Calcium Carbonate Solution in Some Central Mendip Caves, Somerset

By

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In recent years Mr. Smith, Dr. Mead and Mr. Nicholson of this Society have published some results of their investigations into the solution of limestone in the general Bristol area and in Co. Clare (Smith and Mead, 1962; Smith and Nicholson, 1964; Mead, 1964; Smith, 1965). The greatest number of their calcium carbonate figures are derived from the central Mendip Hills where, between December, 1960, and February, 1962, Smith and Mead (1962) sampled four important risings and one large swallet cave, G.B. Cave. The sampling interval was approximately one month.

During the periods May–August of 1960 and 1961 the present author was also sampling $CaCO_3$ solution in the central Mendip Hills, but concentrating largely on the three swallet caves, St. Cuthbert's Swallet, Swildon's Hole and G.B. Cave. The number of stream-sampling sites in each was larger than that used by Smith and Mead in G.B. Cave. The total number of samples analysed was 287. With the exception of two winter collections in G.B. Cave kindly taken by Dr. O. C. Lloyd, sampling was limited to spring and summer conditions. The summer of 1960 was particularly wet underground; 1961 was particularly dry. Collections were timed to sample "high", "average" and "low" water conditions. Thus sampling time intervals were irregular but there is a fair climatic range. Certain of the results are quite surprising; they do not entirely coincide with those of Smith and Mead (1962) and are presented here to indicate some of the lines that further Mendip investigation might follow.

All samples were collected in polythene bottles previously rinsed in distilled water. Most were titrated within 2 to 7 days of collection but the two winter batches from G.B. Cave stood for several months.* Titration was by the Schwarzenbach method (Smith and Mead, 1962), using the standard chemical package sold by British Drug Houses. Routine checking indicated a measuring error of ± 2 parts per million.

SOLUTION PATTERNS IN THE SAMPLE CAVES

In many respects, St. Cuthbert's Swallet, Swildon's Hole and G.B. Cave are closely comparable. They are developed in the base of the Blackrock

* They gave figures quite similar to those published by Smith and Mead for G.B. Cave so that it is unlikely that there was radical deterioration.

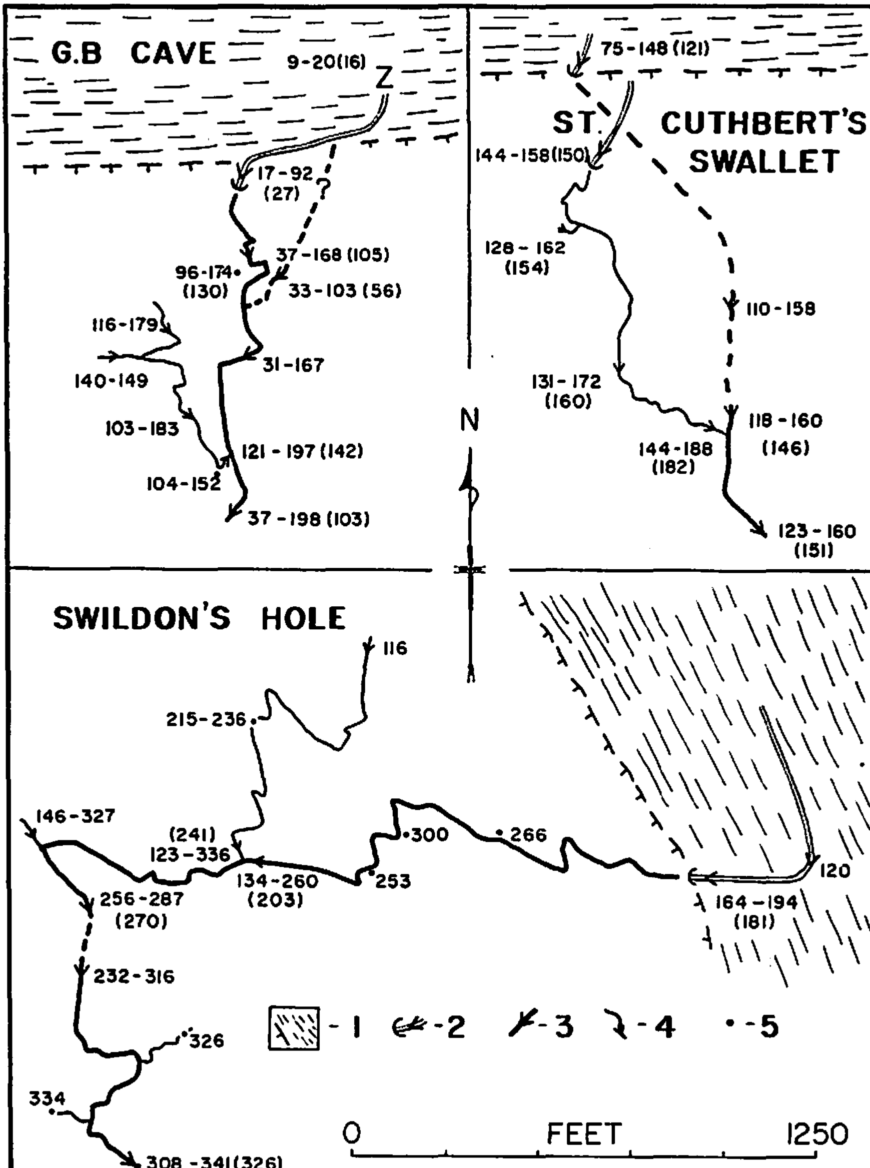

Fig. 11. The major streams for three central Mendip caves showing values for $CaCO_3$ in solution measured during 1960 and 1961. Figures in brackets are mean values where five or more variates are available. (1) The outcrop of the Limestone–Shales. Blank areas are Blackrock Limestone. (2) Surface stream channels with sampling sites. (3) Major underground streams with sampling sites. (4) Important tributary streams underground. (5) Drip samples.

Limestone (Lower Carboniferous), which dips steeply to the south or west. Their erosional enlargement can be attributed almost exclusively to streams collected on the outcrop of underlying Limestone-Shales. The sinks are close to 800 ft. O.D. and the caves are 400–500 ft. deep. In the catchment basins, soils are generally shallow and the cover is largely permanent grass with some heath.

In *Fig.* 11, a majority of the stream sample values cover "high", "average" and "low" water conditions, but those below the important tributary in Swildon's Hole are for "average" and "low" only. In general, the lowest values at a site (stream or drip sample) pertain to high water conditions and *vice versa.* But there are anomalies in every cave. For instance, the largest value at the main stream sink of G.B. Cave, (92 p.p.m.), was measured in summer high water conditions.

The G.B. Cave values are the lowest of the three, St. Cuthbert's Swallet, with its broadly similar length of underground stream channel, is intermediate and Swildon's Hole is highest. This distinction is already apparent at the stream sinks but is shared by tributary streams and drips underground. G.B. Cave figures compare with those published by Smith and Mead (1962, p. 201), with one very important rider—summer samples collected a few days apart at a given site show a considerably wider fluctuation in $CaCO_3$ content than appears in the rather smooth curves of Smith and Mead, which were drawn through samples taken approximately 1 month apart. For example, a large drip near the head of the Gorge increased 50 p.p.m. in 8 days (taken at "average" and "low" stream levels). This is a greater variation at a site than Smith and Mead found at any of their drip stations during the entire 14 months that they observed. It must suggest that the mean values quoted in *Fig.* 11 are of no general significance though they may be used for the limited purpose of comparing the three caves.

Smith and Nicholson (1964, p. 133) have published an illustration of the $CaCO_3$ content of waters in a hypothetical Mendip cave. Although considerable fluctuations in value are allowed at a site, values increase rather steadily down the cave to a maximum of 250 p.p.m. This is matched by a figure of 240 p.p.m. at the rising.

Fig. 11 cannot be said to support this hypothetical case. In the two shorter caves values stop well below the required maximum; in the long cave they march steadily through it.

THE INCREMENT OF CALCIUM CARBONATE IN MAJOR CAVE STREAMS

In *Fig.* 12 each line on the graph represents 1 day's collection. The $CaCO_3$ value at the stream sink is subtracted from all downstream values to obtain a uniform starting point.

In their Co. Clare work, Smith and Nicholson (1964, p. 122 *et seq.*) have stressed the difficulty of determining that the downstream increase in $CaCO_3$ between two consecutive cave-stream stations is to be attributed to solution by *that* stream and not to the admixture of richer waters from drips and small

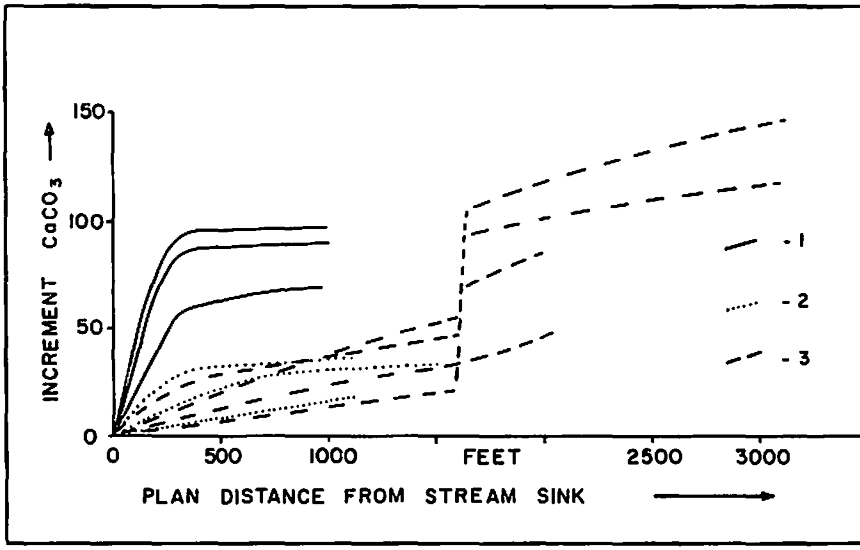

Fig. 12. Downstream increment of calcium carbonate in major cave streams. (1) G.B. Cave. (2) St. Cuthbert's Swallet. (3) Swildon's Hole. The abrupt increase in three of four collections in Swildon's Hole is caused by the entry of the principal tributary in "low" and "average" water conditions. In "high" water conditions (fourth curve), this phenomenon was not observed.

tributaries. This is also a problem in Mendip. It may be that all of the modest increment shown in St. Cuthbert's Swallet is produced by drip and trickle mixing. But, along some sections of the Swildon's stream, qualitative estimates would suggest that the aggregate volume of drip and trickle water is so small compared to that of the major streams that its enriching effect cannot be very large, even if it is supposed that "Mischungskorrosion" (Bögli, 1963) occurs as well. It seems that, when sampled, $CaCO_3$ in the Swildon's stream was increasing rather steadily. The same may be true of St. Cuthbert's, for its curves are similar.

Drip and trickle increment can most confidently be excluded in the upstream section of G.B. Cave. Sampling sites were at the sink and where the two important streams enter the Gorge. Drips and trickles should register more strongly downstream—between sampling sites half-way down the cave (the Bridge) and its terminus. But it will be seen that curves are very flat there: there is little increment of any sort.*

Therefore, the main feature of *Fig.* 12—the contrast between the G.B. Cave régime and that in the other two caves—is held to be valid. The G.B. Cave stream has comparatively little dissolved limestone at the sink. It rapidly adds a great deal in the very steep upper section of the cave and is then exhausted.

*p*H

Smith and Mead (1962, p. 195) have outlined the use of *p*H measurements in the study of cave waters. *p*H values shown in *Figs.* 13 and 14 were measured with a Lovibond Comparator, interpolating to 0·1 *p*H. The Comparator can

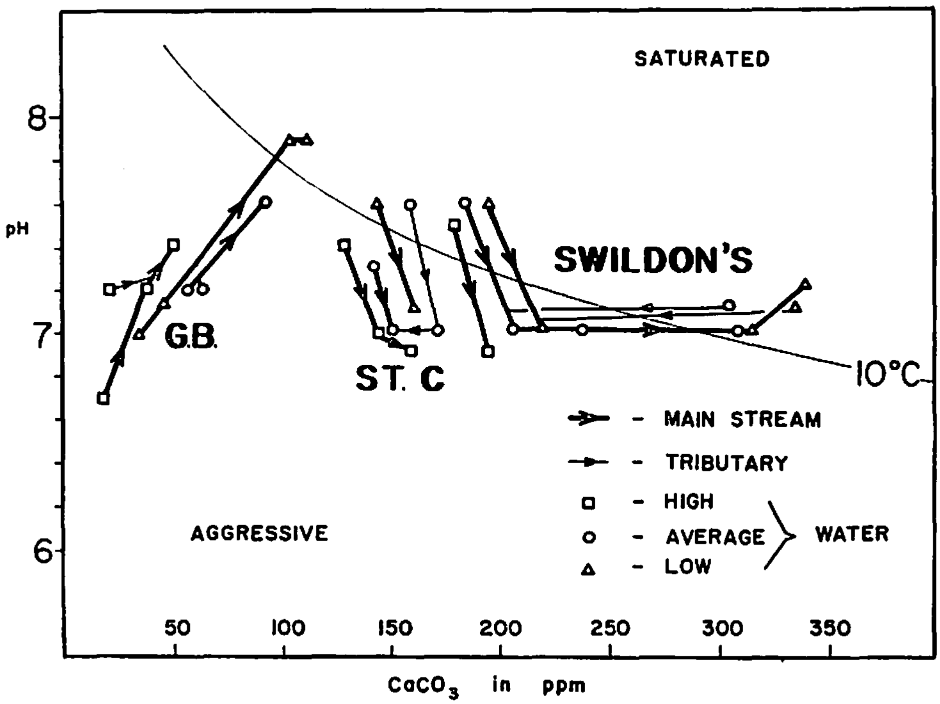

Fig. 13. Calcium carbonate in solution in streams plotted against *p*H for nine collections in the sample caves. Arrows indicate the direction of flow.

only be used in daylight: sink and rising samples were measured at the site but cave samples could only be dealt with on emergence, in some cases 8 hours after collection.

* In two collections (one of winter low water and one of summer low water) there may have been a net loss of as much as 10 p.p.m. of $CaCO_3$ in the main stream between the head and terminus of the Gorge. These collections are not included in *Fig.* 12 as there are no data from the Bridge to function as a check.

*p*H may be very unstable and Picknett (1964, p. 57) has stated that it can be altered substantially by minute traces of other minerals in solution. Cave values in *Figs.* 13 and 14 may therefore be wholly erroneous. But they are,

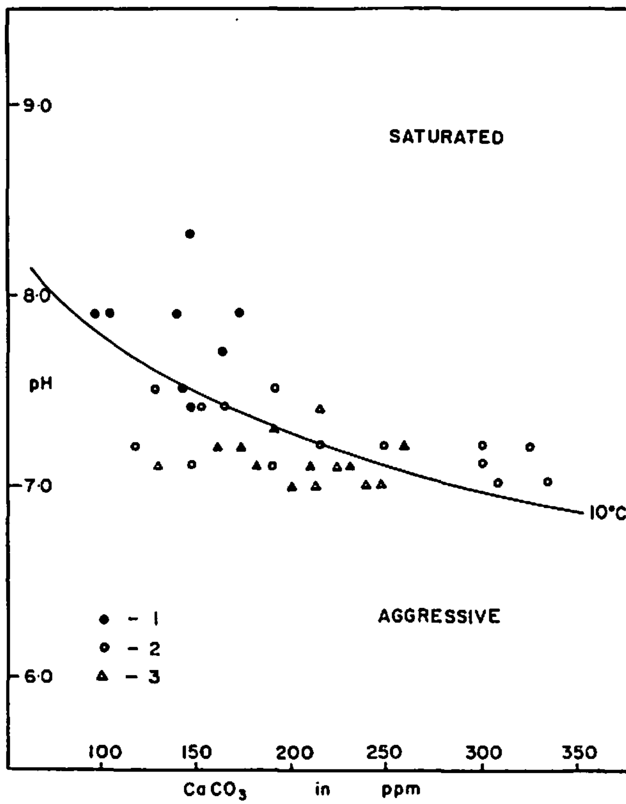

Fig. 14. Calcium carbonate in solution plotted against *p*H. (1) Drip and trickle samples in G.B. Cave. (2) Drip and trickle samples in St. Cuthbert's Swallet and Swildon's Hole. (3) Rising samples from Wells, Wookey Hole, Rodney Stoke and Cheddar.

nevertheless, included because they happen to have turned out consistent and predictable, more so than the $CaCO_3$ in solution.

The curve in *Fig.* 13 is Picknett's line of equilibrium or saturation for pure calcite in solution at 10° C. (Picknett, 1964, Pl. 47). Mendip cave waters do not deviate much from 10° C. but the calcites will rarely be pure. This line is a rough guide only.

The St. Cuthbert's and Swildon's stream waters appear very similar. The greater extent of the latter along the abscissa reflects the much greater length of stream passage that was sampled. Waters are saturated (or nearly so) at the sink but become mildly agressive when measured well inside the cave. G.B. Cave is again distinct; its waters are aggressive at the sink but then proceed rapidly towards the saturation line.

Fig. 14 compares percolating drips and trickles in caves with vigorous discharges at the risings. Most of the values cluster about Picknett's saturation line but the G.B. Cave samples stand well above it.

DISCUSSION

The main finding is that solution *may* differ markedly in different swallet caves. G.B. Cave, also studied by Smith and Mead, is the exception in a sample of three, but this does not mean that it is the exception on a regional scale. Demonstrably, swallet cave studies have not yet obtained a picture of mean conditions. This requires sampling at intervals of a very few days at a large number of sites in a cave, maintained for, say, three periods of 50 days each in the year.

If the apparent contrasts between the swallet streams of G.B. Cave, St. Cuthbert's Swallet and Swildon's Hole are correct, the following explanation may be offered:

The underground stream régimes are dominated by the nature of the surface stream crossing of the Limestone–Shales. The G.B. Cave stream crosses a narrow shale outcrop at right-angles. There is minimum exposure to the interlaminated limestones and thus little $CaCO_3$ in solution at the sink. The St. Cuthbert's stream also crosses a narrow outcrop directly but is flowing through mining dumps with much limestone in them. These may account for its intermediate values at the sink. Swildon's stream follows the strike of a broad shale outcrop where there is maximum exposure to interlaminated limestone. This hypothesis does not explain the almost equally distinctive contrasts between the percolation waters of the different caves. They are unlikely to be derived from the shales.

Smith, Mead and Nicholson have argued that cave waters are of two types—"swallet" and "percolation". The former equilibriate with normal atmospheric CO_2 and (at 10° C.) are capable of dissolving 74 p.p.m. $CaCO_3$ or a little higher. Percolation waters equilibriate with CO_2-enriched soil air and are able to dissolve much more. They supply the greater part of the discharge at the risings.

Mead (1964) discounts entirely the possibility that much of the swallet water may also be CO_2-enriched from soil air whilst it is collecting on the Sandstone or Limestone–Shale outcrops. Yet the figures for Swildon's sink indicate that such enrichment (or something indistinguishable from it) is very important. Smith and Nicholson (1964, p. 135) recognize the possibility but suggest that swallet waters lose their soil-derived CO_2 to the atmosphere whilst they flow in the surface stream channel. It is agreed that this will happen to a varying extent. But if some escape of CO_2 from water to air is allowed here, it must also be allowed when percolation waters drop below the soil, passing through the 200–600 ft. of air-filled fissures in limestone that occur above the regional water-table. The fissure air exchanges with the surface atmosphere, especially in the environs of a man-sized cave—which is the only place where fissure water can be sampled. This is to suggest that the "anaerobic solubility curve", (Smith and Mead, 1962, p. 193), cannot be wholly applied. It is not known what corrections obtain: they seem likely to vary in space and time.

Smith and Mead have reasoned from $CaCO_3$ data at the risings back through the anaerobic solubility curve and postulate that pCO_2 values in the soil (much higher than have been measured) dominate the Mendip solution pattern. Other factors need to be evaluated. CO_2-fixing bacteria in all water and "Mischungskorrosion" may be important. Very high $CaCO_3$ figures for Magnesian and Jurassic Limestone (Smith and Nicholson, 1964, p. 136) suggest that rock composition and fabric are prominent variables.

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