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## FIELDWIDE CHEMICAL AND ISOTOPIC GRADIENTS IN STEAM FROM THE GEYSERS

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### ABSTRACT

Strong fieldwide gradients from southeast to northwest in gas/steam and  $\delta^{18}\text{O}$  have been found in steam produced from wells at The Geysers. These gradients result from recharge from the southeast that has increased liquid saturation in the southern part of the reservoir and flushed gases and high  $\delta^{18}\text{O}$  connate waters to the north and out of the system through surface vents. Variations in the steepness of the gradients are probably related to major venting in the Big Geysers area. Although lateral steam flow and condensation subsequent to flushing explain some local gradients in the southern area, these processes cannot explain the fieldwide variations.

### INTRODUCTION

Except for a small number of wells at the southern edge of the field, all wells at The Geysers yield saturated or slightly superheated steam. Geochemical study of well discharges is, therefore, essentially limited to gases, volatile salts, and isotopes. A small number of gas analyses have been reported for steam from The Geysers. Allen and Day (1927) reported that steam from six of the shallow steam wells drilled from 1921 to 1925 contained notably less  $\text{CO}_2$  (~63%) and more  $\text{H}_2$  (~15%) and  $\text{CH}_4$  (~15%) than steam samples from Lassen Park. The difference was probably due to the presence of far more organic matter in The Geysers sedimentary reservoir rock than in the dominantly volcanic Lassen system. Other than providing this observation, the gas analyses were not very useful to Allen and Day. This paucity of data and interpretation continued until the mid-1980's. Small numbers of analyses were reported by Barnes et al. (1973), Weres et al. (1977), Nehring (1981), and Truesdell et al. (1981) without well locations and without significant interpretation.

Gas chemistry has been successfully applied to geothermometry of hot-water systems (Hulston and McCabe, 1962; and others), but direct application of these methods to vapor-dominated systems suggested that gases were not in equilibrium. Some progress (more at Larderello than at The Geysers) was made by

D'Amore and Truesdell (1980) in applying semi-empirical gas geothermometers, but understanding of Geysers gas chemistry awaited recognition that wellhead steam was a mixture of reservoir vapor and vaporized reservoir liquid.

Applying concepts that Giggenbach (1980) developed for hot-water systems, D'Amore et al. (1982) and D'Amore and Celati (1983) showed that by combining two gas equilibria with gas solubilities both the reservoir temperature and the vapor fraction or effective reservoir steam saturation (called "y") could be calculated. D'Amore and Truesdell (1985) used this method to show that different parts of The Geysers differed greatly in y but relatively little in temperature (figure 1). Southeast Geysers samples showed y values from 0.005 to 0.1, indicating that produced steam originated almost entirely from vaporized liquid, but samples from the central and west Geysers showed y values of 0.1 to 1.0, indicating a much larger contribution of reservoir vapor to produced steam.

The variation in y is directly related to the variation in gas/steam ratio. Representative gas analyses are given in table 1 for low, medium, and high total gas/steam ratios from three areas of The Geysers.

### FIELDWIDE PATTERNS IN STEAM COMPOSITIONS

Studies of the fieldwide gas and isotope chemistry of Larderello steam (Celati et al., 1973; D'Amore et al., 1977) show that, in general, gas concentrations (gas/steam,  $\text{NH}_3$ ) increase from the center of the field toward the edge while concentrations of substances more soluble in liquid ( $^{18}\text{O}$ ,  $\text{H}_3\text{BO}_3$ , Cl) decrease in this direction. These patterns were interpreted by D'Amore and Truesdell (1979) to result from lateral steam movement and condensation that could be modeled as a Rayleigh condensation process. In this process the concentration of each constituent C is related to its original concentration  $\text{C}_0$  and the fraction of remaining steam  $\text{M}/\text{M}_0$  by the equation  $(\text{C}/\text{C}_0) = (\text{M}/\text{M}_0)^{(1/B - 1)}$ , in which B is the distribution coefficient of the constituent between vapor and liquid ( $\text{C}_v/\text{C}_l$ ). Limited supporting data from The Geysers was presented. This model of convective circular-

tion of steam and condensate was used by Calore et al. (1982) to explain observed variations in the depth to the liquid saturated zone at the margins of the Larderello field and to indicate an extension of the field to the east (R. Celati, oral commun., 1981).

From the isotope data of Haizlip (1985), fragmentary published gas data, and many unpublished analyses, it is known that large concentration gradients of gas and isotope constituents exist at The Geysers. Understanding the natural processes which caused these gradients will advance our knowledge of the field and possibly assist exploitation as it did at Larderello.

With the cooperation of some of the major steam producers (GEO Operator Corp., Geysers Geothermal Co., Unocal, and Sante Fe Geothermal), maps have been drawn of gas/steam ratios (in ppm gas by weight) and  $\delta^{18}O$  in steam from the entire drilled Geysers field (figures 2, 3). These maps are highly generalized and represent different densities of data in various parts of the field. Early production data representative of original conditions were sought. Steam compositions indicating influence of injected water have been rejected as have analyses from unusually shallow (gas rich) and low flow rate, subcommercial wells. The maps show variations in only gas/steam ratios and  $\delta^{18}O$ ; other variations in isotopes are shown in figure 4 and in gases in table 1.

#### NON-RAYLEIGH GRADIENTS

Geysers steam shows wide ranges in gas and isotope compositions much larger than those observed at Larderello. The range in gas/steam is from about 150 ppmw (parts per million by weight) to more than 65,000 ppmw (table 1); the published range at Larderello is from 10 to 120 liters STP/kg (approximately 17,000 to 200,000 ppmw). The range in  $\delta^{18}O$  is also larger at The Geysers, -7 to +3 permil compared with -6 to 0 permil at Larderello. The magnitude and direction of these composition gradients at The Geysers are different from those at Larderello and require a different interpretation.

At Larderello composition gradients in the central and Serrazzano zones (about two-thirds of the entire field) are consistent with the Rayleigh condensation model. At The Geysers this model appears to work only in limited areas. One of these areas is at the southern end of the field where steam flow appears to be from west to east, as indicated by gradients in gases and isotopes with increases to the east in total gas and  $NH_3$  and decreases in  $\delta^{18}O$  and B (figure 5). Data supplied by Union Oil Co. (now Unocal) for an unspecified section of the central Geysers show the predicted change in  $CO_2$ , although this could not be compared with changes in other constituents (D'Amore and Truesdell, 1979). These gradients, similar to those in the southeast

Table 1. Gas Analyses from Typical Wells in Three Regions of The Geysers

Northwest Geysers						
	High		Medium		Low	
	ppm (wt.)	mole % w/o $H_2O$	ppm (wt.)	mole % w/o $H_2O$	ppm (wt.)	mole % w/o $H_2O$
Total gas	65,200		29,400		8,410	
$CO_2$	55,500	74.3	26,600	71.8	7,450	69.8
$H_2S$	1,710	2.96	958	3.34	356	4.31
$NH_3$	576	1.99	414	2.89	251	6.08
Ar	--	--	.86	.0026	.11	.0012
$N_2$	560	1.18	270	1.15	48.8	.717
$CH_4$	2,580	9.49	1,020	7.56	161	4.13
$H_2$	347	10.1	225	13.3	73.1	14.9
S/G (mole)	30.7		66.1		227	
Central and West Geysers						
	High		Medium		Low	
Total gas	13,500		5,420		2,620	
$CO_2$	11,500	62.5	4,460	58.5	2,080	53.6
$H_2$	662	4.65	310	5.26	184	6.12
$NH_3$	223	3.13	101	3.41	151	10.0
Ar	<2	<0.01	2.0	0.03	.7	.02
$N_2$	153	1.3	78.3	1.61	35.5	1.44
$CH_4$	851	12.7	412	14.8	131	9.24
$H_2$	133	15.8	57.3	16.4	34.8	19.5
S/G (mole)	133		185		608	
Southeast Geysers						
	High		Medium		Low	
Total gas	982		443		143	
$CO_2$	734	51.9	322	51.1	94.7	43.2
$H_2S$	116	10.6	75	15.3	36.4	21.4
$NH_3$	30	5.46	34	13.9	.3	.37
Ar	1.0	.08	.03	.006	.01	.0062
$N_2$	46	5.17	3.3	.82	2.5	1.79
$CH_4$	43	8.33	3.4	1.54	6.4	8.06
$H_2$	12	18.4	5.3	18.3	2.4	23.8
S/G (mole)	1,724		3,870		11,100	

Geysers (Mohinder Gulati, pers. commun., 1977), may also be due to Rayleigh condensation. This model does not work, however, for northern Geysers as a whole, as shown by the strong increase of both gas and oxygen-18 in steam from the central Geysers to the northwest. The condensation model requires changes in oxygen-18 and gas concentrations to be opposite. In addition, the magnitude of the observed changes in gas/steam, if caused by condensation, would require more than 99.8% condensation in the northern part of the reservoir which seems highly unlikely. The isotope and gas gradients are less definite for the south central Geysers, and data toward the field boundaries are missing or fragmentary.

The reason for the large fieldwide gradients in steam composition must be highly speculative without more data, but some suggestions may be more plausible than others. Faced with explaining the oxygen-18 data, Haizlip (1985) rejected processes involving the fluid alone (boiling, condensation, etc.) and concluded that only a south-to-north increase in the amount of remnant connate water or in the rock/water ratio could explain the isotope gradient.

#### CONNATE WATER

The isotopic similarity of steam from the northwest Geysers with connate or metamorphic waters from the Sulphur Bank mine and Wilbur Spring, 25 and 40 km northwest of The Geysers, was noted by Haizlip (1985). These mineralized thermal waters were described by White et al. (1973) as originating from the metamorphism of connate sea water (original  $\delta^{18}\text{O}$  and  $\delta\text{D}=0$ ) contained in Jurassic marine sediments, with  $\delta^{18}\text{O}$  values increased to +4 to +5 by exchange with silicates and carbonates and  $\delta\text{D}$  reduced to -20 to -30 by exchange with low deuterium marine clays. The Sulphur Bank and Wilbur Spring waters are similar in  $\delta^{18}\text{O}$  to the connate(?) fluids described by Lambert (1976) and Sternfeld (1981) as once present in the central Geysers, and fall approximately along the  $\delta^{18}\text{O}$ - $\delta\text{D}$  trend of northwest Geysers steam (figure 4). Gas compositions are less distinctive. No analyses of Wilbur Spring gases are available, but Sulphur Bank mine gas is mainly  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2$ , and trace  $\text{H}_2\text{S}$  (Nehring, 1981). This gas, collected at the surface, may have lost  $\text{H}_2\text{S}$  and  $\text{H}_2$ , but the high  $\text{CH}_4$  contents and light  $\delta^{13}\text{C}$  in  $\text{CO}_2$  are similar to Geysers samples (-14 for Sulphur Bank; about -13 to -20 for The Geysers; Huebner, 1981, and unpublished data).

#### FLUSHING BY METEORIC RECHARGE

The major gradients in gas and isotope composition of steam are almost certainly due to meteoric recharge entering the reservoir from the southeast. Steam in the southeast Geysers has low gas and  $\delta^{18}\text{O}$  similar to local meteoric water. Similar steam compositions are observed along the southern and southeastern boundaries of Larderello where recent recharge has been induced by exploitation. The effects of this recharge decrease away from the point of liquid entry.

Wells drilled at the southeast and east edges of The Geysers field are known to produce steam-water mixtures or water alone from the same depth as the steam reservoir a few hundred meters away. The similarity between isotopic compositions of local meteoric water and steam from the southeast Geysers adjacent to these water boundaries (figure 4) and the low gas contents of steam in this area suggest that this part of the field was the site of massive recharge to the system. Recharge adjacent to outcrops of the reservoir rock has been observed at Larderello, with

increases in tritium and decreases in gas and  $\delta^{18}\text{O}$  in steam observed over periods of a few years (Calore et al., 1982; D'Amore et al., 1983). The lack of tritium in the steam at the southeast Geysers suggests that recharge is not a rapid process related to present exploitation (as at Larderello) but has occurred over a longer period or from older waters (>60 yr.).

The low gas content, low  $\delta^{18}\text{O}$  composition, and high flows of steam from the southern Geysers all suggest that a large proportion of the reservoir fluid consists of liquid water. This liquid water must be held in small fractures and pores of the reservoir rock coexisting with vapor in larger openings because neither drilling nor seismic observations favor the existence of a large well-defined water-saturated zone within the productive volume of the reservoir. In the northern Geysers there is also no evidence of a well-defined water-saturated zone even to the 5-6 km maximum depths of induced seismicity in the oldest producing zone. In this part of The Geysers high gas and  $\delta^{18}\text{O}$  and lower productivity suggest much lower liquid water contents in the productive reservoir.

#### BOILOFF THEN FLUSHING

The apparent lack of a deep water-saturated zone in any part of The Geysers suggests that the system has undergone a near-complete boiloff of its original liquid. This is in agreement with geologic, petrologic, and simulation studies which all suggest that The Geysers started as a hot-water saturated reservoir and became vapor-dominated through a deficit of fluid recharge to discharge (see for example, White et al., 1971; Lambert, 1976; Preuss, 1985). This process does not necessarily tend to a stable steady state and the vapor-dominated zone can extend downward as long as there is liquid to displace. It is possible that a seismic event or other disturbance could allow liquid to enter the underpressured vapor-dominated reservoir from the side where adequate permeability exists. If cooler liquid water entered a nearly dry vapor-dominated reservoir, its effect would depend on its quantity and the depth of entry. Shallow entry and moderate quantity would favor recharge of liquid suspended in the reservoir while large quantities and deep entry would produce a liquid saturated zone that might be large enough to reverse the process of vapor domination. In either case, with time the liquid would move throughout the reservoir. The movement of suspended liquid would depend on vaporization and condensation and would be relatively slow unless hastened by removal (production) of steam as observed with recent recharge at Larderello. Venting of steam and resulting lateral pressure gradients must be important in causing lateral movement of liquid away from areas of recharge. The relative locations of recharge areas and vents have

apparently influenced the flow of recharge at The Geysers.

#### GRADIENTS RELATED TO VENTS

Although surface alteration is found throughout The Geysers, the greatest concentration is in the area of the Big Geysers (units 1-8) along with the largest natural vents. The distribution of vent areas may explain the smaller gradients in  $^{18}\text{O}$  and gas between the southeast and central Geysers and the steepening gradients to the northwest. Driven by meteoric recharge from the southeast, gases and high  $\delta^{18}\text{O}$  steam would have gradually migrated to these vents and left the system. Strong venting in the central Geysers (the Big and Little Geysers areas) would have allowed extensive flushing and homogenization of fluid compositions between this area and the southeast Geysers, while less venting to the northwest would have allowed less flushing and homogenization.

#### ROCK ALTERATION

If recharge waters enter the system from the southeast, reservoir rocks in this area would undergo the greatest alteration of their oxygen isotopes to reach equilibrium with fresh (unaltered) meteoric water. Reservoir rocks further to the northwest would have been progressively less altered as oxygen-18 in recharge waters increased through exchange with rock or mixture with connate formation waters. The influx of meteoric recharge would also be expected to leach minerals with which it was not in equilibrium. Sulfide minerals and organic matter would be oxidized by air-saturated meteoric recharge; calcite would be dissolved through the refluxing action of steam condensation and downward flow of steam condensate.

#### STEAM MIGRATION

The observed steam composition gradients throw into question some of our assumptions about vapor-dominated systems. If steam circulates freely within these systems, then convection should either homogenize fluid compositions (as it does in most hot-water geothermal systems) or create patterns around upflow zones. The presence of separate zones of active boiling and condensation in the Rayleigh condensation model of D'Amore and Truesdell (1979) can maintain concentration gradients, but as we have seen, gradients at The northern Geysers are generally opposite to that predicted by this model. Seismic evidence suggests that vertical permeability is much greater than horizontal, since microearthquakes induced by steam production can extend 3 km deeper than the wells but only a few hundred meters laterally (Oppenheimer, 1986).

The existence of Rayleigh condensation gradients at the southern margin of The Geysers (figures 2, 3, 5) that are counter to gradients resulting from flushing suggests that flushing occurred and was complete before

the Rayleigh gradients were established. Exploration of this chronology may be possible through petrologic studies.

Present gradients in steam composition suggest that either steam is not very mobile on a fieldwide scale or that rock and liquid compositions control steam compositions on a time scale that is rapid relative to the rate of steam circulation. Both conditions may be true. The original pre-exploitation pressure gradients in the field probably were small, as indicated by shut-in pressures of new wells close to 35 bars in all parts of the field. The pressure drops and steam drainage caused by exploitation may change steam composition patterns but would not be evident in figures 2 and 3 since these represent mostly early data. Of course some areas may have been drained before they were drilled, especially on the margins of the early produced Big Geysers area.

With continued exploitation of The Geysers, reservoir pressure differentials between the reservoir and surrounding ground water will increase and, as at Larderello, increased cold-water recharge may occur and tritium may appear. For this reason the use of tritium as an artificial tracer should be avoided.

#### CONCLUSION

The Geysers geothermal field is large and geologically and geochemically complex with a history that is only starting to be understood. Natural circulation in vapor-dominated systems like The Geysers is locally and on a short time scale dominated by the "heat pipe" mechanism in which upward flowing steam condenses and produces downward flowing condensate driven by volcanic heat supplied to yet undiscovered boiling zones. Larger scale circulation patterns based on lateral steam flow away from boiling zones (and condensate back flow) indicated by "Rayleigh" composition patterns appear to dominate at Larderello and in parts of The Geysers. Large-scale circulation at The Geysers appears to have been dominated by flushing with meteoric water probably initiated by catastrophic breakthrough of liquid at the margin of the system. In this process recharge introduced in the southeast has progressively removed oxygen-18 and gases (including gas-forming minerals) from the reservoir, with effects diminishing from the southeast, where steam is almost gas free and similar in  $\delta^{18}\text{O}$  to local meteoric water, to the northwest, where steam is gas and oxygen-18 rich. The exact roles of residual connate waters and high rock/water ratios in the original fluid compositions flushed by meteoric recharge are not yet known. The association of high permeability with highly flushed fluids suggests that the flushing has had physical as well as chemical effects on the reservoir or that flushing was facilitated by existing high permeability.

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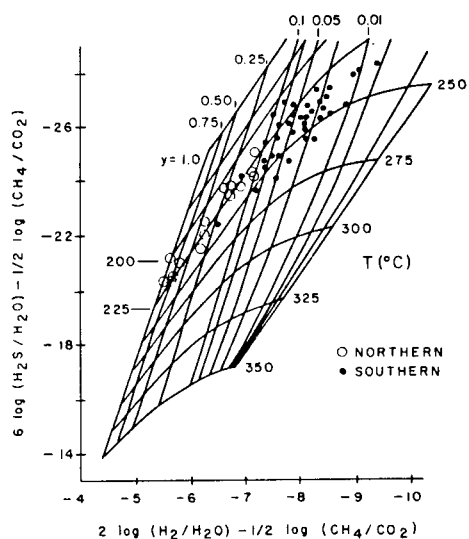


Figure 1. Reservoir temperatures and steam saturation for two areas of The Geysers (from D'Amore and Truesdell, 1985).

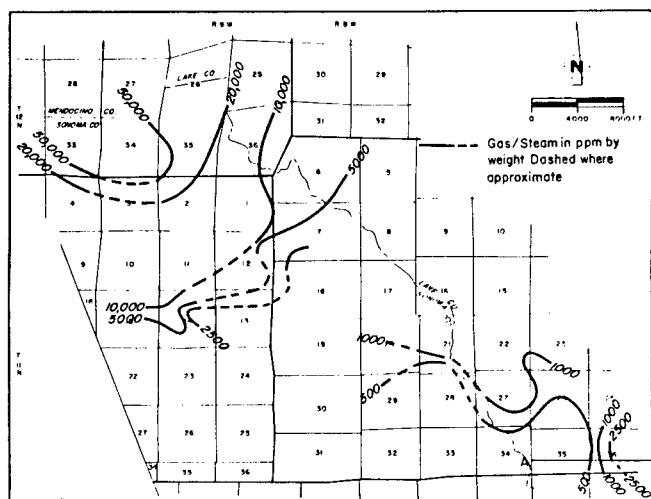


Figure 2. Gas/steam ratios for early production from wells at The Geysers expressed as parts per million by weight. Data from the U.S. Geological Survey and steam-producing companies including GEO Operator, Geysers Geothermal, Unocal Geothermal, and Sante Fe Geothermal.

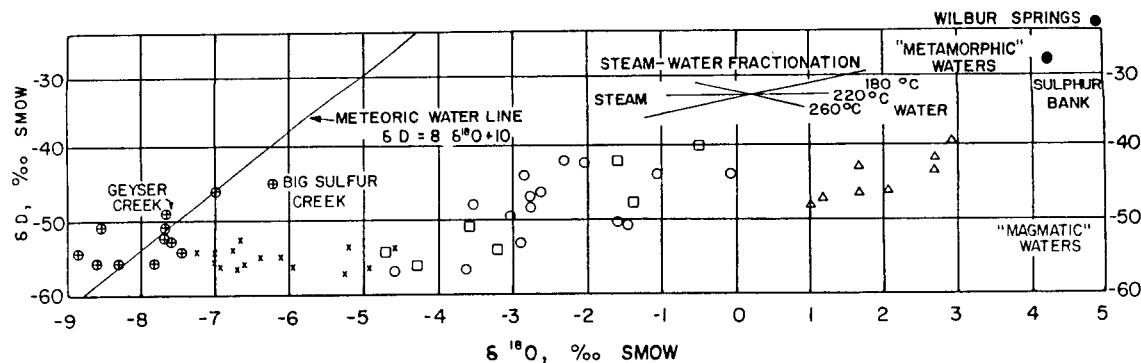


Figure 4. Oxygen-18 and deuterium compositions of early production steam from The Geysers (Data sources as in figure 2). Symbols: x southeast; o central; □ west; Δ northwest; ⊕ meteoric waters; ● connate or metamorphic waters.

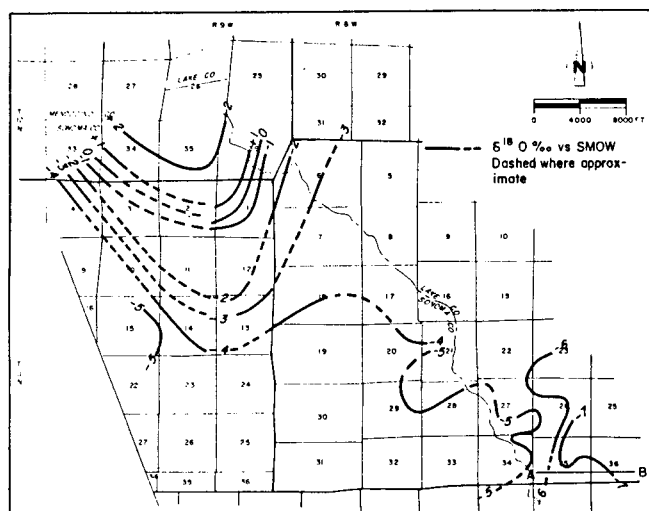


Figure 3. Oxygen-18 compositions of early production steam from The Geysers. Data sources as in figure 2.

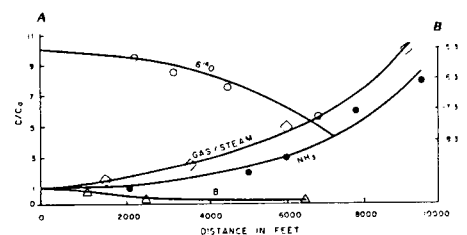


Figure 5. Gradients in steam composition across part of the southern Geysers. Location of cross-section line A-B shown in figures 2 and 3.