

## ORGANIC SPECIES IN GEOTHERMAL WATERS IN LIGHT OF FLUID INCLUSION GAS ANALYSES

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### **ABSTRACT**

Measurement of organic compounds in Karaha-Telaga Bodas and Coso fluid inclusions shows there are strong relationships between H<sub>2</sub> concentrations and alkane/alkene ratios and benzene concentrations. Inclusion analyses that indicate H<sub>2</sub> concentrations > 0.001 mol % typically have ethane > ethylene, propane > propylene, and butane > butylene. There are three end member fluid compositions: type 1 fluids in which alkane compounds predominate, type 2 fluids that have ethane and propylene and no ethylene and propane, and type 3 fluids that have propylene and butylene and no propane or butane. Alkane/alkene ratios increase regularly with depth in Karaha-Telaga Bodas anhydrite and quartz inclusions. Coso analyses show a similar change in benzene and alkane/alkene ratios with sample depth.

Equilibrium calculations show that high-hydrogen fugacities and low temperatures favor alkane compounds, whereas high temperatures and low hydrogen fugacities favor alkene compounds. Benzene, propylene, butylene, and ethylene should form in that order as hydrogen fugacity decreases.

The Coso and Karaha-Telaga Bodas analyses indicate that benzene concentrations and alkane/alkene ratios are directly related to hydrogen fugacity. The large differences in hydrogen fugacity are best explained by boiling, because hydrogen strongly partitions into the vapor phase and is thus stripped from the geothermal fluids. The change in alkane/alkene ratios downhole would be reversed if the reactions were temperature driven. Calculations explain why benzene is a common constituent of geothermal fluids. Methane will react to form benzene at relatively high hydrogen fugacities. The relationship between organic species and hydrogen suggests that equilibrium at Karaha-Telaga Bodas and at Coso is fluid dominated.

### **INTRODUCTION**

A major goal for developing a dual quadrupole fluid inclusion gas analysis system was to study organic species (Norman, 2002). Organic species in geothermal fluids have received little attention because of their low concentrations that have a minor affect on power production. Based on experience with major aqueous gaseous species, we assume that organic species may be used to interpret fluid source, fluid chemistry, and fluid process. Benzene concentrations are also of concern because benzene is a carcinogen for which the US Environmental Protection Agency (EPA) has set a drinking water maximum contaminant level (MCL) of 0.005 ppm (5 ppb).

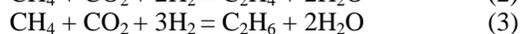
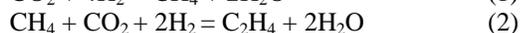
We previously presented ideas on how the distribution of C<sub>1</sub>-C<sub>4</sub> straight chain (alkane or paraffin compounds) and those with a double carbon bond (alkene or olefin compounds) are related to organic compound source (Norman, 2002). Fractionation of C<sub>1</sub>-C<sub>4</sub> simple organic species as a consequence of fluid boiling and condensation was also introduced then (Norman, 2002). Here we present organic fluid inclusion analyses performed on material from two bore holes, one from the Karaha Telaga-Bodas, Indonesia geothermal field, and one from the Coso, California geothermal field. We concentrate on equilibrium between the organic species, and how equilibrium considerations may be used to interpret fluid source and process. The Coso host rock is comprised of gneiss and granite, whereas the Karaha-Telaga Bodas system host rock has abundant organic material, including lakebeds (Moore, 2002; Moore, 2002; Lutz, 1999). By comparing the analyses from the two bore holes, we will show that changes in organic species with depth is best explained by equilibrium driven reactions, and not by wall rock environment.

### **BACKGROUND**

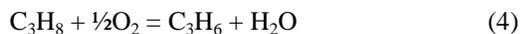
Methane and less, or generally lesser, amounts of higher hydrocarbons compounds that are dissolved in geothermal fluids can be measured in fluid inclusions

(Norman, 1987; Norman, 1996). About 40 species are identified in fluid inclusion analyses (Apodaca, 1987). The most common species after methane are the alkane compounds ethane, propane, butane, and pentane, the alkene compounds ethylene, propylene, and butylene, and the aromatics benzene and toluene. Alkane compounds by far predominate in oil and gas fields and also in geothermal reservoir fluids that occupy sediments with abundant organic material (Desmarais, 1988; Giggenbach, 1986; Giggenbach, 1997).

Organic compounds occur in all geothermal systems, not just those fluxing through sediments. Most notable are the ocean ridge “black smoker” systems that have methane and higher-order organic compounds (Riedel, 2001). There is an increasing body of isotopic evidence that most mid-ocean ridge hydrothermal system organic compounds are formed inorganically by Fischer-Tropsch reactions (Holloway, 1999; Riedel, 2001). This process was demonstrated in the laboratory by Berndt (199). Fischer-Tropsch reactions produce more light hydrocarbon compounds than heavy ones, commonly having  $C_n/C_{n+1} \sim 3$ . The ratio of alkane to alkene compounds formed by Fischer-Tropsch is related to the hydrogen activity as can be seen in reactions 1-3. High hydrogen fugacity will favor formation of ethane over ethylene.



Organic compounds may react during fluid transport. Hence, understanding how this may occur is necessary before a source for geothermal organic compounds based on alkane/alkene ratios is assigned. A simple reaction is the oxidation of an alkane compound to produce an alkene compound. An example is:



Oxidation reactions are possible in geothermal systems near the surface where there is the possibility of significant free oxygen derived from the atmosphere. Under oxygen-free reservoir conditions an appropriate expression for alkane oxidation is:



Our object in this paper is to show via fluid inclusion analyses whether or not geothermal organic compounds change during fluid transport. The dual quadrupole system we use allows the analysis of multiple organic species and hydrogen from the same inclusions or group of inclusions. It is our

assumption that the inclusions that we analyze have remained closed since trapping, and that evidence of organic species oxidation or reduction will be evident from the analyses

## METHODS

Samples of the Karaha-Telaga Bodas borehole are splits of samples studied petrographically and by fluid inclusion microthermometry (Moore, 2002; Moore, 2002). Coso borehole 83-16 chip samples in EGI archives were collected from about 1000 ft intervals. Sample cleaning was done by our standard method of immersing samples in a warm 20% NaOH solution for an hour, multiple rinsing in ultra clean water (prepared by passing reverse osmosis cleaned water through fine filtration, deionization, and charcoal columns), soaking samples overnight in ultra pure water, and then oven drying at 60°C. This process aggressively removes surface organic compounds. Minerals that have iron stains or adhering clays are precleaned using an HCl solution.

Gas analyses were done on a dual quadrupole mass spectrometer analytical system (Norman, 2002). Analyses were performed operating in the crush-fast-scan (CFS) mode (Norman, 1996) and sequentially crushing each sample about 10 times. On some samples less than ten crushes are performed because of a limited number of inclusions, and some crushes are lost because the gas burst is too large, which shuts the vacuum system down. Ideally integrated burst size is 106 to 10<sup>7</sup> counts for an individual crush. Analyses that yield a burst size < 10<sup>4</sup> counts are automatically censored. Species measured include H<sub>2</sub>, He, CH<sub>4</sub>, H<sub>2</sub>O, N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>S, Ar, CO<sub>2</sub>, SO<sub>2</sub>, the C<sub>2</sub>-C<sub>4</sub> alkanes and alkenes, pentane or cyclopentane, toluene and benzene. Gas water ratios are measured to better than 0.2 %, precision for measuring N<sub>2</sub>/Ar ratios in air-filled, synthetic inclusions is < 1%. The analytical system is calibrated with commercial high gas mixtures and the calibration is checked weekly by running our standard HF1 (Hansonburg Fluorite).

## RESULTS

Twenty-nine Karaha-Telagas Bodas well K-33 samples were analyzed. Minerals crushed are quartz, calcite, anhydrite, wairakite, and epidote from which two hundred and three analyses were obtained. Coso chips yielded 91 analyses. Water is the dominant species comprising > 99 mol.% of the volatiles in a majority of the analyses (Table 1). The organic species vary remarkably in K-33 minerals from 13 to > 10,000 ppm/v averaging 841 ppm/v. Fluid inclusion petrography and high gas amounts indicate fluids were trapped with a vapor phase present. Consequently, analyses are considered to be mixtures

bore hole	KTB K33	KTB K33Coso 83-16	
mineral	Calcite	Qtz	Qtz
depth (ft)	3259	5459	7680
Crush	6860H	6933i	6837a
Counts	4590887	1691702	233202.6
(mol.%)			
H2	0.00126	0.13	0.20
He	0.00000	0.00015	0.00015
CH4	0.025	0.035	0.334
H2O	99.7	99.2	98.2
N2	0.23	0.08	1.02
H2S	0.00009	0.00712	0.00071
Ar	0.0039	0.0008	0.0076
CO2	0.033	0.427	0.222
(ppm)			
C2H4	21.8	0.0	0.0
C2H6	1.1	22.4	155.7
C3H6	18.0	0.0	0.0
C3H8	0.0	54.5	0.0
C4H8	49.5	2.2	0.0
C4H10	0.0	18.0	0.0
C5H12	1.7	11.2	0.0
C6H6	27.7	33.5	49.7
C7H10	0.0	3.0	0.0
TORG	119.9	144.8	205.5

Table 1. Representative analyses of Karaha-Telaga Bodas (KTB) and Coso fluid inclusions. Note that KTB calcite analyses show mostly alkene compounds whereas KTB quartz analyses show mostly alkane compounds.

Analysis (ppm)	C2H4	C2H6	C3H6	C3H8	C4H8	C4H10
1	0.0	93.2	14.8	0.0	5.2	7.6
2	0.0	13.6	11.8	0.0	2.0	0.0
3	0.0	7.9	0.0	0.0	3.6	10.8
4	1.7	8.5	6.9	0.0	2.6	0.0
5	0.0	32.4	14.9	0.0	0.0	1.1
6	0.0	29.6	17.1	0.0	1.0	1.0
7	0.0	15.0	11.7	0.0	0.0	0.0
8	0.0	24.6	11.4	0.0	0.7	0.5
9	5.7	2.2	0.0	0.0	1.7	11.0
	<b>Alkane/Alkene</b>		<b>2.46</b>			

Table 2. Nine sequential analyses, # 6862, of Karaha-Telaga Bodas calcite from 3642 ft. that illustrates similar analyses obtained from repeated crushes on a given sample. Fluids are type 2; the average alkane/alkene ratio is 2.46.

of vapor-filled and liquid-filled inclusions. Because the analyses generally will include vapor-dominated and liquid-dominated inclusions, they are assumed to show greater concentrations of organic species than in if only liquid-filled inclusions were opened.

Sample to sample variation in organic species is considerable. However, sequential crushes on a given sample yield similar analyses (Table 2). Benzene is a major organic species that in some analyses equals the amount of methane (Table 1). Some samples show no propane, whereas others show no propylene (Tables 1 and 2). Other samples show little or no ethylene and propylene, but significant ethane and propane. Analyses can be divided into three end member types, plus analyses that appear to have characteristic of two of the types. These end members are analyses with: little or no detectable alkene compounds, which we call type 1 fluids; little or no detectable ethylene or propane, which we call type 2 fluids; and little or no detectable propane and butane, which we call type 3 fluids.

Analyses of Karaha-Telaga Bodas anhydrite inclusions from shallow depths show the highest concentration of alkene compounds, and deep quartz-hosted inclusions show the most alkane compounds. Plotting average alkane/alkene ratios vs. depth (Fig. 1) shows a remarkably linear change in the alkane/alkene ratio with depth for anhydrite and quartz inclusions. Alkane/alkene ratios for calcite-hosted inclusions, however, do not show a similar variation. Benzene amounts show an increase with depth for Karaha-Telaga Bodas analyses (Fig. 2), and benzene varies positively with TORG (total organic compounds excluding methane) (Fig. 3).

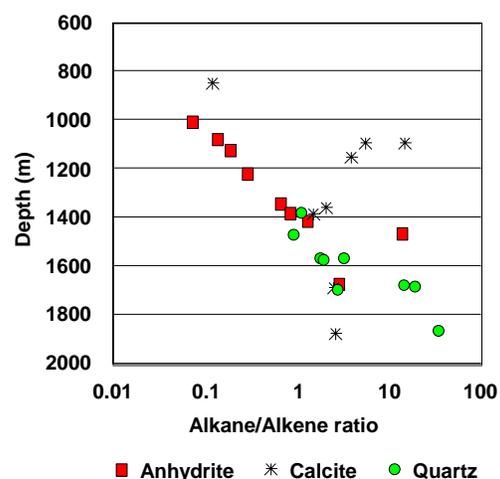


Fig. 1. A plot of the average fluid inclusion gas alkane/alkene ratios versus sample depth for the principal KTB K-33 minerals.

Hydrogen concentrations are related to organic species. Plotting hydrogen vs. alkane/alkene ratios and benzene shows positive relationships (Figs. 4 & 5). However, these plots are somewhat flawed in that the hydrogen detection limit is 0.1 to 1 ppm/v depending on burst size, and no hydrogen was detected in 63 of the Karaha-Telaga Bodas analyses. It would be more appropriate to plot hydrogen fugacity, but this cannot be calculated with accuracy for fluid inclusion analyses that have an excess gas component from vapor-filled inclusions.

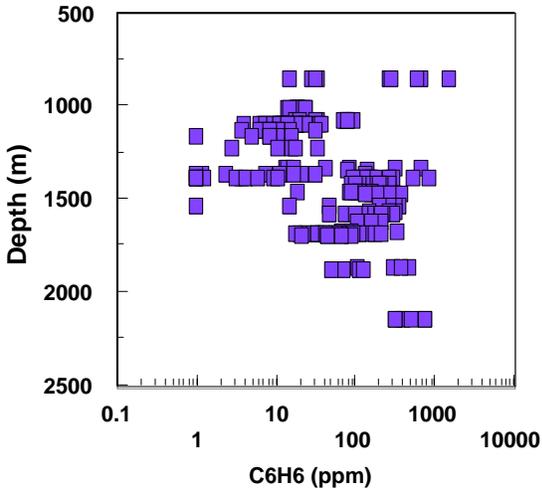


Fig. 2. Variation of KTB K33 fluid inclusion benzene versus sample depth.

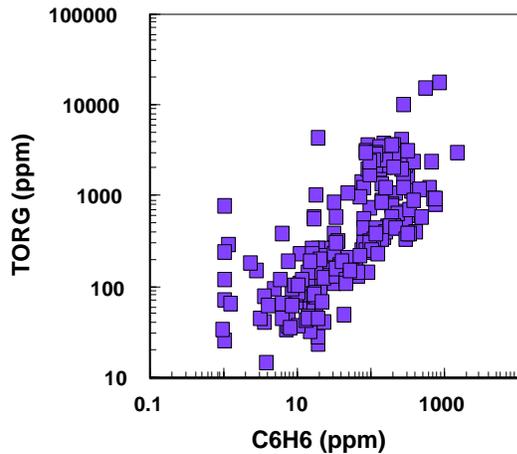


Fig. 3. Variation of KTB K33 fluid inclusion benzene with TORG (total organic compound except methane).

Coso analyses have less organic species, but they show the same changes with depth as observed in the Karaha-Telaga Bodas inclusions. The TORG varies from < 10 ppm/v to about 500 ppm/v. Analyses show that the 1000-3000 ft samples have type 3 and

type 2 fluids, whereas chips from > 6000 ft exhibit type 1 fluids. Benzene shows a systematic increase with depth (Fig. 6).

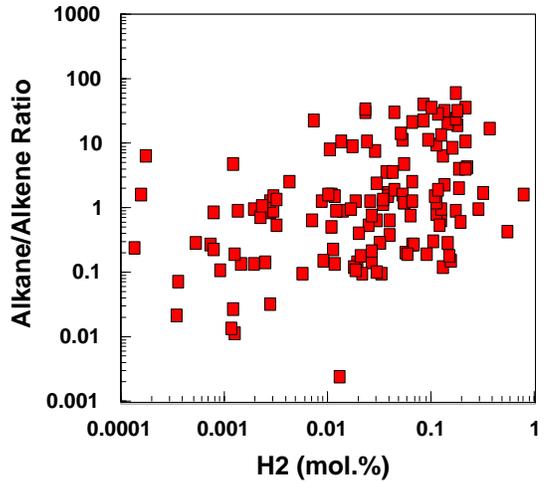


Fig. 4. The relationship between KTB K33 fluid inclusion hydrogen the alkane/alkene ratio.

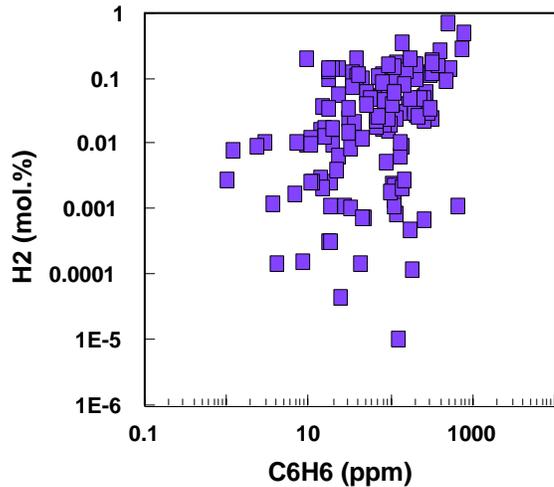


Fig. 5. The relationship between KTB K33 fluid inclusion benzene and hydrogen.

## INTERPRETATION

Boiling can fractionate organic species, but boiling cannot explain the differences in organic species distribution we observed. Figure 4 in Norman et al. 2002 shows that boiling may fractionate ethane and ethylene, and butane and butylene, but it does not

fractionate the pair propane and propylene. Therefore fluid boiling cannot be responsible for the variations in alkane/alkene ratios we measured.

The positive correlation between alkane/alkene ratios and hydrogen indicates that hydrogen fugacity is related to the dominance of alkane vs. alkene species. Reactions of C<sub>2</sub>-C<sub>4</sub> species with hydrogen and benzene are:



These reactions show that the species on the right are favored by high hydrogen fugacities, which agrees with the positive relationship shown in Fig. 4.

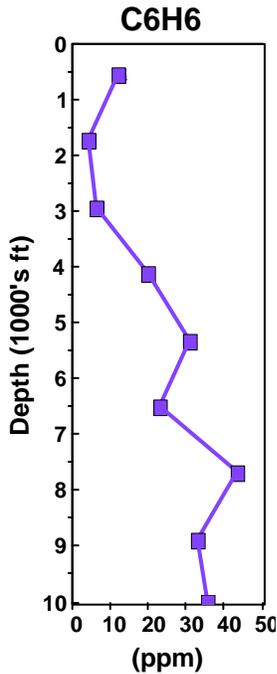


Fig. 6. Fluid inclusion benzene plotted against downhole depth for Coso drill chip analyses.

Equilibrium equations were obtained from the SUPCRT92 database (Johnson, 1992) and plotted (Fig. 7). Figure 7 shows that the end member fluid types we measured can be explained by equilibrium reactions involving hydrogen. Alkane compounds will be stable in high hydrogen fugacity fluids; alkene compounds in low hydrogen fugacity fluids,

and type two fluids will be stable at intermediate hydrogen fugacities.

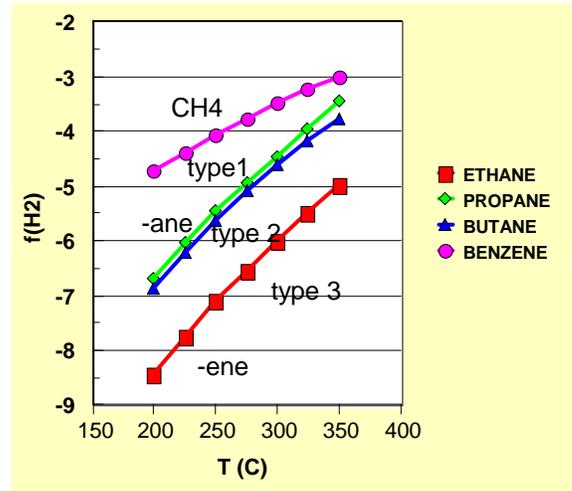


Fig. 7. Equilibrium relationships between ethane and ethylene, propane and propylene, butane and butylene, and methane and benzene. See text for details. Type 1, 2 and 3 fluids will occur were indicated above.

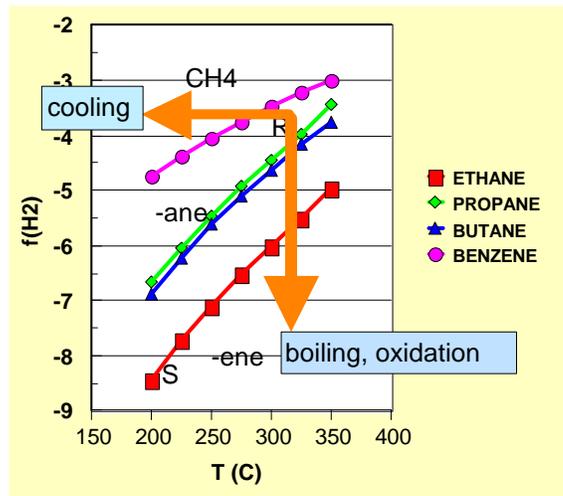


Fig. 8. Equilibrium relationships shown in Fig. 7. Arrows show the changes in species that equilibrium calculations predict when H<sub>2</sub> is lost by boiling, and when fluids cool. R and S are respectively reservoir and steam-heated water conditions

Figure 8 shows that fluid processes may result in oxidation of C<sub>2</sub>-C<sub>4</sub> alkane to alkene compounds or reduction of alkene compounds. These processes are shown diagrammatically in Fig. 8. Cooling will result in reduction of alkene compounds; heating will do the opposite. Hydrogen fractionates into a vapor phase more strongly than any other gaseous species. Therefore, open system boiling will result in hydrogen loss from geothermal fluids, which will promote oxidation of alkane compounds.

The near-linear change from deep alkane-dominated fluids to shallow alkene-dominated fluids recorded in Karaha-Telaga Bodas anhydrite and quartz inclusions may be explained by fluid boiling. The solubility of anhydrite and quartz is primarily dependant on temperature, positively for quartz and inversely for anhydrite. Calcite solubility, on the other hand, is highly affected by pH. Downward-flowing acid steam-heated waters, as described by Moore, (2002), would deposit Karaha-Telaga Bodas anhydrite in response to elevated temperatures. But calcite, which Moore (2002) describes as being deposited by anhydrite parent fluids, would be deposited only if pH was modified by wall rock reactions. Solution cooling or evaporation could only have deposited quartz. Hence, it is understandable why there is a regular change in alkane/alkene ratios with depth in anhydrite and quartz inclusions. For both minerals, deposition occurred continually in response to temperature change- considering that evaporation is also caused by an increase in temperature- that varies regularly with depth. Calcite, however, most likely was deposited at limited times when fluid chemistry was modified, and the alkane/alkene ratios in calcite suggest that at that time in the paragenesis, neither anhydrite nor silica were deposited.

We can envisage why the alkane/alkene ratio varies so regularly with depth in anhydrite inclusions. Steam-heated waters will have little hydrogen because it has low solubility in aqueous fluids. Equilibrium therefore favors alkene organic compounds. When these fluids flowed downward as postulated by Moore (2002), they would encounter upward steaming hydrogen from fluids boiling at depth, or magmatic hydrogen. As depths increased, higher fluid pressures would allow hydrogen to dissolve into the acid waters, which would result in reduction of the alkene compounds. Moore (2002) thinks silica was deposited from the same solutions that formed anhydrite. The nearly identical variation in alkane/alkene ratios in these minerals agrees with that contention.

Changes in alkane/alkene are not related to wall rock reactions. If this was the case, there should be distinct differences between downhole variations in alkane and alkene compounds in Coso vs. Karaha-Telaga Bodas. The regular change in ratios with depth

indicates reactions that are temperature related. Temperature is known to increase with depth at both boreholes studied. However, if equilibrium reactions were solely a function of temperature, the change in alkane/alkene ratios with depth would be opposite from that measured.

Alkane/alkene reactions may be affected by kinetics. However, the regular change in alkane/alkene ratios suggests that equilibrium is rapid in geological time for reactions 6-8. Cooling may result in reduction of benzene to methane, but that would require high hydrogen fugacities. The decrease in benzene with elevation is explained by the accompanying decrease in TORG. The decrease in TORG with elevation suggests fluid dilution or loss of volatiles by boiling as fluids rose, or fluid concentration by evaporation as in descending fluids. The former explanation seems to best-fit Coso, and the evaporation explanation agrees with Moore (2002) for Karaha-Telaga Bodas fluids. The higher amounts of benzene and TORG with depth at Coso indicate that organic species source is associated with deep and high temperature reactions, which agrees with an inorganic source there.

## RAMIFICATIONS

Our data strongly suggest that the distribution of organic species may be used to understand fluid processes and fluid sources. Equilibrium calculations indicate that reservoir organic compounds should be mostly alkanes no matter what the carbon source. At temperatures of 300°C, a hydrogen fugacity of about 10<sup>-4</sup> bars is expected by water-wall rock equilibrium calculation, which would drive the result toward the reduction of alkene compounds. Loss of hydrogen from boiling geothermal fluids will oxidize alkane compounds as they rise under convective flow to shallow depths. Recharging near surface waters may introduce alkene compounds to the deep geothermal system. However, rapid reduction of alkene compounds by hydrogen gas is to be expected in prograding geothermal systems. Therefore, alkane/alkene ratios may be used to identify deep, un-boiled reservoir fluids. Degassed reservoir fluids and steam-heated waters are expected to equilibrate so that alkene compounds prevail. Non-boiling geothermal systems can be identified by a decrease in alkane/alkene ratios with fluid temperature and depth.

Our data indicates that benzene is produced deep in geothermal systems. Equilibrium calculations indicate it will be a stable phase in degassed and steam-heated geothermal waters. The amounts we measure in fluid inclusion analyses is certainly higher than in the fluid phase, but our analyses indicate benzene levels in past Coso and Karaha-Telaga Bodas geothermal fluids must have been far > 0.005

ppm. Our data indicate that benzene concentrations should be expected to be higher in deep, high temperature reservoir fluids.

## **CONCLUSIONS**

Organic species are measured in fluid inclusions that are mixtures of liquid and vapor at concentrations of 10's to 1000's of ppm/v. Concentrations of organic species is greater in Karaha-Telaga Bodas inclusions because wall rocks there include sediments.

Alkene compounds dominate over alkane compounds in shallow Karaha-Telagas Bodas and Coso inclusions. The reverse is true in minerals from deep within the geothermal systems.

There is a near-linear change in average Karaha-Telaga Bodas quartz and anhydrite inclusion alkane/alkene ratios with depth. This change in ratio is best explained by equilibrium reactions in response to higher hydrogen fugacities at depth.

Boiling and subsequent loss of hydrogen from ascending Coso fluids resulted in oxidation of alkane compounds. This process should be common to most high temperature geothermal systems.

Alkane/alkene ratios are a new geochemical tool that can be used to understand geothermal fluid sources and processes.

There is considerable benzene in geothermal waters, and equilibrium calculations show that benzene will be stable during boiling and mixing processes.

## **ACKNOWLEDGEMENTS**

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