Cave Science

The Transactions of the British Cave Research Association

BCRA

Volume 20 Number 3 December 1993

Cave Science

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Cover photo: The entrance chamber of Zhucaojing, Xingwen, once a section of a massive phreatic tube but now drained and breached. Photo by Tony Baker, China Caves Project.

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Transactions of the British Cave Research Association

The Caves and Karst of Xingwen, China

Tony WALTHAM, Dave BROOK and Simon BOTTRELL

Abstract: Xingwen is a spectacular karst formed on a limestone escarpment in Sichuan. It was investigated in 1992 by the China Caves Project. Over 26 km of cave have been mapped, including some very large fossil passages, and there is considerable scope for further exploration. Cave inception and development has been controlled closely by the geology, and a remarkably large proportion of the caves were initiated on the same bedding plane. The limestone surface has areas of young pinnacle karst and older cone karst. Two giant dolines have formed where ancient caves have been breached by sinkhole shafts. Between them, the surface and underground of Xingwen provide a textbook example of karst development on a magnificent scale.

XINGWEN

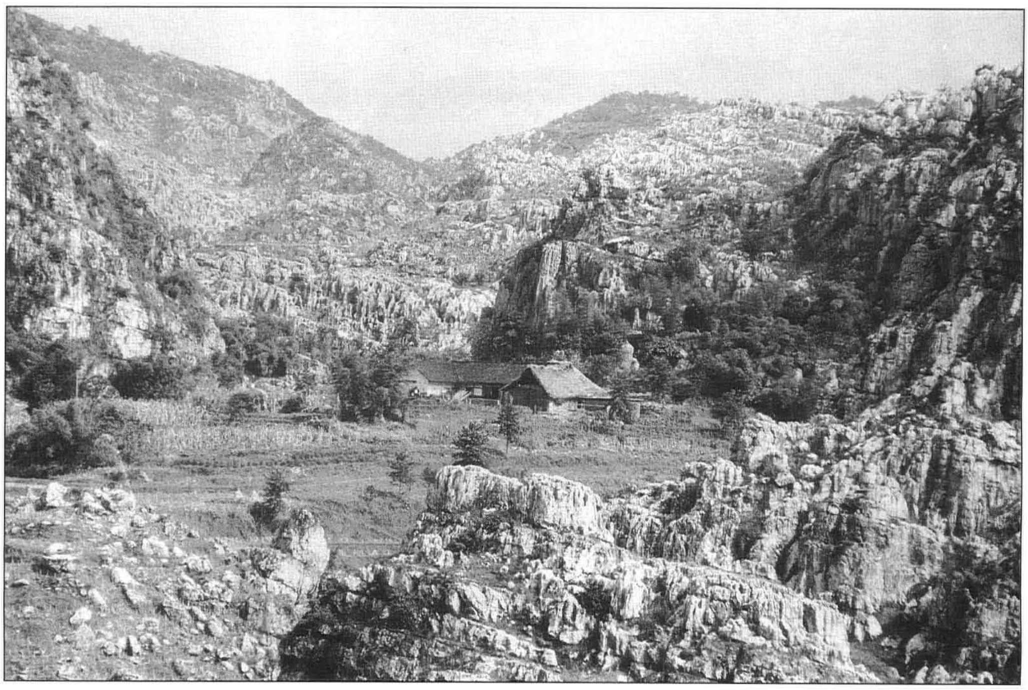
The limestone karst of Xingwen lies in the southern part of Sichuan province. It is 80 km southeast of Yibin, a city on the Chang Jiang (Yangtze River). An escarpment of massive limestone bears some spectacular surface karst landforms, and also houses some systems of very large caves; many of these were mapped in 1992 by the China Caves Project (Waltham and Willis, 1993).

Geologically, Xingwen lies in the fold belt around the southern margin of the Red Basin, and is therefore on the northern edge of the Guizhou limestone highlands. The limestone outcrop at Xingwen traces a thin band in an ellipse round an anticline 60 km long and 20 km across. The best of the karst, at Xingwen, occupies only a 15 km long sector on the southern edge of the anticline (Fig. 1); the dip is only 25-35°, giving a wide outcrop on the limestone dipslope.

The karst is all formed on and in the Permian Maokou and Qixia Formations. Throughout southern China, these beds are known as some of the most cavernous limestones. At Xingwen, they are about 350 m thick.

Like much of China, the Xingwen countryside supports a substantial population. Nearly all the land is farmed, with rice grown on the lower slopes while the limestone hills are planted with corn, tobacco and chilli. Industry exists wherever it can. Beds of coal and pyrite within the sandstone and shale sequence just above the limestone feed thriving sulphur factories at and around Xingwen. These are vital to the local economy; they employ about half the local workforce, but also create some spectacular pollution (Waltham and Willis, 1993; Bottrell, 1993).

Figure 1. Outcrop of the limestone and major stream sinks around Xingwen. The older sandstones are Silurian, lying beneath a major unconformity. The younger sandstones are Triassic, and include a sequence better described as coal measures in their lower part directly above the limestone.



A small farm on a patch of soil within the limestone chaos at the southern end of the Xingwen park.

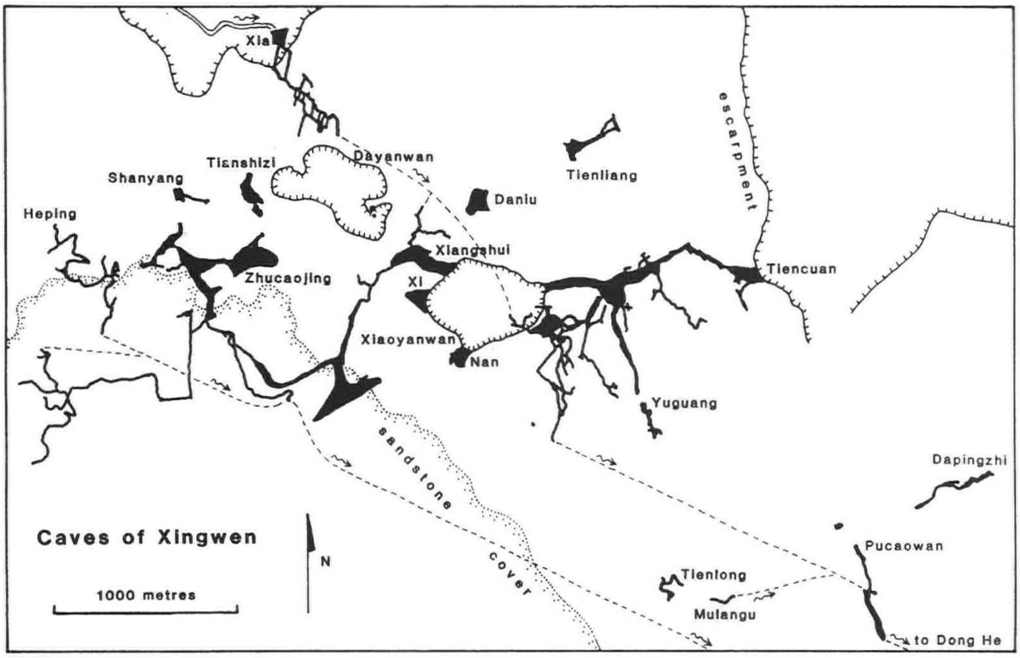


Figure 2. Outline map of the known caves at Xingwen.

The local sulphur industry is in unfortunate conflict with schemes to develop the very considerable tourist potential of Xingwen. The area has been designated a regional park and a large show cave is already open. Some of the limestone landforms are very worthwhile visitor sites, but further development depends on successfully coexisting with the adjacent sulphur factories. The potential of the park offers a fascinating challenge to the county government, and mapping the caves by the China Caves Project was partly in order to improve the database on the site.

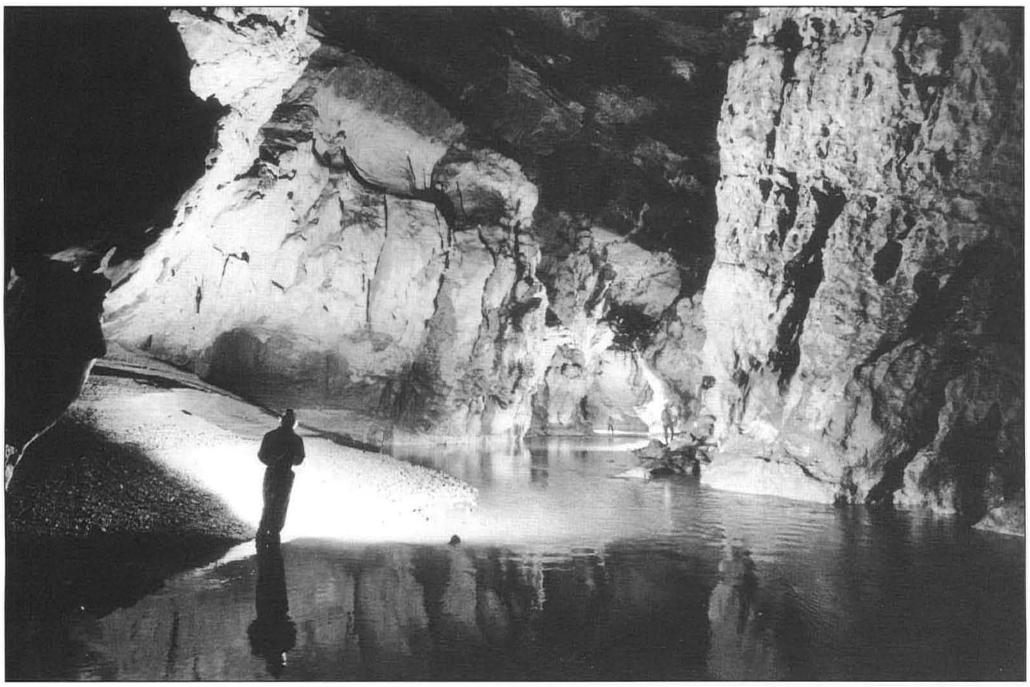
Xingwen has a wet temperate climate. Annual rainfall is 1280 mm. Summers are warm and wet, while winters are cool and dry. Snow is minor at these low altitudes. Natural vegetation is therefore thick, and karstic solutional processes are well supplied with soil carbon dioxide. The karst of Xingwen is mature and its development was not significantly interrupted by Pleistocene climatic deteriorations. The limestone surface is composed of bare karren fields, shilin pinnacle karst and fengcong cone karst; there is no tower karst.

THE CAVES

The limestone at Xingwen forms a massive escarpment facing just east of north. Much of the scarp face is a line of vertical limestone cliffs 100-200 m high. Three components of water enter the limestone. To the north, sandstones beneath the limestone rise to hills in the core of the anticline; rivers and streams from these flow downdip and sink into the base of the limestone. Rainfall directly onto the limestone all sinks underground. To the south, a younger sequence of shales, mudstones and sandstones grades upwards into stronger sandstones which create high ridges and scarps overlooking the karst; streams from these flow onto the limestone and sink into the upper beds near the lower margin of the limestone dipslope.

All this input water has contributed to the development of caves within the limestone. The cave drainage at Xingwen all flows east to a single resurgence, Dong He Dong (Cave River Cave) in the floor of the Daba River valley (Fig. 1). The Daba flows across the limestone outcrop in a deep valley with a minimal gradient; it is the only river which does not sink into the limestone, and it defines the local base level. The limestone escarpment does not have a horizontal crest; for 20 km west of the Daba valley, it rises steadily so that the highest sinks into the limestone are 900 m above the Dong He resurgence.

The main known caves are grouped into a small area, where the Xingwen park is located on a wide section of the limestone outcrop. Figure 2 shows outline position of the mapped caves in this zone (detailed surveys are in Waltham and Willis, 1993). This figure also locates the two massive dolines, Xiaoyanwan and Dayanwan. Alternatively spelled as Xiao Yan Wan (Little Rock Bay) and Da Yan Wan (Big Rock Bay), Xiaoyanwan is confusingly the larger of the two, and is one of the largest dolines in the world.



The river passage along the strike in Dong He Dong, with a dipping bedding plane forming the roof.

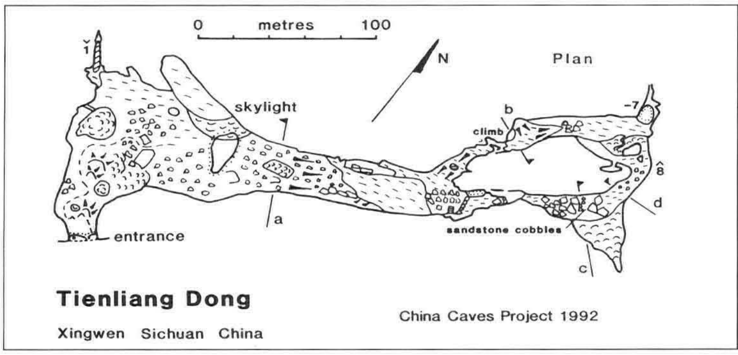


Figure 3. Survey of Tienliang Dong.

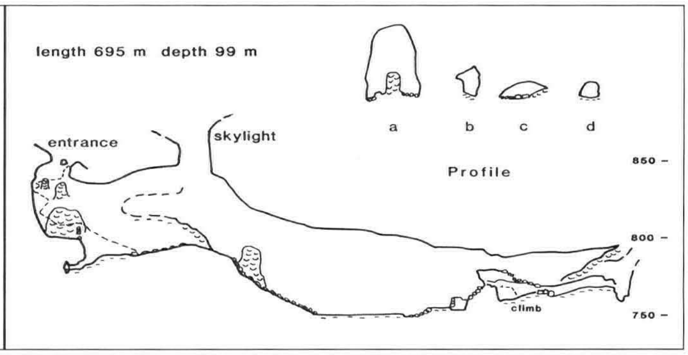
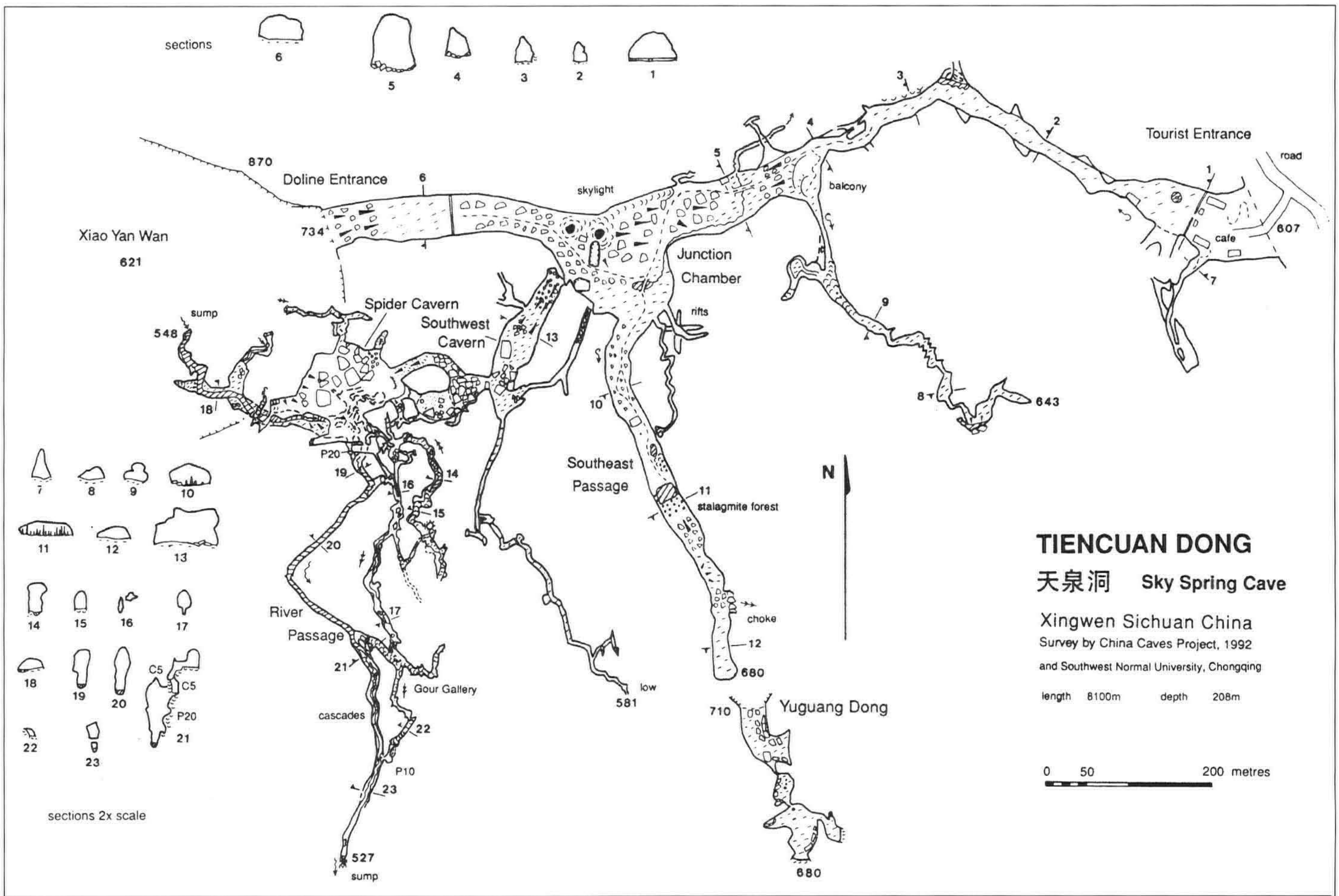
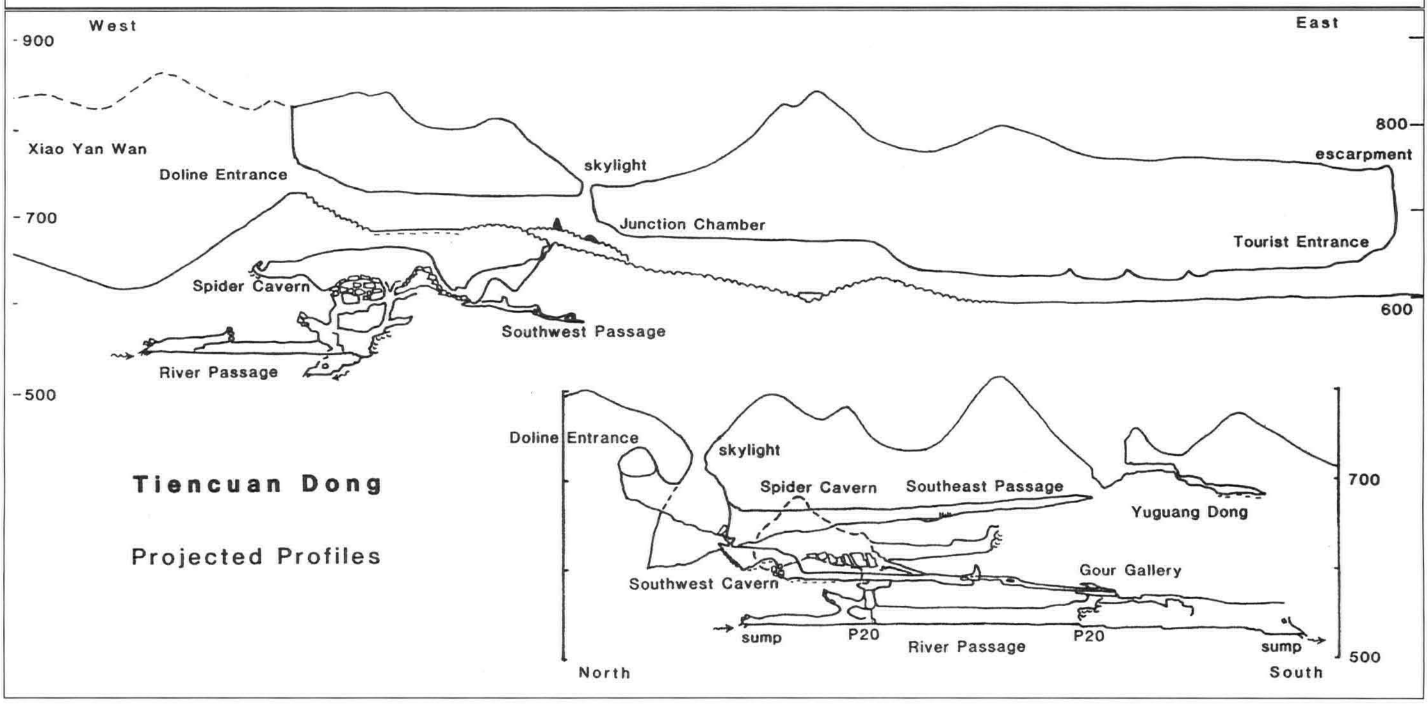


Figure. 4. Survey of Tiencuan Dong.





Morphology of the caves

The main caves are briefly described in order from west to east. Explorations in 1992 were incomplete due to shortage of time, bad weather and, in some caves, bad air. Over 26 km of caves are now known, but there are certainly more caves to be found and mapped.

Heping Dong carries a small stream through most of its 1750 m of passages. The water is polluted, and the Acid Bath is a deep lake 150 m long with a pH of 2.6. Large old passages form the entrance series before the water turns south in immature canyons.

Zhucaojing has 8800 m of mostly large passage. Its entrance chambers are fragments of fossil phreatic trunk passage 50-100 m in diameter; they are now just breached by sinkholes below the sandstone margin. From them, a stream cave drains south to a shaft into a larger passage with bad air. This passes beneath the southern trunk cave, which was another phreatic route from west to east; the passages are mostly 10 m wide and over 25 m high, and include a massive chamber on their south side. To the east, a rift series, frequently flooded in its lower reaches, links to another remnant of massive phreatic trunk (Xiangshui Dong) which opens into the side of the Xiaoyanwan doline. Low level passages to the north carry floodwater from Xia Dong.

Shanyang Dong and Tianshizi Dong are ancient sinkholes now dry and choked before connecting to Zhucaojing.

Xia Dong swallows the largest sinking river at the foot of the escarpment. Its 2200 m of passages have a large clean-washed streamway punching through a complex of parallel rifts.

Daniu Dong and Tienliang Dong (Fig. 3) are fragments of very old phreatic trunk passages now breached by dolines high on the escarpment. Xi Dong and Nan Dong are similar fragments, not so old, now exposed in the walls of Xiaoyanwan.

Tiencuan Dong has 8100 m of passages (Fig. 4). A fossil trunk passage is 30-50 m in diameter for its whole length between entrances in the cliffs of Xiaoyanwan and the escarpment; together with the large dip tube to the south, this is developed as a very spectacular show cave. More passages to the southwest include ancient phreatic tunnels which are choked before they reach Xiaoyanwan, and a number of routes into a lower river passage; this carries the water from Xia Dong but is sumped in both directions.

Yuguang Dong is a truncated continuation of the downdip Tiencuan tunnel (Fig. 4), with its passage far above its inception horizon due to extensive roof collapse.

Mulangu Dong is a large stream sink choked with inwashed clinker after 150 m, and Tienlong Dong is a nearby, unrelated fragment of fossil phreatic tube.

Pucaowan Dong (Fig. 5) swallows a major stream in heavy rain; its normally dry entrance passage descends to a section of the main drain from Tiencuan and Xia Dong.

Dapingzhi Dong has a large passage descending steeply, roughly with the dip (Fig. 6); it is a phreatic remnant heavily modified by collapse.

Dong He Dong (southeast of Fig. 2) has 1860 m of passage in two sections at the area resurgence. Partially drained phreatic tubes follow the bedding roughly along the strike, with downloops flooded and uploops breached by dolines.

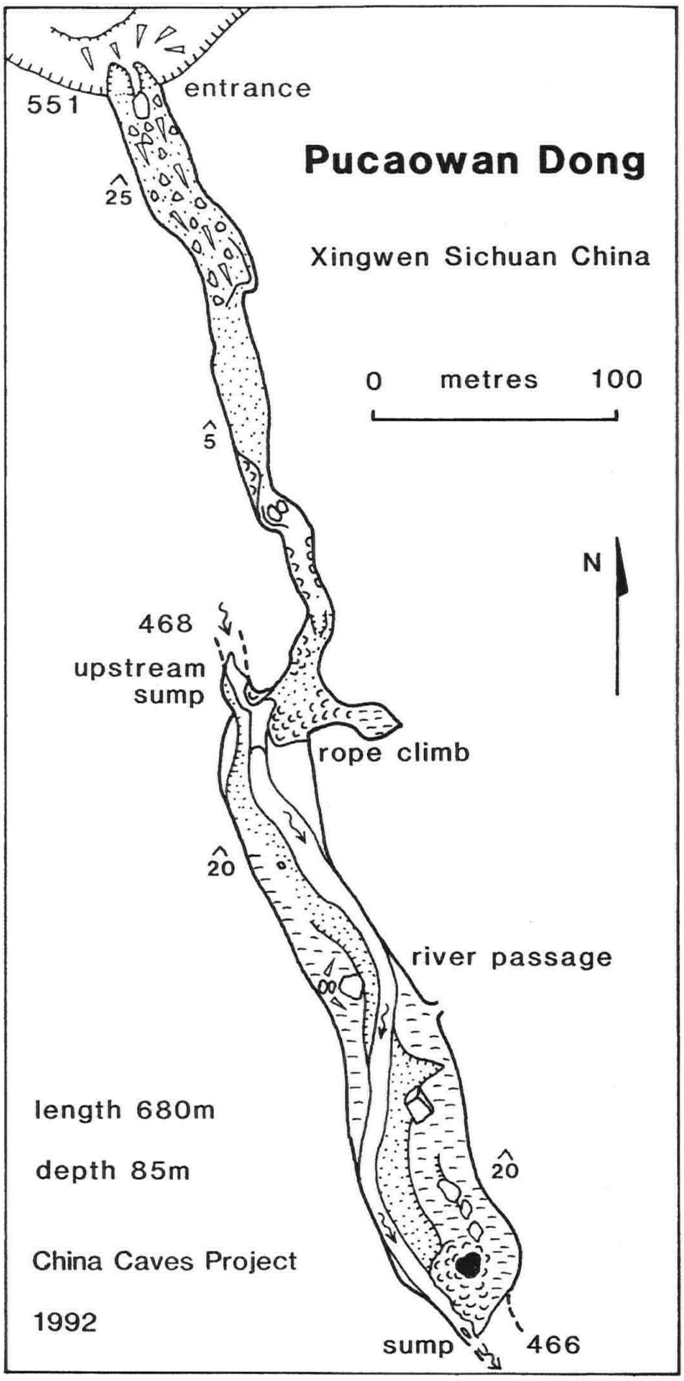


Figure 5. Survey of Pucaowan Dong.

Inception of the caves

The caves of Xingwen present a textbook case of speleogenesis in a dipping limestone. Progressive retreat of the sandstone cover down the dipslope has allowed successive generations of new caves to form; these overlap and invade the older caves, notably as vadose inlets

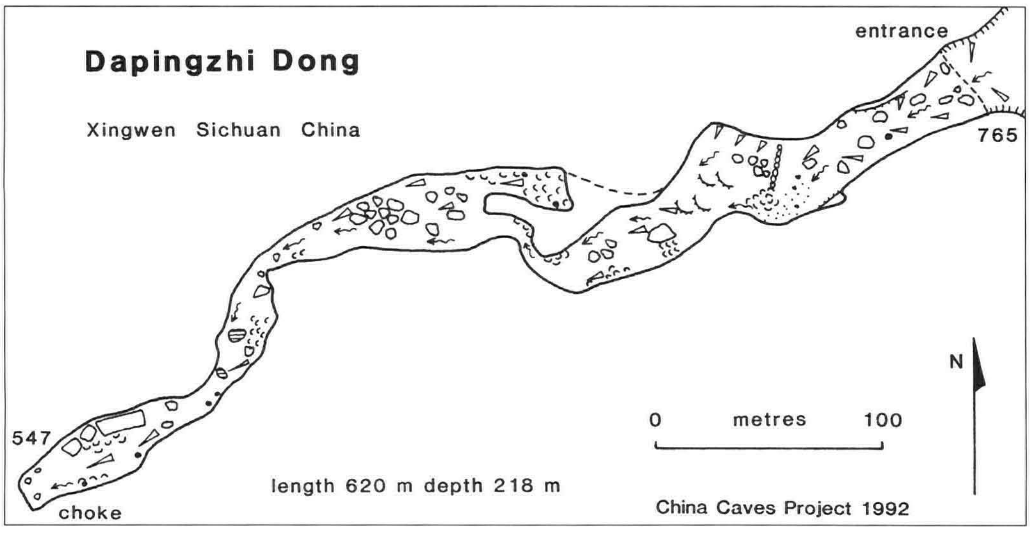


Figure 6. Survey of Dapingzhi Dong.

Base of younger sandstone	
Massive limestones	- 110 m
Xiaoyanwan walkway bedding plane	
Massive limestones	- 55 m
Collapse bedding plane	
Thin bedded limestones	- 25 m
Inception bedding plane	
Massive limestones	- 160 m
Top of older sandstones	

Table 1. Sequence of Permian limestones at Xingwen.

cutting through ancient dewatered phreatic tunnels.

The limestone contains numerous bedding planes, including three very conspicuous horizons which are clearly recognisable in Xiaoyanwan and Tiencuan (Table 1, Figs. 4 and 10). The walkway bedding plane creates a conspicuous notch around much of the vertical perimeter wall in the Xiaoyanwan doline; houses and defensive positions have been built within it, and it now provides a very spectacular walk. There is however minimal cave development associated with it. It appears to be a horizon susceptible to weathering but not to cave inception.

About 80 m below the walkway, the inception bedding plane is barely recognisable in the doline profile, but is of prime importance in the adjacent caves. The main passage of Tiencuan Dong was formed entirely along this horizon; the cave changes level by 45 m in order to follow the inception horizon across a fault at the cave's skylight (Fig. 9). Subsequently, the 25 m of thin-bedded limestones above the initial phreatic tube have collapsed along much of the cave's length. The cave ceiling is now formed at the collapse bedding plane, which underlies a more massive limestone bed. Solution features on the lower cave walls, and collapse fractures above, clearly show the roles of inception, solutional enlargement and collapse. The eastern half of the Tiencuan passage is still close to the main inception horizon; there has been much less collapse, and phreatic rifts survive in the roof (Fig. 4).

This one inception horizon appears to have dominated control of cave development at Xingwen. Because it is dipping, it can provide a complete routeway through the limestone aquifer. All the main fossil passages of both Tiencuan and Zhucaojing appear to have been initiated at or very close to it. The differences in levels are accounted for by the southerly dip. Much of the young streamway in Heping Dong is at a similar horizon, but the vadose streamway in Zhucaojing steps down to lower bedding planes. Pucaowan is largely a strike tube, and Dapingzhi is a dip tube, both at about the same stratigraphic horizon. The tubes at the Dong He resurgence are also in the core of the limestone sequence, at or very close to the same bedding. Only detailed geological mapping of the caves will show if inception was on the one or on a close group of horizons.

It is pertinent to ask why one bedding plane has been such an important horizon of cave inception. Furthermore, it is tempting to suggest that pyrite may have been a critical factor, when the pyrite ores are conspicuous in the immediately overlying clastic sequence. This would be in line with modern recognition (by Lowe, 1992, and others) of the role of pyrite in the very first stages of cave inception. However, the bedding plane has not been examined in detail, and it cannot yet be recognised as anything more than a significant lithological break.

The upper limestones, above the inception bedding plane, have little known sub-horizontal cave development; the old tube in Tienlong Dong may be an exception. There are just very small bedding plane openings in the highest limestones exposed in the sinkhole walls below the cover margin. These sinkholes along the margin feed direct to vertical shafts which penetrate the full depth of the upper limestone.

Limestones below the inception bedding do contain more caves. Xia Dong has been initiated on a zone of bedding planes close to the base of the limestone. The continuation of its youthful passage, in the lower streamway of Tiencuan Dong, is also just above the base of the limestone. In neither of these caves is the underlying sandstone exposed, but the passages of Yanzi Dong, further to the west (Waltham and Willis, 1993), step up and down through the lowest limestone beds and have long lengths with a mudstone or sandstone floor.

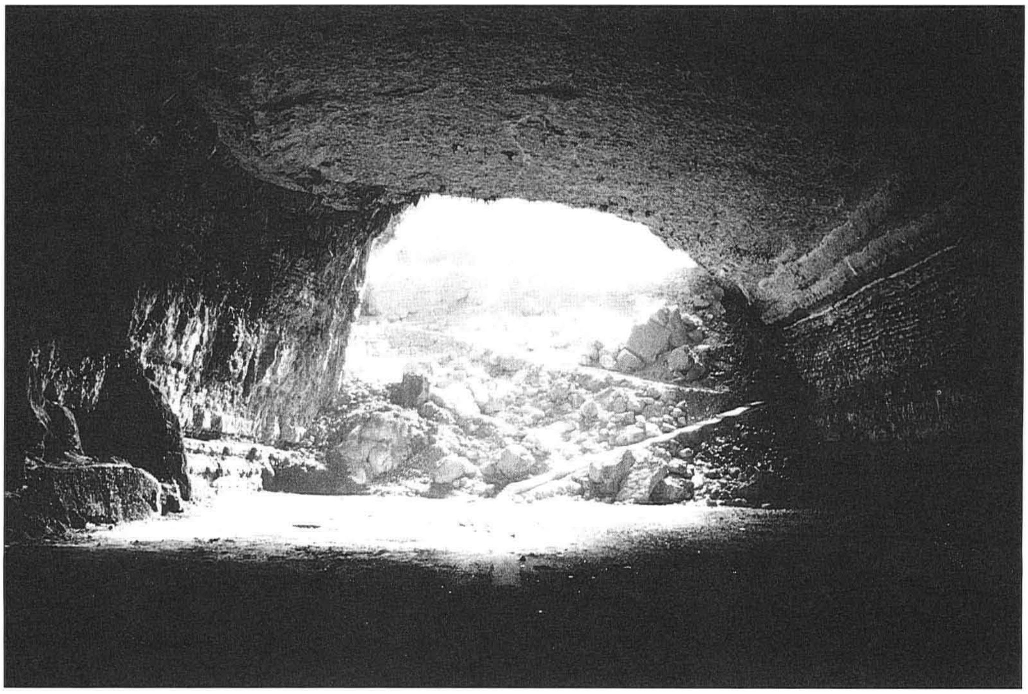
Joints have also been important in the cave initiation. They have been enlarged to form the many ancient and modern inlet shafts swallowing drainage from the sandstone cover. They have guided the phreatic tubes on the inception bedding plane into rectilinear patterns – noticeable in the plan outlines of both western Zhucaojing and the Dong He resurgence caves. The dip of the bedding has meant that these joint-influenced passages have switchback profiles, which encourage sedimentation and choking in the downloops.

The joint influence is most dramatically demonstrated in Xia Dong (Fig. 7). Parallel joints have been opened by phreatic solution into dozens of tall narrow rifts. These have been breached and connected by phreatic tubes which follow the bedding and cut through the joints. The modern cave stream follows one of these tubes; there is another large tube recognisable through much of the joint maze south of the streamway; and there are traces and fragments of at least four roughly parallel tubes. Dip is just west of south, parallel to the joints, and the tubes cut obliquely to the southeast, guided by the hydraulic gradient in the original phreas. Partial drainage followed the early phreatic development, but the tube gradients are still steeper than the local modern hydraulic gradient, so they and the joint rifts are sumped to the southeast. The rifts and the tubes appear to have formed simultaneously. Hanging blades of rock, bounded by joints and undercut along the bedding, have collapsed to aid passage and chamber enlargement.

The role of sulphuric acid

The shales, coals and pyrite ore which overlie the limestone are all pyritic, and their oxidation by groundwaters leads to the production of

Looking towards the western entrance of Tiencuan Dong. The bedding plane roof has been left by collapse of the thinly bedded limestones which are now exposed in the cave walls; inception was on the bedding plane now exposed a few metres up the wall on the left. The floor has been artificially levelled.



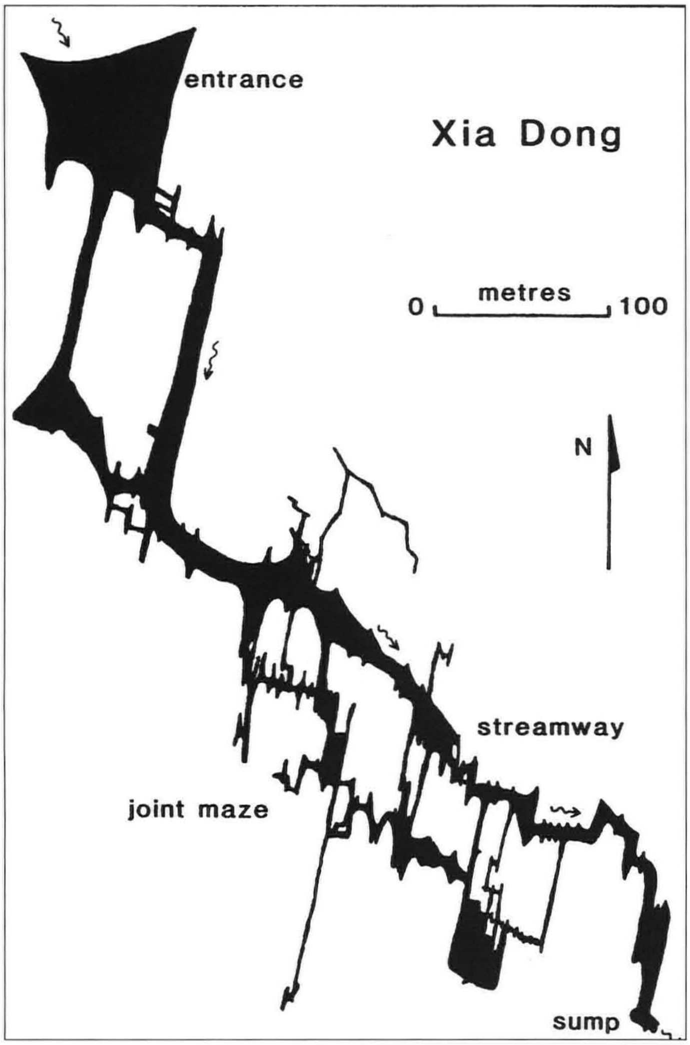
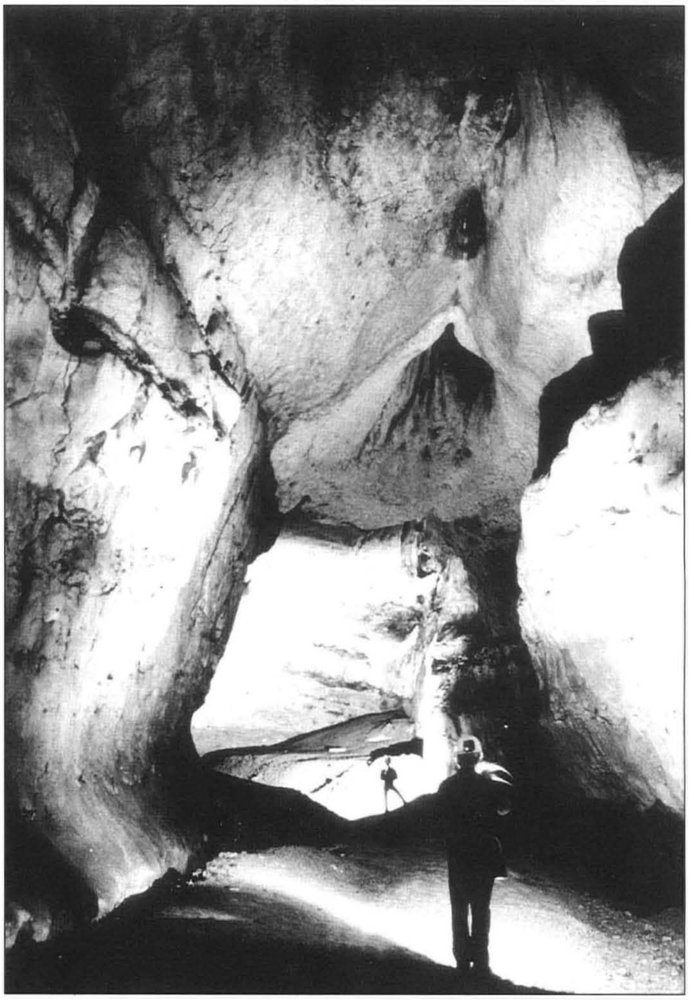


Figure 7. Outline survey of Xia Dong showing the system of parallel joint-controlled rifts.



Phreatic rifts in the roof mark the line of the joint which guided this part of the western passages in Zhucaojing.

sulphuric acid. Natural drainage from the shale slopes has a pH between 3 and 4. Such waters are extremely corrosive; at these pH levels, limestone dissolution rates would be up to to ten times the normal rates achieved by carbonic acid in karst regions (Plummer *et al*, 1978).

Small flows of drainage within the pyrite mines disappear into the mine floors and drain into the underlying limestone. The one metre of mudstone between the main pyrite bed and the limestone is adequately fractured to allow throughflow. This drainage is dilute sulphuric acid with a pH between 2 and 3. The precise role of this acidic water in further cave inception is not known, but its presence cannot be ignored. The implication is that natural waters acidified by passing through the unmined pyrite bed in the distant past may have generated considerable secondary porosity within the upper limestones; this would have been utilized in the development of the dolines, ravines and shaft systems along the limestone cover margin. The same acidic groundwaters may also have contributed significantly to cave inception beneath the mudstone and sandstone cover at sites far away from the limestone outcrops.

Allogenic waters so enriched in sulphuric acid must also have had some impact on continuing cave development. Their net effect, prior to modification of the catchment hydrochemistry by the mining and industrial activities, is difficult to assess. At present there is significantly increased limestone dissolution within the catchment; calcium and magnesium concentrations in the Zingwen karst waters are more than double those recorded at other karst resurgences in nearby parts of China (Bottrell, 1993). However, the modern sulphuric acid sources include the mineral processing waste water and also acid rain, which are unnatural features. In the natural situation, the karst would receive sulphuric acid only in allogenic surface drainage and groundwater seepage from the overlying rock sequence. The natural inputs are significant, but it is difficult to estimate what fraction of the modern acid input they represent.

Enlargement of the caves

The broad pattern of the caves can be recognised in the schematic profile (Fig. 8). Vadose water has always flowed vertically down shafts and/or downdip along bedding planes roughly towards the south. Ultimately the vadose water has met the water table at or close to the level of the contemporary resurgence in the Daba valley to the east.

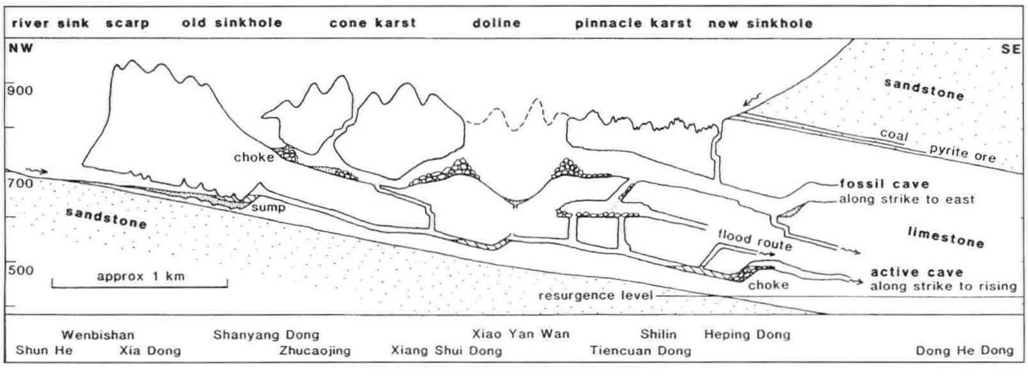
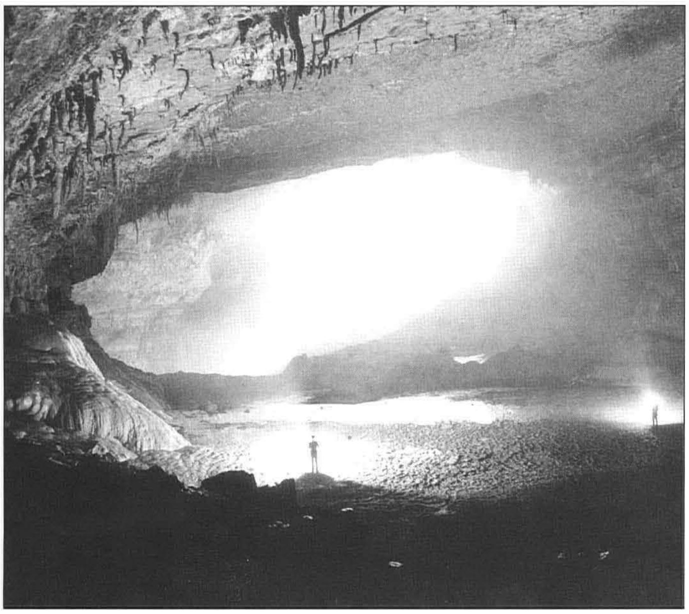


Figure 8. Diagrammatic profile of cave development in the Xingwen escarpment. The profile suffers some distortion because cave development was both down the dip and along the strike; the fossil caves are all at about the same stratigraphic horizon in the middle of the limestone, and the active cave follows very close to the base of the limestone until it reaches the resurgence level.

Phreatic flow has always then been guided by the hydraulic gradient – creating phreatic tubes with an overall orientation a little south of east. Within the phreas, water could climb or fall stratigraphically, and flow concentrated on the major inception horizon (or horizons) close to the middle of the limestone sequence. On the bedding planes, flow looped obliquely up and down to follow the joint traces.

The combination of the dipping limestone, retreating sandstone cover and lowering resurgence level in the Daba valley meant that trunk drains were repeatedly abandoned in favour of parallel new caves developing to the south. These were in the same bedding planes but at lower altitude. Much of the new cave development was underneath the sandstone cover – as the drainage slipped sideways downdip.

The oldest caves are the remnants in Daniu and Tienliang. A later major trunk route was fed by the Heping, Shanyang and Tianshizi sinks; it drained east through the Zhucaojing entrance chambers, through Xiangshui, beneath the site of Xiaoyanwan (not yet formed), and through Tiencuan. Flow may once have left Tiencuan towards the east. Scallops show flow in the east of Tiencuan was towards the west; so the downdip tubes must have developed to take all the flow further south. Southeast Passage runs south down a very low dip, but its profile (Fig. 4) climbs for much of its length due to increasing breakdown towards the south. A sinkhole could have once existed over or in front of the Tiencuan cliff entrance. Simultaneous or later drainage formed the southern fossil trunk route in Zhucaojing, feeding through Xi Dong and Nan Dong into the Spider Cavern area of Tiencuan. Dapingzhi could be a truncated section of ancient phreatic lift, or it could be another downdip input; its origins are obscured by its collapse.



The entrance chamber of Zhucaojing, once a section of massive phreatic tube, but now drained and breached at its upper corner.

The present main drain is even further south, largely under the sandstone cover. The Xia Dong tributary has invaded older sections of passage as it has found a way obliquely downdip; it approaches resurgence level not far beyond its last sighting in Pucaowan Dong.

Destruction of the caves

As is typical of a maturing karst, the abandoned caves of Xingwen have suffered from the twin attacks of sediment choking and surface erosion.

An abundant supply of sediment derives from erosion of the retreating sandstone cover, and is efficiently washed into the caves. There it is joined by plentiful collapse debris from failure of the thin-bedded limestones over the main cave roofs. Downloops in the phreatic trunk caves make effective sediment traps, and become barriers between accessible sections of fossil passage. Some passages in Heping Dong are completely sealed with well consolidated sand, silt and clay, and are now only seen at their exposed ends; they indicate a history of choking and re-excavation which may go back a very long time.

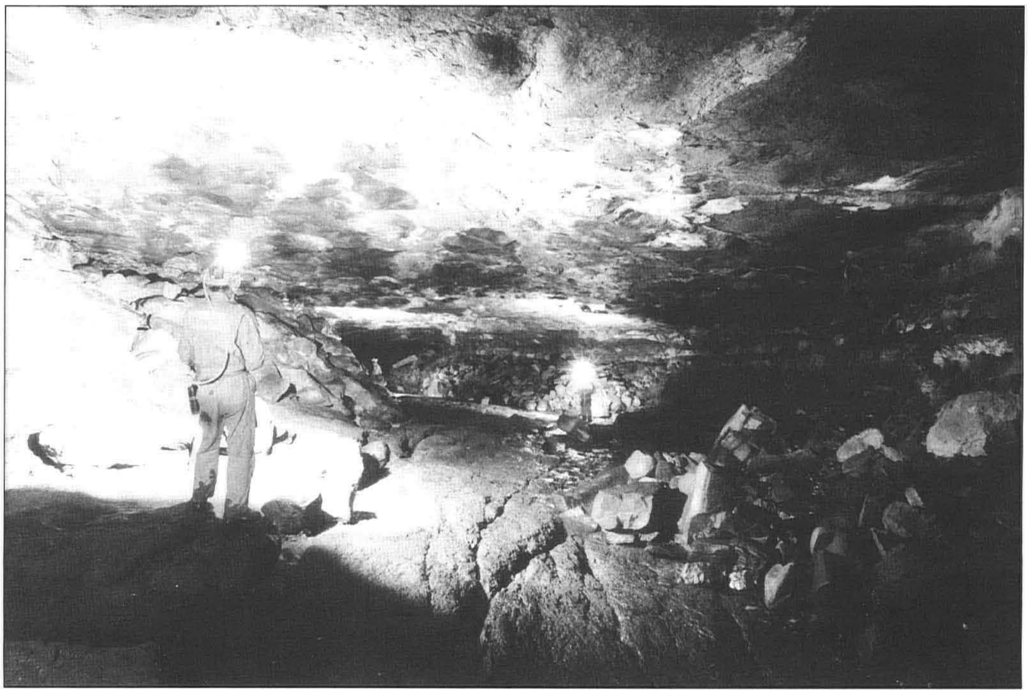
Major backflooding in some of the caves after heavy rain indicates the presence of constrictions with defined flow maxima in the major cave drains. These are probably more sediment or breakdown chokes, of which the clinker choking of Mulangu Dong is an example.

Stalagmite deposition has choked some of the older caves now far out from the sandstone cover; Tianshizi Dong is the most heavily decorated. Calcite deposits are not a major feature of the Xingwen caves, and the forest of narrow cylindrical stalagmites in the Tiencuan show cave is a notable exception.

The caves are ultimately destroyed when surface lowering reaches them, and this accounts for the shortage of caves high on the eroded dipslope. The major loss is when doline floors reach down to the collapse bedding plane (Table 1) which roofs most of the major caves. Streams which invade the older caves may clear them of sediment, but are most destructive where new shafts perforate the old cave roofs; this is particularly important immediately under the edge of the sandstone cover. The giant dolines have formed where the processes of cave destruction have overlapped those of continuing excavation.

THE KARST

The surface landforms of Xingwen are on a scale no less spectacular than the caves beneath. The escarpment cliffs are not fundamentally karstic features, though they do rely on the mechanical strength of the limestone. On the dip slope, the karst has three major elements. The lines of sinkholes along both margins of the limestone outcrop are directly related to the caves. The giant dolines are a feature of both cave and surface erosion. The karst of the shilin pinnacles and the fengcong cones is essentially independent of the caves, except for relying on their provision of underground drainage.



Yanzi Dong has a bedding plane roof created by collapse of the slabs which now litter the floor.

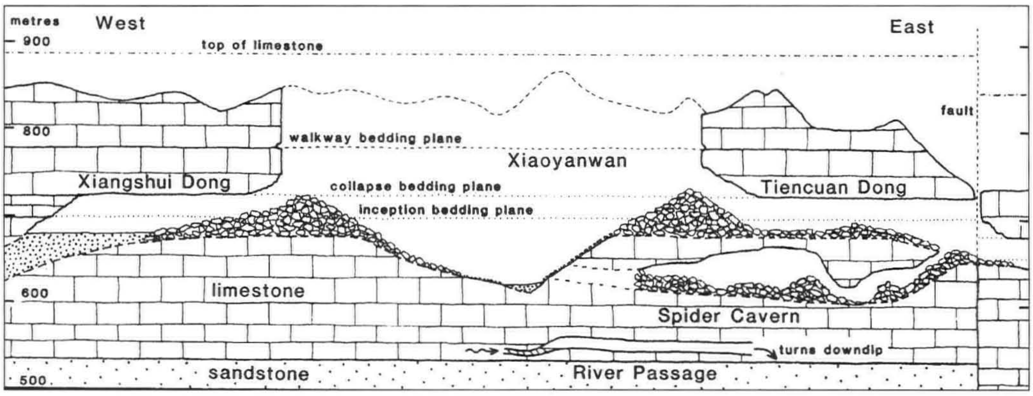


Figure 9. East-west profile through Xiaoyanwan. This is not drawn on the longest axis of the doline, but is displaced to the north to pass through the two larger caves. The profile of Spider Cavern (Zhizhu Dong) is projected from a little to the south.

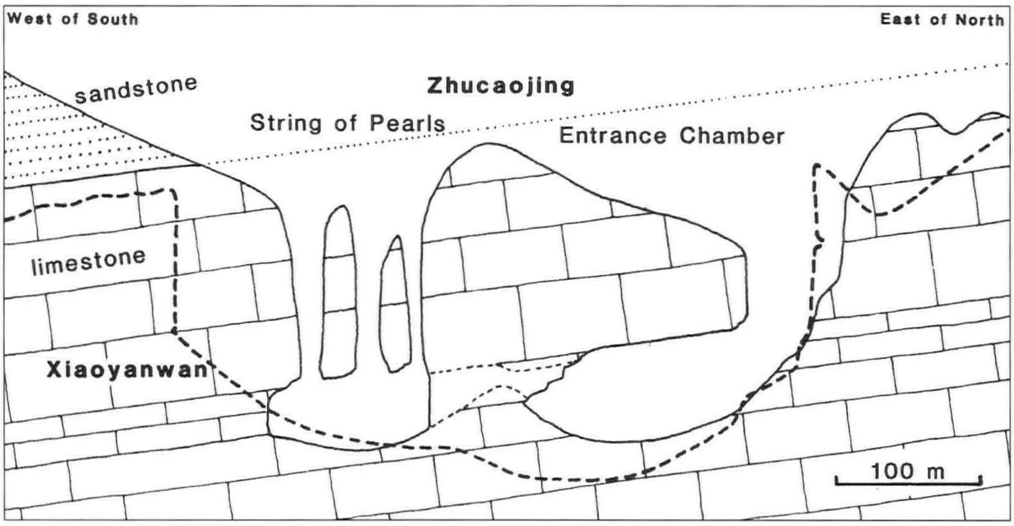


Figure 10. A comparison of parallel profiles drawn through the entrance chambers of Zhucaojing (solid lines) and the Xiaoyanwan doline (heavy broken lines). All collapse debris has been omitted for clarity, and the floors beneath the areas of thicker debris are therefore postulated.

The giant dolines

Xiaoyanwan is a singularly spectacular doline. Over 600 m long and over 400 m on its shortest diameter, it is over 200 m deep and almost completely ringed by vertical limestone cliffs over 100 m high. The dark shadows of three massive cave entrances break the white of the limestone walls; two of these continue into the passages of Tiencuan and Xiangshui Dong (Fig. 9). The floor of the doline is a tiny field of grass; directly below, the river cave from Xia Dong lies beneath 70 m of rock.

The doline lies at the confluence of five very large old cave passages (Fig. 2), and its origins must relate to their disintegration. There is no evidence that a single large chamber existed and collapsed, and the doline lacks any large blocks which would derive from the failure of such a massive roof. The origin of Xiaoyanwan is best conceived by comparison with the entrance chambers of Zhucaojing (Fig. 10). At the latter site, large old phreatic passages now lie just under the edge of the sandstone cover; they have therefore been breached, by both deepening dolines and a series of youthful vertical shafts. It will not be long in geological terms before the Zhucaojing chambers are unroofed and their intervening walls are eroded to create a massive doline. Cliff retreat, kept vertical by undercutting the strong upper limestones, will then produce a copy of Xiaoyanwan.

Dayanwan is a smaller and older doline formed by essentially the same process. With its lower walls, it may represent an evolutionary stage beyond that reached at Xiaoyanwan (Waltham, *in prep*). There may be cave remnants buried by the scree below its walls, but the more irregular profile of its floor suggests that it originated over caves which were smaller and less continuous than those at the other sites.

Though the giant dolines are conspicuous components of the Xingwen karst, they are only localised special events. Except that they are an expression of disintegration of the land surface, they are not part of the more widespread evolution of the karst landforms.

The pinnacles and cones

One of the tourist attractions of Xingwen is the stone forest (shilin) which lies to the southeast of Xiaoyanwan (Fig. 11). As is typical of the Chinese stone forests, this is a pinnacle karst created by solution of joint-guided networks of deep kluftkarren in an exposed bed of massive limestone. The main joints are vertical, so the pinnacles stand to heights of 20 m or more and are deeply fluted by subsidiary karren.

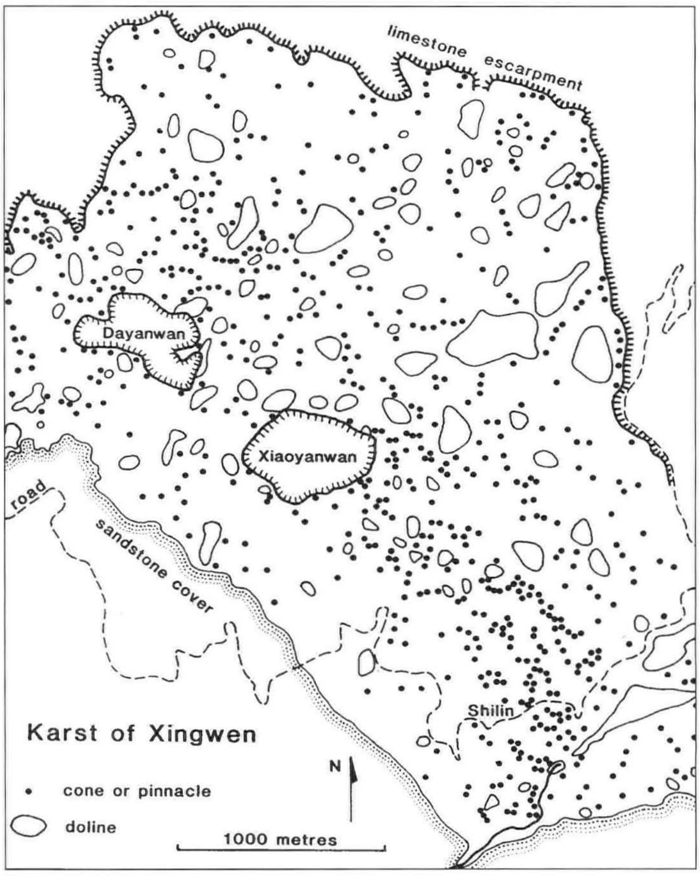
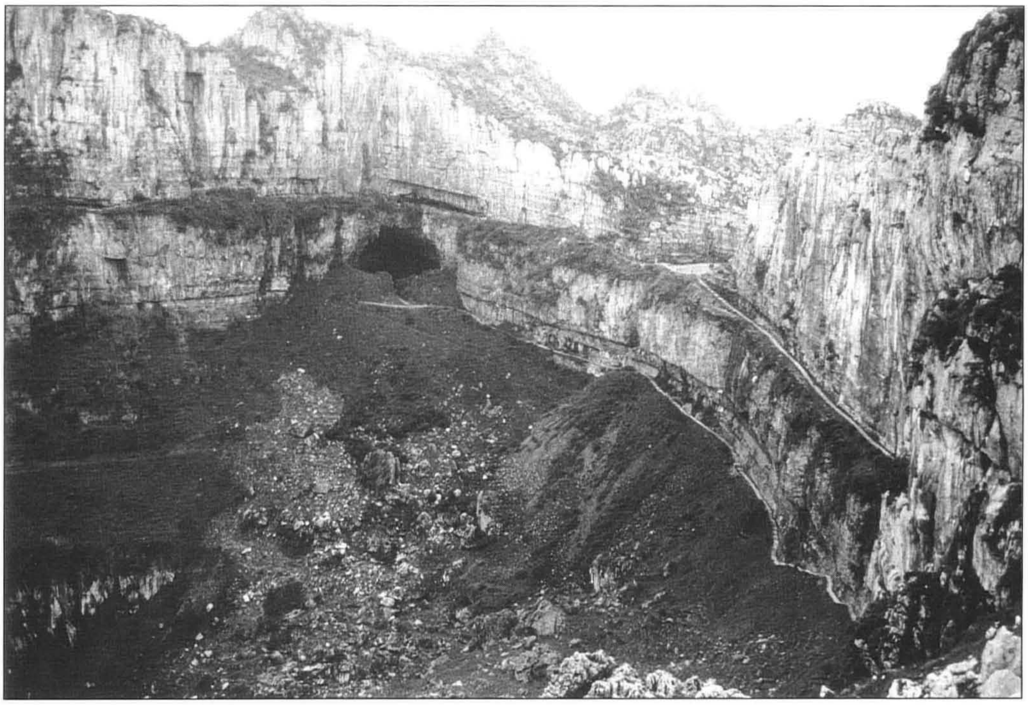


Figure 11. Surface karst landforms of the limestone dipslope at Xingwen. No distinction is made between pinnacles and cones, but most of the closely packed features are pinnacles and the more widely spaced landforms are largely cones.

The giant doline of Xiaoyanwan, viewed from the west; the cave entrance is Tiencuan Dong.



The shilin karst forms an ill-defined belt (recognisable by the highest density of symbols on Figure 11), and is broken by a few wider dolines.

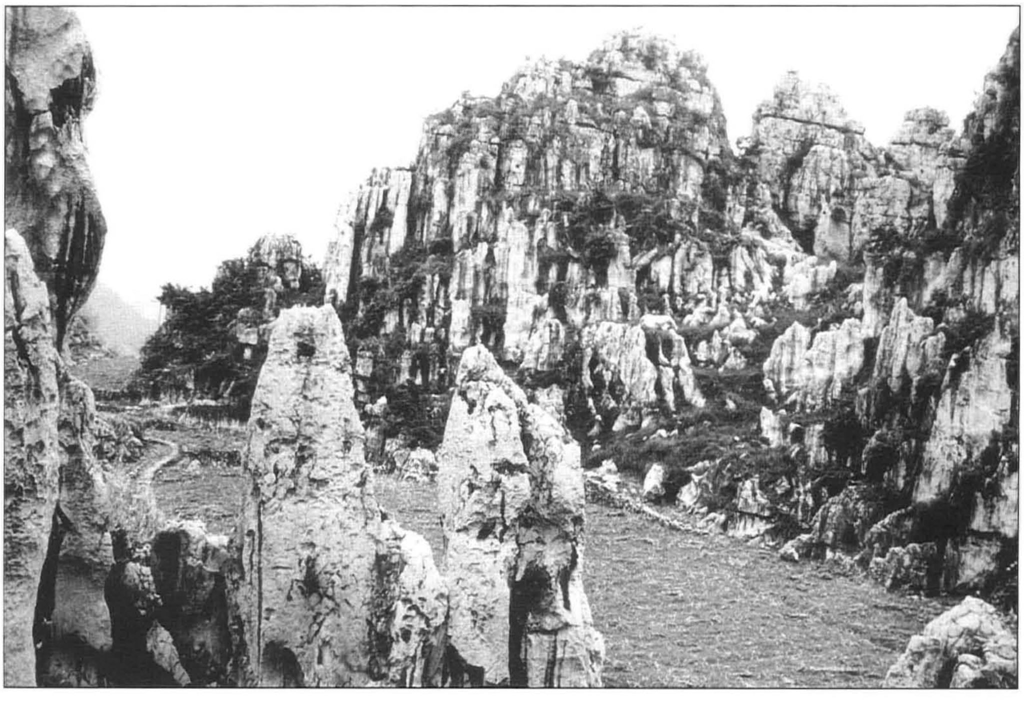
The bulk of the Xingwen park is best described as a landscape of fengcong cone karst. The majority of the hills are true cones in Chinese style (as opposed to the hemispheres of the classical cone karst in Java). Between them lie either dolines, poorly defined valleys or broad saddles. The hills are clustered enough to be described as fengcong; within China, the landscape on most of the dip slope would classify as fengcong depression karst (Smart *et al.* 1986). Many of the cone flanks are covered by small pinnacles, and the doline floors are all alluviated to some degree. Some of the deepest dolines have intersected old caves, and have been modified by collapse into them.

Reference to Figure 11 indicates four zones of karst landforms on the dip slope in the heart of the Xingwen karst. A zone closest to the sandstone cover has little relief and few positive features; some of it is bare limestone, but it mostly has a soil cover, derived from the overlooking slopes, beneath which small stumpy limestone pinnacles (known as stone teeth to the Chinese) are forming. The main zone of pinnacle karst, with the closest spaced positive features contains the Shilin and reaches towards Xiaoyanwan; most of the soil is lost into the deep fissures, and small dolines develop as the pinnacles crumble back. The main zone of cone karst (with a lower density of positive features) passes just northeast of Dayanwan, Xiaoyanwan and Shilin; between the cones the dolines are at their most mature, and increase in size as they get older away from the sandstone cover. A fourth zone of more widely spaced and more degraded cones may exist on the highest, northern, part of the escarpment; dolines are less well defined in this zone.

These zones may be interpreted as an evolutionary sequence, with age increasing with distance from the retreating sandstone cover. Table 2 shows the complete sequence of stages. The cone karst does appear to follow the pinnacle karst. This is because disintegration of the pinnacle microforms runs in parallel with slow growth of the cone and doline macroforms. It is not a direct evolution from pinnacle to cone. The pinnacles are probably best developed in the Shilin area because the steeper slopes into the adjacent Mulangu valley allowed faster removal of the soil which covered the stone teeth.

The cone degradation near the crest of the scarp (Stage 7) is not clearly defined; it may be a relic of a past climatic change, and therefore not a true stage within a single sequence. Inception of the main caves is so deep that their evolution has little direct impact on the parallel evolution of the surface. The exception is where new sinkholes and old caves coincide to form the giant dolines. No absolute time scale can yet be tied to the Xingwen karst, but the eight stages in Table 2 probably span around five million years.

A section of the karst just north of Xingwen Shilin. Some pinnacles still survive, but they are beginning to degrade, and the profile of a cone is emerging.



Stage 1	Newly exposed limestone, stone teeth karren form beneath soil; deep sinkholes along sandstone edge.
Stage 2	Loss of soil into deep fissures, and into the main caves far below.
Stage 3	Pinnacles form into shilin stone forest, by fissure deepening between stone teeth.
Stage 4	Disintegration of pinnacles by erosion, combines with slow expansion of dolines, creating residual cones.
Stage 5	Cone karst reaches maturity, and dolines continue to expand.
Stage 6	Deepening of doline floors, aided by collapse into unroofed caves.
Stage 7	Degrading of cones, and coalescence of dolines.
Stage 8	Total loss of karst, due to retreat of scarp face.

Table 2. Stages in the evolution of the Xingwen karst.

CAVE EXPLORATION

The first cave investigations in Xingwen were by the local people many years ago. They were searching for the cave sediments which can be boiled in water to yield valuable nitrates. Dug pits survive in many of the cave floors, with paths and flights of stone steps leading in from the nearest entrance. The nitrate miners visited all the easily accessible caves – and found their sediment in most of the fossil passages. The mining has now ceased, but some of the older villagers worked in the caves and still know the methods of working.

The caves also underwent a military phase. The bedding notch round the cliffs of Xiaoyanwan was fitted with walls and water channels and could have housed over a hundred people in an unassailable position. Further west, Da Yonzi Dong has an old bandit fort built within its entrance (Waltham and Willis, 1993). More recently, the floors of the huge entrance passages at both ends of Tiencuan Dong were levelled to provide sites for underground factories during the wars of this century.

Since then, the Chongqing Southwest Normal University surveyed 4 km of passage in the show cave section of Tiencuan Dong; but they carried out no new exploration.

In 1992 the China Caves Project visited Xingwen. Their main new explorations were all the southern passages in Zhucaojing (including the link to Xiangshui), all the lower passages in Tiencuan, and most of Heping Dong. They surveyed all the caves, and added the detail to the Chongqing survey of the show cave.

Exploration potential

There is clearly a lot more cave to explore in and around Xingwen. The 1992 explorations were cut short by time and weather; some important open leads remain.

The canal at the northern tip of Xiangshui sumps in wet weather, but in dry conditions offers a long swim following a strong draught. It will lead to a new section of the Xia Dong river passage. This will sump upstream and probably choke downstream (as floodwaters back up); the draught suggests there are open high levels which could relate to Daniu Dong.

Downstream in Heping exploration halted at a pitch. This should drop into a section of streamway carrying very polluted water from the industrial area to the west; bad air will ultimately be encountered. The northern arm at the west end of Zhucaojing also ends in a pitch, which could drop into the same streamway and link the caves. The main streamway in Zhucaojing ends at another pitch into a larger passage; however, this contains seriously bad air, so it probably sumps downstream, but could be open upstream towards Heping.

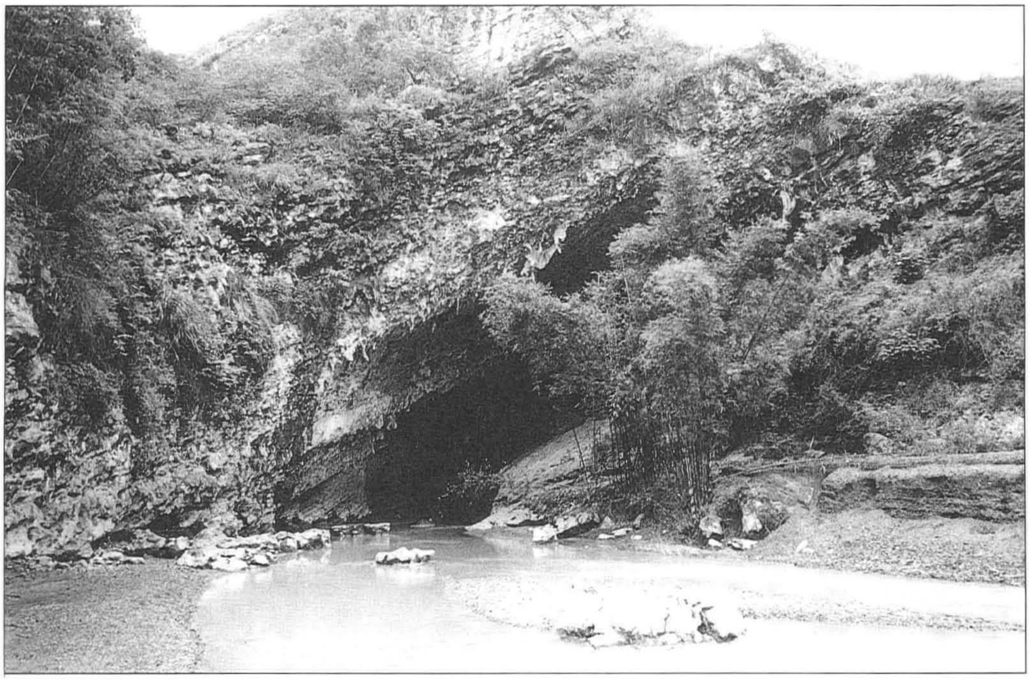
The southerly cave streams of Xingwen are all polluted by inwashed pyrite and wastewater from the mineral processing plants. Oxidation of the pyrite, and subsequent reaction with the limestone (forming spectacular gypsum in parts of Zhucaojing), leaves the cave air depleted in oxygen and enriched in carbon dioxide; a mist of sulphuric acid is also created at some sites. Bad air is a problem with varying degrees of seriousness at the lower ends of unventilated caves carrying the polluted streams; downstream sumps make the worst sites. There are no bad air problems in the fossil caves, stream caves with through ventilation, or any caves on the clean river in Xia Dong.

Adjacent sites

The limestone outcrop continues both east and west of Xingwen (Fig. 1). To the east, a number of large fossil caves are known round the nose of the anticline, but the northern limb of the fold is steeper and the limestone forms a narrow hogsback ridge.

The next major resurgence west of Xingwen is the Longtan rising, over 30 km away (Fig. 1). Numerous sinking streams drain to this, and there must be considerable lengths of open cave awaiting serious exploration; there is over 700 m of relief in the catchment. A number of streams sink into the base of the limestone near the highest outcrops on the saddle between the Xingwen and Longtan catchments. However those visited in 1992 were notably unexciting. Shenfeng Dong (Fig. 12) is a series of large old tubes along and down the dip; 2800 m of passage have a vertical range of 280 m. The Yanzi caves were mapped and extended by the China Caves Project (Waltham and Willis, 1993); 2920 m of collapse-modified passages follow the base of the limestone downdip, reaching a depth of 316 m in the deeper cave. It is not yet known which way these caves drain, but flow estimates in the Xingwen catchment suggest that there is no room for the Yanzi water; they probably all drain to Longtan.

Further west, the Gonxian and Junlian karsts were both visited in 1992 (Bottrell and Willis, 1992). Gongxian is on the western nose of



Water emerges from the dipping limestone at the Dong He resurgence.

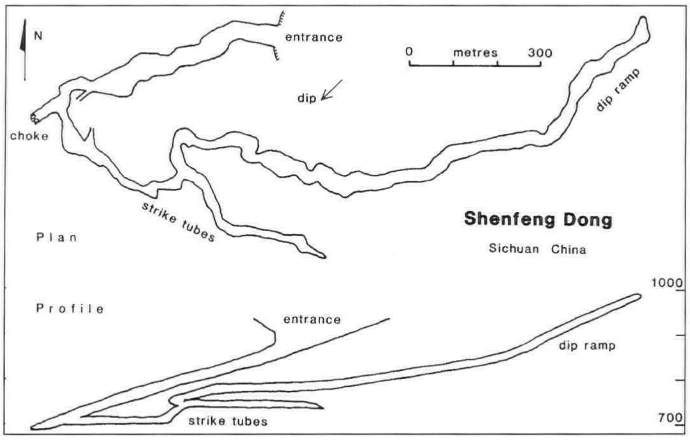


Figure 12. Survey of Shenfeng Dong (from mapping by Chongqing Southwest Normal University).

the anticline which includes Xingwen; it is the more promising area with many known caves, both active and fossil, with open leads awaiting serious investigation.

A KARST CLASSIC

The Xingwen park provides a textbook example of karst development in a massive dipping limestone. The surface karst features are truly spectacular, and their variations across a progressively exposed outcrop permit recognition of evolutionary sequences in the landforms. They are matched by a series of caves with clearly displayed patterns of inception and development. Geological influences on cave genesis are unusally conspicuous.

The stone forest, the giant doline of Xiaoyanwan and some of the caves are all worthwhile tourist destinations. Pollution problems associated with the local sulphur industry are not insuperable, and there is considerable scope for developing tourism in the park. This will make the site more accessible.

.Xingwen is already well known within China for its fine karst landforms. The mapping of the caves in 1992 has greatly added to the database and hence the value of the karst. Xingwen fully deserves wider international recognition by geomorphologists.

THE WORLD'S LARGEST DOLINES

Xiaoyanwan is an extremely large doline; it is not only very spectacular because of its white perimeter cliffs, but is among the largest dolines in the world. It is interesting to compare its dimensions with other known very large dolines. Table 3 lists the statistics of the large dolines, and figure 13 shows their comparative profiles. Sarawak Chamber has been included for comparison; its area matches that of all the large dolines with vertical perimeter walls, though this does not necessarily imply that the dolines were formed by collapses of individual cave chambers.

Garden of Eden, in the Mulu Park, has the largest dimensions. However, it only has cliffs round half of its perimeter; the other half opens from a blind valley draining off adjacent shales. It was formed as the sinkhole and cave at the end of the valley enlarged and broke into a very large cave passage crossing at right angles (Waltham and Brook, 1980). A profile drawn through the remnants of this passage, Deer Cave and Green Cave is impressive (dashed in Figure 13), but any other profile is very asymmetrical. Some may not accept the Garden of Eden as a true doline; it is partly floored by shale.

Luse is the largest of the many giant dolines in the Nakanai Mountains of New Britain. It is thickly forested, lacks any vertical cliffs, and is rather uninspiring in its morphology. In the same karst, the dolines of Ora, Kavakuna and Korikobi each have volumes of over 15 million cubic metres, but all are smaller versions of Luse lacking encircling cliffs (Maire, 1981). El Sotano de Barro is the largest of Mexico's deep pits, and Sarisarinama is the largest of the remarkable dolines in the ancient sandstone plateaux of Venezuela. Another remarkable doline is the Crveno Jezero in Croatia; its greatest diameter is nearly 400 m, though this reduces lower down; its depth is around 220 m, and there is also a lake 250 m deep in part of its floor (Bozicevic and Pepeonik, 1987); impressive statistics, but its volume is probably well under 32 million cubic metres and its appearance is reputed to be not so spectacular.

Xiaoyanwan has a very large area and volume, along with bare perimeter cliffs which are a superb sight. Mynie, another giant doline in the Nakanai Mountains (Maire, 1981), is deeper, and its profile is impressive; it does have vertical walls for its entire perimeter, though these are mostly clad in dense vegetation. These two dolines have elements of verticality which make them far superior to Luse and the Garden of Eden. It is probably best to set aside pure dimensions, and accept that Xiaoyanwan and Mynie are the two most magnificent and spectacular dolines in the world; they are the ultimate examples of their landform type.

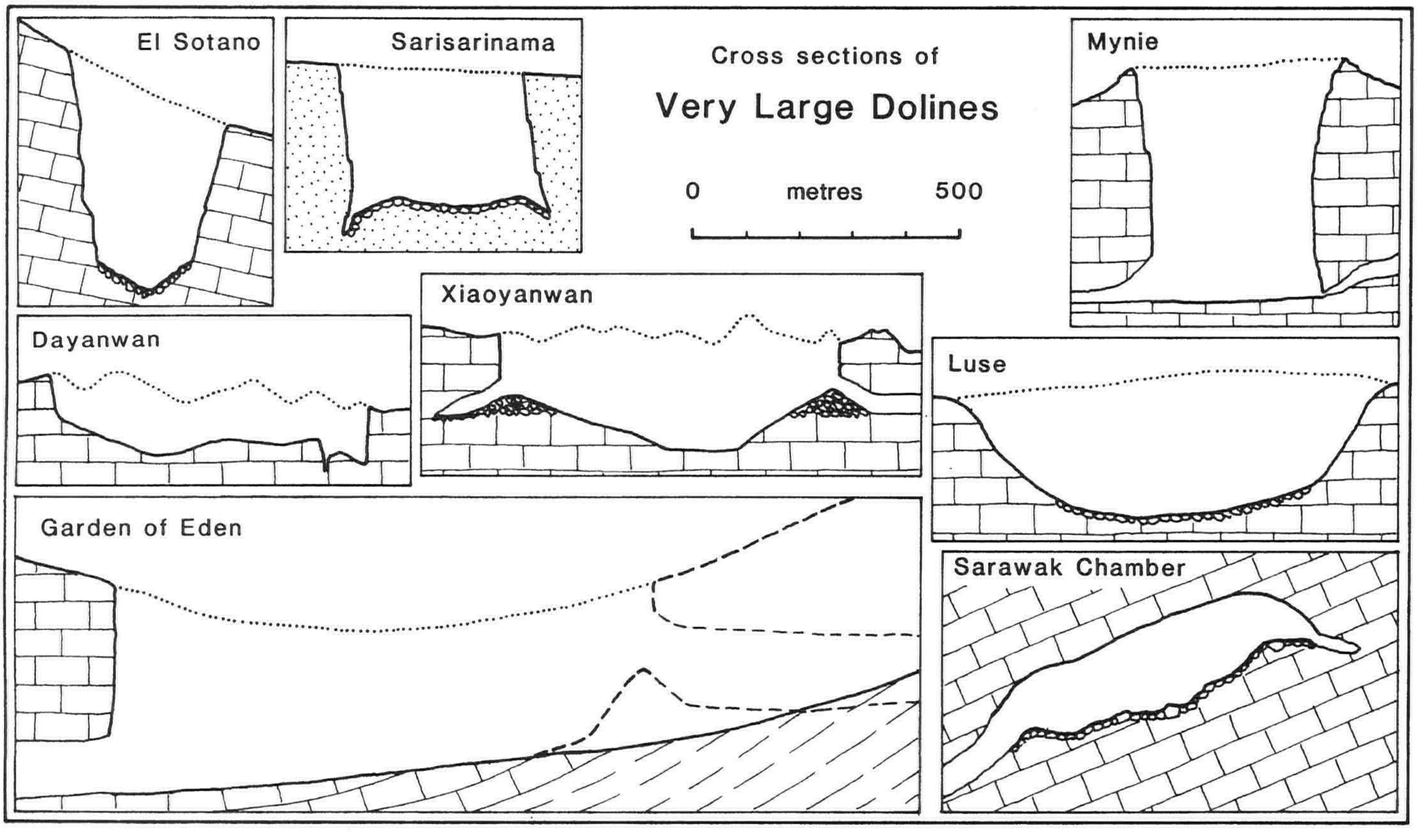


Figure 13. Profiles through some of the world's giant dolines, all drawn to the same scale.

Doline	Location	Depth metres	Diameters metres	Area sq m	Volume cu m
Garden of Eden	Sarawak	200	1200 x 800	750 000	150 000 000
Luse	New Britain	220	800 x 600	380 000	60 000 000
Xiaoyanwan	China	210	650 x 450	196 000	36 000 000
Mynie	New Britain	420	300 x 300	70 000	26 000 000
Sarisarinama	Venezuala	275	340 x 300	72 000	18 000 000
Dayanwan	China	110	680 x 280	164 000	15 000 000
El Sotano	Mexico	380	400 x 200	60 000	15 000 000
Sarawak Chamber	Sarawak	ht 90	700 x 300	165 000	15 000 000

Table 3. Dimensions of the world's very large dolines.

ACKNOWLEDGEMENTS

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The China Caves Project report on Xingwen includes the cave surveys and also material on caves in Guangxi, Tibet and Yunnan. It is available by post for £4.20 from the first author or from BCRA Sales.

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Water Chemistry in the Xingwen Caves, China

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Abstract: The spectacular karst area of Xingwen receives recharge of varying water quality from different catchments. Much of the recharge water contains sulphuric acid derived by oxidation of pyrite, which occurs both naturally and as a result of mining and mineral processing activities. Analyses of water from different catchments feeding the aquifer and within the caves are used to assess the impact of naturally and anthropogenically produced sulphuric acid on the aquifer, both in terms of water quality and its effects on limestone dissolution rates and the development of caves. Net rates of limestone dissolution are certainly enhanced by sulphuric acid at the present day, but much of this is due to anthropogenic effects. Significant amounts of sulphuric acid are however produced by natural pyrite oxidation reactions in catchments underlain by shale and would have played a siginificant role in limestone dissolution and cave development in the past. Inwashed pyritic sediment, the result of mineral processing, pollutes some of the caves and gives rise to highly acidic waters and bad air in the form of acidic mists and low oxygen concentrations.

INTRODUCTION

Xingwen county lies in the south of China's Sichuan Province, approximately 80 km SE of Yibin, a city on the Chiang Jiang (Yangtze River). The limestone escarpment at Xingwen is spectacularly karstified and hosts many large caves which were explored and surveyed during the 1992 China Caves Project (Waltham and Willis 1993). The Xingwen karst is formed in limestones of the middle Permian Maokou and Qixia Formations which have an elliptical outcrop approx. 60 km x 20 km around a major pericline. Xingwen lies on the south side of this pericline, where the limestone dips at around 5-25° and hence there is a wide limestone outcrop on the dip slope (Fig. 1). The limestones unconformably overlie Silurian sandstones and shales, which form the core of the pericline. Upper Permian shales and sandstones overlie the limestones and these contain beds of coal and, almost immediately above the limestone, a 1.5 m thick bed of pyrite ore.

The pyrite and coal deposits form the basis of much of the local industry; coal is mined for domestic fuel as well as for use in conjunction with pyrite in sulphur production and to fuel lime kilns. The mining of coal and pyrite ore and the mineral processing, by which pyrite is beneficiated from the ore, lead to pollution of some waters. Additionally the smelting of pyrite to produce sulphur leads to the release of sulphur dioxide to the atmosphere (with localized smog and "acid rain") and the creation of large slagheaps containing unused pyrite.

A reconnaissance study of the chemistry of the waters of the Xingwen karst aquifer and its feeder catchments was undertaken as part of the 1992 China Caves Project. The Xingwen area has been designated a regional park and has very considerable tourist potential. This conflicts with the local sulphur producing industry and the realization of the future potential of the park presents a fascinating challenge to the county government. Mapping of the caves, determination of the underground drainage routes and examination of

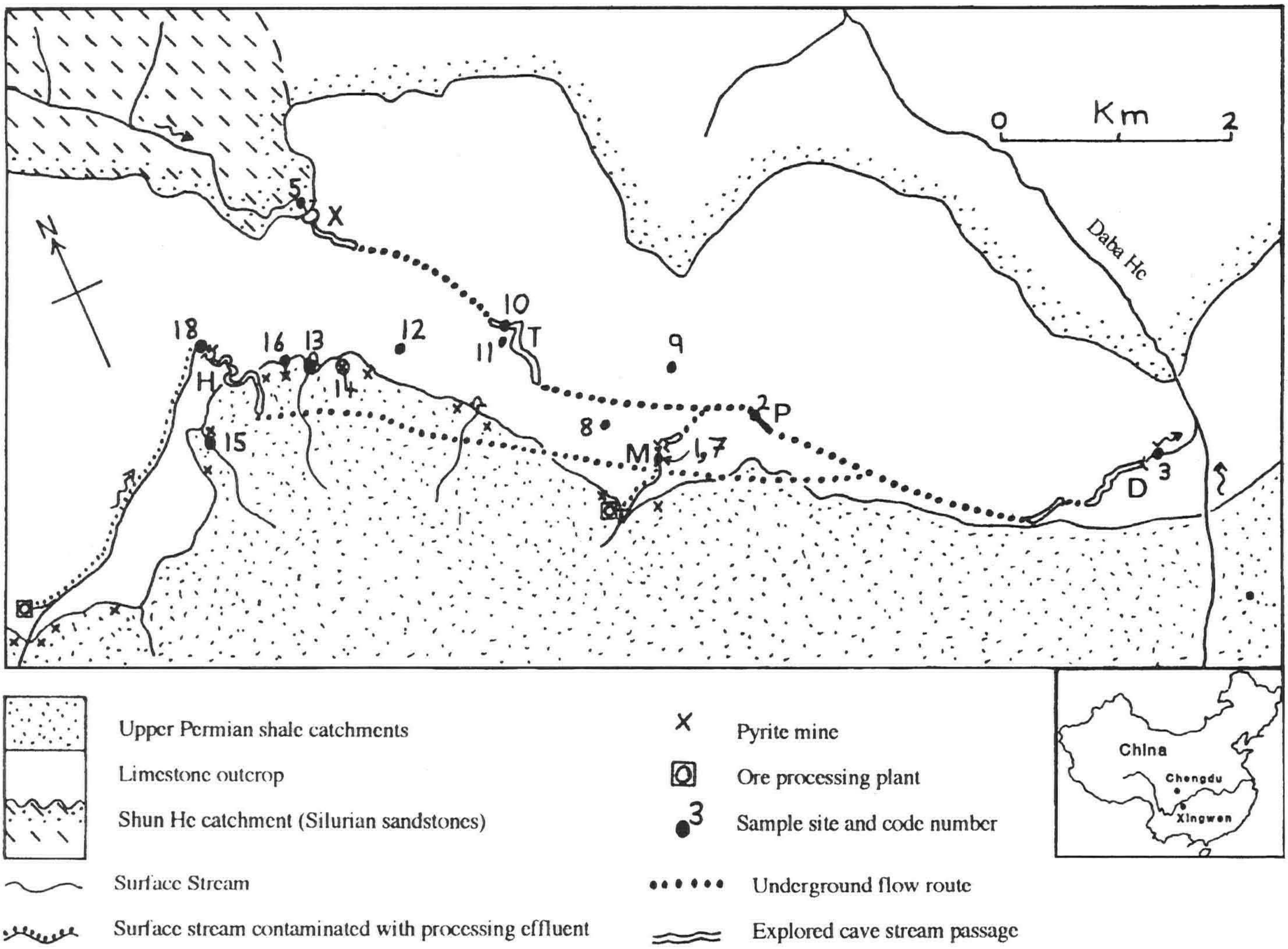

Figure 1. Simplified geology and drainage in the Xingwen karst region. For more detailed area maps see Waltham et al. *(this volume). Catchments and caves referred to in the text are: X = Xia Dong, T = Tiencuan Dong, P = Pucaowan Dong, M = Mulangu, H = Heping, D = Donghe resurgence.*

the extent of industrial impact on the aquifer waters improves the database for future management of the area. The magnitude of the effects of sulphuric acid corrosion, both naturally and anthropogenically produced, on the development of the aquifer can also be assessed through examination of the water chemistry.

CATCHMENTS FEEDING THE XINGWEN KARST AQUIFER

A detailed description of the aquifer and the caves is given by Waltham *et al.* (1993). The catchments discussed below are marked on Fig. 1.

1) Autogenic recharge

All rainfall onto the limestone outcrop sinks. This water collects into percolation flows underground and these percolation inlets augment the allogenic flows from the stream sinks. Where soil is present in fractures, valleys and on doline floors it is intensively but traditionally farmed. The major sulphur works in the area are built on the limestone outcrop. Samples were taken from small percolation inlets into the caves.

2) Silurian sandstone catchments

Rivers drain from these catchments into sink caves at the base of the limestone escarpment. All the catchments are fertile farmland and are intensively but traditionally farmed, with rice, maize and tobacco being the main crops. There is no industrialization of these catchments. Samples were taken at the Xia Dong sink and in the Tiencuan Dong cave river.

3) Permian shale catchments

These catchments are underlain by a pyritic shale-coal sequence and are farmed with varying degrees of intensity. Drainage from these areas feeds into gorge and sinkhole systems in the upper part of the limestone. Samples were taken from streams above the pyrite mines where there was no coal mining activity higher in their catchments.

4) Mine drainage

The pyrite ore bed at the base of the Permian shale sequence (and immediately above the limestone) is worked in a series of mines of various sizes. These work down the dip of the bed into the hillside and are drained through their floors into the underlying limestone aquifer. There are also numerous small coal mines in the sequence above emitting drainage from their entrances and into sinking streams. Sample 14 was taken within a working mine (from a drainage sump pool) and sample 16 from waters issuing from fissures in limestone immediately below an abandoned mine.

5) Streams contaminated with processing tailings

The Mulangu river and the Heping Dong stream are both heavily contaminated by tailings from modern ore processing plant, rendering them highly turbid. Two samples were taken from the Mulangu river on separate occasions and one from the Heping Dong stream. Both rivers sink into caves and carry a considerable load of suspended sediment. There are smaller ore washing plants at many of the mines which discharge similar effluent into sinking streams.

All of the water recharging the Xingwen karst drains out at a single resurgence at Donghe Dong. This is in the Daba river valley, on the south edge of the area; the Daba river crosses the limestone outcrop without sinking and the valley acts as a discharge boundary controlling the base level of groundwater in the aquifer.

SAMPLING AND ANALYTICAL DETAILS

The sampling locations are marked on Fig. 1. As far as possible at least two samples were taken of each of the catchment water types listed above. A further two samples were taken, one at Pucaowan cave in the centre of the aquifer (Loc. 2, Fig. 1) and one at the Dong He resurgence (Loc. 3, Fig. 1), the single resurgence for the Xingwen karst; these will represent mixtures of waters derived from the catchments described above. All the samples were collected at baseflow conditions, prior to the rainfall and flooding which affected the area later in the expedition.

Each sample was collected in a pre-rinsed bottle of known volume when full. Water pH and conductivity were measured in situ in the field or, in the case of two of the samples collected underground, immediately on opening the sample bottle in daylight. Samples were filtered in the field on to pre-weighed filters and two aliquots of the filtrate retained, one acidified with 1% nitric acid for cation analysis and one unacidified for anions. Cations were analysed by ICP-OES and anions by ion chromatography.

Filters and the suspended sediment were rinsed with distilled water and sun-dried in the field. On return they were dried at 110°C and re-weighed to determine suspended sediment concentration. The sediments were examined under a binocular microscope and subsequently analyzed for pyrite by the chromium reduction method (Canfield *et al.* 1986).

PYRITE OXIDATION: NATURAL AND ANTHROPOGENIC

Pyrite (FeS_2) is a common constituent of many sedimentary rocks, usually formed as a result of bacterial processes during diagenesis of the sediment after burial (Berner, 1970). Pyrite and other sulphide minerals are also major constituents of many ore bodies. When exposed to an oxidizing, near surface environment, pyrite and other sulphides become unstable and undergo oxidation reactions. This may involve oxidation by molecular oxygen derived from air (often via oxygenated shallow groundwaters).

$$FeS_2 + 7/2O_2 + H_2O = 2SO_4^{2} + 2H^+ + Fe^{2+} \qquad (1;$$

or may involve another oxidizing agent, e.g. Fe^{3+},

$$FeS_2 + 14Fe^{3+} + 8H_2O = 2SO_4^{2+} + 16H^+ + 15Fe^{2+} \qquad (2.$$

These reactions are often microbially mediated, since energy is released in the transformation of sulphide to sulphate. The stable end products of these reactions are sulphate and protons; essentially sulphuric acid is being produced and the waters become highly acidic.

The process of pyrite oxidation takes place entirely naturally, as part of the normal surface weathering process. However man's activities may accelerate the process beyond its natural rate. This is often the result of mining activities, which modify groundwater flow paths and introduce oxygenated surface waters into previously reducing environments. This gives rise to the phenomenon of Acid Mine Drainage (AMD).

In the Xingwen region pyrite oxidation reactions take place in three situations;

1) As part of natural weathering reactions. The upper Permian shale sequence is pyrite rich and natural weathering by shallow groundwaters involves pyrite oxidation and releases acid sulphate to streams sinking at the limestone contact. This process is less important in the Silurian catchment, since the lithologies here contain less pyrite.

2) As a result of mining operations for pyrite and coal AMD is produced. The mines drain often highly acidic waters through their floors into the limestone or discharge them from adit entrances into sinking streams.

3) Effluent from ore washing plant is discharged into sinking streams and contains significant amounts of fine grained pyrite, which oxidizes in the surface and groundwater. Pyrite oxidation also takes place where the sediment accumulates in groundwater conduits and cave passages in the limestone aquifer. At the same plants, pyrite oxidation will also take place in the slag heaps and contaminate the drainage from these.

A fourth source of acidity and sulphate in the area is 'acid rain' resulting from sulphur dioxide released during the pyrite smelting process. This is a combination of "rain-out" and dry deposition and will be washed into soil and percolation waters in the vicinity of the sulphur production plants.

RESULTS

The water analyses are presented in Table 1. All analyses are reported in mgL^{-1} except pH and conductivity ($mScm^{-1}$). Bicarbonate is assumed to be the balance between anion and cation charge totals, as it was not titrated in the field. For the alkaline waters this gives bicarbonate concentrations of 90-190 mgL^{-1}. For the acid waters the charge balance on the analyses is sensitive to assumptions on the speciation of Fe and Al (H^+ is included in the charge balance based on pH measured using an activity coefficient calculated by a Debye-Hückel model). Many of these analyses give small positive charge excess when Fe and Al are taken as 3^+ (which are more stable at lower pH). Such analyses would balance with no bicarbonate (which would not be stable at pH <4.5) if a proportion of Fe were present as 2^+ or Al as some complex of lower charge. In three remaining cases (samples 14 and 18 and to a lesser degree 13) there is a significant excess of negative charge even when calculated using Fe^{3+} and Al^{3+}. These samples are those with the highest sulphate concentration and the imbalance could be an artefact of the analyses at such high sulphate

Table 1. Analytical data on Xingwen waters. Code numbers refer to sample locations on Fig. 1.

	Rainwater	Percolation waters			Silurian catchment		U. Permian catchment		Mine waters		Streams contaminated with ore processing effluent			Puccaowan Stream	Donghe Resurgence
Code no.	9	8	11	12	5	10	13	15	14	16	1	7	18	2	3
pH	6.24	7.78	7.23	7.57	8.13	7.30	4.09	2.95	2.91	4.56	3.75	3.98	2.60	3.96	4.67
Conductivity	0.07	0.59	0.39	0.41	0.20	0.23	1.40	1.40	7.92	0.73	1.17	1.13	4.80	0.88	0.73
Susp. Sed.	<1	<1	<1	<1	<1	30	<1	<1	<1	100	2590	10200	1360	80	100
Ca	8.6	137.0	77.0	93.0	39.0	46.0	239.0	94.0	440.0	136.0	147.0	169.0	403.0	141.0	149.0
Na	1.0	4.3	1.2	1.5	3.0	3.1	3.6	5.5	7.7	2.8	15.0	15.0	47.0	7.0	6.2
K	0.0	1.2	0.8	0.7	0.8	0.8	1.4	1.1	2.8	0.7	1.9	2.1	4.5	8.8	1.3
Mg	0.24	5.00	4.40	1.70	3.60	4.20	10.80	27.00	125.00	7.70	16.00	16.00	85.00	12.00	11.20
Fe	0.21	0.04	<0.005	<0.005	<0.005	<0.005	0.68	99.00	2800.00	30.00	59.00	57.00	1010.00	11.20	0.09
Al	0.14	0.04	0.02	0.00	0.05	0.05	114.00	25.00	584.00	2.40	40.00	38.00	370.00	24.00	10.80
SO4	17	190	45	97	40	48	1400	760	12800	320	680	780	7000	520	450
NO3	2.10	22.00	11.00	18.00	4.50	4.50	11.10	0.08	<0.05	12.80	7.10	8.40	1.06	7.00	5.20
Cl	0.51	5.20	1.30	2.20	1.10	0.92	3.90	2.43	5.20	1.60	3.50	3.20	5.90	9.70	2.16
F	<0.05	0.23	0.19	0.09	<0.05	0.05	0.65	0.48	15.10	0.28	1.12	1.60	7.60	0.88	0.97
Si	3.8	2.4	2.2	1.66	1.7	1.8	6.6	6.3	50	3.5	6.5	6.2	17.6	3.8	3.8
HCO3 *	5.97	183	190	152	89.0	104	-223	43.1	-1060	155	168	80.6	-1090	42.2	19.8
Total +ve charge (meq)	0.500	7.47	4.28	4.86	2.39	2.80	25.8	16.6	250	9.47	17.2	17.9	128	12.0	9.89

All analyses are in units of mgL^{-1}, except pH, conductivity ($mScm^{-1}$)and +ve charge ($meqL^{-1}$). HCO_3^- was calculated as the difference between total +ve and -ve charge (after accounting for H^+ in acidic waters using an activity coefficient calculated by an extended Debye-Huckel model). Three high sulphate waters have an excess negative charge, for discussion of this see text.

concentration. Alternatively these samples could have contained lower charge sulphur species (such as SO_2 (aq), HSO_3^- or HSO_4^-) when collected, and which have subsequently oxidized to SO_4^{2-} prior to analysis, giving an excess of negative charge.

Rainwater was collected in a cleaned plastic bowl during a heavy rainfall event. It has slightly acidic pH, usual for rainwater, but slightly higher conductivity and higher SO_4 content than pristine rain, probably due to the local atmospheric pollution from sulphur production.

The percolation waters have slightly alkaline pH and relatively low conductivity (0.4-0.6 $mScm^{-1}$). Of note are the high calcium, sulphate and nitrate concentrations of these waters (Table 1). Waters from the Silurian catchment also have alkaline pH and even lower conductivities than the karst percolation waters, with concomitantly lower calcium, sulphate and nitrate.

The waters from the other catchment types are all far more acidic (pH from 4.6 to 2.6) and extremely sulphate rich (320-12,800 mgL^{-1}). This is a clear indication of extensive pyrite oxidation. These waters are also far richer in iron, aluminium and magnesium (Table 1). Concentrations of potassium are similar in all the waters (0.7-4.5 mgL^{-1}). Calcium concentrations in the waters (94-440 mgL^{-1}) are all higher than the Silurian catchment waters (~40 mgL^{-1}) and similar to or higher than the percolation waters (77-137 mgL^{-1}). Sodium is present at similar or slightly higher concentrations (2.8-7.7 mgL^{-1}) in the shale catchments and mine waters compared to the Silurian catchments and percolations waters (1.2-4.3 mgL^{-1}), but at much higher concentrations (15-47 mgL^{-1}) in the rivers contaminated with processing tailings.

The majority of waters contained <1 mgL^{-1} of suspended sediment. The marked exceptions are the streams contaminated by ore processing tailings which contain 1,360-10,200 mgL^{-1}, of which 2.4-7.9% is pyrite (Table 2). The rest of the sediment was composed of rock flour, mainly clay minerals. One of the mine waters (sample 16) also contained suspended pyrite which formed 7.1% of the sediment load (Table 2) the rest being an ochreous ooze, presumably an amorphous precipitate of $Fe(OH)_3$. Sample 10, the river in Tiencuan Dong, draining a Silurian catchment, contained 30 mgL^{-1} of suspended sediment, too little for mineral identification.

Two waters were also sampled from the centre part of the aquifer (Pucaowan cave; sample 2, Fig. 1) and the Donghe resurgence (sample 3, Fig. 1). These represent mixtures of the water types discussed above.

DISCUSSION

Percolation waters

The percolation waters are all essentially calcium bicarbonate solutions, but with significant sulphate and nitrate. The sulphate concentrations are 2.6 to 11 times that in the rainwater sample, and while some of this difference could be accounted for by concentration by evapo-transpiration, it is likely that sulphate is also being added by atmospheric dry deposition. The nitrate concentrations are high considering that there is minimal use of agrochemicals on the limestone soils; however all available soil is farmed and animal slurry is applied as fertilizer and could well be the nitrate source.

Table 2. Pyrite contents of suspended sediment samples. Code numbers refer to sample locations on Fig. 1.

Code No.	Suspended sediment mgL^{-1}	%Pyrite in sediment	Suspended pyrite mgL^{-1}
1	2590	7.85	204
2	80	4.68	4
3	100	4.49	4
7	10200	2.36	241
16	100	7.11	7
18	1360	5.36	73

Non-industrialized catchments

These lie on the Silurian sandstones and upper Permian shales and the runoff water chemistry contrasts markedly between the two substrate types. The Silurian catchments have slightly alkaline, low concentration $Ca\text{-}HCO_3\text{-}SO_4$ waters, while the Permian shale catchment waters are acidic and contain high concentrations of sulphate and aluminium, and high iron in sample 15. High sulphate is the result of pyrite oxidation, and whilst this reaction releases iron, this may subsequently be removed from solution by precipitation of iron hydroxides, a feature commonly observed in the watercourses in these catchments. The high aluminium concentrations result from leaching of aluminosilicate minerals (clays and feldspars) in the shales by these low pH waters.

Industrially contaminated waters

These waters emanate from the ore processing plants and mines. All are extremely sulphate-rich and acidic, due to pyrite oxidation, and all but one have very high aluminium concentrations due to leaching of aluminosilicate minerals at low pH. The exception (no. 16) is partly neutralized (pH 4.6, as opposed to 2.6 to 4 for the others) and demonstrates the pH dependence of aluminium solubility, aluminium being precipitated as the solution is neutralized. The high aluminium and sulphate concentrations and low pH of these waters (together with the possibility of dissolved heavy metals released during pyrite oxidation) renders these waters of very low quality and unusable for drinking or irrigation purposes.

Mixing and evolution of waters in the aquifer

Many of the waters recharging the aquifer have chemistries which are markedly out of equilibrium with calcite. Some components may behave in a conservative fashion on mixing with other types and/or reaction with the limestone aquifer rocks. Others may either be lost from solution due to precipitation of solid phases on neutralization of the more aggressive waters, or gained by reaction of the waters with their suspended sediment load or dissolution of limestone.

On geomorphological grounds the water in Pucaowan cave is believed to be a mixture of the Mulangu and Xia Dong rivers, plus an added percolation water component. If this hypothesis is correct it should be possible to achieve a mass balance for conservative species in the dissolved load of these flows in which the Pucaowan water is the result of the same mixing ratio of the other flows. That is:

$$Q_P.C_P = Q_M.C_M + Q_X.C_X + Q_{Perc}.C_{Perc}. \qquad (3,$$

where Q and C are the discharge and concentration respectively and the subscripts refer to the flows at Pucaowan (P), Mulangu (M), Xia Dong (X) and the percolation component (Perc). Using date Table 1, conservative mass balance was found to apply for fluoride, aluminium and nitrate with discharges of:

$Q_M = 0.62Q_P$,

$Q_X = 0.28Q_P$,

$Q_{Perc} = 0.10Q_P$;

i.e. under baseflow conditions the flow in Pucaowan is 62% from the Mulangu river, 28% from the Xia Dong stream and 10% from percolation water component. The fact that these three species (and numerous trace metals for which analyses are presented by Bottrell *et al. in prep.*) all yield the same conservative mixing ratios and can be taken as confirmation of the hypothesis that the Pucaowan water is indeed a mixture of these three flows. It is perhaps surprising that aluminium should behave conservatively, however the pH of the mixed flow at Pucaowan remains sufficiently low that no aluminium-bearing solid phases are precipitated. The flows at Pucaowan, Mulangu and Xia Dong were all estimated in the field but not gauged (dye tracing detectors were not recovered due to flooding). At the time the samples were taken, the Pucaowan flow was larger than either Xia Dong or Mulangu and the Xia Dong stream was estimated to be smaller than or at most a similar size to Mulangu. This provides further qualitative support for the mixing hypothesis. It is possible that the contaminated flow from Heping Dong (of similar chemistry to the Mulangu river) contributes to the flow at Pucaowan, but this is more likely to join the main flow further downstream, causing the severe bad air problems in Donghe Dong II.

All of the other species analyzed exhibit either an increase or decrease relative to the conservative mixture calculated on the basis described above; these discrepancies are given in Table 3. Sulphate exhibits a substantial increase, presumably due to oxidation of pyrite in the suspended sediment load. Despite the release of iron by pyrite oxidation, iron shows a marked decrease in concentration, over 50mgL^{-1} if the iron released by pyrite oxidation (as gauged by the increase in sulphate concentration) is taken into account. This loss of iron from solution is the result of oxidation and precipitation as ferrous hydroxide:

$$Fe^{2+} + 1/4O_2 + 5/2H_2O = Fe(OH)_3 + 2H^+ \qquad (4.$$

Ferrous hydroxide precipitates are commonly observed as surface scum and wall coatings in the caves.

Calcium and magnesium both show increases over calculated conservative mixing concentrations, which HCO_{3-} shows a decrease. Both of these effects are the result of proton consuming reactions; limestone dissolution:

$$CaCO_3 + H^+ = Ca^{2+} + HCO_{3-} \qquad (5.$$

(where some Mg is substituted for Ca in the carbonate), and conversion of HCO_3^- to CO_2:

$$HCO_{3-} + H^+ = CO_2 + H_2O \qquad (6.$$

From the data in Table 3 the net sink for acidity (protons) to these reactions (carbonate speciation and limestone dissolution) during the traverse of waters from the Mulangu cave entrance to Pucaowan is 3.1meqL^{-1}. Conversely the net production of protons by reactions 1 and 4 is 2.8 meqL^{-1}; thus the acidity produced is, in effect, almost instantaneously balanced by carbonate dissolution and re-speciation. The discrepancy in these two figures is closely matched by the pH change in the waters between Mulangu and Pucaowan.

Three other dissolved species show changes of smaller magnitude (Table 3). Sodium shows a decrease while potassium shows an increase, which are of similar magnitude when considered in charge terms (0.14 and 0.18 meqL^{-1}). This may be the result of an ion-exchange process on the clay component of the processing fines:

$$K\text{-clay} + Na^+ = Na\text{-clay} + K^+ \qquad (7.$$

The increase in chloride is relatively small in charge terms and may be related to leaching of the clay processing fines in these acidic waters. Suspended sediment shows a massive decrease, due to sedimentation in the system at low flow.

In principle a similar analysis of the components present in the discharge from the whole aquifer could be undertaken. However the number of inputs of variable chemistry and the variety of high sulphate sources renders such an approach unreliable on the larger, more complex system. On a qualitative basis, the overall similarity of the Pucaowan and Donghe waters (except that the latter are less acidic; Table 1) implies that similar processes act on all the acid sulphate inputs to the aquifer. Further work is underway to define the relative budgets of acid sulphate sources to the aquifer by distinguishing them on the basis of the sulphur and oxygen isotopic compositions of the sulphate (Bottrell *et al. in prep.*).

EFFECT OF ACID SULPHATE WATERS ON RATES OF LIMESTONE DISSOLUTION IN THE AQUIFER

As shown in the preceding section, the production of acidity by pyrite oxidation causes limestone dissolution within the aquifer. The aim of the following discussion is to assess the impact of this process, both at the present day and in the natural, pre-industrial aquifer. The presence of acidic sulphate recharge to the aquifer affects limestone dissolution in two ways. Since calcite dissolution rates are pH dependant (e.g. Plummer *et al.* 1978) instantaneous rates of dissolution are increased at the lower pH of these waters. Secondly, the total supply of acidity to the system is increased and hence more calcite can be dissolved per unit of water passing through the system. The calculations below are performed for baseflow conditions under which the data were collected. Flood events act to dilute acid sulphate sources, so the net flux of acid into the aquifer per unit time probably remains approximately constant. However flood events redistribute pyritic sediment in the conduits and by introducing oxygenated water may stimulate sulphuric acid production from this source.

The present day

The section of flooded passage between the Mulangu sink and the rising in Pucaowan provides an excellent natural laboratory for the determination of instantaneous dissolution rates in the acid sulphate waters. Since calcite dissolution is, more-or-less, matched by proton release the pH remains approximately constant, near 4. The major unknown is the surface area of the connecting conduit; this is estimated here as the circumference of the passage at the two sumps (c. 10 m in each case) multiplied by the straight-line sump-to-sump

Table 3. Calculated losses and gains of non-conservative components to the Pucaowan cave water.

Species	Calculated conservative mixture concentration mgL^{-1}	Actual concentration mgL^{-1}	Discrepancy mgL^{-1}	meqL^{-1}
Suspended sediment	3100	80	-3000	-
SO_4^{2-}	475	520	+45	+0.94
Ca^{2+}	118	141	+23	+1.15
Mg^{2+}	11.4	12.0	+0.6	+0.06
Fe^{2+}	36	11	-25	-0.90
Including Fe from pyrite oxidation			-51	-1.84
Na^+	10.3	7.0	-3.3	-0.14
K^+	1.6	8.8	+7.2	+0.18
Cl^-	2.7	9.7	+7.0	+0.20
HCO_3^-	122	42	-80	-1.31
Including HCO_3^- from limestone dissolution			-154	-2.52

distance (680 m), giving 6,800 m^2. From Table 3 the excess dissolution of calcite is 0.6 $mmolL^{-1}$ (60 mgL^{-1}); at an estimated discharge of 0.2 cumec this gives 12gs^{-1} $CaCO_3$ dissolved over 6,800m^2 or 1.8$mgm^{-2}s^{-1}$. Plummer *et al.* (1978) give experimental rates of c. $10^{-5.4}$. $mmolcm^{-2}s^{-1}$ for calcite at pH=4, equivalent to 4 $mgm^{-2}s^{-1}$ in the units used here. Given the uncertainties in the flow and area estimates, these rates can be considered to agree within error. This demonstrates that the acid sulphate waters can approach their theoretical maximum instantaneous limestone dissolution rates, which are c. 10 times those reached in carbonic acid solutions (Plummer *et al.* 1978).

Table 4. Calcium and magnesium concentrations of major karst resurgences in China.

	Ca^{2+} mgL^{-1}	Mg^{2+} mgL^{-1}	$CaCO_3$ equivalent $mmolL^{-1}$
Shanxi	50.3	20.7	2.1
Jinan	70.1	12.1	2.2
Guilin	70.9	2.9	1.9
Xingwen	149	11.2	4.2

First three sets of values are regional means for groups of risings in these areas (from Yuan, 1991, p.40)

The bulk affect of the acid sulphate drainage on the Xingwen aquifer can be gauged from the data in Table 4. At baseflow the Donghe resurgence at Xingwen contains effectively twice the dissolved limestone load of other major karst resurgences in this part of China. This excess corresponds to 100 g $CaCO_3$ per second or 9 tonnes per day (equivalent to 5.4 tonnes per day of pyrite oxidation). Thus, on the aquifer scale, the acid sulphate inputs double the amount of limestone removed by each volume of water.

The past effects of natural pyrite oxidation

At the present day the acid sulphate waters clearly have a significant impact on the dissolution of limestone in the aquifer. Two estimates are now made of the magnitude of the effects of pre-industrial pyrite oxidation processes.

The first approach is to consider the size of the present day natural acid sulphate inputs; these consist of minor streams draining the shale slopes. These waters have high sulphate concentrations and very low pH (Table 1) and hence instantaneous dissolution rates when these enter the limestone aquifer will be high. However they are of limited volume, totalling perhaps 10Ls^{-1} at baseflow. Using a sulphate concentration of 1,000 mgL^{-1} to estimate the total acidity released by pyrite oxidation would give 15g $CaCO_3$ dissolution per second or 1.3 tonnes per day, 14% of the present day total. The effects of natural pyrite oxidation processes could well have had a significant effect on the development of the aquifer.

The second estimate considers the effects on the limestone beneath of oxidizing the pyrite in the rocks immediately overlying the aquifer. This would happen naturally as part of the weathering and erosion process, and would take place either as weathering by surface streams or by groundwaters penetrating the sandstone/shale sequence, including the pyrite ore bed. Only the pyrite in the ore bed is considered. Pyrite is also present throughout the shales and coals of the sequence, so this could be considered a minimum estimate; however some acidity could be neutralized by carbonate or silicate reactions in the shales, but there is no carbonate in the ore horizon. Each square metre of limestone surface has a 1.5 m thickness of ore above it at approx 10% pyrite grade, giving 0.42 tonnes pyrite. When oxidized to sulphuric acid, this has the capacity to dissolve 0.7 tonnes $CaCO_3$. This would create 28% porosity in the top 1 m of the limestone, or 2.8% in the top 10 m (or 0.08% if distributed through the full 350 m thickness). Clearly weathering of the overlying shales can have a very significant impact on porosity development in the aquifer. In particular, the acid sulphate groundwater may penetrate from the shales into the underlying limestone and initiate porosity development before the shales are eroded back to expose the limestone surface must be considered. This process may be instrumental in the inception of the spectacularly developed canyon and shaft systems (both active and abandoned) which feed into the caves along the shale contact and in the relatively immature karst exposed nearby (Waltham and Willis, 1993; Waltham *et al.* 1993). These shafts ultimately coalesce to form large dolines (Waltham 1994) and the rapid early development of these shafts by acid sulphate ground- and surface waters may be an essential prerequisite of the scale of doline development at Xingwen.

BAD AIR IN THE XINGWEN CAVES

Bad air conditions were encountered in three of the caves explored in Xingwen: Pucaowan streamway (where the problem was first encountered); Donghe Dong II streamway; and in Bad Air Pitch in Zhucaojing. In all three cases the passage affected is in, or adjacent to, a streamway contaminated by effluent from processing of pyrite ore and is a zone of poor ventilation above a sump.

Characteristics and symptoms associated with the bad air conditions were:

1) A strong sulphurous smell accompanied by watering of the eyes and pulmonary irritation (this was not noticeable in Pucaowan).

2) Shortage of breath and tiredness or exhaustion on even mild exertion, sometimes accompanied by noticeable panting. Panting subsided on cessation of exertion.

3) In Donghe Dong II and Bad Air Pitch the bad air was visible as a distinct layer of haze below normal air.

Symptom 2) is generally similar to effects observed at altitude due to decreased oxygen partial pressure. Noticeable panting is also a symptom of increased CO_2 concentrations in the cave atmosphere. Decreased oxygen partial pressure in these caves would result from consumption of oxygen by pyrite oxidation (reaction 1, above), the pyrite being washed in with the suspended sediment from the ore processing plant (Table 2, above).

The sulphurous smell noted in the more severely affected cave passages probably results from the release of SO_2 into the cave atmosphere. As oxygen partial pressure decreases due to reaction 1, then a reaction such as:

$$FeS_2 + 3O_2 = SO_2 + SO_4^{2-} + Fe^{2+} \qquad (8.$$

producing an intermediate S(IV) compound will become relatively more important, releasing SO_2 to the cave atmosphere. Sulphur dioxide is an acid gas, with a pungent suphurous odour. It is heavier than air and would form a haze and cause irritation to the eyes and lungs. Associated with SO_2 would be aerosols of sulphurous (H_2SO_3) and sulphuric (H_2SO_4) acids. All of these compounds are toxic (Sax 1981, pp. 1133-1135). Additionally dissolution of limestone and release of CO_2 by acidic waters (reactions 5 and 6 above) raises the CO_2 concentration in the cave atmosphere.

This cocktail of effects produces a potentially lethal form of bad air in some of the caves. It is fortunate that the anoxia is associated with SO_2 which is readily detectable by its odour, since blackout and death from anoxia alone are otherwise asymptomatic. Anoxia and high CO_2 concentrations are probably responsible for the immediate symptoms of exhaustion and shortage of breath experienced in the caves. The sulphur species cause watering of the eyes, pulmonary irritation and may be responsible for the longer-lasting symptoms of "poisoning" experienced by some members of the team. Ingestion or skin absorption of dissolved heavy metals from water or spray may also have compounded the poisoning symptoms.

Utimately it is the presence of the inwashed pyrite fines, which continue to consume oxygen and generate acidity within the caves which is responsible for the bad air problems. Since sulphide ores are commonly associated with limestone areas, active mineral processing plants may pose similar threats in other areas. A similar risk obviously exists in abandoned sulphide mines, where remaining ore may be oxidized in situ.

SUMMARY

The Xingwen karst aquifer receives relatively pristine drainage from agricultural catchments on the underlying sandstone; autogenic inputs are contaminated by sulphate from acid rain and/or dry deposition but are rapidly neutralized. All the other inputs to the aquifer are of acid sulphate waters resulting from pyrite oxidation. This occurs partly naturally as a result of weathering processes in catchments underlain by the upper Permian shales and as a result of mining and mineral processing activities. All of the acid sulphate drainage is of extremely low water quality.

Relative to normal karst processes of carbonic acid dissolution the low pH of the acid sulphate waters increases instantaneous limestone dissolution rates by a factor of about 10. The present day acid sulphate inputs double the net rate of limestone removal from the aquifer. In the pre-industrial aquifer the acid sulphate input from shale and ore weathering is estimated to have been around 14% of its present day magnitude. Whilst this would have had a relatively limited impact on the mature karst aquifer, its effect on early porosity development may have been profound.

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Preliminary results on recent palaeomagnetic secular variation recorded in speleothems from Xingwen, Sichuan, China

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Abstract: This study has concentrated on producing the first dated secular variation records from speleothems (secondary cave-calcite deposits) in China. The four samples analysed at present all show excellent correlation in both declination and inclination. Virtual geomagnetic pole positions show evidence for both eastward (7000 to 2900 years b.p.) and westward (2900 years b.p. to the present) drift of the non-dipole field. Features of declination and inclination are also correlatable with those from archaeomagnetic data from China covering a similar time period. Comparison of the inclinations of coeval lateral and central samples have shown inclination errors to be absent. Dating of the palaeomagnetic features has been performed using the well tested uranium-series disequilibrium method. Initial attempts to produce palaeointensity records have been met with little success. Initial rock magnetic studies appear to point to haematite as the dominant carrier of remanence.

INTRODUCTION

The study of magnetisation contained within rocks and artefacts has developed enormously over the past 30 years, to such an extent that our understanding of this phenomenon has led to a revolution in our thinking on the Earth's magnetic field. Enough data is now available to produce models which describe past field behaviour and, to some extent, predict those of the future (Gubbins, 1991; Bloxham and Gubbins, 1986; Bloxham *et al*, 1989). However, these models are largely based on observatory and historical data, limited to the past 400 years. In order to improve the accuracy of these models data is needed from a wide range of localities since observatory data, by its nature, is time constrained. Therefore, to extend the record of the geomagnetic field back into the past we need to study easily datable and consistent recorders of field change.

In China, published records of the long term field variation known as palaeomagnetic secular variation are, so far, obtained from archaeological sources. China, being one of the first civilised countries, has a wide range of archaeological sites, with material suitable for the production of secular variation records. Sites are especially common on the banks of the Yellow and Yangtze rivers, suitable materials being pottery sherds, baked earths, tiles and city walls. Some of these materials may be dated historically (and matched to observatory records) or from their archaeological context or by use of ^{14}C techniques, although not without potential difficulty (Suess, 1970; Ralph, 1972; Stuiver, 1978).

Due to the nature of archaeological materials a continuous record of secular variation is difficult to obtain. Suitable materials are not equally spaced in time and indeed may not be suitable for study; thus 'snapshots' of field variation are produced. Field intensity records can be extracted from unoriented samples but directional data requires samples to be in-situ. Thus the rejection rate may be high and gaps in the record may become apparent. Wei *et al* (1983) show a summary of results obtained from archaeomagnetic research in China covering the last 7000 years (5300 BC - 1900 AD).

Speleothems (secondary calcite formations such as stalagmites, stalactites, and flowstones) have been shown in several publications to be reliable recorders of secular variation (Latham *et al*, 1979; Latham, 1981; Morinaga *et al*, 1989; Perkins and Maher, 1993). They appear to have unique advantages over other materials in that they:-

1. Can be directly and, often, accurately dated using the ^{230}Th - ^{234}U disequilibrium method.
2. Can provide a continuous record of field change with single sample resolutions in the order of 100 years, depending on growth rate.
3. Grow in-situ and hence are easily oriented.
4. Do not appear to be affected by depositional errors of the same magnitude often associated with sedimentary records (Verosub, 1977; Latham, *et al*, 1982).
5. May also provide a combined and non-fragmentary directional and intensity record throughout the period of their growth, although this has yet to be explored fully.

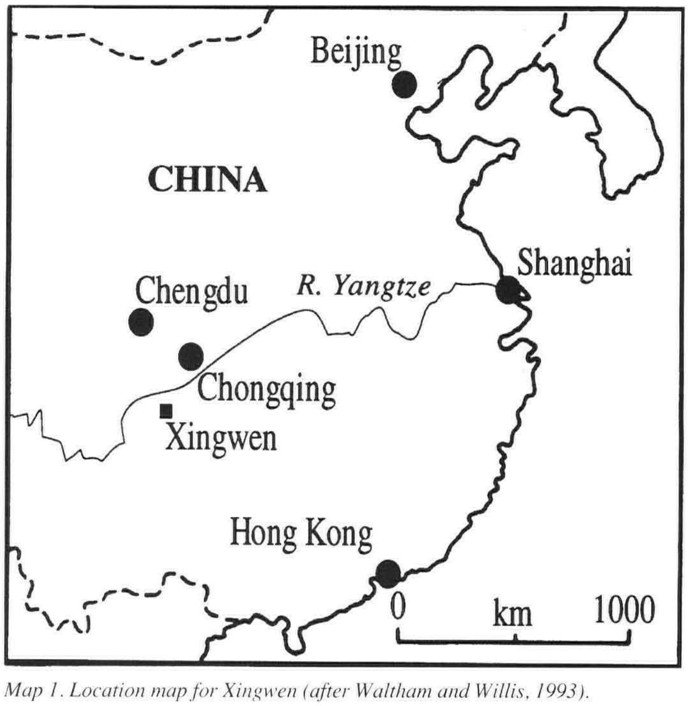
AIMS OF THE PROJECT

In this study, speleothems may provide records of secular variation that are complementary to archaeomagnetic studies and go some way to filling gaps in the current record. It forms part of ongoing research at Liverpool University on recent secular variation in speleothems from Zimbabwe, Guatemala, Mexico, Vancouver Island, the British Isles and Northern Spain. Ultimately the data may be used to extend the field modelling of observatory based data (Gubbins, 1993; Bloxham and Gubbins, 1986; Bloxham *et al*, 1989).

The aim of this particular project was to collect speleothems, in the form of stalagmites, for study of secular variation in China covering the period 0 - 10000 years or as close as possible. Some preliminary results from a Chinese speleothem were published by Liu *et al* (1988) but no attempt was made at direct dating. Similarly, no attempt was made to compare their records to archaeomagnetic records from China. Dating of natural remanent magnetisation (NRM) features using U - The disequilibrium methods available at Liverpool University, provides the necessary dating control, as described by Latham and Schwarcz, (1992). With this achieved it would then be possible to construct dated virtual geomagnetic pole (VGP) positions allowing inferences to be made on ancient field behaviour. Sampling criteria were employed so as to maximise the likelihood of collecting usable speleothems. With data from several samples a composite record of geomagnetic field behaviour should be possible, thus eliminating the problem of fragmentary data such as that from archaeomagnetic studies.

SAMPLING TECHNIQUES AND MEASUREMENT

Xingwen is a large limestone karst area lying on the southern edge of Sichuan province, 70km southeast of Yibin (Map 1). Six stalagmites were collected from two caves in the Xingwen region, two stalagmites from Zhucaojing (Pig Trough Well) and four from Tiencuan Dong (Sky Spring Cave). These caves were explored and surveyed by the 1993 China Caves Project team (Waltham and Willis, 1993).



Map 1. Location map for Xingwen (after Waltham and Willis, 1993).

In order that samples were of sufficient quality for palaeomagnetic and dating work sampling criteria were adhered to. Some of the work at Liverpool has been hindered by the fact that samples, once cut, have magnetisations too weak to be measured even using cryogenic magnetometers or are of such low uranium concentrations that dating is inaccurate. The criteria used during collection are as follows, and are based on this experience and on findings of other speleothem workers (Latham (1982); Lean *(pers comm.))*:

1. Samples must be in-situ for accurate orientation.
2. To collect stalagmites of the correct age range it was assumed that a stalagmite in or near a highly flood prone streamway was active. This could be confirmed by noting if the drip cap was wet and a parent stalactite was present above.
3. Seasonal flooding should inundate the stalagmite allowing accumulation of mud and other detritus on its surface.
4. Stalagmites of sufficient height were taken so as to provide a record of high age resolution.
5. Sample width must be sufficient so as to allow sub-sampling of the central drip cap without inclusion of lateral growth layers.
6. Stalagmites of apparently uniform growth were collected. Samples which appeared to be formed during several periods of growth, as indicated by an upper section of stalagmite growing on an offset lower portion, were avoided.
7. Signs of chemical attack by aggressive ground waters were seen as holes and pits in the drip cap of some potential samples. This could indicate that uranium leaching and migration had taken place leading to dating difficulties.

Sampling in Zhucaojing was made in two areas. PT01 was growing beneath a skylight in a large chamber west of the Entrance Chamber. The remaining samples (PT02, PT03, PT04) were collected from the Lake Sump, an inlet passage off the Downstream Trunk, 400 metres north-east of the Breakdown Chamber (Waltham and Willis, 1993). Figure 1 shows the sampling site for these three stalagmites from Zhucaojing. Stalagmite PT02 appeared to be inundated by a relatively small rise in the water level, due to its proximity to a sump, and would probably be affected by anything more than an average rainfall. However, rainy-season water levels appear to cause the sump and the lake to back up and fill the chamber leading to total submergence of PT02, PT03, and PT04 simultaneously.

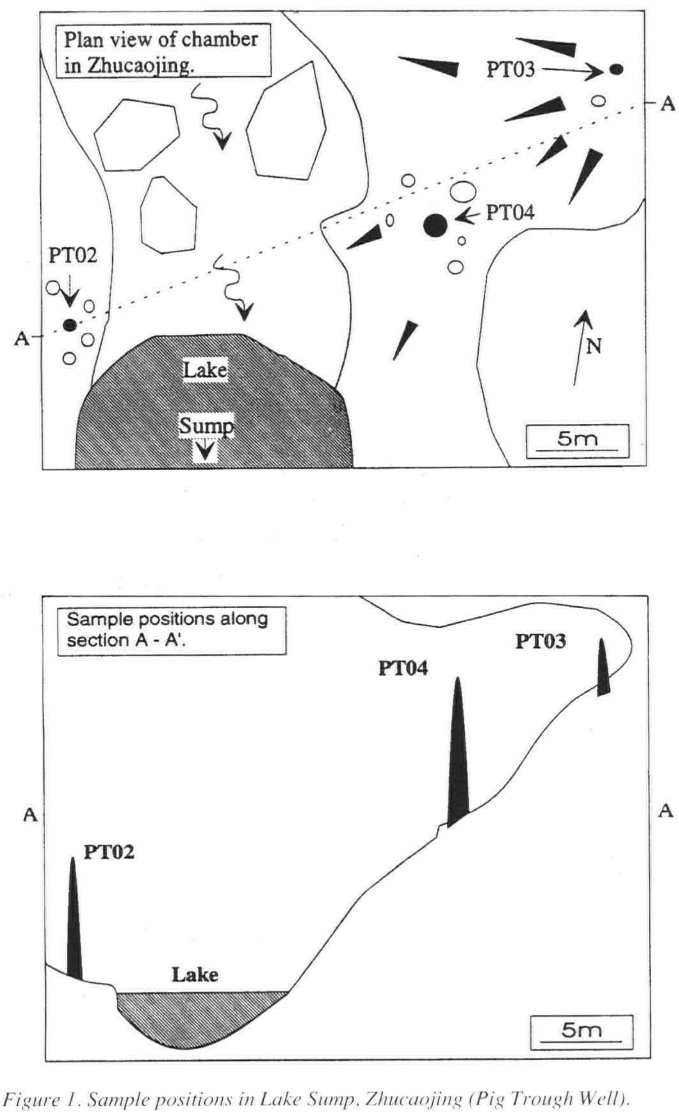


Figure 1. Sample positions in Lake Sump, Zhucaojing (Pig Trough Well).

Samples from Tiencuan Dong were collected from an inlet off the active River Passage 100 metres from the upstream sump (Waltham and Willis, 1993). At the time of collection a small stream was present but evidence of severe flooding is seen in the form of large quantities of mud on the passage floor and sides. SC01 was growing on a ledge 4 metres above the streamway and its base was partially buried in mud. SC02 was found in a similar situation directly opposite SC01 but was 5 metres above the streamway.

The results from four stalagmites, (PT03, PT04, SC01, SC02) obtained at this time in the study, show that the sampling criteria are valid. Only one sample, PT01, from Zhucaojing, has been rejected as it showed signs of chemical alteration and potentially was a poor recorder of secular variation. This fact was not apparent until removed from the cave. The sixth stalagmite, PT02, has not yet been analysed.

Stalagmites were oriented in the cave using an aluminium frame containing a magnetic compass. Scribe marks on opposite sides of the stalagmite and adjustable pointers on the frame allow azimuthal orientation. Horizontal alignment was made with the use of a clear plastic, water filled 3-arm U-tube. Further marks were made on the stalagmite corresponding to water levels in each of the tube arms. Back in the laboratory, samples were cast in plaster in a wooden box, taking into account orientation markings. One vertical slice was sawn from the central drip cap area for sub-sampling, these sub-samples being cut to include as much of the drip cap as possible. Sub-samples in a particular stalagmite were either $14cm^3$ or $6cm^3$. The smaller samples were taken in one case to check if improved resolution was possible, whilst at the same time having large enough samples to measure magnetically.

Sub-samples were measured, in Liverpool, on a cryogenic magnetometer with a minimum sensitivity of 0.2×10^{-8} Am^2kg^{-1}. Corrections were made for the declination of the local field at Xingwen (28.48°N 105.06°W) according to the International Geomagnetic Reference Field (IGRF) accessed through the British Geological Survey. The computer program running the magnetometer makes this correction automatically once the local field value is entered. The program can also correct for inclination if, for example, the samples have been cut 90° out of alignment or to make minor adjustments resulting for cutting errors. Sub-samples from the four analysed stalagmites had NRM intensities ranging from 1.5 to 818 $\times 10^{-8}$ Am^2kg^{-1} whilst mean intensity of individual stalagmites ranged from 33 to 209 $\times 10^{-8}$ Am^2kg^{-1}. This difference in intensity, even from adjacent stalagmites in active streamways, is difficult to explain and may be due to current effects during submergence and subsequent re-emergence and to wash-off effects of resumed drip-water.

For the first stalagmite analysed (SC01) stepwise alternating field (AF) demagnetisation of selected pilot samples was adopted in order to isolate the high stability primary component of remanent magnetisation, whilst removing any viscously acquired remanence. Demagnetisation of the remaining sub-samples was made at a demagnetising field sufficient to remove magnetically soft viscous remanence acquired since sampling, but not high enough to remove the primary magnetisation. In all cases for SC01, the field chosen was 20mT, which was considered to satisfy these criteria. However, to gain increased directional information, all subsequent stalagmites (SC02, PT03, PT04) were subjected to stepwise AF demagnetisation for all sub-samples. This method allows a check on NRM stability throughout the stalagmite and not just for a selected few samples.

Behaviour during AF demagnetisation of representative samples are shown in Figure 2. The majority of sub-samples show a clear primary component and a small viscous component, if at all. Weaker samples tend to have a less stable directional tendency between demagnetisation steps but are not sufficiently dispersed to affect the overall direction. Directions for individual sub-samples were calculated by taking the Fisher mean of the directions from each step after removal of the viscous component until demagnetisation (Fisher, 1953). The α_{95} parameter, the radius of the circle of 95% confidence about the mean, was calculated as a measure of stability.

ROCK MAGNETIC STUDIES

All stalagmites had median demagnetising fields (MDF) in the range 60 - 85mT and the NRM could not be totally removed by 170mT, the highest field attainable on the equipment used. After full AF demagnetisation at 170mT approximately 20% of the original NRM remained (Figure 3). Since so much NRM remains, even at 170mT, the carrier of remanence has a relatively high coercivity compared with results from other speleothem workers (Latham, 1981; Morinaga *et al*, 1989; Perkins and Maher, 1993; Lean *et al*, 1994).

Selected lateral sub-samples from each stalagmite were subjected to incremental thermal demagnetisation up to 700°C in order to study behaviour throughout successive heating stages. Figure 4 shows behaviour of four sub-samples from which general features can be noted. In all cases a sudden drop of 25 to 35% of the total intensity occurs between 70° and 150°C due to unblocking of softer multi-domain grains. Loss of intensity occurs linearly until ~ 400°C where an inflexion point may indicate the presence of some titanomagnetite. Extrapolation of intensity decay from 150° to 400°C to the base line gives Curie temperatures of between 510° and 600°C. The remaining intensity follows a decay path to zero at 700°C, indicating the presence of a mineral with a high blocking temperature, such as haematite. Noel (1990) also suggests the presence of haematite in speleothems from Guangxi province, China.

To further test the mineralogy of the magnetic carriers, isothermal remanent magnetisation (IRM) acquisition was adopted. Acquisition was performed on two pulse magnetometers (5mT - 300mT and 400mT - 4T) and the IRM moment measured on a Molspin spinner magnetometer of minimum sensitivity 0.5 $\times 10^{-5}$ Am^2kg^{-1}. Figure 5 shows IRM acquisition for three sub-samples from SC01. Saturation is not achieved by 4T indicating a high coercivity magnetic mineral, such as haematite. The curve also shows no evidence for an inflexion point at 300mT, the approximate point at which magnetite saturates, thus magnetite is not thought to be present in any significant quantity. Any magnetite present should be visible in the IRM acquisition curve since magnetite has a greater spontaneous magnetisation than haematite.

Susceptibility measurements may also appear to indicate the presence of haematite since bulk susceptibility is either negative (diamagnetic) due to the calcite matrix or weakly positive. Haematite has a low spontaneous magnetisation (0.5 Am^2kg^{-1}) and it is suggested that this is the cause of such low susceptibilities.

Stalagmites in general seem to have a weak magnetisation (Latham *et al*, 1989). This can lead to problems in measurement on all but the most sensitive equipment. The above rock magnetic studies are far from complete but at this stage would seem to point to haematite as the dominant magnetic carrier. Future rock magnetic studies may include use of a Curie balance, thermal demagnetisation of an IRM, thermal demagnetisation of an orthogonal IRM, hysteresis parameters, and low temperature susceptibility studies.

PALAEOMAGNETIC STUDIES

At present, dating analysis has been performed on SC01 only. Growth rate calculated for this stalagmite was 0.087mm a^{-1} with single sample resolution of 275 years. Figure 6 shows declination and inclination for the four samples plotted by height, with an age bar for approximate ages, feature matched to SC01. Equivalent features are marked a,b,c etc. for declination and i, ii, iii etc. for inclination. All records have been subjected to a 3-point smoothing filter. As further dating is completed a more satisfactory idea of the age of all samples will emerge. Apparent agreement between features is excellent, excepting the record for PT04 which has been more problematical to correlate with the other records with the absence of age data.

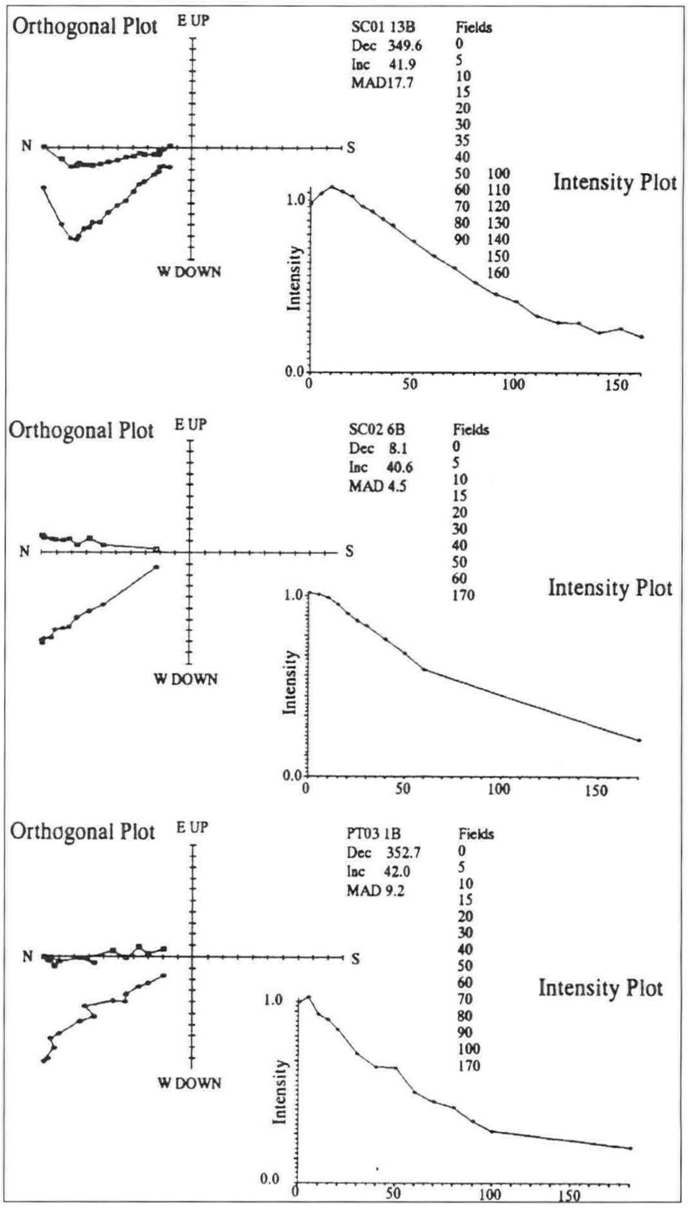


Figure 2. Alternating field demagnetisation behaviour of representative samples from SC01, SC02, PT03.

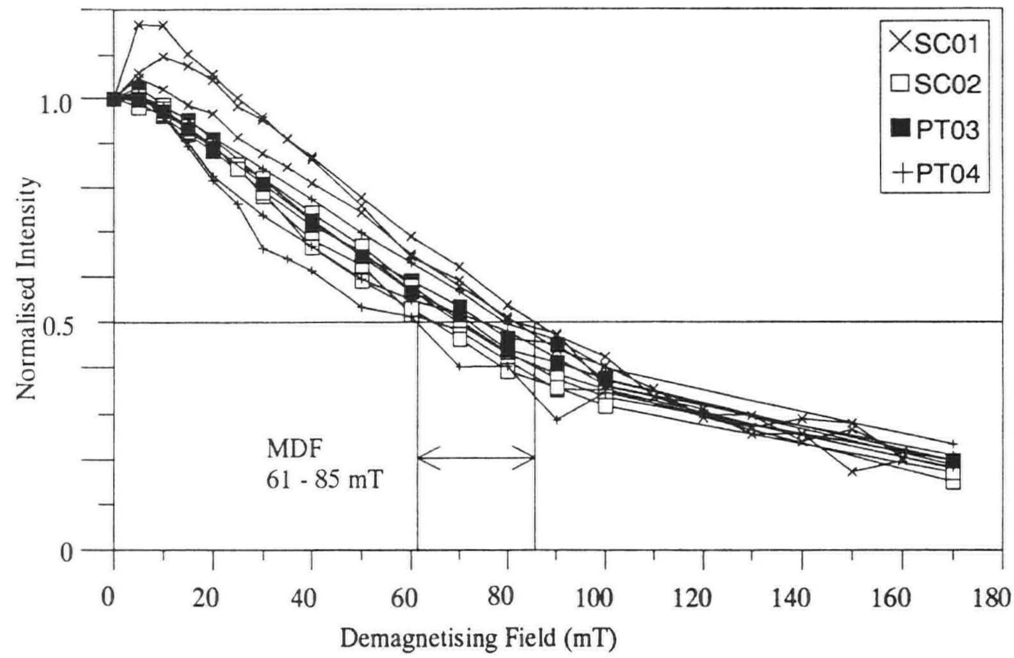


Figure 3. Normalised intensity decay during AF demagnetisation of selected samples from SC01, SC02, PT03 and PT04.

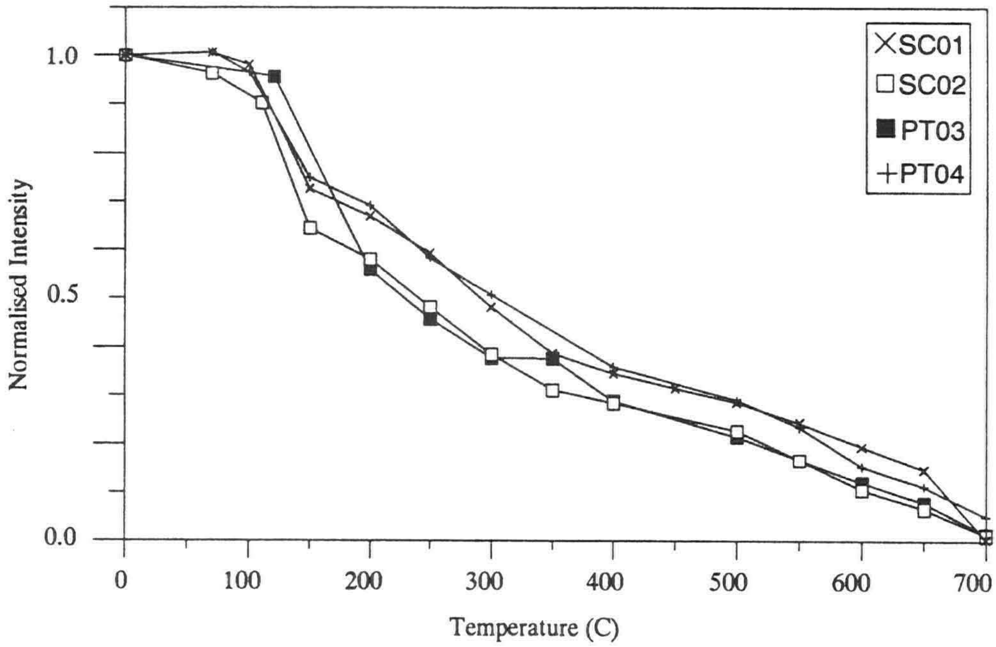


Figure 4. Thermal demagnetisation characteristics of SC01, SC02, PT03, and PT04.

Inclination in the Xingwen region for 0 to 7000 years bp (1990 AD to ~ 5000 BC) ranged from 27° to 57° whilst declination ranged from 20°W to 15°E.

Declinations from SC01, SC02 and PT04 lie to the west of the geocentric axial dipole field (GADF) to which secular variation is presumed to average, but PT03 straddles it. The present day field in China for the Xingwen area, according to the IGRF, lies 1.6° to the west of north. Yukutake and Tachinata (1969) demonstrate that the pattern of secular variation can be described by a stationary non-dipole source with the superposition of a westward drifting non-dipole feature. The influence of a standing non-dipole feature, such as the Mongolian anomaly, and a westward drifting non-dipole field would bias the directions in the manner seen (Yukutake, 1979). Over the past 400 years this positive anomaly has been shown, by observatory records, to have increased in area and intensity. Recent modelling has also shown this positive anomaly to have been present in some form over the past 2.5Myrs (Gubbins and Kelly, 1993).

Slight orientation and/or cutting errors would also help to produce this bias in declination, but since westward bias is apparent in three samples this is presumed unlikely. Samples are also from different caves, with similar degrees of westerly declination bias being seen in Tiencuan Dong and Zhucaojing Dong samples. The mechanism of remanence acquisition in the two caves may be subtly different. Recent modelling by Gubbins and Kelly (1993) has also shown that time averaging does not necessarily produce axial symmetry.

Inclinations are generally shallower than the 47° predicted for Xingwen by the GADF, the mean inclination being 43.3° for all samples. The IGRF model predicts 43° for the present day. The question of possible inclination errors in these samples has been tested by comparing inclinations of central and lateral samples of approximately coeval age. Figure 7 and Table 1 show that, using Fisher statistics, there is clear agreement between the inclinations of central and lateral samples for SC02. Samples are seen to have overlapping or very close α_{95} values, but further examples must be obtained before conclusive evidence for lack of depositional errors is found.

It is interesting to compare the results of Wei *et al* (1983) with the results from this study. Figures 8a and 8b show declination and inclination records from archaeomagnetic studies in China. Although some of the records are not of a particularly high resolution or of great time span, some similarities appear to exist between these and the speleothem records. These similarities are identified using the same notation as per Figure 6. The inclination record of Wei can be correlated to features ii, iii and iv whilst the shorter declination record can only be correlated to features a and b.

Figure 9 shows VGP positions for stalagmites SC01 and SC02, calculated from data that has been subjected to a 3-point smoothing filter. A large degree of similarity is seen in these VGP paths. Generally, an anti-clockwise loop, from 7000 years b.p., is followed by a period of 'wobble' at 3500 years b.p., as the looping direction changes sense to a clockwise loop by 2900 years b.p. continuing to the present day. Clockwise looping is indicative of westward drift

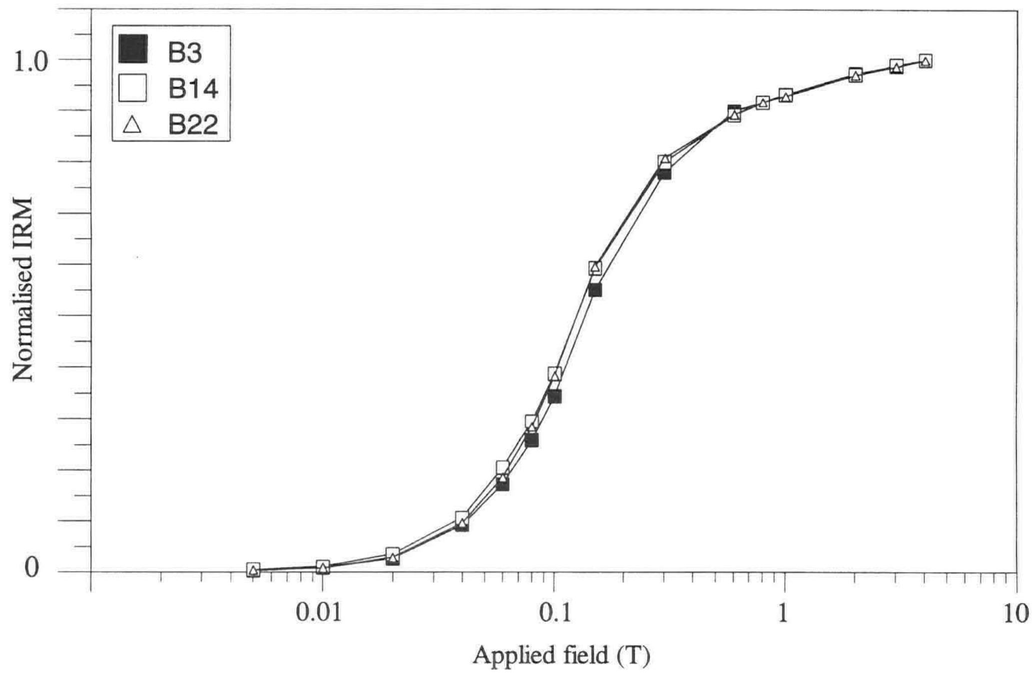


Figure 5. IRM acquisition for samples from SC01.

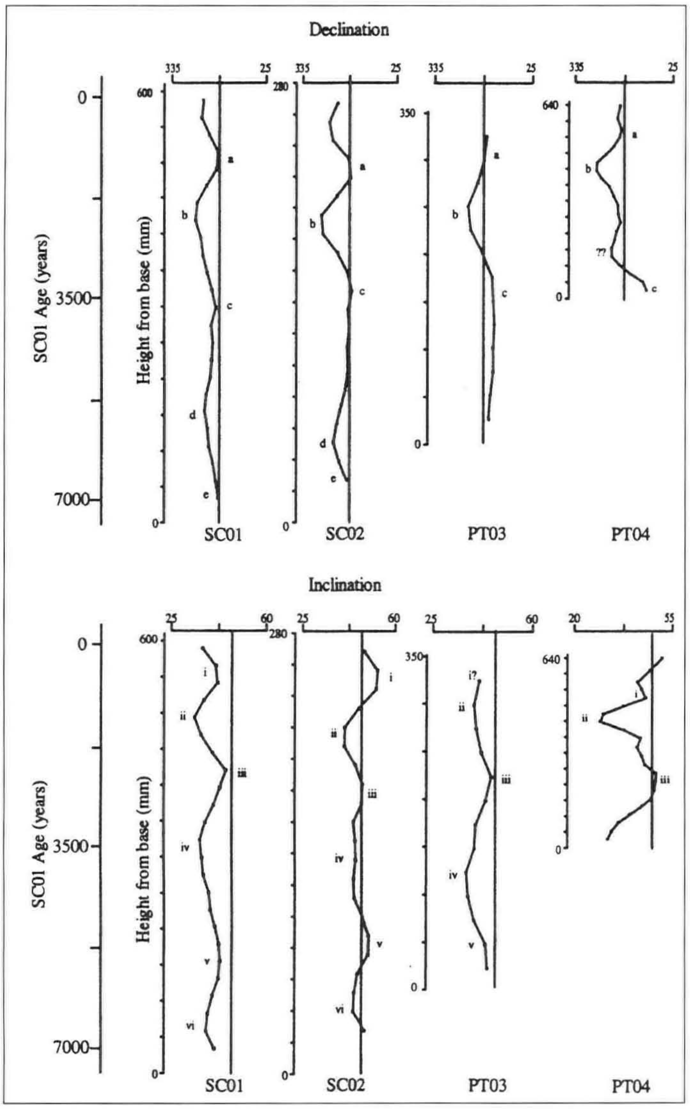


Figure 6. Declination (top) and inclination (bottom) records from SC01, SC02, PT03, PT04 based on data smoothed by a 3-point smoothing filter. Note that age data is for SC01 only and features are matched from this to the remaining samples. The PT04 is more problematical to match without age data.

(Runcorn, 1959). This may indicate the influence of both westward and eastward drift of the non-dipole field although westward drift is thought to predominate in this area at the present time due to the drifting component of the non-dipole field (Yukutake, 1979).

Attempts have been made to extract relative paleointensity records from three of the samples (PT04, PT03 and SC02). An anhysteretic remanent magnetisation (ARM) of 100mT was given to each sub-sample which were then subjected to stepwise AF demagnetisation to check for stability. The remaining ARM at 20mT was then normalised with respect to the NRM at 20mT after taking into account the amount NRM remaining at 170mT. This has met with limited success, with correlation between stalagmites difficult. Latham (1981) and Latham *et al* (1982) also report difficulties in speleothem recording of the past field intensity.

RADIOMETRIC DATING

Uranium series dating has been performed for SC01 sub-samples early on in the study. The fact that samples are destroyed in dating requires that all palaeomagnetic and rock magnetic work is complete before commencement. Dating has begun for PT04 but samples SC02 and PT03 are still undergoing palaeomagnetic studies.

In short, the method uses the growth of isotopes ^{234}U and ^{230}Th into secular equilibrium with parent isotope ^{238}U (i.e. the activities of each isotope per unit time will be at unity) as a measure of time since formation of the calcite from parent drip waters. This is possible due to the different geochemical properties of uranium and thorium. Both isotopes are almost insoluble in their 4^+ states but uranium can be oxidised to its 6^+ state to form uranyl complexes (UO_2^{2+}) which are more soluble than thorium in ground waters of near-neutral pH. Uranium, therefore, is more mobile during weathering than thorium which remains behind in the parent rock. Thus at the time of precipitation of calcite as a speleothem, for example, uranium is

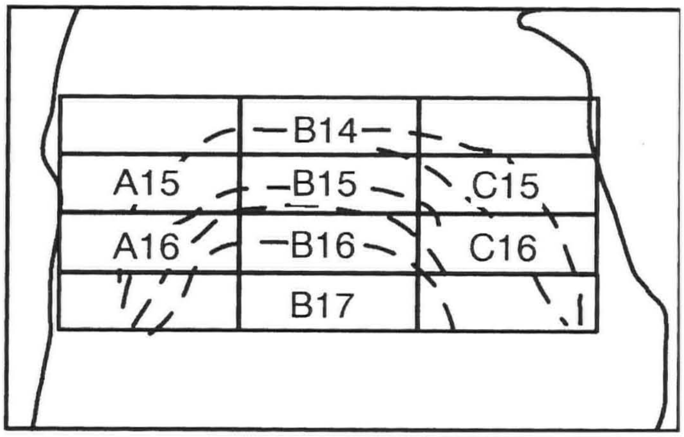


Figure 7. Part of the central slice from SC02 showing position of samples used for inclination checks.

Sample	Declination	Inclination	α_{95}	K
A15	357.9	44.9	0.7	5473
B14	356.5	43.3	1.2	1346
C15	359.4	42.6	1.7	897.2
A16	358.4	44.6	1.4	925.1
15B	2.2	41.2	0.4	9999
C16	3.8	43.0	1.3	1096

Table 1. Checks for inclination and declination continuity between coeval sub-samples in SCO1. a_{95} represents the radius of the circle of 95% confidence about the mean and was calculated as a measure of stability.

present but thorium is absent. From this time onwards uranium decays to its daughter isotopes, and by measuring the activities of the principal isotopes an indication of the age can be ascertained.

Alpha spectrometry was used for the determination of sample activities. An excellent review of speleothem dating can be found in Gascoyne (1984). Ages of up to 350 thousand years (kys) can be determined with relatively consistent repeatability, although mass spectrometry can produce ages up to 500 kys due to greater resolution. Typical alpha-spectrometer accuracy can be in the order of 5 - 10% (Schwarcz, 1989).

Dating of sub-samples from SC01 was not without problems, due to contamination of the sample with detrital thorium. This detrital thorium is seen as a ^{232}Th peak in the alpha spectrum which is assumed to appear in conjunction with detrital ^{230}Th, thus adding to the authigenic ^{230}Th. This results in an apparently greater age for the sample. Corrections can be made for this on the basis that the initial $^{230}Th/^{232}Th$ ratio is known. After Gascoyne (1979) a correction value of 1.5 was adopted. This assumes that the $^{230}Th/^{232}Th$ ratio remains constant throughout the growth of the stalagmite. Dating using this ratio has not been entirely satisfactory since the problem has been compounded due to the young age of the speleothem giving very low ^{230}Th activities (i.e. high counting errors based on counting statistics). An alternative method attempted on SC01 was to calculate the initial $^{230}Th/^{232}Th$ ratio from the topmost sub-sample, assuming zero age, and use this for correcting the subsequent sample ages. This makes the assumption that the top sub-sample is representative of the initial ($t = 0$) $^{230}Th/^{232}Th$ ratio throughout the stalagmite. A ratio of 0.8 was calculated for SC01 and by using this a much improved range of dates was obtained.

A further correction method may be utilised after performing analyses as proposed by Schwarcz and Latham (1989) and tested by Przybylowicz *et al* (1991). Their leachate/leachate (L/L) method is currently being carried out because the presence of ^{232}Th in the alpha spectrum indicates the presence of detrital thorium isotopes which affect the sample ages. This technique involves using the soluble fraction of several coeval samples, with different detrital content, to construct an isochron (a line of constant age). Many calcites contain a detrital component that consists of a mixture of more easily leached isotopes together with those that are more resistant. This may lead to chemical fractionation of isotopes during the initial sample dissolution stage. Even if fractionation does occur, the slope of the isochron of the L/L method, from which the age is calculated, is not affected and therefore dating accuracy may be improved. Difficulty in using this technique with speleothem is increased by the fact that material of coeval age may be in short supply.

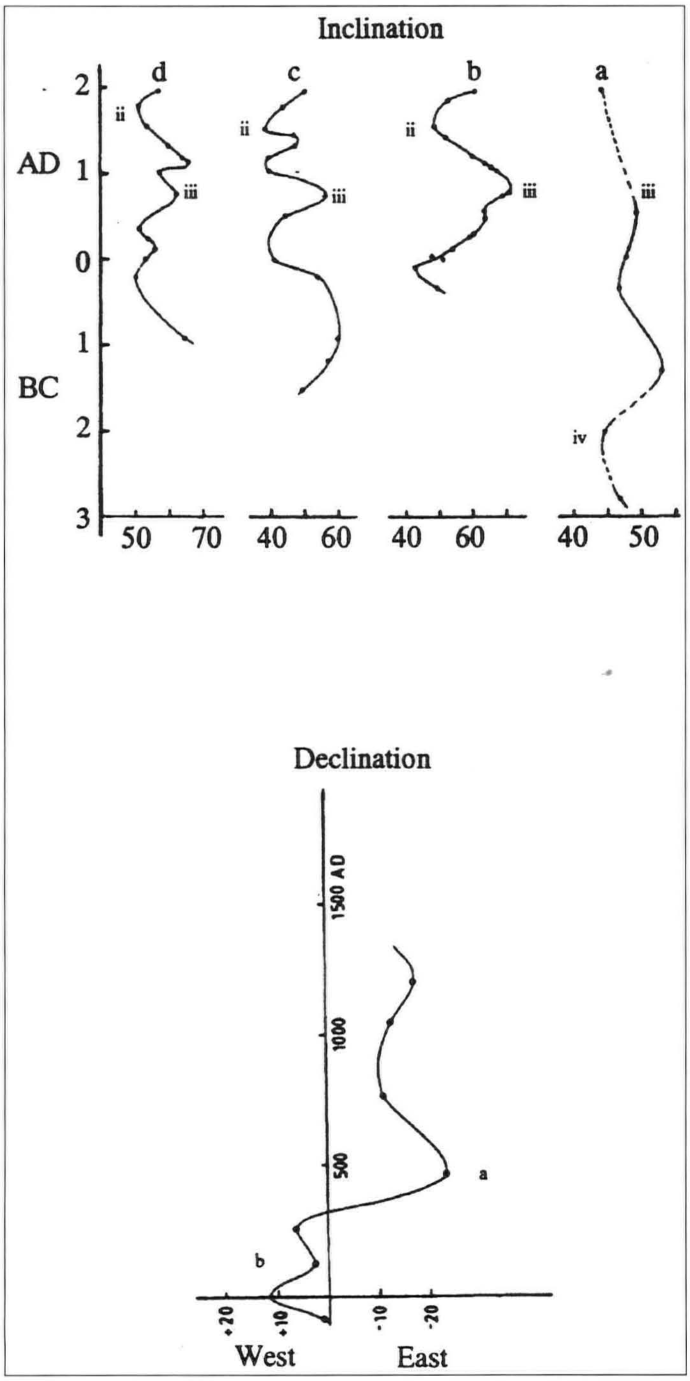


Figure 8a. Variation of inclination for a) Hubei Province b) Henan Province c) Shanxi Province d) Beijing (after Wei et al, *1983).*
Figure 8b. Variation of declination for the Luoyang Region (after Wei et al, *1983).*

CONCLUSION

The results obtained so far are extremely promising. Since the four stalagmites appear to show indisputable correlation, the use of speleothems for secular variation study is justified. The published data available from China so far has been solely based on archaeomagnetic data but this is not of particularly high resolution. The presentation of the results of this study will, hopefully, both complement the existing archaeomagnetic records and go some way to filling the substantial gaps left in the recent record. Further collection of stalagmites from a different area in China would provide a unique opportunity to test for regional differences and to add data to the overall record for China.

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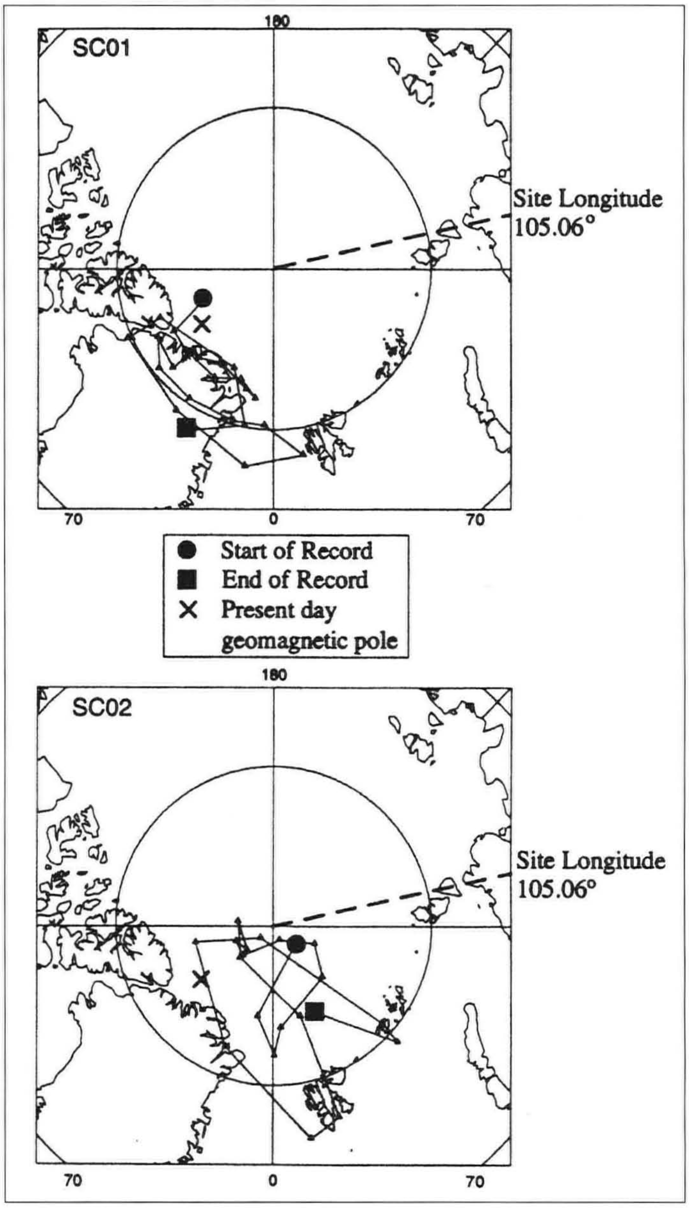

Figure 9. Virtual geomagnetic pole (VGP) positions calculated for stalagmites SC01 and SC02 after using a 3-point smoothing filter.

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Two Caves in Plymouth in 1744 and 1773

Trevor R. Shaw

Abstract: In 1744 Dr. John Huxham published a short account of straw stalactites in a cave at Cattedown. His son, John Corham Huxham, described a new cave in West Hoe in a letter of 1774, which was never published. Both accounts are printed here in full and the probable locations of the caves discussed. The caves were destroyed by quarrying.

About 100 years before the many bone caves of Plymouth were explored in the 19th century and some 220 to 250 years before the present, caves were reported at Cattedown and in the Hoe. Neither cave still exists as they were found in the course of quarrying.

One of these has been mentioned very briefly in the literature (Shaw 1992) but the contemporary manuscript description of the other is still unpublished. Both accounts are printed here in full. That of the cave in the West Hoe, visited in 1773, describes it in considerable detail, but the Cattedown cave is referred to only as the source of a stalactite presented to the Royal Society in 1744.

The exact location of neither cave can be established. The quarries at Cattedown were already vast by 1778 (Fig. 6), but maps showing the progress of quarrying at West Hoe do narrow down the probable position of that cave to one small area.

Aubrey's (1982) reference, written about 1690, to "caves in the rocks by Plymouth", is quite unspecific and, with many areas of limestone in Plymouth in which caves could have been found when building or quarrying, there is no reason to link Aubrey's caves with either the Hoe or Cattedown. In any case, the caves described by the Huxhams were newly entered by quarrying in the next century.

The better known 19th century caves were mostly at Oreston (Pengelly 1872), Cattedown (Worth 1887), and Stonehouse (Worth 1879:104). A small cave was known at the south-eastern corner of the Hoe (Pengelly 1877), and Bellamy (1835) refers to a cave "adjoining the coach road under the Hoe".

There is however one later reference to a stalactite cave known in West Hoe in the first half of the 19th century. Worth (1879:101) writes:

> Caves have occurred on the Western Hoe, the most important of which was described by the Rev. R. Hennah in a communication to the Geological Society. He spoke of it as abounding in stalactites; but as containing no bones of importance.

Richard Hennah (1766?-1846) was Chaplain to the Garrison of Plymouth from 1804 until his death (Horner 1847) and during that period he wrote quite extensively on the fossils of the Plymouth limestone, both in a book (Hennah 1822) and in publications of the Geological Society of London. However a page by page search of the latter, supplemented by a check in Ormerod's comprehensive index (1858) has failed to locate definitely the Hennah communication referred to by Worth. The nearest approach to the report about a cave "abounding in stalactites" on the Western Hoe is this statement (Hennah 1821):

> The caves which occur in the limestone of Plymouth afford stalactitical concretions in great variety of form, and in considerable abundance.

It is possible that a copy of an unpublished letter by Hennah, describing stalactites in a cave at the Western Hoe, might have been seen by Worth over a century ago. No such letter appears to survive in the archives of the Geological Society, and the minutes of the meeting at which his first letters were read imply that these dealt solely with fossil remains in the limestone.

None of the fragments of caves described by Jeffery (1968) can be identified with those dealt with here.

The authors of the two 18th century reports were both named John Huxham and both were Fellows of the Royal Society, but they were two different people, father and son.

THE HUXHAMS

John Huxham, M.D. (1692-1768)

The author of the short account of a cave at Cattedown (Huxham 1746) was a physician of some repute who practised at Plymouth (Fig. 1). Born at Totnes, he trained at Leiden and Rheims, where he became a M.D. in 1717. He published several books on medicine and was elected a Fellow of the Royal Society in 1739, receiving their Copley Medal in 1755. Dr. Huxham developed a quinine drug and recommended fresh vegetable food to reduce scurvy in the Royal Navy. He was buried in St. Andrew's Church, Plymouth (Munk 1887; Moore 1908). His age when he visited the Cattedown cave in 1744 was about 52.

The Rev. John Corham Huxham, M.A. (1723?-1778?)

The John Huxham who described the cave under the West Hoe (Huxham 1774) was the son of the doctor. His date of birth is not known but he matriculated at Exeter College, Oxford, on 22 May 1740, at the age of 17 (Foster 1871). He was elected F.R.S. in 1769 and would have been about 50 years old when he explored the cave. His death probably took place in 1778, for that was the last year in which his name appeared in the printed list of Fellows of the Royal Society.

THE CAVE AT CATTEDOWN

As was usual in the 18th century Dr. Huxham's publication in the Philosophical Transactions of the Royal Society was written as a letter to the Society's Secretary and published in that form. The record of the meeting held on 13 December 1744 (printed here as Appendix I) shows that the letter was read out there before publication. As will be seen from the full title, it dealt with three subjects, two of them medical, but only the part concerning the cave is included in Appendix II.

The stalactite presented to the Society's museum "was found in a Cavern, that was discovered amidst the vast Marble Rocks at *Cat-down* near *Plymouth*." Described as "a cylindrical Tube of twenty Inches long at least . . . and quite hollow", it was evidently what would now be called a 'straw'. The word 'stalactites' (with an s). used at that time, was not an English plural but an earlier form of the word derived from the Latin singular; hence "a . . . Stalactites". The specimen had been brought to Huxham, but he went into the cave the next day and saw some more of these "Tubes". He did not describe the cave itself, nor its location at Cattedown.

The extent of the limestone quarries at Cattedown in 1744 is not known precisely, but by 1778 they were already very large, extending along the southern edge of the Cattedown for some 770 m (Fig. 6).

Figure 1. John Huxham, M.D., F.R.S. An engraving by J. Jenkins of a painting by Thomas Reynell, made probably in 1756 (from Pettigrew, 1840).

Hennah (1822:55) remarks on ". . . the vast quantities of Limestone that have been removed of late years . . . " at Plymouth, and most or at least much of that came from Cattedown. Within that area, therefore, no attempt can be made to identify the position of the cave.

THE CAVE AT WEST HOE

Description

The younger Huxham's (1774) quite detailed description of a cave discovered in a quarry at West Hoe in the spring of 1773 was read at the Royal Society's meeting held on 28 April 1774. The record of the meeting (Appendix III) summarizes it and orders that Mr. Huxham should be thanked for his contribution but it does not authorize publication. It remains therefore as a manuscript in the archives of the Royal Society and is printed here for the first time, in Appendix IV, with permission.

The fact that this paper was not published in the Philosophical Transactions does not necessarily mean that it was thought to be of less value than the earlier one. In the intervening years the membership of the Royal Society had grown and the number of communications submitted had risen also. Furthermore, a higher proportion of those published were scientific in the modern sense rather than just concerned with curious objects.

The cave is described as consisting of several chambers and was well furnished with speleothems. The expression 'Lusus Naturae', used for these formations was often translated as 'sports of nature' or 'freaks of nature' and applied to any mineral deposit of unexpected shape, including fossils whose origin was not then understood by all.

Although the cave entrance was said to be "upon a Level with y^e^ sea Beach" it cannot have been as low as the sea itself. For one thing, the second chamber is described as being two or three feet lower than the first, yet it did not contain water. Furthermore it was "discovered by y^e^ workmen of y^e^ Quarry", presumably in the course of quarrying, and the quarry was certainly not at such a level as to be flooded. Modern maps show the present ground level at the site of the main quarry to be about 8 m above the sea but there may have been some infilling and levelling since the quarry was abandoned. In any case it is clear that the cave was not open to the sea and cannot therefore have been the sea cave described by Jeffery (1968) as being at Rusty Anchor, nearby.

The Location of the West Hoe Cave

Huxham states that the cave was "under a Place called the West Hoe, (where there are several large marble Quarries,)", that it was at a low level (as just discussed) and that "y^e^ Enterance into it is from the west".

Investigating just where the cave might have been is best done by narrowing down the possible area from the present extent of the now disused quarries, with their familiar landmarks round them, to the quarries shown in the less detailed maps of the 18th century. These earlier maps were not only at a small scale, they were also primarily charts for the navigation of Plymouth Sound, showing only features easily recognized from the sea.

The 1973 Ordnance Survey map (Fig. 2) shows West Hoe Park which is still visibly the site of an old quarry. The area marked as West Hoe extends west from this to the immediate surroundings of Millbay, and is all approximately level now, between 7 m and 10 m above sea level, with a sudden steep rise to the north of most of it. In the second half of the 19th century the quarry can be seen from Fig. 3 to have extended over this flat ground as far as the present Radford Road, covering the area now occupied by St. Michael's Church and the terrace housing. The quarry faces shown in Fig. 3 are generally similar to those on the large scale Ordnance Survey map of 1857, and an estate plan of 1875 (West Devon Record Office 874/7/7) shows that this area was still part of the quarry at that date.

Moving further back in time and nearer to Huxham's visit, the first edition of the Admiralty Chart, published in 1822 (Fig. 4), shows the quarry much smaller that it became later. Comparison with Figs. 2 and 3 indicates that this quarry lies about where the southern end of Radford Road and Grand Parade House are now. The same quarry, of

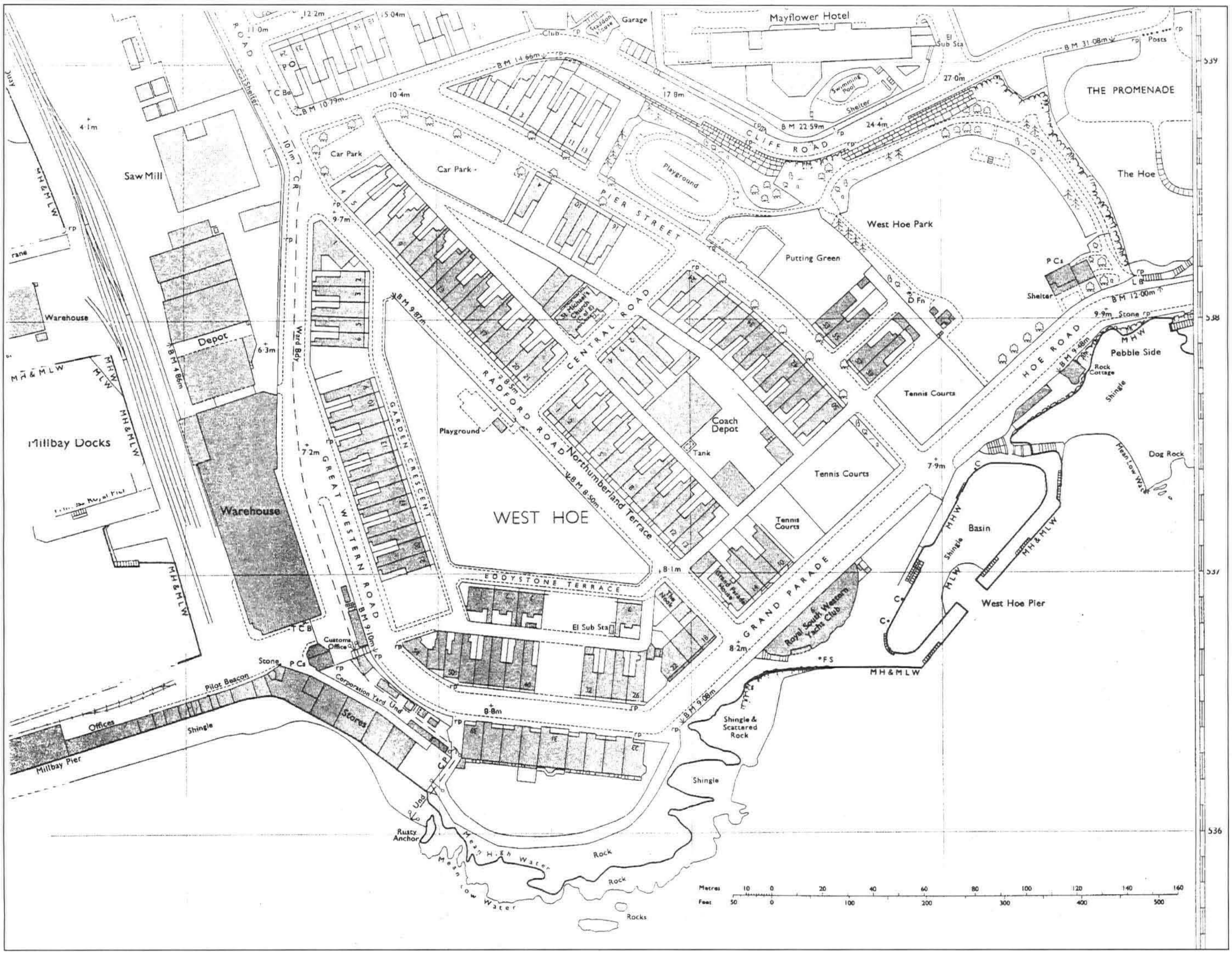

Figure 2. West Hoe, Plymouth. Reduced from the Ordnance Survey 1:1250 plan SX 4753 NW, surveyed in 1949 and revised in 1973 (reproduced with the permission of the Controller of Her Majesty's Stationery Office © Crown copyright).

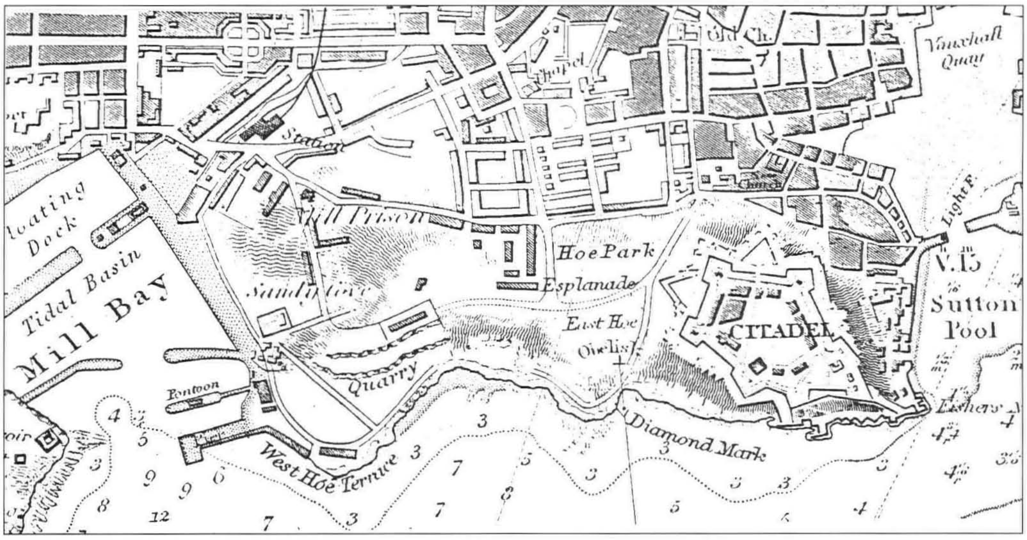

Figure 3. Plymouth Hoe on the Admiralty chart revised to 1859. The quarry at West Hoe was at about its largest size and was still being worked. Scale, as reproduced here, 1:12750 (reproduced by kind permission of the Hydrographer of the Navy).

more or less the same shape and size, is also on the 1788 manuscript survey of the Sound (Fig. 5).

This quarry is, however, not marked on the unpublished survey of 1778 (Fig. 6) which shows very much less detail on land throughout (even the Citadel is represented only by its name). Huxham himself stated that there were several large quarries at West Hoe in 1773, so an omission on the survey does not necessarily imply non-existence. There are therefore two possibilities:

(a) The same quarry did exist at the time of the 1778 survey, perhaps of smaller size, but was omitted as not being a useful landmark for mariners.

(b) Huxham's cave may have been found in the 'Lime Quarry' at the south-east corner of Mill Bay, close to where the presumably long-established 'Kilns' are marked in Fig. 4. This is the quarry referred to by Hennah (1822:30) as the place where he found fossil corals. Hennah describes this as "... the quarry at Mill-Bay, situated near its eastern extremity; . . ." and does not mention West Hoe. Although close to West Hoe, it is not known whether at that time the border of Mill Bay would have been described as part of it. Huxham's comparison of the cave entrance level with that of the "sea Beach" also makes the Mill Bay quarry seem a less likely location although, as Figs. 5 and 6 show, before Mill Bay Docks were built the south-east corner of the bay was not far from the 'sea' of the Sound.

An unpublished survey of the Sound dated 1774 (Hydrographic Office D923/10) is at too small a scale to mark any quarries at all. The presence of the "Three Holes" on this 1774 map and also on the one of 1778 (Fig. 6) at the northernmost point of the central Hoe coastline is not relevant. To be noted on the chart at all they must have formed a distinctive mark recognizable from the sea, such as holes in the south-facing cliff rather than a cave entrance in the west-facing wall of a working quarry.

The most probable location for the cave visited by John Huxham the younger in 1773 is therefore the small quarry shown in the 1788 survey (Fig. 5) as being where the southern end of Radford Road now is. Fifteen years earlier the quarry must have been smaller still but the direction in which it expanded is not known. As the entrance into the cave was from the west, it must have been in the eastern face of the quarry. Nevertheless the other quarry, at Mill bay, is by no means an impossible location.

The vestigial caves in the present West Hoe Park, reported by Jeffery (1968), cannot be associated with Huxham's cave, which was about 150 m further west.

ACKNOWLEDGEMENTS

It is to the Archivist (Mary Sampson) and the Librarian (Sheila Edwards) and her staff at the Royal Society that the existence of this paper is due. By allowing me to work on their collections they made it possible for me to find and copy the unpublished report which is at its centre. All the extracts from their archives are printed here with the kind permission of the President and Council of the Royal Society of London.

I am also particularly grateful to Paul Brough and his staff at the West Devon Record Office in Plymouth, and to Ken Atherton and his staff at the Hydrographic Office of the Ministry of Defence at Taunton, for allowing me to examine many maps, charts and surveys and for allowing some of them to be reproduced here. Drs. M. J. Bishop and Keith Ray of the Plymouth City Museum discussed the problem of locating the caves and made useful suggestions.

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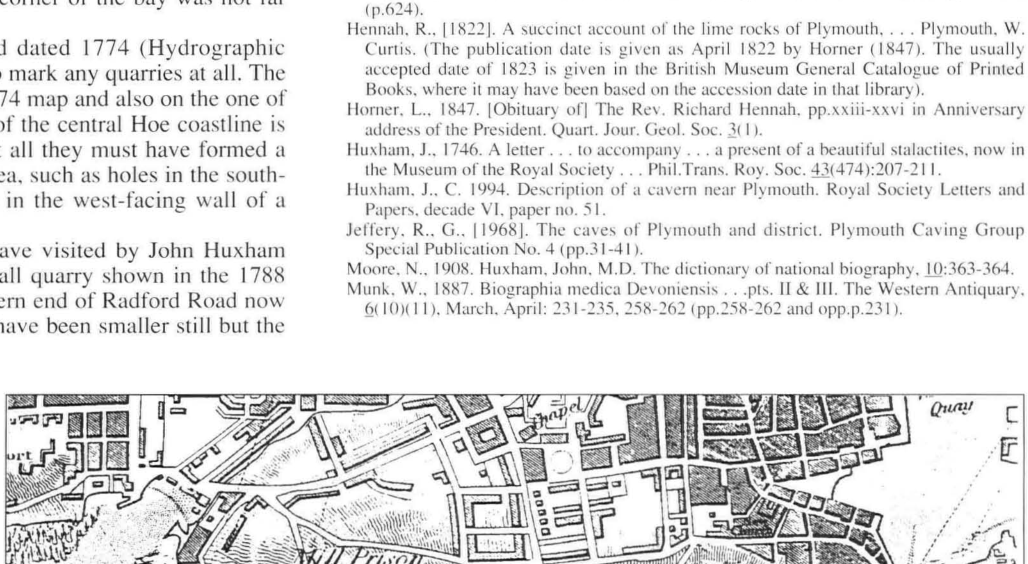

Figure 4. Plymouth Hoe on the first edition of the Admiralty Chart, published in 1822. The West Hoe quarry was quite small, in a position near the present junction of Radford Road and Grand Parade. Scale, as reproduced here, 1:14120 (reproduced by kind permission of the Hydrographer of the Navy.)

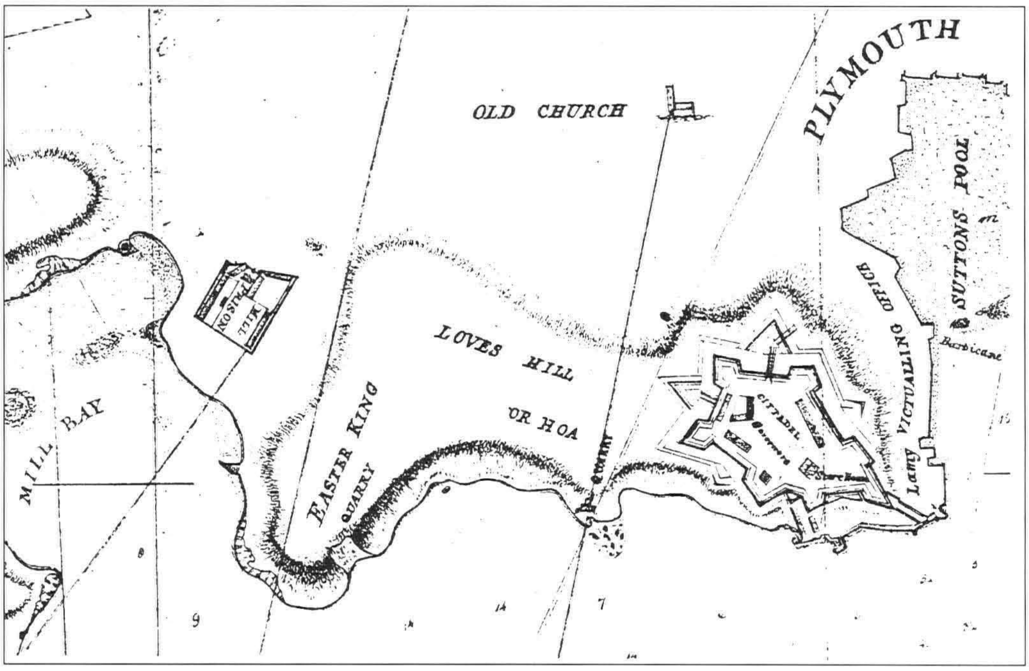

Figure 5. The Hoe from a manuscript chart of Plymouth Sound made in 1788 by James Fraser. The West Hoe quarry was then about the same size as in 1822. The name Easter King has been transferred in error from the western side of Mill Bay. Scale 1:13000 (Hydrographic Office C91, reproduced by kind permission of the Hydrographer of the Navy).

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APPENDIX I
RECORD OF THE ELDER HUXHAM'S LETTER ON A CAVE AT CATTEDOWN BEING READ AT A MEETING OF THE ROYAL SOCIETY ON 13 DECEMBER 1744

(from Journal Book of the Royal Society, vol. 18, 1742-1745, pp.324-325)

A Letter from D[r]. Huxham to D[r]. Mortimer was read dated at Plymouth Sept[r]. 20 1744, serving to accompany a Present of some Stones found in the Kidney of an elderly woman whose Body was opened after her death, the case whereof inclosed was read, and likewise a Present of a very remarkable Stalactites found in a Cavern at Cat-Down near Plymouth.

. . .

This was a hollow Cylindrical Tube about six or eight Inches in length, of a substance in a manner transparent. He says that in this rocky Cavern these Tubes do hang perpendicularly from the top some longer, some shorter, and that this which he sends to the Society was part of one of twenty Inches in length, but they are seldom so long. And they are formed from the petrifying quality of the water which distills through y[e] Crevices of the superiour Rocks.

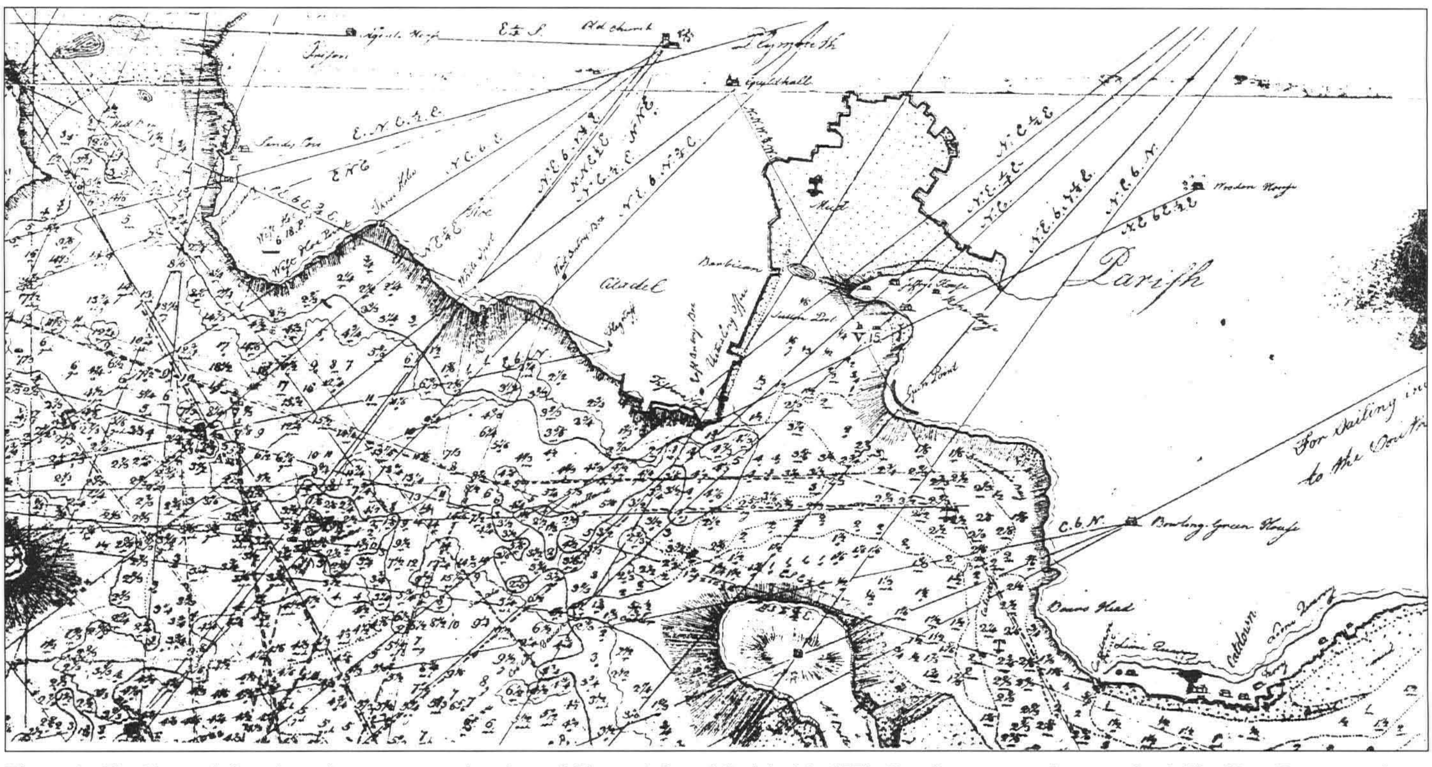

Figure 6. The Hoe and Cattedown from a manuscript chart of Plymouth Sound finished in 1778. Few features are shown on land. The West Hoe quarry is not marked but there is a Lime Quarry at the south-east corner of Mill Bay. The Cattedown quarries are shown on the right hand side of the chart. Scale 1:16000 (Hydrographic Office D881, reproduced by kind permission of the Hydrographer of the Navy).

APPENDIX II
THE ELDER HUXHAM'S ACCOUNT OF STALACTITES AND A CAVE AT CATTEDOWN
(from Philosophical Transactions, vol. 43, no. 474 for June-Dec. 1744, pp.207-211, published in 1746)

XVII. A Letter from John Huxham, M.D. F.R.S. to Cromwell Mortimer, M.D. Secr.R.S. serving to accompany on Account of the Case of one Hannah Hitchcock, one of whose Ureters was grown up; a Present of a beautiful Stalactites, now in the Museum of the Royal Society; and a Drawing of an extraordinary Calculus taken out of the Bladder of a Boy.

Dear Sir,

. . .

In the Box also I have sent one of the more remarkable Stalactites I ever saw. Perhaps it may be a Curiousity even to you. – It was found in a Cavern, that was discovered amidst the vast Marble Rocks at Cat-down near Plymouth. – It hung perpendicularly from the Top of the rocky Cavern, and was a cylindrical Tube of twenty Inches long at least; but was unluckily broke into several Pieces in Bringing to me. This I have sent was by much the longest of them; but Mr. Long (the Master of the Quarries) assured me the Whole was above twenty Inches long, and quite cylindrical, and quite hollow. – I went to the Cave the next Day, and found five or six of such Kind of Tubes, but none above two Inches long. – They all sprang from broad, hollow, protuberating Basis, in some sort as a Nipple arises from the Breast. – These also were cylindrical and hollow. – There were in the same Cavern many other Petrifications, which had formed a kind of hollow Pilasters against its Sides; and also several large solid Masses, which arose from the continual Dropping of the Petrefying Water through the Crevices of the superior Rock. – These all afford very good Alabaster.

. . .

Dear Sir, I have the Honour to be
Your much obliged, and
obedient humble Servant,

Plymouth, Sept. 20.
1744.

J. Huxham

APPENDIX III
RECORD OF THE YOUNGER HUXHAM'S LETTER ON A CAVE AT WEST HOE BEING READ AT A MEETING OF THE ROYAL SOCIETY ON 28 APRIL 1774
(from Journal Book of the Royal Society, vol. 28, 1774-1777 p.69)

A description of a cavern near Plymouth in a letter to the Rev^d Dr. Horsley S.R.S. by the Rev^d M^r Huxham F.R.S. was read.

This Letter contains M^r Huxham's Observations on a cavern or rather nest of caverns, lying near several Marble Quarries, & accidentally found under a place called West-hoe. The several incrustations, petrefactions & Stalactites, which M^r Huxham observed in these Caverns, are described by him as very singular Lusus Naturae. He discovered in them the representations of Festoon curtains with alabaster Fringes, a cascade with three falls, transparent flitches of bacon, two or three kinds of fish, apples, a gigantic hand &c, The description of these and still more extraordinary appearances must be referred to the paper itself.

Thanks were ordered to M^r Huxham for this Communication.

APPENDIX IV
THE YOUNGER HUXHAM'S UNPUBLISHED LETTER ABOUT A CAVE AT WEST HOE
(from Royal Society Letters and Papers, Decade VI, No. 51)

For The Rev^d. D^r. Horsley
[annotated] Description of a Cavern near Plymouth by the Rev^d. J. C. Huxham.
Rec^d. March 5th 1774.
Read April 28 1774
Not to be printed.

Camberwell March 5th.

Rev^d. Sir.

Whilst I was in y^e West last spring, I saw at Plymouth under a Place called the West Hoe, (where there are several large marble Quarries,) a Great Cavern, or rather a Nest of Caverns accidentally discovered by y^e workmen of y^e Quarry, the Inside of w^{ch}: was so curious & uncommon, that I imagine my laying before our worthy Society y^e best account I cou'd give of them, might not prove quite unacceptable, & shall now enter upon it accordingly.

The first Cavern you go into is upon a Level with y^e sea Beach, & y^e Enterance into it is from the west. This may not improperly be styled the Antechamber to y^e Rest; the Breadth, & Length of it is about 14 feet, & y^e upper Part, w^{ch}: is concave, is covered over with various Petrifications, & Incrustations; but as there is nothing very striking in y^e Figure, & Form of these, or different from w^t: is commonly found in such subterraneous Cavities, I shall take no further notice of them. Two, or three feet below y^e Cavern just mention'd, you descend into another of double y^e extent, & a Greater Height. This being lighted up with some candles exhibits to y^r: view, one of y^e most curious, & beautifull Lusus naturae, in so great a variety of Forms, that y^e most Romantic Imagination is scarcely able to form an Idea of it. In one place, you see a Representation of a Festoon Curtain, w^{ch}. is executed in such a noble, & masterlike manner, as defies the utmost Efforts of any Human Art. The Boldness of y^e Folds, & y^e Ease with w^{ch}: the Curtain hangs, is inexpressively striking, & a Fringe at y^e Bottom of two inches deep, formed of exceedingly white Alabaster representing silver Fringe, compleats & beautifies this whole piece of Imagery. In another place, you behold a very natural, & pleasing view of a Cascade, having three Falls; where the Colour of y^e Rock, as well as y^e stream, w^{ch}: falls over it, are pictured with y^e same propriety, & justness. In other parts of y^e same Cavern, you are entertained with strong Representations of Figures like to Flitches of Bacon, some parts of w^{ch}: are transparent, two, or three kinds of Fish, some very regularly shaped Apples, with w^t: is commonly called the Eyes in y^m:, the Representation of a large Gigantic hand, consisting of four Fingers, and a Thumb, by y^e vulgar called y^e Hand of Magog, several Gothic Pillars, & a great number of Beautifull stalactites, & other Petrifications. Another Curiosity which deserves to be particularised is this, that at y^e farther End of this Cavern is a Plano-Concave Enterance of nearly 3 feet in length, & y^e same in Breadth, w^{ch}. from its likeness to an Oven is called by that name. In this Place you have y^e pleasure of seeing several Groupes of petrified miniature Figures placed in a circular Form, some of w^{ch}: represent men, others Trees. They are placed alternately, & if y^e spectator did not know, that the whole was only a Lusus naturae, he wou'd certainly pronounce it to be y^e work of some very ingenious Artist. One of y^e Figures, w^{ch}: stands in the Center of one of y^e Circular Groupes, & w^{ch}: is larger than y^e rest appear to y^e Eye to be drest in y^e Roman Toga, & y^e Habit is exceedingly well done. The Last Thing w^{ch}: I shall take notice of as being curious in this natural Piece of Workmanship is, that close adjoining to y^e oven, w^{ch}: has been mentioned, there is a Figure, w^{ch}: is a very good, & natural Representation of a Copper with a Pipe let into it, as if for ye conveyance of water – I am, Rev.^{d} Sir, Y^r: Obed.^{t}
H^{bl} Serv:^{t} J. Cor^m: Huxham

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Moonmilk mineralogy in some Romanian and Norwegian caves

Bogdan-Petroniu ONAC and Lucretia GHERGARI

Abstract: Ten different moonmilk samples collected in nine caves from Romania and Norway were analysed in order to define their mineralogical and crystallographical features. Using polarizing microscopy, X-ray, SEM and TEM techniques we identified the following crystal morphologies: fibrous, acicular, prismatic and fibrous-lamellar; these were ascribed to two different situations: calcite pseudomorphs after aragonite or vaterite and calcite paramorphs after monohydrocalcite. A ternary system to diagnose various types of moonmilk is proposed.

GENERAL DATA

The term Moonmilk describes white, sometimes yellowish, nanno- or microcrystalline deposits made up of acicular aggregates, which usually show similarity to the well-known porous, skeleton-like texture of palygorskite. Moonmilk deposits generally contain a high amount of water (>52%, Onac, 1993) which can be completely eliminated by heating and later re-absorbed. Moonmilk normally appears as "plastic" deposits which cover cave walls or other calcitic and noncalcitic speleothems. It often can also form flowstone, draperies, stalactites, stalagmites, helictites, rimstone, and even cave pearls.

Definitions of moomilk include the physical macroscopic appearance as well as the character of deposits.

Commonly, the chemical composition of the moonmilk is calcite, but the presence of other carbonates, as well as of some sulphates and phosphates has been mentioned by different authors (Hill & Forti, 1986; Bernasconi (1981) and Fischer (1993) proposed the term of "plastic white mass" or pseudo-moonmilk to be used for all subterranean two-phase systems of which the calcitic or non-calcitic solid phases are less than 90%. In their opinion the term *moonmilk* ought to be applied only for white plastic masses with the solid phase consisting of at least 90% mineralogically verified calcite.

As long as the microcrystalline deposits, irrespective of their composition, represent a well defined type of speleothem, we consider it more useful to keep the term moonmilk without limiting the number of mineral phases which form it.

In respect of the genesis of the moonmilk several theories have been put forward (see Hill & Forti, 1986).

Complex crystallographical and mineralogical observations have to be made in order to explain why completely different mineralogical assemblages deposited from solutions with various anionic and cationic compositions adopt such similar textures.

On the basis of several samples collected from different Romanian and Norwegian caves (Table 1), the present paper will appraise on one hand the compositional diversity of moonmilk deposits formed in similar thermodynamic conditions, and on the other hand the fact that moonmilk deposits with similar structure can form in different thermodynamic conditions.

Table 1. Location and mineral paragenesis of the samples.

Sample	Cave	Minerals
764	A*	Hydromagnesite, aragonite
767	A	Calcite
765	B	Gypsum, calcite
763	C	Calcite
2	Humpleu	Calcite, monohydrocalcite, vaterite
776	Lucia Mică	Calcite, vaterite, aragonite
777	Lucia Mică	Calcite, aragonite
778	Lucia Mică	Calcite, monohydrocalcite
25	Barsa Glacier	Calcite
39	Scarisoara Glacier	Calcite
33	Piatra Altarului	Calcite

* *Caves A, B, C are situated in Norway; their names and location are withheld for conservation reasons.*

The mineralogical and crystallographical studies rely on morphological and compositional observations made through scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The optical properties of crystals larger than 2 μm were determined using a polarizing microscope, while structural data were obtained using X-ray analysis.

All the caves we sampled in Norway are situated north of the Arctic Circle (Nordland fylke) being developed in calcitic and dolomitic marbles of Cambrian-Silurian ages (Lauritzen, 1988). Their physical characteristics are: temperatures <8°C, high humidity (95-100%) and good ventilation (Onac & Fărcas, 1992).

The Romanian caves which provided moonmilk samples are developed either in marble or carbonate rocks of different ages, (Paleozoic-Mesozoic), located in the Bihor Massif-Apuseni Mountains (Fig. 1).

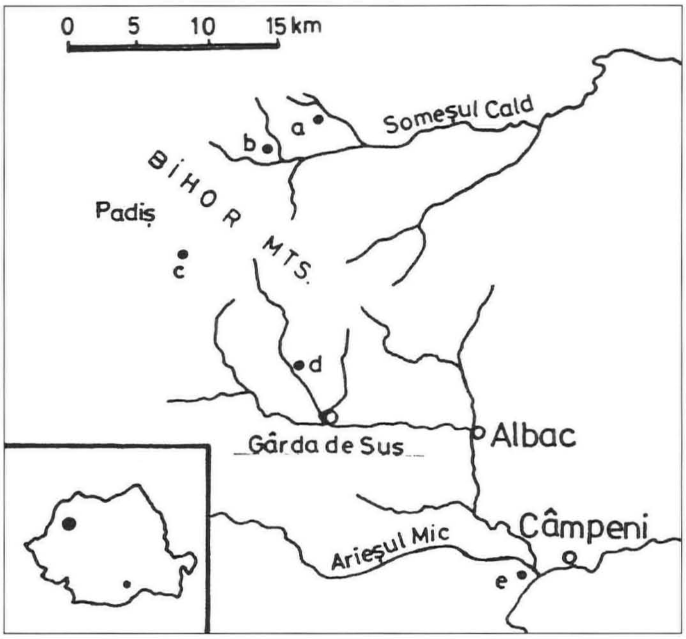


Figure 1. Location of sampled caves from Romania. a: Humpleu Cave; b: Piatra Alterului Cave; c: Barsa Glacier Cave; d: Scărifisoara Glacier Cave e: Lucia Mică Cave.

MINERALOGY OF THE MOONMILK SPELEOTHEMS

The moonmilk samples we analysed can be grouped in two types according to their chemical composition: sulphate-dominated and carbonated-dominated.

Sulphatic moonmilk

gypsum + calcite (sample 765b)

When dry, the samples have a white powdery consistency and are made up by lamellar microcrystals with silky lustre which form delicate aggregates having different habits and sizes (0.1-1.5mm ø). All these microcrystalline aggregates appear rapidly and disappear equally as fast. Large grains with dull lustre ascribed to calcite can be seen within these aggregates.

The normal X-ray spectrum and the secondary X-ray emission spectra obtained using the energy detector (EDX) on a scanning electron microscope showed the presence of two minerals: gypsum and calcite (Fig. 2). The higher intensity of the (200) line of gypsum (comparative with an unoriented sample of spectrum) is due to the preferential orientation of the lamellar crystals which are developed parallel with the face (100). Under the polarizing microscope the gypsum lamellae are practically isotropic because the angle between the optic axis and the normal on (100) is very small (8°). The lamellae are parallel to (100), elongated after the c-axis, sometimes also after the b-axis, showing lamellar twins after (100) or interpenetration twins.

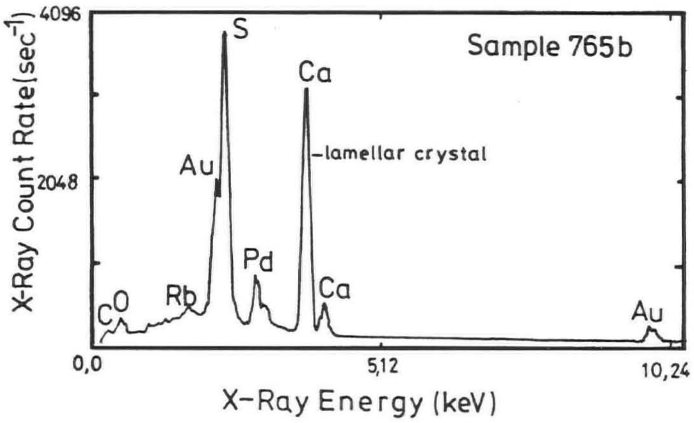
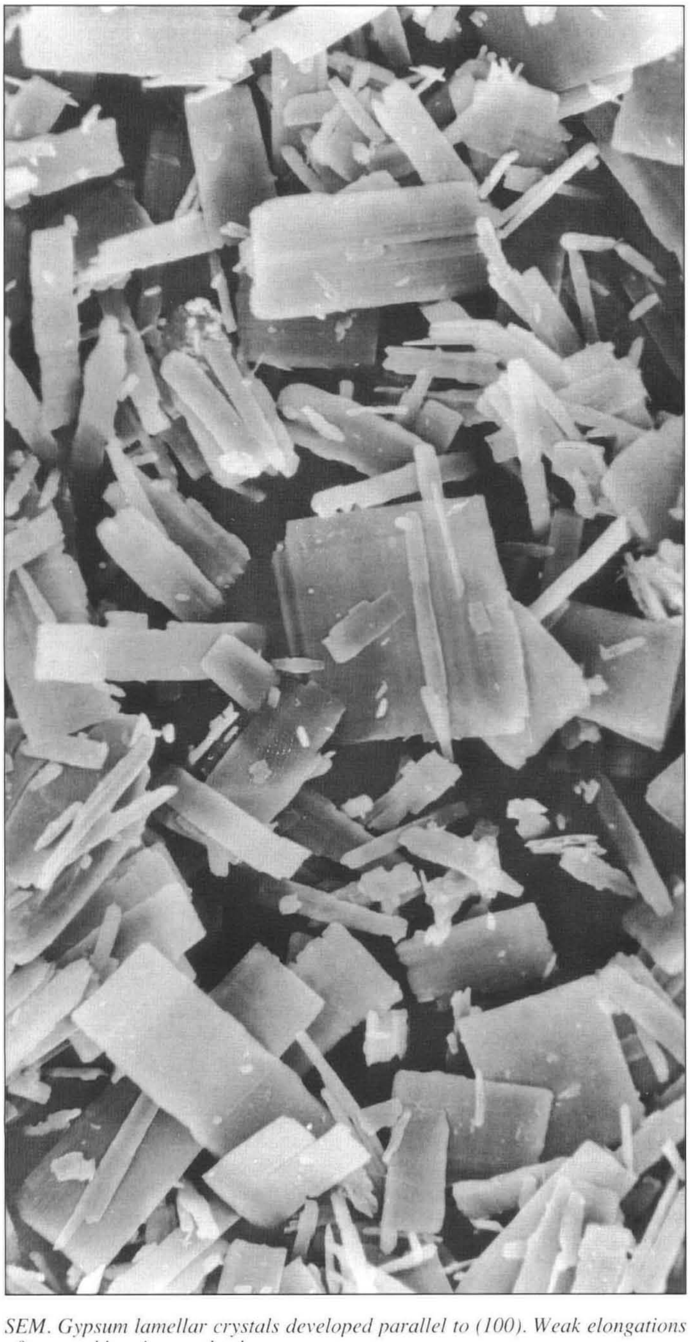


Figure 2. Energy dispersive X-ray (EDX) spectrum of sample 765b.

The calcite found in this sample came from bedrock and consists of grains with corroded edges or small pieces of speleothems affected by dissolution.

Obviously, the crystals' morphology show that gypsum is a neomorphic mineral while the calcite appears as relict clasts which didn't react with sulphuric acid generated by the oxidation of sulphides (e.g. pyrite). In conclusion, in sample 765b both neomorphic gypsum and calcite relicts are present.



SEM. Gypsum lamellar crystals developed parallel to (100). Weak elongations after c and b-axis can also be seen.

Carbonatic moonmilk: Noncalcitic moonmilk

hydromagnesite + aragonite (sample 764)

A sample of white, microcrystalline aggregates was collected from behind some "gypsum balloons" (Onac & Lauritzen, 1994). The aggregates display a colloform appearance building up clusters or irregular forms with rounded surfaces. Macroscopic, the aggregates display dull lustre, but, when magnified up to 20x, fine deposits with a silky lustre can be seen.

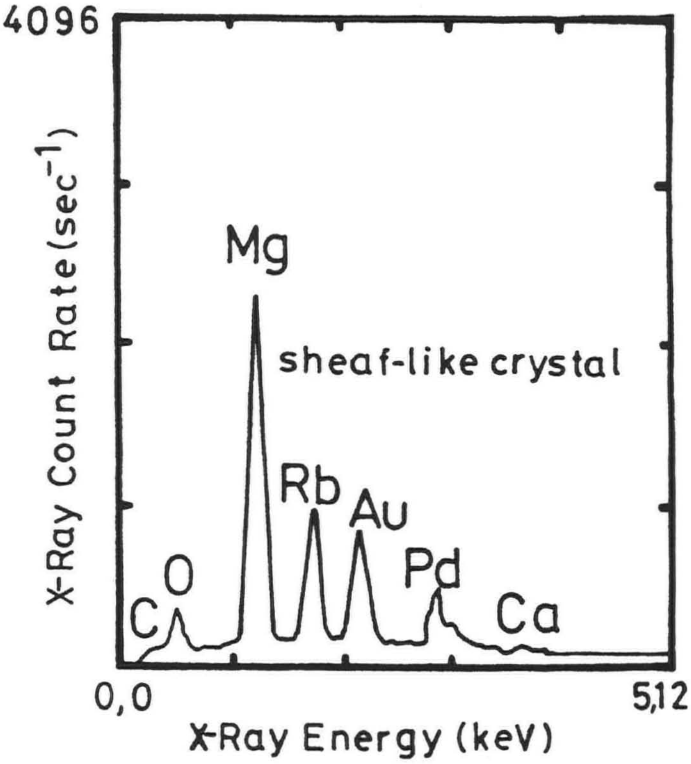


Figure 3. EDX spectrum of white microcrystalline aggregates (sample 764, Norway).

The hydromagnesite (90%) (Fig. 3) forms very thin scaly crystals (0.001x0.01 mm) with symmetric extinction and positive elongation (Nγ || b), being arranged in the shape of sheafs. Mirror-image twins on (100) with elongate lamellae along the c-axis have also been observed.

The aragonite crystals (0.007x0.02 mm) are better developed than the hydromagnesite crystals. Usually they are acicular, forming radiating groups. The crystals have strong relief, strong birefringence and negative elongation. Both minerals have a primary origin.

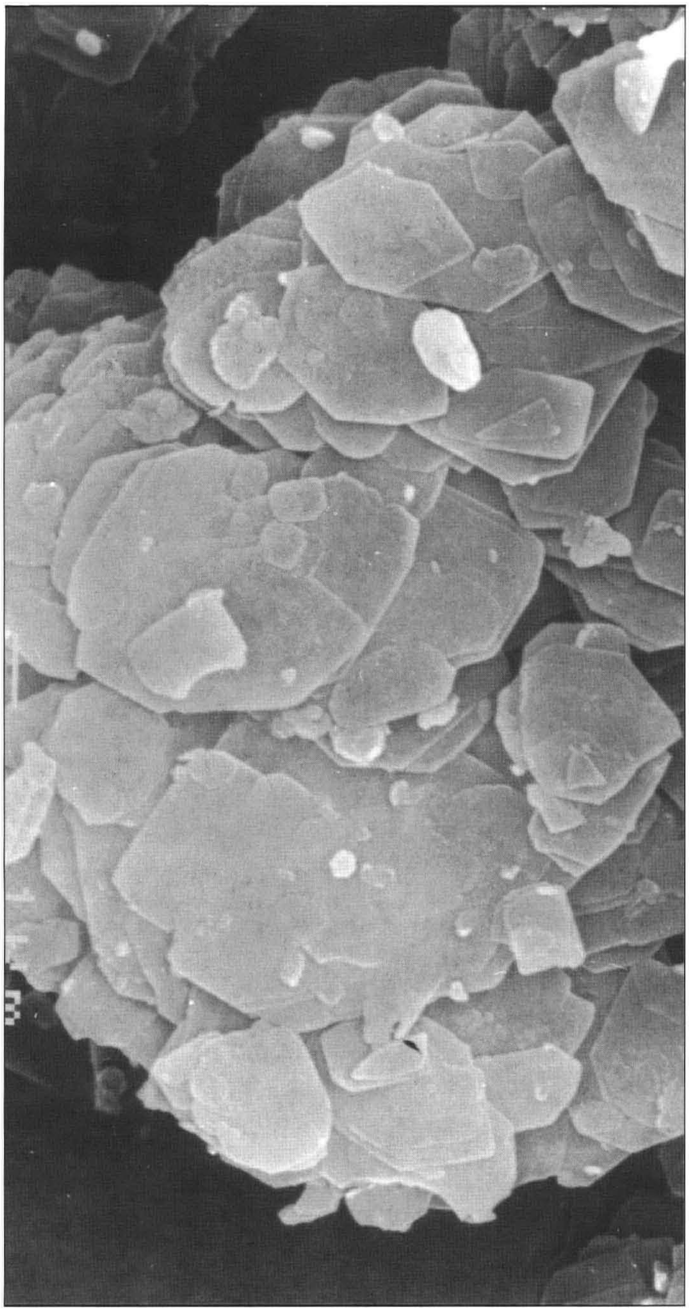
Calcitic moonmilk

The moonmilk with a calcitic composition is by far the most common. Macroscopically all calcitic moonmilk samples look very similar but SEM and TEM analysis showed several morphological differences from one sample to another as a result of various thermodynamic conditions of moonmilk genesis. Three main types of calcitic moonmilk can be described from a morphological point of view:

a) *Fibrous-lamellar* – calcite pseudomorphism after monohydrocalcite.

This type was found in the Humpleu Cave, associated with calcite megascalenohedra close to the cave entrance, as well as in the Room of Wonders where it forms an impressive flow. The sample from this latter occurrence displays an incipient phase of evolution showing both jelly-like and crystallized components. The first one consists of hydrated calcium carbonate which contains vaterite, monohydrocalcite and poorly crystallized calcite while the second one (fibrous-lamellar aggregates) is made up of the same minerals but the quantitative ratio is in the favour of calcite a complete spectrum can be noticed for calcite, while monohydrocalcite, vaterite and aragonite seem to be subordinate (incomplete spectrum due to the small quantity). The amorphous phase was detected between the peaks 11° and 17°Θ.

The sample on which we performed TEM analysis shows fibrous-lamellar crystals which are almost transparent in an electron-beam, having clear straight edges, with equal thickness. During exposure to the electron-beam, the lamellar crystals often suffer local water loss; these peculiar zones modify their transparency, become diffuse-shadowed, and their arrangement is usually diagonal to the crystal elongation. Our observations lead to the idea that monohydrocalcite crystals with fibrous-lamellar habit form first but, given their



SEM. Lamellar hydromagnesite; the lamellae are developed parallel to (100).

instability they rapidly change into calcite (Onac, 1993).

Small quantities of aragonite made up of alternating twins (usually polysynthetic) are also to be found.

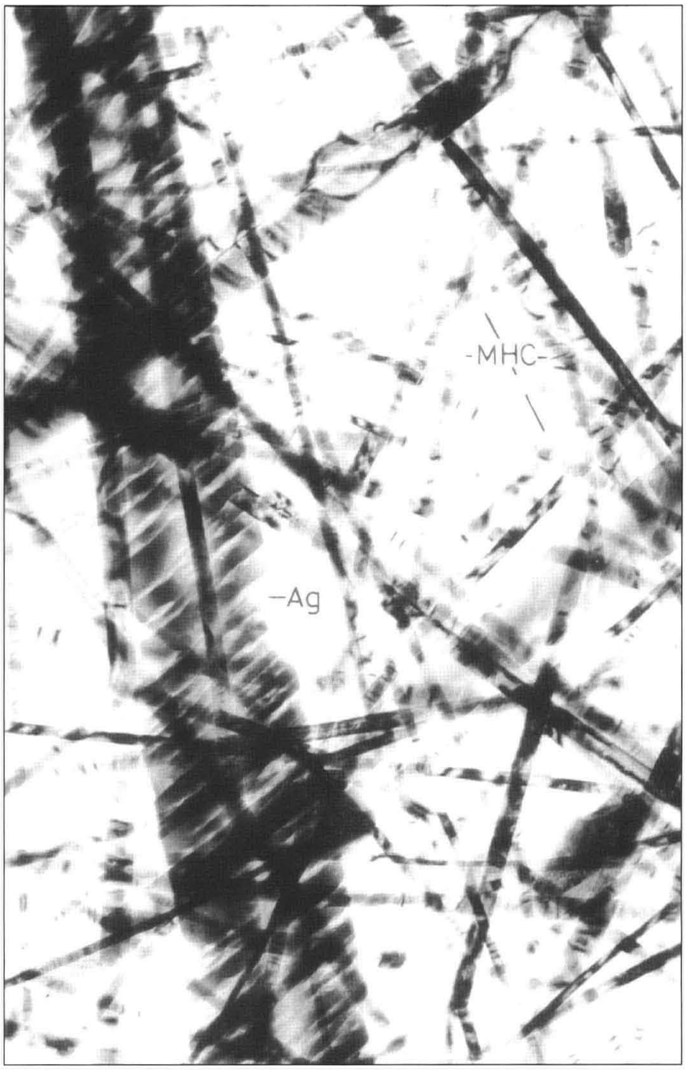
b) *Acicular-prismatic*-paramorphs of calcite after aragonite

Moonmilk made up of crystals, which are in fact paramorphs after aragonite (Onac & Fărcaş 1992), represent the majority of our studied samples.

The morphological types of paramorphism can be divided into two groups; the first one is represented by moonmilk formed from solutions free of impurities (crystals with few dislocations; samples 767, 776, 777, 778). The crystals have an acicular habit, elongated along the c-axis; they appear singly or twinned after (100) (Fig. 4a,b,c). On the TEM it is hard to observe the twins while in SEM images the twinned crystals are easily noticed due to a continuous shadow parallel to the re-entrant angle line.

To the second groups (samples 39, 763) we ascribed crystals having acicular to prismatic habits; most of them display polysynthetic twins. In this group, the crystals are elongated along [111] (Fig. 4d) or [101] and not aloong the c-axis; some crystals have a bladed shape after (010). Interesting intergrowth twins made up of fine lamellar polysynthetic twinned crystals can also be found. A rare type of twinned crystals appear as rhombic plates parallel to (110), outlined by (121) faces and developed in direction of [111] (Fig. 4e).

The differences between the two morphological groups are caused by the crystallization conditions. Polysynthetic twin growth is caused by the high density of dislocations generated by impurities which disturb the crystallization medium.



TEM. Partially pseudomorphosis of calcite after mono-hydrocalcite-MHC- (fibrous-lamellar aggregates) and polysynthetic twinned aragonite (Ag); x10,000.

Calcite formed posterior to the moonmilk deposition often leads to consolidation (cementation) of the former moonmilk aggregates (fibrous-lamellar, acicular, prismatic crystals) in forms of crusts (samples 25, 776, 777, 778).

c) *Microannular*

A drapery-like flowstone made up of calcitic moonmilk has been investigated in Piatra Altarului Cave. SEM and TEM analysis showed an aggregate consisting of pierced grains or annular fragments. This moonmilk speleothem consists of unidentified nannoplankton fragments coming from a weathered limestone with biological components.

Unlike the moonmilk types described above which have been precipitated directly from supersaturated solutions (neomorphism) this last type of moonmilk is just a weathering product with a residual origin.

CONCLUSIONS

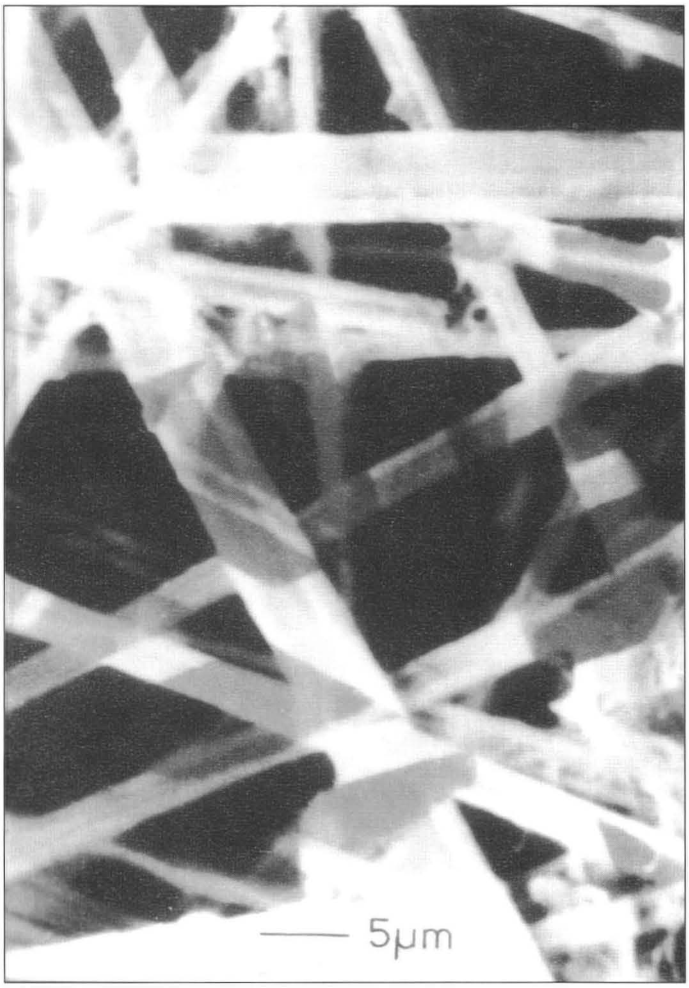
The moonmilk samples we studied are genetically of both neomorphic and residual origin.

The neomorphic moonmilk samples were composed of gypsum, hydromagnesite, monohydrocalcite, vaterite, aragonite and calcite. The following crystal morphologies: fibrous, fibrous-lamellar, prismatic, acicular-prismatic, scaly-like and micro-annular were found to form calcitic moonmilk in both Romanian and Norwegian caves. These morphologies are not actual calcite morphologies but represent:

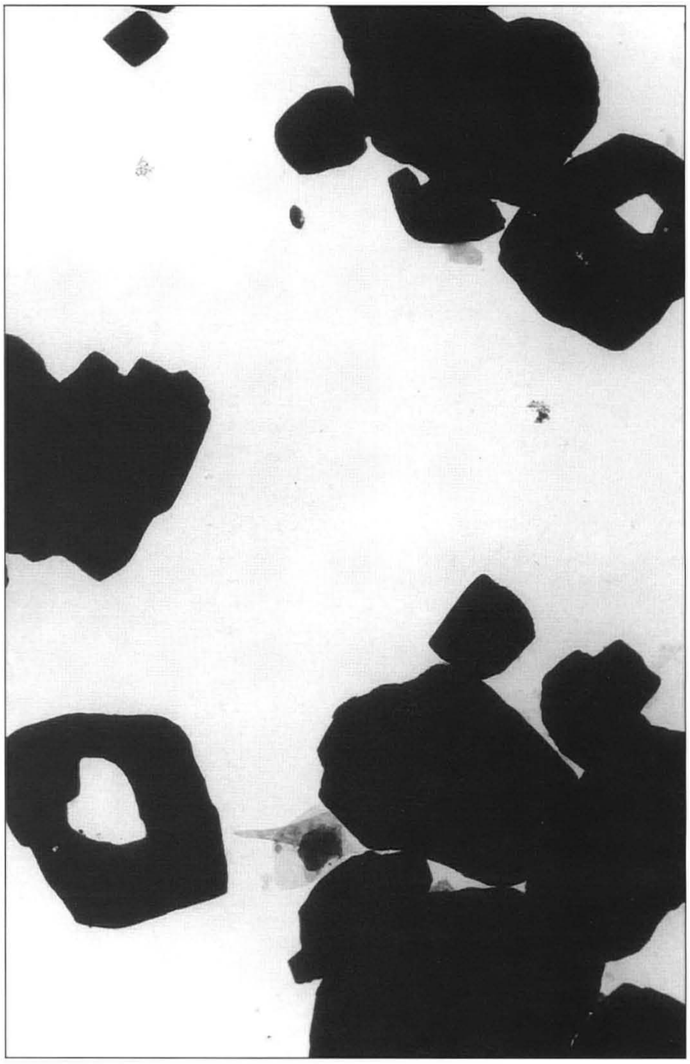
– calcite paramorphs after aragonite or vaterite, and
– pseudomorphism of calcite after monohydrocalcite.

The following mechanism by which fribrous-lamellar or acicular-prismatic calcite crystals (forming moonmilk speleothems) grow is proposed:

$$(nCaCO_3 - mH_2O)_{gel} \rightarrow CaCO_3 - H_2O \rightarrow \text{vaterite} \rightarrow \text{calcite}$$
$$\searrow CaCO_3\ (\text{aragonite}) \rightarrow \text{calcite}$$



SEM. Calcite paramorphosis after aragonite. The acicular crystals are developed parallel with the c-axis. Mirror-image twins can be seen (sample 767).



Microannular and angular calcite crystals (bioclastic) x2,500.

The investigations carried out on different moonmilk speleothems formed of micro- and nannocrystals which retain an important amount of water, suggest that different chemical compositions and origins can be ascribed even if their macroscopic appearances are very similar. Because of this we consider it useful to keep the term moonmilk, which, after laboratory studies, can be shown to have compositional (calcitic, gypsiferous, a.s.o.) and genetical (neomorphic and/or residual and/or biogenic) characteristics.

To define the boundaries of the pure types of moonmilk we suggest the value of 80% and not 90% as Bernasconi (1981) and Fischer (1993) proposed and the names in the ten field of our ternary system to be: 1: neomorphic; 2: biogene; 3: residual; 4: neomorphic + biogene; 5: biogene + neomorphic; 6: biogene + residual; 7: residual + biogene; 8: residual + neomorphic; 9: neomorphic + residual; 10: neomorphic + biogene + residual (Fig. 5).

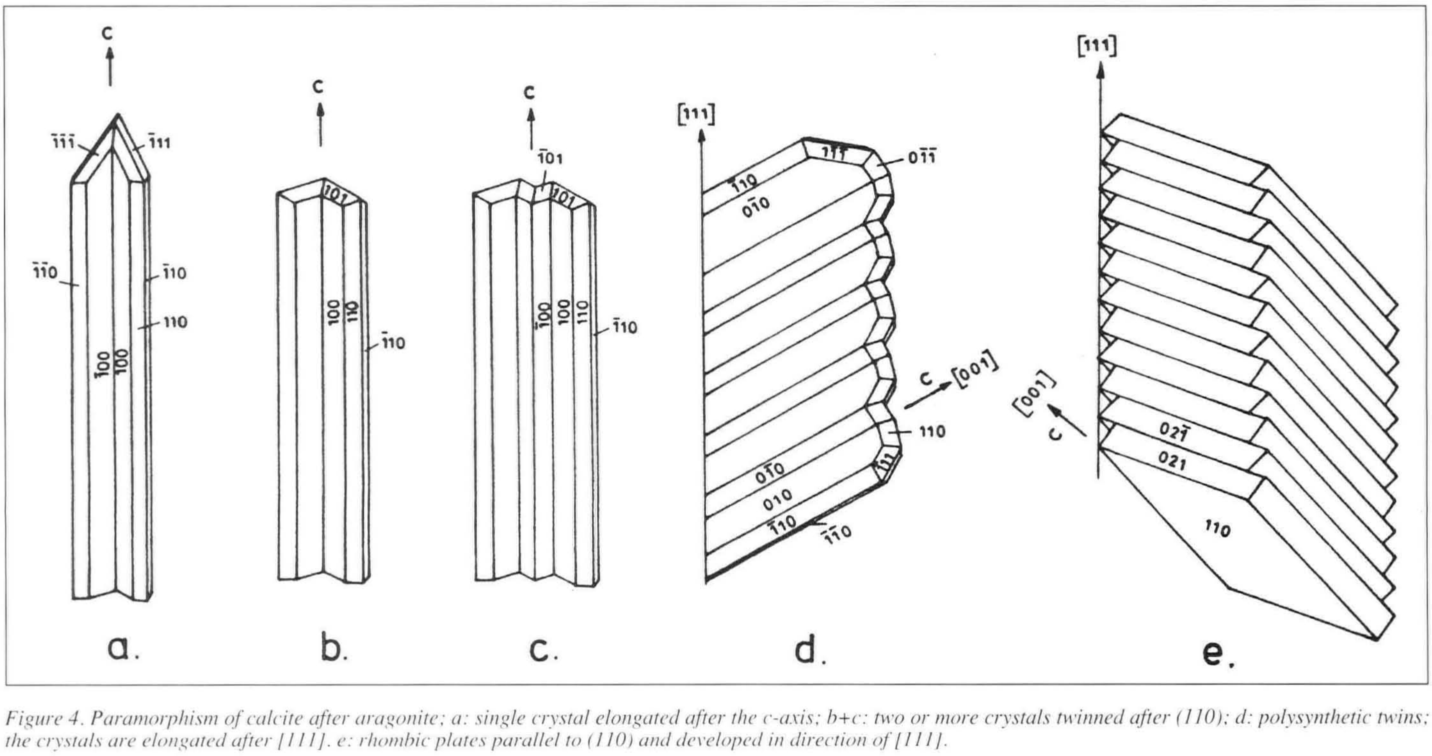


Figure 4. Paramorphism of calcite after aragonite; a: single crystal elongated after the c-axis; b+c: two or more crystals twinned after (110); d: polysynthetic twins; the crystals are elongated after [111]. e: rhombic plates parallel to (110) and developed in direction of [111].

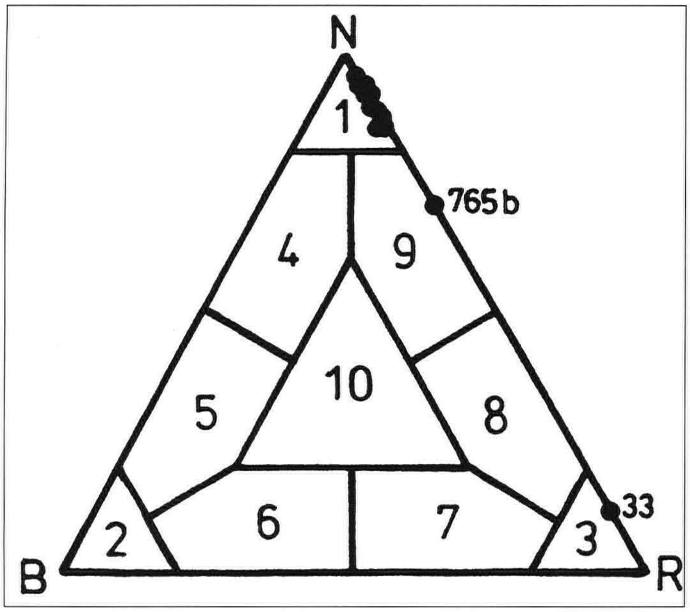


Figure 5. Ternary diagram showing the genetic types of moonmilk. Each dot represents a sample.

ACKNOWLEDGEMENTS

We wish to thank Stein-Erik Lauritzen and Magne Tysseland for their advice and discussions at various time. Thanks are also due to Constantin Goia who collected the samples from the Lucia Mica Cave as well as to Teofil Fărcas for some of the SEM pictures.

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Forum

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

THE PALYNOLOGY OF CAVE SEDIMENTS

S. J. GALE

In their recent discussion of the application of phytolith analysis to cave sediments, Thompson and Maloney (1993) remarked that 'It is generally accepted that pollen preservation is not good under calcareous conditions . . . '. This misconception has probably been fostered by statements to this effect in textbooks on pollen analysis. Faegri and Iversen (1975, p.180), for example, have written '. . . pollen grains . . . may be rather badly corroded in alkaline deposits, even if preservation conditions in general have been favourable.' Yet numerous studies have clearly shown that pollen and other organic-walled microfossils may be preserved in calcareous environments. Thus, Davey (1969) obtained palynomorphs from the Cretaceous Chalk, Turner (in Kerney *et al.*, 1980) recovered pollen from calcareous tufas and Bastin (1979; 1982) has extracted pollen from carbonate speleothems.

It is undoubtedly the case that pollen may not be preserved in highly-oxidising aerobic environments, but such environments should not be confused with those that prevail under calcareous conditions. Indeed, caves contain a wide range of depositional environments in which aerobic and oxidising conditions are not present.

The misconception that pollen is not preserved in cave sediments may be a result of the low pollen influx into caves and the difficulty of extracting sparse quantities of pollen from inorganic sediments. Workers using extraction techniques developed for use on organic sediments such as peats have frequently found it difficult to obtain pollen from inorganic material. However, advances in sample extraction techniques (see, for example, Hunt, 1985) have allowed pollen to be rapidly recovered from large samples of mineral sediment, making it possible to produce pollen diagrams based on large counts of pollen whilst still maintaining a close sampling interval. The success of this approach may be demonstrated by the existence of cave pollen diagrams which display comparable patterns to those of diagrams from surface sites in the area (see, for example, Gale and Hunt, 1985; 1990).

There is a large literature on the pollen analysis of cave sediments which may be unfamiliar to many palynologists. A partial review of this is provided by Hunt and Gale (1986), whilst a useful review of taphonomy and the palynology of cave sediments is given by Coles *et al.* (1989). Other recent work includes that of Scott (1987), Davis (1990) and Gale *et al.* (1993).

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REVIEW

CAVING EXPEDITIONS edited by Dick Willis, published jointly by the Expedition Advisory Centre, Royal Geographical Society (Kensington Gore, London SW7 2AR) and the British Cave Research Association. 3rd edition 1993, 169 pages. ISBN 0-907649-62-9. Price £10.

Some two dozen overseas caving expeditions leave UK each year and they have built up a record of discovery and investigation which no other country can equal. The World's largest caves in the Gunung Mulu National Park of Sarawak have been the prize discovery, but vast cave systems have been explored in Papua New Guinea, China, Mexico, Iran, Russia, Canada, South America and, closer to home, in Spain, Austria, Norway and other parts of Europe.

By chance this book arrived, with a request for review, at the same time as the annual crop of applications to the Ghar Parau Foundation and the Sports Council (the latter being vetted by the Ghar Parau awards committee on behalf of the National Caving Association), so as a Trustee of the Foundation and a member of the awards committee I have been able to take a broad view.

The book itself is an excellent survey of the problems and possibilities for caving expeditions overseas, with chapters written by 23 experts in the subject. As a 3rd edition, opportunity has been taken to iron out a few shortcomings in earlier editions, so there is little left for me to criticize, except that the section on Cave Surveying is perhaps too long and too detailed for a book such as this. Even so, having just read the Ghar Parau applications, I wonder how many of the applicants have looked at this publication or its earlier editions as there is little evidence in some applications. As a result some comments arise.

Personnel: the book emphasizes that moderate sized parties accomplish far more than large ones, yet some applications are for bus loads of 40 or more. Some of these seem to be largely students with very limited experience. Perhaps organizers should think much more carefully about the wisdom of taking such large groups into strange environments where quantity of personnel does not mean quality of results.

Specialists: the book rightly stresses the need for specialists who can interpret the geology and geomorphology but so often the only geologist listed on the application is a second year undergraduate whose expertise is unlikely to be enough for full appreciation of complex geology. As an example, some of the deep Austrian caves favoured by many expeditions are within highly tectonized limestone masses within the Alpine fold belt, but in the expedition reports I have seen little attempt so far to outline the geomorphological evolution of the caves or to relate it to the geological structure. Similarly, many expeditions list speleo-biology as one of their aims, but the only biologist among the personnel is an undergraduate with very little experience of collecting or of taxonomy. And, as the book emphasizes, getting specialists to identify the bugs collected is a battle not helped by the progressive conversion of our national museums into educational fairgrounds.

Presentation and representation: the book does not make these points strongly enough. To take some of the current Ghar Parau applications as an example: they look as though they were written in an alcoholic haze in the pub the night before submission, full of spelling mistakes and marred with sundry smudges and blots. Care and forethought can pay dividends here. If letters to foreign contacts, embassies, ministries etc are presented in this fashion, nobody will take much notice of them. The book also stresses that once in the field in a foreign country cavers are our ambassadors and representatives. Seemly behaviour and goodwill towards the local people are essential, not the denigration of the natives and drunken misbehaviour which occasionally occurs.

Reports and publications: of the two dozen expeditions which leave our shores each year, I see perhaps six reports, and some of these are hardly worth the paper they are written on. Tony Waltham's chapter in this book should be read, learned and inwardly digested by all expedition leaders. A concise objective report on what was found, with appropriate discussion of how that fits into the local geology, geomorphology or hydrology should be compiled as soon as possible after return. Appropriate members of the team should be assigned these tasks, with a clear time limit, enforced by the leader. A report which simply says how clever we were to get to the bottom and wasn't it fun at the local taverna does no good at all. Failure to produce a report at all will almost certainly lead to the refusal of grants for future expeditions, and spoil things for one's successors. If the discoveries and/or analysis are new to speleological knowledge then a suitable article must appear in a national caving journal, such as CAVE SCIENCE. The temptation to do a one-off flimsy on someone's DTP word-processor must be resisted: in ten years time how would anyone locate such reports, regarded by librarians as ephemera? And applications which include hundreds of pounds in their budget for publication are not looked upon favourably, when such journals as CAVE SCIENCE can look after the reports without cost to the expedition funds.

By the time this review is published some of the 1994 expeditions will have set off and others will be in the final stages of preparation. I wish them well and I look forward to seeing their reports in due course.

The Expedition Advisory Centre of the Royal Geographical Society have also commented to the writer that they are concerned at the poor standard and sometimes non-appearance of reports of many expeditions, caving and otherwise, and they have produced an advisory leaflet on report writing which should be obtained by all concerned.

Trevor D. Ford

B.C.R.A. RESEARCH FUNDS AND GRANTS

THE JEFF JEFFERSON RESEARCH FUND

The British Cave Research Association has established the Jeff Jefferson 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 which 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 which 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(s) must be the principal investigator(s), and must be members of the BCRA in order to quality. Grants may be made to individuals or small groups, who need not be employed in universities, polytechnics or research establishments. Information and applications for Research Awards should be made on a form available from Simon Botterill, Dept. of Earth Sciences, University of Leeds.

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, Rowlands House, Summerseat, Bury, Lancs. BL9 5NF. Closing date 1st February.

SPORTS COUNCIL GRANT-AID IN SUPPORT OF CAVING EXPEDITIONS ABROAD

Grants are give annually to all types of caving expeditions going overseas from the U.K. (including cave diving), for the purpose of furthering cave exploration, survey, photography and training. Application forms and advice sheets are obtainable from the GPF Secretary, David Judson, Rowlands House, Summerseat, Bury, Lancs. BL9 5NF and must be returned to him for both GPF and Sports Council Awards not later than 1st February each year for the succeeding period, April to March.

Expedition organisers living in Wales, Scotland or Northern Ireland, or from caving clubs based in these regions should contact their own regional Sports Council directly in the first instance (N.B. the closing date for Sports Council for Wales Awards applications is 31st December).

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 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.
Editor: Dr. Trevor D. Ford, 21 Elizabeth Drive, Oadby, Leicester LE2 4RD. (0533-715265).

CAVES & CAVING — quarterly news magazine of current events in caving, with brief reports of latest explorations and expeditions, news of new techniques and equipment, Association personalia etc.
Editor: Mark Dougherty, 7 Edinburgh Terrace, Armley, Leeds LS12 3RH (0532-639288).

CAVE STUDIES SERIES — occasional series of booklets on various speleological or karst subjects.

No. 1 Caves & 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.

No. 3 Caves & Karst of the Peak District; by Trevor Ford and John Gunn, 1990. Second Edition 1992.

CURRENT TITLES IN SPELEOLOGY — annual listings of international publications
Editor: Ray Mansfield, Downhead Cottage, Downhead, Shepton Mallet, Somerset BA4 4LG.

CAVING PRACTICE AND EQUIPMENT, edited by David Judson, 1984. Second edition 1991.

LIMESTONES AND CAVES OF NORTHWEST ENGLAND, edited by A. C. Waltham, 1974. (out of print).

LIMESTONES AND CAVES OF THE MENDIP HILLS, edited by D. I. Smith, 1975. (out of print).

LIMESTONES AND CAVES OF THE PEAK DISTRICT, edited by T. D. Ford, 1977, (out of print).

LIMESTONES AND CAVES OF WALES, edited by T. D. Ford, 1989.

[redacted]

Obtainable from B.C.R.A. Administrator
B. M. Ellis, 20 Woodland Avenue, Westonzoyland, Bridgwater, Somerset TA7 0LQ