Annual trace element cycles in calcite–aragonite speleothems: evidence of drought in the western Mediterranean 1200–1100 yr BP

EMILY A. McMILLAN,1* IAN J. FAIRCHILD,2 SILVIA FRISIA,3 ANDREA BORSATO3 and FRANK McDERMOTT4

1 School of Earth Sciences and Geography, Keele University, Staffordshire ST5 5BG, UK
2 School of Geography, Earth and Environmental Sciences, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK
3 Museo Tridentino di Scienze Naturali, via Calepina 14, 38100 Trento, Italy
4 Department of Geology, University College Dublin, Belfield, Dublin 4, Ireland


ABSTRACT: Each of two calcitic stalagmites from Grotte de Clamouse, Herault, southern France, displays a discrete aragonite layer dated at around 1100 yr BP. The layer of fanning aragonite crystals is immediately preceded by calcite with Mg and Sr compositions that are uniquely high for the past 3 kyr. Trace element compositions close to the boundary between original aragonite and calcite are consistent with quasi-equilibrium partitioning of trace elements between the phases. Study of modern dripwaters demonstrates that pronounced covariation of Mg/Ca and Sr/Ca ratios in dripwater occurs owing to large amounts of calcite precipitation upflow of the drips that fed the stalagmites. Trace element to Ca ratios are enhanced during seasonally dry periods. Ion microprobe data demonstrate a pronounced covariation of trace elements, including Mg and Sr in calcite, and Sr, U and Ba in aragonite. The mean peak spacing is close to the long-term mean of annual growth rates determined by differences in U-series ages and so the trace element peaks are interpreted as annual. The trace element chemistry of the stalagmites on annual to inter-annual scales thus directly reflects the amounts of prior calcite precipitation, interpreted as an index of aridity. The longer-term context is a multi-decadal period of aridity (1200–1100 yr BP) possibly correlated with an analogous episode in Central America. The arid period culminated in the nucleation of aragonite, but within a decade was followed by a return to precursor conditions. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: stalagmites; annual laminae; trace elements; aridity; palaeoprecipitation.

Introduction

Speleothems grow in a manner that enables them to incorporate geochemical signals indicative of the physical environment in which they grew. Consequently, numerous proxy measures are available for utilisation from speleothem carbonate, potentially yielding high-resolution palaeoclimatic data. Many palaeoclimatic studies on speleothem calcite have tended to focus on stable isotope records (Gascoyne, 1992; McDermott, 2004) and these records interpreted in terms of palaeotemperature or atmospheric circulation (δ18O) and vegetation characteristics (δ13C). Trace element variations in cave waters and speleothems are now better understood in terms of processes (Gascoyne, 1983; Ayalon et al., 1999; Fairchild et al., 2000). Improvements in instrumentation have permitted micrometre-scale analyses on speleothem carbonate facilitating the production of annual to sub-annual resolution trace element records (Roberts et al., 1998, Huang et al., 2001, Finch et al., 2001; Kuczmunow et al., 2003). Annual cycles in trace elements appear to be a normal feature of speleothems from shallow karstic environments (Fairchild et al., 2001). Finch et al. (2003) and Treble et al. (2003) showed a positive relationship between Sr and Ba concentration and rainfall, derived from high-resolution analyses and instrumental records of rainfall variation over the historical period in examples of an aragonitic speleothem from South Africa and a calcitic speleothem from Australia. When combined with high precision U-series dating methods, high-resolution trace element analyses thus offer the potential to provide a tightly constrained palaeoclimatic proxy (Baldini et al., 2002).

The annual nature of trace element cycles has usually been demonstrated by comparison with physical laminae of known annual origin, typically constrained by U-series dating. These physical laminae can be visible optically, or under UV fluorescence, or both (Roberts et al., 1998; Fairchild et al., 2001; Frisia et al., 2003).
Mineralogical change within speleothems is relatively rare and therefore the majority of trace element data refers to primary speleothem calcite. However, annual couplets of calcite and aragonite with seasonally increasing Mg/Ca ratios have been reported from a speleothem from Botswana, and linked to variations in rainfall (Railsback et al., 1994). Finch et al. (2001, 2003) carried out a comprehensive evaluation of the potential for meaningful palaeoclimatic data from trace element variations in speleothem aragonite. They identified a relationship between Sr and Ba which they determined to be representative of variations in rainfall, but found both lateral and vertical variations in composition and as a result meaning-ful relationships were only obtained by averaging out lateral changes. The lateral and vertical trace element variations could reflect sector zoning or growth competition between forms.

Covariations or antipathetic variations in particular elements, for example Mg, Sr, Ba and U, are commonly observed in speleothem calcium carbonate trace element records, but the causes of their variation can be complex (Treble et al., 2003) owing to non-equilibrium incorporation, the presence of micro-domains and the possibility of replacement phenomena. This situation is not helped by the common absence of information on equivalent cave water chemistry. In the case of Sr and Ba, crystal growth kinetics are thought to hold significant influence over their incorporation into speleothem carbonate (Lorens, 1981; Finch et al., 2003; Treble et al., 2003).

Kinetic effects may dominate the incorporation of other trace elements (Fairchild et al., 2001) which, for reasons of ion size (e.g. Mg in aragonite) or charge, do not simply substitute for Ca in the CaCO3 lattice. The incorporation and behaviour of Mg in speleothem calcite is particularly well understood. Its presence is highly dependent on such processes as the amount and extent of prior calcite precipitation in the aquifer overlying the cave, the residence time of storage water in the aquifer and the subsequent supersaturation of the water (Roberts et al., 1998; Hellstrom and McCulloch, 2000; Fairchild et al., 2000; Huang and Fairchild, 2001). The implication is that enhanced Mg can often be interpreted in terms of relatively dry climatic conditions. In this respect, the prior calcite precipitation mechanism is particularly important and is of interest because it affects Sr similarly to Mg. Under relatively dry conditions, cave waters can degas CO2 and promote calcite precipitation. This causes changes in the Mg/Ca and Sr/Ca content of the waters. For Mg (and likewise for Sr):

\[ (Mg/Ca)_{\text{Caco3}} = (Mg/Ca)_{\text{water}} \times D_{Mg} \]

where \( D \) is a partition coefficient that in the case of Mg is thought to vary only with temperature (Huang and Fairchild, 2001). Values for \( D \) are much less than 1 for Mg and Sr and so solutions that have precipitated calcite develop enhanced Mg/Ca and Sr/Ca ratios. Given a particular primary water composition, and knowledge of the value of \( D \), the amount of prior calcite precipitation can be calculated.

In this paper we show how trace element data can be used to characterise a distinctive climatic event recorded in two speleothem samples from the Grotte de Clamouse in southern France. Previous studies on the samples (Frisia et al., 1997, 2002; McDermott et al., 1999) tentatively identified an arid period around 1100 yr BP. This was based on unpublished Mg and Sr data and the occurrence of an aragonite layer, thought to be largely replaced by calcite, but with evidence of preservation of primary \( ^{13}C \) and U contents on a macro-scale. Here we present both low- and high-resolution trace element data, and show how the annual scale of variation strengthens the interpretation of an arid event that may have had regional (Jalut et al., 2000) or even intercontinental (Street-Perrott et al., 2000; Haug et al., 2003) extent.

Site description and modern monitoring

Two stalagmites, CL26 and CL27, 450 and 600 mm long respectively, were collected from Le Balcon and the Grande Carrefour in the uppermost, non-touristic part of Grotte de Clamouse, a cave situated ~30 km west of Montpellier, France (latitude 43° 42′ 33″ N, longitude 3° 36′ 50″ E) (Frisia et al., 1997). Figure 1(A) shows a plan of Grotte de Clamouse and the sampling locations therein. The stalagmites come from cave passages cut in Middle Jurassic oolitic dolomites which have experienced varying degrees of de-dolomitisation (Fairchild et al., 2000). Humidity in the cave passages containing both aragonite and calcite speleothems is relatively stable at 97.5–99% (Frisia et al., 1997).

The cave is set in a typical Mediterranean climate characterised by average annual temperatures of around 14.5°C, mean annual precipitation averaging 766 mm per year with strong seasonality, and prolonged dry summers followed by wetter winter months (Fig. 1(B)). Evaporation often exceeds precipitation during the summer (July–August) resulting in a marked water deficit during this time. Nevertheless, Fairchild et al. (2000) recorded little short-term variation in drip rates indicating a high proportion of storage water in the overlying aquifer. Long residence-time of drip water in the aquifer combined with the porous nature of the bedrock allows the water to de-gas and precipitate calcite along the water flow line above the cave passage, as indicated by strong covariation between Mg/Ca and Sr/Ca ratios in cave dripwater (Fairchild et al., 2000). In principle, this effect should be enhanced during periods of dry weather owing to reduced aquifer recharge causing the composition of the water to evolve away from that which would represent a mixture of calcite and dolomite bedrock (Fig. 1(C)). There is direct evidence or prior calcite precipitation from a reduction in continuously logged electroconductivity during a dry period in late summer 1996. However, we have insufficient measurements of dripwater chemistry and flowrate to be certain of the length of time during which this process occurs during the hydrological year. Fairchild et al. (2000) proposed that, given constant partition co-efficients, Mg/Ca and Sr/Ca ratios of modern-day Clamouse dripwater will be captured in the Mg and Sr contents of speleothem calcite, thus providing a framework for the interpretation of any such patterns found in fossil speleothems.

Both CL26 and CL27 were active when sampled. Their Holocene portions are predominantly made of calcite, but they contain discrete layers of aragonite on average 1–2 mm thick (Fig. 2). The ages of the CL27 and CL26 aragonite layers have been obtained using U-series techniques and are 1167 yr (1122 yr BP) ± 3 for CL26, and 1116 yr (1071 yr BP) ± 4 for CL27 (McDermott et al., 1999; Frisia et al., 2002). The small error estimates reflect the high U content of the samples, but they are based only on internal precision (within-run counting statistics), whereas a more realistic estimate of the error (external precision) is around 18 years, allowing for spike calibration uncertainties.

Methods

ICP analysis

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis was carried out on powders drilled at 2 mm intervals along the growth axis of CL26 and CL27 for
initial trace element analysis. Ten milligrams of powder was dissolved in 1 ml of 5% v/v Aristar Grade mineral acid and topped up to 10 ml. Material from the same powder samples was used for $^{14}C$ and $^{13}C$ stable isotope analysis (McDermott et al., 1999).

SEM analysis

Scanning electron microscope (SEM) analysis was carried out using secondary electron and backscattered electron images at the University of Birmingham using a Philips XL30 ESEM-FEG. The Environmental SEM is used as it offers greater stability, reduced charging effects of non-conductive materials and greater sensitivity for materials with low atomic number.

Thin sections were coated with carbon before being mounted on a stage and put in the sample chamber under vacuum. We used a 25-kV setting as this provided an optimum level of energy to highlight the subtle differences in mean atomic number between calcite and original aragonite when viewed using backscattered electron imagery.

Micro-mineralogical determinations of the primary aragonite layer in a thin section of CL26 were carried out by electron backscatter diffraction (EBSD) using an HKL Channel5 EBSD system on a Phillips XL30CP SEM at Edinburgh University. The mechanical polish was followed by a final colloidal silica polish to remove surface crystal damage and the sample was un-coated. An area around 2 by 1.5 mm was analysed at 4.5 $\mu$m intervals and the electron diffraction patterns solved to differentiate calcite from aragonite.

Ion microprobe analysis

The ion microprobe secondary ion mass spectrometry (SIMS) technique was used for trace element analysis as it offers high spatial resolution and low detection limits for elements that typically define annual layers in speleothems (Roberts et al.,...
Analyses were done on the Cameca ims-4f ion microprobe based within the School of Geosciences, Edinburgh University, on 150 μm thick gold-coated thin sections, using positive secondary ions. The step scan mode was used in which the ion beam moves in automated steps set at predetermined spatial intervals. In this paper, the term ‘ion microprobe track(s)’ refers to step scan analyses, which form a continuous line on the sample, but are made up of discrete steps at 5-μm spacing. Fairchild et al. (2001) give a detailed summary of the operational methods of the ion microprobe, therefore only the specific analytical conditions used for each analysis will be mentioned here. We used an image field of 150 μm and the smallest field aperture, which gave a nominal diameter of the area being analysed of 8 μm. Ablation of the sample by the primary beam precedes the analysis of a given point and tends to remove surface contaminants. The ion microprobe precisely measures the ratio of trace elements to a given major element, in this case calcium. The raw data are converted to ppm by comparison with a set of standards. In this study we used a carbonatitic calcite from Oka to correct Mg and Sr (Mg = 618 ppm and Sr = 10 300 ppm; Roberts et al., 1998). Silica was analysed as an indicator of detrital impurities and analytical peaks coinciding with high Si were removed. High magnification optical microscope images were taken of the sections prior to them being placed in the sample chamber for analysis. This allows the point of analysis to be identified on the sample and enables petrographic examination of the sample. We carried out analyses on both CL26 and CL27, but only present the full results from CL26 as the tangential section of CL27 was less optimal.

**Figure 2** Polished orthogonal surfaces of CL26 (A) and CL27 (B). Discrete, opaque aragonite layers (arrowed) occur within the calcite body of the stalagmites at 68 mm (CL26) and 82 mm (CL27) from the top of the stalagmites. Ion microprobe sections were made from the axial slab of CL26 (A, right) and the lateral section of CL27 (B, right). Scale bars represent 2 cm

**Results**

**Petrography**

We refer to the calcite deposits pre-dating the aragonite layer as calcite (1) and primary calcite that overgrows the aragonite layer as calcite (2). Locally within calcite (1), the backscattered image contrast by SEM is sufficient to reveal rhombic growth zones (Fig. 3(A)) with zigzag terminations defining the outline of crystallites. Calcite (1) displays fibrous growth fabrics as defined by Frisia et al. (2000) and is believed to have formed from dripwaters near, but not at, equilibrium.

The transition from calcite (1) to aragonite is sharp and is marked by a fabric change from fibres to rays (Fig. 3(B)). Rays are clusters of aragonite crystals nucleating from a single point that protrudes into calcite (1), forming a ray-like structure in the plane of section and expanding vertically and laterally in the direction of stalagmite growth (Frisia et al., 2002). The ray crystals display a pseudo-hexagonal cross-sectional geometry characteristic of twinned aragonite crystals and radiate upwards in fan structures up to 3 mm high. The fans end within mosaics of calcite (2). This situation is analogous to some modern Clamouse speleothems where calcite and aragonite co-exist owing to fluctuating supersaturations and the energetic favourability of continued overgrowth on pre-existing crystals. The ray crystals seem to form in carbon and oxygen isotopic quasi-equilibrium with the solution when compared with other aragonite fabrics (Frisia et al., 2000).
Frisia et al. (2002) found, by quantitative X-ray diffraction analysis of 1-mm drilled samples at 2-mm intervals, that the weight % aragonite decreases away from the calcite–aragonite boundary from a maximum of 16%. For our purposes, we needed a more specific documentation of geochemistry and mineralogy on a finer scale. The SEM backscattered electron images (Fig. 3) indicate that the ray crystals are geochemically distinct from the surrounding primary calcite (1) and (2). The EBSD analysis (not presented here in detail) demonstrates that the ray crystals are still composed of aragonite, with indeterminate or calcite solutions to the diffraction patterns being restricted to the boundaries of and outwith the ray crystals. Since we avoided crystal boundaries in our aragonite geochemical traverse of CL26, we are confident that what we analysed was indeed primary aragonite.

**Geochemical context of the aragonite layer**

Figure 4(A) shows ICP trace element data for CL26. Mg and Sr exhibit relatively constant behaviour over the past 2.5 kyr, interrupted by a comparatively high Mg and Sr level in calcite (1) before the aragonite layer (Fig. 4(B)). Values are lower in calcite (2). The aragonite layer itself is both strongly enriched in Sr and depleted in Mg, characteristics which arise from the different partitioning behaviour of aragonite compared with calcite (Morse and McKenzie, 1990). Mg analyses of CL27 display similar characteristics (Fig. 4(C)).

Oxygen isotope ratios reported by McDermott et al. (1999) in the transition zone between secondary replacement calcite and primary calcite in the post-aragonite area overlap. Values are typically around −4.4 to −5.8‰ for δ¹⁸O in calcite <500 years old in CL26 and CL27. Areas of mixed calcite and aragonite yield δ¹⁸O values of −3.5 to −5.2‰ (Frisia et al., 2002). A relative high in δ¹⁸O coincides with textural evidence of non-equilibrium fabrics and mineralogical change, which in combination with present-day observation suggested a relatively dry period around the time of formation of the aragonite layer (McDermott et al., 1999). Higher δ¹³C values are found in aragonite and aragonite–calcite mixtures in CL26 and CL27 (McDermott et al., 1999) (Fig. 4(D) and (E)). The enrichment in δ¹³C values of around 2.5‰ in the original aragonite layer is close to the theoretical expected difference between aragonite and calcite (Morse and MacKenzie, 1990).

High Mg, known to inhibit calcite nucleation and growth (Bischoff and Fyfe, 1968; Burton and Walter, 1987), is a factor in aragonite nucleation, but may not be the only factor. Frisia et al. (2002) identified an inverse relationship between the Mg/Ca ratio of cave dripwater and drip rate, and suggested that slowly dripping highly supersaturated solutions help promote aragonite formation. Immediately prior to aragonite precipitation, the Mg content of the speleothem is seen to increase to its highest level in the previous 1300 years. Hence, the implication is that drip rate was particularly slow at that time. Mg is not readily accepted in the aragonite lattice and therefore its level drops substantially as aragonite precipitation initiates. Mg and Sr levels in calcite (2) are noticeably lower than that of calcite (1). The reason for this becomes apparent when aragonite is considered below.
High-resolution chemical variation

A summary of the overall trends revealed by ion microprobe analysis in Mg and Sr composition in sample CL26 is illustrated in Fig. 5(A). Each data point represents the mean and standard deviation of a scan typically some hundreds of micrometres in length. The overall pattern is similar to that of the ICP data of Fig. 4(A).

Chemical variation within aragonite ray crystals

Initially, the aragonite layer was analysed in sample CL27 and a trend of decreasing Sr and U upwards within the ray crystals was found. However, since both lateral and vertical chemical variability exists in aragonite (Finch et al., 2003), a more careful protocol was later carried out on CL26. As shown by the SEM image in Fig. 6, three parallel traverses were made within a single aragonite crystal (Fig. 6(B)), in addition to some other traverses across the interface between aragonite and calcites (1) and (2).

The ratio of Sr contents of calcite (1) and aragonite at their interface averages 0.16, whereas for calcite (2) and aragonite it is 0.13. These values are consistent with the ratio of partition coefficients of Sr into calcite and aragonite respectively using data from modern dripwaters and precipitates at Clamouse.

For the drip feeding CL26, 1000*Sr/Ca values typically lie between 0.45 and 0.54 (Frisia et al., 2002), whereas at the top of the stalagmite, typical 1000*Sr/Ca values are between 0.07 – 0.08. These data indicate that $D_{Ca}$ for calcite is 0.15, and $D_{Sr}$ for aragonite is approximately unity (Morse and McKenzie, 1990). These results are consistent with the preservation of the original Sr chemistry of the aragonite.

Comparison of results from parallel traces reveals that the overall variation is roughly similar (Fig. 6(B)). Immediately after the onset of aragonite precipitation, Sr, which is easily accepted into the aragonite lattice, shows a steady decline. U
Chemical variation within calcite (1)

A number of step scans were performed in calcite (1): five in section CL26c, eight in CL27 and one in section CL26a. Each scan consisted of between 50 and 130 5-μm steps, representing a sampling of most of the 8 mm of calcite (1) prior to aragonite. All scans revealed cyclic covariation between Mg and Sr. Other elements (H, F, Na and Ba) covaried with Mg and Sr but the data are not presented here. Figure 5(B) illustrates a typical step scan analysis track covering 0.8 mm of calcite (1) approximately 1 mm prior to aragonite nucleation. The pronounced peaks and troughs are interpreted later as annual cycles. The chemical zoning in calcite (1) is shown by the lighter and darker bands on SEM images (Fig. 3(A)). Since a lighter shade indicates a higher mean atomic number and the difference between maximum and minimum Mg concentration in calcite (1) is on average 150 times larger than that of Sr, the darker bands within calcite thus represent high-Mg, high-Sr layers.

Sr varies over a larger range of values compared to Mg, but this is still consistent with variations in prior calcite precipitation being the dominant effect mechanism for change. Prior calcite precipitation results in a rise in aqueous Mg/Ca and Sr/Ca by amounts that are determined by their partition coefficients. Since the Mg partition coefficient (observed to be around 0.035 at Clamouse by comparison of waters with young carbonate precipitates) is smaller than the Sr partition coefficient (around 0.15), Mg/Ca should increase more than Sr/Ca in waters. For example, when 50% of Ca has precipitated from the water, Mg/Ca is expected to have increased by a factor of around 1.08 compared with Sr/Ca. However, comparison of the Sr and Mg ion microprobe data when Mg represents such a condition shows that Sr increases during an average trace element cycle by 1.17 times that of Mg. This probably reflects an increasing kinetic effect on Sr incorporation (Lorens, 1981) during faster growth from more highly supersaturated solutions in the dry season. Overall the kinetic enrichment of Sr compared with Mg is around 26% (1.08*1.17 = 1.26) at the highest Sr and Mg values.

Chemical variation within calcite (2)

Ion microprobe data replicate the overall increasing Mg trend towards aragonite in calcite (1). Along with the lower values of Sr and Mg, the covariation of Mg and Sr, which was so well developed in calcite (1), becomes progressively muted as calcite growth continues after the aragonite period. There are more frequent periods of anti-correlation, and the regularity and definition of annual cycles decreases as growth of calcite continues with many sections of data showing as little as 5 ppm variation between the highest and lowest points. These observations are consistent with relatively minor variations in the amounts of prior calcite precipitation in calcite (2).

Determination of growth rate

Speleothems exhibit laminations which is commonly, but not invariably, annual in origin (Baker et al., 1993; Baker and Genty, 2003). CL26 and CL27 do not contain visible laminae and so we employed a method which involved counting chemical cycles as revealed by ion microprobe analysis as a test of annularity (Baldini et al., 2002). Automated counting methods are only now starting to be introduced for example in counting layers in ice cores (cf. Rasmussen et al., 2002), but could not be used here because of the relatively short segments available. The uncertainty is estimated as plus or minus 10% based on maximum and minimum counts of different operators. Counts were carried out prior to calculation of growth rates from U-series, to avoid systematic bias.

In originally calcitic parts of the speleothems CL26 and CL27, Mg and Sr show covariations of a similar degree to those of Mg/Ca and Sr/Ca in the cave waters (Fig. 1(C)). Marked peaks and troughs suggested a response to regular changes in the cave system, although these variations are more muted in some...
sections of the speleothem. Zhong and Mucci (1989) demonstrate that the precipitation rates of calcite and aragonite are similar to within 25% of each other from a given solution composition, and therefore there is no need to treat each polymorph differently when determining growth rates.

Growth rates were determined by measuring the wavelength of each chemical cycle in sample CL26 and comparing the resulting mean wavelength with the mean annual growth rates calculated from differences in U-series dates. The mean growth rate for the analyses as a whole, using the trace element wavelength method, was 54.9 mm kyr\(^{-1}\) (Fig. 7). This was calculated from the average of the growth rates from each individual step scan. It was found that average growth rates determined by these two independent methods were consistent with each other, suggesting that the chemical cyclicity in the calcite seen in the ion microprobe data are therefore assumed to be annual.

The cyclic trace element variations in Sr in the aragonite crystals (Fig. 5), although not as clear as in calcite (1), were counted and growth rates determined from the results. These were also consistent with the long-term growth rates, indicating that Sr in aragonite has potential for recording primary climatic signals.

**Discussion and aridity model**

**Discussion**

The time during which the aragonite horizons in CL26 and CL27 at Grotte de Clamouse were precipitating is distinctive as these events occur amid a background of relatively stable geochemical conditions during the late Holocene. Increased Mg/Ca alone is insufficient to initiate aragonite precipitation in speleothems (Hill and Forti, 1997) and a number of other factors, such as drip rate, degassing, evaporation and the mechanism of ion transport to crystal growth sites must be taken into consideration (Cabrol, 1978; Frisia et al., 2002). By studying the high-resolution chemical variations surrounding this event we can begin to understand how the system reacts to considerable variations in rainfall on an annual scale.

The path taken by water through an aquifer can be via relatively rapid conduit flow or fracture flow, or by diffuse flow whereby water is contained within pores and voids and is released relatively slowly (Tooth and Fairchild, 2003). Depending on the route by which cave dripwater passes through the aquifer, the sensitivity of the speleothem record can be affected. Storage water has a dominant effect on the dripwater characteristics at Clamouse with little variation after rainfall events (Fairchild et al., 2000). The Mg and Sr results presented here from Clamouse show remarkably strong covariation. Given that enhancement of effects such as prior calcite precipitation is expected to occur during periods of reduced aquifer recharge (rainfall), Mg/Ca ratios should likewise increase. It is notable that Sr, whose incorporation into speleothem calcite and aragonite is suggested to be highly dependent on growth kinetics (Finch et al., 2003; Treble et al., 2003), follows this trend. More commonly, an anti-phase relationship can exist between Mg and Sr in annually laminated speleothems (Roberts et al., 1998; Fairchild et al., 2001). In this case a peak in Mg, accompanied by a trough in Sr (plus U and Ba, Treble et al., 2003), is interpreted as representing the dry season. Such a system is arguably more complex, i.e. Mg is responding to increasing prior calcite precipitation during the dry months with Sr and Ba responding to increased growth rate during wet months.

Grotte de Clamouse speleothems represent a relatively simple case as both Mg and Sr appear to be responding to a common forcing mechanism. The high seasonality to the annual climate influences the controls on the annual trace element signal observed in the speleothems. The seasonal response reflects the conditions within the cave itself, irrespective of the length of water storage in the aquifer. However, the existence of storage means there will be a temporal smoothing of the overall trace element variation year-on-year, which is allowed for in our presentation of multi-year average trends. Seasonal variations in the amount of effective rainfall control the amount of prior calcite precipitation in the flow line in the aquifer and/or cave ceiling above the drip therefore having a subsequent effect on the supersaturation of the cave dripwater. Hence, covariation of Mg and Sr in modern cave waters at Clamouse is transferred to speleothem carbonate as a function of the partition coefficients of Sr and Mg in calcite and aragonite. With this in mind, and considering the annual-scale resolution of the ion microprobe data, we can confidently interpret longer-term trace element variations from speleothems at Grotte de Clamouse.

**Aridity index model**

The chemical changes observed have been argued to be due to seasonal variations in water chemistry driven by varying amounts of prior calcite precipitation, up-flow of the drip feeding the stalagmites. The calcite precipitation is interpreted to represent the degree of degassing that has occurred which is enhanced during periods of low recharge. It is possible to convert our chemical data for CL26 to a single parameter reflecting
the proportion of Ca in the water that was precipitated prior to dripping on the stalagmite and this provides an ‘aridity index’.

The chemical changes around 1200–1100 yr BP are against a background (Fig. 4(A)) of fairly constant Mg and Sr with low points of about 5000 ppm and 28 ppm respectively. If prior calcite precipitation is at a minimum during the precipitation of calcite with such a composition, the higher values can be referred to in terms of amounts of prior calcite precipitation above this background. In order to do this, a common trace element scale for both aragonite and calcite is required. Since Mg and Sr covary, either can be used for this purpose. Sr can be described by a partition coefficient in both aragonite and calcite, whereas the partitioning of Mg into aragonite is not well understood, and so Sr is preferred for this purpose. The Sr content of the primary aragonite can be converted to that expected from primary calcite by multiplying the values by the ratio of the partition coefficients of Sr into aragonite and calcite (0.15).

Given a Sr partition coefficient of 0.15 in calcite, the increase in Sr/Ca in solution resulting from different amounts of prior calcite precipitation can be calculated. Hence the Sr composition of the carbonate can be converted to a scale of the percentage of Ca precipitated from the parent water before the drip reaches the stalagmite. Although in general equilibrium partition coefficients should not be applied to quantitative analysis of kinetically influenced systems, in this case the departure from the equilibrium state is relatively small as is shown by the strong covariation of Sr and Mg. The data are not corrected for the kinetic enrichment of Sr discussed earlier because this applies only to relatively high values of Sr for which the conversion to percentage Ca precipitated is not so sensitive to the Sr value. This percentage Ca precipitated value can be regarded as an aridity proxy and is plotted in Fig. 8. A multi-decadal period of relative aridity climaxing with the onset of aragonite nucleation, followed by a decline in aridity within a few years, is clearly shown. The overall shape of the index is not typical of rainfall records in general, which show multi-year, rather than continuous multi-decadal drought (e.g. Rodrigo et al., 2000). This is likely to be because, although the annual variability shows that there is sensitivity to the seasonal changes in water availability, speleothem records in general tend to have pronounced memory effects, reflecting multi-year water storage (Smith et al., 2004). Therefore, the prolonged high level of the index is likely to reflect a failure of the wetter years to reverse an overall decline in water storage in the aquifer.

The similarity of the declining trend of U and Sr within aragonite of CL27 to that of CL26 indicates that the aragonite layers in both cases reflect the same event, (although there is a small gap in age between the error bars on the dates). Accordingly we average the two dates of 1122 and 1071 years BP on the aragonite layer (which are weighted towards the base of the layer because of the higher U content there) to obtain an approximate age of 1100 years for the onset of aragonite nucleation towards the end of the arid period.

We are able to conclude that based on micrometre-scale chemical analysis and examination of long-term trends throughout the Holocene, an objective picture can be built of the climatic conditions in the last 2.5 kyr, and in particular immediately previous to an aragonite layer precisely dated to around 1.1 kyr in two stalagmites. Our data suggest that over a period of ~100 yr preceding the onset of aragonite precipitation in Grotte de Clamouse the area experienced a cumulative moisture deficiency. This aridity reached a peak around 1100 yr BP (AD 850) triggering a fundamental change in the environmental and kinetic conditions affecting speleothem precipitation in Grotte de Clamouse and causing aragonite to nucleate. These extreme conditions waned within a decade and allowed the cave to return to its antecedent state.

Comparison with palaeoclimatic indicators in other regions

In the wider regional context, there is much evidence that, following early Holocene moist conditions, orbital changes led to the establishment of Mediterranean climate in the latter part of the Holocene (Magny et al., 2002). In addition there is evidence for relatively arid periods superimposed upon this general pattern including a well-documented arid period recorded 1200–1000 cal. yr BP in lake sediments from both Niger and

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**Figure 8** Summary diagram showing the relationship between an aridity index, representing a calculation of the amount of prior calcite precipitation and the mineralogy of speleothems CL26 and CL27 (mineralogy index: 1 = calcite; 2 = mixtures of calcite and aragonite; 3 = aragonite). The aridity index proxy displays a multi-decadal high culminating in aragonite precipitation. It then returns to antecedent conditions over a period of around 10 years.
Ethiopia and also Mexico (Street-Perrott et al., 2000). Our data are also consistent with those presented by Jalut et al. (2000) who used pollen records to reconstruct an arid phase during the interval 1300–1000 yr BP in the region stretching from southeastern France to southeast Spain. This is consistent also with the records from the Sahel where Street-Perrott et al. (2000) refer to a 1200–1100 yr BP arid episode based on Sr/Ca ratios in ostracods from shallow lakes. However, the dating of both these periods is much less precise than in the Clamouse record.

An intriguing correlation with the Clamouse drought record is provided by Central American episodes of multi-year droughts at intervals between AD 760 and 910 reconstructed from the Cariaco Basin Ti content and from lake level variability (Hodell et al., 1995; Haug et al., 2003). These climate changes have been considered as one of the possible causes of the progressive collapse of the Maya civilisation (Hodell et al., 1995). A trans-Atlantic correlation of this drought period was previously argued by Street-Perrott et al. (2000), on climatological grounds as well as on chronological grounds, as drought periods associated with relatively cool north Atlantic conditions tend to follow ENSO events in the Eastern Equatorial Pacific. The concept of intercontinental teleconnected periods of drought is corroborated by the period during 1998–2002 when particular patterns of tropical sea surface temperatures drove a low precipitation anomaly throughout the continental lower mid-latitudes from America through the Mediterranean to the Middle East (Hoerling and Kumar, 2003).

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