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Drip water electrical conductivity as an indicator of cave ventilation at the event scale

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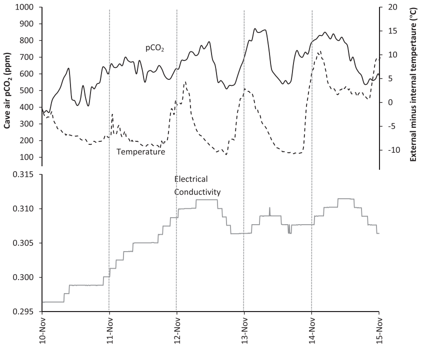
HIGHLIGHTS

- Sub-hourly monitoring assesses cave hydrological and atmospheric variation.
- Cave air CO_2 concentration controls drip water electrical conductivity.
- Cave air pressure can regulate atmospheric ventilation and CO_2 content.
- Cave air CO_2 concentration varies both seasonally and on an event scale.
- Changes in drip water EC can be used as a tracer for cave ventilation and pCO_2.

GRAPHICAL ABSTRACT



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ABSTRACT

The use of speleothems to reconstruct past climatic and environmental change through chemical proxies is becoming increasingly common. Speleothem chemistry is controlled by hydrological and atmospheric processes which vary over seasonal time scales. However, as many reconstructions using speleothem carbonate are now endeavouring to acquire information about precipitation and temperature dynamics at a scale that can capture short term hydrological events, our understanding of within cave processes must match this resolution. Monitoring within Cueva de Asiul (N. Spain) has identified rapid (hourly resolution) changes in drip water electrical conductivity (EC), which is regulated by the pCO_2 in the cave air. Drip water EC is therefore controlled by different modes of cave ventilation. In Cueva de Asiul a combination of density differences, and external pressure changes control ventilation patterns. Density driven changes in cave ventilation occur on a diurnal scale at this site irrespective of season, driven by fluctuations in external temperature across the cave internal temperature threshold. As external temperatures drop below those within the cave low pCO_2 external air enters the void, facilitating the deposition of speleothem carbonate and causing a reduction in measured drip water EC. Additionally, decreases in external pressure related to storm activity act as a secondary ventilation mechanism. Reductions in external air pressure cause a drop in cave air pressure, enhancing karst air draw down, increasing the pCO_2 of the cave and therefore the EC measured within drip waters. EC thereby serves as a first order indicator of cave ventilation, regardless of changes in speleothem drip rates and karst hydrological conditions. High resolution monitoring of cave drip water electrical conductivity reveals the highly sensitive nature of ventilation dynamics within cave

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environments, and highlights the importance of this for understanding trace element incorporation into speleothem carbonate at the event scale.

1. Introduction

Speleothems are important repositories of palaeoclimate information (Fairchild and Baker, 2012). Speleothem carbonate chemistry is routinely used to assess large-scale palaeoenvironmental change, as well as offering the ability to identify annual to sub-annual variations in local meteorology (Treble et al., 2003; Wynn et al., 2014) and vegetation dynamics (Borsato et al., 2007; Fairchild et al., 2010). Although there is a wealth of information to be drawn from cave speleothems, interpretation frequently relies upon understanding site specific controls on carbonate deposition (Spötl et al., 2005; Miorandi et al., 2010). For this reason, a greater emphasis is now being placed upon robust high resolution cave monitoring studies, which aid the interpretation of speleothem chemistry through the characterisation of cave environments (Mattey et al., 2010; Wong et al., 2011).

Drip water conductivity is currently believed to be controlled within the karst zone by the air pressure of CO_2 (pCO_2) in the soil gas and the dissolution of bedrock, then further within the cave chamber according to the pCO_2 of the cave air. The EC characteristics of each drip can then vary on a site-specific basis according to variations in water residence time within the aquifer (Miorandi et al., 2010; Sherwin and Baldini, 2011), the extent of aquifer mixing (Genty and Deflandre, 1998) and potentially prior calcite precipitation (PCP) (Fairchild et al., 2000, 2006; Sherwin and Baldini, 2011). Several studies have observed strong speleothem drip rate/EC relationships, thought to be driven by the karst hydrology. Borsato (1997) and Miorandi et al. (2010) describe a negative EC and drip rate relationship in Ernesto Cave (Italy) whilst Sherwin and Baldini (2011) describe a similar relationship in Crag Cave, (Ireland) during the summer. Studies in Ernesto Cave found that under dry, low drip rate conditions, EC values increase due to enhanced karst water residence time and bedrock dissolution. During periods of high water percolation, EC values fall rapidly, possibly associated with karst water dilution (Miorandi et al., 2010; Sherwin and Baldini, 2011). In contrast, Genty and Deflandre (1998) and Fernández-Cortés et al. (2007) observe increasing EC values during periods of enhanced hydraulic pressure and therefore drip rate. In these latter studies, an increase in EC during periods of high water infiltration is explained by invoking the activation and drainage of a secondary (high EC) aquifer, mainly from water storage in micro-fissures.

However, drip water EC has rarely been discussed through an understanding of carbonate saturation state forced by cave air pCO_2 on a sub-seasonal scale (Sherwin and Baldini, 2011). As karst waters emerge into a cave void, degassing of CO_2 from drip waters is driven by cave air CO_2 concentration (Spötl et al., 2005; Baldini et al., 2008; Tremaine et al., 2011; Wong et al., 2011). An increase in cave air pCO_2 acts to suppress the normal rate of CO_2 degassing from drip waters and in so doing limits the supersaturation of percolating waters. This process in turn, limits the potential for carbonate precipitation and results in an increase in measured drip water EC or Ca^{2+} (Sherwin and Baldini, 2011). Previous work by Sherwin and Baldini (2011) indicates that this control is secondary to a hydrological mechanism and that it operates predominantly during the winter season. At Crag Cave a 1 ppm change in drip water Ca^{2+} would require a 333–667 ppm change in cave air pCO_2. Levels of carbonate supersaturation (reflected through cave drip water pH), also influence the partition co-efficient between trace elements in drip waters and speleothems (Frisia et al., 2005; Fairchild et al., 2010), thereby controlling the record of trace element incorporation into speleothem carbonate for select chemical species (Wynn et al., 2014).

To understand and explain high resolution records of EC, cave monitoring was undertaken in a previously unstudied cave in the Matienzo valley of northern Spain. The sub-hourly resolution of monitoring allows us to link high resolution variability in EC to cave atmospheric pCO_2 dynamics, rather than changes in karst hydrological behaviour. This mechanism of EC control is potentially important for understanding speleothem trace element records, especially at cave sites with very rapidly depositing speleothems or sizeable event scale changes in cave air pCO_2.

2. Site description

The Matienzo region of Northern Spain lies to the east of the Pyrenees mountain range within 40 km of the Northern Iberian coastline. Although famous for decades of cave exploration and for housing thousands of cave systems (Corrin and Smith, 2010) this region has received little scientific scrutiny outside of the geomorphological and archaeological communities. This project has undertaken cave monitoring and speleothem analysis for palaeoenvironmental reconstruction in a single cave system in the heart of the Matienzo karst depression (Fig. 1).

Cueva de Asiul (43° 19′ 0.63″ N, 3° 35′ 28.32″ W; 285 m.a.s.l) is a small, geometrically simple cave system of 75 m length, with an approximate cave volume of 2.7×10^5 l, and lies around 1 km from the village of Matienzo. The cave is easily accessed by a singular small entrance ($<1.5\ m^2$), followed by a well sized passage which is split by a series of larger chambers, ending in a boulder choke (Fig. 2). No active streams exist within the cave but several large pools survive throughout the year, fed entirely by drip waters. Shallow rock overburden ranges from 10 to 40 m (see Fig. 2). The cave is formed within bedded Aptian limestone (approx. 112–124 Ma) broken by a series of thin (<10 m) sandstone lenses (Quin, 2010). The area above the cave system consists of grass and shrub communities, maintained by very low intensity grazing. The soil rarely exceeds depths of 50 cm and is broken by large sections of exposed limestone bedrock and surface scree deposits.

Mean annual air temperature external to the cave site (within 200 m of the cave entrance) is 13.8 °C (4 years of monitoring), similar to longer term averages (14.4 °C) monitored at the nearest GNIP meteorological station in Santander (lat 43.430, long −3.817; 6 m.a.s.l.) (IAEA/WMO, 2014). Daily maximum temperatures are highest during summer (June to August) and drop below freezing in the winter. The Matienzo depression receives approximately 1400 mm/year of precipitation, 40% higher than the 1050 mm/year received in Santander (IAEA/WMO, 2014). The majority of precipitation falls in the winter months, with periods of water excess calculated following Thornthwaite (1948), being limited to the winter and spring months (October–April).

3. Methods

In situ data logging was undertaken in two main locations within Cueva de Asiul. The main monitoring chamber at the rear of the cave (65 m underground) housed three candle shaped speleothem deposits (ASF, ASM and ASR) thought ideal for palaeoenvironmental reconstruction; the second monitoring location is approximately half way through the cave system (40 m underground). Automated cave logging devices operated in conjunction with monthly monitoring visits from February 2011 until December 2013. Detailed methodologies presented here pertaining to cave air pCO_2, drip rate, external rainfall and EC, were collected as part of a wider study addressing the suitability of Cueva de Asiul as a repository for speleothem based palaeoclimate records.

Cave air CO_2 concentration was measured at time intervals of 1 h and soil air CO_2 concentration measured monthly, using a Vaisala GM70 monitor and GMP221 probe with a quoted measurement uncertainty of 2% and observed working uncertainty of 10%, with an operational