# Long-term hydrological changes in northern Iberia (4.9 – 0.9 ky BP) from speleothem Mg/Ca ratios and cave monitoring (Ojo Guareña Karst Complex, Spain)

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## Abstract

An absolute-dated stalagmite from Kaite Cave (Ojo Guareña Karst Complex, N Spain), provides a nearly continuous, high-resolution record of a proxy of regional precipitation patterns through the 4.9 to 0.9 ka BP interval. This record is based in the Mg/Ca ratio of the calcite and its variation through the stalagmite stratigraphy, which is interpreted to be primarily driven by changes in precipitation amount. The calibration of the proxy is supported by the present-day monitoring carried out in the cave for the last 10 years, which reveals a robust inverse relationship between the inter-annual/inter-decadal variability of rainfall and the Mg concentration of dripwaters and precipitating speleothems.

The record of paleoprecipitation, based on 2400 Mg/Ca measurements, shows strong variability at inter-annual to inter-decadal scales, and more subtle but significant changes at secular to millennial scales. This long-term paleohydrological evolution outlines five successive intervals with consistent trends, which are bounded by abrupt shifts in the regional precipitation. These shifts took place at 4.65, 4.2, 2.6, and 1.3 ka BP. Significantly, the intervals of maximum precipitation of the whole record (around 4.9-4.65, 2.6-2.45, and 1.3-1.1 ka BP) can be related with episodes of minimum solar activity, and correlated with cold climatic events elsewhere.

**Keywords:** Speleothem, Karst, Paleohydrology, Mg/Ca, Late Holocene, Iberia.

## Introduction

The characterization of regional precipitation patterns and changes at decadal to millennial time scales in Europe is of major importance to better understand the evolution of human settlements and societies and to improve the knowledge of the climate system on a synoptic scale. However,

information on this climatic parameter beyond the instrumental and historical records is quite scarce because two main reasons: first, the difficulty of getting high resolution, robust paleohydrological records anywhere but particularly in those zones where lakes and wetlands are rare; and second, because the strong spatial variability of rainfall patterns in an area like SW Europe, strongly dependent of the interaction of African subtropical, North Atlantic, and Mediterranean climate systems, which in many cases which in many cases frustrate inter-regional correlations.

This study attempts to contribute in this task by yielding a high resolution series for relative paleoprecipitation changes for the northern part of the Iberian Peninsula (4900 to 900 years BP) based on the changes in the magnesium content through a calcite speleothem which grew in Kaite Cave (900 m a.s.l., Ojo Guareña Karst Complex, N Spain). The analysis of variations in the concentration of trace elements such as magnesium during the growth of calcite speleothems has a high potential as a tool for reconstructing past changes in hydrology, rainfall, and temperature (Trebble et al. 2003; Johnson et al. 2006; Cruz et al. 2007; Fairchild and Treble 2009; Sinclair et al. 2012). These papers also show how that potential is in many cases hampered by the multiple (and in many cases independent) factors that determine the trace element composition of calcite speleothems and the changes in that composition through time. It is for that reason that no general assessments on the hydrological or geochemical functioning of karst systems from a particular emplacement can be made. One part of this hindrance is being solved by progress in experimental laboratory work, which allows for example a better understanding of the factors that modulate the distribution coefficient of each element (e.g., Gascoyne, 1983; Huang and Fairchild 2001, Day and Henderson 2013, Nielsen 2013). Progress can also be made by a rigorous calibration of the signal recorded by the speleothem by means of contemporary Mg/Ca time-series data in the specific conditions of each cave and the routing system of percolating waters until the place of calcite precipitation (e.g., Tremaine and Froelich 2013). In this sense, our paleoclimate interpretation of the magnesium concentration variation through the studied speleothem is supported by a long-term monitoring program (10 years) performed in the cave from where the stalagmite was retrieved.

The studied stalagmite provides a nearly continuous record of the paleohydrological conditions of N Spain over the covered time interval. The series was constructed on a robust time model supported by precise $^{230}$Th absolute dating, and the magnesium content is expressed by Mg/Ca ratios of nearly 2400 analyses performed through the stalagmite by means of Laser Induced Breakdown Spectroscopy (LIBS). The potential of this analytical technique, only tentatively used in speleothem research (e.g., Vadillo et al. 1998; Fortes et al. 2012; Marín-Roldán et al. 2014), is also explored and discussed in the paper.

## Sampling site and studied material

The speleothem studied in this paper, named Buda-100, is a cylindrical and very elongated (112 cm long × 4–6 cm thick) stalagmite, which was retrieved from the Buda Hall in the Kaite Cave (Ojo Guareña Karst Complex, Burgos Province, N Spain, Fig. 1). The sample, fallen and broken in several pieces when collected, was reconstructed and then cut in two longitudinal halves. These pieces (and 19 petrographical thin sections made from them) are preserved in the collection of the Department of Stratigraphy of the Complutense University of Madrid. Buda-100 exclusively consists of calcite and shows two main microfabrics: columnar fibrous calcite (mainly in their axial part), and dendritic in some peripheral areas. Its internal stratigraphy is quite complex in the central part, but much simpler in the periphery, where a pervasive pattern defined by a sub-millimetric lamination is shown. This lamination, according to the age model and the microstratigraphic analysis, is interpreted as annual in origin.

Kaite Cave is quite small (~350 m of maximum length) and relatively shallow (12-20 m below the surface), and is topographically isolated from the main levels of the Ojo Guareña Karst Complex. The cave is 860 m above sea level and the area has a relatively humid, temperate

climate. The region is located in the transition between the two main climatic zones of Western Europe: the Atlantic and the Mediterranean. The climate is warm-temperate, with annual mean temperatures in the range of 10-11 ºC, although these vary notably according the seasons (with mean temperatures over 18 ºC in July-August, and less than 5ºC in January-February). The annual precipitation averages ~720mm (1990–2014 interval, Villarcayo Meteorological Station, Agencia Estatal de Meteorología (AEMET) and Confederación Hidrográfica del Ebro (CHE), W3°34′20″ N42°56′26″, 595 m a.s.l.), with maximum precipitation in November to January but also notable precipitation in April-May, and quite dry summers. During winter, part of the precipitation is snow, which never lasts on the ground more than several days or few weeks. The soil above the cave is shallow (essentially a lithosol) with scarce argillaceous material and organic matter. However, it allows the development of a quite dense cover of small *Quercus* and *Juniperus*. The cave is developed on lightly dipping carbonate unit of Upper Cretaceous (Coniacian) age, which consists of shallow marine, partially dolomitized limestone.

The monitoring program commenced in 2002 at Las Velas Hall, a small gallery adjacent to Buda Hall, both separated ~340 m from the main entrance. The monitoring site is characterized by a stable cave climate: the temperature is 10.40 ± 0.04 ºC and reflects the mean annual temperature outside the cave, the relative humidity exceeds always 99 % and there are no significant air currents (Turrero et al. 2004; 2007).

The seepage water is frequent, with permanent but variable dripping during the year with a definite seasonal effect, and the speleothems are abundant, some of which are growing at the present time. The total volume of dripping water collected seasonally is consistent with an advective flow through the surrounding rock. The data presented in this work correspond to 10 years of monitoring of two points with a "low" and "rapid" flow, with an average annual drip rate of ~ 0.02 mL/min and ~ 0.58 mL/min, respectively.

## Methods

### $^{230}$Th age-dating

Radiometric ages of speleothem calcite can be obtained efficiently with the application of U-series dating techniques on inductively coupled plasma mass spectrometers (ICP-MS) (Shen et al. 2002). With this aim, 14 samples of approximately 150-200 mg of calcite powder were extracted along selected stratigraphic intervals from stalagmite Buda-100 and prepared for $^{230}$Th dating according to the procedures described by Edwards et al. (1987) and Dorale et al. (2004). ICP-MS analyses of stalagmite Buda-100 samples were performed at the Minnesota Isotope Laboratory on a multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS, Thermo Finnigan Neptune) using a MasCom multiplier behind the retarding potential quadrupole (RPQ).

The analytical work of Buda-100 was accompanied by the petrographic study of the speleothem, in order to recognize its internal stratigraphy (e.g., identification of hiatuses and growth patterns), and to detect possible diagenetic features (e.g., micro-dissolution, internal carbonate precipitation, incipient recrystallization). This study was useful in the selection of the extraction points of subsamples for absolute age-datings as well as transects for trace element analyses.

### Mg/Ca measurements

Determination of Mg geochemical data in Buda-100 was conducted by laser induced breakdown spectroscopy (LIBS) (Fig. 2a), at the Complutense University of Madrid in the Department of Analytical Chemistry, using a Q-switched Nd:YAG laser (Quantel, Brio model) operating at

1,064 nm, with a pulse duration of 4 ns. The analyses were performed on the polished surface of the 19 thin sections (mounted on 5x8 cm slabs, 500 μm thick) prepared for petrographical and geochemical analyses (Fig. 2b). Each thin section was placed over an X–Y–Z manual micrometric positionator with a 0.5 mm stage of travel at every coordinate to ensure that each laser pulse impinged on the speleothem. The laser beam was focused on the surface of the speleothem with a 100 mm focal-distance lens. This large working distance allowed easy sample manipulation and plasma light collection while the focusing provided by the lens enabled extremely precise placement of the beam on the speleothem. Emission from the plasma was collected, and then focused into an optical fiber, coupled to a spectrometer. The spectrometer system was a user-configured miniature single-fiber system EPP2000 StellarNet (Tampa, FL, U.S.A.) with a charged coupled device detector (CCD) with a spectral resolution of ±0.5 nm. The wavelength range used was from 200 to 1,000 nm. The detector integration time was set to 100 ms. Each point analyzed was exposed to 3 laser shots before performing the measurements to eliminate any impurity on the surface. The recorded spectra are the average of 20 laser pulses at each single position (Fig. 2c and d). The lateral resolution between spectra was established at 500 μm. The spectral data was processed using an interface created in Matlab software. LIBS data are shown as the ratio of the intensity of Mg versus Ca, Ca being the internal standard. This option is a preventive measure to minimize alteration that can affect the LIBS signal, because of laser-matter interaction during laser ablation. These alterations can be originated by heterogeneity, roughness, variations in the microporosity, etc. of the speleothem surface.

Marín-Roldán et al. (2014) propose a series of experimental proofs to check the quality and reliability of trace element data obtained by LIBS in speleothems. These include tests for (a) uniform plasma temperature (no significant variation in the temperature of the plasma during the experimental measurements allows accurate comparison between the emission intensity of the spectral lines and the corresponding analytical response); (b) homogeneity of data along single growth layers (the absence of significant lateral changes in the trace element composition would allow to recognize the data as representative of each growth layer); and (c) repeatability of the measurements (and the resulting series). These three tests were performed during the measurements with positive results, which are illustrated in Figures 3a, b, and c.

Additionally, the reliability of the LIBS Mg/Ca data was checked by independent analyses, for selected intervals of the stalagmite, by inductively coupled plasma-optical emission spectroscopy (ICP-OES), a more traditional technique which requires of larger amounts of sample (consequently losing the LIBS micrometric resolution). We used a spectrometer Perkin Elmer ICP-OES 5200 DV in the National Research Center of Human Evolution (CENIEH) in Burgos (Spain), which yielded values of Mg in the speleothem of 150 to 400 ppm. The samples analyzed by ICP-OES were drilled using 0.5mm carbide dental burns, sampling areas of 4x4mm, to get approximately 3-8mg of sample. That means that the analytical results yielded by this technique represent non-weighted averages of about 10-20 annual growth layers, whereas the results form LIBS come from about 30 micrograms, and correspond to growth time intervals of several months. Because the very different size of the samples, perfect matches between LIBS and ICP-OES curves should not be expected. However, comparable trends between the two records have been obtained in our study (Fig. 3d).

The positive results in the LIBS evaluation tests (*sensu* Marín-Roldán et al. 2014) and the reasonably good correlation (with the explained limitations) of LIBS and ICP-OES data support our argument that the Mg/Ca measurements for obtaining the time series are representative of the changes in the Mg content in the speleothem through time and can be used for paleoclimate interpretation.

Related to water samples from contemporary monitoring, aliquots representative of the total amount of the seasonal sampling for each drip point were filtered through Millipore filters with pore size 0.45 μm for complete chemical characterization. Magnesium and calcium were analyzed by ion chromatography with METROHM equipment with high-performance Metrosep C3-250 column. Data quality was assessed by replicate samples and sample blanks.

## Cave monitoring: Mg/Ca – climate relationship

Mg content in the calcite of stalagmites is given by the distribution coefficient $K_{Mg} = (Mg/Ca)_{calcite}/(Mg/Ca)_{solution}$. Because $K_{Mg}$ is modulated by temperature, the Mg/Ca ratio in speleothems was considered as a possible paleothermometer in pioneer works (e.g., Gascoyne, 1983). However, according to the experimental work by Huang and Fairchild (2001) about the temperature-dependence of $K_{Mg}$ under laboratory conditions, the temperature variations in the Kaite Cave estimated for the late Holocene (Martín-Chivelet et al. 2011), would be too small to generate significant changes in the Mg/Ca ratios through time in stalagmite such as Buda-100. For this reason, $K_{Mg}$ can be assumed to be roughly constant through time, and thus, the changes in the Mg/Ca in speleothem series should be regarded through the time variability in the hydrochemistry of the cave drip-waters.

These changes in the composition of the drip-water could be related to various processes acting in Kaite Cave:

(a) Differential rates of dissolution of calcite and dolomite in the bedrock, which is favored in the case of Kaite Cave by the mixed dolomitic–calcitic nature of the Cretaceous carbonates. Because of the Mg content of dolomite, this process will affect near exclusively to this element: the aqueous leachates should have lower Mg/Ca relative to the bedrock because of preferential calcite dissolution, but that ratio can rise by increasing water residence times, an aspect that took place during the drier time intervals when the seepage flow decreases. Similar cases were described by Fairchild et al. (2000).

(b) Prior calcite precipitation (PCP), which is favored by the climatic conditions of the Kaite area (Turrero et al. 2015). When percolating, the waters can pass from a dissolution regime to a precipitation regime as they get into areas with lower $pCO_2$ than that which they have previously equilibrated. The resultant degassing leads to calcite precipitation and, consequently also to water enrichment in Mg relative to Ca. PCP is enhanced during dry climatic periods (e.g., Fairchild and Treble 2009), and thus, the higher values in Mg of the dripwaters and of the speleothems should reflect climatic conditions of low rainfall.

The hydrochemical monitoring in Las Velas Hall (Kaite) for the 2002 -2012 interval shows distinctive patterns for both the drip-rate and the Mg/Ca molar ratio in the drip-water (Fig. 4). These patterns are defined by a net progressive increase for the Mg/Ca molar ratio and a negative trend for the drip-rate.

It should be noted that calcium in dripwaters of Kaite does not correlate with magnesium ($r = 0.12$), reflecting that dripwater should not be affected by dilution processes when rainfall increases (Tooth and Fairchild 2003; Baldini et al. 2006), so attention should be paid to dissolution-precipitation processes in the epikarst and the vadose zone affecting the dripwater chemistry.

For a meaningful understanding of these Mg/Ca variations from a hydrological perspective, the inter-decadal rainfall evolution pattern for the area must be considered. A recent study (Confederación Hidrográfica del Ebro, 2012) based in the regional integration and homogenization of meteorological data from 29 observatories, shows a significant decreasing trend in annual rainfall over the Kaite Cave area during the last four decades. Specifically, for the interval 1990-2010 an average annual decrease of -0.7%/year is reported. At a seasonal scale, significant rainfall decrease took place during spring (averaging -2.5%/year), summer (-0.9%/year) and autumn (-0.7%/year) rainfall, while winter rainfall increases (1.3%/year). Our own data, limited to the last ten years, are in accordance with those values.

The decreasing trend in annual rainfall over the Kaite Cave area in recent years coincides with a trend of decreasing drip-rates at the two monitored points in Las Velas Hall (Fig. 4),

demonstrating the link between regional scale hydrological conditions, drip-rates and water chemistry.

Since lower rainfall means less water available for recharging the system, the coexistence of a sharp increase of the Mg/Ca ratio together to a drip-rate decrease points towards changes in the epikarst through water-rock interaction processes. Prior calcite precipitation in the epikarst and/or unsaturated zone is invoked as the process causing progressive increasing in the Mg/Ca molar ratio. It means that a significant storage may occur in the matrix, and in other parts of the system, like the epikarst driving slow fluxes and giving time to the above described processes.

Prior calcite precipitation is considered a long-term (years) water-rock interaction process as a consequence of a continuous decreasing of recharge in the area as reflected during the analyzed period. At seasonal scale lower rainfall during spring, summer and autumn lead to lower recharge and increase of the effect of prior calcite precipitation, being the general inter-annual trend superimposed to that seasonal trend.

## Stalagmite age model

A total of fourteen $^{230}$Th dates were determined for Buda-100 (Table 1). All ages are in correct stratigraphic order and suggest quite constant growth rates for the stalagmite. Petrographic analyses indicate complex internal growth patterns in some parts of the stalagmite but a net continuous growth. Minor hiatal surfaces punctuated the microstratigraphic series. Because their duration is short and difficult to estimate (probably in the range of few years), these hiatuses were not incorporated into the age model. A former chronostratigraphy of the stalagmite based in preliminary data (Cruz et al. 2015), clearly overestimated the duration of two of these surfaces. The age model for this stalagmite was performed by applying the StalAge algorithm (Scholz and Hoffmann 2011). According to this model (Fig. 5) Buda-100 grew between 4900±50 and 950±170 years BP, covering four millennia in the middle to late Holocene. Calculated growth rates are essentially constant through the four millennia, averaging 0.3 mm/year, with two minor exceptions: the rates can exceed 0.5 mm/year in the centuries around 3800 years BP and are as low as to 0.1 mm/year in the last 150 years of the record.

## The Mg/Ca series

2400 Mg/Ca LIBS measurements were performed along Buda-100 and then time-scaled according to the age model to construct the time series of Figure 5. The Mg/Ca intensity ratio averages 0.05 and ranges from 0.02 to 0.13. The series is characterized by a noticeable variability at the shortest timescales, which should be induced mainly by seasonal and interannual changes in the speleothem composition. That variability, of great interest, will not be analyzed in this paper, as further microstratigraphic work is required for its correct understanding. Superimposed on that high frequency variability, longer-term, more subtle changes can be recognized in the speleothem Mg/Ca record. For visually analyzing the longer term changes, the series was smoothed by means of a simple 9-term running average (Fig. 6). Additionally, a spectral analysis was performed on the bulk time series for the identification of cyclic patterns in the Mg/Ca variability. This analysis was performed by means of the Lomb periodogram algorithm, indicated for unevenly spaced time series, and was made with the aid of the PAST software (Hammer et al., 2006). A minor mathematical treatment of the data set was introduced on the original data set prior to the analysis, with the aim of eliminating its long-term positive trend. It was made by subtracting the best-fit linear function from the data. The result, shown in the spectral diagram of Fig. 7, reveals a very significant spectral peak for a period of 210 years, as well as secondary but also significant peaks for 725, 578, 445, 255, and 99 years.The Mg/Ca record is interpreted in terms of paleohydrological changes that occurred in

the region of the cave through time. Variations in the Mg/Ca of the speleothem are mainly determined by the composition of drip-waters, and this composition is strongly dependent of the water-rock interaction occurring in the epikarst. Larger residence times would result in enrichment in Mg/Ca of the water, as a result of several processes which include prior calcite precipitation and/or differential dissolution of calcite and dolomite in the bedrock. Because residence times decrease with higher water recharge, and the recharge depends of the annual amount of precipitation (mainly autumn- winter-spring), the Mg content in the calcite of the speleothem correlates inversely with that meteorological parameter. However, the complex nature of the Mg/Ca record and the inherent limitations of present day monitoring, permit neither the proposal of an absolute quantification nor the calibration of the paleohydrological changes reconstructed from the Mg/Ca record. These are interpreted in terms of "relative" paleoprecipitation variations, e.g., drier or wetter intervals.

It should be noted, however, that despite the noticeable variability of the record over those four millennia, the broad climatic conditions remained quite stable, and that such precipitation variability should occur in a relatively narrow range. Buda-100 stratigraphy reflects (beyond the Mg/Ca variability) that the paleohydrological conditions were stable enough to allow a nearly continuous stalagmite growth at remarkably homogeneous growth rates. And this aspect suggests that, even during the driest periods, the climate was humid enough to allow significant water recharge to maintain stable dripping on the stalagmite.

**Paleohydrological intervals and events**

The Mg/Ca series defines five long-term paleohydrological intervals of moderate amplitude if compared with the high-frequency variability, but with well-outlined trends (Fig. 6). They are bounded by significant events. From older to younger, these intervals and events are:

-1$^{st}$ Interval (4.9-4.65 ka BP): This period is defined by the lowest values in the Mg/Ca ratios, i.e., the climatic conditions are prevailingly wet. No positive or negative trend is clearly appreciated within this interval. Comparing with other areas and proxies, this time is broadly accepted to be a cold episode, and negative temperature anomalies have been reported in Greenland, North America, Africa, and Antarctica (e.g., Wanner et al. 2011, and references therein). In Europe less clear anomalies in the temperatures have been stated, but a notable glacier advance in the Alps has been recently reported between 4.8 and 4.6 ka BP (Luetscher et al. 2011) and an important humid period has been recognized in the eastern Mediterranean (Triantaphyllou et al. 2014).

-Event at 4.65 ka BP. In the stalagmite record, it is marked by an abrupt and intense increase in the Mg/Ca, i.e., a very rapid shift toward drier conditions.

-2$^{nd}$ Interval (4.65-4.2 ka BP): After the 4.65 ka BP event, the Mg/Ca values stay high for approximately two centuries and then started to gradually decrease until the end of the interval. This indicates that, after an initial dry period, the regional climate evolves gradually to more humid conditions. Maximum precipitation was reached at the end of the interval (4.2 ka BP). This whole interval has been considered as cold in northern Europe, with rapid advance of glaciers and the onset of the so-called Neoglacial period. Contrarily to our stalagmite record, in other areas the 4.2 ka BP wet episode is defined by strong dryness, such as in North America (Booth et al. 2005), Mexico (Bernal et al. 2011), the Middle-Est (Weiss et al. 1993; deMenocal 2001; Ayalon and Bar-Matthews 2011), and China (Wang et al. 2005).

-3$^{rd}$ Interval (4.2-2.65 ka BP): The boundary with the previous interval is not marked by an abrupt shift (or event), but by a net change in the trend. After several decades of humid conditions around 2.4 ka BP, the conditions change towards a greater dryness. In fact, this 3$^{rd}$ interval is very long and defined by a net positive trend in the Mg/Ca values (i.e. drier conditions). It shows an internal complex variability, punctuated by several secular episodes of greater dryness (around 3.7 and 3.3 ka BP).

-Event at 2.65 ka BP: Short interval (few decades) defined by an abrupt decrease in the Mg/Ca, which returns to the low values of the onset of the series and the start of the previous interval. This event records a major regional paleohydrological change, with an abrupt increase in precipitation. It can be correlated with episodes of rapid climate change (cooling) in central Europe (e.g., Swindles et al. 2007; Martin-Puertas et al. 2012, Wanner et al. 2011; 2014; and references therein).

-4th Interval (2.6-1.35 ka BP): After the abrupt decrease in the Mg/Ca of the 2.6 ka event, another prolonged interval began, being again defined by a net positive trend in the Mg/Ca series (dryness increase). The fourth interval (2.6 ka – 1.35 ka BP) starts with a 150 yr period of wet conditions followed by a long interval during which the conditions progressively became drier. This interval coincides with the progressive aridification recognized in the western Mediterranean area, conditions which seem to have preceded and accompanied the Romanization of Iberia (Jalut et al. 2000; 2009). The late part of this interval is commonly identified in Europe with the Dark Ages or the Migration Period Cooling (Ljungqvist 2010), with strong human migratory movements.

-Event at 1.35 ka BP: Shift defined by a rapid decrease in the Mg/Ca (which however does not reach values as lower as in the previous events) which abruptly ended the previous dry period.

-5th Interval (1.3-1.0 ka BP): This final period is defined by remarkably low values in the Mg/Ca ratios during the first ~200 years (wet conditions), and a later interval for which the Mg content starts to increase (dryer conditions). A marked humid event, however, is recognized around 1.15 ka BP. The end of this interval, with a clear positive trend, is defined by the top of the stalagmite record. Interestingly, the climatic conditions in this time interval experienced an abrupt change in Europe, which derived in the so-called Medieval Climate Anomaly (MCA). The MCA, which lasted form the 8th to the 14th Century (Martín-Chivelet et al., 2011), was characterized by changes in climate globally, including relative warmth over the North Atlantic/European region and much of the extra-tropical Northern Hemisphere (Esper et al. 2002). The reason why the stalagmite stopped growing remains unclear. The high Mg/Ca values and the final positive trend in the Mg/Ca, coupled with slow speleothem growth rates suggest that the end of the stalagmite development could be related to a reduction of water availability in the cave as a result of a dry period. Trouet et al. (2009) demonstrates that the MCA was characterized by a period of persistent positive North Atlantic Oscillation (NAO) probably starting before 1000 yr BP. This positive phase could determine prolonged dry winter conditions in SW Europe and the Mediterranean.

These paleohydrological intervals should be framed within the variability of the N Atlantic and European climates during the Late Holocene. For the considered interval, the proposed main forcing of climate change is the solar activity (e.g., Wanner et al. 2014). In this sense, we must emphasize that the three episodes of maximum pluviosity recognized in our stalagmite record can be related with periods of Grand Solar Minima (GSM). This correlation points towards a strong coupling between solar activity and precipitation over northern Iberia. Three main GSM occurred during the considered interval, dated at 4.9, 2.8 and 1.3 ka BP (Steinhilber et al. 2009). Two of these GSM (4.9 and 1.3 ka BP) coincides precisely with the onset of two our maximum pluviosity intervals, indicating a rapid and robust response of the paleohydrological regime to the solar activity decrease. The third GSM (2.8 ka BP, 'Homeric Minimum') can be also related with the maximum pluviosity episode that started several decades later, at ~2.65 ka BP. Interestingly, a similar delay was postulated by Swindles et al. (2007) in a well age-constrained continental record in Ireland, where a major paleohydrological shift (to wetter/cooler conditions) also postdated the 2.8 ka BP solar minimum.

Additionally, the spectral analysis of the Mg/Ca time series (Fig. 7) revealed a preponderant cyclicity (maximum spectral power peak) for 210 years (as well as secondary ones for 725, 578, 445, 255, and 99 years). Significantly, that dominant cyclicity in BUDA-100 Mg/Ca record has a comparable period to the Suess solar cycle, recognized by different authors in cosmogenic isotopes records in tree rings and ice-cores (e.g., Dergachev et al. 2000; Vasiliev and Dergachev

2002; Steinhilber et al. 2009). Although the relationships between the Mg/Ca record and the solar cycles need to be further investigated, the identification of frequencies typical of solar cycles in the speleothem record also argues for a strong influence of solar activity changes in the rainfall patterns of SW Europe.

## Conclusions

-The Holocene stalagmite Buda-100, retrieved from the Kaite Cave (Ojo Guareña Karst Complex, N Spain) was radiometrically dated by $^{230}$Th and analyzed by laser induced breakdown spectroscopy (LIBS) for obtaining a high-resolution series of Mg/Ca ratios.

-The stalagmite, which grew from 4.9 to 0.9 ka BP, show significant variations of Mg/Ca, which are primarily driven by changes in the precipitation amount. The calibration of the proxy is supported by the present-day monitoring carried out in the cave for the last 10 years, which reveals a strong inverse relationship between the inter-annual variability of rainfall (and drip-rate) and the Mg concentration of drip-waters and precipitating speleothems.

-The record of paleoprecipitation, based in 2400 Mg/Ca measurements, outlines five successive paleohydrological intervals with consistent trends, and bounded by events that define abrupt shifts in paleoprecipitation. These took place at 4.65, 4.2, 2.6, and 1.3 ka BP.

-Significantly, the intervals of maximum precipitation of the whole record (around 4.9-4.65, 2.6-2.45, and 1.3-1.1 ka BP) can be related with Grand Solar Minima (GSM), and correlated with cold climatic events elsewhere.

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## References

Ayalon A, Bar-Matthews M (2011) Mid-Holocene climate variations revealed by high-resolution speleothem records from Soreq Cave, Israel and their correlation with cultural changes. The Holocene 21:163-171. doi:10.1177/0959683610384165

Baldini JUL, McDermott F, Fairchild IJ (2006) Spatial variability in cave drip water hydrochemistry: Implications for stalagmite paleoclimate records. Chem Geol 235: 390-404. doi: 10.1016/j.chemgeo.2006.08.005

Bernal JP, Lachniet M, McCulloch M, Mortimer G, Morales P, Cienfuegos E (2011) A speleothem record of Holocene climate variability from southwestern Mexico. Quaternary Res 75:104-113. doi:10.1016/j.yqres.2010.09.002

Booth RK, Jackson ST, Forman SL, Kutzbach JE, Bettis III EA, Kreig J, Wright DK (2005). A severe centennial-scale drought in mid-continental North America 4200 years ago and apparent global linkages. The Holocene 15, 321-328. doi: 10.1191/0959683605hl825ft

Cheng H., Edwards RL, Hoff J, Gallup CD, Richards DA, Asmerom Y (2000) The half-lives of uranium-234 and thorium-230. Chem Geol 169: 17–33. doi:10.1016/S0009-2541(99)00157-6

Confederación Hidrográfica del Ebro (2012) Evolución de la temperatura y la precipitación en la cuenca del Ebro. www.chebro.es

Cruz JA, Martín-Chivelet J, Marín-Roldán A, Turrero MJ, Edwards RL, Ortega AI, Cáceres JO (2015) Trace Elements in Speleothems as Indicators of Past Climate and Karst Hydrochemistry: A Case Study from Kaite Cave (N Spain). In: Andreo B, Carrasco F, Durán JJ, Jiménez P, LaMoreaux JW (eds) Hydrogeological and Environmental Investigations in Karst Systems, vol 1. Environ Earth Sci. Springer Berlin Heidelberg, pp 569-577. doi:10.1007/978-3-642-17435-3_64

Cruz Jr FW, Burns SJ, Jercinovic M, Karmann I, Sharp WD, Vuille M (2007) Evidence of rainfall variations in Southern Brazil from trace element ratios (Mg/Ca and Sr/Ca) in a Late Pleistocene stalagmite. Geochim Cosmochim Acta 71:2250-2263. doi:10.1016/j.gca.2007.02.005

Day CC, Henderson GM (2013) Controls on trace-element partitioning in cave-analogue calcite. Geochimica et Cosmochimica Ac 120:612-627. doi: 10.1016/j.gca.2013.05.044

deMenocal PB (2001) Cultural Responses to Climate Change During the Late Holocene. Science 292:667-673. doi:10.1126/science.1059287

Dergachev VA, Raspopov OM, Vasiliev SS (2000) Long-term variability of solar activity during the Holocene. Proc. 1st Solar & Space Weather Euroconference, "The Solar Cycle and Terrestrial Climate", Santa Cruz de Tenerife, Spain (ESA SP-463, December 2000).

Dorale J, Edwards RL, Alexander EC, Jr., Shen C-C, Richards D, Cheng H (2004) Uranium-Series Dating of Speleothems: Current Techniques, Limits, & Applications. In: Sasowsky I, Mylroie J (eds) Stud Cave Sediments. Springer US, pp 177-197. doi:10.1007/978-1-4419-9118-8_10

Edwards RL, Chen JH, Wasserburg GJ (1987) $^{238}U^{234}U^{230}Th^{232}Th$ systematics and the precise measurement of time over the past 500,000 years. Earth Planet Sc Lett 81:175-192. doi:10.1016/0012-821X(87)90154-3

Esper J, Cook ER, Schweingruber FH (2002) Low-Frequency Signals in Long Tree-Ring Chronologies for Reconstructing Past Temperature Variability. Science 295 (5563): 2250-2253. doi: 10.1126/science.1066208

Fairchild IJ, Borsato A, Tooth AF, Frisia S, Hawkesworth CJ, Huang Y, McDermott F, Spiro B (2000) Controls on trace element (Sr–Mg) compositions of carbonate cave waters: implications for speleothem climatic records. Chem Geol 166:255-269. doi:10.1016/S0009-2541(99)00216-8

Fairchild IJ, Treble PC (2009) Trace elements in speleothems as recorders of environmental change. Quaternary Sci Rev 28:449-468. doi:10.1016/j.quascirev.2008.11.007

Fortes FJ, Vadillo I, Stoll H, Jimenez-Sanchez M, Moreno A, Laserna JJ (2012) Spatial distribution of paleoclimatic proxies in stalagmite slabs using laser-induced breakdown spectroscopy. J Anal Atom Spectrom 27:868-873. doi:10.1039/c2ja10299d

Gascoyne M (1983) Trace-element partition coefficients in the calcite-water system and their paleoclimatic significance in cave studies. J Hydrol 61:213-222. doi:10.1016/0022-1694(83)90249-4

Hammer Ø, Harper DAT, Ryan PD (2006) PAST - PAlaeontological STatistics, ver. 1.58. December 7, 2006

Huang Y, Fairchild IJ (2001) Partitioning of $Sr^{2+}$ and $Mg^{2+}$ into calcite under karst-analogue experimental conditions. Geochim Cosmochim Ac 65:47-62. doi:10.1016/S0016-7037(00)00513-5

Jalut G, Dedoubat JJ, Fontugne M, Otto T (2009) Holocene circum-Mediterranean vegetation changes: Climate forcing and human impact. Quatern Int 200:4-18 doi:10.1016/j.quaint.2008.03.012

Jalut G, Esteban Amat A, Bonnet L, Gauquelin T, Fontugne M (2000) Holocene climatic changes in the Western Mediterranean, from south-east France to south-east Spain Palaeogeogr Palaeocl 160:255-290 doi:10.1016/S0031-0182(00)00075-4

Johnson KR, Hu C, Belshaw NS, Henderson GM (2006) Seasonal trace-element and stable-isotope variations in a Chinese speleothem: The potential for high-resolution paleomonsoon reconstruction Earth Planet Sc Lett 244:394-407 doi:10.1016/j.epsl.2006.01.064

Ljungqvist FC (2010) A new reconstruction of temperature variability in the extra-tropical northern hemisphere during the last two millennia. Geografiska Annaler: Series A, Physical Geography 92:339-351. doi:10.1111/j.1468-0459.2010.00399.x

Luetscher M, Hoffmann DL, Frisia S, Spötl C (2011) Holocene glacier history from alpine speleothems, Milchbach cave, Switzerland. Earth Planet Sc Lett 302:95-106. doi:10.1016/j.epsl.2010.11.042

Marín-Roldán A, Cruz JA, Martín-Chivelet J, Turrero MJ, Ortega AI, Cáceres JO (2014) Evaluation of Laser Induced Breakdown Spectroscopy (LIBS) for detection of trace element variation through stalagmites: potential for paleoclimate series reconstruction. J Appl Las Spectrosc 1:7-12

Martín-Chivelet J, Muñoz-García MB, Edwards RL, Turrero MJ, Ortega AI (2011) Land surface temperature changes in Northern Iberia since 4000 yr BP, based on δ13C of speleothems. Global Planet Change 77:1-12. doi:10.1016/j.gloplacha.2011.02.002

Martin-Puertas C, Matthes K, Brauer A, Muscheler R, Hansen F, Petrick C, Aldahan A, Possnert G, van Geel B. (2012) Regional atmospheric circulation shifts induced by a grand solar minimum. Nature Geosci 5:397-401. doi:10.1038/ngeo1460

Nielsen LC, De Yoreo JJ, DePaolo DJ (2013) General model for calcite growth kinetics in the presence of impurity ions. Geochim Cosmochim Ac 115:100-114. doi:10.1016/j.gca.2013.04.001

Scholz D, Hoffmann DL (2011) StalAge – An algorithm designed for construction of speleothem age models. Q Geochron. 6:369-382 doi:10.1016/j.quageo.2011.02.002

Shen G, Wang W, Wang Q, Zhao J, Collerson K, Zhou C, Tobias PV (2002) U-Series dating of Liujiang hominid site in Guangxi, Southern China. J Hum Evol 43:817-829. doi:10.1006/jhev.2002.0601

Sinclair DJ, Banner JL, Taylor FW, Partin J, Jenson J, Mylroie J, Goddard E, Quinn T, Jocson J, Miklavič B (2012) Magnesium and strontium systematics in tropical speleothems from the Western Pacific. Chem Geol 294–295:1-17. doi:10.1016/j.chemgeo.2011.10.008

Steinhilber F, Beer J, Fröhlich C (2009) Total solar irradiance during the Holocene. Geophysical Res Lett 36:L19704. doi:10.1029/2009gl040142

Swindles GT, Plunkett G, Roe HM (2007) A delayed climatic response to solar forcing at 2800 cal. BP: multiproxy evidence from three Irish peatlands. The Holocene 17:177-182. doi:10.1177/0959683607075830

Tooth AF, Fairchild IJ (2003) Soil and karst aquifer hydrological controls on the geochemical evolution of speleothem-forming drip waters, Crag Cave, southwest Ireland. J Hydrol 273:51-68. doi:10.1016/S0022-1694(02)00349-9

Treble P, Shelley JMG, Chappell J (2003) Comparison of high resolution sub-annual records of trace elements in a modern (1911–1992) speleothem with instrumental climate data from southwest Australia. Earth Planet Sci Lett 216:141-153. doi:10.1016/S0012-821X(03)00504-1

Tremaine DM, Froelich PN (2013) Speleothem trace element signatures: A hydrologic geochemical study of modern cave dripwaters and farmed calcite. Geochim Cosmochim Ac 121:522-545. doi:10.1016/j.gca.2013.07.026

Triantaphyllou MV, Gogou A, Bouloubassi I, Dimiza M, Kouli K, Rousakis G, Kotthoff U, Emeis KC, Papanikolaou M, Athanasiou M, Parinos C, Ioakim C, Lykousis V (2014) Evidence for a warm and humid Mid-Holocene episode in the Aegean and northern Levantine Seas (Greece, NE Mediterranean). Reg Environ Change 14:1697-1712. doi:10.1007/s10113-013-0495-6

Trouet V, Esper J, Graham NE, Baker A, Scourse JD, Frank DC (2009) Persistent Positive North Atlantic oscillation mode dominated the Medieval Climate Anomaly. Science 324: 78-80. doi: 10.1126/science.1166349

Turrero MJ, Garralón A, Martín-Chivelet J, Gómez P, Sánchez L, Quejido A, Ortega AI, Martín-Merino MA (2004) Seasonal changes in the chemistry of drip waters in Kaite Cave (N Spain). In: Wanty RB, Seal II RS (Eds) Water–Rock Interaction 11 Balkema Publishers London pp 1407–1410

Turrero MJ, Garralón A, Gómez P, Sánchez L, Martín-Chivelet J, Ortega AI (2007) Geochemical evolution of drip-water and present-growing calcite at Kaite Cave (N Spain). In:

Bullen TD, Wang YX (Eds) Water-Rock Interaction 12 Balkema Publishers Rotterdam pp 1187–1190

Turrero MJ, Garralón A, Sánchez L, Ortega AI, Martín-Chivelet J, Gómez P, Escribano A (2015) Variations in Trace Elements of Drip Waters in Kaite Cave (N Spain): Significance in Terms of Present and Past Processes in the Karst System. In: Andreo B, Carrasco F, Durán JJ, Jiménez P, LaMoreaux JW (eds) Hydrogeological and Environmental Investigations in Karst Systems, vol 1. Environ Earth Sci. Springer Berlin Heidelberg, pp 579-586. Springer-Verlag Berlin Heidelberg 2015. doi 10.1007/978-3-642-17435-3_65

Vadillo JM, Vadillo I, Carrasco F, Laserna JJ (1998) Spatial distribution profiles of magnesium and strontium in speleothems using laser-induced breakdown spectrometry. Fresenius J Anal Chem 361:119-123. doi:10.1007/s002160050846

Vasiliev SS, Dergachev VA (2002) The ~2400-year cycle in atmospheric radiocarbon concentration: bispectrum of $^{14}C$ data over the last 8000 years. Ann. Geophys 20 (1): 115–20. doi:10.5194/angeo-20-115-2002

Wang Y, Cheng H, Edwards RL, He Y, Kong X1, An Z, Wu J, Kelly MJ, Dykoski CA, Li X (2005) The Holocene Asian Monsoon: Links to Solar Changes and North Atlantic Climate. Science 308:854-857. doi:10.1126/science.1106296

Wanner H, Mercolli L, Grosjean M, Ritz SP (2015) Holocene climate variability and change; a data-based review. J Geol Soc 172:254-263 doi:10.1144/jgs2013-101

Wanner H, Solomina O, Grosjean M, Ritz SP, Jetel M (2011) Structure and origin of Holocene cold events. Quaternary Sci Rev 30:3109-3123. doi:10.1016/j.quascirev.2011.07.010

Weiss H, Courty M-A, Wetterstrom W, Guichard F, Senior L, Meadow R, Curnow A (1993) The Genesis and Collapse of Third Millennium North Mesopotamian Civilization. Science 261:995-1004. doi:10.1126/science.261.5124.995

**Figure Captions**

**Fig 1** a) Location map of the Kaite Cave in northern Spain. b) Longitudinal section of the stalagmite Buda-100, used in this study, which was retrieved from the Buda Hall in the Kaite Cave (Ojo Guareña Karst Complex, Burgos province).

**Fig 2** a) Experimental setup for the measurements by laser induced breakdown spectroscopy (LIBS). (b) Example of polished thick section of the stalagmite used for LIBS measurements, in which the microcraters produced by the laser beam on the sample can be observed. (c) Example of spectrum obtained by LIBS, which results from the average of 20 laser pulses at each single position. (d) Detail of the emission peaks, from which the Mg/Ca activity ratio is calculated.

**Fig 3** Experimental tests performed to check the quality and reliability of the analytical data obtained by LIBS in the speleothem. (a) *Lateral homogeneity test*: The graph shows the Mg/Ca intensity ratio measured in 12 points along a single growth layer of the stalagmite, performed to check the lateral homogeneity. Note that the values are remarkably homogeneous except for the points 3 and 4. As can be observed in the microphotograph, these two outliers are produced by a small error in the positioning of the sample, which determined that the laser beam was focused slightly out of the selected micrometric layer. These analyses average the Mg/Ca ratio of the two successive layers. (b) *Replicability test*: Mg/Ca intensity ratios measured for 80 single points along two transects parallel to the growth axis show excellent replicability of the geochemical series. Minor differences between the two records are mainly due to the high resolution of the LIBS micro-sampling and the high variability of the Mg/Ca ratios in the stalagmite at that micrometric scale. (c) *Plasma temperature test*: The plasma temperature was checked by monitoring the ratio of two atomic spectral lines in the LIBS experiment: Ca (I) at 430.8 nm and Ca (I) at 445.4 nm (ICa430.8/ICa445.4). The graphs show nearly constant temperature of the plasma during the experimental measurements, which minimizes the matrix effect and provides more accurate results. (d) Comparison of LIBS results with inductively coupled plasma-optical emission spectroscopy (ICP-OES). The graph allows a visual comparison of LIBS data performed for a segment of the stalagmite and the ICP-OES data performed for the same interval. The correlation is very good, particularly if we consider the strongly different amount of sample required for each analytical technique (milligrams in the case of the ICP, few micrograms in the case of LIBS) and in the different lapse of time represented in the analyzed sample in each case (10-20 years for the ICP vs. one year or less for LIBS).

**Fig 4** A long-term (10 years) record of mean annual calcium concentration and Mg/Ca molar ratio from dripwaters collected seasonally from two points of different drip-rate in Las Velas Hall, Kaite Cave (N Spain) for the period 2002-2012. Dotted lines indicates the drip-rate decreasing and Mg/Ca ratio increasing trends which are consistent with a long-term prior calcite precipitation process as a consequence of a continuous decreasing of recharge in the area in the time interval analyzed, as explained in the text.

**Fig 5** Age depth model obtained with StalAge (Scholz and Hoffmann, 2011) for Buda-100 stalagmite, based on the $^{230}$Th ages of Table I.

**Fig 6** Mg/Ca time series for stalagmite Buda-100, based in 2400 Mg/Ca measurements which were time-scaled with the age model of Figure 5. The red line represents the 9-term running average. The five main paleohydrological intervals described in the text and their general trends are also shown. The Mg/Ca series is interpreted in terms of regional paleohydrological changes through time (see text for discussion).

**Fig 7** Spectral diagram performed for the Mg/Ca series of stalagmite Buda-100. Spectral analyses were performed with the Lomb periodogram algorithm, indicated for unevenly spaced time series (PAST software, Hammer et al., 2006). Numbers labelled in the diagram indicate periodicities (in ky) of the main spectral peaks. The 0.01 and 0.05 significance levels ("white noise lines") are shown.

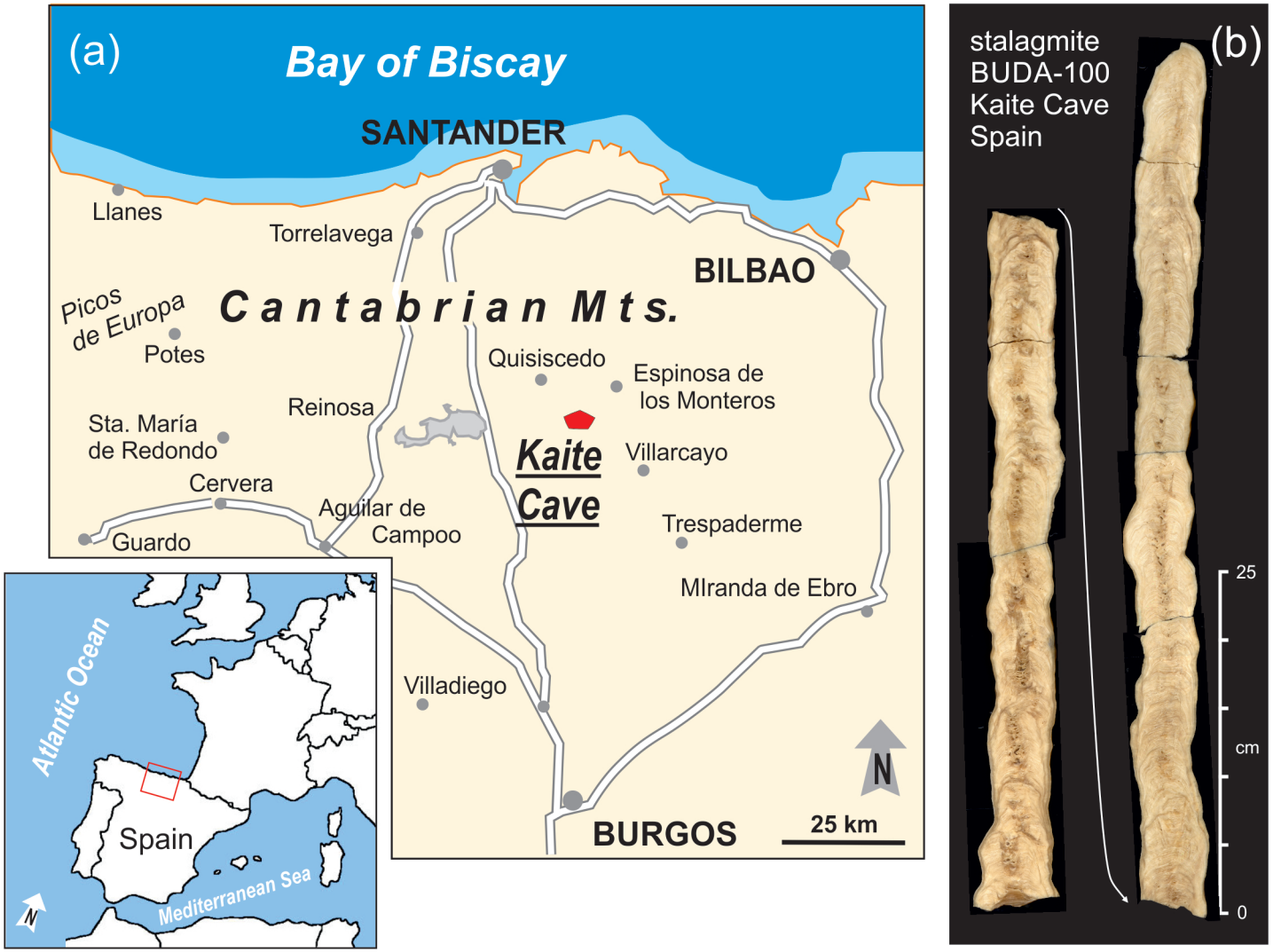
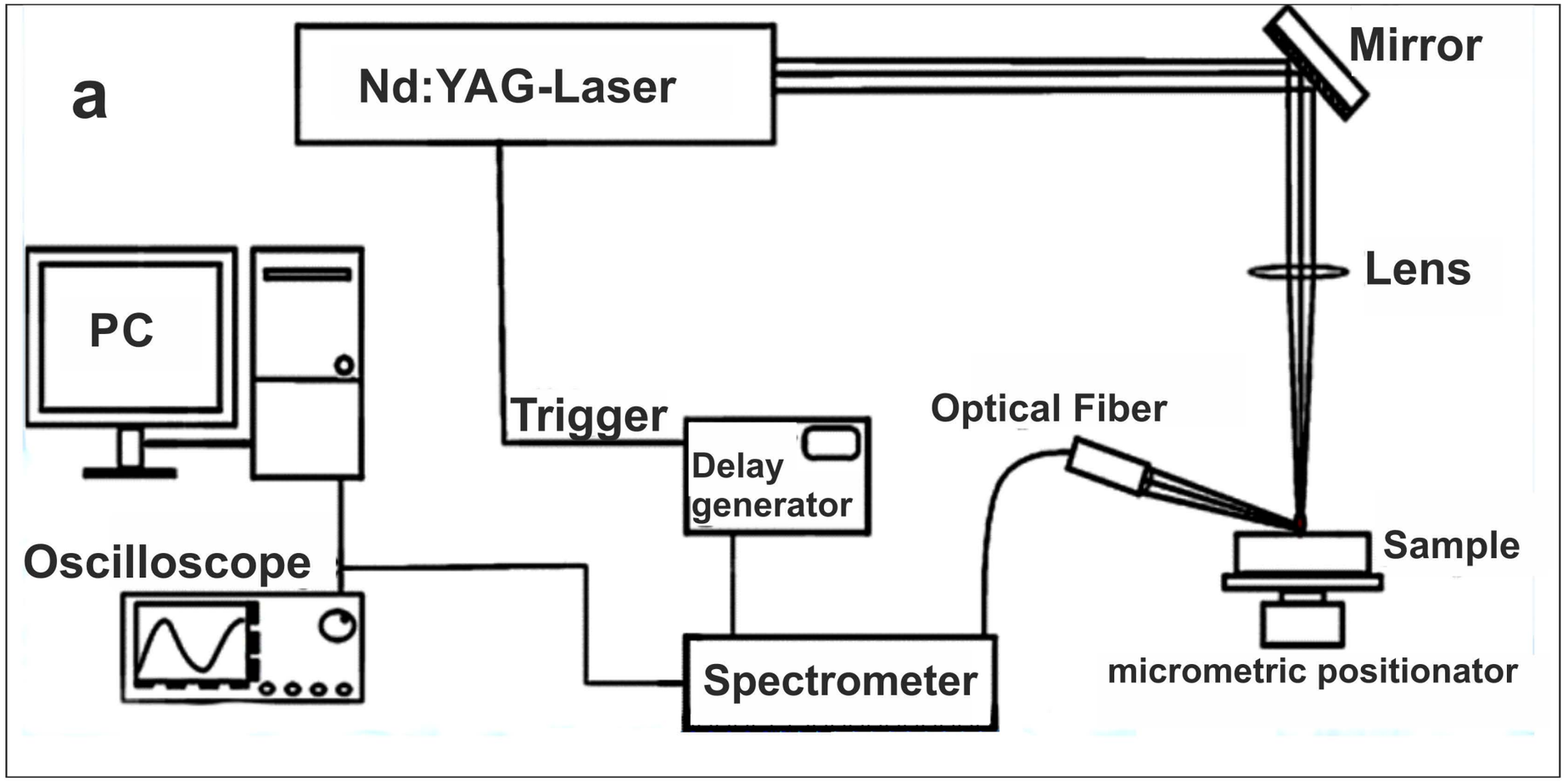
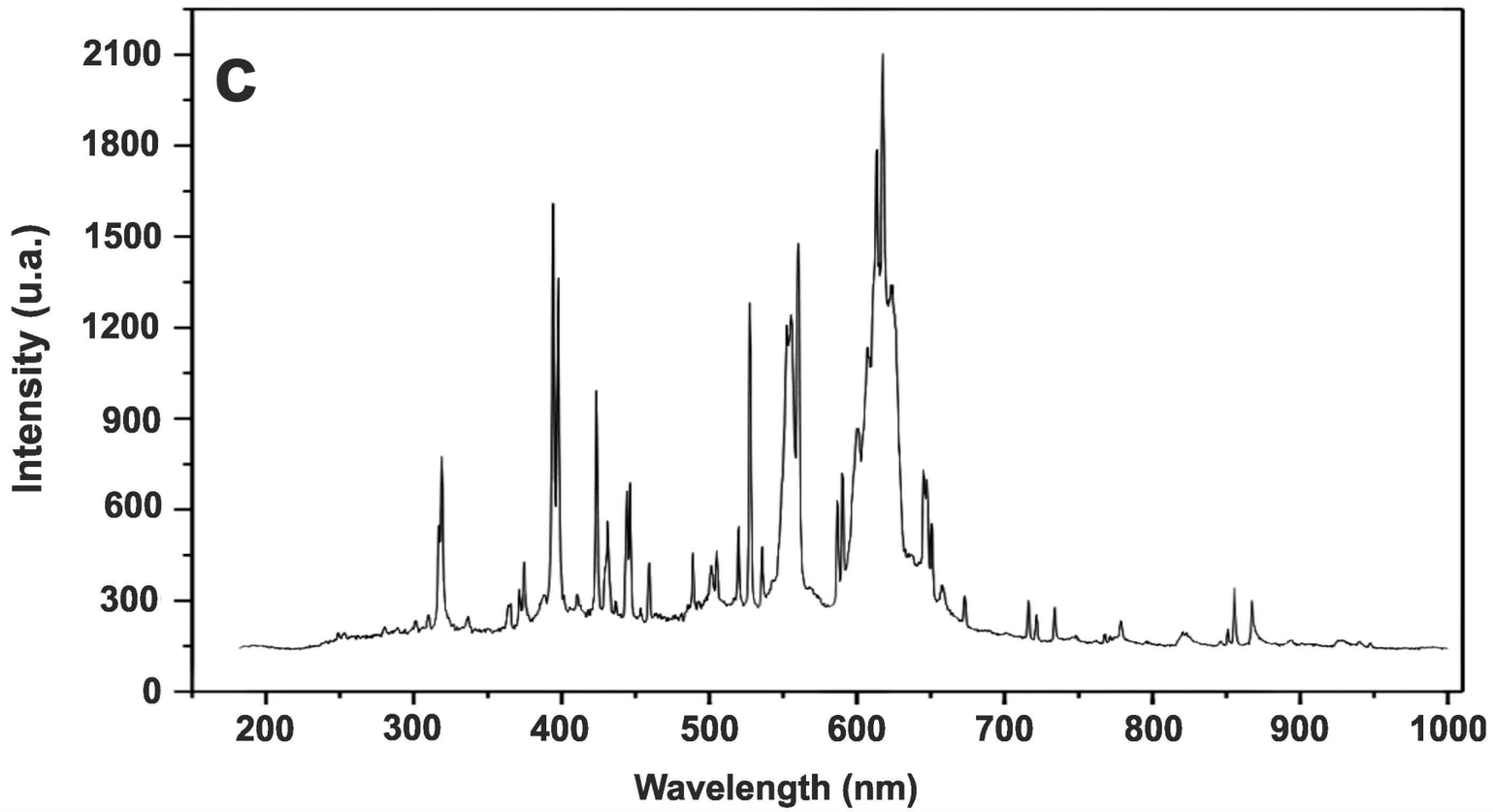
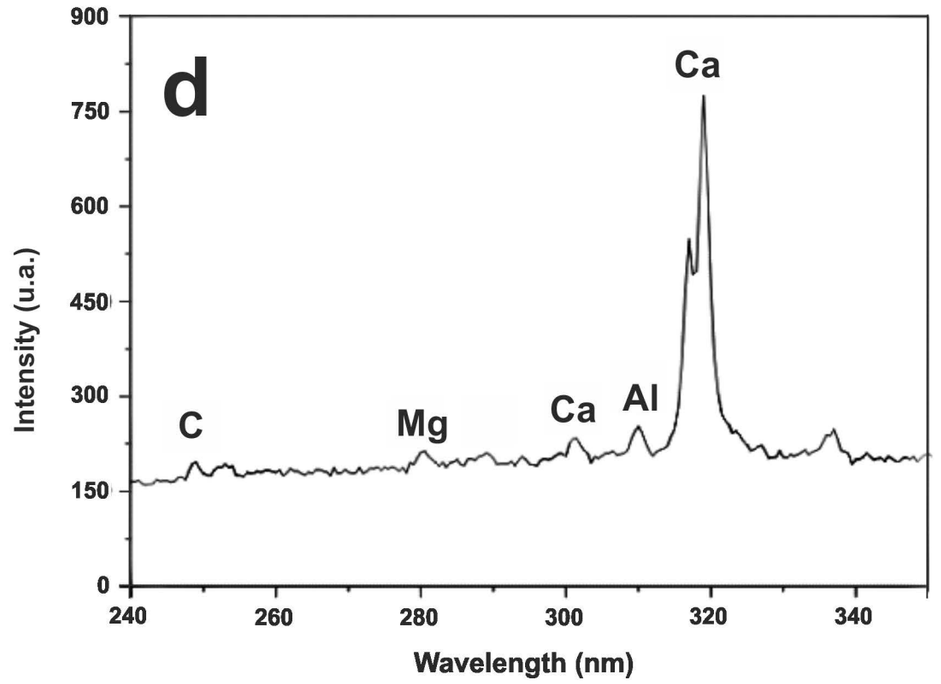



Figure 1 Cruz et al

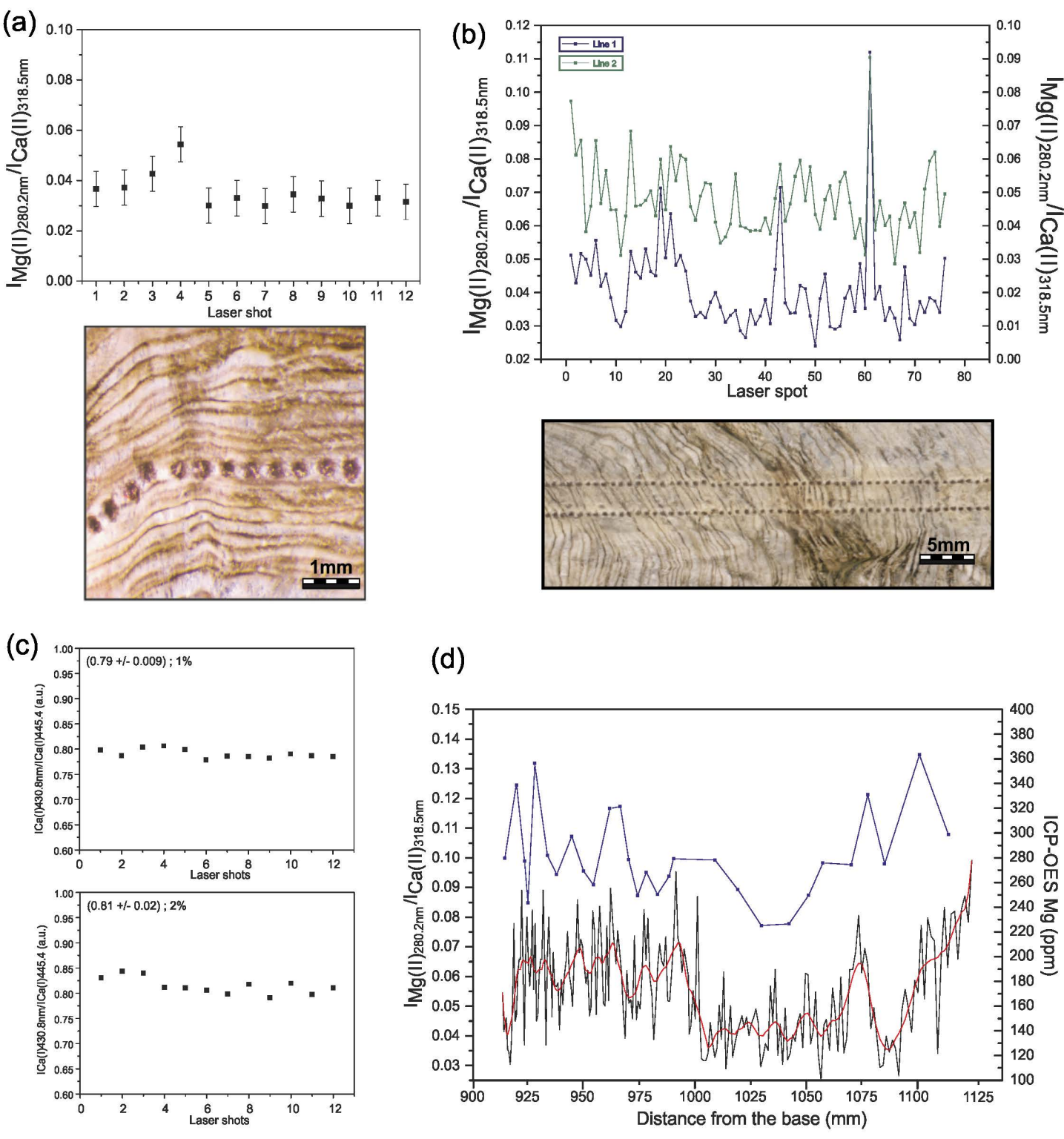




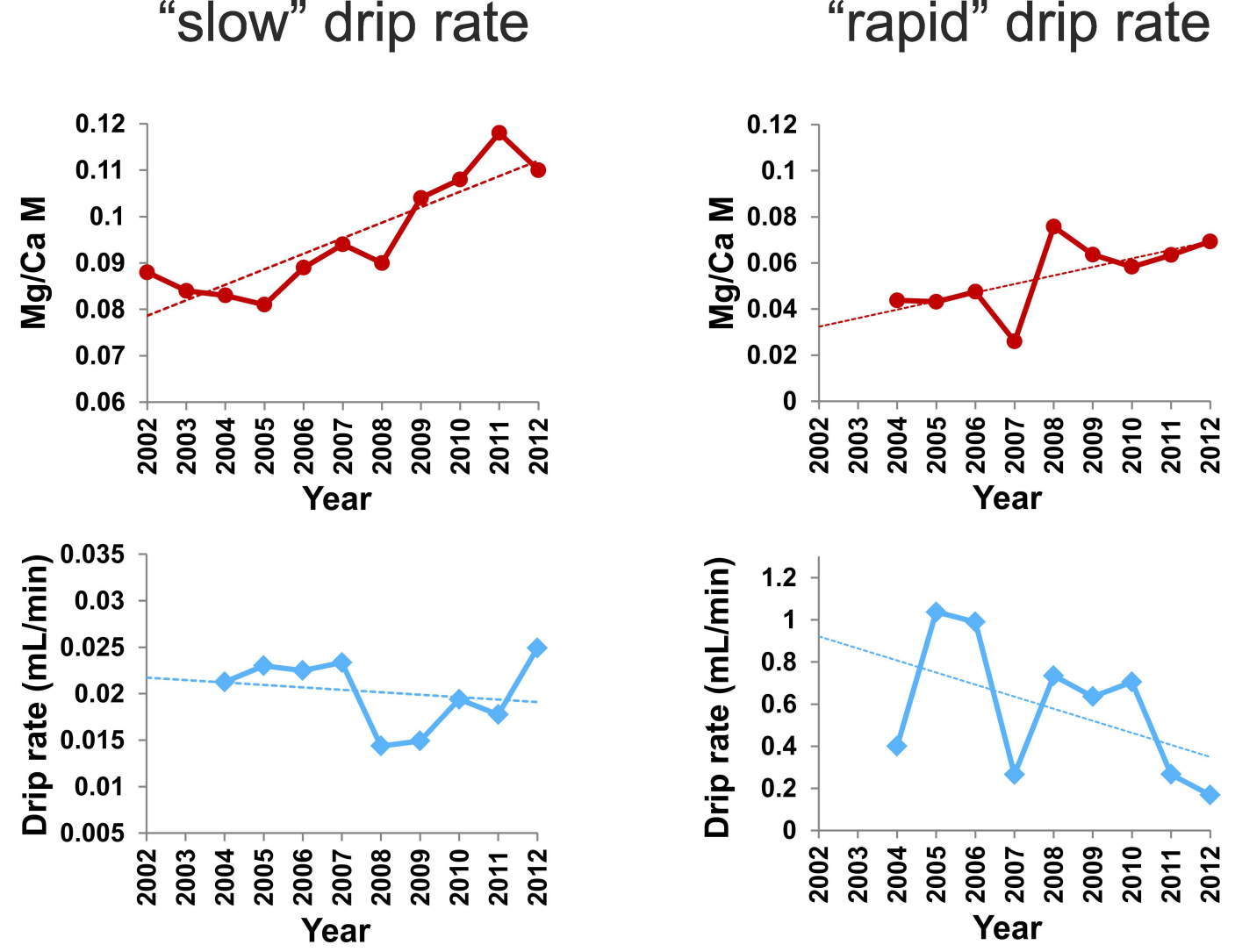


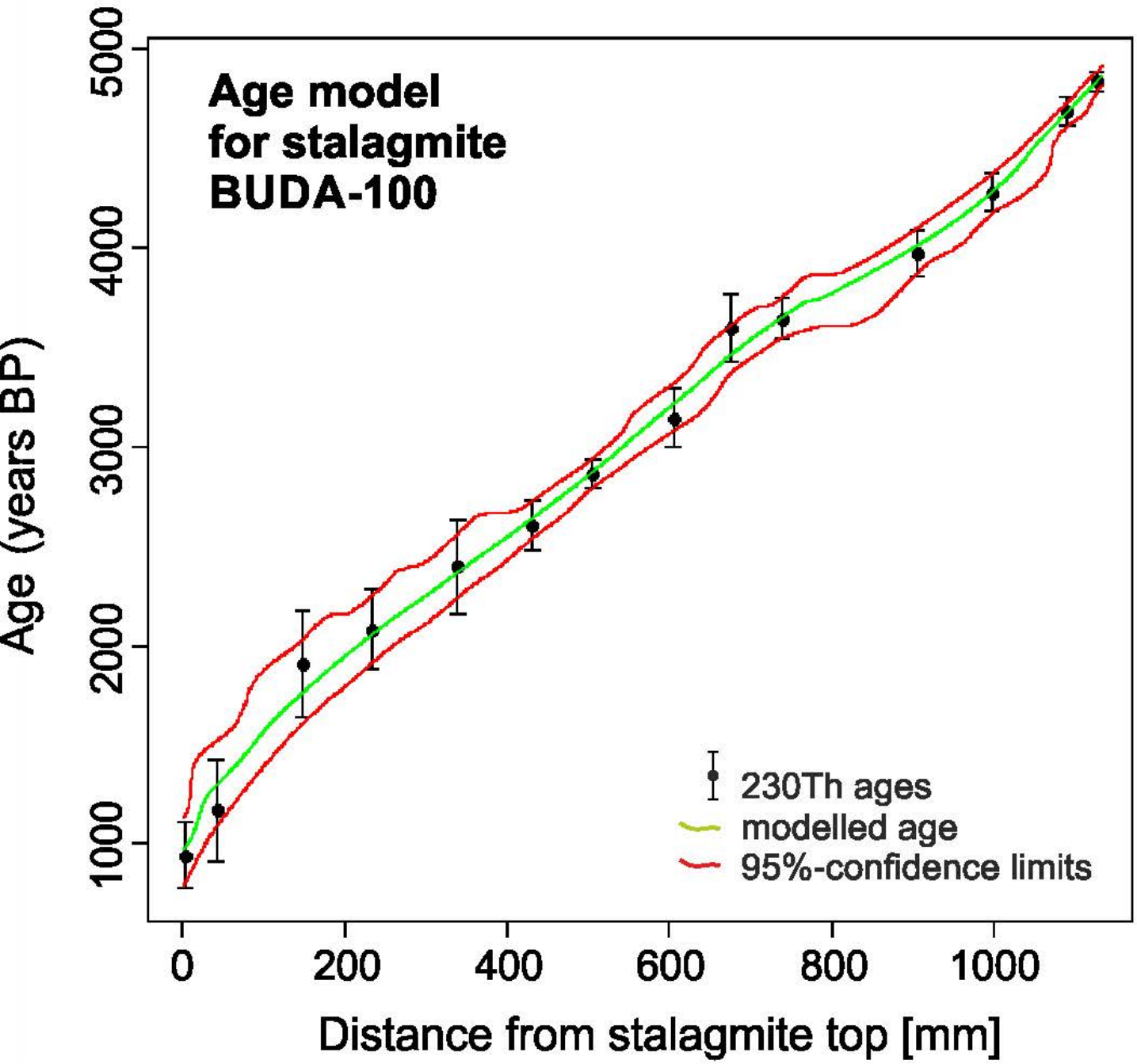




Cruz et al Figure 2

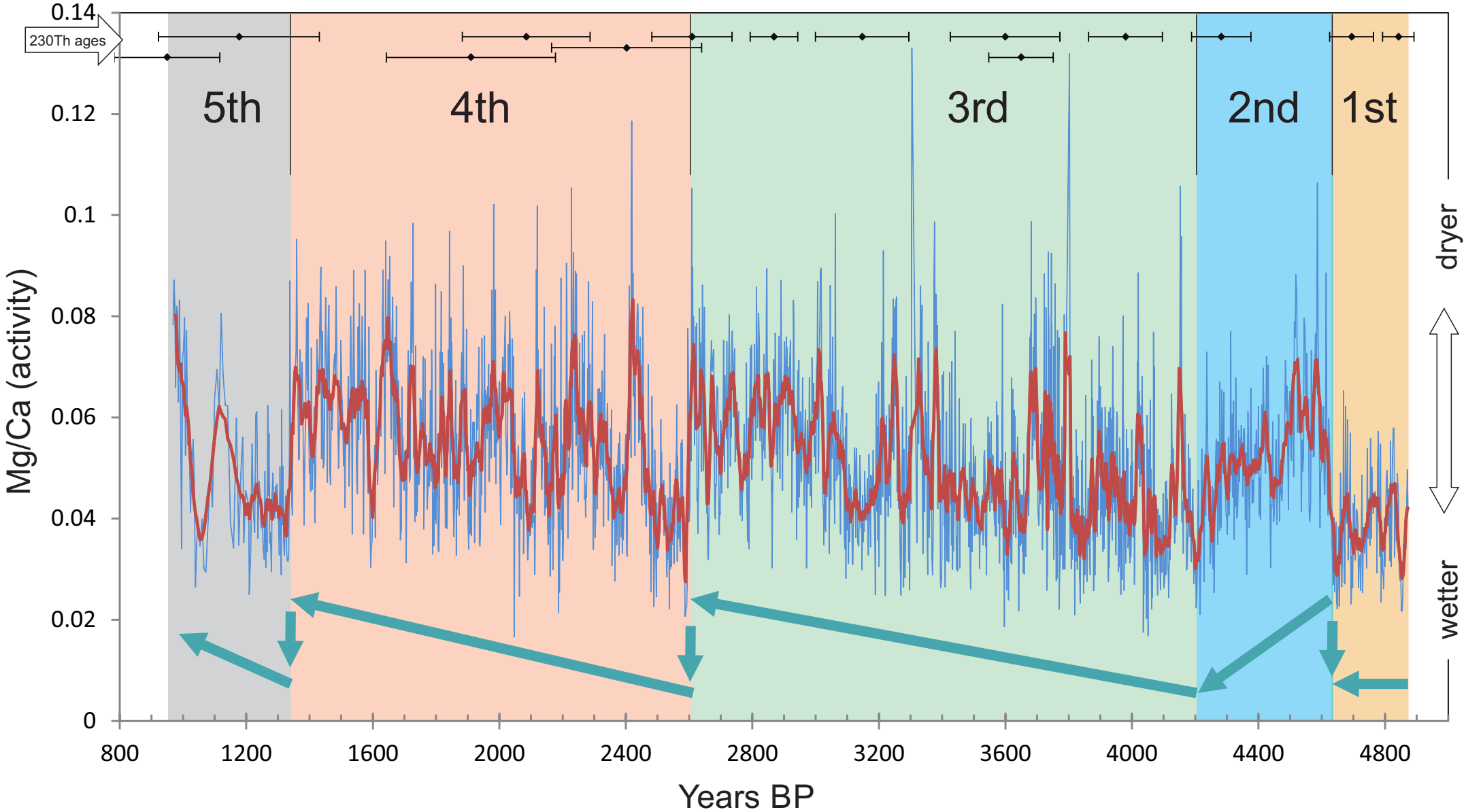



Cruz et al figure 3

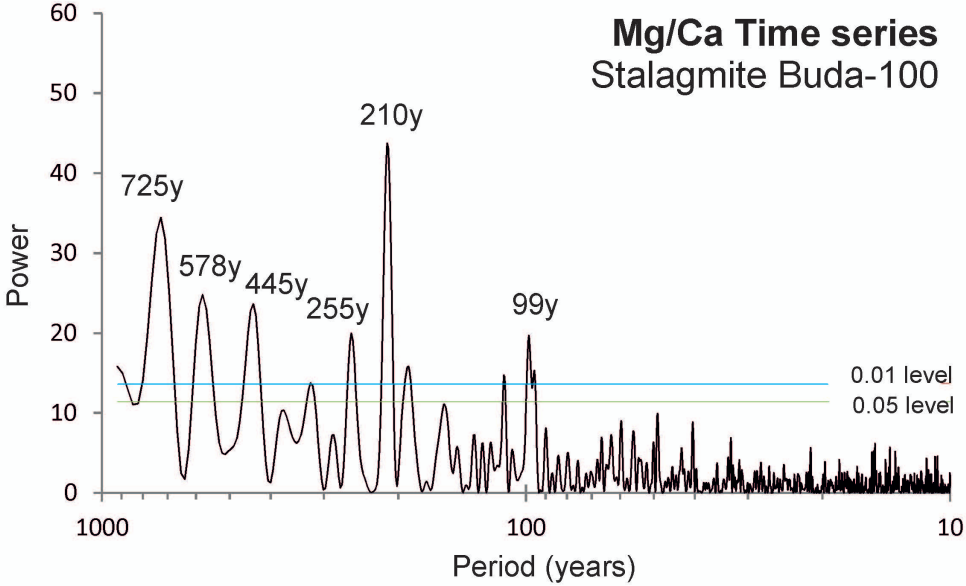

"slow" drip rate
"rapid" drip rate
Mg/Ca M
Drip rate (mL/min)
Year
0.12
0.11
0.1
0.09
0.08
0.07
0.06
0.04
0.02
0
0.035
0.03
0.025
0.02
0.015
0.01
0.005
1.2
1
0.8
0.6
0.4
0.2
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011
2012




CRUZ ET AL FIGURE 5




CRUZ ET AL FIGURE 6


Mg/Ca Time series
Stalagmite Buda-100
60
50
40
30
20
10
0
Power
725y
578y
445y
255y
210y
99y
0.01 level
0.05 level
1000
100
10
Period (years)