George T. Matzko\*

## Abstract

The speleothem formation experiments conducted in the late 1970s by the Society have been resurrected at the Van Andel Creation Research Center. A new experimental apparatus has been constructed, other ancillary equipment collected and testing has begun. The earlier work is reviewed and the results of that research are summarized. The deposition of speleothems from a theoretical per-

# Introduction

The rate of speleothem (stalagmite and stalactite) formation is an intriguing chemical problem that has been investigated by creationists on and off for the last 30 years (Gish, 1989). Creationist interest in this somewhat arcane topic derives from the obvious disparity between descriptions of slow speleothem growth rates normally touted by guides in commercial caverns compared to reports of rapid, even catastrophic, growth of dripstone formations in the uniformitarian and creationist literature (Gardner, 1935; Meyers and Doolan, 1987; Williams, et al., 1976; Williams and Herdklotz, 1977; 1978; Williams, House and Herdklotz, 1981; Williams, 1988b; Wolfrom, 1994). However, for dramatic appeal, nothing can surpass the Carlsbad Bat (Whitcomb, 1973). In October 1953, National Geographic Magazine published a photograph of a bat that was preserved in a stalagmite before it had a chance to decompose (Sutherland, 1953). The same photograph was used as a cover illustration for the September 1971 Quarterly (8:93).

For the sake of clarity, it should be mentioned what is not being considered in this article: the rapid formation of dripstone from concrete-mortared structures. Stalactite growth in this environment does not proceed by the same chemical reaction as it does in natural limestone caves (Williams and Herdklotz, 1977, p. 198; Williams, 1988a; Wise, 1988). Another important but related issue that is not covered in this article is the mechanism by which caves are formed in the first place. For speculaspective, emphasizing the chemical processes involved, is considered. Recent advances in the age dating are examined. The factors that affect speleothem growth are discussed. Recent studies conducted in natural cave environments are mentioned. The kinetics of speleothem precipitation is being studied in an attempt to predict what natural conditions encourage rapid development.

tions on cave formation during and after the Flood, see Williams and Herdklotz, 1977, pp. 197–198; 1978, p. 88. One aspect of this problem which is pertinent to this discussion is the suggestion that sulfuric acid may have played a role in dissolving limestone during the early part of a cave's history (Moorehouse, 1968; Oard, 1998). If some caves have been formed by sulfuric acid dissolution, it may be possible that sulfuric acid also played a role in the formation of some of the older speleothems. Sulfate ions are normally found in water samples taken from caves. For example, calcite precipitating water samples from Warm River Cave, Virginia were found to contain from 128 to 438 mg/L SO<sub>4</sub><sup>2-</sup> during tests in 1984 (Herman and Lorah, 1986). But as far as it is known now, the main effect of CaSO<sub>4</sub> on dissolution and precipitation rates of solid CaCO<sub>3</sub> is a common-ion effect (Buhmann and Dreybrodt, 1987). See earlier experiments on dissolution of limestone and dolomite by acid solutions in Williams and Herdklotz, 1977, pp. 193–194.

# **Chemistry of Speleothem Formation**

What we do know is that the primary chemical agent involved in the formation of speleothems is carbon dioxide. The solubility of calcite in pure water is very small, about 6 ppm at 10°C, but carbonate minerals are readily soluble in acid, and the acid most important to karst processes is carbonic acid, formed by the dissolution of gaseous CO<sub>2</sub>:

 $CO_2 (gas) = CO_2 (aqueous)$  $CO_2 (aqueous) + H_2O = H_2CO_3$ The net reaction for the dissolution of calcite is:  $CaCO_3 + H_2O + CO_2 = Ca^{2+} + 2HCO_3^{-}$ 

<sup>\*</sup>George T. Matzko, Ph.D., Chairman, Division of Natural Science, Bob Jones University, Greenville, SC 29614. Email: gmatzko@mbusa.net

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In most cases it is believed that calcite speleothems are formed when ground water which is supersaturated with CaCO<sub>3</sub> enters a cave. Outgassing of dissolved CO<sub>2</sub> lowers carbonate solubility in these drip waters and leads to crystalline calcite deposition.

The calculation of calcite deposition rates therefore hinges on the combinations and permutations inherent in carbonate equilibria. For example, the concentration of dissolved calcite varies with the cube root of the  $CO_2$  partial pressure as follows (White, 1988, p.130):

$$m_{Ca^{2+}}^{3} = P_{CO_{2}} \frac{K_{1}K_{c}K_{CO_{2}}}{4K_{2}(\gamma_{Ca^{2+}})(\gamma_{HCO_{2}})^{2}}$$

where:

 $K_1$  and  $K_2$  = equilibrium constants for the dissociation of carbonic acid.

 $K_c$  = the solubility product constant for calcium carbonate.

 $P_{CO_2}$  = the partial pressure of carbon dioxide.

 $\alpha$  and  $\gamma$  = the activities and activity coefficients of the respective species.

 $K_{CO_2}$  = a bulk equilibrium constant that describes all neutral carbon bearing species:

$$K_{\rm CO_2} = \frac{\alpha_{H_2\rm CO_3}}{P_{\rm CO_2}}$$

In addition to equilibrium relationships, the kinetics of calcite dissolution and deposition must also be considered. The kinetics are determined by three independent processes (Buhmann and Dreybrodt, 1985a):

 The kinetics of dissolution (or deposition) at the phase boundary between the solvent aqueous system CaCO<sub>3</sub> – H<sub>2</sub>O – CO<sub>2</sub> and the limestone.

• The kinetics of the conversion of CO<sub>2</sub> to carbonic acid.

• Mass transport of the dissolved species, i.e. Ca<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, CO<sub>2</sub> and H<sub>2</sub>CO<sub>3</sub>, by diffusion from and to the phase boundaries.

The first kinetic model that included the three processes listed above, and therefore accounted for the mechanisms taking place at the surface of the CaCO<sub>3</sub> rock, is the Plummer-Wigley-Parkhurst model (Plummer, 1978). The Plummer-Wigley-Parkhurst or PWP equation gives the dissolution rate as a function of the species Ca<sup>2+</sup>, H<sup>+</sup>, HCO<sub>3</sub><sup>-</sup> and H<sub>2</sub>CO<sub>3</sub> at the CaCO<sub>3</sub> surface:

$$F = \kappa_1(H^+) + \kappa_2(H_2 \text{CO}_3^*) + \kappa_3 - \kappa_4(\text{C}a^{2+})(\text{HCO}_3^-)$$

where *F* is the flux of  $Ca^{2+}$  ions.

The first three rate constants are temperature (K) dependent:

$$\log \kappa_1 = 0.198 - 444 T^{-1}$$
$$\log \kappa_2 = 2.84 - 2177 T^{-1}$$
$$\log \kappa_3 = -5.86 - 317 T^{-1}$$

The fourth rate constant is dependent on the activity of the aggressive agent and is given by Plummer, Wigley and Parkhurst (1978). The quantities in round brackets in the PWP equation are the activities of the corresponding species and  $(H_2CO_3^*) = (H_2CO_3^0) + (CO_2)$ . Note that because the PWP equation is a rate equation, containing forward and backward reactions, it is valid for the precipitation of CaCO<sub>3</sub> as well as its dissolution. All that is required is to change the sign of *F* (Inskeep and Bloom, 1985).

The PWP model has been tested extensively under a variety of conditions (Buhmann and Dreybrodt, 1985b; Dreybrodt and Buhmann, 1991; Dreybrodt, et al., 1992; Liu and Dreybrodt, 1997; Fairchild, et al., 1999). During these tests the dissolution or precipitation rates were found to roughly correspond with the equation,

$$R = \alpha \left( \left[ Ca^{2+} \right]_{eq} - \left[ Ca^{2+} \right] \right)$$

(Buhmann and Dreybrodt or B-D model), where  $\alpha$  is a function of CO<sub>2</sub> pressure, thickness of the water film covering the CaCO<sub>3</sub> surface, and temperature.  $[Ca^{2+}]_{eq}$  is the concentration at saturation and when

$$\left[Ca^{2+}\right] \ge 0.2 \left[Ca^{2+}\right]_{eq}.$$

For example, at a  $P_{CO_2}$  of 5 x  $10^{-3}$  atm and a temperature of 10°C,  $[Ca^{2+}]_{eq}$  has a value of 16.2 x  $10^{-4}$  mmol cm<sup>-3</sup> and  $\alpha$ , the rate constant, is equal 1.54 x  $10^{-5}$  cm s<sup>-1</sup> for a laminar core (diffusion layer) thickness of 0.01 cm. Note also that rates of deposition given in mmol cm<sup>-2</sup> s<sup>-1</sup> can be converted into a speleothem growth rate given in cm/yr. by multiplying by the factor 1.17 x  $10^{6}$ -cm<sup>3</sup> s mmol<sup>-1</sup> yr.<sup>-1</sup>. This assumes that the calcite is deposited in such a way that it is compact (Baker, et. al., 1998).

As an example of a theoretical growth rate calculation of a speleothem, assume the laminar flow conditions listed above and a 400 ppm CaCO<sub>3</sub> solution where we have  $[Ca^{2+}] = 0.004$  mmol cm<sup>-3</sup>,

 $\alpha = 1.54 \text{ x } 10^{-5} \text{ cm s}^{-1}$ , and

 $\left[Ca^{2+}\right]_{eq} = 16.2 \text{ x } 10^{-4} \text{ mmol cm}^{-3}.$ 

With these values the B-D model yields a deposition rate of  $3.67 \times 10^{-8}$  mmol cm<sup>-2</sup> s<sup>-1</sup> or a 0.0429 cm/yr. growth rate.

# Age Dating of Speleothems

While a growth rate of 0.0429 cm/yr. may seem impressive, yielding a two and a half-meter stalactite in 6,000 years, it still falls short of the values for recent cave deposits measured by the relatively new, excess <sup>210</sup>Pb technique.

Citing the difficulty in obtaining reliable dates from the <sup>14</sup>C method (Williams and Herdklotz, 1977, p. 198) because of the multiple sources of carbon in speleothems, Baskaran and Iliffe (1993) conducted the first study of short-term (1–100 yr.) growth rates using a relatively short-lived isotope such as <sup>210</sup>Pb. <sup>210</sup>Pb (half-life = 22.1 yr.)

is produced from its gaseous precursor, <sup>222</sup>Rn (half-life = 3.8 d) at a constant rate. Most of the <sup>222</sup>Rn in cave air is presumed to have degassed from ground water at the same time that CO<sub>2</sub> is degassed from the water dripping into caves. Drip waters from the ceilings of caves have high concentrations of <sup>222</sup>Rn. Baskaran and Iliffe (1993) measured the <sup>210</sup>Pb in various sections of a 126-mm soda straw stalactite from Harrel's Cave, Texas. They found that the concentration of <sup>210</sup>Pb exhibits an exponential decrease with distance from the bottom of the soda straw. This data vielded a longitudinal growth rate of 1.1 mm/vr. and an age of 115 yr. A 23mm wide icicle shaped stalactite from the same cave, which formed around a soda straw having a central diameter of 5mm, was tested by the same method and yielded a lateral growth rate of 0.031 mm/yr. with an age of 581 yr. Interestingly, an inner core sample of the same icicle stalactite was analyzed by the <sup>14</sup>C technique and dated at an age of 7460 yr. The authors believe that their values compare favorably with tradition growth rates such as the 2 mm/yr. rate reported by Moore and Sullivan (Moore, 1978).

A Japanese group (Tanahara, et. al., 1998) using the same excess <sup>210</sup>Pb dating method, measured the <sup>210</sup>Pb profiles of two soda straw stalactites collected from a natural cave at Tamagusuku, Okinawa Island, Japan. They obtained growth rates of 2.2 and 5.9 mm/yr. respectively. One would expect growth rates of straws to vary even in a single cave, depending on running and dropping rates of water, but a 5.9 mm/yr. rate over 6,000 yr. is capable of producing a stalactite 35 meters long!

Are higher stalactite growth rates than these possible? What factors could be responsible for producing even greater rates of growth? A growth rate of 5.9 mm/yr. corresponds to a  $[Ca^{2+}]$  of 3.4 x 10<sup>-2</sup> mmol/cm or 3,400 ppm CaCO<sub>3</sub> using values of,  $\alpha = 1.54 \times 10^{-5}$  cm s<sup>-1</sup>, and  $[Ca^{2+}]_{eq} = 16.2 \times 10^{-4}$  mmol cm<sup>-3</sup> in the B-D equation. How are such high concentrations obtained? Consider each of the possible factors in turn.

## Temperature and Speleothem Growth

Calcite speleothems are found to form in caves beneath icefields (Gascoyne and Nelson, 1983). In temperate and tropical climates the dissolved CO<sub>2</sub> required to dissolve limestone formations is thought to primarily come from gas uptake from decaying organic matter (even to the extent of 16–20 % CO<sub>2</sub> in the soil measured during a monsoon in India) [Adams and Swinnerton, 1937]. See Williams and Herdklotz, 1977, pp. 192–193 for a discussion of the CO<sub>2</sub> content of water in natural situations. Such a mechanism is not possible in areas devoid of biological activity; although venting of CO<sub>2</sub> from deep within the earth's crust should not be automatically ruled out.

Dreybrodt (1982) proposed a temperature effect mechanism in order to account for the formation of speleothems in caves covered by glaciers or bare karst. Under a glacier there is abundant melt water at 0°C that can penetrate into the fissures of the limestone rock. On the way through the limestone rock to the cave, its temperature is increased by a few degrees and since the solubility of CO<sub>2</sub> decreases with increasing temperature, the solution becomes supersaturated and the deposition of calcite can occur. By this mechanism alone, a solution with a temperature of 2°C entering a cave with the same temperature can be responsible for a growth rate of  $1 \times 10^{-3}$  cm/yr. all by itself. Depending on the water film thickness, a 5°C differential could easily be responsible for a growth rate of 5 x  $10^{-3}$ cm/yr. Williams and Herdklotz, 1977, pp. 195-197 conducted experiments on the effect of temperature on CaCO<sub>3</sub> solution and deposition. The results are summarized in Tables I and II.

## Pressure Difference and Speleothem Growth

It is well known that  $CO_2$  solubility in water not only increases with decreasing temperature but also increases with increasing pressure. Presumably there is some hydrostatic pressure responsible for pushing the ground water through microscopic fissures in the limestone. Unfortunately, a typical pressure gradient from the surface to the cave ceiling would be difficult to quantify. However, it is safe to say that as the water enters the cave, the pressure on the water drops. As the pressure drops, the solubility would also drop and  $CO_2$  would be free to outgas. Several experiments were run in the 1970s employing this concept, and the results are summarized in Tables I and II.

## Hydrogen Ion Concentration

The equilibrium pH of the  $CaCO_3 - H_2O - CO_2$  system is well defined for every value of CaCO<sub>3</sub> concentration, CO<sub>2</sub> pressure and temperature (White, 1988. p.131). However, in caves, as opposed to controlled laboratory conditions, the pH is often controlled by other reactions in the system (Garrels, 1965, p.75). For example, pH measurements of cave waters in Indian Echo Cave, PA ranged from 7.67 to 9.91 (Holland et. al., 1962). The 9.91 reading came from a "small pool fed largely by water from a soda straw" and had a concentration of 194 ppm CaCO<sub>3</sub> while the water dripping from the soda straw had an average pH reading of 7.74 and a calcium carbonate concentration of 289 ppm. Water samples taken from Luray Caverns, VA by the same group had a pH range from 7.32 to 8.05. One final example: A small calcite precipitating stream named Westerhofbach located near the village of Westerhof, Germany has been studied more recently (Dreybrodt et al.,

Experiment Designation	Test Time (hours)	Description of Rig	Test Solution	Rock Being Dissolved	Test Temp (°C)
А	700	Ref. 1, p. 212	tap water	Indiana	25
		Ref. 2, p. 192	$+CO_2$	Limestone	
В	500	(same as A)	tap water + CO <sub>2</sub> + 5% NaCl	(same as A)	(Same as A)
С	NR	Ref. 2, p. 195	tap water	Indiana Ls,	(same as A)
			$+CO_2$	Beekmantown	× ,
			+ 1% Ācetic acid	Dolomite	
D	450	(same as C)	demineralized	Beekmantown	45-50
			Water + $CO_2$	Dolomite	
Ε	600	(same as C)	(same as D)	(Same as D)	(same as D)
F	500	(same as C)	(same as D)	(same as D)	8-25
G	502	Ref. 3, p. 89	demineralized	(same as D)	25
		*	Water + $CO_2$ + $NH_3$		
Н	500	Ref. 4, p. 205	demineralized	(same as D)	(same as G)
		*	Water + $CO_2$		
Ι	1314	(same as H)	(same as H)	(same as D)	(same as G)
J	600	Ref. 4, p. 207	(same as H)	(same as D)	(same as G)
К	600	(same as J)	(same as H)	(same as D)	(same as G)

Table I. Test Conditions During Calcium Carbonate Dissolution and Precipitation Experiments

NR: Not recorded; LS: Limestone

Ref. 1: Williams et al., 1976; Ref. 2: Williams and Herdklotz, 1977; Ref. 3: Williams and Herdklotz, 1978; Ref. 4: Williams, House and Herdklotz, 1981.

Table II.	Test Results of	Calcium (	Carbonate I	Dissolution	and Prec	cipitation I	Experiment	s.

Experiment Designation	Amount of CaCO ppt. (grams)	93 CaCO <sub>3</sub> ppt. per year (grams)	Amount of Solution Consumed (liters)	Amount of CaCO ppt. per liter of Water (grams)	D <sub>3</sub> Likely Mechanism of CaCO <sub>3</sub> ppt.
А	1.7962	22.51	NR	NA	Pressure Difference
В	4.4554	78.05	209	0.0213	Temperature and
				(	Chemical differencees
С	0	0	NR	0	
D	6.4413	125.36	450	0.0143	Temperature and
					Pressure differences
Е	9.4288	137.66	600	0.0157	(same as D)
F	9.9007	173.46	500	0.0198	(same as D)
G	1.0184	7.08	1260	0.0008	Pressure difference
Н	2.7036	47.37	118	0.0229	(same as G)
Ι	3.9386	26.25	1314	0.003	(same as G)
J	10.6556	155.57	472	0.0226	(same as G)
K	12.8434	187.51	191	0.0672	(same as G)

NR: Not recorded; NA: Not available.

1992). Along the 265-m long stream, the pH varied between 7.69 upstream to 8.48 downstream. The greatest deposition rate  $(6.50 \times 10^{-8} \text{ mmol cm}^{-2} \text{ s}^{-1})$  was measured at station #7 where coincidentally the pH was 8.48. Qualitative pH measurements were made in a natural cave and quantitative pH measurements were made in laboratory situations. These results were reported in Williams et al., 1976, p. 212; Williams, House and Herdklotz, 1981. Carbonates dissolve at a much faster rate in solutions of low pH (Stumm and Morgan, 1996, p. 791). Therefore, it is not unreasonable to suppose that in some cases that limestone is dissolved at a rapid rate by acidic waters close to the surface and becomes increasingly alkaline as the water travels through layers of soil and rock. It would become, as a result, increasingly supersaturated with calcium carbonate before it drips from the cave ceiling. Such a mechanism, though hard to prove, would be more prominent during early stages of a cave's history before the alkalinity has been washed out of the soil and rock.

## Flow Velocity and Turbulence

Weyl (1958) discussed the idea that the rate of solution of calcite is proportional to the flow. White and Longyear (1962) were responsible for introducing the concept of "hydraulic jump," a sudden transition in the distance that water will have penetrated into limestone at 90% saturation, as the velocity increases. This penetration distance increase is not a small effect according to White and Longyear. They state (p.163) that "the effectiveness of solution increases by seven orders of magnitude at the jump." Buhmann and Dreybrodt (1985a) confirmed this hydraulic jump by calculating the dissolution rate using the B-D equation for various boundary layer film thicknesses, d, which are inversely related to velocity and turbulence). For d < 0.003 cm, a increases nearly linearly with d. This is the region in which the conversion of  $CO_2$  into  $H_2CO_3$  is rate determining. At d = 0.03 cm a threshold is reached and above 0.05 cm the dissolution rate decreases. However, in a turbulent system, the rates are determined entirely by surface-controlled processes and the PWP equation holds. Buhmann and Dreybrodt calculated that the rates of dissolution would increase about one order of magnitude for turbulent flow situations. Lauritzen investigated dissolution rates in a phreatic cave conduit by analyzing the chemical composition of the water at the inlet and exit of the conduit (Dreybrodt and Buhmann, 1991). At low flow rates  $(1 \text{ m}^3 \text{ s}^{-1})$  the observed dissolution rates were small, but at flow rates above 10 m<sup>3</sup> s<sup>-1</sup> the dissolution rate increased to maximal value of  $1 \times 10^{-7}$  mmol cm<sup>-2</sup> s<sup>-1</sup>. Further confirmation of the importance of flow rates has come from rotating disk dissolution experiments (Liu and Dreybrodt, 1997). By rotating a calcite disk in solutions of various temperatures and CO<sub>2</sub> partial pressures and measuring dissolution rates by electrical conductivity measurements, Liu and Dreybrodt were able to confirm the applicability of the B-D model for turbulent solutions. For example, at a rotating speed of 100 rpm (10°C,  $P_{CO_2} = 3 \text{ x}$  $10^{-4}$  atm.) the measured dissolution rate was 8.0 x  $10^{-8}$ mmole  $cm^{-2} s^{-1}$ , but at a rotating speed of 3000 rpm the rate had increased to  $28.8 \times 10^{-8}$  mmole cm<sup>-2</sup> s<sup>-1</sup>.

The velocity and turbulence of ground water flow through the cracks and fissures in limestone is a complex subject and rates vary from one karst area to another depending on various geometrical, hydraulic and chemical parameters (Dreybrodt, 1996). However, it is safe to say that calcium carbonate supersaturation will increase during times of higher flow rates such as heavy rain storms and floods. Williams and Herdklotz (1977, pp. 197–198) discussed the possible effect of rapidly-moving, receding Floodwater through limestone fissures. If the depth of water was 1000 ft. above an opening in the rock, the velocity of flow could be as great as 80 ft s<sup>-1</sup>.

## **Drip Rates**

The average molecular accumulation rate between two drops falling onto a calcite surface at a time interval T has been shown by Dreybrodt (Baker, et al., 1998) to be

$$R_{acc} = \frac{\left(c - c_{eq}\right)\delta}{T\left(1 - \exp\left(\frac{T}{\tau}\right)\right)} mmol cm^{-2} s$$

where

$$c_{eq} = (-.01t + 0.72) \cdot 10^{-3} (mol \cdot l^{-1}) \text{ and } \tau = \frac{\delta}{\alpha}$$

where:

 $R_{acc}$  is the accumulation rate assuming that  $T \ge 0.2\delta/\alpha$ .

c is the concentration of Ca in the water film in mmol/cc.

 $c_{eq}$  is the equilibrium concentration of Ca, which depends entirely on the temperature *t* in °C as shown above.

 $\delta$  is the thickness of the water film in cm.

*T* is the interval of time between drops.

 $\tau$  is the time constant and  $\alpha$  is the kinetic constant in cm/s.

It can be seen from the equations above that the maximal growth rates for stalagmites will occur when the drop rate is fast enough to keep the surface covered with a thin film of optimal thickness ( $\cong 0.03$  cm) in order to allow the CO<sub>2</sub> to degas. Perhaps this is one reason why stalactites can sometimes appear with a complementary stalagmite and sometimes not. Stalagmite growth appears to be much more dependent on the drip rate dynamics. In a quantitative study of drip rate Williams, House and Herdklotz (1981, pp. 205–206) found that CaCO<sub>3</sub> deposition increased to a maximum as the drip rate decreased. Then the amount of precipitate decreased upon further lowering of drip rate indicating a possible optimum drip rate for maximum deposition.

# Observations and Experimentation on Speleothem Formation

In the 1970s, those working on the problems associated with speleothem formation were limited to using chemical equilibrium calculations as a starting point to predict the rate of speleothem formation. The theoretical models developed since that time, especially the PWP and B-D models now provide an excellent starting point for calculating actual speleothem growth. For example, it used to be thought that models like these were generally valid for pure substances, but not for natural limestones and dolomites that contain impurities that may have an effect on CaCO<sub>3</sub> dissolution and subsequent precipitation. We now know, in the words of Buhmann and Dreybrodt, that "although foreign ions displace the calcite solution equilibria, by the effect of ion-strength, ion-pairing and the common-ion effect, the kinetics of the dissolution process are hardly changed" from that predicted by the B-D model (Buhmann and Dreybrodt, 1987, p. 89.). In addition to the theoretical advantages offered to workers in the next millennium there are also computer programs on the market that are able to model groundwater behavior in detail. The Van Andel Creation Research Center is in the process of obtaining a software package of this type. The challenge for the experimentalist will be to duplicate the non-equilibrium conditions found in natural settings. For example, natural water laden with CO<sub>2</sub> may travel hundreds of feet through jointed limestone before entering a cave where  $CO_2$  can be released (due to a pressure difference) causing CaCO<sub>3</sub> deposition. Since most test rigs are limited in size, it is almost impossible to achieve a lengthy water travel path that would reflect a natural situation. The only practical solution may be to recycle the test solution thereby increasing the time of exposure to the test rocks as well as increasing the travel length of the fluid in order to effect more calcium carbonate dissolution.

In all of the previous experiments sponsored by the Society, it was found that:

The onset of precipitation...does not occur until a certain "incubation" time...has passed where no apparent precipitation takes place. After this time the precipitate became obvious and growth is visible (Williams, House and Herdklotz, 1981, p. 207).

Also a pH change accompanied the precipitation "event"—the pH of the water with dissolved carbon dioxide and calcium was 8.27. Upon deposition of CaCO<sub>3</sub>, the pH of the solutions was lowered to 8.15 (Williams, House and Herdklotz, 1981, pp. 207–208). This is a puzzling result since it appears to be in opposition to the measurements made in Indian Echo Cave and other locations mention above where the pH generally increases as the CaCO<sub>3</sub> is deposited.

If it can be determined what factors retard precipitation, then eliminate them, reducing the "incubation" time, it may be possible to speed up the precipitation reaction for speleothem formation and growth. If any of the above conditions can be related to the theoretical models presented previously, then considerable insight into speleothem development processes can be gained. This information in turn could, hopefully, be used to predict the conditions necessary for rapid formation.

The test conditions and results from the experiments conducted in the late 1970s are collected and summarized

in Tables I and II. Hopefully, the data are easier to discern in this format rather than scattered throughout the four reports published from 1976–1981. These reports are referenced and any details needed for further study can be found in them. One of the columns in Table II records the amount of CaCO<sub>3</sub> precipitate obtained per liter of water passing through the test rig. Obviously water flow into a vented cave is necessary for the formation of speleothems and generally the more water seeping into a cavern, the more CaCO<sub>3</sub> precipitation will occur (Williams and Herdklotz, 1978, p. 88). Considering a Flood model of earth history, the postulated wet conditions (warm ice age) immediately after the Flood would encourage speleothem formation in caverns in the vadose zone.

## Conclusion

Many times, actual rapid growth rates of speleothems have been observed in caves—as high as 1 inch per 7.5 days (4 inches/month) (Williams, House and Herdklotz, 1981, pp. 208, 226). The trend in literature also has been moving toward faster growth rates especially among those who are pioneering the use of the excess <sup>210</sup>Pb dating method. Additional experiments need to be performed in order to optimize the various factors that have the potential to increase growth rates by another order of magnitude, temperature, pressure, pH and flow gradients all need to be explored again under controlled conditions before we can obtain a definitive answer to this important question.

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