SOME GEOCHEMICAL ASPECTS OF LIMESTONE SOLUTION

by

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Introduction

The last two decades have seen great advances in our knowledge of the origin and development of caves, due largely to the increasing application of quantitative scientific methods to their study. The purpose of this paper is to introduce a few of these more important recent advances to a wider audience of Australian speleologists. My approach will be to first review the basic information essential to any understanding of limestone solution, then to use this information in discussing four aspects of the geochemistry of limestone solution.

Basic Geochemistry of Limestone Solution

For the purposes of this discussion we will restrict ourselves to solution caves formed in limestone. For simplicity limestone will be considered to be pure calcium carbonate ($CaCO_3$), and all calcium carbonate will be considered to be in the form of calcite.

The components which are generally of most importance in limestone solution are calcium carbonate, water, and carbon dioxide (CO_2).

(a) The system $CaCO_3$-H_2O

To what extent is pure water capable of dissolving limestone? Although pure water does not occur in nature, the question is of interest as it indicates how important other components are in dissolving limestone to form caves. Bogli (1960) quotes the following figures:

10 parts per million $CaCO_3$ at 8.7°C
13.1 " " " $CaCO_3$ at 16°C
14.3 " " " $CaCO_3$ at 25°C

From thermodynamic data Garrels and Christ (1965) calculate a value of 12.6 p.p.m. at 25°C. Thus pure water is capable of dissolving a small though significant amount of limestone, and the amount increases with increasing temperature.

(b) The system H_2O-CO_2

Carbon dioxide occurs in the atmosphere to the extent of about 0.03%, or 3 x 10^{-4} atmospheres pressure. Thus natural waters always contain some carbon dioxide dissolved as an impurity. Much higher concentrations can occur in air contained in soil. There is a straight line relationship between the pressure of carbon dioxide in the gas phase, and the concentration dissolved in the water when equilibrium has been reached. As is always the case for gases, the solubility decreases with increase in temperature (see Figure 1).

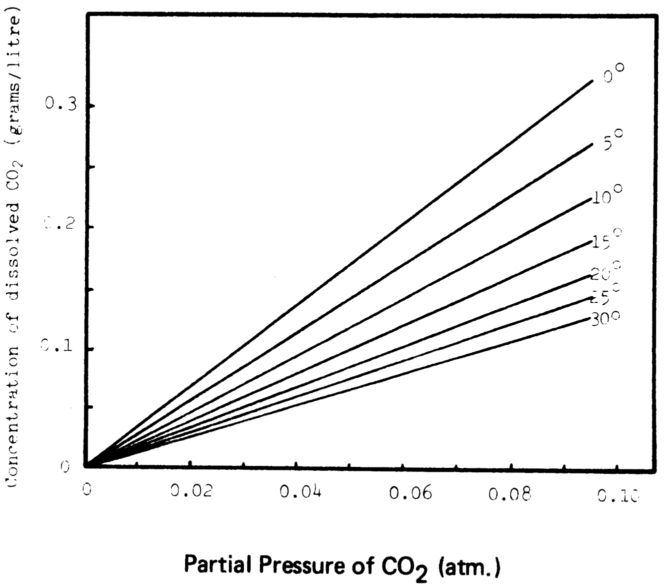


Figure 1 – Relationship between concentration of CO_2 dissolved in water and CO_2 pressure in the gas phase for temperatures between 0° and 30°C. (Modified after Holland et al. 1964)

(c) The system $CaCO_3$-H_2O-CO_2

For this system we must consider two possible situations, one where it remains open to its atmosphere after the addition of the limestone, and another where it is closed.

When calcium carbonate is placed in water containing dissolved carbon dioxide, it dissolves to a much greater extent than it would have had it been placed in pure water. This is because the water and carbon dioxide react with the carbonate ions in the calcium carbonate, converting them to bicarbonate ions.

$$CO_3^{2-} + CO_2 + H_2O \rightleftharpoons 2HCO_3^-$$

This causes more limestone to dissolve until the concentration of calcium and carbonate ions required by its solubility product is reached. As well as allowing more limestone to dissolve, this also allows more carbon dioxide to dissolve. If the system is closed to its atmosphere before the limestone is added, however, no more carbon dioxide is available to take part in further reaction. If we consider the situation at 25°C and for the normal atmospheric partial pressure of carbon dioxide, then according to Garrels and Christ (1965) only 14.1 p.p.m. of calcium carbonate will dissolve, which is very little more than dissolved in pure water (12.6 p.p.m.). If, however, the system is left open to its atmosphere with a fixed partial pressure of carbon dioxide, more carbon dioxide is available to dissolve and react with the calcium carbonate. The result is that much more calcium carbonate dissolves. For the same temperature and carbon dioxide pressure as above, 39.8 p.p.m. of calcium carbonate will be dissolved at equilibrium, or approximately three times that which would have dissolved in pure water (Garrels and Christ, 1965). For any given partial pressure of carbon dioxide the lower the temperature the higher the solubility of calcium carbonate (see Figure 2), and for any given temperature the higher the partial pressure of carbon dioxide the higher the solubility of calcium carbonate (see Figure 3).

Figure 3 clearly illustrates the two situations discussed above. If limestone is placed in water in equilibrium with and open to an atmosphere containing a constant partial pressure of carbon dioxide, the concentration of calcium carbonate in solution will increase until an equilibrium concentration is reached. The path the changing composition will follow at 10°C is shown by the dotted line in Figure 3, where carbon dioxide pressures of 0.1 and 0.01 atmospheres (10^{-1} and 10^{-2} atm.) are shown as examples. If the limestone is placed in water which is in equilibrium with, but no longer open to, an atmosphere with a given partial pressure of carbon dioxide, then in this case the path the changing composition will follow is shown by the dashed line in Figure 3. Clearly the amount of calcium carbonate finally dissolved in this case is much less than for the open system.

Both these situations are important in cave formation. The closed system occurs when water flows into completely filled cave passages, and the open system occurs whenever water is simultaneously in contact with both limestone and a carbon dioxide containing atmosphere, whether this be normal air, or the interstitial atmosphere contained in soil.

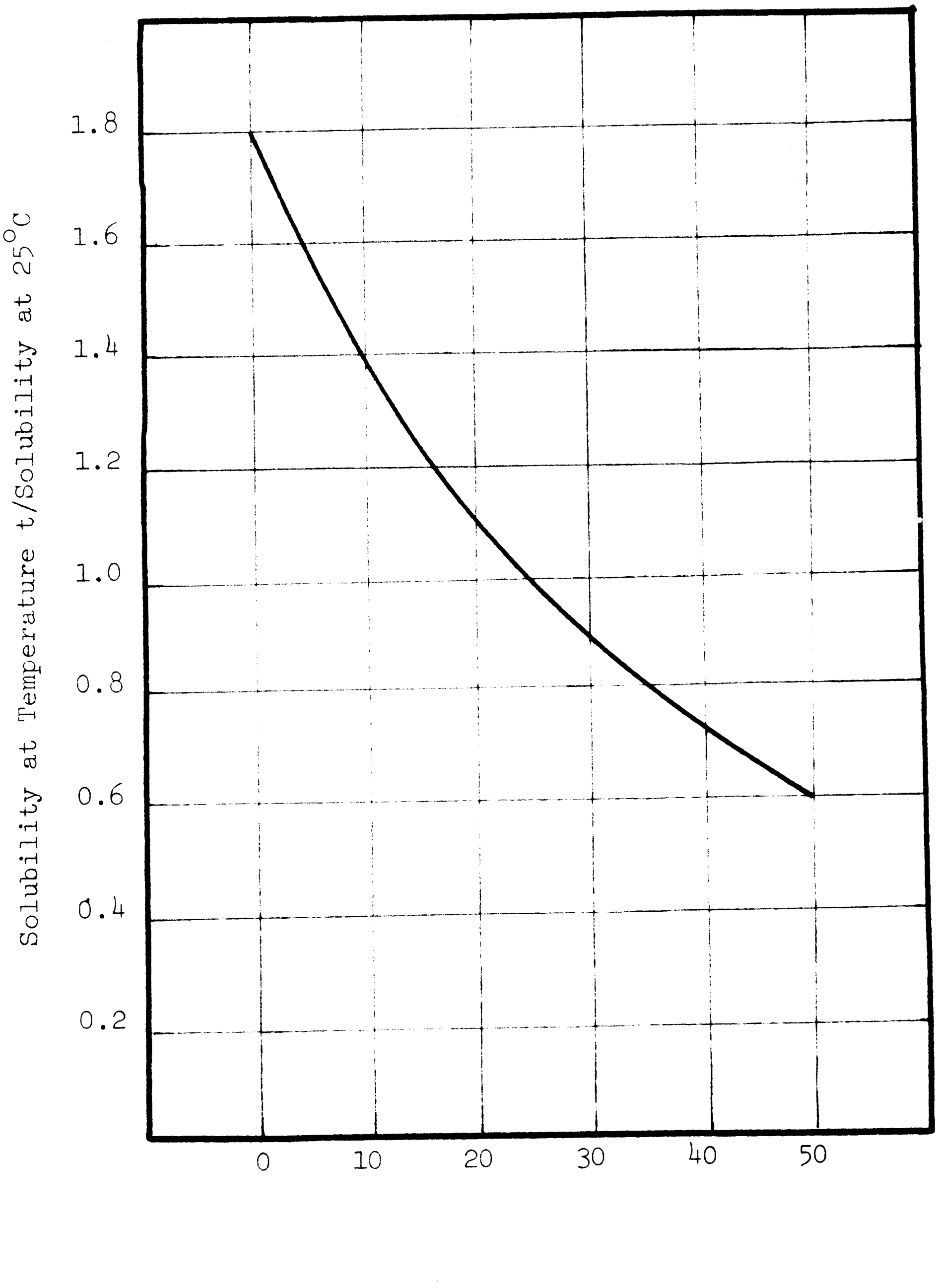
The Mixing Effect

This phenomenon, also known as mixing corrosion or "mischungskorrosion", was first pointed out by Bogli in 1963. The basic concept is extremely simple, and it is amazing that it had not been appreciated before.

As noted above, for a given temperature the amount of calcium carbonate which will dissolve in water depends on the pressure of carbon dioxide. This is usually shown by means of a graph of calcium carbonate concentration versus carbon dioxide pressure. The three types of graph used are shown in Figure 4 (a - c). The first of these is probably the most common (Figure 4a). The two ordinates are both plotted on logarithmic scales, and the resulting graph is a straight line. The second (Figure 4b) is identical to that shown in Figure 3, where the vertical scale is linear, and the horizontal scale is logarithmic. This produces a curve which is concave upwards. The third type of plot, shown in Figure 4c, is not commonly used. In this case both ordinates are linear, and the resulting curve is concave downwards. It is this graph which is of importance in understanding the mixing effect. The same graph is shown in greater detail in Figure 5.

In Figure 5 all waters with compositions which plot in the field below the curve are undersaturated with calcite at their particular carbon dioxide pressure, and will be aggressive towards limestone. Similarly, all waters with compositions which plot in the field above the curve are supersaturated with calcite, and will tend to deposit it. If we take two points A and B on the curve, then these represent two waters, both saturated with calcite at a particular carbon dioxide pressure. If we mix solution A with solution B, then all the possible compositions which can be formed by mixing the two solutions in any proportions, are represented by the straight line joining A and B on the graph. Note that this line always lies in the undersaturated field. Thus even though solutions A and B are both saturated with calcite, mixtures of them are not, and hence are capable of dissolving more calcite. This is what is known as the "mixing effect".

The precise amount of undersaturation produced by mixing two given solutions is difficult to determine, however Thrailkill (1968) shows that the greatest total undersaturation (undersaturation per unit volume times total volume) will occur when the volume of solution A is much greater than that of solution B (probably about 30 times greater). There are several circumstances which would tend to counteract the mixing effect. These are discussed by Thrailkill (1968), who examines the magnitude of the mixing effect, and shows that, given favourable conditions, the mixing effect is clearly capable of playing a major role in cave formation.



Temperature t (°C)

Figure 2 – Effect of temperature on solubility of calcite in water in the presence of atmospheric CO_2. (Hem, 1959)

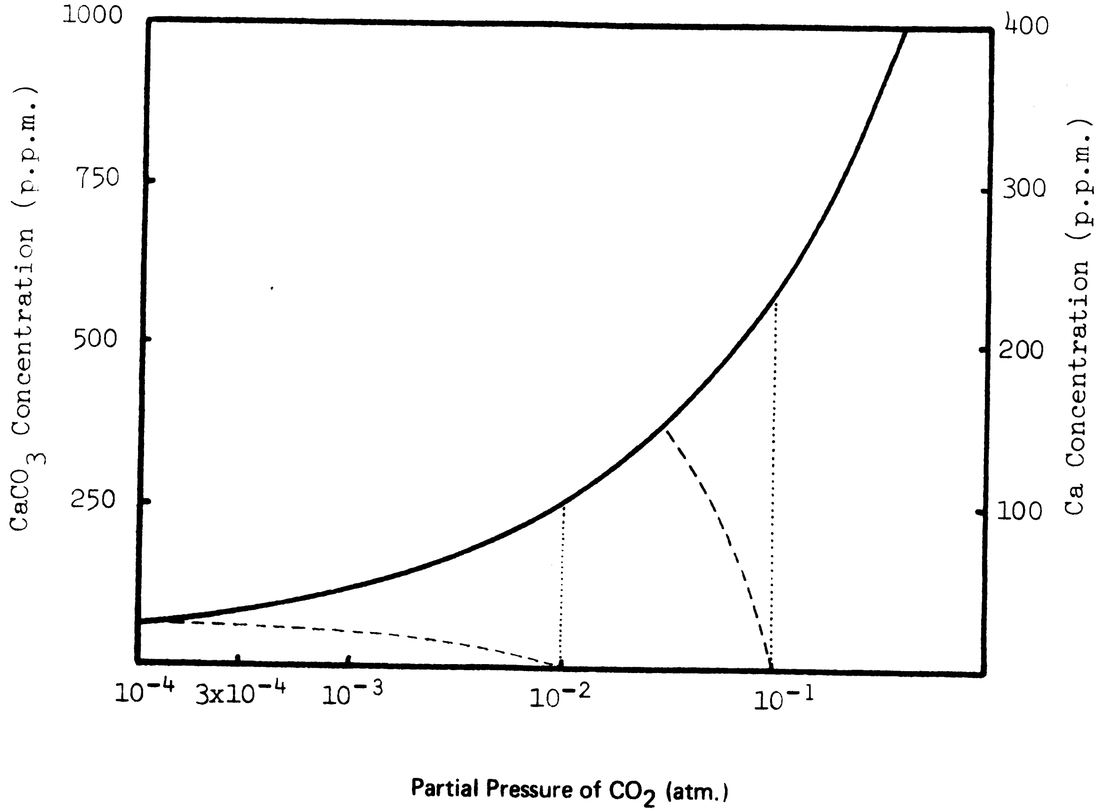


Figure 3 – Changes in composition of carbonated water during equilibration with calcite at 10°C in the presence (dotted lines) and absence (dashed lines) of a vapour phase. See text.

(Modified after Holland et al, 1964)

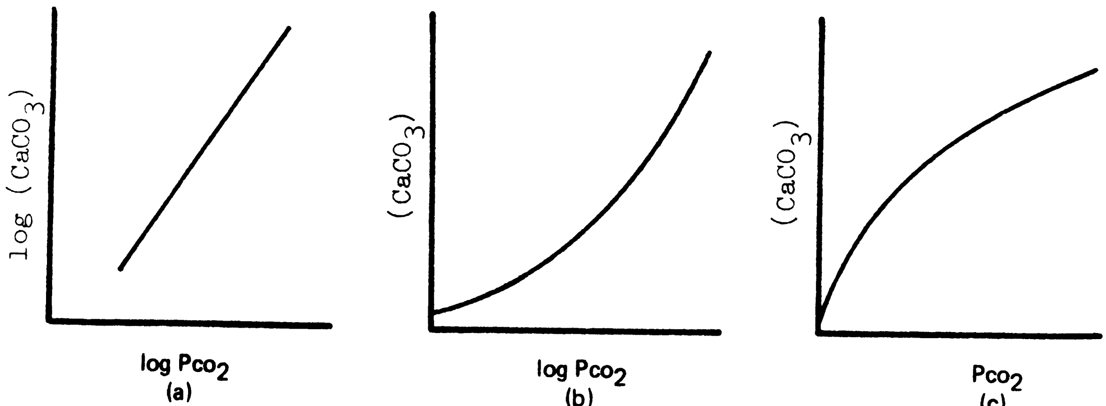


Figure 4 – Standard forms of calcite saturation diagrams. (a) log - log (b) semi-log (c) linear See text.

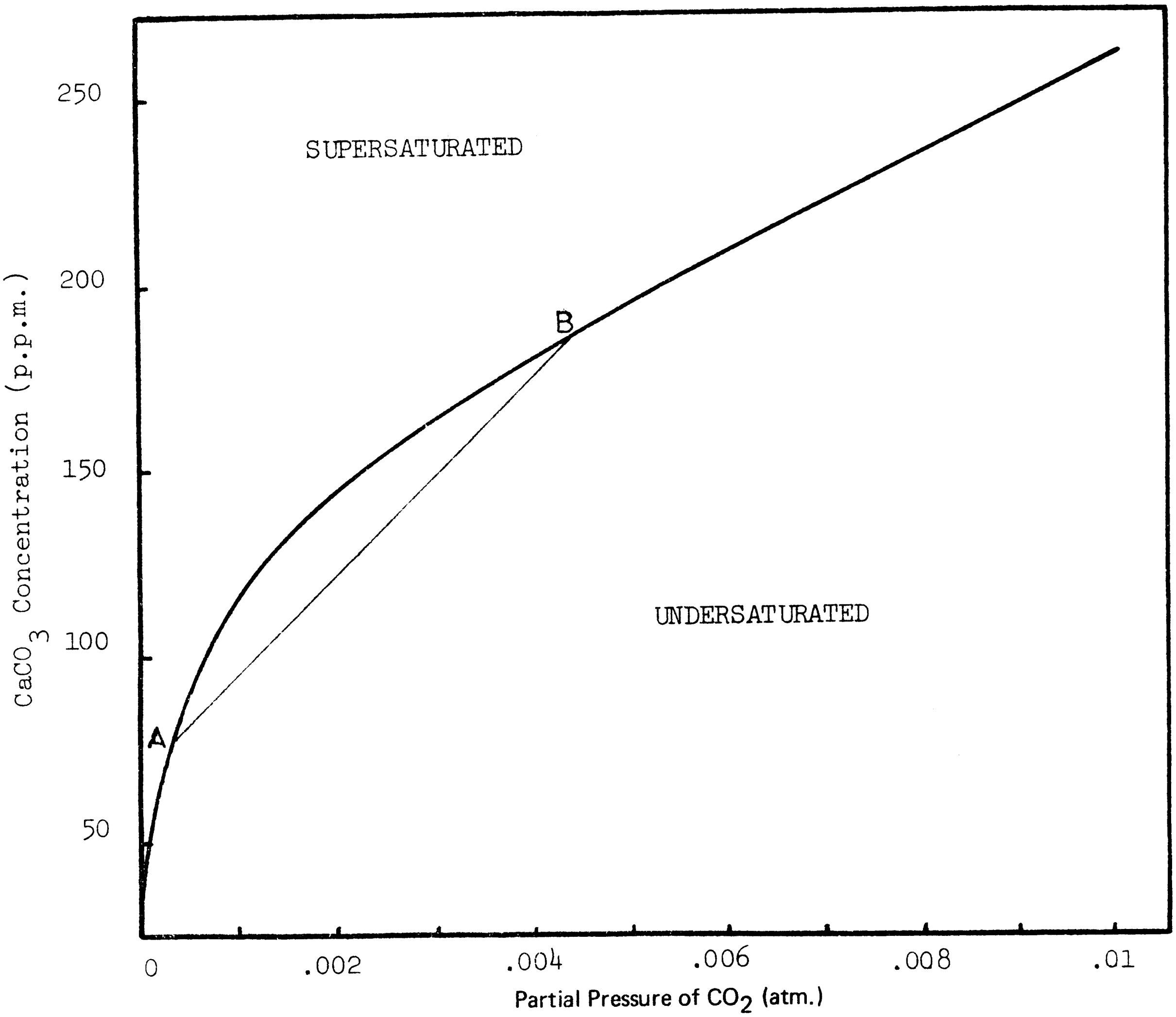


Figure 5 – Solubility of calcite in water at 10°C in the presence of carbon dioxide. See text for explanation.

The mixing effect is probably most important when vadose seepage water mixes with shallow phreatic water. The resulting solution probably explains the common occurrence of horizontal cave systems, apparently formed when completely filled with water, where horizontal geological control is absent (Bogli, 1964).

The Temperature Effect

In (c) above it was noted that for a given partial pressure of carbon dioxide, the lower the temperature the higher the solubility of calcium carbonate (see Figure 2). Hence if water saturated with calcite is cooled, it can then dissolve more calcite, provided that it is still in contact with its atmosphere.

During summer, water infiltrating into limestone may be several degrees warmer than the ground-water body. As it passes through the rock it approaches the rock temperature, and gains additional aggressive power as it cools. Thrailkill (1968) shows that the aggressive power of water, in contact with normal atmospheric carbon dioxide pressure, is appreciably increased by cooling as little as 1C°. It would appear, therefore, that cooling is a likely mechanism for cave excavation, assuming the system is open to a carbon dioxide pressure at least equal to that of the normal atmosphere.

As for the mixing effect, there are several circumstances which may tend to counteract any undersaturation caused by cooling. The kinetics of limestone solution are more favourable then deposition, however, so that even if the net result is no temperature change, or even warming, the temperature effect may still be an effective process in the excavation of caves.

Flow

The chemical process of limestone solution is profoundly influenced by physical conditions. Apart from pressure and temperature, whose influence is obvious, the rate of flow of water in a cave has been considered important by a number of workers. In general, the higher the flow rate the greater the agitation, and agitation favours solution of a solute. This is simply illustrated by the fact that sugar dissolves more rapidly in a cup of tea if it is agitated by stirring.

Kaye (1957) published results of a series of simple experiments which demonstrated clearly that solvent motion is an important factor in limestone solution. When relating his results to cave development he concluded:

> "By comparing the similarity of the plexus of tabular openings of a typical limestone aquifer with an integrated system of tubes filled with water, it can be seen that the velocity of ground-water movement below the water table varies considerably, both from one conduit to another, and within conduits, depending on the role played by the different conduits in draining the system. Because solution rate is affected by relative movement of solvent and limestone, fast-flowing conduits enlarge preferentially over slow-flowing feeder conduits. In consequence a system of openings that were initially all of the same width develops into one of various widths. This certainly must be considered a factor in the solution of large limestone caverns". (Kaye, 1957, p.45)

Another aspect of the influence of flow on cave development was investigated by Weyl (1958). He started with a porous limestone and calculated how far water would penetrate before becoming 90% saturated with calcite. He considered water flowing by laminar flow under gravity down a vertical capillary of given radius. For a radius of 0.02 mm he showed that there is virtually no penetration, while a capillary of 0.25 mm radius permits a penetration of over 1 metre. When the size of the capillary increases to about 1 mm radius turbulence sets in, but by this time penetration is about 500 metres. He also calculated that a fracture will be equivalent to a capillary with radius 0.82 times the width of the fracture, a result which is no doubt more relevant when we are concerned with non-porous limestones.

This particular interest of Weyl's figures is that they show that water can be aggressive after penetrating very considerable distances underground. This is in marked contrast to the conclusion of Bogli (1964), but is to some extent supported by analyses by Back and Hanshaw (1970).

Humic Acids

Many authors have commented on the possible role of humic acids in limestone solution, but in the absence of experimental work have been unable to evaluate their role. Humic acids are extremely complex organic chamicals which are refractory residues in the decay of vegetable matter.

Murray and Love (1929) considered the effects of various low molecular weight acids which occur in plants or are formed by their decay, and they carried out a series of rather naive experiments involving fermentation of leaves. They concluded that "Bacterial action, through formation of organic acids, must be much more effective in making limestones porous than atmospheric carbon dioxide". (Murray and Love, 1929, p.1475). They also comment in their abstract:

> "Experimental evidence shows that, under favorable conditions, these acids may be the most effective solvents of limestone that exist in nature". (Murray and Love, 1929, p.1467)

Although I know of no other work which has been pbulished as yet, further work is presently being done on the geological role of humic acids. This is being done by Mr W. Baker of the Tasmanian Mines Department, Hobart, who at my request ran limestone and dolomite in his apparatus with 0.1% humic acid solution at 25°C. For comparison he also ran them under the same conditions with water saturated with carbon dioxide (closed system). For both limestone and dolomite the 0.1% humic acid solution was approximately three times as effective a solvent as the saturated solution of carbon dioxide, and the limestone dissolved to about twice the extent of dolomite (W. Baker, 1970, pers. comm.).

In another experiment (Baker, 1971, pers. comm.) the solubility of calcite in 0.1% humic acid solution was compared with its solubility under identical conditions in water through which air was bubbled, i.e. an open system with atmospheric partial pressure of carbon dioxide. In this case the humic acid solution was approximately nine times more effective a solvent than the water (10.250 grams calcite compared to 1.175 grams).

A 0.1% humic acid solution is much stronger than would normally be encountered in nature, however humic acids are such potent chemicals that even at much lower concentrations they clearly have a significant role to play. Visitors to western Tasmania will have noticed the characteristic "cold tea" colour of creek water there. This is caused by dissolved humic acids. In this same area the limestone is recessive and usually covered by buttongrass swamps. This is probably due in part to strong solution of the limestone by waters carrying much dissolved humic acid.

The four aspects of the geochemistry of limestone solution considered above are four which I consider important, and generally inadequately known to Australian speleologists. The mixing and temperature effects are especially important as they allow water to gain extra aggressive ability where it will do the most good in forming caves – deep below the surface. The mixing effect also allows a plausible explanation of an otherwise inexplicable phenomenon, the common occurrence of horizontal caves of shallow phreatic origin. Flow phenomena are easily overlooked, but are probably of great importance, particularly in the very early stages of cave development. Very little is known of the influence of humic acids, however it seems probable that in some areas, such as western Tasmania, their influence may be strong.

Much attention has been given to the study of the carbonate minerals, so that a wealth of data is available in the geological and chemical literature. Despite this we seem only now to be getting a reasonable understanding of the geochemical processes operative in forming caves. A proper appreciation of the complexities of the interactions of these processes, however, still seems far off.

Acknowledgments

Permission from W. Baker to publish results of his work on humic acids is gratefully acknowledged. Thanks are due to A. Goede and E. Hamilton-Smith for helpful criticism of the manuscript.

References

Back, W. and Hanshaw, B.B. (1970) Comparison of chemical hydrogeology of the carbonate peninsulas of Florida and Yucatan. *Jour. Hydrology* 10, 330-368.

Bogli, A. (1960) Kalklosung und Karrenbildung: Zeitschrift fur Geomorphologie. Supplement Volume 2. *Internationale Beitrage zur Karstmorphologie*, 4-21.

———— (1963) Beitrag zur Entstehung von Karsthohlen. *Die Hohle* 14, 63-68

———— (1964) Mischungskorrosion – ein Beitrag zum Verkarstungs-problem. *Erdkunde* 18, 83-92.

Garrels, R.M. and Christ, C.L. (1965) Solutions, minerals, and equilibria. Harper and Row.

Hem, J.D. (1959) Study and interpretation of the chemical characteristics of natural water. *U.S.G.S. Water-Supply Paper 1473*

Holland, H.D., Kirsipu, T.V., Heubner, J.S., and Oxburgh, U.M. (1964) On some aspects of the chemical evolution of cave waters. *Jour. Geology* 72, 36-67.

Kaye, C.A. (1957) The effect of solvent motion on limestone solution. *Jour. Geology* 65, 35-46.

Murray, A.N., and Love, W.W. (1929) Action of organic acids on limestone. *Bull. Am. Assoc. Petroleum Geologists* 13, 1467-1475.

Thrailkill, J. (1968) Chemical and hydrologic factors in the excavation of limestone caves. *Geol. Soc. Amer. Bull.* 79, 19-46.

Weyl, P.K. (1958) The solution kinetics of calcite. *Jour. Geology* 66, 163-176.

DISCUSSION

Q *With respect to the work that has been done on the distance that water can travel through a conduit before it becomes saturated – you mentioned that beyond a diameter of perhaps one millimeter the water becomes turbulent therefore the theoretical data starts to break down. Does this turbulence therefore increase the solubility per unit distance and shorten the distance that the water will travel before it becomes saturated?*

A With the change in flow from laminar to turbulent or D'Arcy flow it would increase the turbulence and hence shorten the distance – presumably.

Q *Does this phenomenon of mixture corrosion require water to be under hydraulic head or can it have a free air surface?*

A It will occur in either case. The presence of an air surface would increase the undersaturation. Consider the situation. You have your two bodies of water mixing under air. Having mixed they are capable of dissolving more limestone, but by virtue of the air being present some of its carbon dioxide content will be able to dissolve and hence increase the aggressiveness of the water. So you get solution of the limestone aided by the presence of extra carbon dioxide.

Q *Let's say you have got two saturated solutions, one carrying say 120 p.p.m. and another carrying say 30 p.p.m. How many extra parts per million can the mixed solution take up? I am trying to get this as a kind of measure of the quantitative effectiveness of mixing corrosion.*

A You're pulling figures out of the air and it is very difficult to calculate and certainly not the thing to figure out in my head. Thrailkill actually calculated the effect of mixing corrosion in terms of his "standard undersaturation". At any rate it would probably be easier to glance through his paper later on. Nevertheless in terms of his "standard undersaturation" it is very much greater than the temperature effect. It is very significant.

Q *Noel, you were talking about the formation of the initial cavity and I heard a paper in which it was claimed that cave enlargement was caused mainly during flood pulses, or are you just talking about the initial capillary stage?*

A I'm not only concerned with the initial capillary stage but with cave enlargement as well. The role of flood flow is dealt with by Thrailkill but I chose not to discuss this as one of the aspects presented.

Q *Do you know if anyone has done any sequential measurements of pH as you pass down say a swallet? Presumably the pH ought to become steadily less acid. Starting perhaps with humic acid in the water are any measurements being done on this?*

A You are concerned with the role of humic acids in this?

Q *Well, carbon dioxide would be affecting it too.*

A Consider just humic acids.

C *They would be moving from, well pH 3.5 is the lowest I have found with humic acids and that is an English figure.*

A That would be an average figure.

Q *Do you think it gets as low as that here?*

A What I recall from Bill Baker's solutions, he has gone to great pains to remove stray cations and anions so that it was only humic acid and I think that it had a pH of that order.

Q *How do you determine saturation? Do you use a conductivity meter?*

A In Baker's experiments with humic acids there is no attempt to determine the saturation. The runs were done for a given time. Actually when you get saturation calcium humates precipitate, so actually what you are concerned with is not what the saturation value is but how much it is capable of dissolving in a certain time.

Q *It seems to me that you'd get some idea of the activity of the water by taking a series of pH readings as it goes down. Has it been done?*

A I question that you would learn a great deal from this because you are dealing with very dilute solutions of humic acids perhaps between .01 and .001%, so that probably the pH differences are going to be less than your natural variation anyway, so that it would be difficult to find any particular trend. Also of course under normal conditions you have water from different sources coming in.

C *I did a bit of playing around with pH measurements but we found they weren't accurate. But it will give you some indication of how long the water has been underground and which is going to where, and it might give some additional information which is easier to obtain than by using fluorescein. I have some figures if anyone is interested.*

A I'm inclined to think that you are dealing with such a complex system that the interactions are way beyond our understanding as yet. You are trying to single out one effect from the net result of many things interacting.

C *pH has been found not to be particularly useful because it is strongly affected by changes of temperature as well. There is no set pH at which a solution becomes saturated. What is rather useful is to use a pH meter and then add finely ground limestone to the mixture and measure the pH again and get the difference between a reading where the solution is saturated and a reading where the solution is undersaturated.*