Cave and Karst Science

The Transactions of the British Cave Research Association

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Volume 26 **Number 3** **December 1999**

Isotope geochemistry, Leon Sinks, Florida, USA
Marble speleogenesis, County Donegal, Ireland
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Cave and Karst Science

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Cave and Karst Science

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Cover photo:
Fluorescein dye injection at the opencast fluorspar mine on Dirtlow Rake, Castleton, Derbyshire, UK.
The site is close to Hollandtwine Mine, which was traced to Peak Cavern in 1972 during a joint Pegasus Caving Club/Technical Projects Unit undertaking. Activated charcoal fluocapteurs were used, but only in Peak Cavern. The fluorspar mine trace, carried out by the Limestone Research Group in 1993, showed that tracer went not only to Peak Cavern (c.1,000m) but also to three sites in Bradwell, a straight-line distance of more than 3,100m (see Editorial). Photo by John Gunn.

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EDITORIAL

John Gunn and Dave Lowe

For this Editorial we have decided to break with tradition, by providing some comments and advice on an aspect of cave science that has always been of interest to the wider caving community - the use of water tracing to demonstrate links between sinks, cave streams and springs. Although a wide variety of substances has been used (see for example Ford and Williams, 1989), fluorescent dyes have been most widely used in Britain, particularly optical brightening agents (OBA), sodium fluorescein (CI 45350 Acid Yellow 73) and rhodamine WT (CI Acid Red 388). These all have the advantage that they can be detected in quantities invisible to the naked eye, thereby avoiding the adverse comment that frequently accompanies visible coloration of surface streams! Additionally, they can be adsorbed onto passive detectors (fluocapteurs in technical parlance, but much more commonly referred to as 'bugs'), avoiding the necessity to sit around at every potential emergence site to take regular water samples.

Unfortunately, as is commonly the case with seemingly simple techniques, many dye users are unaware of the potential problems of this approach, perhaps most importantly the risk of recording false 'positive' results. As there have recently been several applications to the BCRA Cave Science Fund, asking for financial support for water tracing experiments, we felt it would be timely and appropriate to raise a few points in this Editorial. Although various legal aspects are mentioned for the information of British readers, there are also points of general relevance to the international readership.

First of all, it is important to be aware that in England, Wales and Scotland the permission of the Environment Agency must be sought prior to introducing any artificial tracer substance into the environment. As well as avoiding the risk of prosecution, this has the advantage that, should a visual coloration result, the Agency are aware of the probable cause, and waste of officer time can be avoided. If there is any possibility of the tracer emerging from a public water supply the Agency will probably insist on the relevant Water Company being consulted, and it would normally be sensible to do this as a matter of routine before consulting the Agency. Fluorescein and rhodamine WT are considered safe for use in the sub-visible concentrations used by responsible and experienced individuals and organisations. The Drinking Water Inspectorate have indicated that it is for the relevant individual Water Company to decide whether rhodamine WT should be used in the catchment of a public groundwater potable supply. They suggest that concentrations of <2 μg/l should not pose a risk to public health over anticipated trace timescales of around one week.

Having obtained the necessary permissions, it is essential to place fluocapteurs, and to collect water samples, to determine the natural luminescence 'background' prior to injection of the tracer. All natural waters have a fluorescence signature that may vary seasonally or through storm events. Failure to recognise and allow for this may compromise the results of a tracing experiment. As an example, a recent student exercise used synchronous scanning fluorescence spectrophotometry to examine canal and river waters around Huddersfield. Here, in an area where, to the best of our knowledge, there have never been <u>any</u> tracing experiments, the waters were shown to contain substances that could have been interpreted as OBA, fluorescein or rhodamine! Of these three, various types of OBA are commonly used in a spectrum of products, including detergents and some animal feedstuffs. We know that some cavers claim to have used OBA with great success as a tracing agent, but we would nevertheless urge caution. Wherever possible cotton wool fluocapteurs should be emplaced some distance <u>upstream</u> of the tracer injection site <u>and</u> at a range of springs additional to those considered 'most likely' to be targeted by the tracer.

In general we prefer to trace with fluorescein and rhodamine rather than OBA. Even then, over the course of many tracing experiments, we have observed sufficient obviously 'false' positive results (e.g. from springs altitudinally higher than the tracer injection points) to make us cautious in interpreting the fluorescence both of water samples and of fluocapteurs.

So, what is 'the average responsible caver' to do? We stress that we have no wish either to belittle any tracing work that has been done, or to stifle any work that will be done, by cavers. However, we do suggest that, wherever possible, the support and advice of an academic, or other individual, with a track record of successful tracing work, and access to a spectrofluorimeter, should be sought. If this proves impossible, and it is necessary to proceed without such a mentor, then we consider the most reliable and 'foolproof' method for tracing in nonpeaty waters to be the use of fluorescein and activated charcoal fluocapteurs. If the charcoal is eluted and there is a very clear fluorescence under UV light, then it is very probable that fluorescein dye has passed the point where the fluocapteur was emplaced. Even then, however, the possibility that the fluorescence is due to the presence of some other substance cannot totally be discounted, and the method will not detect low concentrations of dye.

Our own recent experiences lead us to warn others to beware of:

- false 'positive' tracing results, due to contamination (as described above) and/or longer than expected dye retention times within the rock mass causing 'cross-contamination' whereby dye introduced in one experiment is confused with that introduced during a later experiment;
- apparent 'negative' traces, due either to insufficient time being allowed for slow local dye throughput, or to a failure to recognise the potential for multiple outputs, or to monitor outputs at greater distances from the injection points at all or for a sufficient length of time.

As these possibilities become more generally recognised, demonstrated and accepted, the technical considerations related to carrying out successful water tracing experiments can only become still greater. We believe that paying careful attention to geological considerations, as well as to more conventional questions of landscape (particularly altitude differences), will become an ever more necessary precursor of tracing experiments. For all that, we also suspect that the necessary changes of paradigm and related changes of practice will be slow in coming.

Though we have no intention of questioning any specific accepted 'wisdom' here, we cannot help but wonder how many acknowledged water trace results might be open to question in the light of these considerations. It is easy and reasonable, for example, to accept the veracity of strong visual traces, which are, quite literally, impossible to ignore. However, it might now be appropriate to ask whether these 'obvious positives' might have led to less obvious 'positives' being either overlooked due to premature cessation of monitoring, or not even considered. To give a specific example. In the early 1970s a clear positive trace was reported from Hollandtwine Mine on Dirtlow Rake to Ink Sump in Peak Cavern, Castleton. At the time nobody thought to place fluocapteurs a few kilometres away at the various springs in Bradwell. However, in 1993 we carried out an experiment from a site near Hollandtwine (Dirtlow Pit), confirming that drainage does, indeed, target both Peak Cavern and Bradwell. However, the route is not via Bagshaw Cavern, and this raises the exciting possibility of the existence of a very large, as yet undiscovered, cave system! This trace was replicated recently - and this raises another worrying point: all too few "known" traces have been replicated.

In the case of non-visual dye traces, wherein the connection is confirmed (or not!) by spectrofluorimetric identification (or not) of very low dye concentrations, the possibilities for incomplete or misleading results are greatly multiplied.

As they seem to say quite commonly these days, the 'jury is still out' on this issue. However, while the jury is out, evidence is still being taken, and we would welcome correspondence recounting any thoughts concerning water tracing in general or describing illustrations of unexpected ('positive' or 'negative') water tracing results.

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Ford, D C and Williams, P W, 1989. *Karst Geomorphology and Hydrology.* [London: Unwin Hyman.]

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Uranium and strontium isotopic geochemistry of karst waters, Leon Sinks Geological Area, Leon County, Florida

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Abstract: The Leon Sinks Geological Area (Florida) is a mature karstic area developed on the Oligocene-Miocene Upper Floridan aquifer. This hydrological system is extremely vulnerable to pollution because of the very high permeability of the carbonate aquifer. The threat of water pollution in the study area makes the evaluation of the water sources of the sinkholes necessary.

Uranium and strontium isotopes are used in this investigation as tracers to determine the water sources of sinkholes. Uranium isotopes in water have been shown to be useful as tracers to distinguish sources of mixed waters. Isotopic ratios of strontium are often used as a natural flow tracer, as well, because the $^{87}Sr/^{86}Sr$ ratio of natural waters is a function of soils and rocks with which they have been in contact.

The sinkhole waters in Fisher Sink, Fisher Rise sink, and Lost Stream sink, which originate from the Water Table aquifer (Pliocene-Pleistocene), have higher $^{87}Sr/^{86}Sr$ ratios and lower $^{234}U/^{238}U$ ratios. The waters of Big Dismal and Hammock come from the Upper Floridan aquifer, which has lower $^{87}Sr/^{86}Sr$ ratios and higher $^{234}U/^{238}U$ ratios.

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INTRODUCTION

The Leon Sinks Geological Area lies in the Woodville Karst Plain, which extends from Tallahassee southward to the Gulf of Mexico. The Woodville Karst Plain is a flat to gently rolling, sandy plain with elevations that vary from about 50 feet [c.15m] above sea level along its northern edge to sea level at the Gulf of Mexico. Quartz sand covers limestone rocks, which usually lie at depths of 30 feet [c.9m] or less (Lane, 1988). The Woodville Karst Plain is within the 564,000 acres [c.2,280km^2] of the Apalachicola National Forest, the largest national forest in Florida. Located seven miles [c.12km] south of Tallahassee, Florida, the Leon Sinks Geological Area is an unusual geological area where features of karst topography are visible. It has several prominent wet sinkholes, dry sinkholes, numerous depressions, a natural bridge, a disappearing stream, and swamps. The area is still evolving – new sinkholes may appear at anytime.

Tallahassee, the Capital of Florida, is a rapidly expanding urban area. Although industrial pollution does not constitute a serious threat, contaminated storm water runoff, sewage disposal, and sanitary landfills have the potential to pollute the natural water resources of the Leon Sinks Geological Area. Most of the precipitation on the surface in Tallahassee finds its way into lakes, which are connected with the Leon Sinks Geological Area by sloughs and creeks. Pollution of the aquifers may occur if sinkholes are used in the disposal of polluted water or wastes (Hendry and Sproul, 1966). The aquifers of the Leon Sinks Geological Area may be recharged with the polluted storm water run off through sinkholes and natural conduits, which carry surface water directly into the aquifers. The hydrological system in the Leon Sinks Geological Area is extremely vulnerable to pollution because of the very high permeability of the limestone aquifer and its unconfined exposure to direct recharge. The surface waters enter here and form part of the recharge to the Upper Floridan aquifer system. Hence, there is a serious potential for pollution to enter the aquifer at places such as these sinkholes. The threats of water pollution in the study area make the evaluation of the water sources of the springs and sinkholes necessary, and the environmental conditions of sinkholes should be closely monitored.

The uranium activity ratio ($^{234}U/^{238}U$) varies widely in natural waters (Osmond and Cowart, 1976). In many cases, each surface and aquifer water has its own fingerprint, which is determined by two easily measured parameters: the uranium concentration and the ratio of $^{234}U/^{238}U$. In a closed system, ^{234}U and ^{238}U will be in equilibrium ($^{234}U/^{238}U=1$). However, in open systems, e.g. where dissolution of aquifer rocks occurs and water circulation takes place, the activity ratio of these two isotopes can vary and is not equal to 1. These cases are in disequilibrium. The uranium isotopic disequilibrium method has been applied extensively to delineate many hydrological regimes in various sandstone and carbonate aquifer systems world wide (Osmond *et al.*, 1968; Kigoshi, 1971; Osmond and Cowart, 1976; Cowart, 1980; Tikhonov, *et al.*, 1986; Kronfeld *et al.*, 1991; Bonotto and Andrews, 1993; Lienert *et al.*, 1994; Hussain, 1995). Uranium isotopes, which often have characteristic isotope ratios for zones of recharge, can be used to complement the interpretations based on strontium isotopes.

The ratio of $^{87}Sr/^{86}Sr$ in natural waters is a function of the soils and rocks with which they have been in contact. Isotopic ratios of Sr can provide valuable information about groundwater flow conditions and are often used as a natural flow tracer (e.g. Johnson and Depaolo, 1997). Collerson *et al.*, (1988) studied the $^{87}Sr/^{86}Sr$ ratios of ground waters from the Great Artesian Basin of Australia. Substantial flowpath-related variability of $^{87}Sr/^{86}Sr$ is observed in groundwaters in the Trout Lake watershed of northern Wisconsin (Bullen *et al.*, 1996). The $^{87}Sr/^{86}Sr$ ratio is also used in studying the interaction between groundwater and lake water in a mantled karst system (Katz and Bullen, 1996). Notsu *et al.* (1991) found strontium isotopic ratios are essential to identification of the source materials of soluble components in hot spring or mineral spring waters. On the basis of those studies, strontium plays a very important role as a natural tracer in hydrology.

Limestones and dolomites of the Ocala Group (Late Eocene), the Suwannee Limestone (Oligocene), and the Chattahoochee and St. Marks formations (Early Miocene), which constitute the Upper Floridan aquifer, contain a significant amount of strontium. Overlying these carbonate rocks are the limestone of the Torreya Formation (Early-Mid Miocene) and the clastic sediments of the Miccosukee Formation (Late Miocene to Pliocene), which have distinctly different sources of strontium isotopes from those of the marine carbonate rocks. Clays and soils usually have greater strontium isotopic ratios than those of marine carbonate rocks. Each of the marine carbonate units, which form the matrix of the Upper Floridan aquifer, has a distinctly different $^{87}Sr/^{86}Sr$ (generally less than 0.7090), and the clays and sands, which cap the carbonates, have a yet different strontium ratio (generally greater than 0.7090). Therefore, the ratio of $^{87}Sr/^{86}Sr$

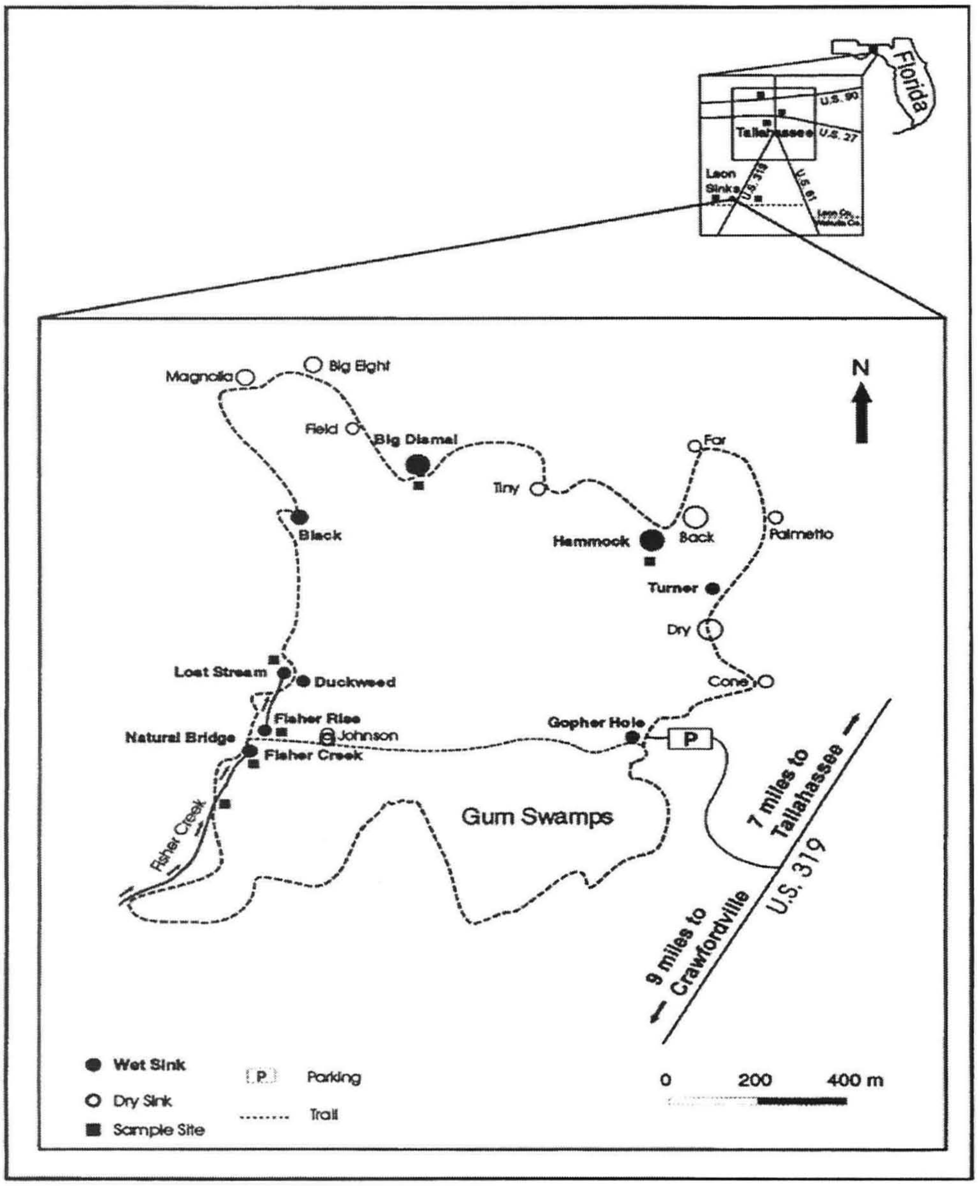

Figure 1. Location of the Leon Sinks Geological Area and sample sites, Leon County, Florida.

in each of the water sources will also be distinct, because each of the water sources has a different water-rock interaction history.

The objectives of this study are to examine the uranium and strontium isotopic signatures of the Leon Sinks Geological Area, to determine probable water sources of the Leon Sinks Geological Area on the basis of the uranium and strontium fingerprints, and to evaluate if uranium and strontium isotopes can be useful in tracing regional surface and ground water movement.

The results will help refine techniques for studying the interactions between water and rock and between groundwater and surface water. The developed technique should be applicable to many other carbonate and sandstone aquifer areas and watersheds in the world.

HYDROGEOLOGICAL SETTING

The Leon Sinks Geological Area is located in Leon County, Florida (Fig. 1). The study area is a mature karstic area with many sinkholes, circular depressions, submerged caves, a natural bridge, a disappearing stream, water table ponds, cavernous openings, and swamps. The aquifers of the Leon Sinks Geological Area consist of the Upper Floridan aquifer and the Water Table aquifer (Fig. 2). In the study area the Upper Floridan aquifer system, which is one of the most productive aquifers in North America (Hendry and Sproul, 1966), is composed of four Tertiary carbonate units: the Ocala Group, the Suwannee Limestone, the Chattahoochee Formation, and the St. Marks Formation. These are composed of pale orange calcirudite, greyish orange dense dolomites and pale biocalcarenitic or silty limestones. They also contain several intermittent thin beds of clay. The Upper Floridan aquifer is overlain unconformably by the semi-permeable Torreya Formation and the impermeable Miccosukee Formation. The Torreya Formation is composed of sandy limestones, which form the Water Table aquifer. The Miccosukee Formation, composed of silts, sands and gravels of varying coarseness, unconformably overlies the Torreya Formation. The Miccosukee Formation is covered by permeable Pleistocene to Recent undifferentiated sands and clays.

The present topography of the Leon Sinks Geological Area is the result of hundreds of thousands of years of karstic evolution. Rainfall absorbs carbon dioxide from the air and from decaying vegetation to become a weak acid. This is dramatically proven at the Leon Sinks Geological Area. The pH values of the surface waters from the area are approximately 3-5 (Tables 1 and 2). The acidic water slowly dissolves the limestone as it moves through underground pore spaces and fractures in the bedrock. Over time, these cavities become larger and create a network of passages that carry ever-increasing volumes of water. When the cavities become large enough, the remaining surface layer collapses, leaving a sinkhole or depression at ground level. The sinkhole continues to evolve and new sinkholes appear frequently throughout the surrounding plain.

A disappearing stream occurs when a surface stream flows down into a conduit system. Fisher Creek, a disappearing stream, which originates in eastern Gadsden County, Florida, flows into Fisher Creek Sink at the south side of the natural bridge. After flowing for a short

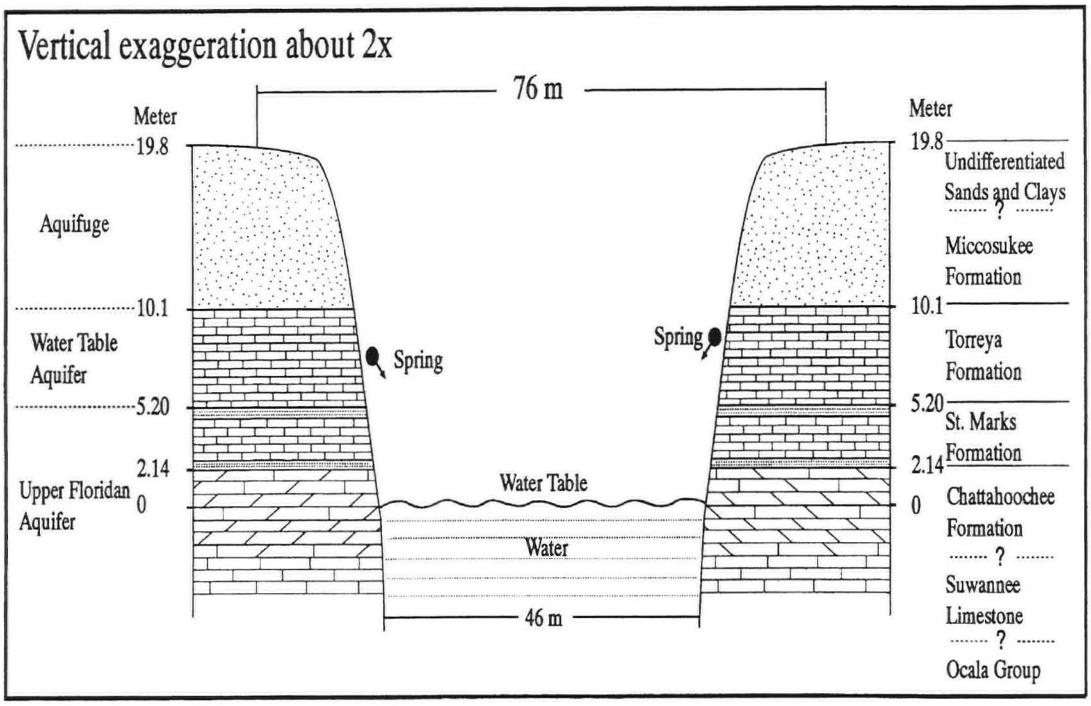

Figure 2. Cross section of Big Dismal sink, with geological and hydrological units.

distance underground it emerges at Fisher Creek Rise, north of the natural bridge. It then flows about 500 feet [c.150m] at the surface, before finally disappearing underground again into Lost Stream sink.

Dry sinks form when covering materials subside into depressions or small cavities in more shallow limestone layers. Therefore, the dry sinks, such as Dry Sink, Magnolia Sink and Big Eight Sink, have formed in shallow limestone layers.

Hammock Sink and Big Dismal Sink are two famous wet sinks in this area. Rocks crop out on the western side of Hammock Sink and represent the local bedrock, upon which the soil has developed during the rock weathering process. The beds of this rock are nearly horizontal and parallel in nature. To the north of Tiny sink, a sandy soil with higher elevation is encountered. The sand is from dunes that were formed near an ancient shoreline. The modern shoreline of the Gulf of Mexico is about 20 miles [c.32km] south of the Leon Sinks Geological Area.

Big Dismal sink, a large wet sink, formed suddenly by a collapse process when an underground cavity became so large that the weight of the overlying material could no longer be supported. Big Dismal has a diameter of approximately 250 feet [c.75m] and its walls are about 65 feet [c.20m] high above water level. No streams flow into it. The outcrop at Big Dismal Sink is composed of the Chattahoochee Formation, St. Marks Formation, Torreya Formation (Hawthorn Group), and Miccosukee Formation (Fig. 2). Differentiation between the St. Marks Formation and the Chattahoochee Formation is predominantly on the basis of mineral composition: the St. Marks is calcite, whereas the Chattahoochee is dolomite. Usually, the St. Marks is harder, more recrystallised, has more moldic porosity, and lacks substantial quantities of quartz sand. The Chattahoochee typically is relatively soft, fine-grained and homogeneous, and contains very fine quartz sand. The Torreya in this area is very sandy, crumbly, moldic limestone and is discontinuous. Another, thinner, section exposing the Chattahoochee Formation can be found at the natural bridge. No other sinks in the area expose as thick a section as that at Big Dismal Sink.

METHODS

A total of sixteen water samples have been collected from the study area and its environs. Eleven water samples were collected from the Leon Sinks Geological Area and the other five water samples from its neighbouring areas to compare the uranium and strontium data from Leon Sinks itself with regional background uranium and strontium data. The sink samples were collected from the sinkholes. Fisher Sink, Fisher Rise and Lost Stream were tannic in colour at the times of sampling. Big Dismal and Hammock, however, had been clear in colour during the course of this study. Ten water samples were analysed for strontium isotopic composition and twelve water samples for their uranium isotopic composition and uranium concentration. The locations of water samples collected from Leon Sinks Geological Area are shown in Fig. 1.

Water samples were filtered through 0.45µm filter paper to remove any particulate organic matter or fine sediment that may interfere in the analytical processing. The samples were acidified to pH=1~2 with high-purity HNO_3 and stored in sealed polyethylene bottles.

About 100ml of water samples is needed for strontium isotopic analysis. Strontium is separated from the bulk of other elements by standard ion exchange techniques using HCl as the eluent. The sample is then dissolved in 0.25N HNO_3 and placed on a tungsten (W) filament and is then ready for mass spectrometry. $^{87}Sr/^{86}Sr$ ratios are measured on a Finnigan MAT 262 multiple-collector thermal ionisation mass spectrometer (TIMS). All reported values of the $^{87}Sr/^{86}Sr$ ratio are then corrected for the presence of ^{87}Rb, normalised to $^{86}Sr/^{88}Sr$=0.1194 because of thermal isotopic fractionation, and are precise to 0.000010 or better at the 95% confidence level.

Generally, 14-litre water samples are enough for uranium analysis. Pretreatment is necessary and involves the addition of 2ml of ^{232}U tracer spike, 5ml of clean dilute iron nitrate ($Fe[NO_3]_3$) solution, and 20ml of clean 8N nitric acid into 3.5-litre sample containers. Uranium and iron are co-precipitated after heating the bottles to 100°C and adding 20ml of ammonium hydroxide (NH_4OH). Ferric hydroxide flocculates scavenge many elements, including the uranium, and eventually settle on the bottom of the bottle. The flocculates are separated, dried, and dissolved in clean 8N hydrochloric acid (HCl). An ether extraction step is necessary to separate uranium from iron. After ether extraction, the sample is allowed to evaporate to dryness before the anion exchange process is conducted to separate other elements from uranium and to purify the uranium. The sample is then dried and dissolved in 5ml of clean 2N ammonium chloride (NH_4Cl, pH=2.52-2.60). The electroplating is conducted with an electroplating assembly set for an hour and the planchet is flamed for 30 seconds to fix the deposited radionuclides on the planchet. The sample is then ready for alpha spectrometric analysis. The long-term average uncertainty for both $^{234}U/^{238}U$ ratios and uranium concentrations at the FSU U/Th laboratory ranges from 0.02 to 0.04 (ppb for concentration).

Samples	Location	Type	Date	pH Value	U (ppb)[a]	$^{234}U/^{238}U$[b]
4923	Fisher Creek	River	10/9/96	2.97	0.02	2.15
4893	Fisher Sink	Sink	8/23/96		0.06	2.19
4547[c]	Fisher Rise	Sink	11/6/94		0.047	1.095
4546[c]	Lost Stream	Sink	11/6/94		0.035	1.008
4501[c]	Hammock	Sink	2/19/94		0.649	0.695
4550[c]	Hammock	Sink	11/6/94		0.504	0.778
4549[c]	Big Dismal	Sink	11/6/94		0.358	0.818
4921	Jump Creek	River	10/9/96	3.8	0.09	1.08
4883	Lake Jackson	Lake	7/30/96	6.25	0.03	1.65
4896	St. Marks River	River	8/30/96	4.6	0.04	2.48
4973	City Well 5	Well	3/14/97		0.46	1.01
4967	City Well 12	Well	3/14/97		0.48	0.88

Table 1. Uranium data of waters from Leon Sinks Geological Area and related regional surface and ground waters.

(a) Uncertainty (2σ) ranges from ±0.02 to ±0.04;
(b) Uncertainty (2σ) ranges from ±0.02 to ±0.04;
(c) Data from Whitecross (1995).

RESULTS

Twelve water samples were analysed for uranium isotopic ratios and uranium concentrations (Table 1). This group of water samples can be categorised into three types:

- samples from the Leon Sinks Geological Area itself;
- samples from the surface water (Jump Creek, Lake Jackson, and St. Marks River);
- samples from the Upper Floridan aquifer (City Well 5 and City Well 12) in neighbouring areas.

Jump Creek is about 0.6 miles [1km] west of the Leon Sinks Geological Area, whereas St. Marks river is about a mile [1.5km] east of the Leon Sinks Geological Area. Lake Jackson is located in Tallahassee.

The uranium activity ratios range from 0.695 to 2.48 and the concentrations range from 0.02ppb to 0.649ppb for the water samples from the Leon Sinks Geological Area and neighbouring areas (Table 1). The water samples from Fisher Creek, Fisher Sink, Fisher Rise sink, and Lost Stream sink have lower uranium concentrations and higher uranium activity ratios. Their uranium concentrations range from 0.02ppb to 0.06ppb, whereas their uranium isotopic ratios range from 1.008 to 2.19. The water samples of Lake Jackson, St. Marks River, and Jump Creek, which are collected from neighbouring areas, also have a lower uranium concentration and a higher uranium ratio. The uranium concentrations for the three neighbouring surface water samples range from 0.03ppb to 0.09ppb and their uranium isotopic ratios range from 1.08 to 2.48. Water samples from two deep sinks (Hammock and Big Dismal) and two City wells (Well 5 and Well 12) have higher uranium concentrations (0.358ppb~0.649ppb) and lower uranium isotopic ratios (0.695~1.01). The uranium isotopic data are plotted using uranium activity ratio ($^{234}U/^{238}U$) versus uranium concentration (U) (Fig. 3). Two different zones can be established:

- the Upper Floridan aquifer zone with a high uranium concentration and a low activity ratio;
- the Water Table aquifer zone with a low concentration and a high activity ratio.

However, the water from different sites probably has its own distinctive source, as demonstrated by their uranium data signatures. Hammock sink and Big Dismal sink are being supplied from the same water source that underlies the City of Tallahassee. Therefore, the recharge area for Hammock sink and Big Dismal sink is located in northern Leon County, Florida.

The strontium data of water samples collected from Leon Sinks Geological Area and its neighbouring areas are listed in Table 2. The strontium ratios ($^{87}Sr/^{86}Sr$) range from 0.708099 to 0.711099 for all the water samples collected in this study. The sink water samples from the Leon Sink Geological Area range from 0.708099 (Hammock sink) to 0.711099 (Fisher Rise sink). Waters from Fisher Sink, Fisher Rise sink, and Lost Stream sink have higher strontium ratios (0.7090330.711099), and thus they are related to surface water and Water Table aquifer because the regional surface waters from Fisher Creek, Lake Jackson, and St. Marks River have higher strontium ratios (0.709416~0.710837). The water sample from Hammock sink has a relatively lower strontium ratio (0.708099), which should be related to the Upper Floridan aquifer because the two City Well water samples have similar strontium ratios (0.708232 and 0.708345) to that of Hammock samples. The variation of seawater $^{87}Sr/^{86}Sr$ throughout Phanerozoic time is well studied (Burke *et al.*, 1982). A detailed record of the $^{87}Sr/^{86}Sr$ ratio in seawater during the last 100 million years was determined by measuring the ratio in 137 well-preserved and well-dated fossil foraminifera samples (Hess *et al.*, 1985). It is assumed that the average carbonate $^{87}Sr/^{86}Sr$ ratio should be the same as the average $^{87}Sr/^{86}Sr$ ratio in foraminifera, and groundwater inherits

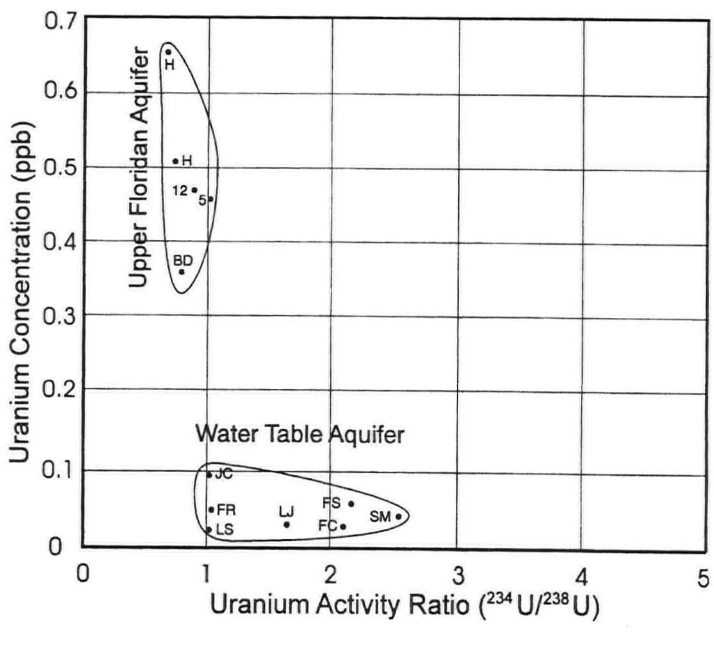

Figure 3. Plot of $^{234}U/^{238}U$ versus uranium concentration for water samples from Leon Sinks Geological Area and regional surface and ground waters.
Keys: BD=Big Dismal, FC=Fisher Creek, FR=Fisher Rise, FS=Fisher Sink, H=Hammock, JC=Jump Creek, LJ=Lake Jackson, LS=Lost Stream, SM=St. Marks, 5=Well 5, 12=Well 12.

Samples	Location	Type	Date	pH Value	$^{87}Sr/^{86}Sr$	$\pm 2\sigma$
4923	Fisher Creek	River	10/9/96	2.97	0.710837	±0.000010
4893	Fisher Sink	Sink	8/23/96		0.710462	±0.000008
Lsw2	Fisher Rise	Sink	2/7/98		0.711099	±0.000016
4894	Lost Stream	Sink	8/30/96	6.4	0.709033	±0.000008
4922	Lost Stream	Sink	10/9/96	3.21	0.709133	±0.000009
Lsw3	Hammock	Sink	2/7/98		0.708099	±0.000009
4883	Lake Jackson	Lake	7/30/96	6.25	0.709416	±0.000009
4896	St. Marks River	River	8/30/96	4.6	0.710424	±0.000016
4973	City Well 5	Well	3/14/97		0.708345	±0.000010
4967	City Well 12	Well	3/14/97		0.708232	±0.000011

Table 2. Strontium isotopic ratios of waters from the Leon Sinks Geological Area and related regional surface and ground waters.

the $^{87}Sr/^{86}Sr$ ratio fingerprints from the carbonates. The strontium isotopic ratio data in this study are plotted on Hess's $^{87}Sr/^{86}Sr$ ratio-age line (Fig. 4).

DISCUSSION

The water samples from Fisher Sink, Fisher Rise sink, and Lost Stream sink, which are all located in the south-west portion of the Leon Sinks Geological Area, have low uranium concentrations (0.035ppb~0.06ppb) and high uranium activity ratios (1.008~2.19). They have similar uranium fingerprints to that of surface waters (Fisher Creek, Jump Creek, Lake Jackson, and St. Marks River) (Table 1). Fisher Sink, Fisher Rise sink, and Lost Stream sink have a similar origin with Fisher Creek and Jump Creek, located in the south of the Leon Sinks Geological Area. A surface water influence is further supported by the tannic nature of these three waters. It is possible that the tannic water observed in these three sinks came from an environment similar to that of Fisher Creek and Jump Creek. Hammock and Big Dismal sinks have higher uranium concentrations (0.649ppb and 0.504ppb for Hammock and 0.358ppb for Big Dismal) and lower uranium activity ratios (0.695 and 0.778 for Hammock and 0.818 for Big Dismal). Big Dismal and Hammock plot in the same area as Well 5 and Well 12 in Fig. 3, and therefore, Big Dismal and Hammock have an Upper Floridan aquifer signature.

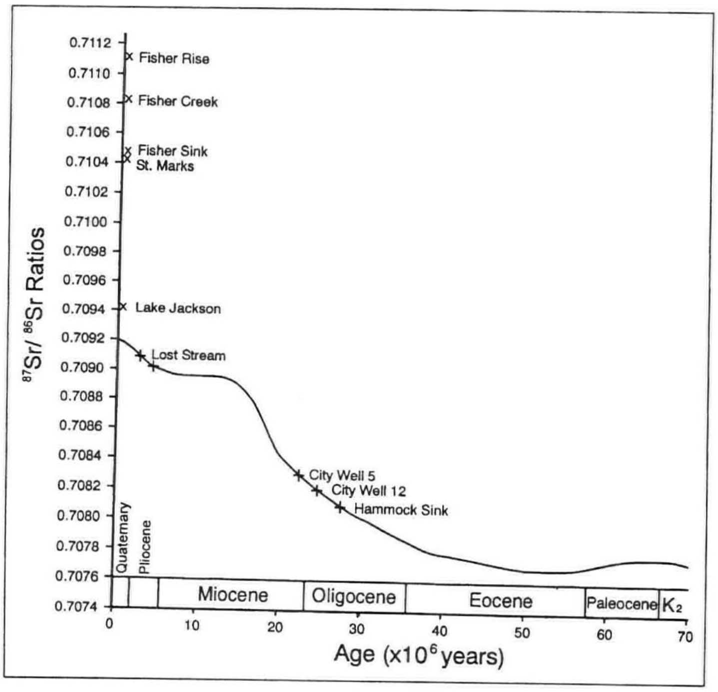

Figure 4. Plot of $^{87}Sr/^{86}Sr$-age for water samples from Leon Sinks Geological Area and regional surface and ground waters. The $^{87}Sr/^{86}Sr$-age line, which is based on Hess et al. (1986), represents the best estimate of seawater $^{87}Sr/^{86}Sr$ ratio versus time.

Surface water samples from Leon Sinks Geological Area (Fisher Creek) and its neighbouring areas (Lake Jackson and St. Marks River) have a higher strontium ratio ranging from 0.709416 (Lake Jackson) to 0.710837 (Fisher Creek). Groundwater samples from City Well 5 and City Well 12, which draw water from the Upper Floridan aquifer, have lower strontium ratios (0.708345 and 0.708232). The data for two groundwater samples (City Wells) and one sinkhole water sample (Hammock) fall on the $^{87}Sr/^{86}Sr$-age line. We can conclude that the waters originate from the Oligocene (Suwannee Limestone)-Miocene (Chattahoochee and St. Marks formations) of the Upper Floridan aquifer (Fig. 4). The strontium ratios for Fisher Sink and Fisher Rise sink are 0.710462 and 0.711099, respectively, which are beyond the normal carbonate strontium ratios. Other sinkhole waters may originate from the Water Table aquifer or be related to surface water because the largest seawater $^{87}Sr/^{86}Sr$ ratio is 0.7092 (modern oceanic water). This indicates that they have nothing to do with the carbonate Upper Floridan aquifer. One possibility is that they all originate from the Water Table aquifer, which contains clastic sediments (clays and sands). The two water samples of Lost Stream sink fall to the left end of the $^{87}Sr/^{86}Sr$-age trend line. The Lost Stream sink probably is a mixture of surface water (high strontium ratio) and groundwater (low strontium ratio) because the Lost Stream sink is only 650 feet [200m] from Fisher Rise, which has the highest strontium ratio. The Lost Stream sink water samples were collected at different times and almost identical strontium ratios were obtained (0.709033 and 0.709133). Hence, the strontium ratios are basically constant for a single site.

CONCLUSIONS

This study has demonstrated the effectiveness of both uranium and strontium isotopes in discriminating groundwater sources. The surface water samples have higher uranium isotopic ratios ($^{234}U/^{238}U$) and lower uranium concentrations, whereas the groundwater samples or karstic water samples have lower uranium isotopic ratios and higher uranium concentrations.

The sink water samples (Big Dismal and Hammock) from the deep ground have a high uranium concentration and a low uranium activity ratio, whereas the sink water samples (Fisher Sink, Fisher Rise sink, and Lost Stream sink) from the shallow ground have a low uranium concentration and a high uranium isotopic ratio.

On the basis of uranium isotopic fingerprints, sink waters from Hammock and Big Dismal carry the regional groundwater (Upper Floridan aquifer) signature, whereas the sink waters from Fisher Sink, Fisher Rise sink, and Lost Stream are dominated by shallow groundwater (Water Table aquifer) and surface water components, which are affected by Pleistocene sands and clays.

On the basis of $^{87}Sr/^{86}Sr$ ratio-age plotting, the water of Hammock sink originates from the Suwannee Limestone (Oligocene) of the Upper Floridan aquifer whereas the sink waters in Fisher Sink, Fisher Rise sink, and Lost Stream sink result from the Water Table aquifer and probably have surface water components influenced by the strontium signature of Pleistocene sands and clays.

Fisher Sink, Fisher Rise sink, and Lost Stream sink may be contaminated by storm water runoff from the Tallahassee urban area, because they have the uranium and strontium signatures of regional surface waters. Big Dismal and Hammock are not polluted by urban storm runoff, because they have the same uranium and strontium signatures as those for the water samples from the Upper Floridan aquifer.

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Water studies in Wookey Hole Cave, Somerset, UK

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Abstract: Water samples were collected by members of the Cave Diving Group from the River Axe in Wookey Hole Cave between the Entrance and Wookey 23. The samples were analysed for all major constituents, enabling ion balances to be used to assess analytical reliability. The results showed that water in the Static Sump at the beginning of Wookey 23 had very much less magnesium than water in the Main Stream between the surface and Sump 22. This result was confirmed by the analysis of a second set of samples. The results of the remaining constituents showed that water in the Static Sump had the same origin as that in the River Axe. Only magnesium bicarbonate concentrations were different. A third set of samples included a sample from Sump 25. Results showed that the location of the "Unknown Junction", from where water flows to the Static Sump by a different route from the majority of the River Axe, is upstream of Sump 25. Analytical difficulties were caused by high concentrations of suspended calcium carbonate in the river during high water conditions in the winter of 1996/97, and part of the paper deals with analytical problems caused by such suspensions in the River Axe.

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INTRODUCTION

Between 1966 and 1975, Stenner analysed many samples from the River Axe at Chamber 3 of Wookey Hole Cave (NGR ST532480). Magnesium concentrations varied from 18×10^{-5} M to 46×10^{-5} M, the concentrations being higher in low flow. In August 1974, there was a higher magnesium concentration in a sample from the 5th Chamber than in a sample taken a few days later from the 9th Chamber. Two possibilities were evident. There could be a gradient in magnesium from Wookey 9 to Wookey 5, or there could have been general changes in Mg levels between the two dates, with no magnesium gradient between the two sites.

When the two alternative explanations were considered, two facts were thought to be significant. Firstly, according to a survey of the cave (Hanwell, 1970), the River Axe flows from limestone into Triassic conglomerate at Wookey 12, approximately only 50m upstream of Wookey 9. Secondly, it had relatively recently been demonstrated that when hard water that is low in magnesium, with zero aggressiveness, is shaken with powdered dolomite, magnesium from the dolomite will dissolve in the water (Stenner, 1971). The two facts made the first explanation more likely to be true. A study of water samples from deeper in the cave would be worthwhile, and might explain the data from 1974. In 1996, Gee was regularly diving to Chamber 22, "pushing" the aven that trends towards a surface feature (Gee, 1996). He agreed to combine some of these trips with a study of water chemistry in the cave. To supplement analyses carried out by Stenner, Knights analysed samples for sulphate and nitrate by ion chromatography. The inclusion of data for these two ions completed the determination of all ions present in significant concentrations. This made it possible to calculate ion balances and thereby assess the accuracy of the analytical data (Knights and Stenner, 1999). Gee was joined in the project by Chapman and Stell of the Somerset Section of the Cave Diving Group.

METHOD

Samples were collected from the tops of the major loops of the River Axe, at Chambers 3, 9, 20 and 22. At Wookey 23, samples were taken from the Static Sump. At Wookey 22, the sample was taken from Sump 22 above the point of entry of the main stream (coming from Sting Corner in Wookey 24, and shown in the results as Sump 22). The location of the sample sites is shown in Fig. 1 (after Hughes, 1982). A collection was started on 30.11.96, but after collecting samples from Chambers 3 and 9, the trip had to be abandoned. Samples were collected on 14.12.96, and 25/26.01.97. On 25.01.97, an extra sample was taken in Wookey 22, deep below the surface at the point where the Axe enters through boulders (Sample 22B). Water levels in November and December were extremely high. In January the water level had fallen, but it was still higher than usual.

The results from the samples collected in December 1996 and January 1997 were utterly unexpected, and the implications were intriguing. A high priority was placed on making another collection, including samples from upstream of Wookey 23. A series of attempts to collect a set of such samples was made between March 1997 and early July 1997, all of which failed. At last the gremlins were defeated, and a third collection of samples was made on 20.07.97 from the same sites as on 14.12.96, with the important addition of a sample from Wookey 25, immediately before the long descent into the 25th Sump.

METHODS OF ANALYSIS

Samples were analysed for total hardness and aggressiveness by titrating with standard EDTA, and alkaline hardness by titrating with standard HCl, as soon as possible after collection. Samples were later analysed for chloride (by $AgNO_3$ titration), potassium and sodium (by flame emission spectrophotometry), magnesium (by atomic absorption spectrophotometry), and sulphate and nitrate (by ion chromatography). Knights carried out the ion chromatography determinations. The analytical methods have been described in detail elsewhere (Knights and Stenner, 1999). The following standard errors have been calculated (as $10^{-5} \times$ Molar, ~ ppm as $CaCO_3$):

Total hardness, calcium and aggressiveness to $CaCO_3$, 0.8; alkaline hardness 3.0; non-alkaline hardness, 3.8; magnesium, 0.17; sodium, 0.13; potassium, 0.05; chloride, 2.6; sulphate, 0.3; nitrate, 0.23.

The cation/anion balances quoted in Tables 1 to 3 indicate the reliability of the recent analyses.

The unit chosen in this study was $10^5 \times$ Molar. By making this choice, the data for the species associated with water hardness are

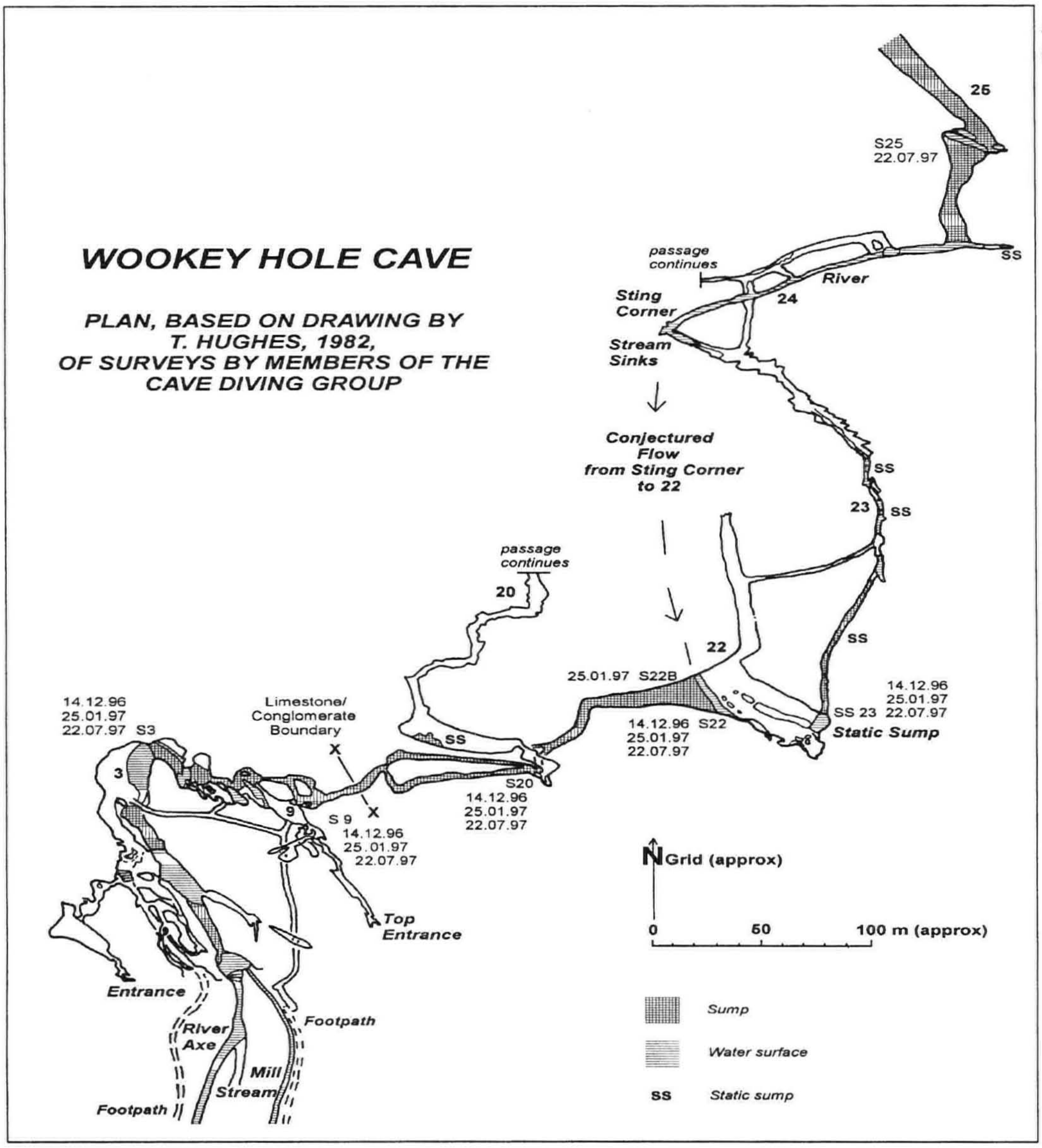

Figure 1. Location of Wookey Hole Cave. (Based on Hughes, 1982.)

numerically identical (to within analytical precision limits) to parts per million (ppm) calcium carbonate, the unit widely used by limestone geomorphologists. The unit was especially suitable when calculating ion balances.

When concentrations of "colloidal" calcium carbonate were detected, they were estimated by the method proposed earlier (Stenner, 1969). The initial total hardness was measured by a rapid titration to the first "unstable" endpoint. The final total hardness was measured by continuing to a final, stable, endpoint. The difference between the two values is a measure of the "colloidal" calcium carbonate concentration.

Because solid calcium carbonate dissolves much more rapidly at pH 4.5 than at pH 11, and in the alkalinity titration it is essential to wait for a stable end point, this determination inevitably includes both the dissolved and the suspended calcium carbonate. The dissolved carbonates were therefore found from the alkalinity data by subtracting the concentration of suspended calcium carbonate.

RESULTS AND DISCUSSION

The effects of colloidal suspensions of calcium carbonate on the results in Tables 1 to 3

Samples had also been taken from the Axe at the surface and in Chambers 3 and 9II on 30.11.96, when the river was extremely high after heavy rain. The water was very cloudy, and analysis of the samples was very difficult because of high quantities of suspended calcium carbonate. Filtering the samples did not remove the suspension. The "colloidal" calcium carbonate interfered seriously with the total hardness and alkaline hardness titrations (see separate discussion, below). In particular, it made a reliable alkalinity titration impossible.

The water in the Axe was completely clear by 12.12.96, but in spite of the complete absence of any visual warning of a likely problem, every sample contained very large concentrations of "colloidal" calcium carbonate. This once again made reliable alkalinity determinations impossible, and reduced the accuracy of total hardness titrations. It was impossible to estimate the concentrations of "colloidal" calcium carbonate by the usual method, because titration of a sample to a stable end point could not be achieved, and alkalinity data could not be corrected. Data in Table 1 confirm the seriousness of consequent errors. There were seriously large imbalances between anions and cations. Because negative values for non-alkaline hardness are impossible, the results are clearly grossly in error, the result of the alkalinity figures being too high. Titration of the sample from the Wookey Hole Road Bridge with HCl to a final stable end-point made it possible to obtain a minimum estimate of the concentration of "colloidal" calcium carbonate; 41 ppm as $CaCO_3$. However, because of the nature of this titration, it was inevitable that the initial value of the alkalinity would be too high, and would include a substantial percentage of the suspended calcium carbonate. The ion imbalance suggests that it was 60 ppm too high, but the non-alkaline hardness figure suggests a lower figure; approximately 49 ppm too high. So the true concentration of the colloidal calcium carbonate was probably either 89 or 101 ppm as $CaCO_3$.

Site	Total Hardness	Mg	Ca	Alkaline Hardness	Non-Alkaline Hardness	Cl^-	K	Na	SO_4^{2-}	NO_3^-	Coll.	Ion Balance
Road Bridge.	*245.6*	34.6	*211*	*(259)*	*(-14)*	45.5	3.9	30.3	14.8	45.0	>41	113
3rd Chamber	*274.2*	33.9	*240*	*(261)*	*(14)*	47.1	4.2	30.3	11.8	46.8		55
9th Chamber	*239.7*	33.5	*206*	*(258)*	*(-19)*	45.5	4.0	31.0	15.3	37.4		116
Sump 20	*233.4*	34.4	*199*	*(257)*	*(-23)*	43.9	4.1	30.9	14.5	43.1		128
Sump 22	*267.9*	32.3	*236*	*(255)*	*(17)*	45.5	4.0	30.2	14.1	45.0		72
S.Sump W 23	*211.5*	9.8	*202*	*(235)*	*(-23)*	42.3	4.2	34.2	14.1	40.8		119

Table 1. Data for samples collected 14th December 1996. Units: $10^5 \times M$ (as specified; non-alkaline hardness di-valent, ion balance mono-valent). Total, Mg, Ca, alkaline hardness and non-alkaline hardness figures are identical to concentrations in ppm as calcium carbonate. "Coll." represents the estimated concentration of "colloidal" calcium carbonate. The accuracy of figures in italic script is seriously lower than usual because of analytical difficulties caused by the colloidal

Site	Total Hardness	Mg	Ca	Alkaline Hardness	Non-Alkaline Hardness	Cl^-	K	Na	SO_4^{2-}	NO_3^-	Coll.	Ion Balance
Road Bridge.	279.7	42.2	238	253	27.0	47.9	4.0	34.5	12.4	39.3	1.5	19
3rd Chamber	274.7	42.2	233	255	20.0	46.3	4.0	33.8	17.3	37.6	1.5	40
9th Chamber	281.2	43.0	238	254	26.9	47.9	5.0	34.0	17.3	42.9	1.5	32
Sump 20	277.7	42.6	235	253	24.7	47.1	4.0	34.2	11.4	36.8	1.5	19
Sump 22B	281.2	42.0	239	252	29.4	46.3	4.0	34.4	11.0	36.0	1.5	8
Sump 22	276.1	42.4	234	249	26.8	45.5	4.1	34.1			3.1	
S.Sump W23	251.8	13.6	238	231	20.4	40.6	3.8	36.2	13.6	42.7	3.8	30

Table 2. Data for samples collected 25th – 26th January 1997. Units: $10^5 \times M$ (as specified; non-alkaline hardness di-valent, ion balance mono-valent). Total, Mg, Ca, alkaline hardness and non-alkaline hardness figures are identical to concentrations in ppm as $CaCO_3$. "Coll." represents the estimated concentration of "colloidal" calcium carbonate.

Site	Total Hardness	Mg	Ca	Alkaline Hardness	Non-Alkaline Hardness	Cl^-	K	Na	SO_4^{2-}	NO_3^-	Coll.	Ion Balance
Road Bridge.	289.8	35.0	255	250	40.2	43.9	4.6	35.2	12.0	27.6	0.0	24
3rd Chamber	285.4	33.8	254	247	38.7	42.3	4.6	37.5	14.0	34.5	0.0	14
9th Chamber	*Coll.*	35.6	*Coll.*	*Coll.*	*Coll.*	44.7	4.6	37.8	13.9	30.6		
Sump 20	289.4	34.6	255	250	39.8	42.3	4.6	36.5	13.8	41.4	0.0	9
Sump 22	287.0	34.8	252	249	38.2	42.3	4.8	33.4	14.6	33.2	0.0	10
S.Sump W23	270.6	11.9	259	239	31.9	39.8	9.7	28.8	11.0	8.6	0.0	32
Sump 25	286.7	35.4	251	251	35.9	44.7	4.6	32.8	10.0	32.3	0.0	5

Table 3. Data for samples collected 20th July 1997. Units: $10^5 \times M$ (as specified; non-alkaline hardness di-valent, ion balance mono-valent). Total, Mg, Ca, alkaline hardness and non-alkaline hardness figures are identical to concentrations in ppm as $CaCO_3$. "Coll." represents the estimated concentration of "colloidal" calcium carbonate.

Samples from 25/26.01.97 contained small concentrations of "colloidal" calcium carbonate (1.5 to 3.8 ppm $CaCO_3$. The alkalinity was corrected by subtracting the value obtained in the total hardness for the "colloidal" calcium carbonate.

Samples from 20.07.97 were free of "colloidal" calcium carbonate, with the single exception of the sample from Wookey 9, in which the "colloidal" calcium carbonate concentration was too high to permit the determination of total, alkaline or calcium hardness. Why this single sample was affected is a mystery. Perhaps a factor in the collecting or handling of the sample triggered the formation of the suspension.

The results in Tables 1 to 3 show that the presence of "colloidal" calcium carbonate causes serious ion balance problems. The method suggested by Stenner in 1969 for determining concentrations of "colloidal" calcium carbonate, and correcting data for consequent errors in alkalinity and non-alkaline hardness, is clearly very "approximate". The true "colloidal" calcium carbonate content is likely to be greater than this estimate, and there is an unsolved analytical problem here.

Comments on the results from 14.12.96

The results from samples collected on 14.12.96 had the following features:

1. At every site, large concentrations of "colloidal" calcium carbonate were present.
2. At every site except the Static Sump in Wookey 23, magnesium concentrations were very similar. Within the ranges of concentrations found in the present study, and within the range of pH in the water, although magnesium can be added, its natural removal is not possible.
3. Concentrations of chloride, sulphate, nitrate, potassium and sodium at all sites, including the Static Sump in Wookey 23, were similar.
4. At the Static Sump and chambers 20 and 9, calcium levels were very similar.

Water Sample	Unsaturated sample $10^{-5} \times M$ (~ ppm $CaCO_3$)			Sat. AR $CaCO_3$	Sat. Rock sample 1 (Ca:Mg = 30.0)		Sat. Rock sample 8 (Ca:Mg = 1.0)	
No.	Alk. H	Ca	Mg	ΔTH	ΔCa	ΔMg	ΔCa	ΔMg
8	209.5	229.9	18.9	0.0	-1.6	0.4	0.9	2.8
10	243.5	245.3	43.3	-13.6	-8.8	2.0	0.4	6.0

Table 4. Results of saturating water from two Mendip risings (Cheddar No.1, Water sample 8, Rodney Stoke, Water sample 10) with powdered limestone (Rock Sample 1), powdered dolomite (Rock Sample 8) and with powdered AnalaR $CaCO_3$. Concentrations $10^{-5} \times M$ (~ ppm as $CaCO_3$). From Stenner, 1971, Table 2 (p.292).

Comment 2, above, will be examined in more detail. The precipitation of magnesium as magnesium hydroxide will not take place from a solution containing 50×10^{-5} M Mg when the pH of the water is less than 11. This pH is far above the range that can exist naturally in the subterranean River Axe, so removal of magnesium by this means can be ruled out. Indeed, laboratory measurements made after shaking natural waters with powdered limestones and dolomites have in every case led to an increase of magnesium in solution, rather than a reduction (Stenner, 1971, Table 1 p.290, Table 2 p.292). Two illustrative examples have been extracted and are presented in Table 4. The first sample, from Cheddar 1st Rising had alkaline and total hardness, calcium and magnesium concentrations similar to those reported from the Wookey 23 Static Sump, and was originally in equilibrium with pure calcite. When shaken with powdered dolomite, this sampled dissolved magnesium, with no statistically significant change in dissolved calcium. It is an example of incongruent dissolution of dolomite. The increase of Mg was, however, small, perhaps because only very small quantities of powdered dolomite were added to the water samples. However, in the second sample, from Rodney Stoke Rising, a larger quantity of magnesium passed into solution, in spite of magnesium concentrations having already been high, and the original water sample having been supersaturated with respect to calcite.

Thus there is evidence of the ability of magnesium carbonate to pass into solution by the incongruent solution of dolomite, but no evidence to suggest the removal of magnesium from solution.

Despite the analytical difficulties, the results show that the explanation of magnesium variations in the Axe which, prior to this study had been thought to be most likely, was completely incorrect. There was no magnesium gradient in the River Axe between Wookey 23 and the Entrance.

The outstanding feature of the result from 14.12.96 was the low magnesium level in the Static Sump in Wookey 23. At the same time, the concentrations of many constituents in the sample were the same as in the other samples from the River Axe. It seemed possible that water in the Static Sump had the same origin as water in the Axe, except that the latter water had dissolved a considerable quantity of magnesium. A further set of results was needed to clarify the situation, because there was a remote possibility that the similarities in the other hydro-chemical characteristics could have been a coincidence.

The higher Ca contents in Wookey 22 and 3 samples were thought to have caused by inaccuracies in the total hardness titrations. It is possible that the fraction of very small particles in the "colloidal" calcium carbonate was higher in these two samples, and a significant quantity of this fraction had been included in the rapid titration to the first unstable end-point. A further set of samples was needed to resolve the uncertainties.

In conclusion, the very first set of samples had produced very exciting results. There were uncertainties caused by the unfilterable suspended calcium carbonate. If larger samples had been available, it would have been possible to try using a high-speed centrifuge, or to make conductivity measurements to investigate calcium and "colloidal" calcite concentrations in more detail. However, the planned collections had proved to be feasible, they were carried out, and the maximum possible quantity of information was extracted from these samples.

Comments on the results from 25/26.01.97

The set of samples collected on 25/26.01.97 showed the following features:

1. Except at the Static Sump at Wookey 23, magnesium concentrations were very similar to each other, but significantly higher than on 14.12.96, when the flow had been substantially greater.
2. Concentrations of calcium, sodium, potassium, sulphate, nitrate and chloride were very similar at all sites. The data sets for sodium and sulphate on the two dates were different. The data comprehensively supported the suggestion from the 14.12.96 results; that water in the Static Sump in Wookey 23 had the same origin as water in the Axe. While there had been a remote possibility that the similarities on 14.12.96 could have been a coincidence, there is no possibility whatsoever that the different results from 25/26.01.97 could also have been a coincidence. It is possible that flow of water from the unknown location upstream into the Static Sump only takes place within certain discharge limits. Therefore there may be occasions when water in the Static Sump does not share the same chemical characteristics with the Main Stream.
3. The sample collected underwater in Wookey 22, from where the river from Sting Corner enters the sump through boulders, gave results that were indistinguishable from those from the surface of the sump pool.

Because concentrations of suspended calcium carbonate were low, alkaline hardness data were more reliable, and total hardness and calcium data were considerably more reliable. The increase of magnesium between the Static Sump and Wookey 22 was accompanied by an equal increment of alkaline hardness (within practical limits). The conclusion is that magnesium from $MgCO_3$ in dolomite or dolomitic limestone had dissolved as $Mg(HCO_3)_2$. There was no change in calcium in true solution in the water.

Comments on the results from 20.07.97

The most important result was from the sample from Sump 25. Results from this sample were similar to those from the main flow of the River Axe at all points downstream, whereas the magnesium, alkaline and total hardness results from the Static Sump were once again significantly different from those in all other samples. This result had a considerable consequence on the understanding of the hydrology of the cave. Some of the minor abnormalities in the data from the Static Sump are likely to be the consequence of the static sump having been "stagnant" for several weeks, during which time several parties of divers had visited the site.

THE HYDROCHEMISTRY OF WOOKEY HOLE CAVE

The hypothesis is that in December 1996 and January 1997, water in the Static Sump in Wookey 23 did indeed have the same origin as water in the River Axe.

The following paragraph describes the position after examining the results from December 1996 and January 1997. Following directly from the hypothesis of the origin of water in the Static Sump, there must be an "Unknown Junction" yet to be discovered, at some point upstream, where all the water in the Axe had a composition similar to that in the Static Sump. From this "Unknown Junction", a small fraction of the Axe flowed into a route leading to the Static Sump. The majority of the Axe flowed through a different route to Wookey 22, and in this route it entered a zone of dolomite or dolomitic limestone. Here, the physical conditions (such as turbulent mixing) were such that the water dissolved the substantial concentration of magnesium carbonate seen in the results.

The results show that on 25.01.97, the water dissolved a higher concentration of magnesium between the "Unknown Junction" and Wookey 22 than on 14.12.96. However, on both occasions, no change in magnesium was detectable in the considerable distance from Wookey 22 to the Entrance. These are very important observations, for which there are three possible explanations.

1. The "Unknown Junction" is a very large distance upstream of Wookey 22 (much farther than the distance from Wookey 22 to the Entrance).
2. The distance upstream is not crucially important, the most important factor being that the main body of the Axe flows through a zone where the physical conditions especially favour and maximise the dissolution of magnesium from the dolomite. This possibility presents a problem. When, in higher flow, water arrives at Wookey 22 with lower levels of magnesium, it follows that it must arrive there with a capacity to dissolve more magnesium. Yet from Wookey 22 to the Entrance it fails to dissolve any more magnesium, in spite of contact with dolomitic conglomerate from Wookey 12 to the entrance.
3. [This is a modification of the second possibility]. Downstream of the "Unknown Junction", a part of the Axe flows through a dolomite zone where physical conditions encourage rapid reactions between water and rock, becoming saturated with magnesium to close to the low-flow value of approximately 50×10^{-5} M Mg. As flow increases, this water is mixed with an increasing proportion of low-magnesium water overflowing from the route to the Static Sump. This would explain the variable, flow-dependent concentration of magnesium in the Axe arriving at Wookey 22.

The results from the samples collected on 20.07.97 added nothing new to this particular aspect of the study, except to suggest the probability that, in normal flow conditions, the chemical characteristics of the Axe at Wookey 22 and Wookey 25 are the same.

Whichever explanation turns out to be the best explanation, results in the present studies have some implications.

1. Water from the four major separate sources of the Axe (Swildon's Hole, Eastwater Cavern, St. Cuthbert's Swallet and - by far the biggest source - percolation water) must have coalesced upstream of the "Unknown Junction". The size of any inlet stream this side of the junction (and hence this side of Wookey 25) must be too small to produce a measurable change in the chemical parameters of the Axe.
2. Important new information provided by samples collected on 20.07.97 concerned the location of the "Unknown Junction". The results proved that the "Unknown Junction" lies beyond the present known limits of the cave; i.e. upstream of Wookey 25.
3. The possibility of making important discoveries in a route from the Static Sump to the "Unknown Junction" is very real.
4. There must be a zone of dolomite, dolomitic limestone or dolomitic conglomerate upstream of Sump 25, between Wookey 25 and the "Unknown Junction".
5. Where water from the "Unknown Junction" encounters the zone of dolomite, dissolutional activity will have caused considerable localised cavern enlargement (which could be masked by massive localised cavern breakdown). This is a direct consequence of the large quantity of magnesium carbonate being dissolved by the large river in a localised zone of the underground river system.

The present considerations do not imply that water in the Static Sump will always have the same chemical characteristics as water in the Axe, apart from elevated magnesium bicarbonate. On the first two sample dates, the flow of the Axe was high, and it is possible that as flow falls, a level might be reached when water from the "Unknown Junction" ceases to flow to the static sump. Water in the static sump will then reflect the levels of salts in the Axe the last time it flowed to the pool, and not the current levels in the river. This will not negate the conclusions drawn from the results presented here.

The present paper describes the present state of the understanding of the hydrology of the Wookey Hole system. There are opportunities to refine this understanding before an attempt is made to explore this part of the cave. The survey shows that there are more static sumps in Wookey 23, an intriguing one in Wookey 25 and another one in Wookey 20. In the near future it is planned to analyse samples from these additional static sumps (together with a sample from Sting Corner). It is also planned to analyse a selection of mud samples from Wookey 23 (because only those samples deposited in the last two thousand years by the St. Cuthbert's Swallet to the River Axe system will have a high lead content).

The present sets of water analyses have been compared with data from analyses of samples collected between 1966 and 1979. A summary of the earlier data is presented in Table A1 in the Appendix, and discussed briefly in the Appendix. A summary of the results of the analyses of all of the surface samples collected from the Axe at Wookey Hole in 1996 and 1997 is also published in the Appendix, in Table A2.

"COLLOIDAL" CALCIUM CARBONATE IN THE RIVER AXE

"Colloidal calcium carbonate" created a difficulty that was encountered in the analysis of water samples from the River Axe. When reliability of analytical data was assesses by making ion balances, it was noted that even small quantities of "colloidal" calcite caused serious imbalances (Knights and Stenner, 1999). Chemists from Bristol Water plc routinely analyse samples of the river at the pumping station several miles downstream, where water is pumped from the river to Cheddar Reservoir. Manual titrations for total hardness are no longer carried out in the Bristol Water laboratories (manual methods having been replaced by automatic instrumental methods of analysis). However, old laboratory notebooks kept by Bristol Water refer to occasional periods when suspended material in the Axe interfered with EDTA titrations for hardness at this monitoring station (D Johnson, Chief Chemist, Bristol Water plc, 1998, personal communication).

When natural water samples were shaken with powdered limestones and dolomites, to provide data for comparison with data obtained using pure calcite (Stenner, 1971, pp.293–294), colloidal suspensions were created. Except in the water samples saturated with a chert sample that contained 69% acid insoluble residue (which failed to clear), the suspensions cleared after 24 hours, presumably as a result of a dynamic equilibrium between the suspended "colloidal" particles, the solution, and the larger particles in the excess solid. The behaviour of many samples during total hardness and alkalinity titrations proves that these samples contain suspended calcium carbonate. Examination of residues from one such sample bottle proved that, in this sample, the calcium carbonate was in the form of calcite (S Bottrell, University of Leeds, 1999, personal communication). As this sample also contained silica, it is possible that the calcite had crystallised around the nucleus of a grain of sand. Because the range of particle sizes has not been measured, the suspended material has been described in the present paper as "colloidal" calcium carbonate.

A semi-stable suspension of calcium carbonate, in which the particles are too small to be removed by filtration, is a rough definition of so-called "colloidal" calcium carbonate. It is revealed by an unstable end point in titrations for total hardness (Stenner, 1969, p.180). When the apparent end-point of the titration has been reached, if the solution is allowed to stand for about 30 seconds, the colour reverts from cornflower-blue to claret if the sample contained "colloidal" calcium carbonate. The concentration of "colloidal" calcium carbonate may be determined by titrating quickly to the first end-point (measuring the calcium and magnesium in true solution), then continuing to a final stable end-point. The difference between the two burette readings gives an estimate of the concentration of "colloidal" calcium carbonate.

The alkaline hardness titration is normally unsuitable for determining the "colloidal" calcium carbonate concentration. In this titration, it is necessary to leave the solution standing for at least two minutes to ensure the pH truly reaches the inflection-point pH (Rose, 1983), irrespective of whether a pH meter or a colorimetric pH indicator is used. Because particulate calcium carbonate passes into solution faster at pH 4.5 (the pH at the alkaline hardness titration end-point) than it does at pH 10 (the pH of the buffered sample during the total hardness titration), the alkaline hardness titration normally determines the sum of dissolved and "colloidal" carbonates. In other words, titrating quickly to a first end-point is not possible in alkaline hardness titrations.

This is the explanation of the methods used to estimate dissolved salts plus "colloidal" calcium carbonate in the 25/26.01.97 samples. However, on 30.11.96 and 14.12.96, this method failed, probably because unusually large concentrations of "colloidal" calcium carbonate were present. Possibly because of the presence of unusually large sizes of particles, it took longer than usual for suspended calcium carbonate to dissolve after the first end-point had been reached. In the total hardness titrations, a stable cornflower-blue colour was never reached. Eventually, loss of ammonia from the solution, with a consequent drift of pH, caused the colour of the indicator to degrade before this stage could be reached. (This analytical difficulty was also noted by Bristol Waterworks chemists). One alkaline hardness titration succeeded in providing an estimate of the minimum possible concentration of "colloidal" calcite, 41 ppm calcite (quoted previously), which is certainly an underestimate of the true value of the "colloidal" calcium carbonate concentration.

The results displayed in Table 1 confirm the magnitude of the errors in alkaline hardness titrations, the consequence of colloidal calcium carbonate having been titrated as alkaline hardness. Since the values obtained for alkaline hardness were too high, there were two consequences. Firstly, non-alkaline hardness figures were too low. Note the impossible negative non-alkaline harness results. Secondly, seriously large anion/cation imbalances, shown in Table 1, were found. If the ion imbalance were to be used to estimate "correct" values for the alkaline hardness, there are interesting consequences. In the data for the static sump in Table 1, for example, the alkaline hardness would fall by (119/2) ppm to 175 ppm $CaCO_3$, and the non-alkaline hardness would rise from an impossible value to a more reasonable value of 37 ppm $CaCO_3$. However, the same reasoning could be applied to the data in Table 2. In this set of samples, in which colloidal calcium carbonate was detected and estimated, ion balances and examination of non-alkaline hardness data combine to suggest that concentrations of colloidal calcium carbonate had been underestimated. The results from Chamber 3 and the static sump both had higher ion imbalances than usual, and non-alkaline hardness values were lower than usual. This suggests that alkaline hardness values were too high, because of a higher "colloidal" calcium carbonate content than had been estimated. There is a very tempting research project here, waiting for someone to pick up!

The fact that the Axe dissolved Mg as $Mg(HCO_3)_2$ from dolomite without dissolving Ca raises a question: What happened to the $CaCO_3$ in the dolomite as $MgCO_3$ dissolved? The chemistry of dolomite dissolution was considered next. In experiments referred to above (See Table 4), when water samples were shaken with powdered dolomites and dolomitic limestones, they all dissolved magnesium. With water similar to that in the Static Sump in Wookey 23 and a rock sample with a Molar Mg:Ca ratio of 1, incongruent dissolution of the dolomite took place. It is possible that when $MgCO_3$ in dolomite dissolves, the $CaCO_3$ component of the dolomite contributes to the calcium carbonate crystals in suspension.

However, on 14.12.96, water in the static sump, which had yet to come into contact with the dolomitic limestone, had an extremely high "colloidal" calcium carbonate load! Back to square one again! This fascinating cave is certainly in no hurry to give up its secrets. Work is continuing.

SUMMARY

On any occasion, there was no variation in any measured hydro-chemical component of the River Axe from Sump 25 to the Entrance. In particular, there was no magnesium gradient in the River Axe.

1. The points of confluence of the tributaries that make up the River Axe are all upstream of Sump 25.
2. The Static Sump in the 23rd Chamber contained magnesium concentrations that were significantly lower than those in the River Axe.
3. Concentrations of magnesium and alkaline hardness were lower in the Static Sump, by an equal quantity, than those in the River Axe, while those of calcium, sodium, potassium, chloride, sulphate and nitrate were the same, proving that they shared the same origin.
4. There is a considerable possibility that exploration of the Static Sumps will result in the discovery of important extensions.
5. At an unknown distance upstream of Sump 25, the River Axe (still a single unit) has the same composition as the Static Sump in the 23rd Chamber. The physical conditions in which most of the River Axe acquires varying concentrations of magnesium bicarbonate are not known.
6. At times, analysis of samples for total, calcium and alkaline hardness have been made difficult by the presence of large concentrations of suspended calcium carbonate.

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APPENDIX

	Temp° C	Total Hardness	Mg	Ca	Alkaline Hardness	Non-Alkaline Hardness	Agg.	Cl^-	K	Na	SO_4^{2-}	T.An val=2	D.O. %	Pres/ E.coli
No.	14	16	14	14	16	16	7	8	3	3	3	1	3	1
Mean	9.94	273	27.8	249	240	33.0	-0.2	58.5	4.3	27.5	20.5	37	89.8	90
S.D.	0.13	15.4	6.6	14.3	12.3	8.1	9.3	5.8	0.5	2.3	2.18		7.3	
RSD	1.3	5.6	28.6	5.7	5.1	24.6	-5900	9.9	11.6	8.1	10.6		8.1	
Min.	9.7	244	18	219	212	22	-17	46	3.8	25.0	18		84	
Max.	10.1	295	45.5	267	260	50	11.2	64	4.8	29.2	28		98	

Table A1. A summary of hydro-chemical characteristics of the River Axe at Wookey Hole between 1966 and 1978. Most of the samples were collected from the 3rd Chamber.

Site	Total Hardness	Agg	Mg	Ca	Alkaline Hardness	Non-Alkaline Hardness	Cl^-	K	Na	SO_4^{2-}	NO_3^-
No.	6	4	6	6	4	4	6	6	6	4	4
Mean	273.6	-4.2	41.3	232	252	32.4	45.8	4.08	23.4	12.9	39.3
S.D.	15.8	1.44	6.0	14.0	1.6	4.9	2.13	0.39	3.2	1.07	7.2
RSD	5.8	34.8	14.4	6.0	0.6	15.0	4.66	9.5	9.5	8.3	18.2
Min.	246	-6.5	34.6	211	250	27.0	42.3	3.7	29.5	12.2	27.6
Max.	290	-2.8	51.3	255	254	40.2	47.9	4.6	38.8	14.8	45.3

Table A2. Results of analyses of samples collected from the River Axe at Wookey Hole Bridge in 1996 and 1997.

Whereas most of the hydro-chemical characteristics of the Axe have been stable over the period of more than thirty years, there appears to be one exception. A single sample, collected on 21.08.68, was analysed for sulphate, chloride and total anion content. The results showed the water had a nitrate content that was too low to be detected. This conclusion was supported by a good anion/cation balance for the sample. Although this was the result of the analysis of a single sample, there is an identical situation at the Cheddar Rising. A single sample, collected from the Cheddar Yeo spring on 8.10.68 was analysed for sulphate, chloride and total anion, and in this sample the concentration of nitrate was also too low to have been detected by this method. At this spring, nitrate concentrations are also much higher now than the detection limit for nitrate implied by the methods used in 1968 to 1970. The nitrate concentrations at the Cheddar Yeo spring are now in the range of 22×10^{-5} to 42×10^{-5} M, which is very similar to the range in the Axe at Wookey Hole. Thus in the two major springs which feed the River Axe, both of which had levels of nitrate in 1968 that were too low to determine, there are now very significant nitrate levels in the springs themselves. This clearly indicates that the ground-waters that supply the two springs have become contaminated by nitrates.

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FOOTNOTE

Some of the data in the present paper were discussed at the local BCRA. meeting at Priddy in November 1998. It was suggested that the chemistry of the water in the Static Sump in Wookey 23 could have been affected by water overflowing into Wookey 23 from the Axe at Sting Corner in very high flood conditions. One of the authors, Clive Stell, has made two trips to Wookey 23 in flood conditions, and reported that there was a stream flowing in Wookey 23 on both occasions. It was flowing ***OUT*** of Wookey 23 ***TOWARDS*** Sting Corner. Whatever else may be concluded from this observation, it proves conclusively that there is a flow of water from other than the known main stream, into Wookey 23. There will be more about this, and other on-going research in the cave, in the future.

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Geological guidance of speleogenesis in marble of the Dalradian Supergroup, County Donegal, Ireland

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Abstract: Pollnapaste is a small but complex cave developed in marble of the Dalradian Supergroup near Lettermacaward in County Donegal, at the mouth of the Gweebarra River. Speleogenesis has largely been guided by variations in marble band lithology during inception and the early stages of void formation, but as the cave developed the influence of this banding declined. Solubility contrasts, between marble and metadolerite, and the configuration of the intrusions have provided later and greater guiding effects. Phreatic development appears largely strike-related, with only minor dip tubes connecting different segments. Metadolerite or quartz aquicludes have created perched zones of saturation, in which the early stages of the cave's development occurred. Breaching of these aquicludes allowed progressive lowering of the phreas and development of vadose passages along fractures cutting across the strike. There is no conclusive evidence for any pre-Devensian development of the cave system and the main passage development is presumed to be entirely late-glacial to post-glacial in age, although inception may have occurred much earlier.

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INTRODUCTION

The results of an investigation of an area of karst in County Donegal, adjacent to Gweebarra Bridge (Fig.1), near Lettermacaward, between Glenties and Dungloe is described. The karst is unusual in an Irish context. It has formed within a sequence of deformed metasediments belonging to the Dalradian Supergroup, which have locally been metamorphosed to impure banded marble. The main feature within the marble outcrop is an active stream cave known as Pollnapaste. Most caves in Ireland are formed in Carboniferous Limestone, which is widespread throughout the country. Though not extensive, Pollnapaste is interesting. It exposes considerably more of the geological structure and lithological variety in three dimensions than can be determined from surface exposures. Despite the practical restrictions of the cave environment on mapping the geological structure, it provides an opportunity to examine the influence of the geology on the normal karstic development of highly deformed marble, compared to that of the relatively undisturbed Carboniferous Limestone.

Though surveyed to BCRA grade 5c, representation of the cave in two dimensions is difficult on account of the three-dimensional complexity of the system. Thus, the survey (Figs. 2, 3) can be considered to indicate only the general configuration and relationships of the various passages. Despite the system's complexity, the original sketch survey (Fig.4) made by David Johnston as part of his undergraduate thesis is a testimony to his ability to comprehend

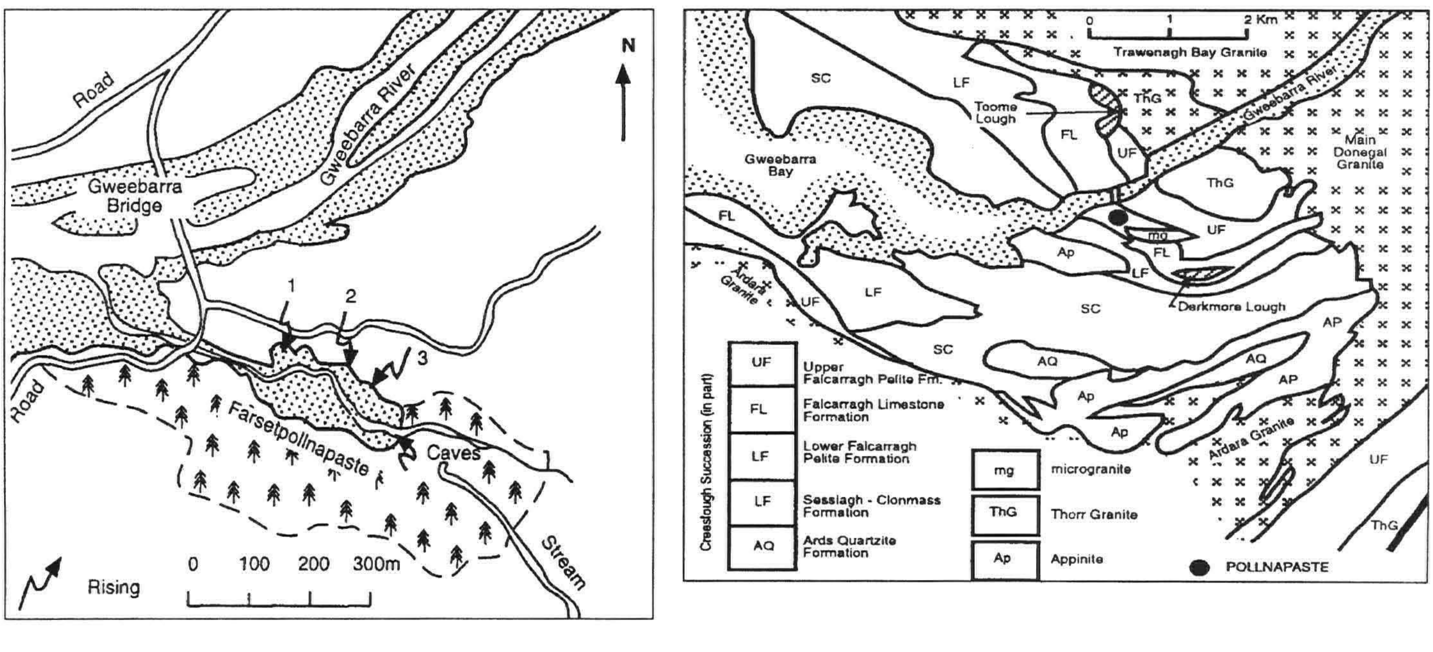

Figure 1. Locality map of Pollnapaste and simplified geological map of the area. Numerous metadolerite bodies are excluded for clarity.

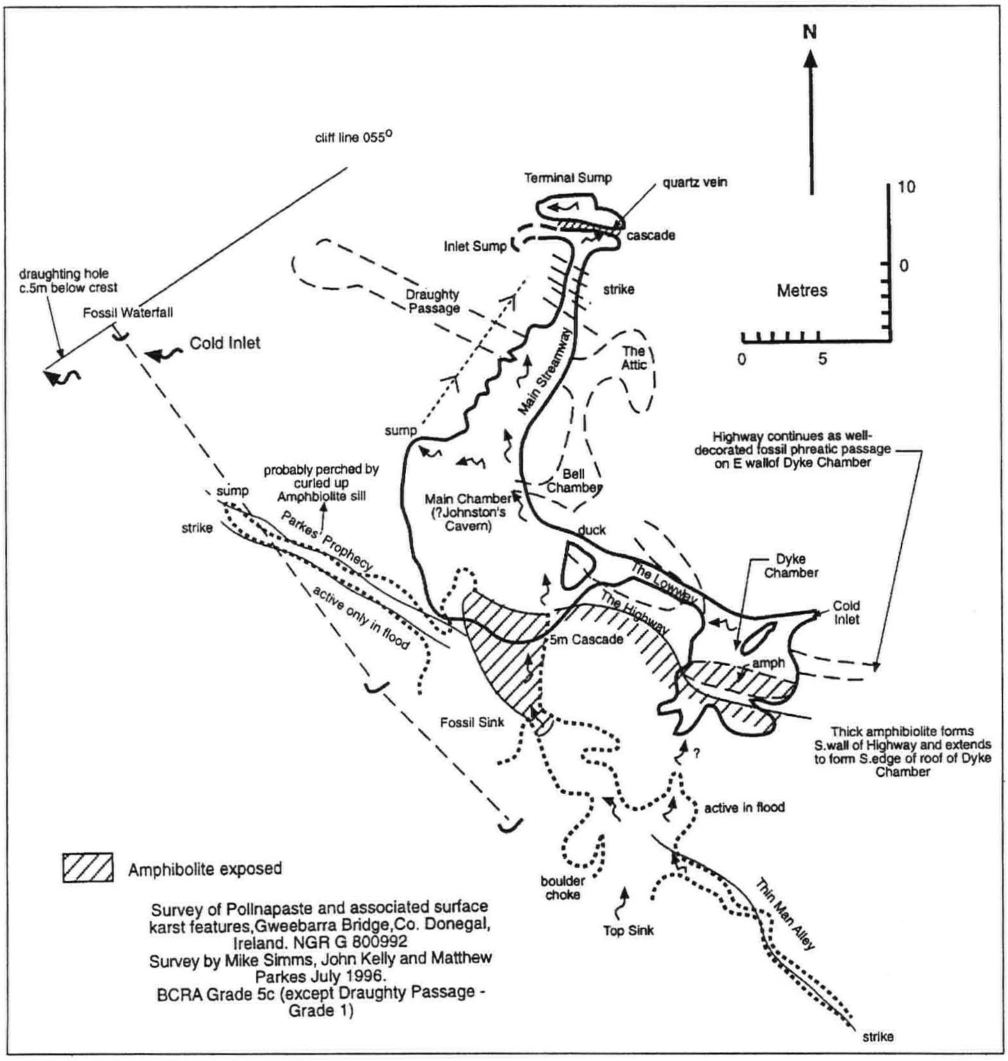

Figure 2. Survey of Pollnapaste and associated karst features.

complex three-dimensional structures. His untimely death in 1995, just before this study was undertaken, leaves the analysis poorer, for want of his potential input.

LOCATION AND SETTING

Pollnapaste (a corruption of Pollnapeiste - the cave of the worm or serpent) is situated above and to the southeast of Farsetpollnapaste (which translates approximately as the ford at the shallows at the cave of the worm or serpent) in Kincrum Townland, a few hundred metres southeast of Gweebarra Bridge, in central County Donegal (Fig.1).

The cave is shown on the 1:10,560 scale map (Donegal 65) of the area, and has been known to geologists for some decades, but was first noted in the caving press only recently (Anon, 1989). A river draining from Derkmore Lough flows on the surface for about 800m before sinking into Pollnapaste. The resurgence lies just above high tide level in the muddy embayment of Farsetpollnapaste. The steep-sided enclosed valley is heavily wooded, with both native woodland and some modern plantations.

A second, sub-parallel, stream flows from the area just north of the cave. It does not sink but flows down a steep-sided valley, which is

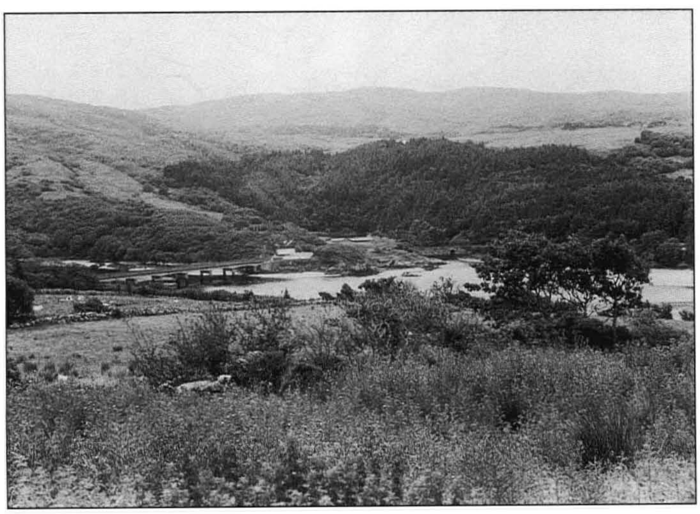

Plate 1. An overview from Lettermacaward southeast into Farsetpollnapaste (photo by M Parkes).

Plate 2. A view into Farsetpollnapaste; Pollnapaste and the resurgence are hidden within the trees at the far end (photo by M Parkes).

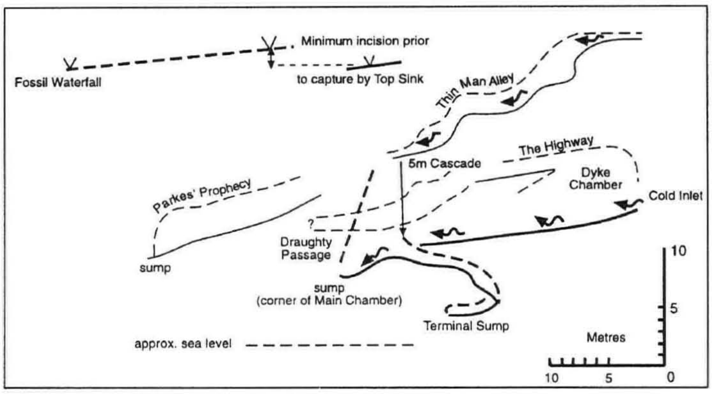

Figure 3. *Section of Pollnapaste and associated karst features.*

locally gorge-like and has at least one abandoned cave on its western flank (The Den - see below). It reaches Farsetpollnapaste at the same point that the resurgence from Pollnapaste issues, and the two flows combine for a few metres before reaching the tidal pool.

GEOLOGY

The cave is developed within the Falcarragh Limestone Formation, part of the local Creeslough Succession, which has been correlated with the Neoproterozoic Appin Group of Scotland. The latter is the basal group of the three that comprise the Dalradian succession in northwest Donegal. This thick sequence of diverse sedimentary rocks was metamorphosed in late Proterozoic or early Palaeozoic times. The metasedimentary rocks are bounded by late Caledonian granites; the Main Donegal Granite to the northeast, the Trawenagh Bay pluton to the northwest and the Ardara pluton to the southwest. A small deformed granite intrusion is also present within the metasedimentary succession a few hundred metres to the southeast of Pollnapaste. Whereas most of the metasediments are quartzitic or pelitic, sporadic carbonates in the sequence have been metamorphosed to marble. In the inferred environment of deposition of the carbonates, it is likely that they were dolomitised shortly after deposition.

In the Gweebarra area the Falcarragh Limestone Formation is composed of interbedded pelites and marbles in the lower part, passing up into a marble-dominated unit with thin bands of quartzite and psammite, each about 2cm thick and laterally persistent. The cave is developed within this banded marble. Total outcrop thickness of the main marble is difficult to measure because of the structural complexity, but nowhere is it more than a few tens of metres. Karstic development coincides with the limits of the banded marble, and hence is confined to a narrow belt, on the south side of the estuary.

Plate 3. Fossil sink, and the entrance to Pollnapaste. The relict waterfall lies over the col in the centre (photo by M Simms).

Polyphase deformation and metamorphism has affected the succession. The major structure of the area comprises northeast facing recumbent folds, on which upright upward facing folds have been superimposed. Dolerite intrusions, altered to amphibolite grade by the metamorphism are widely distributed throughout the marble and are the oldest igneous rocks present.

DESCRIPTION OF THE CAVE

A stream flows from Lough Derkmore through a wooded gully before reaching Top Sink, where it disappears into a sump pool among boulders on the west floor of a high but very short cave. The cave appears to back up completely in high water conditions. From the right an inlet stream called Thin Man Alley ascends steeply for almost 20m before becoming too low for further progress.

This apparently restricted cave is accompanied by a far more impressive cave developed beneath a deep adjacent depression, reached by climbing over the col between them. The depression is steep-sided with a rock wall above the cave around about half of the circumference, forming a natural amphitheatre. This is termed Fossil Sink, as the original flow through the sinkhole has been captured via Top Sink. The flow passes through a small sump in Top Sink, and reappears amongst the boulders in Fossil Sink and flows over a shelf to cascade into the cave.

A 5m drop (requiring a ladder) leads into an irregular high cavern, termed Main Chamber. A metadolerite sill is conspicuous along the southern edge of the roof and has been breached near where the cascade enters. The stream crosses the Main Chamber floor and largely sumps in the northwest corner, although some water continues down a

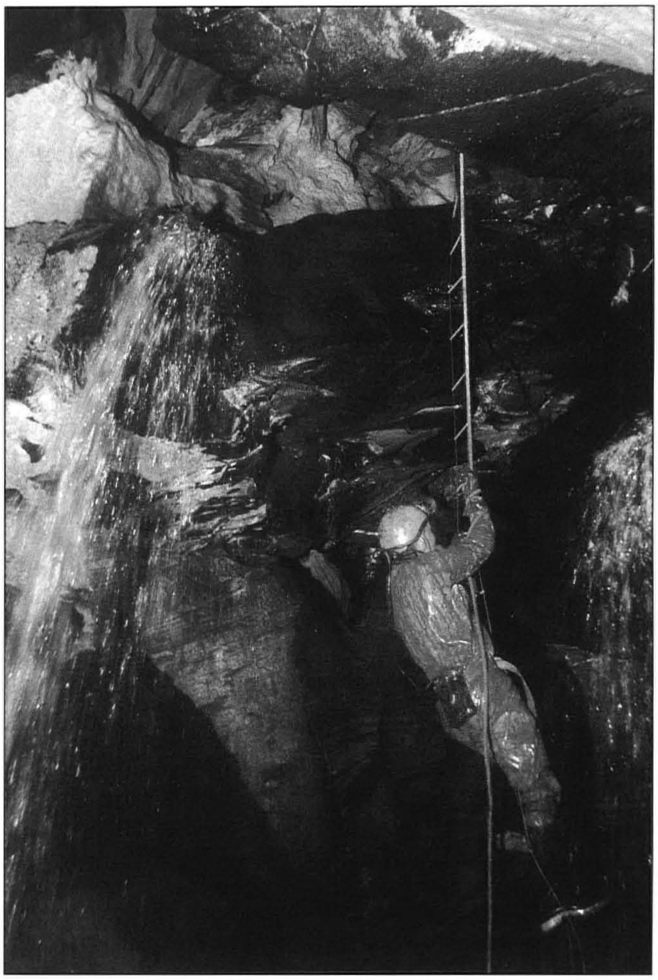

Plate 4. Entrance pitch in Pollnapaste, with metadolerite visible above ladder (photo by T Faulkner).

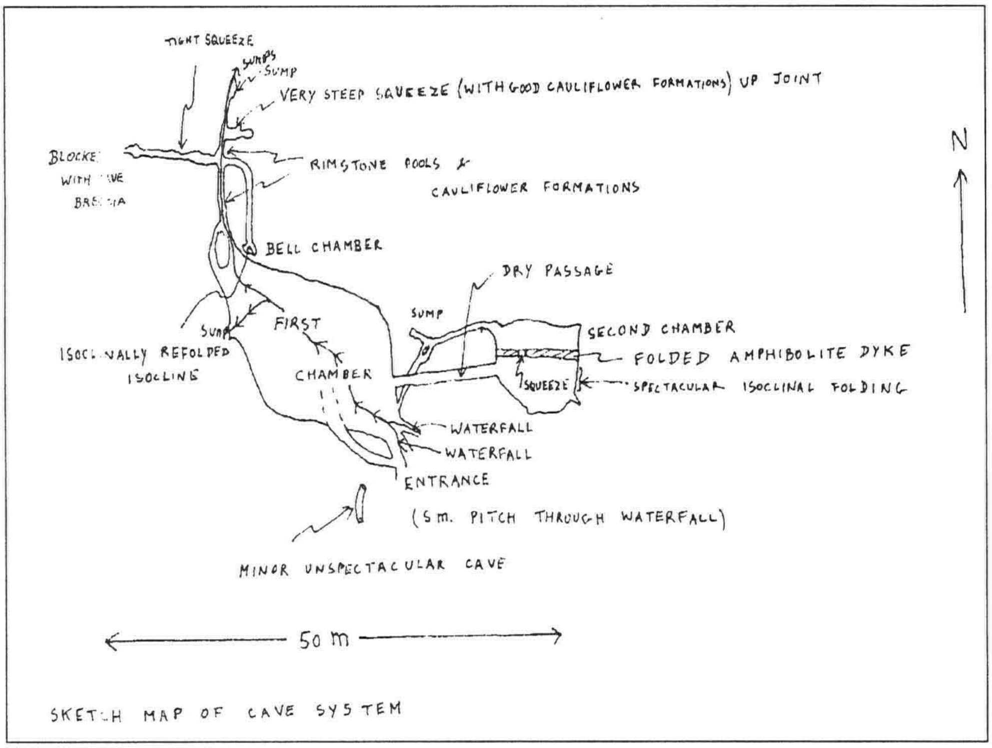

Figure 4. Dave Johnston's sketch survey (Johnston, 1980).

narrower canyon type streamway. This widens where a climb up to the right leads to heavily calcited sections called the Attic (on the left) and Bell Chamber (on the right), the latter named from a prominent formation. From here the Main Chamber and the Main Streamway can be seen but not entered.

Also at this point, on the opposite side of Main Streamway, a higher level passage (Draughty Passage) can be entered. After a short distance it is almost blocked by a stalagmite boss and gour dam. It has not been surveyed beyond these, but descends a metre or so into a lower and broader section of passage, floored by re-sedimented peat underlain by sand. It continues over muddy cobbles for another 2 to 3m, before becoming too low for further progress. At this point it is probably less than 5m from the cliff edge.

The Main Streamway passes these side passages into a few metres of tubular section passage that was the former sump, and end of the cave. The way on was blocked by a thin aquiclude, which has been breached, dropping into a small shaft, at the base of which is the present terminal sump. Immediately before the cascade, a small inlet stream enters on the left probably returning some of the flow from the sump in the Main Chamber.

From the foot of the waterfall in the Main Chamber, a low wet crawl (The Lowway) behind boulders leads via a narrow rift into the second main part of the cave, Dyke Chamber. This is named after a substantial folded metadolerite dyke that forms a wall across the middle of the chamber. It averages about 10 to 50cm in thickness, about 2m in height and is crossed either through a small triangular window at its base, or a very low squeeze underneath.

This chamber can also be reached by a climb up to a mud-floored, dry high-level passage, the Highway, which emerges at the top of the dyke. From this point a choked relict passage descends to the northwest. A small, very cold, inlet stream enters in the northeast corner. The folding of the banded marble is perhaps best seen in this chamber, although the whole cave exhibits it well, except where it is obscured by calcite deposits.

Close by the cave entrance is a second cave, termed Parkes' Prophecy. It was anticipated that this might provide an alternative entrance route into the Main Chamber or to the Draughty Passage area. In fact, it sumps after about 15m of steeply descending narrow rift passage.

PRESENT HYDROLOGY

Most of the water flow in the main surface stream sinks in Top Sink, which sumps almost immediately. Some of the water enters a sump, perched by the metadolerite sill, to cascade into the southwest corner of Dyke Chamber. The remainder continues via a short duck/sump (depending on water volume), to become the waterfalls into the main chamber. Within the cave the main flow is directly across the Main Chamber. Rather than all flowing down the main streamway passage, much of the flow actually sumps in the lowest section of the Main Chamber. The water almost certainly reappears in a small dissolutional inlet tube low on the left near the final sump.

The resurgence for the system lies at about 2m above sea level in Farsetpollnapaste. A separate small stream to the north sinks just upstream of here, but is insufficient to account for the outflow of the rising. A series of flood risings up to 4m higher than the main rising lie on the slope behind. There are several other flood risings around the north shore of Farsetpollnapaste, though not necessarily associated with the main cave system (Fig.1).

- At site (1) is a series of open joints in marble dipping steeply to the north. One wall has indistinct small (<2cm) scallops;
- At site (2) is another series of open joints in marble dipping steeply to the north;
- At site (3) is a 1.5m-wide joint-guided rift with open joints at the back,. and evidence that water resurges at times.

INFLUENCE OF GEOLOGY ON CAVE DEVELOPMENT

Overall structure

The local strike of metamorphic foliation is northwest to southeast, and the prevailing dip of the marble is northeastwards, steepening from about 30 to 40° in Main Chamber to near vertical in the downstream part of the Main Streamway. Beneath the thick metadolerite sill roofing the Main Chamber the marbles appear more intensely folded. This is

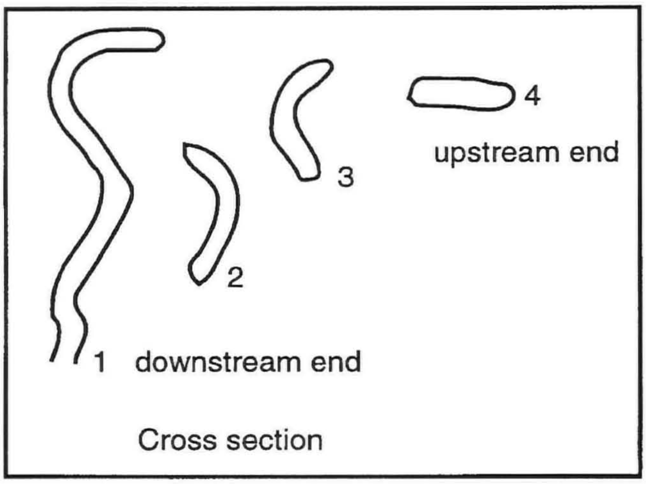

Figure 5. Sketch sections through Thin Man Alley (approximate locations shown on Figure 2).

particularly evident adjacent to the waterfall and in the southern half of Dyke Chamber.

Lithological variation

Lithological variation (between paler, more soluble, carbonate and darker, less soluble, silicate-rich layers) within the marble is seen as stripes or banding, possibly reflecting an original limestone and shale bedding. The bands are strongly folded, isoclinally in places. Apparently the banding and folding have had little influence beyond the initial phases of dissolution, which appears to have favoured the purer carbonate horizons. In Thin Man Alley, the passage morphology is clearly guided by open subvertical folds in the marble, forming a narrow rift where a particularly soluble marble band has been dissolved out (Fig.5). At the upstream limit the marble band is almost horizontal and the passage is a rather waterlogged flat-out crawl. As it descends, the passage develops into an inclined rift, first dipping northeastwards, then curving round to dip southwestwards and then, towards its downstream end, swinging back to a very steep northeasterly dip. Similarly the passage morphology in the furthest, narrower, parts of Draughty Passage mirrors the folding in a carbonate horizon.

The passage in Parkes' Prophecy is also lithologically-guided, developed along a purer carbonate band in parts. However, in the lower part of Pollnapaste, in the main streamway, a dissolutional tube cuts directly through the bedding, at about 90° to strike. It appears unaffected by lithological variation in the marble but clearly was initially joint guided. In several places the joint is visible in the roof. The passage is now epiphreatic and a vadose trench has developed in its floor. Flood levels, as indicated by debris in the cave, suggest that the water level commonly backs up. Water level here has been lowered by the removal of a perched sump. This has happened in the last few years where a cavers' breakthrough (Anon 1990a, b) resulted in the removal of a quartz vein dam and altered a flooded section into a small waterfall shaft into an aven above the terminal sump.

Dyke Chamber, which best displays the folded banding in its walls, demonstrates that once an initial inception stage is passed, the overall cave dissolutional development is largely independent of the lithological banding. In the aven walls and throughout the cave many thin insoluble bands are seen to be boudinaged. This is the irregularly pinched out appearance caused by differential stretching during the metamorphic deformation and folding. This may account for their relative unimportance once cave passages reach a certain size. Also,

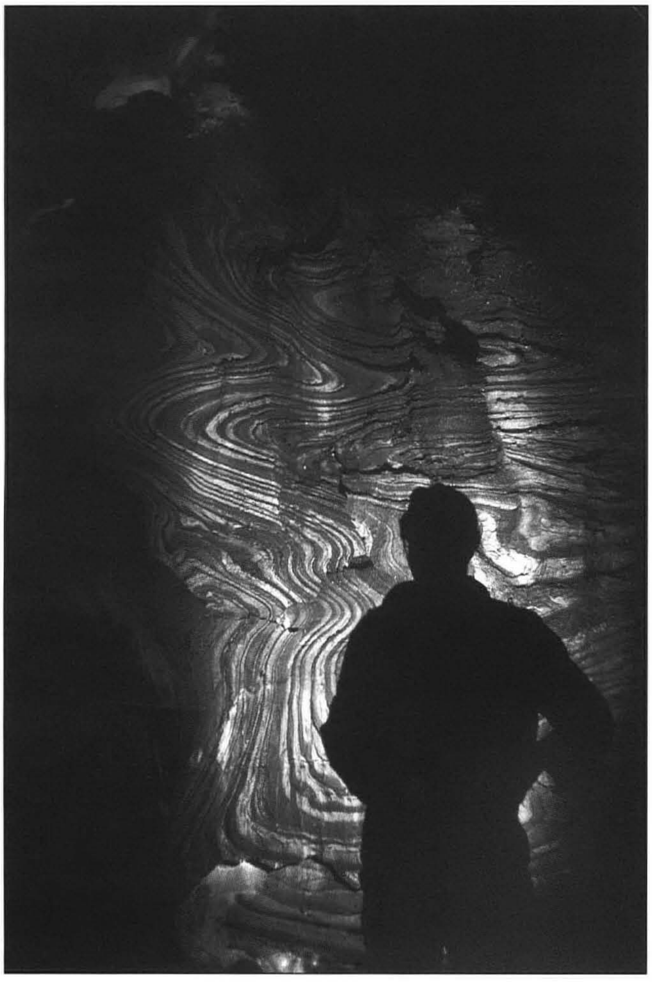

Plate 5. Folded lithological banding in the marble in Dyke Chamber (photo by J Kelly).

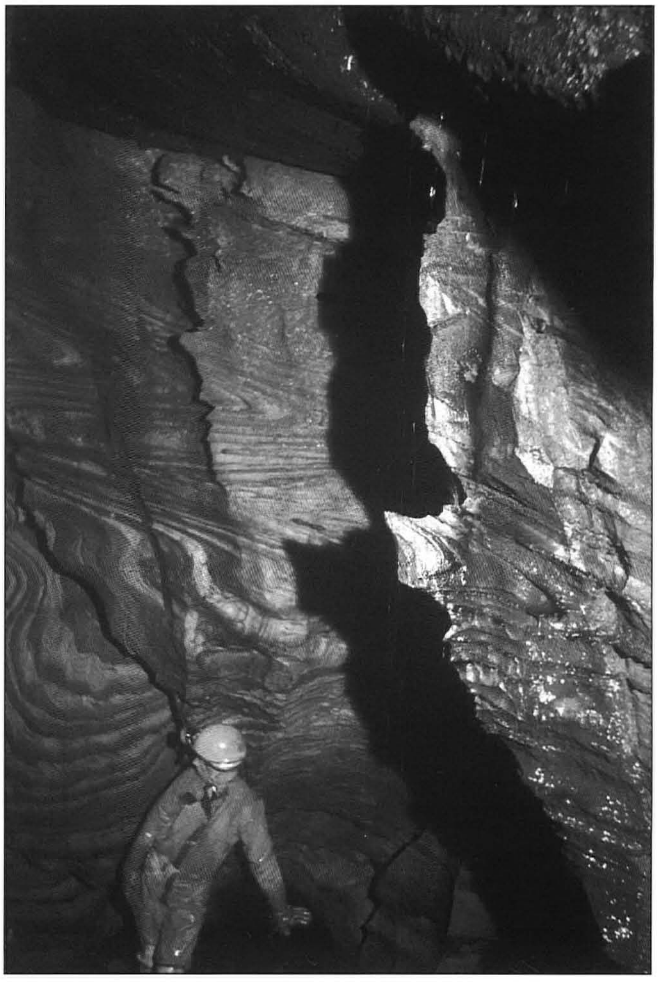

Plate 6. Folded lithological banding in the marble in Dyke Chamber, viewed from the Highway (photo by T Faulkner).

Plate 7. Folded lithological banding in the marble in Dyke Chamber (photo by T Faulkner).

some 'insoluble' bands are actually partly calcareous, and are brittle and degraded by dissolution, breaking off when weight is placed on them.

Once a passage has become large enough to allow sediment to move freely within it, corrasion becomes a major factor in cave enlargement, adding to dissolutional effects. Most parts of the cave, except The Highway passage (which is mud floored) and the high, heavily calcited, sections such as The Attic and Bell Chamber, are floored with broken rocks, including clasts of metadolerite. The relative importance of this corrasion was impossible to determine. Although scalloping is locally present on the cave walls, the lithological banding is a stronger influence and the more soluble paler bands are less prominent than the less soluble darker ones. The texture of all the marble is extremely granular and abrasive to the touch.

Intrusive igneous rocks

The other main rock type present in the cave is readily distinguished by touch alone, as it is smooth, hard and slimy. The rock is a metadolerite (although there are also some manganese/iron oxide blackened quartz veins). Essentially, igneous intrusions of basic magma within the limestone, both dykes and sills, have been metamorphosed with the limestone. They are distributed throughout the cave and are insoluble, providing impermeable barriers. In many smaller passage sections the morphology is clearly limited by the presence of a metadolerite, forming one wall of the passage along the strike of the intrusion.

The roof of the main chamber clearly exposes a thick (about 60 to 100cm) sub-horizontal metadolerite body. This sill has been folded into a monocline, across which the stream flows between the lowest point in Top Sink and the lip of the waterfall. It dips gently downstream before curving sharply upwards to become vertical or slightly overturned. The boudinage of this metadolerite and the associated minor fault displacement at the hinge of the fold are clearly visible in the roof of the Main Chamber just to the north of the waterfall cascade. This must have been the point at which the aquiclude was breached. Prior to that it must have been very effective at supporting a perched aquifer, with water flow descending northwestward along the trough of the monocline. The present line of the waterfall drop into the cave is only about 2 to 3 metres back from this, due to its erosional retreat.

East of the waterfall, the northern limb of the metadolerite monocline is exposed along the entire southern wall of The Highway, continuing across the upper part of the wall along the southern side of Dyke Chamber. This appears to form a partial barrier to flow from

Plate 8. Phreatic windows in the northern part of Dyke Chamber (photo by T Faulkner).

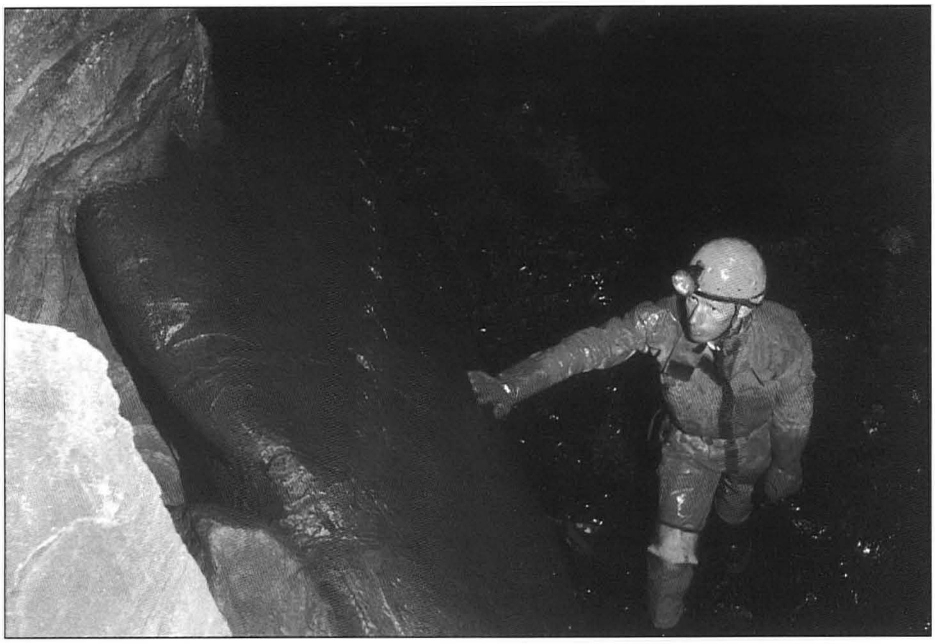

Plate 9. Looking down on the smooth surface of part of the dyke in Dyke Chamber (photo by T Faulkner).

Top Sink, creating the perched sump that lies immediately north of the lower end of Thin Man Alley. At times of low flow a small volume of water trickles over the lip of this barrier but the clean-washed walls and floor of Dyke Chamber indicate that it takes large volumes of water in flood, presumably all via this perched sump.

In Dyke Chamber, the influence of the metadolerite aquiclude is less clear cut. The dyke remains as a wall (about 2m high and varying from 5 to 60cm thick), in a straight line across the middle of the aven (although folded from top to floor with horizontal axes), separating the aven into two parts. It would seem that the aven development has reached a scale where it proceeded, simply by expanding around the dyke without being materially influenced by it. On the east wall of Dyke Chamber, opposite The Highway and at only a slightly higher level, is a short section of relict dissolutional phreatic passage developed along strike and extensively choked with a spectacular array of speleothems. This represents the upstream continuation of the Highway-Bell Chamber-Draughty Passage conduit. The influence of the east-west dyke in the development of Dyke Chamber may have been less significant than seems apparent at first. Several active and relict passages converge in this location. The older passages are situated above the dyke and hence cannot have been influenced directly by it. After the abandonment of The Highway, subsequent flow routes have maintained a northward flow despite increasing exhumation of the dyke. Increasing incision of passages downstream (to the north) of the dyke eventually allowed an alternative route to develop beneath the dyke at the western end of the chamber.

Fracturing and jointing

The marble displays few fractures and joints, and only locally did they exert any major influence on cave development. The breach of the metadolerite roof of the Main Chamber at a small fault (with a displacement of only tens of centimetres) that can be seen from the climb up to the Highway is the most significant example. The second is the orientation of the dissolutional tube section upstream of the terminal sumps. This is at right-angles to the banding in the marble, and is joint guided. Fracturing post-dates the igneous intrusions and the main ductile deformation.

SURFACE KARST GEOMORPHOLOGY

The limited outcrop of marble displays extensive dissolutional sculpture in the exposures in the forest and valley sides, although these are much obscured by vegetation. Small caves other than The Den (see below) are probably more common than searches have indicated. The only other large-scale feature, apart from the cave and its sinks, is an apparent former waterfall and lake above the cave entrances. This is a shallow depression area, with a distinct lowest point, on the cliff edge, above the cave entrance. The exposures near the lip are heavily karstified and some expanded joints are big enough to allow access to a caver.

Two scenarios could have caused these features. The thick metadolerites, especially the one seen in the roof of the Main Chamber, may have formed a hydrological barrier that forced most of the stream to flow on the surface. It would have ponded up in a small lake with a waterfall outlet over the cliff edge. The development of a subterranean flow through fractures in the metadolerite would have breached the hydrological barrier and would rapidly have formed a cave with the flow diverted underground, as is seen now.

The features observed can also be explained by postulating a model where the flow was always largely subterranean. However, during glacial or interglacial times, with extensive permafrost conditions, the water was unable to drain via the cave but was diverted over the top of the cave sinks on the surface, forming the waterfall outlet.

Cave development

The oldest series of passages in the cave would appear to be the Highway-Bell Chamber-Draughty Passage conduit. The source of the water was to the southeast, presumably from a sink upstream of the present sink, but possibly from the next stream to the north. The single trunk conduit of The Highway developed along strike immediately beneath and to the north of the metadolerite monocline. It was connected to Bell Chamber by a series of anastomosing dip-tubes, the lower part of which may have been destroyed by collapse and enlargement of Main Chamber. The upper halves of these dip-tubes are still preserved in the roof. The whole area of Bell Chamber and The Attic, where not obscured by speleothem growth, has a rounded dissolutional morphology with smooth or indistinctly scalloped walls and roof. This conduit then descends obliquely along a northwest-dipping joint to the final strike tube of Draughty Passage, from which water probably resurged above the base of the cliff to the northeast of the relict waterfall.

A second drainage route developed along strike on the up-dip side of the metadolerite monocline, and may initially have been contemporaneous with that just described on the down-dip side. However, the relatively immature vadose morphology of this second drainage route suggests it is more recent. This is the Thin Man Alley-

Parkes' Prophecy conduit, which descends from southeast to northwest. Thin Man Alley presumably was, and still is, fed by minor sinks upstream of the main sinks. It may once have formed a continuous passage but has since been breached by downcutting and collapse in the region of Fossil Sink.

Fossil Sink may have developed as an invasion inlet to the Parkes' Prophecy conduit prior to breaching of the metadolerite monocline. The small depth of incision, less than 2m, that occurred below the surface outlet prior to capture by Top Sink suggests that Fossil Sink operated only briefly or only as a flood overflow in the early stages of development of Top Sink. Much of the large size of the Fossil Sink doline is due to later collapse along major joints, rather than direct erosion or dissolution.

Breaching of the metadolerite monocline in the region of the waterfall effectively drained much of the perched phreas that existed on its upstream side, although the aquiclude still remains effective elsewhere, such as in creating the perched sumps at the downstream end of Parkes' Prophecy and adjacent to Dyke Chamber. Much of Main Chamber has developed subsequent to this breaching event, through erosion, dissolution and collapse. The vadose streamway flowing north from Main Chamber has developed during this late phase of cave development. A series of closely spaced fractures, with which the much earlier Bell Chamber-Attic series is also associated, has allowed this vadose streamway to cut straight across the bedding, which here is near vertical. The quartz vein that now forms the lip of the final cascade clearly formed an aquitard until breached by the caver action. It probably still forms an aquitard to east and west of this point, accounting for the position of the inlet sump entering from the west just on the upstream side of the cascade.

Timing of cave development

The development of inception horizons (Lowe and Gunn, 1997) could have occurred at any stage in the history of the marble in this region. If it actually occurred, the early dolomitisation of limestones, prior to metamorphism, may have influenced the rock mass to produce inception horizons. The metamorphism and folding itself may similarly have influenced the inception and gestation stage of speleogenesis, but the timing and mechanism of such influence is speculative.

Whereas inception of suitable horizons was probably considerably earlier, the assessment of the cave's configuration in relation to the geology and particularly the landscape indicates that the main development was late- or post-glacial. The area was glaciated extensively during at least the last glacial advance (Midlandian), and probably several preceding this. These glaciations will have altered the pre-glacial landscape dramatically and have had a profound influence on the present landscape features. This poses the question of whether the cave was 'inherited' from an earlier landscape pre-dating the last glacial maximum. It is possible to speculate that the cave had developed in a closed system of largely confined drainage beneath the metadolerite aquiclude long before late Quaternary times, with the last glaciation merely exposing the system to near surface levels, and allowing modifications by surface drainage elements. Equally, it is possible to invoke a sub-glacial, high pressure, hydraulic environment for the origins of Pollnapaste, but the following sequence of events is most compatible with the cave's features:

- inception of speleogenic horizons at unknown time;
- glacial scouring of the landscape ending after the last glacial maximum at 15,000 years ago;
- reinstatement of surface drainage across the Falcarragh Limestone, and epikarstification;
- brief operation of shallow lake and waterfall outlet, before breaching of the metadolerite aquicludes allowed diversion of drainage underground;
- main development of cave passages in sequence described above.

The relatively large size of the Main Chamber (15m x 8m x 6m high), and the presence of abandoned high-level passages well-decorated with speleothems, might tend to suggest that the cave is older than the 10 to 12,000 years that have elapsed since the final retreat of the ice sheets. However, a more detailed analysis of the cave in its regional context does not necessarily support a pre-glacial origin for even the earliest parts of the system.

Relationship to Derkmore Lough

Derkmore Lough occupies a glacially-scoured basin on the western slopes of Derkbeg Hill. This lough and the stream that drains from it into the cave clearly post-date the end of the last glaciation. The development of all phases of the cave can be linked to various incision levels of the present stream and the role of aquicludes in creating perched phreases. There is nothing to suggest that even the oldest parts of the system are not related to this stream. Such a close relationship between the underground conduits and surface features would be unlikely to have survived a major episode of glaciation.

Relationship to the relict waterfall

The relict waterfall and the dry valley that lies between it and Fossil Sink are such subtle features that they must post-date the last ice movements. The shallowness of the dry valley indicates that it operated for only a very short time, but it also indicates that the underground drainage through the cave had yet to develop. It is unlikely that the marble could support such surface flow in the presence of any significant pre-glacial cave system at such shallow depth. The possibility that through-flow was prevented by blockages of glacial sediment fill is not borne out by examination of the system, which lacks any significant sediment fill other than the banks of fluvial gravel directly associated with present, or earlier, drainage routes. Glacial

Plate 10. The shallow dry valley depression between Fossil Sink and the relict waterfall (photo by M Simms).

sediments that might have blocked the cave would show a very different distribution, being preserved in alcoves and passages well away from the present or former streams that would have removed them.

Speleothem growth

The abundance and size of the speleothems in many of the high-level parts of the system, and their apparent inactive state, might at first suggest a considerable age. However, much of this speleothem growth is of crumbly, 'cauliflower' stalagmite with a very open texture, indicating rapid growth. The reason for this type of stalagmite growth occurring here is unclear, although it appears to be characteristic of marble caves (Trevor Faulkner, University of Huddersfield, pers. comm. Oct. 1997). At present no U-series dating has been undertaken on speleothems, but may be tried in the future.

Incision rates

Less than 2m of incision occurred between abandonment of the relict waterfall route and abandonment of the Fossil Sink in favour of Top Sink. The col between Top Sink and Fossil Sink now lies almost 8m above the floor of Top Sink, implying some 10m of incision in total. However, there is an obvious nick point close to the point where the surface stream swings round to the northwest into Top Sink, with a significant increase in gradient downstream of this. Upstream of the nick point the incision is significantly less than 8m, though the exact figure is unknown. It is probably less than 4m. This would give a total incision of perhaps 6m in 10,000 years, or 60cm per ka. This is very fast but not impossible considering the high rainfall, the important role of abrasion by clastic debris and of dissolution by acid drainage from blanket peat, and the high hydrological gradient from the upland to the coast.

OTHER SITES IN THE AREA

A limited exploration for other caves across the marble outcrop in this area failed to locate any other sites, except for The Den. Although Flautist's Cave is known to exist on the Lettermacaward side of the Gweebarra River, much of the northern part of the outcrop is either lake-covered (Ranny Lough, Toome Lough) or else so flat-lying as to make caves unlikely, other than flooded sections accessible only to divers. There are wooded gullies and sections of the slope down to the river that could well contain caves, but the area is relatively densely populated and farmed due to the higher fertility of the soils on marble compared to those on other lithologies.

It should be noted that references to caves in County Donegal are few and those that exist have in some cases been given erroneous names. The classic 'Caves of Ireland' by Coleman (1965) refers to a few small caves in Donegal, but they are in the Carboniferous Limestone in the south of the county. One is in Ballynacarrick Townland, and this may have been mistakenly used as the name for Pollnapaste (Anon, 1990a, b). Confusingly, there is also an area called Ballynacarrick some kilometres upstream from Gweebarra Bridge.

Flautist's Cave (Lettermacaward side of Gweebarra River)

This site was not located during this study, despite making local enquiries. The first description (Anon, 1990c) of it was by Adam Jones, an Oxford University geologist mapping in the area in 1989. It is about 11m long and consists of a single chamber that stops abruptly against a metadolerite sill. A very small waterfall flows over the sill, into a pool that contained brown trout, despite the whole cave being polluted with domestic rubbish. The height averages 1.5m but rises to over 2m at the back of the cave. It would seem that here too the metadolerite has acted as a strong influence on cave development (Fig.6).

The Den

This cave is situated on the south side of the small stream valley to the north of Pollnapaste, which meets the rising of the cave just before the sea. A climb down into a choked pot leads only into a second dry chamber less than 3m high, with flowstone on the walls (Fig.7). This site is entirely inactive and is probably unconnected to Pollnapaste.

COMPARISON WITH OTHER AREAS WITH MARBLE CAVES

Some exploration of caves in marble, including a 10m-deep pot, in the Connemara Dalradian Supergroup sequence has been reported (Anon, 1990b), though these have not been surveyed in detail. None appears to be extensive. They lie within the outcrop of the Lakes Marble

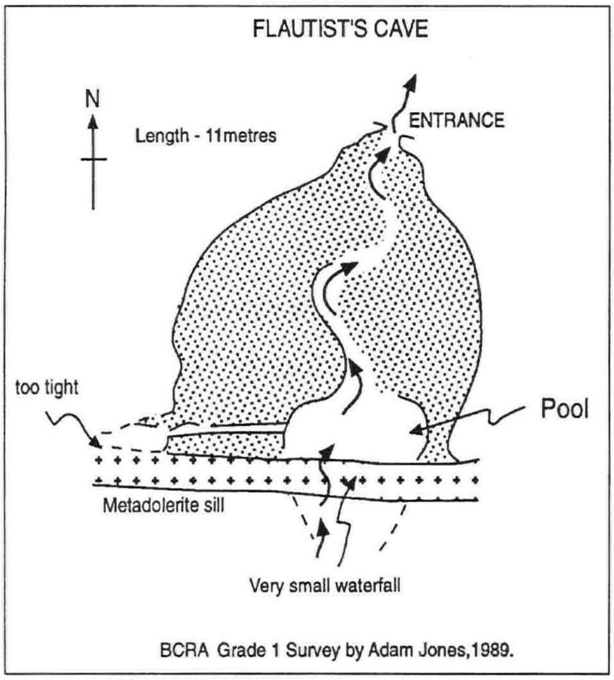

Figure 6. Flautist's Cave: sketch survey by Adam Jones.

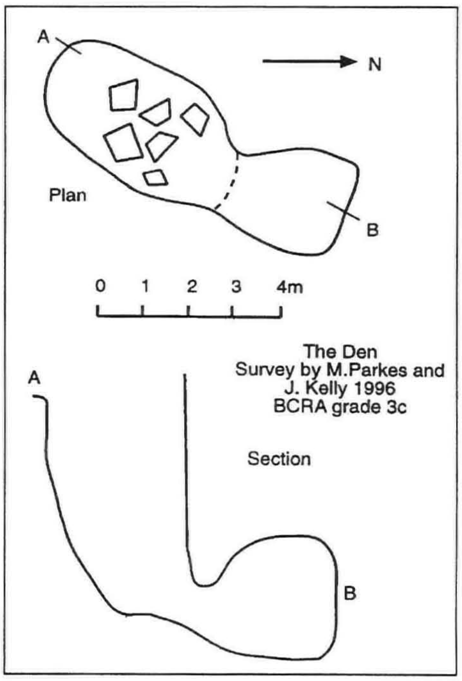

Figure 7. Survey of The Den.

Formation of the Argyll Group, a unit younger than the Falcarragh Limestone. The well-known Connemara Marble, a distinctive green marble, has a restricted outcrop, but may contain caves too.

Within Britain, only Scotland has Dalradian Supergroup marble lithologies of comparable nature. However, here only a few caves are known and all are relatively short. The cave at the highest altitude in Britain, Uamh nan Uachdar, in the Grampians, is 60m long and was described by Young (1992). It was noted as within a marble of the Dalradian Supergroup by Waltham *et al.* (1997). No details of its speleogenesis are known. From its description (a single wet rift with one oxbow) the cave is probably immature compared to Pollnapaste.

However, although Pollnapaste may be relatively unusual in an Irish context, caves in marble are relatively common in Norway and have been described extensively (e.g. Bottrell, 1987; Faulkner and Newton, 1990, 1995; Lauritzen *et al.*, 1991). (Davies (1986) also notes that they are common in New Zealand). Geological guidance of speleogenesis has been analysed in Lower Glomdal (Bottrell, 1988) and Greft Stream Cave (Holbye, 1983; see also Ford and Williams, 1989, Fig. 2.12, p.40). Examination of these reports suggests that a complex variety of influences has acted in forming the caves and, as at Pollnapaste, discrimination of the various factors is difficult. Cowle and Wilcock (1982), for example, describe Kvandalhola found in 1979. The description and illustrations reveal complex relationships with the geology, in comparable striped marbles.

Faulkner (1983) recorded many caves in Norway's marbles. Though few observations regarding the influence of geology were recorded, the important role of igneous intrusions is clear. For example, Arch Cave consists of a single passage divided into parallel passages by igneous intrusive rocks.

In 1990, Faulkner and Newton recorded many caves in south Nordland within several varieties of marbles. Despite numerous geological observations, it is difficult to gain a clear picture of any guiding factors operating exclusively or predominantly, other than the karstic nature of the marble compared to surrounding lithologies.

By contrast, a survey of Scandinavia's deepest cave, RJR (Lauritzen *et al.*, 1991) demonstrates at least some geological influences on the cave's development. Lithology is important because the cave (nearly 2km long and 580m deep) is in one 20 to 30m-thick marble band, yet the thickest of three marble bands has no known caves. The third main band supports caves too, yet all three dip steeply in parallel. The caves are immense compared to the band thickness of the host outcrops.

Recent work by Faulkner and Newton (1995) has presented more detailed geological observations related to speleogenesis of other caves in south Nordland, Norway. Aside from the obvious relationship of the karst and caves to the marble outcrop, the authors observed a preferential development of caves in narrow bands of marble, too small to be represented on most geological maps. Three main marble lithologies were identified, with caves commonly formed at contacts between marble and non-marble lithologies, or between striped and grey marble types. Intrusions, or contacts of other impure bands, are also noted as forming cave walls, waterfalls and sumps.

The most detailed analysis of Norwegian marble caves was by Bottrell (1988), following his earlier descriptive report (Bottrell 1987) of caves in the purer grey or yellow striped marbles in Lower Glomdal, Rana. His summary of genetic influences on cave sites indicates that the purer grey marble contains the majority of caves, and those in the yellow marbles are commonly restricted to specific bands. Qualitatively, fractures are of secondary importance in cave passage genesis, though they determine position and orientation of passages within the speleogenic lithology. Significant passages in the yellow marble seem to have developed in highly fractured zones.

In terms of passage morphology, those within single homogeneous units have ideal tubular shape, but as soon as dimensions extend beyond that unit or band, modification occurs and development continues only in one horizon. Fractures imposed variable but secondary guidance of passage shape, in a similar fashion to that of Pollnapaste.

CONCLUSION

Investigation of a small but complex cave system developed in deformed Dalradian Supergroup marbles intruded by dolerites, has demonstrated the relative roles of lithology and structure in cave development. Conduit inception has primarily been along strike or down dip within more soluble bands, but in some instances fractures have had an overriding influence. The presence and configuration of non-carbonate horizons (intrusive igneous rocks and quartz veins) has had an important influence on subsequent cave development, particularly with regard to draining of the phreas. The available evidence suggests that the cave development phase is largely post-glacial in age.

ACKNOWLEDGEMENTS

This paper is dedicated to Dr David Johnston, who mapped the rocks of the area and explored the cave in 1980, and first showed the cave to the lead author. David's tragic death in 1995 came just before he was to join this investigation of the caves. The project would not have been possible without the award of a Praeger Grant, administered by the Royal Irish Academy, for which we are very grateful. We particularly thank Trevor Faulkner for extensive discussions and generous provision of photographs for this paper. Pam Fogg and Dave Scott also assisted in discussion, and Adam Jones supplied Pam Fogg with information about Flautist's Cave. Special thanks to Elaine Cullen for preparing the figures. The valued comments of the referees have significantly improved the paper.

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Carbon monoxide poisoning: a potential hazard to speleologists?

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Abstract: Many speleologists habitually employ acetylene lamps as an aid to cave exploration. Acetylene generated from calcium carbide burns incompletely in acetylene lamps, and production of carbon monoxide appears likely. In order to establish the potential hazard of carbon monoxide poisoning during speleological activities, an experiment was carried out during a rescue training exercise of the National Speleologic Rescue Service of Lombardy, Italy. Fifteen voluntary rescue technicians provided venous blood samples before and after 14 hours of caving, in enclosed spaces with poor air circulation. The data show a clear and statistically significant decrease of blood carboxy-haemoglobin, probably due to the effects of hyperventilation in surroundings that are effectively free of carbon monoxide.

INTRODUCTION

Carbon monoxide (CO) is a major cause of illness and death. It is produced endogenously in small amounts, and forms as a product of incomplete combustion of hydrocarbon fuels. It is colourless, odourless and undetectable to the human senses (Weaver, 1999). Fire and associated smoke inhalation are responsible for most accidental fatalities associated with CO. Accidental CO-poisoning occurs typically from the use of defective or improperly installed household appliances that operate on combustible fuels including gas, oil, coal, wood and kerosene (Fisher, 1999).

Carbon monoxide binds reversibly to haemoglobin (Hb), with an affinity approximately 240 times that of oxygen, leading to a corresponding reduction in the total oxygen-carrying capacity of the blood, with resultant tissue hypoxia. With an affinity of this magnitude, even low-level exposure is associated with severe toxicity (Ilano and Raffin, 1990). Most of the signs and symptoms of CO-poisoning can thus be ascribed to the resultant tissue hypoxia. The severity of the observed symptoms correlates roughly with the observed level of carboxy-haemoglobin (COHb). Neurological and cardiovascular manifestations are common, including fatigue, headaches, dizziness, difficulty in thinking, nausea, dyspnoea, weakness, and confusion. Marked tachycardia and tachypnoea are also common, as the cardiovascular and pulmonary systems try to compensate for the reduced peripheral oxygen delivery. Prolonged hypoxia due to high CO levels may lead to cardiac arrhythmia or arrest, and to a variety of neurological sequelae. Non-lethal CO exposure is frequently misdiagnosed due to the nonspecific nature of its symptoms.

Speleologists commonly employ acetylene lamps in cave exploration, often staying in caves for a long time, frequently in enclosed spaces, where acetylene lamps are the sole source of light. Acetylene generated from calcium carbide contains impurities and burns incompletely in acetylene lamps, leading to production of a large amount of particulate carbon in the form of "lamp-black". Carbon monoxide (CO) production is hence likely, and a CO poisoning hazard is a theoretically possible. Chlorates, nitrites, nitrates, benzol derivatives and toluol (methyl-benzene) could also be produced, depending upon the degree of impurity, and methaemoglobin (MetHb) could be detected. MetHb is a derivative of haemoglobin in which ferrous iron is oxidised to the ferric state. MetHb is a dysfunctional haemoglobin, in that it is unable to combine reversibly with oxygen and carbon monoxide. As Hb is oxidised continuously into MetHb and subsequently reconverted to haemoglobin, it is normal for small amounts of MetHb (<1.5%) to be present in blood.

In order to establish the real hazard of CO-poisoning during speleological activities, an experiment was carried out in the Stoppani Cave (LoCo 2021, Lombardy-Italy) during a rescue training exercise of the National Speleologic Rescue Service of Lombardy (9th group – speleo, Corpo Nazionale Soccorso Alpino e Speleologico). Carboxy-oxymetric analysis was performed on blood samples.

SUBJECTS AND METHODS

Fifteen voluntary rescue technicians (14 male and 1 female) provided reference venous blood samples at the start of the training exercise in Stoppani Cave. All the subjects were non-smokers, to prevent any possible influence of cigarette-derived CO. Training continued for 14 hours, and involved carrying a speleological stretcher through enclosed spaces with poor ventilation. The team members worked together, close to one another, during the entire time. Intense physical effort stimulated secondary tachycardia and hyperventilation. A second venous blood sample was collected from each technician at the end of the rescue training.

Blood samples were stored in lithium heparin at low temperature, in hermetically sealed test tubes (Vacutainer) and analysed the following day at the Emergency Medicine Division of the Maggiore Hospital in Milan. Blood analyses were performed with an IL 682™ CO-Oximeter (Instrumentation Laboratory), measuring carboxy-haemoglobin (COHb) and methaemoglobin (MetHb).

Sample Group 1	COHb	MetHb
Mean value	1.2	0.35
Standard deviation	0.290	0.237

Sample Group 2	COHb	MetHb
Mean value	0.94	0.4
Standard deviation	0.217	0.192
P	0.002	0.534

Table 1. *COHb and MetHb mean values and standard deviations in the 15 blood samples in Groups 1 and 2 (taken before and after the rescue exercise respectively). The probability values (P) that the difference between the Group 1 and Group 2 results is due to chance are also shown.*

RESULTS

COHb and MetHb mean values and standard deviations in blood sample groups 1 and 2 (initial values and final values respectively) are shown in Table 1.

A Student's *t*-Test was performed in order to establish any possible statistically significant differences, and the probability values *(P)* that the difference is due to chance are shown in the last line of Table 1.

Normal MetHb and COHb values are, respectively, <1.5% and <4% of total Hb (<8% in smokers).

DISCUSSION

Toxic MetHb becomes relevant only if the level of toxic substances exceeds normal enzymatic reducing capacity. MetHb levels fall rapidly during blood storage, even at low temperature, and meaningful results can be obtained only on freshly drawn blood. So, even if data show no statistically significant variation of MetHb, it is impossible to infer on this basis whether calcium carbide-derived acetylene combustion (usually rich in impurities) contains toxic derivatives.

In contrast, COHb remains quite stable for several hours after collection, and storage in airtight tubes can help to prevent bonds breaking. The results of COHb analysis are therefore valid.

The data clearly show a statistically significant decrease of blood COHb, probably due to hyperventilation by the test subjects in relatively CO-free surroundings.

Increased heart and respiratory rates brought about by exertion could enhance COHb formation if CO were present. Thus, its reduced levels in the post-exercise blood samples lead to the conclusion that CO is effectively absent or at minimal, non-toxic, levels under the conditions of the experiment.

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Land values around Cango Cave, South Africa, in the 19th century

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Abstract: The conditions surrounding the land tenure around South Africa's Cango show cave and the responsibilities for the Cave, beginning in the early nineteenth century, are discussed briefly. Details of local land prices, derived from historical documents, give a clear indication of the value of the cave, and confirm that minor government officials and the land owners must have made a very good living from the Cave until their monopoly was terminated by the Colonial Government in 1891.

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Cango Cave, South Africa's leading show cave, is situated in the Swartberg foothills, about 27km north of Oudtshoorn, near the western boundary of the original farm No.28. This has been known variously as De Kombuis, Kombuis, Combuys, Kombuys and Combuis. The legal owner is, and always has been, the State, by virtue of the following servitude, which Governor Lord Charles Somerset had inserted into the original title deed of 10 January 1820:

"... on condition that he (van der Westhuizen) and the future proprietors of the place Combuis shall have no right whatever to that part of the ground where the Mouth of the Grotto is situated; that the same shall be left perfectly free and undisturbed and be considered as public property; that he shall at any future period suffer a road to be cut across the land to the said Grotto ..."

The responsibility for the Cave was vested in the Magistrate at George. He delegated responsibility to the local Field Cornet and, to avoid the necessity of motivating for extra salary to pay for this additional duty, he allowed the Field Cornet to charge visitors 10 rix dollars for each party, and to keep same in lieu of salary[1]. Ten rix dollars (then equal to 15 pre-decimalisation UK shillings or £0-75) was equivalent to about £45 sterling in today's devalued currency[2]. This arrangement also ensured that the Magistrate was not required to audit the Cave accounts.

These arrangements might have been agreeable to the Magistrate and to the Field Cornet, but they were not good for the Cave, which was attracting visitors despite the poor access roads[3]. It was a perfectly legal situation, whereby a part-time minor Government official, ex officio, had acquired a potentially valuable monopoly.

The Cave was in need of improvements for the benefit of the visitors, there being no gate, toilets, tea room, access road and outspan. The owner, i.e. the Colonial Government, did not consider voting money for the Cave, even though it was the stated policy that the Cave should be conserved. The Field Cornet, despite his potentially valuable monopoly, did not spend money on the Cave, because he was subject to dismissal, having no security of tenure. The owner of the surrounding land did not invest, because he derived no guaranteed income from the Cave. The only facilities provided were a portable ladder for the descent into Van Zyl's Hall[4], and flaming torches for illumination.

Although the Magistrate was not required to audit the Cave accounts, he did instruct the Field Cornet to keep a visitors' book. There is, however, no record of the numbers of visitors to the Cave, if only because the Field Cornets had a vested interest in under-reporting them. If they had been seen to be making a large income from the Cave they would have had to pay tax on it. Additionally, the Government could have been expected to appoint a salaried manager, and to keep the income from the Cave.

For over sixty years Field Cornets Louis Botha Sr. and Jr. lived 3 hours' ride away at Vinknestrivier on the back road to Calitzdorp. They would have been unable to watch the Cave, and must therefore have come to some arrangement with the owners of the surrounding land.

Nevertheless, some idea of the value of the Cave to the Field Cornet and to the surrounding landowner can be got from the changing land values during the nineteenth century (Tables 1 and 2). In 1825

Purchaser	Transfer No. and Date	Amount (£)
Daniel Jacobus du Plessis	141 of 21 June 1839	210
John O'Connel	60 of 18 Jan. 1847	300
Petrus Jacobus Botha	99 of 14 Dec. 1848	650
Petrus Jacobus Nicolaas Botha	235 of 30 Jan. 1868	225

Table 1: Non-Cango Cave land share transactions 1839 - 1868.

Purchaser	Transfer No. and Date	Amount (£)
Petrus Jacobus Terblans	141 of 21 June 1839	210
Theunis Jacobus Botha	85 of 25 May 1846	262½
Jacobus Johannes Schoeman	1 of 04 Jan. 1847	300
Wynand Petrus du Plessis	189 of 25 Jan. 1853	850
Louis Jacobus Kleynhans	319 of 25 July 1868	1625
Herman van der Veen	320 of 25 July 1868	1125

Table 2: Cango Cave land share transactions 1839 - 1868.

Combuis was subdivided, the 509 hectares surrounding the entrance to Cango Cave becoming known as Grootkraal. In 1839 equal shares in Grootkraal were sold for £210 each. The increase in value of the share that controlled Cango Cave (Tables 1 and 2) illustrates well the profitability of the Cave. That share increased in value by 674% over 29 years, whereas value of the other share increased by a mere 7%[5].

Because these postulated agreements were private, there is no record of the details. Nevertheless, the apparently anomalous peak value of the non-Cango Cave share - £650 in 1848 - compared with £300 the previous year for the Cango Cave share, deserves further comment. The £650 non-Cave share was bought by Petrus Jacobus Botha[6], and transferred twenty years later to his son for a mere £225[7]. Petrus Jacobus Botha was son of Louis Johannes Botha Jr.[8] - Field Cornet of Vinknestrivier from 1837. This decline in value of his share indicates that, for whatever reason, he was unable to come to a lasting agreement with his father!

The Cave share increased in value by £1,415 over 29 years, compared with an increase of only £15 for the non-Cave share. Especially in the middle of the nineteenth century, when wealthy city dwellers were not buying farms for aesthetic reasons,, the purchase price of a farm depends to a large extent on the anticipated future income. Assuming that:

1) the £1,400 difference can be explained by the anticipated Cave receipts;

2) the takings would be divided equally between the Field Cornet and the shareholder; and

3) the purchaser (Louis Jacobus Kleynhans) expected to recover his outlay in ten years,

a rough calculation suggests that the annual number of visiting parties averaged:

$$\frac{140 \times 2}{0{\cdot}75} = 373 \text{ parties or, in round figures, 1 party per day.}$$

Unfortunately this simple idea is confounded by the precipitous 31% drop in the value of the share when it was immediately transferred to Herman van der Veen for £1,125. Van der Veen was an expatriate Hollander, who described himself as a shopkeeper[9]. His Dutch origin and the reduced purchase price suggest that he was a better businessman than was Kleynhans - a farmer, probably of poor education[10].

Although details of the financial arrangements between the Field Cornets and surrounding landowners are unknown, the above evidence confirms that the Cave was profitable. This was eventually appreciated by the Colonial Government, which terminated the Field Cornet monopoly in 1891. The owner of the surrounding land, Herman Wilhelm Johannes van der Veen (son of Herman), was appointed Caretaker. Although a salary of £18 per annum had been suggested by the Oudtshoorn Divisional Council, the Government reduced the entrance fees to the equivalent of 5 UK shillings (or £0-25 in modern currency) for a single visitor, 1 shilling and sixpence (£0-075) each for a party not exceeding 5 in number, and 1shilling (£0-05) each for a party exceeding 5 in number. Children were admitted at half price. Again, these fees accrued to the Caretaker in lieu of salary[11]. These fees, reduced by between 67% and 93%, confirm that until 1891 the Field Cornet and the owner of the surrounding land must have been making a very good living from the Cave.

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Some observations on the occurrence of channel karren-like features in flooded karst conduits in the Yorkshire Dales, UK

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Abstract: Channel karren-like features are described, occurring on sediment free rock surfaces in flooded conduits. Direct observation during times of increased flow indicates an origin, at least in part, due to abrasion by moving sediment.

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REPORT AND DISCUSSION

Channel karren are a common feature of bedrock surfaces in karst terrains and are recorded occurring locally within caves (e.g. Workman, 1997). Recent observations by the authors in the flooded conduits of the cave system behind Gods Bridge risings in Chapel-le-Dale, North Yorkshire, have revealed a number of occurrences of similar features on mainly sediment-free rock surfaces. These features are morphologically most similar to rundkarren, having a typically rounded cross-section and smooth crests (Fig.1). Some of the grooves are clearly visible from some distance away, because the characteristic dark brown patina that coats rock surfaces in flooded conduits in the Yorkshire Dales is commonly absent. Such grooves are seen as pale lines against a dark background. The features occur in two different settings. One set occurs on steeply sloping rock surfaces, commonly forming a step in the floor of the passage. They run down the steepest part of the exposed surface in an almost straight line. The courses of the channels show little sinuosity and commonly run from the very top to the very bottom of the exposed bedrock. The grooves are aligned along the direction of flow in the conduit and, unlike those reported from relict conduits (e.g. Workman 1997), are not associated with an inception horizon. Examples can be seen in Joint Hole main passage and at the Hindenberg Wall (Fig.2).

The other set forms around openings where smaller passages and fissures join larger conduits, with many entering in the floor of the larger conduits. These grooves form a radial pattern around the mouth of the smaller passage. The grooves are rounded, with rounded crests, but tend to become wider and shallower away from the opening, becoming narrower and deeper towards the mouth of the smaller passages. The grooves may converge towards the mouth of the smaller passage. This type can occur on less steeply dipping rock surfaces. An example of this type can be seen at the Blue Rift in Joint Hole main passage (Fig.2).

Careful selection of diving conditions has allowed observation of some of these features during times of increased flow. In conditions of high discharge the grooves found on the steps in the floor of the passages often have a stream of sand grade sediment particles trickling down them (Fig.3). This downward movement of sediment is most commonly seen during dives soon after a flood pulse has passed through the conduit. In the radial type, sand grade particles can be seen being ejected from the smaller conduits and carried above the floor of the larger conduit by the current of water entering from the smaller conduit. The particles then fall to the floor some distance away from the entrance to the smaller passage, where they roll back down the grooves, back into the smaller passage. Both authors have observed this circulation of sediment particles on several separate occasions.

Direct observation by the authors of sediment movement in vertical segments of active phreatic conduits has revealed sediment particles up to cobble size being lifted vertically by the current. If the particles moved out of the main current in the phreatic lift, or collided with other particles being carried by the current, they fell back down to the floor, commonly rolling against the walls.

The karren-like features are at least in part a result of abrasion by moving sediment particles, rather than being of wholly dissolution origin as are karren occurring on the land surface. They are seen most commonly in cave systems with high sediment loads, such as Joint Hole and Hurtle Pot in Chapel-le-Dale (Cordingley, 1999), Black Keld

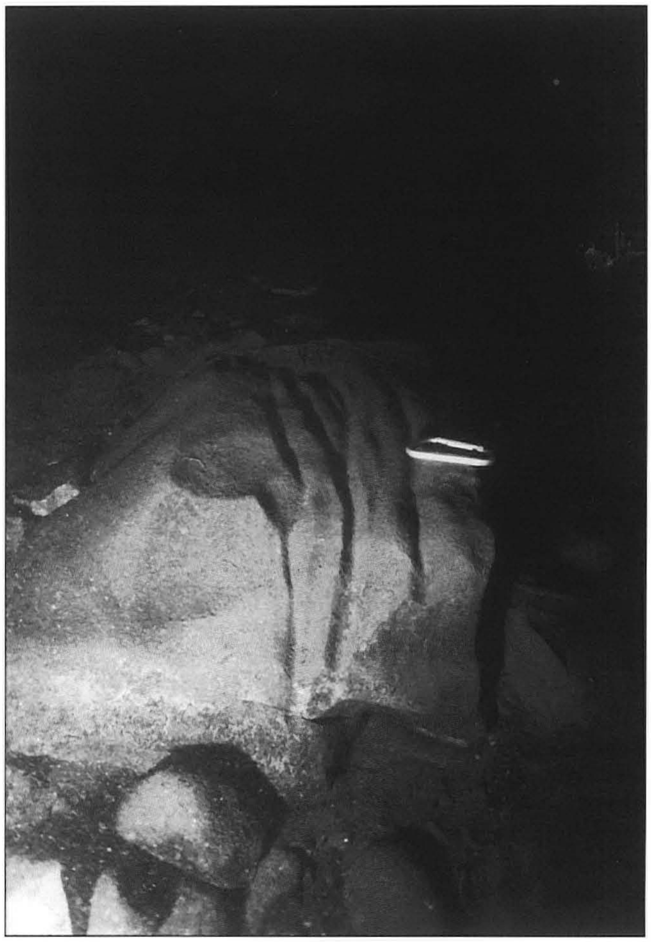

Figure 1. Channel karren-like features in Joint Hole main passage, Chapel-le-Dale, North Yorkshire.

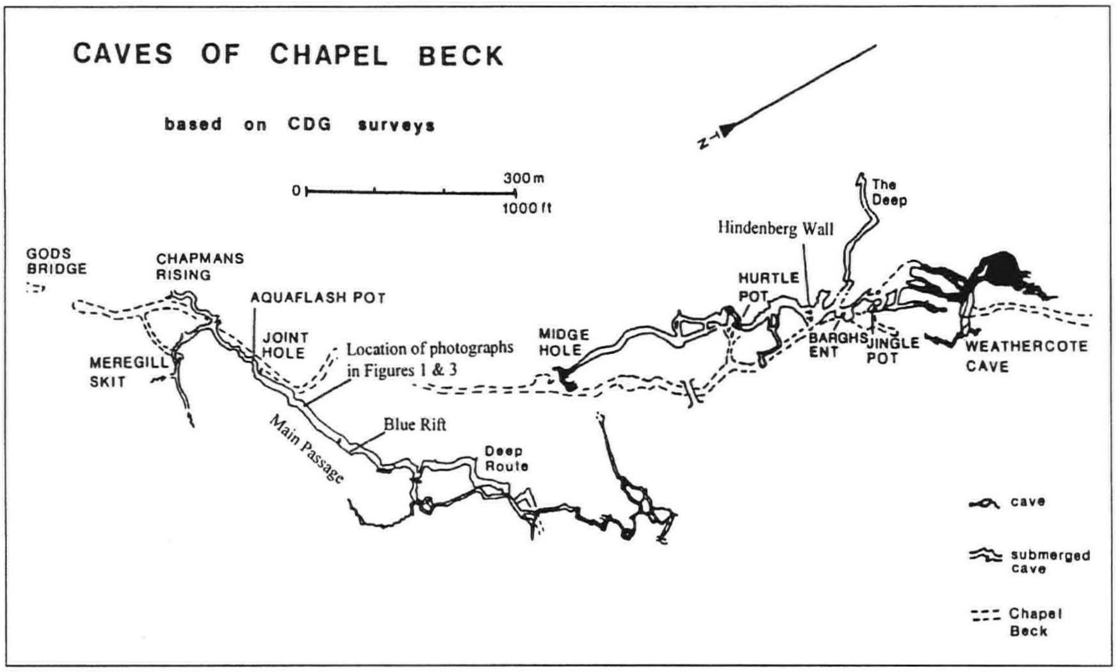

Figure 2. Plan of the caves of Chapel Beck. Reproduced from Brook et al (1996) with permission.

in Wharfedale and Lancaster Hole, Easegill (Cordingley, 1992). The absence of the dark brown patina commonly seen elsewhere in these passages in the base of the grooves may be due to abrasion by sediment particles moving down the grooves. Although it is not possible to show that dissolution is not involved in the inception or later development of these features, there is no positive evidence that dissolutional processes play any greater role than they do on other, un-grooved, exposed bedrock surfaces in phreatic conduits.

The role of abrasion in cave development has received relatively little attention. Though commonly alluded to (e.g. Ford and Williams, 1991, pp.306-307), very few results of studies into the effects of abrasion have been published. Newson (1971) concluded that there is both hydraulic and geological potential for abrasion in many swallet-linked cave streamways, though his study did not benefit from direct observation in active phreatic conduits. Observations by the authors suggest that abrasion plays an active role in phreatic conduit development in systems carrying a high sediment load.

True karren are dissolutional features (Lowe and Waltham, 1995; Ford and Williams, 1991), and rundkarren are formed largely under soil profiles (Lowe and Waltham, 1995). As the features described in this paper are, at least in part, due to abrasion, strictly they cannot be called karren. It is therefore proposed to call these karren-like features found in active phreatic conduits 'pseudo-karren'.

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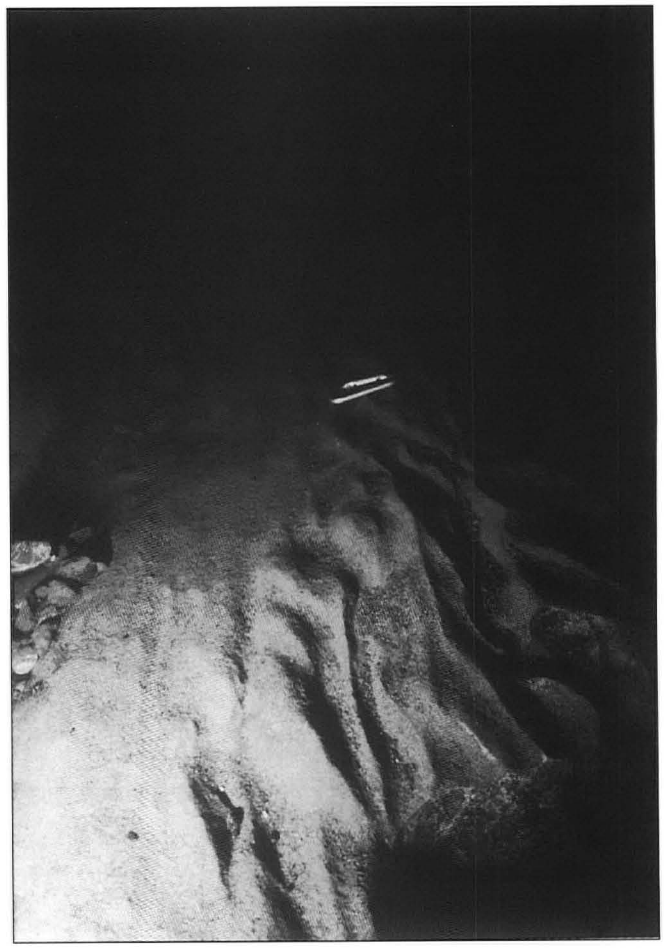

Figure 3. Channel karren-like features in Joint Hole main passage, Chapel-le-Dale, North Yorkshire showing sand grade sediments in the grooves.

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GEOLOGICAL FACTORS THAT HAVE INFLUENCED THE DEVELOPMENT OF MARBLE ARCH CAVE, CO. FERMANAGH, NORTHERN IRELAND

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Marble Arch is the longest cave system (>4,500m) in the Cuilcagh karst of County Fermanagh, and the sixth longest in Ireland (Kelly & Jones, 1995). It is named after a natural rock bridge, the Marble Arch, that forms part of a karst window complex at the present resurgence. Both names are misleading, as the nearest outcrop of marble (Dalradian Supergroup) is some 50km to the northwest. In fact, the Marble Arch is formed within rocks of the Dartry Limestone Formation, which is part of the Dinantian (Lower Carboniferous) succession of northwestern Ireland. Much of the Dartry Limestone Formation comprises mud mound limestones, previously termed Waulsortian (Lees, 1961 & 1963, Schwartzacher, 1961 and Lees *et al.*, 1985), that have a maximum thickness of about 340m. Each mound initially grew by the accumulation of micrite mud without a skeletal reef-like framework, and as such the lime mud could accumulate only below storm base. As the sediment of the Dartry Limestone Formation began to accumulate, tectonic activity lowered the sea floor rapidly below the photic zone, dramatically reducing carbonate production and nearly 'drowning' the mound accumulations. To compensate for the increasing depth, framework-building organisms developed individual mud mound centres upwards as they attempted to regain the photic zone. In the process, a submarine topography with highs up to 100m above the mean sea floor level was formed. Within the stratigraphy the near drowning of the Dartry Limestone mud mound accumulations is recorded by a thin (to 35cm) carbonate shale intramound horizon some 30m above the base of the formation. From sinks to rising the Marble Arch cave system traverses almost all of the mud mound sequence. However, lithological guidance of conduit inception is observed only where flow has intersected the intramound horizon. Faults and fractures have guided all other conduit growth. The guiding roles of the tectonic framework and the intramound horizon are considered in terms of the conduit inception and development sequence, and the latter is considered in the context of the overall evolution of the Irish landscape.

ORDER AND DISORDER IN THE KARSTS AND CAVES OF CENTRAL SCANDINAVIA

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The Caledonide nappes of central Scandinavia lie in a descending sequence from the Atlantic coast of Norway to the Caledonide thrust front, some 200km to the east in Sweden. To determine possible regional trends, the study area was subdivided into 20 zones on a tectono-stratigraphical basis. Metacarbonate outcrops occur in most nappes in the study area, but their number, mean length, mean area and angle of dip generally decline as the nappes are descended. Many metacarbonate outcrops in the western part of the area are close to vertical and commonly occur as long, narrow, north to south aligned, "stripe karsts". Karst caves have formed in all carbonate-bearing nappes down to the lower Køli Nappes. A provisional classification of karst as *Vertical stripe karst, Angled stripe karst* or *Non-stripe karst* is proposed. Caves of all complexities from a single linear passage to a complex multilevel network occur in all karst types, but distinctive suites of internal morphological features can be recognised for each. Caves in vertical stripe karst appear to have features similar to those in strictly horizontal sedimentary limestones, within the confines of their narrow containing outcrops. The number of caves and the total cave dimensions in each zone appear to show no systematic trend when normalised against the total *length* of zonal carbonate outcrop. The vertical distributions of the carbonate outcrops and their cave entrances are essentially random within the constraints of the local topography, and it seems that cave dimensions are not related to contemporary catchment areas. The vertical ranges of cave systems are always much smaller than the vertical ranges of the containing carbonate outcrops. It is tentatively suggested that caves in *vertical stripe karst* have formed entirely within an upper zone of fractured rock that has a maximum thickness of 50m. It is further suggested that as cave dimensions and their internal morphologies show few systematic trends across the zones, then similar cave inception, cave development and cave removal processes operate, and have operated, across the whole study area.

SUB-SURFACE RADIO LOCATION AT SKIN-DEPTH DISTANCES

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Several techniques of sub-surface radio-location all rely on a VLF magnetic dipole producing a quasi-static field. However, at distances approaching a skin depth, the field lines depart from this simple model resulting in inaccurate depth and position estimation. This paper describes a technique for increasing the accuracy of radio-location at large distances.

Sub-surface radio-location has application in the mining industry, and in cave rescue, cave surveying and civil engineering. A typical procedure is to place a horizontal transmitter (vertical magnetic dipole) underground and to calculate its position by making several measurements of field direction and/or magnitude using a receiver on the surface. Techniques have been devised that allow the transmitter to be tilted by an unknown amount (the so-called "dead body" problem). However, these systems still assume that the receiver lies in the near-field, and they may require cumbersome 3D frame antennas to measure field magnitude and direction.

At distances approaching a skin depth, signal strength and field-angle methods become increasingly inaccurate - e.g. at two skin depths the error approaches 20%. However, for best signal/noise ratio (SNR) it has been shown that the field distance should be roughly three skin depths. A location technique that did not depend on near-field behaviour could take advantage of this and, by careful choice of frequency, we could optimise SNR or antenna size.

Ideally, with known ground conductivity, a full application of the field equations would suffice. In practice, conductivity is unknown and the field equations do not provide a solution. Nevertheless, this paper will present an algorithm which, WITHOUT knowing conductivity, results in a depth error of under 1% at two skin depths. This has been confirmed by simulations and by practical tests at 200m depth using a 4kHz beacon. Other enhancements to the basic radio-location procedure will be described. Instead of using a 3D antenna, two co-axial solenoids can measure magnitude and gradient of the vertical field component which are required for the new algorithm. The use of a stationary antenna system means that ultra-low bandwidth receivers can be used, to give an increase in SNR.

This new algorithm allows radio-location to be extended to regions where far-field effects distort the field lines and make conventional location difficult. Further simulations are planned for inhomogeneous ground, together with practical tests using a wideband VLF channel-sounder. The task of verifying the algorithm analytically has not yet been attempted.

CARBON FLUX AND AQUIFER EVOLUTION IN THE SOUTH CENTRAL KENTUCKY KARST

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The geometries of carbonate karst aquifer "plumbing systems", and the rates at which they evolve, depend on the fluxes of water and CO_2 through them. A one year, high temporal resolution study of flow and carbonate chemistry within the humid-subtropical Mammoth Cave System's Logsdon River quantifies significant variations in these fluxes over storm and seasonal time scales. Undersaturated storm waters dissolve rock within a 25-30m-thick flood zone. Waters were only undersaturated, and thus capable of dissolving the aquifer framework, 31% of the year. Rates of aquifer evolution are thus strongly influenced by time-varying processes. Although flood conditions occur during a small percentage of the time, they dominate chemical passage enlargement. Of the $7.8x10^3 \pm 1.9x10^3$ kg ha^{-1} of total inorganic carbon leaving the river's $25km^2$ catchment during the year, 1% entered the aquifer as recharge, 57% was derived from carbonate mineral dissolution, and 42% was produced by biological activities. The inorganic component of the atmospheric "young" CO_2 sink was $3.4x10^3 \pm 8.5x10^2$ kg ha^{-1} yr^{-1}. A dual approach, coupling quantitative modelling with calibration and refinement of the models by careful measurement of processes within real karst aquifers, provides a framework for developing a comprehensive understanding of karst system behaviour.

NEW OBSERVATIONS ON THE HYDROGEOLOGY OF THE NORTHERN WHITE PEAK

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Previous research on the hydrology of the northern White Peak has focused on the margins where streams that have their headwaters on Namurian strata sink after flowing onto the Carboniferous Limestone. The majority of the known cave passage is associated with these sinks or the resurgences to which they drain. Away from the margins there is surprisingly little evidence that there has ever been any concentrated recharge, with few large dolines. Hence, it has been assumed that this area has been dominated by diffuse recharge draining to a poorly integrated fracture / fissure system. The presence of a relatively large number of springs, most of which are characterised by a low, fairly constant discharge and high concentrations of dissolved carbonates supports this assumption. However, there are a small number of relict passages, such as the large passages of Water Icicle Close Cavern, that suggest things may not be quite so simple and that in some areas at least there have been periods of conduit / cave development in the past. Not unrelated is the question of how the driving of lead mine soughs have changed the hydrology of the area. A small number of soughs discharge a large flow of water and it is by no means clear where this was discharged before the soughs were driven. The situation has, regrettably, not been clarified by two recent water tracing experiments that yielded somewhat surprising results, or rather non-results, and it is suggested that a great deal of further work will be needed before the hydrogeology of this complex area can be understood.

RECENT ARCHAEOLOGICAL, SPELEOLOGICAL, AND PALAEOENVIRONMENTAL RESEARCH IN THE CAVES OF THE MAKAPANSGAT VALLEY, SOUTH AFRICA

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Every year since the summer of 1997, the Makapansgat Middle Pleistocene Research project, under the direction of Dr Anthony Sinclair, of the University of Liverpool, and Patrick Quinney, of the University of the Witwatersrand, has been undertaking studies into all aspects of archaeological research in the Makapansgat area of the Northern Province, S. Africa. During this period a number of important new sites have been discovered of archaeological, palaeo-anthropological, or purely speleological interest. The majority of these are open stone tool sites but a good number are the mined remnants of fossil bearing palaeocaves, and also previously unknown more modern caves.

This paper is an overview of the recent new cave and palaeocave discoveries as well as re-evaluations and the application of new techniques at old well known sites, such as the Limeworks Australopithecine palaeocave. In the summer of 1999, samples were taken from 4 cave sites in the valley in an attempt to date the sites by reversal magnitostratigraphy. Samples where also taken from these four and one other cave site, to undertake a magnetic susceptibility study into various aspects of the caves and their exterior environment, including the presence and possible utilisation of fire by hominids.

STRATIGRAPHICALLY-GUIDED DRAINAGE IN THE SLAUGHTER CATCHMENT, FOREST OF DEAN, UNITED KINGDOM: A CONCEPTUAL MODEL

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Lying in the northwest of the Forest of Dean, the Slaughter Resurgence is a major though in some ways paradoxical rising, fed by a web of allogenic inputs and background autogenic drainage east of the River

Wye. It is clear that the conduit system "behind" the Slaughter Resurgence is of fundamental importance to the modern underground drainage of a wide area. However, the relationships between this system and the local geology, and between the system and four other (lesser) resurgences are less obvious. Based upon a broad knowledge of the geology, the confirmed drainage connections and the known cave passages, a conceptual model of one possible set of relationships between geology and underground drainage is described.

A MULTI-PROXY STUDY OF SPELEOTHEMS

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Cave speleothems offer the potential to provide an improved palaeoclimate and palaeoenvironmental record as, unlike many other terrestrial records, their cave environment protects them from destruction by surface erosion, allowing long sequences to be preserved. Speleothems provide a climatic signal by the timing and rate of their growth and also through the palaeoenvironmental signals they contain including oxygen and carbon isotopes, but of particular interest in this study, are the pollen and organic acids trapped in the speleothem calcite. Conventional sources of such organic remains such as lake and bog sediments are constrained by the fact that they can only be dated back to about 40Ka by ^{14}C dating. Beyond this limit the Middle Pleistocene terrestrial record has not been precisely dated, it is based on faunal and floral correlations.

Speleothems on the other hand, are particularly well suited for dating through the application of U-series thermal ionisation mass spectrometry back to 350Ka BP. This makes them especially advantageous for palaeoclimate studies, as it allows an absolute timeframe to be determined for the records they contain, specifically, in this case, pollen and organic acids. The technique of extracting pollen from speleothems to study palaeoenvironmental change is relatively new in Britain where traditionally wetland sediments have been analysed, but elsewhere studies have shown these pollen spectra to be representative of contemporary surface vegetation. The fluorescence properties of organic acids in the speleothems are also being studied as a complementary record to the pollen. If climatically induced variations in the rate of organic matter breakdown are reflected in changes in the composition of organic acids in the soil and their fluorescence properties, then a climatic signal may be preserved.

U-Th dating of speleothems in the current study has shown growth to have taken place during both interstadial and interglacial periods, ranging in age from about 120Ka to 8Ka. The pollen spectra obtained from interglacial samples (both the last interglacial and early in the Holocene) comprise typical assemblages with a wide range of thermophilous trees and shrubs being represented (including *Quercus*, *Fraxinus*, *Alnus*, *Corylus* and *Hedera*). Warmth-loving species are also present in a flowstone that has been dated at c. 72-66Ka, suggesting that the climate in such interstadial periods was warmer than previously thought. These pollen records are complemented by the organic acid fluorescence records of soil humification.

The analysis of pollen and organic acid records from cave speleothems is a significant new approach in palaeoclimate and palaeoenvironmental research in Britain. It provides palynological records for time periods for which few suitable sediments are available (specifically interstadials), and for which precise absolute ages can now be obtained through U-Th dating.

THE KARSTIFICATION OF THE PERMIAN STRATA EAST OF LEEDS, UK

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The outcrop of Permian strata to the east of Leeds exhibits a variety of karstic and palaeokarstic features. The area is crossed by an extensive network of dry valley systems and lacks surface water. Two different karst types are recognised: dolomite and dolomitic limestone karst and gypsum karst. Dolomite and dolomitic limestone karst is characterised by small isolated dolines whereas gypsum karst is characterised by large-scale dolines, many occurring in groups. An appreciation of the karstic nature of parts of the Permian outcrop is becoming increasingly important because of pressure from development and waste disposal.

ANNUAL RESOLUTION SPELEOTHEM PROXY RECORDS OF NORTH ATLANTIC CLIMATE FOR THE LAST 3,000 YEARS FROM UAMH AN TARTAIR, SCOTLAND

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Luminescent organic matter in stalagmites may form annual bands, allowing growth rate to be precisely determined. Stalagmite growth rate may be controlled by climate, so annual bands can be used to derive long precipitation records. A continuously banded stalagmite from Uamh an Tartair, a cave in NW Scotland, was used to provide a 1100 year annual growth rate record. Growth rate of this stalagmite was calibrated against historical meteorological records and demonstrated a strong correlation with mean annual P/T. Given that temperature has varies by ~ ±1 °C over the last several hundred years, we use stalagmite growth rate to reconstruct mean annual precipitation. The location of the cave means that precipitation is closely linked to the North Atlantic Oscillation, for which a record is also derived. This suggests that changes in the North Atlantic Oscillation state was an important control on European climate over the past millennium. Ongoing research is extending this record by the analysis of three additional stalagmites from the site dating back to at least 3,600 years BP.

POSTER PRESENTATIONS

HUMAN REMAINS FROM CLOGHERMORE CAVE, COUNTY KERRY, IRELAND

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Cloghermore Cave was surveyed in the 1980s but it is only recently that the archaeological importance of the extensive deposits of animal and human bone in the cave has been recognised. In 1999 the Irish Heritage Service financed a programme of archaeological investigation in the cave, during which a concealed entrance to the cave was discovered with evidence of usage in antiquity. Inside the cave the main surface concentrations of bone were retrieved and some of the principal areas of bone deposit were excavated. Radiocarbon analysis of a single human bone specimen gave a date of 800 - 1000 AD, and further dating of animal and human remains is in progress. The human remains include individuals of all ages and both sexes, and the estimated minimum number of individuals MNI in the whole assemblage is 18. Unlike Britain, there are several examples in Ireland of the use of caves for the deposition of human remains in the early medieval period, a practice that is also alluded to in some of the Irish heroic legends.

RECONSTRUCTION OF BOMB ^{14}C TIME HISTORY RECORDED IN FOUR MODERN STALAGMITES BY AMS MEASUREMENTS – IMPORTANCE FOR CARBON TRANSFER DYNAMICS

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Understanding carbon transfer dynamics in karst areas enables a better interpretation of the carbon isotope content measured in stalagmites ($\delta^{13}C$, ^{14}C) as well as an estimation of the dead carbon proportion (dcp), which allows a better understanding of the dissolution processes and correction of the ^{14}C speleothem ages. Powder samples have been microdrilled on vertical stalagmite polished sections. AMS ^{14}C measurements can be made with only 10 mg of $CaCO_3$, which corresponds, for fast growth rate stalagmites, to 1 or 2 years of deposition. The chronology is given by 1) laminae counting when these are regular enough to suppose that they are annual (visible or luminescent under UV light : Fau-stm14, Han-stm5, SU-96-7; 2) by a specific mark (in the case of Pos-stm4 where we found a black carbon layer due to the explosion of a gas storage in the cave in 1944). This study yields the following results. Firstly, that the ^{14}C activity of the stalagmites is sensitive to atmospheric ^{14}C bomb input and this sensitivity can be characterised by two simple factors: 1) the amplitude damping effect (D) which is the percentage of amplitude attenuation in the stalagmite time series when compared to the atmosphere time series; 2) the inertial effect (I) which is the time delay, in years, between 1964 (date of the atmospheric ^{14}C peak) and the maximum of ^{14}C activity observed in the stalagmite time series. D and I are linked together and characterise the sensitivity of the local karst system to the carbon transfer into speleothems. Secondly, that the ^{14}C activity of the stalagmite can been modelled using atmosphere ^{14}C activity time series, isotope fractionation processes and three components of soil organic matter; the correlation coefficient R^2 between modelled and measured values is 0.99. Finally, thanks to the model, the dead carbon proportion from the old SOM degradation has been estimated at 1%; dead carbon due to the limestone dissolution is between 9.0 and 12.2% ±1.5 % for open system conditions (Fau-stm14, Han-stm5 and Pos-stm4) and close to 40% for closed system conditions (SU-96-7). This work demonstrates that most of the carbon transfer dynamics is controlled in the soil by SOM degradation rates; the shape of the modelled curves ($a^{14}C$ and $\delta^{13}C$) are already determined by the combination of the three different SOM components. The time delay between atmosphere and stalagmite ^{14}C activity peaks shows that there is an inertial effect of several years (i.e. > 10yr), which is important to know when interpreting other chemical analyses made in annual laminae of speleothems. The ^{14}C activity time series of modern stalagmites brings new information about the carbon transfer into karst and highlights the role of the soil in the dynamics of the transfer, such ^{14}C time series can bring valuable information for those who are studying the dynamics of soil.

ADAPTIVE DIGITAL COMMUNICATIONS FOR SUB-SURFACE RADIO PATHS

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Low frequency sub-surface radio is used for communications with miners and cavers. The signal attenuation is dependent on frequency and on the electrical conductivity of the ground. In addition, the optimum frequency for communications is dependent on depth below the surface; and on the degree of noise and co-channel interference. An adaptive communications system makes use of a channel-sounding technique by transmitting a wideband signal and deriving the signal/ noise ratio (SRN) as a function of frequency. The communications system can thereby alter its transmission frequency, and other parameters, to optimise SNR under different conditions. The same principles are relevant to applications in sub-surface radio location, archaeology and geophysics.

LOW-COST IMPLEMENTATION OF A SPEECH COMPRESSION SYSTEM

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A method is described for compressing analogue speech waveforms to reduce the peak/mean ratio without adversely affecting the speech intelligibility or acceptability. Equipment is currently being constructed to allow quantitative measurements to be made of this method. One proposed application for this type of speech processing is in communications to cavers, pot-holers and miners where a low SNR is combined with high ambient noise. Other applications would include public address systems and deaf-aids.

SUBFOSSIL AMPHIBIAN AND REPTILE FAUNAS FROM BRITISH AND IRISH CAVES

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Historically, very little work has been carried out on subfossil amphibians and reptiles (herpetofaunas) from caves in the British Isles, despite these being intrinsically rich sources of their bones. Herpetofaunal remains are often very abundant in caves, sometimes more so than other vertebrates, and this large volume of previously untapped data has important implications for palaeoenvironmental reconstruction and biogeography. Recent work has identified Late Pleistocene and Holocene amphibian and reptile assemblages from caves in Devon, Somerset, Herefordshire, Derbyshire, Staffordshire, Lancashire, Dyfed, Clwyd and Highland Region. Caves in Wales and southwest England show that at least seven species reached Britain during the Lateglacial. Very soon after their certain extinction during the arctic Younger Dryas, thermophiles such as natterjack toad (*Bufo calamita*) were amongst the first postglacial immigrants in an open landscape. Direct AMS radiocarbon dating gives detailed insights into the timing of immigration and biogeographical history during the Lateglacial and Holocene.

A SPELEOTHEM PALAEOENVIRONMENTAL RECORD FROM LANCASTER HOLE, YORKSHIRE

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Two flowstones obtained from Lancaster Hole, Yorkshire have been analysed for pollen and organic acids and dated by TIMS U-Th dating. Such records may be long ranging due to the protective cave environment in which they are preserved, and have the particular advantage over conventional organic pollen bearing sediments in that they can be dated much further back in time (up to 350Ka) than radiocarbon dating has allowed.

In the current study, pollen has been extracted from the flowstones, sub-sampling according to the growth periods shown by the TIMS U-Th dating. The pollen is well preserved, at concentrations of 1-5 grains per gram of calcite. The earliest period of growth has been dated to 132 to 127Ka, during the last interglacial. The pollen obtained from this section is typical of interglacial conditions, the spectra including such thermophilous species as oak, alder, ash, and hazel.

The pollen records obtained from the later growth phases, dated to interstadial periods 5c, 5a and 3 are significant, as such pollen records from organic sediments during the last cold period are rare. The two flowstones overlap at around 101Ka and their pollen spectra are similar in character, including, most notably, oak, ash and hazel, along with a wide range of herbs. The pollen spectra from stages 5a and 3 also have oak represented, along with some alder and hazel. The presence of such thermophilous species during interstadial periods indicate that the climate at these times may not have been as severe as previously thought, and such records compare well with those obtained from long French pollen sequences covering the same time periods.

The luminescence characteristics of the organic acids in both samples have been analysed and suggest significant variations in the overlying soil and vegetation characteristics over the last 130Ka, with significant variation between each growth period. The organic acid signals for the period when both flowstones overlap (101Ka) are not identical (one indicating well humified soils the other more wet conditions) and this is probably due to the extreme local nature of this signal.

THE ECOLOGY and CONSERVATION OF AQUATIC INVERTEBRATES IN THE PEAK-SPEEDWELL CAVE SYSTEM, CASTLETON, DERBYSHIRE

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The aquatic invertebrate community of the Peak - Speedwell cave system, which lies within the Castleton Caves SSSI, has been studied through a programme of monthly sampling over a two year period. The data have been used to assess the faunal biodiversity and the conservation value of the aquatic communities. This is of particular importance as the ecological value of the cave SSSI has not previously been assessed. The impacts of contemporary anthropogenic activities, principally agricultural practices, quarrying and recreational caving, are discussed in relation to their potential to degrade the fragile subterranean ecosystem.

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Forum

Readers are invited to offer thesis abstracts, review articles, scientific notes, comments on previously published papers and discussions of general interest for publication in the Forum of Cave and Karst Science.

All views expressed are those of the individual authors and do not necessarily represent the views of the Association unless this is expressly stated. Contributions to the Cave and Karst Science Forum are not subject to the normal refereeing process, but the Editors reserve the right to revise or shorten text. Such changes will only be shown to the authors if they affect scientific content. Opinions expressed by authors are their responsibility and will not be edited, although remarks that are considered derogatory or libellous will be removed, at the Editors' discretion.

CORRESPONDENCE

Comments on the Paper "A history of cave exploration in the Northern Pennines, United Kingdom, up to 1838", by S A Craven.

Dear Editors,

I read Stephen Craven's paper in the August 1999 Transactions *[Cave and Karst Science]* (Craven, 1999) with interest, as I am fortunate enough to possess a copy of the second edition of West's Guide to the Lakes (West, 1780). This was the first edition to include the Addenda containing the articles by John Hutton, Adam Walker, *et al.*

It would also seem that this was the first time John Hutton's *"A Tour to the Caves"*, appeared in print. The Preface to West's second edition includes the words *"And a friend of the publishers has communicated an original article called A Tour to the Caves, which it is hoped will not only entertain, but be found particularly accurate as a matter of fact"* (West, 1780, p.iii). The paper itself is titled *"A Tour to the Caves of the West-Riding of Yorkshire in a Letter to a Friend Now First Printed"* (West, 1780, p.238). The underlining is mine.

This suggests to me that Hutton's paper first appeared in this edition of West's Guide to the Lakes, rather then as a work in its own right in the same year, as implied by Dr Craven (Craven, 1999, p.54). I suspect that the publisher, Richard and Urquhart of London, commissioned John Hutton to write his account specifically for incorporation into the new edition of West's Guide, but having read it, realised that the result also merited a separate publication.

In the same edition is reprinted the article by Adam Walker entitled *"A Description of Some Natural Curiosities in the Western Edge of Yorkshire"*. This states definitively that the article was first published in The General Evening Post of 25 September 1779 (West, 1780, p.232), as suggested by Dr Craven.

Incidentally, Dr Craven (Craven, 1999, p.54) does Adam Walker a disservice when he says that the following passage is erroneously describing Chapel-le-Dale (West, 1780, p.235):

> *"In our road to Settle we met with the Ribble, which tumbles into a deep cavern, and is lost in the bowels of the mountain for upwards of three miles, when it issues again into daylight, and with a continued roar makes its way to Settle."*

The three pages preceding the paragraph containing the extract, are devoted to an impressively accurate description of Hurtle Pot, Jingle Pot, and Weathercote Cave, together with the salient features of the hydrology of the valley. Walker was well aware that the Chapel-le-Dale water emerged at God's Bridge and flowed on to Ingleton before joining the Lune (West, 1780, p.234).

The words in question follow an account of an ascent of Ingleborough from Chapel-le-Dale, which he undertook immediately after his exploration of Weathercote Pot. A more logical interpretation of the passage is that he is describing Alum Pot, which he may have encountered on a descent over Simon Fell. Alternatively, he could have paid a visit to Alum or Hull Pot on his way to Settle. Either way, the description should simply be regarded as one of a number of additional highlights in an article that is devoted primarily to descriptions of Chapel-le-Dale and Malham, and **not** as a description of Chapel-le-Dale.

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Stephen Craven responds:

I have looked at Mr Gardner's comments, and thank him for them. Since writing the paper I have acquired a copy of West's 2nd Edition (1780) *Guide to the Lakes*, and confirm the comments in the Preface.

However, I beg to differ with Mr Gardner's interpretation of Adam Walker's description of the River Ribble north of Settle. Ordnance Survey sheet 90 (Wensleydale) confirms my memory of the Ribble flowing above ground north of Settle. It does **not** flow underground for more than 3 miles. Thus, I still maintain that Walker confused Ribblesdale with Chapel-le-Dale.

Dear Editors,

Comments on the Report "Speleothem Deterioration at Cango Cave, South Africa", by S A Craven.

Craven's article (1999) deals mainly with speleothem deterioration in the two proximal chambers, which constitute the main tourist attraction of the Cango Caves. That the formations in this part of the cave are dominantly inactive, dull and corroded, was first noticed a long time ago, but was investigated scientifically only recently. King (1958) observed the corrosion, as did Marker (1975), who attributed it to several phases of dissolution due to fluctuations of the water-table during the Tertiary. After having identified the mondmilch-like material coating the speleothems as apatite, Martini (1987) suggested that at least a great part of the decay was due to bat guano, a widespread phenomenon in a number of caves in southern Africa (Martini and Kavalieris, 1978). Craven (1994) paid little attention to the mineralogical aspect and proposed that the damage is due mainly to human alteration of the micro-climatic conditions. In 1998, during several visits to the cave, the author drew Craven's attention to the importance of the apatite coatings and, consequently, he wrote the article that is the object of this comment. Although his article presents a fair review of the subject, a few obvious flaws must be addressed.

Referring to the apatite coating, Craven uses the term *"phosphate material"*, which is obviously not very informative. To justify his choice of term, he quotes Fleischer and Mandarino (1995), who recommend implicitly that the term apatite is not used, but suggest instead the use of the various end-member names of this well defined mineral group (fluorapatite, carbonate-hydroxylapatite, etc.). However, these end-members differ very little from each other and, whereas the recommendation is theoretically correct, it is impractical. Indeed, it is easy to identify apatite by X-ray diffraction, but to further ascertain the mineralogical composition is more difficult and in some cases virtually impossible. This is especially true for many cave occurrences, where the apatite is generally microcrystalline and impure, commonly displaying variable composition within a single sample. It must be remembered that recommendations of this type are not absolute and that the final word should be a reflection of the specific usage. For instance, the term apatite is still used widely by petrologists. A recent example is found in an article by Tapper and Kuehner (1999), published in a prestigious mineralogical review. It is clear that Craven should have used the word "apatite".

A more important point to discuss is Craven's model for the evolution of calcite deposition in the proximal chambers. He visualizes that originally the speleothems were coated only with "phosphate mineral" but, when calcite deposition resumed after bats abandoned the cave at the end of the 19th century, new calcite covered the apatite. After 1945, due to a considerable increase in the number of visitors, the recent calcite was re-dissolved due to a rise of the CO_2 level in the cave atmosphere, thus re-exposing the apatite.

This model is not consistent with descriptions Craven quotes from historical sources. These indicate that during the early 19th century the speleothems were generally active and glistering, which is practically no longer the case today. This evidence formed the basis of his previous model (Craven 1994), which suggested that speleothem corrosion was the result of two centuries of human visits. Nevertheless, he does not reject these historical observations, but nor does he discuss them, even though they conflict with his model. Although Craven does not describe recent deposition of calcite on apatite, it seems that such deposits do occur in rare spots, from the entrance to the deepest part of Cango I (Martini, *personal observation*). The thickness of post-apatite calcite varies considerably from place to place, from less than one millimetre to several tens of centimetres. In the latter case the calcite is certainly prehistoric, whereas in the former case it could possibly be recent. This suggests that the covering of apatite by calcite is not necessarily human related, but is linked simply to natural variation of the intensity both of ground water seepage and guano accumulation. Both processes may, or may not, occur simultaneously at different localities, as they may be controlled by very local conditions and not by regional effects, such as climatic variations.

Craven's model of re-solution of a very recent calcite coating is still more hypothetical. Here too, he neither describes field evidence nor provides references to sub-contemporaneous observations to support his idea. The description by King (1958), dating not later than the early nineteen-fifties, suggests that the state of the speleothems in the proximal chambers was the same then as it is today. He observed recent deposits of calcite only *"in a few instances"*. A widespread neo-deposition of calcite, active from the end of the 19th century to 1945, therefore seems unlikely.

It is doubtful that conditions for calcite dissolution are met at present. Due to the proximity of the cave entrance the atmosphere in these chambers is dryer and has a lower CO_2 level than the air deeper in the cave. CO_2 levels range from less than 0.1% to 0.6%, with the latter value being reached only when the number of visitors is exceptionally high (Craven, 1996; Grobbelaar, 1996). Considering that in the deeper parts of the cave CO_2 levels are higher (>1%) and that calcite is nevertheless still being deposited (e.g. Martini, 1987), it appears very unlikely that calcite is being dissolved in the proximal chambers. On the contrary, the conditions outlined above suggest that enhanced deposition is taking place, as is evidenced by the fact that, where seepage still occurs, rapid calcite deposition is observed (Craven, 1996, 1999). Where no new deposition is observed, which is in more than 90% of the cases, there is no seepage and the flowstone is dull and dry. Thus, a deficiency of drip water is the probable explanation for non deposition of calcite.

In conclusion, it is likely that the state of speleothem degradation in the two proximal chambers is dominantly natural and has not altered drastically during the past two centuries, with the exception of the removal of fragile speleothems. The widespread corrosion and apatite coatings, commonly several centimetres thick, did not form in a few decades, but during many centuries. The historical reports of *"glistering formations"* were probably exaggerated, as was commonly the case at a time when caves were still regarded as a strange and dreadful world.

Lamp flora, graffiti and vandalism, especially in the narrow deepest part of the cave, are the most important causes of anthropogenic damage in Cango Cave. The most urgent conservation issue is the protection of the undeveloped sections, that is Cango II and III, which are by far the most beautiful. A thorough quantitative assessment of the cave meteorology and imposition of a strict visit control policy can address this issue.

ACKNOWLEDGEMENTS

The text was read critically by P Wipplinger of the Council for Geoscience.

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Dear Editors,

Speleothem deterioration at Cango Cave, South Africa: Reply to comments by J E J Martini.

Thank you for the opportunity to reply to Dr Martini's comments on my postulated mechanism for the deterioration of the speleothems in Cango Cave.

Dr Martini takes exception to my use of the phrase *"phosphate material"* to describe the matt, powdery, coatings on the speleothems, and prefers the word *"apatite"*. I made it clear in my paper (Craven, 1999) that I wished to avoid a semantic argument, and still do. It does not matter, for the purposes of my hypothesis, whether the powder is called *"apatite"*, *"fluorapatite"*, *"carbonate-hydroxylapatite"*, or *"phosphate material"*. Indeed, Dr Martini concedes that they *"...differ very little from each other..."*. Hill and Forti (1997) confirm that, *"... most phosphate minerals are ... of interest only to the mineralogist..."* and, like Fleischer and Mandarino (1995), they do not allow apatite the status of a mineral. I will, therefore, leave the mineralogists to debate this semantic problem.

Dr Martini's further comments are welcomed, because they make an important contribution to the debate about the causes of the speleothem deterioration in the Cango show cave. I did not intend to imply that my phosphate material hypothesis is the only mechanism involved, and I apologise for not having made that clear. Speleothem deposition and dissolution is a reversible, and multi-factorial, process; thus, no one variable must be considered in isolation. I agree with Dr Martini that several different processes have taken place at different times and in different parts of the Cave.

Dr Martini questions the reliability of the historical sources, some of which may or may not be exaggerated. Nevertheless, they are the only nineteenth century records available, and therefore have to be considered. Thus, on 16 September 1808 were reported: *"eternally trickling water"*, *"water came when one* [stalactite] *broke ... off"*, and *"the continual drip"* (Faure, 1824). On 08 September 1816 were present, *"various baths or cisterns of water as clear as crystal"* (Thom, 1816). In 1822 there were *"several basins of clear water"* (Thompson, 1823); on 06 December 1830 *"troughs full of perfectly clear cold water which had percolated through the strata above"* (Harrison, 1830). It is worth remembering that December is in the middle of the hot, dry, season in the southern Cape. Harrison was not writing with intent to publish, and he has a reputation for a *"high standard of accuracy"* (Crail, 1958).

In 1840 the roof of Botha's Hall was *"covered with innumerable small and delicate icicle-looking stalactites, each with a huge drop of pure water hanging from their extremities"* (Sherwill, 1842).

I will not encroach further upon your space with additional reports of the water in Cango Cave during the nineteenth century. If the water had not been present, the several visitors would have had no evidence to exaggerate.

As Dr Martini pointed out, King (1958) reported that the speleothems are, *"...not generally in a state of active growth; apparently they flourished when the quantity of water percolating into the Caves was greater"*. Nevertheless, several of my elderly patients, knowing of my interest in Cango Cave, have spontaneously mentioned their visits to the Cave in the 1940s, 1950s and even 1960s. Their independent memories are of a wet Cave with moist speleothems. I accept that this is anecdotal information. The inescapable evidence shows, however, that Cango Cave is today much drier than it was in the nineteenth century, and probably than it was in the middle of the twentieth century.

The conclusion to be drawn is that several factors are operating to bring about the deterioration of the speleothems, none of which can be discussed in isolation (Craven, 1994). These include:

1. Deficiency of drip water, as mentioned by Dr Martini, who does not speculate on the causes therefor. It is unlikely to be due to reduced rainfall (Craven, 1988). A more probable explanation, to which I alluded in my recent paper (Craven, 1999), is:

2. Vegetation changes overlying the Cave. The nature of the original vegetation in the Cango Valley, before the settlers disturbed the veld, is unknown. In 1808 the entrance was surrounded by *"bullrushes, bushes, shrubs and ... high forests"* which sheltered *"swallownests, bees, leopards, porcupines, dassies and other wild animals"* (Faure, 1824). This description is confirmed by an early nineteenth century watercolour (Von Molendorf, n.d.), another watercolour of 1872 (Michell & Michell, 1872) and a postcard from the 1890s (Ravenscroft, n.d.). All three illustrations are remarkably similar, and reveal little change during half a century. Postcards dating from the 1930s, 1960s and 1990s show that the vegetation has since become stunted.

Other factors to be considered are:

3. Carbon dioxide changes within the Cave. Although this has been treated elsewhere (Craven, 1996), it is topical because of arguments, which I believe to be specious, currently being promoted by the Cave Management (Gerstner, 1999) with the support of the University of the Orange Free State (Grobbelaar *et al.*, 1996). Other things being equal, a high CO_2 level in the Cave will cause dissolution of the speleothems. Therefore (according to the managerial argument) if an artificial entrance is driven at the end of the show Cave, the resulting ventilation will reduce the CO_2 and encourage speleothem deposition. This argument is easily refuted by noting the high CO_2 levels in Cango II and III, where the speleothems are very much alive.

It is not known whether the high CO_2 levels in the distal parts of the Cave are natural, or represent the accumulation of two centuries of visitors' expired CO_2 and burned hydrocarbons, or a combination of both. This could be investigated by collecting air and water carbon-14 samples at different places within the Cave (Vogel, 1996).

4. Temperature changes within the Cave.

5. Relative humidity changes within the Cave.

6.Air flow within the Cave. This may well have changed since 1964 when the artificial entrance was driven, with no air-tight door, immediately to the north of the natural entrance. At some time in the past the gate on the natural entrance was covered with a fibreglass screen, thereby restricting air flow.

The object of these comments is to reply to Dr Martini, and NOT to write a dissertation on the various inter-related variables that contribute to the deterioration of the speleothems in Cango I. While I agree with Dr Martini that the undeveloped sections, i.e. Cango II and III, must be protected, I still believe that it is possible and desirable for some restoration to be encouraged in the Show Cave. The presence of newly deposited calcite in the Registry and in Botha's Hall shows that if the Cave environment, and that overlying the Cave, can be manipulated appropriately, within a few decades there will be a greatly improved cave. This will require long-term monitoring and applied research to identify which of the several variables are responsible for the deterioration, and for which manipulation will be feasible.

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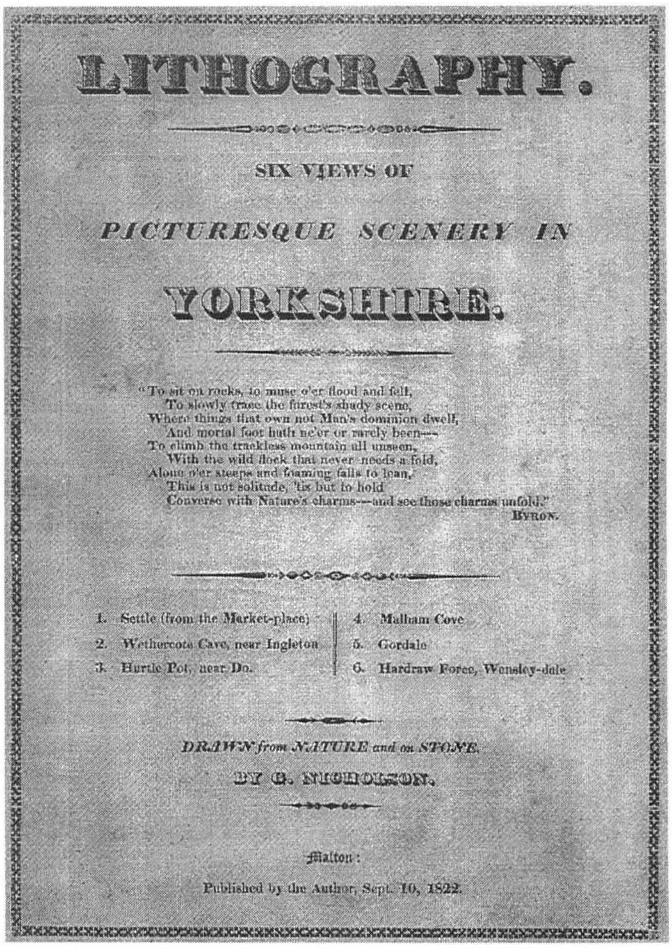
Dear Editors,

Stephen Craven's recent paper on the history of cave exploration in the Northern Pennines[1] has filled a great need. By reprinting extracts from the source materials up to 1838, he has made them available to those working on the individual caves of the region, as well as to those studying the broader development of cave exploration in England and elsewhere. Craven has combined his knowledge of the early literature and a close familiarity with the area, enabling him to suggest possible identification of such places as "Johnson's Jacket Hole".

But, even Craven has not been able to find an original copy of George Nicholson's 1822 lithograph of Hurtle Pot. This is not surprising, for the British Library does not have the book in which it appears, and I too have been unable to trace one in any public collection in the UK. Nor is it listed in J R Abbey's standard reference book *"Scenery of Great Britain and Ireland in aquatint and*



LITHOGRAPHY.

SIX VIEWS OF

PICTURESQUE SCENERY IN

YORKSHIRE.

"To sit on rocks, to muse o'er flood and fell,
To slowly trace the forest's shady scene,
Where things that own not Man's dominion dwell,
And mortal foot hath ne'er or rarely been---
To climb the trackless mountain all unseen,
With the wild flock that never needs a fold,
Alone o'er steeps and foaming falls to lean,
This is not solitude, 'tis but to hold
Converse with Nature's charms---and see those charms unfold."
BYRON.

1. Settle (from the Market-place)
2. Wethercote Cave, near Ingleton
3. Hurtle Pot, near Do.
4. Malham Cove
5. Gordale
6. Hardraw Force, Wensley-dale

DRAWN from NATURE and on STONE,
BY G. NICHOLSON.

Malton:
Published by the Author, Sept. 10, 1822.

Figure 1. The front cover of George Nicholson's book.

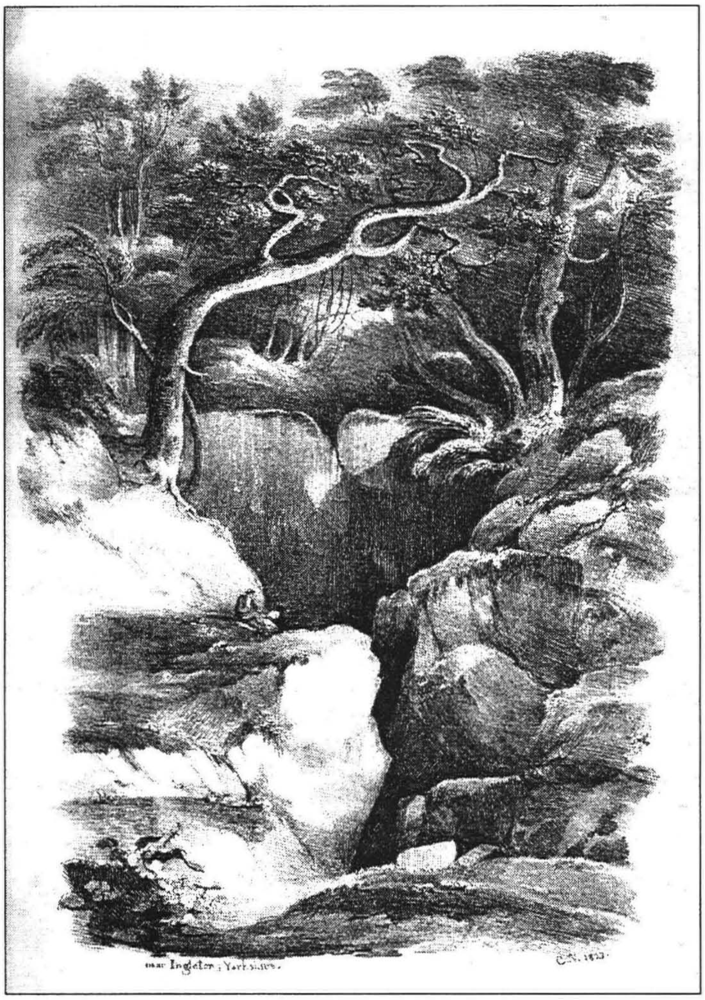


Figure 2. Nicholson's (1822) picture of Hurtle Pot.

lithography 1770 – 1860 ..."[2]. Only a poor impression of what the picture look like can be gained from the small-size modern reproductions that appeared first in a newspaper of 1959[3] (with its very coarse half-tone screen) and then, equally small and coarse, in a local booklet[4] and (reversed, left for right) in a magazine[5]. It is the earliest known picture of the cave and it deserves high quality reproduction.

Fortunately there is a complete original copy of George Nicholson's book *"Six views of Picturesque Scenery in Yorkshire"*[6], in the library of the Karst Research Institute at Postojna. The book is of large size (500mm by 350mm) and consists of a printed front cover (Fig.1) on unwatermarked wove paper, (no title page), the six lithographs on thicker wove paper watermarked 1816 on three of the six sheets, and an unprinted back cover. The third picture, of Hurtle Pot (Fig.2), is lettered *"near Ingleton; Yorkshire"* at the bottom left, and *"G:N. 1822"* at the bottom right (the "G" looks more like a "C" in most of the pictures). The picture itself measures 359mm by 252mm. It shows the entrance of the hole seen from the south side. The book now in Postojna was bought in London in 1959, for two pounds sterling.

George Nicholson (1887 – 1878) was probably the nephew and pupil of the better-known Yorkshire watercolour painter Francis Nicholson (1753 – 1844), who also produced some lithographs[7].

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SCIENTIFIC NOTE

THE UNDERGROUND FLOW OF THE RIVER SKELL, NEAR RIPON, NORTH YORKSHIRE, UK

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Carbonate, argillaceous and evaporite rocks of late Permian age crop out in a narrow belt to the east of the Pennines from Tyne and Wear to Nottinghamshire. Dissolution of evaporites in the sequence has produced a large number of dolines, which have been described mainly (though not exclusively) in the Ripon area. The dolines form a major hazard for civil engineering projects and have been the subject of a number of papers (Smith, 1972; Cooper, 1986, 1988, 1995, 1996, 1998; Cooper and Burgess, 1993; Paukstys *et al.*, 1997; Waltham and Cooper, 1998). In comparison, the karstification of the carbonate units in the Permian sequence has received little attention in the geological literature. A number of caves are recorded in the carbonate units (Brook *et al.*, 1988), though some are of tectonic origin (Lowe, 1974, 1978). Caves thought to be of dissolutional origin occur in Maltby, South Yorkshire (Ryder, 1975, 1979, 1981; Lowe, 1994) and Cresswell Crags, North Nottinghamshire (Ryder, 1975; Waltham *et al.*, 1997). Dolines occur on the carbonate units (Lowe, 1994; Murphy in press) though due to the intensive agricultural use of the soils formed on the Permian outcrop they are often quickly filled in. Dry valley systems are also a feature of the Permian outcrop, though they are believed to be formed by surface run-off furnished by the melting of a seasonal snow cover (Straw and Clayton, 1979), so may be partly periglacial rather than totally karstic landforms.

Sinking streams are rare; most water enters the aquifer by direct infiltration. However, the River Skell to the west of Ripon flows underground for approximately 2km (Fig.1) when crossing the outcrop of the Cadeby Formation (previously known as the Lower Magnesian Limestone (Smith *et al.*, 1986)). Under normal summer flow conditions the water sinks at the foot of a cliff at [SE 284691] (Fig.2) and resurges through superficial deposits near Hell Wath cottages at [SE 289699], approximately 40m lower. The sinking of the River Skell is described in the early Geological Survey memoirs covering the area (Fox-Strangways, 1873, 1908; Fox-Strangways *et al.*, 1886). Kendall and Wroot (1924) also refer to the sinking of the River Skell. They describe only half the water passing underground and place the sink at approximately [SE 282689], with the rising being

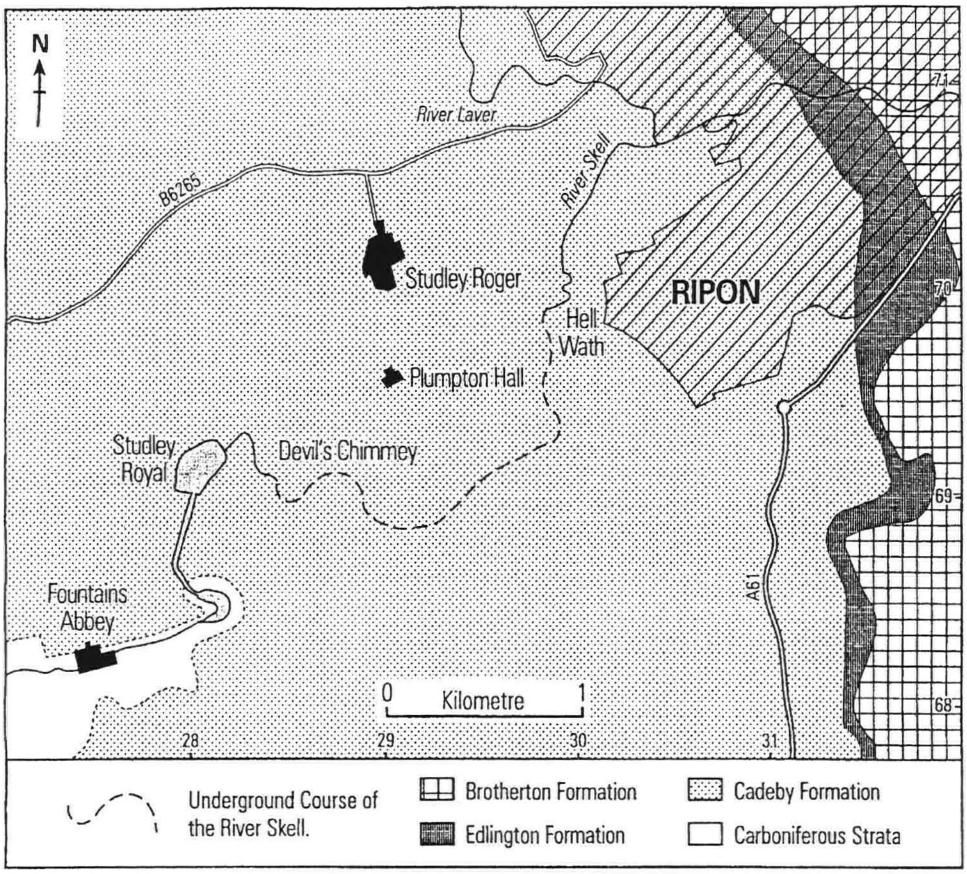

Figure 1. Location of the River Skell, Ripon.

only half a mile down the valley. Presumably this indicates that the site was visited at a time of elevated water levels. Lowe (1974, 1978) repeats Fox-Strangways' description, and mentions the possibility of enterable down-dip cave development. Cooper (1986) comments on the lack of springs and sinking streams on the Cadeby Formation outcrop and mentions the sinking of the River Skell as the most notable example.

Two cave fragments are described by Brook *et al.* (1988) at the base of the cliff above the usual stream sink. These are called Devils Chimney Caves. Cave No.1 is a 12m crawl into a chamber, with the apparent way on collapsed. Cave No.2 is a 5.5m crawl that becomes too low. Both entrances are blocked at present. Neither cave is associated with the present water flow, and they may represent fragments of a relict higher level of development in the postulated cave system. Fox-Strangways (1873, 1908) comments on the occurrence of sediment-filled caves in quarries in Studley Park.

The sinking and rising 2km away and 40m lower of the River Skell is the finest example of underground flow recorded on the outcrop of the Cadeby Formation. It provides clear evidence of karstification of the dolomites and dolomitic limestones of the Cadeby Formation, which is commonly overshadowed by the sometimes spectacular effects of karstification of the evaporites higher in the Permian succession. Whereas the causes and effects of evaporite dissolution are the subjects of an increasing literature, the effects of karstification on the carbonate units and its implications should not be ignored.

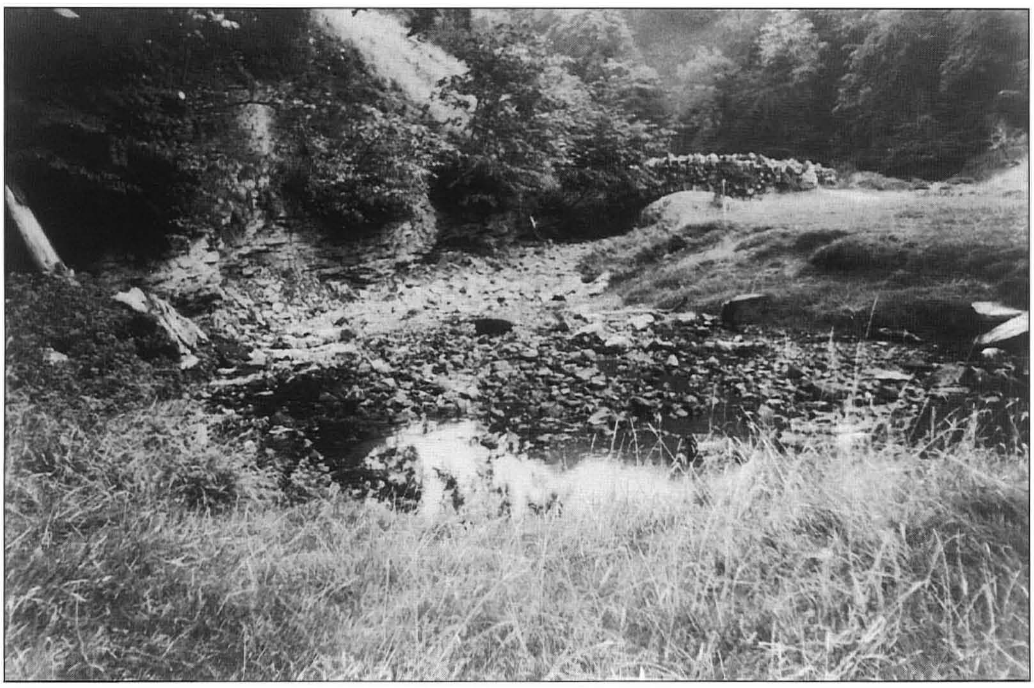

Figure 2. The river Skell passing underground at its normal summer flow position.

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BOOK REVIEW

Dearne, M J and Lord, T C, 1998. *The Romano-British Archaeology of Victoria Cave, Settle. Researches into the Site and its Artefacts.* British Archaeological Reports, British Series 273. John Hedges, Oxford. 166pp. ISBN 0-86054-957-7. Price £37.

Victoria Cave, near Settle in North Yorkshire, is one of a number of British caves, containing important archaeological and palaeontological materials, that were systematically explored during the second half of the nineteenth century. The modern professional archaeological literature frequently contains disparaging remarks about the activities of antiquarians and collectors of curiosities of the last century. Thus, it is worth noting that Joseph Jackson, the amateur collector who discovered the cave, reported his initial archaeological finds promptly to the appropriate authority (the Secretary of the Society of Antiquaries of London). Also, the subsequent investigations undertaken by the Settle Caves Exploration Committee at Victoria Cave between 1870 and 1878 were conducted under the auspices of the British Association, and were advised by a scientific panel that included some of the most distinguished geologists and archaeologists of the day. The excavation and recording methods employed at Victoria Cave were based on the innovative principles pioneered by William Pengelly at Kent's Cavern in Devon, and included the use of a state-of-the-art technique - photography - to monitor the progress of the work.

A principal aim of the excavations of the 1870s was to corroborate and provide a stratified context for Joseph Jackson's earlier discovery of a hyena jaw in the cave. This objective was achieved in 1872, when a preglacial bone-bearing deposit was located under an accumulation of later sediments at a depth of nearly 5m. To this day, Victoria Cave is best known as one of Britain's key Pleistocene faunal sites, dating to the last interglacial (when hippopotami roamed the verdant hills of Craven), with the consequence that the cave's rich panoply of Roman artefacts has been neglected. Dearne and Lord's new monograph at last restores the balance, and provides the definitive catalogue of the coins, brooches, pottery and other manufactured items found in the cave that can be dated on typological grounds to the Romano-British period.

Martin Dearne's researches on Victoria Cave form part of a larger project undertaken in collaboration with Keith Branigan, with the aim of synthesising the extensive evidence for the use of caves in Roman Britain. Tom Lord, curator of most of the surviving finds from the 1870s excavations as well as the bulk of the archive material relating to Victoria Cave, is also an experienced cave archaeologist. In addition to the work of the two main authors, the volume includes contributions from nine other specialists in Roman archaeology, so the volume as a whole has excellent credentials and a high standard of scholarship. Reconstructing the history of the excavations and establishing the provenance of the finds has proved a major exercise, as finds from other cave sites in the Settle area have been confused with those from Victoria Cave. Also, many finds from the original excavations have disappeared and are known today mainly from earlier inventories and the original site notebooks.

Despite more than half of the book being taken up by an illustrated catalogue of the archaeological finds, the work is not merely descriptive, but also aims to place the cave in its regional setting and establish the function of the site during the Romano-British period. Dearne and Branigan's earlier research on Romano-British caves has provided archaeological criteria that distinguish between opportunistic, domestic, industrial and ritual usage. Although Victoria Cave clearly falls into the latter category there are no signs of definite modification or decoration of the cave or of symbolic artefacts that are unequivocally associated with a particular deity, and there is no evidence for burial activity inside the cave. One possibility is that adherents of Mithraism, a secretive and exclusively Roman cult that was associated especially with the military, used the cave. During the third century AD the Mithraic cult rivalled Christianity in popularity in the Roman Empire, and its rites were often centred on subterranean locations where initiation and endurance tests took place (a peculiar blend of recreational caving and freemasonry, to use a modern analogy).

In summary, this book is a specialised monograph that is more likely to find a home in academic libraries than on the shelves of the general reader. However, it is worth consulting as a standard of the level of detail now expected in the publication of artefacts from archaeological caves, as well as an example of the amount of information that can be still be gleaned from excavations that took place more than a century ago.

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THESIS ABSTRACT

SHARRATT, N J, 1998

Ecological aspects and conservation of the invertebrate fauna of the sandstone caves of Table Mountain, Cape Town.

MSc Thesis, University of Natal (Pietermaritzburg), South Africa, August 1998.

The Cape peninsula caves are temperate sandstone caves supporting 21 invertebrate species that are endemic to the peninsula. Thirteen of these are troglobitic Gondwanan relicts, including several highly troglomorphic, phylogenetically unique and rare species. According to the criteria listed in the *IUCN Red List Categories* (1994), *Peripatopsis alba* and *Spelaeogriphus lepidops* should be considered Critically Endangered, their extent of occurrence being less than 100km^2. Data Deficient species such as *Protojanira leleupi, Paramelita barnardi, Hahnia* sp.nov., Dermaptera sp.nov., *Cryptops stupendus* and *Cthoniella cavernicola* are also likely to be Critically Endangered. The remaining endemic troglobites and troglophiles should be considered Endangered on account of their limited distributions (extents of occurrence <5,000km^2). Management-orientated research and long term population monitoring of these species are conservation priorities.

Eighty-five cavernicolous invertebrates were recorded from Peninsula caves. Six new species, including two highly troglomorphic (blind and depigmented) species of Dermaptera and Hahniidae (Araneae) were discovered.

Abundances were established by visual counting of individuals in quadrats along transects into Bats' and Wynberg caves, Table Mountain. Environmental variables were measured at each quadrat. The rhaphidophorid, *Speleiacris tabulae*, was the most common censussed invertebrate, its distribution being correlated positively with bat guano on which it fed. It, in turn, served as food source for troglobitic predators and scavengers and is therefore considered to be a keystone species.

Abundance and species richness were compared between caves and between zonally-defined habitats within caves. Abundances were generally greater in Bats' Cave, while Wynberg Cave was more species rich. Community distribution patterns and correlations with environmental variables were analysed using hierarchical clustering and two-dimensional ordination plots generated by CLUSTER, MDS and BIO-ENV programs within the PRIMER software package (Clarke and Warwick, 1994). Communities were primarily correlated with the zonal physical environment and secondarily with food availability. Relative humidity was the environmental variable most strongly and uniformly correlated with community patterns, with temperature and moisture availability also being of importance. The distributions of several troglobitic species were correlated positively with crevice availability, and evidence is presented to suggest the existence of a 'crevice community'. This community should be considered an additional cave biotope with its own set of ecological parameters.

RESEARCH FUNDS AND GRANTS

THE BCRA RESEARCH FUND

The British Cave Research Association has established the BCRA Research Fund to promote research into all aspects of speleology in Britain and abroad. Initially, a total of £500 per year will be made available. The aims of the scheme are primarily:

a) To assist in the purchase of consumable items such as water-tracing dyes, sample holders or chemical reagents without which it would be impossible to carry out or complete a research project.
b) To provide funds for travel in association with fieldwork or to visit laboratories that could provide essential facilities.
c) To provide financial support for the preparation of scientific reports. This could cover, for example, the costs of photographic processing, cartographic materials or computing time.
d) To stimulate new research that the BCRA Research Committee considers could contribute significantly to emerging areas of speleology.

The award scheme will not support the salaries of the research worker(s) or assistants, attendance at conferences in Britain or abroad, nor the purchase of personal caving clothing, equipment or vehicles. The applicant must be the principal investigator, and must be a member of the BCRA in order to qualify. Grants may be made to individuals or groups (including BCRA Special Interest Groups), who need not be employed in universities or research establishments. Information about the Fund and application forms Research Awards are available are available from the Honorary Secretary (address at foot of page).

GHAR PARAU FOUNDATION EXPEDITION AWARDS

An award, or awards, with a minimum of around £1000 available annually, to overseas caving expeditions originating from within the United Kingdom. Grants are normally given to those expeditions with an emphasis on a scientific approach and/or exploration in remote or little known areas. Application forms are available from the GPF Secretary, David Judson, Hurst Farm Barn, Cutler's Lane, Castlemorton, Malvern, Worcs., WR13 6LF, UK. Closing dates for applications: 31st August and 31st January.

THE E.K.TRATMAN AWARD

An annual award, currently £50, made for the most stimulating contribution towards speleological literature published within the United Kingdom during the past 12 months. Suggestions are always welcome to members of the GPF Awards Committee, or its Secretary, David Judson, not later than 1st February each year.

BRITISH CAVE RESEARCH ASSOCIATION PUBLICATIONS

CAVE AND KARST SCIENCE - published three times annually, a scientific journal comprising original research papers, reviews and discussion forum, on all aspects of speleological investigation, geology and geomorphology related to karst and caves, archaeology, biospeleology, exploration and expedition reports.
Editors: Dr. D J Lowe, c/o British Geological Survey, Keyworth, Notts., NG12 5GG, UK and Professor J Gunn, Limestone Research Group, Dept. of Geographical and Environmental Sciences, University of Huddersfield, Huddersfield, HD1 3DH, UK.

CAVES AND CAVING - quarterly news magazine of current events in caving, with brief reports or latest explorations and expeditions, news of new techniques and equipment, Association personalia etc.
Editor: Hugh St Lawrence, 5 Mayfield Rd., Bentham, Lancaster, LA2 7LP, UK.

CAVE STUDIES SERIES - occasional series of booklets on various speleological or karst subjects.
No. 1 *Caves and Karst of the Yorkshire Dales;* by Tony Waltham and Martin Davies, 1987. Reprinted 1991.
No. 2 *An Introduction to Cave Surveying;* by Bryan Ellis, 1988. Reprinted 1993.
No. 3 *Caves and Karst of the Peak District*; by Trevor Ford and John Gunn, 1990. Reprinted with corrections 1992.
No. 4 *An Introduction to Cave Photography;* by Sheena Stoddard, 1994.
No. 5 *An Introduction to British Limestone Karst Environments;* edited by John Gunn, 1994.
No. 6 *A Dictionary of Karst and Caves*; compiled by Dave Lowe and Tony Waltham, 1995.
No. 7 *Caves and Karst of the Brecon Beacons National Park;* by Mike Simms, 1998.
No.8 *Walks around the Caves and Karst of the Mendip Hills;* by Andy Farrant, 1999.

SPELEOHISTORY SERIES - an occasional series.
No. 1 The Ease Gill System-Forty Years of Exploration; by Jim Eyre, 1989.

BCRA SPECIAL INTEREST GROUPS

SPECIAL INTEREST GROUPS are organised groups within the BCRA that issue their own publications and hold symposia, field meetings etc.
Cave Radio and Electronics Group promotes the theoretical and practical study of cave radio and the uses of electronics in cave-related projects. The Group publishes a quarterly *technical journal* (c.32pp A4) and organises twice-yearly field meetings. Occasional publications include the *Bibliography of Underground Communications* (2nd edition, 36pp A4).

Explosives Users' Group provides information to cavers using explosives for cave exploration and rescue, and liaises with relevant authorities. The Group produces a regular newsletter and organises field meetings. Occasional publications include a *Bibliography* and *Guide to Regulations* etc.

Hydrology Group organises meetings around the country for the demonstration and discussion of water-tracing techniques, and organises programmes of tracer insertion, sampling, monitoring and so on. The group publishes an occasional newsletter.

Speleohistory Group publishes an occasional newsletter on matters related to historical records of caves; documentary, photographic, biographical and so on.

Cave Surveying Group is a forum for discussion of matters relating to cave surveying, including methods of data recording, data processing, survey standards, instruments, archiving policy etc. The Group publishes a quarterly newsletter, Compass Points (c.16pp A4), and organises seminars and field meetings.

Copies of BCRA publications are obtainable from: Ernie Shield, Publication Sales, Village Farm, Great Thirkleby, Thirsk, North Yorkshire, YO7 2AT, UK.
BCRA Research Fund application forms and information about BCRA Special Interest Groups can be obtained from the Honorary Secretary: John Wilcock, 22 Kingsley Close, Stafford, ST17 9BT, UK.