Field Studies 5 (1981) 365–387

THE TUFA DEPOSITS OF THE MALHAM DISTRICT, NORTH YORKSHIRE

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ABSTRACT

Tufa is a soft, porous, calcareous rock that forms in springs, waterfalls and lakes of limestone regions. The Malham district provides many examples from the thin films coating the surface of pebbles to complex screens. Goredale Beck is probably the best example of a tufa-depositing stream in the British Isles.

Deposition is a chemical process, apparently assisted by the presence of certain mosses and algae, and typically occurs where subterranean water, rich in carbon dioxide and supersaturated with calcite, issues onto the surface. The loss of carbon dioxide to the atmosphere alters the pH of the water and causes precipitation of calcium carbonate within about 80 m of the feeder spring. The chemistry involved is explained in appendices. As tufa is so easily damaged by human interference special efforts should be made to conserve the more important deposits.

INTRODUCTION

CALCAREOUS TUFA is a soft, porous, calcareous rock formed in springs, waterfalls and lakes in limestone regions. *Tufa* is a name applied to any soft, porous rock although it is generally reserved for the rock just described. Tufa is often confused with *travertine*, a name derived from Tiburtine, the region surrounding the Tiber in Italy, where this material was once quarried. Travertine is identical in composition to calcareous tufa but it is a hard, non-porous variety used for building. Travertine is often formed from tufa by recrystallisation and infilling of the pores. Both deposits are recent in origin and their formation continues today. Certain limestone cave formations, e.g. dripstone, stalagmites and stalactites have a similar texture and composition and they are formed by a similar process.

Tufa formation has excited the interest of biologists and geologists as its formation appears to be closely associated with certain plants. The possible role of plants in tufa formation was described by Cohn (1864) who suspected that algae growing within the deposit abstracted carbon dioxide from the water resulting in the precipitation of calcium carbonate, the principal constituent of tufa. Cohn's hypothesis was often cited in later studies, and Rothpletz (1892) suggested that the algae actually secreted the material. Unfortunately there was little experimental work at this time, so the comments of the original investigators were often not questioned and were copied verbatim. The luxuriant growth of bryophytes on tufa was also noted (Emig, 1918) and bryophyte photosynthesis, by removing carbon dioxide from water, is considered by many bryologists today to be the mainspring of tufa formation.

Many inorganic processes could also give rise to tufa formation, such as temperature changes (Ek and Pissart, 1965), evaporation (Kindle, 1927) and pH changes brought about by the diffusion of aqueous carbon dioxide into the atmosphere (Barnes, 1965). Recent studies suggest that plants play an important *physical* rather than *chemical* role in tufa formation (Gruninger, 1965; Pentecost, 1978). It is now fairly well established that the material is deposited as a result of the chemical changes which occur when calcareous spring water feeding the streams, comes into contact with the atmosphere, yet the complex interrelationships between accreting material and the associated organisms, many of which become cemented into the rock, are little understood. The surface of tufa provides an environment of slow sedimentation often followed by rapid removal. Organisms inhabiting tufa must contend with both of these processes.

Tufa and travertine deposits have been described from every continent except Antarctica. Deposits are usually found in fast flowing calcareous streams, particularly where there are waterfalls where tufa "curtains" or "screens" develop, so-called because of their green, mossy surfaces. There are several splendid tufa-falls in Europe such as those at Tivoli near Rome, Urach (30m) and Gütersteiner (110 m) in Germany, and the Topolje Falls (30 m) in the Karst region of Jugoslavia. In this last region, tufa formation may be sufficiently rapid to cause the damming of rivers and streams (Golubic, 1969). Tufa also forms around certain hot springs such as those in Yellowstone National Park and in some districts tall mounds, resembling termite hills, develop. The formation of "mound springs" is not dependent upon thermal water and some rudimentary mounds occur close to Malham Tarn (Fig. 1).

FIG. 1.
A tufa hummock close to the source of Gordale Beck, below Great Close Hill. This mound is about 0.4 m high and 1 m wide at its base and is densely vegetated with bryophytes and grasses. Although associated with a line of calcareous springs, the development of these hummocks is not fully understood.

The distribution of tufa deposits near Malham.

The main areas of tufa deposition in the Malham area are shown in Fig. 2. The streams giving rise to the deposits are confined to the slopes of High Mark, north of the Field Centre. There are at least twenty five major springs in this area (Ternan, 1971) but not all of these feed the streams which give rise to tufa deposits. Some springs discharge directly into streams such as Cowside Beck, in which deposits are

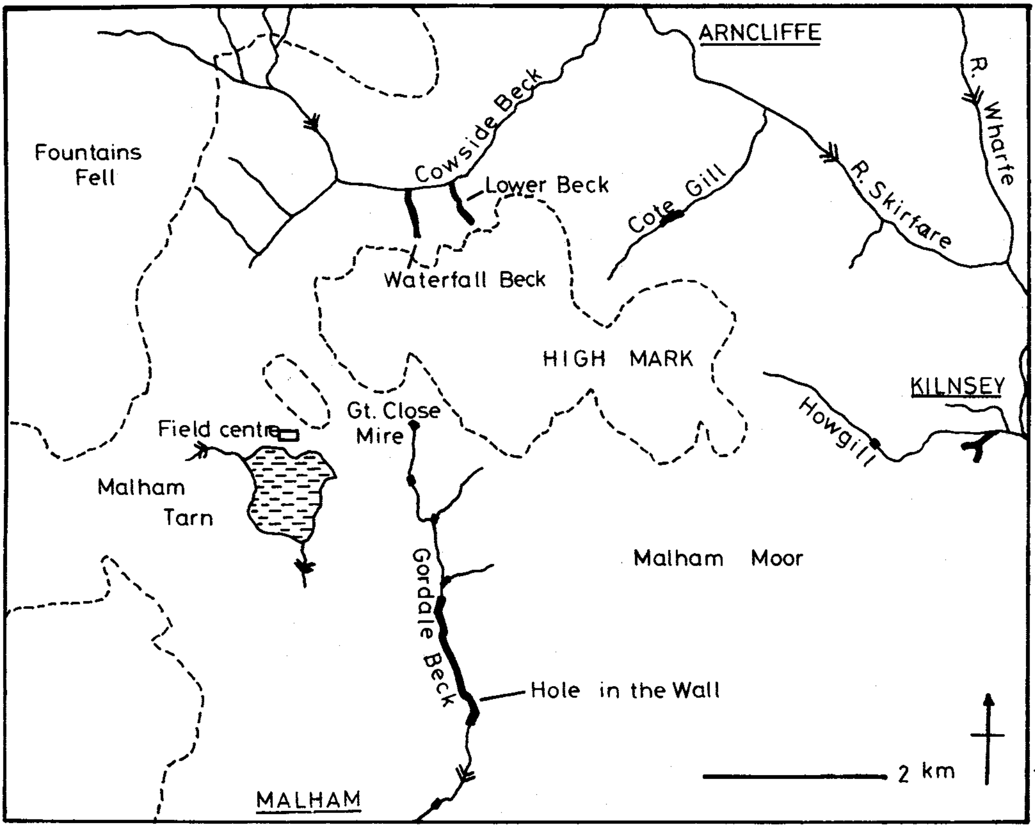

FIG. 2.

Map showing the positions of the main tufa-depositing streams and tufa deposits in the Malham area.
streams and rivers with direction of flow
tufa deposits
457 m (1500 ft.) contour

few, whilst the waters of others soon disappear underground so that contact with the atmosphere is brief and insufficient to promote precipitation of calcium carbonate. Precipitation is accelerated by good mixing, turbulence and aeration caused by steep stream gradients. This is well demonstrated in Gordale Beck, probably the best example of a tufa-depositing stream in the British Isles. Gordale Beck rises from a collection of springs situated around Great Close Mire, east of the Field Centre. From this point, to Mastiles Bridge (National Grid Reference SD/911656), the stream gradient is about 1:50. There are few tufa deposits in the stream bed although a few tufa hummocks (Sinker, 1960) occur in the mire. Below the bridge, the gradient increases to 1:14 and tufa covers large areas of the stream bed.

There are four other important tufa streams in the area. These are Waterfall Beck (SD/908698), which is 770 m in length, with a total fall of 143 m before its confluence with Cowside Beck, and about 400 m east, a similar but less accessible stream named "Lower Beck" by Pentecost (1975) which also flows into Cowside Beck. Cote Gill (SD/940697) also contains extensive deposits of tufa about 600 m from the springheads and all three streams contain large waterfalls with fine tufa curtains on High Mark. Large quantities of tufa also occur in a small tributary of

Howgill near Kilnsey (SD/973673), noteworthy for a number of small tufa dams which are rare in the British Isles. Tufa deposits are far less common in streams rising from the adjacent limestone hills. Examples may be seen near Alum Pot and Clapham Beck on Ingleborough, and near Kettlewell. The reasons for the scarcity of deposits in these areas will be discussed later. Thin, spongy incrustations of tufa, or *Krustenstein* (Kann, 1941), often occur around the margins of calcareous lakes. The rocks in the littoral of Malham Tarn are covered with a thin (approx. 5 mm) layer of *Krustenstein* and this provides a harbour for many protozoa, invertebrates and algae (Holmes, 1965; Lund, 1961). Studies on the colonisation of artificial substrata left in the Tarn indicate that the deposit is continuously disturbed, broken up and redeposited. Its distribution in the tarn is dependent upon the distribution of littoral rocks and stable peat surfaces (Fig. 3). Series of narrow grooves may be seen on the rocks beneath the *Krustenstein,* giving the surface a gnawed appearance. Similar structures, called *galets sculptés*, have been described from the Lac d'Annecy by Le Roux (1908) and attributed to limestone corrosion caused by respiring algae and bacteria. However, the *galets sculptés* in the Tarn appear to be due to the burrowing activities of the caddis *Tinodes waeneri* (Holmes, 1965).

Travertine deposits are scarce and appear to have resulted from the recrystallisation of tufa, which has been exposed to the atmosphere for long periods. The best examples may be seen in parts of Gordale, below the Hole in the Wall (Fig. 13). In the British Isles, the most extensive deposits of *exposed* tufa are found in the Malham district, but large deposits also occur in North Wales, Derbyshire and Gloucester-

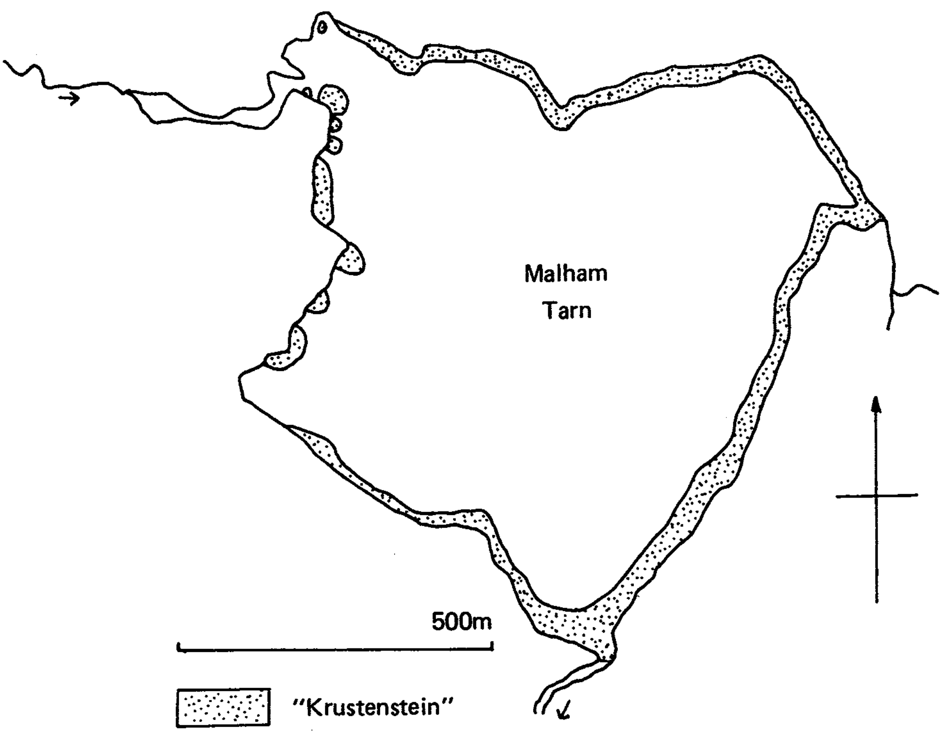

FIG. 3.
The distribution of *Krustenstein* in Malham Tarn.

shire. In fact, most highly calcareous springs are tufaceous and deposits may be expected to occur in any limestone district.

Tufa composition and formation

An analysis of thirteen tufa samples from the Malham area indicated that the deposits consist of almost pure calcium carbonate in the form of calcite (mean: 91.8 per cent, range 78-97 per cent, see Table 1). Small quantities of quartz-silt are always present, together with traces of organic material consisting of entrapped plant and animal remains. Traces of iron and manganese occur and the former is probably responsible for the ochraceous colour of travertine. Magnesium also occurs (mean 0.16 per cent, range 0.05-0.82 per cent) but magnesium calcite, which is an important marine biogenic mineral, was not detected by X-ray diffraction analysis. This suggests that the element is associated with the detrital organic matter. The total phosphate phosphorus content was about 10^4 times higher than that of the associated waters and was probably released from the organic remains.

The porosity of the samples varied from 44-67 per cent (Table 1) so that only about half of the volume of the material consists of calcite. Typical porosities for travertine range from 5-20 per cent (Pentecost, 1975). Thin sections of surface deposits reveal a porous, heterogeneous structure (Fig. 4) of microcrystalline calcite which is randomly distributed or, in the presence of algae and bryophytes, sometimes regularly distributed upon the cell wall surfaces. Numerous voids with dimensions ranging from a few micrometres to several decimetres occur within the deposits as a result of resolution or the decay of entrapped organic matter. Several are evident in Fig 4. The calcite is usually present as irregular crystals, 0.1-5 µm in diameter, but when recrystallisation occurs, as in Harry's Screen (see page 381) in Gordale, euhedral crystals (i.e. those with distinct faces) up to 3 mm long, may be seen.

Table 1. *Composition of tufa deposits near Malham Tarn Field Centre*

Locality and National Grid Reference	SD/	Composition of surface sample, %						
		$CaCO_3$	Mg	Fe	Mn	organic matter	inorganic residue	porosity
Malham Tarn	890668	79.5	.31	.06	.03	12.8	6.2	—
Gordale Beck	915641	96.6*	.14	nd	.01	1.9	.8	44
,,	914646	95.7	.05	.05	nd	1.5	2.7	66
,,	915641	96.2	.03	.08	nd	2.2	1.5	55
Waterfall Beck	908695	86.8	.11	.09	.02	6.0	6.7	67
,,	908696	95.4	.14	.03	nd	2.4	1.5	48
,,	908696	92.6	.14	.03	.006	4.8	1.9	64
,,	908698	94.8	.14	.002	nd	3.5	1.0	65
,,	908700	94.7	.14	.03	.006	2.8	1.8	—
Lower Beck	914697	93.2	.02	.04	nd	3.4	3.2	50
,,	913702	95.8	.03	.07	nd	1.9	2.2	61
Howgill	975673	94.7*	.04	.04	.022	0.9	4.3	50
Crystal Beck	913743	78.0	.83	.06	.03	16.3	1.6	—
Mean		91.8	.07	.045	.01	4.7	2.7	57

nd not detected
* not accreting

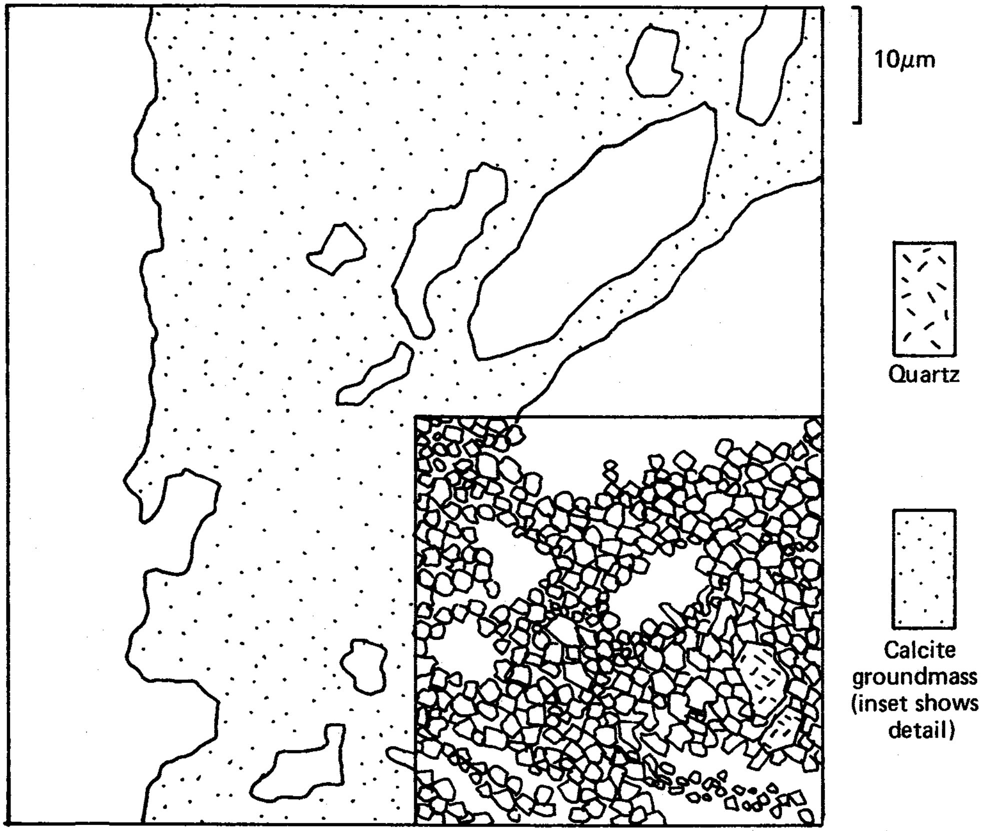

FIG. 4.
Diagram of a thin section of tufa from Waterfall Beck, showing the microcrystalline, porous structure and the "ghosts" of filamentous Cyanobacteria sheaths. Silt particles are present also.

Water chemistry

The tufa streams occur within a limestone catchment and the waters contain 100-200 mg l^{-1}* of both calcium and bicarbonate, with smaller quantities of sulphate, chloride, sodium and magnesium (Tables 2 and 3). Because of the complexity of underground water systems in karst regions, the catchment areas of the streams cannot be defined with certainty. The springs feeding Gordale Beck and Malham Tarn rise at the level of the impervious Silurian basement (O'Connor, 1964; Smith and Atkinson, 1977) but many others issue within the limestone sequence, probably along impervious partings in the limestone. The tufa springs in the area all have approximately the same chemical composition, with a calcium: magnesium ratio of 40:1, but the concentration of solutes varies considerably. For instance, Gordale Beck and the Howgill tributary have persistently harder waters than the rest (Table 2). There is also a regular temporal variation in the water hardness of some streams, notably Gordale and Waterfall Beck. This is probably related to variations in soil temperature and a favourable hydrological system (Pitty, 1968). Soil temperature determines, to a considerable degree, the bacteriological activity of the soil and hence the respiration rates of these organisms. This, in turn, determines the carbon

* mg l^{-1} = milligrammes per litre.

Table 2. *Some general chemical characteristics of the springheads of tufa-depositing streams near Malham Tarn.*

Springhead	pH	t°C	Ca^{++}(mM l^{-1})	HCO_3^- (mM l^{-1})	SATCAL	Date
Cote Gill	7.5	7	1.25	2.20	0.94	5.2.78
Cowside Beck	7.6	7	1.41	2.70	1.01	14.5.73
Gordale Beck	8.2	16	1.87	3.78	1.12	,,
Howgill	7.5	8	1.27	2.27	0.94	5.2.78
Howgill tributary	7.4	9	1.77	3.68	1.00	14.5.73
Lower Beck	8.0	7	1.31	2.65	1.06	,,
Waterfall Beck	7.5	6	1.37	2.74	1.00	,,

Table 3. *Detailed analyses of tufa-depositing waters near Malham Tarn (springheads, excluding Malham Tarn)*
(μM l^{-1})

Component	Malham Tarn (mid-lake)	Gordale Beck	Howgill tributary	Waterfall Beck
Ca^{++}	1140	1690	1755	1299
Mg^{++}	38	31	85	28
Na^+	320	164	261	153
K^+	16	24	15	7
HCO_3^-	2040	3150	3540	2650
CO_3^{--}	37	28	24	7
$CO_2+H_2CO_3$	11	28	48	99
P (total reactive)	0.09	0.09	0.01	0.04
SO_4^{--}	162	148	154	120
NO_3^-	0.07	0.06	0.10	0.03
pH	8.5	8.2	8.1	7.5
t°C	9	15	10	6
date	14.5.73	13.5.73	13.5.73	13.5.73

dioxide partial pressure (i.e. concentration) in the soil atmosphere. This gas reacts with water to form carbonic acid, the principal agent of limestone solution (see Appendix 1). South-facing catchments will tend to have warmer, bacteriologically more active soils resulting in a calcium-rich groundwater and it is interesting to note that the waters of Gordale Beck, rising from south-facing slopes, are significantly harder than those of north-facing Waterfall Beck, nearby (Fig. 2, Table 3).

Detailed studies of Waterfall Beck (Fig. 5) and Gordale show that the concentrations of calcium and total carbon dioxide (C_t, Appendix 1), decrease downstream. This fall is attributed to a diffusional loss of carbon dioxide from the water to the atmosphere, and photosynthetic uptake by aquatic plants. This results in the supersaturation of the waters with calcite since much of the carbon dioxide gained by the water from the carbon dioxide rich soil atmosphere is lost once the waters regain contact with the air. There are therefore three carbon dioxide "sinks", or removal processes, for these waters, (a) the atmosphere, (b) photosynthesis and (c) calcite precipitation. It is possible to estimate (a + b) and c separately since calcium carbonate precipitation and the fall in C_t can be measured independently (Appendix 2). For example, the data obtained for 17.8.1974 (Figs 5 and 6) show a total down-

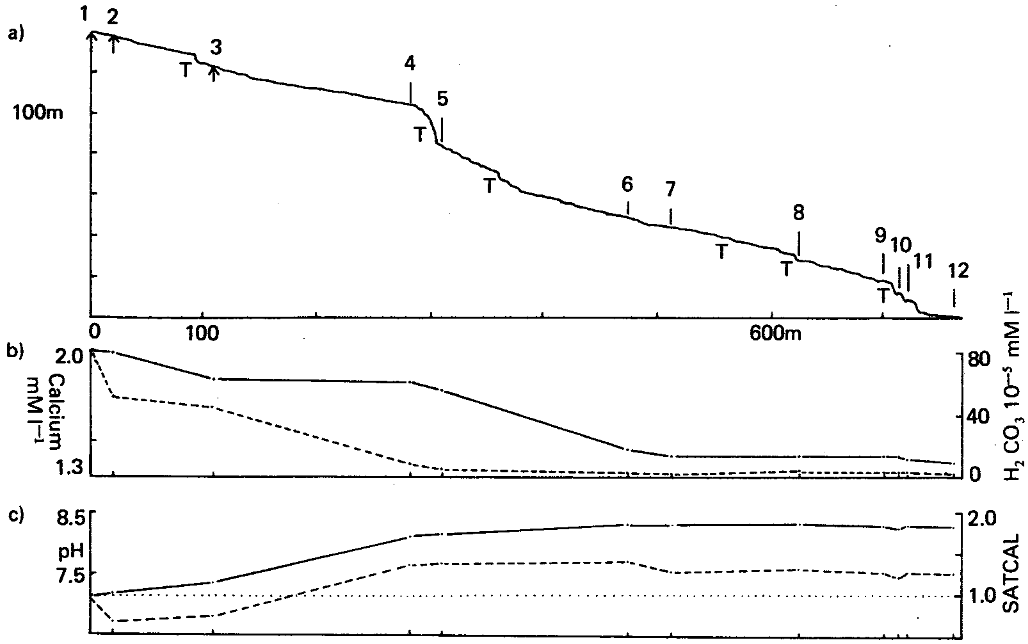

FIG. 5.

(a) A profile of Waterfall Beck showing the water sampling sites (1-12), the feeder springs (arrows) and the major tufa deposits (T). The vertical scale is exaggerated by a factor of 1.8.

(b) Changes in the chemical composition of the waters downstream; calcium (full lines) and aqueous carbon dioxide (broken lines).

(c) Changes in chemical composition indicated by pH (full lines) and SATCAL (broken lines). The dotted line shows the SATCAL = 1.0 level.

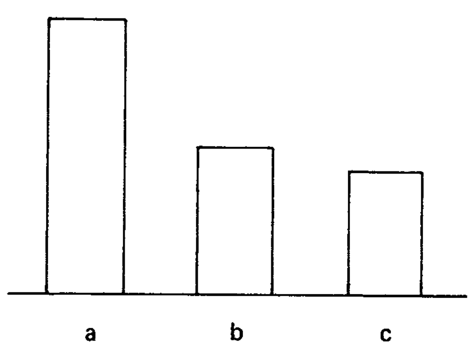

FIG. 6.

The partition of the losses in total carbon dioxide in Waterfall Beck on 17.8. 1974. (a) The difference in the total carbon dioxide concentration between the springhead and the lowest sampling point on Waterfall Beck (1.46 mM.).

(b) Carbon dioxide lost to the atmosphere and plants (0.79 mM).

(c) Carbon dioxide lost as precipitated calcium carbonate (0.66 mM).

stream loss of 1.46 mM carbon dioxide, of which 0.66 mM was removed by precipitation as calcite, and 0.79 mM was lost to the atmosphere and photosynthesis. When the total losses of carbon dioxide are plotted against the springhead carbon dioxide concentration (Fig. 7) they are found to be positively correlated ($r = 0.955$, $p < .001$) and this suggests that a diffusional loss of gas to the atmosphere is the dominant mechanism of carbon dioxide loss.

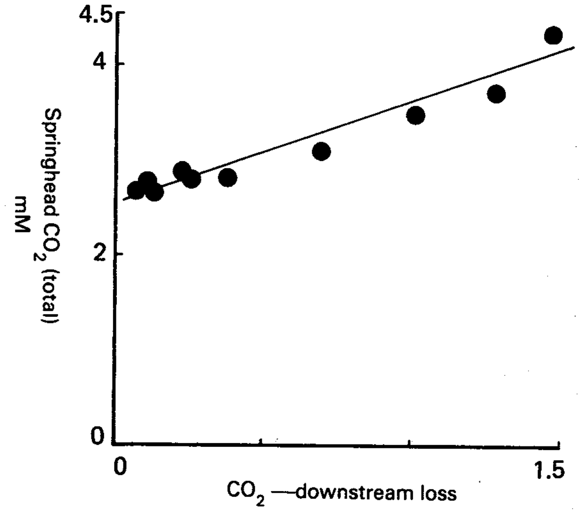

FIG. 7.
The relationship between the total carbon dioxide concentration at the Waterfall Beck springhead and the resulting downstream loss of carbon dioxide between sampling stations 1 and 12.

Detailed chemical analyses taken from twelve sites along Waterfall Beck (Fig. 5) indicated a mean loss of calcium by precipitation of 0.1 mM (range: 0-0.67) between 1972-6. The greatest losses of calcium occurred between sites 4 and 8, where most of the tufa was found, which indicates that the precipitation occurs just prior to, or simultaneously with tufa deposition. A rapid fall in carbonic acid (see Appendix 1) is apparent between sites 1 and 4, and below site 5 the concentration becomes steady at about 3×10^{-5} M, and the loss of gas to the atmosphere precedes the precipitation of carbonate by several minutes in this stream.

The photosynthetic uptake of carbon dioxide by plants growing in the beck will be negligible. It could be argued that since the uptake of gas by the plants is also diffusion controlled, the two mechanisms could not be distinguished. However, there are six reasons for supporting the atmospheric diffusion process: (1) The total downstream loss of carbon dioxide does not peak during the summer, and winter losses sometimes exceed summer losses; (2) The loss of gas is greatest over the waterfalls, but aquatic plants are not confined to these alone; (3) The greatest loss of carbon dioxide occurs between sites 1 and 4 where aquatic vegetation is sparse; (4) Algal productivity in this stream bed has been shown to be extremely low (Pentecost, 1978) although bryophytes also abound; (5) The carbon dioxide uptake by the algae becomes saturated at low light intensities (Pentecost, 1978) so that photosynthesis is only diffusion controlled under special circumstances, but data for the beck bryophytes are lacking; (6) Controlled aeration experiments in the laboratory gave the same results as those found in the beck (Pentecost, 1975). This is also supported by the work of Cole and Bachelor (1969) and Jacobson and Usdowski (1975) but it should not be assumed that photosynthesis is *always* negligible. In long stretches of slow-flowing productive water, photosynthetic uptake could outweigh the diffusional loss to the atmosphere (Barnes, 1965).

The SATCAL values for Waterfall Beck (see Appendix 1 for details) suggest that supersaturation of the waters with calcite occurs within about 80 m of the feeder springs. Most of the springwaters in the district possess SATCAL values close to 1.0 (Table 2) which indicates that the waters rise close to chemical equilibrium with the soil atmosphere. The pH values at the springheads range from 6.7-7.7 but they rapidly rise to values of 8.1-8.5 downstream, reflecting the gas exchange previously noted.

The hardness of the Malham Tarn waters is known to vary seasonally, possibly because of the photosynthetic activities of the extensive *Chara* beds (Lund, 1961; Pitty, 1971). However, the calcium and carbon dioxide levels are consistently lower than those of the adjacent tufa streams (Table 3) and the SATCAL value is usually close to 1.0, although the Tarn is also fed by springs issuing from the same limestone formation. The reduced hardness may be due to the long residence time of the Tarn waters (about 1 yr) combined with good mixing and a high surface area to volume ratio. The equilibration process is complicated by the extensive precipitation of calcite by the stonewort *Chara globularis* (Pentecost, unpublished data). The growth of these *Chara* beds might account for the variability of water hardness and pH across transects of the tarn (A. Morton, personal communication; Pentecost, unpublished data).

Flora and fauna

The flora and fauna of several European tufa deposits have been described (Gregory, 1911; Pia, 1933; Wallner, 1933; Symoens, 1949; Gruninger, 1965; Dürrenfeldt, 1978) and indicate that bryophytes and algae are the predominant biological components. This is also the case for the British deposits but the literature is scanty and of a more specialised nature (Fritsch and Pantin, 1946; Proctor, 1960; Pentecost, 1978). The most abundant bryophyte of the Malham screens is *Cratoneuron commutatum* (Figs 8, 9 and 10) which occurs on all of the major deposits and often attains 100 per cent cover. It is a polymorphic species and the various growth forms appear to be related to the rate of flow of water. In fast water the stems are almost entirely stripped of their "leaves" and during spate periods large patches of the moss are torn away, although regeneration soon occurs from stems deeply embedded within the deposits. In sheltered sites with slowly dripping water, the moss grows out into broad pinnate fronds. *Cratoneuron filicinum*, a related but more delicate species, is less common and grows intermingled with *C. commutatum*. Neither species has been found fertile in this habitat. *Pellia fabbroniana* is also common, particularly in Gordale where it may form extensive patches (Fig. 9) on tufa developing between boulders in the stream bed. It prefers more sheltered sites than *Cratoneuron* and is less often washed out. Other bryophytes are less abundant although *Gymnostomum curvirostre* and *G. aeruginosum* are locally common in Gordale, particularly near the Hole in the Wall. Tufa seepages have a more diverse flora than screens with, in addition to the above species, *Riccardia pinguis, Eucladium verticillatum* and *Bryum pseudotriquetrum*. Proctor (1960) has recorded *Cinclidotus fontinaloides* and *Barbula tophacea* from the district.

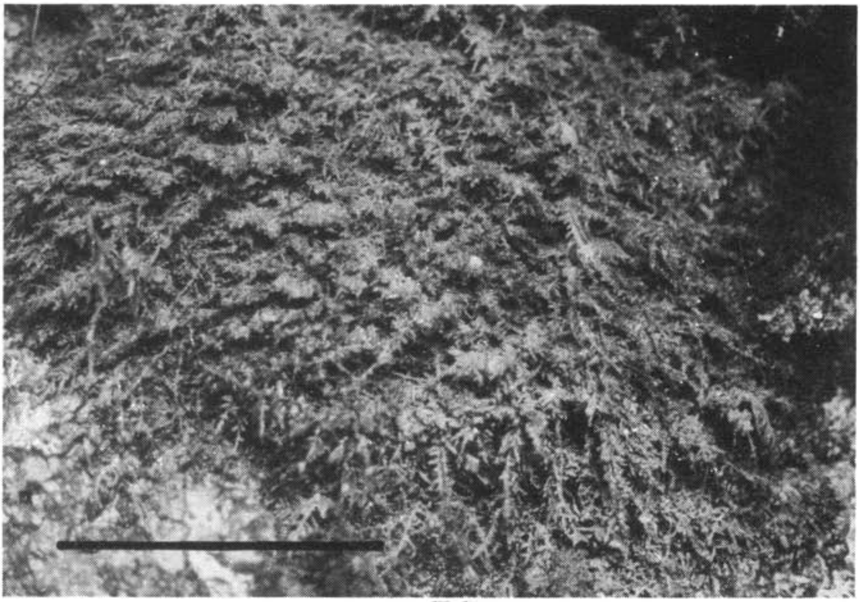

FIG. 8.
A tufa seepage colonised by *Cratoneuron commutatum* in lower Gordale. This broadly pinnate growth form is characteristic of seepages. The moss in the lower part of the photograph is encrusted with *Schizothrix*-tufa. Bar = 10cm.

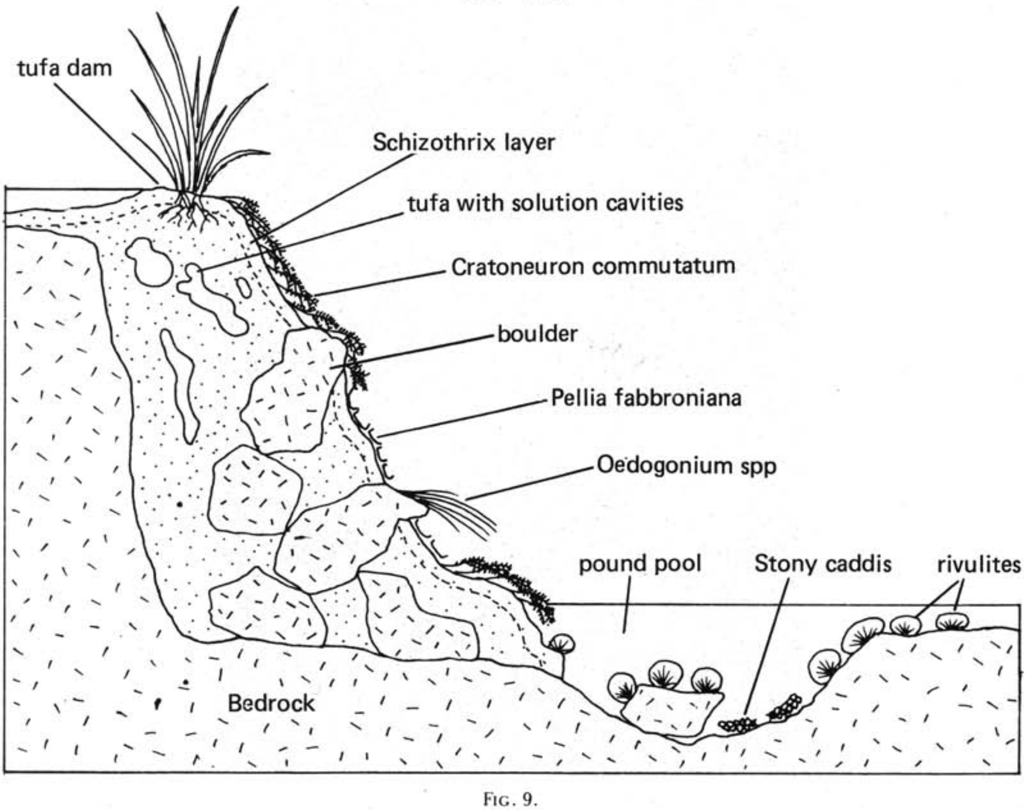

FIG. 9.
Diagrammatic section across a tufa deposit in Gordale Beck, illustrating the habits of the flora and fauna.

Other species, which are otherwise abundant in the streams, appear to be scarce or absent upon the deposits, e.g. *Brachythecium rivulare, Eurhynchium riparioides* and *Thamnium alopecurum.* Several uncommon bryophytes occur on tufa seepages and hummocks and these include *Amblyodon dealbatus, Fissidens adianthoides, Orthothecium rufescens, Philonotis calcarea, Leiocolea bantriensis, Moerkia flotowiana* and *Preissia quadrata.* Vascular plants are uncommon upon accreting tufa in Britain but *Sesleria caerulea, Veronica beccabunga, Geranium robertianum* and *Pinguicula vulgaris* occur upon the Gordale deposits. The diversity of the flora of tufa appears to increase as the rate of flow of water over the material decreases.

Tufa possesses a rich algal flora dominated by filamentous Cyanobacteria. These plants are the cause of the yellow-brown colouration of fresh deposits and they play an important role in tufa formation. The algae are mainly endolithic (i.e. below the rock surface) and the commonest species is *Schizothrix calcicola,* a minute filamentous plant which lives in the uppermost 2-3 mm of the deposit and associated bryophytes (Figs 9 and 10). This species belongs to the Oscillatoriaceae, a family renowned for their gliding movements which appears to result from the secretion of mucilage (Castenholz, 1973). The surface skin of the *Schizothrix* layer is tinted yellow by caro-

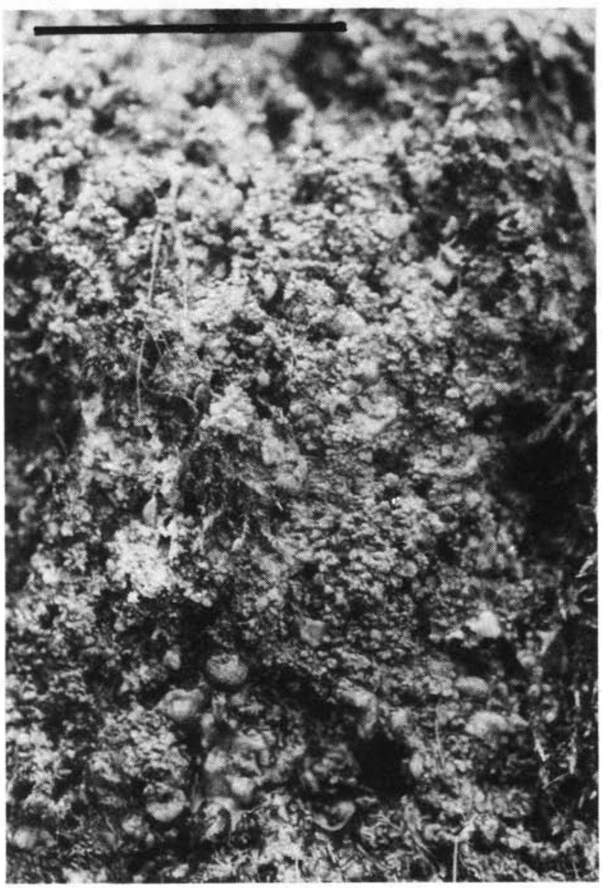

FIG. 10.
Detail of a tufa screen surface in Waterfall Beck. Strands of the moss *Cratoneuron commutatum* are growing on a tufa surface made nodular by encrusted colonies of *Schizothrix calcicola.* Bar=10 cm.

tenoid pigments within the cells. Beneath this skin, the pigment is present in much lower concentration and the plants appear blue-green in colour owing to the unmasking of the phycobilin pigments. This suggests that carotenoid formation may be connected with the high light intensities which may occur at the tufa surface. This is supported by the observation that the yellow pigmentation is absent from deep hollows and beneath bryophytes. The *Schizothrix* filaments are surrounded by a gelatinous sheath which may greatly exceed the filament diameter. As the filaments glide over the substratum, the sheath is discarded and these remain in large numbers beneath the living algal layer. The mucilage is eventually destroyed by micro-organisms so that the remains become scarce in old deposits and travertine.

The degree of light transmission by tufa is such that *S. calcicola* may grow photosynthetically 1-2 mm below the deposit surface (Pentecost, 1978). This plant frequently develops into hemispherical colonies, densely encrusted with calcite, which give tufa a nodular appearance (Fig. 10). Other Oscillatoriaceae also occur, notably *Phormidium incrustatum* (Naeg.) Gom. (also known as *Microcoleus vaginatus* (Vauch.) Gom: the taxonomy of this group is currently in a state of flux) and *Schizothrix fasciculata*. These species have broader trichomes (filaments) but they are otherwise morphologically similar to *S. calcicola*. Coccoid Cyanobacteria often occur intermingled with the filamentous forms, notably *Gloeocapsa calcarea* and *Aphanocapsa grevillei*.

The most conspicuous tufa-forming species, but not the most abundant, is *Rivularia haematites* which occurs as dark olive-brown buttons upon stones in tufa streams (Fig. 11). This species does not form thick, laminated "screens" of tufa but it is a major "crust" former, particularly in Gordale Beck and the *Krustenstein* of Malham Tarn. *Rivularia* traps calcite particles upon the surface of its mucilaginous sheaths and the particles continue to grow into crystals considerably larger than those found associated with *S. calcicola*. However, this species is non-motile so that it cannot move towards the light once covered with deposit. Some of the large *Rivularia* colonies in Gordale and Waterfall Beck may by 15-25 years old (see later). These colonies grow close to the water surface and often form a well defined zone around deep pools. During dry spells, the colonies frequently become exposed to the air. Their thick sheaths and hemispherical shape may be advantageous under these conditions by reducing their rate of dessication. *Scytonema myochrous* is one of the few Cyanobacteria which grows on the surface of tufa rather than within it. The species forms dark brown colonies consisting of branched, non-motile filaments and it is a characteristic plant of tufa screens in the area. The sheath is narrow and less mucilaginous than those of the previous species which might explain why the plant remains free of calcite encrustation.

Although the Cyanobacteria dominate the algal flora of tufa in terms of biomass, other algae are usually present, often in large numbers. The commonest of these is *Gongrosira debaryana,* an encrusting member of the green algae (family Chaetophorales) consisting of an irregular plate of cells from which large numbers of short branches arise. The species forms bright green colonies upon tufa but it is most abundant upon encrusted stones in fast flowing streams. Another green alga, the desmid *Oocardium stratum* is far less common, at least, in its typical form. The alga was recorded as abundant in Gordale Beck by West and West (1899) but it appears to be rare now. The most recent records are those of C. A. Sinker (May, 1959, on a cushion of *Bryum pseudotriquetrum)*. Later visits to the site by Sinker were

FIG. 11.
Rivularia haematites colonies encrusting a stone in Gordal Beck. The largest colonies are probably about 5 years old. They often fuse to form a continuous crust. Bar = 1 cm

unsuccessful but C. Sinclair (personal communication) rediscovered the species in November 1970.* Both sites of collection are in lower Gordale. *O. stratum* also possesses a thick mucilaginous envelope and it is an abundant and well known tufa-former on the continent (Wallner, 1933).

The deposits possess a rich diatom flora, dominated by small *Achnanthes* species. A surface sample of tufa from Waterfall Beck yielded the following species

Achnanthes exilis (dominant)	*Amphora ovalis*	*C. ventricosa*
A. affinis	*Caloneis bacillum*	*Denticula* sp.
A. lanceolata	*Cymbella delicatula*	*Navicula tripunctata*

All of these plants are motile but none is restricted to this type of habitat. One unusual feature of the flora is the regular appearance in spring of *Chrysonebula holmesii,* a coccoid Chrysophyte (Lund, 1953) virtually unknown apart from its occurrence upon the Malham deposits. This plant produces great quantities of

*The Author has since found the species at three sites in Waterfall Beck in 1981.

mucilage resulting in the formation of large patches of thick white jelly over the deposits, particularly those in Waterfall Beck, Lower Beck, and the Howgill tributary. The opacity of the mucilage is due to the deposition of calcite although the carbonate is not incorporated into the underlying deposit, as the mucilage is sloughed off once the streams are in spate. The growth disappears almost entirely during late summer and winter.

Other algae also occur, particularly among the bryophytes during spring and summer. These include species of *Oedogonium, Zygnema, Spirogyra* and *Vaucheria*. The growths are epiphytic or epilithic and the plants do not become encrusted with calcite although this has often been noted on the continent (Pia, 1933). A minute crustose lichen, *Thelidium microcarpum* (Pentecost and Fletcher, 1974) sometimes grows intermixed with the algae.

Despite many studies of the fauna of Malham, little is known of the animals inhabiting the tufa excluding those associated with the encrustations in the littoral of Malham Tarn (Holmes, 1965). Invertebrates are a conspicuous feature of tufa deposits; species of *Rhyacophila* (Trichoptera) are common among *Cratoneuron* together with certain tardigrades. A recent study by Dürrenfeldt (1978) of some German deposits indicated a limited but highly specialised fauna of *Pericoma, Protonemura* and *Nemoura*, with some species showing adaptations to the accreting environment. Further studies along these lines at Malham would seem desirable.

Growth rates and geomorphology

Although there are no precise measurements of flow rates in tufa streams, estimates of 10-50 l sec^{-1} have been made for Waterfall Beck, resulting in an annual loss of calcite by precipitation of about 5-20 tonnes. How much of this is incorporated into tufa is uncertain. The growth rates of the tufa deposits in Howgill are 0.2-0.34 mm a^{-1} (Pentecost, 1978) and detailed studies of *Rivularia* incrustations in the area gave rates of 0.2-1.6 mm a^{-1}. Tufa deposits possess a regular laminated structure due to seasonal differences in algal growth rates; thin, dense layers are produced in winter when growth is minimal, followed by a wide spongy layer in the summer. Thus, under favourable conditions, deposition rates can be determined indirectly from the periodicity of the laminations (Pentecost, 1978) although caution must be exercised since narrow layers might also be produced in the summer, if the flow of water temporarily ceased (Schmidle, 1910).

The scarcity of tufa in the adjacent areas is probably connected with the capping of the surrounding hills with Millstone Grit and Yoredale sediments. These rocks give rise to poor, acidic soils and the waters draining them become "channelled" so that they have a concentrated effect upon the underlying limestone, producing potholes and caves (Moisley, 1953). The soils, being poor, may also be bacteriologically less active, resulting in a soil atmosphere poor in carbon dioxide. Also, the channelling effect means that waters have less time in contact with the limestone, and they often rise in an "aggressive" state (i.e. capable of dissolving the rock, see Appendix I). Consequently, tufa formation is less likely to occur, and this may explain why Cowside Beck, which is fed by springs rising on High Mark and Fountains Fell, contains few deposits and the stream bed shows evidence of corrosion.

Tufa is a soft rock and it is rapidly destroyed by mechanical abrasion. Large fragments are broken off by stones carried along by the water when the streams are in spate. This can result in a dynamic equilibrium whereby tufa formation equals the rate of erosion once a certain degree of growth has occurred. This may explain the parabolic shape of some of the larger screens. Gregory (1911) termed these "constructive waterfalls" but erosion eventually overtakes accretion. This is most evident in Gordale, where the waterfalls have cut back through the hard limestone to produce the gorges below the Hole in the Wall and Janet's Foss. Furthermore, Gordale Beck has cut through 1.1 m of bedrock since its change in course, which presumably occurred in 1730 (see discussion in Moisley, 1953). Erosion of the Hole in the Wall screen nearby, is also evident (Fig 12). The water originally flowed about 3 m to the west of its present course, at a slightly higher level. The shape of the tufa deposits is not always determined by erosion. In small rivulets close to the spring-heads, and in seepages, tufa develops into hummocks, small tufa dams and grotesque stalagmitic masses.

There are extensive banks and terraces of tufa in Gordale, above the cascades. Many of these now stand 2 m or more above the present water level and they are covered in vegetation. The deposits contain the remains of Cyanobacterial nodules,

FIG. 12.
The "Hole in the Wall", Gordale. The beck waters have flowed through the hole for about 250 years. The water flowed once along a line shown by the narrow left hand trickle and there is a much eroded tufa deposit below it. The main flow cascades over a large tufa screen about 7 m high.

encrusted caddis cases and twigs. In addition, peculiar structures called *oncolites* occur. These are small rounded pebbles, about 1 cm in diameter, composed of concentric layers of tufa built around a foreign nucleus. They are structurally similar to, but much larger than, recent oolites. Oncolites are formed in lakes, streams and tropical seas and they are always associated with Cyanobacteria. Modern oncolites are extremely rare in the British Isles and they do not appear to be forming in Gordale Beck at present. They appear to require gentle water currents, which enable the oncolites to roll and accrete carbonate over their entire surface. "Water biscuits" are flattened oncolites known from Australia and the United States, but not Britain (Mawson, 1929; Golubic, 1973).

The colonisation of Harry's Screen by plants

Harry's Screen is the name given here to the large, non-accreting tufa deposit west of the Hole in the Wall in Gordale (it is named after Harry Gill, who has recently retired after managing the Field Centre estates for many years). This deposit is situated upon the earlier course of Gordale Beck and it is at least 250 years old (Fig. 13). It is now well vegetated and about 50 per cent of its area is covered with soil to a depth of 3-8 cm. The flora (Table 4) consists mainly of grasses but the exposed tufa is colonised by algae, bryophytes and lichens and totals 47 species. Although the substratum is essentially the same, the flora is quite different from that of the accreting deposits, being that of a typical limestone soil in the area. The exposed tufa has become indurated to form travertine close to the surface and this protects the soft layers beneath. The cavernous hollow at the base is eroding rapidly, but the indurated layers possess fine laminations and some areas show the remains of *Cratoneuron* which have been "petrified" *in situ*. These structures have been termed "bryoliths" by Boros (1925).

The use and conservation of tufa and travertine

Travertine has been used as a building and ornamental stone since antiquity, e.g. in the construction of Hadrian's Villa near Rome. The picturesque, cavernous varieties have been exploited for use in garden rockeries throughout Britain but travertine is not commonly employed as a building material because of its scarcity. However, Gundulf, the Bishop of Rochester, used a local source in the construction of

Table 4. *The flora of Harry's Screen*

Algae	Lichens	*Toninia lobulata*	*Draba muralis*
Gloeocapsa calcarea	*Caloplaca heppiana*	*Verrucaria nigrescens*	*Festuca ovina*
Nostoc muscorum	*Cladonia pocillum*	*V. sphinctrina*	*Geranium robertianum*
Schizothrix calcicola	*Collema fragile*		*Hieracium* sp.
Trentepohlia sp.	*Gyalecta jenensis*		*Scabiosa columbaria*
	Lecidea lurida		*Sedum acre*
	Lepraria crassisima	Vascular plants	*Senecio jacobaea*
Bryophytes	*Leptogium schraderi*	*Anemone nemorosa*	*Sesleria caerulea* (dom.)
Camptothecium lutescens	*Placynthium nigrum*	*Arabis hirsuta*	*Silene dioica*
C. sericeum	*Protoblastenia immersa*	*Asplenium trichomanes*	*Taraxacum officinale*
Conocephalum conicum	*P. ruperstris*	*Bellis perennis*	*Thymus drucei*
Ctenidium molluscum	*Solorina saccata*	*Campanula rotundifolia*	*Urtica dioica*
Pottia lanceolata	*Squamarina crassa*	*Cystopteris fragilis*	*Valeriana officinalis*
Riccardia pinguis	*Thelidium microcarpum*	*Dactylis glomerata*	*Veronica chamaedrys*

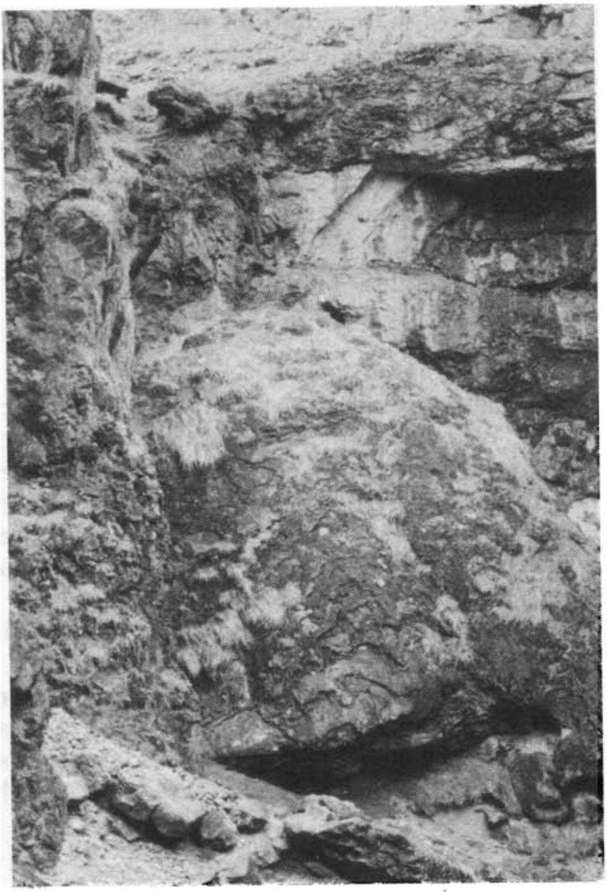

FIG. 13.
Harry's Screen in Gordale. This old deposit, which is eroding rapidly at the edges due to trampling, is about 15 m high. The screen surface is vegetated mainly by the grass *Sesleria caerulea*. The small white patches are thalli of the limestone lichen *Squamarina crassa*. Gordale Beck flows through the "Hole in the Wall" about 10 m to the right of this photograph. The lip of the old waterfall can be seen top left.

St. Leonards Tower in Kent in 1077 (Fielding, 1893) and the "Towfe" stone of Gloucestershire was used in buildings of Worcester and Glastonbury. A particularly fine and laminated variety of travertine occurs at Matlock Bath and this has been used in some of the town's public buildings. Here, the deposition of tufa sometimes occurs in the absence of Cyanobacteria (Pentecost, 1975) and the process is exploited in the "petrifying well" where objects are suspended in the springwater and become encrusted with a layer of tufa. The "well" at Knaresborough operates in the same manner but Cyanobacteria are always present there. No petrification (i.e. replacement of material by carbonate) actually occurs at these wells.

Extensive deposits of postglacial tufa occur at several sites in the British Isles (see references in Pentecost, 1978) but accretion has long since ceased at most of them. Some of these deposits have been quarried for lime or marl in the past, but those in the Malham district do not appear to have been utilised, probably because of abundant supplies of good quality limestone and the inaccessibility of the travertine sites.

These activities obviously bear upon the conservation of deposits. Whilst quarrying is unlikely to threaten the tufa screens of the Malham area, there are other factors which could eventually threaten their existence. The Bourne Brook near Cambridge and the Conestoga Creek in the United States were once celebrated sites of tufa deposition, but water pollution, land drainage and dredging have destroyed the sites completely (Golubic, 1973; Pentecost, 1975). Increase in the phosphate loading of a stream may be important since phosphates are known to inhibit calcite nucleation, and thus "poison" tufa deposition. Water pollution is unlikely to affect the High Mark streams but damage due to trampling and collecting is already a cause for concern. Gordale is most at risk, because of its proximity to the road and its well publicised scenic beauty. Apart from the accelerated erosion caused by trampling, over-collecting may endanger some of the plants and animals inhabiting the material e.g. *Oocardium stratum* and *Orthothecium rufescens*. It is unfortunate that the richest and most interesting site should be also the most accessible, and for this reason, the collecting of samples below the Hole in the Wall should be discouraged. At the same time, every encouragement should be given to continue the research into the genesis and biology of this remarkable material.

Acknowledgements

I wish to thank the staff of Malham Tarn Field Centre for their generous assistance and advice, and for the suggestions and information given by Prof. G. E. Fogg, Mr. C. A. Sinker and Dr. C. Sinclair. Part of this work was submitted as a PhD degree funded by the NERC.

References

Barnes, I. (1965). Geochemistry of Birch Creek, Inyo Co., California; a travertine-depositing creek in an arid climate. *Geochimica Cosmochimica Acta,* **29**, 85-112.

Boros, A. (1925). Two fossil species of mosses from the Diluvial lime tufa of Hungary. *Bryologist,* **28**, 29-32.

Castenholz, R. W. (1973). Movements, In: *The Biology of the blue-green Algae* (N. G. Carr and B. A. Whitton, Eds), 320-339.

Cohn, F. (1864). Über die Entstehung des travertine in der Wasserfallen von Tivoli. *Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie Abhandlung,* **40**, 580-610.

Cole, G. A. and Bachelder, G. L. (1969). Dynamics of an Arizona travertine-forming stream. *Journal of the Arizona Academy of Science,* **5**, 271-283.

Dürrenfeldt, A. (1978). Untersuchungen zur Besiedlungsbiologie von Kalktuff faunistische, ökologische und elektronenmikroskopische Befunde. *Archiven für Hydrobiologie,* Suppl., **54**, 1-79.

Edmond, J. M. (1970). High precision determination of titration alkalinity and carbon dioxide content of seawater by potentiometric titration. *Deep Sea Research,* **17**, 737-750.

Ek, C. and Pissart, A. (1965). Dépôt de carbonate de calcium par congélation et teneur en bicarbonate des eaux résiduelles. *Comptes rendus de l'Académie de Science,* **260**, 929-932.

Emig, W. H. (1918). Mosses as rock builders. *Bryologist,* **21**, 25-29.

Fielding, C. H. (1893). *Memories of Malling,* H.C.H. Oliver, West Malling, Kent.

Ford, (1970). Characteristics of limestone solution in the Southern Rocky Mountains and Selkirk Mountains, Alberta and British Columbia. *Canadian Journal of Earth Science,* **8**, 585-609.

Fritsch, F. E. and Pantin, C. F. A. (1946). Calcareous concretions in a Cambridgeshire stream. *Nature,* **157**, 397-399.

Golterman, H. L. (1969). *Methods for the chemical analysis of freshwaters.* IBP Handbook No. 8, Blackwell, London.

GOLUBIC, S. (1969). Cyclic and non-cyclic mechanisms in the formation of travertine. *Verhandlungen der Internationalen Vereinigung für theoretische und angewandte Limnologie,* **17**, 956-961.

GOLUBIC, S. (1973). The relationship between blue-green algae and carbonate deposits. In: *The Biology of the Blue-green Algae.* (N. G. Carr and B. A. Whitton, Eds.) 434-472. Blackwell, London.

GREGORY, J. W. (1911). Constructive waterfalls. *Scottish Geographical Magazine,* **27**, 537-546.

GRUNINGER, W. (1965). Rezente Kalktuffbildung im Bereich der Uracher Wasserfalls. *Abhandlung von Karst und Hohlenkunde,* E2, 1-113.

HOLMES, P. F. (1965). The natural history of Malham Tarn. *Field Studies,* **2**, 199-223.

JACOBSON, R. L. and USDOWSKI, E. (1975). Geochemical controls on a calcite precipitating spring. *Contributions to Mineralogy and Petrology,* **51**, 65-74.

KANN, E. (1941). Krustenstein in Seen. *Archiven für Hydrobiologie,* **37**, 432-504.

KINDLE, E. W. (1927). The role of thermal stratification in lacustrine sedimentation. *Transactions of the Royal Society of Canada,* **21**, 1-36.

LE ROUX, M. (1908). Récherches biologiques sur le lac d'Annecy. *Annales Biologique lacustre,* **2**, 220-402.

LUND, J. W. G. (1953). New or rare Chrysophyceae II. *Hyalobryon polymorphum* n. sp., and *Chrysonebula holmesii* n. gen., n. sp. *New Phytologist,* **52**, 114-123.

LUND, J. W. G. (1961). The algae of the Malham Tarn district. *Field Studies,* **1**, (3) 58-72.

MAWSON, D. (1929). Some South Australian algal limestones in the process of formation. *Quarterly Journal of the Geological Society of London.* **85**, 613-620.

MOISLEY, H. A. (1953). Some karstic features in the Malham Tarn district. *Annual report of the Council for the Promotion of Field Studies,* 1953/4, 33-42.

O'CONNOR, J. (1964). The geology of the area around Malham Tarn, Yorkshire. *Field Studies,* **2**, 53-82.

PENTECOST, A. (1975). *Calcium carbonate deposition by blue-green algae.* Ph.D. Thesis, University College of North Wales, Bangor.

PENTECOST, A. (1978). Blue-green algae and freshwater carbonate deposits. *Proceedings of the Royal Society, London,* **B 200**, 43-61.

PENTECOST, A. and FLETCHER, A. (1974). Tufa, an unusual lichen substrate. *Lichenologist,* **6**, 100-102.

PIA, J. (1933). Die Rezenten Kalksteine. *Mineralogische und Petrologische Mitteilung, Erganzungsband,* **1**, 1-419.

PITTY, A. F. (1968). Calcium carbonate content of karst water in relation to flow-through time. *Nature,* **217**, 939-940.

PITTY, A. F. (1971). Biological activity and the uptake and re-deposition of calcium carbonate in lake waters. *Environmental letters,* **1**, 103-109.

PROCTOR, M. C. F. (1960). Mosses and liverworts of the Malham district. *Field Studies,* **1**, (2) 61-85.

ROTHPLETZ, A. (1892). On the formation of oolite. ***American Geologist,*** **10**, 279-282.

RUSSELL, E. W. (1961). *Soil conditions and plant growth.* Longmans, Green and Co., London.

SCHMIDLE, W. (1910). Postglaziàle Ablagerungen im Nordwestlich Bodenseegebeit. *Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie Abhandlung,* **2**, 104-122.

SINKER, C. A. (1960). The vegetation of the Malham Tarn area. *Proceedings (Scientific) of the Leeds Philosophical and Literary Soceity,* **8**, 1-37.

SMITH, D. I. and ATKINSON, J. C. (1977). Underground flow in cavernous limestones with special reference to the Malham area, *Field Studies,* **4**, 597-616.

STUMM, W. and MORGAN, J. J. (1970). *Aquatic Chemistry.* Wiley Interscience, London and New York.

SYMOENS, J. J. (1949). Note sur des formations de tuf calcaire observés dans le bois d'Hautmont. Bulletin de la Societie Botanique de Belge, 82, 81-90

TERNAN, J. L. (1971). *Karst water studies in the Malham area, north of the Craven Fault,* PhD. Thesis, University of Hull.

WALLNER, J. (1933). *Oocardium stratum* Naeg, Eine wichtige tuffbildende Alge Südbayerns, *Planta,* **20**, 287-293.

WEST, G. S. and WEST, W. (1899). The alga-flora of Yorkshire. *Transactions of the Yorkshire Naturalists Union,* **5**, 1-239.

WOOD, E. D., ARMSTRONG, F. A. J. and RICHARDS, F. A. (1967). Determination of nitrate in sea water by cadmium-copper reduction to nitrite. *Journal of the Marine Biological Association of the United Kingdom,* **47**, 23-31.

Appendix I

Pure water, exposed to the atmosphere, will contain a trace of carbon dioxide in solution. Some of this gas reacts with the water to form a small quantity of carbonic acid, which gives the water a slightly acidic reaction with a pH of 6-6.5 (eq. 1).

$$CO_2 + H_2O \rightleftharpoons \underset{\text{carbonic acid}}{H_2CO_3} \tag{1}$$

Carbonic acid dissociates almost completely into bicarbonate, carbonate and hydrogen ions (eqs. 2 and 3).

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \tag{2}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{--} \tag{3}$$

Calcium carbonate, the principal constituent of limestone, can react with some of these hydrogen ions to produce soluble calcium bicarbonate (eq. 4).

$$H^+ + CaCO_3 + HCO_3^- \rightleftharpoons Ca(HCO_3)_2 \tag{4}$$

The amount of calcium carbonate which is dissolved depends upon the concentration of carbonic acid, which in turn, depends upon the concentration of carbon dioxide in the air. As the quantity of carbon dioxide (usually expressed as the partial pressure) in the atmosphere increases, the dissolution of limestone increases. Waters charged with carbonic acid and capable of dissolving limestone are often described as "aggressive". In industrial regions, atmospheric pollution by other acid-generating gases, e.g. sulphur dioxide, may increase this "aggressiveness".

The concentration of carbon dioxide in the atmosphere is approximately constant (0.03 per cent by volume), but the soil atmosphere, through which much rainwater passes, generally has a higher and more variable partial pressure of carbon dioxide which enhances limestone solution. Provided that the water is in contact with the limestone for a time sufficient for the reactions to go to completion, then a relationship between calcium carbonate solubility and the partial pressure of carbon dioxide may be sought. This is achieved by solving a series of equilibrium equations (Stumm and Morgan, 1970; p. 180) for an open system at a specified temperature, pressure and ionic strength. The solution is involved but it is readily obtained using computer methods. Some results, using this method (Pentecost, 1975) are shown in Fig. 14 where the mean calcium levels for Waterfall Beck, Gordale and Malham Tarn have been added. The results suggest that these waters were in contact with a soil atmosphere containg about 0.4-1 per cent carbon dioxide, i.e. a 13-30 fold enrichment over that of the air. These values are consistent with those obtained from actual soil samples (Russell, 1961).

An equilibrium equation describing the solubility of calcite in pure water is necessary to solve the equation above. This is the *solubility product* for calcite. The solubility product, K_s, is a constant at a given temperature, pressure and ionic strength. For calcite, K_s is the product of the concentrations (written in square brackets in eq. 5) of the calcium and carbonate ions in pure water. Evidently,

$$K_s = [Ca^{++}][CO_3^{--}] \tag{5}$$

a calcite-water system will contain a trace of carbon dioxide derived from the carbonate ions of the mineral itself (eqs. 2 and 3). The solubility product describes an equilibrium condition for the solution. If the concentration of either (or both) ions change, then the solubility product will change. If the changes result in the product increasing above the equilibrium value, then precipitation of some calcium carbonate may result, since the system will attempt to regain its equilibrium position. If the product descreases, dissolution of calcium carbonate may occur, for the same reason. Providing that the concentration of calcium and carbonate ions in solution is known, K_s may be determined and its value compared with tabulated values to determine whether the solution is in equilibrium with calcite. A more convenient method is to derive a "saturation index" for calcite. A good index is that described by Ford (1970), called SATCAL. This is defined as:

$$\text{SATCAL} = \frac{pK_s\ (\text{tabulated})}{pK_s\ (\text{calculated from sample})}$$

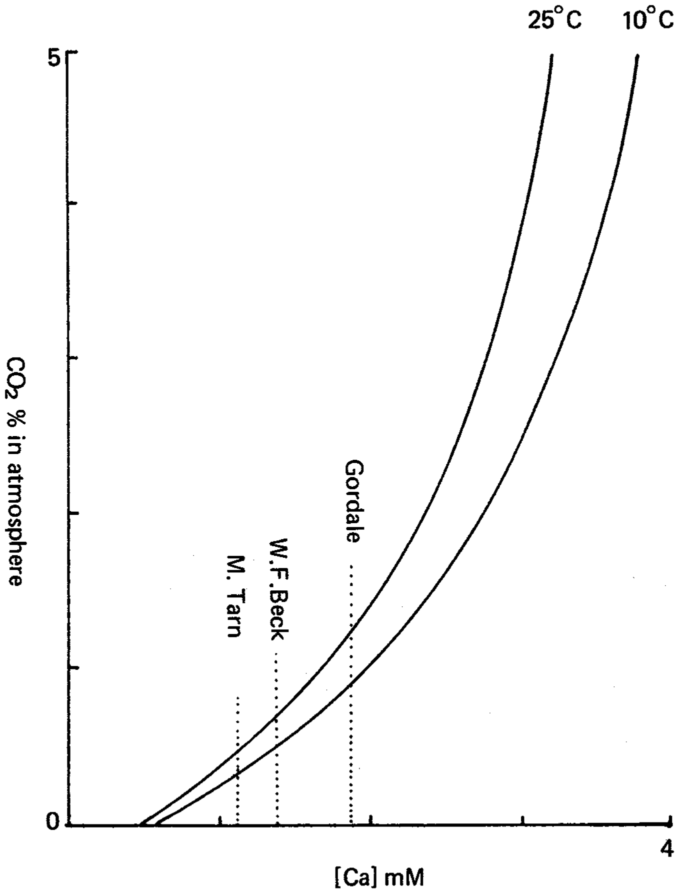

FIG. 14.
The relationship between atmospheric carbon dioxide concentration and the solubility of calcite (expressed as the calcium concentration) at two temperatures.

Where pK_S is the negative logarithm of K_S (c.f. pH).
SATCAL may be understood as follows:

SATCAL = 1	Water in equilibrium with calcite.
SATCAL < 1	Undersaturation, calcite dissolution possible, waters "aggressive".
SATCAL > 1	Supersaturation, calcite precipitation and tufa formation possible.

Note that sparingly soluble minerals such as calcite, supersaturate to a high degree so that precipitation does not necessarily occur if SATCAL > 1. The spring waters of High Mark had SATCAL values close to 1.0 (p. 372) indicating an equilibrium condition, but this situation soon changed once the carbon dioxide-rich waters contacted the air, as previously described, leading to calcite supersaturation, precipitation and tufa formation (eq. 6).

$$Ca(HCO_3)_2 \rightleftharpoons \underset{\text{tufa}}{CaCO_3\downarrow} + \overset{\text{atmosphere}}{\overset{\text{photosynthesis}}{CO_2\uparrow}} + H_2O \qquad (6)$$

Appendix II
Methods of analysis

(i) Dissolved cations. Ca, Mg, K, Na, Mn, Fe, Sr.
Atomic absorbtion spectrophotometry.

(ii) Total carbon dioxide and the carbon dioxide species.
High precision alkalinity titration of Edmond (1970). Total carbon dioxide is the concentration of all the carbon dioxide species in water. This is usually written as C_t, where

$$C_t = [CO_2\,(aq)] + [H_2CO_3] + [HCO_3^-] + [CO_3^{--}] + [\text{complexes}].$$

Since H_2CO_3 is only a small fraction of the CO_2 in solution, the two are combined as the composite, i.e. $[H_2CO_3] + [CO_2\,(aq)] = [H_2CO_3^*]$. The concentration of the individual species, necessary for the computation of SATCAL, was obtained from a computer programme devised by the author, although tables and library programmes are now readily available for this purpose. Complex formation (e.g. $CaHCO_3^+$) may cause errors in this method, but an independent check indicated that the concentration of complexes was negligible (see Stumm and Morgan, 1970).

(iii) pH:
EIL glass electrode, installed at the Field Centre. Many values were double-checked using a colorimetric method.

(iv) Sulphate, total reactive phosphate:
Golterman (1969)

(v) Nitrate:
Wood *et al,* (1967)

(vi) Tufa analysis.
Dried samples were decalcified with 0.1 N hydrochloric acid, the residue washed, dried and reweighed. The organic and inorganic, acid-insoluble fractions were determined by difference after wet-oxidation (conc. $H_2SO_4 + K_2Cr_2O_7$, 300°C).