



What determines the calcium concentration of speleothem-forming drip waters?



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ABSTRACT

Cave drip water calcium ion concentration is a primary determinant of speleothem deposition and growth rate. The factors that determine drip water calcium ion concentrations are the soil and vadose zone CO₂ concentrations, and the hydrogeochemical evolution of the water from soil to cave. Here, we use a systematic literature review of cave drip water calcium concentrations, combined with PHREEQC equilibrium modelling, to investigate the global relationship between calcium concentration and surface climate. Our results are discussed in the context of understanding the climatic and environmental controls on drip water calcium concentration, speleothem growth rates and proxies of past climate and environmental change. We use an empirical, global soil CO₂ concentration–temperature relationship to derive PHREEQC modelled cave drip water calcium concentrations. The global mean modelled drip water calcium concentration is close to that observed, but it over-predicts at high and low temperatures, and significantly under-predicts at temperate conditions. We hypothesise that closed system hydrochemical evolution due to water saturation is an important control on carbonate dissolution at colder temperatures. Under warmer conditions, for example temperate climates with a dry and hot or warm summer, seasonally-limited water availability can lead to: < 100% soil cover; water-limitations on microbial and root respiration; wildfire; and prior calcite precipitation, all of which limit drip water calcium concentrations. In temperate climates with no dry season, higher CO₂ concentrations than modelled from soil values are necessary to explain the observed drip water calcium values, which we propose is from an additional source of CO₂ from microbial activity and root respiration in the vadose zone during open system hydrochemical evolution.

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1. Introduction

Cave drip water calcium ion concentration is the primary determinant of speleothem growth rate (Dreybrodt, 1999; Baker et al., 1998); other growth rate determining factors are temperature, drip rate, water film thickness, and cave air CO₂. Understanding the global characteristics of drip water calcium ion concentration are therefore relevant to our understanding of the spatial distribution of speleothem formation, understanding how speleothem growth rates vary over time (Tan et al., 2006), and improving our understanding of paleoenvironmental information contained within speleothem growth rate variations (Baker et al., 2015; Mariethoz et al., 2012; Stoll et al., 2015).

Cave drip water calcium ion concentrations are a product of the carbonate dissolution process, and the subsequent evolution of this water. The typical dissolution of limestone by carbonic acid commences in the soil and vadose zone, due to the elevated concentrations of CO₂ in the soil (Brook et al., 1983) and vadose zone (Atkinson, 1977). Given long enough vadose zone residence times,

infiltrating water may reach saturation calcium concentration as carbonate mineral dissolution is a relatively fast process (Dreybrodt, 1988). The composition (primarily Ca and HCO₃) of the saturated solution will depend on whether the dissolution evolves in either an open or closed system with regard to CO₂ (Appelo and Postma, 2005). Additional factors affecting dissolution include additional CO₂ generated from microbial or root respiration occurring within the karst unsaturated zone (Meyer et al., 2014), mixing corrosion (Dreybrodt, 1981), common-ion effects and temperature (Appelo and Postma, 2005) and the oxidation of sulphides (Spötl et al., 2002). Organic acids can both decrease Ca (suppress calcite dissolution, Wilkins et al., 2001) and increase Ca (reduce the effective saturation of calcite by chelating Ca ions in solution, Braissant et al., 2003), and may be important in systems with high concentrations of dissolved organic carbon. Depending on the hydrogeology of the karst, infiltrating water may be held in fractures, voids or caves where calcium may be lost from solution by calcite precipitation along the flow path (prior calcite precipitation, Fairchild et al., 2000).

Despite the complexity of processes that can determine speleothem-forming drip water calcium ion concentrations, Genty et al. (2001) reported an empirical linear regression between mean annual temperature

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and drip water calcium ion concentration ($n = 30$) for a study of ten European cave sites:

$$[\text{Ca}] \left(\text{mg L}^{-1} \right) = 17.66 \times T \left(^\circ\text{C} \right) - 78.02 \quad \left(R^2 = 0.63 \right). \quad (1)$$

However, this relationship excluded one site (Clamouse Cave) which had a summer dry season (or Mediterranean climate) and a Köppen–Geiger soil classification of Csa (Table 1; Peel et al., 2007). This site had lower drip water calcium ion concentrations than predicted. All other sites contributing to Eq. (1) were from sites classified as temperate with no dry season and warm summers (Köppen–Geiger classification Cfb).

A related empirical correlation has also been identified between the growing season soil carbon dioxide concentrations and surface climate parameters such as mean annual temperature and actual evapotranspiration (AET) (Brook et al., 1983):

$$\log(\text{PCO}_2) = -2.48 + 0.03 T \quad \left(R^2 = 0.64 \right) \quad (2)$$

$$\log(\text{PCO}_2) = -6.28 + 1.48(\log(\text{AET})) \quad \left(R^2 = 0.66 \right). \quad (3)$$

This permits the possibility of predicting soil carbon dioxide concentrations from climate data, and using this to determine infiltration water carbonate dissolution and the resulting equilibrium calcium concentration in drip waters.

Here, we investigate the extent to which temperature determines the calcium concentration of speleothem-forming drip waters through both modelling and empirical approaches. First, we update the Genty et al. (2001) dataset of European cave drip water calcium concentrations with a meta-analysis of the literature to empirically investigate the global relationship with surface temperature. Secondly, we use a geochemical speciation equilibrium modelling approach to model the carbonate system evolution of infiltration waters, using the predicted growing season soil carbon dioxide concentration from Brook et al. (1983) as an input, as this study provides a global empirical relationship between temperature and soil carbon dioxide concentration. Through a comparison of the two approaches, we can improve our understanding of the processes determining drip water calcium concentration, and determine the extent to which it is climate controlled. We discuss our results in the context of improving our understanding of speleothem growth dynamics, including growth rate variations over time and the use of growth rate as a paleoenvironmental proxy.

2. Methods

For the meta-analysis of temperature and calcite data from the literature, we undertook a database search to identify papers which contained both speleothem-forming drip water calcium concentration data and surface climate data. Papers which reported data from anthropogenically-impacted sites (for example, high pH drips from lime; e.g. Hartland et al., 2011) were excluded from the compilation. For caves with drip sites which were sampled multiple times within a year, we obtained a mean and standard deviation (SD) for each drip site. In other cases, we obtain a mean and SD for the cave as a whole. The new data compilation includes published data from several studies (Gascoyne, 1983; Spötl et al., 2005; McDonald et al., 2007; Karmann et al., 2007; Asrat et al., 2008; Wynn et al., 2008; Riechelmann et al., 2011; Wong et al., 2011; Oster et al., 2012; Prasanna et al., 2014; Moreno et al., 2014; Wu et al., 2015; Treble et al., 2015). To this we added our own unpublished data from the UK from Stump Cross Cavern (Baker, unpublished data) and additional data from Uamh an Tartair (Fuller, 2007), and Australian cave data from Glory Hole Cave (Coleborn unpublished data), Cathedral Cave (Andersen, unpublished data),

Yonderup Cave (Nagra et al., in review), and Wildman's Cave (Flemons, 2015).

To model the carbonate system hydrochemically and derive the equilibrium Ca concentration expected, we used PHREEQC (Parkhurst and Appelo, 1999). We modelled the equilibrium calcium ion concentration from an initial soil PCO_2 , and using a variety of environmental conditions. These included the temperature-dependence of calcite dissolution, open and closed system evolution, common-ion effects, the initial ionic concentration of rainfall and increased ionic strength due to evapotranspiration. The open system dissolution was modelled by equilibrating a constant PCO_2 with calcite (for example, at 25 °C, $K_{\text{CaCO}_3} = 10^{-8.48}$) in pure water. Physically this represents a system where calcite is dissolved in the same location as the CO_2 is produced or a system where the CO_2 is not transport limited (i.e. as in the unsaturated zone). For the closed system dissolution the modelling was done in two steps. First the soil water was equilibrated with the target PCO_2 in pure water. Then the soil water charged with this amount of CO_2 was brought into equilibration with calcite and thus the CO_2 is partially consumed to reach equilibrium (i.e. $\text{PCO}_2 \neq \text{constant}$). Physically this represents a system where calcite is dissolved at a location that is isolated from the zone of CO_2 production in the soil. The open system, with other parameters kept equal, therefore produces a higher Ca concentration than a closed system. Increasing solution ionic strength is known to decrease solute activities and increase solubility for minerals whereas common-ion effects could potentially decrease the solubility (Appelo and Postma, 2005). To quantify this effect, measured rainwater water samples from Hubbard Brook and De Kooy and a 1:1000 diluted seawater sample mimicking rainwater in coastal zones (Appelo and Postma, 2005) were used as input solutions and equilibrated with PCO_2 and calcite. Further increasing ionic strength mimicking the effect of evapotranspiration on soil solutions was achieved by equilibrating a 1:100 diluted seawater sample. The 1:1000 and 1:100 dilution of seawater would equate to concentrating the ions in a coastal rainwater sample by 1–2 orders of magnitude.

3. Results

3.1. Meta-analysis of drip water data

Table 1 presents the speleothem-forming drip water calcium concentrations and mean annual surface air temperatures from our literature analysis. Also reported are the mean annual precipitation and the Köppen–Geiger climate classification (Peel et al., 2007). Mean drip water calcium concentrations range from 0.81 mmol L^{-1} (Clamouse Cave, France) to 5.20 mmol L^{-1} (La Faurie Cave, Dordogne, France), which is identical to that reported by Genty et al. (2001). The mean annual surface air temperatures range from 6.5 °C (Ernesto Cave, Italian Alps) to 25.3 °C (Niah Great Cave, Borneo), a range approximately double that reported in Genty et al. (2001) (6.5 °C to 15.5 °C).

The results of the meta-analysis are shown graphically in Fig. 1. The data from Genty et al. (2001), excluding the Clamouse Cave site, yield a statistically significant correlation between temperature and calcium ion concentration (Eq. (1)). However, the larger dataset reveals no correlation with temperature ($r = 0.00$, $n = 134$). Most notably, cave drip water calcium concentrations above ~14 °C are lower than that predicted by the Genty et al. (2001) regression using mean annual temperature as a predictor. The Clamouse Cave data groups with data from two Western Australia caves, also in a Mediterranean climate region (Köppen Geiger classification Csb). We undertook further statistical analysis of the dataset to explore the relationship between drip water calcium concentration and mean annual precipitation, and between drip water calcium concentration and temperature for temperate sites with and without dry seasons (Köppen–Geiger classifications Cf vs Cs). None yielded statically significant relationships for linear, non-linear simple or multiple regressions, with the exception for a subset of sites with Köppen–Geiger classification Cfb (temperate, no dry season) and

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