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Active deposition of calcareous tufa in Wessex, UK, and its implications for the 'late-Holocene tufa decline'

Andy Baker[1] and Michael J. Simms[2]

([1]Department of Geography, University of Exeter, Amory Building, Rennes Drive, Exeter, EX4 4RJ, UK; [2]Department of Geology, Ulster Museum, Botanic Gardens, Belfast BT9 5AB, UK)

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Abstract: Recent publications have suggested that deposition of calcareous tufa and travertine in the British Isles has declined since the mid-Holocene. Several causal mechanisms have been postulated which include changes in both palaeoenvironmental and palaeoecological conditions. Results presented here for actively depositing tufa in the Wessex region of southwest England suggest that there has been significant under-reporting of contemporary tufa deposition. This factor must be taken into consideration in any investigation of a possible tufa decline in the late Holocene. Geochemical and environmental conditions at 26 tufa deposition sites are reported in order better to elucidate the climatic and environmental factors which constrain contemporary tufa deposition, and to achieve a better understanding of the controls on Holocene deposition.

Key words: Tufa, travertine, Holocene deposition, environmental change, geochemistry, Wessex, England.

Introduction

Calcareous tufa or travertine are secondary carbonate deposits which form primarily from the degassing of calcium carbonate rich waters (Pentecost, 1993). Several mechanisms have been proposed as to their formation, including both purely inorganic from the carbonate degassing process (e.g. Dreybrodt *et al*., 1992; Liu *et al*., 1995), as well as organic assisted deposition, through plant photosynthesis changing the CO_2 balance of the waters (Spiro and Pentecost, 1991).

Inorganic deposition of tufa can be explained using the theory of calcite deposition, where waters which are saturated with calcium degas on exposure to the atmosphere and precipitate calcium carbonate:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O \quad (1)$$

Several studies have investigated the chemistry of tufa deposition (Jacobson and Usdowski, 1975; Herman and Lorah, 1987; Michaelis *et al*., 1984; Liu *et al*., 1995). In an alternative mechanism, tufa may be deposited at springs where the cooling of thermally heated groundwaters occurs, and where dissolution has been enhanced by the action of sulphates, e.g. in geological areas with associated gypsum or metal sulphide deposits. In the case of the latter, this leads to the following reactions for the case of iron pyrite:

$$FeS_2 + 3.5\ O_2 + H_2O \rightarrow Fe^{2+} + 2H_2SO_4 \quad (2)$$

$$CaCO_3 + 2H_2SO_4 \rightarrow Ca^{2+} + SO_4^{2-} + CO_2 + H_2O \quad (3)$$

$$CO_2 + H_2O + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^- \quad (4)$$

demonstrating that one mole of pyrite releases two of sulphuric acid and that this, in turn, liberates more CO_2 to react with the limestone. When degassing occurs, tufa is deposited as $CaCO_3$ and the spring waters will be enriched in sulphate.

In addition to understanding the chemistry of tufa deposition, the rate of deposition can also be calculated from the chemical kinetics. This has been demonstrated in a series of papers by Dreybrodt *et al*. (Dreybrodt and Brumann, 1991; Dreybrodt *et al*., 1992) and Liu *et al*. (1995). They demonstrate that the rate of growth can be predicted by the equation:

$$\text{growth rate} = \alpha\ ([Ca^{2+}]_{eqm}\text{-}[Ca^{2+}]) \quad (5)$$

where α is dependent on temperature, the flow conditions (turbulent or laminar) and the thickness of the water film flowing over the tufa. In an extension to this work, Buhmann and Dreybrodt (1987) also demonstrated that common-ion effects may also increase or decrease growth rate.

The role of organic factors in the deposition of tufa is less clearly understood. The presence of organic matter such as leaves, twigs and moss may provide nuclei for the precipitation of calcium carbonate. In addition, cyanobacteria have been reported to

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have a role in tufa deposition (Pentecost, 1978). However, the role of photosynthesis is less well determined, especially where conditions are temperate, as is the case for British examples, or where tufa springs have a significant flow velocity rather than slow seepage flow and ponded water conditions which may aid the concentration of CO_2 produced from photosynthetic action.

Recent research has suggested that tufa deposition is sensitive to climatic and environmental change. In a review of possible factors affecting tufa deposition, Goudie *et al*. (1993) detail 26 possible causes for cessation of tufa deposition. These were divided into those caused by changes in discharge, water chemistry and catchment conditions respectively. A summary of these factors is presented in Table 1. It is apparent that these factors can be related to the geochemical and kinetic equations listed above. For example, tufa deposition is sensitive to changing groundwater calcium (equation 5) so there may be a decline in total growth abundance or in growth rate if groundwater calcium ion concentrations decrease. Alternatively, an increase may occur if the calcium concentration rises. Both changes are possible due to the impacts of changing farming practices (e.g. liming) or acid-rain deposition. The reader is referred to Goudie *et al*. (1993) for a more detailed discussion of the factors listed in Table 1.

Several authors, including Goudie *et al*. (1993) and Griffiths and Pedley (1995) have recognized a late-Holocene tufa decline in the UK (Figure 1); a similar decline has been suggested for several regions of Europe (Stirn, 1964; and see references in Pentecost, 1995). If tufa deposition has declined, or is still declining, then this has important environmental consequences as tufa springs provide a rare alkaline habitat. The evidence for this apparent tufa decline has been amassed from radiometric dating analyses as well as from published accounts of active and inactive tufa sites. Both environmental and climatic causes for the decline have been postulated. However, radiometric evidence is problematic as tufa cannot be dated by ^{14}C of the calcium carbonate since there is an unknown 'dead carbon' fraction, although organic inclusions within the tufa can be dated if present. Similarly, U-Th analyses are often inaccurate or imprecise, due either to high detrital contamination or to open system deposition causing uranium isotope mobilization. Both radiometric methods also suffer from sample bias as 'top' dates are rarely obtained from long sequences as this part is normally of little interest to the Holocene scientist. Finally, the size of sample of Holocene tufa published in Pentecost (1993) and Goudie *et al*. (1993) is too small for reliable interpretation of any trends in tufa deposition in the Holocene. Field survey would be the most precise method of determining the abundance of both contemporary and fossil tufa deposits, in order to get a better understanding of any tufa decline. To the authors' knowledge, only one survey has been undertaken in the British Isles. This took the form of a literature review rather than a field survey (Pentecost, 1993), and reviewed the distribution, mineralogy, size and age of 160 tufa deposits in the British Isles, caused predominantly by the degassing of calcium bicarbonate rich waters. Tufa deposition at all but one site was of calcite; the largest tufa was 81 ha in extent (Caerwys, Clywd); and most of the largest observed sites were fossil features. A total of 105 sites were active, 55 were inactive and most sites were associated with limestone formations, primarily Carboniferous limestone (33.7%) and Cretaceous chalk deposits (17.6%).

The review of Pentecost (1993) was the first of its kind for the British Isles. However, the contention that there has been a late-Holocene tufa decline, with a possible climatic or environmental cause requires a more detailed investigation to be undertaken. As Goudie *et al*. (1993) comment:

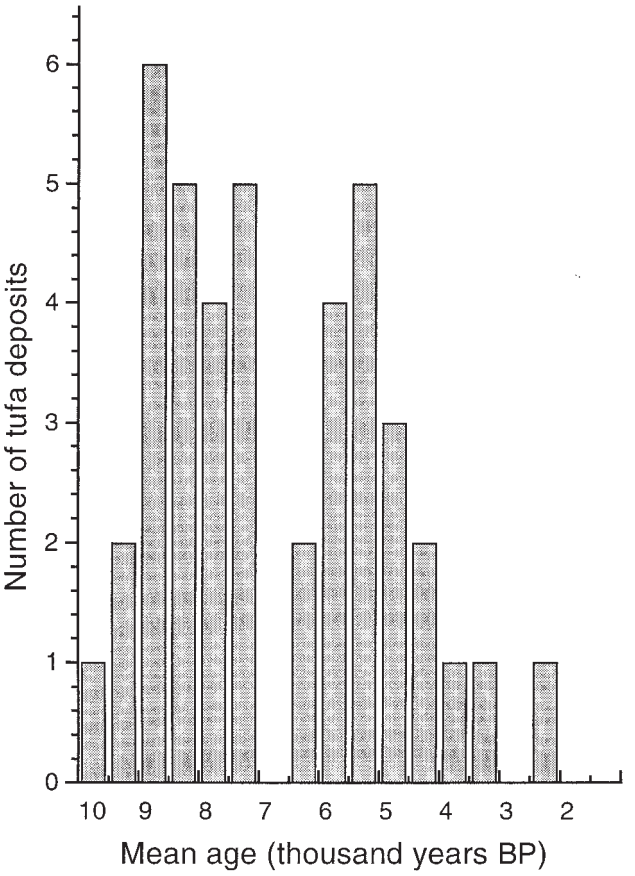

Figure 1 Age distribution of Holocene tufa (after Goudie *et al*., 1993; Griffiths and Pedley, 1995).

Table 1 Hypotheses to explain a decline in tufa deposition (summarized from Goudie *et al*., 1993). A decline in each of the factors is assessed as to whether it would generate a decline (–) or increase (+) in tufa deposition, and each factor is categorized as being either climatic (C) or anthropogenetically (A) induced

Hypothesis	Possible effect	Cl/An
Changes in discharge volume or variability		
– discharge variation associated with changes in precipitation	±	C
modification of surface drainage	±	A
Changes in water chemistry		
– due to increased soil erosion	–	C/A
– due to changes in soil chemistry	±	C/A
– due to change in soil thickness and thus P_{CO_2})	–	C/A
– due to deforestation/afforestation	±	C/A
– due to general water pollution	±	A
– due to acid deposition	+	A
Changes in catchment environment		
– deforestion/deforestation leading to change in water temperature regime	±	C/A
– introduction of livestock causing trampling	–	A
– change in temperature which may change the rate of tufa deposition	–	C/A
– devegetation of floodplains making them more susceptible to channel migration	–	C/A
– quarrying and culverting	–	A
– channel regulation	±	A
Self-limiting tufa deposition		
– tufa growth damming itself	–	–

In many parts of Europe there appears to be evidence for a decline in tufa deposition rates since the mid-Holocene. However, the veracity of this trend needs to be investigated further by undertaking more dating of tufa deposits, but with full knowledge of the limitations of many of the available techniques. Moreover, monitoring needs to be undertaken of more sites of tufa deposition to check whether present day rates are as low as often maintained and also to ascertain under what catchment conditions tufa deposition is active today.

It is the latter that we investigate here, by undertaking a detailed geochemical survey of tufa deposition sites in the Wessex Region (here defined as the unitary authorities of Somerset and North Somerset), in order to determine both their mode of formation, their catchment conditions and also their number and extent.

Site description and methods

An approximately 1000-km^2 study area was defined, bounded by Bristol, Bath, Castle Cary and Taunton (Figure 2). This area was chosen on account of varied land use and geology. In terms of land use, the region is dominated by improved pasture land, with limited mixed farming in the south of the region; 1995 census results demonstrate 58 000 out of 272 000 hectares under tillage (mostly wheat and stock-feed), and 199 000 hectares of grassland (34 000 hectares under five years old; 152 hectares over five years old; 13 000 hectares rough grazing; Ministry of Agriculture, Fisheries and Food, 1995). Within the area covered by the survey a number of distinct aquifers can be identified in the Palaeozoic and Mesozoic successions. The basic characteristics of these are summarized below.

Carboniferous Limestone

The Carboniferous Limestone succession of the Mendip Hills reaches about 1000 m in thickness. It is dominated by massive, fairly pure limestones and clastic units, of sand or mud, are confined almost exclusively to the basal Lower Limestone Shale and the very top of the Carboniferous Limestone (Waltham *et al*., 1997). Minor shale partings may occur at any level within the succession but are of little hydrological significance. The Palaeozoic succession in and around the Mendip Hills has been folded into a series of elongate domes such that the central upland core of Old Red Sandstone now acts as the main allogenic catchment for recharge to the Carboniferous Limestone aquifer. Porosity in the Carboniferous Limestone is very low but permeability along fractures and bedding planes locally may be high, producing the dissolutional conduits, or caves, characteristic of the area. Throughflow in these conduits is rapid compared with other aquifers and at discharge the water typically is unsaturated.

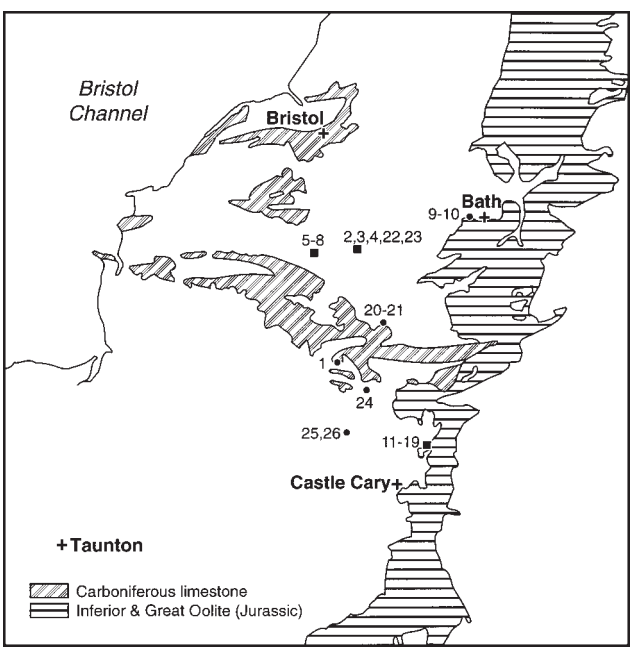

Figure 2 Map of the tufa sites of the Wessex region.

Triassic, Mercia Mudstone Group

The Mercia Mudstone Group is a major aquiclude in which permeability is extremely low. However, in the upper part of the succession a number of minor calcareous units, nowhere more than a few metres thick, act as minor aquifers and discharge springs at outcrop. The most extensive of these aquifers is the Butcombe Sandstone, a coarse, sometimes conglomeratic, sandstone of fairly high porosity. Many of the clasts are of Carboniferous Limestone or reworked Triassic pedogenic or lacustrine limestone. Sulphates, in the form of gypsum (calcium sulphate) and celestine (strontium sulphate) are present in minor amounts in the Mercia Mudstone Group and this may well account for the sulphate component of some spring waters.

Triassic, Penarth Group (Rhaetic)

The dark pyritous mudstones of the lower part of the Penarth Group form an important aquiclude. Nonetheless, minor springs may be associated with thin sandstones within the succession.

Lower Jurassic, Lower Lias

The lower part of the Lower Lias, often called the Blue Lias, is characterized by alternations of thin (typically 5–30 cm thick) argillaceous limestones intercalated with calcareous mudstones. The latter act as aquitards between the limestones, with jointing and other fractures allowing water flow through the thin mudstone bands. Porosity of the limestones is low but conduit flow can develop along joints and at the junction of limestones and mudstones; solutionally enlarged joints have been observed at outcrop at several sites. The thinness of the limestones and resultant close spacing of fractures, and their separation by relatively impermeable mudstones, prevents the development of direct flow paths. Hence flow-through time probably is considerably greater than for the larger Carboniferous Limestone conduits and so the water frequently is saturated at the point of discharge.

Adjacent to some parts of the Mendip Hills the typical mudstone-limestone alternations of the Lower Lias are not seen. Instead a carbonate-dominated succession is seen in which much of the Lower Lias is developed as massive bioclastic limestones which lithologically, and hydrologically, are similar to the Carboniferous Limestone.

Lower Jurassic, Middle Lias

In parts of Somerset the Middle Lias succession comprises, in part, a sequence of fairly porous calcareous sands, the Pennard Sands. These are underlain by impermeable silts, with springs at the junction of the two units. Recharge to the Pennard Sands at the sites visited is autogenic and flow through the aquifer is diffuse, with water typically saturated at discharge.

Middle Jurassic, Great Oolite

Both the Great Oolite and the underlying Inferior Oolite are important aquifers. Porosity is much higher than in the Carboniferous Limestone, although fissure flow also is important. The prevalence of one or other at a particular site may have an important bearing on whether the water at discharge is saturated or not. Recharge to the aquifer is autogenic while springs from the Great Oolite typically discharge at the junction with the underlying Fullers Earth Clay aquiclude.

Springs were located within the chosen study region using OS 1:25 000 maps. A random selection were visited between January and July 1996, chosen from locations identified by the authors as being potentially suitable for tufa precipitation (primarily where springs were associated with geological boundaries and the overlying rock was known to be calcareous). In addition, the location of known or probable tufa sites was provided by local wildlife trusts, ecological consultancies and the Environment Agency; these localities were also visited. For each tufa depositing site, the local geological and environmental conditions were noted. Water samples for geochemical analysis were taken in 125-ml glass bottles with glass stoppers. These were filled to the top, kept cool and analysed within 24 hours for pH with a 0.01 precision meter and HCO_3^- by titration with 0.1 M HCl. The remaining solution was then acidified with 14 M HNO_3 and Ca^{2+}, Mg^{2+}, Sr^{2+}, Na^+, K^+, Cl^- and SO_4^{2-} determined by AAAS. Total ion chemistry was calculated using WaterEqf (Plummer *et al*., 1976) and, where ion balance error was under 10%, the saturation indexes were calculated. Water geochemical samples are point samples; for a complete analysis of the characteristics of the springs a complete annual cycle would need to be investigated. However, previous geochemical studies have suggested that intra-annual changes in source chemical characteristics are of the order of only ± 20% (Michaelis *et al*., 1984; Herman and Lorah, 1987; Dreybrodt *et al*., 1992); three of the sites presented here were also sampled at regular intervals to confirm this characteristic. Although subtle variations in tufa depositional characteristics on a diurnal to seasonal timescale may be missed by our sampling strategy, point data does provide a useful indicator of basic geochemical properties.

Results

Twenty-six tufa depositing springs were visited in the course of this study. The spatial distribution of these sites is plotted in Figure 2, and the water geochemical and site environmental data presented in Table 2. Detailed site descriptions can be found in the Appendix. The tufa sites can be considered in terms of their number and size, as well as site geology, environment and water geochemistry.

The number of tufa sites

Previous work indicated that only five tufa sites are present within the region studied here, of which only one is active. Pentecost (1993) lists Bath Spa (active, but a thermal spring), Horton Court (National Grid Reference ST/766850, inactive), Midsomer Norton (ST/643538, inactive), Rodney Stoke (ST/476497, inactive) and Wookey Hole (ST/532480, inactive). In this study we have not undertaken a survey of inactive sites, although this is a feasible future project. Of the 40 springs we chose to investigate, 26 were depositing tufa. Our sample was biased towards spring sites issuing from calcareous rocks in the region, which may suggest an overestimate of the absolute total number of tufa sites from all rock types in the region. Nonetheless, our results clearly demonstrate that considerable underreporting of tufa deposition is occurring. This is particularly highlighted by the fact that we have visited only *c*. 10% of all the springs issuing from limestone rocks in the region, suggesting that the total number of tufa deposits in the region may exceed 200, a figure greater than the national total cited in Pentecost (1993).

The size of the tufa sites

The size of the active sites visited in this study are small compared with other active sites in the country which have been reported in the literature and compared with fossil sites reported in Pentecost (1993). However, there probably has been considerable bias

Table 2 Sites of active tufa deposition are listed below. Environment and geochemical conditions are also listed. Geochemistry samples were point samples during the period 1/96 to 6/96

Site No.	Site-ID	Location	OS Grid Reference (All within ST grid square)	Geology	Vegetation	pH	Alkalinity	SO_4^{2-}	Ca^{2+}	Mg^{2+}	K^+	Na^+	Cl^-	Ion Balance	Sat. Index Calcite	Sat. Index Aragonite	Sat. Index Dolomite	Sat. Index Magnesite
							mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	%				
1	Fountain	Dulcotte, near Wells	565446	Triassic Mudston or Carboniferous Limestone	Unknown	7.51	6.0	0.18	2.23	1.23	0.17	1.18	1.12	4.7	0.30	0.15	0.25	0.36
2	Fort Main	Cinderlands Brake, Stoweay	601594	Lower Lias, Triassic	Secondary Woodland	7.24	4.8	n.d.	2.74	0.11	0.01	0.73	0.45	9.2	0.04	0.12	-1.44	-1.79
3	Fort-2T	" secondary flow	601594	Lower Lias, Triassic	-	7.74	3.6	n.d.	2.23	0.07	0.09	1.30	0.60	15.9	0.30	0.14	-1.07	-1.67
4	Fort-2B	" secondary flow	601594	Lower Lias, Triassic	-	8.41	3.8	n.d.	2.21	0.07	0.00	0.29	0.64	3.9	0.97	0.81	0.28	0.99
5	CG-1	Cook's Gully, Nempnett Thrumpwell	534595	Butcombe Sandstone, Jurassic	Secondary Woodland	8.11	6.6	0.67	2.43	1.92	0.04	0.66	0.72	3.9	0.94	0.78	1.68	0.43
6	CG-2	"	534595	Butcombe Sandstone, Jurassic	-	8.14	6.6	0.49	2.40	1.72	0.06	0.54	0.55	3.9	1.04	0.88	1.84	0.49
7	CG-3	"	534595	Butcombe Sandstone, Jurassic	-	8.07	5.6	2.03	5.80	2.19	0.04	0.53	0.67	22.3	1.13	0.97	1.76	0.31
8	CG-4	"	534595	Butcombe Sandstone, Jurassic	-	8.14	6.0	1.06	3.03	1.56	0.02	0.31	0.28	5.9	1.01	0.85	1.65	0.32
9	West	Vernham Wood, Odd Down, Bath	731618	Great oolite, Jurassic	Coppiced woodland	6.94	5.2	1.40	7.54	0.67	0.23	1.00	0.94	22.6	0.25	0.09	-0.64	1.20
10	East	Vernham Wood, Odd Down, Bath	731618	Great oolite, Jurassic	-	7.82	4.0	0.91	3.63	0.24	0.12	0.80	0.96	11.4	0.63	0.47	-0.01	0.95
11	Saite Lane	Batcombe	693388	Inferior Oolite, Jurassic	Grass	8.38	5.8	0.15	2.28	0.35	0.10	0.94	0.26	0.4	1.16	1.01	1.42	-0.05
12	Lower Source	Moor Lane, Batcombe	692386	Inferior Oolite, Jurassic	Grass	7.36	5.0	0.30	2.60	0.95	3.72	0.87	4.10	1.4	0.13	0.02	-1.26	-1.71
13	Main Source	Hydraulic Ram, nr Batcombe	673369	Inferior Oolite, Jurassic	Grass	8.18	4.4	0.30	2.75	0.09	0.03	0.30	0.58	3.4	0.94	0.78	0.30	0.95
14	Lower Culvert	Moor Lane, Batcombe	692386	Inferior Oolite, Jurassic	Grass	7.79	4.0	0.47	2.83	0.13	0.08	0.30	0.58	6.1	0.53	0.37	-0.38	-1.22
15	Main source	Carrot Hill Farm, nr Batcombe	674373	Inferior Oolite, Jurassic	Grass	8.62	5.6	0.07	2.80	0.17	0.03	0.33	0.45	0.8	1.45	1.30	1.60	0.16
16	Secondary	Carrot Hill Farm	674373	Inferior Oolite, Jurassic	Grass	8.58	4.6	0.22	2.68	0.16	0.03	0.32	0.99	0.0	1.32	1.16	1.32	0.31
17	Mid source	Moor Lane, Batcombe	692384	Inferior Oolite, Jurassic	Grass	7.36	4.0	0.43	2.70	0.12	0.05	0.30	0.28	7.1	0.09	0.07	-1.26	-1.66
18	Source	Moor Lane, Batcombe	694382	Inferior Oolite, Jurassic	Grass	7.98	5.0	0.30	2.63	0.12	0.03	0.31	0.42	1.4	0.78	0.62	0.14	0.96
19	Secondary	Hydraulic Ram, nr Batcombe	673369	Inferior Oolite, Jurassic	Grass	8.62	5.0	0.13	2.55	0.09	0.03	0.30	0.49	1.2	1.37	1.22	1.21	0.48
20	Wood	Hay Street, Ston Easton	631538	Rhaetic and Lower Lias, Triassic	Woodland	7.83	5.4	0.10	2.90	0.11	0.02	0.39	0.40	3.3	0.71	0.55	0.10	-1.12
21	Trough	Hay Street, Ston Easton	631538	Rhaetic and Lower Lias, Triassic	Woodland	7.41	5.2	0.07	2.90	0.11	0.03	0.12	0.39	3.5	0.28	0.13	0.95	-1.54
22	East	Tynemoor Wood, Temple Cloud	609595	Lower Lias, Triassic	Secondary Woodland	7.85	5.2	nd	2.65	0.19	0.01	0.20	0.36	2.0	0.64	0.48	0.01	-0.95
23	West	"	609595	Lower Lias, Triassic	Secondary Woodland	7.58	5.6	nd	2.51	1.18	0.02	0.28	0.48	16.2	0.37	0.21	0.30	-0.38
24	Source	Trivvell, near Croscombe	600438	Rhaetic and Lower Lias, Triassic	Grass	7.31	nd	0.19	2.95	0.12	0.02	0.46	0.63	nd	nd	nd	nd	nd
25	Cascade	Washingstones Gulley, West Pennard	565376	Middle Lias Pennard Sands, Jurassic	Secondary Woodland	8.31	nd	0.75	2.65	0.60	0.09	0.82	0.53	nd	nd	nd	nd	nd
26	Cascade	Withal Combe, West Pennard	570377	Middle Lias Pennard Sands, Jurassic	Secondary Woodland	8.45	nd	0.85	2.70	0.58	0.06	0.86	0.60	nd	nd	nd	nd	nd
	Mean of all sites					**7.91**	**5.09**	**0.53**	**2.97**	**0.57**	**0.20**	**0.56**	**0.71**	**6.54**	**0.71**	**0.58**	**0.29**	**-0.73**
	Standard Deviation of all sites					**0.47**	**0.95**	**0.50**	**1.15**	**0.66**	**0.72**	**0.32**	**0.73**	**6.71**	**0.44**	**0.44**	**1.09**	**0.73**

towards the reporting of only the larger tufa deposits, with smaller deposits being ignored or overlooked. The largest sites observed here are at Tynemoor Wood (sites 22 and 23 in Table 2; Figure 3), where tufa deposition is occurring along a 500-m length of stream, and at Odd Down (sites 9 and 10) where active deposition is just part of a 1000-m^2 tufa cascade. Typical downstream length of tufa deposition is 1–500 m, and barrage/cascade height is 1–5 m. The size of contemporary tufa deposits in the region may explain the underreporting of deposits, and may suggest that there has been a decrease in the size of tufa deposits as opposed to a simple decline in the number of sites, which in turn reflects the climatic change over the Holocene.

The geology of the tufa sites

All the sites reported here have been found associated with lithological boundaries directly associated with Jurassic or Triassic rocks. Somewhat surprisingly, none have been found directly associated with the Carboniferous Limestone even though this comprises some 40% of the total outcrop of carbonate rocks in the region of study. The data presented in Table 2 suggests that the bulk of tufa deposition is due to the bicarbonate chemistry, rather than through sulphate effects (only deposition at the base of the Butcombe Sandstone at sites 5–8 demonstrate an important sulphate effect). Hence the lack of tufa deposition associated with the Carboniferous Limestone must be due to other factors. One possible explanation is the substantially higher porosity of at least some of the Mesozoic aquifers, notably the Jurassic oolites, compared with the Carboniferous Limestone, which has a very low porosity but high permeability through fissue flow. This produces a relatively high storage capacity and long residence time in the Jurassic oolites, as demonstrated by dye tracing experiments (Smart, 1977). This in turn would permit supersaturation of the water with respect to calcium carbonate and thus promote tufa deposition. However, the Carboniferous Limestone in the region differs in only minor respects from that found in northern England, the Peak District of Wales, areas where tufa deposition is occurring today (Pentecost, 1993; Waltham *et al*., 1996).

The local environmental conditions

Most of the sites located were in woodland (58%), although there are some exceptions (e.g. deposition over a fountain at Dulcote). The predominance of tufa deposition within woodland may suggest that this has an influence on tufa deposition. For example, woodland may increase the calcium concentration of the local groundwater through the maintenance of a high soil CO_2 concentration (Miotke, 1974) or provide precipitation nuclei for tufa deposition, e.g. branches and twigs. Alternatively, the presence of tufa in woodland may reflect the destruction of many tufa sites as a result of the intensification of farming practices; hence it is preserved today only in relatively undisturbed areas such as woodland. Of the above hypotheses, the former seems unlikely as the tufa sites are being formed through inorganic rather than organic processes (Table 1). Similarly, vegetation influences on tufa deposition would generally involve the change in calcium concentration of the groundwaters, which would be expected to affect a large area and not a localized spring. This has been observed through a doubling of spring water calcium ion concentration emitted from the Carboniferous limestone in the region at Cheddar Rising over the last 40 years, an increase which has been attributed to intensification of farming practices (Richards, 1987). Such an increase in calcium ion concentration would, however, increase the likelihood of tufa deposition. Data on agricultural change in the region, although limited by change in the census area as county boundaries have altered and by problems of false returns from farmers, does suggest that there has been an intensification, but of the form of a consistent decrease in the percentage of rough grazing land in the region from ~10% to ~5% over the last 50 years (Table 3). Thus intensification of farming in the region may remain the most likely cause of tufa decline, with historically documented sites such as the large cascade at Stowey Church (ST\599594) being obliterated through the conversion of rough grazing to permanent pasture.

Table 3 Percentage agricultural land use for the county of Somerset. Note a consistent decline in rough grazing and arable at the expense of permanent grassland. For source of data, see text; note that Somerset county decreased in area between 1974 and 1996, which may affect the returns

Land use	1950	1951	1976	1977	1995
Grassland: rough grazing	10.2	10.2	7.6	7.3	4.8
Grassland: > five years old	59.0	60.9	59.2	58.0	55.9
Arable	30.7	28.9	31.5	32.6	21.3

Figure 3 The cascade at Tynemoor Wood (site 23).

The geochemistry of the tufa sites

As previously stated, tufa spring deposition is predominantly controlled by inorganic, geochemical processes. The data presented in Table 2 add weight to this argument, as the geochemistry is dominated by the CO_2-HCO_3-$CaCO_3$ system. Springwater pH is in the range 7.5 to 8.7, and initial calcium concentrations range from 2.2 to 7.5 $mmol^{-1}$, all significantly above that of equilibrium (0.6–0.8 mmol l^{-1}) concentration as indicated by the positive saturation indexes with respect to calcite. No correlation is apparent between the geochemistry of the waters and either land use or geology (with the exception of the sulphate-rich springs issuing from the Butcombe Sandstone).

Has there been a late-Holocene tufa decline?

Results presented here suggest that there has been a considerable underreporting of active tufa deposition. This observation in turn suggests that the same has occurred for fossil sites. Our results demonstrate that, if there has been a decline in tufa deposition over the Holocene, it has taken the form of a decline in large tufa deposits (>1000 m^2) as opposed to small sites (<1000 m^2), rather than an actual decline in the number of tufa deposition sites. If this is true, then this may still be a climatically driven response, with the more fractured Carboniferous Limestones of the region having a greater sensitivity to climate change over the Holocene, because of their shorter groundwater residence time and fewer total number of springs with higher discharge compared to neighbouring Jurassic and Triassic rocks. If such a decline in large-scale tufa deposition has occurred then it might reflect not only possible hydrological variations in groundwater flow over the 10^3 years timescale but, perhaps more importantly, the effect of agricultural 'improvements' and the intensification of farming which has led to increased culverting and ploughing-in of sites over the decade to century timescale. There remains a need for further regional studies to see if this trend is repeated elsewhere in the British Isles and further afield, in particular at sites of more and less intensive land use as well as in regions of differing geology. In addition, the recognition of tufa sites has taken on a new importance because the alkaline spring water (typically pH 7.5 to 8.0; Table 2) associated with them provides a unique habitat for several bryophytes, in particular *Cratoneurion commutatum* (Pentecost, 1995). This species is currently protected under the EU habitat directive (SACS), where member states are required to identify the best examples and conserve them. Two *Cratoneurion* sites were observed in this study.

The results presented here suggest that the hypothesis presented by Griffiths and Pedley (1995), that tufa deposition occurred primarily in a period of low atmospheric CO_2 in the early Holocene, is highly unlikely. First, significant active deposition is occurring today, a time of atmospheric CO_2 well above their 'window'. Second, the geochemical theory of carbonate deposition suggests that a change in atmospheric CO_2 from 3×10^{-4} to 3×10^{-3} atm will only change the critical saturation level of calcium necessary for tufa deposition from 0.63 $mmol^{-1}$ to 0.93 mmol l^{-1} (from Dreybrodt, 1988; Dreybrodt *et al.*, 1992). This range in CO_2 is much greater than that experienced over the Holocene, and indeed is higher than that predicted for future climate change, yet the change in groundwater calcium concentration is such that it would not cause the cessation of any of the sites investigated here (Table 2).

Future research needs to undertake detailed studies at a wide range of tufa depositing sites over annual and daily field cycles in order to gain a better understanding of the geochemistry of the tufa depositing waters, their growth rate, and their sensitivity to seasonal and environmental change. Only through the application of both contemporary calibration and improved radiometric dating results can Holocene and Quaternary tufa deposits be included with any confidence in the reconstruction of climatic and environmental change through the use of abundance diagrams and through isotope, pollen, macrofossil and trace element analyses.

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Appendix – site descriptions

Sites with associated water chemistry

1) Dulcote, near Wells (ST 565446). Fountain at road junction with culverted spring in roadside wall opposite. Presumably derived from Carboniferous Limestone which outcrops in the inlier of Dulcote Hill nearby. Possibly rising through thin Triassic mudstone cover; the Triassic mudstones in this area contain minor occurrences of gypsum (calcium sulphate) which may account for the chemistry of the water at this site. Extensive tufa encrustation.

2–4) Cinderlands Brake, Stowey (ST 601594). Several springs issuing from alternating limestones and mudstones near base of Lower Lias. This part of the Lower Lias comprises centimetre to decimetre-scale alternations of argillaceous limestones and calcareous mudstones. Minor tufa cascades.

5–8) Cook's Gully, Nempnett Thrubwell (ST 534595). Several springs issuing from calcareous unit in upper part of Mercia Mudstone Group. This unit may be the Butcombe Sandstone, which contains a significant calcareous component, or from a thin lacustrine limestone unit a few metres lower in the succession. Extensive tufa cascades for some distance downstream.

9–10) Vernham Wood, Odd Down, Bath (ST 731618). Several springs issuing from junction of Great Oolite limestones with Fullers Earth Clays beneath. The Great Oolite has a relatively high intergranular porosity compared with other limestones in the region, such as the Lias limestones and the Carboniferous Limestone. Major tufa deposition over considerable area, though much disrupted by landslipping.

11–19) Batcombe Sites: Saite Lane (ST 693388); Moor Lane (ST 692386), Carrot Hill Farm (ST 674373). Many springs issue from the base of the Inferior Oolite which forms the local hills. Tufa deposition is extensive, encrusting ditches and forming substantial cascades along the stream within the village for many hundreds of metres. Tufa persists at localities where substantial field improvements have occurred.

20) Wellow Brook, Ston Easton (ST 630539). Minor springs issuing from Penarth Group (Rhaetic). The Penarth Group contains minor limestones and calcareous sands but otherwise is predominantly mudstones, often with substantial quantities of iron pyrite in the lower part of the sequence. The main aquifer here probably is the overlying thin limestones of the basal Lower Lias, with some flow along fractures in the Penarth Group towards outcrop. Extensive fossil tufa deposits are evident from material thrown out of animal burrows.

21) Hay Street, Ston Easton (ST 631538). Tufa encrusted water trough and culvert fed from limestones in the Lower Lias. The Lower Lias succession here is of a condensed facies dominated by limestones with only very minor mudstone units.

22–23) Tynemoor Wood, near Clutton (ST 609595). Minor springs issuing from alternating limestones and mudstones in lower part of Lower Lias where faulted against Mercia Mudstones. Large tufa cascades.

24) Titwell, near Croscombe (ST 600438). Spring issuing from base of massive Lower Lias limestones or the Penarth Group (Rhaetic) beneath. The Lower Lias in this area is in a massive, condensed facies with no significant mudstone intercalations. Major tufa cascade with grottos where stream descends into valley.

25) Washing Stones Gully, Pennard Hill (ST 565376). Seepage springs from Middle Lias Pennard Sands overlying impermeable siltstones. The Pennard Sands are calcareous and have a moderately high porosity. Eastern tributary has major tufa cascade at confluence; western branch shows no tufa deposition.

26) Withial Combe Nature Reserve (ST 570377). Seepage springs from Middle Lias Pennard Sands above impermeable siltstones. Intermittent tufa deposition, with major cascade on western tributary.

Sites with no water chemical analyses/sites adjacent to study region

27) Magotty Pagotty, Copley Wood, near Kingweston (ST 511310). Minor springs issuing from alternating limestones and mudstones near base of Lower Lias. Minor tufa encrustations along stream.

28) Pit Farm, Butcombe (ST 516621). Extensive seepage from calcareous units, either the Butcombe Sandstone or a thin lacustrine limestone, within Mercia Mudstone Group. Large tufa deposits.

29) Aust Cliff (ST 565896). Seepage from Penarth Group (Rhaetic) and basal Lias limestones, particularly adjacent to faults cutting southern end of cliff. Tufa cascades.

30) Sedbury Cliff, near Chepstow (ST 557932). Numerous springs issuing from alternating limestones and mudstones near base of Lower Lias about 20 m above foot of cliff. Large fallen masses of tufa lie at base of cliff.