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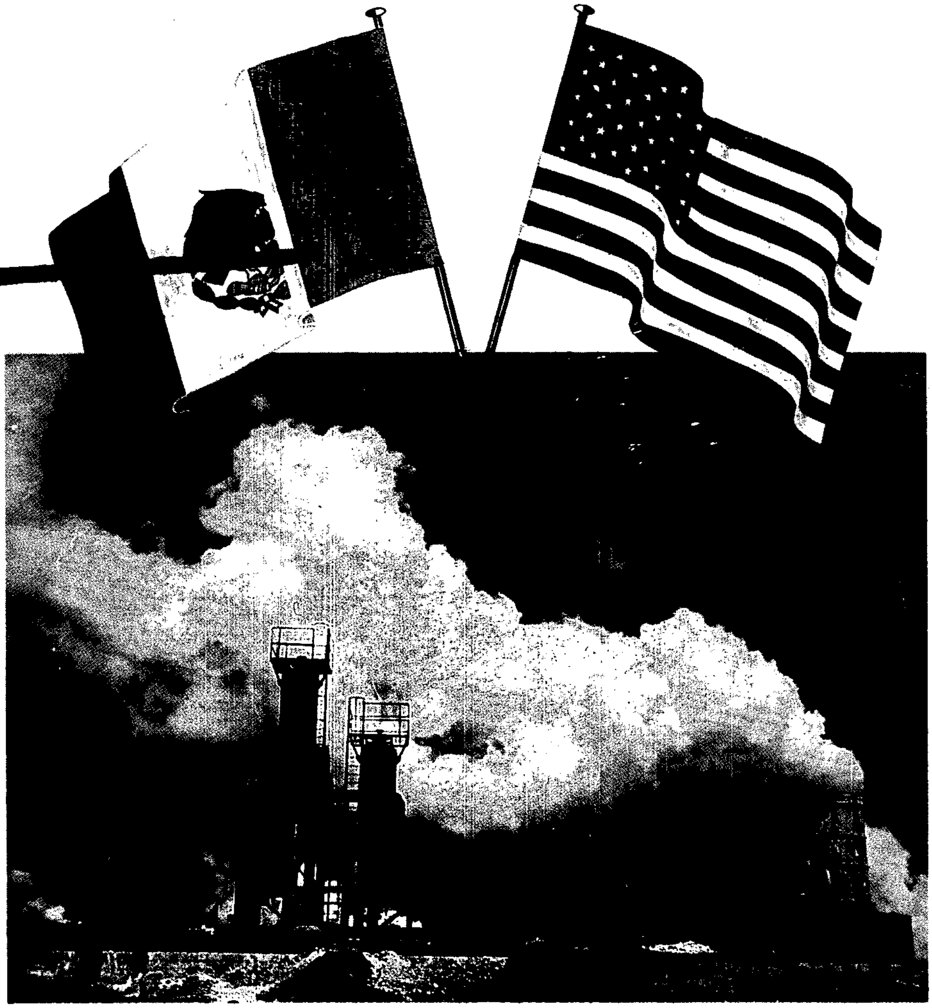

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A REVIEW OF PROGRESS IN UNDERSTANDING THE FLUID GEOCHEMISTRY OF THE CERRO PRIETO GEOTHERMAL SYSTEM

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ABSTRACT

Fluid geochemistry has played a major role in our present understanding of the Cerro Prieto geothermal system. Fluid chemical and isotopic compositions have been used to indicate the origin of water, salts and gases, original subsurface temperature and fluid flow, fluid-production mechanisms, and production-induced aquifer boiling and cold-water entry. The extensive geochemical data and interpretation for Cerro Prieto published from 1964 to 1981 are reviewed and discussed. Fluid geochemistry must continue to play an important role in the further development of the Cerro Prieto field.

INTRODUCTION

Geochemistry has played an important role in the exploration and development of the Cerro Prieto geothermal field. The natural hot springs and fumaroles were surveyed and analysed in the first phase of exploration. In this survey ion and gas ratios were used to indicate zones of maximum thermal activity. During the development (heating up) of production wells, fluid samples were collected and analysed at frequent intervals. On the basis of Na/K ratios, a model of subsurface flow was developed which agrees in all essential with recent models based on much more extensive data. After the field came into production, geochemical studies have concentrated on the application of geothermometers, on the origin of the water, gases, and salts in the geothermal fluid, on mineral alteration, and on fluid-production mechanisms. In this paper we will review the results of these studies of the Cerro Prieto geothermal field to show the wide applicability of fluid geochemistry in geothermal studies.

GEOCHEMISTRY OF SURFACE MANIFESTATIONS

The surface expression of the Cerro Prieto field consists of numerous hot spring and fumaroles to the south and west of the field. These were analysed and described by Mercado (1968). It was found that the temperatures of the vents correlated with the ratios K/Na and Cl/SO_4 in hot-spring waters. The total flow of the surface vents was estimated as 5 x 10^6 m^3 per year at an average temperature of 60°C, corresponding to a heat flow of 3 x 10^{14} cal/year. Using these analyses of the spring waters, Fournier (1979) showed that chloride-enthalpy relations indicated an aquifer temperature of 335°C, the maximum temperature later found in the deeper wells of the field. Restudy of the surface manifestations by Vallette and Esquer Patiño (1981) showed that the salinity and chemical character depended on the type of spring. Some spring waters sampled in both of these studies appeared to have cooled conductively from reservoir fluid and had the same Cl concentration as the reservoir (9000 mg/kg), but differ in overall chemistry. Compared to well waters, spring waters have higher Mg and SO_4 and lower K and SiO_2, indicating reequilibration at lower temperatures and surficial oxidations of H_2S. During the time between these surveys (1964(?)-1979), the area of manifestations decreased about 60%, and changes in salinity and temperature ocurred probably due to the exploitation of the field.

FIELD MODELS BASED ON CHEMICAL THERMOMETRY

The analysis of well fluids was started with the earliest drilling. Analyses of water and gas were cited by Alon and Mooser (1964) in the description of drilling and testing well M-3. By 1968 most of the wells later used to produce 75 MWe (in 1973-74) had been drilled and tested and produced fluids analyzed. These early analyses and analyses of production fluids to 1977 were compiled by Mañón et al. (1977). Cerro Prieto wells under development (heating up) are initially flowed at slowly increasing rates with variable amounts of cooling by conduction and steam loss resulting in variable salinity at the surface. Although the salinity of these fluids depends on the flow rate, the ratios of major ions are not significantly affected. Mercado (1968, 1970, 1976) proposed, therefore, a calibration of the Na/K ratios at Cerro Prieto based on downhole and enthalpy-derived temperatures and used these ratios

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to describe subsurface fluid flow in the field.

The model of subsurface fluid flow proposed by Mercado in 1976 (Fig. 1) contains most of the features of our present models based on resistivity (Wilt and Goldstein, 1981), downhole logs (Halfman et al., this symposium), rock alteration and oxygen isotopes (Williams and Elders, 1981), as well more complete fluid geochemistry. High-temperature water initially below 2-km depth and with Na/K of 4.5 flows up and to the west from the area east of M-53. This water mixes along its upper boundary with a tongue of cold water (initial Na/K = 100) flowing from east to west and at its lower boundary with a tongue of cooler water (initial Na/K = 30) flowing from west to east. The temperature of the hot upflow was overestimated because Mercado (1970) used unrealistic high temperatures in his calibration of the Na/K geothermometer apparently derived in part from total enthalpy measurements on wells with excess steam. From Mercado's (1970) calibration the temperatures ranged from 400°C (Na/K = 4.5) for his deep fluid to 260°C (Na/K= 9.5) for his coolest well fluid (M-9). The Na/K and Na-K-Ca geothermometers applied to chemical analyses of waters from production wells collected after 1973 and later-flowing downhole measurements suggest that the highest fluid temperatures are actually near 330°C. Higher temperatures (to 350°C?) are to be found at greater depths, but the fluids probably cannot circulate at these temperatures due to precipitation of quartz (Fournier, 1977).

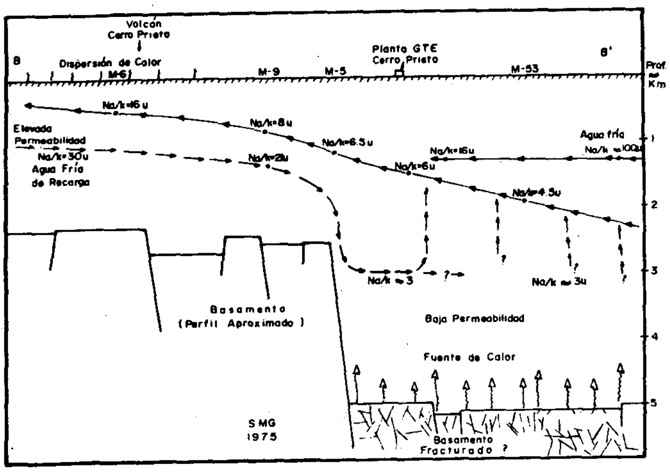

Figure 1. Southwest to northeast cross section of the Cerro Prieto field according to the model of Mercado (1976) based on fluid Na/K ratios.

A similar approach to that of Mercado was used by Alfredo Mañón and his coworkers (Mañón et al., 1979; Fausto et al., 1979; Fausto et al., 1981) in tracing the variation in temperature and salinity based on analyses of fluid from wells in development and production. Mañón et al. (1979) defined a new calibration of the Na-K-Ca geothermometer to correct for apparent underestimation of temperature above 300°C by the original calibration. Using analyses from 1973 to 1977 they found decreases in temperature of 10° to 20°C and chloride of 370 to 670 mg/l per year although some wells showed little change or even increases. The areas to the east and south of the production area (CPI) were found to contain higher temperature fluids although the correlation with chloride was poor, probably due to flow of fluids to earlier drilled wells, or perhaps in part to problems mentioned earlier in collecting representative samples from wells under development. This did not improve after production began. Fausto et al. (1979, 1981) extended these observations to new wells as drilled and, following the earlier work by Mañón et al. (1977) and Mazor and Mañón (1979), distinguished conservative, reactive and indefferent elements from their correlation with chloride. Each of these papers presented analyses of fluid from newly drilled wells and countours of indicators of temperature and salinity. These models of the distribution of temperature and direction of fluid flow in the field did not differ from that of Mercado (1976), although many new supporting data were added. In particular, the edges of the productive field have been determined except to the northwest. The discovery of higher temperature fluid under the production field (E series wells) is also noteworthy.

ISOTOPIC CHANGES IN WELL DISCHARGE FLUID

Since 1977 we have mentioned yearly the isotopic composition of water and steam from production separators. Complete data for 1977 was presented by Truesdell et al. (1981), and the areal distribution of 1977 total fluid ^{18}O values was presented by Truesdell et al. (1979a). Deuterium (and to a lesser extent oxygen-18) is a conservative constituent of the fluid and may be used to trace the movement of water within the reservoir and the mixing of waters of different origin. In 1977 deuterium and chloride concentrations were strongly correlated and showed mixture of brine with dilute Colorado River water. The distribution of ^{18}O values showed unaltered fluids at the margins of the field with isotopically lighter water in the center, indicating drawdown of cooler, less oxygen isotope shifted water from above and the side. Later measurements have shown that this process is continuing. Figure 2 shows the changes in ^{18}O and D for selected wells: M-5, a well with relatively stable enthalpy and Cl; M-31, a well with average drops in enthalpy and Cl; and M-21A with relatively great drops in enthalpy and Cl. In all wells the ^{18}O has dropped. The most in M-31 and M-21A, least in M-5. The deuterium has dropped strongly in M-31 and M-21A and has been stable in M-5. The local cold groundwater (at 100-300 m depth) is about -13 in ^{18}O and -103 D (Truesdell et al., 1979a; Makdisi et al., this Symposium), which suggests that in early 1982, M-31 (and probably M-21A) fluid was three-quarters diluted with cold groundwater while M-5 fluid was only one-fifth diluted. The oxygen-18 map of the field (fig. 3) shows a large area of ^{18}O less than -9 compared to a small area in 1977 (see Truesdell et al., 1979). The deep fluids from the β aquifer (in parenthese in fig. 3) show higher ^{18}O (and D) values than fluids from the α aquifer in agreement with the genesis of lower temperature waters by cold-water mixing suggested by Truesdell et al. (1981) and Grant et al. (1981). The area of isotopic change (with allowance for the wells) is open to allowance for the depth of the wells) is open to the northeast, suggesting that most cold water is coming from this direction.

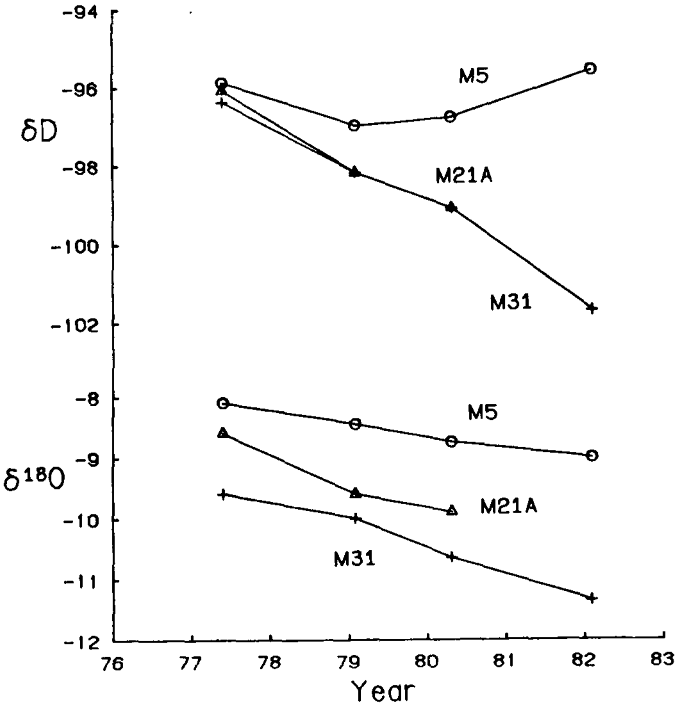

Figure 2. Changes in δ^{18}O and δD with time for fluid feeding selected wells.

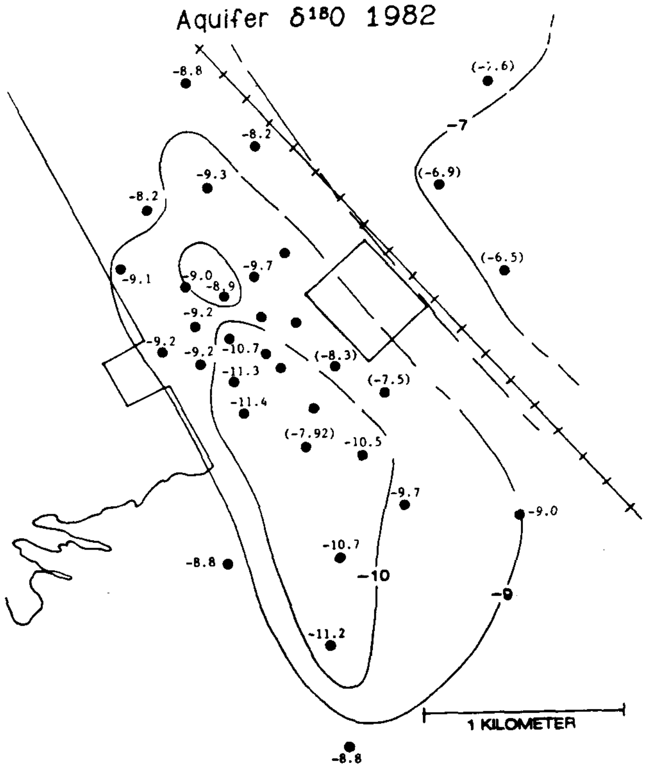

Figure 3. Distribution of ^{18}O in the fluid feeding production wells in 1982. Fluids from the deeper β aquifer are indicated by parentheses.

PRODUCTION MECHANISMS FROM GEOCHEMICAL INTERPRETATIONS

Mercado (1970, 1977) used Na/K ratios to indicate that producing was from two aquifers in certain wells (M-20, M-15A, M-21A, and M-39). For these wells the Na/K ratio showed that changes of flow rate caused lower or higher temperature water to enter by flowing down the annulus around the casing or up adjacent abandoned wells. The use of geochemical data to trace fluid feed to individual wells was continued by Fausto et al. (1981). They showed interference effects of wells around M-8, also discussed in this paper and by Goyal et al. (this symposium), as well as describing chemical and production histories of new wells.

Mercado's (1977) interpretation of high enthalpy wells, such as M-21A, involved flow of steam and higher enthalpy water from greater depths with flashing of the water in the formation to produce high surface chloride concentrations. This is similar to the interpretation of Truesdell at al. (1977, 1979b) and Grant et al. (1981) which also calls upon aquifer boiling but does not require deeper, higher temperature fluids. Instead, Grant et al. (1981) (and the earlier papers) suggest that near-well boiling is common at Cerro Prieto and that boiling zones expanding into hot rock produce high enthalpy fluids by heat transfer from the rock.

TIME CHANGES IN ENTHALPY AND CHEMICAL TEMPERATURES

Changes in aquifer temperature and the effects of local near well boiling are clearly shown on graphs of time vs. temperatures indicated by Na-K-Ca, silica and enthalpy (the temperature of liquid water with the measured enthalpy) (Grant et. al., 1981). The silica geothermometer equilibrates rapidly and indicates temperatures near well bottom (Goyal et al., 1981, and imput, data). Boiling in the aquifer near the wells lowers temperatures as reflected by the silica geothermometer. In contrast the Na-K-Ca geothermometer is slow to equilibrate as those at Cerro Prieto. Therefore, it indicates the temperature away from the influence of near well boiling. The expansion of a near-well boiling zone into new hot rock will cause heat transfer to the fluid and excess steam with high indicated enthalpy temperatures. As the boiling zone stabilizes, the enthalpy temperatures agree with Na-K-Ca temperatures. Silica temperatures will still be low, because the well bottom temperature is lower than the aquifer temperature. If all three temperature indicators agree, then the well has an all liquid feed. Figure 4 shows indicated temperatures for M-14 which had a small amount of local boiling when first opened, but generally has had an all liquid feed. The opposite condition is shown by M-31 (fig. 5), which had a large enthalpy excess (and silica deficiency) which decreased until 1980 when its boiling zone stabilized. The stabilized boiling zone still produced low well-bottom temperatures reflected by low silica. Well M-8 (fig. 6) shows interference effects in the coalescing boiling zone feeding several nearby wells. From the opening of the well in early 1974 there was some boiling, but the opening of M-21A caused a great decrease in aquifer pressure and a jump in the enthalpy of M-8. Note that silica dropped at the same time. This occured again in mid-1976 when M-27 was opened, and near the end of 1977 when M-46 was opened and its flow combined with that of M-8 in a common separator. The enthalpy increase in mid-1980 may be due to the effects of an eartquake. Interference in M-8 is also discussed by Fausto et al. (1981) and Goyal et al. (This Symposium).

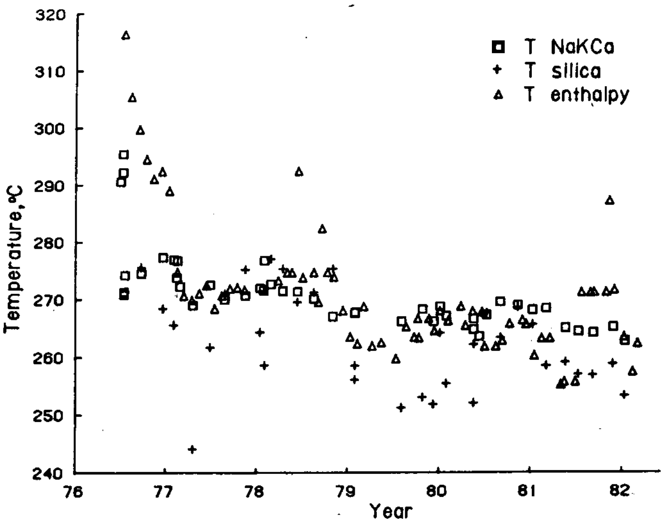

Figure 4. Changes with time in NaKCa, silica and enthalpy temperatures for fluid from well M14. This well has had a predominantly all-liquid feed with little near-well boiling.

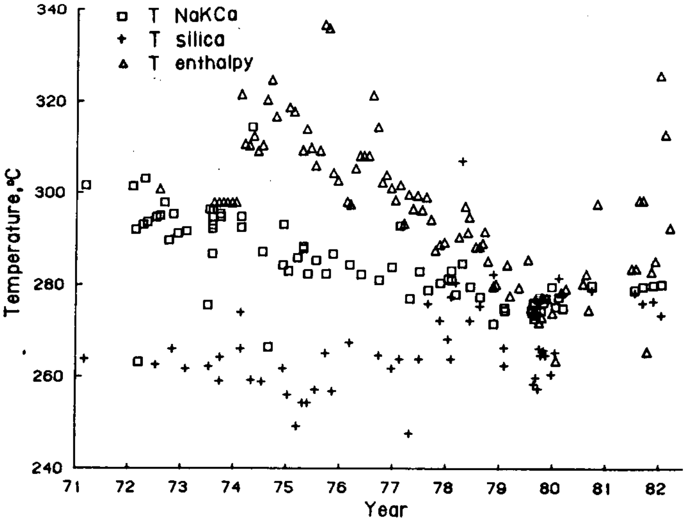

Figure 5. Changes with time for fluid temperatures for fluid from well M31. This well shows near-well boiling with an expanding boiling front which stabilized in 1980.

Further evidence on the origin of excess enthalpy from local boiling or general boiling is provided by the radon and ammonia measurements of Semprini and Krugger (1981). These authors found that both Rn and NH_3 are correlated with enthalpy. They conclude from Rn results that boiling in the aquifer could be either local (with boiling fronts to about 200 m from the wellbore) or general, but that the NH_3 results favor general boiling with excess steam (containing NH_3) moving to the wells. They did not consider the possibility that the NH_3-enthalpy correlation results from

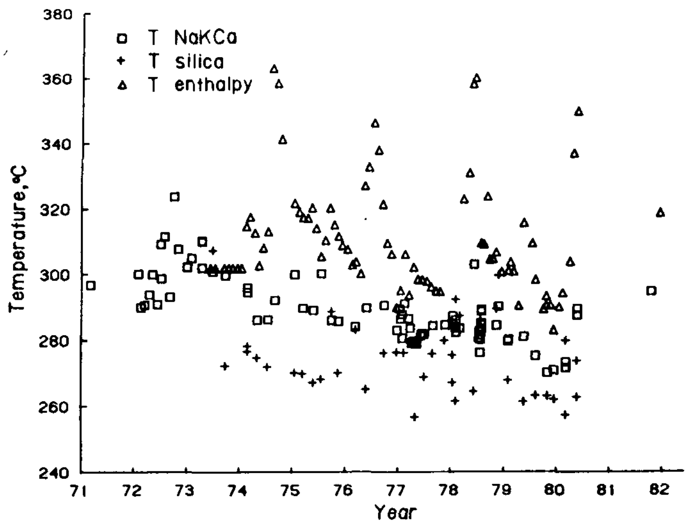

Figure 6. Changes with time for fluid temperatures of well M8. The boiling front of this well expanded rapidly when nearby well M21A was opened (mid 1974) and again in mid 1976 when well M-27 was opened. The opening of M46 and diversion of its flow into the M8 separator caused similar effects in 1977 as did an earthquake(?) in 1980.

exothermic formation of NH_3 from N_2 and H_2 in the cool near-well zones resulting from local boiling in which low near-well temperatures correlate with high enthalpy (compare enthalpy and silica temperatures in figs. 4-6).

COLD WATER ENTRY AND THE EXISTENCE OF A CAPROCK.

Geochemical data first suggested that pressure drawdown was causing cooler, more dilute water to enter the field from the sides and above (Truesdell et al., 1977, 1979b). The contrast of this behavior with that of Wairakei, where fluid removed from the reservoir is replaced by steam, suggest that sealing of the Cerro Prieto aquifer from surrounding cold waters is not as complete as at Wairakei. Using the original enthalpy-chloride relationship obtained from early fluid production and the observed changes in chloride and enthalpy to 1980, Grant et al. (1981) were able to calculate the effective porosities of the rocks through which fluids moved to the wells. The pattern of the observed declines in chloride and enthalpy suggested that the old Cerro Prieto field (CPI) lacked a "cap rock" in the accepted sense and that it was a "leaky aquifer" (Grant and O'Sullivan, this Symposium). The relative unimportance of general boiling in the aquifer was also shown by the high retention of atmospheric noble gases described by Mazor and Truesdell (1981). The behavior of deeper wells feeding Cerro Prieto power plants II and III will be monitored closely for chemical changes indicating production mechanisms in this part of the field.

THE ORIGIN OF WATER, GASES, AND SALTS

Mercado (1968) suggested that magmatic gases supplied heat, water, and possibly other substances to the deep fluids but that these mixed with cold meteoric at dephts below 2.5 km (fig. 1). At shallower dephts more meteoric water, principally from the Colorado River to the east, mixes with the hot upflow. Thus, Mercado assumes some magmatic fluid (water and gas), but the major contribution to the water is from the Colorado River. Some salts are assumed to be dissolved from the rock, and temperature and rock interactions control ion distributions.

Coplen (1972) analysed one Cerro Prieto well fluid and found it similar to central Imperial Valley groundwaters, which originate from infiltration of Colorado River water with little contribution from local precipitation and none from seawater. Rex (1972) found the Cl/Br ratio of the Cerro Prieto waters to be similar to coastal seawater and suggested an evaporite source for the dissolved salts.

Based on Rex's work, isotopic studies of Crosby et al. (1972) and many new chemical and isotopic data, Truesdell et al. (1981) suggested that the water in the Cerro Prieto system is Colorado River water which has circulated deeply and mixed with a hypersaline, oceanic brine. This mixture was altered by high-temperature rock reactions similar to those found experimentally and in coastal geothermal systems, and lost Mg, Ca and SO_4 and gained Li, K, SiO_2 and trace elements. During ascent it mixed with more Colorado River water and cooled, reequilibrating with rocks accordingly to reach the present compositions.

Although all evidence points to the water and salts of the Cerro Prieto geothermal fluid having originated from Colorado River water and oceanic brines respectively, the gases in the fluid may have a different origin. Isotope compositions of sulfur and carbon in the dissolved gases (Truesdell et al., 1979a, and Janick et al., this Symposium) are permissive of a magmatic origin although mixed sedimentary sources are also possible. De Marais et al. (1981 and this Symposium) have shown convincingly that light hydrocarbons in the fluid originate from the thermal breakdown of organic matter (coal and organic-rich shale) contained in the sediments. This in situ breakdown is temperature-dependent and provides additional tracing for fluid movement.

The only unequivocal magmatic constituent of the fluid other than heat is the helium-3 isotope which is being outgassed from the mantle and is only enriched relative to atmospheric composition in volcanic gases, young volcanic rocks, and high-temperature geothermal fluids. Welhan et al. (1978) found that the Cerro Prieto fluids had ^{3}He/^{4}He ratios 6.3 times that of the atmosphere. This ratio is similar to that of fluids from the Salton Sea field in the Imperial Valley with similar or higher temperatures and a similar geologic setting to Cerro Prieto. Higher ^{3}He/^{4}He isotope ratios have been found at Yellowstone, Kilauea, and elsewhere, but the Cerro Prieto ratios clearly indicate introduction of mantle He. Since young volcanic rocks may contain mantle helium, it is not certain wheter the helium reaches the fluid directly or through rock leaching.

SUMMARY

Geochemical have been widely applied to fluids from the Cerro Prieto geothermal field. Geochemistry has proved particularly useful in identifying the original temperatures and sources of aquifer fluids and in detecting aquifer boiling and cold-water entry resulting from exploitation. Fluid from Cerro Prieto have been useful in the study of hydrothermal gas and mineral equilibria and kinetics at aquifer temperature of 240°to 340°C.

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