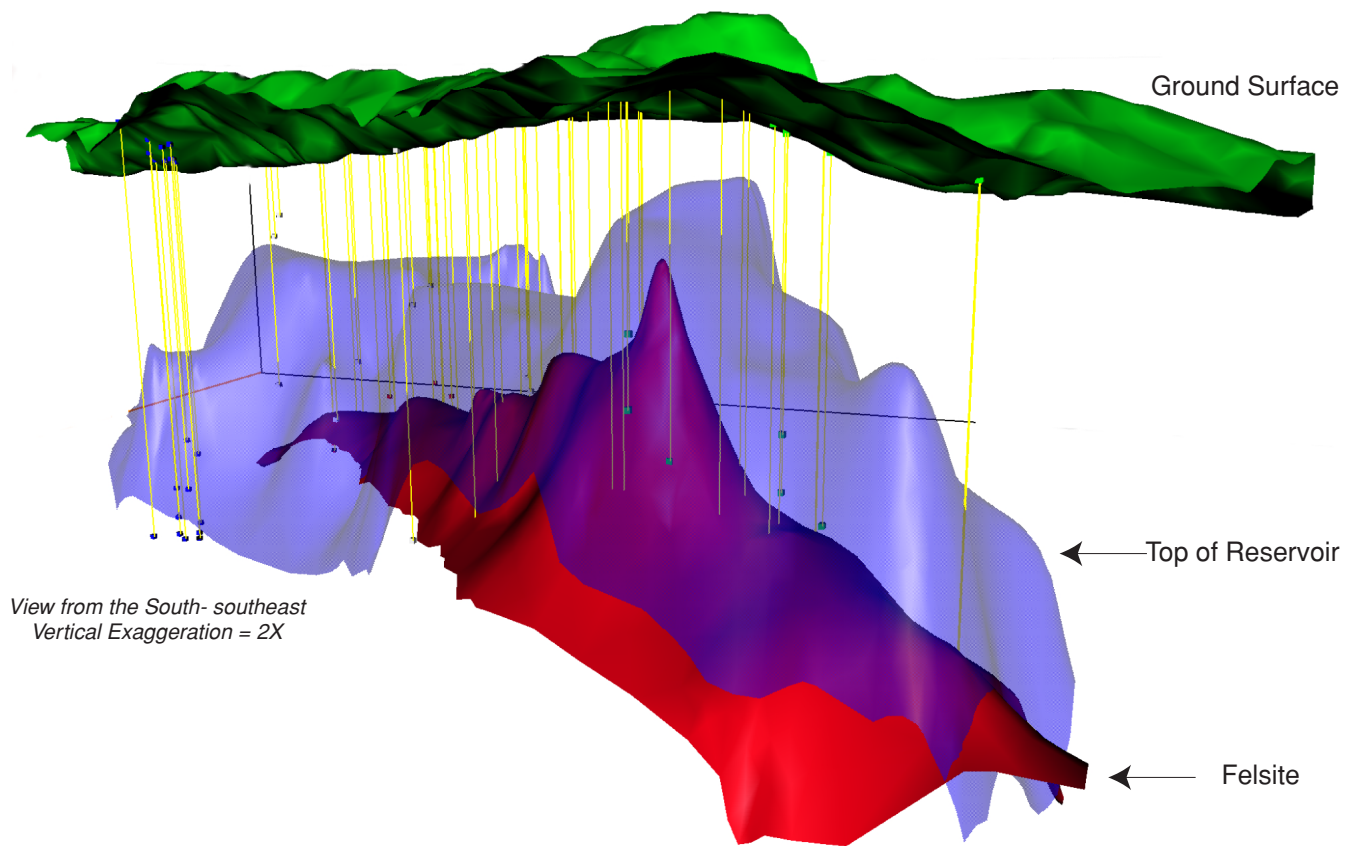


# Gas and isotope geochemistry of 81 steam samples from wells in The Geysers geothermal field, Sonoma and Lake Counties, California, U.S.A.

Open-File Report 99-304



# **Gas and Isotope Geochemistry of 81 Steam Samples from Wells in The Geysers Geothermal Field, Sonoma and Lake Counties, California, U.S.A.**

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**U.S. DEPARTMENT OF THE INTERIOR  
U.S. GEOLOGICAL SURVEY**

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## ABSTRACT

The Geysers geothermal field in northern California, with about 2000-MW electrical capacity, is the largest geothermal field in the world. Despite its importance as a resource and as an example of a vapor-dominated reservoir, very few complete geochemical analyses of the steam have been published (Allen and Day, 1927; Truesdell and others, 1987). This report presents data from 90 steam, gas, and condensate samples from wells in The Geysers geothermal field in northern California. Samples were collected between 1978 and 1991. Well attributes include sampling date, well name, location, total depth, and the wellhead temperature and pressure at which the sample was collected. Geochemical characteristics include the steam/gas ratio, composition of non-condensable gas (relative proportions of CO<sub>2</sub>, H<sub>2</sub>S, He, H<sub>2</sub>, O<sub>2</sub>, Ar, N<sub>2</sub>, CH<sub>4</sub>, and NH<sub>3</sub>), and isotopic values for  $\delta D$  and  $\delta^{18}O$  of H<sub>2</sub>O,  $\delta^{13}C$  of CO<sub>2</sub>, and  $\delta^{34}S$  of H<sub>2</sub>S. The compilation includes 81 analyses from 74 different production wells, 9 isotopic analyses of steam condensate pumped into injection wells, and 5 complete geochemical analyses on gases from surface fumaroles and bubbling pools.

Most samples were collected as saturated steam and plot along the liquid-water/steam boiling curve. Steam-to-gas ratios are highest in the southeastern part of the geothermal field and lowest in the northwest, consistent with other studies. Wells in the Northwest Geysers are also enriched in N<sub>2</sub>/Ar, CO<sub>2</sub> and CH<sub>4</sub>,  $\delta D$ , and  $\delta^{18}O$ . Well discharges from the Southeast Geysers are high in steam/gas and have isotopic compositions and N<sub>2</sub>/Ar ratios consistent with recharge by local meteoric waters. Samples from the Central Geysers show characteristics found in both the Southeast and Northwest Geysers.

Gas and steam characteristics of well discharges from the Northwest Geysers are consistent with input of components from a high-temperature reservoir containing carbon-rich gases derived from the host Franciscan rocks. Throughout the geothermal field, the carbon-isotopic composition of CO<sub>2</sub> is consistent with derivation of carbon from Franciscan metasedimentary rocks. NH<sub>3</sub> concentrations are high in most Geysers well fluids, and are 2-3 orders of magnitude greater than would be expected in a the gas phase exhibiting homogeneous equilibrium at normal reservoir temperatures and pressures. Evidently, NH<sub>3</sub> is flushed from the Franciscan host rocks at a rate that exceeds the reaction rate for NH<sub>3</sub> breakdown.

Many wells show clear influence by fluids from re-injection wells where steam condensate has been pumped back into the geothermal reservoir. Six wells were resampled over the time period of this study. One of these six wells was strongly affected by a nearby injection well. Three of the six resampled wells showed some signs of decreasing liquid/steam within the geothermal reservoir, consistent with "drying out" of the reservoir due to steam withdrawal. However, two wells exhibited little change.

Analyses of gases from five surface manifestations (fumaroles and bubbling pools) are roughly similar to the deeper geothermal samples in both chemical and isotopic composition, but are lower in soluble gases that dissolve in groundwater during transit toward the surface.

## INTRODUCTION

The following report contains gas and isotope analyses of fluids discharged from steam wells in The Geysers geothermal field, Sonoma, Lake and Mendocino Counties, California. These samples were collected and analyzed by a variety of USGS scientists over a period of 20 years. Though sampling and analytical methodologies were not always identical, we have made every effort to ensure that the data are consistent and comparable, and we believe the data published herein are accurate within the precisions reported. In addition to analytical data and locations, we have provided additional information on the wells, such as their total depth, depth of casing, temperature, and pressure, to aid workers in their use of the data.

## ACKNOWLEDGMENTS

Gas sampling and analysis began in the mid-1970s under the guidance of Dr. Alfred H. Truesdell. USGS Menlo Park employees involved in work on The Geysers included Nancy Nehring, Mary Stallard, Terrie Winnett, Marianne Guffanti, Terry Cheatham, and Julie Kennedy. In addition, a variety of USGS people helped with sample analysis, including Carol Kendall, Bill Evans, L. Doug White, Steve Silva, Mark Huebner (all from Menlo Park), Tyler Coplen (Reston), and W.C. Pat Shanks III (Denver). We appreciate the assistance and cooperation of Brian Koenig, Tom Powell, and Phil Molling (Unocal Corporation), Tom Box and Joe Beall (Calpine Corporation), John Stackleberg and Jill Haizlip (Geo Corporation and CCOC), Deb Bergfeld (University of New Mexico), and Ken Stelling and Ali Khan of the Division of Oil, Gas, and Geothermal Resources, California Department of Conservation. This work was partially funded through the Department of Energy-U.S. Geological Survey Interagency Agreement No. DE-AI-01-91-CE-31020. Joe Moore (EGI) and Julie Donnelly-Nolan (USGS) carefully reviewed the manuscript.

## BACKGROUND

### ABOUT THE GEYSERS

The Geysers steam field is a vapor-dominated geothermal reservoir located in the Mayacmas Range in northern California, about 150 km north of San Francisco (fig. 1). It covers about 150 km<sup>2</sup> on the border of Lake, Mendocino, and

Sonoma Counties. In vapor-dominated systems, water is present as both liquid and steam, though vaporized water constitutes the pressure-supporting medium. Thus, these reservoirs are significantly underpressured with respect to a hydrostatic load and must be tightly sealed by low-permeability rocks to prevent the system from being flooded by colder infiltrating ground water (White and others, 1971).

The Geysers is the most obvious manifestation of a large heat-flow anomaly associated with the adjacent Clear Lake volcanic field, a late Pliocene to Holocene magmatic system

(Hearn and others, 1981, 1995; Donnelly-Nolan and others, 1981). The Geysers steam field is oriented northwest-southeast, parallel to the southwest edge of the volcanic field. It is bordered to the southwest and northeast by active NW-trending faults of the San Andreas fault system. Apparently, these faults and associated lithology changes act as permeability barriers that contain the geothermal system (Goff and others, 1977).

Though the total electrical generation of The Geysers exceeded 2,000 MW in the late 1980s, current production

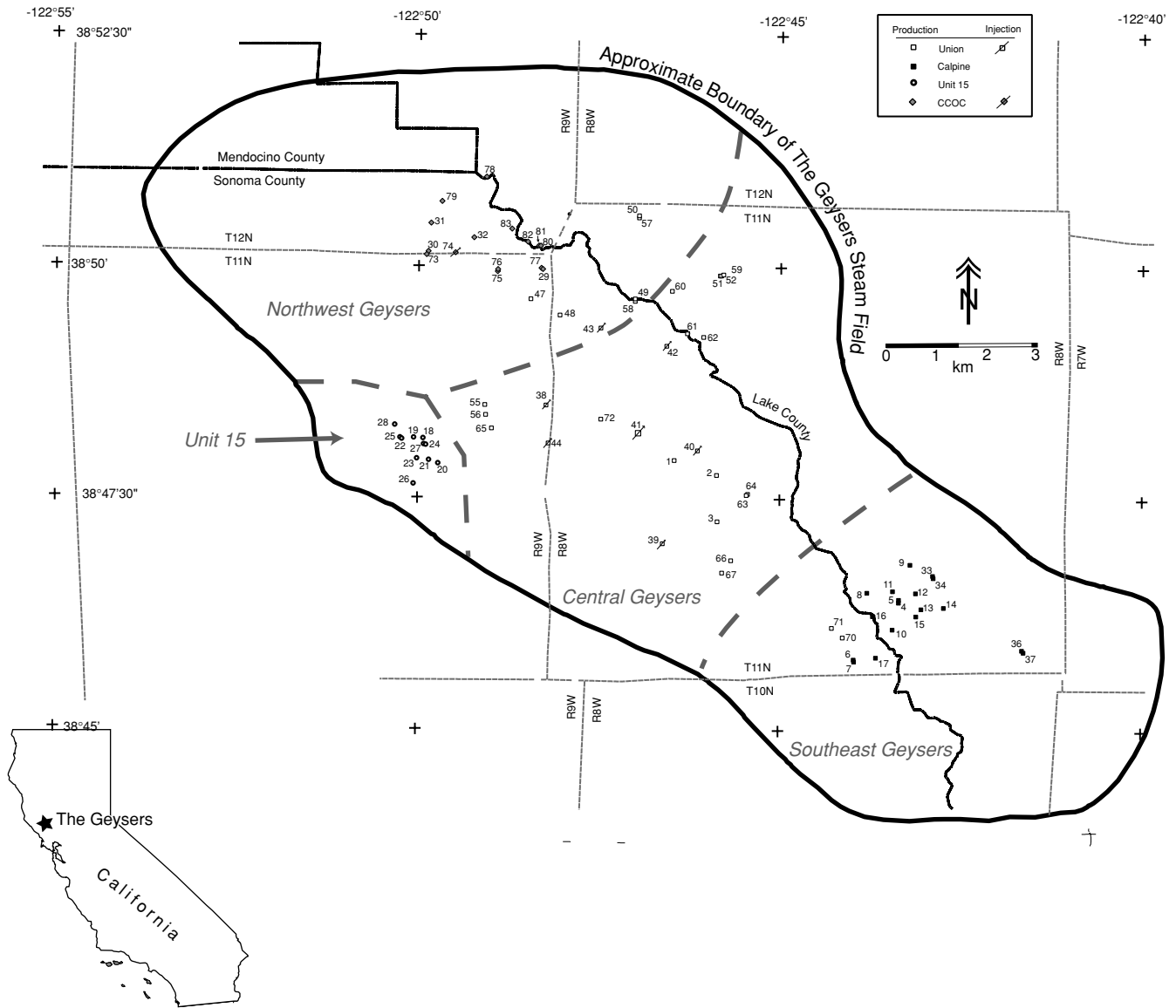


Figure 1.—Well locations for this study. Well symbols (see legend) correspond to the geothermal operator that operated the well at the time of sampling. Unit 15 wells, operated at the time by GEO Corp., are listed by their unit name. Injection wells are designated by small arrows that pass through the symbol. Latitude and longitude tics, county boundaries and some township and range boundaries are shown to give context relative to other published maps. Gray lines indicate informal region boundaries that separate the field into Southeast, Central, Northwest and Unit 15 sectors. They are not necessarily consistent with terminology used in other studies. The outline of the steam field is from California Division of Oil and Gas (1992).

is < 1,000 MW from 300-400 active wells. In 1998, geothermal operators began piping treated wastewater from Lake County to The Geysers to recharge the geothermal system. In the future, wastewater from Santa Rosa also may be injected. Both of these projects are likely to change the chemistry and isotopic composition of steam and gas discharges from The Geysers. As such, the analyses reported here will be useful in tracking future changes in the composition of steam from The Geysers.

## HISTORY OF THE GEYSERS STEAM FIELD

The Mayacmas Range never contained actual geysers, but early explorers to the region did find fumaroles, mud pots, and steaming ground. In the late 19th century, the Geysers Resort, built where Geyser Canyon intersects Big Sulphur Creek, was popular as a spa capable of hosting 200

guests. Koenig (1992) reviewed the history of geothermal development at The Geysers, and the following few paragraphs summarize material in his review. Though the first attempt to generate electricity was a commercial failure, it did provide enough power to light The Geysers Resort in the late 1920s. B.C. McCabe established the Magma Power Company in the early 1950s and completed 6 wells between 1955 and 1957. Magma, together with Thermal Power, signed a contract with the Pacific Gas and Electric Company (PG&E) to provide steam for electricity generation in late 1958. PG&E Unit 1, The Geysers first power plant, came “on line” in June 1960, with a 12.5-MW turbine generator. These initial wells were less than 1,400 ft (427 m) deep, but as later exploration spread NW and SE, significant steam resources were found at greater depth. By 1965, drilling had spread to the northwest and southeast along Big Sulphur Creek (fig. 2), and some wells exceeded 5,000 ft (1,524 m) in depth. Several more powerplants were constructed in the late 1960s, and the cumulative generating capacity of the steam field reached 192 MW by late 1971.

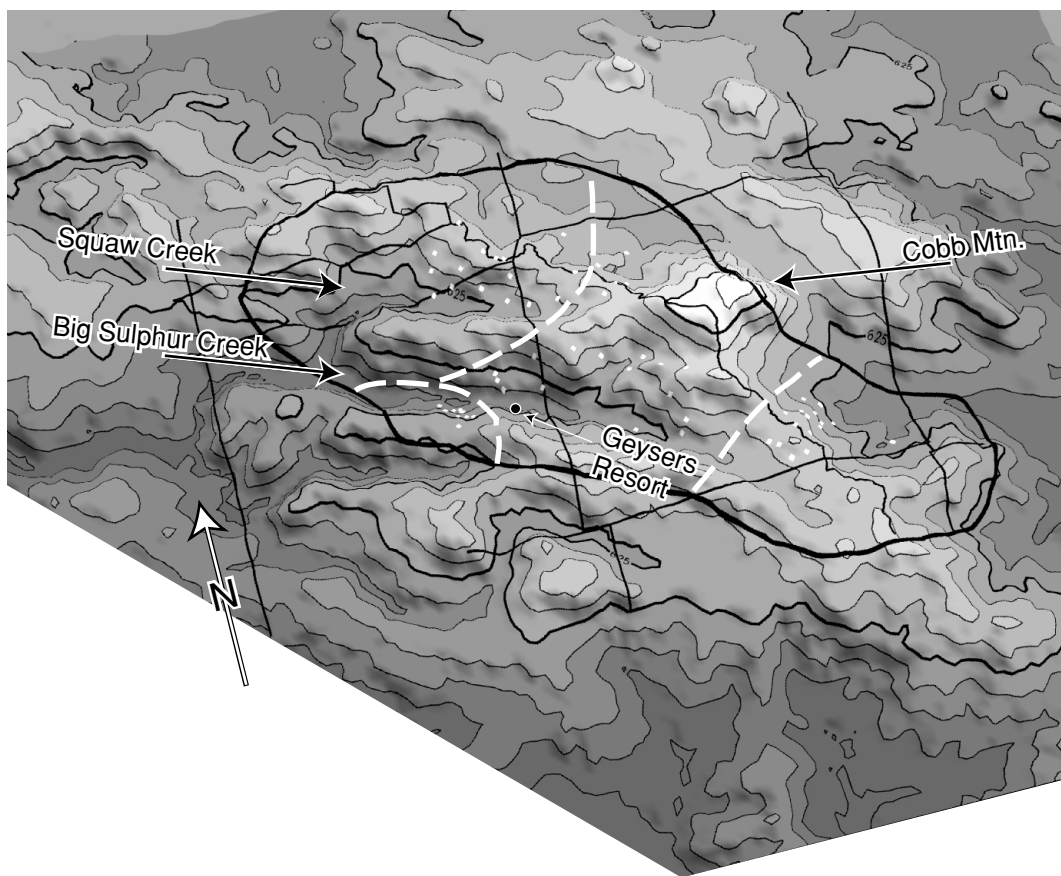


Figure 2.—Perspective image of the topography of The Geysers region as seen from the south-southwest (vertical exaggeration =3X). Contour interval is 125 meters. The two bold contour lines are at 625 and 1,250 m. The steam-field boundary, county lines, and township and range boundaries (as in fig. 1) are overlain, as are the well locations (white dots). The white lines denote the four regions as outlined in the text and shown in fig. 1. Scale varies throughout the diagram but can be estimated by comparison of the field outline to that in fig. 1. The trend of the steam field clearly mimics that of the regional topography.

The energy crisis of 1973-74 spurred a large increase in geothermal exploration and development in subsequent years, and the electrical generating capacity at The Geysers reached 943 MW by late 1980, making it the largest power-producing geothermal area in the world. Development continued at a rapid pace through much of the 1980s, despite decreased steam prices and the increasingly common transfer of ownership of geothermal wells between companies.

Environmental regulations combined with the need to increase steam pressures led to reinjection of cooled, condensed steam into former production wells. Although Unocal (a.k.a. Union Geothermal) had begun a limited reinjection program in the Central Geysers as early as 1969 (Gambill, 1992), it was not until the early 1980s that the Northern California Power Agency (NCPA) and Calpine, operating in the

Southeast Geysers, began to reinject condensed steam (Klein and Eney, 1992; Beall and others, 1992).

By 1989, the operating capacity at The Geysers had reached over 2,000 MW. The rate of exploration finally slowed as steam prices decreased and exploration costs increased due to the great depths (>10,000 feet: 3,048 m) that were needed to find steam at the margins of the field (Koenig, 1992). At the same time, pressure declines within the field caused additional problems. Some powerplants operated below capacity, and others were forced to close. In 1995, the steam field was producing about 1,200 MW, approximately 60% of its capacity, but still the largest geothermal field in the world. In all, ~770 deep wells have been drilled into the geothermal system (locations for sampled wells are shown in figs. 1 and 2).

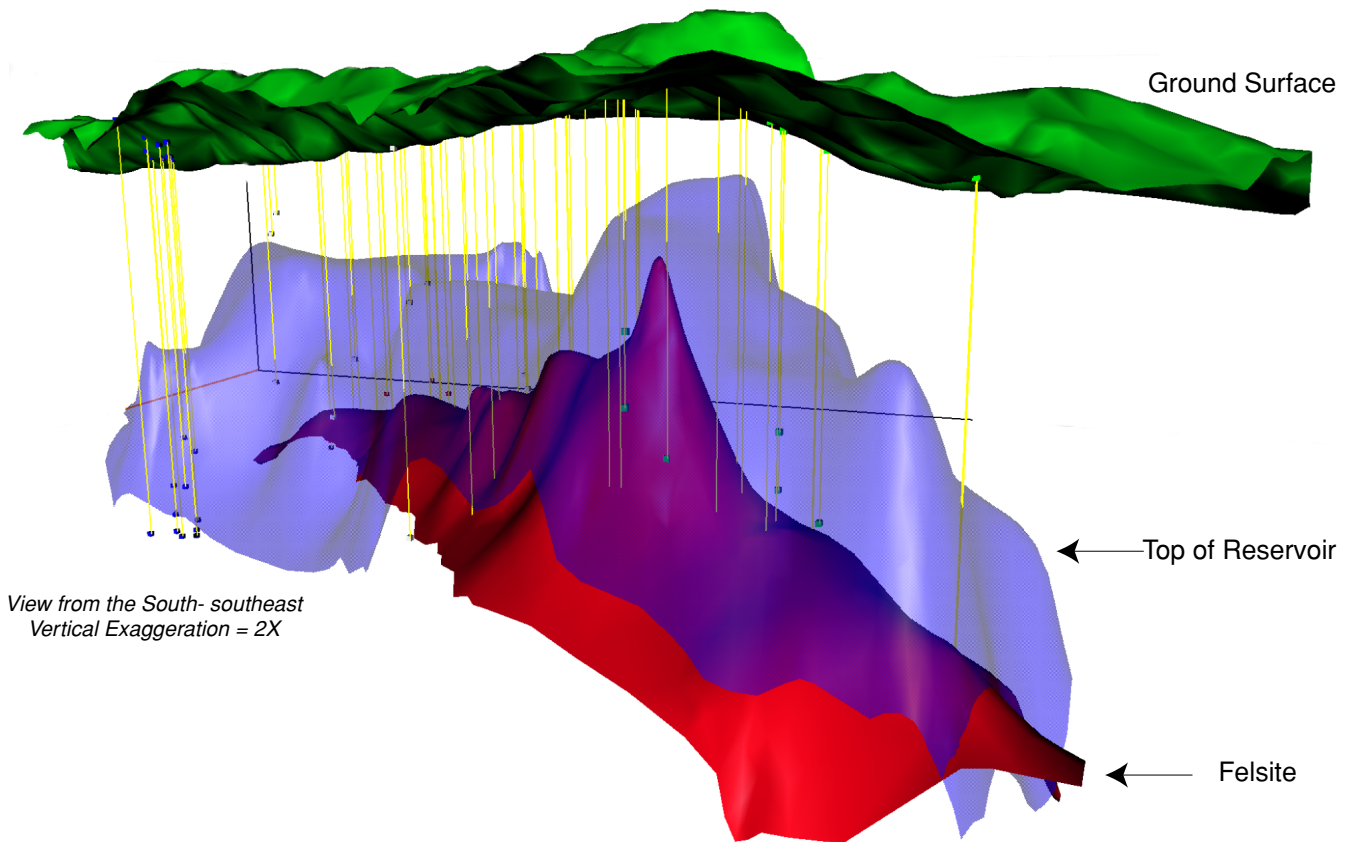


Figure 3.—Schematic diagram of the “felsite” intrusion, overlying geothermal reservoir and surface topography at The Geysers steam field: view is from the south-southeast (700 m beneath the ground surface). Vertical exaggeration equals 2X. The red surface is the intrusion/pluton, which intrudes closest to the surface toward the center of the diagram, in the south-central Geysers. The blue surface represents the top of the geothermal reservoir. Green is surface topography. Yellow lines represent the approximate location and depths of wells, with small squares at the well bottoms. In reality, most wells are inclined (deviated), and are thus not accurately depicted by the vertical lines on the figure. The felsite and reservoir surfaces were constructed with data from the “Top of Reservoir” and “Top of Felsite” maps in Unocal and others (1992) and are approximate representations of the actual geometries of these features. Note the location of the wells at the left side of the diagram, from the Unit 15 site, which are found at the edge of the geothermal reservoir. The reservoir itself is everywhere located above the felsite and mimics its general shape. Scale varies throughout the diagram.

## GEOLOGY OF THE GEYSERS RESERVOIR

The Geysers geothermal field lies within the central belt of the Franciscan Complex, an assemblage of deep oceanic deposits formed in the Mesozoic Era and early Tertiary Period. In this region, the Franciscan assemblage consists primarily of regionally metamorphosed graywacke, argillites, and cherts. Numerous thrust faults result in a complex overlapping of these rock types with Franciscan melange, serpentinite, and greenstones (McLaughlin, 1981). Most of the thrusting occurred contemporaneously with sedimentation and subduction.

During the last 2-3 million years, northwest-oriented, strike-slip faults have formed as part of the San Andreas fault system and offset many of the thrust packages within the steam field. The Colloiyami and Mercuryville strike-slip faults form the northeast and southwest edges of The Geysers field, respectively creating a geometry for the steam field that is elongate parallel to the faults of the San Andreas system.

The steam field is also coaxial with a large composite intrusion (fig. 3), informally known as "the felsite" (Schriener and Suemnicht, 1981). This composite intrusion of granite, granodiorite, and microgranite porphyry was emplaced at about 1.1-1.2 Ma (Dalrymple, 1993; Grove and others, 1998) and is thought to be an intrusive equivalent of Cobb Mountain dacite and rhyolite, part of the Clear Lake volcanic field (Hulen and Walters, 1993; Hulen and others, 1997b). It appears highly likely that the geothermal system was created by intrusion of "the felsite" to create a liquid-dominated reservoir about a million years ago (Sternfeld, 1981; McLaughlin and others, 1983; Moore and Gunderson, 1995; Hulen and Nielson, 1996). Besides its heat, the "felsite" may have induced some of the fracturing that has created the permeability necessary to sustain an economic geothermal system (Hulen and Walters, 1993). The liquid-dominated reservoir was characterized by studies of fluid inclusions and oxygen isotopes (Moore and Gunderson, 1995) and appears to have persisted until 0.28-0.25 Ma, when venting and consequent boiling produced the present-day geothermal system (Shook, 1995; Hulen and others, 1997a, b). More recent, underlying, unsampled intrusions likely provide the heat that is being "mined" by the current geothermal system (Hearn and others, 1981; Truesdell and others, 1987; Donnelly-Nolan and others, 1993). The presence of recent intrusions is consistent with  $^3\text{He}/^4\text{He}$  ratios in geothermal discharges (Kennedy and Truesdell, 1996) and the very high temperatures ( $\sim 340^\circ\text{C}$ ) recorded in deep wells in the Northwest Geysers (Walters and others, 1992).

The productive portion of the geothermal reservoir is primarily located in weakly metamorphosed Franciscan rocks but extends down into the felsite intrusion and its surrounding biotite-hornfels-grade aureole. Most of the reservoir rocks are not highly porous, ranging from 1 to 5 percent (Gunderson, 1992a), and thus the steam appears to be located primarily in fractures, though there is some disagreement on the orienta-

tion of the most important steam-bearing fractures (cf. Thompson and Gunderson, 1992; Beall and Box, 1992). Mapping of  $\delta\text{D}$  anomalies caused by reinjection of condensate provides evidence that many steam-bearing fractures have a NNE trend (Beall and others, 1992), consistent with WNW regional extension.

## CHARACTERISTICS OF THE GEYSERS STEAM RESERVOIR

As noted above, The Geysers reservoir is a vapor-dominated reservoir that is underpressured with respect to a hydrostatic pressure gradient. As suggested by White and others (1971) and modeled by Pruess (1985) and Shook (1995), vapor-dominated systems represent heat pipes wherein upward-flowing steam condenses to liquid droplets at the base of the caprock, which then flow back down through the reservoir. Such a mechanism can account for the very high heat flow in the region, where heat is transported up toward the surface as steam. White and others (1971) proposed that a deep boiling brine should underlie the geothermal system and that pressures would therefore return to hydrostatic levels at depth. To date, evidence for a deep water table remains elusive, though fluid-inclusion evidence shows that dense, saline liquids have existed during the history of The Geysers geothermal system (Moore and Gunderson, 1995).

Because the reservoir contains both steam and liquid water droplets, the compositions of well discharges are a function of the relative amounts of the two phases available for transport to the surface (Truesdell and White, 1973; Truesdell and others, 1987). The relative reservoir steam saturation (the proportion of steam to liquid water + steam, or "y" value) can be estimated by using a combination of gas equilibria and gas solubility equations (D'Amore and Celati, 1983; D'Amore and Truesdell, 1985). The latter authors found that well discharges from the Southeast Geysers were composed mostly of recently boiled liquid water ( $y = 0.01$  to  $0.05$ ), whereas fluids from the Northwest Geysers were predominantly derived from reservoir steam ( $y = 0.1$  to  $1.0$ ). These fieldwide characteristics can partially be traced to different temperature reservoirs that have been identified.

The Geysers steam field is divided into two principal reservoirs, a normal-temperature reservoir and a high-temperature reservoir (NTR and HTR), which appear to be hydrologically connected. In the NTR, temperatures are close to  $240^\circ\text{C}$ , with a pressure around 35 bars. Pressures in the HTR are only marginally higher, though temperatures normally exceed  $300^\circ\text{C}$  and have been measured as high as  $342^\circ\text{C}$  (Walters and others, 1992). The host rock for the NTR is normally Franciscan graywacke; though the HTR is found typically in the hornfels, no obvious changes in lithology occur as one passes from the NTR to the HTR (Walters and others, 1992). Moreover, the temperature and pressure gradients be-

tween the reservoirs are continuous. Wells that extend into the HTR, such as the Prati wells from the Northwest Geysers, pass through the NTR, and so sampled fluids represent a mixture of steam and gas from both reservoirs. Though the HTR may reside beneath the NTR throughout The Geysers steam field, it has only been sampled in the Northwest and North-Central Geysers, where wells extend below the 5,900 ft (1,798 m) bsl elevation at which the HTR is located. Kennedy and Truesdell (1996) conjecture that the low  $\gamma$  and absence of evidence for the HTR in the Southeast Geysers may be due to the greater meteoric recharge (from Cobb Mountain) and greater heat conduction due to the shallower reservoir depths.

Geochemically, there are a number of obvious trends that differentiate the Southeast Geysers from the Northwest Geysers. Steam discharges in the Southeast Geysers have an isotopic signature of slightly oxygen-exchanged meteoric water that is similar to present-day streams and springs in the region (Truesdell and others, 1987). In contrast, samples from the Northwest Geysers have elevated  $\delta^{18}\text{O}$  and  $\delta\text{D}$  and show far less influence of present-day meteoric water. Haizlip (1985) suggested that this isotopically enriched water was equivalent to "connate" or formation waters (derived from ancient seawater) that discharge from Franciscan and Great Valley sediments and are found throughout the Clear Lake volcanic field (White and others, 1973). Donnelly-Nolan and others (1993) proposed that this end member is instead evolved meteoric fluid that has undergone near-closed-system, repeated boiling episodes within Franciscan rocks in areas of high heat flow. Whatever its origin, Gunderson (1992b) showed that the trend in steam discharges is also accompanied by changes in the oxygen-isotope composition of host rocks in the geothermal reservoir. In the Southeast Geysers, host rocks have lower  $\delta^{18}\text{O}$  than in the Northwest Geysers, consistent with higher meteoric-water/rock ratios over the history of the geothermal system. Apparently, natural recharge of meteoric water occurs mainly in the southeast part of the field (Truesdell and others, 1987).

The Northwest Geysers is also characterized by higher gas/steam ratios than the rest of the field, part of which is due to the influence of the high-gas-to-steam HTR (Walters and others 1992). The higher gas content of the Northwest Geysers wells may be due partly to the high temperatures associated with the HTR, which causes breakdown of organic matter in Franciscan rocks, and to the lesser flushing by meteoric water in that part of the field over the lifetime of the system (Gunderson, 1992b). Steam from the Northwest Geysers and parts of the Central Geysers are also high in HCl (Haizlip and Truesdell, 1989), values of which can reach nearly 100 ppm in bulk steam (Kennedy and Truesdell, 1996). This has caused considerable corrosion-related problems, and the operating companies have created mitigation systems to raise the pH of condensing steam in the wellbore (Bell, 1989).

Gas samples from the Northwest Geysers have been shown to have high  $^3\text{He}/^4\text{He}$  ratios (R/Ra of 6.3 to  $>8.3$ ; Torgerson and Jenkins, 1982; Kennedy and Truesdell, 1996), up to values typical of MORB. Kennedy and Truesdell (1996)

interpreted these values to indicate modern magma degassing beneath the Northwest Geysers, possibly extending south underneath the entire geothermal field. The degree to which a magmatic input influences the noncondensable-gas content (other than He) of The Geysers geothermal fluids is not clear.

## SAMPLE COLLECTION

Sampling procedures, described in greater detail in Fahlquist and Janik (1992), are summarized below. Because The Geysers geothermal reservoir is a steam field rather than a liquid-dominated field, samples could be directly taken from the sampling port on an insulated steam line near the well-head. All acid mitigation systems were deactivated to prevent sample contamination and to ensure minimal condensation of fluid in the wellbore before sample collection. In addition, precautions were taken to prevent condensation at the inlet to the sampling apparatus.

The high temperatures of well fluids required careful cooling prior to collection in the sample bottle. A double-coil condenser of 1/4-in.-O.D. stainless-steel tubing was connected to the steam line by a regulating valve. The first coil was immersed in water that was allowed to boil, effectively reducing the temperature of the sample to about 100°C. The second coil was placed in an ice-water bath, which condensed the water vapor and reduced the sampling temperature to about 30°C. Flow rate was regulated by a valve connected to the end of the second coil. The steel coil was then connected to the sample bottle with silicone tubing.

The gas sampling bottle, a modified-Giggenbach bottle (Nehring and Truesdell, 1977) with known volume, was weighed, 1/4- to 1/3- filled with a known amount of 4 N NaOH solution, and then evacuated so that the internal pressure of the bottle approximated that of the vapor pressure of the NaOH solution.  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ , and  $\text{NH}_3$  were dissolved in the NaOH solution, which was diluted by condensed steam. Other gases (He, Ar,  $\text{N}_2$ ,  $\text{CH}_4$ , and  $\text{H}_2$ ) filled the headspace in the bottle. Sample collection was complete when: (1) the vacuum in the head space had disappeared and the bottle's internal pressure approached atmospheric pressure, or (2) if the caustic solution had become nearly saturated with soluble gases (typically only for fumaroles), or (3) if addition of condensed steam caused the bottle to become more than 75% full.

Steam condensate was collected from the silicone tubing at the outlet of the condenser for isotopic analysis. Samples were collected in 60-mL glass bottles and fitted with airtight caps to prevent evaporation.

Five samples were collected from surface manifestations. G95-01, 02, 03, and 04 were collected by inserting a funnel into standing water in Hot Springs Creek and at Old Geysers. Gas passing through the funnel was collected into an evacuated gas bottle partly filled with caustic solution, as above. This sampling configuration results in loss of soluble gas components such as  $\text{NH}_3$ , which dissolve in the standing



water. Sample G96-01 was collected from a fumarole at mile-post 2.51 on Big Sulphur Creek Road. A titanium tube was placed directly in the vent, mud was packed around the tube to prevent air entrainment, and the Ti tube was connected to a gas bottle with silica-rubber tubing. Condensates were collected by coiling the sampling tube and placing it in a bucket of water, causing the steam to condense before flowing into a 60-mL glass bottle with threaded top. Bubbles of non-condensable gas were allowed to escape. The condensate was kept significantly below 100°C to prevent boiling and significant evaporative loss, which would affect the isotopic composition of the sample.

## SAMPLE ANALYSIS

Gases in the sample-bottle headspace ( $H_2$ , He, Ar,  $CH_4$ ,  $N_2$  and  $O_2$ ) were analyzed by gas chromatography at Menlo Park. After measuring the initial pressure in the headspace, two Carle AGC 111 gas chromatographs with thermal conductivity detectors were connected to a common sampling inlet system to allow the samples to be injected at known pressures less than 1 atmosphere (Fahlquist and Janik, 1992). One chromatograph used Ar as a carrier gas, and the other used He. Before the sample analyses, standards of known composition were used for calibration. Sample concentrations were determined by reference to the peak areas for the standards.

After the gas analysis, the total volume of caustic (with dissolved sample gases and added steam condensate) was determined. In addition, part of the caustic liquid was isolated for a density determination that was necessary for later quantification of the total gas analysis.  $NH_3$  within the caustic solution was determined by gas-sensing electrode. For all samples except those collected in 1981 (G81 samples),  $CO_2$  was liberated from the caustic solution by addition of phosphoric acid on a stable-isotope-extraction line. The number of micromoles of  $CO_2$  was noted for a given volume of caustic solution. The evolved  $CO_2$  was then kept for later isotopic analysis of  $\delta^{13}C$ . G81 samples had their  $CO_2$  concentrations quantified by precipitation of carbonate as  $SrCO_3$ , a technique that is not as accurate as direct evolution of  $CO_2$  gas by addition of phosphoric acid. Earlier analyses, including those of Nehring (1981), overestimated  $CO_2$  because the amount of precipitated  $Sr(OH)_2$  was not accounted for and was assumed to be  $SrCO_3$ .  $H_2S$ , present in the solution as sulfide, was oxidized to sulfate with  $H_2O_2$  and then precipitated as  $BaSO_4$  by addition of  $BaCl_2$  to the solution, which first had been acidified with HCl to remove  $CO_2$ . Sulfide was quantified by determining the mass of  $BaSO_4$  precipitated per volume of caustic. For many samples, the  $BaSO_4$  was analyzed subsequently for its  $\delta^{34}S$  by mass spectrometry.

The mass of water added to the sample bottle during sample collection (as steam condensate) was then quantified by subtracting the masses of all previously determined components. Afterwards, the mass and volume fraction of all

sample constituents was determined. Full details on sample analysis are available in Fahlquist and Janik (1992).

## RESULTS

Tables 1 through 5 contain well attributes, sample geochemistry from production wells, mean well compositions, characteristics of injection wells, and temporal trends for sample geochemistry, respectively. Appendix I provides further documentation on sample acquisition, units, and context for data interpretation. Below, we provide short summaries of observed trends in The Geysers geochemistry data set.

Before proceeding, it is worth noting that well discharges are not substantially different in composition than those collected in 1925 and analyzed by Allen and Day (1927). Their analysis of Well 6, a 487-ft-deep well near The Geysers Resort (fig. 2) showed ~18,000 ppm by weight non-condensable gases, composed of 65.2%  $CO_2$ , 14.65%  $H_2$ , 15.40%  $CH_4$ , 3.45%  $N_2+NH_3$  and 1.35%  $H_2S$  (all in mol%), within the range of compositions noted in this study.

## SURFACE ELEVATION

Surface elevations of the sampled wells ranged from 506 to 1,037 m. The highest elevation in the steamfield is over 1,400 m on the summit of Cobb Mountain (fig. 2). The lowest elevation is about 250 m, at the confluence of Squaw and Big Sulphur Creeks in the Northwest Geysers. The topography is highly mountainous and irregular and is deeply dissected by numerous streams wherever the surface geology consists of Franciscan rocks. In contrast, the drainage network is only poorly developed on Cobb Mountain and the other highly porous Clear Lake volcanics, (Goff and others, 1977; Kennedy and Truesdell, 1996). As mentioned above, the terrain has a distinctive northwest trend caused by Quaternary faulting.

## TOTAL DEPTH

Most wells are over 2,000 m deep, with the exception of some of the older ones, such as Sulphur Bank 8 and 15, drilled in the early 1960s. Wells in the Northwest Geysers are the deepest, extending up to and over 3,000 m (fig. 3).

## TEMPERATURE

Temperatures measured at the wellheads were quite consistent at 175 to 195°C. Temperatures reported to DOGGR have a wider range, plausibly because they represent more variable conditions (shut-in, bleed, etc.), whereas the USGS samples were taken during normal operations. As shown in

figure 4, most samples fall within the steam region of a temperature versus pressure plot, but right along the saturation line for liquid water. Samples with the highest temperatures and pressures, presumably reported to DOGGR immediately after being shut-in, approach the conditions expected for the initial reservoir before to development (White and others, 1971). Such samples have pressures and temperatures close to the maximum enthalpy of saturated steam (235°C and 30.6 bars). A few samples have high temperatures at relatively low pressures and plot well within the steam field. Some of these samples come from the Northwest Geysers and may have some input from the high-temperature reservoir (HTR).

### PRESSURE

Most wellhead pressures ranged from 8 to 10 bars and reflect pressures along the univariant curve for saturated steam (see above).

### pH FIELD VERSUS pH LAB

Field measurements of pH were typically 0.5 to over 3.0 log units lower than corresponding measurements of the same samples in the lab. This is likely due to degassing of CO<sub>2</sub> between field sampling and laboratory analysis. Samples from the Northwest Geysers appear to have had slightly higher field pHs and lower laboratory pHs.

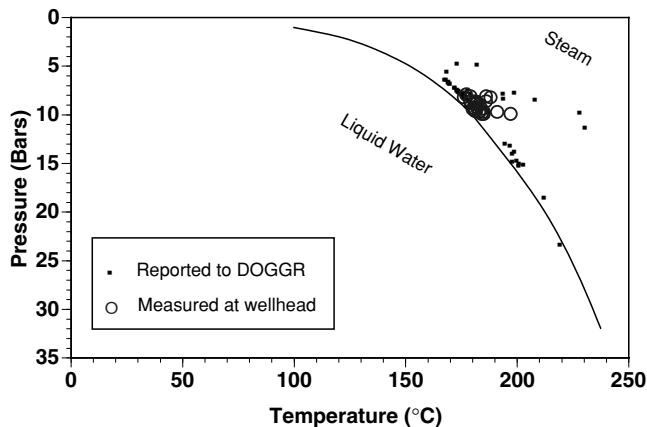


Figure 4.—Temperature versus pressure for Geysers wells as measured at wellhead. Unfilled circles represent data measured at wellhead by operator on day of sampling. Small filled squares are data reported to the California Division of Oil, Gas, and Geothermal Resources for the month that sampling took place. Most of the data fall very close to the steam/water phase boundary, though some samples appear to lie totally within the steam field.

### STEAM TO GAS (MOLAR) AND GAS/STEAM

The wells from the Southeast Geysers were consistently higher in steam to gas than the Central And Northwest Geysers wells (fig. 5). Some of the Northwest Geysers wells contained over 5 % non-condensable gas. In contrast, most Southeast Geysers wells had less than 1000 ppm gas by weight.

### NONCONDENSABLE-GAS COMPOSITIONS

CO<sub>2</sub> concentrations in production-well fluids varied from 23.4 to 79.2 mol% of the noncondensable gases; however, most samples had 50-70% CO<sub>2</sub>. Some fumaroles tended to have more CO<sub>2</sub>, presumably because they had low NH<sub>3</sub> and H<sub>2</sub>S due to condensation of steam and loss of soluble gas to shallow ground and surface waters. CO<sub>2</sub> concentrations were higher in the Northwest Geysers than to the southeast and correlated negatively with H<sub>2</sub>S, steam/gas, and H<sub>2</sub> (fig. 5, 12a).

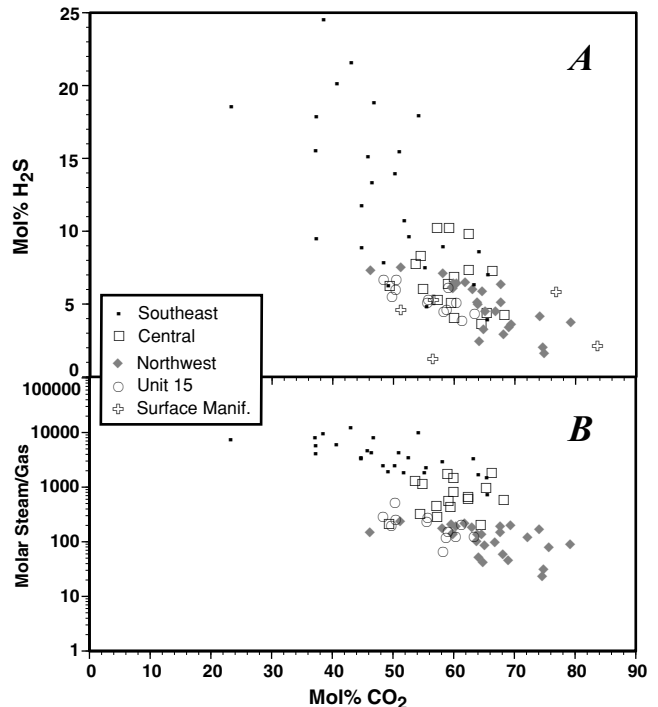


Figure 5.—Mol% CO<sub>2</sub> vs. mol% H<sub>2</sub>S and molar steam/gas for The Geysers wells and surface manifestations. **A.** The two gases show a clear negative correlation in all parts of the steam field. Samples from the Southeast Geysers are highest in H<sub>2</sub>S. **B.** The regions of the field are easily differentiated on a plot of molar Steam/Gas versus mol% CO<sub>2</sub>. Steam/gas clearly increases as one proceeds from northwest to southeast. Unit 15 wells have similar CO<sub>2</sub> to the Central Geysers but have lower steam/gas.

### $H_2S$

$H_2S$  concentrations varied from 1.6 to 24.4%, though most sample concentrations ranged from 3 to 9%. The highest relative concentrations were found in the Southeast Geysers wells, though given the low gas/steam in those samples, the absolute concentrations of  $H_2S$  would not be high.  $H_2S$  correlated strongly with  $H_2$  (fig. 6).

### $He$

$He$  concentrations were very low. Most were below detection, though a few constituted up to 0.07% of the noncondensable gases.

### $H_2$

$H_2$  concentrations varied from about 7 to 33% of the noncondensable gases. Most samples had between 10 and 30%  $H_2$ . As previously stated, a plot of  $H_2$  vs.  $H_2S$  shows a strong correlation between these two gases (fig. 6).

### $O_2$

As expected for a reduced geothermal system with high  $H_2S$ ,  $H_2$ , and  $CH_4$  concentrations,  $O_2$  concentrations were very low, even in samples with  $N_2/Ar$  ratios consistent with incorporation of air or air-saturated water. For example, G90-25 had very high  $N_2$ , and  $N_2/Ar$ , consistent with addition of air,

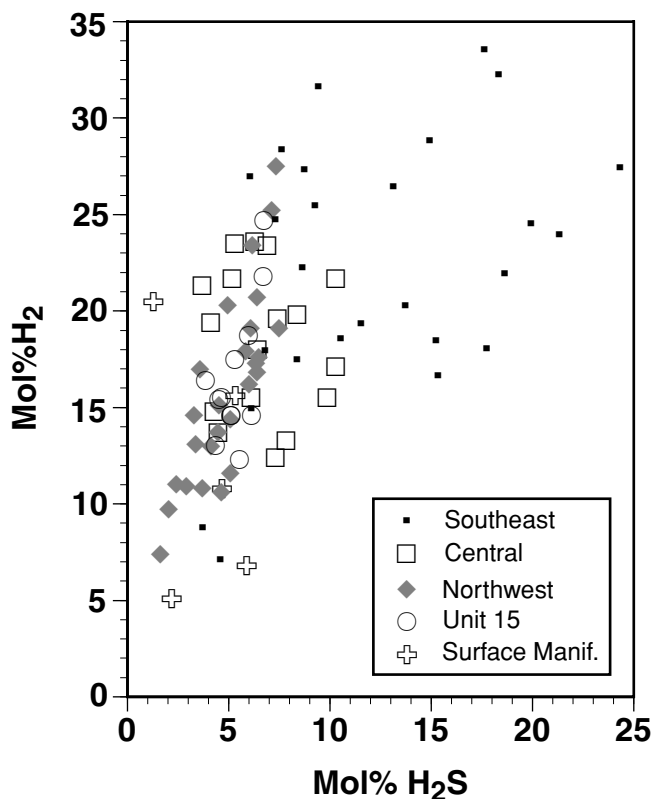


Figure 6.—Mol%  $H_2S$  vs.  $H_2$  in noncondensable gas from The Geysers wells. The two gases show a clear positive correlation in all parts of the steam field. Symbols as in fig. 5.

but the  $O_2$  had been reacted out prior to sampling or analysis.  $O_2$  reacts rapidly with steel casing and steam in the wellbore (producing  $H_2$ ). Only in samples where air was introduced during actual sampling is there likely to be any  $O_2$  entering the sample bottle. The only samples with significant  $O_2$  were the two surface manifestations collected as gas bubbling through water in Hot Springs Creek.

### $Ar$

$Ar$  concentrations were uniformly low, and generally below 0.1% of the noncondensable gas. The sample with the highest  $Ar$  content, G81-15 from the McKinley 1 well, was also unusual for having extremely low  $CO_2$  and high  $H_2$ . Air may have entered the wellbore at some stage, diluting the gaseous components in the geothermal fluid, and reacting with the steel casing to produce oxidized iron and  $H_2$ . In general, samples with the highest  $Ar$  concentrations had  $N_2/Ar$  ratios between that of air and air-saturated water (fig. 7).

### $N_2$

Most samples had  $N_2$  concentrations between 1 and 5 mol% of the noncondensable constituents, though a few had much higher values, presumably due to addition of air or large amounts of gas from air-saturated water. In general,  $N_2$  concentrations did not correlate positively with  $N_2/Ar$  ratios. However, they did correlate strongly with  $CH_4$  (fig. 8), as would be expected for thermal breakdown of organic matter.

### $CH_4$

$CH_4$  concentrations ranged from less than 1 to over 20 mol% of the noncondensable gas, though most samples tended to fall in the range of 3 to 13%. The highest values were found in the Unit 15 wells.  $CH_4$  concentrations generally correlated positively with gas/steam,  $CO_2$  and  $N_2$ .

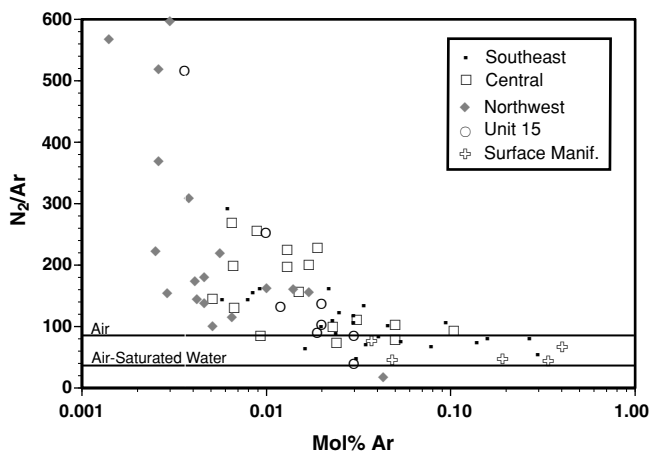


Figure 7.—Mol%  $Ar$  vs.  $N_2/Ar$  ratio for noncondensable gas from The Geysers wells and surface manifestations. Most samples with more than about 0.02 mol%  $Ar$  have  $N_2/Ar$  similar to that expected for atmosphere and meteoric water. Low- $Ar$  samples often tend to have much higher  $N_2/Ar$ . Samples from the Northwest Geysers have the highest  $N_2/Ar$ . Symbols as in fig. 5.

$NH_3$ 

$NH_3$  concentrations had a similar range to those of  $CH_4$ , most falling in the range of 3 to 12% of the noncondensable gases. The highest values were found in the Northwest Geysers (CCOC and Unit 15 wells), though high values were also found in other areas. Unlike  $CH_4$ , there was no obvious correlation between high  $NH_3$  and high gas to steam ratios.

 $N_2/Ar$ 

Though samples reach ratios as low as 18, the majority of The Geysers gas samples had  $N_2/Ar$  ratios greater than that of air (84) or air-saturated water (ASW: 38). Over 17 samples, primarily those with high gas/steam ratios had  $N_2/Ar$  over 200, and a number of others had very high values but were unquantified because their Ar concentrations were below the detection limit. The  $N_2$  in samples with  $N_2/Ar$  less than ASW probably has undergone partial conversion to  $NH_3$ .

 $\delta D$  and  $\delta^{18}O$  in steam

$\delta D$  plotted against  $\delta^{18}O$  range from close to the meteoric-water line to an oxygen-shifted endmember similar to magmatic and metamorphic fluids (fig. 9) and are consistent with values from Truesdell and others (1987) and Beall and others (1992). The most  $\delta^{18}O$ -shifted samples were those with high gas-to-steam ratios, found primarily in the Northwest Geysers. Waters pumped into injection wells was much higher in  $\delta D$ , consistent with evaporative fractionation at the surface to create isotopically heavy residual waters. Some Union samples collected in 1990 (primarily from the Southeast and Central Geysers) appeared to show some mixing with this injection-derived heavy water (similar trends discussed in detail in Beall and others, 1992). Southeast Geysers samples showed the greatest influence of meteoric water. Samples from the Northwest Geysers were strongly shifted towards a heavy-oxygen, high-deuterium end member and showed no obvious mixing with any reinjected fluid. The isotopically enriched end member is discussed further below.

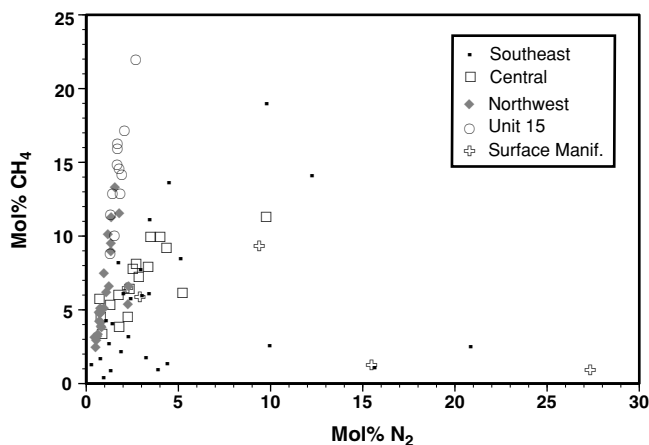


Figure 8.—Mol%  $N_2$  vs. mol%  $CH_4$  for noncondensable gas from The Geysers wells and surface manifestations. The two species are highly correlated in all parts of the field, though the slope of trends of  $N_2$  versus  $CH_4$  is different in the Northwest Geysers than for the Central Geysers.

 $\delta^{13}C$  in  $CO_2$ 

Samples from throughout the field had  $\delta^{13}C$  tightly clustered between about  $-12$  and  $-15\text{‰}$ , with no obvious trends within this range. Values of this magnitude are significantly lower than magmatic values ( $-8$  to  $-4\text{‰}$ ; Allard and others 1977; Allard, 1979) or carbon values from most marine carbonates (Rollinson, 1993). However, they are significantly greater than values typically associated with the breakdown of organic materials in sedimentary rocks, which are usually  $< -20\text{‰}$  (Rollinson, 1993).

 $\delta^{34}S$  in  $H_2S$ 

Though the two laboratories that provided sulfur-isotopic analyses gave values that differed somewhat, both gave values near zero (the total range for both data sets was  $-3.3$  to  $+1.9\text{‰}$ ). Such values are consistent with (but do not prove) an igneous source of sulfur to The Geysers geothermal reservoir.

## DISCUSSION

## RELATIVE GAS ABUNDANCES ACROSS THE GEYSERS STEAM FIELD

Molar steam-to-gas ratios averaged 4180 in wells from the Southeast Geysers; in contrast, they averaged 830 in the

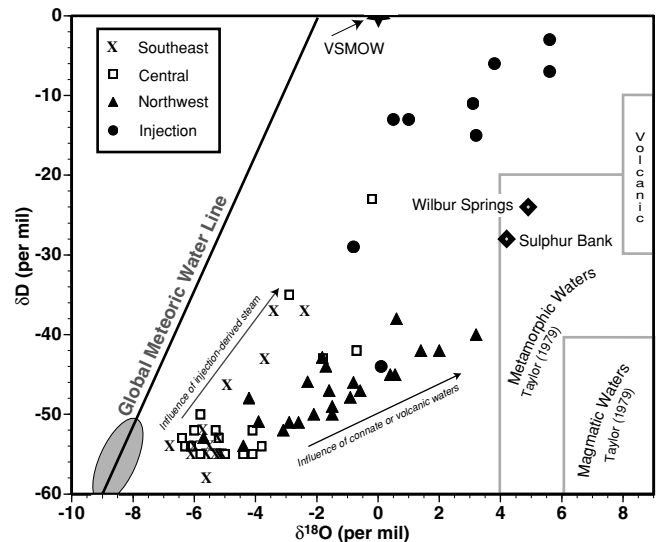


Figure 9.— $\delta^{18}O$  vs.  $\delta D$  for steam condensed from The Geysers wells. Units in permil relative to VSMOW. Samples from wells of the Southeast Geysers plot close to the global meteoric-water line, as do some samples from the Central Geysers. Some of these wells plot on a trend toward injection-derived steam. Samples from the Northwest Geysers form a trend toward an isotopically heavy end member similar to connate waters described by White and others (1973). Metamorphic and primary magmatic water boxes from Taylor (1979). Volcanic (andesitic) gas box from Giggenbach (1992). The global meteoric water line is from Craig (1961). Local meteoric-water (gray box) from Gunderson (1992).

Central Geysers, 130 in the Northwest Geysers, and 220 in Unit 15 wells (Table 3). Central Geysers wells were more variable, and some of these wells may receive input from the HTR.

Looking only at the noncondensable-gas compositions, Southeast Geysers wells had higher relative  $H_2S$  and  $H_2$  and lower  $CO_2$  than the other parts of the field (fig. 10). Organic gases were highest in the Northwest Geysers: Unit 15 had the highest proportion of  $CH_4$ , though Northwest Geysers wells had the highest relative  $NH_3$ . The Northwest Geysers wells also had the highest relative  $CO_2$  concentrations. Fumarole samples were different from well fluids in that they lacked  $NH_3$  and had higher relative proportions of  $CO_2$ ,  $N_2$ , and other gases (particularly  $O_2$  and Ar; figs. 7, 10, 11a).

General trends also appear in X-Y plots of noncondensable-gas abundances and ratios. A plot of  $CH_4$  vs.  $N_2$  shows that these two components correlate strongly throughout The Geysers field, though the slope of the trend for  $N_2$  vs.  $CH_4$  is different for the Northwest Geysers and Unit 15 parts of the field as compared to that in the Central and Southeast Geysers wells (fig. 8). Ternary diagram of  $CH_4$  or He with  $N_2$  and Ar identify strong trends away from air and meteoric-influenced fluids toward He- and  $CH_4$ -rich end members (fig. 11a, b). The Unit 15 and Northwest Geysers wells form a trend distinct from that shown by the Central Geysers wells and away from a component more elevated in Ar. Bubble diagrams, where the symbol size corresponds to a third variable, demonstrate that the  $N_2$  and  $CH_4$ -rich component in Northwest Geysers well fluids is also high in gas/steam and  $CO_2$  (fig. 12).

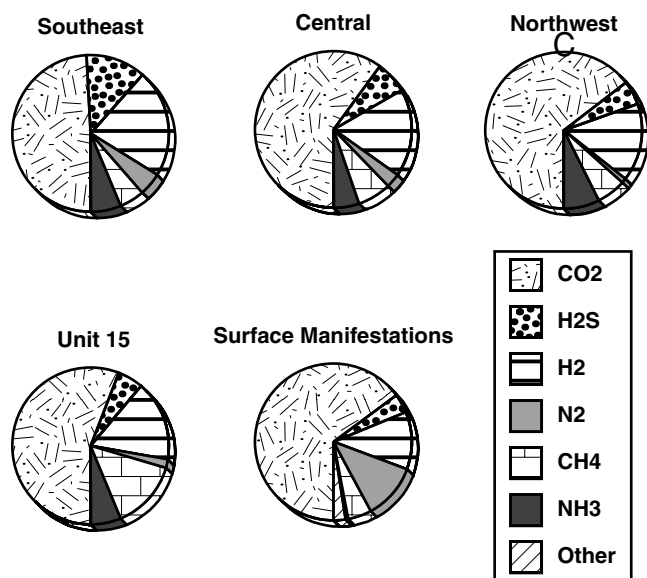


Figure 10.—Pie diagrams illustrate the relative amounts of various noncondensable gases in The Geysers well discharges.  $CO_2$  dominates the noncondensable fractions from all wells but is most abundant in the Northwest Geysers. Wells from the Southeast Geysers are highest in  $H_2S$  and  $H_2$ , whereas Unit 15 wells contain the highest  $CH_4$  concentrations.

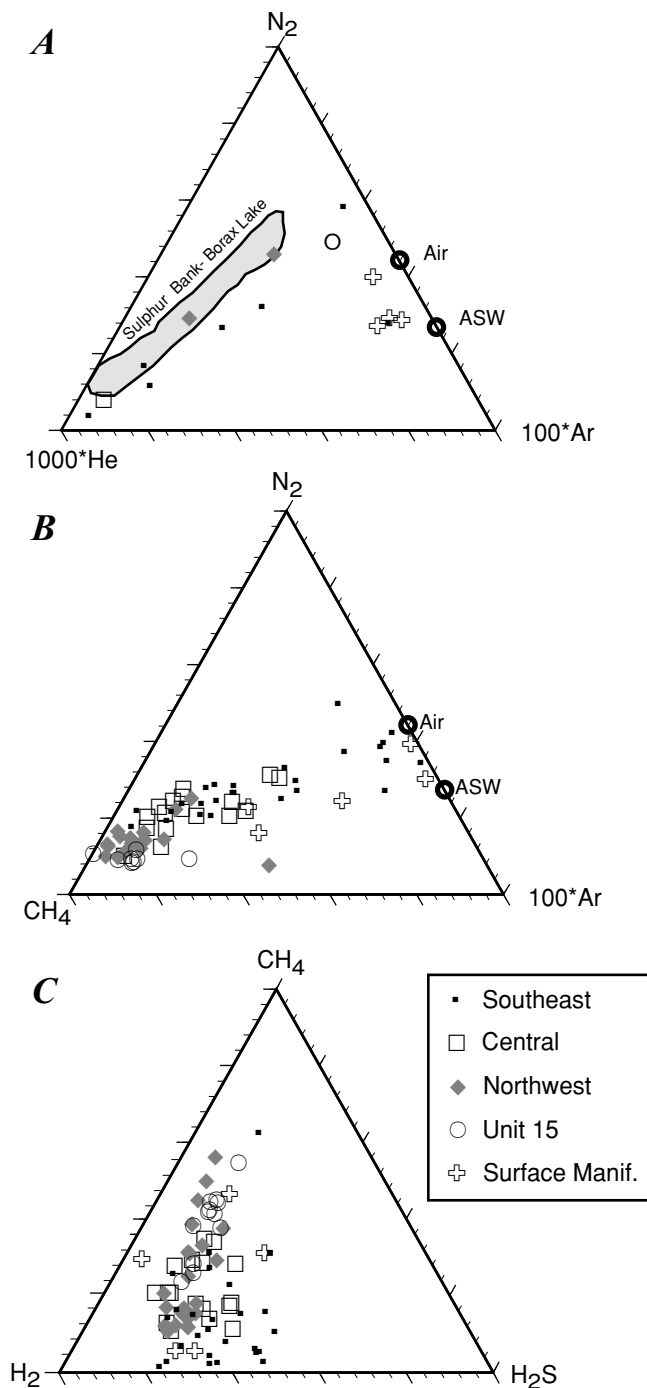


Figure 11.—Ternary diagrams for noncondensable gases from The Geysers steam field. **A.**  $N_2$ – $100^*Ar$ – $1000^*He$  diagram shows that samples range from air-saturated-water (ASW)- and air-derived- end members toward a He-enriched component consistent with either crustal or magmatic input to the system. The Geysers samples follow a trend similar to that for samples from the nearby Clear Lake volcanic field (Sulphur Bank-Borax Lake trend of Goff and others, 1995). **B.**  $N_2$ – $100Ar$ – $CH_4$  diagram has a similar trend to A, but toward a  $CH_4$ -rich organic/sedimentary endmember. **C.**  $CH_4$ - $H_2$ - $H_2S$  ternary figure demonstrates the high  $H_2$  and  $H_2S$  of most samples from the Southeast Geysers as compared to those from Unit 15 and Northwest Geysers wells, which trend toward a very  $CH_4$ -enriched composition.  $H_2/H_2S$  of Geysers well fluids is relatively constant.

There are two basic end members of Geysers gases. The first end member is high in  $\text{CH}_4$ ,  $\text{CO}_2$ , gas/steam, and  $\text{N}_2/\text{Ar}$  and is typically found in the Northwest Geysers, both in the Prati wells (CCOC) and Unit 15 (fig. 5b, fig. 11b, fig. 12). This type of sample is typified by Prati 25 (G91-10). The other end member is found in the Southeast Geysers. It is

lower in  $\text{CO}_2$ , and  $\text{CH}_4$  and higher in  $\text{H}_2\text{S}$  and  $\text{H}_2$  (fig. 11c, 13).  $\text{N}_2/\text{Ar}$  values are closer to air-saturated water (fig. 7), gas/steam ratios are low (fig. 13a), and  $d\text{D}$  and  $d^{18}\text{O}$  values (fig. 9) are only slightly removed from those found in local meteoric water. A representative sample of this group is McKinley 3 (G81-16).

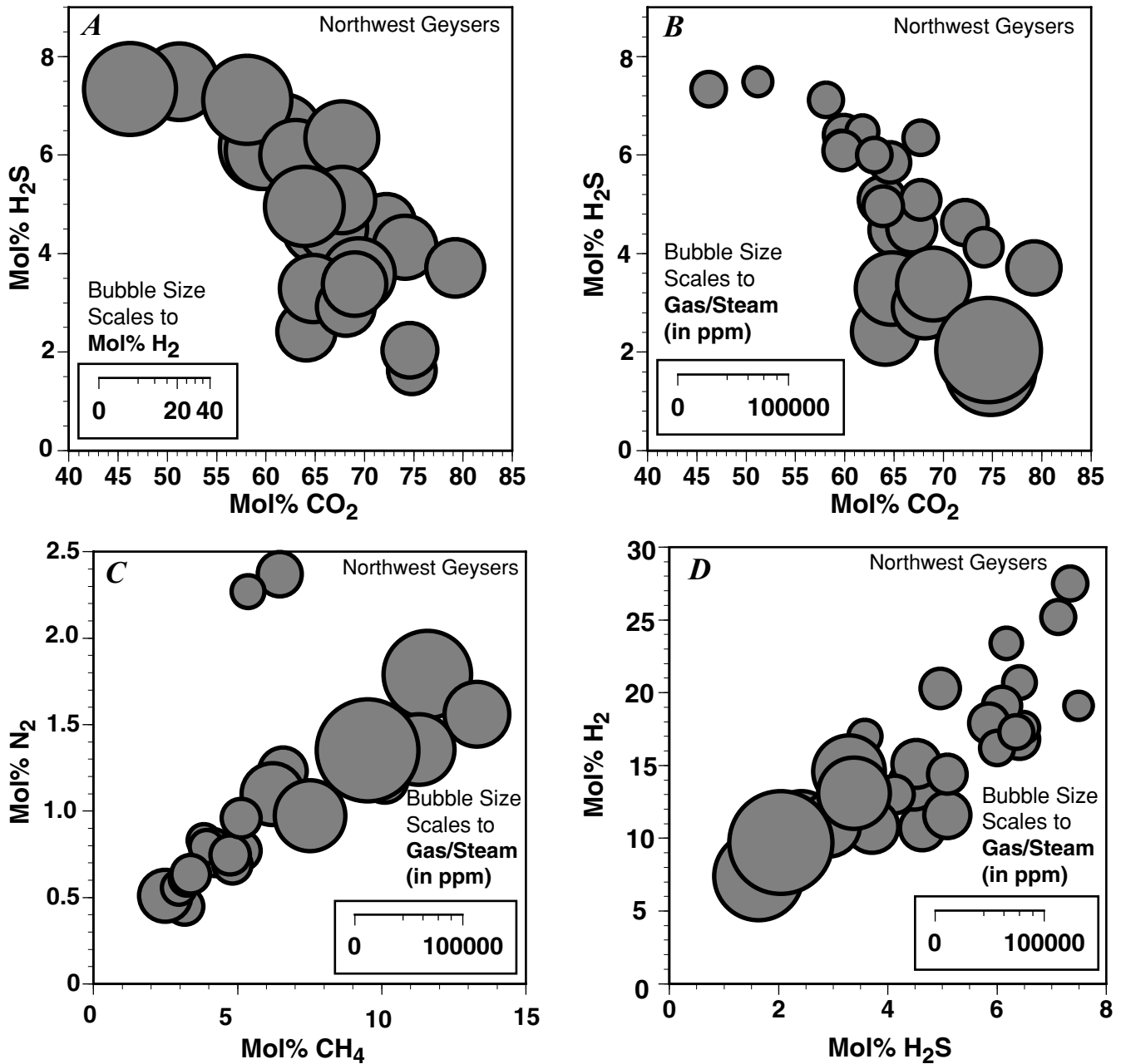


Figure 12.—Bubble diagrams for wells of the Northwest Geysers. The size of the symbol corresponds to the concentration of a third variable whose name and scale are shown as insets to each figure part. **A.** Mol%  $\text{CO}_2$  vs. mol%  $\text{H}_2\text{S}$  for Northwest Geysers wells with mol%  $\text{H}_2$  plotted as bubble diameter. **B.** Mol%  $\text{CO}_2$  vs. mol%  $\text{H}_2\text{S}$  for Northwest Geysers wells with gas/steam (in ppm by weight) plotted as bubble size. **C.** Mol%  $\text{CH}_4$  vs. mol%  $\text{N}_2$  for Northwest Geysers wells with gas/steam (in ppm by weight) plotted as bubble size. **D.** Mol%  $\text{H}_2\text{S}$  vs. mol%  $\text{H}_2$  for Northwest Geysers wells with gas/steam (in ppm by weight) plotted as bubble size. In general,  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{CH}_4$ , and gas/steam are positively correlated.  $\text{H}_2$  and  $\text{H}_2\text{S}$  are positively correlated with each other and negatively correlated with the previously mentioned variables.

$\text{NH}_3$  concentrations are very high in the Northwest Geysers (fig. 10) but tend to decrease in the samples with the very highest gas/steam (fig. 14). In the Central Geysers,  $\text{NH}_3$ ,

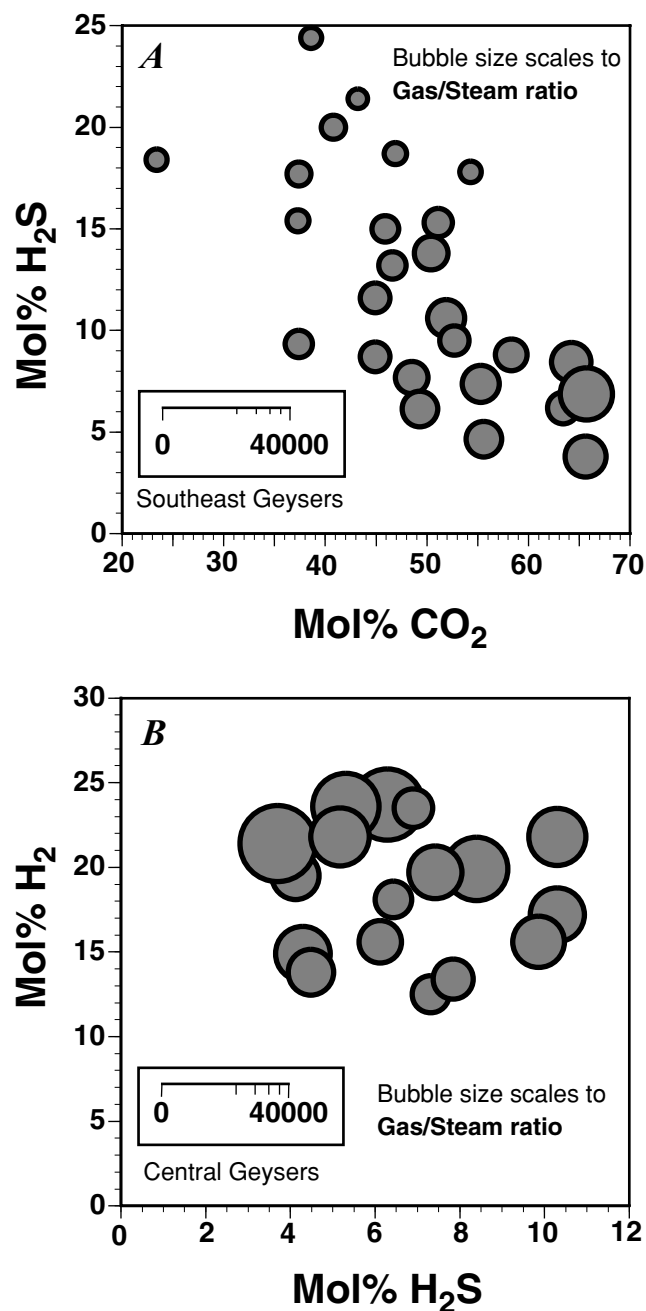


Figure 13.—Bubble diagrams for wells from the Southeast and Central Geysers. **A.** Mol%  $\text{CO}_2$  versus mol%  $\text{H}_2\text{S}$  for noncondensable gases from the Southeast Geysers. Bubble diameter corresponds to gas/steam ratio. Samples from the Southeast Geysers are higher in  $\text{H}_2\text{S}$  and lower in  $\text{CO}_2$  than the Central and Northwest Geysers. As in the Northwest Geysers, samples with low  $\text{H}_2\text{S}$  are higher in  $\text{CO}_2$  and gas/steam. **B.** Mol%  $\text{H}_2\text{S}$  versus  $\text{H}_2$  for noncondensable gases from the Central Geysers. Bubble diameter corresponds to gas/steam (in ppm by weight). There are no strong correlations among the three variables, though the range of gas/steam in this part of the field is considerable.

appears to correlate with  $\delta\text{D}$  as a result of reinjection of steam condensate (see below). The relative abundance of  $\text{NH}_3$  relative to  $\text{N}_2$  and  $\text{H}_2$  is much higher than would be expected at equilibrium, as is discussed in the next section.

### EQUILIBRIUM, MIXING, AND CONDENSATION IN THE GEYSERS RESERVOIR

Numerous indicators hint that the sampled fluids from The Geysers reservoir were not in equilibrium with each other, and moreover, individual constituents within a single gas sample do not typically attain equilibrium. This is complicated by the observation that Geysers well discharges are a mixture of reservoir steam and liquid, all of which is flashed to steam during withdrawal (Truesdell and others, 1987), and would be unlikely to attain equilibrium.

Figure 15 displays a plot of temperature versus  $\log \text{H}_2/\text{H}_2\text{O}$ , as modified from figure 4 of Giggenbach (1987). The Geysers samples are plotted as a field (in gray) that completely includes all samples from the present study. Temperature is chosen to be  $250 \pm 50^\circ\text{C}$ , which brackets the downhole temperatures measured in most parts of the field. Samples from The Geysers plot between the Ni/NiO and magnetite/hematite buffers. The range of  $\text{H}_2/\text{H}_2\text{O}$  is striking, given the homogeneity of temperatures in the geothermal reservoir. Most of the samples with the lowest  $\text{H}_2/\text{H}_2\text{O}$  values are from the Southeast Geysers. By accounting for the higher steam saturation in that part of the field, and calculating only that part of the  $\text{H}_2$  and  $\text{H}_2\text{O}$  introduced directly by reservoir steam,

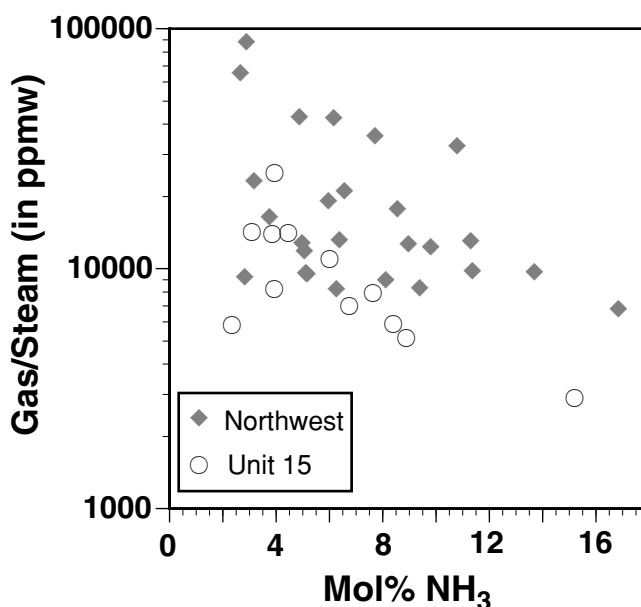


Figure 14.—Mol%  $\text{NH}_3$  vs. gas/steam (in ppm by weight) for wells of the Northwest Geysers. Though  $\text{NH}_3$  concentrations are quite high in the Northwest Geysers, concentrations actually decrease with increasing gas/steam ratio.

the  $H_2/H_2O$  values are much more similar and plot between  $\sim -2.5$  and  $-3.0$  (discussed in figure caption: solubility data for  $H_2$  from Giggenbach (1980) and  $y$  values calculated with method of D'Amore and Truesdell, 1985). Such values are appropriate for a geothermal reservoir rock containing both ferric and ferrous iron.

The Geysers data, plotted on a graph of log of the concentrations of  $(NH_3)^2/(N_2 \cdot xH_2O)$  versus the log of the concentrations of  $CH_4/CO_2$  (fig. 16) implies a very different oxidation state than that displayed in fig. 15. The reaction boundaries, taken from Giggenbach (1987), appear to show that

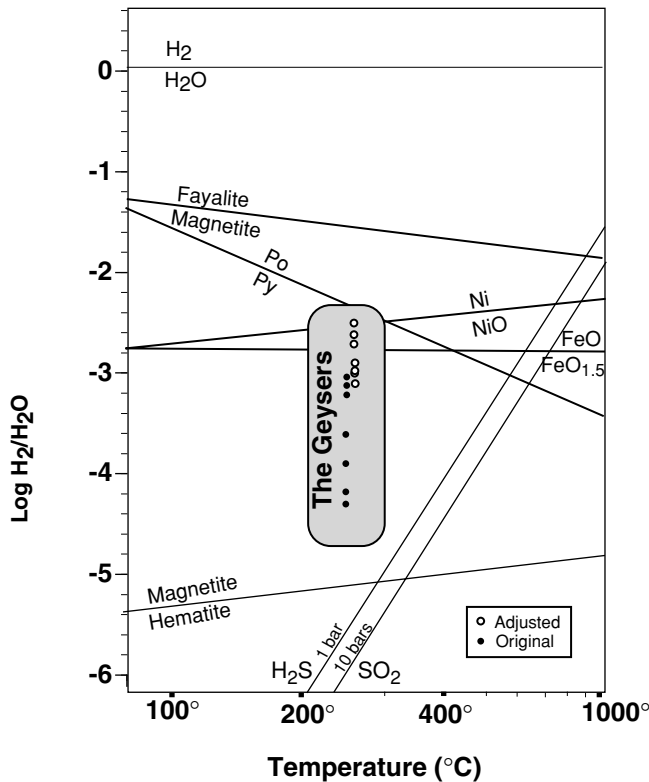


Figure 15.—Log  $H_2/H_2O$  vs.  $T$  for wells from The Geysers steam field. For simplicity, all samples are plotted at  $250 \pm 50^\circ C$ . Mineral and gas buffers from Giggenbach (1987, Fig. 4). Analyses of samples from production wells plot homogeneously throughout the gray box. The filled circles represent samples A86-4, A86-9, G88-15, G90-7, G90-20, G90-25, and G91-02. The unfilled circles are the same samples corrected to account for  $H_2O$  derived from reservoir liquid boiled during steam withdrawal. The  $y$  values (a fraction equal to  $H_2/H_2O$  from steam divided by  $H_2O$  from both reservoir steam and liquid) were estimated from figure 4 of Truesdell and others, (1987). Steam/liquid partition coefficient for  $H_2$  was from Giggenbach (1980) and calculated for  $240^\circ C$ . For clarity, samples are offset along the X-axis from their uncorrected equivalents and do not imply different temperatures. The figure demonstrates great heterogeneity of  $H_2/H_2O$  for bulk well discharges, but similar  $H_2/H_2O$  values calculated for the steam fraction within the reservoir. It thus appears that  $H_2$  has an approximately equilibrium concentration within the steam phase of the reservoir and is in equilibrium with typical crustal Fe-buffering assemblages.

Geysers samples plot at more reducing conditions than the magnetite/fayalite equilibrium and equilibrated at temperatures above  $600^\circ C$ . Boiling of reservoir liquid does not account for the high  $NH_3$  concentrations because  $NH_3$  still partitions strongly into the vapor, and samples with the highest calculated  $y$  value (as determined from fig. 4 of Truesdell and others, 1987) have some of the highest values of  $(NH_3)^2/(N_2 \cdot xH_2O)$ . Both plots cannot be correct; and in fact, it appears that the amount of  $NH_3$  in The Geysers samples far exceeds that which could be in equilibrium with the rest of the geothermal fluid at geothermal temperatures and typical crustal oxidation states.

Geochemical modeling with SOLVGAS (Symonds and Reed, 1993) demonstrates that  $NH_3$  from The Geysers steam field is several orders of magnitude more abundant than would be expected at typical reservoir temperatures and pressures ( $240^\circ C$  and 30 bars). SOLVGAS can calculate the equilibrium distribution of gas species, given an input composition, temperature, and pressure. Calculated  $N_2/NH_3$  ratios are more than 160 times greater than those actually observed. The  $H_2$ ,  $H_2O$ ,  $CH_4$ , and  $CO_2$  were consistent with equilibrium at 30 bars and  $\sim 235^\circ C$  for sample G90-11, and with an equilibrium temperature of  $297^\circ C$  for sample G91-10 from the Northwest Geysers. However, inclusion of  $NH_3$  in the calculations proved unsuccessful. Calculated  $NH_3$  concentrations would

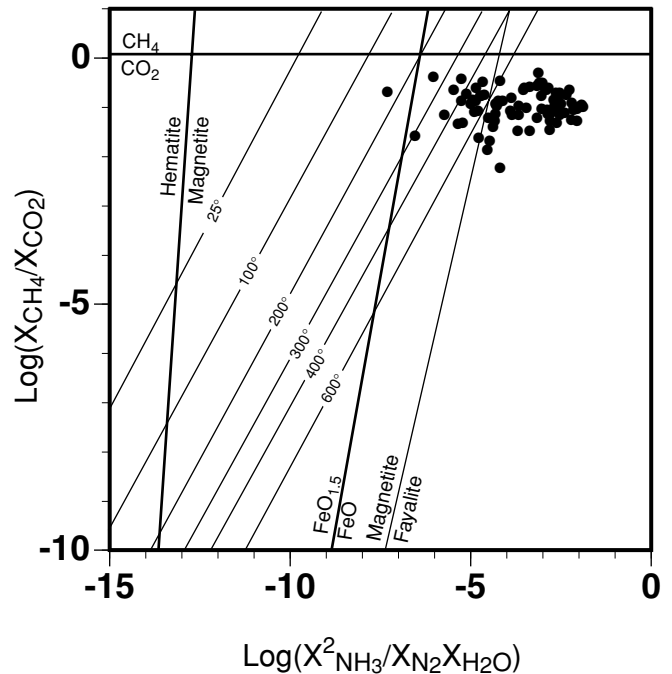


Figure 16.—Plot of  $\log(X_{CH_4}^2/(X_{N_2} \cdot X_{H_2O}))$  vs.  $\log(X_{CH_4}/X_{CO_2})$  for well discharges from The Geysers steam field. Apparent oxidation states are below that of the quartz-fayalite-magnetite buffer for most samples. Accounting for gases derived from reservoir liquid (as in fig. 15) does not significantly change the plot because both  $NH_3$  (numerator) and  $H_2O$  (denominator) are important components of the liquid phase.



not match actual concentrations except at temperatures below 100°C, resulting in poor fits for the other components.

Calculations by Eugster (1972) for conditions of 500 K (227°C) show that the relative  $\text{NH}_3$  and  $\text{N}_2$  concentrations of typical Geysers samples such as G81-09 are consistent with  $\text{H}_2$  fugacities of  $\sim 0.5$  bars, more than 100 times those likely at the  $\sim 30$  bars total pressure of The Geysers reservoir. The  $\text{NH}_3$  is either coming from great depth ( $>250$  bars pressure) or, more likely is being produced locally by thermal breakdown of Franciscan-hosted organic materials, which also produces the abundant  $\text{CH}_4$ . Evidently, the  $\text{NH}_3$  does not have sufficient time to equilibrate in The Geysers reservoir. Giggenbach (1987) noted that  $\text{NH}_3$  was the slowest of the geothermal gases to equilibrate.

### SOURCES OF COMPONENTS IN THE GEYSERS FLUIDS

**End member #1 — Northwest Geysers:** Samples from the Northwest Geysers are unique in composition, as discussed above, and are characterized by high  $\text{CO}_2$ ,  $\text{CH}_4$ , and gas/steam, relatively high  $\text{NH}_3$ , and low  $\text{H}_2\text{S}$  and  $\text{H}_2$ . Such characteristics imply a strong component of fluid from the HTR (Walters and others, 1992).

As noted by several workers, there is also an obvious trend in the isotopic composition of Northwest Geysers well samples away from a meteoric end member towards an isotopically heavy composition that is similar to both connate and magmatic waters (Haizlip, 1985; Walters and others, 1992; D'Amore and Bolognesi, 1993; Kennedy and Truesdell, 1996). The gas samples in this study, particularly from the Northwest Geysers, are consistent with this observation. Fluids with a strong meteoric signature come from the southeast part of the field; e.g., most Southeast Geysers samples consistently plot with  $\delta^{18}\text{O}$  between  $-5$  and  $-7\text{‰}$  and with  $\delta\text{D}$  between  $-50$  and  $-60\text{‰}$ . Other Southeast Geysers samples trend toward the composition of evaporated steam condensate that has been pumped back into the ground (as discussed below). In contrast, the Northwest Geysers samples point toward an end member with around  $-4\text{‰}$   $\delta^{18}\text{O}$  and  $-40\text{‰}$   $\delta\text{D}$ , which could feasibly extend into the region commonly associated with high-temperature volcanic gas or steam (shown on fig. 9). However, these same samples have characteristics that are inconsistent with a simple magmatic origin, and are more representative of connate (sedimentary) or metamorphic fluids, which have compositions that can overlap with those of magmatic fluids (White and others, 1973).

One example of this connate/metamorphic signature is the  $\delta^{13}\text{C}$  of  $\text{CO}_2$  in the Geysers samples, which is very similar throughout the field, ranging only from  $-11.7$  to  $-15.0\text{‰}$  VPDB (most are between  $-12$  and  $-14\text{‰}$ ). As discussed by Bergfeld and others (1999), such values are typical of Franciscan carbonate veins (see also Sternfeld, 1981; Lambert and Epstein, 1992). Carbon isotopes from vein carbonate in Franciscan graywackes, taken from a core drilled in the

bottom of Sulphur Bank 15 (SB-15) cluster around a value of  $-12\text{‰}$ , with all values ( $n = 24$ ) falling between  $-9$  and  $-15\text{‰}$  (Bergfeld and others, 1999). Both metamorphic veins and younger hydrothermal veins yield values similar to those for  $\text{CO}_2$  from gas samples in this report. Bergfeld and others (1999) concluded that modern gases have derived their carbon primarily from these older metamorphic calcite veins, mixed with some carbon from organic materials in the Franciscan rocks. There is no evidence for significant magmatic carbon input to the system, which should have a value of  $-4$  to  $-8\text{‰}$  (Allard and others, 1977; Allard, 1979; Rollinson, 1993). Analyses of  $\delta^{13}\text{C}$  in  $\text{CH}_4$  are also low ( $-29$  to  $-33\text{‰}$  VPDB, see footnote to table 2), and imply a thermally derived sedimentary component of methane to The Geysers system (see also Shigeno and others, 1987; Bergfeld and others, 1999).

Another characteristic inconsistent with magmatic input to The Geysers reservoir fluid is the high  $\text{CH}_4$  and  $\text{NH}_3$  concentrations in the high gas/steam wells of the Northwest Geysers. These two gases are unstable at magmatic temperatures and crustal oxidation states and are typically added to geothermal and volcanic discharges by relatively low-temperature addition from sedimentary and metamorphic sources (Symonds and others, 1994; Giggenbach, 1987). Ternary diagrams of  $\text{N}_2$ -Ar- $\text{CH}_4$  show a clear trend from an air-saturated meteoric water end member toward a  $\text{CH}_4$ -rich source most obvious in the Northwest Geysers and Unit 15 (fig. 11). Gunderson (1992b) also noted the trend toward gas-rich compositions in the Northwest Geysers and attributed it to the greater thickness of Franciscan reservoir rock in the Northwest Geysers, relative to felsite, and the lesser flushing of the northwest part of the field by recharge of meteoric water.

This nonmeteoric end member is also obvious in the  $\text{N}_2/\text{Ar}$  ratios of high gas/steam fluids, which exceed 300 in 7 samples and are far greater than the atmospheric ratio of 84. High  $\text{N}_2/\text{Ar}$  is also found in springs and gas vents all over the Clear Lake volcanic field, as discussed by Goff and others (1995) and Goff and Janik (1993). For example, Goff and Janik (1993) reported high values at the Herman Pit of Sulphur Bank Mine ( $\text{N}_2/\text{Ar} = 248$ ), at Jones Hot Spring (191), and at the Kelseyville methane well (195). Even higher values were listed by Jenden and others (1988) for natural gases from deep wells in the California Great Valley. These gases had  $\text{N}_2/\text{Ar}$  ranging from  $>200$  to several thousand, with one sample having a ratio of 22,000. These extraordinarily high values were attributed by Jenden and others (1988) to production of  $\text{N}_2$  by thermal decomposition of organic matter and/or oxidation of ammonium in sheet silicates of the Franciscan assemblage believed to underlie the Great Valley strata in the California Great Valley.

It is therefore reasonable to postulate that the high  $\text{CH}_4$ , gas/steam ratios and  $\text{N}_2/\text{Ar}$  in the Northwest Geysers is from a Franciscan sedimentary/metamorphic component to The Geysers gases. The high temperatures and high  $^3\text{He}/^4\text{He}$  (Kennedy and Truesdell, 1996) may also indicate an input of magmatic heat and mantle-derived noble gases to the Northwest Geysers. The sulfur-isotopic signature from Geysers

steam samples (close to 0‰ CDT) are also compatible with a magmatic origin but could conceivably be explained as the composition of H<sub>2</sub>S in equilibrium with Franciscan-seawater-derived sulfate (~+20 to +30 ‰ CDT) that is dissolved into the liquid phase in the geothermal reservoir. Norman and others (1998) found excess H<sub>2</sub>S in fluid inclusions from The Geysers reservoir and attributed it to magmatic input of sulfur-rich gases and low kinetic rates of breakdown by reaction with rock.

**End member #2 — Southeast Geysers:** In comparison to end member #1 from the Northwest Geysers, the well discharges typical of the southeast part of The Geysers field are higher in H<sub>2</sub>, H<sub>2</sub>S, and H<sub>2</sub>O, the latter which is relatively unshifted in its isotopic composition. This reflects higher meteoric recharge to the Southeast Geysers (Truesdell and others, 1987), a greater integrated water/rock ratio over time, and less resulting influence of gases from argillaceous Franciscan Complex metagraywackes (Gunderson, 1992b). The high H<sub>2</sub> concentrations are consistent with the high steam/gas. H<sub>2</sub> is relatively fast at equilibrating in geothermal systems (Giggenbach, 1987), and the high H<sub>2</sub> values reflect the higher steam abundances and reduction of H<sub>2</sub>O to H<sub>2</sub> at geothermal temperatures. As mentioned above, H<sub>2</sub>/H<sub>2</sub>O ratios in gases from the Southeast Geysers are low due to the addition of liquid water from the reservoir during production. H<sub>2</sub>S values are high due to partial equilibrium sulfide (Norman and others, 1998) and lower dilution with high CH<sub>4</sub>-CO<sub>2</sub> Franciscan-derived gases. Compared with many geothermal systems (Ellis, 1979), The Geysers gases are quite low in CO<sub>2</sub>, averaging less than 50% of the noncondensable gases in the Southeast Geysers wells. The concentrations of carbon gases are highest in the Northwest Geysers and lowest in the southeast. Again, this likely reflects the greater flushing of the Southeast Geysers over time by meteoric waters, resulting in most of the Franciscan-derived carbon gases having been swept from the southeast part of the reservoir (Truesdell and others, 1987; Gunderson, 1992b).

### EFFECTS OF RE-INJECTION

The most obvious signs of reinjected steam condensate in the samples from this study are those from the Southeast and Central parts of the field. On a plot of  $\delta D$  vs.  $\delta^{18}O$ , (fig. 9), one can discern a trend from an <sup>18</sup>O- and D- depleted end member toward the field represented by the eight injection wells which are considerably enriched in D and <sup>18</sup>O due to low temperature (<100°C) evaporation. The trend is distinct from that shown by wells from the Northwest Geysers, which points toward a more <sup>18</sup>O-enriched “connate” water that is distinct from the injected steam condensates (table 4). The trend implies that injected fluids have migrated from injection wells to be reboiled and returned to the surface through production wells. Simple mixing calculations (based on data

from the injection wells and those Southeast Geysers samples closest to the meteoric water line) indicate that as much as 25-40% of the steam in some wells appears to be derived from reinjected fluids. The sample with the most obvious “injectate” signature also has the highest NH<sub>3</sub> concentration of any sample from The Geysers that we analyzed (fig. 17). Given the high solubility of NH<sub>3</sub> in liquid H<sub>2</sub>O, it is likely that some of this gas dissolves in condensing steam in the wellbore and then remains in the steam condensate during cooling at the surface before reinjection. Samples with a high proportion of “injectate” would then have higher NH<sub>3</sub> concentrations than the typical Geysers well fluid (already very

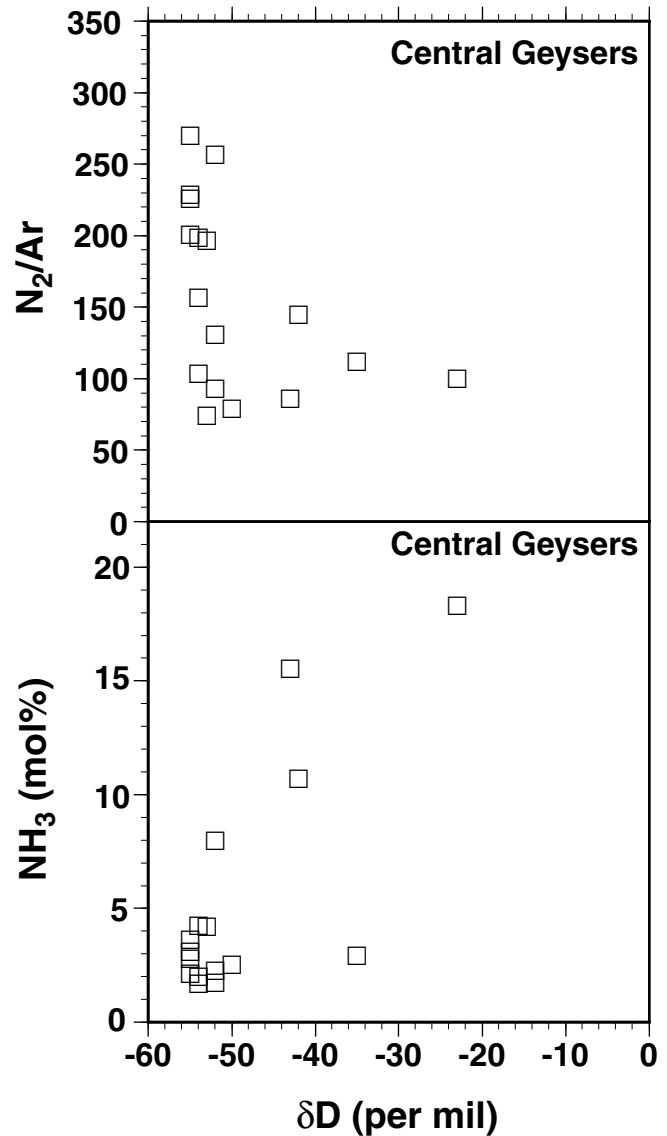


Figure 17.—Plot of  $\delta D$  (‰) of steam condensate vs. mol% NH<sub>3</sub> and N<sub>2</sub>/Ar from the noncondensable-gas portion of well discharges from the Central Geysers. Samples enriched in  $\delta D$  also have higher NH<sub>3</sub> concentrations and N<sub>2</sub>/Ar ratios consistent with derivation from atmosphere or air-saturated water. Such trends are consistent with significant input of reinjected, evaporated steam condensate.

high as noted above). Increased  $\text{NH}_3$  in well discharges of the Southeast Geysers were discussed by Beall (1993), who discusses the use of  $\text{NH}_3$  as a tracer for injectate.

Figure 17 also demonstrates that Central Geysers wells with the highest  $\delta\text{D}$  also have  $\text{N}_2/\text{Ar}$  ratios that are consistent with higher contributions of air-saturated water, as would be expected for steam condensate that had sat at the surface before reinjection.

As discussed below, the 1991 sampling of Prati 38 (Northwest Geysers) also showed obvious influence of "injectate," with increased  $\text{NH}_3$  and steam/gas.

### TEMPORAL CHANGES IN THE GEYSERS FLUIDS

Seven wells in the database were resampled over time (once each: table 5). The three samples from the Southeast Geysers, CA956#1, McKinley 3 and Abel 1 were resampled 7.5, 6 and 20 months after the original samplings, respectively. Each showed increased gas/steam and mol%  $\text{CO}_2$ , decreased  $\text{NH}_3$ , and decreased  $\text{H}_2\text{S}$ . The decreases in  $\text{NH}_3$  and  $\text{H}_2\text{S}$  would indicate a lesser influence of a liquid phase in the reservoir, as both gases are relatively soluble in any condensed phase. If the liquid phase were still abundant but were undergoing progressive boiling, one would expect increased abundance of soluble gases over time, and decreased gas/steam ratios, as most gases are only slightly soluble and would boil away early. Instead, the opposite is true. Most likely, the amount of saturated liquid feeding these two wells decreased during the interval between sampling. Loss of this liquid phase would increase permeability through small cracks in the reservoir where adsorbed liquids would originally reside, potentially resulting in increased migration of gas and steam through regions previously occupied by  $\text{NH}_3$ - and  $\text{H}_2\text{S}$ -rich liquids. Reduction of reservoir liquid is consistent with the progressively lower reservoir temperatures and pressures observed as a result of production and withdrawal of reservoir fluids over time (Truesdell and White, 1973).

Beall and Box (1993) noted a similar increase in noncondensable gas with time, as well as an increase in the mole fraction of  $\text{CO}_2$ . They attribute the change to reduction of reservoir pressures, causing open-system flow of  $\text{CO}_2$ -rich gases into the Southeast Geysers from below the geothermal reservoir. Their explanation is similar to that offered above, but infers an external source of noncondensable gas to the reservoir, rather than simply a decrease in saturation of the system and flow of noncondensable gases already present.

There was little change in Rorabaugh A-4 (Unit 15) in the two years between sampling. Changes in Prati State 24 (Northwest Geysers) were also small. Prati 25 (Northwest Geysers) had increased gas/steam, which was accompanied by an increased  $\delta\text{D}$ , implying a greater proportion of the Franciscan "connate" component (discussed in previous section) over time. The composition of Prati 38 (Northwest Geysers) changed markedly over the 3 years between sampling

trips and appears to have been influenced by the nearby injection well (Prati 9). Compared with the 1988 samples of Prati 38, the 1991 sampling is higher in Ar and has a lower  $\text{N}_2/\text{Ar}$  ratio, indicating a greater influence of air-saturated water. The gas/steam ratio decreased markedly between 1988 and 1991, and the  $\text{NH}_3$  concentration increased by 250%, as would be likely if there were a strong "injectate" signature.

### FUMAROLE COMPOSITIONS AS COMPARED WITH WELL DISCHARGES

When compared with the relative noncondensable-gas abundances of well discharges, the fumaroles are low in  $\text{H}_2\text{S}$  and  $\text{NH}_3$ . These gases have relatively high solubility in the  $\text{O}_2$ -rich meteoric waters that geothermal fluids would have to pass through to reach the surface.  $\text{N}_2$ , Ar, and  $\text{O}_2$  are all higher in the fumarolic gases, as might be expected for surface emanations. The  $\text{N}_2/\text{Ar}$  ratio is also consistent with input of air-saturated water.  $\text{CH}_4$  and  $\text{H}_2$  are about the same as samples in the well-discharge database and  $\text{CO}_2$  is somewhat higher. The  $\delta^{13}\text{C}$  of  $\text{CO}_2$  from the fumaroles is the same as that of  $\text{CO}_2$  from the geothermal reservoir.

### CONCLUSIONS

- This database of geothermal fluid analyses from the Geysers contains chemical data on 81 production-well discharges and 9 injection wells from, the Northwest, Central, and Southeast Geysers, Unit 15 (westcentral Geysers), and 5 surface manifestations in the Central Geysers. Wellhead temperatures and pressures correspond to the liquid-water/steam boiling curve or slightly superheated conditions.
- Evidence for recharge of meteoric water is most obvious in samples from the Southeast Geysers, where steam has an isotopic composition close to that of slightly oxygen-exchanged present-day precipitation and  $\text{N}_2/\text{Ar}$  ratios are similar to or slightly higher than air-saturated water. The noncondensable component in Southeast Geysers geothermal fluids is enriched in  $\text{H}_2$  and  $\text{H}_2\text{S}$ .
- Many of the differences between the Northwest Geysers and Southeast Geysers can be explained by higher temperatures and considerable contributions of carbon-rich gases from the host Franciscan assemblage to the Northwest Geysers. The Franciscan component is manifested in the high concentrations of  $\text{CO}_2$  and  $\text{CH}_4$ , the low  $\delta^{13}\text{C}$  of  $\text{CO}_2$  and  $\text{CH}_4$ , and the high  $\text{N}_2/\text{Ar}$ . In contrast, there is evidence for greater input of meteoric water (recharge) to the Southeast and a longer history of meteoric water-rock reaction, which would have depleted the local Franciscan rocks of their carbon-rich component and caused both rock and fluid to have isotopic compositions

more similar to meteoric water.

- Contributions of magma-derived gas to the Northwest Geysers has been suggested by Kennedy and Truesdell (1996) and may be responsible throughout the field for the near-zero values for  $\delta^{34}\text{S}$  of  $\text{H}_2\text{S}$ . The high  $\text{N}_2/\text{Ar}$  of the Northwest Geysers may be explained either by a magmatic input or a sedimentary input (the explanation favored herein).
- The abundance of  $\text{NH}_3$  is too high to reflect equilibrium within the geothermal reservoir, even if it were derived partially due to boiling of liquid condensate. Apparently,  $\text{NH}_3$  enters the system due to breakdown of Franciscan-hosted organic materials and reacts too slowly with the other gaseous components to reach equilibrium.
- Seven wells resampled during this study show some increases in  $\gamma$  (steam/liquid+steam) in the reservoir and some influence of injection-derived condensate. Several wells showed no appreciable change in discharge composition.
- Surface manifestations are similar in chemical and isotopic composition to deep fluids but have higher  $\text{CO}_2$  and lower  $\text{NH}_3$  and  $\text{H}_2\text{S}$ .  $\text{N}_2/\text{Ar}$  ratios reflect air-saturated water.

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A P P E N D I X

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## APPENDIX I: DESCRIPTION OF DATA TABLES

**TABLE 1. WELL ATTRIBUTES**

**Sample #:** Denotes an individual visit to a particular well. All samples collected by USGS personnel begin with the letter “G”. Unit-15 wells were collected in 1986 by Geo Corporation and begin with the letter “A”. Samples A87-1 and A87-2 were collected by Mr. Tom Box of Calpine Corporation in 1987. The number following the initial letter represents the year in which the sample was collected (19XX). The final number denotes the order in which the samples were collected during that year.

**Well:** The full name of the well. G95 and G96 samples are from surface manifestations rather than wells.

**Region:** S= Southeast; C= Central; N= Northwest; U= Unit 15. In order to facilitate plotting of the geochemical data, the steam field was divided into 4 regions. The boundaries of these regions are shown in fig. 1. The limits were chosen partly based on geography and partially based on steam/gas ratios.

**API Number:** The official designation of the well as listed by the California Division of Oil, Gas, and Geothermal Resources (DOGGR).

**Map #:** The number assigned to the well in figure 1.

**Well Type:** Wells are listed as production or injection, depending on what they were used for at the time of collection. Reinjection became mandatory, due to environmental concerns, in the late 1960s, before the first sampling for this study. G95 and G96 samples are from bubbling pools and fumaroles rather than wells.

**Year Drilled:** The year that the well was first put into production.

**Operator:** The company utilizing the well at the time of sampling. CGC= Calpine Geysers Corporation, CCOC=Coldwater Creek Operator Corporation, Union= Unocal Geothermal Company.

**Current Operator:** All wells sampled for this study that are now active are utilized by Calpine. The former CCPA wells are inactive and the Unit 15 wells are abandoned.

**Latitude:** Latitude of the well listed in decimal degrees. Data are from varied sources, including Reed (1982), California Division of Oil and Gas (1992), and public records available through the California DOGGR.

**Longitude:** Longitude of the well listed in decimal degrees. Data are from varied sources, including Reed (1982), California Division of Oil and Gas (1992), and public records available through the California DOGGR.

**Latitude:** Latitude of the well listed in meters (Universal Transverse Mercator Zone 10). Data were generated from the latitude records above.

**Longitude:** Longitude of the well listed in meters (Universal Transverse Mercator Zone 10). ). Data were generated from the longitude records above.

**Section-Township-Range:** The section, township, and range where the well is located.

**Sample Date:** The date of sampling in year/month/day.

**Surface Elevation:** The ground elevation, in meters, at the site of the well.

**Total Depth:** The well depth, in meters, measured relative to the surface elevation.

**Casing Depth:** The depth to which the well was fully cased before sampling, relative to the surface elevation, in meters. Perforated casing is not included.

**Wellhead T:** The temperature of the well discharge at the sampling

point on the Earth’s surface, in °C. This is usually significantly lower than the downhole reservoir temperature. Stated value represents the temperature of the discharge on the day of sampling, as supplied by the operator to the USGS.

**Wellhead P:** The pressure of the well discharge at the sampling point on the Earth’s surface. This is usually significantly lower than the downhole reservoir pressure. Stated value represents the pressure of the discharge on the day of sampling, as supplied by the operator to the USGS. Pressure in bars (absolute, corrected from gauge pressure), with psi (lbs/in<sup>2</sup>) in parentheses.

**Wellhead T\*:** Because we did not obtain wellhead temperatures at the time of collection for all of our samples, we have included the temperature of the well discharge, in °C, as reported by the operator to the California DOGGR for the reporting period of the month of sampling. The temperature represents a single individual temperature measurement during that month, and could be strongly affected by well conditions such as shut-in, blowoff, etc. As such, it may be different from the wellhead temperature at the time of sampling.

**Wellhead P\*:** Because we did not obtain wellhead pressures at the time of collection for all of our samples, we have included the pressure of the well discharge as reported by the operator to the California DOGGR for the reporting period of the month of sampling. The pressure represents a single individual pressure measurement during that month, and could be strongly affected by well conditions such as shut-in, blow-off, etc. As such, it may be different from the wellhead pressure at the time of sampling, and could be different than typical operating conditions. Pressure in bars (absolute, corrected from gauge pressure), with PSI (lbs/in<sup>2</sup>) in parentheses.

**TABLE 2. GAS GEOCHEMISTRY**

**Sample #:** Same as “Sample #” in table 1.

**Well:** Same as “Well” in table 1.

**Region:** Same as “Region” in table 1.

**Sample Type:** All wells in this table are production wells. G95 and G96 samples are from bubbling pools and fumaroles rather than wells.

**Sample Date:** The date of sampling in year/month/day.

**pH-field:** The pH of condensate as measured at the sampling site.

**pH-Lab:** The pH of condensate as measured in the USGS laboratory.

**Steam/Gas:** Ratio of moles of steam (H<sub>2</sub>O) to moles of non-condensable gas (CO<sub>2</sub>+H<sub>2</sub>S+H<sub>2</sub>+O<sub>2</sub>+Ar+N<sub>2</sub>+CH<sub>4</sub>+NH<sub>3</sub>) in the bulk fluid withdrawn from well.

**Gas/Steam:** Ratio of mass of noncondensable gas to mass of steam (x10<sup>6</sup>).

**CO<sub>2</sub>, H<sub>2</sub>S and other non-condensable gases:** Concentrations in mole percent of the noncondensable portion of the sampled fluid (without H<sub>2</sub>O).

**N<sub>2</sub>/Ar molar ratio:** The molar ratio of N<sub>2</sub> to Ar in the sampled fluid. The ratio in air is 83.6, whereas that of air-saturated water at standard temperature and pressure is 38.

**δD:** The hydrogen-isotopic composition of condensed steam in units of permil, relative to Vienna Standard Mean Ocean Water (VSMOW) where:

$$\delta D = \left( \frac{(D/H)_{sample} - (D/H)_{VSMOW}}{(D/H)_{VSMOW}} \right) \times 10^3$$



Samples collected in 1990-91 were measured in the laboratory of Tyler Copen in Reston, VA. Analytical precision is 1 per mil. G78- and G81-samples were measured in the laboratory of R. Harmon at the Scottish Universities Research and Reactor Centre, Glasgow.

$\delta^{18}\text{O}$ : The oxygen-isotopic composition of condensed steam in units of permil, relative to Vienna Standard Mean Ocean Water (VSMOW) where:

$$\delta^{18}\text{O} = \left( \frac{^{18}\text{O}/^{16}\text{O}_{\text{sample}} - (^{18}\text{O}/^{16}\text{O})_{\text{VSMOW}}}{(^{18}\text{O}/^{16}\text{O})_{\text{VSMOW}}} \right) \times 10^3.$$

Samples from 1990-91 were measured in the laboratory of Tyler Copen in Reston, VA. Analytical precision is 0.2 permil. G81-1 to G81-5 were measured in the laboratory of J.R. O'Neil, Menlo Park, CA. G78 samples were measured by L. Doug White in the laboratory of I. Barnes, Menlo Park, CA. All others were measured in the laboratory of C. Kendall, Menlo Park, CA.

$\delta^{13}\text{C CO}_2$ : The carbon-isotopic composition of  $\text{CO}_2$  in units of permil relative to the standard Peedee belemnite (VPDB). Samples were measured in the laboratory of C. Kendall in Menlo Park. Analytical precision is 0.2 permil.

$\delta^{34}\text{S (D)}$ : The sulfur-isotopic composition in  $\text{H}_2\text{S}$  in units of permil relative to Canyon Diablo Troilite (CDT). Measured in the laboratory of W.C. Pat Shanks III in Denver, CO. Analytical precision is  $\pm 0.2$  permil.

$\delta^{34}\text{S (M)}$ : The sulfur-isotopic composition in  $\text{H}_2\text{S}$  in units of permil relative to Canyon Diablo Troilite (CDT). Measured by S. Silva in the laboratory of C. Kendall in Menlo Park, CA. Analytical precision is  $\pm 0.2$  permil.

**TABLE 3. MEAN COMPOSITION OF ANALYSES**

This table is divided into columns that contain the mean composition of wells for the four regions of The Geysers geothermal field and superjacent surface manifestations. The row indicators are the same as columns in table 2 and use the same units. The mean compositions are for *all* wells in this compilation, not solely those indicated as representative of initial reservoir conditions.

**TABLE 4. INJECTION WELLS**

**Sample #:** Denotes an individual visit to a particular well. All samples collected by USGS personnel begin with the letter "G".

**Well:** The full name of the well.

**Year Drilled:** The year that the well was first put into production.

**Sample date:** The date of sampling in year/month/day.

$\delta\text{D}$ : The hydrogen-isotopic composition of water in the steam condensate prior to reinjection. In units of permil, relative to Vienna Standard Mean Ocean Water (VSMOW). Measured in the laboratory of Carol Kendall in Menlo Park, CA. Analytical precision is 1 permil.

$\delta^{18}\text{O}$ : The oxygen-isotopic composition of water in the injectate fluid before injection. In units of permil, relative to Vienna Standard Mean Ocean Water (VSMOW). Measured in the laboratory of Carol Kendall in Menlo Park, CA. Analytical precision is 0.2 permil.

**TABLE 5. TEMPORAL VARIATIONS**

**Well:** The full name of the well.

**Sample #1:** Same as "sample #" in tables 1 and 2. The first sampling of the well. The letter (G) indicates sampling by USGS personnel. The first number represents the year sampled, whereas the second number (after the dash) is for the sample number within the year.

**Sample #2:** Same as "sample #" in tables 1 and 2. The second sampling of the well. The letter (G) indicates sampling by USGS personnel. The first number represents the year sampled, whereas the second number (after the dash) is for the sample number within the year.

**G/S #1:** Gas/steam ratio (in ppm by weight) for the first sampling.

**G/S#2:** Gas/steam ratio (in ppm by weight) for the second sampling.

**$\text{N}_2/\text{Ar}$  #1:**  $\text{N}_2/\text{Ar}$  for the first sampling.

**$\text{N}_2/\text{Ar}$  #2:**  $\text{N}_2/\text{Ar}$  for the second sampling.

**$\delta\text{D}$  #1:**  $\delta\text{D}$  (in permil relative to VSMOW) for the first sampling.

**$\delta\text{D}$  #2:**  $\delta\text{D}$  (in permil relative to VSMOW) for the second sampling.

**$\text{NH}_3$  #1:**  $\text{NH}_3$  concentration in noncondensable gas (in mol%) in first sampling.

**$\text{NH}_3$  #2:**  $\text{NH}_3$  concentration in noncondensable gas (in mol%) in second sampling.

**$\text{H}_2\text{S}$  #1:**  $\text{H}_2\text{S}$  concentration in noncondensable gas (in mol%) in first sampling.

**$\text{H}_2\text{S}$  #2:**  $\text{H}_2\text{S}$  concentration in noncondensable gas (in mol%) in second sampling.





Geysers Steam Field  
Mean Composition of Analyses

	Southeast Geysers	Central Geysers	Northwest Geysers	Unit 15	Surface Manifestations
pH-field	4.9	5.4	6.2		
pH-lab	7.2	7.7	7.7	8.2	
Steam/Gas	4,180	830	130	220	-
Gas/Steam	630	3,250	21,650	10,260	-
CO <sub>2</sub> (mol%)	49.0	59.7	65.0	56.0	64.9
H <sub>2</sub> S (mol%)	12.3	6.72	4.91	5.35	3.88
He (mol%)	0.0161	0.0077	0.0014	0.0004	0.0021
H <sub>2</sub> (mol%)	22.3	18.6	15.9	16.7	11.9
O <sub>2</sub> (mol%)	0.0135	0.046	0.0081	0.0375	2.30
Ar (mol%)	0.058	0.0237	0.0075	0.017	0.204
N <sub>2</sub> (mol%)	4.66	2.96	1.04	1.76	11.5
CH <sub>4</sub> (mol%)	5.14	6.99	6.06	14.3	4.86
NH <sub>3</sub> (mol%)	6.19	5.33	7.24	6.21	0.512
N <sub>2</sub> /Ar	118	157	239	169	58
δD (per mil)	-53	-49	-47	-49	
δ <sup>18</sup> O (per mil)	-5.1	-4.3	-1.4		
δ <sup>13</sup> C CO <sub>2</sub> (per mil)	-13.5	-13.3	-12.4	-12.7	-13.1
δ <sup>34</sup> S (D) (per mil)	0.9	0.8	0.5	1.3	
δ <sup>34</sup> S (M) (per mil)	-0.2	-0.6	-0.5	-0.9	

Injection Wells

Sample #	Well	Year Drilled	Sample Date	$\delta D$	$\delta^{18}O$
<b>G90-00</b>	D.X. State 4596-72	1982	90/12/11	-29	-0.8
<b>G90-00</b>	D.X. State 4596-61	1983	90/12/11	-15	3.2
<b>G90-00</b>	Geysers Development Corp. (GDC) 05	1980	90/12/11	-13	1.0
<b>G90-00</b>	Geysers Devel. Corp. (GDC) 26	1984	90/12/11	-3	5.6
<b>G90-00</b>	Geysers Devel. Corp. (GDC) 88-12	1971	90/12/11	-7	5.6
<b>G90-00</b>	BEF 42B33	1984	90/12/11	-13	0.5
<b>G90-00</b>	LF State 4597- 23 (Lakoma Fame)	1979	90/12/11	-11	3.1
<b>G90-00</b>	CMHC 06 (Cobb Mtn. Hunting Club 6)	1978	90/12/11	-6	3.8
<b>G91-03</b>	Prati 09	1983	91/06/24	-44	0.1

Well	Sample #1	Sample #2	G/S #1	G/S #2	N <sub>2</sub> /Ar #1	N <sub>2</sub> /Ar # 2	δD # 1	δD # 2	NH <sub>3</sub> # 1	NH <sub>3</sub> #2	H <sub>2</sub> S #1	H <sub>2</sub> S #2
			ppm	ppm					Mol%	Mol%	Mol%	Mol%
CA 956#1	G81-12	G88-14	176	622	393	44	-54	-58	9.04	3.91	24.40	8.80
McKinley 3	G81-16	A87-1	270	500	73	61	-55	-	7.02	5.36	17.70	9.50
Rorabaugh A-4	A86-3	G88-10	5,990	5,220	-	132	-	-49	8.40	8.89	6.72	6.75
Prati State 24	G88-6	G91-6	9,034	9,557	181	567	-49	-50	8.10	5.15	6.41	7.12
Prati 38	G88-7	G91-2	21,307	6,872	519	115	-51	-38	6.56	16.84	4.48	7.49
Prati 25	G88-8	G91-10	65,219	88,655	597	-	-49	-42	2.65	2.88	1.63	2.04
Abel1	A87-2	G88-11	668	979	107	86	-	-55	7.35	4.99	7.68	7.37