DEPARTMENT OF THE INTERIOR
UNITED STATES GEOLOGICAL SURVEY

WATER-RESOURCES INVESTIGATIONS 79-35
OPEN-FILE REPORT

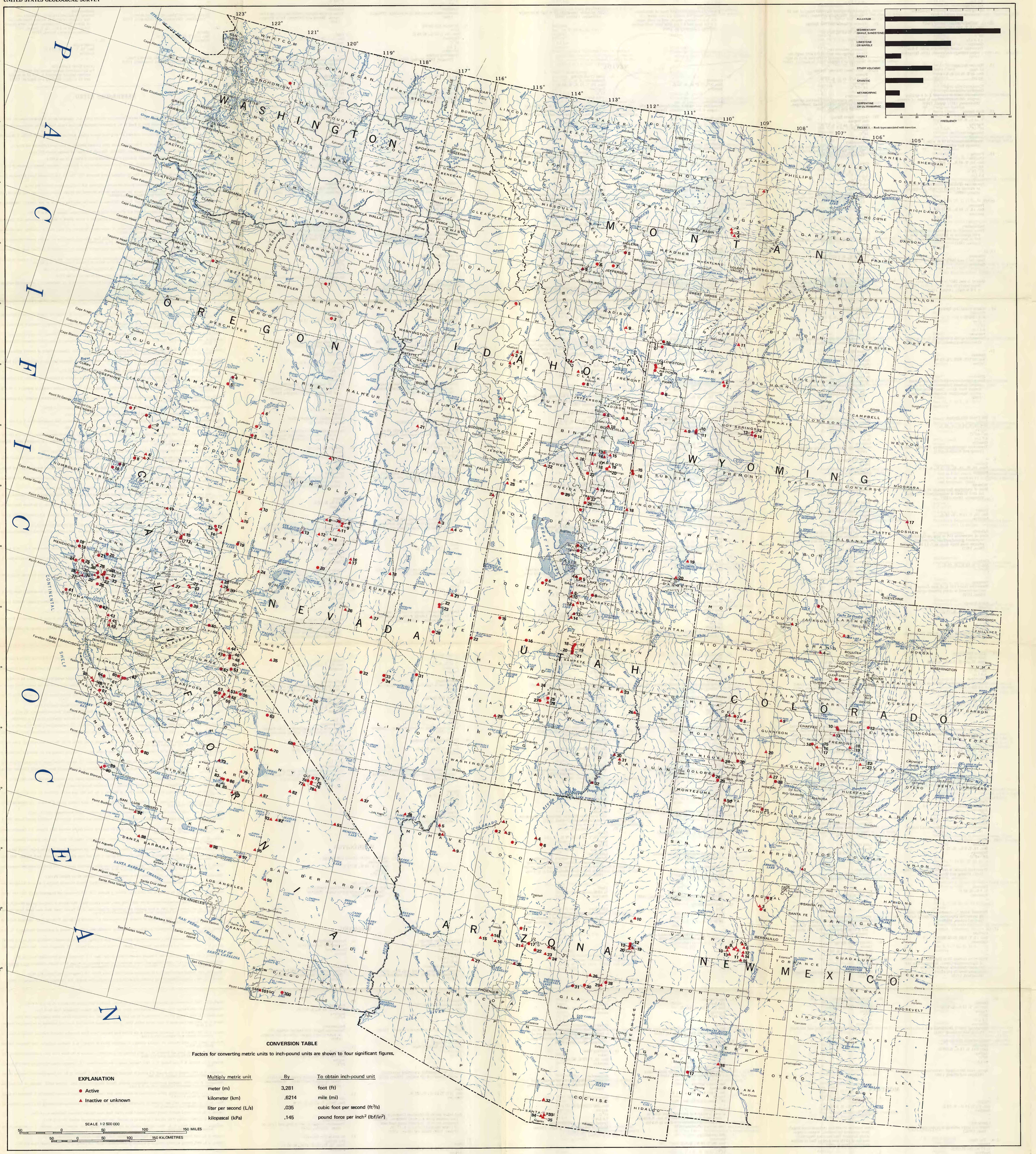

FIGURE 1. – Rock types associated with travertine

CONVERSION TABLE

Factors for converting metric units to inch-pound units are shown to four significant figures.

Multiply metric unit	By	To obtain inch-pound unit
meter (m)	3.281	foot (ft)
kilometer (km)	.6214	mile (mi)
liter per second (L/s)	.035	cubic foot per second (ft^3/s)
kilopascal (kPa)	.145	pound force per inch² (lbf/in^2)

EXPLANATION

- Active
- Inactive or unknown

SCALE 1:2 500 000

MAP SHOWING OCCURRENCES OF SPRING-DEPOSITED TRAVERTINE IN THE CONTERMINOUS WESTERN UNITED STATES

By
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1979

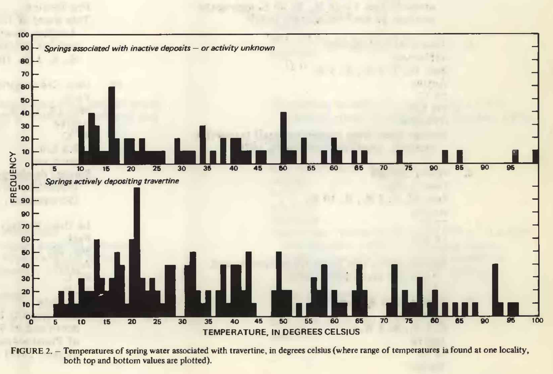

FIGURE 2. – Temperatures of spring water associated with travertine, in degrees celsius (where range of temperatures is found at one locality, both top and bottom values are plotted).

CHEMICAL CHARACTERISTICS OF SELECTED WATERS THAT DEPOSIT TRAVERTINE

	Concentration range (mg/L)				Percentage of cations or of anions	
	Maximum	Minimum	Median	Mean	Maximum	Minimum
Cations:						
Ca[1]	494	4	150	179	68	2
Mg	355	<1	40	53	33	<1
Na (or Na+K)	3,520	14	340	681	94	5
Anions:						
HCO_3+CO_3[1]	8,370	<1	780	1,214	89	2
SO_4	1,730	5	400	467	89	1
Cl	2,330	3.2	210	521	64	1

[1] Both Ca and carbonate species are probably underestimated because of precipitation of $CaCO_3$ between spring orifice and sampling site or in container between time of sampling and of analysis, or both.

UNCERTAINTIES

Of Location

The locations of travertine deposits shown on the map and indicated on the master table are the best representations the authors could make in light of several uncertainties. Where section, township, and range locations were given in the key reference, the information was referred to a quadrangle map, thence to the appropriate State base map where the township grid appeared at reduced scale, and thence to the still smaller-scale map of this report. The last transfer was made by reference to lines of latitude and longitude, drainage, relations to county lines, and directions and distances from those cities that are shown. Older publications commonly identified locations as "about three miles north of west from Greenburg" or some similar statement. Although each deposit location is given on the master table at least to township and range, the fact that some locations involve interpretation should be recognized.

Of Activity

Uncertainties regarding activity of deposition stem from two sources; 1) failure of the original report to say that deposition was or was not taking place, and 2) the fact that springs change in activity both with respect to discharge and with respect to their ability to form travertine. The result is, in part, that various reports of discharge and temperature of water are cited where the deposit is known to be inactive (spring discharges from beneath the travertine mound, for instance), or where activity of deposition is unknown from the report in the literature.

Discharge and temperature date in this report are all "as of" the visit by an investigator—and some of those date back to the late 19th century. Conditions at any of the reported occurrences may be different today compared to when the information reported here was gathered.

With respect to references, we have tried to cite one principal reference—commonly, but not exclusively, the first that contained a reasonably complete description and location. Those data have been supplemented by liberal use of information in Stearns and others (1937), and Waring (1965), although those "standard" references are not individually cited unless one was the sole reference found or where half or more of the information came from one of them.

TRAVERTINE FORMATION

Travertine is commonly thought to be calcite or aragonite formed either by agitation of water or evaporation (Gary and others, 1972, p. 752). Documented modes of deposition of travertine in the Western United States have shown that dolomite and the entire solid solution of calcite (from $CaCO_3$ to $CaMg(CO_3)_2$) should be added to the minerals forming travertine deposits and that evaporation has little if any bearing on most travertine deposits.

The calcareous materials, calcite, aragonite, and dolomite form travertine deposits from aqueous solutions that became at least slightly supersaturated with respect to the minerals deposited. The supersaturation may occur by loss of carbon dioxide (CO_2) from solution to the air, gain of CO_2 from the air, commingling of two chemically different and incompatible aqueous solutions, or by loss of CO_2 through photosynthesis.

In a study of travertine deposition from hot springs, Friedman (1970) showed on the basis of stable isotope evidence that evaporation of water was slight. He showed that the deposition of the travertine was by loss of CO_2 to the air. Friedman further showed that for kinetic reasons the isotopic fractionation of the carbon 13 (^{13}C) between aqueous solution and the travertine, relative to the PDB standard in permil ($^o/oo$), decreased from a difference of 4.8 $^o/oo$ at 75°C to 0 $^o/oo$ at 20°C.

Quite different results were found for travertine depositing from a spring on Pescadero Creek, Santa Clara County, California. The spring is in the southwest 1/4 section 23 of township 11 south, range 3 east and issues from Franciscan greywacke of presumed late Mesozoic age along the Sargent fault. The spring-water composition, given in the table below may be interpreted in the light of earlier reported work. The rather high silica and magnesium concentrations are typical of CO_2-rich metamorphic water (Barnes, 1970; White and others, 1973) reacting with serpentinite (Barnes and others, 1973). Although serpentine is not exposed at the spring, it is present in outcrop a short distance westward along the fault and almost surely occurs below the spring. The CO_2-rich water commonly issues from creeping segments of active faults (Barnes and others, 1975; Irwin and Barnes, 1975).

The spring water has a carbon dioxide partial pressure (P_{CO_2}, in the table above) far above the .03 kPa found in the earth's atmosphere, so CO_2 is lost from solution. Loss of CO_2 to air leads to precipitation of magnesian calcite as travertine. Most of the carbon remains as bicarbonate (HCO_3^{-1}) in the water and is thus a key to the source of the carbon. The value of the ^{13}C in solution, -7.29 $^o/oo$, is typical of mantle-derived CO_2, and is out of isotopic equilibrium with the CO_2 of the air (-7 $^o/oo$) by about -7.3 $^o/oo$. Thus CO_2 will be lost from solution as $^{13}CO_2$ and $^{12}CO_2$. The dissolved carbon is also out of isotopic equilibrium with respect to $^{14}CO_2$. While $^{13}CO_2$ and $^{12}CO_2$ are lost from solution to the air, $^{14}CO_2$ enters the solution to yield spuriously young ages of both travertine and dissolved carbon (table 2). The enrichment of the travertine in ^{14}C and ^{13}C may be due to the $MgCO_3$ content of the magnesian calcites which are enriched in the heavier carbon isotopes (O'Neil and Barnes, 1971) relative to the $CaCO_3$ end member of the calcite solid solution. The interpretation of the isotopic compositions of travertines may be ambiguous. If only the travertine isotopic composition (-0.06 $^o/oo$) were known, the obvious interpretation of the carbon source would be a marine carbonate (+4 to -4 $^o/oo$, Craig, 1953). Such an interpretation is clearly wrong from the composition known for the dissolved, mantle-derived carbon. The problem is that the isotopic fractionation between dissolved and precipitated carbon may be none (Friedman, 1970) to nearly an equilibrium fractionation as reported here.

Low temperature formation of serpentine from olivine and pyroxenes yields waters of pH values up to 12.0 (Barnes and O'Neil, 1969). The solutions, as they emerge, contain no detectable carbonate (CO_3^{-2}) and up to 53 mg/L (milligrams per liter) calcium ion (Ca^{+2}). The solutions gain CO_2 from the overlying air and deposit aragonite, calcite, or both, with a kinetic isotopic fractionation of about 10 $^o/oo$ in ^{13}C, with the travertine depleted in ^{13}C (O'Neill and Barnes, 1971).

In a companion study of conglomerates and travertines, it was shown that travertines could also form by dispersion of magnesium- (Mg^{+2}) and HCO_3^{-1}-rich solutions into Ca^{+2}-rich HCO_3^{-1}-poor solutions (Barnes and O'Neil, 1971). The travertines are unusual because they are composed of calcite ranging in composition from $CaCO_3$ to $Ca_{.5}Mg_{.5}CO_3$ and dolomite ranging in composition from $Ca_{.6}Mg_{.4}CO_3$ to $Ca_{.5}Mg_{.5}CO_3$. Although they showed the solid solutions were due to dispersions of two chemically incompatible waters, they did not provide a chemical explanation of the reaction mechanism to yield the solid solutions. The Mg^{+2}-HCO_3^{-1}-rich waters contain so much HCO_3^{-1} that up to 10 percent of the Mg^{+2} exists in the ion pair $(MgHCO_3)^+$. The ion pair is large and singly charged and has a low charge density relative to Mg^{+2}. The ion pair is thus much less hydrated than Mg^{+2}. It is polar, with the Mg end positive with respect to the HCO_3 end and is thus attracted to the negatively charged surface of the crystals of solid carbonates. The addition of the ion pair to the crystal surface and loss of the hydrogen ion adds anhydrous layers of $MgCO_3$ to the growing crystal and thus provides an effective mechanism for growing $MgCO_3$-rich solid solutions in low temperature, dilute waters.

Possibly the most common mode of formation of travertine is from leaching of calcium carbonate from rocks by ground water and subsequent deposition of travertine in stream channels. Plants take up CO_2 from air and respire CO_2 through their roots. As a consequence, the amount of CO_2 in soil atmospheres may be appreciably greater than that in the earth's atmosphere. Calcium carbonate dissolved in a CO_2-rich water may reprecipitate when CO_2 is lost from solution after the ground water enters a stream channel. A detailed study of a travertine-depositing stream in an arid climate (Barnes, 1965) showed the CO_2 loss was almost entirely by photosynthesis, and evaporative effects were less than detectable. There is a tendency for travertine to form on obstructions such as leaves, twigs, and stones. As the travertine continues to accumulate, it forms rims to pools on the downstream side. The fundamental cause of the accumulation is a greater time rate of supply of unstable (supersaturated) solution per unit area of substrate where the water velocity is greater. The maximum development in stream channels is a series of pools separated by rims of travertine.

As noted earlier and in the following figure, many kinds of rocks yield travertine. There is a problem in that many granites yield CO_2 from mantle sources. Some of the CO_2-rich springs in granitic terranes yield travertine and some do not. Apparently CO_2-rich water cannot leach the calcium from the silicates; if they could, travertine deposits would form in all granitic rocks. Where travertine occurs in silicate rock terranes, it may be assumed that $CaCO_3$ also occurs, either disseminated and hence overlooked, or as a subsurface lenses or masses of marble, limestone or other calcareous materials. Otherwise the calcium may not be supplied to form the travertine.

Travertine deposition does not seem to depend upon the temperature of the springs as shown in the figure below. Because the deposition of travertine is independent of temperature, evaporation of water is not an important cause of deposition. The supersaturation and consequent travertine deposition is due to the chemical reasons given earlier.

CHEMICAL AND ISOTOPIC COMPOSITIONS OF A SPRING ON PESCADERO CREEK, CALIFORNIA AND PRECIPITATES FROM THE SPRING WATER

(Concentrations in mg/L; ^{13}C compositions to the PDB standard in permil ($^o/oo$); pressure in kilopascals (= 0.01 bar). $SrCO_3$ is total dissolved CO_2 species, chiefly HCO_3 - precipitated by addition of an ammoniacal $SrCl_2$ solution.)

SiO_2	108	CO_2 (aq)	530
Al	0.48	HCO_3	2,540
Fe	2.0	CO_3	1.5
Ca	39	SO_4	2
Mg	145	Cl	2,300
Na	2,170	F	0.7
K	60	Br	6.1
NH_4	8.9	I	5.9
		B	88
pH	6.78	$\delta^{13}C$ travertine (calcite)	-0.06
P_{CO_2}	35.5	$-\delta^{14}C$ $SrCO_3$	922±5
kP	0.03	Apparent age; years B.P., $SrCO_3$	20,500±450
$\delta^{13}C$ $SrCO_3$	-7.29	$-\delta^{14}C$ travertine	839±5
		Apparent age; years B.P., travertine	14,670

SPRING-DEPOSITED TRAVERTINE IN ELEVEN WESTERN STATES

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OCCURRENCE OF TRAVERTINE BY STATES

EXPLANATION

Descriptions of deposits are given, where known, in eight items for each occurrence as follows:

a.	Name	e.	Temperature of associated spring
b.	County	f.	Discharge of spring
c.	Section, Township, Range	g.	Rock(s) at orifice
d.	Reported depositional activity	h.	Comments and reference(s)

ARIZONA

1. -
Coconino
Not surveyed
Inactive
-
"Large flow"
Limestone
Travertine deposits occur along 8 km reach of river. (M. E. Cooley, 1978, written commun.)

2. Havasu Spring
Coconino
Tps. 32-33 N., R. 4 W. (proj.)
Active
21°C
1,900 L/s
Limestone
Much travertine occurs below spring. Other occurrences reported at Mooney and Bridal Veil Falls (Galbraith, 1941; Metzger, 1961)

3. Elves Chasm
Coconino
Not surveyed
Inactive
-
3.5-14 L/s (various measurements 1923-65)
Limestone
Eight travertine remnants occur; two larger enclose Elves Chasm to heights 20-165 m above Colorado River. (M. E. Cooley, 1978, written commun.)

4. -
Coconino
Unsurveyed
Unknown
-
-
Limestone
Travertine occurs in at least 7 places in Marble Canyon along Colorado River (Cooley, 1976)

5. -
Mohave
T. 31 N., R. 15 W.
Inactive
-
-
Limestone
Three erosional remnants of travertine extend as much as 120 m above Lake Mead. (M. E. Cooley, 1978, written commun.)

6. Blue Spring
Coconino
T. 32 N., R. 7 E. (proj.)
Active
21°C
> 2600 L/s
Redwall Limestone
Causes extensive deposits in channel of Little Colorado River. (Cooley, 1976)

7. -
Coconino
T. 31 N., Rs. 1, 2 E.
Active
-
-
Redwall Limestone
Travertine is forming in bed of Hermit Creek, Grand Canyon National Park. (Metzger, 1961)

8. -
Mohave
Secs. 4, 9, T. 30 N., R. 14 W.
Inactive
-
-
Sedimentary; limestone
Travertine forms cliff extending 245 m above arm of Lake Mead. (M. E. Cooley, 1978, written commun.)

9. -
Mohave
Secs. 2, 3, 4, T. 27 N., R. 11 W.
Inactive
-
-
Limestone
Three travertine deposits range from 60-245 m above Colorado River; the two larger ones are south of river. (M. E. Cooley, 1978, written commun.)

10. -
Apache
Sec. 35, T. 21 N., R. 28 E.
Unknown
-
-
Tertiary gravel
Travertine was mapped in several occurrences near St. Johns. (Harrell and Eckel, 1939, pl. 1)

11. Montezuma Well
Yavapai
Sec. 31, T. 15 N., R. 6 E.
Active
22°-28°C
55-80 L/s
Sedimentary
Discharge deposits nearly 90 kg of $CaCO_3$ per day. (Cole and Bachelder, 1968; T. H. Thompson, 1977, oral commun.)

12. Stinking Spring

17. Fossil Creek Springs
Gila
Sec. 14, T. 12 N., R. 7 E.
Active
21°C
1,180 L/s
Limestone
Many new orifices open as some are sealed by travertine. Inactive terrace nearby is roughly 1.5 km long, 150 m wide, and extends several hundred meters up slope of mountain. It is much larger than present depos-