Climate Variability During the Middle-Late Pleistocene Based on Stalagmite from Órganos Cave (Sierra de Camorra, Southern Spain)

C. Jiménez de Cisneros, E. Caballero, B. Andreo and J.J. Durán

Abstract Paleoclimatic reconstruction in southern Spain has been investigated in this study using stable isotope analyses from Órganos Cave (Southern Spain). A combination of $\delta^{18}O$ and $\delta^{13}C$ analyses with uranium-series dating and δD values of the water extracted from stalagmite fluid inclusions makes it possible to obtain an isotopic record during 340–370 ky BP (MIS10). The profile shows the climatic evolution in the area and we can see a colder early stage with small fluctuations that change to warmer conditions at the end, coinciding with the start of the interglacial stage MIS9.

Keywords Speleothems · Paleoclimate · Pleistocene · Stable isotopes · Fluid inclusions

1 Introduction

Variations in $\delta^{13}C$ and $\delta^{18}O$ values of calcite speleothem have been widely recognized as a powerful tool to reconstruct the paleoclimate/environment of terrestrial areas (e.g. Banner et al. 1996; Bar-Matthews et al. 2000; McDermott 2004; Fairchild et al. 2006; McDermott et al. 2006; Spötl and Mangini 2007). During the late twentieth century, the main focus of research was on $\delta^{18}O$ records in

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speleothems as paleotemperature indicators. Support for a paleoclimatic record based on growth frequencies of speleothems can be obtained from the dated deposits themselves, by variations in ^{13}C and ^{18}O of calcite along the growth axes of deposits that formed in isotopic equilibrium with the groundwater. The precise dates that can be obtained on these records using the U-Th technique potentially enable high chronostratigraphic resolution (Edwards et al. 1987; Musgrove et al. 2001; Marshall et al. 2009).

Fluid inclusions, representing fossil seepage water, are formed in speleothems when small volumes of drip water become trapped within the precipitating calcite. The oxygen isotope ratios of speleothem calcite and hydrogen isotope ratios of speleothem fluid inclusion are water-isotope tracers, which enable the calculation of paleotemperatures (Mathews et al. 2000; Dennis et al. 2001; Genty et al. 2002; Verheyden et al. 2005; Vonhof et al. 2006; Jiménez de Cisneros et al. 2011; Jiménez de Cisneros and Caballero 2013).

In this paper we present a paleoclimate record of the western Mediterranean. The stalagmite from southern Spain (Málaga province) is dated by ^{230}Th/^{234}U, ranging in age from 340 to 370 ky BP. Continental records during this period are scarce not only in the western Mediterranean (Jiménez de Cisneros et al. 2003; Durán et al. 2004; Muñoz-García et al. 2007; Dominguez-Villar et al. 2008; Moreno et al. 2010; Bartolomé et al. 2012; Jiménez de Cisneros and Caballero 2013; Durán et al. 2013) but also worldwide, which enhances the interest of this work.

2 Location and Geological Setting

Órganos or Mollina cave is located in Malaga province (Southern Spain, Fig. 1) at 650 m above sea level and was formed in Lower Jurassic dolomites of the External Zone of the Betic Cordillera. The unsaturated zone above the cave is several tens of metres thick and comprises fissured but poorly karstified dolomites and limestones with diffuse flow behaviour. Stalagmite sample was collected in the inner part of the cave, which has only one entrance. Hence dripwaters would not have been subject to evaporation or rapid degassing, which is important for stable isotope variations in the calcite. It is a stalagmite EM-MO over 56 cm long formed by laminated calcite. Colour is predominantly white with some alternating black bands. Thin-section analysis indicates suitability for preserving a quasi-continuous climate record in the whole of the sample. Examination of thin-sections reveals that apparent texture/colour changes are due to the alternating density of fluid inclusion and minor clays or organics. Crystal fabric is predominantly large and columnar in nature favouring deposition in equilibrium with its corresponding drip water (Kendall and Broughton 1978).

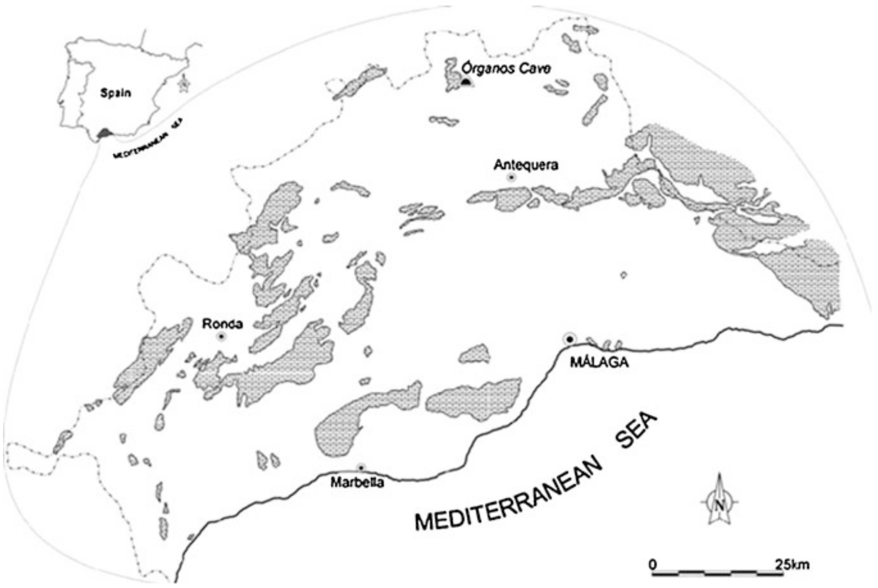


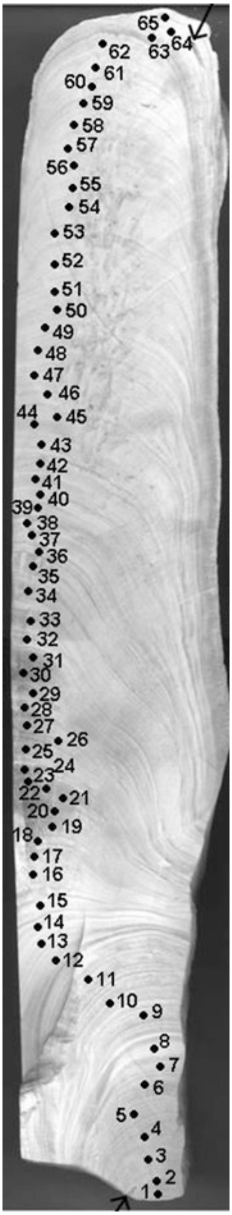
Fig. 1 Location map, showing the situation of the Órganos Cave, southern Spain

3 Analytical Methods

The mineralogical composition of the samples was determined by X-ray diffraction, using a Panalytical X‘PERT pro diffractometer. The stalagmite was cut along its growth axis after retrieval from the cave in order to expose its growth laminae and to permit checks for a secondary alteration.

The sampling for this isotopic study was carried out using a dental-drill. Samples for stable isotope analyses of less than 10 mg were drilled. The drill was cleaned with HCl and water in between samples, in order to avoid sample contamination. Samples for stable isotope analysis were typically taken at 2–5 mm intervals along the growth axis of the stalagmite (Fig. 2). In total, 65 samples were analysed, including 12 supplementary samples to check the isotopic equilibrium with the Hendy Test (Hendy 1971). CO_2 was extracted from calcite at 70° by reaction with H_3PO_4 (McCrea 1950) using a VG Micromass preparation line. Data were corrected for fractionation using the carbonate-phosphoric acid fractionation factors for calcite. Results are reported as ‰ versus the PDB standard for carbonates. Paleotemperatures were calculated using the Sharp (2007) equation. Analytical precision was 0.1‰ for $\delta^{18}O$ and 0.05‰ for $\delta^{13}C$ based on replicate measurements of an internal carbonate standard. The isotopic composition of percolating water from which the flowstone calcite precipitated can be determined by analysing water released from fluid inclusions trapped within the carbonate matrix (Jiménez de Cisneros et al. 2011).

Fig. 2 Stalagmite EM-MO from Órganos Cave formed during MIS10. Small black circles show the position of the samples used for stable isotope analyses



U-series analyses were carried out using multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS). The small calcite samples required (100–500 mg) mean that thin growth phases and hiatuses can be easily resolved.

High precision (typically ~0.5 %) allows growth phase length to be more precisely constrained. U-Th isotopic measurements were undertaken on a ThermoFinnigan Neptune MC-ICPMS, (Bristol Isotope Group facilities, University of Bristol, UK).

4 Results

Results from the XRD analysis show that the studied material consists of calcite. Most of the calcite is homogeneous, made of clear palisade crystals with fine growth laminations. Speleothem mineralogy and fluid inclusions are interpreted to be primary, which permits to conclude that fluid inclusion isotope composition is undisturbed since the time of formation.

The stalagmite was tested with the Hendy test for isotopic equilibrium. Samples taken along a single growth layer should show no signs of kinetic isotopic fractionation. The test results show a variation of less than 0.4‰ in $\delta^{18}O$ values and no sequential enrichment in the $\delta^{13}C/\delta^{18}O$ plot. This indicates that speleothem growth is in isotopic equilibrium with the drip water and that the calcite isotopic values do not reflect kinetic effects.

Figure 3 shows the variation of $\delta^{18}O$ and $\delta^{13}C$ from the base to the top of the stalagmite versus time. The $\delta^{18}O$ values vary from −4.30 ‰ to −5.95 ‰ and the $\delta^{13}C$ vary from −3.63 ‰ to −6.03 ‰. We have extracted inclusion water using the method by Jiménez de Cisneros et al. (2011). Water released from inclusions was analysed and the mean values were −4.7‰ $\delta^{18}O_w$ and −29.2‰ δD. Analytical uncertainties are 1.5‰ for δD and 0.5‰ for $\delta^{18}O$.

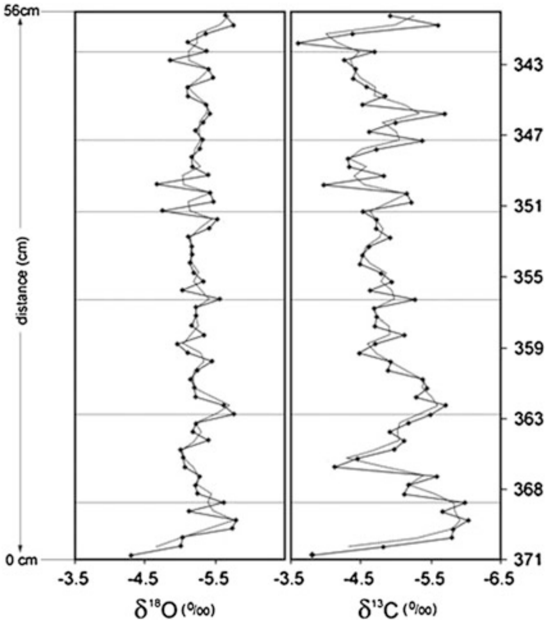


Fig. 3 $\delta^{18}O$ and $\delta^{13}C$ plotted against depth in the stalagmite. The dating results are shown to the right of the figure

The calculated ages from Uranium series $^{230}Th/^{234}U$ are 340–370 ky from the base to the top of the stalagmite. Precipitation rates were calculated by measuring the distance between points of known age. If a uniform stalagmite growth rate is considered, this means an accretion rate of about 1.8 cm/1,000 years. This rate is interpreted to represent consistent flow rates of meteoric water through the local country rocks into the cave.

5 Discussion

Calcite of stalagmites mainly originates from the seepage of rainwater. Although temperature is the major controlling variable for $\delta^{18}O$ carbonate values in speleothems, it should be stated that there are two competing temperature effects controlling the speleothem $\delta^{18}O$ values. These are an increase in the $\delta^{18}O$ (less negative) values of meteoric water related to warming and a decrease in the $\delta^{18}O$ (more negative) speleothem data corresponding to increased temperatures within the cave.

The $\delta^{18}O$ and $\delta^{13}C$ values for stalagmite when combined with the $^{230}Th/^{234}U$ ages, help to reconstruct a continuous paleoclimate record over the 340,000–370,000 years ago, being the interval during which this stalagmite was formed. This period is characterized by values of precipitation, temperature and vegetation cover very favorable in this area for the development of speleothems (Durán 1996; Durán et al. 2004). Samples precipitated under thermodynamic equilibrium conditions are expected to display the following criteria: a) no correlation between $\delta^{18}O$ and $\delta^{13}C$ along a single growth layer and b) constant $\delta^{18}O$ and variable $\delta^{13}C$ values along a single growth layer. The stalagmite samples yielded positive results in the Hendy test (Hendy 1971), suggesting that calcite precipitation occurred under conditions of (or near to) the isotopic equilibrium. $\delta^{18}O$ values remained almost constant in each growth layer, showing only minor changes (under 0.4 in all cases). Figure 3 shows the carbon and oxygen stable isotope records obtained along the growth axes of stalagmite. These plots depict no significant correlation between carbon and oxygen values, a finding that also supports isotopic equilibrium during precipitation.

An alternative test of thermodynamic equilibrium is by comparing the $\delta^{18}O$ values of fluid inclusions with those of the surrounding calcitic matrix. Assuming that the inclusions and the surrounding calcite are coeval, and that the oxygen isotope composition of trapped fluids did not vary over time, published water/calcite equilibrium calibrations can be used to reconstruct cave paleotemperatures, and to assess whether these temperature predictions are physically realistic. To obtain the absolute temperature variation for a given $\delta^{18}O$ variation an independent estimate of $\delta^{18}O_w$ should be done, using fluid inclusion studies. The mean values of paleotemperature obtained were 17–18 °C and in this case we used the $\delta^{18}O_w = -4.7‰$ mean value of water extracted in the samples (Sharp 2007). The oxygen isotope record shows an overall increasing trend from the eldest growth

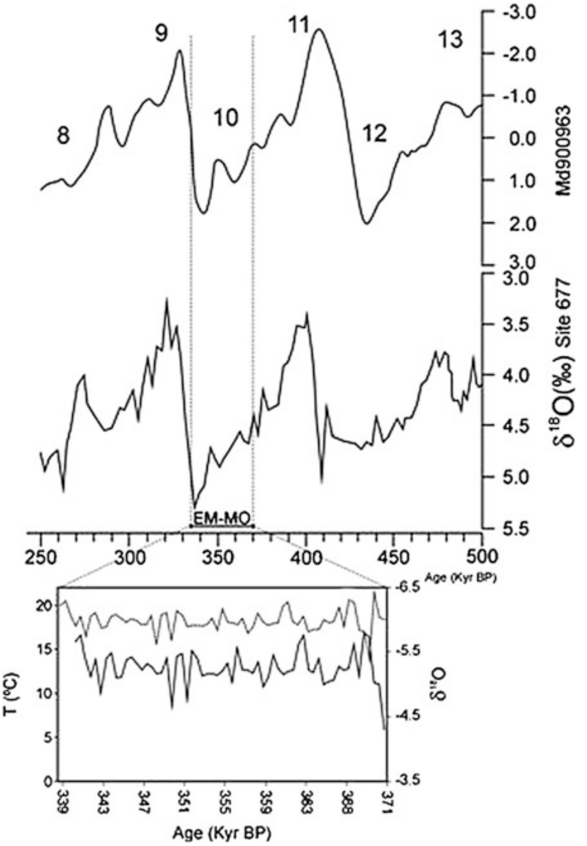


Fig. 4 The growth period of the stalagmite EM-MO matches the glacial period (MIS10) in the global sea level curve from ODP Site 677 (Shackleton et al. 1990) and MD 99003963 (Bassinot et al. 1994). δ^{18}O record obtained in the stalagmite from Órganos Cave

period (17–20 °C) which may be interpreted as representing the Middle–Late Pleistocene late warming (340,000–370,000 years ago).

A temperature-time profile using δ^{18}O from the speleothem as proxies for temperature is plotted on Fig. 4 together with those obtained from site 677 (Shackleton et al. 1990) and MD99003963 (Bassinot et al. 1994). The speleothem record contains several very sharp changes in δ^{18}O being the sign of rapid cooling and warning trends. In order to interpret δ^{18}O fluctuations in a paleoclimatic sense, the relationship between δ^{18}O and temperature must be assessed. The relatively enriched oxygen isotope ratios in the oldest part of the stalagmite (end of MIS10) indicate a colder period followed by a slightly warmer one (start of MIS9). Our paleoclimate records are generally concordant with data obtained in isotopic studies of deep marine sediments, confirming that we are recording global climatic events (Williams et al. 1988; Dotsika et al. 2010; Moreno et al. 2013).

6 Conclusions

This study presents terrestrial Middle–Late Pleistocene paleoclimate results from a stalagmite from southern Spain (Málaga). The stalagmite is dated by ^{230}Th/^{234}U, ranging in age from 340 to 370 ky BP.

δ^{18}O values for individual speleothem layers are consistent with equilibrium deposition of individual speleothem layer. Paleoclimatic information was gained by dating periods of stalagmite growth and measuring δ^{18}O and δD of speleothem calcite and fluid inclusions respectively.

The isotopic record of stalagmite shows a deposition under colder conditions (MIS10) followed by a warmer period (MIS9).

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