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## GASEOUS SPECIES IN FLUID INCLUSIONS: A TRACER OF FLUIDS AND INDICATOR OF FLUID PROCESSES

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### ABSTRACT

Quantitative bulk analysis of fluid inclusion volatiles measures the composition of trapped geothermal liquids and vapor. Fluid-inclusion gas-analyses may identify fluid boiling and mixing, and the analyses can be used as a fluid tracer. Fluid boiling is indicated by excess gaseous species. Linear arrays of data points on gas ratio diagrams indicate fluid mixing. Nitrogen-argon ratios are used to discriminate atmospheric from magmatic volatiles. Crustal components in geothermal fluids are best indicated by concentrations of methane and helium. Methane strongly correlates with other organic compounds, and N<sub>2</sub>-Ar-CH<sub>4</sub> plots are similar to N<sub>2</sub>-Ar-He diagrams. Alkene to alkane ratios of C<sub>2-7</sub> organic species indicate the oxidation state of geothermal fluids. The Geysers inclusion analyses are an example of how inclusion fluids may be used to understand the paleo hydrology of a geothermal system.

### INTRODUCTION

The objective of this paper is to demonstrate how bulk fluid-inclusion gas-analyses can indicate geothermal processes, be used as a tracer, and record the geochemistry of paleo geothermal systems. Although fluid inclusion gas analyses have been made for many years, interpretations have been simple; mainly analyses are used for the identification of species. Fluid-inclusion gas-analyses that include 6 or more compounds hold a wealth of information when properly interpreted. A good analogy are whole rock analyses that to the untrained observer appear similar, but contain much information when interpreted by a petrologist.

The principal hypotheses for the interpretation of quantitative, fluid-inclusion gas-analyses are:

1. Fluid inclusion gas chemistry has not changed since trapping except for possible equilibration of species at lower temperatures.
2. The amount of volatiles contributed by secondary inclusions to a bulk analysis is negligible.

Hypothesis one is similar to the hypothesis central to all fluid inclusion analysis; that is that inclusions have remained a closed systems since trapping (Shepherd et. al., 1985). A concern about H<sub>2</sub> loss from inclusions has been expressed (Mavrogenes and Bodner, 1994). Hydrogen diffuses through quartz, however it is not clear if hydrogen diffusion will affect inclusions residing in bedrock. Hydrogen is measured in fluid inclusions by Raman spectroscopy (Dubessy, et al., 1988) and mass spectrometry (Norman and Sawkins, 1987). The common measurement CH<sub>4</sub> and H<sub>2</sub>S in fluid inclusions shows that hydrogen diffusion does not result in the oxidation of reduced species. Helium has a higher diffusion rate through most minerals than H<sub>2</sub>. The occurrence of measurable amounts of He in inclusions (Norman and Musgrave, 1994), as well as measurement of H<sub>2</sub> in fluid inclusions, suggest that H<sub>2</sub> loss from fluid inclusions is minimal.

Hypotheses two is commonly made by those analyzing inclusion fluids, for example bulk fluid-inclusion deuterium analysis. Most minerals have some secondary inclusions, but these occupy far less volume than primary inclusions. Primary fluid inclusions generally are three dimensional, hence have larger internal volumes than the two-dimensional secondary-inclusions on fracture planes. We choose not to analyze minerals that have few primary inclusions and a high density of secondary inclusions.

### PREVIOUS WORK

Isotopic ratios of rare gases and H-, O-, C-, and S-bearing volatiles are widely used as tracers in the study of geothermal fluids. Application of these analyses to fluid inclusions, save for inclusion water, is far less common because of analytical problems extracting and measuring minute quantities of fluid-inclusion gaseous species. Giggenbach (1986) put forth that gas chemistry, specifically ratios of the nonreactive species N<sub>2</sub>-Ar-He, can be used as a tracer. Norman and Musgrave (1995) explore fluid

inclusion N<sub>2</sub>-Ar-He ratios as tracers of paleo geothermal fluids. They concluded that fluid inclusion N<sub>2</sub>-Ar-He ratios are valuable for interpreting fluid sources.

## METHODS

Inclusions volatiles are measured by thermal decrepitation followed by cryogenic separation (TDCS) and crush-fast-scan (CFS) methods. Both methods use a quadrupole mass spectrometer to measure the liberated inclusion volatiles (Fig. 1). Procedures for bulk measurements done by thermally decrepitating fluid inclusions are given in Norman and Sawkins (1987). Volatiles are cryogenically separated into liquid-N<sub>2</sub>-noncondensable, liquid-N<sub>2</sub>-condensable, and aqueous fractions. A liquid N<sub>2</sub>-cooled charcoal trap may be used to separate active noncondensable gaseous species from rare gas species. The quantity of each fraction is determined by pressure measurement in a known volume and the gas ratios are measured by a quadrupole mass spectrometer. Analytical precision is 5% or less for most species. Sample size is typically 2 g, but quantities 1/50 of that are analyzed.

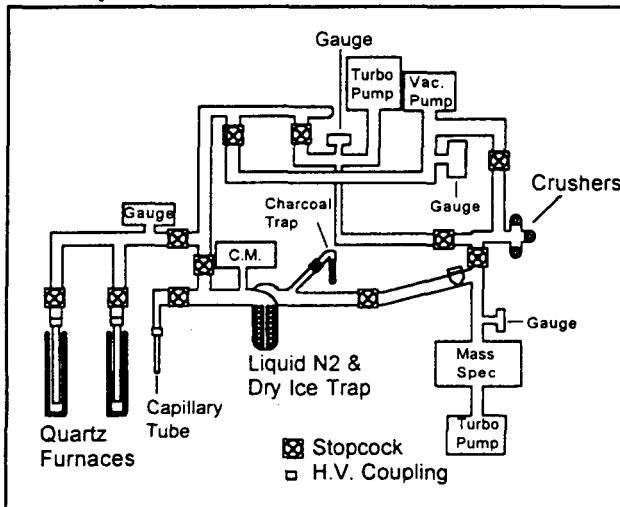


Fig. 1. The gas analysis system at New Mexico Tech. High vacuum is supplied by two turbo pumps. Volatile species are measured with MKS® capacitance manometer and a Balzers® QMS 420 quadrupole mass spectrometer controlled with Quadstar® software.

The CFS method involves opening inclusions by a swift crush in the vacuum chamber housing the mass spectrometer. Volatiles released are quickly removed by the vacuum pumping system in one or two seconds. Meanwhile, the pulse of inclusion volatiles is recorded by operating the quadrupole in a fast scan

mode with measurements every 100 to 200 milliseconds. The CPS method measures fewer inclusions than can be measured by the TDCS method. Opening a 10 to 20 micron inclusion, or group of smaller inclusions of equivalent volume, provides the ideal amount of volatiles for measurement. A 40 micron inclusion swamps the vacuum system and the system crashes. Five to fifteen crushes are made on a 0.2 g sample with the expectation that some crushes will be failures by opening too many inclusions. The CFS method is fast and simple, but the precision is 10 to 20%, and some species are difficult to detect because of interferences. Ammonia is rarely detected because of the interference of secondary water peaks at m/e = 17 and 16; He at concentrations below 30 ppm is interfered with by the tail on the H<sub>2</sub> peak; and CO peaks fall on those of CO<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and C<sub>2-7</sub>, organic species. Only in The Geysers inclusions has it been possible to detect inclusion H<sub>2</sub> above secondary H<sub>2</sub> created during ionization of H<sub>2</sub>O, CH<sub>4</sub>, H<sub>2</sub>S and C<sub>2-7</sub> organic species.

TDCS analyses have fewer problems with interference between species because the volatile sample is divided into three or four fractions. However, thermal decrepitation has its own analytical problems. Heating above the homogenization temperature (T<sub>h</sub>) is required to decrepitate inclusions in most cases. During heating inclusion volatiles equilibrate to temperatures near that of the furnace, hence yielding elevated H<sub>2</sub> and CO concentrations (Norman et al. 1991a). This can be corrected by calculating the equilibrium assemblage of species at T<sub>h</sub> (Norman et al. 1991a). Ammonia is rarely detected because it breaks down when heated to furnace temperatures.

Analysis of split samples by the two methods yields similar values for major species, though there are some differences in the analyses produced. Thermal decrepitation yields higher ratios of C<sub>5-6</sub> to C<sub>2-3</sub> organic species (Apodaca, 1987) than liberated by crushing. This is thought to result from adsorption of heavier organic species on mineral surfaces made during crushing.

## BOILING

Boiling in past geothermal systems is easily recognized by fluid inclusion gas analysis. The accepted criteria for identifying fluid boiling is the petrographic observation of a vapor and liquid phase trapped at the same time and temperature. Gas analyses of inclusions that indicate boiling differ from analyses of inclusions comprised of liquid-rich

inclusions (Fig. 2). They have higher gas/water ratios than is reasonable and exhibit large analysis to analysis variation in gas-water ratios. The variations in gas-water ratios are a consequence of opening different proportions of liquid- and vapor-rich inclusions. Comparison of depth and pressure estimates based on geological and gas analysis demonstrates that some analyses have unreasonable amounts of gaseous species. If even one vapor-rich inclusion is opened in a mixture of liquid and vapor-rich inclusions, the analysis will indicate higher amounts of gaseous species than in the trapped liquid. Simply, the analysis will yield excess gaseous species. Hence, the calculations we make assuming the analyses represent trapped liquid are in error. It follows that bulk fluid inclusion analysis of contemporaneously trapped vapor and liquid will rarely yield the true composition of a paleo geothermal fluid.

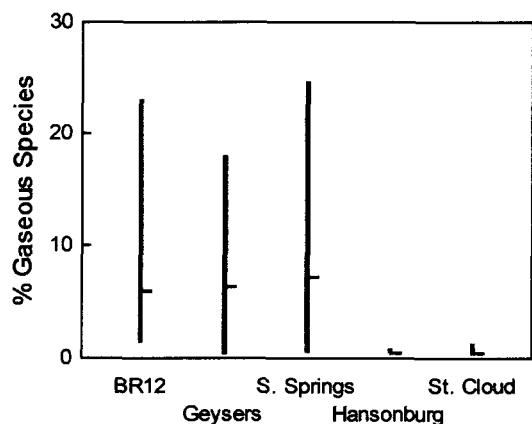


Fig. 2. Comparison of fluid-inclusion compositions between boiling and non-boiling geothermal systems. Bars indicate the range of measurements, vertical ticks are averages. Boiling systems are Broadlands, The Geysers, and Sulphur Springs. Non-boiling systems are the mineral deposits at Hansonburg and St. Cloud NM (Norman et. al., 1991b). BR12 and Hansonburg analyses are by the CFS method, the others are by the TDCS method.

Analyses of inclusions trapped under boiling conditions show broad variations in gas ratios (Fig. 2). The distribution of data in Fig. 3 can be explained by modeling fluid boiling. Modeling requires an estimate of the trapping temperature, fluid salinity, and fluid gas chemistry. The first two are obtained by fluid-inclusion microthermometry, or in the case of opaque minerals, analysis of well fluids. Gas chemistry of the boiling liquid is estimated from

graphs; a composition from the center of a cluster of data is generally chosen. The composition of liquid and vapor phases is calculated for  $y$  (molar ratio of the vapor produced) ranging from 0.001 to about 0.06 so that  $> 90\%$  of fluid volatiles have partitioned into the vapor phase. It is not important that the correct value of  $y$  is known, or if the geothermal system was open or closed to vapor loss. The value of the model is to demonstrate that the range of compositions measured can reasonably be explained by an admixture of vapor- and liquid-rich inclusions derived from a single fluid. Boiling models for Amanse inclusion analyses (Fig. 3) clearly demonstrate that analyses for each generation of quartz can be explained by a single fluid that was boiling. In light of the modeling, the data indicate that each generation of quartz was deposited by a fluid that had a unique gas chemistry.

#### MULTIPLE SOURCES

The distribution of analyses made on a single generation of Broadlands quartz, however, can not be explained by fluid boiling (Fig. 4). Modeling does, however, confirm that some of the scatter in the data is explained by fluid boiling (Fig. 4c). The analyses indicate multiple fluid sources or evolution of fluid gas chemistry. Bulk fluid-inclusion gas-analyses alone can not alone indicate if data represent: 1) mixing of two fluids; 2) heterogeneous trapping of two fluids; 3) varying rates of wall rock reaction by a single fluid; or 4) evolution of the geothermal system. However, other information such as spatial and temporal variations in fluid-inclusion gas-chemistry, stable isotope analyses, and fluid-inclusion temperature-salinity diagrams may help in choosing between the alternatives. Alternative 1 is difficult to demonstrate if fluid inclusions indicate boiling. The process recorded could be mixing of a vapor plume, say from a magma, with an aqueous phase. Mixing of this type will not be indicated on fluid inclusion temperature-salinity diagrams.

End member compositions may be roughly estimated by plotting the analyses on several ternary diagrams (Fig. 4) and by factor analysis. Exact fluid compositions may not be determined by bulk analysis of inclusions that exhibit a wide variation in composition. The data can, however, indicate if different generations of minerals were deposited by fluids that different gas chemistry (Fig. 3). Geothermal systems vary in fluid-inclusion gas-chemistry (compare Figs. 4 and 5). St. Cloud fluid inclusions have  $N_2/Ar$  ratios

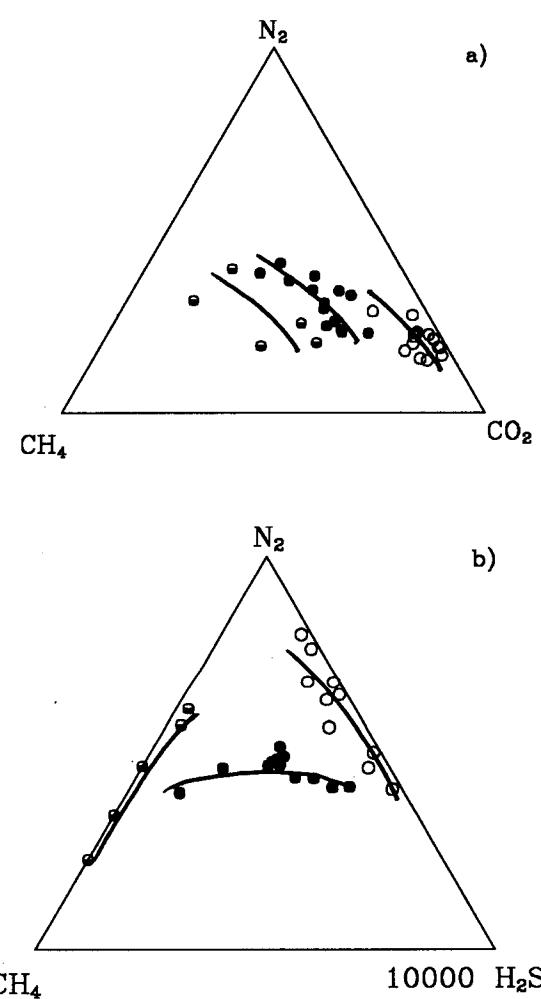


Fig. 3. Ternary plots of fluid inclusions from the Amanse mesothermal Au deposit, Ghana: a) a  $\text{N}_2\text{-CH}_4\text{-CO}_2$  diagram; and b) a  $\text{CO}_2\text{-CH}_4\text{-H}_2\text{S}$  diagram. Filled circles are analyses of vertical vein quartz, half-filled circles are analyses of rock-forming quartz in granite, and open circles are analyses of late horizontal veins. Lines represent boiling models calculated by choosing a fluid composition near the center of each cluster of data. The line spans the extent of liquid and vapor compositions possible by closed system boiling at 300 °C. All analyses are made by the CFS method.

about that of air-saturated ground water (ASW) at 20 °C and relatively constant  $\text{CO}_2/\text{CH}_4$  ratios from analysis to analysis. Broadlands 12 inclusions differ both in the gas ratios and the distribution of values exhibited.

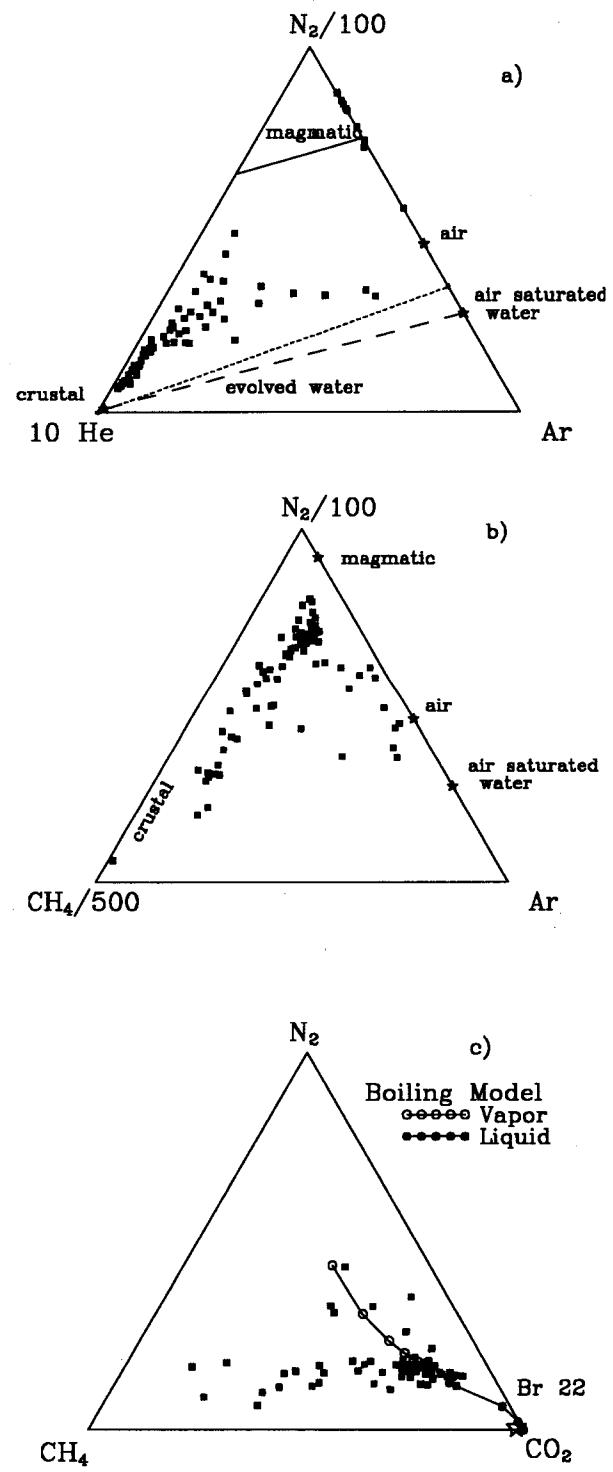


Fig. 4. Eighty fluid inclusion analyses of a single piece of Broadlands quartz: a) a  $\text{N}_2\text{-Ar-He}$  diagram; b) a  $\text{N}_2\text{-Ar-CH}_4$  diagram; and c) a  $\text{N}_2\text{-CH}_4\text{-CO}_2$  diagram. Boiling was modeled at 260 °C. All analyses were made by the CFS method.

## INTERPRETING FLUID SOURCE

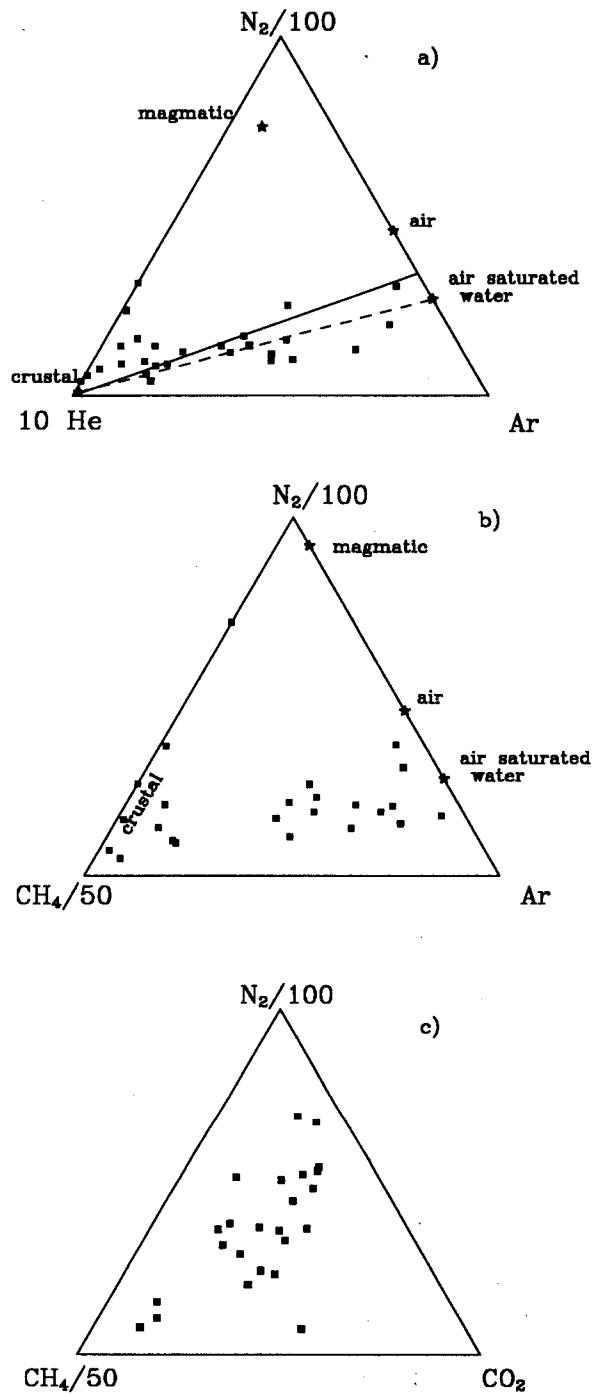


Fig. 5. Fluid inclusion analyses of the St. Cloud paleo geothermal system that deposited Cu-Ag ores at temperatures about 250°C and depths of 900 m from 0 to 4 eq.wt% NaCl nonboiling solutions (Norman et al. 1991b): a) a N<sub>2</sub>-Ar-He diagram; b) a N<sub>2</sub>-Ar-CH<sub>4</sub> diagram; and c) a N<sub>2</sub>-CH<sub>4</sub>-CO<sub>2</sub> diagram. All analyses were made by the TDCS method.

We consider three volatile sources; these are atmosphere, crust, and magma. An atmospheric component is the least equivocal to determine. Gaseous species have ratios similar to ASW, but with minor or no O<sub>2</sub> similar to the gas chemistry of deep circulating ground waters.

Magmatic gaseous species include N<sub>2</sub>, Ar, CO<sub>2</sub>, CO, H<sub>2</sub>, He, SO<sub>2</sub>, and H<sub>2</sub>S. Giggenbach (1986) pointed out that felsic magmatic volatiles have N<sub>2</sub>/Ar > air, which has been verified by others (Giggenbach and Glover, 1991; Hedenquist and Aoki, 1991). Elevated N<sub>2</sub>/Ar ratios, however, do not uniquely identify magmatic volatiles. Crustal volatiles may also have N<sub>2</sub>/Ar > air, the most common example is natural gas (Norman and Musgrave, 1995).

Volatiles derived from crustal rocks include CO<sub>2</sub>, He, H<sub>2</sub>S, N<sub>2</sub>, Ar, CH<sub>4</sub>, and C<sub>2-7</sub> organic species. Strong correlations between fluid inclusion CH<sub>4</sub> and C<sub>2-7</sub> organic species are measured in geothermal systems underlain by carbonaceous rocks. For example, the correlation coefficient (R<sup>2</sup>) for CH<sub>4</sub> and C<sub>n</sub>H<sub>n</sub> (estimated total C<sub>2-7</sub> organic species) for BR12 and St. Cloud analyses are respectively 0.94 and 0.86. The minor amounts of organic species in ASW and volcanic gases indicate CH<sub>4</sub> is a good choice to represent crustally derived volatiles in geothermal systems associated with carbonaceous rocks.

The differences in gas chemistry between St. Cloud and Broadlands (Fig. 4 and 5) must reflect differences in fluid sources and geothermal processes. St. Cloud fluid-inclusion chemistry is consistent with a geothermal system comprising mixed evolved and meteoric waters or meteoric waters that accumulated various amounts of CH<sub>4</sub>, CO<sub>2</sub>, and H<sub>2</sub>S from a crustal source. A second possibility is heterogeneous trapping of a shallow circulating meteoric water that had a gas chemistry similar to ASW and a deep circulating meteoric fluid that had accumulated CH<sub>4</sub>, CO<sub>2</sub>, He, and H<sub>2</sub>S. Statistical analysis of fluid inclusions T<sub>b</sub> and T<sub>m</sub> measurements indicates heterogeneous trapping of two fluids (Norman et al. 1991b).

Broadlands gas chemistry indicates all three fluid sources. Poor correlation of N<sub>2</sub> in Broadlands inclusions with organic species suggest N<sub>2</sub> is not derived from underlying sediments. The N<sub>2</sub>/Ar > ASW for most analyses therefore indicates a magmatic source. Broadlands gas chemistry is consistent with a deep circulating meteoric water that interacts with

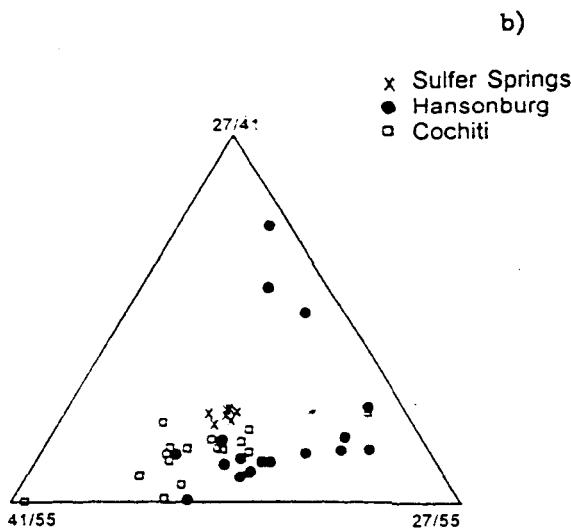
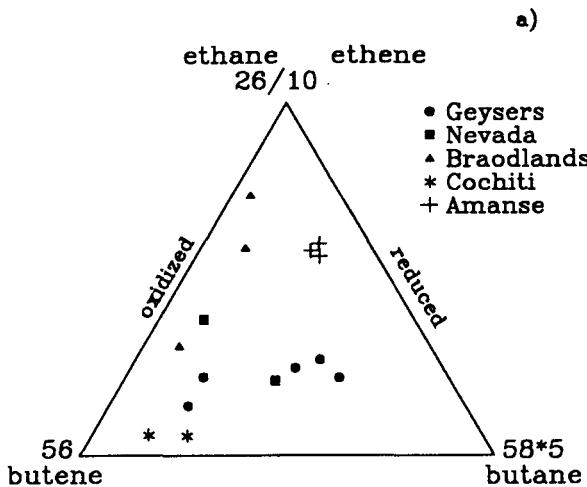


Fig. 6. Analysis of organic species. Plots are m/e peak heights rather than the amounts of various species: a) a m/e plot of peaks 26, 56, and 58 that shows the relative proportions of butene, butane, and lighter organic species; b) a plot of m/e peak ratios. Peaks 27, 41, and 55 are major peaks alkene compounds. Data are from both TDCS and CFS analyses.

the basement turbidites to varying degrees and accumulates upward fluxing magmatic volatiles. There is supporting evidence that the interruptions made from Figs. 4 and 5 are correct. St. Cloud He and

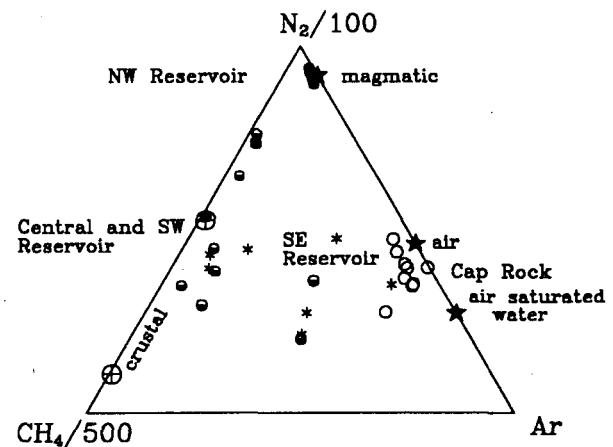


Fig. 7. Analysis of The Geysers fluid inclusions: filled circles are inclusions from the NW part of the reservoir; half-filled circles are analyses of inclusions from the SE, SW, and central part of the reservoir; open circles are analyses of cap rock minerals; the circle with cross are analyses of calcite in Franciscan rocks outside the geothermal system; and stars are analyses of reservoir steam.

stable isotopic analyses do not indicate magmatic volatiles (Norman and Musgrave, 1995), whereas the opposite is true of Broadlands (Giggenbach, 1986). Interaction of fluids with turbidites in basement rocks has been inferred from B/Cl ratios of Broadlands fluids (Ellis, 1979).

#### ORGANIC SPECIES

Organic species other than methane are generally trace gases. They can provide information on the oxidation state of geothermal systems and homogeneity of fluids. Over 23 organic species have been measured in inclusion fluids (Apodaca, 1988). The most common species after CH<sub>4</sub> are C<sub>2-4</sub> alkenes and alkanes. Oxidation of alkanes produces alkenes:



Hence, ratios of fluid inclusion alkane to alkene compounds indicates the oxidation state of the trapped fluid. Figure 6a illustrates ratios of fluid inclusion butane to butene as well as showing the ratio of C<sub>2</sub> to C<sub>4</sub> compounds. Homogeneity of organic constituents fluids are illustrated on plots like Figs. 6a and 6b.

There is an apparent relationship between basement rocks and the oxidation state of  $C_{2-7}$  organic species. Amanse, Getchell (Nevada), and The Geysers occur within thick sequences of marine carbonaceous sediments and the analyses have more reduced organic species than those from the other geothermal systems. Heavier organic compounds do not partition as strongly into a vapor phase, hence may be considered as residual species. It is not clear why the organic compounds in some inclusions are more homogeneous than others. This may reflect variation in the source rocks.

### THE GEYSERS

The Geysers is a good system to test fluid inclusion gas analyses as an indicator of fluid sources. Fluid inclusions and stable isotope analyses indicates a magmatic input into the NW part of the reservoir and connate fluids in the SE part of the geothermal system (Moore, et. al. 1989). Analyses of inclusions from The Geysers and Franciscan sediments suggest three sources (Fig. 7). Inclusions from the cap rock indicate a significant ASW component. Inclusions from the NW part of the reservoir indicate a strong magmatic component. Much different are inclusions in Franciscan calcite that are  $CH_4$ -and He-rich. Gas analyses indicate an increasing component of fluids typical of Franciscan rock in the southern part of the reservoir. The Geysers inclusions we measured comprise both liquid-and vapor-dominant types indicating trapping when the reservoir was filled with water. Remarkably, the fluid inclusion gaseous species we measure are similar to those reported in the steam reservoir. The fluid inclusion analyses indicate a paleo hydrology wherein reservoir fluids interfaced with shallow flowing meteoric waters at the position of the present cap.

### DISCUSSION

The data presented here are consistent with the 2 hypotheses. If  $H_2$  was lost by diffusion one would expect fluid-inclusion gas-analyses to consist of an oxidized assemblage of gaseous components, or plot on ternary diagrams in straight lines toward oxidized species. Inclusions from St. Cloud, for example, indicate quite consistent  $CH_4/CO_2$  ratios in all inclusions (Fig. 5). If inclusions were modified by post trapping events, or if a large percentage of secondary inclusions were analyzed, inclusion chemistry should be similar to the last geothermal event. There is no indication of this in our data. Analyses from Amanse and Broadlands show the opposite. Amanse

inclusions have distinctly different compositions and no evidence of overprinting by later geothermal events. Remarkably these inclusions are 2 Ga. Broadlands inclusions indicate a broad range in fluid geochemistry that is different from present well fluids. The analyses do not indicate any secondary inclusions similar in composition to present reservoir fluids.

Fluid inclusion bulk analyses does not give the same information as a reservoir fluid gas analyses. Bulk inclusion analyses may yield an average composition over some length of time, or an analysis of heterogeneously trapped fluids. Statistically there will be variations in multiple analyses if inclusions do not have identical gas chemistry. Differences between analyses aid in the interpretation of past reservoir processes, be it boiling (Fig. 2) or multiple sources of gaseous components (Figs. 4 and 5).

Gas analyses may detect a different type of fluid mixing than is illustrated by analysis of dissolved solids, such as chlorine. Gaseous species may separate during boiling and move independently from the parent liquid. Hence, fluid mixing indicated by gas analyses may result from the addition of a vapor derived by boiling from one liquid, to a second fluid. In addition, volatiles may be derived from the wall rock along fluid channelways by fluid-rock chemical reactions and accumulation of gaseous species in wall-rock pore-spaces by diffusion. These possibilities increase the number of hypotheses regarding sources of gaseous components in a geothermal system. By way of example, possible explanations for the organic constituents in Broadlands fluids are: 1.) mixing of a convectively driven meteoric fluid with fluids in equilibrium with basement sedimentary rocks; 2.) addition to reservoir fluids of an organic-compound-rich vapor derived from the basement rocks by magmatic heating; and 3.) interaction of reservoir fluids with basement rocks. Other types of data are needed to decide between the possible hypotheses.

### CONCLUSIONS

Analyses of inclusion volatiles can be used as a tracer in geothermal systems. Meteoric waters, evolved waters, and magmatic fluids can be expected to have differ compositions of volatile species. Hence, it is possible indicate fluid sources from fluid-inclusion gas-analyses. Ratios of  $N_2$  to  $Ar > air$  is a good, but not perfect indicator of magmatic volatiles. Methane as well as He are valuable components to characterize fluids that have accumulated volatiles

due to reactions in crustal rocks. Analyses of fluid inclusions show distinct chemical differences between geothermal systems and spatial variation and temporal variations within a geothermal system. It is possible to deduce the past hydrology of a geothermal system from spatial variations of fluid-inclusion volatiles.

Geothermal processes can be inferred from fluid-inclusion gas-analyses. Fluid boiling is the most strait forward interpretation. Distributions of gas data that are not explained by fluid boiling can be attributed to fluid mixing, heterogeneous trapping of fluids from different sources, and wall rock reactions. Selection of the best hypothesis may require other types of geochemical data.

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