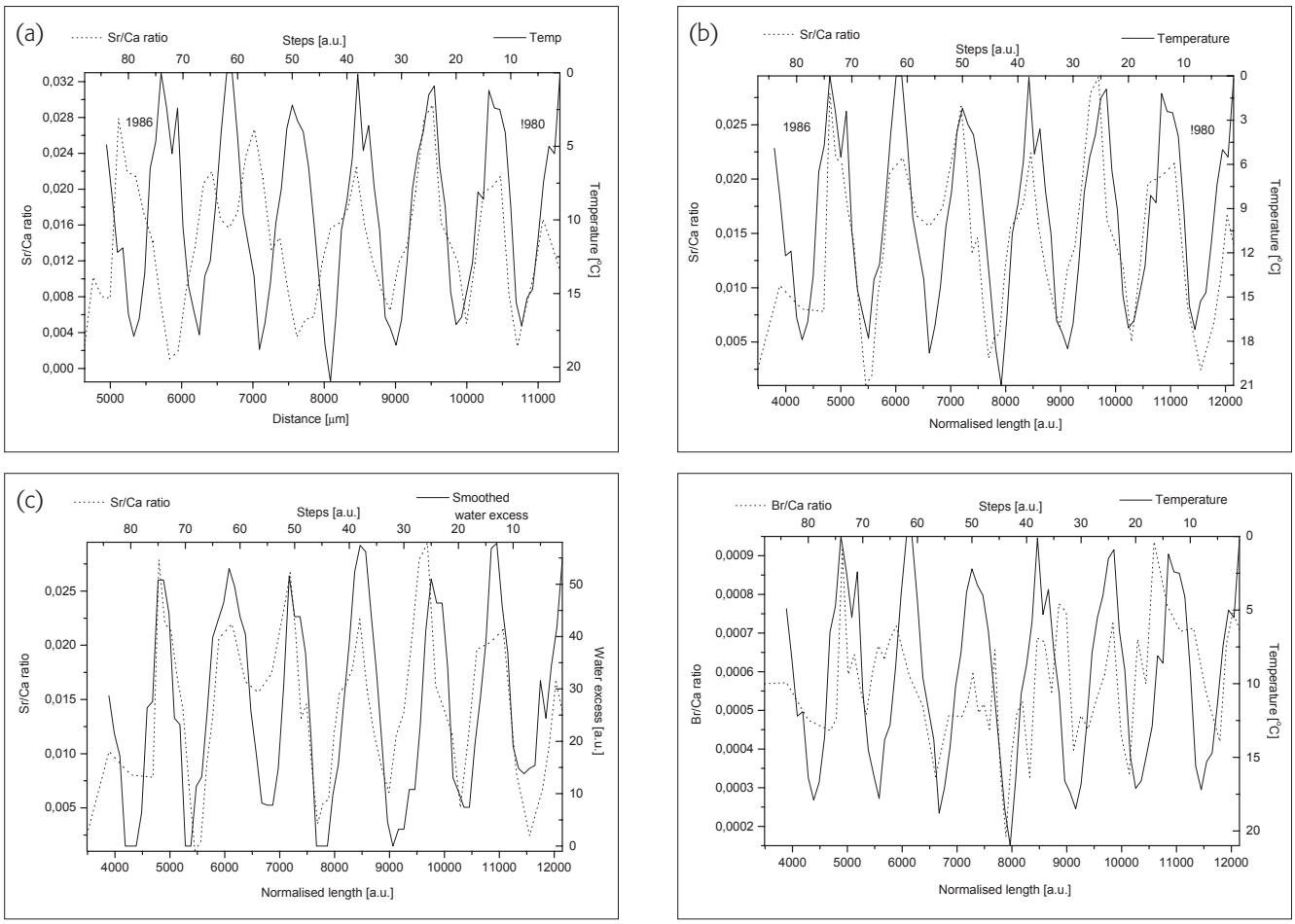

Figure 3. (a) Comparison of temperature distribution estimated on monthly basis and chemical Sr/Ca profile, all corresponding to the scan line in Figure 1. (b) Comparison of temperature distribution estimated on monthly basis and chemical Sr/Ca profile, recalculated for the uniformised year widths. The figure covers the full year increments from the line on Figure 1. (c) Comparison of inverted and smoothed water excess distribution with the chemical Sr/Ca profile. The same range as in (b). (d) Comparison of the normalised Br/Ca profile with the temperature distribution.

An Eclipse E400 optical microscope was used to trace the variability of the consecutive dark and bright layers. The microscope was equipped with a Coolpix 950 digital camera (Nikon Europe BV) to take photos of the fragments of interest. The digital images were analysed using the Lucia G image analysis program, in order to extract the optical profiles along the vertical growth axis of the stalagmite. Annual alternations were clearly visible on these profiles leading to an accurate absolute time scale: 1992 at the top, 1960 somewhere near the bottom and 1948 at the base. All other data, such as the profile of the signal of backscattered electrons and the elemental distributions were compared to the optical profile morphology. Regardless of how closely they followed the optical image, there were always discrepancies between the optical images and mappings, sometimes very small (as for Sr/Ca or Br signals).

Results

In this article, we focus our attention on a selected fragment of a speleothem having an image with the annual lamellae for a six-year period. A photomicrograph of a fragment of a spelothem is shown in Figure 1. The selection is only for visual reasons—simply, longer increments are more obscure from the point of view of our eyes. Nevertheless, the whole of the rest of the speleothem is built up in the same way and we can easily prove the same conclusions. The results are supported on the linear optical scan, extracted by use of the MicroImage 4.0 program from the photos of the speleothem. It is the reference line for the all other results. In parallel, the chemical analysis by the use of the synchrotron-based X-ray microfluorescence device was performed, along the same line. Several elemental signals could be detected. Some of them, such as Zn, Fe and Pb, were randomly distributed and we could not detect any reasonable connection between these signals and the morphological features of the speleothem as revealed by its optical profile. The distribution of raw signals of calcium, the main element, gave no clear indications of links between the morphology of the sample and its composition. Only Sr and, partially, Br signals gave scans correlated with the optical profiles. In particular, normalisation of the Sr signal against the Ca gave a plot similar to the optical profile, see Figure 2. It is also easy to see in Figure 2 and important to note how closely correlated are the chronol-

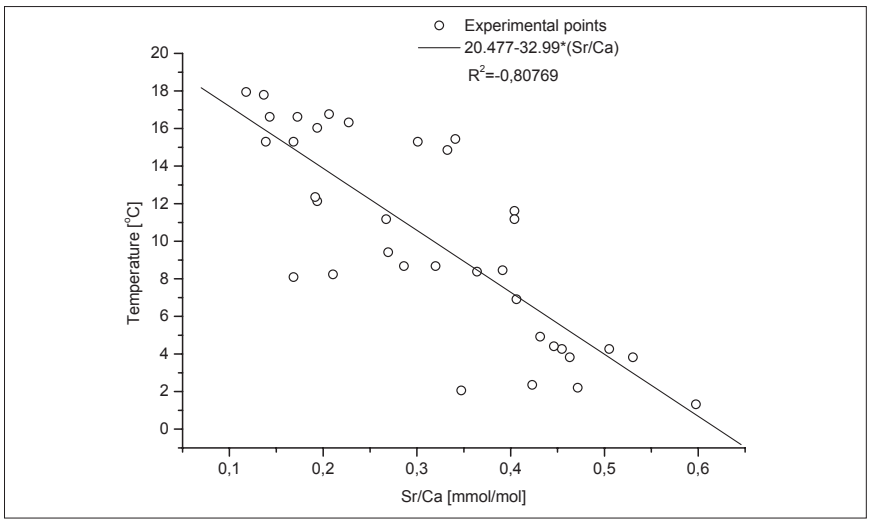

Figure 4. Linear fit of Sr/Ca ratio as a function of the temperature.

ogy and the optical profiles. After the annual growth zones were established—and the chronology was determined, the use of relevant climatic data becomes possible. Figure 3(a) shows the inverted annual temperature distributions superimposed on the Sr/Ca stalagmite profile. Coincidence is observed towards the right side of the figure—the figure was adjusted to the first of the years—1980 being one. Later on, the curves start to deviate from each other. Although not shown here, a very similar result was obtained when smoothed data on water excess was superimposed on the Sr/Ca profile.

Among the results obtained by using the electron microprobe, the most spectacular was that showing that Mg and Ca were linked by a kind of hyperbolic relationship:

$$Mg/Ca = 1/(Ca - 4) \qquad (1)$$

where the concentrations are in weight percents. The function describing this relationship is called a homographic one. Moreover, some amounts of Na, K, Cl, Al and Si were found, with some pairs of them (Na and Cl, Al and Si) strictly correlated with each other (data not shown here).

Deciphering of climatic data

The results obtained need to be presented on a more convenient base. We should note that all the climatic data obtained from the meteorological station are always presented in equal steps, e.g. on a monthly basis. Second, anyone can easily observe that the annual growth laminae of the speleothems are unequal, and sometimes quite different. That both lines in Figure 3(a) are moderately similar is only a random case. One of the reasons is that the sequence is relatively short and would be significantly disturbed over a longer distance. Nevertheless, one can improve the situation by correcting the results. This correction is in the recalculation of the ring width to the normalised value. When such an operation is carried out, the new profiles are observed, see Figure 3(b), and then the coincidence of the curves—the inverted temperature and chemical Sr/Ca ones is striking. One should remember, that the normalisation procedure used in this work operates on a one-year long cycle of normalisation. It is obvious that finer normalisation, e.g. on a monthly basis, would improve the coincidence even more. However, some part of the uncertainty is irreparable and results from disruptions in the speleothem structure. It is worth emphasising that the relationship shown in Figure 3(b) correlates with the external, outside-cave temperature and not the temperature of the speleothem as it formed in the cave.

If the water excess distribution profile is created and smoothed (the original data on the water excess are strongly scattered), then that new profile can also be correlated with the chemical Sr/Ca data, see Figure 3(c). The correspondence is again quite noticeable. A further correlation exists between the Br/Ca normalised signal and the temperature distribution, see Figure 3(d).

The correspondence of the data concerning the temperature and Sr/Ca ratio was studied further. After rejecting a number of bad points (~13%), and transforming the data to the chemical units (mmols of Sr against moles of Ca), the correlation between the remaining set of data was quite striking for a natural object. The relation is a first order polynomial, see Figure 4:

$$t[°C] = 20.48 - 694.2 \times (Sr/Ca) \qquad (2)$$

We are aware that it is the Sr/Ca ratio that can potentially be a function of the temperature and not the contrary, but this way of presentation is more useful. Indeed, simply, having established a Sr/Ca ratio one can decipher the temperature or, similarly, the water excess.

The comparison of this Equation (2) with Equation (1) testifies at once that the relationship between Mg signal and temperature is non-linear and complicated. It cannot be used for the deciphering of the climate in this case.

The studies on the Godarville speleothem have proved the correspondence of the optical with some of the chemical (Sr/Ca) results. Moreover, the chemical results could be linked to climatic data, the inverted temperature and smoothed water excess data. This correlation has clear climatic significance. The peaks in the Sr/Ca ratio corresponded to the minima in the temperature and they occured in the December–February periods. These enable the particular cave years to be assigned. This discovery for the Godarville was significant since it was not intuitively clear what was meant by "cave year". The relationship between the water excess and the chemical results was similarly striking. Thus, deciphering the temperature and water excess data from the chemical measurements gives the very promising possibility of establishing climatic conditions. The suggested reliability coefficient is impressive for a natural object. However, it is essential to recalculate the data for equal incre-

ments of growth, otherwise it is difficult to compare the climatic database characterised by the equal time periods with the variable annual speleothem growth increments. Although there are some other published papers showing the distribution of Sr/Ca in connection with the calendar year and the correlation between this chemical signal and precipitation,[6–8] this correlation in our work is only similar but not analogous to that in a paper by Johnson *at al*.[9] The mechanisms governing the speleothem formation were somewhat different. Nevertheless, we have shown that perhaps one day a scientist reading the purely spectrometric (chemical) indications on a stalagmite will translate this to the temperature or water excess and attribute this to precisely the year and even the season it occured.

Acknowledgements

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