



## Research papers

# Isotopic characterization of cave environments at varying altitudes on the eastern Adriatic coast (Croatia) – Implications for future speleothem-based studies



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## ABSTRACT

An important step in the implementation of paleoclimate reconstructions from speleothems (cave carbonate deposits) is to evaluate the sensitivity of the host cave environment to regional climate. Accordingly, we studied three caves at different altitudes (74 m, 570 m and 1250 m a.s.l.) along a transect from the Dalmatian islands to Velebit Mountain peaks in coastal Croatia to characterize their environments in terms of each cave's suitability to host speleothems that would be capable of yielding robust paleoclimate reconstructions. We conducted cave microclimate (2-years) and dripwater (1-year) monitoring and analysed the isotopic composition of precipitation, cave dripwater and modern spelean calcite. As for the water isotopic imprints, the isotopic values of meteoric waters reaching the two lower-altitude caves, in spite of an altitude difference of 500 m, lie on local meteoric water lines (LMWLs) of similar slope and intercept ( $\delta^2\text{H} = 6.61 \times \delta^{18}\text{O} + 4.92$  and  $\delta^2\text{H} = 6.69 \times \delta^{18}\text{O} + 6.86$ ). Their slopes lower than that of GMWL indicate enhanced evaporation during the warm season. As expected, the LMWL of the highest cave region ( $\delta^2\text{H} = 7.83 \times \delta^{18}\text{O} + 14.45$ ) resembles the slope of the GMWL, but the values of deuterium excess obtained for all three caves (between 15.2‰ and 16.6‰) match that of western Mediterranean-sourced waters (~15‰). Monthly *d*-excess values suggest Atlantic-sourced air masses can reach the sites throughout the year but never dominate the rainfall composition. The altitude effect was noted both in precipitation and in dripwater isotopic composition, but with notably different  $\Delta\delta^{18}\text{O}/100$  m gradients (−0.33‰ and −0.11‰, respectively). Stable isotope variations of the dripwaters in all caves were attenuated in relation to the rainwater, even those of the drip sites with fracture-flow behaviour.

Based on stable cave microclimate conditions, relatively steady discharges, and modern calcite apparently precipitated at or close to isotopic equilibrium with dripwater, the two caves at lower altitudes show the greatest potential for future paleoclimate studies. The cave at the highest altitude experiences large cave air temperature amplitudes (5.3 °C) and pronounced ventilation, making the isotopic signal susceptible to kinetic fractionation which might preclude quantification of environmental changes, but on the other hand it accentuates isotopic events, making them easier to identify.

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## 1. Introduction

After the dominance of ice and deep-sea cores, it has been suggested that the future in paleoclimate studies might belong to speleothem science (Henderson, 2006), especially with intensified multi-proxy (isotopes, fabrics, trace elements etc.) and parallel-

proxy (proxies from tree rings, lake sediments etc.) approaches (Fairchild et al., 2006). Speleothems, which are secondary (mostly) carbonate deposits precipitated from cave water (dripping, seeping, flowing, impounded), can record the rainwater isotope signal that is transmitted through the epikarst to the cave. Since the 1960's, the potential of speleothem stable oxygen isotopes as a valuable paleoclimate proxy has been recognized (Hendy and Wilson, 1968). Under equilibrium conditions, the speleothem  $\delta^{18}\text{O}$  value is dependant only on two variables – dripwater  $\delta^{18}\text{O}$  and the cave temperature, the latter controlling equilibrium frac-

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tionation between dripwater and calcite (Hendy, 1971; Lachniet, 2009). Successful interpretation of climate proxy records archived in speleothems depends on understanding the temporal and spatial variability of dripwater hydrology and composition (Baldini et al., 2006; Fuller et al., 2008) which is, in turn, the result of complex processes in the epikarst during the transition of the atmospheric water to the cave. Studies of the isotope hydrology of this pathway and the implications for speleothem paleoenvironmental records have been conducted worldwide (Bar-Matthews et al., 1996; Cruz et al., 2005; Baldini et al., 2006; McDonald and Drysdale, 2007; Beddows et al., 2016; Fuller et al., 2008; Matthey et al., 2008; Miorandi et al., 2010; Oster et al., 2012; Johnston et al., 2013; Riechelmann et al., 2013; Feng et al., 2014; Genty et al., 2014; Moreno et al., 2014; Luo et al., 2014), emphasizing the importance of the characterization of those site-specific processes. The necessity of thorough monitoring is underscored and recommended in order to assess the representativeness of key variables, to identify hydrological seasonality, water transit times in the karst, and finally to determine which speleothems may provide the most robust records of climate events (McDermott, 2004; McDonald and Drysdale, 2007; Beddows et al., 2008, 2016; Riechelmann et al., 2011).

The eastern Adriatic coast is still understudied in terms of paleoclimate, having only few speleothem-based paleoenvironmental (Surić et al., 2005a, 2005b, 2009, 2010; Surić and Juračić, 2010) and paleoclimate studies (Lončar, 2012; Rudzka et al., 2012). Research on stable isotopes in regional precipitation (Krajcar Bronić et al., 1998, 2006; Horvatinčić et al., 2005; Vreča et al., 2006; Barešić et al., 2011; Roller-Lutz et al., 2013; Hunjak et al., 2013) was not aimed at speleothem applications, but the data nonetheless provide a sound basis for ongoing study focused on the reconstruction of the regional boundary between continental European and Mediterranean atmospheric influences. As demonstrated in Alpine speleothems (Luetscher et al., 2015), this boundary has been migrating during past glacial-interglacial cycles, governing temperature, precipitation and vegetation distribution.

Here we present cave microclimate monitoring, precipitation isotope composition, cave dripwater and modern calcite data that provide a basis for interpreting future high-resolution paleoclimate reconstructions. We selected three caves at different altitudes along a transect from the north Dalmatian islands to the Velebit Mountain peaks. Strašna peć Cave on Dugi otok Island (74 m a.s.l.), Manita peć Cave in Velika Paklenica canyon (Velebit Mountain, 570 m a.s.l.) and Spilja u Zubu Buljme Cave (Velebit Mountain, 1250 m a.s.l.) were chosen to estimate how altitude influences the isotope signal in meteoric water, and subsequently in dripwater and speleothems. This is essential for estimating past atmospheric influences on the cave environment. Variations in cave drip rates, responses to surface events, and fluctuations in the isotope composition of waters help characterize the karst aquifers, while testing for equilibrium fractionation between drip waters and modern calcite, along with other hydrological properties, provides a solid foundation on which to base the selection of speleothems for sampling. In addition to the three caves studied here, data from previous work on adjacent Modrič Cave (Kuhta et al., 1999; Surić et al., 2010; Rudzka et al., 2012) is also incorporated.

## 2. Study area and site description

The research was conducted on the eastern Adriatic coast (Croatia) along a transect from the islands to the Velebit Mountain peaks (Dinaric Alps) (Fig. 1). The overall distance between the endmembers is 53 km, although the mountain ridge with the highest studied cave is only 7.5 km from the coastline. The studied caves are

similar in size, depth and morphology (Fig. 1; Table 1), but their climatic settings differ substantially.

Spilja u Zubu Buljme (ZB) is located at 1250 m a.s.l. under the Velebit Mountain peak, on the flank of a former glacier valley. A simple ascending channel (up to 1318 m a.s.l.) with a total length of 239 m (Fig. 1a) has formed in Upper Jurassic limestone. According to the large amount of unconsolidated debris within the cave, it is possible that, until recently, the cave funnelled material shattered by frost action from the upper, presently closed, entrance. Our study site lies 200 m from the entrance, and 40 m above it. According to Köppen-Geiger classification (Peel et al., 2007), a Df (humid boreal) climate dominates, and the snow cover can last from a few days to several months. As there is no meteorological station in the vicinity, we used data from nearby Zavižan station (1594 m a.s.l.), located 63 km NW from ZB cave with MAAT of 4.2 °C (1986–2015; Croatian Meteorological and Hydrological Service/CMHS, 2016) which also shares similar climate characteristics.

The mid-altitude cave Manita peć (MP) was also formed in Upper Jurassic limestone on the flank of the Paklenica canyon in the Velebit Mountain. Our study site is at the end of simple descending and spacious chambers with heights up to 40 m, and situated 150 m from and 40 m below the entrance level (Fig. 1b). The climate type at this site, which is only 3.7 km from the coast, but at an elevation of 570 m, is Cfb (temperate humid with warm summers). The closest rain gauge station (Parići village) lies 3.5 km to the north, at a similar altitude, and during the 1991–2000 period the mean annual precipitation was 1037 mm (CMHS, 2015). Until this study, air temperature data for the MP cave area did not exist. We used instead data from the coastal Starigrad station (MAAT = 16.1 °C for 1992–2014), which is very close to the MP cave (3.7 km), but with an altitude difference of ca. 560 m.

The lowermost Strašna peć Cave (SP) is located on the open-seaward side of Dugi otok Island (74 m a.s.l.). It was formed in Upper Cretaceous limestone and also consists of descending chambers (Fig. 1c). We conducted sampling and measurements at the bottom of the cave, 100 m from the entrance at –30 m relative to the entrance. The dominant climate type is Csa, i.e. Mediterranean climate with hot summers. MAAT measured 18 km NW of the site on the same island (Božava station, 1998–2014) and 21 km SE (Sestrica Vela Island station, 1981–2014) was 16.4 °C and 16.5 °C, respectively (CMHS, 2015). Mean annual precipitation is 826 mm and 592 mm, respectively (CMHS, 2015). Generally, the amount of precipitation on Croatian islands decreases from north to south, and from the mainland coast to the open sea. Consequently, the significantly lower annual precipitation on Sestrica Vela Island station (about half of the coastal Starigrad station/12 m a.s.l.) can be attributed to the station's southerly position, distance from the coast (20 km), and the absence of any orographic effect, since the small island on which the station is located has a maximum elevation of only 55 m a.s.l.

Previously investigated Modrič Cave (MOD) is a horizontal system consisting of two channels with total length of 829 m. It is located 130 m from the coast, with the entrance at 32 m a.s.l. MAAT at the nearest meteorological station Starigrad (8 km from the cave) was 16.1 °C and a mean annual precipitation was 1193 mm (1992–2014; CMHS, 2015).

Due to the positions of all caves in the epikarst and shallow vadose zone near the summits, their recharge areas are limited, and the sources of the cave dripwater are restricted to local precipitation without any influence of mixing with the groundwater aquifer. Owing to the up to 140 m thick overburden, the infiltration elevations (i.e. altitudes of the catchments) are just slightly above the elevations of the caves. Modification of the isotopic composition of water can occur during its transition through the soil zone and epikarst, but in our case where the caves are overlain by

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