CONF-8208109-Vol.2-7

CUARTO SIMPOSIO SOBRE EL CAMPO GEOTERMICO DE CERRO PRIETO BAJA CALIFORNIA, MEXICO

AGOSTO 10 - 12. 1982
GUADALAJARA, JAL.
Organizado por
Comisión Federal de Electricidad
en cooperación con el
United States Department of Energy,
Division of Geothermal Energy

ACTAS/PROCEEDINGS

VOLUMEN 2

Coordinadora Ejecutiva
de Cerro Prieto
Mexicali, Baja California
México

Earth Sciences Division,
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

CARBON-13 VARIATIONS IN FLUIDS FROM THE CERRO PRIETO GEOTHERMAL SYSTEM

C. J. Janik*, N. L. Nehring*, M. A. Huebner**, and A. H. Truesdell*
*U.S. Geological Survey, Menlo Park, California, U.S.A.
**U.S. Geological Survey, Denver, Colorado, U.S.A.

ABSTRACT

The carbon isotope compositions of CO_2 in steam from Cerro Prieto production wells have been measured for 1977, 1979, and 1982. Variations in the $\delta^{13}C$ values are caused by production-related changes in the chemical and physical parameters of the geothermal system. In 1977, most CO_2 in the reservoir was isotopically light ($\delta^{13}C = -6.4 \pm 0.4$). Heavier CO_2 was produced from wells in the center of the field (M5,M26,M27) due to deposition of isotopically light calcite caused by near-well boiling. In 1979 nearly all wells showed relatively heavy CO_2, probably due to expansion of aquifer boiling and calcite precipitation. In 1982, many wells in the central part of the field were shut in. The amount of drawndown decreased and as temperatures and pressures near the wells increased, the boiling zones collapsed. The CO_2 in the fluid then exchanged with the precipitated calcite and became isotopically lighter. The sensitivity of carbon isotopes to calcite precipitations caused by aquifer boiling and to reequilibration with this deposited calcite upon decrease of boiling suggests use as an indicator of these aquifer processes.

Surficial CO_2 of thermal origin was collected in 1981. Generally, the carbon-13 contents were close to CO_2 from production wells except for high-temperature mud pots and fumaroles containing isothopically light CO_2 derived from near surface alteration of organic matter.

INTRODUCTION

Carbon isotope studies have been included in several investigations of the Cerro Prieto geothermal field. Elders et al., (1977, 1978) used the carbon-13 compositions of calcite in sandstones and shales from well cuttings to provide information on fluid flow and to better understand the history of the hydrothermal system; Des Marais et al. (1981, and this symposium) used carbon isotope measurements to determine the major source for hydrocarbons in the Cerro Prieto reservoir; Crosby et al. (1972) and kakdisi et al., (this symposium) reported isotopic compositions of dissolved carbon species in studies of Mexicali Valley groundwaters; and Truesdell et al., reported limited data for carbon-13 in CO_2 of the thermal fluids. This study presents extensive measurements of carbon isotope compositions of CO_2 from Cerro Prieto production wells and surface manifestations collected over a period of six years. This data is compared with earlier published data in an attemp to show relationship between the various carbon species in the system.

The $^{12}C/^{13}C$ ratio in CO_2 may be used to determine the origin of CO_2 in a geothermal fluid (Craig, 1963) and to monitor reactions involving carbon species in a hydrothermal system (Ohmoto and Rye, 1979). Physical changes in the Cerro Prieto geothermal reservoir induced by steam production affect the compositions of gases in the system (Nehring and Valette-Silver, this symposium). These changes should be reflected by variations in the carbon-13 composition of the CO_2. Carbon in CO_2 from surface emanations should differ from that of reservoir CO_2 due to exchange reactions with carbon contained in rock and groundwater at lower temperatures.

SAMPLE COLLECTION AND ANALYSES

Steam samples were collected in April-May, 1977, Jan-Feb. and May, 1979, and Jan. 1982, Steam from the central steam outlet tube of production separators was cooled in a stainless steel condenser, and the total flow (gas and condensate) was collected in evacuated 300ml Pyrex bottles containing 100ml of 4N NaOH (Nehring and Truesdell, 1978). Spring samples were collected in June-July, 1981, by Nehring and Vallette-Silver (this symposium). Gas was trapped in a partially submerged inverted funnel and collected throuhg Tygon tubing into the same type of gas collection bottle used for steam sampling.

With this collection method, virtually all the CO_2 in the samples is dissolved in the NaOH solution. A 10ml aliquot of this solution is acidified with 4N HCL to pH 9-10 and precipitated as $SrCO_3$ by adding an excess of $SrCl_2$-saturated NH_4OH. The acification minimizes coprecipitation of hydroxides. The $SrCO_3$ precipitate (containing some strontium hydroxide, borate and silicate) is

DISCLAIMER

Table 1. Carbon-13 contents and mole fractions of CO_2 in reservoir fluid from Cerro Prieto production wells. Mole fractions of CO_2 were calculated using data from gas analyses by N. L. Nehring.

Well	1977		1979		1982	
	$\delta^{13}C$	CO_2 mole-frac. $x10^3$	$\delta^{13}C$	CO_2 mole-frac. $x10^3$	$\delta^{13}C$	CO_2 mole-frac. $x10^3$
M-5	-5.2	0.97*	-5.4	1.59	-5.5	1.50
M-8+M46			-5.1	1.80		
M-11	-6.8	1.14	-5.1	1.04	-5.7	1.07
M-14	-6.4	1.49	-5.3	1.51	-5.2	0.31*
M-19A	-6.4	1.43	-5.4	1.15	-5.8	1.36
M-21A			-4.9	1.51		
M-25	-5.8	1.57			-6.1	1.58
M-26	-5.1	1.05*	-5.9	1.17	-5.3	1.39
M-27	-5.4	3.20	-5.1	1.95		
M-29	-6.0	0.87	-5.6	0.91	-5.6	1.30
M-30	-6.9	1.09			-5.7	1.07
M-31	-6.2	1.70	-5.0	1.41	-5.6	1.88
M-35			-5.4	1.01	-6.2	0.86
M-42	-6.8	1.11	-5.7	1.16	-5.6	1.18
M-45			-5.2	2.37		
M-48			-5.9	1.11	-6.7	0.91*
M-50			-5.5	2.15	-5.5	1.33
M-51			-5.3	1.67	-5.3	2.10
M-53**			-6.2	2.19	-5.3	1.87
M-84**			-5.0	2.12	-5.6	3.65
M-90			-5.3	1.47	-5.7	1.06
M-91			-5.5	1.20	-5.4	0.97
M-101					-5.6	1.19
M-102**					-5.1	0.76*
M-103**			-5.3	1.21		
M-104**					-5.3	0.63*
M-105			-5.2	1.47	-5.4	1.69
M-114			-6.5	0.82	-5.6	0.81
M-130			-5.1	1.19	-5.5	1.67
E-2**					-6.3	1.35
E-4**					-6.0	1.98

* Samples have unusually low gas/steam ratio.
** Deep wells which draw fluid from the β aquifer.

Table 2. Carbon-13 in CO_2 (gas) from surface expressions of the Cerro Prieto geothermal system. Descriptions were provided by N. L. Nehring and J.N. Valette-Silver (this symposium).

Location	Description	$\delta^{13}C$
N-3	Cold spring in canal	- 4.2
N-5	20°C pool, acid altered area	- 4.2
N-7	30°C pool, depositing pyrite	- 4.5
N-18	Cold pool, depositing S or FeS_2	- 4.6
N-20	80°C pool, depositing pyrite	- 5.5
N-31*	100°C fumarole in canal	-14.5
N-36	100°C mudpot, depositing pyrite	- 9.2
N-43	90°C spring in marsh	- 8.3
Near N-46	Spring near edge of Laguna Volcano	- 7.4
N-50	Cold pool	- 6.1
N-61	Cold spring in canal	- 6.1

* Collected in Jan. 1978. All other samples were collected in June-July 1981.

filtered on cellulose acetate membrane filter paper, washed, vacumm dried, and sieved to assure isotopic uniformity. CO_2 is then liberated from the $SrCO_3$ with orthophosphoric acid (McCrea, 1950) and analyzed for carbon isotopes in a double collecting mass spectrometer. $\delta^{13}C$ values are reported in permil relative to PDB and are accurate to ± 0.2. The results of the analyses are presented in tables 1 and 2.

ORIGIN OF CO_2

Possibly sources of CO_2 in the Cerro Prieto geothermal system include (1) oxidation of reduced carbon (methane, coal and other organic matter contained in sedimentary rocks and recharge water), (2) decarbonation reactions involving the destruction of calcite to form calc-silicate minerals, (3) dissolution reactions in which calcite is leached from the sedimentary rocks in the aquifer, (4) upflow of primary CO_2 from a deep magmatic source, and (5) introduction of atmospheric CO_2 dissolved in groundwater recharge. Carbon of different $\delta^{13}C$ values may be contributed by each of these sources.

Figure 1 compares carbon isotope compositions of CO_2 from Cerro Prieto production wells and surface features with available data for carbon-13 in other carbon components of the Cerro Prieto geothermal system. The $\delta^{13}C$ ranges of carbon-bearing materials reported by Craig (1963), Taylor et al. (1967), and Ohmoto and Rye (1979) are also shown. The range of carbon-13 in CO_2 from Cerro Prieto wells ($\delta^{13}C = -4.9$ to -6.9) could indicate a magmatic origin but more likely results from a mixture of CO_2 derived from decarbonation of detrital marine carbonates and from oxidation of organic carbon, both plentiful in the Cerro Prieto reservoir rock.

At high-temperature reservoir conditions, decarbonation reactions produce CO_2 which is enriched in $\delta^{13}C$, and dissolution reactions produce CO_2 which is isotopically similar to the parent calcite (Ohmoto and Rye, 1979). If equilibrium is maintained between CO_2 and calcite, the carbon-13 content is greater in CO_2 by approximately +0.3 to + 2.7 per mil at temperatures from 200 to 400°C. At temperatures less than

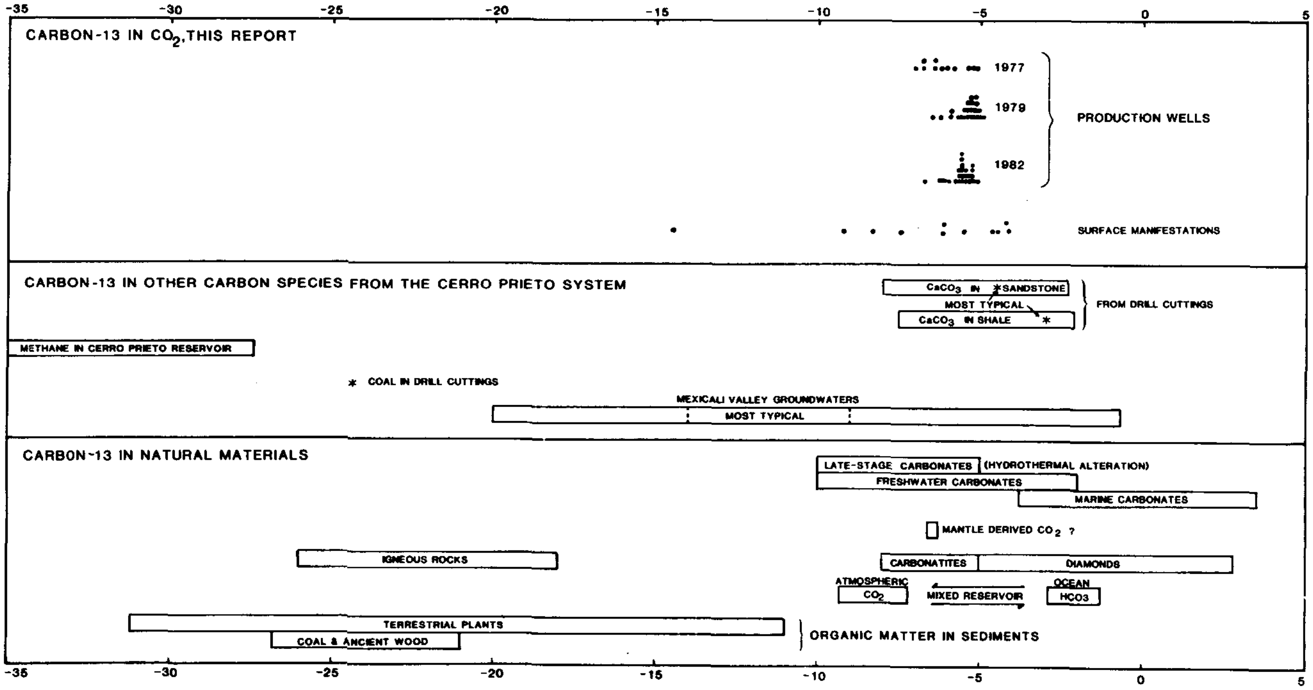

Figure 1. Carbon-13 contents of CO_2 from Cerro Prieto wells and surface manifestations compared with carbon isotope data for other carbon species in the Cerro Prieto geothermal system and with compositions of possible source materials. Carbon isotope data for carbon species in the Cerro Prieto system (other than CO_2) are from Des Marais et al., 1981, and this symposium; Makdisi et al., this symposium; and Elders et al., 1977, 1978. $\delta^{13}C$ ranges for carbon-bearing materials are from Craig, 1963; Taylor et al., 1967; and Ohmoto and Rye, 1979.

192°C, the CO_2 is isotopically lighter in carbon relatively to the calcite (Bottinga, 1968). Larger fractionation factors are observed between CO_2 and CH_4. In addition, $\delta^{13}C$ values of CO_2 in fluids increase with decreasing oxygen fugacity and decreasing CO_2/CH_4 ratios (Ohmoto and Rye, 1979).

Carbon-13 in CO_2 from surface manifestations range from $\delta^{13}C = -4.2$ to -14.5. This suggests that reservoir CO_2 is isotopically modified by addition of light CO_2 from organic matter and by exchange with detrital carbonate. CO_2 in acid surface springs may be heavier than deep CO_2 because of assition of CO_2 from complete dissolution of detrital and cementing carbonates ($\delta^{13}C$ 0). The isotopically light carbon may represent a contribution of CO_2 from near-surface oxidation of carbon in organic-rich sediments (and possibly in groundwaters) to light hydrocarbons (Des Marais et al., 1981; Nehring and Valette-Silver, this symposium).

TEMPORAL AND SPATIAL VARIATIONS

Figures 1 and 2 show that the carbon-13 content of CO_2 in the thermal fluid has clearly changed between 1977 and 1982. For 1977 well samples, the mean value is $\delta^{13}C = -6.1 \pm 0.6$ with 55 percent of the samples having values from -6.2 to -6.9. Samples from 1979 contain heavier carbon with an average $\delta^{13}C = -5.4 \pm 0.4$, and 54 percent of these values ranging from -4.9 to -5.3. The CO_2 appears to be returning to a lighter composition in 1982, having an average $\delta^{13}C = -5.6 \pm 0.4$ with only 42 percent of the samples containing heavier carbon.

Figure 2 shows that the major fraction of CO_2 in the reservoir has not significantly changed with time. The values cluster between 0.75 to 2.25 ($x10^{-3}$), and averages are $1.42 \pm .44$ and $1.36 \pm .64$ for 1977, 1979, and 1982, respectively. Therefore, changes in the isotopic composition of CO_2 in the reservoir cannot be due to changes in the total CO_2 content of the thermal fluid. Although average CO_2 concentrations were essentially constant, there is a positive correlation between CO_2 concentrations and $\delta^{13}C$ values for each year's samples (Fig. 2). Steam from new wells and steam with very low gas/steam ratios are exception to this trend (Table 1).

In 1977, the CO_2 was isotopically heavier near the center of the field and was progressively lighter towards the northwest and southwest (Fig. 3). Steam from wells M5, M26, and M27 was more than 1 permil heavier in carbon than the average value (-6.4) for CO_2 from the remaining wells. This average value may represent the carbon isotope composition of the CO_2 in the reservoir fluid during the early stages of production. Wells M-11, M-14, and M-42 are outside the area most affected by drawndown as observed by Truesdell et al., (1979b). In addition, enthalpy and silica data for these wells indicate that they were not affected by near-well boiling in 1977 (Grant et al., 1981). The $\delta^{13}C$ value for CO_2 from M-11 (-6.8) may be most representative of reservoir CO_2 in the natural state, prior to production. This well was producing at low-flow conditions relative to the other wells and had an average gas to steam ratio for wells in 1977 (Nehring and D'Amore, 1981).

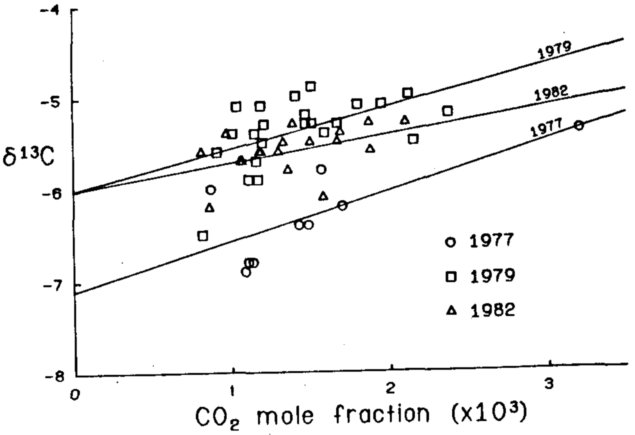

Fig. 2 $\delta^{13}C$ in CO_2 from production wells versus the mole-fraction of CO_2 in the reservoir fluid for 1977, 1979 and 1982. A linear regression of each data set is also shown. Data is from table 1. Samples from deep wells and samples with low gas/steam ratios are not included.

$\delta^{13}C$ en el CO_2 de pozos productores versus la fracción de mol CO_2 en el flúido del yacimiento para 1977, 1979 y 1982. También se muestra una regresión lineal de cada conjunto de datos, los cuales provienen del Cuadro 1. No se incluyen muestras de pozos profundos ni muestras con razones gas/vapor bajas.

The carbon-13 contents of CO_2 from the three central wells strongly indicate that physical and chemical processes associated with the production can affect the isotopic composition of reservoir CO_2. The $\delta^{13}C$ enrichment of CO_2 from wells M-5, M-26 and M-27 appear to be related to local boiling effects in the reservoir. Grant et al. (1981) suggested that decreasing pressures and temperatures associated with fluid withdrawal cause an enthalpy rise in the fluid near the well due to heat transfer from the rock. This result in increased boiling accompanied by a transfer of most gases to the steam phase and a concentration of salts in the liquid phase. Decreasing CO_2 pressure in the liquid causes precipitation of calcite near the well by the reaction:

$$Ca^{++} + 2HCO_3^- = CaCO_3 + CO_2 + H_2O.$$

The CO_2 from this reaction enters the vapor phase produced by boiling. Therefore, the initial CO_2 in the steam should have a carbon-13 compositions near the expected value for CO_2 in the reservoir (-6.4 to -6.8), but with degassing of the fluid and a greater contribution of CO_2 from precipitation of isotopically ligher calcite neat the well, the values should become more positive.

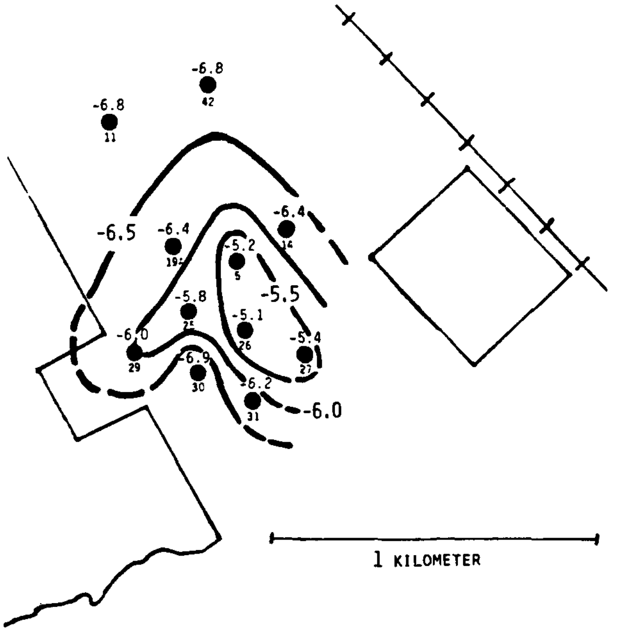

Fig.3. $\delta^{13}C$ distribution pattern for CO_2 for production wells, 1977.
Patrōn de distribuciōn del $\delta^{13}C$ para el CO_2 de pozos productores, 1977.

The distribution of $\delta^{13}C$ values in 1979 shows very little field-wide variation in the carbon-13 contents of CO_2 (Fig. 4). The isotopically heavy CO_2 observed for only three wells in 1977 is now funded in most wells in production. Analyses of carbon-13 in CO_2 from wells in the same region sampled in 1977 ($\delta^{13}C$ = -5.3 ± 0.3) indicate that effects due to fluid withdrawal and boiling are more widespread. Well M-21A, having the heaviest value, is an extreme case of production-related change in the isotopic composition of CO_2 in the reservoir fluid. Only wells M-114 and M-53, located far north of the main production zone, have lighter values associated with an indisturbed reservoir. Both are new wells. Gas chemistry (Nehring and Valette-Silver, this symposium), physical data (CFE), and geologic evidence (Lyons and Van de Kamp, 1979) suggest fluid communication between M-48 and M-84. Therefore, an average value for $\delta^{13}C$ in CO_2 from these wells is used in figure 4.

In 1982, several wells in the central part of the field were taken out of production in an attempt to retard the enthalpy and flow decreases caused by overproduction of the reservoir. The shutting-in of these wells may be causing a change in the carbon-13 content of the thermal fluid.

The $\delta^{13}C$ values do not vary widely in 1982, but most wells have the same or lighter values than they did in 1979 (Fig. 5). A contour reversal is developing with the lightest values in the center and the heaviest values toward the margins of the field, possibly caused by solution of calcite from former zones of near-well boiling. As in 1979, an average composition is used for wells M-48 and M-84. The new two deep wells, E-2 and E-4, are not considered in determining the contours. Production of these wells

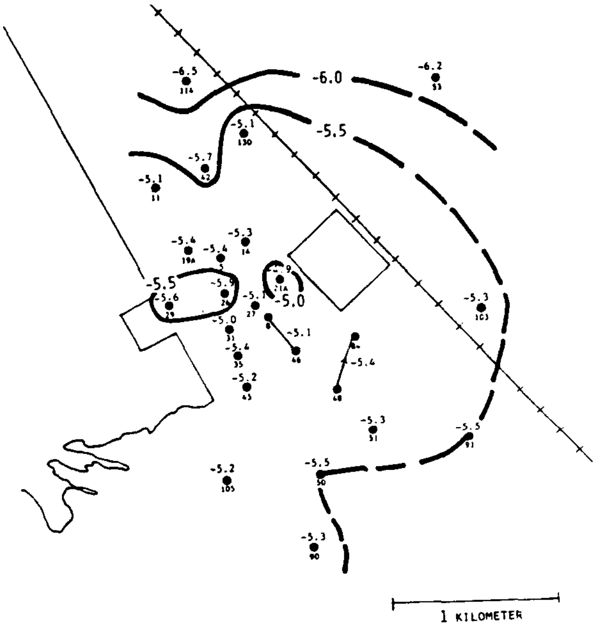

Fig.4. $\delta^{13}C$ distribution pattern for CO_2 for production wells, 1979.
Patrōn de distribuciōn del $\delta^{13}C$ para el CO_2 de pozos productores, 1979.

began in mid to late 1981. Both have high steam fractions and high enthalpy associated with boiling near the well bottom. The $\delta^{13}C$ values for these wells may represent the transition from the ligther composition of CO_2 in the indisturbed reservoir to the heavier isotopic composition caused by degassing of fluids and calcite precipitation near the well. M-53, M-102, and M-104, which also tap the deeper aquifer, have been producing for 2 to 4 years and have more positive values similar to those observed near the center of the field in 1979.

Figure 6 shows the distribution of $\delta^{13}C$ for CO_2 from surface features in the geothermal system. CO_2 from cold pools and warm springs to the northwest is isotopically heavier with increasing distance from the production wells. The carbon-13 contents of CO_2 from these springs and pools are greater than for deep reservoir CO_2. Similar features southwest of the production field have CO_2 which is isotopically similar to or lighter than CO_2 from deep wells. In general, there appears to be a negative correlation between the temperature of the feature and the $\delta^{13}C$ value (see table 2). The highest temperature features, N-36 and N-31, have the lightest $\delta^{13}C$ values. Gases from these features also contain large amounts of higher hydrocarbons (Nehring and Valette-Silver, this symposium) suggesting that the isotopically light CO_2 is produced by alteration of organic matter probably near the surface.

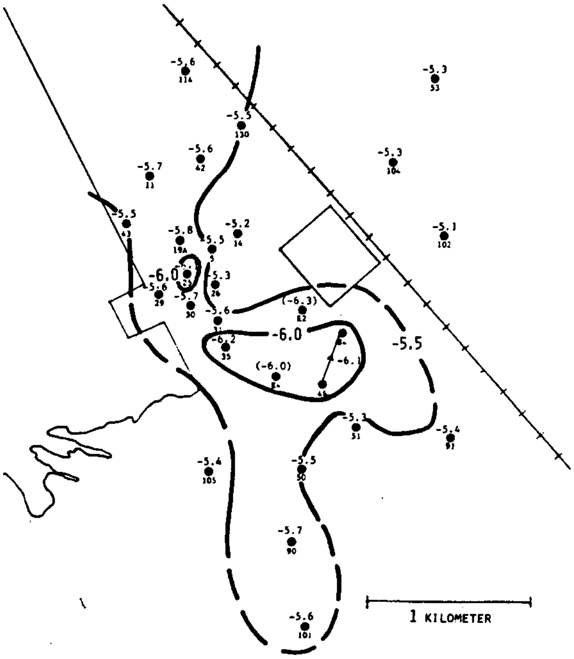

Fig.5. $\delta^{13}C$ distribution pattern for CO_2 for production wells, 1982.
Patrón de distribución del $\delta^{13}C$ para el CO_2 de pozos productores, 1982.

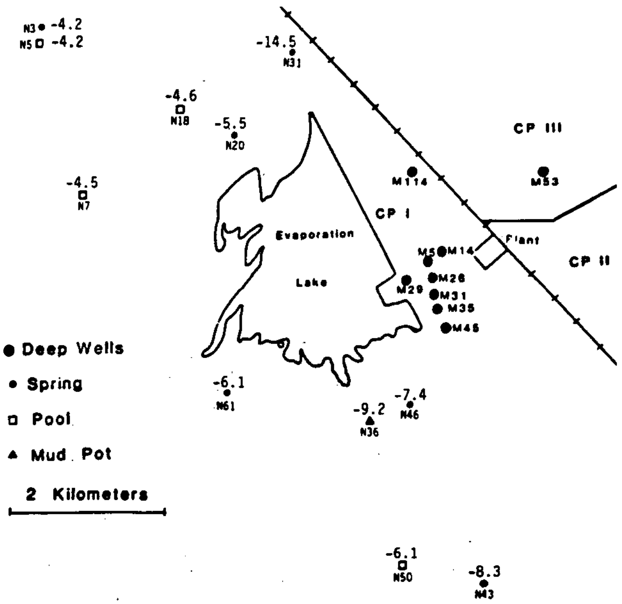

Fig. 6 Location map of surface manifestations in the Cerro Prieto geothermal system and $\delta^{13}C$ values for CO_2 from 1981 collection. Mapa de ubicación de las manifestaciones superficiales en el sistema geotérmico de Cerro Prieto y valores de $\delta^{13}C$ para el CO_2 de la recolección de 1981.

SUMMARY

The carbon-13 content of CO_2 from producing wells at Cerro Prieto has shown changes with time and location in the field that indicate the deposition of calcite in near-well boiling zones and later re-solution. The source of the carbon may be magmatic but is probably of mixed sedimentary origin with CO_2 from some surface features heavily influenced by decomposition of organic matter.

ACKNOWLEDGMENTS

We thank our colleagues at the Comisión Federal de Electricidad for facilitating the sample collections and for providing physical data. We also thank D. DesMararais for helpful comments, A. Cook for drafting figure 1, and P. Bennett and G. Fong for help in producing the paper.

REFERENCES

Bottinga, Y., 1968, Calculation of fractionation factors for carbon and oxygen exchange in the system calcite carbon-dioxide-water, J. Phys. Chem.,

v. 72, p. 800-808.

Craig, H., 1963, The isotopic geochemistry of water and carbon in geothermal areas, in Tongiorgi, E., ed., Nuclear geology on geothermal areas Spoleto, 1963: Consiglio Nazionale delle Ricerche, Laboratorie di Geologia Nucleare, Pisa, p. 17-54.

Crisby, J.W. III, Chatters, R.M., Anderson, J. V., and Fenton, R.L., 1972, Hydrologic evaluation of the Cerro Prieto goethermal system utilizing isotope techniques: Washington State University, College of Engineering Research 72/11-5, 30 p.

DesMarais, D.J., Donchin, J.H., Nehring, N.L., and Truesdell A.H., 1981, Molecular carbon isotopic evidence for the origin of geothermal hydrocarbons: Nature, v. 22, p. 826-828.

DesMarais, D.J., Stallard, M.L., Nehring N.L., Truesdell, A.H., 1982, Hydrocarbon production the Cerro Prieto geothermal field, this symposium.

Elders, W.A., Olson E.R., Hoagland, J.R., Barker, C.E., Johnson, P.D., and Collier, P., 1977. A comprehensive study of samples from geothermal reservoirs: Petrology and light stable isotope geochemistry of wells M-48, M-84, M-90, M-91, M-92, and Prian-1 in the Cerro Prieto geothermal field, Baja California, México: Univ. Calif. Riverside report UCR/IGPP-77/37, 153p.

Elders, W.A., Hoagland, J.R., Olson E.R., McDowell, S.D., and Collier, P., 1978, A comprehensive study of samples from geothermal reservoirs: Petrology and light stable isotope geochemistry of twenty-three wells in the Cerro Prieto geothermal field Baja California, México: Final report to the Dept. of Energy/ Lawrence Berkeley Laboratory, 264 p.

Grant, M.A., Truesdell, A.H., and Mañón, M.A., 1981, Production induced boiling and cold water entry in the Cerro Prieto Geothermal Reservoir indicated by chemical and physical measurements, in Proc., 3rd. Symp. on the Cerro Prieto Geothermal Field, Baja California, México: Report LBL-11967, p. 221-247.

Lyons, D.J., and Van de Kamp, P.C., 1979, Subsurface geological and geophysical study of the Cerro Prieto geothermal field, in Proc., 2nd. Symp. on the Cerro Prieto Geothermal Field, Baja California, México, p. 173-195.

Makdisi, R.M., Truesdell, A.H., Coplen, T.B., Thompson, J.M., and Sánchez, R.J., Geochemical evolution of Mexicali Valley groundwaters, this symposium.

McCrea, J.M., 1950, On the isotopic chemistry of carbonates and a paleotemperature scale, J. Chem. Phys., v. 18, no. 6, p. 849-857.

Nehring, N.L., and D'Amore, F., 1981, Gas Chemistry and thermometry of the Cerro Prieto goethermal field: Proc. 3rd. symposium on the Cerro Prieto Geothermal Field Baja Calif., México LBL Report 11967, p. 178-184.

Nehring, N.L., and Truesdell, A.H., 1978, Collection of chemical, isotope and gas samples from geothermal wells, in Proc., 2nd., Workshop on Sampling Geothermal Efficients, Las Vegas, Nevada, Feb. 1977: Enviromental Protection Agency Report EPA-600/7-78 121, p. 130-140.

Nehring, N.L., and Valette, J.N., 1982 Gas reactions in the Cerro Prieto reservoir, this symposium.

Truesdell, A.H., Rye, R.O., Pearson, F.J., Olson E.R., Nehring, N.L., Whelan, J.F., Huebner, M.A., and Coplen, T.B., 1979, Preliminary isotopic studies of fluids from the Cerro Prieto Geothermal Field: Geothermics, v. 8, p. 223-229.

Truesdell, A.H., Mañón, M.A., Jiménez S., M., E., Sánchez, A., A., and Fausto L., J.L., 1979b, Geochemical evidence of drawdown in the Cerro Prieto geothermal field: Geothermics,v. 8 p. 257-265.

Ohmoto, H., and Rye, R.O., 1979, Isotopes of sulfur and carbon, in Barnes, H.L., ed., Geochemistry of hydrothermal are deposits: New York, Wiley and Sons, p. 509-567.

Taylor, H.P., Jr., Frechen, J., and Degens, E. T., 1967, Oxygen and carbon isotope studies of carbonatites, Leacher See District, West Germany and the Alno District Sweden: Geochim. et al., Cosmochim. Acta, v. 31 p., 407-430.