

HAVASU CANYON - A NATURAL GEOCHEMICAL LABORATORY

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HAVASU CANYON--A NATURAL GEOCHEMICAL LABORATORY

Robert Giegengack,¹ Elizabeth K. Ralph,¹ and Alan M. Gaines²

INTRODUCTION

Havasu Creek, one of the few perennial streams that discharge into the Colorado River within the Grand Canyon, represents a site where the fortuitous combination of water chemistry and valley configuration has enabled us to place realistic limits on the reliability of radiocarbon dates of calcareous tufa, a material whose widespread distribution in areas of the world now quite dry has been interpreted as testimony of once-wetter climates or greater ground-water flux.

THE RADIOCARBON METHOD³

Radiocarbon, or radioactive ^{14}C , is produced in the upper atmosphere when low-energy neutrons, continually generated by interaction of cosmic rays with the atmosphere, collide with the nuclei of ^{14}N atoms, displacing a proton from each nucleus so affected. The resulting unstable nuclide, ^{14}C , decays spontaneously to ^{14}N by emission of a β^- particle. The best measurement of the half-life of this decay process is $4,730 \pm 30$ calendar years. Equilibrium between rate of production and rate of decay of ^{14}C in the atmosphere is thought to have been established at a concentration of 10^{-12} ^{14}C atoms per stable carbon atom, prior to the artificial enrichment of atmospheric ^{14}C by excess neutrons released in atmospheric nuclear-bomb tests since 1945.

Radioactive ^{14}C reacts chemically like the stable C isotopes and is rapidly oxidized to $^{14}\text{CO}_2$, which is utilized in plant photosynthesis more or less as if it were one of the lighter, stable carbon isotopes. During the life of a typical plant, continual contact with the atmospheric carbon reservoir by plant respiration maintains a $^{14}\text{C}/^{12}\text{C}$ ratio in live plant tissue approximately equal to that in the atmosphere; when the plant dies, however, the ^{14}C content diminishes as spontaneous decay continues in the absence of respiration.

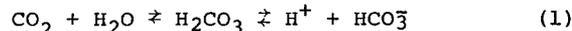
Animals that build their tissues from materials ingested as green plants likewise maintain within their bodies a $^{14}\text{C}/^{12}\text{C}$ ratio equivalent to that of the atmosphere. Since the half-life of ^{14}C is long with respect to the lifetimes of most plants and animals, even predators high in the food chain can be expected to maintain the atmospheric $^{14}\text{C}/^{12}\text{C}$ ratio in their tissues. As in plants, however, contact with the atmosphere, however indirect, is broken at the death of an animal, after which radioactive decay proceeds without replenishment of ^{14}C via the food chain.

¹⁴If it can be assumed that (1) the atmospheric $^{14}\text{C}/^{12}\text{C}$ ratio has been approximately constant for the last 45,000 years, and (2) that carbon has not been added to or removed from a given sample after its death, then it follows that determination of the $^{14}\text{C}/^{12}\text{C}$ ratio within the dead organism and comparison of that ratio to the assumed atmospheric

ratio will lead to a determination of the time that has elapsed since death of the organism, given the accuracy of the measured half-life.

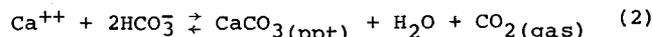
Radiocarbon concentrations below that remaining after 7 or 8 half-lives are below the limit of detection of contemporary instrumentation. Thus, applicability of this dating method at the present time is effectively limited to the last 45,000 years.

In addition to the straightforward organic pathways described above, students of radiocarbon are interested in mechanisms that fix atmospheric carbon directly in geologic materials without involving the biosphere. For example, rain falling through the atmosphere dissolves CO_2 according to the equation:

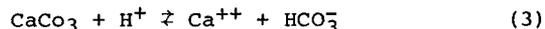


Rain that falls on the Earth's surface may evaporate, may flow directly to the ocean as surface runoff, or may infiltrate through the soil zone to become part of the ground-water system. In passing through the organic litter on the soil surface, CO_2 generated by oxidation of that litter is dissolved according to equation (1); since soil air may contain as much as 100 times more CO_2 than does the atmosphere, most of the HCO_3^- in ground water is derived from the soil.

If such water should emerge from the subsurface as a spring and lose excess CO_2 the relatively undersaturated atmosphere, HCO_3^- may combine with dissolved Ca^{++} , present in abundance in virtually all ground water, to form a precipitate (CaCO_3) whose radiocarbon age is approximately equal to the residence time of the water in the subsurface, if the age of the leaf litter is assumed to be small:



If a ground-water parcel should encounter limestone bedrock, the H^+ ion provided by dissociation of H_2CO_3 will bring about dissolution of CaCO_3 :



Such HCO_3^- will have no measurable ^{14}C if the limestone is older than 45,000 years.

If such a water sample should emerge at the ground surface and release CO_2 to the relatively undersaturated superjacent atmosphere, the reaction of equation (2) will occur, and CaCO_3 will be precipitated that owes its C to the atmosphere, the soil zone, and all limestones it may have encountered during subsurface flow. The radiocarbon age of the resultant CaCO_3 will be something between 0 (the age of atmospheric carbon) and infinity (the age of the limestone), not an encouraging range of values to the geologist who might try to establish the time of precipitation, or to the hydrologist bent on establishing ground-water flow rates. In exceptional cases, very young water samples may retain enough artificially enriched atmospheric carbon to yield "ages" something less than 0!

Despite this discouraging assessment of the potential problems of using inorganically precipitated fresh-water carbonate materials for radio-

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³For a more comprehensive discussion of the geophysics of radiocarbon than will be presented here, see Ralph 1971.

carbon dates, many geologists choose to date inorganic carbonate samples in the absence of more reliable organic material.

We have identified Havasu Canyon, Arizona, as a natural laboratory in which to test empirically the extent of departure of carbonate ages from true ages of precipitation.

HAVASU CANYON, ARIZONA

Havasu Creek, Arizona, rises from perennial springs on the floor of Havasu Canyon and falls 1,470 feet in 10 miles of flow to the Colorado River; the five major waterfalls on the map and on the accompanying long profile (Figure 1) account for approximately 420 feet of this descent.

The spring water emerges from alluvium overlying the Lower Slope Member of the Supai Formation (E.D. McKee, pers. comm. 1973). The creek flows through the underlying Redwall and Temple Butte Limestones, and enters the Colorado River in the upper part of the Muav Limestone (E.D. McKee, pers. comm. 1973; see also McKee 1969; McKee and Gutschick 1969; McKee and Resser 1945; see also Figure 2).

The Havasu Springs represent the discharge point of the Coconino Trough, a subsurface watershed that drains \pm 3,500 square miles of northern Arizona (Cooley 1963; see Figure 2). Both temperature (\sim 20°C) and discharge of the springs are remarkably constant (see Table 1), unlike those properties of most other permanent water sources that enter the Colorado River in the Grand Canyon (see Johnson and Sanderson 1968, Table 1); this suggests that the residence time of water in the ground, within the C Multiple Aquifer System of Cooley (1963), is long. The approximate mean discharge of 60 cfs represents 0.25"/yr of precipitation over the watershed, about 1/50 of the mean annual precipitation of 12".

Havasu Creek maintains a permanent community of Havasupai Indians, who practice agriculture on alluvium on the canyon floor near the village of Supai, using Havasu Creek water for irrigation.

In Table 2 we present data from a number of chemical analyses of the water.

The water that emerges from the Havasu Springs carries CO₂ in solution far in excess of what would be present if the water were in chemical equilibrium with the atmosphere. As CO₂ is lost (see equation [2]), CaCO₃ is first precipitated at loci of microturbulence, such as bed or bank obstructions or even twigs of streamside trees that hang in the water. Precipitation of CaCO₃ on such obstructions increases the interference that the obstructions present to streamflow; this enhances local turbulence which leads to accelerated precipitation.⁴ Thus, individual tufa structures may grow to considerable size and may come to span the width of the stream as a complex of festooning, anastomosing tufa ridges that support small waterfalls, separated by quiet, deep pools. The first⁵ such tufa dam has been constructed near mile 2.5,

⁴A direct chemical precipitation of CaCO₃ from fresh water is called tufa while it is still soft; recrystallization of such a sediment, typically after emergence, results in a more durable sediment known as travertine (e.g., see Pettijohn 1957).

⁵The map and long profile of Figure 1 are marked at half-mile intervals. The origin, point 0.0, is a short distance above the present location of the springs and exactly 10 miles, measured along the sinuous course of Havasu Creek on USGS 15' quadrangles Supai, Ariz. (1962), Kanab Point, Ariz. (1962), and Tuckup Canyon, Ariz. (1962), from the mouth of Havasu Creek at the Colorado River.

just below the village of Supai.

Tufa structures are well developed from mile 2.5 to mile 7.2, just below Beaver Falls. This central length includes the five major waterfalls (see Figure 1), all of which cascade over scarps composed entirely of tufa; it is clear that each waterfall has occupied a series of positions along the scarp in recent years (see discussion in James 1900; Wampler 1959; also compare photographs in the two books).

The tufa geometry we have discussed here is not permanent. Individual structures are in a constant state of change, under normal circumstances the result of continual minor diversion of the stream as some tufa structures grow faster than others. Wholesale modification of tufa morphology occurs whenever heavy local rainfall generates surface runoff in the canyon watershed. Water from such floods typically is undersaturated with respect to CaCO₃. Thus, tufa structures may be both dissolved in part and mechanically damaged by the force of water during a flood. A major flood in August 1954 dramatically modified tufa morphology in the central reach of the creek (Black 1955); other floods in historic time have altered the forms of Supai, Navajo, Havasu, and Beaver Falls (James 1900; Iliff 1954; Wampler 1959).

Modification of the course of Havasu Creek, either gradually or catastrophically, results in the drowning of streamside trees. Many of these eventually topple into the creek, where they sink to the bottom of ooze-floored pools or float downstream, to become logged in developing tufa structures. The floors of many pools are covered with a tangle of intertwined, waterlogged branches. Many dams fairly bristle with wood fragments; to a first approximation, those lowest in the wall of a given dam are the oldest.

During June 1969 we collected samples of modern tufa-encrusted wood at frequent intervals along the stream (see figure 3). We assumed that the time that intervenes between the death of a tree in Havasu Canyon and the incorporation of a piece of its wood in a growing tufa dam is not long; thus the first layer of CaCO₃ that is precipitated on the surface of the wood should have the same ¹⁴C age as the wood itself. If we should find that there is a significant difference between ¹⁴C age of the wood and the ¹⁴C age of the first layer of tufa, that difference is a measure of the C-isotope disequilibrium between the stream water, from which the tufa precipitated, and the atmosphere, from which the wood C is derived, at the point in the stream where precipitation began and at the time the tree died.

GEOCHEMICAL DATA

We have measured radiocarbon activity in 9 sample pairs,⁶ chosen to avoid very young samples that might have been contaminated by bomb carbon; these measurements are recorded in Table 3. The disequilibrium values in column 6 of table 3 were obtained by subtracting the wood age from the tufa age for each sample pair. Each such value is an expression of the magnitude of the C-isotope dis-

⁶Two such pairs, from miles 9.53 and 9.70, are from samples of tufa-encrusted wood lying on the stream bank in the lower reach of the creek. Field evidence suggested that these samples had been transported after precipitation began. Disequilibrium values obtained from these two samples are represented by open circles on the plot of Figure 4. The departure from the trend of one of these values supports the interpretation that that sample, at least, was transported and redeposited.

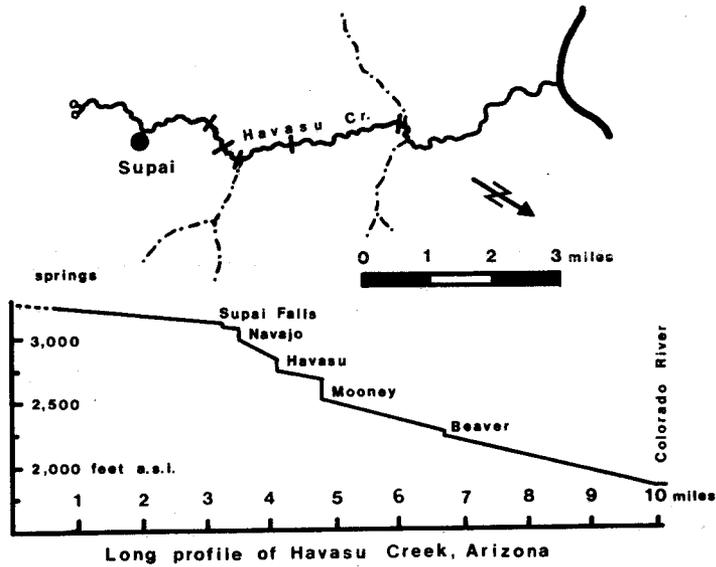
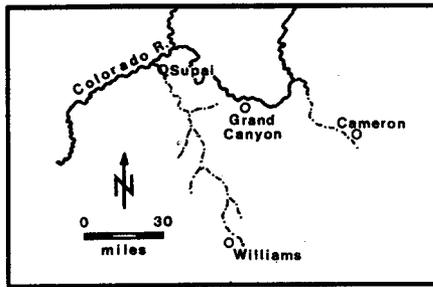


FIGURE 1. Map and long profile of Havasu Creek, Arizona.

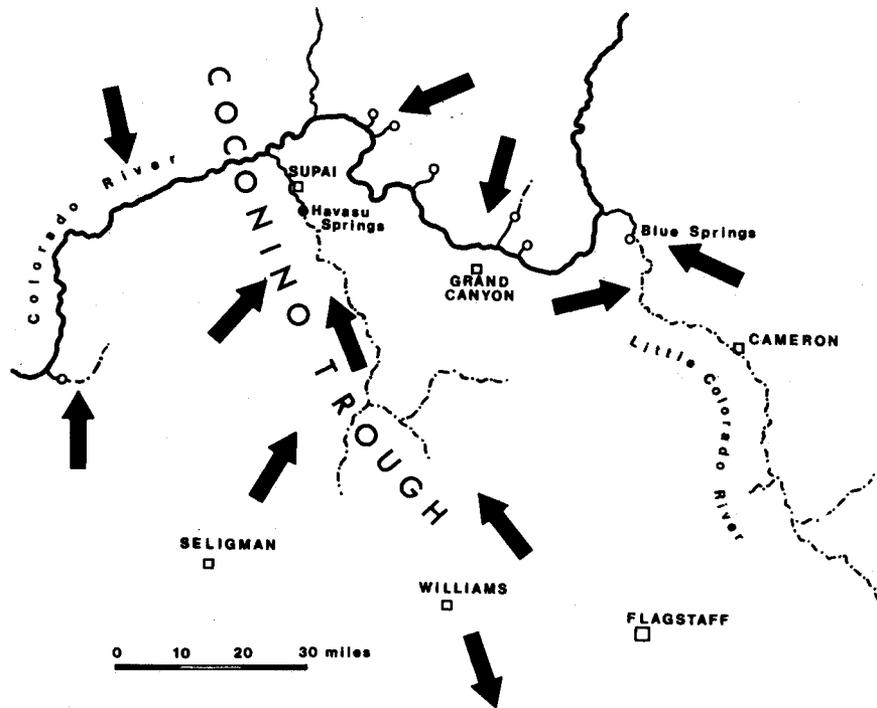


FIGURE 2. Subsurface watershed of Havasu Springs, Arizona. Solid circle is Havasu Springs; other springs are represented by open circles. Arrows indicate general direction of flow of subsurface water.

TABLE 1. Discharge measurements of Havasu Creek, Arizona.

Date measured	Sample locality	Discharge (cfs)	Source of data	Remarks
9/13/23	mouth	74.5	1	may include local surface runoff
5/20/50	mouth	60.0	1	
10/20/50	mouth	63.8	1	
6/14/51	mouth	59.3	1	
6/16/51	mouth	63.3	1	
6/17/51	mile 0.8	59.3	2	
6/12/52	mouth	62.9	1	
6/13/52	mouth	65.7	1	
6/01/54	mile 5.0	61.5	3	
6/12/54	mile 1.0	63.3	3	
4/06/65	mouth	66.5	1	
6/25/65	mouth	60.0	1	estimate
8/07/65	mile 0.8	59.5	4	
11/12/67	mile 0.8	61.8	4	
6/29/68	mile 1.3	49.8	4	
6/29/68	mile 4.7	49.6	4	
8/23/68	mile 4.7	53.7	4	
8/23/68	mile 1.0	60.4	4	
12/28/68	mile 1.0	66.6	4	

Sources: 1. Johnson and Sanderson, 1968, table 1, p. 11.
 2. *ibid.*, table 2, p 13.
 3. Wampler, 1959, p 12.
 4. Measurements by personnel of the U.S. Geological Survey. Provided by E. H. McGavock, Sub-district Chief, Water-Resources Division, U.S. Geological Survey, Flagstaff, Arizona.

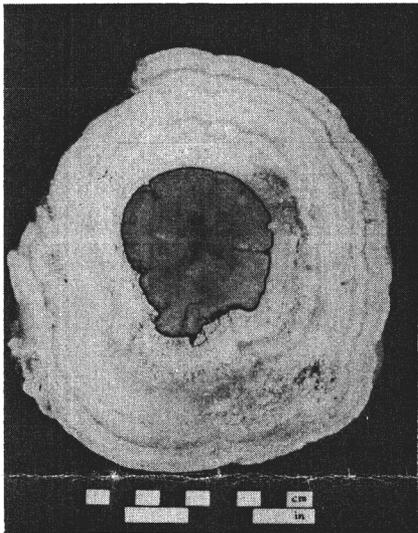


FIGURE 3. A typical section through a tufa-encrusted wood sample.

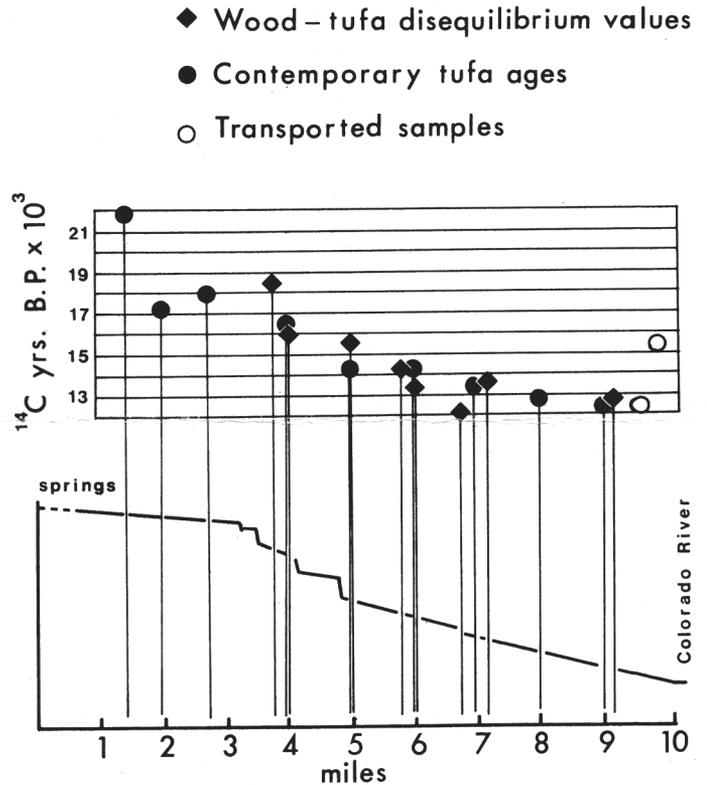


FIGURE 4. Plot of wood-tufa disequilibrium values and contemporary-tufa ages against the long profile of Havasu Creek.

TABLE 2. Chemical analysis of water from Havasu Creek. Except where otherwise noted, concentrations are expressed as milligrams/liter (mg/l) or parts per million (ppm); in dilute solutions, the units are essentially identical.

SAMPLE LOCATION	Date of collection	Temperature °C	Ca	Mg	Na + K	HCO ₃	CO ₃	SO ₄	Cl	F	NO ₃	SiO ₂	Dissolved solids, mg/l, calculated	Dissolved solids, residue on evap.	Hardness as CaCO ₃		Percent Na	Na-absorption ratio	Specific conductance (micromhos at 25°C)	pH	Source of data	Remarks
															Ca, Mg	non-CO ₃						
~ mile 8.0	1924?	-	154	63	3	283	-	90	68	-	-	-	657	705	-	-	-	-	-	-	1	a
mile 1.4	10/20/50	21	133	48	27	588	0	36	48	.2	1.4	-	584	-	530	48	10	-	1,030	-	2	
mile 1.4	6/17/51	22	-	-	-	574	0	-	46	-	-	-	-	-	-	-	-	-	1,000	-	2	
mile 1.4	8/7/65	-	74	45	36	416	0	36	48	.2	-	-	-	444	368	27	-	-	820	7.7	2	
mile 3.6	6/16/51	-	-	-	-	384	0	-	47	-	-	-	-	-	-	-	-	-	752	-	2	
Spring mile 4.9	6/16/51	22	109	47	36	526	0	44	48	0	0	-	543	-	466	34	15	.7	959	-	2	b
~ mile 7.0	6/16/51	21	52	47	28	338	tr	38	48	0	.3	-	380	-	323	46	16	.7	704	-	2	
mile 9.9	6/16/51	21	-	-	-	304	tr	-	48	-	-	-	-	-	-	-	-	-	661	-	2	
mile 0.8	8/7/65	-	74	45	36	416	0	36	48	.2	-	-	-	-	368	27	-	-	820	7.7	3	
mile 0.6	12/28/66	21	118	45	33	542	0	38	46	.3	-	18	565	-	478	34	-	-	973	7.7	3	
mile 0.8	11/12/67	21	125	32	40	523	0	40	45	.2	-	18	558	-	446	18	-	-	961	7.4	3	
mile 1.3	6/29/68	20	134	43	42	602	0	38	50	.3	-	20	623	-	512	18	-	-	1,050	7.2	3	
~ mile 2.0 irr. ditch	6/29/68	-	134	44	39	600	0	35	50	.3	-	20	618	-	514	22	-	-	1,040	7.4	3	c
mile 4.8	6/29/68	21	78	44	39	428	0	38	49	.3	-	24	483	-	376	26	-	-	837	7.7	3	
~ mile 1.0	8/23/68	-	132	44	46	600	0	35	58	.3	-	25	636	-	510	18	-	-	1,050	7.5	3	
mile 4.8	8/23/68	-	78	44	41	436	0	36	48	.3	-	23	485	-	374	16	-	-	836	7.8	3	

Sources: 1) Wampler, 19. , p. 12. 2) Johnson and Sanderson, 1968, table 2, p. 13. 3) Analyses by personnel of the U.S. Geological Survey. Provided by E.H. McGavock, Subdistrict Chief, Water-Resources Division, U.S. Geological Survey, Flagstaff, Arizona

Remarks: a) Date of collection unknown; analysis reported 12/10/24. Concentrations converted from citation as grains/gallon. HCO₃ reported as CaCO₃ and MgCO₃. b) Sample collected from spring inflow below Mooney Falls. c) Sample collected from irrigation ditch; water flows to ditch directly from Havasu Creek.

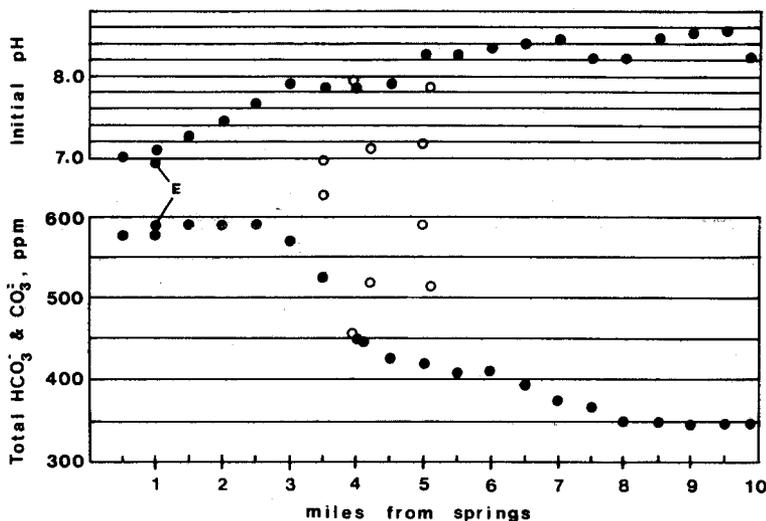


FIGURE 5. Results of in situ titration of water of Havasu Creek and of springs entering the stream. Solid circles represent titrations of stream waters; open circles represent titrations of water from springs entering Havasu Creek. The two points labeled E are from the East Branch of Havasu Creek near the springs; other points from the same mile position are from the West, or main Branch, of Havasu Creek. See text for fuller description.

TABLE 3. Radiocarbon data list.

PENN Lab No.	Field sample No.	Corrected mile post	Material	¹⁴ C age (5568)*	Wood-tufa disequilibrium value	Direct disequilibrium value	Remarks
WOOD-TUFA SAMPLE PAIRS							
P-2167	69HC 6.30 TW2	3.70	wood	modern			
P-2166	69HC 6.30 TW2	3.70	tufa	19,720 ± 300	19,720		
P-1632	69HC 5.97 TW1	4.03	wood	137 ± 42			
P-1642	69HC 5.97 TW1	4.03	tufa	17,010 ± 570	17,010		
P-1987	69HC 5.00 TW1	5.00	wood	<20			
P-2044	69HC 5.00 TW1	5.00	wood	<20	16,090		run twice
P-1988	69HC 5.00 TW1	5.00	tufa	16,105 ± 176			
P-1899	69HC 4.25 TW1	5.75	wood	216 ± 46			
P-1898	69HC 4.25 TW1	5.75	tufa	15,040 ± 250	14,820		
P-1897	69HC 4.00 TW1	6.00	wood	436 ± 40			
P-1896	69HC 4.00 TW1	6.00	tufa	14,580 ± 210	14,140		
P-1694	69HC 3.27 TW1	6.73	wood	567 ± 56			
P-1695	69HC 3.27 TW1	6.73	tufa	13,080 ± 190	12,510		
P-2254	74HC 0.87 TW1	9.13	wood	modern			
P-2253	74HC 0.87 TW1	9.13	tufa	13,680 ± 250	13,680		
P-1631	69HC 0.47 TW1	9.53	wood	196 ± 48			redeposited?
P-1641	69HC 0.47 TW1	9.53	tufa	13,030 ± 300	12,830		redeposited?
P-2037	69HC 0.30 TW1	9.70	wood	440 ± 40			redeposited
P-2038	69HC 0.30 TW1	9.70	tufa	16,390 ± 230	16,160		redeposited
CONTEMPORARY-TUFA AGES							
P-2252	74HC 8.60 CT	1.40	tufa	22,850 ± 550		22,850	
P-2251	74HC 8.00 CT	2.00	tufa	18,110 ± 250		18,110	
P-2329	74HC 7.10 CT2	2.70	tufa	19,030 ± 260		19,030	
P-2318	74HC 6.00 CT	4.00	tufa	17,460 ± 260		17,460	
P-2239	74HC 5.00 CT	5.00	tufa	15,370 ± 180		15,370	
P-2319	74HC 4.00 CT	6.00	tufa	15,430 ± 180		15,430	
P-2320	74HC 3.00 CT	7.00	tufa	14,452 ± 180		14,450	
P-2321	74HC 2.00 CT	8.00	tufa	13,790 ± 170		13,790	
P-2322	74HC 1.00 CT	9.00	tufa	13,490 ± 170		13,490	
WOOD-STRATIGRAPHIC AGES							
P-2211	74HC 3.29 OW1	6.71	wood	3,170 ± 50			
P-2212	74HC 6.149 OW1	3.851	wood	modern			
P-2213	74HC 5.80 OW1	4.20	wood	1,670 ± 50			
P-2214	74HC 6.00 OW1	4.00	wood	250 ± 40			
P-2215	74HC MFTOP OTW1	5.21	wood	480 ± 50			
P-2216	74HC 3.60 OTW2	6.40	wood	920 ± 50			
P-2217	74HC 3.60 OW1	6.40	wood	740 ± 40			
P-2218	74HC 5.85 OW1	4.15	wood	130 ± 50			

*Many laboratories choose to retain the half-life value on which many thousands of ages were based in the early days of the method. To convert ages referred to the 5,568 half-life to citation with respect to the 5,730 half-life, multiply the former by 1.03.

o ¹⁴C-sample location
ages in ¹⁴C years B. P.

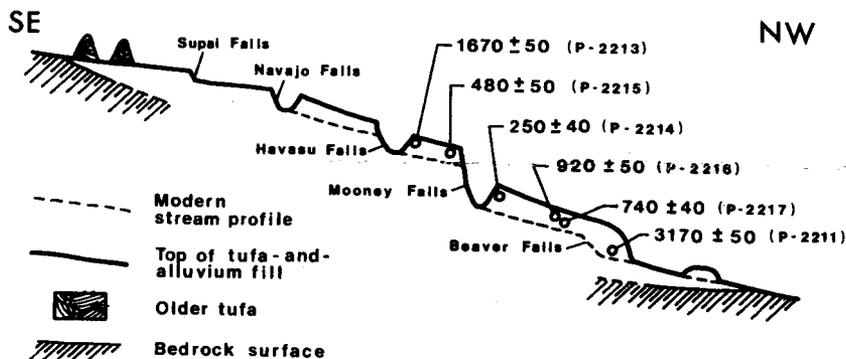


FIGURE 6. Schematic long profile of Havasu Creek, showing distribution of ¹⁴C ages of alluvial fill and older tufa. All ¹⁴C samples represented here are of wood.

equilibrium between the creek water and the atmosphere at the site where precipitation began and at the time the tree died. These disequilibrium values are plotted on the long profile of Havasu Creek in Figure 4. From this plot it is clear that the difference between the tufa age and the wood age decreases systematically with distance downstream. This trend represents gradual equilibration of the C-isotope spectrum of HCO_3^- in the water with that of CO_2 in the atmosphere as a result of gaseous exchange across the air-water interface; this exchange is probably most effective under conditions of severe turbulence.

In June 1974 we attempted to precipitate SrCO_3 directly from stream water to establish an equilibrium curve controlled by ^{14}C activity in the modern atmosphere, but we were unable to exclude from the vessels in which precipitation was to take place fine detrital particles of CaCO_3 carried in suspension in the water. Instead, we collected, at half-mile intervals, samples of CaCO_3 precipitated on stream-bank moss and on cottonwood leaves suspended in the water; we reasoned that the samples were safely young if chlorophyll was still preserved within the calcite encrustations.

Radiocarbon ages of such contemporary-tufa samples are also listed in Table 3 and plotted on Figure 4. The congruence of the two equilibration curves, well within the range of the standard radiocarbon-age error, is surprising, inasmuch as the C-isotope spectrum represented by the calcite of the contemporary tufa is equilibrating with an atmosphere whose concentration of ^{14}C is roughly 60% greater than the concentration in the atmosphere with which equilibration should have taken place prior to A.D. 1945.

Stable-isotope ratios were determined routinely for all dated samples; corrections based on such measurements would not significantly alter the values of Table 3. Additional stable-isotope ratios are being acquired for selected samples. These data will be reported elsewhere.

In addition to exchange of CO_2 between water and the atmosphere, which the curves of Figure 4 clearly show is occurring, carbon is being lost from the water by precipitation of CaCO_3 as tufa, by aquatic photosynthesis, and by degassing of CO_2 , the mechanism that triggers precipitation. We undertook a program of titration of the creek water in situ, using the technique developed by Barnes (1964, 1965), to measure the rate of downstream diminution of dissolved carbon species. Titration was accomplished by adding increments of a standard acid to a measured volume of creek water with a micrometer pipette, and monitoring the resulting changes in pH of the samples with a battery-powered pH meter. The equivalence point of each titration was determined graphically from the inflection point of the curve of pH vs. added volume of standard acid. In these waters, the titration alkalinity so determined is a good measure of HCO_3^- concentration (Berner 1971:56).

In Figure 5 we have plotted both initial pH of the sample and the calculated concentration of HCO_3^- against distance downstream; the systematic diminution of total dissolved carbon in the water is apparent.

ALLUVIAL HISTORY

In addition to the modern generation of tufa, Havasu Canyon preserves evidence of a lengthy and probably complex history of deposition of detrital sediment and precipitation of CaCO_3 . Thick masses of sediment that predate the modern configuration of the long profile of Havasu Creek are preserved near Navajo Falls, just below Havasu and Mooney Falls, and along a half-mile of the canyon above and below the position of the fall now called Beaver Falls. Each of the waterfalls is direct-

ly underlain by calcareous tufa, supported by a column of alluvial sediment of unknown thickness. Between the waterfalls the canyon walls are encrusted with benches of crystalline travertine, often many tens of feet above the modern stream bed. No bedrock is exposed in the stream bed above the mouth of Beaver Canyon, at mile 6.7; below this point tufa structures are discontinuous and less well developed. Such sediment may never have been precipitated, either because the total concentration of HCO_3^- is lower here (see Figure 5), or because the reduced gradient of Havasu Creek below Beaver Falls (see Figure 1) minimizes turbulence. Alternatively, surface runoff from Beaver Canyon may have prevented buildup of tufa by removing the sediment as fast as it was precipitated.

The village of Supai itself and the agricultural economy of its inhabitants are built on a broad alluvial fill on the canyon floor.

Wherever natural cuts permit examination of the internal stratigraphy of these deposits, it is clear that the bulk of the sediment consists of alluvial sands, silts, and gravels, derived principally from the Supai Formation, and deposited by running water. Little if any precipitated CaCO_3 is present below the top of the column, which is everywhere veneered with a layer of calcareous travertine as much as 6 feet thick. The simplest interpretation of this sequence is that the bulk of the sediment was deposited from water derived from surface runoff during a single alluvial period that was characterized by more abundant rainfall than the area receives today. The tufa veneer was precipitated under conditions like those of today, when the only depositional process of importance is direct chemical precipitation of CaCO_3 . Recent incision of the combined sedimentary fill has produced the scarps of Navajo, Havasu, and Beaver Falls; historic incision has reduced Beaver Falls to a steep succession of low tufa dams developed on older travertine.

Distribution of older fill along the long profile of Havasu Creek is shown schematically in Figure 6. It is possible from this plot to reconstruct an end-fill profile along the top of the travertine veneer over the sedimentary fill. At the time that such a condition might have prevailed, Navajo Falls would not have existed, Havasu and Mooney Falls would have been much lower than they are today, and Beaver Falls would have been an imposing cataract at the confluence of Beaver Creek with Havasu Creek. Two masses of crystalline travertine protrude above that profile against the east wall of the canyon near Supai Village; presumably they were precipitated during an earlier period of valley alluviation.

Wood fragments are common in the travertine cap that veneers the sedimentary fill, rare within the mass of detrital sediment, and have not been observed in the two masses of older travertine. Enough wood samples have been recovered to impose a broad chronology on the later alluvial history of the canyon. The dated samples appear in the date list of Table 3 and are plotted on the profile of Figure 6.

The oldest date yet acquired from within the alluvial column is $3,170 \pm 50$ ^{14}C years B.P. (P-2211) obtained from the bole of a tree in growth position buried in sandy alluvium at the base of what is now Beaver Falls. We do not know how much alluvium underlies that sample. A wood sample enclosed in the crystalline travertine capping the sedimentary fill at mile 6.40 yielded an age of 920 ± 50 (P-2216); wood from crystalline travertine precipitated nearby against the alluvial fill during incision yielded an age of 740 ± 40 (P-2217). Wood samples both from the travertine cap and from tufa dams in the bed of the modern stream give ages

from 0 to 600 ^{14}C years B.P.

We can summarize the late alluvial history as follows: Some time before 3,000 B.P. a mass of alluvium, delivered by surface runoff from the plateau surface, began to accumulate in Havasu Canyon. By 900 B.P. contribution of detrital sediment from that source had ceased, and a thick veneer of CaCO_3 was precipitated directly over the alluvium, presumably from water derived from the subsurface. Incision of the tufa-veneered sediment began soon after 900 B.P., and has proceeded at different rates in different parts of the canyon. The present configuration of the long profile of Havasu Creek is rapidly changing as that incision proceeds.

The existence of two masses of crystalline travertine, lacking in wood fragments and extending above the top of the fill deposited during this latest accumulation, suggests that the canyon has experienced more than one such episode of alluviation.

Such deposits are not unique to Havasu Canyon; there are numerous localities within the Grand Canyon where masses of travertine mark the positions of springs that are no longer active.

CONCLUSIONS

The study of carbon-isotope geochemistry and alluvial history of Havasu Creek reported here is not complete, but several major conclusions can already be drawn:

1. Equilibrium of the C-isotope spectrum of HCO_3^- ion in solution in Havasu Creek with the C-isotope spectrum of atmospheric CO_2 is proceeding at least as far as the mouth of the creek; even if we assume a linear equilibration rate and no addition of water below the main complex of springs, approximately 9 additional miles of turbulent flow would be required to bring about total equilibration.

2. Radiocarbon ages of calcareous tufa precipitated at spring orifices or from flowing surface water should not be interpreted as real ages unless limits can be placed on the magnitude of the probable error represented by the C-isotope disequilibrium between the water and the contemporary atmosphere.

3. Havasu Creek has experienced a history of variation in stream regimen. A recent period of alluviation began before 3,000 P.B. and terminated by 900 B.P.; the present time of active incision and rapid and dramatic change of configuration of the creek began before 700 B.P.

We must learn more about the recent history of Havasu Canyon before we attempt to correlate climatic inferences drawn from evidence of variation in stream regimen at this locality with the pattern of recent climatic change described from elsewhere on the Colorado Plateau. Our growing understanding of the mechanisms that control precipitation of calcareous tufa in Havasu Creek may enable us to draw conclusions of paleoclimatic significance from masses of calcareous tufa and travertine that bear witness to periods of greater groundwater flux in other parts of the Grand Canyon.

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LITERATURE CITED

- BARNES, IVAN. 1964. Field measurement of alkalinity and pH. U.S. Geological Survey Water-Supply Paper 1535-H:H1-H17.
- _____. 1965. Geochemistry of Birch Creek, Inyo County, California--a travertine depositing creek in an arid climate. *Geochim. et Cosmochim. Acta* 29:85-112.
- BERNER, R. A. 1971. Principles of chemical sedimentology. McGraw-Hill.
- BLACK, D. M. 1955. Natural dams of Havasu Canyon, Supai, Arizona. *Science* 121:611-612.
- COOLEY, M. E. 1963. Hydrology of the Plateau Uplands Province. In Annual report on ground water in Arizona, Spring 1962 to Spring 1963, by N. D. White, R. S. Stulik, E. K. Morse, and others: Ariz. State Land Dept. Water-Resources Report 15:27-38.
- ILIFF, F. G. 1954. People of the blue water. Harper and Bros., New York, 271 p.
- JAMES, G. W. 1900. In and around the Grand Canyon. Little, Brown, and Co., Boston, 241 p.
- JOHNSON, P. W., and R. B. SANDERSON. 1968. Spring flow into the Colorado River--Lees Ferry to Lake Mead, Arizona. Arizona State Land Department Water-Resources Report No. 34, 26 p.
- MCKEE, E. D. 1969. Stratified rocks of the Grand Canyon. U.S. Geological Survey Professional Paper 669:-B:23-58.
- MCKEE, E. D., and C. E. RESSER. 1945. Cambrian history of the Grand Canyon Region. Part 1, stratigraphy and ecology of the Grand Canyon Cambrian. Carnegie Inst. Washington Pub. 563: 3-168.
- MCKEE, E. D., and R. C. GUTSCHICK. 1969. History of the Redwall Limestone of northern Arizona. *Geol. Soc. America Memoir* 114, 612 p.
- PETTIJOHN, F. J. 1957. Sedimentary rocks. Harper and Bros., New York, 718 p.
- RALPH, E. K. 1971. Carbon-14 dating. In Dating techniques for the archeologist, coedited by Henry N. Michael and Elizabeth K. Ralph, MIT Press, p 1-48.
- WAMPLER, JOSEPH. 1959. Havasu Canyon--gem of the Grand Canyon. Howell-North Press, Berkeley, California, 121 p.