

Abstract

Here we present a new speleothem isotope record (POM2) from Ascunsă Cave (Romania) that provides new data on past climate changes in the Carpathian-Balkan region from 8.2 ka until present. This paper describes an approach towards constraining the effect of temperature changes on calcite $\delta^{18}\text{O}$ values in stalagmite POM2 over the course of the Middle Holocene (6–4 ka), and across the 8.2 and 3.2 ka rapid climate change events. Independent pollen temperature reconstructions are used to constrain the temperature-dependent component of total isotopic change in speleothem calcite. This includes the temperature-dependent composition of rain water attained during vapour condensation and during calcite precipitation at the given cave temperature. The only prior assumptions are that pollen-derived average annual temperature reflects average cave temperature, and that pollen-derived coldest and warmest month temperatures reflect the range of condensation temperatures of rain at the cave site. This approach constrains a range of values between which speleothem isotopic changes should be found if controlled only by surface temperature variations at the cave site. Deviations of measured $\delta^{18}\text{O}_c$ values from the calculated range are interpreted towards large-scale hydrologic change independent of local temperature.

Following this approach, we show that an additional 0.6‰ enrichment of $\delta^{18}\text{O}_c$ in the POM2 stalagmite was caused by changing hydrological patterns in SW Romania during the Middle Holocene. Further, by extending the calculations to other speleothem records from around the entire Mediterranean Basin, it appears that all Eastern Mediterranean speleothems recorded a similar isotopic enrichment due to changing hydrology, whereas all changes recorded in speleothems from the Western Mediterranean are fully explained by temperature variation alone. This highlights a different hydrological evolution between the two sides of the Mediterranean.

Our results also demonstrate that during the 8.2 ka event, POM2 stable isotope data fit the temperature-constrained isotopic variability, with only little hydrologic change at most. In the case of the 3.2 ka event, the hydrological factor is more evident. This

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implies a potentially different rainfall pattern in the Southern Carpathian region during this event at the end of the Bronze Age.

This study brings new evidence for disturbances in Eastern Mediterranean hydrology during the Holocene, bearing importance for the understanding of climate pressure on agricultural activities in this area.

1 Introduction

The impact of Holocene rapid climate changes on human communities in the Eastern Mediterranean region was documented by Weninger et al. (2009). Staubwasser and Weiss (2006) showed that rapid climate change events can alter the hydrological cycle, putting pressure on agricultural societies and sometimes leading to their demise. This paper attempts to bring new information about the response of hydrology to temperature change in different parts of Europe, focusing on the Carpathian-Balkan region.

In the region surrounding the Eastern Mediterranean, proxy records suggest that conditions were more humid during the Early Holocene compared to present-day moisture budgets (Rossignol-Strick, 1999; Rohling et al., 2002). Enhanced freshwater flux roughly between 10 000 yr before present (10 ka) and 6 ka led to stratification and sapropel formation in the Eastern Mediterranean, whereas depleted $\delta^{18}\text{O}$ values in lacustrine calcareous microfossils and endogenic carbonate deposits suggest less evaporation across the region during that time compared to the present day. A stacked oxygen isotope record generated from lake proxies around the Eastern Mediterranean shows a general drying trend between 6 and 4 ka (Roberts et al., 2008). A pattern of increasing $\delta^{18}\text{O}$ values is documented in speleothem records from south-central Europe and the Eastern Mediterranean (McDermott et al., 2011, and references therein). This has been suggested by McDermott et al. (2011) to reflect less rainfall from Atlantic-sourced moisture reaching the Eastern Mediterranean region during the Late Holocene.

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Due to the topographic complexity and rather sparse data distribution, reports from across the Carpathian-Balkan region do not provide yet a unified view on past environmental change, but rather point to possibly contrasting Holocene hydroclimatic evolution at regional scale (Feurdean et al., 2008; Magyari et al., 2013). Lake records from the southern Balkans, such as Ioannina, Greece (Frogley et al., 2001) and Prespa and Ohrid, Macedonia (Leng et al., 2010) indicate high humidity throughout the Early Holocene, whereas paleolimnological records from Steregoiu, NW Romania (Feurdean et al., 2007) and Sfânta Ana Lake, central Romania (Magyari et al., 2009), suggest that lower humidity persisted in the area. At Sfânta Ana, a volcanic crater lake with no outflow, water levels began to rise only after 7.4 ka (Magyari et al., 2009).

Several Holocene speleothem records are available from the Romanian Carpathians (Onac et al., 2002; Tămaş et al., 2005; Constantin et al., 2007). Trends towards higher values seen in these time series throughout the Holocene were interpreted as reflecting rising temperatures. McDermott et al. (2011) followed on the interpretation of European speleothem records documenting decreasing rainout gradients across the Holocene on a longitudinal transect. However, a more specific distinction between hydrology and temperature-driven changes requires further research because interpreting stable oxygen isotope records from speleothems in terms of palaeoclimate is not generally straightforward (McDermott, 2004; Lachniet, 2009; Tremaine et al., 2011). For example, the effects of temperature and hydrologic changes may cancel each other out as cave temperature and rainfall temperature affect speleothem $\delta^{18}\text{O}$ values in opposite directions. Changes in seasonality of both rainfall and calcite precipitation are difficult to detect (Baker et al., 2011). Furthermore, moisture sources and transport trajectories, which generally affect the stable isotopic composition of meteoric water in Europe (Rozanski et al., 1982), may respond to regional-scale climate changes in contrast to local ones. Consequently, specific temperature or hydrological information is rarely directly quantifiable from speleothem stable isotope records. An example is the muted or even absent signal around the 8.2 ka cold event in speleothem $\delta^{18}\text{O}$ records throughout Romania (Tămaş et al., 2005; Constantin et al., 2007), despite this event

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being clearly identifiable in peat bog pollen records (Feurdean et al., 2007), in Balkan lake records (Pross et al., 2009; Panagiotopoulos et al., 2013), as well as in the Aegean Sea (Marino et al., 2009). This ambiguity of speleothem $\delta^{18}\text{O}$ records with respect to climatic events and transitions raises the question of how more specific information on the nature of climate change can be extracted from this proxy.

In this study we present a new speleothem isotopic record from Ascunsă Cave located on the eastern slopes of the Carpathian Mountains in Southern Romania (Fig. 1), in an area under periodical Mediterranean hydroclimate influences (Bojariu and Paliu, 2001; Apostol, 2008). We combine information from regionally averaged pollen-based temperature reconstructions from Europe across the Holocene (Davis et al., 2003) with the new oxygen isotope data from Ascunsă Cave, alongside a detailed comparison with published speleothem records from Romania (Onac et al., 2002; Tămaş et al., 2005; Constantin et al., 2007) and the Mediterranean (McDermott et al., 1999; Bar-Matthews et al., 2003; Drysdale et al., 2006; Vollweiler et al., 2006; Verheyden et al., 2008; Fleitmann et al., 2009). We also attempt to constrain the regional-scale hydrologic information inherent by speleothem $\delta^{18}\text{O}$ change across the Holocene, focussing on Mediterranean climate trends observable after 6 ka (Mayewski et al., 2004; Roberts et al., 2008, 2011; McDermott et al., 2011).

Finally, local pollen data sets (Feurdean et al., 2008; Bordon et al., 2009) are used to constrain selected rapid climate shifts associated with the 8.2 ka and the 3.2 ka events.

2 Materials and methods

2.1 Cave setting and stalagmite characteristics

Ascunsă Cave is located on the eastern slopes of Mehedinţi Mountains, Southern Carpathians (45.0° N, 22.6° E, 1050 m alt.) in south-western Romania (Fig. 1). It is a 400 m long and over 200 m deep contact cave developed by river erosion of

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3 Results and discussion

3.1 U-series dating results and growth model

The U-Th ages suggest that the stalagmite started growing around 17.2 ka, but most of the growth occurred between 8.2 ka and the present. The age model for the Holocene part of the stalagmite (Fig. 5) is based on eleven U-Th ages with typical dating uncertainties ranging between 1 and 6 % (2σ) (Table 1). The stalagmite was active at the time of sampling, thus the age at the top (77.4 cm) is assumed to be 0 (relative to 2009, the year of sampling) and is used as an additional tie point in the growth model calculation. The ^{238}U concentration varies between 18 and 50 ng g^{-1} , and ^{232}Th concentration ranges between 0.1 and 12.2 ng g^{-1} . Dating uncertainties are therefore mainly resulting from small U concentration and a significant correction for initial Th, combined with the young age of the stalagmite which yields low $^{230}\text{Th}/^{232}\text{Th}$ activity ratios (< 10) for six of the age determinations. Two samples (POM 09-2/III and POM 09-2/VI) are entirely dominated by detrital Th, with $^{230}\text{Th}/^{232}\text{Th}$ activity ratios < 0.5 and have not yielded resolvable U-Th ages.

We measured U and Th isotopes on a sample from the top of the actively forming stalagmite in order to assess a reliable correction factor. The results show a ^{238}U concentration of $18.3 \pm 0.1 \text{ ng g}^{-1}$ and a ^{232}Th concentration of $12.2 \pm 0.1 \text{ ng g}^{-1}$. The measured ^{230}Th in the top sample is assumed to be entirely of detrital origin and the apparent age of 8.3 ka a result of initial thorium contamination. The $^{230}\text{Th}/^{232}\text{Th}$ activity ratio of this sample is 0.6 ± 0.05 , which indicates detrital activity ratios for $^{230}\text{Th}/^{232}\text{Th}$, $^{234}\text{U}/^{232}\text{Th}$ and $^{238}\text{U}/^{232}\text{Th}$ of 0.6 ± 0.05 , if we assume the detritus to be in secular equilibrium. We note that this factor is well within the range of the bulk earth value of 0.8 ± 0.4 (Wedepohl, 1995). We therefore use the value of 0.6 with a conservative uncertainty of 50 % to correct for initial Th.

The growth model of stalagmite POM2 (Fig. 5) was generated using the StalAge algorithm of Scholz and Hoffmann (2011).

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3.2 Cave monitoring results

Monitoring data show a stable average temperature of $8.2 \pm 0.6 \text{ }^\circ\text{C}$ at the stalagmite site. Relative humidity is also stable around $94 \pm 2.5 \%$ during the year, especially at sampling sites POM2 (where stalagmite POM2 was sampled) and POM B situated deeper inside the cave (Table 2).

Isotope measurements of drip waters at POM2 site show rather consistent values for both $\delta^{18}\text{O}$ ($-10.57 \pm 0.04 \text{ }‰$) and δD ($-70.58 \pm 0.20 \text{ }‰$), during the autumn–winter months. This may indicate an efficient mixing of waters in the aquifer, without capturing any individual rain events.

Analysis of calcite farmed on glass plates also revealed relatively constant values with mean $\delta^{13}\text{C}$ of $-10.30 \pm 0.8 \text{ }‰$ and $\delta^{18}\text{O}$ of $-7.91 \pm 0.2 \text{ }‰$ for both POM2 and an adjacent stalagmite, POM X (Table 3).

We constructed a local drip water line for Ascunsă Cave (Fig. 6) using $\delta^{18}\text{O}$ and δD values of drip waters from all three sampling sites. Compared to the global (GMWL) and Mediterranean (MMWL) meteoric water lines, the Ascunsă groundwater line (AGWL) is defined as $\delta\text{D} = 6.9 \times \delta^{18}\text{O} + 2$ and plots above the GMWL. This could indicate either the existence of enrichment processes at local scale or a mixture between humid Atlantic and drier Mediterranean vapour sources.

To test the existence of equilibrium fractionation conditions at the POM2 site, we used drip water $\delta^{18}\text{O}$ values to calculate a theoretical $\delta^{18}\text{O}$ value of the farmed calcite, using the equation given by Tremaine et al. (2011):

$$1000 \ln \alpha = 16.1 (\pm 0.65) \times 10^3 T^{-1} - 24.6 (\pm 2.2).$$

The resulting value of $-8.5 \pm 0.1 \text{ }‰$ is slightly below the average of $-7.9 \text{ }‰$ measured on calcite farmed at POM2 and POM X sites. Although the 0.6 $‰$ offset from generally predicted values could indicate some kinetic fractionation, calcite precipitation can still be considered to have taken place close to equilibrium during the monitored period. However, calculations using the equations in Kim and O'Neill (1997) and Day and Henderson (2011) returned theoretical $\delta^{18}\text{O}$ values of -9.2 and $-9.6 \text{ }‰$, respectively, well

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record variations in hydrologic climate characteristics, such as rainfall seasonality, evaporation, and concurrent input from different moisture sources (McDermott, 2004; Fairchild et al., 2006; Lachniet, 2009). Assuming that (1) calcite precipitation temperature in the cave reflects the annual average surface air temperature that oscillates very little year around (see also Table 2) and (2) the coldest and warmest months define the range of temperature-controlled oxygen isotope fractionation during condensation of rain, we calculate an expected range for relative changes of $\delta^{18}\text{O}$ in speleothem records based entirely on temperature variation. For that purpose, we employ pollen-based reconstructions of the annual average surface air temperature (TANN – Temperature ANNUal), surface air temperature of the coldest month (MTCO – Mean Temperature of the COldest month), and surface air temperature of the warmest month (MTWA – Mean Temperature of the Warmest month) for two zonal sectors from central Europe and the Mediterranean, respectively (Davis et al., 2003). We use the empirical equation of Tremaine et al. (2011) for temperature-dependent oxygen isotope fractionation during calcite precipitation:

$$1000 \ln \alpha = 16.1 \left(10^3 T^{-1} \right) - 24.6. \quad (1)$$

For the $\delta^{18}\text{O}$ -temperature relationship in rainwater we use the empirical global mid-latitude relationship suggested by Rozanski et al. (1993):

$$\delta^{18}\text{O}/\Delta T = 0.58\text{‰}\text{°C}^{-1}. \quad (2)$$

For calcite precipitation, $\Delta\delta^{18}\text{O}/\Delta T$ is $\sim -0.18\text{‰}\text{°C}^{-1}$ (Tremaine et al., 2011), therefore the combined temperature effect in speleothem $\delta^{18}\text{O}$ is dominated by rainfall temperature and resulting changes in drip water $\delta^{18}\text{O}$.

We consider rather relative than absolute the changes across the Holocene time intervals of interest. We then compare the calculated temperature-constrained range of relative $\delta^{18}\text{O}$ variation with the one measured in several Carpathian speleothem

records in order to identify the likelihood of additional changes in other climate parameters (e.g. rainfall seasonality, evaporation from the soil, or variable moisture sources and pathways).

If only temperature variability contributed to the observed difference between two time intervals of interest, this change in $\delta^{18}\text{O}_c$ will plot inside the range calculated from the pollen input data TANN, MTCO and MTWA. Ideally, the position inside that calculated range should reflect the unchanged annual distribution of rainfall above the cave, but see discussion of uncertainties in the appendix. If any hydrologic factor had changed along with temperature, the observed change of $\delta^{18}\text{O}_c$ may fall outside the calculated temperature constrained range. For example, a significant change in rainfall seasonality should result in the observed change of $\delta^{18}\text{O}_c$ plotting above the range if the proportion of summer rain increased. The proportional increase of summer rain may of course be the result of additional summer rain, or a reduction of winter rain. Other hydrologic factors, such as a different proportion of moisture from the Mediterranean and the Atlantic, respectively (see Fig. 6), or a different isotopic composition of the sea surface in either two source regions, may also cause the observed $\delta^{18}\text{O}_c$ to fall outside the temperature constrained range.

3.3.3 Temperature and hydrology-related changes in speleothem $\delta^{18}\text{O}$ records from Romania and the Mediterranean basin

We analyse the broad $\delta^{18}\text{O}$ change across the time interval 6–4 ka as outlined above for the Romanian stalagmites and also for a selection of southern European records. For simplicity, this isotopic transition is defined as the difference between the average $\delta^{18}\text{O}$ during the 4–2 and 8–6 ka intervals ($\Delta\delta^{18}\text{O}_{6-4\text{ka}}$).

The pollen-based temperature reconstructions by Davis et al. (2003) divide Europe into six main regions: north-western (NW), north-eastern (NE), central-western (CW), central-eastern (CE), south-western (SW) and south-eastern (SE). The boundary between central and southern zones is 45°N , the boundary between western and eastern zones is 15°E . This places the Alps and much of northern Italy inside the CW zone

The large scale pattern across the Mediterranean suggests different forcing of climate change over the West and the East respectively, but also a common cause of hydrologic change over the Eastern Mediterranean domain. In principle, three aspects may contribute to the observed hydrologic change in the East: (1) different rainfall seasonality, (2) a change in proportion of moisture source, and (3) a different isotopic composition of the moisture sources. Higher $\delta^{18}\text{O}$ values could be the result of more rain falling in the warmer months during Late Holocene, but this is unlikely because of large scale subsidence over the Eastern Mediterranean region due to the Asian monsoon (Rodwell and Hoskins, 1996; Staubwasser et al., 2006). As a result, there are virtually no rainfalls during summer in the Levant, and are significantly reduced over SE Europe. The summer months are those with lowest rainfall in SW Romania. Subsidence and accompanying low humidity over the Eastern Mediterranean may, however, have increased evaporation, which would be in agreement with rising summer temperatures in SE Europe across the Holocene (Davis et al., 2003). Evaporation in soil and epikarst drives drip water $\delta^{18}\text{O}$ towards more positive values, resulting in higher $\delta^{18}\text{O}$ in speleothem calcite (Bar-Matthews et al., 1996; Fairchild et al., 2006).

Alternatively, the proportion of summer rain could have been also higher if winter rainfall decreased. McDermott et al. (2011) suggested lower rainout efficiency during winter along a West-East transect across central Europe. However, higher winter temperatures only in the Western Mediterranean region (Davis et al., 2003) would increase the temperature gradient between SW Romania and the source of cyclones in the Gulf of Genoa, possibly leading to increased rainout efficiency in South Europe.

Another factor that may have added to the observed increase in speleothem $\delta^{18}\text{O}$ is a change in the isotopic composition of the Mediterranean mixed layer. A steadily increasing $\delta^{18}\text{O}$ by almost 1‰ is recorded in tests of surface dwelling foraminifera from the Aegean Sea between 8 and 4 ka BP, which is uncorrelated with the abundance of cold water species (Rohling et al., 2002). In the Adriatic Sea, an increase by 0.5‰ was recorded at the same time (Siani et al., 2010). As such, a combination of warmer summer temperatures, enhanced evaporation from the soil, and higher $\delta^{18}\text{O}$ of the

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Eastern Mediterranean moisture source are currently the favoured explanation for the observed increase in $\delta^{18}\text{O}$ of speleothems from the Eastern Mediterranean domain.

3.3.4 The $\delta^{13}\text{C}$ record

Interpretation of speleothem $\delta^{13}\text{C}$ data is generally hampered by a host of local factors such as changes in soil CO_2 production and content, closed versus open system dissolution of carbonates in the soil/epikarst system, residence time and mixing of waters along the pathway to the drip point, or solution degassing (Hendy, 1971; Bar-Matthews et al., 1996; Fairchild et al., 2006).

Percolating water degassing could be greater during certain periods at POM2 sampling site, as the CO_2 content of the cave's atmosphere drops from ~1800 ppm in November–December to ~1000 ppm in April–May. This seasonal variation in the CO_2 content of cave air is likely the combined result of soil CO_2 productivity and cave ventilation (Spötl et al., 2005; Kowalczyk and Froelich, 2010; Frisia et al., 2011; Tremaine et al., 2011; Riechelmann et al., 2013).

At the POM A site, which is the shallowest and closest to the entrance, the $p\text{CO}_2$ reaches a minimum value of 760 ppm, well above values of outside air (between 200 and 310 ppm). The two deeper sites, POM2 and POM B, show even less ventilation, with minimal values of 960 ppm. This indicates that cave ventilation is moderate (although continuous) at Ascunsă Cave.

Supposing that the cave ventilation regime remained unchanged during the Middle Holocene, cave air $p\text{CO}_2$ was probably controlled mostly by soil/vegetation dynamics. If so, higher speleothem $\delta^{13}\text{C}$ values are indicative of reduced CO_2 input from the soil and/or prior precipitated calcite (Fairchild et al., 2000). These two processes could be the result of increasing drought conditions and might have been responsible for producing the upward trend observed in $\delta^{13}\text{C}$ values during the Middle Holocene. This situation is consistent with the increasing drought implied by oxygen isotopes in our stalagmite.

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3.3.5 The 8.2 and 3.2 ka events

The 8.2 ka climate change event (Alley et al., 1997; Rohling and Pälike, 2005) is one of the most prominent events of environmental change in the Holocene. Pollen assemblages from northern Romania (Feurdean et al., 2008), Macedonia (Bordon et al., 2009) and Greece (Pross et al., 2009), testate amoebae from northern Romania (Schnitchen et al., 2006), speleothem carbon stable isotopes from Israel (Bar-Matthews et al., 2000) and marine faunal composition from the Aegean Sea (Rohling et al., 2002) document a decrease in winter temperature and precipitation, while summer conditions remained rather stable. Similar to other Romanian stalagmites (Tămaş et al., 2005; Constantin et al., 2007), the POM2 $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ records do not show significant variations across the 8.2 ka event. The only indication of changing environmental conditions is that the growth rate was 8 times higher during this event compared to the rest of the Holocene in the Ascunsă Cave.

Figure 10 shows a comparison of $\Delta\delta^{18}\text{O}$ for pollen temperature-constrained and measured oxygen isotope values for the 8.2 and 3.2 ka events. For the 8.2 ka event, $\Delta\delta^{18}\text{O}$ is calculated as the difference between a 500-yr interval succeeding the event (8.1–7.6 ka) and the event itself (8.3–8.1 ka). Here we used pollen-based temperature reconstructions as follows: for V11 Cave, those from the Steregoiu peat bog in northern Romania (Feurdean et al., 2008), and for Ascunsă Cave, the Lake Maliq in Macedonia (Bordon et al., 2009).

The shift in isotopic values after the 8.2 ka event at Ascunsă Cave is seemingly explained by the pollen-based temperature rise (Feurdean et al., 2008; Bordon et al., 2009). Nevertheless, as calcite values from Ascunsă are closer to summer values, a hydrological influence on these values could be argued for. As the annual reconstructed pollen temperature rose after the 8.2 ka event, so did the cave temperature. Supposing that rainfall $\Delta\delta^{18}\text{O}/\Delta T$ slope was identical to present day, the decreasing $\delta^{18}\text{O}$ values change resulting from a warmer cave atmosphere must have been offset by the increasing of the $\delta^{18}\text{O}$ values stemming from higher rainfall temperature in

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winter. Yet, no significant change in $\delta^{18}\text{O}$ is observed in the record. Observed $\delta^{18}\text{O}$ values fall within but close to the low $\delta^{18}\text{O}$ summer end of the calculated temperature-constrained range (Feurdean et al., 2008; Bourdon et al., 2009). As such, the lack of a clear $\delta^{18}\text{O}$ signal across the 8.2 ka event can also be explained by a relative increase of the amount of winter infiltration after the event, thereby increasing the proportion of lower $\delta^{18}\text{O}$ in drip water. A possible scenario for the 8.2 ka cold event itself would be that overall lower drip water $\delta^{18}\text{O}$ values associated with lower annual temperatures were offset by a larger proportion of summer rainfall.

The 0.6‰ increase in $\delta^{18}\text{O}$ values after the 3.2 ka event in the Ascunsă record was analysed by comparing the periods 3.0–2.5 ka with 3.2–3.0 ka. These intervals are similar at Poleva (Constantin et al., 2007), showing a comparable structure, although with a small difference in chronology. At Poleva, the two intervals are 2.95–2.53 and 3.07–3.01. The difference in timing is most probably a result of differences in age determinations, while still within uncertainties. The magnitude of rising isotope values after the event is outside the pollen-defined change in $\delta^{18}\text{O}_c$ due to temperature, thus it likely reflects a hydrologic change. The interval is coeval with events documented in both archaeological and palaeoclimate records around the Eastern Mediterranean (see review in Drake, 2012) that may have led to the demise of the Late Bronze Age (Kaniewski et al., 2010). Associated to this cold event, a decrease of the Aegean Sea winter surface temperatures was documented by Rohling et al. (2002), whereas a drop of the Dead Sea level reflects drier conditions in the Eastern Mediterranean (Migowski et al., 2006). In northern Romania, testate amoebae data indicate a dry phase between 3.39 and 3.03 ka (Schnitchen et al., 2006), while pollen-based temperature reconstructions clearly show decreased annual and winter values (Feurdean et al., 2008).

The temperature-constrained isotopic change calculated using pollen reconstructed temperatures from Maliq Lake (Bordon et al., 2009) lies between -0.2‰ for the cold season and 0.4‰ for summer months. The measured value from Ascunsă Cave is 0.6‰ ; this offset towards higher values possibly indicates that hydrological processes were responsible for this enrichment. The Mediterranean plays an important role as

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winter moisture source in south-western Romania (Bojariu and Paliu, 2001). The ^{18}O depleted waters associated with the 3.2 ka event could be the combined result of lower temperatures at the cave site and a decreased Mediterranean input resulting from less winter evaporation of sea surface waters. Reduced sea surface temperatures also imply more depleted $\delta^{18}\text{O}$ values for winter moisture contributing to the downtrend observed in the Ascunsă isotope time series. After the 3.2 ka event, as cave temperature rose, the isotopic processes affecting calcite precipitation would have lowered $\delta^{18}\text{O}$ values. However, this effect might have been overwritten by raising summer temperatures, possibly accompanied by evaporation, similar to developments observed at the Middle Holocene transition.

4 Conclusions

The stable isotope record of Ascunsă Cave in southern Romania was used to identify centennial to millennial climate change during the Holocene in this area. Between 6 and 4 ka, $\delta^{18}\text{O}$ gradually shifted towards higher values and we show that the Atlantic source effect was not the main isotopic driver for this well-defined isotopic shift.

By using a new approach to discriminate between the effects of temperature and hydrology on speleothem $\delta^{18}\text{O}$ values, we demonstrate that this shift not only reflects rising regional temperatures as documented by pollen assemblages (Davis et al., 2003), but also a combination of hydrologic influences.

The approach presented in this study relies on using pollen-based temperature reconstructions to constrain temperature-driven isotopic changes of speleothem calcite. This method can use any independent temperature reconstructions and considers the isotopic fractionation occurring during water vapour condensation and calcite precipitation. A constrained range of temperature-driven isotopic changes between winter and summer is obtained, and departures from this range suggest that additional factors ultimately control the isotopic variability over the studied period.

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Using this approach we find that the Middle Holocene enrichment in SW Romania was 0.6‰ greater than the maximum values, likely associated with rising temperatures. We further extended the calculation to other speleothem records in the Eastern and Western Mediterranean and western Romania (Urşilor Cave). In the Atlantic-dominated western Romania, isotopic change largely followed temperature variations, revealing different climate response of these two regions separated by the Southern Carpathian mountain range.

We also show that during the Middle Holocene, $\delta^{18}\text{O}$ in Western Mediterranean speleothems responded mostly to temperature change. At the same time, other processes such as enhanced evaporation rates or gradual enrichment in isotopic composition of surface waters could have contributed to the observed isotope change in areas influenced by the Eastern Mediterranean climate.

We analysed two rapid climate changes, at 8.2 and 3.2 ka. At Ascunsă Cave, the 8.2 ka event is characterized by a growth rate 5–6 times greater than during the rest of the Holocene. Nevertheless, the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values show low variability, whereas the 3.2–3.0 ka period is well defined by a 1.5‰ depletion in $\delta^{18}\text{O}$. The low isotopic variability during the 8.2 ka event seems to reflect only temperature variations, but hydrologic conditions such as relatively more summer vs. winter rainfall at Ascunsă and V11 caves cannot be ruled out.

During the 3.2 ka event, the thermic and hydrological impact on speleothem isotope values is obvious at Ascunsă Cave, reflecting decreased winter temperature and a lower and perhaps isotopically-lighter Mediterranean moisture input.

Appendix A

Calculation method of temperature constrained isotope values

The calculation of the temperature-related part of an observed change in speleothem calcite $\delta^{18}\text{O}$ from pollen-based temperature reconstructions relies on two basic

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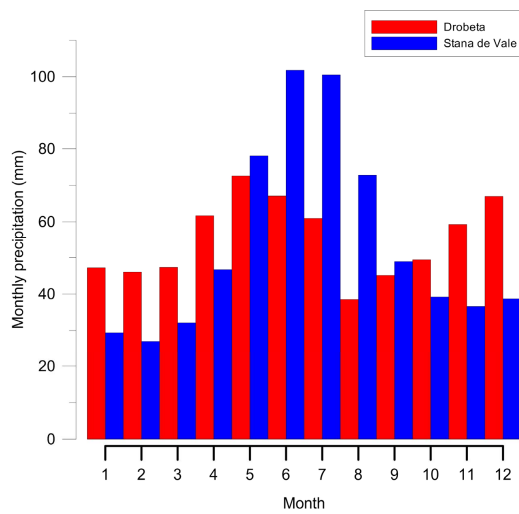


Fig. 2. Average monthly precipitation quantities at stations Drobeta and Stâna de Vale (data from Dragotă and Baci, 2008).

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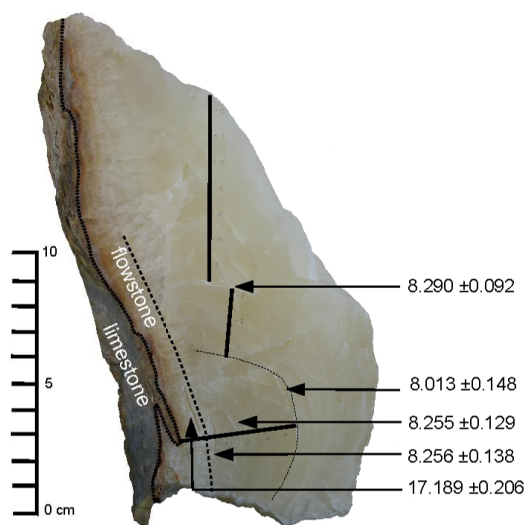


Fig. 3. Base of stalagmite POM2 (ages are given in ka).

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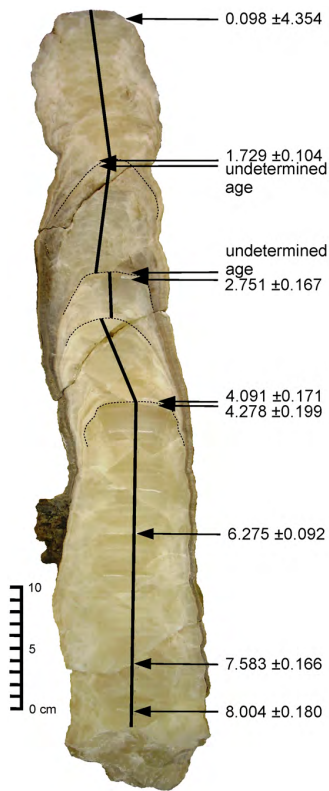


Fig. 4. Upper part of stalagmite POM2 (ages are given in ka).

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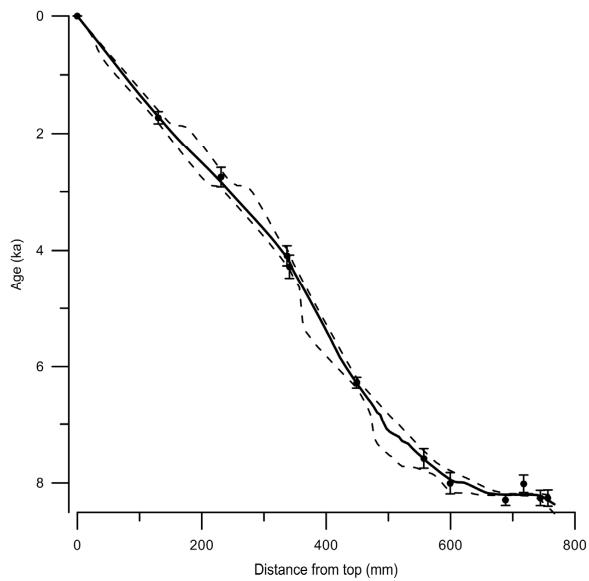


Fig. 5. The growth model (solid line) of stalagmite POM2 with 95 % confidence intervals (dashed lines).

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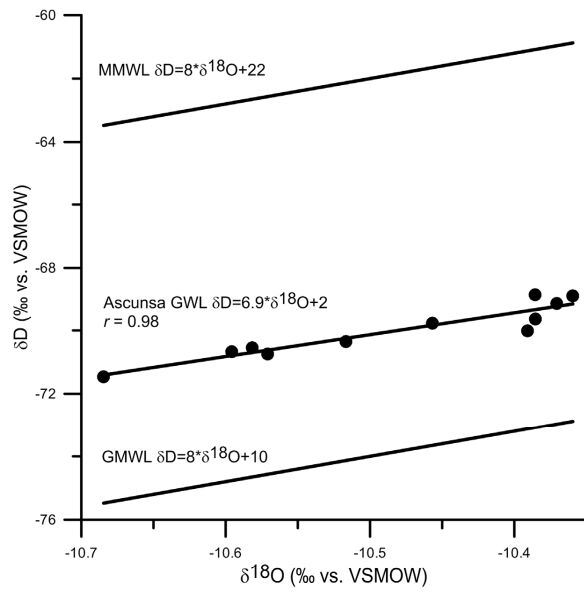


Fig. 6. Comparison between GMWL – global (Craig, 1961) and MMWL – Mediterranean meteoric water lines (Gat and Carmi, 1970), as well as Ascunsa Cave groundwater line.

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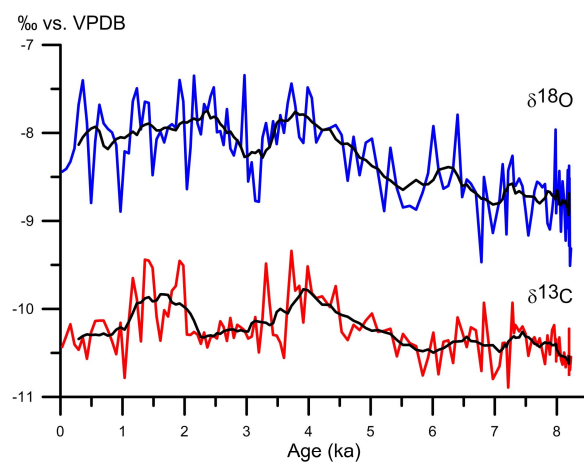


Fig. 7. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ profiles of stalagmite POM2 with 9-point smoothed values (black).

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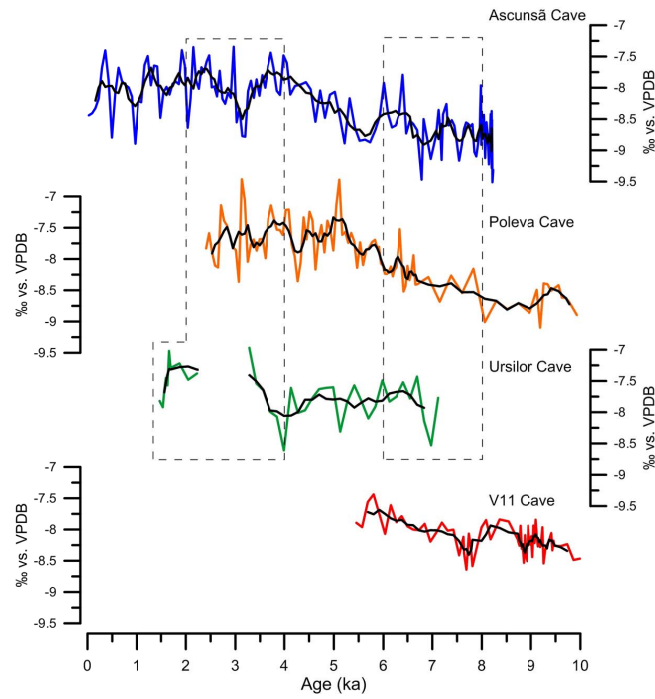


Fig. 8. Comparison between $\delta^{18}\text{O}$ records from Ascunsă, Poleva, Urșilor and V11 caves. Isotopic values predicted by McDermott et al. (2011) for low altitude caves at 22°E longitude are represented as dashed line. Dashed line boxes represent the time windows (2–4 and 6–8 ka) for which the average isotopic values were calculated.

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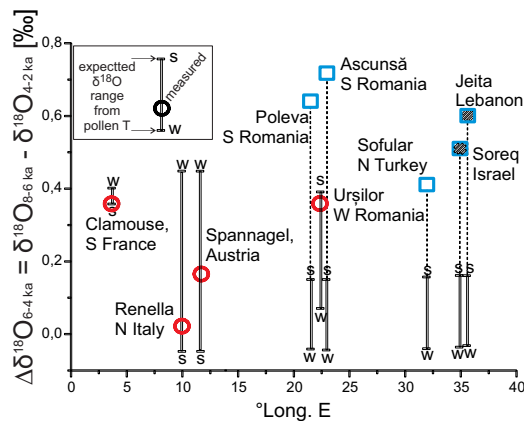


Fig. 9. Comparison of isotopic changes in stalagmites across different longitudes in Europe and predicted isotopic change in winter and summer precipitated calcite in the interval 6–4 ka.

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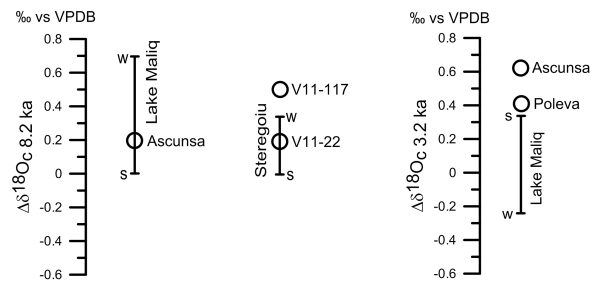


Fig. 10. Comparison of isotopic changes in stalagmites from Ascunsă, Poleva and V11 caves with expected oxygen isotope change constrained by pollen temperature reconstruction in winter and summer, for the 8.2 ka event (left) and the 3.2 ka event (right). $\Delta\delta^{18}O$ as defined in the text.