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Recent flowstone growth rates: Field measurements in comparison to theoretical predictions

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Abstract

The model of calcite precipitation kinetics of D. Buhmann and W. Dreybrodt, based on the rate laws of L.N. Plummer et al., is used to predict cave flowstone growth rates. These theoretically modelled growth rates are compared to actual growth rates of recent samples found in cave and mine sites in southwest England. A good agreement is found between modelled and actual growth rates within the 95% confidence level of the determinations, although in general modelled growth rates overestimate actual growth rate by between 2.4 and 4.7 times. Several reasons for this overestimation are discussed, including uncertainties arising from the experimental data of L.N. Plummer et al., seasonal shut-off of water flow onto the flowstones and significant variations in the growth rate determining parameters during the period of flowstone growth. For one flowstone an underestimation of growth rate is observed and is explained by the presence of rimstone pools which pond water on the sample surface.

1. Introduction

Flowstones (also known as sinter or travertine) are inorganic secondary calcite precipitates found in caves, and formed by deposition of calcite on the bed of a cave stream or seepage flow. The most important mechanism for flowstone deposition is the degassing of groundwaters which contain elevated carbon dioxide concentrations (Holland et al., 1964; Ford and Williams, 1989); the elevated CO_2 being derived from the high partial pressures of CO_2 in the soil atmosphere generated by microbial processes and root respiration (Dorr and Munnich, 1986).

In a recent papers, Buhmann and Dreybrodt (1985a, 1985b) have established a theoretical model for the kinetics of calcite dissolution and precipitation, based on the rate laws of Plummer et al. (1978). This model takes into account the three processes which occur during the deposition of a flowstone: (1) chemical reactions at the calcite–solution interface; (2) diffusional transport of species through the solution to the surface of the solid; and (3) slow conversion of carbon dioxide into protons and bicarbonate ions. It was shown that these processes could be combined into a linear rate equation of the form:

$$R=\alpha([\mathrm{Ca}^{2+}]_{\mathrm{eq}}-[\mathrm{Ca}^{2+}]) \quad (\mathrm{mmol\ cm^{-2}\ s^{-1}}) \tag{1}$$

where α is a rate constant depending on P_{CO_2}, temperature and the geometry of flow (details are presented in Buhmann and Dreybrodt, 1985a, b); and $[Ca^{2+}]_{eq}$ is the Ca^{2+} concentration at saturation. The square brackets denote concentrations.

In subsequent papers the model was extended by the consideration of foreign ions and ion pairs (Buhmann

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and Dreybrodt, 1987) and the inclusion of turbulent flow effects (Dreybrodt and Buhmann, 1991). In a study of a calcite precipitating stream, Dreybrodt et al. (1992) determined that in a turbulent flow situation the growth rate model overpredicted the actual growth rate by an order of magnitude due to the omission of diffusion boundary layer effects. However, no studies have been undertaken to compare the growth rates predicted from the model with actual rates on cave flowstones, where deposition is from a thin water film and under laminar flow conditions, and the molecular diffusion of the reactants may be rate determining.

Recently, improved dating precision has allowed the determination of the growth rates of flowstones deposited in the Quaternary time period by both mass spectrometric uranium series dating (Li et al., 1989; Baker et al., 1993) and annual luminescence banding (Baker et al., 1993, 1995). There is thus potential for the use of the growth rate model to interpret these Quaternary growth rate variation. In this study we compare predicted growth rates derived from the model of Buhmann and Dreybrodt (1985a) with those measured for recently deposited flowstone samples, in order to determine the adequacy of the model.

2. Experimental methods and results

Recent growth rates were determined for flowstones which had grown in mines or excavated caves, where it was possible to estimate the maximum time duration since their deposition from the date of opening of the mine or cave [a technique used by Orr (1952)]. Samples of flowstones were then taken, and their thickness measured. This gives an estimate of growth rate, which must be considered a minimum, since it can not be assumed for certain that speleothem deposition occurred immediately after mine opening or cave excavation. Despite this problem, this approach gives a better estimate of actual growth rate than analysing the weight gain of calcite slabs placed on flowstone surfaces. Experiments showed that the errors associated with this approach were too large for useful comparisons with theoretical growth rate to be made, primarily because the minimum thickness of the calcite slabs was significantly thicker than the water film (Baker, 1993). Flowstone thickness determinations also allow for multiple samples to be taken from each flowstone in order to investigate the change in growth rate with distance from the water source. Between two and eleven samples were taken from each individual flowstone, and the thickness of each was measured a minimum of six times using a ± 0.1-mm-precision Vernier caliper. In total thirty samples were taken from seven flowstones, care being exercised to make these samples as small and discretely located as possible in order to conserve the speleothems.

Flowstone growth rate measurements were made in two caves, Kent's Cavern and Dolebury Levy. Kent's Cavern is developed in the Devonian limestones at Torquay, Devon, SW England. The flowstones sampled were situated below the level of a former stalagmite floor excavated by W. Pengelly between 1865 and 1880 during archaeological investigations (Proctor and Smart, 1989). The second sampling location was Dolebury Levy, an adit situated in the Lower Limestone Shales of the Carboniferous Limestone Series at Rowberrow, Mendip Hills. The adit was wholly excavated by Dr. Benjamin Somers in 1830 in search of haematite and ochre (Gough, 1967; pp. 173–175 and 243–245). Details of the sample locations for both sites are presented in Baker (1993).

A second set of measurements were also made to determine the growth rate controlling variables; calcium concentration, temperature and water flux (film thickness, discharge and seasonality of water flow) which are required in the model (Eq. 1). Cave air P_{CO_2} was not measured, but assumed to be $3 \cdot 10^{-4}$ atm. This approximation does not have a significant effect on growth rate, as shown by Buhmann and Dreybrodt (1985a), and detailed later in Table 4. Measurements were made over the course of the annual hydrological cycle within the period May 1991 to October 1992.

Calcium concentration in the cave waters feeding the flowstone were measured using standard ethylene diamine tetraacetate (EDTA) titrations. Water was collected in 125-ml glass sample bottles filled to the top and stoppered to prevent degassing, and the titrations were performed in the minimum possible time (usually <24 hr from collection). Samples were collected as close to the water source in the cave as possible (to prevent degassing), taking care not to include particles of bedrock or mud which might contaminate the sample. Where possible, calcium concentrations were also obtained at the base of the deposit to determine the change in calcium saturation over the surface of the flowstone. For some samples, water drip rates were frequently so slow as to make the collection of water samples for titration impossible. Film thickness measurements were obtained on the flowstones, using a Vernier spherometer. At least six measurements of film thickness were obtained per site. Where possible, a measure of discharge was also obtained by recording the drip rate onto the flowstone. Occasional temperature measurements were also made to confirm that the water temperatures approximate to the mean annual temperature for the region (9–11°C; Wigley and Brown, 1977).

For all samples, the flowstone thickness measurements and the calculated (minimum) growth rates are shown in Table 1. The measured calcium concentrations, water film thicknesses and discharges are presented in Table 2. All measurements made in this study varied between 10° and 11°C. A value of 10°C is used in all growth rate calculations.

3. Discussion

Data presented in Table 1 show that growth rates derived from the thickness measurements are of a similar order of magnitude (0.009–0.050 mm yr^{-1}), the exception being for the top of sample KC-91-1, where significantly elevated growth rates were measured (0.130–0.261 mm yr^{-1}). Such a significant decrease in growth rate downstream would suggest a long water residence time, with degassing of CO_2 as the water flowed over the sample resulting in a decrease in calcium concentration (see later discussion). For all other samples there was no observed variation in flowstone thickness down the length of individual flowstones. Given this finding, it is appropriate in further calculations to consider average growth rates and averaged present-day conditions.

Calcium concentrations and hydrological data are presented in Table 2. Calcium concentrations were not determined for DL-91-2 and DL-91-3 as the flows feeding these flowstones were too slow for sample collection; two titrations from fast dripping sources near the samples measured 1.63 and 1.90 mmol l^{-1}, the same concentration as that measured at DL-91-1. All three sites are in the same bedrock, at a similar depth and with identical surface vegetation; therefore it is assumed that the calcium concentration of DL-91-2 and -3 is the same as that for DL-91-1. For two samples, KC-91-1 and -8, the calcium concentration was determined both at the water source and at the base of the

Table 1
Flowstone thickness and growth rate data

Distance (cm)	Slope (°)	Thickness (mm)	Growth rate (mm yr^{-1})
KC-91-1:			
Top:			
15	5	30.57 ± 4.75	0.261 ± 0.041
30	5	23.03 ± 6.37	0.217 ± 0.060
32	5	15.88 ± 5.05	0.130 ± 0.041
45	5	23.82 ± 4.36	0.174 ± 0.032
Base:			
75	80	3.74 ± 1.18	0.033 ± 0.010
90	70	1.98 ± 0.92	0.017 ± 0.008
105	75	1.98 ± 1.00	0.017 ± 0.009
120	75	2.63 ± 0.92	0.023 ± 0.008
125	80	2.12 ± 0.44	0.018 ± 0.004
147	85	1.01 ± 0.60	0.009 ± 0.005
150	85	1.30 ± 0.58	0.011 ± 0.005
KC-91-5:			
21	85	1.68 ± 1.36	0.015 ± 0.012
42	85	2.68 ± 1.18	0.023 ± 0.010
KC-91-8:			
63	85	4.12 ± 1.16	0.036 ± 0.010
69	85	5.70 ± 0.66	0.050 ± 0.006
KC-91-10:			
15	50	4.36 ± 1.42	0.038 ± 0.012
30	50	5.95 ± 1.84	0.052 ± 0.016
45	50	4.33 ± 0.64	0.038 ± 0.006
60	50	3.25 ± 1.41	0.028 ± 0.012
DL-91-1:			
20	90	3.43 ± 0.42	0.021 ± 0.003
40	90	3.05 ± 0.92	0.019 ± 0.006
40	90	2.95 ± 0.66	0.018 ± 0.004
60	90	2.66 ± 0.56	0.016 ± 0.005
DL-91-2:			
30	90	2.26 ± 0.90	0.014 ± 0.006
60	90	3.17 ± 1.14	0.020 ± 0.007
90	90	2.46 ± 0.66	0.015 ± 0.004
110	90	3.38 ± 0.56	0.021 ± 0.003
DL-91-3:			
30	90	3.16 ± 0.86	0.020 ± 0.005
50	90	2.69 ± 0.88	0.017 ± 0.006
75	90	3.17 ± 0.40	0.020 ± 0.003

The slope of the flowstone surface is measured to the nearest 5°, sampling distance from the drip/seep source to the nearest cm. Uncertainties in flowstone thickness are 1σ derived from multiple measurements made upon each sample. Growth rates are minima, based on sample deposition starting on cave or mine excavation.

Table 2
Calcium ion concentrations, water film thickness and discharge rate and timing for the seven flowstone samples

Site	Calcium (mmol l^{-1})	Water film thickness (mm)	Discharge	
			($l\ s^{-1}$)	nature
KC-91-1				
(top)	2.64 ± 0.32 ($n=8$)	0.158 ± 0.125 ($n=3$)	$(5.2 \pm 4.7) \cdot 10^{-5}$ ($n=8$)	continuous
(base)	1.77 ± 0.38 ($n=3$)			
KC-91-5	1.67 ± 0.38 ($n=4$)	0.069 ± 0.047 ($n=4$)	$(4.9 \pm 5.8) \cdot 10^{-6}$ ($n=4$)	winter only
KC-91-8				
(top)	2.49 ± 0.15 ($n=5$)	0.086 ± 0.060 ($n=4$)	$(11.0 \pm 6.7) \cdot 10^{-5}$ ($n=4$)	winter only
(base)	2.17 ± 0.16 ($n=3$)			
KC-91-10	2.34 ± 0.72 ($n=9$)	0.073 ± 0.061 ($n=4$)	$(2.2 \pm 1.2) \cdot 10^{-5}$ ($n=8$)	continuous
DL-91-1	1.90 ± 0.11 ($n=5$)	0.048 ± 0.040 ($n=5$)	$(2.7 \pm 1.9) \cdot 10^{-4}$ ($n=5$)	winter only
DL-91-2	n.d.	0.047 ± 0.019 ($n=4$)	$(5.4 \pm 1.7) \cdot 10^{-7}$ ($n=6$)	continuous
DL-91-3	n.d.	0.038 ± 0.027 ($n=4$)	$(1.5 \pm 0.7) \cdot 10^{-6}$ ($n=6$)	continuous

n = number of sampling occasions over the seasonal cycle. Error terms are the 1σ errors, reflecting seasonal variations. n.d. = not determined.

flowstone. In each case, the calcium concentration was lower at the latter, suggesting that water flow rates were slow enough for significant degassing of CO_2 to occur. However, there appears to be no corresponding decrease in growth rate with increasing distance from the drip source (Table 1). Water film thickness measurements are not statistically different between all flowstones sampled. This is because of both the limited range of drip discharges and the large error terms associated with the film thickness measurements. These errors are a function of the naturally variable thickness of water over the heterogeneous flowstone surfaces. The hydrological characteristics of the flowstones separate them into two groups. KC-91-1, KC-91-10, DL-91-2 and DL-91-3 were observed to have a continuous drip source and remain wet all year around. KC-91-5, KC-91-8 and DL-91-1 were all observed to have water flows for only 4–6 months during winter and early spring.

The mean and one standard deviation calcium concentrations for each site, together with the mean and ±1 standard deviation for all film thicknesses measured in this study (0.075 ± 0.055 mm) were used in the calculation of model growth rates. The water temperature was taken as equal to the mean annual temperature of 10°C, and the partial pressure of carbon dioxide in the cave atmosphere was assumed constant at $3 \cdot 10^{-4}$ atm, giving a value of $[Ca^{2+}]_{eq}$ of $6.3 \cdot 10^{-4}$ mmol cm^{-3} (from Table 2; Buhmann and Dreybrodt, 1985a). Modelled growth rates were calculated using Eq. 1 listed above. The value of α was interpolated from data presented in Buhmann and Dreybrodt (1985a, table 2), and was determined to be $4.9^{+2.9}_{-2.5} \cdot 10^{-6}$ cm s^{-1} (the range of values dependant on the variable film thickness). The growth rate was converted from mmol cm^{-2} s^{-1} to mm yr^{-1} by multiplying by $1.174 \cdot 10^7$, assuming a molecular weight of $CaCO_3$ of 100.09 g mol^{-1}; calcite density of 2.689 g cm^{-3} and that $3.15 \cdot 10^7$ s occur in a year (Dreybrodt, 1980). A comparison of the modelled growth rates and the (minimum) growth rates determined from sample thickness are shown in Table 3. Except for the top 50 cm of site KC-91-1, actual growth rates are lower than that predicted by the model by 2.4–4.7 times. However, if the 2σ (rather than 1σ) standard deviation error ranges of both the actual and modelled growth rates are taken into consideration, then there is no significant difference between the two.

3.1. Comparison of modelled and observed growth rates

Although there is no difference between modelled and observed growth rates at 2 standard deviations, there is a consistent overprediction of growth rate by the model. Several explanations for this pattern may be suggested. Firstly, sample growth may have commenced significantly more recently than when the cave or mine was excavated. While this is possible, for example Berner (1980) demonstrated that seeding was

Table 3
Comparison of modelled and actual growth rates for all flowstone sites

Site	Modelled growth rate (mm yr^{-1})	Actual growth rate (mm yr^{-1})	Modelled/actual mean growth rate
KC-91-1			
(top)	0.09 ± 0.06	0.201 ± 0.049	0.4
(base)	0.09 ± 0.06	0.019 ± 0.009	4.7
KC-91-5	0.06 ± 0.04	0.018 ± 0.007	3.3
KC-91-8	0.10 ± 0.06	0.039 ± 0.011	2.6
KC-91-10	0.10 ± 0.06	0.041 ± 0.011	2.4
DL-91-1	0.07 ± 0.04	0.019 ± 0.003	3.7
DL-91-2	0.07 ± 0.04	0.018 ± 0.004	3.9
DL-91-3	0.07 ± 0.04	0.019 ± 0.003	3.7

Modelled mean and 1σ errors are calculated as described in the text. Mean and 1σ errors for the actual growth rate calculated from sample thickness estimates from each of the sites.

necessary before crystal growth could start, this is unlikely to explain the magnitude of the observed overprediction of 2.6–4.7 times. Secondly, the calcium concentrations and discharge may have decreased significantly over the last 100–150 yr. However, this is considered unlikely. While human induced vegetation changes may decrease calcium concentration, the Dolebury Levy site is situated in a nature reserve which has not undergone significant change in vegetation. Furthermore, agricultural land use changes are generally observed to increase calcium concentrations (by a factor of up to 2 × on the Mendip Hills; Richards, 1987), rather than decrease them. In fact, had changes in calcium concentration occurred, then the observed relationship between calcium concentration and growth rate (see next section) would not be present. Changes in discharge are also not considered likely as changes in precipitation are not generally recognised as significant over this time period.

A third factor which could explain the disparity between observed and modelled growth rates is the effect of seasonal shut-off of water flow during the summer. However, a sensitivity of growth rate to seasonally limited discharge was not observed. Three of the seven samples for which rates could be determined (KC-91-5, KC-91-8 and DL-91-1; Table 3) had a water supply for only 4–6 months. However, the growth rates observed for these samples are not significantly different from those which were wet all year (KC-91-1, KC-91-10, DL-91-2 and DL-91-3); see Table 3. Had continuous growth for KC-91-5, KC-91-8 and DL-91-1 been possible, an increase of 2–3 times the observed values would be expected (to 0.036–0.054, 0.078–0.116 and 0.038–0.057 mm yr^{-1}, respectively). This would be in closer agreement to that theoretically modelled (0.06, 0.10 and 0.07 mm yr^{-1}, respectively). However, this fails to explain the overprediction of growth rate for sites with continuous water supply.

Alternatively, it seems possible that the uncertainties implicit within the Plummer et al. (1978) kinetic model upon which the growth rate model is based may explain the discrepancy in growth rates. Reddy et al. (1981) noted that a range of up to 2 times is present in the rates determined from Plummer et al. (1978) dissolution experiments. However, Buhmann and Dreybrodt (1985a) show that for the thin (0.1 mm) water films observed here, the errors in the Plummer et al. (1978) equations are not significant as molecular diffusion within the water film is rate determining. Uncertainties in the Plummer et al. (1978) equations may become important for the thick water films observed at the top of sample KC-91-1 (discussed later). Other complicating factors may also be important. For example, Compton and Daly (1984) reported a significantly higher value for the rate constant k_2 derived from dissolution experiments using a rotating disc compared to that from the powdered calcites of Plummer et al. (1979). Hence surface roughness may be important in controlling precipitation and dissolution rates. Using freshly cleaved crystals, Compton et al. (1986) showed that initial rate of dissolution was very slow, but that the rate increased as dissolution progressed and surface roughness increased. The higher surface roughness of speleothems compared to that of the calcite used in the

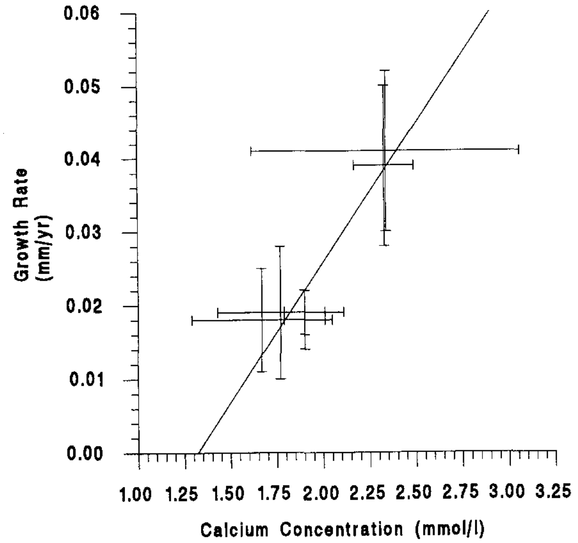

Fig. 1. Relationship between growth rate and calcium concentration for the seven flowstone samples. *Error bars* are 1σ; the linear regression line described in the text is shown. Where calcium concentrations were determined at both the water source and the base of the flowstone, the mean value is plotted here. Only growth rate data for the base of KC-91-1 are plotted.

dissolution experiments may thus cause a significant increase in actual growth rate compared to the model (W. Dreybrodt, pers. commun., 1993), although the magnitude of this effect would probably not explain the large disparity observed in this study.

3.2. Sensitivity of modelled growth rates to controlling parameters

The data collected also allow investigation of the sensitivity of observed growth rates to the determining parameters: temperature, calcium concentration, film thickness and seasonally limited discharge. The observed growth rate of the flowstone samples and the measured calcium concentrations demonstrate a weak but statistically significant relationship ($r=0.81, n=7$, significant at a 95% confidence level); with an increase in growth rate with increased calcium concentration (Fig. 1). In the case of the hydrological parameters, no significant correlation was observed between film thickness and discharge over the seasonal cycle ($r=0.43$, $n=12$, not significant at a 95% confidence level). This may be a function of amalgamating data from all the flowstone samples (which may have differing discharge–film thickness relationships) or simply results from the limited range of sample discharges. Although film thickness does not vary between samples, discharge does exhibit seasonal limitations, with three of the seven sites becoming dry in the summer, those with continuous flow (KC-91-1/-10, DL-91-2/-3) have an observed growth rate of 0.023 ± 0.008 mm yr^{-1} ($n=18$), not significantly different from those with 4–6 months of winter flow (KC-91-5/-8, DL-91-1) with a growth rate of 0.025 ± 0.007 mm yr^{-1} ($n=8$). These results suggest that for this limited sample set the calcium concentration is of greater importance to growth rate than either the seasonality of water supply or water film thickness for these samples.

The observed sensitivity of growth rate can be compared to that predicted according to Eq. 1. Table 4 shows the effect of increasing the growth rate determining variables individually by 50% from the average value observed for all sites in this study. It can be seen that growth rate is most sensitive to changes in calcium concentration, although a significant sensitivity to water film thickness and temperature are also predicted. The former was not observed in our field data due to the lack of a relationship between discharge variations and water film thickness, but may be observable from a larger sample size of flowstones which cover a greater variability in discharge. Only minor differences in temperature occur between sample sites, and we are not able to confirm this relationship from our field data.

3.3. Explaining the elevated growth rate of KC-91-1

A final important observation is of the very high growth rate for the upper part of KC-91-1, which is an order of magnitude higher than that observed for any other flowstone at the site, and is greater than that pre-

Table 4

Sensitivity of growth rate to a 50% increase in the value of each of the variables from the mean value observed in Kent's Cavern and Dolebury Levy

Variable	Mean	Growth rate change ($mm\ yr^{-1}$)
Calcium concentration	2.00 mmol l^{-1}	+0.037
Water film thickness	0.08 mm	+0.025
Temperature	10°C	+0.018
CO_2 partial pressure	$3\cdot10^{-4}$ atm	+0.007

Table 5
Flow measurements made upon KC-91-1, KC-91-5 and KC-91-8

Sample	Drip rate ($l\ s^{-1}$)	Velocity ($cm\ s^{-1}$)	Film thickness (cm)	Reynolds number
KC-91-1	$7.5 \cdot 10^{-5}$	0.20	0.6	0.95
KC-91-1	$7.5 \cdot 10^{-5}$	0.66	0.6	3.122
KC-91-5	$1.5 \cdot 10^{-4}$	0.33	0.08	0.21
KC-91-8	$3.8 \cdot 10^{-4}$	0.18	0.08	0.11

Drip rates are those measured at the time of the velocity determination; all values fall within the 2σ range of drip rates measured over the annual cycle (Table 2). The Reynolds number is defined as equal to $\rho v d/\mu$, where ρ is the density of water, v is the velocity, d is the water depth and μ the viscosity of water at 10°C (0.01307 g cm^{-1} s^{-1}).

dicted from model. There are several potential explanations of this observation. Firstly, it may be due to the development of turbulent flow, which would lead to growth rates an order of magnitude higher than under laminar flow conditions (Buhmann and Dreybrodt, 1985a). A test to see if turbulent flow was present was undertaken at three sites (KC-91-1, -5 and -8) by placing a drop of Rhodamine WT dye onto the flowstone surface and measuring the velocity of the labelled water down the flowstone. Water drip rate and film thickness were also recorded, and together these variables can be used to derive the Reynolds number (R_e), an index of flow regime. Typical flow velocities were in the range 0.01–0.2 cm s^{-1} (for drip rates between $4 \cdot 10^{-5}$ and $8 \cdot 10^{-4}$ l s^{-1}) (Table 5). For KC-91-1, the calculated Reynolds numbers (Table 5) were in the range 0.1–4, and demonstrate no likelihood of turbulent flow occurring.

A second cause of the elevated growth rate may be the shallow gradient at the top of the flowstone, where rimstone pools are present, with lower growth rates observed on the steeply sloping sides. Thus slope angles may cause increased water residence times and high water film thicknesses, allowing additional degassing of CO_2. This is supported by the significant difference in the calcium concentration of the source water and that at the base of the flowstone (Table 2). A third factor may be the thicker water film; film thickness at the upper sample site on which rimstone pools were visible was 6.4 mm (1σ uncertainty = ±3.2 mm; $n = 14$), significantly deeper than that observed on the steeper sloping face of the sample (0.158 ± 0.125 mm, Table 2). The thicker water film may allow some movement within the water, increasing the rate of molecular diffusion and thus growth rate. Alternatively, the ponding may permit a continual supply of water, giving continuous deposition, whereas lower down the sample the flowstone may become dry under some conditions. (In fact, throughout the year of observations, a water film was observed over the whole sample.) Further research is needed to investigate the effect of irregularities on the flowstone surface in increasing residence times and maintaining high water film thickness.

4. Conclusions

Flowstone growth rates were measured on seven samples. Measured growth rates were minima, and ranged between 0.018 and 0.201 mm yr^{-1}. These are within the 2σ error range predicted by Eq. 1 for modern temperature, calcium concentration, water film thickness and cave air P_{CO_2} conditions, although growth rates were generally overpredicted by the model by between 2.4 and 4.7 times This may be a result of uncertainties in the rate constants derived from experimental studies of calcite dissolution, possibly relating to differences in surface roughness of the experimental calcites compared to natural surfaces. The model also predicted the sensitivity of growth rate to calcium concentration which was observed in the field data.

This study has important implications for the palaeoclimatic interpretation of flowstone growth rates, suggesting that the model of Buhmann and Dreybrodt (1985a) may be used to interpret growth rates. Modelled sensitivity of growth rate shows a complex dependence on temperature, calcium concentration and discharge. In this study calcium was shown to be the predominant control, although an inadequate range of discharges, film thicknesses and water temperatures were observed. Further work is needed over a longer timescale, during which variations in both temperature, discharge and calcium concentration may have occurred. Such investigations are now possible with the use of annual luminescence banding and mass spectrometric uranium series dating for samples which have grown during periods of known palaeoclimate (e.g., the Holocene in the U.K.).

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References

Baker, A., 1993. Speleothem growth rate and palaeoclimate. Ph.D. Thesis, University of Bristol, Bristol (unpublished).

Baker, A., Smart, P.L., Edwards, R.L. and Richards, D.A., 1993. Annual growth banding in a cave stalagmite. Nature (London), 364: 518–520.

Baker, A., Smart, P.L., Barnes, W.L., Edwards, R.L. and Farrant, A.R., 1995. The Hekla 3 volcanic eruption recorded in a Scottish speleothem? Holocene, 5(2) (in press).

Berner, R.A., 1980. Early Diagenesis: A Theoretical Approach. Princeton University Press, Princeton, N.J., 250 pp.

Buhmann, D. and Dreybrodt, W., 1985a. The kinetics of calcite dissolution and precipitation in geologically relevant situations of karst areas, 1. Open system. Chem. Geol., 48: 189–211.

Buhmann, D. and Dreybrodt, W., 1985b. The kinetics of calcite dissolution and precipitation in geologically relevant situations of karst areas, 2. Closed system. Chem. Geol., 53: 109–124.

Buhmann, D. and Dreybrodt, W., 1987. Calcite dissolution kinetics in the system H_2O–CO_2–$CaCO_3$ with the participation of foreign ions. Chem. Geol., 64: 89–102.

Compton, R.G. and Daly, P.J., 1984. The dissolution kinetics of Iceland spar single crystals. J. Colloid Interface Sci., 101: 159–166.

Compton, R.G., Daly, P.J. and House, W.A., 1986. The dissolution of Iceland Spar crystals — the effect of surface morphology. J. Colloid Interface Sci., 113: 12–20.

Dorr, H. and Munnich, K.O., 1986. Annual variations of the ^{14}C content of soil CO_2. Radiocarbon, 28: 338–345.

Dreybrodt, W., 1980. Deposition of calcite from thin films of natural calcareous solutions and the growth of speleothems. Chem. Geol., 29: 89–105.

Dreybrodt, W. and Buhmann, D., 1991. A mass transfer model for the dissolution and precipitation of calcite from solutions in turbulent motion. Chem. Geol., 90: 107–122.

Dreybrodt, W., Buhmann, D., Michaelis, J. and Usdowski, E., 1992. Geochemically controlled calcite precipitation by CO_2 outgassing: Field measurements of precipitation rates in comparison to theoretical predictions. Chem. Geol., 97: 285–294.

Ford, D.C. and Williams, P., 1989. Karst Geomorphology and Hydrology. Unwin-Hyman, London, 601 pp.

Gough, J.W., 1967. The mines of Mendip. David and Charles, Newton Abbot, 227 pp.

Holland, H.D., Kirsipu, T.W., Huebner, J.S. and Oxburgh, U.M., 1964. On some aspects of the chemical evolution of cave waters. J. Geol., 72: 36–67.

Li, W.-X., Lundberg, J., Dickin, A.P., Ford, D.C., Schwarcz, H.P., McNutt, R. and Williams, D., 1989. High precision mass-spectrometric uranium-series dating of cave deposits and implications for palaeoclimate studies. Nature (London), 339: 334–336.

Orr, P.C., 1952. Excavations in Moaning Cave. St. Barbara Mus. Nat. Hist. Bull., No. 1, 19 pp.

Plummer, L.N., Wigley, T.M.L. and Parkhurst, D.L., 1978. The kinetics of calcite dissolution in the CO_2–water systems at 5 to 60°C and 0.0 to 1.0 atm CO_2. Am. J. Sci., 278: 179–216.

Plummer, L.N., Parkhurst, D.L. and Wigley, T.M.L., 1979. Critical review of the kinetics of calcite dissolution and precipitation. In: E.A. Jenne (Editor), Chemical Modelling in Aqueous Systems. Am. Chem. Soc., Washington, D.C.

Proctor, C.J. and Smart, P.L., 1989. A new survey of Kent's Cavern, Devon. Proc. Univ. Bristol Speleol. Soc., 19: 422–429.

Reddy, M.M., Plummer, L.N. and Busenberg, E., 1981. Crystal growth of calcite from calcium bicarbonate solutions at constant P_{CO_2} and 25°C: a test of a calcite dissolution model. Geochim. Cosmochim. Acta, 45: 1281–1289.

Richards, D.A., 1987. The influence of post-war land-use change on the total hardness of the waters of the Cheddar Falls, Somerset. Dissertation, University of Bristol, Bristol (unpublished).

Wigley, T.M.L. and Brown, M.C., 1977. The physics of caves. In: T.D. Ford and C.H.D. Cullingford (Editors), The Science of Speleology. Academic Press, London, pp. 329–358.