PROCEEDINGS, Twenty-Ninth Workshop on Geothermal Reservoir Engineering
Stanford University, Stanford, California, January 26-28, 2004
SGP-TR-175

GEOTHERMAL FLUID PROPENE AND PROPANE: INDICATORS OF FLUID

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ABSTRACT

The use of fluid inclusion gas analysis propene/propene ratios is investigated. Ratios of these species are affected by geothermal fluid temperature and oxidations state. Our purpose is to determine if analyses of these species in fluid inclusions these species to can be used to interpret fluid type, history, or process. Analyses were performed on drill cuttings at 20ft intervals from four Coso geothermal wells. Two wells are good producers, one has cold-water entrants in the production zone, and the fourth is a non-producer. The ratios show distinct differences between producing and the nonproducing wells. Propane-dominate fluids are associated with cool water entrants.

INTRODUCTION

Data presented by at the 2003 Stanford Geothermal Workshop (Norman et al., 2003) show that oxidation state, temperature, and fluid processes affect the C_2-C_6 organic compound concentrations. Here we test the hypothesis that fluid inclusion organic compounds analyses can be used to indicate fluid source and fluid processes. The fluid inclusion organic compounds that we examine are those measured in Fluid Inclusions Technology analyses of Coso drill chips described in detail in Dilley et al. (2004) elsewhere in this volume. Our goal is to determine if organic compound analysis is an additional valuable tool with which to interpret fluid inclusions gas analyses.

COSO WELLS

Coso wells chosen for analysis are BLM-N33-7, Navy 1 37-9, BLM 84-30, and 58a-18, which we will respectively refer to as Wells 1, 2, 3 and 4. Well 1 is an exceptional producer below 6,000 ft; Well 2 is a production bore hole but there are entrants of cold water into the well, principal production is from a fracture at the borehole bottom; Well 3 is a non producing well; and Well 4 is a producer. Bed rock is a mixture of alluvium and basalt flows to depths of about 1000 to 2000 ft, that overlie a Jurassic-age metamorphic crystalline complex intruded by granites. About a spoonful of drill chips from achieved samples were collected at 20 ft. intervals. Chips were sent to Fluid Inclusion Technologies (FIT), Tulsa OK for analysis. Fluid inclusion gas analysis is performed by crushing the chips in vacuum and measuring the volatiles released by a coupled series of 4 quadrupole mass spectrometers. Raw data are peak heights for m/e^- (mass/charge) ranging from 1 to 180 (Fig.1). Dilley et al., 2004 report that m/e^- peak ratios 44/15 (CO_2/CH_4), and 28/40 (N_2/Ar) as well the peak 34 (H_2S) can indicate the presence of bore hole fractures and fluid source, and can differentiate producing from nonproducing wells.

FLUID INCLUSION ORGANIC SPECIES

Geothermal organic species other than methane are generally at ppm concentrations. Figure 1b shows the FIT analysis of Well 2 chips from 6780 ft depth plotted on a linear scale. The three large peaks at 18, 28, and 44 are interpreted to be H_2O (gram formula weight - gfw 18), N_2, (gfw 28), and CO_2 (gfw 44). Organic species are evident when the analysis is plotted using a logarithmic scale (Fig. 1a). Peaks at m/e$^-$ 24-27, 30-31, 37-39, and 41-43, and those > 48 with exception of peak 64 are organic compounds created in the mass spectrometer. Generally the lighter organic species predominate as is shown in Fig. 1. Careful examination of spectra like that shown indicates the presence of both alkane and alkene compounds. Oxidation-reduction reactions can be written for C_2-C_4 alkane and alkene species:

$$C_2H_4 + H_2 = C_2H_6 \qquad (1)$$
$$C_3H_6 + H_2 = C_3H_8 \qquad (2)$$
$$C_4H_8 + H_2 = C_4H_{10} \qquad (3)$$

And for benzene and methane:

$$C_6H_6 + 9\ H_2 = 6\ CH_4 \qquad (4)$$

Plotting these reactions on a log f (H_2) vs T diagram (Fig. 2) shows that species change with temperature and fluid oxidation state. A decrease in fluid temperature may result in alkene compounds and benzene reacting with H_2 to form alkane compounds and methane. The opposite may occur by loss of H_2 resulting from fluid boiling.

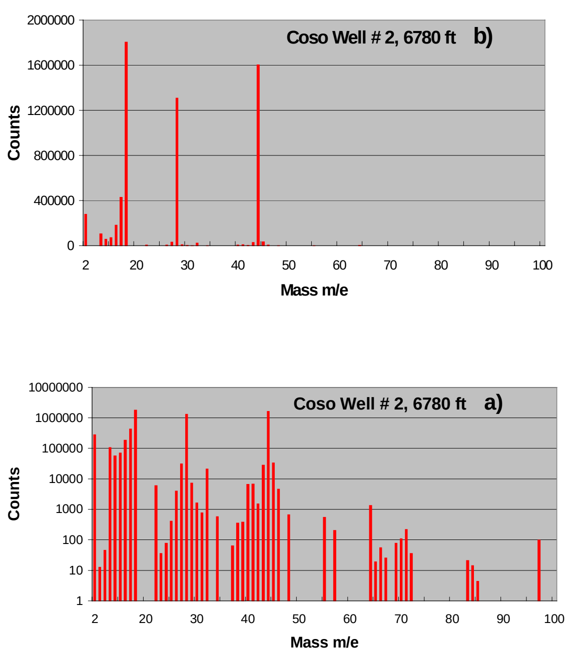


Figure. 1. Mass spectra for the analysis of Well 2 drill chips from 6780 ft.: a) has a log scale, b) has a linear scale. The prominent peaks in both graphs at masses 18, 28, and 44 are respectively water, N_2, and CO_2.

The ratio of propane to propene was chosen for study for several reasons. The light hydrocarbon compounds are generally more common in geothermal fluids than the heavier compounds, as

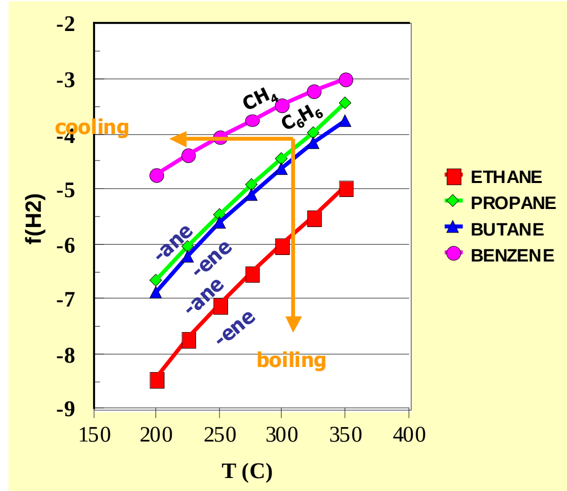


Figure. 2. A diagram showing equilibrium between alkane and alkene compounds, and methane and benzene. Arrows show how species will change in 300C fluids that cool or loose H_2 by boiling: -ane refers to alkene compounds such as ethane, -ene refers to alkene compounds.

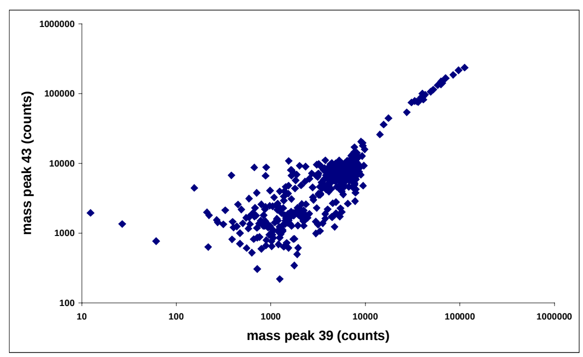


Figure. 3. Plot of Well 2 mass peak 43 verses mass peak 39.

evidenced in Fig. 1. Another reason for choosing these species is that the pentane/pentene ratio is little fractionated by fluid boiling (Norman et al, 2003). This is not true for the C_2 and C_4 compounds. The mass peaks of propane and propene are not interfered with as badly as are the peaks for ethane and ethane. Analyses from FIT are peak heights. There is no simple way to determine quantitatively the concentrations of individual species. We do not know the exact cracking outlines of propane and propene, however the patterns of major and minor peaks are similar for all mass spectrometers. Hence we know that propane, which has the same gfw as CO_2, has a major fragmentation peak at 43. Propene (gfw 42) has a major peak at 39, which is a lesser fragmentation peak for propane. So, we assume we can use the ratios of m/e$^-$ peaks 43/39 to quantify variations in the ratios of these species.

METHODOLOGY

Of concern when we plot mass peaks is that the peaks we choose truly represent the species we assign to them. As explained in Dilley et al. (2004), the way we test our assumptions about mass peaks is to plot two peaks we presume represent the same species against one another. We know that peak 43 represents propane plus fragments of higher order organic compounds, and peak 39 represents propene and fragments of higher heavier organic compounds that Includes propane. The plot of peak 43 versus peak 39 for Well 1 analyses (Fig. 3) shows a linear trend for about 18 of the 423 analyses performed. This linear array of data indicates that the inclusions with the highest concentrations of organic compounds have primarily propane. The poor correlation for most of the analyses indicates that the 43 and 39 peaks, for the most, part represent different organic compounds

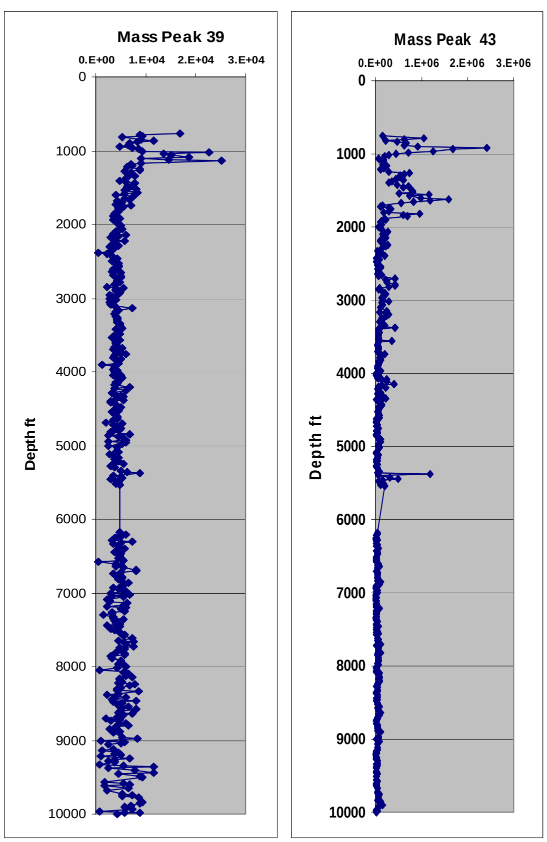


Figure. 4. FIT analyses of peaks 39 (left) and 43 (right) plotted verses depth for Well 1.

RESULTS

Analyses of peak 39 and 43 show little variation when plotted versus depth. The analysis of Well 1 chips is an example (Fig. 4). Ratios of these peaks do show significant differences from well to well, and with depth (Fig. 5). Megascopically the 43/39 ratios of nonproductive Well 3 inclusions (Fig. 5c) are distinctly different from analyses of the other wells The Well 3 43/39 ratios indicate that propene concentrations are much greater than propane, and there in little variation in the ratios from top to bottom of the bore hole. Well 1 show ratios that commonly are as high as 50 to > 100 in the upper 5,500 ft of the borehole. The bottom 5000 ft of Well 1 has ratios that are more homogeneous from sample to sample, and vary form about 10 to about 20. Well 2 ratios show higher values for the interval between 7,000 and 8,400 ft. Well 4 ratios are fairly homogeneous with depth, and vary from about 10 to about 40.

Dilley et al. 2004 conclude that high H_2S contents of Well 2 inclusions from about 4,500 ft to 6,500 ft indicate entrants of steam-heated waters. We do not see any difference in Well #2 43/39 ratios over that interval, but do see a change in ratios at depths > 6,500 ft. Downward migrating waters precipitate calcite and oxidize reduced iron bearing minerals. Calcite and hematite recorded on the Well 2 mud log is plotted on Fig. 6. This figure shows that calcite and hematite occurs at depths from about 4,000 ft to about 9,100 ft.

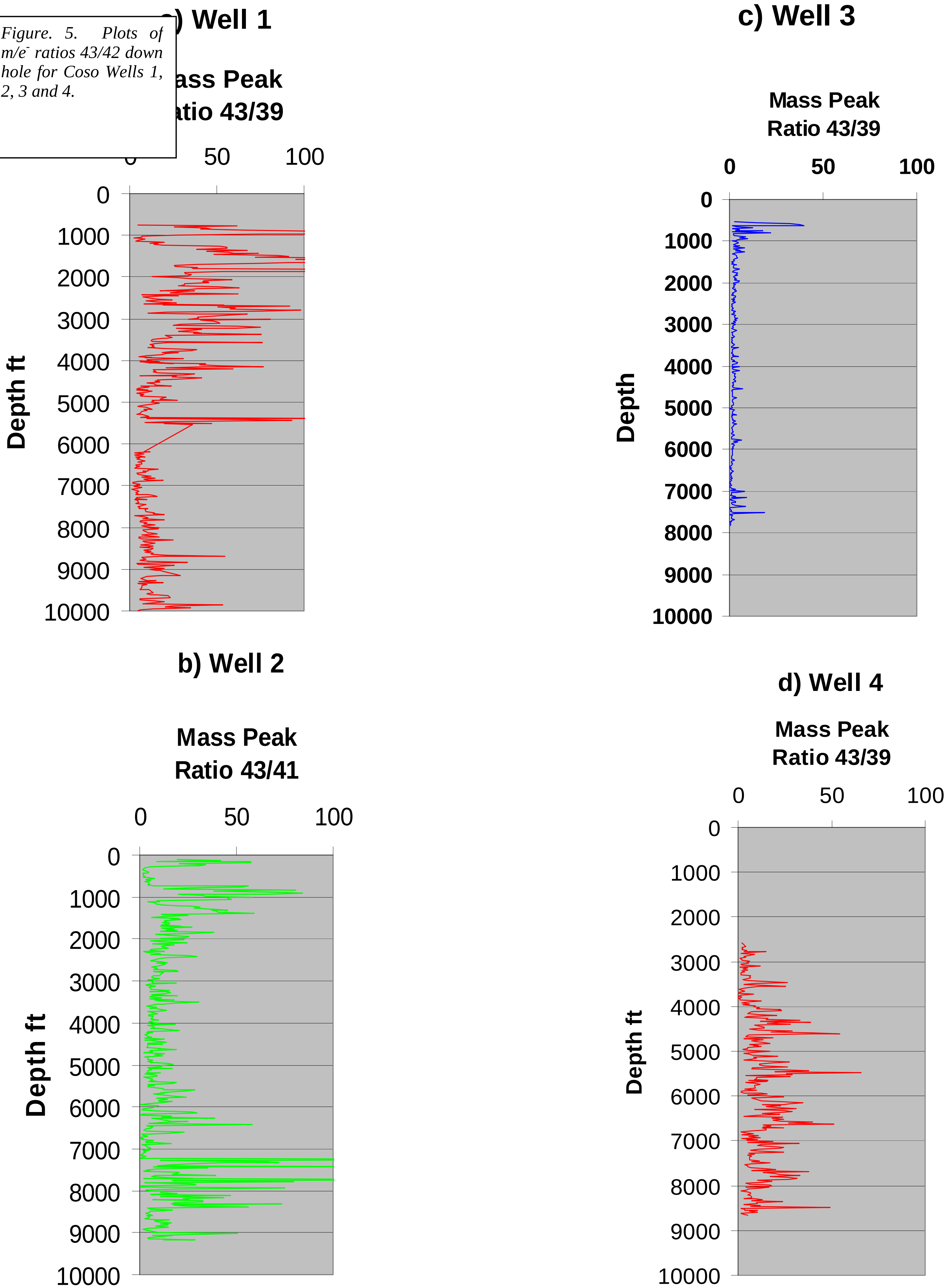
Water is the principal volatile in geothermal fluid inclusions. The water peak, therefore, is an indicator of the fluid inclusion density. Mass 18 is plotted versus depth for the four wells (Fig. 7). Well 3 clearly stands out by having lower and more uniform water values than producing well chips.

INTERPRETATION

Background Inclusions

It is reasonable to expect that Coso host rocks have inclusions that could date from the metamorphosed or granite intrusion. We expect that the modern geothermal system has formed new inclusions within the same rock. The homogeneous set of analyses we obtained from Well #3 chips are consistent with inclusions that were trapped during a regional event like metamorphism. The low water values for Well 3, and much higher values for the other wells, is constant with a flux of Recent geothermal waters through the Coso bed rocks near these bore holes.

Figure. 5. Plots of m/e⁻ ratios 43/42 down hole for Coso Wells 1, 2, 3 and 4.



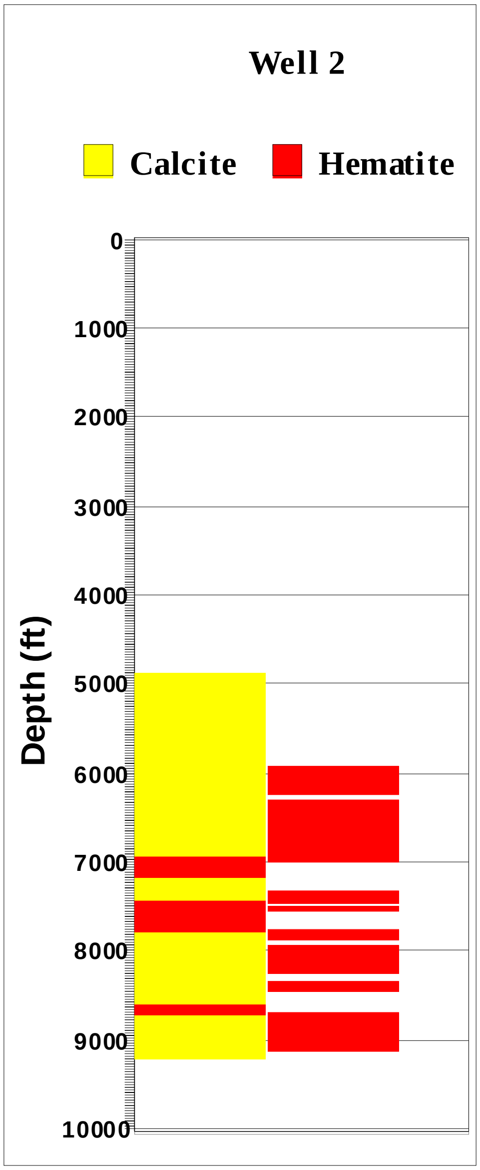


Figure. 6. Occurrence of calcite and hematite in Well 2 drill chips. Data compiled from the Well 2 mud log.

The higher sample-to-sample variation in water and 43/39 ratios in Wells 1, 2 and 4 chip analyses can be explained considering that Well 3 typifies Coso bedrock background fluid inclusions. Dilley et al. (2004) show that peaks in gas concentrations and ratios are associated with fractures. It stands to reason that a higher density of new fluid inclusions will form near fractures. If this is the case then the sample-to-sample heterogeneity in Well 1, 2 and 4 34/39 ratios can be explained as admixtures of Recent and background inclusions. However, admixtures of background and Recent inclusions cannot easily explain the large variation in Well 1 43/39 ratios because the water analyses indicate that Recent inclusions dominate top to bottom in Well 1 chips. The analyses rather indicate that there is more than one Recent fluid trapped in Well 1 inclusions.

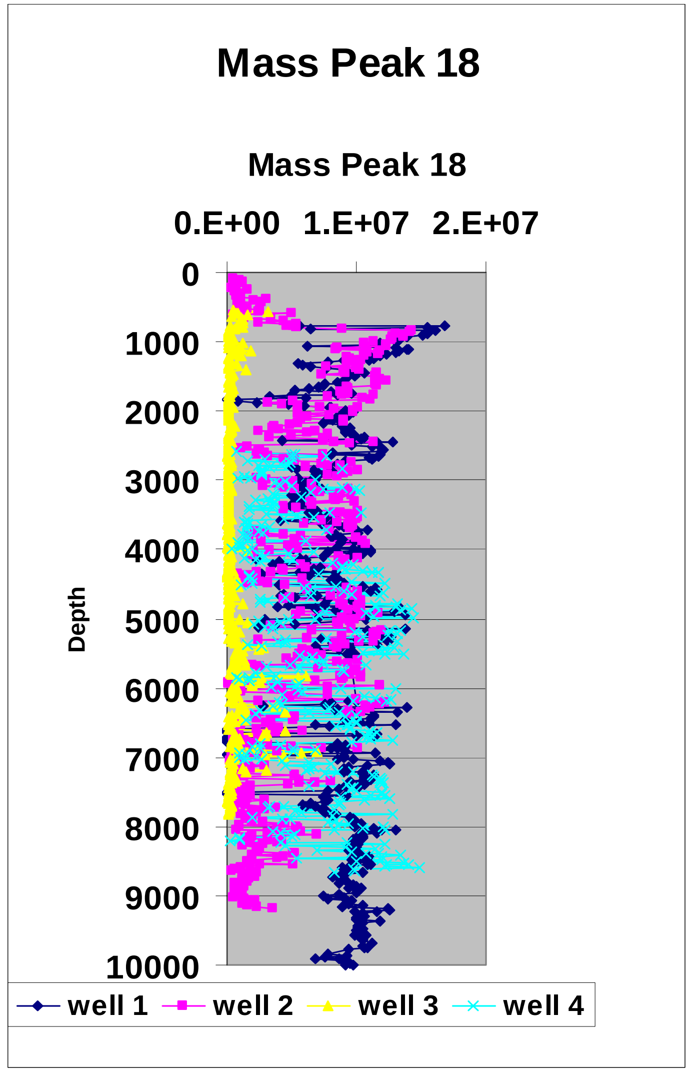


Figure. 7. Comparison of the water peak, m/e = 18, analyses of drill chips from Wells 1, 2, 3, and 4.

Fluid Types and 43/30 Rations

The rather consistent Well 1 39 and 43 peak heights (fig. 4) suggests that the concentration of C_3 compounds varies little from top to bottom of the crystalline bed rock. However the 43/39 ratios show a difference between the lower producing section of the well and the upper 5,500 ft. The higher ratios in chips from the upper portion of the well can be explained by lower temperature propane dominant solutions fluxing through the top half of the well. Reservoir fluids appear to have ratios somewhat above background, but significantly less than the values in upper 5,500 ft of Well 1.

The high Well 2 43/39 ratios between 7,200 and 8, 400 maybe explained by entrant of propane-bearing fluids like occur at the top of Well 1. Calcite and hematite, in this lower portion of the well suggest recharge of high oxidation state cool waters. Calculation shows that at 200 C propane and hematite can coexist.

Well 2 temperature logs in Fig. 5, Lorie Dilley et al. (2004) indicated that the hot-water-bearing-fractures are below 8,600 ft., That same interval has 43/39 ratios between 10 and 20 which from Well 1 and Well 4 analyses is typical of reservoir fluids.

We see no distinctive ratio at the depths in Well2 where H_2S values suggest entrants of steam-heated waters. That is consistent with the chemistry of propane and propene. Boiling and condensation do not affect the ratios of two. Hence condensed vapor form boiling reservoir fluids would be expected to have the same 43/39 ratios as the reservoir fluids. However, if fluids cool significantly during condensation this could result in reduction of propene to propane. It is possible that ratios of 10 to 20 represent propene and a fragment of a higher hydrocarbon species that has a fragmentation peak at 43. It that case cooling may be insufficient to change the 43/39 ratio.

Dilley's plots of Well 2 N_2/Ar and CO_2/CH_4 ratios show multiple peaks for the depth interval 7,200 to 8,400 ft. Well 2 analyses with higher N_2/Ar and CO_2/CH_4 values ratio are attributed to fractures carrying reservoir fluids. Well 2 analyses with higher N_2/Ar and CO_2/CH_4 have low 43/39 ratios. The opposite is true for analyses with lower N_2/Ar and CO_2/CH_4 ratios. These high N_2/Ar and CO_2/CH_4 agree with what the analyses we expect if there are fractures transporting reservoir fluids. Well 2 analyses with high N_2/Ar and CO2/CH_4 values ratio are, therefore, attributed to fractures carrying reservoir fluids. The lower 43/39 ratios in these zones is with magmatic N_2/Ar ratios is consistent with our megascopic observations that reservoir fluids have 34/39 ratios of about 10 to 20. Overall the Well 2 analyses suggest that between 7,200 and 8,400 there are interspersed fractures with bearing reservoir and cool surface fluids.

These data for Well 2 may indicate a through going structural zone that penetrates to the surface. Our analyses suggest that at times these fractures are occupied by reservoir fluids, and at times filled with recharging cool fluids. The data do not tell us if the events occur at the same time. Well 2 temperature logs indicate that either today there is no flow in fractures at depths of 7,200 to 8,400 ft., or that flow of reservoir fluids and recharge waters is about equal.

CONCLUSIONS

- Coso drill-chip fluid-inclusion analysis 43/39 ratios show variations from bore hole to bore hole, and with depth in individual bore holes.
- The 43/39 ratios for the most part represent ratios of propane/propene.
- The 43/39 ratios are an indicator of cool surface waters fluid entrants into deep Coso bore holes.
- The 43/39 ratios are a valuable tool in interpreting FIT fluid inclusion analyses.

ACKNOWLEDGMENTS

This study was supported by a grant from the California Energy Commission "Fluid Inclusion Stratigraphy: A New Inexpensive Method for Geothermal Reservoir Assessment". The views in this paper are those of the authors, and in no way reflect that of the CEC.

REFERENCES

Dilley, Lorie M, David I. Norman, and Brian Berard (2004), Fluid Inclusion Stratigraphy: a New Method For Geothermal Reservoir Assessment, Preliminary Results: PROCEEDINGS, Twenty-Ninth Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, California, January 26-28, 2004.

Norman David I. and Joseph N. Moore (2003) Organic Species in Geothermal Waters in Light of Fluid Inclusion Gas Analyses: PROCEEDINGS, Twenty-Eighth Workshop on Geothermal Reservoir Engineering,