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Geothermal Resources Council *Transactions*, Vol. 21, September/October 1997

Origin and Chemical Evolution of The Geysers, California, Hydrothermal Fluids: Implications From Fluid Inclusion Gas Compositions

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ABSTRACT

The compositions of fluid-inclusion gases from hydrothermally altered rocks at The Geysers were determined to evaluate their origins. Samples dominated by magmatic fluids have N_2/Ar ratios much greater than air and high $^3He/^4He$ ratios. Fluid inclusion populations dominated by connate waters also have high N_2/Ar ratios but are enriched in CH_4. A noble gas analysis of one sample indicates that it has high contents of radiogenic He and a low R/Ra ratio. These samples are found mainly in the northwest Geysers. Samples from the southeast and central Geysers generally have N_2/Ar ratios between air and air-saturated water indicating a significant component of meteoric recharge, and lower CH_4 contents. Despite their meteoric signature, He isotopic compositions record the influence of a magmatic input. Similar N_2-Ar-CH_4 ratios characterize the modern steam.

Introduction

The gas compositions of geothermal fluids are sensitive indicators of their source areas and the processes affecting them (Kennedy et al., 1985; Giggenbach, 1986; Kennedy and Truesdell, 1996; Norman et al., 1996). Norman and Musgrave (1993) and Norman et al. (1996) have shown that the interpretational techniques used to evaluate the gas compositions of modern fluids can also be applied to fluid inclusion gas analyses. In this paper, we apply these techniques to the gas compositions of fluid-inclusions from The Geysers. Although this geothermal system is presently vapor-dominated, Moore and Gunderson (1995) demonstrated that many of the inclusions formed when the system was liquid-dominated. Thus, these inclusions provide information on the sources and evolution of the fluids that gave rise to the present vapor-dominated conditions.

Geological Setting

The Geysers is located in the Mayacmas Mountains on the southwestern edge of the Clear Lake volcanic field, about 150 km north of San Francisco (Figure 1). The active geothermal system appears to be closely related to an underlying hypabyssal granitic intrusion (Schriener and Suemnicht, 1981) that ranges in age from more than 1.4 to 0.95 Ma (Dalyrmple, 1992; Pulka, 1991). Younger rhyolite dikes were emplaced in the southeast at 0.57 Ma while measured temperatures of up to 342°C (Walters et al., 1988) and high $^3He/^4He$ ratios (R/Ra values up to 8.3; Kennedy and Truesdell, 1996) in steam from the northwest attest to more recent activity. Although the influence by the youngest intrusives on the present geothermal system appears to be most evident in the northwest, high R/Ra values in steam from the southeast suggests that it's influence may extend underneath much of the geothermal field but is buffered by deep meteoric recharge from the southeast (Kennedy and Truesdell, 1996).

Mineralogic, fluid inclusion, and isotope relationships, combined with $^{40}Ar/^{39}Ar$ spectrum dating indicate that the present vapor-dominated conditions evolved from a liquid-dominated geothermal system at about 0.25 to 0.28 Ma (Moore and Gunderson, 1995; Hulen et al., 1997). Alteration of the metagraywacke reservoir rocks by the early hydrothermal waters produced distinctive mineral assemblages. Within 600 m of the intrusive contact, the rocks were altered to a biotite-rich hornfels containing phengite, chlorite, and biotite. Veins within the hornfels contain biotite ± tourmaline ± actinolite ± clinopyroxene ± epidote + quartz + potassium feldspar (paragenesis 1). With increasing distance from the intrusion, the veins are characterized by actinolite ± epidote ± ferroaxinite ± prehnite + quartz + potassium feldspar (paragenesis 2); epidote ± chlo-

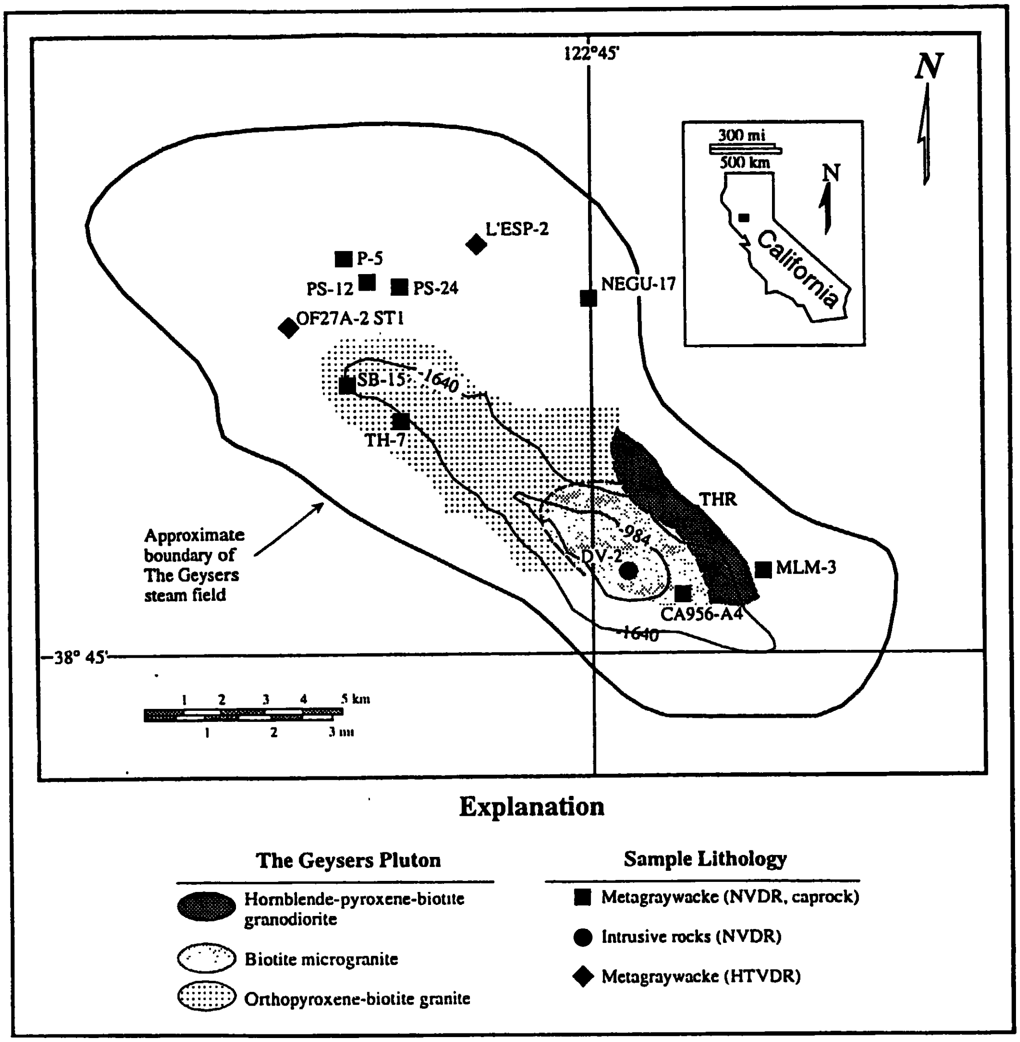

Figure 1. Map showing the distribution of sample locations and the major intrusive phases of The Geysers pluton. Abbreviations: L'ESP = L'esperance-2; P = Prati; PS = Prati State; SB = Sulphur Bank; THR = Thorne. The following refer to regions of the present-day reservoir NVDR = normal vapor-dominated reservoir; caprock; HTVDR=high-temperature vapor-dominated reservoir. The contours show the extent of the reservoir at different elevations relative to mean sea level.

rite + quartz + potassium feldspar (paragenesis 3); and calcite + quartz + potassium feldspar (paragenesis 4).

Moore and Gunderson (1995) used fluid inclusions to demonstrate that 5 different fluids were involved in this alteration. They recognized a high-temperature hypersaline (25 weight percent NaCl equivalent) brine, a moderate salinity connate or metamorphic water with a salinity in excess of 5 weight percent NaCl equivalent, steam that is locally enriched in noncondensable gases; a low salinity, moderate temperature (200°C) steam condensate, and a low salinity, lower temperature meteoric water.

Sample Selection, Distribution, and Characteristics

Fluid-inclusion gas analyses were performed on veins that had been characterized by Moore and Gunderson (1995) or Hulen et al. (1997). These samples provide a complete transect across the thermal system from the upper parts of the pluton to the weakly altered rocks in the outer parts of the metamorphic aureole it formed. The distribution of the sample locations, their relationship to the present-day configuration of the steam reservoir, and the host lithologies are shown in Figure 1.

In addition to the well samples, carbonate-quartz veins from outcrops near SB-15 and from Elk Mountain, located outside The Geysers field were analyzed to establish background gas compositions. Surface samples from The Geysers were considered appropriate for background measurements because previous whole-rock isotope studies by Moore and Gunderson (1995) and Lambert and Epstein (1992) had shown that near surface rocks were essentially unaltered by The Geysers thermal system.

Analytical Methods

Major and minor gases, including H_2O, CO_2, CH_4, H_2S, H_2, N_2, Ar, and $C_{2\text{-}7}$ organic species were analyzed by quadrapole mass spectrometry after being released from the inclusions by either thermal decrepitation and cryogenic separation (TDCS method) or crushing (crush-fast scan (CFS) method). Details of the analytical techniques are described by Norman and Sawkins (1987) and Norman et al. (1996).

Both methods have advantages and limitations. In general, the TDCS method provides greater precision and allows analysis of a larger number of species because the sample is cryogenically separated into liquid N_2 noncondensible, liquid N_2 condensable, and aqueous fractions. Analytical precision is 5% or better for most species. However, the inclusions must be heated above their homogenization temperatures (typically to 400° to 500°C) before they will decrepitate. As the inclusions are heated, H_2, CO, CO_2, and CH_4 reequilibrate to the furnace temperature. Ratios between conservative species (e.g. He, N_2, Ar, etc.) are, however, unaffected. The data can be "corrected" by calculating the equilibrium concentrations at the average fluid-inclusion trapping temperature. Such corrections, however, assume that the inclusion population was adequately sampled and that they were trapped at the same temperature and contained the same gas compositions. Because these assumptions cannot be verified, and it can be shown that the relative positions of the samples are generally not greatly affected by "correcting" the CH_4 contents of the samples, no "corrections" were applied to the TDCS data shown in the ternary diagrams below.

The CFS method involves crushing the inclusions in the vacuum chamber housing the mass spectrometer. Crushing measures far fewer inclusions than does decrepitation. Opening a 10 to 20 micron inclusion or group of smaller inclusions of equivalent volume provides the ideal amount of volatiles for the analysis. The precision of the CFS analyses is 10 to 20%. However, concentrations of He below 30 ppm can not be detected because of interferences with other gases.

The noble gases were analyzed in a magnetic sector noble gas mass spectrometer after the samples were crushed under vacuum in a sample preparation line connected directly to the mass spectrometer. The exsolved gas was purified by passing it over a series of metal alloy getters to remove reactive constituents (e.g. CO_2, H_2O vapor, N_2, etc.). The residual noble gas fraction was then adsorbed on activated charcoal cooled to 27°K. The noble gases were released separately by heating the charcoal to a pre-determined temperature and then admitted to the mass spectrometer. The abundances of He, Ne, and Ar isotopes in each sample were determined. A procedural blank (gas processed without crushing) was analyzed prior to each sample. The blank amounts were: $^4He = 2.3\text{-}9.0 \times 10^{-11}$ cc STP ($^3He = 0.7\text{-}3.0$ cc STP), $^{22}Ne = 3.2\text{-}4.9 \times 10^{-12}$ cc STP, and $^{36}Ar = 0.6\text{-}1.3 \times 10^{-10}$ cc STP. The isotopic compositions of the Ne and Ar in the blanks were atmospheric within error and, therefore, a blank correction was applied to the measured gas amounts but not to the sample isotopic data. The He blanks consistently have ^3He in excess of ^4He relative to atmospheric composition ($^3He/^4He$ about 23 Ra) and the sample He compositions have been corrected accordingly.

Results

One hundred forty CFS and TDS analyses were performed on the samples. With the exception of quartz from Prati-5 (1271 m), the principle component of the fluid inclusions was H_2O, which ranged from 67.1 to more than 99 mole percent. CO_2 and CH_4 made up the bulk of the remaining gases in these samples. CFS analyses yielded concentrations of CO_2 that ranged from 2.4×10^{-4} to 11.5 mole percent whereas CH_4 ranged from 6.2×10^{-5} to 8.7 mole percent. Quartz from Prati-5 (1271 m) contains numerous vapor-rich inclusions and the analyses are enriched in noncondensible gases. H_2O contents of inclusions in this sample ranged from 25.9 to 86.3 mole percent, CO_2 from 8.3 to 50.6 mole percent and CH_4 from 2.6 to 32.7 mole percent. Hydrocarbons ($C_{2\text{-}7}$) were present in most samples but only in trace amounts, and typically comprised less than 1.5 mole percent.

The results of the noble gas analyses are shown in Table 1 as concentrations and as F(i) values, where F(i) is the $i/^{36}Ar$ sample ratio normalized to the ratio in air. The isotopic compositions of Ne and Ar were indistinguishable from air. In general, the samples are characterized by low gas concentrations. The similarity of the $F(^{22}Ne)$ values to air-saturated water $[(F^{22}Ne).0)]$ suggests that meteoric water has had an influence on the noble gas inventory in the fluid inclusions (e.g. DV-2). $F(^{22}Ne)$ values approaching 1.0, however, implies that other processes or sources may also play a significant role, such as air entrapment or contamination.

Determination Of Fluid Sources

Fluids formed in different geologic environments may be characterized by distinctive gas ratios or noble gas contents (Kennedy et al., 1985; Giggenbach, 1986; Norman and Musgrave, 1993; Norman et al, 1996; Hiyagon and Kennedy, 1992). Meteoric volatiles have N_2/Ar, ^{22}Ne, ^{84}Kr, and $^{132}Xe/^{36}Ar$ between air and air-saturated water. Volatiles associated with magmatic fluids include N_2, Ar, CO_2, H_2, H_2S, and He with R/Ra values 0.1 and N_2/Ar ratios exceeding 100. The presence of high N_2/Ar ratios in themselves, however, is not a good indicator of a magmatic influence. Hiyagon and Kennedy (1992) found N_2/Ar ratios up to 200 in natural gas fields influenced by connate waters. Gases of crustal origin are identified primarily by low $^3He/^4He$ ratios (.1 Ra) and by the presence of CH_4 and hydrocarbons ($C_{2\text{-}7}$). However, some gases often associated with magmatic fluids can also be derived from crustal rocks, such as CO_2, H_2S, and N_2 and CH_4 can be produced abiogenically in hydrothermal systems.

Figure 2 shows the He x 10-N_2/200-Ar ratios of fluid inclusions determined by TDCS analysis and the averages of multiple CFS analyses of samples from SB-15. The data define two groups. With the exception of DV-2 (point 1), samples containing tourmaline and/or biotite (paragenesis 1) or actinolite (paragenesis 2) are characterized by N_2/Ar ratios much greater than air and low He contents. The compositions of these samples implies that gases of a magmatic or crustal origin dominate and that there has been little, if any, influence of meteoric fluids. The presence of a magmatic component is further suggested by the occurrence of hypersaline inclusions in OF27A2-

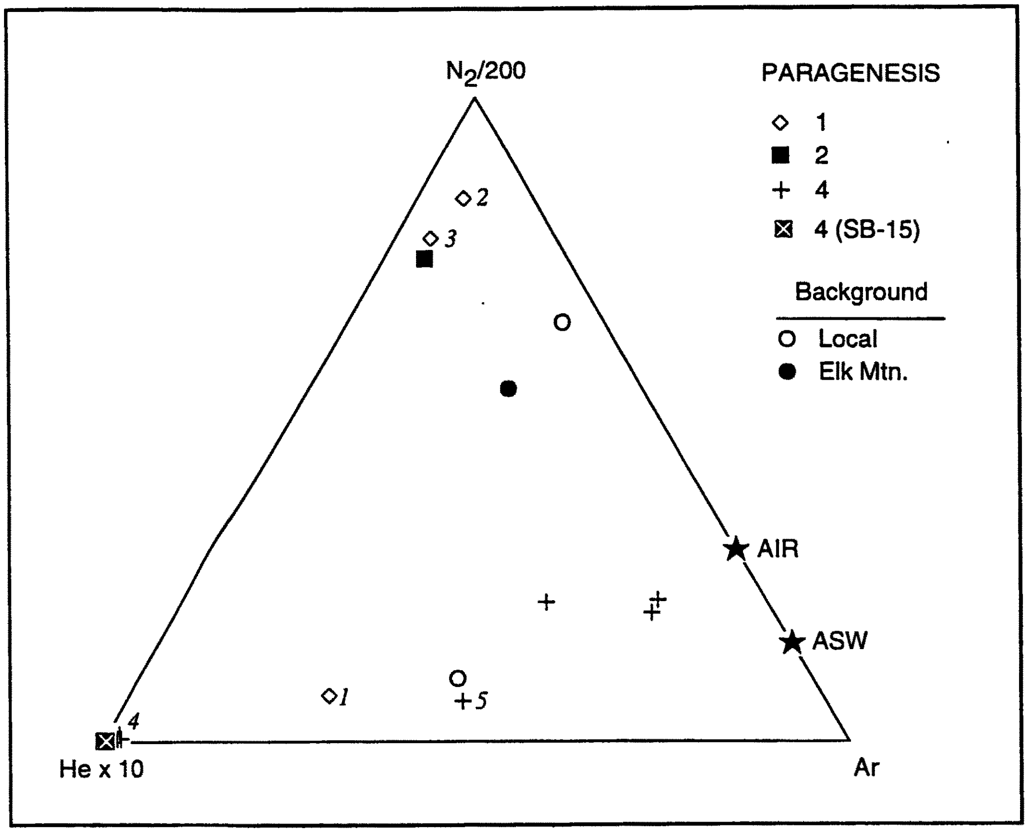

Figure 2. Ternary diagram showing He x 10-N_2/200-Ar ratios of fluid inclusion gases. Paragenses 1-4 refer assemblages characterized by tourmaline and or biotite (1), actinolite ± ferroaxinite (2); epidote + quartz (3), and calcite + quartz (4). Local background samples were collected from a pad near SB-15 (see Figure 1); the sample from Elk Mountain is from outside the field. Numbers in italics within the triangle refer to the following samples: 1 = DV-2; 2 = OF27A-2ST1; 3 = L'esperance-2; 4 = SB-15 (459 m); 5 = Thorne-6 (1216 m). ASW = air-saturated water.

ST1 (point 2) and L'esperance-2 (point 3). The second group is characterized by N_2/Ar ratios close to air-saturated water. Samples in this group are from the southeast and central parts of the field and include inclusions from DV-2 (point 1), which also contains hypersaline inclusions. The samples in this group define a trend that would be expected from interactions with meteoric waters that had accumulated varying amounts of crustal He. Samples containing paragenesis 4 are from the caprock or uppermost part of the steam reservoir.

The noble gases are enriched in ^{4}He/^{36}Ar relative to meteoric water (F(^{4}He) about 0.25) and except for inclusions in DV-2, are also enriched relative to air. Inspection of Table 1 shows that the magnitude of the enrichment is inversely correlated with the concentration of ^{36}Ar indicating that, except for L'esperance-2, the samples can be considered mixtures of two independent components; one enriched in ^{36}Ar (meteoric water or air) and the other enriched in total He with a ^{3}He/^{4}He ratio of about 6 Ra (Figure 3). It is noteworthy that the isotopic composition of the inclusion fluids is similar to the low end of the values (6.3 to 8.3 Ra) measured in the present-day production steam (Kennedy and Truesdell, 1996). Inclusions in L'esperance-2 require an additional component with a much higher He content relative to Ar and a ^{3}He/^{4}He ratio of about 0.5 Ra (Figure 3). These ratios indicate a significant crustal contribution which is consistent with the high CH_4 contents discussed below. The low R/Ra value of inclusions in L'esperance-2 was unexpected because of the presence of hypersaline inclusions and the high N_2/Ar ratio of the sample. Apparently, the inclusions in this sample record the influx of connate or metamorphic fluids with high N_2/Ar, high CH_4/N_2, and low ^{3}He/^{4}He ratios. These fluids may have been responsible for the formation of chlorite after biotite in veins deposited in this sample. The influence of meteoric recharge is most pronounced in the noble gas data from quartz + tourmaline veins in DV-2. Inclusions in this sample have the highest ^{36}Ar concentration, the lowest F(^{22}Ne), and as noted above, N_2/Ar ratios indicative of a meteoric source. However, the ^{3}He/^{4}He ratio requires a magmatic contribution.

CH_4/500-N_2/100-Ar Relationships and Comparison with Modern Steam

He concentrations of many of the samples analyzed by the CFS method could not be determined because of interferences, and data on this species is unavailable for the representative analyses of the early steam compiled by Truesdell et al. (1987). However, based on correlations between CH_4 and the C_{2-7} , Norman et al. (1996) suggested that CH_4 could be used as an indicator of a crustal source. This work provides further support for the use of CH_4 as a proxy for He. Analysis of 88 CFS determinations from SB-15 yielded a correlation coefficient between log CH_4 and log C_{2-7} of 0.78, and with the exception of data from a depth of 315 m, correlation coefficients for the remaining 7 depth intervals ranged from 0.84 to 0.98.

Table 1. Relative abundances of noble gases. OF27A-2ST1(a) and (b) refer to tourmaline- and quartz-rich fractions of the same vein.

Sample	Mass analyzed (gm)	[^{36} Ar] 10^{-9} ccSTP/gm	F (^{4}He)	F(^{22}Ne)	[^{4}He] 10^{-9} ccSTP/gm	[^{3}He] 10^{-9} ccSTP/gm
Thorne-6 (1216 m)	0.0770	—	—	—	33.4	28.1
SB-15 (459 m)	0.9846	—	—	—	0.6	0.6
SB-15 (460 m)	0.8475	2.13	3.885±0.001	0.926±0.116	1.4	1.5
L'esperance-2	0.2800	1.54	56.493±0.104	0.824±0.113	14.5	1.0
OF27A-2ST1(a)	0.2988	1.65	9.129±0.008	0.791±0.207	2.5	2.6
OF27A-2ST1(b)	0.1662	1.38	10.623±0.016	0.870±0.430	2.4	2.4
DV-2	0.1463	3.85	0.608±0.002	0.428±0.172	0.4	0.6

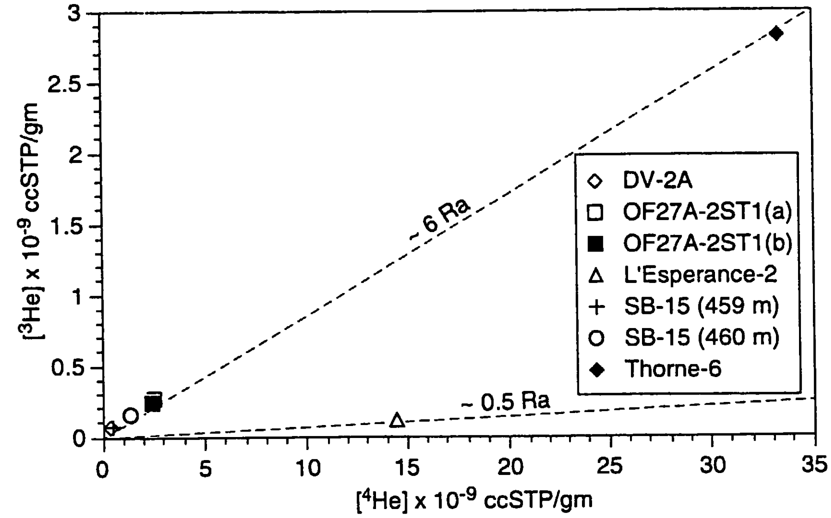

Figure 3. Concentrations of ^{3}He plotted against ^{4}He for samples from The Geysers. Refer to Figure 1 for sample locations.

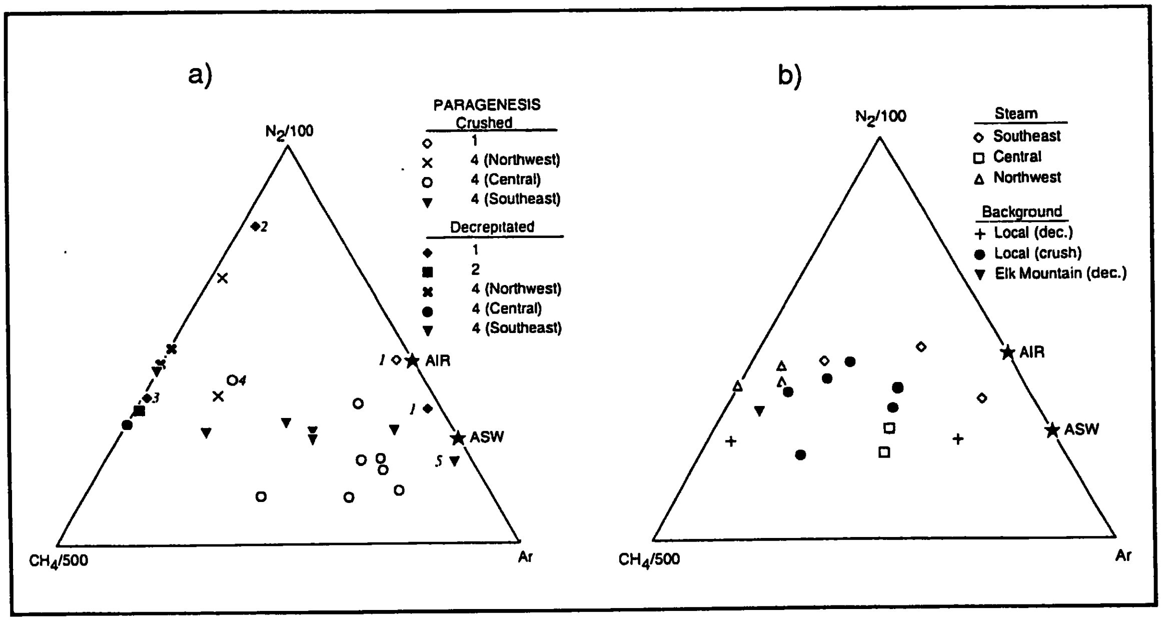

Figure 4. Ternary diagram showing CH_4/500-N_2/100-Ar ratios of samples from (a) The Geysers wells and (b) the present-day steam and background samples. The abbreviations and numbering are the same as the same as those used in Figure 2.

Figure 4 shows the average $CH_4/500-N_2/100-Ar$ ratio for each sample calculated from the CFS analyses (Figure 4a) and for comparison, the compositions of the present-day steam and background samples (Figure 4b). Overall, these data present a picture of the hydrothermal system that is consistent with conclusions obtained from the analyses illustrated in Figure 2. The most significant feature of Figure 4 is the strong similarity between the gas ratios of the fluid inclusions and the steam, suggesting that both have been influenced by similar fluid sources and/or processes. As a group, analyses of steam and inclusion fluids from the northwest Geysers are characterized by the highest CH_4 contents and N_2/Ar ratios much greater than air-saturated water. CFS analyses from the southeast and central Geysers have lower average CH_4 contents than those from the northwest, and like the TDCS analyses, yield N_2/Ar ratios similar to air-saturated waters. Variations in the CH_4 contents of the inclusion fluids are consistent with the He data discussed above and suggest that the inclusion fluids represent meteoric waters that have reacted to varying degrees with the basement rocks. Continued recharge of meteoric water is demonstrated by the $\delta^{18}O$ and δD values of the steam (Truesdell et al., 1987). In contrast, the high N_2/Ar ratios of the northwest samples imply little infiltration of contemporary waters while the higher CH_4 contents of the steam suggests less extensive reaction between the hydrothermal fluids and the reservoir rocks. These interpretations are supported by heavy $\delta^{18}O$ and δD contents of the steam from the northwest and by whole-rock oxygen data indicating that the Franciscan rocks in the northwest are typically less isotopically exchanged than those in the central and southeast Geysers (Moore and Gunderson, 1995; Walters et al., 1996). Taken together, the fluid-inclusion gas data provide evidence that the patterns of fluid circulation and meteoric recharge seen today were developed prior to The Geysers becoming vapor-dominated and that permeabilities have always been higher in the southeast than in the northwest.

Conclusions

The gas compositions of the fluid inclusions have been used to document the importance of magmatic, connate or metamorphic, and meteoric fluids during the evolution of The Geysers hydrothermal system. Inclusion populations of a dominantly magmatic origin are found in tourmaline-bearing veins in the biotite hornfels sampled in the present-day high-temperature vapor-dominated reservoir by well OF27A-2ST1. These inclusions are characterized by high- temperature halite-saturated brines, N_2/Ar ratios much greater than air, and He isotopic ratios of approximately 6 Ra. High-temperature hypersaline fluid inclusions were also observed in biotite-bearing veins from the high-temperature reservoir penetrated by L'esperance-2, and in tourmaline + quartz veins found in the plutonic rocks in DV-2. Although veins in L'esperance-2 are characterized by high N_2/Ar ratios, the associated He isotopic ratio of 0.5 Ra indicates overprinting of the magmatic signature by connate or metamorphic fluids and that high N_2/Ar ratios do not in themselves indicate a magmatic influence. It is noteworthy that inclusions in L'esperance-2 not only have one of the highest N_2/Ar ratios, they also have one of the highest CH_4 contents. The fluid inclusions in DV-2 have high water contents (H_20 99 mole percent) and N_2/Ar ratios similar to meteoric water, suggesting that meteoric recharge may have occurred in the southeast part of The Geysers prior to the onset of vapor-dominated conditions at about 0.25 to 0.30 Ma (Hulen et al., 1997).

Ternary plots of N_2, Ar, and CH_4 demonstrate a striking similarity between the compositions of the modern steam and fluid-inclusion gases from the normal vapor-dominated reservoir and the overlying caprock. Steam and inclusion gases from the northwest Geysers have the highest N_2/Ar ratios and CH_4 contents. Lower N_2/Ar ratios are found in the southeast and central Geysers. Variations in these ratios are compatible with gradients in the isotopic compositions of the steam (Truesdell et al., 1987) and imply higher contributions of meteoric recharge in the southeast compared to the northwest. Large-scale gradients in reservoir rock permeabilities are also suggested by whole rock $d^{18}O$ data which indicate lower integrated water/rock ratios in the northwest Geysers (Moore and Gunderson, 1995; Walters et al., 1996). Taken together, the CH_4, N_2/Ar, and isotope data imply that permeabilities have always been highest in the southeast and central Geysers.

Despite variations in the salinities, gas compositions, and temperatures of the inclusions, or their relative distance from the pluton, noble gas analyses document widespread flux of magmatic gas through the hydrothermal system. He isotopic ratios of the inclusion gases in most samples are near 6 Ra and, thus, require the input of a magmatic fluid. The presence of a magmatic component in the inclusion fluids raises the possibility that other gases, including H_2S and H_2 also have a magmatic origin.

Acknowledgments

Funding for JNM and MCA was provided by the Department of Energy under contract No. DE-AC07-95ID13274. Work by BMK was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Geothermal Technologies of the US Department of Energy under contract No. DE-AC03-76SF00098.

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