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 CO_2 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 CO_2 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 CO_2 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 CO_2 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 CO_2. 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 CO_2 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 HCO_3) of the saturated solution will depend on whether the dissolution evolves in either an open or closed system with regard to CO_2 (Appelo and Postma, 2005). Additional factors affecting dissolution include additional CO_2 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:

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

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):

$$\log(PCO_2) = -2.48 + 0.03\ T \quad \left(R^2 = 0.64\right) \tag{2}$$

$$\log(PCO_2) = -6.28 + 1.48(\log(AET))\left(R^2 = 0.66\right). \tag{3}$$

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, $K_{CaCO3} = 10^{-8.48}$) 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. $PCO_2 \ne$ 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-Gieger 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-Gieger classification Cfb (temperate, no dry season) and

Table 1

Cave drip water calcium concentration and climate data, including cave location and drip water identification and publication source (where data is published). n/d = no data available. Climate zones are the Köppen-Geiger classification as used by Peel et al. (2007): Af = tropical rainforest, Am = tropical monsoon, Cf = temperate without dry season (Cfa = hot summer, Cfb = warm summer), Cs = temperate with dry summer (CSa = hot summer, Csb = warm summer), ET = polar (alpine climate).

Publication	Location	Drip ID	Drip water [Ca] mmol L^{-1}		Mean annual surface air temperature (°C)	Mean annual precip (mm)	Climate zone
			Mean	SD			
Genty et al. (2001)	Villars, Dordogne, France	Vi#1A	3.45	0.45	12.4	1005	Cfb
		Vi#1B	4.40	0.68			
		Vil4	3.60	0.70			
		Vi#10A	3.10	0.88			
		Vi#10B	2.65	0.50			
	La Faurie, France	Fau14	5.03	0.75	12.9	1005	Cfb
		Fau13	5.20	0.70			
		Fau11	3.80	0.83			
		Fau10	3.88	0.95			
		Fau8	3.90	0.73			
		Fau6	3.83	0.78			
	Prou-meyssac, France	Pro1	3.83	0.78	13.6	884	Cfb
		Pro2	3.65	0.60			
		Pro3	2.63	0.63			
	Postojna, Slovenia	PR2	1.73	0.09	8.7[a]	1326	Cfb
		PR3	1.79	0.07			
		Ent	2.00	0.26			
		Bri	1.39	0.25			
	Bath, England	bfm96p	2.58	0.21	10.5	814	Cfb
		bfm963	2.63	0.28			
		bfm96b	2.53	0.35			
		bfm96f1	2.53	0.25			
		bfm96f4	2.18	0.22			
		bfm96f2	2.62	0.35			
		bfm96j	2.30	0.35			
	Assynt, Scotland	SU967	0.93	0.10	7.2	1955	Cfb
	Clamouse, France	Clam1A	1.11	0.05	14.5	766	Csa
		Clam1B	1.10	0.05			
		Clam2	0.89	0.05			
		Clam3	0.96	0.05			
		Clam4	0.81	0.05			
	Mendips, England	GB Cave	1.59	0.39[b]	10.0	900	Cfb
	England	Poole's Cavern	2.43	0.17[b]	9.0	1329	Cfb
	Italy	Ernesto	1.33	0.13	6.5	n/d	ET
Wu et al. (2015)	Xueyu Cave, SW China	Site1	4.38	0.43	17.2	1072	Cfa
		Site2	1.84	0.72			
		Site3	2.01	0.57			
Prasanna et al. (2014)	Niah Great Cave, NW Borneo	D5	1.93		25.3[c]	2814	Af
		D6	1.13				
		D8	3.49				
Moreno et al. (2014)	Molinos Cave, NE Spain	Site 1	2.53	0.87	12	500	CSa
Riechelmann et al. (2011)	Bunker Cave NW Germany	TS1	2.33	0.18	10.6	920	Cfb
		TS2	1.81	0.17			
		TS3	1.80	0.23			
		TS5	1.69	0.09			
		TS6	2.20	0.50			
		TS7	2.13	0.25			
		TS8	1.95	0.12			
Wong et al. (2011)	Natural Bridge Caverns, TX, USA	NBVC	0.95	0.60	19.6	740	Cfa
		NBBC	1.38	0.27			
		NBGN	1.17	0.54			
		NBFT	3.26	0.50			
		NBEL	1.71	0.35			
		NBWS	2.92	.32			
		NBFE	2.84	0.43			
		NBCD	1.47	0.65			
		NBCA	1.62	0.43			
Fuller (2007)	Uamh an Tartair, Assynt, Scotland	S1	1.39	0.31	7.2	1955	Cfb
		S2	1.27	0.02			
		S3	1.30	0.17			
		S5	1.35	0.14			
		S6	1.21	0.02			
		S7	1.29	0.20			
		S8	1.27	0.17			

Table 1 (*continued*)

Publication	Location	Drip ID	Drip water [Ca] mmol L^{-1}		Mean annual surface air temperature (°C)	Mean annual precip (mm)	Climate zone
			Mean	SD			
		S12	1.36	0.19			
		S13	0.99	0.14			
		SU031	1.76	0.25			
		SU032	1.63	0.11			
Baker (unpublished)	Stump Cross Caverns, UK	Calcite Pillars 1a	2.29	0.48	8.1	836	Cfb
		Calcite Pillars 1	2.31	0.31			
Andersen (unpublished)	Wellington Caves, NSW, Australia	All	2.20	0.97[b]	18.1	629	Cfa
Treble et al. (2015)	Golgotha Cave, WA, Australia	1A	1.24	0.24	14.75	1113	Csb
		1B	1.16	0.26			
		2A	1.16	0.26			
		2B	1.29	0.26			
		2E	1.89	0.19			
McDonald et al. (2007)	Kooringa Cave, Wombeyan, NSW	K1	2.23	0.53	11[d]	848	Cfb
		K2	1.63	0.39			
		K3	2.78	0.44			
	Wollondilly Cave, Wombeyan, NSW	W1	2.33	0.41	14.5[d]		
		W2	2.8	0.60			
		W2A	2.67	0.40			
		W3	2.50	0.63			
		W5A	2.51	0.63	10.2[d]		
		W6A	2.38	0.31			
		W6C	3.18	0.61			
Flemons (2015)	Wildman's Cave, Wombeyan, NSW, Australia	All	2.40	0.41[b]	13.5[d]		
Spötl et al. (2005)	Obir Cave, Austria	HA	1.33	0.12	6.8	1350	ET
		SH1	1.28	0.10			
		PH1	1.19	0.12			
Asrat et al. (2008)	Rukiessa Cave, Ethiopia	All	1.4	0.83[b]	19.5	1014	Cfb
	Achere, Ethiopia	All	3.13	1.88[b]			
	Goda Mea, Ethiopia	All	2.57	0.65[b]			
Karmann et al. (2007)	Santana Cave, Brazil	ESF	2.23	0.14	18.9	1589	Cfb
		EE2	1.45	0.04			
		EE1	1.32	0.04			
		EIF	1.53	0.35			
		SGR1	1.67	0.16			
Wynn et al. (2008)	Crag Cave, Ireland	R	2.84	0.12	9.6	900	Cfb
		X	3.43	0.83			
		Y	3.33	0.21			
		CC-Bil	4.57				
Oster et al. (2012)	Black Chasm Cavern, CA, USA		1.84	0.36	12.3	1100	Csb
Tremaine and Froelich (2013)	Hollow Ridge Cave, FL, USA	SJA	1.05		18.8	1377	Cfa
Coleborn (unpublished data)	Glory Hole Cave, NSW, Australia	G1	2.48	0.12	9.4	1158	Cfb
		G10	2.32	0.29			
		G13	2.04	0.78			
		G3	2.23	0.65			
		G4	2.00	0.72			
		G6	1.80	0.88			
		G7	1.74	0.93			
		G8	1.94	0.81			
		LR1	1.33	0.62			
		M10	2.15	0.42			
		M13	1.71	0.73			
		M14	1.48	1.04			
		M2	2.01	0.67			
		M4	1.65	1.10			
		M8	2.36	0.33			
Nagra et al. (in review)	Yonderup Cave, WA, Australia	1A	1.20	0.6	15.1	664	Csb
		2A	1.42	0.20			
Gascoyne (1983)[c]	Cascade Cave, Vancouver Is	V1	1.03		7.8	n/d	n/d

Table 1 (*continued*)

Publication	Location	Drip ID	Drip water [Ca] mmol L^{-1}		Mean annual surface air temperature (°C)	Mean annual precip (mm)	Climate zone
			Mean	SD			
		V2	1.39		7.1		
		V3	1.41		6.9		
		V4	1.21		6.9		
		V6	1.57		6.9		
	Jamaican Caves	J1, J7	1.06		24.1	n/d	Am
		J5, J13	1.67		23.0		
		J6, J9	1.26		22.3		
		J3	1.43		23.5		
		J10	1.62		23.4		
		J11	1.17		22.6		
		J12	1.45		24.0		

[a] Temperature data from Domínguez-Villar et al. (2015).
[b] Standard deviation is that of all drips within the cave, not for an individual drip.
[c] Surface air temperature unknown–drip water temperature reported.
[d] Surface air temperature unknown, mean annual cave air temperature reported.

mean annual temperature < 15 °C. This subset of sites can be considered to have no water-limitation (no dry season and relatively low evaporation in all months) and are those with the same climate as those in Genty et al. (2001). For these 78 drip water from 15 caves in Europe and SE Australia, a positive correlation between temperature and drip water calcium ion concentration persists for this larger dataset:

$$Ca\left(mmol\ L^{-1}\right) = -0.711 + 0.303\ T(°C)\quad \left(R^2 = 0.46\right). \qquad (4)$$

3.2. Modelled drip water chemistry

Fig. 2 presents the PHREEQC modelled equilibrium drip water calcium concentrations for a range of initial carbon dioxide concentrations and environmental conditions. Drip waters are modelled for the temperature range 5–25 °C, open and closed system evolution, and a range of initial ionic strengths which represent actual rainwater compositions and their subsequent ionic enrichment due to evapotranspiration. Fig. 2 demonstrates that temperature has a significant effect on equilibrium drip water Ca (through its effect on calcite solubility) so that the solubility of calcite decreases with increasing temperature for the same PCO_2. Carbonate mineral dissolution within a closed system will decrease drip water Ca, relative to open system dissolution, due to exhaustion of the limited CO_2 pool in the infiltrating soil water. Closed system dissolution might be expected where saturated peatland overlies the limestone (e.g. at the cooler climate sites in northwest Scotland and northern Norway), as well as at sites where there is a separation between the source of CO_2 production and the location where the limestone is dissolved (e.g. the Waitomo district of New Zealand Gunn, 1981). In reality soil water chemical composition varies with rainfall and aerosol/dust source, soil mineral composition and soil residence time. The effects of the initial solution composition and enrichment of rain derived solutes due to a combination of evaporation and transpiration of the soil solution have negligible effects on the final drip water calcium concentration for low to moderate ionic strengths. The results for the two rainwater samples (Hubbard Brook and De Kooy) and the 1:1000 diluted seawater are indistinguishable from pure water equilibrated with calcite at 25 °C (Fig. 2). Only as the ionic strength increases towards that of 1:100 diluted seawater (equivalent to concentrations of Na of 4.85 mmol L^{-1} and Cl of 5.66 mmol L^{-1}) is there a noticeable
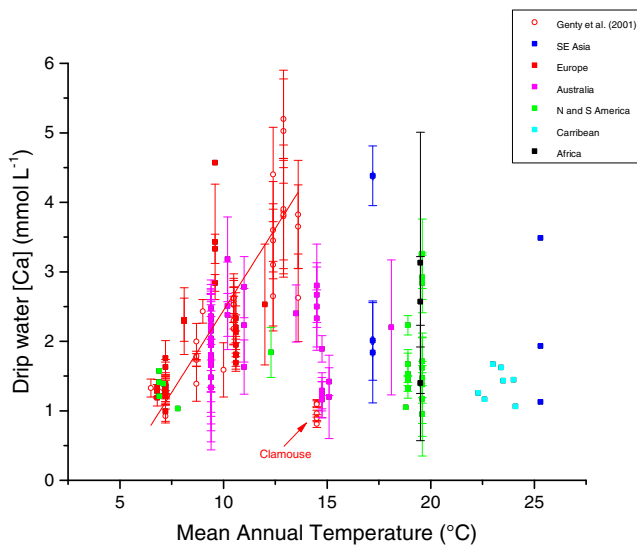

Fig. 1. Comparison of cave drip water calcium ion concentration and mean annual air temperature. Red open circles are data published in Genty et al. (2001). Error bars represent the 1 standard deviation for an individual drip or a cave site (see Table 1). The regression line is fitted to the Genty et al. (2001) dataset, excluding the sites from Clamouse Cave.
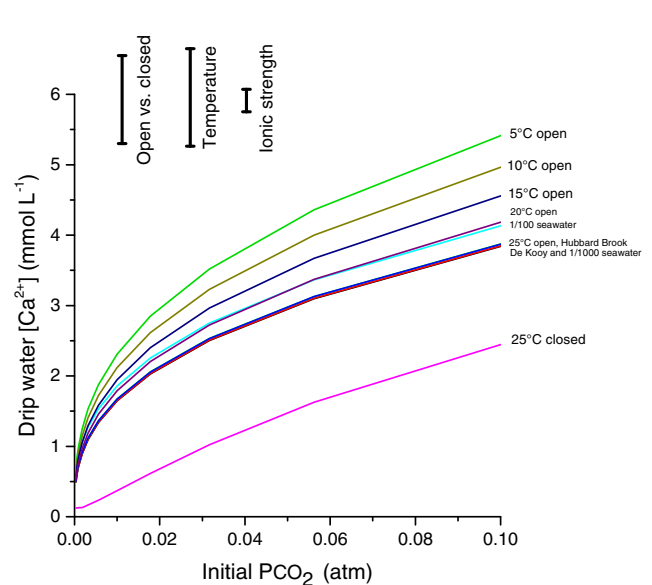

Fig. 2. PHREEQC modelled drip water calcium concentrations for a range of environmental conditions. Vertical bars show the ranges for temperature (5–25 °C), open vs closed system evolution, and initial water composition 0–0.01% seawater.

effect with increased Ca concentration due to formation of aqueous complexes and reduced ion activity. In contrast, the ranges of drip water Na and Cl for the sites in this paper (where measured) are shown in Table 2. Only Cathedral Cave and Golgotha Cave have concentrations of Na and Cl near the modelled 1:100 diluted seawater. The modelled increase in solubility is therefore at the upper end of the measured range and probably only relevant for caves in coastal zones with high salt input to the soils or for caves in semi-arid and arid zones with high evapotranspiration. The latter are also likely to be water limited and have low soil CO_2 production and therefore a lower Ca concentration than predicted by Eqs. (1) or (4).

We used the global empirical correlation between growing season soil CO_2 and temperature (Brook et al., 1983) (Eq. (2)) to investigate a possible temperature–drip water calcium concentration relationship. For two of our sites (Golgotha Cave and Glory Hole Cave, Australia), we can validate the use of this empirical relationship between temperature and soil carbon dioxide concentration at two sites where we have measured soil carbon dioxide concentration data. At the montane Glory Hole Cave (Köppen-Gieger climate Cfb), with surface mean annual air temperature of 9.3 °C, the predicted soil carbon dioxide concentration (log(PCO_2) from −2.20) underestimates the observed summer (Dec-Mar) soil CO_2 (log (PCO_2) = −1.72) but falls within the observed annual range (log (PCO_2) from −1.72 to −2.70) (Coleborn et al., 2016). However, at the Mediterranean (Köppen-Gieger climate zone Csb) Golgotha Cave, the predicted log(pCO_2) of −2.04 overestimates the observed annual range of soil carbon dioxide concentration (log(pCO_2) from −2.2 to −2.4) (Treble et al., 2015). This observation is considered further in the discussion.

Fig. 3 shows the cave drip water calcium concentration data in comparison to the PHREEQC modelled drip water calcium concentration using the PCO_2 input parameters derived from Brook et al. (1983). The open system modelled drip water calcium concentration increases from 1.69 mmol L^{-1} at 0 °C to 2.15 mmol L^{-1} at 30 °C. This increase with increasing temperature demonstrates the relative importance of PCO_2 on modelled drip water calcium concentration, rather than temperature alone, which would decrease calcium ion concentrations with increasing temperature. The modelled drip water calcium concentrations are within the range of the global cave drip water dataset (2.03 ± 0.89 mmol L^{-1}; n = 130). Speleothem forming drip waters are higher than that predicted by the global soil carbon dioxide model at mean annual temperatures of 10–14 °C. Drip water calcium ion concentrations can be lower than that modelled at all temperatures, but Fig. 3 shows that this is most likely at mean annual temperatures above 14 °C. The correlation between drip water calcium ion concentration and temperature is not significant (r = 0.04, n = 130) and has no explanatory power. Notable is the observation that within-cave variability in drip water calcium concentrations is large and that it can be greater than any between-cave variability for caves at similar temperatures or in similar regions (Table 1, Fig. 3). This observation of within-cave variability is compelling evidence for the importance of local-scale processes determining drip water calcium concentrations.

4. Discussion

Fig. 3 demonstrates that global mean modelled drip water calcium concentration from open system dissolution of calcite is in close

agreement with the observed global mean of drip water. However, observed drip water calcium concentrations are generally higher than modelled at temperate climate conditions (10–14 °C), and lower than modelled for warmer temperatures. Processes in addition to the soil carbon dioxide concentration–temperature relationship therefore have additional influence on the drip water calcium ion concentration, and these are considered in turn below.

4.1. Processes decreasing drip water calcium concentration

4.1.1. Closed system calcite dissolution

Water geochemical evolution under a closed system control requires the separation of the location of the CO_2 production (e.g. the soil) and the calcite dissolution by a zone of water saturation. This is most likely at sites where there is typically a water excess in most months, and the overlying soils are therefore saturated for much of the year. For example, two sites with mean annual temperatures < 10 °C but contrasting water availability are Uamh an Tartair (Northwest Scotland) and Glory Hole Cave (Australian Snowy Mountains). At Uamh an Tartair, high annual total precipitation limits surface organic matter decomposition to the extent that a blanket bog overlies the cave, and mean drip water calcium ion concentrations (0.99 to 1.76 mmol L^{-1}; Fuller, 2007) are below that predicted for an open system (1.8 mmol L^{-1}). At Glory Hole Cave, lower rainfall totals lead to intermittent soil saturation and the overlying vegetation is dominated by snow gum forest. Here, cave drip water mean calcium ion concentrations are higher (1.3 to 2.5 mmol L^{-1}). A closed system evolution of drip waters at Uamh an Tartair is consistent with the explanation of high percentages of 'dead' carbon (geologically old ^{14}C) in speleothems at the site (Genty et al., 2001) and a soil saturation control on drip water calcium concentration at Uamh an Tartair is in agreement with the interpretation of speleothem growth rate derived paleoclimate records (Proctor et al., 2000; Trouet et al., 2009; Baker et al., 2015), which demonstrate that growth rate inversely correlates with mean annual precipitation and the North Atlantic Oscillation.

4.1.2. Prior calcite precipitation

Vadose zone waters which are supersaturated with respect to calcite may precipitate some or all of this excess calcite prior to the drip water being measured at a particular speleothem forming drip site. Therefore, if prior calcite precipitation (PCP) has occurred, either in the karst unsaturated zone (Fairchild et al., 2000), or on a stalactite within the cave (Treble et al., 2015) then it will lead to a decrease in the measured drip-water calcium ion concentration. The amount of PCP would be expected to increase with increasing residence time of the water in karst voids and/or with slower water flow on stalactite surfaces, and therefore at a global scale it would be expected to increase with decreasing water availability.

In our dataset, the drip sites at Golgotha Cave (Western Australia) have been demonstrated to undergo in-cave PCP (Treble et al., 2015), with PCP related to drip rate. There, the low flow-site (1A, Table 1) with demonstrated PCP has a mean calcium concentration of 1.24 ± 0.24 mmol L^{-1}, in contrast to the high flow site (2E, Table 1) which has less PCP and a calcium concentration of 1.89 ± 0.19 mmol L^{-1} which is similar to that modelled (1.90 mmol L^{-1}). PCP has also been attributed to speleothem records from Clamouse Cave (McMillan et al.,

Table 2
Cave drip water Na and Cl concentrations. Either the range or mean and standard deviation are shown.

| Location	[Na] (mmol L^{-1})	[Cl] (mmol L^{-1})	Publication
Ernesto Cave, Italy	0.017 ± 0.009	0.023 ± 0.011	Fairchild et al. (2000)
Grotte de Villars, France	0.14–0.32	0.15–0.37	Baker et al. (2000)
Clamouse Cave, France	0.27 ± 0.10	0.30 ± 0.13	Fairchild et al. (2000)
Natural Bridge Caverns, TX, USA	0.13–0.87	n.d	Musgrove and Banner (2004)
Cathedral Cave, NSW, Australia	0.025–2.47	0.005–2.91	Andersen (unpublished data)
Golgotha Cave, WA, Australia	2.31–3.35	2.76–4.48	Treble et al. (2015)
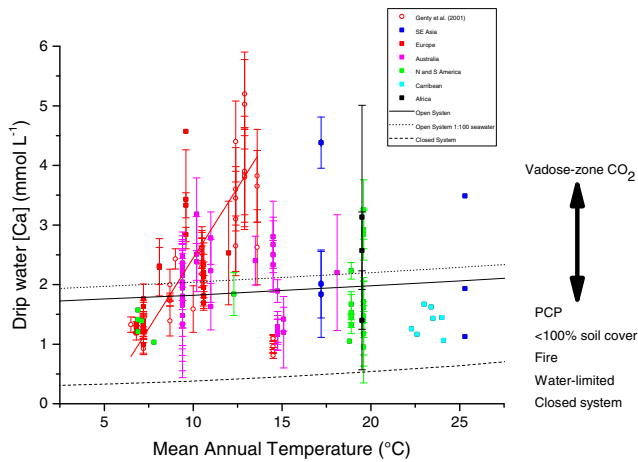
Fig. 3. Observed and modelled speleothem-forming drip water calcium ion concentrations. Observed data is the same as presented in Fig. 1. PHREEQC modelled data uses the Brook et al. (1983) relationship between PCO_2 and temperature, and is shown for open system evolution (solid line), open system evolution with ionic strength of a 1:100 diluted seawater (dotted line) and closed system evolution (dashed line). Additional processes affecting drip water calcium concentration and discussed in Section 4 are shown on the right hand side.

2005; Fairchild and Treble, 2009): Clamouse Cave drip water calcium ion concentrations fall in the range 0.8 to 1.1 mmol L^{-1}, well below the modelled value (1.9 mmol L^{-1}). Both of these sites have a Mediterranean climate classification, and we hypothesise that PCP is a likely factor for the observed, lower-than-modelled, calcium concentrations at many sites with a seasonally limited water balance.

4.1.3. Incomplete (<100%) soil cover

The open system modelled drip water calcium concentration (from 1.69 mmol L^{-1} at 0 °C to 2.15 mmol L^{-1} at 30 °C) presumes a complete surface soil cover. Mixing of karst waters which originate from areas of soil cover with those which have a bare bedrock source would be expected to lead to drip waters with calcium concentration lower than that modelled. Soil cover may be less than 100% in recently glaciated regions, in arid climates where vegetation growth and therefore soil formation are limited, and in regions which experience soil loss (e.g. those with very steep terranes or those which experience intense wild-fires). At our Australian sites, soil cover is incomplete at Wildman's Cave, Wombeyan; Cathedral Cave, Wellington; and site 1A at Yonderup Cave, Yanchep; and complete at Golgotha Cave and Glory Hole Cave. Additionally, drip water samples from Yonderup Cave were from a post-wildfire recovery period. At Yonderup Cave, site 1A had 70% soil cover whereas site 2A had complete soil cover, and drip water calcium concentrations appear to reflect this soil cover (1.20 ± 0.6 mmol L^{-1} and 1.42 ± 0.20 mmol L^{-1} respectively). However, when comparing between sites, drip water calcium ion concentrations does not necessarily fall below those modelled (e.g. Wildman's Cave observed 2.40 ± 0.41 mmol L^{-1} vs modelled 1.86 mmol L^{-1}; Cathedral Cave, Wellington 2.20 ± 0.97 mmol L^{-1} vs modelled 1.95 mmol L^{-1}), demonstrating that multiple processes determine drip water calcium concentrations.

4.1.4. Fire and water-limited CO_2 production

Water availability is an essential requirement for microbial respiration, and in water-limited environments microbial respiration and CO_2 production may be limited by moisture availability. Our modelling uses a temperature–soil CO_2 empirical relationship that does not explicitly include water availability. A lack of available water, especially in the growing season, may also limit vadose zone CO_2 production from root respiration and/or microbial respiration (see Section 4.2.1).

Wildfire has also been shown to limit soil carbon dioxide concentrations. Coleborn et al. (2016) demonstrate from sites in the Snowy

Mountains, Australia, that soil carbon dioxide concentrations at forested karst sites which have experienced wildfire may be lower than non-burnt karst sites for up to 5–10 years, due to the time taken for tree growth to recover and root respiration to return to pre-fire levels. Treble et al. (2016) report a multi-year increase in drip water calcium concentrations at Golgotha Cave, Australia: modelling of this data attributed this increase to a long-term rise in unsaturated zone CO_2 due to the recovery of forest growth following fires.

At both the Golgotha Cave and Glory Hole Cave, Australia, we have soil carbon dioxide concentration data. At Golgotha Cave, a forested site in a Mediterranean climate zone, soil CO_2 concentrations were over-predicted by Eq. (2), demonstrating a possible overestimation of soil CO_2 concentration post-fire in a water limited environment. This factor will therefore affect predicted drip water calcium ion concentrations, in addition to the recognised effects of PCP (Section 4.2). At Glory Hole Cave, a forested site in a montane climate zone which was last impacted by wildfire in 2003 AD, observed and predicted soil carbon dioxide concentrations are in better agreement.

4.2. Processes increasing drip water calcium concentration

4.2.1. Additional vadose zone CO_2

For all temperatures, but particularly at mean annual temperatures between 10 and 14 °C, higher CO_2 concentrations than modelled from growing season soil carbon dioxide concentrations alone are necessary to explain the observed drip water calcium values. Additional carbon dioxide sources occur in the vadose (or unsaturated) zone, termed 'ground air CO_2' by Atkinson (1977). Vadose zone microbial communities will contribute additional CO_2 from microbial respiration (Fairchild and Baker, 2012) and deep rooted trees will contribute carbon dioxide at depth from root respiration (for example, see Meyer et al., 2014; Treble et al., 2015). Evidence of a ubiquity of biologically sourced carbon over inorganic (geological) sourced carbon comes from the widespread observation of speleothem geological (or 'dead carbon') at values far lower that 50% (typically 15 ± 5% dead carbon, Genty et al., 2001; Fairchild and Baker, 2012; Noronha et al., 2015).

Vadose zone microbial respiration would be expected to be ubiquitous, its activity proportional to temperature but limited by carbon supply and, in arid conditions, water availability. As such, vadose zone microbial respiration would be expected to decline in water limited, arid environments with limited soil cover, and reach a maximum level in warm and wet climates such as those experienced in monsoon regions and temperate climates. The presence of root respiration from tree roots within the vadose zone may occur within a wide range of climates and environments, but would be least likely in the cold (e.g. tundra) and warm (e.g. desert) extremes. Ernesto Cave (6.5 °C), although one of the coldest sites in our dataset, has a bimodal distribution of calcium concentrations, the higher concentration sites requiring an additional PCO_2 source (Fairchild et al., 2000).

Within our drip water dataset, the majority of forested cave sites have drip water calcium concentrations above that predicted for open system evolution from a soil CO_2 endmember, the exceptions being one drip site at Postojna (sampled at 120 m depth below surface, compared to other sites with higher calcium concentration at 37 m and 10 m below surface, and the deep site is therefore more likely to have more geochemically evolved drip water that has undergone PCP), 27% of the drips at Glory Hole Cave, Australia, and four of the five drips at Golgotha Cave, Australia (where PCP has been shown to be the dominant process).

We can utilise our hydrochemical model to predict the total (soil and vadose zone) CO_2 concentration required to generate the observed drip water calcium values under open system conditions. For a mean annual temperature of 10 °C, drip water calcium concentrations of 3.0 mmol L^{-1} require an initial $\log(PCO_2)$ of −1.58, and concentrations of 4.0 mmol L^{-1} require a $\log(PCO_2)$ of −1.25. At 15 °C, a drip water calcium concentration of 3.0 mmol L^{-1} requires an initial $\log(PCO_2)$ of

−1.49, and a concentration of 4.0 mmol L^{-1} requires a log(PCO$_2$) of −1.15. Approximated to a ppm volume, this is the equivalent increase from a modelled soil CO$_2$ of 6600 ppm to a combined soil and vadose zone CO$_2$ of 26,000–56,000 ppm (10 °C) and from a modelled soil CO$_2$ of 9300 ppm to a combined soil and vadose zone CO$_2$ of 32,000–71,000 ppm. These values compare reasonably to the original 'ground air carbon dioxide' calculations of Atkinson (1977), who suggested for the Mendip Hills, UK, an unsaturated zone CO$_2$ concentration of 1.5 to 3.0% which was nearly constant throughout the year, and sourced from the decay of organic matter washed or leached from the soil by percolation water. A seasonally varying 'ground air' or epikarst source of CO$_2$ from 3.0 to 10% has also been required to explain the geochemical evolution of groundwater in karst aquifers in the Dordogne, France (Peyraube et al., 2012, 2013, 2014), close to the drip water cave sites of Genty et al. (2001, 2014) reported here. Our modelled CO$_2$ are also very similar to observed vadose zone CO$_2$ values reported for Nerja, Spain, with maximum vadose zone CO$_2$ measured in boreholes of 55,000 ppm in comparison to maximum soil CO$_2$ of 6900 ppm (Benavente et al., 2010). Nerja is situated in a Mediterranean climate and has a mean annual temperature of 18.8 °C, suggesting that even in water-limited environments, 'ground air' or vadose zone CO$_2$ can be significantly higher than soil CO$_2$ concentrations. Faimon et al. (2012) report log(PCO$_2$) of cave drip waters of −1.53 in the Moravian Karst, Czech Republic, which greatly exceeded that of the overlying soil (−2.72), and a deep epikarst source of CO$_2$ was inferred. Similarly, Treble et al. (2015) reverse modelled Golgotha Cave drip water to restore the solutions to the chemistry at the point of equilibrium with the source CO$_2$, accounting for PCP effects. This resulted in a log(PCO$_2$) of −2.04 ± 0.04, in agreement with the value predicted by the Brook et al. relationship, but higher than shallow soil CO$_2$ measurements at this site (−2.2 to −2.4). Treble et al. (2015) attribute this to evidence for enhanced CO$_2$ production at depth by the deep-rooted trees overlying Golgotha Cave.

4.2.2. Seasonal bias in drip water geochemistry

In many of the European cave sites, a temperate climate leads to warm and relatively dry summers, followed by relative wet and mild winters. An autumn 'flush' of water with relatively high carbon dioxide concentrations could additionally explain the higher than modelled cave drip water calcium concentrations at many of the European cave sites. A similar seasonal bias can be hypothesised for caves in monsoon regions, where recharge is likely to be biased to the warmer, wet monsoon season. However, the global soil carbon dioxide equations of Brook et al. (1983) already considers the growing season soil CO$_2$ concentrations rather than the annual mean, which should therefore account for any seasonal bias in drip water chemistry related to a growing season 'flush' of waters with a high CO$_2$ source. Additionally, the temperature sensitivity is not sufficient to explain the observed drip water calcium concentrations e.g. an increase in temperature from 10 °C to 20 °C only increases drip water calcium from 1.98 to 2.15 mmol L^{-1}.

5. A conceptual framework for drip water calcium ion concentration

Our results can be used to provide a conceptual framework for expected drip water calcium concentrations under a variety of environmental and climatic changes. In summary, a combination of geochemical modelling and literature drip water calcium values demonstrates that drip water calcium ion concentrations of speleothem-forming drip waters:

1) Have no relationship with mean annual temperature, except for a subset of sites where mean annual temperature is <14 °C and there is no dry season.

2) Are under-predicted from growing season soil carbon dioxide concentrations, especially in temperate climate regions (Köppen-Geiger classification Cfb and mean annual temperatures <14 °C).

3) Can be greater than modelled by open-system evolution of waters from a soil carbon dioxide source due to the additional contribution of vadose zone CO$_2$, which can be significant even in seasonally water-limited environments.

4) Can be less than that modelled by open-system evolution of waters from a soil carbon dioxide source due to the effects of (i) wildfire, bare-rock surface and water-limitations on CO$_2$ production in water-limited environments (ii) closed system evolution, most likely in cold, water-saturated environments, and (iii) prior calcite precipitation, which can occur in all environments but which is most likely in water-limited climates.

Several of these factors affecting drip water calcium concentration can occur simultaneously, and may occur over different timescales. Fig. 4 presents a variety of scenarios for hypothetical cave drip waters over the Quaternary timescale, scenarios relevant to the understanding of the time and rate of speleothem growth. Fig. 4a presents a scenario for glacial–interglacial climate change at a water limited site. Conceptually based on the Australian sites at Wellington or Golgotha Cave, we consider the effects of an ~6.5 °C decrease in Australian summer annual temperature between glacial and stadial periods (Chang et al., 2015), and the associated decrease in evaporative water loss. We hypothesise that this will lead to decreased PCP and less water-limitation during glacial and stadial periods compared to interglacial and inter-stadial conditions, which would be similar to today where calcium concentrations are lower than modelled. Fig. 4b presents a scenario of changing landcover over the timescale of an interglacial, conceptually based on a northwest European cave site. Soil cover increases after the last glacial period, followed by increases in forest cover in the Holocene climatic optimum. The scenario presents the effects of an increase in soil
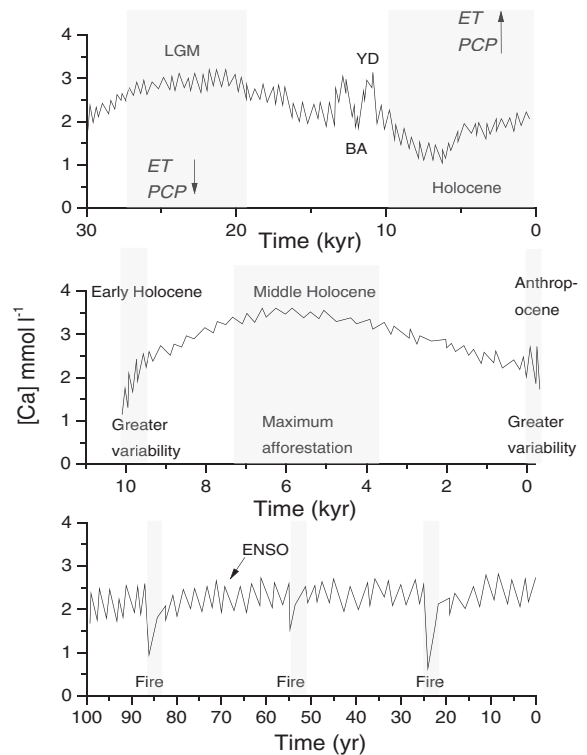

Fig. 4. Conceptualisation of cave drip water calcium concentration variations over timescales of: (a) glacial–interglacial climate change in a water-limited site (LGM – Last Glacial Maximum, YD - Younger Dryas stadial, BA – Bølling-Allerød interstadial, ET – evapotranspiration, PCP – prior calcite precipitation). (b) The current interglacial (the Holocene) for a generic European site. Greater variability is hypothesised at the start and end of the Holocene due to soil, vegetation and landscape instability after the last glaciation, and land-use change in the modern period (the Anthropocene). (c) The last 100 years for a forested, fire-prone site in an ENSO region.

microbial respiration and subsequent root respiration, together with increased soil cover and associated soil and vadose zone CO_2 production, over the timescale of 10^3–10^5 years based on a typical European Holocene example (Mauri et al., 2015). Fig. 4c presents a scenario of the effects of wildfire at a forested site over 10^1–10^3 years. Conceptually based on the observed soil CO_2 data of Coleborn et al. (2016) in SE Australia, a region affected by climate variability due to the El Niño Southern Oscillation (ENSO), the scenario presents multi-year variability in drip water calcium concentrations based on changes in moisture availability, and multi-decadal impacts of wildfire due to forest cover loss and changes in root respiration.

6. Conclusions

We observe no correlation between drip water calcium concentration and temperature in our meta-analysis of global sites. This finding contradicts that of Genty et al. (2001) which considered sites from just one region, that of Europe. Our modelling approach suggests that drip water calcium concentrations are relatively complacent to temperature, except in the special case of sites in a Köppen-Geiger Cfb climate zone with mean annual temperature <14 °C. In this climate zone, our comparison of drip water calcium concentration to that predicted from soil carbon dioxide concentration alone demonstrates that this correlation is driven by both soil and vadose zone carbon dioxide. Globally, many factors other than temperature are more important in determining speleothem-forming drip water calcium concentration, including vadose zone carbon dioxide production, wildfire and prior calcite precipitation. These factors may operate at a small-scale, from individual flow-path to watershed, and generate substantial within-cave variability in drip water calcium concentrations.

Calcium concentration is a primary determinant of speleothem growth rate (Baker et al., 1998; Dreybrodt, 1999), together with temperature, drip rate and cave air carbon dioxide concentration. It is also a fundamental control on calcite saturation of drip waters and their ability to form speleothems. The lack of correlation between calcium concentration and temperature for most climate regions suggests that speleothem growth rate will be insensitive to temperature changes. Instead, growth rates are more likely to reflect a multitude of competing processes which include PCP, fire, forest growth and vadose zone microbial respiration. With respect to anthropogenic impacts on speleothemforming drip waters, our results suggest that cave and karst management should consider local-scale impacts from overlying land-cover change, including forest, soil and fire management, and that these are likely to be more important than the direct effects of anthropogenic global warming. With respect to the use of speleothem growth rate as a proxy record of past climates and environments, our results suggest that it is only in special cases where speleothem growth rate is likely to have a climate sensitivity e.g. in water-limited or water-sensitive environments where water supply and drip rate are the dominant control on growth rate.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.gloplacha.2016.06.001.

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