Growth Mechanisms of Speleothems in Castleguard Cave, Columbia Icefields, Alberta, Canada

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GROWTH MECHANISMS OF SPELEOTHEMS IN CASTLEGUARD CAVE, COLUMBIA ICEFIELDS, ALBERTA, CANADA*

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ABSTRACT

In spite of its location beneath high alpine terrain and active glaciers, Castleguard Cave contains many actively growing calcite speleothems. Four hypotheses as to their growth mechanism were tested against field data on water chemistry, temperatures, CO_2 content of cave air, and evaporation rates. The hypotheses were (1) that a biogenic source of high PCO_2 is unlikely, so calcite deposition by CO_2 degassing would require a nonbiogenic source; (2) warming of water after entering the cave, or in passage through the rocks above it might cause calcite supersaturation; (3) calcite might be deposited because of evaporation of seepage; and (4) waters dissolving several Ca-bearing minerals might precipitate calcite as the least soluble by the common-ion effect. The field data indicate that hypothesis (4) accounts for most calcite deposition, with groundwaters evolving by dissolving dolomite incongruently and by oxidizing pyrite to sulfuric acid. The acid dissolves carbonate minerals and the CO_2 evolved slightly raises the PCO_2 of the solution. Considerable calcite supersaturation is achieved at almost constant PCO_2 and no biogenic CO_2 source need be invoked. Of the alternative mechanisms, evaporation contributes no more than a few percent of total calcite deposition, while temperature effects may make a smaller contribution. An important implication for paleoclimate studies is that, given suitable conditions of mixed gypsum-limestone or dolomite-limestone terrain or rocks containing abundant pyrite, calcite speleothems can form even under glaciers provided cave temperature is above 0°C. Thus, ancient speleothems generally indicate air-filled caves and lack of continuous permafrost, but do not necessarily imply vegetated soils.

INTRODUCTION

Speleothems (stalagmites, stalactites, and flowstones of calcite) are abundant and often very large in tropical and temperate caves, but in arctic and alpine caves, actively growing speleothems are small and uncommon or are absent. Castleguard Cave is an interesting exception to this generalization. In spite of its situation beneath modern glaciers, it contains small active speleothems wherever suitable slow seepage and drips of water occur. This paper discusses the chemical pathways which lead to calcite deposition in such an environment.

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ROLE OF GAS-PHASE CO_2

Numerous studies in the temperate and tropical zones have shown that groundwaters in carbonate rocks have partial pressures of CO_2 (PCO_2) of around $10^{-2.0}$ atm or more, compared with $10^{-3.5}$ atm for the air above the earth's surface. The extra CO_2 is acquired in the soil, where the interstitial atmosphere has PCO_2 of $10^{-2.0}$ to $10^{-1.0}$ atm. If a water equilibrated with such a PCO_2 first becomes saturated with calcite by dissolving limestone and subsequently enters an open cave where the air has a PCO_2 less than the solution, degassing of CO_2 will occur from water to air. The solution becomes supersaturated with respect to calcite, which may be precipitated as speleothems if the kinetics of the various reactions allow it. This is widely considered to be the normal mode of calcite speleothem formation (e.g., White, 1976). Obviously, this mechanism requires a gas source from which the groundwater can acquire an elevated PCO_2. Such a source seems unlikely at Castleguard, where Ford (1971) has measured the chemistry of springs, snowmelt, and glacier fed streams. His data (Ford, 1971, Table 1) give a mean PCO_2 of $10^{-3.2}$ for tundra streams and pools, $10^{-3.6}$ to $10^{-3.3}$ for glacier waters, $10^{-3.6}$ for snow-patch meltwater and $10^{-3.7}$ atm for karst springs. In the southern Canadian Rockies as a whole, Ford (1971) demonstrates a marked difference in chemistry between waters originating above and below the treeline. Those from below treeline have the higher Ca, alkalinity, and PCO_2. Waters above the treeline have PCO_2 equal to the atmospheric value or less. A similar pattern was reported from Norway by Lauritzen (1981).

As an initial hypothesis, we should expect that the Castleguard Cave waters have evolved from an initial PCO_2 in equilibrium with the atmosphere ($10^{-3.64}$ atm at 2000 m a.s.l.). Moreover, if CO_2 degassing is important in the deposition of calcite in the cave, then some non-atmospheric source of CO_2 is needed, since the cave atmosphere is unlikely to have a PCO_2 less than the outside air.

Three further initial hypotheses relate to means whereby calcite might be precipitated from waters which have evolved from an initial PCO_2 of $10^{-3.6}$ atm.

CHANGE IN PCO_2 AND DEGASSING FOLLOWING A RISE IN TEMPERATURE

The solubility of calcite decreases with temperature at a given PCO_2. At Castleguard the cave temperature ranges up to 4°C, so that infiltrating waters may dissolve calcite at 0°C near the surface and then be warmed as they pass through the deeper strata. Warming will produce slight supersaturation and may cause precipitation of calcite. Recently this mechanism has been discussed in detail by Dreybrodt (1982), who takes the theoretical case of a water which dissolves calcite at 0°C while in equilibrium with the atmosphere. The water reaches equilibrium with respect to calcite under open-system condi-

tions (i.e., free access of gaseous CO_2 to the solution) and then infiltrates through the rock where it is gradually warmed under closed-system conditions (i.e., no CO_2 exchange with a gaseous reservoir). The warming raises the PCO_2 of the solution with little or no change in Ca content, so that when the water enters a cave the excess CO_2 may degas to the atmosphere, producing slight supersaturation with respect to calcite. Dreybrodt (1982) applies a chemical kinetic model derived from experimental work by Plummer et al. (1978) to demonstrate that quite fast rates of speleothem growth may theoretically be possible by this mechanism.

EVAPORATION OF PARENT SOLUTION

In temperate caves evaporite minerals such as gypsum commonly occur where very slow seepages of sulfate-bearing water are evaporated by cold air blowing through the cave and being warmed by heat from the walls. This situation exists par excellence at Castleguard, and the cave contains a suite of hydrated carbonates and sulfates occurring as crusts on walls and crystals in sediments, all apparently of evaporite origin (Harmon et al., 1983, this symposium). Evaporation has been demonstrated to occur and its rate has been estimated (Atkinson et al., 1983). Possibly the calcite speleothems also precipitate in response to progressive concentration of calcite-saturated seepage and pool waters. Thrailkill (1971) established that calcite deposition in Carlsbad Caverns (New Mexico) was due to a combination of evaporation and degassing of CO_2.

COMMON-ION EFFECTS DURING MINERAL DISSOLUTION

Wigley (1973a, 1973b) has published two valuable theoretical studies of chemical evolution in the systems, calcite-gypsum-water, and calcite-dolomite-water. He demonstrates that if a water is first saturated with respect to calcite, under given temperature and PCO_2 conditions, then subsequent dissolution of either gypsum or dolomite will produce supersaturation and precipitation of calcite. This arises because more Ca is added to the solution from the new mineral, increasing the ion activity product,

$$IAP_{cte} = aCa^{2+} \cdot aCO_3^{2-} \qquad (1)$$

and the calcite saturation index,

$$SI_{cte} = \log (IAP/K_{cte}), \qquad (2)$$

where K_{cte} is the equilibrium solubility constant for calcite. At Castleguard the rocks above the cave consist of closely interbedded limestones and dolomites containing abundant pyrite and scarcer gypsum. The right mineralogical setting exists for common-ion effects to cause calcite to precipitate from solutions moving through the strata, and this may be an explanation for growth of the calcite speleothems.

FIELD MEASUREMENTS

To investigate these four initial hypotheses, measurements were made of water chemistry, temperatures of rock, water and air, evaporation rates, and PCO_2 of the cave air. Two traverses were made through the cave, from the entrance as far as Holes-in-the-Floor in April 1979 and as far as the Ice Blockage in April 1980. Ford et al. (1983, this symposium) provide maps and topographic details of Castleguard Cave.

Water samples were collected from three types of site: flows of water eroding cave walls, seepages and drips depositing speleothems, and calcite-lined pools fed by drips or slow seepage. One sample was taken from the perennial spring outside the cave. Temperature was measured at site for several samples, but for others was assumed equal to local air temperature. Alkalinity and pH were determined inside the cave (1979) or immediately

following removal to the surface (1980). Samples were filtered, acidified, and stored for analysis of Ca, Mg, Na, K, Cl and SO_4 in the laboratory. Completed analyses were assessed for charge balance between major cations and anions. Those with an imbalance greater than 5.5% were rejected. The aqueous model computer program WATSPEC (Wigley, 1977) was used to compute ionic species abundances, PCO_2, and saturation indices of calcite, dolomite, and gypsum (Table 1).

The CO_2 content of cave air was measured volumetrically with a Draeger portable gas analyzer and converted to a partial pressure for standard atmosphere conditions at 2000 m a.s.l. (Smithsonian Institution, 1966). Details of temperature and relative humidity measurements are given in Atkinson et al. (1983, this symposium).

RESULTS AND DISCUSSION OF HYPOTHESES

CO_2 Relations Between Water and Cave Air

Figure 1 presents measurements of the PCO_2 of the cave air. Overall mean PCO_2 in the 2 yr was $10^{-3.82}$ atm ($n = 29$, c.v. $= 48\%$) which compares well with the global atmospheric value of $10^{-3.64}$ atm at 2000 m a.s.l. There is no trend of CO_2 levels through the length of the cave and no evidence of detectable enrichment of the cave air by degassing of waters or other CO_2 sources.

The calculated PCO_2 of the water samples is compared with the cave air in Figure 2. The 1979 samples overlap the measured PCO_2 range but some 1980 waters have PCO_2 slightly greater than the air. The contrast between years could possibly be due to differences in procedure or instrumentation but this is thought unlikely. Partial pressures of up to twice the atmospheric value of CO_2 occur in some waters. Degassing of this CO_2 may help to precipitate calcite in the cave.

Figure 3 is a plot of pH against molarity of HCO_3^-. Langmuir (1971) showed that waters dissolving calcite follow one of two types of paths across such diagrams. Initial pH of the sample depends upon its initial PCO_2. The sample may evolve in contact with a gas phase of this PCO_2, so that CO_2 used in solution of carbonate minerals is replaced by dissolution of the gas ("open system"), or it may be removed from the gaseous CO_2 source while it dissolves calcite ("closed system"). The plotting positions of most Castleguard waters is consistent with their evolution along an open-system (or near-open system) path with PCO_2 between $10^{-3.3}$ and $10^{-3.6}$ atm.

The source of the slight enrichment of CO_2 is believed to be reaction between carbonate minerals and sulfuric acid produced by pyrite oxidation in the rocks above the cave. This is discussed in more detail below.

Temperature Changes in Waters Entering the Cave

Table 2 compares the temperatures of waters entering

the cave with air and rock temperatures at the same site. The final column shows the maximum potential change which the water would experience in reaching the same temperature as local air or rock. In every case this change is less than 1°C. The change in calcite saturation index that such a small warming or cooling would produce is less than ±0.01, much less than the experimental uncertainty of ±0.1 in estimating the index from chemical analyses. Since the calcite saturation indices of depositing drips and pools range from -0.04 to 0.83 with mean 0.29 ($s = 0.25$, $n = 20$), it seems very unlikely that precipitation of calcite is caused by the small change in the index which would be produced by temperature changes after entering the cave, especially as many drips become cooler, tending to reduce their degree of calcite supersaturation. This conclusion is reinforced by detailed measurements of a drip 1220 m from the entrance. The water at this site falls from the tips of small stalactites located beneath cracks in the roof. The stalactites indicate that the drip deposits calcite over the long term, and on both occasions of sampling it was supersaturated with respect to calcite. The drops of water fall about 1 m onto a steeply sloping wall, down which they spread as a film for 2.5 m before collecting in small pools on a ledge. There are thin crusts and flowstones of calcite on the wall and in the pools. The water in the film had cooled from 2.50°C at entry to 2.05°C just below the point where it fell onto the wall, and by the time it had reached the pool its temperature was the same as that of the rock, 2.00°C. At least at the time of measurement, temperature changes in this drip were small but in a direction such as to decrease the degree of supersaturation with respect to calcite, and can have played no part in the deposition of speleothem.

I now consider the hypothesis elaborated by Dreybrodt (1982) that calcite supersaturation may be produced by

TABLE 1

Chemical analysis of Castleguard Cave waters

Site	Distance from entrance (m)	Type[a]	Temp (°C)	pH	Ca	Mg	Na	K	Alk[b]	SO$_4$	pPCO$_2$	Sat. index Cal.	Sat. index Dol.	Sat. index Gyps.	Ca from calcite, dolomite, and gypsum C	D	G	Alk/SO$_4$
							(mmol L^{-1})								(mmol L^{-1})			
April 1979																		
S12 Helictite Passage	1200	D	2.0	8.47	0.69	0.89	0.052	0.008	2.11	0.46	3.49	0.23	0.31	-2.18	-0.67	0.89	0.46	4.59
S4 P24	1520	E	3.1	8.95	0.95	0.84	0.087	0.012	2.39	0.62	3.95	0.87	1.44	-1.95	-0.52	0.84	0.63	3.85
S15 First Fissure	2590	E	2.5	8.30	0.60	0.64	0.052	0.010	1.70	0.50	3.41	-0.06	-0.36	-2.18	-0.54	0.64	0.50	3.40
S9 First Fissure	2740	E	2.6	8.38	0.69	0.58	0.033	0.010	1.74	0.42	3.48	0.09	-0.16	-2.20	-0.32	0.58	0.423	4.14
S7 Grottoes	3670	D	3.2	8.90	0.90	1.85	0.52	0.11	2.51	1.70	3.89	0.75	1.58	-1.63	-1.47	1.85	0.52	1.48
S8 Grottoes	3670	P	3.2	8.50	0.82	1.21	0.16	0.013	2.11	1.15	3.53	0.31	0.55	-1.77	-1.55	1.22	1.15	1.83
S13 Grottoes	3950	D	3.3	8.48	0.67	0.76	0.078	0.012	1.62	0.70	3.61	0.13	0.08	-2.01	-0.79	0.76	0.70	2.31
S3 Camp 1	4200	D	3.5	8.50	0.87	1.87	0.10	0.019	3.26	1.17	3.35	0.51	1.11	-1.79	-2.17	1.87	1.17	2.79
S11 Holes-in-Floor	4300	P	3.8	8.72	0.90	2.67	0.27	0.020	2.92	2.23	3.63	0.63	1.51	-1.57	-2.89	2.67	1.12	1.31
S10 First Fissure	2900	E	2.8	8.91	0.60	0.59	0.070	0.010	1.56	0.56	4.08	0.48	0.70	-2.13	-0.55	0.59	0.56	2.79
S14 Helictite Passage	850	D	1.6	8.41	0.60	0.90	0.22	0.014	2.49	0.34	3.36	0.19	0.27	-2.35	0.66	0.91	0.35	7.32
April 1980																		
S7 Welcome Crawl	4210	D	3.3	8.35	0.71	0.85	0.070	0.015	2.26	0.65	3.34	0.17	0.17	-2.04	-0.79	0.86	0.65	3.48
S8 A62	4775	E	2.1	8.13	0.64	0.39	0.017	0.008	1.59	0.34	3.26	-0.22	-0.93	-2.28	-0.09	0.39	0.34	4.68
S9 Next Scene	4240	P	3.3	8.28	0.64	1.28	0.13	0.020	2.16	0.88	3.29	0.02	0.09	-1.98	-1.52	1.28	0.88	2.45
S10 Second Fissure	5960	D	2.8	8.24	1.05	1.31	0.16	0.015	2.62	1.18	3.17	0.25	0.33	-1.68	-1.44	1.31	1.18	2.22
S11 Holes-in-Floor	4470	D	3.2	8.50	1.55	2.90	0.29	0.018	4.56	2.32	3.22	0.83	1.69	-1.35	-3.67	2.90	2.32	1.97
S12 Grottoes	3950	D	3.5	8.27	0.82	0.89	0.083	0.010	1.93	0.98	3.32	0.07	-0.06	-1.81	-1.05	0.89	0.98	1.97
DW Second Fissure	6175	D/E	2.8	8.20	0.82	0.85	0.052	0.010	1.61	0.86	3.34	-0.07	-0.39	-1.85	-0.89	0.85	0.86	1.87
W3 Cave Spring			2.7	8.31	1.29	0.61	0.087	0.015	2.00	0.85	3.35	0.31	0.05	-1.68	-0.18	0.62	0.85	2.35
S1A Grottoes	4210	P	3.3	8.28	0.53	1.11	0.070	0.008	2.21	0.68	3.28	-0.04	0.00	-2.15	-1.26	1.11	0.68	3.25
S2A Grottoes	3670	P	3.0	8.44	0.74	1.09	0.21	0.051	2.33	0.82	3.42	0.27	0.45	-1.94	-1.17	1.09	0.82	2.84
S3A Grottoes	3670	P	3.0	8.30	0.79	1.14	0.17	0.015	2.34	0.93	3.28	0.16	0.22	-1.87	-1.28	1.14	0.93	2.52
S4A First Fissure	2830	P	2.2	8.34	1.02	1.80	0.31	0.010	3.29	1.46	3.18	0.40	0.77	-1.63	-2.24	1.80	1.46	2.25
S5A Grottoes	3670	D	3.1	8.45	0.76	1.03	0.18	0.015	2.10	0.93	3.48	0.24	0.37	-1.88	-1.20	1.03	0.93	2.26
S6A Holes-in-Floor	4580	D	2.8	8.54	0.99	1.64	0.17	0.020	3.21	1.28	3.39	0.58	1.13	-1.69	-1.93	1.64	1.28	2.51
S2 Helictite Passage	1220	D	2.8	8.26	0.83	0.63	0.096	0.010	2.20	0.34	3.26	0.15	-0.07	-2.21	-0.14	0.63	0.34	6.47
S3 First Fissure	2590	E	2.2	8.18	0.68	0.52	0.078	0.020	1.66	0.40	3.30	-0.14	-0.66	-2.21	-0.24	0.52	0.40	4.15
S5 First Fissure	2740	E	2.5	8.17	0.84	0.37	0.061	0.015	1.52	0.45	3.32	-0.09	-0.80	-2.07	0.01	0.37	0.45	3.38

[a] E—eroding flow; D—depositing flow or drip; P—calcite-lined pool.
[b] Alkalinity in meq L^{-1}.

water warming in the rocks above the cave, producing a slight increase in PCO_2, which in turn produces degassing and supersaturation when the water comes into contact with the cave air. Detailed examination of this hypothesis shows that the PCO_2 and saturation index which would be produced by the maximum temperature change possible at Castleguard (4°C) are far smaller than the slight CO_2 enrichments and larger saturation indices actually observed in the cave waters. For example, Dreybrodt indicates (1982, Figure 1) that a 4°C temperature change should increase PCO_2 by some 15% from an initial value of $10^{-3.52}$ to $10^{-3.46}$ atm. If all the excess CO_2 is degassed on reaching a cave, a calcite saturation index of 0.02 would result. These figures may be compared with an average PCO_2 in calcite-depositing waters of $10^{-3.36}$ ($n = 20$, $c.v. = 33\%$), representing an 89% increase in PCO_2 over the atmospheric value of $10^{-3.64}$ atm. This is far bigger than Dreybrodt's hypothesis can explain and also larger than can be accounted for by errors in chemical analysis. Likewise, the mean calcite saturation index of depositing waters is 0.29, more than ten times larger than the value of 0.02 expected from a 4°C warming alone.

Warming along the lines suggested by Dreybrodt may therefore contribute slightly to calcite deposition in Castleguard Cave, but it is insufficient to account fully for observed values of PCO_2 and calcite supersaturation. Other factors must also play a part.
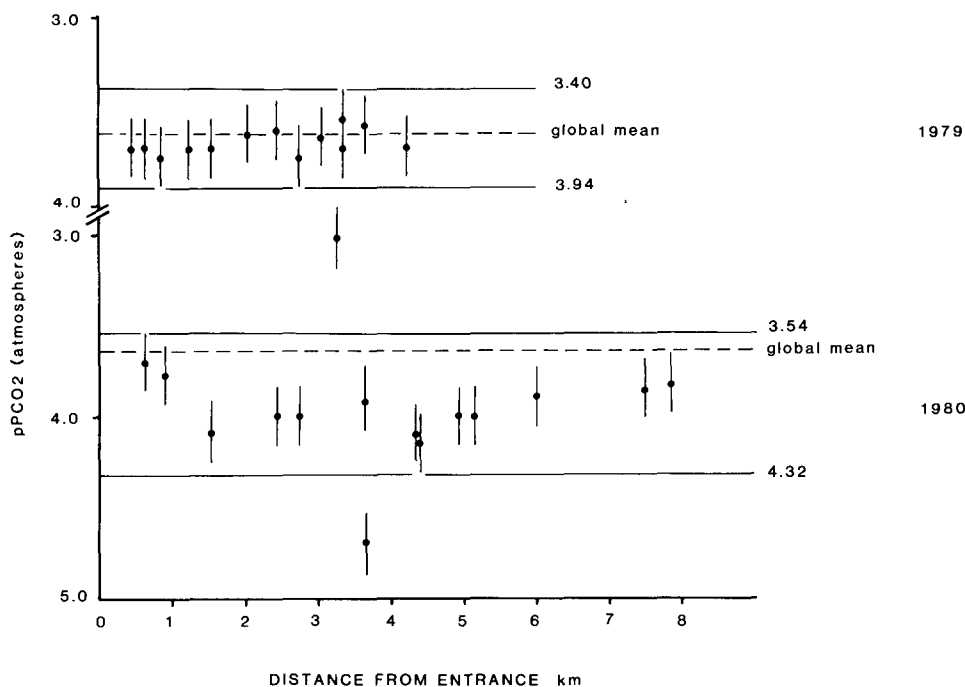

FIGURE 1. Carbon dioxide concentrations in air in Castleguard Cave. Concentrations were measured volumetrically but are expressed as partial pressure. $pPCO_2 = -\log PCO_2$ in atmospheres.
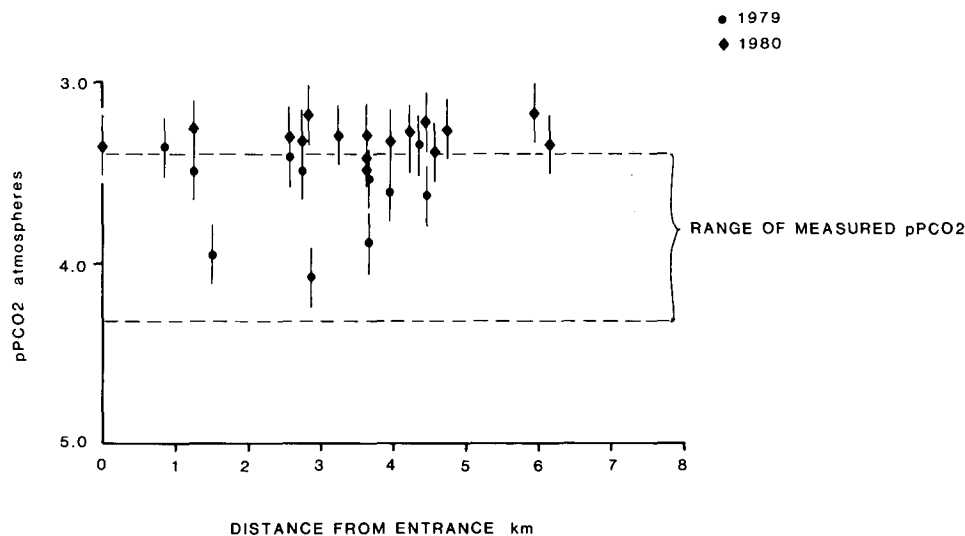

FIGURE 2. Carbon dioxide partial pressures (PCO_2) of water samples in Castleguard Cave.

CALCITE DEPOSITION RESULTING FROM EVAPORATION

The role of evaporation in deposition of pure calcite speleothems may be assessed from both a physical and a chemical standpoint.

From the physical standpoint, likely maximum growth rates resulting from evaporation may be estimated. Except in the entrance zone where evaporation is ca. 14 mm yr^{-1} during winter, evaporation is 1.4 to 2.5 mm yr^{-1} in the first half of the cave (Atkinson, 1983, this symposium). True annual rates will be less than this because the cave wind blows outwards from the entrance for 4 to 5 mon each year, when evaporation in the first half of the cave will be zero, and net evaporation will be confined to the Second Fissure. Thus, 2 mm yr^{-1} is a reasonable estimate for the maximum long-term evaporation rate from the walls throughout most of the cave.

Estimate of maximum linear growth rates of flow-stones, etc., is given by,

$$\frac{dX}{dt} = \frac{E \cdot m\mathrm{Ca} \cdot 10^{-4}}{\rho_c} \text{ mm yr}^{-1} \tag{3}$$

where dX/dt is the rate of increase of thickness of a flow-stone (or length of a stalagmite), E is the evaporation rate, $m\mathrm{Ca}$ is the calcium content of the parent solution in mmol L^{-1} and ρ_c is the density of calcite, 2.65×10^3 kg m^{-3}. This expression assumes that the speleothem surface is kept continually moist and that the solution has a constant Ca concentration as a result of any increase in $m\mathrm{Ca}$ due to evaporation being exactly balanced by precipitation of calcite at constant PCO_2. For Castleguard, $E \approx 2$ mm yr^{-1} and $m\mathrm{Ca}$ averages 0.84 mmol L^{-1} ($s = 0.22$, $n = 20$), which implies an average annual growth rate of 6.3×10^{-5} mm yr^{-1} due to evaporation.
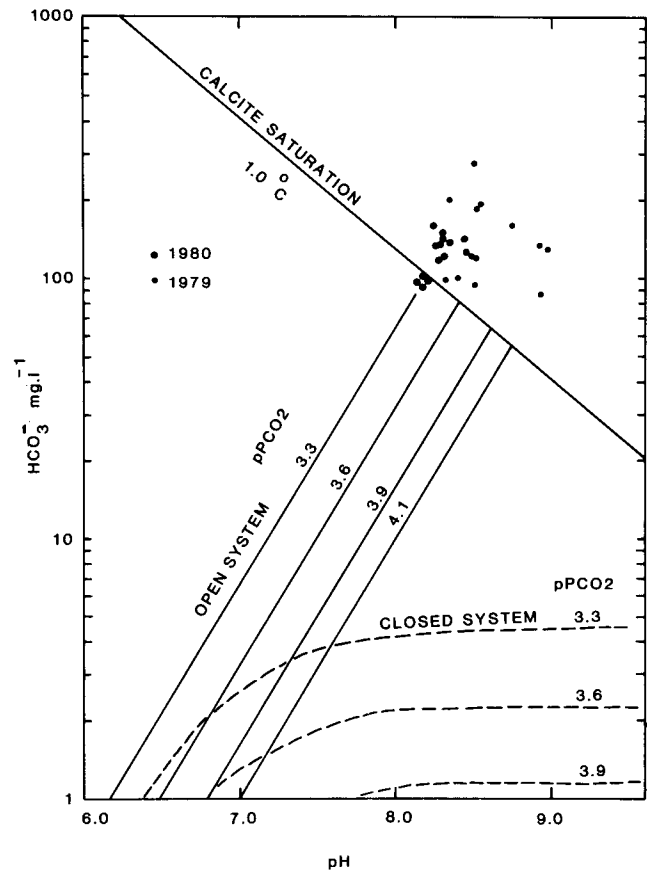

FIGURE 3. Plot of pH against HCO$_3^-$ for Castleguard Cave waters. Overlapping pionts are omitted for clarity. Open- and closed-system evolution paths are shown for different values of initial PCO$_2$.

TABLE 2

Comparison of water, air temperature, and rock temperature, 1980[a]

Site	Distance from entrance (m)	Type[b]	Water temp (°C)	Air temp (°C)	Rock temp (°C)	Maximum potential temp change (°C)
S1	850	D	1.95 cooling to 1.70	1.6	1.60, 1.70	−0.35
S1A	1220	D	2.50 cooling to 2.00	2.13	2.00	−0.5
S5	2740	E	2.5	2.8	2.2	+0.3
S6	2900	E	2.8	2.5	2.3	−0.5
S2A	3670	D,P	3.1 cooling to 2.9	3.2	3.1	−0.2
S12	3950	D	3.5		3.2	−0.3
S8	4775	E	2.1	2.6	2.3	+0.5
	ca. 5000	E	2.1	2.9		+0.8
S10	5960	D	2.9	3.1	2.8	+0.2
DW	6175	D/E	2.6	2.7	2.4	−0.3

[a]Temperatures quoted to two decimal places were measured to ±0.05°C with a Grant thermistor; values quoted to one decimal place were measured to ±0.2°C with a mercury thermometer.

[b]See Table 1 for explanation.

Actual average deposition rates of recent flowstones are not known with great precision. Actively growing examples are typically 10 to 100 mm thick although larger specimens are known. The maximum possible age for flowstone deposited since the maximum Wisconsinan glaciation is around 10,000 yr, as indicated by the age distribution of speleothems dated by U-series methods (Gascoyne et al., 1983, this symposium). Therefore, the minimum growth rates of flowstone have order of magnitude 10^{-3} to 10^{-2} mm yr^{-1}. This implies that the maximum probable growth rate by evaporation is between 6 and 0.6% of the minimum probable total growth rate for flowstones. While evaporation may contribute to flowstone growth, it is inadequate to account for more than a small part of it.

A slightly different approach may be used to estimate the growth rate of a soda straw stalactite. They are usually hollow and for the present discussion I shall assume an external radius of 2 mm with a central canal of 1 mm radius. Using an equation common in cloud physics (Fletcher, 1962; Byers, 1965; Wigley, 1975), the rate of evaporation from a spherical droplet (i.e., a drop hanging from the tip) is given by

$$\frac{dm}{dt} = k^* \cdot r \cdot E^* \cdot \zeta \cdot \rho_a \qquad (4)$$

where dm/dt is the rate of change of mass of the drop, k^* is a constant which depends upon temperature, r is the drop radius, E^* is the vapor pressure deficit as a function of the saturated vapor pressure, ζ is a ventilation factor of the order of unity, and ρ_a is the density of the air. For conditions in Castleguard Cave beyond a few hundred meters from the entrance, $k^* \approx 6.10^{-7}$ m^2 s^{-1} (Wigley, 1975: 82), $r = 2.10^{-3}$ m, $E^* \approx 0.03$, and $\rho_a \approx$ 1 kg m^{-3}. Then

$$\frac{dm}{dt} \approx 3.6 \times 10^{-11} \text{ kg s}^{-1}. \qquad (5)$$

The same assumptions as before allow us to calculate the rate of calcite deposition in response to evaporation from the drop. The volume rate of deposition is

$$\frac{dV_{CaCO_3}}{dt} = \frac{1}{\rho_w} \cdot \frac{1}{\rho_c} \cdot \frac{dm}{dt} \cdot \frac{mCa}{10} \text{ m}^3 \text{ s}^{-1} \qquad (6)$$

where ρ_w and ρ_c are water and calcite densities in kg m^{-3} and mCa is calcium concentration in mmol L^{-1}. For $\rho_w \approx 10^3$, $\rho_c = 2650$, $dm/dt \approx 3.6 \times 10^{-11}$, and $mCa \approx$ 0.84 we have

$$\frac{dV_{CaCO_3}}{dt} \approx 1.14 \times 10^{-18} \text{ m}^3 \text{ s}^{-1}. \qquad (7)$$

In a soda straw stalactite this volume will be added to the outer annulus of the stalactite and not to the central canal. The area of the annulus is 9.4×10^{-6} m^2 and thus

the linear growth rate of the stalactite produced by evaporation is 1.2×10^{-13} m s^{-1} or 3.8×10^{-3} mm yr^{-1}. In 10,000 yr evaporation could produce a soda straw stalactite 38 mm long. In fact, most straws in Castleguard are much longer than this, with many specimens around 500 mm long and a few of about 1000 mm. The actual growth rate of stalactites appears to be at least an order of magnitude greater than could be produced by evaporation alone. This result is comparable to that deduced above for flowstones.

From the chemical standpoint, Thrailkill (1971) detected the effects of evaporation in Carlsbad Caverns by demonstrating an evolutionary sequence of waters in which Mg was concentrated by evaporation while Ca remained constant or decreased due to precipitation of calcite at constant PCO_2. Figure 4 is a plot of Ca and Mg in Castleguard waters and at first appears to exhibit a broadly similar "evaporation trend." Eroding flows occupy positions close to the line on which Ca:Mg = 1.0, suggesting equilibration with dolomite as the main control on the Ca:Mg ratio. Depositing drip and pool waters trend away from the eroding flows with Mg contents increasing about five times more rapidly than Ca (Figure 4). While evaporation may have contributed to this trend, it is most unlikely to explain it entirely. A more than four-fold increase of Mg relative to eroding flows is exhibited by some waters. If due entirely to evaporation of an initial "eroding flow" type of water, this would imply that some 75% of the parent solution had already been evaporated by the time the water sample was taken. Such high figures might just be feasible in a few pools or films fed by the slowest seepage, but they are most unlikely to arise in drips falling frequently enough for a sample to be collected in a few minutes or hours. Yet several drips exhibit some of the highest enrichments in Mg relative to Ca (Figure 4). In fact, the trend of Mg and Ca in Figure 4 can be satisfactorily explained by incongruent solution of dolomite and solution of $CaSO_4$ leading to calcite precipitation, as explained in the next section.

In summary, both physical and chemical evidence suggest that evaporation plays only a minor part in the precipitation of pure calcite speleothems in Castleguard Cave. However, evaporation is of great importance in the growth of hydrated carbonate and sulfate crystals, crusts, and wall coatings, as discussed by Harmon et al. (1983, this symposium).

COMMON-ION EFFECTS

Most of the chemical features of Castleguard Cave waters, including the deposition of calcite speleothems, can be explained by supposing the waters to have evolved by simultaneously dissolving ideal dolomite (Ca:Mg = 1.00) and calcium sulfate at constant PCO_2. Wigley (1973a, 1973b) has studied the theoretical evolution of waters in gypsum-calcite and dolomite-calcite environments. He demonstrated the chemical evolution diagrammatically by plotting the amounts of dissolved Ca which

were derived respectively from gypsum ($CaSO_4$), dolomite ($CaMg[CO_3]_2$), and calcite ($CaCO_3$). Versions of his diagrams, recalculated for a temperature of $2.5°C$ and a PCO_2 of $10^{-3.64}$ atm are shown in Figure 5. The axes are defined as follows:

G = Ca derived from gypsum = mSO_4
D = Ca derived from dolomite = mMg
C = Ca derived from calcite = $(mCa_r - mMg - mSO_4)$.

All concentrations are in millimoles per liter. Values of C, D, and G have been calculated for each water sample and are listed in Table 1. Almost all values of C are negative, which strongly suggests that most of the waters have deposited a calcium mineral, presumably calcite, while dissolving dolomite and $CaSO_4$. Also shown in Table 1 are saturation indices with respect to calcite, dolomite, and gypsum. All of the depositing drip and pool waters are supersaturated with respect to calcite, most are supersaturated with respect to dolomite, but all are strongly undersaturated with respect to gypsum.

Figure 5a shows how calcite may be precipitated in the simple gypsum-calcite system. A water in equilibrium with air at $PCO_2 = 10^{-3.64}$ atm, but containing no Ca in solution, lies at the origin. If brought into contact with both calcite and $CaSO_4$ (envisaged as gypsum in the diagram), it will dissolve both and move along some radial path such as the line OA. At A, calcite saturation is reached, but continuing dissolution of $CaSO_4$ is possible, moving the solution parallel to the G axis, carrying it above the calcite saturation line. If calcite can be precipitated so as to keep the solution at equilibrium with calcite, then the path AB will be followed. At all times after A is reached, the solution will lie on or above the calcite saturation line,

until it eventually reaches the point C where it is saturated with respect to both minerals. A similar evolutionary path is possible in the simple dolomite-calcite system (Figure 5b). In this case, precipitation of calcite is due to the incongruent dissolution of dolomite.

On the gypsum diagram (Figure 5a), the Castleguard waters lie far below the calcite saturation line and it is quite clear that a simple common-ion effect between calcite and gypsum is not sufficient to account for the supersaturation with respect to calcite listed in Table 1. Because the waters have dissolved dolomite, they lie far from the pure calcite-gypsum plane of Figure 5a. On Figure 5b the data lie close to both the calcite and dolomite saturation lines, but mostly slightly below them. Again, it is clear that incongruent dissolution of dolomite is not by itself a complete explanation of the supersaturation and precipitation of calcite from the samples, particularly as many are in fact supersaturated with respect to dolomite. Thus, the true evolution of the waters must involve simultaneous dissolution of dolomite and $CaSO_4$. This is shown schematically in Figure 6.

Figure 6 is a diagram of the calcite saturation surface in the trimineralic system involving calcite, ideal dolomite, and gypsum at a PCO_2 of $10^{-3.64}$ atm. The principal planes containing the CG and CD axes are from Figures 5a and 5b, respectively, and the contours of the calcite saturation surface are constructed on an isometric projection. The Castleguard data show a spread down the calcite saturation surface in what appears to be an evolutionary trend.

Pure meltwater in contact with air would lie at the origin of the diagram. The Eldon and Pika formations above the cave consist of interbedded dolomites and calcites. The initial evolutionary path is therefore envisaged as lying close to the CD plane and rising to meet the
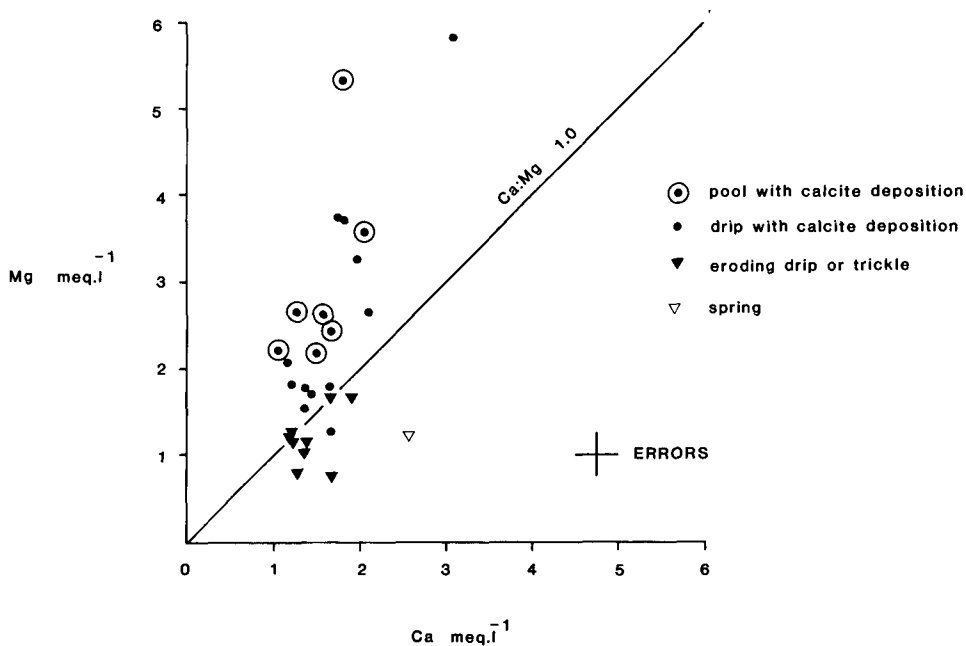

FIGURE 4. Calcium and magnesium in Castleguard Cave waters.

calcite saturation surface as both calcite and dolomite are dissolved. Once the calcite saturation surface is reached, incongruent dissolution of dolomite begins and the solution will move along a path across the saturation surface (or more likely parallel to it but somewhat above it). The first sampled waters are eroding flows lying somewhat away from the CD plane. They are close to saturation with calcite but still capable of dissolving dolomite. Further evolution is by incongruent dissolution of dolomite moving the water down the calcite saturation surface into the region where C is negative, i.e., more calcite has been precipitated than was originally dissolved. Even-

tually, the intersection of the calcite saturation surface with the dolomite saturation surface will be reached. Following the evolutionary trend beyond this point, the dolomite saturation surface lies below the calcite surface (see Figure 5b). Precipitation of calcite remains the controlling reaction, however, as precipitation of dolomite is normally inhibited kinetically. Most of the depositing drip and pool samples are supersaturated with dolomite (Table 1).

Continuing evolution of waters from the point where dolomite becomes saturated cannot be due to incongruent dolomite dissolution alone. However, the calcite satura-
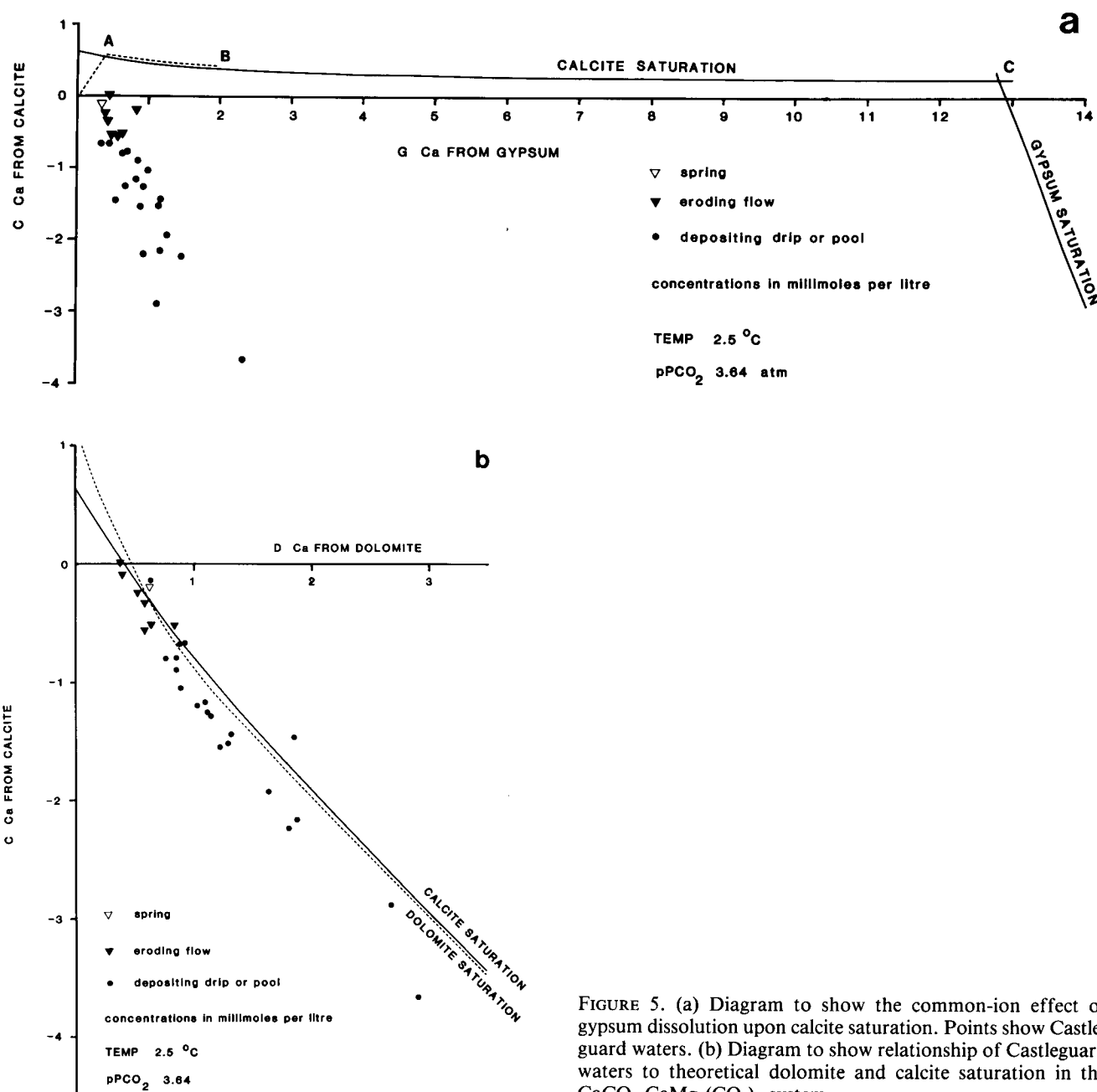

FIGURE 5. (a) Diagram to show the common-ion effect of gypsum dissolution upon calcite saturation. Points show Castleguard waters. (b) Diagram to show relationship of Castleguard waters to theoretical dolomite and calcite saturation in the $CaCO_3$-$CaMg (CO_3)_2$ system.

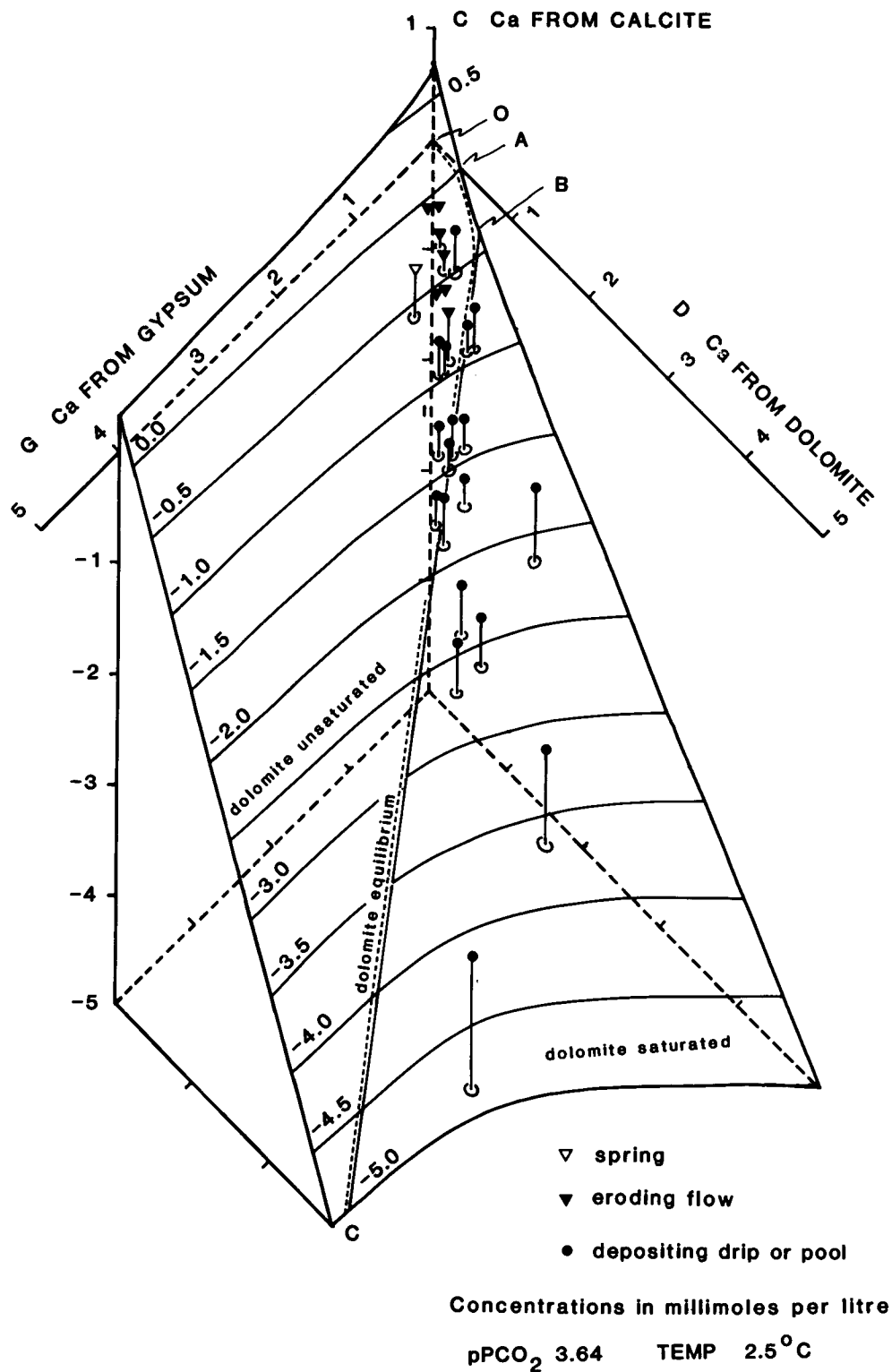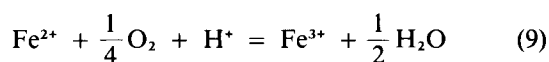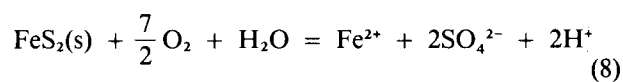FIGURE 6. Generalized model of the evolution of Castleguard waters in the $CaCO_3$-$CaMg(CO_3)_2$-$CaSO_4$-H_2O system at 2.5°C and PCO_2 = $10^{-3.64}$ atm. Contoured surface is calcite saturation surface. Line of mutual calcite and dolomite saturation is also shown. Vertical bars show relation of data points to surface.

tion surface in Figure 6 is inclined towards the G axis. Continuing addition of $CaSO_4$ to the solution moves the evolving waters both down the calcite saturation surface (as the common-ion effect precipitates calcite) and away from the CD plane. One might expect the precise path of evolution to be controlled by the line of intersection of the calcite and dolomite surfaces, but this is not in fact the case at Castleguard because the sulfate derives mainly from oxidation of pyrite, not gypsum.
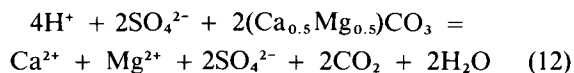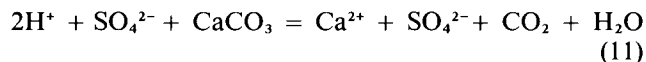
Several lines of empirical evidence support the evolutionary model just outlined. First, Figure 4 shows that the calcite depositing waters evolve away from their supposed parents, the eroding flows, by dissolving Mg. Concentrations of Ca also increase, but by a smaller amount, as would be expected if evolution were by simultaneous dissolution of $CaSO_4$ and incongruent dissolution of dolomite. Second, a plot of saturation indices shows a high degree of correlation between calcite and dolomite (Figure 7), particularly among depositing drip and pool waters. Close examination of Figure 7 confirms the role of SO_4 in driving the evolution of the sampled waters. In Figure 7a the concentrations of SO_4 are shown against each point. This is effectively the value of G and there is a clear trend from low values among depositing waters close to the origin to high values as saturation indices of calcite and dolomite increase. Similarly, in Figure 7b, the saturation index with respect to gypsum becomes larger, i.e., the solution moves towards gypsum equilibrium, as saturation indices of calcite and dolomite increase.

So far, this discussion of common-ion effects has assumed that the source of SO_4 is gypsum. In fact, at Castleguard it is much more likely to be from oxidation of pyrite in the carbonate rocks above the cave. Pyrite occurs as small crystals scattered through the rock at all levels in the succession and especially on bedding surfaces in the Stephen Formation. In the Eldon and Pika formations larger crystals and small nodules occur while rusty weathering spots contain partially oxidized pyrite surrounded by iron oxyhydroxides. In contrast, gypsum is much less common or abundant and was only observed as a vein filling in the upper Cathedral limestone.

The chemical reactions involved in the oxidation of pyrite are outlined by Stumm and Morgan (1981: 469–471) and may be summarized as

$$FeS_2(s) + \frac{7}{2}O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+ \tag{8}$$

$$Fe^{2+} + \frac{1}{4}O_2 + H^+ = Fe^{3+} + \frac{1}{2}H_2O \tag{9}$$

$$Fe^{3+} + 3H_2O = Fe(OH)_3(s) + 3H^+ \tag{10}$$

Thus, each mole of pyrite oxidized releases two moles of sulfuric acid. As demonstrated by Vear and Curtis (1981) for the weathering of shales in England, this acid reacts almost immediately with carbonates.

$$2H^+ + SO_4^{2-} + CaCO_3 = Ca^{2+} + SO_4^{2-} + CO_2 + H_2O \tag{11}$$

$$4H^+ + 2SO_4^{2-} + 2(Ca_{0.5}Mg_{0.5})CO_3 = $$
$$Ca^{2+} + Mg^{2+} + 2SO_4^{2-} + 2CO_2 + 2H_2O \tag{12}$$

Each mole of pyrite oxidized adds 2 mol of calcium or magnesium sulfate to the solution. Furthermore, the CO_2 evolved may dissolve to produce carbonic acid, making possible the dissolution of up to a further 2 mol of carbonate mineral per mole of pyrite. One effect of this would be to slightly increase the PCO_2 of the solution in conditions where gas exchange was restricted, such as where water percolates in narrow fissures or fractures. This may account for the slightly elevated PCO_2 observed in some Castleguard waters.

That pyrite oxidation is indeed an important reaction at Castleguard is confirmed by Figure 6. The path $OABC$ shows the theoretical evolution of a water which first dissolves dolomite, then gypsum and dolomite. Once dolomite saturation is reached at B, addition of gypsum moves the water on a path parallel to the G axis, causing it to precipitate calcite and rendering it unsaturated with respect to dolomite. More dolomite is dissolved with the overall effect of causing the water to follow the line BC on which equilibrium with calcite and dolomite are both maintained. The field data do not follow this trend at all, but indicate greater dissolution of dolomite than the addition of gypsum alone would allow. Mass balance calculations show that the additional Mg comes from solution of dolomite by sulfuric acid and carbonic acid generated from pyrite oxidation.

Stable isotope analyses by Gascoyne and Nelson (1983, this symposium) give $\delta^{13}C$ values for Holocene calcite speleothems in the range -1.5 to $+1.6°/_{oo}$ PDB. Harmon et al. (1983, this symposium) note a similar compositional range for flowstone 73010 which grew from 155,000 to 93,000 yr ago. These compositions are much heavier than is normal in temperate-zone speleothems, but they are consistent with the proposed evolution of the depositing waters by incongruent dissolution of dolomite and common-ion precipitation of calcite. The heavy isotopic compositions are most likely due to much of the carbon in solution derived from the rock ($\delta^{13}C \approx 0$ to $2°/_{oo}$) following pyrite oxidation. Molar ratios of alkalinity (expressed as HCO_3^-) to SO_4 vary from 1.3 to 7.3, averaging 3.1 ($s = 1.4$, $n = 28$). Since each mole of sulfate produced by pyrite oxidation introduces up to 2 mol of carbon from the rock into solution, it is probable that between a quarter and all of the carbon in the sampled waters is isotopically heavy carbon originating from the rock. The exact proportions of atmospheric and lithic carbon will depend upon the amount of pyrite oxidized and dissolved, and upon the degree of CO_2 isotopic exchange that the solution has with a gas reservoir. The reservoir comprised by the air in fissured rocks has roughly the same volume as the percolating water itself, so gas exchange and dilution of the heavy carbon isotopes by atmospheric CO_2 ($\delta^{13}C = -7°/_{oo}$) may be quite

A.

CALCITE SATURATION INDEX

DOLOMITE SATURATION

INDEX
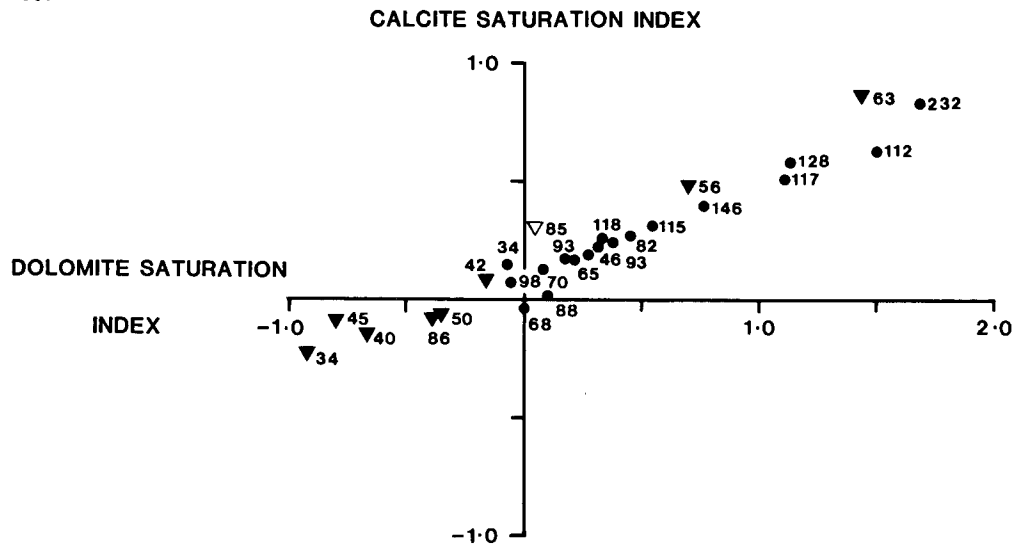
▽ spring

▼ eroding flow

● depositing drip or pool

B.

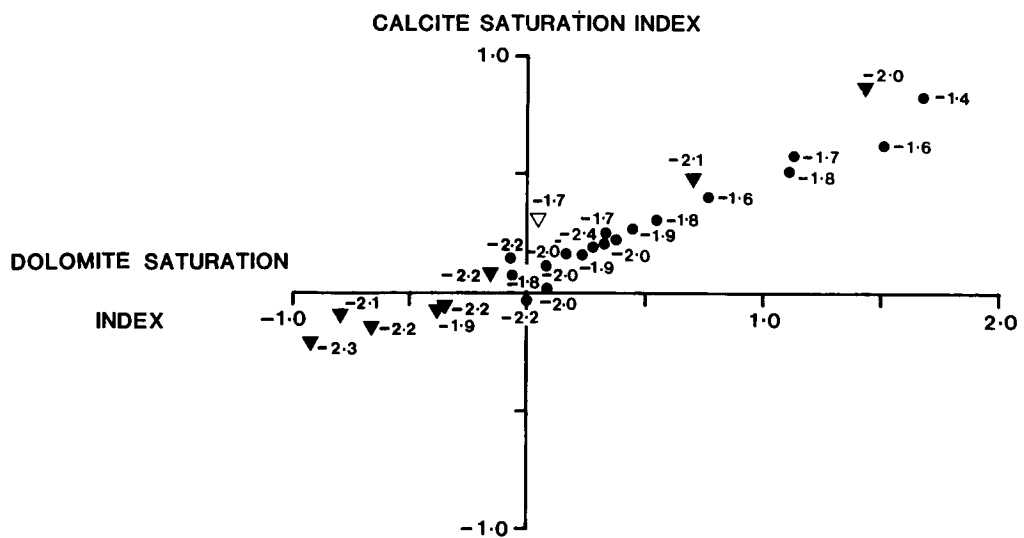CALCITE SATURATION INDEX

DOLOMITE SATURATION

INDEX

FIGURE 7. (A) Plot of saturation indices of calcite and dolomite in Castleguard waters. Numbers against points indicate SO$_4$ concentration in units of $100 \times$ mmol L^{-1}. (B) As for Figure 7(A), but numbers against points show saturation index with respect to gypsum.

limited. Indeed, with CO_2 being evolved from reaction between sulfuric acid and carbonate minerals, the isotopic composition of CO_2 gas in some smaller fissures may be expected to be similar to the 0 to $+2°/_{oo}$ of the rock. This type of situation is a hybrid between the classical "open" and "closed" systems (Garrels and Christ, 1965; Deines et al., 1974; Wigley et al., 1978). The solution is *chemically* open to CO_2 exchange with a gas phase with PCO_2 roughly constant at $10^{-3.3}$ to $10^{-3.6}$ atm. But it is *isotopically* closed (or partially closed) because the isotopic composition of the gas phase CO_2 is itself strongly influenced by exchange with the solution and/or direct release of CO_2 from reaction of H_2SO_4 with the rock.

CONCLUSIONS AND IMPLICATIONS FOR PALEOCLIMATIC STUDIES

The following conclusions may be drawn from the detailed discussion of the field data in the light of the four initial hypotheses:

(1) The Castleguard Cave waters originate from melting of snow and ice and have evolved under predominantly open-system conditions with respect to exchange of CO_2 between solutions and a gas reservoir. The PCO_2 of this reservoir is on average slightly greater than that of the global atmosphere.

(2) The principal chemical reactions between rock and water are as follows: (a) dissolution of calcite and dolomite by carbonic acid, (b) oxidation of pyrite to sulfuric acid and iron oxyhydroxides, (c) dissolution of calcite and dolomite by sulfuric acid, and (d) precipitation of calcite. Supersaturation and precipitation of calcite results primarily from common-ion effects in the system $CaCO_3$-H_2SO_4-$CaMg(CO_3)_2$-H_2O-CO_2 at near constant temperature and PCO_2. The slightly higher than atmospheric values of PCO_2 are probably due to the CO_2 released when sulfuric acid reacts with carbonate minerals.

(3) The isotopic composition of recent calcites reported by Gascoyne and Nelson (1983, this symposium) appears to be consistent with the chemical evolution proposed. More modeling is needed of hybrid systems which have more than one source of CO_2 with different isotopic compositions.

(4) Although the common-ion effect is the main process producing calcite speleothems, small contributions may also be made by degassing of CO_2 from the slightly CO_2-enriched drip waters and by warming of the waters during passage from the surface to the cave. Actual precipitation of calcite, as opposed to supersaturation of the solution, may be stimulated by slight evaporation of calcite-depositing seepages or pools, but this is not a quantitatively significant cause of the calcite speleothem growth.

These conclusions have important consequences in the area of paleoclimatology. With the advent of U-series dating of speleothems (see Gascoyne et al., 1983, this symposium), several authors have interpreted age distributions of speleothem dates in paleoclimatic terms. Harmon et al. (1977) studied four areas of the Rocky Mountains which are at present marginal for speleothem growth and showed that episodes of growth alternated with periods of little or no growth in a manner consistent with the deep-sea isotopic record of global oscillations in climate and ice-volume. Ford (1976) used speleothem dates to illuminate the history of glaciation and interglacials in the Nahanni region of Northwest Territories, Canada, with the implication that speleothems were interglacial deposits. Gascoyne (1981) has published an age-histogram of dates from northwest England and suggests that it reflects interglacials when abundant speleothem growth occurred, glacials (i.e., periods of cold climate but without ice sheets necessarily being present) when speleothem growth was restricted, and episodes of glaciation when speleothem growth ceased. Atkinson et al. (1978) suggested a similar interpretation for the age distribution of dates from southwest and northwest England.

All of these authors based their interpretation, implicitly or explicitly, upon the supposition that speleothems grow primarily by degassing of CO_2, and that the elevated PCO_2 required is supplied by the air of a well-vegetated soil (see Atkinson et al., 1978, for a review). The Castleguard Cave speleothems are growing beneath modern ice sheets and provide direct proof that speleothem growth is possible without involvement of biogenic CO_2. The present study, by demonstrating the mechanism of speleothem deposition at Castleguard, allows us to be more specific about the paleoclimatic deductions which may be made from the occurrence of ancient speleothems. Given suitable geological conditions such as occur at Castleguard, the minimum climatic requirement for speleothems to grow at least slowly is a supply of water. The only circumstances in which water is likely to be totally cut off is where the cave temperature is below 0°C or where a warm cave lies beneath truly continuous permafrozen ground. The latter case may occur in the distal part of First Fissure at Castleguard, where the walls are dry and there are no actively growing speleothems apart from evaporite minerals. This section of the cave lies beneath the coldest part of the overlying topography, with mean annual temperatures of about -6.5°C.

Suitable geological conditions for the growth of speleothems without biogenic CO_2 are those where common-ion effects or incongruent dissolution of dolomite are likely, specifically mixed gypsum-limestone or limestone-dolomite terrain and any carbonate terrain in which pyrite is abundant. Geochemically suitable terrain is probably best identified by the Ca:Mg and Ca:SO₄ ratios of water draining from it. High values of these ratios indicate a

predominantly Ca-HCO$_3$ water which is unlikely to produce speleothems without CO$_2$ degassing. Low values indicate a Ca-Mg-HCO$_3$-SO$_4$ water in which similar

groundwater evolution to that at Castleguard may be at least possible in periods of cold climate.

ACKNOWLEDGMENTS

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