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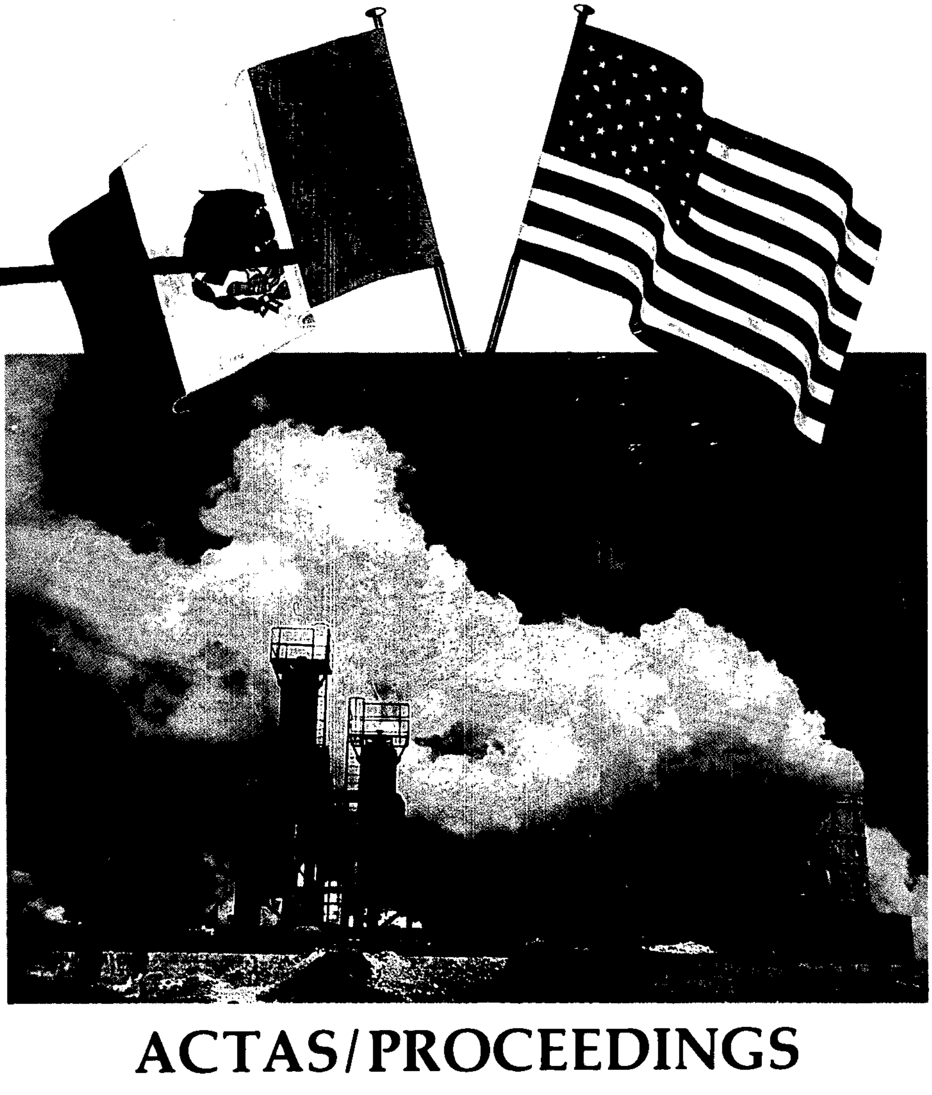

ACTAS/PROCEEDINGS

VOLUMEN 2

Coordinadora Ejecutiva
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GAS REACTION IN THE CERRO PRIETO RESERVOIR

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Abst ~~INTRODUCTION~~

Gases in an undisturbed geothermal reservoir should be in equilibrium with the surrounding rock and water. Production of fluid at rapid rates may cause physical changes in the reservoir that are reflected as changes in gas composition. At Cerro Prieto production has lowered the reservoir pressure enough in places to induce boiling in the aquifer, leading to high enthalpy, low production and eventual drawndown of cold water into the reservoir. These changes are reflected in gas compositions.

Differences in gas composition between well and surface samples reflect changing equilibrium in temperature-dependent chemical reactions and a mixture of gases dissolved in groundwater.

COLLECTION AND ANALYSIS OF GASES

Steam samples were collected for gas analyses in April-May 1977 and January 1982. Steam was tapped from the central steam outlets of production separators, cooled to near 30°C through a stainless steel condensing coil, and collected in evacuated 300-mL bottles containing 100mL of 4N NaOH (Nerhing and Truesdell, 1978). Total flow from the condenser (gas and condensate) was collected in sample bottles.

Gas samples from surface features were collected in June-July 1981. Gas was trapped in an inverted funnel and collected in a bottle identical to that used for steam samples.

Analyses for major gases were made by wet chemistry (H_2O, CO_2, and H_2S), specific ion electrode (NH_3), and gas chromatography (He, H_2, CH_4, Ar, O_2, and N_2). Gas compositions of the 1977 (well) samples were presented by Nehring and D'Amore (1982). Compositions for 1981 (surface features) and 1982 (well) samples are shown in Tables 1 and 2.

CHANGES IN GAS COMPOSITIONS FROM WELLS BETWEEN 1977 AND 1982.

Comparasion of gas compositions from production wells between 1977 and 1982 show changes which can be explained by physical processes ocurring in the reservoir such as boiling of the reservoir fluid and drawndown of cold water into the reservoir. The mole fraction of gas in the reservoir in 1977 (Fig. 1) shows the effects of boiling in the reservoir. Wells M-20, M-21A, M-27, M-8, and M-35 have high total gas contents owing to boiling near the well bottoms. This boiling was first observed by Truesdell et al. (1979) as excess enthalpy in the well fluid. Boiling causes bicarbonate (HCO_3) to disproportionate into CO_2 and

Table 1. Gas compositions (molar) Cerro Prieto surface features. All samples collected June-July 1981 except N-31 collected January 1978. ND= not determined.
Composición del gas (en moles) de las manifestaciones superficiales de Cerro Prieto. Todas las muestras se recolectaron en junio-julio de 1981, a excepción del N-31 que se recolectó en enero de 1978. ND=no se determinó

Location	Description	CO_2	H_2S	NH_3	He	H_2	Ar	O_2	N_2	CH_4
N-3	Cold spring in canal	97.2	0.84	0.0066	0.00012	0.0028	0.025	0	0.80	1.07
N-5	20°C pool	94.3	2.02	0.023	0.00022	0.0018	0.041	0	1.39	2.19
N-7	30° pool	97.8	1.03	0.0078	0.000037	0.0042	0.0059	0	0.17	1.01
N-18	Large cold pool	88.4	0.22	0.034	0.0019	0.00071	0.056	0	2.18	8.82
N-20	60°-80° C pool	79.9	0.99	0.065	0.00064	1.87	ND	0	2.42	14.8
N-31	100°C fumarole along canal	80.7	1.25	12.5	0	3.61	0.046	0	1.97	0.23
N-36	Small 100°C pool	83.0	3.54	1.83	0.00036	0.66	0.13	0	5.81	4.73
N-43	90°C spring in marshy pool (southernmost feature)	88.1	1.40	0.083	0	1.88	0.094	0	2.78	5.52
N-46	Spring near edge of Lagana Volcano lake	77.1	2.78	0.090	0.00061	1.73	0.15	0.53	8.88	8.11
N-49	Large cold pool	63.6	1.06	0.075	0	0.00039	(O_2)	3.98	22.6	6.51
N-50	Large cold pool	80.8	2.21	0.058	0.0015	0.028	0.12	0	4.64	11.7
N-61	Cold spring in canal	91.8	0	0.085	0	0.012	(O_2)	0.80	2.58	4.25

DISCLAIMER

Table 2. Gas compositions (molar) of 1982 Cerro Prieto production fluids.
Composición del gas (en moles) de los flúidos de producción en Cerro Prieto en 1982. No se detectó O_2

Well	Steam fraction	Gas/ Steam $x10^3$	CO_2	H_2S	NH_3	He	H_2	Ar	N_2	CH_4
M-5	0.303	5.79	85.64	4.87	1.60	0.00046	3.14	0.013	0.54	4.23
M-11	.280	4.52	84.87	5.79	1.83	.00063	2.09	.028	1.60	3.79
M-14	.215	1.72	85.15	3.63	.62	.00016	6.54	.011	.47	4.00
M-19A	.283	5.65	85.35	5.39	1.57	.00047	3.20	.014	.57	4.04
M-25	.335	5.54	85.04	5.69	1.55	.00012	3.15	.014	.55	4.11
M-26	.273	6.02	84.42	6.69	1.55	.00022	2.66	.016	.62	4.01
M-29	.211	7.09	86.73	4.53	1.59	.00044	2.88	.014	.57	3.80
M-30	.269	4.72	84.49	5.57	1.94	.00049	3.85	.018	.66	3.68
M-31	.377	6.05	82.43	5.81	1.51	.00031	4.58	.019	.73	5.10
M-35	.280	3.73	82.33	5.26	1.70	0	4.11	.024	.95	5.68
M-42	.224	6.12	86.33	4.51	2.36	.00061	1.80	.015	.60	4.29
M-43	.228	4.90	85.48	5.88	1.99	.00080	2.14	.016	.67	3.85
M-48	.372	2.94	83.00	5.56	2.49	0	5.47	.021	.78	3.82
M-50	.303	5.24	83.86	5.57	1.73	.00026	3.80	.020	.74	4.31
M-51	.411	6.05	84.41	5.43	1.47	.00025	4.40	.016	.64	3.72
M-53	.325	6.77	84.93	5.12	1.43	.00025	4.71	.0085	.37	3.49
M-84	.708	6.36	80.99	5.58	1.21	0	10.34	.0087	.38	2.48
M-90	.264	4.82	83.45	5.07	1.64	.00029	3.41	.028	1.06	5.30
M-91	.309	3.82	82.10	7.34	2.35	.00086	3.81	.023	.96	3.56
M-101	.313	4.72	80.79	8.14	2.44	.00058	2.75	.018	.75	5.18
M-102	.759	1.17	85.55	4.23	1.98	0	5.18	.0032	.17	3.22
M-104	.558	1.35	83.61	4.10	1.05	0	7.16	.0052	.24	4.19
M-105	.420	4.85	82.75	5.92	1.88	.00083	5.22	.019	.79	3.69
M-114	.215	4.48	84.07	6.32	1.75	.0011	1.62	.019	.81	5.36
M-130	.296	6.68	84.25	5.38	2.44	.00024	3.68	.011	.45	3.95
E-2	.397	4.02	84.34	6.93	2.17	.00040	3.87	.012	.49	2.52
E-4	.511	4.82	80.34	6.57	1.14	0	9.11	.022	1.12	2.60

No O_2 was detected.

carbonate (CO_3^{2-}). This causes the amount of CO_2 being released into the steam phase to increase and, since CO_2 is the major gas, the total gas content increases. A second, smaller boiling zone may be present around M-19A and M-25.

No very high gas contents (>$2.0x10^{-3}$ mole fraction on Fig. 1) were found in 1982. Wells M-20, M-21A, and M-27 were shut in at the time collections were made because of low enthalpies and low production. Despite a lack of data from these wells, expansion of the boiling zone observed in 1977 apparently has been halted and, at least near M-31 and M-35, may have receded. A small boiling zone may still be centered around M-25.

In two instances, pairs of neighboring wells show an unusually low gas content in one well and unusually high content in the other (M-48 and M-84, M-35 and M-31). It appears steam formed near the well with low gas content is being discharged by the neihboring well. Enthalpy measurements support this hypothesis.

The amount of N_2 in the reservoir has substancially increased between 1977 and 1982 (Fig. 2). This increase in N_2 (1982 contours) correlates well with the decrease in aquifer chloride observed in 1977 (Fig.3). Truesdell et al. (1979) proposed that the decrease in chloride was due to drawndown of cold water into the reservoir. One would expect an increase in N_2 and Ar in the reservoir because the solubilities of these gases are greater in cold water than in hot water. Oxygen would react with H_2S and be removed. All of these changes were observed.

RELATIONSHIP OF SURFACE FEATURES AND WELLS

Mercado (1975) presented temperature distributions for the Cerro Prieto field. These data showed temperature contours rising from the northeast toward the southwest. Cold water from the Sierra Cucapâh intrudes from the west at a depth of about 1,000m. Thermal water reaches

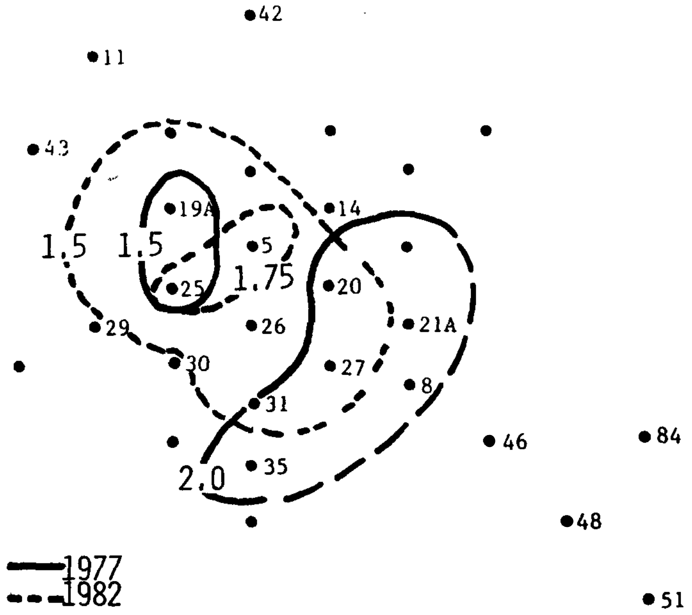


Fig. 1. Mole fraction gas (x10^3) in reservoir (CPI)
Gas en fracción de mol (x10^3) en el yacimiento (CPI).

the surface northwest and southwest of the geothermal field and is expressed as hot pools, mud pots, etc. (Fig. 4).

Chemically, the gas composition of surface features should be related to gas composition of wells. Differences should be caused by reactions with groundwaters and reequilibration to lower temperatures. A triangular plot of three major gases, CO_2, H_2S, and N_2 (Fig. 5), shows that surface features have lost H_2S and gained N_2 relative to the wells. Loss of H_2S is greater in surface features northwest of the production field than in those features to the southwest. H_2S is lost by a combination of two processes reaction with metal oxides and silicates to form metal sulfides (particularly pyrite) or reaction with oxygen in air or air dissolved in water to form sulfates. The first process appears to be dominant at Cerro Prieto.

Nitrogen content is greater in the southern surface features than in the northern ones. In addition, the nitrogen content decreases away from the production field within each group. This is because of a greater percentage of cold, Colorado River water in the surface features nearest the field.

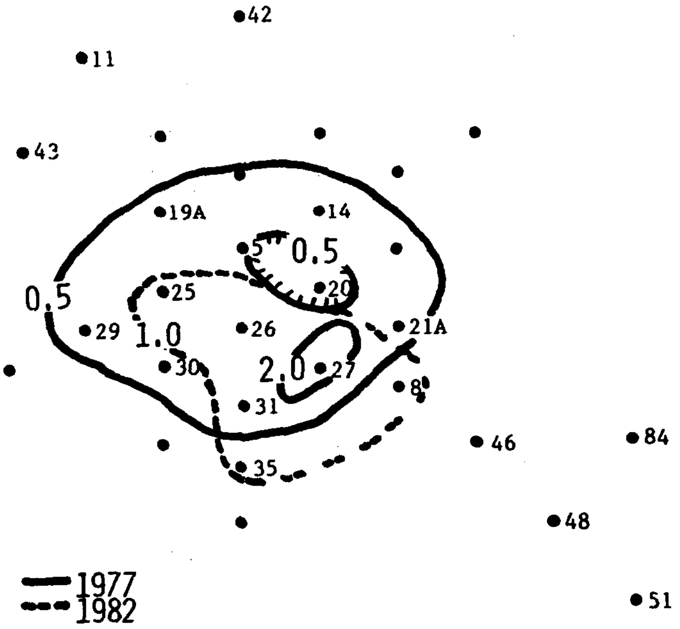


Fig. 2. Mole fraction N_2 in reservoir (CPI)
N_2 en fracción de mol en el yacimiento (CPI).

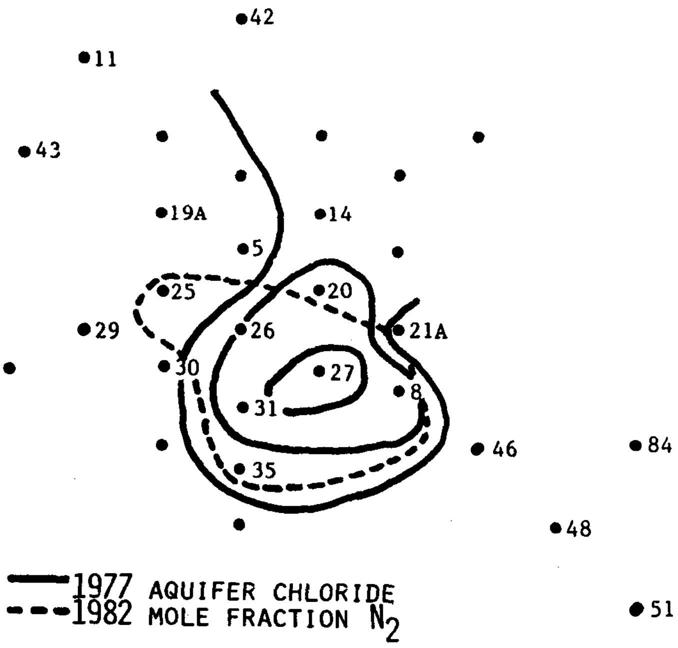


Fig. 3. Comparison between aquifer chloride and mole fraction N_2 in reservoir (CPI)
Comparación entre los cloruros del acuífero y el N_2 en fracción de mol en el yacimiento (CPI).

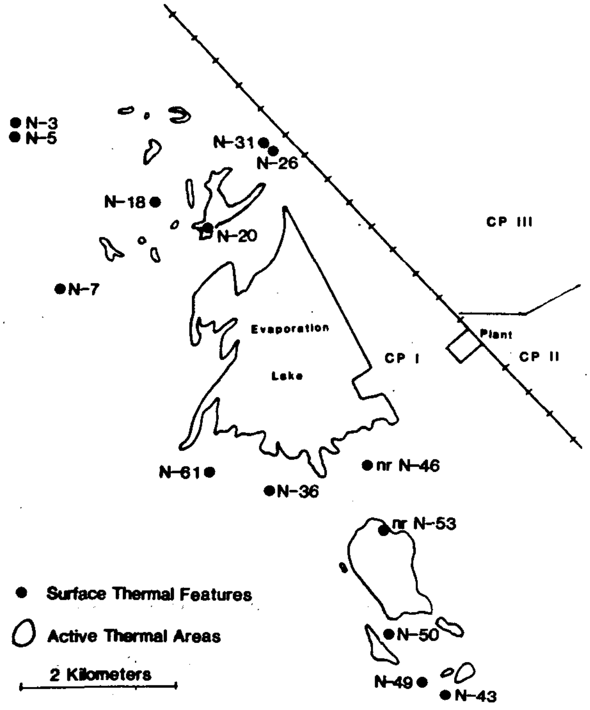


Fig.4. Location of surface features analyzed for gases
Ubicación de las manifestaciones superficiales analizadas respecto a gases.

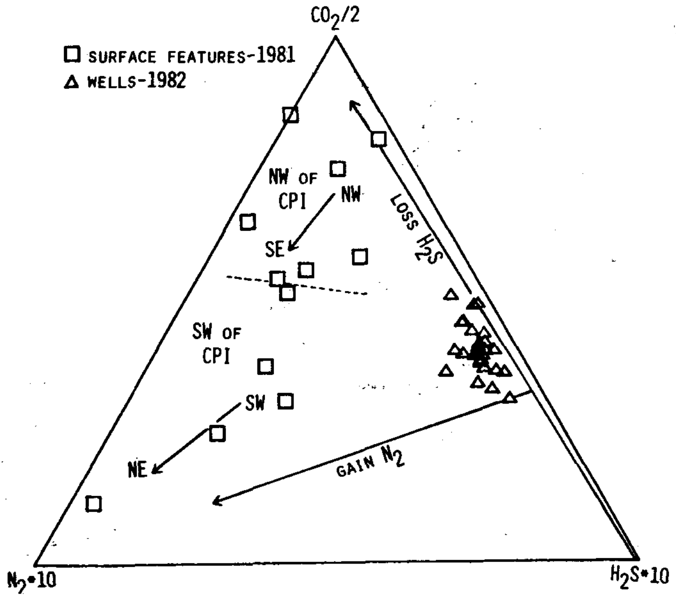


Fig.5. CO_2-N_2-H_2S triangular diagram of Cerro Prieto wells and surface features showing loss of H_2S and gain of N_2 in surface gases
Diagrama triangular CO_2-N_2-H_2S de los pozos y las manifestaciones superficiales de Cerro Prieto que muestra la pérdida de H_2S y la obtención de N_2 en gases superficiales.

HYDROCARBON GASES IN SURFACE AND WELLS*

The distribution of hydrocarbon gases from surface features and wells falls into three groups that are related to the temperature/time regime:

(1) wells about 3000m deep, with measured near 340°C (for example, well E-2);

(2) wells about 1000m deep, with measured temperatures near 290°C (for example, M-31);

(3) surface features (for example, N-31-a 100°C fumarole).

Fig. 6 plots the hydrocarbon distributions in these three samples; table 3 identifies the hydrocarbons present by peak number and lists their semiquantitative concentrations. Although compositions intermediate to those presented here also were obtained, those presented are representative.

Samples near 340°C contain very few hydrocarbons, and the abundance of those present were low relative to methane (Figs. 6a and 7). Two explanations are possible: (1) coal is decomposing directly into small straight-chain hydrocarbons (C1-3) and benzene, or (2) intermediate compunds form which are highly unstable near 340°C and decompose almost immediately to C1-3 hydrocarbons. The increased concentration of high molecular weight (C4-7) straight-chain and branched hydrocarbons at 290°C (Figs. 6b and 7) favor the second explanation. Many of these compounds would be considered intermediate between coal and methane. Lower temperatures would allow higher concentrations of these compounds to accumulate before decomposition occured. Carbon isotope data for the individual hydrocarbons (DesMarais, personal communication) supports this theory.

Slow decomposition of intermediate hydrocarbons is even more evident in the surface samples (Figs. 6c and 7). Methane concentration in these samples is substantially lower relative to other hydrocarbon concentrations than in samples from higher temperature regimes. Hexanes (C6) and heptanes (C7) are second only to methane in concetrations. At 100°C or less, intermediates appear to break down very slowly, if at all.

SUMMARY

Interpretation of gas compositions of well fluids in 1977 support chemical evidence for a large boiling zone around wells M-20, M-21A, M-8, M-27 and M-35. Substancial changes in gas compositions from 1977 to 1982 suggest the boiling

Table 3. Peak identification and semiquantitative concentrations of hidrocarbons in representative wells.
Identificación de hidrocarburos en pozos representativos por número pico y sus concentraciones semicuantitativas.

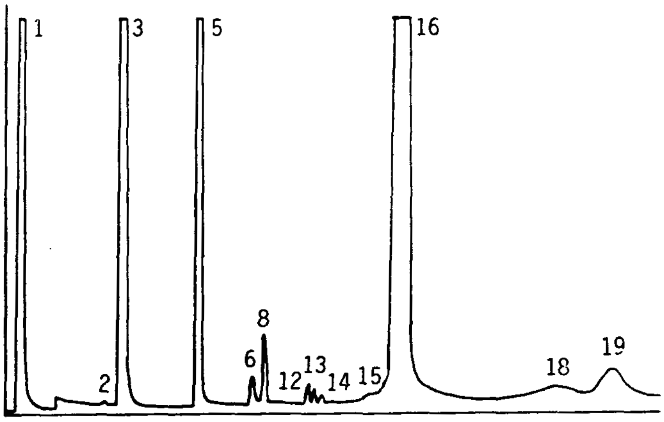
Peak	Hydrocarbon	Well		
		E-2	M-31	N-31
1	Methane	25,000	50,000	2,000
2	Ethene	0.05	2	9
3	Ethane	3,500	15,000	45
4	Propene	0	0	3
5	Propane	250	4,000	15
6	2-methylpropane	6	550	10
7	1-butene	0	0	15
8	n-butane	10	1,000	75
9	2-butene	0	0	7
10	2,2-dimethylpropane	0	2	0.01
11	1-pentene	0	0	1
12	2-methylbutane	2	250	4
13	n-pentane	2	300	7
14	Cyclopentane and 2-pentene	1	200	4
15	n-hexane	1	1,000	30
16	Benzene	2,000	6,000	900
17	Unidentified C7	0	300	25
18	Unidentified C7 (n-heptane?)	2	300	50
19	Toluene	8	1,000	250

zone is no larger expanding and has possibly receded due to shutting in of some the wells. The 1982 distributions shows drawndown of groundwater into the reservoir from above.

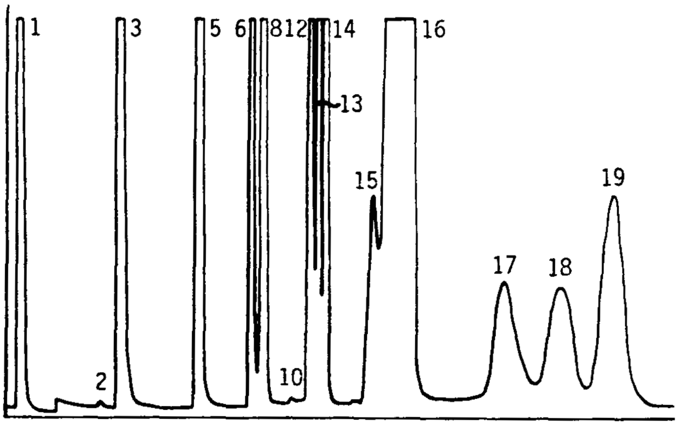
Gas compositions from surface features indicate a loss of H_2S and increase in N_2 relative to the wells. H_2S is lost by reaction with metal ions to form metal sulfides or with air to form sulfate. Nitrogen is introduced with groundwater from the east mixing with thermal water as it ascends to the surface.

Hydrocarbon compositions show large variations owing to rapid re-equilibration with changes in temperature.

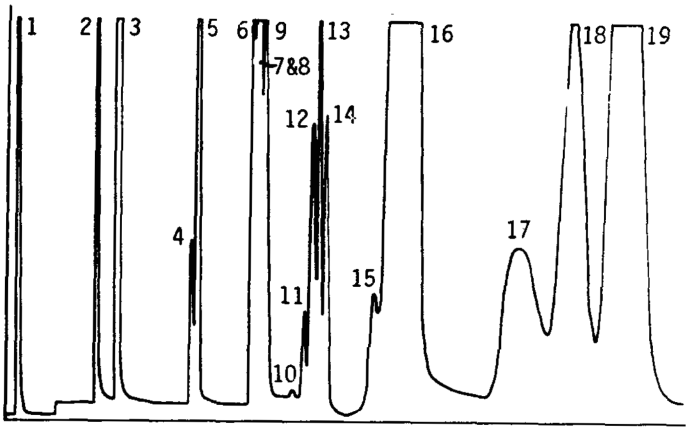
*This section on hydrocarbons has been submitted and accepted for representation at the 1982 Geothermal Resources Council annual meeting.



A. Well E-2 340°C, 2000 m



B. Well M-31 290°C, 1000 m



C. Fumarole N-31 100°C, surface

Fig. 6. Chromatograms of hydrocarbons
Cromatogramas de hidrocarburos.

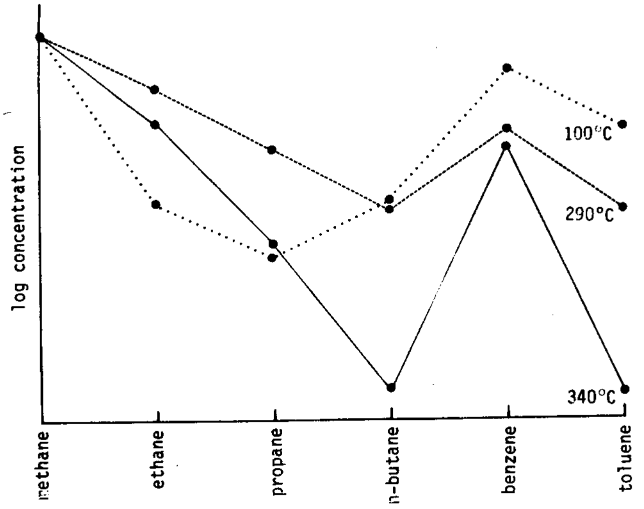


Fig.7. Relative abundances of selected hydrocarbons from wells E-2, M-31, and fumarole N-31
Cantidad relativa de hidrocarburos seleccionados de los pozos E-2, M-31 y fumarola N-31.

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