

## Sources and fractionation processes influencing the isotopic distribution of H, O and C in the Long Valley hydrothermal system, California, U.S.A.

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**Abstract**—The isotopic ratios of H, O and C in water within the Long Valley caldera, California reflect input from sources external to the hydrothermal reservoir. A decrease in  $\delta D$  in precipitation of  $0.5\text{‰}$   $\text{km}^{-1}$ , from west to east across Long Valley, is caused by the introduction of less fractionated marine moisture through a low elevation embayment in the Sierra Nevada Mountain Range. Relative to seasonal fluctuations in precipitation ( $-158$  to  $-35\text{‰}$ ),  $\delta D$  ranges in hot and cold surface and groundwaters are much less variable ( $-135$  to  $-105\text{‰}$ ). Only winter and spring moisture, reflecting higher precipitation rates with lighter isotopic signatures, recharge the hydrological system. The hydrothermal fluids are mixtures of isotopically heavy recharge ( $\delta D = -115\text{‰}$ ,  $\delta^{18}\text{O} = -15\text{‰}$ ) derived from the Mammoth embayment, and isotopically lighter cold water ( $\delta D = -135\text{‰}$ ,  $\delta^{18}\text{O} = -18\text{‰}$ ). This cold water is not representative of current local recharge. The  $\delta^{13}\text{C}$  values for dissolved carbon in hot water are significantly heavier ( $-7$  to  $-3\text{‰}$ ) than in cold water ( $-18$  to  $-10\text{‰}$ ) denoting a separate hydrothermal origin. These  $\delta^{13}\text{C}$  values overlie the range generally attributed to magmatic degassing of  $\text{CO}_2$ . However,  $\delta^{13}\text{C}$  values of metamorphosed Paleozoic basement carbonates surrounding Long Valley fall in a similar range, indicating that hydrothermal decarbonization reactions are a probable source of  $\text{CO}_2$ . The  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of secondary travertine and vein calcite indicate respective fractionation with  $\text{CO}_2$  and  $\text{H}_2\text{O}$  at temperatures approximating current hydrothermal conditions.

### INTRODUCTION

THREE major chemical elements in hydrothermal fluids, H, O and C, typically originate from sources external to active hydrothermal reservoirs. The sources, mechanisms and pathways by which these chemical components are introduced can provide important information on fluid circulation paths, chemical evolution and energy potential associated with these hydrothermal systems. Sources of H and O, present principally as water, may include meteoric recharge, modern or ancient sea water, mineral dehydration, and magmatic dewatering (WHITE, 1974). The D and  $^{18}\text{O}$  contents in water are commonly employed to assess the origins of hydrothermal fluids, the amount of boiling and mixing in the geothermal reservoir and the extent of water–rock reaction (TRUESDELL and HULSTON, 1980). Carbon is present in very low concentrations in most volcanic rocks. Therefore, abundant C in dissolved carbonate,  $\text{CO}_2$  gas, and secondary carbonate minerals must also be derived from external sources including meteoric recharge, decarbonization of sedimentary rocks and magmatic degassing of  $\text{CO}_2$  (CRAIG, 1953; ARNORSSON and BARNES, 1983; BARNES *et al.*, 1988). One common method of differentiating C sources is

the  $^{13}\text{C}/^{12}\text{C}$  isotopic ratio of the hydrothermal fluids (TRUESDELL and HULSTON, 1980).

The issues of source and transport of water and C, outlined above, are addressed in the present study of isotopic distributions in the Long Valley hydrothermal system. The Long Valley caldera is situated in a  $450\text{ km}^2$  elliptical depression along the eastern front of the Sierra Nevada in east central California, U.S.A. (Fig. 1). Long Valley, a classic example of volcanic caldera, was formed approximately 0.7 Ma ago by structural collapse concurrent with the eruption of  $\sim 500\text{ km}^3$  of Bishop Tuff (BAILEY *et al.*, 1976). Subsequent intracaldera volcanism caused resurgence of the west central part of the caldera floor. Rhyolitic domes have developed in the western margins of the caldera as recently as 500–600 a ago (MILLER, 1985).

Areas of present-day hot spring discharge are distributed primarily around the southern and southeastern sides of the resurgent dome. Major spring features occur at Casa Diablo and Hot Creek (Fig. 1). Additional springs occur across Long Valley terminating along the eastern side of Lake Crowley on the extension of the caldera ring-fracture system. In contrast, no hot springs occur within the caldera to the west of Casa Diablo. However, commercial and

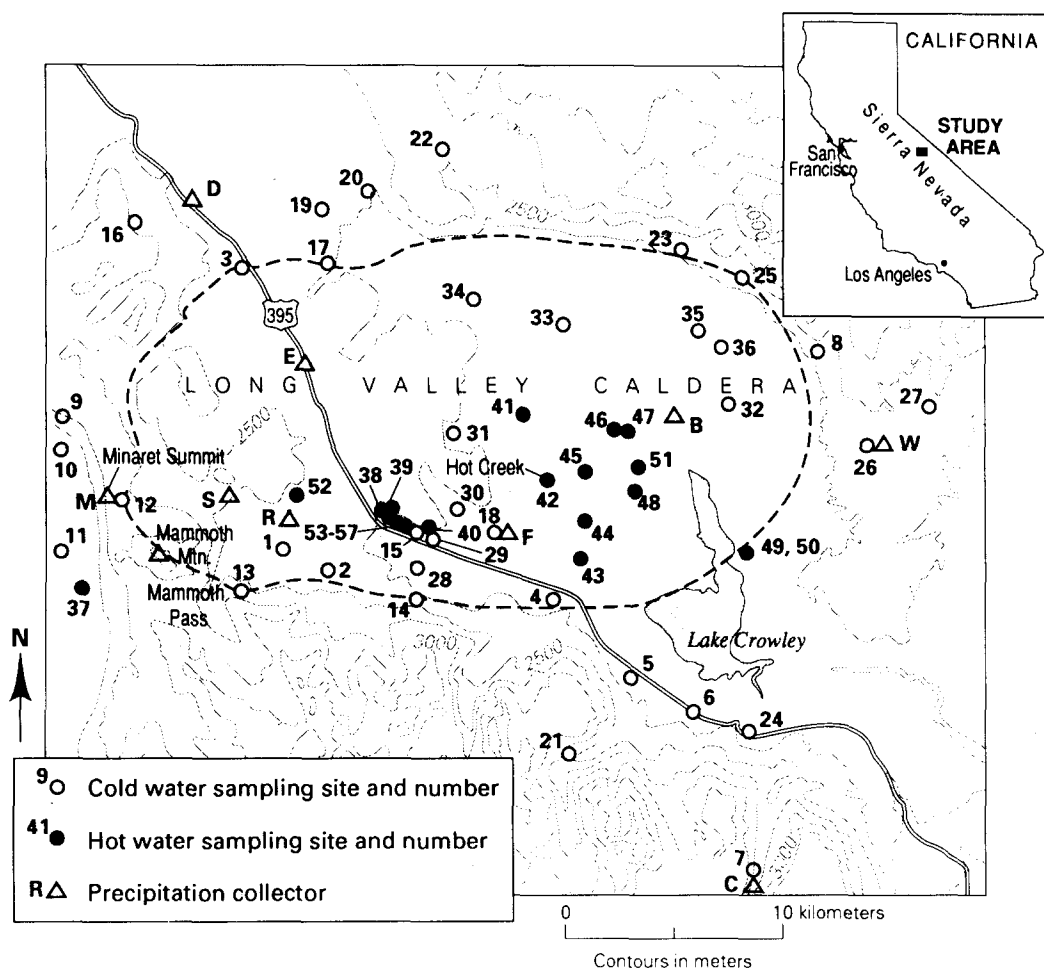


FIG. 1. Topographic setting and sampling locations within Long Valley and the surrounding area. Data for indicated sites are presented in Tables 1 and 2.

scientific drilling (WOLLENBERG *et al.* 1987) have recently intersected thermal waters in excess of 200°C at <400 m depth in the western moat demonstrating that this lack of surface hydrothermal features is related more to topography and shallow circulation of cold groundwater than to the absence of the high-temperature reservoir at depth. Based on temperature, heat flow and chemical data, the current conceptual model of the geothermal system is of deep recharge into volcanic fill and underlying basement rocks from the eastern front of the Sierra Nevada to the west of Long Valley (SOREY, 1985). This water is conductively heated by shallow magmatic intrusions underlying the western moat area. The hydrothermal fluid is then transported upward along fault systems into shallow aquifers and laterally along the hydrological gradient, discharging from hot springs to the east.

MARINER and WILLEY (1976), in the first systematic study of D and  $^{18}\text{O}$  distributions in hot springs in Long Valley, emphasized the isotopically mixed character of most of the thermal water. Based on a mixing line, MARINER and WILLEY (1976) concluded

that the hydrothermal reservoir has recharged from a single isotopically heavy meteoric source. After subsequent  $^{18}\text{O}$  enrichment by exchange with reservoir rocks, the hydrothermal fluids progressively mixed with a lighter meteoric water in the discharge zone producing the isotopic variations observed in the hot springs.

In further refining the mixing model, SOREY *et al.* (1978) concluded that the initial recharge water was heavier in  $^{18}\text{O}$  and D than suggested by MARINER and WILLEY (1976). SOREY *et al.* (1978) also demonstrated significant regional isotopic differences across Long Valley with cold waters from the eastern rim of the caldera being the lightest and waters from the western rim the heaviest. These authors proposed that such isotopic distributions could be used to delineate recharge sources of hydrothermal fluids in Long Valley. Based on enthalpy- $\delta^{18}\text{O}$  and enthalpy- $\delta\text{D}$  plots, FOURNIER *et al.* (1979) suggested that the isotopic compositions of the springs reflected boiling at  $T > 282^\circ\text{C}$ , a temperature yet to be encountered by exploratory drilling. Compilations of additional isotopic data for Long Valley were presented by FARRAR

*et al.* (1985, 1987, 1989). In interpreting more recent isotopic compositions from drill holes, RDO-8, MBP-1 and MBP-3 in the western moat, SHEVENELL *et al.* (1987) concluded that the thermal springs to the east were isotopically diluted as initially proposed by MARINER and WILLEY (1976).

More limited work has focused on the origin of C in the Long Valley hydrothermal system. Measurements of  $\delta^{13}\text{C}$  of  $\text{CO}_2$  gas ( $-5$  to  $-7\text{‰}$ ) at the Casa Diablo wells led TAYLOR and GERLACH (1984) to conclude that  $\text{CO}_2$  is supplied to Long Valley from a magmatic source. However, more extensive  $^{13}\text{C}$  data from Casa Diablo and a number of hot springs (WINNETT and JANIK, 1986) indicated significant regional and seasonal variations ( $-5.0$  to  $10.5\text{‰}$ ) reflecting changes in sources and fractionation processes which are not indicative of a direct magmatic source. WINNETT and JANIK (1986) also found that  $\delta^{13}\text{C}$  values decreased from west to east possibly reflecting mixing with C derived from leaching of old lake beds and hydrothermal deposits.

The objectives of the present work are to characterize the distributions of D,  $^{18}\text{O}$  and,  $^{13}\text{C}$  in the Long Valley hydrothermal fluids, to investigate potential source terms for  $\text{H}_2\text{O}$  and C, and to characterize geochemical, hydrological and meteorological processes which control their distributions.

## METHODOLOGY

Nine precipitation collectors were installed within Long Valley to determine the variability of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  in recharge waters. The collectors were situated to reflect differences in lateral distribution, elevation and climate evident in Long Valley (Fig. 1). Precipitation at three of the sites, Minaret Summit, Rock Creek and Deadman Summit had been previously sampled between 1969 and 1971 by FRIEDMAN and SMITH (1972). The collection technique, described by CLAASSEN *et al.* (1986), consisted of suspension of double polyethylene bags inside vertically supported 360 cm or 510 cm diameter cylindrical ducting. A narrow orifice

(<50 mm) was situated about two-thirds of the way down from the top of the bags to minimize evaporation. Integrated samples were collected at monthly to quarterly intervals. Comparisons with a standard precipitation collector at the U.S. Forest Service office at Mammoth Lakes indicated quantitative agreement in precipitation volumes.

Samples for D and  $^{18}\text{O}$  isotopes were collected in sealed 25 ml glass bottles from the precipitation collectors and from a number of hot and cold springs, wells and surface waters in and adjacent to Long Valley (Fig. 1). Samples for  $^{13}\text{C}$  were precipitated in the field using  $\text{SrCl}_2$  and  $\text{NH}_3\text{OH}$ . Isotopic samples from the geothermal production wells, MBP-1 and MBP-3, were collected as total flow samples by condensation in an ice bath. Water was obtained from the RDO-8 well using a downhole sampler after bailing. Calcite samples were acquired for  $^{13}\text{C}$  isotope analysis from surficial spring deposits and from fracture fillings in core from the RDO-8 and 44-16 wells. Analyses of D,  $^{18}\text{O}$ , and  $^{13}\text{C}$  in the fluid and rock samples were performed by the U.S. Geological Survey, Menlo Park, California and Geochron Laboratories, Cambridge, Massachusetts.

## RESULTS

### D and $^{18}\text{O}$ isotopes in precipitation

The isotopic composition of precipitation (relative to SMOW) sampled as rain and snow at the designated collectors between 1984 and 1987 are listed in Table 1 and plotted in Fig. 2a. The distribution of the data is described by the linear regression fit of

$$\delta\text{D} = 7.6 \delta^{18}\text{O} - 0.5 \quad (1)$$

(solid line, Fig. 2a). The dashed diagonal line in the figure is the global meteoric line initially defined by CRAIG (1961),

$$\delta\text{D} = 8.0 \delta^{18}\text{O} + 10. \quad (2)$$

The close similarity in slopes in Eqns 1 and 2 indicates that atmospheric fractionation processes such as under-cloud evaporation (GAT and DANSGAARD, 1971) do not significantly affect the isotopic signature for precipitation even in the more arid portions of Long Valley. Precipitation does, however, exhibit a wide variability in isotopic composition from  $-158$  to  $-35\text{‰}$  for  $\delta\text{D}$  values and  $-20.6$  to  $-2.8\text{‰}$  for  $\delta^{18}\text{O}$  values. Such distributions undoubtedly reflect a number of complex processes involving the origin and direction of storm tracks, the elevation and temperature of condensation, the degree of isotopic equilibrium obtained during condensation, and whether precipitation occurs as rain or snow.

The preceding processes are reflected in the seasonal variations of  $\delta\text{D}$  values shown in Fig. 3a. The data clearly indicate that isotopically lightest precipitation (mean average =  $-110\text{‰}$ ) falls during the winter months while isotopically heaviest precipitation (mean average =  $-60\text{‰}$ ) predominates during the summer. Comparable seasonal variations were obtained for  $^{18}\text{O}$ . The winter isotopic compositions approximate those of snow elsewhere in the central Sierra Nevada Mountains (FRIEDMAN and SMITH,

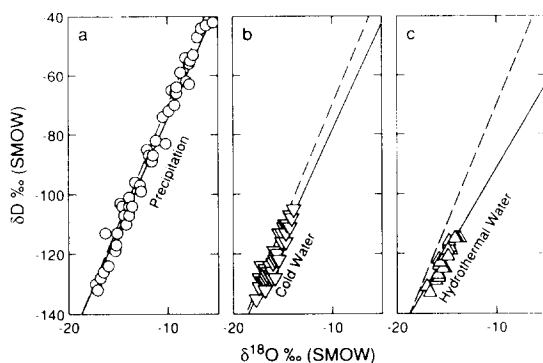


FIG. 2. Plots of  $\delta\text{D}$  vs  $\delta^{18}\text{O}$  values for (a) precipitation, (b) cold surface and groundwaters, and (c) hydrothermal fluids. Dashed lines correspond to the CRAIG (1953) meteoric line and solid lines to the linear regression fits to respective fluids as defined by Eqns 1, 3 and 4 in the text.

Table 1.  $\delta D$  and  $\delta^{18}O$  values for precipitation in Long Valley between 1984 and 1987. Data are tabulated for specific collector sites shown in Fig. 1. Distance is radial from Minaret Summit as shown in Fig. 4

Precipitation collector	Elevation (m)	Distance (km)	Date	$\delta D$ (‰)	$\delta^{18}O$ (‰)
Minaret Summit (M)	3102	0	27-06-1984	-103	-14.8
			10-11-1984	-90	-8.7
			12-02-1987	-107	-13.9
Maintenance Station (S)	2548	5.0	05-01-1984	-110	-14.2
			31-07-1984	-74	-10.5
			25-04-1984	-89	-11.7
			02-08-1984	-64	-9.1
			10-10-1984	-65	-9.6
			21-05-1986	-101	-13.9
			12-02-1987	-124	-16.0
Ranger Station (R)	2396	8.3	05-01-1984	-117	-15.2
			07-02-1984	-85	-12.1
			24-04-1984	-87	-11.5
			10-10-1984	-53	-7.4
Escape Road (E)	2332	11.3	22-05-1986	-104	-13.6
			27-06-1984	-158	-20.6
			01-08-1984	-44	-6.6
			11-10-1984	-66	-9.2
			21-05-1986	-107	-14.4
			19-10-1986	-70	-9.3
Deadman Summit (D)	2451	13.9	19-10-1986	-132	-17.1
			25-04-1984	-99	-12.7
			28-06-1984	-130	-17.3
			19-10-1986	-124	-16.5
Fish Hatchery (F)	2157	17.1	21-02-1987	-122	-16.5
			05-01-1984	-113	-16.3
			07-02-1984	-96	-13.3
			24-04-1984	-89	-11.6
			27-06-1984	-74	-9.0
			31-07-1984	-55	-7.7
			09-10-1984	-43	-6.1
Benton Crossing (B)	2078	27.0	19-05-1986	-83	-10.2
			21-10-1986	-63	-7.8
			05-01-1984	-128	-16.8
			07-02-1984	-104	-14.6
			24-04-1984	-97	-12.8
			31-07-1984	-37	-4.1
			11-10-1984	-35	-2.8
Rock Creek (C)	2560	31.7	19-05-1986	-113	-15.1
			27-06-1984	-109	-12.5
			10-10-1984	-54	-8.2
			19-05-1986	-126	-16.5
Watterson Trough (W)	2460	36.1	21-10-1986	-72	-9.9
			31-04-1984	-130	-5.4
			11-10-1984	-62	-8.1
			19-05-1986	-119	-15.3
			21-10-1986	-66	-9.1

1972; KROUSE *et al.*, 1977; SMITH *et al.*, 1979). Based on a nonturbulent adiabatic fractionation model proposed to explain D distributions across eastern California (SMITH *et al.*, 1979), average winter precipitation of  $-110\text{‰}$  at Long Valley would result from condensation as snow at a temperature of  $-15^{\circ}\text{C}$  at an elevation of 4000 m. These are realistic winter atmospheric conditions over the crest of the Sierra Nevada Mountains immediately west of Long Valley.

Precipitation rates between 1984 and 1987 were calculated from measured fluid volumes and sampling intervals for the various collectors. Significant variations in rates (Fig. 3b) are attributable to the

geographical diversity in collector locations (Fig. 1). Annual precipitation in western Long Valley has been previously estimated at  $>150\text{ cm}$ , while in the eastern portion of Long Valley at Lake Crowley, precipitation is  $<30\text{ cm}$  (SOREY *et al.*, 1978). About 75% of this precipitation was reported to have occurred as snow between November and April. Precipitation rates averaged over Long Valley for the present data (solid line, Fig. 3b) approached a maximum of  $0.25\text{ cm d}^{-1}$  during wettest winter months and a minimum of  $0.05\text{ cm d}^{-1}$  during the driest fall months. A comparison of Figs 3a and 3b indicates that a distinct correlation exists between high rates of



Table 2. Isotopic compositions of surface waters, groundwaters, and hydrothermal fluids in Long Valley determined in the present study

Sample	Date	Temp. (°C)	δD (‰)	δ <sup>18</sup> O (‰)	δ <sup>13</sup> C (‰)
Cold surface and groundwaters					
1. Mammoth Creek	26-06-1983	6	-114	-15.7	—
2. Sherwin Creek	28-04-1984	3	-121	-15.7	—
3. Deadman Creek	18-11-1983	8	-122	-15.8	—
4. Convict Creek	25-04-1984	6	-122	-15.4	—
5. McGhee Creek	26-04-1984	5	-123	-16.0	—
6. Hilton Creek	25-04-1984	8	-123	-16.0	—
7. E. Fork Rock Creek	25-04-1984	7	-126	16.1	—
8. Wilfred Canyon	01-06-1984	12	-128	-16.7	—
9. Agnew Meadow Spring	10-10-1984	7	-113	-15.4	—
10. Upper Soda Spring	09-10-1984	8	-110	-14.8	-7.4
11. Soda Spring	10-10-1984	14	-110	-14.6	-6.5
12. Minaret Summit Spring	02-08-1984	8	-108	-14.1	-12.3
13. Mammoth Rock Spring	09-10-1984	7	-111	-14.9	-9.7
14. Laurel Spring	17-11-1983	10	-128	-16.7	-14.3
15. Sheriff Substation Spring	25-04-1984	12	-113	-14.7	-8.3
16. Hartley Spring	01-08-1984	8	-119	-15.9	-17.9
17. Big Spring	18-11-1983	11	-125	-16.6	-15.6
18. Fish Hatchery Pool	16-04-1984	10	-124	-16.3	—
19. Alpers Canyon Spring	03-08-1984	15	-125	-16.8	—
20. Clark Canyon Spring	03-08-1984	10	-127	-16.6	—
21. Buzztail Spring	03-08-1984	5	-128	-17.4	—
22. Bald Mtn Spring	03-08-1984	11	-125	-16.8	-16.4
23. Aspen Spring	21-05-1986	8	-127	-16.2	—
24. Round Valley Spring	25-04-1984	6	-135	-17.7	—
25. Sanchez Spring	21-05-1986	8	-124	-17.2	—
26. Watterson Trough	25-04-1984	7	-131	-17.4	—
27. E. Watterson Trough	21-05-1986	6	-128	-16.1	—
28. Gravel Pit Well	21-10-1986	8	-115	-15.4	—
29. Sheriff Substation Well	17-11-1983	9	-116	-15.1	—
30. Long Canyon Well	10-10-1984	18	-105	-13.9	—
31. Little Antelope Valley	10-10-1984	10	-126	-16.5	—
32. Well LV21	20-04-1984	11	-132	-16.8	—
33. Windmill 31P1	20-05-1986	6	-125	-16.8	—
34. North Windmill	24-04-1984	9	-132	-16.8	—
35. Windmill 35N1	20-05-1986	10	-107	-14.3	—
36. Windmill 2A	20-05-1986	10	-129	-16.8	—
Hydrothermal fluids					
37. Reds Meadow Spring	07-02-1984	45	-110	-14.7	-3.6
38. Casa Diablo Spring	18-11-1983	92	-118	-13.2	-3.0
39. Meadow Spring	11-10-1984	64	-119	-14.6	-4.1
40. Colton Spring	03-08-1984	70	-116	-14.2	-3.0
41. Little Hot Creek Spring	17-11-1983	80	-125	-15.2	-3.4
42. Hot Creek Spring	27-06-1983	91	-121	-14.0	-4.1
43. Whitmore Spring	17-11-1983	33	-129	-16.1	-6.2
44. N. Whitmore Spring	17-11-1983	50	-123	-15.7	-5.1
45. Horse Shoe Spring	11-10-1984	31	-125	-15.4	—
46. Mondale Spring	07-11-1984	18	—	—	-5.3
47. Dome Spring	11-10-1984	58	-123	-15.7	-5.7
48. Little Alkali Lake Spring	11-10-1984	33	-124	-15.9	-4.9
49. Layton Spring 'a'	24-04-1984	50	-131	17.0	-6.0
50. Layton Spring 'b'	24-04-1984	18	-133	-16.7	—
51. Big Alkali Lake Spring	11-11-1983	50	-127	-15.8	-6.0
52. RDO-8 Well	15-11-1986	201	-115	-14.3	-4.9
53. MBP-1 Well	07-01-1984	168	-114	-13.2	—
54. MBP-2 Well	18-11-1983	—	-115	-12.9	-5.0
55. MBP-3 Well	12-07-1985	171	-116	-14.8	—
56. MBP-4 Well	05-01-1984	—	-114	-13.9	—
57. MBP-5 Well	05-01-1984	—	-111	-13.4	—

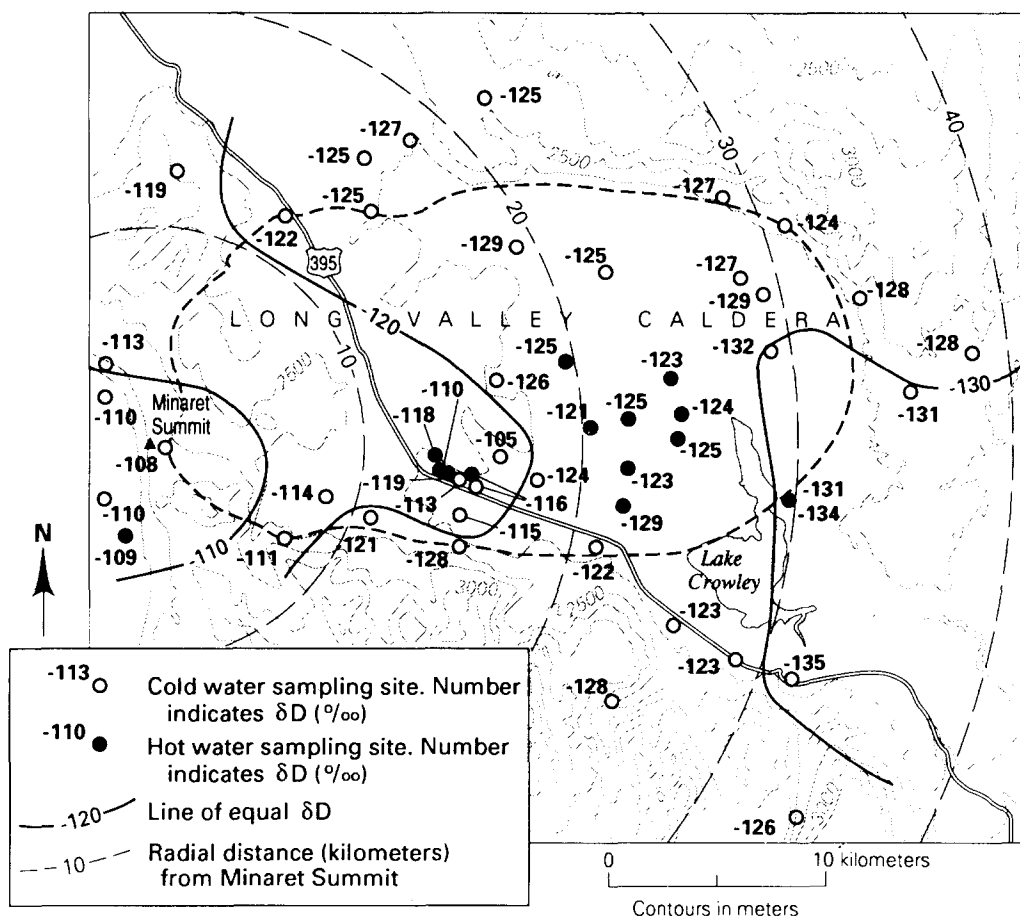


Fig. 4. Geographical distribution of  $\delta D$  in cold and hot waters in and adjacent to Long Valley.

### Carbon isotope distributions

The  $\delta^{13}C$  values of hot waters in Long Valley increase with both increasing total dissolved C and temperature (Table 2, Fig. 5). The lightest  $\delta^{13}C$  values for cold groundwaters ( $-18$  to  $-12$ ‰) overlap isotopic values expected for soil gas  $CO_2$  derived from plant respiration during Calvin and Hatch-Slack photosynthesis (HILLAIRE-MARCHEL, 1986). The increase in  $\delta^{13}C$  values with total C in cold groundwater appears to reflect a mixing of this soil zone source with small proportions of hydrothermal fluids which have cooled conductively. Water samples that exhibit above-ambient temperatures ( $>15^\circ C$ ) are significantly heavier in  $^{13}C$ . Although WINNETT and JANIK (1986) proposed that  $\delta^{13}C$  values increased in the thermal water from west to east across Long Valley, the present data reveal no obvious regional trends (Table 2). The  $\delta^{13}C$  values of the hydrothermal fluids appear to be complex functions of reservoir  $^{13}C$ , groundwater mixing,  $CO_2$  loss from boiling, and dissolution and precipitation of carbonate mineral phases.

### Isotopic equilibrium with calcite

The O and C composition of the hot water can be combined with data for coexisting secondary carbonates to assess isotopic fractionation within the hydrothermal reservoir and to estimate present and past temperatures of secondary calcite deposition (Table 3). Calcite is formed in two types of hydrothermal environments in Long Valley; as surficial travertine deposits associated with hot-spring discharge, and as vein and fracture fillings within the deeper hydrothermal reservoir. The travertine deposits are primarily forming under current hot spring conditions. The only exceptions are the Layton Springs deposits which appear to have been formed under past sublacustrine conditions. The vein calcite samples are from drill core from multiple depths in the RDO-8 hole and from a single depth in the 44-16 hole. The present hydrothermal fluids in contact with these deposits are in chemical equilibrium with respect to  $CaCO_3$  (WHITE and PETERSON, 1990). However, the specific age of vein deposits is not known.

The isotopic fractionation factor,  $\alpha$ , describing

Table 3. Carbon and oxygen isotope analysis for coexisting hydrothermal fluids and calcite and a comparison between measured and calculated temperatures (°C) based on <sup>13</sup>C fractionation between calcite and CO<sub>2</sub> (Eqn 7) and <sup>18</sup>O fractionation between calcite and water (Eqn 8)

		Rock (‰)		Water (‰)		Temperature		
		δ <sup>13</sup> C	δ <sup>18</sup> O	δ <sup>13</sup> C	δ <sup>18</sup> O	measured	<sup>13</sup> C	<sup>18</sup> O
Spring travertine								
Reds Meadow Spring		+1.7	+15.8	-3.6	-14.7	48	76	15
Hot Creek		+1.5	-7.2	-1.5	-15.8	92	113	54
Dome Spring A		+2.6	+15.9	-5.7	-15.7	58	42	11
Dome Spring B		+1.8	+15.9	-5.7	-15.7	58	50	11
Mammoth Rock Spring		-0.3	+14.2	-9.7	-14.9	18	31	25
Layton Spring A		+3.5	—	-9.3	-13.7	33	6	—
Layton Spring B		+1.9	—	-9.3	-13.7	33	17	—
Layton Spring C		+1.3	—	-9.3	-13.7	33	22	—
Little Hot Creek		-0.7	—	-3.4	-15.2	83	119	—
Big Alkali Lake Spring		-0.3	+13.2	-6.0	-15.8	50	70	22
Colton Spring		+0.1	+14.4	-3.0	-14.2	93	112	24
Little Alkali Lake Spring		—	+16.7	-4.9	-15.9	48	—	7
Vein calcite in the hydrothermal reservoir								
RDO-8	317 m	-5.3	-5.4	-4.9	-14.3	164	205	211
	405 m	-7.0	-7.1	-4.9	-14.3	175	307	251
	503 m	-4.1	-3.3	-4.9	-14.3	173	167	173
	521 m	-3.2	-2.0	-4.9	-14.3	171	146	154
	541 m	-6.1	-8.4	-4.9	-14.3	198	244	288
	547 m	-5.8	-7.6	-4.9	-14.3	200	229	264
	568 m	-6.5	-8.5	-4.9	-14.3	196	268	292
	611 m	-4.6	-3.9	-4.9	-14.3	198	182	183
	613 m	-5.7	-7.4	-4.9	-14.3	189	222	259
44-16	2500 m	-3.0	-1.9	-4.8	-14.9	205	230	125

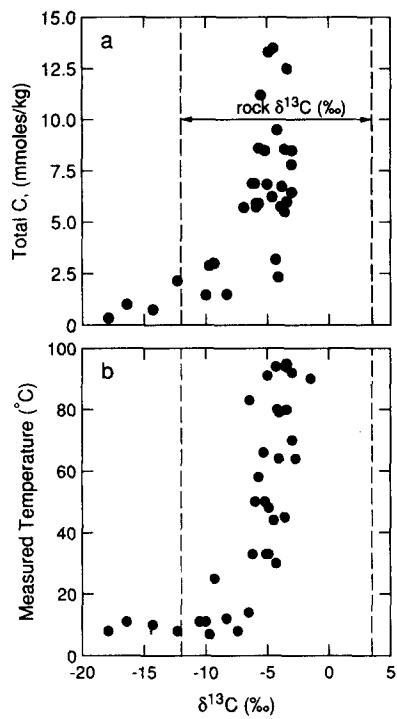


FIG. 5. Total dissolved C and measured temperatures plotted as functions of δ<sup>13</sup>C values for (a) cold groundwater and (b) hydrothermal fluids. The indicated range for rock δ<sup>13</sup>C values is for Paleozoic metasediments surrounding Long Valley.

either <sup>13</sup>C or <sup>18</sup>O partitioning between calcite (c) and dissolved species in water (w) is expressed as

$$\alpha = \frac{1000 + \delta(^{13}\text{C}, ^{18}\text{O})_c}{1000 + \delta(^{13}\text{C}, ^{18}\text{O})_w} \tag{5}$$

The <sup>13</sup>C fractionation between calcite and the fluid phase is expected to be a function of temperature (*T*, K) and the proportions of various carbonate species present in the fluid phase. The fractionation between calcite and aqueous bicarbonate at <150°C, has been described by the relation (BOTTINGA, 1968; MOOK *et al.*, 1974)

$$10^3 \ln \alpha_{\text{CaCO}_3\text{-HCO}_3} = 1.435(10^6 T^{-2}) - 9.483(10^3 T^{-1}) + 17.7. \tag{6}$$

The fractionation between calcite and CO<sub>2</sub> is expressed by the relation (BOTTINGA, 1968)

$$10^3 \ln \alpha_{\text{CaCO}_3\text{-CO}_2} = 2.988(10^6 T^{-2}) - 7.666(10^3 T^{-1}) + 2.461. \tag{7}$$

These fractionation factors are plotted as functions of temperature in Fig. 6a. Predicted <sup>13</sup>C fractionation between CaCO<sub>3</sub> and CO<sub>2</sub> is significant at low temperature, decreases rapidly with increasing temperature, and is minimal at measured reservoir temperatures of 200°C. In contrast, predicted <sup>13</sup>C fractionation between CaCO<sub>3</sub> and HCO<sub>3</sub> is slight up to 150°C.



Measured  $\delta^{13}\text{C}$  values in the vein calcite at a reservoir temperature of  $\sim 200^\circ\text{C}$  is only weakly fractionated with respect to the fluid phase (Table 3 and Fig. 6a) and reflects  $^{13}\text{C}$  equilibrium with  $\text{CO}_2$ . At high temperatures and near-neutral pH, carbonate species are generally chemically associated and dominated by dissolved  $\text{CO}_2$  (WHITE and PETERSON, 1990). The heavier  $\delta^{13}\text{C}$  is more strongly fractionated in the lower temperature travertine deposits relative to the hot-spring fluids. The continued apparent isotopic equilibrium of  $^{13}\text{C}$  between the travertine and  $\text{CO}_2$  is unexpected because  $\text{HCO}_3^-$ , and not dissolved  $\text{CO}_2$  is the dominant aqueous C species at the temperatures and atmospheric pressures of the hot-spring environment. Rapid degassing of  $\text{CO}_2$  prior to and during hot spring discharge was found to cause  $^{13}\text{C}$  disequilibrium between  $\text{CO}_2$  and  $\text{HCO}_3^-$  in the Long Valley hot springs (WINNETT and JANIK, 1986). Apparent isotopic equilibrium of  $^{13}\text{C}$  between travertine and dissolved  $\text{CO}_2$  has been described in a number of active hot spring systems (TURI, 1986).

Fractionation of  $^{18}\text{O}$ , occurring between calcite and water, and between calcite and dissolved  $\text{CO}_2$  gas, can be described by the respective fractionation factors expressed as functions of temperature (O'NEIL *et al.*, 1969),

$$10^3 \ln \alpha_{\text{CaCO}_3-\text{H}_2\text{O}} = 2.78(10^6 T^{-2}) - 2.89 \quad (8)$$

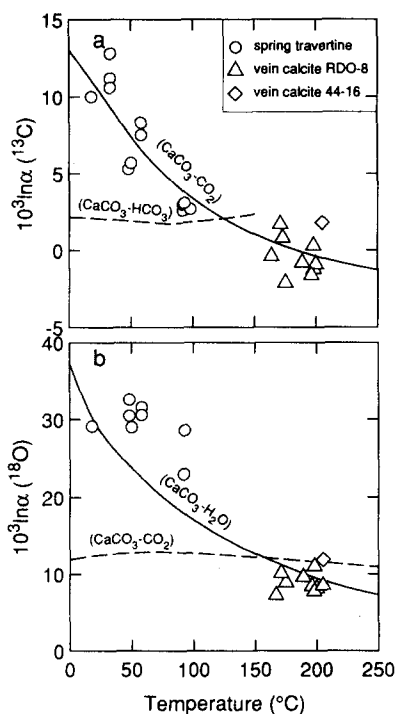


FIG. 6. Comparison of temperature effects on the fractionation of (a)  $^{13}\text{C}$  and (b)  $^{18}\text{O}$  between calcite and dissolved aqueous species. Solid and dashed lines are experimental fractionation factors defined in the text. Points are measured temperatures and fractionation values calculated from data in Table 3.

and

$$10^3 \ln \alpha_{\text{CaCO}_3-\text{CO}_2} = -1.803(10^6 T^{-2}) + 10.61(10^3 T^{-1}) - 2.780. \quad (9)$$

The  $\text{CaCO}_3$ - $\text{CO}_2$  fractionation (Eqn 9) is clearly temperature insensitive compared to  $\text{CaCO}_3$ - $\text{H}_2\text{O}$  fractionation (Eqn 8) which decreases strongly with increasing temperature (Fig. 6b).

The observed 10‰ difference in  $\delta^{18}\text{O}$  values between vein calcite and fluids at  $\sim 200^\circ\text{C}$  (Table 3) correlates closely with the predicted  $\text{CaCO}_3$ - $\text{H}_2\text{O}$  fractionation (Eqn 8). The extent of fractionation in the lower temperature travertine hot spring deposits is significantly greater ( $\sim 30\text{‰}$ ) and exceeds both the predicted  $\text{CaCO}_3$ - $\text{CO}_2$  and the  $\text{CaCO}_3$ - $\text{H}_2\text{O}$  fractionations. Similar discrepancies for  $\delta^{18}\text{O}$  values have been noted in other hot spring-travertine systems (GONFIANTINI *et al.*, 1968; TURI, 1986). Most travertine deposits do not form in the orifice of the actively discharging hot spring from which the fluid isotopic samples were collected, but rather around the spring periphery where maximum  $\text{CO}_2$  loss and lower temperatures have probably occurred making the actual fractionation less than is apparent from Fig. 6b.

The calculated  $^{13}\text{C}$  and  $^{18}\text{O}$  fractionation temperatures (Eqns 8 and 9) for the vein calcite from the RDO-8 well can be compared to measured temperature profile (Fig. 7) to assess possible changes in the thermal history of the hydrothermal reservoir. Also plotted are the ranges of homogenization temperatures measured for a number of primary and secondary fluid inclusions in calcite at depths of 503, 541 and 642 m in the RDO-8 well (JOE MOORE, University of Utah Research Institute, written commun.). The data demonstrate that calcite samples exhibiting close agreement between  $^{13}\text{C}$  and  $^{18}\text{O}$  fractionation temperatures also have comparable measured and

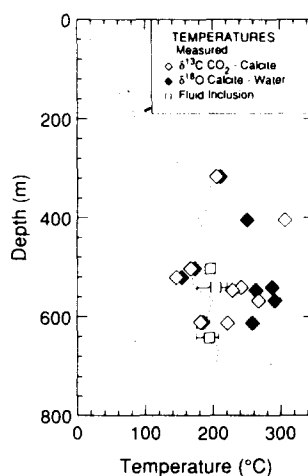


FIG. 7. Comparison of measured temperature profiles in the RDO-8 drill hole with calculated temperatures based on  $^{18}\text{O}$  and  $^{13}\text{C}$  fractionation (Eqns 7 and 8) and fluid inclusion annealing temperatures.

fluid inclusion temperatures. This correlation suggests that these calcites are forming under present chemical and temperature conditions. However, some of the calcites exhibit fractionation temperatures approaching 300°C (Table 3), significantly in excess of present measured reservoir temperatures. The temperature discrepancy of up to 50°C between  $^{13}\text{C}$  and  $^{18}\text{O}$  fractionation for these calcites could indicate that possible non-equilibrium isotopic fractionation has occurred, probably due to recrystallization and isotopic exchange prior to formation of the more recently equilibrated calcites. Such temperature discrepancies could also be enhanced by past changes in the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  contents of the hydrothermal fluid. Therefore, whether these apparent fractionation temperatures actually reflect past higher reservoir temperatures is difficult to ascertain. The isotopic data clearly indicate that significant calcite precipitation has not occurred at temperatures lower than present conditions in the RDO-8 drill hole.

## DISCUSSION

The significant spatial variability in  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values of precipitation appears to be related to the extreme topographic relief within and surrounding Long Valley. More than 2000 m of vertical relief exist between the crest of the Sierra Nevada and the floor of Long Valley caldera which are separated by a lateral distance of <10 km. Meteorological studies have documented the effects of upslope conditions and corresponding decreases in condensation temperatures on the progressive depletion of D and  $^{18}\text{O}$  isotopes in precipitation as storm fronts rise over mountainous terrain (SMITH *et al.*, 1979). However, no correlation is found between the elevation of the precipitation collectors and the D and  $^{18}\text{O}$  water contents (Table 1). This lack of correlation is due to the fact that major winter storm tracks generally approach Long Valley from the Pacific Ocean, placing it on the leeward side of much of the significant precipitation that falls on the western slope of the Sierra Nevada.

The only exception to the generally strongly fractionated nature of precipitation which falls on the eastern side of the Sierra Nevada is the relatively heavy D and  $^{18}\text{O}$  contents of local precipitation in the vicinity of Mammoth Mountain which is centered in an embayment within the NW–SE trending Sierran crest (Fig. 1). Directly north and south of Mammoth Mountain are Minaret and Mammoth Passes situated at elevations of ~2900 m, or 1000 m lower than the Sierran crest farther to the north and south. Adjacent to this embayment is the San Joaquin River Canyon which nearly bifurcates the Sierra Nevada from the south-west. Storms moving from the west up the San Joaquin drainage pass through the Mammoth embayment at anomalously low elevations relative to the

rest of the Sierra Nevada. The net effect of this window is to decrease precipitation and upslope fractionation of D and  $^{18}\text{O}$  on the western slope and increase precipitation with an isotopically heavier marine imprint to the east.

The above effects can be simplistically modeled by plotting  $\delta\text{D}$  of precipitation as a function of radial distance from a point source centered in the Mammoth embayment which is assumed to be Minaret Summit. The spatial relation is clearly demonstrated (Fig. 4) by the concentric contours centred on Minaret Summit. This model assumes that once the storms have passed through the confines of the embayment, the resulting isotopically heavy precipitation spreads outward to the east across Long Valley. At increasing distances from the embayment, this heavier signature is progressively diluted by isotopically lighter precipitation which has passed over the Sierran crest at higher elevations to the north and south. In addition, as the clouds move eastward, rainout effects progressively lighten the isotopic composition of precipitation across Long Valley.

Although wide variations exist for D contents in winter and spring precipitation at specific collector sites, a negative correlation is evident between average  $\delta\text{D}$  values and distance of the site from Minaret Summit (Fig. 8). Precipitation at sampling stations close to the Mammoth embayment at Minaret Summit, Mammoth Maintenance Station, and the Mammoth Ranger Station are isotopically heavier than sites in eastern Long Valley at Watterson Trough and Benton Crossing. This correlation is not simply related to the distance from the Sierran crest. Rock Creek, located directly east of the crest but to the south of the embayment (Fig. 1), exhibits some of the lightest isotopic values of any of the precipitation sites. The elevation of the Sierran crest directly to the

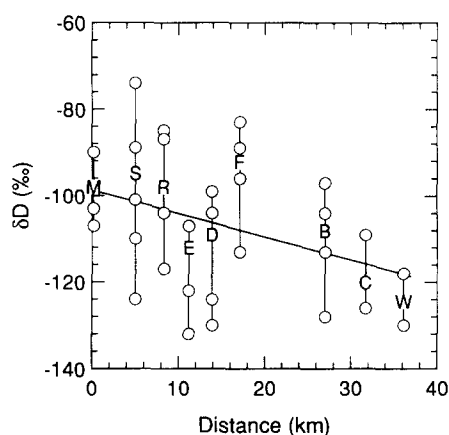


Fig. 8. The distribution of  $\delta\text{D}$  values in winter and spring precipitation samples (January–May) plotted as a function of collection distance from Minaret Summit. Letters correspond to collectors listed in Table 1 with locations plotted in Fig. 1. The solid line is the linear regression fit through the data.

west of Rock Creek is  $>4000$  m, which effectively fractionates D toward lighter isotopic compositions before the storm fronts reach the site. The linear regression fit to the precipitation data (Fig. 8) indicates a  $\delta D$  decrease of  $\sim 0.5\text{‰ km}^{-1}$  occurring radially outward from the Mammoth embayment. Precipitation at the Escape Road collection site appears anomalously light and precipitation at the Fish Hatchery anomalously heavy relative to this concentric trend.

The distributions of  $\delta D$  values in cold and hydrothermal waters are plotted as functions of radial distance from the Mammoth embayment in Fig. 9. The vertical  $\delta D$  scale is significantly reduced relative to Fig. 8, reflecting less variability due to greater integration of precipitation events. This natural averaging is also responsible for the greater apparent negative correlation between  $\delta D$  values and distance for individual samples. The mean linear regression for the fluids (solid line, Fig. 9) indicates that  $\delta D$  decreases an average of  $0.6\text{‰ km}^{-1}$ , a gradient which is relatively close to  $0.5\text{‰ km}^{-1}$  obtained for precipitation (Fig. 8).

MARINER and WILLEY (1976) and SOREY *et al.* (1978) suggested isotopic mixing models involving a single deep hydrothermal fluid source and one or more shallow cold groundwater sources to explain the D and  $^{18}\text{O}$  isotope distributions in hydrothermal fluids within Long Valley. A further refinement of the plot of  $\delta D$  vs  $\delta^{18}\text{O}$  values for hydrothermal and cold waters, which formed a basis of their model, is shown in Fig. 10. The trend in  $\delta D$  and  $\delta^{18}\text{O}$  data for hot waters (Eqn 4) can be explained by mixing a heavy hydrothermal water, approximating RDO-8 and MBP well isotopic compositions ( $\delta D = -115\text{‰}$ ,  $\delta^{18}\text{O} = -14.3\text{‰}$ , Table 2), with a second isotopically light cold-water component. Only Reds Meadow Hot Spring, situated west of the Sierra Crest falls appreciably off this mixing trend, signifying a separate

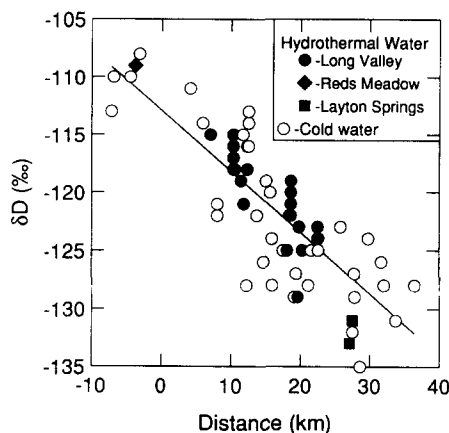


Fig. 9. The distribution of  $\delta D$  in cold groundwater and surface water (open circles) and hydrothermal fluids (solid points) plotted as a function of collection distance from Minaret Summit. The solid line is the linear regression fit through the data.

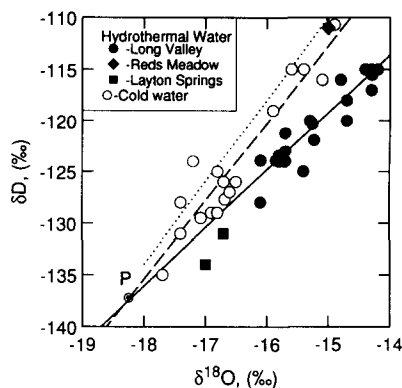


Fig. 10. Plot of  $\delta D$  vs  $\delta^{18}\text{O}$  for hot and cold fluids. Solid line is linear regression fit to the Long Valley hydrothermal data (Eqn 4). The dashed line is the fit to cold water data (Eqn 3) and dotted line is meteoric line (Eqn 2). The intercept P is the projected composition of the cold water end member.

peripheral hydrothermal system. The Layton Springs data are also excluded from this analysis because of its isolated location on the eastern margin of the ring fracture system.

The source area for the isotopically heavy recharge can be bracketed between the  $-110$  and  $-120\text{‰}$   $\delta D$  isograds shown in Fig. 4. Waters directly to the east, north and south of Casa Diablo, including the resurgent dome area and the north and south rims of the caldera are isotopically too light ( $< -120\text{‰}$ ) to be recharge to the hydrothermal system. In contrast, waters associated with Mammoth Mountain and areas to the west of the Sierra crest appear to be too heavy ( $> -110\text{‰}$ ) if RDO-8 and MBP waters are indicative of the unmixed hydrothermal end member. Based on the  $\delta D$  distributions, the eastern front of the Sierras north-west of Casa Diablo and north of Mammoth Mountain appears to represent the most probable area of recharge to the hydrothermal reservoir. The respective  $\delta D$  and  $^{18}\text{O}$  content of the light cold water mixing component can be calculated to be  $-138\text{‰}$  and  $-18.2\text{‰}$ , based on the interception of the hydrothermal mixing line (solid line) with the cold-water meteoric line (dashed line) (Point P, Fig. 10).

Cold groundwaters contain minimal concentrations of Cl and B compared to the hydrothermal fluids in Long Valley (FARRAR *et al.*, 1985, 1987, 1989). As required for two component mixing, a linear relation exists between Cl and  $\delta D$  values (Fig. 11a), and between B and  $\delta D$  values (Fig. 11b). The intercepts of these mixing lines produce a  $\delta D$  value for the cold-water end member of  $\sim -135$  to  $137\text{‰}$  which is in close agreement with the D- $^{18}\text{O}$  intercept of  $-138\text{‰}$  (Fig. 10). The position of any specific fluid composition along either the isotopic or elemental mixing lines should quantitatively reflect the proportions of the hot and cold fluids. Both isotopic and chemical mixing indicate that between 50 and 100% of the mixed fluid is composed of the initial hydro-

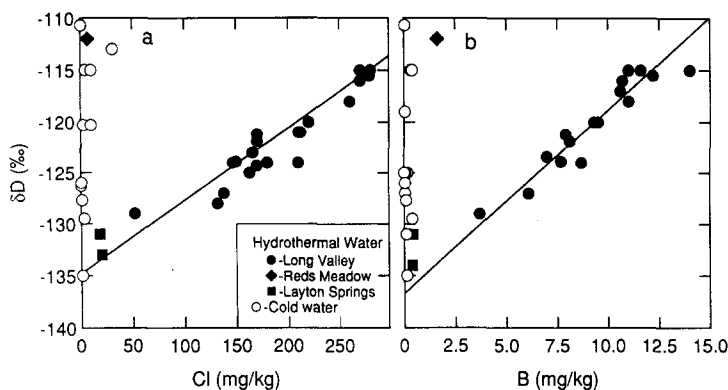


Fig. 11. Plot of  $\delta D$  vs (a) Cl and (b) B for cold and hydrothermal fluids in Long Valley. Solid lines are linear regression fits to the Long Valley hydrothermal data.

thermal component. The only exception is Whitmore Spring which is significantly more dilute and contains young recharge water based on a  $^3H$  content of 4.6 TU.

The predicted end-member cold water component with a  $\delta D$  value of  $-135$  to  $-138$ ‰ is light relative to measured precipitation within Long Valley (Fig. 1). Only a single cold spring, located at Round Valley (Fig. 4), exhibits a D composition as light as  $-135$ ‰. This spring and comparable areas of recharge delineated by the  $< -130$ ‰ isograd (Fig. 4) occur exclusively to the south and east of Long Valley at distances of up to 20 km from the hydrothermal discharge points. Much of this potential recharge area is arid and is down-gradient relative to current water levels for the shallow hydrothermal system (SOREY *et al.*, 1978).

In addition to variations attributed to differing geological source areas, temporal changes in meteorological conditions can also effect D and  $^{18}O$  recharge composition. Paleoclimatic data for the Great Basin area directly to the east of Long Valley indicate that slightly cooler climates existed 1.2–1.5 ka ago during the last pluvial period (BENSON, 1978). Groundwaters recharged during this period are depleted in  $\delta D$  by  $\sim 3$ – $5$ ‰ due to lower mean annual condensation temperatures (WHITE and CHUMA, 1987). The possibility exists that older waters, recharged at slightly cooler temperatures, also exist at depth in the central and eastern portions of Long Valley. Thermal reversals in well logs for this area indicate that cold water underlies the lateral thermal plume (SOREY, 1985) and therefore represents a potential source of mixing. In addition,  $^3H$  values for mixed waters in the eastern portion of the caldera are  $< 1$  TU indicating an older source of cold water relative to Whitmore Spring and other mixed waters to the west.

Unlike D and  $^{18}O$  compositions, the heavy  $\delta^{13}C$  contents of the hydrothermal fluids clearly indicate that dissolved C is not derived from meteoric recharge water in Long Valley (Fig. 5). This con-

clusion is also supported by analysis of fluids from the MBP-1 and MBP-3 wells which indicate that  $^{14}C$  in the total flow was  $< 1.2\%$  modern. This percentage corresponds to an apparent age of  $> 32$  ka, which is much older than the estimated fluid residence time in the Long Valley reservoir (1.2 ka, WHITE and PETERSON, 1990). This discrepancy implies that the C source is principally comprised of radiogenically dead C not related to recent recharge.

One potential C source in Long Valley is magmatic degassing of  $CO_2$ . Such a scenario is supported by a similarity between the range in  $\delta^{13}C$  for hydrothermal fluids and erupting volcanic systems ( $-3$  to  $-6$ ‰; TAYLOR and GERLACH, 1984). Based on seismic data and heat flow models, it has been postulated that one or more magma bodies have been recently injected at shallow depth (4.5 km) beneath Long Valley (SAVAGE *et al.*, 1987). NEWMAN *et al.* (1988) indicated that the parent rhyolitic magma in the recent Mono Craters system contained abundant  $CO_2$  (1 wt%), which during upward transport, degassed under closed-system conditions to form gas-rich bubbles. The remaining  $CO_2$  in the glass, erupted at the surface, is generally  $< 30$  ppm. Such extensive loss of C for a cooling magma body beneath Long Valley could therefore transfer significant  $CO_2$  to an overlying convecting hydrothermal system. The possibility of injection of mantle-derived  $CO_2$  is also supported by corresponding increases in the  $^3He/^4He$  ratio and decreases in  $He/CO_2$  over the central portion of Long Valley (WHELAN *et al.*, 1988) although seasonal changes in these parameters complicate this interpretation (HILTON and CRAIG, 1989). A secondary older magmatic source of C is also contained in the volcanic rocks in the caldera. Although the total C content of the Bishop Tuff is not known but is assumed to be low, extensive rock-water interaction could mobilize this component into the fluid phase. Presumably the  $\delta^{13}C$  of this C source would be indistinguishable from that of a modern magmatic input.

While such evidence indirectly indicates a possible

Table 4. Carbon isotopic compositions of Paleozoic metasediments surrounding the volcanic reservoir rocks of Long Valley. Geological controls from RHINEHART and ROSS (1964)

Unit	Rock	Age	$\delta^{13}\text{C}$ (‰)
Mount Baldwin Formation	Marble	Pennsylvanian	0.0
Buzztail Formation	Hornfels	Ordovician	-0.5
Mount Morrison Sandstone	Sandstone	Silurian-Ordovician	-0.9
Mount Aggie Formation	Hornfels	Ordovician	-1.2
Convict Lake Formation	Quartzite	Ordovician	-1.2
Lake Dorothy Hornfels	Hornfels	Pennsylvanian	-6.7
Undifferentiated metasediments	Limestone	—	-7.7
Bright Dot Formation	Quartzite	Pennsylvanian	-10.7
Undifferentiated metasediments	Limestone	—	-11.9

magmatic source of  $\text{CO}_2$  for reservoir fluids in Long Valley, it fails to consider the alternate explanation that much of the C was derived from pre-existing carbonate rocks. Ordovician through Permian metasedimentary rocks crop out to the northwest and southeast in areas immediately outside the ring fracture system which defines the structural boundaries of the Long Valley caldera (RHINEHART and ROSS, 1964). These same metasedimentary rocks have also been encountered during drilling at Casa Diablo and underlying the Bishop Tuff in the 44-16 hole. Although these rocks are dominated by quartz-rich hornfels, they contain subordinate amounts of marble and other carbonate-rich rocks. Recent data on  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of hydrothermal fluids (GOFF *et al.*, 1990) also suggest hydrothermal circulation through these rocks.

The  $\delta^{13}\text{C}$  values of carbonate-rich facies of these metasedimentary rocks collected from surface outcrops outside the boundaries of the Long Valley caldera are listed in Table 4. These data range from 0.0‰ for the Mount Baldwin Marble, a  $\delta^{13}\text{C}$  generally representative of marine carbonate rocks, to significantly lighter values approaching -12‰ for undifferentiated metasediments sampled immediately northwest of the Long Valley ring fracture system. Such variability in isotopic values denotes extensive fractionation associated with metamorphism caused by the intrusion of the Sierra Nevada Batholith. The range in these  $\delta^{13}\text{C}$  values, particularly for the more highly fractionated metasediments, is comparable to the  $\delta^{13}\text{C}$  composition of the hydrothermal fluids in the overlying volcanic rocks (Fig. 5). At temperatures near 200°C, the approximate temperature at the volcanic-metasediment interface encountered in the 44-16 well, the fractionation of  $^{13}\text{C}$  between calcite and  $\text{CO}_2$  is essentially zero, thereby supporting the similarity between fluid and carbonate rock isotopic ratios. The single analysis of calcite vein material in the metasediments at the bottom of the 44-16 hole had a  $\delta^{13}\text{C}$  value of -3.0‰ which is comparable to fluids and vein material found in the overlying volcanic reservoir rocks. The  $^{13}\text{C}$  isotope data do not conclusively prove that metasedimentary rocks are the principal source of C in the hydrothermal reservoir. However, the possibility of

hydrothermal interaction with C-containing sedimentary rocks seems more likely than with a deeper and as yet unproven cooling magma body.

### CONCLUSIONS

This paper describes the sources and the hydrological and geochemical processes that control the observed distributions of D,  $^{18}\text{O}$ , and  $^{13}\text{C}$  in Long Valley fluids. The extent of D and  $^{18}\text{O}$  variability in precipitation within the relatively small geographical confines of Long Valley is controlled by seasonal and topographic effects. The isotopic distribution can be explained by a simple point source model representing the intrusion of isotopically heavy precipitation through the embayment in the Sierran crest. Relative to typical precipitation on the leeward side of the Sierras, this precipitation is not as strongly fractionated by upslope conditions existing to the west of the mountains. The ranges in  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values are found to be comparable in both cold and hot waters within Long Valley but show less variability than seasonal precipitation variations. Due to higher precipitation rates and lower transpiration rates, only isotopically light winter and spring recharge occurs.

The isotopic compositions of the hot waters discharging from Long Valley can be described as two component isotopic and chemical mixtures involving 50–100% isotopically heavy hydrothermal fluid enriched in Cl and B and inversely proportional amounts of isotopically light dilute cold water. The source of recharge to the hydrothermal reservoir is uniquely defined by the regional distribution of  $\delta\text{D}$  values to lie within the Mammoth embayment. The source of the light cold water component is defined by the intersection of both isotopic and/or chemical-isotopic mixing lines. The resulting  $\delta\text{D}$  value is generally lighter than current precipitation or surface and groundwaters within Long Valley and may represent older deep groundwater.

The  $\delta^{13}\text{C}$  values of total C in hot waters in Long Valley are significantly heavier than for cold waters indicating a separate hydrothermal source. The range in  $\delta^{13}\text{C}$  values overlies that generally attributed

to magmatic degassing of CO<sub>2</sub>. However,  $\delta^{13}\text{C}$  data on carbonates from the metamorphosed Paleozoic basement also correspond to fluid  $\delta^{13}\text{C}$  values indicating that hydrothermal decarbonization reactions are likely. For  $^{13}\text{C}$  and  $^{18}\text{O}$ , isotopic equilibrium exists between fluids and calcite in the high temperature reservoir but not in hot spring discharge. Fractionation temperatures in the former case are compatible with current hydrothermal conditions.

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