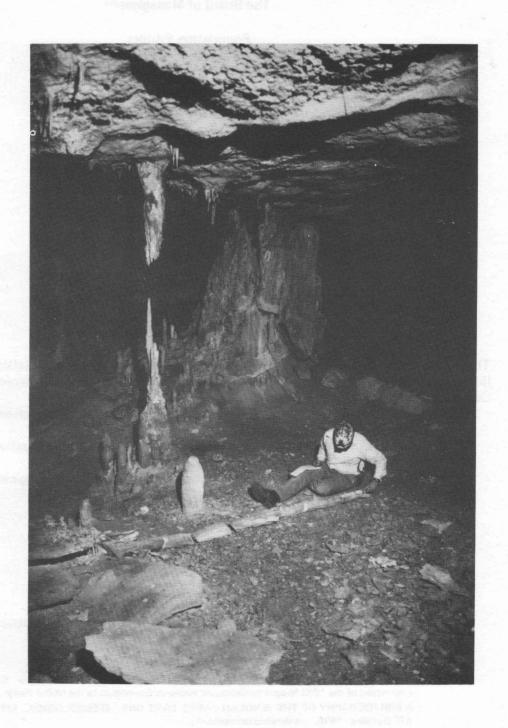
JOURNAL OF AUSTRALASIAN CAVE RESEARCH



World's longest halite stalagmite, Webbs Cave, Nullarbor Plain.

Photograph by Adrian Davey

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Cover Photograph: This fallen stalagmite, broken in ten pieces across a thoroughfare in Webbs Cave, Nullarbor Plain, is the longest halite stalagmite on record in the world at 2.78 m. It has been removed for its safety and display, and for scientific study, to the Western Australian Museum.

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COLOUR IN SOME NULLARBOR PLAIN SPELEOTHEMS

J.R. Caldwell, A.G. Davey, J.N. Jennings, A.P. Spate

Abstract

Chemical and mineralogical analyses of 18 speleothem samples from Nullarbor Plain caves are related to their colours ranging from white to black through browns and reds. Iron, manganese and organic compounds are the pigments responsible but their effect is variable according to their manner of incorporation in the speleothems and possibly also to the intervention of clay minerals. Closer studies are necessary to unravel these aspects and to investigate sequences of colour in speleothem growth.

INTRODUCTION

The colour of speleothems is a matter of interest to many Australian speleologists yet few data have been published about this aspect of our caves. It has recently been brought to the fore by the work of Spate and Ward (1980) on the blackness of much calcite decoration in Jersey Cave, Yarrangobilly, N.S.W.. Manganese is commonly called on to explain this colour but in this case organic carbon appears to be the cause, with bushfires its ultimate source.

Although Nullarbor Plain caves have been thought to be poor in speleothems (Jennings 1962), the course of investigation has shown this not to be so, and there is considerable variation in colour in their decorations. There is also advantage here for the study of colour because of the prevalence of salt crystallisation wedging which results in much fallen and fractured material, obviating the need to do any damage to obtain samples for analysis. This paper will discuss the colour of a range of samples from the Nullarbor.

METHODS

Loose dusts on the samples were removed by compressed air jet.

The colours of the surface of the samples, of dry powder ground from bulk fractions of them and of dry powder from organic acid - leached residues from them were determined with Munsell colour chart.

Partial chemical analyses were made:-

carbonate-CO2 by volumetric calcimeter (expressed as CaCO3)

Mg/Ca atomic ratio by Chave's XRD peak shift method (Chave 1952) and/or Na2EDTA titration

iron by colorimetric measurement of thiocyanate complex (expressed as Fe_2O_3)

manganese by colorimetric measurement of generated permanganate ion (expressed as MnO_2) SO4 by gravimetric barium sulphate method

inferred Na₂SO₄ by excess sodium over Na(K)Cl (at expense of CaSO₄)

 ${\tt CaSO_4.2H_2O}$ by mathematical construction from ${\tt SO_4}$ minus inferred ${\tt Na_2SO_4}$

Cl by Mohr titration

Na/K ratio by flame photometer, lithium internal reference

P2O5 by gravimetric phosphomolybdate method

SiO₂ by weight loss from ignited HF-H₂SO₄ residues

organic carbon by Schollenberger wet (280°) combustion and titration method

N by Kirsten's Dumas method (NiO catalyst, 1050° ignition)

(NH₄)₂O by MgO fusion and distillation into boric acid.

 $\rm H_2O(60^{O})$ was obtained by oven drying $\rm 20^{O}-60^{O}$ and laboratory pH by visual display meter.

X-ray diffraction was carried out on a number of the samples by means of a Norelco diffractometer with copper target, nickel β - filter and scintillometer detector.

RESULTS

Table 1 presents the analyses from 8 dominantly calcite samples, hand specimens of which range from white to black.

Table 1 Calcite specimens

No.	Munse Color		L	Per	centag	ges		Per	centa	ges			Munsell	
Sample N	Hand specimen surface	Bulk	Na/K	Organic	Fe203	Mn02	Fe/Mn	80 ₄	C1	CaCO ₃	pН	Bulk mineralogy	dry pigment	Pigment mineralogy by XRD
1	10YR8/4 to 10YR8/3	5YR8/1	ND	nil	.07	nil	-	ND	ND	ND	ND	Mg.03calcite	ND	ND
2	10YR4/4 to 10YR7/4	5YR8/1	ND	nil	.05	nil		ND	ND	ND	ND	Mg.05calcite	ND	ND
3	10YR8/3	10YR8/1	ND	nil	.03	nil	-	ND	ND	ND	ND	Mg.03calcite	ND	ND
4	5YR3/2- 5YR5/6 coating 7.5YR7/4 crystals	5YR8/1	ND	nil	.17	.001	>100	ND	ND	ND	ND	Mg _{.03} calcite	2.5YR4/7	illite >kaolin= quartz. No iron mineral resolved
5	10YR3/1	10YR8/2	ND	.12	.01	nil	-	ND	ND	ND	ND	Mg.05calcite	10YR2/1	
6	2.5YR 2.5/0	10YR8/2	ND	.16	.01	.00	1		ND	ND	ND	Low-Mg calcite	ANTEN ANTEN	riva efficier relacion de re-
7	7.5YR8/4	7.5YR8/4	320	.03	2.04	.14	15.9	1.7	.9	94	9.25	Mg.03calcite	2.5YR3/6	kaolin=goethite >haematite
8	5YR4/7 with 5YR7/6 carbo- nate gra- nules	5YR6/6	150	.05	8.58	1.08	8.8		1.6		9.40	Mg.03calcite	2.5YR3/4	haematite >kaolin >>goethite (tr) kaolin >> illite/montmor- illonite

Calcium/magnesium atomic ratio thus: $Mg_{.03}$ calcite = $(Ca_{.97}Mg_{.03})CO_{3}$

- = not applicable ND = not determined tr = trace (as) = CO_2 expressed as $CaCO_3$ >> much greater than

From Snake Pit (N133) two samples of acicular crystalline fragments from a speleothem of unknown nature are of low magnesian calcite and respectively very pale brown (sample 1) and dark yellowish brown (sample 2) in colour. However the only pigment determined chemically is a small proportion of Fe₂O₃ which is slightly greater in the pale brown than in the dark brown specimen (cf. Kral 1976). This suggests that the difference between the two resides in a superficial staining of the crystals by the iron, not properly estimated by analysing the samples in bulk. The bulk samples in powder form were indistinguishable in colour.

Sample 3, a coarsely crystalline, rhombohedral low magnesian calcite fragment from Witches Cave (N193), is very pale brown in colour. It has an even lower content of Fe $_2$ O3 than the previous samples and this was the only colouring component detected. This reinforces the conclusion that analysis of the sample in bulk may be misleading.

A piece of low magnesian calcite flowstone (sample 4) from Weebubbie Cave (N2), with acicular crystals radial to the accumulation surface, is yellowish red on the outside but its crystals are pink. It has a little more iron than the three previous samples but this is still a small constituent. This may be rendered more effective as a pigment by the presence of a clay component of illite and kaolin, and of some quartz; the iron may coat these impurities.

Both sesquioxide and clay could be residual from the bedrock, the Abrakurrie Limestone in the cases of N133 and N193, from the Nullarbor and Wilson Bluff Limestones with N2 (see analyses in Lowry 1970). Derivation from surface soil is also possible; in this case the materials may be aeolian as well as residual in origin.

Sample 5 is a very dark grey, low magnesian calcite fragment from a speleothem, most likely a stalactite, from Webbs Cave (N132). The fracture surfaces show that the colour extends through the body of the specimen though the outside is darkest. Sample 6 is also from Webbs Cave, part of a stalagmite, and of black calcite, with its colour uniformly through the specimen. The organic carbon content is slightly greater than that of sample 5. Both samples become white when ground to powder. The chemistry of these specimens suggests their colours are due to a small organic content through the crystal lattice. Humic matter disseminated through the body of a speleothem can affect its colour powerfully. Transport by percolation water from the surface is the

probable supply mechanism. Kral (1976) attributes the grey to black colours of dripstones in the Demanova valley caves in Slovakia, which lack manganese, to soil colloids, without, however, indicating whether these may have a humic content.

It is apposite to mention here the composition of sample 9, also from Webbs Cave (Table 2). This is from an irregular floor deposit, of black to dark brown colour; its surface is partly accumulational and smooth, and partly fractured and angular. It has a vitreous lustre and is largely made up of amorphous organic matter, together with a significant component of colourless weddellite, $\text{Ca}(\text{C}_2\text{O}_4).2\text{H}_2\text{O}$ (crystalline calcium oxalate dihydrate). There is a gypsum fraction. The amorphous organic matter must be the chief pigment, though 0.49% of Fe₂O₃ may contribute. Such material could provide at low concentrations a substantial supply of colouring for speleothems. Its origin will be discussed below.

e No.	Munsel Colour	-		Perce	ntage	es			Pe	rcent	ages				Munsell Colour	
Sample	Hand specimen surface	Bulk dry powder	Na/K	Organic Carbon	Fe203	Mn0 ₂	Fe/Mn	804	C1	CaCO3	P ₂ 05.	H ₂ 0(60)	pН	Bulk mineralogy	Dry pigment	Pigment mineralogy by XRD
9	7.5YR2/0 to 7.5YR3/2	10YR3/4		27.35		.003	>100			(as)	1.85		7.17	amorphous organics gypsum, weddellite (no urea)	7.5YR4/4 (organic) 10YR6/4 (oxalate)	amorphous organics 65%, weddellite 14%, (gypsum) (silica)
10	2.5YR5.5/0	5YR7/1	ND	.13	.08	.01	7	ND	ND	ND	ND	ND	ND	calcite	ND	ND

Table 2 Miscellaneous deposits

Dark-coloured, angular carbonate gravels of uncertain origin are sometimes found in Nullarbor caves. Sample 10 from Mottled Cave (N27) is representative; its pigmentation runs through the interior of the clast and a small component of organic carbon, the likely source of colour, is probably of surface origin. The presence of these black gravels in the caves supports the idea of surface supplies of organic carbon as speleothem pigment and if they suffer remobilisation by solution, they could serve as a secondary source of it within the caves.

Reverting to Table 1, there remain samples 7 and 8 from the smooth surfaced banks of fine-grained clastic material, known as 'coffee-and-cream' at the beginning of the Easter Extension of Mullamullang Cave (N37). The 'cream' (sample 7) consists of pink crystallised powder. It is coloured by some 2% of goethite and haematite. Kaolin is also present. The 'coffee' (sample 8) is a reddish yellow granular deposit, which is in parts slightly coherent. It is granule- to silt-sized and there are occasional crystallised fragments - thin rods less than 1 mm in diameter and bits of curving cave flowers. Low magnesian calcite forms only three-quarters of this material and there is a significant gypsum content. However its stronger colour comes from the bigger haematite fraction, reinforced by manganese dioxide. There is also clay, mainly kaolin.

Although the bulk of the 'coffee-and-cream' is salt-wedged detritus from the Abrakurrie Limestone roof, there is also a concentration of insoluble residues from the bedrock and perhaps from the surface, together with an addition of soluble salts brought by percolation water from the surface. Similar deposits are found in a number of Nullarbor Caves, with a range in their colour variation.

Table 3 comprises data from 8 evaporite samples.

White crusts coat the breakdown around the lakes of Mullamullang Cave. These are represented here by a single sample (11) from White Lake, which consists almost entirely of gypsum, with a small halite component. This result differs markedly from the statement by Anderson (1964) that there is 'a thick calcite encrustation' around White Lake. Wigley and Hill (1966), however, give an analysis in which again CaSO4 is dominant at 75% of the content, with 5.4% NaCl; in addition they found 14.9% of MgSO4. Analyses of White Lake water show it is dominantly a chloride-sulphate water, with a lesser bicarbonate component; sodium is the main cation, with Mg and Ca about equally abundant but much less than Na. At saturation, salts will be deposited in the order - calcium sulphate, magnesium sulphate, calcium carbonate, sodium chloride. On this count, our analysis and that of Wigley and Hill are congruent on a trend of increasing concentration of the water of the lake.

Sample 12 from Kelly Cave (N165) is a fragment of a halite stalactite, which owes its whiteness and translucency to its high purity. So also with the cave cotton (Hill 1976) from the same cave (sample 13) where it floats down from the roof persistently - at least when people are in the chamber. Likewise sample 14 from Mullamullang Cave consists of almost pure halite as white curving flowers.

Table 3 Evaporite specimens

No.	Munse: Colou	The second secon		Per	centa	ages		Pe	ercent	ages					Munsell Colour	ing Linguis The case in
Sample	Hand specimen surface	Bulk dry powder	Na/k	Organic	Fe ₂ 03	MnO_2	Fe/Mn	SO4	C1	CaCO ₃	рН			Bulk mineralogy XRD	Dry pigment	Pigment mineralogy by XRD
11	5YR8/1	5YR8/1	260	nil	nil	nil	-	ND	.7	nil	7.60	0		gypsum	Zingo	er repekter. Srip Laker
12	5YR8/1	5YR8/1	800	nil	nil	ni1	-	ni1	ND	ni!	6.8	5		halite	-	-
13	5YR8/1	5YR8/1	700	nil	nil	nil	-	ni1	ND	.4 (as)	7.50	0		halite	-	Granina da
			dase.		4			CaSO4.2H20	NaCl		%Si0 ₂	%H20(60)	%Na ₂ SO ₄			
14	10YR8/1	10YR8/1	500	ND	ND	ND		ND	98.4	.0	1.1	ND	.0	halite, minor quartz		
15	2.5YR2/0	10YR2/1	40	. 21	6.0	6.2	1.1	78.2	2.1	.1	2.5	4.4	.2	(78%) gypsum	7.5YR2/0	pyrolusite >goethite =haematite
16	10YR2/1 to 10YR3/3	10YR3/1	900	.08	9.5	6.1	1.7	74.0	3.0	.1	3.2	3.5	.2	(74%) gypsum	5YR3/2	pyrolusite =goethite =haematite
17	5YR3/3 to 5YR4/4	10YR4/5	400	.03	9.6	1.7	6.3	79.0	1.0	.1	2.9	5.1	.2	(79%) gypsum	2.5YR4/6	haematite =goethite
18	5YR3/3	10YR4/6	500	.03	10.8	1.3	9.2	77.4	2.1	. 4	2.2	5.3	.2	(77%) gypsum, calcite	2.5YR4/6	haematite =goethite

Samples 19 and 20 (Table 4) are from the interior and the surface of a 2.78 m fallen stalagmite from Webbs Cave. Its white interior is 95.8% halite and other colourless substances analysed amount with it to 99.4%; there are no pigmented residues. The surface is very pale brown to light yellow brown; this colour is due to a small proportion of iron and to a little more organic carbon. In the surface skin there is more gypsum and calcite in the form of sand and silt sized crystals than in the body of the stalagmite. They are thought to be due to re-solution and re-deposition. There is a half-round re-solution channel running down the side of the stalagmite, which near the base goes inside it, emerging as a cylindrical hole at the base. There are also lighter coloured trails of secondary deposition over the outside of the speleothem. The more soluble sodium chloride was differentially removed in this process. The pigments may have been incorporated into the reworked skin in this process of resolution and re-deposition.

Table 4 Webb Cave 2.78 m halite stalagmite

V d	Mun: Cole	sell our													
bei	me tead	Bulk		Per	centa	ges						a pertu	Na	C1 %	Mary and A
	Specimen surface	powder	Ca	Mg	Na	K	C1	so ₄	нсо3	Br	н20	Na/K	total	anhyd	rous
19	10YR8/1	10YR8/1	. 29	.12	37.52	.72	58.30	.06	.15	. 20	2.04	52.1	95.8	99.0	
20	10YR7/3	> 63µ	Oning High	7.5Y	R8/2	sand	grains		gypsi	ım +	low-Mg	g calci	te	21 5080 21 5080	after
	10YR6/4	< 63 µ	47	10YR	25/3	silt			gypsı	um +	low-Mg organi		te + 0.	8%	halite removed by H ₂ O
		ore No		(101	R8/3 af	ter c	organics	remo	oved b	у Н20	02) 0.4	% Fe.	Nil Mn.		II IIII

Along with sample 14, white halite, the reddish brown samples 17 and 18 and the black samples 15 and 16 come from a single area of crust deposit in the Salt Cellars of Mullamullang Cave. This deposit has an irregular surface of both crystallised facets and small roughish knobs. Some of these knobs are white and consist entirely of gypsum. But the strongly coloured areas are only about three-quarters gypsum. The reddish brown samples (17,18) owe their colour to haematite and goethite, the former preponderant. There is some manganese dioxide present but the Fe/Mn ratio remains high. The blackness of samples 15 and 16 is clearly due to the manganese, the Fe/Mn ratio being much lower. The manganese occurs as pyrolusite (Figure 1). There is also more organic carbon present than in the other samples from the crust but this may not be significant. Some of the pigments are disseminated through the deposit as separate mineral crystals, not simply as surface or crystal interface coats. A strict relationship of colour to mineralogy is suggested for this crust deposit.

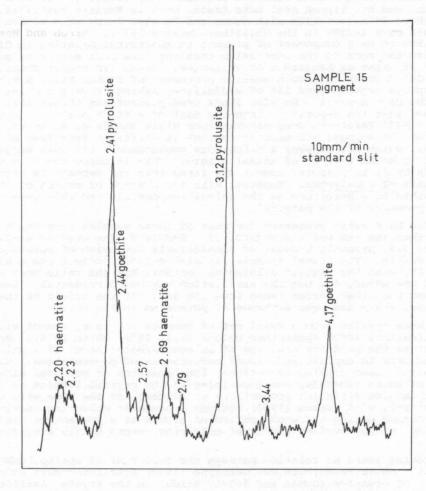


Figure 1 X-ray diffractogram of pigment from a black gypsum crust from Mullamullang Cave, Nullarbor Plain.

DISCUSSION

It is evident that even in this karst with limited vegetation, and so meagre humus supplies, blackness can have different explanations. Some samples owe this colouring to organic matter. Other samples are black from manganese, however. Black gypsum has scarcely been recorded before; Deal (1962) mentions black selenite needles from Jewel Cave, S. Dakota. The pyrolusite responsible for the black colour in Mullamullang Cave was readily determinable by x-ray diffraction in contradistinction to occurrences of this mineral previously reported from caves where XRD was difficult (Hill 1976; White 1976; Moore 1981).

Cave cotton has been found of gypsum, mirabilite and epsomite in caves before but in the Nullarbor Caves it is made of halite as well as gypsum. Extrusion will be the mechanism common to all mineral species of this kind of speleothem.

White halite speleothems - crusts, helictites, stalactites, stalagmites, columns and cave cotton - are recorded from a number of Nullarbor caves (Wigley and Hill 1966; Lowry 1966; Davey 1978). Halite deposition is not due simply to the caves being dry but also to the fact that they are set in a dry climate. The region is fed with cyclic salt, both by oceanic spray and from dusts blown from playas and salinas

inland. The Webbs Cave 2.78 m stalagmite, varying from 0.2 m to 0.1 m in diameter, may be the largest halite speleothem yet recorded in the world, much larger than the 0.5 m stalagmite from the interior desert province of Xingiang Province, now in the Museum of Geology in Beijing, China (Jennings 1976).

Amber coloured gypsum stalactites and helictites up to at least 50 cm length are found in Nullarbor caves, with twinning characteristic of some, and Appleyard (1980) has associated their growth with the dry climate and also large temperature differences in summer between the surface (where summer storm rains leach gypsum from soils) and the cave atmosphere. This may well be so but gypsum speleothems do not have so much climatic restriction as halite ones; substantial gypsum decoration occurs in the drier parts of wet climate caves, e.g. in Puketiti Flower Cave, the King Country, New Zealand.

Weddellite has been recorded previously by Bridge (1973) from Jingemia Cave, Watheroo, and Mt. Tippan near Lake Rason, both in Western Australia. In the latter case, there is association with guano and he also found this mineral in bat guano from Petrogale Cave (N200) in the Nullarbor (Bridge 1977). Birch and West (in prep.) find weddellite to be a component of pigment in Aboriginal painting in Cloggs Cave, Buchan, Victoria, and come to the conclusion that the likeliest source is as decomposition product of urine of kangaroos or wallabies. Green (in prep.) describes a black, botryoidal deposit in a rock shelter northwest of Broken Hill, N.S.W., which has 35% of amorphous organics and 15% of weddellite, making it very similar in composition to the Webbs Cave deposit. He also finds urea present and thinks this is derived from rat urine and that the deposit is from the nest of a stick nest rat (Leporillus conditor.) Bridge (1975) refers to dung bitumen from Wigie Mia Cave, W. Australia, and attributes it to rat droppings; its mineral content is different from that of the Webb Cave material, which has however a bituminous appearance. All this suggests that the black deposit in Webbs Cave is of animal origin. This is supported by a palynological analysis by J. Luly (pers. comm.) who finds that the deposit is rich in pollen dominantly of Eucalyptus. Together with the absence of chitin of insect origin, this points to a herbivore as the animal responsible and this does not rule out a rat as the producer of the material.

The Na/K ratio presented for most of these samples from the Nullarbor is much higher than the sea water standard, 28. Sample 9, the organic sample, has a low ratio of 3.2, probably because of considerable accession of potassium of presumed animal origin. The gravel (sample 10) with organic content has a high Na/K ratio 77. Sample 15, with the highest pyrolusite content, has the ratio most approximating to that of sea water, 40, but the association may be coincidental. Sample 19 has a ratio of 52 and the other ratios range from 150-900. If the origin of the halite is mainly sea spray, there has been exchange of potassium in the soil.

These results from a small set of samples are in agreement with textbook generalisations about speleothem colour (Hill 1976; White 1976). However they demonstrate the need for analyses of an even greater level of sophistication than employed here to explain individual occurrences of pigmentation. Surface staining, penetration along crystal interfaces, interspersion of coloured minerals through a matrix of white minerals, and impurities in the crystal lattice of a white matrix mineral involve different proportions of pigment for the same effect on colour. The distinction of Jakucs (1962) between syngenetic colouring, defined as an inner colour formed during the whole period of growth of a speleothem, and postgenetic colouring, namely surface and crust colouring, seems hardly adequate, given this variety.

Having found no relation between the colour of 24 speleothems and their trace elements - Mg,Sr,Fe,Mn,P,Zn,Cu, Gascoyne (1977) attributed dark colouration to the presence of organics (humic and fulvic acids) in the crystal lattice. However, Palyi (1960-1965) suggests that there may be quite subtle links between certain metals and organics on the basis of study of stalactites in some Hungarian caves. He thinks that certain bacteria oxidise iron II and manganese II to iron III and manganese IV, which are then incorporated into calcite but protected by humic colloids, probably as metal-organic chelates (cf. Manskaya & Drozdova 1968).

Apart from the general interest of speleothem colour, it is clear from these possible explanations of differences in pigmentation that a more refined study of colour in speleothems, where these possess growth layers of different colours and where there are speleothem sets of different colours side by side in succession, may furnish evidence relating to surface environmental change.

This paper was submitted for publication before an important contribution by White (1981), which describes a more elaborate study of the kind advocated above, reached us. It adds reflectance spectrophotometry to chemical analysis, x-ray diffraction and optical microscopy as used here. White's conclusions may be related to this paper thus.

By adding to the evidence for deep reds to be attributable to haematite and goethite, White's paper supports our explanation of the strongly coloured 'coffee' of the 'coffee-and-cream' deposit from Mullamullang Cave and indirectly strengthens the view that the reddish brown crusts of gypsum from that cave owe their colour to iron oxides also.

However, it implicitly casts doubt on the same explanation for the pale brown to yellowish red and pink of some calcite speleothems which have lower iron oxide contents. White finds that many yellow to brown calcites lack such impurities and

he calls on organic pigments for the generality of weakly coloured speleothems in this range of colour. Organic carbon is not present in our relevant Nullarbor samples (1 to 4) and it seems inadvisable to discount the lower but still far from negligible iron content of the 'cream' of the complex 'coffee-and-cream' of Mullamullang Cave. So it may be premature as yet to exclude altogether a role for iron oxides in this range of speleothem colour. There are indications above that interaction of iron oxides with organic compounds and clay may enhance their colour effect.

Nevertheless this paper has been concerned to identify sources of organics, accepted here as the cause of dark brown to black colour of many Nullarbor speleothems. We have no reason to oppose the idea that some, perhaps the majority, of the lighter coloured cave decorations depend on organics. This reinforces our view that a more careful study of colour in speleothems may be a source of information about changes in the surface condition of karst.

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GLACIATION AND KARST IN TASMANIA: REVIEW

AND SPECULATIONS

Kevin Kiernan

Abstract

The evolution of Tasmanian karsts is fundamentally interwoven with the history of Quarternary climatic change. Specifically karstic processes were periodically overwhelmed by the influence of cold climate which exerted strong controls over thermal, hydrological and clastic regimes. While these episodes of cold climatic conditions have temporally dominated the Quaternary, their legacy may be under-represented in present karst landforms. There is no general case with respect to the consequences for karst of the superimposition or close proximity of glacial ice. The pattern of events in each area will be dependent upon the interaction between local and zonal factors. A number of Tasmanian karsts which may have been influenced by glaciation are briefly discussed.

INTRODUCTION

Many of Tasmania's karsts lie in close proximity to, or within, areas which were covered by glacial ice during the Pleistocene. These areas were subjected to massive variations of thermal regime, hydrological regime and clastic load during the waxing and waning of the glaciers. Still other Tasmanian karsts were influenced by periglacial processes during the glacial stages and even those in nearly coastal situations at low altitude must have been influenced by fluctuations in the base level brought about by Quaternary sea level changes. It may be concluded that no Tasmanian karst escaped the cold touch of the Pleistoscene.

Whether that touch was deathly cold, and stopped the pulse of karstification, or whether that pulse was quickened, is a question fundamental to the understanding of Tasmanian karst. Several authors have concluded that cave development was inhibited during cold climatic episodes due to factors ranging from a diminution of rhizogenic soil water acidulation to the freezing of free water (e.g. Halliday, 1954; Warwick, 1971) or by the infilling of karstic conduits by clastic sediments(Rudnicki, 1967; Hladnik and Kranjc, 1977). However caves in the Canadian Rocky Mountains and elsewhere have been generated during the presence of ice sheets (Ford, 1977; Sweeting, 1972) and there clearly exists a need to be cognizant of the differing thermal regimes between and even within glaciers, and of the abundance of meltwater and tools for corrosion which characterise many temperate glaciers. The object of this note is merely to raise some possibilities which might be borne in mind and tested as the exploration and study of Tasmania's karst proceeds.

KARST AND GLACIATION: SOME TASMANIAN PROBLEMS

The task of unravelling the chronology and degree of Quaternary climatic change in Tasmania is in its infancy, a fact which must inhibit to some extent elucidation of the interaction of palaeoclimate with karst development. Nonetheless, through localised studies of the glacial chronology adjacent to karst areas it may prove possible to gain considerable insight into the question. Indeed such localised studies probably represent the most desirable direction in which to proceed since there seems no reason why the response to a particular set of climatic conditions should necessarily be the same everywhere.

Indeed, evidence of the effect upon Tasmanian karst of glaciers appears at first glance to be contradictory. The weathering of igneous clasts in tills around the Mount Anne massif in south-western Tasmania suggests at least two glacial stages are represented in the deposits (Kiernan 1980a). Probably during the earlier, more extensive stage a glacier over 400 metres thick in the Timk Valley deposited dolerite erratics on the karstified north-east ridge of the mountain. Portions of large karstic shafts formed in the dolomite high on the northern wall of the valley are exposed in section and may represent preglacial karst truncated by the direct or indirect effects of ice erosion. While this suggests erasure of karst during glaciation, the converse may also occur. Glaciers with a temperate thermal regime may themselves contain a karst-like hydrological network (Clayton, 1964; Halliday, 1976, 1979; Kiernan, 1979; 1980b) which may enhance carbonate karst development where glacial ice overlies soluble rock and a low ice velocity inhibits glacial erosion. In the headwaters of the Dante Rivulet in Tasmania's central West Coast Range there exists evidence both for incomplete removal of surface karren by superincumbent glacial ice, and perhaps also the generation of subglacial caves during the Last Glacial Stage.

This possibility is clearly dependent upon the availability of meltwater and probably abrasive materials, and also upon low ice velocities (Kiernan 1980a, 1981).

A third effect may be neither destructive nor constructive to caves but rather to render them inert. Considerable aggradation has been suggested in and near Exit Cave in south-eastern Tasmania by proglacial streams carrying a high clastic load during glacial times (Goede, 1968). In south-central Tasmania a reversion to surface drainage has been suggested in the Junee karst due to the infilling of caves by a destabilised slope mantle in a periglacial environment (Goede, 1973). Thick fills of coarse gravels with a matrix of silty or clayey sand are common in Tasmanian caves (Burns, 1960; Goede and Murray, 1977). These poorly sorted sediments are dominantly allogenic. The gravels reach a calibre of 20 centimetres or more, are poorly rounded and frequently display facetting. They probably reflect mechanical weathering in cold climatic conditions. Transport was accomplished by streams of higher energy than those which presently occur within the caves and occurred over fairly short distances. These streams were probably fed by meltwater. Some caves infilled in this manner have later been removed from "cold storage" through erosion of the sediments after a return to milder climatic conditions and a diminution in the calibre of the clastic load. This has occurred in the Nelson River area of western Tasmania and elsewhere. However, ponding of glacial meltwaters within or adjacent to the ice margin may provide a sediment trap which effectively eliminates larger calibre materials from the clastic load that might otherwise result in very rapid cave infilling.

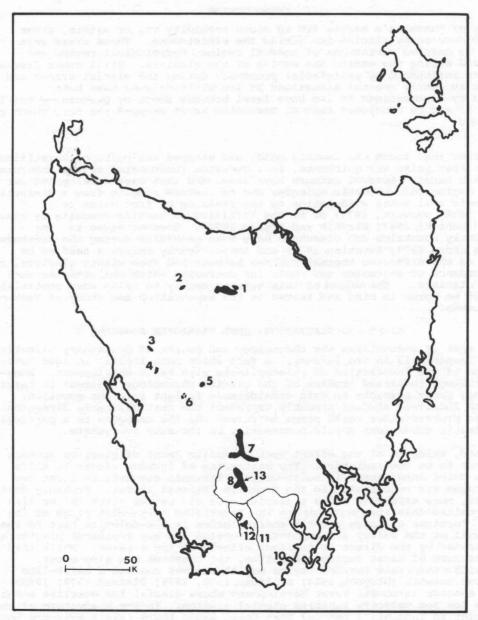


Figure 1. Localities mentioned in text:
1. Mole Creek, 2. Lake Lea, 3. Dante Rivulet, 4. Nelson River,
5. Mount Ronald Cross, 6. Frenchmans Cap, 7. Junee-Florentine,
8. Mount Anne-Weld River, 9. Cracroft River, 10. Ida Bay, 11. Picton River, 12. Lake Sydney, 13. Lake Timk.

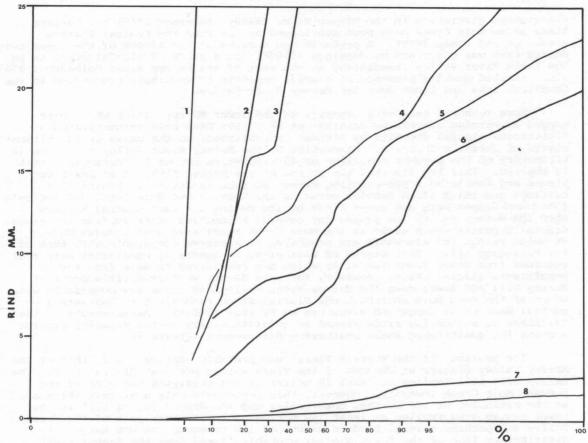


Figure 2. Cumulative percentage frequency curves for maximum thicknesses of weathering rinds developed on dolerite clasts within glacial deposits of the Mersey River Valley, Tasmania:

1. Railton-till. Maximum recorded thickness is 250mm. 2. Mersey Hill, Mole Creek - till. 3. Tarleton - outwash terrace. 4. Mersey River bank 200 metres upstream from Croesus Cave - till. 5. Union Bridge, Mole Creek - till. 6. Parangana damsite - till. 7. Latero-terminal moraine 2.3 kilometers east from Rowallan Dam - till. 8. Last Glacial Maximum limit 1 kilometer north from Rowallan Dam - till.

Palaeoclimatic factors may offer an explanation for the distribution of particular karst features, such as meltwater swallets near former ice-sheet margins (Handel et al., 1978). In a number of Tasmanian karsts caves occur parallel to valley sides a short distance within the limestone margin. One possible reason for such a configuration lies in the release of tectonic stresses, which besides being responsible for much internal cavern breakdown may also provide jointing in a limestone mass that guides speleogenesis. Hence caves along valley margins may be due to the production of sheeting joints through unloading of pressure following surface erosion (Renault, 1970; Warwick, 1971, Jennings, 1970; 1980). However this configuration may also be explicable in terms of cold climatic conditions, with vadose invasion caves (Malott, 1937) being developed through the diversion of drainage to valley margins by obstructions such as sediments or ice upon the valley floor. Such a situation appears to have been involved in the evolution of the D'Entrecasteaux River anabranch in Exit Cave.

The latter suggestion has also been raised with respect to the system of caves associated with the underground course of Mole Creek in central northern Tasmania, where the decanting of proglacial meltwater against the margins of an Ordovician limestone ridge by fluvioglacial sediments was hypothesised to have promoted solutional opening of the limestone leading ultimately to an underground breach of a surface drainage divide (Jennings and Sweeting 1959). However, this demonstrates some of the difficulties in the investigation of such phenomena in the absence of a detailed picture of the glacial chronology as the thesis was developed in the context of a now outmoded monoglacial model and prior to the recognition of field evidence which indicates a far greater extent of ice during pre Last Glacial time. It also encounters some possible difficulties with respect to apparent aggradation in some caves concurrently with the elaboration of others, although the two need not necessarily be mutually exclusive.

An alternative perhaps more compatible with present, but still incomplete knowledge of the glacier systems of the Mole Creek area lies in the meltwater being decanted not from proglacial fans but laterally from the margins of a more extensive earlier ice body. While the Parangana damsite 17 kilometres south-west from Mole Creek has for some time been regarded as the downstream limit of

Pleistocene glaciation in the Mersey River Valley (Paterson 1965) the Western Tiers above Mole Creek have been overlapped by ice from the Central Plateau (Jennings and Ahmad 1959). A probable end moraine on the slopes of the Tiers near Scotts Cave was described by Jennings (1967). In a study of glacial deposits in the Forth River Valley immediately to the west of the Mersey River Colhourn (1976) also remarked upon the presence of glacial deposits of uncertain provenance in the Chudliegh area and lower down the Mersey River Valley.

More recently extensive deposits in the lower Mersey Valley which were mapped as Permian gravels by Jennings et al.(1959) have been reinterpreted as Pleistocene glacial deposits by Kiernan (unpublished) on the basis of constituent clasts of Jurassic dolerite. Glaciation of the Mersey River Valley to within 12 kilometers of the present coastline or 45 kilometres beyond the Parangana limit is implied. This ice diverted the course of the Mersey River in at least two places and inundated a pre-existing karst surface at Railton. Frost-riven outcrops and thick slope mantles occur on the Tiers above Mole Creek and indicate that these slopes were not swept clear by ice during the Last Glacial Maximum when the Mersey Valley ice proper lay several kilometres upstream from Parangana. Glacial deposits which occur in the Mole Creek karst area near Croesus Cave, at Union Bridge and elsewhere are weathered to a degree comparable with that of the Parangana till. This degree of weathering is generally consistent with that recorded from other Tasmanian sites which are considered to date from the penultimate glacial stage. However, far more deeply weathered tills occur at Mersey Hill and lower down the Mersey River Valley and these are comparable with those of the much more ancient Linda Glacial Stage recognised in Tasmania's central West Coast Range and elsewhere by Kiernan (1980a). Measurements of the thickness of weathering rinds formed on dolerite clasts in the deposits provide a means for quantifying these weathering differences (Figure 2).

Ice pouring off the Western Tiers was probably confluent with that of the Mersey Valley Glacier at the foot of the Tiers during pre Last Glacial time. The Mersey Hill till implies at least 60 metres of ice overlying the site of the present Mole Creek township. However, this represents only a minimum thickness as the extension of ice further down-valley and the deposition of till in the Lower Beulah area implies at least 160 metres of ice in that part of the Mersey Valley and perhaps several hundred metres of ice to swamp the Gog Range. A distributary lobe of the Forth Glacier probably flowed down the Dasher River Valley to merge with the Mersey ice and leave Mt. Roland standing as a nunatak, (Kiernan, unpublished work). The extent of this Pleistocene ice cover probably had profound implications for the development of karst in the area.

Possible glacial diversion of drainage to valley margins has also been invoked to explain the configuration of Judds Cavern and other caves in the South Cracroft Valley in southern Tasmania (Goede, 1975; Gilleson and Taylor, 1980), however here again inadequate knowledge of the glacial geomorphology and chronology is a stumbling block. Only topographic evidence of a highly equivocal nature has to date been advanced for the existence of an appropriately located glacier. One study recognises putative glacial deposits in the nearby middle Huon River Valley and tills within the adjacent Picton River catchment (Colhoun and Goede, 1979) but it does not address itself to any low level glaciation around the Cracroft karst and provides no direct evidence for ice in this area of the South Cracroft Valley.

However, the existence of a small glacier at a higher elevation which flowed northeast for at least 1.5 kilometres on the opposite side of the Cracroft-Picton divide during the Last Glacial Stage is unequivocal. During an earlier stage this glacier extended to a low elevation down the Farmhouse Creek valley towards the Picton River, and depending upon the extent of this earlier glaciation it is conceivable some ice may have spilled over the Picton-Cracroft divide towards the Cracroft karst, but it may not have extended far. A small stream which sinks high on the Picton side of the divide breaches it underground to re-emerge in Judds Cavern (Goede, 1975). This stream may have been ponded by the ice margin hence this may represent glacial diversion.

SOME ALPINE KARST LANDFORMS

The study of the interaction between karst and glaciation is also complicated by a degree of equifinality in landform evolution resulting from the processes operating in the two domains. The development of enclosed depressions by both glacial and karstic processes demonstrates a degree of convergence in alpine landform evolution. In the glacial instance enclosed depressions are formed by erosional overdeepening or by glacigenic deposition, while karstic depressions are the product of solution processes operating from the surface downwards or of mechanical collapse of rock into subjacent voids of solutional origin. Subjacent dolines may occur within surficial deposits of glacigenic origin where such deposits overlie soluble rock. Sinkholes are developed within a till mantle which overlies Ordovician limestone near Lake Lea in central northern Tasmania and in till underlain by dolomite at Carbonate Creek in western Tasmania. Similar forms occur in the fluvioglacial deposits which mantle limestone near Caveside in the Mole Creek area.

A depression which is primarily of glacial origin may focus postglacial drainage and promote karst development. A depression initially of karstic origin may in certain circumstances form a favourable site for ice accumulation during colder climatic conditions. Such a landform may represent an irregularity in the long profile of a glacier and promote differential ice flow rates which accentuate the depression by glacial erosion. Hence in areas where both glacial and karst processes coincide there may be difficulty in attributing such a landform to a single specific origin. Some lake basins in the Frenchmans Cap National Park in western Tasmania have been suggested to be former karstic depressions elaborated by glacial ice (Peterson 1966), while in the Mount Anne area Lake Timk lies within a glacially over-deepened basin now drained underground through Palaeozoic dolomite. The Lake Sydney cirque near the Cracroft karst is similarly drained underground through Gordon Limestone.

Ford (1977) has developed a four-fold classification of landforms developed within such contexts. Postglacial karst forms entirely follow glaciation, owing little to glacial processes. A Tasmanian example may be found in karren forms on the high altitude dolomite outcrops of Mt. Anne, Mt. Ronald Cross or Frenchmans Cap. Karstiglacial forms are primarily of glacial origin, but have been adapted and modified by karst processes. The Lake Timk depression may serve as a Tasmanian example, as the karst drainage associated with it appears immature and the basin clearly owes much to glacial processes which have been accentuated by aspect and the Anne massif snowfence. On the other hand, glaciokarstic forms are of solutional origin but have been subsequently modified by glacigenic processes. This is the origin advanced some years ago for some of the Frenchmans Cap lakes (Peterson, 1966). Several glaciokarsts exist in Tasmania. Finally, preglacial karst forms antedate and have not been morphologically modified by glacial action.

CONCLUSION

Temporally, episodes of cold climatic conditions have dominated the Quaternary, and during these periods the processes which we regard as characteristic of karst were overpowered. This has neither been necessarily destructive nor constructive of karst, but as a first approximation it would seem that the evidence for cave elaboration under cold climatic conditions is disproportionately small (Kiernan, in prep.). Where glacial ice and carbonate rock coincide, there is no necessary general case as to the influence upon karst development. Local factors such as topography and its effect upon microclimate, ice movement, glacier thickness and hydrological regime will interact with zonal influences and processes.

Probably upwards of one dozen Tasmanian karsts were over-ridden by glaciers during the Pleistocene. Others lay marginal to ice during those same episode's. Some karst which were over-ridden during pre Last Glacial times assumed marginal positions during the most recent episode of Tasmanian glaciation. Some of these essentially alpine karsts are inaccessible and little explored, but others are easy of access. While it would be premature to speculate too widely on the implications of the glaciers, it seems likely that they exerted a considerable influence upon the existence and location of many Tasmanian caves.

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ISOTOPIC COMPOSITION OF PRECIPITATION, CAVE DRIPS AND ACTIVELY FORMING SPELEOTHEMS AT THREE

TASMANIAN CAVE SITES

A. Goede, D.C. Green, R.S. Harmon

Abstract

Monthly samples of precipitation and cave drips were collected from three Tasmanian cave sites along a north-south transect and their $^{18}\text{O}/^{16}\text{O}$ ratios determined. At one station D/H ratios were also measured and the relationship between $\delta^{18}\text{O}$ and δD values investigated. The $^{18}\text{O}/^{16}\text{O}$ and D/H ratios of monthly precipitation show marked seasonality with values correlating strongly with mean monthly temperatures. The effect of temperature on $^{18}\text{O}/^{16}\text{O}$ ratios appears to increase as one goes southwards and is at least twice as strong at Hastings $(.61^{\circ}/_{\circ\circ} \text{ SMOW}/^{\circ}\text{C})$ as it is at Mole Creek $(.28^{\circ}/_{\circ\circ} \text{ SMOW}/^{\circ}\text{C})$.

Irregularities in the seasonal pattern of $^{18}\text{O}/^{16}\text{O}$ change are particularly pronounced at Hastings and in the Florentine Valley and can be attributed to the amount effect. For $\delta^{18}\text{O}\text{values} > -5.5^{\circ}/_{\circ}\circ$ the combined data from the three Tasmanian stations show an amount effect of .026°/ $_{\circ}\circ$ SMOW/mm.

Cave drips show apparently random, non-seasonal variation in $^{18}O/^{16}O$ isotopic composition but the weighted mean of the $^{18}O/^{16}O$ isotope composition of precipitation provides a good approximation to their mean $^{18}O/^{16}O$ isotopic composition. In contrast the D/H ratios for a cave drip site in Little Trimmer Cave, Mole Creek, show a distinct seasonal pattern.

The $^{18}\text{O}/^{16}\text{O}$ and $^{13}\text{C}/^{12}\text{C}$ ratios have been determined for a number of actively forming speleothems. With respect to $^{18}\text{O}/^{16}\text{O}$ it is found that speleothems at the three sites are being deposited under conditions approaching isotopic equilibrium. The $^{13}\text{C}/^{12}\text{C}$ ratios of these speleothems are highly variable but the generally less negative values found in Frankcombe Cave (Florentine Valley) compared with the other two sites may reflect the effects of recent clear felling in the area.

METHODS

Three pairs of surface and underground sample sites were selected. The sites were chosen along a north-south transect and located in karst areas likely to provide speleothem material suitable for yielding palaeoenvironmental information from isotopic analyses (Figure 1). At each surface site a monthly raingauge was installed while at each cave site plastic funnels connected to containers were placed under two cave drips in close proximity. In addition a set of sheathed maximum and minimum thermometers (Dobros, nos. 1001 and 1002), mounted on a wooden board, was located close to the cave drip collectors. At Mole Creek and in the Florentine Valley the surface site was located in close proximity to the cave entrance. At Hastings, because of the dense forest at the cave site, the monthly raingauge was installed at The Chalet approximately 3 km SSE of the cave and at a significantly lower elevation. The site has the advantage of a meteorological station so that daily precipitation and temperature data are available for the period of record. Table I gives details of the three cave sites and the nearest meteorological stations.

All sites were visited monthly as close as possible to the middle of the month. These visits commenced in December 1978 for the Mole Creek and Florentine Valley sites and in January 1979 for Hastings. At all three sites they continued for the whole of 1979. At each surface site the accumulated precipitation was measured and water samples collected for $\delta^{18}0$ and δD isotopic analysis. At underground sites the actual, minimum and maximum temperatures were read and the thermometers reset during each visit. Water samples were collected from cave drips for $\delta^{18}0$ analysis as well as analysis of calcium and total hardness. The analysis of hardness variations in cave drips is reported in another paper (Goede, 1981). Samples were also collected for δD analysis at one of the two cave drip sites at each of the three localities. δD samples for precipitation and seepage have so far been analysed only for the Mole Creek station.

Isotopic analyses of precipitation and seepage samples for $\delta^{\,1\,8}\text{O}$ were made using a VG Micromass 602D mass spectrometer. Isotopic analyses for δD were carried out at the Scottish Universities Research and Reactor Centre at East Kilbride.

Some problems were encountered during collection of the data. The maximum thermometer installed in King George V Cave, Hastings, proved to be unreliable and its readings have been excluded from consideration. It had originally been intended to accumulate all drip waters between visits but in the case of Little Trimmer and Frankcombe Caves drip rates proved to be so rapid that the 25 litre containers used frequently overflowed. To reduce the problem of collecting a representative sample in this circumstance hoses were inserted deep into the containers to allow thorough mixing of the contents before they overflowed. Instantaneous drip rates, obtained by timing drip water accumulation over a short time period, were measured from July (Frankcombe Cave) and August (Little Trimmer) onwards.

At Hastings problems of overflowing did not arise but both drip sites dried up progressively during the period of sampling due to the long drought which affected south-eastern Tasmania during 1979. At King George V Cave even the spring rainfall maximum which occurred from August to October failed to re-activate the drips because of the unusually dry preceding soil conditions. Therefore it was not possible to collect cave drip samples from this site from July onwards.

ANALYSIS OF OBSERVATIONS

Precipitation patterns

The monthly precipitation totals for the period mid-December 1978 to mid-December 1979 are shown in Figures 2, 3 and 4.

At Mole Creek the driest monthly period was December-January (41 mm) and the wettest, August-September (199 mm) (Figure 2). There was a major rainfall maximum in winter and spring (July-October) and a minor maximum in March-April. Precipitation for the period was 1385 mm which is close to the mean annual precipitation for the area. The record can be regarded as representing a typical year.

In the Florentine Valley the driest monthly period was February-March (27 mm) and the wettest August-September (176 mm) (Figure 3). Precipitation for the period was 1090 mm which was well below the mean annual precipitation for the area estimated to be at least 1500 mm. During the year precipitation was highest in late winter and spring and lowest in late summer.

At Hastings daily rainfall amounts from the meteorological station were available as well as totals form the monthly gauge. The annual precipitation amount at the Bureau of Meteorology station was 1090 mm compared with 976 mm from the monthly gauge (Figure 4). Amounts from the monthly gauge were always slightly below those from the station. Since these differences were no larger during the summer than during the winter they are not due to evaporation from the monthly gauge but appear to have resulted from either local site difference or bias in one or both of the gauges. Both annual amounts were well below the mean annual precipitation of 1367 mm recorded for the station (Bureau of Meteorology, 1975). The graph shows two precipitation maxima; one in March-May and the other in July-October with extremely dry conditions intervening from January to March and May to July.

TABLE I. Details of cave sites and nearest meteorological stations.

Site	Longitude	Latitude	Altitude		Mean Annual · Precip. (mm)
* Little Trimmer Cave Mole Creek	146 ⁰ 15'E	41°34'S	460	9.2†	7 ms 24-318 388
Goderick, Deloraine	146 [°] 38'E	41°31's	253	10.7	1061
Frankcombe Cave, Florentine Valley	146 [°] 27'E	42°32'S	400	9.2†	teri be <u>r</u> amatan Sa Depenyasi-C
Maydena	146 ⁰ 36'E	42 ⁰ 46'S	267	10.2	1230
King George V Cave, Hastings	146 ⁰ 51'E	43 ⁰ 23'S	180	9.9†	
* The Chalet, Hastings	146 ⁰ 53'E	43 ⁰ 25'S	40	10.9	1367

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

Isotopic composition of precipitation

The three stations show the pronounced pattern of seasonal variation in the $^{18}\text{O}/^{16}\text{O}$ ratio characteristic of mid-latitudes, (Figures 2, 3 and 4), and termed the temperature effect by Dansgaard (1964). Precipitation was isotopically heavy during the summer months and isotopically light during the winter months. The Mole Creek record displayed the most regular seasonal pattern although even here the precipitation for December 78 - January 79 was unusually heavy isotopically. It was also a particularly dry month.

The patterns for Hastings and the Florentine Valley were less regular but once again it was not noticeable that isotopically heavy values tended to be characteristic of dry months which tended to be more common at the two stations because of the southeast Tasmanian drought. This phenomenon of variation in isotopic composition depending on the quantity of monthly precipitation has been described as the amount effect by Dansgaard (1964). He has attributed it to the following factors:

- (1) Variation in the isotopic composition of newly formed condensate as a result of cooling during the condensation process. The amount of precipitation is related to the amount of cooling.
- (2) Fractionation by isotopic exchange between the drops and the environmental vapour through which they fall on the way down.
- (3) Evaporation from falling drops where they pass through low humidity air at lower elevations.

All three factors will lead to a negative correlation between $\delta^{\,1\,8}\text{O}$ values and the precipitation amount.

When values of $\delta^{1\,8}O$ for monthly precipitation were plotted against monthly precipitation amounts for all three stations it was found that the amount effect was apparent for $\delta^{1\,8}O$ values > -5.5°/.. (Figure 5). Correlation analysis gave a coeficient of r = -.65. Student's t test showed this correlation to be highly significant (p >> .001). The equation to the line of best fit (reduced major axis) was determined as:

$$\delta^{18}O = -.0256 P_m - 1.521$$
 (1)

This indicates that values of δ^{18} 0 become isotopically lighter by approximately 1°/ $_{\circ}$ 0 for every 40 mm increase in monthly precipitation.

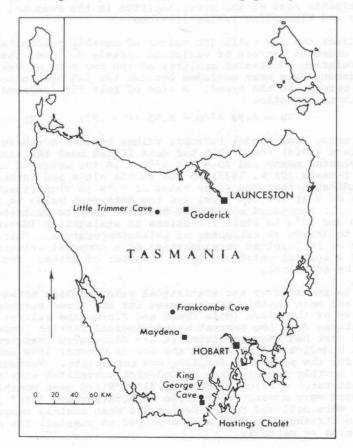


Figure 1. Location map of the cave sites and nearest climatic stations.

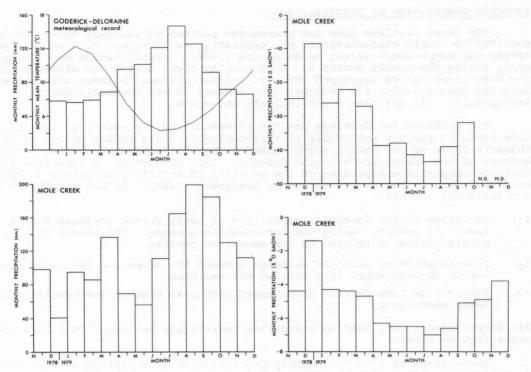


Figure 2. Thirty year meteorological record at Goderick (Deloraine) together with monthly precipitation amounts, δD and $\delta^{\,1\,8}O$ values for the period December 1978 to December 1979 at Little Trimmer Cave, Mole Creek.

Dansgaard (1964) states that the amount effect is found all the year round at most tropical stations and in the summer time at mid-latitudes. However, it appears that during the drought conditions prevailing in southeastern Tasmania during 1979 the amount effect was noticeable during a few winter months (Figure 5). It appears to explain most of the irregularities in the seasonal pattern found at the Hastings and Florentine Valley stations.

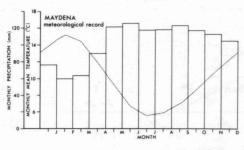
At Mole Creek the D/H ratio (δD value) of monthly precipitation was also measured. The seasonal pattern of variation closely followed that of the $\delta^{18}O$ value. In correlation regression analysis of the two sets of values (Figure 6) the December-January data were excluded because the isotope values were clearly anomalous with respect to the trend. A line of best fit (reduced major axis) is obtained with the equation.

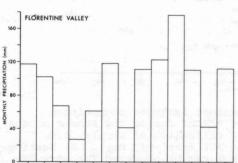
$$\delta D = 6.98 \ \delta^{18}O + 5.65 \ (r = .97)$$
 (2)

When comparing mean annual isotopic values between northern hemisphere stations Dansgaard (1964) found that the data fitted best the line $\delta D=8.1\,\delta^{1\,8}O+11$ for unweighted means and $\delta D=8.0\,\delta^{1\,8}O+10$ for weighted means. The application of t-tests (Silk, 1979) to the sample slope and intercept terms of equation (1) indicates that the slope value of 6.98 is significantly lower than the slope value of 8 at the 10% level and the intercept value is not significantly different from 10. Dansgaard's equation has been used to describe the relationship between δD and $\delta^{1\,8}O$ in fluid inclusions in stalagmites (Schwarcz et al., 1976) in order to arrive at estimates of palaeotemperature. This may not be a valid procedure as it involves consideration of a temporal relationship at one site instead of a spatial relationship at a number of sites. The two relationships need not be identical.

In order to investigate the statistical relationships between monthly isotope values and mean monthly temperatures for the three surface sites it was necessary for two of the sites (Mole Creek and Florentine Valley) to obtain mean monthly temperatures from the nearest meteorological station (Goderick and Maydena). After the field work had been completed it was discovered that temperature measurements at Goderick had ceased at the end of October 1978 and that the Maydena record for the period of sampling was incomplete. Fortunately, it was found that mean monthly temperatures at Goderick correlated very closely with those of the Palmerston station (146°59'E, 41°47'S) and mean monthly temperatures at Maydena correlated very closely with those at Strathgordon (146° 3'E, 42°46'S). The Palmerston data were utilised to synthesize the mean monthly temperature values at Goderick and the Strathgordon data were employed to complete the mean monthly temperature records at Maydena.

Since sampling was done about the middle of each month, corresponding mean monthly temperatures were obtained by taking the average of the two months overlapping the inter-sample period. For Mole Creek and the Florentine Valley the estimates have been corrected for the differences in elevation between the rainfall station and the meteorological station. The correction factor used is 1° C/150 metres (Haltiner & Martin, 1957).





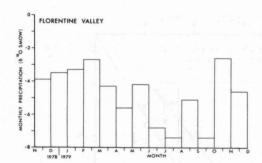
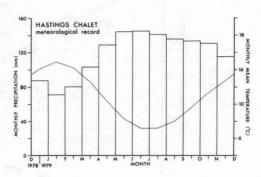
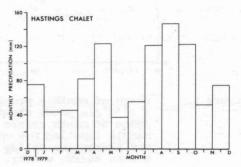


Figure 3. Thirty year meteorological record at Maydena together with monthly precipitation amounts and $\delta^{1\,8}$ O values for the period December 1978 to December 1979 at Frankcombe Cave, Florentine Valley.





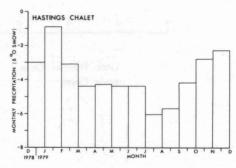


Figure 4. Thirty year meteorological record at Hastings Chalet together with monthly precipitation and $\delta^{18}O$ values for the period January 1979 to December 1979.

Regression analysis was carried out to relate $\delta^{\,1\,8}\,O$ and $\delta\,D$ values to mean monthly temperatures (T_m) for the three rainfall stations (Figure 7). Equations to the reduced major axes are:

Mole Creek: $\delta^{18}O = .28T_m - 8.13 (r=.91)$ (3)

 $\delta D = 1.78T_{m} - 50.4 (r = .95)$ (4)

Florentine Valley: $\delta^{18}O = .39T_m - 8.78 (r = .76)$ (5)

Hastings: $\delta^{18}O = .61T_{m} - 10.13 \ (r = .86)$ (6)

In the analyses the Mole Creek data for December-January were again excluded because the isotope values were anomalous with respect to the trend. The temperature coefficients (slope values in the above equations) increase as one goes further south and this could well be due to the increased amount effect resulting from the unusually dry conditions prevailing in southeastern Tasmania during the sampling period.

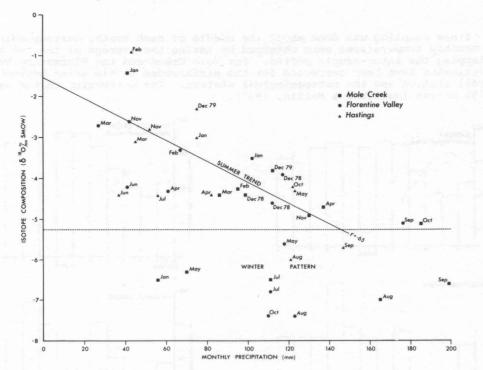


Figure 5. Graph of monthly precipitation against isotopic composition ($\delta^{18} \text{O}^{\circ}/_{\circ} \circ$ SMOW) shows the amount effect during the summer months. (Name of month refers to month of collection of sample, e.g. sample labelled May covers period mid April-mid May). At Hastings and Florentine Valley amount effect can be observed for very dry months during winter.

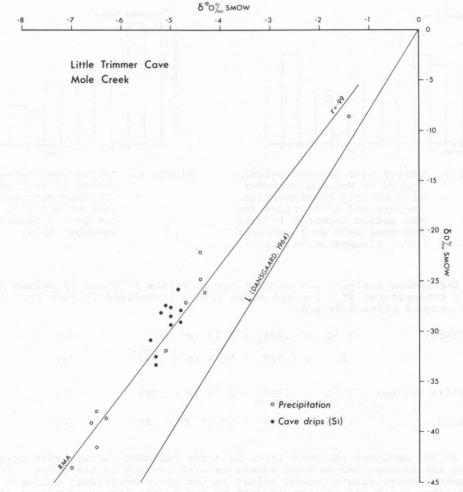


Figure 6. Relationships between monthly $\delta^{18}O$ and δD values for precipitation and cave drip (S_1) at Little Trimmer Cave, Mole Creek.

Cave temperatures

At each of the three cave sites the minimum and maximum temperatures were read monthly and the actual temperature at the time of the visit (instantaneous temperature) was also noted. Maximum temperature values for King George V Cave have been disregarded because the thermometer proved to be unreliable. The cave temperature ranges (°C) for 1979 are shown in Figure 8.

The mean annual temperatures calculated for the three caves from the instantaneous temperature measurements are:

Little Trimmer Cave	9.5°C
Frankcombe Cave	8.3°C
King George V Cave	9.4°C

These values should be compared with the mean annual temperatures calculated in Table I for the surface sites. At Mole Creek the agreement is close with the mean cave temperature 0.3° C higher than the calculated mean annual surface temperature. At Hastings a comparison shows the mean cave temperature to be 0.5° C lower than expected and in the Florentine Valley it is 0.9° C below the estimated mean annual surface temperature.

There is a marked contrast in the annual temperature range of the three cave sites. From north to south minimum temperature ranges are 0.9, 0.3 and 0.2°C while instantaneous temperature ranges are 1.2, 0.3 and 0.1°C. Maximum temperatures ranges are available only for Little Trimmer Cave 1.0°C and Frankcombe Cave 0.6°C. It is clear that Little Trimmer Cave has by far the greatest annual temperature range (approx. 1.0° C), the range at Frankcombe Cave is much smaller (approx. 0.4° C) while the cave site temperature variation for King George V Cave is extremely small (approx. 0.15° C). Only at Little Trimmer Cave is there a clearcut seasonal pattern. It is weakly developed in Frankcombe Cave and not at all in King George V Cave.

The reasons for the contrast between the three sites are not clear. All three have small entrances and are lacking in detectable air currents and all three sample sites are well removed from known entrances and from permanent underground streams. After the conclusion of the sampling programme the authors received information that Little Trimmer has a second entrance and this may explain the greater temperature variation at this site. It is also possible that other entrances, unknown to speleologists, exist closer to one or more of the sample sites but no evidence for this was found.

The long term temperature control on the cave atmosphere must be the surrounding bedrock (Lange, 1954, 2 refs). In the absence of significant air movement at the three sites, seasonal temperature variations by means of cave seepage waters entering through the roof of the caverns may be superimposed on the long term control. This would be most likely to have a significant effect where large amounts of seepage water move rapidly from the soil profile through the bedrock to the cave. If this is a factor it may go some way towards explaining the nearly constant temperature conditions in King George V Cave. This cave experienced very little seepage during 1979 compared with the other two. The site is also located in a permanently dry passage, while the other two sites are located in passages which may carry small flows of water after a prolonged period of heavy precipitation.

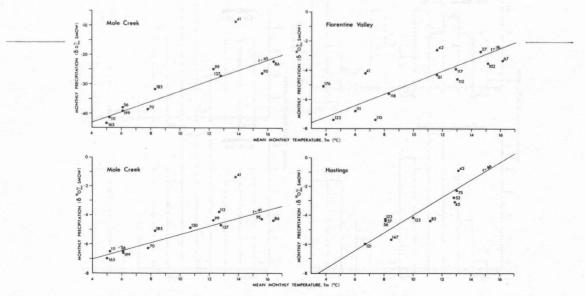


Figure 7. Statistical relationships between $\delta^{1\,8}\text{O}$ (SMOW) values and mean monthly temperatures at the three stations as well as the relationship of δD SMOW values and mean monthly temperatures at Mole Creek.

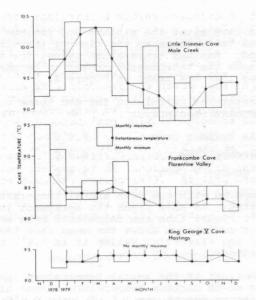


Figure 8. Monthly temperature observations at three cave sites.

Cave seepage rates

Since the water containers installed to collect seepage water overflowed during most months, at least in Little Trimmer and Frankcombe Caves, few absolute measurements of the amounts of drip water between monthly visits are available from these sites. Instantaneous drip rates were measured in Little Trimmer from August onwards and in Frankcombe Cave from July onwards. They are shown in Table II.

Like streamflows the drip rates show extreme variability with very high rates occurring during, and shortly after, periods of heavy rainfall and very low rates following prolonged drought conditions.

Isotopic composition of cave drips

Monthly samples of water were analysed from all six cave drip sites to determine the $^{18}\text{O}/^{16}\text{O}$ ratio. For the Hastings sites only a partial record was available because the drips dried up progressively during the year. In Little Trimmer Cave at drip site S1 the D/H ratio was determined for 11 out of 13 months of record. The patterns of variation are shown in Figure 9. The amount of isotopic variation in cave drip waters is reduced compared with that of precipitation (cf. Figures 2,3 and 4) presumably indicating the very considerable amount of storage and mixing of water in the soil.

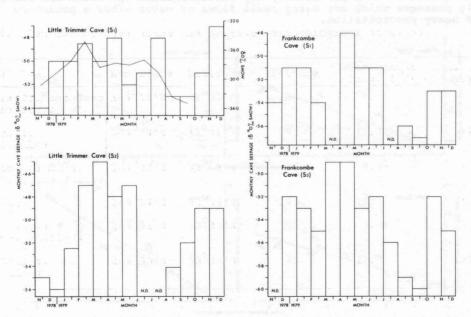


Figure 9. Monthly measurements of the isotopic composition of cave drip in Little Trimmer and Frankcombe Caves.

There is a marked contrast in the behavious of D/H and $^{18}\text{O}/^{16}\text{O}$ values. The former maintain the seasonality of pattern that characterises the precipitation at the surface site although there is clearly a lag effect of approximately two months for both the summer maximum and the winter minimum. The $^{18}\text{O}/^{16}\text{O}$ values still show a surprising range of variation with several isolated peaks of isotopically heavy values and with an almost complete removal of the seasonal cyclic pattern. The causes of non-seasonal variations in the $^{18}\text{O}/^{16}\text{O}$ values of drip waters are not known.

TABLE II. Instantaneous drip rates of cave seepage waters in litres/hour

Litt	le Trimmer C	ave	Fra	Frankcombe Cave				
Date	Sl	S2	Date	Sl	S2			
-	_		24/7/79	.054	1.147			
9/8/79	1.147	9.556	14/8/79	.420	3.211			
11/9/79	.459	14.556	17/9/79	2.918	6.040			
8/10/79	1.758	17.393	16/10/79	.510	3.058			
9/11/79	.076	.917	15/11/79	.031	.287			
11/12/79	.008	.612	10/12/79	3.823	5.734			
Mean	.690	8.601	Mean	1.293	3.246			

The weighted mean values of precipitation can only be compared with the arithmetic means of cave drip samples since average drip rates between monthly visits are not known.

In the case of Little Trimmer and Frankcombe Caves isotopic means of precipitation and cave drips are comparable but in the case of King George V Cave the cave drips are much lighter isotopically than would have been expected. The fact that the drips in King George V Cave dried up during the period of record suggests that the seepage water collected is not related to precipitation during 1979 but may well be derived from precipitation which fell during the previous winter. The fact that the cave drips failed to respond to the substantial spring rainfall from July to October (Figure 4) suggests a high capacity for water storage in the soil mantle and possibly low permeability of the Permian caprock above the cave. At drip site Sl in Little Trimmer the different behaviour of the $\delta^{18}O$ and δD content of water as it passes through the soil and overlying rock means that the close relationship found between the two sets of values for precipitation (Equation 2) is significantly lost in this movement. The equation for the relationship in cave drip waters is

$$\delta D = 10.78 \ \delta^{18}O + 25.52 \ (r = .70)$$
 (7)

The correlation just reaches significance at the $2^{\circ}/_{\circ}$ level. The application of t-tests indicates that neither the intercept term nor the slope value is significantly different from the corresponding values in Dansgaard's equation for the meteoric water-line.

TABLE III. Comparison of mean isotopic values (SMOW) between precipitation and cave drips.

Site		Precipi (weight	tation ed mean)		drips etic mean)
Little Trimmer Cave (Mole Creek)	s ₁	-32.78	δD°/00	-29.13	δD°/00
(Mole Cleek)	sı	-5.40	δ ¹⁸ 0°/00	-5.04	δ 180°/00
	s ₂	-5.40	Call Ala	-5.04	n
Frankcombe Cave (Florentine Valley)	s ₁	-5.27	(-5.26	1 1 2 2 2 2 2
(Florentine valley)	s ₂	-5.27	oga n -Engada Haligager 2u	-5.38	i galoù Mi igiza ev
King George V Cave (Hastings)	s ₂	-4.76*		-5.82	in which is the second

^{*} Value adjusted for difference in altitude using a value of -0.40°/...δ180/

TABLE IV. Isotopic composition (PDB) of actively forming speleothems from three Tasmanian caves.

Sample No.	Cave	Nature of material	δ 180°/00	δ 1 3 C°/00
OX12	Little Trimmer	straw	-3.8	-8.0
OX15	Left is Adams: This	mere milalistik "Adultik bet ber ki ki Turun dipermikanan mere	-3.5	-9.7
OX19	m m	flowstone	-3.8	-13.7
OX20	TI .	п	-3.5	-13.5
OX2	Frankcombe	Straw	-4.0	-8.4
OX3	mortal Anna Promot Assets	and the plant of the man	-3.6	-6.2
OX7	II .	n .	-3.7	-5.7
OX1	King George V	Straw	-3.7	-12.0
OX5	н	nded 2	-3.1	-10.1
OX8			-3.7	-10.4
OX9	н	PT N. 1876	-3.7	-8.7
OX10		31 (1) (1) (1) (1) (1) (1) (1) (1) (1) (1	-3.8	-7.9
OX11	н	n (1865)	-4.0	-10.3

TABLE V. Calculated temperatures of calcite deposition

Cave Site	Observed Mean nnual Temp. (°C)	Calculated Minimum	-	tures (°C) Maximum
Little Trimmer	9.5	9.4	10.0	10.6
Frankcombe Cave	8.3	8.6	9.3	10.3
King George V (using seepage data)	9.4	4.6	6.8	8.1
King George V (using precipitation data	9.4	9.3	11.2	12.6

Isotopic composition of speleothems

In order to determine whether present day deposition of calcite in the three caves is occurring under conditions of isotopic equilibrium, actively growing tips of straw stalactites were collected and analysed for their oxygen and carbon isotopic composition (Harmon, Schwarcz & Ford, 1978). In the case of Littler Trimmer Cave two samples of flowstone that had formed on plastic funnels used to collect cave drip water during 1979 were also analysed. A total of thirteen analyses was carried out and the results are shown in table IV.

Calculating average values for the three sites we obtain

	δ ¹⁸ O°/° PDB	$\delta^{13}C^{\circ}/\circ \circ PDB$
Little Trimmer Cave	-3.65	-11.23
Frankcombe Cave	-3.77	- 6.77
King George V Cave	-3.67	- 9.90

With the aid of these values and knowing the mean isotopic composition of cave drip water it is possible to calculate the temperature of deposition since the $^{18}\text{O}/^{16}\text{O}$ ratio of calcite formed in equilibrium with water decreases with increasing temperature. The equilibrium constant for the system calcitewater has been determined by O'Neil et al.(1969) and subsequently modified by O'Neil et al.(1975) as

$$10^3 \text{ ln K}_{C-W} = 2.78 \ 10^6 \text{T}^{-2} - 2.89$$
 (8)

where $K_{C-W} = (^{18}O/^{16}O)_{C}/(^{18}O/^{16}O)_{W}$ and T is the absolute temperature.

Using the mean isotopic composition of the seepage water at the three cave sites, temperatures of deposition were calculated for the mean, lowest and highest $^{18}\text{O}/^{16}\text{O}$ isotope ratio values of speleothems from each of those sites. Since it has already been suggested that the seepage water collected in King George V Cave during 1979 was not typical for this site the calculations were repeated using the weighted mean isotopic composition of precipitation adjusted for the difference in altitude between the cave and the surface station. The results of these calculations are shown in Table V.

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Considering the small number of samples of calcite involved, the limitations of accuracy of measurement of $\delta^{1\,8}O$ values and the fact that arithmetic means of the isotopic composition of seepage had to be used the agreement with observed temperatures is considered quite satisfactory.

The King George V Cave seepage waters do not appear to be representative of normal conditions. As has been suggested earlier they appear to be abnormally light isotopically. Ignoring these results in Table V the calculated temperatures are slightly higher at all three sites than the observed values. This may well reflect slight differences in calibration of $\delta^{\,1\,8}\text{O}$ values between laboratories.

It is confirmed that speleothems currently forming at the three sites investigated are depositing calcite under conditions of isotopic equilibrium.

The $^{12}\text{C}/^{13}\text{C}$ isotope ratios are highly variable but values for Frankcombe Cave are significantly heavier isotopically than for the other two sites. This may be due to recent clearfelling and burning in the area.

ACKNOWLEDGEMENTS

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ERRATA

A. Goede. Variation in hardness of cave drips at two Tasmanian sites.
Helictite 19 (2), 1981.

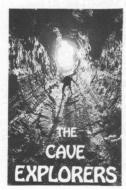
page 58, Table 1, for Golderick read Goderick

page 63, paragraph 5, lines 6 and 7 should read:b) there will be a greater surface area of contact with both the depositional surface and the cave atmosphere.

page 66, paragraph 3, line 7 should read: points to a rapid loss of calcium carbonate by deposition in the cave environment when the rate of flow of the cave drip is low.

page 66, paragraph 7, line 10, after 'drip' insert 'rate'.

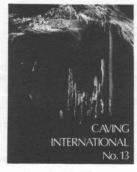
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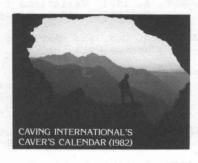
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G. Francis

Abstract

The unusual occurrence of the mineral metastrengite ($FePO_4.2H_2O$) in a cave on Manus Island is described. Its formation is attributed to the interaction of biogenic materials containing phosphates and ferruginous sediments derived from insoluble residues in the limestone bedrock.

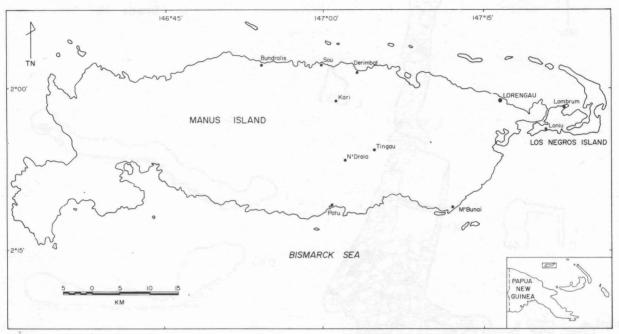
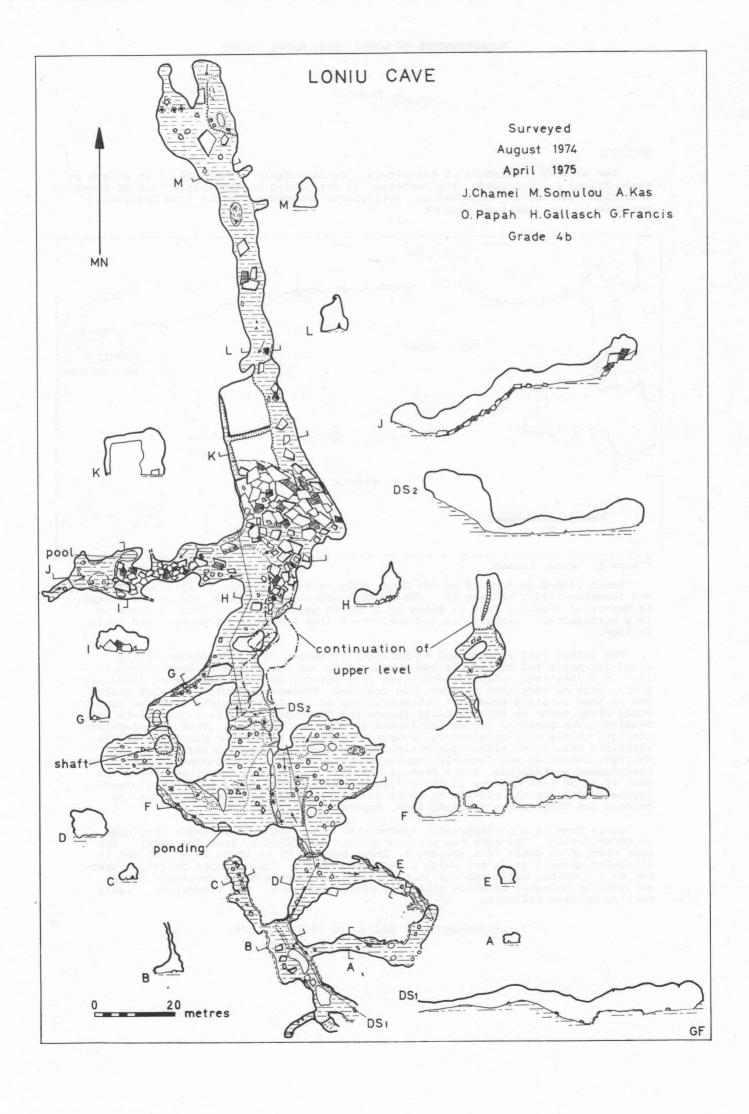


Figure 1. Manus Island

Manus Island is located on the Outer Melanesian Island Arc at latitude $2^{\circ}S$ and longitude $147^{\circ}E$ (Figure 1). The eastern extremity of Manus, Los Negros Island, is separated from the rest of Manus by a narrow passage. Loniu Cave is situated in a northeasterly trending raised reef which lies between this passage and Loniu Village.

The raised reef is composed of Naringel Limestone, which is predominantly algal-foraminiferal biomicrite and biomicrudite and has in places been recrystallised or dolomitized. Samples collected from outcrop are invariably pure carbonate rocks, with no more than 4% insoluble residue. However exposures in Lolak quarry and in road cuttings show that concentrations of insoluble residue from the limestone often occur as stylocumulate (Logan and Semeniuk, 1986, 6) along joints and bedding plane partings and as infiltrate in solution cavities. This stylocumulate consists mainly of clay minerals, quartz, magnetite, pyrite and marcasite and is sometimes associated with cryptocrystalline silica and goethite reactate. The Naringel Limestone was formerly considered to be of Plio-Pleistocene or Early Pleistocene age (Jaques, 1976; Francis, 1977). However the writer now considers that it is of Late Miocene to Early Pliocene age, on the basis of micropalaeontological dates for the underlying Lauis Sandstone which have been determined by Belford and Chaproniere (Jaques, 1980, Appendix 2).

Loniu Cave is a nothephreatic system with about 500 m of passages developed on three levels. The cave has previously been described by Francis (1977). The main chamber in Loniu Cave (Figure 2, Cross Section F) is about 60 m long and is elongated along a joint set which trends about $080^{\rm O}$. This chamber contains numerous wall pockets, bellholes and joint ceiling cavities and has developed almost entirely by phreatic solution with only minor breakdown. The floors are largely mantled by cave sediment.



Two sedimentary units are present. The lower unit is a porous yellow-brown to brown silt which varies from friable to hard in consistency. A dark brown botry-oidal crust with fibrous texture is often present. This unit is at least 1 m thick but its base is rarely exposed. Microscopically it consists of 10-20 micron squat prismatic crystals which are brownish-green with slightly pleochroic reddish-violet bands along cracks and grain boundaries. X-ray diffraction analysis indicates that both the porous silt and the surface crust are metastrengite (FePO₄.2H₂O).

Metastrengite occurs in phosphatized andesite on Malpelo Island in the Eastern Pacific, where phosphate derived from bird guano has reacted with ferromagnesian minerals in the volcanics (McConnell, 1943). It has also been reported from Liberia, where solution caves developed in iron ore (mainly hematite) have coatings of metastrengite along cave walls and along joint wall cavities (Axelrod et al., 1952). Axelrod and his co-workers consider that the metastrengite has formed through reactions between bat guano and iron ore. Metastrengite occurs in Western Australia (Gorman, 1976), but no site details are given in the abstract of this paper provided by P.J. Bridge. The occurrence of ferruginous phosphate in a limestone cave is unusual, in that phosphatic cave fill is commonly dominated by calcic phosphates such as apatite (including collophane), whitlockite and monetite (c.f. Bridge, 1973).

It seems likely that the phosphate in Loniu Cave has formed through reactions between bat guano and ferruginous oxide and sulphide minerals in cave earth which is derived from insoluble residue in the limestone (including stylocumulate). Earthy phosphate derived from bird guano is present in shallow vertical caves and crevice karst corridors on Nauna Island, to the east of Manus (White and Warin, 1964, 52). Since the main chamber in Loniu Cave has no direct connection with the surface and the phosphatic mineralisation is confined to cave sediment rather than the enclosing limestone, bat guano deposited in the cave is a much more likely source for the phosphate than bird guano which was deposited on the surface.

The metastrengite silt is overlain by a black reddish-brown (5YR 2/2) sandy clay loam with strong crumb structure which is up to 0.3 m thick. The loam is very acid (pH 3.5-4.0) and its detrital grains are mainly quartz and goethite. Organic material such as termite appendages and wing cases is abundant. This loam has probably been brought into the cave by termites, which have constructed runways of similar material along fractures and through pores in the limestone. Thus biogenic processes have been particularly important for sedimentation in Loniu Cave

ACKNOWLEDGEMENTS

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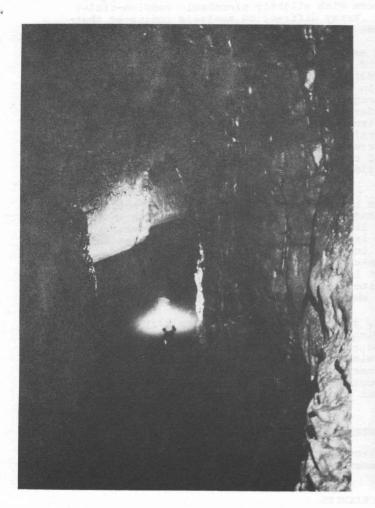
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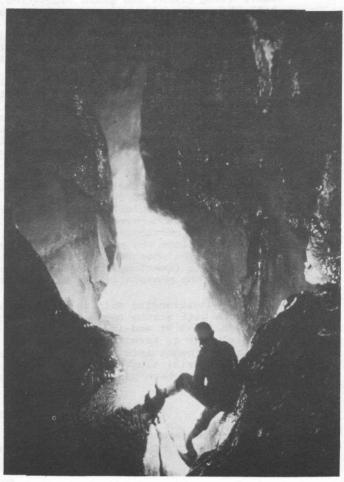
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Cover Photograph: This fallen stalagmite, broken in ten pieces across a thoroughfare in Webbs Cave, Nullarbor Plain, is the longest halite stalagmite on record in the world at 2.78 m. It has been removed for its safety and display, and for scientific study, to the Western Australian Museum.



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