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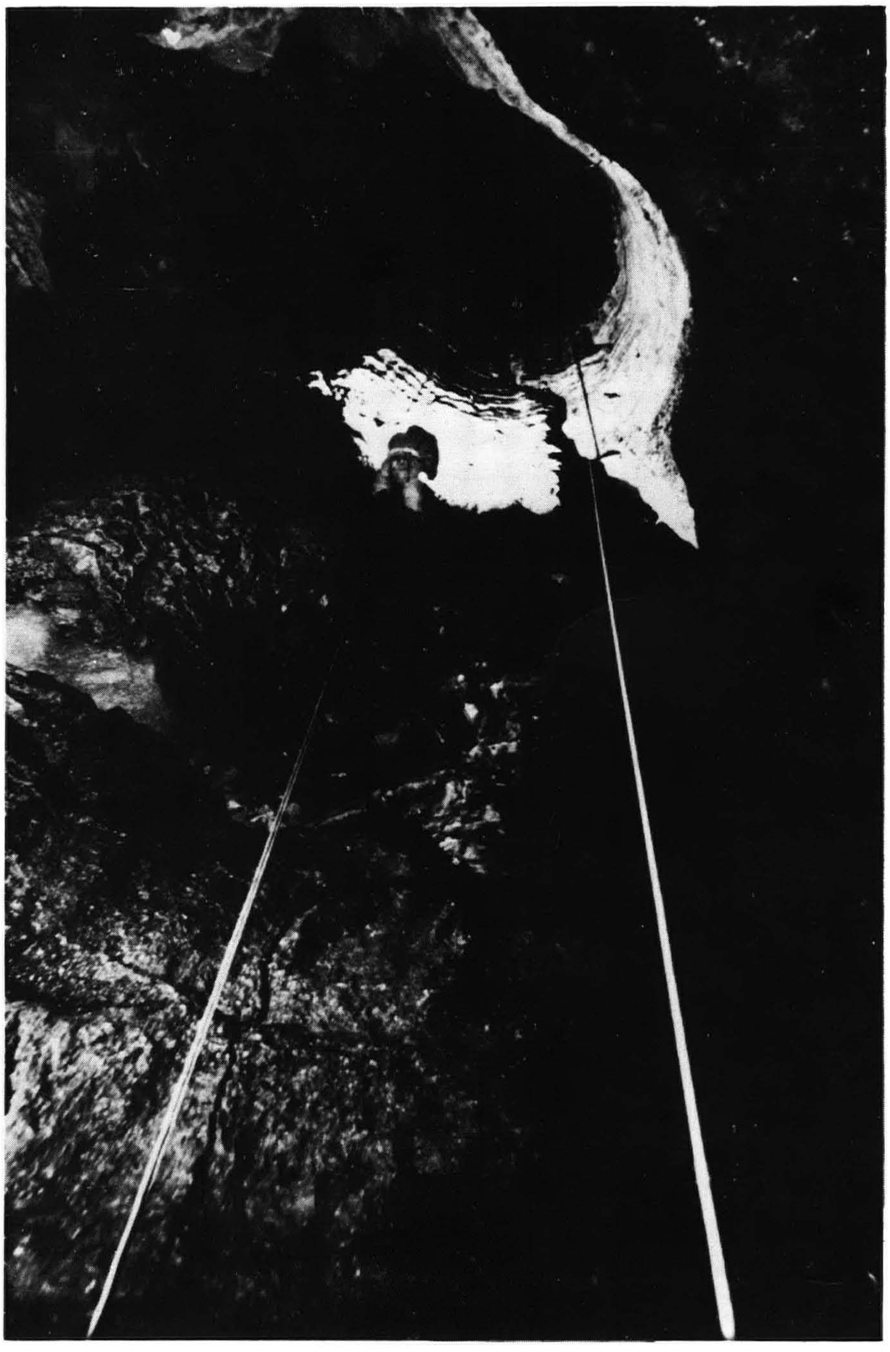
TRANSACTIONS

BRITISH CAVE RESEARCH ASSOCIATION

Volume 8 Number 1 March 1981

Cueva El Guarataro

BRITISH CAVE RESEARCH ASSOCIATION

NOTES FOR CONTRIBUTORS

Articles for publication in the Transactions may cover any aspect of speleology and related sciences, such as geology, geomorphology, hydrology, chemistry, physics, archeology and biology. Articles on technical matters such as caving techniques, equipment, diving, surveying, photography and documentation are also accepted for publication as well as expedition reports, historical and biographical studies.

These notes are intended to help authors to prepare their material in the most advantageous way so as to expedite publication and to reduce both their own and editorial labour. It saves a lot of time if the rules below are followed. All material should be presented in as close a format as possible to that of the Transactions. Text should be typed double-spaced on one side of the paper only. If typing is impractical, clear neat handwriting is essential. Subheadings, sectional titles etc., within an article should follow as far as possible the system used in the Transactions. In any case, they should be clearly marked, and a system of primary, secondary and tertiary subheadings, if used, should be clearly indicated and double-checked before submission.

All material should be accompanied by an abstract stating the essential results of the investigation for use by abstracting, library and other services.

References to previously published work should be given in the standard format used in the Transactions. In the text the statement referred to should be followed by the relevant author's name, the date, and sometimes page number, in brackets. Thus: (Bloggs, 1999, p. 99). All such references cited in the text should be given in full, in alphabetical order, at the end. Thus: Bloggs, B. 1999. The speleogenesis of Bloggs Hole. Bulletin X Caving Assoc. vol. 9, pp 99-199. Books should be cited by author, date, title, publisher and where published. Periodical titles should be appreviated in World List of Scientific Periodicals format if possible.

Acknowledgments: anyone who has given a grant or helped with the investigation, or the preparation of the article, should be acknowledged briefly. Contributors in Universities and other institutions are reminded that grants towards the cost of publication may be available and they should make appropriate enquiries as early as possible. Expedition budgets should include an element to help publication, and the editor should be informed at the time of submission.

Illustrations: line diagrams and drawings must be in BLACK ink on either clean white paper or card, or on tracing paper or such materials as kodatrace. Anaemic grey ink and pencil will not reproduce! Illustrations should be designed to make maximum use of page space. If photo-reduction is contemplated all lines and letters must be large and thick enough to allow for their reduction. Letters must be done by stencil, letraset or similar methods, not handwritten. Diagrams should be numbered in sequence, Fig. 1, Fig. 2, etc., and referred to in the appropriate place in the text by inserting (Fig.1) etc., in brackets. Captions should be typed on a separate sheet if they are not an inherent part of the diagram.

Photographs are welcome. They must be good clear black and white prints with sharp focus, and not too much contrast. Prints about 15 x 10 cm (6 x 4 inches) are best. Experienced authors may make up their complete photo pages (Plates) with captions printed or electro-typed in, but other authors should lightly pencil the photo number on the back, type the caption on a separate sheet and indicate in the text the point where the photo is referred to: Thus: (Photo 1) etc.

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Speleological expeditions have a moral obligation to produce reports (contractural in the cases of recipients of awards from the Ghar Parau Foundation). These should be concise and cover the results of the expedition as soon as possible after the return from overseas, so that later expeditions are informed for their planning. Personal anecdotes should be kept to a minimum, but useful advice such as location of food supplies, medical services etc., should be included.

Authors may order reprints of their contribution for their own private use. The order must be notified to the editor at the time of submission. Orders after publication cannot be accepted.

If you have any problems regarding your material, please consult the editor in advance of submission. (Dr. T.D. Ford, Geology Department, University of Leicester, Leicester LE1 7RH. Phone 0533-554455 ext. 121 or 0533-715265).

ERRATUM The diagrams below were inadvertently missed from T. Atkinson's note on page 206 of TRANSACTIONS vol. 7, no. 4.

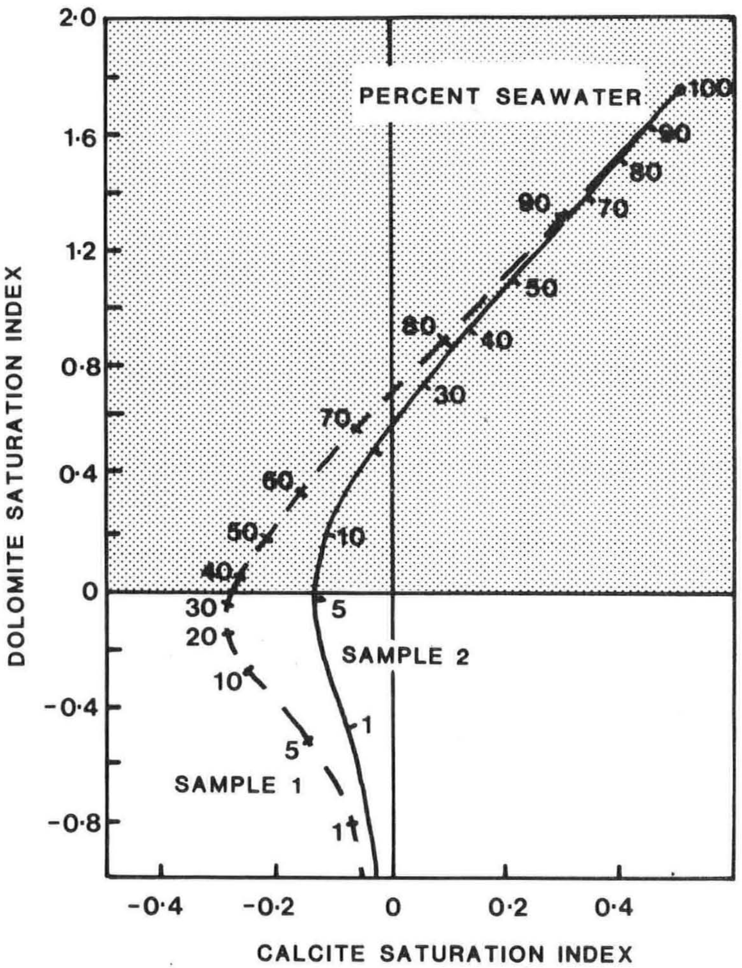


Fig. 1. Calcite and dolomite saturation index changes for mixing of two saturated pure calcite solutions with seawater. Sample 1 (broken line) has $PCO_2 = 10^{-2}$ atm. Sample 2 (solid line) $PCO_2 = 10^{-3}$ atm. The region that favours growth of dolomite is shaded. Saturation index is zero in saturated solutions, negative when under-saturated and positive when super saturated.

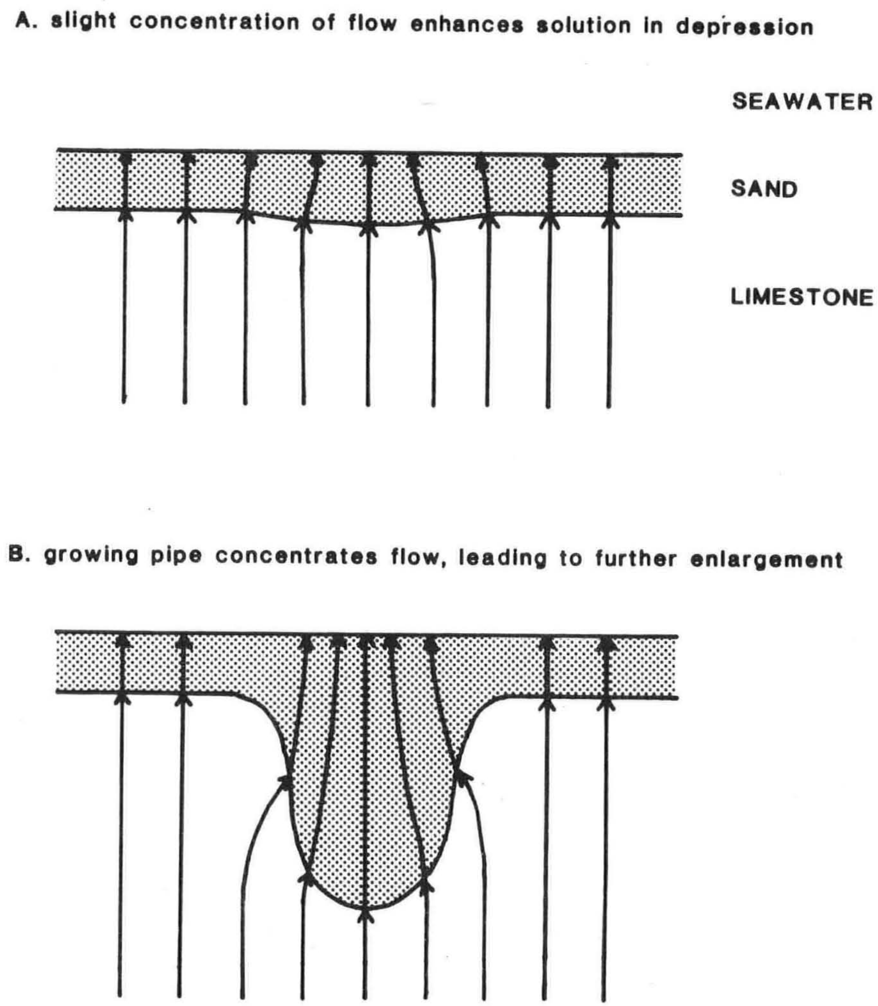


Fig. 2. Diversion of groundwater flow lines by pipe growth. (a) incipient depression on limestone surface, (b) Pipe forming by diversion of flow lines.

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# TRANSACTIONS OF THE BRITISH CAVE RESEARCH ASSOCIATION

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Cover picture: Prussiking up the 250 metre entrance pitch of Cueva El Guarataro, Venezuela. Photo by D. Checkley.

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# CAVES OF THE SERRANIA DE SAN LUIS, EDO. FALCON: THE BRITISH KARST RESEARCH EXPEDITION TO VENEZUELA, 1973

Compiled and edited by Phil Chapman and Dave Checkley

## SUMMARY

The 1973 British-Venezuelan Expedition to the San Luis Mountain region found numerous caves and shafts. Descriptions of 25 caves and 37 shafts are given, together with the surveys of the more important caves.

## INTRODUCTION

In 1973 eight British cavers visited Venezuela for six months. They were Dave Checkley (leader), Mel Gascoyne (treasurer, hydrologist), Mike Farnworth (transport officer), Phil Chapman and Gerry Swift (zoologists), Richard Matthews (geologist), Roger Nichols (catering officer, photographer) and John Gardner (equipment officer, diver). Jack Sheldon joined us for the latter part of our stay.

On our return to Britain, a full report was prepared for publication in Venezuela, but the publisher eventually declined to proceed. A shorter version was then prepared for publication in Spain and this too was not published. Meanwhile an account has been published of the hydrology of the Serrania (Gascoyne, ) and the biology of the caves (Chapman, 1980). This latter paper briefly summarises the geology and geomorphology of the area. The present paper describes the expedition and the caves explored. Further details of the scientific work will be published elsewhere.

## THE EXPEDITION AND THE PLACE

In April, 1971, the original organisers, the Northern Exploration Group, sought information on the caves of Brasil, Bolivia, Venezuela and other parts of South America. A few contacts were made, of whom by far the most helpful was Dr. Eugenio (Gene) de Bellard Pietri, a speleologist, who wrote enthusiastically of huge caves and deep shafts awaiting exploration in the remote jungle areas of Venezuela. His letters welcoming a British team were always a source of inspiration and, taking advantage of his local knowledge, the group, now centered on Dave Checkley and Mike Farnworth and based at Lancaster University, decided to visit a little known mountain range in northern Venezuela (Fig. 1). The late Brigadier Glennie, President of the British Cave Research Association, agreed to be the Patron, providing a fund of knowledge and sound advice.

It soon became apparent that an expedition to such a remote location would be very costly and we set about fund raising. The first step was to get our ideas down on paper in some marketable form and to this end we compiled an illustrated booklet in which we tried to present our scientific projects as excitingly as possible, stressing exploration not only of the caves, but also of the whys and wherefores of the cave environment. Over 500 copies were sent to firms, grant bodies and interested parties. Few firms replied, and most refused to help. Where firms did help, it was most generously and they are acknowledged at the end of this report. Of grant-awarding bodies, only the Gilchrist Foundation made a small donation. In the end our main sponsor was Lancaster University, to whom we extend our sincere thanks.

The expedition set off in February 1973. After nineteen sun- and wine-drenched days on board ship, punctuated by calls at Vigo, Tenerife and Kingston, Jamaica, we were welcomed at La Guaira by Gene de Bellard and enjoyed his hospitality in Caracas. With his help, beaurocratic formalities were soon tidied up and we left for Falcon and the Serrania de San Luis.

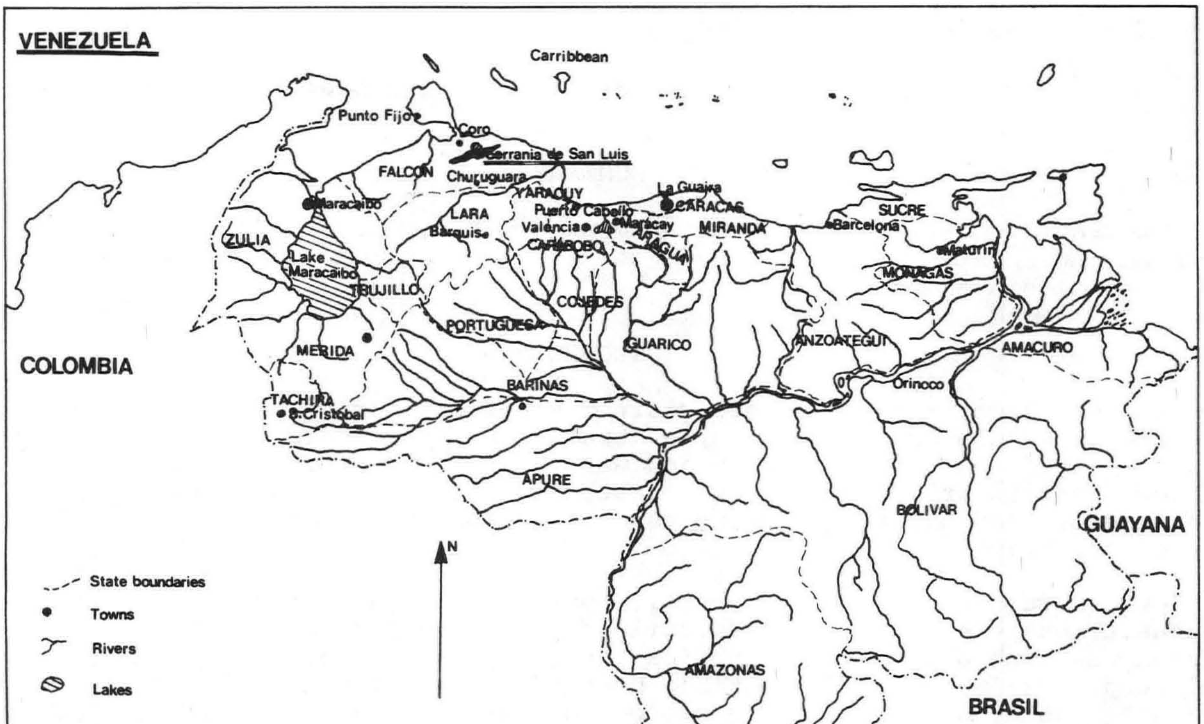


Fig. 1.

The state of Falcon lies in the north-west of Venezuela, bounded to the north by the Caribbean and to the west by the oilfields of Lake Maracaibo. The state capital, Coro, lies in a 20 km wide desert strip fringing the sea. Looking south from Coro, the Serrania de San Luis appears as a long, green, cloud-strewn range of hills standing out in sharp contrast to the greys and browns of the surrounding desert scrub. On the northern flank of the Serrania, rivers rising at the resurgences of Meachiche, Siburua and San Antonio wind their way northwards through the desert to the Embalse El Isiro, a man-made reservoir.

There are two roads into the Serrania. The first climbs steeply through desert scrub to La Chapa, then on into more lush montane forest, crossing the watershed at the 1370 metre high Penasco pass before dipping into the eastern end of the Curimagua valley basin. The second route is signposted to Churuguara and runs south-west across the plain from Coro before lazily climbing into the arid western part of the Serrania. The region's highest peak, Cerro Galicia, at 1500 metres, is skirted on its southern flank, after which the road drops into the western end of the valley basin and Curimagua village.

The long, enclosed valley basin has two steep east-west ridges running along its edges and terminates abruptly in the east with a craggy north-south scarp. Transverse ridges chop the basin into four parts. The Curimagua section drains to the Sumidero del Trapichito, a prominent sink below the cliffs of La Bandera mountain. The two central sub-basins, the Acarite and Camburales valleys, are long, narrow, and cliff-bound. The easternmost and largest drainage basin contains the village of Uria and drains into the Hondo de Uria, a sink which feeds the great spring at Hueque on the southern slope of the Serrania.

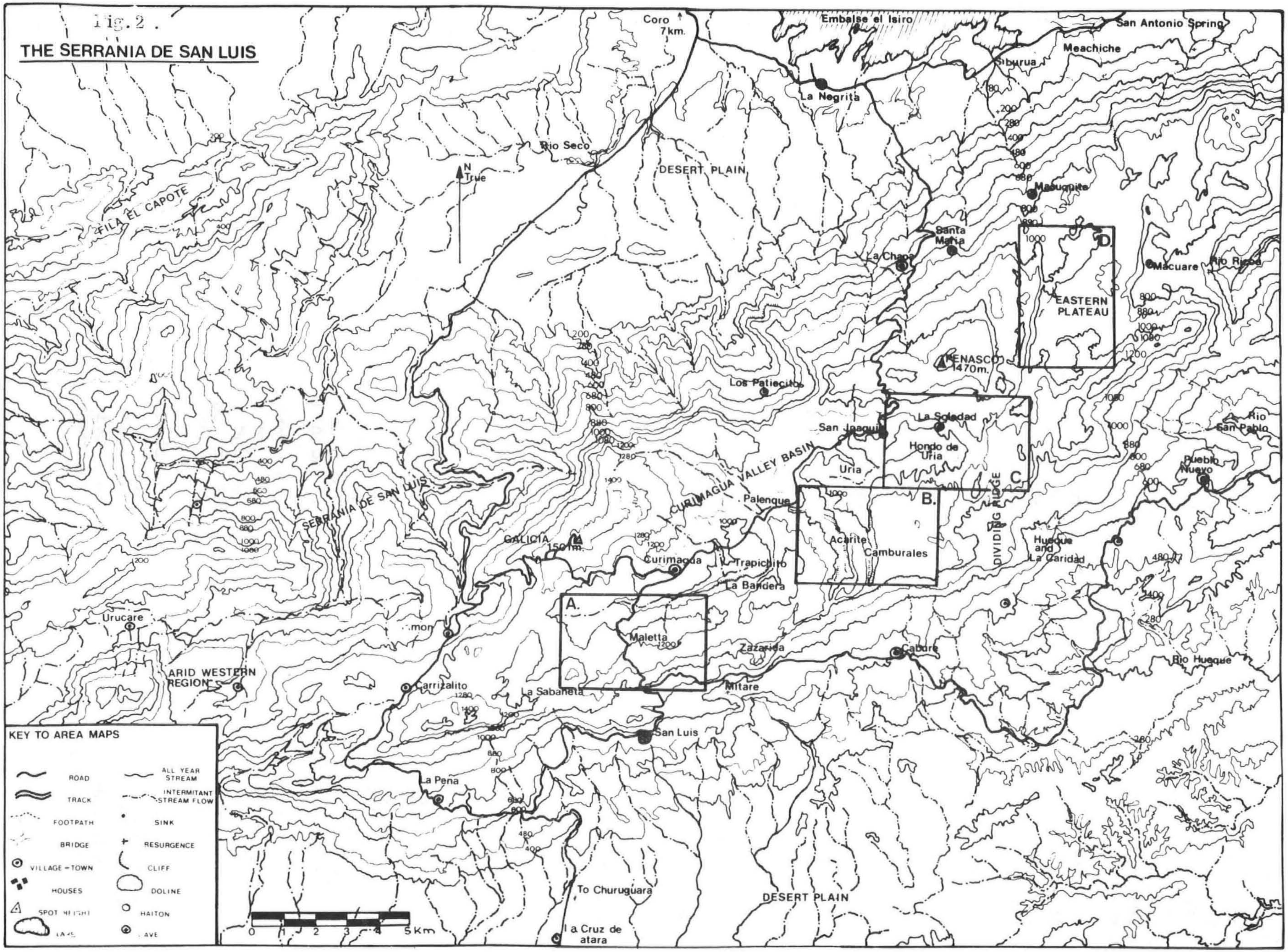



Fig. 2.
THE SERRANIA DE SAN LUIS

The way south from Curimagua lies over flat-topped Maletta mountain, location of el Guarataro, the deepest shaft in South America, then down via endless hairpin bends to a junction. To the west is San Luis, a pleasant town centered on a large resurgence, and to the east is Cabure. Just below the road a short way beyond is another large resurgence called Mitare which supplies Curimagua with potable water via a pumping station. Running along the Cabure road, an impressive line of cliffs about 10 km long mark the edge of the limestone. Below the eastern end of these cliffs sits the colourful town of Cabure and a little beyond is an uphill track to the Hueque resurgence.

The expedition was extremely fortunate in being loaned the use of the local community center in Curimagua as its base. The village was ideally placed, being served by three all-weather roads, water, and electricity supplies. The center consisted of a fenced-off area of about 700 $m^2$ containing a building resembling a large, open Dutch barn with a raised and partially enclosed stage at one end (used as a sleeping area and a complex of four rooms at the other (equipment store, food store, kitchen and laboratory). There can be no doubt that the final success of the expedition was due in large measure to the excellence of this base.

At the time of our visit, the local economy was dominated by small scale farmers ("campesinos"). Farms were centered in the fertile valley basin where the major crops were sugar cane, coffee, maize. Besides these, there were a few fairly large banana plantations and orange groves, scattered avocado pear and papaya trees, guava, pineapples and sweet lemons. Steeper forested slopes, and especially dolines, were cultivated on the traditional slash-and-burn system which produced a few poor crops of beans or maize, after which the denuded soil was abandoned to scrub forest which was often almost impenetrable and proved a major obstacle to cave-hunting. Numerous well-kept tracks linking often remote cultivated plots to the villages allowed us to reach known caves relatively quickly and easily.

The staple food of the Campesinos was maize and beans. The maize was ground to a flour and baked into small, doughy, disc-shaped "arepas" which were eaten with a spicy stew or soup containing black beans, yuca meat, chicken or goat. The social life of the men centered on the numerous bars where small bottles of ice-cold beer were consumed in quantity. Over-rapid consumption by thirsty cavers invariably led to violent hiccuping, possibly our most frequent health problem ! Dancing to music played on the cuatro (a small guitar-like instrument) with assorted percussion was a pastime enjoyed by one and all.

None of the team had previous experience of tropical rainforest, but most soon learned to wield a machete and to avoid poisonous snakes, spiders and scorpions. The long, irritant spines of forest palms and the biting insects were harder to escape. Local guides were invaluable in leading us to known caves, and indeed we were shown so many that their exploration and study occupied most of our stay and we had little time left over for cave hunting, though productive sorties were made to the eastern forests of the Serrania and the shaft-studded Maletta mountain.

In all, the expedition spanned six months and included two brief visits to the Andean province of Merida where some caving was done in addition to much mountain climbing. Occasional weekend visits to the fleshpots of Punto Fijo provided welcome breaks from constant caving and helped sustain morale and good health.

A time analysis for the expedition shows that 30% of all man-days were spent underground, including 18% spent in cave or shaft exploration with a further 17% of the total devoted to scientific work. Only one man-day in four was spent at base camp. The free provision of four-wheel drive vehicles and their maintenance by the local government based in Coro had much to do with this efficient use of time, as did the pleasant climate and country and good relationships with the community and within the team.

THE CAVES AND HAITONES (SHAFTS)

This section details all significant caves and shafts visited by the expedition. Locations are shown on the area maps (Figs. 2-6). 'F' numbers refer to the registration of the entrances in the Atlas Espeleologico de Venezuela by E. De Bellard Pietri, Biblioteca de la Academia de Ciencias Fisicas, Matematicas y Naturales, Volumen 1X1970. Where numbered shafts entered significant caves the description is given in the caves section. Numbers given were painted in a prominent place by the entrances of all haitones.

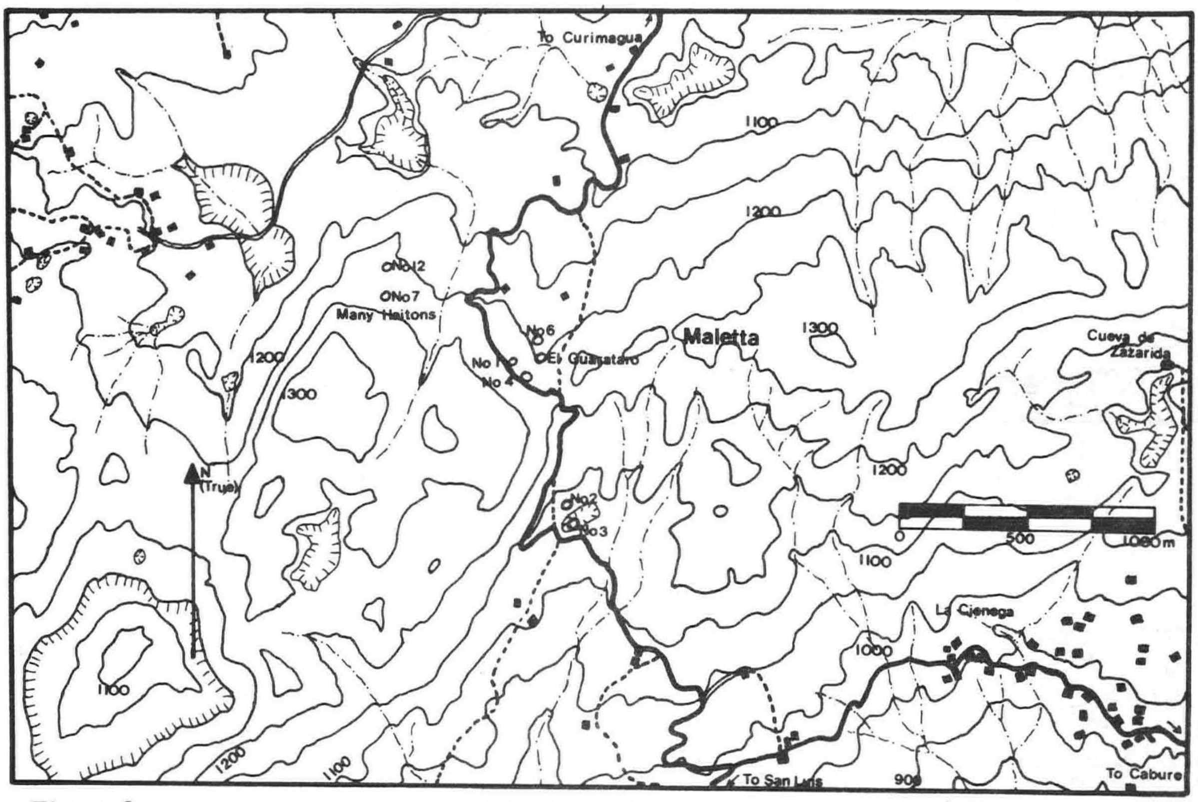



Figure 3 **AREA MAP A - MALETTA**

Cueva de Macuquita (Fig. 7).

Location:- Lat. 11° 15' 52"
Long. 69° 34' 19"
Plan length 320 m.
Depth 115 m.

From the village of Macuquita follow the southward running track for about one kilometre. A smaller track leads off after 30 minutes walk, in a south-west direction contouring around the spur. Eventually the track leads into a valley running north to south formed between two ridges. In the valley entrance there is a large doline which contains the cave entrance in a small cliff.

Description

The entrance is large and dips steeply north into a massive and dangerous boulder choke. Two obscure eight metre pitches through loose boulders, lead down to a large passage.

Here a side passage leads off which is narrow at first but soon opens into a large steeply descending passage which terminates in another boulder choke. This is the deepest point in the cave.

The main passage continues down the bedding and leads to a large terminal chamber. Several small shafts and passages were explored in the boulder floor. A very collapsed dip tube, sink cave formed mainly in limestone and shale.

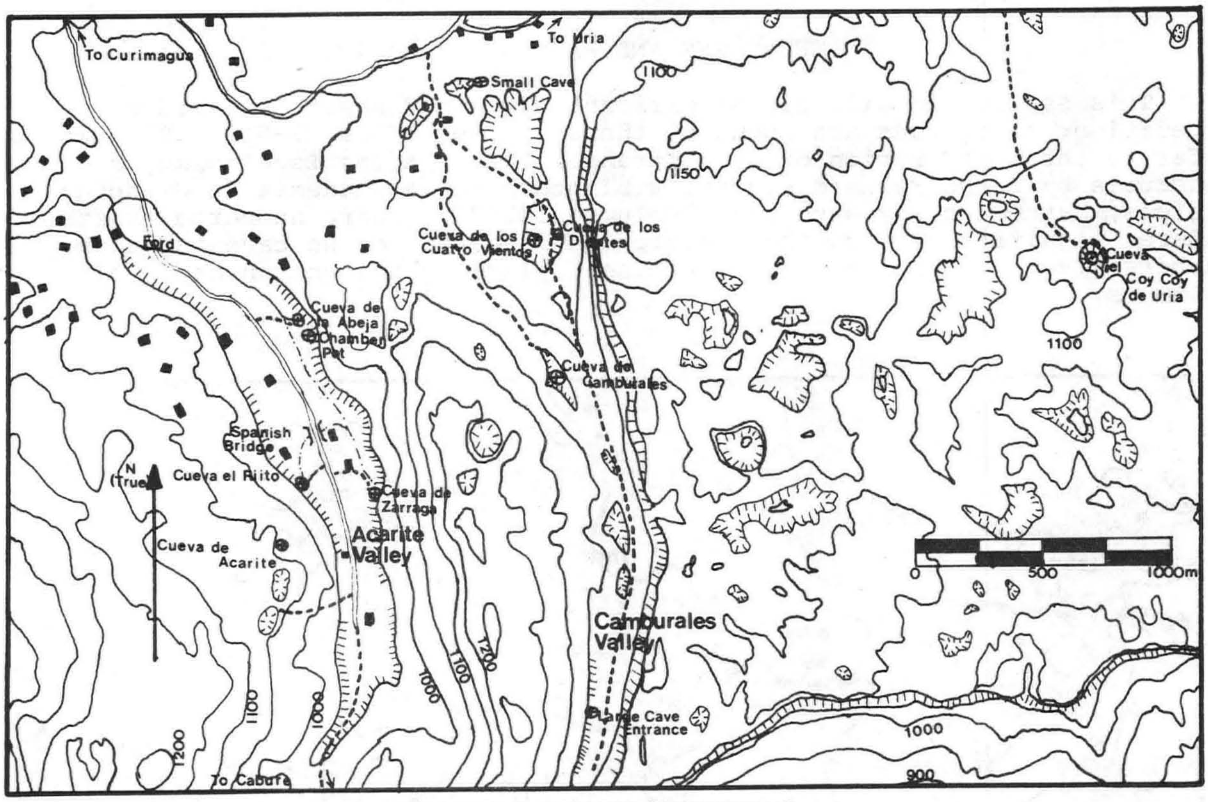



Figure 4 AREA MAP B-ACARITE CAMBURALES

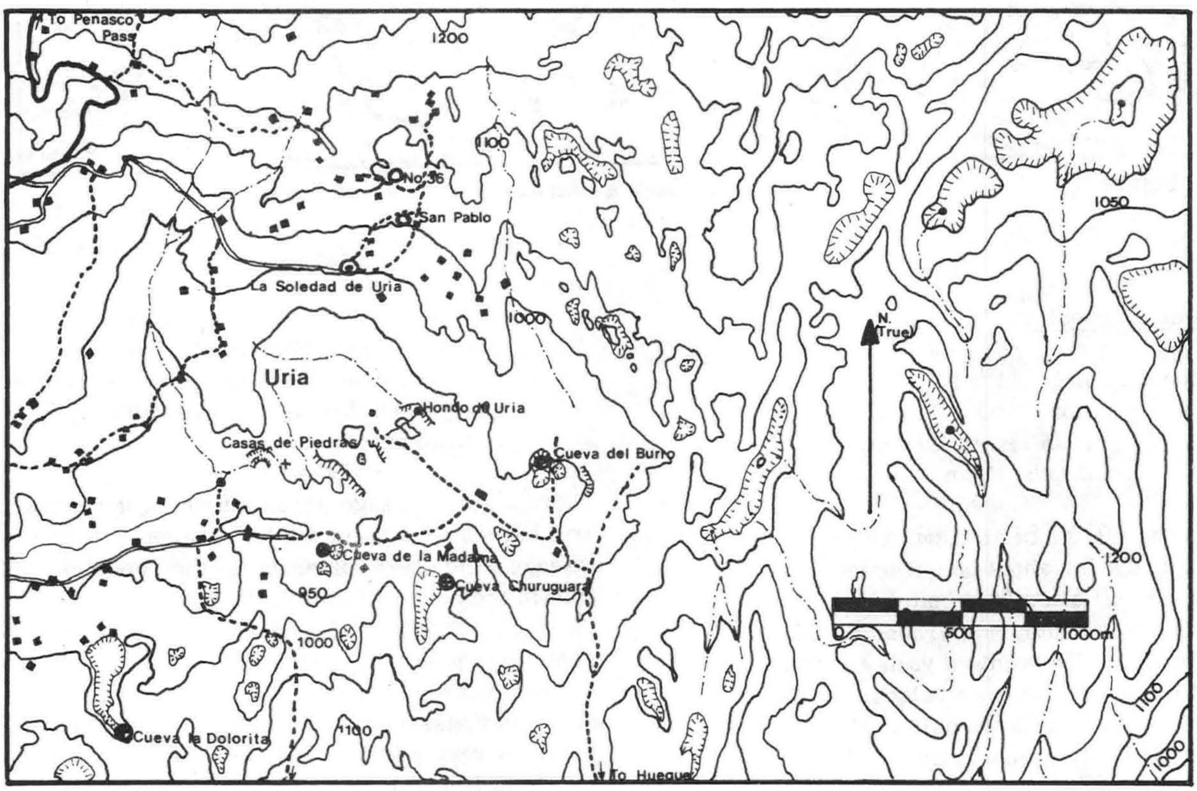
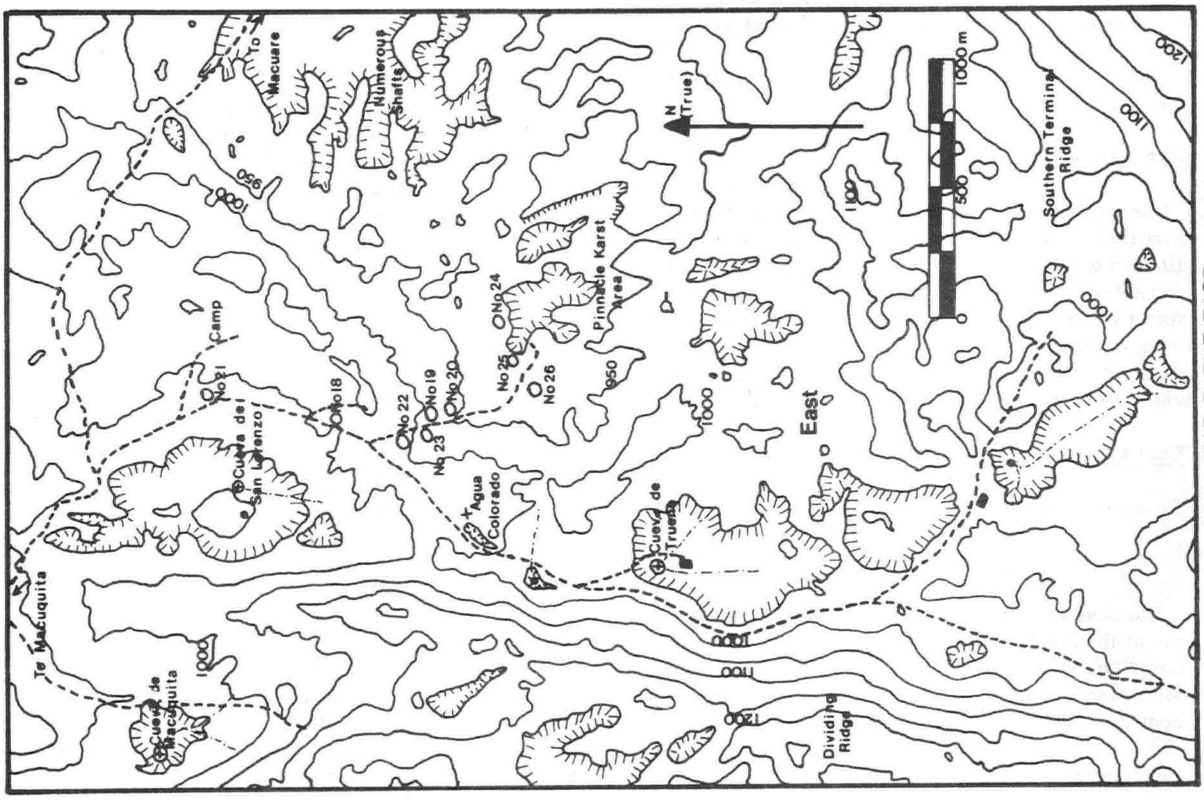



Figure 5 AREA MAP C-URIA




AREA MAP D-THE EAST

Fig. 6.

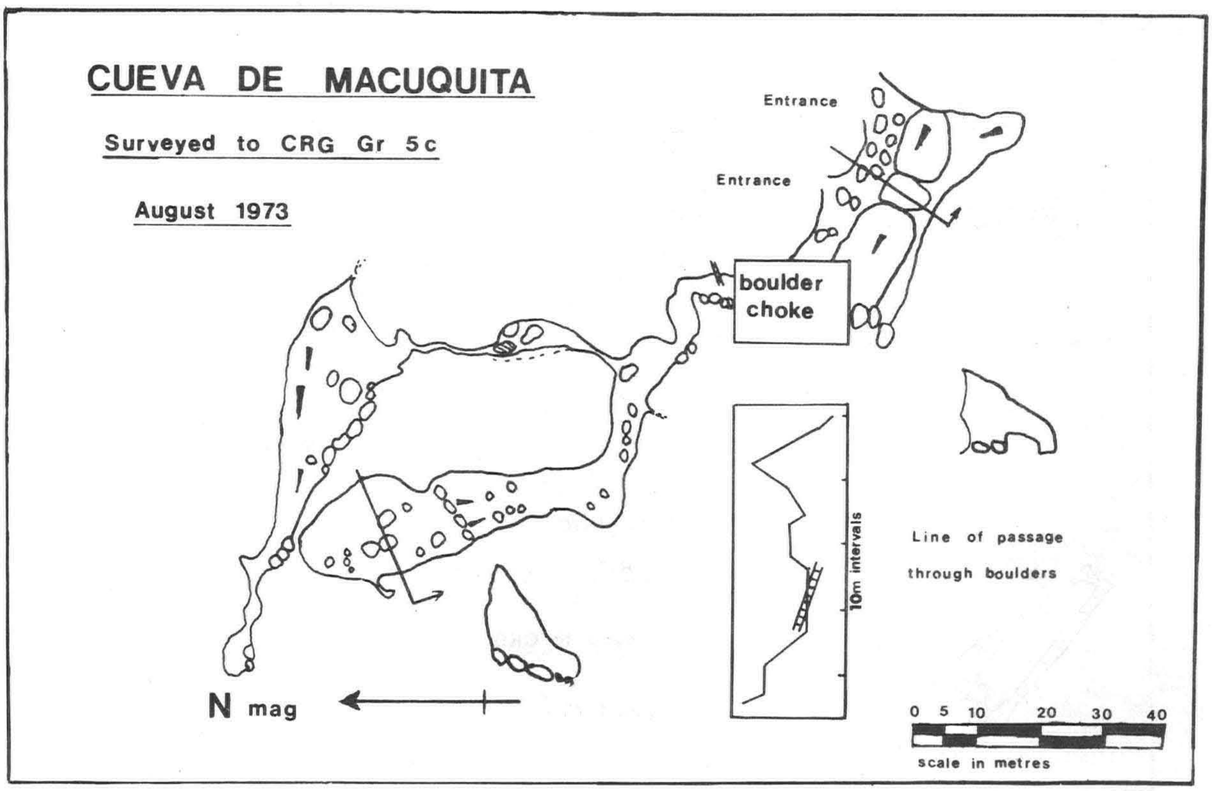



Fig. 7. Survey of Cueva de Macuquita.

Cueva el Riito de Acarite F 49. (Fig. 8).

Location:- Lat. 11° 10' 5"
Long. 69° 37' 6"
Plan length 450 m.

Follow the cobbled Spanish road south down the Acarite valley, pass over a narrow bridge and continue to a shrine. The cave entrance is situated in a small cliff east of the track and 30 m. before the shrine.

Description.

The cave entrance has a concrete area, and a stream bed leading from it. The cave is normally flooded to the roof but in dry periods can be entered for several hundred metres, the whole being in water of varying depths. It ended in a sump. The cave is an old, now largely abandoned, resurgence level with local amenity value for washing, bathing and water supply.

Cueva de los Dientos

Location:- Lat. 11° 11' 17"
Long. 69° 37' 08"
Plan length 250 m.

The cave is situated in the bottom of the large doline at the northern end of Camburales valley. It is below the large rock face on the valley's eastern side, and has a small entrance beneath a large boulder.

Description

The cave initially takes the only passable line through a maze of boulders. At the lowest point of the boulder choke a stream and series of passages are met. The stream is the same water as found in Cueva de los Cuatro Vientos, and it finally disappears into the boulders.

Cueva de la Rata (Fig. 9).

Location:- Lat. 11° 10' 20"
Long. 69° 39' 00"
Plan length 128 m.

Take the track to Trapichito main sink, and bear left through a coffee plantation after about 500 metres. Follow a small stream until it sinks below a large boulder at the base of a cliff. The entrance is on the opposite side of the boulder.

Description

The cave consists of a long vadose stream passage containing water which varies from knee to waist deep. There are several avens off this passage. Daylight can be seen from one of them. The cave ends in a boulder choke.

Cueva de Zarraga (Fig. 10).

Location:- Lat. 12° 10' 45"
Long. 69° 37' 30"
Plan Length 1,150 m.

Take the Acarite track and follow it for about three kilometres until the bridge is crossed. Continue until a shrine is seen, and take the path off to the left. Pass behind the house and walk in a south-eastward direction to the main cave entrance at the base of the cliffs.

Description

From the large entrance the cave drops steeply down a boulder slope into a chamber. To the left a well decorated passage leads through to daylight again. To the right a complex series of low wet crawls lead to another entrance. Straight on, a climb over large boulders leads to a low level passage on the right hand side. An awkward route through boulders leads to a large muddy passage. A sharp left bend reveals a small vadose passage containing a stream. This runs mainly parallel, but at a low level, to the main passage, linking with it occasionally. The main passage finally ends in a steep climb up an immense choke. The low level passage goes via a sump into a long and difficult draughting crawl through boulders, finally becoming too tight.

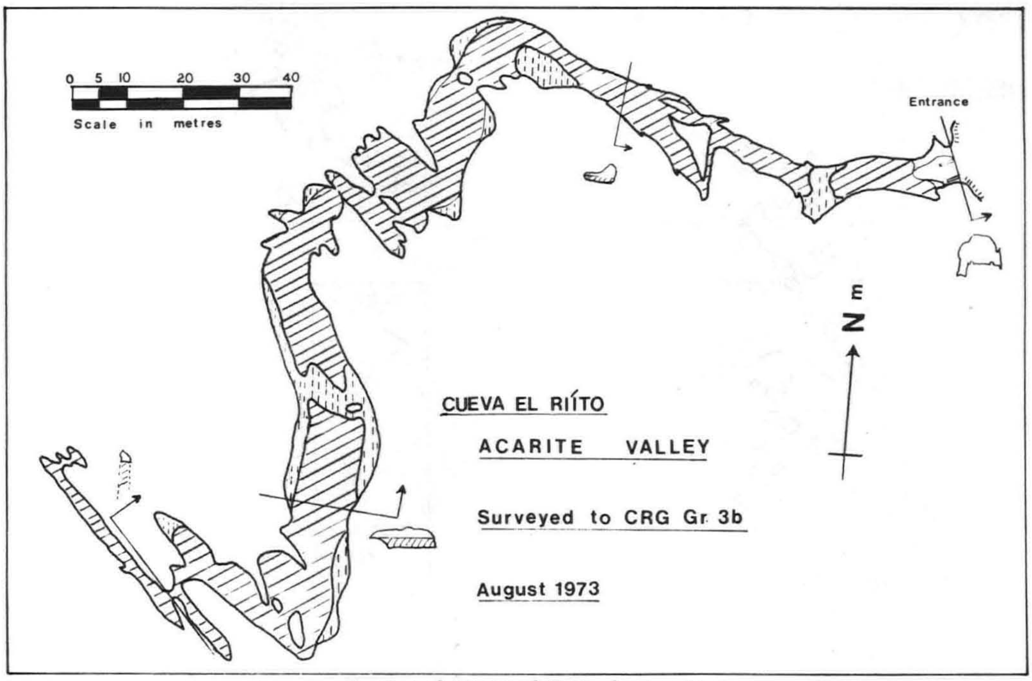



Fig. 8. Survey of Cueva el Riito de Acarite.

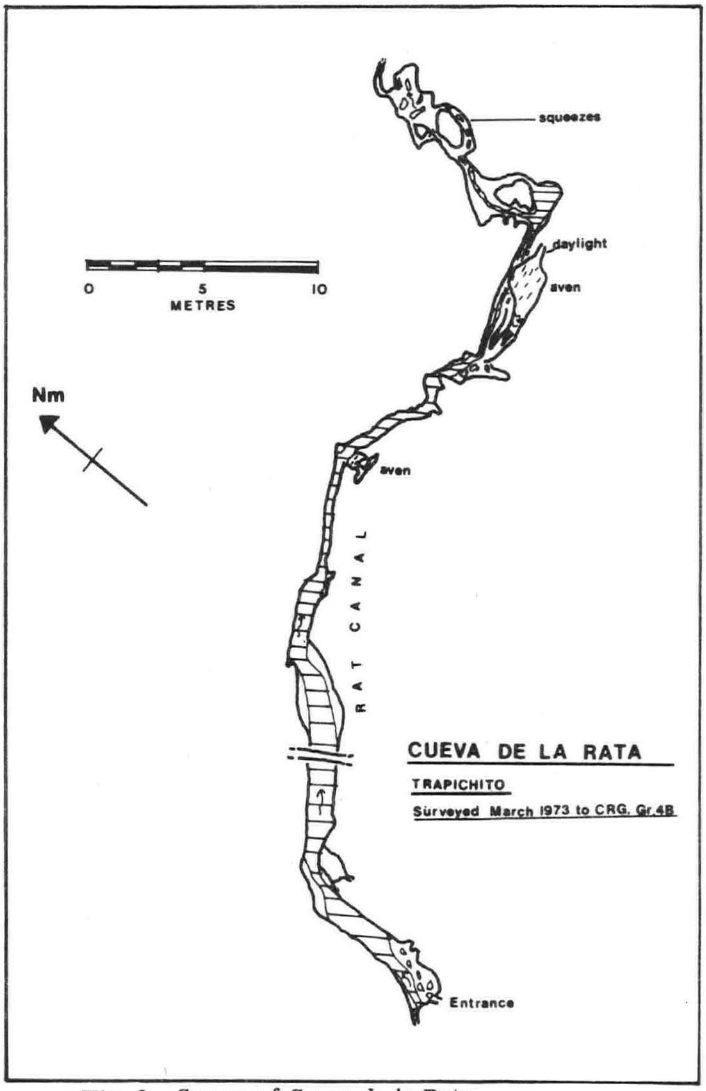



Fig. 9. Survey of Cueva de la Rata.

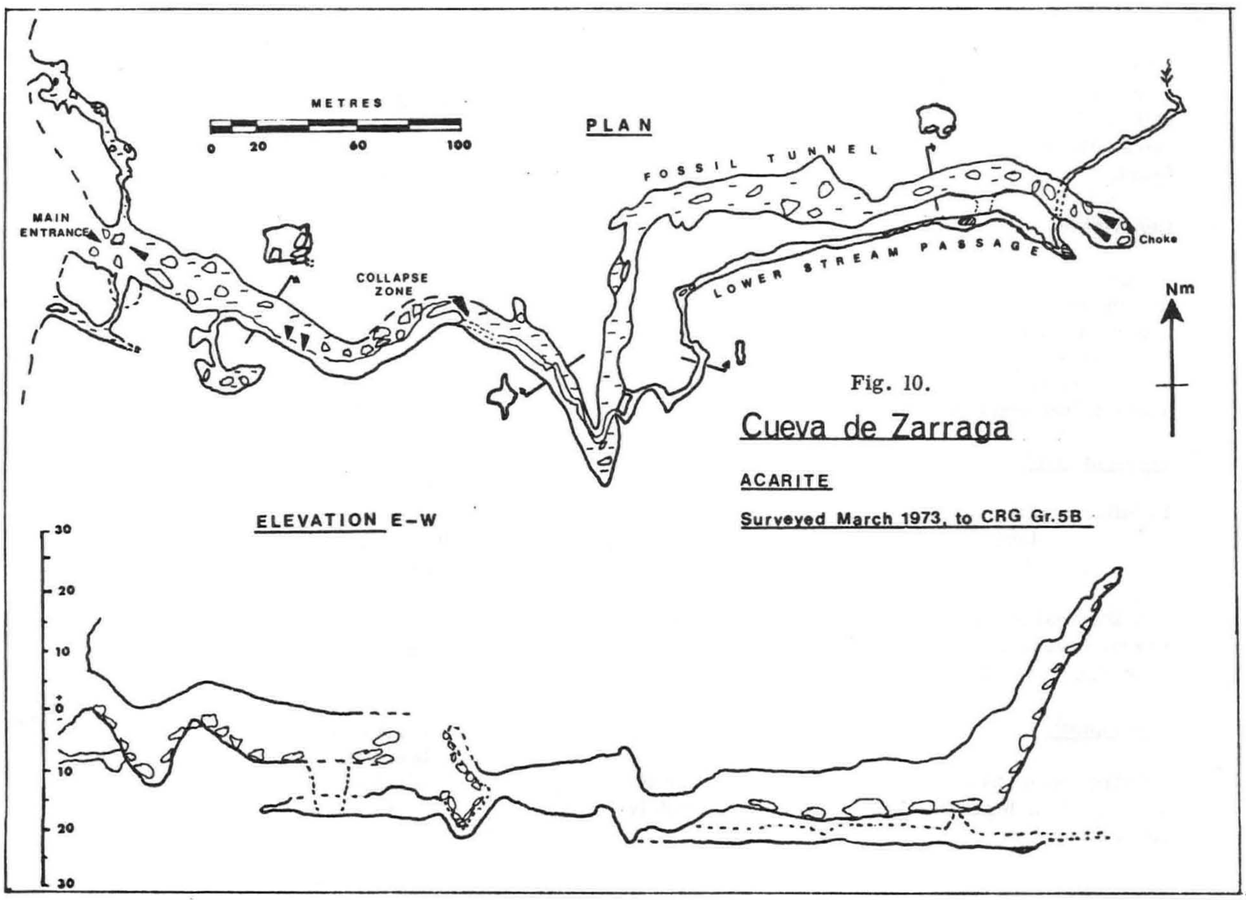



Fig. 10.

Cuevo del Burro (Fig. 11).

Location:- Lat. 11° 12' 25"
Long. 69° 35' 48"
Plan length 580 m.

Take the left fork in the track from San Joaquin and drive east to the sugar cane factory. Take the main path straight on, eventually going down through a sugar cane plantation to meet another path. At this junction turn right, and follow the path, taking the left hand fork at the junction subsequently reached. About 1 Km. from there, at the top of a rise, a well vegetated doline can be seen to the left. At the bottom of this is the cave.

Description

From the entrance below a small cliff a steep slope leads down to a boulder chamber where running water can be heard. A series of squeezes down through boulders leads to a large stream passage. Upstream is a large breakdown chamber, from which a high level passage takes off. After a low section on gravel, the cave ends in two sumps, one being a large flooded bedding plane. The cave is a conduit for the Hondo de Uria water. It accounted for one sixth of the flow from Hueque resurgence, and is the main drain for the eastern end of the valley.

Chamber Pot (Fig. 12).

Location:- Lat. 11° 10' 18"
Long. 69° 37' 59"
Plan Length 450 m.

The cave is situated beneath the rock face at the entrance to and on the eastern side of Acarite valley. 100 m. to the south of Cueva de la Abeja, two small entrances at the base of the cliff are found.

Description

From the bottom of the 13 metre entrance pitch, low and high level routes begin. Large chambers are characteristic of the high level, and the low level is a vadose stream passage. At the end a short, attractive section containing a few formations is reached before the choke.

Cueva de Acarite F 50

Location:- Lat. 11° 10' 30"
Long. 69° 37' 40"
Plan length 100 metres

On the west side of Acarite valley approximately 100 m. beyond the resurgence cave, and 100 m. above the valley floor.

Description

A large open chamber with an arch entrance 35 m. wide by 20 m. high. The chamber is approximately 100 metres in length with no side passages.

Cueva de Zazarida

Location:- Lat. 11° 9' 8"
Long. 69° 39' 52"
Approximate length 100 m.

Follow the track, by a stream bed, up the last valley before Mitare pumping station, going east on the Cabure road. Branch left after a short distance and walk up another stream bed until an area containing numerous sinks is reached.

Description

It is a small sink cave with a short entrance climb down. A small clean stream passage ends in a choked bedding plane downstream. A parallel passage can be entered and there are many oxbows.

Cueva de los Cuatro Vientos (Fig. 13).

Location:- Lat. 11° 11' 14"
Long. 69° 37' 10"
Plan length 880 m.

Follow the track along the base of the imposing Camburales cliffs, then break off to the right into the banana plantation in the largest doline, to find the entrance under a small cliff.

Description

A draughting, low crawl entrance, followed by a clamber down boulders, leads to a large chamber which has mud banks on three sides. On the right is a tight inlet passage; whilst to the left, leads to a small chamber, containing attractive formations. Straight on is the main passage. This is 20 metres high, contains a stream, and has large mud banks on either side. 100 metres upstream is a boulder pile covered with mud. Here also is the junction of two passages. To the left is a canal passage 200 metres long; whilst on the right, the main stream flows over a series of gours. Upstream involves a climb up the mud slope and a further climb ends the cave when the floor meets the roof. This is an old phreatic tunnel cave.

Cueva el Coy Coy de Uria F 55 (Fig. 14).

Location:- Lat. 11° 11' 12"
Long. 69° 35' 58"
Plan length 1,100 m.
Depth 90 m.

Take the San Joaquin track past the bar and continue until reaching the fork. The left hand branch is followed to a second fork. A path leads off here, on the right, and after a short climb, the left hand branch is taken to a cleared doline area. From there the path leads directly to the Coy Coy doline where several climbs are necessary to skirt around the entrance cliff.

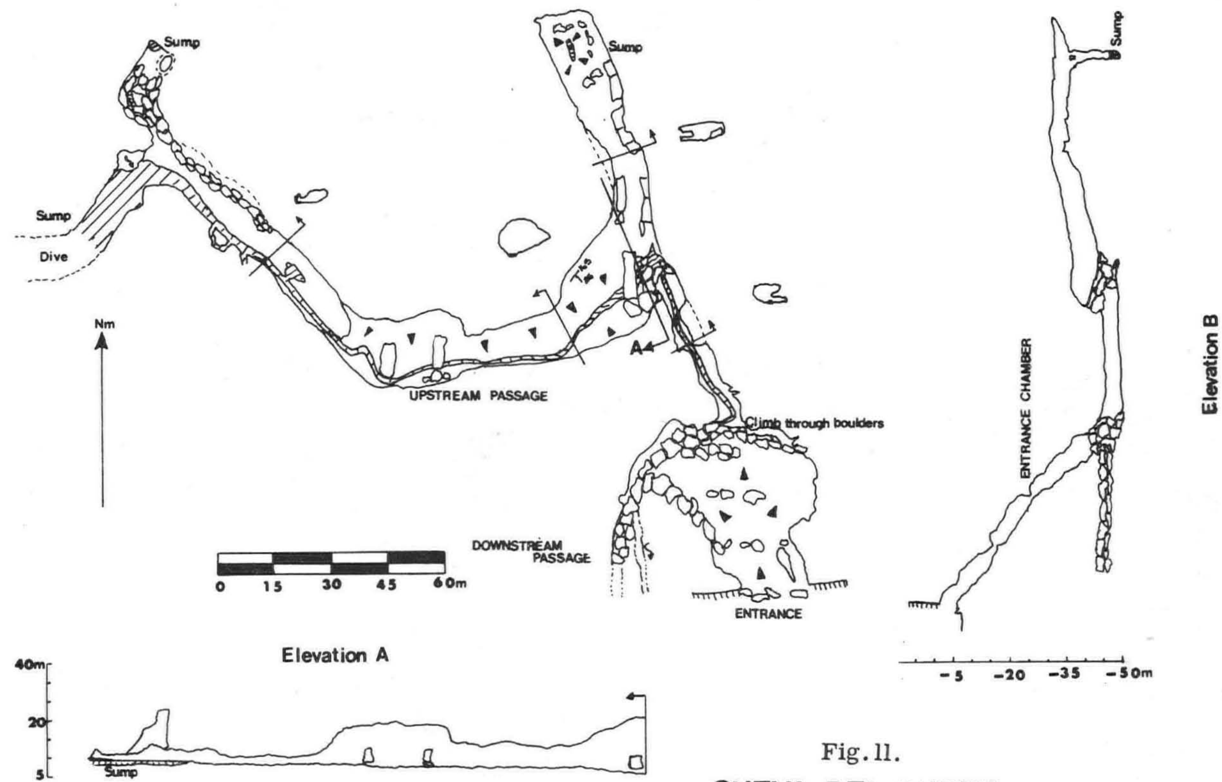



Fig. 11.

**CUEVA DEL BURRO**
**Surveyed March 1973 CRG Gr. 5b**

Fig. 12.

**CHAMBER POT**
Length 450 m
Depth 23 m
**CRG Gr 5b**

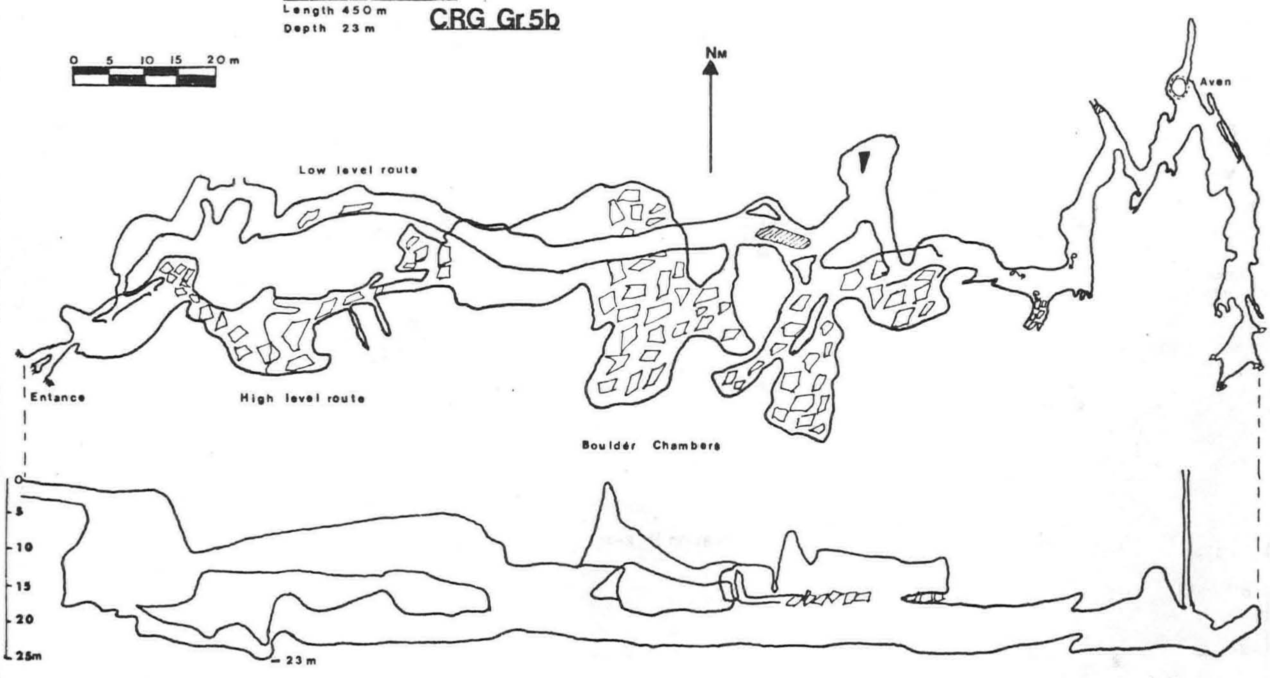


Fig. 13. **CUEVA DE LOS QUATROS VIENTOS**

**CRG Gr 5b**

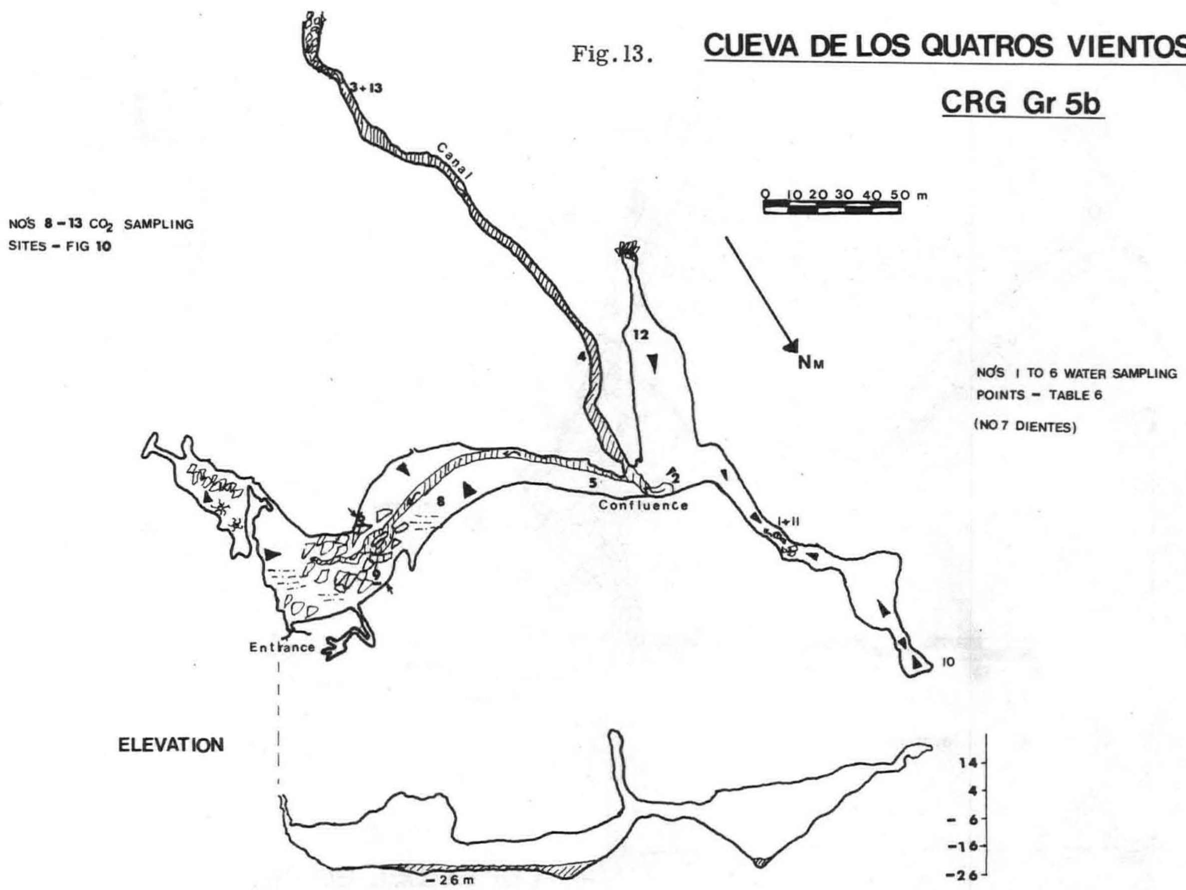
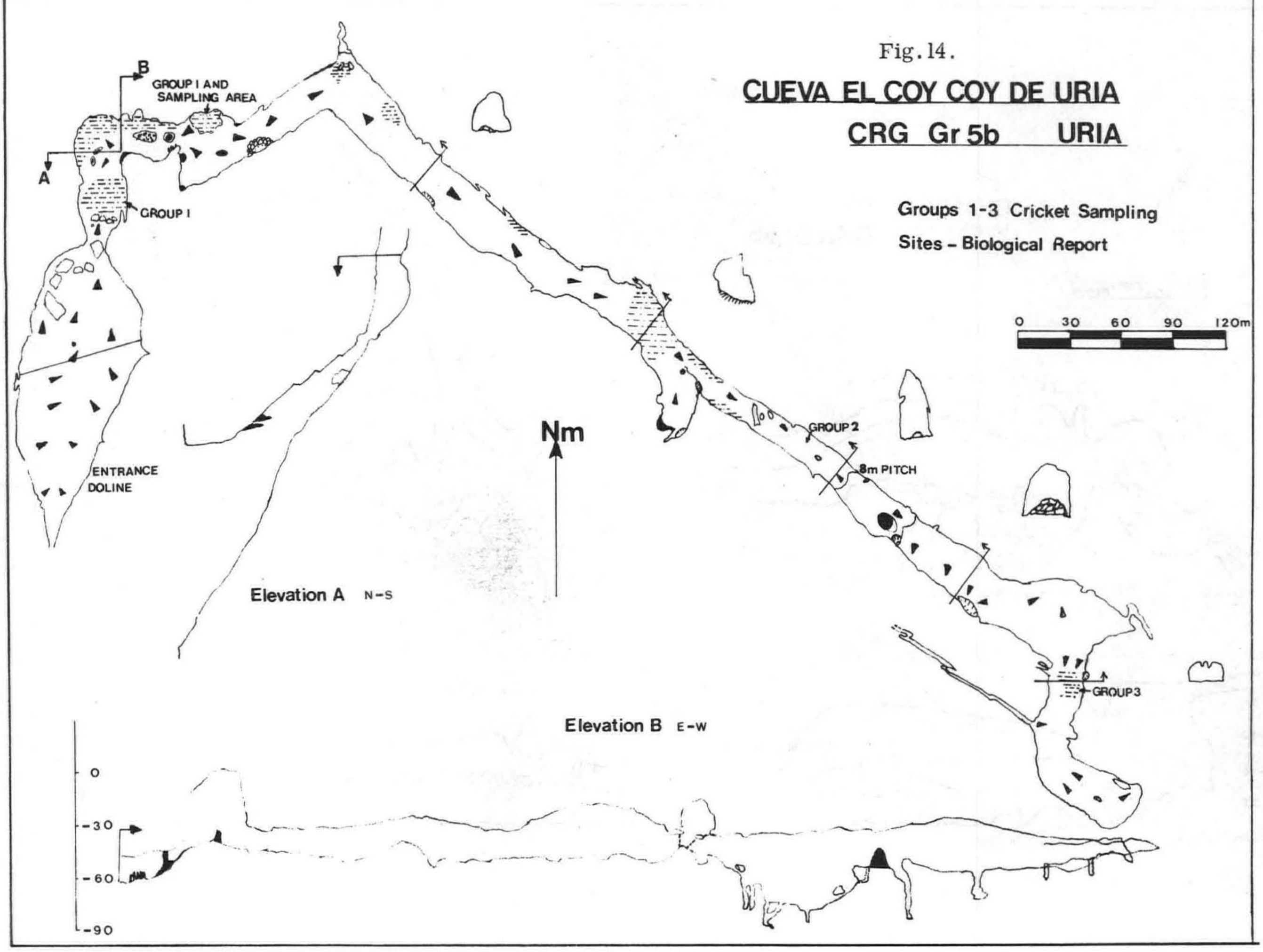


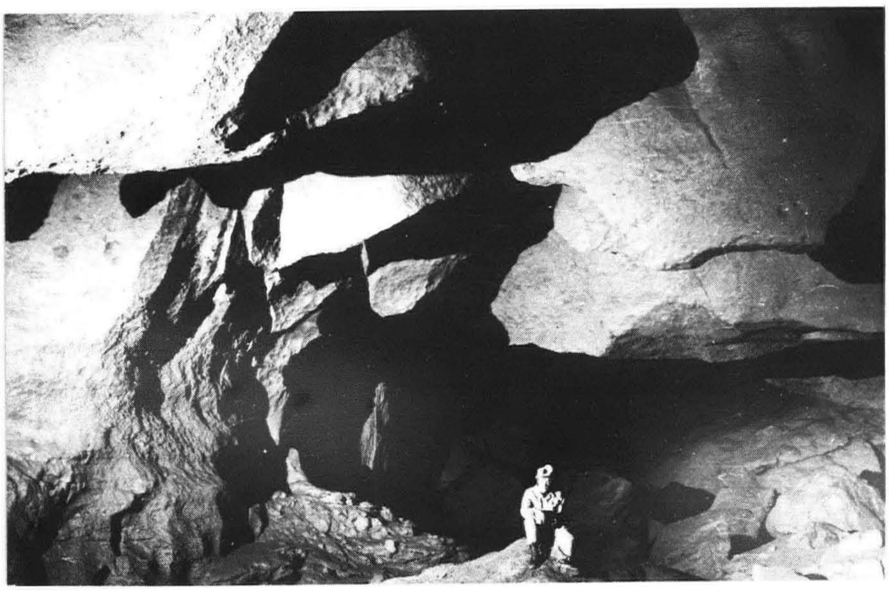

Fig. 14.

**CUEVA EL COY COY DE URIA**

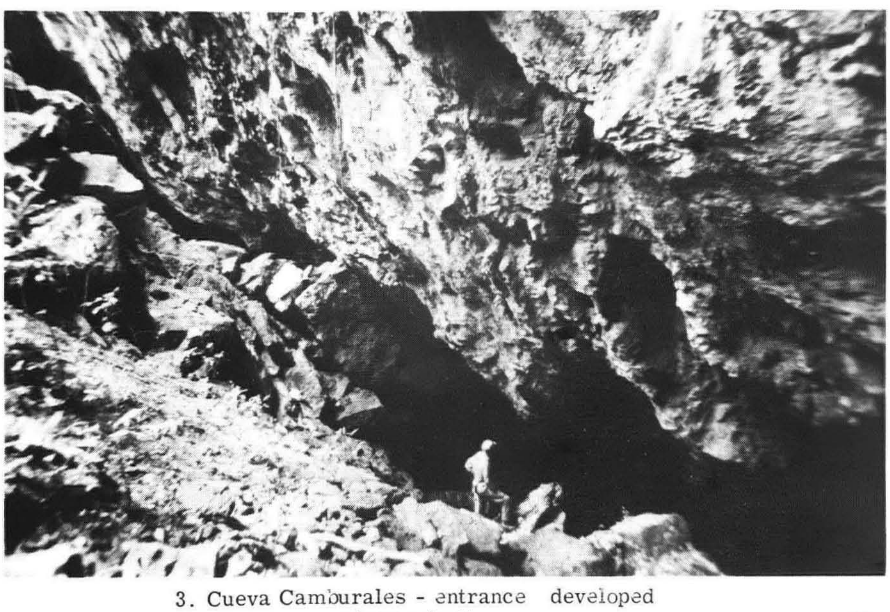
**CRG Gr 5b URIA**



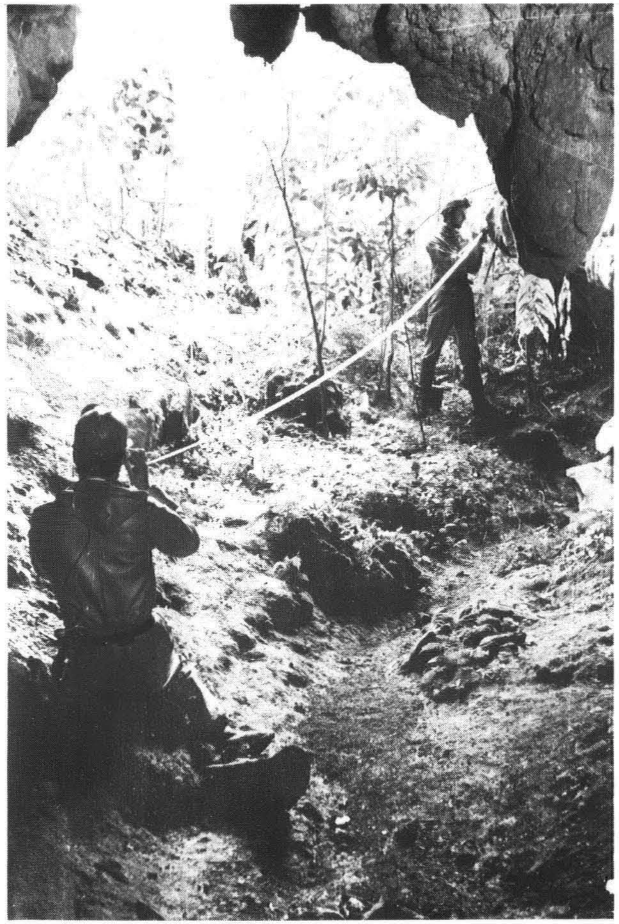
1. Cueva Camburales



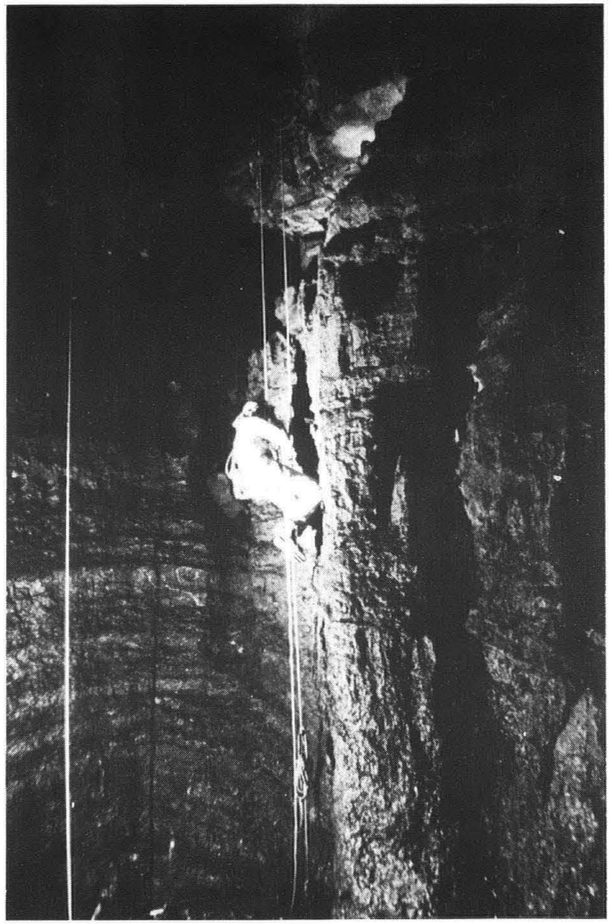
2. Cueva Zarraga - roof pendants



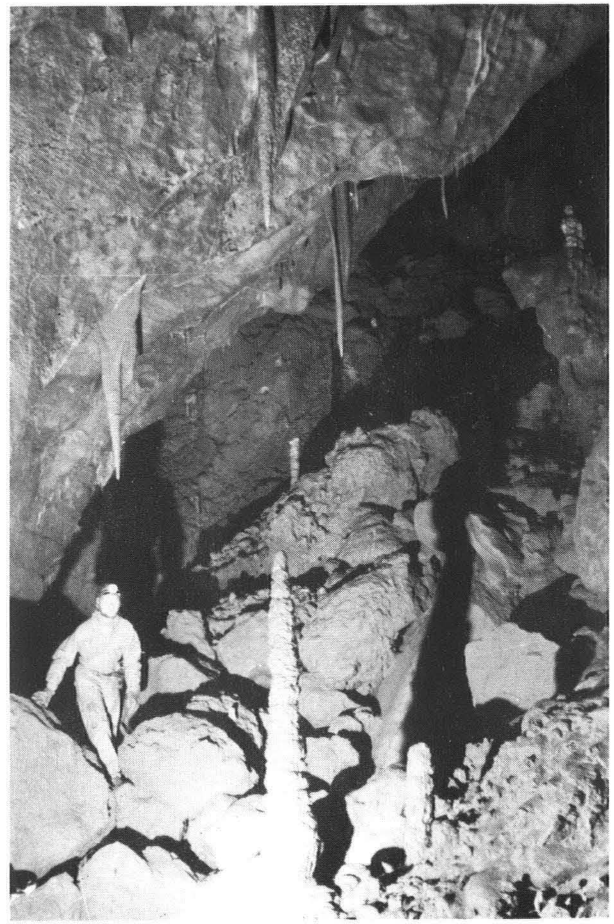
3. Cueva Camburales - entrance developed along a fault



1. Surveying in Cueva Zarraga



2. Prussiking in El Guarataro entrance shaft



3. Boulder choke in Cueva Zarraga

Description

An impressive entrance slope leads via an awkward climb to the first guacharo inhabited chamber. This large chamber is typical of what is a huge tunnel cave. After passing innumerable stalactite formations, a short climb is reached which leads to the second guacharo roost chamber. This is the largest chamber in the cave. The continuation of the guano-floored chamber is a passage full of boulders which goes on to a series of awkward climbs down through boulders. Eventually a vertical wall of calcite is reached but a bedding to the left and tight tube allows for an easy ascent. The latter sections of passage are unstable and very collapsed. At two points in the terminal choke area are to be seen human footprints in the mud. There is an archeological site in the entrance doline, of this large collapsed phreatic tunnel.

Cueva de Trinidad No. 4 (Hueque Cave) (Fig. 15).

Location:- Lat. 11° 11' 00"
Long. 69° 33' 58"
Plan length 450 m.

Walk up the Rio Hueque above the tourist waterfalls until a dry stream bed joins it on the left. Continue up this bed for about one kilometre to the base of a large cliff, where the entrance is obvious.

Description

From the entrance chamber two parallel vadose stream passages lead to the sump chamber. Just before this chamber a phreatic maze leads off to the right.

Also from the entrance chamber a passage leads off left until a well decorated chamber is reached. The cave is described in more detail in the geological study. There are four other caves to the west at the base of the same cliff.

Cueva de Chasea

Location:- Lat. 11° 10' 18"
Long. 69° 38' 55"
Plan length 24 m.

Entrance is situated at the top of the cliff above Cueva de la Rata

Description

A four metre crawl leads into a small chamber, which contains bat guano. No passages continue from there.

Practice Pot

Location:- Lat. 11° 09' 15"
Long. 69° 35' 20"

Situated in a cliff on the south side of the doline below the village of Trapichito, beneath La Bandera.

Description

It is approximately 16 metres long and 6 metres deep. It ends in a boulder and mud choke.

Cueva del Guarataro (Fig. 18).

Location:- Lat. 11° 09' 09"
Long. 69° 41' 17"
Plan length 640 m.
Depth 305 m.

The entrance shaft is situated to the east of the San Luis-Curimagua road. At the summit of the pass, descend into the first field to the east of the road, and the entrance is on the eastern side of the clearing, surrounded by trees.

Description

The entrance is very impressive. The first pitch of 52 metres lands on a small bridge spanning the shaft. The second drops from there 112 metres to a large floor. At the eastern end of this floor, and after a short climb up, the top of the 55 metre third pitch is reached. A further 19 metre pitch follows immediately from the bottom.

At this point is met a vadose passage containing a small stream and it continues downwards until a 6 metre pitch drops into a larger streamway. This can be followed upstream to a large aven, or downstream via two more pitches and many short climbs to a terminal choke.

Cueva de Camburales (Fig. 16).

Location:- Lat. 11° 10' 00"
Long. 69° 37' 17"
Plan length 780 metres

Take the track into Camburales valley, and keep the western fork, so contouring around the dolines. When a large clearing is reached, head off right, to cross the fence at the far end of the clearing. Large cliffs, and an obvious entrance are soon seen to the south.

Description

At the bottom of the steep entrance slope a climb down through the calcited boulders leads to a large entrance passage. Left down a steep mud slope, leads to a stream and a climb up in the roof to a collapsed rift and massive rubble pile. Right leads down to a stream passage, an easily by-passed duck and a series of large guano filled chambers. The cave ends with a low passage and impenetrable choke.

Cuevas Casas de Piedras (Fig. 17).

Location:- Lat. 11° 12' 25"
Long. 69° 36' 17"
Plan length 350 metres

Take the track out of San Joaquin towards the Hondo de Uria. The Uria stream is reached by taking a left fork downhill. Follow the stream through a sugar plantation to the obvious entrance.

This cave system is well known to the local people.

Casa de Piedra No. 1. F. 53

Once past the low entrance the passage is large and comes into daylight in an enclosed area, which was once a chamber.

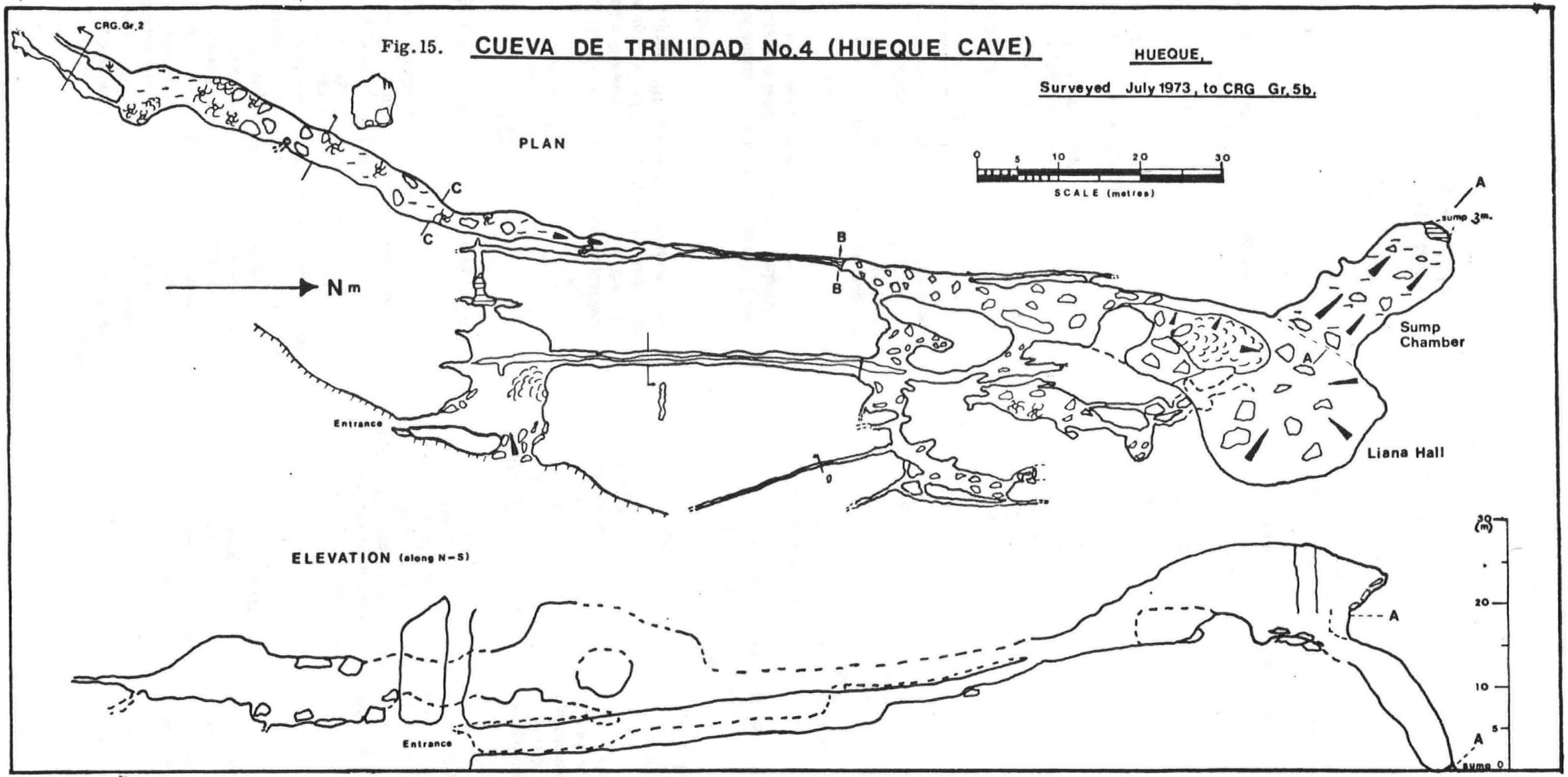



Fig. 15. CUEVA DE TRINIDAD No.4 (HUEQUE CAVE)

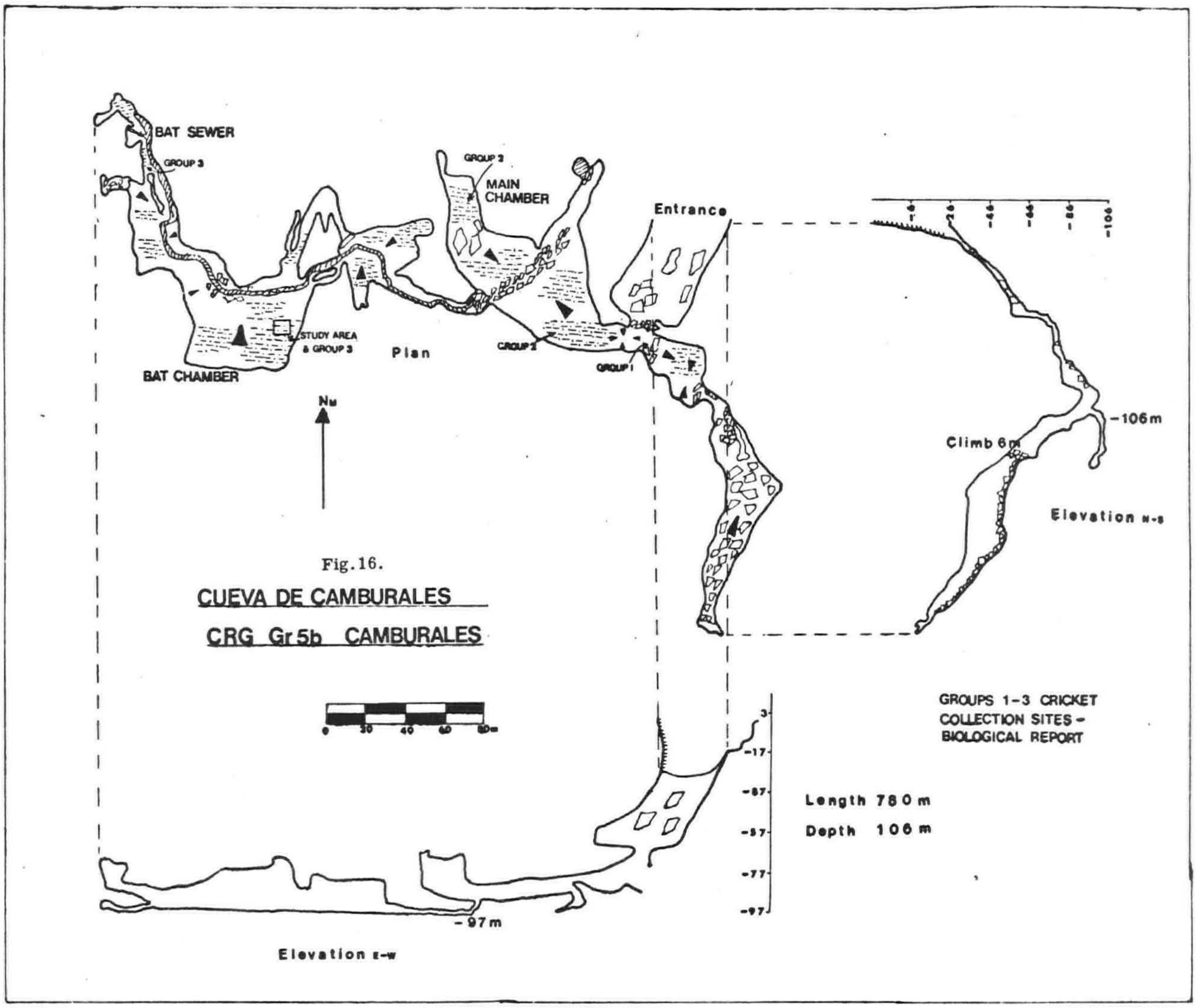



Fig.16.

CUEVA DE CAMBURALES

CRG Gr5b CAMBURALES

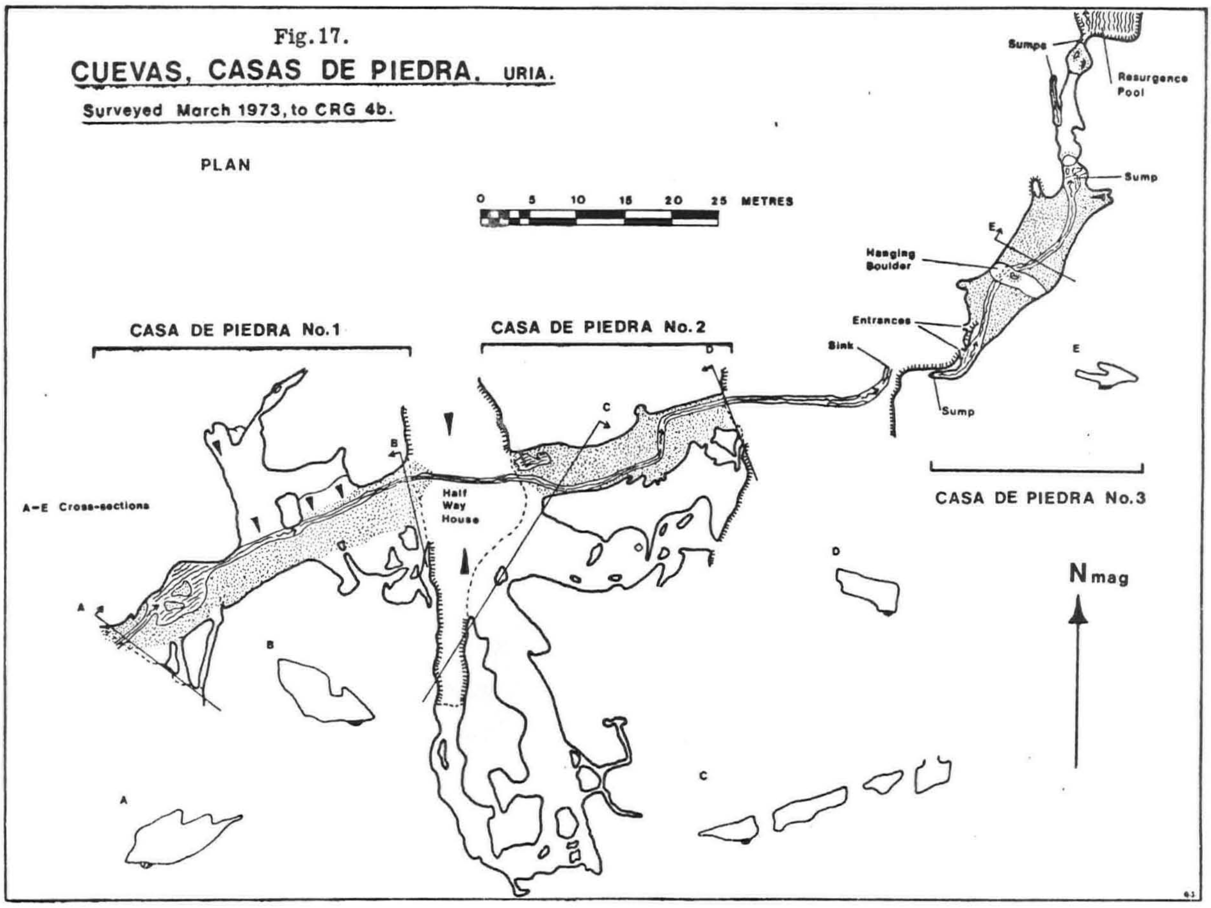



Fig.17.

CUEVAS, CASAS DE PIEDRA. URIA.

Surveyed March 1973, to CRG 4b.

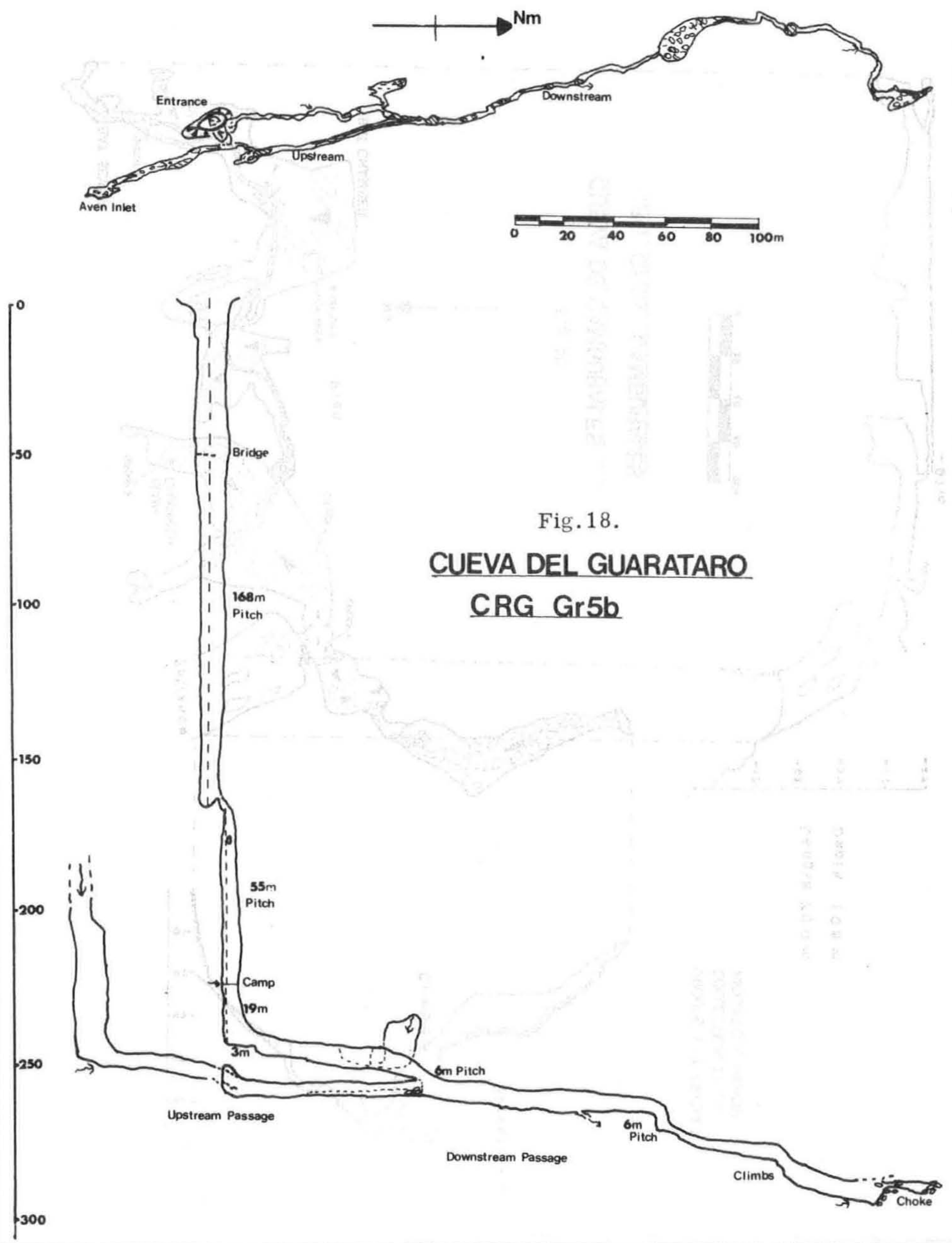



Fig. 18.

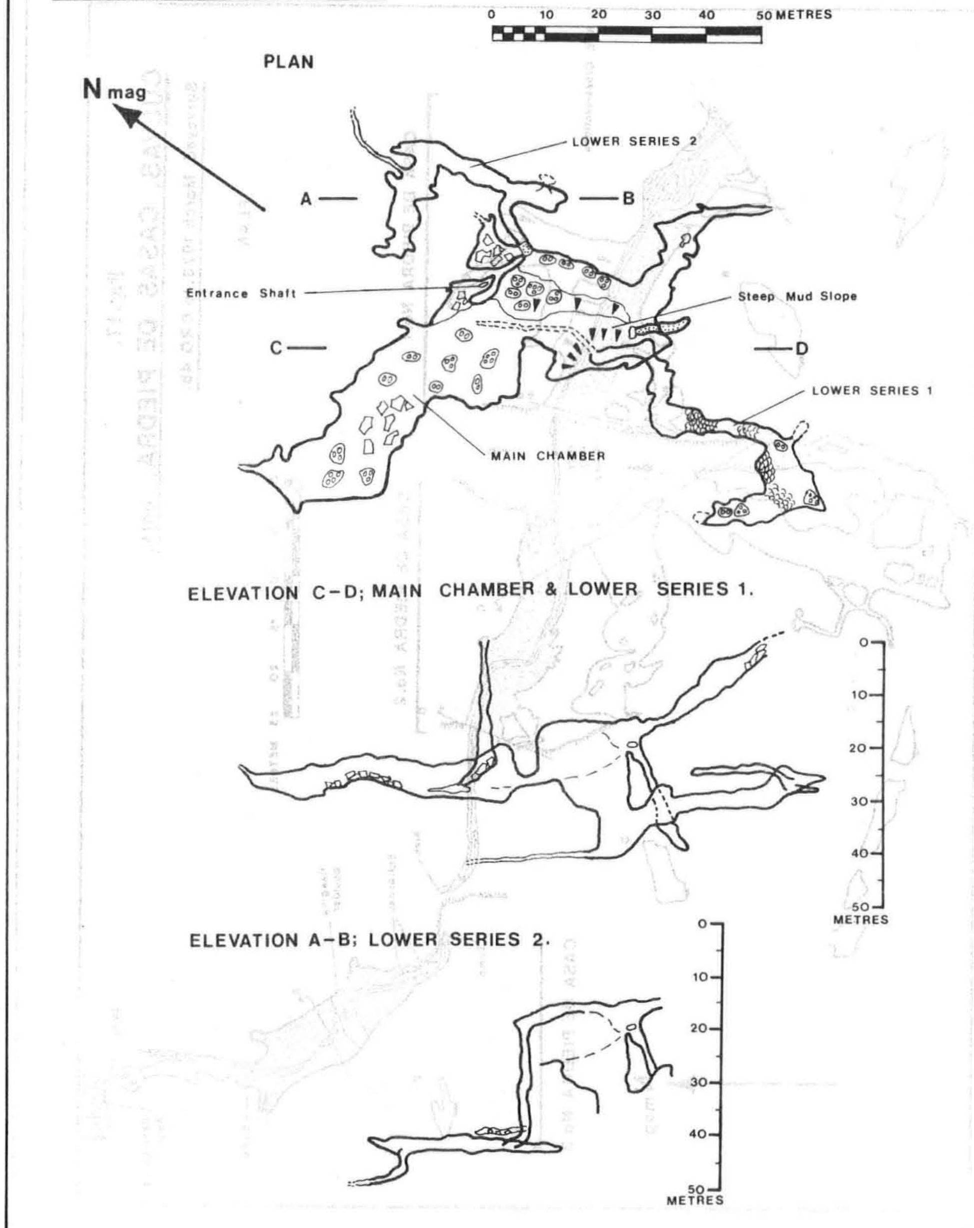
CUEVA DEL GUARATARO

CRG Gr5b

CUEVA DE LA MADAMA

Surveyed June 1973, to CRG 5b.

Fig. 19.



Casa de Piedra No. 2. F. 54

The stream continues through the second casa for 60 metres, then comes out into daylight again before sinking beneath a cliff and entering the third casa. In the collapse area between the first and second casas three passages lead off to the right.

Casa de Piedra No. 3. F. 87

There are several entrances in the cliff face into this smaller cave passage. The stream continues through it until it sumps at the far end. Just above the sump the exit leads out to a small resurgence pool.

This system follows the strike of the beds through a small ridge for the first and second Casas while the third runs up-dip.

Cueva de la Madama. F. 138 (Fig. 19).

Location:- Lat. 11° 12' 13"
Long. 69° 36' 06"
Plan length 320 metres
Depth 50 metres

The cave is situated beyond the termination of the Uria track at the sugar-cane factory. The continuing path is followed for 400 metres up the hill and the narrow entrance is situated in a small doline on the right.

Description

The entrance pitch of 24 metres leads into a large chamber 85 metres long and 20 metres wide. This chamber has many stalactite formations, as has most of the cave. At the southern end of the chamber a 55° mud slope leads to a vertical drop of 11 metres into a lower passage. This lower section is well decorated and picturesque upstream. Downstream a narrow muddy trench leads to a mud choke. At the eastern end of the large chamber another pitch of 20 metres can be descended into a further series of passages. It is an old system, being in part of phreatic origin. After numerous collapses, the cave has now become well calcited and stabalized. The narrow stream passage in the first lower series almost certainly represents a recent re-invasion of the system.

Cueva del Trueno. F. 141 (Fig. 20).

Location:- Lat. 11° 14' 47"
Long. 69° 34' 04"
Surveyed length 347 metres
Depth 42 metres

This cave is situated along the main path south from Macuquita. After almost two hours walk the path trends west and the cave is in the large doline to the left. The cave entrance is in the north side of the doline, at the end of a dry stream bed and above some boulders.

Description

The cave is an active sink. As the system strikes different beds different passage forms are seen. The initial stream passage opens out after 80 metres when it strikes a shale bed and a collapse chamber is developed. Once this boulder choke has been negotiated the passage continues low and wet at first, but soon develops into a rift. Then follows a series of pools, which are in sandstone beds, until again the cave opens out into a large passage 8 metres high. After only another 40 metres the way on is blocked by a collapse, where the passage hits the shales.

Cueva del Pajaro (Fig. 21).

Location:- Lat. 11° 09' 10"
Long. 69° 39' 55"
Surveyed length 541 metres
Depth 63 metres

Travelling east from San Luis to Cabure, follow the track up the second valley after the water pumping station. The lower entrance is near to the sugar cane factory, at the head of the valley, in a small doline. The cave entrance is well known to the local people and has been partially explored before.

Description

The cave is a straight forward active vadose canyon passage but both upper and lower entrances are collapses into the system. The breakdown area of the upper entrance is clean fluted limestone but the collapses in the interior of the cave are caused by the system hitting beds of sandstone and shale. The system of small passages near the lower entrance are in clean limestone and are very markedly joint controlled.

Cueva la Dolorita (Uruguay)

The left fork out of San Joaquin and the turning off for Coy Coy are taken. Along this path the right fork is followed until the large doline is reached.

Description

La Dolorita is the western entrance whilst Uruguay is to the east. The connecting passage is a large tunnel full of rotting calcite formations. After 60 m. a roof collapse is reached and the continuation is to the left for a further 120 m. to the Uruguay doline.

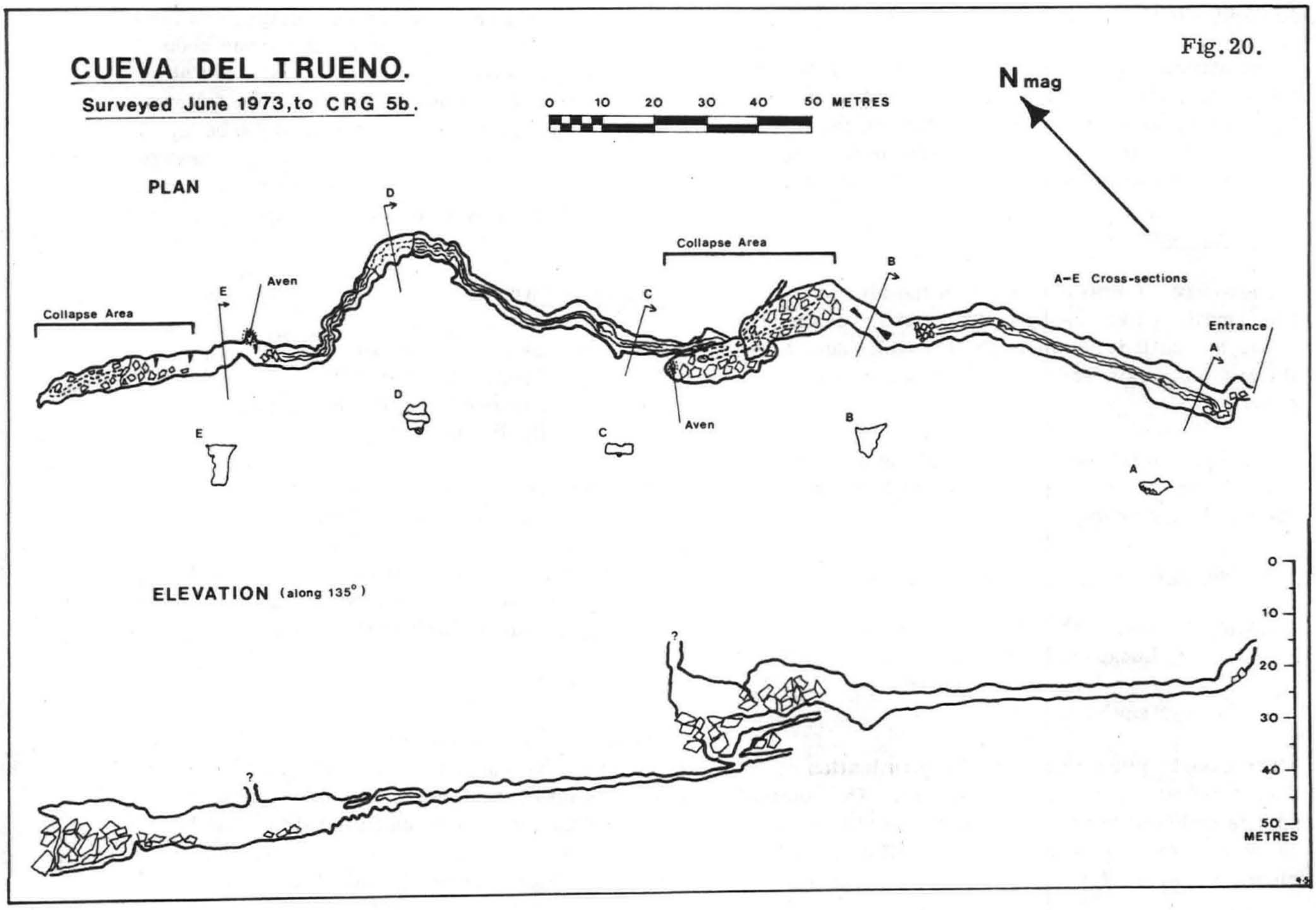
Cueva de la Abeja (Fig. 22).

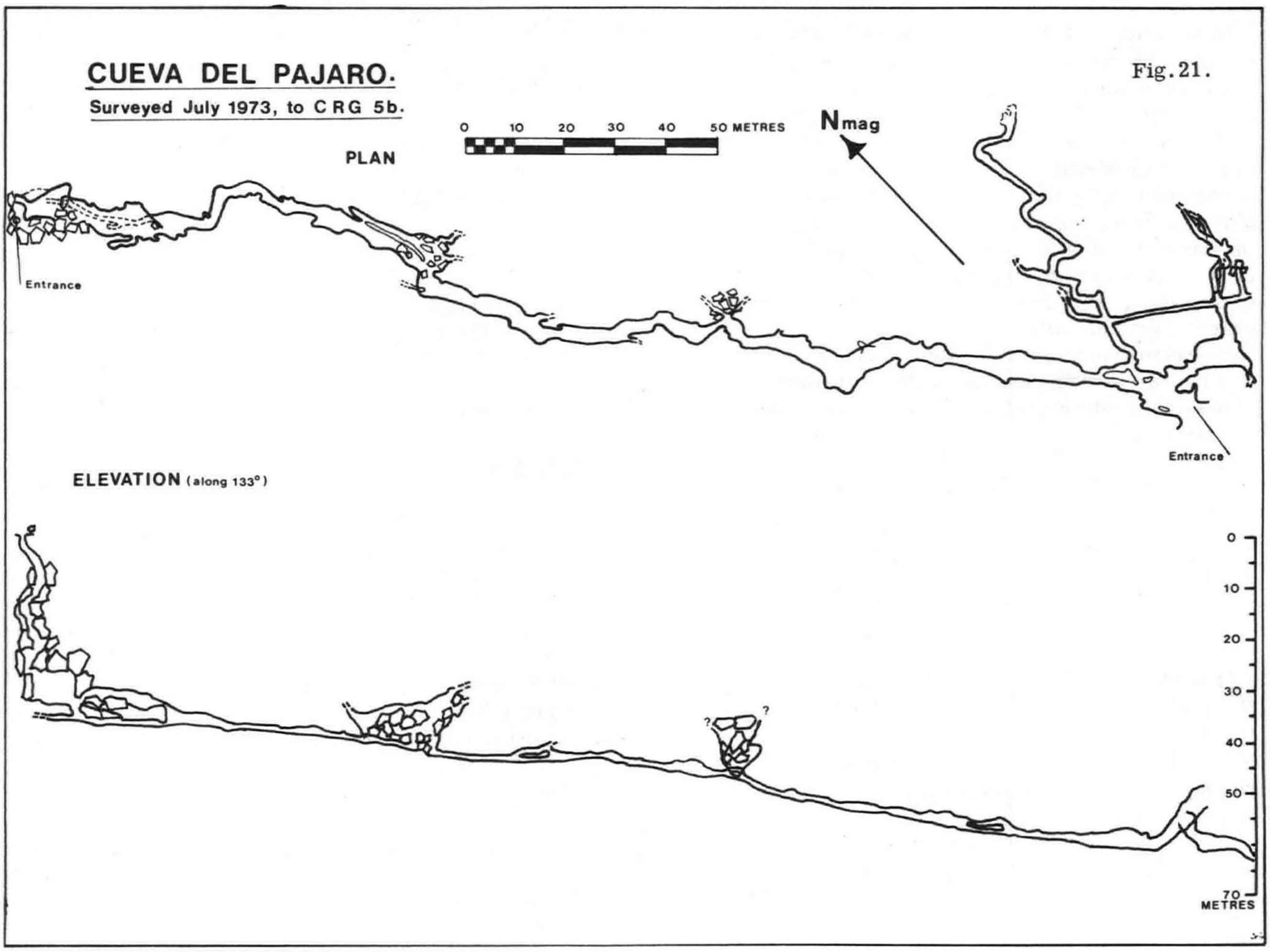
Location:- Lat. 11° 10' 20"
Long. 69° 37' 59"
Plan length 270 m.

The cave is situated beneath the rock face on the eastern side and at the northern end of Acarite valley. The entrance is above the sink of the small stream running down the valley and under a large square-cut overhang.

Description

The cave contains a small stream, and has a variety of passage types including some restricted water-filled passage. The entrance is a short pitch down through a series of huge boulders. After passing through reasonably dry passage a narrow water


CUEVA DEL TRUENO.
Surveyed June 1973, to CRG 5b.
0 10 20 30 40 50 METRES
N mag
PLAN
Collapse Area
Aven
Collapse Area
A–E Cross-sections
Entrance
Aven
ELEVATION (along 135°)
0
10
20
30
40
50
METRES
Fig. 20.


CUEVA DEL PAJARO.
Surveyed July 1973, to CRG 5b.
0 10 20 30 40 50 METRES
N mag
PLAN
Entrance
Entrance
ELEVATION (along 133°)
0
10
20
30
40
50
70
METRES
Fig. 21.

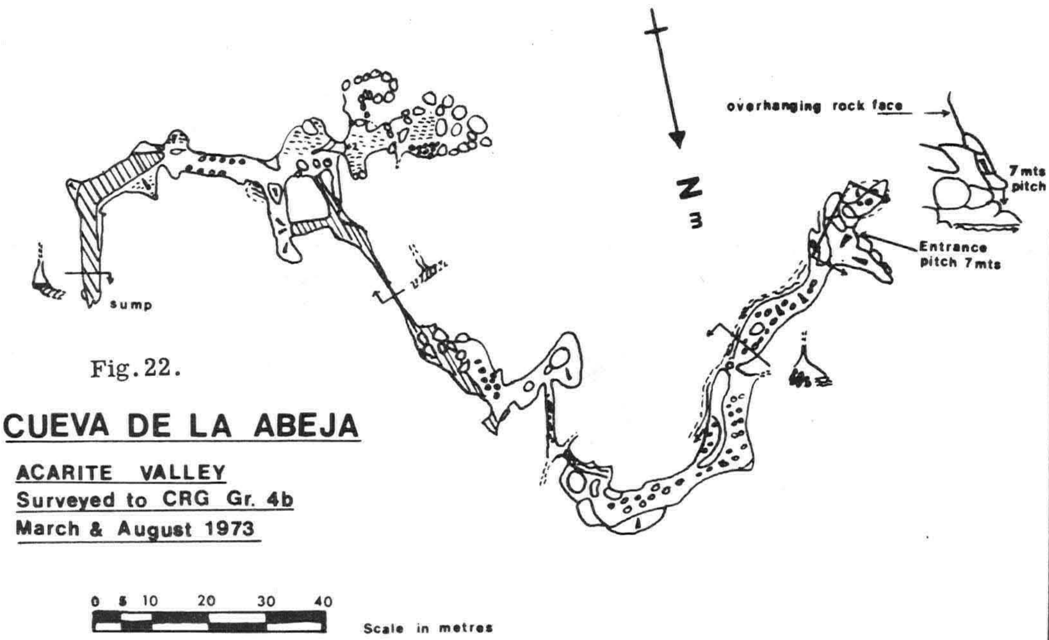



Fig. 22.

**CUEVA DE LA ABEJA**

**ACARITE VALLEY**
**Surveyed to CRG Gr. 4b**
**March & August 1973**

filled passage is encountered. In very dry weather it is possible to pass through the restriction into a large passage beyond. To the right a dry high level system can be entered which ends in a boulder choke. To the left a wide passage can be followed to the long terminal pool.

Cueva de Churuguara (Fig. 23).

Location: Lat. $11^{\circ}$ 12' 08''
Long. $69^{\circ}$ 35' 50''
Plan length 425m.
Depth 95m.

At the end of the left fork of the track out of San Joaquin is a sugar cane factory. A path leads on from there and the first right hand fork is taken. Bear left immediately after this point and contour round a large doline. From then onwards is ill-defined and skirts round some rock pinnacles from whence it is a five minute walk to the entrance shaft.

Description

A 16m. pitch leads to a sloping ledge and from there it is a further 40m to the cave level. The main way on from there is obvious, but a short climb up a mud slope to the left of a hole in the floor leads via a low passage to the rest of the cave. The whole of this part of the cave is well decorated. It is part of an old phreatic system.

Cueva de San Lorenzo (Fig. 24).

Location: Lat. $11^{\circ}$ 15' 39''
Long. $69^{\circ}$ 33' 55''
Plan length 440m.
Depth 237m.

From the village of Macuquita take the main southward bound track up the hill. After an hour's walk a large cleared doline is reached. The path skirts this to the left and continues south until an even larger cleared doline is seen. Avoid paths entering on the left hand side and follow the track to the southern end of the doline. A path takes off down into the doline and the entrance is five minutes walk from it down a stream bed.

Description

An 11m pitch leads to a steeply descending passage. The cave continues in similar fashion to a terminal choke. Two 10m. ladders are required and ropes make the ascent easier. Most of the cave is formed in sandstone or shale beds, and follows them down dip.

Cueva de San Pablo

Location: Lat. $11^{\circ}$ 12' 56''
Long. $69^{\circ}$ 35' 54''
Plan length 144m.
Depth 72m.

Take the path up the hill from behind the church in La Soledad de Uria. Take the right hand fork to where the ground levels out. 100m. before a house on the left hand side of the path in a shallow depression, is the entrance shaft.

Description

An impressive abseil to a boulder floor is followed by a low down dip passage. A large chamber is entered at roof height and an 11m. pitch lands on a boulder floor. The passage continues down to a boulder choke. The cave takes a small stream.

## HAITONES

Haiton One. F133

Location:- Lat. $11^{\circ}$ 09' 08''
Long. $69^{\circ}$ 41' 20''

Situated on the north east of the Curimagua to San Luis road, on the summit of the pass over Maletta.

Depth. 9 metres

Comments.

The entrance is a large, collapsed shaft. It leads to a loose and dangerous rift continuation.

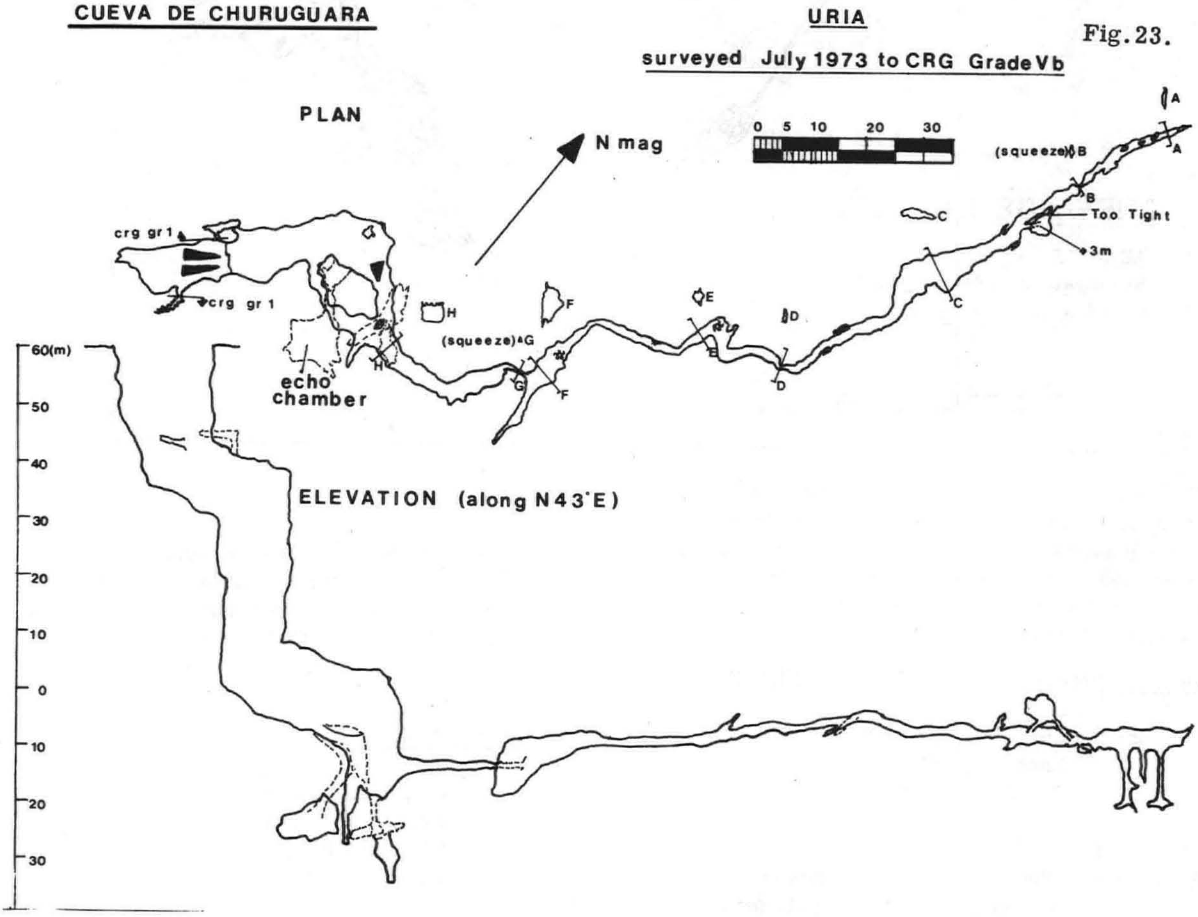

CUEVA DE CHURUGUARA
URIA
surveyed July 1973 to CRG Grade Vb
PLAN
N mag
0 5 10 20 30
(squeeze) B
Too Tight
3m
crg gr 1
crg gr 1
(squeeze) G
echo chamber
60(m)
50
40
30
20
10
0
10
20
30
ELEVATION (along N43°E)

Fig. 23.

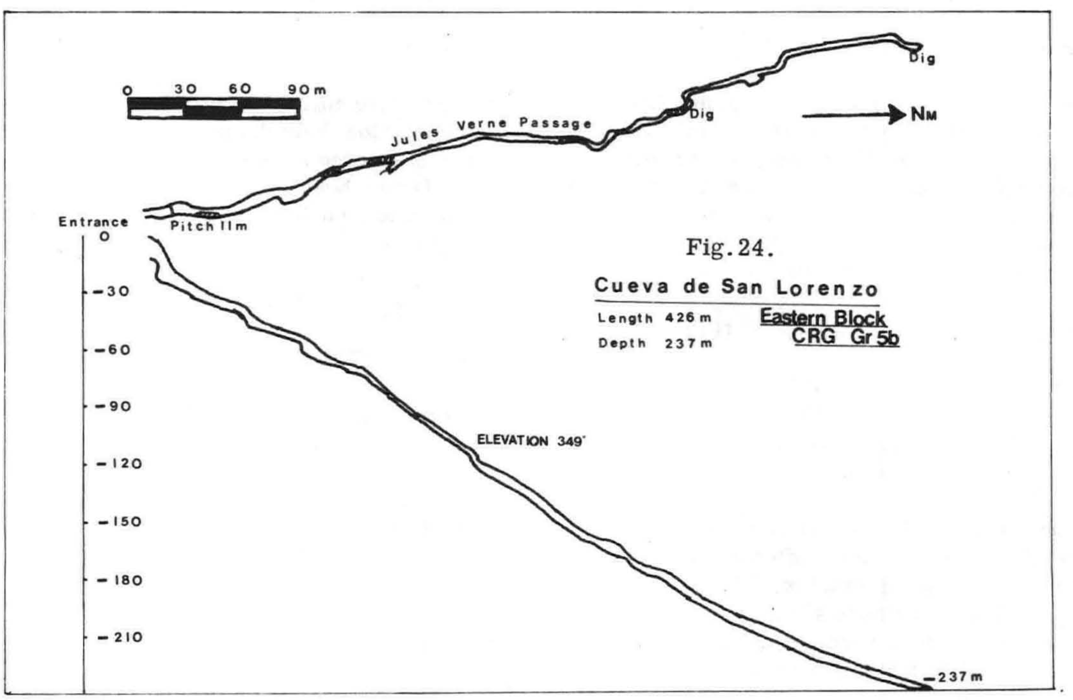

0 30 60 90 m
Jules Verne Passage
Dig
Dig
NM
Entrance
Pitch 11m
0
-30
-60
-90
-120
-150
-180
-210
ELEVATION 349°
-237 m
Cueva de San Lorenzo
Length 426 m
Depth 237 m
Eastern Block
CRG Gr 5b

Fig. 24.

Haiton Two. F 62

Location:- Lat. 11° 08' 50"
Long. 69° 41' 10"

It is in a large doline on the north east side of the Curimagua to San Luis road. Sitting on the south side of the Maletta ridge, it lies at the lowest point of a cutting containing an electric power line.

Depth. 34 metres.

Comments.

The haiton is situated in the midst of a cultivated doline. It is formed along a joint which closes and becomes impassable at the bottom.

Haiton Three. F 63

Location:- Lat. 11° 08' 50"
Long. 69° 41' 10"

In the same doline as haiton two, but slightly further south.

Depth. 30 metres. Length. 10 metres.

Comments.

The entrance is a large open rift with the north side sloping steeply into the haiton. After 30 metres the shaft finishes with a boulder floor.

Haiton Four. F 64

Location:- Lat. 11° 09' 08"
Long. 69° 41' 20"

On the north east side of the Curimagua to San Luis Road, at the summit of the pass over Maletta ridge.

Depth. 26 metres. Length 20 metres.

Comments.

The entrance is a large open rift running at approximately 70 degrees magnetic, bearing along a joint. The rift leads to a second daylight shaft, which ends in a boulder choke.

Haiton Five. El Guarataro

See - Cave Descriptions list.

Haiton Six. F 83.

Location:- Lat. 11° 09' 13"
Long. 69° 41' 17"

On the north east side of the Curimagua to San Luis road, on the summit of the pass over Maletta. Pass through a group of large boulders at the northern end of the No. 5 clearing, to the top of the Haiton.

Depth. 110 metres

Comments.

A large entrance shaft leads to an obvious ledge at minus 28 metres. It then continues down as a narrow tube until becoming impassable. The lower section necessitates the use of ladders.

Haiton Seven

Location:- Lat. 11° 09' 19"
Long. 69° 41' 36"

On the west side of the Curimagua to San Luis road half a kilometre before the summit of the pass over the Maletta ridge. Take the track beneath telegraph poles until a water pipe line is reached. Follow the pipe for a short distance south. Turn west along an obvious track leading to a long cultivated area, about one kilometre from the road.

Depth 161 metres.

Comments.

The entrance is at the western end and on the northern side of the cultivated area. The shaft has a visible ledge at minus 17 metres and ends in an impassable tight rift bearing 280 degrees.

Haiton Eight

Location:- Lat. 11° 12' 02"
Long. 69° 36' 33"

Situated on the south side of the Uria basin, just off the Coy Coy track, next to a large cleared doline.

Depth 15 metres

Comments.

A wide entrance bridged by boulders.

Haiton Nine Cueva de la Madama

See - Cave Descriptions list.

Haiton Ten El Charro

Location:- Lat. 11° 13' 54"
Long. 69° 37' 02"

On the western side of the Coro to Curimagua road, to the north of the pass over Penasco. Five hundred metres down the hill from the summit, a track leads from the road to a stream which runs into the haiton.

Depth 10 metres Length 12 metres

Comments

The stream running into the haiton is used by the local people for domestic purposes.

Haiton Eleven Liron

Location:- Lat. 11° 10' 36"
Long. 69° 30' 40"

To the south east and above the village of Trapichito is a sugar cane plantation. Somewhere amidst the cane is the small rift like entrance beneath the sandstone capping.

Depth 90 metres Length 20 metres

Comments

The haiton consists of two shafts joined by an eye-hole and ends in a rift bearing 85 degrees magnetic.

Haitones Twelve and Thirteen

Location:- Lat. 11° 09' 28"
Long. 69° 41' 32"

Comments

Two small Haitones 6 metres deep bearing 0 degrees magnetic.

Haitones Fourteen, Fifteen, Sixteen and Seventeen

Location:- Lat. 11° 09' 22"
Long. 69° 41' 40"

These haitones are situated on a rise above and to the west of haiton number seven.

Haitones Fourteen, Fifteen, Sixteen and Seventeen

| Number | Depth | Entrance size |
|---|---|---|
| 14 | 90 metres | 3 x 9 metres |
| 15 | 70 metres | 7 x 5 metres |
| 16 | 27 metres | 5 x 3 metres |
| 17 | 42 metres | 4 x 1½ metres |

Comments

A group of haitones all very similarly placed on Maletta, normally ending with boulder floors.

Haiton Eighteen

Location:- Lat. 11° 15' 31"
Long. 69° 33' 57"

Situated approximately half a kilometre before Agua Colorado, on the eastern side of the track running south from the village of Macuquita. The entrance is a 6 metres long 2 metres wide shaft behind a campesino shelter in a large doline.

Depth 20 metres.

Haitones, Nineteen, Twenty, Twenty-two, twenty-three, Twenty-four, Twenty-five and Twenty-seven.

Location

| Number | Lat. | Long. | Depth | Entrance |
|---|---|---|---|---|
| 19 | 11° 15' 18" | 69° 33' 45" | 12 metres | 5 x 5 m |
| 20 | 11° 15' 16" | 69° 33' 43" | 12 metres | 5 x 5 m |
| 22 | 11° 15' 16" | 69° 33' 50" | 40 metres | 1 x 1 m |
| 23 | 11° 15' 16" | 69° 33' 48" | 15 metres | 2 x 1 m |
| 24 | 11° 15' 13" | 69° 33' 40" | 7 metres | 2 x 1 m |
| 25 | 11° 15' 10" | 69° 33' 40" | 8 metres | 5 x 1 m |
| 27 | 11° 15' 08" | 69° 33' 36" | 40 metres | 4 x 5 m |

These haitones are situated east south east of Agua Colorado up to a kilometre from it. Branch eastwards half a kilometre before Agua Colorado, leaving the main south bound track from Macuquita. They are all close to this minor track.

Comments.

A series of haitones in a large doline area, some obvious and others quite obscure.

Haiton Twenty-one.

Location:- Lat. 11° 15' 44"
Long. 69° 33' 48"

Situated on the eastern side of the track running southwards from the village of Macuquita. Approximately one kilometre before reaching Agua Colorado, a few metres from this main track.

Depth. 36 metres.

Comments.

The entrance is a series of three holes, beneath a small rock face just visible from the track. Two of the shafts connect, and all are formed along a rift bearing 185 degrees magnetic.

Haiton Twenty-six

Location:- Lat. 11° 15' 04"
Long. 69° 33' 40"

A large entrance amongst rock pinnacles south east of Agua Colorado, and slightly south of No. 24.

Depth 51 metres.

Comments.

The most impressive entrance in the area 10 metres wide and 30 metres long. The shaft ends in a chamber with a boulder floor.

Haiton Twenty-eight

Location:- Lat. 11° 07' 55"
Long. 69° 36' 38"

On the south side of the Uria basin in the region of Coy Coy. The entrance is a slit amongst boulders high on the side of a cultivated doline - very obscure and overgrown.

Depth 52 metres

Comments.

The shaft ends with a boulder floor.

Haiton Twenty-nine

Location:- Lat. 11° 11' 56"
Long. 69° 36' 37"

On the south side of the Uria basin turning off the Coy Coy track. In the south west corner of a large doline, beneath a large boulder.

Depth 14 metres

Comments.

A rift ending with a boulder floor.

Haiton Thirty Rusia

Location:- Lat. 11° 11' 58"
Long. 69° 36' 42"

Situated on the south side of the Uria basin to the west of a large cleared doline, encountered on the path up to Coy Coy.

Depth 40 metres Length 14 metres

Comments.

The entrance is situated amongst boulders in dense undergrowth. A narrow sloping shaft leads to a chamber with many formations.

Haiton Thirty-one Churuguara

See - Cave Descriptions list.

Haiton Thirty-Two Chomo de Diablo

Location:- Lat. $11^{o}$ 09' 20"
Long. $69^{o}$ 39' 55"

Travelling east from San Luis to Cabure follow the track up the second valley after the water pumping station. Pass a sugar cane factory and haiton thirty-three, to where the path levels out in a field - a group of trees conceals the entrance.

Depth 26 metres

Comments.

A large shaft with a ledge halfway down, and boulder floor.

Haiton Thirty-Three Pajaros

Location:- Lat. $11^{o}$ 09' 10"
Long. $69^{o}$ 39' 50"

Just before haiton thirty-two in a very large doline.

Depth 50 metres

Comments.

The haiton has one vertical side and one sloping steeply.

Haiton Thirty-Four

Location:- Lat. $11^{o}$ 12' 55"
Long. $69^{o}$ 36' 02"

Situated above the village La Soledad de Uria to the north, on the hill above the church. Follow the track by the church to a house, behind which is the haiton. An obscure, overgrown entrance in a clearing.

Depth 20 metres

Comments.

The shaft ends in a rift blocked with boulders.

Haiton Thirty-Five

Location:- Lat. $11^{o}$ 13' 00"
Long. $69^{o}$ 35' 55"

A few hundred metres North and above Haiton thirty-four. A small obscure entrance at the site of a cleared doline.

Depth 34 metres

Comments.

The shaft leads into a rift which narrows and becomes impassable.

Haiton Thirty-Six Cueva de San Pablo

See - Cave Descriptions list.

Haiton Thirty-Seven

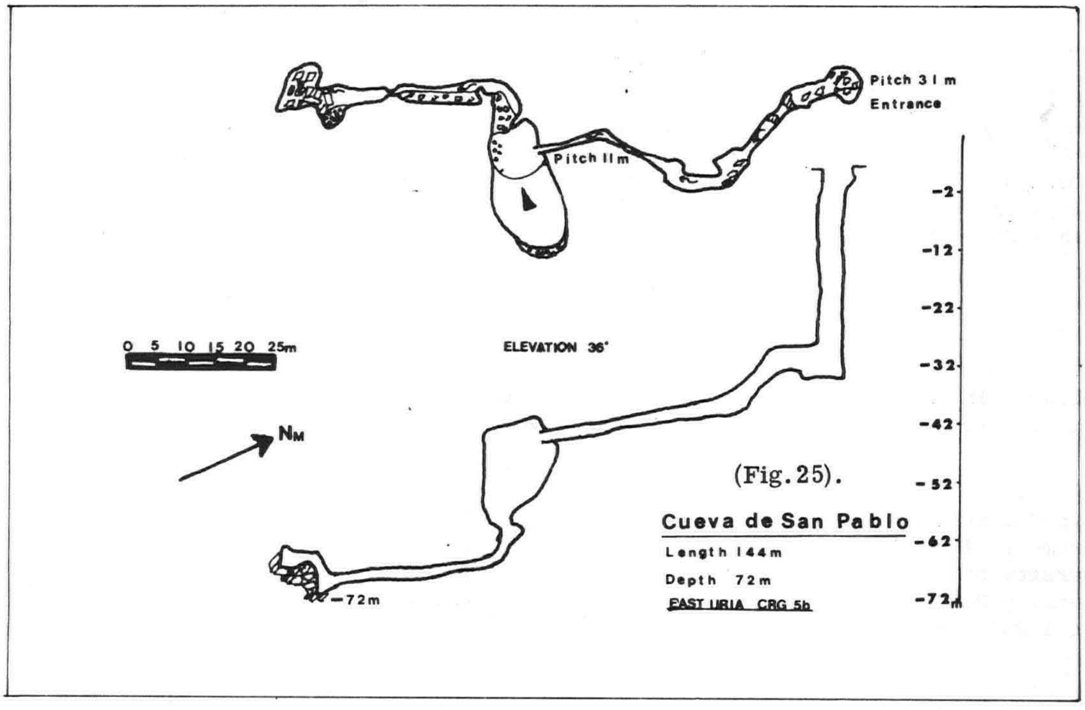
Location:- Lat. $11^{o}$ 9' 50"
Long. $69^{o}$ 39' 00"

A good track going south from Trapichito climbs La Bandera west of the sink area and cliffs. A fork east on the top leads in a roughly easterly direction for one kilometre to the entrance. The path is here intermittent and difficult to follow.

Depth 198 metres

Comments.

A large rift entrance, spanned by a rock bridge leads into a large chamber and descending passage with ledges. The bottom horizontal rift continuation was a little too tight to pass along and time was short.




(Fig. 25).

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Carlos J. Naranjo
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Gascoyne, M.

Philip Chapman,
Department of Geography
University of Bristol,
University Road,
Bristol BS8 1SS

David Checkley,
Department of Diagnostic Radiology,
The Medical School,
University of Manchester,
Oxford Road,
Manchester 13

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# IN SITU CHEMICAL ANALYSES OF CARBONATE WATERS

R. W. Crabtree, S. T. Trudgill, A. M. Pickles and M. I. Cowton

ABSTRACT

Graduated plastic syringes were used for in situ titrations for alkalinity and calcium. The results were comparable to in situ measurements using conventional glassware but both differed from the results of sample analyses made within a few hours in the laboratory. The differences were largely interpretable in terms of degassing of $CO_2$ in the laboratory samples.

## INTRODUCTION

Chemical analysis of waters where carbonate equilibria dominate the solute system may be unreliable because degassing of carbon dioxide during transport and storage may substantially alter the carbonate equilibria. In situ analyses are preferable to analyses on transported samples but the use of conventional glassware in caves and other field sites is often not easy. We report comparative work on analyses of carbonate water samples from caves and other karst waters using in situ titrations and laboratory titrations for calcium and alkalinity. Syringes were used for the in situ titration work and were found (a) to be as reliable as conventional glassware for in situ titration, but easier to handle and (b) to yield results which differed from those obtained using stored and transported samples; the differences were largely interpretable in terms of degassing processes during storage procedures, as shown by calculations of saturation indices and $pCO_2$ values.

## EXPERIMENTAL

Conventional titration glassware was used alongside calibrated medical quality plastic syringes. The syringes used were Luer syringe units from Everett Medical Products Ltd., Mitcham, Surrey, England. Titre delivery was compared between syringes and burettes and replicate samples were analysed using both methods. 50 ml syringes (5 ml graduation) were used for sample collection and dispensing; 10 ml syringes (0.5 ml graduation) were used for the titre.

Alkalinity titrations were performed using 0.02 N hydrochloric acid, standardised with borax solution, and using a BDH 4.5 indicator (Stenner, 1969). Calcium was analysed using 0.025 M EDTA with potassium hydroxide buffer and ammonium purpurate indicator (Schwarzenbach & Flaschka, 1965). pH was measured using a portable Walden Precision Apparatus temperature-compensated pH meter, with combined electrode, powered by two pp9 9 v batteries. Temperature was measured by a glass mercury thermometer. The saturation index values with respect to calcite were calculated using the WATSPEC computer programme (Wigley, 1977).

In both the case of the syringe and the burette, titration was performed in a 100 ml conical glass flask with a white paper surface below for ease of colour change detection. Titrations performed in cave environments were carried out in the light of electric NIFE cells. The syringe titration apparatus fitted into a watertight ammunition box of 10 x 7 x 3½ inches (25.4 x 17.78 x 8.89 cm) dimensions, which was capable of being carried intact through rugged cave environments. A 25 ml sample was taken straight from the stream using a 50 ml syringe and then placed into the flask making sure that no air bubbles were present. The buffer and indicator were added using plastic dropping bottles. The titre was dispensed using the 10 ml syringe (again making sure that no air bubbles were present), adding it dropwise to the flask, shaking the flask with each drop; 1 drop was equivalent to 0.1 ml. The titrations were thus performed within about two minutes of sampling.

## SYRINGE ACCURACY

The amounts dispensed by the syringe were calibrated in the laboratory against an 'A' grade glass burette graduated to 0.1 ml. A tube was connected to the burette tip and the syringe tip and the syringe deliveries were checked against the rise in the burette levels. The results are shown in Table 1. The agreements are within 2.5% and the syringe is less accurate for small quantities. This is largely due to a slight stiffness in the plunger operation, and with practice this can be overcome without overshooting a graduation mark.

TABLE 1. COMPARISON OF SYRINGE AND BURETTE ACCURACY

RESULTS OF 10 COMPARISONS PER SYRINGE VOLUME

| TOTAL DELIVERED BY SYRINGE (ml) | MEAN AMOUNT RECORDED ON BURETTE (ml) | MEAN DIFFERENCE ml | % |
|---|---|---|---|
| 10 | 9.76 ± 0.04 | - 0.24 | - 2.4 |
| 25 | 24.8 ± 0.08 | - 0.2 | - 0.8 |
| 30 | 29.7 ± 0.0.03 | - 0.3 | - 1 |
| 50 | 49.9 ± 0.11 | - 0.1 | - 0.2 |

TABLE 2. LABORATORY REPLICATION WITH SYRINGE AND BURETTE, $HCO_3^-$ mg/1

| TEMPERATURE, °C | pH | SYRINGE | BURETTE |
|---|---|---|---|
| 19.0 | 7.4 | 380.6 | 385.4 |
| 19.0 | 7.4 | 380.6 | 399.7 |
| 20.0 | 7.5 | 380.6 | 399.7 |
| 20.5 | 7.5 | 380.6 | 385.4 |
| 20.0 | 7.5 | 380.6 | 383.0 |
| | MEAN | 380.6 | 390.6 |

DIFFERENCE OF MEANS 10.0 mg/1 = 2.56%

TABLE 3. FIELD REPLICATION WITH SYRINGE AND BURETTE, $HCO_3^-$ mg/1 MAGNESIAN LIMESTONE WELL, NR.SHEFFIELD

| | SYRINGE | BURETTE |
|---|---|---|
| | 440 | 432 |
| | 448 | 436 |
| | 432 | 422 |
| | 432 | 464 |
| | 432 | 428 |
| | 432 | 430 |
| | 440 | 436 |
| | 436 | 434 |
| | 436 | 424 |
| | 452 | 424 |
| MEAN | 438 | 433 |
| | $\sigma$ = 0.17795 | $\sigma$ = 0.30097 |
| | VAR. = 0.0285 | VAR = 0.0852 |

DIFFERENCE = 5 mg/1 = 1.14%

$$\text{VAR.} = \frac{\sum yi^2}{N} - \frac{(\sum yi)^2}{N}$$

where yi = $i^{th}$ observation

## SYRINGE AND BURETTE REPLICATION

Table 2 shows the results for laboratory alkalinity titrations on five replicates of well water, sampled on 19.9.78 from the Magnesian Limestone east of Sheffield. The well surface was 7.1 m below the surface with free air circulation above and a metal cover at ground level. The results differ by 2.56%.

Table 3 shows results from replicate field analyses from one bulk sample at the same well on 4.11.78, well level, 1.2 m from the surface, temperature 10°C. Using a Mann Whitney 'U' test there are no significant differences between the sets of data for syringes and burettes at the 99.5% level. Syringe and burette analyses may thus differ slightly, but the differences are negligible and less than or equal to differences in results for replications using one method alone.

## FIELD ANALYSES AND LABORATORY ANALYSES

Polythene sample bottles of 1.5 mm wall thickness and 250 ml capacity, with air tight screw caps were used for sample collection. As polythene is permeable to carbon dioxide diffusion, glass bottles with ground glass stoppers were also used for sample collection. Samples were kept for varying lengths of time before analyses and in some cases kept in a refrigerator at 2°C before analyses.

Table 4 shows results for replicate analyses between syringes and burettes from samples in the Malham Tarn Field Centre area, North Yorkshire, U.K. on 18.4.79. The calcium replication is good but the alkalinity replication shows lower values for the syringes.

Table 4. REPLICATIONS OF SYRINGE AND BURETTE, $HCO_3^-$ mg/l, $Ca^{2+}$ mg/l, MALHAM TARN FIELD CENTRE, N. YORKSHIRE; LABORATORY ANALYSES WITHIN 8 HOURS USING POLYTHENE BOTTLES

| | n | MEAN $HCO_3^-$ | σ | VAR. | MEAN $Ca^{2+}$ | σ | VAR. |
|---|---|---|---|---|---|---|---|
| **FIELD** | | | | | | | |
| SYRINGE | 10 | 147.29 | 21.46 | 414.3 | 69.78 | 12.61 | 143.04 |
| BURETTE | 20 | 183.89 | 42.11 | 1685.36 | 65.54 | 12.02 | 137.15 |
| DIFFERENCE (Methods) | | +36.6 | | | -4.24 | | |
| **LABORATORY** | | | | | | | |
| SYRINGE | 20 | 152.23 | 19.64 | 366.61 | 63.36 | 10.29 | 100.59 |
| BURETTE | 20 | 179.43 | 25.69 | 627.21 | 53.70 | 10.17 | 98.18 |
| DIFFERENCE (Methods) | | +27.2 | | | -9.66 | | |

DIFFERENCES (FIELD TO LABORATORY) SYRINGE: +4.94; BURETTE: -4.46

TABLE 5. REPLICATIONS FOR STORAGE IN PLASTIC AND GLASS BOTTLES, MALHAM TARN FIELD CENTRE, N. YORKSHIRE, $HCO_3^-$ mg/l; $Ca^{2+}$ mg/l

FIELD
BURETTE
n = 20 T°C = 6.8

| | MEAN | σ | VAR. |
|---|---|---|---|
| pH : | 7.56 | 0.356 | 0.114 |
| $HCO_3^-$ : | 183.89 | 42.11 | 1685.36 |
| $Ca^{2+}$ : | 65.54 | 12.02 | 137.15 |

LABORATORY : 8 HOURS STORAGE

| | POLYTHENE BOTTLES n = 20 T°C = 10.5 | | | GLASS BOTTLES n = 20 T°C = 12.0 | | |
|---|---|---|---|---|---|---|
| | MEAN | σ | VAR. | MEAN | σ | VAR. |
| pH : | 7.62 | 0.305 | 0.086 | 7.62 | 0.31 | 0.086 |
| $HCO_3^-$ : | 179.43 | 29.69 | 627.21 | 180.09 | 31.65 | 890.14 |
| $Ca^{2+}$ : | 53.7 | 10.17 | 98.18 | 60.67 | 22.80 | 467.88 |
| **24 HOURS STORAGE** | | | | | | |
| pH : | 7.55 | 0.22 | 0.05 | 7.47 | 0.22 | 0.04 |
| $HCO_3^-$ : | 146.8 | 21.54 | 440.08 | 183.47 | 33.04 | 1037.58 |
| $Ca^{2+}$ : | 67.84 | 11.92 | 134.89 | 54.77 | 12.34 | 144.67 |

TABLE 6. REPLICATION FOR IN SITU CAVE ANALYSES AND SURFACE ANALYSES, G.B. CAVE, MENDIP HILLS, SOMERSET.

| | | n | MEAN | $\sigma$ |
|---|---|---|---|---|
| 1) CAVE TITRATION - SYRINGE | $T^{o}C$ | 10 | 5.5 | 1.29 |
| | pH | 10 | 8.0 | 0.49 |
| | $HCO_3^-$ | 10 | 150.81 | 79.93 |
| | $pCO_2$ | 10 | 2.94 | 0.34 |
| 2) STORAGE 4 HOURS SURFACE TITRATION - BURETTE POLYTHENE BOTTLES | $T^{o}C$ | 10 | 6.9 | 0.61 |
| | pH | 10 | 8.08 | 0.10 |
| | $HCO_3^-$ | 10 | 224.97 | 138.45 |
| | $Ca^{2+}$ | 10 | 37.2 | 20.94 |
| | calcite sat. | 10 | 0.204 | 0.46 |
| | $pCO_2$ | 10 | 2.90 | 0.29 |
| 3) STORAGE 20 HOURS LAB. TITRATION - BURETTE POLYTHENE BOTTLES | $T^{o}C$ | 10 | 10 | - |
| | pH | 10 | 8.09 | 0.15 |
| | $HCO_3^-$ | 10 | 233.26 | 140.61 |
| | $Ca^{2+}$ | 10 | 38.2 | 20.77 |
| | calcite sat. | 10 | 0.26 | 0.37 |
| | $pCO_2$ | 10 | 2.892 | 0.336 |
| 4) STORAGE 20 HOURS LAB. TITRATION - BURETTE GLASS BOTTLES | $T^{o}C$ | 3 | 14.5 | - |
| | pH | 3 | 8.5 | 0.0 |
| | $HCO_3^-$ | 3 | 151.27 | 8.43 |
| 5) STORAGE AT 2°C FOR 12 DAYS LAB. TITRATION - BURETTE GLASS BOTTLES | $T^{o}C$ | 3 | 14.5 | - |
| | pH | 3 | 7.97 | 1.10 |
| | $HCO_3^-$ | 3 | 68.87 | 14.95 |
| | $Ca^{2+}$ | 3 | 27.33 | 7.57 |

Table 5 shows the values for storage in plastic and glass for waters taken in the Malham Tarn Field Centre area, North Yorkshire, U.K. on 18.4.79. Storage lead to a decrease in alkalinity and the samples in glass bottles lost less than the plastic ones.

Table 6 shows the results of analyses of drip and stream samples from GB Cave, Mendip Hills, Somerset, U.K. Table 7 shows the data broken down by environment. A decrease in alkalinity values is seen with storage and an increase in saturation index and loss of carbon dioxide is evident; this is especially true of drip samples.

TABLE 7. GB CAVE WATER SAMPLE RESULTS

| | $T^{o}C$ | pH | $HCO_3^-$ mg/l | $Ca^{2+}$mg/l | $pCO_2$ | calcite sat. |
|---|---|---|---|---|---|---|
| a) <u>ENTRANCE DRIP</u> | | | | | | |
| <u>IN CAVE</u> | 7.0 | 8.3 | 234.4 | - | 3.02 | |
| (Syringe) | 7.0 | 8.3 | 239.1 | - | 3.01 | |
| SURFACE | 8.0 | 8.2 | 312.3 | 52.0 | 2.81 | 0.72 |
| (Burette) | 8.0 | 8.2 | 312.3 | 52.0 | 2.81 | 0.72 |
| LABORATORY (20 HOURS POLYTHENE BOTTLES) (Burette) | | | | | | |
| | 9.0 | 8.0 | 307.4 | 54.0 | 2.61 | 0.55 |
| | 9.0 | 8.0 | 307.4 | 54.0 | 2.61 | 0.55 |
| b) <u>CAVE DRIP</u> | | | | | | |
| <u>IN CAVE</u> | 7.0 | 8.4 | 348.9 | - | 2.95 | |
| (Syringe) | 7.0 | 8.4 | 348.9 | - | 2.95 | |
| SURFACE | 7.0 | 8.0 | 439.2 | 70.0 | 2.47 | 0.77 |
| (Burette) | 7.0 | 7.9 | 444.1 | 68.0 | 2.36 | 0.66 |
| LABORATORY (20 HOURS POLYTHENE) (Burette) | | | | | | |
| | 10.0 | 8.0 | 458.7 | 70.0 | 2.44 | 0.82 |
| | 10.0 | 7.9 | 458.7 | 70.0 | 2.33 | 0.73 |
| LABORATORY (20 HOURS; GLASS) (Burette) | | | | | | |
| | 14.5 | 8.4 | 122.0 | 70.0 | 3.40 | 0.74 |

Table 7 - continued

| | | | | | | |
|---|---|---|---|---|---|---|
| c) MAIN INLET | | | | | | |
| IN CAVE | 4.5 | 7.1 | 73.2 | - | 2.33 | |
| (Syringe) | 4.5 | 7.1 | 73.2 | - | 2.33 | |
| SURFACE | 6.5 | 8.1 | 97.6 | 20.0 | 3.20 | -0.24 |
| (Burette) | 6.5 | 8.0 | 102.5 | 20.0 | 3.08 | -0.32 |
| LABORATORY (20 HOURS, POLYTHENE) (Burette) | | | | | | |
| | 10.0 | 8.1 | 156.2 | 20.0 | 2.99 | -0.00 |
| | 10.0 | 7.9 | 68.3 | 20.0 | 3.14 | -0.53 |
| LABORATORY (glass) (Burette) | | | | | | |
| | 14.5 | 8.5 | 146.4 | 20.0 | 3.40 | 0.42 |
| LABORATORY (glass, fridge) (Burette) | | | | | | |
| | | 7.6 | 51.6 | 36.0 | | |
| d) TOP OF WATERFALL | | | | | | |
| IN CAVE | 4.5 | 8.0 | 92.7 | - | 3.12 | |
| (Syringe) | 4.5 | 8.0 | 92.7 | - | 3.12 | |
| SURFACE | 6.5 | 8.1 | 131.8 | 24.0 | 3.07 | -0.05 |
| (Burette) | 6.5 | 8.0 | 131.8 | 18 | 2.97 | -0.26 |
| LABORATORY (Polythene) (Burette) | | | | | | |
| | 10.0 | 8.2 | 141.5 | 22.0 | 3.13 | 0.10 |
| | 10.0 | 8.2 | 131.8 | 22.0 | 3.16 | 0.07 |
| LABORATORY (glass) (Burette) | | | | | | |
| | 14.5 | 8.5 | 146.4 | 24.0 | 3.40 | 0.49 |
| LABORATORY (glass, fridge) (Burette) | | | | | | |
| | | 9.2 | 77.5 | 24.0 | | |
| e) SUMP | | | | | | |
| IN CAVE | 4.5 | 8.2 | 102.5 | - | 3.28 | |
| (Syringe) | 4.5 | 8.2 | 102.5 | - | 3.28 | |
| SURFACE | 6.5 | 8.2 | 141.5 | 24.0 | 3.15 | 0.08 |
| (Burette) | 6.5 | 8.1 | 136.6 | 24.0 | 3.06 | -0.04 |
| LABORATORY (Polythene) (Burette) | | | | | | |
| | 10.0 | 8.3 | 151.3 | 26.0 | 3.20 | 0.29 |
| | 10.0 | 8.2 | 151.3 | 26.0 | 3.10 | 0.19 |
| LABORATORY (glass) (Burette) | | | | | | |
| | 14.5 | 8.5 | 161.0 | 18.0 | 3.36 | 0.42 |
| LABORATORY (glass, fridge) (Burette) | | | | | | |
| | | 7.1 | 77.5 | 22 | | |

## DISCUSSION

The data presented suggest that the use of syringes provides a viable alternative to burettes for field titrations, though the replications are better for calcium than for alkalinity. With care in the use of the syringe in the dispensing of the titre the titration can be made to be as accurate as burette titrations. Using dilute titre also increases accuracy, as overshooting the mark by one drop causes a lower error. The best method remains field titration using calibrated glassware but for expedition and in situ cave measurements, the syringes are to be preferred; any inaccuracies due to the method would appear to be far less than those due to degassing during transport out of the cave system.

In terms of the interpretations of the data on field to laboratory changes, the $pCO_2$ values for glass bottles are all greater than any other values. This implies that leaching of carbonate could be taking place from the glass; bacterial decomposition of organic matter and $CO_2$ production is a further possibility. The effect is not seen in the polythene bottles used, which are permeable to $CO_2$ and the samples suffer the greatest loss of $CO_2$. Losses from the cave to the laboratory are not necessarily the largest where the $pCO_2$ is the highest; they appear to be greatest when the disequilibrium between the natural system and the atmospheric is greatest, i.e. the drip samples, equilibriated with bedrock conditions, show the greatest cave - surface losses while the stream system shows the least losses; or even slight gains.

It is clear that in situ analyses differ from surface analyses in a way that is non-systematic in that it cannot be allowed for in a simple cave - surface conversion factor; the differences are interpretable largely in terms of differences in $pCO_2$ between the measured system and atmospheric; syringes provide a viable method of rapid in situ titrations.

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R. W. Crabtree, S. T. Trudgill, A. M. Pickles
and M. I. Cowton,
Geography Department,
University of Sheffield,
S10 2TN

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# AN INVESTIGATION OF THE CALCIUM CONCENTRATIONS OF CAVE STREAMS AND RESURGENCE WATERS

W. Gascoine

ABSTRACT

From the study of cave streams and laboratory experiments with limestone in carbon dioxide treated water, results have been obtained which indicate that the solution process of limestone in peaty or rain water results in underground streams containing both calcium salts in solution and calcium carbonate as a colloidal suspension, as well as organic calcium complexes in some cases.

Laboratory work with bicarbonate solutions gives results which indicate that the process by which the colloidal suspensions are formed can be summarised as:-

1. $CO_2 + H_2O \rightleftharpoons H_2CO_3$
2. $H_2CO_3 + CaCO_3 \longrightarrow Ca^{2+} + 2\ HCO_3^-$
3. $HCO_3^- \rightleftharpoons CO_2 + OH^-$
4. $HCO_3^- + OH^- \longrightarrow CO_3^{2-} + H_2O$
5. $Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3$ colloidal.

## INTRODUCTION

Estimations of the calcium content of resurgences in the limestone area of South East Wales and of streams in the caves in that area have led to the conclusion that streams which are supersaturated with respect to calcium carbonate almost always carry a considerable proportion of their calcium as insoluble though microscopic suspensions.

The suspensions would appear to be of either calcium carbonate from the upper limestones or some organic calcium salt derived from lignin acids present in the peaty water which feeds the caves in the region.

Laboratory experiments have been performed in an attempt to simulate the field data obtained using water and limestone from local swallets and caves and also a series of experiments has been done to attempt to explain why and how the suspensions appear.

It is hoped that the study will continue and expand into a more detailed analysis of the properties of cave and resurgence waters and comment, criticism and guidance from the readers of this article will be welcomed by the author.

## FIELD STUDIES

### The resurgences

The limestone resurgences in the Clydach Gorge, Gwent, are mostly resurgences from known caves in the area, largely those in the oolite beds below Mynydd Llangattwg. Most of these connections have been proved in recent years using dyes and Lycopodium spores and thus a relatively detailed water flow pattern is available for the mountain and the gorge.

The significant resurgences used in this study are associated with Ogof Agen Allwedd and Ogof Craig a Fynnon, with some others included for completeness. Analysis of the waters carried out by the author in the laboratories of a local college shows the presence of several calcium salts in all the samples, with a corresponding variation in the streams within the caves which feed these resurgences (Figs. 1 & 2, Table 1).

TABLE 1

The calcium concentrations are expressed as micrograms of $CaCO_3$ per cubic centimetre of solution.

| Resurgence | $[CaCO_3]$ estimated by Flame Photometer | $[CaCO_3]$ estimated by Flame Photometer after $H^+$ treatment | $[CaCO_3]$ estimated by EDTA titration |
|---|---|---|---|
| 1. Limekiln (1) | 56 | 88 | 97 |
| 2. Limekiln (2) | 42 | 56 | 68 low water |
| 3. Blackrock | 24 | 26 | 32 |
| 4. Waterfall | 12 | 12 | 16 |
| 5. Capel (1) | 41 | 56 | 65 |
| 6. Capel (2) | 52 | 76 | 90 low water |
| 7. Rock and Fountain | 67 | 105 | 126 |
| 8. Elm Hole (1) | 34 | 51 | 54 |
| 9. Elm Hole (2) | 39 | 51 | 64 low water |
| 10. Pwll y Cwm (1) | 35 | 43 | 53 |
| 11. Pwll y Cwm (2) | 40 | 52 | 70 low water |
| 12. Clogwyn | 39 | 49 | 70 |
| 13. Gisfaen (1) | 38 | 52 | 56 |
| 14. Gisfaen (2) | 44 | 55 | 70 low water |

The estimation by Flame Photometry was done using an EEl instrument with a suitable filter to mask the presence of other metal ions ($Na^+$ is present in low concentrations in the waters, 8 to 10 $\mu g.cm^{-3}$). The estimation was comparative using a standard solution of 100 $\mu g.cm^{-3}$ as a full-scale deflection and deionised water as a zero standard.

In addition several samples of water containing known $Ca^{2+}$ concentrations were estimated on the instrument to ensure that the scale deflection was giving readings that could be directly converted to concentration values.

The acid treatment estimation was carried out on the same samples after treatment with concentrated HCl (20 drops to 100 $cm^3$ was found to be sufficient to give a lasting acidity); the estimations were then done on the Flame Photometer.

The EDTA estimation for $Ca^{2+}$ was carried out using the standard technique listed in Analytical Chemistry texts with Murexide as indicator. (Total hardness, $Ca^{2+}$ and $Mg^{2+}$, was also checked with some samples to confirm the relevance of the values obtained using Murexide indicator).

These results seem to indicate that the cave waters as they emerge from the mountain into the river gorge carry calcium in several forms:

(a) as calcium ions in solution, probably from carbonate and bicarbonate, capable of estimation by Flame Photometry;

(b) as microscopic particles of $CaCO_3$ carried by the stream and only able to be estimated accurately after treatment with acid has caused them to dissolve;

(c) as some other calcium compounds, stable to acid treatment, but capable of being decomposed by EDTA and thus estimated. These could be organic compounds of calcium formed by the peaty nature of the waters entering the limestone, or by some other complex which is resistant to acid.

The origins of the resurgences are given below for completeness and to explain why the cave streams that were subsequently sampled were so chosen.

The Limekiln stream, Ogof Capel and the Rock and Fountain resurgences are fed by streams in Ogof Craig a Ffynnon. The surface origins of these streams are not known except for one feeder (Pwll Coedog) which is 1km from the gorge and high on Mynydd Llangattwg. The cave extends well beyond this point at a depth of approx. 130m (Gascoine, 1978).

Elm Hole and Pwll y Cwm are resurgences for the Ogof Agen Allwedd stream which originates from several feeders all of which are over 4km distant on the Northwest flank of Mynydd Llangattwg; some have been positively identified whilst others are as yet only suspected of being feeders. The resurgences are also fed by water from Ogof Darren Cilau and Llangattwg Swallet, also 4km distant.

Ffynnon Gisfaen is the resurgence point for much of the water sinking on Western Mynydd Llangattwg and Eastern Mynydd Llangynidr. Tests using Lycopodium spores on swallets up to 7km distant have shown positive results at Ffynnon Gisfaen; no known cave is associated with the water flow (Gascoine, 1980).

The waters issuing from Ogof Clogwyn, Blackrock Cave and the Waterfall resurgence are of unknown source and may or may not contain soft water from feeders close to the resurgence: the others mentioned above almost certainly do not have any soft water inlets.

The pH of all these resurgences is in the range 7.6 to 8.0.

The cave streams

Streams in Ogof Agen Allwedd, Ogof Craig a Ffynnon and Ogof Eglwys Faen have been sampled under medium water conditions to see if they are also carrying suspended calcium salts in similar proportions to the resurgences (Figs. 3 & 4, Table 2).

All the samples taken show this property and the proportions are remarkably similar in all the caves. Attempts to obtain samples from inlets where the streams enter the cave, having percolated through the overlying limestones have also shown that, even under those conditions, suspended calcium salts are present.

The samples were taken in sealable plastic bottles which were filled completely and stored at below 12°C until analysis was carried out, to try and prevent any re-solution occurring with a rise in temperature.

TABLE 2

| Stream | $[CaCO_3]$ estimated by Flame Phot. | $[CaCO_3]$ estimated by Flame Phot. after $H^+$ treatment | $[CaCO_3]$ estimated by EDTA titn. |
|---|---|---|---|
| Agen Allwedd | | | |
| 1. R. H. inlet | 34 | 43 | 56 |
| 2. L. H. Inlet | 52 | 72 | 92 |
| 3. Entrance inlet | 52 | 75 | 102 |
| 4. Confluence | 42 | 60 | 72 |
| 5. 1st choke | 44 | 60 | 75 |
| 6. 2nd choke | 46 | 61 | 76 |
| 7. 3rd choke | 36 | 44 | 58 |
| Craig a Ffynnon | | | |
| 8. 1st choke chamber | 67 | 94 | 132 |
| 9. N. W. inlet | 52 | 72 | 96 |
| 10. R. H. sump | 66 | 97 | 126 |
| Eglwys Faen | | | |
| 11. St. Patricks | 76 | 100 | 130 |
| 12. Main chamber | 49 | 70 | 80 |
| 13. Bird chamber | 48 | 66 | 76 |
| 14. Entrance rift | 52 | 78 | 88 |
| 15. E. Aven | 50 | 72 | 84 |
| 16. W. Series stream | 47 | 66 | 76 |

The calcium estimations were carried out in the same way as for the resurgence samples and, with the similar results obtained, the same conclusions can be drawn. In addition, however, it can also be concluded that water entering limestone very quickly attains an equilibrium position where it is carrying calcium salts in both solution and suspension.

The pH of all these streams is in the range 7.6 to 8.0

The results obtained from these field studies have led on to a study of the solution of limestone in the laboratory using deionised and peaty water and oolite from the Carboniferous Limestone of South Wales. In addition the possible effects of other anions in the stream waters have been studied.

## LABORATORY STUDIES

Investigations of limestone samples treated with $CO_2$ saturated water

It is well documented in literature and has been independently ascertained by the author, that the caves under study are present in the bands of Oolitic limestone near the base of the Carboniferous Limestone and thus it is these limestones that have been used in all the subsequent investigations. Samples of Gilwern, Blaen Onneu and Pwll y Cwm Oolite were broken into small pieces, mixed and used in the following experiments.

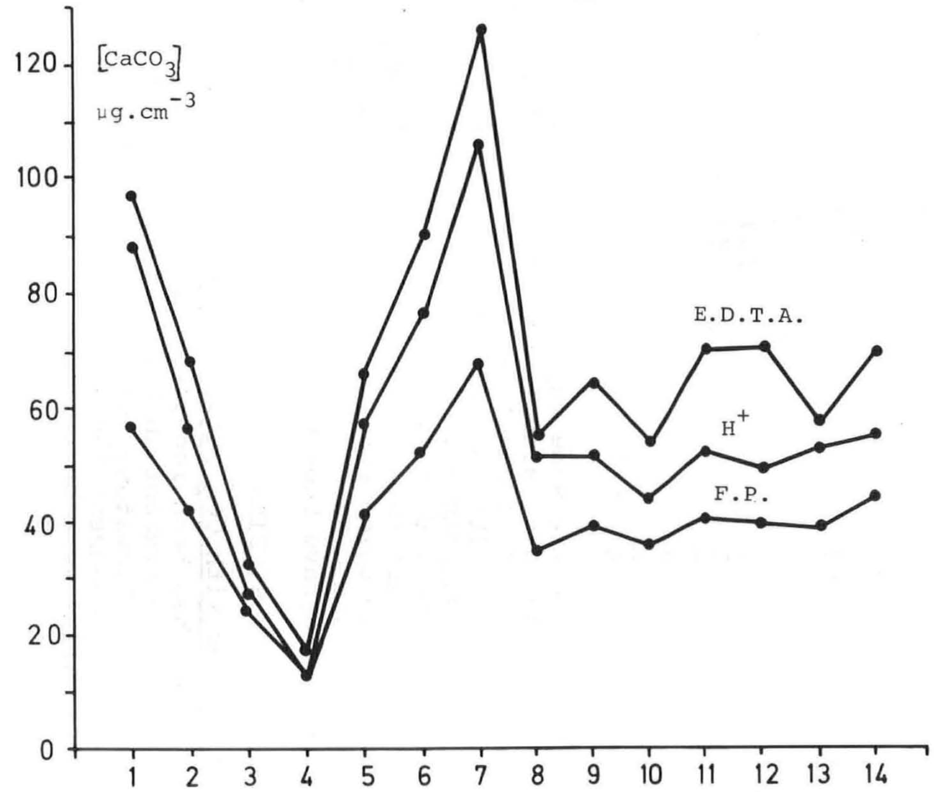


FIGURE 1. THE CLYDACH RESURGENCES

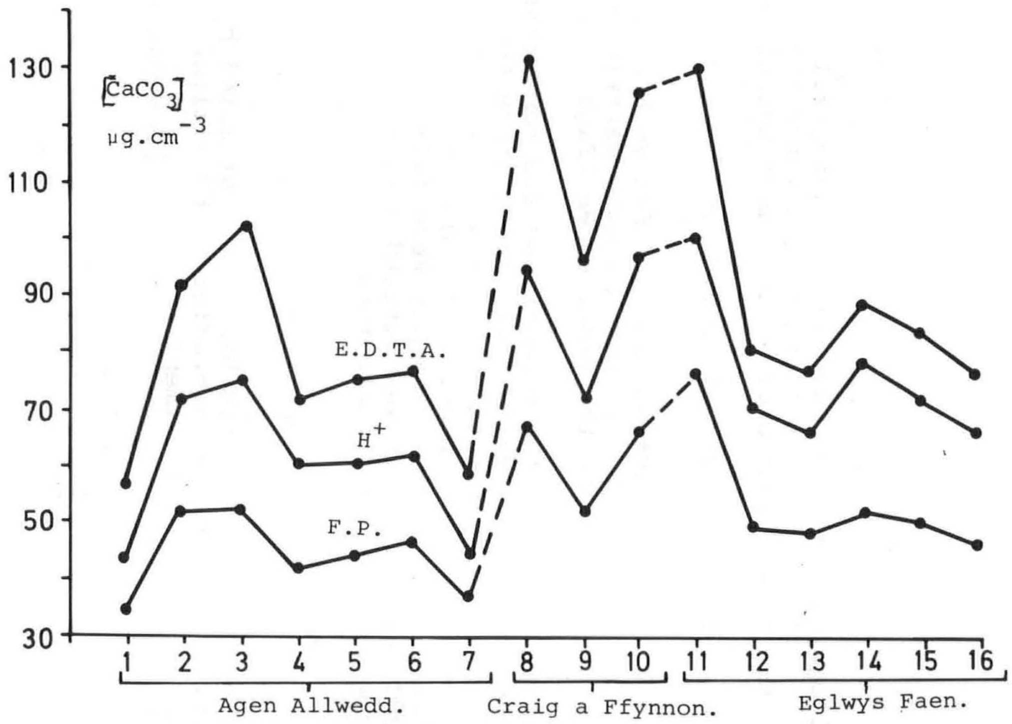


FIGURE 3. THE CAVE STREAMS

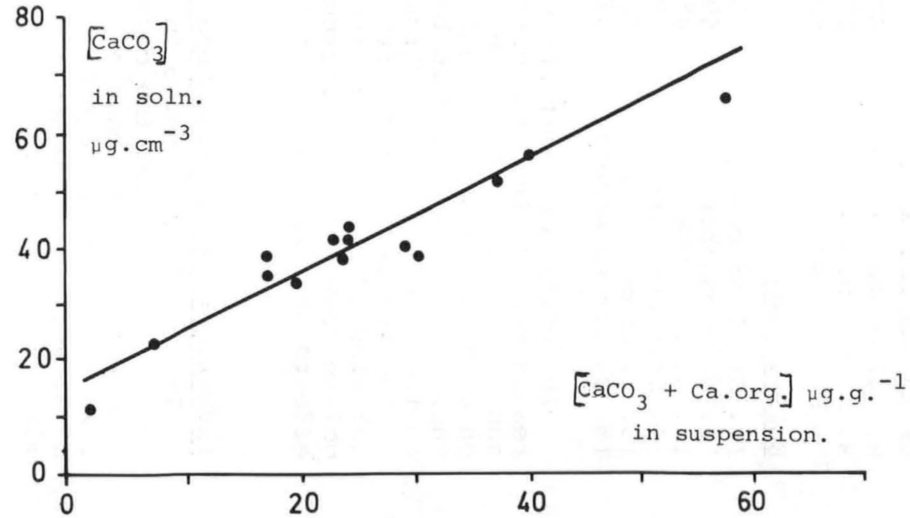


FIGURE 2.

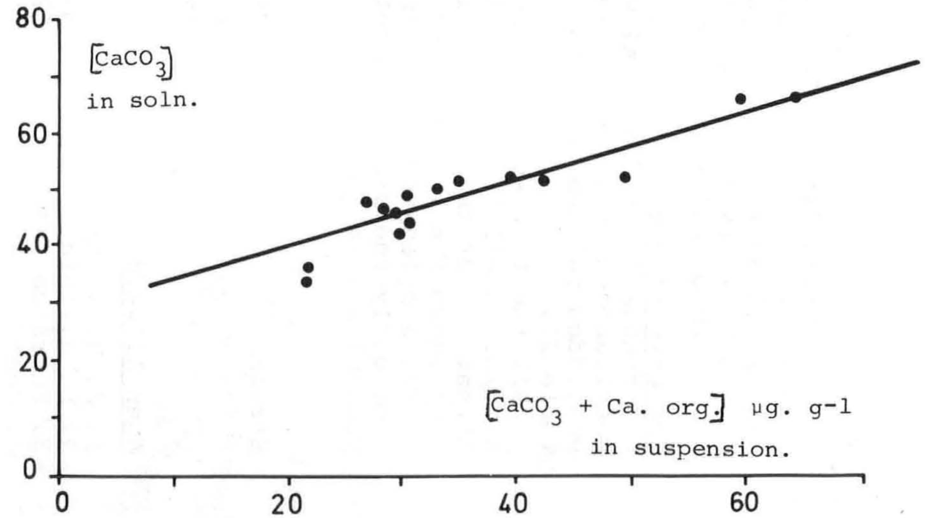


FIGURE 4.

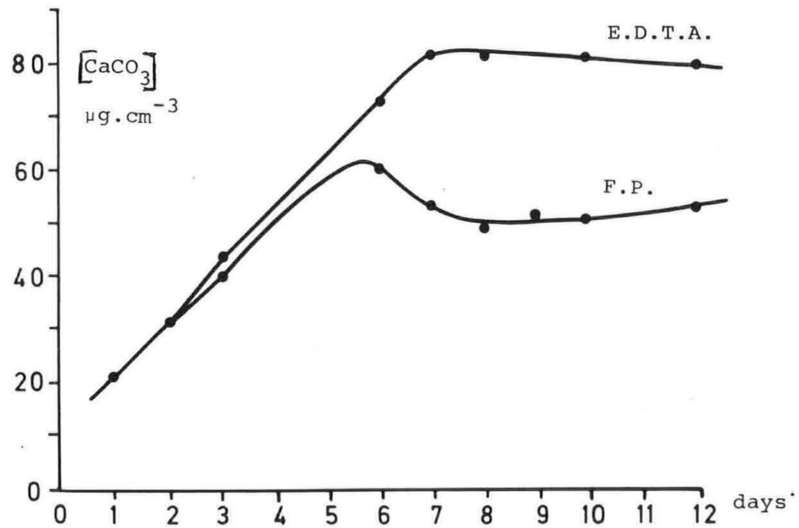


FIGURE 5. (Pure water)

SOLUTION OF OOLITE

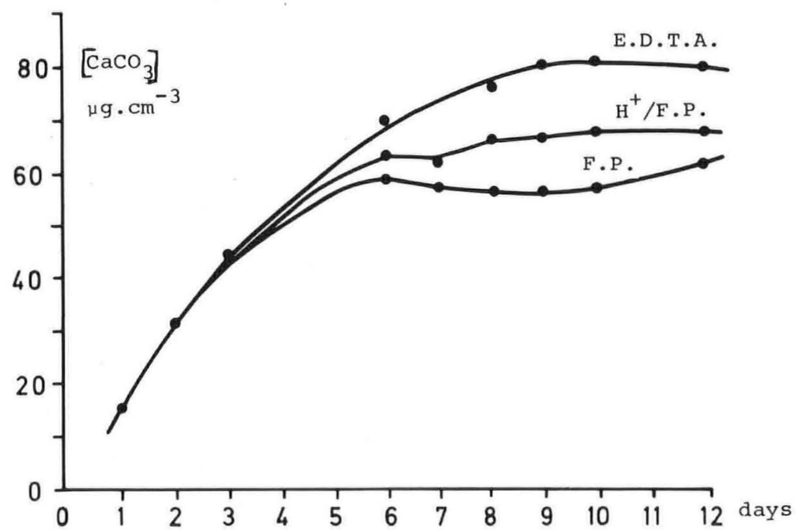


FIGURE 6. (Peaty water)

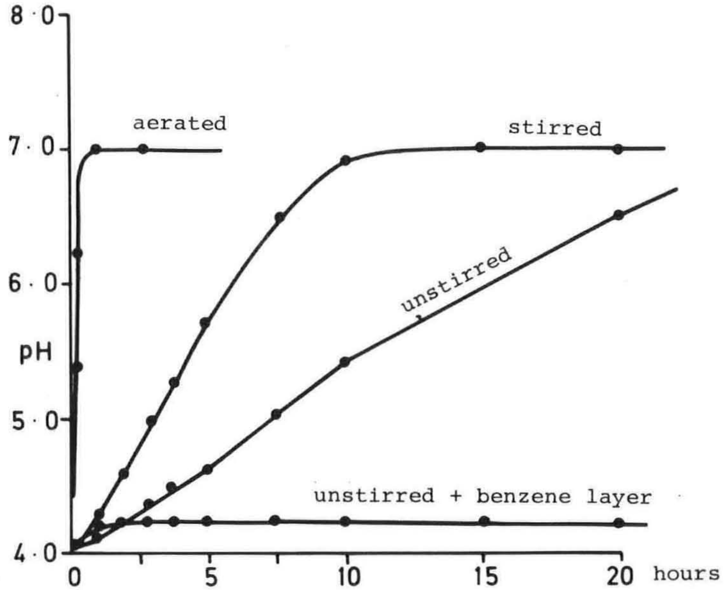


FIGURE 7.

DECOMPOSITION OF '$H_2CO_3$' and $HCO_3^-$ at 12°C

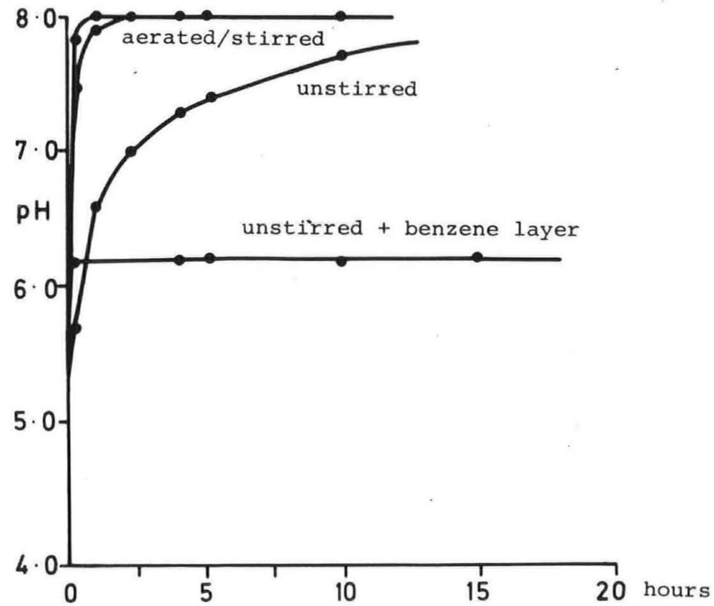


FIGURE 8.

Deionised water

Pieces of the oolite were placed in a large flask and deionised water was added ($800cm^3$). The contents were then saturated with water-washed $CO_2$ from a Kipps apparatus until the pH fell to 4.1 (the minimum value obtained) and then were continued to be treated for a further 5 minutes. After this the flask and contents were allowed to stand at room temperature for several days. Samples of the solution were taken at intervals for analysis by Flame Photometry, acid treatment and EDTA titration, and the results of the calcium estimations are shown on Table 3 and on Figure 5.

TABLE 3

Initial pH of water 7.1
pH after $CO_2$ saturation 4.3

| Time (days) | $[CaCO_3]$ Flame Phot. | $[CaCO_3]$ $H^+$/Flame Phot. | $[CaCO_3]$ EDTA titn. |
|---|---|---|---|
| 0 | 0 | 0 | 0 |
| 1 | 20 | 20 | 20 |
| 2 | 30 | 30 | 30 |
| 3 | 40 | - | 44 |
| 6 | 60 | 72 | 72 |
| 7 | 52 | 82 | 82 |
| 8 | 49 | - | 80 |
| 9 | 50 | pH steady at 8.0 | |
| 10 | 50 | - | 80 |
| 12 | 52 | 77 | 78 |

It can be seen that the solution process of oolite (in this case analysis showed it to be 87% $CaCO_3$) proceeds normally until around 30 $\mu g.cm^{-3}$ $CaCO_3$ is present in solution, when some precipitation commences; solution then continues to a maximum value of around 60 $\mu g.cm^{-3}$, to be followed by a steady decline in the concentration of dissolved calcium. The concentration of the total calcium in both solution and suspension rises to a constant value of around 80 $\mu g.cm^{-3}$.

On such experiments a fine film of precipitate is visible after a few days on the lower surface of the flask. It should also be noted that acid treatment of the solution and estimation by Flame Photometry gave $CaCO_3$ concentrations that were identical to those estimated by EDTA titration, organic matter being absent as pure water was used.

Peaty water

Pieces of some oolite placed in peaty water (initial pH 4.2) taken from the Mynydd Llangattwg moor and $CO_2$ treated in the same way, gave the calcium concentrations shown in Table 4 and on Figure 6.

TABLE 4

Initial pH of water 4.2
pH after $CO_2$ saturation 4.1

| Time (days) | $[CaCO_3]$ Flame Phot. | $[CaCO_3]$ $H^+$/Flame Phot. | $[CaCO_3]$ EDTA titn. |
|---|---|---|---|
| 0 | 2 | | |
| 1 | 15 | - | 15 |
| 2 | 32 | - | - |
| 3 | 44 | - | 45 |
| 6 | 59 | 61 | 68 |
| 7 | 56 | 62 | - |
| 8 | 56 | 67 | 76 |
| 10 | 56 | 66 | 80 |
| 12 | 61 | 66 | 78 |

pH of final solution 7.9

The brown colour of the peaty water made the end-point of the EDTA titration difficult to see: carbon treatment had little effect on the colour and no effect on the total calcium concentration of the solution, i.e. the organic complex is not absorbed by carbon.

Again, the solution process produces a slight peak in the concentration of soluble calcium and also evidence of a suspension; there was in this case a brown flocculant precipitate noticeable after a day or two. (Attempts to produce an infra-red spectrum of the dried precipitate failed to give any real evidence of its nature and work is continuing on this aspect of the study).

These results indicate that, as the solution of oolite in the laboratory gives a similar equilibrium mixture to that which occurs in caves and resurgences, it is likely that a similar process is occurring in the upper limestones of Mynydd Llangattwg, the suspensions being present in quantity by the time the water reaches the level of the cave passages some 130 m down in the limestone sequence.

Further investigations

1. The experiments with oolite and $CO_2$ saturated waters were repeated using a pump to aerate the solution continually after it was saturated with $CO_2$, to try to speed up the process and/or ascertain if there was any significant difference in the resulting solution. Over-heating of the pump meant that the experiment could only be carried out for a few hours at a time, but the results showed a similar trend was followed in aerated as in still solutions, e.g. after aeration for 6 hours, a solution of deionised water saturated with $CO_2$ on oolite gave an analysis:-

pH 8.0, $[CaCO_3]$ by Flame Photometry $50\mu g.cm^{-3}$

$[CaCO_3]$ by EDTA titration $85\mu g.cm^{-3}$

2. The sulphate concentrations of cave and resurgence waters in the Llangattwg and Clydach areas are around $15\mu g.cm^{-3}$ and the chloride concentrations around $10\mu g.cm^{-3}$, so Flame Photometric estimations of solutions containing only sulphate ions (from $MgSO_4$ and $(NH_4)_2SO_4$) and chloride ions (from HCl) in these concentrations were carried out to ascertain if any readings were obtained from these ions. None was obtained.

It can be assumed therefore that the presence of these ions does not interfere with the results from the Flame Photometry and the acid treatment is indeed dissolving some colloidal or fine particulate form of calcium carbonate.

3. To verify the above statement, a laboratory experiment using pure $CaCO_3$ treated with $CO_2$ saturated water was carried out and the results were as follows; after 12 days, analysis gave:-

pH 8.0, $[CaCO_3]$ by Flame Photometry $32\mu g.cm^{-3}$

$[CaCO_3]$ by Flame Photometry after acid treatment $45\mu g.cm^{-3}$

and $[CaCO_3]$ by EDTA titration $46\mu g.cm^{-3}$

4. To date all attempts to filter out the suspension of calcium carbonate have failed. Filters down to 2um pore size have been tried as has centrifugation on standard laboratory centrifuges.

Use of finer filters may succeed.

Investigations of solutions of $CO_2$ in deionised water

Assuming some of the acidity in the water percolating into caves on Mynydd Llangattwg is due to dissolved $CO_2$, a series of experiments was performed where $CO_2$ was bubbled into deionised water and the solution allowed to stand with pH electrodes immersed in it;

(a) without stirring
(b) with stirring
(c) with aeration with air and $O_2$ gas
(d) without stirring and with a layer of an immiscible liquid on the surface of the solution (benzene was used in the experiments).

The temperature of the solutions was 12°C in each case.

The change in pH was then recorded over a period of up to 24 hours: the results (Fig. 7) show no appreciable change in aerating with air or oxygen gas, although there was a difference in the final pH of 0.3 units in the solution.

The inference gained from the experiments is that the loss of $CO_2$ to atmosphere is the controlling factor in the pH change and prevention of the loss by a benzene layer effectively stops the process: in the equilibrium:-

$$H_2CO_3 \rightleftharpoons CO_2 + H_2O$$

loss of $CO_2$ causes decomposition of $H_2CO_3$, which is largely present as hydrated $CO_2$ anyway (Kern, 1960).

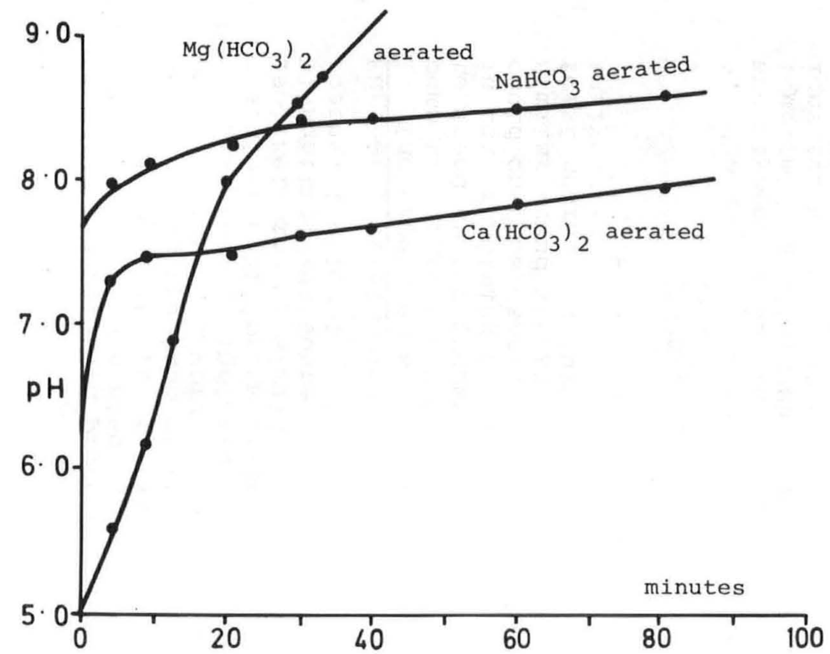

FIGURE 9 DECOMPOSITION OF BICARBONATES

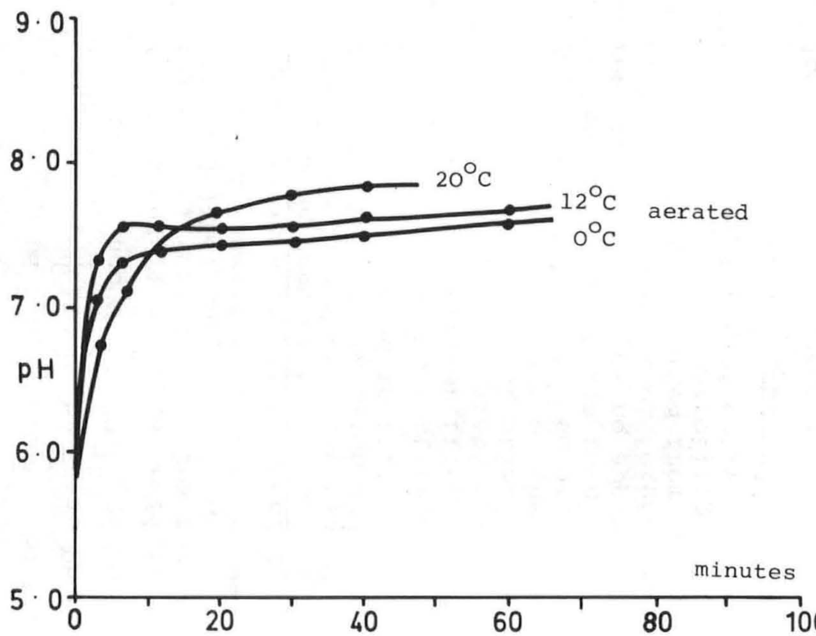

FIGURE 11. TEMPERATURE EFFECTS AND SEEDING

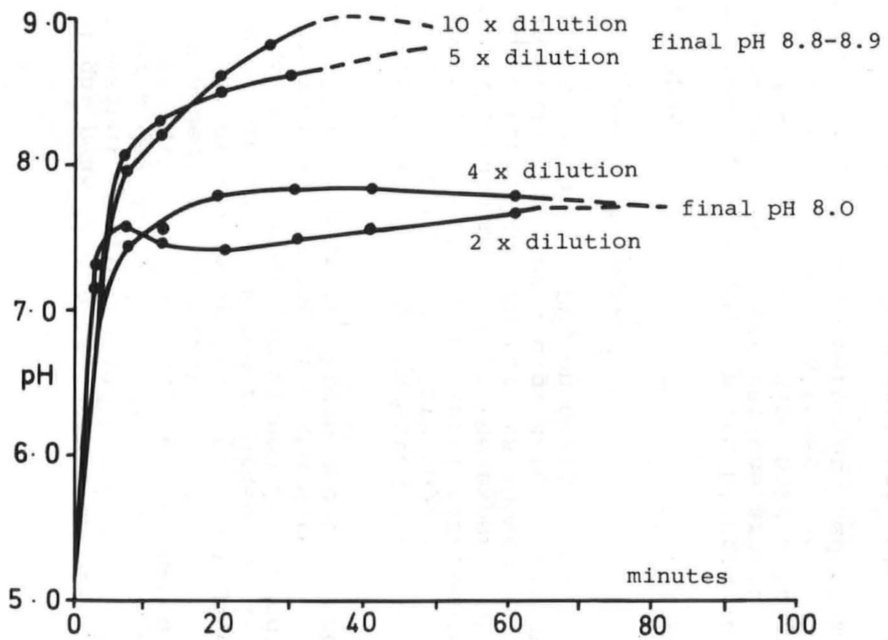

FIGURE 10. $(Ca(HCO_3)_2)$

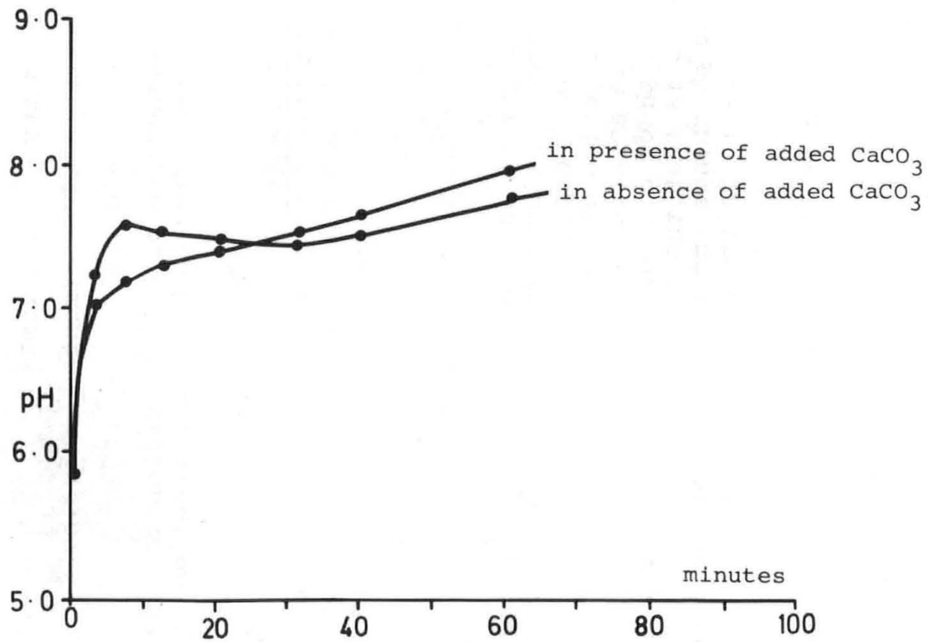

FIGURE 12.

Investigations of the decomposition of bicarbonate ions in solution

As it is widely accepted that solution of limestone by $CO_2$ enriched water results in the production of bicarbonate ions, the following experiments were carried out to study the decomposition of such ions under various conditions.

1. $CO_2$ gas was bubbled into limewater (calcium hydroxide solution) until the pH was at a minimum value; the solution was then allowed to stand with pH electrodes immersed in it at 12°C.
   (a) without stirring
   (b) with stirring
   (c) with aeration with air and $O_2$ gas
   (d) without stirring and with a benzene layer on the surface of the solution.

The change in pH was recorded for up to 24 hours and again no appreciable difference in the rate of decomposition was noted in aerating with air or $O_2$ gas; rapid aeration much accelerated the pH change and the presence of a benzene layer virtually stopped the process (Fig. 8). The inference is that, again, the loss of $CO_2$ to atmosphere is the rate-controlling factor in the decomposition, so it is proposed that the mechanism for bicarbonate ion decomposition may be:-

$$HCO_3^- \rightleftharpoons CO_2 + OH^-$$

This mechanism is widely quoted in literature especially in pH ranges of 8.0 and above (Welch et al., 1969).

The levelling off of the pH was accompanied by a slow precipitation of $CaCO_3$ from solution and then a slow rise in pH to 8.0 followed. This is the pH of a saturated solution of $CaCO_3$ in deionised water: the value was also checked by experiment later.

It seems likely therefore from these results that, where the concentration of $HCO_3^-$ is sufficiently high, the decomposition process will follow a mechanistic route:-

step 1 $\quad HCO_3^- \rightleftharpoons CO_2 + OH^-$

step 2 $\quad HCO_3^- + OH^- \rightleftharpoons CO_3^{2-} + H_2O$

These mechanisms are also quoted in literature at the pH of the experiments.

2. A further set of experiments carried out on solutions of bicarbonates which do not decompose to produce a carbonate precipitate, re-inforces the proposed mechanism. No levelling off of pH occurs as the $OH^-$ produced in step 1 is not consumed in the $CO_3^{2-}$ precipitation (step 2).

The results for sodium and magnesium carbonate are on Fig. 9.

$MgCO_3$ is not precipitated if the original solution used is prepared from $Mg(OH)_2$ and $CO_2$, as, at the temperature of the experiment (12°C) $MgCO_3$ is more soluble in water than $Mg(OH)_2$.

3. To verify that the precipitation of $CaCO_3$ is indeed the reason for the levelling off of the pH at around 7.6, the series of experiments was repeated using saturated limewater solutions diluted with deionised water to differing degrees (Fig. 10).

Dilution of the limewater up to a factor of four times resulted in a levelling off of pH and precipitation of $CaCO_3$ from the solution, a four times dilution giving a solution of about 400 µg of $CaCO_3$ per $cm^3$ of water. The precipitation was often slow and progressed for a considerable time after the pH curve levelled off. The pH in all cases ultimately attained a value of 8.0. Limewater solutions diluted in excess of four times did not give precipitation of $CaCO_3$ and the pH climbed steadily through the experiment to 8.8 or 8.9.

Previous work indicates that $CaCO_3$ may have precipitated in more experiments but aeration caused loss of $CO_2$ to occur rapidly and the precipitation step, being a relatively slow process, did not have time to occur.

Referring to the work with oolite + $CO_2$ + $H_2O$ the peak in the curve of $[CaCO_3]$ estimated by Flame Photometry may be present because of this slow precipitation falling behind the initial decomposition of $HCO_3^-$ producing $OH^-$; indeed peaks have occurred from time to time on the other decomposition curves of $HCO_3^-$ from treated limewater.

4. The decomposition of $HCO_3^-$ that has been discussed in the work so far has also been carried out at different temperatures to see if temperature is a significant factor in the process (Fig. 11).

Experiments carried out at 0°C, 12°C and 20°C with aeration did not give significant differences that could be attributed to temperature, although the 12°C curve did show the slight peak mentioned before. As the work is to study changes in cave waters, which are always below 12°C, no higher temperatures were used.

5. Similarly the decomposition was repeated at 12°C with and without the added presence of limestone chippings (the oolite mixture used in earlier experiments) The results showed that there is a possibility of added limestone seeding the precipitation of $CaCO_3$ (Fig. 12), although the results are by no means conclusive.

The premise therefore is that limewater saturated with carbon dioxide gas, produces bicarbonate ions which, largely independent of temperature or the presence of limestone, decompose in the following way:-

$$\text{step 1} \quad HCO_3^- \rightleftharpoons CO_2 + OH^-$$
$$\text{step 2} \quad HCO_3^- + OH^- \rightleftharpoons CO_3^{2-} \quad H_2O$$

Step 2 comes to equilibrium dependant on the concentrations of carbonate and bicarbonate present and the solubility of calcium carbonate at the temperature of the experiments; with low concentrations the step can be very slow in occurring.

## CONCLUSIONS

From the fieldwork and laboratory work done so far it is proposed that:-

(a) Peaty water sinking into limestone strata will contain dissolved carbon dioxide as well as lignin acids.

$$H_2O + CO_2 \rightleftharpoons H_2CO_3$$

(b) It will dissolve limestone to produce bicarbonate ions in solution (as well as organic calcium complexes).

$$H_2CO_3 + CaCO_3 \longrightarrow Ca^{2+} + 2HCO_3^-$$

(c) Aeration of this water within the rock fissures will enable decomposition of the bicarbonate to occur producing hydroxide ions and resulting in a rise in pH to between 7.6 and 8.0

$$HCO_3^- \rightleftharpoons CO_2 + OH^-$$

(d) The hydroxide produced will often cause a second process to occur resulting in the production of a colloidal or finely divided suspension of calcium carbonate,

$$HCO_3^- + OH^- \rightleftharpoons CO_3^{2-} + H_2O$$
$$CO_3^{2-} + Ca^{2+} \rightleftharpoons CaCO_3 \text{ (solid)}$$

(e) As a result, cave streams carry suspensions though the system and these are still present in the resurgence waters even after the streams have flowed long distances over long periods of time in the cave.

(f) The calcium ions in solution are capable of being estimated by Flame Photometry, whereas acid treatment is necessary for the carbonate suspension to be estimated and EDTA titration will give the total calcium present.

Whether these suspensions play a part in the production of stalagmite or travertine has yet to be ascertained, as has the exact nature of the organic calcium complexes carried by the streams. Further work may shed some light on these problems.

## ACKNOWLEDGEMENTS

Thanks are due to Ian Penney and other C.S.S. members for their co-operation over several years.

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# ASPECTS OF THE GEOLOGY OF TWO CONTRASTED SOUTH AFRICAN KARST AREAS

Margaret E. Marker

"Dedicated to the memory of Pop Sweeting".

ABSTRACT

The general characteristics of two contrasted South African karst assemblages are compared. The northeastern Transvaal karst is developed on proterozoic Malmani dolomite of the Transvaal System whereas the eastern Cape karst is associated with the sandy Alexandria Formation of the Tertiary Coastal Limestones. Geological information has been collated and preliminary lithological analyses are reported. The differences between the two rock types are stressed in an attempt to explain the karst variation.

As late as 1972 the statement that 'karsts are relatively rare in central and southern Africa' (Sweeting 1972, p.8) could still be accepted. Since then, however, the increasing tempo of karst research has revealed the extent and complexity of southern African karst regions. Potential karst host rocks are widespread and give rise to considerable regional variation in karst landform assemblage characteristics (fig. 1). Such geographical variation in assemblage has been attributed to the differing interplay of parameters significant to karst evolution. Historically, stage of development, climatic controls of the solution process and lithological factors have been accorded chief weight, in that order, but others are also of significance.

In view of 'Pop' Sweeting's sustained interest in South African karst discoveries and his association with pioneer work on their karst lithologies, it seems appropriate to devote this memorial paper to geological aspects of two contrasted South African karst assemblages.

The two areas are the karst provinces of the northeastern Transvaal and of the Eastern Cape. The northeastern Transvaal karst province is associated with the eastern limb of the Proterozoic Malmani dolomite, in an 300 km arc from Potgietersrus (latitude 25°S) to Carolina (latitude 26°S). The Alexandria Formation of the Tertiary Coastal Limestones, that hosts the Eastern Cape karst, is situated astride 33°50'S between the Sundays River and the Great Fish River. By virtue of their locations these two areas have contrasted climatic regimes (fig. 2). The northeastern Transvaal karst lies within the subtropical summer rainfall regime. Annual rainfall, being controlled by relief that ranges from 1 800 to 500 m, varies from 2 000 mm along the eastern escarpment to 550 mm in interior valleys. The lower 30 - 250 m Coastal Limestones are affected by coastal cyclonic disturbances and may receive rain in any month although spring and autumn maxima are usual.

## KARST CHARACTERISTICS

The northeastern Transvaal karst may be subdivided into a northern, Strydpoort mountain region, dissected by steeply incised valleys and a southern, Blyde region where valley development is more advanced and karst plains associated with cones are characteristic (fig. 3). The Strydpoort has a slightly greater amount of thin soil-covered or bare slopes with a concomitant more marked development of karren types. Both areas have characteristic karst hydrology and extensive cave systems. Point input of surface waters is rare, underground waters being derived from surface infiltration. Chemical concentration in karst waters tends to be higher in the north than in the south, a feature apparently constant throughout the evolution of the karst assemblage since tufa deposits, many now relict in the landscape, are virtually confined to the northern karst. Although undoubtedly karstic, the density of karst landforms is relatively low, being inhibited by a high ratio of surface runoff on steep slopes, the deep residuum and the age of the karst.

The complex karst of the sandy limestones of the coastal Alexandria Formation is in complete contrast. Enclosed hollows of varying dimensions predominate and caves are absent. Shallow dolines (pans) are most common and their present distribution extends beyond the limits of the limestone outcrop suggesting that they may have been let down through thin limestone into underlying Cape System rocks. Poljes and uvalas, associated with blind valleys, are more localised, being concentrated immediately inland of the coast between

Table 1. SUMMARY OF KARST CHARACTERISTICS

| AREA | N E TRANSVAAL<br>Blyde (N) | <br>Strydpoort (S) | E CAPE |
|---|---|---|---|
| GEOLOGY<br>Rock<br>Age | Transvaal System<br>Malmani dolomite<br>Proterozoic | | Coastal Limestones<br>Alexandria Formation<br>Tertiary |
| SURFACE COVER | Slight | Slight | Deep soil or sands |
| MEAN ELEVATION (m) | 1 400 | 1 600 | 60 - 250 |
| Mean Range relief | 500 | 600 | 200 |
| CLIMATE | | | |
| T°C max. | 20 | 20 | 22 |
| T°C min. | 11 | 11 | 14 |
| Rainfall p.a. (mm) | 900 | 700 | 650 |
| LANDFORM ASSEMBLAGE | | | |
| Pan dolines | | | * |
| Shaft dolines | * | * | |
| Funnel dolines | * | * | * |
| Uvalas | | | * |
| Poljes | | | * |
| Karst plains | * | * | |
| Cones | * | | |
| Caves | * | * | |
| Karren | * | * | only coastal |
| Springs | * | * | * |

Table 2. ASPECTS OF THE SOUTH AFRICAN GEOLOGICAL SUCCESSION

| | | | |
|---|---|---|---|
| QUATERNARY | | | |
| TERTIARY | Coastal Limestones | | |
| MESOZOIC | | | |
| PALAEOZOIC | Cape System ($\pm$ 3,0 - 3,3 million years) | | |
| PRE-CAMBRIAN | | | |
| PROTEROZOIC | Transvaal System ($\pm$ 2 200 million years) | Pretoria Series | |
| | | Malmani Dolomite | Mixed Zone<br>Upper Dolomite & Chert<br>Chert poor Zone<br>Lower Dolomite & Chert<br>Transition Zone |
| | | Black Reef Formation | |

Springmount and Boknes (fig. 4). These poljes flood after heavy rain to drain through dolines in the alluvial covered floors. Larger poljes such as Zuney and Kaba Kloof have considerable non-karst catchments and probably owe their dimensions to the greater volume of aggressive floodwaters. Underground drainage appears to be organised into discrete karst channels since major springs emerge along the coast at the basal contact of the limestone. The hydrology is complicated, however, by the effects of Cenozoic marine stillstands that have resulted in a stepped topography and a number of discrete, former piezometric levels. Furthermore the limestone itself is progressively younger seawards having been deposited as a veneer on a suite of Cape System benches (Ruddock 1968). This results in springs inland, additional to those of the major aquifer emergences along the coast.

The distinction between the localised polje-uvala karst and the more extensive but lower density pan doline karst is probably a function of the thickness of limestone available. Inland and eastwards the limestone is usually patchy and thin (2 - 3 m) whereas at C Padrone itself, 37 m of limestone resting on Cape System rocks, are known and at Thornhill in the centre of a uvala concentration over 100 to 150 m of sands and limestone overlie older rocks.

## GEOLOGICAL CONTRASTS

The contrast in karst characteristics from the northeastern Transvaal to the eastern Cape is marked (table 1). The distinction is maintained by the karst host rocks. Malmani dolomite forms the lower part of the Proterozoic Transvaal System (table 2). By virtue of its age and depositional history it is a highly lithified, well-jointed sparitic dolomitic limestone. In the eastern Cape, the Coastal Limestones are dominantly Tertiary in age and correspondingly less lithified. The limestones are recognised as being progressively younger towards the coast. Cretaceous fossils have been recorded from Lower Need's Camp and Bathurst and Birbury outcrops contain an Eocene fauna (Siesser 1972). Nearer the coast fossils are scarce and the precise age of the deposits is unknown. They pass upwards with little change into Pleistocene calcareous aeolianite sandstones.

### The Malmani Dolomite

In the Transvaal a high proportion of all karst landforms occur within the upper part of the Lower Dolomite and Chert Zone and in the Chert-poor Zone of the Malmani dolomite (table 2). The close interbedding of chert with dolomite in the Bread and Butter Series of the Upper Dolomite and Chert Zone tends to restrict the development of other than a particular form of karren. The Malmani dolomite is essentially a magnesian limestone containing some purer limestone beds. It is believed to have been deposited under cyclic conditions (Button 1973) as a shallow, off-shore deposit characterised by algalmat development (Erikssen 1975). In chemical composition it is variable as to the range of calcium and magnesium content and in the highly variable proportion of silica in the form of quartz grain inclusions (table 3).

Table 3 CHEMICAL COMPOSITION

Malmani Dolomite[1]

| | CaMg Ratio | CaO % | MgO % | $SiO_2$ % | $(FeAl)_2O_3$ % | MnO % |
|---|---|---|---|---|---|---|
| Maloney's Eye | 1 : 0.64 | 29.6 | 18.9 | 2.8 | 2.9 | - |
| Krugersdorp | 1 : 0.69 | 26.6 | 18.2 | 8.7 | 3.5 | 1.1 |
| Pretoria | 1 : 0.37 | 33.5 | 12.2 | 12.2 | 0.9 | 0.3 |

| Alexandria Limestone[2] | $CaCO_3$ | $MgCO_3$ | $SiO_2$ + insol | $(FeAl)O_3$ |
|---|---|---|---|---|
| A Crystalline | 77.3 | 1.4 | 14.5 | 2.0 |
| B Soft Compact | 63.5 | 2.2 | 29.5 | 2.6 |

[1]Quoted from various sources in unpub. Ph D thesis Wits Univ 1971.

[2]Averaged from figures quoted by Wybergh 1920.

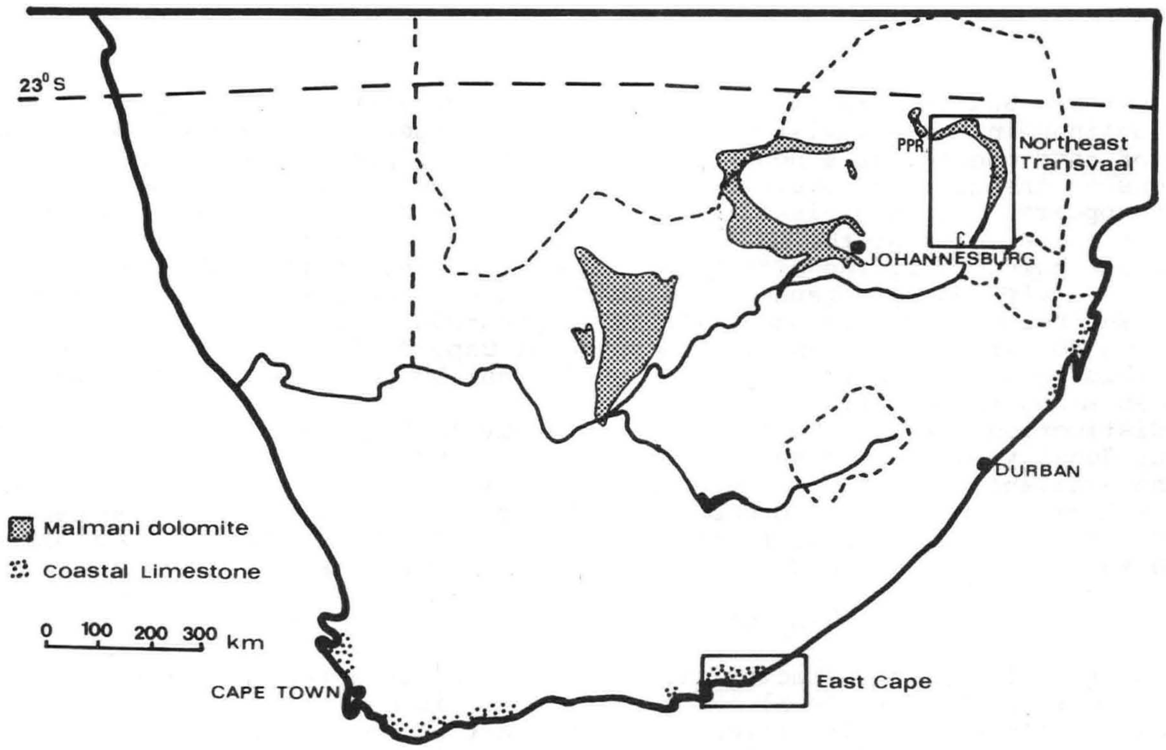


Fig.1 Karst areas of South Africa (PPR= Potgietersrus, C= Carolina)

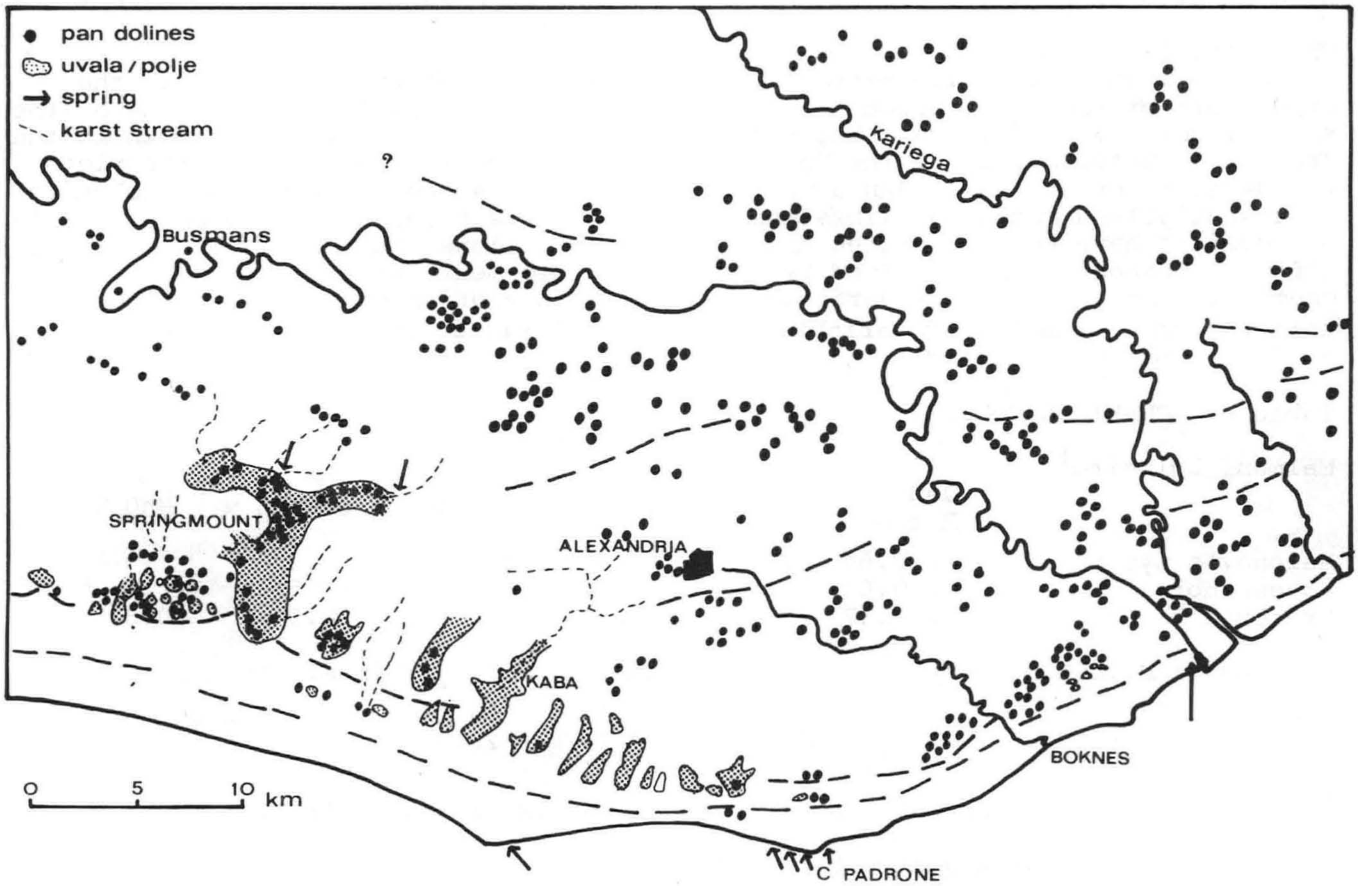


Fig.4 A portion of the Eastern Cape karst region developed on Alexandria Formation limestone

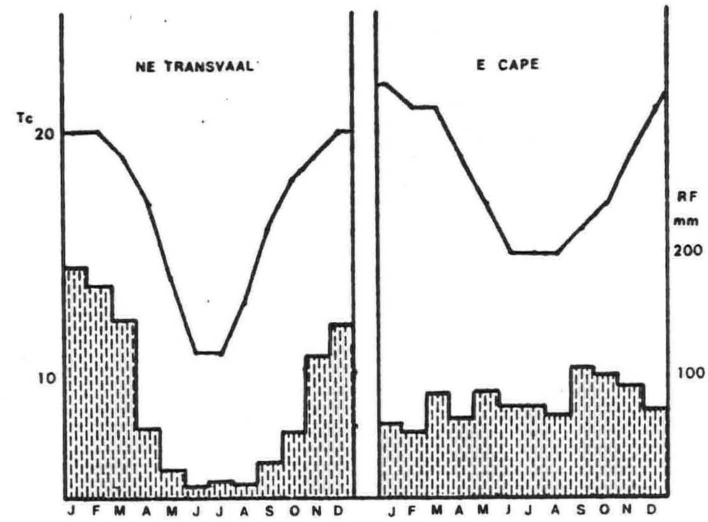


Fig.2 Climatic conditions in the Northeast Transvaal and East Cape.

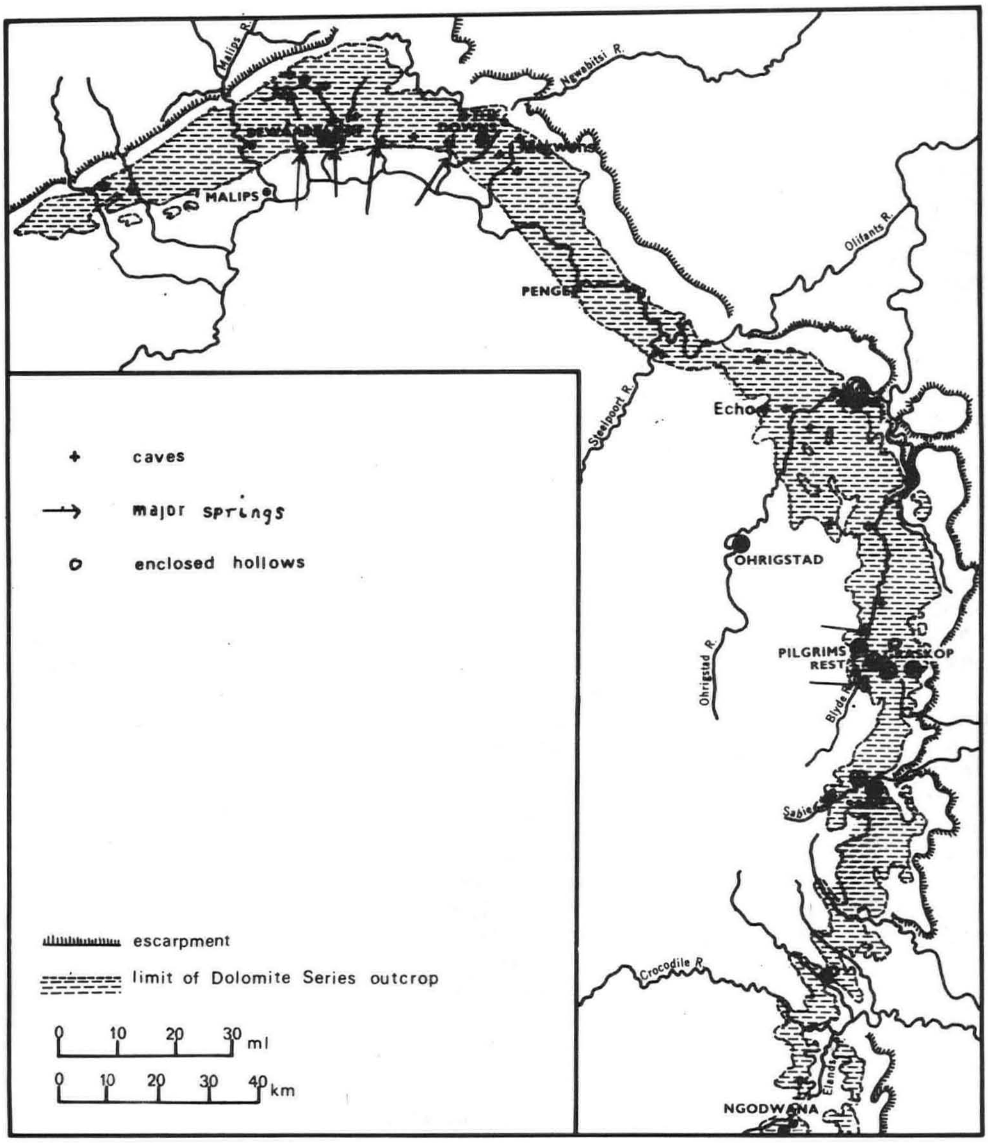


Fig.3 Northeastern Transvaal karst region on Malmani dolomite

More significant than the impurities actually within the dolomite beds, which are less than 12% by weight, is the proportion of interbedded chert, shale and quartzite. These insoluble bands have influenced karst evolution significantly. The rubbly waste mantle on most slopes results from the weathering of the high proportion of insoluble material within the Malmani dolomite. The red earth, a weathering product of the insoluble material, has been washed down to choke the alluviated karst plains and many of the cave systems.

The beds are rarely massive for they are interrupted by horizontal partings and by chert both in bands and as stromatolitic structures. Well-developed joints are characteristic and marked lineaments (major joints) appear to be derived from underlying structures. Since a period of erosion preceeded the deposition of the overlying Pretoria Group, the uppermost beds of the Malmani dolomite now consist of a silicified chert lag breccia variable in stratigraphic position from north to south. Variation in thickness is thus in part due to differences in deposition and in part to subsequent erosion. Thickness is greatest in the centre of the Strydpoort region where it reaches 1 700 m. It thins somewhat west towards Potgietersrus and markedly southwards to 1 000 m in the north of the Blyde region and to only 100 m near Carolina (Button 1973).

Lithologically the dolomites are also variable* (table 4). They range from finely granular, clean dolomitic limestones to a granular inter-mixture of dolomite and calcite resulting from recrystallisation. This series pass into much coarser types : contorted limestones with complex textures to some suggestive of metamorphosed sediments. Some are deformed and the constituents foliated and aligned. In every case where such stress effects are apparent, there is an association with tectonic movements. Incipient dolomitisation is a feature, although thin sections do not show coarse large plates of dolomite such as are seen in European dolomite (table 4). The distinct dolomite rhombs, however, often exhibit dark margins believed to indicate weathering during deposition or consolidation. Recrystallisation, a further stage in alteration, is frequent. Granular calcareous cement between the dolomite rhombs increases pore space and is itself susceptible to solution weathering. These factors render the rocks more susceptible to solution than are dolomites usually.

The Alexandria Formation

In the eastern Cape precise description of the Alexandria Formation are scarce. Most exposures overlie a basal conglomerate of beach origin, resting on older Cape System rocks. Engelbrecht (1962) described the formation as consisting of conglomerates, limestone and sandstone in lenses rather than beds. The limestone is brown to cream crystallised on the surface but softer at depth. Lateral facies variation is significant and lenses of rolled pebbles derived from the underlying rocks are frequent. Wybergh (1920) quoted a section consisting of 1.2 m soft yellow shalky limestone resting on 1.2 m of compact shelly limestone with pebbles on 0.6 m beach conglomerate. A borehole at Glendower passed through 6 m calcareous sandstone resting on 27 m of limestone. At Seaview west of C Padrone, 118 m limestone overlies 11 m calcareous sandstone resting on Cape System shale. Neither constituents nor depths are consistent.

These sandy limestones or calcareous sandstones are inshore or onshore sediments of marine and aeolian provenance. It has been suggested that the thicker, upper deposits are largely of aeolian origin (Engelbrecht 1962). Nevertheless the unsorted nature of the silica constituents would seem to preclude an aeolian origin (table 4). In size range and assortment the grains differ markedly from those from present dune or beach deposits.

The limestones tend to be harder and more crystalline inland where they occur at higher altitudes and are older. Nearer the coast the limestones are friable, rapidly weathering to the constituent sand grains. Considerable chemical variation has been noted (Wybergh 1920) but it appears possible to distinguish the more crystalline, harder, purer limestones from the softer calcareous sandstone (table 5).

*The analyses on which this description is based were carried out by Dr. G. S. Sweeting in 1970.

Table 4. LITHOLOGICAL CHARACTERISTICS OF THE MALMANI DOLOMITE

| AREA | SITE | % POROSITY | RATE OF REACTION WITH HCl | % CALCITE | TYPE OF DOLOMITE | DETAILS |
|---|---|---|---|---|---|---|
| SOUTH BLYDE | Cave | 0,38 | 3 | 0,5 | pure dolomite | fine-medium texture, orderly arrangement of rhombic grains in close contact, little cement, no recrystallisation |
| | Cave | 0,53 | 3 | 5,5 | distorted dolomite | fine-medium texture, fractured dark-rimmed rhombs in grey cloudy matrix, much quartz in grains & aggregates, signs of stress |
| | Doline | 0,26 | 3 | 15,8 | dolomite | medium texture, abundant granular matrix, occasional minute quartz grains, conspicuous pore space |
| | Karren | 0,35 | 4 | 0,8 | incipient dolomite | fine granular texture, grains & veins of calcite, grey muddy cement, incipient dolomitisation, some recrystallisation |
| | Karren | 0,13 | 2 | 0,5 | dolomite | fine grain texture, powdery fine granular cement, many quartz grains |
| NORTH STRYDPOORT | Cave | 1,05 | 4 | 7,5 | dolomite | very fine textures, small dolomite grains, close packing |
| | Cave | 0,15 | 1 | 1,5 | siliceous dolomite | irregular arrangement of intermixed dolomite, calcite & quartz in patches or mosaics |
| | Doline | 0,35 | 3 | 0,1 | dolomite | fine texture, granular cement, small isolated patches of secondary calcite, rare quartz grains, recrystallisation |
| | Karren | 0,34 | 5 | 1,6 | siliceous dolomite | fine-medium texture, irregular rhombs, grey cement, abundant mosaics & patches of quartz, signs of stress |
| | Karren | 0,03 | 5 | 40,0 | dolomite limestone | irregular arrangement of intermixed dolomite, calcite & quartz + large calcite patches, signs of lamination from stress |
| | Karren | 0,10 | 3 | 0,1 | dolomite | fine even texture, dolomite & calcite in clean cement, high porosity |

POROSITY calculated after 24 hours immersion in water.
RATE OF REACTION measured on a nominal scale 1 - 5 (maximum = 5).
All microscopic analyses of Malmani Dolomite samples carried out by Dr G S Sweeting

Table 5 CHEMICAL VARIATION IN COASTAL LIMESTONES

| | % insoluble $SiO_2$ etc | % $(FeAl)_2O_3$ | % $CaCO_3$ | % $MgCO_3$ |
|---|---|---|---|---|
| A Crystalline limestones | 14.5 | 2.0 | 77.3 | 1.4 |
| B Soft compact limestones | 29.5 | 2.6 | 63.5 | 2.2 |

(Average figures derived from Wybergh 1920)

The latter are dominantly coastal and younger although no hard and fast distinction can be sustained.

Limited preliminary sampling and laboratory analyses have been undertaken (table 6). The variability of these limestones in all parameters is confirmed. The limestones can be said to consist of subrounded to subangular quartz grains of variable sizes with some admixture of alien insoluble materials. Fossils, even in a comminuted state, are relatively rare. Powder micrite is the dominant matrix material. In the weakly consolidated samples the quantity is small. Firmer samples have a denser matrix. Slight recrystallisation and alteration to form sparry rims round the sand grains occurs in a few samples. Degree of

Table 6. LITHOLOGICAL CHARACTERISTICS OF THE COASTAL LIMESTONES

| | SITE | % POROSITY | RATE OF REACTION WITH HCl | % LOSS IN HCl ($CaCO_3$) | STRUCTURE | MATRIX | GENERAL DESCRIPTION |
|---|---|---|---|---|---|---|---|
| INLAND A ± 200 m | Bathurst 1 | 2,7 | 3 | 28 | Hard | Sparite rims | Unsorted medium to small subrounded Si grains with Fe staining in partially altered micrite matrix |
| | Bathurst 2 | 2,2 | 5 | ? | Fairly hard | Dom. sparite small amount micrite | Unsorted subangular large (,75 mm) Si grains shell fragments in dominantly sparitic cement |
| | Birbury 1 | 5,6 | 4 | 23 | Fairly hard | Dense micrite | Moderately sorted medium to fine subrounded Si grains in firm micrite matrix |
| | Birbury 2 | 1,0 | 2 | 5 | Hard conglo-merate | Recrystallised micrite becoming sparite | Unsorted angular Si grains with varied other minerals, boulders and fossils in altered micrite cement |
| | Thornhill | 5,7 | 5 | 16 | Mod Consol | Dense micrite | Moderately sorted medium small sub-rounded Si grains with some impurities |
| | Patoskop | 0,6 | 3 | 60 | Very hard crystal-line | Sparite as flow-stone | Fine Si grains with large Ostrea fossils in flowstone sparite |
| ± 100-150 m B | Kaba Kloof | 1,8 | 4 | 13 | Friable | Restricted micrite + platy calcite | Sorted small rounded Si grains and shell fragments with platy calcite |
| | Langkloof | ? | 5 | 11 | Friable | Partially crys-talline micrite | Relatively wellsorted medium to fine subrounded Si grains in partially altered micrite matrix |
| | Langebos | ? | 4 | 15 | Friable | Powder micrite | Assorted small to very fine rounded Si grains in powder micrite matrix |
| | Springmount | 0,7 | 5 | 14 | Mod consol | Dense micrite | Unsorted medium-small subrounded Si grains and other minerals in micrite matrix |
| < 60 m C | C Padrone | 8,3 | 4 | 13 | Hard calcrete | Micrite with sparite rims all sparite on surface | Unsorted small subangular Si grains sparitic cement |
| | Cannon Rocks | 11,0 | 4 | 10 | Hard compact | Dense micrite | Unsorted medium to small subrounded Si grains in micrite cement |
| | Port Alfred 1 | - | 4 | 26 | Mod consol | Micrite powder | Assorted small subrounded Si grains in powder micrite matrix |
| | Port Alfred 2 | 14,7 | 4 | 61 | Mod consol | Micrite slight crystallisation | Moderately sorted medium-small sub-rounded Si grains in micrite matrix |

alteration shows some correlation with distance inland. At higher elevations and in exposed surface samples where calcretisation has occurred, consolidation and recrystallisation is much more marked. These samples have a lower percentage of quartz grains as though re-working had permitted loss of some of the grains and compaction of calcite at depth.

The Alexandria Formation limestones are thus in reality calcareous sandstones. They undoubtedly host a complex surface karst and hydrological system yet their impurity creates a weak rock susceptible to fast disintegration and production of surface sands. The distribution of karst forms suggests that the solution process is joint controlled yet joints are rarely visible in the limited surface exposures. Solution must act on the matrix material where water entry is concentrated. The lack of caves can be attributed directly to the incoherent host rock.

## FINAL ASSESSMENT

The northeastern Transvaal Malmani dolomite karst is entirely different from the eastern Cape Coastal Limestone karst. The former is associated with a sparitic, well-jointed compact, resistant magnesian limestone whereas the latter is developed on incompletely lithified, incoherent sandy limestones. In the former, karst density is low although individual landforms may be of large dimensions. In the latter, surface karst densities are high in selected areas. The marked differences in karst assemblages have, by implication, been attributed to geological differences and in particular to lithology. Nevertheless climatic conditions also differ. Consideration must be given to the influence of climatic parameters. In the northeastern Transvaal, annual temperature ranges from 20° to 11°C. In the eastern Cape the range is 22° to 15°C (fig. 2). Such differences are almost insignificant, more particularly as everywhere in South Africa water availability is the chief constraint. In the northeastern Transvaal, annual total precipitation varies from 2 000 mm to about 550 mm away from the Escarpment and in rainshadow valleys. In addition 26% variance in annual precipitation is the norm. Precipitation totals in the eastern Cape are similarly variable and relief dependant, ranging from 960 mm near the coast south of Alexandria to 450 mm inland close to the Sundays river. In the summer rainfall Transvaal, the solution process is virtually ineffective between the end of March and October because of both lack of water and lack of biotic $CO_2$ during plant dormancy. Drought years cause further restrictions. In the eastern Cape seasonal drought is of lesser significance than annual variation. In both areas karst solution is thus restricted by prevailing climatic conditions. The degree of difference in the climatic parameters, however, appears to be too slight to explain the marked variation in the karst assemblages. Furthermore, work in the northeastern Transvaal has already indicated that climatic differences exert too small a control to account for the assemblage differences, so these have been attributed to lithological variation.

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Margaret Marker,
Geography Department,
University of Fort Hare,
Alice, Cape Province.

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