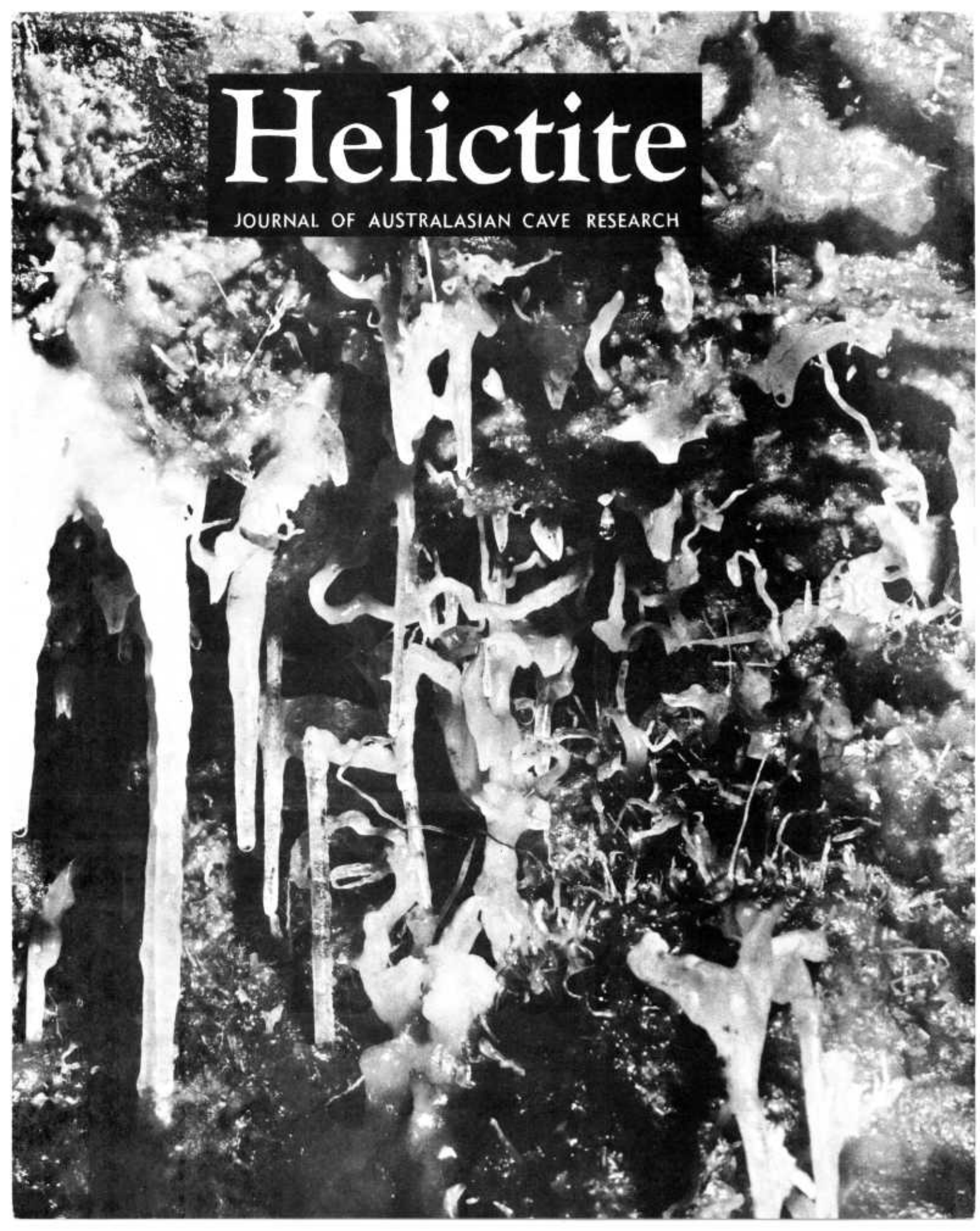


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NEW SPELEOLOGICAL JOURNAL

Studies in Speleology is the annual journal of the Association of the William Pengelly Cave Research Centre, United Kingdom. This association, administered from London, was founded in December, 1962, for the furtherance of cave study, conservation and research. The first issue of the journal which appeared in July, 1964, contains articles from many parts of the world on cave areas and fauna.

The publication is well produced and illustrated with numerous photographs and maps. A high standard has been set, and it is to be hoped that this can be maintained. The cost of the journal is Estr 1 a year for members of the association, and £1.5.0 for non-members. Enquiries should be addressed to M.A. Rennie Esq., Hon. Membership Secretary, Association of the P.C.R.C., 40 Bradley Gardens, Ealing, London, W 13, U.K.

NEW DEEP CAVE IN NEW ZEALAND

New Zealand speleologists in December, 1964, reached the bottom of a pothole near Mt. Owen, southwest of Nelson, South Island. The depth of the chasm, estimated by ladder pitches, is 925 ft making it the second deepest cave in New Zealand. The pot was descended almost entirely by wire ladder. The deepest cave in N.Z. is Harwood Hole, Takaka Hill, northwest of Nelson. It is almost 1,300 ft deep. Both caves occur in Mt. Arthur marble, but are widely separated. The expedition was lead and organised by the Nelson Speleological Group and included members of several other N.Z. caving societies.

ERRATA

The last two references in the paper "Calcium and Magnesium in Karst Waters", by Mr. I. Douglas, were accidentally left out during the typing of this issue. See page 36.

YANET'EVA, O.K. 1954 : Solubility of Dolomite in Water in the Presence of Carbon Dioxide. Izvest. Akad. Nauk. S.S.S.R., Otdel. Khim. Nauk, 1954 : 1119 - 1120.

YANAT'EVA, O.K. 1955 : Solubility in the System $\text{CaCO}_3\text{-MgCO}_3\text{-H}_2\text{O}$ at Various Temperatures and CO_2 Pressures. Zhurn Obskhei Khim., 25 : 234 - 237.

CALCIUM AND MAGNESIUM IN KARST WATERS

-Some Notes on Karst Processes in Dolomitic Carbonate Rocks-

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The basic textbooks and reference sources in speleology (Kunsky, 1954; Trombe, 1952, and Warwick, 1962) describe the process of solution of carbonate rocks in terms of the system $\text{CaCO}_3 - \text{H}_2\text{O} - \text{CO}_2$, making little or no reference to the role of MgCO_3 in the solution process. The widespread occurrence of dolomitic rocks amongst the older sedimentary formations of Australia, e.g., at Buchan, Victoria, and Camooweal, Queensland, makes some knowledge of the complexity of solution processes in rocks containing dolomite highly desirable for the understanding of the development of caves in this continent. This paper is intended to review the scattered literature on this topic and to describe what is known of the behaviour of the system $\text{CaO} - \text{MgO} - \text{CO}_2 - \text{H}_2\text{O}$.

Mineral Composition of Carbonate Rocks

The principal minerals forming carbonate rocks are calcite, aragonite and dolomite. Calcite (CaCO_3) crystallises in the trigonal system, and is the most common mineral in limestones. Aragonite, which has the same chemical composition as calcite but which crystallises in the orthorhombic system, is produced in shells of crustaceans or as a primary deposit from hot springs, but is liable to be converted to the more stable form of calcite. Dolomite, the double carbonate, $\text{MgCO}_3 \cdot \text{CaCO}_3$, crystallises, like calcite, in the trigonal system. Dolomite is commonly used as a rock term, like limestone, but Dunbar and Rodgers (1957, p 219) recommend the use of the term dolostone for sedimentary rocks containing more than 50 percent of the mineral dolomite.

Classifications of carbonate rocks are made either on a genetic or chemical basis. The following chemical classification based on that given by Pettijohn (1957, p 418) reflects the wide range of chemical composition of carbonate rocks.

Table 1, on the following page, sets out the nomenclature of calcitic and dolomitic carbonates.

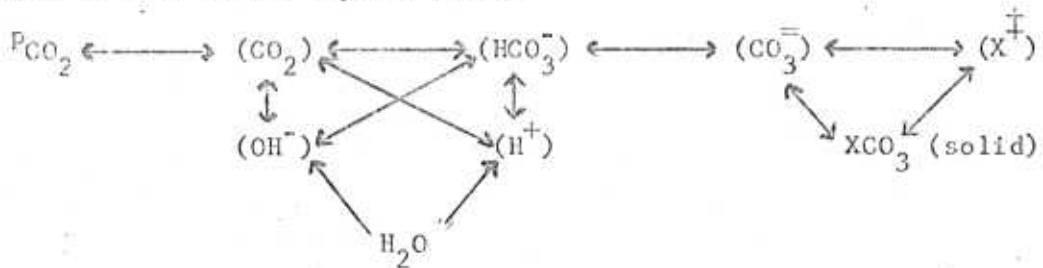
Table 1: Calcitic and Dolomitic Carbonates

<u>Type</u>	<u>% Dolomite</u>	<u>Approx. MgO Equivalent %</u>	<u>Approx. MgCO₃ Equivalent %</u>
Limestone) 0 to 10*	(0 to 1.1	0 to 2.3
Magnesian Limestone)		(1.1 to 2.1	2.3 to 4.4
Dolomitic Limestone	10 to 50	2.1 to 10.8	4.4 to 22.7
Calcitic Dolostone	50 to 90	10.8 to 19.5	22.7 to 41.0
Dolostone	90 to 100	19.5 to 21.6	41.0 to 45.4

(* Dolomite is not present in high calcium limestones; magnesium carbonate is in solid solution in calcite.)

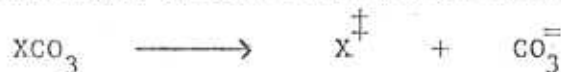
Chemistry of Carbonate Rock Solution

The general equilibrium governing the solution of carbonate minerals is the product of a chain of partial equilibria involving the carbonate material, water and carbon dioxide. The complete equilibrium can be expressed in this form (Roques, 1961):

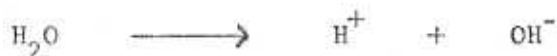


in which X represents either calcium or magnesium or both ions (the divalent cation) making up the particular carbonate in the system under examination. The reactions which occur to make up this general equilibrium can be expressed in the following equations:

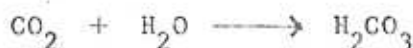
- (1) The dissociation of the carbonate mineral at the solid liquid interface into magnesium and/or calcium ions and carbonate ions:



- (2) The ionic dissociation of water:



- (3) The equilibrium of hydration:



(4) The dissociation of carbonic acid:



(5) The combination of hydrogen and carbonate ions:



(6) The equilibrium of absorption of carbon dioxide (CO_2) into the water from the atmosphere, which depends on the concentration of carbon dioxide in the water, the coefficient of absorption and the partial pressure of CO_2 in the atmosphere.

All these reactions are reversible. For example, a reduction of the partial pressure of the CO_2 in the atmosphere will cause a loss of CO_2 from the water to the air, with a reduction in the carbonic acid concentration, and thus result in the precipitation of some of the carbonate mineral which has been taken into solution. The important factor is that a change in conditions affecting any of these equations will affect the whole of the general equilibrium of the carbonate mineral - water - carbon dioxide system.

The behaviour of calcium alone in this system is fairly well known, having been described by Trombe (1952), Hutchinson (1957), Carrels (1960) and Schoeller (1962), to mention but a few of the recent writers on calcium carbonate equilibria, and will not be enlarged on further. With the range of composition of carbonate rocks as great as shown above, obviously it cannot be assumed that the solution mechanism described for pure calcium carbonate is that which controls the natural solution of carbonate rocks. Unfortunately it is not sufficient to describe the solubility of magnesium carbonate minerals or dolomite, in addition to those for calcium carbonate, to obtain the complete picture of the solution of carbonate rocks, as natural processes will involve some form of action which is a compromise between the ideal cases. However, as the discussions among geomorphologists turn to the subject of the relative aggressivity of karst waters in different climatic zones; as the chemical composition of karst waters is used in the interpretation of the geological conditions of the carbonate rocks from which they drain; and as the water resources engineers introduce sophisticated methods for the calculation of the aggressivity of groundwater in areas of carbonate rocks, it is thought worthwhile to attempt to summarise the nature of the solution processes in carbonate rocks containing magnesium.

Solubility of Magnesium Carbonate Minerals

The solution of dolomite and dolomitic rocks depends not only on the solubility of the double carbonate, $\text{MgCO}_3 \cdot \text{CaCO}_3$, but also on the relative solubility of calcium carbonate minerals and magnesium carbonate minerals.

Magnesite ($MgCO_3$) is hardly ever found as separate crystals, but it is present in many organic limestones and magnesian limestones in solid solution with calcite. Magnesium carbonate thus occurs in carbonate rocks as part of crystals largely consisting of calcium carbonate. Solution of these minerals will depend on the stability of the mineral and the behaviour of the magnesium and calcium components. Before the solubility of dolomite is examined, it is therefore essential to compare the solubility of magnesium carbonate and calcium carbonate.

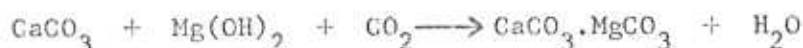
To understand the solubility of magnesium carbonate it is necessary to examine the forms in which $MgCO_3$ occurs in nature. Under marine conditions:

$MgCO_3$ is only precipitated at temperatures over $100^\circ C$;

$MgCO_3 \cdot 3H_2O$ (nesquehonite) is precipitated between $16^\circ C$ and $100^\circ C$;

$MgCO_3 \cdot 5H_2O$ (the pentahydrate) is precipitated at and below $16^\circ C$.

A precipitation of $Mg(OH)_2$ (brucite) may occur in warm sea water of high pH, but it is thought to revert to $MgCO_3$ on the return of normal CO_2 pressure; nevertheless, in spite of the lower pH, because the reaction is slow, the $MgCO_3$ will not redissolve, but will crystallise on to any available nuclei, such as calcite (having the same crystal system) with or without Mg already in solid solution (Fairbridge, 1957, p 135),



This slowness with which magnesium carbonate comes out of solution also has important implications in the evolution of groundwaters passing through and emerging from carbonate rocks.

Despite the remarks of Fairbridge on the behaviour of brucite under marine conditions, it appears that at CO_2 pressures below about 0.00035 atmospheres at temperatures between $18^\circ C$ and $25^\circ C$, which are just the crucial temperatures and pressures for natural conditions at the ground surface, brucite is the stable mineral form. Above these levels, nesquehonite is the stable form (Pietsch, 1939, p 315). It is important to note these differences, as much of the solubility data in the chemical literature refers only to one or other of these forms of magnesium carbonate. The diversity of the published results makes direct comparisons difficult. As a first basis for comparison, the solubilities of various carbonate minerals in CO_2 -free water, devoid of contact with the atmosphere, are given in Table 2, based on data used by Pietsch (1939) and Hutchinson (1957).

The differences in solubility of the various magnesium minerals probably account for some of the contradictory statements in the literature. Fairbridge (1957, p 163) discusses the formation of dolostone by the sub-aerial process of leaching of limestones resulting in the concentration of

Table 2: Solubility of Some Carbonate Minerals in Pure Water at 25°C

		<u>Parts per million (ppm)</u>		<u>epm*</u>	
CaCO_3	Calcite	4.5 - 5.8	(Ca)	0.22 - 0.29	(Ca)
CaCO_3	Aragonite	5.6 - 6.2	(Ca)	0.28 - 0.32	(Ca)
MgCO_3	Magnesite	16.2	(Mg)	1.32	(Mg)
Mg(OH)_2	Brucite	2.65	(Mg)	0.22	(Mg)
$\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$	Nesquehonite	212	(Mg)	17.4	(Mg)

*Equivalents per million = $\frac{\text{ppm} \times \text{valency}}{\text{atomic weight}}$

the less soluble MgCO_3 . However, he notes that in some cases, e.g. some crinoidal limestones where the MgCO_3 is reduced to less than one to two percent, although the uneached crinoid stems may have about 20 percent MgCO_3 , there is a curious preference "for what is normally less soluble MgCO_3 ." Hem (1959) has produced curves for the solubility of calcium carbonate and magnesium carbonate at 25°C and at various CO_2 pressures which are shown in Figure 1. These curves clearly indicate the greater solubility of magnesium carbonate at all pressures; however, the curve for magnesium carbonate is derived from the data for nesquehonite published by Kline (1929). Before the solubility of dolomite or dolomitic rocks can be understood, it is essential to understand the nature of the magnesium carbonate at the solid/liquid interfaces at which solution is taking place. This is a complex problem, and at this stage of investigation there is little evidence from observations or experimental results on which to base a brief description of the processes involved.

Solubility of Dolomite

The solution mechanism of dolomite is the same as that for the other carbonate minerals, except that under ordinary atmospheric and aqueous conditions it goes into solution less rapidly (Clarke, 1924, p 580). As dolomite is a double carbonate ($\text{MgCO}_3 \cdot \text{CaCO}_3$) it would be expected that the double carbonate molecules would go into solution as units, that is that dolomite is congruently soluble, and that variations in CO_2 partial pressure would not affect this congruent solubility (Pietsch, 1961, p 1357). However, experimental data show that at low CO_2 partial pressures at 25°C dolomite is incongruently soluble, with more magnesium than calcium coming into solution. At CO_2 pressures of about one atmosphere at 25°C dolomite is congruently soluble, but at higher pressures it is again incongruently soluble, with more calcium than magnesium being dissolved (Pietsch, 1961, p 1357; Yanat'eva, 1954, 1955). Thus experimental data comparable with natural conditions on the ground surface suggest that there should be pref-

erential solution of magnesium from dolomite. However, the conditions controlling the solution of carbonate rocks are not always those of the atmosphere at the ground surface. Solution may take place beneath a soil layer, or along cavities within the rock mass, under conditions quite different from those on the surface.

Normally the CO_2 pressure of soil air is many times greater than that of the atmosphere. This pressure increases with depth, as shown in the following table, and may be 100 times that of the atmosphere in cracks in the bedrock (Biro, 1959, p 142).

Table 3: Percentage by Volume of Carbon Dioxide in Soil Air of Cacao Soils of River Estate, Trinidad. (Mohr and Van Baren, 1954)

<u>Depth in cm</u>	Wet Season Oct./Jan. CO_2 % total volume	Dry Season Feb./Mar. CO_2 % total volume
Atmosphere	0.03	0.03
10	6.5	0.5
25	8.5	1.6
45	9.7	3.2
90	10.0	5.2
120	9.7	6.8

These contrasts in CO_2 partial pressure within the zone of solution of carbonate rocks mean that on bare rock surfaces, such as those of karren, there may be incongruent solution of the dolomite minerals, whereas in underground systems there may be congruent solubility. The picture is further complicated by the time factor, for experimental data suggests that if the solubility experiments are carried on until equilibrium is reached, the quantities of magnesium and calcium which have by then been dissolved from the mineral will show congruent solubility (Pietsch, 1961, p 1358). Equilibrium conditions may however not be reached under natural conditions, especially when there is rapid movement of water through a carbonate rock mass, or rapid wetting of and runoff from a rock surface. Conditions will also be different where groundwaters contain acids other than carbonic acid, or where waters are saline, as for example in the evolution of coastal landforms in dolomitic rocks.

The Calcium:Magnesium Ratio

Hem (1959) has suggested that the ratio of calcium to magnesium (computed from equivalents per million) in natural waters may be a guide to their origin. Waters which have dissolved only dolomite and from which no precipitation of carbonate minerals has taken place, would be expected to have a calcium:magnesium ratio of 1.0 if the solubility of dolomite is congruent. Yanat'eva's (1954, 1955) data at a CO_2 partial pressure of

0.0012 atmospheres do not include direct results for dolomite alone, but for mixtures of dolomite and calcite, and dolomite and magnesite:

Table 4: Solubility of Some Carbonate Minerals at a Carbon Dioxide Partial Pressure of 0.0012 Atmospheres at 25°C. (Yanat'eva, 1955)

	Equivalents per million	
	<u>Calcium</u>	<u>Magnesium</u>
Calcite	1.6	0
Calcite and Dolomite	0.79	1.75
Dolomite and Calcite	0.81	2.03
Dolomite and Magnesite	0.64	2.23
Magnesite	0	3.06

Yanat'eva's inference about the incongruent solubility of dolomite under these conditions is made from a diagram in which the concentrations of calcium in solution are plotted against the concentrations of magnesium (Figure 2). A central line at 45° to the vertical, representing the composition of dolomite, passes to the left of the points obtained from the solution of the two mixtures containing dolomite, instead of between them, as it does at the same temperature at a CO₂ partial pressure of one atmosphere. Thus from the calcite and dolomite mixture more magnesium carbonate was dissolved than would have been expected from dolomite alone.

In the absence of comparable experimental data, Yanat'eva's results can only be compared with those obtained from the analysis of cave waters. This has recently been done by Holland, Kirsipu, Huebner and Oxburgh (1964) who have investigated the evolution of cave waters in three cavern systems in the eastern U.S.A. (Indian Echo Cave and Carpenter Cave in Pennsylvania, and the Luray Caverns in Virginia). The waters from the Luray Caverns are of special interest as this system occurs in the calcitic dolostone of the Beekmantown Formation. At the point where water samples were collected dripping from the cave ceiling, where there was least possibility of their composition having been modified by precipitation following their emergence from the rock mass into the lower CO₂ partial pressure of the cave, the observed Ca:Mg ratios ranged from 0.97 to 0.82. Elsewhere in the cave much lower ratios occurred as a result of precipitation of calcium carbonate on actively growing cave formations. These ratios of just below 1.0 suggest that under the conditions in the calcitic dolostone above the Luray Caverns, the dolomite is dissolved congruently. Arguing from their analytical results, Holland and co-workers suggest that the partial pressure of CO₂ in the soil is of the order of 0.1 to 0.2 atmospheres, which is of the order suggested by Birot as quoted above. At such a pressure it is quite probable that the solubility of dolomite is congruent.

The high magnesium concentrations found in some of the waters of the Luray Caverns caused Holland and co-workers (1964, p 59) to doubt the solubility values determined by Yanat'eva. For the solubility of dolomite at a CO₂ partial pressure of one atmosphere, Yanat'eva's results are:

<u>Temperature °C</u>	<u>Calcium ppm</u>	<u>Magnesium ppm</u>
0	10.7	10.1
25	6.14	6.10
55	6.02	6.06

These can be compared with the waters with the highest magnesium concentrations found in the Luray Caverns:

<u>Temperature °C</u>	<u>Calcium ppm</u>	<u>Magnesium ppm</u>
17.1	4.82	6.88
?) Probably	5.12	6.66
?) 12.0	2.36	6.64
?) to 16.0	5.16	6.62

These high magnesium concentrations are about equal to those for the solubility of dolomite at a CO₂ partial pressure of one atmosphere for the temperatures measured. It is doubtful that such a pressure would occur in the soil zone or in cavities within the rock, and Holland and co-workers conclude that Yanat'eva has underestimated the solubility of dolomite. They have recalculated the solubility of dolomite and suggest that at a CO₂ partial pressure of one atmosphere and a temperature of 25°C, the concentration would be of the order of 11 to 12 ppm of both calcium and magnesium. This revised figure for the solubility of dolomite is similar to that determined by Halla (Pietsch, 1961, p 1356).

It has been suggested (Pal'vev, 1956; Pietsch, 1961) that waters dissolving dolomite will only obtain a Ca:Mg ratio of 1.0 when they have reached equilibrium; and that while they are undersaturated they may have a higher concentration of magnesium than calcium. This could be an explanation for the Luray Caverns waters always having a Ca:Mg ratio of less than 1.0. Nevertheless, this is not borne out by analyses of underground stream waters, sampled by the writer, from the Cambrian dolostones and calcitic dolostones of the Durness area of Sutherland, Scotland. Although the Cambrian carbonate rocks of this area vary from limestones to dolostones, most of them are highly dolomitised, and Ford (1959) noted no preferential development of solution phenomena in any division of the Durness Limestone Formation.

The results in Table 5 suggest the congruent solubility of dolomite at quite low temperatures, although the CO₂ partial pressures in the solution

FIG. 1 SOLUBILITY OF CALCIUM AND MAGNESIUM CARBONATES AT 25° C.
(Based on graphs by Hem, 1959)

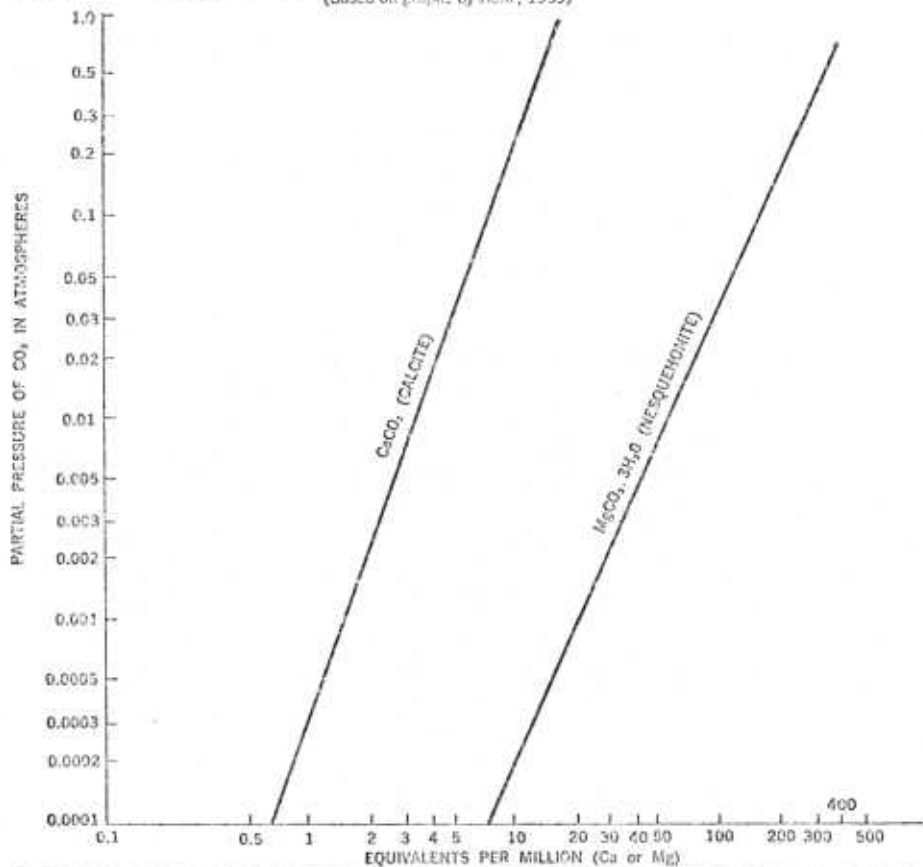


FIG. 2 SOLUBILITY IN THE SYSTEM CaCO₃—MgCO₃—H₂O
AT CO₂ PARTIAL PRESSURE = 0.0012 Atm.
and 25° C. (after Yanat'eva, 1955)

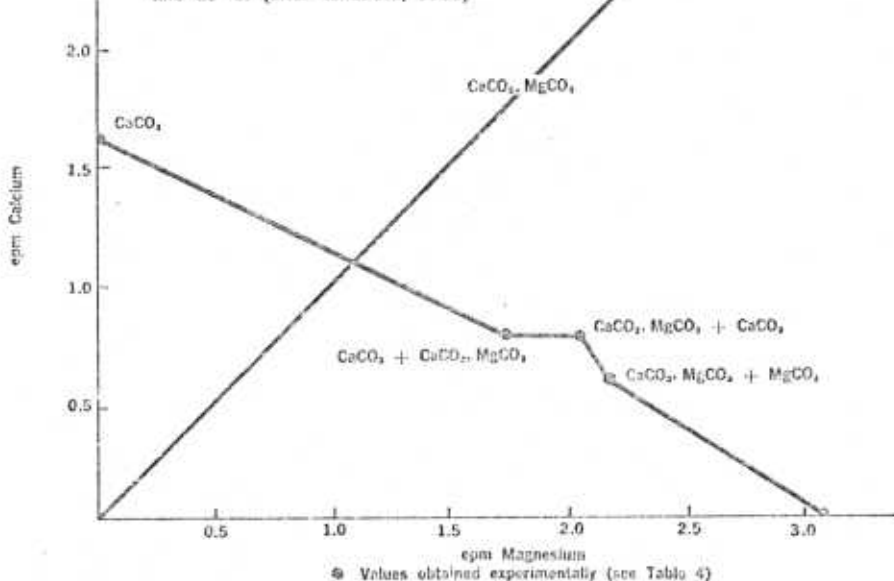


Table 5: Calcium and Magnesium in Sutherland Karst Waters

	<u>Temperature °C</u>	<u>Ca ppm</u>	<u>Mg ppm</u>	<u>Ca:Mg Ratio</u>
Stream near Keoldale	9.5	1.90	2.30	0.83
Stream at Sangomere	7.5	2.15	2.14	1.00
Stream emerging in Smoo Cave	9.0	1.30	1.40	0.93

zones which they drain are quite unknown. In fact all the field observations on waters from areas of dolostone seem to suggest congruent solubility. As these analyses are few and scattered it is not possible to draw direct conclusions as to the true nature of karst processes in dolostones and other carbonate rocks containing dolomite. Yanat'eva's data must be compared with more laboratory studies, and many more observations in caves and surface waters of karst areas will be needed to get a full picture. The work by Holland and his collaborators has been a very significant step in this direction.

Calcium Carbonate Precipitation and the Ca:Mg Ratio

The Ca:Mg ratio has been widely used in Hungary (Holly, 1962) to determine the source of underground waters and the reliability of a spring. However, a value of the ratio near unity does not always indicate that the water has emerged from a dolostone. A low value of the ratio may result from the precipitation of calcium carbonate which goes out of solution much more readily than magnesium carbonate. As noted above, magnesium tends to remain in solution for a long time after conditions of CO₂ partial pressure and temperature which induced its solution have been changed. This is the typical situation which occurs when a water emerges from the rock mass into the cave atmosphere. There is a loss of CO₂ from the water to the cave atmosphere, and the precipitation of calcium carbonate to form dripstone and flowstone decorations. In Indian Echo Cave, Holland and co-workers (1964, p 45) noticed that there was water dripping from a soda-straw stalactite into a number of pools. The calcium concentration of the water in the pools was less than that of water dripping from the stalactite, but the magnesium content remained nearly constant. In the Luray Caverns also, the calcium concentration of water dripping from the ceiling of the cave decreased markedly as it flowed over a stalactite to a collecting point below, the magnesium content remaining essentially constant.

Evaporation and the Ca:Mg Ratio

The Ca:Mg ratio is also affected by evaporation. Under such conditions an undersaturated water will not only become supersaturated, but the magnesium concentration will increase, and precipitation will prevent a proportionate increase of the calcium concentration, with a resulting lowering

of the Ca:Mg ratio. The writer noticed this occurring in streams rising in the Tertiary limestones of Al Jabal al Akhdar of northern Cyrenaica.

Table 6: Calcium and Magnesium in Cyrenaican Waters

	<u>Temp. °C</u>	<u>Ca ppm</u>	<u>Mg ppm</u>	<u>Ca:Mg ratio</u>
Water from irrigation channel in Wadi Darnah abt. 4 km below spring	27.2	2.79	2.71	1.03
Water from wadi at El Atrun, abt. 5 km below spring	25.0	1.90	2.06	0.92
Water from fountain of Apollo at Cirene (Shahhat)	22.2	2.74	0.82	3.34

These samples were collected in the afternoon at the beginning of September, towards the end of a long dry season when evaporation is intense. In both wadis below the springs, water is lost by evaporation and infiltration into the gravels of the stream beds. Deposits of calcium carbonate are found on the pebbles beneath the water, and the high concentrations of magnesium carbonate can be explained solely in terms of this evaporation and precipitation process, no dolostones or calcitic dolostone having yet been recorded among the Eocene limestones from which these waters emerge. The water from the fountain of Apollo which is some 600 metres above the wadis, in the Oligocene limestones near the summit of the Jabal, has had a shorter passage through the limestone and has been exposed to the atmosphere for a shorter time. The water thus has a lower magnesium content than the coastal samples, although there has probably already been some loss of calcium carbonate, as there is a large tufa screen where the water emerges from the rock. Thus here is an instance of Ca:Mg ratio being very close to unity, yet being quite unrelated to the solution of dolomite. Neither this explanation of the Ca:Mg ratio, nor the possibility of prior precipitation of CaCO_3 , have been considered by Jennings (1963, p 4) or Jennings and Sweeting (1963, p 55) in discussions on karst waters from Yarrangobilly, Cliefden and the Kimberley Ranges, which the writers thought might be derived from dolomitic terrains.

With reference to the increase in concentration of magnesium in surface streams draining karst areas, the writer has noted that evaporation may be important in summer in the Carboniferous Limestone area of Derbyshire, England. At one site where water samples were collected over several months, the water is impounded to form a mill pond, exposing a large water surface for evaporation. The samples were collected at the outlet, and magnesium concentrations varied from 1.06 to 1.48 ppm in winter (February-March) and from 1.80 to 2.08 ppm in summer (June-July), but there was no difference in the calcium concentration from winter to summer. The stability of the

calcium content is probably caused by constant precipitation of calcium carbonate on the bed of the mill pond, as this water is always saturated with calcium carbonate. The possibility of the magnesium content being affected by the discharge of water through the mill pond can be ruled out as most of the solute concentration is made up of calcium bicarbonate, the calcium content varying from 4.52 to 6.25 ppm according to the flow through the pond and not according to the season.

Concluding Remarks

This paper has emphasised the lack of general understanding of speleogenetic processes in dolomitic rocks, and has stressed the difficulties of making accurate studies of the solubility of carbonate rocks. Although geomorphologists and speleologists have tended to neglect this aspect of karst morphology, basic data on the solubility and porosity of dolomitic carbonate rocks is becoming increasingly available as a result of research by groundwater and petroleum geologists. This work is published in such journals as the Bulletin of the American Association of Petroleum Geologists, the Water Supply Papers of the United States Geological Survey, and the Journal of Hydrology. There is now scope for the correlation of this basic data with the results of studies of cave and other karst waters, as has been done by Holland and co-workers. Particular attention should be paid to the mineralogy, chemical composition and lithology of the rocks involved and care taken to sample waters systematically through the whole range of hydrologic conditions from peak floods to extreme drought. Such field studies should be accompanied by laboratory studies of solubility and porosity, both of the rocks of the area being studied and of individual carbonate minerals.

There has been some progress along these lines by speleologists in Europe, notably in Switzerland, Austria, Hungary and Czechoslovakia. However, although the Alps contain many fine cave systems in dolomitic rock, the writer knows of no publication which compares karst processes in limestones and dolostones. Unfortunately the diversity of journals and of languages in which such a work might appear has prevented a complete examination of all the literature.

Despite the possibility of a considerable European contribution to this problem of karst processes in dolomitic rocks, the writer feels that the semi-arid environment of Australia provides conditions sufficiently different from those in Europe to warrant the study of such processes in this Continent. In the early stages of this study, the regular sampling of cave and associated surface waters could be made in any cave system which was being visited regularly for exploration, survey, or biological studies. When samples are taken from flowing water, the rate of flow should be determined. If samples are taken from stagnant water bodies, the depth of such pools should be measured. Comparisons of such measurements permit the estimation of the effects of dilution by floods or concentration by evapo-

ration. Temperature and pH measurements of the water being sampled should also be made at the time of sample collection.

The collation and extension of this preliminary work and the associated laboratory studies, would eventually have to be taken over by full-time research teams. The writer hopes that perhaps this could be done by a Cave Research Institute, perhaps similar to the Underground Laboratory of the National Centre of Scientific Research at Moulis, France. Such a speleological research station in Australia could make a wide range of observations on both the hydrological and geological aspects of caves, and on the biology of cave fauna and flora.

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A NOTE ON CLOUDMAKING BY CAVES

Little work on cave meteorology has yet been carried out in Australia, although some observations on cave air currents were made on the Nullarbor Plain (noted for its "blowholes") in 1957 by L. Bishop of the Sydney University Speleological Society, and in 1964 by I. Wood of the University of New South Wales Speleological Society. Yet cave weather and climate are most interesting fields of study as it is hoped to indicate in this note discussing one facet of cave meteorology.

In the winters of 1955 and 1956, Canberra Speleological Society parties often came out of the 65 Foot Pitch from the Main Chamber of the Dip Cave, Wee Jasper, N.S.W., in the evening or at night. On a number of occasions we noted a column of mist over this entry and the neighbouring vent. No doubt this was happening simultaneously over the Daylight Hole, an even deeper shaft, but since we did not frequent this spot at night it has not been noted by the writer. The mist columns occurred on calm, clear evenings when the outside air temperature was falling rapidly towards freezing point, and below.

Such mist formation is a well-known phenomenon and the explanation is straightforward. The rock walls of a cave have a great heat capacity and act as a moderating influence on cave atmosphere. As a result, in a cave like the Dip Cave, with a number of large chambers and no disturbing underground river, air temperature remains at a steady level except close to the entrances. In the Dip the air temperature holds to 13.3°C (56°F) and relative humidities are high, generally over 90 percent. The result on a cold night is that the air inside the cave is warmer and lighter than the outside air. So it rises through the higher openings in the system to be replaced by colder air entering at the lower entrances. If there is much wind, the escaping cave air is dissipated into the huge mass of the atmosphere; on a calm night, there is a much more gradual mixing of cave and outside air through turbulence just above the vent. The mixing of two air masses, at different temperatures but neither saturated with water vapour, can result in a mixture which is supersaturated. Condensation to give a mist can then take place (Brunt, 1941, p 47). This is what happened at the Dip.

The converse of this process has been noted on one occasion in the Daylight Chamber in the same cave. On November 29, 1957, a great cloud of mist was seen billowing around the roof where the shaft from the Daylight Hole widens between 70 and 50 feet up from the chamber floor. The motions of this mist showed there was a downward current. It was a hot, sunny day outside, 32.2°C (90°F) and of high humidity (a physiological impression, not determined instrumentally). The much colder and denser cave air must have been draining from the lower entrances. The top of the No. 4 Extension shaft, for instance, is 70 feet below the Daylight Hole. This outward draining of cold air induced an inflow from above into the Daylight Chamber where it was cooled to dewpoint by mixing with the cave atmosphere. In this circumstance some cooling by direct contact with the cave walls, steady at 13.3°C, would also be

taking place. This, however, would result chiefly in dew condensing on the walls themselves, a process which Trombe (1952, p 120) has claimed to be of great importance in the hydrology and morphological processes of some caves.

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A B S T R A C T S

REVISION OF THE RHAPHIDOPHORIDAE (ORTHOPTERA) OF NEW ZEALAND. PART XI - A NEW SPECIES BELONGING TO THE GENUS GYMNOPECTRON HUTTON, 1897, FROM THE POOR KNIGHTS ISLANDS. By Aela M. Richards. Trans. Roy. Soc. N.Z. Zoology, 2 (24), 1962 : 203 - 207.

A new species of Rhaphidophoridae belonging to the genus Gymnoplectron giganteum Richards is described from a cave on Tawhiti Rahi, one of the Poor Knights Islands situated off the northeast coast of the North Island of New Zealand. G. giganteum is the largest representative of the family recorded from New Zealand, an adult male reaching a length of 18 inches from the tip of its antennae to its hind tarsi. - A.M.R.

MAMMAL SUB-FOSSILS FROM BASALT CAVES IN SOUTH-WESTERN VICTORIA. By N.A. Wakefield. Vict. Nat., 80 (9), 1964 : 274 - 278.

Mammal sub-fossils are recorded from four sites in the Byaduk Caves and from the Natural Bridge near Mount Eccles 12 miles south and 22 miles south-south-west respectively from Hamilton, Victoria. A total of 28 species are listed, and their relative abundance at each site is recorded. It is assumed that the Masked Owl (Tyto novae-hollandiae) and the small Barn Owl (Tyto alba) were responsible for most of the deposits. The remainder could be the remains of prey of quolls (Dasyurus quoll). All specimens belong to a modern fauna, with the exception of a single specimen of the rock wallaby (Petrogale penicillata).- A.M.R.

VOLCANIC PHYSIOGRAPHY OF THE WESTERN PLAINS OF VICTORIA. By C.D. Ollier and E.B. Joyce. Proc. Roy. Soc. Vic., 77 (2), 1964 : 357 - 376.

A description of the volcanic physiography of the Western Plains of Victoria, including the volcanic hills which dot the Plains. Overall vulcanicity probably extended from earliest Pleistocene times to the Recent. The paper is valuable to speleologists in providing a background to lava cave

development and siting in this area. Discussion includes types of volcanoes, vent features, lava flow features, nature of eruptions, weathering, soils, erosion, dating of volcanoes and sequence of vulcanicity in Victoria. Lava caves are referred to briefly from Byaduk, Mt. Eccles, Mt. Hamilton, Mt. Warrnambool, Parwan, Mt. Porndon and Mt. Gisborne. Fossils have been found in some of the lava caves and these give a minimum age of their flow; the volcano and caves may have been in existence for a very considerable time before fossil entry.- E.A.L.

CAVES AND RELATED FEATURES OF MOUNT ECCLES. By C.D. Ollier. Vict. Nat., 81 (3), 1964 : 64 - 71.

Mount Eccles, located five miles west of Macarthur about halfway between Hamilton and Port Fairy in Victoria, was formerly the centre for eruption of large quantities of basalt. Many unusual volcanic features occur in this area which is remarkable also for having in one small area a variety of lava caves formed in several different ways. Types include a contorted cave in layered lava, lava tunnel caves, and an open vent 100 ft deep leading from a small spatter cone. This shaft ends in a small chamber sealed with large boulders of frothy lava. Discussion follows on the possible geological history of Mount Eccles.- E.A.L.

McEACHERN CAVE, NELSON. By C.D. Ollier. Vict. Nat., 81 (7), 1964 : 195 - 197.

This is a young cave in Oligocene limestone near Nelson, close to the border between Victoria and South Australia. The importance of this small cave is the infill with a variety of sediments up to at least eight feet thick, and associated with an assemblage of bones. McEachern Cave is, in fact, the first Victorian cave discovered containing stratified deposits. These are now being extensively studied by several people. Ollier points out that there has been a gradual emergence of this part of Australia from beneath the sea and that the coastal area is topographically younger than the inland parts. He mentions the need for further work to document the probable sequence of cave development from the well-developed Naracoorte Caves to the simple young caves of the Nelson area near the coast.- E.A.L.

POST-PLISTOCENE CHANGES IN THE MAMMALIAN FAUNA OF BORNEO - Archaeological Evidence from the Niah Caves. By Lord Medway. Studies in Speleology, 1 (1), 1964 : 33 - 37.

In the archaeological deposits at Niah Cave, Sarawak, which have been dated by C 14 techniques, mammalian remains from levels representing periods earlier than B.C. 17,613 + or - 190 provide a sample of the later Upper Pleistocene fauna of lowland Borneo. At least 50 species have been recognised, although not all can be finally identified. Of those identified, the majority are still extant in Borneo although one, a giant pangolin, is totally extinct, another, the Malay tapir, no longer occurs on the island, and two more, the Sumatran rhinoceros and the orang-utan, nowadays have a restricted distrib-

ution in Borneo, not including the Niah region. In addition, several extant species are represented by Pleistocene congeners of slightly larger average size. Two other mammals, the lesser gymnure and the ferret-badger, today have a limited montane distribution; their presence in the deposit suggests a lowering of the mean ambient temperature by about 5°C during the end of the Pleistocene. Of other large mammals which might have been expected, neither the Javan rhinoceros, the Indian elephant, nor the tiger are represented, although a fragmentary canine crown, attributable to a young tiger, has been recovered from Neolithic levels.

THE NEW ZEALAND GLOW-WORM. By Aola M. Richards. Studies in Speleology, 1 (1), 1964 : 38 - 41.

The glow-worms of the celebrated Glow-worm Grotto of Waitomo Cave, North Island, New Zealand, are the larvae of a mycetophilid fly. The larvae prey upon midges which they capture by means of sticky fishing-lines suspended from the roof of the cave. The light emitted by the larvae serves as a lure for the prey. The unique density of the population of glow-worms in this cave results from the existence of ideal ecological conditions, notably the existence of an abundant food supply in the shape of goats which breed in the mud banks of the subterranean river, and permanent darkness.- E.B.B.

BORNEO CAVES - With Special Reference to Niah Great Cave. By Tom Harrisson. Studies in Speleology, 1 (1), 1964 : 26 - 32.

There are many caves in Borneo. Most of them contain either significant prehistoric materials or specialised life, or both. With recent advances in studies at the Niah Caves and elsewhere in Sarawak (Borneo), there is a base line for further exploration, but little point in the somewhat indiscriminate and always single-angled approach which has damaged, or ecologically destroyed, so many cave sites elsewhere in South-east Asia recently. A more thoughtful, long term and conservational approach is discussed and illustrated in this paper by the Curator of the Sarawak Museum, who has pioneered in this field since 1947.

NOTES ON MICROCHIROPTERAN BATS. By J.L. McKean and L.S. Hall. Vict. Nat., 81 (2), 1964 : 36 - 37.

Notes are recorded of observations on feeding, breeding habits and swimming behaviour of microchiropteran bats in Victoria and New South Wales. In 1956, the diet of a colony of lesser long-eared bats (Nyctophilus geoffroyi) in a house at Mt. Martha, Victoria, was found to consist of moths and small beetles; 95 percent of the remains consisted of moths' wings and 5 percent of elytra. The colony of bent-winged bats (Miniopterus schreibersi) in a sea cave near Warrnambool, Victoria, also has a diet consisting mainly of moths and many moth wings have been found in the cave. The authors claim this as the only reference to moth remains in caves inhabited by M.

schreibersi. (In October, 1964, moth wings were collected from the Abercrombie Caves by the reviewer. These caves also contained a colony of M. schreibersi.- Editors).

Observations on a maternity colony of N. geoffroyi living under the bark of a live rough-barked gum tree north of Booligal, N.S.W., indicates that this species regularly gives birth to twins. All other known species of microchiropteran bats give birth to single young.

McKean and Hall have also observed that N. geoffroyi can float on water and move across the surface by beating its partly extended wings. In the Vict. Nat., 81 (4), p 104, 1964, E. Hamilton-Smith notes that a specimen of M. schreibersi from Duke's Cave, Buchan, Victoria, after being knocked into water, swam across the surface for about 18 inches and then took flight without much difficulty.- A.M.R.

FOX PREDATION ON CAVE-BATS. By P.D. Dwyer. Aust. J. Sci., 26, 1964 : 397 - 398.

Consistent predation upon the bent-winged bat, Miniopterus schreibersi blepotis, and little bent-winged bat M. australis, by a fox (Vulpes vulpes) was followed at Yessabah Bat Cave, near Kempsey, N.S.W., between March 1961 and September 1963. Predation was indicated by portions of wings that were discarded and accumulated at specific sites in the intervals between visits. The fox usually caught bats in portions of the cave where their flight path was relatively restricted. Wing elements representing a minimum of ten M. australis and 476 N. s. blepotis were collected from Yessabah during the period mid-July 1960 to mid-September 1962 (The latter date is probably a misprint for 1963). The author writes that for M. s. blepotis this represents a predation rate of 12.5 bats/month or 150/year. The maximum estimated size of the M. s. blepotis colony at Yessabah for any single date was about 1,500, so approximately 10 percent of this number were being taken annually by this predator. The highest rate of predation occurs during the autumn months and corresponds to the autumn peak in colony size that results from an annual influx of juvenile bats. No minor peak in predation corresponding to the spring peak in colony size is evident.- A.M.R.

VERTEBRATE REMAINS FROM THE NULLARBOR CAVES, WESTERN AUSTRALIA. By E.L. Lundelius, Jr. J. Roy. Soc. W. Aust., 46, 1963 : 75 - 80.

Six caves - Cocklebidy Cave, Murra-el-elevyn, Madura Cave, Webb's Cave, Snake Pit and Abrakurric Cave - located along the southern edge of the Nullarbor Plain (see map by E.G. Anderson in Helictite, 2 (4), p 125) have yielded the remains of Pleistocene and Recent vertebrates. The Recent material extends the known range of one species of mouse, Pseudomys (Thetomys) occidentalis Tate, 600 miles eastward from the south-western part of Western Australia to Murra-el-elevyn, and indicates that it is a part of the Recent fauna of the Nullarbor Plain. Remains of Potorous Desmarest (the rat kan-

garoo) from Webb's Cave are intermediate morphologically between Potorous platyops from Western Australia and P. morgani from Kangaroo Island, South Australia. Webb's Cave also contains remains of Sarcophilus harrisi Boitard (the Tasmanian devil) in association with recently introduced species. This indicates a very recent disappearance of this animal from the Australian mainland. In the lower, red soil unit of Madura Cave, a lower third premolar of the kangaroo Sthenurus and a wombat tooth similar in size to Phascolumys parvus have been found. The presence of Sthenurus in Pleistocene deposits in this area suggests a more humid climate at that time. Faunal lists are given for all six caves examined. - A.M.K.

NEW CARABIDAE (COLEOPTERA) FROM NEW ZEALAND CAVES. By E.B. Britton. Ann. Mag. nat. Hist., Ser. 13, 6, 1963 : 625 - 634.

New carabidae are described from caves in the Nelson and West Coast districts of the South Island of New Zealand. In the subfamily Trechinae the new monotypic genus Erebotrechus Britton is erected. This genus is related to Duvaliomimus Jeannel, but among other characters is distinguished by extreme reduction of the eyes. E. infernus Britton has been collected from the Fox River Caves near Charleston, and from a cave on Newton Flat, on the south side of the Buller River. A new species of Duvaliomimus, E. pluto Britton, is described from Fenian Creek Cave north of Westport, and from Oparata, West Nelson. A key is given to the eight species of Duvaliomimus.

In the subfamily Harpalinae, tribe Stenolophini, three new species are described: Syllectus magnus Britton is recorded from Profanity Cave, near Inangahua on the Buller River; S. spelaeus Britton from Nile River Cave, Charleston; a small cave at Newton Flat, Buller River; Little Cave, Paturau, Nelson, and Huia Cave, Kaka, Tallmor, Nelson; and Pholeodytes cerberus Britton from Oparata, near Karamea, and Fenian Creek Cave, Paturau. - A.M.R.

SUBTERRANEAN FRESHWATER PRAWNS (CRUSTACEA : DECAPODA : ATYIDAE) IN AUSTRALIA. By W.D. Williams. Aust. J. Mar. Freshw. Res., 15, 1964 : 93 - 106.

This paper describes two new species of freshwater prawns belonging to the genus Parisia Holthuis. P. gracilis Williams and P. unguis Williams were collected by Mr. W. Penman from limestone caves near Katherine, Northern Territory. The relationships of these species to each other, and to the previously described species of the genus are discussed at length. This is the first record of Parisia from outside Madagascar, and it brings to four the total number of atyids known only from subterranean waters in Australia. The specimens were collected from Brennon's Brook, about 300 ft beneath the surface of the ground, and about 1,400 ft from the entrance to the cave system. -A.M.R.