A Study of Limestone Solution in North-west Co. Clare, Eire

By

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New chemical techniques have resulted in a number of recent quantitative studies concerned with the process and rate of limestone solution. These studies have usually been based upon the analysis of only a small number of water samples, the number of underground samples being particularly limited. The results presented in this paper are an attempt to analyse a large number of samples from a variety of sites in a relatively limited area of limestone. The results for varying types of site are presented under separate headings, namely swallets, simple canyon passage caves, cave systems, risings, cave drips and wells. In conclusion an attempt is made to outline a "model" to describe the overall pattern of solution for the area.

The major limitation of this study was that samples could only be collected during a restricted period of time. The majority of samples were collected between July 5th and 19th, 1963, but a reconnaissance survey undertaken in July, 1961, is referred to where appropriate. Most of the samples were analysed within 24 hours of their collection. The samples were titrated using E.D.T.A. (for details of the method see Ingle Smith and Mead, 1962, p. 209). The titration is for calcium content, but in order to render the results comparable to other similar work the results are presented in terms of parts per million (hereafter p.p.m.) calcium carbonate. The absolute range of error was of the order of 5 p.p.m. $CaCO_3$.

No specific reference is made in the paper to water temperatures or magnesium carbonate content. These were, however, studied in the field; the temperatures during the period of study varied from 9° C. to 18° C. and are only of real importance in comparing the results with those of climatically different areas. The magnesium values constituted, in all cases, only some 5 per cent of the calcium value.

A location map relevant to the locality discussed has been previously published by the University of Bristol Spelæological Society (Ollier and Tratman, 1956, Plate 6). Reference is also made to specific cave plans published by this Society.

SWALLETS

Throughout the period of study in July, 1963, samples were collected from the swallets at Pollcahercloggaun East and Pollcragreagh (Ollier and

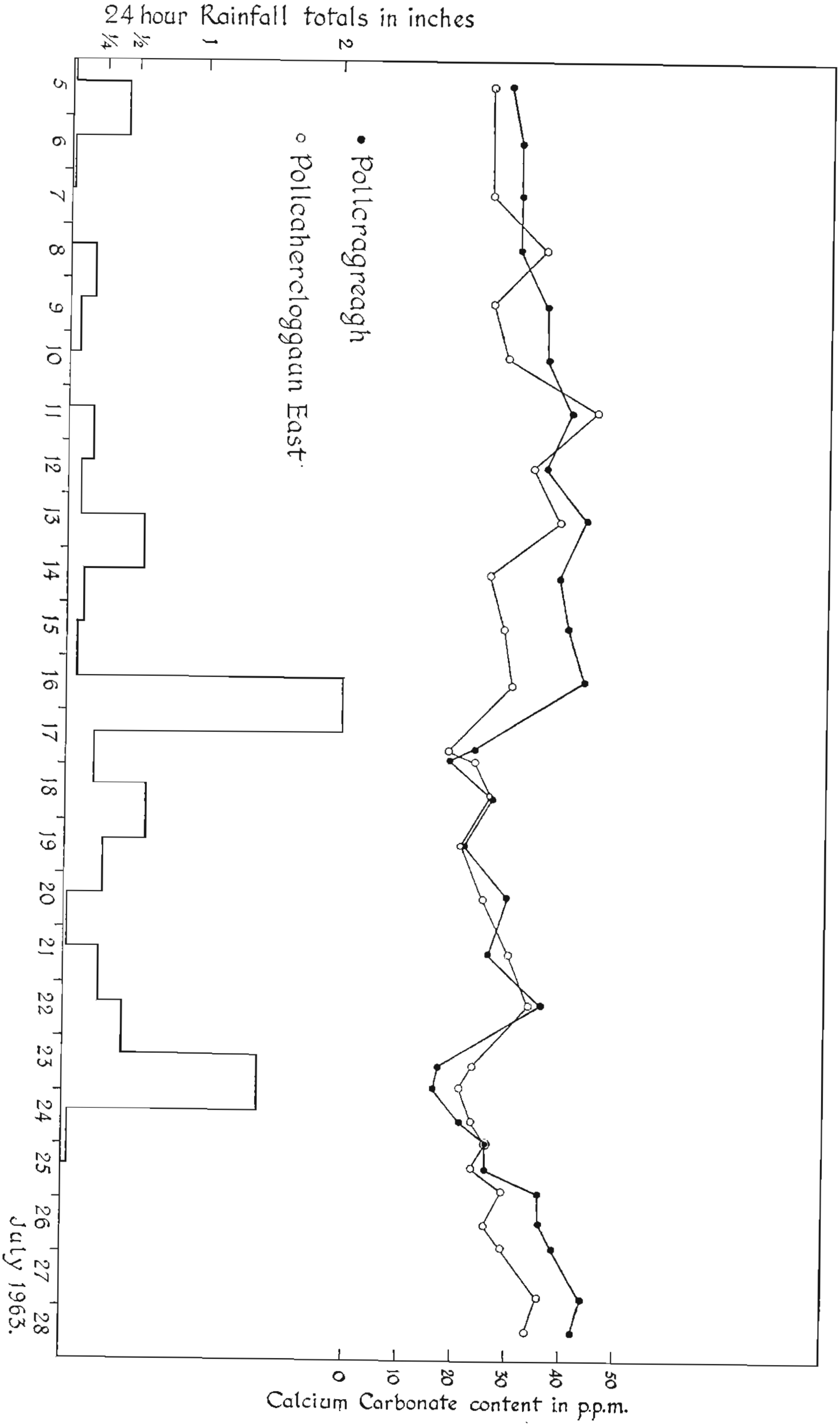

Fig. 19.—Relationship of rainfall to calcium content for the swallets Pollcragreagh and Pollcahercloggaun East.

Tratman, 1956, Plate 6, E13 and E12)* at least once a day (the time of collection was noted). The variations in calcium content (expressed in p.p.m. $CaCO_3$) are shown in *Fig.* 19. The values for Pollcahercloggaun East vary from a maximum of 45 p.p.m. $CaCO_3$ to a minimum of 18 p.p.m. $CaCO_3$ whilst Pollcragreagh exhibits a variation from 44 to 16 p.p.m. $CaCO_3$. There is a distinct relationship between variations in calcium content and rainfall figures. There is clearly a lag effect between the rainfall peaks and the corresponding minima of calcium content. The nature of the rainfall observations, which are 24-hour rain-gauge totals observed at 9 a.m. on the day of observation, and the frequency of the water sampling do not enable an accurate figure to be given for this time lag, but it appears to be of the order of 12 hours.

The rainfall totals in *Fig.* 19 are from the station at Corkscrew Hill, which is situated at an elevation of some 650 ft. on the south-eastern slopes of Poulacapple in the townland of Doonyvardan. This situation is considered to reflect the rainfall conditions experienced in the catchment areas of the two swallets studied more accurately than the other neighbouring meteorological stations at Kilfenora or Ballyvaughan.

In addition to the regular sampling of these two swallets, samples were collected from some twenty-five other swallets. Because of the variation of calcium content with discharge it is considered unwise to give an overall average for these swallets. The values for eight small streams feeding the Poulnagollum–Poulelva cave system between Pollnua (E4) to the north and Bullock Pot to the south give an average of 12 p.p.m. $CaCO_3$, the highest figure being 21 p.p.m. and the lowest 8 p.p.m. (for location see Collingridge *et al.*, 1962, *Fig.* 52). All eight samples were collected on July 18th; the relationship of these figures to the prevailing rainfall conditions can be seen from *Fig.* 19. Three other swallets in the Polldubh area (B1–B3) give values of 3, 13 and 25 p.p.m. $CaCO_3$ for July 14th. St. Catherine's I (D5), Ia and III (D6) give values of 45, 38 and 40 p.p.m. $CaCO_3$ respectively, the date of collection was July 15th.

The sampling undertaken in July, 1961, was less detailed than in 1963 but is of interest due to a prolonged spell of continuous rainfall, the station at Corkscrew Hill recording some 9 in. in 5 days. The resulting floods were the most severe experienced in the area for twenty or more years. The calcium content of the swallet water was greatly reduced. Polldonough (B7) with a value of 15 p.p.m. $CaCO_3$ can be considered typical of these conditions; values obtained under more normal discharge conditions in July, 1961, were 38 and 45 p.p.m. $CaCO_3$ and on July 15th, 1963, the value was

* Hereafter the reference letter and number given in brackets after a named site refer to this map.

40 p.p.m. $CaCO_3$. Under flood conditions the majority of swallets yielded a figure of less than 20 p.p.m. $CaCO_3$; a notable exception was Noughaval at 85 p.p.m. $CaCO_3$.

The calcium figures for swallet streams presented above do not correspond closely with the values given for this area by Corbel (1957, p. 371). Corbel states the calcium values for the swallets in the Poulnagollum–Poulelva area as in the range 45–55 p.p.m. $CaCO_3$; however, the number of samples analysed, the run-off conditions and the method of chemical analysis employed are not discussed. The values given by Corbel closely match those of Coleman and Dunnington (1944, Appendix I, p. 129) obtained from four samples of swallet water; again the run-off conditions are not discussed, the calcium values were ascertained by soap solution methods.

CAVES

The caves of north-west Co. Clare can be considered to be of two types. There are those caves that, in a generalized manner, can be regarded as simple canyon passages and are fed by a single stream swallet. Secondly, there are the more complex caves with several series of passages fed by a number of stream swallets; these we can term cave systems. In detail this division is more difficult to sustain as the following account will illustrate.

Simple Canyon Passage Caves

Attempts were made to study the calcium content of streams flowing in simple canyon passage caves in the hope that the increase of calcium content between the entrance swallet and the furthest accessible point of the cave stream would enable the rate of solutional erosion of the cave passage to be assessed. However, no conclusive results were obtained, due to the fact that measurable increases in the calcium content of the stream water were either associated with the junction of small underground tributaries or increases in calcium content were within the range of error of the method of titration. In addition to these complications a small quantity of highly calcium-rich water was added to the stream by drips falling from the cave roof.

Measurements of this kind were attempted in a number of canyon passage caves. The results for three such caves, considered typical of the overall pattern, are presented below.

Cullaun 1 (C1). The values show a gradual increase in calcium content. However, studied in more detail this simple pattern is perhaps somewhat misleading. Samples collected on other occasions demonstrated that the solution process in the section above the "Normal Entrance" is not simple. There are many seepages whose volume and calcium content are sufficient to influence the calcium content of the main stream. In addition to the seepages there is also a major tributary. This tributary has only flowed over some

(Samples collected on July 10th.)

Location	A	B
Stream at the surface, flowing on shale	—	12·5
Deep, open U-shaped channel, at surface	60	21
Typical subterranean canyon passage	210	22·5
"Normal Entrance", unroofed passage	800	40
First Vertical Feature	1,150	48
(Two Pissers)	(1,650)	(78)
	1,725	58
(Main Tributary)	(1,740)	(73)
	2,400	63
Just upstream of First Bedding Plane	3,350	60
Top of First Pot	3,600	70

Column A—Distance from the shale/limestone boundary in feet.
Column B—Calcium content in p.p.m. $CaCO_3$.
Locations and values in brackets are for tributaries to the main Cullaun 1 Stream.

200 ft. of limestone and joins the main stream some 400 ft. above the "Normal Entrance"; this has some dilution effect. The Two Pissers and the "Main Tributary"* derive water from both Cullaun Zero-1 and Cullaun Zero although they may also be influenced by additional underground feeders. The relatively long distance travelled by these streams may account for their calcium content being in excess of the main Cullaun 1 stream at their points of junction.

The figures for Cullaun 1 show a rapid increase in the calcium values in the initial part of the stream course, and despite the complications mentioned above this rapid increase is typical of the results from other swallets in the area of study.

Pollcahercloggaun West (*E*14) *and West*-1. (Samples collected on July 10th.)

Pollcahercloggaun West-1

Distance from cave entrance in feet	0	368	700	1,070	1,660
Calcium content in p.p.m. $CaCO_3$	52·5	55	57·5	57·5	67·5

The stream in Pollcahercloggaun West-1 is small and flows in a narrow canyon passage. The only appreciable additions are two strong drips at approximately 1,400 ft. from the entrance. Pollcahercloggaun West joins West-1 at 1,660 ft.; it is similar in size and passage form and has flowed a comparable distance from the shale edge. The calcium content of Pollcahercloggaun West at the junction is 70 p.p.m. $CaCO_3$. Both streams flow for a short distance over limestone after leaving the shales and before their points of engulfment. On July 14th the calcium values at the swallets were, for West-1 47·5 p.p.m. $CaCO_3$ and for West 42·5 p.p.m. $CaCO_3$. A

* The "Main Tributary" is the stream referred to, mistakenly, as the "Main Stream" by Acke (1954, p. 13).

value for the West stream 200 ft. above the swallet and situated on the shale was 28 p.p.m. $CaCO_3$. The strong initial "pick-up" of calcium is again suggested.

Cullaun 5 (C5). The terminal figure for Cullaun 5 was 68 p.p.m. $CaCO_3$. This overall figure is the resultant of several individual feeders whose values are 73 (the main stream), 103, 35, 83, 35 and 48 p.p.m. $CaCO_3$. The value of 103 p.p.m. $CaCO_3$ was from a strongly "misfit"* stream flowing from Cullaun 5b and the value of 83 p.p.m. $CaCO_3$ is from a small seepage. The volume of all the tributaries in Cullaun 5 is approximately equal to the volume of the main stream at the cave entrance. Here again the complex yields a final figure of approximately 70 p.p.m. $CaCO_3$ and those tributaries of Cullaun 5 and of other simple canyon passage caves that have calcium values markedly in excess of 70 p.p.m. $CaCO_3$ are not of the "simple canyon passage" type.

A more detailed study was made for the Cullaun 5d† tributary. The calcium values for samples collected on July 7th were as follows:

Location	Distance from Cave Entrance in Feet	Calcium Content in p.p.m. $CaCO_3$
Entrance	20	30
	75	30
	200	32·5
Waterfall—Top	420	42·5
Waterfall—Bottom	420	42·5
	1,000	45
Water leaves passage	1,500	42·5

The only measurable increase, outside the range of error of the titration, in Cullaun 5d, is probably accounted for by a small tributary (48 p.p.m. $CaCO_3$) and a number of drips some 300 ft. from the entrance.

Cave Systems

Two cave systems were studied in some detail, namely the Doolin Cave System and the Poulnagollum–Poulelva Caves. The former is the simpler system and the average calcium carbonate values for two sets of samples collected on July 8th and 15th, 1963, are given in *Fig.* 20.‡

Samples collected on July 6th, 1963, exhibit a similar overall pattern, although the values are lower than for the "average" values plotted in *Fig.* 20, e.g., St. Catherine's 1 entrance (D5), 30 (average 48), Aran View tributary

* The passage is an old original route, beheaded near 5b. It now carries only minor streams, mostly small trickles under ordinary flow.

† Not on map.

‡ The cave survey from which *Fig.* 20 was drawn is basically that of Robertson *et al.* (1956, Plate 7).

(D2), 135 (171) and Fisherstreet Pot (D1), 83 (118) p.p.m. $CaCO_3$. This suggests that the calcium content of all the major components of the cave system varies markedly with discharge conditions. The nature of the run-off conditions for July 6th, 8th and 15th can be assessed from the rainfall amounts given in *Fig.* 19.

Considering the average figures it is noticeable that the swallets in the St. Catherine's branch of the system exhibit values of some 40 p.p.m. $CaCO_3$ and the tributaries have values of some 70 p.p.m. $CaCO_3$. In the lower parts of the cave system the values of stream samples may well be complicated by the possibility of water seeping in from the surface Aille River which crosses directly over the line of the cave. The cave roof is only some 20–30 ft.

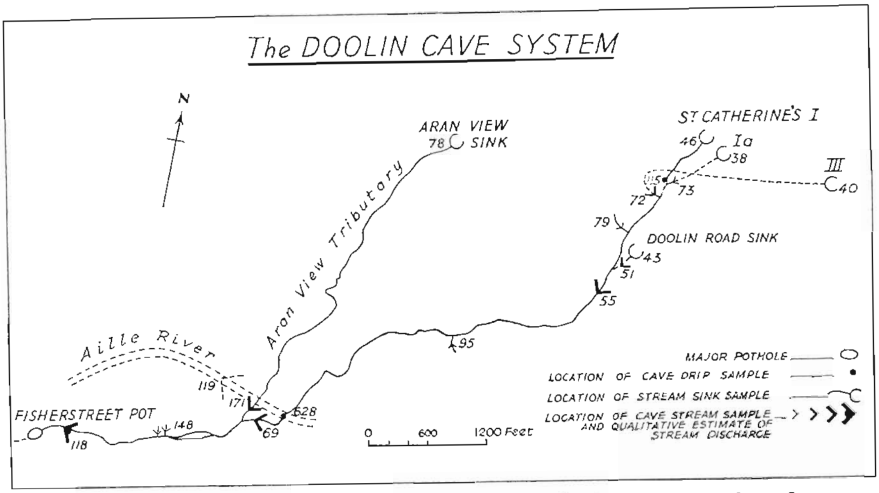

Fig. 20.—Location and calcium content of water samples in the Doolin Cave System. (All figures are in p.p.m. $CaCO_3$.)

beneath the river bed. In times of low discharge the Aille River does not flow as a surface stream far beyond this section of its course.

The calcium content of the Aran View Tributary is surprisingly high. The stream has a normal surface swallet but it has been artificially modified by a farmer's canal producing a rather complex situation under normal flow conditions. The canal crosses over the cave south of the swallet and its waters percolate into the cave at various points. More intensive water sampling in this locality is needed to clarify the situation and to explain the high calcium content of the Aran View water.

Poulnagollum–Poulelva. The Poulnagollum–Poulelva cave system is extensive having a total passage length of nearly 7 miles. A survey of this system has been recently published (Collingridge *et al.*, 1962) and this has rendered it possible for an attempt to be made at a comprehensive survey of the calcium content of the waters of this cave. Water samples were obtained from some thirty-six separate locations in this system, the majority from cave streams. Samples were collected from many of these locations on several occasions during July, 1963, up to a maximum of five. Samples from some of these sites had been collected and analysed in July, 1961. A schematic modification of the 1962 survey is given in *Fig.* 21.

The locations of the sampling points of the streams in the Poulnagollum–Poulelva system, together with the average calcium carbonate values, are given in *Fig.* 21.

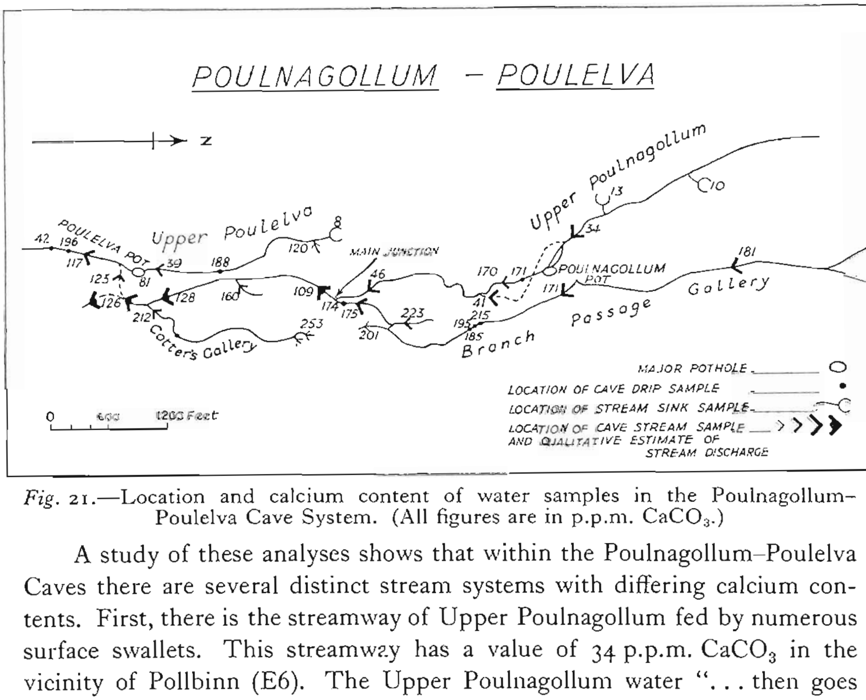

Fig. 21.—Location and calcium content of water samples in the Poulnagollum–Poulelva Cave System. (All figures are in p.p.m. $CaCO_3$.)

A study of these analyses shows that within the Poulnagollum–Poulelva Caves there are several distinct stream systems with differing calcium contents. First, there is the streamway of Upper Poulnagollum fed by numerous surface swallets. This streamway has a value of 34 p.p.m. $CaCO_3$ in the vicinity of Pollbinn (E6). The Upper Poulnagollum water "... then goes off to the right, crosses the roofs of Shaft Gallery and Gunman's Cave, passes through Pollbeg, and reappears as the First Waterfall in Poulnagollum" (Collingridge *et al.*, 1962, p. 221). Analysis of the water at the First Waterfall, at a distance of at least 400 yd. from the Pollbinn sample and collected on the same day, gives a value of 40 p.p.m. $CaCO_3$. Thus the stream described by Collingridge is substantiated by a consideration of the calcium values, it has also been verified by methylene-blue dye tests carried out by this Society and earlier by dye tests conducted by Coleman and Dunnington (1944, p. 129), who quote a figure for the First Waterfall of 65 p.p.m. $CaCO_3$.

The mean value for the stream in Gunman's Cave, from our observations, was 170 p.p.m. $CaCO_3$. Two analyses in July, 1963, gave 158 and 171 and three values of 183, 170 and 161 p.p.m. $CaCO_3$ were obtained in July, 1961. Coleman and Dunnington (1944, p. 129) give a figure of 120 p.p.m. $CaCO_3$ for Gunman's Cave. Corbel (1957, p. 371) also quotes an identical figure to that of Coleman and Dunnington, although he qualifies the sample as "... les eaux stagnantes". In the many years that this Society has visited this cave system the stream in Gunman's Cave has never ceased to flow. These earlier figures for Gunman's Cave do not accord closely with the values obtained by us in 1961 or 1963, which were collected under a wide range of discharge conditions.

The water from Gunman's and Shaft Gallery unites with the flow from the First Waterfall to form the Main Stream of Poulnagollum.

The calcium values in *Table I* show that in Branch Passage Gallery, on four out of five occasions, the difference in calcium carbonate content over a distance of some 800 yd. was within the range of error of the titration methods used. There seem to be two factors which influence the calcium carbonate content of the united Main Stream. First, variations in the calcium carbonate content of the component streams and, secondly, variations in the relative volumes of the two streams involved. *Table I*, in addition to summarizing the calcium figures for part of the Poulnagollum–Poulelva system, also gives the ratio of stream volumes for the Main Stream and the stream from Branch Passage Gallery. The ratio varies with discharge conditions, the samples for July 17th were collected during the subsiding period of a flood, the water level being higher than on any other occasion when the cave was visited in 1963.

Table I

Location	Dates (July 1963)					Mean
	6	12	14	17	18	
First Waterfall	40	43	48	34	39	41
Branch Passage Gallery at Muddy Link (nr. Poulnagollum Pot)	165	173	163	175	181	171
Branch Passage Gallery at Main Junction*	165	173	163	175	196	175
Main Stream at Main Junction	43	46	58	42	42	46
Main Stream, 100 ft. below Main Junction	95	94	128	110	112	109
Ratio of volume of Main Stream to Branch Passage Gallery Stream	4:3	5:3	1:2	1:1	6:5	1:1

The figures in the table are all p.p.m. $CaCO_3$.

* This is the combined waters of Branch Passage Gallery and Branch Passage, the latter component being quite small.

The Branch Passage Gallery stream was not sampled above its junction with the Muddy Link. The source of this stream is twofold. The stream in Branch Passage Gallery East originates beneath a peat-floored depression. There is no swallet associated with this depression, the surface water reaching the stream below by percolation. The Branch Passage Gallery West stream is fed, in part at least, from a group of small swallets along the shale/limestone edge. Dye tests have verified this connexion. It is not clear if the manner of flow is by means of streams in cave passages of limited size or by more impeded flow along joints and bedding planes. Further sampling is required before a more detailed picture of the limestone solution in this portion of the Poulnagollum–Poulelva cave system can be given.

The flow below Main Junction has a mean value from five observations of 109 p.p.m. $CaCO_3$. This value has increased to 128 p.p.m. $CaCO_3$ in the stream just before the junction with the stream from Cotter's Gallery; this increase is accomplished in a distance of some 2,000 ft. A large part of this increase may be due to a tributary joining the main cave stream from the Low Road passage with its higher calcium content of 160 p.p.m. $CaCO_3$. Thus, as with the canyon passage caves, changes in the calcium content of cave streams are probably related to complications of tributary passages. The Cotter's Gallery stream has a value of 212 p.p.m. $CaCO_3$ but its volume is small and it has little effect on the calcium content of the main stream. A short distance below this point the main stream leaves the major cave passage and can only be followed for a short distance.

The situation after this is more complex, but a portion of the Poulnagollum water joins the Poulelva Main Stream as a tributary near to Poulelva Pot; this tributary has a value of 123 p.p.m. $CaCO_3$. The combined flow in the Poulelva Streamway has a value of 117 p.p.m. $CaCO_3$ before the passage which leads to Killeany Rising becomes impassable. Samples collected from Killeany Rising on the same day show a value of 120 p.p.m. $CaCO_3$, but again the situation is complicated since water from at least two swallets is known to join underground with the water flowing from the Poulelva Streamway to Killeany. The swallets concerned are Pollcahircloggaun East and Pollcragreagh.

WELLS

A limited number of water samples were collected from wells. Their location is given in *Table II*. These samples, whilst few in number, were collected from a number of widely scattered localities in the limestone. The majority of the samples were collected in July, 1961.

High calcium values were obtained from two neighbouring wells in the townland of Doolin. One of the wells (1) gave a value of 280 p.p.m. $CaCO_3$ and the other (2) 270 p.p.m. $CaCO_3$. Also in excess of 250 p.p.m. $CaCO_3$

was the sample from a quarry pump (3) which gave a value of 275 p.p.m. $CaCO_3$. This pump, however, yielded a value of 238 p.p.m. $CaCO_3$ 2 days after the peak of the 1961 floods. A pump at Ballymurphy (4) gave 248 p.p.m. $CaCO_3$.

In a slightly different category are the wells situated approximately over the line of the underground streamway between Owenterbolea (F2) and Upper St. Brendan's (F3). Samples from the first of these wells (5) produced values of 190 p.p.m. $CaCO_3$ 2 days after the flood peak of 1961 and after a further 3 days the value was 195 p.p.m. $CaCO_3$. It is worth while to note that at the flood maximum this well began to discharge water in the manner of a natural rising and the value was at least as low as 70 p.p.m. $CaCO_3$. A sample from the second well (6) under normal flow conditions gave a value of 155 p.p.m. $CaCO_3$.

Two further sampling sites near Cahercloggaun (7) and at Tobercornan (8) are perhaps better classified as small risings, the water in these two cases not being raised to the surface manually by pumping. The former, which has a much smaller and slower flow than the latter, gave a value of 223 p.p.m. $CaCO_3$ and the latter 182 p.p.m. $CaCO_3$. Both were collected under moderate discharge conditions in the area in July, 1963.

Table II. LOCATION OF WELLS*
(O.S. 6 in. to 1 mile)

1.	Clare sheet 8	E. 2·5 in.,	N. 12·1 in.
2.	Clare sheet 8	E. 2·5 in.,	N. 11·4 in.
3.	Clare sheet 8	E. 31·9 in.,	N. 19·4 in.
4.	Clare sheet 9	E. 15·0 in.,	N. 12·8 in.
5.	Clare sheet 8	E. 35·8 in.,	N. 17·3 in.
6.	Clare sheet 8	E. 33·0 in.,	N. 17·4 in.
7.	Clare sheet 4	E. 35·6 in.,	N. 0·4 in.
8.	Clare sheet 2	E. 14·3 in.,	N. 10·3 in.

RISINGS

The risings associated with the Coolagh River and Doolin Cave systems are thought to be of a submarine nature and are therefore not available for sampling. A number of small risings occur on the beach at Doolin Strand but their calcium content, varying between 25 and 50 p.p.m. $CaCO_3$, demonstrates that they are not the resurgences of the Doolin Cave system, the terminal values of that system at Fisherstreet Pot (*Fig.* 20) being of the order of 100 p.p.m. $CaCO_3$. The corresponding values for the surface Aille River

* The Irish Ordnance Survey maps of this scale do not at present carry any grid nor are the latitude and longitude recorded. An arbitrary system of reference is given in the table below based on measurements from the south-west corner of each sheet. The measurements are given to the nearest $\frac{1}{10}$ in. (approximately 88 ft.) in the form of eastings and northings. Each O.S. sheet measures approximately 36·3 in. W–E, and 24·2 in. S N.

at the time of collection of the Doolin Strand samples was also some 100 p.p.m. $CaCO_3$. However, other risings are exposed at low tide which were not sampled and these may be related to the Aille River–Doolin Cave system. The origin of the water feeding the beach risings is not clear.

Killeany Rising (F4) is fed by water from several distinct swallets and cave systems. Dye tests conducted at times of low or moderate discharge conditions have demonstrated that water from the west side of the valley appears only at the west side of the rising and that water from the east of the valley reappears at the east of the rising. The known feeders from the west are Poulnagollum–Poulelva, Pollcragreagh and Pollcahercloggaun East, whilst proven drainage lines from the east are from Cullaun 1 and its tributaries, possibly from Cullaun 2.

The combined surface flow from Killeany Rising returns underground at Owenterbolea (F2) to reappear at Lower St. Brendan's Rising (also known as St. Brendan's Well). In times of increased run-off the water rises at Upper St. Brendan's Rising (F3), which is situated between Killeany and Lower St. Brendan's Risings. Subterranean tributaries also feed into this system. A known tributary, verified by a dye test, is from Pollcahercloggaun West which joins the main flow between Owenterbolea and Upper St. Brendan's, as probably does Cullaun 3.

Detailed sampling was undertaken at Killeany and Lower St. Brendan's throughout the period of study and the results are presented in *Fig.* 22. During the course of the sampling at Killeany Rising it became apparent that the calcium values were somewhat irregular. On detailed investigation it was found that the water from the western side of the rising contained a differing amount of calcium to that of the eastern side. The results are shown separately in *Fig.* 22 after July 13th.

As with the swallets, there is a correlation between calcium minima and discharge maxima. A rough qualitative assessment of the discharge conditions was obtained by considering the position of the point of re-engulfment of the water issuing from Killeany Rising. For discharge of a larger order the depth of the water at Killeany road bridge was measured. The pattern of discharge conditions thus obtained is also plotted in *Fig.* 22. The lag between the discharge and its associated calcium minimum and the corresponding rainfall maximum cannot be accurately stated. It appears, however, that the time lag for the risings is very similar to that for the swallets (cf. *Figs.* 19 and 22). For each distinct minimum calcium value at Killeany Rising (i.e., July 17th, 19th–20th and 23rd–24th) the Poulnagollum–Poulelva water reaches its lowest value before that of the Cullaun water and the Lower St. Brendan's Rising is the last to respond. In order to give closer quantitative values to the time lags involved more frequent sampling would be required. The figures for 1961 exhibit similar characteristics. The

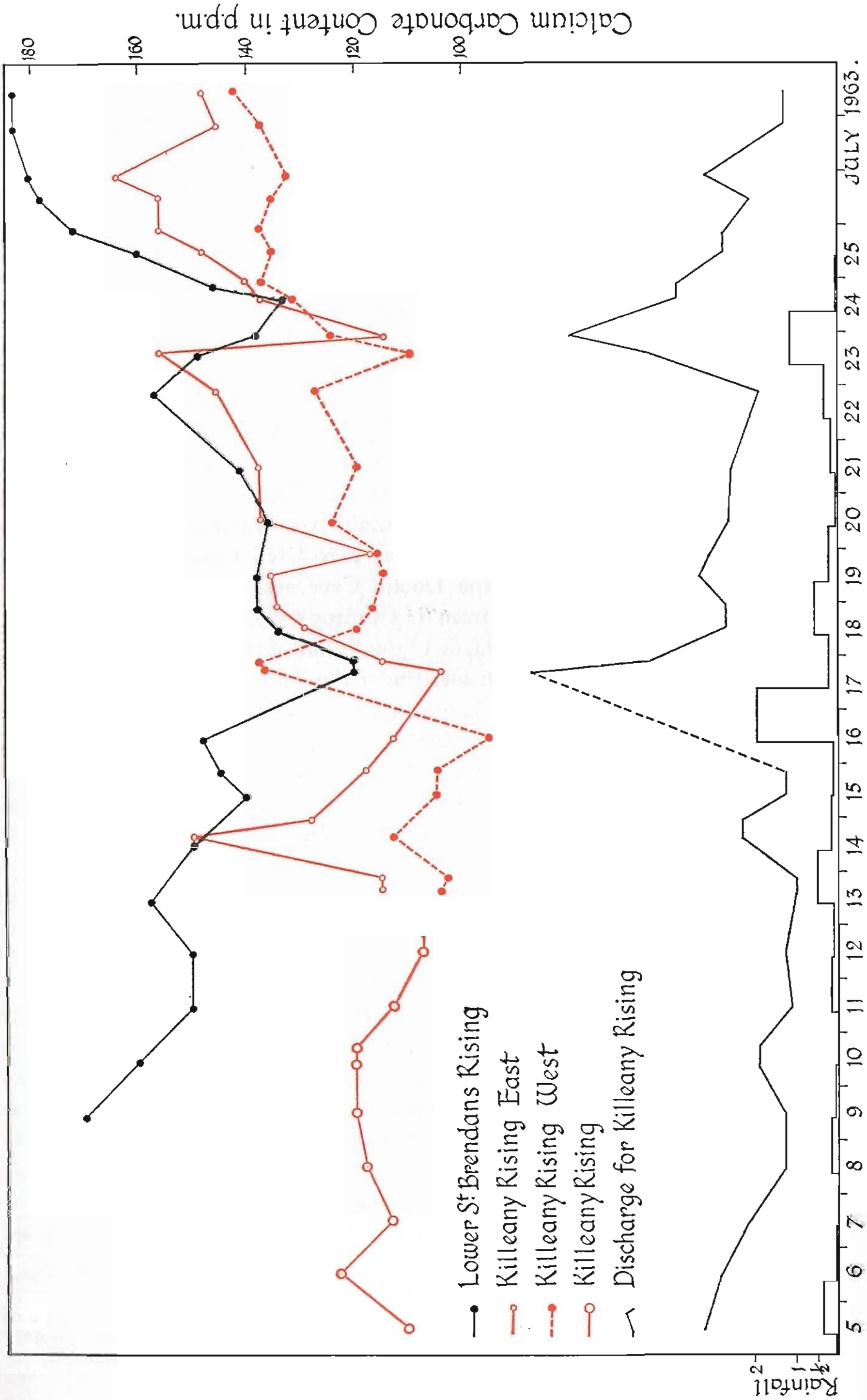

Fig. 22.—Relationship between rainfall, discharge and the calcium content of selected risings.

minimum figure recorded for Lower St. Brendan's Rising fell as low as 88 p.p.m. $CaCO_3$ after the period of heavy rain mentioned above.

A limited number of calcium determinations were obtained for risings associated with the Upper Fergus River (Clare 16). These values were markedly higher, a repeated set of values for four risings varying between 173–260 p.p.m. $CaCO_3$. Again the danger of using only a limited number of values to obtain an overall "average" figure is apparent.

CAVE DRIPS*

Drips were collected from ten sites in the Poulnagollum–Poulelva cave system (for their location see *Fig.* 21). Eight of these sites had values between 171 and 196 p.p.m. $CaCO_3$. A single sample from Cotter's Gallery gave 261 whilst another value was 42 p.p.m. $CaCO_3$. The latter sample was fed directly from an aven† and, as such, naturally has greater affinities with water from swallets than with water that has percolated through the overlying bedrock. Similar values for the Doolin Cave system showed comparable figures, five analyses varying from 113 to 295 p.p.m. $CaCO_3$ (see *Fig.* 20). Mention should, however, be made of one result of some 600 p.p.m. $CaCO_3$, where the main cave passage passes under the Aille. This figure is thought to be due to a heavy natural contamination of the sample by iron which adversely affects the particular titration used (Schwartzenbach, 1957, p. 65). A figure of 420 p.p.m. $CaCO_3$ for water associated with the "Bloody Guts" formation in Cullaun 2 is thought to be due to the same cause. The unusual colour, for the Co. Clare area, of this stalactite perhaps indicates localized iron contamination.

Three values for the Fergus River Cave were 245, 300 and 307, and for Polldubh 185 and 214 p.p.m. $CaCO_3$.

DISCUSSION OF RESULTS

From the above account, which attempts to outline the sites and calcium values of the water samples collected in north-west Co. Clare, it is possible to outline a "model" to describe the limestone solution of the area. The results have been separately presented from the theory in the belief that whilst the observed facts remain of value to later work the theory is clearly of a more ephemeral nature.

One major difficulty in discussing the results is that there is a lack of similar detailed quantitative work on the solution of other limestone areas.

* The term "drip" is used in this paper for water which joins an underground cave passage from the roofs or walls by free fall. There is considerable variation in the volume of water flowing in unit time from any individual drip. After periods of prolonged rain some drips supply volumes of water comparable to small tributary streams.

† The main roof of the cave into which the aven opens is considerably less than 100 ft. below the surface.

The only comparable published study of which the authors are aware is of similar work on Mendip undertaken under the auspices of this Society (Ingle Smith and Mead, 1962). In the limestone area of Mendip the solution model is as follows. Precipitation percolates through the soil cover and reaches equilibrium with the carbon dioxide in the soil air; this is considerably higher than the atmospheric carbon dioxide content. The carbon dioxide content of this percolation water is then utilized in dissolving the calcium carbonate which is the dominant constituent of the limestone. The percolation water finally reappears at the resurgences around the periphery of

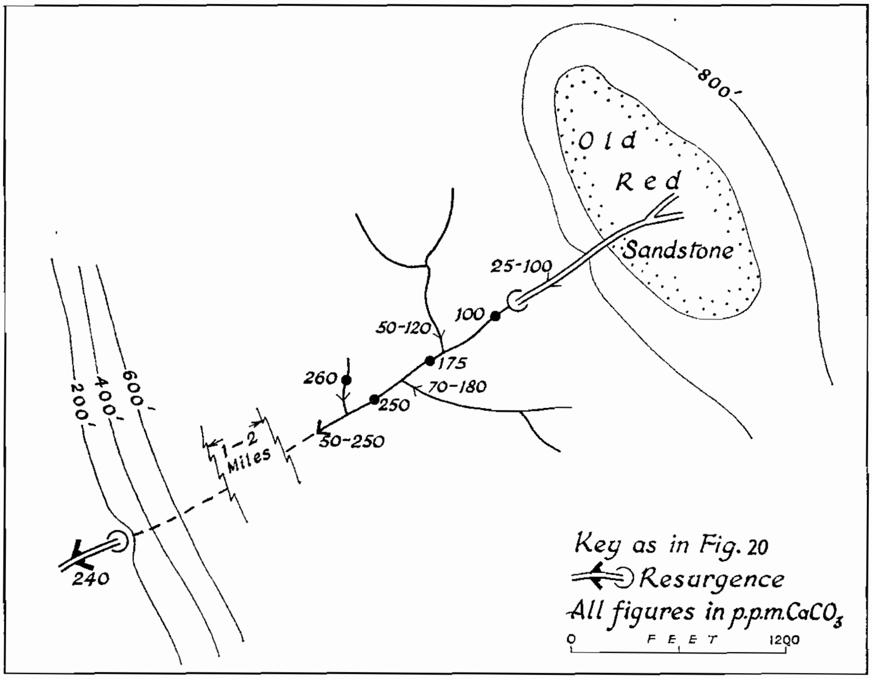

Fig. 23.—Calcium content of subterranean water samples of a hypothetical Mendip cave, Somerset.

Mendip. Intermediate stages in the process can be investigated by a study of the calcium content of the streams and drips in the underground cave passages. The calcium carbonate content of the Mendip risings is of the order of some 235 p.p.m. $CaCO_3$ and, with limited exceptions, remains constant regardless of changes in discharge conditions. The drip water in the caves has a calcium carbonate content which is generally less than 235 p.p.m. calcium carbonate. The Mendip results also show some evidence that the calcium values of the drip water increase with the depth of the drip below the surface, i.e., that water with a high carbon dioxide content obtained from the soil air takes some time to become saturated with calcium carbonate. The proportion of the water at the risings which is of a true swallet origin is thought to form only a fraction of the total discharge (Tratman, 1963, p. 50), the bulk of the discharge at the risings is water of a percolation nature. A diagram showing the typical calcium carbonate values associated with the varying sites in this model is given in *Fig.* 23.

The model for north-west Co. Clare (*Fig.* 24) is of a different nature. The majority of water flowing through the caves is of swallet origin. The catchment area for the swallet water is generally on the shale areas which lie

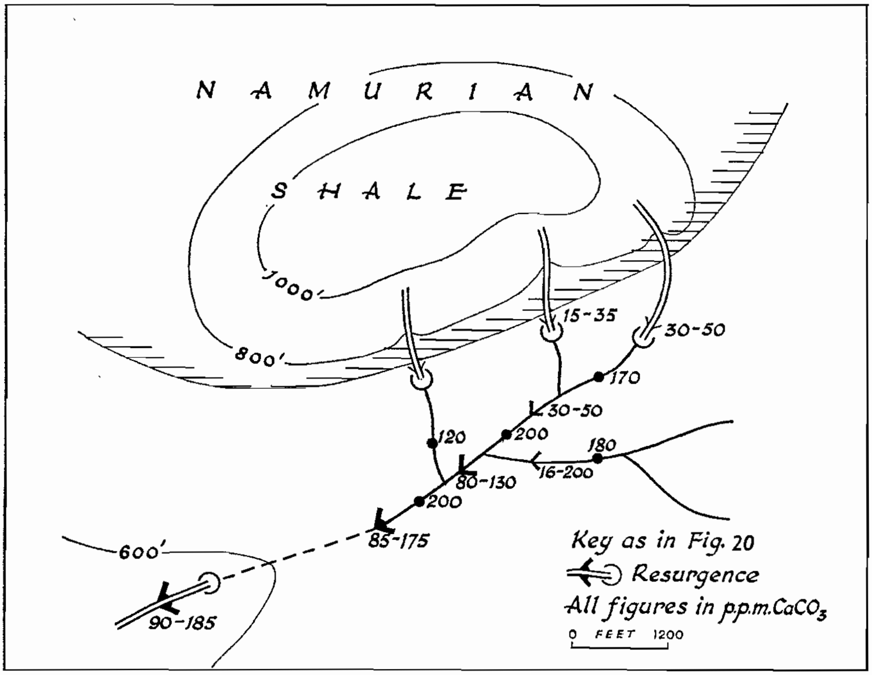

Fig. 24.—Calcium content of subterranean water samples of a hypothetical cave in north-west Co. Clare.

stratigraphically and topographically above the limestones. The major swallets are associated with limestone/shale junction, although the catchment area for some of the smaller cave streams is situated on the limestone outcrop. This situation is borne out by the data outlined above. Cave streams that are fed from stream swallets have low calcium contents, whilst the cave streams with high calcium values are thought to be dominantly fed by water of percolation origin. In the former category is the streamway of Upper Poulnagollum with values of 30–40 p.p.m. $CaCO_3$. In the latter category is the stream in Gunman's Cave with a mean value of 170 p.p.m. $CaCO_3$. The stream in Branch Passage Gallery may, in part at least, owe its high calcium content to the fact that it, too, is fed by percolation water (see p. 127).

It is of interest to note that the simple canyon passage cave streams and the swallets generally exhibit values of less than 70 p.p.m. $CaCO_3$. The maximum calcium value that can be dissolved by water with a carbon dioxide content in equilibrium with the normal atmosphere is 74 p.p.m. $CaCO_3$ at 10° C. It seems possible, therefore, that the water in surface streams is only capable of dissolving some 70 p.p.m. $CaCO_3$. It could be argued that the water in such streams is fed in part from water that has reached the surface stream after percolation through a limited thickness of soil, i.e., the water discharged by the streams is not solely direct surface run-off according to the strictest definition. The delay in response of the surface stream run-off to the corresponding rainfall peak illustrates this lag effect. However, the excess of carbon dioxide that this stream water has acquired by percolation through a limited soil cover may well be lost rapidly back into the atmosphere due to the turbulent nature of the stream flow.

This interpretation, although simple in outline, appears to the authors to be well illustrated by the calcium values of the samples studied in north-west Co. Clare. In this context detail is given in the Appendix to the calcium values for streams studied in the Pyrenees in the summer of 1963. Here there is no close cover of vegetation but the calcium values of surface streams are very similar to those described from Co. Clare. In both areas once the streams begin to flow on limestone there is a rapid initial uptake of calcium carbonate to a value of approximately 40 p.p.m. $CaCO_3$.

Naturally the picture becomes more complex when subterranean streams fed dominantly by swallet stream and percolation water merge (as illustrated in *Table I*). In addition to the complication of these streams of differing origins becoming tributary to one another, there is a small addition of water of a percolation origin, drip water, direct to the cave streams. Since the calcium content of this drip water in the Co. Clare area is normally far in excess of the calcium values for the cave streams they therefore tend to increase the calcium content of the streams.

The risings fed by this complex of stream and drip water show calcium values intermediate between the values of swallet and percolation water. The risings vary markedly in their calcium content in relation to discharge, high discharge being associated with low calcium values, and vice versa. This conflicts with the model for the Mendips outlined earlier. However, in the Co. Clare model there is a short and direct link between the cave streamways and the risings which is not the case in the Mendips. The cave water in Co. Clare, in the caves here studied, spends a comparatively short time underground before reappearing at the risings, whilst in the Mendips it seems possible to think in terms of a water table concept. The water, once it has reached the water table, maintains a constant calcium value from season to season. This constant calcium figure can be regarded as a "saturation" value, the percolating soil water enriched with carbon dioxide from the soil atmosphere having dissolved its maximum possible calcium content. Thus in a simple model the saturation values are controlled by the carbon dioxide content of the soil air.

In both the Mendips and Co. Clare the calcium values for the percolation water, as collected from various drips, are very similar. Further, the calcium values obtained from the wells in north-west Co. Clare, except under the abnormally high discharge conditions of 1961, suggest that there is a maximum calcium value of between 200 and 300 p.p.m. calcium carbonate. Wells are situated at sites which give a reliable water supply, even in times of drought. Most wells, therefore, can be thought of as fed dominantly by percolating water which has attained its saturated calcium value in respect to the available soil carbon dioxide. Thus it is possible to compare the calcium figures for the risings and wells on Mendip to the calcium figures for the wells sampled in Co. Clare. These two figures are similar in the 200–300 p.p.m. $CaCO_3$ range.

Lithologically the Carboniferous limestones of both Co. Clare and the Mendip are similar. However, the saturation values for other British limestones which are at present under study are not necessarily in the same range of values. Values for the Chalk of southern Britain do appear to be similar in the 200's in terms of p.p.m. $CaCO_3$, but the values for springs associated with various limestone members of Jurassic sequence of the southern Cotswolds are markedly higher, in the high 300's, and preliminary figures for the Magnesium limestone of north-eastern England give higher figures again. All these limestones are relatively pure in that they are essentially composed of calcite or calcite plus a subordinate content of dolomite. The variations in calcium content of the waters associated with these limestones can perhaps be interpreted as due to variations of the carbon dioxide content of the soil air.

The overall picture of the calcium content of limestone waters in north-west Co. Clare is one of complexity rather than simplicity. The model put forward is an attempt to identify a pattern out of this apparent complexity, a pattern which may well be considered as illustrating the soil carbon dioxide hypothesis for limestone solution as first presented by Adams and Swinnerton (1937). The authors have not calculated an overall weathering rate for the area of the form outlined by Corbel (1959) and somewhat refined for use in this area by Williams (1963). The reason for this is that the overall complexity of the solution pattern, and particularly the variation of the calcium content of the rising waters with discharge, makes such a calculation difficult without more detailed information. Particularly it should be noted that when stream discharge is high the calcium values are much reduced and that this factor must be allowed for in calculating overall weathering rates which utilize an annual discharge figure for the streams concerned.

Further investigations in the area along the lines of the work described above would be enhanced if more detailed measurements could be obtained for the relationships of rainfall and stream discharge.

It is hoped that the hypotheses outlined in the latter part of this paper may act as a starting point for further work of this kind in Co. Clare; work for which this Society is admirably suited.

ACKNOWLEDGEMENTS

The collection of water samples which forms the basis of the work described in this paper would have been impossible without the generous assistance of many members of the University of Bristol Spelæological Society. The authors would like to express their thanks to all those who helped in this way.

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APPENDIX

In August, 1963, a reconnaissance expedition organized by this Society visited the Central Pyrenees. The base camp was situated some 8 km. to the west of Mte. Perdido (Mont Perdu) at a height of 2,450 m. in the valley of the Salerons which drains south to the Ordessa Valley. The immediate area of the camp was composed entirely of limestone; however, the streams in the valleys only flowed underground intermittently. There were a number of semipermanent snowfields in the vicinity of the camp, many of these fed small streams. Glacially eroded landforms, slightly modified by recent frost action, were abundant. Vegetation was absent over much of the area and was only continuous on the most favourable sites, of which those in the valleys were the most conspicuous. The overall impression was of a landscape in which solutional karstic forms were fast evolving, although at present the area could reasonably be said to exhibit the early youthful phase of the karstic cycle. In this respect the limestone features could be contrasted to the Grotte Casteret and its associated more fully developed karstic features which occurred some 3 km. to the east and at a height approximately 300 m. greater than the base camp elevation. These features are not thought to be genetically related to the present landscape.

Analysis of water samples for their calcium content was undertaken in the field using comparable methods to those described earlier. The precipitation in the summer of 1963 for this area was abnormally high and the cloud cover correspondingly above average. However, the run-off was rapid and, except during periods of heavy rain, the dominant water supply was from snow melt. Water issuing from snow banks showed a negligible calcium content and *p*H's of 5·0–5·5 were recorded.*

Analyses of surface streams showed values of 40–55 p.p.m. $CaCO_3$. These streams were composed dominantly of snow-melt water from the snow banks. Their length was rarely in excess of half a kilometre. They were normally sampled at small stream sinks.

In the Salerons valley there were a number of small risings fed by streams whose underground course was of limited length. The calcium values of these risings varied between 45 and 70 p.p.m. $CaCO_3$; the majority of values were between 60 and 65 p.p.m. $CaCO_3$. One rising (used as the water supply for the camp) was observed to fluctuate in volume daily, the maximum discharge at sunset (approximately 20.00 hr.) was at least five times greater than the minimum discharge at sunrise. The calcium content was also found to fluctuate:

August 10th	10.00 hr.	90 p.p.m. $CaCO_3$
	13.00	85
	15.45	47
	19.00	50

The water temperatures can be taken as constant throughout the day.

The fluctuations in flow were clearly related to diurnal variations in snow melt. The corresponding changes in calcium content may be due to variations in velocity of stream flow giving differing time for solution to take place, or due to the varying proportions of "percolation" water from the flat comparatively well-vegetated area up valley in relation to the water originating as snow melt.

Additional samples were obtained during an intensive rain storm when a completely dry rift-like cave became extremely wet. The catchment area was small and the vertical distance to the surface did not exceed 7 m. The water reappeared at a small permanent rising some 10 m. below the cave.

1. Strong flow from cave roof, 5 minutes after rain began—23 p.p.m. $CaCO_3$.
1. Flow slackening, 15 minutes after rain began—43 p.p.m. $CaCO_3$.
2. Permanent cliff foot rising before rain—60 p.p.m. $CaCO_3$.
3. Permanent cliff foot rising 20 minutes after rain—50 p.p.m. $CaCO_3$.

Measurements in temporary pools on open bare limestone collected on two separate occasions gave the following readings:

1. Immediately rain stopped—15 p.p.m. $CaCO_3$.
   Half an hour after rain stopped—19 p.p.m. $CaCO_3$.
2. Half an hour after rain stopped—12·5 p.p.m. $CaCO_3$.
   One hour after rain stopped—15 p.p.m. $CaCO_3$.

It is suggested that the above results are indicative of rapid limestone solution. Additionally the relatively low calcium content of the water of this limestone area is thought to be related to the low soil carbon dioxide values which are in turn due to the sparse development of vegetation.

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* The *p*H values were obtained by the use of *p*H papers and can therefore be regarded as only a rough indication of the true values.