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INTERPRETING GEOTHERMAL PROCESSES AND FLUID SOURCES FROM FLUID INCLUSION ORGANIC COMPOUNDS AND CO_2/N_2 RATIOS

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ABSTRACT

The distribution of organic species is explored using data acquired from a new dual quadrupole system that routinely measures eighteen gaseous species. The process of condensation and its affect on gas distribution is modeled, and a new discrimination diagram based on total gaseous species and the CO_2/N_2 ratio is introduced.

We conclude that organic species concentrations indicate source; that pyrolysis of organic material produces significant aromatic compounds; that Fischer-Tropsch reactions produce organic species dominated by methane; CO_2/N2 vs. total gas plots are useful for illustrating boiling and condensation processes; and Cerro Prieto gas concentration are consistent with the gaseous species being modified by input of magmatic volatiles.

INTRODUCTION

This report is the sixth in a series of papers presented at the Stanford Geothermal Workshop concerning geothermal gaseous species. Out goal here is to explore interpretations of organic species concentrations and how gas ratios are affected by condensation and boiling processes. We have a new dual quadrupole mass spectrometer system that makes better analyses of fluid inclusion organic species, hence will again address the interpretation of organic fluid inclusion species. Little can be said about organic species in present geothermal systems because organic species are infrequently measured.

Condensation is an accepted feature of geothermal systems, but there is little analyses of how this process affects gaseous species. The condensation processes commonly considered are steam-heated waters, and transfer of magmatic volatiles to meteoric waters circulating to depth in volcanogenic geothermal systems (Giggenbach, 1997). Condensation and boiling are difficult to differentiate in geothermal water analyses or in fluid inclusion studies because there is a liquid and vapor phase present during both processes. We will, however, demonstrate that boiling and condensation fractionate gaseous species in a different manner; hence gas ratios can indicate which process was operating. We will show that gas ratios in several geothermal systems agree with the hypothesis that deep-circulating waters accumulate volatiles from deep-seated magmatic sources. We will also look at evidence for open system boiling in geothermal systems.

ORGANIC COMPOUNDS

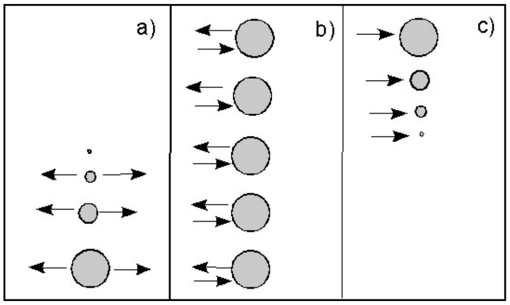
Light organic compounds (LOC) other than methane occur in geothermal fluids at concentrations typically 1 to 5% that of CO_2. Giggenbach, 1997 reports that these compounds are principally alkanes (single-bonded compounds) such as are found in sedimentary oil and gas. However, high concentrations of alkene compounds (a species with one double bond, such as propylene) are reported in geothermal systems discharging on mid-ocean ridges (Welhen et al. 1988). Pyrolysis of organic material produces mostly alkanes (North, 1985) whereas Fischer-Tropsch reactions produce both alkane and alkene compounds (Stokewell et al., 1988). Pyrolysis may produce more C_2-C_6 compounds whereas Fischer-Tropsch reaction produce LOC with ratios of $C_2/C_1 = C_3/C_2 = C_4/C_{4=}$ about 0.3 (Berndt et al., 1996). Experimental data shows that alkanes react with Fe^{2+}-bearing rock to produce alkenes. Also, alkenes and alkanes are recently reported among volcanic gases (Capaccioni et al., 2001). Norman et al. 1997 and Norman et al. 2001 shows that ratios of alkenes to alkanes are related to host rock, and that organic species distributions characteristic of Fischer-Tropsch reactions are common in fluid inclusions.

The concentrations and ratios of LOC should provide information about the source of organic species and degree of wall-rock reactions. However, boiling and condensation will fractionate organic species because of the broad range in solubility of LOC. Therefore we first look at the affect of these processes on LOC concentrations, then we present fluid inclusion LOC concentrations from several geothermal systems and interpret the distributions.

BOILING AND CONDENSATION

Fluid boiling is identified in geothermal waters and fluid inclusions by a number of methods. These include observation of vapor-dominant and liquid-dominant inclusion pairs that have that have similar homogenization temperatures (Th), measurement of "excess gas" when performing bulk fluid inclusion gas analysis (Norman et al., 1996), and modeling fluid inclusion gas compositions (Norman et al., 1996, Moore et al., 2001). In geothermal well discharges excess enthalpy, gas/water ratios, and equilibrium calculations on gas concentrations (Giggenbach, 1986) are used to identify boiling.

Condensation is a two-step process (Fig. 1). Vapor entering a fluid undersaturated with gaseous species will dissolve into the fluid (Fig.1a) and the gaseous species concentrations will increase until the vapor pressure of the gaseous species and water equal the ambient pressure. At that time bubbles will pass through the fluid and an equilibration will occur whereby the vapor pressure of each species in the liquid will change in order to equal the partial pressure of each gaseous species in the vapor. Over time the aqueous gaseous species will change in concentrations until they equal the partial pressure of the species in the incoming vapor. Generally during the equilibrium process, low solubility species will go into the bubbles, and high solubility species will enter the fluid (Fig. 1b).



Figuare 1: A cartoon illustrating the condensation process and boiling process: a) Vapor entering a liquid undersaturated in gaseous species will sorb the vapor until $P_{H2O} + P_{g.s} = P$ *(g.s. = gaseous species, P= total pressure on the liquid); b) Then vapor bubbles will pass through the liquid exchanging gaseous species until the partial pressure of each gaseous species in the liquid equals that in the vapor; c) If the pressure or temperature decreases, say at some alter time, the liquid will boil releasing the newly acquired and prior gaseous species.*

METHODS

Gas analyses were performed on an improved quadrupole mass spectrometer analytical system (Fig. 2). The new system operating in the crush-fast-scan (CFS) mode uses twin quadrupoles in order to double the number of species measured. Species routinely measured include H_2, He, CH_4, H_2O, N_2, O_2, H_2S, Ar, CO_2, SO_2 , the C_1-C_4 alkanes and alkenes, pentane, cyclopentane, toluene and benzene. A third high vacuum system and a hydrocarbon-free backing pump on the quadrupole vacuum system were added to the facility. The new system has about a factor-of-ten better sensitivity over the previous system we used because the operating pressure is a factor of ten lower.

All measurements reported here were performed by the CFS method described in Norman et al. (1996). Gas water ratios are measured to better than 0.2 %, precision for measuring N_2/Ar ratios in air-filled, synthetic inclusions is about 1%.

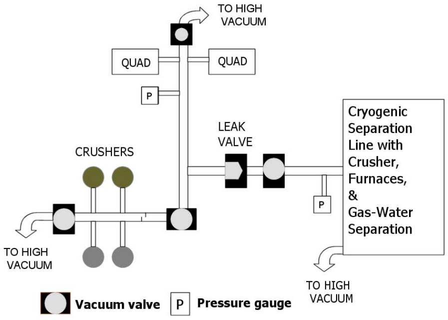


Figure 2: A schematic diagram of the dual quadrupole fluid inclusion gas analytical system.

RESULTS

Table 1 displays typical analyses produced by the new quadrupole system. On the table slope refers to the negative slope of the C_1-C_4 compounds when plotted on a Schultz-Flory plot; A/E refers to the ratio of C_2-C_4 alkane to alkene compounds. These analyses show the high variability in C_2H_4 and C_2H_6 concentrations, and the overall great variation in the total organic species concentrations. Benzene in some analysis is second only to methane in abundance.

Calculation confirms that organic species distributions change as a consequence of boiling. Gas partition coefficients were calculated from solubility data compiled by (Prini and Crovetto, 1989). They show a wide variation with C_2H_4 coefficient higher than methane and C_4H_8 quit low (Fig. 3). Changes in species distribution are calculated for a fluid in which concentrations of alkene and alkane species are the same, y (the steam fraction) = 0.01, T = 300 C and the distribution is that expected from Fischer-Tropsch reactions, $C_{n+1}/C_1 = 0.3$. The results show that both the vapor and liquid phase species plot with a concave downward shape (Fig. 4). The C_1-C_4 organic species strongly partition into the vapor phase save butylene that mostly remains in the liquid phase. Moderate boiling removes most all ethylene from the

Table 1: Representative analyses of fluid inclusions by the CFS (crush-fast-scan) method (Norman et al, 1996) done on the new dual quadrupole system.

location	Karaha	Karaha	Karaha	Coso
well	T-8	T-8	T-8	83-16
Sample	1045m	781m	1197m	5301m
material	PY +ACT	ANHY	QTZ	CHIP
Crush	6684D	6685D	6686D	6835C
(mol.%)				
H2	0.067	0.0000	0.062	0.0058
He	0.00010	0.00003	0.00034	0.00002
CH4	0.17	0.010	0.12	0.029
H2O	96.69	99.68	97.32	99.61
N2	1.6	0.027	1.0	0.25
H2S	0.00072	0.00022	0.0024	0.00022
Ar	0.020	0.00028	0.0120	0.0021
CO2	1.3	0.29	1.4	0.1
SO2	0.00000	0.00016	0.00138	0.00066
(ppm/v)				
C2H4	74.2	2.0	0.0	18.7
C2H6	89.6	0.0	78.3	0.0
C3H6	0.0	0.0	0.0	2.0
C3H8	143	2.8	59	0.6
C4H8	346	0.2	0.0	0.0
C4H10	128	2.0	21.7	0.0
C5H10	895	0.0	0.0	0.0
C6H6	40	1.0	36	51.0
C7H10	16	1.1	2.3	0

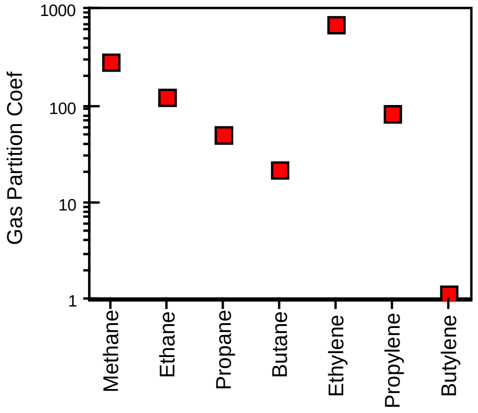


Figure 3: Calculated gas partition coefficients for C_2-C_4 alkane and alkene compounds at 300 C in pure water. The 300 C partitioning coefficient for methane (Giggenbach, 1980) is added for comparison.

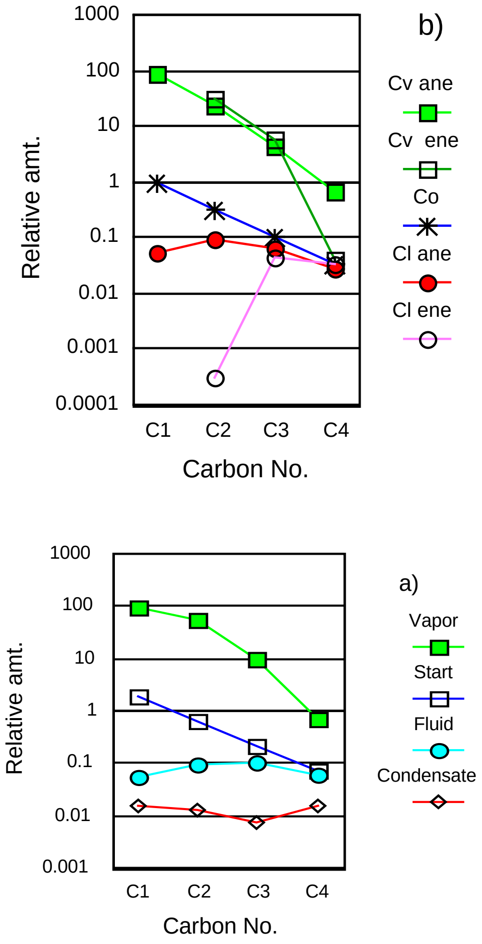


Figure 4: Modeled fractionation of a 50:50 mixture of alkane and alkene species, see text for details: a) shows distribution of vapor and liquid for a steam fraction (y) = 0.01, and the distribution when the vapor is added to a cooler water; b) shows the relative concentrations in vapor (C_v) and liquid (C_l) of alkanes (ane) and alkenes (ene) species for fluids plotted in Fig. a).

liquid. Modeling condensation of the vapor released by boiling shows a near-flat distribution of concentrations slightly concave upwards.

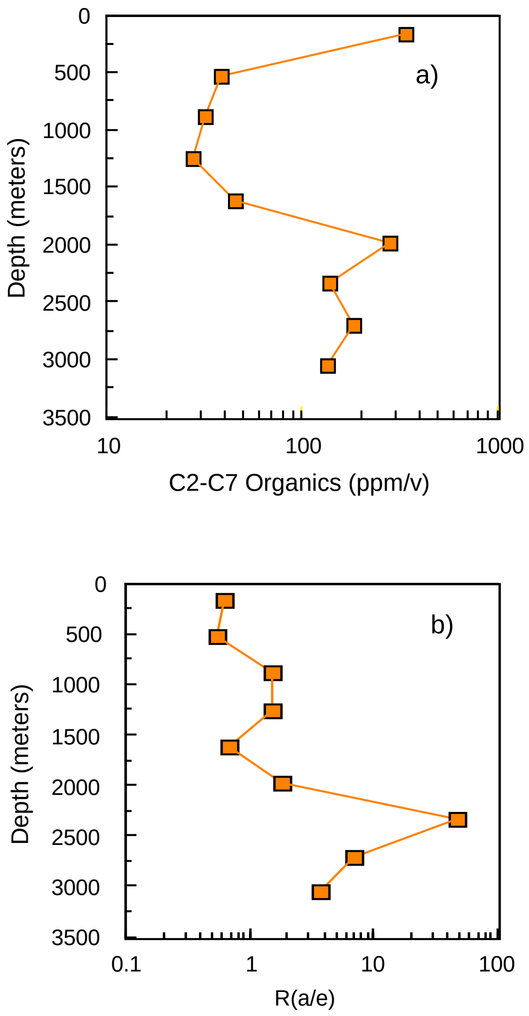


Figure 5: Average concentrations of organic species in fluid inclusions from Coso, CA drillhole 83-16: a) concentrations verses depth; b) the molar ratio of alkane to alkene species vs. depth.

Organic species in the Coso, CA fluid inclusions show higher concentrations at production depths of > about 1800m (6000 ft) and an increasing proportion of alkene species in shallower waters (Fig. 5). Organic species concentrations again are high in the sallowest sample. On Schultz-Flory plots (Fig. 6) Coso fluid inclusion organic species plot generally straight slopes through $C_{3.}$ The average C_{n+1}/C_n for 76 analyses = 0.297. Species above C_3 were not detected in many analyses.

Karaha-Telaga Bodas, Indonesia inclusions from drill hole T-8 show higher levels of heavier organic spies, in particular the aromatic compounds benzene, toluene, and cyclopentane (Fig. 7). Data plot similar to analyses of the same species measured in oil field brines (North, 1986). The C_2-C_4 species are mostly alkanes. The average alkane/alkene ratio for 89 analyses is 23.

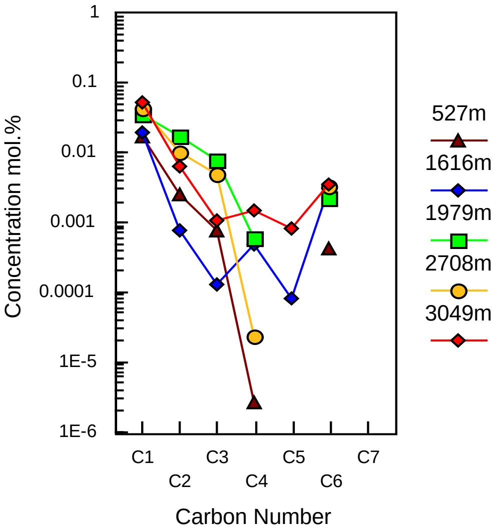


Figure 6: Representative analyses of Coso 83-16 fluid incisions from several depths plotted on a Shultz-Flory diagram.

We introduce the CO_2/N_2 vs. total gas discriminations diagram. The CO_2/N_2 vs. total gas plot is divided into three fields (Fig. 8). Excess gas levels attributed to boiling are defined as concentrations > 1.5 mol.% similar to the excess gas histogram we introduced previously (Norman, 1996). The boundary between excess gas and gas-cap is placed at 20 mol.% based on experience and reasoning. In order to measure total gas > 20 mol.% we must either open only vapor-dominant inclusion with > 20 mol. % gaseous species, or open a mixture of liquid dominant and vapor-dominant inclusion with the later containing significantly > 20 mol.% total gas. Boiling geothermal fluids can produce vapor with > 20 % total gas, but this requires a very small y, and hence will be of rare occurrence. Therefore, there must be special conditions that trap vapor so that repeated analyses indicate> 20 mol.% gaseous species. We have measured total gas as high as 37% in The Geysers fluid inclusions (Moore, et al., 2001) for which there is abundant evidence that the inclusions were trapped in the early stages of gas cap formation. Hence, we argue that high gas/water ratios measured in multiple analyses are most probably vapor trapped during formation of a gas cap than vapor generated by minor boiling. Gas partition coefficients for CO_2 and N_2 differ considerably, hence boiling will result in significant fractionation in the ratios of these species between gas and liquid phases. The different slopes for boiling and condensation trends are obtained by calculation. By way of example, Fig. 9 and Fig. 10 shows models of open-system fluid boiling and condensation. Gas analysis of fluid inclusions trapped under boiling conditions is expected to include a mixture of liquid-filled and vapor-filled inclusions, hence a series of bulk analyses could lie anywhere in the space bounced by liquid and gas-filled inclusion (Fig. 9). Under special conditions, a series of analyses on a single sample will plot should plot in a linearly on a CO_2/N_2-total gas diagram assuming that the source fluid composition was constant. If a series of crushes opens only liquid- or vapor-filled inclusions are opened, the analyses will plot along a line with high negative slope if fluids were trapped after they had

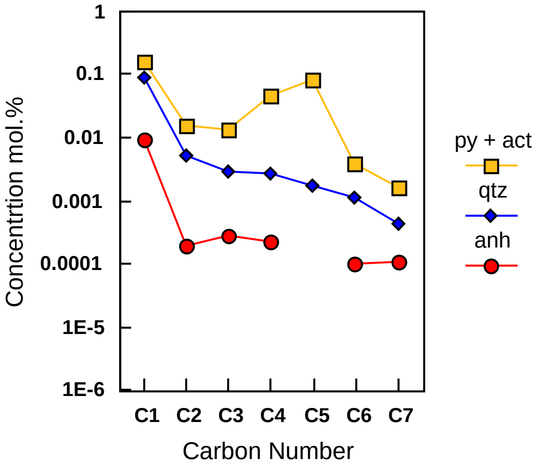


Figure 7: Shultz-Flory plots of representative Karha T-8 fluid incision analyses: py is pyrite, act is actinolite, qtz is quartz, and anh is anhydrite. Minerals from 700 to 1000m.

undergone different degrees of boiling. Opening mixtures of vapor- and liquid-dominant inclusions that were trapped having undergone similar degrees of boiling, will yield analyses that lie along a tie line between the liquid and vapor curves that have a less, but always, negative slope. Figure 10 shows two models for vapor condensation at 300 C. The fluids have 0.2 mol.% CO_2 and N_2 with ratios of CO_2/N_2 at 10 and 50, and were assumed undersaturated with respect to the two species. A vapor 10 % CO_2 and N_2 with a CO_2/N_2 ratio of 10 was added until P = P_{H2O} + 30 bars, then continue flow of the vapor was allowed until the fluid and vapor came to equilibrium. These calculations show that during the equilibrium stage the change in CO_2/N_2 plots with a positive slope. The slope varies with fluid temperature and the CO_2/N_2 ratio of the added fluid. Generally, slopes are higher for higher fluid temperatures and higher CO_2/N_2 ratios. Therefore, we expect that analyses of fluid inclusions randomly trapped during a condensation process will exhibit a positive slope.

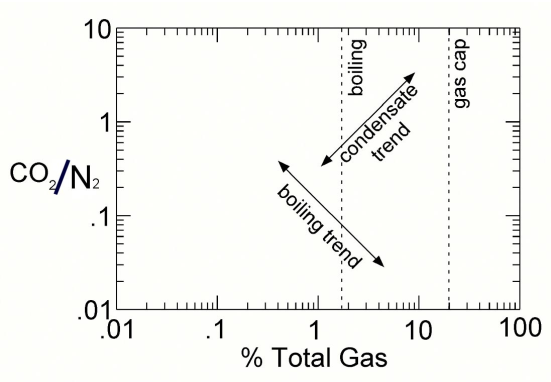


Figure 8: The CO_2-N_2 vs. total gas species discrimination diagram. See text for an explanation.

Coso fluid inclusions analyses from well 64-16 plotted on a CO_2/N_2 vs. total gas diagram shows opposite slopes. The analyses of Wairakite from deep in the geothermal system show a positive slope (Fig.10), whereas analyses of bladed calcite show a negative slope. Analyses of Karaha inclusions from well T-8 show a regular change in total gas with depth (Fig. 11). The analyses, as a group, plot with a positive slope. Cerro Prieto well discharge analyses, supplied by Cathy Janek, show a positive trend on a CO_2/N_2 vs. total gas diagram. Plotting the same analyses against N_2/Ar ratios show that analyses with higher CO_2/N_2 ratio have higher (magmatic) N_2/Ar ratios.

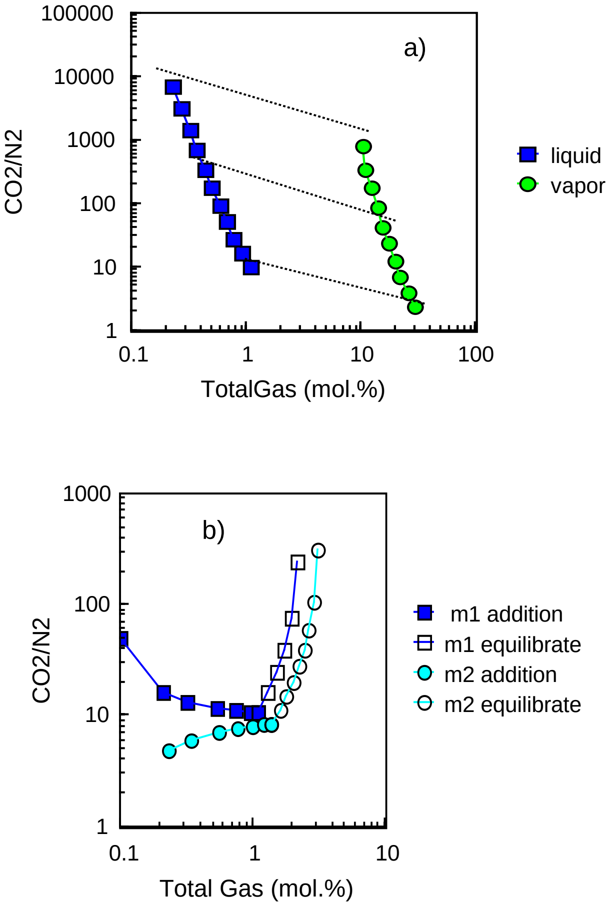


Figure 9 a) An open system boiling model showing how the CO_2--N_2 ratio changes in the liquid and vapor phases with increasing steam fraction. Starting conditions are 300 C, P_{total} = P_{H2O} + $P_{g.s.}$. Each symbol is the result of a 1C decrease in temperature. Dotted line ties coexisting liquid and vapor compositions. b) Modeling condensation for two starting fluids m1, 0.2 mol.% gaseous species, CO_2/N_2 = 10 and m2, 0.2 mol.% gaseous species, CO_2/N_2 = 50. The added vapor has a CO_2-N_2 ratio of 10, P= P_{H2O} + 30 bars. Filled boxes are the change in composition during the solution stage, open symbols are the changes in composition when $P_{g.s.}$ +P_{H2O} = P_{total}. The upper most symbols are represent final equilibrium between liquid and the added steam.

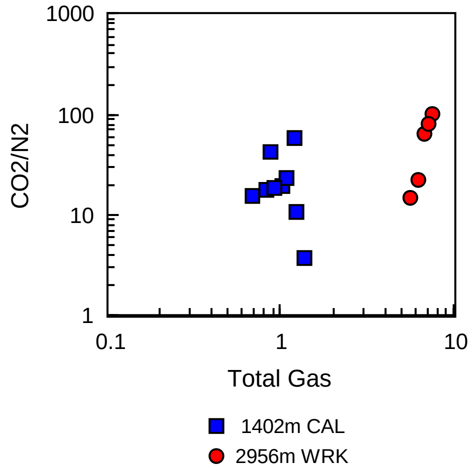


Figure 10: Analyses of Coso well 64-16 fluid inclusions; filled symbols are analyses of calcite from 1402 m. Open symbols are analyses of Wairakite from 2956m.

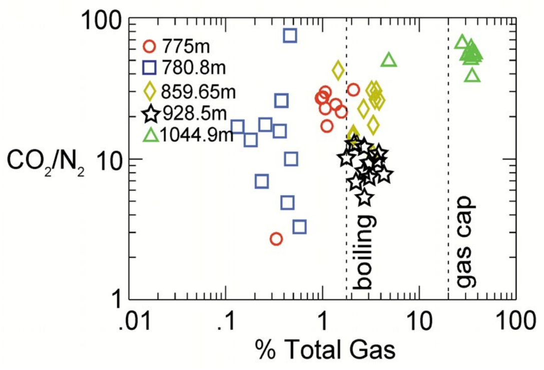


Figure 11: Plot of Karaha T-8 analyses from several depths.

DISCUSSION

Organic Species Sources:

Coso and Karha analyses of organic fluid inclusion species indicate that the distribution of species can indicate source. Total concentrations of organic species verses that increase with depth in the reservoir, the preponderance of alkanes, and the C_{n+1}/C_n ratios in Coso inclusions are consistent with formation by Fischer-Tropsch reactions. Fischer-Tropsch reactions produce H_2, and we can see in Table 1 there is a correlation between H_2 concentrations and presence of organic species. The occurrence of benzene in Coso inclusions could be due to DOW - process reaction of methane with graphite in wall-rock. Karaha organic species that are preponderantly alkanes and cyclic hydrocarbon agree with generation by pyrolysis of organic material in wall rocks. We suspect the sample-to-sample variability in slope on Shultz-Flory plots (Fig.6) is a consequence of analyzing a mixture of vapor- and liquid-filled inclusions.

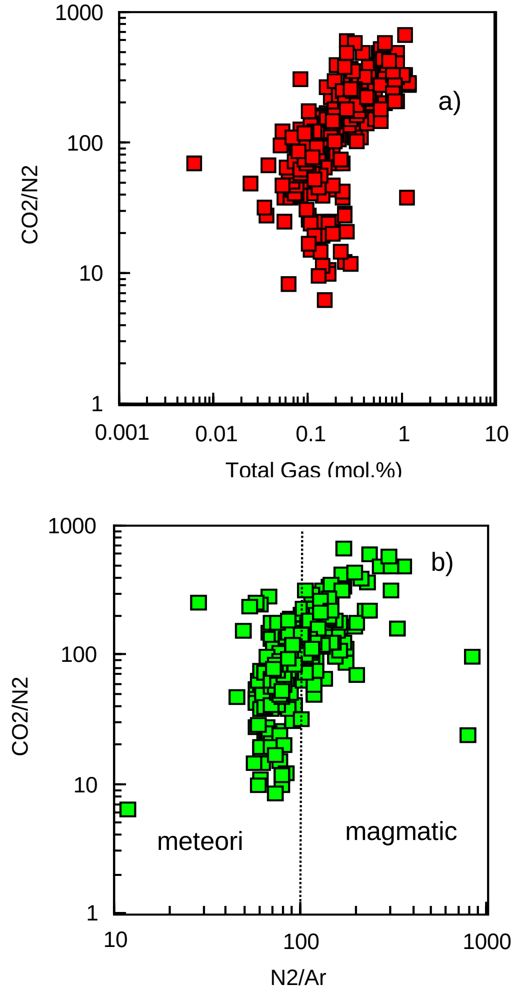


Figure 12: Cerro Prieto analyses supplied by Cathy Janek: a) plotted on a CO_2/N_2-Total Gas discrimination diagram; b) plotted on a CO_2/N_2 - N_2/Ar diagram. On b) the N_2/Ar ratios characteristic of air saturated water and volcanic gases are shown.

Distribution and Concentrations

Formation of geothermal organic species requires minerals or organic material to react with the fluid. For both type of reactions the resulting concentrations of the various LOC species should be related to temperature and depth, which we see in Coso analyses. Modeling illustrates that moderate fluid boiling can remove most organic species from geothermal fluids leaving residual species like butylene and benzene. Fluid inclusion analyses of boiling fluids that include vapor-filled inclusions will be enriched in methane, ethylene and like insoluble gaseous species. Modeling shows that a condensation process will result in a fluid with proportionally more of the soluble species that includes the aromatic organic species, butylene, H_2S, and CO_2. The high concentrations of heavier organic species, and the increase in CO_2/N_2 with depth in Karha fluid inclusions can be explained by a condensation processes.

A condensation process, oxidation of alkane to alkene species at higher levels in the system, or greater production of alkene species at lower temperatures might explain the increase in alkane to alkene ratio with depth at Coso. Modeling shows that condensation should result in a more flat distribution of species when plotted on Schultz-Flory diagrams, and we do not see this in Coso analyses. There is little data on how the production of alkane and alkene species varies with temperature in natural systems. Hence, the best explanation is that the change in alkene species with depth seen in Coso inclusions is related to oxidation of alkane compounds as fluids approached the surface.

The CO_2/N_2 vs. Total Gas Diagram

The data analyses we present show that the CO_2/N_2 vs. total gas diagram can explain gas distributions. The distribution in bladed-calcite fluid-inclusion CO_2/N_2 is consistent with fluid boiling. The same logic can be applied to the high CO_2 concentrations associated with the deep Coso wairakite.

Karaha inclusions were trapped the as a gas cap was forming (see Moore et al. elsewhere in this volume). Overall the data (Fig. 11) suggest condensation process supplied gaseous species to the geothermal system. Fluid inclusion CO_2-N_2 ratios suggest that near-surface fluids were not boiling, or exhibit as in the case of sample at 780m, open system boiling. The deeper samples indicate boiling, and the deepest samples from which is now in the gas cap, shows evidence of gas-cap formation. The data plotted on the CO_2/N_2-total gas diagram certain agree with present gas cap depth, and show a logical change in process with depth.

Cerro Prieto analyses when plotted on a CO_2/N_2 vs. total gas diagram (Fig. 12) show that the diagram can equally well be applied to geothermal well analyses. The diagrams indicate two fluids, one with lower CO_2-N_2 ratios that has N_2/Ar ratios < 100, and a second group of analyses for which CO_2/N2 increase collinearly with N_2/Ar ratios. The low N_2/Ar analyses are explained as circulating meteoric fluids. A condensation process involving addition of magmatic volatiles can explain the second and larger group of analyses. Gas analyses plotted on the CO_2/N_2 diagram strongly suggest that Cerro Prieto fluid compositions are modified by condensation-equilibration processes that increase fluid CO_2/N_2 and N_2/Ar. Hence, the plot agrees with the hypothesis (Giggenbach, 1997) that deeply circulating geothermal waters acquire a magmatic component as well as heat.

CONCLUSIONS

1. The source of hydrocarbon species is indicated by ratios of alkane to alkene species, and by C_{n+1}/C_n ratios.

2. Pyrolysis of organic material in wall rocks forms significant amounts of the aromatic organic species..

3.Fischer-Tropsch reactions produce organic species dominated by methane, and are characterized by the occurrence of alkane species.

4.The CO_2/N_2 vs. total gas diagram is useful for showing fluid boiling and condensation processes.

5. Gaseous species in geothermal systems are continuously modified by condensation and boiling processes.

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