

## METHANE AND EXCESS N<sub>2</sub> AND Ar IN GEOTHERMAL FLUID INCLUSIONS

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### ABSTRACT

Examination of thousands of fluid inclusion gas analyses has led us to question some working hypotheses associated with interpretations of N<sub>2</sub>/Ar ratios in geothermal volatiles. Fluid inclusion gas analyses, some confirmed by analyses of present fluids, indicate that geothermal fluids have N<sub>2</sub> and Ar concentrations about 10 times greater than in air saturated water. Also, high N<sub>2</sub>/Ar ratios are associated with lower concentrations of Ar, rather than increased N<sub>2</sub> in all geothermal systems we have studied. These observations contradict commonly held ideas about how geothermal systems operate and there are no apparent explanations. We introduce a CO<sub>2</sub>/CH<sub>4</sub> vs. N<sub>2</sub>/Ar diagram. It illustrates fluid sources and processes better than a ternary diagram, and defines fluid compositions that have organic nitrogen.

### INTRODUCTION

Giggenbach (1986) introduced the idea that N<sub>2</sub>-Ar-He ratios of geothermal gases may identify the source of volatiles in geothermal fluids. He attributed geothermal N<sub>2</sub>-Ar ratios greater than air to additions of magmatic gases because volcanic gases have N<sub>2</sub>/Ar > air. He attributed elevated geothermal helium concentrations to the accumulation of crustal radiogenic helium. Norman and Musgrave (1993) apply Giggenbach's ideas to fluid inclusion gas analyses, and recognize the ambiguity in the interpretation of geothermal helium concentrations. At a the 21<sup>st</sup> Stanford Meeting (Norman et al., 1996) we introduced the use of a N<sub>2</sub>ArCH<sub>4</sub> ternary diagram to interpret the source of geothermal volatiles. Hydrologists use helium accumulation ages to date ground waters, but in geothermal systems magmas can supply helium in great abundance. The only way to differentiate the two sources of helium is by isotopic analysis, which is a laborious process. Methane is a better species with which to identify the crustal component in geothermal fluids. For all practical purposes, methane is not among the gaseous species in volcanic vapors nor does it occur in meteoric water, but methane is common in sedimentary formation fluids. We have subsequently

plotted fluid inclusion analyses on N<sub>2</sub>ArCH<sub>4</sub> diagrams to interpret fluid sources (e.g., Moore et al., 1997, and Moore et al. 1999).

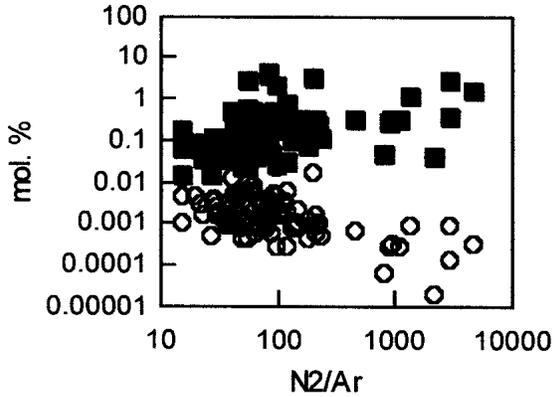
This paper explores some hypotheses behind the application of N<sub>2</sub>-Ar-CH<sub>4</sub> ratios as a tracer. Data we have accumulated in the past few years raises questions about the rationale underlying our use of N<sub>2</sub>-Ar-CH<sub>4</sub> diagrams. Here we look in detail at controls on N<sub>2</sub>/Ar ratios, the amounts of nitrogen and argon in fluids, the sources of methane in geothermal fluids, and how to interpret organic nitrogen.

### GAS ANALYSES

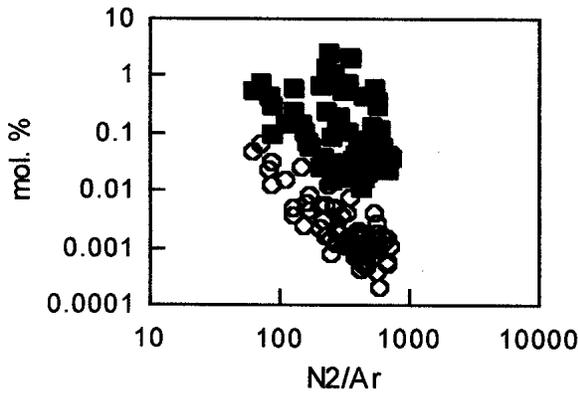
All fluid-inclusion gas-analyses reported here were done by the CFS (crush-fast-scan) method described in Norman et al. (1996). A swift crush in a vacuum chamber housing a quadrupole mass spectrometer opens a few inclusions. The vacuum pumping system removes the volatiles released in one or two seconds. Meanwhile, the mass spectrometer operating in the peak hopping mode, scan rates are about 200 milliseconds, records the pulse of volatiles. We make ten to twenty sequential crushes on about a 200 mg sample with the expectation that some crushes will be failures by opening too many or too few inclusions for analysis. The precision of gas/water ratios is 10 to 20%; ratios of gaseous species are duplicated with a variation less than 5%.

### THE N<sub>2</sub>/Ar RATIO

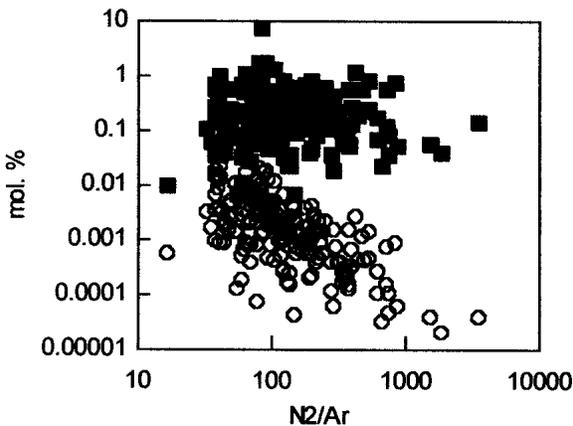
We thought, following Giggenbach (1986), that geothermal-fluid N<sub>2</sub>/Ar ratios > ASW (air saturated water) are the result of adding a nitrogen-rich magmatic component to circulating meteoric waters. Stable isotopic studies show the amount of magmatic water in most active geothermal systems is less than 10%. So we reasoned, the magmatic component is added as a gaseous-specie-rich vapor. If this is true, hybrid fluids should have elevated concentrations of nitrogen whereas argon concentrations should be similar to those in ASW. However, we see no evidence for this supposition in our data.



*Fig. 1 Concentrations of Tiwi, Mat 25 fluid inclusion N<sub>2</sub> and Ar plotted against the N<sub>2</sub>/Ar ratio, filled symbols are N<sub>2</sub>, open symbols are Ar.*



*Fig. 2 Concentrations of Broadlands BR12 fluid inclusion N<sub>2</sub> and Ar plotted against the N<sub>2</sub>/Ar ratio, filled symbols are N<sub>2</sub>, open symbols are Ar.*



*Fig. 3 Concentrations of Lepanto, Philippines fluid inclusion N<sub>2</sub> and Ar plotted against the N<sub>2</sub>/Ar ratio, filled symbols are N<sub>2</sub>, open symbols are Ar.*

Plots of nitrogen and argon against N<sub>2</sub>/Ar show that they relate N<sub>2</sub>/Ar ratios to concentrations of argon, not nitrogen. Figures 1 to 5 show examples of fluid inclusion analyses of present and past geothermal systems. The pattern in the data is the same for low salinity geothermal systems like Broadlands and Tiwi, low salinity past geothermal systems like Lepanto, and high salinity geothermal past systems like the Tyrone Copper porphyry deposit. The Geysers fluid inclusion analyses exhibit the same pattern as do the few analyses of early The Geysers' steam. If low N<sub>2</sub>/Ar ratios represent meteoric water and dissolved volatiles, the only way to explain the data is by mixing that fluid with some liquid containing dissolved gases that have a high N<sub>2</sub>/Ar ratio. Also, the gas/water ratio has to be about the same in the two liquids. The water component of the high N<sub>2</sub>/Ar ratio fluid cannot be magmatic. Stable isotopic studies do not support this idea. For example the present Broadlands geothermal gases have high N<sub>2</sub>/Ar ratios (Giggenbach, 1986) but the waters are primarily meteoric. An explanation for the Fig.1 to 5 data also has to be compatible the dilemma posed in the following section.

#### CONCENTRATIONS OF N<sub>2</sub> AND Ar

If our working hypothesis is correct, we should measure nitrogen and argon concentrations at the concentrations in ASW in some inclusions. There is an extensive literature on concentrations of nitrogen and rare gas species in ground waters reviewed in Norman and Musgrave (1993). Air species concentrations in surface water are in equilibrium with the atmosphere at the recharge water temperature. Because nitrogen and rare gas species are non reactive, they persist for long times in groundwater. The solubility of gaseous species in water varies by a factor of about two between zero and 30 C. Thus, analysis of gaseous species concentrations allows estimates of groundwater recharge temperature, and by inference to past climates, to estimates of age.

We cannot find one analysis that suggests nitrogen and argon concentrations similar to ASW in examining more than 5,000 analyses made in the past few years. Some examples are on Fig. 6 to 9. These figures that show near ASW N<sub>2</sub>/Ar ratios, which therefore plot along the line of N<sub>2</sub>/Ar = 50, have nitrogen and argon concentrations an order of magnitude or greater than that of ASW. Many samples we measure have assemblages of vapor-rich and liquid-rich inclusions. Therefore, we can explain analyses that show concentrations of nitrogen and argon a thousand times that in ASW as dominated by gaseous species released from vapor-filled inclusions. Gas partitioning calculations easily demonstrate that such concentrations are possible in a vapor separated

from ASW. We have selectively graphed analyses of quartz that have no observable vapor-filled inclusions (Fig. 6) and they show concentrations of nitrogen and argon 10 to 100 greater than ASW values.

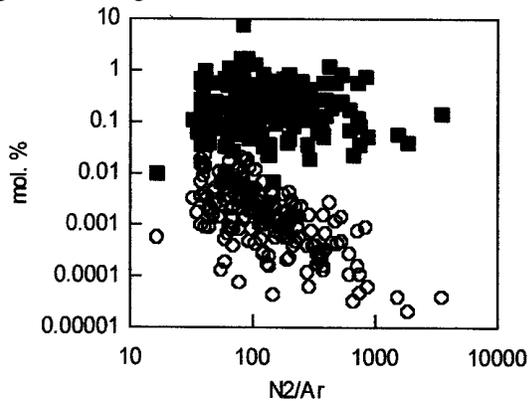


Fig. 4 Concentrations of N<sub>2</sub> and Ar in Tyrone Copper porphyry deposit, New Mexico, fluid inclusions plotted against the N<sub>2</sub>/Ar ratio. Filled symbols are N<sub>2</sub>, open symbols are Ar.

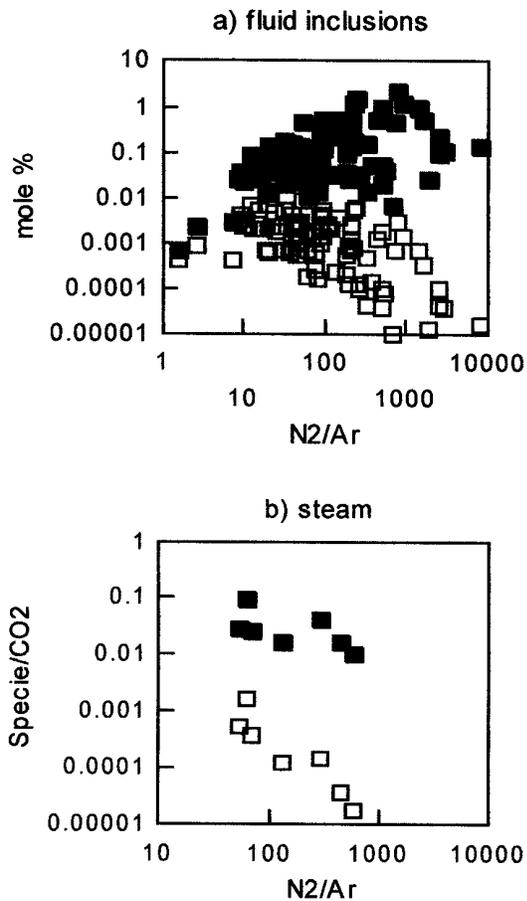


Fig. 5 Concentrations of N<sub>2</sub> and Ar in The Geysers a) fluid inclusions, b) steam plotted against the N<sub>2</sub>/Ar ratio. Filled symbols are N<sub>2</sub>/CO<sub>2</sub>, open symbols are Ar.

Like N<sub>2</sub>/Ar ratios discussed above, excess argon and nitrogen seem universal to all the geothermal systems, present and past, that we study.

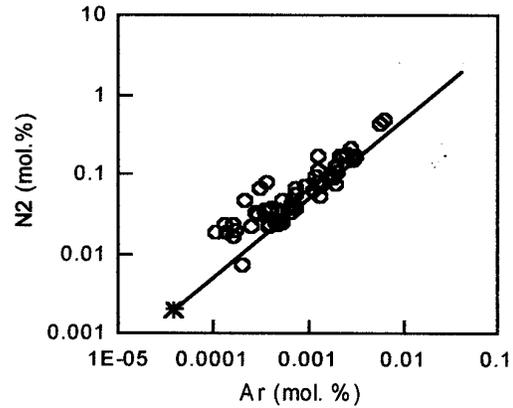


Fig. 6 Concentrations of N<sub>2</sub> and Ar in fluid inclusions form an unnamed epithermal Ag-Au deposit in Turkey. The line is drawn at a N<sub>2</sub>/Ar = 50, about that of ASW, fluid inclusion analyses are open circles, the star is the value for ASW, analyses of geothermal waters, if included, are a filled box.

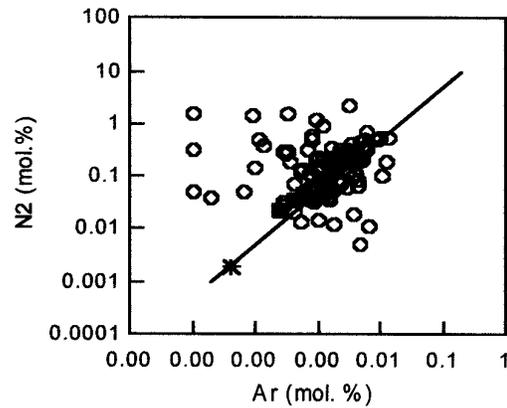


Fig. 7 Concentrations of N<sub>2</sub> and Ar in Tiwi, Mat 25 fluid inclusions. See fig. 6 for the explanation.

The analytical system and data reduction program was checked meticulously, and we found no problems. Air contamination cannot explain excess amounts of nitrogen and argon because we always monitor analyses for air (at mass peak 32) and reject those few analyses that include appreciable air. Musgrave (1992) mentions the high amounts of nitrogen and argon in fluid inclusions from Sulphur Springs, Valles Caldera, New Mexico. Musgrave also points out that analyses of Baca (Valles Caldera) geothermal waters exhibit about 10 times more nitrogen and argon than ASW. In Fig. 7 we compare three analyses of Tiwi, MAT 25 well fluids to our fluid inclusion gas analyses of minerals from the same bore hole. The concentration of nitrogen and argon in present MAT 25 fluids is more than 10 times the concentration of nitrogen and argon in ASW, and the compositions overlap with some of our fluid

inclusion analyses. The Tiwi and Baca analyses validate our analyses and suggest that excess nitrogen and argon is an overlooked property of geothermal waters. Excess nitrogen and argon in Tiwi fluids are also remarkable because some recharge waters at Tiwi include sea water that has less dissolved gaseous species than fresh water because of the salting out effect.

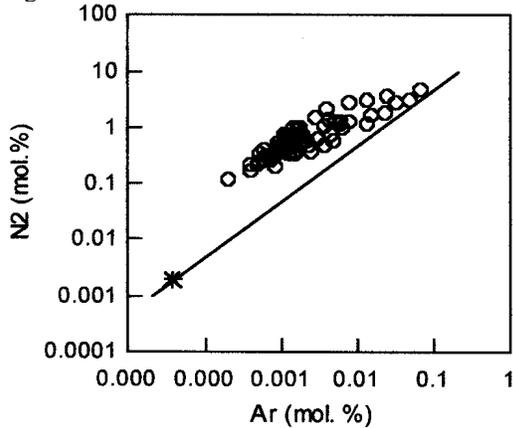


Fig. 8 Concentrations of  $N_2$  and Ar in Broadlands Br12 fluid inclusions. See fig. 6 for the explanation.

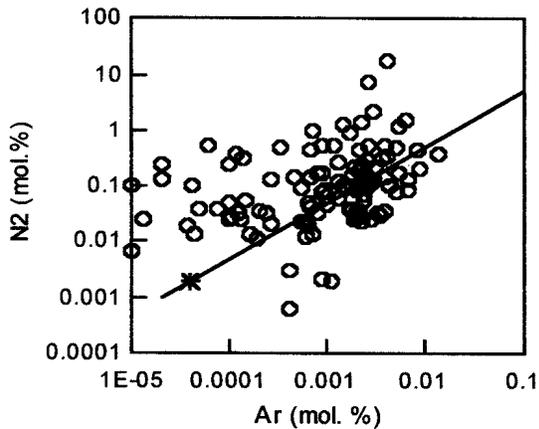


Fig. 9 Concentrations of  $N_2$  and Ar in The Geysers fluid inclusions. See fig. 6 for the explanation.

The lowest amounts of fluid inclusions nitrogen and argon measured in our facility are in late calcite and barite from the Pipeline deposit in Nevada (Fig. 10). Many of these analyses yield a consistent  $N_2/Ar$  ratio of about 42, which is a ratio typical value for ground water, yet these analyses have three to ten times more nitrogen and argon than ASW. Some fluid inclusion gas analyses of Pipeline and other geothermal minerals record argon at or below ASW concentrations. Nevertheless, these inclusions invariably have  $N_2/Ar$  ratios  $>$  ASW and nitrogen levels greater than in ASW.

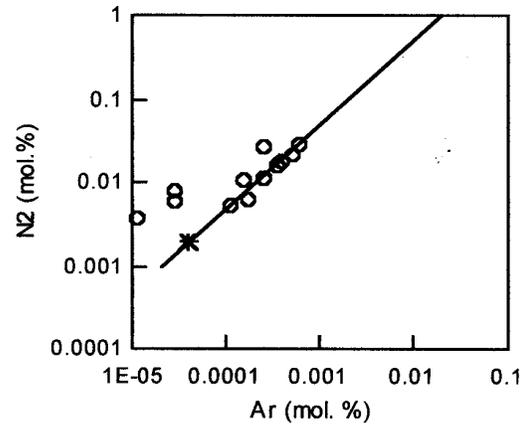


Fig. 10 Concentrations of  $N_2$  and Ar in the Pipeline gold deposit, NV, late calcite and barite.

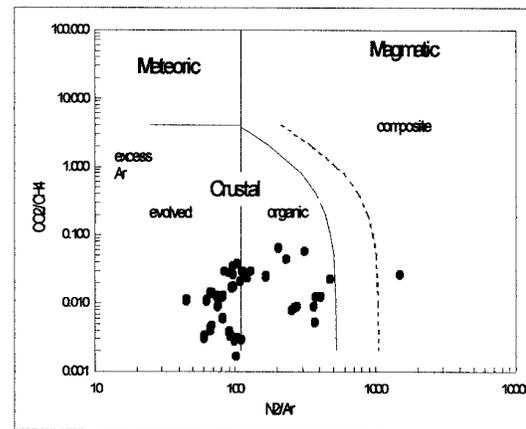


Fig. 11 Analyses of Franciscan Formation fluid inclusions, see text for details.

It is apparent to us that the working hypothesis we have used in the interpretation of  $N_2/Ar$  ratios is flawed, not in the source of the species, but the pathways of gaseous species into geothermal systems. A simple explanation is that geothermal fluids “dry out” by loss of water to hydrous minerals. This would require water rock ratios (w/r) of 0.1 or lower because chlorite, which has the greatest amount of bound water among common alteration minerals, contains about 10 wt.% water. Although w/r of 0.1 and less have been documented for a few ore depositing geothermal systems, overall stable isotopic studies suggest higher ratios for geothermal systems (Taylor, 1997). Barring “drying out” the data indicate that circulating meteoric waters in geothermal systems are charged with nitrogen and argon derived from meteoric waters. There are additions of magmatic volatiles and organic nitrogen to geothermal fluids, but in geothermal systems like Tiwi,  $N_2/Ar$  ratios indicate a predominately meteoric

source of nitrogen and argon (Moore et al., 1997; Norman et al., 1997).

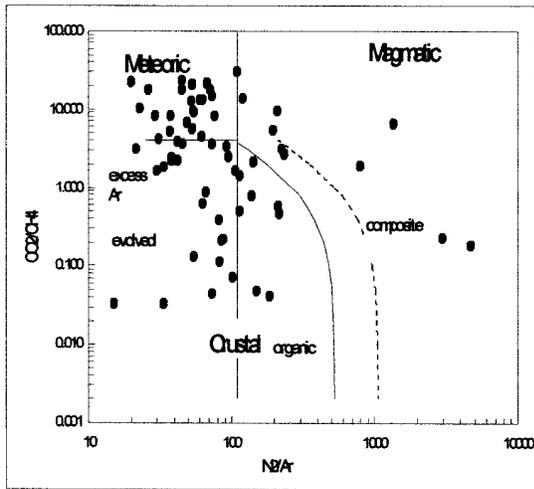


Fig. 12 Analyses of Tiwi, Mat 25 fluid inclusions.

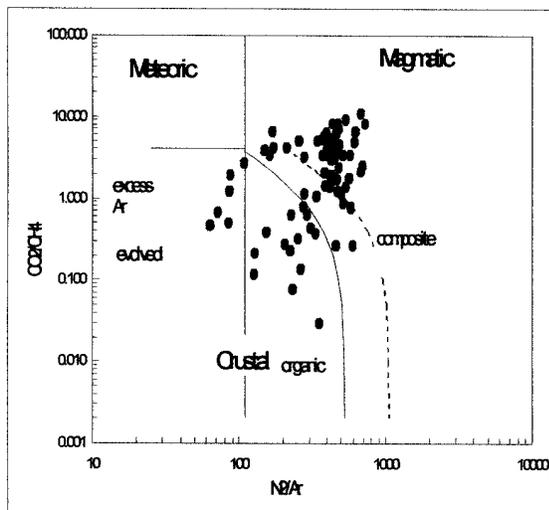


Fig. 13 Analyses of Broadlands BR12 fluid inclusions.

Boiling and condensation processes can explain excess concentrations of nitrogen and argon and why argon appears to control the  $N_2/Ar$  ratio. A separated vapor phase may dissolve in gaseous-specie-poor, possibly cooler liquid, consequently increasing the amount of dissolved gas. The data in Fig. 1 look like there is an upward limit on nitrogen of about 1%. Gaseous species that dissolved in an aqueous liquid is limited to amounts where the partial pressures of the gaseous species and water equals the reservoir pressure. Liquids can only hold up to 1% nitrogen in shallow geothermal systems at pressures of 500 bars or less. At 300 C the vapor pressure of 1% nitrogen in water is about 190 bars, the vapor pressure of water is 86 bars and there has to be allowance for

other gaseous species. Ratios of nitrogen and argon are retained in a boiling-condensation process because the solubility constants of the two species are similar. Modeling a boiling-condensation process shows that increasing nitrogen and argon concentrations about a factor of ten is possible. Consequently, a gas-stripped residual liquid about 10 times the volume of the gas-rich fluid is produced. We have no record of such a fluid in our fluid inclusion analyses, nor can we find one mentioned in the literature.

### METHANE

We introduced the use of methane as a tracer species because gas ratios plotted on ternary  $N_2$ -Ar- $CH_4$  diagrams resembled ratios plotted on  $N_2$ -Ar-He diagrams. For arguments given above, methane is a logical species to use for indicating the crustal component in thermal fluids. Also, analyzing methane is easier than helium because methane generally occurs in higher concentrations, and there is no ambiguity about the origin of the species as there is with helium. One of our concerns is that organic material, which produces methane, also contains nitrogen. Natural gases commonly have significant concentrations of nitrogen. Add mixed organic nitrogen will increase the  $N_2/Ar$  ratio thus falsely suggesting magmatic ratios. We propose use of a  $CO_2/CH_4$  vs.  $N_2/Ar$  diagram that can differentiate fluids bearing significant organic nitrogen (Fig. 11). On the diagram the meteoric water field refers to near surface recharging waters that have high  $CO_2/CH_4$  ratios, and  $N_2/Ar$  ratios between 25 and 110 (Norman et al. (1997). Crustal fluids, by our definition, are meteoric fluids that approach equilibration with crustal rocks and may have additions of gaseous species derived from wall rocks such as the organic species, helium, nitrogen, and hydrogen sulfide. Meteoric waters evolve by equilibration which results in reduction of  $CO_2$  to  $CH_4$  (Giggenbach, 1997). The equilibrium  $CO_2/CH_4$  ratio varies with temperature and rock type. We arbitrarily draw a line at  $CO_2/CH_4 = 4$  that represents equilibration with crystalline rock at 200 C. Fluids in contact with sedimentary organic material may have lower  $CO_2/CH_4$  ratios than fluids of same temperature in equilibrium with crystalline rock. We estimate the amount of organic nitrogen that a geothermal fluid might acquire from sediments by considering that organic material in rocks is principally from plants. We used the average molar ratio of nitrogen to carbon in humic acids of 0.05/1 (Sposito, 1989) to estimate the amount of organic nitrogen that rocks might produce with methane. The area on Figure 10 labeled "organic" is where calculation shows there may be sufficient organic nitrogen to increase  $N_2/Ar$  appreciably above ASW. The calculated "organic" field depends on the choice of total carbon dioxide and methane in a fluid; we

choose 1 and 2 mole %. The diagram also illustrates relative oxidation states of fluids. Calculation can relate carbon dioxidemethane ratios to oxygen and hydrogen fugacity.

Figures 11 to 13 illustrate the utility of the  $\text{CO}_2/\text{CH}_4$  vs.  $\text{N}_2/\text{Ar}$  diagrams. Figure 11 shows fluid inclusion analyses of calcite and quartz stringers in the Franciscan Formation collected near, but outside, The Geysers geothermal field. We expected inclusion fluids in equilibrium with the organic-rich Franciscan rocks at low grade metamorphic temperatures. The analyses all plot in our crustal field and some analyses exhibit  $\text{N}_2/\text{Ar} > \text{ASW}$  that we interpret to result from additions of organic nitrogen. Figure 12 shows Tiwi volatiles to be the result of meteoric fluids that are interacting with organic compound-bearing rocks, or are admixtures of meteoric waters and waters with a crustal component. In contrast, Broadlands 12 analyses indicate an admixture of magmatic and crustal volatiles (Fig. 13).

### **CONCLUSIONS**

1. We poorly understand the causes for nitrogen and argon concentrations in geothermal fluids.
2. Fluid inclusion gas data plotted on the  $\text{CO}_2/\text{CH}_4$  vs.  $\text{N}_2/\text{Ar}$  diagram we introduce presents a clearer picture of volatile sources and geothermal processes than data plotted on a  $\text{CO}_2\text{N}_2\text{Ar}$  ternary diagram. The plot also shows the relative oxidation state of inclusion fluids.

### **ACKNOWLEDGMENTS**

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