

The Solution of Limestone

With special reference to Mendip

By

D. INGLE SMITH, B.Sc., M.Sc., and D. G. MEAD, B.Sc.

GENERAL INTRODUCTION

It has long been realized that the erosion of limestone and in particular the formation of extensive cave systems is due to the fact that the rock is slightly soluble in water. This causes the water flowing from limestone regions to contain dissolved calcium carbonate and it is said to be "hard". Many authors have written about the solution of limestone, but a number of the accounts have been incomplete or inaccurate. Moreover, there have been very few actual measurements of the amount of limestone carried off in solution and in no case has a regular series of measurements been made over a year or more. The present paper attempts to rectify some of these omissions. It is divided into two parts. Part 1 is a detailed, and it is hoped accurate, account of the chemistry of the solution process and references are given to earlier theoretical papers on the subject. Part 2 is a presentation of some of the numerous measurements of the hardness of water samples that the authors have made. The results are discussed and comparison is made with theoretical predictions. Whilst it is shown that the theory of limestone solution by waters containing dissolved carbon dioxide is correct, it is apparent that there are many details which require further explanation. Experimental details of the titrations used to determine water hardness are given in an appendix.

Although the present paper is the result of close collaboration at all stages between the two authors, the principal contribution of D. G. M. is towards the chemical aspects and of D. I. S. to the geomorphological aspects of the account. However, both accept full responsibility for the whole of the paper.

PART I

CHEMICAL THEORY

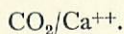
INTRODUCTION

Limestone consists for the most part of calcium carbonate (CaCO_3) present as calcite, and so the study of its solution by water is essentially the study of the solution of calcium carbonate. Various workers have measured the solubility of calcium carbonate in pure water, free from dissolved air, and

have obtained a figure of about 12 parts per million (p.p.m.) at 10° C. It is generally known, and the present work confirms the point, that most water found in caves and issuing from resurgences in limestone regions contains considerably more dissolved calcium carbonate than 12 p.p.m. The investigation of this problem forms the central theme of the work outlined below.

It is well known that limestone is soluble in acids and this has led to the idea that the water entering limestone masses might be slightly acidic in nature. Thus Bamber (1951) and Miller (1952), respectively, suggest that "humic acids" and "organic acids" in cave waters may be responsible for the high solubility of calcium carbonate. Such acids could be derived from animal and plant life of the covering soil. Another possibility that has been put forward is that the calcium carbonate may not be dissolved in the water, but may be present in the colloidal form. Bamber (1951) considers this may be of importance, while Hutchinson (1957, p. 671) believes that only a small part of the calcium carbonate is likely to be present in the colloidal form. Thirdly, it has been realized for a long time that the gas carbon dioxide (CO₂) when dissolved in water, enhances the solubility of calcium carbonate. The gas could be derived either from the atmosphere or from organic sources in the soil, or perhaps both. The importance of carbon dioxide has been recognized by many authors, for example, Adams and Swinnerton (1937), Bamber (1951), Bögli (1960), Chantry (1949), Corbel (1957), Fraipont (1951), Hutchinson (1957, p. 662), Johnston (1915), Johnston and Williamson (1916), Kendall (1912), Miller (1952), Pill (1951) and Trombe (1952, p. 207).

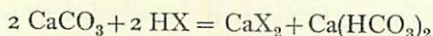
The first step in investigating the high solubility of limestone is to decide which of the three possible mechanisms (organic acids, colloidal calcium carbonate or carbon dioxide) is likely to be of importance in aiding the process of solution. It is possible to make a decision on this point by studying the water appearing at the risings and this has been done by the present authors. One part of the sample was analysed for calcium carbonate and a second part was analysed for "total carbon dioxide".* This is a measure of the total amount of carbon dioxide present in the solution in the forms of free carbon dioxide, carbonic acid, carbonate and bicarbonate (*see* p. 194). From these results it was possible to calculate the ratio by molecules:



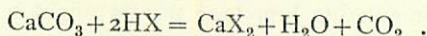
A ratio of 1 would indicate that there were equal numbers of calcium ions and carbon dioxide molecules (combined or free). This situation would arise if the limestone were present in the colloidal form, the colloidal particles being simply calcium carbonate, containing equal numbers of calcium ions

* For note on experimental method, see appendix.

and carbonate ions. If the limestone had been dissolved by an organic acid (say HX) according to the following equation:



there would be an equal number of calcium and bicarbonate ions and the ratio would be 1. However, if there were an excess of the organic acid, carbon dioxide might be expelled from solution and the overall equation would be:

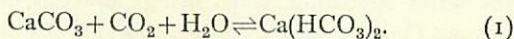


In this case there would be no carbon dioxide left in solution and the ratio would be zero. The final possibility is that carbon dioxide may have assisted solution according to equation (1) (below). In this reaction, the product is calcium bicarbonate which contains twice as many carbon dioxide molecules (present as bicarbonate ions) as calcium ions and so a ratio of 2 would be obtained.

The present results, though not as precise as the authors would wish, indicate a ratio close to 2 and this is taken as strong support for the belief that the high solubility of limestone, at least in the Mendip Hills, is due to the presence of carbon dioxide in the surface waters. The limestone is therefore present in solution as calcium bicarbonate.

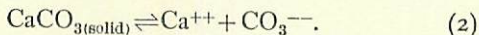
THEORY OF THE SOLUTION OF LIMESTONE BY CARBON DIOXIDE

Before discussing the origin of the carbon dioxide, it is necessary to describe the chemistry of the process of solution and in particular how the solubility of the limestone varies with differing amounts of available carbon dioxide. It will be assumed that limestone is composed entirely of calcium carbonate; whilst this is, of course, not completely accurate, it is satisfactory for the present purpose. Most papers on the subject of limestone solution quote the following equation:



Although this gives a correct indication of the reactants and products of the reaction, it tells little of how the reaction actually takes place.

The first stage in the solution process consists of calcium carbonate going into solution to give calcium ions and carbonate ions:



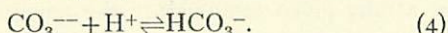
This is a reversible reaction and the position of equilibrium can be defined in terms of the solubility product k :

$$[\text{Ca}^{++}] \times [\text{CO}_3^{--}] = k, \quad (3)$$

where the square brackets indicate the concentrations of the ions concerned. And k is a constant, characteristic of calcite; it varies slightly with temperature, but is not appreciably affected by the presence of other ions in solution.

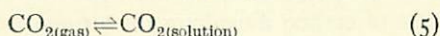
Equation (3) indicates that if carbonate ions are removed from solution to decrease $[\text{CO}_3^{--}]$, more calcium ions are produced by solution of calcium carbonate until the product of $[\text{Ca}^{++}]$ and $[\text{CO}_3^{--}]$ returns to k .

A mechanism by which carbonate ions may be used up is by their reaction with hydrogen ions (H^+) to produce bicarbonate ions:

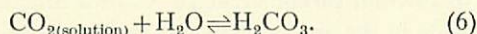


Hydrogen ions are produced by acids, so the latter are able to increase the solubility of calcium carbonate by reacting with the carbonate ions produced in the primary process (2). It is thus reasonable to suppose that if there are, for example, organic acids present in the water when it comes in contact with the limestone, more calcium carbonate will be dissolved than would be dissolved by pure water.

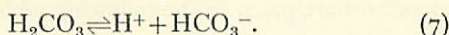
In practice the most important acid present in cave waters is carbonic acid which is derived from carbon dioxide. This gas dissolves in water:



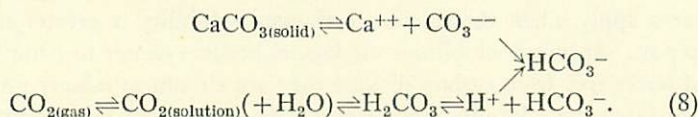
and part of it reacts with the water to give carbonic acid:



In common with all acids, it ionizes to give hydrogen ions and anions; in this case the anions are bicarbonate ions:



It is these hydrogen ions that react with the carbonate ions as described in equation (4) to increase the solubility of the calcium carbonate. The overall scheme of the process can be represented as follows:



It can be seen that bicarbonate ions are derived from two distinct sources, namely calcium carbonate and carbon dioxide, although of course, once formed, the ions from the two sources are chemically indistinguishable. It is also apparent that the carbon dioxide aids the calcium carbonate solution not because it produces an ion common to both parts of the solution process (bicarbonate ion), but because it is acidic and produces hydrogen ions. It can in fact be shown on chemical grounds that this production of a common ion is a hindrance to the solution process and that an acid of similar strength which did not itself form bicarbonate ions could cause a higher limestone solubility.

The next topic to be considered is what determines how much calcium carbonate can be dissolved by a given amount of water with the participation

of carbon dioxide. The most important variable is the concentration of dissolved carbon dioxide in solution and this depends on two factors:

- i. The percentage of carbon dioxide in the air above the water.
- ii. The temperature.

The solution of gases by water has been extensively studied and it has been found that at any given temperature the amount of gas that dissolves is proportional to the percentage of gas in the air (assuming constant atmospheric pressure—Henry's Law). It has also been found that the amount of gas dissolved decreases with increasing temperature. Applying these generalizations to the present problem, it would be expected that a low temperature and a high percentage of carbon dioxide in the air would increase the amount of carbon dioxide in solution and hence increase the amount of calcium carbonate dissolved by a given volume of water.

A variety of workers, as reviewed by Frear and Johnston (1929), have measured the solubility of calcium carbonate as a function of temperature and of percentage of carbon dioxide in the air and have found these predictions to be correct. The best available figures quoted in this review for the solubility of calcium carbonate at 10° C. as a function of the percentage of carbon dioxide in the air are shown as the "equilibrium solubility" curve in *Fig. 42*, and it can be seen that the solubility is greatly increased by the carbon dioxide. Factors for converting the solubilities at 10° C. to solubilities at other temperatures are given in the following table:

Temperature °C	0	10	20	30	50
Factor	1.28	1.00	0.78	0.64	0.43

These figures apply when the calcium carbonate solubility is greater than about 30 p.p.m. At lower solubilities the factors become nearer to 1 until in the case of water free from carbon dioxide they are all almost exactly unity.

It is seen that the solubility is somewhat increased by low temperatures. It is likely that temperature affects the solubility of calcium carbonate, not only by affecting the solubility of carbon dioxide, but also by its effect on all the other reactions. However, the factors were determined experimentally and so include all these possibilities.

An important point about the "equilibrium solubility" curve is that it is necessary for the water to be continuously in contact with air of the specified carbon dioxide content all the time that the limestone is dissolving. If this is not the case, the calcium carbonate will have a lower solubility. The reason for this can be found from a study of equation (1). This indicates that the carbon dioxide is not merely acting as a catalyst for the solution process; it actually takes part in the reaction and is used up by it. If the water is in contact with air containing the specified amount of carbon dioxide, as the

carbon dioxide in solution is used up, more dissolves from the air. In fact calcium carbonate and carbon dioxide dissolve simultaneously, each aiding the solution of the other. This goes on until equilibrium is reached, and the amount of calcium carbonate dissolved at this point is given by the "equilibrium solubility" curve as a function of the percentage of carbon dioxide in the air.

It is likely that sometimes in nature the water is not continuously in contact with air containing the specified percentage of carbon dioxide. For example, it is possible that the pure water first comes into contact with air

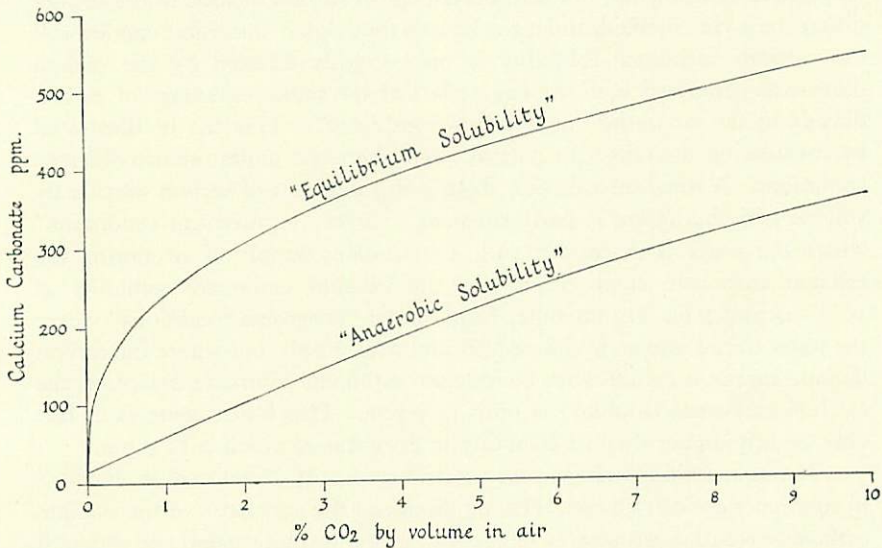


Fig. 42.—Calcium carbonate solubilities at 10°C.

containing a particular percentage of carbon dioxide then trickles into the joints and fissures in the limestone mass where there is little or no circulation of air and no continuous supply of carbon dioxide to replenish that used up by the calcium carbonate solution reaction. The calcium carbonate solubility would then be less than that indicated on the "equilibrium solubility" curve, if the relevant percentage of carbon dioxide were taken to be that of the air initially in contact with the water. From a knowledge of the solubility of carbon dioxide in pure water and the percentage of carbon dioxide in the air, it is possible to calculate the amount of carbon dioxide dissolved in the pure water at equilibrium by applying Henry's Law. It is then possible to calculate how much calcium carbonate this solution could dissolve, bearing in mind that some of the carbon dioxide remains in solution as "equilibrium CO₂" (see p. 195). The authors have calculated how much calcium carbonate may be

dissolved by water initially in contact with air containing various amounts of carbon dioxide and the results are presented as the "anaerobic solubility" curve in *Fig. 42*. As stated above, the figures are based on the assumption that once the water reaches the limestone, there is no further contact with any carbon dioxide supply.

The curves in *Fig. 42* show that for a given percentage of carbon dioxide in the air, when conditions are such that the "anaerobic solubility" curve is applicable, the calcium carbonate solubility is less than that which obtains when conditions are such that the "equilibrium solubility" curves are relevant. In particular, at low but not zero percentage of carbon dioxide in the air, the difference is very marked, and it can be seen that under "anaerobic conditions" the calcium carbonate solubility is only slightly affected by the carbon dioxide as compared with the large effect of the same percentage of carbon dioxide in the air under "equilibrium conditions". This can be illustrated by considering the effects of normal atmospheric air under the two different conditions. Normal air contains about 0.033 per cent of carbon dioxide by volume and this figure is fairly constant. Under "equilibrium conditions" where the water is in contact with a continuous supply of air during the calcium carbonate solution process, the calcium carbonate solubility at 10° C. is 74 p.p.m. On the other hand, under "anaerobic conditions" where the water comes into an initial equilibrium with the air, but where the carbon dioxide supply is cut off when the calcium carbonate solution takes place, the calcium carbonate solubility is only 14 p.p.m. This latter figure is in fact only slightly higher than its solubility in pure water, which is 12 p.p.m.

It was mentioned above that determinations of "total carbon dioxide" in solution were carried out. Having discussed the chemistry of the calcium carbonate solution process, it is possible to see in more detail the different forms in which the carbon dioxide can be present. The set of equations (8) indicate all the possibilities.

1. *Carbonate Ion* (CO_3^{--}). This is derived from calcium carbonate. A study of the solubility product equation (3) indicates that when much calcium carbonate has been dissolved and the concentration of calcium ions is high, the concentration of carbonate ions is low. In solutions containing fewer calcium ions, there are more carbonate ions present.

2. *Bicarbonate Ions* (HCO_3^-). These ions are derived from the carbon dioxide and from the calcium carbonate. Most of the "total carbon dioxide" in solution is generally present in this form and hence the limestone when dissolved is said to be in the form of calcium bicarbonate. It should be noted, however, that it is not possible to obtain solid calcium bicarbonate; it only exists in solution.

3. *Carbonic Acid* (H_2CO_3). This is formed from carbon dioxide and water, equation (6). It is never likely to be present in high concentration as

the equilibrium position in equation (6) is with the concentration of $\text{CO}_{2(\text{solution})}$ much higher than the concentration of H_2CO_3 .

4. $\text{CO}_{2(\text{solution})}$. This is carbon dioxide physically dissolved and is the only part of the "total carbon dioxide" in which carbon dioxide molecules, as such, are present. The amount present at equilibrium is uniquely determined by the percentage of carbon dioxide in the air (assuming normal atmospheric pressure) and the temperature. It does not depend on how much calcium carbonate has been dissolved.

When limestone has been dissolved and equilibrium has been established under "equilibrium conditions" (free supply of air), there is still some free carbon dioxide present in solution. The amount is equal to the carbon dioxide solubility under the prevailing conditions, where "solubility" refers to the amount of gas dissolving in water when no chemical reaction takes place. This acts as a form of "chemical buffer" preventing the series of reactions, (8), from taking place in the reverse direction. Hence this carbon dioxide is known as "equilibrium carbon dioxide". It is instructive to see what happens when the percentage of carbon dioxide in the air is changed so as to make the concentration of $\text{CO}_{2(\text{solution})}$ different from this equilibrium value. If some of the carbon dioxide is removed from solution, the buffer action is reduced and the reactions, (8), take place in reverse and calcium carbonate is deposited. However, this is a slow reaction and may take many days or even months to reach completion. On the other hand, if the concentration of carbon dioxide is increased, the reactions (8) go forward and more calcium carbonate is dissolved (assuming there is limestone present). Such a solution is said to be "aggressive" and the amount of carbon dioxide in solution above the equilibrium value is said to be "aggressive carbon dioxide".

The amount of hardness in a solution can be expressed in a number of different ways. When converting from one to another, it should be remembered that 100 p.p.m. calcium carbonate is the same as 40 p.p.m. calcium or 56 p.p.m. calcium oxide or 182 p.p.m. calcium bicarbonate. In all cases expression of the hardness in p.p.m. or mg. per litre give the same numerical value.

*p*H AND AGGRESSIVE CARBON DIOXIDE

The *p*H of a solution is a measure of its acidity or alkalinity, neutral solutions having a *p*H of 7. In acid solutions the *p*H is less than 7 and in alkaline solutions it is greater than 7. Any chemical solution of a definite composition has a definite *p*H, and in the case of a solution containing known amounts of carbon dioxide and calcium carbonate, it is possible to calculate the *p*H of the solution. Generally speaking, carbon dioxide tends to make the solution acid and calcium carbonate to make it alkaline. The *p*H of an equilibrium mixture of water, carbon dioxide and calcium carbonate depends

on the amount of the latter two reactants that have been dissolved. The solution is generally approximately neutral, but becomes slightly more acid as more carbon dioxide and calcium carbonate dissolve to produce a more concentrated equilibrium mixture. For example, water with 250 p.p.m. calcium carbonate and an equilibrium amount of carbon dioxide has a pH of 7.4 (Trombe, 1952, p. 232). However, if there is an excess of carbon dioxide or calcium carbonate the solution is respectively more acid or more alkaline than the equilibrium mixture, and this property can be of diagnostic value. For example, if the solution is found to be more acid than would be the case with a solution of the same calcium carbonate content at equilibrium, then it can be concluded that there is an excess of carbon dioxide and the solution is therefore aggressive. Thus the possible aggressiveness of a solution can be determined by measuring its pH instead of by a direct measurement of aggressive carbon dioxide which is more difficult experimentally. Both methods, of course, require a knowledge of the calcium carbonate content of the solution under investigation.

As far as the authors are aware, no one has previously made a direct determination of total carbon dioxide in order to calculate the amount of aggressive carbon dioxide in cave waters, but several attempts have been made to employ pH determinations to assess the aggressiveness of such waters. The authors found that collecting samples in a cave and bringing them back to the laboratory for pH determination gave unreliable results and it is considered that the only satisfactory method would be to measure the pH of the water in its natural environment with a portable glass electrode pH meter. It is hoped to do this in the near future. Colour indicators are unlikely to be sufficiently accurate, particularly under poor lighting conditions in a cave.

THE RATE OF THE SOLUTION PROCESS

Discussion has so far been centred on the position of equilibrium in the solution process and not on how rapidly it is attained. The fact that extensive cave systems develop at all in limestone indicates that the solution process is not particularly rapid; if it were, the water would become immediately saturated on reaching the limestone and would have no aggressive power left to dissolve calcium carbonate when it reached lower levels. At a given temperature, the rate of solution probably depends on a variety of factors. One of the most important is likely to be the degree of turbulence of the water, greater turbulence causing more rapid solution (Weyl, 1958). If uptake of carbon dioxide from the air is the rate determining step, then the degree of turbulence of the air and water at the air/water interface would affect the rate. When comparison is made between the rates of limestone solution in different parts of the world, an important variable is likely to be the temperature. This may range from $0^{\circ}C$. in arctic conditions to over $40^{\circ}C$. under

tropical conditions and this would cause a large change in the rate of solution. As a rule of thumb, it is often stated that the rate of a chemical reaction doubles for every 10° C. rise in temperature, which indicates a sixteenfold increase in reaction rate on going from 0° to 40° C. As far as the authors are aware, no detailed laboratory study has been made on this topic and so no more reliable estimate of the effect of temperature on solution rate is available at present.

It was found in the present work that the temperature of the risings and of most of the samples taken in G.B. Cave varied only between 9° and 10.5° C. throughout the year and so the effect of temperature as a variable has not been considered. However, in comparing our results with those of a climatically different area, it would be necessary to bear in mind a possible difference in prevailing temperature between the two regions and a consequent differing solution rate.

PART 2

DISCUSSION OF RESULTS

Geomorphologists have expressed interest in the landforms associated with limestone for many years. Indeed, W. M. Davis early recognized the uniqueness of limestone scenery. In his writings he makes specific reference to the effects that the solubility of limestone has on the evolution of karstic landforms. The writings of geomorphologists have, however, been dominantly of a qualitative nature, concerned essentially with the description of landforms associated with the karstic cycle. Few have attempted to assess quantitatively the manner in which these landforms have been produced. Similarly, studies concerning the evolution of cave systems are frequently descriptive and theoretical. Since the work of Davis, geomorphologists have been preoccupied with the establishment of the various stages in the karstic cycle rather than with the processes by which landforms themselves are formed. Because the dominant erosive processes acting in limestone areas are closely connected with the fact that water, particularly when rich in carbon dioxide, is capable of dissolving limestone, it is possible from an analysis of water samples to obtain quantitative information as to manner and rate of the solution processes that are active.

The results outlined below are based upon the analysis of approximately a thousand water samples collected over a period of some fifteen months from a variety of sites on and around the Mendip Hills. The emphasis has been upon regular sampling from carefully chosen sites in order to assess the variations in the amount of limestone which is carried off in solution. Other workers who have made similar analyses have frequently based their observations upon the results obtained from random samples rather than repeated sampling from the same locality (e.g., Sweeting and Gerstenhauer, 1960; Corbel, 1957). This random method has frequently been forced upon these

authors by the fact that they did not reside in the location from which the samples were obtained. A study of the available literature suggests that the only really comparable study to the work here described was that of Roques (1959) and in this instance the samples were collected for the summer period only and the relationships of dissolved limestone to water discharge conditions were not given.

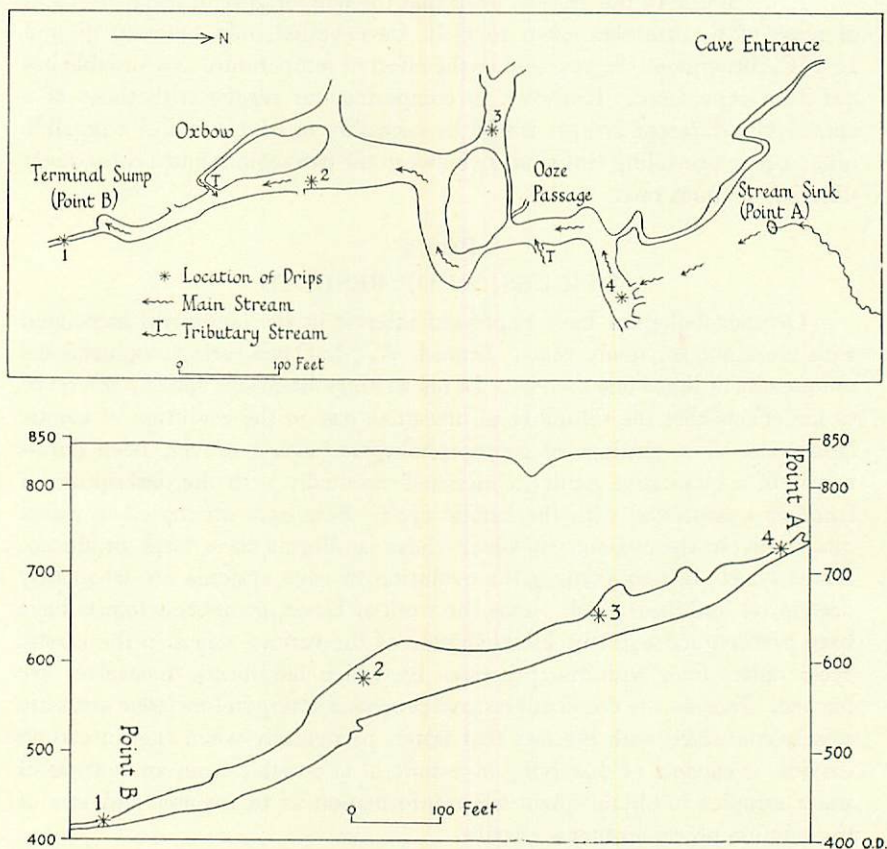


Fig. 43.—Side elevation and plan of the gorge in G.B. Cave.
(After Crickmay and Bendall, 1951.)

OBSERVATIONS ON G.B. CAVE

The underground samples referred to in this paper were collected from G.B. Cave. This particular cave was selected since it involved the minimum of spelæological difficulty in the collection of the samples and has been surveyed to an accuracy of C.R.G. grade 6-7 (Crickmay and Bendall, 1951). Samples were collected from the stream sink (point A, Fig. 43) and from the same

stream at its lowest point in the cave (point B), the terminal sump. The samples were collected on the same day and within an hour or so of each other. Also at the time of collection of the surface sample the discharge of the entrance stream was noted. An approximate value for the discharge of this small surface stream was obtained by measuring the velocity and depth of the water flowing in a stream cross-section of known dimensions. Since

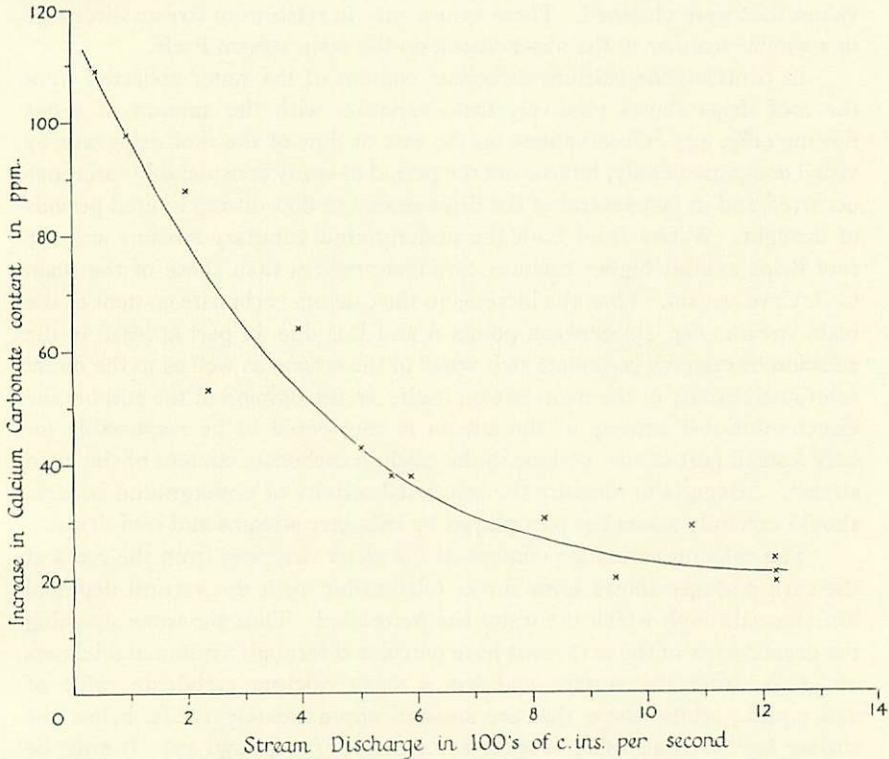


Fig. 44.—Difference in calcium carbonate content between points A and B as a function of stream discharge.

the stream was small, measurements of discharge obtained in this way should not be taken as indicating anything but a relative value. On all occasions the sample from B showed a higher value for dissolved calcium carbonate than A. The difference between the values obtained at A and B varied according to the stream discharge (*Fig. 44*). It can be seen that this difference in calcium carbonate content varied inversely with the stream discharge.

It is apparent that the water at B does not consist solely of surface water that had previously passed point A, since, during periods of drought, the

surface stream dries up completely (*Fig. 45*) whilst throughout the period of study the stream at B continued to flow. The water that is added to the subterranean section of the stream comes from two sources, (*a*) from underground stream tributaries, "stream water", and (*b*) from drips issuing from the roofs of underground cave passages or "percolation water". Observations on the underground tributary streams are given in *Fig. 46* and these demonstrate the considerable fluctuations in the calcium carbonate values that were obtained. These values vary in relation to stream discharge in a similar manner to the observations on the main stream itself.

In contrast, the calcium carbonate content of the water collected from the roof drips shows relatively little variation with the amount of water flowing (*Fig. 47*). Observations on the rate of flow of the roof drips was by visual comparison only, but during the period of study considerable variations occurred and in fact several of the drips ceased to flow during limited periods of drought. Waters from both the underground tributary streams and the roof drips exhibit higher calcium carbonate figures than those of the main G.B. Cave stream. Thus the increase in the calcium carbonate content of the main stream (*Fig. 45*) between points A and B is due, in part at least, to the addition of calcium carbonate rich water to the stream as well as to the direct solutational activity of the main stream itself. In the opinion of the authors the direct solutational activity of the stream is considered to be responsible for only a small part of the increase in the calcium carbonate content of the main stream. Attempts to measure the solutational activity of underground streams should carefully assess the part played by tributary streams and roof drips.

The calcium carbonate content of the water dripping from the roofs of the cave passages shows some direct relationship with the vertical depth of limestone through which the water has percolated. Thus the water reaching the deeper parts of the cave must have percolated through a minimal thickness of 440 ft. from the surface and has a mean calcium carbonate value of 240 p.p.m., whilst those that are situated approximately 120 ft. below the surface have a mean value of some 120 p.p.m. (*Figs. 43 and 47*). It must be stressed, however, that the water dripping from the roof of the cave need not necessarily have taken the shortest path from the ground surface above nor need the speed of flow of the drips be strictly comparable. But bearing in mind these factors a rough correlation exists between the calcium carbonate content of the water from the drips and the distance from the ground surface to the point from which the water falls from the cave roof. This strongly suggests that the drips in the shallower parts of the cave are not saturated with calcium carbonate in respect of the carbon dioxide content of the water forming the drips. The heights of both the ground surface and the roofs of the cave passages are taken from the G.B. Cave survey (Crickmay and Bendall, 1951), the location of the drips sampled is given in *Fig. 43, (1-4)*.

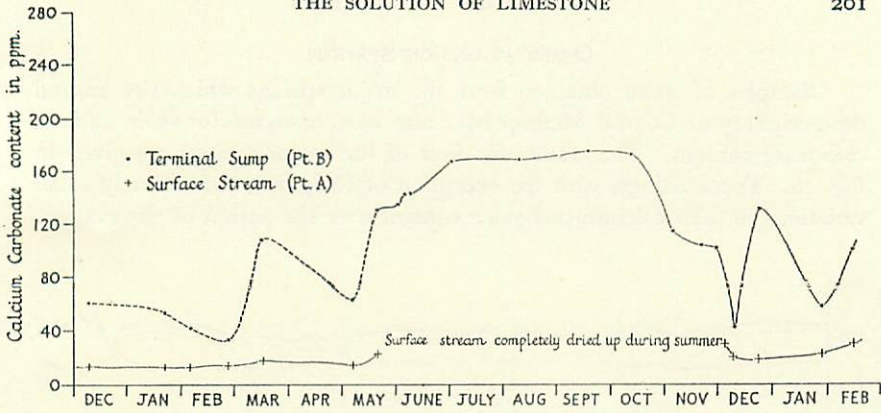


Fig. 45.—Calcium carbonate content of the G.B. Cave stream at points A and B.

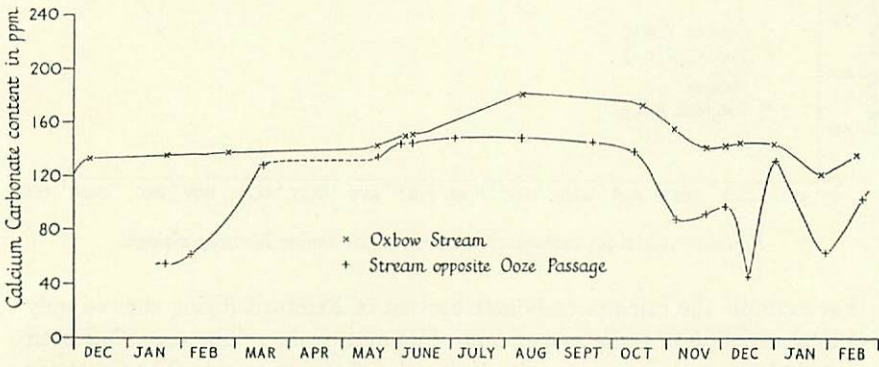


Fig. 46.—Calcium carbonate content of two underground tributary streams.

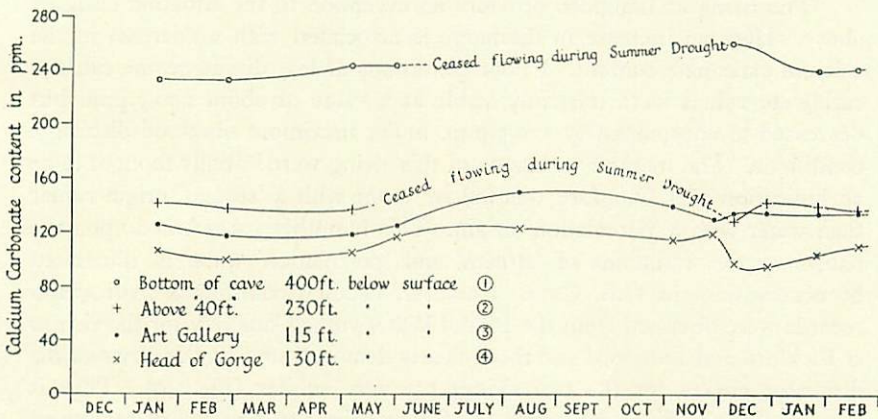


Fig. 47.—Calcium carbonate content of selected drips.
The dates in all the figures are from Dec. 1960 to Feb. 1962.

OBSERVATIONS ON SPRINGS

Samples of water obtained from the major springs which rise around the periphery of Central Mendip have also been analysed for their calcium carbonate content. The results for four of the major springs are given in *Fig. 48*. These risings, with the exception of Langford, showed only small variations in their calcium carbonate content over the period of observation.

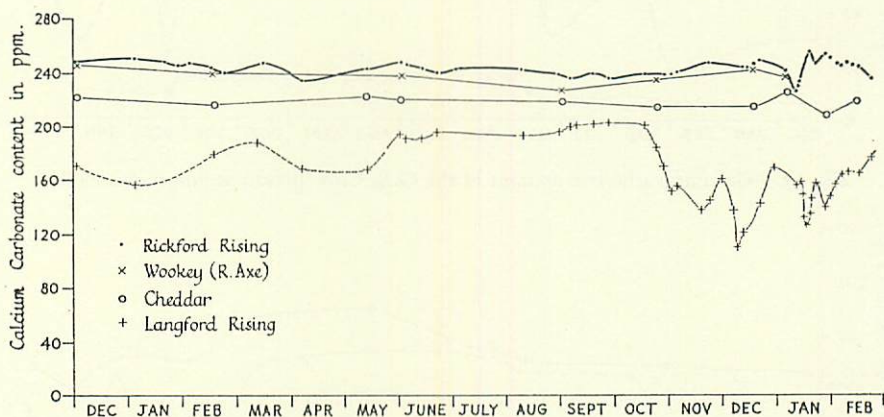


Fig. 48.—Calcium carbonate content of the major Mendip risings.

For example the calcium carbonate content of Rickford Rising showed only a total variation of some 11 per cent of its mean value. The rising has been sampled on some sixty occasions during the period of study. The figure for the risings at Cheddar and Wookey Hole (R. Axe) showed similar variations to these more detailed observations at Rickford.

The rising at Langford provides an exception to the situation outlined above. Here an increase in discharge is associated with a decrease in the calcium carbonate content. Under conditions of low discharge the calcium carbonate values were relatively stable at a value of about 200 p.p.m. but decreased to approximately 120 p.p.m. under maximum observed discharge conditions. The marked variations of this rising were initially thought to be an indication that Langford was fed by water with a 'stream' origin rather than water with a 'percolation' origin. This hypothesis was based upon the nature of the variations of 'stream' and 'percolation' water as illustrated by observations in G.B. Cave. However, detailed continuous hydrograph records were obtained from the Bristol Waterworks Company for the risings at Rickford and Langford and these clearly demonstrate that the forms of the discharge curves for the two risings are very similar (*Fig. 49*). Thus it appears that the discharge response of both risings to a period of prolonged

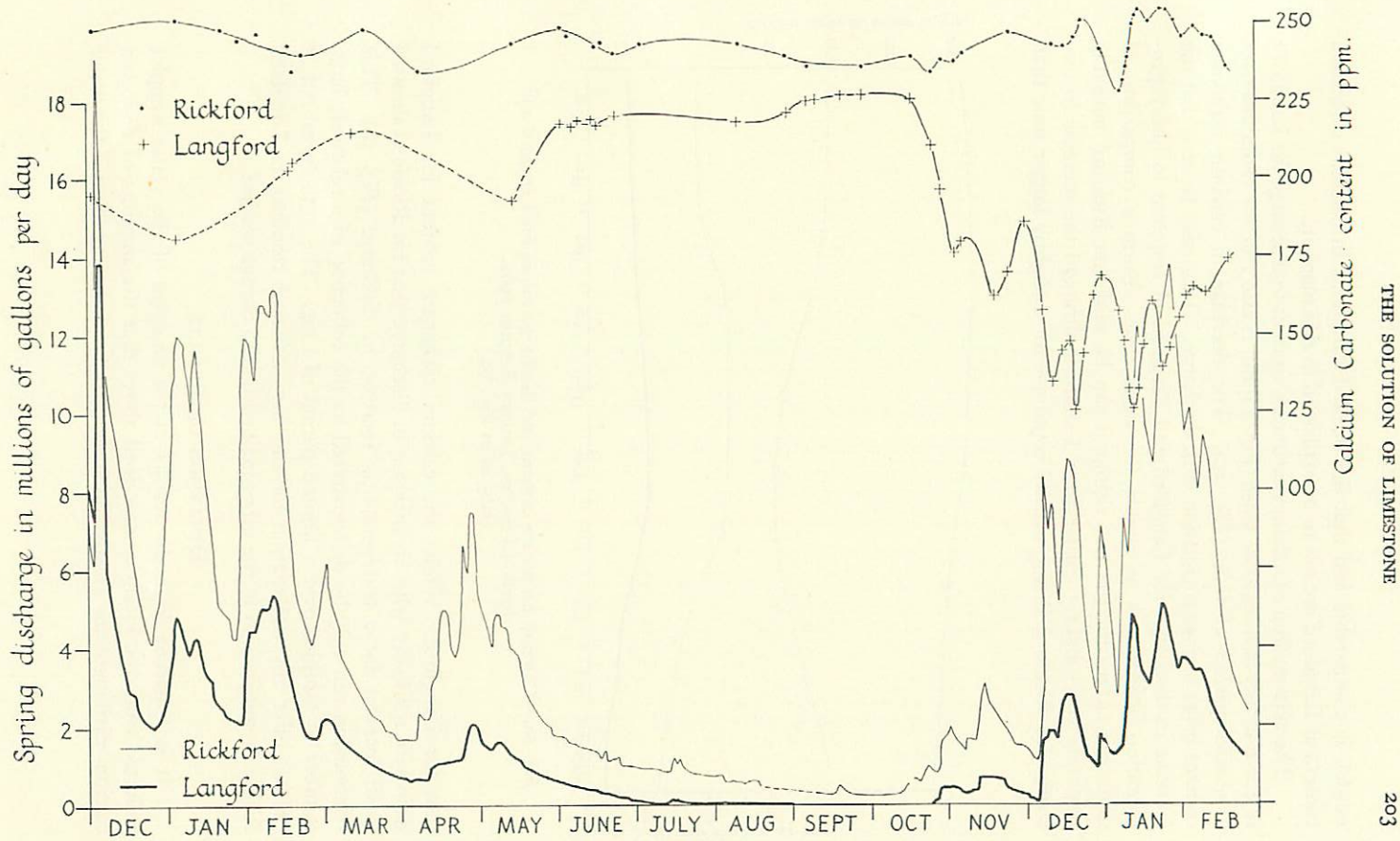


Fig. 49.—Calcium carbonate content and discharge values for Langford and Rickford risings.

rainfall is comparable and that the marked variations in calcium carbonate content at Langford are not to be explained in this manner.

The relationship of calcium carbonate content to discharge for Langford is true not only in a seasonal sense (*Fig. 49*) but is also true for variations over a smaller period of time (*Fig. 50*). The decrease in calcium carbonate content bears a close correlation with discharge. It can also be seen that the increase in discharge for Langford and Rickford in response to heavy precipitation commences at almost the same time. From a comparison of discharge curves for the two risings it can be said that Rickford normally responds very slightly earlier than Langford although the increase in discharge for Rickford Rising usually continues for a slightly longer time than

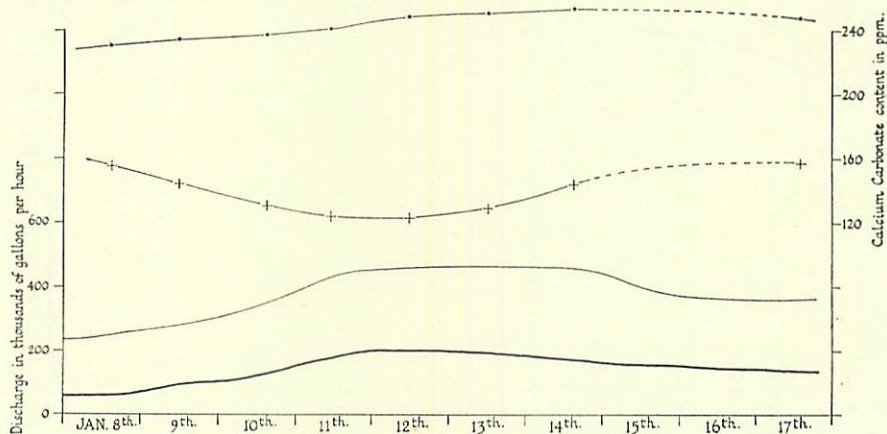


Fig. 50.—Calcium carbonate content and discharge values for Langford and Rickford risings, January 8–17th, 1962. (Key as in *Fig. 49*.)

that for Langford. Whilst the calcium carbonate content for Langford decreases markedly with an increase in discharge that for Rickford shows a small increase for a corresponding increase in discharge (*Fig. 50*). This relationship can only be demonstrated by the collection of a relatively large number of samples over a limited period of time. The authors cannot at present offer any explanation for the very different response of Langford Rising in comparison to the other major Mendip risings studied.

DISCUSSION OF RESULTS

It is apparent from the results of the analyses of the water samples collected from the localities described above that the amounts of dissolved calcium carbonate are greatly in excess of those to be expected if the water

responsible for the solution initially contained carbon dioxide derived only from the free atmosphere (*Fig. 42*). Adams and Swinnerton (1937) were the first to draw attention to the fact that the carbon dioxide content of the air within the soil was very much higher than that of the atmosphere itself and that this higher carbon dioxide content was responsible for the large quantities of calcium carbonate carried off in solution from limestone areas. No figures are available for the carbon dioxide content of Mendip soils but by utilizing the published figures for soil carbon dioxide from areas of comparable climate and vegetation cover some interesting facts emerge. Russell (1950, Table 78, p. 340) gives soil carbon dioxide figures from which it is clear that particularly high carbon dioxide concentrations are to be expected under a "grassland cover". The surface of Mendip taken as a whole falls within this classification and most certainly the ground overlying G.B. Cave is grass covered. The mean figure given by Russell for the carbon dioxide content of the soil air associated with a grass cover is 1.6 per cent, i.e., a figure some fifty times greater than the atmospheric value. From *Fig. 42* this carbon dioxide, under "equilibrium" conditions, would be sufficient to dissolve some 280 p.p.m. calcium carbonate at 10° C. A large number of measurements show that the subterranean temperatures of the caves on Mendip and of the risings remain at about 10° C. regardless of season.

This figure of 280 p.p.m. accords remarkably closely to the observed values of the calcium carbonate content of water at the risings. Further it has been shown experimentally that the water at the risings has a "total carbon dioxide" value that demonstrates the water to be saturated with calcium carbonate in respect of the available carbon dioxide. These findings provide field corroboration of the views expressed by Adams and Swinnerton.

However, other aspects of the fieldwork demonstrate that this relatively simple relationship of observed calcium carbonate content and soil carbon dioxide content, even allowing for some inaccuracy in the figures used for the soil carbon dioxide, may not give a completely reliable picture.

First, the process of solution is thought to be by water passing through the soil and establishing a carbon dioxide content in equilibrium with that of the soil air and then the carbon-dioxide enriched water passing out of the soil into the fissures and joints of the bedrock. In this case the "anaerobic solubility" curve is more applicable than the "equilibrium solubility" curve. Thus from *Fig. 42*, the amount of calcium carbonate that would be dissolved at 10° C. is 84 p.p.m. The higher values that are observed in practice may indicate that the carbon dioxide content of the soil air is considerably in excess of the 1.6 per cent assumed as a reasonable figure for the Mendip soils. It would certainly seem a reasonable supposition that "anaerobic" conditions are to be expected in the joints and fissures in the bedrock through which the water percolates.

Secondly, the analyses of the cave drips (*Fig. 47*) tentatively indicate that the depths through which the water containing carbon dioxide from the soil air has percolated bears a direct relationship to the amount of calcium carbonate dissolved. The inference here is that the drips at shallow depths with values of about 120 p.p.m. still contain "aggressive carbon dioxide" and given sufficient time the calcium carbonate content of the water would increase still further. Thus the drips from the deepest parts of G.B. Cave exhibit values of 240 p.p.m. calcium carbonate, this water having percolated through a considerably greater thickness of limestone. The similarity of this value to that of the water at the risings tentatively indicates that the drips at the deepest parts of the cave are saturated with respect to the carbon dioxide content of the water. It should be noted that if the "anaerobic solubility" curve is applicable to these drips then the initial carbon dioxide content must be much greater than that assumed from a study of Russell's work. No absolute figures for the speed of percolation have been obtained but it seems that the speed of solution suggested by Bögli (1960, *Fig. 5*, p. 9) from theoretical considerations is too rapid. Bögli considers that the bulk of the solution of limestone by carbon dioxide rich water takes place within a period of less than an hour and will be virtually complete within sixty hours, although Bögli is considering the part played by solution in the formation of surface Karren forms. Qualitative observations on the response of the rate of flow of the G.B. Cave roof drips to precipitation suggest that this rate does not apply in the case studied. The authors are of the opinion that the time necessary for the water flowing in joints and fissures to reach equilibrium with the dissolved carbon dioxide should be thought of in terms of days rather than hours.

A third difficulty of the relatively simple picture outlined by Adams and Swinnerton is the lack of any marked seasonal variation in the amounts of dissolved calcium carbonate going off in solution. This is apparent from the analyses of the drips (*Fig. 47*) which shows a total variation of only some 15 per cent over the period of observation. This lack of seasonal variation is even more readily seen from the figures for dissolved calcium carbonate obtained from the risings (*Fig. 48*). However, in the theory of limestone solution outlined above, the amount of limestone that can be dissolved is dependent on the amount of carbon dioxide in the soil. All published works on soil air (e.g., Russell and Appleyard, 1915; Boynton and Compton, 1944) stress seasonal variation in the carbon dioxide content and so one would accordingly expect a seasonal variation in the calcium carbonate content of the water from the risings. The varying amount of carbon dioxide in the soil is due to a varying level of activity during the year of various plant and microbacteriological processes which produce the carbon dioxide.

A possible explanation of this anomaly between theory and observation may be due to the soil depth from which the samples of soil air were obtained by the workers mentioned above. Boynton and Compton produce graphs which show the variations of soil carbon dioxide throughout the year obtained from samples taken at different soil depths. The maximum depth considered by these authors is 5 ft. whilst the results of Russell and Appleyard are from shallower depths. It is possible that seasonal amplitude of these variations in carbon dioxide content will decrease with depth in the soil until at the base of the soil horizons the values will not exhibit a marked seasonal variation. To confirm this suggestion further field observation is clearly needed. The present state of knowledge is succinctly put by Boynton and Compton (1944, p. 114) in the following quotation: "The carbon dioxide percentage was higher in gas from the heavier subsoils than in gas from the sandy loam subsoil and increased with depth . . . for a given soil and depth, the maximum percentages of carbon dioxide seemed to occur during mid-summer."

A fourth problem concerns the fact that after a period of rain the discharge of the risings increases within a matter of several hours but (with the exception of Langford) the calcium carbonate content of the water shows only a minor change (*Fig. 48*). Thus the additional water issuing from the risings after the rain must also be saturated with calcium carbonate but if the additional water has only recently fallen as rainwater the observations on the drips suggest that insufficient time would have elapsed for the carbon dioxide enriched soil water to have percolated down to depth and to have become saturated with calcium carbonate. This difficulty may be resolved by suggesting that the water flow is at depth and that recently fallen rainwater causes water already saturated to be expelled from the risings. However, the method of water flow necessary to give this result is difficult to envisage. In fact it would seem that the situation at Langford with a decrease in calcium carbonate content corresponding to an increase in discharge conditions represents most closely the expected conditions and that the other risings represent a situation that is more difficult to explain! The results given by Roques (1959) for summer observations of calcium carbonate content for various risings in the French Causse concur with the results for the majority of the major Mendip risings.

Despite these difficulties it is clear that the ideas of Adams and Swinerton concerning the importance of carbon dioxide from the soil air in the solution of limestone are acceptable. In fact they provide the only simple answer to the question of the origin of the large quantities of calcium carbonate carried off in solution from limestone areas. Preliminary observations of the quantity of calcium carbonate present in springs in other West Country limestone areas show the results to be significantly different from

those from Mendip. Detailed observations from a selection of risings associated with the Cotswold escarpment to the north of Bath show a calcium carbonate value considerably higher than that for the Mendip risings. The mean figures for the Cotswolds is 290 p.p.m. compared to 235 p.p.m. for Mendip. All the Cotswold springs sampled gave higher results than those obtained from any Mendip rising. This is not to be explained by differences in the nature of the water flow through these limestones of rather contrasting types. It is considered that the answer to this is probably to be found in differences of soil type associated with the two limestone areas, the difference in soil type affecting the amount of carbon dioxide present in the soil air. It is hoped to extend the work outlined above to include a study of the reasons for the variations of calcium carbonate content of waters associated with limestone areas of varying geological types.

The water samples collected from the various sites mentioned above have also been analysed for magnesium carbonate content. However, for both the Mendip and Cotswold regions the magnesium carbonate content of the waters represents only a small proportion of the total hardness, normally between 5 and 10 per cent of the calcium carbonate figure. Therefore discussion has been limited to the calcium carbonate figures alone.

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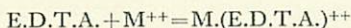
APPENDIX

E.D.T.A. TITRATIONS

As the titrations form the basis of the quantitative aspects of the present work, a description of them is given below. A full account of the theory and practice of E.D.T.A. titrations is given by Schwarzenbach (1957)* and the present methods are based on this account.

Theory

The titrations rely on the unique properties of E.D.T.A. (ethylene-diamine tetra-acetic acid). This is a colourless organic substance which is a strong complexing agent for metal ions in aqueous solution: that is, it reacts with them to form a complex compound:



where M⁺⁺ is a divalent metal ion. As the complexes are soluble and also colourless, there is no visible change in the solution when the reaction takes place, and so it is necessary to follow the course of the reaction with a so-called metal indicator. These are soluble dyes whose colour depends on whether or not specific metal ions are present in solution. This is only true, however, if the solution is buffered to the correct pH. Thus, as E.D.T.A. solution is added to a suitably buffered solution containing metal ions and the appropriate metal indicator, the colour suddenly changes at the end-point when all the metal ions have been complexed with E.D.T.A. From the amount of E.D.T.A. required to cause the colour change, the concentration of the metal ion originally present in the water sample can be calculated.

Two different titrations were employed:

- i. A titration to give the calcium ion (Ca⁺⁺) concentration. From the result, the calcium carbonate content was calculated.
- ii. A titration to give the sum of the calcium ion and the magnesium ion (Mg⁺⁺) concentrations. This result with that of (i) on another part of the same water sample was used to calculate the magnesium carbonate content.

Procedure

Titration (i) for Ca⁺⁺. 100 ml. of the water sample to be examined was measured out exactly in a measuring cylinder and placed in a 250-ml. conical flask that had been rinsed with distilled water. About 2 ml. of the pH 12 (*see below*) buffer solution was added to the flask and was followed by a few drops of the ammonium purpurate indicator, which gave the solution a reddish-purple colour. The titration was then carried out by adding 0.025 molar E.D.T.A. from a 25-ml. burette until the colour had changed to a pure mauve without any trace of red. When doing this, it was helpful to compare the sample being titrated with one containing similar solutions but with

* Schwarzenbach, G., 1957, *Complexometric Titrations* (trans. and revised by H. Irving), p. 132. London.

excess E.D.T.A. The volume (V_1) of E.D.T.A. required to reach the end-point was read off from the burette. The calcium carbonate content of the original water sample was then given by:

$$\text{CaCO}_3 \text{ content} = 25 \times V_1 \text{ parts per million (p.p.m.)}$$

where V_1 is in ml.

Titration (ii) for $\text{Ca}^{++} + \text{Mg}^{++}$ (standard method). This titration was carried out in a manner similar to the previous one, except that the 2 ml. of pH 12 buffer was replaced by the same amount of pH 10 buffer and the ammonium purpurate indicator was replaced by a few drops of Erio-T indicator. The colour change in this case was from red to blue and the last trace of red vanished at the end-point. If V_2 was the volume in ml. of E.D.T.A. required to reach this end-point, then the so-called "total hardness" of the water sample was given by:

$$\text{Total hardness} = 25 \times V_2 \text{ p.p.m.}$$

expressed in p.p.m. CaCO_3 (i.e., the water had the same hardness as one containing $25 \times V_2$ p.p.m. calcium carbonate).

From the results of titrations (i) and (ii) on different parts of the same water sample, the magnesium carbonate content was calculated as follows:

$$\text{MgCO}_3 \text{ content} = 21.1 \times (V_2 - V_1) \text{ p.p.m.}$$

It is not possible from a single E.D.T.A. titration to obtain directly the magnesium carbonate content of the sample, so if the latter is required, it is necessary to carry out the two titrations described above.

Titration (ii) for $\text{Ca}^{++} + \text{Mg}^{++}$ (improved method). It was found that titration (ii) carried out by the standard method did not give reliable or reproducible results when examining fairly hard water samples (total hardness above 100 p.p.m. CaCO_3): in particular, it was sometimes found that the volume of E.D.T.A. required for titration (ii) was less than that required for titration (i) ($V_2 < V_1$) and this indicated a negative amount of magnesium carbonate, which was plainly impossible. Two other symptoms of trouble were a cloudiness in the solution after adding the pH 10 buffer, and a gradual reversion of the solution colour to red after it had achieved the end-point colour of blue. These observations suggested that the trouble was caused by precipitation of part of the calcium carbonate by the alkaline buffer, and an alternative procedure was devised which prevented this from taking place.

It was first necessary to carry out titration (i) on one part of the water sample in the usual way, in order to get an idea of the approximate value to be expected for V_2 , ($V_2 \approx V_1$). The second 100 ml. part of the water sample was then placed in a flask and a volume of E.D.T.A. about 1 ml. less than V_1 was added from the burette. At this stage the normal amount of pH 10 buffer and Erio-T indicator were added, and the titration completed by adding more E.D.T.A. from the burette until the end-point was reached. V_2 was then the total volume of E.D.T.A. added from the burette in the two parts of the titration, and the calculation was exactly as before.

The use of this improved method for fairly hard water samples gave reproducible results and in no case was a "negative value" for the magnesium carbonate content encountered. It was therefore considered more reliable than the standard method. It should be added that no difficulty of this kind was found with the calcium carbonate titration (i) and the authors believe that the standard method is satisfactory even for hard water samples (up to 350 p.p.m. calcium carbonate).

ACCURACY OF THE RESULTS

It is estimated that each titration should be accurate to within ∓ 3 p.p.m. However, the constancy of some of the magnesium carbonate content results indicates that they are probably more accurate than this figure suggests.

PREPARATION OF SOLUTIONS

Buffer pH 12

This is an approximately 2 N solution of sodium hydroxide. It is made up by dissolving about 80 g. of sodium hydroxide in 1,000 ml. of water. The solution keeps indefinitely in a stoppered bottle.

Buffer pH 10

This is made up by dissolving 70 g. of ammonium chloride in 570 ml. of concentrated ammonia (S.G. = 0.880) and making the solution up to 1,000 ml. with water. This solution keeps indefinitely in a stoppered bottle.

E.D.T.A.

(This is an abbreviation for the Disodium salt of ethylene-diamine tetra-acetic acid dihydrate). The 0.025 molar solution is made up by dissolving 9.306 g. of E.D.T.A. in water and making up to exactly 1,000 ml. in a graduated flask. The solution should be kept in a stoppered borosilicate (e.g., Pyrex) vessel and keeps indefinitely.

Ammonium Purpurate Indicator Solution

This is made up by dissolving 0.02 g. of solid in 10 ml. of water. (The exact strength of the solution is not at all critical.) The solution does not keep and should be made up fresh for each batch of titrations.

Erio-T Indicator

This is the same strength as the ammonium purpurate solution except that it is made up in absolute alcohol, not water. The solution keeps for several months. (Again the exact strength is not at all critical.)

In all cases distilled water rather than tap water should be used and all the reagents should be pure.

An alternative method of obtaining the solutions is to purchase them ready made up. The British Drug Houses Ltd. (B.D.H.) market a pack containing all the necessary chemicals either made up as a concentrated stock solution or as pellets of known weight. The kit is specially prepared for water hardness determinations and contains full instructions for its use. The use of such a pack removes the need for an accurate chemical balance.

"TOTAL CARBON DIOXIDE" DETERMINATIONS

As the procedure for the determination of the total carbon dioxide content of the water samples is not at present sufficiently accurate, it is not intended to describe it in any detail. However, the method consists of acidifying a known volume of the sample and boiling to expel all the carbon dioxide, which is then passed into a U-tube containing soda-lime, where it is absorbed. The increase in weight of the soda-lime gives, directly, the total amount of carbon dioxide in the water sample.