A high-resolution late Holocene speleothem record from Kaite Cave, northern Spain: $\delta^{18}O$ variability and possible causes

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Abstract

A high-resolution calcite oxygen stable isotopic ($\delta^{18}O$) record, covering the past 4000 years, was obtained from Kaite Cave, northern Spain. The record has a mean $\delta^{18}O$ value of -6.25‰ VPDB and a range of 2‰. Spectral analysis of the $\delta^{18}O$ data shows significant periodicities of 2400–1900, 600, 150, 27, and 22 years. The amplitudes during these periods range from 0.2‰ to 2‰. Factors controlling the isotopic ratio in the speleothem were evaluated. The calcite is most likely precipitated under equilibrium conditions, with the cave calcite $\delta^{18}O$ interpreted as a proxy of oxygen isotopic composition in local rainwater. Other factors such as temperature or fractionation in the karst system prior to calcite precipitation are considered of negligible or of minor importance. Mechanisms affecting rainfall isotopic composition were also investigated on different time scales. Precipitation amount is the primary factor controlling the high-frequency $\delta^{18}O$ oscillations. Other climate parameters, such as changes of storm tracks may have significant contributions on centennial and millennial time scales.

1. Introduction

Calcite $\delta^{18}O$ composition is one of the most common proxies used in paleoclimate reconstructions from speleothems (Schwarcz, 1986; Dorale et al., 2003; McDermott, 2004; Fairchild et al., 2006). The final values recorded in calcite speleothems depend on the $\delta^{18}O$ values of drip water, cave temperature, fractionation in the vadose zone, and possible diagenetic alteration after deposition. Variation of oxygen isotopic composition in cave calcite, therefore, could be related to cave environment and local climate if calcite precipitates under equilibrium conditions. When one of these parameters is dominant, the isotopic record may be interpreted in terms of this factor (e.g., temperature, rainfall amount, changes of storm tracks). Unfortunately, one factor does not always dominate throughout the record and different climatic elements may contribute at different time scales. In general, the stable isotope signal is the response of a mixture of climatic contributions (e.g., Niggemann, 2003a).

The oxygen isotopic composition recorded in Holocene stalagmites varies significantly from one place to another, frequently from −2‰ to −10‰ VPDB. However, for a single speleothem sample, the values generally oscillate within 1–3‰ VPDB along the growth axis (e.g., McDermott et al., 1999; Bar-Matthews et al., 2003; Holmgren et al., 2003). Variability in speleothem records from different regions may have different modes of oscillation. Samples from monsoonal regions are commonly characterized by large amplitudes of long-term $\delta^{18}O$ oscillations, such as up to 2‰ variations throughout the Holocene as a response of ITCZ migration (e.g., Wang et al., 2005). On short time scales (i.e., decadal), the fluctuations of these records, however, have smaller amplitudes, ranging from 0.5‰ to 1‰ (e.g., Dykoski et al., 2005). Another oscillation mode is represented by speleothem profiles from locations influenced by the Polar Front, which do not record significant variations during much of the Holocene (Lauritzen and Lundberg, 1999b; McDermott et al.,

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2001). The only trend observed in these records is restricted to their early Holocene portions. During the early Holocene, continental ice sheets were still retreating and oxygen isotopic ratios of seawater were decreasing from typical glacial values to interglacial numbers. However, during the late Holocene, speleothem $\delta^{18}O$ compositions tend to fluctuate about average values without general trends. Short-term $\delta^{18}O$ oscillations in these records are about 1–3‰, while long-term oscillations have amplitudes <1‰. Therefore, high-frequency $\delta^{18}O$ fluctuations recorded in speleothems are of interest.

In this study, a high-resolution calcite stalagmite $\delta^{18}O$ record, covering the past 4000 years, was obtained from Kaite Cave, northern Spain. Possible causes of the $\delta^{18}O$ variability were evaluated to understand contributions to the total variance. Additionally, spectral analysis and separation of the record on different frequencies are carried out. Identification of $\delta^{18}O$ variations on various time scales could help determine the degree to which different sources contribute to the final $\delta^{18}O$ signal.

2. Regional setting

The study area, Kaite Cave, is located at the southern foothills of the Cantabrian Range, only 50 km inland, in northern Spain (43° 2′ N, 3° 39′ W, 860 m above sea level, Fig. 1). The regional climate is temperate and humid, with less frequent rain in summer, but no obvious dry season. Moisture is mainly from the Atlantic Ocean, brought by westerly winds. Most rains are related to Polar Front incursions into southern Europe. The position of the region affected by incursions depends on the latitudinal migration of the Icelandic Low and Azores High pressure cells during the year. When these cells shift to the south during winter, the wet season is established. Rains are less frequent when the cells migrate to the north in summer (Font Tullot, 1983). Espinosa de los Monteros, 10 km to the east and 100 m lower in elevation than the cave, is the closest meteorological station. The mean annual temperature recorded at this station is 11.9 °C, the annual precipitation is 1052 mm, and the potential evapotranspiration is only 707 mm.

The Ojo Guareña Karst Complex is the largest cave in Spain with >100 km of mapped passages (Martín Merino, 1986). The sub-horizontal passages of the karst complex were formed during river down cutting in the area (Eraso, 1986). The gallery where the stalagmite sample was collected represents the highest level of the system. Kaite Cave is a 300-m long gallery developed 10–15 m under the surface. Because of a number of rockfalls, portions of Kaite Cave are largely isolated from the atmosphere, with a stable microclimate and no appreciable air currents. These parts of the cave were discovered in the 1980s. Speleothem samples were collected from a deep gallery, where the microclimate and properties of drip waters were recorded (Turrero et al., 2004a). Humidity is very high throughout the year (>98%). Drip waters were saturated in calcite throughout the year, but some yearly oscillations are also observed. Seasonal delay was seen in hydrochemical parameters with respect to the rainy season (3–6 months), which suggests short residence time ($<\frac{1}{2}$ year) for water in the aquifer. This is in accord with the shallow bedrock layer above the cave gallery. Nevertheless, most drips are constant and temperature is ~10.4 °C around the year (Turrero et al., 2004b).

3. Sample and methods

A speleothem sample, LV5, was collected from Kaite Cave. LV5 is a 1.06 m long stalagmite that had been broken and was lying on the floor of the cave when collected. No current calcite precipitation was observed at the original site of LV5. The stalagmite has a complicated growth history with several hiatuses and evidence for intervals of dissolution. The sample was entirely composed of calcite, confirmed by petrographic observations and X-ray analysis. Varying textures are observed including alternation between dense amber and porous white calcite. Banding is common for much of LV5. However, band counting is difficult in places due to irregular layer morphologies and periods of chaotic growth. The bands are thicker, more regular and more easily distinguished in the dense calcite portions, while they become thinner, more irregular and in cases, undifferentiable in the white porous calcite portions. Dense calcite sections have thicker diameters of the stalagmite than white porous sections. Some evidence for dissolution is visible in portions of the sample. The present work was carried out on the upper 0.31 m of stalagmite LV5 (LV5 Top, Fig. 2), in which there is no obvious evidence for dissolution. The relatively stable growth rate in this portion of the sample allows evaluation of a continuous $\delta^{18}O$ record and its temporal variability.

The age scale of the record was determined by U–Th dating. A Finnigan ELEMENT inductively coupled plasma magnetic sector mass spectrometer (ICP-MS) was used for uranium and thorium isotope determinations. Chemical procedures and age calculations follow descriptions in Edwards (1988), Cheng et al. (2000), Shen et al. (2002), and Dorale et al. (2004). Stable isotopes of oxygen and carbon were analyzed in a Finnigan MAT-252 mass spectrometer fitted with a Kiel Carbonate Device III. Subsamples were collected along the central axis of the sample, with a 0.5mm dental drill. Duplicates from LV5 Top were performed every 20 samples, resulting in $\delta^{18}O$ reproducibility better than 0.1‰. Additionally, a "Hendy Test" was carried out in this section of the sample to evaluate lateral isotopic variability and test for equilibrium calcite precipitation.

4. Results

4.1. Geochronology

Eleven U–Th dates were obtained for LV5 Top. One additional date was obtained from the base of LV5 Top,

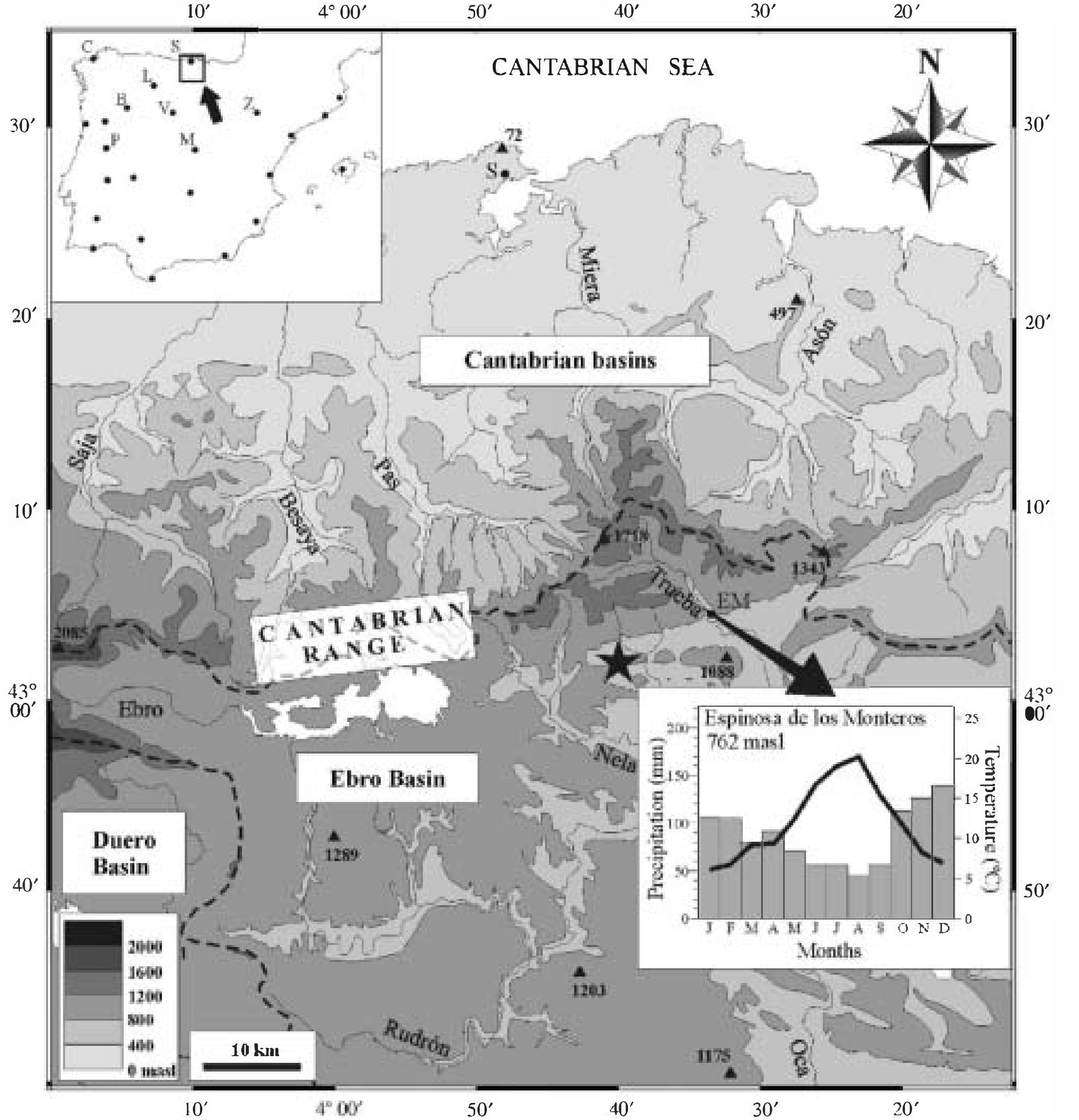

Fig. 1. Regional map of the Cantabrian Range. Names of the main rivers and altitudes of significant summits in meters are shown for reference. Kaite Cave is indicated with a star. Cantabrian, Mediterranean and Atlantic hydrographic limits, are depicted with dashed lines. The city of Santander (S) and the meteorological station Espinosa de los Monteros (EM) are also indicated. Climograma at Espinosa de los Monteros is also included in the graph. Dots in the Iberian Peninsula graph are the meteorological stations of the ISOHIS database. Stations for which information is reported in Table 3 are indicated with letters.

stratigraphically below a dissolution surface (Fig. 2). The subsamples were drilled along stratigraphic layers and the mean width of drilling was 3 mm. A 150 500 mg calcite powder was used for each analysis. The uranium concentrations of the subsamples range from 85 to 210 ppb. Measured $^{230}Th/^{232}Th$ ratios were generally high, except for three subsamples which correspond to younger ages (Table 1). A generic bulk earth $^{230}Th/^{232}Th$ ratio ($4.4*10^{-6} \pm 2.2*10^{-6}$ atomic ratio) was applied to correct for initial ^{230}Th. All ages are in stratigraphical order, and

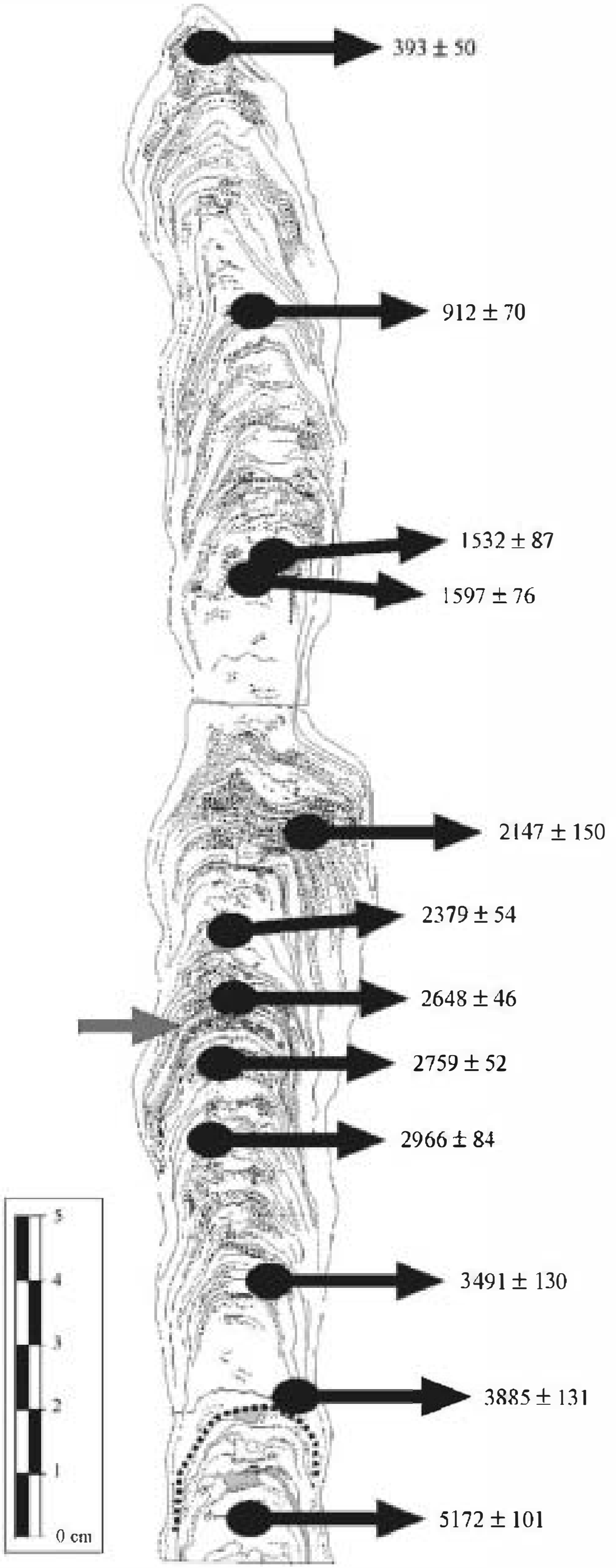

Fig. 2. Sketch of the LV5 Top stalagmite. The results of U–Th dating are indicated along the sample. A hiatus at the base of the sample, indicated by a thick dotted line, was confirmed by petrographic observations and dates. Grey arrow and dots indicate the layer with the "Hendy test". Four main periods of white porous calcite precipitation are easily observed because of scarce banding and thinner sections.

no sign of diagenetic alteration was observed under petrographic examination. Therefore, the system has been considered chemically closed since calcite deposition.

Stalagmite LV5 Top grew continuously from approximately 3900 a before the present (BP) to 310BP. Growth rate ranges from 45 to 120 μm/a, which is relatively constant in comparison with other stalagmite samples from Kaite Cave, for which growth rates change from >1500 to <150 μm/a (Domínguez-Villar et al., 2004). Given the 0.5mm drill bit diameter and speleothem growth rate, each stable isotope analysis integrates, on average, 5.6 ± 1.2 years (1σ error). The sample interval for $\delta^{18}O$ analysis corresponds to 10.6 years on average.

4.2. $\delta^{18}O$ composition, variability and spectral analysis

A total of 350 stable isotope analyses were done on LV5 Top. Tests for equilibrium include a lack of correlation between $\delta^{13}C$ and $\delta^{18}O$ along the whole record ($r^2 = 0.02$) (Fig. 3a). Additionally, the "Hendy Test" gives a low correlation between isotopic ratios along a single layer ($r^2 = 0.26$), and no $\delta^{18}O$ enrichment towards the sides of the stalagmite (Fig. 3b). This suggests that the calcite was likely deposited under equilibrium conditions (Hendy, 1971). The overall variability of the $\delta^{18}O$ record is 1.96‰ VPDB, with a mean value of −6.25‰. The isotopic values represent a normal population (Table 2, Fig. 4).

A clear long-term oscillation dominates the $\delta^{18}O$ record, although high-frequency large-amplitude variations are superimposed on this millennial-scale fluctuation. Spectral analysis with the Redfit application (Schulz and Mudelsee, 2002) yielded significant periodicities on millennial, centennial, and decadal time scales (Fig. 5). The data were not filtered or smoothed prior to analysis. The overestimation factor was four for the Lomb Scargle Fourier transform. A 50% overlap of two segments with a rectangular window-type was applied. The most significant frequency was between 1/1900 to 1/2400 a^{-1}. This frequency range was broad because only two cycles were covered in the record. Nevertheless, they are still representative (Schulz and Stattegger, 1997), although a longer record would be desirable. At high frequency, there are other significant periods (i.e., ~22 a) at the 99% confidence level. Some caution should be used in interpretation because of possible aliasing effects due to proximity to the Nyquist frequency. At centennial time scales, two periodicities are identified at the 95% confidence level, at around 600 and 150 a. Finally, significant periodicities at the 90% confidence level are common at centennial and decadal time scales. Each periodicity has a characteristic $\delta^{18}O$ amplitude. Millennial-scale oscillations have the lowest $\delta^{18}O$ amplitude (0.2 0.5‰), whereas decadal oscillations have large amplitudes (1 2‰). Such amplitudes are similar to other records from Western Europe during late Holocene time (Lauritzen and Lundberg, 1999b; Linge et al., 2001; McDermott et al., 1999, 2001; Niggemann et al., 2003b; Frisia et al., 2006), but not in records from monsoonal

Table 1
U-Th dates from LV5 Top stalagmite from Kaite Cave, Spain

Sample name	Distance from the base (cm)	^{238}U (ppb)	^{230}Th/^{232}Th (atomic)	δ^{234}U measured	^{230}Th/^{238}U (activity)	Age (yr BP) uncorrected	Age (yr BP) corrected	δ^{234}U initial (corrected)
LV5 5C	105.1	124.7±0.17	0.000124±0.000014	148.8±2.3	0.00485±0.00052	409.2±49.7	392.8±50.4	149.0±2.3
LV5 5B	98.7	127.4±0.32	0.000049±0.000002	139.9±3.6	0.01101±0.00053	1006.7±51.5	911.6±70.1	140.3±3.6
LV5 5AII	93.1	109.9±0.20	0.000083±0.000004	148.7±2.7	0.01747±0.00078	1620.2±75.5	1531.7±87.4	149.4±2.7
LV5 5AI	92.6	114.0±0.23	0.000119±0.000005	146.8±2.8	0.01786±0.00072	1660.0±69.5	1596.9±76.2	147.6±2.8
LV5 4C	87.1	148.9±0.61	0.000045±0.000002	149.3±4.7	0.02537±0.00096	2381.8±93.3	2147.4±149.7	150.3±4.7
LV54BT	84.6	79.7±0.13	0.000269±0.000012	166.4±2.3	0.02614±0.00052	2419.2±50.1	2379.3±54.0	167.6±2.4
LV5 4BIV	83.4	158.9±0.26	0.000219±0.000005	164.8±1.9	0.02906±0.00039	2702.4±37.4	2647.7±46.3	166.1±1.9
LV5 4BIII	82.0	210.7±0.54	0.000425±0.000018	149.3±4.7	0.02989±0.00051	2788.0±49.8	2758.9±52.0	163.6±2.5
LV5 4BI	80.1	93.5±0.17	0.000406±0.000016	150.3±2.8	0.03172±0.00084	2998.7±82.6	2966.2±84.2	151.6±2.8
LV54A	76.8	86.7±0.13	0.000518±0.000027	147.3±3.4	0.03696±0.00131	3520.3±129.0	3490.5±129.9	148.8±3.5
LV5 3CIII	74.3	98.4±0.45	0.000171±0.000007	148.9±6.4	0.04177±0.00120	3986.4±120.8	3884.6±130.8	150.6±6.5
LV5 3C II	72.1	90.0±0.19	0.005835±0.000017	151.2±3.4	0.05423±0.00099	5210.8±99.6	5172.1±101.4	153.4±3.5

Decay constant values adopted from Cheng et al. (2000). The errors are always 2σ errors.

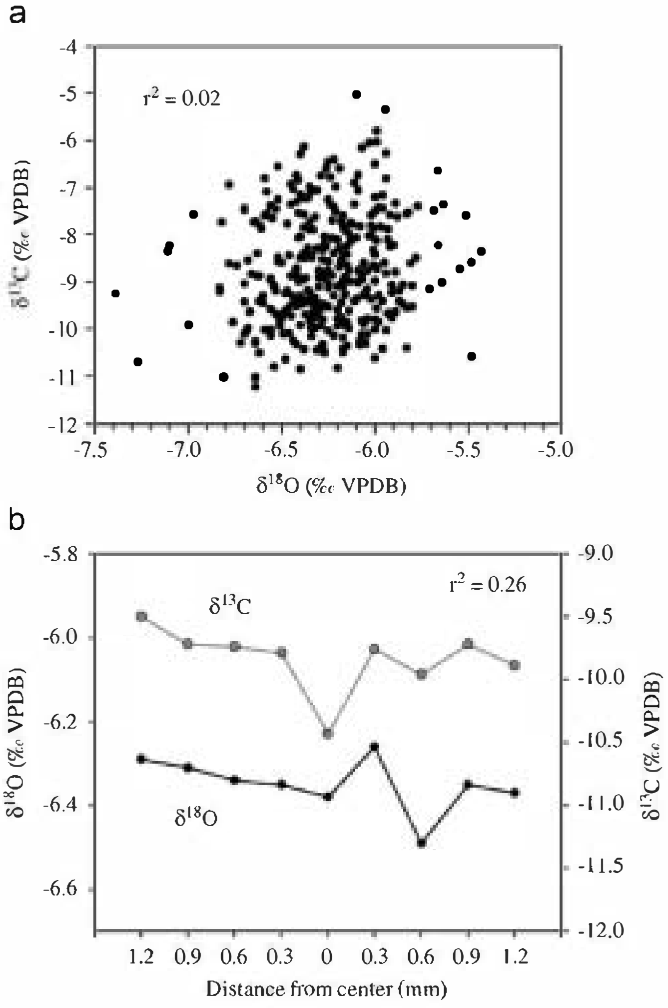

Fig. 3. Equilibrium condition tests on LV5 Top stalagmite. (a) Carbon and oxygen isotopes along the whole record showing the lack of correlation. (b) Carbon and oxygen isotope composition along a single layer showing spatial distribution and correlation. Both tests suggest that calcite was deposited under quasi-equilibrium conditions.

Table 2
δ^{18}O population statistics

Parameter	Value
Average	−6.26‰
Maximum value	−5.43 ‰
Minimum value	−7.39 ‰
Variance	0.085
Standard deviation	0.292
Normality test (Kolmogorov Smirnov)	
Normality	Yes (>90%)
K–SD	0.036
p-value	>0.10

regions (Fleitmann et al., 2003; Wang et al., 2005; Wang et al., 2006). Therefore, the decrease in amplitude from millennial to decadal periodicities is probably not a progressive smoothing of the data. Rather, it may record the characteristics of the δ^{18}O record as a function of different time scale.

5. δ^{18}O variability in the system

5.1. *Factors affecting calcite δ^{18}O*

Many factors could control the speleothem δ^{18}O signal in Kaite Cave, such as diagenesis, fractionation in the vadose zone above the cave, cave temperature, and the δ^{18}O value of local rainwater (e.g., McDermott, 2004; Richards and Dorale, 2003). Petrographic evidence suggests that calcite crystals in LV5 Top have not undergone recrystallization. In addition, calcite precipitation was under quasi-equilibrium conditions. However, other fractionation in the system may not be ignored (Fig. 6). Evaporation of rainwater in the soil or vadose zone is possible (Ayalon et al., 1998). Rainfall in the region is

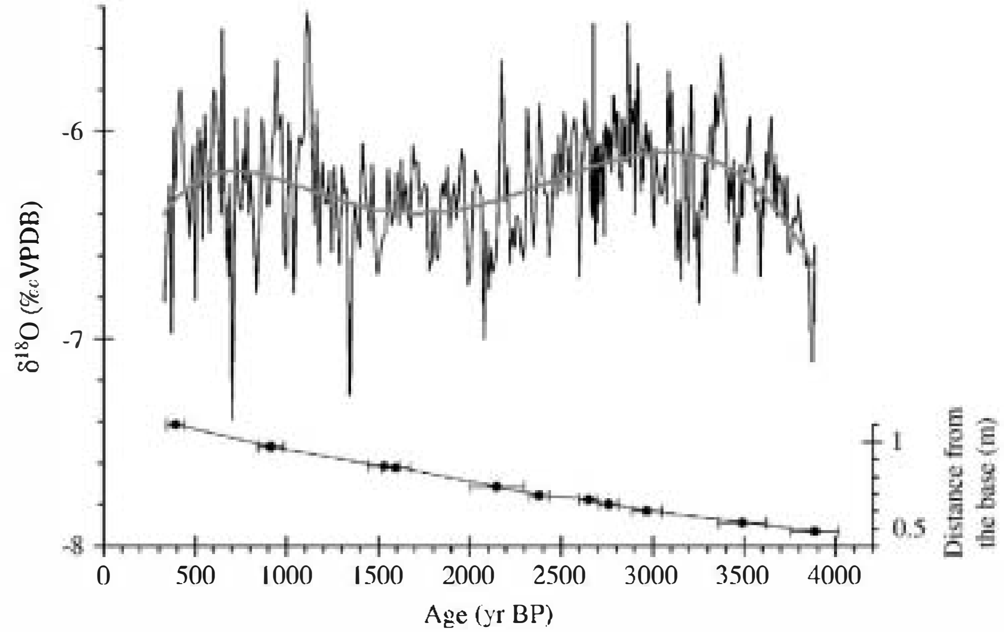

Fig. 4. LV5 Top $\delta^{18}O$ record versus time. The general long-term oscillation is plotted with a grey line. Growth rates are indicated at the base of the graph with corresponding errors. Note the lack of coincidence of isotope values with texture shown in Fig. 2.

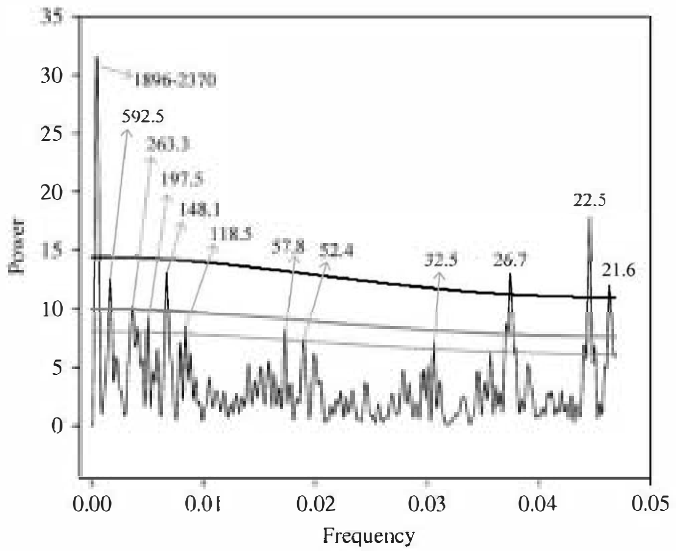

Fig. 5. Spectral analysis of LV5 Top series. Confidence limits are obtained with a χ^2 test at different statistical limits: black bold line at 99%, grey bold line at 95% and grey line at 90%. The numbers at the top of each significant peak correspond to the periodicity duration in years.

several hundred millimeters higher than potential evapotranspiration, suggesting that evaporation is not as important as in semiarid regions. Therefore, the evaporation effect is probably minor, although it cannot be totally ruled out, as discussed further below.

The other two factors affecting calcite composition are cave temperature and rainwater $\delta^{18}O$ composition. Temperature affects the calcite-water fractionation factor so that calcite $\delta^{18}O$ changes by −0.23‰/°C at equilibrium (O'Neil et al., 1969; Friedman and O'Neil, 1977). As cave temperature is currently seasonally stable, possible variations are due to longer term temperature variations. Temperature also affects the isotopic composition of rainfall, with an opposite sign for most regions, including the Kaite Cave region. Rainwater isotope composition is critical for the $\delta^{18}O$ signal in the speleothem. As the calcite precipitation was under quasi-equilibrium conditions, dripping water $\delta^{18}O$ values are recorded directly in the stalagmite and only modulated by cave temperature (Schwarcz, 1986). Therefore, drip water $\delta^{18}O$ mainly resembles the local rainwater $\delta^{18}O$ composition. Thus, oxygen isotope variations in the sample are largely recording $\delta^{18}O$ composition changes of rainwater.

5.2. *Evaluating speleothem $\delta^{18}O$ variability*

In the Iberian Peninsula, rainwater $\delta^{18}O$ has been systematically monitored by the ISOHIS database network (IAEA, 2004). Here, the importance of climatic factors in the cave system based on local rainwater data is quantified. Twenty-four meteorological stations have been set up in the Iberian Peninsula to monitor the monthly rainwater oxygen composition, with available data since 1961 (IAEA, 2004). Seven have records longer than 10 years. The mean range of annual $\delta^{18}O$ variability at these stations is 2.49 ± 0.71‰, similar to the variability found in other European stations (Rozanski et al., 1993). The largest fluctuations occur on the order of 3 15 years. As in this stalagmite sample, when data are averaged over 5 years, the rainfall variability is not totally smoothed. Therefore, short-term rainfall $\delta^{18}O$ fluctuations could contribute to the record as much as 2‰. Rainwater $\delta^{18}O$ variability

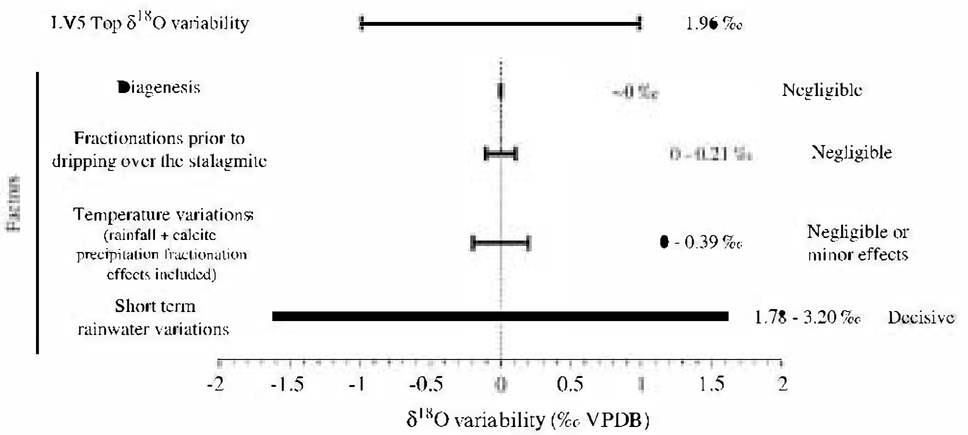

Fig. 6. $\delta^{18}O$ composition variability in LV5 Top and factors affecting the karst system. Speleothem and isotope ranges of various factors are graphically and numerically shown. The black rectangle in the range represents the minimum variability. Isotope ranges reflect inter-annual variability. If speleothem isotope sampling comprises several years, these ranges should be smoothed according to sample resolution (i.e., ~5a in LV5 Top). Assessment of each factor in LV5 Top record is also included.

Table 3
Relation between rainfall oxygen isotope composition and climate for the closer meteorological stations of the ISOHIS database to the Cantabrian Range

Meteorological station[a]	Altitude (masl)	$\delta^{18}O_{weighted}$ (‰VPDB)	$\delta^{18}O$/temperaure (‰VPDB/°C)	r	$\delta^{18}O$/precipitation (‰VPDB/mm)	r
Santander (S)	52	−6.12	+0.246	0.45	−0.0150	0.43
León (L)	913	−8.70	+0.340	0.62	−0.0325	0.57
Valladolid (V)	735	−7.71	+0.236	0.50	−0.0383	0.49
Zaragoza (Z)	247	−5.68	+0.291	0.66	−0.0286	0.27
Madrid (M)	655	−6.76	+0.320	0.59	−0.0216	0.19
Bragança (B)	690	−7.02	+0.294	0.14	−0.0150	0.44
A Coruña (C)	57	−5.49	+0.035	0.10	−0.0125	0.67

The location of the stations is plotted in Fig. 1. Elevation of each meteorological station and weighted mean rainfall value of oxygen isotope compositions also reported. Relations of oxygen isotope compositions with temperature and precipitations taking account monthly values. Correlation factor (r) indicates the grade of reliability of such gradient.
[a]Source data and additional infornation from IAEA (2004).

mainly controls the high-requency oscillations recorded in LV5 Top.

Quantitative evaluation of the fractionations in the system before calcite precipitation inside the cave (e.g., epikarst evaporations) was accomplished by estimating the average rainwater $\delta^{18}O$ value with an interpolation of rainwater data from the IAEA database. The interpolation comprises data from all the stations in the Iberian Peninsula, and the corrected latitude and altitude have been applied (Bowen and Wilkinson, 2002). The estimated mean rainwater $\delta^{18}O$ at Kaite Cave site has a value of -7.92 ± 0.45‰ VSMOW. Calcite precipitated under isotopic equilibrium from this water has a $\delta^{18}O$ value of −6.46‰ VPDB (using the equation from Kim and O'Neil, 1997). Some of the stations used in the interpolation only have two years of measurements recorded during the lighter isotopic phase of rainfall (years 2000 and 2001). The measurements recorded during the subsequent years (unpublished data from the IAEA), if included, will give a mean rainfall oxygen composition slightly heavier (Araguás-Araguás, personal communication). Nevertheless, difference between the average value in LV5 Top (−6.25‰) and the interpolated rainwater composition (−6.46‰) is only 0.21‰. This difference would be even smaller using the data from stations with a longer monitoring history. Therefore, a maximum value for the $\delta^{18}O$ difference between the speleothem calcite and the calcite theoretically precipitated from local rainwater under equilibrium conditions is ~0.2‰. In conclusion, $\delta^{18}O$ fractionation introduced before the drip enters the cave is minor to negligible.

To calculate how much local temperature contributes to the $\delta^{18}O$ variability in the record requires further examination of the relationship between the oxygen isotopic composition of local rainfall and the surface temperature. The two data sets, collected from the five meteorological stations closest to Kaite Cave (<300 km), are positively correlated, with gradients ranging from +0.24 to +0.34‰/°C ($r = 0.45$ 0.66, Table 3). Taking into account the fractionation during calcite deposition related to thermal effects (−0.23‰/°C), the final temperature dependence in the speleothem $\delta^{18}O$ variability ranges from

+0.01 to +0.11‰/°C. The mean annual temperature oscillates less than 3.5 °C at the local meteorological stations for the last ~50 years. As the isotope sampling intervals cover several years (~5 a), a 5 year filter is applied to the meteorological data accordingly. Once filtered with a five year moving average, temperature oscillations on the order of ~2 °C could be expected to be recorded in this stalagmite. This short-term temperature change is also in agreement with the maximum temperature fluctuations suggested for the late Holocene (Lamb 1977; Roberts, 1998). Such ~2 °C temperature change would induce an isotopic variability in a range of 0 0.2‰. Therefore, direct temperature effects are of minor significance, falling close to the resolution of instrumental error. As a consequence, the LV5 Top signal is largely contributed from local rainfall changes.

5.3. *Mechanisms affecting $\delta^{18}O$ variability in rainwater*

Various factors could affect the $\delta^{18}O$ variability in local precipitation, such as latitudinal and altitudinal position of a site, its distance from ocean source, surface temperature and precipitation amount (Dansgaard, 1964; Gat, 1996; Darling et al., 2006). On short-time scales, many of them are relatively stable for the same site. Precipitation amount and temperature are commonly invoked to explain rainwater $\delta^{18}O$ variations. When investigating paleoclimate on long-time scales, other factors may need to be examined as well, for instance, changes in ocean $\delta^{18}O$ composition, migration of ocean currents with different compositions, variations in moisture sources, temperature difference between source and location of precipitation, or additional non-oceanic water vapor (Lauritzen and Lundberg, 1999a; McDermott, 2004). Oscillations caused by mechanisms at short- and long-time scales are summarized in Table 4.

Rainfall amount is the dominant contributor to the rainwater $\delta^{18}O$ in this area, with a relationship ranging from −0.0125 to −0.0383‰/mm ($r = 0.43$ to 0.67) based on the observed data from the IAEA stations along the Cantabrian Range ($n = 4$). Inter-annual variability of the rainfall amount is several hundred to more than one thousand mm in the area. After smoothing that precipitation data with a 5-year filter (to have a resolution equivalent to this speleothem record), the rainfall variability still has amplitudes of several hundred mm (typically ~200mm). This variation in rainfall amount could explain >2‰ of $\delta^{18}O$ in this speleothem record. The longest rainfall $\delta^{18}O$ record with a similar geographic setting to Kaite Cave is from Penhas Douradas (P in Fig. 1). This station is located in a mountainous area in Portugal, near the Atlantic. The rainfall record at this station indicates that depleted isotopic ratios are observed when precipitation increases in the rainy season ($r = 0.85$). This confirms the rainfall amount effect in the region and the importance of the seasonal distribution of rainfall. The short-time speleothem $\delta^{18}O$ variations are interpreted in terms of rainfall amount or the amount of precipitation during the rainy season. Higher local rainfall leads to lower calcite $\delta^{18}O$, and vice versa.

On longer time scales (centennial to millennial), other climate factors, such as persistent atmospheric or ocean current anomalies, could contribute significantly to speleothem $\delta^{18}O$. In northern Spain, the ocean is the major source for water vapor, with non-oceanic sources of moisture insignificant. Most of the precipitation that comes from the Atlantic, although the Mediterranean Sea is important in the western Iberian Peninsula (Font Tullot, 1983; Martín-Vide and Olcina Cantos, 2001). Water from the western Mediterranean Sea comes directly from the Atlantic through the Strait of Gibraltar, and the isotopic

Table 4
Possible mechanisms affecting oxygen isotopic composition of rainwater in Cantabrian Range region, including estimations of $\delta^{18}O$ ranges and assessment about its significance in speleothem signal variability

Duration of oscillations	Mechanism	Isotope ranges	Assessment of mechanism and comments
Short-term	Temperature changes	0–0.2‰	Negligible
	Amount of precipitation variability	1–3‰	Decisive
Long-term	Temperature changes	0–0.2‰	Negligible or minor effects
	Amount of precipitation variability	>1‰	Important. More precipitation implies depleted isotope values
	Storm track variations[a] (Source of moisture isotope composition + temperature differences between source and destiny region + distance from source area)	>1‰	Important. Migration of the Polar Front to the north implies lighter isotope values. This mechanism is of different sign to amount of precipitation that also is affected by displacements of climate belt. Both mechanisms together seem to affect in some decimals as a maximum to the final variability ($n*10^{-1}$‰)
	Changes in isotope composition of ocean source region	$n*10^{-1}$‰	Important.

[a]Note that storm tack variations frequently cause changes in amount of precipitation, however, we have removed that effect to separate amount effect from moisture source effect.

composition of precipitation from the western Mediterranean Sea is not discernible from those of the Atlantic origin (Plata, 1994; Araguás-Araguás and Díaz Teijeiro, 2005). As a result, long-term rainfall $\delta^{18}O$ variations in Spain are mainly caused by migration of the Polar Front and rainfall amount changes. Shifts in the Polar Front affect rainfall amount as well as moisture source. To clarify the importance of these two effects, they are described separately, using latitudinal migration or storm tracks as an indicator of moisture source, and total precipitation to evaluate the amount effect. Latitudinal migration of pressure cells affects the moisture source within the North Atlantic, the temperature gradients between origin and destination, and the distance from moisture source. These variations can be reflected in the isotopic composition in rainfall events with a depletion of $\delta^{18}O$ values (>1‰) when the system shifts to the north (Aragúas-Araguás and Díaz Teijeiro, 2005). Consistent shifts therefore contribute to rainwater $\delta^{18}O$ variations. On the other hand, displacement of the Polar Front to the south will contribute more rain in southern Europe (Zorita et al., 1992; Bolle, 2003). In Northern Spain, there is a weak negative correlation between the NAO index and the amount of winter precipitation (Rodríguez-Puebla et al., 1998). Despite the weak correlation, southward migration of the Polar Front causes slight increases in local rains (Gómez Navarro et al., 1999). Even with minor increases in local rainfall, the $\delta^{18}O$ value of rainfall can be depleted >1‰, because of the large gradient between the precipitation amount and oxygen isotope values (Table 3). Variations in moisture source and rainfall amount are both responses to latitudinal migrations of the climatic belt on long-term time scales. However, their isotopic consequences are opposite (i.e., when the pressure cells shift to the south, more rainfall is recorded in northern Spain. However, the moisture source is closer and the ocean $\delta^{18}O$ composition is heavier, and vice versa. So, rainfall $\delta^{18}O$ would be low due to the amount effect while it could become high because of the heavier source and shorter trajectory). Although both mechanisms are able to cause oscillations >1‰, the two factors will tend to cancel each other resulting in a significantly smaller amplitude.

A change in the isotopic composition of the oceanic source can additionally affect the rainwater $\delta^{18}O$. Global ocean isotopic composition is believed to be nearly stable since deglaciation (Bard et al., 1996). Particular currents in the ocean, however, have different isotopic compositions. This is the case for subtropical and subpolar waters in the North Atlantic. The oceanic Polar Front that approximately depicts the northern limit of the Gulf Stream has a considerable isotopic gradient (>1‰) between the south (heavier) and the north (lighter) waters (Schmidt, 1999; Bigg and Rohling, 2000; Schmidt and Mulitza, 2002). Migration of the Gulf Stream has been reported during the late Holocene (Keigwin and Pickart, 1999), which affects the exact position of water masses with different isotopic compositions in the North Atlantic. Changes in $\delta^{18}O$ composition of planktonic foraminifera have been shown all along the North Atlantic with oscillations ranging from 0.5‰ to 0.7‰ (Keigwin, 1996; Marchal et al., 2002; Lund and Curry, 2004). Although some of this range is explained in terms of SST variations, part of this change could be caused by changes in the local composition of ocean water because of current migration (Duplessy et al., 1992, 1993). Although quantitative evaluation of this mechanism is complicated, small $\delta^{18}O$ changes might be possible due to the sharp isotopic gradient in the North Atlantic and the considerable displacement during current migrations.

In summary, rainfall amount is the most significant mechanism affecting rainwater $\delta^{18}O$ variations at high-frequency time scales. On longer time scales, persistent atmospheric or oceanic anomalies may influence the rainfall $\delta^{18}O$, although the amplitudes are relatively small. Therefore, the rainfall $\delta^{18}O$ recorded in this speleothem sample is the response of a mixture of mechanisms with different amplitudes on different time scales.

6. Mechanisms on different time scales

The main cause of the $\delta^{18}O$ variability in the LV5 Top record is the change of rainfall isotopic composition, whereas temperature and kinetic fractionation have minor or negligible effects. The rainfall $\delta^{18}O$ is mostly related to annual precipitation amount or precipitation amount during the rainy season. However, other factors including modification of atmospheric or oceanic circulation patterns must also be considered.

The $\delta^{18}O$ record has different amplitudes of oscillations on different time scales. The larger fluctuations are likely explained by rainfall amount, while low-amplitude oscillations could be the result of other mechanisms. The different amplitudes of $\delta^{18}O$ variations on various time scales are clearly illustrated in Fig. 7. The record has been divided in three types of signals. Long-term $\delta^{18}O$ variation is on the millennial time scale, as seen in spectral analysis, and was obtained using a 6th order polynomial equation. $\Delta^{18}O$ was subsequently obtained once the millennial-scale oscillation was removed. The resulting time series represents decadal fluctuation. To illustrate centennial oscillation, the $\Delta^{18}O$ signal is smoothed with an 11 point moving average to obtain filtered $\Delta^{18}O$ (which results signal >100a filtered). The three time series have obviously different amplitudes of $\delta^{18}O$ variations. The amplitude for each time series depends directly on the chosen filter. Here, different filters are used to calculate amplitude ranges, which were selected from the frequencies obtained with spectral analysis (Fig. 5).

Both the centennial and millennial-scale $\delta^{18}O$ oscillations range from 0.2‰ to 0.5‰, while the decadal variability ranges from 1‰ to 2‰. Only the amount effect is able to explain the large amplitude of the decadal oscillation. However, the centennial to millennial-scale $\delta^{18}O$ variability could record a combination of variations of rainfall amount, changes in ocean source isotopic

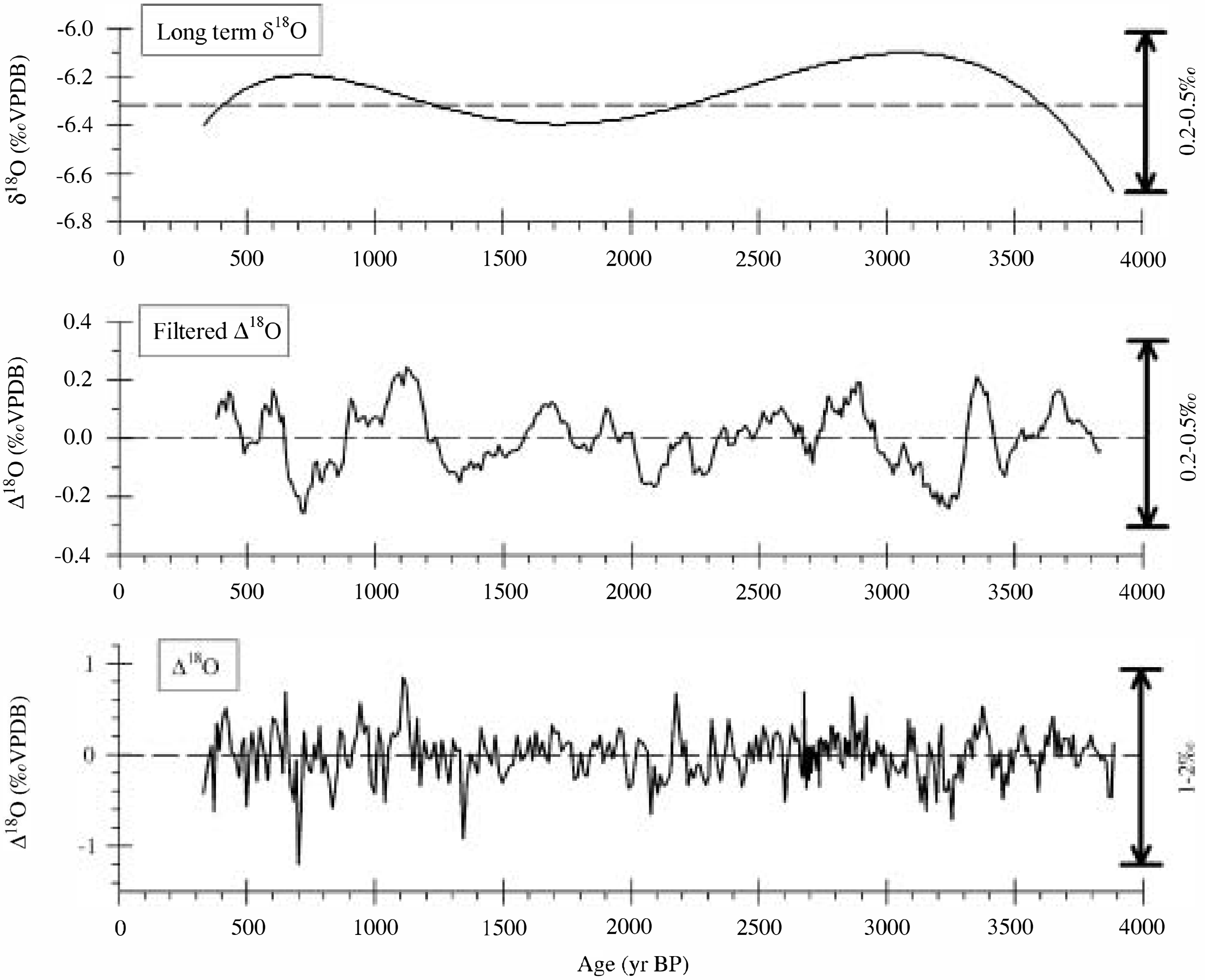

Fig. 7. Speleothem $\delta^{18}O$, filtered $\Delta^{18}O$ and $\Delta^{18}O$ time series from LV5 Top (see text for explanation). The three time series illustrate separately the millennial, centennial, and decadal variabilities of LV5 Top. Note that the oxygen isotopic scale is different for each graph.

composition or changes in storm tracks. As a result, even if much of the variability is explained in terms of rainfall amount, the possibility of changes in ocean or atmosphere dynamics which result in millennial and centennial-scale fluctuations in the record cannot be discarded.

7. Conclusions

A high-resolution $\delta^{18}O$ record was obtained, covering much of the last 4000 years, from a calcite stalagmite sample, LV5 Top, collected from Kaite Cave, northern Spain. The total amplitude of the $\delta^{18}O$ signal is ~2‰, although different amplitudes have been recognized depending on time scale. Spectral analysis shows representative periodicities from decades to millennia. The decadal oscillations show amplitudes in the range of 1–2‰, while on centennial to millennial time scales, the record is characterized by a variability of 0.2–0.5‰. Possible causes of the isotope signal have been examined. The $\delta^{18}O$ signal recorded in LV5 Top is the result of variations in rainwater composition, whereas temperature and kinetic fractionation have minor or negligible effects. Mechanisms affecting changes in rainwater composition have also been described. Rainfall amount or amount of precipitation during the rainy season is the mechanism that contributes most to the variability, which is able to cause fluctuations >2‰. Other mechanisms, however, could be also important, such as long-term changes in storm tracks or variations in isotopic composition of the moisture source from the ocean, which may induce fluctuations <1‰. These secondary mechanisms are negligible at high frequencies, but could be partially responsible for oscillations on centennial or millennial time scales. Therefore, the record is largely explained in terms of paleoisotopic rainwater composition. Climatic causes for that composition could be mainly related to rainfall amount, although interpretations should be cautious since at long-term time scales the record could be the response of a variety of mechanisms.

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