HYDROLOGICAL IMPLICATIONS FROM ^{14}C PROFILING OF UK TUFA

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ABSTRACT. Tufa is a superficial, secondary deposit of calcium carbonate which accumulates on precipitation from emergent spring waters. It occurs as discrete, localized masses in regions of calcareous country rock.

In the United Kingdom, deposits vary widely in structure and thickness but little is known of the rate of deposition. Some deposits contain laminae assumed to represent annual growth increments and which should contain a ^{14}C and stable isotope record related to the original water from which it was precipitated.

Investigations are reported on tufa from three areas of different limestones in the United Kingdom (Northwest Yorkshire, South Derbyshire and North Oxfordshire).

Hydrologically, the dating of tufa by ^{14}C involves the same problems as the dating of groundwater. In the case of actively forming tufa, however, it is possible to derive a sequence of measurements, beginning with present day deposition, which clearly demonstrates the applications of age corrections.

At Gordale Scar, Northwest Yorkshire, a profiling study of laminated tufa appears to show bomb trial ^{14}C to a depth of 18mm below the surface, with almost constant values around 50 percent modern (raw data) from 18 to 48mm below the surface. The ^{14}C content of surface tufa lies within the seasonal range of ^{14}C measurements from the parent stream waters.

Results of 50 percent modern in the sequence are consistent with the simplest correction procedures based on $\delta^{13}C$ balance and the observed $\delta^{13}C$ change on tufa precipitation is a practical demonstration of the fractionation factor ϵ_{17}. However, the application of corrections to active, surface tufa and parent waters collected monthly over a period of study (14 months) from all three sites, produce results higher than would be expected from published world ^{14}C levels.

INTRODUCTION

Tufa deposits form at or near the emergence of spring waters in limestone regions. Terrestrial $CaCO_3$ deposition occurs from Ca-bicarbonate solutions via the overall reaction:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + H_2O + CO_2\uparrow \text{ (Usdowski, Hoefs, and Menschel, 1978)}$$
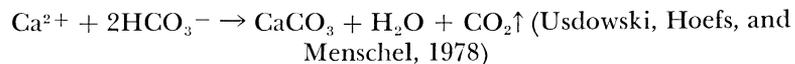
In the United Kingdom, tufa deposits achieve thicknesses of up to 5m and little is known of the rate of accumulation. Tufa deposits are intimately associated with the emergence of groundwaters at springs. The isotopic dating of tufa has considerable relevance to the dating of groundwaters.

In this investigation levels of ^{14}C in active surface layers of tufa and parent waters are compared. A record of past levels, including the bomb trial input since 1954 was sought in samples taken at depth and from profiling of a near surface sequence.

The report includes examples of downstream and seasonal isotopic changes related to exchange with the atmosphere, CO_2 degassing, tufa deposition, etc. Differences of stable isotope composition of active tufa and stream waters provides a practical demonstration of the known isotopic fractionation in $CaCO_3$ deposition (Deines, Langmuir, and Harmon, 1974; Friedman, 1970; Gonfiantini, Panichi, and Tongiorgi, 1968).

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Study areas

Gordale Scar, Malham, N Yorkshire, Grid Ref (GR) SD 91556406

The area consists of massively bedded, well jointed Carboniferous Limestone with a very low matrix porosity. Water movement, underground is confined almost entirely to fissures opened up along joint and bedding-plane weaknesses.

The stream, Gordale Beck, originates from five major springs (eg, station A, fig 1A) which flow for ~ 3.5km over shallow waterfalls into a gorge at Gordale Scar. Tufa mounds are common where turbulent waterflow over rock steps creates waterfalls, with maximum accumulation as the stream passes through the gorge via two major waterfalls, forming the upper and lower mounds (station B-C, fig 1A).

During periods of low rainfall the waters sink underground into the rock above the major waterfalls, (eg, 'sink' on 22.6.78, fig 1A). This seasonal drought is the probable origin of the laminated structure of the upper and lower mounds. Further downstream (station D), two springs of constant flow join Gordale Beck and at Janets Foss (station E) a waterfall deposits unlaminated tufa.

Water samples were collected at the stations and sink position in figure 1a. Samples were taken monthly at station D. Also surface scrapings of active tufa were collected from encrusted boulders and from the upper and lower mounds. A number of bedrock samples were collected from above the stream level.

Dunsley Springs, Matlock, Derbyshire, GR SK 2701 5679

A lenticular tufa deposit overlies Carboniferous Limestone on a steeply inclined (~26°) valley side. Water issues from two springs (eg, station A, fig 1B) and flows across the deposit via two deeply incised channels. Active tufa accumulation only occurs in zones of turbulent waterflow in the stream channels. Apart from this, the deposit is inactive at present.

Water samples were collected at the springs and at station B. Monthly water samples were taken at station B. Surface scrapings of active tufa were collected from the stream channels and bedrock samples from the catchment area of the springs.

Priory Mill, Chipping Norton, Oxfordshire, GR SP 3335 2977

The area consists of Upper Jurassic limestone (< 10m thickness) overlying effectively impermeable Upper Lias clay. Tufa is actively accumulating below several springs that emerge at the limestone-clay interface. Deposition occurs on the gently inclined slope (~ 1.8°) for a distance of ~ 500m.

Water samples were collected from all the springs, for example station A in figure 1C. Water samples were taken monthly at station B. One scraping of active surface tufa was collected 2m upstream of station B, and bedrock samples were taken within the spring catchment area.
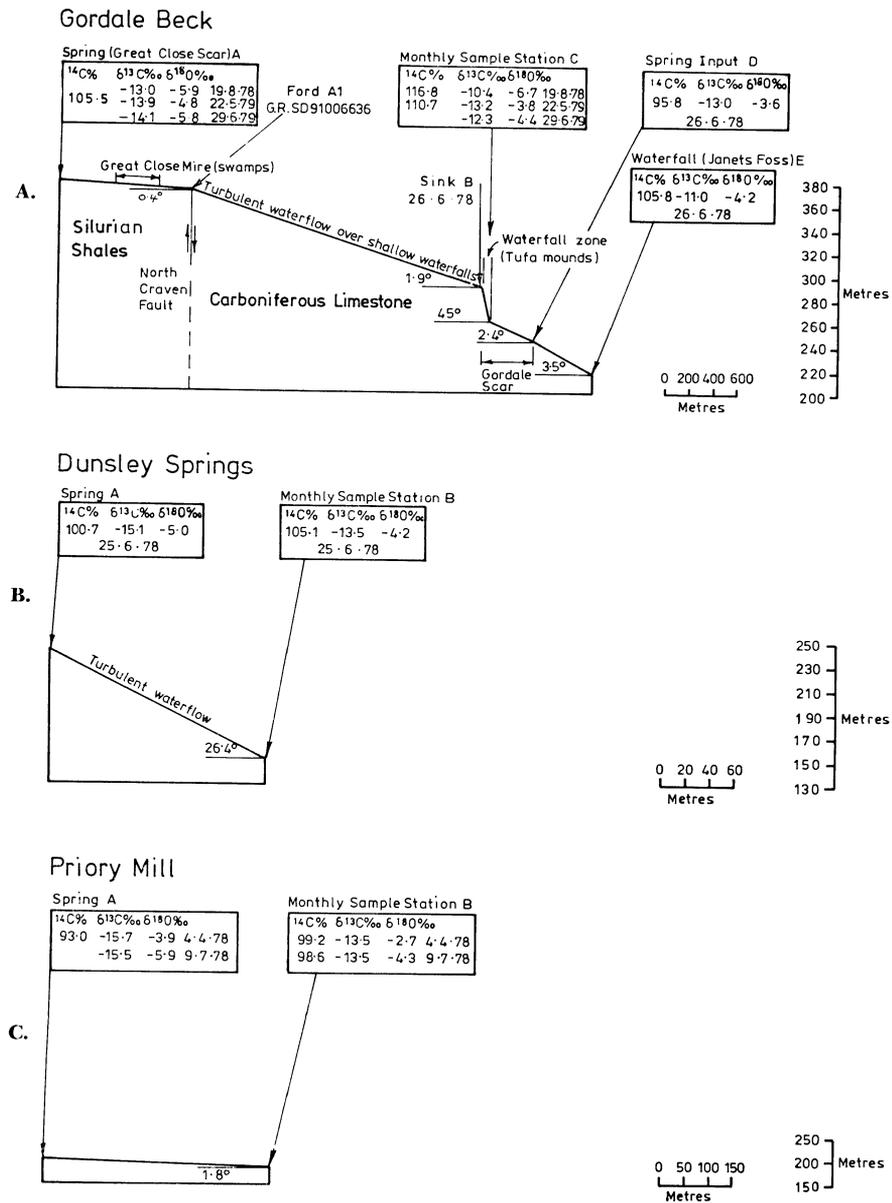
Gordale Beck

Spring (Great Close Scar) A		
¹⁴C%	δ¹³C‰	δ¹⁸O‰
	−13·0	−5·9 19·8·78
105·5	−13·9	−4·8 22·5·79
	−14·1	−5·8 29·6·79

Monthly Sample Station C		
¹⁴C%	δ¹³C‰	δ¹⁸O‰
116·8	−10·4	−6·7 19·8·78
110·7	−13·2	−3·8 22·5·79
	−12·3	−4·4 29·6·79

Spring Input D		
¹⁴C%	δ¹³C‰	δ¹⁸O‰
95·8	−13·0	−3·6
	26·6·78	

Ford A1
G.R. SD91006636

Sink B
26·6·78

Waterfall (Janets Foss) E		
¹⁴C%	δ¹³C‰	δ¹⁸O‰
105·8	−11·0	−4·2
	26·6·78	

Great Close Mire (swamps)

A.

Silurian
Shales

North
Craven
Fault

Carboniferous Limestone

Turbulent waterflow over shallow waterfalls

Waterfall zone
(Tufa mounds)

Gordale
Scar

0 200 400 600
Metres

Dunsley Springs

Spring A		
¹⁴C%	δ¹³C‰	δ¹⁸O‰
100·7	−15·1	−5·0
	25·6·78	

Monthly Sample Station B		
¹⁴C%	δ¹³C‰	δ¹⁸O‰
105·1	−13·5	−4·2
	25·6·78	

B.

Turbulent waterflow

0 20 40 60
Metres

Priory Mill

Spring A			
¹⁴C%	δ¹³C‰	δ¹⁸O‰	
93·0	−15·7	−3·9	4·4·78
	−15·5	−5·9	9·7·78

Monthly Sample Station B			
¹⁴C%	δ¹³C‰	δ¹⁸O‰	
99·2	−13·5	−2·7	4·4·78
98·6	−13·5	−4·3	9·7·78

C.

0 50 100 150
Metres

Fig 1. Profiles of the tufa-depositing streams showing downstream isotopic variations.

Analytical procedures

Water sample analysis

A precipitation of 100 liters of sample water (150 to 200ppm $CaCO_3$) was made for ^{14}C analysis using $BaCl_2$ in an alkaline solution. The dried $BaCO_3$ was reacted with $\sim$ 100 percent H_3PO_4 (containing P_2O_5), and the product CO_2 converted to benzene for liquid scintillation counting using a standard technique.

For stable isotopes a separate 1 liter precipitation giving $SrCO_3$ was reacted with $\sim$ 100 percent H_3PO_4 to produce the most reliable CO_2 (according to Pearson, 1972, pers commun), for mass spectrometer measurement (Micromass 602C). $\delta^{13}C$ and $\delta^{18}O$ values are given relative to PDB, following the computational procedures outlined by Craig (1957). Replicate analysis of $\delta^{13}C$ and $\delta^{18}O$ agreed within a standard deviation better than $\pm$ 0.1‰ for $\delta^{13}C$ and $\pm$ 0.2‰ for $\delta^{18}O$. One ^{14}C replicate analysis agreed to within 0.1 percent modern, however a $\pm$ 1 percent error is applied to all ^{14}C levels quoted.

The dry weight of $SrCO_3$ (g/liter) is a useful check measurement of total carbonate alkalinity derived by other techniques.

The influence of included organic matter on the observed stable isotope composition is important as surface tufa samples contain abundant moss. This was investigated by the acidification of two samples of homogenized marble chips, one with a 50 percent by weight content of moss. Negligible differences of $\delta^{13}C$ 0.2‰ and $\delta^{18}O$ 0.5‰ were observed; therefore, sample pretreatment by roasting in helium (Epstein and others, 1953) was considered unnecessary.

A 1 liter sample of water was taken for tritium analysis. Field measurements of air and water temperature, pH, carbonate hardness (acidimetric titration, expressed in ppm $CaCO_3$) were also collected.

Tufa analysis

Active tufa was scraped to a depth of 2 to 8mm from an area of 100 to 150cm². The total material from each scraping was subdivided into one large sample for ^{14}C ($\sim$80g) and two small samples for stable isotope measurements. An *in situ* block of laminated tufa was taken for ^{14}C profiling from the active surface of the lower tufa mound at Gordale Scar. The problems of removing successive layers of 2 to 4mm thickness from this block were due to the undulating surface and weakly cemented structure. The problems were overcome by casting the block in $CaSO_4$ and removing individual layers at specific depths, controlled by using an engineer's surface gauge and superimposed grid pattern.

RESULTS AND DISCUSSION

Comparison of isotopic compositions of actively forming surface tufa and parent stream waters

In table 1, comparative measurements of $\delta^{13}C$, ^{14}C, and $\delta^{18}O$ are given from active surface tufa and stream waters from the three study areas.

Enrichment due to fractionation effects during $CaCO_3$ precipitation is clearly demonstrated in the average $\delta^{13}C$ values and provides a practical example of isotopic separation in a natural system. The separation factor, the difference between the isotopic composition of the dissolved carbonate (s) and the precipitated carbonate (P), is expressed as,

$$\epsilon_{13} = \delta P - \delta s$$

ϵ_{13} is frequently used in groundwater dating corrections in cases for which the precipitation and solution steps of carbonate water evolution under 'closed-system' conditions have to be allowed (Wigley, Plummer, and Pearson, 1978; Downing and others, 1977). It is noted that the values from table 1 of $\epsilon_{13} = +2.4‰$ (Gordale Scar) and $\epsilon_{13} = +2.0‰$ (Priory Mill) are similar to those used in groundwater corrections by Downing and others (1977). The value of $\epsilon_{13} = +6.6‰$ at Dunsley Springs is beyond the range normally considered for ϵ_{13}. It is also inconsistent with the measured pH (7.7) and average water temperature (8.7°C) according to the pH, water temperature and ϵ_{13} relations given by Wigley, Plummer, and Pearson (1978) and further investigations will be necessary to explain it.

The effect of enrichment on precipitation should ideally also be demonstrated in the comparative measurements of ^{14}C in the tufa and parent waters. Table 2 lists the observed and expected values calculated by invoking the usually applied factor of 2 difference between the $\delta^{13}C$ and implied $\delta^{14}C$. No useful comparison is seen to exist. From the practical viewpoint it was to be expected that an exact comparison would be difficult to achieve due to the problem of scraping off only that layer that strictly applied to the current water. Deeper layers might have higher or lower ^{14}C levels as a result of seasonal fluctuations as demonstrated in figure 2. On average, however, the ^{14}C levels are tending to decline and the inclusion of earlier than current layers might very

TABLE 1

Isotopic composition of active tufa and parent waters at three sites

Site	Type	Colln period	No. of samples	$\delta^{13}C$ (‰)	^{14}C (% modern)	$\delta^{18}O$ (‰)
Gordale Scar	tufa	18.11.77	4	-9.3 ± 0.9	113.8 ± 5.2	-6.2 ± 0.3
	water	20.11.77 to 22. 5.79	10	-11.7 ± 1.2 ($\epsilon_{13} = +2.4$)	111.2 ± 3.9	-4.0 ± 1.6
Dunsley Springs	tufa	22.10.78	2	-7.1 ± 2.0	106.0 ± 2.2	-6.7 ± 0.1
	water	10. 2.78 to 30. 6.79	9	-13.7 ± 0.9 ($\epsilon_{13} = +6.6$)	102.6 ± 2.2	-4.2 ± 2.9
Priory Mill	tufa	9.12.77	1	-11.6 ± 0.1	97.0	-5.8 ± 0.2
	water	9.12.77 to 1. 7.79	11	-13.6 ± 0.4 ($\epsilon_{13} = +2.0$)	100.3 ± 2.8	-4.1 ± 07

Notes: Results are the means of the indicated number of samples taken with the $\pm$ 1 sigma population standard deviation. Individual values are given graphically in figure 2.

well exaggerate the apparent enrichment as seen to be the case at Gordale Scar and Dunsley Springs. The negative enhancement shown for Priory Mill is probably not significant since it is based on only one tufa sample which is being compared with the mean of eleven water samples taken over an approximately 1½ year period.

The more important conclusions of the ^{14}C measurements (table 1) are, firstly, that significantly different levels are found at the three sites (ranging from 97 percent to approximately 114 percent) and secondly, that the levels of ^{14}C in tufa and parent waters are self-consistent, the apparent differences lying within the observed seasonal range of the parent waters (fig 2).

For δ^{18}O, the main difference between the tufa and water (precipitated carbonate) that was not expected is the apparent fractionation on tufa deposition giving more negative values in all three cases. The difference may not be significant, however, as the tufa represents spot sampling (samples taken on a single day) whereas the water sample values are the means of samples taken over an extended period (more than one year in all cases).

Seasonal and downstream isotopic variations

^{14}C, δ^{13}C, δ^{18}O, temperature and alkalinity variations over the period of study are given in figure 2. Isotopic variations downstream are shown in figure 1. The results from each site are separately discussed.

At sample station C (fig 1A) in Gordale Scar, ten samples were taken from 20.11.77 to 22.5.79 (fig 2A). Water and air temperatures follow each other closely, indicating rapid water temperature equilibration with the air due to turbulent waterflow. Fluctuations over a range from 2°C to 17.5°C (water) and from 0.5°C to 18°C (air) are observed. Alkalinity variations show little seasonality. ^{14}C levels vary from $\sim$ 105 percent to 116 percent with the suggestion of higher values in late summer and lower values in winter. The ^{14}C values are well correlated to higher water temperatures considering the limitations of spot check measurement of water temperatures. ^{14}C levels have shown a general decline of $\sim$ 3 percent over the 16-month sampling period. From the variations in δ^{13}C, ^{13}C enrichment is apparently related to increased ^{14}C and water temperature measurements; this suggests exchange of atmospheric CO_2 (δ^{13}C $\sim$ $-8‰$, ^{14}C $\sim$ 135 percent) across the air-water interface especially at elevated temperatures (Pearson, Fisher, and

TABLE 2

Expected and observed differences in ^{14}C between actively forming tufa and parent waters due to isotopic separation

Site	ϵ_{13} (‰)	Expected difference (%)	Observed difference (%)
Gordale Scar	+2.4	+0.5	+2.6
Dunsley Springs	+6.6	+1.3	+3.4
Priory Mill	+2.0	+0.4	−3.3
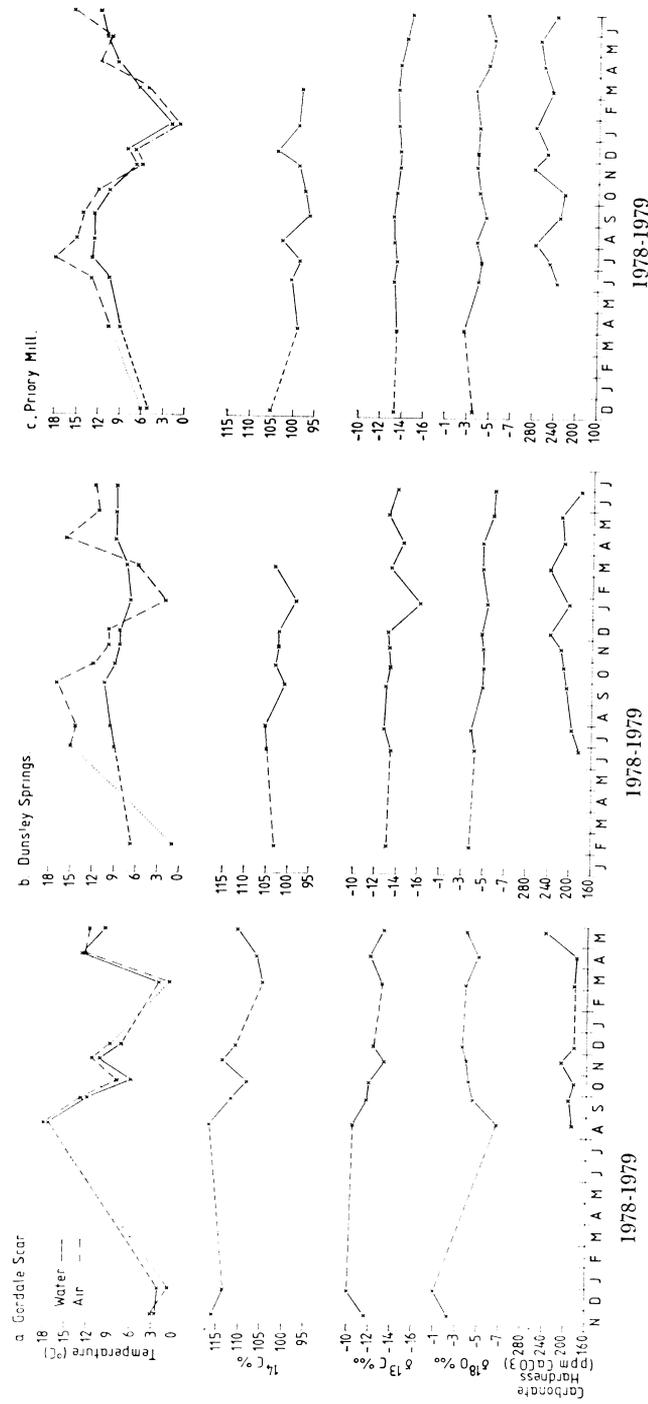
Fig 2. Seasonal variations in temperature, ¹⁴C, δ¹³C, δ¹⁸O and alkalinity of stream waters from tufa sites.

Plummer, 1978) and under conditions of turbulent waterflow (Broecker and Walton, 1958) during the long distance and steep gradient between the springs and sample station. However, field measurement of pCO_2 in the stream waters are essential to confirm this. $\delta^{18}O$ measurements show little seasonality or correlation with temperature.

Downstream isotopic variations in Gordale Beck are shown in fig 1A. Samples taken on 22.5.79 at stations A and C show a downstream increase in ^{14}C of 5.2 percent, $\delta^{13}C$ of $+0.7\%_0$. Also samples taken on 26.6.78 at stations D and E show a similar downstream increase in ^{14}C of 10 percent, ^{13}C of $+2\%_0$ (these stations are considered in isolation of waters upstream, eg, at B, since in this period the waterfall zone between B and C was completely dry. The measurement, 109.2 percent ^{14}C, at B on 26.6.78 is, therefore, irrelevant in this argument).

The downstream enrichment in $\delta^{13}C$ of $0.7\%_0$-$2.0\%_0$ may be due to calcite precipitation and CO_2 degassing (Usdowski, Hoefs, and Menschel, 1978). The observed ^{14}C enrichment cannot be accounted for by isotopic fractionation and it is suggested that progressive, downstream exchange of atmospheric CO_2 with the stream waters occurs between the stations samples due to aeration.

At Dunsley Springs, station B (fig 1B), nine samples were taken from 10.2.78 to 8.3.79 (fig 2B). Water temperatures show less variability than air temperatures due to the short distance of flow from the springs to station B. Alkalinity values show no marked seasonality.

^{14}C levels vary from ~ 99 percent to ~ 106 percent, with significant correlation of higher ^{14}C values to higher water temperatures. During the 13-month period of sampling, ^{14}C levels show a tendency to decline, but not by more than a few percent, with insignificant $\delta^{13}C$ and $\delta^{18}O$ variations over the period.

The downstream isotopic variations at Dunsley Springs are shown in fig 1B. On the 25.6.78 samples taken at station A and B show a downstream increase in ^{14}C of 4.4 percent, $\delta^{13}C$ of $+1.6\%_0$. The greater downstream enrichment in ^{14}C cannot be accounted for by the change in $\delta^{13}C$ and considering the steep stream channel gradient ($\sim 26°$), exchange with atmospheric CO_2 is again considered likely.

At Priory Mill, station B (fig 1C), 11 samples were taken from 9.12.77 to 9.3.79 (fig 2c). Water and air temperatures show a marked seasonality, which is not reflected in the isotope or alkalinity values.

^{14}C levels randomly fluctuate from ~ 97 percent to 105 percent and any possible decline over the sampling period is less marked.

Downstream isotopic variations on samples taken on 4.4.78 at stations A to B demonstrate increases in ^{14}C of 6.2 percent and $\delta^{13}C$ of $2.2\%_0$. The possibility of atmospheric CO_2 exchange at this site is less obvious due to the low gradient ($\sim 1.8°$) involved and general lack of turbulent waterflow conditions.

Isotopic profiling of a tufa sequence

The laminated, relatively impermeable structure of the tufa mounds at Gordale Scar was the most suitable for shallow sequence sampling of

recent tufa layers. The tufa at Dunsley Springs and Priory Mill contains cavities often partially or fully infilled with a different generation of calcite to the matrix.

From the shallow sequence of samples taken from the tufa block at Gordale Scar it was aimed to provide a profile of ^{14}C levels related to the increase in ^{14}C levels in the atmosphere of ~ 100 percent to ~ 190 percent from 1954 to 1964. In addition, four samples were taken at the base and mid-position of the exposed tufa mound to determine its time span.

The ^{14}C, $\delta^{13}C$, and $\delta^{18}O$ values are plotted against depth in figure 3. With increasing depth ^{14}C levels rapidly fall from ~ 113 percent to ~ 65 percent at 15mm. The observed ^{14}C levels (table 1) suggest a factor of ~ 80 percent for the relation of stream water, at Gordale Scar to current atmospheric levels. If this factor is applied to the profile, the rapid increase in ^{14}C levels from 15mm below the surface is reasonably

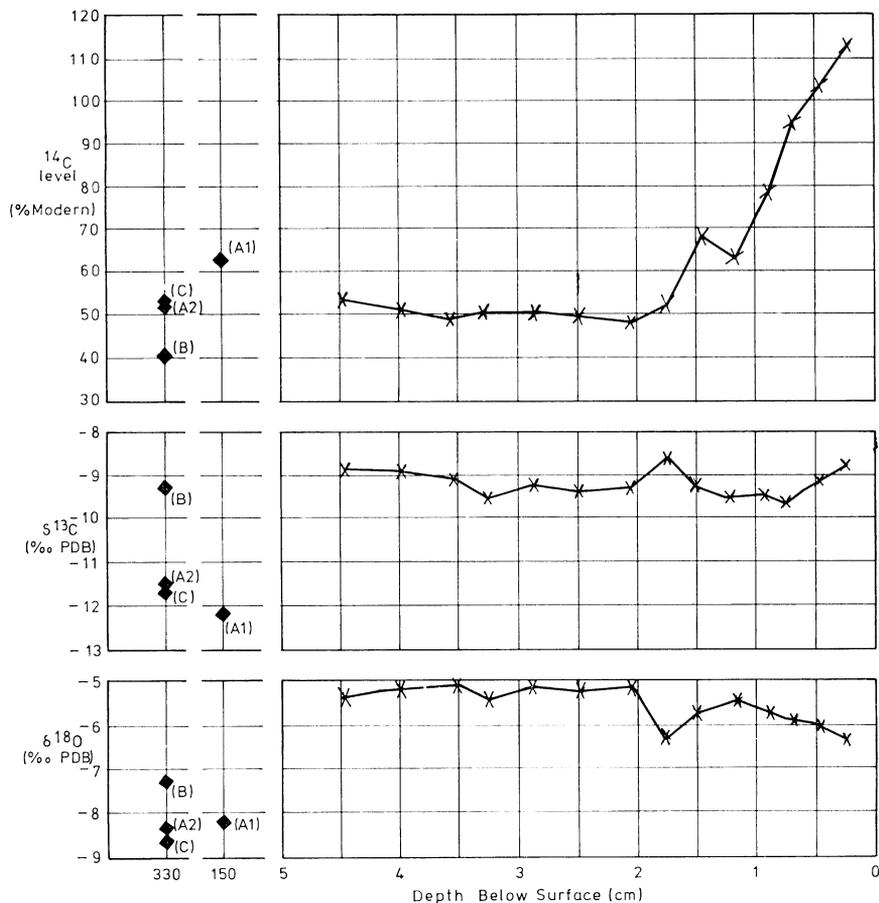Fig 3. Profiles of ^{14}C, $\delta^{13}C$, and $\delta^{18}O$ of a laminated tufa sequence.

consistent with the input of bomb trial ^{14}C. The sharp peak in ^{14}C levels reached in 1964 does not occur in the profile probably because each sample layer taken ($\sim$3.5mm) spans several years of accumulation. From the section on seasonal and downstream isotopic variations, above, a general decline in ^{14}C levels of a few percent in $1\frac{1}{2}$ years in the stream waters sampled at Gordale Scar and Dunsley Springs is consistent with the decrease in atmospheric ^{14}C levels since 1964. With more data it should be possible to specify the period of decline.

At 15mm in the sequence, an abrupt change in tufa structure indicated an erosion surface, hence a possible time gap in the sequence. In figure 3, ^{14}C levels decrease rapidly from $\sim$ 65 percent to 52 percent from 15 to 18mm depth and the levels are almost constant at $\sim$ 50 percent to a depth of 45mm.

A simple interpretation of the ^{14}C profile, without considering a possible time gap would give support to groundwater correction procedures based on approximate 50:50 mixing of biogenic and rock carbon, which gives a correction factor of 2 to the raw data. If this factor of 2 is also applied to the ^{14}C levels of the present day stream waters in table 1, corrected ^{14}C levels of greater than 200 percent are produced which exceed the bomb trial ^{14}C peak level of $\sim$ 190 percent only reached in 1963-1964. This would imply a 14-year residence time of water at all sites sampled. Tritium levels at the sites range from 33 ± 2 TU to 86 ± 4 TU which is below the major input of tritium as rainfall in 1963-1964 of over 1000 TU. (This would have decayed to $\sim$ 400 TU in 1978). Underground waterflow velocities between sinks and springs measured by Smith and Atkinson (1977) near to Gordale Scar gave 1.7km/day to 4.7km/day implying conduit flow through solutionally widened fissures. As similar underground waterflow conditions exist in the area of Gordale Beck, a residence time of days rather than years was expected. The 'factor 2' correction mentioned above is, therefore, inapplicable to the ^{14}C profile data.

The $\delta^{13}C$ levels through the sequence show little variation, $-9.2 \pm 0.3\%_o$, indicating a constant mix of biogenic and rock carbon during the period of deposition, and a mean value which is consistent with ϵ_{13} measured at present. $\delta^{18}O$ values show more variation, $-5.5 \pm 0.5\%_o$, and there is a weak inverse correlation (r = -0.14) between $\delta^{18}O$ and $\delta^{13}C$ values. However, the basal and mid-position samples A1, A2, and C (fig 3) deviate from the average $\delta^{13}C$ of the shallow sequence by $-2\%_o$, although sample B $\delta^{13}C - 9.3\%_o$ is consistent.

A possible explanation of figure 3 can be developed by considering variable rates of tufa accumulation above and below the erosion surface and the implications of partial atmospheric CO_2 exchange with the stream waters. At present, tufa accumulation rates vary over the surface of the tufa mound. Mechanical erosion is seen to occur in the main waterflow channels which strips away friable tufa layers. Active tufa deposition is confined to areas of shallow waterflow in the spray zone

of the waterfall. The migration of the main waterflow channels across the mound surface gives rise to unconformable sequences of tufa.

In figure 3, the basal sample B ($^{14}C = \sim 40$ percent), taken at $\sim$ 330cm, suggests rapid tufa accumulation maybe in terms of cm/year, below the erosion surface. A shift in position of the main waterflow channel into such an area of rapid deposition would quickly remove tufa layers deposited in periods when ^{14}C was equivalent to ~ 50 percent — 65 percent. A further migration of the channel would allow renewed tufa deposition in the abandoned channels at ^{14}C levels of ~ 65 percent. A subsequent period of slow tufa accumulation, in terms of $\sim$ mm/year, above the erosion surface, would then explain the rapid increase in ^{14}C levels from ~ 65 percent to 113 percent over a depth of 15mm.

CONCLUSION

The following conclusions may be drawn from this study:

1) At the three sites investigated, it was demonstrated that actively forming tufa had similar, directly related, ^{14}C levels to those of the parent stream waters.

2) Hydrologic correction procedures based on simple mixing of biogenic and rock carbon were found inapplicable in the cases considered. However, the observed fractionation of $\delta^{13}C$ on tufa deposition provided a practical and useful demonstration of the separation factor ϵ_{13} commonly used in groundwater age corrections.

3) Evidence of atmospheric CO_2 exchange with stream waters, which enhances the expected biogenic carbon input, was supported by the correlation of ^{14}C and $\delta^{13}C$ variations to the water temperatures from measurements taken over an extended period. Also, downstream variations in ^{14}C and $\delta^{13}C$ give added support to this hypothesis.

4) The general decline in ^{14}C levels in the stream waters at all sites is consistent with the known gradual decrease in atmospheric ^{14}C levels since 1964. This may eventually lead to more precise dating of the stream waters by means of correcting their raw ^{14}C values to equivalent atmospheric ^{14}C levels. Suggested preliminary correction factors are: Gordale Scar ~ 80 percent, Dunsley Springs ~ 79 percent, and Priory Mill ~ 75 percent.

5) The record of ^{14}C levels in discrete layers of the tufa is demonstrated over the recent past. Extension beyond this seems feasible with due attention to the depositional and petrographic characteristics. Promise is, thus, given that ^{18}O (and hence, temperature) records will also be preserved and enable the eventual reconstruction of the relevant climatic history.

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