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# DISTRIBUTION OF OXYGEN ISOTOPES AND NONCONDENSIBLE GAS IN STEAM AT THE GEYSERS

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## ABSTRACT

The earliest available isotopic and noncondensable gas analyses have been compiled from around The Geysers geothermal field to estimate pre-exploitation conditions. The observed fieldwide gradients in isotopes and gases provide evidence for several different physical processes which combine to control reservoir fluid compositions. These processes include water-rock, water-steam, and rock-gas interactions.

Oxygen isotopes of Geysers steam generally become heavier from southeast to northwest and from the margins of the field toward the center. Throughout the field there is a good correlation between steam isotopic composition and reservoir rock isotopic composition. It is inferred from this that water-rock interaction exerts the predominant control on steam isotopic composition. Fieldwide lateral and vertical gradients in steam isotopes suggest steam condensation and/or meteoric recharge at the top and margins of the field.

The noncondensable gas content of early Geysers steam generally increases concentrically outward from a low in the south-central part of the field. This pattern is consistent with a fieldwide Rayleigh condensation cell, but because of a strong correlation with reservoir rock type is thought to be related to lithology as well. Lithologic factors which may affect gas content include reservoir rock type, alteration mineralogy, and the "thermal maturity" of organic material in the reservoir graywacke.

## INTRODUCTION

Dry, superheated steam is produced from over 400 wells at The Geysers. This steam is produced predominantly out of a reservoir of Franciscan graywacke and underlying silicic batholith. The noncondensable gas and isotope composition of the steam produced from Geysers wells can be used to evaluate processes and conditions within the reservoir. Noncondensable gases measured in produced steam, for example, can be interpreted in terms of (1) processes that generate gas, (2) chemical reactions among gas species, (3) solubilities in liquid and vapor phases, and (4) physical processes which concentrate or dilute the gases (D'Amore and Truesdell, 1979; D'Amore, Celati and Calore, 1982; McCartney and Lanyon, 1989). The oxygen and hydrogen isotopes of steam, on the other hand, can be interpreted in terms of fluid source(s), isotopic interaction with rock, and liquid-vapor interaction within the reservoir.

Together, these geochemical tools can be used to look at both the initial state of the reservoir and its responses to over 25 years of production. Analyses from early in the production history of an area more closely reflect processes occurring on a geological time scale, whereas later samples show influences of production and injection-related processes.

In this paper I focus on geological processes related to the natural evolution of the field. I present a generalized compilation of early production steam oxygen isotope and total noncondensable gas data for The Geysers. Lateral and

vertical gradients in composition are then interpreted with respect to processes occurring in the reservoir prior to field exploitation. Finally, a model is presented which describes the interpreted pre-exploitation conditions and processes.

### DISTRIBUTION OF OXYGEN ISOTOPES

A generalized map compiling steam oxygen isotope data from production wells throughout The Geysers is shown in Figure 1. The contours used in this map are adapted from Truesdell and others (1987) with the addition of proprietary unpublished analyses. The data represent a wide time window but were chosen to be as close to initial production conditions in each development block as possible. Well spacing, and hence sample density, is not uniform throughout the field, and well depth was not considered when compiling the map. No samples were used, however, from the shallow, low pressure reservoir in the thermal area. All values are presented in per mil relative to SMOW.

In the eastern half of the field, oxygen isotopes in Geysers steam become heavier away from the margins of the field. Wells close to the margins of the field have  $\delta^{18}\text{O}$  values closest to local meteoric water ( $\delta^{18}\text{O} = -7$  to  $-8$  per mil).  $\delta^{18}\text{O}$  values increase to greater than  $-4$  per mil along the axis of the field. In the western half of the field,  $\delta^{18}\text{O}$  values increase with a considerably steeper gradient to a maximum near the northern edge of the field. Steam  $\delta^{18}\text{O}$  values increase in this direction to values as high as  $+3$  per mil, which is more than 10 per mil heavier than local meteoric water (Truesdell and others, 1987).

In addition to the lateral gradients in  $\delta^{18}\text{O}$  observed at The Geysers, there are also significant vertical gradients. The most reliable way to measure these gradients, given a lack of downhole steam samples, is to compare isotopes

from adjacent wells that produce from discrete and significantly different depths. This has been done in Figure 2, where tie-lines join depth and isotope data from pairs of wells drilled off the same pad. For each well, the depth is an average depth of steam entries, weighted for steam entry magnitude. In every case,  $\delta^{18}\text{O}$  increases with depth. The increases range from about 0.3 to 1.5 per mil per 1,000 feet depth. The pairs of wells shown come from all areas other than the northwestern end of the field, so the variation with depth appears to be characteristic of the majority of the field. Walters and others (1988) report a similar trend in the northwestern region as well. Deep wells that penetrate the high-temperature reservoir (HTR) typically produce steam that is isotopically enriched by about 0.6 per mil compared to shallower wells that produce out of the "normal" temperature reservoir. This is the same sense of vertical zonation seen elsewhere in the field, but as discussed later, may not be related to the same process.

### DISTRIBUTION OF NONCONDENSIBLE GAS

A generalized map compiling total noncondensable gases (TNCG) in steam from production wells throughout The Geysers is shown in Figure 3. The map is based on contours from Truesdell and others (1987) and proprietary unpublished analyses. The ages of the analyses again vary but largely reflect the timing of development in various parts of the field. The earliest available data are presented. The data are contoured in parts per million by weight (ppmw) and represent the sum of all analyzed gases.

Like the isotope data, gas data from The Geysers can best be described in two geographical parts. In the southeastern three fourths of the field, gases are concentrically zoned about a northwest-southeast trending minimum centered in the Little Geysers area. TNCGs are as low as

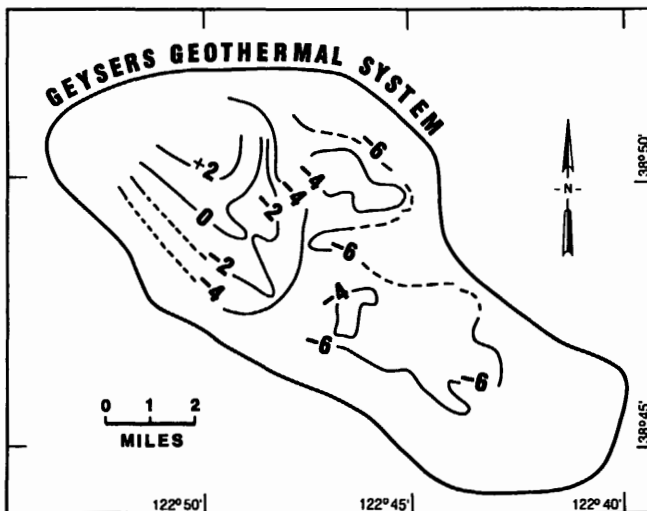


Figure 1. Map showing generalized distribution of oxygen isotopes in "early" steam produced at The Geysers. Contours represent  $\delta^{18}\text{O}$  in per mil relative to SMOW. Data are from unpublished Unocal analyses and Truesdell and others (1987).

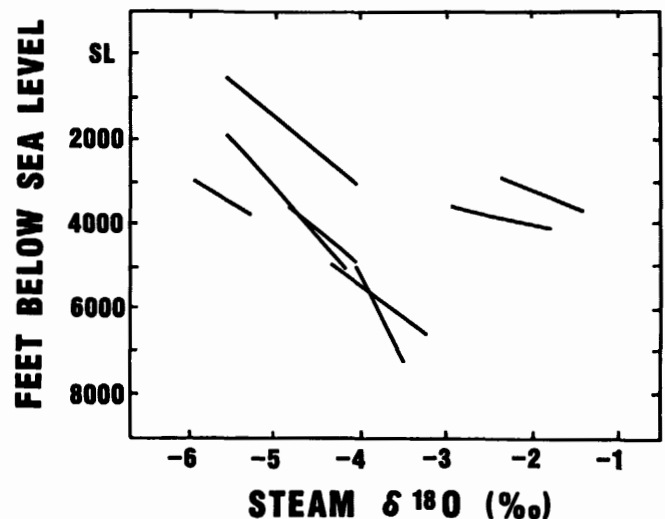
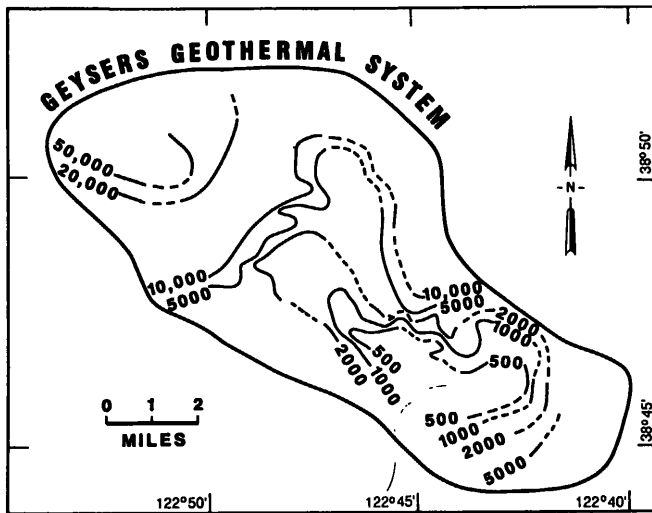


Figure 2. Plot of steam  $\delta^{18}\text{O}$  versus depth for pairs of Geysers wells. Tie-lines connect pairs of wells drilled from the same location that produce from appreciably different depths. Depths represent weighted averages of all recorded steam entries.



**Figure 3.** Map showing generalized distribution of total noncondensable gas in "early" steam produced at The Geysers. Contours in parts per million by weight. Data from unpublished Unocal analyses and Truesdell and others (1987).

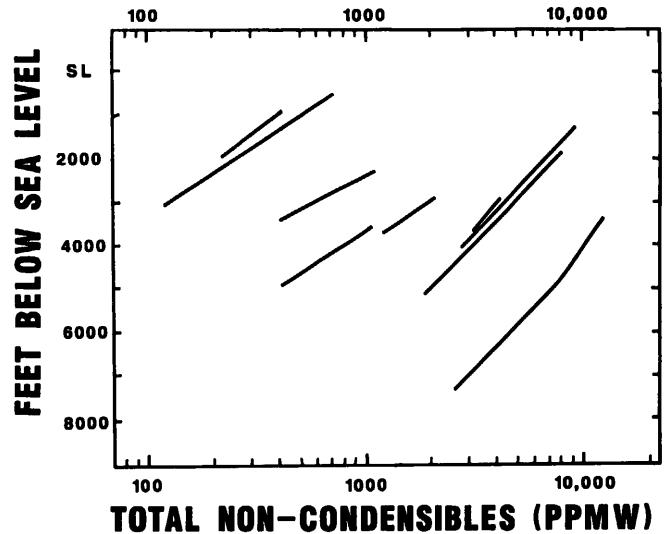
100 ppmw in the center of the gas low, and increase to more than 10,000 ppmw to the north and northwest. In the northwest part of the field, gases again appear to increase toward the edge of the field, but the contours do not appear concentric about the southeast Geysers low. Rather, TNCGs appear to be concentrically zoned about a 50,000 ppmw high near the northwestern edge of the field.

In addition to lateral variations, gases also show a vertical zonation. Vertical zonation of gas in the reservoir can be measured in the same way as oxygen isotopes: using pairs of wells which produce from appreciably different depths. In the case of gases, however, it is more important to work with wells which produce from distinct intervals to avoid interzonal mixing-related distortion of the depth relationship. Figure 4 shows the vertical zonation of TNCG in a number of such pairs of wells. The data are presented as in Figure 2. Again, the only area not represented is the northwestern quarter of the field. The TNCGs increase geometrically upward, doubling every 800 to 1,500 vertical feet. This geometric gradient appears to be slightly higher in shallow, low-gas areas compared to deeper, higher gas areas.

In contrast to the isotope data, noncondensable gases in the northwestern part of the field show a reversed vertical zonation compared to gases in the rest of the field. Walters and others (1988) report that deep steam from the HTR is higher in TNCG than in the overlying "normal" reservoir. This reversal in the vertical zonation may be of key importance in interpreting the nature of the HTR.

### INTERPRETATION

The  $\delta^{18}\text{O}$  values seen in Geysers steam (Figure 5) have previously been attributed to interaction between reser-



**Figure 4.** Plot of total noncondensable gas versus depth for pairs of Geysers wells. Tie-lines connect pairs of wells drilled from the same location that produce from appreciably different depths. Depths represent weighted averages of all recorded steam entries.

voir rock and water of meteoric origin (Craig, 1963). This conclusion is drawn for two reasons. First, the isotopically lightest steam produced at The Geysers is very similar in composition to average local creek water, suggesting a meteoric origin. Second, the large  $\delta^{18}\text{O}$  shift coupled with a smaller  $\delta\text{D}$  shift is exactly that expected from interaction of meteoric water with oxygen-rich, hydrogen-poor rocks such as Franciscan graywackes. The origin of isotopic variation in fluids from most other large geothermal systems can be similarly explained (Sheppard, 1986).

If water-rock interaction is the primary effect on  $\delta^{18}\text{O}$  at The Geysers, then the rocks in contact with reservoir steam (initially present mostly as liquid) should show evidence of this isotopic equilibration. Figure 6 is a plot of initial  $\delta^{18}\text{O}$  of steam versus average whole rock reservoir graywacke  $\delta^{18}\text{O}$  for a number of Geysers wells. The solid dots represent wells which produce only from the "normal" temperature reservoir and the open dots represent wells which produce at least in part from the HTR. Steam from both the "normal" and HTR shows good isotopic correlation with reservoir rock, indicating that water-rock interaction is an important process in the steam reservoir. Given that bulk rock porosity is probably around 5 percent, the instantaneous water-rock ratio in the reservoir is quite low. Therefore steam (water) isotopic composition in the pre-exploitation Geysers reservoir is largely buffered by rock composition. Scatter away from the isotherms is probably due to incomplete rock equilibration and/or Rayleigh fractionation as discussed below and shown on Figure 6. Steam from the HTR is similar in isotopic composition to steam from the "normal" reservoir, but shows the effect of water-rock equilibration at high temperatures.

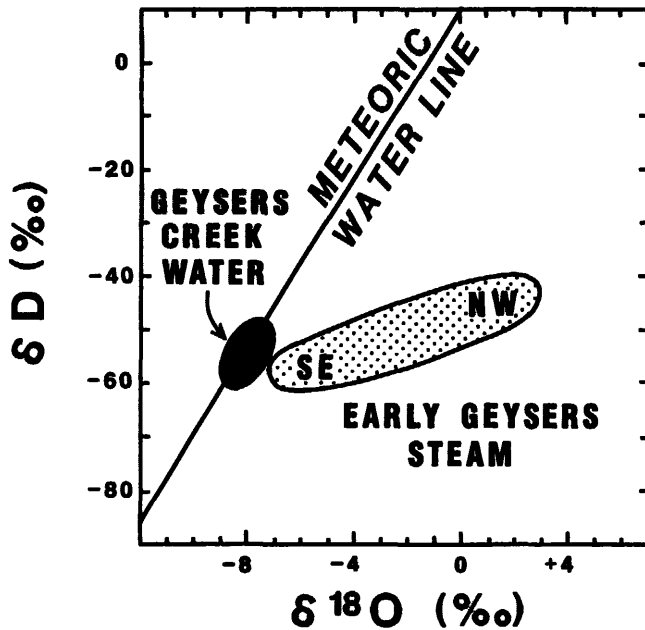


Figure 5. Geysers creek water and "early" steam isotopic compositions. In general,  $\delta^{18}\text{O}$  of steam increases from southeast to northeast. Data from unpublished Unocal analyses and Truesdell and others (1987).

The wide range of steam and rock isotopic compositions in The Geysers reservoir point to widely varying integrated water-rock ratios, both in the "normal" reservoir and the HTR. Figure 7 shows the same data as Figure 6 with calculated integrated water-rock ratios required to achieve various current rock-steam compositions (Taylor, 1974). Water-rock ratios in excess of two by mass imply that an enormous amount of water pervasively circulated through much of the Geysers reservoir. The water has not flowed through the reservoir uniformly, however, as calculated water-rock ratios are relatively low in graywackes from the northwestern Geysers (Figure 7). Oxygen isotopes in graywacke generally are more strongly depleted closer to the felsite, suggesting that much of this fluid circulation occurred in direct response to the igneous intrusion of the underlying silicic batholith. The fact that integrated water-rock ratios are highest near the southern, western, and eastern margins of the field (i.e.  $\delta^{18}\text{O}$  is lowest; Figure 1) suggests that this is where meteoric recharge is at least in part coming from. This recharge must be relatively slow, however, as the reservoir remains vapor-dominated.

While the isotopic composition of reservoir rock grossly controls steam composition, the vertical zonation of steam isotopes does not appear to be related to rock isotopes. This vertical zonation is antithetic to measured vertical zonation of rock isotopes and suggests a second modifying process (Figure 8). I propose that the second process is fractional or Rayleigh condensation (D'Amore and Truesdell, 1979). Heat flow through The Geysers reser-

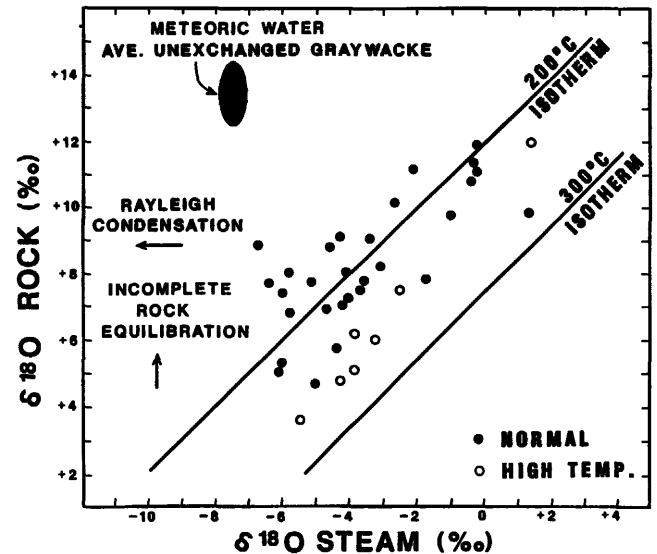


Figure 6. Plot of steam and reservoir rock  $\delta^{18}\text{O}$  for Geysers wells. Solid dots represent wells that produce only from "normal" ( $\sim 240^\circ\text{C}$ ) temperature reservoir. Open circles represent wells that produce at least partly from the high temperature ( $>250^\circ\text{C}$ ) reservoir. Data are from unpublished Unocal analyses and Walters and others (1988). Isotherms are for quartz-water (Clayton and others, 1972) and closely approximate a produced steam-reservoir rock fractionation.

voir is predominantly vertical and is accomplished by heat-pipe-style vertical counterflow of steam and condensate (White, Muffler and Truesdell, 1971; Pruess, 1985). This vertical flow of condensing steam, which is presumed relatively constant through time due to roughly constant conductive heat loss above the reservoir, has established a relatively steady state gradient in steam (and equilibrated pore liquid) isotopes. In this process, oxygen-18 is progressively removed upward through condensation. This vertical gradient in  $\delta^{18}\text{O}$  is superimposed on the larger lateral gradients which are related predominantly to water-rock interaction. Further evidence in support of Rayleigh condensation is seen in the vertical zonation of noncondensable gases. Increased TNCGs toward the top of the reservoir again show the effect of condensation during heat-pipe-style steam-condensate counterflow.

Except for the northwestern end of the field, field-wide gradients in TNCGs appear to support a lateral Rayleigh condensation cell in addition to the vertical cell. TNCGs increase laterally from a low near the central axis of the field outward in all directions. The increase by more than two orders of magnitude in TNCG from the axis of the field to the edge would require condensation of more than 99 percent of the original steam. Such condensation would cause a large negative shift in the residual steam's oxygen isotopes. However, only a small shift is observed. This apparent discrepancy could be reconciled through isotopic re-equilibration of steam, water, and rock near the margins of the reservoir. Alternatively, the hundred fold increase in TNCG lateral may be related to the process described below.

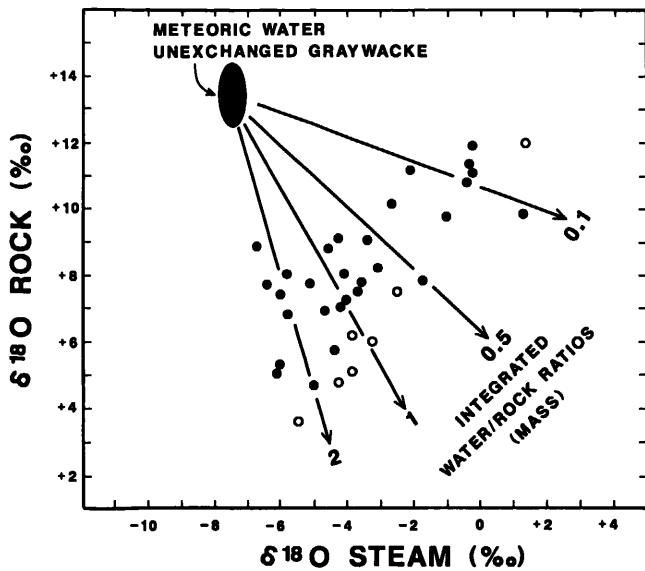


Figure 7. Same data as Figure 6 showing model integrated water-rock ratios required to generate "early" Geysers reservoir conditions. Initial conditions based on Unocal analyses: steam  $\delta^{18}\text{O} = -8$  per mil; rock  $\delta^{18}\text{O} = +13.4$  per mil.

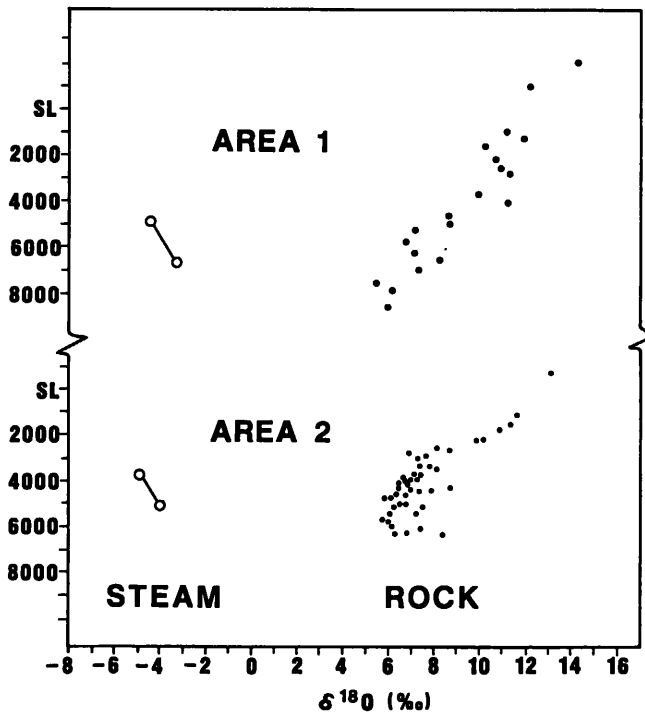


Figure 8. Variation of oxygen isotopes of steam and rocks with depth in two areas at The Geysers. In both areas, steam becomes isotopically lighter and rocks become isotopically heavier with depth.

There is a strong correlation between the spatial distribution of TNCGs and the distribution of rock types in The Geysers reservoir. Figure 9 is a map showing the generalized depth in feet below sea level (down to 6,000 feet subsea) of the batholithic "felsite" which underlies graywacke in the reservoir. This unit has been penetrated by more than 100 drill holes, so its location is well known. Comparison of Figure 3 with Figure 9 shows that the area

of shallowest felsite corresponds precisely with the area of the lowest gas, and the northwest-trending axis of the felsite corresponds with the axis of the gas contours. It is suggested here that this lithologic correspondence with TNCG is not coincidence. Rather, the gas low in the southeast part of the field is related to a lack of carbonaceous source material in the reservoir rocks there. The reservoir in the Little Geysers area consists of a very thin section of high contact metamorphosed Franciscan rocks underlain by felsite. Virtually all of the calcite and organic material was driven out of the Franciscan rocks during the contact metamorphic event, and none exists in the felsite, so there is very little source material to generate gas. In contrast, areas toward the margins of the field have higher TNCG at least in part because they have more source material for that gas. Rocks toward the edges of the reservoir have a large proportion of argillaceous Franciscan graywacke which has not been subjected to high contact metamorphic temperatures. This results in significantly greater amounts of organic material and calcite remaining, and so these rocks are considerably more "fertile" for generation of gases.

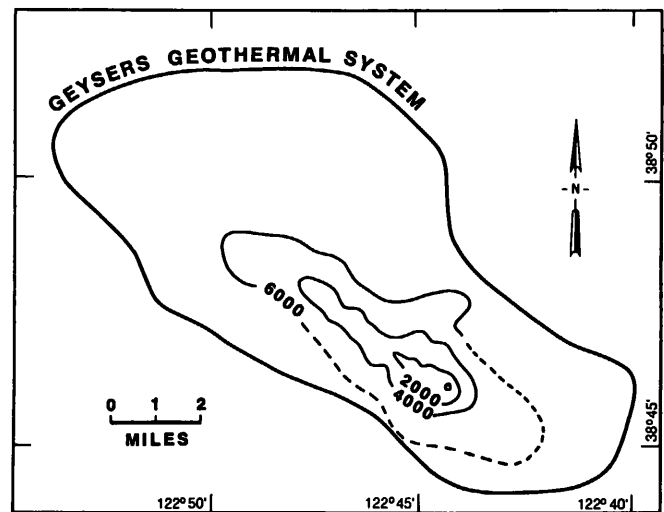


Figure 9. Map showing generalized top of silicic "felsite" batholith in Geysers reservoir (down to 6,000 feet below sea level). Contours are in feet below sea level.

Very high TNCGs at the northwest end of the field are probably related to a combination of three factors. First, the very low integrated water-rock ratios calculated for this area imply that the reservoir rock and hence gases have not been "flushed" by large quantities of circulating fluid. The predominantly graywacke reservoir should therefore be relatively fertile for the generation of gas as suggested by Truesdell and others (1987). Second, the deep reservoir in this region is at considerably higher than "normal" temperatures. Gas generation in this zone should be enhanced because of those higher temperatures. Third, the pressure-temperature conditions in the deep, high temperature reservoir lie distinctly in the vapor field of a water phase diagram, suggesting the absence of free liquid

water (Walters and others, 1988). The gas content of steam produced only from in situ vapor and adsorbed water would be higher than in steam produced in other areas of the field which comes in large part from boiled pore liquid.

### RESERVOIR MODEL

Geochemical data suggest several processes have combined to control the composition of steam produced early in the exploitation history of The Geysers reservoir. The emplacement of a small silicic batholith over the period 2.4 to 0.9 Ma caused nearby contact metamorphism of and initiated fluid circulation in Franciscan graywacke. The fluid was of meteoric origin, and circulation was most intense in what is now the southeastern part of the producing field where the batholith is shallowest. Very little fluid circulated through what is now the northwestern end of the field. The high calculated water-rock ratios in some areas imply that there must have been significant outflow from, and recharge into, the reservoir during this period.

After the liquid-dominated system had established spatial and isotopic characteristics, the hydrothermal system boiled down to become vapor dominated. In response to this boil-down, the vapor-dominated "heat pipe" became the predominant mechanism of vertical heat transport (Figure 10). Gases continued to evolve from the Franciscan graywacke in the reservoir and the vertical gradient of increasing gas upward was established in response to heat pipe-induced Rayleigh distillation. Lateral flow of steam from the center of the field toward the edges may have been caused by either conductive heat loss and/or the thermal effects of slow liquid recharge at the reservoir boundaries. This lateral flow resulted in increasing gas toward the edges of the field. However, increased gas generation from more available calcite and organic material near the margins of the field probably also had a large influence on the lateral TNCG gradients.

Much of the fluid in the reservoir was held as a gas-steam-water mixture in microfractures and pores. Oxygen isotopes in this mixture were controlled by two competing processes. On a field-wide basis, oxygen isotopes of steam and water were largely buffered by equilibration between water and reservoir rock. The pattern related to water-rock interaction was modified by vertical heat-pipe-driven Rayleigh distillation of steam. This condensation process established vertical isotopic gradients through depletion of oxygen-18 from the top of the reservoir. These vertical gradients were superimposed on the larger scale lateral field-wide gradients. The isotopic similarity of steam near the margins of the field to local meteoric water suggests at least historic, if not ongoing, recharge in those areas.

### ACKNOWLEDGEMENTS

I would like to thank Unocal Geothermal for permission to publish. I would also like to thank GEO Operator, Geysers Geothermal, Santa Fe Geothermal, and NCPA for permission to use analyses of samples obtained through data trade in this paper.

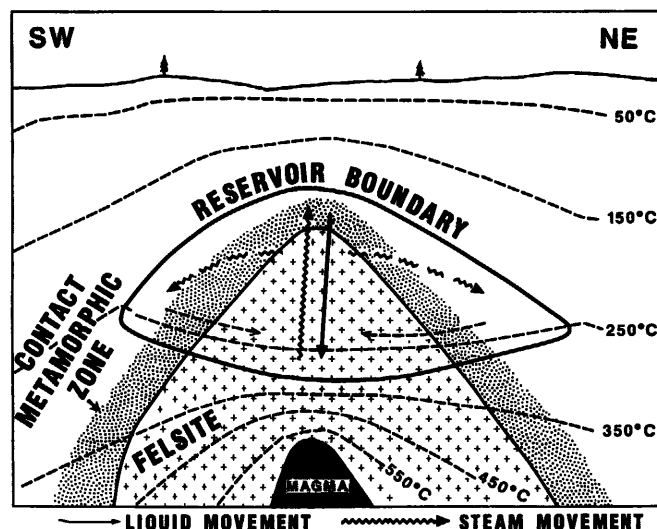


Figure 10. Schematic model of pre-exploitation Geysers reservoir showing flow of liquid and steam. Predominant flow of steam and water is vertical, with only a small lateral component. Hatched area represents reservoir rocks containing calcite and organic material. Diagram is not to scale.

### REFERENCES

- Clayton, R.N., O'Neil, J.R., Mayeda, T.K., 1972. Oxygen isotope exchange between quartz and water, *Journal of Geophysical Research*, v. 77, no. 17, p. 3057-3067.
- Craig, H., 1963. The isotopic geochemistry of water and carbon in geothermal areas, in: *Nuclear Geology of Geothermal Areas*, E. Tongiorgi, ed., Pisa Consiglio Nazionale della Ricerca, Spoleto, p. 17-53.
- D'Amore, F. and Truesdell, A.H., 1979. Models for steam chemistry at Larderello and The Geysers, 5th Stanford Workshop Geothermal Reservoir Engineering, Stanford, California, p. 283-297.
- D'Amore, F., Celati, R. and Calore, C., 1982. Fluid geochemistry applications in reservoir engineering (vapor-dominated systems), 9th Stanford Workshop on Geothermal Reservoir Engineering, p. 295-307.
- McCartney, R.A. and Lanyon, G.W., 1989. Calculation of steam fractions in vapor-dominated geothermal systems using an empirical method, 14th Stanford Workshop on Geothermal Reservoir Engineering, Stanford, California, p. 7.
- Preuss, K., 1985. A quantitative model of vapor dominated geothermal reservoirs as heat pipes in fractured porous rock, *Geothermal Resources Council Transactions*, v. 9-2, p. 353-361.
- Sheppard, S.M.F., 1986. Characterization and isotopic variations in natural waters, in J.W., Taylor, H.P. Jr., O'Neil, J.R., eds., *Stable Isotopes in High Temperature Geological Processes*, Valley, Mineralogical Society of America Reviews in Mineralogy, v. 16, p. 165-183.
- Taylor, H.P. Jr., 1974. The application of oxygen and hydrogen isotope studies to problems of hydrothermal alteration and ore deposition, *Economic Geology*, v. 69, p. 843-883.
- Truesdell, A.H., Haizlip, J.R., Box, W.T., and D'Amore, F., 1987. Fieldwide chemical and isotopic gradients in steam at The Geysers, 12th Stanford Workshop on Geothermal Reservoir Engineering, Stanford, California, p. 241-246.
- Walters, M.A., Sternfeld, J.N., Haizlip, J.R., Drenick, A.F. and Combs, J., 1988. A vapor-dominated reservoir exceeding 600°F at The Geysers, Sonoma County, California, 13th Stanford Workshop on Geothermal Reservoir Engineering, Stanford, California, p. 73-81.
- White, D.E., Muffler, L.J.P., and Truesdell, A.H., 1971. Vapor-dominated hydrothermal systems compared with hot-water systems, *Economic Geology*, 66-1, p. 75-97.