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OVERABUNDANCE OF GASEOUS SPECIES AND THE SOURCE OF ORGANIC COMPOUNDS IN GEOTHERMAL FLUIDS

David I. Norman[1], Nigel J.F.Blamey[1] and Joseph N. Moore[2]

1. New Mexico Tech, Socorro, NM 87801 (dnorman@nmt.edu)
2. EGI, University of Utah, Salt Lake City, UT 84108 (jmoore@esrilan.esri.utah.edu)

ABSTRACT

The problem of excess N_2, Ar and possibly CH4 is revisited. Examination of Cerro Prieto well discharges show that wells have N_2 and Ar concentrations up to ten times greater than > ASW and concentrations as low as one tenth that of < ASW. Integrated average concentrations are, however, about that of ASW. Cerro Prieto fluids show a positive correlation between excess N_2 and Ar, and enthalpy. The low-enthalpy Steamboat Springs fluids similarly have N_2 and Ar concentrations < ASW. Analysis of Mothra Black Smoker inclusions yields N_2/Ar ratios similar to ratios in vent fluids, which shows that excess N_2 and Ar are not due to measurement error. The distribution of Cerro Prieto gaseous species suggests a boiling-like process was responsible for the depletion of gaseous species in low N_2-Ar fluids, and condensation explains fluids with N_2 and Ar > ASW. Three inferences from the data are that: 1) the minerals in which we study fluid incisions are deposited by fluids with excess N_2 and Ar, hence represent only part of the fluid history; 2) the mechanism responsible for fluids depleted in, and with excess N_2 and Ar is a local process because both depleted and excess N_2-Ar waters are observed in Cerro Prieto, and 3) the most accurate estimate of reservoir gas chemistry is obtained from geothermal fluids that have N_2 and Ar concentrations near that of ASW. A mechanism proposed for enriching fluids in H_2, N_2, Ar, and CH_4 calls on wallrock boiling and bubble trapping to sequester these species, then solution of bubbles at times of elevated pressure and temperature that occurs when fractures close.

Our analysis of black-smoker-mineral fluid inclusions indicates similar CO_2/CH_4 ratios as reported in the present vent fluid, thus verifying our fluid inclusion analyses. Some analyses of organic compounds in Tiwi, The Geysers, and Coso fluid inclusions show a Schultz-Flory distribution characteristic of a Fisher-Tropsch reaction. Experimental evidence indicates that "black smoker" methane is produced by Fisher-Tropsch reactions involving olivine and magnetite at temperatures of 300 C or more. We hypothesize that deep circulating fluids subject to Fisher-Tropsch relations show an inverse relationship between N_2/Ar and CO_2/CH_4 ratios, whereas geothermal fluids that have an organic source of methane will show a positive correlation between N_2/Ar and CO_2/CH_4 ratios. The Geysers and Broadlands fluid inclusions and Cerro Prieto fluids show a positive relationship between N_2/Ar and CO_2/CH_4 ratios, whereas Tiwi and Coso fluid inclusions exhibit a negative correlation. Mineral alteration by methane-producing reactions will in time limit the amount of methane produced. Therefore, we expect that both inorganic and organic CH_4 will be mainly generated early in the life of a geothermal system.

INTRODUCTION

Our goal is to interpret geothermal-system fluid-inclusion volatile-analyses. In the 1999 Stanford Workshop paper (Norman and Moore, 1999) we pointed out that concentrations of N_2, Ar, and CH_4 in geothermal fluid inclusion are greater than that reported in reservoir fluids. Here we revisit this subject with new data and new explanations.

FLUID INCLUSION N_2 AND AR

In virtually all analyses of inclusion volatiles we perform N_2 and Ar concentrations are greater than concentrations of these species in 20 C air saturated water (ASW) (Norman and Moore, 1999). This raises questions about whether fluid inclusion gas analyses truly represent past geothermal fluid chemistry, and if they do, what is the process by which N_2 and Ar are concentrated? Other questions, granting our analyses are valid, are why are N_2 and Ar depleted fluids not trapped in fluid inclusions and do present geothermal systems show a range in N_2 and Ar concentrations? Our underlying assumption is that since geothermal waters are comprised mostly of meteoric waters, and meteoric waters have N_2 and Ar concentrations near that of ASW, geothermal fluids should have N_2 and Ar concentrations near that of ASW. Remarkably, there is scant information to back this assumption. An analysis of the Tiwi Mat 25 well supplied to us by UNOCAL (Norman and Moore, 1999) indicates present fluids have N_2 and Ar concentrations about 10 times greater than ASW. Excess N_2 and Ar (excess N_2 and Ar being concentrations > than that in ASW) could be more common than generally thought. Therefore USGS analyses of Cerro Prieto and Steamboat Springs fields obtained from Cathy Janik were studied to determine reservoir N_2 and Ar concentrations. Recent fluid inclusion material was sought so we could relate present fluid-gas compositions to fluid inclusion analyses. Fluid inclusion analysis of well-scale mineralization was attempted but the results are hard to interpret. Several Black Smoker pipe fragments and analyses of vent fluid were obtained from Deborah S. Kelley University of Washington (Seattle). Kelley collected the samples in the summer of 1999 during a program that harvested the Finn pipe from the Mothra Black Smoker System, East Pacific Rise. Here we report fluid inclusion analyses of active Black Smoker sulfide minerals that we compare to vent fluid analyses. Black smoker chimneys rise and collapse in time spans of s few years, hence the inclusions represent fluids present no more than a few years prior to sampling.

Results

Downhole fluid compositions were calculated from the Cerro Prieto data set, and analyses were censored were there are only partial analyses and if y > 0.5. Replicate analyses were averaged. Data subsets were prepared by selecting analyses for which N_2/Ar ratios are similar to ASW. We selected analyses that have N_2/Ar > 30 and < 100 and for which total nitrogen (combining N_2 and NH_3 analyses) as N_2 ratios with Ar are > 30 and <100. The censored data set comprises 234 analyses, and the subsets respectively 226 and 159 analyses. The respective average N_2/Ar ratios are 52, 48, and 78.

Concentrations of N_2 and total nitrogen as N_2 were plotted against Ar for the censored analyses and the subsets. All plots show that nitrogen and Ar concentrations vary by about two orders of magnitude with average concentrations near that of ASW (Fig. 1). A plot of other Cerro Prieto gaseous species verses Ar and N_2 indicate positive correlations with CH_4 and H_2 concentrations. There is no relationship between the N_2/Ar ratio and concentrations of N_2 and Ar, and there is no correlation between N_2 or Ar and CO_2 concentrations. Tiwi and Coso fluid inclusion analyses show similar relationships. Nitrogen (Fig. 2) and Ar show a positive relationship with the steam

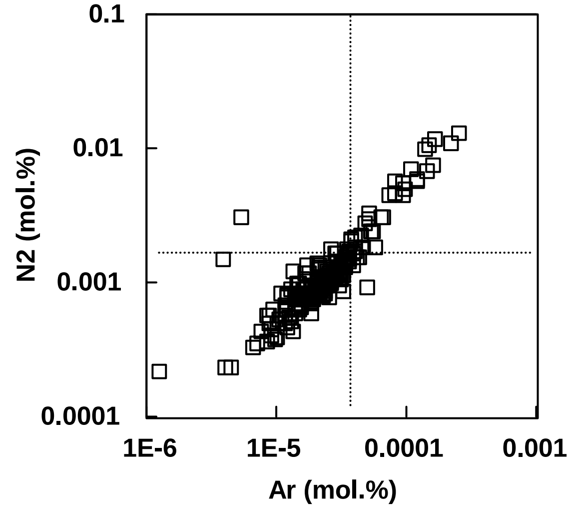

Fig. 1 Analyses of 234 Cerro Prieto wells. Dotted lines are ASW values.

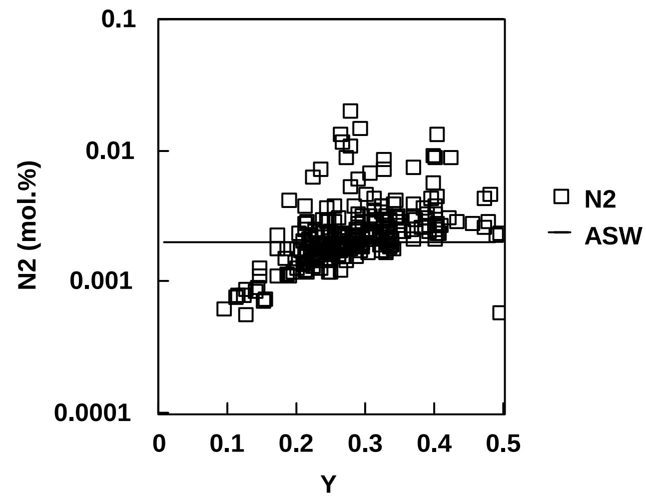

Fig.2 Cerro Prieto well N_2 plotted against the steam fraction "y". A similar looking plot is obtained by plotting Ar vs. y. The N_2 value for ASW is plotted for reference.

fraction (y), and by inference enthalpy. A plot of total nitrogen (as N_2) vs. Ar for the low enthalpy Steamboat Springs geothermal waters (Fig. 3) shows that all analyses indicate N_2 and Ar concentrations < ASW.

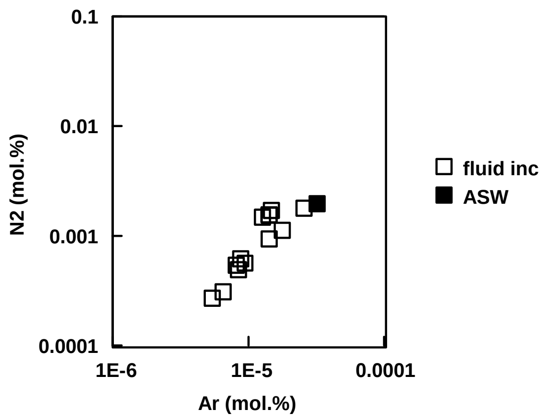

Fig. 3 Steamboat Springs nitrogen and argon concentrations. Compared to ASW. Analyses were censored as outlined in the text.

Analyses of total nitrogen for five selected Cerro Prieto wells sampled periodically over about 12 years show that gaseous species concentrations vary over time. (Fig. 4). Most wells show several nitrogen maxima with nitrogen concentrations well above ASW values, and times when levels were below that in ASW. Integrating N_2 for each well in figure indicates that total N_2 discharge over a period of about 12 years is about that of ASW. The steam fraction of each well varies with time, and this variation roughly tracks that of trace gas concentrations (Fig. 5).

Black Smoker fluid inclusion analyses performed by the crush-fast-scan (CFS) method (Norman et al. 1996) show concentrations of N_2 and Ar, and N_2/Ar similar to those in Mothra vent fluids (Fig. 6 and 7).

<u>Discussion</u>

Analysis of Black Smoker minerals indicates our fluid inclusion analyses of N_2 and Ar closely approximate the chemistry of past fluids. The vent fluids analyses also illustrate that excess N_2 and Ar

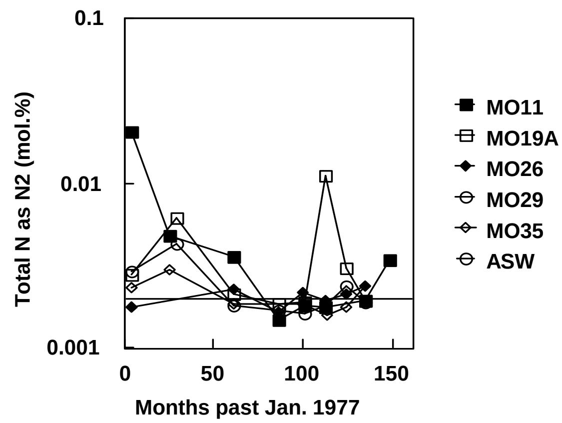

Fig. 4 Analyses of five selected Cerro Prieto wells done over a period of about 12 years starting in 1977. The ASW value is shown for reference.

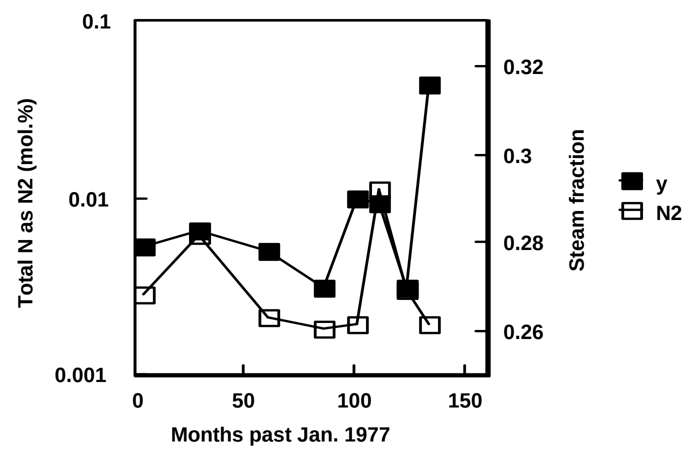

Fig. 5 Comparison of the measured steam fraction "y" and total nitrogen measured over about twelve years for Cerro Prieto well MO19.

is a common phenomenon in geothermal fluids. Numerous stable isotope studies have shown that black smoker fluids are comprised mostly of seawater and Mothra Black Smoker fluids have N_2/Ar ratios similar to seawater. Therefore the occurrence of excess N_2 and Ar in Mothra fluids most logically is the result if a geothermal process.

The occurrence of excess N_2 and Ar in Cerro Prieto and Mothra fluid indicates that our measurement of excess N_2 and Ar is common in geothermal fluids. The lack of any correlation between the N_2/Ar ratio and concentrations of N_2 and Ar strongly suggest that higher concentrations of these species is not

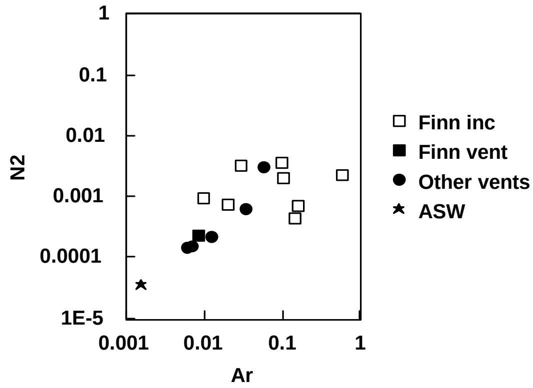

Fig. 6 A comparison of Mothra Black Smoker fluid inclusion analyses to vent fluids. Finn refers to a specific pipe, inc is an abbreviation for fluid inclusion. Note that Mothra vent fluid N_2 and Ar concentrations of are well above that of 20 C seawater (ASW).

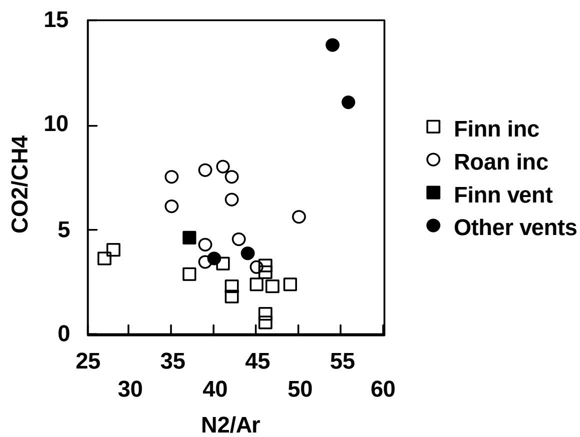

Fig. 7 A comparison of Mothra Black Smoker fluid inclusion analyses to analyses of vent fluids. Finn and Roan refer to a specific pipes, inc is an abbreviation for fluid inclusion. Note that the analyses are plotted on a linear scale and not a logarithmic scale as we commonly do for gas ratio plots.

from addition of magmatic volatiles that typically have ratios of about 80 in basaltic volcanic gases, and 200 to 2000 in felsic volcanic systems. Because concentrations of N_2 and Ar vary from well to well at Cerro Prieto, and with time, the concentrating process must be local and small scale.

Correlations of N_2 and A with the gaseous species that strongly partition from liquid to vapor suggest vapor separation must be part of the concentrating mechanism. The correlation of N_2 and Ar with the steam fraction indicates that the concentrating mechanism is related to fluid temperature. Low concentrations of N_2 and Ar in Steamboat Springs wells are consistent with this idea.

Phase separation, i.e. boiling, may occur in gas-charged geothermal waters when pressure or temperature is lowered. A geyser-like process that could account for excess N_2 and Ar in geothermal fluids, and changes in y value with time, is as follows:
1. Boiling occurs in wallrock adjacent to a fracture, and the bubbles formed are trapped due in pore spaces. The "y" value is small, hence a major portion of the trace gaseous species H_2, CH_4, N_2, and Ar that strongly fractionate into a vapor are transferred into bubbles. Only a fraction of CO_2 is because the "y" values is small and the CO_2 partitioning coefficient is lower.
2. Mineral precipitation in the fracture in time limits or stops flow, hence the pressure in the vein and in the pore space increases. Under increased pressure and temperature bubbles dissolve and gaseous species contained in the bubbles then diffuse creating a highly gas-charged fluid.
3. The fracture opens allowing the fluids to exit now charged with more N_2, Ar, CH_4, and H_2 then the parent fluid contained. Vigorous boiling accompanied by fluid temperature decrease results in vein mineral precipitation.
4. Pressure and temperature in the vein drops allowing boiling to start again in pore spaces, and the cycle repeats.

In natural geothermal systems mineral precipitation will occur mainly in step 3 of the process when fluid flow is rapid, and the fluids physio-chemical parameters are changing rapidly. The limited fluid flow during steps 1 and 2 limits mineral precipitation, and hence fluid inclusion formation.

METHANE-RICH FLUIDS

Previously we considered that fluid inclusion methane was from organic sources, or from low temperature equilibrium with Fe^{2+}-Fe^{3+} in wall rocks (Norman and Moore, 1999). Hence we suggested CH_4 as a good tracer for evolved meteoric waters. However, there is evidence that methane can be produced by Fischer-Tropsch type reactions at temperatures of 300 C or more (Kelley, 1996; Potter et al., 1998) This process was demonstrated in laboratory (Berndt,1996) and stable isotope studies of methane rich fluids at Black Smokers an in Kola peninsula intrusives indicate abiogenic methane (Kelley, 1996; Potter et al., 1998).

Fischer-Tropsch reactions can produce methane concentration greater than that of CO_2. In Fischer-Tropsch reactions higher order organic compounds are produced whose concentrations fall linearly on a logarithmic Schultz-Flory plot. Organic compound concentrations were analyzed in fluid inclusions and plotted on Schultz-Flory plots in order to test for abiogenic organic species.

There are also lingering doubts as to why we commonly measure CO_2/CH_4 ratios in geothermal system fluid inclusions much lower that in present fluids. Organic compounds wet most minerals, and methane is highly soluble in organic liquids. It was postulated that organic compounds might be concentrated in fluid inclusions buy a wetting mechanism, and thus yield false high analyses of organic compounds. Therefore, Mothra Black Smoker minerals were analyzed because the source fluids are rich in methane. If fluid-inclusion organic-compound wetting occurs, it was thought that extremely high organic-compound concentrations should be analyzed in fluid inclusions that formed in methane-rich black-smoker vent fluids.

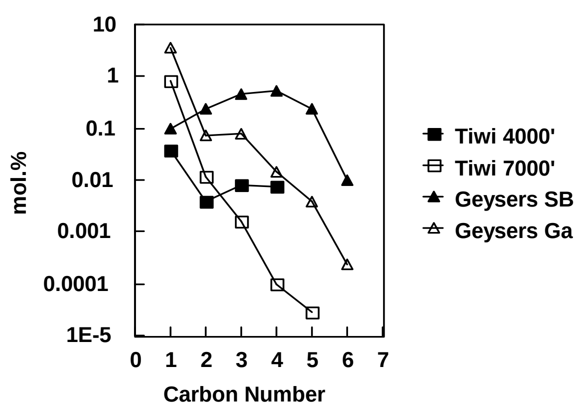

Fig. 8. A Schultz-Flory plot of fluid-inclusion organic species from the Tiwi and The Geysers geothermal systems. Fischer-Tropsch type reactions create logarithmically linear distributions of organic species.

<u>Results</u>

Analyses of Mothra inclusions shows that we measured similar CO_2/CH_4 ratios as are in present vent fluids (Fig. 7). Schultz-Flory plots of Tiwi Mat 25 drill core inclusions from depths of 4000 and 7000 feet depth show respectively a nonlinear and a linear distribution of hydrocarbon species (Fig. 8). Similarly, some inclusions from The Geysers have hydrocarbons that appear abiogenic others do not (Fig. 8). Fluid inclusion analyses of Coso (Fig. 9) show a broad distribution in CO_2/CH_4 ratios. A Schultz-Flory plot of sample 68-6, 8680' quartz and epidote analyses exhibit a linear organic species distribution (Fig. 10). Inclusions in this sample homogenize at or above 300 C, and N_2/Ar ratios range up to 1154.

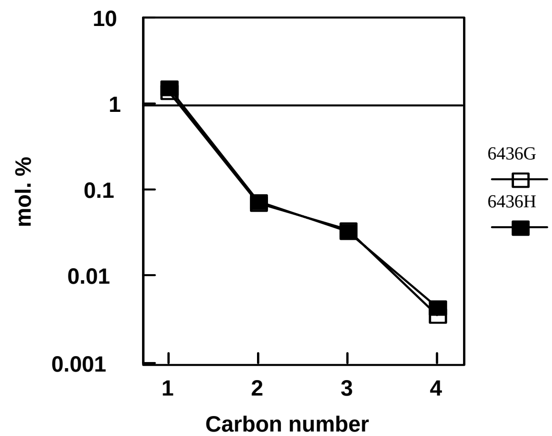

Fig. 9 Analyses of Coso fluid inclusions.

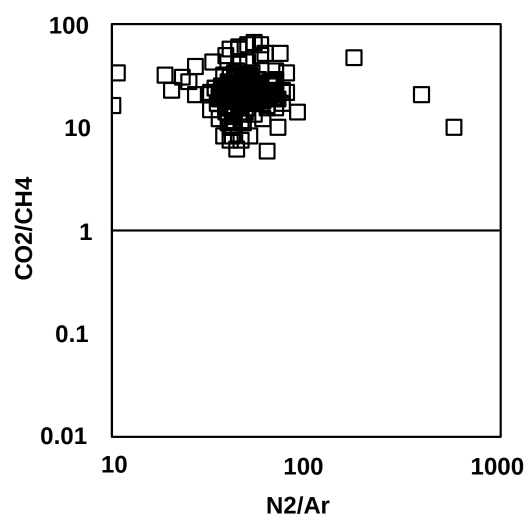

Fig. 10 A Schultz-Flory plot of two sequential organic species analyses done on Coso sample 68-6. See text for details.

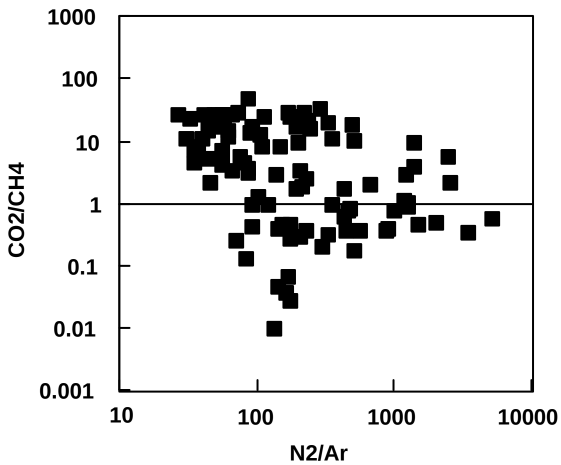

Fig. 11 Cerro Prieto analyses. Note that fluids are dominantly meteoric.

Analyses of Cerro Prieto wells shows a limited range in CO_2/CH_4 ratios, and N_2/Ar ratios indicate the present fluids are almost entirely meteoric. The analyses plot with a weak positive slope suggesting a minor input of magmatic volatiles.

Discussion

Mothra analyses indicate that our fluid inclusion measurements of CO_2/CH_4 are accurate (Fig. 6). Note that the plot is with linear scales rather than logarithmic type we generally use on CO_2/CH_4 vs. N_2/Ar (see Fig. 7). We rejected the idea of fluid inclusion organic wetting to explain low CO_2/CH_4 fluid inclusion analyses. If this was true, there should be a relationship between mineral type and CO_2/CH_4 because of the different mineral affinities for wetting hydrocarbon compounds. This we do not see.

Linear Shultz-Flory plots of fluid inclusion organics suggest that some inclusions have abiogenic methane produced by the Fischer-Tropsch like reactions. Linear organic specie distributions in high temperature Coso inclusions, and deep Tiwi inclusions agree with formation of abiogenic methane at temperatures of 300 C. It is not clear if abiogenic is methane produced by reactions under 300 C by the mechanism proposed by Giggenbach (1997), or if this reactions yields heavy hydrocarbons. As a working hypothesis we assume that abiogenic methane is produced by fluids fluxing

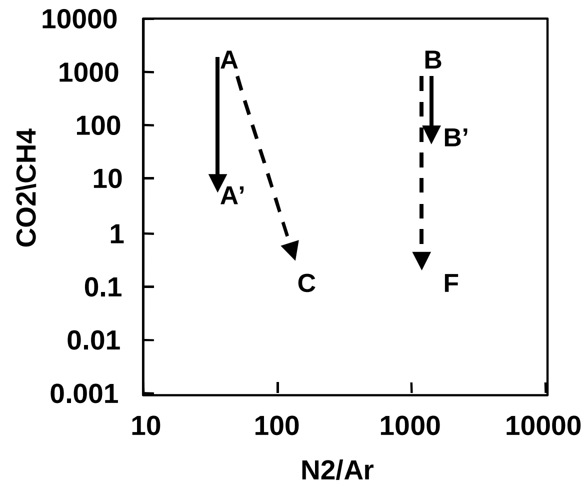

Fig. 12 A diagram to illustrate evolutionary paths of magmatic and meteoric fluids. Both types of fluid initially have very low CH_4 concentrations. Meteoric water starts out at A and evolves towards A' by equilibrium reactions proposed by Giggenbach (1997). Meteoric fluids in contact with organic rich sediments will evolve towards C gaining CH_4 and some N_2 (Norman et al., 1997). Magmatic fluids at B will increase methane content by equilibrium reactions with wall rock and evolve to B'. None equilibrium Fischer-Tropsch reactions may produce much more methane, and magmatic fluid gas rations will move towards F. See the paper by Blamey and Norman elsewhere in the volume for an example of how we label fields on CO_2/CH_4-N_2/Ar diagrams.

in near proximity to an intrusion and thus has accumulated a magmatic volatile component. If this was the case, then we would expect fluid compositions to evolve as diagramed on Fig. 12. Possible mixing relationships referring to Fig. 12 are between fluid A' and B', A' and F, C and B' and C and F'. Coso fluid inclusion analyses (Fig. 7) show A'-F mixing. An example of C-B' mixing is Broadlands BR22 fluid inclusion analyses (Fig. 13, Norman and Moore, 1999). Gas analyses plotted on a CO_2/CH_4 vs. N_2/Ar diagram show an overall negative slope for A'-F mixing and a positive slope for Broadlands-like mixing. The Geysers analyses plot like Broadlands, and Tiwi analyses plot like Coso.

Future work will be on firmly establishing the occurrence of geothermal abiogenic organic compounds using Shultz-Flory plots. We have yet to investigate the effects of boiling and condensation on organic species distributions. Fischer-Tropsch reactions may only occur when there are intrusive rocks high in reduced iron. Broadlands and The Geysers intrusives are granites, and granite is a low iron rock.

The Mothra analyses, and systematic differences in CO_2/CH_4 ratios between different geothermal system fluid inclusions strong argue that our analyses are valid. The higher amounts of methane we measure see in fluid inclusions has several explanations. Generation of by wall rock reactions, and leaching biogenic methane from sediments will decease with time. Hence, higher methane concentrations in fluid inclusions that in geothermal waters may indicate an old geothermal system. Also, the concentrating method discussed above for nitrogen also concentrates methane. We hypothesize that deep circulating fluids subject to Fisher-Tropsch relations will show an inverse relationship between N_2/Ar and CO_2/CH_4 ratios, whereas geothermal fluids that have an organic source of methane will show a positive correlation between N_2/Ar and CO_2/CH_4 ratios. The Geysers and Broadlands fluid inclusions and Cerro Prieto fluids show a positive relationship between N_2/Ar and CO_2/CH_4 ratios, whereas Tiwi and Coso fluid inclusions exhibit a negative correlation. Coso fluid-inclusion organic-compounds, like Tiwi fluids, show a Fisher-Tropsch relationship whereas most of The Geyser inclusion fluids do not.

CONCLUSIONS

1. Fluid inclusion analyses of methane, N_2 and Ar represent parent fluid chemistry.
2. Cerro Prieto shows cyclic behavior during which at times N_2, Ar, H_2 and CH_4 are increased by a factor of 2.
3. Fluid inclusions are primarily formed during times excess gas is expelled from geothermal systems. Hence, fluid inclusion analysis gives only half the geothermal story.
4. Abiogenic methane occurs in some inclusion fluids.
5. The relatively higher amounts of methane that we commonly measure in fluid inclusions are the result can be biogenic or abiogenic. In either case methane best formed early in the life of a geothermal system.

ACKNOWLEDGEMENTS

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