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A late-Holocene climate record in stalagmites from Modrič Cave (Croatia)

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ABSTRACT:

Few terrestrial Holocene climate records exist from Southeastern Europe despite its important geographic position as a transitional climatic zone between the Mediterranean and mainland continental Europe. In this study we present new petrographic and stable isotope data for two Holocene speleothems from Modrič Cave, Croatia (44°15′N, 15°32′E), a coastal Adriatic site (120 metres inland). Modern meteorological and cave conditions have been monitored for two years to understand the links between the climate variability and the stable isotope time-series records in speleothems. Typical of a Mediterranean-type climate, a negative water balance exists between April and September, so that recharge of the aquifer is restricted to the winter months. The weighted mean δ¹⁸O of the rainfall is -5.96‰ (2σ = 2.83), and the weighted mean D/H rainfall value is -36.83‰ (2σ = 19.95), slightly above the Global Meteoric Water Line (GMWL), but well below the Mediterranean Meteoric Water Line (MMWL). Modern calcite from the tops of each stalagmite exhibits δ¹⁸O values that are close to isotopic equilibrium with their respective drip water values. Unfortunately, the relatively young ages and low uranium contents (c. 50 ppb) of both stalagmites hamper the use of U-series dating. Radiocarbon dates have been used instead to constrain their chronology using a dead carbon correction. Aside from some Isotope Stage 3 material (c. 55 ka), both stalagmites were deposited during the late Holocene. Climatic conditions during the late Holocene are inferred to have been sufficiently wet to maintain stalagmite growth and any hiatuses appear to be relatively short lived. Inferred changes in the stalagmite diameters during deposition are linked to δ¹³C and δ¹⁸O variations, indicating alternating periods of drier and wetter conditions. Drier conditions are inferred for the late Roman Ages warm period and the mid-Medieval Warm Period (MWP). Wetter conditions are associated with the Little Ice Age period.
1. Introduction

Published Holocene paleoclimate records for the circum-Mediterranean region, indicates significant differences between the eastern and western basins (e.g. Brayshaw et al., 2011; Bar-Matthews et al., 1997; Kuzucuoğlu et al., 2011; Magny et al., 2002; Peyron et al., 2011; Giraudi et al., 2011; Zanchetta et al., 2011; Martin-Puertas et al., 2010). Holocene climate reconstructions from Croatia can provide a link between the two Mediterranean sub-basins. While numerous studies of the Holocene terrestrial vegetation history of this central Mediterranean region have been published (Sadori et al., 2011), many of the lake sediment sequences on which reconstructions are based are poorly dated, or are sampled at a resolution that is too coarse to discern sub-millennial late Holocene environmental change. An additional complication is that many terrestrial late Holocene pollen records are compromised by anthropogenic effects (e.g. deforestation and cultural changes), making it difficult to disentangle human- and climate-induced vegetation change in the region (e.g. Di Rita and Magri, 2009; Mercuri et al., 2011).

Information about past climates in the region has also been derived from Adriatic Sea sediment cores. By contrast with the lake sediment records, many of the measurable proxies in these marine cores (e.g. planktonic and benthic foraminifera assemblages) are relatively unaffected by human induced changes on the adjacent continents, particularly in the more distal sites (Oldfield et al., 2003; Sangiorgi et al., 2003; Piva et al., 2008). In the recent work of Piva et al. (2008) for example, foraminifera assemblages, along with palaeomagnetic secular variations and aquatic pollen indicators were investigated in a set of marine sediment cores from the Western Adriatic shelf and the Southern Adriatic deep basin to reconstruct a high resolution record of environmental and climatic conditions for the past 6,000 years. The abundance of foraminifera species indicative of warm/dry conditions was found to increase markedly during climatic optima such as the Medieval Warm Period (MWP) and the Roman Ages, events for which there is a significant body of independent documentary, archaeological and historic evidence. Thus, repeated peaks in the occurrence of Globigerinoides sacculifer (an oligotrophic, shallow-water dweller typical of warm tropical environments, that currently only appears in the Western Mediterranean at the end of summer), reflects warm conditions associated with the MWP and Roman Ages. Similarly, the last occurrence of G. sacculifer marks the onset of the ‘The Little Ice Age’ (LIA), recognised as a cold and relatively wet period in this region. According to Piva
et al. (2008), two peaks in *Valvulineria complanata* (an opportunistic benthic species associated with a high availability of organic matter as a result of increased river discharge), match well with the coldest phases of the LIA: the so-called Fernau (1590-1630 AD) and Napoleon (1810-1820 AD) intervals. Cold and humid intervals were thus linked to a substantially increased river discharge, suggesting enhanced rainfall during the cold phase of the LIA.

Speleothem records have the potential to give a perspective on the terrestrial environmental changes that may have accompanied the changes recorded in the marine realm discussed above. However, relatively few studies have been published on speleothems from this part of Europe. Previous work from Croatia focused mainly on submerged samples from submarine caves along the Eastern Adriatic coast (Surić and Juračić, 2010). Horvatiničić et al. (2003) reported δ¹³C and δ¹⁸O time-series records for Holocene speleothems and tufas from Croatia (Plitvice Lakes, Zrmanja, Krupa and Krka Rivers) and Slovenia (Postojna Cave, and Podstenjšek Creek). Most samples were dated using the ¹⁴C method, but a few from the Krka and Plitvice areas were dated by U-series (Srdoč et al., 1994; Horvatiničić et al., 2000). Most of the speleothems and all of the tufas indicate late Holocene deposition, although some stalagmites commenced growing during the Late Glacial (c. 15-12 ka BP).

A recent study of speleothems from three Croatian caves (Lončar et al., 2011) revealed depositional intervals similar to those reported by Surić and Juračić (2010); however some samples also indicate Holocene deposition (4 ka to present) similar to that reported here.

Rogerson et al. (2011) presented a stalagmite record from Ponor Jazbina v Rovnjah, Slovenia, for the period c. 9 to 0.5 ka BP. Relatively arid early Holocene conditions were inferred on the basis of slow growth rates and pronounced Sr/Ca maxima. Of more relevance to the present study is the record for the last 4ka BP from this Slovenian site. Changes in δ¹⁸O and Sr/Ca in this Slovenian stalagmite suggest considerable late Holocene climate variability. Lower δ¹⁸O values, coupled with minima in Sr/Ca are associated with well documented cool climatic phases such as the Little Ice Age and the Late Roman Ages/early Dark Ages, implying reduced aridity. By contrast, higher δ¹⁸O values and maxima in Sr/Ca ratios are associated with the Medieval Warm period, interpreted by Rogerson et al. (2011) to reflect increased aridity. These authors also suggested that millennial scale climate changes during the Holocene were caused by shifts
in atmospheric circulation, resulting in greater precipitation during cool phases, and reduced precipitation during the warmer periods.

A stalagmite from Ceremosnja Cave, eastern Serbia dated using the radiocarbon method due to its low uranium content, preserves a record back to $2,300 \pm 40$ yr BP (Kacanski et al., 2001). Its paleoclimate record based on stable isotope data indicates two warm periods between c. 2,275 and 2,050 yrs BP and 1480-960 yrs BP, terminating with a colder phase from 960 BP to the present. Gradually decreasing $\delta^{18}O$ values in this speleothem during the last 2000 years were interpreted as a cooling trend, but their suggested 5°C decrease in temperature is difficult to reconcile with the available pollen data for the region (Wanner et al., 2008; Davis et al., 2003). Thus, changes in $\delta^{18}O$ at least in part, are likely to reflect temporal changes in the oxygen isotope ratio of precipitation rather than temperature change alone.

This study presents new data for two speleothems (MOD-21 and MOD-22) from Modrič Cave, Croatia with the aim of reconstructing aspects of late Holocene climate change in a region that can provide links between the two Mediterranean sub-basins. Stalagmite MOD-22 was the more suitable for paleoclimate studies, and is the main focus of this paper.

2. Site and sample description

Modrič Cave (44° 15' 24.6" N, 15° 32' 14.16" E) was discovered in 1985 AD close to the eastern Adriatic coastline of Croatia, approximately 30 km north east of Zadar (Figure 1). This sub-horizontal cave developed along a faulted contact zone between the Adriatic and the Dinaric structural complexes of the Upper Cretaceous Adriatic carbonate platform (Herak, 1986). The limestone thickness above the cave ranges from c.1 to 30 m, and its entrance (1.8 m x 1.3 m) faces the coast, at an elevation of 32 metres above sea level (m.a.s.l.), (Surić et al., 2010). The cave extends eastwards and branches into two main passages (Figure 1; Miko et al., 2002). All investigations reported here were conducted in the north passage. The south passage contains evidence for human activity (bones and pottery) as well as bone fragments of Upper Pleistocene fauna (skull of cave bear *Ursus spelaeus*) (Malez, 1987).
The region is characterised by a Mediterranean temperate humid climate with hot summers (Cfa type; Köppen, 1936). Vegetation consisting of C3 plants, mainly scrubby grassland with small isolated bushes, is developed on a thin (<0.5m) terra-rossa soil containing limestone fragments.

In June 2008, two in situ stalagmites (MOD-21 and MOD-22) were retrieved from the cave (Figure 1). In January 2009, three temperature loggers and two Stalagmate® drip loggers were installed to monitor cave environmental conditions and to characterise the hydrological behaviour of the drip sites that fed the two sampled stalagmites. Additionally, a Pluvimate® rain-gauge was installed outside the cave, approximately 500 meters from the entrance. Water samples from two drip feeders (MODW-21, MODW-22) and rainfall were collected monthly from July 2008 to June 2010 for isotopic analysis.

Drip site MODW-22, the feeder drip of stalagmite MOD-22 is located ~ 150 m from the cave entrance (Figure 1), approximately 22 metres below the surface. Drip site MODW-21, the feeder drip to stalagmite MOD-21 is located ~210 m from the entrance, at a depth of 22 metres below the surface. This chamber is well isolated from the rest of the cave by two constrictions: no. 3 and no.13 (Figure 1).

The cave air temperature and the drip-rates at the MODW-21 and MODW-22 sites were monitored from January 2009 to October 2010 using Tinytag Aquatic® temperature loggers, with a resolution of 0.01°C. The drip logger at MODW-22 failed in 2009, and the data are available from November 2009 to October 2010 only. Due to periodic clogging of the external Pluvimate® rain gauge, a data from three nearby meteorological stations: Zadar-Zemunik (88 m.a.s.l. and 23 km from Modrič; NOAA, 2010), Zadar-Puntamika (7 m.a.s.l and c. 30 km from Modrič site; CMHS, 2010) and Starigrad-Paklenica (12 m.a.s.l. and 8 km from Modrič; CMHS, 2010) were used to calculate the water balances at the cave site using the Thornthwaite evapotranspiration model (Thornthwaite, 1948; McCabe and Markstorm, 2007). All three sites exhibit the highest temperature in July and August (c. 25 ºC), and a strong water deficit during the summer months. Recharge of the aquifer thus appears to be restricted to the winter and early spring (November-March).

Stalagmite MOD-22, the primary focus of this paper, was an actively growing, 28 cm long stalagmite when collected (Figure 2a, 2b). Its feeder drip is a long (approximately 1.5 m) single
stalactite. The opaque white calcite in MOD-22 is softer and more porous than in MOD-21. Along the whole stalagmite there are several darker layers (c. 1-5 mm thick), some of which include visible clay-rich horizons.

Speleothem MOD-21 was an actively growing 23.5 cm long stalagmite located approximately 210 metres from the cave entrance under the Jellyfish formation (Figure 2c, 2d). During its early stages of deposition MOD-21 appears to have had two feeder drips, although all analyses are focused along the central axis of the stalagmite. Analysis of visible changes in the carbonate petrography of MOD-21 and radiocarbon dating revealed an erratic growth rate. The record from this speleothem is shown in detail in the supporting electronic information (Appendix S1).

3. Methods

A 0.1 mm diameter dental drill bit was used to obtain ~3 mg of carbonate powder from stalagmite MOD-22 at 2.5 mm intervals along its growth axis, producing 111 samples. The time interval between successive drill holes represents approximately 16 years on average in MOD-22, but this varies between 4 and 26 years, depending on the growth rate.

Oxygen and hydrogen isotope measurements on the water samples were carried out at SILLA (Stable Isotope & Luminescence Laboratory) at the University of Birmingham, UK. All water data were normalised to V-SMOW standards. Analysis of the first batch (c. 50%) of stable isotope measurements on the carbonates were carried out at the Stable Isotope Laboratories at Royal Holloway University of London (UK), and second batch was analysed by Iso-Analytical laboratory (UK). All data for carbonates are reported relative to the V-PDB standard.

A small number of U-series isotope measurements were carried out at University College Dublin, using a ThermoFisher Neptune® multi-collector inductive coupled plasma mass spectrometer (MC-ICP-MS) equipped with an Aridus® desolvation nebulizer. Sample preparation prior to column chemistry involves suspending c. 200 mg of calcite powder in deionised H₂O in a 15 ml teflon Savillex beaker and spiking with a mixed spike (²³³U-²³⁶U-²²⁹Th). After spiking, samples were dissolved gradually in 7M HNO₃ and left to equilibrate for c.
24 hours. BioRad AG 1X8 Resin (200-400 mesh) ion exchange columns were used for U and Th separation and purification.

All radiocarbon measurements were conducted by the Poznan Radiocarbon Laboratory, Poland, using a 1.5 SDH-Pelletron Model Compact Carbon AMS using the Oxalic Acid II (OxII) standard (Goslar et al., 2004). Radiocarbon dates were calibrated using the age calibration program OxCal4 (Bronk Ramsey, 2009) with IntCal 09 calibration curves (Reimer et al., 2009).

4. Results

4.1 Cave air temperature

The mean annual air temperature (MAAT) for the years 1961-2000 from the Zadar Puntamika and Starigrad meteorological stations (1992–2010) is 14.43 ºC and 16.00 ºC respectively. Meteorological data from the Starigrad station (c. 8 km NW from Modrič and 12 m a.s.l.) were used as a proxy for external air temperature at the Modrič site.

Temperature logger TL1, located nearest the cave entrance (Figure 1), recorded an average air temperature of 12.96 ºC (2σ = 4.1), but this site partly reflects seasonal variations in external air temperature with a range of c. 7.42 ºC and a delay of c. 2 months relative to the seasonal changes in external air temperature. By contrast, temperature logger TL2, deployed at the MODW-22 drip site (Figure 1), exhibits a much more stable temperature with a mean annual value of 15.46 ºC (2σ = 0.08). The amplitude of seasonal variations at this site is c. 0.19 ºC, markedly lower than at TL1. As expected, temperature logger TL3 (at drip site MODW-21, Figure 1) shows the most stable temperature of all three sites. Small temperature variations do occur at this site, but their amplitude (0.09 ºC) is very small. The mean cave air temperature value calculated from one full year of data from TL3 is 15.64 ºC (2σ = 0.04). Overall, the air temperature in the interior of the cave (loggers TL2 and TL3) record relatively constant temperatures that are similar to those of the nearby Starigrad meteorological station.
4.2 Drip rate and rainfall data

The objective of this part of the study was to characterise the hydrological behaviour of the drip sites (MODW-21 and MODW-22) that feed stalagmites MOD-21 and MOD-22 to aid with the interpretation of the stalagmite stable isotope data. Data from both drip loggers, along with rainfall data from the Pluvimate® logger at Modrič, were converted from drips per hour to millilitres per day based on the radius of the feeding stalactites (Collister and Mattey, 2008). These data were compared with the rainfall record inferred for the Modrič site (Figure 3) and with two other meteorological stations: Zadar-Zemunik (NOAA, 2010) and Starigrad (CMHS, 2010). In general, the rainfall events occur at the same time, but the magnitude of precipitation events at Starigrad is greater than that recorded at Modrič. The Modrič precipitation record is in reasonable agreement with that from Zadar. Summer months tend to be relatively dry at Modrič over the short monitored period, with the exception of July 2009, when a heavy rainfall event was recorded. A similar rainfall event occurred simultaneously at the Zadar station.

Drip site MODW-22 is a very slow drip (average c. 1 drip/4.77 min), and it remained relatively insensitive to precipitation events over the period of its monitoring from October 2009 to September 2010, Figure 3). The drip logger data are in good agreement with field observation in June 2008, when MODW-22 was observed to drip approximately every 5 minutes, before and after rainfall. Unfortunately, the MODW-22 record from January to October 2009 is unreliable due to the logger failure, and is not shown in Figure 3. During the period from November 2009 to February 2010, the drip rate remained quite constant with the average value of 19.23 ml/day (average drip rate of 1 drip/6.21 min), but showed a sharp increase in mid-February, followed by a gradual decrease to an average value of 30 ml/day (c. 1 drip/3.52 min). At the beginning of July 2010, recording was interrupted for 9 days. From mid-July to September 2010, drip MODW-22 shows lower average drip rate of 19 ml/day. The average amount of water entering through this drip site during the entire period is c. 25.19 ml/day (755.80 ml/month).

Drip MODW-21 is faster than MODW-22, with an average drip rate of 48.28 ml/day, but is much more sensitive to rainfall events. The amount of water dripping at this site is very variable, but overall there is a gradual decrease from the winter towards the summer months (Figure 3). Drip-rates at MODW-21 increased with a c. 2 to 5 day delay in response to intense rainfall events, as seen in the Starigrad and Zadar meteorological stations (Pluvimate® logger was
blocked). This delay is approximately constant, and is especially prominent during the period from January to May 2009. From June 2009 to October 2009 MODW-21 appears to be unresponsive to rainfall events, possibly due to a high evapotranspiration rate and a negative water balance at this time of year.

During the periodic visits to the cave for water collection it was noticed that both drip sites never dried up completely. Overall, the drip rate data from MODW-21 and MODW-22 are in good agreement with the monthly water balance calculations using the Thornthwaite evapotranspiration model (Thornthwaite, 1948; McCabe and Markstorm, 2007) based on the record from meteorological stations that indicate a strong summer water deficit and recharge of the aquifer mostly during the winter months. The smoother trends of MODW-22 and the persistence of its drip flow during the summer of 2010 points to a greater fracture controlled storage component than at MODW-21. In the scheme of Smart and Friederich (1987), both sites are classified as ‘seepage flow’ drips.

4.3 Drip and rain water isotope data

The residence time of water in the bedrock above the cave, and the nature of the moisture sources can be investigated using drip water and rainfall D/H and δ¹⁸O. Knowledge of the water residence time in the aquifer is crucial to detect possible seasonal biases in the speleothem δ¹⁸O signal. A drip site fed by water with a very short residence time for example could be biased towards the seasonal rainfall isotope signal associated with the wet season. As discussed below, this appears unlikely for the Modrič drip sites studied here.

The δ¹⁸O and D/H data for rainfall (Figure 4) sampled monthly for nearly two years at Modrič, exhibit some seasonal variability, with lower values in the winter months (weighted mean δ¹⁸O = -6.93‰, mean D/H = -43.30‰ SMOW), and higher values in the summer months (mean δ¹⁸O = -5.30‰, mean D/H = -32.50‰ SMOW). The weighted mean δ¹⁸O is -5.96‰ (2σ = 2.83), and the range of δ¹⁸O is 5.38‰ V-SMOW. The weighted mean D/H rainfall value is -36.83‰ (2σ = 19.95).
By comparison with the rainfall data, the oxygen isotope ratios at MODW-21 are buffered, and show only limited seasonal variability of c. 1.08‰ V-SMOW (Figure 4). Thus, the annual mean δ\(^{18}\)O for this site for the year 2009 is -6.40‰ (2\(\sigma\) = 0.54). Site MODW-22 shows somewhat more seasonal variability (c. 2.18‰, V-SMOW) during the analyzed period (June 2008 to September 2010), and its annual mean value for the year 2009 is -5.19‰ (2\(\sigma\) = 1.6). The mean δ\(^{18}\)O from drip site MODW-22 perhaps coincidentally shows a value close to the weighted summer mean δ\(^{18}\)O of rainfall from Modrič, while mean δ\(^{18}\)O from MODW-21 is close to the weighted winter mean δ\(^{18}\)O of rainfall. Drips at the MODW-22 site show higher δ\(^{18}\)O values in winter (December to March) and lower values in summer and appear to be strongly out of phase with rainfall values (Figure 4). The partial preservation of seasonal δ\(^{18}\)O variability in the MODW-22 drip data suggests a ‘piston-flow’ behavior in which newly recharged rainfall pushes through previously stored, partly-mixed water.

The annual mean D/H value of MODW-21 drip water for the year 2009 is -38.33‰ (2\(\sigma\) = 4.51), and that from MODW-22 for the same period is -28.15‰ (2\(\sigma\) = 13.41). Overall, the δ\(^{18}\)O and D/H values for drip-waters from MODW-21 are more strongly buffered than those from MODW-22.

The D/H and δ\(^{18}\)O data for drip and rainfall waters were also used to investigate the vapour sources of the rainfall that predominantly recharge these sites. The Global Meteoric Water Line (GMWL) and the Mediterranean Meteoric Water Line (MMWL) are shown in Figure 5a, along with the Modrič drip and rainfall data. This figure shows that the Modrič water samples plot closer to the GMWL (D/H = 8* δ\(^{18}\)O+10) than the MMWL (D/H = 8* δ\(^{18}\)O+22). The Local Meteoric Water Line (LMWL) is given by D/H = 8* δ\(^{18}\)O+13. Also shown for comparison is the Local Meteoric Water Line for the Zadar region (Vreča et al., 2006). For comparison, the averaged data from the Croatian, Italian and Slovenian GNIP sites are also shown in figure 5a (IAEA/WMO, 2006). Figure 5b illustrates an inverse correlation between the average monthly rainfall amount and δ\(^{18}\)O of rainfall at the Zadar GNIP station that influenced speleothem δ\(^{18}\)O.
4.4 Age model of MOD-22

Unfortunately, the Modrič stalagmites are characterised by low uranium contents (typically c. 50-70 ppb in MOD-22 and c. 30 ppb in MOD-21), young ages and relatively high $^{232}$Th contents, making U-series dating impossible (Table 1). Attempts to apply corrections for the detrital contamination in the Holocene U-series age determinations for MOD-22 (Table 1) were unsuccessful, because of their very low $^{230}$Th/$^{232}$Th ratios (typically <3) and young ages. Corrected ages were very sensitive to the choice of $^{230}$Th/$^{232}$Th in the detrital component and as a result meaningful ages could not be calculated. Corrected ages that were in line with the corrected and calibrated $^{14}$C ages for MOD-22 (discussed below) required detrital $^{230}$Th/$^{232}$Th values of c. 1.2 to 1.5, within the range of $0.8 \pm 0.8$ (2σ) commonly used for detrital thorium corrections (Richards and Dorale, 2003).

For these reasons, radiocarbon and U-series dating methods have been combined in an attempt to constrain a chronological model for these speleothems (Table 1 and 2, Table S1 in Appendix S1). Because radiocarbon activities in stalagmites are strongly affected by the incorporation of ‘dead’ carbon from limestone and aged soil-derived carbon, raw $^{14}$C activities must be first corrected for this reservoir effect (called here as a dilution effect - DE) prior to calibration. Dead carbon values can vary between and within different cave sites, depending on vegetation cover, soil productivity, hydrological factors and limestone dissolution rates (e.g. Genty et al, 1999; Genty and Massault, 1999; Genty et al., 2001; Rudzka et al., 2011). The age calibration program OxCal (Bronk Ramsey, 2009) was used to calibrate the $^{14}$C data using calibration curves from Reimer et al. (2009). Calibrated dates reported in Table 2 and Table S1 (Appendix S1) were chosen with the highest probability.

For stalagmite MOD-22, the dead carbon value was estimated using a quasi-linear growth rate model for the sample, with the top surface of the stalagmite anchored to the present-day (active when collected). The uncorrected $^{14}$C data to the DE value, (black solid curve in Figure 6) from stalagmite MOD-22 increase monotonically with distance, indicating quasi-linear growth rates. This points towards relatively stable soil carbon turnover and relatively constant limestone dissolution rates. The c. 1050 year offset when comparing these $^{14}$C data with the last data point (anchored by the year of collection) (Figure 6) is taken to reflect the ‘dead carbon’ effect for this sample. This corresponds to a dead carbon value of approximately 12.5% (Table 2, Figure 6).
Probability density functions of calibrated dates from stalagmite MOD-22 calculated after a correction to the DE value of 12.5% are shown in Figure 7.

The six $^{14}$C measurements from MOD-22 indicate that it was a fast growing, late Holocene stalagmite. Deposition commenced around 331 ± 96 AD (1619 ± 96 cal BP) (Table 2), and continued at an almost linear rate prior collection in 2008 (Figure 6). Its average growth rate is 304 μm/yr. In detail however, this rate varies between the dated intervals, with a noticeable increase in growth rate between 1345 ± 59 and 1580 ± 96 years AD (605 ± 59 and 370 ± 96 cal BP), at a distance 155-35 mm from the top.

4.5 Speleothem isotope data

‘Hendy tests’ on MOD-22 (Figure 8a) show no correlation between the $\delta^{18}$O and $\delta^{13}$C along the examined laminae, indicating no evidence for strong disequilibrium (kinetic) isotope fractionation effects. The stable isotope record for stalagmite MOD-22 shows only moderate variations along the whole time series (Figure 8b). $\delta^{18}$O varies by about 2‰ and $\delta^{13}$C by about 4‰. The mean $\delta^{18}$O value is -4.11‰ V-PDB (2σ = 0.93), and the mean $\delta^{13}$C value is -7.37‰ V-PDB (2σ = 1.74). Through the whole period of deposition of MOD-22 there are two distinctive trends of increasing $\delta^{18}$O, first in the interval between 245 mm and 190 mm from the top and again between 150 mm and 85 mm from the top. $\delta^{13}$C shows at least five increasing trends through the time series (black arrows, Figure 8b).

Based on the modern drip water $\delta^{18}$O values for both stalagmites MOD-21 and MOD-22, and the present-day cave temperature, model $\delta^{18}$O values for modern calcite were calculated using equations from Craig (1965), Friedman and O’Neill (1977), Kim and O’Neill (1997), Coplen (2007), Dietzel et al. (2009) and Tremaine et al. (2011). Values obtained based on the Friedman and O’Neill (1977) and Kim and O’Neill (1997) calculations, are c. 1‰ higher than the measured $\delta^{18}$O values for MOD-21 and MOD-22. Values obtained using calculations from Dietzel et al. (2009) are c. 0.5‰ higher than measured values for MOD-21 and MOD-22. Calculations based on the equations of Craig (1965), Coplen (2007) and Tremaine et al. (2011) seem to reflect the measured $\delta^{18}$O values to within 0.65‰ implying calcite deposition close to isotopic equilibrium (e.g. McDermott et al. 2011)
5. Interpretations

Overall, there are no high amplitude seasonal variations in the cave air temperature at sites MODW-21 and MODW-22 (c. 0.09 °C and 0.19 °C respectively), indicating that both of these sites faithfully record the MAAT of the region averaged over multi-annual time scales. Drip sites MODW-21 and MODW-22 both display a ‘seepage flow’ character in the Smart and Friedrich (1987) classification. However, the MODW-21 drip site responds more rapidly to rainfall events, particularly from autumn to early spring, suggesting some ‘seasonal drip’ character. The presence of a small storage water reservoir and a ‘seepage flow’ component in the MODW-21 drip site could account for its behaviour from January 2009 to May 2009. The fact that most of stalagmite MOD-21 grew rapidly over a short time interval in the late Holocene (Figure S2b) strongly suggests relatively constant water infiltration during this period.

By contrast with MODW-21, drip site MODW-22 is characterised mostly by a ‘seepage flow’ character (Figure 3). The drip rate increases between February and March 2010, and after that it decreases very gradually, remaining essentially insensitive to rainfall events. This type of drip rate behaviour suggests aquifer re-charge during the winter, and its slow exhaustion during the subsequent months.

Rainfall at the Modrič site is probably derived from a combination of several sources. The data for the cave and meteoric waters are close to the Global Meteoric Water Line (GMWL) on a plot of D/H and δ¹⁸O which indicates a predominance of moisture from the Atlantic Ocean. The data from MODW-21 drip site plot entirely on the LMWL of Vreča et al. (2006); however data from drip site MODW-22 plots above this LMWL, possibly suggesting slower infiltration through the soil and consequently greater evaporation effects. The latter effect causes possible isotope enrichment prior to infiltration (Wackerbarth et al., 2010).

Drip waters from MODW-21 do not show large temporal variations in either D/H or in δ¹⁸O, suggesting relatively efficient mixing of waters above the drip site, despite its more ‘flashy’ hydrological response (Figure 3). The marked attenuation of the seasonal meteoric water D/H and δ¹⁸O signals suggests a relatively long (multi-annual) residence time for the water feeding MODW-21. While the MODW-21 drip waters do not follow the D/H and δ¹⁸O of rainfall, the
site is hydrologically responsive to the rainfall events, suggesting the presence of a fracture controlled stored water reservoir (buffering of isotopic signal).

Site MODW-22 exhibits higher D/H and δ¹⁸O values during the winter, and appears to be out of phase with the seasonal trends in meteoric δ¹⁸O and D/H. Overall, mean δ¹⁸O from MODW-22 displays has a value similar to that of summer rainfall mean δ¹⁸O, and is higher than the mean δ¹⁸O value for MODW-21. Delayed and attenuated seasonal signals in the isotopic record of MODW-22 and a relatively constant drip rate suggests a piston-flow type behaviour with incomplete mixing between the summer- and winter-recharged waters. Nonetheless, its hydrological behaviour indicates the presence of an important base-flow component that is not seen in MODW-21 (Figure 3). Assuming that the present-day hydrological (drip-rate) characteristics of these sites have remained relatively constant, the drip monitoring data indicate that the two sites have different hydrological thresholds. Thus, site MODW-21 and by inference stalagmite MOD-21, would be expected to cease dripping (growing) during prolonged (multi-annual) drought periods, whereas the more important storage component of MODW-22 could permit continued dripping (and growth) during prolonged dry intervals.

Age models based on ¹⁴C dates and DE corrections indicate that both stalagmites were deposited in the late Holocene, apart from some Marine Isotope Stage 3 material (c. 55 ka) near the base of MOD-21 (Supporting information, Appendix S1). The climatic conditions during the late Holocene were therefore sufficiently wet to maintain stalagmite growth, and any hiatuses in MOD-22 appear to be relatively short.

Because the radiocarbon chronology depends on the ‘dead carbon’ correction, it should be used cautiously for paleoclimatic interpretations. Nonetheless, an attempt was made to identify intervals of wetter and drier conditions (Figure 9) based on petrography and the stalagmite diameter. Using the rationale of Railsback et al. (2011), wetter periods are inferred when a growth layer (or layers) flow down and drape over a previously deposited layer on the flanks of the stalagmite, whilst drying trends are inferred when layers are narrower and are perched upon previously deposited layers. Based on these assumptions, we infer at least five intervals of different climatic regimes in MOD-22 (drying trends – arrows in Figure 9).
Based on the corrected and calibrated $^{14}$C ages, the approximate duration of previously recognised distinctive climatic intervals recorded during the late Holocene, (e.g. Roman Warm Period (RWP), Dark Ages cold phase, Medieval Warm Period (MWP) and Little Ice Age (LIA)) are also shown (Figure 9).

Drier conditions, recognized by a gradual narrowing of stalagmite MOD-22 during deposition, are usually associated with trends towards higher $\delta^{13}$C (e.g at c. $512 \pm 76$ AD and $900 \pm 76$ AD, Figure 9). At least five such drying-out trends are highlighted on Figure 9. In this interpretation, two very pronounced drier episodes occur in the lower part of MOD-22. This is consistent with the more compact character of the calcite. Using the available chronology, these two dry episodes appear to correspond relatively well with the RWP and the transition from Dark Ages to the MWP, and are in good agreement with Piva et al (2008) and Rogerson et al. (2011) who suggested warmer and drier conditions during these two late Holocene periods in the Adriatic region. Drier/warmer conditions during the transition from Dark Ages to the MWP are also noticed in the stalagmite record from Ceremosnja Cave, eastern Serbia (Kacanški et al., 2001).

Overall, relatively wet conditions dominate the middle to upper part of MOD-22 (between 1348 ± 59 AD and 1580 ± 96 AD) and growth rates were exceptionally high. In this interval the calcite is more porous and overlapping layers are more pronounced (Figure 9). In this interval, the subsequent layers wrap over the previously deposited layers for almost the whole length of the speleothem (marked with dashed lines highlighting the growth layers on the stalagmite scan Figure 9). However, two shift to higher $\delta^{13}$C values during this interval are noticed and are interpreted as drying out trends. $\delta^{18}$O tends to be relatively low during this interval, consistent with wetter conditions and an influence of rainfall amount on $\delta^{18}$O (Figure 5b). This wet interval inferred from MOD-22 indicates increased rainfall and colder conditions at the beginning of the LIA in agreement with Piva et al. (2008) and Rogerson et al. (2011).
6. Conclusions

Dead-carbon corrected and calibrated radiocarbon ages from both stalagmites indicate that deposition occurred mostly during the late Holocene, aside from some Marine Isotope Stage 3 material (c. 55 ka) at the base of stalagmite MOD-21 (Supporting information, Appendix S1).

Drip site MODW-22, the feeder to stalagmite MOD-22 indicates a water storage component, which is reflected in the continuous growth of MOD-22. This permitted continuous stalagmite growth during prolonged (multi-annual) dry periods such as the Roman Warm Period (RWP) and Medieval Warm Period (MWP). Overall, the data indicate alternating wet and dry conditions during the late Holocene. Drier conditions inferred for the late RWP and early MWP are also consistent with the previously published studies by Piva et al. (2008) for the region. Inferred drier conditions during the MWP are consistent with the suggestion that this interval was dominated by a persistent positive North Atlantic Oscillation (NAO), leading to drier conditions in the circum-Mediterranean region (Trouet et al., 2009).

The hydrological data for drip site MODW-21, the feeder to stalagmite MOD-21, indicates a minimal water storage component consistent with its erratic growth history. In order to sustain speleothem growth at this site, sustained relatively wet conditions are essential. These conditions probably existed during the interval when MOD-21 grew very rapidly, as indicated by the two almost identical radiocarbon dates at points along the growth axis that are c. 70 mm apart (Supplementary data). However the absolute timing of this interval is uncertain. Previous studies by Piva et al. (2008) and Magny et al. (2009) indicate that LIA was a wet period in this region. This wet phase is consistent with the fast growth rates observed in stalagmite MOD-22 during this interval (Figure 7), and with its stable isotope data and growth layer geometry. It is possible that MOD-21 also grew rapidly during the LIA, but this would require an unusually high DE value (c. 20%) to correct its \(^{14}\text{C}\) dates (Supplementary data).

Overall, the study indicates relatively constant climatic conditions during the late Holocene. However there is evidence from accelerated deposition rates and growth layer geometry for a wetter period during the early LIA compared with late Holocene average. Relatively linear growth rates in MOD-22 during the inferred drier intervals indicate that changes in hydrological conditions were not sufficient to cause prolonged cessations of speleothem deposition.
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Figure and tables captions

**Figure 1.** Layout of Modrič cave showing the location of the temperature loggers: TL1, TL2, TL3 and the drip sites: MODW-21 and MODW-22. The locations of the sampled speleothems MOD-21, MOD-22 are also shown.

**Figure 2.** Studied speleothems and drip sites in Modrič cave; A) MODW-22 drip site with in-situ stalagmite MOD-22; B) cross-section of stalagmite MOD-22 with the location of drill pits for U-series (U) and radiocarbon dates (RC); C) drip site MODW-21 with in-situ stalagmite MOD-21; D) cross-section of stalagmite MOD-21 with the location of drill pits for U-series (U) and radiocarbon dates (RC). Two hiatuses in MOD-21 are marked with solid black lines. Sampling points for stable isotopes are visible along the growth axis. Dashed lines on the stalagmite’s scans indicate the layers used for the Hendy test.

**Figure 3.** A two year daily record of rainfall at Modrič (black solid curve) and drip rates for MODW-21 and MODW-22 (bold grey and bold black curves respectively). Also shown is the daily rainfall record from two meteorological stations: Starigrad (dashed curve) and Zadar-Zemunik (thin grey curve). Rainfall data is plotted in mm/day on the left-hand axis (increasing downwards) and drip rate data is plotted in ml/day on the right-hand axis (increasing upwards). Periods during which some loggers failed are also shown.

**Figure 4.** A two year record of water isotopes (D/H and δ^{18}O) from Modrič rainfall water and the two drip sites: MODW-21 and MODW-22. Arrows labelled ‘A’ and ‘C’ represent the mean δ^{18}O and D/H for drip waters from sites MODW-22 and MODW-21 respectively. Arrows labelled ‘B’ represent weighted mean δ^{18}O and D/H in the rainfall.

**Figure 5.** A) Plot of Local Meteoric Water Line (LMWL) for Modrič site. GNIP stations from Croatia (Zadar, Zagreb, Zaviza-Mt. Velebit, Komiza-Vis Island, Dubrovnik, Malinska Krk and Plitvice), Slovenia (Ljubljana, Portoroz Airport and Kozina) and Italy (Ancona and Trieste) are given for the reference. The Global Meteoric Water Line (GMWL), Mediterranean Meteoric Water Line (MMWL) and Local Meteoric Water Line (LMWL) taken from Vreča et al. (2006)
are also plotted; B) Plot of the δ¹⁸O data from Zadar GNIP station showing the amount effect for the rainfall data from this region.

**Figure 6.** Calculation of dilution effect (DE) of ¹⁴C data from stalagmite MOD-22. Dashed curve shows calibrated ¹⁴C data after applying DE = 12.5% correction taken directly from the MOD-22 growth rate. Black solid curve represents ¹⁴C data for MOD-22, uncalibrated and uncorrected to the DE value.

**Figure 7.** Probability density functions for ¹⁴C date calibrations from stalagmite MOD-22 after correction to the DE value (12.5 ± 0.1%). Dashed lines indicate calibrated age based on the range of ¹⁴C dates that displayed the highest probability. Black line indicates preferred age model based on the ¹⁴C dates with the highest probability and the distance from the top (0 mm) of the stalagmite is shown on the right-hand axis.

**Figure 8.** A) Hendy test for stalagmite MOD-22. Each sample set was drilled from the single growth layer (distances are measured from the top: A-25 mm, B-85 mm and C-135 mm). Distance was measured from the stalagmite central axis (schematic diagram inserted); B) Stable isotope record with the position of the radiocarbon dates for MOD-22.

**Figure 9.** Interpretation of stable isotope record from the stalagmite MOD-22. Interpretation of wetter and drier intervals based on MOD-22 petrography and the growth layer geometry during different deposition stages is shown using the methodology suggested by Railsback et al. (2011). Dashed lines on the MOD-22 scan highlight the growth character of layers, as shown schematically to the right of the picture. Horizontal dashed lines highlight the intervals of different climatic conditions based on the stalagmite petrography and growth layer pattern after Railsback et al. (2011). The arrows indicate interpreted drying-out trends recorded by δ¹³C in the stalagmite. The duration of RWP: 250 BC – 450 AD (2200 – 1500 cal BP) and Dark Ages (DA): 450 – 800 AD (1500 – 1150 cal BP) are from Desprat et al. (2003). The time-frames for the MWP were set at 800 – 1250 AD (1150 – 700 cal BP) based on a number of publications (Lamb, 1965; Broecker, 2001; Desprat et al., 2003; Trouet et al., 2009; Jungclaus et al., 2010). The timing and duration of the LIA was set to 1350 – 1860 AD (600 – 90 cal BP) based on previously published work (Bond, 1999; Desprat et al., 2003; Jungclaus et al., 2010).
Table 1. U-series measurements performed on stalagmites MOD-21 and MOD-22. Note that dates highlighted in bold were not considered further due to their high uncertainty. The detrital Th correction shown here for illustrative purposes is for \( \frac{{\text{^{230}Th}}}{{\text{^{232}Th}}} = 1 \)

Table 2. Results from \(^{14}C\) measurements on MOD-22. Measured \(^{14}C\) activity \( (a^{14}Cm) \) was corrected to dilution effect \( (DE\%) \). The raw \(^{14}C\) age was calibrated to years BP (1950) and AD/BC using OxCal (Bronk Ramsey, 2009) and calibration curves from Reimer et al. (2009). The highest probability age range is shown in bold.