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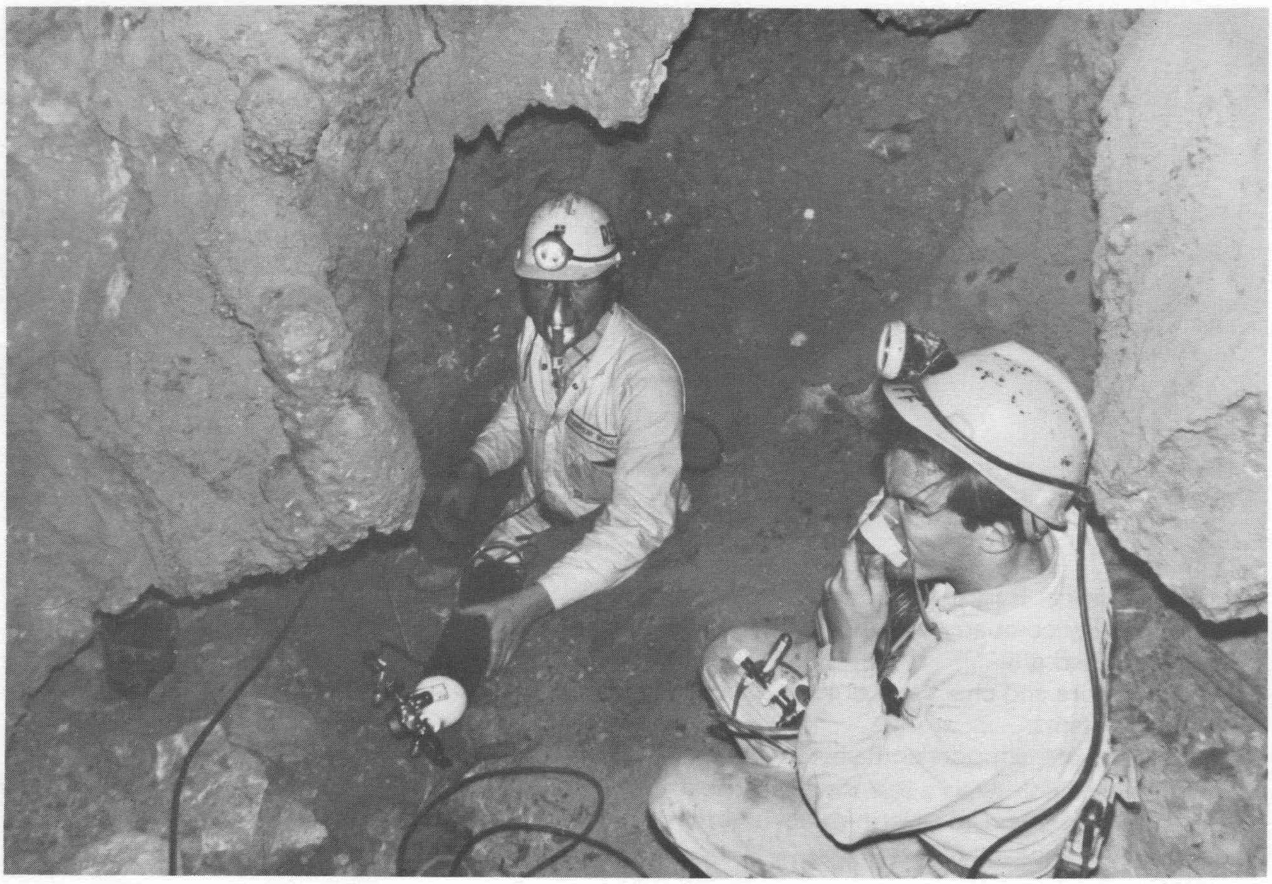

CO_2 Measurements at Wellington Caves

Photograph by R. Armstrong L. Osborne

HELICTITE

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This Journal was (and is) intended to be wide ranging in scope from the scientific study of caves and their contents, to the history of caves and cave areas and the technical aspects of cave study and exploration. The territory covered is Australasia in the truest sense— Australia, New Zealand, the near Pacific Islands, New Guinea and surrounding areas, Indonesia and Borneo.

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REVIEW

CAVES AND KARST OF THE MULLER RANGE, by J.M. James and H.J. Dyson. Atea 78, in conjunction with the Speleological Research Council, Sydney, 1980. Pp. 150. Price $15.00.

This is one of the most impressive speleological expedition reports I have seen; impressive because of its professional standards and comprehensive coverage. It conveys the results of the 'Atea 78' expedition to the Muller Plateau in the Southern Highlands of Papua New Guinea. This was the third expedition to the area, others being in 1973 and 1976, and was launched with one major objective, the exploration of Atea Kananda and with a strong commitment to scientific studies.

The expedition was ambitious and large. It had 49 members from 5 different countries, though the majority (34) were from Australia, and in addition engaged 13 local assistants. The sheer size perhaps explains why the text and tables don't agree in the numbers employed and involved. However, the fact that it received recognition from 5 official bodies in Papua New Guinea is a tribute to the quality of its leadership and to the useful results of previous expeditions. The value of the work done and the standard of its presentation in this report amply justifies that support.

The book is divided into 20 chapters and 9 appendices, involving 26 authors. The material presented covers every official aspect of the expedition - personal details that commonly colour cavers' reports thankfully having being left out - and it is well supported by 40 maps, 29 figures, 25 tables and 60 plates. So there's a wealth of information. After a short introductory chapter by Julia James in which she outlines the purpose and organization of the expedition, and prospects for the future (Mamo 82), the next nine chapters - occupying well over a third of the book - provide a regional speleology of the expedition area. These contributions follow a similar pattern, outlining previous information and giving good accurate descriptions, aided by acceptable half-tone illustrations and well drawn maps of consistent style, of the major sites of interest. They conclude with a speleological assessment of each area, which is a useful guide for future expeditions. The chapter on the Atea Area, as might be expected, is the largest and concludes that the locality should still produce a considerable amount of new cave passage particularly in the vicinity of the Atea Gorge. The main cave, Atea Kananda, is also deemed worthy of a great deal of further exploration.

The following ten chapters present the results of the systematic scientific aspects of the expedition: geology, meteorology, hydrology, surface geomorphology, water chemistry, cave sediments, subterranean geomorphology, botany, vertebrate fauna, and biospeleology. The geology is well handled in an authoritative manner and provides an invaluable basis for further work in the area. The meteorology is brief but useful, being particularly important from the safety point-of-view, as well as complementing the hydrology. It was interesting to read in the latter chapter that the discharge of the river in the Atea Doline has been revised downwards from an enthusiastic visual estimate of 11 $m^3 s^{-1}$ made in 1973 to a measured estimate of 4 $m^3 s^{-1}$ on this expedition, but even with that 'loss' it's still a big river to contend with in a cave. The data presented on the relationship between rainfall, flood peaks, and ducks closing (Figure 13:3) is important for the safety of future expeditions. Some minor confusion shows up in the hydrology chapter over Rhodamine WT (or was it B?) and where it got to. Figure 13:1 shows the tracer route for Rhodamine WT, but the text and Table 13:1 state that it was Rhodamine B. Furthermore, on the figure both the Rhodamine and optical brightener converge at detector point 25 (Atea Resurgence), whereas the table indicates that only the optical brightener emerged there, the Rhodamine only being found (weakly) at site 26 (Yu Nali). In view of the admitted inconclusive nature of the Rhodamine B test, the conclusion endorsing the use of this dye in the tropics is hardly justified.

The chapter on Surface Geomorphology commences with outlines on structural geomorphology and soils and then deals in some detail with karst landforms, subdividing the latter into Small Scale Solution Sculpture, Closed Depressions, Karst Areas, and the Drainage System and Fluviokarst. The text on karst features is generally descriptive rather than explanatory and successfully avoids confusing the reader with difficult and often ambiguous karst terminology, although the distinction between uvalas and glades is rather arbitrary. There also appears to be some uncertainty over whether the Atea Doline is a collapse or solution feature. From its description it seems like a predominantly collapse doline, but the text (p. 94) suggests that it was developed by the removal of material through solution rather than collapse. The numerical and areal significance of the subjacent karst depressions developed in a siltstone caprock over limestone is a particularly important feature of the geomorpholgoy. The origin of such depressions and their significance for the style of the polygonal karst relief which develops from them is something that requires further investigation. The chapter makes a valuable contribution to the discussion on the relative roles of climate and geology in determining karst landform distribution, and concludes that local geology is of greatest significance.

The Water Chemistry chapter is very brief and in fact concentrates on an assessment of limestone solution rates. The values calculated are not very helpful, as the data base is inadequate and a distinction needs to be made between autogenic and allogenic components.

The all-pervading cave mud was clearly quite a feature of the expedition, and David Gillieson's chapter on Clastic Sediments does it justice, being dealt with right down to scanning electron microscope level. Both this and the previous five chapters form a good background against which to interpret the Underground Geomorphology, which is well handled in Chapter 17. Some good points are made about the complications introduced by mixed sedimentary sequences on speleogenesis, that are relevant beyond Papua New Guinea. Jennings' new term "nothephreatic" also gets an airing (soaking?), showing its usefulness even if most of us have an aversion to yet more jargon.

The systematic section terminates with three short biological chapters on Botany, Vertebrate Fauna, and Biospeleology. The latter is the most detailed, and the most important because so little is known about the biology of caves in this part of the tropics. The chapter presents a preliminary list of cavernicolous fauna and useful comments for those wishing to collect specimens in the area.

The report concludes with nine appendices, in fact occupying almost a third of the volume. These mainly cover expedition logistic detail on food, medical, transport, equipment,finance and other topics. The information represents a valuable summary of experience of considerable importance for those planning future expeditions.

Atea 78 was clearly a successful expedition and although not gaining the glamour of an international depth record, it accomplished much more worthwhile science than most other speleological expeditions. The book is not balanced in the sense that equal weight is given to each topic - some chapters are very light - but the cumulative importance of its findings is considerable. The reference list alone is the best available source of literature on caves and karst in Papua New Guinea. Mamo 82 will have a high standard to match.

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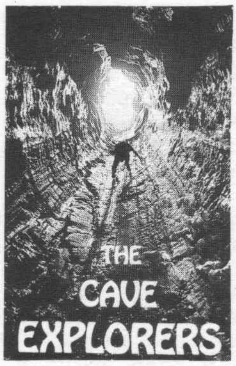

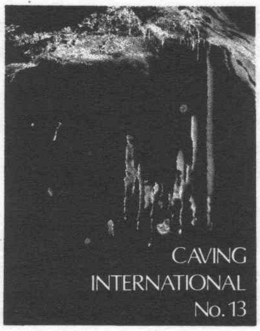

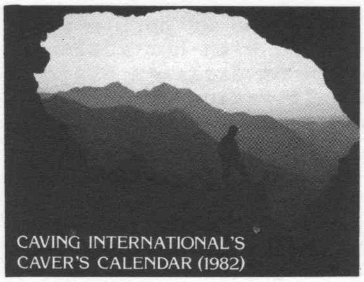

GEOMORPHOLOGY AND PAST ENVIRONMENTS AT NOMBE ROCKSHELTER, SIMBU PROVINCE, PAPUA NEW GUINEA

David S. Gillieson and Mary-Jane Mountain

Abstract

The geomorphic development of a limestone rockshelter in the Chimbu region of New Guinea is outlined. The sedimentary sequence and associated artifactual material are described and related to regional chronology. Disturbance of the rockshelter deposits by seismic and erosive processes is indicated, and must be borne in mind when excavating and analysing material from similar sites.

INTRODUCTION

This paper presents preliminary results of the excavations at Nombe rockshelter, a prehistoric site in the Chimbu region of the PNG Highlands. An excavation by J. Peter White in 1964 (White, 1972) revealed the potential of the site and its stratigraphic complexity. Subsequently excavation by Mary-Jane Mountain demonstrated the presence of extinct fauna and apparent occupation over a long time period. Because of the complexity of the site David Gillieson was asked to undertake geomorphological and sedimentological studies at the site during the 1979 season. At this early stage of analysis no dates are available, so recourse has been made to the regional chronology. Any dating of events or material is therefore provisional.

This paper will firstly provide a brief overview of Highlands prehistory to place Nombe in its cultural context. This is followed by details of the site location, geology and geomorphology. The archaeological deposits will next be described and some preliminary interpretations of their significance made.

FROM HUNTING TO HORTICULTURE

By 40,000 years ago groups of hunter gatherers were entering greater Australia, which at that time included the continuous land masses of New Guinea, Australia and Tasmania. In New Guinea, the earliest dates associated with human material come from the Papuan montane site of Kosipe, where stone tools and charcoal are dated at 26,870 ± 590 BP (White, Crook and Ruxton, 1970). At Kosipe and Manim (Christensen, 1975) early levels are probably associated with the seasonal exploitation of mountain Pandanus *(P.julianettii)*. By 18,000 BP men and women had settled parts of the Eastern Highlands (Watson and Cole, 1978) and the necessary adaptation from a coastal to a montane economy has broad implications for man-land relationships in the tropics. It is possible that early settlers of the Highlands exploited the rich ecotone on the boundary of montane forests and alpine grasslands, the latter being more extensive during the last glacial (25,000-14,000 BP) (Hope and Hope,1976).

By 9,000 BP people were constructing drains for water management presumably associated with horticulture at Kuk near Mt Hagen (Golson, 1977). An intensification of drainage system development at about 6,000 BP is probably associated with cultivation of staples such as taro. The introduction of sweet potato may have caused an increase in population density and land use pressure due to its wider environmental tolerance and faster maturation. Much of the dating of these systems has been by correlation of dated sequences of tephra (volcanic ash).

A great deal of our knowledge of Highlands prehistory comes from excavations in caves and rockshelters (Bulmer, 1975; White, 1972; Christensen, 1975).Occupation at these sites goes back at least 10,000 years and continues to the present in some areas. The stone tool assemblages associated with the earliest levels are characterised by waisted blades, flaked pebble tools and large steep edged scrapers. These rockshelter assemblages are paralleled in those from some open sites. Waisted blades do not persist in the archaeological record more recently than about 4,000 BP, but several specimens have edge grinding and there appears to be a technological overlap with the more recent lenticular polished axe/adzes. At the Yuku site Bulmer (1975) notes that flakes struck from polished axe/adzes are present in a stratum dated between 4,500 - 7,000 BP. The earliest evidence for marine shell in a Highland archaeological context is c.10,000 BP (White, 1972).

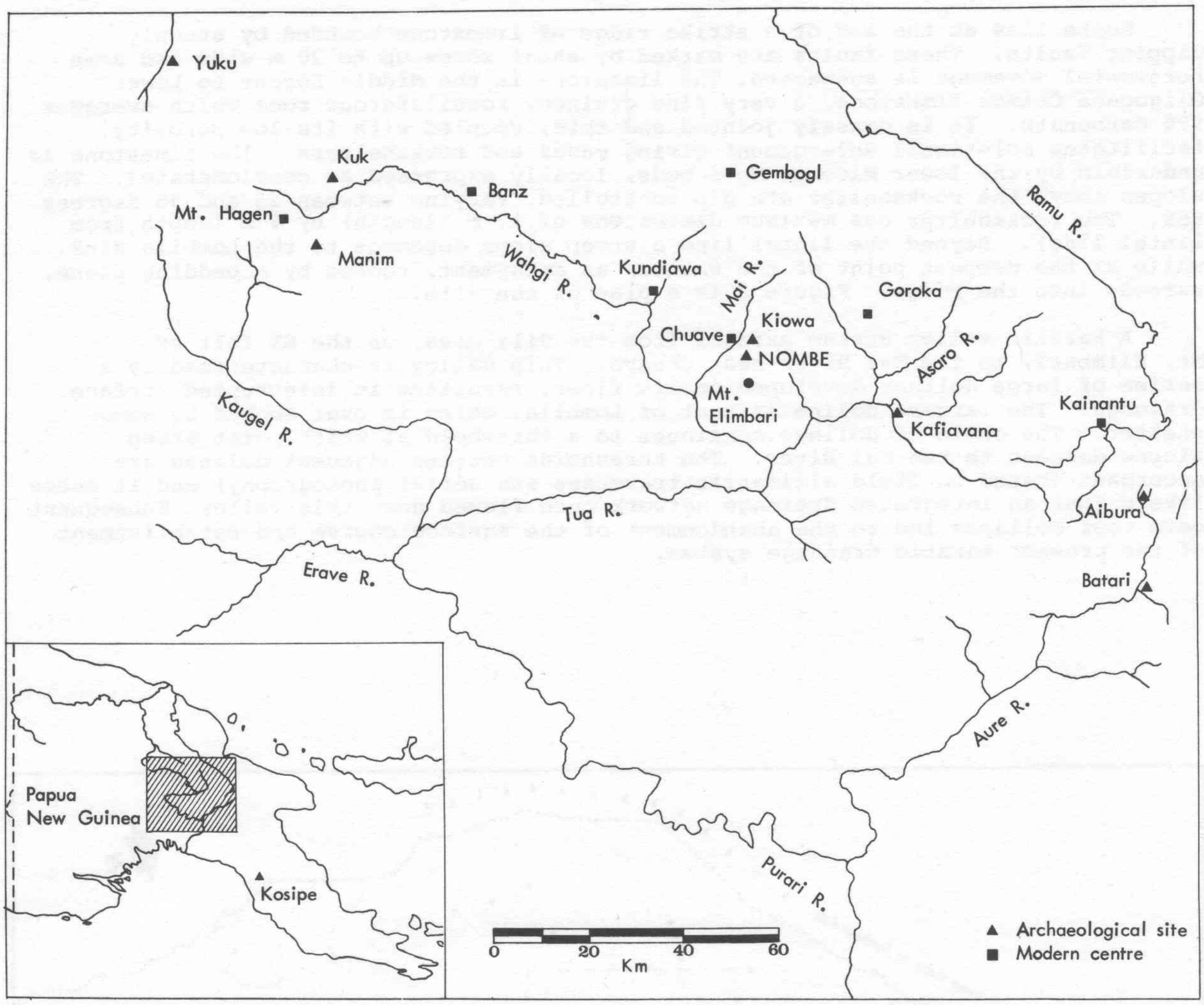

Figure 1: Archaeological sites in the PNG Highlands mentioned in the text.

One further topic of interest is the presence of extinct fauna and its possible association with mankind. Remains of *Diprotodon* dated to 33,000 BP have been recovered from swamp deposits near Tari (Williams *et al.*, 1972) and at Kiowa rockshelter Bulmer (1975) associates the remains of *Thylacinus* with levels dated between 6,000 and 10,000 BP. Certainly there is a demonstrable overlap between the arrival of hunters in the Highlands and the existence of large fauna later to become extinct. The fauna that has been recovered from clear levels of human exploitation in Highlands sites comprises mainly arboreal animals including a wide range of possums, also tree kangaroos and bats. There are also many smaller animals such as bandicoots and rodents.

NOMBE IN TIME AND SPACE

Travelling up the Purari River from the Gulf of Papua, a number of river junctions are passed and eventually, ascending the Tua River, the prominent peak of Mt Elimbari is seen. Elimbari effectively separates the Wahgi and Asaro river basins, and is a faulted limestone massif uplifted during the Pliocene (Bain and McKenzie, 1974). Nombe is a long rockshelter located on the NE side of Elimbari at an altitude of 1,600 m. It lies on a major walking track which connects the Asaro valley to the Mai river at Chuave (see location map, Figure 1).

Nombe lies at the end of a strike ridge of limestone bounded by steeply dipping faults. These faults are marked by shear zones up to 20 m wide and some horizontal movement is suspected. The limestone is the Middle Eocene to Lower Oligocene Chimbu limestone, a very fine grained, fossiliferous rock which averages 97% carbonate. It is densely jointed and this, coupled with its low porosity, facilitates solutional enlargement giving caves and rockshelters. The limestone is underlain by the lower Miocene Movi beds, locally expressed as conglomerates. The slopes above the rockshelter are dip controlled, varying between 25 and 35 degrees ESE. The rockshelter has maximum dimensions of 17 m (length) by 8 m (depth from lintel line). Beyond the lintel line a steep slope descends to the Lombila sink, while at the deepest point of the shelter an embayment, roofed by a bedding plane, extends into the ridge. Figure 2 is a plan of the site.

A karstic valley system extends from the Pila area, on the NE fall of Mt. Elimbari, to the Mai River near Chuave. This valley is characterised by a series of large dolines developed in its floor, resulting in interrupted surface drainage. The largest doline is that of Lombila, which is over looked by Nombe shelter. The chain of dolines continues to a threshold at which point steep slopes descend to the Mai River. The thresholds between adjacent dolines are accordant (based on field altimetric traverses and aerial photography) and it seems likely that an integrated drainage network once flowed down this valley. Subsequent cave roof collapse led to the abandonment of the surface course and establishment of the present karstic drainage system.

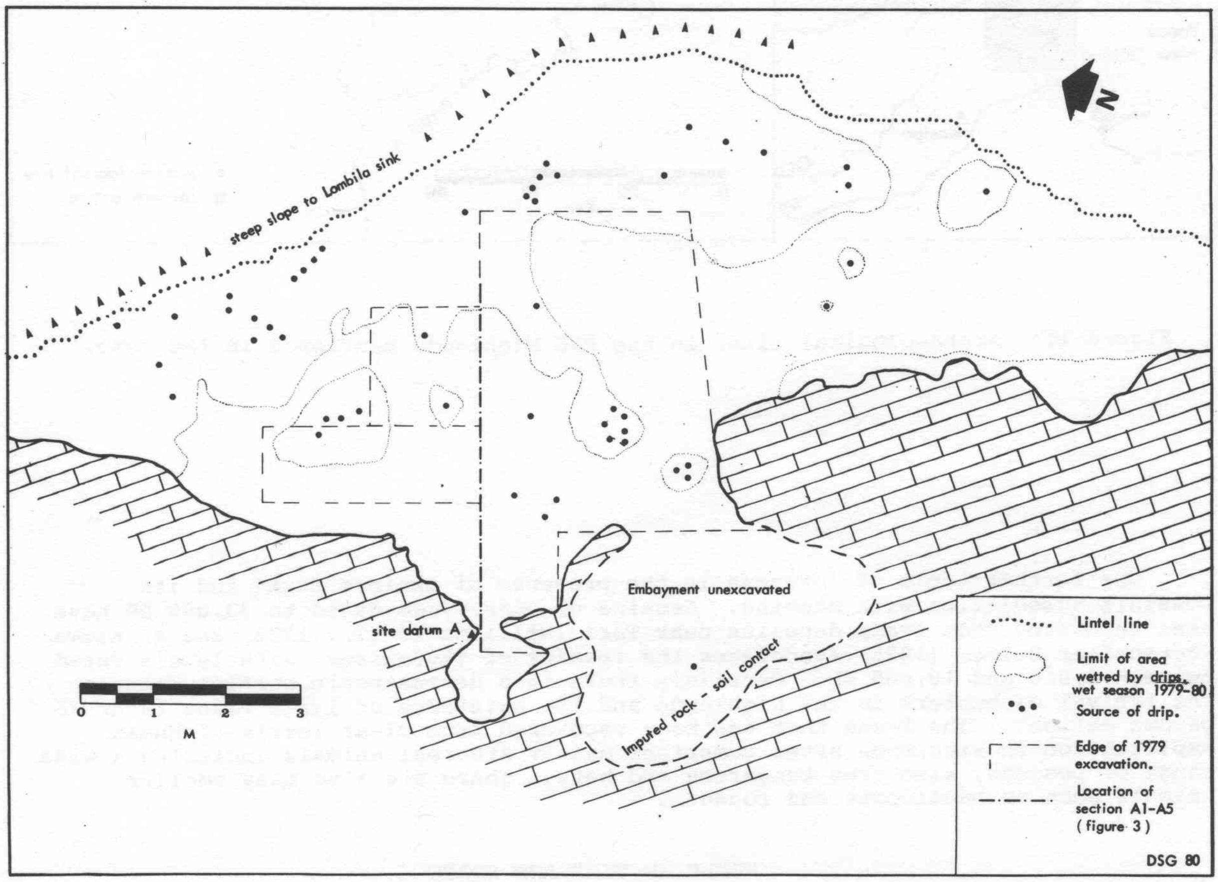

Figure 2: Plan of Nombe rockshelter showing area wetted by roof drips during excavations of late 1979 and location of section in Figure 3.

Further evidence for this is gained from relict clastic sediments located on the thresholds themselves, and at the entrance to Fato Cave, some 300 m west of Nombe. It is suggested here that at the initial stages of its development, Nombe acted as a karst spring feeding this drainage system. It is at the same level as the thresholds between the dolines and is probably the infilled lower entrance of a major cave system to which entry can be gained 30 m south of Nombe. A 4 m cliff provides access to a series of strike controlled galleries whose northernmost termination is a deep channel cut in sediments. It is suggested that this channel connects with the rear of Nombe and is the course to the former spring. The present entrance to the cave is the result of wall and roof collapse, exposing a formerly fluvial cave. Solutional scallops and rock pendants suggest the former flow regime. This system would have collected drainage from fissures and small dolines on the ridge above Nombe.

Through time, any cave conduit carrying suspended sediment may decline in competence, resulting in deposition of the clastic sediment load. In the case of Nombe, this deposition may have been facilitated through block fall from the cliff providing impoundment. The karst spring would become progressively blocked until only the largest flows would emerge, entrenching the accumulated sediments. Following this blockage, other conduits in the rock mass would become active, resulting in spring emergence elsewhere on the slope. Such a spring exists, lower on the slope below Nombe. The combination of high rainfall and pure limestone has resulted in highly calcareous percolation and groundwater. Thus calcium carbonate deposition is widespread. Large stalactites have formed within the Nombe shelter and the effect of their dripwater is noticeable in the underlying sediments. Solutional roof pockets have acted as conduits for percolation water (at least seasonally) and extensive sheets of flowstone have built up on the underlying sediments. Subsequent slumping of the sediments has left these exposed in the roof with adhering cultural deposits.

The morphology and trends of rock surfaces, speleothems and sediments suggest that a former outflow trench existed, cut into the basal clay sediments in the southern part of the site. It is therefore likely that the lowest elements in the Nombe stratigraphy may be the result of infilling of a karst spring, and may therefore have the characteristics of fluvial cave sediments.

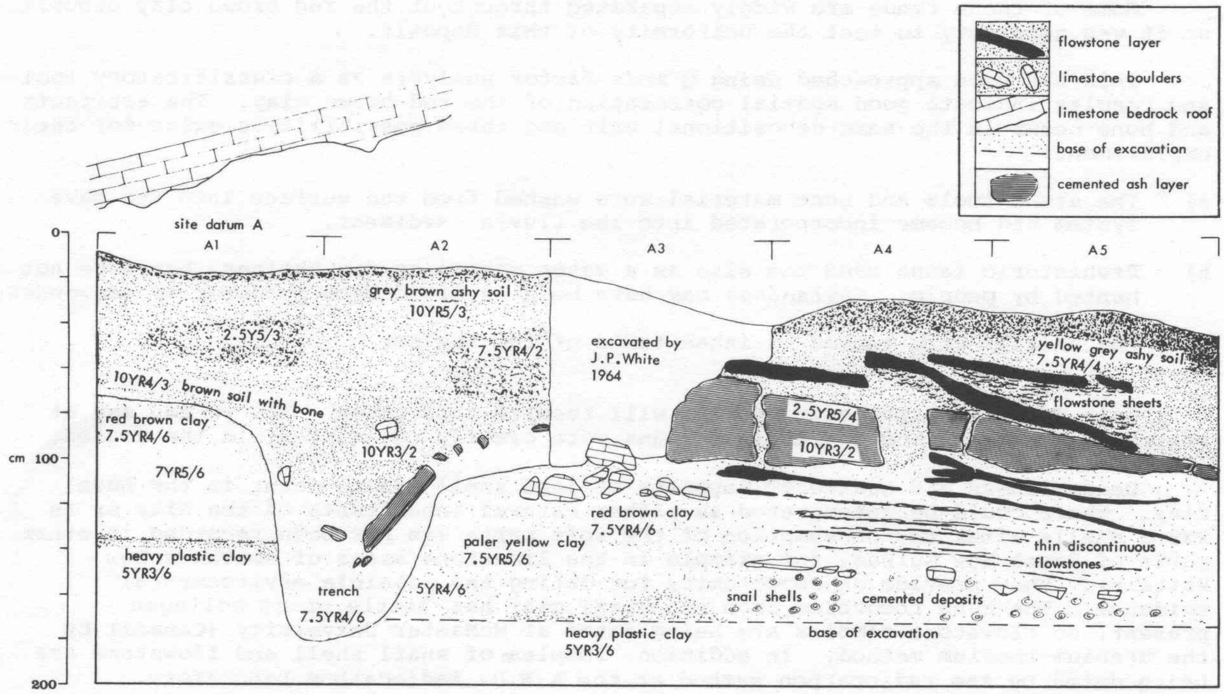

Figure 3: Section diagram of north face of squares A1 to A5, running east from site datum A, as recorded during 1979 excavations.

THE DEPOSITS AT NOMBE

Figure 3 is a section diagram running from the rear of the shelter to the dripline. On this diagram three main stratigraphic units can be discerned:

1. the basal red brown clay, with varying degrees of carbonate cementation.
2. above the clay, a sequence of flowstones, brown earths, cemented deposits and ash layers. This unit is largely absent from the western end of the section due to the disturbance caused by the digging of a trench subsequent to the formation of the cemented ash layers.
3. the uppermost loose, organic loams and ashy soils with abundant artifacts.

Each of these units will be discussed in turn.

1. The basal red brown clay (Munsell 7.5 YR 5/6) underlies a-1 the excavated site and only in one area is its base reached. At the NW corner of the shelter it is underlain by weathered limestone blocks, probably roof fall. The unit varies from a fine, plastic brown clay to a coarsely aggregated cemented clay, depending on the amount of carbonate deposition. The fine, plastic clay occurs at the lowest levels of the excavation and may well be devoid of human associations. The bulk of the deposit is a granular clay whose textural analysis (Figure 4) shows a strong mode in the fine clay fraction. This texture is consistent with that of fluvial cave sediments from montane PNG, a grain size envelope of which is superimposed on the relevant curve in Figure 4. On dispersion the other members of this unit show markedly similar texture supporting both the origin and textural uniformity of this basal unit. The coarse fraction is chiefly small limestone fragments, sparse pulverised bone and stone, and burnt soil nodules. The sediment is alkaline (pH 7.9) with organic carbon content low at 0.13 - 1.39%, and phosphorus also low at 0.08 - 0.58%. There is not a high density of artifactual material in this unit. Most appears to be concentrated in the SE sector of the excavation amongst cemented blocks and flowstones. The fauna is well preserved and includes *Thylacinus*, *Zaglossus*, and *Protemnodon* sp. The latter is of interest as it is a browsing animal indicating exploitation of grasslands (Plane, in White, 1972), whilst the *Thylacinus* has not yet been dated in PNG to a period earlier than 6 - 9,000 BP. The presence of these two genera would indicate that at the time of the formation of the deposit the inhabitants were within reach of the grassland fauna of the late Pleistocene period. The stone tools found in this unit include waisted blades of slatey hornfels, pebble tools, large scrapers and rectangular blades with some edge polish, again consistent with an early date.

Some of these finds are widely separated throughout the red brown clay deposit, so it was necessary to test the uniformity of this deposit.

This has been approached using Q mode factor analysis as a classificatory tool and results indicate good spatial correlation of the red brown clay. The artifacts and bone occur in the same depositional unit and three possibilities exist for their emplacement:

a) The stone tools and bone material were washed from the surface into the cave system and became incorporated into the fluvial sediment.

b) Prehistoric fauna used the site as a water source or for shelter, but were not hunted by people. *Thylacinus* may have been involved as a predator or scavenger.

c) The animals were hunted by inhabitants of the shelter.

Only detailed taphonomic studies will resolve this issue. All we can say at present is that man and the extinct fauna were clearly co-existent in the region.

Dense lenses and scattered deposits of land snail shells occur in the basal clay. These could be interpreted as either natural inhabitants of the site or as waste shells after the consumption of the soft parts (as has been recorded in other parts of Papua New Guinea, for example in the limestone areas of southern New Britain). They provide an opportunity for dating and possible environmental evidence. The bone recovered from the basal clay has little or no collagen present, so flowstone samples are being dated at McMaster University (Canada) by the uranium-thorium method. In addition, samples of snail shell and flowstone are being dated by the radiocarbon method at the A.N.U. Radiocarbon Laboratory. The results should provide an internally calibrated chronology for this important deposit.

2. Above the basal clay are mixed deposits of flowstones, cemented earths and ash layers, some cemented. The flowstones are mostly thin and discontinuous, and can be related to roof drips. They provide a dateable discontinuity in sediment deposition. The cemented brown earths closely resemble the basal clay and probably represent diminishing additions to, and reworking of, this deposit. The cemented ash deposits were initially thought to be tephras, but extensive checking in the vicinity has failed to find any surficial tephra mantles. It is more likely that at least some of the Nombe deposits are the result of fire ash deposition in shallow depressions and a gour

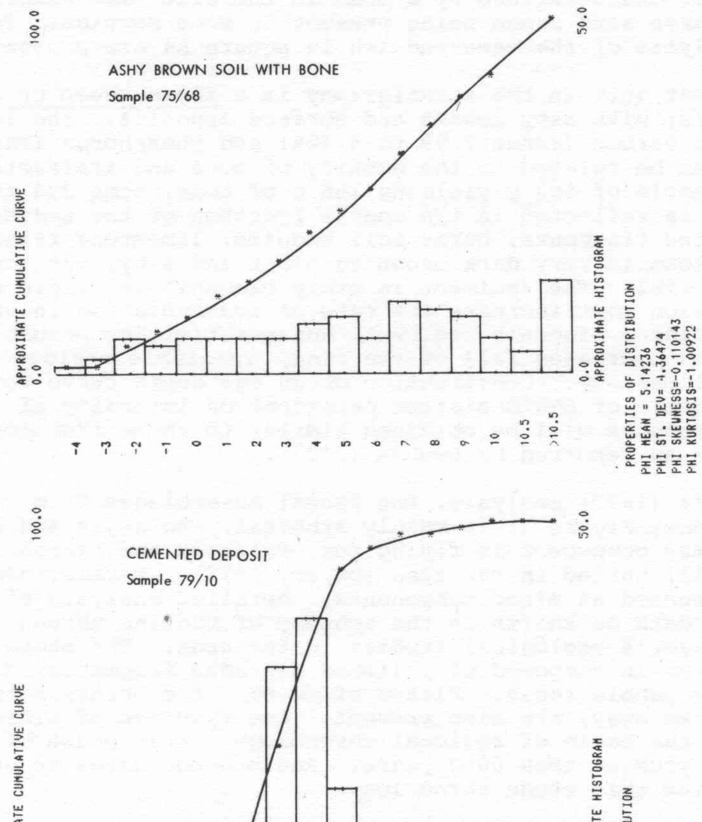

Figure 4: Selected particle size analyses, in phi units for Nombe sediments, showing histograms, cumulative curves and granulometric statistics. The dotted grain size envelope superimposed on the red brown clay cumulative curve is formed from the cumulative curves of 17 stream sediment samples from Selminum Tem cave, Hindenburg Plateau, PNG.

pool. The calcareous ash deposits are sealed in by flöe calcite, itself overlain by partially cemented ashy soil. A scalloped calcite rim and microgour sloping surface are also present. The cemented ash has been disturbed after lithification and one large block and several fragments are present in the fill of a trench excavated from a much higher level into the red brown clay. The texture of these ashy deposits is characterised by a mode in the slit size range, with a secondary mode in the coarse sand range being present in some samples. In Figure 4 the results of analysis of the cemented ash in square A4 are presented.

3. The uppermost unit in the stratigraphy is a loose, deep brown organic loam (Munsel 5 YR 3/2) with ashy lenses and surface deposits. The lower sediment is rich in organic carbon (range 2.99 to 8.46%) and phosphorus (range 0.23 to 1.49%). These values can be related to the density of bone and artifacts in the deposit, a bulk density sample of 500 g yielding 156 g of bone, some 300 fragments. This faunal density is reflected in the coarse fraction of the sediments, which is made of bone and stone fragments, burnt soil nodules, limestone fragments and charcoal. The uppermost loam is very dark brown to black and ashy, but contains much less artificial material. The sediment is truly biogenic in origin and this mode of sediment accession must increase the rate of sedimentation in shelters like Nombe. As well as providing biogenic sediment, human activities probably promote spalling of the walls and increased fall of the fine, insoluble residue that fills fine cracks in the limestone. Construction of an age depth curve for the site should refine this picture of sedimentation dependent on intensity of occupation. It is expected that results will be obtained similar to those from coastal sandstone shelters in NSW as reported by Hughes (1977).

From White's (1972) analysis, the faunal assemblages from the upper unit (above) the top flowstone, Figure 3) is mainly arboreal, *Phalanger* and *Pseudocheirus* spp. A large secondary component is flying fox, *Dobsonia* and *Pteropus* spp. All these animals are still hunted in the area (Dwyer, 1975). Peramelidae and Macropodidae are also represented as minor components. Detailed analysis of the faunal material should provide data on shifts in the economy of hunting through time and be comparable with Dwyer's ecological studies in the area. The stone tool assemblage in the upper stratum is composed of polished axe/adze fragments, small flake tools and cores, and some pebble tools. Flakes of *gaima*, the hornfels from the Kafetu quarry some 15 km away, are also present. One specimen of pierced marine shell was recovered. On the basis of regional chronology, this phase of site occupation may be regarded as younger than 6000 years. Radiocarbon dates on charcoal and snail shell will refine this crude chronology.

Some of this uppermost material has intruded lower strata along cracks in the flowstone or cemented ash (Figure 3). This intrusion may be the consequence of several interrelated processes, namely:

1) slumping of the deposits following truncation by water erosion at the dripline.

2) seismic activity causing slumping and cracking of the deposits.

3) solutional enlargement of joints in the underlying limestone and settling of sediment into the joints, resulting in loss of support for overlying deposits.

Given this probability of slumping and disturbance in limestone cave and rockshelter deposits due to seismic, erosive and solutional processes, it is probably unwise to attempt fine vertical subdivisions of the stratigraphy when analysing artifactual material, unless a detailed examination of the stratigraphy reveals no signs of disturbance.

CONCLUSIONS

Continuing analysis of the types and proportions of both faunal remains and stone tools from the Nombe excavations will provide information on technological and economic change over a long time period, from the late Pleistocene to the historic. This period covers the introduction of horticulture into the Highlands. Given that this innovation would have had profound effects on the lifestyle, we may therefore gain further insights into the dynamics of hunter gatherer societies and their interactions with the tropical montane environment.

Nombe is fairly typical of a large number of rockshelters in the Highlands. Most tend to be located at lithological or structural boundaries which have acted as points for seepage emergence. Subsequent infilling has obscured the evidence for this spring activity which is detectable from bedrock morphological evidence and sediment characteristics. The presence of roof drips acts to consolidate sedimentary deposits and associated cultural material resulting in the formation of unusual deposits such as cemented fire ashes. Flowstone layers in the stratigraphy provide dateable discontinuities and may be especially useful where other dateable material has been lost by leaching. At Nombe the loose, ashy upper deposits are largely anthropogenic in origin and are composed of occupation debris and some surficial organic matter. The rate of deposition of such sediments may be rapid. Slumping and disturbance, the result of seismic activity and the solutional opening of bedrock joints, may necessitate coarse vertical divisions in the analysis of cultural material. In such a geomorphically mobile landscape as that of the PNG

Highlands, it is false to assume stability in cave and rockshelter deposits. Positive evidence of stability, such as conformable strata and lack of intruded strata, must be gained by a careful examination of the site stratigraphy.

Despite these problems, rockshelter deposits are protected from erosion and weathering and therefore offer excellent opportunities for the reconstruction of past man-fauna and man-land interactions.

ACKNOWLEDGEMENTS

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TOWARDS AN AIR QUALITY STANDARD FOR TOURIST CAVES: STUDIES OF CARBON DIOXIDE ENRICHED ATMOSPHERES IN GADEN - CORAL CAVE, WELLINGTON CAVES, N.S.W.

R. Armstrong L. Osborne

Abstract

Carbon dioxide enriched atmospheres are not uncommon in Australian caves and have posed a safety problem for cavers. Carbon dioxide enrichment of a tourist cave's atmosphere is a management problem which can only be approached when standards for air quality are applied. In Gaden - Coral Cave two types of carbon dioxide enrichment are recognised: enrichment by human respiration and enrichment from an external source. Standards for air quality in mines and submersible vehicles are applicable to tourist caves. A maximum allowable concentration of 0.5% carbon dioxide is recommended as the safe, but not the most desirable, air quality standard for tourist caves.

INTRODUCTION

Concentrations of carbon dioxide and oxygen in cave atmospheres can be very different from those found in normal air. Normal dry air at sea level contains 20.95% oxygen and 0.3% carbon dioxide with the remainder being nitrogen and traces of inert gases.

Exposure of humans to atmospheres in which carbon dioxide is enriched or oxygen depleted relative to normal air will result in physiological stress. When found in caves these atmospheres are called "foul air" (James, Pavey and Rogers, 1975).

In this paper a study of carbon dioxide enriched atmospheres in Gaden - Coral Cave, Wellington Caves N.S.W. and a review of existing standards for air quality are used to define an air quality standard for tourist caves.

Types of Carbon Dioxide Enrichment

James (1977) recognised three distinct types of carbon dioxide enrichment in cave atmospheres. James' "Type I" situation involved addition of carbon dioxide to the cave atmosphere with a dilution of other air components. Such air would typically contain 0.3% CO_2 and 20.8% O_2. In "Type II" carbon dioxide has replaced oxygen. This is the "normal" form of "foul air" and could contain 3% CO_2 with 18% O_2.

"Type III" atmosphere is fairly unusual and has oxygen significantly more depleted than "Type II". This type of atmosphere is known as "stink damp" as it often contains hydrogen sulfide.

Sources of Carbon Dioxide

James (1977) recognised six sources of carbon dioxide in cave atmospheres:

1) diffusion of gaseous carbon dioxide into the cave
2) evolution from cave waters
3) production by micro-organisms
4) respiration of plants and animals
5) burning of hydrocarbons
6) volcanic emissions

Of these, source six is irrelevant to Australian conditions, source five should not occur in tourist caves and source one simply indicates that a primary source exists outside the confines of the cave.

Water in contact with air and percolating through the soil absorbs carbon dioxide, becomes acidic ($CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$) and dissolves limestone ($CaCO_3 + H^+ \rightleftharpoons Ca^{2+} + HCO_3^-$) (Picknett, Bray and Stenner, 1976).

On entering a cave the water may liberate carbon dioxide into the cave atmosphere, reversing these equilibria, and deposit calcium carbonate. This is believed to be the origin of the carbon dioxide in James (1977) "Type I" atmosphere.

Micro-organisms, either feeding on washed-in organic matter or on pollutants in cave waters, may produce carbon dioxide either by aerobic or anaerobic respiration. This is believed by James (1977) to be a major source of carbon dioxide in cave atmosphere.

Respiration by plants and animals is usually considered to be a minor source of carbon dioxide. In tourist caves however, significant numbers of humans breathe the air and their contribution to carbon dioxide production must be considered. A resting adult exhales about 500 ml of air in each breath (Crofton and Douglas, 1975). At a resting rate of 12 breaths per minute this is about 6 litres of air of which four percent is carbon dioxide. In a tourist cave with poor ventilation and high usage this could be a significant source of carbon dioxide.

Seasonal Behaviour of Carbon Dioxide

Air movement occurs between caves and the outside air as a result of several mechanisms outlined by Wigley and Brown (1976). An important mechanism is gravitational movement of dense cold air into caves and warm light air out of caves.

Air in caves tends to be insulated from seasonal temperature changes so that in summer it is much cooler and denser than outside air and in winter it is warmer and less dense than outside air. If caves have two entrances at different elevations this will result in the "chimney effect" and the cave will "breathe".

Where carbon dioxide enrichment has been studied, for example, at Bungonia (James, 1977) and Wellington (this work), caves either have single entrances or multiple entrances at roughly the same topographic level making "chimney effect" unimportant. In these areas summer atmospheric temperatures exceed cave temperatures both day and night resulting in carbon dioxide enriched air being trapped in the cave for most of the summer. In late summer and early autumn the night temperatures begin to drop below cave temperatures and carbon dioxide enriched air is drawn from deep in the caves into parts of the cave near the surface where it is usually absent. It has been found in this study that during March carbon dioxide enriched atmospheres pose their most serious threat to safe cave management.

Physical Effects of Carbon Dioxide Enrichment

Atmospheric air provides the body with a source of oxygen and a sink for carbon dioxide. Carbon dioxide is lost from the blood to the air by a process of diffusion.

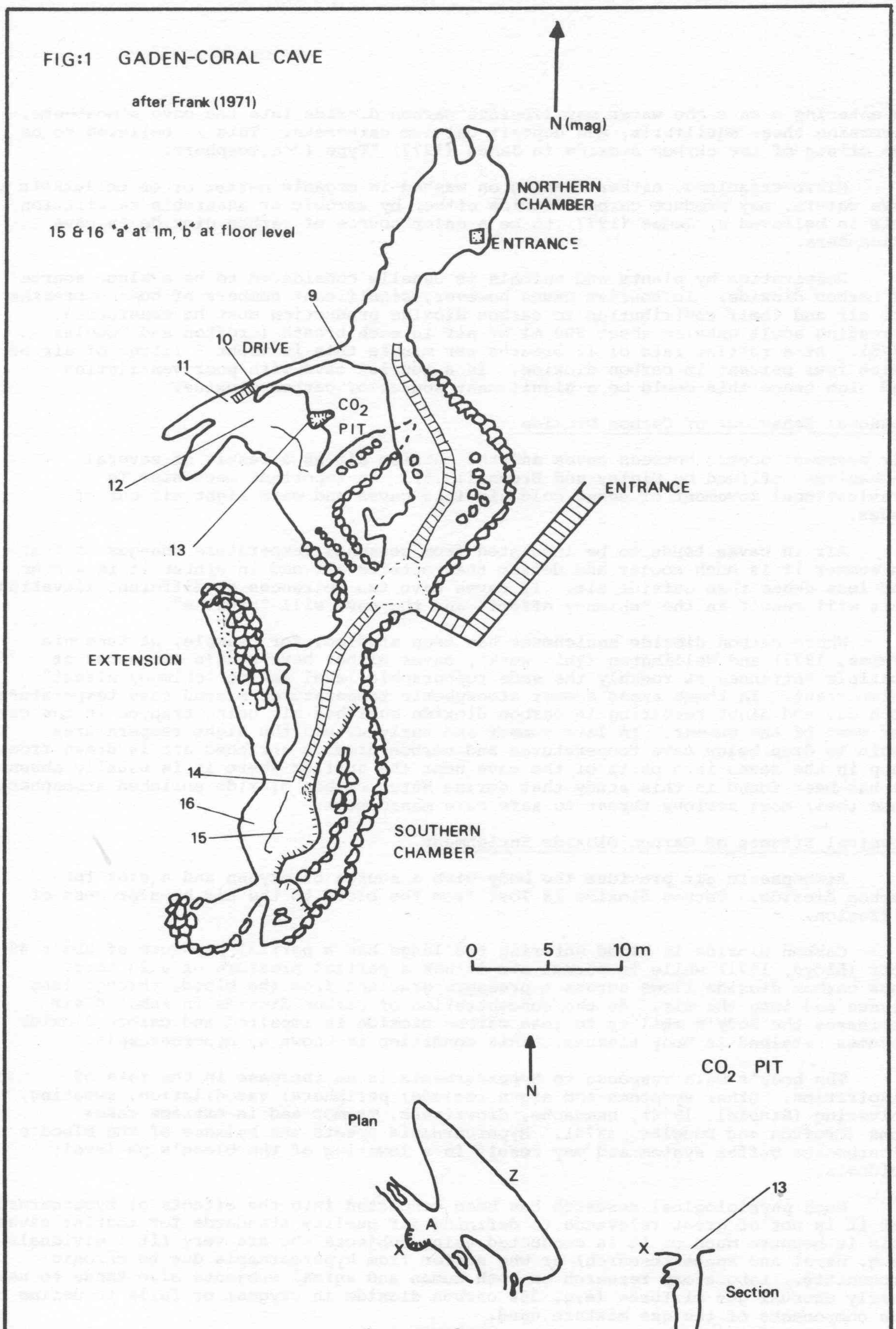
Carbon dioxide in blood entering the lungs has a partial pressure of about 46 torr (Lloyd, 1971) while in normal air it has a partial pressure of 0.23 torr. Thus carbon dioxide flows across a pressure gradient from the blood, through lung tissue and into the air. As the concentration of carbon dioxide in inhaled air increases the body's ability to lose carbon dioxide is impaired and carbon dioxide becomes retained in body tissues. This condition is known as hypercarnapia.

The body's main response to hypercarnapia is an increase in the rate of respiration. Other symptoms and signs include; peripheral vasodilation, sweating, shivering (Stupfel, 1974), headache, drowsiness, tremor and in extreme cases coma (Crofton and Douglas, 1975). Hypercarnapia upsets the balance of the blood's bicarbonate buffer system and may result in a lowering of the blood's pH level: acidosis.

Much physiological research has been conducted into the effects of hypercarnapia but it is not of great relevance to defining air quality standards for tourist caves. This is because much of it is conducted using subjects who are very fit individuals (e.g. naval and space research) or who suffer from hypercarnapia due to chronic bronchitis. Laboratory research on both human and animal subjects also tends to use fairly unusual gas mixtures (e.g. 30% carbon dioxide in oxygen) or fails to define all the components of the gas mixture used.

Chronic exposure to carbon dioxide enriched atmospheres in the range of 0.03 to 3 percent carbon dioxide has been studied by Weitzman, Kinney and Luria (1969). They found that long term exposures caused impairment to both night vision sensitivity and colour sensitivity for green.

FIG:1   GADEN-CORAL CAVE



after Frank (1971)

15 & 16 'a' at 1m, 'b' at floor level

Sketch Map Only

J.L. Bartlett

6 September 1978

STUDIES IN GADEN - CORAL CAVE

Wellington Caves have long been recognised as containing carbon dioxide enriched atmospheres. Ramsay (1882) reported "foul air" in the caves and how it affected candles. Trickett (1900) reported "foul air" in Gaden - Coral Cave and recommended that it should not be developed for tourist use. Frazer (1958) made an instrumental study of carbon dioxide enrichment at Wellington Caves and reported 12.4% carbon dioxide in the lower part of Gaden - Coral Cave.

Although data presented here have not been previously published, they formed the basis of advice to Wellington Shire Council and part of the Master Plan for Wellington Caves (Osborne, 1980).

Methods

Values for carbon dioxide and oxygen are given in volume percent. Measurements were made using either a Drager "Multi Gas Detector" with CH 2501 and CH 23501 tubes or a G.F.G. "Uni Gas" instrument calibrated to normal atmospheric air.

Gaden - Coral Cave

Gaden - Coral Cave is the smaller of two caves open for public inspection at Wellington Caves. It consists (Figure 1) of a north - south trending rift, dipping to the west, divided into a northern and southern section by a pile of breakdown. An artificial entrance connects with the cave at the apex of the breakdown pile. This entrance originally entered the cave at right angles to its axis but was altered in the late 1960s so that a bend towards its base brings the entrance passage roughly parallel to the cave axis.

The Northern Chamber is developed in bedrock and connects to the surface through a narrow vertical shaft. An artificial drive to the west leads to the lower section of the cave. Here the walls are composed of red porous sediment and helictites have developed on parts of them. A 3 m deep shaft in the floor is called the CO_2 pit.

Steps lead from the base of the entrance passage to the Northern and Southern Chambers which contain coralloid speleothems for which the cave is renowned. The steps leading to the Southern Chamber are steeper than those to the north and pass through an area decorated with stalactites and flowstone.

Carbon Dioxide Enriched Atmospheres

Carbon dioxide enriched atmospheres are found in two regions of the cave. Air in the CO_2 Pit is always enriched and this enrichment usually extends through the lower section of the cave. On many occasions this has extended to within 1 m of the junction of the drive with the Northern Chamber.

Carbon dioxide enrichment occurs less frequently in the Souther Chamber. Enriched air ponds below track level in this area and may intrude into the tourist level. Concentrations of carbon dioxide in the Southern Chamber are considerably less than those in the CO_2 Pit and environs.

CO_2 Pit and Lower Section

Previous studies of the CO_2 Pit commenced in 1954 (Lane and Richards, 1963) and culminated with the work of Frazer (1958). Using a Fyrite "Carbon Dioxide Indicator" Frazer recorded: 12% CO_2 with 22% O_2 (January 1958), 12.5% CO_2 with 20.5% O_2 (April 1958) and 13.5% CO_2 with 20% O_2 (May 1958) for air within the CO_2 Pit.

The concentrations of carbon dioxide found by Frazer are higher than those found in this study (maximum in the CO_2 Pit of 9%), but they do illustrate a relative lack of oxygen depletion. When concentrations of carbon dioxide have been found to exceed 4% they have usually been associated with a relative lack of oxygen depletion (Table 1). This suggests that much of the carbon dioxide is not being produced within the cave by biological activity, but is being added to the cave from an external source via the porous sediments.

Following flood rains in September 1978 it was found that the area around the CO_2 Pit was free from excessive carbon dioxide. On the morning of September 6 the CO_2 Pit was entered by J. Bartlett, G. Price and the author using oxygen assisted breathing and a sketch map produced (Figure 1). An attempt to re-enter the CO_2 Pit. later that afternoon and produce a survey was aborted when 9% CO_2 was measured 2 m down the CO_2 Pit and highly carbon dioxide enriched air was found to be spilling out from the CO_2 Pit into the chamber above.

TABLE 1 AIR COMPOSITION: CO_2 PIT AND ENVIRONS

Position locations numbered on Figure 1.

Dräger measurements marked with "d", remainder by G.F.G.

DATE	TIME	LOCATION	CO_2%	O_2%
1/77	1809 hrs	11 2 m off floor	3 d	
1/77	1810	11 floor	6 d	
1/77	1812	13	7 d	
1/77	1814	12	2 d	
23/3/78		11	5 d	
24/3/78	1125	11	5.8 d	
25/3/78	1135	9	1 d	
5/9/78		13	- d	
6/9/78	1010	13 2 m down Pit	4 d	
6/9/78	1102	13 Root Chamber	3.8 d	
6/9/78	1407	13 2 m down Pit	9 d	
5/5/80	1757	9	0.5	21
5/5/80	1759	10	0.5	20.5
5/5/80	1800	11	1.5	20
5/5/80	1802	12	4.5	17
5/5/80	1803	12	5.5	17
5/5/80	1804	13	Off scale	11
6/5/80	1502	9	0.5	20
6/5/80	1505	10	1.6	20
6/5/80	1506	11	3	19
6/5/80	1519	11	3	17
6/5/80	1520	12	Off scale	Not recorded
18/4/81	1419	9	0.5	21
18/4/81	1420	10	0.6	21
18/4/81	1622	9	0.8	21
18/4/81	1523	10	1	21
18/4/81	2058	9	0.5	21
18/4/81	2059	10	0.5	20.8
18/4/81	2101	11	4	18
18/4/81	2102	12	9.5	14
18/4/81	2348	9	1.0	21
18/4/81	2349	10	1	21
18/4/81	2350	11	5	18
18/4/81	2351	12	Off scale	14
18/4/81	2352	13	Off scale	10
19/4/81	1424	9	1.3	21
19/4/81	1425	10	1.5	20.6

Southern Chamber

Carbon dioxide enrichment was first recognised as a problem in the Southern Chamber when guides complained of headaches during Easter 1978 (24-27 March 1978) Measurements (Table 2) showed that a maximum of 3.8% CO_2 was present in the tourist section and that (at the time) tourists were spending from 10 to 15 minutes in air with carbon dioxide contents ranging from 1.5% up to that value.

Enrichment usually occurs only in the tourist section of the Southern Chamber during summer and autumn months. Extensive measurements have shown that small concentrations of carbon dioxide are found here associated with almost equal amounts of oxygen depletion. This is then a Type II atmosphere indicative of local carbon dioxide production by biological activity.

The Southern Chamber has a volume of roughly 250 cubic metres and during peak tourist seasons 20 people spend up to 20 minutes in it seven times a day. This amounts to 47 man hours of carbon dioxide production at a rate of at least 14.4 litres per hour. Thus, assuming the tourists were in a resting state, 677 litres of carbon dioxide would be produced which would cause a daily increase of 0.27% in the carbon dioxide content of the air. Since the tourists are not in a resting state the quantity of carbon dioxide produced would be more than this. This production, combined with the poor ventilation of this section of the cave, accounts for much of the carbon dioxide enrichment that occurs in the Southern Chamber.

Air below path level and in the low passage leading to the north is often carbon dioxide enriched when that in the Southern Chamber tourist area is not. This enrichment probably has the same source as that in the CO_2 Pit and would add to the effect of the tourists during periods of high enriched air mobility (particularly March) to produce the conditions found over Easter 1978.

TABLE 2 AIR COMPOSITION: SOUTHERN CHAMBER

Position locations numbered on Figure 1.

Dräger measurements marked with "d", remainder by G.F.G.

DATE	TIME	LOCATION	CO_2%	O_2%
1/77		16b	2 d	
1/77		Extension	1 d	
1/77		Extension	2 d	
1/77		Extension	4 d	
23/3/78	2005	15a	1.5 d	
24/3/78	1120	15a	2 d	
25/3/78	1140	15a	2 d	
25/3/78	1153	15a	3.8 d	
25/3/78	1535	15a	1.75d	
25/3/78	1552	15a	2.1d	
26/3/78	1040	15a	2 d	
26/3/78	1152	15a	2 d	
5/9/78	2000	15a	0.17d	
5/5/80	1837	14	0.5	20
5/5/80	1840	15b	0.5	20
5/5/80	1841	16a	1.5	19.5
5/5/80	1842	16b	2.0	19
6/5/80	1428	14	0.6	21
6/5/80	1429	15a	0.6	21
6/5/80	1430	15b	1	21
6/5/80	1431	16a	1.5	20
6/5/80	1432	16b	3	19
6/5/80	1453	14	0.5	20
6/5/80	1454	15a	0.5	20
6/5/80	1454	15b	0.5	20
6/5/80	1455	16a	1	20
6/5/80	1455	16b	2.5	19
7/5/80	1424	14	1.25	21
7/5/80	1430	15a	1.3	20.9
7/5/80	1430	15b	1.5	21
7/5/80	1431	16a	2.5	19
7/5/80	1431	16b	4.0	19
7/5/80	1435	15a	1	20.9
7/5/80	1436	15b	1.25	20.9
7/5/80	1438	16a	2.5	19
7/5/80	1439	16b	3.5	19
7/5/80	1540	14	0.5	19
7/5/80	1542	15a	0.5	19
7/7/80	1542	15b	0.6	19
7/5/80	1543	16a	1	19
7/5/80	1543	16b	3	18
18/4/81	1431	14	0.5	18
18/4/81	1432	15a	0.5	20.2
18/4/81	1433	15b	0.6	20.2
18/4/81	1633	14	0.5	20
18/4/81	1634	15a	0.5	20
18/4/81	1634	15b	0.5	20
18/4/81	1636	15a	0.25d	
18/4/81	2125	14	0.5	20.8
18/4/81	2129	15a	0.6	21
18/4/81	2129	15b	0.5	21
19/4/81	1436	14	0.6	20
19/4/81	1437	15a	0.6	20
19/4/81	1438	15b	0.5	20

Source of Carbon Dioxide in the CO_2 Pit.

When it contains only low concentrations of carbon dioxide the atmosphere of the CO_2 Pit and environs resembles that of the Southern Chamber. Low concentrations of carbon dioxide and almost equivalent amounts of oxygen depletion are probably the result of tourist activity in the Northern Chamber. The enriched air is displaced down the drive by fresh air entering the cave via the vertical entrance to the Northern Chamber.

The origin of high concentrations of carbon dioxide in the CO_2 Pit, however, remains problematical. It has been suggested previously that the association of high concentrations of carbon dioxide with a lack of equivalent oxygen depletion indicates that much of the carbon dioxide is not locally produced. Possible sources of this carbon dioxide are now considered.

If the sediments are the immediate source of the carbon dioxide then it must either be generated within them or in places in contact with them. Generation within the sediments could result from either inorganic precipitation of carbonate in the pore spaces by vadose water or biological activity.

Generation in places in contact with the sediments could occur either in air or water filled cavities. Fissures receiving detritus from the surface contain carbon dioxide produced by microorganisms. This carbon dioxide could diffuse through the sediments and into the cave.

At Wellington Caves, bodies of still water are located in Cathedral, Mitchell's and Lime Kiln Caves. This water develops extensive deposits of flöe calcite on its surface indicating that degassing and consequent deposition of carbonate are occurring.

If these bodies of water represent small parts of an extensive groundwater system that has little contact with the air then degassing from it into the sediments could be a major source of carbon dioxide. If there were any pollution of this water then it would be an even more effective source.

Recent exploration in Lime Kiln Cave (Osborne *et al.*,in press) indicates that the pools in this cave are part of an extensive groundwater system. This suggests that evolution of carbon dioxide from cave waters is a possible major source of carbon dioxide infiltration into Gaden - Coral Cave.

AIR QUALITY AND TOURIST CAVE MANAGEMENT

Tourist caves are taken in this paper to be those developed caves to which the public may gain access by payment of a fee. They may be traditional guided caves or self-guided caves. One group of caves not conisdered here but to which serious attention needs to be given are those caves to which access is unrestricted either by regulation or need for equipment other than lights and which are frequented by members of the public rather than members of the caving community. Grill Cave at Bungonia is an example of this type of cave.

Managers of tourist caves have a legal and moral responsibility to ensure that patrons and employees are protected from foreseeable dangers to their health and safety. Accumulation of carbon dioxide in a cave beyond acceptable limits represents such a danger.

It is essential therefore to know:-

a) whether there is carbon dioxide enrichment in a particular cave.
b) what type and level of enrichment occurs,
c) what are acceptable standards for tourist cave air,
d) what management strategies are required,

in order for a management authority to fulfil its duty of care. It has been shown that a study like this can establish the first two requirements.

Air Quality Standards

Air in tourist caves need to be safe both for tourists who are exposed to it for a short period of time and guides who are repeatedly exposed to it. The quality should also be desirable so that the effects of poor quality, although safe, air do not detract from the experience of the tourists or the efficiency of the guides. The environment in a mine or a submersible vehicle is analogous to that of a cave. Air quality standards for these environments are used to develop standards for tourist caves.

For mines, legislation in both New South Wales (N.S.W.,1912) and Great Britain (Great Britain, 1954) require that the carbon dioxide content of mine air shall not exceed 1.25% and that the oxygen content shall not fall below 19%. Should this occur ventilation is deemed to be inadequate and entry into such an atmosphere is proscribed. Stricter legislation in the United States (Bureau of Mines, 1953) and the U.S.S.R. (Skochinsky and Komarov, 1969) has a maximum allowable concentration of 0.5%. The threshold limit value for carbon dioxide, the maximum value to which nearly all workers can be repeatedly exposed for long periods without adverse effect, is 0.5% (National Coal Board, 1970).

Designers of submarines and diving bells need to provide an atmosphere in which both carbon dioxide and oxygen concentrations are kept within strict limits. The American Bureau of Shipping (1979) requires that the carbon dioxide content of these atmospheres be kept at or below 0.5%.

Giving advice to cavers, James *et al.* (1975) suggested that care and experience are required when entering cave atmospheres where the carbon dioxide level exceeds 1%.

When applying these standards to tourist caves it must be remembered that tourists range considerably in both age and fitness and that guides are repeatedly exposed to the cave atmosphere. These considerations should lead us to err on the side of caution.

Observations in Gaden - Coral Cave have shown that, at concentrations of 0.25% carbon dioxide and 20% oxygen, tourists developed peripheral vasodilation and commented on the poor state of the air on leaving the cave. Although by all the above standards these conditions must be considered "safe" they cannot be considered desirable.

Management of a Carbon Dioxide Enriched Tourist Cave

Where it has been established, by a proper study, that a tourist cave's atmosphere is unacceptably carbon dioxide enriched, strategies for management need to be developed. The foundations of these strategies are likely to be either permanent modification of a cave's ventilation or a programme of monitoring resulting in controlled usage.

Permanent ventilation improvements are being experimented with for Gaden - Coral Cave. The two factors that make this the approach of choice for Gaden - Coral Cave are its proximity to the surface and the coincidence of high levels of carbon dioxide enrichment with periods of maximum tourist demand.

Where caves are remote from the surface or where a number of caves are developed allowing a distribution of cave usage, management by monitoring and controlled usage would seem most appropriate. Even with permanent ventilation improvements it may still be necessary to monitor caves during autumn when carbon dioxide mobilization may exceed ventilation capacity. The extent and type of monitoring required for each cave situation should be determined as part of the initial study.

RECOMMENDATIONS

The following recommendations are made for the guidance of tourist cave managers:-

1) A proper study should be made whenever there is any doubt as to the quality of the atmosphere or adequacy of ventilation in a tourist cave.
2) Wherever air quality is found to be unacceptable a plan of management to deal with the problem should be drawn up for the cave.
3) The following considerations should be taken into account when defining safe and desirable air quality standards for tourist caves.
    a) Tourists and guides must not be exposed to atmospheres that fail to meet statutory conditions for mines (CO$_2$ over 1.25% or oxygen less than 19%).
    b) Management strategies should ensure that the atmosphere in a tourist cave does not exceed the threshold limit value for carbon dioxide (0.5%).
    c) It is not desirable that tourists or guides should develop symptoms or signs of hypercarnapia. In caves where significant exercise is required (e.g. many steps) air quality may need to be considerably better than the threshold limit value. (Carbon dioxide may need to be less than 0.1%)

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VARIATION IN HARDNESS OF CAVE DRIPS AT TWO TASMANIAN SITES

Albert Goede

Abstract

Thirteen consecutive monthly samples were collected from two drip sites at each of two Tasmanian caves: Little Trimmer at Mole Creek and Frankcombe Cave in the Florentine Valley. At one of the two drip sites in Little Trimmer a positive relationship was found between the logarithm of precipitation and the total hardness without any detectable lag effect. No such relationship was detected at the other drip site despite its close proximity. At both drip sites the hardness values fail to show a seasonal pattern and are clearly unrelated to surface temperature variations. In strong contrast both drip sites in Frankcombe Cave showed significant seasonal variation and close positive correlation with mean monthly temperature with lag times of one and two months respectively. At one of the two drip sites the influence of monthly precipitation on variations in drip hardness could also be detected. The strong temperature dependence of cave drip hardness values at these sites may well be due to soil exposure to direct insolation following recent clear-felling and burning of the vegetation in the area.

INTRODUCTION

A programme of sampling has been carried out in two caves in different major Tasmanian karst areas, Little Trimmer at Mole Creek and Frankcombe Cave in the Florentine Valley (Figure 1). Two drip sites were sampled monthly in each cave over a period of thirteen months. Few studies of this kind have been previously described. Pitty (1966) made monthly measurements of water hardness at a number of seepage points in Poole's Cavern, Buxton, Derbyshire in England. Using the statistical method of partial correlation coefficients he was able to show significant relationship between drip hardness on the one hand and the climate elements of temperature and precipitation on the other, especially when lag effects were taken into account. He also considered the possible causal relationships between climatic and climate-controlled factors and water hardness.

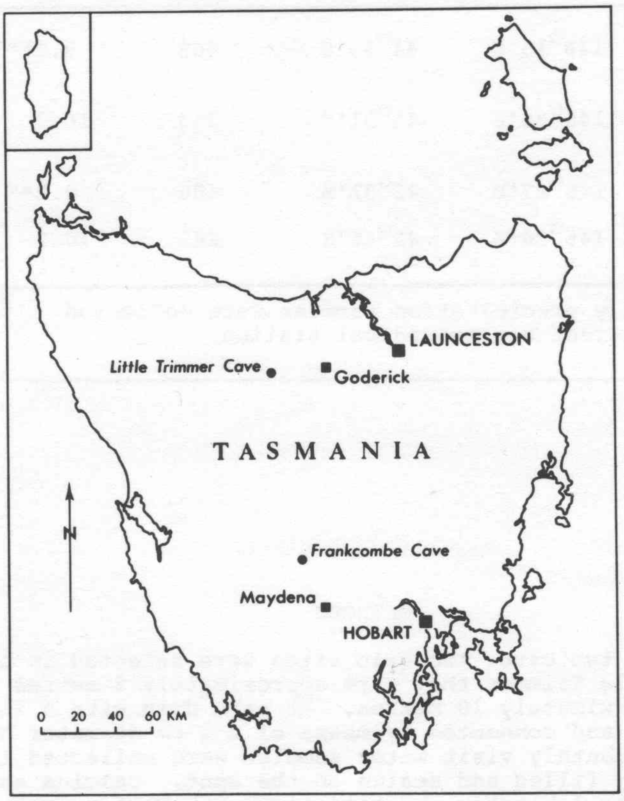

Figure 1 - Location map of cave sites and nearest climatic stations.

Jennings (1979) carried out a similar monthly sampling programme for two years in Murray Cave, Cooleman Plain, Australia but also made measurements of CO_2 in the cave atmosphere and in the soil above the cave. However, he found that "lagged correlation on a weekly and 3 weekly basis of individual drip hardness on air temperature and precipitation yielded few significant results". He concluded that there was only a weak case for dominance of hardness by temperature through rhizosphere CO_2 and no evidence which would support the hypothesis of dominance of antecedent precipitation.

In the present work, precipitation data was measured at surface sites in close proximity to each cave entrance. At each of the two sites a monthly raingauge was installed and visited monthly as close as possible to the middle of the month. Temperatures were not measured at the surface sites but were calculated from mean monthly temperatures at the two nearest meteorological stations of Goderick (near Deloraine) and Maydena (Figure 1). For further information see Goede, Green & Harmon (in press). Details of the cave sites and nearest meteorological stations are given in Table 1. Data for the stations were obtained from 'Climatic Averages Australia' (Bureau of Meteorology, 1975). Sample collections from both surface and underground sites were made monthly for a period of thirteen months from December 1978 to December, 1979).

Both caves are developed in Gordon Limestone of Ordovician age and the hills in which they are located are composed entirely of this rock.

TABLE 1 Details of cave sites and nearest meteorological stations

Site	Longitude	Latitude	Altitude (m)	Mean Annual Temp (°C)	Mean Annual Prec. (mm)
*Little Trimmer Cave, Mole Creek	146°15'E	41°34'S	460	9.2**	-
Golderick, Deloraine	146°38'E	41°31'S	253	10.7	1061
*Frankcombe Cave Florentine Valley	146°27'E	42°32'S	400	9.2**	-
Maydena	146°36'E	42°46'S	267	10.2	1230

* Sites where monthly precipitation samples were collected
** Estimated from nearest meteorological station.

METHODS

In each of the two caves two drip sites were selected in close proximity to each other. In Little Trimmer they were approximately 2 metres apart and in Frankcombe Cave approximately 10 metres. At each drip site a 21 cm diameter plastic funnel was installed and connected by means of a 2 cm diameter hose to a 25 litre container. On each monthly visit water samples were collected in polythene bottles which were completely filled and sealed on the spot. Calcium and total hardness were determined in the laboratory by titration with EDTA as soon as possible after collection (Douglas, 1968). At the time of analysis specific conductivity was also measured. It had originally been intended to accumulate all drip waters between visits but drip rates proved to be more rapid than anticipated so that the containers frequently overflowed. To minimize the problem of taking a representative sample in this circumstance hoses were inserted deep into the containers so that any water would have mixed thoroughly with the contents before it overflowed. This probably caused some bias in hardness values towards the latter part of the sampling period. There are some advantages in obtaining mean hardness values over a period of time rather than the point values of samples collected at wide intervals of time as did Pitty and Jennings. These investigators related the hardnesses to climatic parameters averaged over periods of time of varying lengths.

Instantaneous drip rates were measured during visits from July (Frankcombe Cave) and August (Little Trimmer) onwards. Maximum and minimum instantaneous drip rates recorded for the four sites were

Little Trimmer:	S_1	.008 - 1.758	litres/hour
	S_2	.612 -17.393	litres/hour
Frankcombe Cave:	S_1	.031 - 3.823	litres/hour
	S_2	.287 - 6.040	litres/hour

The principal purpose of the monthly sampling programme was to collect precipitation and seepage waters for isotopic analysis of $^{18}O/^{16}O$ and D/H ratios and to relate these measurements to the isotopic composition of actively forming speleothems (Goede, Green & Harmon, in press). To this end monthly air temperature measurements were also taken at the cave drip sites. Little Trimmer was found to have a mean annual temperature of 9.5°C with a range of 1.2°C and Frankcombe Cave a mean annual temperature of 8.3°C with a range of 0.3°C.

DRIP HARDNESS

As might be expected, calcium and total hardness are very closely related at all four drip sites (Figures 2 and 3). Mean values of the sites are as follows:

		Total Hardness (p.p.m.)			No. of Observations
		Mean		S.D.	
Little Trimmer Cave (Mole Creek)	S_1	231	±	43.3	13
	S_2	308	±	17.9	12
Frankcombe Cave (Florentine Valley)	S_1	198	±	18.6	13
	S_2	211	±	15.5	12

Little Trimmer

The two drip sites are only 2 metres apart but differ markedly in their mean total hardness values and their degree of variability (Figure 2). Applying Student's t test the difference between the means is found to be highly significant ($p <<< .001$). In order to determine the extend to which total hardness variations at the two drip sites are related, correlation analysis was carried out ($r = .60$, $p < .05$). Only 36% of the variation in one drip is statistically 'explained' in terms of the other.

When mean monthly hardness (H_{S1}) for drip site S_1 are graphed against monthly precipitation amounts (P_m) for the same periods (Figure 4) a non-linear relationship is found which is best represented by the equation

$$H_{S1} = 225,02 \log P_m - 222.91 \; (r = .68) \qquad (1)$$

This positive relationship is significant ($p = .01$) and indicates that nearly half (45.9%) of the variations in drip hardness at S_1 can be attributed to variation in precipitation amounts during the same monthly periods. Residual values do not shown any relationship to mean monthly surface temperature.

Investigating the same type of relationship for drip site S_2 no significant correlation exists ($r = .27$, $p >> .20$). Total hardness values for S_2 do not exhibit a seasonal trend indicating that they are not related to surface temperature variations.

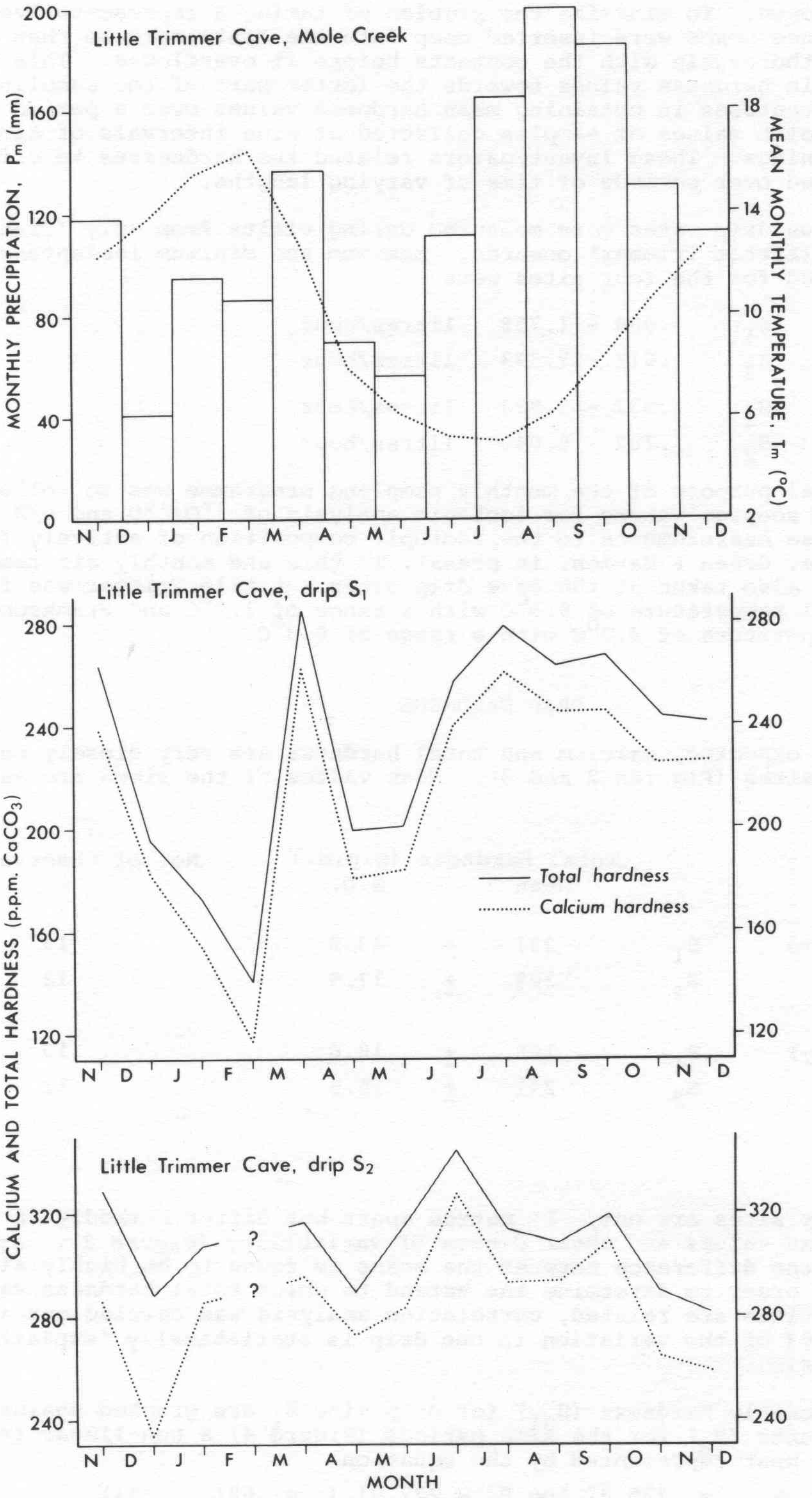

Figure 2 - Monthly precipitation and calculated mean monthly temperature for surface site at Little Trimmer. Monthly total and calcium hardness values for cave drips S_1 and S_2 in the same cave.

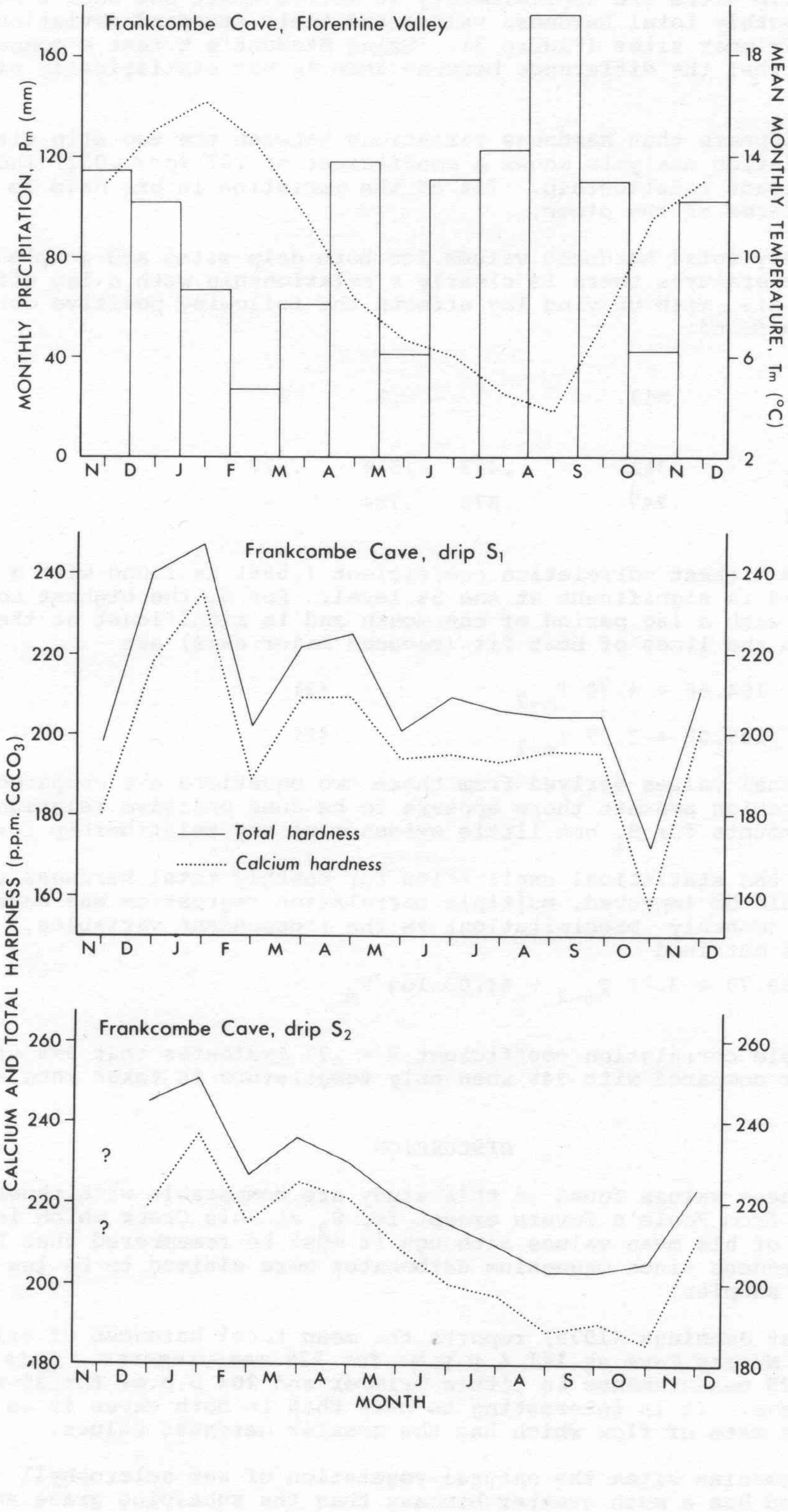

Figure 3 - Monthly precipitation and calculated mean monthly temperature for surface site at Frankcombe Cave. Monthly total and calcium hardness values for cave drips S_1 and S_2 in the same cave.

Frankcombe Cave

The two drip sites are approximately 10 metres apart but show a much greater similarity in monthly total hardness values and their standard deviations than do the two Little Trimmer sites (Figure 3). Using Student's t test a comparison of the two means shows that the difference between them is not statistically significant $(.05 << p < .10)$.

Again it appears that hardness variations between the two drip sites are related. Correlation analysis shows a coefficient of .87 $(p << .001)$ indicating a highly significant relationship. 75% of the variation in one drip is statistically 'explained' in terms of the other.

When monthly total hardness values for both drip sites are graphed against mean monthly temperatures there is clearly a relationship with a lag effect between the two (Figure 5). With varying lag effects the following positive correlation coefficients are found:

Lag time (months)	Nil	1	2	3
S_1	.361	.479	.586	.427
S_2	.747	.870	.784	-

For S_1 the highest correlation coefficient (.586) is found with a lag period of two months and is significant at the 5% level. For S_2 the highest coefficient (.870) is found with a lag period of one month and is significant at the 0.1% level. The equations to the lines of best fit (reduced major axes) are

$$H_{S1} = 164.86 + 4.70\ T_{m-2} \qquad (2)$$

$$H_{S2} = 185.08 + 3.77\ T_{m-1} \qquad (3)$$

When residual values derived from these two equations are compared with monthly precipitation amounts there appears to be some positive relationship with precipitation amounts for S_1 but little evidence of any relationship for S_2.

To see if the statistical explanation for monthly total hardness values for drip site S_1 could be improved, multiple correlation regression was carried out with T_{m-2} and log P_m (monthly precipitation) as the independent variables. The following relationship was obtained

$$H_{S1} = 89.73 + 3.76\ T_{m-2} + 44.03 \log P_m$$

The multiple correlation coefficient R = .77 indicates that 59% of the variance is accounted for compared with 34% when only temperature is taken into account.

DISCUSSION

Mean hardness values found in this study are comparable with those reported by Pitty (1966) from Poole's Cavern except for S_2 at Mole Creek which is significantly higher than any of his mean values although it must be remembered that Pitty measured only calcium hardness since magnesium carbonates were claimed to be low or non-existent in his samples.

In contrast Jennings (1979) reports the mean total hardness of drip measurements in Murray Cave as 141.4 p.p.m. for 228 measurements. This compares with 268 p.p.m. for 25 measurements in Little Trimmer and 204 p.p.m. for 25 measurements in Frankcombe Cave. It is interesting to note that in both caves it is the drip with the greater rate of flow which has the greater hardness values.

At the Tasmanian sites the natural vegetation of wet sclerophyll forest is more vigorous and has a much greater biomass than the subalpine grassland at Cooleman Plain. Since the provenance of soil CO_2 is predominantly biogenic it is expectable that the Tasmanian sites would yield much higher hardness values than Murray Cave.

Little Trimmer

As mentioned earlier a significant positive relationship is found when total hardness values of cave drip S_1 are correlated with the logarithm of monthly precipitation. It is clear that the response of total hardness to precipitation is a rapid one with no detectable lag effect.

Pitty (1966) tabulates eleven factors which could cause differences in the quantities of carbonates dissolved in karst water. Five of these are controlled by precipitation and three can be expected to have a positive correlation with carbonate hardness. They are:

1) Increased precipitation causing an increase in biotic activity.
2) Greater solution with faster flow.
3) Greater solution with increased pressure.

Factor 1) cannot apply in the case of S_1 because firstly it would take time for the increased moisture to boost the carbon dioxide concentration in the soil and secondly time is also required for the soil water to take up carbonate and move down to the roof of the cavern. Goede, Green & Harmon (in press) using monthly measurements of the deuterium-hydrogen ratio of both precipitation and S_1 seepage have shown that the average time taken by the water to reach the S_1 seepage point after falling as precipitation is approximately 2 months.

Clearly factors 2) and 3) are more plausible mechanisms because their effects would be felt much more rapidly. However, one might have expected them to be more effective with higher precipitation amounts much in excess of those required to saturate the soil. In contrast the evidence shows that total hardness values respond most strongly when monthly precipitation amounts are small.

Another possibility that must now be considered is 4) that more loss of carbon dioxide, hence more deposition of calcium carbonate per unit volume of water occurs when the rate of cave drip is low since

a) it makes more time available for these processes to operate before the drip falls.
b) there will be greater surface area of contact with both the depositional surface and the soil temperature.

Clearly the drip rate of S_1 is highly variable and much lower than S_2.

As pointed out, drip S_2 has little similarity with S_1 in terms of its temporal pattern of hardness variation. The S_2 pattern suggests a weak positive correlation with monthly precipitation and a weak negative one with mean monthly temperature but neither approaches statistical significance. The minima in December-January and April-May seem to correlate with similar minima in the graph for S_1 and probably indicate periods of moisture deficiency. The third minimum from July to September is weakly represented in the S_1 graph and probably indicate periods of moisture deficiency. The third minimum from July to September is weakly represented in the S_1 graph and may reflect an excess of water causing saturation of the soil. Figure 4 also hints at a possible fall in hardness when mean monthly precipitation amounts exceed 140 mm. Most likely the S_2 pattern represents the complex interaction of a number of factors relating to both temperature and precipitation.

Frankcombe Cave

The presentation of data and analysis of results are shown graphically in Figures 3 and 5. Hardness variations at the two drip sites are much more closely related to each other and both appear to be predominantly controlled by a temperature related factor with a lag time from one to two months showing a positive relationship with hardness.

Pitty (1966) listed six factors which are temperature controlled. Out of the six, four could apply to the Florentine Valley and of these only two would lead to a positive relationship between carbonate hardness and temperature. They are

1) greater output of carbon dioxide with increased biotic activity at higher temperatures
2) gain in soil carbon dioxide with photosynthesis due to increased root respiration.

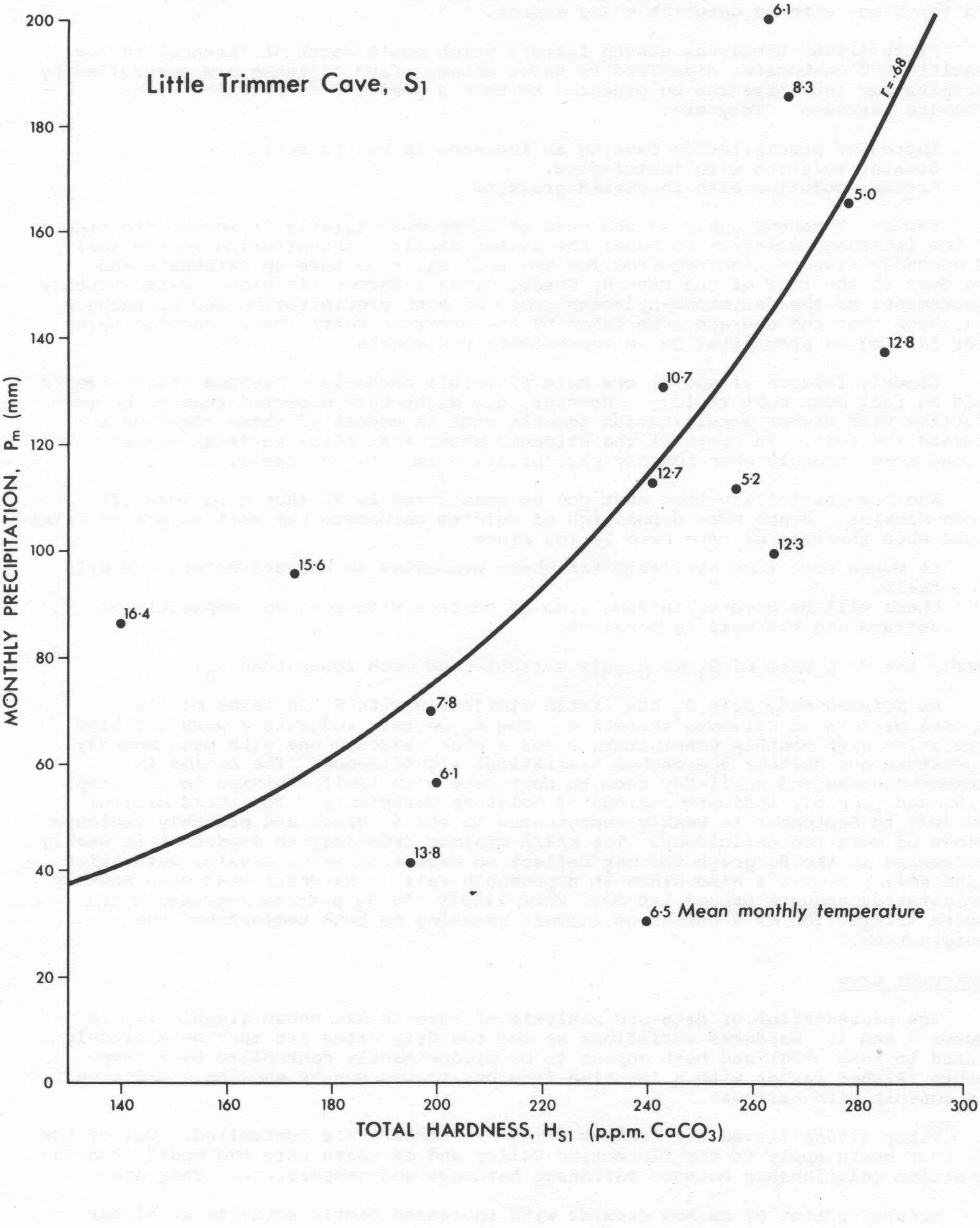

Figure 4 - Relationship between total hardness and monthly precipitation for drip site S_1 in Little Trimmer.

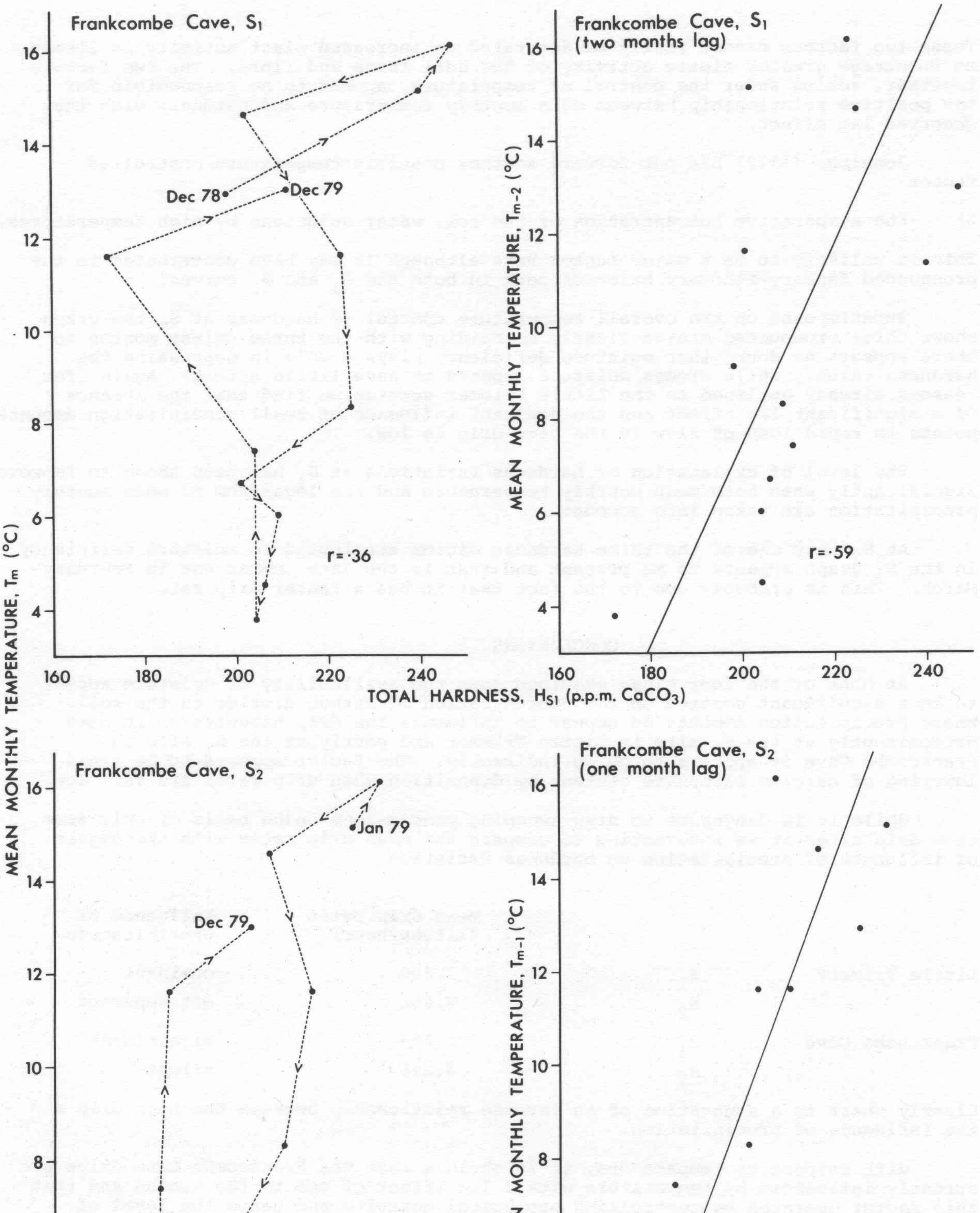

Figure 5 - Relationships between total hardness and mean monthly temperature illustrating lag effects for drip sites S_1 and S_2 in Frankcombe Cave.

These two factors cannot really be separated as increased plant activity is likely to encourage greater biotic activity of the soil fauna and flora. The two factors together, acting under the control of temperature, appear to be responsible for the positive relationship between mean monthly temperature and hardness with the observed lag effect.

Jennings (1979) has put forward another possible temperature-controlled factor

3) the evaporative concentration of the soil water solutions by high temperatures.

This is unlikely to be a major factor here although it may have contributed to the pronounced January-February hardness peak in both the S_1 and S_2 curves.

Superimposed on the overall temperature control of hardness at S_1 the graph shows three pronounced minima clearly coinciding with the three driest months so there appears no doubt that moisture deficiency plays a role in depressing the hardness values, while excess moisture appears to have little effect. Again, for reasons already outlined in the Little Trimmer section we find that the absence of a significant lag effect and the dominant influence of small precipitation amounts points to rapid loss of flow if the cave drip is low.

The level of explanation of hardness variations at S_1 has been shown to improve significantly when both mean monthly temperature and the logarithm of mean monthly precipitation are taken into account.

At S_2 only one of the three hardness minima attributed to moisture deficiency in the S_1 graph appears to be present and that is the late summer one in February-March. This is probably due to the fact that it has a faster drip rate.

CONCLUSIONS

At none of the four sites examined does the availability of moisture appear to be a significant control on the concentration of carbon dioxide in the soil. Where precipitation amounts do appear to influence the drip hardness as it does predominantly at the S_1 site in Little Trimmer and partly at the S_1 site in Frankcombe Cave it appears to do so indirectly. The factor appears to be rapid lowering of calcium carbonate content by deposition when drip rates are very low.

While it is dangerous to draw sweeping conclusions on the basis of only four cave drip sites it is interesting to compare the mean drip rates with the degree of influence of precipitation on hardness variation

		Mean drip rates (litres/hour)	Influence of precipitation
Little Trimmer	S_1	.690	dominant
	S_2	8.601	not apparent
Frankcombe Cave	S_1	1.293	significant
	S_2	3.246	slight

Clearly there is a suggestion of an inverse relationship between the mean drip and the influence of precipitation.

With respect to temperature, it is obvious that the Frankcombe Cave drips are strongly influenced by temperature with a lag effect of one to two months and that this factor operates by controlling biological activity and hence the level of carbon dioxide in the soil.

The area above Frankcombe Cave was clear-felled and burned a couple of years before the start of measurements and although a partial weed-cover had established itself and regrowth of forest species commenced the soil temperature can be expected to be still strongly influenced by direct insolation. In contrast at Mole Creek the hill above Little Trimmer is covered by mature wet sclerophyll forest that has not been recently burned and has been subject only to selective logging a considerable time ago.

It would be interesting to resume sampling of the Frankcombe Cave drip sites some years from now when forest cover has re-established itself in order to assess the extent to which the behaviour of the cave drips will have changed.

ACKNOWLEDGEMENTS

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DETERMINATION OF KARST WATER AGGRESSIVENESS BY ARTIFICIAL SATURATION: A COMPARISON OF RESULTS OBTAINED USING LIMESTONE AND REAGENT GRADE CALCIUM CARBONATE.

D.L. Dunkerley

Abstract

Trials of the method of estimating the aggressiveness of karst water by artificial saturation (Stenner, 1969) were made on stream and spring waters in limestone country at Buchan, Victoria. Saturation was brought about with both laboratory reagent grade calcium carbonate and also with powdered local limestone. Resulting estimates of the initial degree of saturation varied considerably. The differences amounted to an average 5.6% (maximum 8.0%) in aggressiveness estimated from change in total hardness, 8.8% (maximum 14.0%) using calcium hardness, and 9.4% (maximum 31.0%) using magnesium hardness. Whilst the average differences between the two sets of results are not great, and certainly do not prohibit the use of the original Stenner method, they do serve to indicate that in particular individual cases misleading results can be obtained if local limestone is not used. Possible reasons for the differing behaviour of the two materials are suggested.

INTRODUCTION

There are three classes of method by which the capacity of karst waters to dissolve additional limestone (known as aggressiveness) may be estimated. In the first, readily-measured properties of the water, such as its pH, temperature and calcium carbonate content, are used in conjunction with simple models of the behaviour of carbonate solutions in order to distinguish between saturated or supersaturated samples and those which are still aggressive. Qualitative estimates of the degree of departure from saturation may also be obtained using these methods, exemplified by the well-known Trombe curves (Sweeting, 1972). However, such techniques are based on gross oversimplifications of the chemistry of karst waters, and should only be used to give very general indications of aggressiveness.

A second class of methods relies on much fuller and more realistic models of water chemistry employing precisely-known physical constants to estimate the concentrations of the many ions and ion-complexes which may be present in a natural water sample. These values may then be used to calculate a degree of saturation with respect to a particular compound such as calcium carbonate. These methods involve extensive computations which are normally run on a computer (e.g. Truesdell and Jones, 1974; Wigley, 1977), and are quite unsuitable for use in the field. In addition they require much more extensive details of the chemistry of the water than are needed by methods in the first class. The absolute minimum requirement is for precisely known values for calcium and magnesium ion concentrations, field temperatures and pH, and alkalinity. More complete analyses, including concentrations of sodium, potassium, chloride and sulphate ions for example, permit more reliable results to be obtained. Concentrations of some of these species are quite difficult to determine accurately, and the need for such data is a disadvantage of these sophisticated solution models.

Intermediate between these two groups of methods in terms of ease of use are those techniques in which two identical water samples are collected, one being placed in contact with excess calcium carbonate and allowed to equilibrate, and the other left undisturbed. After equilibration, the concentration of carbonates in the saturated sample is compared with that in the untreated sample. The direction in which the water hardness changed on equilibration with excess carbonate reveals whether the water was saturated or aggressive, aggressive waters taking up additional material, and supersaturated samples depositing it. The amount of material deposited or taken into solution provides a quantitative estimate of aggressiveness. This method has been investigated by Stenner (1969, 1971) and widely applied. It may be applied in the field with the use of standard hardness titrations or with electrical conductivity measurements used as an alternative (see Bray, 1976; Allbutt, 1977).

The great advantage of measuring the actual hardness change in the presence of excess calcium carbonate, argued by Stenner (1969), is that no chemical theory or assumptions need be invoked. Further, no accurate measurements of pH or of parameters other than water hardness are required. Stenner (1969) used reagent grade calcium carbonate powder to induce saturation for two reasons. First, he argued that the absence of impurities in pure calcite simplifies the reactions during artificial saturation, and second, the material is finely powdered, making the procedure quite fast (about two hours to equilibrium).

The use of materials other than pure calcium carbonate was examined by Stenner (1971), who found that crushed limestones could yield quite different results. Similar findings arose in the work of Trudgill (1976) on Aldabra Atoll in the Indian Ocean. Trudgill estimated the aggressiveness of sea water using the Stenner method modified through the use of crushed local carbonate rocks and pure magnesium carbonate. He found that the various forms of carbonate gave differing estimates for the degree of aggressiveness of a water sample. Sea water generally appeared supersaturated when analysed with pure calcium carbonate but unsaturated when powdered local rock was used.

In general, Trudgill (1976, p. 172-173) found that actual rock solubility (i.e., water aggressiveness) was greater than predicted from tests using pure materials. He concluded that "....the only way to predict limestone solubility may be through the use of rock powders rather than of pure chemicals." (Trudgill, 1976, p. 173).

The work reported in this paper was carried out to determine whether such effects would occur in surface waters in limestone terrain, and if so, to assess their magnitude.

THE STUDY AREA

The samples analysed came from the Buchan and Murrindal rivers and from a small spring feeding into Fairy Creek, which are all located on the Devonian limestones in the Buchan area, East Gippsland, Victoria. The rocks within this area range from dolomites to quite pure limestones containing over 96% calcium carbonate (Teichert and Talent, 1958).

The streams and spring at the time of sampling were flowing freely, and were apparently free of suspended sediment.

FIELD AND LABORATORY PROCEDURES

Six field sites were selected for sampling, with the aim of observing waters of widely differently hardness. Riverine sites were located at varying distances along the streams after their entry on to the limestone, and the spring was included to give a sample having high total hardness.

At each site six samples were collected in 250 ml polythene bottles which were washed twice beforehand in the water to be sampled. Two were sealed without modification, for replicate hardness analyses; the remaining four samples were used to give replicates saturated with powdered local limestone and pure calcium carbonate.

The samples containing added carbonate material were periodically agitated to ensure good contact with the water, and analysed several days later in the laboratory. Thus, ample time for equilibration was allowed, following the work of Stenner (1969). Prior to analysis, the samples were allowed to stand for 24 hours to allow all particles to settle.

Total and calcium hardness for each sample were determined on 50 ml aliquots by standard complexometric titrations (Schwarzenbach and Flaschka, 1969) using BDH hardness tablets and BDH EDTA as the complexone. Magnesium hardness was found by subtraction.

Replicate samples were analysed for each treatment at each site to permit assessment of the repeatability of the analyses. This is necessary in order to be able to interpret apparent differences in hardness among the various treated and untreated samples.

RESULTS

The results of the 84 titrations are presented in Table 1.

Waters of widely varying hardness are represented, total hardness for example ranging from 36 ppm to 536 ppm calcium carbonate equivalent.

The mean difference in results of total hardness determinations on replicate samples was 0.90 ppm (maximum 10ppm); for calcium hardness the values were 0.76 ppm (maximum 6 ppm), and for magnesium hardness (found by difference) 1.24 ppm (maximum 9 ppm). In many cases replicate samples gave identical results.

Differences in hardness between samples saturated with reagent grade calcium carbonate and with local limestone are considerably greater. These differences amount to a mean of 7.7 ppm (maximum 22 ppm) for total hardness, 10.8 ppm (maximum 32 ppm) for calcium hardness, and 6.3 ppm (maximum 26 ppm) for magnesium hardness. These values are 5-15 times greater than the mean differences between replicate samples noted above, and cannot therefore be attributed to imprecision in the analyses.

In most cases, more local limestone dissolved to reach saturation than did pure calcium carbonate; likewise, less carbonate was precipitated from initially supersaturated solutions in the presence of local limestone than in the presence of pure calcium carbonate.

Averaged over the 14 sets of samples, the results contained in Table 1 indicate a difference in apparent aggressiveness determined by the two methods of 5.6% (maximum 8%) when using change in total hardness as recommended by Stenner (1969). Differences based upon change in calcium hardness averaged 8.8% (maximum 14%), while magnesium hardness estimates averaged 9.4% (maximum 31%). While these differences are not great, formal t-tests reject the hypothesis that there is no difference between the results of the two methods at the 0.001 significance level. There is not disagreement however between the two methods in the identification of supersaturated and aggressive samples, so that for this purpose they may be used interchangeably, at least at this site. Work at other sites may reveal different effects.

POSSIBLE REASONS FOR THE OBSERVED DIFFERENCES

No data are yet available on the detailed chemical composition of the various limestones occurring in the Buchan area, so that a full analysis of the mechanisms of carbonate dissolution there cannot yet be made. Some speculations based upon published work are however possible.

Terjesen and his co-workers (Erga and Terjesen, 1956; Terjesen *et al.*, 1961) have found that very small concentrations of certain metal ions in solution can reduce the equilibrium concentration of calcium carbonate by significant amounts, and also retard the rate of approach toward equilibrium. They have proposed a number of theories to describe the physical processes involved in the inhibition of dissolution of calcium carbonate. Nestaas and Terjesen (1969) favour the theory that metal cations act by occupying the active sites or "kinks" in the molecular structure of the carbonate, hence preventing the removal of calcium ions from the lattice. They have shown that in the presence of 10^{-5} moles of scandium ions per litre, such effects may reduce the equilibrium concentration of calcium carbonate by 50%. The effect of inhibiting solution is produced by many metal ions in solution; Terjesen *et al.* (1961) have ranked the major ions in order of decreasing effectiveness as inhibitors as follows:

Pb^{2+}, La^{3+}, Y^{3+}, Cd^{2+}, Cu^{2+}, Au^{3+}, Zn^{2+}, Ge^{4+}, Mn^{2+}

Natural limestones may contain some of these elements at significant concentrations. Chyi *et al.* (1978) for example provide analyses of Kentucky limestones containing in excess of 17 ppm La and 4 ppm Sc. However, lead is not commonly found in limestones at concentrations above about 10 ppm (e.g., see Graf, 1962). This metal is however often contained in reagent grade chemicals. The pure calcium carbonate used in the present work lists 10 ppm heavy metals as lead among other trace contaminants, and lead is the most effective inhibitor of dissolution noted by Terjesen *et al.* (1961). Hence it is possible that in the case of the present work the pure calcium carbonate contained more lead and other inhibitors than does the local Buchan rock, and that this accounts for the greater apparent solubility of the latter. If this behaviour in fact occurs, then limestones in other areas may behave quite differently and might display a lower apparent solubility than reagent grade chemicals. This would certainly add weight to the case for the use of local rock powders where this is possible, and would raise an additional obstacle to the use of sophisticated chemical solution models of the kind referred to earlier, in that trace metal concentrations would have to be added to the already extensive list of analyses needed for their use.

TABLE 1: RESULTS OF TITRATIONS ON UNMODIFIED AND ARTIFICIALLY SATURATED SAMPLES*

		HARDNESS (ppm)								
		UNTREATED SAMPLE			SATURATED WITH REAGENT GRADE CALCIUM CARBONATE			SATURATED WITH CRUSHED LIMESTONE		
LOCATION		TOT.	Ca	Mg.	TOT.	Ca	Mg	TOT.	Ca	Mg
MURRINDAL R.	A	70	38	38	78	42	43	82	50	38
	B	70	38	38	78	42	43	82	48	40
MURRINDAL R.	A	112	68	52	112	68	52	120	72	57
	B	112	68	52	112	66	55	120	70	59
SPRING ABOVE FAIRY CK.	A	520	398	145	456	356	119	464	376	104
	B	518	396	145	458	354	123	460	378	97
BUCHAN R.	A	38	20	21	50	30	24	56	38	21
	B	36	20	19	48	30	21	54	36	21
BUCHAN R.	A	48	28	24	58	40	21	62	42	24
	B	46	30	19	58	38	24	62	42	24
SPRING ABOVE FAIRY CK.	A	536	420	138	474	348	150	490	370	142
	B	532	429	133	464	432	145	486	374	133
MURRINDAL R.	A	86	48	45	90	54	43	98	60	45
	B	86	50	43	88	52	43	96	58	45

* Replicate samples are designated A and B for each site. Total and calcium hardness values are expressed as $CaCO_3$ equivalent; magnesium hardness is expressed as $MgCO_3$ equivalent.

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