

More on the Use of Fluid Inclusion Gaseous Species as Tracers in Geothermal Systems

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ABSTRACT

This paper continues previous efforts to develop the science of fluid inclusion gas analysis. The principal objective is to generate and refine interpretations of fluid source and hydrothermal process from analyses of fluid inclusions volatiles.

A good knowledge of magmatic gas compositions is necessary in order to identify magmatic volatiles in fluid inclusions. Ratios of N_2 , Ar, and CO_2 in magma were measured in magmatic glass inclusions. Heating inclusions to glass melting temperatures yields reproducible measurements that cluster tightly on ratio diagrams. Analyses by cold crushing were not reproducible.

Measured ratios of N_2 to Ar in some inclusions approximate that of air and show a larger range of ratios from analysis to analysis than is possible to obtain from meteoric water. Contamination by air was suspected. However, modeling shows that these ratios are to be expected in vapor and liquid evolved from boiling meteoric waters. Tiwi inclusions serve as an example. They are mixtures of vapor-dominated and liquid-dominated inclusions trapped during fluid boiling. The NJAr ratios for most inclusions range from 30 to 105, which are the ratios expected in vapor and residual liquid when meteoric water is boiled. Overall most Tiwi fluid inclusion gas compositions are consistent with a boiling meteoric fluid that has reacted with country rock accumulating organic compounds.

Explanations for enigmatic, fluid-inclusion N_2 /Ar ratios far less than those in air saturated water (ASW) are investigated. Partitioning of N_2 into the vapor phase during boiling can not explain the N_2 /Ar ratios nearing one that are commonly measured in geothermal fluid inclusions. Tiwi inclusions that have N_2 /Ar ratios < ASW have lower N_2 concentrations than inclusions with NJAr ratios near that of ASW.

These fluids occur primarily in the highly altered roof zone of the geothermal system. The best explanation is reduction of N_2 to form NH_3 , driven by decreasing fluid temperature or incorporation of NH_3 into phyllosilicate minerals.

Kazakhstan mineral deposit inclusions that have low N_2 /Ar ratios have the same N_2 concentrations as inclusions with normal ratios. Anomously low NJAr ratios are the consequence of high concentrations of Ar. An explanation is accumulation of radiogenic Ar from wall rocks. Analysis of Ar isotopes in one sample of Sulfur Springs quartz that has NJAr ratios < ASW yielded indicates a $^{40}Ar/^{39}Ar$ ratio above air. This suggests that fluid inclusions may contain radiogenic Ar accumulated from wall rocks in sufficient concentrations to change the N_2 -Ar ratio. Calculation indicates that the low NJAr ratios measured in Kazakhstan inclusions are possible by accumulation of radiogenic Ar only if the water to rock ratio is on the order of 0.01 to 0.001 and the K-rich rocks are in excess of several million years old. This implies that low NJAr ratio fluids can only be generated once in the lifetime of a geothermal system, and most probably are formed early in the history of a geothermal system.

INTRODUCTION

The use of fluid inclusion gas chemistry to understand the geothermal processes and determine the source of fluids has been demonstrated (Norman et al. 1993, 1996). But this is a recent field of investigation, and our ability to interpret fluid inclusion gas chemistry is far from perfect. This paper further explores the application of fluid inclusion gas analyses to understanding geothermal systems.

In general, an analysis of fluid inclusion gases can be interpreted in the same manner as an analysis of reservoir fluid. But, there are some significant differences. Fluid inclusion analyses do not have the precision of well gas analyses and bulk fluid inclusions analyses will yield an average analysis over some unknown length of time. Analysis of inclusions by the crush-fast-scan (CFS) method opens one or a few inclusions, however the spatial and time relations among the inclusions is not known. Using the CFS method to analyze vapor-dominant and liquid-dominant inclusions trapped together under boiling conditions yields analyses of trapped vapor and liquid at an unknown "y" (steam fraction) value. Most

likely, each inclusion was trapped at a different time. Therefore, the gas chemistry of single vapor-dominant and liquid-dominant inclusions may not represent equilibrium between vapor and liquid. On the other hand, fluid inclusions can uniquely provide samples of geothermal fluids trapped over an extended period of time at vertically and horizontally distributed sites. Inclusions analysis together with thermometric analysis potentially can provide a four dimensions picture of a geothermal system. Hence the impetus to fully understand the analyses of fluid inclusion volatiles.

METHODS

Inclusion volatiles are measured by thermal decrepitation followed by cryogenic separation (TDCS), and by the cold-crushing-fast-scan (CFS) method. Both methods use a quadrupole mass spectrometer to measure the liberated inclusion volatiles (Fig. 1). Procedures for bulk measurements done by thermally decrepitating fluid inclusions are given in Norman and Sawkins (1987). Volatiles are cryogenically separated into liquid-N₂-noncondensable, liquid-N₂-condensable, and aqueous fractions. A liquid N₂-cooled charcoal trap may be used to separate active noncondensable gaseous species from rare gas species. The quantity of each gas fraction is determined by pressure measurement in a known volume and the gas ratios are measured by a quadrupole mass spectrometer. Analytical precision is 5% or better for most species. Sample size is typically 2 g, but quantities as small as 50 mg are analyzed. A bakeout period of one day is commonly used while heating to 125 to 200 C. Fluid inclusions are decrepitated at temperatures of 400 to 500 C; magmatic glass inclusions are heated to 1100 to 1200 C.

The CFS method involves opening inclusions by a swift crush in the vacuum chamber housing the mass spectrometer. Volatiles released are quickly removed by the vacuum pumping system in one or two seconds. Meanwhile, the pulse of inclusion volatiles is recorded by operating the quadrupole in a fast scan mode with measurements every 100 to 200 milliseconds. The CPS method measures far fewer inclusions than is measured by the TDCS method. Opening a 10 to 20 micron inclusion, or group of smaller inclusions of equivalent volume, provides the ideal amount of volatiles for a CPS analysis. Opening a 40 micron inclusion swamps the vacuum system and the system crashes. Five to twenty crushes are made on about a 200 mg sample with the expectation that some crushes will be failures by opening too many

inclusions. The CFS method is fast and simple, but the precision is 10 to 20%, and some species are difficult to detect because of interferences.

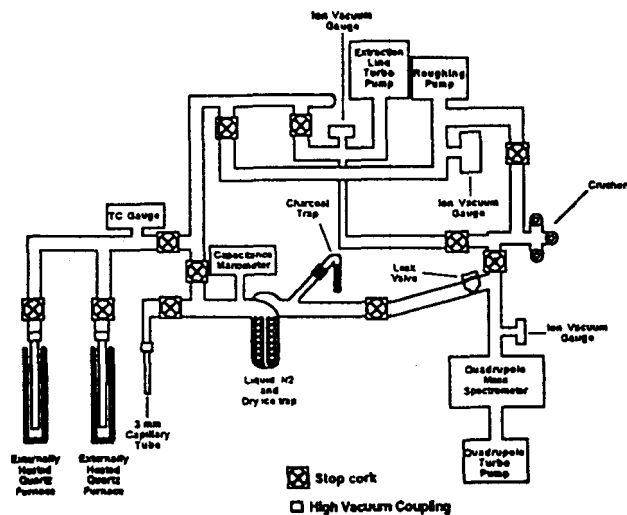


Fig. 1. The gas analysis system at New Mexico Tech. High vacuum is supplied by two turbo pumps. Volatile species are measured with MKSQ capacitance manometer and a Balzers® QMS 420 quadrupole mass spectrometer controlled with Quadstar® software.

Ammonia is rarely detected in CFS analyses because of the interference of secondary water peaks at $m/e = 17$ and 16 ; He at concentrations below 30 ppm is interfered with by the tail on the H₂ peak; and CO peaks fall on those of CO₂, N₂, CH₄, and C₂, organic species. Small amounts of admixed air is commonly detected during CFS measurements, which is estimated from the amount of O₂ measured. The concentrations of inclusion N₂, Ar and CO, can be corrected for air contamination assuming all O₂ measured represents admixed air. The source of air contamination is mostly likely air trapped on grain boundaries and micro-cracks. Air contamination can be eliminated by prolonged baking. However, in the interest of expediency, and to minimize H₂ and He diffusion from inclusions, prolong baking of samples is not done.

MAGMATIC VOLATILES

It is of great interest to be able to identify magmatic volatiles in fluid inclusion liquids. There is a considerable body of evidence that magmatic volatiles, save from basalts, have N₂/Ar > air (see references cited in Norman et al. 1993 and 1996). Further, Groff (1996) has shown a positive correlation between fluid inclusion N₂/Ar and magmatic hydrogen

isotopic values in inclusions from two mineral deposits. We use diagrams like Fig. 2a to interpret fluid inclusion gas chemistry with the tacit understanding that the magmatic field represents volatiles from andesitic magmas. This diagram does not agree well with actual analyses of volcanic gases (Fig. 2b). Analyses in the He corner of Fig. 2b are from basaltic volcanoes. It is not clear if these compositions should be ignored because basaltic magmas are petrogenetically related to some felsic melts. Admittedly some of the analyses suggest contamination of volcanic gases and magma by air and ground water, but the degree of contamination is hard to quantify. In reality, our data base for assuming that magmatic volatiles can be identified by their N_2/Ar ratio is far from perfect. Hence, an effort was made to measure magmatic N_2 -Ar-He directly by analysis of magmatic glass inclusions. Ideally, analyses of glass melts should provide better estimates of magmatic N_2 -Ar-He ratios than volcanic gas analysis because

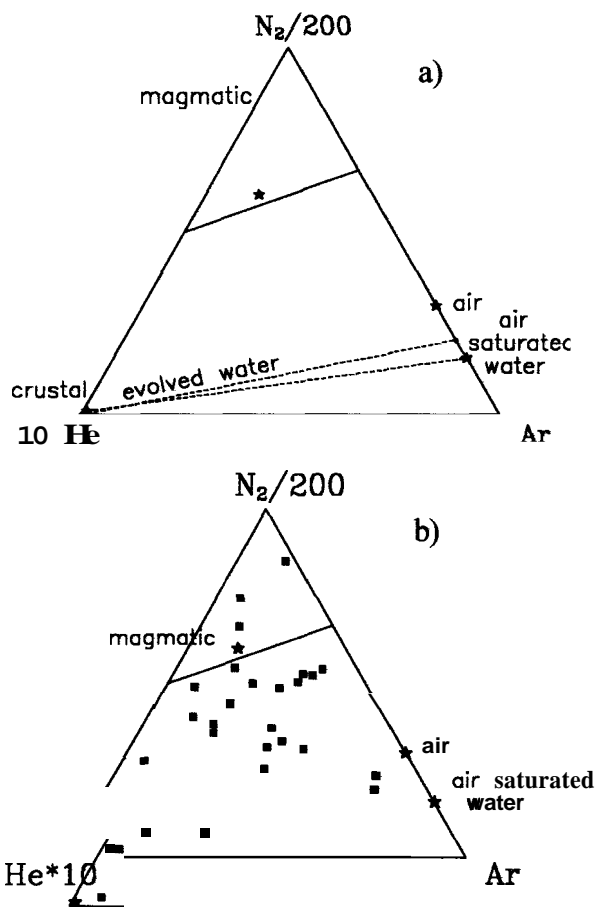


Fig. 2 a) Diagram for interpreting source of fluid inclusions volatiles from Norman et al. 1993 and 1996. b) Analyses of volcanic gases (Reyes and Giggenbach, 1992)

the melt is trapped in at depths beneath near surface sources of contamination.

Glass in feldspar megacrysts from the Mt. Erebus volcano in Antarctica and glass in Taupo volcanic quartz phenocrysts was analyzed (Fig. 3). Analyses of eight different megacryst samples by the TDCS method yielded identical ratios within analytical uncertainty (Fig. 3a). They show that the alkaline Erebus magma has N_2/Ar ratios \gg air. The feldspars and glass were heated to fusion in vacuum, hence the analysis should be representative of the gaseous species trapped in the melt. There could, however, be some He loss by diffusion from Erebus glass during the day-long bakeout at 200 C under vacuum preceding the analysis. Unfortunately, there are no analyses of Erebus volcanic gasses with which to compare the measurements. The good agreement between multiple analyses argues that they represent magmatic gas. Loss of volatiles by leakage, or contamination introduced along fractures, is expected to increase the variance of multiple analyses.

One sample each of Erebus and Taupo glass were analyzed by the CFS method (Figs. 3b and 3c). It was hypothesized that a majority of the gaseous species would partition into the bubbles seen in the glass. Hence, it was thought, a meaningful analysis could be obtained by crushing. The results are disappointing, and difficult to interpret. There appears to be air contamination of the volatiles liberated during crushing even though virtually no O_2 was measured. Rapid cooling during eruption may have opened micro cracks on phenocryst surfaces. The O_2 could have been lost by oxidation and some He may have diffused into the fractures from magma inclusions. It is clear that baking prior to TDCS analysis eliminates the air-like volatiles released by crushing. Analyses of Taupo and other glass inclusions are planned to be done by the TDCS method. This type of analysis appears to hold great promise for yielding reliable ratios of magmatic N_2 , Ar, and He.

BOILING AND N_2/Ar RATIOS

The N_2/Ar of ground water varies from about the 38 of air saturated water (ASW) to about 52 (Fig.2a). Analyses of fluid inclusions from some present geothermal systems, for example, that Valles, NM geothermal system (see Norman et al, 1993) plot mostly in the idealized evolved water field on Fig. 2a. St. Cloud, NM Ag-Cu deposit fluid inclusion analyses plot in a similar fashion (Fig. 4b).

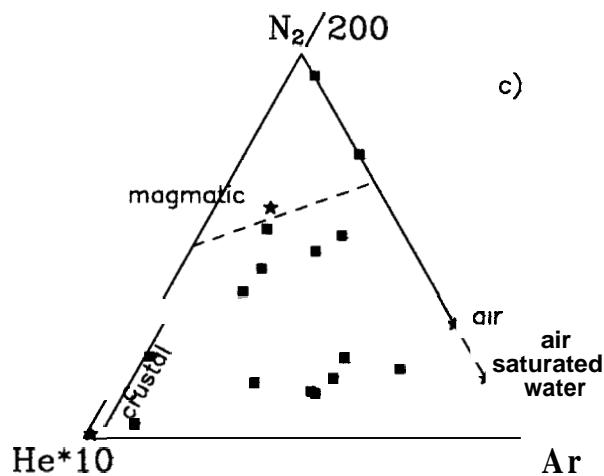
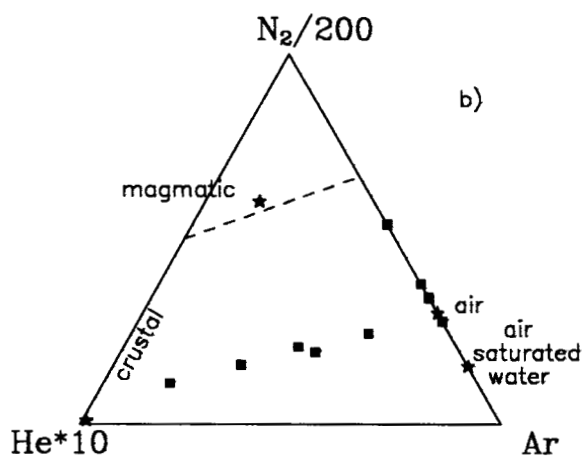
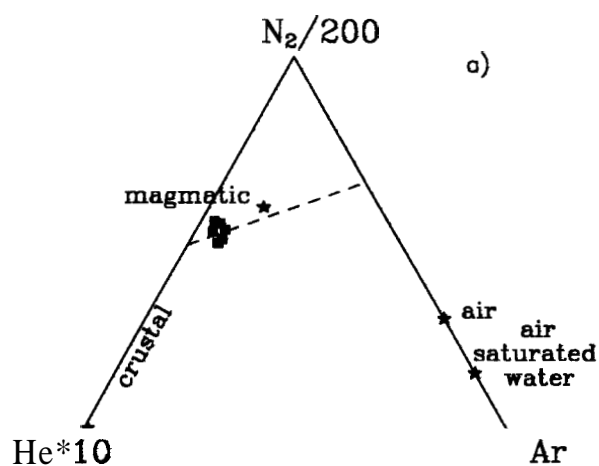


Fig. 3 Analyses of magmatic glass inclusions: a) analysis of 8 samples of MT Erebus inclusions in feldspar megacrysts by the TDCS method; b) analysis of one Erebus samples by the CFS method; c) analysis of one sample of Taupo magmatic glass in quartz phenocrysts.

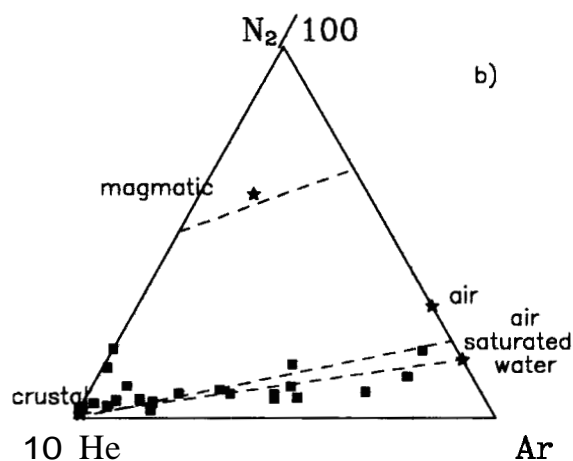
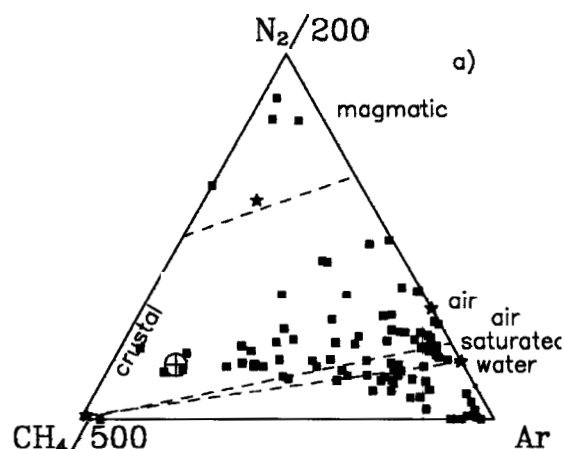


Fig. 4 Analyses of aqueous fluid inclusions in quartz and calcite from a) Mat 25 well, Tiwi geothermal system and b) the St. Cloud-US Treasury mine, NM (Norman et al., 1991)

But analyses like this are in the minority. Tiwi inclusions exhibit, for example (Fig 4a), a wide range in N_2/Ar ratios, and few analyses fall into the field for evolved water in Fig. 2. Many Tiwi ratios are near that of air suggesting possible air contamination far larger than that indicated by admixed O_2 in the analysis. One difference between St. Cloud and Tiwi inclusions is that the former all are the two phase, liquid-dominant type, whereas Tiwi inclusions comprise both liquid- and vapor-dominant varieties. The gas partition coefficients for N_2 and Ar vary by about a factor of two. Therefore, a vapor separated from a liquid at a low y value has about double the N_2/Ar ratio of these species than in the unboiled liquid. Vapor separated from meteoric water will have a N_2/Ar ratio about that of air! A CFS

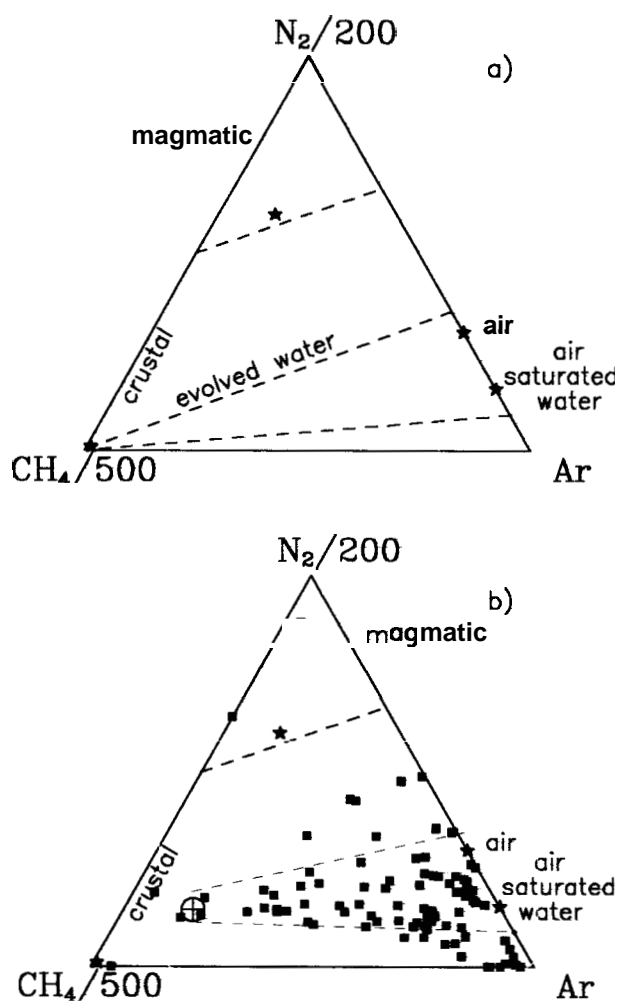


Fig. 5 a) Interpretation diagram similar to Fig. 2a. The lower dashed lines indicate the calculated field of N_2/Ar ratios (data from Prini and Crovetto, 1989), expected when boiling meteoric waters are trapped in fluid inclusions. b) Analyses of Tiwi fluid inclusions. Lower dotted lines are tie lines drawn from the calculated maximum and minimum N_2/Ar ratios calculated in a) to the calculated crustal component in the fluids (Moore et al. 1997).

analysis of inclusions trapped under boiling conditions will yield an analysis of trapped vapor in one crush, in another an analysis of trapped liquid, and in some cases analysis of both types of inclusions. Therefore, analysis of inclusions trapped under boiling conditions will have an analysis to analysis difference in N_2/Ar ratios. We calculated the range in N_2/Ar expected in meteoric water inclusions trapped under boiling conditions (Fig. 5a).

The expanded range for meteoric fluids simplifies the interpretation of Tiwi analyses. The field made by drawing tie lines (Fig. 5b) between the calculated N_2/Ar extremes for boiling meteoric water and the statistically determined crustal end member (Moore, et al. 1997) includes most of the analyses. This illustrates that the gas chemistry of most Tiwi inclusions is consistent with a meteoric fluid source.

LOW N_2/Ar FLUIDS

A number of Tiwi fluid inclusions have $N_2/Ar \ll$ than ASW (Fig. 4a). Some analyses have N_2/Ar near 1 (Table 1). Similar low N_2/Ar ratios are measured in inclusions from other active and past geothermal systems including Sulphur Springs, The Geysers, 6 ore deposits in Mexico and an ore deposit in Kazakhstan (Fig. 6). In general, inclusions with $N_2/Ar \ll$ ASW:

- are common, but are not measured in inclusions from every geothermal system studied
- only occur in a minority of inclusions from one geothermal system
- may occur in all inclusions within a single gram-size sample.

Boiling ASW will not create fluids that have N_2/Ar ratios less than about 15. Possible explanations for fluids with this chemistry are:

- 1) Fluid accumulation of radiogenic Ar from K-bearing minerals
- 2) N_2 occurring as NH_3 that is not detected
- 3) Magmatic gas with a low N_2/Ar ratio

There is no evidence to support idea of a low N_2/Ar magmatic gas, however knowledge of magmatic gas compositions is so limited that the idea can not be out of hand rejected.

Closure temperatures for radiogenic Ar loss from K-bearing minerals ranges from 200 to 400 C, hence geothermal fluids may force Ar out of K-bearing minerals. Measurement of the Ar isotopic composition of inclusions fluids in one sample of Sulphur Springs quartz that has a $N_2/Ar = 5$ indicates excess radiogenic argon ($^{40}Ar/^{36}Ar_{sample} / ^{40}Ar/^{36}Ar_{air} = 1.4$). This measurement demonstrates that inclusions may contain significant concentrations of radiogenic Ar.

The reason for low-ratios is illustrated in plots of Ar and N_2 concentrations versus N_2/Ar (Fig. 7). Kazakhstan analyses with $N_2/Ar <$ ASW are

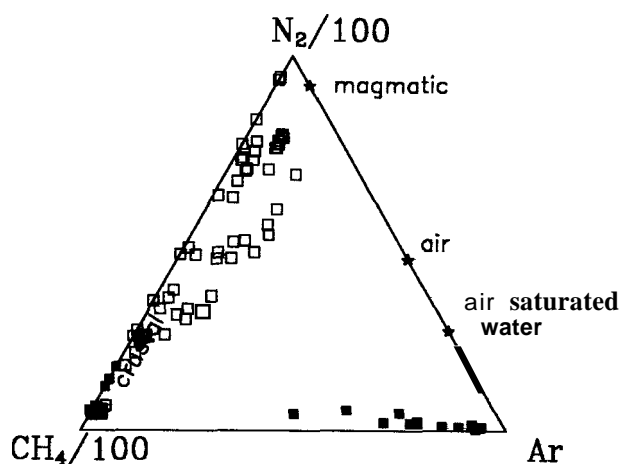


Fig. 6 Analysis of Kazakhstan mineral deposit fluid inclusions. The filled symbols are analyses obtained from one sample of quartz.

associated with increasing relative amounts of Ar (Fig. 7a). This is evident in the analyses presented in Table 1 also. Figure 7a is consistent with development of low-ratios from additions of radiogenic Ar to circulating meteoric fluids.

Calculations were done in order to demonstrate that sufficient radiogenic Ar could be derived from crustal rocks to significantly lower N_2/Ar ratios (Fig. 8). It was assumed for purposes of calculation that:

- 1) Fluids had a starting N_2/Ar ratio of 38.
- 2) Concentrations of Ar and N_2 started at concentrations in 20 C ASW.
- 3) There was no loss in Ar or N_2 from the fluid.
- 4) All radiogenic Ar was removed from rock.
- 5) There was no prior loss of radiogenic Ar from minerals.

The calculations show that N_2/Ar ratios of 5 or less can only occur if water rock ratios are very small and the rocks have remained closed to Ar loss for millions of years. This implies that low N_2/Ar fluids can form only once in the lifetime of a geothermal system; only a small volume of low N_2/Ar fluid can be formed; low-ratio fluids can not develop in coeval volcanic rocks; and low-ratio fluids must be generated early in the history of a geothermal system. Low-ratio fluids have the greatest chance of originating in billion year old granites. Conversely, calculations show that low-ratio fluids can not form in young basic terrains. The origin of Ar in low-ratio fluid inclusions will be confirmed by Ar isotopic

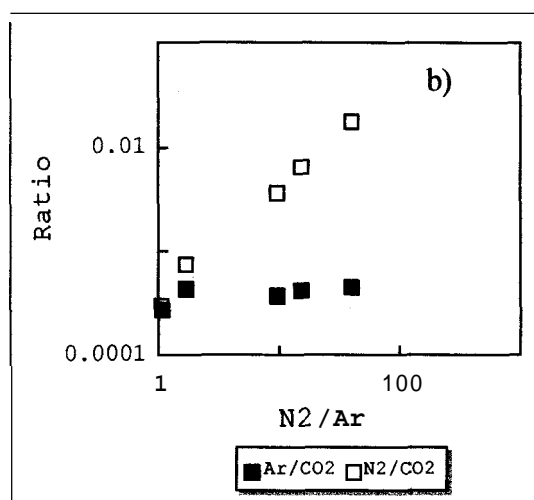
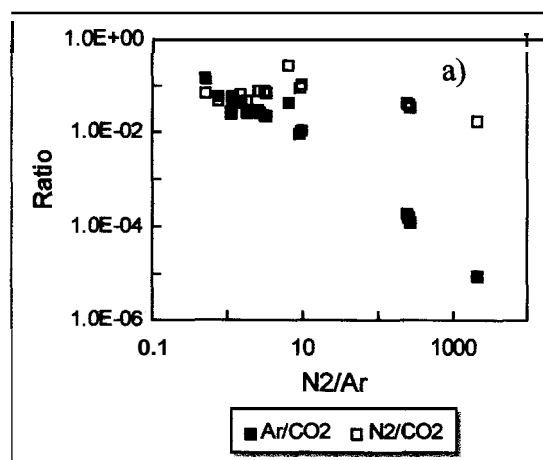


Fig. 7 Relative concentrations of fluid inclusion N_2 and Ar versus N_2/Ar in samples that have some ratios \ll ASW: a) Kazakhstan inclusions, b) Tiwi inclusions. The plots demonstrate that Kazakhstan low-ratio fluids are the result of increasing fluid concentrations, whereas Tiwi low-ratio fluids result from decreased amounts of N_2 .

analysis now in progress. The most exciting aspect of the identification of low N_2/Ar ratio inclusions may be their use to identify early formed mineralization in geothermal systems.

All low N_2/Ar ratio fluids may not form by accumulation of radiogenic Ar. Low-ratio Tiwi inclusions are associated with a decreased relative amounts of N_2 (Fig. 7b). This could be the result of N_2 reduction by hydrogen to form NH_3 that we did not detect. Mat 25 inclusions, which have low ratios, are from the upper most part of the drill core and associated

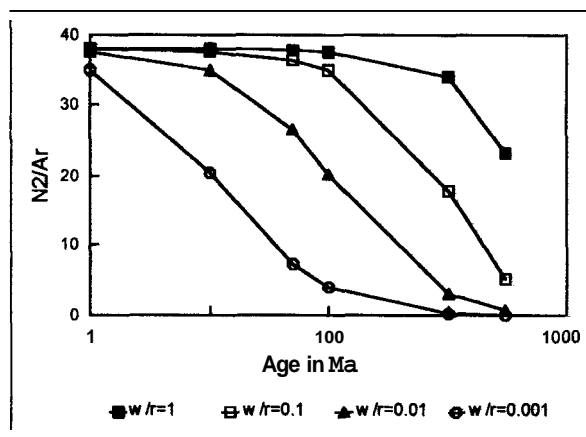
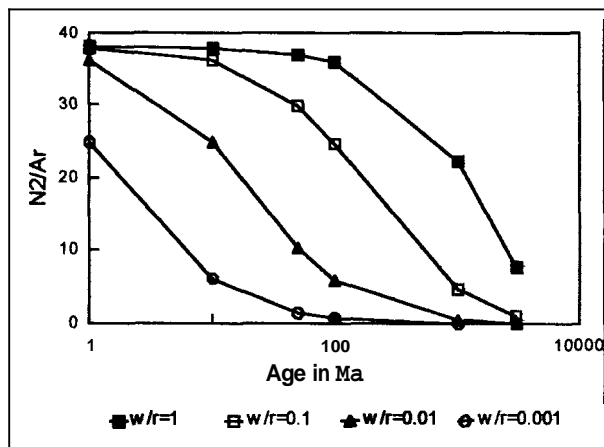


Fig. 8 Calculated N_2/Ar ratios in geothermal fluids as function of water to rock ratio (w/r) and age (or years from the last heating event), see text for details. Upper diagram is for a granitic rock with 5% K, the lower diagram is calculated for rock with 0.8% K.

with extensive illite alteration. Incorporation of NH_3 into phyllosilicate minerals may have driven the decrease in fluid N_2 as would reduction of N_2 to W . The latter can occur in response to decreasing fluid temperature.

CONCLUSIONS

1. Analysis of magmatic glass inclusions shows great promise for obtaining accurate magmatic ratios of N_2 -Ar-He. The analyses of Erebus glass

inclusions confirms that hypothesis that magmatic gases have $N_2/Ar \gg$ than air.

2. Modeling N_2/Ar ratios in boiling systems demonstrates that analyses of inclusions trapped under boiling conditions are expected to have a broad range in N_2/Ar ratios, even though the fluid prior to boiling had a restricted range of values. Fluid inclusion N_2/Ar ratios about that of air is expected in vapor derived from meteoric waters. A range of N_2/Ar ratios in inclusion volatiles from about 15 to about 120 measured in one sample can be used to affirm fluid boiling.

4. Inclusion fluids may have N_2/Ar ratios less than 15. These may form by accumulation of radiogenic Ar from country rocks or incorporation of N_2 , as NH_3 into alteration minerals. Argon isotopic analysis can confirm additions of radiogenic Ar to inclusion fluids. However, plotting N, and Ar normalized to a major species such as CO_2 can illustrate if low ratios are associated with increasing relative amounts of Ar or decreasing amounts of N_2 .

5. Low N_2/Ar fluids that formed by accumulation of radiogenic Ar are small in volume and can only form once in the history of a geothermal system. Identification of such fluids should prove of great value in identifying early formed mineralization in a geothermal systems.

TABLE 1 Water-free analyses of fluid inclusions volatiles by the CFS method.

	Kazakhstan		Tiwi	
(mol.%)				
H_2	13.3	0.99	nd	nd
He	0.027	nd	nd	0.044
CH_4	35.3	20.0	0.58	5.0
N_2	3.5	1.4	0.029	6.8
H_2S	0.001	0.010	0.018	0.19
Ar	1.4	0.001	0.027	0.15
CmHn	0.30	0.13	nd	nd
CO_2	46.1	77.4	99.2	87.8
N_2/Ar	2.6	2120	1.1	45

nd = none detected

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