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A Compilation of Gas Geochemistry and Isotopic Analyses from The Geysers Geothermal Field: 1978-1991

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ABSTRACT

We present 45 chemical and isotopic analyses from well discharges at The Geysers geothermal field and summarize the most notable geochemical trends. H_2 and H_2S concentrations are highest in the Southeast Geysers, where steam samples have δD and $\delta^{18}O$ values that reflect replenishment by meteoric water. In the Northwest Geysers, samples are enriched in gas/steam, CO_2, CH_4, and N_2/Ar relative to the rest of the field, and contain steam that is elevated in δD and $\delta^{18}O$, most likely due to substantial contributions from Franciscan-derived fluids. The $\delta^{13}C$ of CO_2, trends in CH_4 vs. N_2, and abundance of NH_3 indicate that the bulk of the non-condensable gases are derived from thermal breakdown of organic materials in Franciscan meta-sediments.

Introduction

Despite the prominence of The Geysers as the world's largest geothermal field (formerly producing at ~2000 MWe), there are very few published chemical analyses of steam and non-condensable gas (Allen and Day, 1927; Nehring, 1981; Truesdell *et al.*, 1987). Recently, Lowenstern *et al.*, (1999) published a USGS Open-File Report with the first full geochemical analyses of well discharges from The Geysers steam field. Below, we list a subset of these analyses that are most representative of The Geysers steam field and we summarize some of the key geochemical trends contained in the *entire* data set. Herein, our discussion focuses primarily on the sources of steam and non-condensable gases in the geothermal fluids.

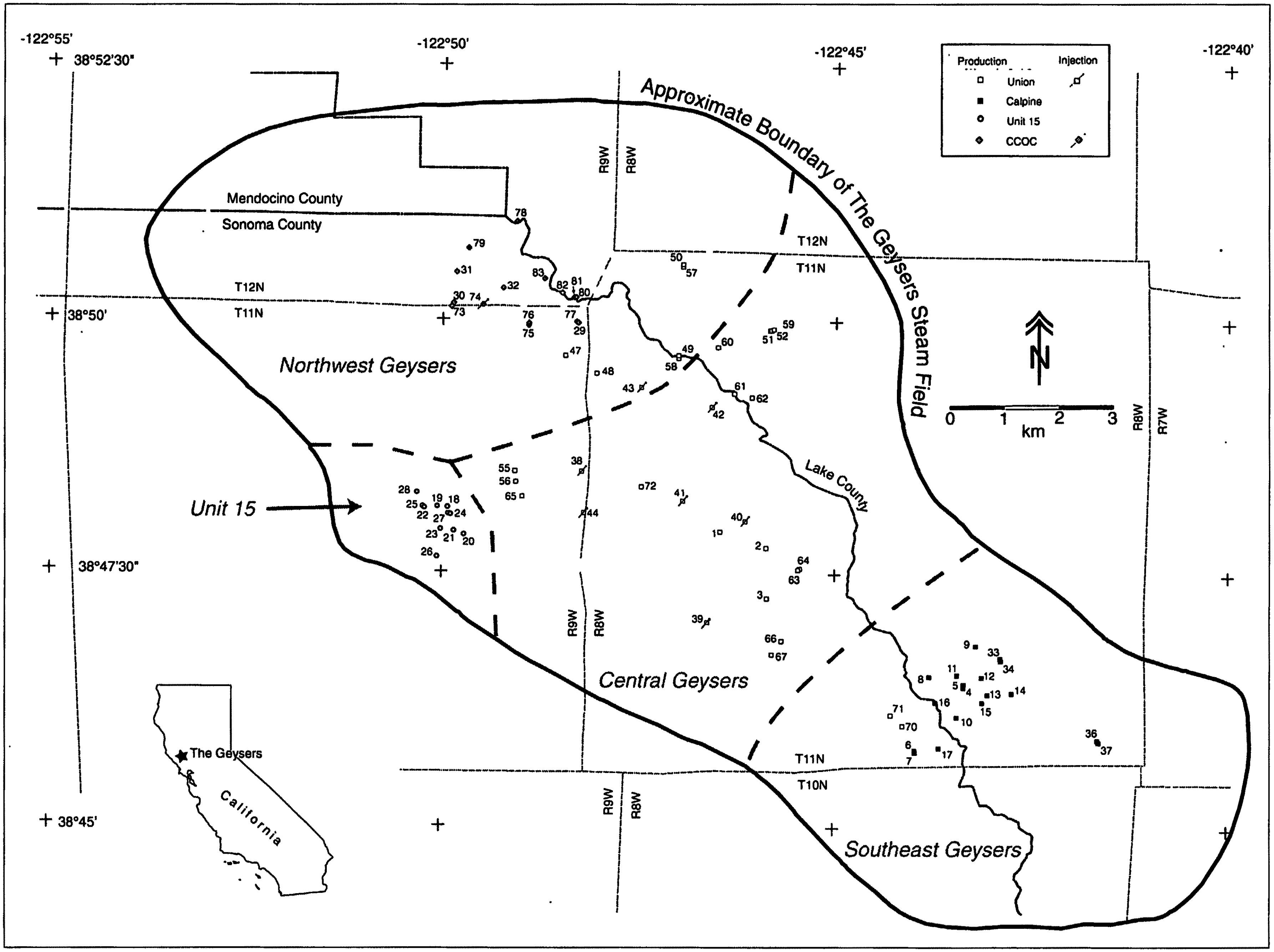
Characteristics of The Geysers Steam Field

The Geysers is a vapor-dominated geothermal field (Figure 1, overleaf) located within the Mayacamas Range in northern California, about 150 km north of San Francisco and at the margin of the Clear Lake volcanic field (Hearn *et al.*, 1981). In vapor-dominated systems, water is present both as liquid and steam, though vaporized water constitutes the pressure supporting medium (White *et al.*, 1971). The present system is believed to have boiled down from a previous liquid-dominated reservoir about 0.28 Ma (Moore and Gunderson, 1995; Hulen *et al.*, 1997; Moore *et al.*, 1998). The Geysers geothermal system was apparently initiated by heat from a composite granitoid intrusion ("the felsite"; Schriener and Suemnicht, 1981) emplaced about 1.1 Ma; and the system has since been sustained by subsequent (unsampled) intrusions (Kennedy and Truesdell, 1996; Grove *et al.*, 1998). Though part of the geothermal reservoir is located within the felsite, most is hosted by Franciscan complex meta-sediments.

At the wellhead, The Geysers steam is superheated; however, within the deeper reservoir, H_2O is contained both as steam and interstitial liquid. Well discharges are thus a function of the relative amounts of the two phases available for transport to the surface (Truesdell *et al.*, 1987). D'Amore and Truesdell (1985) found that y (the proportion of steam to that of liquid water + steam) was very low in the Southeast Geysers ($y = 0.01$ 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. In the Northwest and north-Central Geysers, the 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 (Walters *et al.*, 1992). In the NTR, temperatures are close to 240°C with a pressure around 35 bars. Pressures in the underlying HTR are similar, though temperatures normally exceed 300°C and have been measured as high as 342°C (Walters *et al.*, 1992). Wells that extend into the HTR pass through the NTR, so that sampled fluids represent a mixture of steam and gas from both reservoirs. Kennedy and Truesdell (1996) conjecture that the low y and lack of evidence for the HTR in the Southeast Geysers may be due to the greater meteoric recharge and greater heat loss by 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

Figure 1. Well locations for this study. Symbols correspond to geothermal operator at time of sampling. 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.



signature that is similar to present-day streams and springs in the region (Truesdell *et al.*, 1987). In contrast, samples from the Northwest Geysers have enriched $\delta^{18}O$ and δD values 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 that originate from Franciscan and Great Valley sediments and are found throughout the Clear Lake volcanic field (White *et al.*, 1973). Gunderson (1992) showed that the oxygen isotope composition of host rocks in the Northwest Geysers is also enriched in $\delta^{18}O$.

The Northwest Geysers is also characterized by higher gas/steam ratios than the rest of the field (Truesdell *et al.*, 1987; Walters *et al.*, 1992). This may be due partially to: 1) the high temperatures associated with the HTR, causing greater breakdown of organic matter in Franciscan rocks, and 2) to the lesser flushing by meteoric water over the lifetime of the system (Gunderson, 1992). Steam from the Northwest Geysers and parts of the Central Geysers is also elevated in HCl (Haizlip and Truesdell, 1989), which has caused considerable corrosion-related problems. Lastly, gas samples from the Northwest Geysers have high $^{3}He/^{4}He$ ratios (R/Ra of 6.3 to 8.3; Kennedy and Truesdell, 1996), up to values typical of MORB. Kennedy and Truesdell (1996) interpreted these values to indicate present-day magma degassing beneath the Northwest Geysers, possibly extending south underneath the entire geothermal field.

Sampling and Analysis

Sampling procedures are described in detail by Fahlquist and Janik (1992) and Lowenstern *et al.*, (1999). All samples were taken directly from the sampling port on an insulated steam line near the wellhead at isoenthalpic condition with acid mitigation systems deactivated to prevent sample contamination and to ensure minimal condensation of fluid in the wellbore prior to sample collection. The fluid was drawn into an evacuated bottle containing 4N NaOH solution. Sample analysis was by a combination of gas chromatography (N_2, Ar, He, O_2, CH_4 and H_2), gravimetry/ volumetry (CO_2, H_2O and H_2S), selective-ion electrode (NH_3) and mass spectrometry ($\delta^{13}C$). Steam was also collected as condensate for isotopic analysis of $\delta^{18}O$ and δD by mass spectrometry.

Results

Table 1 (overleaf) contains sample number, well name, location, and gas and isotope composition. Lowenstern *et al.*, (1999) provide additional information on well latitude, longitude, depths and casing, wellhead temperatures and pressures, sulfur isotopes and other well and sample attributes for 81 samples. In addition, they provide data for nine re-injected steam condensates and five surface manifestations (fumaroles and bubbling/boiling pools). Table 1 contains mostly samples believed to be representative of The Geysers prior to significant development. They are similar to the nine representative compositions listed by Truesdell *et al.*, (1987). Even so, it must be stressed that samples for this study do not reflect a single point in time within the geothermal reservoir; Southeast Geysers wells were sampled principally in 1981, whereas data from the Central Geysers are primarily from 1990. Moreover, our published dataset is likely to vary somewhat from present-day compositions at The Geysers which are affected by re-injection of steam condensate and treated wastewater, and by long-term pressure declines (Beall *et al.*, 1992; Beall and Box, 1993). Well discharges that more obviously reflect these latter processes are listed in Lowenstern *et al.*, (1999).

Table 2. Mean compositions of well discharges.

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	SE	C	NW	U15	Surf.
Gas/Steam (ppm)	630	3250	21,650	10,260	---
CO_2 (mol%)	49.0	59.7	65.0	56.0	64.9
H_2S (mol%)	12.3	6.72	4.91	5.35	3.88
He (mol%)	0.0161	0.0077	0.0014	0.0004	0.0021
H_2 (mol%)	22.3	18.6	15.9	16.7	11.9
O_2 (mol%)	0.0135	0.046	0.0081	0.0375	2.30
Ar (mol%)	0.058	0.0237	0.0075	0.017	0.204
N_2 (mol%)	4.66	2.96	1.04	1.76	11.5
CH_4 (mol%)	5.14	6.99	6.06	14.3	4.86
NH_3 (mol%)	6.19	5.33	7.24	6.21	0.512
N_2/Ar	118	157	239	169	58
δD H_2O (‰)	-53	-49	-47	-49	
$\delta^{18}O$ H_2O(‰)	-5.1	-4.3	-1.4		
$\delta^{13}C$ CO_2 (‰)	-13.5	-13.3	-12.4	-12.7	-13.1

SE= Southeast Geysers; C= Central; NW= Northwest; U15 = Unit 15; Surf. = Surface Manifestations

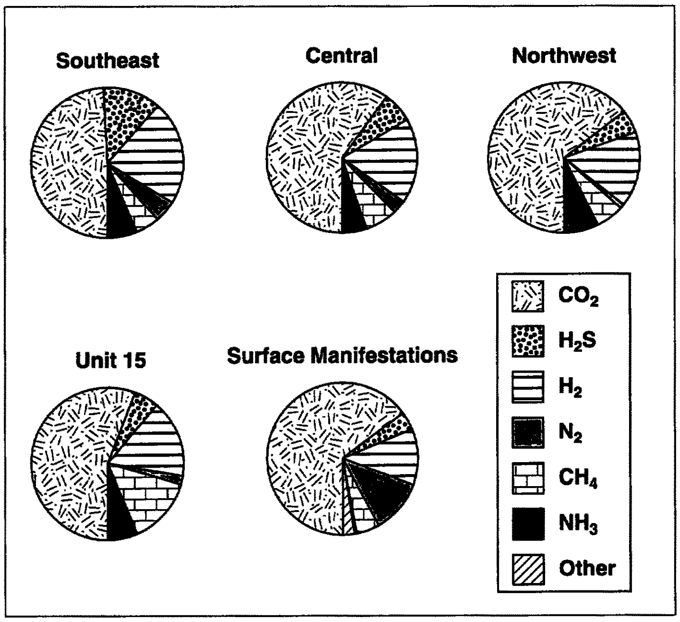

Figure 2. Relative amounts of various non-condensable gases in The Geysers well discharges.

Table 1. Gas geochemistry of samples from The Geysers.

Sample#	Well	Region* & Map#	Gas/Steam (ppm by wt.)	CO_2 mol%	H_2S mol%	He mol%	H_2 mol%	O_2 mol%	Ar mol%	N_2 mol%	CH_4 mol%	NH_3 mol%	N_2/Ar	δD H_2O (per mil)	$\delta^{18}O$ H_2O (per mil)	$\delta^{13}C$ CO_2 (per mil)
G78-05	LF State 4597-18	C(1)	3,062	59.2	10.3	bdl	17.2	0.003	0.050	5.23	6.24	2.06	105	-54	-6.1	-12.4
G78-07	LF State 4597-16	C(3)	1,002	66.3	7.31	bdl	12.5	0.27	0.017	3.37	7.96	2.23	202	-55	-5.0	-13.2
G81-01	D&V-A1	S(4)	443	51.1	15.3	bdl	18.3	bdl	0.0058	0.82	1.54	13.90	141	-54	-6.0	
G81-03	CA 958-37-34 (956#3)	S(6)	192	54.3	17.8	bdl	17.9	0.0140	0.0093	1.47	3.97	4.92	158	-55	-5.6	
G81-04	CA 958-37A-34	S(7)	143	43.2	21.4	bdl	23.8	bdl	0.0062	1.79	8.06	0.37	289	-55	-5.1	
G81-05	D&V-3	S(8)	276	40.8	20.0	0.0054	24.4	bdl	0.0085	1.29	2.59	11.90	152	-58	-5.6	
G81-09	Thorne 6	S(9)	745	50.4	13.8	0.0037	20.1	bdl	0.030	3.08	5.83	7.76	103	-53	-6.8	
G81-13	Thorne 3	S(11)	984	51.9	10.6	bdl	18.4	bdl	0.079	5.17	8.33	5.46	65	-47	-4.9	
G81-17	MLM1	S(14)	403	46.6	13.2	bdl	26.3	bdl	0.030	3.46	5.98	4.64	115	-53		
G81-16	McKinley 3	S(13)	270	37.4	17.7	bdl	33.4	bdl	0.054	3.95	0.81	7.02	73	-53	-6.1	
A86-4	Rorabaugh A-7	U(21)	11,177	59.1	6.14	bdl	14.7	bdl	0.0057	1.44	12.9	6.01	253			-12.5
A86-6	Rorabaugh A-10	U(23)	14,500	63.4	4.37	bdl	13.1	bdl	0.0035	1.81	14.6	3.10	516			-12.4
A86-8	Rorabaugh A-18	U(25)	8,024	49.8	5.55	bdl	12.4	bdl	0.032	2.70	22.0	7.63	85			
A86-9	Rorabaugh A-22	U(26)	7,123	55.6	5.14	bdl	14.7	bdl	0.017	1.72	16.0	6.75	102			-12.2
A86-10	Rorabaugh A-27	U(27)	8,378	61.3	3.87	bdl	16.5	bdl	bdl	1.86	12.9	3.93	-			-13.3
A86-11	Filley1	U(28)	25,534	58.3	4.53	bdl	15.5	bdl	bdl	1.72	16.3	3.95	-			
A87-1	McKinley-3	S(13)	500	52.7	9.50	0.030	31.5	0.0147	0.0164	1.00	0.28	5.36	61			
A87-2	Abel 1	S(33)	668	48.5	7.68	0.0047	28.2	0.038	0.023	2.46	5.62	7.35	107			
G88-6	Prati State 24	N(29)	9,013	60.4	6.41	0.00048	20.7	0.006	0.0046	0.831	3.83	8.10	181	-49	-1.5	-12.9
G88-7	Prati 38	N(30)	21,207	65.1	4.48	bdl	13.7	0.020	0.0026	1.35	8.98	6.56	519	-51		-12.1
G88-8	Prati 25	N(31)	65,324	74.8	1.63	bdl	7.4	0.013	0.0030	1.79	11.58	2.65	597	-49		-11.8
G88-13	CA 956A 56-34 (956#2)	S(17)	498	44.9	3.70	bdl	22.1	0.011	0.046	4.55	13.51	6.49	99	-54		-14.2
G88-16	Davies Est. 5	S(37)	1,344	65.6	3.79	bdl	8.64	0.0065	0.034	4.46	1.21	5.31	131	-58		-12.8
G90-02	Ottoboni St.4596 -15	N(47)	8,255	59.6	6.17	bdl	23.4	bdl	bdl	0.806	4.17	6.25	-	-48	-0.9	-12.4
G90-03	Ottoboni St.4596-14	N(48)	8,371	61.8	6.48	bdl	17.6	0.0019	0.0041	0.714	4.23	9.38	174	-43	-1.8	-12.7
G90-04	D.X. 4596 -45	N(49)	11,837	74.1	4.13	bdl	13.0	0.0014	0.0029	0.4495	3.16	5.05	155	-51	-3.9	-11.8
G90-05	L'Esperance 2 (LESP-2)	N(50)	9,253	69.4	3.58	bdl	17.0	bdl	0.014	2.27	5.36	2.82	160	-48	-4.2	-12.3
G90-06	GD Horner State 4596-9	C(51)	2,057	60.0	4.12	bdl	19.5	bdl	0.019	4.37	9.30	3.17	230	-55	-4.4	-13.3
G90-07	NEGU 15	C(52)	3,177	68.3	4.29	bdl	14.9	bdl	0.017	2.73	8.20	1.76	158	-54	-3.8	-13.1
G90-10	Sulphur Bank -15	C(55)	4,944	54.5	8.39	0.0077	19.9	0.0043	0.0051	0.744	5.78	10.8	146	-42	-0.7	-13.1
G90-12	CA State 92-6	N(57)	16,763	72.2	4.63	bdl	10.7	bdl	0.015	2.37	6.46	3.74	158	-53	-5.7	-11.8
G90-14	NEGU 17	C(59)	8,552	64.5	3.70	bdl	21.4	0.0046	0.0089	2.30	6.70	1.82	258	-52	-6.0	-13.0
G90-15	GD Horner State 4596-7	C(60)	5,634	57.3	5.31	bdl	23.6	bdl	0.013	2.55	7.82	3.78	198	-53	-5.2	-13.3
G90-17	D.X. State 4596-87	C(62)	3,822	59.5	5.17	bdl	21.8	0.015	0.013	2.86	7.29	3.71	227	-55	-4.1	-13.2
G90-19	Angeli 3	C(64)	2,888	62.4	7.42	bdl	19.7	bdl	0.0065	1.76	6.10	2.86	271	-55	-5.8	-13.1
G90-21	Beigel 3	C(66)	952	59.0	6.43	bdl	18.1	bdl	0.050	4.02	9.99	2.61	80	-50	-5.8	-13.1
G91-01	Prati 37	N(73)	43,034	64.8	3.29	bdl	14.6	bdl	bdl	1.356	11.29	4.87	-	-42	1.4	-12.5
G91-05	Prati State 12	N(76)	12,298	59.8	6.09	bdl	19.1	bdl	bdl	0.691	4.82	9.80	-	-45	0.4	-12.5
G91-07	Prati State 54	N(77)	13,217	64.6	5.85	bdl	17.9	bdl	bdl	0.746	4.74	6.37	-	-50	-1.5	-12.4
G91-08	Prati 27	N(78)	32,705	68.1	2.92	bdl	10.9	bdl	bdl	1.098	6.21	10.78	-	-46	-0.8	-12.3
G91-09	Prati 39	N(79)	42,766	69.0	3.38	bdl	13.1	bdl	bdl	0.973	7.51	6.15	-	-40	3.2	-12.2
G91-10	Prati 25	N(31)	88,700	74.6	2.04	bdl	9.7	0.0047	bdl	1.351	9.51	2.88	-	-42	2.0	-12.3
G91-11	Prati State 01	N(80)	9,775	63.0	6.00	bdl	16.2	bdl	0.0025	0.556	2.96	11.36	222	-51	-2.6	-12.5
G91-13	Prati 14	N(82)	12,671	67.7	5.09	bdl	14.4	0.0110	0.0046	0.634	3.37	8.96	138	-51	-2.9	-12.6
G91-14	Prati 50	N(83)	12,866	63.9	4.96	bdl	20.3	0.0073	0.0026	0.959	5.12	4.96	369	-47	-1.6	-12.4

First two numbers indicate year sampled. * Regions shown on Fig. 1 (S=Southeast, N=Northwest, U=Unit 15, C=Central). Number in parentheses is sample no. on Fig. 1.

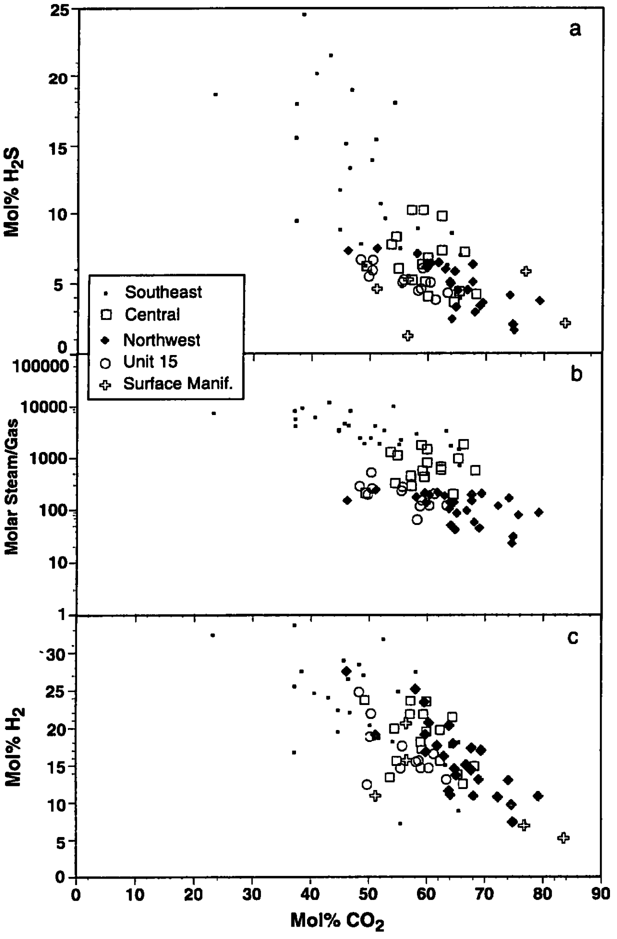

Figure 3. Mole % CO_2 versus (**a**) H_2S, (**b**) molar steam/gas and (**c**) H_2 for The Geysers wells and surface manifestations.

Gas to steam ratios (ppm by weight) averaged 630 in wells from the Southeast Geysers; in contrast, they averaged 3,250 in the Central Geysers, 21,650 in the Northwest Geysers and 10,260 in Unit 15 wells (Table 2, previous page). These averages reflect the entire 81 analyses listed in Lowenstern *et al.* (1999) and not solely those in Table 1 (the accompanying figures also summarize *the entire dataset*). Looking only at the non-condensable gas compositions, Southeast Geysers wells had higher relative H_2S and H_2, and lower CO_2 than the other parts of the field (Figure 2, previous page). The total of $CO_2 + CH_4 + NH_3$ was highest in the Northwest Geysers and Unit 15.

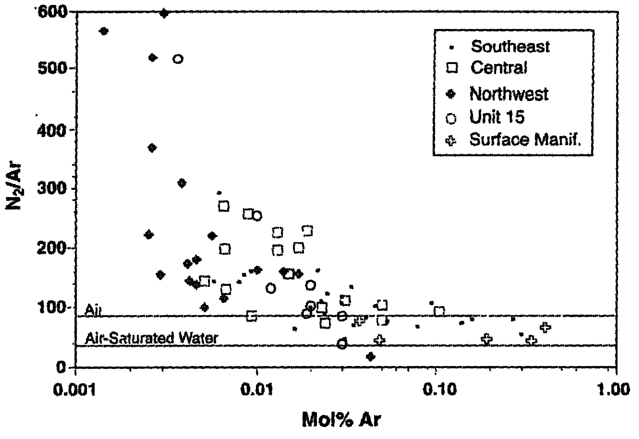

Figure 4. Mole % Ar versus N_2/Ar for non-condensable gas from The Geysers wells and surface manifestations.

We observe two basic types of gases from The Geysers. The first is high in CH_4, CO_2, gas/steam and N_2/Ar, and is common in the Northwest Geysers. Prati 25 (G91-10) is typical of such samples (Table 1). The other type is found in the Southeast Geysers. It is lower in CO_2 and CH_4, and higher in H_2S, and H_2 (Figure 3). N_2/Ar values are closer to those of air and/or air-saturated water (Figure 4). A representative sample of this group is McKinley 3 (G81-16; A87-1).

Re-sampling of individual wells over 5 to 10 years (Lowenstern *et al.*, 1999) showed gradual drying out of the reservoir (increases in gas/steam), increases in CO_2 and decreases in H_2S, consistent with the findings of Beall and Box (1993). However, some wells showed clear influence of nearby injection wells, either in their stable isotopic composition, decreases in gas/steam, or increases in NH_3 derived from re-injected condensate (see also Beall *et al.*, 1992).

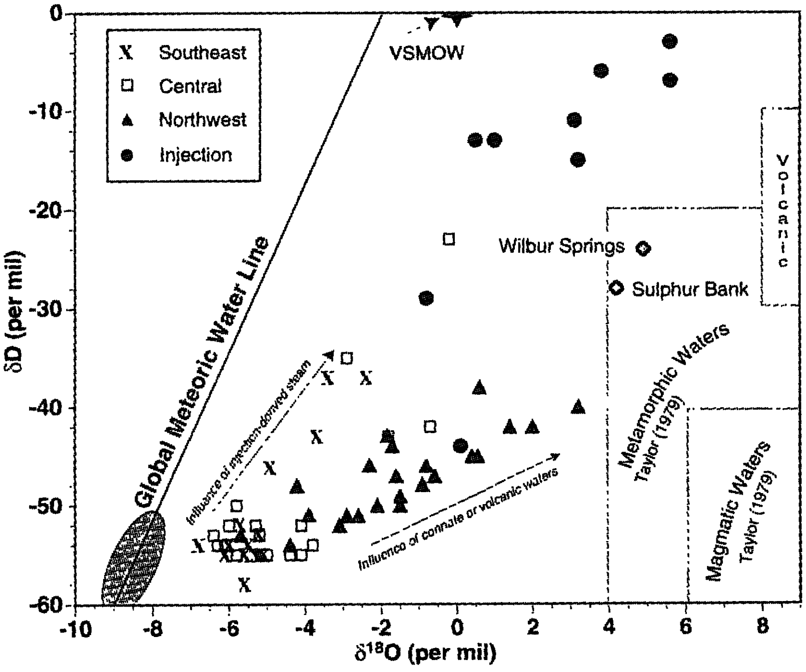

Figure 5. $\delta^{18}O$ versus δD for steam condensed from The Geysers wells. Samples from wells of the Southeast Geysers plot close to the global meteoric water line and local meteoric water (gray ellipse), as do some samples from the Central Geysers. Some of these wells plot on a trend toward injection-derived condensate. Samples from the Northwest Geysers form a trend toward an isotopically heavy end-member similar to connate or volcanic waters. References used to construct the diagram are listed in Lowenstern *et al.*, (1999).

Sources of Gas and Steam in The Geysers Fluids

We can identify several sources of components to gases and steam at The Geysers. Most Southeast Geysers well discharges plot with $\delta^{18}O$ between –5 and –7 ‰ and with δD between –50 and –60 ‰, consistent with slightly ^{18}O-shifted meteoric water. Other Southeast Geysers samples trend toward the composition of evaporated steam condensate that has been re-injected (Figure 5). In contrast, samples from the Northwest Geysers with their high CO_2, CH_4 and gas/steam, relatively high NH_3, and low H_2S and H_2, have characteristics that imply a strong component of fluid from the HTR (Walters *et al.*, 1992). In samples with the highest gas/steam, and thus the greatest signature from the HTR, the steam is enriched in an isotopically heavy component (Figure 5). Such a trend has been noted before and attributed as due to either introduction of magmatic fluids (e.g., D'Amore and Bolognesi, 1993) or connate/Franciscan waters (Haizlip, 1985) similar to those found in the Clear Lake volcanic field and surrounding region (White *et al.*, 1973; Goff *et al.*, 1995).

We interpret the gas abundances and ratios of Northwest Geysers samples to be most consistent with their derivation in large part due to thermal breakdown of organic materials in Franciscan-hosted sediments and conclude that the trend in δD and $\delta^{18}O$ is also best explained by such an origin. Strongly supporting this "Franciscan" signature is the $\delta^{13}C$ of CO_2 in the Geysers samples, which is very similar throughout the field, ranging only from –11.7 to –15.0 ‰ VPDB (most are between –12 and –14‰). Bergfeld *et al.*, (1999) found that such values are typical of Franciscan carbonate veins and concluded that gas at The Geysers has derived its 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, although magmatic carbon in this setting could be somewhat lighter in $\delta^{13}C$ than the typical MORB values of –4‰ to –8‰ (Rollinson, 1993).

Another characteristic consistent with a crustal source of CO_2 in The Geysers reservoir is the high CH_4 and NH_3 concentrations throughout the field and particularly 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 breakdown of sedimentary and metamorphic sources at relatively low-temperatures (Symonds *et al.*, 1994). Such sources could supply the abundant CO_2 as well. A ternary N_2-100*Ar-CH_4 diagram (Figure 6) shows a clear trend from a meteoric water/ air-saturated water end-member towards a CH_4-rich source that is high in N_2/Ar (>200). Samples from the Northwest Geysers and Unit 15 are closest to the CH_4-N_2 tieline because they are least mixed with an air-saturated water end-member. General trends for the entire field are observed even within the Northwest Geysers samples themselves (Figure 7). In these wells, gas/steam, CH_4 and N_2 are positively correlated, and negatively correlated with H_2 and H_2S (Lowenstern *et al.*, 1999). The strong positive correlation of CH_4 and N_2 (Figure 8 and 7a: CH_4/N_2 ~9) and the trend in Figure 6 seems to imply that excess N_2 enters The Geysers system from the same source as the CH_4. If so, N_2/Ar ratios would be expected to be strongly affected by sedimentary sources.

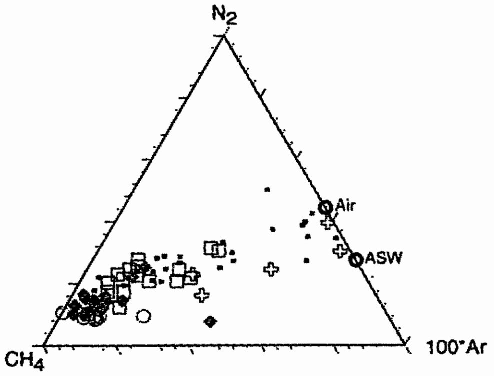

Figure 6. N_2 vs. 100xAr vs. CH_4 for Geysers wells and surface manifestations. Symbols as in Figures 3 and 4. ASW= air-saturated water.

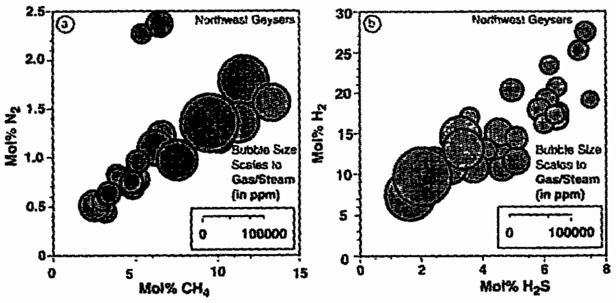

Figure 7. Bubble diagrams for wells of the Northwest Geysers. The size of the symbol corresponds to third variable shown as inset. **a.** Mol% CH_4 vs. mol% N_2 vs. gas/steam. **b.** Mole% H_2S versus mole% H_2 vs. gas/steam.

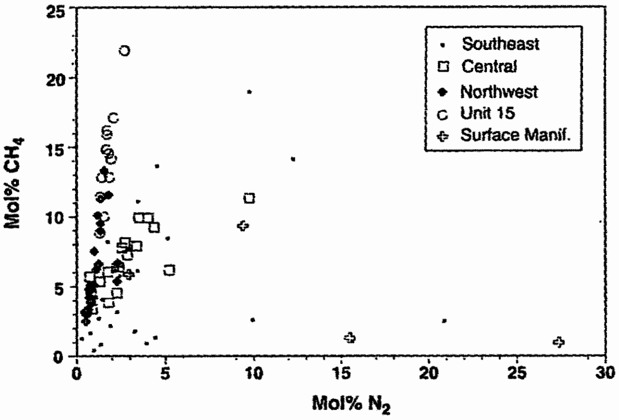

Figure 8. Mole % N_2 versus mol% CH_4 for non-condensable gas from The Geysers wells and surface manifestations.

Indeed, N_2/Ar ratios exceed 300 in 7 samples, 6 of which are from high gas/steam wells from the Northwest Geysers or Unit 15. The values are far greater than the atmospheric ratio of

84 (Figure 4) and are comparable to N_2/Ar found in many springs and gas vents from the Clear Lake volcanic field, as discussed by Goff *et al.*, (1995) and Goff and Janik (1993). Jenden *et al.*, (1988) report N_2/Ar for natural gases from deep wells in the California Great Valley that range from >200 to several thousand, with one sample having a ratio of 22,000. These extraordinarily high values were attributed to production of N_2 by thermal decomposition of organic matter and/or oxidation of ammonium in sheet silicates of the Franciscan assemblage believed to underlie the host strata. High N_2/Ar can also be associated with an arc-magmatic signature, where sedimentary materials are transferred to the mantle wedge either during subduction or magma ascent (Giggenbach 1992). The high N_2/Ar of magmas is thus inherited, directly or indirectly, from meta-sediments.

We conclude that the CH_4, and NH_3 abundances, N_2/Ar, gas/steam ratios, and stable isotope geochemistry of samples from the Northwest Geysers are best explained as reflecting a Franciscan meta-sedimentary source (White *et al.*, 1973; Haizlip, 1985). Convincing evidence for the continuing presence of mid-crustal magma chambers in this region is indicated by: 1) the young volcanism of the Clear Lake volcanic field, 2) the presence of a large, hot, and shallow geothermal system, and, 3) the high $^3He/^4He$ in gases from many Northwest Geysers wells (Kennedy and Truesdell, 1996). Nevertheless, it appears that the chemical input of steam and gas to The Geysers, with the exception of He, is still dominated by meteoric and meta-sedimentary sources.

Conclusions

- As shown in other studies, the geochemical variability of wells from The Geysers is strongly correlated with geography. Samples from the Northwest Geysers are high in CO_2, CH_4, NH_3, N_2/Ar and gas/steam. Those from the Southeast Geysers are enriched in H_2S and H_2 and contain steam isotopically similar to local meteoric water or re-injected steam condensate.
- Chemical and isotopic characteristics of discharges from the Southeast Geysers indicate greater meteoric recharge to that part of the field and a longer history of water-rock interaction (Gunderson, 1992; Truesdell *et al.*, 1987).
- Gas chemistry and isotopic characteristics of samples from The Geysers are consistent with a strong meta-sedimentary input, likely caused by boiling of connate waters and thermal breakdown of sedimentary organic materials within or beneath the reservoir. Such processes are most obvious in the Northwest Geysers where there is a greater thickness of Franciscan sediments, less meteoric recharge, and evidence for recent magmatic heating.

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References

Allen, E.T., and Day, A.L., 1927, "Steam wells and other thermal activity at The Geysers California." Carnegie Institution of Washington, Publication 378, 106p.

Beall, J.J. and Box, W.T., Jr., 1993, "The future of noncondensible gas in the Southeast Geysers steamfield." *Geothermal Resources Council Trans.*, v. 17, p. 221-225.

Beall, J.J. and Box, W.T., Jr., and Enedy, S.L., 1992, "Recovery of injected condensate as steam in the South Geysers field." C. Stone, ed., Monograph on The Geysers Geothermal Field: Davis, California, *Geothermal Resources Council Spec. Rpt.* No. 17, p. 151-157.

Bergfeld, D., Goff, F., and Janik, C.J., 1999, "Carbon isotope systematics and CO_2 sources in The Geysers-Clear Lake region, Northern California." *Geothermics,* in revision.

D'Amore, F. and Bolognesi, L., 1993, "Isotopic Evidence for a magmatic contribution to fluids of the geothermal systems of Larderello, Italy, and The Geysers, California." *Geothermics*, v. 23, p. 21-32.

D'Amore, F., and Truesdell, A.H., 1985, "Calculation of geothermal reservoir temperatures and steam fraction from gas compositions." 1985 International Symposium on Geothermal Energy: *Geothermal Resources Council Trans.*, v. 9, pt. 1, p. 305-310.

Fahlquist, L. and Janik, C, 1992, "Procedures for collecting and analyzing gas samples from geothermal systems." *U.S. Geological Survey Open-File Report* 92-211, 19 p.

Giggenbach, W.F.,1992, "The composition of gases in geothermal and volcanic systems as a function of tectonic setting." Y.F. Kharaka and A.S. Maest, eds., *Water-Rock Interaction: Proceedings* WRI-7, AA. Balkema, Rotterdam, p. 873-878.

Goff, F., and Janik, C.J., 1993, "Gas geochemistry and guide for geothermal features in the Clear Lake region, California." J.J. Rytuba, ed., *Active Geothermal Systems and Gold-Mercury Deposits in the Sonoma-Clear Lake Volcanic Fields, California.* Society of Economic Geologists Guidebook Series, v. 16, p. 207-261.

Goff, F., Janik, C.J., and Stimac, J.A., 1995, "Sulphur Bank Mine, California: An example of a magmatic rather than metamorphic hydrothermal system?" *World Geothermal Congress,* Florence Italy, 18-31 May 1995, p. 1105-1110.

Grove, M., D'Andrea, J., Harrison, T.M., McKeegan, K.D., Dalrymple, G.B., and Hulen, J.B., 1998, "High precision Pleistocene U-Pb Zircon ion microprobe granite emplacement ages from The Geysers geothermal system, CA." *Trans., Am. Geophys. Union,* v. 79, p. F 951.

Gunderson, R.P., 1992, "Distribution of oxygen isotopes and noncondensible gas in steam at The Geysers." C. Stone, ed., Monograph on The Geysers Geothermal Field: Davis, California, *Geothermal Resources Council Spec. Rpt.* No. 17, p. 133-138.

Haizlip, J.R., 1985, "Stable isotopic composition of steam from wells in the northwest Geysers, The Geysers, Sonoma County, California." *Geothermal Resources Council Trans.*, v. 9, no. 1, p. 311-316.

Haizlip, J.R. and Truesdell, A.H., 1989, "The correlation of noncondensible gas and chloride in steam at The Geysers." *Geothermal Resources Council Trans.*, v. 13, p. 455-460.

Hearn, B.C., Jr., Donnelly-Nolan, J.M., and Goff, F.E., 1981, "The Clear Lake Volcanics." R.J. McLaughlin and J. Donnelly-Nolan, eds., Research in the Geysers-Clear Lake Geothermal Area, northern California: *U.S. Geological Survey Professional Paper* 1141, p. 25-45.

Hulen, J.B., Heizler, J.A., Stimac, J.A., Moore, J.N., and Quick, J.C., 1997, "New constraints on the timing of magmatism, volcanism, and the onset of vapor-dominated conditions at The Geysers steam field, California." *Proceedings of the 22nd Workshop on Geothermal Reservoir Engineering,* Stanford University, Stanford, CA, p. 75-81.

Jenden, P.D., Kaplan, I.R., Poreda, R.J., and Craig H., 1988, "Origin of nitrogen-rich natural gases in the California Great Valley: Evidence from helium, carbon and nitrogen isotope ratios." *Geochim. Cosmochim. Acta,* v. 52, p. 851-861.

Kennedy, B.M., and Truesdell, A.H., 1996, "The Northwest Geysers high-temperature reservoir: Evidence for active magmatic degassing and implications for the origin of The Geysers geothermal field." *Geothermics,* v. 25, p. 365-387.

Lowenstern, J.B., Janik, C.J., Fahlquist, L., and Johnson, L.S., 1999, "Gas and isotope geochemistry of 81 steam samples from wells in The Geysers geothermal field, Sonoma and Lake Counties, California, USA." *U.S. Geological Survey Open File Report* 99-304, in press.

Moore, J.N., and Gunderson, R.P., 1995, "Fluid inclusion and isotopic systematics of an evolving magmatic-hydrothermal system." *Geochim. Cosmochim. Acta,* v. 59, p. 3887-3907.

Moore, J.N., Anderson, A.J., Adams, M.C., Aines, R.D., Norman, D.I., and Walters, M.A., 1998, "The fluid inclusion and mineralogic record of the transition from liquid-to vapor-dominated conditions in The Geysers geothermal system, California." *Stanford Geothermal Workshop,* v.23, 211-218.

Nehring, N.L., 1981, "Gases from springs and wells in The Geysers-Clear Lake area." R.J. McLaughlin and J. Donnelly-Nolan, eds., Research in the Geysers-Clear Lake Geothermal Area, Northern California: *U.S. Geological Survey Professional Paper* 1141, p. 205-209.

Rollinson, H.R., 1993, "Using Geochemical Data: Evaluation, Presentation, Interpretation." *Longman Scientific and Technical Ltd.*, Essex, U.K., 352 p.

Schriener, A., Jr., and Suemnicht, G.A., 1981, "Subsurface intrusive rocks at The Geysers geothermal area, California." Proceedings of the Symposium on Mineral Deposits of the Pacific Northwest-1980: *U.S. Geological Survey Open File Report* 81-355, p. 295-302.

Symonds, R.B., Rose, W.I., Bluth, G.J.S. and Gerlach, T.M., 1994, "Volcanic-gas studies: Methods, results, and applications." M.H. Carroll and J.R. Holloway, eds., Volatiles in Magmas: Mineralogical Society of America, *Reviews in Mineralogy,* v. 30, p. 1-66.

Truesdell, A.H., Box, W.T., Jr., and Haizlip, J.R., 1987, "A geochemical overview of The Geysers (California) geothermal reservoir." M.K. Horn, ed., Transactions 4th Circum-Pacific Energy and Mineral Resources Conference, Singapore, August 1986, p. 487-499 (reprinted *in* C. Stone, ed., Geothermal Resources Council Spec. Rpt. No. 17, p. 121-132.).

Walters, M.A, Haizlip, J.R., Sternfeld, J.N., Drenick, A.F., and Combs, J., 1992, "A vapor dominated high-temperature reservoir at The Geysers California," C. Stone, ed., Monograph on The Geysers Geothermal Field: Davis, California. *Geothermal Resources Council Spec. Rpt.* No. 17, p. 77-87.

White, D.E., Barnes, I., and O'Neil, J.R., 1973, "Thermal and mineral waters of non-meteoric origin, California coast ranges." *Geol. Soc. Am. Bull.,* v. 84, p. 547-560.

White, D.E., Muffler, L.P.J., and Truesdell, A.H, 1971, "Vapor-dominated hydrothermal systems compared with hot water systems." *Econ. Geol.,* v. 66, p. 75-97.