H$_2$S CONCENTRATIONS IN GEOTHERMAL AND HYDROTHERMAL FLUIDS – A NEW GAS GEOTHERMOMETER

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ABSTRACT

Several gas geothermometers exist that have applications in the geothermal industry. Most are based on the CO_2-CH_4-H_2-H_2O system but none involve H_2S, a gas that is always present in geothermal systems.

The equilibrium reactions for water-magnetite-pyrite-pyrrhotite-H_2S-CO_2-CH_4 were first described by Norman et al. (1998) to explain approaching equilibrium from the hot and cold sides. Equilibrium is based on the reaction:

$$2Fe_3O_4 + 12H_2S + CO_2 = 6FeS_2 + 10H_2O + CH_4$$
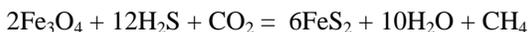
Fluid-rock equilibria modeling using PHREEQC v.2.10 confirms that the H_2S content increases approximately five fold for every 50°C increase in temperature. The H_2S concentration increases from 0.0003 mole % at 200°C to 0.008 mole % at 300°C. A formula to calculate temperature based on H_2S concentration is presented for the 200-300°C range and is valid for non-boiling low-salinity fluids.

Key words: H_2S, gas, geothermometer, geothermal, hydrothermal, fluid inclusions, gas analysis, pyrite, magnetite, pyrrhotite

INTRODUCTION

The concept of gas geothermometry is not new (Giggenbach, 1980; D'Amore and Panichi, 1980). Several geothermometers are established for application to the geothermal industry (Henley et al., 1984), the most commonly applied based on the H_2-CO_2-CH_4-H_2O system. Gas geothermometers based on other chemical systems exist, the N_2-NH_3 system being an example. Irrespective of the compounds applied, gas geothermometers share common factors. For a geothermometer to be successful, the equilibrium concentration of species present in the system must be temperature dependent and reflect the maximum temperature conditions.

Other constraints that apply include: achievement of equilibrium; each species concentration must be accurately determined; and retrogressive reactions must not have occurred.

Fluid inclusion gas analysis shows that the H_2S content of geothermal fluid inclusions is variable. The sulfur that occurs in geothermal systems is sourced within the earth's crust by equilibrium reactions between pyrite, pyrrhotite, magnetite and hydrothermal fluid. The equilibrium reaction for water-magnetite-pyrite-pyrrhotite is described by Norman et al. (1998). Irrespective of the fluid source, the fluid chemistry will evolve by interaction between fluid and rock. Equilibrium for any given temperature is reached when the fluid H_2S activity is in equilibrium between pyrite and magnetite, or once a mineral is totally replaced.

The aim of this paper is to introduce a new gas geothermometer for non-boiling fluids controlled by magnetite-pyrite-pyrrhotite-water equilibrium. The geothermometer is determined for low-salinity fluids and a correction is suggested to allow the H_2S geothermometer's application under brine conditions.

BACKGROUND

The CO_2-CH_4-H_2S-H_2O-magnetite-pyrite-pyrrhotite equilibrium conditions are described in Norman et al. (1998) to explain the distribution of H_2S in geothermal systems. The equilibrium reaction is as follows:

$$2Fe_3O_4 + 12H_2S + CO_2 = 6FeS_2 + 10H_2O + CH_4$$
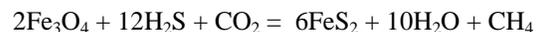
Equilibrium concentrations of H_2S controlled by magnetite-pyrite-pyrrhotite vary in some geothermal systems from the theoretical equilibrium established by calculation. Norman et al. (1998) explain this variation in terms of approaching equilibrium from the hot or cold sides. Values for H_2S in solution that exceed equilibrium

conditions at a given temperature are explained by fluids being hotter than the surrounding rocks; these sulfur-rich fluids will cause sulfidation of magnetite. Conversely, colder fluids entering a geothermal system acquire H_2S by the destruction of pyrite to form magnetite thereby releasing H_2S into the hydrothermal fluid. If all pyrite has reacted or if equilibrium is achieved at a lower temperature, then the fluid may have a lower H_2S content than expected.

The H_2S concentration in equilibrium with pyrite, magnetite and pyrrhotite is very temperature sensitive, implying that this reaction could be successfully applied to gas geothermometry. However, the equilibrium conditions in the diagrams of Norman et al. (1998) are calculated for pure water conditions using SUPCRT. Salinity has a pronounced effect on the H_2S concentration by virtue of changing the H_2S activity. Equilibrium conditions calculated by Blamey (2000) for a change in ionic strength from 8 to 25 weight percent NaCl equivalent (hereafter wt % NaCl equiv) show a broad range in the H_2S equilibrium concentration at 300ºC. A salinity correction must therefore be required if the H_2S geothermometer is to be applied to hydrothermal brines.

Geothermometers based on equilibrium conditions are only valid if specific criteria are met. These criteria include: no boiling or phase separation; achievement of equilibrium conditions; no modification of the fluid prior to analysis; and accurate H_2S analysis.

Fluid inclusion homogenization temperatures measured by microthermometry are either equal to or less than the trapping temperature. If Th is known to be <Tt then an isochore is plotted. In some cases, Th may be as much as 100ºC less than Tt (Blamey, 2000) and therefore finding an alternative approach to constraining temperature becomes important. Another consideration is whether source fluid equilibrium gas ratios are preserved in calcite-hosted fluid inclusions. The reliability of CO_2-CH_4-H_2 based gas geothermometers for calcite-hosted fluid inclusions is unknown under low gas-water conditions, owing to bicarbonate re-equilibration at ambient temperatures.

The application of CO_2/CH_4 ratios to estimate equilibrium temperatures is presented by Giggenbach (1997). Quartz fluid inclusion CO_2/CH_4 ratios measured by quadrupole mass spectrometry confirm that gas geothermometry is valid for fluid inclusions (Blamey and Norman, 2002). However, equilibrium conditions between CO_2 and calcite might result in changes to the CO_2 concentration by the production of HCO_3^- and thereby invalidate the H_2-CH_4-CO_2 gas geothermometer for gases hosted within calcite. A H_2S geothermometer that is not affected by equilibrium reactions with the host mineral might offer an alternative.

METHODOLOGY

Samples are analyzed by crushing samples *in vacuo* to liberate their fluid inclusion volatiles for analysis by quadrupole mass spectrometry. The quadrupole mass spectrometer is calibrated using Scotty gas mixtures as well as three in-house fluid inclusion standards. Accurate measurement of fluid inclusion H_2S concentration depends on calibration of all significant gases and water (see Norman and Blamey 2001 for the calibration method). It should be noted that gas concentrations reported for gas analysis are in mole percent whereas a simple conversion can be made into molar concentrations for the modeling program.

Geochemical modeling is conducted using PHREEQC version 2.10. The program monitors the significant species that one enters and calculates equilibrium concentrations at desired temperatures. The llnl.dat thermo-dynamic database is favored and is valid up to a maximum temperature of 300ºC. Geothermal well UTAH STATE 52-21 is selected as a starting chemistry for modeling, principally because the well's 206°C temperature approximates to the lower modeling temperature limit. Equilibrium phases are magnetite, pyrite, pyrrhotite, quartz, sericite, K-feldspar, albite, and a 0.1 CO_2/CH_4 ratio.

A serious consideration for those willing to attempt the H_2S geothermometer is the effect of fluid salinity. Since this gas geothermometer is dependent on H_2S as a concentration and not gas ratios, saline fluids require special treatment owing to the increase of the H_2S activity coefficient (aH_2S) and Henry's Law constants (K_H). To correct for salinity, the Henry's Law constant for H_2S is calculated using formulae presented by Drummond (1980). A rough guide to correcting for salinity is as follows. The ratio between K_H at the same temperatures for pure

water conditions and the desired salinity is calculated ($K_{H\ pure\ water}/K_{H\ brine}$). The analyzed H_2S is then divided by this ratio, correcting the lower H_2S concentration analyzed in the brine to a higher value compatible with pure water conditions. A more accurate and recommended method would be to use PHREEQC to model the change in activity coefficient in response to salinity increase.

RESULTS

The data gained from geochemical modeling is presented in table 1 and figures 1 and 2. The data is converted from molar concentration into mole percent and compared to the 200, 250 and 300°C values originally determined by Norman et al. (1998) using SUPCRT.

PHREEQC modeling for well UTAH STATE 52-21 is in very close agreement with the H_2S content reported by Norman et al. (1998) at 200°C (Table 1). At 250°C there is a 3°C difference that increases to 10°C at 300°C. In the 200-300°C temperature range the H_2S concentration increases from 0.0003 to 0.008 mole percent for pure water and low-salinity fluids. The H_2S concentration increases almost logarithmically in response to a linear increase in temperature (Fig. 2).

Table 1. *Results from PHREEQC modeling using a starting chemistry equivalent to well UTAH STATE 52-21. The output is reported in both molar concentration and mole percent. The H_2S values reported by Norman et al. (1998) are given for comparison; there is close agreement around 200°C whereas a 10°C difference occurs at 300°C.*

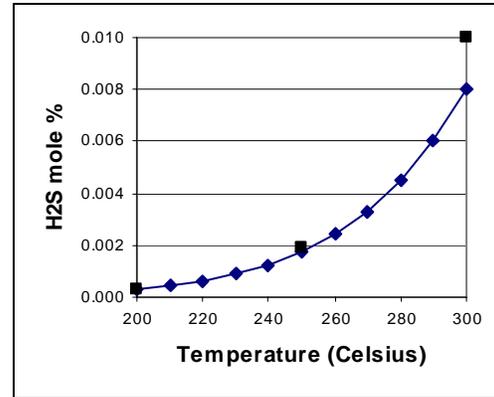| Temp (°C)	PHREEQC output (H_2S molar concentration)	PHREEQC output (H_2S mole %)	Norman et al. (1998) values (H_2S mole %)
200	1.64e-4	2.95e-4	2.98e-4
210	2.40e-4	4.32e-4	
220	3.46e-4	6.23e-4	
230	4.94e-4	8.89e-4	
240	6.97e-4	1.25e-3	
250	9.72e-4	1.75e-3	1.875e-3
260	1.34e-3	2.41e-3	
270	1.83e-3	3.29e-3	
280	2.48e-3	4.46e-3	
290	3.33e-3	5.99e-3	
300	4.43e-3	7.97e-3	1.0e-2

Figure 1. *Plot of H_2S (mole %) vs temperature (°C) for the results from PHREEQC modeling (dark blue diamonds). For comparison the original data from Norman et al. (1998) are plotted in black squares.*
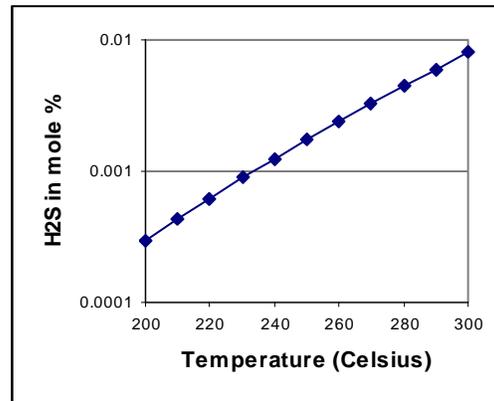

Figure 2. *Plot of H_2S (mole %) vs temperature (°C) for the PHREEQC modeling data showing that the relationship between H_2S and temperature is almost logarithmic.*

An example that shows the effect of salinity on H_2S equilibrium concentrations is presented in Blamey (2000), using an example from a Carlin-type gold deposit. Ore-stage quartz fluid inclusions that have a modal salinity of about 8 wt % NaCl equiv have a 295-323°C trapping temperature range and 0.0007-0.03 mole percent H_2S content (Blamey, 2000). For comparison the data is plotted on the CO_2/CH_4 vs H_2S equilibrium diagram presented by Norman et al. (1998) for pure water conditions (Figure 3a) and for the same diagram modified and corrected for 8 wt % NaCl equiv (Figure 3b).

DISCUSSION

There is a clear correlation between temperature and H_2S content controlled by pyrite-pyrrhotite-magnetite-water equilibrium in geothermal and hydrothermal systems. Although differences between PHREEQC modeling and the original SUPCRT modeling (Norman et al., 1998) occur, these differences are possibly due to the choice of thermodynamic database.

The success to applying this H_2S geothermometer depends on accurate H_2S analysis and calculation of the equilibrium temperature using a relatively simple formula. Clearly a complex formula that exactly matches the data can be found, however, for simplicity the following formula is applied:

$$T = \log(X)*A + B \quad \text{………(equation 1)}$$

For equation 1, T = temperature in Celsius, X = H_2S concentration in mole percent, and A and B are values determined by linear regression for the 200-250 and 250-300°C segments of the data. The H_2S content at 250°C is approximately 0.00175 mole percent and therefore when applying the geothermometer, H_2S values below 0.00175 mole percent will use different A and B values than above 0.00175 mole percent (see table 2).

Table 2. *Values for the constants A and B as they apply to equation 1. Note that values for A and B differ above and below 0.00175 mole percent H_2S.*

	For H_2S <0.00175 mole %	For H_2S >0.00175 mole %
A	64.68	75.85
B	427.8	458.6

Differences between figures 3a and 3b demonstrate the need for a salinity correction. The equilibrium fields for pyrite, magnetite and pyrrhotite change in response to the salinity increasing from 0 to 8 wt % NaCl equiv. If the H_2S gas geothermometer were to be applied without a salinity correction (Fig. 3a), then one might expect a lower temperature (around 235°C) that is 60°C below the minimum trapping temperature measured by microthermometry. By correcting for salinity (Fig. 3b) the lower H_2S analyses correspond to the lower 295°C trapping temperature. The higher H_2S concentrations are attributed to approaching equilibrium from the hot side (Norman et al., 1998) and might indicate source temperatures above 350°C. Clearly

without a salinity correction, the application of the H_2S gas geothermometer to brines would result in large errors.

CONCLUSION

The H_2S geothermometer based on pyrite-pyrrhotite-magnetite equilbrium is viable in the 200-300°C range for low-salinity geothermal and hydrothermal fluids. In all likelihood the geothermometer is viable above 300°C but PHREEQC modeling only applies the llnl thermodynamic database up to 300°C. Gas separation by boiling will render the H_2S geothermometer invalid and therefore should only be applied to non-boiling systems.

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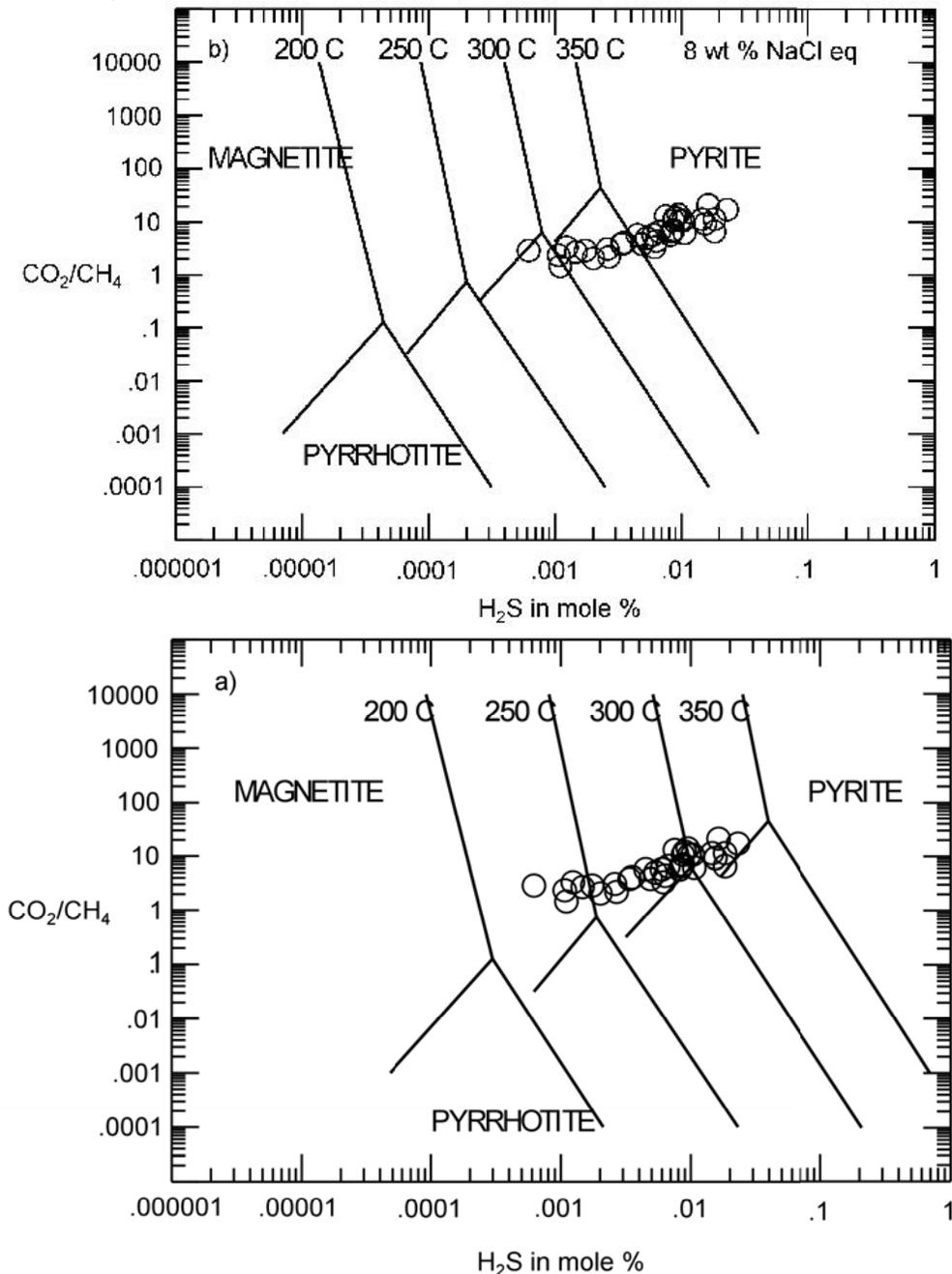
Figure 3. Plot of CO_2/CH_4 vs H_2S in mole % for ore-stage mineralization at the Pipeline Mine. See text for details. Diagrams are modified after Norman et al. (1998).